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Potential Ecological Risk Assessment of Heavy Metals Contamination in Surface Sediments of Ikpoba River, Southern Nigeria

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Abstract
The potential ecological risk assessment of heavy metals contamination in surface sediments of Ikpoba River, Edo State was estimated in this study after assessment of heavy metal concentrations in surface sediments from seven stations of the study area. Heavy metals were analyzed in the sediments using Atomic Absorption Spectrophotometer. The index of geo-accumulation for the metals (Lead (Pb); Iron (Fe); Nickel (Ni) and Copper (Cu)) studied were less than zero showing that the stations sampled were unpolluted with heavy metals. Contamination factor followed same pattern. Generally, there was a low potential ecological risk for heavy metal contamination to sediment dwelling organisms. However, station 4 (Capitol) was moderately contaminated and extremely enriched with Cu. Heavy metal values in this study were below the EPA limits for sediments except station 4 which was heavily polluted with Cu following the EPA guidelines. Regular monitoring and assessment of pollution load of Ikpoba River is recommended.

Key words: Metals; Contamination; Risk; Aquatic; Sediment

Introduction

Water bodies all over the world have been exposed to an array of harmful pollutants as a result of the industrial revolution in recent years. Heavy metals are among the most common environmental pollutants and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources (Iwuoha *et al*., 2012). The strong binding affinity of heavy metals result in low concentrations in water and high concentrations in sediments. This strong binding affinity is dependent on various factors such as the sediment particles, the properties of the adsorbed compounds and the prevailing physicochemical conditions (Al-Hejuje *et al*., 2018). In many ways, sediments are considered as a reservoir and sink for heavy metals in the aquatic ecosystem and under changing environmental conditions, these metals may be released to the water column by various processes of remobilization. Geochemical study of sediments to evaluate the concentration of heavy metals is necessary as it helps to assess the ecotoxic potential of the river sediments (Iwuoha *et al*., 2012).

Environmental quality indices are powerful tools for the development, evaluation and converging of raw environmental information to decision makers, managers and the public (Iwuoha *et al*., 2012). These indices evaluate the degree to which the sediment associated chemical status might adversely affect aquatic organisms and also enable sediment assessors and managers to effectively diagnose and interpret sediment quality (Caeciro *et al*., 2005). This enables ranking and prioritizing of contaminated areas for further investigation. Several numerical sediment quality indices have been developed to provide interpretative tools for assessing chemical pollution (Al-Hejuje *et al*., 2012). Among these methods are the Sediment Quality Guidelines (SQGs), contamination factor (CF), contamination degree (CD), pollution load index (PLI), geoaccumulation index (I_{geo}), and potential ecological risk index (RI) (Ghrefat *et al.,* 2011; Khuzestani & Souri 2013; Zarei *et al.,* 2014, Enuneku *et al*., 2018).

In Nigeria, most domestic sewage and industrial effluents from both rural and urban areas are released into the environment without proper treatment (Asibor *et al*., 2015). Ikpoba River being a major river within the Benin metropolis is not an exception to this menace. The present study is thus aimed at investigating the concentration and distribution of heavy metals (Pb, Cu, Fe, Cd) in Ikpoba River to assess the pollution status as well as the potential ecological risk indices using enrichment factor (EF), geo-accumulation index (I_{geo}), contamination index and potential ecological risk index.

Materials and Methods

Study area

Ikpoba River (Lat 6.5ºN, Long 5.8ºE) is located in Benin City, Edo State in Southern Nigeria. The study area is situated within the Western Littoral Hydrological area of Nigeria (Akintola, 1986). Its headwater originates from North West of Benin City and flows north to south through the city. The river flows through a dense rain forest where the allochthonous input of organic matter from the surrounding vegetation is derived through run-off from the surface of the soil. The vegetation of Ikpoba River consists of rainforest which is secondary in nature and has been greatly subjected to deforestation and other anthropogenic activities. The study area is composed essentially of the secondary rainforest vegetation type and majorly composed of grasses, shrubs, epiphytic ferns, water hyacinth (*Eichorrnia carssipes*) palm trees (*Elaeis guinenses*), bamboo trees (*Bambusa bambusa*), and rubber tree (Ibezute *et al*., 2016). The riparian communities are sparsely populated and their main activities are farming, fishing and palm-wine tapping. Industrial wastes and water from drainage channel are discharged into the river at several points especially at the Benin City storm water discharge point.

Station 1 (6.4532°N, 5.6095°E) was at the Iguosa Stretch of the River; Station 2 (6.4513°N, 5.6162°E) was at Evwomore; Station 3 (6.4105°N, 5.6372°E) was at Ekosodin axis; Station 4 (6.4049°N, 5.6389°E) was at Capitol directly under the bridge at the fringe of University of Benin; Station 5 (6.3761°N, 5.6461°E) was at Upper Lawani (storm water discharge point) ; station 6 (6.3517°N, 5.6467°E) was at the slaughter house and station 7 (6.3343°N, 5.6636°E) was at the Guinness Brewery.

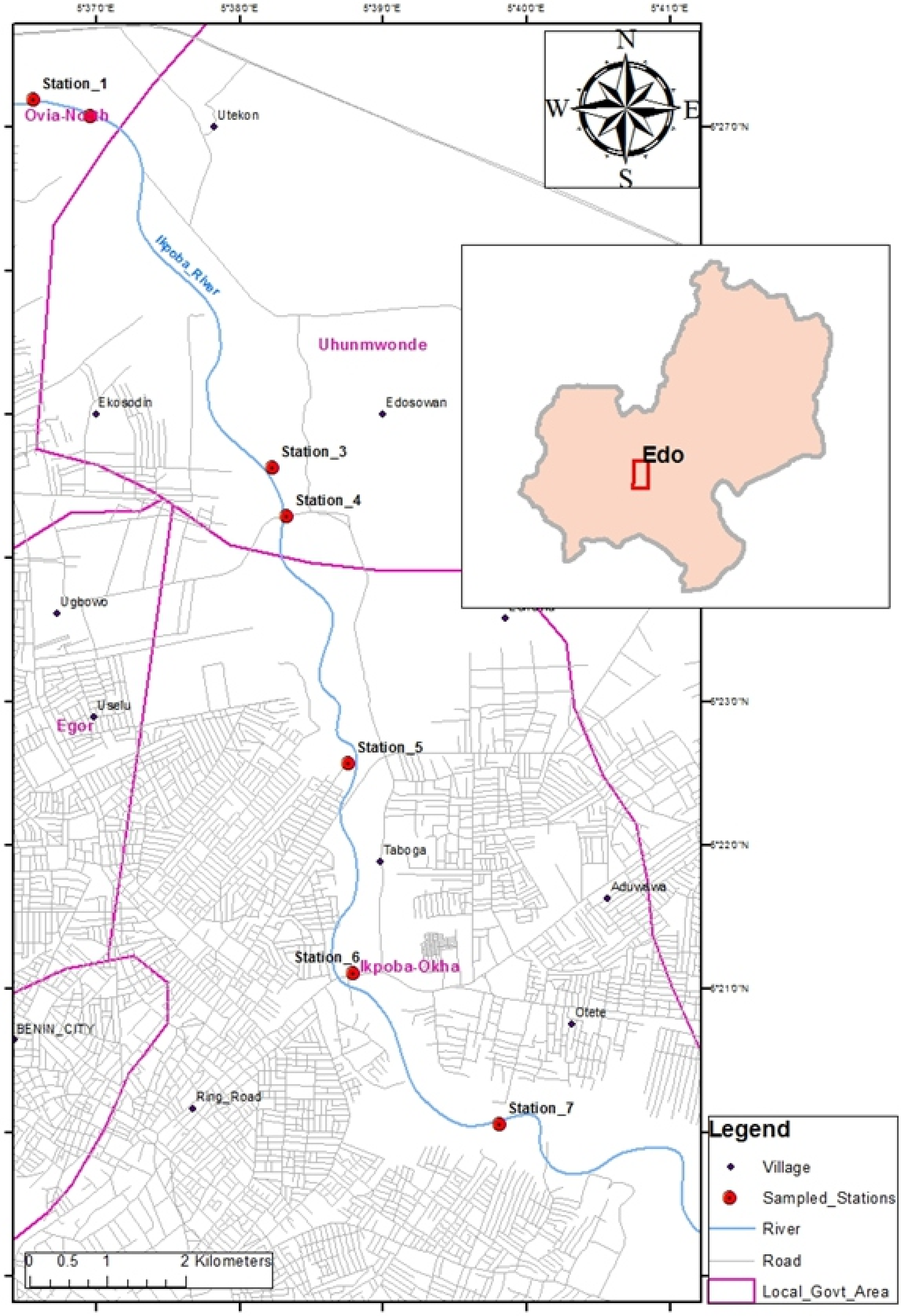

Figure 1: *Map sowing the study area along Ikpoba River*

Sample Collection and Analysis

Collection of Sediment Samples

Twenty-one (21) superficial sediment samples (0-5cm) (Maanan *et al.* 2015) were collected using a Van Veen grab from October to December 2018. They were collected from seven stations of the river beginning from the source downwards as it traverses the city. The sampling stations were chosen based on the prevailing stresses including the Benin City storm water discharge point.

Chemicals and reagents

All chemicals and reagents were of

analytical grade. Materials and reagents used included 72% HNO_3 (BDH), 37% HCl (JHD). In order to construct the calibration curves, working standard solutions for Cd, Pb, Cu, Ni, Fe and Zn were freshly prepared by diluting an appropriate aliquot of standard solutions containing 1000 ppm with serial concentrations for each element using 0.1%HNO_3. Glassware and polyethylene containers were cleaned and soaked in 10% HNO_3 for 48 hours and then rinsed thoroughly with deionized water.

Sample Digestion and Heavy Metal Analysis

In the laboratory, the soil samples were air dried for 48 hours and grounded with ceramic mortar and pestle. Digestion of soil samples was carried out after the modified method of Likuku *et al.*, 2013 and Massadeh *et al.*, 2017). Then 1g of sample was digested in 10ml freshly prepared aqua regia (3:1, HNO_3:HCl) in a hot sand bath on a hot plate for 45 minutes. It was allowed to cool. Twenty (20) ml of distilled water was then added. Then it was filtered through a whatman filter paper (110 mm) into a 100ml standard flask. It was made up to mark with distilled water. Samples were then analysed for heavy metals using atomic absorption spectrophotometer (Buck Scientific, 210 VGP).

Sediment Contamination

To determine the degree of contamination by a specific metal and distinguish natural and anthropogenic inputs EFs, I_{geo}, E_I, RI were computed.

Efs (Equation 1) were computed by comparing the measured metal levels to the pre-industrial levels. To avoid anomalies in the calculation of the enrichment, geochemical normalization based on the concentration of a conservative element is commonly employed. Fe, Al, Sc, Mn and Li are usually used as the conservative reference element (Wang *et al.*, 2018). The aim of normalization is to correct changes in the nature of sediments which may influence contaminant distribution (Iqbal and Shah, 2014). In this study, Fe was chosen as the conservative element for normalization. Fe is normally characterized by high natural concentrations and so can hardly be enriched by anthropogenic sources.

$$EF = \frac{M_x/Fe_x}{M_b/Fe_b} \quad \text{..........................Equation 1}$$

where EF is the enrichment factor, M_x and Fe_x are the metal and Fe content of the sample. M_b and Fe_b are the metal and Fe background shale contents in the continental crust (Salomons and Forstner, 2012; Khodami *et al.* 2016).

The calculated EFs will be profiled using the classification reported by Sakan *et al.* (2009). where;

EF<1: no enrichment
1<EF<3: minor enrichment
3<EF<5: moderate enrichment
5<EF<10: moderately severe enrichment
10<EF<25: severe enrichment
25<EF<50: very severe enrichment
EF>50: extremely severe enrichment

I_{geo} (Equation 2) is a criterion commonly used to estimate heavy metal pollution in surface sediments (Muller 1969, Zhenwu *et al* 2015). It reflects the degree of contamination of the sediment by a metal. It is computed using the relationship.

$$Igeo = \log_2\left(\frac{C_n}{1.5 \times B_n}\right) \quad \text{..........................2}$$

where C_n is the measured level of the metal, n in the sediment and Bn is the background concentration of the metal (average shale concentration as given by Turekian and Wedepohl 1961) while 1.5 is the factor compensating background data for data correction due to lithogenic effect. Muller (1969) characterized I_{geo} into seven classes beginning from class 0 to class 6.

*I*geo ≤ 0 (grade 0), unpolluted
0 < *I*geo ≤ 1 (grade 1), slightly polluted
1 < *I*geo ≤ 2 (grade 2), moderately polluted
2 < *I*geo ≤ 3 (grade 3), moderately severely polluted
3 < *I*geo ≤ 4 (grade 4), severely polluted
4 < *I*geo ≤ 5 (grade5), severely to extremely polluted
*I*geo > 5 (grade 6), extremely polluted.

Assessment of Potential Ecological Risk

The quantitative approach developed by Hakanson (1980) was used to estimate the potential ecological risk of heavy metal pollutants in sediments. PERI reflects the susceptibility of biological populations to toxic substances. The main function of potential ecological risk index is to indicate the contaminant agents and where contamination studies should be given priority. PERI (Equation 3) was estimated to assess the degree of heavy metal pollution in sediments according to the toxicity of heavy metals and the response of the environment.

$$\text{PERI}_{i=} \sum E_f^i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

$$E_f^i = T_r^i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

where PERI_i is the sum of all risk factors for heavy metals in sediments ie sum of monomial potential ecological risk indices. E_f^i (Equation 4) is the monomial potential ecological risk factor, *Cf* is the contamination factor and T_r^i is the toxic response factor which represents the potential hazard of heavy metal contamination by indicating the toxicity of particular heavy metals and the environmental sensitivity to contamination. According to Hakanson (1980), Cd, Cu, Ni and Pb have toxic response factors of 30, 5, 5 and 5 respectively (Hsu *et al*. 2016).

Contamination factor was estimated by dividing the mean heavy metal concentration in this study by its corresponding average shale concentration.

$$\text{CF} = \frac{\text{Mean metal concentration at contaminated site}}{\text{Metal average shale concentration}} \qquad (5)$$

Hakanson categorized CF values into four grades ie

CF<1: class 1 with low CF

1 ≤ CF<3: class 2 with moderate CF

3 ≤ CF<6: class 3 with considerable CF

CF ≥ 6: class 4 with very high CF

As suggested by Hakanson (1980), E_f^i <40 indicates a low potential monomial ecological risk; 40< E_f^i <80 is a moderate ecological risk; 80< E_f^i <160 is a considerable ecological risk; 160< E_f^i <320 is a high ecological risk and E_f^i > 320 is a very high ecological risk. PERI_i < 95 indicates a low potential ecological risk; 95 < PERI_i < 190 is a moderate ecological risk; 190 < PERI_i < 380 is a considerable ecological risk and PERI_i > 380 is a very high ecological risk.

Results

The summary table for heavy metal concentration in sediments of the Ikpoba River are as shown in Table 1. The variation in concentration of Pb, Ni and Fe in the stations were significant indicating that the stations had varying concentration of the metals.

EF and Igeo of individual metals are shown in Table 2. EF for station 1 showed that the station was minimally enriched with Pb, Ni and Fe with moderately severe enrichment with Cu. Station 2 and 3 were minimally enriched with Ni and Fe and moderately severely enriched with Cu. In station 4, there was extremely severe enrichment with Cu. Station 5 had moderately severe enrichment with Cu. In station 6, there was minor enrichment with Ni and Fe and severe enrichment with Cu. Station 7 had moderately severe enrichment with Pb and Ni with minor enrichment with Fe while Cu was very severely enriched. The enrichment factor ranged between 0.17 – 6.06 for Pb, 0.70 to 5.08 for Ni, 0.69 to 1.93 for Fe and 7.11 to 80.90 for Cu. For Pb, Ni and Fe, the lowest and highest enrichment factors were in station 5 and 7 respectively. This pattern was different for Cu as the highest enrichment factor (80.90) was observed in station 4 while the lowest observed in station 1. Igeo were all ≤ 0 (grade 0) for the metals in all the stations. The CF, monomial E_f^i and PERI for heavy metals in the sediments are shown in Table 2. The CF for all the stations were < 1 except station 4 with a CF of 1.47 with Cu. This indicates that station 4 is moderately contaminated with Cu as 1 < CF < 3. The monomial E_f^i for each of the heavy metals were all less than 40. PERI which is the sum of the monomial ecological risk for the metals were 1.01 for station 1, 1.06 for station 2, 0.89 for station 3, 7.48 for station 4, 0.89 for station 5, 1.82 for station 6 and 3.66 for station 7. The values were all less than 40 indicating low potential ecological risk.

Table 1: Summary Table for heavy metal concentration in sediments of Ikpoba River between September and November, 2018

Stations	Heavy metals (mg/kg)				
	Pb	**Ni**	**Fe**	**Cu**	**Cd**
Station 1					
Mean ± SD	0.83±0.30[b]	2.10±0.16 [b]	857.82±159.45 [ab]	5.81±2.52	BDL
Min	0.48	2.00	748.66	4.36	
Max	1.05	2.28	1040.80	8.72	
Station 2					
Mean ± SD	0.32±0.16 [a]	2.29±0.44 [b]	1104.76±501.01 [b]	7.27±2.52	BDL
Min	0.19	2.02	613.90	4.36	
Max	0.50	2.80	1615.34	8.72	
Station 3					
Mean ± SD	0.15±0.13 [a]	1.61±0.54 [ab]	1236.28±29.64 [bc]	6.63±2.19	BDL
Min	0.00	1.00	1208.80	4.36	
Max	0.25	2.02	1267.69	8.72	
Station 4					
Mean ± SD	0.17±0.03 [a]	1.23±0.39 [ab]	746.53±81.11 [ab]	66.17±101.36	BDL
Min	0.15	1.00	654.38	4.36	
Max	0.20	1.68	807.10	183.14	
Station 5					
Mean ± SD	0.06±0.11 [a]	0.87±1.10 [a]	594.06±115.49 [a]	7.27±5.03	BDL
Min	0.00	0.00	507.08	4.36	
Max	0.19	2.10	725.09	13.08	
Station 6					
Mean ± SD	0.07±0.12 [a]	0.57±0.33 [ab]	965.97±62.76 [bc]	15.29±5.73	BDL
Min	0.00	1.00	922.30	11.00	
Max	0.20	2.07	1037.89	21.80	
Station 7					
Mean ± SD	2.20±0.46 [c]	0.35±0.20 [c]	1651.85±426.97 [c]	23.87±3.58	0.007 ±0.01
Min	1.90	6.07	1171.00	21.80	0.00
Max	2.73	6.68	1986.55	28.00	0.02
P value	**$p < 0.001$**	**$p < 0.001$**	**$p < 0.05$**	**$p > 0.05$**	

P < 0.001 highly significant, p < 0.05 significant. Similar superscripts indicates no significant difference based on DMR test

Table 2: EF and I_{geo} of individual metals in sampled stations

	Pb		Ni		Fe		Cu		Cd	
Station	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}
1	2.27	-5.18	1.70	-5.60	1.00	-6.37	7.11	-3.54	0.00	0.00
2	0.88	-6.55	1.85	-5.48	1.29	-6.00	8.89	-3.22	0.00	0.00
3	0.41	-7.64	1.31	-5.98	1.44	-5.84	8.10	-3.35	0.00	0.00
4	0.46	-7.49	1.00	-6.37	0.87	-6.57	80.90	-0.03	0.00	0.00
5	0.17	-8.89	0.70	-6.88	0.69	-6.90	8.89	-3.22	0.00	0.00
6	0.18	-8.81	1.15	-6.16	1.13	-6.20	18.70	-2.14	0.00	0.00
7	6.06	-3.77	5.08	-4.02	1.93	-5.42	29.18	-1.50	0.00	0.00

Table 3: CF, Monomial E_f^i and PERI for heavy metals in sediments of sampled stations

	Pb		Ni		Fe		Cu		Cd		
Station	Cf	E_f^i	Cf	E_f^i	Cf	E_f^i	Cf	E_f^i	Cf	E_f^i	**PERI**
1	0.04	0.21	0.03	0.15	0.02	0.00	0.13	0.65	0.00	0.00	**1.01**
2	0.02	0.08	0.03	0.17	0.02	0.00	0.16	0.81	0.00	0.00	**1.06**
3	0.01	0.04	0.02	0.12	0.03	0.00	0.15	0.74	0.00	0.00	**0.89**
4	0.01	0.04	0.02	0.09	0.02	0.00	1.47	7.35	0.00	0.00	**7.48**
5	0.00	0.02	0.01	0.06	0.01	0.00	0.16	0.81	0.00	0.00	**0.89**
6	0.00	0.02	0.02	0.10	0.02	0.00	0.34	1.70	0.00	0.00	**1.82**
7	0.11	0.55	0.09	0.46	0.03	0.00	0.53	2.65	0.00	0.00	**3.66**

Table 4: EPA heavy metal Guidelines for sediments (mg/kg)

S/N	Metals	Not polluted	Moderately polluted	Heavily polluted	Present Study
1	Pb	<40	40 – 60	> 60	0.00 – 2.73
2.	Ni	<20	20 – 50	>50	0.00 – 2.27
3.	Fe	ND	ND	ND	507.08 – 1986.55
4.	Cu	< 25	25 – 50	>50	4.36 – 183.14

Discussion

The pollution status of sediments of the Ikpoba River was assessed in this study using Igeo, EF, CF, monomial E_f^i and PERI. The results of this study indicated that there was a low PERI for heavy metal contamination to sediment dwelling organisms. Station 4 was extremely enriched with Cu. Igeo for all the metals were less than 0 indicating that the stations sampled were unpolluted with heavy metals. The contamination factor followed same pattern as the EF and Igeo as the values for all the metals were less than one except Cu in station 4. This shows that station 4 was moderately contaminated and extremely enriched with Cu. Generally, sediments of all the sampling stations along the Ikpoba River were unpolluted with heavy metals. This observation is germane as the heavy metal values in this study are below the EPA limits for sediments except station 4 which was heavily polluted with Cu following the EPA guidelines. Similar findings have been reported by Ogbeibu *et al*., (2014) and Asibor *et al.*, (2015). Bearing in mind the vulnerability of the Ikpoba river to contamination by heavy metals from domestic and industrial wastes, regular monitoring and assessment is recommended.

Conclusion

In this study, there was a low potential ecological risk for heavy metal contamination to sediment dwelling organisms. However, station 4 (Capitol) was moderately contaminated and extremely enriched with Cu. Heavy metal values in this study were below the EPA limits for sediments except station 4 which was heavily polluted with Cu following the EPA guidelines. Regular monitoring and assessment of pollution load of Ikpoba River is recommended.

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