Sciknow Publications Ltd.
Natural Environment

NE 2014, 2(1):1-9
DOI: 10.12966/ne.05.01.2014

Using Pollution Load Index and Geoaccumulation Index for the Assessment of Heavy Metal Pollution and Sediment Quality of the Benin River, Nigeria

Anthony E. Ogbeibu*, Michael O. Omoigberale, Ifeanyi M. Ezenwa, Joyce O. Eziza and Joy O. Igwe

Department of Animal and Environmental Biology, Faculty of Life Sciences, University of Benin, Benin City, Nigeria

*Corresponding author (Email: ogbeibu@yahoo.com)

Abstract - A study on the characterization of sediment quality was conducted along a stretch of the Benin River, Niger Delta, Nigeria, between June and December, 2011 to evaluate the impact of anthropogenic activities. Five stations were selected from Ajimele to Koko for the investigation. Samples were analysed using standard methods. The results showed that the sediment was slightly acidic across the study stations. There was no significant difference ($P > 0.05$) in the mean concentrations of organic carbon, total nitrogen, exchangeable anions and zinc, while electrical conductivity, chloride, nitrate, phosphate, sulphate, sodium, potassium, calcium, magnesium, exchangeable base, iron, chromium, manganese, lead and nickel showed significant difference ($P<0.05$). *A posteriori* Duncan Multiple Range (DMR) test revealed that with the exception of Nickel, the concentrations of these parameters at stations 4 and 5 were not significantly different from each other, but were significantly higher ($P<0.05$) than those of stations 1, 2 and 3. Estimated Pollution Load Index (PLI) and geo-accumulation index (Igeo) revealed that the sediments at all stations were practically uncontaminated by heavy metals. The significant spatial variation recorded in the concentrations of some parameters used in characterizing the sediment quality is a reflection of impacts of anthropogenic activity on quality of this river.

Keywords - Sediment Physico-chemistry, Pollution Load Index, Geo-accumulation Index, Benin River

1. Introduction

Sediments embody critical elements of aquatic ecosystems. They are collections of fine, medium, and coarse grain minerals and organic particles that are found at the bottom of lakes and ponds, rivers and streams, bays, estuaries, and oceans [1]. Data from sediments can provide information on the impact of distant human activity on the wider ecosystem. The composition of sediment sequences provides the best natural archives of recent environmental changes [2].

Sediment acts as both carrier and potential sources of contaminants in an aquatic environment and can serve as a pool that can retain or release contaminants to the water column by various processes of remobilization [3, 4]. Sediment-associated contaminants especially the heavy metals have the potential to cause direct effects on sediment-dwelling organisms and can indirectly adversely affect man and other animals at the higher trophic levels. Thus, information on sediment quality conditions is essential for evaluating the overall status of aquatic ecosystems.

Recent studies on the sediment quality of water bodies in Nigeria include the works of [5, 6, 7, 8, 9, 10, 11, 12]. The sediment of Benin River like the sediments of most aquatic ecosystem in the Niger Delta region of Nigeria is contaminated with different pollutants including organic and inorganic compounds such as crude oil and refine products through normal operations as effluents, operational failures, sabotage and vandalization of facilities into the adjourning water bodies. Often times as these components get to the water body, they finally settle at the sediment which acts as a sink of contaminants in aquatic systems [1].

The need to assess the state of the sediment quality of the Benin River has become imperative in view of the health implications since untreated effluents from the adjourning industries are discharged into the river, and the water is used for domestic activities by people living in the catchment area. This study reports the levels of the physico-chemical parameters and the heavy metals of the sediments of a stretch of Benin River with the aim of evaluating the pollution status of the River.

2. Study Area

The study was conducted along an approximately 30.62 km stretch of Benin River situated in the North Central part of Delta State (Lat. 05^0 54' 14.9"– $05^0$59'54.9"N; Long. 05^0 41'

50.7"- 05^0 27' 006"E) (Fig. 1).

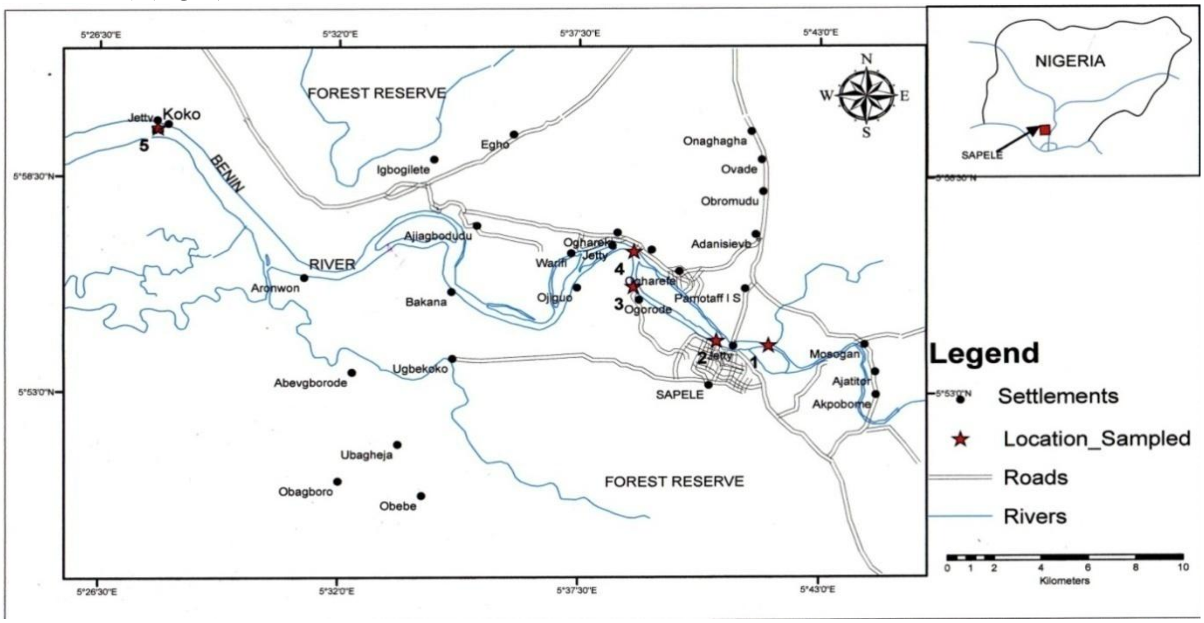

Fig. 1. ***Map of study area showing sampling stations***

Three distinct longitudinal zones could be recognized in this river, the upper freshwater zone, the middle transitional zone with salinity fluctuations and the lower coastal zone which is predominately saline. The present study was conducted in the upper freshwater reaches in the commercial town of Sapele and Koko town. Five sampling stations were investigated along the study stretch. The predominant vegetation includes *Pandanus candelabrum, Elaeis guineensis, Azolla africana, Nymphaea lotus, Salvinia nymphellula, Echinochloa pyramidalis* and *Pistia stratiotes.* Many human activities within and around this river include dredging, logging, fishing, boating, watercraft maintenance, discharging of petroleum products, saw-milling, transportation, laundering, bathing and swimming. The river also receives effluents from many industries such as ASCA oil, Rain oil, Cybernetic, Optima, Total Asphalt blending plant, Ogorode power station and abattoirs sited close to it.

3. Materials and Methods

Sediment samples were collected following the standard procedure described by APHA [12]. The samples were air-dried at room temperature, further dried in an oven at $105^{O}C$ and then crushed to a fine texture in a ceramic mortar, and thereafter sieved mechanically using a 0.5 mm mesh sieve. The following physico-chemical parameters pH, electrical conductivity, nitrate, sulphate, chloride, phosphate, total nitrogen, organic carbon, exchangeable A and B, oil and grease, sodium, calcium, magnesium, potassium and heavy metals namely Iron, copper, lead, Manganese, Nickel and Chromium were analyzed using methods adopted from APHA [12] and Radojevic and Bashkin [13].

4. Data Analysis

Inter station comparisons were carried out to test for significant differences in the physico-chemical conditions using parametric analysis of variance (ANOVA) and Duncan Multiple Range (DMR) test were used to test for significant difference among stations and also to locate site(s) of significant difference.

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 for each site was evaluated using the procedure of Tomlinson *et al.* (15):

$$PLI = (CF1xCF2xCF3x.......CFn)^{1/n}$$

Where: n = number of metals and 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 [15] the PLI value > 1 is polluted while PLI value < 1 indicates no pollution.

The geo-accumulation index (Igeo) values were calculated for the different metals using the equation of Mullers [16]: $I_{geo} = \log_2 (Cn/1.5Bn)$

Where: Cn = measured concentration of element n in the sediments

Bn = geochemical background for the element n

Muller [17] 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 geochemical 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 [19] were considered as the background values.

5. Results

Table 1 shows the summary of the mean concentrations for the physico-chemical parameters of sediments at the study stations, and the results of statistical analysis.

Table 1. Summary of Spatial Variability in Physical and Chemical Characteristics of Sediments from Benin River

zz	Station 1 $\bar{x}$ ±SD	Station 2 $\bar{x}$ ±SD	Station 3 $\bar{x}$ ±SD	Station 4 $\bar{x}$ ±SD	Station 5 $\bar{x}$ ±SD	P-Value
pH	5.21 ± (5.10-5.40)	5.31 ± 0.16 (5.10-5.50)	5.26 ± 0.13 (5.10-5.40)	5.08 ±0.22 (4.80-5.30)	5.24 ±0.15 (4.98-5.40)	P>0.05
EC (µS/cm)	115.71 ±21.05^{B} (94.0-146.0)	123.57 ±20.39^{B} (99.0-155.0)	140.0 ±26.98^{B} (99.0-171.0)	592.71 ±447.85^{A} (105.0-956.0)	727.9 ±429.6^{A} (255.0-1215.0)	P<0.001
Org. Carbon (%)	0.82 ±0.13 (0.69-1.09)	0.86 ±0.13 (0.73-1.12)	0.89 ±0.15 (0.71-1.18)	0.87 ±0.16 (0.69-1.16)	2.23 ±2.30 (0.80-7.28)	P>0.05
Total Nitrogen (%)	0.08 ±0.02 (0.05-0.11)	0.09 ±0.01 (0.07-0.11)	0.09 ±0.02 (0.07-0.12)	0.09 ±0.02 (0.07-0.12)	0.22 ±0.23 (0.08-0.73)	P>0.05
Cl^{-} (mg/kg)	31.64 ±10.21^{B} (18.34-43.80)	35.18 ±9.97^{B} (20.37-46.5)	38.68 ±9.62^{B} (20.37-48.9)	174.39 ±138.65^{A} (21.6-286.8)	213.4 ±167.6^{A} (76.50-540.12)	P<0.001
NO_3^{-} (mg/kg)	2.53 ±2.21^{B} (0.12-4.83)	2.70 ±2.33^{B} (0.13-5.13)	2.97 ±2.52^{B} (0.14-5.40)	18.13 ±16.68^{A} (0.14-31.64)	9.45 ±11.51^{A} (0.14-33.86)	P<0.05
PO_4^{3-} (mg/kg)	1.00 ±0.71^{B} (0.09-1.75)	1.00 ±0.82^{B} (0.10-1.86)	1.09 ±0.89^{B} (0.10-1.96)	6.58 ±6.04^{A} (0.11-11.47)	3.85 ±3.88^{A} (0.78-12.28)	P<0.05
SO_4^{2-} (mg/kg)	2.76 ±2.24^{B} (0.11-5.11)	2.98 ±2.32^{B} (0.15-5.43)	3.28 ±2.49^{B} (0.22-5.71)	19.27 ±17.52^{A} (0.22-33.46)	10.35 ±11.96^{A} (0.31-35.81)	P<0.05
Na (Meq/100g)	4.29 ±3.41^{B} (0.29-7.88)	4.59 ±3.58^{B} (0.34-8.37)	5.01 ±3.91^{B} (0.34-8.80)	29.71 ±27.05^{A} (0.42-51.62)	15.44 ±18.71^{A} (0.87-55.24)	P<0.05
K (Meq/100g)	5.69 ±4.48^{B} (0.27-10.41)	6.20 ±4.58^{B} (0.44-11.05)	6.76 ±5.00^{B} (0.37-11.62)	45.65 ±34.38^{A} (0.51-68.14)	20.5 ±24.6^{A} (1.77-72.92)	P<0.05
Ca (Meq/100g)	2.85 ±2.60^{B} (0.09-5.55)	3.06 ±2.73^{B} (0.14-5.89)	3.33 ±2.99^{B} (0.10-6.19)	20.76 ±19.22^{A} (0.19-36.33)	10.74 ±13.27^{A} (0.37-38.87)	P<0.05
Mg (Meq/100g)	2.45 ±2.14^{B} (0.19-4.67)	2.61 ±2.25^{B} (0.22-4.96)	2.88 ±2.42^{B} (0.25-5.22)	17.55 ±16.10^{A} (0.31-30.59)	9.01 ±11.20^{A} (0.43-32.74)	P<0.05
Exchangeable Bases. (Meq/100g)	15.25 ±12.65^{B} (1.10-28.51)	16.32 ±13.30^{B} (1.21-30.27)	17.84 ±14.48^{B} (1.15-31.83)	107.34 ±97.93^{A} (1.43-186.69)	55.29 ±68.10^{A} (3.44-199.77)	P<0.05
Exchangeable Anions. (Meq/100g)	5.66 ±1.65 (3.10-7.59)	6.12 ±1.59 (3.26-8.06)	6.72 ±1.45 (4.78-8.48)	8.91 ±3.14 (5.12-11.47)	5.75 ±3.16 (3.06-12.28)	P>0.05
Fe (mg/kg)	1.88 ±1.39^{B} (0.32-3.36)	2.03 ±1.43^{B} (0.40-3.57)	2.23 ±1.55^{B} (0.40-3.75)	12.73 ±11.43^{A} (0.42-21.99)	7.03 ±7.71^{A} (0.63-23.53)	P<0.05
Cr (mg/kg)	0.25 ±0.18^{B} (0.03-0.44)	0.28 ±0.17^{B} (0.04-0.47)	0.32 ±0.19^{B} (0.05-0.49)	1.68 ±1.46^{A} (0.05-2.87)	1.18 ±1.08^{A} (0.11-3.07)	P<0.001
Zn (mg/kg)	2.00 ±1.63 (0.22-3.71)	2.18 ±1.66 (0.32-3.94)	2.39 ±1.80 (0.32-4.14)	6.38 ±5.58 (0.34-10.90)	4.17 ±3.38 (1.61-11.66)	P>0.05
Cu (mg/kg)	0.24 ±0.22^{B} (0.01-0.47)	0.26 ±0.23^{B} (0.01-0.50)	0.29 ±0.24^{B} (0.01-0.52)	1.75 ±1.61^{A} (0.01-3.06)	0.88 ±1.14^{A} (0.00-3.27)	P<0.05
Mn (mg/kg)	0.63 ±0.36^{B} (0.19-1.02)	0.72 ±0.33^{B} (0.29-1.09)	0.79 ±0.34^{B} (0.29-1.14)	3.97 ±3.36^{A} (0.31-6.69)	3.52 ±2.83^{A} (0.47-7.77)	P<0.01
Pb (mg/kg)	0.15 ±0.13^{B} (0.00-0.29)	0.16 ±0.14^{B} (0.01-0.31)	0.18 ±0.15^{B} (0.01-0.33)	1.10 ±1.01^{A} (0.01-1.91)	0.58 ±0.69^{A} (0.02-2.05)	P<0.05
Ni (mg/kg)	0.14 ±0.05^{C} (0.03-0.19)	0.17 ±0.06^{C} (0.05-0.25)	0.20 ±0.10^{B} (0.06-0.39)	0.75 ±0.50^{A} (0.13-1.23)	0.47 ±0.35^{A} (0.13-1.23)	P<0.001

P > 0.05 – No significant difference; P < 0.05 – Significant difference; P < 0.001 – Highly significant difference;

Means with the same superscript in the same row are not significantly different

5.1. *Hydrogen – ion concentration (pH)*

The pH was slightly acidic with a mean range of between 5.04 in station 4 and 5.30 in station 2. There was no significant difference (P>0.05) in the mean pH values of the study stations.

5.2. *Electrical Conductivity (EC) and Chloride (Cl^-)*

Fluctuations in mean conductivity values which ranged from the lowest value (118.83 µS/cm) in station 1 to the highest value (670.67 µS/cm) in station 4 (Fig. 2). The chloride concentration varied from 33.71 mgl^{-1} in station 1 to 210.3 mgl^{-1} in station 5 (Fig. 3). Analysis of variance (ANOVA) showed significant difference (P< 0.05) in the mean conductivity and chloride values among the study stations. *A posteriori* DMR test showed that stations 4 and 5 which were not significantly different (P>0.05) from each other were significantly higher (P<0.05) than stations 1, 2 and 3 which were not significantly different (P>0.05) from each other.

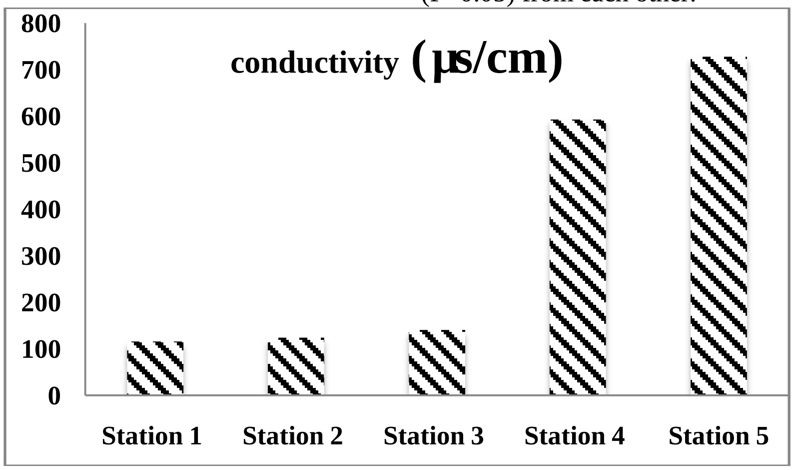

Fig. 2. Spatial variations of Conductivity in the study stations

5.3. *Organic carbon and Total Nitrogen*

The mean organic carbon values ranged from 0.83% in station 1 to 2.27% in station 5. There was no significant difference (P>0.05) among the stations. The mean total nitrogen was highest (0.23%) in station 5 and lowest (0.08%) in stations 1 and 2. There was no significant difference (P>0.05) in the mean total nitrogen concentration of the study stations.

5.4. *Nitrate, Phosphate and Sulphate*

Spatial variations in the concentrations of these parameters are shown in Figure 3. The concentration of nitrate varied from a mean of 2.53 mg/kg in station 1 to 18.13 mg/kg in station 4.

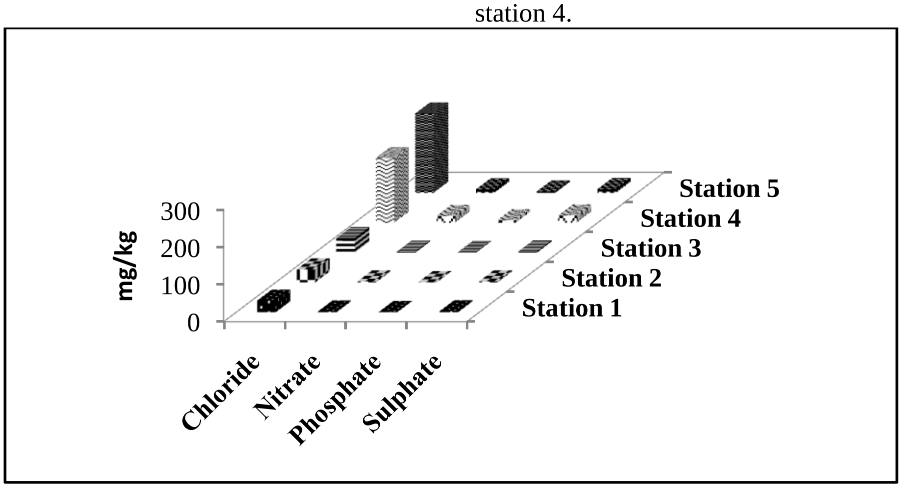

Fig. 3. Spatial variations of Chloride, nitrate, Phosphate and sulphate in the study stations

The mean phosphate value was lowest (1.00 mg/kg) in stations 1 and 2, while the highest value (6.53 mg/kg) was recorded in station 4. The sulphate concentration varied significantly in the study stations, with the lowest mean concentration (2.76 mg/kg) in station 1 and the highest (19.27 mg/kg) in station 4. The mean concentrations of nitrate, phosphate and sulphate showed significant difference (P< 0.05) among the study stations. *A posteriori* DMR test showed that stations 4 and 5 which were not significantly different (P>0.05) from each other were significantly higher (P<0.05) than the other stations.

5.5. Sodium and Potassium

Variation in mean sodium concentration ranged from 4.29 meq/kg in station 1 to 29.71 meq/kg in station 4, while the mean potassium concentration varied from 5.69 meq/kg in station 1 to 45.65 meq/kg in station 4 (Fig. 4).

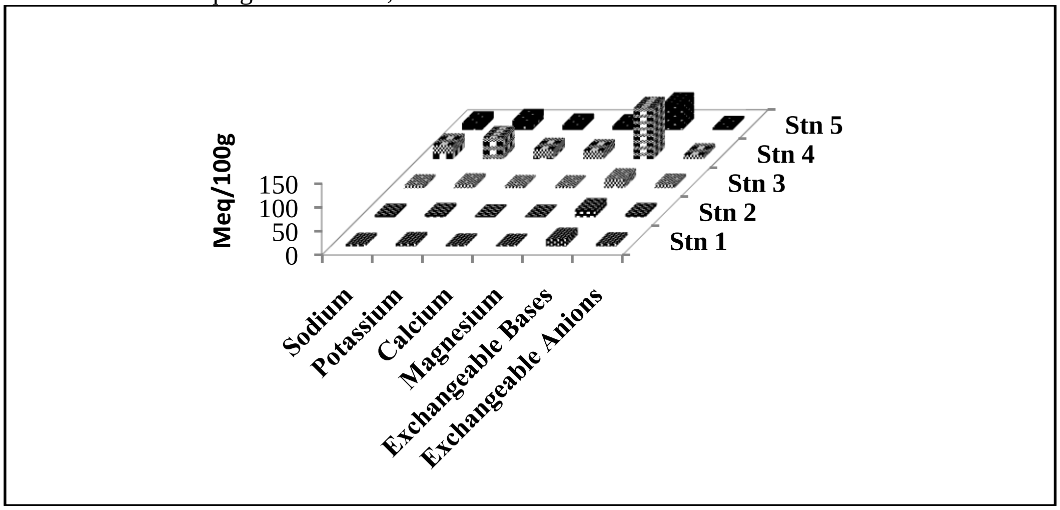

Fig. 4. Spatial variations of the alkali earth metals and exchangeable ions in the study stations

The mean values of both parameters were significantly different (P<0.05) among the study stations. *A posteriori* DMR test showed that stations 4 and 5 which were not significantly different (P>0.05) from each other, but were significantly higher (P<0.05) than the other stations.

5.6. Calcium and Magnesium

The concentration of these alkaline earth metals varied significantly in all stations (Fig. 4). Calcium had the lowest mean value of 2.85 meq/kg in station 1 and the highest (20.76 meq/kg) in station 4. The mean value of magnesium ranged from 2.45 meq/kg in station 1 to 17.55 mg/kg in station 4. The mean values of both parameters were significantly different (P<0.05) among the study stations. Further analysis using DMR test showed that stations 4 and 5 which were not significantly different (P>0.05) from each other were significantly higher (P<0.05) than stations 1, 2 and 3 which were not significantly different (P>0.05) from each other.

5.7. Exchangeable Bases and Anions (Meq/100g)

The mean values of exchangeable bases fluctuated between 15.25 meq/100g in station 1 and 107.34 meq/100g in station 4 (Fig. 4). Analysis of variance (ANOVA) showed significant difference (P< 0.05) in the mean exchangeable bases values among the study stations. *A posteriori* DMR test showed that stations 4 and 5 which were not significantly different (P>0.05) from each other were significantly higher (P<0.05) than the other stations. The mean value of exchangeable anions was lowest (5.66 meq/100) in station 1 and highest (8.91 meq/100g) in station 4 (Fig. 4). The mean value of this parameter was not significantly different (P > 0.05) among the study stations.

5.8. Heavy metals

The heavy metals determined in this study include iron, chromium, zinc, copper, manganese, lead and nickel. Spatial variations in their mean values are shown in Figure 5. The mean values of iron ranged between 1.88 mg/kg and 12.73 mg/kg, while the mean chromium was highest (1.68 mg/kg) in station 4 and lowest (0.25 mg/kg) in station 1. The mean zinc value ranged from 2.00 mg/kg (station 1) to 6.38 mg/kg (station 4). The mean copper was highest (1.75 mg/kg) in station 4 and lowest (0.24 mg/kg) in station 1, while the mean manganese concentration was lowest (0.63 mg/kg) in station 1 and highest (3.97 mg/kg) in station 4 (Fig. 7). Analysis of variance (ANOVA) revealed the same trend in spatial variation of these heavy metals. There was a significant difference (P< 0.05) among the study stations, and *a posteriori* DMR test showed that stations 4 and 5 which were not significantly different (P>0.05) from each other were significantly higher (P<0.05) than the rest of the stations.

There was a distinct spatial variation for lead and nickel. The maximum concentration of Pb (1.10 mg/kg) was recorded at station 4, while the minimum value (0.15 mg/kg) was detected at station 1. The values of lead at various stations were subjected to one way ANOVA, there was high significant differences (P<0.01) was recorded. *A posteriori'* DMR test revealed that stations 4 and 5 significantly higher than stations 1, 2 and 3. The mean concentration of nickel ranged from 0.14 mg/kg in station 1 to 0.75 mg/kg in station 4, and inter-station difference was highly significant (P<0.01). *A posteriori* DMR test showed that stations 4 and 5 were significantly higher (P<0.01) than station 3, which in turn was significantly higher (P<0.01) than stations 1 and 2.

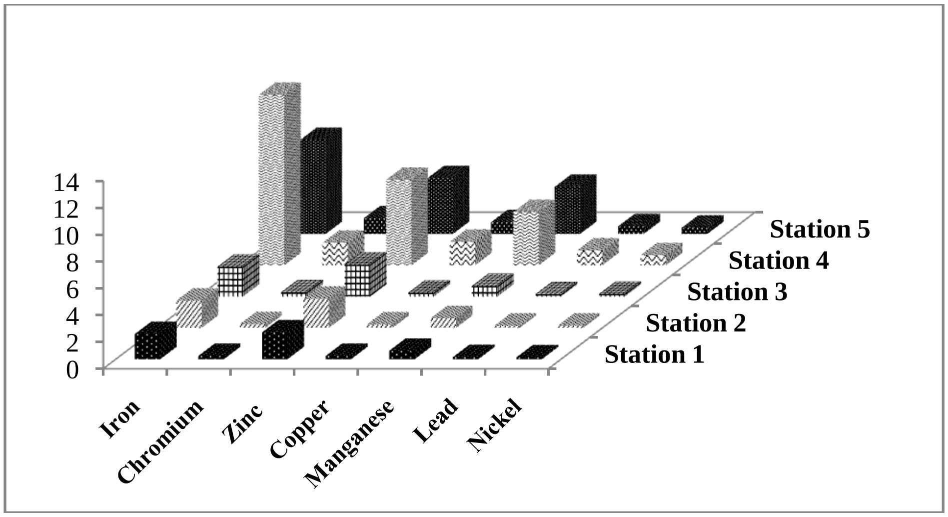

Fig. 5. Spatial variations of the heavy metals in the study stations

5.9. Determination of Sediment Contamination by Heavy Metals

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 of > 1 signifies pollution, while PLI value < 1 indicates no pollution. The PLI values recorded for all the stations were below 1 (Fig. 6). Thus the sediment of the study stretch of Benin River is unpolluted.

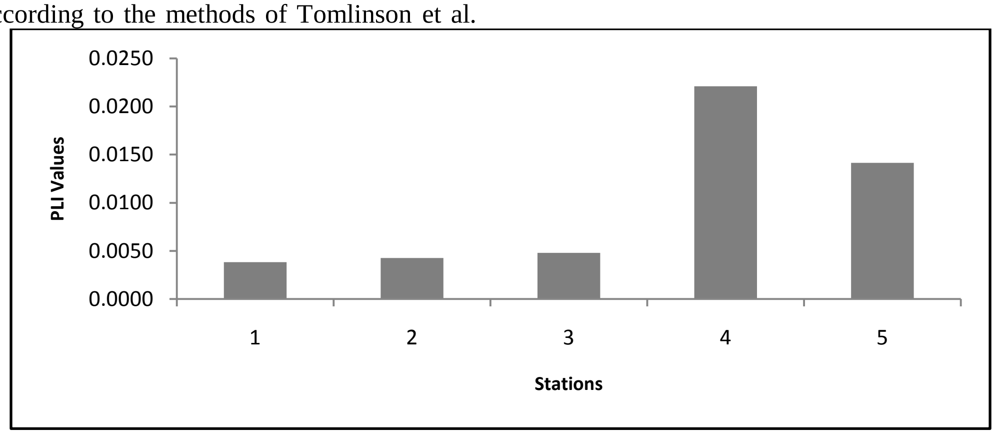

Fig. 6. Spatial Variations in the PLI Values

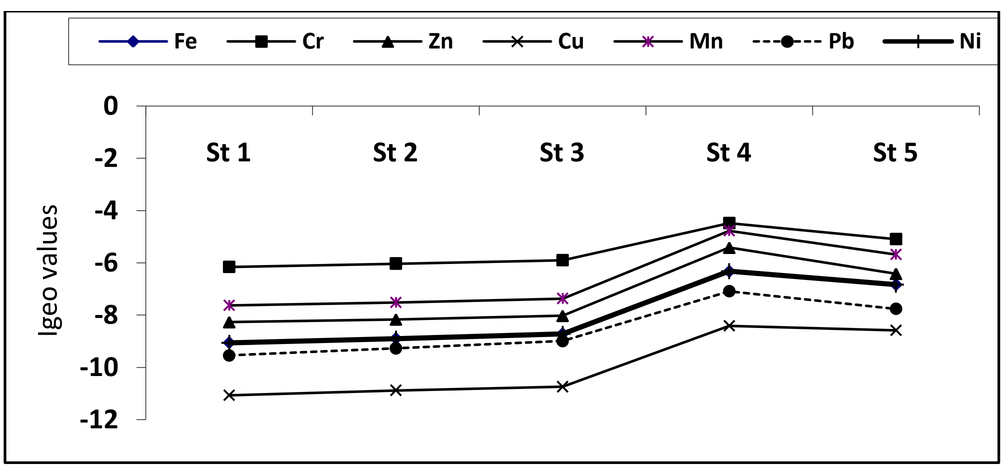

Fig. 7. Spatial Variations in the Igeo values

The calculated Igeo values are presented in Table 2 and the variations are shown graphically (Fig. 7). It is evident from the figure that the Igeo values for all the metals fall in class '0' in all the five sampling locations, indicating that there is no pollution from these metals in the Benin River sediments. The Igeo values were consistent with those derived for PLI. All metals had concentrations below the EPA regulatory limits for sediment (Table 3).

Table 2. Summary of Pollution Load Index (PLI) and Geo-accumulation Index (Igeo)

	Stations				
	1	**2**	**3**	**4**	**5**
PLI	0.0038	0.0043	0.0048	0.0221	0.0141
Geo-accumulation Index (Igeo)					
Fe	-9.061	-8.899	-8.717	-6.326	-6.836
Cr	-6.158	-6.03	-5.899	-4.482	-5.096
Zn	-8.266	-8.164	-8.024	-5.418	-6.416
Cu	-11.069	-10.88	-10.744	-8.41	-8.582
Mn	-7.626	-7.515	-7.366	-4.776	-5.684
Pb	-9.54	-9.266	-8.992	-7.091	-7.761
Ni	-9.061	-8.899	-8.717	-6.326	-6.836

Table 3. EPA heavy metal Guidelines for Sediments (mg/kg)

S/n	Metals	Not polluted	Moderately polluted	Heavily polluted	Present study
1.	Iron	ND	ND	ND	1.88 – 12.73
2.	Chromium	<25	25 – 75	>75	0.25 – 1.68
3.	Zinc	<90	90 - 200	>200	2.0 – 6.38
4.	Copper	<25	25 – 50	>50	0.24 – 1.75
5.	Manganese	<300	300 – 500	>500	0.63 – 3.79
6.	Lead	<40	40 – 60	>60	0.15 – 1.10
7.	Nickel	<20	20 – 50	>50	0.14 – 0.75

6. Discussion

Although water 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. Sediments have been described as a ready sink of pollutants where they concentrate according to the levels of pollution [19]. The levels of physico-chemical parameters and trace metals in river water determine the quality of the sediment.

In this study, the higher values of sediment physico-chemical parameters in stations 4 and 5 indicated the anthropogenic contributions especially the improper discharge of wastes from various human activities and the industrial oil sub-sector in the study area. The level of homogeneity observed in pH of the sediment is similar to the observation of Davies and Tawari [9] in the Okpoka Creek, upper Bonny Estuary and Iwegbue et al. [20] reported that lower pH value is typical of the anaerobic sediments of the Niger Delta. The range of conductivity and chloride values recorded in this study showed a progressive increase from the upstream stations towards the downstream stretch of the river (stations 4 and 5). These observed variations might be as a result of the distinct longitudinal zones along the stretch of the river and their proximity to the Atlantic Ocean.

The values of total organic carbon (TOC) recorded in this study are lower than values reported by Ogbeibu [21] for the Ethiope-Benin River, but similar to values from selected major rivers in south-western Nigeria documented by Etim and Adie [22]. Extreme concentrations of TOC levels below 0.05% and above 3% have been implicated in decreased benthic abundance and biomass. The mean TOC obtained in the sediments from the study were within the risk associated values recommended by Hyland et al. [23]. Nitrate and phosphate play a significant role in surface water eutrophication. They are essential nutrients required for plant growth and their presence in surface water and sediment are primarily enriched by agricultural activities. The higher values of nitrate and phosphate recorded at stations 4 and 5 could be attributed to farming activities, the predominant land use practice in the catchment areas of these study sites. High level of phosphate has been linked to agricultural land use around riverine areas and runoff during the rainy season [24]. Other possible sources of phosphate and nitrate are rock deposits, interaction between water and sediment and decaying plants and animals at the bottom of the river.

Significantly higher values of the alkali earth metals were recorded in the perturbed stations 4 and 5. The exchangeable anions showed some degree of homogeneity across the study stations, which conforms to the acidic nature of the river.

The concentrations of the heavy metals Fe, Cr, Cu, Mn, and Pb were higher in stations 4 and 5 with the highest anthropogenic impact. The mean concentrations of Fe were lower when compared with the reported values of 28.1-33.7 mg/kg for Orogodo River sediments [6], 31.19-58.34 mg/kg in the sediments of river Ngada [25] and 867.8-7195.0 mg/kg in the Benin River [21]. These changes are attributable to the nature of the anthropogenic activities carried out on the hinterland and within the river. The pH of the water influences the solubility of the metals and this in turn affects their ability to settle on the sediment. Fe has been reported to occur at high concentrations in Nigerian soil/sediment [26].

Chromium reaches water bodies primarily from the discharge of industrial wastes and disposal of products containing the metal [13, 25]. The values recorded in this investigation were lower when compared to the mean values of 14.89-21.79 mg/kg for the bottom sediment of Ekpan creek [27]. These values of zinc recorded did not compare favourably with the mean values obtained by Ihenyen [28] and Ogbeibu [21] in the sediment of this river. These differences might be due to temporal and spatial variation and pollution from sewage effluent that has high zinc content [30]. Copper showed similar variation with zinc. Puyate et al. [6] and Ogbeibu [21] recorded higher values in the sediments of Orogodo River and Benin River respectively. High levels of copper have been implicated in anaemia, liver and kidney damage, stomach and intestinal irritation [31]. The values of Mn recorded in this study were quite low when compared with the values recorded by Okafor and Opuene [5] in the sediments of nearby Taylor Creek.

Lead is toxic to humans and its major anthropogenic sources include the use of lead as a petrol additive, runoff from the cities, discharge of improperly treated waste effluents, sewage sludge and the use of pesticides containing lead compounds [13]. The high concentration of lead recorded in station 4 might be due to the nature of anthropogenic activities associated with petroleum products. The range (0.15-1.10 mg/kg) of lead recorded in this study was lower than the values (3.8-10.00 mg/kg and 4.85-8.52 mg/kg) obtained by Ogbeibu [21] and Olomukoro and Azubuike [27] in sediments Benin River and Ekpan creek respectively. The mean concentration of nickel showed similar spatial pattern like others with the highest and lowest values encountered in stations 4 and 1 respectively. The range obtained in this study was much lower than the values of Ogbeibu [21] in sediments at Benin River.

The pollution load index (PLI) and the Geo-accumulation Index (Igeo) have been used extensively in the assessment of sediment pollution by heavy metals [31, 15, 32, 33, 34, 35, 36]. The results of the present evaluation revealed that the sediment of the study stretch of the Benin River is unpolluted by heavy metals. The PLI was less than 1 for all stations and the Igeo values for the various heavy metals were below 0, thus indicating practically uncontaminated condition. The Igeo values were consistent with those derived for PLI. These results were corroborated by the fact that the values of heavy metals in the sediments were below the EPA guidelines for sediment limit, an indication that the sediment of the Benin River was not polluted by heavy metals. However, the level of these metals in the environment has increased tremendously in the past decades as a result of human input and activities [37]. The implication of this is that these heavy metals pose risk of contamination or pollution of the sediments and overlying surface water. Studies have shown that the concentrations of physico-chemical parameters in sediments are positively correlated with the concentration levels in the overlying water; therefore, continuous assessment is highly essential to minimize the potential health hazards of the inhabitants in the catchment areas who depend of the river water for domestic, agricultural and fishing purposes.

7. Conclusion

The Benin River which is the major source of fish for the local communities also represents an important route for the transportation of petroleum and allied products. The quality of the surface water and sediment is of great importance for the sustainable use of the river. The significant spatial variation recorded in the concentrations of some parameters used in characterizing the sediment quality is a reflection of impacts of anthropogenic activity on quality of this river. This study, however, allayed the fear of possible heavy metal pollution in the sediment of the study stretch, but without precluding the need for continuous monitoring of both sediment and water quality to match the potential threat from industrialization.

8. References

[1] Adams, W. J., Kimerle, R. A., and Barnett, J. W. Jr. (1992). Sediment quality and aquatic life assessment. *Environmental science and technolo*gy 26(10), 1865-1875.

[2] Fagbote, E. O., and Olanipekun, E. O. (2010). Evaluation of the status of heavy metal pollution of sediment of agbabu bitumen deposit area, Nigeria. *European journal of scientific research,* 41(3), 373-382.

[3] Marchand, C., Lalliet, V. E., Baltzer, F., Alberic, P., Cossa, D., and Baillif, P. (2006). Heavy metals distribution in mangrove sediments along the mobile coastline of French Guiana. *Mar. Chem.,* 98, 1-17.

[4] Davies, O. A., and Abowei, J. F. N. (2009). Sediment quality of lower reaches of Okpoka Creek, Niger Delta, Nigeria. *European Journal of Scientific Research,* 26(3), 437-442.

[5] Okafor, E. C., and Opuene, K. (2007). Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments. *Int. J. Environ. Sci. Tech*., 4(2), 233-240.

[6] Puyate, Y. T., Rim-Rukeh, A., and Awatefe, J. K. (2007). Metal Pollution Assessment and Particle Size Distribution of Bottom Sediment of Orogodo River, Agbor, Delta State, Nigeria. *Journal of Applied Sciences Research*, 3(12), 2056-2061.

[7] Adeyemo, O. K., Adedokun, O. A., Yusuf, R. K., and Adeleye, E. A. (2008). Seasonal changes in physicao-chemical parameters and nutrient load of river sediment in Ibadan city, Nigeria. *Global NEST Journal*, 10(3), 326-336

[8] Oribhabor, B. J., and Ogbeibu, A. E. (2009). Concentration of heavy metals in a Niger Delta mangrove creek, Nigeria. *Global journal of environmental sciences,* 8(2), 1-10.

[9] Davies, O A., and Tawari, C. C. (2010). Season and tide effects on sediment characteristics of trans-Okpoka Creek, upper bonny Estuary, Nigeria. *Agric. Biol. J. N. Am.,* 1(2), 89-96.

[10] Ezekiel, E. N., Hart, A. I., and Abowei, J. F. N. (2011). The Sediment Physical and Chemical Characteristics in Sombreiro River, Niger Delta, Nigeria. *Research Journal of Environmental and Earth Sciences,* 3(4), 341-349.

[11] Adepoju, M. O., and Adekoya, J. A. (2012). Distribution and assessment of heavy metals in sediments of the river Orle, Southwestern Nigeria. *Journal of Sustainable Development and Environmental Protection,* 2(1), 78-97.

[12] APHA (American Public Health Association), AWWA (American Water Works Association), WPCF (Water Pollution Control Federation), 1998: Standard methods for the examination of water and waste water. 20^{th} ed., Washington, DC 1325pp.

[13] Radojevic, M., Bashkin, V. N. (1999). Practical environmental analysis. Royal school of chemistry, Thomas Graham house, science park Cambridge, UK. 645pp.

[14] Tomlinson, D. C., Wilson, J. G., Harris, C. R., and Jeffrey, D. W. (1980). Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index. *Helgol. Wiss. Meeresunters,* 33, 566-575.

[15] Chakravarty, I. M., and Patgiri, A. D. (2009). Metal Pollution Assessment in Sediments of the Dikrong River, N.E. India. *J Hum Ecol,* 27(1), 63—67

[16] Muller, G. 1969. Index of geo-accumulation in sediments of the Rhine River. *Geo. J.,* 2(3), 108-118.

[17] Muller, G. (1981). Die Schwermetallbelstung der sedimente des Neckars und seiner Nebenflusse: eine estandsaufnahme. *Chem. Zeitung*, 105, 157–164.

[18] Turekian, K. K., and Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. Geol. Soc. *Am. Bull*., 72, 175 – 192.

[19] Onyari, M. J., Muohi, A. W., Omondi, G., and Mavuti, K. M. (2003). Heavy metals in sediments from Makupa and Port-Reitz Creek systems. *Kenyan Coast Environ. Int.* 28(7), 639-647.

[20] Iwegbue, C. M. A., Nwajei, E. G., and Arimoro, F. O. (2007). Assessment of contamination by heavy metals in the sediment of Ase River, Niger Delta, Nigeria. *Research journal of environment science,* 1(5), 220-228.

[21] Ogbeibu, A. E. (2011). Oil spill tracking and characterization – A case study of oil pollution in the Ethiope-Benin River, Niger Delta, Nigeria. IAIA Conference, Puebla, Mexico.

[22] Etim, E. U., and Adie, G. U. (2012). Assessment of Qualities of Surface Water, Sediments and Aquatic Fish from Selected Major Rivers in South-Western Nigeria. *Research Journal of Environmental and Earth Sciences,* 4(12), 1045-1051.

[23] Hyland, J., Karakassis, I., Magni, P., Petrov, A., and Shine, J. (2000). Summary Report: Results of initial planning meeting of the United Nations Educational, Scientific and Cultural organization (UNESCO) Benthic Indicator Group, 70pp.

[24] Erhunmwunse, N. O., Dirisu, A. R., and Ogbeibu, A.E. (2013). Managing eutrophication in nigeria inland waters. *Journal of Water Research and Protection (JWARP)* **5,** 743-746

[25] Akan, J. C., Abdulrahman, F. I., Sodipo, O. A., Ochanya, A. E., and Askira, Y. K. (2010). Heavy metals in sediments from River Ngada, Maiduguri Metropolis, Borno State, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology.* 2(9), 131-140.

[26] Adefemi, O. S., Asaolu, S. S., and Olaofe, O. (2007). Assessment of the physico-chemical status of water samples from major dams in Ekiti State, Nigeria. *Pak. Nu*t. 6(6), 657-659.

[27] Olomukoro, J. O., and Azubuike, C. N. (2009). Heavy Metals and Macroinvertebrate communities in bottom sediment of Ekpan Creek, Warri, Nigeria. *Jordan Journal of Biological Sciences,* 2(1), 1-8.

[28] Ihenyen, A. E. (2001). Heavy metals in sediments of the Benin River estuary and its environs, western Niger Delta, Nigeria. *Environ. Sci.,* 6, 551-559.

[29] Allen, S.E. (1989). Chemical analysis of ecological materials. Blackwwell Scientific publications. 368pp.

[30] Turnland, J. R. (1988). Copper nutrition, bioavailability and influence of dietary factors. *J. Am. Dietetic Assoc.,* 1, 303-308.

[31] Priju, C. P., and Narayana, A. C. (2007). Heavy and Trace Metals in Vembanad Lake Sediments. *Int. J. Environ. Res.,* 1(4), 280-289

[32] Harikumar, P. S., Nasir, U. P., and Mujeebu R. M. P. (2009). Distribution of heavy metals in the core sediments of a tropical wetland system. *Int. J. Environ. Sci. Tech*., 6 (2), 225-232

[33] Mohiuddin, K. M., Zakir, H. M., Otomo, 1. K., Sharmin, 1.S., and Shikazono, 1. N. (2010). Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. *Int. J. Environ. Sci. Tech*., 7 (1), 17-28

[34] Bentum, J. K., Anang, M., Boadu, K. O., Koranteng-Addo, E. J., and Owusu A. E. (2011). Assessment of heavy metals pollution of sediments from Fosu Lagoon in Ghana. *Bull. Chem. Soc. Ethiop*., 25(2), 191-196.

[35] Rabee, A. M., Al-Fatlawy, Y. F, Abd own, A. N., and Nameer, M. (2011). Using Pollution Load Index (PLI) and Geoaccumulation Index (I-Geo) for the Assessment of Heavy Metals Pollution in Tigris River Sediment in Baghdad Region. *Journal of Al-Nahrain University* 14 (4), 108-114

[36] Iwuoha, G. N., Osuji, L. C., and Horsfall, M. Jnr. (2012). Index Model Analysis Approach to Heavy Metal Pollution Assessment in Sediments of Nworie and Otamiri Rivers in Imo State of Nigeria. *Research Journal of Chemical Sciences,* 2(8), 1-8

[37] Prater, B. E. (1975). The metal content and characteristics of Steelwork effluents discharging to the Tees estuary. *Water Pollut. Control*., 74, 63-78.