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Levels of Trace Metals in surface Sediments from Kalabari Creeks, Rivers State, Nigeria

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***KEYWORDS*:** Kalabari creeks, surface sediment, anthropogenic, trace metals, domestic effluent.

ABSTRACT: The study investigated the levels of six trace metals V, Cu, Pb, Cd, Fe and Ni in surface sediment of Kalabari creeks. Surface sediments of about 0-2cm depth were collected from June 2009 to April 2010 at two months interval to cover the rainy and dry seasons. Bulk scientific atomic absorption spectrophotometry (AAS) model 200A was used to analyze the samples. The results obtained revealed that the mean levels of the metal occurred in the order Fe > Ni > Cu > Pb >V = Cd, which were 4,767.06 ± 076.5mg/kg, 20.90 ± 10.47mg/kg, 14.67 ± 12.03mg/kg, 1.63 ± 1.16mg/kg respectively. Vanadium and cadmium were below detection limit (BDL) <0.001 in all the samples. The overall mean levels of trace metal in sediment in the rainy season was in the order Fe > Ni > Cu > Pb > Cd = V, while in the dry season, the order was Fe > Cu >Ni > Pb > Cd = V. The results obtained agreed with WHO and FEPA now Federal Ministry of Environment (FMENV) set standard for sediment. © JASEM

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Introduction: **Nigeria** is among the non-industrialized country in the world. Despite this, the country is faced with pollution of its environment; water, air and land. Most of the human activities in Nigeria have resulted to the contamination of the environment. Substances such as crude oil, plastic waste, domestic waste, industrial effluent are major sources of pollutants in the environment (Ellis, 1989, Adewoye *et al.*, 2005, Farombi *et al.*, 2007, Ayandiran *et al.*, 2009). Heavy metals such as lead, cadmium and mercury are not essential for man. Unlike nickel, iron, zinc, copper and vanadium which are essential. However, excess levels in human food can be poisonous. According to Forstner and Prosi (1979) the harmful effects of heavy metals as pollutants result from incomplete biological degradation. Therefore, these metals tend to accumulate in the aquatic environment. Heavy metals are non-biodegradable and once they enter the environment, bioaccumulation occurs in every phases of the environment both sediment and water, by means of metabolic and biosorption process (Hodson, 1988, Carpene *et al.*, 1990, and Wicklund-Glynn, 1991). Stephen (2004) reported the importance of the monitoring of pollution levels of heavy metals in aquatic system, so that approximate measures of the potential hazard can be attained. This measure should give an estimation of the type of effect that could be expected after exposure of heavy metal, in developed country like USA higher levels of metals are often found in the costal sediment. Adriano (2001), reported elevated levels of heavy metals concentrating in USA soil and sediment to be an average of 7.4 ppm. Arsenic concentration was reported in sediment as having average of 33.7ppm (with a range from <0.450 to 455ppm while mercury is 5 to 100 ppb).

Copper is a micronutrient for both plants and animals at low concentration; however, it may become toxic to some forms of aquatic life at elevated concentrations. Thus copper concentrations in natural environments and its biological availability, are important. Naturally occurring concentrations, of copper have been reported from 0.03 to 0.23μg/l in surface sea waters and from 0.2 to 3.0 μ g/l in freshwater system (Bowen, 1985). Copper concentrations in location receiving anthropogenic inputs such as mine tailing discharges can vary anywhere from natural background to 100μg/l (Lopez and Lee, 1977; Hem, 1989) and have in some cases been reported in the 200,000μg/l range in mining area. Mining, leather and leather products, fabricated metal products and electrical equipment are a few of the industries with copper-bearing discharges that contribute to anthropogenic inputs of copper to surface waters (Patterson *et al, 1998).*

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Another metal is nickel, it occurs in the environment only at very low levels. Nickel tetra-carbonyl $Ni(CO_4)^{2+}$ is particularly known to be poisonous. Human use nickel for different applications; the most common application is the use as an ingredient of steel and metal product, it can be found in common metal products such as jewelry. An uptake of large quantities of nickel can cause allergic reactions such as skin rashes mainly from jewelry, asthma and chronic bronchitis, birth defects, respiratory failure, etc. The analysis of trace metal in sediment permits pollution detection that could escape water analysis and provides information about the critical sites of the system under consideration (Horsfall and Spiff, 2005).

Based on the importance of sediment in aquatic environment, this study was conducted in Kalabari creeks in the lower reaches of New Calabar River in the Niger Delta. The area was chosen for the study because it received domestic, industrial, agricultural, and natural runoff from a heavy populated and fast growing industrial city – Port Harcourt. Most of the companies or industries located in Port Harcourt are oil and gas companies. The aim of the study is to ascertain levels of these metals – nickel, vanadium, copper, iron, lead, and cadmium in sediment, whether its present level agrees with the levels recommended by WHO and FEPA now FMENV (Federal Ministry of Environment).

METERIALS AND METHODS

Study area: Kalabari creek is located in the lower reaches of New Calabar River. This area consist of some settlements/communities whose main activities is fishing and cultivation of crops which are their source of livelihood. There were five sampling points; Ogbakiri, Tombia, Okporota, Buguma and Sama all along the creeks in the New Calabar River. These creeks are less than two kilometers from Port Harcourt main town, where many industries and companies are cited. The industrial, domestic and water runoff from these creeks empty into the Atlantic Ocean. The area normally witness low and high tides, during high tide, seawater are carried to these area and debris are deposited on the sediment surface. During rainy season, large volumes of water are carried from the hinter land to these creeks.

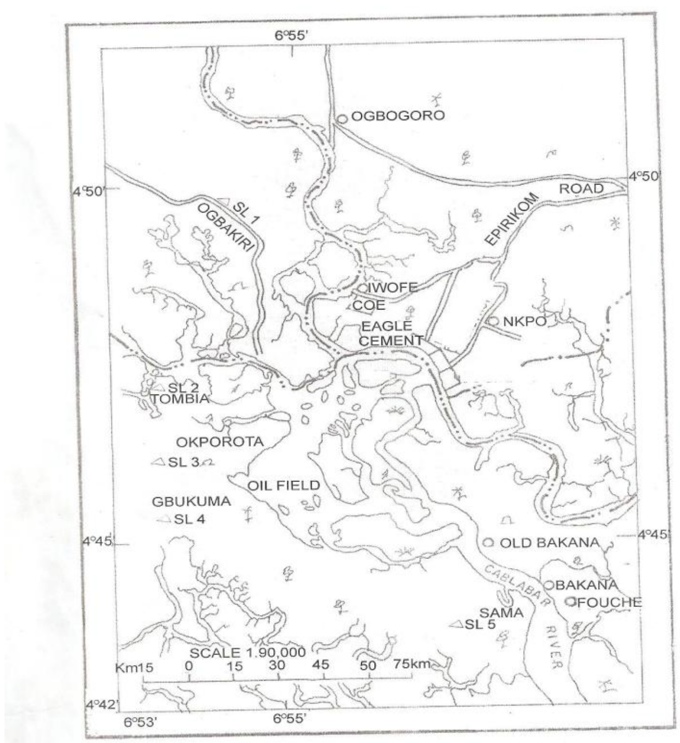

Fig. 1: Map showing lower reaches of New Calabar River and sampling sites.

*Sampling and Analysis***:** The sediment samples were collected from five sampling stations from June 2009 to April 2010 to cover two seasons, dry and wet/rainy. The rainy season covers from June to October 2009 and dry season covers from December 2009 to April 2010. The samples were collected at two months interval. 2cm^3 of top sediment were collected from each site and rap in polythene bags and stored in a cooler packed with ice blocks. About 5g of the sediment samples were removed and dried at 105^{0}C and were homogenized in a mortar. Two grams of the powdered sediment samples were further dried to constant weight and 1.0g were accurately weighed into 50ml volumetric flasks with Sartorous analytical balance model 2842. To each of the volumetric flask, 3ml of concentrated nitric acid (HNO_3), 1ml perchloric acid ($HClO_4$) 60% and 1ml sulphuric acid H_2SO_4 in the ratio of 3:1:were added and heated on a hot plate to near dryness. The content of each flask was diluted with 5ml of de-ionized water and were heated for 30 minutes. Then 10ml of de-ionized water was added and filtered with Whatman No. 1 filter paper and preserved pending analysis. Samples were analyzed using Buck Scientific atomic absorption spectrophotometer model 200A equipped with air-acetylene flame.

RESULTS AND DISCUSSION

Table 1: Seasonal trace metal levels in surface sediments of Kalabari Creeks in mg/kg

Site	V		Ni		Cu		Fe		Pb		Cd	
	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry
1	BDL	BDL	42 ± 12.7	25.6 ± 5.15	19.3 ± 1.7	21.6 ± 5.2	559.7 ± 120.9	25983 ± 3742.2	3.06 ± 0.54	0.98 ± 0.26	BDL	BDL
2	BDL	BDL	32.5 ± 14.89	23.7 ± 6.25	6.48 ± 0.92	48.3 ± 10.53	515.9 ± 275.2	933.5 ± 258.0	1.9 ± 0.14	1.22 ± 0.62	BDL	BDL
3	BDL	BDL	7.42 ± 5.9	15.2 ± 4.3	1.43 ± 0.59	17.9 ± 16.70	8795 ± 13803.2	18586 ± 2932.3	0.77 ± 0.13	2.49 ± 0.73	BDL	BDL
4	BDL	BDL	12.1 ± 4.9	35.62 ± 9.11	0.603 ± 0.37	15.4 ± 1.77	22662 ± 2849.1	14546 ± 15468.2	0.29 ± 0.10	5.13 ± 1.7	BDL	BDL
5	BDL	BDL	9.82 ± 5.3	8.33 ± 11.10	0.46 ± 0.73	15.3 ± 10.4	253.1 ± 22.5	2222 ± 515	0.16 ± 0.19	0.37 ± 0.05	BDL	BDL
Overall Mean Std dev.	BDL Nil	BDL Nil	20.77 ± 15.51	24.43 ± 10.72	5.66 ± 8.02	23.72 ± 13.98	6557.14 ± 9702	7777.1 ± 8172.63	1.24 ± 1.23	2.04 ± 1.89	Nil Nil	Nil Nil

BDL: Below detection limit

Table 2: Mean monthly values of trace metals in sediment in rainy and dry seasons of Kalabari Creeks in mg/kg

Parameter	June 2009	August 2009	October 2009	December 2009	Feb. 2010	April 2010
V	BDL	BDL	BDL	BDL	BDL	BDL
Ni	18.56 ± 13.27	24.65 ± 25.98	19.1 ± 8.94	25.47 ± 6.31	24.18 ± 12.24	15.47 ± 9.98
Cu	5.45 ± 7.36	5.9 ± 8.91	5.61 ± 7.84	26.84 ± 10.17	21.11 ± 21.7	27.35 ± 16.06
Fe	3043.53 ± 5187.07	7220.64 ± 0622.22	337.24 ± 88.84	9067.16 ± 8454.35	9163.58 ± 11188.71	9970.1 ± 92739.78
Pb	1.36 ± 1.46	1.17 ± 1.19	1.18 ± 1.07	1.91 ± 1.92	2.57 ±2.61	1.63 ± 1.24
Cd	BDL	BDL	BDL	BDL	BDL	BDL

Table 3: One-way analysis of variance (ANOVA) of significance difference of trace metals in sediment in rainy and dry seasons.

		Sum of squares	df	Mean Square	F	Sig.
Jun.09	Between Groups	384688860	5	7693771.957	1.716	.169
	Within Groups	1.1E+008	25	448429.192		
	Total	1.5E+008	29			
Aug.09	Between Groups	5.4E+008	5	108575912.2	2.827	.038
	Within Groups	9.2E+008	24	38408964.78		
	Total	1.5E+009	29			
Oct.09	Between Groups	460766.2	5	92153.240	68.819	.000
	Within Groups	32137.376	24	1339.057		
	Total	492903.6	29			
Dec.10	Between Groups	3.4E+008	5	68360771.06	6.233	.001
	Within Groups	2.6E+008	24	10967761.51		
	Total	6.1E+008	29			
Feb.10	Between Groups	3.5E+008	5	69830363.58	3.347	.020
	Within Groups	5.0E+008	24	20864644.86		
	Total	8.5E+008	29			
Apr.10	Between Groups	4.1E+008	5	82688717.58	3.393	.019
	Within Groups	5.8E+008	24	24370847.01		
	Total	1.0E+008	29			
Mean	Between Groups	2.1 E+008	5	42716521.03	3.645	.014
	Within Groups	2.8E+008	24	11719118.47		
	Total	4.9E+008	29			

F critical = 2.76 *Alpha = 0.05*

Table 4: Correlation of trace metals levels in sediments samples in rainy and dry seasons 2009/2010 in mg/kg with months.

		Jun.09	Aug.09	Oct.09	Dec.09	Feb.10	Apr.10	Mean
Jun.09	Pearson Correlation	1	**	**	**	**	**	**
	N	30						
Aug.09	Pearson Correlation		1	**	**	**	**	**
	Sig. (2-tailed)	.834**						
	N	.000	30					
		30						
Oct.09	Pearson Correlation			1	**	**	**	**
	Sig. (2-tailed)	484**	.572**					
	N	.007	.001	30				
		30	30					
Dec.09	Pearson Correlation			.746**	1	**	**	**
	Sig. (2-tailed)	.812**	.962**	.000				
	N	.000	.000	30	30			
		30	30					
Feb.10	Pearson Correlation	.833**		.596**		1	**	**
	Sig. (2-tailed)	.000	.999**	.001	.967**			
	N	30	.000	30	.000	30		
			30		30			
Apr.10	Pearson Correlation	.814**		.592**		.999**	1	**
	Sig. (2-tailed)	.000	.997**	.001	.961**	.000		
	N	30	.000	30	.000	30	30	
			30		30			
Mean	Pearson Correlation	.856**		.621**		998**	995**	1
	Sig. (2-tailed)	.000	.997**	.000	.976**	.000	.000	
	N	30	.000	30	.000	30	30	30
			30		30			

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

The mean levels of all the trace metals analyzed in sediment samples varied from one site to another and with season, except vanadium and cadmium. There was no significant difference at $p<0.05$ in the mean levels of all the metals.

The mean concentration of vanadium and cadmium was below detection limit (BDL) <0.01 in both rainy and dry seasons. This result indicates that there was no significant level of vanadium in the environment. This means that the major source of pollution is domestic rather than crude oil or petroleum products. This implies that the oil activities in the area do not have any impact on the levels of vanadium and cadmium in these results as indicated in tables (1) and (2).

The mean level of nickel reveals that the highest concentration occurred at site 4 as shown in table 1. However, the overall mean in rainy and dry seasons were 20.77 $\pm$ 15.5 and 24.43 $\pm$ 10.72 mg/kg respectively. On the other hand, the mean monthly variation of the metal as shown in table 2 reveals that the highest concentration of the metal (Ni) occurred in December 2009. The monthly variation of nickel in the sediment was in the order December > August > February > October > June > April. However, the overall data revealed that the highest mean levels occurred in the dry season, when compared to the rainy season. This result agreed with the facts that in dry season, less loads are being carried and physio-chemical processes, the chemical component are adsorbed on the various matrixes of the river system biota, sediment and water. Similar results were reported by (McGreer *et al.*, 2000, Rajotter and Coutre, 2002, Forambi *et al.*, 2007,). Contrary results were obtained in the levels of heavy metals in sediment of lower Olifants River (Turekian, 1977, Peres and Pihan, 1991, Seymore *et al.*, 1996, Vindohini, 2008). The mean level of nickel correlated significantly at the 0.01 level (2-tailed) in all the months and sites. There was no significant difference in mean level of nickel with other metals. The levels obtained in the study fall within WHO and FMENV standard set values.

Copper levels in sediment varied from one location to another. This variation could be seen in the tables 1 and 2 respectively. Table 1 revealed that in the rainy season, the overall mean is 5.66 $\pm$ 8.02 mg/kg, whereas 23.72 $\pm$ 13.98 mg/kg was reported in the dry season. The results indicated that highest level of copper was recorded in site (2). This site is the first to receive the stormwater runoff which carried the debris and effluent in drains from Port Harcourt City. The distribution of copper in the sediment of Kalabari creek is similar to those reported in the New Calabar River both in the Niger Delta area (Horsfall and Spiff, 2002).

The result of one-way analysis of variance as presented in table (3) (ANOVA) at $p<0.05$ indicates significant difference in the mean levels of Cu in all the month except in June. However, the element correlated significantly at the 0.01 level (2-tailed) between all the metals in every month as indicated in table 4. High concentration of copper observed in the sediment was probably due to high anthropogenic and natural processes. This is in accordance with the observation by (Hughes and Plos, 1978, Bezuidenhout *et al.*, 1990, Seymore, 1994, Oronsaye and Ogbebo, 1995, Senthil *et al.*, 2008, Horsfall and Spiff, 2002, Okafor and Opuene, 2006), who stated that copper mainly accumulated in sediment.

Iron is one of the important elements in the environment. The results revealed that iron recorded the highest levels of all the metals in the sediment compartment. The distribution of iron in the sediment is similar to levels of copper and nickel. The mean levels of iron ranged from 9970.1 $\pm$ 92739.78 to 337.24 $\pm$ 88.84mg/kg. Elevated levels of iron have been reported by (Okoye *et al.*, 1991, Okafor and Opuene, 2007). High level of the metal (Fe) was reported in Humic acid which is one of the component of sediment Horsfall and Spiff, 2005. Humic acid are basic component of sediment which can trap or attract metals. According to the authors, Humic and Fulvic acid cycle distribute trace/heavy metals in the sediment. High level of Fe in sediment may occur as a result of natural and anthropogenic source, most of the substances we use in our home contained Fe as one of the alloy.

The distribution of lead in sediment samples is similar to iron levels. The level of lead (Pb) varies from sites to seasons. The overall mean value of lead in the rainy season was 1.24 $\pm$ 1.23 mg/kg and 2.04 $\pm$ 1.89 mg/kg in the dry season respectively. The results revealed that dry season recorded the highest levels of Pb. Elevated levels were observed in February in the dry season. The highest levels of Pb was 2.51 $\pm$ 2.61 mg/kg, while the lowest was 1.17 $\pm$ 1.18 mg/kg in August. The result obtained in this study is similar to those reported previously from the Niger Delta environs, (Kakulu and Osibanjo, 1988, Horsfall and Spiff, 2002). However, the result obtained was contrary to those reported by Topouoglou *et al.*, 2002 and Ngugen *et al.*, 2005. Highest level of Pb was recorded in the dry season when compared to the rainy season. This is due to the fact that sediment become less diluted with fresh water, effluent either from rain or drainage, hence the levels of the metal (Pb) tend to be higher in this period when compared to the rainy season. The results of one-way analysis of variance (ANOVA) at $p<0.05$ indicate significant difference in all the months except in June, and no significant with sites. The mean levels of Pb in sediment samples were below FEPA now (FMENV) and WHO standard except in dry season when there were elevated levels as indicated in table 1.

Conclusion: The finding indicates that the mean levels of vanadium and cadmium were below detection limit (BDL) <0.001 in both seasons. The results indicate that there was no significant level of vanadium and cadmium in the environs. This means that the major source of pollution is domestic waste, rather than crude oil or petroleum products. This implies that that oil activities in the area do not have any impact on the levels of vanadium and cadmium in the sediment in all the sites. However, elevated levels of Ni, Pb, Fe and Cu were obtained in the study area. The level of these metals reported presently in this study will not pose any threat to the pollution of area i.e Kalabari creek. The results obtained in this study were below WHO and FMENV (Federal Ministry of Environment) former FEPA. More studies should be conducted in the area especially since sediment serves as trapped or reservoir for pollutants such as heavy metals. The results revealed that the major source of pollution in the area is anthropogenic excluding oil exploitation and exploration.

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