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Geochemical Index, Ecological Risk and Enrichment Factor of Heavy Metals in Sediments at Drainage Discharge Points into the New Calabar River, Rivers State Niger Delta, Nigeria

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Abstract Sediment samples were obtained from points where drainage of effluents were discharge into the New Calabar River. The samples were collected for a period of four months and analyzed for heavy metals using atomic absorption spectrophotometer (AAS). The heavy metals examined were iron (Fe), manganese (Mn), lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr) and zinc (Zn). The result of the heavy metals showed that the mean values of the measured heavy metals were Fe (177.111±16.984mg/Kg), Mn (47.946±2.245mg/Kg), Pb (3.102±0.254mg/Kg), Cd (0.216±0.132mg/Kg), Ni (4.537±0.466mg/Kg), Cr 4.156±1.154mg/Kg) and Zn (2.298±1.009 mg/Kg). The results of the heavy metals were then analyzed using some pollution indices so as to determine their input sources and implication in the environment. Contamination factor examination results showed that the sediment is not polluted with any of the heavy metals, some of them were at the preliminary stage of contamination. Geochemical index assessment of the heavy metals showed uncontamination of sediment with heavy metals and further to it indicated a non-anthropogenic source of heavy metals, which more or less indicated natural sources of heavy metals in the sediment. Ecological risk factor assessment showed that the sediment heavy metals do not pose any risk to ecological existence of biomes. Enrichment factor analysis indicated that there was significant enrichment with Mn, Pb, Cr and Cu in the stations, very high enrichment with Ni in the stations, butthere was a range of significant enrichment to extremely high enrichments with Cd in the sediments at the sampled points. Therefore, the point of drainage discharge into the river should be adequately monitored to prevent excessive discharge of heavy metals.

Keywords Geochemical index, ecological risk, enrichment factor, heavy metals, sediment

Introduction

The understanding that the earth is undergoing life-threatening environmental complications as a result of fast depreciation of natural resources is increasing. The destruction of nature due to human survival strategic activities has culminated in putting the continuous existence of the ecosystem at risk. The desire for a better living has resulted in migration to urban areas which have caused the clustering of human population explosion at specific areas of the world. This has further culminated in fear of certain environmental health conditions because of the enormous amount of wastes discharged in these areas [1].

It is a well-known fact that sediments quality has been duly compromised due to the influence of anthropogenic activities. These activities, has culminated into the ever rising amount of heavy metals that are present in water

environments such as sediment. Sediment as the ultimate sink for environmental toxicants have been documented to absorb tenacious and deadly substances to concentrations which are many folds greater than that which the water matrix holds [2-3].

The presence of heavy metals in the environment can be traced to human and rock sources and are characterized by stability and tenacity when discharged into waters and sediments. When the concentrations of these metals are higher than required in the aquatic environment, they become sources or reasons for concern because they are injurious and are not subject to biodegradation naturally. The presence of these metals in sediment is a sign of hazard to marine life in numerous ways, particularly because when the flow pattern becomes turbulent, they are re-suspended back to the water matrix [4-6], they are accumulated in bottom dwelling aquatic animals that forage for food in sediments and also put back to the food chain and web to yield a variety of metabolic, physical and biological conditions [7-8].

At the time when the effect of human activities has contributed immensely to the aquatic heavy metal burden, the biological, geological and chemical processes within the ecosystem is being changed. This change in the properties of the environmental cycle and contaminant agents are precursors of toxic environment to aquatic creatures [9]. Sediments are central constituents of the natural ecosystem where poisonous chemicals gather. The accumulation of these component toxicants is occasioned over multifarious physical and chemical adsorption pathways which is a factor of the type and composition of the sediment background and the physicochemical characteristics of the compounds adsorbed [10-11]. Most often, the presence of heavy metals in the environment beyond threshold levels are due to human activities. The pathways, concentrations and toxicity of contaminant agents for instance heavy metals present in the coast of water environment is a common concern because of their high toxicity to plants and animals and the extent to which they can alter the prime output of the shoreline environs [12]. Therefore, this article was carried out to examine the geochemical, ecological risk and enrichment factor of heavy metals concentrations in drainage discharge point along the New Calabar River, Port Harcourt, Nigeria.

Materials and Methods

Collection and Preparation of Sediment Samples

The collection of sediment samples was achieved with the use of plastic trowel to scoop the surface of the sediment to a depth of 10 cm. They were immediately put into polyethene bags and placed in ice-cold containers and moved to the laboratory. The sediment samples were allowed to air dry freely to constant weight for four weeks. The samples were finely ground and hard particles removed without crushing them. Before maceration of the samples, they were sorted to remove pieces of wood, leaves, bones and stones. The fine samples were sieved with 2 mm mesh into pre-cleaned glass bottles and stored in a dry cupboard.

The finely pulverized particles were digested using a mixed volume of hydrochloric acid (HCl) and nitric acid (HNO_3) in a 3:1 ratio. The digestion was done in a Teflon container at 110 °C. The final solutions werefiltered into 100 ml Erlenmeyer volumetric flask and made up to 50 ml mark with de-ionized water. The filtrates were transferred into 50 ml plastic vials and tightly closed and then refrigerated at 4 °C for 10 days before analysis to be done.

The final filtrates were analyzed using flame atomic adsorption spectrophotometer (AAS), 71096 SolaarThermo Elemental detector model. Triplicate examination of the samples were done and the results computed as mean±SD. The result obtained were validated by the method of Marcus and Edori, (2016). The data obtained were subjected to statistical analysis using excel package in a personal computer.

Assessment of Heavy Metals Pollution Using some Indices

Different pollution indices were used to assess the level of effect posed by heavy metals on the environmental ecology of the area investigated. The indices used were contamination factor, pollution index, geo-accumulation index, ecological risk factor and enrichment factor.

Contamination Factor

The level of contamination of sediment by the heavy metals was assessed using the contamination factor. It describes the contamination status of any sediment contaminated with heavy metals. It is a sole factor examination of individual metals in environmental media. The contamination factor was proposed by Lacatusu [13] and expressed as:

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

Where CF is the contamination factor, Cm is the concentration of the examined metal and Cb is the standard value recommended for the metal by standard organizations, national values or specific values from supposed uncontaminated sites considered as background value. In this case, the national background values proposed by DPR [18] was used for all the calculations.

Pollution Index

The pollution index is a joint assessment index that establishes the level of pollution associated with the combined effect of all the individual metals examined.

The Pollution Index (PI) equation applied is mathematically shown as:

Pollution Index (PI) = n√(CF1 X CF2 X CF3 X… X CFn)

Where, CF, Cb, Cm and n represents contamination factor, background value, metal concentration and n = number of metals examined

The interpretation of the values observed for contamination factor and pollution index are based on the significance of intervals chart proposed by Lacatusu [13] as follows:

<0.1 (very minor contamination), 0.10-0.25 (minor contamination), 0.26-0.5 (reasonable contamination), 0.51-0.75 (severe contamination), 0.76-1.00 (very severe contamination) 1.1-2.0 (minor pollution), 2.1-4.0 (reasonable pollution), 4.1-8.0 (severe pollution), 8.1-16.0 (very severe pollution) and >16.0 too much pollution.

Geo-accumulation index (I-geo)

The geochemical index which was suggested by Muller [14] was used to categorize the category of contamination of the sediment by heavy metals and also predict the sources of the metals and other chemical species that might be present in the medium (sediment or soil). It is a sole factor index of distinct metal evaluation that relates the value of the heavy metal gotten from a given sediment sample with that of original (uninfluenced) value or the average value of the metal in shale.

Geo-accumulation index was calculated based on the formula of Muller [14] as;

$$\mathrm{I-geo} = \log 2\,(\frac{Cn}{1.5\,Bn})$$

Where, Cn = Concentration of heavy metal in the sediment.

Bn = Geochemical background value of the metal in shale

The 1.5 value introduced is due to possibility of changes that may occur from background data geological differences. The interpretation of the eight classes of I-geo grouping (0 -7) and interpretations are given as: class 0 is I-geo ≤ 0 (practically uncontaminated), class 1 is 0 < I-geo < 1 (uncontaminated to moderately contaminated), class 2 is 1<I-geo<2 (moderately contaminated) 3 is 2 < I-geo < 3 (moderately to heavily contaminated), class 5 is 3 < I-geo < 49 (heavily contaminated), class 6 is 4 < I-geo < 5 (heavily to extremely contaminated) and 7 is 5 < I-geo < 6 (extremely contaminated).

Ecological Risk Factor (ERF)

The ecological risk factor (ERF) is used to state the probable environmental hazard of a single metal or other contaminants present somewhat in river environment [15].

The formula is arithmetically expressed as:

$ERF = Tr\ x\ CF$

Where Tr = toxic-response factor for a given chemical specie and

CF= the contamination factor of the specie.

The terminologies used to interpret the ecological risk factor (ERF) are;

ERF <40 is low risk, 40≤EFR<80 is moderate risk, 80≤EFR<160 is considerable risk, 160≤EFR<320 is high risk and ERF≥320 very high risk.

Enrichment Factor

The data for enrichment factor (EF) is used to evaluate between regional geochemical changes, besides the forecasting of the origin and source of heavy metals distribution in any surrounding [6].

The formula which was first suggested by Buat-Menard and Chesselet [16] and was applied to estimate the enrichment factor. This is simply expressed as:

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

Where C_n (sample) = concentration of the studied element,

C_{ref} (sample) = concentration of the studied reference element in the environment,

B_n = background value of the reference element and

B_{ref} = background value of the reference element in the reference environment in average shale [17], but for this work, the DPR [18] were used as the background concentrations.

The reference element used in this research is iron (Fe), whose target value is given by DPR [18] as 38000 mg/Kg. The categories and terminologies for interpretation of the different value ranges for enrichment factor was put forward by Sutherland *etal*. (2000) and they are; EF < 2 is deficient to minimal enrichment, 2 ≤ EF < 5 is moderate enrichment, 5 ≤ EF < 20 significant enrichments, 20 ≤ EF 40 is very high enrichment and EF > 40 extremely high enrichments.

Results and Discussion

The results of the heavy metals are shown in Table 1. Iron (Fe) values in the stations varied from 163.891±24.085 - 201.087±3.744 mg/Kg. The highest value was observed at the Iwofe Jetty station and the lowest value observed at the Minipiti station. The mean concentration of Fe within the experimental period was 177.111±16.984 mg/Kg. The results of Fe in the examined sediments in the various stations in the present work are lower than those of Mohd *et al*. [19], in Balok River sediments in Pahang, Malaysia, where concentrations of Fe ranged from 32244 – 67104 mg/Kg and also those of Balamurugan *et al*. [1], in the Sediments of Kodaikanal Lake, Tamil Nadu, India, where very high values of Fe within the range of 102000 – 109000 mg/Kg were observed.

The results for manganese (Mn) concentrations in the examined stations showed that it varied between 44.833±1.424 – 50.042±0.264 mg/Kg. The highest concentration of Mn was observed at the Minipiti station and the least at the Police Post station. The mean concentration of Mn within the experimental period was 47.946±2.245 mg/Kg. The observed concentrations of Mn in sediments from effluents ensuing from drainage at the discharge points in the present work is slightly lower than the values observed in sediment at the point where the Mediterranean Sea exchange water with the Boughrara lagoon in southeastern Tunisia, in which concentration values were in the range of 66.8 – 91 mg/Kg [12] and also lower than those of Yousry *et al*. [20], in Nile bed sediments, where concentrations of Mn varied from 15.60 – 4536.40 mg/Kg.

The results for lead (Pb) concentrations in the examined stations showed that it varied between 2.863±0.203 - 3.453±0.317mg/Kg. The highest concentration ofPb was observed at the Minipiti station and the least at the Police Post station. The mean concentration of Pb within the experimental period was 3.102±0.254mg/Kg. Pb levels observed in the present work is lower than those of Bassey and Ifedayo [21], in two notable creeks of the Great Kwa River, Southeastern Nigeria, where they observed concentrations in the range of 16.58 - 25.2 mg/Kg in Mbat Abbiati Creek and 15.55 - 37.65 mg/Kg in Oberakhai Creek and also the values observed in sediments of Kodaikanal Lake Tamil Nadu, India, where the observed concentrations ranged from 20 - 97 mg/Kg [1].

The results for cadmium (Cd) concentrations in the examined stations showed that it varied between 0.050±0.015 - 0.372±0.033 mg/Kg. The highest concentration ofCd was observed at the Iwofe Jetty station and the least at the Police Post station. The mean concentration of Cd within the experimental period was 0.216±0.132 mg/Kg. the concentrations of Cd in this work is higher than those of Marcus and Edori [22], in sediments of Bomu and Oginigba Rivers, where Cd was not detected in any of the sediment samples, but within the value range observed in sediment samples from the main stream of the new Calabar River, in which concentrations ranged from 0.004 – 0.29 mg/Kg [23].

The results for nickel (Ni) concentrations in the examined stations showed that it varied between 4.133±0.570 - 5.190±0.439 mg/Kg. The highest concentration on Ni was observed at the Iwofe Jetty station and the least at the

Minipiti station. The mean concentration of Ni within the experimental period was 4.537±0.466 mg/Kg. Ni content in the sediment from the effluent discharge points (this present work) is within the range of the observed values (2.02 - 5.0 mg/Kg) in the New Calabar River [23], but lower than the values of 8.19±2.25 -18.07±2 mg/Kg in sediments of theBushehr province of the northern Persian Gulf [24].

The results for chromium (Cr) concentrations in the examined stations showed that it varied between 2.937±0.168 - 5.705±0.796 mg/Kg. The highest concentration of Cr was observed at the Iwofe Jetty station and the least at the Minipiti station. The mean concentration of Cr within the experimental period was 4.156±1.154 mg/Kg. The measured value of Cr in the sediments at the effluent discharge points are lower than the values observed in the sediments of the Bushehr province of the northern Persian Gulf, whose mean values ranged from 10.19±5.97 – 16.82±3.05 mg/Kg [24] and also those of Haxhibeqiri *et al*. [25], in sediments from surface sediments of in Drini Bardhë River, Kosovo, where concentration values ranged from 43.1 - 265.4 mg/Kg.

The results for copper (Cu) concentrations in the examined stations showed that it varied between 1.374±0.332- 3.702±0.226 mg/Kg. The highest concentration of Cr was observed at the Iwofe Jetty station and the least at the Minipiti station. The mean concentration of Cr within the experimental period was 2.298±1.009 mg/Kg. The measured value of Cu in the sediments at the effluent discharge point were lower than those of Bibak *et al*. [24], in sediments of the Bushehr province of the northern Persian Gulf, whose mean values ranged from 3.45±0.77 - 5.5±2.83 mg/Kg and also lower than the values of Cu observed in Bomu and Oginigba Rivers, Port Harcourt, Nigeria where the mean concentration for each river sediment was 66.301 ±38.152 and 74.610 ± 27.152 for Bomu and Oginigba Rivers respectively [22], but within the same value range observed by Nwineewii *et al*. [23], in New Calabar River sediment where concentrations were in the range of 1.38 - 4.07 mg/Kg.

The observed mean concentrations of each heavy metal examined in the sediments at the discharge points into the New Calabar River in the present work were generally lower than values quoted in the DPR [18] target values for the concentrations of individual heavy metal in soil or sediment. The low level of heavy metals observed in the present work may be due to the geologic nature of the soil within the area and the nature of waste passed to the drainage, which were eventually discharged to the river. Other factors that may have been responsible for the low concentrations of the heavy metals might be due to influences that are associated with fluctuations in lithological contributions, water and sediment dynamics, flow pattern, ecological landscapes, traditional influences and the nature of the vegetation [26]. Also, the natural organic matter of the sediment enhances the capacity of the sediment to hold more or less of heavy metals within its matrices and further added to this is the nature of metal-organic complexes that are possibly formed in the sediments can form associations that can either hold large or little quantity of heavy metals [27].

Table 1: Heavy metals concentrations at the different drainage discharge points

Heavy Metals	**Stations**			**Mean±SD**	**DPR [18]**
(mg/Kg)	**Iwofe Jetty**	**Minipiti**	**Police Post**		**Value**
Fe	201.087±3.744	163.891±24.085	166.354±14.348	177.111±16.984	38,000
Mn	48.963±2.304	50.042±0.264	44.833±1.424	47.946±2.245	850
Pb	2.990±0.070	3.453±0.317	2.863±0.203	3.102±0.254	85
Cd	0.372±0.033	0.227±0.072	0.050±0.015	0.216±0.132	0.8
Ni	5.190±0.439	4.133±0.570	4.287±0.318	4.537±0.466	35
Cr	5.705±0.796	2.937±0.168	3.827±0.103	4.156±1.154	100
Cu	3.702±0.226	1.374±0.332	1.818±0.236	2.298±1.009	36

The contamination factor of the heavy metals are shown in Table 2. The contamination factor values for Fe varied from 0.004 – 0.005, Mn varied from 0.053 – 0.059, Pb varied from 0.034 – 0.041, Cd varied from 0.063 - 0.465, Ni varied from 0.118 – 0.148, Cr varied from 0.029 – 0.057 and Cu varied from 0.038 – 0.103. Following the data obtained for the different values in each of the heavy metal and being interpreted on the basis of intervals of contamination factor [13], showed that the sediments from the different stations were not contaminated with Fe, Mn, Pb and Cr. The sediment was uncontaminated with Cd at the Police Post station, but reasonable contaminated at the Iwofe Jetty and Minipiti stations. The sediment was not contaminated with Cu at the Minipiti and Police Post

stations but very minor contamination at the Iwofe Jetty station. Ni in sediment showed minor contamination in all the three stations examined. The results of the contamination factor of the heavy metals can generally indicate that the sediment is yet to be polluted by any of the metals. This is because the observed values were yet far below the values of the reference concentrations of each of the individual metals.

Table 2: Contamination factor of heavy metals at the different drainage discharge points

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	**Minipiti**	**Police Post**
Fe	0.005	0.004	0.004
Mn	0.058	0.059	0.053
Pb	0.035	0.041	0.034
Cd	0.465	0.284	0.063
Ni	0.148	0.118	0.123
Cr	0.057	0.029	0.038
Cu	0.103	0.038	0.051

The results of geochemical index of the heavy metals from the different stations are given in Table 3. The different geochemical accumulation index in individual metals showed that Fe varied from -2.176 to -2.273, Mn was -1.104 to -1.151, Pb was -1.262 to -1.344, Cd was -1.076 to -0.422, Ni was -0.705 to -0.803, Cr was -1.119 to -1.413 and Cu was -0.862 to -1.295. the typical range of the results of the I-geo analysis of the heavy metals fall into the 0 category, which implies that the sediments were practically uncontaminated by the heavy metals. Furthermore, the result points out to the fact that anthropogenic influence of heavy metal input may have been very little or negligible or that as a result of the tidal nature of the river, at high tide whatever may have been deposited are like washed off to the main stream of the river.

Table 3: Geochemical index of heavy metals at the different drainage discharge points

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	**Minipiti**	**Police Post**
Fe	-2.176	-2.273	-2.273
Mn	-1.112	-1.104	-1.151
Pb	-1.331	-1.262	-1.344
Cd	-0.208	-0.422	-1.076
Ni	-0.705	-0.803	-0.785
Cr	-1.119	-1.413	-1.295
Cu	-0.862	-1.295	-1.167

The ecological risk factor values of the metals from sediments collected from the drainage discharge points are shown in Table 4. The values showed the following variation; Mn (0.053 – 0.059), Pb (0.169 – 0.2013), Cd (1.875 – 13.95), Ni (0.591 – 0.742), Cr (0.059 – 0.114) and Cu (0.191 – 0.514). The ecological risk factor values observed in the sediment showed very slight variation between the station in all the heavy metals examined except for Cd which showed a slightly noticeable variation with Iwofe station having a value up to 13.93 when compared to those of Minipiti (8.514) and Police Post (1.875) stations. The inference that can possibly be deduced from the ecological risk factor data obtained from this study when compared with Håkanson [15], indicted that the heavy metals posed no risk to the ecological environment. This assertion is based on the fact that all the observed values were below 40, which is the base point of ecological risk factor assessment.

Table 4: Ecological Risk factor of heavy metals at the different drainage discharge points

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	**Minipiti**	**Police Post**
Mn	0.058	0.059	0.053
Pb	0.176	0.203	0.169
Cd	13.95	8.514	1.875
Ni	0.742	0.591	0.613
Cr	0.114	0.059	0.077
Cu	0.514	0.191	0.253

The enrichment factor values of the metals from sediments collected from the drainage discharge points is shown in Table 5. The values showed the following variation; Mn (10.886 – 13.650), Pb(6.647 – 9.419), Cd (14.277 – 87.873), Ni (27.380 – 28.022), Cr (6.810 – 10.781) and Cu (8.849 – 19.433). The enrichment factor values for the heavy metals when juxtaposed with the interpretation proposed by Sutherland *et al*. [28], in the different intervals of enrichment by heavy metals showed that the sediments were significantly enriched with Mn, Pb, Cr and Cu in all the stations. Ni in sediment showed very high enrichment in all the stations, Cd in the sediment showed significant enrichment in the police post station but showed extremely high enrichments at the Iwofe jetty and Minipiti stations. The enrichment factor values implicated anthropogenic contribution of heavy metals (although not yet close to the reference value) in the investigated stations [23].

Table 5: Enrichment Factor of heavy metals at the different drainage discharge points

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	**Minipiti**	**Police Post**
Mn	10.886	13.650	12.048
Pb	6.647	9.419	7.694
Cd	87.873	65.791	14.277
Ni	28.022	27.380	27.979
Cr	10.781	6.810	8.742
Cu	19.433	8.849	11.536

Conclusion

The values of the heavy metals examined in the sediment in this work is still at levels that are yet to pollute the sediment. The contamination factor results showed that the sediment is free from pollution. Geochemical accumulations indicated non contamination by any of the heavy metals and also showed that the concentrations of the metals were still within natural occurrence stages. Ecological risk assessment indicated a sediment that is free of risk to biological inhabiters of bottom sediment and enrichment factors assessment showed that the sediments were extensively enriched with heavy metals at varying degrees. Although, the sediment seems safe at the moment, yet proper surveillance should be put in place to avoid any serious input of heavy metals through these routes to the river.

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