

*Full Length Research Paper*

# Seasonal variation of enrichment and contamination of heavy metals in the surface water of Qua Iboe River Estuary and adjoining creeks, South-South Nigeria

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Received 19 December, 2013; Accepted 8 April, 2014

Seasonal variation of the distribution pattern, enrichment and contamination of some heavy metals (Cd, Cr, Fe, Pb, Zn, Ni and Cu) in surface water of Qua Iboe river estuary and adjoining creeks were investigated using physicochemical parameters. The results of wet season mean concentrations (mg/l) were: Cd ( $0.09 \pm 0.02$ ), Cr ( $0.05 \pm 0.02$ ), Cu ( $0.05 \pm 0.01$ ), Fe ( $10.68 \pm 1.91$ ), Pb ( $0.06 \pm 0.01$ ), Zn ( $0.08 \pm 0.03$ ) and Ni ( $7.4 \pm 1.31$ ) while the dry season mean concentrations (mg/l) revealed Cd ( $0.06 \pm 0.02$ ), Cr ( $0.04 \pm 0.02$ ), Cu ( $0.02 \pm 0.004$ ), Fe ( $7.36 \pm 1.94$ ), Pb ( $0.03 \pm 0.008$ ), Zn ( $0.03 \pm 0.01$ ) and Ni ( $5.17 \pm 1.73$ ). The wet season mean concentration of heavy metals were higher than the dry season. Concentration data were processed using Pearson correlation matrix to identify the inter-relationships between physicochemical parameters as well as the sources of heavy metals. The results showed that salinity, pH and temperature among others played a significant role in the adsorption/desorption and dissolution of heavy metals in the surface water. The Enrichment factor (*EF*) calculated during the wet season in surface water ranged from 0.2 to 2.9 while the *EF* calculated during the dry season ranged from 0.2 to 1.9. During wet season, Cd, Cu, Fe, Pb and Zn showed minor surface enrichments while Cr and Ni showed no enrichment. During dry season, Cd, Fe and Zn were moderately enriched in surface water while Cr, Cu, Pb and Ni were not enriched. Surface enrichment was attributed to atmospheric deposition, released of sediment bound metals to the surface, dissolution/erosion of coastal sediments as well as anthropogenic input. The computed degree of contamination indicated that the river system was moderately contaminated during dry season but highly contaminated during wet season. The implication is that during flooding which is consequent upon climate change, there will be higher degree of contamination of Qua Iboe River estuary and adjoining creeks.

**Key words:** Heavy metals, seasonal variations, surface enrichments and contamination, Qua Iboe estuary.

## INTRODUCTION

Pollution refers to the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in deleterious effects such as harm to living resources, hazards to human health, hindrance to marine activities including

fishing, impairment of quality for use of sea water and reduction of amenities (GESAMP, 1993).

Estuarine pollution may be defined as the human introduction to an estuary of any substances such as chemicals and waste products that are hazardous or

potentially harmful to the estuarine ecosystem (Tomlinson et al., 1980). This includes pollutants that are directly toxic to plants and animals, as well as materials that overload the estuary's capacity to assimilate wastes and thus deplete essential oxygen (Tomlinson et al., 1980).

Rivers and creeks are direct recipients of industrial waste and municipal sewage. They also drain urban, suburban, and rural areas where they collect more pollutants and litter. As they move toward the coast, they gather or join the waters of other streams (Süren et al., 2007). They eventually reach the sea, usually via an estuary, the area where fresh and salt water meets. Most of the estuaries themselves are bordered by dense population and industrial development that add significantly to the water's pollution load.

Heavy metals are chemical elements with a specific gravity that is at least four to five times the specific gravity of water at the same temperature and pressure (Garbarino et al., 1995; Duruibe et al., 2007) and are among the most common environmental pollutants and their occurrence in waters, sediments and biota is as a result of inputs from natural or anthropogenic sources which may include wind-blown dust, forest fires, gas flaring, atmospheric deposition through rain fall, industrial and urbanization processes such as fossil fuel combustion, waste incineration, industrial effluents discharge, sewage, paints, etc. (Wittmann et al., 1981). The pollution of surface water bodies, especially with heavy metals, has gained a global concern over the industrial age (Uwah et al., 2013). This is because the primary producers which are the building block of the marine food web inhabit the photic zone. The introduction of environmental pollutants into the aquatic systems is a common phenomenon in Nigeria (Abu and Egenonu, 2008). Urbanization and industrialization is one of the main indices of national and global development, but sometimes, while it enhances the quality of life, it also poses serious threats to the management of the natural ecosystem and public health (Umoren and Onianwa, 2005).

The existence of heavy metals in surface water has led to serious concerns about their influence upon aquatic flora, fauna as well as human populace who subsist on aquatic resources. In surface water, most heavy metals adhere to particulate matter and are taken up by planktons and benthos, animals, most of which are filter feeders (Schubel and Kennedy, 1984). Consequently, the toxins are concentrated in the pelagic food chains and many particles combine chemically in a manner highly depletive of oxygen, causing estuaries to be anoxic (Law, 2000).

Once these particles are incorporated into the marine

ecosystem, they quickly become absorbed into the food web leading to mutations, change in tissue matter, biochemistry, behavior, reproduction and suppress growth in marine life as well as disease which can be harmful to humans (Selman, 2007). The persistence and non-biodegradability of heavy metals may result in their bioaccumulation and bio-magnification in the marine environment and thus they are also known as 'chemical time bombs' (Salati and Moor, 2009). The concentration of most metals in river system varies significantly between seasons and also dependent on the geology of the study area (Ogri et al., 2011).

Water quality is defined in terms of chemical, physical and biological content and the quality changes with season and geographical areas (Suski et al., 2006). Important physical and chemical parameters influencing the aquatic environment are pH, salinity, temperature, rainfall, dissolved oxygen and carbon dioxide, total suspended and dissolved solids, heavy metals contaminants, etc (Suski et al., 2006).

The study of the seasonal variation, enrichment and the level of contamination of heavy metals with respect to physicochemical parameters in the surface water of Qua Iboe River estuary become imperative because the estuary is very rich in nutrients and as a result mothers wide varieties of fishery resources. This present study is aimed at assessing the seasonal variation in concentration of some heavy metals (Cd, Cr, Cu, Zn, Pb, Ni, and Fe) in surface water of Qua Iboe River estuary and adjoining creeks with a view to identify the controlling factors, the sources of enrichment / distribution patterns as well as the level of contamination of the estuary.

## MATERIALS AND METHODS

### Description of the study area

The Qua-Iboe River originates from Umuahia in Abia State, Nigeria. It traverses through the rain forest and communities of Abia State and empties its water into the Atlantic Ocean via its estuary in Ibendo Local Government Area (via Eket) of Akwa Ibom State, Nigeria. It covers a distance of about 150 to 180 km. The estuary of the river lies in close proximity to the Exxon – Mobile oil terminal and effluent treatment and discharge site. Human settlements, economic and social activities thrive along the bank of the estuary. The inhabitants depend on the water of the estuary for some of their domestic, economic and recreational activities. Fishing is the major occupation of the inhabitants (Nemerow, 1986). Most of those involved in oil exploitation and processing live in the Qua-Iboe Terminal community and the off-shore platform. Some at the communities at the bank of the estuary include Qua Iboe Terminal (QI-T), Ukpenekeang, Mkpanak, Ukpenekeang, Iwuochang, Atasi and Ikoro-Ihub. These communities are approximately 2 to 3 km

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apart along the course of the river. The estuary exchanges organic and inorganic materials with the ocean through tidal backwash and mixing (Nemerow, 1986). The notable creeks are the Stubbs and Douglass which forms one of the major tributaries of the estuary (Figure 1).

### Sample collection, preservation and analysis

Eight surface (Approx. 1 m) and subsurface (Approx. 4 m depth) water samples were collected using a Nansen bottle water sampler from eight study locations along the estuary and adjoining creeks in 2012. Upon retrieval, the water was emptied into decontaminated plastic bottles. About one litre of each sample was preserved by adding 10 ml of 6 N Nitric acid and stored at 5°C. The water samples for heavy metal analysis were filtered through Whatman filter paper No. 1, and 1000 ml of the filtered samples were acidified to pH 2 with 20 ml of 6 N HNO<sub>3</sub>. Standard solutions for Fe, Zn, Cu, Pb, Co and Cd were prepared according to the analytical methods for atomic absorption spectrophotometry (Mathis and Cummings, 1973). Physical parameters (temperature, salinity, dissolved oxygen (DO), pH, electrical conductivity (EC), total suspended solids and total dissolved solids) were determined *in-situ* using appropriate analytical equipment as described by APHA (1992).

### Ecological risk assessment

The ecological risk assessment was carried out using enrichment factor (EF) and contamination factor (Cf).

#### Enrichment factor (EF)

Enrichment factor is a measure which gives the relative abundance of a contaminant over background values (Uwah et al., 2013). To identify the anomalous metal contamination, chemical normalization of the heavy metal concentration data to a conservative element Fe was employed since Fe is the only element occurring mostly from lithogenic source from this area.

According to Ergin et al. (1991), the metal enrichment factor (EF)

is defined by the equation:  $EF = \frac{M_{Fe}^{sample}}{M_{Fe}^{background}}$ , where  $\frac{M}{Fe}^{sample}$  is the ratio of metal and Fe concentrations in the surface water, and  $\frac{M}{Fe}^{background}$  is the ratio of the metal and Fe concentrations in the background data (subsurface water) of the study area. The factor is thus summarized in the Table 1.

#### Contamination factor (Cf) adapted from Hakanson (1980) model

The model calculates for each heavy metal a contamination factor (Cf) which is defined as:  $CF = \frac{C_{sample}}{C_{background}}$  where,  $C_{sample}$  and

$C_{background}$ , respectively refer to the mean concentration of a pollutant in the surface water and the background (subsurface water) of the study area.

A modified model provides a measure of the degree of overall contamination in surface water of the study area and it is expressed as  $Cd = \frac{\sum_{i=1}^n Cf_i}{n}$  where Cd is the degree of contamination, n is the number of analyzed elements and  $Cf_i$  is  $C_{i,T}$  element (or pollutant). The factors are thus summarized in Table 2.

## RESULTS AND DISCUSSION

Descriptive statistics of heavy metals (Cd, Cr, Cu, Fe, Pb, Zn and Ni) pollution and physicochemical parameters (temperature, pH, salinity, dissolve oxygen, total suspended solids (TSS) and total dissolve solids (TDS)) in surface water studied at 8 locations during dry and wet season are presented in Tables 3 and 4, respectively. During dry season (Table 3 and Figure 4), the mean concentrations (mg/l) of Cd (0.06 ± 0.02), Cr (0.04 ± 0.02), Cu (0.02 ± 0.004), Fe (7.36 ± 1.94), Pb (0.03 ± 0.008), Zn (0.03 ± 0.01) and Ni (5.17 ± 1.73) obtained in surface water of the study area were generally lower than the mean concentration (mg/l) of Cd (0.09 ± 0.02), Cr (0.05 ± 0.02), Cu (0.05 ± 0.01), Fe (10.68 ± 1.91), Pb (0.06 ± 0.01), Zn (0.08 ± 0.03) and Ni (7.4 ± 1.31) obtained during the wet season (Table 4 and Figure 4). The concentration data obtained during both seasons were also lower than their corresponding background values (Tables 3, 4, Figures 2 and 3).

These results agrees with the results obtained by Godwin et al. (2004) for seasonal variations of heavy metals concentration in the study area and was attributed mainly to surface runoffs and anthropogenic inputs. The higher values of coefficient of variation (CV) (Tables 3 and 4) for the metals indicates varying levels of input in the study area. On the other hand, the mean concentration of Ni, Cd and Pb during dry and wet seasons (Tables 3 and 4) were higher than WHO standard of 0.7, 0.02 and 0.01 mg/l, respectively. These metals concentrations may pose some deleterious effects on pelagic marine organisms. On the contrary, the mean concentrations of Fe, Zn, Cu and Cr were lower than WHO standards of 50, 1.0, 2.0 and 0.5 mg/l, respectively for flowing water.

The seasonal variation in concentrations of heavy metals as well as physicochemical parameters in surface water in Qua Iboe River estuary suggests higher atmospheric deposition during wet season, salt water intrusion, and effects of tides (Kuppusamy and Giridhar, 2006). The low surface water temperature during the wet season could have been affected by high precipitation and high humidity.

The surface water temperature during dry season (Table 3) was higher than the value recorded during wet season (Table 4). Metabolic rate and the reproductive activities of aquatic life are controlled by water temperature. This may have led to the scavenging of the depleted metallic elements alongside with nutrients from the surface water resulting in their low concentration during the dry season. Metabolic activity increases with a rise in temperature, thus increasing the demand for oxygen by fish. However, an increase in river temperature also led to a decrease in dissolve oxygen (DO), limiting the amount of oxygen available to these aquatic organisms. With a limited amount of DO, fishes in this system may become stressed. The low levels of

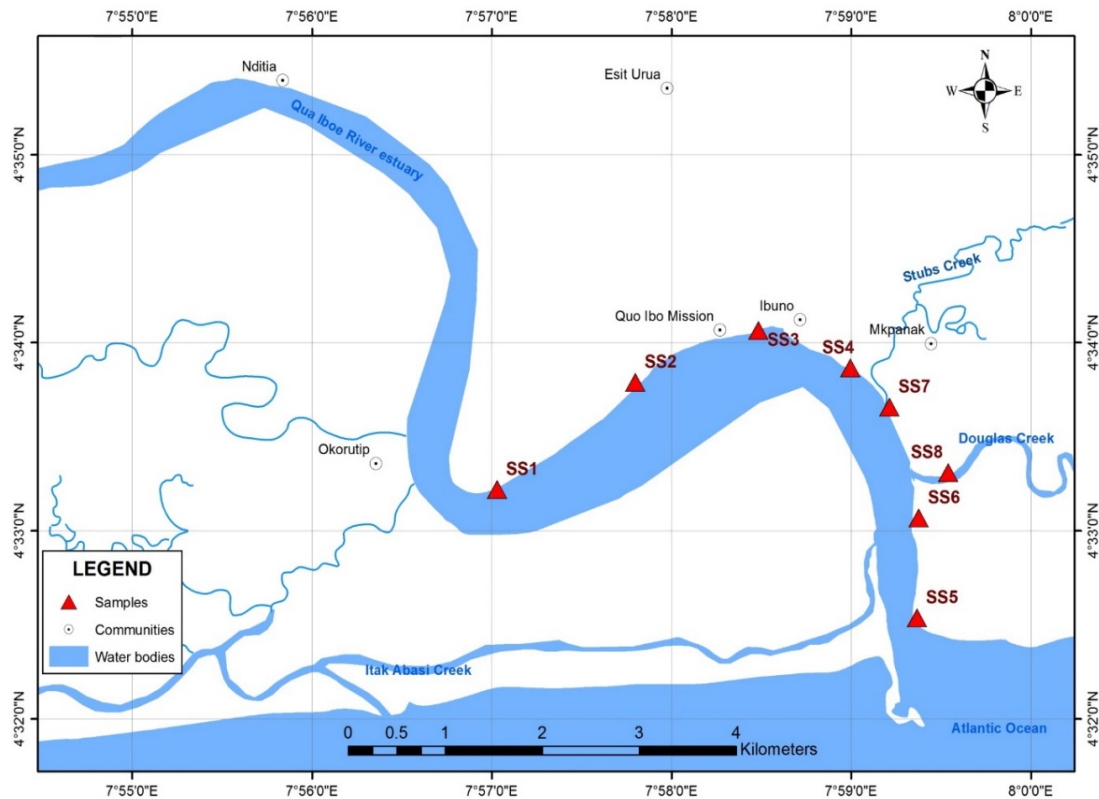


Figure 1. Map of the study area showing the sampling stations.

Table 1. Enrichment factor model for heavy metals contamination in surface water.

Enrichment factor (EF) values	Degree of contamination
$EF \leq 1$	No enrichment
$EF \leq 3$	Minor enrichment
$EF 3-5$	Moderate enrichment
$EF 5-10$	Moderately severe enrichment
$EF 10-25$	Severe enrichment
$EF 25-50$	Very severe enrichment
$EF > 50$	Extremely severe enrichment

Source: Birch (2003).

Table 2. Degree of contamination model for heavy metals in surface water.

Cd values	Water quality
$Cd < 1.5$	Nil to low degree of contamination
$1.5 \leq Cd < 2$	Low degree of contamination
$2 \leq Cd < 4$	Moderate degree of contamination
$4 \leq Cd < 8$	High degree of contamination
$8 \leq Cd < 16$	Very high degree of contamination
$16 \leq Cd < 32$	Extremely high degree of contamination
$Cd > 32$	Ultra high degree of contamination

Source: Hakanson (1980).

**Table 3.** Physicochemical parameters of water samples from Qua-Iboe River estuary and adjoining creeks during dry season.

Variable	Mean	CV (%)	Min	Max	Background concentration (mg/l)
Temp (°C)	27.35 ± 1.52	5.57	25.65	29.46	
Sal (‰)	14.22 ± 0.59	4.14	13.5	15.09	
pH	10.23 ± 1.22	11.93	8.95	12.61	
EC ( $\mu\text{cm}^{-1}$ )	3.99 ± 0.89	22.5	2.8	5.9	
DO (mg/l)	7.37 ± 0.24	3.26	7.15	7.75	
TDS (ppm)	14281 ± 3043	21.31	10450	18400	
TSS (ppm)	1208 ± 628	51.95	680	2685	
Cd (mg/l)	0.06 ± 0.02	46.72	0.02	0.09	0.03 ± 0.001
Cr (mg/l)	0.04 ± 0.02	76.59	0.01	0.08	0.02 ± 0.001
Cu (mg/l)	0.02 ± 0.004	63.79	0.01	0.04	0.01 ± 0.004
Fe (mg/l)	7.36 ± 1.94	26.37	3.49	9.36	4.15 ± 0.916
Pb (mg/l)	0.03 ± 0.008	38.89	0.02	0.06	0.02 ± 0.009
Zn (mg/l)	0.03 ± 0.01	50.73	0.01	0.05	0.01 ± 0.008
Ni (mg/l)	5.17 ± 1.73	33.48	2.23	7.14	2.56 ± 0.080

**Table 4.** Physicochemical parameters of water samples from Qua-Iboe River estuary and its associated creeks during wet season.

Variable	Mean	CV (%)	Min	Max	Background concentration (mg/l)
Temp (°C)	25.19 ± 0.73	2.93	24.38	26.58	
Sal (‰)	11.17 ± 0.22	1.99	10.89	11.5	
pH	7.15 ± 0.10	1.43	7.35	10.42	
EC ( $\mu\text{cm}^{-1}$ )	6.02 ± 1.38	23.07	5.06	8.61	
DO (mg/l)	5.71 ± 0.68	11.91	4.85	6.85	
TDS (ppm)	13925 ± 4119	29.57	9200	20240	
TSS (ppm)	1710 ± 850	49.71	1000	3600	
Cd (mg/l)	0.09 ± 0.02	55.56	0.03	0.10	0.05 ± 0.020
Cr (mg/l)	0.05 ± 0.02	42.30	0.02	0.09	0.02 ± 0.008
Cu (mg/l)	0.05 ± 0.01	22.45	0.04	0.07	0.03 ± 0.010
Fe (mg/l)	10.68 ± 1.91	17.90	7.45	12.45	5.43 ± 1.144
Pb (mg/l)	0.06 ± 0.01	27.87	0.04	0.08	0.02 ± 0.006
Zn (mg/l)	0.08 ± 0.03	63.63	0.03	0.18	0.03 ± 0.005
Ni (mg/l)	7.41 ± 1.31	17.67	5.48	8.88	3.32 ± 1.402

dissolve oxygen recorded during wet season (Table 4) may have been as a result of high rate of microbial-mediated oxidation of contaminant from surface run-off into the water body.

Salinity is a measure of the dissolved salts in the water. The results shows that salinity was higher during dry season (Table 3) than during the wet season (Table 4) and this may be attributed to high surface evaporation, low flow of water, decrease in water level and salt water intrusion as a result of tidal influx (UNESCO, 1993). During dry season (Table 5), significant correlation were observed between Salinity and all heavy metals (Cd ( $p < 0.05$ ), Cr ( $p < 0.01$ ), Cu ( $p < 0.01$ ), Fe ( $p < 0.01$ ), Pb ( $p < 0.05$ ), Zn ( $p < 0.01$ )) except Ni. This may have been one of the factors responsible for the decrease in the levels of

heavy metals in the surface water during this season as the metals ions may have become immobile by the salt ion.

The conductivity of water is a function of the concentration of dissolved ions (Asuquo, 1999). Though conductivity is not of human or aquatic health concern, but because it is easily measured, it can serve as an indicator of other water quality problems. Increase in water conductivity indicates sources of dissolved ions in the vicinity. However, the mean value recorded during dry season (Table 3) was higher than the mean value recorded during wet season (Table 4). During dry season, significant correlations ( $p < 0.01$ ) were observed between electrical conductivity and Cr as well as Fe. No significant correlations were observed during the wet

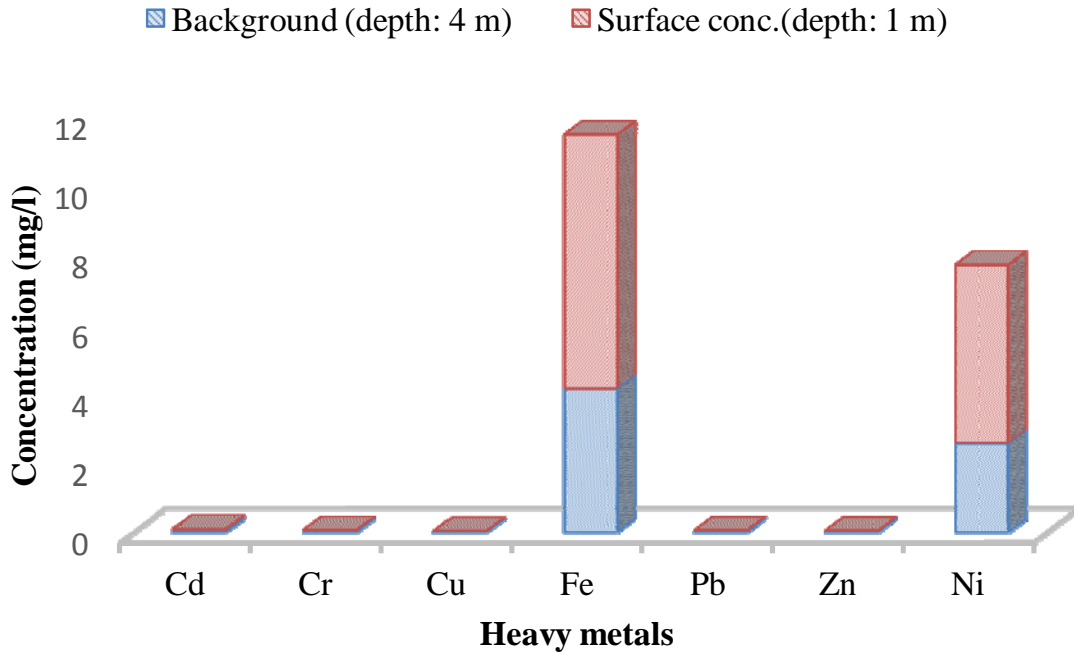


Figure 2. Bar chart showing the variation in surface concentration over background during dry season.

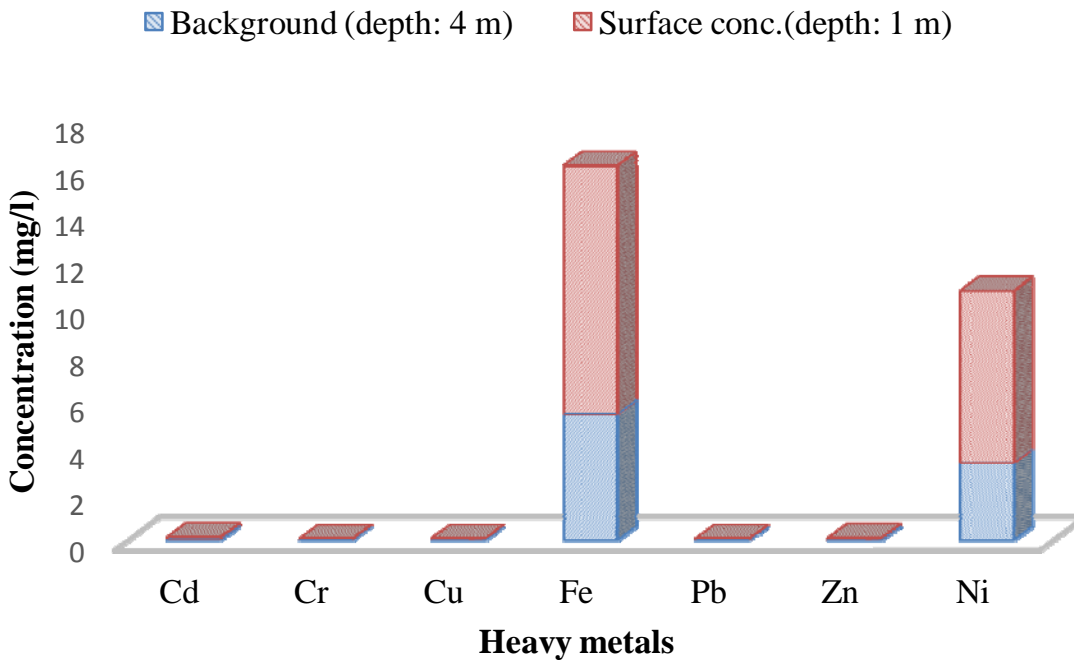
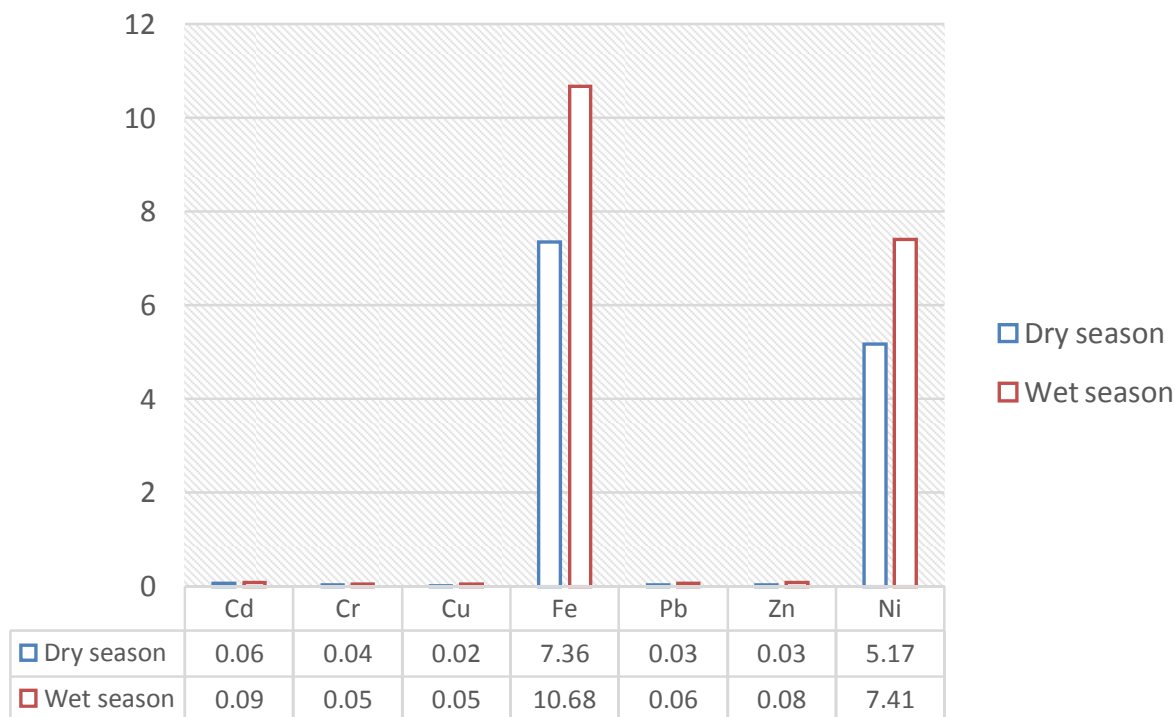


Figure 3. Bar chart showing the variation in surface concentration over background during wet season.

season (Table 6). The low values obtained during the wet season may be due to dilution of the surface water by rain and high input of fresh water from river into the estuary. The high values may show that the water is brackish (Asuquo, 1999).

Total suspended solids (TSS) may enter the water body through surface run-offs, that is, erosion by rain water, upland soil erosion, and land sliding etc. This is evident in the higher mean levels ( $17010 \pm 580$  ppm) recorded during wet season (Table 4) than during the dry season



**Figure 4.** Bar chart showing the mean heavy metals concentration in surface water during dry and wet seasons.

**Table 5.** Pearson correlation matrix of physicochemical parameters and heavy metals in surface water from Qua-Iboe River estuary and its associated creeks during dry season.

	Temp	Sal	pH	EC	DO	TDS	TSS	Cd	Cr	Cu	Fe	Pb	Zn
<b>Sal</b>	0.610 <sup>a</sup>												
<b>pH</b>	0.937 <sup>a</sup>	0.682 <sup>a</sup>											
<b>EC</b>	0.532 <sup>b</sup>	-0.043	0.428										
<b>DO</b>	0.071	-0.072	-0.001	0.288									
<b>TDS</b>	0.639 <sup>a</sup>	0.662 <sup>a</sup>	0.862 <sup>a</sup>	0.080	-0.031								
<b>TSS</b>	-0.218	-0.414	-0.423	0.282	0.840 <sup>a</sup>	-0.609							
<b>Cd</b>	0.240	0.558 <sup>b</sup>	-0.092	0.364	-0.052	0.646 <sup>a</sup>	-0.523						
<b>Cr</b>	0.005	0.633 <sup>a</sup>	0.044	0.678 <sup>a</sup>	-0.293	-0.040	0.334	-0.014					
<b>Cu</b>	-0.127	0.885 <sup>a</sup>	-0.298	0.490 <sup>c</sup>	-0.267	-0.532	0.676 <sup>a</sup>	0.577 <sup>b</sup>	0.668 <sup>a</sup>				
<b>Fe</b>	0.889 <sup>a</sup>	0.635 <sup>a</sup>	0.809 <sup>a</sup>	0.658 <sup>a</sup>	-0.322	0.474 <sup>c</sup>	-0.226	0.350	0.115	0.011			
<b>Pb</b>	-0.252	0.531 <sup>b</sup>	-0.300	-0.339	0.255	-0.283	-0.238	0.178	-0.211	0.282	-0.063		
<b>Zn</b>	0.435 <sup>c</sup>	0.955 <sup>a</sup>	0.498 <sup>c</sup>	-0.057	0.724 <sup>a</sup>	0.493 <sup>c</sup>	-0.246	0.063	-0.144	-0.297	0.527 <sup>b</sup>	-0.010	
<b>Ni</b>	-0.593	-0.858	-0.559	-0.077	0.143	-0.399	0.168	-0.225	0.245	0.390	-0.626	0.259	-0.884

a\* significant at  $p < 0.01$ , b\* significant at  $p < 0.05$  and c\* not significant.

(1208 ± 628 ppm) (Table 3). In the water body, they are present either as suspended load or bed load. High levels of suspended solids may reduce light penetration, decrease algal growth and also leads to low algal productivity and reduction in aquatic invertebrates. During dry season, significant correlations between TSS and Cu ( $p < 0.01$ ) was observed and during wet season TSS

correlated significantly with Cd ( $p < 0.05$ ), Zn ( $p < 0.01$ ) and Ni ( $p < 0.05$ ). This result is in agreement with high enrichment factors of Cd and Zn during the wet season indicating anthropogenic inputs.

pH is the measure of acidity or alkalinity of the water. It is one of the key environmental parameter that determines the survival, physiology, metabolism and

**Table 6.** Pearson correlation matrix of physicochemical parameters and heavy metals in surface water from Qua-Iboe River estuary and its associated creeks during wet season.

	Temp	Sal	pH	EC	DO	TDS	TSS	Cd	Cr	Cu	Fe	Pb	Zn
Sal	0.784 <sup>a</sup>												
pH	-0.406	-0.282											
EC	0.584 <sup>b</sup>	0.479 <sup>c</sup>	0.076										
DO	0.321	0.471	0.190	-0.180									
TDS	0.879 <sup>a</sup>	0.509 <sup>b</sup>	-0.569	0.566 <sup>b</sup>	-0.175								
TSS	0.224	0.372	-0.059	-0.500	-0.019	-0.017							
Cd	-0.232	-0.072	0.025	0.240	0.241	-0.175	0.508 <sup>b</sup>						
Cr	-0.550	-0.116	0.011	-0.204	0.497 <sup>c</sup>	-0.487	-0.100	0.196					
Cu	-0.701	-0.498	0.225	-0.118	0.700 <sup>a</sup>	-0.513	-0.373	0.748 <sup>a</sup>	0.621 <sup>a</sup>				
Fe	-0.006	-0.166	0.092	0.444 <sup>c</sup>	0.208	0.321	-0.390	0.378	0.140	-0.509			
Pb	-0.153	-0.053	0.301	-0.260	0.651 <sup>a</sup>	-0.224	0.223	-0.060	-0.415	-0.175	-0.162		
Zn	0.226	0.339	0.019	-0.362	-0.117	-0.072	0.839 <sup>a</sup>	-0.475	0.051	-0.371	-0.492	-0.230	
Ni	-0.565	-0.239	0.495 <sup>c</sup>	-0.332	0.286	-0.536	0.579 <sup>b</sup>	0.019	0.654 <sup>a</sup>	0.548 <sup>b</sup>	0.342	0.041	0.224

a\* significant at  $p < 0.01$ , b\* significant at  $p < 0.05$  and c\* not significant.

**Table 7.** Enrichment factor (EF) values of heavy metals in surface water during dry season.

Station/Element	Cd	Cr	Cu	Fe	Pb	Zn	Ni
SW1	1.5	0.06	0.6	1.0	0.1	3.1	0.5
SW2	1.4	0.0	1.0	1.0	0.9	1.6	0.1
SW3	1.8	0.1	0.8	1.0	0.3	2.8	0.5
SW4	0.9	0.04	1.0	1.0	0.8	2.1	0.6
SW5	2.2	0.07	0.9	1.0	1.1	1.7	1.0
SW6	1.8	0.09	1.1	1.0	0.9	1.4	0.9
SW7	1.1	0.9	0.8	1.0	1.3	1.1	0.8
SW8	0.6	0.0	0.8	1.0	0.6	1.7	0.1
Mean	1.4	0.2	0.9	1.0	0.8	1.9	0.6
%litho	24					30	
%Anthro	76					70	

growth of aquatic organisms (Ramanathan et al., 2006). Higher values were recorded during dry season (Table 3) than in the wet season (Table 4). Lower coefficient of variations during both seasons suggests even distribution in surface water along the study locations. On the other hand, there was no significant correlation between pH and all heavy metals except Fe ( $p < 0.01$ ) during dry season (Table 5). Higher values of pH leads to alkalinity and this may have led to the adsorption of these elements unto particulate matter. During wet season (Table 6), there were positive correlations though not significant between pH and all heavy metals. This may to some extent led to the dissolution of the heavy metals in surface water during the wet season. This is particularly important because the solubility of metal hydroxides increases as pH decreases (Elder, 1988).

Pearson correlation matrix analysis on the concentration data during dry and wet seasons are given in Tables 5 and 6, respectively. It was carried out to

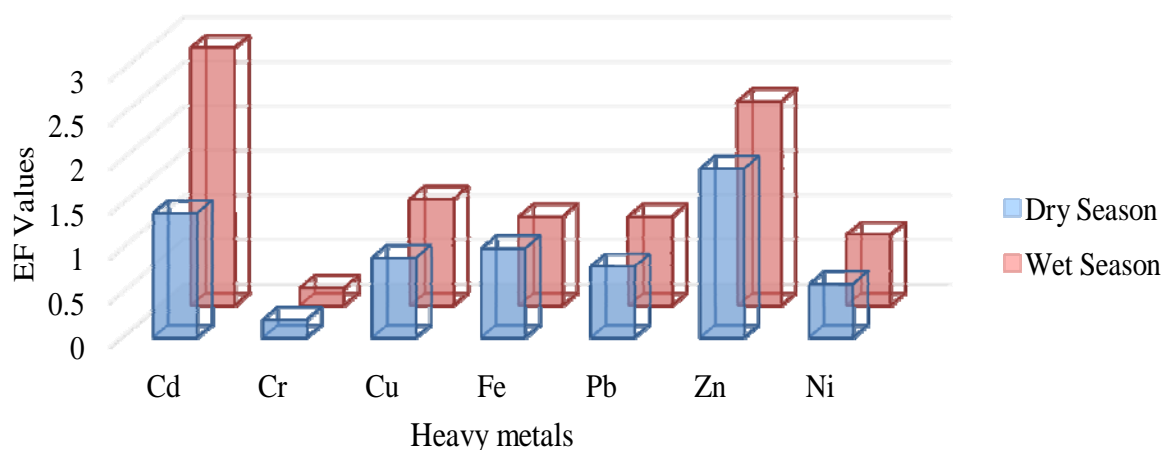
assess possible similar sources of the metals. The heavy metals with positive correlation were considered to have similar sources. Table 5 shows that during the dry season, there were significant correlation between Cd and Cu ( $p < 0.05$ ), Cr and Cu ( $p < 0.01$ ), Zn and Fe ( $p < 0.05$ ) indicating similar sources of inputs. However, during the wet season (Table 6), there were significant correlations between Cd and Cu ( $p < 0.01$ ), Cr and Cu ( $p < 0.01$ ), Cr and Ni ( $p < 0.05$ ). Insignificant correlations observed between other heavy metals in this study indicate diverse source of input. The results of enrichment factor (EF) in surface water during dry and wet season are presented in Tables 7 and 8, respectively.

The results obtained from the enrichment factor (EF) determination indicate that the surface water were more enriched with heavy metals (Cd, Cr, Cu, Fe, Pb, Zn and Ni) during wet season than dry season (Tables 8, 7 and Figure 5).



**Table 8.** Enrichment factor (EF) values of heavy metals in surface water during wet season.

Station/Elements	Cd	Cr	Cu	Fe	Pb	Zn	Ni
SW1	3.2	0.1	1.0	1.0	0.2	3.2	0.8
SW2	3.1	0.0	1.1	1.0	1.3	2.1	0.2
SW3	2.8	0.3	1.2	1.0	1.1	2.2	0.7
SW4	2.6	0.1	1.1	1.0	1.3	2.6	0.9
SW5	2.1	0.1	1.4	1.0	1.3	2.1	1.1
SW6	3.0	0.2	1.3	1.0	1.0	2.2	1.2
SW7	3.2	0.0	1.2	1.0	0.6	1.9	0.3
SW8	3.4	0.6	0.9	1.0	1.1	2.1	1.2
Mean	2.9	0.2	1.2	1.0	1.0	2.3	0.8
%litho	15		40			20	
%Anthro	85		60			80	

**Figure 5.** Bar chart showing seasonal variation of heavy metals enrichment in surface water of the study area.

The Enrichment factor (*EF*) calculated during the wet season ranged from 0.2 to 2.9 while the *EF* calculated for dry season ranged from 0.2 to 1.9. According to Birch (2003) model (Table 1), Cd, Cu, Fe, Pb and Zn showed minor enrichments while Cr and Ni showed no enrichment during wet season (Table 8). During dry season, Cd, Fe and Zn were moderately enriched while Cr, Cu, Pb and Ni were not enriched. The higher *EF* values of heavy metals signify that the source of contamination is anthropogenic while the lower values show lithogenic origin. It was evident here that Cd and Zn recorded the highest factors in surface water and greater percentages of inputs are linked to anthropogenic sources. The primary anthropogenic sources of zinc in the environment (air, water, soil) are related to mining and metallurgical operations involving zinc and use of commercial products containing zinc (Eduljee et al., 1986).

Domestic waste, shipyard, automotive and industrial effluent also releases good amount of Zn into the aquatic

environment (Garcia and Millan, 1998). Besides, household products which include powder and liquid laundry detergents, shampoos, toilet tissue and other cleaning product may also contribute to the zinc load into the aquatic environment (Tezcan and Ozbay, 1984). The possible sources of Cd in the surface water may be from atmospheric fall-out, fossil fuel combustion, release of sediment bound-metal.

The degree of heavy metals contamination in surface water of the study area water during dry and wet seasons (Table 9) shows the contamination trend: SW1>SW6>SW8>SW4>SW2>SW7>SW3>SW5 and SW1>SW8>SW3>SW4>SW6>SW1>SW7>SW5, respectively. The trend shows that the station with the ID: SW1 showed very high degree of contamination during dry season and extremely high degree of contamination during wet season. On the other hand, the least contaminated station with the ID: SW5 showed nil to low degree of contamination during both seasons. The mean degree of contamination during dry season shows that

**Table 9.** Degree of contamination of surface water of the study area with heavy metals during dry and wet season.

Station	Cd values	
	Dry season	Wet season
SW1	14.0	22.6
SW2	2.3	1.86
SW3	0.91	4.28
SW4	2.73	3.10
SW5	0.65	0.61
SW6	3.76	2.69
SW7	2.15	1.20
SW8	3.56	6.99
Mean	3.76	5.41

the surface water of the study area was moderately contaminated but highly contaminated during wet season.

### Conclusion

The seasonal variation, distribution pattern, enrichments and contamination of heavy metals in 16 samples of surface water (approximately 1 m) in Qua Iboe River estuary and adjoining creeks studied along 8 stations showed elevated concentrations during the wet season months as compared to the dry season months and was attributed mainly to atmospheric deposition, erosion and washing of domestic wastes containing these pollutants into the water body. The physicochemical parameters (temperature, salinity, pH, total dissolve solids, electrical conductivity, dissolve oxygen and total suspended solids) also had seasonal effects in the adsorption/dissolution and distribution of these substances in the surface water.

The enrichment factor analysis indicated that the metals (Cd, Cr, Cu, Fe, Pb, Zn and Ni) were more enriched during wet season than during the dry season. The higher enrichments of Cd and Zn indicated anthropogenic input including dumping of domestic wastes, and runoff from land. The mean contamination factors of all the heavy metals studied indicated high degree of contamination of the surface water during wet season as compared to the dry season. Consequently, the implication is that during flooding which is consequent upon climate change, there will be higher degree of contamination of the surface water of Qua Iboe River estuary and adjoining creeks. Climate change adaptation measures should be such as will minimize surface run off into the river system to reduce the pollution of the water body.

### ACKNOWLEDGEMENTS

The authors acknowledge Dan, S. F, Michael Dan,

Usenobong Umoh of Department of Marine Chemistry, Akwa Ibom State University-Nigeria for assisting during the field sampling. Mr. E. Effiom and Dr. Osabor all of Department of Pure and Applied Chemistry, University of Calabar for assisting immensely during the analysis.

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