Geoenvironmental Assessments of Heavy Metals in Surface Sediments from Some Creeks of the Great Kwa River, Southeastern Nigeria

Bassey Edem Ephraim* and Ifedayo Olumide Ajayi
Department of Geology, University of Calabar, P. M. B. 1115, Calabar
* E-mail of the corresponding author: basseyephraim@unical.edu.ng

Abstract
In southeastern Nigeria, the Great Kwa River watershed which was originally covered by tropical rainforest has now become a beehive of various agricultural, extractive and industrial activities. The present study focused on the investigation of the current level and distribution of seven heavy metals (Pb, Zn, Cu, Ni, Cr, Cd, As) collected from surface sediment at 12 stations, located within Mbat-Abbiati and Oberakkai Creeks of the Great Kwa River. Results show that the measured heavy metals have an abundance trend in the order Zn>Cr>Ni>Cu>Pb>As>Cd for sediments from Mbat-Abbiati and Zn>Cr>Ni>Pb>Cu>As>Cd for sediments from Oberakkai Creek. Enhanced concentrations and significant spatial variation was recorded for heavy metals in sediments from Oberrakai Creek as against what obtains in sediments from Mbat-Abbiati Creek. The pollution status was evaluated using Enrichment Factor (EF), Index of Geoaccumulation (Igeo), Contamination Factor (Cf), Degree of Contamination (Cd) and Pollution Load Index (PLI). Indication from both the contamination factor and degree of contamination is that all the measured heavy metals, excluding Pb and Cd, exhibits low contamination status in the sediment. Based on geoaccumulation index, the sediments are generally classified as unpolluted with regards to the measured heavy metals. The computed Enrichment Factors (EF) showed that some heavy metals (Pb, Zn, Cr, Cd) have EF values of up to 1, which indicates enrichment through lithogenic and anthropogenic sources. Further screening revealed that more than 55% of the calculated EF values for the Pb, Zn, Cr and Cd are from lithogenic sources, thereby suggesting that the main sources of pollution are geogenic materials, probably sourced through mining and quarrying activities that thrive within the catchment region. Results of the Pollution Load Index conclude that sediments from both Mbat-Abbiati and Oberakkai Creeks are generally unpolluted.
Keywords: Geoenvironment, pollution, sediment, Nigeria, Great Kwa River

1. Introduction

Heavy metals, which can be sourced through anthropogenic and geologic sources, are stable and persistent environmental contaminants of coastal waters and sediments. Elevated concentrations of these metals in aquatic ecosystems are of major concern due to their toxicity and non-biodegradable nature. These metals pose a threat to aquatic life in various ways, notably, through re-suspension into the water column from geochemical re-cycling (Ahmet *et al.*, 2005; Al-Haidarey *et al.*, 2010; Campbell & Tessier 1996), accumulation in benthic fauna that feed on sediments, and ability to enter the food chain to produce a range of metabolic and physiological disorders (Barakat *et al.*, 2012; Kumar *et al.*, 2012; MacFarlane *et al.*, 2006). Aquatic sediments serve as a pool that can retain or release these heavy metals to the water column by various processes of remobilization (Caccia *et al.*, 2003; Pekey 2006; Marchand *et al.*, 2006). On a weight per square meter basis, the uppermost superficial sediments constitute the largest heavy metals reservoir in aquatic systems (Al-Haidarey et. al. 2010). The heavy metals always occur in concentrations that usually exceed the levels of the overlying water by 3 to 5 orders of magnitude so that bioavailability of even a minute fraction of the total sediment's heavy metal content assumes significant importance (Defew *et al.*, 2004; Zabetoglou *et al.*, 2002). A number of serious health problems can develop as a result of excessive uptake of dietary heavy metals Also, the consumption of heavy metal-contaminated food can seriously deplete some essential nutrients in the body causing a decrease in immunological defences, intrauterine growth retardation, impaired psycho- social behaviour, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer (Arora 2008). Thus, the continuous identification, quantification and assessment of heavy metals in aquatic system should be encouraged, given its immense health benefit (Addo *et al.*, 2011).

In Nigeria, studies on the assessment of the contamination status of heavy metals on river sediment have been vigorously pursued over the last couple of years (see for instance, Aderinola *et al.*, 2009; Butu & Iguisi 2013; Chindah *et al.*, 2009; Davies *et al.*, 2006; Ladigbolu & Balogun, 2011; Majolagbe et. al, 2012; Olubunmi & Olorunsola, 2010; Puyate *et al.*, 2007; Uwah *et al.*, 2013; Uzairu *et al.*, 2009). The present study focused on two Creeks of the Great Kwa River in Southeastern Nigeria

The Great Kwa River watershed was originally covered by tropical rainforest but has now become a beehive of agricultural, road construction, forestry, industry, mining and quarrying activities (Efiong 2011). The establishment of mostly the quarrying/mining activities within the catchment area of the River, together with the intense agricultural practice in the area is bound to impact negatively on the quality of the aquatic ecosystem. Other areas of environmental concern in the basin includes the numerous human activities within and around this river, notably, dredging, logging, fishing, boating, watercraft maintenance, saw-milling, transportation, laundering, bathing and swimming, etc. These activities could result in eutrophication, nutrient enrichment, toxic chemical contamination, sedimentation and other problems that plague coastal waters, with consequent attendant ecological and economic impacts on the aquatic ecosystem. There is therefore need for constant quality monitoring and evaluation of the ecological integrity of the aquatic ecosystem in view of the health implications. The present study was therefore designed to document the current state of heavy metals concentration in sediments of Mbat-Abbiati and Oberekkai Creeks of the Great Kwa River in southeastern Nigeria. The primary objectives include, (1) to provide preliminary data of heavy metal (Pb, Zn, Cu, Ni, Cr, Cd, As) concentration and distribution on the study area, (2) to employ various means of assessments, including the use of various indices to assess the current pollution status of the river basin, and (3) to evaluate impacts on industrial and economic activities in the study area. The justification for the work is the fact that Mbat-Abbiati and Oberekkai Creeks are well positioned to receive effluents from the various agricultural, mining and quarrying activities which flourish within the neighborhood.

2. Materials and Methods

2.1 Study Area and Sampling Site Description

The present study considered two Creeks, namely Mbat-Abiati Creek in Abiati village and Oberekkai Creek in Oberekkai village. The area of study is therefore delimited by Latitude 5°05'N and 5°06'N and latitudes 8°27'E and 8°29'E, situated within present-day Akamkpa Local Government Area of Cross River State, southeastern Nigeria (Fig. 1). Mbat-Abiati and Oberekkai Creeks empty into the Great Kwa River. The Great Kwa River takes its rise from the Oban Hills in eastern Nigeria, flows southwards and discharges into the Cross River Estuary around latitude 4o45'N and longitudes 8o20'E. The lower reaches of the River drains the eastern coast of Calabar Municipality. The lower Great Kwa River is characterized by semi-diurnal tides and extensive mud flats. The study region is characterized by tropical climate with distinct alternating dry and wet seasons. Based on data measured by the National Meteorological Agency, the area is associated with warm temperatures ranging between 26 °C to 32 °C and a bi-modal rainfall pattern averaging approximately 2,300 mm annually. The annual mean daily relative humidity and evaporation is in the range 76 – 86% and 3.85 mm/day respectively (Petters *et al.*, 1989). Moist, evergreen forest-type vegetation exists in unaltered areas, while herbs, shrubs and few trees are cultivated in the altered portions of the area. Thick, riparian forest fringes most streams and in the area. The topography of the study area is typified by plains under 200m above sea level which dominates the land surface of the area. The study area is also an integral part of the Calabar Flank, which is unique in many respects. In terms of sediments, the Calabar Flank is underlain by Cretaceous Sedimentary rock deposits comprising sandstones, limestones, marlstones and shales. The Mfamosing Limestone Formation is the main Carbonate – bearing deposit occurring within the study area and it is the thickest carbonate body in Nigeria (Reijers & Petters 1987).

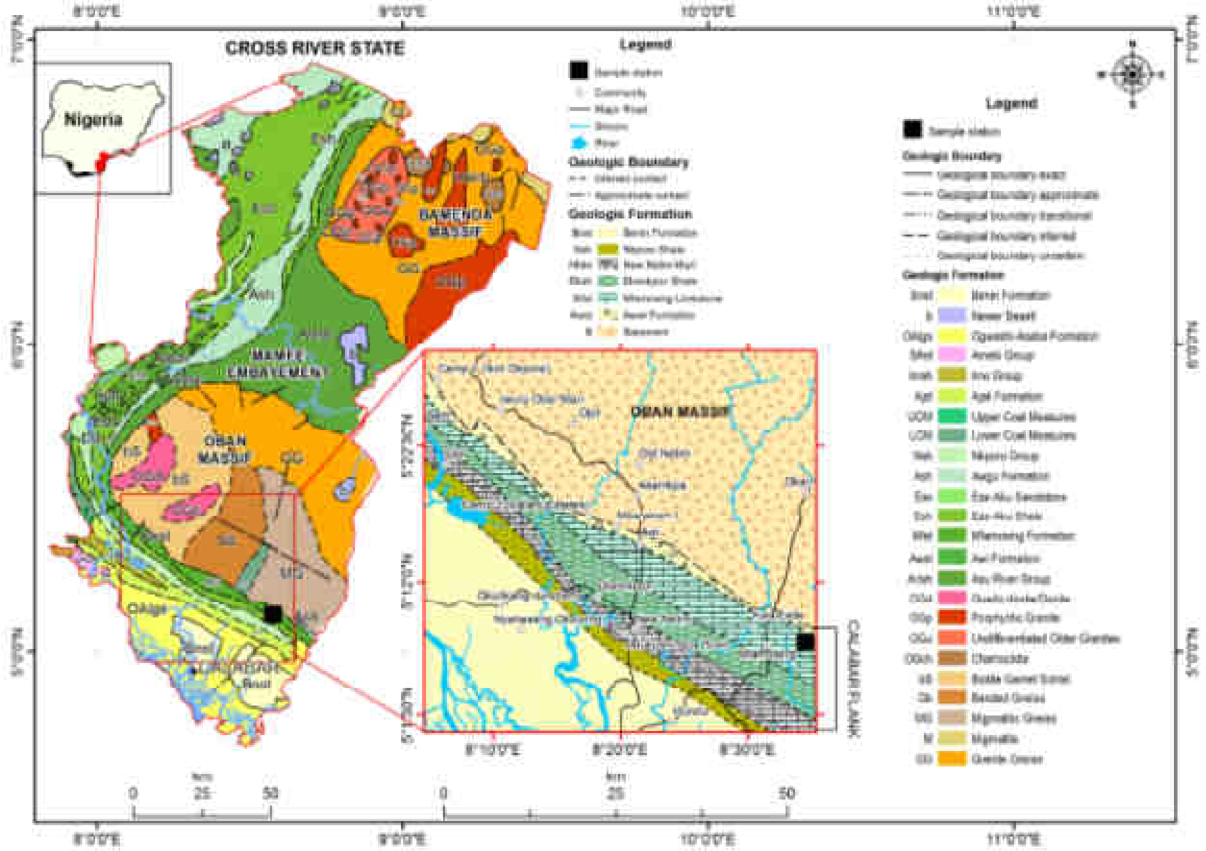

Figure 1. Geological map of Cross River State in southeastern Nigeria, showing the geology of study area

2.2 Sampling and Laboratory Techniques

A total of twelve (12) sizeable surface sediment samples were strategically collected from different locations beneath the drainage channels of the two Creeks selected for study. All the sampling points were appropriately located using the Global positioning System (GPS), and identifiable landmarks in adjoining land areas to the sampling points were also recorded. At each sampling point, surface sediment samples were taken at a depth of 0 – 10 cm, drained of water in situ and then quickly packed into well-labeled, sterile cloth bags which were previously thoroughly washed and dried before use. The choice of surface sediments was due to the fact that this layer controls the exchange of metals between sediments and water (Barakat *et al.*, 2012; El Nemr *et al.*, 2006). Also, Solomons & Forstner (1984) reported that heavy metals tend to be concentrated in the finer grain sizes of sediment. The collected samples were transported to Soil Science Laboratory of University of Calabar, Nigeria, where they were air-dried for three weeks under room temperature of about 30ºC. The drying was necessary to eliminate organic matter and moisture contents, amongst other undesirable components. After drying, individual samples were disaggregated, and sieved through a 2-mm plastic sieve to remove large debris, gravel-size materials, plant roots, animal shells and other waste materials. Finer fractions, not only concentrate iron oxide/hydroxide, organic matter, aluminum, clay minerals, but also have the largest capacity to bind particle reactive trace metal contaminants relative to coarser particles (>2 mm size). The prepared samples were then package, labeled and stored in clean closed plastic bags for subsequent analysis. Considerable precautions were taken to avoid contamination during drying, grinding, sieving and storage.

Prior to the analysis, 0.5g of each sample was weighed into the digestion flask and digested to complete dryness with an acid solution, comprising H2O-HF-HClO4-HNO3 in the ratio 2:2:1:1. Afterward, about 50% of HCl was added to the residue and heated using a mixing hot block. The solution was cooled and homogenized before being transferred to test-tubes where it was brought to volume using dilute HCl. Sample splits of 0.25g was then analyzed for heavy metals using the ICP-ES (Inductively Coupled Plasma-Emission Spectrometry) technique at the Geochemistry Laboratory of Acme Analytical Laboratories, Vancouver BC, Canada. All the sediment samples were analyzed for total concentrations of Pb, Zn, Cu, Ni, Cr, Cd, As, Al.

The accuracy of the analytical procedure used was reputedly cheeked by analyzing duplicate samples and repeatedly analyzing reference samples (STD OREAS24P), and comparing the obtained values with the expected values. The quality control samples represented 10% of the total analytical load. The duplicates samples were treated identically. The percentage recovery from 93 to 105%, while precision is within 5%.

Details on the sampling, treatments and analysis of the sediment samples are in Ajayi (2014).

2.3 Determination of Contamination Factor (Cf) and Degree of Contamination (Cd)

Both Contamination Factor (Cf) and the Degree of Contamination (Cd) are widely employed to determine the contamination status of sediment. Cf values were measured using the expression below:

$$Cf = C_{metal} / C_{background}$$

Cmetal is the concentration of metal in sediment, while Cbackground is the background value for the metal. The average composition of shale from Turekian & Wedepohl (1961) was used as background values for the metals. The degree of contamination (Cd) was computed as the sum of the determined contamination factors (Cf) for each of the measured heavy metals in the site.

2.3 Determination Index of Geoaccumulation (I_{geo})

The Index of Geoaccumulation (I_{geo}), which involves comparing observed concentration of the metal (n) in the sediment with pre-industrial levels or background levels, was used to assess the level of heavy metal pollution in the sediments. The I_{geo} was calculated, using the method of Muller (1979) & Abrahim & Parker (2008), as follows:

$I_{geo} = \log_2 ([C_n]/ 1.5* [B_n])$

Where, Cn is the measured concentration of element 'n' in the sediment and Bn is the geochemical background for element 'n' which is either directly measured in pre-civilization sediments of the area or taken from the literature. In the present study, the average composition of shale from Turekian & Wedepohl (1961) was considered appropriate. The factor 1.5 is introduced to include possible variations of the background values that are due to lithologic variations in the sediment.

2.4 Determination of Enrichment Factor (EF)

To evaluate the magnitude of contaminants in the environment, Enrichment Factors (EF) were computed following the method of Atgin *et al.* (2000) and Simex & Helz (1981), as follows:

$EF = (C_M/C_{Al})_{sample}/(C_M/C_{Al})_{Earth's\ crust}$

Where, $(C_M/C_{Al})_{sample}$ is the ratio of concentration of measured heavy metal (C_M) to that of Al (C_{Al}) in the sediment sample and $(C_M/C_{Al})_{Earth's\ crust}$ is the same reference ratio in the Earth's crust. The values taken as the average abundance of Pb, Zn, Cu, Cd, Cr, As and Ni (20, 95, 45, 0.3, 90, 4.72 and 68 mg kg-1, respectively) in the reference Earth's crust were the average composition of shale, from Turekian & Wedepohl (1961). Aluminium (the reference value being 47,200) was selected as the reference element.

2.5 Determination of Pollution Load Index (PLI)

The pollution load index (PLI) proposed by Tomlinson *et al.* (1980) was also used in this study. The PLI for a single site is the nth root of n number multiplying the contamination factors (CF values) together:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots CF_n)^{1/n}$$

Where CF is the contamination factor, n is the number of metals.

3. Analysis and Discussions of Results

3.1 Heavy Metal Abundance

The concentration of heavy metal and relevant statistical summaries for sediments of Mbat-Abbiati and Oberekkai Creeks is given in Table 1, while the graphic illustration of the mean abundance of the heavy metals is presented as Fig 2.

TABLE 1. Concentration of heavy metals (mg/kg Dry Weight) in sediments of Mbat- Abbiati and Oberakhai Creeks of the Great Kwa River, SE Nigeria

		Pb	Zn	Cu	Ni	Cr	Cd	As	Al
Mbat Abbiati Creek	**AS-1**	25.22	81.8	22.88	26.6	70	0.27	0.3	58,900
	AS-2	20.61	86.8	21.88	25	62	0.3	1.5	55,000
	AS-3	18.28	83.9	25.25	25.3	57	0.28	0.4	47,700
	AS-4	16.58	87.9	27.05	28.5	58	0.43	1.3	43,300
	AS-5	17.58	82.8	25.94	25.9	56	0.32	0.6	48,700
	AS-6	16.66	81.1	25.21	24.5	53	0.32	2.1	43,800
	MIN	16.58	81.1	21.88	24.5	53	0.27	0.3	43,300
	MAX	25.22	87.9	27.05	28.5	70	0.43	2.1	58,900
	MEAN	19.16	84.05	24.7	25.97	59.33	0.32	1.03	49,567
	ST.DEV	3.32	2.75	1.94	1.44	5.99	0.06	0.71	6,219
Oberakhai Creek	**OS-1**	26.56	107.8	26.91	30.4	72	0.46	0.2	73,400
	OS-2	15.55	59.4	16.33	21.2	47	0.23	0.6	42,800
	OS-3	19.92	82.7	22.55	23.8	56	0.35	0.6	48,700
	OS-4	37.65	130.6	24.61	51.9	120	0.11	2.3	161,600
	OS-5	26.24	105.3	26.6	29.9	66	0.36	1.6	65,300
	OS-6	21.69	73.5	22.21	23.9	63	0.2	0.3	72,900
	MIN	15.55	59.4	16.33	21.2	47	0.11	0.2	42,800
	MAX	37.65	130.6	26.91	51.9	120	0.46	2.3	161,600
	MEAN	24.6	93.22	23.2	30.18	70.67	0.29	0.93	77,450
	ST.DEV	7.6	26.07	3.9	11.25	25.66	0.13	0.83	43,112

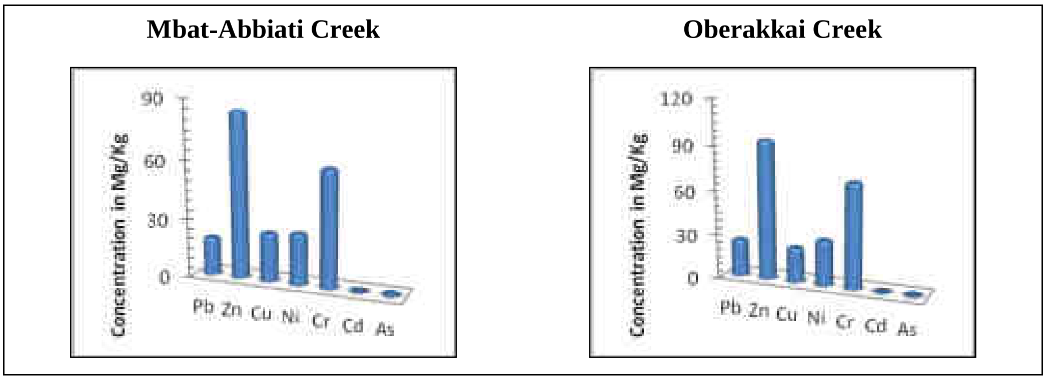

Figure 2. Mean abundance of heavy metals in sediment of Mbat Abbiati and Oberakkai Creek of the Great Kwa River

A cursory appraisal of Table 1 and Fig. 2 show the respective abundance trend recorded for sediments of Mbat – Abbiati and Oberrakai Creeks as: Zn>Cr>Ni>Cu>Pb>As>Cd and Zn>Cr>Ni>Pb>Cu>As>Cd. Also revealed were the relatively enhanced concentrations and significant spatial variation in concentrations recorded for each of the heavy metals in sediments of Oberrakai Creeks as against what obtains in sediments of Mbat Abbiati Creeks (Table 1).

As shown in Table 1, the heavy metal concentrations (mg kg-1 dry weight) of sediments of Mbat Abiati Creeks can be summarized as follows: 19.16±3.32 for Pb, 84.05±2.75 for Zn, 24.7±1.94 for Cu, 25, 97±1.44 for Ni, 59.33±5.99 for Cr, 0.32±0.06 for Cd, 1.03±0.71 for As and 30183 ±4186 for Fe. Similarly, the heavy metal concentrations (mg kg-1 dry weight) of sediments of Oberakhai Creeks (Table 1) can be summarized as follows: 24.60±7.60 for Pb, 93.22±26.07 for Zn, 23.20±3.90 for Cu, 30.18±11.25 for Ni, 70.67±25.66 for Cr, 0.29±0.13 for Cd, 0.93±0.83 for As and 28,517 ±10,284 for Fe. Indication is that Zn and Cd respectively constitute the highest and lowest abundance in terms of concentrations in both sediments of Mbat – Abbiati and Oberrakai Creeks.

3.2 Comparison of the mean concentration of heavy metals in the investigated sediments with Geochemical Benchmarks, Sediments Quality Guidelines and Metal Concentrations in Sediments of other Local and Regional Rivers

The mean concentration of heavy metal in sediments of Mbat-Abbiati and Oberekkai have been compared with the concentrations of heavy metals in the widely utilized World average shale composition of Turekian & Wedepohl (1961), EPA Ecological Screening Values (EPA, 1995), Canadian Interim Sediment Quality Guidelines, comprising Threshold Effect Concentration (TEC) and Probable effect concentration (PEC) (Environment Canada 1995, 2002), Dutch Soil Quality Standards which is made up of the Target and Intervention values (MHSPE 1994), as well as with sediments of various other local and regional rivers. These criteria are shown in Table 2.

Table 2. Mean values (mg kg-1) of heavy metals contents of the studied sediments, in comparison with geochemical background data, sediment quality guidelines, toxicological reference, and other local and regional river sediments

Class	DESCRIPTION		Pb	Zn	Cu	Cd	Ni	As	Cr
Present study	Mbat-Abbiati Creek		19.16 (±3.32)	84.05 (±2.75)	24.7 (±1.94)	0.32 (±0.06)	25.97 (±1.44)	1.03 (±0.71)	59.33 (±5.99)
	Oberrakai Creek		24.6 (±7.60)	93.22± (26.07)	23.20 (±3.9)	0.29 (±0.13)	30.18 (±11.25)	0.93 (±0.83)	70.67 (±25.66)
Geochemical background	Average composition of Shales[a] (Turekian & Wedepohl, 1961)		20	95	45	0.3	68	4.72	90
Sqg and other toxicological reference values for river sediments and soils	EPA Ecological Screening Values[b]		30.2	124	18.7	1	15.9	7.24	52.3
	Canadian ISQG[c]	TEC	35	123	35.7	0.596	18	5.9	37.3
		PEL	91.3	315	197	3.53	35.9	17	90
	Dutch Soil Quality Standard[d]	Target Values	85	140	36	0.8	35	29	100
		Intervention Values	530	720	190	12	210	55	380
Local and international river sediments	River Kubanni Sediments[e]		-	103.7	-	-	-	2.04	24.3
	Ajawere River Sediments[f]		27.96	14.63	16.02	3.39	3.75	12.38	43.24
	Cross River Sediment[g]		56.51	108.77	-	1.85	7.03	2.05	0.97
	Day River Sediment, Morocco[h]		109.01	100.13	108.62	1.27	-	-	102.27
	Japan River Sediment[i]		23.1	118	30.6	0.158	25.1	9.32	65.2

Note: TEC= Threshold effect concentration; PEL= Probable effect level; ISQG= Interim sediment quality guideline.

[a]Turekian & Wedepohl (1961); [b]EPA (1995); [c]Environment Canada (2002); [d]MHSPE (1994); [e]Butu &

Iguisi (2013);
[f]Oyekunle *et al.* (2011); [g]Ekwere et al (2013) ; [h]Barakat et al (2012); [i]Gamo (2007)

It is observed that the mean concentrations of heavy metal in sediments of Mbat-Abbiati and Oberekkai are generally lower than values quoted in the EPA Ecological Screening Values (EPA, 1995), in both TEC and PEC of the Canadian Interim SQG (Environment Canada, 1995, 2002), as well as in values recorded for both Target and Intervention values of the Dutch Soil Quality Standards (MHSPE, 1994) (Table 2). The only exceptions in this regards is the fact that Cd appears to be slightly enriched in the sediments of Mbat-Abbiati and Oberekkai compared to that of the World average shale composition of Turekian & Wedepohl (1961). Similar trend is observed for Ni and Cr when the mean contents are related to the TEC values of the Canadian Interim SQG (Environment Canada 1995, 2002), and for Cu and Ni when compared with the EPA Ecological Screening Values (EPA 1995).

In comparison with sediments of various local and regional rivers, there is a general depletion trend recorded for most of the heavy metal compositions of sediments of Mbat-Abbiati and Oberekkai, apart from the fact that Zn, Cu, Ni, and Cr contents are higher than what obtains in the Ajawere River Sediments (Oyekunle *et al.*, 2011). A similar trend is displayed by Ni and Cr when the mean concentrations of heavy metal in sediments of Mbat-Abbiati and Oberekkai Creeks are compared with those of the Cross River Sediment (Ekwere *et al.*, 2013)). Also, Cd and Cr are comparatively higher in the River Kubanni Sediments of Zaria northwestern Nigeria (Butu & Iguisi 2013) and in the Japan River Sediment (Gamo 2007).

3.3 Assessment of Heavy Metal Contamination

It is often beneficial to involve various indices in geoenvironmental assessments. Some of the indices employed in the present study include: Contamination Factor (Cf), Degree of Contamination (Cd), Index of Geoaccumulation (Igeo), Enrichment Factor (EF) and Pollution Load Index (PLI).

3.3.1 Assessment according to Contamination Factor (CF) and Degree of Contamination

Computed contamination factor (Cf) and degree of contamination (Cd) is shown in Table 3, where it is observed that the computed contamination factors (Cf) for sediments from Oberrakhai Creek are larger than those of sediment from Mbat-Abbiati Creek. For instance, 7.70, 6.56 and 6.44 represents the recorded degree of contamination (Cd) for sediments of Stations OS-4, OS-1 and OS-5 respectively, and all these are from Oberrakhai Creek. These values are larger than the highest degree of contamination (Cd) of 5.71 measured in sediment of Station AS-4, situated in Mbat-Abbiati Creek.

Table 3: Contamination Factor (Cf) and Degree of Contamination Cd) for sediment samples from Mbat-Abbiati and Oberekkai Creeks of the Great Kwa River, SE Nigeria.

Location/Sample Station		**Pb**	**Zn**	**Cu**	**Ni**	**Cr**	**Cd**	**As**	**DEGREE OF CONTAMINATION (Cd)**
		Contamination Factors (Cf)							
Mbat-Abbiati Creek	**AS-1**	1.26	0.86	0.51	0.39	0.78	0.90	0.06	5.48
	AS-2	1.03	0.91	0.49	0.37	0.69	1.00	0.32	5.35
	AS-3	0.91	0.88	0.56	0.37	0.63	0.93	0.08	5.13
	AS-4	0.83	0.93	0.6	0.42	0.64	1.43	0.28	5.71
	AS-5	0.88	0.87	0.58	0.38	0.62	1.07	0.13	5.14
	AS-6	0.83	0.85	0.56	0.36	0.59	1.07	0.44	5.32
	MEAN	0.96	0.88	0.55	0.38	0.66	1.07	0.22	5.36
Oberakhai Creek	**OS-1**	1.33	1.13	0.6	0.45	0.8	1.53	0.04	6.56
	OS-2	0.78	0.63	0.36	0.31	0.52	0.77	0.13	3.88
	OS-3	1.00	0.87	0.5	0.35	0.62	1.17	0.13	5.08
	OS-4	1.88	1.37	0.55	0.76	1.33	0.37	0.49	7.70
	OS-5	1.31	1.11	0.59	0.44	0.73	1.20	0.34	6.44
	OS-6	1.08	0.77	0.49	0.35	0.7	0.67	0.06	4.57
	MEAN	1.23	0.98	0.52	0.44	0.78	0.95	0.20	5.70

Considering the contaminations level terminologies associated with Cf values, shown in Table 4, all the measured heavy metals, excluding Pb and Cd, can be described as exhibiting low contamination status in sediment of both Mbat – Abbiati and Oberrakhai Creeks. However, Pb and Cd and probably Zn appear to display slightly moderate contamination level in both Creeks.

Table 4. Contamination Factor and Level of Contamination (Hakanson 1980)

Contamination Factor (Cf)	**Level of Contamination**
Cf<1	Low contamination
1≤Cf<3	moderate contamination
3≤Cf<6	considerable contamination
Cf>6	Very High contamination

On the basis of the mean values of Cf, sediments of Mbat-Abbiati Creek are enriched for metals in the order:

Cd>Pb>Zn>Cr>Fe>Cu>Ni>As, while that for Oberakhai Creek is of the order: Pb>Zn> Cd>Cr>Fe>Cu>Ni>As

3.3.2 Assessment according to Geo-accumulation Index (I_{geo})

The geo-accumulation index (Igeo) scale, proposed by Muller (1981) consists of seven grades (0-6) ranging from uncontaminated to highly contaminated, as shown in Table 5.

Table 5. Muller's Classification for the Geo-Accumulation Index

Igeo Value Range	Class	Sediment Quality
≤0	0	uncontaminated
0 – 1	1	from uncontaminated to moderately contaminated
1 – 2	2	moderately contaminated
2 – 3	3	from moderately to strongly contaminated
3 – 4	4	strongly contaminated
4 – 5	5	from strongly to extremely contaminated
≥6	6	extremely contaminated

The Igeo values and their corresponding contamination intensity for heavy metals in sediments from Mbat-Abbiati and Oberekkai Creeks are presented in Table 6 and the variations are shown graphically (Fig. 3).

It is evident from the figure that the Igeo values for all the metals fall in class '0' in all the twelve sampling locations (except at sampling sites OS-1 for Cd and OS-4 for Pb), indicating that there is no pollution from these metals in the investigated sediments.

On the basis of the mean values of Igeo, sediments of Mbat-Abbiati Creek are enriched for metals in the order: Cd>Pb>Zn>Cr>Fe>Cu>Ni>As, while that for Oberakhai Creek is of the order: Pb>Zn> Cd>Cr>Fe>Cu>Ni>As

Table 6: Geoaccumulation Index Values for sediment samples from Mbat-Abbiati and Oberekkai Creeks of the Great Kwa River, SE Nigeria.

	Pb	Zn	Cu	Ni	Cr	Cd	As
AS-1	-0.25	-0.8	-1.56	-1.94	-0.95	-0.74	-4.56
AS-2	-0.54	-0.72	-1.63	-2.03	-1.12	-0.58	-2.24
AS-3	-0.71	-0.76	-1.42	-2.01	-1.24	-0.68	-4.15
AS-4	-0.86	-0.7	-1.32	-1.84	-1.22	-0.07	-2.45
AS-5	-0.77	-0.78	-1.38	-1.98	-1.27	-0.49	-3.56
AS-6	-0.85	-0.81	-1.42	-2.06	-1.35	-0.49	-1.75
Mean Igeo Values	-0.66	-0.76	-1.46	-1.98	-1.19	-0.51	-3.12
OS-1	-0.18	-0.4	-1.33	-1.75	-0.91	0.03	-5.15
OS-2	-0.95	-1.26	-2.05	-2.27	-1.52	-0.97	-3.56
OS-3	-0.59	-0.79	-1.58	-2.1	-1.27	-0.36	-3.56
OS-4	0.33	-0.13	-1.46	-0.97	-0.17	-2.03	-1.62
OS-5	-0.19	-0.44	-1.34	-1.77	-1.03	-0.32	-2.15
OS-6	-0.47	-0.96	-1.6	-2.09	-1.1	-1.17	-4.56
Mean Igeo Values	-0.34	-0.66	-1.56	-1.83	-1	-0.8	-3.43
Igeo Class	0	0	0	0	0	0	0
REMARKS	Unpolluted	Unpolluted	Unpolluted	Unpolluted	Unpolluted	Unpolluted	Unpolluted

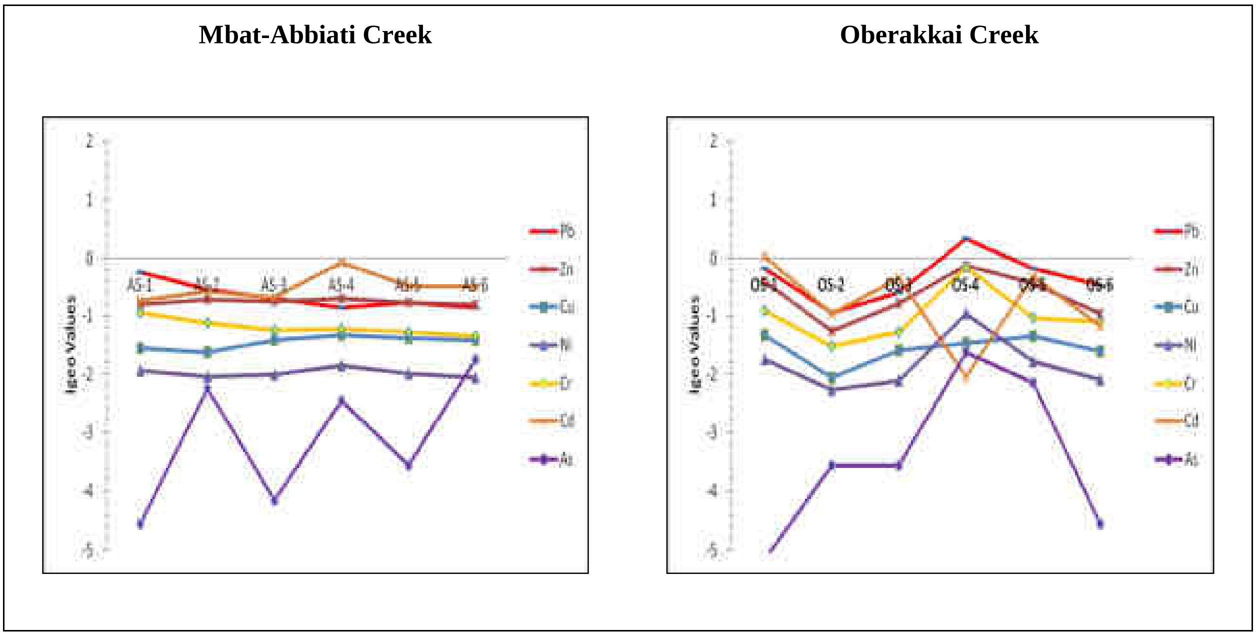

Figure 3. Spatial variations in the Igeo values of sediments from Mbat-Abbiati and Oberakkai Creeks of the Great Kwa River

3.3.3 Assessment according to Enrichment Factor (EF)

The Enrichment Factors (EF) of all the heavy metals measured in the sediment samples of Mbat-Abbiati and Oberrakhai Creeks of the Great Kwa River are presented in Table 7. The computed EF values are generally <2.00, which are not considered significant according to Atgin *et al.* (2000). However, when interpreted following the method used by Birch (2003), where EF<1 indicates no enrichment, <3 indicates minor enrichment, 3 – 5 show moderate enrichment, 5 – 10 denote moderately severe enrichment, 10 – 25 denote severe enrichment, 25 – 50 denote very severe enrichment and >50 refer to extremely severe enrichment, it becomes obvious that the investigated sediments can generally be classified as reflecting minor enrichments with regards to the measured heavy metals.

Table 7: Enrichment Factors for sediment samples from Mbat-Abbiati and Oberekkai Creeks of the Great Kwa River, SE Nigeria.

		Pb	Zn	Cu	Ni	Cr	Cd	As	AL
Mbat-Abbiati Creek	AS-1	1.88	1.29	0.76	0.58	1.16	1.34	0.09	1.00
	AS-2	1.65	1.46	0.78	0.59	1.10	1.60	0.51	1.00
	AS-3	1.69	1.63	1.04	0.69	1.17	1.72	0.16	1.00
	AS-4	1.68	1.88	1.22	0.85	1.31	2.91	0.56	1.00
	AS-5	1.59	1.57	1.04	0.69	1.12	1.93	0.23	1.00
	AS-6	1.67	1.72	1.13	0.72	1.18	2.14	0.89	1.00
	MIN	1.59	1.29	0.76	0.58	1.10	1.34	0.09	1.00
	MAX	1.88	1.88	1.22	0.85	1.31	2.91	0.89	1.00
	MEAN	1.69	1.59	0.99	0.69	1.17	1.94	0.41	1.00
	ST.DEV	0.10	0.21	0.19	0.10	0.07	0.55	0.30	0.00
Oberakhai Creek	OS-1	1.59	1.36	0.72	0.54	0.96	1.84	0.05	1.00
	OS-2	1.60	1.29	0.75	0.64	1.07	1.58	0.26	1.00
	OS-3	1.80	1.57	0.91	0.63	1.12	2.11	0.23	1.00
	OS-4	1.03	0.75	0.30	0.42	0.73	0.20	0.27	1.00
	OS-5	1.77	1.49	0.80	0.59	0.99	1.62	0.46	1.00
	OS-6	1.31	0.93	0.60	0.42	0.84	0.80	0.08	1.00
	MIN	1.03	0.75	0.30	0.42	0.73	0.20	0.05	1.00
	MAX	1.80	1.57	0.91	0.64	1.12	2.11	0.46	1.00
	MEAN	1.52	1.23	0.68	0.54	0.95	1.36	0.22	1.00
	ST.DEV	0.30	0.32	0.21	0.10	0.15	0.71	0.15	0.00

Further appraisal of the enrichment Factors (EF) data showed that some heavy metals (Pb, Zn, Cr, Cd) have enrichment factors of up to 1, which indicates enrichment through lithogenic and anthropogenic sources (Praveena *et al.*, 2007; Neto *et al.*, 2006; Huang & Lin, 2003; Shotyk *et al.*, 2000). It therefore becomes necessary to define the percentage of enrichment that is due to lithogenic sources and that due to anthropogenic influences. This discrimination was accomplished, following the method of Hernandez *et al.* (2003); the formulas employed are as follows:

$$[C_M]_{Lithogenic} = [C_{Al}]_{Sample} \, X \, ([C_M]/[C_{Al}])_{Lithogenic}$$

$$[C_M]_{Anthropogenic} = [C_M]_{Total} - [C_M]_{Lithogenic}$$

Where $[C_M]_{Lithogenic}$ and $[C_M]_{Anthropogenic}$ represents enrichment due to lithogenic and anthropogenic source respectively. Other components are as defined earlier, under determination of Enrichment Factor (EF).

The results showed that more than 50% of the calculated EF values for Pb, Zn, Cr and Cd are from lithogenic sources (Fig. 4). The sources of pollution therefore include geogenic materials, much of which are most likely sourced from dispersion or lithogenic influx arising from the robust quarrying and mining activities within the area.

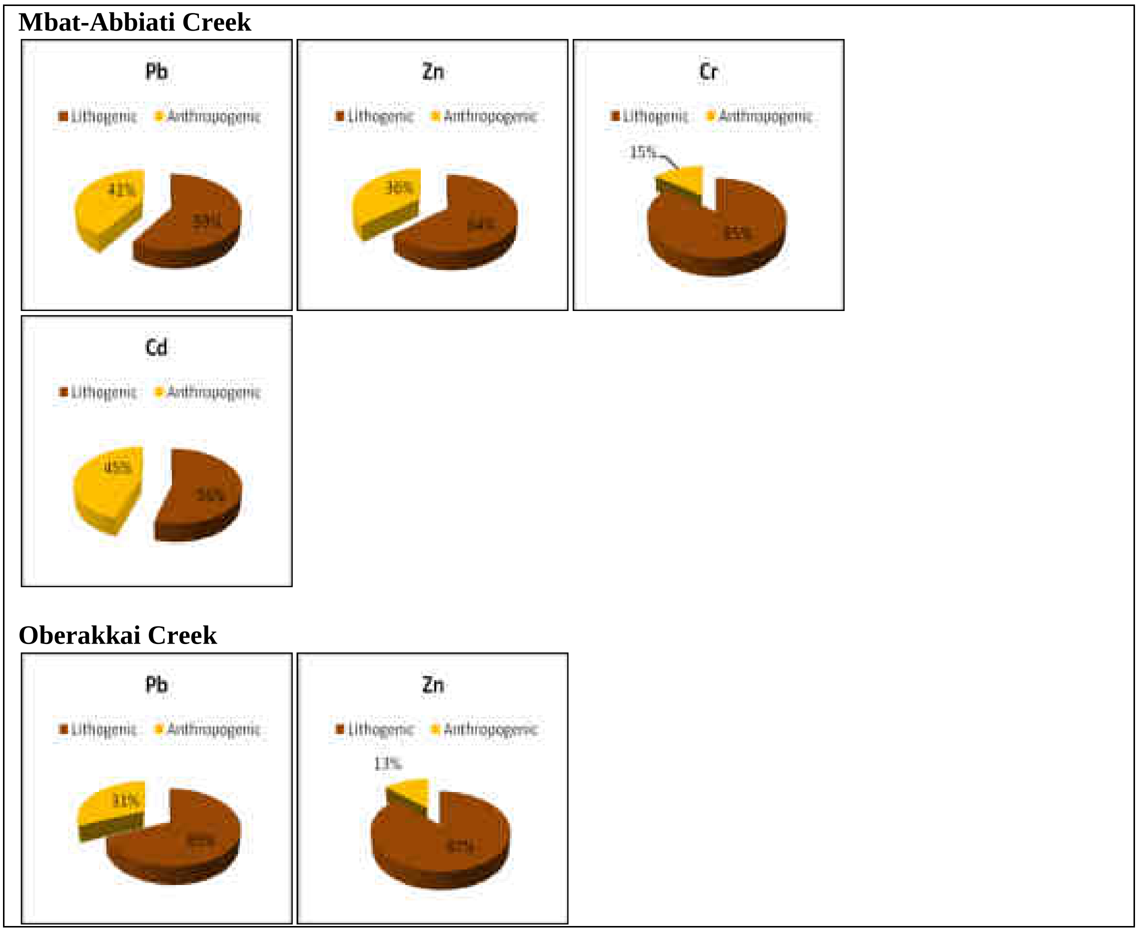

Figure 4. Lithogenic and anthropogenic proportions of enriched heavy metals in sediments of Mbat-Abbiati and Oberakkai Creeks of the Great Kwa River

3.3.4 Assessment according to the Pollution load index (PLI)

The Pollution Load Index provides a simple, comparative means for assessing a site or estuarine quality: a value of zero (0.0) indicates perfection, a value of one (1.0) indicate only baseline levels of pollutants present and values above one > 1.0) indicate progressive deterioration of the site and estuarine quality (Tomlinson *et al.*, 1980).

Computed Pollution Load Index (PLI) values for sediments of Mbat-Abbiati and Oberrakhai Creeks are presented in Table 8. As shown in Table 8, PLI values of sediments of the Mbat-Abbiati Creek ranged from 0.006 to 0.029 with an average of 0.018, while that of Oberrakhai Creek vary between 0.001 and 0.247 with an average of 0.025. Indication from both dataset is that sediments from both Creeks are unpolluted.

4. Summary and Conclusion

The results of this study supply valuable information about heavy metal contents of sediment from different sampling stations in Mbat-Abiati and Oberekkai Creeks of the Great Kwa River. The order of the mean

concentrations of tested heavy metals in sediments of Mbat – Abbiati and Oberrakai Creeks is respectively Zn>Cr>Ni>Cu>Pb>As>Cd and Zn>Cr>Ni>Pb>Cu>As>Cd. Contamination Factor (Cf) and Degree of Contamination (Cd), Geoaccumulation Index (Igeo), Enrichment Factor (EF), have been successfully applied for the assessment of contamination status of sediments from Mbat – Abbiati and Oberrakai Creeks.
Indication from both the contamination factor and degree of contamination is that all the measured heavy metals, excluding Pb and Cd, exhibits low contamination status in the sediment. Based on geoaccumulation index, the sediments are generally classified as unpolluted with regards to the measured heavy metals. The computed Enrichment Factors (EF) showed that some heavy metals (Pb, Zn, Cr, Cd) have EF values of up to 1, which indicates enrichment through lithogenic and anthropogenic sources. Further screening revealed that more than 55% of the calculated EF values for the Pb, Zn, Cr and Cd are from lithogenic sources, thereby suggesting that the main sources of pollution are geogenic materials, probably sourced through mining and quarrying activities within the catchment region. Results of the Pollution Load Index conclude that sediments from both Mbat-Abbiati and Oberakkai Creeks are generally unpolluted.

Table 8: Pollution Load Index (PLI) for sediment samples from Mbat-Abbiati and Oberekkai Creeks of the Great Kwa River, SE Nigeria.

		POLLUTION LOAD INDEX
Mbat-Abbiati Creek	**AS-1**	0.007
	AS-2	0.020
	AS-3	0.006
	AS-4	0.029
	AS-5	0.009
	AS-6	0.024
	MEAN	0.018
Oberakhai Creek	**OS-1**	0.014
	OS-2	0.001
	OS-3	0.006
	OS-4	0.247
	OS-5	0.081
	OS-6	0.001806
	MEAN	0.024524

Results of the present study show that the sediment of the Great Kwa River was not polluted by heavy metals. However, the level of these metals in the environment has increased tremendously in the past decades. The implication of this is that these heavy metals pose risk of contamination or pollution of the sediments and overlying surface water. There is therefore need for consistent monitoring of both the sediment and overlying waters. Further research should cover a wider area and made to also incorporate organic compounds (pesticides, PAHs and PCBs) for better results.

References

Addo, M. A., Okley, G. M., Affum, H. A., Acquah, S. & Gbadago, J. K. (2011), "Water Quality and Level of Some Heavy Metals in Water and Sediments of Kpeshie Lagoon, La- Accra, Ghana", *Res. J. Environ. Earth Sci.* 3, 487-497.

Aderinola, O.J., Clarke, E.O., Olarinmoye, O.M., Kusemiju, V. & Anatekhai, M.A. (2009), "Heavy Metals in Surface Water, Sediments, Fish and Perwinkles of Lagos Lagoon", *American-Eurasian J. Agric. & Environ. Sci.* 5 (5), 609-617

Ahmed, A., Dilek, D. & Fatih, D. (2005), "Bioaccumulation, detection and analyses of heavy metal pollution in sultan marsh and environment", *Water, Air and Soil Pollution* 164, 241- 255.

Ajayi, I. O. (2014), "Phytoremediation investigations in Mbat Abbiati and Oberakkai in southeastern Nigeria", *Unpublished MSc thesis*, University of Calabar, Calabar. 153p

Al-Haidarey, M. J. S., Hassan, F M., Al-Kubaisey, A R A. & Douabul A A Z. (2010), "The Geoaccumulation Index of Some Heavy Metals in Al-Hawizeh Marsh, Iraq", *E-Journal of Chemistry*, 7(S1), S157-S162

Arora, M., Kiran, B., Rani, S., Rani A., Kaur, B. & Mittal, N. (2008), "Heavy metal accumulation in vegetables irrigated with water from different sources". *Food Chemistry* 111, 811–815

Atgin, R. S., El-Agha, O., Zararsiz, A., Kocatas, A.. Parlak, H. & Tuncel, G., (2000), "Investigation of the sediment pollution in Izmir Bay: trace elements", *Spectrochim. Acta B* 55 (7), 1151-1164

Barakat, A., El Baghdadi, M., Rais, J. & Nadem, S. (2012), "Assessment of Heavy Metals in Surface Sediments of Day River at Beni-Mellal Region, Morocco", *Research Journal of Environmental and Earth Sciences* 4(8), 797-806.

Birch, G. (2003), "A scheme for assessing human impacts on coastal aquatic environments using sediments". In Woodcoffe C. D. & Furness R. A. (eds.), Coastal GIS 2003, *Wollongong University Papers in Center for Maritime Policy*, 14, Australia. Retrieved from http://www.ozestuaries.org/indicators /DEF_sediment_scheme.html.

Butu, A.W. & Iguisi, E.O. (2013), "Concentration of heavy metals in sediment of river Kubanni, Zaria, Nigeria", *Comprehensive Journal of Environment and Earth Sciences*. 2(1), 10 - 17

Caccia, V.G., F.J. Millero & A. Palanques (2003), "The distribution of trace metals in Florida Bay sediment. Mar", *Pollut. Bull.*46(11), 1420-1433.

Campbell, P G C & Tessier, A (1996), "Ecotoxicology of Metals in the Aquatic Environment: Geochemical Aspects", In Newman M C & Jagoe C H (ed.s), Ecotoxicology: *MI Lewis Publishers, Chelsea*, 11-58.

Chindah, A. C., Braide, S. A., Amakiri, J. & Chikwendu, S.O.N (2009), "Heavy Metal Concentrations in Sediment and Periwinkle –Tympanotonus fuscastus in the Different Ecological Zones of Bonny River System, Niger Delta, Nigeria", *The Open Environmental Pollution & Toxicology Journal* 1, 93-106

Davies O. A., Allison M.E & Uyi, H. S. (2006), "Bioaccumulation of heavy metals in water, sediment and periwinkle (Tympanotonus fuscatus var radula) from the Elechi Creek, Niger Delta". *African Journal of Biotechnology* 5 (10), 968-973

Defew, L., Mair, J., Guzman, H. (2004), "An assessment of metal contamination in mangrove sediments and leaves from Punta Mala Bay, Pacific Panama". *Marine Pollution Bulleti*n 50 (50), 547-552.

Efiong, J. (2011), "Changing Pattern of Land Use in the Calabar River Catchment, Southeastern Nigeria". *Journal of Sustainable Development* 4 (1), 92 – 102

El-Nemr, A., A. Khaled & Sikaily, A. E. (2006). "Distribution and statistical analysis of leachable and total heavy metals in the sediments of the suez gulf", *Environ. Monit. Assess*. 118, 89-112.

Environment Canada. (1995), "Interim Sediment Quality Guidelines, Soil and Sediment Quality Section Guidelines Division", Ecosystem Conservation Directorate, Evaluation and Interpretation Branch, Ottawa, Ontario

Environment Canada (2002), "Canadian sediment quality guidelines for the protection of aquatic life: Summary table".http://www.doeal.gov/SWEIS/OtherDocumen/328%20envi%20canada%202002.pdf

Environmental Protection Agency (EPA). (1995), "Ecological Screening Values".In: Supplemental Guidance to RAGS: Region 4 *Bulletins-Ecological Risk Assessment*, Bull..2, Atlanta,Georgia.
http://www.epa. gov/region4/wastepgs/ofiecser/otsguid.htm

Gamo, T. (2007), "Environmental geochemistry" (In Japanese), *Baihu-kan, Japan*, 118-119.

Hakanson, M. (1980), "An ecological risk index for aquatic pollution control-a sedimentological approach", *Water Research* 14, 975–1001.

Hernandez, L., Probst, A., Probst, J. L. & Ulrich, E. (2003), "Heavy Metal Distribution in Some French Forest Soils: Evidence for Atmosphere Contamination". *The Science of Total Environment* 312, 195-210.

Huang, K. & Lin, S. (2003), "Consequences and Implications of Heavy Metal Spatial Variations in Sediments of the Keelung River drainage basin, Taiwan". *Chemosphere* 53, 1113-1121.

Kumar, M., Balwant K. & Pratap K. P.(2012), "Characterization of Metals in Water and Sediments of Subarnarekha River along the Projects' Sites in Lower Basin", *India Universal Journal of Environmental Research and Technology* 2 (5), 402-410

Ladigbolu, I.A, Balogun, K.J (2011), "Distribution of Heavy Metals in Sediments of Selected Streams in Ibadan. Metropolis, Nigeria", *International Journal of Environmental Sciences* 1 (6), 1186 – 1191

Macfarlane, G.R.; Schreider, M. & Mclennan, B. (2006), "Biomarkers of heavy metal contamination in the red fingered marsh crab, Parasesarma erythodactyla", *Archives of Environmental and Contamination Toxicology* 51(4), 584-593.

Majolagbe, A O., Osibanjo, O, Yusuf, K. A. & Olowu, R. A. (2012), "Trace Metals Distribution and Contamination in the Surface Marine Sediments of Roro Bay in Lagos, Nigeria" 02 (02), 69-78

Marchland, C.E., E. Lalliet Verges, F. Baltzer, P. Alberic, D. Cossa & P. Baillif, (2006), "Heavy Metals in Mangrove Sediments along the Mobile Coastline of French Guiana", *Marine Chemistry* 98, 1-17.

MHSPE (Ministry of Housing, Spatial Planning, and Environment) (1994), "Intervention Values and Target Values - Soil Quality Standards", *Directorate-General for Environmental Protection, Department of Soil Protection, The Hague, The Netherlands*, 9 May 1994

Muller, G. (1979), "Schwermetalle in den sedimenten des Rheins-VeraÈnderungenseit. Umschau" (79:778-783), In: Green-Ruiz, C. & PaÂez-Osuna, F. (2001). Heavy metal Anomalies in Lagoon Sediments related to Intensive Agriculture in Altata-Ensenada del PabelloÂn coastal system (SE Gulf of California). Environment International 26, 265-273.

Neto, J. A. B., Gingele, F. X., Leipe, G. & Brehme, I. (2006), "Spatial Distribution of Heavy Metals in Surficial

Sediments from Guanabara Bay: Rio de Janeiro, Brazil", *Environmental Geology* 49, 1051–1063.

Olubunmi, F. E. & & Olorunsola, O. E. (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

Oyekunle, J. A. O., Ogunfowokan, A. O., Akanni, M. S. & Torto, N. (2011). Seasonal Mean Levels of Heavy Metals in Water and Associated Sediments from Ajawere River in Oke - Osun Farm Settlement, Osogbo, Nigeria. Proceedings of the Environmental Management Conference, Federal University of Agriculture, Abeokuta, Nigeria, pp 350-372.

Peckey, H., 2006. Heavy Metals Pollution Assessment in sediments of the Izmit bay, Turkey. Environmental Monitoring and Assessment, 123: 219-231.

Praveena, S. M., Radojevic, M., Abdullah, M. H. & Avis, A. Z. (2007), "Factor-cluster analysis and enrichment study of mangrove sediments – An example from Mengkabong Sabah", *The Malysian Journal of Analytical Sciences* 2(2), 421 - 430

Puyate, Y.T., Rim-Rukeh, A. & 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

Reijers, T. J. A. & Petters, S. W. (1987), "Depositional environments and diagenesis of Albian carbonates on the Calabar Flank, SE Nigeria. Journal of Petroleum Geology" 10, 283-294.

Shotyk, W., Blaser P., Grunig, A. & Cheburkin A. K. (2000), "A New Approach for Quantifying Cumulative, Anthropogenic, Atmospheric Lead Deposition using Peat Cores from Bogs: Pb in Eight Swiss Peat Bog Profiles", *Science of the Total Environment* 249, 281 –295.

Simex, S. A. & G. R. Helz, (1981), "Regional geochemistry of trace elements in Chesapeake Bay", *Environ. Geo* 3, 315-323.

Solomons, W. & Forstner, U. (1984), "Metal in the Hydrocycle", *Springer Verlag*, New York, 21–22.

Tomlinson, D. C., Wilson, J. G., Harris, C. R. & Jeffery, D. W. (1980), "Problems in the assessment of heavy metals level in estuaries and the formation of a pollution index". *Helgol. Wiss. Meeresunters* 33 (1-4), 566-575.

Turekian, K. K. & Wedepohl, K. H. (1961), "Distribution of the elements in some major units of the earth's crust". *Journal of Geological Society of America* 72, 175–192.

Uwah, I. E., Dan, S. F., Etiuma, R. A. & Umoh, U. E. (2013), "Evaluation of Status of Heavy Metals Pollution of Sediments in Qua-Iboe River Estuary and Associated Creeks, South-Eastern Nigeria". *Environment and Pollution* 2 (4), 110-122

Uzairu, A., Harrison, G.F.S., Balarabe, M. L. & Nnaji, J.C. (2008), "Concentration levels of trace metals in fish and sediment from Kubanni river, northern Nigeria", *Bull. Chem. Soc. Ethiop*. 23(1), 9-17

Zabetoglou K, Voutsa D, & Samara C. (2002), "Toxicity and Heavy metal contamination of surficial sediments from the Bay of Thessaloniki (Northwestern Aegean Sea) Greece", *Chemosphere* 49, 17-26.