

Assessment of Heavy Metal Loadings of Water and Sediment of River Enumabia in Orokam, Benue State, Nigeria

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Abstract

Enumabia being the only surviving river in Orokam community gave us the concern to assess the concentration of heavy metals in water and sediment in the river. 20 samples of water and Sediment were taken from four (4) different points 20 meters apart and analysed for heavy metals by the use of AA-700 Dual Atomizer Atomic Absorption Spectrophotometer in Energy Research Centre, University of Nigeria, Nsukka. In water, the concentration of Fe ranges from 0.7669 to 0.9214 mg/l, Pb ranges from 1.3300 to 1.7210 mg/l, As ranges from 0.9032 to 2.0120 mg/l, and there was no concentration of Hg, Cr and Al. The concentration of metals in the water samples are at the range of permissible limit set by World Health Organization (WHO) except Pb, and As that are fairly higher than the permissible limit. In sediment, the concentration of Fe ranges from 128.8812 to 113.9563 mg/l, Pb ranges from 0.2500 to 0.9520 mg/l, Cr ranges from 0.1240 to 0.6676 mg/l, Al ranges from 10.0000 to 16.0000 mg/l, As ranges from 0.0000 to 1.1240 mg/l, Cu ranges from 0.2420 to 0.8490 mg/l and there was no concentration of Hg. The concentration of Fe, Pb, Cr and As in the sediment exceeded the standards set by WHO. This presence could be detrimental to plant, human being and aquatic life. Since there is fast accumulation of toxic and carcinogenic metals present in the water and sediment samples collected from Enumabia River in Orokam there is need for a follow up study to determine how the human and aquatic lives have been affected.

Keywords: Heavy Metals; Sediments; Water; Concentration; WHO; River; Atomic Absorption Spectrophotometer.

I. INTRODUCTION

Heavy metals are any metallic chemical elements that have high relative densities and they are toxic and poisonous at low concentrations. Representatives of heavy metals are Mercury (Hg), Cadmium (Cd), Arsenic (As), Chromium (Cr), Thallium (Tl), and Lead (Pb) [1]. Heavy metals (HMs) are those metallic elements having an atomic number

considerably above 20 and density greater than 5 gcm^{-3} which make them exhibit the properties of metal [2].

Heavy metals are chemical elements with properties of metalloids that have high specific gravity and are poisonous irrespective of the levels. Some illustrations include Pb, As, Hg, Cd, Zn, Ag, Cu, Fe, Cr, Ni, Pd, and Pt. These metals are discharged into the physical surroundings by both innate and human activities such as industrial effluents, automobiles exhaust, and prospecting. Unlike living matter pollutants,

heavy metals cannot be transformed into harmless natural state by bacterial activities and have tendency to build up in living beings. In fact, most of them are agents that cause cancer [1]. Heavy metals like Cu, Zn, and Fe play a worthwhile role in plant embryology, but heavy metals such as Pb, Cd, Cr, and Hg are dangerously toxic to human and her environment [2].

Sediments are solid materials such as loose sand, clay, silt and other soil particles that established at the bottom of a body of water. Sediment can come from soil erosion, or from the festering of plants and animals. Denudation agents like wind, water and ice help carry these particles to rivers, lakes and streams. Sediment eroding into water bodies reduces the quality of water for drinking, wildlife and the land encompassing the water bodies [3].

Heavy metals pollution is a peril to our environment as they are leading adulterating agents of water and sediment. Heavy metals debasement in sediment and water has many harmful effects and thus is of great worry to the public health, agricultural production, and environmental health [5]. The soil pollution is mainly due to indiscriminate discarding of industrial and urban wastes as well as usage of agricultural chemicals while water pollution is primarily caused by channeling industrial wastes, sewage disposition, petroleum contagion, and agricultural drainage water [6].

Rivers are depicted to be one of the major media for pollutant and heavy metal transportation either via denudation agents or sediment of the river [7]. Hence there's need to examine the metal levels in the sediment of the river.

This study is aimed at examining the pollution levels of metal concentration from water and sediment samples collected from River Enumabia, quantify the content of heavy metals in water and sediment collected from River Enumabia using AA-Dual Atomic Atomizer Absorption Spectrophotometer (AAS) and provide a data base index on the concentration of metals peculiar to the study area.

II. STUDY AREA

This research was conducted in the only surviving river in Orokam Community, Ogbadibo Local Government Area of Benue State (see Plate I). Orokam geographical coordinates are 60° 59' 0" North, 70° 35' 0" East.

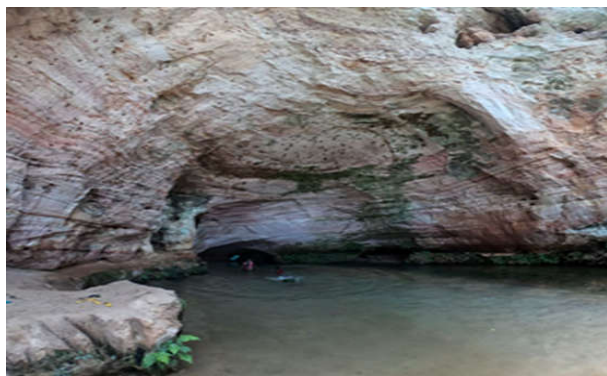


Plate I Photograph of the Study Area (Enumabia River)

III. MATERIALS AND METHODS

A. Water sample analysis

Twenty (20) samples of water were obtained from Enumabia River in Orokam Community in Ogbadibo Local Government Area, Benue State. Five (5) from the siege (point A), another five (5), 20 meters away from the siege (point B), another five (5) samples 40 meters away from the siege (Point C), and finally another five samples 60 meters away from the siege (Point D). The samples were collected 20 meters interval based on human activities in the water. At point A there was no major activity like bathing and washing of clothes, but only fetching of drinkable water, at point B the only human activities at that point is bathing, at point C the major human activity is washing of clothes and at point D there is no major human activities. The staunchness of heavy metals was done by putting 5 ml of concentrated HNO_3 and 10 ml of concentrated HCl into a 150 ml of the water sample collected. The solution was covered with a wash glass and heated at 105 °C till the volume reduced to 20 ml before being allowed to cool. Later, the final volume was adjusted to 120 ml with analytes water and duplicates were processed on a regular basis to phantom precision. The concentrations of Cu, Hg, Cr, K, Ar, Zn, Fe and Pb in the extract of water were evaluated using the AAS.

B. Sediment Sample Analysis

Twenty (20) Sample of sediments were collected using a polythene bag, five (5) each from different points same as water samples and labelled as A, B, C and D respectively. The samples were then enclosed in a sterilized polythene bags and taken to Energy Research Centre University of Nigeria, Nsukka. After oven-drying (at 115 °C) for few hours, the sediment samples were granulated (pulverized) mechanically and passed through a 1.50 mm sieve and for further analysis. The filtered sediment samples were educed using the humid digestion method (HDM). Thereafter, thorough digestion of the filtrate sediment samples was carried out. Two gram (2 g) each of dried granulated sediments was put into a 100 ml conical flask, and later, a 20 ml samples dissolved in 15 ml of 1:1 HNO_3 : blended, heated to 98 °C to dryness, and afterword refluxed for 20 minutes without boiling. After cooling, 8 ml of concentrated HNO_3 was once again added and allow to flow back (refluxed) for 40 minutes till brown effluvium were generated. The solutions were evaporated to about 7 ml on cloak set at 105 °C with a watch glass over it. After cooling the emanating samples, 3 ml of and 4 ml of 40 % were added to each sample, and the solutions placed on the heating cloak to start the oxidation of peroxide until fizziness receded. The containers were cooled and the acid-peroxide residue heated to about 10 ml at 105 °C. Afterwards 15 ml of concentrated hydrochloric acid (HCl) was added to the sample's residue, and the solutions were placed on the heating source and refluxed for 20 minutes at 105 °C. The Whatman No. 45 filter paper was used to filter the obtained

residue, put into a 150 ml volumetric flasks, and then made up to the mark with distilled water. Subsequently, the filtrates was taken for heavy metal analysis using AAS.

IV. RESULTS AND DISCUSSION

A. Concentration of Metals in Water

Results obtained from the AA-700 Dual Atomizer Atomic Absorption Spectrophotometer (AAAS) of the water collected from four (4) different points of Enumabia River in Orokam, Benue State carried out at Energy Research Centre, University of Nigeria, Nsukka, in milligram per litre (mg/l) is presented in Table I, while graphs of concentration (mg/l) against metals in water at points A, B, C and D are presented in Fig. 1, 2, 3 and 4 respectively.

Table I. Concentration in mg/l of Metals in Water Samples from Enumabia River.

Sample ID	Metals						
	Fe	Hg	Pb	Cr	Al	As	Cu
A	0.7669	0.0000	1.5000	0.0000	0.0000	0.9032	0.0323
	0.7421	0.0000	1.4000	0.0000	0.0000	0.9321	0.0323
	0.7244	0.0000	1.5100	0.0000	0.0000	0.9421	0.0323
	0.7233	0.0000	1.5000	0.0000	0.0000	0.9321	0.0232
	0.7344	0.0000	1.6000	0.0000	0.0000	0.9213	0.0432
B	0.7869	0.0000	1.3300	0.0000	0.0000	1.0240	0.0243
	0.6755	0.0000	1.3230	0.0000	0.0000	1.0433	0.0233
	0.7423	0.0000	1.4322	0.0000	0.0000	1.0324	0.0022
	0.6732	0.0000	1.3322	0.0000	0.0000	0.9542	0.0503
	0.7324	0.0000	1.3300	0.0000	0.0000	1.0234	0.0332
C	0.8559	0.0000	1.6214	0.0000	0.0000	2.0120	0.0432
	0.7853	0.0000	1.6214	0.0000	0.0000	2.0750	0.0444
	0.9032	0.0000	1.5233	0.0000	0.0000	2.0420	0.0433
	0.8843	0.0000	1.6234	0.0000	0.0000	1.9320	0.0421
	0.7320	0.0000	1.7210	0.0000	0.0000	2.5571	0.0432
D	0.9214	0.0000	1.7210	0.0000	0.0000	2.1120	0.0522
	0.9340	0.0000	1.7221	0.0000	0.0000	2.1122	0.0421
	0.9211	0.0000	1.7321	0.0000	0.0000	2.4410	0.0521
	1.0012	0.0000	1.6940	0.0000	0.0000	2.5022	0.0452
	0.9321	0.0000	1.7420	0.0000	0.0000	2.6601	0.0551

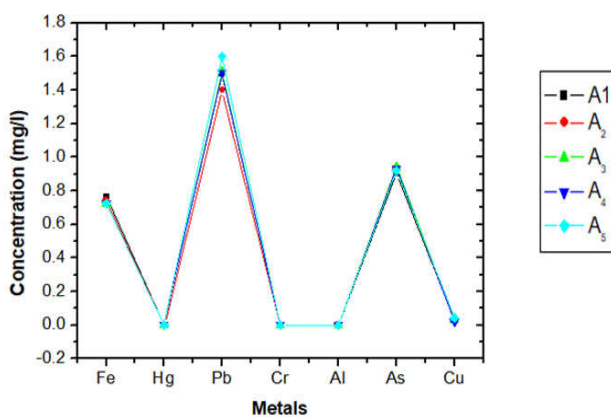


Fig. 1 Graph of Concentration (mg/l) against Metals in water at point A

At point A, lead (Pb) has the highest concentration as depicted by the graph in all the samples collected from that point, follow by Arsenic (As), Iron (Fe) and Copper in that order. While there is no presence of Mercury (Hg), Chromium (Cr) and Aluminium (Al).

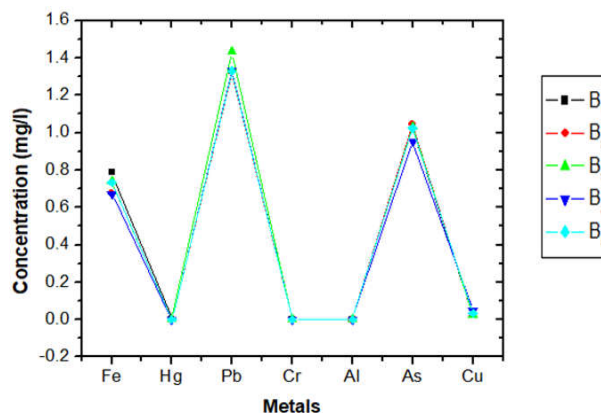


Fig. 2 Graph of Concentration (mg/l) against Metals in water at point B

At point B, lead (Pb) has the highest concentration as depicted by the graph in all the samples collected from that point lesser than the concentration in samples A, follow by Arsenic (As), Iron (Fe) and Copper in that order. While there is no presence of Mercury (Hg), Chromium (Cr) and Aluminium (Al).

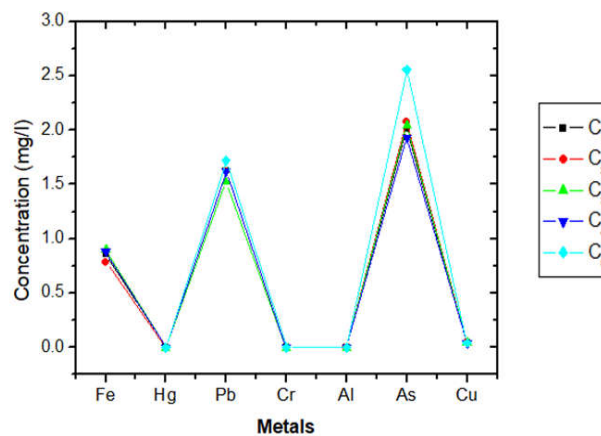


Fig. 3 Graph of Concentration (mg/l) against Metals in water at point C

At point C, Arsenic (As) has the highest concentration as shown by the graph in all the samples collected from that point, follow by Lead (Pb), Iron (Fe) and Copper in that order. While there is no presence of Mercury (Hg), Chromium (Cr) and Aluminium (Al). The concentration of Arsenic at point C may be due to the dirt and chemicals from textiles that are been washed regularly at that point.

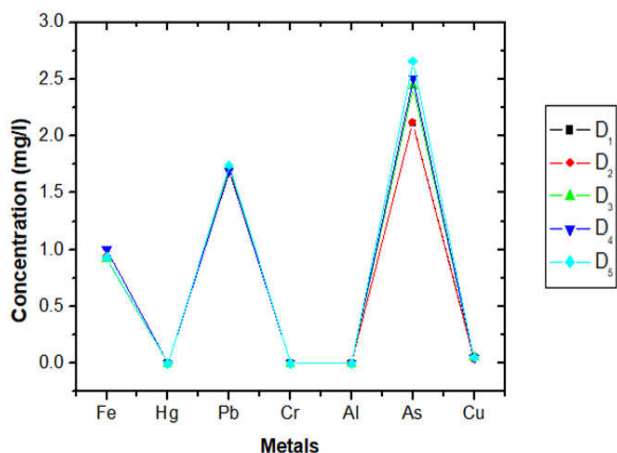


Fig. 4 Graph of Concentration (mg/l) against Metals in water at point D

At point D, Arsenic (As) has the highest concentration as shown by the graph in all the samples collected from that point, follow by Lead (Pb), Iron (Fe) and Copper in that order. While there is no presence of Mercury (Hg), Chromium (Cr) and Aluminium (Al).

B. Concentration of Metals in Sediment

The results obtained from the AA-700 Dual Atomizer Atomic Absorption Spectrophotometer (AAS) of the sediment collected from four (4) different points, five (5) samples each of Enumabia River in Orokam, Benue State carried out at Energy Research Centre, University of Nigeria, Nsukka in milligram per litre (mg/l) is presented in Table II, while graphs of concentration (mg/l) against metals in Sediment at points A, B, C and D are also presented in Fig. 5, 6, 7 and 8 respectively.

Table II. Concentration in mg/l of Metals in sediment Samples from Enumabia River.

Sample ID	Metals						
	Fe	Hg	Pb	Cr	Al	As	Cu
A	122.1834	0.0000	0.9520	0.6267	16.0000	0.0000	0.2420
	123.3412	0.0000	0.9655	0.5523	16.0000	0.0000	0.2324
	142.2310	0.0000	1.0012	0.6621	15.0000	0.0000	0.2422
	122.1723	0.0000	0.9341	0.6432	16.0000	0.0000	0.2340
	121.1840	0.0000	0.9033	0.7324	16.0000	0.0000	0.3421
B	124.3493	0.0000	0.7520	0.1240	14.0000	1.1240	0.4290
	123.5901	0.0000	0.7522	0.1223	14.0000	1.1234	0.4290
	122.6689	0.0000	0.7520	0.2313	13.0000	1.3421	0.4213
	124.6721	0.0000	0.7721	0.4521	14.0000	1.2231	0.6012
	124.5621	0.0000	0.7651	0.1321	14.0000	1.3214	0.4321
C	128.8812	0.0000	0.2500	0.2212	10.0000	0.2213	0.8290
	127.7410	0.0000	0.3400	0.2213	11.0000	0.2213	0.7911
	126.4521	0.0000	0.2400	0.2213	10.0000	0.2211	0.8311
	128.5321	0.0000	0.2300	0.2144	12.0000	0.2131	0.8971
	128.4521	0.0000	0.2300	0.2214	10.0000	0.2111	0.8290
D	113.9563	0.0000	0.5000	0.6676	12.0000	1.2124	0.8490
	113.9741	0.0000	0.5200	0.7661	12.0000	1.2214	0.8290
	113.9231	0.0000	0.5000	0.6661	13.0000	1.2341	0.7921
	113.2314	0.0000	0.5400	0.6712	11.0000	1.2311	0.8490
	114.0124	0.0000	0.4900	0.6213	14.0000	1.2121	0.8812

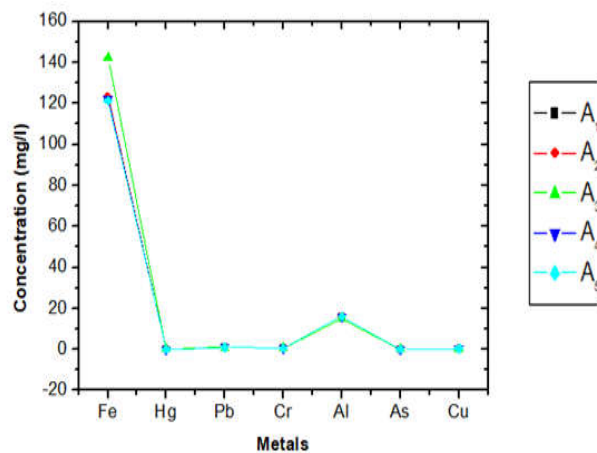


Fig. 5 Graph of Concentration (mg/l) against Metals in Sediment at point A

At point A, Iron (Fe) has the highest concentration as shown by the graph in all the sediment samples collected from that point, followed by Aluminium (Al), Chromium (Cr), Lead (Pb) and Copper (Cu) in that order. While there is no presence of Mercury (Hg), and Arsenic (As). The absence of these two metals may be hold to the fact that there were no much human activities at that point other than fetching of drinkable water.

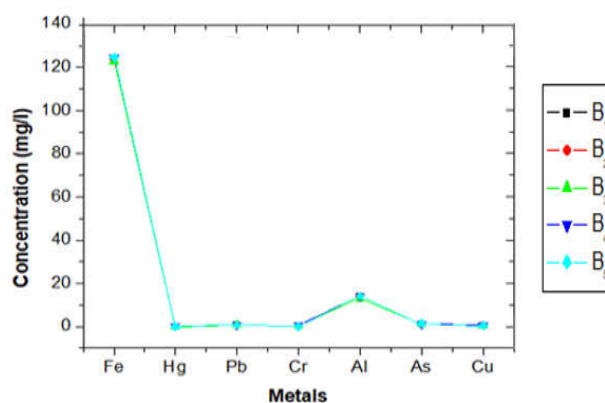


Fig. 6 Graph of Concentration (mg/l) against Metals in Sediment at point B

At point B, Iron (Fe) still has the highest concentration as shown by the graph in all the sediment samples collected from that point, followed by Aluminium (Al), Arsenic (As), Chromium (Cr), Lead (Pb) and Copper (Cu) in that order. While there is no presence of only Mercury (Hg). There is a significance difference in the concentration of Arsenic at point A and B. At point A there is no trace of Arsenic but in B, there are significance values of Arsenic in all the samples collected at that point due to high human activities at that point.

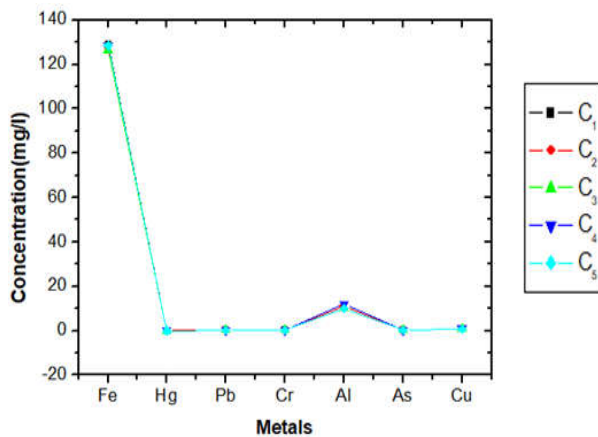


Fig. 7 Graph of Concentration (mg/l) against Metals in Sediment at point C

At point C, Iron (Fe) still has the highest concentration as shown by the graph in all the sediment samples collected from that point, followed by Aluminium (Al), Arsenic (As), Chromium (Cr), Lead (Pb) and Copper (Cu) in that order. While there is no presence of Mercury (Hg).

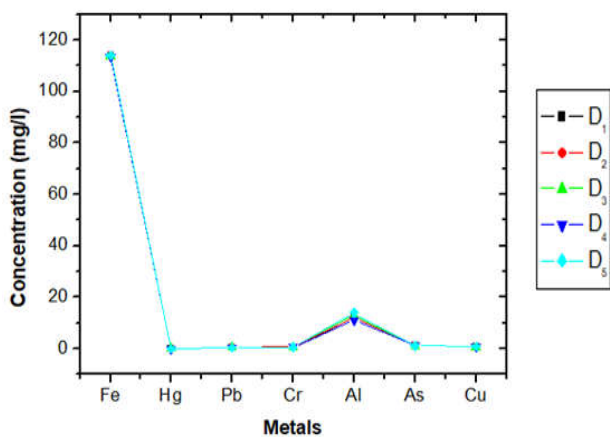


Fig. 8 Graph of Concentration (mg/l) against Metals in Sediment at point D

At point D, Iron (Fe) still remain highest in concentration as shown by the graph in all the sediment samples collected from that point, followed by Aluminium (Al), Arsenic (As), Chromium (Cr), Lead (Pb) and Copper (Cu) in that order. While there is no presence of on Mercury (Hg).

The concentration of metals in the sediment in milligram per kilogram (mg/kg) is given in Table III using (1).

$$C = \frac{Df}{M} \tag{1}$$

C is the concentration of metals in mg/kg or concentration of metals in the sediment in mg/l, Df is the dilution factor and M is the mass of the sample.

Noting that,

$$Df = \frac{50/12}{\text{mass of each sample}} \tag{2}$$

Table III. Concentration in mg/kg of Metals in sediment Samples from Enumabia River.

Sample ID	Metals						
	Fe	Hg	Pb	Cr	Al	As	Cu
A	1211.4158	0.0000	9.3474	6.2136	158.6357	0.0000	2.3994
	1231.3122	0.0000	9.2413	6.2412	141.4231	0.0000	2.0013
	1241.4310	0.0000	8.9414	7.0023	158.6231	0.0000	2.7713
	1412.2120	0.0000	9.4218	6.2310	158.0132	0.0000	2.4132
	1232.4321	0.0000	9.4532	6.2324	158.4121	0.0000	2.5412
B	1290.3811	0.0000	7.8333	1.2602	145.8333	11.7083	4.4688
	1314.3421	0.0000	7.5321	2.1414	141.5131	8.0001	3.7612
	1240.2316	0.0000	8.0012	2.7713	144.6131	11.9141	4.0942
	1134.4012	0.0000	8.0121	1.7141	145.7413	9.0012	4.0024
	1341.3421	0.0000	7.8231	1.8823	145.7413	11.8141	4.9903
C	1265.4468	0.0000	2.4547	2.1719	98.1871	2.1729	8.1299
	1234.2310	0.0000	2.0123	2.4121	101.9612	3.0002	8.9924
	1421.3421	0.0000	2.0101	3.0012	98.4141	3.0025	7.0081
	1231.4321	0.0000	2.2425	2.8813	98.6134	2.8961	8.0024
	1614.4321	0.0000	2.4320	2.6262	99.0013	2.3412	7.9923
D	1087.0125	0.0000	4.7694	6.3681	114.4662	11.5649	8.0985
	1241.0123	0.0000	4.5412	5.0001	117.0001	9.0132	8.9924
	1226.4310	0.0000	4.6324	5.6132	114.9417	10.0012	8.5421
	1213.8101	0.0000	5.0202	6.9924	114.8145	11.0012	9.0024
	1052.0012	0.0000	4.2310	6.9242	112.9141	10.9741	8.9920

Table IV compares the limit set by some regulatory bodies as stated by [8], [9], [11], [13], [14], [15] and [16] with this research to ascertain the permissible limit of the concentration of heavy metals in the sediment collected from Enumabia river in Orokam community.

Table IV. Limits of metals in water and Sediment set by regulatory bodies

SAMPLE	METALS												
	Water (mg/l)	Fe	Hg	Pb	Cr	Al	As	Cu	Zn	Cd	Ni	Cl	References
Water	0.50	0.006	0.01	0.05	0.1	0.01	2.00	5.00	0.01	0.07	5.00		[8]
	-	-	-	2.00	0.9	-	0.05	-	-	-	-	-	[9]
	-	-	10	50	-	-	-	-	-	-	-	-	[11]
	-	-	-	0.05	-	-	-	-	-	-	-	-	[13]
	0.30	-	0.01	-	-	-	2.00	-	-	-	-	-	[16]
Sediment (mg/kg)	-	-	0.20	0.10	-	-	-	-	-	-	-	-	[13]
	-	-	0.20	-	-	-	-	-	-	-	-	-	[14]
	-	-	0.30	-	-	-	-	-	-	-	-	-	[15]
	-	-	2.00	0.50	-	-	20	-	-	-	-	-	[9]

Equally, Table V compares the limit set by some regulatory bodies as stated by [8], [10] and [12] with this research to ascertain the permissible limit of the concentration of heavy metals in the water samples collected from Enumabia river in Orokam community.

Table V. Limits of Detection in Water.

Metals	Limit of Detection in Water	References
Fe	-	-
Hg	0.61 μ g/l by ICP; 51 μ g/l by AAS; 0.051 μ g/l by cold vapour AAS	[12]
Pb	11 μ g/l by AAS	[10]
Cr	0.05-0.21 μ g/l by AAS	[8]
Al	-	-
As	0.1 μ g/l by ICP-MS; 2 μ g/l by AAS	[8]
Cu	0.02-0.11 μ g/l by ICP, 0.51 μ g/l by AAS	[8]

C. Characteristics of Water Sample

1) Iron (Fe) : The concentration of Fe recorded in the samples from Table I shows that sample D has highest concentration than samples A, B, and C. This is due to the fact that sample D was collected farthest away from the source (source of the water) which must have been contaminated by external factors via denudation agents. The concentration of Fe in the water samples gotten from the points sorts from 0.7669 (A) -1.0012(D) mg/l. The concentration of Fe in the water samples collected from the four (4) different points is limited compare with the establishment standard by NESREA (20mg/l) [16] and WHO (0.5-50mg/l) [8].

2) Mercury (Hg): There was no concentration of Hg in any of the samples collected as shown in Table I.

3) Lead (Pb): The value of the concentration of Pb recorded in the water sample samples according to Table I, shows that samples collected from point D has the highest concentrations of Pb compared with samples collected from A, B and C respectively. The concentration ranges from 1.3300 – 1.7420 mg/l. The concentration value of Pb in the water samples collected from Enumabia river is higher than the range set by WHO (0.01mg/l) [16].

4) Chromium (Cr): There was no concentration of Cr in any of the samples collected as shown in Table I.

Aluminium (Al): There was no concentration of Al in any of the samples collected as shown in Table I.

5) Arsenic (As) : The concentration of As from the result in Table I depicted that samples collected from point D has the highest concentrations of As compare with samples collected from A, B, and C respectively. The As concentrations in the water samples ranges from 0.9032 –2.6601mg/l. The concentration of As in the water samples collected from Enumabia river is higher than the range set by WHO (0.01mg/l) [8].

6) Copper (Cu): The concentration of Cu in the collected samples as shown in Table 1 ranges from 0.0243 –0.0551mg/l, depicting that the concentrations of Cu is highest in the samples collected from point D sample than A, B and C. The concentration of Cu in the water samples collected from Enumabia river is at the range set by WHO (0.05-0.15mg/l) [9].

D. Characteristics of Sediment Samples

1) Iron (Fe): The concentration of Fe recorded from the analysis of the sediment samples collected from four (4) different points is given in Table II in mg/l. It was shown

that samples collected from C has highest concentration of Fe compare to the concentrations in the samples collected from A, Band D respectively. The concentration of Fe in the samples collected is higher than the range set by WHO (25mg/l) [8].

2) Mercury (Hg): There was no concentration of Hg in any of the samples collected as shown in Table II.

3) Lead (Pb): The concentration of Pb in the sediments collected and analyzed using AAS was recorded as given in Table II in mg/l shows that the concentrations of Pb is highest in the samples collected from point A compare to the samples collected from point B, C and D respectively do to the fact that they was no much human activities at point A other than fetching of water, there was no much interference with the primordial value of lead. The concentration of Pb in the samples collected is fairly higher than the range set by WHO (0.3mg/l) [15].

4) Chromium (Cr): The concentration of Cr in the sediments collected and analyzed using AAS was recorded in Table II in mg/l, shows that the concentration of Cr is highest in the samples collected from point D compare to the samples collected from point A, B and C respectively. The concentration of Cr in the samples collected is fairly higher than the range set by WHO (0.5mg/l) [9].

5) Aluminum (Al): The concentration of Al in the sediments collected and analyzed using AAS was recorded in Table II in mg/l, and it shows that the concentration of Al is highest in the samples collected from point A compare to point B, C and D. The concentration of Al in the samples collected in the area is at the range set by WHO (20 mg/l) [16].

6) Arsenic (As): The concentration of As in the sediments collected and analyzed using AAS that was recorded in Table II in mg/l, shows that the concentration of As is highest in the samples collected from point D compare to the samples collected point A, B and C. The concentration of As in the samples collected in the area is fairly higher than the range set by WHO (0.01mg/l) [8].

7) Copper (Cu): concentration of Cu in the sediments collected and analyzed using AAS that was recorded in Table II in mg/l, shows that the concentration of Cu is highest in samples collected from point D compare to the samples collected from point A, B and C. The concentration of Cu in the samples collected in the area is at the range set by WHO (2mg/l) [2].

V. CONCLUSION

This study revealed that water and sediment samples collected from the only surviving river (Enumabia River) in Orokam, Ogbadibo Local Government Area of Benue State detailed some significant heavy metal concentration that call for further adequate observations and monitoring to circumvent and curb the incessant increase of some toxic and carcinogenic metals like Lead (Pb), Chromium (Cr) and Arsenic (As) which are beyond the tolerable bounds set by

World Health Organization (WHO) and other regulatory bodies.

Since there is fast accumulation of toxic and carcinogenic metals present in the water and sediment samples collected from Enumabia River in Orokam there is need for a follow up study to determine how the human and aquatic lives have been affected.

Routine monitoring and assessment of the only surviving river in Orokam Community should be done every quarterly on annual basis to prevent indiscriminate accumulation of toxic and carcinogenic metals in the river.

Consequently the degree of contamination of the analyzed metals is not terrifyingly high, strides should be taken by Law Environmental Protection Agencies to ensure that such river is not contaminated further. Such baseline would help appropriate agencies to formulate policies on metal contamination and monitoring for environmental impact assessment.

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