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Seasonal Effects on Nutrient and Bioactive Element Distributions in the Surface Sediments of Calabar River, Calabar, South-East Nigeria

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Abstract
The contamination of metals (Fe, Zn, Ni, Mn, Mg, Cd, Cr and Pb) and abundance of nutrients (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, TN and TP) in the surface sediment of Calabar river during wet and dry seasons of the year was studied to evaluate their distribution, ecological risk and possible resource limitation within the ecosystem. The result obtained showed that average concentration of nutrient increased in the order PO_4^{3-}(0.61) < TP (1.99) < NO_2^-(2.11) < NH_4^+(5.74) < NO_3^-(33.10) < TN (48.42) µM while that of metals were Cd (0.18) < Cr (1.61) < Mn (1.80) < Zn (3.42) < Pb (5.33) < Ni (7.18) < Mg (21.64) < Fe (38.44)mg/kg for wet season and PO_4^{3-}(0.57) < TP (1.76) < NO_2^-(2.49) < NH_4^+(4.996) < NO_3^-(31.24) < TN (47.10)µM and metals, Cd (0.28) < Cr (0.899) < Mn (3.588) < Zn (4.60) < Pb (4.60) < Ni (7.73) < Mg (17.12) < Fe (31.96)mg/kg for dry season. Considering the sediment quality guideline classification, ERL/ERM, TEL/PEL and LEL/SEL, these metals pose no environmental risk. Also, several standard indices: EF, CF, MPL, Cd, MCd, RI and PERI were used to evaluate the sediment pollution status and its ecological risk and the result showed no contamination and low environmental risk. The Redfield ratio of NO_3^-: PO_4^{3-} and TN: TP for these study sites were within 16: 1 and 30: 1 during the dry season. However, during the wet season NO_3^-: PO_4^{3-} got very high to about 54: 1. This is an indication of PO_4^{3-} limitation and excess NO_3^-. Finally,statistical analysis including Pearsonrank order correlation ɤ, Spearman correlation, ANOVA and Turkey HSD multiple comparison were applied to evaluate the sources and the significance in their relationship at probabilities levels of p< 0.1, p<0.05 and p<0.01.

Keywords: Seasonal, Distribution, Risk assessment, Surface Sediment, Calabar river

Introduction

Aquatic sediment, particularly in urban environments, accumulates metal pollutants from a variety of sources at much higher concentrations than corresponding water columns. Weathering of rocks and soils, as well as multiple anthropogenic activities caused by the discharge of industrial and urban wastes into water bodies, are the primary contributors (Singh et al., 2005). Heavy metals, among these pollutants, have sparked widespread concern due to their toxicity, abundance, persistence, and subsequent accumulation in aquatic habitats (Lin et al., 2013; Yang et al., 2012). Metal concentrations in sediment are not an isolated factor; rather, they interact with surrounding environmental factors. Therefore, research into the relationship between these elements and various environmental factors is required to comprehensively evaluate the metals' impact on the ecosystem. Thus, the distribution of metals in sediment could be used to investigate anthropogenic impacts on aquatic ecosystems and assess the risk posed by waste discharges (Yi et al., 2011). According to Adeniyi and Afolabi (2002), the significance of trace metals in marine sediment is becoming a global concern that must be properly assessed.

Eutrophication, along with oxygen limitation (anoxic coastal water), is caused by increased input of reactive nitrogen, phosphorus, or phosphate from detergent discharges, industrial, domestic, and urban runoffs, and fertilizers of farmlands. These substances may then go through reactions like ammonification, nitrification, denitrification, and anammox (Tuominen et al., 1998; Herbert, 1999; Hulth, 2004) or phosphate cycles (Anil, 2003). Nitrogen mineralization and benthic metabolism are severely harmed by this, and higher-level animals are also impacted. Karlson and associates (2007) dead zones, ecological harm, and even climate change could result from this. Because they serve as the transitional zone between the terrestrial and marine environments, coastal regions and estuaries are especially affected by excessive nutrient input. Many coastal regions around the world, including the Black Sea, the Baltic Sea, and the Gulf of Mexico, have been found to have anoxic coastal waters (Diaz& Rosenberg, 2008).

One of the most important coastal regions in southeast Nigeria is Calabar and its environs. They are renowned for the wealth of marine life that can be found in the nearby rivers and estuaries, including the Calabar River (fig. 1). A significant portion of the teaming population's economic, social, and health resources are represented by these resources. A vast amount of urban waste, including sewage, household, mechanic, hospital, power plant, and fertilizer waste from farms, is carried by the Calabar River as it flows through the densely populated city of Calabar. Anthropogenic activities and their associated discharges pose a significant ecological threat to aquatic ecosystems. This research aims to examine the concentrations, pollution levels, and risk contributions of various heavy metals and nutrients. The assessment will utilize several parameters, including pollution index, contamination factor, ecological risk indices, and toxic units (Hakansonet al., 1980; Harikumaret al., 2009) as well as the Redfield ratio (Redfield, 1958).

Study Location

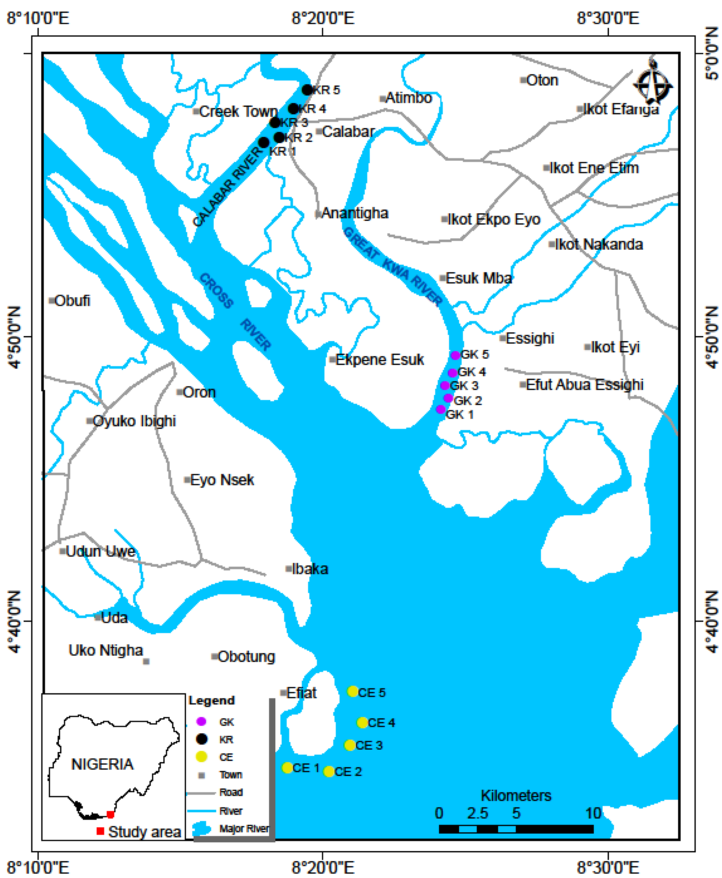

Figure 1. A map showing the study location: Calabar River (N 4.956770^0 E 8.304764^0) represented as KR (1-5)

Materials and Methods

Sample Collection and Preparation

Sediment samples were collected from the upper 5 cm layer at five different stations along the Calabar River. Care was taken during the collection process to minimize disturbance, as the upper 5 cm is more chemically and biologically active than deeper layers, facilitating chemical exchanges between the sediment and water (Dalia et al., 2014).A total of ten sediment clusters were collected during both the wet and dry seasons (July and February, respectively) from the Calabar River (KR), comprising five samples per season. A sediment grab sampler was utilized for this process. Each sample was stored in dark polyethene bags and treated with hydrochloric acid (HCl) to halt biological activity. The sampling containers were preconditioned with a 5% nitric acid solution and then thoroughly rinsed with distilled water before sampling. The collected samples were placed in a cooler with ice and transported to the laboratory for subsequent chemical analyses.

Analytical processes

Nutrient analysis:

The nutrient analysis was conducted following the methodology outlined by (Hou et al., 2013). The total nitrogen (TN) in the sediment was measured using the Kjeldahl nitrogen method, while the total phosphorus (TP) was assessed through a spectrophotometric approach.

Heavy metal analysis

The US EPA's Method 200.2 procedures were modified to assess the levels of Fe, Mn, Ni, Mg, Zn, Cd, Cr, and Pb. About 0.5 grams of dried and uniformly mixed sediment was measured and placed into a 50-mL conical flask for digestion, along with 2.8 mL of 1:1 HNO_3 and 7 mL of 1:4 HCl. After digestion, the resulting sample extract was analyzed for metal content using an ICP/AES instrument (SPECTRO SpectroCiros CCD, an inductively coupled plasma atomic emission spectrometry device manufactured by Spectro Analytical Instruments in Germany).

Pollution was evaluated using conventional tools including the Geo-accumulation index, Enrichment factor, Contamination factor, Ecological risk index, and Toxic units (Hakanson, 1980; Taylor, 1964) as used by Gopal et al. (2017) and Swarnalataet al. (2013).

Results

The results obtained in this research are presented in the following tables and figures.

Table 1: Concentration of nutrients and bioactive elements (mg/kg) from Calabar River (coordinates, N 4.956770°, E 8.304764°) during the wet season.

Sample ID	Nutrients		NO_3^-	NO_2^-	NH_4^+	PO_4^{3+}	TN	TP
KR1			42.4	2.02	4.92	0.48	53.9	1.91
KR2			38.3	1.98	7.71	0.32	59.2	1.45
KR3			28.6	1.69	6.17	0.65	44.5	3.01
KR4			23.5	2.82	4.88	0.74	42.4	2.1
KR5			32.7	2.06	5.01	0.86	42.1	1.46
Bioactive element	**Fe**	**Zn**	**Mn**	**Mg**	**Ni**	**Cd**	**Cr**	**Pb**
KR1	38.2	4.34	2.94	14.3	5.45	0.83	0.93	3.80
KR2	48.9	6.12	1.02	24.2	7.45	0.03	1.77	5.33
KR3	57.2	4.33	2.13	13.8	9.21	0.16	2.02	2.11
KR4	23.8	9.32	2.14	29.5	9.16	0.31	1.73	1.60
KR5	24.1	2.54	0.78	26.4	4.65	0.33	1.60	4.28

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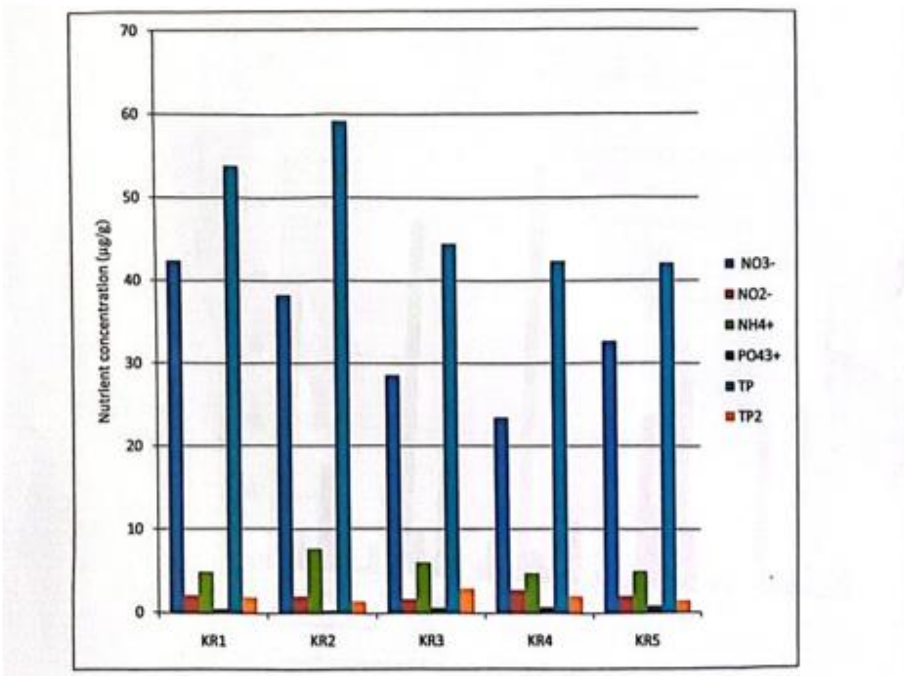

Figure 2: Concentration of Nutrients in the sediments of Calabar River during wet season.

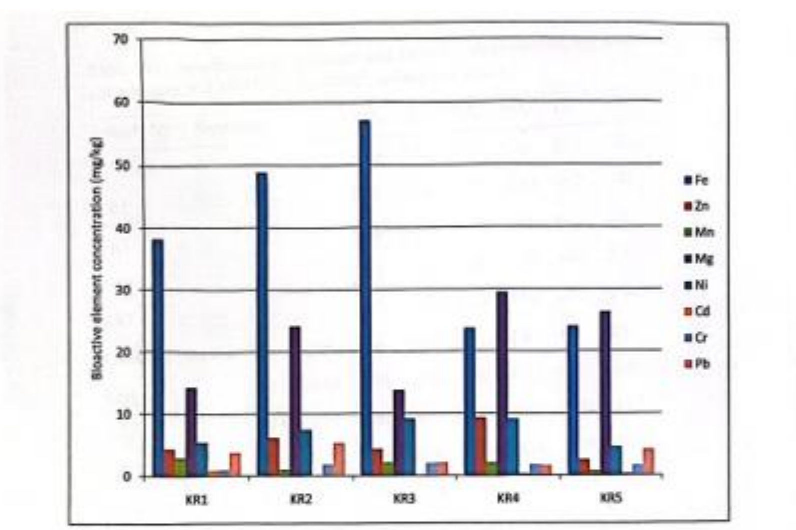

Figure 3: Concentrations of bioactive elements (mg/kg) in the sediments of Calabar River during the wet season.

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Table 2: concentration of nutrients and bioactive elements(mg/kg) from Calabar River (coordinates, N 4.956770°, E 8.304764°) during the dry season

Sample ID	Nutrients		NO_3^-	NO_2^-	NH_4^+	PO_4^{3-}	TN	TP
KR1			21.8	1.82	5.08	0.32	33.1	2.01
KR2			42.4	2.12	3.84	0.43	51.9	2.11
KR3			32.4	1.43	6.14	0.84	47.1	1.98
KR4			24.3	1.28	5.34	0.61	49.3	4.01
KR5			35.3	2.16	4.58	0.65	54.1	2.33
Bioactive Element	**Fe**	**Zn**	**Mn**	**Mg**	**Ni**	**Cd**	**Cr**	**Pb**
KR1	29.3	5.34	0.88	16.3	8.43	0.13	0.66	4.32
KR2	31.4	3.23	1.43	16.8	5.78	0.18	1.86	6.19
KR3	44.3	4.76	1.34	11.5	2.96	0.57	0.49	2.34
KR4	28.4	6.45	2.57	21.4	12	0.08	0.41	2.28
KR5	26.4	3.22	1.93	19.6	9.48	0.42	0.44	4.26

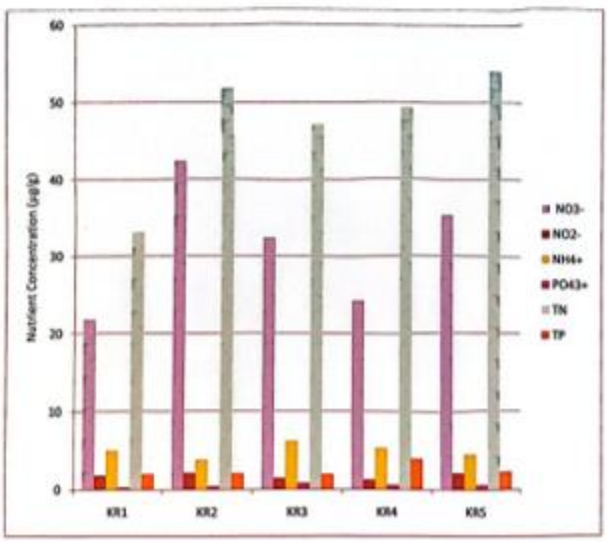

Figure 4: Concentration of Nutrients in sediments of Calabar River during Dry season

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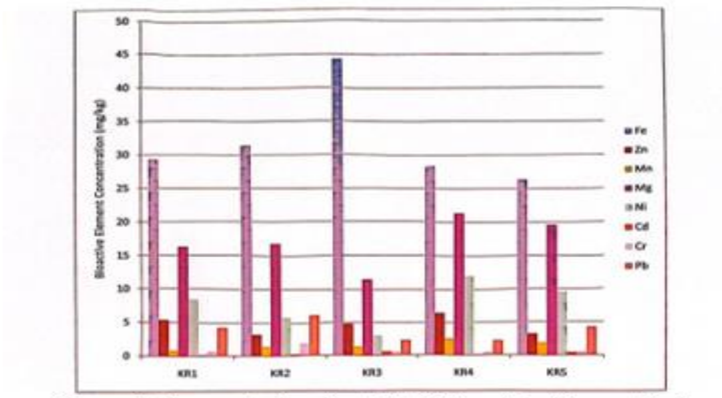

Figure 5: Concentration (mg/kg) of Bioactive Element in the sediments of Calabar River during Dry season.

Table 3: Range, Mean and Standard deviation of Nutrients in sediments of Calabar River (in KR) for wet and Dry Seasons

Nutrients		Wet Season	Dry season
NO_3^-	Range	23.5 – 42.4	21.8 – 42.4
	Mean	33.10 ± 3.759	31.24 ± 4.18
NO_2^-	Range	1.69 – 2.82	1.28 – 2.16
	Mean	2.114 ± 0.185	1.76 ± 0.199
NH_4^+	Range	4.88 – 7.71	3.84 – 5.34
	Mean	5.738 ± 0.613	4.996 ± 0.429
PO_4^{3-}	Range	0.32 – 0.86	0.32 – 0.84
	Mean	0.61 ± 0.213	0.57 ± 0.101
TN	Range	42.10 – 59.20	33.1 – 54.1
	Mean	48.42 ± 3.855	47.1 ± 4.129
TP	Range	1.45 – 3.01	1.98 – 4.01
	Mean	1.986 ± 0.315	2.488 ± 0.431
TN:TP		21-1	19-1
NO_3^-: PO_4^{3-}		54.3-1	54.8-1

Mean ± SD obtained from values of all five (5) stations of the study site

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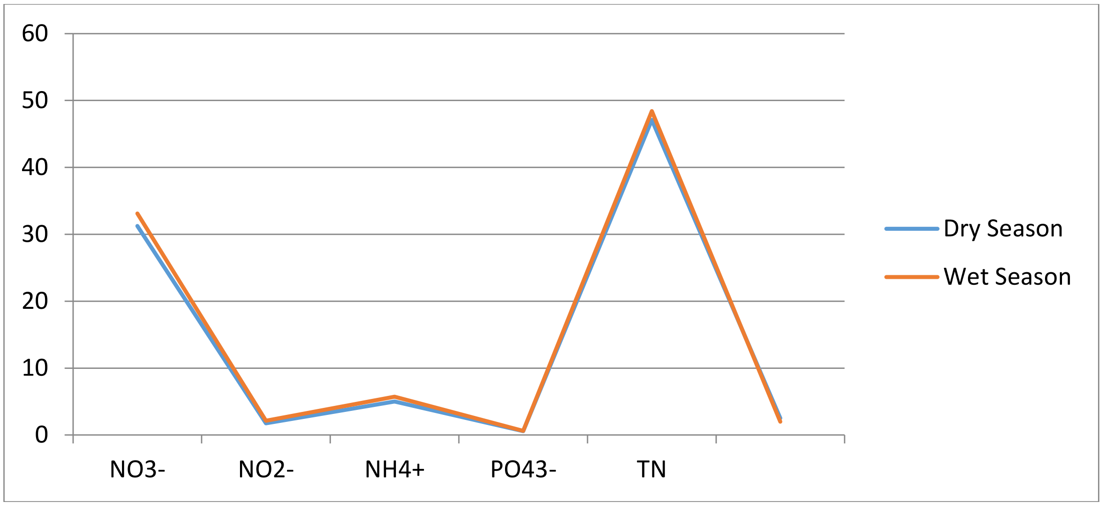

Figure 6: Mean concentration of nutrients in the sediments of Calabar River during wet and dry seasons.

TABLE 4: Range, Mean and Standard deviation of heavy metals from Calabar River (KR) sediments

Element		**Wet season**	**Dry season**
Fe	Range	23.8 – 57.2	26.4 – 44.3
	Mean	38.44 ± 7.422	31.96 ± 3.581
Zn	Range	2.54 – 9.32	3.23 – 6.45
	Mean	5.33 ± 1.343	4.6 ± 0.697
Mn	Range	0.78 – 2.94	0.88 – 1.93
	Mean	1.802 ± 0.445	4.6 ± 0.322
Mg	Range	13.8 – 29.5	11.5 – 21.4
	Mean	21.64 ± 3.591	17.12 ± 1.884
Ni	Range	4.65 – 9.21	2.96 – 12
	Mean	7.184 ± 1.046	7.73 ± 1.738
Cd	Range	0.03 – 0.33	0.08 – 0.57
	Mean	0.183 ± 0.37	0.276 ± 0.47
Cr	Range	0.93 – 2.02	0.44 – 1.865
	Mean	1.61 ± 0.59	0.899 ± 0.74
Pb	Range	1.60 – 5.30	2.288 – 6.193
	Mean	3.424 ± 1.35	3.88 ± 1.25

Mean ± SD Mean of triplicate determinations

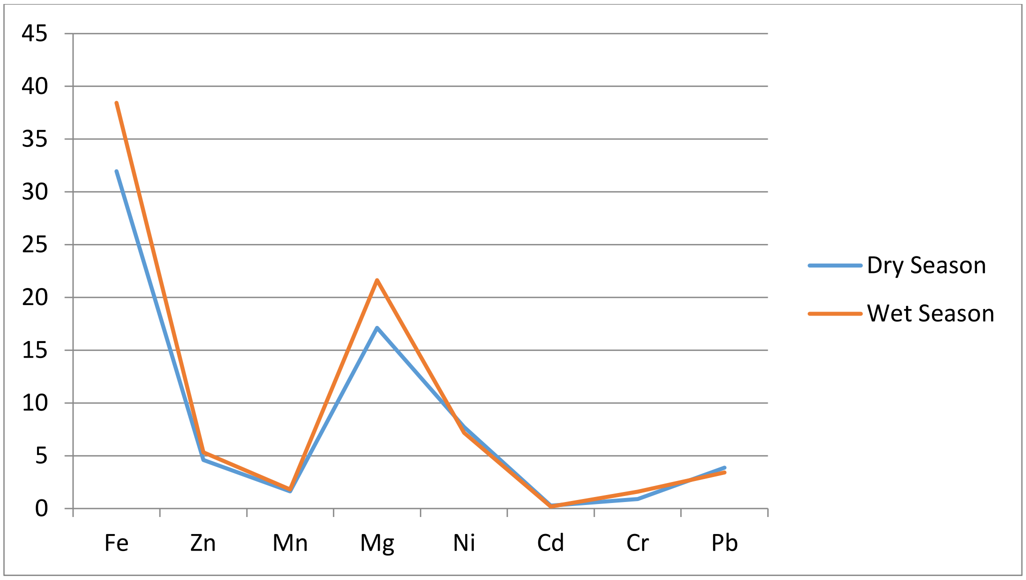

Figure 7: Mean concentration of bioactive elements in the sediments of Calabar River during wet and dry seasons.

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Table 5: Pollution assessment factors

	Fe	Zn	Mn	Mg	Ni	Cd	Cr	Pb
Geoaccumulation index (Igeo)								
Wet season	-11.19	-4.44	-9.82	-	-4.03	-3.18	-6.58	-5.64
Dry season	-11.39	-4.56	-9.87	-	-4.01	-2.09	-4.89	-4.74
Enrichment factor								
Wet season	1	130.60	3.54	-	123.00	279.80	20.46	51.19
Dry season	1	123.61	3.19	-	203.11	438.47	11.23	57.74
Contamination factor								
Wet season	5.00×10^{-4}	0.076	1.897×10^{-3}	-	0.096	0.229	0.016	0.040
Dry season	5.676×10^{-4}	0.066	3.383×10^{-3}	-	0.075	0.345	0.061	0.046

Table 6: Ecological Risk Index for metals of the Calabar River sediments.

Location	Fe	Zn^{1}	Mn	Ni^{5}	Cd^{30}	Cr^{2}	Pb^{5}	PERI	Remark
Wet season1		0.076	-	0.479	13.264	0.032	0.193	14.049	low Ecological Risk
Dry season 1		0.066	-	0.519	10.356	0.123	0.229	11.293	Low Ecological Risk

Tris not available for Mn therefore, no Ri was obtained.

Table 7: Toxic Unit of Bioactive Elements (Pederson *et al.*, 1998)

	Fe	Zn^{270}	Mn	Ni^{35}	$Cd^{3.53}$	Cr^{9}	$Pb^{91.3}$	Potential Acute Toxicity ΣTU
Wet Season	-	0.020	-	0.205	0.052	0.018	0.037	0.332
% contribution	-	6.02	-	61.75	15.66	5.42	11.15	100.00
Dry Season	-	0.016	-	0.224	0.078	0.01	0.043	0.371
% contribution	-	4.31	-	60.38	21.02	2.70	11.59	100.00

PEL values for Fe and Mg were not available; therefore TU could not be calculated

Discussion

Nutrients: The presence of all the analyzed nutrients was revealed at the five sites of the river in increasing order of phosphate $PO_4^{3-} < NO_2^- < NH_4^{3+} < NO_3^- <$ TN. However, on average a slight variation of TP > NO_2 was observed during the wet season. The red field ratio was evaluated to be 54.3: 1 and 54.8: 1 for NO_3^-: PO_4^{3-} during wet and dry seasons respectively. While TN: TP showed 21.2: 1 and 18.9: 1 for wet and dry seasons respectively. The nitrite: phosphate ratio is very high and shows a strong indication of phosphate limitation and excess nitrite which can lead to eutrophication and oxygen depletion which may further result in anoxia and hypoxia for both wet and dry seasons within this location. This location therefore requires serious monitoring and actions taken to avoid this location becoming a dead zone very shortly. However, practically the nutrients except TP were higher during the wet season. These values were compared with values obtained from researchers worldwide and were found to be within range as reported by Diaz and Rosenberg (2008) that dead zones are increasing among coastal areas worldwide. These could be associated with highly uncontrolled anthropogenic activities.

Heavy metals

The concentrations of the studied heavy metals (Fe, Zn, Ni, Mn, Cr, Cd and Pb) detected in the surface sediment of Calabar River were as seen in Tables 1, 2 and 4 and Figures 2, 4 and 5. They showed a decreasing trend of Fe > Ni,

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higher than Zn, > Pb, > Mn, > Cr, > Cd for both wet and dry seasons. Though Fe, Zn, and Cr were of higher concentration in the wet season, Mn, Ni, Cd and Pb were of higher concentration in the dry season. All the values obtained were compared with standard values given by RSMENR (2002) and the sediment quality guidelines for metal concentration as recorded by Parsaudet al. (1993) and McDonald et al. (1991) and were found to be below the targeted values and thus this region could be declared unpolluted with respect to these metals. This sediment does not pose any danger concerning these metals. Considering the various instruments used to assess the pollution/contamination status of the sediment, the following were established: that the environment is yet unpolluted with low ecological risk and low potential acute toxicity, as presented in Tables 5 – 7.

Conclusion

This environment can be declared safe concerning these bioactive elements, but excess nitrate and deficient phosphate were observed. This could be dangerous, shortly resulting in a dead zone of this River. Therefore, policies to control nitrate inflows into the location, particularly from farmlands and other anthropogenic activities, should be enacted and effectively monitored.

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