Spatio-Temporal Variations of Heavy metals Concentrations in Sediments of Qua Iboe River Estuary, South-South, Nigeria.

ABSTRACT

Studies on spatio-temporal variation in heavy metal concentrations in Sediments from Qua Iboe River Estuary, South-South, Nigeria was conducted between January, 2022 and December, 2022 with the aim of understanding the route sources of heavy metal concentration within the system. Sediment samples were collected monthly from five stations taking cognizance of areas with high, medium and low human activities along the estuary. The samples collected were analyzed using standard protocol as recommended by APHA. Mean values of heavy metals in sediments for wet and dry seasons were as follows: Cadmium (0.20±0.04 and 0.19±0.04 mg/kg), Chromium (0.35±0.07 and 0.28±0.05 mg/kg), Copper (0.97±0.15and 10.94±0.14 mg/kg), Iron (130.79±13.69 and 115.29±10.19 mg/kg), Lead (0.56±0.06 and 0.54±0.06 mg/kg), Zinc (19.36±2.24 and 18.71±2.78 mg/kg). Heavy metal concentrations in sediments were below the DPR target / intervention limits with exception of iron without a standard. Analysis of variance and paired sample t-test revealed significant (p = 0.05) spatial variation but no seasonal variations were observed respectively. The result obtained from this study showed that heavy metals levels were below DPR target / intervention limit which shows moderate level of anthropogenic activities within the study area. However, constant monitoring of aquatic ecosystem is strongly recommended.

Keywords: Spatial, Temporal, variation, sediment, Heavy Metal, Nigeria.

1.0 Introduction

Sediments reflect past and current status of the environment as well as providing crucial information on the impact of pollution sources (George and Efiom, 2017). Sediment is an integral component of aquatic ecosystem providing habitat, feeding, spawning and rearing ground for many aquatic organisms (George and Efiom, 2017). Sediments plays a vital role in the remobilization of contaminants in aquatic ecosystem under certain environmental 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 benthic zone (Moses, *et. al*, 2015).

Consequently, sediments enriched with trace metals may affect the health of marine organism and aquatic ecosystem. 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 (Obasahan, 2008).

Trace metal assessment in aquatic media is necessary, because the intensity of toxicity of many metals and their compounds are becoming a threat to environmental health. Trace metals below and above a certain threshold results in metabolic disorders, and some of them especially As, Cd, Cr, Hg, Pb, Se, Co and V may constitute serious health hazards to humans as well as other forms of living things (George *et. al*., 2013). Therefore, assessment of trace metals with high accuracy and sensitivity in aquatic ecosystem is very important in monitoring their environmental impact, pollution and toxicity (Efiom and George, 2018).

Sediments are sensitive indicators for monitoring and evaluation of contaminants in water bodies (George and Efiom, 2017). The bottom sediments are a reservoir for heavy metals and therefore earn distinct consideration in the planning and design of aquatic pollution research studies (Loska and Wiechula, 2003). Several studies on the impacts of human activities on aquatic sediments have been reported - Chindah, *et. al.*, (2009); Akpan and Thompson, (2013); Uwah, *et. al.* (2013); Benson, *et. al.* (2016); George and Efiom, (2017) and Efiom and George, (2018) Thus, the aim of this study is to evaluate the level of heavy metal concentrations in the bottom sediments of Qua Iboe River Estuary and relate it to the anthropogenic activities in the area.

2.0 Materials and Methods

2.1 Study area

The Qua Iboe River Estuary (QIRE) (Fig. 1) lies within latitude 4º 30´ to 4º 54'N and longitude 7º 30´ to 8º 00' E on the South Eastern Nigeria coastline. It is a meso-tidal estuary having tidal amplitude of 1m and 3m at neap and spring phases respectively (Uwah *et.al*. 2013). Sediments are brought into the estuary by longshore drift, tidal flow, waves and river transport. Coarse to medium-grained sand occurs mostly in the mouth of the estuary and middle of the main channels where the tidal current is strong but most parts of the banks and creeks where the tidal current are weak are characterized by fine sand, silt and clay. The latter has high affinity for pollutants such as hydrocarbon and heavy metals (Uwah *et.al.* 2013). The climate of the area is characterized by a long-wet season usually lasting from May to November and a short period of dryness from December to April. The QIRE is comprised of tidal creeks (most notably Stubb creek and Douglas creek), lagoons, wetlands, and tributaries fringed with mangrove vegetation made up of species of Avicennia, Rhizophora and Nypa. The coastal vegetation of the area is mainly thick mangrove swamp. The main occupation of the inhabitants include large scale fishing employing the use of fishing vessels, small scale fishing by artisanal fishermen employing the use of fishing boats, farming activities involving the use of agrochemicals, boat construction, sand mining for commercial purposes as well as timber logging of mangrove vegetation as fuel wood (Ekwere, et.al. 1992).

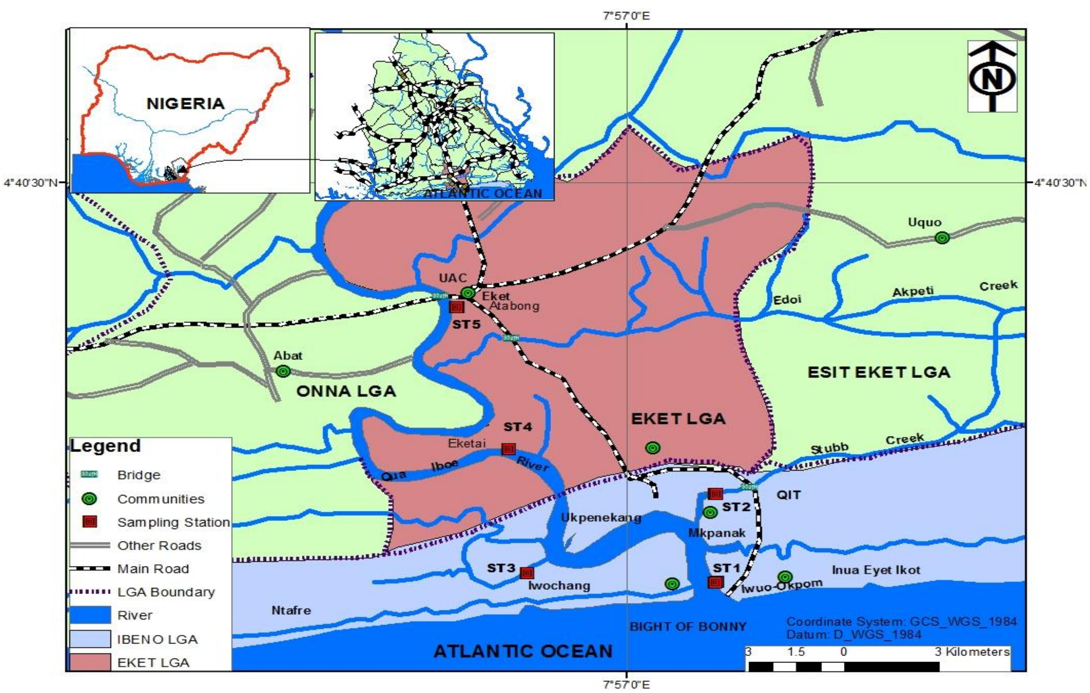

Fig 1: Map of the study area showing sampling stations in Qua Iboe River Estuary

2.2 Study Locations

Station 1

Station 1 is the discharge point; it receives waste from the market and domestic waste from the inhabitants of the community. Other coastal activities in this station include, large scale fishing using fishing vessels, small scale fishing with motorized boats with possible oil and fuel spills from the boat engine and open defecation into the Estuary. Station 1 is a pure mangrove plots comprising of *Avicennia africana* cohabiting with *Achrostichum aureum.* This station is located at Iwuokpom between latitude 4^0 32´ N and longitude 7^0'58' E.

Station 2

Station 2 is the Exxon Mobil - QIT terminal. This is where off-loading of finished petroleum product from ship to pipelines is done and fishing activities is also high in this station. Other coastal activities include, large scale fishing using fishing vessels, small scale fishing with motorized boats with possible oil and fuel spills from the boat engine, gas flaring and disposal of domestic waste from inhabitants of the community into the Estuary. Station 2 is a mixed mangrove vegetation comprising *Nypa fruticans, Avicennia africana, Rhizophora mangle* and *Achrostichum aureum.* This station is located at Mkpanak between latitude 4^0 34´ 09.9'' N and longitude 7^0 58' 32.8'' E.

Station 3

This is a commercial station with a large market located at the River side, domestic wastes from human households is being emptied into the River. Other coastal activities in this station include, large scale fishing using fishing vessels, small scale fishing with motorized boats with possible oil and fuel spills from the boat engine, boat construction, disposal of market / domestic waste and open defecation into the Estuary. This is a landing site for fishermen and distribution to other sectors and also a boat park for movement of goods and people within the estuarine communities. Station 3 is a characteristic of mono-specific mangrove vegetation subjugated by *Nypa fruticans* interlaced with few stands of *Elaise guineensis.* The station is located at Iwuochang between latitude 4^0 32´ N and longitude 7^0 55'E.

Station 4

Station 4 is the discharge point; it receives run-off from agricultural farmlands and wood industry sited 1.5 km from the river bank. Fishing activities in this station is minimal employing the use of motorized boat by artisanal fishermen and for transportation of wood with possible oil and fuel spill from the boat engine. Dredging is one of the major coastal activities sited in this station. Station 4 is a secondary swamp forest composed of diverse species such as *Pandanus candelabrum*, *Elaise guineensis*, *Pycnathus angolensis*, *Raphia hookeri* , *Musanga cercropiodes*, *Barteria nigritiana*, *Anthocleista djalonensis* with *Cytrospermum sengalensis*, *Afzelia nephtytis* and *Smilax anceps* as undergrowth. This station is located at Eketai between latitude 4^0 35' N and longitude 7^0 54'E.

Station 5

Station 5 is the discharge point; it receives effluents from urban / drainage discharge, abattoir which is usually flooded during high tide, effluents from auto-mechanic workshop and car wash activities. A fringing vegetation dominated by species such as *Symphonia globulifara, Pandanus candelabrum, Cytrospermum senegalenses, Alstonia boonei, Elaise guineensis and Vossia cuspidate*. This station is located at Atabong between latitude 4^0 38' N and longitude 7^0 54' E.

2.3 Samples Collection

Sediments samples were collected monthly between Januaryand December, 2022; covering the dry and wet seasons.The samples were collected with Van Veen grab sampler. 5 grab samples were collected at each sampling station and were combined together into a stainless-steel bowl to make a composite sample. A total of three hundred subsamples and 60 composite samples were collected, dried, ground and sieved.

2.4 Laboratory Analysis

2.4.1 Determination of Trace Metals

1 g of air - dried sediment was weighed accurately and sieved through 2 mm sieve on a foil paper and transferred to a 250 ml conical flask. A measured volume of well - mixed acid, Perchloric acid, nitric acid and sulphuric acid in the ratio 1: 2: 2 was transferred into the flask containing the sediment sample in the fume hood. The sample was heated for about (15 - 20 minutes) in the hot plate until a white fume was observed. The digestion was stop and allowed to cool. After cooling, 20 ml of distilled water was added and boiled to bring the metal into solution. The solution was filtered through Whatman 42 filter paper in a 100 ml volumetric flask and make up to mark with distilled water and then transferred to 100 ml plastic can for AAS analysis. Heavy metals were determined using Atomic Absorption Spectrophotometer (model GBC scientific AASGF 3000) according to APHA, (1998, 2008).

2.5 Data Analysis

Statistical package for Social Sciences (SPSS) version 20 was employed to compute Mean, variance and standard error in the data. Also, one-way analysis of variance (ANOVA) and Least Significant Difference (LSD) test were employed to separate significant differences in mean values computed for stations while paired sample t-test was used to compare the seasons. The probability level was set at $p = 0.05$. Correlation analysis tested the association between various parameters along sampling stations.

3.0 Results

3.1 Mean Heavy Metal Concentrations in Sediments

The mean range of cadmium values recorded in the stations were 0.03±0.0 mg/kg (Atabong) – 0.52±0.06 mg/kg (Eketai) (Table 1). The spatial variation of cadmium showed significant difference ($p<0.05$). Eketai was significantly higher than the other stations while Iwuochange was significantly higher than the control (Ataobong). . Seasonal variation between the dry and wet season showed no significant difference ($p > 0.05$) (Table 2). Fig. 2 showed the spatial and temporal variations of cadmium concentration.

Table 1: Mean spatial variations in heavy metals in Qua Iboe River Estuary

Heavy Metal	Iwuokpom	QIT	Iwuochang	Eketai	Ataobong	DPR Limits
Cd.	$0.12±0.02^{bc}$	$0.14±0.05^{bc}$	$0.19±0.03^{b}$	$0.52±0.06^{a}$	$0.03±0^{c}$	0.80
Cr.	$0.08±0.04^{c}$	$0.13±0.01^{c}$	$0.47±0.01^{b}$	$0.83±0.06^{a}$	$0.03±0^{c}$	100
Cu.	$1.64±0.11^{a}$	$0±0^{c}$	$1.37±0.06^{b}$	$1.64±0.05^{a}$	$0.01±0^{c}$	36
Fe	$150.22±4.18^{b}$	$147.79±5.85^{b}$	$139.59±6.28^{b}$	$170.67±2.25^{a}$	$0.46±0.03^{c}$	-
Pb	$0.55±0.06^{c}$	$0.72±0.01^{b}$	$0.57±0.04^{c}$	$0.84±0.05^{a}$	$0.002±0^{d}$	85
Zn	$24.95±4.49^{a}$	$24.58±4.42^{a}$	$13.08±0.97^{b}$	$27.85±2.05^{a}$	$0.29±0.02^{c}$	140

Means with different superscripts along the same row are significantly different (Duncan's test) $p<0.05$

Table 2: Seasonal Variations in Heavy Metals in Qua Iboe River Estuary

	DRY	WET
Cadmium	$0.20±0.04^{a}$	$0.19±0.04^{a}$
Chromium	$0.35±0.07^{a}$	$0.28±0.05^{a}$
Copper	$0.97±0.15^{a}$	$0.94±0.14^{a}$
Iron	$130.79±13.69^{a}$	$115.29±10.19^{a}$
Lead	$0.56±0.06^{a}$	$0.54±0.06^{a}$
Zinc	$19.36±2.24^{a}$	$18.71±2.78^{a}$

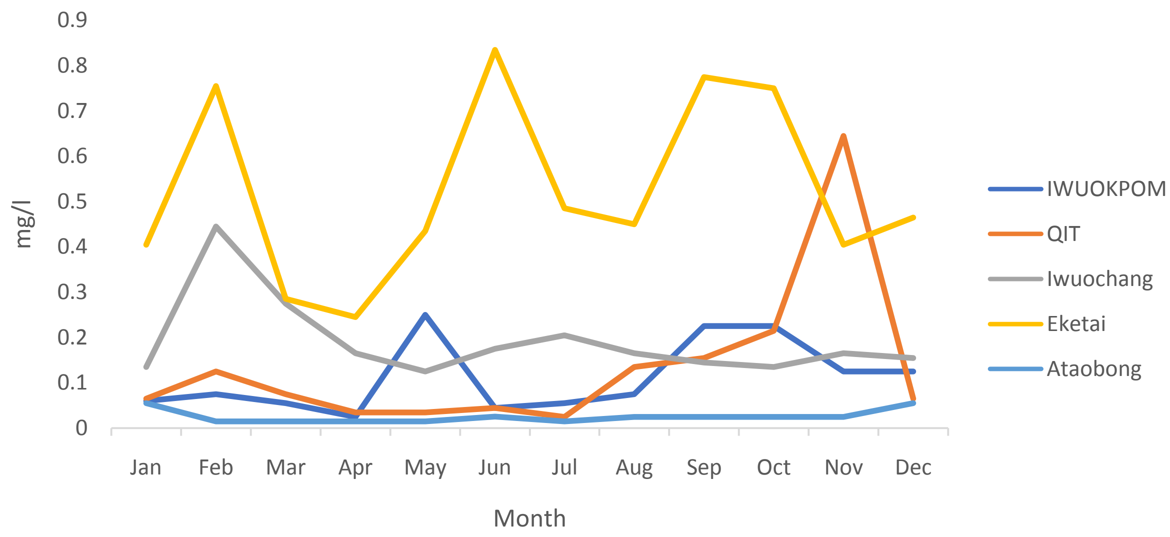

Fig.2: Spatio-Temporal Variations of Cadmium in Qua Iboe River Estuary

The mean values recorded for chromium were from 0.03±0.00 mg/kg (Atabong) - 0.83±0.06 mg/kg (Eketai). Significant spatial variation ($p < 0.05$) was observed for chromium. Eketai and Iwuochange were significantly higher than the other stations. However, there was no significant seasonal variation (Table 2). Fig. 3 showed the spatio-temporal variations of chromium.

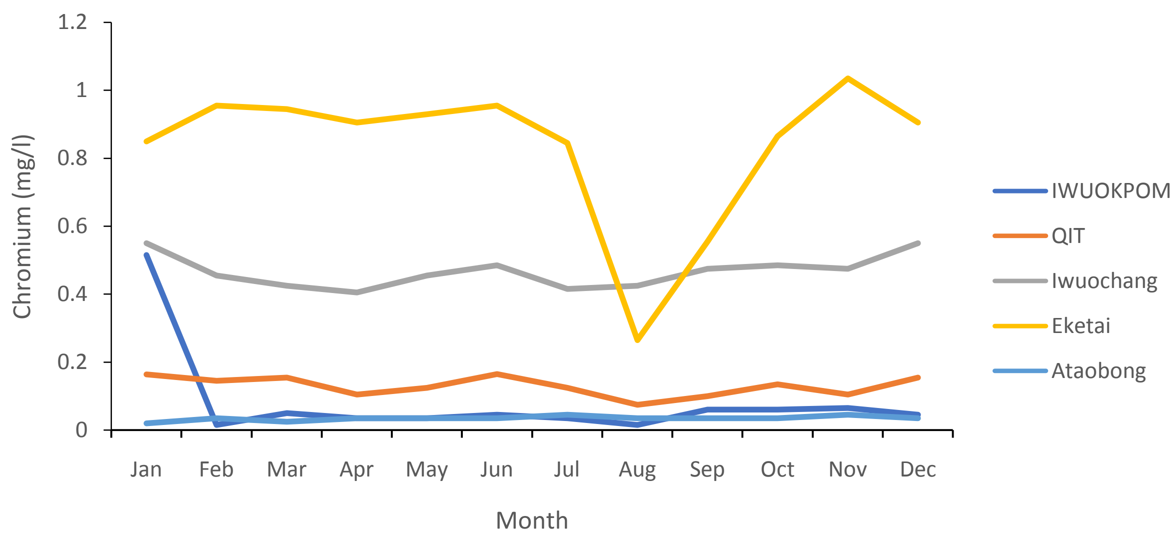

Fig. 3: Spatio-Temporal Variations of Chromium in Qua Iboe River Estuary

Mean Cu values recorded in the stations were 0.00±0.00 at (Atabong) – 1.64±0.05 mg/kg at (Eketai) and (Iwuokpom) respectively (Table 1). The spatial variation of copper showed significant difference ($p<0.05$). Iwuokpom and Eketai were significantly higher with the lowest value recorded at QIT. Seasonal variation between the dry and wet season showed no significant difference ($p > 0.05$) (Table 2). Fig. 4 showed the spatial and temporal variations of cadmium concentration during the study duration.

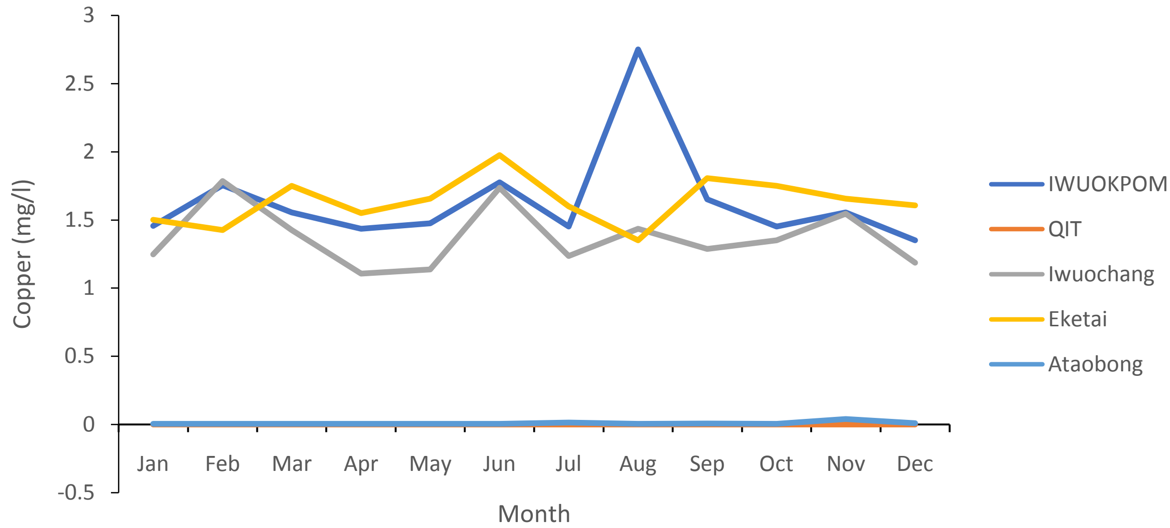

FIGURE 4: SPATIO-TEMPORAL VARIATIOINS IN COPPER IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022).

Fe values recorded spatially across the stations were 0.46±0.03 at (Atabong) – 170.67±2.25 mg/kg at Eketai (Table 1). Significant spatial variation ($p<0.05$) was observed for iron during the study duration. Eketai recorded higher Fe values with the lowest value recorded at Atabong. Seasonal variation between the dry and wet season showed no significant difference ($p > 0.05$) (Table 2). Fig. 5 showed the spatial and temporal variations of iron concentration during the study duration.

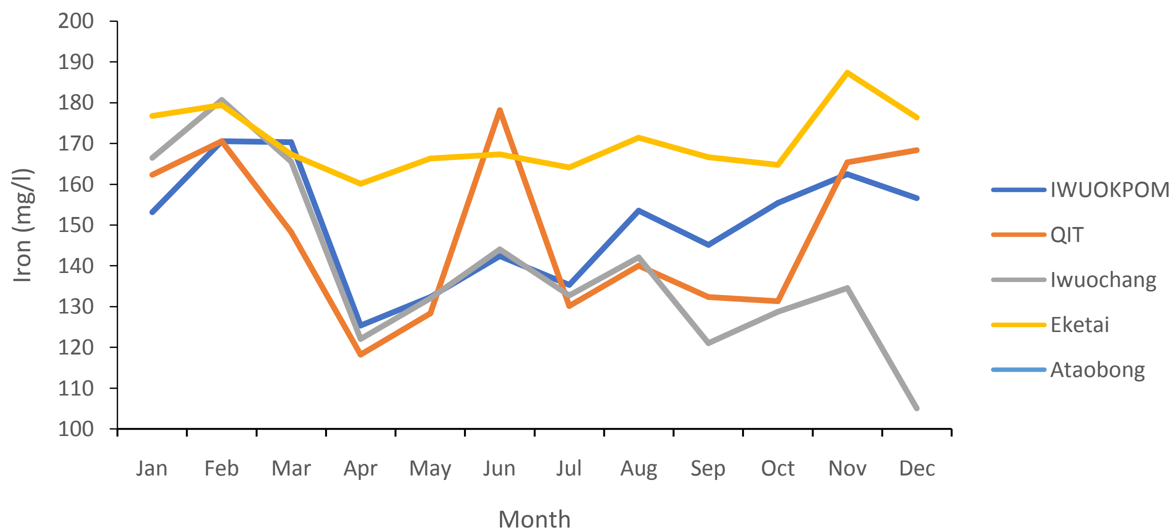

FIGURE 5: SPATIO-TEMPORAL VARIATIOINS IN IRON IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022)

The mean values Pb computed spatially during the study range between 0.002±0.00 at (Atabong) - 0.84±0.05 at (Eketai) (Table 1). Significant variation at p = 0.05 was computed for Pb spatially but there was no significant difference recorded temporally during the period of study (Table 1 and 2). Fig. 6 shows the temporal and spatial variation in Pb throughout the study duration.

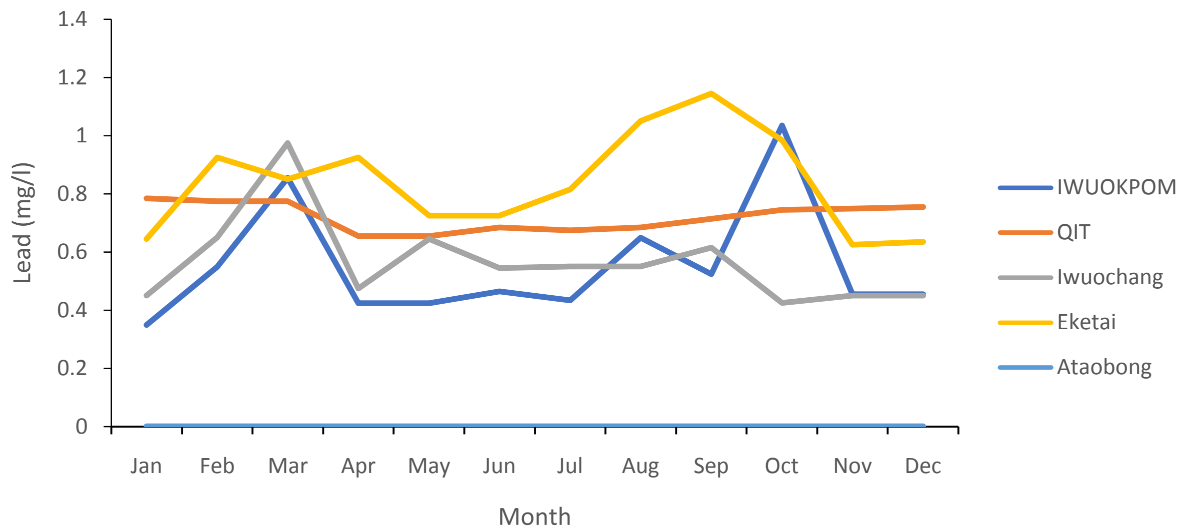

FIGURE 6: SPATIO-TEMPORAL VARIATIOINS IN LEAD IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022)

Mean Zn values computed spatially during the study range between 0.29±0.02 at (Atabong) - 27.85±2.05 at (Eketai) (Table 1). Significant variation at p = 0.05 was observe for Zn across the stations but there was no significant difference recorded between seasons (dry and wet) during the period of study (Table 1 and 2) respectively. Fig. 7 shows the temporal and spatial variation in Zn throughput the study duration.

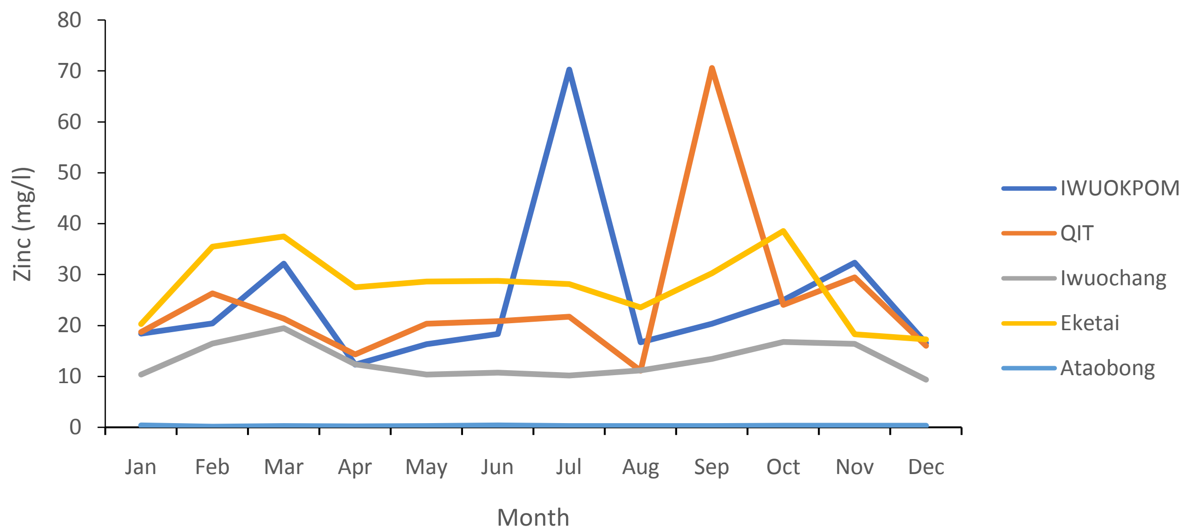

FIGURE 7: SPATIO-TEMPORAL VARIATIOINS IN ZINC IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022).

4.0 Discussion

The results showed higher dry season mean values of heavy metal concentration than wet season values. This result agrees with earlier reports by George and Efiom, (2017); Efiom and George, (2018). This trend may be due to dilution of metal concentration during the rainy season by direct precipitation / run off from adjourning lands or reduction in human / industrial activities as a result of the rains. The concentrations of heavy metals in each of the stations were related to the levels of human activities in each of these stations. The high values of heavy metal concentration recorded at Eketai are a clear evidence of the levels of anthropogenic activities in the stations.. These activities included, dredging, wood lumbering, boat transportation, agricultural activities, bathing, washing of clothes and cars and indiscriminate disposal of both domestic and industrial waste. All the metals investigated in both seasons were below the Department of Petroleum Resources (DPR) target / intervention limits for sediment quality guideline exception of iron that does not have DPR target limit (DPR, 2002). The results of this study is consistent with related studies (Olatunji and Osibanjo, 2012, Ideriah, *et. al*. 2013; George and Efiom, 2017; Efiom and George, 2018).

High level of iron in sediment of this study area and other parts of Nigeria have been reported (Udosen, *et. al*. 2007; Issa, *et. al*. 2011; Opaluwa, *et. al*. 2012, George and Efiom, 2017; Efiom and George, 2018).
Furthermore, the high concentration of Fe in sediment may be attributed to the nature of the soil and the levels of human activities in and around the study area. High levels of iron in Nigerian soils have been documented by Oluwu, *et.al*. (2010).

Generally, the elemental concentrations of heavy metal in sediments are not only attributed to anthropogenic and lithogenic routes but also on the textural characteristics of the sediment such as the level of organic matter, mineral composition and depositional environment of the sediments (Pourang, *et.al*. 2005). Fine sediments (mud) dominate QIRE and heavy metals are assumed to be more connected with smaller grain size particles. This assertion was buttressed by (Saeed and Shaker, 2008) that stated that the concentration of metals in sediment depends on the quantity of organic matter and its particle size.

5. Conclusion

This study was designed to assess the connections between anthropogenic activities and the observed status of sediment quality from Qua Iboe River Estuary (QIRE), Nigeria. The values of iron was high when compared to other metals. However, the sediment quality guideline value for iron according to Department of petroleum Resources is not known which made it difficult to conclude if the concentration observe during the study was within or above the threshold limit while the results for other heavy metals such as Cd, Cr, Cu, Pb and Zn were below the DPR target / intervention limit. Nevertheless, the levels of heavy metals observed in the sediment of QIRE reveal evidence of anthropogenic activities within the study area. If the trend continues without curtailing the level of human activities, it may pose severe risk to benthic dwelling organism. This calls for the need to educate the rural dwellers on proper management and disposal of waste and also industries should adhere to proper treatment and minimization in the discharge of industrial waste which has been identified as one of the major sources of heavy metals within the study area.

6.0 References

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