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Heavy Metals Pollution in Surface Water and Sediment of Lower Cross River System in Akwa Ibom State, Nigeria.

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Abstract *This study analyzed some heavy metals in surface water and sediment from Cross River system in Akwa Ibom State, Nigeria. Water and sediment samples were collected from Ibaka, Oron, Nwaniba, Ayadehe, Okopedi and Enwang and analyzed for the concentration of some heavy metal ions using atomic absorption spectrophotometer. The results obtained from the analysis indicated that mean concentrations of Cd, Pb, Cr, Co, Cu, Se and Ni in surface water were 13.69±8.97, 20.53±10.60, 18±11.47, 25.81±13.91, 26.9±11.0 1.18±0.32 and 32.67±26.16 µg while the corresponding mean concentrations in the sediments were 0.52±0.24, 57.78±15.60, 16.22±5.48, 7.52±2.28, 69.81±16.90, 0.75±0.44 and 6.87±2.26 µg/g, respectively. The results of surface water and sediment quality were compared with some guidelines which revealed no serious contamination risk to man and aquatic organism for surface water and some degree of contamination at some stations for the metals under study in sediment samples.*

Key Words; Pollution, heavy metals, surface water, sediment, Cross River.

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1.0 Introduction

One of the most important issues facing today's communities is the entry of pollutants into the environment through anthropogenic, natural and industrial processes (Espinoza *et al*., 2005; Kane et al. 2012; Prabu, 2009). Consequently, increasing level of urbanization and industrialization coupled with population explosion have created future risk for the health of the water ecosystem. Aquatic pollution arises due to introduction of contaminants at the level and concentrations that can be injurious to the aquatic environment or other members of the environment through the food chain. Intrusion of wastes to the aquatic environment may affect several properties of water including organoleptic, physicochemical properties (such as colour, salinity, pH, temperature, biochemical oxygen demand, chemical oxygen demand, etc) and heavy metals (Salomons *et al*., 1995). Among all forms of water pollution, heavy metal pollution has received serious concern because most of them are toxic (above certain concentrations) and could persist in the environment for a long period of time (compared to other pollutants). Impact of bioaccumulation of heavy metal contaminated water is magnified when the metal is transferred along the food chain (Osu and Odoemelam, 2015). Some heavy metals are toxic even at very minute concentration and can create excessive toxicity if not controlled (Herawati *et al.,* 2005). Concentration of most pollutants at the point source may differ significantly from those at the non-point source especially for a non-steady water body. However, heavy metal pollutants have been found to display different behaviours from one other because the sediment acts as a sink for heavy metals (Campbell *et al.,* 1988; Cheggour *et al.,* 2005; Luoma, 1989; Di

Toro *et al.,* 1990; McCready *et al.,* 2006) According to Adeyemo *et al*. (2008), sediments also act as a natural buffer and filter system in the natural cycle of water and are important habitat and main nutrient source for aquatic animals.

In view of their impact in the aquatic system, some studies have been reported on the pollution of some water bodies by heavy metals. Islam *et al*. (2015) found high concentrations of some heavy metals in water (Cr>Cu>As>Ni>Pb>Cd) and sediment (Cr>Ni>Cu>Pb>As>Cd) from Korotoa River. They reported that the heavy metal levels determined exceeded the safe limits for drinking water. Although their study indicated low mobility (except Cd and Pb), calculated contamination factor and geoaccumulation index indicated moderate to heavy contamination by chromium, arsenic and lead ions. Calculated pollution index indicated progressive deterioration of the sediment quality. Varol (2011) reported eminent contamination of water and sediment of the Tigris River using contamination factor, pollution load index, geochemical index and enrichment factor. Copper contamination was alarming because there was a nearby copper mining site around the study area. High level of anthropogenic intrusion of heavy metals into the water and sediment was reported by the researcher. Sundaray *et al*. (2011) carried out geochemical speciation and risk assessment in a river estuarine sediment of the Mahanadi Basin, India. They found that the risk of cadmium, nickel and lead ions is due to their high availability in the exchangeable form. Risk profile was also established due to association, ability to co-precipitate and special affinity towards carbonate. Geo and Chen (2012) reported that Bohai Bay was one of the most polluted rivers in China. Risk factor analysis indicated heavy metal pollution particularly by cadmium due to high mobility. Other heavy metals in the sediment and water did not show significant pollution risk.

Most of the reported research carried out on heavy metal pollution of water and sediment in the Cross-River systems are concentrated in the upper Cross River systems (Akpan, and Thompson, 2013; Ayotunde *et al*., 2011, 2013, Eddy and Ukpong, 2013). Since there exist point source and non-point pollution and the ability of other part of the river system to be contaminated by pollutant sources that are quite different from the those along the upper channel, (Ali *et* al., 2016; Islam *et al.,* 2014; Varol and Sen, 2012) then there is need for an independent work on the status of heavy metal pollution in the lower Cross River. Therefore, the aim of the present study was to investigate the extent of heavy metal pollution of water and sediment in the lower part of Cross River.

2.0 Materials and Methods

2.1 Study area description

The Cross River lies between latitudes 4 º 30 ′ and 5 º 15 ′N and longitudes 8 º 00 ′ and 8 º 15′E and flows from the neighbouring Cameroon Republic through Ikom and Obubra in Cross River State, Afikpo in Ebonyi State, Okopedi in Itu, Oron to Ibaka in Mbo Local Government Area of Akwa Ibom State and into the Atlantic Ocean, covering about 352 kilometers. The river is a major source of water for the highly populated and predominantly rural population of the area. Six sampling stations were selected from the lower Cross River and within major communities along the bank of the river. The sampling stations included Ibaka, Oron, Nwaniba, Ayadehe, Okopedi and Enwang, covering a distance of about 95 kilometers (from Ibaka to Okopedi).

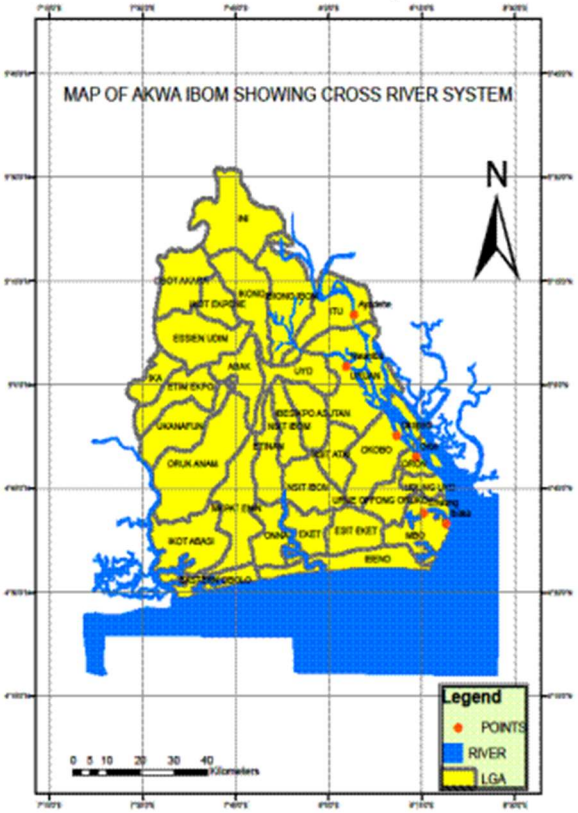

Fig. 1; map of study area showing sampling stations along Cross River

2.2 Sample collection

Water samples for trace metal analysis were collected with 1000 mL high density polyethylene bottles and acidified in-situ with 2.0 ml concentrated HNO_3 and placed in an ice-chest for transport to the laboratory where it was kept in a refrigerator at <4°C until analysis. Bottom sediment samples (at the depth of 0-5.0 cm) were collected using a stainless-steel hand trowel from each point where water samples were taken. All samples were properly labelled before preservation and analysis.

2.2 Sample treatment

An aliquot of 200 ml of the stirred water sample was filtered into a clean beaker and 3 ml of concentrated HNO_3 was added. The beaker was heated on a boiling water bath to concentrate the solution to about 15 ml. The digested water sample was allowed to cool and filtered into a 50 mL volumetric flask and made up to the mark with deionized water before transferring the content to a polyethylene sample bottle for atomic absorption spectrophotometric analysis. The bottom sediment was treated by digesting 1 g of the air-dried sample in a 200 mL platinum crucible with 10 mL of a mixture of concentrated HNO_3 and $HClO_4$ (4:1 v/v). The mixture was heated to near dryness on a water bath. On cooling, the residue was reconstituted in 5 mL HNO_3, filtered through Whatman No 1 filter paper into a 50 mL volumetric flask and made up to the mark with deionized water. The digests were stored in polyethylene bottles ready for analysis. A reagent blank was also prepared at the same time.

2.3 Determination of concentrations of metal ions

Concentrations of Cd, Pb, Cr, Co, Cu, Se, and Ni ions in water and sediment were determined using atomic absorption spectrophotometer (UNICAM 939/59).

3.0 Results and Discussions

Mean concentrations of Pb^{2+}, Cr^{6+}, Co^{2+}, Cu^{2+}, Se^{4+} and Ni^{2+} in water and sediment samples from Ibaka, Oron, Nwaniba, Ayadehe, Okopedi and Enwang are presented in Tables 1 and 2, respectively.

Mean concentration of Cd ion in water ranged from. Mean concentrations of cadmium in the sediment samples were lower than the corresponding concentrations in the water. This suggests that the contamination may be recent or the exchange rate for cadmium ions from the sediment to the water and vice versa favoured accumulation of Cd^{2+} in the water than in the sediment. The presence of some anions such as carbonates and associated metal oxides such as Fe-Mn oxides has been found to sequester other heavy metals and create association to form complexes (Sundaray *et al*., 2011).

Table 1. Mean concentration (µg l^{-1}) of heavy metal ions in surface water from lower Cross River.

Sampling station	Cd	Pb	Cr	Co	Cu	Se	Ni
Ibaka	9.50±4.8	28.17±10.6	23.67±10.37	39±15.19	36.0±13	1.47±0.31	59±30.69
Oron	20.5±13.29	13.5±7.09	20.5±9.16	17.33±7.87	20.0±5.	1.26±0.28	35.33±30.95
Nwaniba	13.83±7.81	13.0±3.90	10.67±4.23	11.67±5.24	19.0±9	1.17±0.21	12.0±2.19
Ayadehe	16.33±10.63	26.67±9.91	19.0±17.42	27.17±3.54	26.0±6	1.03±0.05	22.5±7.56
Okopedi	10.0±3.56	16.0±4.90	11.0±2.53	16.83±4.62	28.0±9	1.04±0.49	15.83±5.95
Enwang	12.0±7.13	25.83±13.64	23.17±14.11	36.83±15.09	32.0±13	1.13±0.31	51.33±23.63
Mean±SD	13.69±8.97 (64.49)	20.53±10.60 (51.65)	18±11.47 (63.71)	24.81±13.91 (56.07)	26.9±11 (40.74)	1.18±0.32 (27.02)	32.67±26.16 (80.08)
Range	BDL-44	2-43	4-53	5-55	10-55	0.23-1.82	5-95

**** Coefficient of Variation (%) in parenthesis**

Table 2. Heavy metal concentrations (μg g^{-1}) in sediment from lower Cross River

Sampling Station	Cd	Pb	Cr	Co	Cu	Se	Ni
Ibaka	0.72±0.17	76.88±10.10	24.1±1.51	7.45±0.73	92.03±8.71	0.97±0.50	6.37±0.99
Oron	0.39±0.09	55.52±13.52	19.43±2.68	7.83±3.39	78.55±14.13	0.52±0.55	9.18±3.30
Nwaniba	0.63±0.13	67.42±5.61	16.38±2.07	9.68±0.77	67.05±8.91	0.43±0.33	7.93±1.19
Ayadehe	0.55±0.10	47.54±5.66	13.74±2.52	7.94±1.17	50.60±5.63	0.55±0.27	6.58±1.03
Okopedi	0.69±0.14	60.38±7.43	9.72±3.27	7.95±1.40	75.97±10.26	0.85±0.30	7.12±0.94
Enwang	0.11±0.09	41.02±14.12	14.07±5.38	4.30±1.47	53.83±7.57	1.17±0.12	4.00±1.63
Mean±SD	0.52±0.24 (46.25)	57.78±15.60 (27)	16.22±5.48 (33.79)	7.52±2.28 (30.32)	69.81±16.90 (24.21)	0.75±0.44 (58.67)	6.87±2.26 (32.90)
Range	0.06-0.85	27.6-88.1	6.7-26.1	2.9-11.2	41.3-103.1	0.01-1.43	2.8-12.2

****Coefficient of variation, CV (%) in parenthesis; SD = Standard deviation**

In order to test for the statistical differences between concentration of heavy metal ions in water and in the sediment (including Cd^{2+}). t-test statistics was used. Calculated values of 't' were obtained using the following formula,

$$t = \frac{\overline{X_2} - \overline{X_1}}{\sqrt{\frac{s_2^2}{n_2} + \frac{s_1^2}{n_1}}} \quad (1)$$

where X_2 and X_1 are means of sample set 2 and 1, respectively, while the corresponding standard deviations are S_2 and S_1, respectively, n_1 and n_2 are the sample size for set 1 and 2, respectively. Calculated t-values are presented in Table 3. It is seen from the results that there is a significant difference between concentrations of cadmium ions in water and sediment ($t_{cal} > t_{tab}$ at $\alpha = 0.05$ and 0.01) as shown in Table 3. The significant differences are applicable to concentrations of cadmium ion in all the sampling stations and for the overall mean. Therefore, concentration of cadmium ion in the water is significantly higher than the concentration in the sediment. Coefficient of determination was very low while Pearson correlation coefficient (r) was negative indicating that cadmium ion concentration in the water increases as its concentration in the sediment decreases. This also implies that the observed trend may be due to a shift in equilibrium between the concentration of cadmium in the water and sediment due to reasons explained earlier.

Table 3: Calculated t-values for heavy metals in water and sediments

Station	Cd	Pb	Cr	Co	Cu	Se	Ni
Ibaka	5.4841	18.5436	0.2161	4.9036	20.8282	0.9623	70.3298
Oron	4.5394	16.0316	0.5386	1.4060	23.1862	1.4069	7.7393
Nwaniba	5.0697	30.5653	3.9403	15.3472	19.6656	1.7442	3.8344
Ayadehe	4.4532	9.1609	2.0403	6.2687	12.4941	1.4697	9.4082
Okopedi	7.8394	21.8910	0.9206	13.8457	18.9322	0.3703	5.8134
Enwang	5.0024	4.9935	3.5702	7.4427	7.9588	-0.1057	16.3175
Grand mean	7.5165	12.6144	0.7489	0.5319	14.3659	0.8543	8.3824
R^2	0.1048	0.0257	0.3287	-0.7293	0.0410	0.0332	0.2497
R	-0.3237	-0.3237	0.5733	4.9036	0.2025	0.181	-0.4997

**** R^2 is the coefficient of determination while r is the Pearson correlation coefficient**

****Tabulated t-values are 2.132 at α = 0.05 and 3.747 at α = 0.01**

Correlation between cadmium ion and other metals in the water did not reveal any unique association (Table 4) which confirmed the existence of exchange of cadmium ion between the sediment and the water. However, there was a strong evidence from Pearson correlation analysis of correlation between cadmium and lead and also between cadmium and cobalt in the sediment (r =0.657 and 0.559 for lead and cobalt ions, respectively) as shown in Table 5. Such remarks could not be observed for other metals even if R-values were positive (except for Se^{4+}) because R-values are very weak and also Indicate weak association between the observed components

Table 4: Pearson Correlation Coefficient of Trace Metal of Surface Water Samples from Cross River System

	Cd	Pb	Cr	Co	Cu	Se	Ni
Cd	1						
Pb	0.016	1					
Cr	0.043	0.251	1				
Co	-0.109	.698[a]	.569[a]	1			
Cu	-0.075	.579[a]	.371	.591[a]	1		
Se	0.238	0.078	0.193	0.261	0.192	1	
Ni	-0.063	.553[a]	.528[a]	.804[a]	.541[a]	0.301	1

Comparison of mean concentration of cadmium ions in sediments with different sediment quality requirement (Table 6) indicate that there is no serious contamination in the lower Cross River due to cadmium ion. Mean lead ion concentration in the surface water of the lower Cross River ranged from 13.0 to 28.17 µg/L. Highest mean concentration (28.17 µg/L) of Pb was recorded at Ibaka while the least concentration (13.0 µg/L) was recorded at Nwaniba

Table 5: Pearson Correlation Coefficient of Trace Metal in Sediment from Cross River

Cd	Pb	Cr	Co	Cu	Se	Ni
657[a]	1					
).127	.463[a]	1				
559[a]	.376	0.150	1			
489	.651[a]	.600[a]	0.276	1		
.349	-0.186	0.010	-.450	0.013	1	
).299	0.156	0.187	.392	0.298	.346	1

**** a dignify that correlation is significant at the 0.05 level (2-tailed).**

. Calculated Pearson correlation coefficient for lead in water and sediment was negative (R = -0.3237) as indicated in Table 3. This indicate that there is a competition in the distribution of lead and cadmium ions between the water and the sediment since both metals are divalent. The association between lead and cadmium in water was very weak (Table 4) but positive in sediment (Table 5). From the results presented in Table 3, there is a significant difference between the concentration of lead in water and sediment of the lower Cross River. Also, the concentration of lead ion in sediment is significantly higher than the concentration in the water at all sampling locations at α = 0.05 and 0.01 (Table 3)

Table 5: Comparison of sediment metal concentration (µg g^{-1} dry weight) of Cross River with Sediment Quality Guidelines (SQGs)

Metal ion	C (µg g^{-1} dry weight)	NOAA		FDEP		CCME (marine)		CCME (fresh)		Ontario		Contamination Level
		ERL[+]	ERM[a]	TEL	PEL[+]	IG[c]	PEL[+]	IG[c]	PEL[+]	LEl[+]	SEL	
Cd	0.52±0.24 (0.06 - 0.85)	1.2	9.6	0.68	4.21	0.7	4.2	0.6	3.5	0.6	10	No contamination
Pb	57.18±5.60 (27.6-88.1)	46.7	218	30.2	1.12	30.2	1.12	3.5	91.3	3.1	2.50	Intermediate
Cr	16.22±5.48 (6.7-26.1)	81	37.0	52.3	1.60	62.3	16.0	37.3	90.0	2.6	1.10	Intermediate
Co	7.52±2.28 (2.9 -11.2)	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	50*	50*	Not ranked
Cu	69.81±6.90(41.3-10.39)	3.4	28.0	18.7	10.8	18.7	10.8	15.7	1.97	16	10	Intermediate
Se	0.75±20.44 (0.01-1.43)											
Ni	6.87±2.26 (2.8-12.2)	20.9	51.6	15.9	42.8	n.g*	n.g*	n.g*	n.g*	16	75	No contamination

****ERL = Effect Range Low; ERM = Effect Range Median; TEL = Threshold Effects Level; IG = Interim Guideline; PEL = Probable Effect Level; LEL = Low Effect Level; SEL = Severe Effect Level; *ng = no guideline; SQG = Sediment Quality Guideline.**

The highest concentrations of chromium (23.67 µg/L), cobalt (39.00 µg/L), copper (36.00 µg/L), selenium (1.47 µg/L) and nickel (59.00 µg/L) ions in the surface water of lower Cross River were recorded at Ibaka while the lowest concentrations of chromium (10.67 µg/L), cobalt (11.67 µg/L), copper (19.00 µg/L) and nickel (12.00 µg/L) ions were observed at Nwaniba with that of selenium (1.03 µg/L) at Ayadehe.

In the sediment, highest mean concentrations for cobalt, selenium and nickel ions were observed at Nwaniba (9.68 µg/g), Enwang (1.17 µg/g) and Oron (9.18 µg/g), respectively whereas Ibaka had the highest mean concentrations of cadmium (0.72 µg/g), lead (76.88 µg/g), chromium (24.1 µg/g) and copper (92.01 µg/g). However, the corresponding least concentrations for chromium, copper and selenium were recorded at Okopedi (9.72 µg/g), Ayadehe (50.60 µg/g) and Nwaniba (0.43 µg/g), respectively while the lowest concentrations for cadmium (0.11 µg/g), lead (41.02 µg/g), cobalt (4.30 µg/g) and nickel (4.00 µg/g) were obtained from Enwang. Concentrations of the metal ions investigated were found to be significantly different from each other except foe selenium at Ibaka and cadmium at Ibaka, Oron and Okopedi (Table 3).

From the inter-correlation Table for the concentrations of metal ions in water, it is observed that chromium ion displayed relatively weak association with cobalt ($r = 0.569$) but very weak with other metals ($r < 0.4$). Cobalt showed strong and significant association with nickel ($r = 0.804$) and relatively weak association with copper ($r = 0.591$) but very weak with selenium ($r = 0.261$). Copper showed relatively strong and significant correlation ($r = 0.541$) with only nickel. Nickel also displayed relatively positive correlation with chromium and lead ions as shown in Table 4.

In the sediment sample, no strong positive or negative correlation was observed. However, relatively strong positive correlation was observed between copper and lead ($r = 0.651$), copper and chromium ($r = 0.600$) and between lead and cadmium ($r = 0.657$). Comparison of mean concentrations of chromium, copper, selenium and nickel with quality requirements from different agencies (Table 6) indicates that there was intermediate contamination of the sediment of the lower Cross River except for nickel (no contamination), selenium and cobalt where records were not provided.

4.0 Conclusion

The study of surface water and sediment quality of the lower Cross River in Akwa Ibom State revealed that the river had no serious contamination at the time of investigation. However, intermediate contaminations were observed with respect to lead, chromium and copper, indicating the possibility of a future threat to the quality of this aquatic environment if activities releasing these metal ions are not cheeked.

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