Geo-accumulation and Ecological Risks of Heavy Metals in Sediments of Andoni River, Rivers State, Niger Delta, Nigeria

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Abstract: - **The effect of human activities on natural environment has led to alterations in the natural state of the environment, which has led to contamination or pollution at different levels. Sediment samples collected from Andoni River, Rivers State, Nigeria, were analyzed for heavy metal content. The result revealed that the concentrations of the heavy metals were in the order Fe > Zn > Mn > Cu > Cd > Pb > As. Contamination factor analysis indicated that all the metals at the different stations fall within uncontamination to contamination category except Cu which was observed to fall within moderate contamination, Cd which was within moderate contamination at Mbiaka station and Zn where all sediment samples indicated pollution. Pollution load index analysis indicated a contamination free sediment. Geo-accumulation index analysis of sediment heavy metals showed that the sediment is uncontaminated with Fe, Mn, Pb and As, slightly contaminated with Cu and Cd (at some stations) and extremely contaminated with Zn. Ecological risks analysis showed asediment whose heavy metal content did not pose risk to the ecology, but if the condition continuous unabated, may be at risk of Zn and Cd. Therefore, controlled effort be applied to ascertain the anthropogenic input sources of Zn and Cd in the environment to avoid near future effects.**

Keywords: **Geo-accumulation, ecological risk, sediment, heavy metals, anthropogenic activities, contamination**

I. INTRODUCTION

Waterpollution majorly arises from anthropogenic inputs above natural background concentration within a specified environment. The presence of environmental toxicants or pollutants in any ecological environment whether aquatic or terrestrial reduces not only the quality of such environment but also its use or applicability by natural dwellers (both plants and animals) within such locality (Krishna *et al*., 2009; Ibrahim *et al*., 2016). Global attention has greatly shifted to the contamination of aquatic environments by heavy metals. This not only because of its toxicity, but also its persistence and abundance in the environment (Islam *et al*., 2015). Natural factors and human activities affect the concentration or abundance of heavy metals in the environment (Khan *et al*., 2008). Rapid increase in the number of industries and population drift to urban centres has led to increased levels of heavy metals and organic pollutants in the environment (Sedky *et al*., 2013).

Heavy metals are considered as important intermediates of pollution in aquatic environments and public health studies (Khaled *et al*., 2012). This is due to the fact that they can induce certain disease conditions and also when they are released they get deposited on sediment and can later be immobilized depending on the prevailing condition within the environment (Marcus and Edori, 2016). Heavy metals sometimes are found at trace concentrations. They can be immobilized within the sediment through re-suspension, absorption, precipitation and co-precipitation with other elements in the form of oxides and hydroxides (Mohiuddin *et al.*, 2010; Awofolu *et al*., 2005) and also undergo complex formation reactions.

Heavy metals do not undergo biodegradation, and so can be concentrated along the food chain. Therefore, their toxic effects in most cases are felt or observed at points that are distances removed from the source of pollution (Tilzer and Khondker, 1993). Human exposure to heavy metals have been associated with several diseased conditions in man, animals and plants, more especially when they are present at high concentrations (Saha and Hossain, 2011).

In order to properly monitor and restore the integrity of any water body, there is the need to adequately protect the sediment quality of that aquatic system. This will further help to preserve aquatic life, wild life and human well-being (Issa *et al.*, 2011). Sediment is known to be the final sink for pollutants in aquatic systems and also a very important part of aquatic ecosystem. It serves as a habitat, food source, spawning ground and rearing areas for many aquatic plants and animals (Issa *et al*., 2011).

This study was therefore carried out to examine the concentration of some heavy metals in sediment in Andoni River, Rivers State, Niger Delta, Nigeria.

II. MATERIALS AND METHODS

Study Area

Andoni is an urban area located in Rivers State, South-South Nigeria. It has an estimated area of 233km^2 and with a population of about 211,009 people. The area lies on the latitude 4^{o}27′0′N and 4^{o}35′0′N and longitude 7^{o}29′0′E and 7^{o}39′0′E. Andoni has 76 towns and villages and the occupation of the inhabitants is mainly fishing. The Andoni River system comprises of many creeks. However, the study was restricted to five locations that where carefully chosen. They were chosen to cover the entire area, the locations were Iwoma and Otukloko in North central, Egedem in North-East, Mbiaka in the West and Inyonkon in the South.

Sample Collection

Samples were collected from bottom sediment at low tide using a grab sampler. The samples were collected to a depth of 10 cm from five locations. Within a location, three samples were taken and mixed together to form aggregate sample. Samples were collected three times at four-month interval within the sampling year. The sediment samples were immediately transferred into plastic polythene bags and placed in iced packed containers. The samples were transported immediately to the Department of Chemistry Laboratory, where the samples were stored.

Sample Preparation

The sediment samples were air dried to constant weight for a period of two weeks. Thereafter, they were homogenized to fine powder in ceramic mortar with a pestle. Stones and solid particles such as sticks and vegetables were selectively removed before grounding it to powder. The homogenized sediment particles were sieved with 2mm plastic mesh.

Sample Digestion

Precisely 2.0 g of the homogenized samples were weighed out and transferred to Teflon cups. A mixture of three acids, nitric acid (HNO_3), perchloric acid ($HClO_4$) and hydrochloric acid (HCl) were added in the ratio of 3:2:1 respectively. The acids-sediment mixture was digested in a water bath for 2 h at a temperature of 120^{o}C. Furthermore, 20 ml of deionized water was added to the mixture and continued heating for another 1 h. The content was allowed to cool and then filtered into sample bottles using Whatman size 2 filter paper. The filtrate was made up to 25 ml with deionized water and stored frozen (4^{o}C) for 24 h before being transferred to the laboratory for metallic analysis.

Laboratory Analysis of Heavy Metals

The digests were subjected to heavy metal analysis using atomic absorption spectrophotometer (AAS) model SE-71906, UK. Further validation of the data was done according to the method described in Marcus and Edori, (2016). The results were then recorded as mean ± SD.

Model Assessment

Different assessment models were used to evaluate the concentration of heavy metals in the sediment to ascertain the level of contamination or pollution of the sediment and also to determine their sources.

Contamination Factor (Cf) and Pollution Load Index

The contamination factor proposed by Lacatusu (2000) is given mathematically

as; $CF = \frac{Concentration\ \ of\ metal\ in\ measured\ \ sample\ (Cm)}{Concentrat\ ion\ of\ metal\ at\ backgroud\ \ level\ (Cb)}$,

while pollution load index which was originally suggested by Thomilson *et al*., (1980) was determined using the formula

$$PLI = CFI\ \times CF2\ \times CF3\ \times CF4 \ldots\ldots\ldots\ldots \times CFn)1/n$$

The CF and PLI are used in ranking the contamination or pollution of sediment by individual and combined effect element(s) respectively in any medium.

Where, CF = contamination factor, n = number of metals, Cm = measured metal concentration, Cb = background value. Here, the DPR (2002) target values for individual heavy metal was used as the background value. The values gotten were deduced based on the table of intervals of contamination or pollution provided(Lacatusu, 2000).

Geo-accumulation index (I-geo)

The Muller (1981) equation was used to calculate the I-geo as;

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

Cn = measured concentration of heavy metal, Bn = Geochemical background concentration in shale (represented in this case with DPR (2002) values for Nigeria). The number 1.5 was added due to possible variations that may arise in the background as a result of lithological differences. The interpretation of the data obtained was explained on the basis of seven classes of geo-accumulation index (Muller,1981).

Ecological Risk Factor (E_f)/ Potential Ecological Risk(PER)

The risk factors evaluation (E_f and PER) assess the ecological risk potential of a single contaminant and ecological risk assessment and the effects of several metals pollutants in sediment or soil respectively. The equations for the parameters are;

$$\text{Ef} = Tr\ \times \text{Cf and } PER = \sum E_f$$

Tr = toxic-response factor a given metal and CF= the contamination factor for the measured metal. Toxic response factors values are given as; Cu = Pb = 5, Cd = 30, Zn = 1, As = 10, Mn = 1 and Fe not available. Therefore, the final calculations were done by excluding the values of Fe.

The values obtained were interpreted according to terms used to interpret Ef and PER (Thomilson *et al*., 1980).

III. RESULTS AND DISCUSSION

The concentrations of the different heavy metals assessed in the sediments of Andoni River is given in Table 1. The concentrations of Fe in the sediments of Andoni River varied between 1051.33 ± 30.04 -5581.43±45.38 mg/Kg. The value of Fe obtained in the present research is higher than the values obtain in sediments of Tembi River River, Iran (Shanbehzadeh *et al*., 2014) and those of New Calabar River, Rivers State, Nigeria (Nwineewii *et al*., 2018).More so, the value of Fe observed is lower than the average value in shale. Fe is a component of blood and is responsible for its red coloration. The high level of Fe observed from the stations, might be either from geologic conditions or from different navigations and explorations within the area.

The concentrations of Zn observed in sediments from the different stations varied from 1456.91±27.25 - 4312.65±62.11 mg/Kg. These values obtained in the different stations are higher than the world average value in shale. These values as observed disagrees with the findings of Marcus and Edori, (2016) in Oginigba and Bomu Rivers, Rivers State, Nigeria, Nwineewii *et al*., (2018) in New Calabar River, Rivers State, Nigeria, despite the fact that all the rivers were in the same brackish environment. Zn is very important to plants and animals. Its importance more especially lies in its ability to catalyze the replication and transcription of enzymes and proteins (Galdes and Vallee 1983). High intake of Zn especially at over dose levels causes retarded growth and reproduction associated disorders (Nolan 2003). However, certain side effects disease symptoms are associated with Zn toxicity (Fosmire 2001).

Manganese (Mn) concentrations in sediments from different stations in Andoni River varied from 111.26±13.92 - 327.49±12.67 mg/Kg. these values are lower than the 850 mg/Kg average value in shale. The concentrations of Mn in this study is lower than the values observed in sediments of a Tropical River, Chottanagpur Plateau, India (Manoj and Padhy, 2014) and those of Yang et al., (2016) in surface sediments from a water reservoir in Zhejiang Province, China.

The concentrations of Cu in the present study varied from 18.66±4.12 - 91.58±6.33 mg/Kg in the stations. These values are either higher or lower than the world average value in shale. Sediment content of Cu as observed in this study is higher than those of Bhattacharya *etal*., (2008) in sediments of West Bengal India, but within the range of the values observed by Yang *et al*., (2016) in surface sediments in water reservoir in Zhejiang Province, China. The sources of Cu in any aquatic environment such as sediment include exploration and exploitation of minerals by mining industries and production of metals, shore weathering and other metal based activities. The importance of Cu lies in its usefulness in metabolic activities of animals and plants. However, children are not expected to be exposed to elevated levels of Cu due to its effect on them at high levels.

The concentrations of Pb in the sediment samples ranged from undetected (<0.01±0.00) - 1.02±0.00 mg/Kg. These values are lower than the average shale value. These values are lower than the values obtained in Turag River, Bangladesh (Bhuyan and Islam, 2017) and those observed in sediment samples from Qingshan Reservoir, China (Wu *et al*., 2014). The low level of Pb in this work may be attributed to non Pb producing activities within the area and also from the geologic composition of the shoreline soil and absence of Pb in runoffs transported into the river. Although the major form of transportation within the area is water transportation, which make use of gasoline, yet the value of Pb is negligible. This might imply that the gasoline might be free from the notable additive, tetra ethyl lead.

The concentrations of Cd in this research ranged from 0.35 ± 0.08 - 1.21±0.10 mg/Kg in the stations. Values obtained for Cd in the sediments were either lower or higher than shale value. The obtained values of Cd in the present research is higher than the values of Nwineewii et al., (2018) in the new Calabar River, but within the values of Ghaleno *et al*., (2015) insediments of water reservoir, Chah Nimeh of Sistan, Iran.

The concentrations of As in the sediments of Andoni River from the different stations varied from 0.27 ± 0.00 – 0.82 ± 0.06 mg/Kg which is lower than the average value in shale. These values are lower than those of Yang *et al*., (2016) in water reservoirs in Zhejiang Province, East of China and those of Wu *et al*., (2014) in Hongfeng and Baihua Reservoirs on the Yunnan-Guizhou Plateau in Southwest China. As exists in many oxidation states (+2, +3, +5 etc). It is a known human and animal poison even at very low concentrations (WHO, 2010). When animals contact As, either orally or dermally, the most affected part is the gastro intestinal track (Smith and Steinmaus, 2007) and is associated with different ailments.

Table 1: Concentration of heavy metals in sediment from selected stationsin Andoni River system in mg/Kg

Location	Fe	Zn	Mn	Cu	Pb	Cd	As
Iwoma	1051.33±30.04	1514.23±40.27	111.26±13.92	91.58±6.33	<0.01±0.00	0.35±0.08	0.27±0.00
Mbiaka	4610.09±27.63	4312.65±62.11	130.04±21.31	25.94±2.54	1.02±0.00	1.21±0.10	0.60±0.04
Egedem	5581.43±45.38	2796.78±33.63	327.49±12.67	18.66±4.12	1.01±0.00	0.72±0.00	0.52±0.13
Otukloko	2145.59±26.14	1456.91±27.25	127.04±10.22	75.26±11.05	<0.01±0.00	0.52±0.02	0.82±0.06
Inyonkon	1095.21±16.05	1743.53±29.13	138.94±15.95	56.04± 8.66	0.10±0.00	0.67±0.12	0.35±0.01

The contamination factor of the individual metals and the pollution index of the metals is given in Table 2. The contamination factor of the metals investigated showed that Fe varied from 0.0277 – 0.147in the stations. The values of contamination factor obtained for Fe showed non-contamination of the sediment with Fe. The contamination factor values observed for Zn varied between 10.407 – 30.805 in the stations. These values indicated very high to extremely polluted sediment with Zn. The values for Mn, Pb and As fall within the range of uncontaminated sediment with the different metals. The value range for Cu was 0.518 – 2.544, which indicated that the river sediments were either uncontaminated or moderately polluted with Cu and those of Cd fell within the values of 0.438 – 1.513, which symbolizes slight to low contamination. The assessment of the extent of contamination of any river sediment is based on the interpretation established in the criteria for contamination of the sediment as in this case. The criteria as given by Singovszka and Balintova, (2016) are as follows; CF > 1is classified as low contamination, 1 ≤ CF < 3 is moderate pollution, 3 ≤ CF < 6 is considerable pollution and CF > 16 is very high or extremely polluted sediment. Pollution load index of the different stations examined indicated very slight pollution by the metallic elements.

Table 2: Contamination factor (CF) and pollution load index of heavy metals in sediment from selected stations in Andoni River

Location	Fe	Zn	Mn	Cu	Pb	Cd	As	PLI
Iwoma	0.0277	10.816	0.131	2.544	0.00	0.438	0.27	0.477*
Mbiaka	0.121	30.805	0.153	0.721	0.012	1.513	0.60	0.462
Egedem	0.147	19.977	0.385	0.518	0.0119	0.90	0.52	0.441
Otukloko	0.0565	10.407	0.149	2.091	0.00	0.65	0.82	0.707*
Inyonkon	0.0288	12.454	0.163	1.557	0.0012	0.838	0.35	0.228

*Pb values not part of the calculation otherwise the result would have been 0.00

The geo-accumulation index of the metals is given in Table 3. The geo-accumulation index (I-geo) of the individual metals showed that Fe varied from 0.0184 – 0.0979, Zn varied between 6.933 – 20.536, Mn fell within the range of 0.087 – 0.257, Cu was observed to be within the range 0.345 – 1.696, Pb values ranged from 0.00 – 0.008, Cd values were within 0.433 – 1.008 and As values ranged from 0.18 – 0.547. These values when compared with the intervals of contamination or pollution as proposed by Muller, (1981) and Mohiuddin*et al.*, (2010) showed that all the stations were uncontaminated with Fe, Mn, Pb and As since they were within the category or claas of 0 (Igeo < 0). Cu was uncontaminated at Mbiaka and Egedem stations, but was moderately contaminated in Iwoma, Otukloko and Inyonkon stations. These stations were in the class 1 category (0 < Igeo < 1) of Cu contamination. The degree of contamination of Cd in the examined stations showed uncontamination except at Mbiaka that fall within the class 1. The values observed for Zn were all within the class 6, which is very high or extreme contamination (geo ≥ 5 Class 6, extremely contaminated). The I-geo result showed total anthropogenic Zn sources, while all other metals might have little or total absence of anthropogenic input sources.

Table 3: Geo-accumulationindex (I-geo) of heavy metals in sediments from selected stations in Andoni River

Location	Geo-accumulation index of Heavy Metals						
	Fe	Zn	Mn	Cu	Pb	Cd	As
Iwoma	0.0184	7.211	0.087	1.696	0.00	0.292	0.18
Mbiaka	0.0809	20.536	0.102	0.480	0.008	1.008	0.40
Egedem	0.0979	13.318	0.257	0.345	0.0079	0.60	0.347
Otukloko	0.0376	6.938	0.100	1.394	0.00	0.433	0.547
Inyonkon	0.0192	8.303	0.109	1.038	0.0008	0.558	0.233

The ecological risk factor and potential ecological risk index is given in Table 4. Zn values ranged from 10.407 – 30.805, Mn values ranged from 0.131 – 0.163, Cu ranged from 2.9 – 12.72, Pb values ranged between 0.00 – 0.06, Cd values ranged from 13.148 – 45.39 and As values ranged from 2.7 – 8.2. The PERI values ranged from 8.711 – 86.013. The results of the ecological risk factor and potential ecological risk index of the individual metals and their combined effects indicated that in all the examined stations, they do not pose any form of risk to the ecological system. This is due to the fact that all the values were within E < 30 (low risk) except for Mbiaka station that Zn is slightly above 30 and Cd is 45.39 which are in the category of E_f = 30 - 60 (moderate risk). For the PERI results, proposed values by Hakanson, (1981) revealed that all the stations were lower than the stipulated value for low risk PERI < 110 (low risk).

Table 4: Ecological risk factor (E_f)/ potential ecological risk index (PERI) of heavy metals in sediments from selected stations in Andoni River

Location	Ecological Risk Factor of Heavy Metals						
	Zn	Mn	Cu	Pb	Cd	As	PERI
Iwoma	10.816	0.131	12.72	0.00	13.148	2.7	63.815
Mbiaka	30.805	0.153	3.605	0.06	45.39	6.0	86.013
Egedem	19.977	0.385	2.9	0.0595	27.0	5.2	55.522
Otukloko	10.407	0.149	10.455	0.00	19.5	8.2	48.711
Inyonkon	12.454	0.163	7.785	0.006	25.14	3.5	49.048

IV. CONCLUSION

The indices used in the examination of the sediment heavy metals quality or condition in this study has to do with human (anthropogenic) contribution. They effectively revealed that the sediments were contaminated with Zn, Cu and Cd, but the contamination levels have not risen to the extent of pollution as to cause toxic effects or responses from aquatic organisms. The observed contamination of the sediment can cause decline in ecological environments of the river examined. This, if allowed to persist for a long time, especially for Zn, Cu and Cd. At the present condition, these metals can be made available to water through re-suspension process and can be freely taken in by edible aquatic animals, which will consequently affect the food chain negatively. Therefore, effort should be put in place to handle the input sources which we could not identify in the present study.

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