Concentration, Ecological Risk and Enrichment Factor Assessment of Selected Heavy Metals in Sediments from New Calabar River, Nigeria

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ABSTRACT: The New Calabar River is an important commercial river in Rivers State. Surface sediment samples were collected from four stations and analyzed for some heavy metals concentrations. The results obtained revealed that the concentrations of the metals were iron (Fe) > zinc (Zn) > nickel (Ni) > chromium (Cr) > copper (Cu) > lead (Pb) > cadmium (Cd) > arsenic (As). Their respective mean values were; Fe, 147.84 ± 90.13; Zn, 5.49 ± 2.01; Ni, 3.50 ± 1.48; Cr, 3.42 ± 1.00; Cu, 2.48 ± 1.11; Pb, 2.42 ± 1.09; Cd, 0.089 ± 0.12 and As, 0.006 ± 0.005 mg/Kg. The results were further evaluated with some model indices (contamination factor, ecological risk and enrichment factor assessments. Sediment contamination factor analysis showed that the sediments were slightly contaminated. Ecological risk assessment revealed that the metals at the present concentrations are not harmful or cannot cause risk to the environment. However, enrichment factor analysis indicated that all the metals had significant anthropogenic enrichment at the various stations except As at Aluu, Choba and Iwofe and Cd at Aluu. Therefore, adequate and continuous monitoring should be put in place to prevent upsurge of anthropogenic heavy metals input into the river.

In recent years, the accumulation of heavy metals in the environment has received increased attention from both scholars and officials saddled with legislation. This attention is primarily due to their harmfulness and persistence in the surrounding environment and consequent buildup in aquatic plants and animals (Guan *et al***.,** 2014**)**. The quality of sediments is a very important factor in defining the pollution forms or nature of river or marine systems. This is because they act as both transporters and sinks for environmental pollutants, and also provides important historical information of pollution and the input sources of pollutants into the aquatic systems (Forstner and Wittmann, 1981; Devesa-Rey *et al*., 2010). Heavy metal concentrations higher than required levels have toxicological character in aquatic environment. The buildup of trace metals in any water environment and sediments is contingent on diverse influences, which are the type of sediment constituents and the physicochemical conditions under which the environment is operating (Nemr *et al*., 2007). Generally, the discharge of heavy metals and other environmental pollutants to the shoreline zones is on the increase majorly due to the fact that economic activities is on the rise worldwide (Nasehi *et al.,* 2012). Since sediments is the final sink for contaminants and pollutants, at certain concentrations, these contaminants or pollutants are re-suspended back to water and also are accumulated most especially on bottom dwelling biota, which are always in close association with the sediment. Current research have shown that pollutants, for instance heavy metals, carbon-based compounds, nutrients and disease causing organisms in sediments are universal and portend considerable hazards to humans and the aquatic populations (Maanan *et al*., 2015; Benson *et al*., 2016).

Despite the limitations of sediment quality procedures and background standards, they are extensively used determining or assessing different risk associated with heavy metal contamination in any water environments (Burton, 2002). Numerous experimental and numerical methods have similarly been established or developed in reaction to ecological concerns and as valueble pollution tools for observing water systems. Therefore this work was done to examine the concentrations, ecological risk and enrichment factor of some heavy metals in the New Calabar River

MATERIALS AND METHODS

Description of the Study Area: The New Calabar River is bordered in longitude 7°60'E and latitude 5°45'N in

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the coastal region of Rivers State, Niger Delta, Nigeria. The river releases its water to the Atlantic Ocean. The Rumuolumeni/Akpor area where the river cut across is one of the industrial hubs of the state and come next to Trans Amadi Industrial Layout. Industries situated along its bank discharge its effluents into it. The river is under constant navigation by oil and allied industries and its under constant dredging and forest operations (transportation of log of wood). The University of Port Harcourt and the Ignatius Ajuru University of Education are sited along its bank. There is the recent addition of illegal oil bunkering activities in the river.

Sample Collection and Preparation: Sediment samples were collected with the aid of plastic trowel during low tide and wrapped with polythene bags to avoid contaminations and taken to the laboratory. In the laboratory, the samples were air dried until there was no weight change. Thereafter, the samples were macerated in a ceramic mortar with a pestle and sieved with 1mm mesh. The obtained powdered sediments were then stored in tightly closed glass bottles. Two grams (2g) of the dried sediment was digested according to the method of Marcus and Edori, (2016) and thereafter filtered to obtain the digest.

Sample Analysis: The digests were then analysed with atomic absorption Spectrophotometer (AAS) to obtain the concentrations of the heavy metals.

Model Assessments: The results obtained for the heavy metals were then assessed with model equations on contamination and pollution to ascertain their implications on the environment. These models include contamination factor, ecological risk index and enrichment factor.

Contamination Factor: The Contamination Factor (CF) of the heavy metals measured was calculated as (Lacatusu, 2000):

$$CF = \frac{Cm}{Cb}$$

Where Cm = the measured concentration of metal in the sample and Cb is the background concentration of the same metal in average shale or any other standard (for this study it is DPR standard). The interpretation of contamination index is based on the following intervals as proposed by Lacatusu (2000) CF = 0 – 1.0 signifies contamination; 1.1- 4.0, slight to moderate pollution; 4.1-8.0 Severe pollution; 8.1-16.0 Very severe pollution; >16.0 Extreme pollution.

Ecological Risk: The Ecological risk (Er) assessment of Heavy metals was calculated as (Hakanson, 1980):

$$Er = Tr \text{ x } CF$$

Where Tr is the toxic response factor (numerical values are assigned to individual elements) and CF is the contamination factor of single metals. The terms used to interpret ecological risk is based on the suggestion of Hakanson (1980), they are: Er <40, low ecological risk; 40 < Er ≤80, reasonable ecological risk; 80 < Er ≤160, significant ecological risk; 160 < Er ≤320, pronounced ecological risk; and >320, severe ecological risk; (2)

Enrichment Factor: The Enrichment Factor (EF) analysis of the measured heavy metals was calculated as (Buat-Menard and Chesselet, 1979):

$$EF = \frac{(Cn/Cref)sample}{(Bn/Bref)}$$

Where Cn is the concentration of metal measured in the sample, Cref is the concentration of the reference material (in this study it is Fe), Bn is the background concentration of the examined metal and Bref is the concentration of the reference element (Fe). The Enrichment factor classes were predicted on the foundation of the following categories: EF < 2 absence to negligible enrichment, EF = 2-5 reasonable enrichment, EF = 5-20 severe enrichment, EF = 20-40 excessive enrichment and EF>40 exceptionally high enrichment (Manno *et al*., 2006).

RESULTS AND DISCUSSION

The results of heavy metals concentrations in the sediment are given in Table 1. The concentrations of Nickel (Ni) obtained at Choba station was the highest and followed by Iwofe station, while Aluu and Elibrada had the same value. The value ranged from 2.02 – 5.05 mg/Kg. The results obtained were below permissible limit value proposed by DPR. This result is far below the values obtained on sediments in Euphrates River, Iraq (Emad *et al.* (2012). The low values obtained in sediments at the various locations can be attributed to river current which moves most of the dissolved metals that should have settled within the river bed. Cadmium (Cd) values within the sampled stations ranged from 0.004 – 0.032 mg/Kg. The values obtained were lower than the 0.8 mg/Kg (the average value in shale). However, these values corroborated the findings of Ideriah *et al.,* (2012) on sediments of Abonnema shoreline, in Akuku Toru local government area, Rivers State, Nigeria. Though Cadmium at high concentration is harmful but the result from this work

shows no reason for concern. The concentrations of lead (Pb) ranged from 1.43 - 4.12 mg/Kg. These values showed the presence of lead addition to the sediment. These values are very low when compared to those observed by Saha and Hossain, (2011) in Buriganga River, Bangladesh, which ranged from 60.3 to 105.6 mg/Kg. Lead (Pb) is a poisonous metal and have carcinogenic characteristics. It also inhibits the effectiveness of many natural systems in the body. Increased concentration of Pb could be poisonous and

could cause serious disease. Iron (Fe) concentrations in the sediment varied from 13.67 – 247.99 mg/Kg. Although Iron (Fe) is beneficial to both human and animals, but dangerous if consumed in high amount. The observed values of Fe in the sediment at the different locations are lower than the world average value and the DPR requirement for soil and sediment in Nigeria. Iron plays an important role in blood circulation and also the centre of the haem-porphrin in blood (Edori and Kpee, 2018).

Table 1: Heavy Metal Concentration in Sediment from New Calabar River

| Heavy Metal (mg/L) | Location | | | | | |
	Elibrada	Aluu	Choba	Iwofe	Mean±SD	DPR Standard
Ni	2.02	2.02	5.05	4.90	3.50±1.48	3.5
Cd	0.032	0.004	0.031	0.29	0.089±0.12	0.8
Pb	1.50	1.43	2.61	4.12	2.42±1.09	85
Fe	13.67	120.79	247.99	208.90	147.84±90.13	38000
Cu	1.38	1.50	4.07	2.98	2.48±1.11	36
Zn	3.10	3.99	6.84	8.01	5.49±2.01	140
As	0.002	0.002	0.013	0.007	0.006±0.005	1.0
Cr	2.88	2.09	4.05	4.66	3.42±1.00	100

The concentrations of Copper (Cu) varied from 1.38 – 2.98 mg/Kg within the sampled stations. All the results were below average levels or concentration in shale. The levels of copper in sediment from this work were far below those reported by Singh and Upadhyay, (2011) on sediments of Ramgarh Lake, UP, India. The low level of copper may be attributed to the fact that industries within these areas do no release copper into the environment. Zinc (Zn) levels in this study varied from 3.10 – 8.01 mg/Kg within the stations. This value is very low when compared with the DPR standard of 36 mg/Kg. Also, in this study, the values were lower than those observed by Mohammed and Folorunsho (2015) in samples within Kaduna metropolitan city, Northern Nigeria. The low level of Zinc metal was not far fetch as there are relatively little activities that could influence the release of Zinc into the environment. Secondly the housing areas are far away from the sampled site. The level of arsenic (As) recorded across all the locations ranged from 0.002 – 0.013 mg/Kg. the observed value of As in this work is lower than those of the world average value in shale and DPR standard. Arsenic even at very low concentration is poisonous and very harmful (Edori and Kpee, 2016). Therefore, its release to any environmental media should be discouraged. Chromium (Cr) was observed to fall within the range of 2.09 – 4.66 mg/Kg within the sampled stations. These results were below the average value in shale and DPR requirement in soil and sediment. This was far below works by Saha and Hossain (2011) in Bangladesh rivers sediment. This concentration of chromium is high and could be due to continuous human activities along the coast of these stations. The

contamination factor values are given in Table 2. The contamination factor values calculated from the heavy metals results showed that all the sediment bound metals in the different stations fall within the 0-1 range (which is no contamination to negligible contamination), except Ni at Choba and Iwofe which were within the slight to moderate contamination range. This implies that anthropogenic input were minimal or insignificant. Contamination factor is used to interpret the extent of heavy metals impact on the contamination of any environment (water, sediment, soil or air) (Edori and Kpee, 2017).

Table 2: Contamination Factor (CF) of Heavy Metals in Sediment Samples from New Calabar River

Metal	Elibrada	Luu	Choba	Iwofe
Ni	0.577	0.577	1.443	1.4
Cd	0.04	0.005	0.039	0.363
Pb	0.018	0.017	0.031	0.048
Fe	0.000	0.003	0.007	0.005
Cu	0.038	0.042	0.113	0.083
Zn	0.022	0.029	0.049	0.057
As	0.002	0.002	0.013	0.007
Cr	0.029	0.021	0.041	0.047

Table 3: Ecological Risk Assessment of Heavy Metals in Sediments from New Calabar River

Metal	Elibrada	Aluu	Choba	Iwofe
Ni	2.885	2.885	7.215	7.00
Cd	1.20	0.150	1.170	10.89
Pb	0.09	0.085	0.155	0.240
Cu	0.19	0.210	0.565	0.415
Zn	0.022	0.029	0.049	0.057
As	0.020	0.020	0.130	0.070
Cr	0.058	0.042	0.082	0.094

Table 4: Enrichment Factor of Heavy Metals in Sediments from New Calabar River

Metal	Elibrada	Aluu	Choba	Iwofe

Ni	1604.349	1604.349	221.092	254.667
Cd	111.192	1.573	5.938	65.941
Pb	49.055	5.293	4.705	8.817
Cu	106.559	13.108	17.324	15.123
Zn	61.553	8.966	7.486	10.408
As	5.559	0.629	1.992	1.273
Cr	80.059	6.575	6.208	8.477

The ecological risk assessment of the experimental data is given in Table 3. The values obtained for ecological risk for all the metals examined in this study were below the base value of 40 (the beginning point of ecological risk assessment). This implies that the examined metals do not pose ecological risk or threat to the environment. This observation is in agreement with the findings of Mahmoud *et al*., (2017) in surface sediments of New Valley, Western Desert, Egypt. .

The enrichment factor values from the present study is given in Table 4.The values obtained in this study showed that Ni was exceptionally enriched in all the sample stations, Cd was exceptionally enriched at the Elibrada and Iwofe stations, Pb, Cu, Zn and Cr are exceptionally enriched at the Elibrada station. Cd at Aluu, As at Aluu, Choba and Iwofe showed absence to negligible enrichment. All the other metals showed severe enrichment in the remaining stations. The result obtained for enrichment factor is an indication of anthropogenic influence on the presence of some of the metals in the environment (Han *et al*., 2006).

*Conclusion***:** The results of this investigation offered important information on the level of metal contamination in the surface sediments of the New Calabar River within the Elibrada – Iwofe axis of the river. The order of distribution of the metals were Fe > Zn > Ni > Cr > Cu > Pb > Cd > As. Contamination factor and ecological risk assessment indicated heavy metals risk free environment. However, enrichment factor analysis showed signs of anthropogenic influence in the heavy metals input into the environment. Thus providing basis for continuous monitoring.

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