ELEMENTAL CONCENTRATION IN SEDIMENTS ALONG CROSS RIVER IN CROSS RIVER STATE, NIGERIA

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ABSTRACT

Elemental analysis was carried out on sediment samples obtained at a depth of 0 – 15cm, from eleven beaches along the Cross River channel using Energy Dispersive X-ray Fluorescence (EDXRF) technique. Sixteen elements potassium, K, calcium, Ca, titanium, Ti, vanadium, V, chromium, Cr, manganese, Mn, iron, Fe, nickel, Ni, zinc, Zn, germanium, Ge, gallium, Ga, strontium, Sr, yttrium, Y, rubidium, Rb, zirconium, Zr and copper, Cu in the sediments were determined. The results obtained show that the elements concentration ranged from 5.205 – 33280.000 ppm. Fe was the most abundant element with concentration range of 1952.511 – 33280.000ppm, Y and Cu with the concentrations of 61.006ppm and 10.724.000ppm were only detected in sediments from Assigha beach. Inter- element correlation showed very strong correlation between Fe – Ti, Ti – Ca and Mn – Ti with the correlation coefficient r = 0.977, r = 0.902 and r = 0.920 respectively. From the result of cluster analysis and inter – correlations, elements said to be solid earth recycling markers were predominantly higher in concentration pointing to intensive erosion in the adjourning areas of the river.

INTRODUCTION

Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of body of water (Davies and Abowie, 2009). Sediments can come from the erosion of bedrocks and soil or from the decomposition of plants and animals.

Data from sediments can provide information on the impact of distinct human activity on the wider ecosystem (Olubunmi and Olurunsola, 2010). Sediment load and composition is highly influenced by the type and intensity of agricultural land used which play a role in determining the organism which survives in the water body. Sediment analysis is important in evaluating qualities of total ecosystem of a body of water (Adeyamo *et al*, 2008).

There exist a close relationship between sediment texture and morphology with high concentration of elements occurring in the fine – grained sediment (clay) of the submarine troughs and shelf valleys and lowest in the sandy shelf sediments. Conversely, it is obvious that the concentration of elements (metals) varies directly with grain size. Grain size is the most fundamental property of sediment particles affecting their entrainment, transport and deposition and ultimately determines the level of elemental concentration in sediments. Owing to the importance of grain size in sediment analysis, various grain sizes were aptly represented during sampling for the study. Sixteen sediment samples ranging in particle size from 1.0×10^{-6}m to 2×10^{-3}m and to a depth of 0cm to about 15cm were obtained from eleven locations along the Cross River channel in Cross River State of Nigeria.

In this study Energy Dispersive X – ray Fluorescence (EDXRF) was applied for the determination of concentration of elements present in sediments obtained from the Cross River in Cross River State, Nigeria. By normalizing the elements detected to iron and taking element

– element correlations in addition to hierarchical cluster analysis of the elements detected, the possible sources of these elements were predicted.

The aim of this study is to evaluate the elemental composition of sediments from the study location, determine major sources of these elements as well as assess the relationship between sediments grain size and the concentration of elements in sediment.

MATRIALS AND METHODS

Study Area

The Cross River takes its source from the Cameroon highlands and run through Cross River State, Ebonyi and Akwa Ibom State in Nigeria and empties itself into the Atlantic Ocean. The Cross River State portion of the river was sectioned out for this study. It lies between $8^0\ 00^1$E and $8^0 45^1$E and between $5^0 45^1$N and $6^0$00N. Geologically, the study area lies on the Oban Massif and the Calabar flank geological formation. The major human activities prevalent in the area are agriculture and fishing. Sediment were obtained from eleven beaches along the river channel; Assigha, Okangha, Etigidi, Ikom town, Ikpalegwa, Ajere, Afam, Ekpokpa, Ekori, Okuni and Ediba beach.

Sample Preparation

Sediments were collected along the middle course of the Cross River. Sediment samples collected were air dried and 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.

Elemental Analysis

The elemental analysis of the sediment samples were carried out by 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. The spectra data analysis was done with the 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 fit into the sample holder in turns and each irradiated with x –ray beams for 1000s.

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.

RESULTS AND DISCUSSION

Table 1 shows the physical characteristics of sediments from the various sediment locations and Tables 2 and 3 list the concentration of elements detected by EDXRF. Sixteen elements were detected in the sediments namely K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, Rb, Sr, Y and Zr.

Cu and Y were detected in sediments from Assigha beach with the concentration of 10.724ppm and 61.006ppm respectively. The concentration of Fe was the highest followed by that of K. On the average the concentration of element in the sediments analyzed is as follows; Fe > K > Ti > Ca > Ge > Ga > Zr > Rb > Mn > Sr > V > Cr > Zn > Ni > Y > Cu. The ranged of elements in the sediments was 33280.00ppm to 4.026ppm.

The concentrations of elements were observed to vary with sediment's grain size. Elements such as Fe, K, Ca, Ti, Mn, Ge and Sr, show increase in concentration as the grain size decreases. Their concentration was observed to be higher in sediments with size range of 1mm to 3.9µm (mud sediments). However, Zn, Cr, and Ni were observed to increase in their concentration as the grain size increases. Their concentration in grain size ranging from 1mm to 2mm (very coarse sand) was higher than in mud sediments.

Table 1: Physical characteristics of sediments

Sediments location	Sediments size range	Aggregate class	Other names	Colour
Assigha beach 01	0.25 – 1mm	Coarse and 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 08	3.9 - 125µm	Silt and very fine sand	Sand and mud	Black
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 in 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

The Pearson's rank 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).

Table 3: Result of EDXRF analysis of sediments

Sediment Location	Elements and their concentration in 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
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

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 $CaCo_3$ – ash free. The high positive correlation between Fe and Ti confirms their Ti – Fe schist origin. Nickel and vanadium, manganese and titanium were fairly positively correlated presuming possible input from agricultural activities and from the engine boats used in transportation along the river.

Also there is a high positive correlation between Mn, Zr and Fe suggesting that they are from the same source. This also account for the positive correlation between Rb and Zr. Ga and Ge show a strong positive correlation pointing to the fact that they originates from the same source.

Generally, low correlation coefficients between elements suggest that they come from different sources. Cluster analysis is a widely used classification approach for environmental purposes with its hierarchical and non – hierarchical algorithm (Massart and Karfman, 1983). Cluster analysis divides data into groups (clusters) that are meaningful, useful or both. If meaningful groups are the goals the clusters should capture the natural structure of the data.

In this study a hierarchical cluster analysis of fourteen elements detected in the sediments was carried out to ascertain possible origin of the elements. The result of the cluster analysis (Figure 1) shows three distinctive groups. The first cluster is made up of Ni, Zn, Cr, V, Mn, Sr, Zr and Rb, the second clusters comprise of Ga, Ge, Ti, Ca and Fe and the third cluster contains K and Fe. From the result of the cluster analysis element in each of the cluster can specifically be said to come from the same source.

Hierarchical Cluster Analysis

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                     Rescaled Distance Cluster Combine

  C A S E       0         5        10        15        20        25
Label      Num  +---------+---------+---------+---------+---------+

Ni            6  -+
Zn            7  -+
Cr            3  -+
V             2  -+
Mn            4  -+
Sr           10  -+
Zr           12  -+
Rb           11  -+
Ga            9  -+-----------------------------------------------+
Ge            8  -+                                               |
Ti            1  -+                                               |
Ca           13  -+                                               |
Fe            5  -------------+-----------------------------------+
K            14  -------------+
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Figure 1: Dendrogram of cluster of elements in sediments from the middle course Cross River.

Principally, elements from the first cluster stem from natural background due to the rock mineral weathering, with little input from some of the elements such as Mn, V, Cr and Ni from anthropogenic activities. Elements in the second cluster are elements that occur abundantly in the earth crust and has found their way into the sediment deposit by the process of mineral weathering and natural soil erosion. And the third cluster which Fe and K belongs to is basically due to mineralogy of the study area reflecting the predominant mineral rock type; magnetite and alkali feldspar.

Figures 2 – 4 show the concentrations of elements in sediments with grain size between 0.625mm – 0.0028mm (silt and mud) and observed to be higher than that with grain size that range between 1mm – 0.25mm (sand). The concentration of potassium was observed to be higher in mud sediments than sand as reflected in sediments from Ekpokpa 13, Ajere 10, Ikom 07 and Okangha 04 which are all mud sediments. The concentration of calcium was observed to be higher in mud sediments than in sand. The least concentration of calcium was in sediment from Ediba 16 (227.317ppm). The highest concentration of Ti was recorded in mud sediment from Ikom 07 (5905.967ppm) and the least concentration in sand sediment from Etigidi 05 (287.298ppm). The highest concentration of chromium was observed in mud sediment from Ikpalegwa 08 (169.268ppm), and the least recorded in sand from Ikom 06 (74.744ppm). Except for Ikom 07 and Assigha 01, the concentration of Cr in sand sediments was observed to be higher than that of the mud sediments.

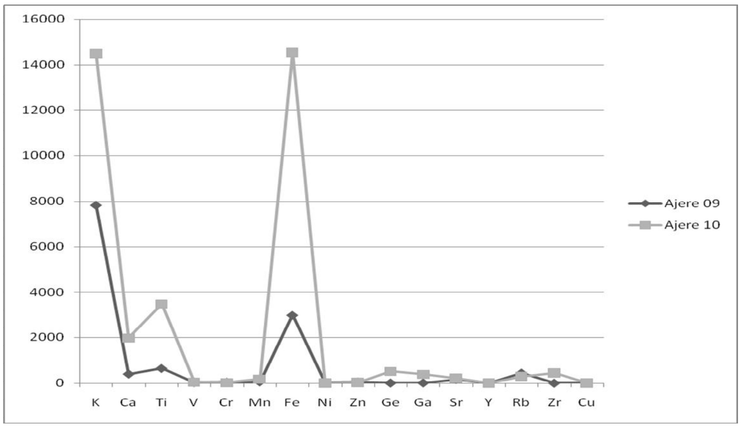

Figure 2: Variation of elemental concentration with particulate size in sediments from Ajere beach

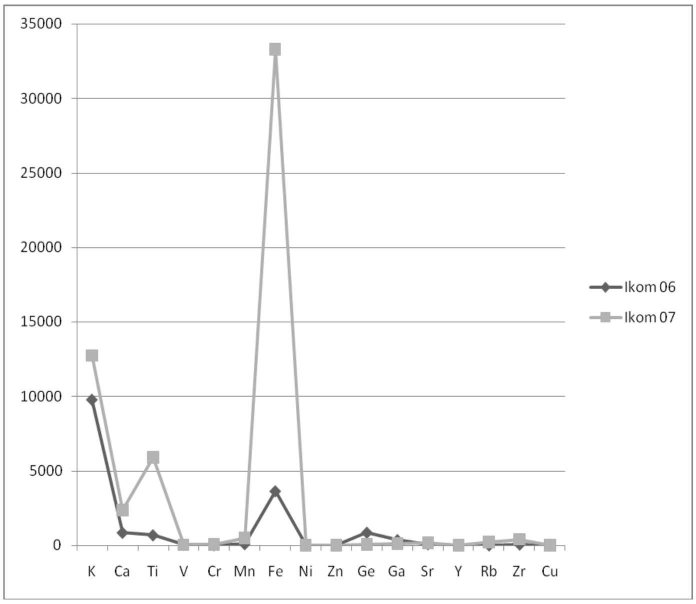

Figure 3: Variation of elemental concentration with grain size in sediments from Ikom beach

The concentration of manganese ranges from 58.742 – 492.789ppm with the highest value observed in mud sediment from Ikom 07 and the least in sand sediment from Ajere 09. Manganese's concentration in the sediments varies inversely with sediment grain size. Iron recorded the highest concentration in the entire observation with a concentration of 33280.000ppm in mud sediment from Ikom 07. The least concentration of iron was recorded in sand sediment from Ediba 16 with a concentration of 1952.511ppm. In all the sediment locations where sediments of different grain sizes were sampled, it was observed that the concentration of iron was higher in the mud sediments than in sand sediments.

The concentration of nickel ranged from 4.026ppm – 128.188ppm with the highest concentration recorded in the sand sediment from Assigha 01 and the lowest in mud sediment from Ekpokpa 12. Generally, nickel was observed to be high in sand sediment than in mud sediments, showing that the concentration of Ni in sediments increases as grain size increases. The highest concentration of Ge was recorded in sediment from Ediba 16 (1667.490ppm) and the least concentration in sand sediment from Ajere 09 (7.857ppm).

The concentration of strontium ranges from 55.762 – 392.805ppm with highest value observed in mud sediment from Afam 11, and the least value in sand sediment from Okangha 03.

Rubidium concentration values observed ranges from 200.503ppm to 444.137ppm, with the highest concentration recorded in sediment from Ikpalegwa 08. Rubidium was not detected in sediments from Assigha beach, Okangha 03, Etigidi 05 and Ikom 07. Apart from Cr and Ni that shows distinctive increase in concentrations with increase in grain size, the concentration of other elements such as K, Ca, Ti, V, Zn, Mn, Fe, Ge, Ga, Sr, Y, Rb and Zr increases as grain size decreases. This is shown in Figures 2, 3, and 4.

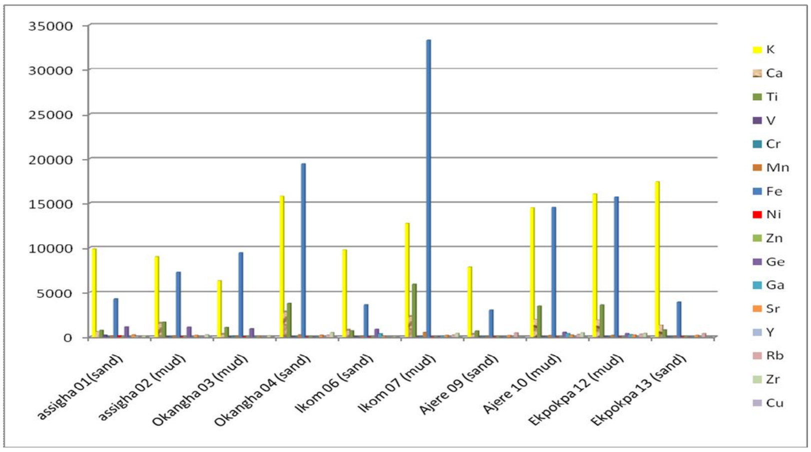

Figure 4: Chart showing variation of elemental concentration with sediment grain size

CONCLUSION

Elemental analysis of sediments revealed the contributions of major sediments sources (bedrock, soil, and decomposition of organisms), to the sediment deposit. The correlation of elements detected and the cluster analysis provided veritable means of identifying the elemental sources and major contributors to the observed level of elemental concentration.

The high concentration of K, Ca, Ti, Ge, Ga, Rb, and Sr in the sediments analyzed may be attributed to the contributions of bedrocks, littoral contributions and organic matter in the case of Ca. The concentration of elements was observed to be higher in mud sediments than in sand sediments implying an inverse relationship between the concentration of elements in sediments with grain size, except for Ni and Cr whose concentration was observed to be higher in sand than in mud sediments

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