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Heavy Metals in Rivers and Sediments from Two Southwestern States of Nigeria

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Abstract

Anthropogenic sources of heavy metals to coastal cities and their environment are mostly through the various water bodies. This study aimed at using the Potential Ecological Risk (PER) index to characterize rivers and sediments for possible environmental impact. Ten water and ten sediment samples from both Igbokoda and Apapa in Southwest, Nigeria were collected between March and, August 2018 and analysed for heavy metals. The water and sediment grab samples were treated using standard procedures. The filtrate from the sediment was made up of the 50 cm^3 mark with distilled water and used for seven heavy metals determination using Atomic Absorption Spectrophotometry (AAS). Zn has the highest mean concentration (>150 mg/Kg) in the sediments from both sites. The remaining six metals have remarkably low concentration <15 mg/Kg in both rivers and sediments. The Contamination Factor (CF) and the Pollution Load Index (PLI) calculated for each metal in the sediments implied 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 is an indication of a potential hazard to the food chain; it needs attention and also prevention. It may also suggest that the Igbokoda water is unsafe for aquatic, biota, recreational and other beach activities. This study therefore recommends that a proper treatment of wastewater and sewages be properly carried out before fluxing into both the Igbokoda and Apapa water bodies.

Keywords: Sediments, River water, Heavy metals, Pollution Load Indices, Contamination factor

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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, and oceans as well as in the open land and that contaminate the groundwater [3,4]. 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 [5]. 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 [6].

Heavy metals are so dangerous because they tend to bio-accumulate [7]. 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 exposure to such metals continues 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 have become problems of increasing significance from an ecological, evolutionary, nutritional, and environmental perspective [8].

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 behaviour 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 [9]. 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 [10,11] and thereby providing a record of catchments input into aquatic ecosystems [12]. The favorable 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 [13]. 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 chains. Some information provided by these previous studies is also associated with source pollution of the heavy metals and the risk assessment criteria. Dearth of information and data for the coastal rivers under investigation has prevented the stakeholders concerned with ecosystem management to evaluate appropriately the potential risks from heavy metals. The present study is targeted at comparing the levels of contamination of sediments and their associated rivers from two coastal towns in the southwestern part of Nigeria using the potential ecological risk PER methods. The PER status will show specific metal pollution status or 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

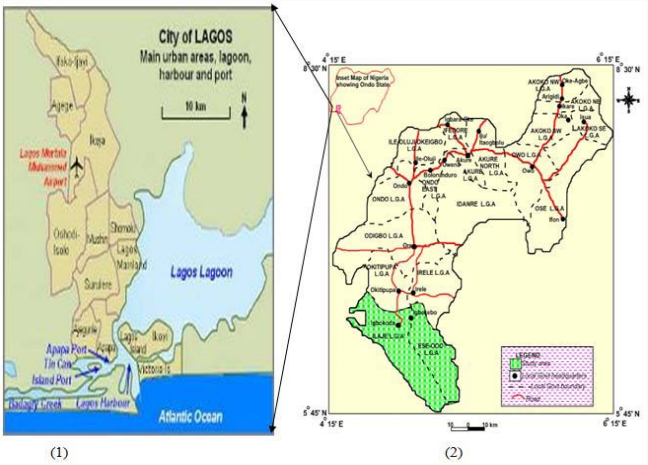

Plate 1: Map of the study area (1) Map of Lagos state showing Apapa Port (2) Map of Ondo showing Igbokoda.

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. At each location, about 2-3 Kg sediment samples were collected from the surface layer (0-15cm depth) using a stainless steel Peterson grab sampler (20x12 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.

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 about 200 mL distilled water thrice. The water samples collected were preserved by adding 2mL of Concentrated HNO_3 acid to fix the samples.

Methods

Heavy metals determination in water: The water samples were first digested with conc. HNO_3 before analysis of the heavy metals 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 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 Whatman 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

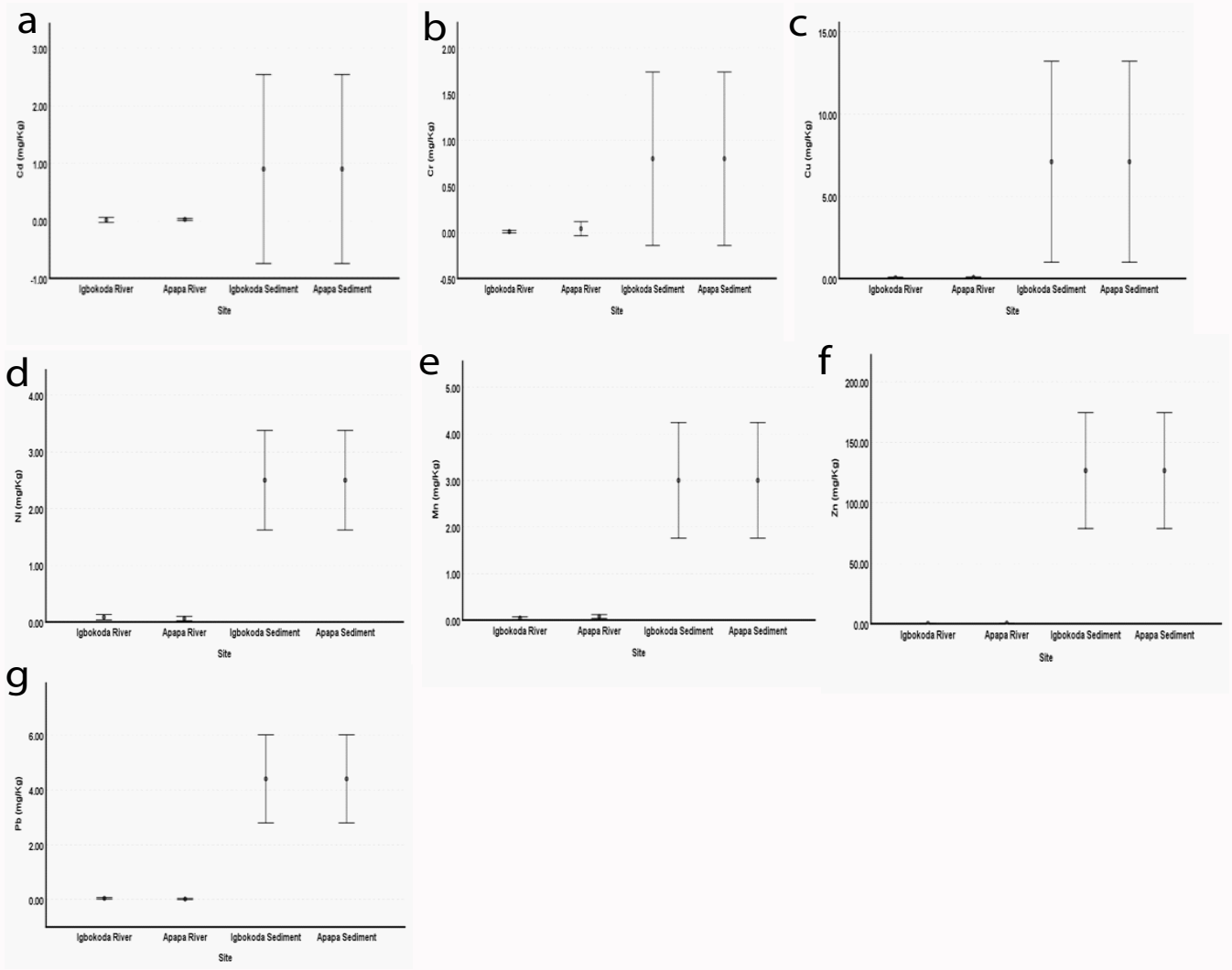

Figure 1(a-g): Comparative mean metal concentration of seven heavy metals in rivers and sediments from Igbokoda and Apapa. (Values are Mean ± S.D for five sample number (n=5).

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 [14,15]. 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:

Metal Concentration in µg/g= (AAS Reading in$^{\mu g}/_{ml}$ $^{x \text{ volume of digest in ml}}$)/Weight of sample in g ……..(i)

Contamination factor: The Contamination Factor (CF) was calculated as described by [16] and modified by [2]:

CF = Metal concentration in sediment/Base value for the metal ……(ii)

The base value for each metal was reported by 16 modified by [2] and represents the average composition of the surface rocks. 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 [17].

Pollution load index: Pollution Load Index (PLI) was computed according to [16] using equation (iii).

PLI = $(CF1 \times CF2 \times CF3 \times \ldots CFn)^{(1/n)}$ ……(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 [18] proposed equations (iv) and (v) which were used to calculate PER:

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

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

where,

C^i_f is the single element contamination factor, C^i is the content of the element in samples and C^i_n is the background value of the element.

The sum of C^i_f for all metals represents the integrated pollution degree (C_d) of the environment. E^i_r is the potential ecological risk index and T^i_r 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 [18-20].

PER is the comprehensive potential ecological risk index, which is the sum of E^i_r. 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 (mg/Kg) 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 % composition of the metals in river water is in the decreasing order of 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.

Assessments of contamination and pollution in sediments

The contamination factor (C^if) for individual metal and degree of contamination (Cd) are presented in Table 1. The two sites, Igbokoda and Apapa showed low contamination (Cd< 6) for all

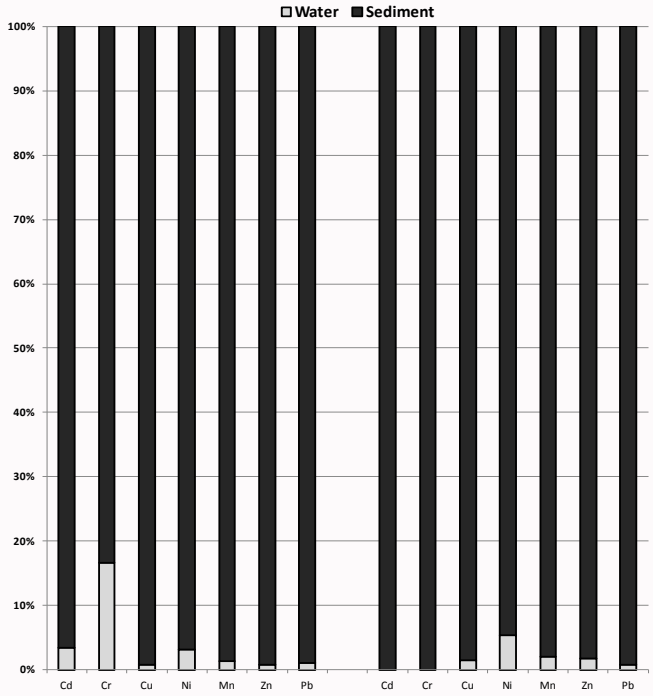

Figure 2: Percentage composition of seven heavy metals in rivers and sediments from Igbokoda and Apapa, south west, Nigeria (Values are Mean±S.D for five sample number (n=5).

the metals in the sediments. The table can be interpreted as shown in Table 2, that the contaminated sites pose low potential risk to the surrounding ecosystems. This observation is akin to that reported by [21]. Overall, the C^if 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 1).

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 [19,21]. Extent of pollution increases with the increase of numerical PLI value. As per above grade system, the sediments are not polluted, since PLI of the sediments from the two sites 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 over time unless waste and effluents coming from the anthropogenic activities in the coastal rivers are 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.

Four categories of C^if, four categories of E^ir, and four categories of PER, as shown in Table 2 were defined [22]. Combining the potential ecological risk index of individual metals (E^ir) and the Potential Ecological Risk index (PER) (Table 3) with their grades (Table 2), 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 1: Contamination factor, degree of contamination and contamination level of seven heavy metals in sediments from Igbokoda and Apapa, South west, Nigeria.

Site	Contamination Factor (CF)							Degree of Contamination	Contamination level
	Cd	Cr	Cu	Ni	Mn	Zn	Pb		
Igbokoda	1.41	0.01	0.18	0.04	0.05	1.89	0.00	3.60	Low
Apapa	0.13	0.03	0.24	0.05	0.04	1.58	0.00	2.10	Low

Table 2: Indices and grades of potential ecological risks of some heavy metal pollution [22].

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	C_d<5	Low contamination	E^i_r<40	Low risk	RI<40	Low risk
1 ≤$C^i_{f<}$3	Moderate	5≤C_d<10	Moderate contamination	40≤E^i_r<80	Moderate Risk	65≤RI<130	Moderate risk
3 ≤$C^i_{f<6}$	Considerable	10≤C_d<20	Considerate contamination	80≤E^i_r<160	Considerable risk	130≤RI<260	Considerable risk
C^i_f≥3	High	C_d≥5	High contamination	160≤E^i_r<320 E^i_r ≥5	High risk Very high risk	RI≥5	Very high risk

Table 3: Potential Ecological risk factor, risk index and pollution degrees of seven 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	0.90	0.24	1.89	0.02	45.37	Low Risk
Apapa	3.90	0.06	1.20	0.30	1.58	0.02	6.79	Low Risk

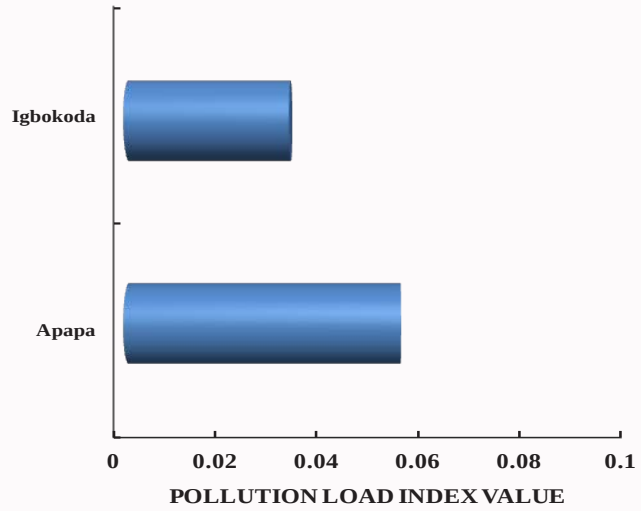

Figure 3: Pollution Load Index (PLI) of the total heavy metals in sediments from Apapa and Igbokoda in southwestern part Nigeria.

The PER represents the sensitivity of various biological communities to different toxic substances and illustrates the potential ecological risk caused by hazardous materials. Cd contributes significantly to the PER of the environment and may originate from anthropogenic activities [19,23,24]. 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.

Conclusion

This study on the pollution status of sediments contaminated by some heavy metals used the method of potential ecological risk indices. According to the method, 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 almost same orders' Cd>Zn>Cu>Ni>Cr/Pb in Igbokoda sediments but with the order Cd>Zn>Cu>Ni>Cr>Pb for the Apapa Sediments.

The results of the sediment quality assessments from the two locations showed that the sediments are moderately contaminated by the metals and the pollution may be attributed to pollution through anthropogenic activities. Contamination assessment of sediments might provide substantial evidence on water management techniques and indicates the need for remediation and the protection of river waters. Further studies on the dynamics of heavy metals between the water and the sediments may be required to fully understand the contribution of sediments to river contamination processes. A metal speciation study is also vital for understanding its transport and fate in the water and sediments. Cd metals needs be given strict monitoring because of its high PER value in sediments.

References

1. Pawan KB. Heavy Metals in Environment. Lambert Academic Publishing. 2012.
2. Youssef DH, El-Said GF. A comparative study between the levels of some heavy metals in the sediments of two Egyptian contaminated environments. Chemistry and Ecology. 2010; 26: 183-195.
3. Chen Z, Saito Y, Kanai Y, Wei T, Li L, Yao H, et al. Low concentration of heavy metals in the Yangtze estuarine sediments, China: a diluting setting. Estuarine Coastal Shelf Sci. 2004; 60: 91-100.
4. Loska K, Wiechula D. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemosphere. 2003; 51: 723-733.
5. Mohamed A, Hassaan AE, Fedekar FM. Environmental Assessment of Heavy Metal Pollution and Human Health Risk. American Journal of Water Science and Engineering. 2016; 2: 14-19.
6. Zhang LP, Ye X, Feng H, Jing Y, Ouyang T, Yu X, et al. Heavy Metal Contamination in Western Xiamen Bay Sediments and Its Vicinity, China. Marine Pollution Bulletin. 2007; 54: 974-982.
7. Yuan C, Shi J, He B, Liu J, Liang L, Jiang G. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environ Int. 2004; 30: 769-783.

8. Arif TJ, Mudsser A, Kehkashan S, Arif A, Inho C, Qazi M, et al. Heavy Metals and Human Health: Mechanistic Insight into Toxicity and Counter Defense System of Antioxidants. Int J Mol Sci. 2015; 16: 29592-29630.

9. DelValls TA, Forja J, Gonzalez-Mazo E, Gomez-Parra A, Blasco J. Determining contamination sources in marine sediments using multivariate analysis. Trends Anal Chem. 1998; 17: 181-192.

10. Kronvang B, Laubel A, Larsen SE, Friberg N. Pesticides and heavy metals in Danish streambed sediment. Hydrobiologia. 2003; 494: 93-101.

11. Milenkovic N, Damjanovic M, Ristic M. Study of heavy metal pollution in sediments from the iron gate (Danube River), Serbia and Montenegro. Polish J Environ Stud. 2005; 14: 781-787.

12. Mwamburi J. Variations in trace elements in bottom sediments of major rivers in Lake Victoria's Basin, Kenya. Lakes Reservoirs. 2003; 8: 5-13.

13. Casper ST, Mehra A, Farago ME, Gill RA. Contamination of surface soils, river water and sediments by trace metals from copper processing industry in the Churnet River Valley, Staffordshire, UK. Environ Geochem Health. 2004; 26: 59-67.

14. Chale FMM. Trace metal concentrations in water, sediments and fish tissue from Lake Tanganyika. Sci Total Environ. 2002; 299: 115-121.

15. Martin JM, Meybeck N. Elemental mass-balance of material carried by major world rivers. Marine Chemistry. 1979; 7: 173-206.

16. Tomlinson DI, Wilson JG, Harris CR, Jeffrey DW. Problems in the assessment of heavy metals levels in estuaries and the formation of a pollution index, Helgol. Meeresunters. 1980; 33: 566-567.

17. Badr NBE, El-Fiky AA, Mostafa AR, Al-Mur BA. Metal pollution records in core sediments of some Red Sea coastal areas, Kingdom of Saudi Arabia. Environ Monit Assess. 2009; 155: 509-526.

18. Guo W, Liu X, Liu Z, Li G. Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. Proc Environ Sci. 2010; 2: 729-736.

19. Islam MS, Ahmed MK, Al-Mamun MH, Masunaga S. Potential ecological risk of hazardous elements in different land-use urban soils of Bangladesh. Sci Total Environ. 2015; 512-513: 94-102.

20. Xu ZQ, Ni SJ, Tuo XG. Calculation of heavy metals toxicity coefficient in the evaluation of potential ecological risk index. Environ Sci Technol. 2008; 31: 112-115.

21. Rashed MN. Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast. Egypt J Hazard Mater. 2010; 178: 739-746.

22. Proshad R, Islam MS, Haque MA, Hoque MF, Ahmed S. Apportionment of hazardous elements in agricultural soils around the Industrial vicinity of Bangladesh. SF Journal of Environmental and Earth Science. 2018; 1: 1-8.

23. Mass S, Scheifler R, Benslama M, Crini N, Lucot E, Brahmia Z. Heavy metal concentrations in soil and wild plants growing around Pb–Zn sulfide terrain in the Kohistan region, northern Pakistan. Microchem J. 2011; 99: 67-75.

24. Luo XS, Yu S, Zhu YG, Li XD. Trace metal contamination in urban soils of China. Sci Total Environ. 2012; 421-422: 17-30.