

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

## ABSTRACT

Studies on spatio-temporal variation in heavy metal concentrations in benthic 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 and provide result which will allows policy-makers and local actors to design programs and policies that will help improve upon the existing practices and mitigate future contamination problems. Sediment samples were collected monthly ~~in-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 and other contaminants in sediments for wet and dry seasons were as follows: Cadmium ( $0.20 \pm 0.04$  and  $0.19 \pm 0.04$  mg/kg), Chromium ( $0.35 \pm 0.07$  and  $0.28 \pm 0.05$  mg/kg), Copper ( $0.97 \pm 0.15$  and  $10.94 \pm 0.14$  mg/kg), Iron ( $130.79 \pm 13.69$  and  $115.29 \pm 10.19$  mg/kg), Lead ( $0.56 \pm 0.06$  and  $0.54 \pm 0.06$  mg/kg), Zinc ( $19.36 \pm 2.24$  and  $18.71 \pm 2.78$  mg/kg). Heavy metals concentrations in sediments were below the DPR target / intervention limits ~~with~~ exception of iron ~~without a which set-standard, is not established~~. Analysis of variance and paired sample t-test revealed significant ( $p = 0.05$ ) spatial variation but no seasonal variations were observed respectively. However, the series of activities evident, coupled with the findings of this study further justify the need for appropriate monitoring and management of our indigenous water bodies.

**Keywords:** Spatio, Temporal, variation, benthic sediment, Heavy Metal, Nigeria.

## 1.0 Introduction

Sediments reflect the ~~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 ~~areas-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~~. 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).

Benthic Sediments are sensitive indicators for monitoring and evaluation of contaminants in ~~waterbodies~~. The bottom sediments are a reservoir for heavy metals and therefore earndistinct 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 ~~has-beinghave been~~ reported ~~;~~ Chindah, *et. al.*, (2009); George and Efiom, (2017); Akpan and Thompson, (2013); Uwah, *et. al.* (2013); Efiom and George, (2018) and Benson, *et. al.* (2016).

Thus, the aim of this study is to evaluate the level of heavy metal concentrations ~~in benthic-the bottom~~ sediments of Qua Iboe River Estuary and ~~examine the correlation between the observed anthropogenic activities within the study area and the levels of heavy metal recorded, relate it to the anthropogenic activities in the~~

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**Comment [None2]:** Which other contaminants was considered in this study?

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area. It is expected that the result from this study will help complement existing data which will help policy makers in the proper planning and policies that will help abate pollution.

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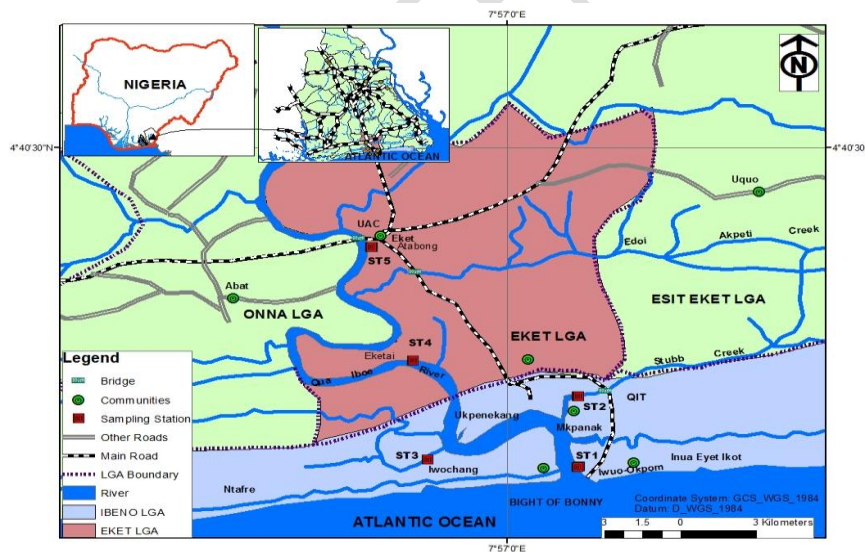
## 2.0 Materials and Methods

### 2.1 Study area

The Qua Iboe River Estuary (QIRE) lies within latitude  $4^{\circ} 40' 30'' \text{N}$  and longitude  $7^{\circ} 57' 0'' \text{E}$  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 (Uwahet.al. 2013). Sediments are brought into the estuary by longshore drift, tidal flow, waves and River-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 (Uwahet.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 weather 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 excavation-mining for commercial purposes as well as timber logging of mangrove vegetation as fuel wood (Ekwere, et.al. 1992). The sampling sites are made up of four examined-sites located at the lower reach of the estuary and a control site located at Atabong (Fig. 1). The global positioning system (GPS) coordinates of the different sites are: Iwuokpom ( $40^{\circ} 32' \text{N} - 70^{\circ} 58' \text{E}$ ), Mkpanak ( $40^{\circ} 34' 09.9'' \text{N} - 70^{\circ} 58' 32.8'' \text{E}$ ), Iwochang ( $40^{\circ} 32' 50'' \text{N} - 70^{\circ} 55' 03'' \text{E}$ ), Eketai ( $40^{\circ} 35' \text{N} - 70^{\circ} 54' \text{E}$ ), Atabong ( $40^{\circ} 38' \text{N} - 70^{\circ} 54' \text{E}$ ). The control site (Atabong) is free from oil exploration and production activities and has less coastal activities compared to the examined-othersites. Figure 1 is a map of the study area indicating the sampling sites

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

### 2.2 Samples Collection

Sediments samples were collected monthly ~~for one year (between January, 2022 and December, 2022; covering a period spanning~~ the dry and wet seasons. ~~of the study area using~~ 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.

## 2.3 Laboratory Analysis

### 2.3.1 Determination of Trace Metals

1 g of air - dried sediment was weighed accurately and ~~passed-sieved~~ through (2 mm sieve) ~~on a -with~~ 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 makes 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).

### 2.4 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 ~~obtained across~~ recorded in the stations ~~during the period of survey~~ were  $0.03 \pm 0.01$  mg/kg (at Atabong) –  $0.52 \pm 0.06$  mg/kg (at Eketai) (Table 1). ~~Within the five sampling stations, the~~ The spatial variation of cadmium showed significant difference ( $p < 0.05$ ). Eketai was significantly higher than the other stations while Iwuochang was significantly higher than the control (Ataobong), at  $p = 0.05$  during the study period. Seasonal variation between the dry and wet season showed no significant difference ( $p > 0.05$ ) at  $p = 0.05$  (Table 2). Fig. 2 explain showed the spatial and temporal variations of ~~in~~ cadmium concentration.

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

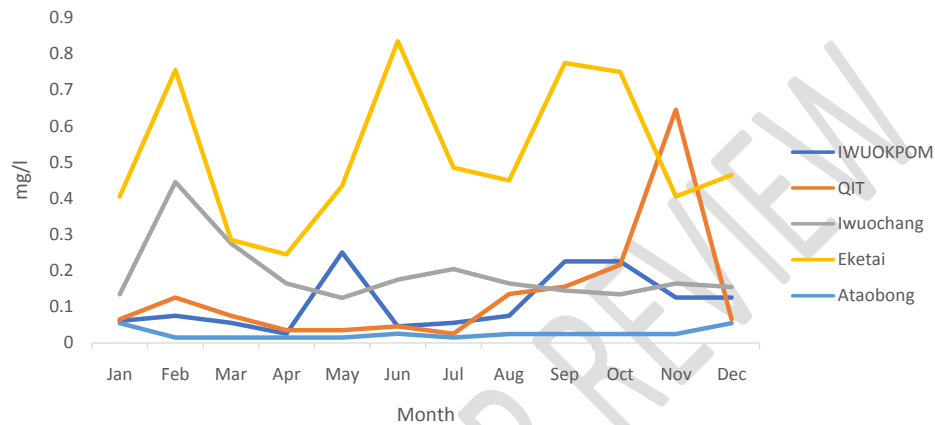
Heavy Metal	Iwuokpom	QIT	Iwuochang	Eketai	Ataobong	DPR Limits
Cd.	$0.12 \pm 0.02^{bc}$	$0.14 \pm 0.05^{bc}$	$0.19 \pm 0.03^b$	$0.52 \pm 0.06^a$	$0.03 \pm 0^c$	0.80
Cr.	$0.08 \pm 0.04^c$	$0.13 \pm 0.01^c$	$0.47 \pm 0.01^b$	$0.83 \pm 0.06^a$	$0.03 \pm 0^c$	100
Cu.	$1.64 \pm 0.11^a$	$0 \pm 0^c$	$1.37 \pm 0.06^b$	$1.64 \pm 0.05^a$	$0.01 \pm 0^c$	36
Fe	$150.22 \pm 4.18^b$	$147.79 \pm 5.85^b$	$139.59 \pm 6.28^b$	$170.67 \pm 2.25^a$	$0.46 \pm 0.03^c$	-
Pb	$0.55 \pm 0.06^c$	$0.72 \pm 0.01^b$	$0.57 \pm 0.04^c$	$0.84 \pm 0.05^a$	$0.002 \pm 0^d$	85
Zn	$24.95 \pm 4.49^a$	$24.58 \pm 4.42^a$	$13.08 \pm 0.97^b$	$27.85 \pm 2.05^a$	$0.29 \pm 0.02^c$	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
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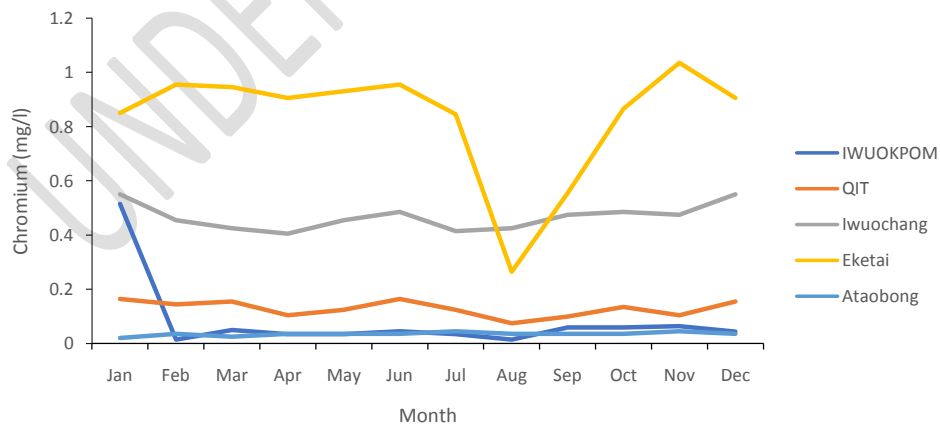
Cadmium	0.20±0.04 <sup>a</sup>	0.19±0.04 <sup>a</sup>
Chromium	0.35±0.07 <sup>a</sup>	0.28±0.05 <sup>a</sup>
Copper	0.97±0.15 <sup>a</sup>	0.94±0.14 <sup>a</sup>
Iron	130.79±13.69 <sup>a</sup>	115.29±10.19 <sup>a</sup>
Lead	0.56±0.06 <sup>a</sup>	0.54±0.06 <sup>a</sup>
Zinc	19.36±2.24 <sup>a</sup>	18.71±2.78 <sup>a</sup>



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

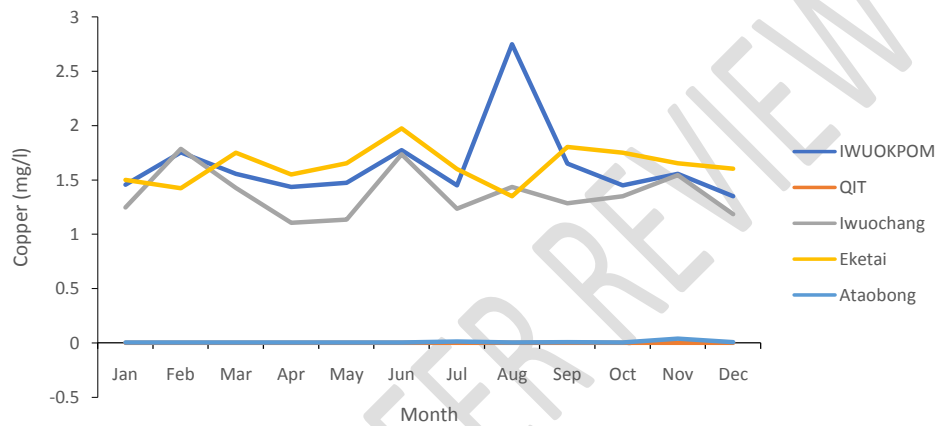
The mean values recorded for chromium across the sampling stations ranged between from 0.03±0 mg/kg (at-Ataobong) - 0.83±0.06 mg/kg (at-Eketai). Significant spatial variation ( $p < 0.05$ ) - at  $p = 0.05$  - was observed for chromium. Eketai and Iwuochang were significantly higher than the other stations. However, there was no significant seasonal variation difference as regards seasons (Table 2). Fig.3 showed the spatio-temporal variations of chromium across the stations in the different month of study.



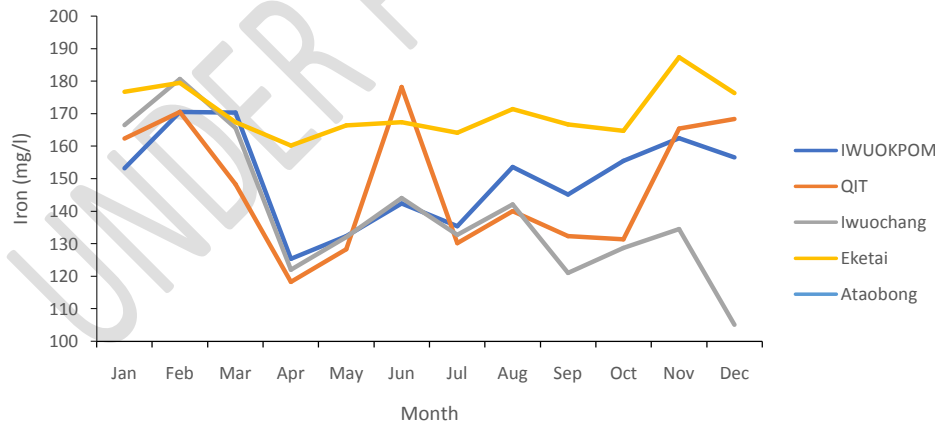
**Fig.URE3: Spatio-Temporal VariatioinsVariationsIn-ofChromium in Qua Iboe River EstuaryFOR WET AND DRY SEASON (January, 2022 -December, 2022).**

The mean values for Cu, Fe, Pb and Zn computed spatially during the study range between  $0\pm 0$  at QIT -  $1.64\pm 0.05$  at Iwuokpom and Eketai respectively for copper,  $0.46\pm 0.03$  at Atabong -  $170.67\pm 2.25$  at Eketai for iron,  $0.002\pm 0$  at Atabong -  $0.84\pm 0.05$  at Eketai for lead and  $0.29\pm 0.02$  at Atabong -  $27.85\pm 2.05$  at Eketai for zinc (Table 1). Significant variation at  $p = 0.05$  was computed for Cu, Fe, Pb and Zn across the stations but there was no significant difference recorded between dry and wet season during the period of study (Table 1 and 2) respectively. Fig. 4 – 7 shows the temporal and spatial variation in Cu, Fe, Pb and Zn respectively throughout the study duration.

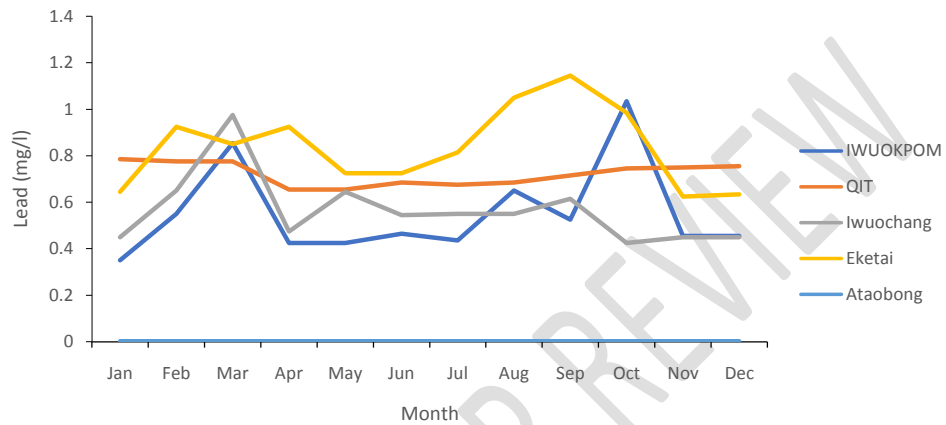
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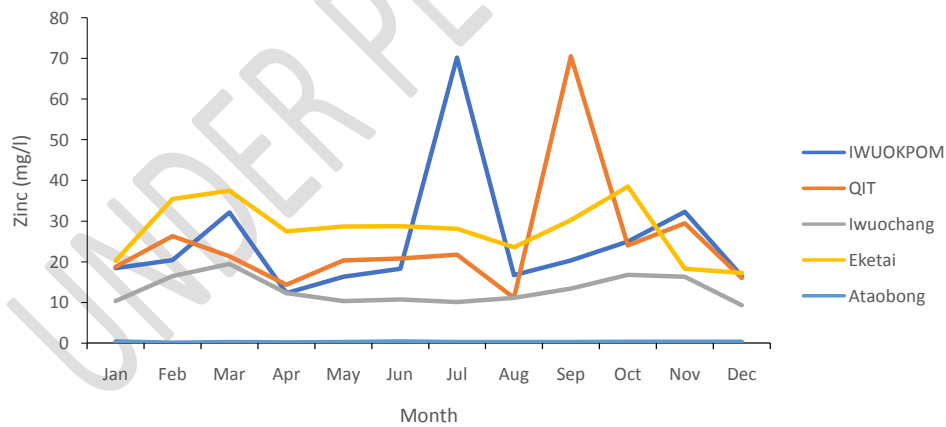
**FIGURE 4: SPATIO-TEMPORAL VARIATIOINS IN COPPER IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022).**



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



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



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

#### 4.0 Discussion

The results ~~computed for this study~~ 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 adjoining lands or reduction in human / industrial activities as a result of the rains. The concentrations of heavy metals ~~computed for in~~ each of the stations ~~in this study~~ were ~~adjudge-based or related to~~ the levels of human activities ~~emanating from in~~ each of these stations. The high ~~values of heavy metal concentration recorded at Eketai~~ ~~is values of heavy metal concentration recorded at Eketai~~ are a clear evidence of the levels of anthropogenic activities ~~sited in this in the~~ station, ~~during the study~~. 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~~ ~~which the DPR target limit is not known~~ (DPR, 2002). The results of this study ~~ies are~~ consistent with related studies ~~y conducted by~~ (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 ~~has have been reported~~ ~~reported~~ ~~(by other authors~~ (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~~ ~~is 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) ~~who 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 ~~recorded during the study~~ 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 observed 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 ecological 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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**Comment [None14]:** These should be included in the detailed description of the study station instead here.

**Comment [None15]:** This you didn't achieve because you presented your results superficially without relating their variations to the anthropogenic activities in the stations. First of all you didn't describe the stations in details for one to identify which anthropogenic activity is unique to each and the ones that can influence heavy metal contamination.

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**Comment [None17]:** There is none. Some parameters are like that. What you can do is to compare your results with studies done in the same region or related studies

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**Comment [None20]:** Which industries, what type of wastes, in which station are they located, up or downstream of that station

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