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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

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 $^\circ\text{C}$ 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 cm^3 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 mortar, 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 cm^3 conical flask. The digestion was carried out with 20 cm^3 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

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

Contamination factor

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

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

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:

$\text{CF} < 1$, low contamination; $1 < \text{CF} < 3$, moderate contamination; $3 < \text{CF} < 6$, considerable contamination; and $\text{CF} > 6$, high contamination [16].

Pollution load index

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

$$\text{PLI} = (\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \dots \times \text{CF}_n)^{1/n} \quad (\text{iii})$$

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].

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

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

where,

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

C_n 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 $\pm$ 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.

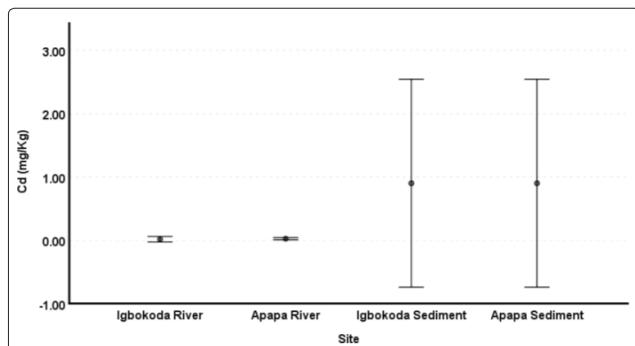


Figure 1a

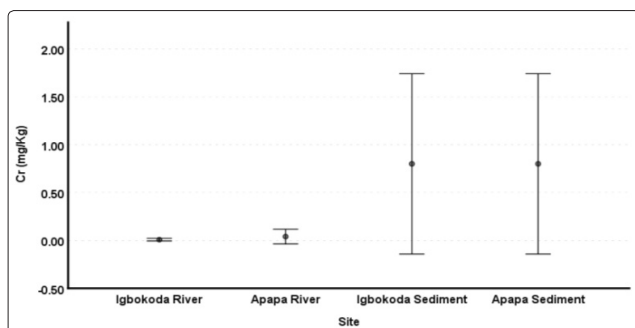


Figure 1b

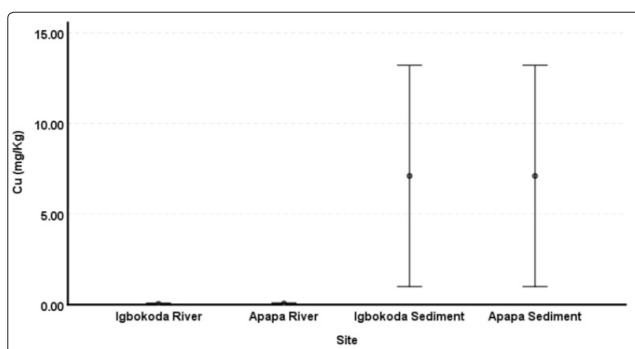


Figure 1c

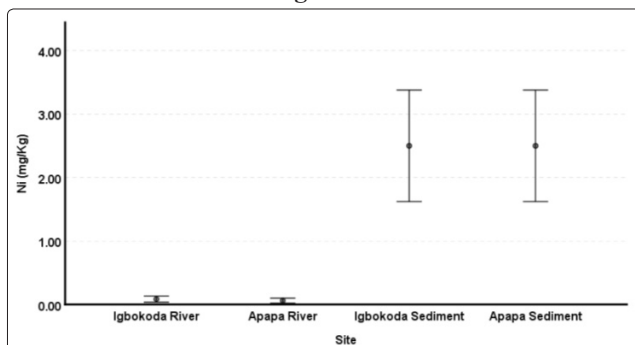


Figure 1d

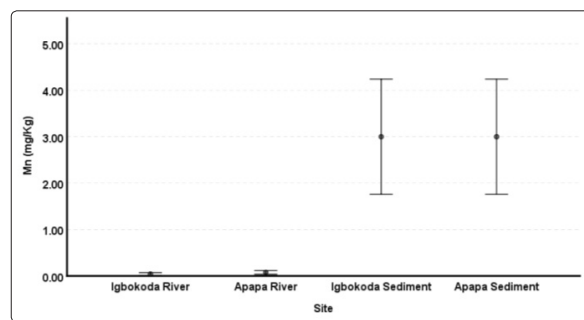


Figure 1e

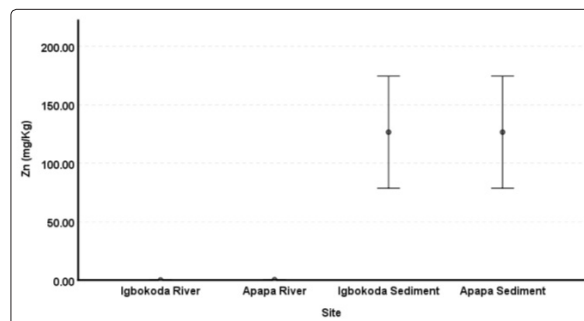


Figure 1f

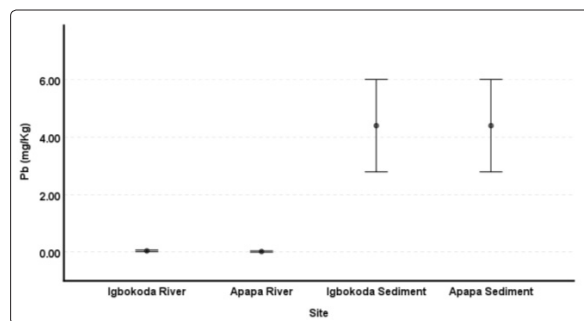


Figure 1g

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

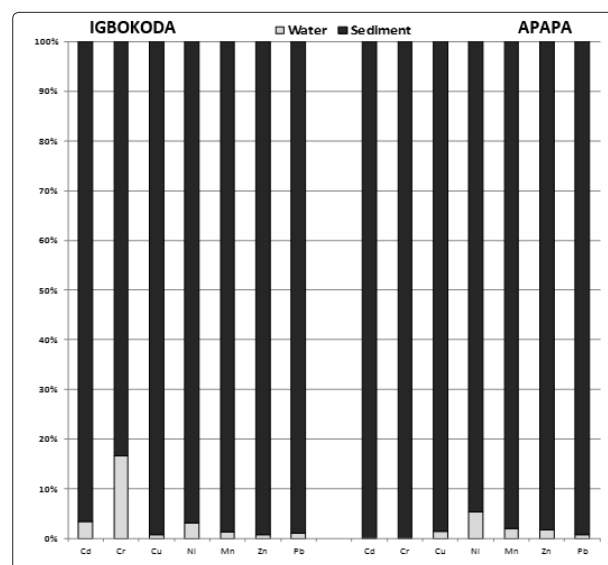


Figure 2: Percentage composition of hazardous metals in river water and sediments from Igbokoda and Apapa, south west, Nigeria

Assessments of Contamination and Pollution in Sediments

The contamination factor (C_f) 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 C_f 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 C_f, four categories of E_{ir}, and four categories of PER, as shown in Table 3 [21]. Combining the potential ecological risk index of individual metals (E_{ir}) 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 _f	Contamination degree of individual metal	Degree of Contamination	Contamination degree of the environment	E _{ir}	Grade of Ecological risk of individual metal	Risk index (PER)	
C _f < 1	Low	Cd < 5	Low contamination	E _{ir} < 40	Low risk	RI < 40	Low risk
1 ≤ C _f < 3	Moderate	5 ≤ Cd < 10	Moderate contamination	40 ≤ E _{ir} < 80	Moderate Risk	65 ≤ RI < 130	Moderate risk
3 ≤ C _f < 6	Considerable	10 ≤ Cd < 20	Considerate contamination	80 ≤ E _{ir} < 160	Considerable risk	130 ≤ RI < 260	Considerable risk
C _f ≥ 3	High	Cd ≥ 5	High contamination	160 ≤ E _{ir} < 320	High risk	RI ≥ 5	Very high risk
				E _{ir} ≥ 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 (E _{ir})						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

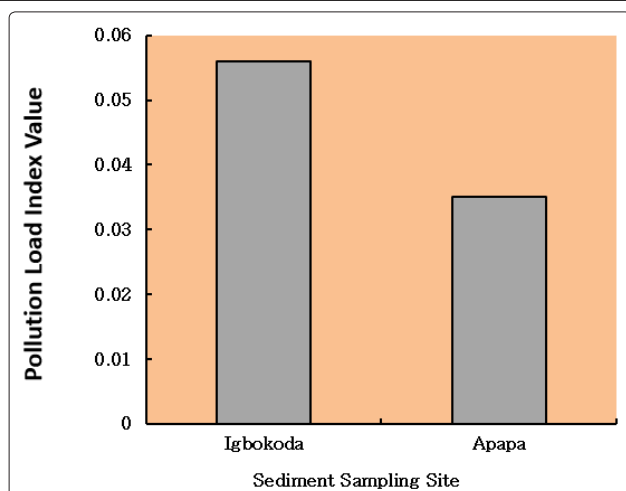


Figure 3: Pollution load index (PLI) of hazardous metals in sediments from two sites in South Western Nigeria

Conclusion

For the study of the pollution status of sediments contaminated by some heavy metals the method of potential ecological 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 contaminated by the metals and their pollution can be attributed to industrial pollution through anthropogenic activities. Contamination assessment of sediments may provide 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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