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Full Length Research Paper

Hydrobiological constraints of trace metals in surface water, coastal sediment and water lily of Calabar River, Nigeria

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Trace metals concentrations in surface water, sediment and water lily (*Nymphaea lotus*) samples from the banks of Calabar River, a major tributary of Cross River Estuary, Nigeria were determined. The results revealed average concentrations 0.017, 0.010, 37.08 and 0.025 mg/l, respectively, for As, Cd, Fe and Pb in surface water samples, which exceeded Federal Environmental Protection Agency (FEPA) maximum guideline values. Elevated levels of heavy metals (As, 1.251 mg/kg; Cd, 0.038 mg/kg; Co, 0.509 mg/kg; Cu, 3.78 mg/kg; Fe, 35.48 mg/kg; Mn, 10.72 mg/kg; Ni, 0.732 mg/kg; Pb, 1.355 mg/kg; V, 0.427 mg/kg; and Zn, 8.665 mg/kg) in sediment samples indicated anthropogenic influences while, measured concentrations in *N. lotus* were typical of a growing plant.

Key words: Trace metals, coastal sediment, *Nymphaea lotus*, Calabar River Estuary.

INTRODUCTION

In recent times, much concern is on ascertaining the eco-environmental quality due to increased human, domestic and industrial activities. Pollution by heavy metals has been of considerable public and scientific interest in the light of the evidence of their extreme toxicity to humans and biological systems.

Literature on heavy metals accumulation in surface waters, sediment and plants along the banks of Calabar River is very scanty. Available publication by Ukpong (1995) is mainly on the physical and chemical properties of mangrove soils of the Cross River Mangrove Swamp and associated Creeks. The most recent report is on the physicochemical characteristics and anthropogenic pollution of the surface waters of the River (Asuquo, 1999). The same author observed that the physicochemical attributes of the river were higher during the flood tide than the ebb tide. Total hydrocarbon levels (22.0-55.8 mg/l) were identified above the tolerable limits while iron concentration (1.55±0.42 mg/l) was below Federal Environmental Protection Agency (FEPA) limit recommended for near shore waters.

Calabar River constitutes a major inlet into the land and is often utilized as main transportation route. Generally, it is a multi-use resource with fishery as its dominant use. It also serves as receiving water for domestic and industrial wastes. Although the Calabar River experiences regular tidal inundations, there are fluctuations in salinity between the rainy and drier months, with high salinity (3.8±0.6%) recorded for the dry season while low salinity (0.5±0.6%) occurs in the rainy season (Ukpong, 1991).

In an attempt to generate information on the eco-environmental characteristics of the Calabar River, the heavy metals accumulation potentials in surface water, sediment and water lily from the banks of Calabar river was investigated.

MATERIALS AND METHODS

The Calabar River is a major tributary of Cross River, originating from the Oban Hill, Nigeria and flows through black shale and siltstone, clayey sand, silt and alluvial deposits before entering the Cross River at Alligator Island. It is located off the Atlantic beach ridge coast in Southeastern Nigeria. It is situated between latitudes 04º 55' N and 05º 00'N and by longitudes 08º 15'E and 08º 23'E (Figure 1).

Sampling locations designated $_{ST}$NP (Ekorinim beach), $_{ST}$CA (Calcemco jetty), $_{ST}$CL (Cross lines beach) and $_{ST}$DN (Edibe edibe

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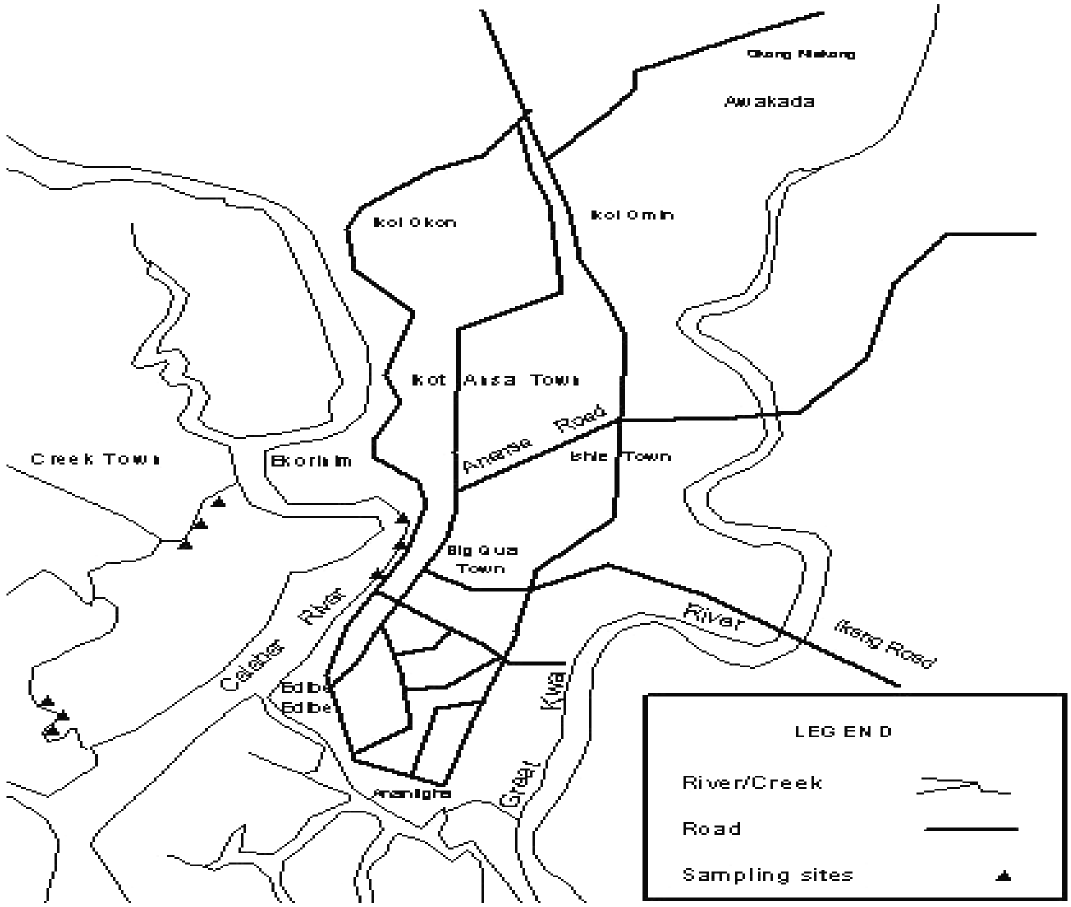

Figure 1. Calabar Municipality showing Sampling sites.

beach) were established at interval along the bank of the river. At each location, three samples each of surface water, coastal sediment and water lily (*Nymphaea lotus*) were collected. Surface water samples were collected in 1 litre polyethylene bottles, just below 0.5 m depth of the water surface, and filtered through 0.45 µm Millipore filter paper. Intertidal sediment samples collected were oven dried at 70 - 100ºC, gently crushed with a rolling pin, and sieved to collect the <63 µm grain size. 1.0 g of each sediment sample were extracted using 10 ml 0.25 M HNO_3 and and 20 ml 0.25 M H_20_2. Samples of water lily were collected from the designated points along the banks of the river. The samples were obtained manually and rinsed with deionized water to remove adhered impurities. The fresh leaves of the plants were carefully cut using stainless scissors and placed in polyethylene bags. These were dried at 60ºC, milled and dried again at 105ºC. 1.0 g of each dried samples was extracted using a mixture of trioxonitrate (V) acid and hydrogen peroxide acid as described by Radojevic and Baskin (1999) in 100 ml Kjedhal digestion flasks. All the samples were analysed for elemental composition was performed using Pye Unicam 939/959 AAS.

RESULTS AND DISCUSSION

The concentration of Pb, Ni, V, Zn, Fe Co, Cd, Mn, Cu and As in surface water, *N. lotus* and surficial sediments of Calabar River are presented in Tables 1, 2 and 3. Table 4, 5 and 6 present the correlation matrices for sediment, surface water and N. lotus samples respectively, showing values of Pearson's correlation coefficient ($p<0.05$, $n=4$) for pairs of heavy metals at the four locations.

The concentrations of As, Cd, Fe and Pb in water samples were generally high with mean values of 0.017±0.006, 0.010, 37.08±11.23 and 0.025±0.018 mg/l, respectively. These average values, however, exceeded maximum guideline values of 0.01, 0.003, 0.3 and 0.01mg/l respectively recommended for nearshore waters (FEPA, 1999). The high concentration levels of these heavy metals could be attributed to anthropogenic sources arising from solid and liquid wastes discharged by cottage industries located in the area. Ni, Cu, Zn concentration levels were significantly low in the water samples. Ni and Cu maintained a constant average level of 0.010 mg/l at the four stations except at $_{ST}$Cl where 0.009 mg/l value was recorded for Cu. Table 2 shows that the average concentration levels of heavy metals in N. lotus at all stations were within the typical amounts of risk elements in plants (Vecera et al., 1999). However, Fe average concentration was relatively high in *N. lotus* with the highest level of 54.40 mgkg-1 dry weight recorded at

Table 1. Concentrations of heavy metals in surface water samples from Calabar River.

Metals	Heavy metals concentration (mg/l)				
	$_{ST}$**CL**	$_{ST}$**NP**	$_{ST}$**CA**	$_{ST}$**DN**	**Mean**
As	0.010	0.025	0.015	0.018	0.017
Cd	0.010	0.010	0.010	0.010	0.010
Co	0.010	0.010	0.010	0.010	0.010
Cu	0.009	0.010	0.010	0.010	0.010
Fe	42.00	22.00	36.00	48.30	37.08
Mn	0.010	0.010	0.010	0.010	0.010
Ni	0.010	0.010	0.010	0.010	0.010
Pb	0.010	0.048	0.010	0.030	0.025
V	0.050	0.080	0.103	0.065	0.075
Zn	0.042	0.016	0.007	0.013	0.019

Table 2. Concentrations of heavy metals in sediment samples from Calabar River

Metals	Heavy metals concentration (mg/kg)				
	$_{ST}$**CL**	$_{ST}$**NP**	$_{ST}$**CA**	$_{ST}$**DN**	**Mean**
As	1.227	1.265	1.240	1.270	1.251
Cd	0.026	0.014	0.050	0.062	0.038
Co	0.536	0.438	0.417	0.646	0.509
Cu	2.765	2.961	3.643	5.752	3.780
Fe	33.00	33.80	36.10	39.00	35.48
Mn	3.587	10.44	13.55	15.30	10.72
Ni	0.413	0.674	0.842	1.00	0.732
Pb	1.363	1.388	1.018	1.650	1.355
V	0.138	0.249	0.572	0.750	0.427
Zn	8.845	8.542	7.416	9.856	8.665

Table 3. Concentrations of heavy metals in *Nymphaea lotus* samples from Calabar River

Metals	Heavy metals concentration (mg/kg)				
	$_{ST}$**CL**	$_{ST}$**NP**	$_{ST}$**CA**	$_{ST}$**DN**	**Mean**
As	0.088	0.162	0.113	0.140	0.126
Cd	0.013	0.008	0.003	0.025	0.012
Co	0.010	0.010	0.010	0.010	0.010
Cu	0.535	0.870	0.997	1.325	0.932
Fe	21.40	23.60	38.45	54.40	34.46
Mn	3.276	3.223	3.227	3.920	3.412
Ni	0.142	0.649	0.186	0.724	0.425
Pb	0.055	0.257	0.122	0.182	0.154
V	0.090	0.216	0.069	0.200	0.144
Zn	4.273	4.406	3.960	6.380	4.755

the downstream station $_{ST}$DN. This shows that N. lotus has greater tendency to accumulate Fe, Zn, Mn, and Cu than As, Cd, Co, Ni, Pb, and V. Moreover, Fe, Zn, Mn, and Cu concentrations were in the range 21.40 to 54.40 mg/kg, 4.273 to 6.380 mg/kg, 3.276 to 3.920 mg/kg and 0.535 to 1.325 mg/kg, respectively. The heavy metal content in *N. lotus* at the four locations studied may be presented in order of decreasing concentrations as Fe >Zn>Mn>Cn>Ni>Pb>V>As>Cd>Co.

Table 2 is a summary of the concentrations and the mean levels of heavy metals in the surficial sediments of the Calabar River Estuary. From these results, the concentration of Cd was generally low with a mean value of 0.038 mg/kg. The average concentrations for As, Co, Ni, V and Pb (1.251, 0.509, 0.732, 0.427 and 1.355 mg/kg, respectively) were similarly low. However, Fe, Mn, Zn, and Cu levels were relatively high especially at $_{ST}$DN location. Enhanced concentrations Fe, Mn, Zn and Cu were observed at $_{ST}$DN location. The trend in heavy metal distribution in order of decreasing average concentration can be presented as Fe> Mn> Zn> Cu> Pb>As>Ni> V> Co> Cd.

Table 4. Correlation matrix* for coastal sediment samples giving values of Pearson's correlation coefficients, r, for pairs of heavy metals (p<0.05,n=4).

Parameters	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	V	Zn
As	1	0.205	0.307	0.619	0.582	0.705	0.697	0.603	0.518	0.492
Cd		1	0.517	0.863	0.915	0.696	0.786	0.126	0.926	0.218
Co			1	0.729	0.564	0.119	0.279	0.849	0.401	0.923
Cu				1	<u>0.973</u>	0.761	0.859	0.557	0.909	0.592
Fe					1	0.864	0.937	0.360	0.980	0.392
Mn						1	<u>0.985</u>	0.802	0.912	0.043
Ni							1	0.192	<u>0.961</u>	0.174
Pb								1	0.174	<u>0.985</u>
V									1	0.203
Zn										1

Significant correlations (p<0.05) are underlined.

Table 5. Correlation matrix* for surface water of Calabar River, giving values of Pearson's correlation coefficients, r, for pairs of heavy metals (p=0.05,n=4).

Parameters	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	V	Zn
As										
Cd	-		-	-	-	-	-	-	-	-
Co	-	-		-	-	-	-	-	-	-
Cu	0.74	-	-		-0.29	-	-	0.53	0.72	-0.97
Fe	-0.67	--	-			-	-	-0.57	-0.45	0.20
Mn	-	-	-	-	-		-	-	-	-
Ni	-	-	-	-	-	-		-	-	-
Pb	0.94	-	-	0.53	-0.57		-		0.02	-0.31
V	0.35	-	-	0.72	-0.45	-	-	0.02		-0.83
Zn	-0.57	-	-	-0.97	0.20	-	-	-0.31	-0.83	

Table 6. Correlation matrix* for *N. lotus* from Calabar River, giving values of Pearson's correlation coefficients, r, for pairs of heavy metals (p=0.05,n=4).

Parameters	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	V	Zn
As										
Cd	-		-	-	-	-	-	-	-	-
Co	-	-		-	-	-	-	-	-	-
Cu	0.74	-	-		-0.29	-	-	0.53	0.72	-0.97
Fe	-0.67	--	-			-	-	-0.57	-0.45	0.20
Mn	-	-	-	-	-		-	-	-	-
Ni	-	-	-	-	-	-		-	-	-
Pb	0.94	-	-	0.53	-0.57		-		0.02	-0.31
V	0.35	-	-	0.72	-0.45	-	-	0.02		-0.83
Zn	-0.57	-	-	-0.97	0.20	-	-	-0.31	-0.83	

The linear correlation coefficients calculated for heavy metal in the sediment samples at the four locations indicated that Cu/Fe, Fe/V, Mn/Ni, Ni/V and Pb/Zn correlations had significant linear correlation coefficients (mostly larger than critical r=0.950).

This study has confirmed that sediments are important hosts for toxicant metals. It has been shown that sediment permit the detection of trace metals that may be either absent or in low concentration in the water column. As presented, the concentrations of heavy metals studied in the surface water and N. lotus samples can be relatively low but the concentrations in the sediments may be elevated. The occurrence of enhanced concentrations of trace metals in coastal sediments such as that obtained from Calabar River can be a good indication of man-induced pollution rather than by natural enrichment through geological weathering.

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