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INDEX MODEL APPROACH OF HEAVY METALS POLLUTION ASSESSMENT IN SEDIMENT QUALITY OF OKPORKU RIVER, OGOJA, CROSS RIVER STATE NIGERIA

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ABSTRACT

Evaluation of heavy metal pollution in sediment in Okporku River, Okoja, Cross River State was carried out between October and December, 2014. Three sampling stations were selected for this study. Samples were analyzed using Atomic Absorption Spectrophotometer. The heavy metals determined in this study include lead, chromium, iron, copper and cadmium. The mean ± standard deviation values of cadmium was 0.033±0.006mg/kg, chromium was 0.051± 0.005mg/kg, copper was 0.050 ± 0.001mg/kg, Iron was 0.095 ± 0.007mg/kg and Lead was 0.024 ± 0.020mg/kg. There were significant differences (P<0.05) in cadmium, chromium, copper, iron and Lead in the stations sampled. Assessment of the heavy metal load of Okporku River revealed that the sediment is not heavy metal-polluted. The PLI was less than 1 for all stations indicating unpolluted and the Igeo values for iron fell in class '0' in all the 3 sampling stations, indicating that there is no pollution, Lead fell in class '3' in station 3 indicating moderately to heavily contaminated condition in these stations and class '0' in station 2 of the first month and I, 2 and 3 in the second and third month indicating practically uncontaminated condition in these stations, in class '6' in station 1, 2 and 3 indicating extremely contaminated condition for iron and for chromium in station 1 and 3. These were values below the Environmental Protection Agency (EPA) permissible limits for sediment. However, the continuous build-up of the metal contaminants can be checked if relevant government agencies ensure strict compliant of industrial standards which stipulate treatment of industrial wastes before the discharge of such contaminated effluents/wastes into the River.

Keywords: Heavy metals, Pollution, Accumulation, Sediment, Okporku River.

1. INTRODUCTION

Sediment is the loose sand, clay, silt and other soil particles that are deposited at the bottom of water body or accumulated at other depositional sites. Sediments can emanate from the erosion of bedrocks and soil or from decomposition of plants and animals (Akpan and Thompson, 2013). Heavy metals are among the most common environmental pollutants and their occurrence in waters and biota indicate the influence of natural or anthropogenic activity. Heavy metals are chemical elements having atomic weights between 63.546 and 200.590 and a specific gravity that is 5 times greater than that of water. The existence of trace metals in aquatic environments usually lead to serious concerns about their influence on plant and animal life (Iwuoha *et al,* 2012). Geo-accumulation index is the quantitative measure of the degree of pollution in aquatic sediment. It consists of seven grades ranging from unpolluted to very extremely polluted (Andem *et al.,* 2015). Pollution load index is a quick tool used to compare the pollution status of different environment. Pollution load index is use to determine the pollution severity and its variation along the different sample stations (Adel mashaan rabee *et al.,* 2011). Sediments are an important repository for various pollutants such as pesticides and heavy metals. These play a significant role as sensitive indicators for monitoring contaminants in aquatic systems. Aquatic organisms inhabiting polluted sediments are considered to be important carriers as sink for heavy metals in the hydrological cycle and reflect the current quality of the system as well as provide information on the impact of pollution sources (Ebru and Baha, 2012). Waste materials including organic and inorganic chemicals, terrestrial runoff, liquid effluents, and leachate carrying chemicals originating from numerous urban, industrial, and agricultural sites eventually accumulate in sediments. Anthropogenic and natural pollutants cause the accumulation of heavy metals in marine sediments. So, the majority of heavy metal emissions from anthropogenic sources accumulate in river and ocean sediments (Ebru and Baha, 2012). All heavy metals exert toxic effects at some level of concentration. They originate from mining, smelting, electroplating, and other industrial processes that have metal residues in their wastes and also through non-point source surface run off. Some specific local sources include discharge from smelters (Cu, Pb, Ni), metal based industries (Zn, Cr, Cd from electroplating), paint and dry formulators (Cd, Cr, Cu, Pb, Zn, Hg and Se), and petroleum refineries (As, Pb). The pollution of the aquatic environment with heavy metals due from urbanization and industrial development has become a major problem in recent years (Ebru and Baha, 2012). Heavy metals discharged into aquatic systems may be immobilized within the stream sediment by main processes such as adsorption, flocculation and co-precipitation (Barakat *et al.,* 2012).Heavy metals exist in water in colloidal, particulate and dissolved phases with their occurrence in water bodies being either of natural origin (e.g. eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin(that is; solid waste disposal, industrial or domestic effluents, harbor channel dredging) (Momodu and Anyakora, 2009). No work has been done on heavy metal pollution in Okporku River. This study will provide baseline line information on the degree of heavy metal pollution of the River. Findings from this research shall add to the knowledge of the inhabitants of the area of the effects of the sediment body studied.

2. MATERIALS AND METHODS

2.1. Description of the study area

Okporku River is geographically located between latitude 6°44'48.5"N and longitudes 08°6'22.9"E (Fig. 1). The area is found in the derived Guinea Savannah vegetative zone, which experiences humid tropical climate with marked dry (November-March) and rainy (April-October) seasons. The mean relative humidity of the area varies from 50-75%, with the estimated annual rainfall range between 1750 and 2000 mm. The annual temperature varies from 27-28°C. The geological formation of the area consists of the crustacean sediment made from the sedimentary formation of shells and the sandstones group (Akpan-idiok *et al*, 2012). The area has a number of surrounding villages with over 4000 ha of abundant land for irrigation agriculture. It is sandwiched between two major commercial agricultural towns: Ogoja and Okuku, all in Cross River State. It has a population of about 4,649 people out of which about 70% are farmers. The major economic activities in the area are crop production and fishing at small scale. The major crops grown include: Cassava, maize, yam, melon, groundnut and vegetables. The vegetation around the Okporku River is not of the Nypa palms or Mangrove or the Achy Gums occasioned by the typical fresh water swamp environment but were plants of other species growing on the shore of the river (Akpan-idiok *et al*, 2012).

2.1.1. Sampling station

Three sampling stations were chosen along the river course. The co-ordinates of the samplings stations were taken using geographic positioning system (GPS) and approximate distances of the stations were calculated.

Station 1

This station is the control point and upstream since the activities around this station is minimal or absent. This station is called 'Itakpana', and geographically located between Latitude 06°45'34.9"N and Longitude 08°42'04.6"E. The community drink from this river and also by farmers who pass through here to their farms and the channel is bordered by a swamp used in growing rice.

Station 2

This Station is the first downstream and is geographically located between Latitude 06°44'46.6"N and Longitude 08°39'58.8"E. This station is called 'Ehohokpa', is polluted due to agricultural wastes that are discharged into the river.

Station 3

This station is second downstream station, it is called 'Urubri', and is geographically located between Latitude 06°43'29.2"N and Longitude 08°40'27.8"E. this station forms a sort of confluence in the middle which empties into the Okpauku river. Activities around this station includes bathing, washing of clothes and motorcycles and fishing (but not on a commercial scale) that is carried out here.

2.2 Collection of Samples

Sediment samples were collected into a sterile polythene bag using hand trowel from three different sample stations. Sample collected commenced from the month of September to the month of November, 2014 between 9am to 3pm., then the sediment sample were taken to the Department of Chemistry, University of Calabar for analysis.

2.3 Analysis for Heavy metals

Sediment samples collected were subjected to standard laboratory analytical procedures as described by APHA (2005). The samples were air dried and sieved in 500μm mesh. 1.5 g of the fine sediment were weighed into Teflon vessels and 3.0 ml of 37% HCL, 6 ml of 65% HNO_3 and 0.25 mL of 30% H_2O_2 were added and thoroughly mixed. The mixtures were then digested in ethos 900 microwave digester for 26 min. The digested samples were allowed to cool in a water bath for 30 min and the concentrations of the Cadmium (Cd), Chromium (Cr), Iron (Fe), Lead (Pb) and Copper (Cu) were determined using Perkin-

Elmer Analyst 300 Atomic Absorption spectrophotometer (AAS).

2.4. Statistical Analysis

Data obtained were subjected to Descriptive Statistics for mean, range and standard. Inter station comparisons were carried out to test for significant differences in the Heavy metals presence using parametric analysis of variance (ANOVA) and Duncan Multiple Range (DMR) test was used to separate the mean values among stations. To determine the magnitude of heavy metal contamination in the sediment, the Pollution Load Index (PLI) and geo-accumulation Index (Igeo) were employed.

Pollution load index (PLI) for each station were evaluated using the procedure of Tomlinson *et al.* (1980) adopted by Andem *et al.*, 2015

$PLI = (CF1 \times CF2 \times CF3x............CFn)^{1/n}$ .... (1)

Where: n = number of metals

CF = contamination factor

CF = Metal concentration in sediment/Background values of the metal

PLI is a potent tool in heavy metal pollution evaluation. According to Chakravarty and Patgiri (2009) the PLI value > 1 indicates pollution

PLI value < 1 indicates no pollution.

The geo-accumulation index (Igeo) values were calculated for the different metals using the equation of Mullers (1969) adopted by Andem *et al.*, 2015

$Igeo = \log_2 (Cn/1.5Bn)$... .... (2)

Where;

Cn = measured concentration of element n in the sediments

Bn = geochemical background for the element n

Muller (1981) proposed seven classes of the geo- accumulation index.

Class 0 = Igeo <0 (practically uncontaminated)

Class 1= 0 < Igeo < 1 (uncontaminated to moderately contaminated)

Class 2 = 1 < Igeo < 2 (moderately contaminated)

Class 3 = 2 < Igeo < 3 (moderately to heavily contaminated)

Class 4 = 3 < Igeo < 4 (heavily contaminated)

Class 5 = 4 < Igeo < 5 (heavily to extremely contaminated)

Class 6 = 5 < Igeo (extremely contaminated)

Class 6 is an open class and comprises all values of the index higher than Class 5. The elemental concentrations in Class 6 may be hundred fold greater than the geo-chemical background value.

In these computations, the world average concentration of Cr (90 mg/kg), Zn (95 mg/kg), Cu (50 mg/kg), Pb (20 mg/kg), Mn (900 mg/kg) and Ni (68 mg/kg) reported for world shale (Onyari *et al.*, 2003) were considered as the background values.

3. RESULTS

3.1. Heavy metals in Sediment

Summary of the mean concentrations for the metals of sediments at the study stations and the calculated F-values of one way analysis of variance measured in Okporku River were presented in Table 1 and 2. Also, summary of Pollution Load Index (PLI) and Geo-accumulation Index (Igeo) on sediment quality of Okporku River is presented in Table 3. The heavy metals determined in this study include lead, chromium, iron, copper and cadmium. Spatial variations in their mean values are shown in Figure 4. The mean ± standard deviation of cadmium was 0.033 ±0.006mg/kg and the range was between 0.028-0.039mg/kg the highest mean value for cadmium was shown in station 1 and the lowest was in station 2 (Table 1). The mean ± standard deviation of Chromium was 0.051 ±0.005mg/kg and the range was between 0.046-0.055mg/kg the highest mean value for Chromium was recorded in station 3 and the lowest was in station 2 (Table 1). The mean ± standard deviation of Copper was 0.050 ±0.001 mg/kg and the range was 0.049-0.051mg/kg. The highest mean value for Copper was shown in station 1 and the lowest was in station 2 (Table 1). The mean ± standard deviation of Iron was 0.095 ±0.007 mg/kg and the range was 0.089-0.103mg/kg. The highest mean value for Iron was shown in station 2 and the lowest was in station 1(Table 1). The mean ± standard deviation of Lead was 0.024 ±0.020 mg/kg and the range was 0.00-0.036mg/kg. The highest mean value for Lead was shown in station 3 and the lowest was in station 2 respectively (Table 1). All the heavy metals assessed showed significant differences across the stations sampled. Analysis of variance (ANOVA) revealed the same trend in spatial variation of these heavy metals (Table 2).

3.2 Pollution Load Index and Geo-accumulation Index

The Pollution Load Index (PLI) was calculated for each of the study stations according to the methods of Tomlinson *et al.* (1980). A PLI value > 1 signifies pollution, while PLI value < 1 indicates no pollution. The PLI values recorded for all the stations were below 1 (Table 3 and Figure 2). Thus the sediment of the study stretch of Okporku River is unpolluted. The calculated Igeo values are presented in Table 3 and the variations are shown graphically (Figure 4). It is evident from the figure that the Igeo values for chromium fell in class '1' in sampling station 1 indicating uncontaminated to moderately contaminated and class "0" in sampling stations 2 and 3, indicating no pollution in these stations. Chromium, Copper, Iron and Lead fell in class "0" in all sampling stations indicating no pollution. The Igeo values were not consistent with those derived for PLI. All trace metals had concentration below the EPA regulatory limits for sediment except for iron which was detectable (Table 4).

4. DISCUSSION

Sediment quality is usually employed as a pollution indicator by contaminants including trace metals; sediments can provide a deeper insight into the long-term pollution state of the aquatic environment (Andem *et al.,* 2015). Sediments have been described as a ready sink of pollutants where they concentrate according to the levels of pollution (Onyari, *et al.,* 2003). High levels of copper have been implicated in anaemia, liver and kidney damage, stomach and intestinal irritation. Lead is toxic to humans and its major anthropogenic sources include petrol where it is used as additive, runoff from the cities, discharge of untreated waste effluents, sewage sludge from shipping activities and some pesticides (Ogbeibu *et al*., 2014). The concentrations of Lead was higher in station 1 while copper was still higher in station 1, these could be as a result of anthropogenic disturbances associated with some untreated wastes produced by humans and sewage sludge around the River. The mean concentrations of these elements were lower when compared to that Akan *et al*., 2010 in River Ngada. These could be attributed to the fact that anthropogenic disturbances embedded in the shoreline were discharged into the River. Chromium is an abundant element in the earth crust. It occurs in oxidized forms ranging from Cr^{2+} to Cr^{6+}. Only Cr^{3}+ and Cr^{6}+, are, however of biological importance. Industrial effluent is a major source of chromium followed by urban run-off (Majolade *et al*., 2012). The values recorded in this study were lower when compared to the mean values reported by Olomukoro and Azubuike, 2009 in Ekpan Creek and higher when compared with the mean value given by Ogbeibu *et al.,* 2014 in Benin River. These differences could result in different sampling frequencies and period. The pollution load index (PLI) and the Geo-accumulation Index (Igeo) have been used extensively in the assessment of sediment pollution of trace metals (Bentum *et al*., 2011). The results of the present evaluation revealed that the sediment of the study stretch of the Okporku River is unpolluted by heavy metals. The PLI was less than 1 for all stations indicating unpolluted and the Igeo values for iron fell in class '0' in all the 3 sampling stations, indicating that there is no pollution from these metals in the Okporku River sediments, lead fell in class '3' in station 3 indicating moderately to heavily contaminated condition in these stations and class '0'in station 2 of the first month and 1,2 and 3 in the second and third month indicating practically uncontaminated condition in these stations and copper fell in class '3' in station 1,2 and 3 also indicating moderately to heavily contaminated condition in these stations , in class '6' in station 1, 2 and 3 indicating extremely contaminated condition for Iron and for Chromium in station 1 and 3. These results point to the fact that the trace elements in sediments were below the EPA permissible limits for sediment, an indication that the most areas of the Okporku were not polluted except for a few pockets contaminated. The concentrations of heavy metals in sediments varied according to the rate of particle sedimentation, the rate of heavy metals deposition, the particle size and the presence or absence of organic matter in the sediments. The concentration of Cd, Cr, Cu, Fe and Pb in Okporku sediments observed in this study ranges between 0.028 – 0.039, 0.046 – 0.055, 0.049 – 0.051, 0.089-0.103 and 0.00-0.036 mg/kg dry weight sediment for the metals respectively. Iron recorded high concentrations when compared with other metals assessed (Table 1).this may be due to the high concentration of these metals in suspended (Adel mashaan rabee *et al.,* 2011). The increase in the level of these metals is anthropogenic-based and constitutes a serious risk to humans and animals using the river water for various purposes. Similar observations were also made for Ona River situated in Akpata, Ibadan, Oyo state of Nigeria (Andem *et al.,* 2015).

5. CONCLUSIONS

Okporku River is one of the major Rivers in Ijegu Community of Yala Local Government Area of Cross River State. Local communities use this River for fishing and agricultural activities. Finding from the evaluation and characterization of sediment quality sampled in this study reflects the impacts of anthropogenic activities on quality of the river. However, the continuous build-up of the metal contaminants can be checked if relevant government agencies ensure strict compliant of industrial standards which stipulate treatment of industrial waste before discharging such contaminated effluents/wastes into River. Therefore, regular assessment is highly recommended to minimize the potential health hazards of the people who surely depend on the River water for fishing and agricultural purposes.

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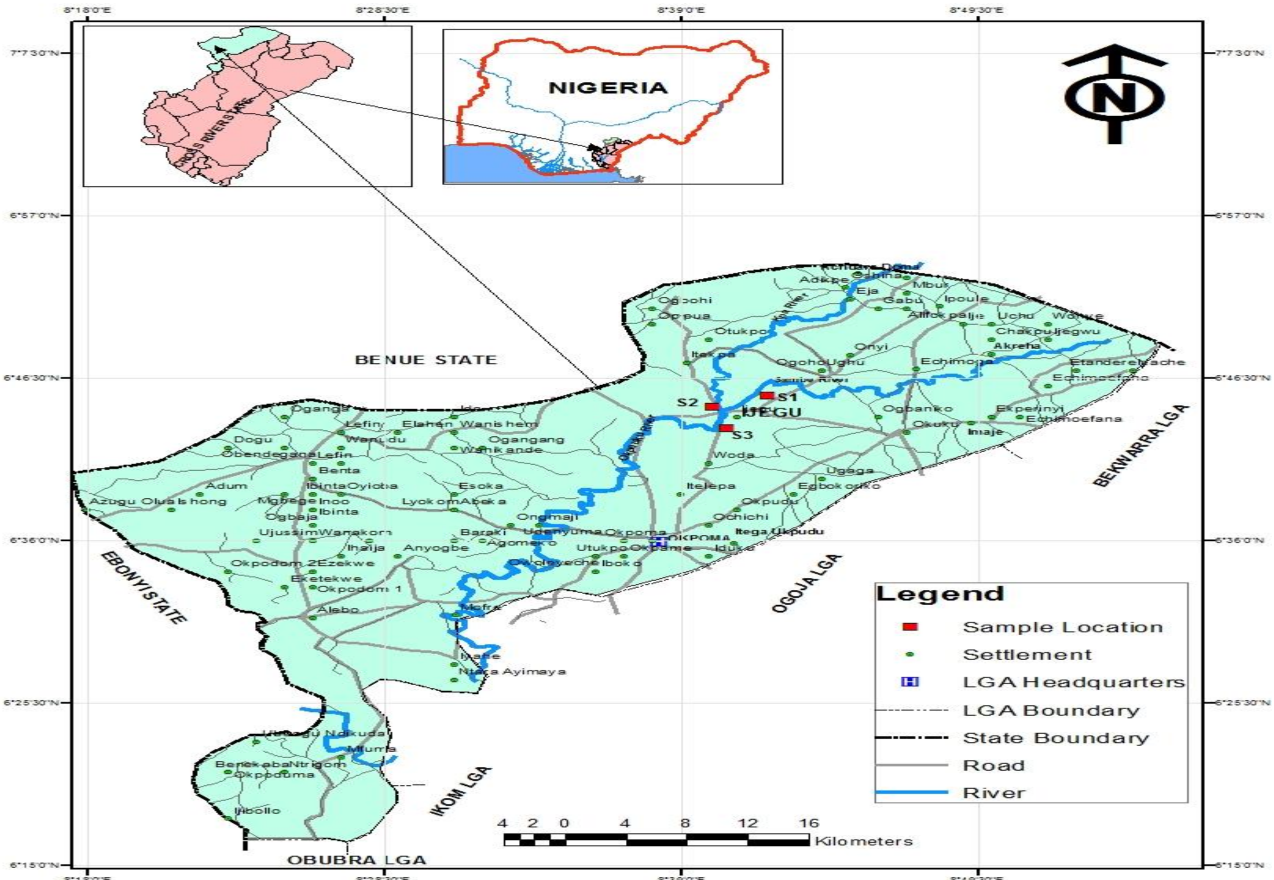

Figure 1: Map of Study Area Showing Sampling Stations (1-3).

Table 1: Spatial variability in Heavy metals of Sediment from Okporku River

	Stations				
Heavy metal (mg/kg)	S1 (Itakpana) Mean ±S.D	S2 (Ehohokpa) Mean ±S.D	S3 (Urubri) Mean ±S.D	Overall Mean ± S.D	Overall Range
Cadmium (Cd)	0.039 ±0.004 (0.035-0.042)	0.028 ±0.002 (0.026-0.030)	0.032 ±0.003 (0.029-0.034)	0.033 ± 0.006	0.028-0.039
Chromium (Cr)	0.052 ±0.001 (0.052-0.053)	0.046 ±0.004 (0.042-0.049)	0.055 ±0.002 (0.052-0.056)	0.051±0.005	0.046-0.055
Copper (Cu)	0.051 ±0.004 (0.046-0.054)	0.049 ±0.004 (0.044-0.052)	0.049 ±0.007 (0.041-0.053)	0.050±0.001	0.049-0.051
Iron (Fe)	0.089 ±0.009 (0.079-0.097)	0.103 ±0.011 (0.095-0.116)	0.093 ±0.007 (0.087-0.100)	0.095±0.007	0.089-0.103
Lead (Pb)	0.035 ±0.060 (0.00-0.104)	0.00-0.00 (0.00-0.00)	0.036 ±0.062 (0.00-0.107)	0.024±0.020	0.00-0.036

Table 2: Calculated F-values of one way analysis of variance measured in Okporku River

Heavy metal (mg/kg)	F- values	F-Critical	P-value	Inferences
Cadmium (Cd)	24.403	18.513	0.039	P<0.05
Chromium (Cr)	23.990	18.513	0.039	P<0.05
Copper (Cu)	24.030	18.513	0.039	P<0.05
Iron (Fe)	23.076	18.513	0.041	P<0.05
Lead (Pb)	24.609	18.513	0.038	P<0.05

Table 3: Pollution Load Index (PLI) and Geo-Accumulation Index (Igeo) on Surface Sediment of Okporku River

	Stations		
Parameters	S1 (Itakpana)	S2 (Ehohokpa)	S3 (Urubri)
PLI	0.041	0.122	0.038
	Geo-accumulation Index (Igeo)		
Cadmium (Cd)	-0.890	-0.810	-0.840
Chromium (Cr)	-1.280	-1.840	-1.950
Copper (Cu)	-1.680	-1.670	-1.670
Iron (Fe)	-1.760	-1.860	-1.780
Lead (Pb)	-1.610	0.000	-1.620

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

Metals	Not polluted	Moderately polluted	Heavily polluted	Present study
Iron	ND	ND	ND	0.079-0.116
Chromium	<25	25 – 75	>75	0.042-0.056
Cadmium	ND	ND	>11.9	0.026-0.042
Copper	<25	25-50	>50	0.041-0.054
Lead	<40	40-60	>60	0.00-0.107

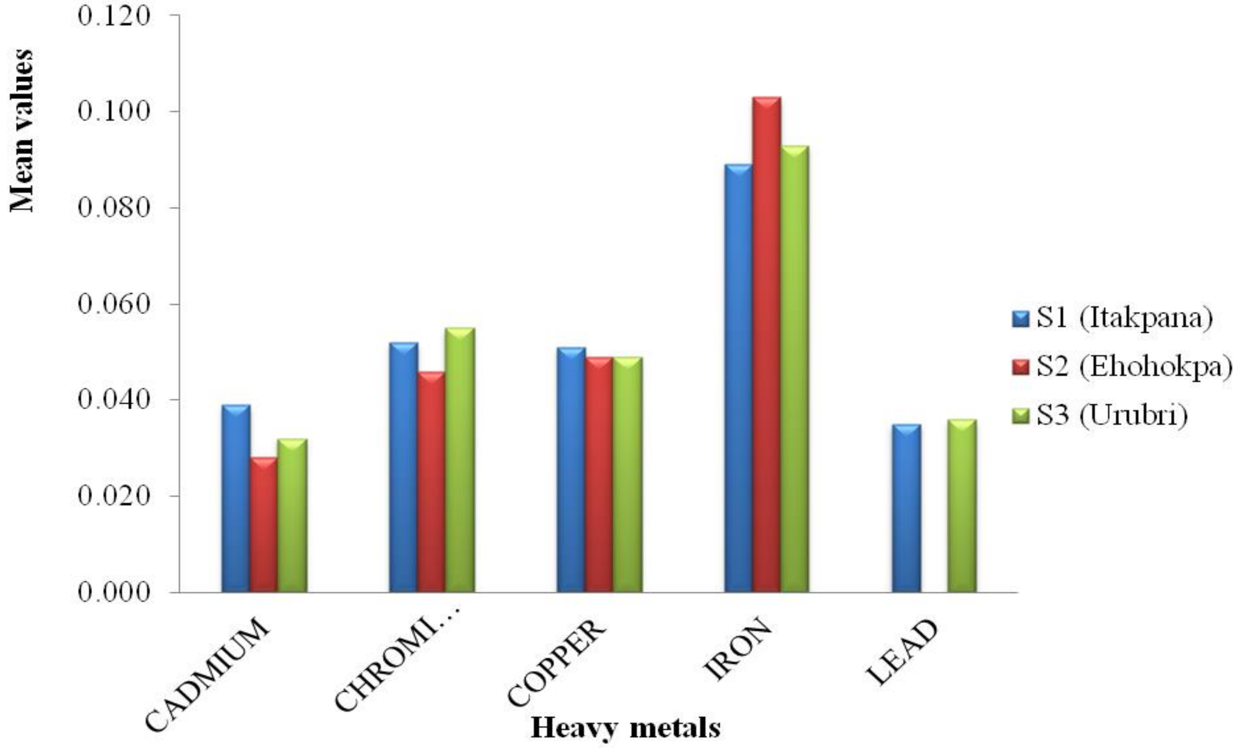

Figure 2: Spatial variations of heavy metals in Okporku River

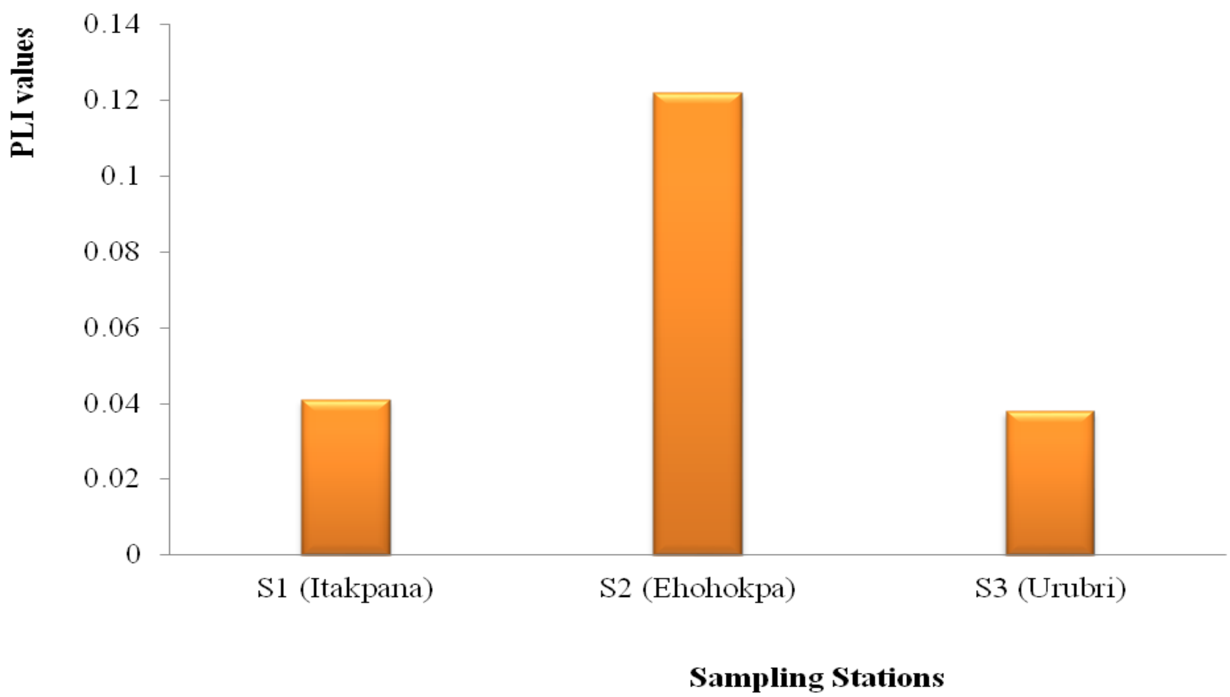

Figure 3: Spatial variations in the PLI value

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