

Assessment of Heavy Metals Associated with bottom Sediment of Asejire Reservoir, Southwest Nigeria

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ABSTRACT. A study on the characteristic of sediment quality of Asejire Reservoir was conducted to evaluate the heavy metal content of the reservoir. Twenty stations were selected, samples and analyzed using standard methods. The result showed that the sediment was slightly acidic across the study stations, with low conductivity and organic matter content. The heavy metals order of dominance was: Fe>Pb>Cu>Zn>Mn>Al>Ba>Ni>Cr. The mean concentration levels of all the heavy metals were lower than mean background value except Fe, Cu and Pb. However, calculated Enrichment Factor (EF) values for all the heavy metals investigated showed that they were less than 1.5 (<1.5), suggesting that the heavy metals were all derived mainly from natural sources such as bedrock materials and weathering processes.

INTRODUCTION

Sediments are materials formed due to transportation and deposition of organic and mineral matter found at the bottom of oceans, lakes, ponds and rivers [1]. The sediments are formed either from allochthonous or autochthonous materials or from both. The materials ranged fine to coarse grain minerals [2]. Data from sediments provide information on the impact of distant human activity on the wider ecosystem.

Heavy metals accumulate in sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds [3, 4]. The high contamination of aquatic system with toxic heavy metals is of major concern to the society because these elements are not biodegradable and their elevated uptake by crops and aquatic organisms may also affect food quality and safety [5]. It is a source of serious concern to government regulatory agencies and environmentalist. Though heavy metals play important roles in our society as most of them are vital raw materials in most industries, (Cu, Se, Zn, etc.) and as essential materials in the maintenance of some metabolic activities in human bodies, others at certain concentrations have been implicated in health complications in the liver, lung, intestine, blood etc.

Heavy metals accumulate in sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds [3, 4]. The dissolution and adsorption processes are influenced by several physicochemical parameters such as pH, dissolved oxygen, salinity, redox potential, organic and inorganic carbon contents and the presence in water phase of some anions and cations that can bind or co-precipitate the water-dissolved or suspended pollutants [6].

The determination of the chemical characteristics of sediments, on which benthic invertebrate animals live, is very important in the assessment of the health of the aquatic environment [7]. Heavy metals particles deposited into water either directly or indirectly washed off surfaces into water courses either react with the constituents of the water or settle to the bottom where they react with the sediments.

Various studies have demonstrated that several watercourses are contaminated by heavy metals from discharged human wastes (8-12). Recent studies on the sediment heavy metal quality of

water bodies in Nigeria include the works of [13-15]. In Nigeria, most domestic sewage and industrial effluents from both rural and urban areas are released into the environment without proper treatment. The wastewaters eventually find it to lakes and reservoirs within their catchment basins. About 30% of human generated waste found their way into rivers and reservoirs.

STUDY AREA

Asejire Reservoir is a manmade lake that was created in November 1970 by the impoundment of River Osun and officially opened in 1972. River Osun catchment basin extends from longitudes $003^{\circ} 55' E$ to $005^{\circ} 05' E$ and latitudes $06^{\circ} 35' N$ to $08^{\circ} 20' N$. However, the catchment area of Asejire Reservoir is from longitudes $004^{\circ} 07' 017'' E$ to $004^{\circ} 08' 925'' E$ and in length from latitudes $07^{\circ} 21' 48'' N$ and $07^{\circ} 26' 84'' N$ (Figure 1). It was primarily created to supply domestic and industrial water, although some ancillary benefits such as fishing activities have also emerged [16]. The reservoir receives the bulk of its water input from two rivers, Rivers Osun and its main tributary River Oba.

From the data supplied by the Oyo State Water Corporation of Nigeria, the catchment area of the dam is $7,800 \text{ km}^2$ and the impounded area is 23.42 km^2 (2,342 hectares). The dam has a normal pool elevation (water level) of 150 m and maximum flood elevation of 152.4 m. The surface area of the reservoir is about 24 km^2 . Its gross storage capacity is approximately 7,403.4 million litres per day while its discharge capacity is 136.26 million litres per day with maximum water capacity of about 675 m^3 .

The reservoir supply water to more than two million inhabitants of Oyo and Osun states. It is used by industries located within these states, while more that 20 artisanal fishermen depends on it for their daily living. With the aforementioned enormous significance of the reservoir, no detailed scientific investigation has been carried out to investigate heavy metals concentration and distribution in the sediments of the reservoir which is an important component of the food web and fishery of the reservoir.

MATERIAL AND METHODS

Sampling was carried out aboard canoe every two months for two annual cycles (June 2012 – March 2014) using an improvised Van Veen grab sampler of 0.04 m^2 ($0.2 \text{ m} \times 0.2 \text{ m}$) for sediment collection. The reservoir was divided into three sections (lower reach, mid-basin and upper reach), with an established 20 stations.

Analysis of sediments was based on air-dried samples. The samples were spread in a flat tray and allowed to dry under normal room temperature. The air-dried sediment samples were gently crushed with a pestle in a porcelain mortar and sieved through a 2mm sieve. Samples were digested in 10ml of concentrated nitric acid (70%) for two hours at $170^{\circ} C$ before the residue was diluted, filtered in volumetric flasks [17]. After digestion, the concentrations of the metals were analyzed by flame atomic absorption spectrophotometer using Perkin Elmer 3100 Flame Atomic Absorption Spectrophotometer with direct aspiration.

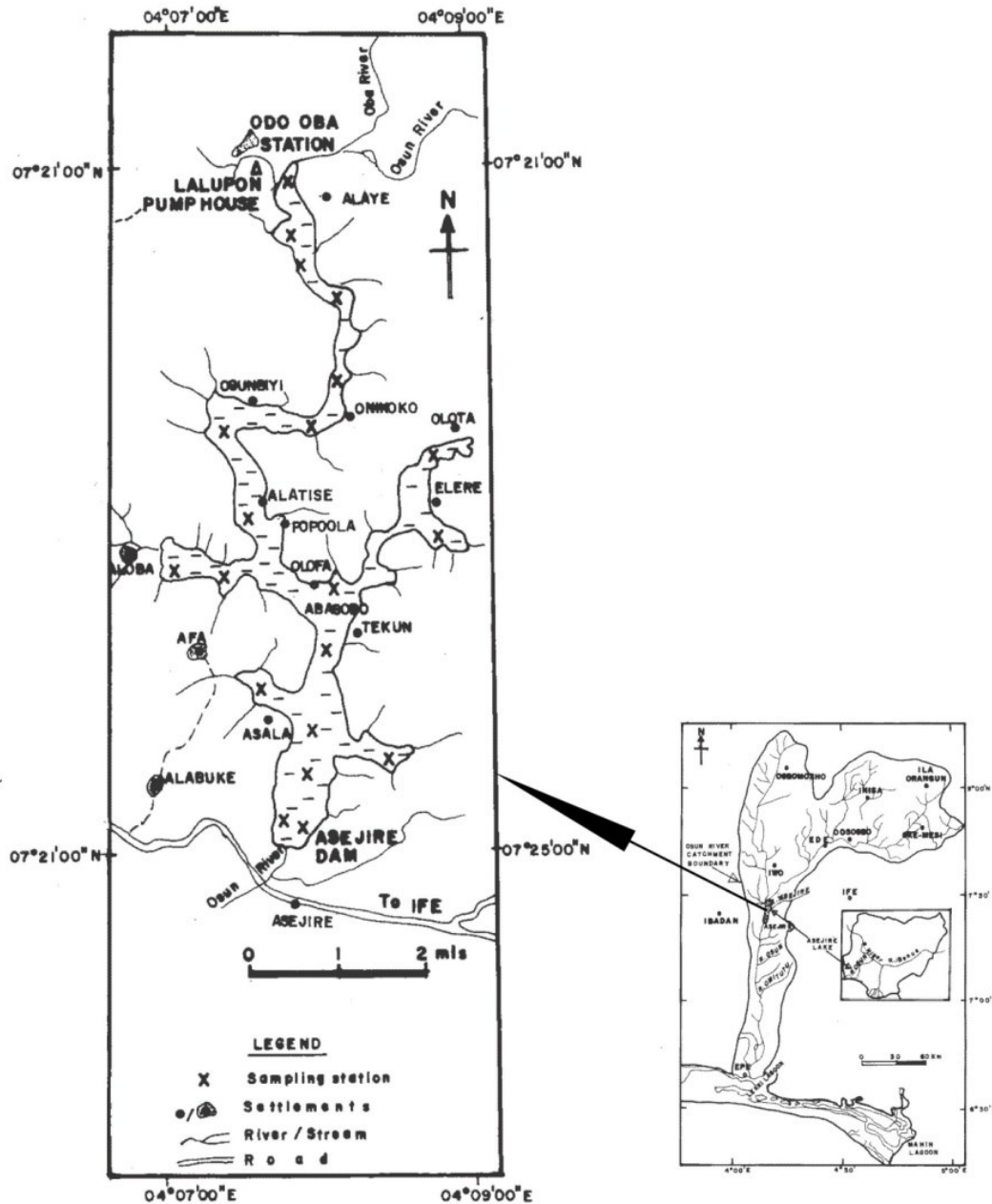


Figure 1: Map of Osun River Basin showing Asejire Reservoir, catchment basin and sampling locations

According to [18, 5], the Enrichment Factor (EF) is defined as the ratio of metal and Fe concentration of the sample with the ratio of metal and Fe concentration of the background values of the metals being investigated. This is summarized below:

$$EF = (M/Fe)_{\text{sample}} / (M/Fe)_{\text{background}}$$

Where:

$(M/Fe)_{\text{sample}}$: The ratio of metal and Fe concentration of the sample

$(M/Fe)_{\text{background}}$: The ratio of metal and Fe concentration of the background

All the statistical analyses were carried out using the Palaeotological Statistics [19], Statistical Package for Social Sciences (SPSS) Software package for biological data analysis and Statistical Ecology [20].

RESULTS

A summary of the physico-chemical parameters showing the conductivity, pH, temperature and organic carbon of the sediment of the study area are given in Table 1. pH was slightly acid ranging from 5.49 (Station 2) to 6.54 (Station 6), with mean value of 5.94 ± 0.32 . Fluctuations in mean conductivity ranged from 242.8 – 571.7 $\mu\text{S}/\text{cm}$, with an average value of $387.7\mu\text{S}/\text{cm}$. Temperature ranged from 28.6 to 29.3 (28.9 ± 0.15) while organic carbon content of the sediment ranged from 1.06% (Station 11) to 3.88% in Station 7 with a mean of $2.54 \pm 0.62\%$.

Table 1: Mean physico-chemical parameters of sediment from different locations

Station	Conductivity (μScm^{-1})		pH		Temperature ($^{\circ}\text{C}$)		Organic Carbon (%)	
	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
1	571.7	76.24	5.55	0.308	29.0	0.742	2.82	1.211
2	538.3	62.98	5.49	0.186	29.3	0.663	3.12	1.434
3	528.3	70.40	5.66	0.421	29.1	0.565	2.70	1.050
4	502.9	91.06	5.68	0.298	29.0	0.565	2.69	1.623
5	242.8	30.32	6.25	0.324	28.7	0.851	2.79	1.468
6	278.5	57.70	6.54	0.353	29.0	0.444	2.11	1.168
7	540.0	139.87	5.52	0.254	28.7	0.277	3.88	1.941
8	466.4	112.28	5.57	0.160	29.0	0.493	3.36	1.180
9	460.2	97.64	5.60	0.251	29.6	0.525	2.33	1.211
10	259.6	68.98	6.30	0.250	28.6	0.709	1.07	0.727
11	263.9	62.06	6.07	0.523	28.9	0.881	1.06	0.873
12	298.1	57.31	6.13	0.673	28.7	0.488	1.86	1.288
13	329.7	111.10	6.43	0.494	28.8	0.631	2.11	1.791
14	290.1	93.16	6.21	0.351	28.8	0.381	2.63	2.062
15	421.5	127.25	5.62	0.237	28.8	0.484	3.34	1.370
16	394.2	95.96	5.74	0.352	28.8	0.533	3.30	1.431
17	451.1	114.88	5.85	0.399	28.8	0.328	3.26	1.727
18	293.9	72.92	6.17	0.481	28.8	0.466	1.94	1.253
19	308.5	62.00	6.22	0.574	29.1	0.577	1.56	0.920
20	314.4	88.74	6.24	0.474	29.0	0.656	2.78	1.039
Minimum	242.80		5.49		28.61		1.06	
Maximum	571.66		6.54		29.26		3.88	
Mean	387.71		5.94		28.90		2.54	
S.d.	99.754		0.315		0.154		0.624	

The heavy metals contents of the sediment of the studied reservoir are presented in Tables 2. The concentrations of the heavy metals in the sediment showed thus: $\text{Fe} > \text{Pb} > \text{Cu} > \text{Zn} > \text{Mn} > \text{Al} > \text{Ba} > \text{Ni} > \text{Cr}$. Their average concentrations (mg kg^{-1}) range from 26298.2 – 56966.0 (39978.8 ± 8710.2) for Fe, 32.2 – 121.9 (72.0 ± 27.4) for Pb, 14.8 – 75.4 (43.7 ± 21.6) for Cu, 11.7 – 28.3 (20.9 ± 3.2) for Zn, 0.32 – 2.13 (1.50 ± 0.47) for Mn, 1.18 – 1.65 (1.38 ± 0.12) for Al, 0.36 – 0.70 (0.52 ± 0.06) for Ba, 0.02 – 0.10 (0.05 ± 0.02) for Ni and 0.02 – 0.05 (0.03 ± 0.01) for Cr. A close look on the data shows that concentrations of Fe, Cu and Pb were higher than the average concentrations of World Sediment background level (Table 2). However, concentrations of the other six metals were considerably lower than the average concentrations of the World Sediment background level. Such discrepancies between concentrations of elements in the area of study with those of mean World Sediments are indicative of considerable deviations in geological units [21].

Table 2: Mean Heavy metal concentration (mgkg^{-1}) in Asejire Reservoir

Station	Al		Fe		Zn		Cu		Pb		Ba		Cr		Mn		Ni	
	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.	x	s.d.
1	1.28	0.24	36975	15985	18.40	11.0	60.93	18.8	120.0	32.7	0.54	0.22	0.03	0.01	1.06	1.24	0.04	0.05
2	1.39	0.32	55355	19958	22.41	9.9	72.74	15.7	121.1	34.2	0.51	0.26	0.03	0.01	2.13	1.48	0.06	0.05
3	1.37	0.29	45394	17754	25.30	15.4	75.40	12.6	104.9	41.9	0.70	0.24	0.03	0.01	1.54	1.24	0.03	0.02
4	1.43	0.27	56334	32626	25.21	13.1	66.33	9.1	121.9	32.5	0.58	0.20	0.02	0.01	1.79	1.00	0.09	0.09
5	1.36	0.27	33077	10578	17.09	10.5	24.44	15.9	35.7	15.9	0.58	0.18	0.04	0.02	2.03	1.15	0.07	0.07
6	1.45	0.25	30075	11256	23.09	11.1	26.61	21.0	48.9	17.1	0.63	0.18	0.02	0.01	1.08	0.98	0.07	0.07
7	1.55	0.22	52138	23060	20.62	10.8	57.88	20.0	106.7	44.7	0.59	0.22	0.03	0.01	1.77	1.26	0.06	0.07
8	1.52	0.33	50610	19524	23.08	12.1	70.26	13.1	91.7	35.8	0.50	0.23	0.02	0.01	1.78	1.45	0.07	0.07
9	1.19	0.27	56966	19862	22.81	12.1	72.08	12.0	80.5	44.6	0.52	0.26	0.03	0.01	2.07	1.18	0.04	0.04
10	1.22	0.19	26809	15118	22.06	10.7	20.61	14.9	40.2	21.5	0.40	0.12	0.02	0.01	1.38	1.61	0.10	0.13
11	1.29	0.27	28293	11806	15.12	7.4	18.45	12.9	48.1	18.7	0.43	0.12	0.02	0.00	0.32	0.53	0.06	0.09
12	1.28	0.24	26298	13068	20.66	8.4	23.85	12.3	49.3	13.2	0.47	0.16	0.04	0.02	0.66	0.96	0.06	0.07
13	1.31	0.16	32828	19467	26.21	14.0	27.38	12.8	43.7	16.0	0.47	0.25	0.04	0.03	0.63	0.86	0.04	0.05
14	1.54	0.38	37643	17877	28.31	14.1	31.57	15.0	34.3	15.5	0.36	0.19	0.03	0.01	1.86	1.73	0.07	0.06
15	1.58	0.41	44340	17515	17.73	9.0	60.55	20.9	76.5	20.6	0.47	0.21	0.03	0.01	2.01	1.33	0.04	0.04
16	1.50	0.35	36760	12828	19.29	7.6	66.33	15.6	98.5	27.5	0.49	0.22	0.03	0.01	1.94	1.30	0.06	0.06
17	1.18	0.25	45797	19771	22.63	13.5	50.17	17.0	65.8	28.5	0.49	0.19	0.04	0.01	1.94	1.61	0.03	0.02
18	1.24	0.29	37876	14362	11.67	8.2	14.83	9.8	59.8	30.6	0.55	0.26	0.05	0.04	1.13	1.37	0.03	0.04
19	1.65	0.38	34447	13281	17.36	10.9	14.86	11.1	60.7	20.2	0.50	0.21	0.02	0.01	1.09	1.27	0.02	0.01
20	1.21	0.31	31563	17370	18.25	11.3	18.40	13.3	32.1	13.9	0.54	0.27	0.03	0.01	1.87	1.60	0.03	0.02
Min	1.18		26298.19		11.67		14.83		32.15		0.36		0.02		0.32		0.02	
Max	1.65		56966.00		28.31		75.40		121.94		0.70		0.05		2.13		0.10	
X	1.38		39978.78		20.86		43.68		72.02		0.52		0.03		1.50		0.05	
s.d.	0.121		8710.188		3.245		21.584		27.367		0.058		0.007		0.469		0.018	
Background value	7.2		4.1		95		50		20		-		90		900		68	

*Ogbeibu *et al.* (2014)

The calculated enrichment factor of the sediment heavy metals in the reservoir is indicated Table 3. Enrichment Factor showed that virtually all the metals investigated have a factor below 1.

Table 3: Enrichment Factor (EF) of heavy metals in sediment of Asejire Reservoir

Stations	Al	Zn	Cu	Pb	Cr	Mn	Ni
1	1.97E-05	2.10E-05	1.40E-04	7.00E-04	3.30E-08	1.30E-07	6.73E-08
2	1.43E-05	1.70E-05	1.10E-04	5.00E-04	2.40E-08	1.80E-07	6.73E-08
3	1.72E-05	2.40E-05	1.40E-04	5.00E-04	3.40E-08	1.50E-07	6.73E-08
4	1.45E-05	1.90E-05	1.00E-04	4.00E-04	1.50E-08	1.40E-07	9.99E-08
5	2.34E-05	2.20E-05	6.00E-05	2.00E-04	5.00E-08	2.80E-07	1.22E-07
6	2.74E-05	3.30E-05	7.00E-05	3.00E-04	3.00E-08	1.60E-07	1.40E-07
7	1.69E-05	1.70E-05	9.00E-05	4.00E-04	2.30E-08	1.50E-07	7.48E-08
8	1.71E-05	2.00E-05	1.10E-04	4.00E-04	2.00E-08	1.60E-07	8.71E-08
9	1.19E-05	1.70E-05	1.00E-04	3.00E-04	2.50E-08	1.70E-07	4.23E-08
10	2.59E-05	3.60E-05	6.00E-05	3.00E-04	3.90E-08	2.30E-07	2.16E-07
11	2.60E-05	2.30E-05	5.00E-05	4.00E-04	3.10E-08	5.00E-08	1.28E-07
12	2.77E-05	3.40E-05	7.00E-05	4.00E-04	7.10E-08	1.10E-07	1.38E-07
13	2.27E-05	3.40E-05	7.00E-05	3.00E-04	5.40E-08	9.00E-08	7.69E-08
14	2.32E-05	3.20E-05	7.00E-05	2.00E-04	3.50E-08	2.20E-07	1.15E-07
15	2.03E-05	1.70E-05	1.10E-04	4.00E-04	2.70E-08	2.10E-07	5.95E-08
16	2.33E-05	2.30E-05	1.50E-04	6.00E-04	3.20E-08	2.40E-07	9.84E-08
17	1.47E-05	2.10E-05	9.00E-05	3.00E-04	4.10E-08	1.90E-07	3.46E-08
18	1.86E-05	1.30E-05	3.00E-05	3.00E-04	6.00E-08	1.40E-07	5.47E-08
19	2.73E-05	2.20E-05	4.00E-05	4.00E-04	3.10E-08	1.40E-07	3.06E-08
20	2.19E-05	2.50E-05	5.00E-05	2.00E-04	4.00E-08	2.70E-07	4.78E-08
Min.	1.19E-05	1.33E-05	3.21E-05	1.87E-04	1.46E-08	5.08E-08	3.06E-08
Max	2.77E-05	3.55E-05	1.48E-04	6.65E-04	7.15E-08	2.80E-07	2.16E-07
Mean	2.07E-05	2.36E-05	8.55E-05	3.63E-04	3.59E-08	1.72E-07	8.84E-08
S.d.	4.20E-06	5.31E-06	2.79E-05	8.50E-05	1.05E-08	4.52E-08	3.50E-08

DISCUSSION

Many environmentalists have use water as pollution indicator by contaminants including heavy metals, but sediment can provide a deeper insight into long-term pollution state of aquatic environment [22, 2]. Sediments have been described as sink of pollutants whereby they concentrate according to the levels of pollution [23]. The result of the physico-chemical analysis as reported in Table 1 shows the sediment of the reservoir to exhibits small fluctuation in pH values. The pH also tends to be slightly acidic. The slightly acidic nature of all the sampling points in the reservoir may be due to the humic acid formed from decaying organic matter. The level of homogeneity observed in pH of the sediment is similar to the observations with reported works for bottom sediment of other water bodies in Nigeria [24, 25, 13]. [26, 27] reported that lower pH value is typical of the anaerobic sediments.

The low conductivity may be attributed to the low content of soluble salts in sediments as reported by [28]. The low organic matter (2.54 ± 0.62) may be related mainly to the low organic matter flux to sediments due to low discharge of domestic and industrial wastewaters from the catchment basin. Similar low values from selected major rivers in Southwestern Nigeria have been documented by [29]. Extreme concentrations of organic carbon levels below 0.05% and above 3% have been implicated in decreased benthic abundance and biomass [2]. The mean organic content obtained in the sediments from the study were within the risk associated values recommended by [30].

In other to assess the metal content in reservoir sediments, it is important to establish the natural levels of these metals and also make comparisons with values reported from other local and regional metal-contaminated rivers and reservoirs. Apart from natural contributions, heavy metals may be incorporated into the aquatic system from anthropogenic sources such as solid and liquid wastes of industries. Some degree of contamination may be caused from fall out of industrial emissions from the atmosphere.

The background value gives the normal abundance of an element [31]. The mean concentration levels of all the heavy metals were lower than mean background value except Fe, Cu and Pb. Concentration of Fe, Cu and Pb are uniformly higher than the background value. The high value of Fe in the reservoir is not unusual, as this phenomenon has been reported to be dominant in most tropical aquatic ecosystem [32, 13, 14, 33, 9]. Lead is toxic to humans and is a major anthropogenic sources included in the use of lead as petrol additives, runoff from cities, discharge on improperly treated waste effluents, sewage sludge and the use of pesticides containing lead compounds. The high concentration of Pb recorded might be due to the nature of anthropogenic activities within the catchment basin especially from motor mechanic workshops. Copper also showed a higher value in the reservoir sediment compared to the background values. [13] recorded similar high values in the sediments of Orogodo and Benin Rivers respectively. High levels of copper have been implicated in anaemia, liver and kidney damage, stomach and intestinal irritation.

To ascertain the probable sources of the metals, enrichment factor were calculated for the stations. According to [34], EF values smaller than 1.5 suggest that heavy metals derived from mainly natural sources such as weather processes, while EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. [35] divided the contamination into different categories based on EF values. If $EF < 2$, it suggests deficiency to minimal metal enrichment. However, if value of EF is greater than 2, it suggests various degrees of metal enrichment. The results of EF factor reveal that the mean EF values of all elements were below 1.5 suggesting that a significant portion of heavy metal in Asejire Reservoir is delivered from mainly natural sources as shown in Table 3.

CONCLUSION

Asejire Reservoir is a major source of water for domestic and industrial uses for more than two million inhabitants in the Southwest of Nigeria. It is also a source of fish for the local communities. The quality of the surface water and sediment is of great importance for the sustainable use of the

reservoir. The significant spatial variation recorded in the concentration of some parameters used in characterizing the sediment quality is a reflection of impacts of anthropogenic activity on the quality of the reservoir water. This study, however allayed the fear of possible heavy metals pollution in the sediment, but without precluding the need for continues monitoring of both sediment and water quality to match the potential threat from industrialization and discharge of untreated waste from the catchment basin into the reservoir.

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