Journal of Natural Sciences Research
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.3, No.11, 2013

Seasonal Variations in Heavy Metal Status of the Calabar River, Cross River State, Nigeria

Ewa, E.E.[1], Iwara, A.I.[2], Offiong, V.E.[3], Essoka, P. A.[1], & Njar, G.N[1]

1. Dept. of Geography & Environmental Studies, University of Calabar, Nigeria.
2. Dept. of Geography, University of Ibadan, Nigeria.
3. Dept. of Urban & Regional Planning, CRUTECH, Calabar, Nigeria
   Corresponding author's email:iwaradream2008@gmail.com

Abstract
The study examined heavy metal status of the Calabar River in Cross River, Nigeria. Surface water samples were collected during the wet and dry seasons for ten months across five stations and analyzed for heavy metal parameters using standard methods. Result showed that the concentrations of iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), lead (Pb) and total hydrocarbon (THC) in the dry and wet seasons were low and within WHO and FEPA tolerable limits The proportion of copper (Cr), cadmium (Cd), barium (B), nickel (Ni), vanadium (V) and mercury (M) were not detected indicating the absence of these metals in the sampled stations. The low levels of heavy metal contents across the sampled stations showed they were not polluted and as such suitable for aquatic live. Independent samples test result indicated seasonal difference in the proportion of Fe, Zn, Cu, Pb and THC ($p<0.01$).The study identified runoff from industrial, agricultural and residential areas as sources of heavy metal pollution in the wet season and effluent discharges from industrial and municipal wastes as major sources of pollution of the Calabar River in the dry season. To sustain the ecological status of the Calabar River, waste management practice of waste re-use through the use of retention ponds is encouraged.

Introduction
World-wide, heavy metal contamination in water, sediment or plant is an increasing environmental concern (Ahmed et al., 2005). In different parts of the world, rivers have been used as a major sink of industrial and municipal wastes as well as a recipient of toxic and solid waste from agricultural runs off. Water pollution by heavy metals due to human activities is causing serious ecological problems in many regions of the world. Metals which are discharged into natural waters at increased concentrations in sewage, industrial effluents or from mining operations can have severe toxicological effects on humans and aquatic ecosystems (Mondol et al., 2011). Heavy metals are environmental pollutants, and their occurrence in water, soil and plant indicates the presence of natural or anthropogenic sources (El Bouraie et al., 2010). The main natural sources of metals in waters are chemical weathering of minerals and soil leaching.
The anthropogenic sources are usually associated with industrial and domestic effluents, urban storm, water runoff and landfill among others (Zarazua et al., 2006). Human and industrial activity has disturbed the natural environment, particularly the aquatic ecosystems. The production and use of heavy metals has led to widespread environmental contamination and cause of concern now in urban and rural areas. Some of these compounds are the object of study because of their toxicity and ubiquity and they are known to remain stable in the aquatic environment (Singh and Singh 2006). Heavy metals are non-degradable and harmful to plants, aquatic organisms and human health at certain levels of exposure (Mustafa and Nilgun, 2006; Singh and Upadhyay, 2012). The Calabar River is adjoined by the Calabar Port Authority, residential, agricultural and mangrove land-uses.

The Calabar Port ecosystem contributes immensely to the economic development and environmental security of the state and country as a whole (Offiong et al., 2012), but, the presence of industries and increasing urbanization in the area are immensely affecting the water resources available. The poor effluent management from industries has negatively impacted on the water quality resulting in the change of its natural contents. The industrial activities in the area include food processing, fuel bunkering, corrugated iron sheets, logging and shipping. The most serious risks of industrial production activities in the area include air and water pollution which stems from the discharge of effluents (in gaseous, solid and liquid forms) without prior treatment into the Calabar Rivers. This perhaps is of great concern to the terrestrial and aquatic environment. Indeed, the Calabar River is a major sink of industrial, agricultural and municipal wastes in the area. The present study was carried out to assess the seasonal proportion of heavy metal in the Calabar River.

Materials and methods
Study Area
The Calabar River was the study environment found in Calabar, Cross River State. The river encloses Esuk Nsidung Calabar south Adiabo brige in Odukpani Local Government Areas. The Calabar River is a major tributary of the Cross River, originates from Oban hills Nigeria and flows through black shale and siltstone,

clayey, sand and silts deposits, before entering the estuary at Alligator Island (Etim and Enyenihi, 1991). The River has an estimated area of 54,000 square kilometers and stretches about 25km to the south of the river. The Calabar River is hydro-dynamically homogenous. Dissolved particulate materials are transported by surface current from the estuary into Creeks and upper reaches of Calabar River within the industrial area of Esuk Nsidung to Adiabo-Bridge head during semi diurnal tide (Asuquo et al., 1999). The river is a recipient of toxic substances from industrial, agricultural and municipal discharges

Sampling Technique

Surface water samples were collected bi-monthly for the wet and dry seasons. A total of 10,800 water samples were collected for both dry and wet seasons for ten months across five study stations. Samples were collected for water quality assessment and bacteriological studies along the industrial area of the Calabar River, using a mini research boat (Plankton Fisher). The samples were collected within the industrial distance area of 16,704.3 meters seaward (author field survey) that is, from Adiabo bridge head to Esuk Nsidung beach. This covers five geo-referenced equidistance stations of 3,340.3 metres each. Water samples for physico-chemical parameters were collected using 1-liter plastic containers and stored in cool box at approximately 4^0C; while heavy metal and hydro-carbon samples were collected with glass bottles, preserved with metallic acid before laboratory analysis.

Analytical Methods

pH, electric conductivity (EC), total dissolved solids (TDS) and dissolved oxygen (DO) were measured with a multi-meter, while chemical oxygen demand (COD), sodium, sulphate, nitrate, salinity, calcium, ammonium, phosphate, potassium, and magnesium were determined according to the method by APHA-AWWA (2005). Biological oxygen demand (BOD) was determined in sample and concentration after 5 days incubation in DO bottles at 20^o C (APHA, 1998).Hardness was determined by standard EDTA titration methods (DWAF, 1992). Fecal coliform counts were performed using the standard membrane filtration method. The mfc was used for fecal coliform counts, while total hydrocarbon (THC) was determined using as spectrophotometer (API-RP-45).

Data Analysis

Obtained heavy parameters were grouped in two different periods (wet and dry season) and the SPSS for windows (Version 20.0) was used for analysis. Independent samples test was used to find out if the parameters differed between the two seasons, while Pearson's correlation was employed to understand the nature of association between the parameters.

Results and discussion

Table 1 show that the pH level is alkaline with pH values ranging from 6.10 to 7.10. The pH value is high in the dry season and low in the wet season with average values of 7.03 and 6.30 respectively. This implies that the pH level of the stream may not affect the metal solubility and hardness of the water. A river with high alkalinity levels according to Ipeaiyeda & Onianwa (2011) will be able to supply adequate amounts of carbonate, bicarbonate and hydroxide ions in solution to bind up free protons and metals. Increase in alkalinity level during the dry season reduces water acidity of the Calabar River as reflected in measures of water pH (7.03). A river with high pH generally contains elevated levels of dissolved solids (Ipeaiyeda & Onianwa, 2011). The pH values obtained across the Calabar River in both seasons were within WHO and FEPA maximum tolerable level of 8.5 respectively.

The Table indicates that the concentration of iron (Fe) was high with an average value of 7.032 mg/L in the dry season, while the value was low in the wet season with an average value of 6.30 mg/L (Table 1). The Fe values in both seasons fell within WHO and FEPA maximum tolerable level of 50 mg/L respectively. The generally low concentrations of Fe in the river imply it does not have the potentials to disrupt aquatic life and cannot cause adverse effects on aquatic organism within the vicinity. Zinc (Zn) content was observed to be relatively high in the dry season, but low in the wet season with mean values of 0.03 mg/L and 0.02 mg/L respectively. Zn values in values both seasons happened to fall within WHO tolerable level of 1.0 mg/L. This shows that the river contains the right proportion of Zn which is an essential plant and human nutrient element. The low concentration also implies the Calabar River is ideal for domestic uses and adequate to support aquatic life (Iwara et al., 2012). Copper (Cu) concentration was high in the wet season and low in the dry season with average values of 0.26 mg/L and 0.17 mg/L respectively. Cu values in both seasons were far below WHO and FEPA maximum tolerable level of 2 mg/L respectively. The Cu content across the course of the Calabar River is not toxic to aquatic life as such would not cause any damage to aquatic organism. Copper is one of the most toxic metals to aquatic organisms and ecosystems and it is moderately soluble in water and binds easily to sediments and organic matter. Solomon (2009) noted that fish and crustaceans are 10 to 100 times more sensitive to the toxic effects of copper than are mammals; and that algae especially blue-green algae species, are 1,000 times more sensitive to the toxic effects of copper than are mammals. The increase in Cu content in the wet season may be attributed to the weathering of rock mineral pollution and an increase in organic pollution from runoff

For manganese (Mn), high value in surface water was recorded in the wet season with an average value of 0.65 mg/L, while low concentration in Mn was noticed in the dry season with an average value of 0.06 mg/L. Mn values in the dry season happened to fall within WHO tolerable level of 0.5 mg/L, its concentration in the wet season was above WHO tolerable limit of 0.5 mg/L. The high concentration of Mn in the wet season implies the river would facilitate algae growth during this season (Nwankwoala et al., 2011).The high value of Mn concentration in the wet season was attributed to the dilution of the Calabar River. This is in agreement with other studies (Rajmohan and Elango, 2005) as well as runoff from industrial effluents within the river catchment (Mondol et al., 2011).

In addition, high lead (Pb) proportion at the five sites was recorded in dry season, while low values were recorded in the wet season with average values of 3.1 mg/L and 0.40 mg/L respectively (Table 1). Pb values in both seasons were above WHO and FEPA tolerable levels of 0.01 mg/L respectively. The values recorded in the dry season were fare above WHO and FEPA acceptable limits compared to the values recorded in the wet season. The high levels of Pb in the dry season may be attributed to industrial and agricultural discharge (Mason, 2002). The proportion of chromium (Cr), cadmium, barium, nickel, vanadium and mercury were not detected throughout the study, indicating the absence of these metals in the sampled stations across the Calabar River (Table 1). This undetectable level of heavy metal was also reported by Asuquo et al., (1999) for Calabar South and Bakassi.

Nevertheless, the concentration of total hydrocarbon (THC) was found to be high in the wet season withan average value of 27.99 mg/L, while low values were recorded in the dry season with an average value of 21.07 mg/L. THC values in both seasons were very far above WHO and FEPA maximum tolerable level of 10 mg/L respectively. The high THC value in the dry season may be attributed to runoff from crude oil activities from industries within the river catchment. Similar studies observed high THC concentration in wet than during the dry season (Olsen et al., 1993). The heavy metals content in the Calabar River are associated with crude oil activities and municipal waste discharges within the river catchment. Chindah and Sibeudu (2003) attributed the predominance of heavy metals in the river system to oil industries activities and municipal waste charges within the river vicinity.

Table 1: Summary of heavy metal parameters

Parameters	Water parameters				Water standards	
	Dry season		Wet season			
	Range	Mean	Range	Mean	WHO	FEPA
pH	6.9-7.10	7.03	6.1-6.6	6.30	6.5-8.5	6.5-8.5
Iron (mg/L)	0.018-0.04	0.03	0.018-0.03	0.02	50	50
Zinc (mg/L)	0.0184-0.06	0.03	0.0224-0.14	0.08	1.0	
Copper (mg/L)	0.126-0.22	0.17	0.03-0.32	0.26	2	2
Manganese (mg/L)	0.022-0.24	0.07	0.026-0.10	0.65	0.5	
Lead (mg/L)	2.0-4.40	3.1	0-2	0.40	0.01	0.01
Chromium (mg/L)	0	-	0	-	0.5	0.5
Cadmium (mg/L)	0	-	0	-	0.02	
Barium (mg/L)	0	-	0	-	0.01	0.01
Nickel (mg/L)	0	-	0	-	0.7	0.7
Arsenic (mg/L)	0	-	0	-	-	
Vanadium (mg/L)	0	-	0	-	0.01	0.01
Mercury (mg/L)	0	-	0	-	0.001	0.001
THC (mg/L)	19.46-24.88	21.70	25.74-31.44	27.99	10	10

Furthermore, the result in Table 2 gives information on the seasonal differences in heavy metal concentration in the Calabar River. It indicates that the proportion of Fe, Zn, Cu, Pb and THC differed significantly between the dry and wet seasons, whereas, the amount of Mn in the water body of the Calabar River did not differ significantly between both seasons. This implies that the proportion of metals in the river is seasonal dependent as its amount either increases or decreases. For example, Pb proportion increased during the dry season, while Cu amount in the river was observed to be high in the wet season as a result of mineral weathering and runoff from industrial, agricultural and residential land-uses.

Table 2: Independent samples test result of the difference in heavy metal contents

	Seasons	Mean	Std. Error Mean	t-Value
Fe (mg/L)	Dry season	0.030	0.002	2.452*
	Wet season	0.023	0.001	
Zn (mg/L)	Dry season	0.029	0.004	4.490**
	Wet season	0.082	0.011	
Cu(mg/L)	Dry season	0.172	0.010	2.913**
	Wet season	0.259	0.028	
Mn (mg/L)	Dry season	0.071	0.021	0.956 ns
	Wet season	0.049	0.008	
Pb(mg/L)	Dry season	3.100	0.331	6.348**
	Wet season	0.405	0.266	
THC (mg/L)	Dry season	21.702	0.550	7.960**
	Wet season	27.994	0.568	

**Significant at 1% alpha level
*Significant at 5% alpha level
ns = not significant at 5% alpha level

Pearson's correlation matrix in the dry and wet season

The Pearson's correlation matrix in Table 3a indicates positive and negative associations between the parameters. It shows that high positive and significant correlations existed between THC and Zn; while positive and insignificant association were observed between Fe and pH, Zn and Fe, Zn and Ph, Cu and Ph, ph and Pb, Pb and Fe, Pb and Zn among others. The positive relations is an indication that increase in one of the parameters results in a resultant increase in the other and vice versa The positive associations imply that the assigned parameters are influenced by similar anthropogenic and natural factors. On the other hand, negative and insignificant associations were also observed between Mn and pH, THC and pH, Cu and Zn, Mn and Zn, Mn and Cu and THC and Mn. These negative associations indicate that increase in one of the parameters results in the decrease of the other and vice versa. The negative associations suggest that the metals do not have identical sources of pollution, as their sources of pollution differ. It is perhaps an indication of varied pollution sources.

Table 3a: Pearson's correlation matrix in the dry season

Parameters	pH	Fe	Zn	Cu	Mn	Pb	THC
pH	1						
Fe	0.124	1					
Zn	0.240	0.434	1				
Cu	0.202	0.298	-0.056	1			
Mn	-0.029	0.408	-0.085	-0.097	1		
Pb	0.276	0.455	0.455	0.517	0.274	1	
THC	-0.023	0.312	0.660*	0.038	-0.048	0.548	1

*Significant at 5% alpha level

Furthermore, for the wet season, negative and significant correlation was observed between THC and Mn; while insignificant associations were observed between MNe and pH, Cu and Fe, Cu and Zn, Mn and Zn, Mn and Cu, Pb and Fe, Pb and Zn, THC and Pb among others (Table 3b). While, positive and insignificant associations were observed between Mn and Fe, Pb and Mn, THC and Fe, THC and Zn, and between THC and Cu. As usual, the negative associations suggests varied sources of pollution between the parameters, while positive association is an indication of common and similar pollution sources (Iwara et al., 2012).

Table 3b: Pearson's correlation matrix in the wet season

Parameters	pH	Fe	Zn	Cu	Mn	Pb	THC
pH	1						
Fe	0.02	1					
Zn	0.331	-0.018	1				
Cu	0.382	-0.235	-0.080	1			
Mn	-0.212	0.436	-0.467	-0.458	1		
Pb	-0.462	-0.129	-0.071	-0.487	0.543	1	
THC	-0.029	0.077	0.317	0.356	-0.685*	-0.315	1

*Significant at 5% alpha level

Conclusion

The results reveal that the proportion of heavy metal in the Calabar River indicates no potential threat to aquatic life as the measured parameters are low and within WHO and FEPA permissible levels for surface water. Both seasons have substantial influence on the proportion of metals in the river, and the proportions of Fe, Zn, Cu Pb and THC differ in both seasons. The study identifies runoff from industrial, agricultural and residential areas as sources of pollution in the wet season and as effluent discharges from industrial and municipal wastes as major sources of pollution of the Calabar River in the dry season. To sustain the ecological status of the Calabar River, waste management practice of waste re-use through the use of retention ponds is encouraged.

References

Ahmed, A., Dilek, D. and Fatih, D. (2005) Bioaccumulation, detection and analyses of heavy metal pollution in sultan marsh and environment. *Water, Air and Soil Pollution,* 164: 241.

APHA (1998) Standard method for the examination of water and waste water 20th ed. American Public Health Association Washington, DC.

APHA-AWWA (2005) Standard method for water and waste water Examination. 21st edition. American water works Association; Washington, DC.

Asuquo, F.E., Ogri, O.R. and Bassey, E.S. (1999) Distribution of heavy metals and total hydrocarbons in coastal waters and sediments of Cross River, South-eastern Nigeria. *International Journal of Tropical Environment,* 1 (2): 1 – 19.

Chindah, A. C. and Sibeudu, O. C. (2003) Levels of Hydrocarbons and heavy metals in sediment and a decapod crustacean (Crab – Uca Tangeri) in the Bonny/New Calabar River Estuary, Niger Delta. *Pollut J Environ Protect*, 25/26: 55-71

DWAF (1992) Analytical methods Manual, TR 151. Department of Water Affairs & Forestry, Pretoria.

El Bouraie, M.M., El Barbary, A.A., Yehia, M.M. & Motawea, E.A. (2010) Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt. Suo, *61(1): 1–12.*

Etim, L. and Enyenihi, U.K. (1991) Annual cycle of condition and flood season spawning in *Galatea Paradoxa* (Born, 1977) from the Cross River, Nigeria. *Tropical Freshwater Biology*, 2: 243 – 248.

Ipeaiyeda, A.R. and Onianwa, P.C. (2011) Pollution effect of food and beverages effluents on the Alaro River in Ibadan City, Nigeria. *Bull. Chem. Soc. Ethiop.,* 25(3): 347-360.

Iwara, A. I., Njar, G. N., Deekor, T. N., and Ita, A. E. (2012) Effect of Adiabo abattoir on the water quality status of Calabar River in Odukpani, Cross River State, Nigeria. *Continental J. Environmental Sciences*, 6 (2): 36 – 43.

Mason, C. F. (2002) Biology of freshwater pollution. 4rd ed. Essex Univ. England. 387 pp.

Mondol, M.N., Chamon, A.S., Faiz, V. and Elahi, S.F. (2011) Seasonal variation of heavy metal concentrations in water and plant samples around Tejgaon Industrial area of Bangladesh. *Journal of Bangladesh Academy of Sciences,* 35 (1): 19-41.

Mustafa, S. and Nilgun, D.E. (2006) Copper(II)-rubeanic acid coprecipitation system for separation-preconcentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations. *J. Haz. Mat.,* 137: 1035-1041.

Nwankwoala, H. O., Udom, G. J. and Ugwu, S. A. (2011) Some heavy metal investigations in groundwater sources in Yenagoa, Bayelsa State, Nigeria. *Journal of Applied Technology in Environmental Sanitation,* 1 (2): 163-170.

Offiong, R. A., Iwara, A. I., Njar, G. N. and Atu, J. E. (2012) Effects of industrial activities on the structure and floristic pattern of vegetation within the Calabar Port Authority, south-southern Nigeria. *Journal of Geography and Geology,* 4 (1):203 – 211.

Olsen, C. R., Larsen, I. L., Mulholland, P.J., et al., (1993) The concept of an equilibrium surface applied to

particles sources and contamination distribution in estuarine sediment. *Estuar*, 16: 683-96.
Rajmohan, N. and Elango, L. (2005) Distribution of iron, manganese, zinc and atrazine in groundwater in parts of Palar and Cheyyar River Basins, South India. *Environ. Monit. Assess.,* 107: 115-131.
Singh, J., Upadhyay, S.K., Pathak, R.K. and Gupta, V. (2011) Accumulation of heavy metals in soil and paddy crop (*Oryza sativa*), irrigated with water of Ramgarh Lake, Gorakhpur, UP, India. *Toxicol. Environ. Chem.,* 93(3): 462-473.
Singh, V.K. and Singh, J. (2006) Toxicity of industrial wastewater to the aquatic plant *Lemna minor L. Journal of Environmental Biology,* 27:385-390.
Solomon, F. (2009) Impacts of copper on aquatic ecosystems and human health. Retrieved from<MINING.com>
Zarazua G., Ávila-Pérez P., Tejeda S., Barcelo-Quintal, I. and Martínez T.(2006) Analysis of total and dissolved heavy metals in surface water of a Mexican polluted river by Total Reflection X-ray Fluorescence Spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy,61, 1180-1184.