

Assessment of heavy metal contamination of sediments along the cross river channel in Cross River state, Nigeria

¹Akpan, I. O., Thompson, E. A.²

Department of Physics University of Calabar, Calabar, Nigeria

Abstract: Sixteen sediments samples were obtained from eleven beaches along the Cross River channel in Nigeria. The sediments were analysis for heavy metal contaminants such as Fe, Cu, Mn, Cr, Zn, Hg, Pd, Cd, Ni, Ti and V during the wet season of the year 2011 using EDXRF. Hg, Pd, Cd were not detected from all the samples. The most abundant metal detected was iron. Enrichment Factor (EF) of the heavy metal contaminants in the sediments calculated ranged from 20.000 – 0.133, indicating significant enrichment of the sediments sampled at some locations due to human activities. The geo-accumulation Index (I_{geo}) calculated shows no contamination to moderate contamination.

Key words: Sediments, heavy metals, Enrichment factor, geo-accumulation index, contaminants, elements

I. Introduction

Sediment is the loose sand, clay, silt and other soil particles that is deposited at the bottom of body of water or accumulated at other depositional sites. Sediments can emanate from the erosion of bedrocks and soil or from the decomposition of plants and animals.

Mucha et al, (2003) opines that sediments are the ultimate sink of contaminants in the aquatic system. Information glean from study of sediment provides a better view on the impact of distinct human activity on the wider ecosystem. Sediment load and composition is highly reflective of the type and intensity of agricultural land used which is a lead in determining the health and survival of aquatic organisms. Its composition provides the best natural archives of recent environmental changes.

According to Martins et al (1997), sediment besides being a habitat, it also major source of nutrient for aquatic organisms, hence an assessment of the concentration of metal contaminants, their enrichment level and the extent to which to these metals has pollute the sediment is imperative.

Living organisms require trace amount of some heavy metals but excessive levels can be detrimental to the organisms (Vries *et al*, 2007), with the exception of lead, cadmium and mercury which are toxic even in low concentrations (Galas-Gorcher, 1991).

Multi-elemental analysis of sediment may reveal the presence of heavy metals which are contaminants and may have toxic influence on ground water and surface water and also on plants, animals and humans (Suciu *et al*, 2008). Accumulation of trace metals occur in upper sediment in aquatic environment by biological and geochemical mechanisms may become toxic to sediment-dwelling organisms and fish, resulting in death, reduced growth, or impaired reproduction and lower species diversity (Praleena *et al*, 2007). These elements also occur naturally in rocks forming minerals and ore minerals; here they can reach the environment from natural processes (Akinmosin *et al*, 2009).

Heavy metals may accumulate to a toxic level in sediments without visible signs. This may occur from normal geological phenomenon such as ore formation, weathering of rocks and leaching or due to increased population, urbanization, industrial activities, agricultural practices, exploration and exploitation of natural resources (Ajayi and Osibanjo, 1981).

Sediment analysis is vital to assessing qualities of total ecosystem of a water body in addition to water sample analysis practiced for many years, because it reflects the long term quality situation independent of the current inputs (Adeyamo et al, 2008).

In this study energy dispersive x – ray fluorescence (EDXFR) as a veritable multi element analytical tool was applied for the determination of the concentration of metals present in the sediments obtained from 13 beaches along the Cross River in Nigeria.

By normalizing the metals detected to iron the enrichment factor (EF) of each metal was assess thereby determining the extent to which the sediments has been enriched with a particular metal. Also the geoaccumulation index (I_{geo}) of metal contaminants was as well determined to assess the pollution status of the sediments under study.

This study is aim at assessing the level of heavy metal enrichment in the sediments as well as the contamination status.

Study Area

The Cross river take its source from the Cameroon highlands and run through Cross River state, Ebonyi state and Akwa Ibom state in Nigeria and finally emptied itself into the Atlantic ocean. The Cross River state portion of the river was section out for this study. The area under study lies between longitude $8^{\circ} 00^{\prime} E$ and $8^{\circ} 45^{\prime} E$ and latitude between $5^{\circ} 45^{\prime} N$ and $6^{\circ} 00^{\prime} N$. Geologically, the study area lies on the Oban Massif and the Calabar flank geological formation. The rock type found in the area is predominantly migmatite-gneiss-schist complex and granitoid (Orajaka, 1964). The principal rock minerals associated with these are; quartz, feldspar and magnetite. The major human activities prevalent in the area are agriculture and fishing. Sediment were obtained from eleven beaches along the river channel; Assigha beach, Okangha beach, Etigidi beach, Ikom town beach, Ikpalegwa beach, Ajere beach, Afam beach, Ekpokpa beach, Ekoribeach, Okuni beach and Ediba beach.

II. Experimental

Sampling and Sample preparation

Sediments were collected along the middle course of the Cross River in Cross river state, Nigeria. The sampling was done using the core sampling device. Sediment samples collected were air dried before presented for further preparation. The sediments samples were categorized into sand and mud grain sizes. At the Centre for Energy Research and Development (CERD), Obafemi Awolowo University Ile – Ife, the samples were ground into fine powder using an agate mortar. The grounded samples were pressed into 13mm diameter pellets by applying a pressure of about 6 – 8 torr without binder with the aid of a CARVER Model manual pelletizing machine. The pelletized samples were then taken for elemental analysis.

Analysis

The elemental analysis of the sediment samples were carried out by an Energy Dispersive X –Ray Fluorescence (EDXRF) spectrometer.

The spectrometer consist of portable ECLIPSE – 111 silver tube x – ray machine with beryllium window, XR – 100CR model high performance thermoelectrically cooled Si – Pin photodiode detector powered by PX2CR power supply and a 8006A MCA.

The spectra data analysis was done with the Axil fitting programme contained in the QXAS software package supplied by the International Atomic Energy Agency (IAEA), Vienna.

The tube voltage and current were maintained at 25.0KV and 0.050mA respectively during irradiation of samples. The pelletized samples were fitted into the sample holder in turns and each irradiated with x –ray beams from the x –ray for a live of 1000 seconds.

However, to maintain quality assurance in the analysis of sediments, a NIST 1646a Estuarine Sediment standard was used for calibration. The method used for the analysis of the sediments was by direct comparison of count rate.

III. Results and discussion

Table 1 shows the physical characteristics of the sediments from the various sediment locations along the Cross River channel. Table 2 and 3 list the concentration of elements detected by EDXRF.

Cu and Y were only detected in sediments from Assigha beach with concentrations of 10.724ppm and 61.086ppm respectively. Copper happens to be one of the metal contaminants but its concentration in sediment at Assigha beach was below the threshold value recommended by the consensus – base sediment quality guide lines, as such, the sediments were not polluted by Cu.

In heavy metal contamination assessment of sediments, apart from determining the level of enrichment and the pollution status, it is important to take a correlation analysis of the metals detected as this will certainly aid in suggesting possible sources of the metal contaminants. The correlation coefficients are as shown on table 4.

The correlation analysis of elements shows a high positive correlation between potassium (K) and calcium (Ca), titanium (Ti), iron (Fe), strontium (Sr) and Zirconium (Zr), with the following correlation coefficients K – Ca (0.839), K – Ti (0.717), K – Sr (0.823), K – Zr (0.679).

Calcium is highly positively correlated with titanium Ca – Ti (0.902), with manganese; Ca – Mn (0.748), with iron; Ca – Fe (0.831), with strontium; Ca – Sr (0.682) and with zirconium; Ca – Zr (0.859).

Titanium shows high correlation with manganese; Ti – Mn (0.920), with iron; Ti – Fe (0.977), and with zirconium; Ti – Zr (0.893).

Vanadium correlates positively with nickel; V – Ni (0.698), and with germanium; V – Ge (0.531). There exist a high positive correlation between manganese and iron; Mn – Fe (0.963) and manganese with zirconium Mn – Zr (0.739). Iron and zirconium correlates positively; Fe – Zr (0.838). Germanium and gallium

correlates positively; Ge – Ga (0.644). Strontium and Zirconium also exhibits positive correlation Zr – Sr (0.576).

Zinc correlates negatively with potassium; Zn – K (-0.526), with titanium; Zn – Ti (-0.605), with manganese; Zn – Mn (-0.596) and with iron; Zn – Fe (-0.628). Also germanium and potassium shows a negative correlation Ge – K (-0.698).

It was observed that Ca correlates strongly positively with K, Ti, Mn, Fe, Sr and Zr, suggesting the diluting influence of both organic matter and carbonate, that means the sediments analyzed were not CaCO₃ – ash free.

The high positive correlation between Fe and Ti confirms their Ti – Fe schist origin. Nickel and vanadium correlates fairly positively confirm their input petroleum products. Manganese and titanium were fairly positively correlated presuming possible input from agricultural activities specifically from pesticides.

Also there is a high positive correlation between Mn, Zr and Fe suggesting that they are from the same source.

A high positive correlation between Sr, Zr and K confirms solid earth recycling as stated by Patchet et al, (1984). This also account for the positive correlation between Rb and Zr.

Ga and Ge show a strong positive correlation pointing to their common littoral originates.

Generally, low correlation coefficients between elements suggest that they come from different sources. Enrichment Factor (EF)

Enrichment factor (EF) can be used to differentiate between the metal originating from anthropogenic activities and those from natural procedure, and to assess the degree of anthropogenic influence. Sutherland (2000), gives the definition of enrichment factor as stated below;

Enrichment factor is defined as $EF(X) = \frac{(X/N)_{\text{sample}}}{(X/N)_{\text{control}}}$

EF(X) is the enrichment factor for the metal X,

(X/N)_{sample} is the ratio of the concentration of metal X to major metal N (Fe or Al) in the sample.

(X/N)_{control} is the ratio of the concentration of the metal X to major metal N (Fe or Al) in a reference material such as the control sample.

Both aluminum (Al) and iron (Fe) can be used as the metal for normalization because their anthropogenic sources are small compared to natural sources (Herlz, 1976).

In this study the metals were normalized to iron.

In a bid to reduce the effect of grain size, metal concentrations maybe discussed in terms of the enrichment factor. The use of enrichment factors allows for comparison of sediments from different environments and the comparison of sediments whose metal contents were obtained by different analytical technique (Cantillo, 1982).

Orth and Wells (2009) opines that a common approach to estimate the extent to which the sediment has been impacted (naturally and anthropogenically) with heavy metal is to calculate the enrichment factor (EF) for metal concentration above uncontaminated background levels.

Generally, the values of the enrichment factor below evaluate the level of impartation of the sediment by the metals.

EF ≤ 1 No enrichment

EF < 2 Minimal enrichment

EF 2 – 5 Moderate enrichment

EF 5 – 20 Significant enrichment

EF > 40 Extremely high enrichment

Enrichment factors of 2.952, 3.436 and 5.676 for potassium were recorded in sediments from Assigha 01, Ikom 06, Ajere 09 and Ekpokpa 13 respectively. With exception of sediments from Etigidi 05 with EF(Ti) of 1.790, sediments from all other sample locations recorded EF(Ti) that range from 4.337 – 2.005 (see table 5).

Sediments from Etigidi 05, Ikom 06 and Ajere 09 were found to have EF(V) of 3.001, 3.571 and 2.829 respectively. High EF(V) of 13.628, 11.501 and 10.971 in sediments from Assigha 01, Ediba 16 and Ekori 14 respectively were obtained.

EF(Cr) in sediments under study ranged from 10.692 to 0.769 (see table 5) the highest recorded in sediments from Ajere09. High EF(Mn) of 5.181, 4.708, 3.472 and 3.306 were obtained in sediments from Etigidi 05, Ediba 16, Assigha 01 and Ikom 06 respectively.

Assigha 01 recorded a very high enrichment factor of 20.000 for Nickel followed by Ediba 16 with EF(Ni) of 11.200. Ekpokpa 13, Ajere 09 and Etigidi 05 recorded appreciable EF(Ni) (see table 5). EF(Zn) for sediments from most of the sample locations were generally low with the exception of that from Ediba 16 and Ajere 09 which recorded an EF(Zn) of 7.758 and 5.667 respectively.

Germanium recorded very high enrichment factors ranging from 35.000 to 0.066 (see table 5).

Enrichment factors for Gallium in sediments from Ikom 06, Etigidi 05, and Ekori 14 were quite significant but Ediba 16 recorded the Highest EF(Ga) of 43.005.

EF(Zr) of 2.702 and 2.222 were obtained in sediments from Assigha 01 and Etigidi 05 while that from other sediments locations were generally low. EF(Sr) of below 4.00 but greater than 2.00 was recorded in sediments from Assigha 01, Ajere 09 and Ekpokpa 13.

Enrichment factors of 9.618, 6.261 and 9.459 were recorded for Rb in sediments from Ediba 16, Ekpokpa 13 and Ajere 09 respectively.

Sediments from Assigha beach is significantly enriched with V, Ni and Ge. From the Pearson correlation analysis V and Ni are strongly related suggesting that they are from the same source. K, Ti, Cr, Mn, Zn and Sr enriched sediments from this location moderately.

Sediments from Okangha beach is only significantly enriched with Cr but moderately enriched with Ti while other metals detected enrich it minimally. Sediments obtained from Etigidi beach is significantly enriched with Cr, Mn, Ni, Ge and Ga. Its shows moderate enrichment from V, Zn and Zr. Ikom beach sediments on the average was observed to be moderately enriched with all the metals detected from it. Sediment from Ikpalegwa beach shows moderate enrichment for Cr and Ti, it was not enriched with Ni, V, Sr and Zn, but was minimally enriched with other metals. Sediments obtained from Ajere beach averagely was significantly enriched Cr and Rb and other metals enriched it moderately with the exception of Ge and Ga. Afam's beach sediment was only moderately enriched with Ti, other metals show minimal enrichment. Sediments from Ekpokpa beach was moderately enriched with K, Ti, Cr, Mn, Ni, Sr and Rb, other metals detected minimally enriched it. Ekori' beach sediment was significantly enriched with V Ge, and Ga. And moderately enriched with Ti, Cr, Ni, Zn and Rb. Besides Vanadium which moderately enriched sediment from Okuni beach other metals minimally enrich it. Sediment from Ediba beach was significantly enriched with V, Cr, Ni, Zn, Ge, Ga and Rb but moderately enriched with Mn and Ti.

Geo-accumulation Index

The geoaccumulation index I_{geo} proposed by Muller (1979) has been employed to evaluate pollution of sediments by heavy metals. The I_{geo} of a metal in sediment can be calculated with the formula;

$$I_{geo} = \log_2 C_{metal} / 1.5 C_{metal}(\text{control})$$

Where;

C_{metal} is the concentration of the heavy metal in the enriched sample

$C_{metal}(\text{control})$ is the concentration of the metal in the unpolluted control

The factor 1.5 is introduced to minimize the effect of the possible variation in the background or control values which may be attributed to lithological variations in the sediment (Mediola et al, 2008).

The Muller geo-accumulation index has seven classes depending on it value

$I_{geo} < 0$ No pollution

$I_{geo}: 0 - 1$ Not or minimal pollution (class 1)

$I_{geo}: 1 - 2$ Moderately polluted (class 2)

$I_{geo}: 2 - 3$ Moderately polluted to polluted (class 3)

$I_{geo}: 3 - 4$ Polluted to strongly polluted (class 4)

$I_{geo}: 4 - 5$ Strongly polluted (class 5)

$I_{geo}: 5 - 6$ Strongly polluted to very strongly polluted (class 6)

$I_{geo}: > 6$ Very strongly polluted (class 7)

The geo-accumulation index (I_{geo}) has been widely used to assess the degree of metal contamination or pollution in terrestrial, aquatic and marine environments (Tijani et al, 2009).

Table 6 shows the geo-accumulation indices (I_{geo}) for metal contaminations in the sediments obtained from eleven beaches along the Cross River channel.

Sediments from Ikom 07 and Ikpalegwa 08 recorded the highest Ti I_{geo} of 3.39 and 3.15 respectively. I_{geo} of 2.75, 2.63, 2.75, 2.68 and 2.95 for were obtained in sediments from Okangha 04, Ajere 10, Afam 11, Ekpokpa 12 and OKuni 15 respectively. For vanadium, the I_{geo} of 2.49, 2.51 and 1.14 were recorded in sediments from Assigha 01, Ekori 14 and Ediba respectively. Geoaccumulation index of V from other sample locations were below 1. Sediments from Okangha 03, Ikom 07 and Ikpalegwa 08 recorded I_{geo} of 1.51, 1.21 and 2.38 respectively. As shown in table 6, I_{geo} of Mn range from -0.31 to 2.75 to, with the highest value obtained in sediment from Ikom 07.

High I_{geo} of Ni of 3.06, 1.14 and 1.10 were recorded in sediments from Assigha 01, Ekpokpa 13 and Ediba 16 respectively.

Amongst the heavy metal contaminants detected Zinc had the least I_{geo} with the highest value of 0.74 recorded in sediment from Ajere 09. Sediments from Ikom 07 and Ikpalegwa 08 recorded I_{geo} of Fe of 1.71 and 1.14 respectively and these values were the most appreciable I_{geo} of Fe.

From the geoaccumulation indices, sediments from Ikom 07 and Ikpalegwa 08 are contaminated with Ti. Those from Okangha 04, Ajere 10, Afam 11, Ekpokpa 12 and Okuni 15 are moderately polluted with Ti. On the average the entire sediment analyzed is moderately polluted with Ti.

Sediments from Assigha 01, Ediba 16 and Ekori 14 were moderately polluted with vanadium. Sediments from the other sample locations are free from V contamination.

Besides Ikpalegwa 08, Ikom 07 and Okangha 03, whose sediments are moderately contaminated with Cr, those from other locations were not contaminated with it.

Sediments obtained from Okangha 04, Ikom 07, Ikpalegwa 08, Ajere 10, Afam 11, Ekpokpa 12 and Okuni 15 were moderately contaminated with Mn. Averagely sediments analyzed was moderately polluted with Mn.

Apart from sediments obtained from Assigha 01, Ekpokpa 13 and Ediba 16 which were moderately contaminated with Nickel, those from other locations show no Ni contamination. The entire sediments analyzed were not polluted by Zinc.

Only Ikom 07 and ikpalehwa 08 were mildly contaminated with Fe.

IV. Conclusion

Accumulation of trace metals occur in upper sediments in aquatic environments by biological and geochemical mechanisms and become toxic to sediment inhabiting organisms and fish, culminating in death, growth reduction and lower species diversity (Praveena et al, 2007). Heavy metal contaminants in trace amounts also occur in rock forming minerals and ore minerals; hence they can reach the environment from natural processes. Heavy metals can find its way into the aquatic systems naturally from normal geological phenomena such as ore formation, weathering of rocks and leaching or due to increase population, urbanization, industrialization, agricultural practices, exploration and exploitation of natural resources (Ajaji and Osibanjo, 1981).

Sediments have been reported to form the major repository of heavy metals in aquatic system while both natural and human influences could make the concentration of heavy metals in the water high enough to be of ecological significant. Bioaccumulation and enhancement is capable of leading to toxic level of these metals in fish, even when the exposure is low.

According to Charis and Abbasi (2005), fish are notorious for their ability to concentrate heavy metals in their muscles and since they are vital part of human nutrition, they need to be carefully screened to ensure that unnecessary high level of some toxic metals are not being transferred to man through consumption.

Metals such as, K, Ca, Ge and Ga does not possess any danger to the environment even at high concentration, although K in the presence of phosphorus and nitrogen may enhance eutrophication of water bodies.

Strontium, zirconium and rubidium are not toxic to the environment but their naturally occurring radioactive isotopes may have serious health implications is living organisms are exposed to them.

The metal contaminants detected in the sediments analyzed namely; Ti, V, Cr, Mn, Zn, Cu and Fe are toxic to the environment as well as have a wide range of health issues associated with their contamination. These health issues include; irritation, skin rash, respiratory failure, birth defects, asthma, allergies, heart disorder, cancer, kidney disorder, diabetes, etc.

Anthropogenic sources of these metal contaminants in the area under study are mainly agricultural; since almost all heavy metals are normal components of mineral fertilizers, lime and pesticides. These agro chemical and additives are commonly used in this area. The principal source of vanadium is the petroleum product used in engine boats for transport along the river.

Table 1: physical characteristics of sediments

Sediments location	Sediments size range	Aggregate class	Other names	Colour
Assigha beach 01	0.25 – 1mm	Coarse median sand	Sand	brown
Assigha beach 02	1 – 62.5µm	Silt and clay	Mud	Light brown
Okangha beach 03	1 – 3.9µm	Clay	Mud	Dark brown
Okangha beach 04	62.5 - 125µm	Very fine sand (freshly deposited)	Sand	Light brown
Etigidi beach 05	1 – 2mm	Very coarse and coarse sand	Sand	Light brown
Ikom beach 06	0.5 – 1mm	Coarse sand	Sand	Light brown
Ikom beach 07	1 – 62.5µm	Silt and clay	Mud	Reddish brown
Ikpalegwa beach	3.9 - 125µm	Silt and very fine	Sand and mud	Black

08			sand		
Ajere beach 09	0.5 – 1mm		Coarse sand	Sand	Light brown
Ajere beach 10	3.9 – 62.5µm		silt	Mud	Brown
Afam beach 11	1 – 62.5µm		Silt and sand	Mud	Brown
Ekpokpa beach 12	1 – 62.5µm		Silt and sand	Mud	Brown
Ekpokpa beach 13	0.25 – 0.5mm		Medium sand	Sand	Light brown
Ekori beach 14	125 - 250µm		Fine sand	Sand	Light brown
Okuni beach 15	1 – 62.5µm		Silt and clay	Mud	Brown
Ediba beach 16	1 – 2mm		Very coarse sand	Sand	Light brown

Table 2: Result of EDXRF analysis of sediments

Sediment location	ELEMENTS AND THEIR CONCENTRATION (PPM)						
	K	Ca	Ti	V	Cr	Mn	Fe
Assigha beach 01	9850.000	583.582	730.524	203.402	19.528	106.689	4261.277
Assigha beach 02	9010.000	1652.222	1669.492	42.113	24.288	133.165	7259.915
Okangha beach 03	6286.06 0	400.604	1039.523	19.874	92.492	94.398	9438.553
Okangha beach 04	15800.000	2885.432	3766.875	34.485	20.124	235.087	19440.000
Etigidi beach 05	1597.138	253.355	287.298	30.546	35.984	108.462	2906.724
Ikom beach 06	9750 .000	843.434	677.074	45.515	12.54	86.281	3624.085
Ikom beach 07	12740 .000	2383.053	5905.967	42.507	74.744	492.789	33280 .000
Ikpalegwa beach 08	17520 .000	3372.653	5000.566	40.179	169.268	270.348	22360.000
Ajere beach 09	7831.379	400.604	648.891	29.758	<41.712	58.742	2990.128
Ajere beach 10	14480.000	1970.015	3482.094	39.176	23.048	172.524	14540.00
Afam beach 11	17700.00	2742.514	3797.439	53.464	30.088	215.349	17580.00
Ekpokpa beach 12	16050.00	1904.493	3595.359	54.216	24.776	184.303	15670.00
Ekpokpa beach 13	17370.00	1288.429	774.158	27.144	<18.396	67.725	3908.681
Ekori beach14	6450.271	627.973	1012.194	205.524	28.7	76.471	5339.149
Okuni beach15	16450.0	3475.511	4340.391	29.903	40.644	278.543	20150.00
Ediba beach16	1737.949	227.371	396.248	79.251	<15.144	66.346	1952.511

Table 3: Result of EDXRF analysis of sediments

SEDIMENT LOCATION	ELEMENTS AND THEIR CONCENTRATION (PPM)								
	Ni	Zn	Ge	Ga	Sr	Y	Rb	Zr	Cu
Assigha beach 01	128.188	29.531	1090.471	ND	228.375	61.006	ND	123.954	ND
Assigha beach 02	27.247	50.327	1083.135	ND	185.669	ND	ND	239.36	10.724
Okangha beach 03	21.375	28.883	899.271	ND	<55.762	ND	ND	144.548	ND
Okangha beach 04	5.205	23.488	ND	ND	199.142	ND	200.503	473.668	ND
Etigidi beach 05	21.872	32.415	1012.232	606.36	ND	ND	ND	128.617	ND

Assessment of heavy metal contamination of sediments along the cross river channel in Cross River

Ikom beach 06	15.107	23.766	850.371	354.036	79.407	ND	ND	54.788	ND
Ikom 07	<5.704	18.560	56.235	111.003	175.743	ND	213.326	401.783	ND
Ikpalegwa beach08	14.737	26.918	613.206	375.552	187.193	ND	444.137	611.223	ND
Ajere beach09	28.532	55.987	7.857	10.625	168.524	ND	444.137	ND	ND
Ajere beach10	8.569	23.766	512.961	379.953	214.077	ND	284.823	446.36	ND
Afam beach11	12.806	36.541	636.189	408.315	392.805	ND	230.423	442.583	ND
Ekpokpa beach 12	<4.026	18.186	380.442	262.104	226.773	ND	320.442	388.183	ND
Ekpokpa beach 13	33.679	35.94	ND	ND	185.699	ND	384.297	ND	ND
Ekori beach14	30.076	46.090	1338.393	733.011	97.828	ND	356.320	ND	ND
Okuni beach 15	6.020	19.421	ND	230.319	239.965	ND	252.183	312.8	ND
Ediba beach16	32.769	50.003	1667.49	1219.007	ND	ND	294.926	ND	ND

ND: NOT DETECTED

Table: 4 Result analysis of control sample

Elements	Concentration (ppm)
Fe	6783.213
Mn	48.670
Cr	21.613
Zn	22.348
Ni	10.210
V	24.024
K	5310.381
Ge	165.531
Ga	98.143
Sr	86.961
Rb	106.236
Zr	134.581
Ti	374.432
Ca	589.356

	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Zn	Ge	Ga	
Sr	Rb	Zr										
K	1											
Ca	.839**	1										
Ti	.717**	.902**	1									
V	-.251	-.327	-.283	1								
Cr	.186	.353	.450	-.228	1							
Mn	.508*	.748**	.920**	-.244	.413	1						
Fe	.632**	.831**	.977**	-.286	.478	.963**	1					
Ni	-.270	-.459	-.487	.698**	-.190	-.383	-.471	1				
Zn	-.526*	-.530*	-.605*	.211	-.202	-.596*	-.628**	.239	1			
Ge	-.698**	-.569*	-.541*	.531*	-.111	-.490	-.540*	.387	.423	1		
Ga	-.460	-.247	-.197	.250	-.107	-.206	-.240	-.120	.262	.644**	1	
Sr	.823**	.682**	.582*	-.013	-.022	.404	.493	-.011	-.234	-.506*	-.444	1
Rb	.400	.308	.313	-.047	.235	.115	.219	-.298	.169	-.381	.186	.250
Zr	.679**	.859**	.893**	-.316	.467	.739**	.838**	-.413	-.588*	-.387	-	
	.200				.576*	.154	1					

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Table 4 correlation matrix of elements

Table 5: Enrichment Factors

Sediment location	K	Ti	V	Cr	Mn	Ni	Zn	Ge	Ga	Zr	Sr	Rb
Assigha 01	2.95 2	3.10 5	13.62 8	3.461	3.472	20.00 0	2.091	10.48 8	ND	2.702	2.26 6	ND
Assigha 02	1.58 5	4.16 4	1.657	2.538	2.542	2.467	2.091	16.11 1	ND	1.136	2.57 0	ND
Okangha 03	0.58 8	2.00 5	0.600	7.461	1.389	1.467	0.909	3.902	ND	0.297	1.19 5	ND
Okangha 04	1.03 8	3.50 9	0.486	0.769	1.667	0.133	0.364	ND	ND	0.515	1.87 8	0.65 6
Etigidi 05	0.70 2	1.79 0	3.000	9.462	5.181	5.000	3.363	14.27 0	14.38 6	2.222	ND	ND
Ikom 06	3.43 6	3.38 4	3.571	2.615	3.306	2.733	1.970	9.615	6.731	0.762	1.71 1	ND
Ikom 07	0.48 9	3.21 4	0.343	1.692	2.056	0.133	0.182	0.066	0.227	0.606	0.40 6	0.40 8
Ikpalegwa 08	1.00 1	4.05 1	0.486	5.769	1.681	0.400	0.364	1.123	1.152	1.379	0.64 8	1.26 1
Ajere 09	3.34 5	3.93 1	2.829	10.69 2	2.722	6.333	5.667	0.107	0.241	ND	2.84 3	9.45 9
Ajere 10	1.27 2	4.33 7	0.743	1.231	1.653	0.400	0.485	1.443	1.800	1.545	1.14 8	1.24 8
Afam 11	1.28 6	3.91 3	0.857	1.308	1.694	0.466	0.606	1.484	1.600	1.273	1.17 4	0.83 4
Ekpokpa 12	1.30 8	4.15 6	0.971	1.231	1.639	0.133	0.364	0.996	1.152	1.247	1.12 5	1.30 6
Ekpokpa 13	5.67 6	3.58 9	1.971	3.615	2.403	5.733	2.788	ND	ND	ND	3.71 0	6.26 1
Ekori 14	1.54 3	3.43 3	10.97 1	4.077	1.986	3.733	2.606	10.27 0	9.469	ND	1.42 9	4.24 8
Okuni 15	1.04 3	3.90 2	0.429	1.538	1.917	0.133	0.303	ND	0.786	0.783	0.92 9	0.79 6
Ediba 16	1.13 7	3.67 6	11.57 1	6.000	4.708	11.20 0	7.758	35.00 0	43.05 5	ND	ND	9.61 8

ND Not Detected

Table 6: Geoaccumulation Index of Heavy Metals

Sediment locations	Ti	V	Cr	Mn	Ni	Zn	Fe
Assigha 01	0.38	2.49	-0.73	0.55	3.06	-0.18	-1.26
Assigha 02	1.57	0.22	-0.42	0.87	0.83	0.59	-0.49
Okangha 03	0.89	-0.86	1.51	0.37	0.48	-0.21	-0.11
Okangha 04	2.75	-0.06	-0.69	1.69	-1.56	-0.51	0.93
Etigidi 05	-0.97	-0.23	0.15	0.57	0.51	-0.05	-1.81
Ikom 06	0.27	0.34	-1.37	0.24	-0.02	-0.49	0.36
Ikom 07	3.39	0.24	1.21	2.75	-1.42	-0.85	1.71
Ikpalegwa 08	3.15	0.16	2.38	1.89	-0.06	-0.32	1.14
Ajere 09	0.20	-0.28	0.36	-0.31	0.90	0.74	-1.77
Ajere 10	2.63	0.12	-0.49	1.24	-0.84	-0.49	0.52
Afam 11	2.75	0.12	-0.11	1.56	-0.26	0.12	0.79
Ekpokpa 12	2.68	0.59	-0.39	1.34	-1.93	-0.88	0.60
Ekpokpa 13	0.46	-0.41	-0.82	-0.11	1.14	0.10	-1.38
Ekori 14	0.85	2.51	-0.18	0.07	0.97	0.46	-0.93
Okuni 15	2.95	-0.27	0.33	1.93	-1.35	-0.79	0.99
Ediba 16	-0.51	1.14	-1.10	-0.13	1.10	0.58	-2.38

References

- [1] Adeyemo, O. K., Adedokun, O. A., Yusuf, R. K and Adeleye, E. A. (2008). Seasonal changes in physio-chemical parameters and nutrient load of river sediment in Ibadan city, Nigeria. *Global Nest Journal* 10(3): 326 – 336.
- [2] Asaah, A. V. and Abimbola, A. F. (2005). Heavy metal concentrations and distribution in surface soil of the Bassa Industrial zone, Doula, Cameroon. *The Journal for science and Engineering* 31(2A): 147 – 158.
- [3] Ajayi, S. O. and Osibanjo, O. (1981): pollution studies in Nigerian Rivers , water quality of some Nigerian Rivers, *Environmental pollution (series B)*2: 87 – 95.
- [4] Akinmosin, A., Osinowo, O. and Oladunjoye, M. A. (2009): Radiogenic components of the Nigerian tarsand deposits. *Earth Sci. Res. J.* 13(1): 64 – 73.
- [5] Chen, M. L. and Harris, W. (1999): Baseline concentration of 15 trace elements in Florida surface soil *J. Environmental quarterly* 28: 1173 – 1181.
- [6] Galas – Gorchers, H (1991): Dietary intake of patricide residues; cadmium, mercury and lead. *Food add.* 8: 793 – 800.
- [7] Mediolla, L. L., Domingues, M. C. D. and Sandoval, M. R. G. (2008). Environmental Assessment of and Active Tailings Pile in the state of Mexico (Central Mexico). *Research Journal of environmental science* 2(3): 197 – 208.
- [8] Morse, J. W., Presley, B. J., Taylor, R. J., Benoit, G. and Santschi, P. H. (1993): Trac metal chemistry of Galveston Bay; water, sediments and biota, *Mar Environ. Res.* 36: 1- 37
- [9] Orth, R. A. and Wells, D. V. (2009): Sedimentation analysis of New Germany Lake, Coastal and Estuarine Geology Report 10, Department of Ntaural Resources, Maryland.
- [10] Olubumi, F. E. and Olorunsola (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.
- [11] Praveena, S. M., Radojevie, M., Abdullahi, M. H. and Avis, A. Z. (2007). Factor – cluster analysis and enrichment study of mangrove sediments – An example from Mengkabong Sabali. *The Malaysian Journal of Analytical Science* 2(2): 421 – 430
- [12] Suci, I., Cosma, C., Todica, M., Bolboaca, S. D. and Jantschi, L. (2008): Analysis of soil heavy metal pollution and patern in central Transylvanian. *Int. J. Mol. Sci.* 9: 434 – 453.
- [13] Sutherland, R. A. (2000): Bed sediment associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology* 39: 611 – 637.
- [14] Vries, W., Romkens, P. F. A. M. and Schutz, G. (2007): Critical soil concentrations of cadmium, lead and mercury in view of health effect on humans and animals. *Reviews of Environmental contamination and Toxicology* 191: 91 - 130
- [15] Wisconsin Department of Natural Resources (2003). Consensus based sediment quality guidelines recommendations for use and application. Department of Interior, Washington D. C. 20240 pp 17.
- [16] Zwanziger, H. and Geiss (1997): chemometrics in environmental analysis. *Wienheim, J wiley*