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# Spatial and Seasonal Variation in the Contamination Indices of Trace Metals in Sediment from Qua Iboe River Estuary, South-South, Nigeria

**Moses, E. A., Etuk, B. A. And Udosen, E. D.**
Department of Chemistry, University of Uyo, Uyo, Akwa Ibom State

## ABSTRACT

This study was conducted to determine the levels of trace metals in sediments from Qua Iboe river estuary(QIRE), Nigeria and assess their extent of contamination. Sediment samples were collected from five designated stations and one reference station along QIRE in the dry and wet seasons and analysed for trace metals using atomic absorption spectrophotometer. Geo-accumulation indices, enrichment factors, pollution load indices, degree of contamination and contamination factors were estimated using suitable models. Concentration of metals in mg/kg during the dry season were: Pb (0.03-4.57), Cd (0.04-0.65), V (0.03-0.58), Cr (1.54-3.69), Ni (1.74-5.18), Fe (23.60-41.87), Zn (7.20-14.52). The ranges for the wet season were Pb (0.10-1.65), Cd (0.06-0.53),V (0.04-1.75), Cr(0.31-2.89), Ni (1.18-5.37), Fe(27.04-31.87), Zn (5.03-14.93). Levels of trace metals investigated were below the sediment quality guidelines except Fe. Contamination indices revealed that the sediments from Qua Iboe river estuary were contaminated with respect to the indices considered in this study. Enrichment factors and geo-accumulation indices indicated anthropogenic sources of pollution especially for Pb, Cd and V. There is need for regular monitoring of the aquatic ecosystem to minimize sediment contamination which may pose ecological risk to benthic and pelagic organisms.

**Keyword**: *Trace Metals; Contamination Indices; Sediment; Qua Iboe River Estuary.*

## 1. INTRODUCTION

Trace metals are natural constituent of sediments and the concentrations of these metals in river sediments reflect the occurrence and abundance of certain rocks or mineralized deposit and drainage of the river [1]. However, at a particular level in the environment they may be toxic to the aquatic ecosystem and because trace metals cannot be degraded, persistence in the environment is inevitable.Sediments are repositories for physical debris and sinks for various pollutants such a pesticides, polycyclic aromatic hydrocarbons and trace metals from natural and man-made sources. The ability of sediments to act as sinks for toxic metals and polycyclic aromatic hydrocarbons have been reported by several authors [2, 3, 4].

Sediments play a role in the remobilization of contaminants in aquatic system under certain conditions. The availability of metals in aquatic system is mediated by sediment- water exchange process that may result in the release or remobilization of pollutants from the sediment bed. Trace metals can be present in amounts several times higher than their natural background levels and pollute marine sediments in coastal regions near industrial areas [1]. Consequently, sediments enriched with trace metals may affect the health of marine organism and aquatic ecosystem.

The lower reach of Qua Iboe River was chosen for the study because of oil exploitation and exploration activities in the area. The presence of a petrochemical industry and allied companies at the proximity of the study area has increased the population density of the area in recent times. This has resulted in increase in the volume of industrial, domestic and agricultural wastes generated. High values of trace metals in sediments from Nigerian aquatic environment have been linked to industrialization, urbanization, agricultural activities, high human population and reworking of sediments by microorganisms [5].

The analysis of sediments is an important step in mapping possible exposure pathways to various aquatic organisms, since contaminants in sediments may be bioavailable to sediment dwelling organisms. Information on trace metal distribution and enrichment in sediment is important in detecting, tracing and monitoring pollution sources in an aquatic system [5, 6]. Sediments and biological organisms such as fish and oysters are good indicators of pollution where pollutants escape water analysis [7].

Several studies were conducted on the level of trace metals in sediment from QIRE[8, 9, 10].The aim of the present study was to evaluate the spatial and seasonal variations of trace metals in sediments, determine the degree of anthropogenic pollution and assess the degree of contamination of sediments from Qua Iboe river estuary (QIRE) using different models such as contamination factor, degree of contamination, enrichment factor, geo-accumulation index and pollution load index.

## 2. MATERIALS AND METHODS

### 2.1 The study area and site description

Qua Iboe river is about 150km long, it originates from Umuaha hills and transverses sedimentary terrains and develops into extensive meanders before emptying into the Atlantic Ocean, with creeks and channels islands common throughout the length of the estuary. The lower reach of the estuary is situated close to a petrochemical effluent treatment and discharge plant. The sampling sites are made up of five examined sites located at the lower reach of the river and a control site located at EkpeneUkpa. The global positioning system (GPS) coordinates of the different sites are : Okoroutip (4°55'5"N - 7°54'47"E), Ukpenekang (4°27'2"N - 8° 3'5"E), Iwochang ( 4°36'50"N – 7°50'03"E), Douglas creek (4°30'55"N – 8°07'E), Stubb creek (4°34'41"N – 7°59'47"E), EkpeneUkpa(4°47'90"N – 7°50'03"E). The control site (EkpeneUkpa) is about 27km from the examined sites and is free from oil exploration and production activities. Figure 1 is a map of the study area indicating the sampling sites

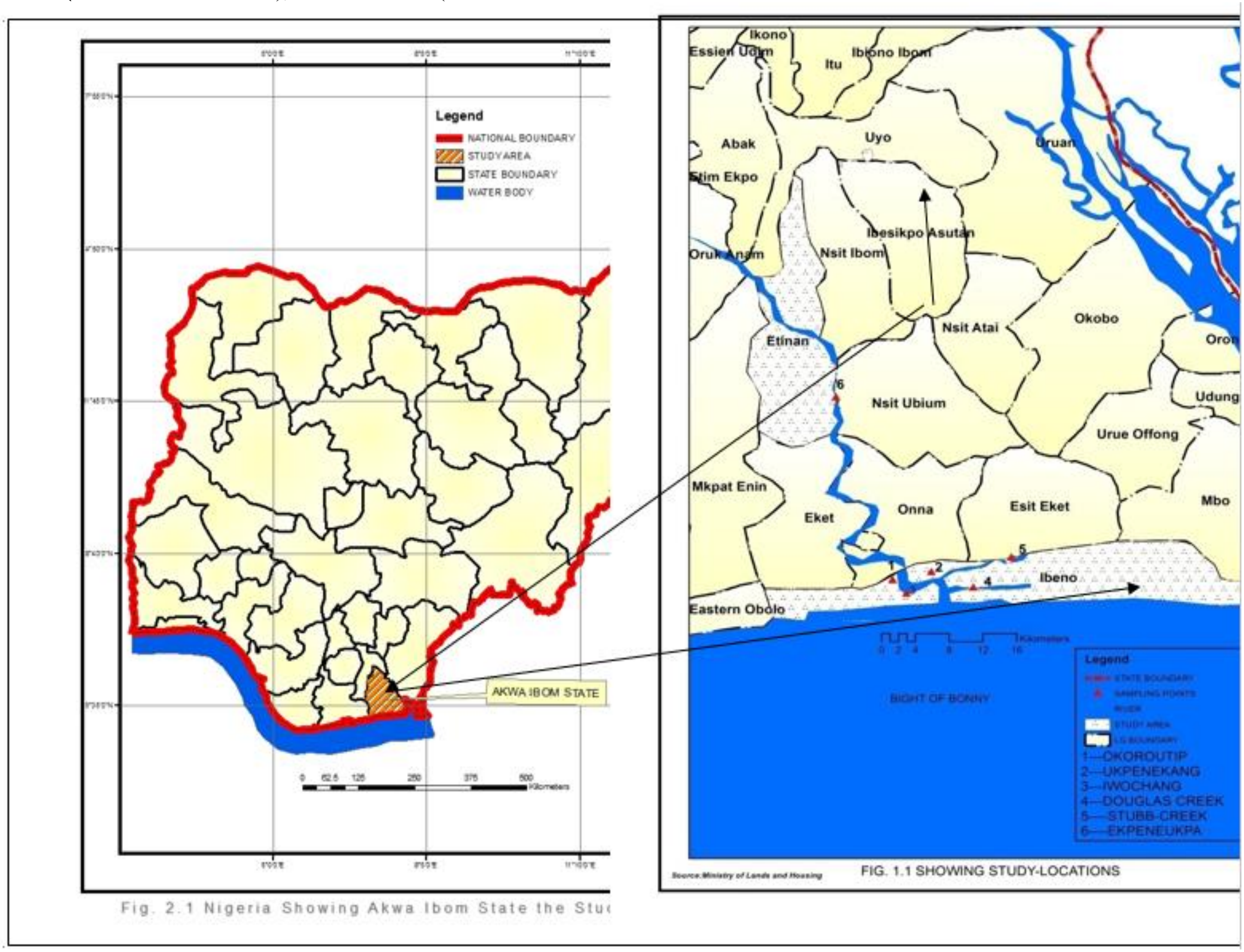

Fig. 2.1 Nigeria Showing Akwa Ibom State the Stu

FIG. 1.1 SHOWING STUDY-LOCATIONS

### 2.2 Samples and sampling

Grab sediments were collected monthly for one year (November , 2013 to October, 2014) period spanning the dry and wet seasons of the study area using a plastic spatula sampler. 5 grab samples were collected at each sampling location and were combined together into a stainless steel bowl to make a composite sample. A total of three hundred and sixty subsamples and 72 composite samples were collected, dried, ground and sieved.

### 2.3 Determination of trace metals

About 1g of dried samples was weighed into a 100ml beaker and the digestion of the metal was done using perchloric acid and nitric acid in the ratio 4:1[11]. After appropriate digestion, the trace metals were determined using atomic absorption spectrophotometer (Unicam, 939/959 model). All analyses were performed 3 days after sampling. The accuracy of the determination was assessed by the analysis of a certified reference material (Marine sediment, IAEA 256) for each batch of the analysis and recoveries in the range of 96% - 104% was obtained.

### 2.3 Data analysis

In order to assess the contamination indices of sediment from Qua Iboe river estuary, analytical data were subjected to pollution models expressed in (1-6).

 

**2.3.1 Contamination factor:** Contaminant factor (CF) was calculated using the equation

$$C_F^i = \frac{c_{O-1}^i}{c_n^i} \quad [12] \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

where; $C_{O-1}^i$ is the conc. of the examined element in the examined environment and $C_n^i$ is the conc. of the examined element in the reference environment.

2.3.2 $The\ degree\ of\ contamination\ (Cd) = \sum CF \ldots\ldots\ldots\ldots\ldots\ldots(2)$

2.3.3 $Modified\ degree\ of\ contamination = \frac{Cd}{n} \ldots\ldots\ldots\ldots\ldots\ldots(3)$

where: n = no of pollutants and Cd = degree of contamination

2.3.4 $Pollution\ Load\ index = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots \times CF_n)^{1/n} \ldots\ldots(4)$

PLI was calculated by the equation proposed by [13] where: CF =contamination factor and n = number of pollutants

2.3.5 $Enrichment\ Factor$

$$= \frac{[metal\ in\ sediment]/[Fe\ in\ sediment]}{[metal\ in\ control]/[metal\ in\ sediment]} \qquad (5)$$

The metal enrichment factor defined by the above equation is used to evaluate the actual level of elemental contamination and Fe is used as the normalizing metal because it is the major sorbent phase for trace metals and is a quasi-conservative tracer of the natural metal-bearing phases [14].

2.3.6 $Geoaccumulation\ index$

$$= log_2 \frac{Cn}{1.5Bn} \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where :Cn = concentration of the metal in sediment, and Bn = concentration of the metal in the reference environment and 1.5 accounts for variation in the background data due to lithogenic effects

**2.4 Statistical Analysis**

All values are expressed as mean ± standard deviation. Student's t-test was used to compare between means and a P < 0.05 was considered statistically significant. Pearson correlation coefficient was used to examine the relationship between metal pairs in sediment and cluster analysis was used to assess common pollution sources between sampling sites. Statistical analyses were performed using SPSS statistics 17.0 windows.

## 2.5 3. RESULTS

### 2.5.1 Trace metals concentration

Concentrations of trace metals in sediment of QIRE for dry and wet seasons from the five designated locations and one reference location are presented in Tables 1 and 2 below respectively. The highest value was recorded for iron at Stubb creek during the dry season while the lowest value was recorded for vanadium at EkpeneUkpa during the wet season. The variation of trace metals for the wet season and dry season followed the trend: Fe > Zn > Ni > Cr >Pb> V > Cd. The concentrations of Fe, Zn, Ni and Cr were higher in the dry season than wet season while the concentrations of Pb, Cd and V were higher in the wet season than dry season. Nosignificant difference existed between the mean of the two seasons (P<0.05).

The stability of the metal in both seasons was predicted using their coefficient of variation (CV) values. The result reveals that Cd at Iwochang during the wet season recorded the highest value (CV = 90.5%), being the least stable while the least CV values for the trace metals was recorded by Ni at the same station during the wet season (CV = 0.70%). This result indicates that Ni was the most stable metal in this study.

**Table 1: Trace Metal Concentration In Sediment From Qua Iboe River Estuary (QIRE) During The Dry Season Mg/Kg**

| Location | Pb | | Cd | | V | | Cr | | Ni | | Fe | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) |
| Okoroutip | 0.33±0.18 | 54.50 | 0.04±0.03 | 75.00 | 0.58±0.26 | 44.80 | 2.86±0.53 | 18.50 | 5.18±0.24 | 4.60 | 31.03±8.82 | 28.40 | 14.01±7.40 | 52.00 |
| Ukpenekang | 0.13±0.04 | 30.70 | 0.05±0.02 | 40 | 0.28±0.15 | 53.6 | 1.60±0.12 | 7.50 | 2.71±0.82 | 30.20 | 30.20±2.95 | 9.70 | 7.92±0.34 | 4.29 |
| Iwochang | 0.51±0.20 | 39.20 | 0.47±0.16 | 34 | 0.16±0.14 | 87.5 | 2.49±0.50 | 20.00 | 3.18±1.37 | 43.00 | 32.08±9.69 | 30.20 | 13.77±4.37 | 31.70 |
| Douglas | 0.50±0.26 | 52.00 | 0.43±0.19 | 44 | 0.47±0.21 | 61.7 | 3.58±0.43 | 12.00 | 2.37±0.29 | 12.20 | 34.74±8.33 | 23.90 | 13.01±2.18 | 16.80 |
| Stubb | 4.57±2.90 | 63.40 | 0.40±0.01 | 2.5 | 0.25±0.04 | 16 | 3.69±0.25 | 20.00 | 4.78±0.48 | 10.00 | 41.81±7.55 | 18.10 | 14.52±2.49 | 15.00 |
| Control | 0.03±0.01 | 33.30 | 0.65±0.03 | 60 | 0.03±0.02 | 66.6 | 1.54±0.58 | 37.6 | 1.74±0.28 | 16.00 | 23.60±4.27 | 18.00 | 7.20±1.08 | 15.00 |
| Average | 1.01 | | 0.24 | | 0.30 | | 2.63 | | 3.33 | | 32.24 | | 11.78 | |
| LEL | 31 | | 0.6 | | ------- | | 26 | | 16 | | 10.38 | | 120 | |
| TEL | 35.8 | | 0.99 | | --------- | | 43.5 | | 22.7 | | 10.30 | | 120 | |
| PEC | 12.8 | | 4.95 | | --------- | | 111 | | 48.6 | | 20.30 | | 111 | |

**Table 2: Trace Metal Concentration in Sediment from Qua Iboe River Estuary (QIRE) During the Wet Season Mg/Kg**

| Location | Pb | | Cd | | V | | Cr | | Ni | | Fe | | Zn | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) | Mean | CV (%) |
| Okoroutip | 1.63±0.26 | 15.90 | 0.20±0.05 | 25.00 | 0.60±0.08 | 13.30 | 2.51±0.18 | 7.17 | 5.37±2.50 | 46.00 | 28.14±4.41 | 15.30 | 14.93±1.19 | 7.90 |
| Ukpenekang | 1.82±0.43 | 23.60 | 0.11±0.07 | 63.60 | 0.72±0.02 | 2.76 | 1.61±0.21 | 13.00 | 4.44±0.65 | 14.6 | 27.04±0.82 | 3.00 | 5.03±3.20 | 64.00 |
| Iwochang | 2.04±0.13 | 6.37 | 0.53±0.48 | 90.50 | 0.73±0.19 | 17.80 | 2.40±0.21 | 8.70 | 1.13±0.008 | 0.70 | 25.50±1.78 | 6.90 | 6.08±2.07 | 34.00 |
| Douglas | 1.66±0.08 | 4.81 | 0.41±0.29 | 70.70 | 1.75±0.05 | 2.80 | 0.31±0.24 | 7.76 | 3.10±0.21 | 6.80 | 29.41±2.33 | 7.90 | 4.98±3.00 | 60.00 |
| Stubb | 1.68±0.18 | 10.70 | 0.38±0.06 | 15.70 | 0.56±0.02 | 3.50 | 2.89±0.62 | 21.40 | 3.62±0.22 | 6.00 | 31.87±2.38 | 9.50 | 9.21±1.29 | 14.00 |
| Control | 0.10±0.05 | 50.00 | 0.06±0.04 | 66.60 | 0.04±0.03 | 75.00 | 0.53±0.10 | 18.86 | 1.18±0.25 | 21.10 | 27.11±1.54 | 5.60 | 12.33±0.54 | 4.30 |

2.5.2*Contamination indices*

Tables 3 and 4 reveals the contamination factor of each trace metal, the degree of contamination, the modified degree of contamination and pollution load index for both seasons. In the dry season, the result for the contamination factor ranged from 1.00 for the trace metals at the control station to 17.00 for Pb at Iwoachang while for the wet season the range was 1.00 for all the trace metals at the control site to 20.00 for Pb at Iwoachang. The highest CF value in this study was recorded for lead (20.4) at Iwoachang during the wet season while the least CF value was recorded for Zn at Douglas creek during the wet season.

The range for degree of contamination (CD), modified degree of contamination (Mcd) and pollution load index during the dry season was 7.00 – 177.22, 1.00 – 25.32, and 1.32 – 4.04 respectively. The highest values for the three contamination indices were recorded at Stubb creek while the lowest values were recorded at the control site. For the wet season, the range for degree of contamination (CD), modified degree of contamination (Mcd) and pollution load index was 7.00 – 76.38, 1.00 – 10.91 and 1.32 – 4.40. The highest values for the above-mentioned indices during the wet season were recorded at Douglas creek while the lowest values were recorded at the control site. In this study, the PLI values of sediments from QIRE recorded an average of 3.08 in the dry season and 2.86 in the wet season.

Tables 5 and 6 reveal the enrichment of trace metals in sediment of QIRE in both seasons. For the dry season, the enrichment factor ranged from 1.00 for all the trace at the control site to 12.44 for Pb at Iwoachang while the enrichment factor ranged from 1.00 for all the trace metals at the control site to 40.00 for V at Douglas creek. Tables 7 and 8 reveals the result of geo-accumulation index of trace metals in sediment from QIRE during the wet and dry season. The decrease in the Igeo values was as follows: Pb> V > Cd > Cr > Ni > Zn > Fe. The geoaccumulation index ranged from - 0.91 for Cd at Okoroutip to 6.67 for Pb at the Stubb creek during the dry season while the wet season values ranged from - 0.67 for Fe at Iwoachang to 4.87 for V at Douglas creek.

**Table 3: Table of contamination factor degree of contamination, (CD), modified degree of contamination (MCd), pollution load index (PLI) for QIRE sediment during the dry season**

| Location | Pb | Cd | V | Cr | Ni | Fe | Zn | CD | MCD | PLI |
|---|---|---|---|---|---|---|---|---|---|---|
| Okoroutip | 11.00 | 0.80 | 19.30 | 1.86 | 2.97 | 1.31 | 1.91 | 39.15 | 5.60 | 3.03 |
| Ukpenekang | 4.33 | 1.00 | 19.30 | 1.03 | 1.55 | 1.27 | 1.10 | 29.58 | 4.23 | 2.11 |
| Iwoachang | 17.00 | 9.40 | 5.30 | 1.61 | 1.83 | 1.34 | 1.91 | 38.39 | 5.48 | 3.49 |
| Douglas creek | 16.60 | 8.60 | 15.60 | 2.32 | 1.36 | 1.40 | 1.81 | 47.69 | 6.81 | 4.04 |
| Stubb creek | 1.52 | 8.00 | 8.30 | 2.39 | 2.75 | 1.77 | 2.01 | 177.22 | 25.32 | 5.85 |
| EkpeneUkpa | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 7.00 | 1.00 | 1.32 |

**Table 4: Table Of Contamination Factor (CF), Degree Of Contamination, (CD), Modified Degree Of Contamination (Mcd), Pollution Load Index (PLI) For QIRE Sediment during the Wet Season**

| Location | Pb | Cd | V | Cr | Ni | Fe | Zn | CD | MCD | PLI |
|---|---|---|---|---|---|---|---|---|---|---|
| Okoroutip | 16.3 | 3.33 | 15.00 | 4.73 | 4.55 | 1.06 | 1.21 | 46.18 | 6.59 | 4.18 |
| Ukpenekang | 18.2 | 1.83 | 18.00 | 3.03 | 3.76 | 1.08 | 0.41 | 46.13 | 6.62 | 3.14 |
| Iwoachang | 20.4 | 8.83 | 18.25 | 4.52 | 0.96 | 0.94 | 0.49 | 54.39 | 7.77 | 3.51 |
| Douglas creek | 16.6 | 6.83 | 43.00 | 5.85 | 2.62 | 1.08 | 0.40 | 76.38 | 10.91 | 4.40 |
| Stubb creek | 16.8 | 6.33 | 14.00 | 5.45 | 3.06 | 1.18 | 0.75 | 47.57 | 6.79 | 4.18 |
| EkpeneUkpa | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 7.00 | 1.00 | 1.32 |

**Table 5: The Enrichment Factor for Sediment from QIRE In The Dry Season**

| Location | Pb | Cd | V | Cr | Ni | Fe | Zn |
|---|---|---|---|---|---|---|---|
| Okoroutip | 8.15 | 0.60 | 14.64 | 1.41 | 2.26 | 1 | 1.53 |
| Ukpenekang | 3.38 | 0.70 | 7.29 | 1.51 | 1.22 | 1 | 0.85 |
| Iwoachang | 12.44 | 6.90 | 3.92 | 1.19 | 1.35 | 1 | 1.41 |
| Douglas creek | 11.33 | 5.83 | 10.62 | 1.55 | 0.93 | 1 | 1.22 |
| Stubb creek | 85.5 | 4.53 | 4.69 | 1.35 | 1.52 | 1 | 1.13 |
| EkpeneUkpa | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

**Table 6: The Enrichment Factor for Sediment from QIRE During The Wet Season**

| Location | Pb | Cd | V | Cr | Ni | Fe | Zn |
|---|---|---|---|---|---|---|---|
| Okoroutip | 15.40 | 3.14 | 14.00 | 4.47 | 4.27 | 1 | 1.14 |
| Ukpenekang | 17.20 | 1.84 | 18.09 | 3.07 | 3.77 | 1 | 0.41 |
| Iwoachang | 21.73 | 9.36 | 19.45 | 4.82 | 0.99 | 1 | 0.52 |
| Douglas creek | 15.32 | 3.78 | 40.00 | 0.54 | 2.44 | 1 | 0.36 |
| Stubb creek | 14.32 | 5.39 | 11.91 | 4.64 | 2.61 | 1 | 0.63 |
| EkpeneUkpa | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

**Table 7: Geoaccumulation Indices of Trace Metals In Sediments From QIRE During The Dry Season**

| Location | Pb | Cd | V | Cr | Ni | Fe | Zn |
|---|---|---|---|---|---|---|---|
| Okoroutip | 2.87 | -0.91 | 3.69 | 0.31 | 0.99 | 0.07 | 0.40 |
| Ukpenekang | 1.53 | -0.58 | 2.64 | -0.53 | 0.05 | -1.48 | -0.45 |
| Iwoachang | 3.50 | 2.65 | 1.83 | 0.11 | 0.55 | 0.16 | 0.35 |
| Douglas creek | 3.47 | 2.52 | 3.38 | 0.63 | -0.14 | -0.18 | 0.27 |
| Stubb creek | 6.67 | 2.42 | 2.47 | 0.68 | 0.87 | -0.58 | 0.43 |

**Table 8: Geoaccumulation Indices of Trace Metals in Sediments From QIRE During The Wet Season**

| Location | Pb | Cd | V | Cr | Ni | Fe | Zn |
|---|---|---|---|---|---|---|---|
| Okoroutip | 3.44 | 2.74 | 3.32 | 1.66 | 1.60 | -0.50 | -0.31 |
| Ukpenekang | 3.60 | 1.87 | 3.58 | 1.02 | 1.30 | -0.59 | -1.88 |
| Iwoachang | 3.77 | 4.14 | 3.60 | 1.60 | -0.65 | -0.67 | -1.60 |
| Douglas creek | 3.47 | 3.77 | 4.87 | 1.96 | 0.81 | -0.47 | -1.89 |
| Stubb creek | 3.49 | 3.66 | 3.22 | 1.86 | 1.03 | -0.35 | -1.01 |

### 2.5.3 Correlation and Hierarchical cluster analysis

During the dry season, significant positive correlation was observed between the following metal pairs: Pb- Cr ( r = 0.633), Cd-Zn (r = 0.638), Zn-Cr ( r = 0.863), Zn-V ( r = 0.537) and Zn- Fe ( r = 0.706). During the wet season, significant positive correlation was observed between the following metal pairs: Cr-Cd ( r = 0.767), Cr- V ( r = 0.719) and Fe- Cr ( r = 0.537) while negative correlation was observed between the following pairs: Zn – Pb ( r = -0.508) and Zn – Cd ( r = -0.455).

Hierarchical cluster analysis (HCA) was used in the classification of the sampling locations into polluted sites with similar or different pollution status. Figures 1 and 2 reveal two primary clusters for both seasons. During the dry season, similar source of pollution was observed for Iwoachang, Okoroutip, Douglas creek and Stubb creek while similar pollution source was observed for Ukpenekang and EkpeneUkpa. Similar spatial distribution pattern was observed in the wet season. Furthermore, two primary clusters and three major groupings were identified based on the individual trace metals concentration (Figures 3 and 4).

**Table 9: Pearson's Correlation Matrix of Trace Metals in Sediment from QIRE during the Dry Season**

| | Pb | Cd | V | Cr | Ni | Fe | Zn |
|---|---|---|---|---|---|---|---|
| **Pb** | **1** | | | | | | |
| **Cd** | **0.454a** | **1** | | | | | |
| **V** | **-0.058a** | **-0.041a** | **1** | | | | |
| **Cr** | **0.633b** | **0.679a** | **0.541a** | **1** | | | |
| **Ni** | **0.518a** | **0.143a** | **0.475a** | **0.522a** | **1** | | |
| **Fe** | **-0.127b** | **0.423b** | **0.321b** | **0.421b** | **0.430b** | **1** | |
| **Zn** | **0.495a** | **0.638b** | **0.537b** | **0.863b** | **0.785a** | **0.706b** | **1** |

**Table 10: Pearson's Correlation Matrix of Trace Metals in Sediment from QIRE during the Wet Season**

| | Pb | Cd | V | Cr | Ni | Fe | Zn |
|---|---|---|---|---|---|---|---|
| **Pb** | **1** | | | | | | |
| **Cd** | **0.643a** | **1** | | | | | |
| **V** | **0.553a** | **0.537a** | **1** | | | | |
| **Cr** | **0.772a** | **0.767b** | **0.719b** | **1** | | | |
| **Ni** | **0.408a** | **-0.267b** | **0.193b** | **0.314a** | **1** | | |
| **Fe** | **0.080a** | **0.116a** | **0.208** | **0.537b** | **0.466b** | **1** | |
| **Zn** | **-0.508b** | **-0.455c** | **-0.616b** | **-0.217** | **0.214c** | **0.174a** | **1** |

**a = not significant**
**b = significant at P < 0.05**
**c = significant at P < 0.01**

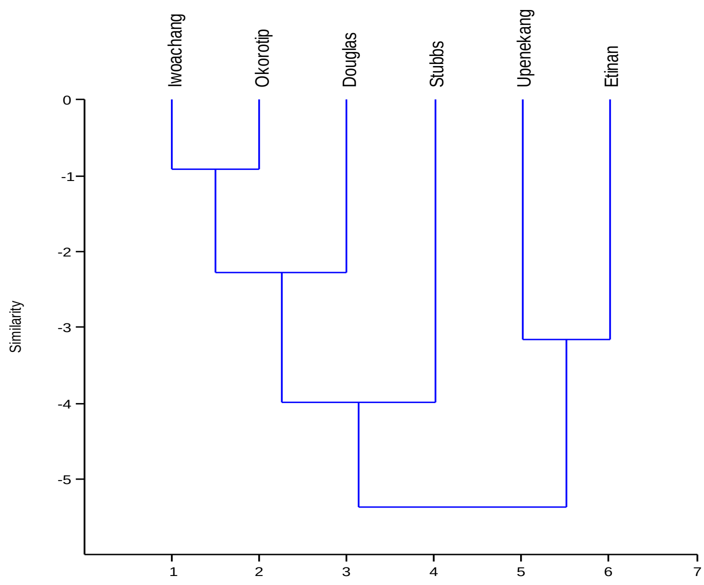


**Figure 1: Dendrogram showing spatial distribution of trace metals in sediment (Dry season )**

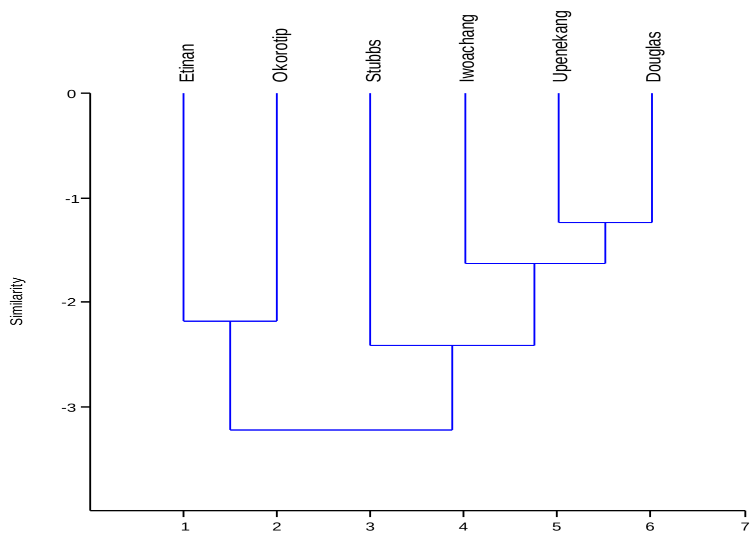


**Figure 2 :Dendrogram showing spatial distribution of trace metals in sediment (wet season)**

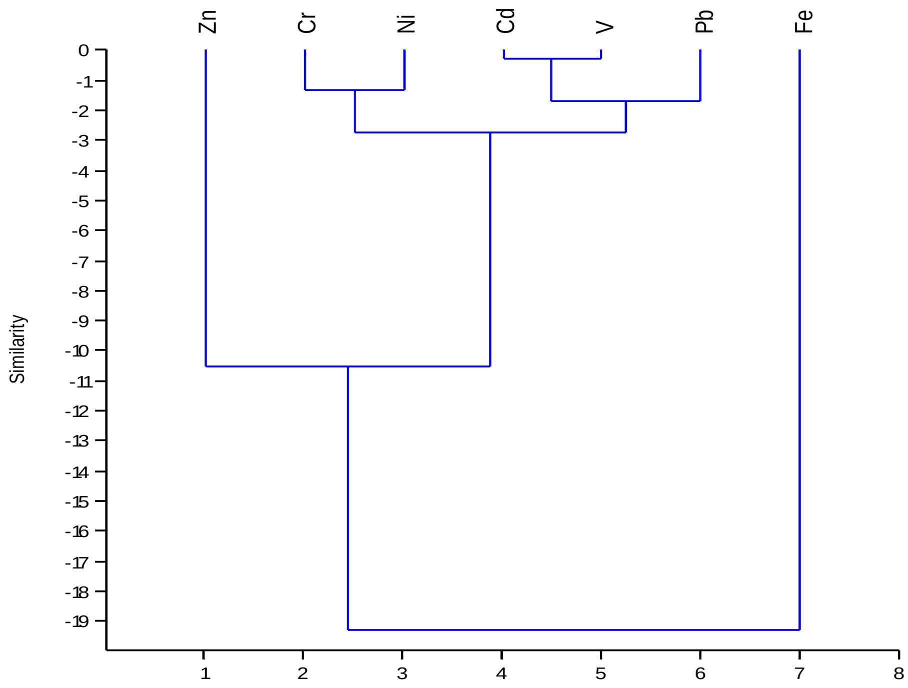


**Figure 3: Dendrogram showing metals trend in sediment during the dry season**

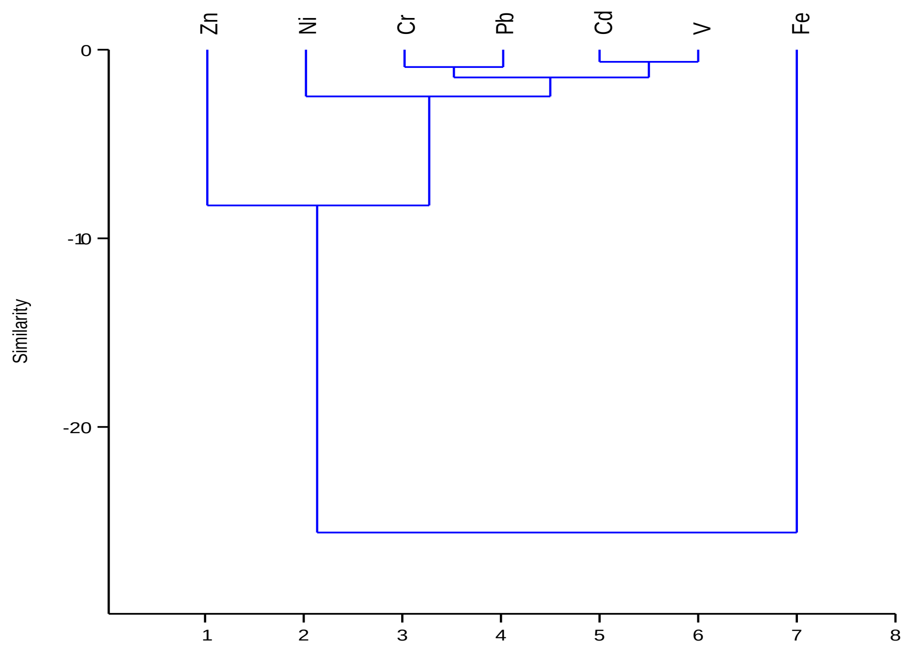


**Figure 4: Dendrogram showing metals trend in sediment during the wet season**

# DISCUSSION

### Trace metals concentration

In this study, higher dry season mean values of trace metals than wet season values were observed. This trend may be due to adsorption to sediment particles because of reduced water volume usually associated with increase evaporation rate in the dry season [5] or metal dissolution as a result of low water pH[14].Higher levels of trace metals in the studied sites compared to the control sites confirms the fact that the control site has a lower pollution status compared to other locations

.

All the metals investigated in both seasons were below the sediment quality guideline except iron [15, 16]. The results from this studies were higher than values reported by [5,11] but lower than values reported by [2, 10]. The highest level was obtained at Stubb creek during the dry season and the lowest level was obtained at Ekpene Ukpa during the same season. High level of iron in sediment of this study area and other parts of Nigeria has been reported by other authors[10, 11, 17]. Most of the pipelines used in conveying oil from the platform to the treatment sites are made up of iron, ferro-chromium materials and alloys of zinc and iron which when corroded can result in the release of these metals into the aquatic ecosystem. Moreover, the concentration of Fe in sediment may due to the nature of soil along the aquatic ecosystem and high levels of iron in Nigerian soils has been reported [4].

Generally, elemental concentrations of sediments depends not only on anthropogenic and lithogenic sources but also on the textural characteristics such as organic matter, mineralogical composition and depositional environment of the sediments [18]. Fine sediments (mud) dominate QIRE and trace metals are believed to be more associated with smaller grain size particles. This assertion was supported by [19]who stated that the concentration of metals in sediment depends on the amount of organic compound and its particle size. Other factors that affect the abundance of metals in sediments include the trace metal content of the rock and parent material of soil formation [20].

### Contamination indices

According to [21], CF < 1 indicates low contamination, 3≤CF≤6 indicates moderate contamination while CF≥6 indicates high contamination factor. On the basis of the above classification, QIRE sediments recorded very high contamination for Pb, Cd and V in both seasons. However, the contamination of Cd at Okoroutip and Ukpenekang was low and can be categorized into class I. Considerable contamination was recorded for Cr and Ni in the dry season while Cr and Ni revealed moderate contamination in the wet season. The value of contamination factor for Fe and Zn was low for both seasons. In addition, the degree of contamination of all the trace metals investigated in this study was very high [22].

The high CF values for Pb and Cd recorded in this study may be due to pollution sources such as industrial waste from non-treatment of oil field waste from petrochemical plants discharged into the ecosystem, agricultural run-off and other anthropogenic inputs. The pollution load index provides a simple comparative means for assessing and comparing an estuarine sediment quality. A value of zero or less than one indicates perfection, a value of (1.0) indicates baseline level of pollutants present and values above one indicate progressive deterioration of the estuarine quality [13, 23].Since the value of PLI was greater than one for all the sampling sites in both seasons, there is need for immediate intervention and rectification to ameliorate the level of pollution in sediments from QIRE.

Enrichment factor (EF) is an important aspect of geochemical studies used to differentiate between metals originating from anthropogenic (non-crustal) source and geogenic (crustal) sources [14, 22]. Enrichment factor values greater than one indicates minor sediment contamination, 0 < EF < 10 indicates contamination from natural origin for instance soil or parent rock while EF values greater than 10 are considered to be from anthropogenic sources [24].

For the studied locations, the enrichment factor for Pb and V for all the stations apart from the control site indicate anthropogenic source of contamination in the wet season while lead at Iwoachang, Douglas creek and Stubb creek and vanadium at Okoroutip and Douglas creek indicate anthropogenic contamination in the dry season. For other trace metals apart from Pb and V, their source of contamination may be natural (EF< 10).

Generally, zinc, nickel, chromium and cadmium showed minor to moderate enrichment for both seasons while lead and vanadium demonstrated severe enrichment to very severe enrichment. In this study, the enrichment factor for trace metals in the wet season was higher than that of the dry season. This may be due to run-offs, and tidal incursions and flooding. This corroborates with the research undertaken by [25] who reported higher enrichment factor values in the wet season than the dry season. The finding in this study is consistent with the results of other studies [14, 22].

Geoaccumulation Index (Igeo) of sediment was classified by Muller and based on Muller [26] classification, lead at Stubb creek was extremely polluted (6.67), Okoroutip and Ukpenekang were moderately polluted while Iwoachang and Douglas creek were severely polluted during the dry season. In addition, lead in the wet season was severely polluted while vanadium and cadmium were moderately to severely polluted for both seasons.

In both seasons, Igeo values for iron in this study was less than one showing that the sediment was not contaminated with respect to the above classification. This makes iron a suitable normalizer for sediments in this study area. The finding for iron in this study is similar to the report of [14]. In this study, Fe is used as a conservative tracer to differentiate natural from anthropogenic pollution source. According to [27], identification of anomalous metal concentration and evaluation of metal abundance is achieved by geochemical normalization of the trace metal data to a conservative element e.g Al, Fe, Si. Iron may be chosen as normalization element because its origin is exclusively lithospheric.

The result in this studies suggest possible geo-accumulation of Pb, Cd and V and background concentration for Fe, Zn, Ni, Cr in sediments from QIRE. Accumulation of trace metals in sediments tends to pose threats to aquatic life due to re-suspension into the water column from geochemical cycling, bioaccumulation in benthic organisms, biomagnification through the aquatic food web and remobilization [2]. In addition, most trace metals are transferred through the food chain via the following pathway: sediment----zoobenthos-----benthonic canivores---- human [20].

**Correlation and Hierarchical cluster analysis**

Significant correlations between metal pairs imply that they may have co-accumulation potentials, same anthropogenic pollution or natural pollution source and chemical association between trace metals in a particular area [28,29]. In this study, the chemical association observed between Pb, Cr, Fe,V, Cd and Zn may be due to their similarity in chemical structure, valency and their ability to replace each other in their ores or reaction sites. Manahan [30] reported that cadmium is very similar to zinc and these metal are found in oxidation state of +2 and frequently undergo geochemical processes together. Cadmium occurs naturally in ores together with zinc, lead and copper [31]. In the wet season, an inverse relationship was observed between Zn- Cd, Zn-Pb and Zn - V. When (HCA) was used to explain the spatial distribution and sources of trace metals in sediments from six sampling sites from QIRE, the designated sites were found in the same cluster while the control site was found in a different cluster. The above classification may be due to the concentration of the metals at the sampling sites, their degree of contamination and PLI values .In addition, the inclusion of Okoroutip in the cluster with low trace metal contamination may be due to the seasonal effect of flooding and dilution of the trace metal concentration in the wet season. Similar trend was observed in another study [32]. Figures 3 and 4 reveal that the pollution source of iron and zinc may be crustal while the pollution due to V, Cr, Ni, Cd, and Pb may be man-made.

## 4. CONCLUSION

This study was designed to determine the levels of some trace metals in sediment from Qua Iboe River Estuary (QIRE), Nigeria and evaluate their sediment contamination indices. The highest value was recorded for iron at Stubb creek during the dry season while the lowest value was recorded for vanadium at EkpeneUkpa during the wet season. Only iron was above the sediment quality guideline stipulated by National Oceanic and Atmospheric Administration while the results for sediment contamination indices reveal that Pb,V and Cd are capable of causing potential ecological risk to sediment dwelling organism. This calls for proper treatment and minimization in the discharge of petrochemical waste which been identified as the major sources of lead, cadmium and vanadium in the above estuary.

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