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Determination of Heavy Metal Contamination in Sediments of the Anambra River

Juliana A Israel [1], Glory J Okore [2,*], Chinyere J Madichie [1], Magdalene N Akanbi [3], Kenneth O Amanze [2], Pamela I Okeke [2] and Gabriel C Eze [4]

[1] Chemistry Department, Federal College of Education (Tech Umunze) Anambra State, Nigeria

[2] Chemistry Department, Alvan Ikoku University of Education Owerri Imo State, Nigeria

[3] Polymer Engineering Department, Federal University of Technology, Owerri, Imo State, Nigeria

[4] Western Illinois University

* Correspondence: okore.glory@alvanikoku.edu.ng

Abstract

This work investigated six heavy metals (Pb, Hg, Cd, Mn, Fe and As) in sediment samples of the Anambra River collected from five sampling points at 1km from each other. The Anambra River cuts across several towns and flows into River Niger in Anambra State Nigeria. A total of forty sediment samples were used for the study. The samples were collected from November 2017 to Feb 2018 (dry season sampling) then from May 2018 to August 2018 (wet season sampling). Metal ion concentration in the sediments was determined using Atomic Absorption Spectrophotometer (AAS). Experimental results showed the concentration of metals in the order of Fe > Mn > As > Cd > Hg > Pb (Dry season) and Fe > Mn > As > Hg > Pb > Cd (wet season). In both seasons iron, manganese and arsenic recorded higher values than other metals. Results from Contamination Factor (CF) calculation showed that all the metals analyzed (except for arsenic) exert low contamination effect on the sediment samples in both seasons. Arsenic exerts considerable contamination in dry season. This study provided information on heavy metal concentration in sediment, magnitude of contamination, likely ecological risk to man and other living organisms within the Anambra River catchment area.

Keywords: heavy metals; contamination; sampling; ecological risk; Anambra river

Introduction

Anambra River, originally called Omambala River is in Anambra State Nigeria. The river has a length of 210 km and passes through Anambra East, Anambra West, Anyamelum, and Oyi local government areas and emptied itself at River Niger in Onitsha Anambra State.   Inhabitants around the Anambra River catchment area are mainly fishermen and peasant farmers. Fertilizers, herbicides, and pesticides are normally used in agricultural activities along the riverbanks. Again, the presence of the Otuocha market within the site of study leads to the release of degradable and non-degradable solid waste from the market directly into the river. These anthropogenic activities- sewage disposal, solid waste disposal, and agricultural activities using fertilizers, herbicides, pesticides, coal ash from local ovens used by fish sellers for grilling fishes around the riverbank are washed out as run-off into the river and this results in an increase in the pollution level of the river.   Poor sanitary conditions within the communities result in the indiscriminate dumping of municipal solid waste into the river. Two climatic seasons are prevalent in Anambra State – the rainy season which starts from March to October and the dry season (November to March). The rainy season is characterized by heavy downpours, heavy flooding, soil leaching, ground infiltration, and water percolation. There are generally lower temperatures and relatively high humidity during the rainy season. The dry season is characterized by higher temperatures, low humidity, extensive aridity, and a lot of particulate generation. Rural dwellers within the Anambra River catchment area depend majorly on Anambra

River and its tributaries for water, for domestic purposes such as drinking, cooking, bathing, laundry and processing of farm produce like cassava, melon, bitter leaves, etc. With the recent increase in the use of chemicals such as fertilizers, herbicides and pesticides in agriculture, surface water bodies such as streams, lakes, and rivers are prone to pollution due to the influx of agricultural run-off and dumping of domestic wastes into water bodies The sitting of Otuocha market at the bank of Anambra River and the unrestricted use of the river as the washing zone for automobiles pre-disposes the river to a high level of anthropogenic pollution. Automobiles are known to commonly emit some poisonous gases and elements such as lead (Pb) since it has been established that Nigerian gasoline contains a significant amount of Pb that can adversely affect the environment when released [1,2].The danger inherent in heavy metal pollution of surface water, the bioaccumulation and biomagnification of toxic metals on aquatic organisms in the water, and the possible transfer to human life through the food chain, there is a need for a periodic check on the quality of this river on which many residents in Otuocha and its environs depend. Emeka et al [3] assessed the concentration of some heavy metals in water samples from Anambra River using atomic absorption spectrophotometric method, and discovered that the concentrations of Cd, Pb, Ni, Mn and Hg were reasonably higher than WHO, SON and EU permissible limits for portable water. The pollution index of the above- mentioned metals were also found to be higher than the threshold value of 1.0, which indicates high level of pollution as found in the study.

Ayogu et al. [4] evaluated the contamination level of heavy metals in Anambra drainage basin's sediment by collecting twelve samples from the basin upstream and downstream in wet and dry seasons and discovered that some of the samples exceeded the threshold pollution index value of 1, thus signifying high pollution levels. Hoang et al. [5] studied the contamination of Houijing river in Taiwan, by collecting samples from surface water and sediments from five sites suspected to be likely to be contaminated by industrial activities for a period of five years and discovered that two sites which were close to industrial discharge point were the most contaminated. Malvandi [6] evaluated the degree of pollution of Zarrin-Gol River through the determination of the concentration of some heavy metals and metalloids in samples collected from the river and discovered that arsenic and selenium levels were quite high and could be regarded as pollutants to the river. Patel et al. [7] assessed the level of contamination of river water and sediments along the basin of Svamanmukhi river and found substantial pollution of the river with iron and manganese, and the river basin with chromium, lead, copper and zinc, contamination values of which exceeded the Indian averages, but were far below the world averages. Zhang et al. [8] assessed the level of pollution of Zijang river sediment by determining the concentration of some heavy metals found therein. By applying geoaccumulation and ecological risk index, they discovered contaminations by cobalt, zinc, copper, cadmium, manganese, antimony and lead, which came agricultural and mining activities within the area of study. Islam et al. [9] also used geo-accumulation index and contamination factor to assess the level of pollution of Femi River and discovered that silver, cobalt and mercury levels were either moderate or high, while arsenic, chromium and lead were at zero or low levels of pollution. Wu et al. [10] evaluated the pollution levels of heavy metals in the sediment samples of selected urban rivers and found levels of accumulation of cadmium, chromium and mercury which pose high toxicity levels to benthic organisms and ecological risks, as well. Siddique et al. [11] analysed sediment samples from lower Meghna River for heavy metal contamination, using atomic absorption spectrophotometry, and geo-accumulation and pollution load index, and found out that there was no contamination of heavy metals within the studied area.

Materials and Methods

Sampling: Samples of the river sediments were collected at five different locations (1kilometre apart, marked A-E) along the river. Forty-sediment samples were used for the study. The samples were collected from November 2017 to February 2018 (dry season sampling), then May 2018 to August 2018 (rain season sampling). Sampling was done during the morning hours when all the pollutants are expected to be evenly distributed across different compartments and media of the river. Three samples of sediments were collected at each of the sampling sites. A representative sediment sample for each sampling site was obtained by mixing the three samples collected at each point. The representative sample was then dried and stored in a labeled plastic bag until it is required for laboratory analysis.

AAS Analysis of the Sediment Samples

Extraction of metals from the sediments was done by mixed acid digestion [11,12]. Heavy metal concentration in the sediment samples was determined using Varian AA240 Atomic Absorption Spectrophotometer.

Results and Discussion

The analysis of sediment samples collected from the Anambra River within the area of study (Otuocha) showed the presence of Fe, Mn, Cd, Pb, Hg, and As in different concentrations. Tables 1 and 2 showed the overall mean concentration of the individual metals along the sampled points for both seasons. From Table 1 it is seen that the mean concentrations of all the metals tested for in sediment samples were in the order of Fe > Mn >As > Cd > Hg > Pb while Table 2 showed the metal concentration in the order of: Fe> Mn > As > Hg > Pb > Cd. In both seasons, Fe concentration is found to be the highest while Cd concentration is the least.

Table 1. Mean concentration of heavy metals (mg/l) in sediment along with the sampled points in Dry season (Nov -Feb).

	A	B	C	D	E	Mean & std
Pb	`0.447	0.280	0.320	0.255	0.218	**0.304** ± 0.13
Hg	0.597	0.754	0.225	0.263	0.375	**0.387** ± 0.15
Cd	0.818	0.195	0.564	0.704	0.014	**0.459** ± 0.34
Mn	5.764	5.493	4.277	3.437	3.504	**4.495** ± 1.09
Fe	19.887	18.464	21.377	18.815	18.220	**19.353** ± 1.30
As	3.389	2.66	3.311	2.584	3.760	**3.141** ± 0.51

Table 2. Mean concentration of heavy metals (mg/l) in sediments along with the sampled points in Wet season (May -Aug).

	A	B	C	D	E	Mean & std deviation
Pb	0.206	0.127	0.119	0.203	0.010	**0.133** ± 0.08
Hg	0.370	0.189	0.400	0.603	0.00	**0.303** ± 0.03
Cd	0.065	0.043	0.045	0.108	0.041	**0.060** ± 0.03
Mn	3.378	3.968	3.427	3.268	2.433	**3.295** ± 0.55
Fe	43.139	44.913	43.913	44.632	44.556	**44.297** ± 2.5
As	0.260	0.260	0.300	0.200	0.190	**0.240** ± 0.05

Comparison of heavy metal levels in the sediment of Anambra River with other studies and guidelines.

Table 3. Comparison of heavy metal levels (mg/kg, dry weight) in the sediment of the present study with other studies and guidelines.

Metals	Present Study	[a]Aladja river Sediment	[b]Evbiob sediment	PEC	USEPA
Pb	0.304	0.25	0.10	12.8	30.2
Hg	0.387	-	-	-	-
Cd	0.459	0.96	0.05	5.0	0.68
Mn	4.495	2.05	6.27	-	15.9
Fe	19.353	6.48	49.65	20.03	-
As	3.141	-	-	-	-

Oyakhilome [14].

The similarity in the distribution pattern is seen in the high concentrations of iron (Fe) and manganese (Mn) in the sediments from the three rivers. While the Fe concentration in sediments from the Anambra River (the present study) and that of Aladja river sediment are below the PEC permissible value, Fe concentration in sediments from Evbiob River is higher than the PEC limit. Manganese and lead concentrations in sediments from the three rivers are below the permissible limits of PEC and USEPA.

Pollution Index Models

Various models have been developed to assess heavy metal contamination in sediment which include the Contamination Factor (CF), Pollution Load Index (PLI), and Geoaccumulation Index (Igeo). Some of these models provide useful information, reducing large data for easy understanding by policymakers [15].

To assess the heavy metal pollution levels and extent of contamination in sediment, the data obtained for the heavy metal concentrations were used to calculate the above-listed pollution indices.

Contamination Factor (Cf)

Contamination factor (C_f) is the ratio obtained by dividing the concentration of each metal in the water or sediment by the upper permissible value or its background value.

$$C_f = \frac{\text{Analytical value for the ith conc}}{\text{Permissible limit for the ith conc.}} \tag{1}$$

$$C_f = C_o / C_n \tag{2}$$

where C_o is the concentration of the heavy metal in the examined environment and C_n is the concentration of the metal in the reference environment. The background concentrations were taken as the target value (mg/kg) of the Department of Petroleum Resources. These values are: Fe - 38000, Zn - 140, Pb - 85, Co - 20, Cu - 36, Cr - 100, Ni - 35, Mn - 850, As - 1.0 and Cd - 0.8.

C_f values were interpreted as $C_f < 1$ = low contamination; $1 < C_f < 3$ moderate contamination; $3 < C_f < 6$ = considerable contamination and $C_f > 6$ = very high contamination.

The contamination factor values of heavy metals in the sediments of Anambra River in dry season follows the order As > Cd > Hg & Mn > Pb > Fe while that of wet season follows the order As > Cd > Mn > Hg > Pb > Fe (see Tables 4 and 5). In the dry season, all the metals exert a low contamination effect except for Arsenic. The river sediment is considerably contaminated by Arsenic in the dry season. In the wet season, all the metals exert a low contamination effect on the sediment. The contamination effect of toxic metals on the sediments of the river could be attributed to the indiscriminate dumping of solid waste and liquid effluents from domestic and industrial sources into the river.

Table 4. Contamination Factor of Sediment Samples in the dry season.

	A	B	C	D	E	Mean
Pb	0.005	0.003	0.004	0.003	0.003	0.004
Hg	0.006	0.008	0.002	0.003	0.004	0.005
Cd	1.02	0.243	0.705	0.885	0.002	0.571
Mn	0.007	0.006	0.005	0.004	0.004	0.005
Fe	0.0005	0.0005	0.0006	0.0005	0.0005	0.0005
As	3.40	2.66	3.31	2.58	3.76	3.14

Table 5. Contamination Factor of Sediment Samples in the wet season.

	A	B	C	D	E	Mean
Pb	0.002	0.002	0.004	0.002	0.001	0.002
Hg	0.004	0.002	0.004	0.006	0	0.003
Cd	0.08	0.050	0.056	0.135	0.051	0.074
Mn	0.004	0.005	0.004	0.004	0.003	0.004
Fe	0.001	0.001	0.001	0.001	0.001	0.001
As	0.260	0.260	0.300	0.200	0.190	0.240

Pollution Load Index (PLI)

The Pollution Load Index (PLI) demonstrates the general contamination level by considering the overall toxicity of all observed heavy metals. The PLI is the nth root of the aggregation of contamination factors in the research area. PLI provides a temporal and spatial overall indication of pollution in the environment which can be of assistance in environmental governance [16]. The Pollution Load Index (PLI), as proposed by Tomilson *et al*, [17] was used to assess the quality of river sediment.

To identify the metal contamination as a total scale in sediment, Tomilson *et al,* [17] recommended an equation for calculating the Pollution Load Index (PLI) as;

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots\ldots CFn)\ 1/n \tag{3}$$

where n is the number of metals.

PLI > 1 indicates pollution and demonstrates the dynamic deterioration of the quality, whereas PLI< 1 low contamination. PLI value of zero indicates the starting point of becoming infected.

The PLI provides a comparative means for assessing water quality at the respective locations. For Anambra River, the PLI values for both seasons are less than one, indicating low contamination of the river sediments.

$$\text{Pollution Load Index (PLI) for dry season,} =$$

$$\sqrt[6]{0.004 \times 0.005 \times 0.571 \times 0.005 \times 0.0005 \times 3.14} \tag{4}$$

$$= \sqrt[6]{8.965 \times 10^{-11}} = 0.021 \tag{5}$$

$$\text{Pollution Load Index (PLI) for wet season} =$$

$$\sqrt[6]{0.002 \times 0.003 \times 0.074 \times 0.004 \times 0.001 \times 0.240} \tag{6}$$

$$= \sqrt[6]{4.262 \times 10^{-13}} = 0.011 \tag{7}$$

Geoaccumulation Index (I-geo)

The Geoaccumulation Index (I-geo) is used to assess the extent of metal pollution in soil samples. The I-geo was estimated using the following equation:

$$\text{Igeo} = \log_2 \left(\frac{C_m}{1.5 C_b} \right)$$

(8)

where Cm is the concentration of the metal in the sample, Cb is the background value of the metal, 1.5 is the background matrix correction factor due to lithogenic effects; hence, this index is used to analyze natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. The background value taken is considered from the world average value in shale (mg/kg) of the metals determined in the study.

The values are Fe = 47200, Zn = 95, Pb = 20, Co = 19, Cu = 45, Cr = 90, Ni = 68, Mn = 850, As = 13, Hg = 37.5 and Cd = 0.3.

I-geo < 0 – uncontaminated, 0 < I-geo < 1 – moderately contaminated, 1 < I-geo < 2 – moderately to heavily contaminated, I-geo < 3 – heavily contaminated, 3 < I-geo < 4 – heavily to extremely contaminated, 4 < I-geo < 5 – extremely contaminated.

Table 5. Geoaccumulation Index (I-geo) of Sediment samples from Anambra River (Dry season).

	A	B	C	D	E	Mean
Pb	0.004	0.003	0.003	0.003	0.002	0.003
Hg	0.016	0.020	0.006	0.007	0.010	0.012
Cd	0.547	0.130	0.377	0.471	0.009	0.307
Mn	1.3×10^{-3}	1.3×10^{-3}	1.0×10^{-3}	8.1×10^{-4}	8.2×10^{-4}	0.001
Fe	8.454×10^{-5}	7.850×10^{-5}	9.088×10^{-5}	8.00×10^{-5}	7.746×10^{-5}	8.230×10^{-5}
As	0.05	0.041	0.051	0.040	0.058	0.048

Table 6. Geoaccumulation Index (I-geo) of Sediment samples from Anambra River (Wet season).

	A	B	C	D	E	Mean
Pb	0.002	0.001	0.001	0.002	0.0001	0.001
Hg	0.010	0.005	0.010	0.016	0	0.008
Cd	0.043	0.029	0.030	0.072	0.027	0.040
Mn	7.97×10^{-4}	9.37×10^{-4}	8.09×10^{-4}	7.71×10^{-4}	5.74×10^{-4}	7.77×10^{-4}
Fe	1.83×10^{-4}	1.91×10^{-4}	1.87×10^{-4}	1.89×10^{-4}	1.89×10^{-4}	1.88×10^{-4}
As	0.004	0.004	0.005	0.003	0.003	0.004

The Geoaccumulation Index values obtained in this study (for both seasons) were all below one which indicates low contamination of the water sediment. Ranking in order of decreasing contributions in dry season showed Cd > As > Hg > Pb > Mn > Fe while that of wet season is Cd > Hg > As > Pb > Mn > Fe.

Discussion

From the analytical results, it was observed that in both seasons, Fe has the highest concentration followed by Mn. Similar observation was recorded for iron in Qua Ibeo river estuary, Aladja River, and Ogba River [18]. The high loads of iron and manganese in the sediment could be attributed to lithological or crustal origin as well as man's anthropogenic activities. According to Oyakilome [14], Iron and Manganese have been known to be commonly high in Nigerian soils; moreover, the pattern of distribution of these metals might suggest that the level of heavy metals in the sediments is both natural and anthropogenic influences   In agreement, Oyakilome [14]   noted that in rural areas, the metal content of soil/sediment can be assigned mainly to rock weathering and of course, erosion and wastes that are generated due to human activities, and are discharged on land around the rural environment. Such wastes are transported by run-off water into surrounding water bodies when it rains. Manganese is one of the most abundant metals in the earth's crust, usually occurring with iron [13].

The relatively high level of Arsenic can be from man's anthropogenic activities as Arsenic and its compounds, especially the trioxide, are used in the production of pesticides, treated wood products, herbicides, and insecticides.   Pesticides, herbicides, and insecticides are commonly used by farmers, so the possibility of residual amounts of these agrochemicals being discharged into the river during a rainstorm cannot be ruled out.   In both seasons the concentration of lead in the river sediments is low relative to the concentration of other metals. This is contrary to the findings of Igweilo and Onyenmechi [19] who posited that soil lead levels in and around the Anam River are high and may pose adverse health problems. The presence of lead can be attributed to man's anthropogenic activities.

Conclusions

Discharge of untreated solid wastes and agricultural run-off into the Anambra River could have contributed to the pollution of the river as shown by the result of this analysis. Iron and Manganese recorded higher concentrations in the sediments samples analyzed. Calculated pollution assessment indices; Contamination Factor and Pollution Load Index of heavy metals showed that the river requires special treatment before it can be used for domestic activities.

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