Spatio-Temporal Variation in Heavy metals Concentration in Benthic Sediment 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 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 sediment for wet and dry seasons were as follows: Cadmium (0.20±0.04and 0.19±0.04mg/kg), Chromium (0.35±0.07and 0.28±0.05mg/kg), Copper (0.97±0.15[a]and 10.94±0.14mg/kg), Iron (130.79±13.69and 115.29±10.19mg/kg), Lead (0.56±0.06and 0.54±0.06mg/kg), Zinc (19.36±2.24and 18.71±2.78mg/kg). Heavy metals concentrations in sediments were below the DPR target / intervention limit exception of iron 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 for many aquatic organisms (George and Efiom, 2017). Sediments plays 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 impacts of human activities on aquatic sediment has being 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 concentration in benthic sediment 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. It is expected that the result from this study will help complement existing datawhich will help policy makers in the proper planning and policies that will help abate pollution.

2.0 Materials and Methods

2.1 Study area

The Qua Iboe River Estuary lies within latitude 4º 40´30´´N and longitude 7º 57´0´´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 dry 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 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. The global positioning system (GPS) coordinates of the different sites are: Iwuokpom (40 32´ N - 70'58' E), Mkpanak (40 34´ 09.9'' N - 70 58' 32.8'' E), Iwochang (40 32´50" N – 70 55'03"E), Eketai (40 35' N – 70 54'E), Atabong (40 38' N – 70 54' E). The control site (Atabong) is free from oil exploration and production activities and has less coastal activities compared to the examined sites. Figure 1 is a map of the study area indicating the sampling sites

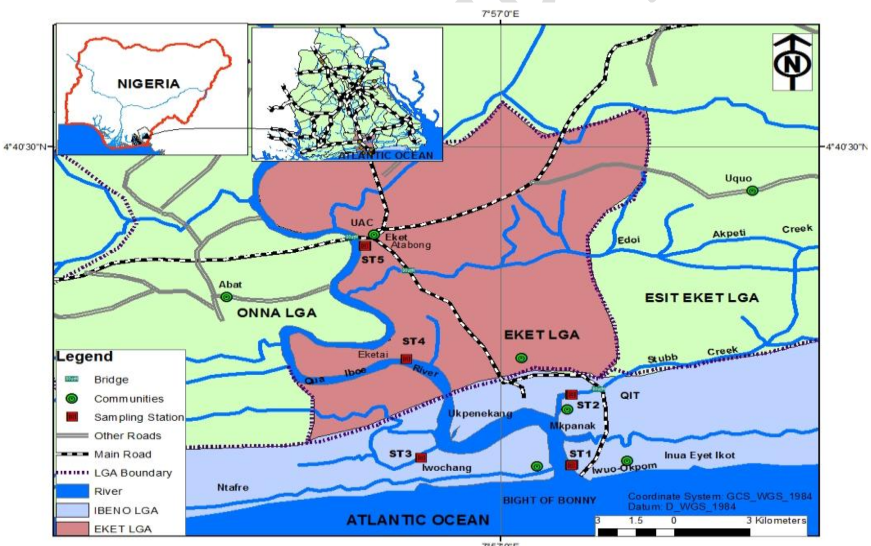

Fig 1: Map of the study area showing sampling stations in Qua Iboe River Estuary

2.2 Samples Collection

Sediments samples were collected monthly for one-year (January, 2022 and December, 2022) period spanning the dry and wet seasons of the study area using 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 weigh accurately and passed through (2 mm sieve) with foil paper and transfer 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 transfer into the flask containing the sediment sample in the fume hood. 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 boil to bring the metal into solution. The solution was filtered through Whatman 42 filter paper in a 100 ml volumetric flask and makes to mark with distilled water and then transfer 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 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 the stations during the period of survey were 0.03±0 at Atabong – 0.52±0.06 mg / kg at Eketai(Table 1). Within the five sampling stations, the spatial variation of cadmium shows significant difference at $p = 0.05$ during the study period. Seasonal variation between the dry and wet season shows no significant difference at $p = 0.05$ (Table 2). Fig. 2 explain the spatial and temporal variation in cadmium concentration.

Mean values recorded for chromium across the sampling stations range between 0.03±0at Atabong - 0.83±0.06 at Eketai. Significant spatial variation at $p = 0.05$ was observed for chromium. However, there was no significant difference as regards seasons (Table 2). Fig.3 shows the variations across the stations in the different month of study.

The mean values for Cu, Fe, Pb and Zn computed spatially during the study range between 0±0at QIT - 1.64±0.05 at Iwuokpom and Eketai respectively for copper, 0.46±0.03 at Atabong - 170.67±2.25 at Eketai for iron, 0.002±0at Atabong - 0.84±0.05at Eketai for lead and 0.29±0.02 atAtabong - 27.85±2.05at 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 throughput the study duration.

TABLE 1: Mean SPATIAL VARIATIONS IN HEAVY METALS IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (FROM January, 2022–December,2022)

Heavy Metal	IWUOKPOM	QIT	IWUOCHANG	EKETAI	ATAOBONG	DPR Intervention Limit
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

Comment [GdG1]: I believe that the authors should represent the results in the form of a boxplot, as they would be very explanatory, as well as the application of descriptive statistics

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 FOR WET AND DRY SEASON (January, 2022 -December, 2022)

	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]

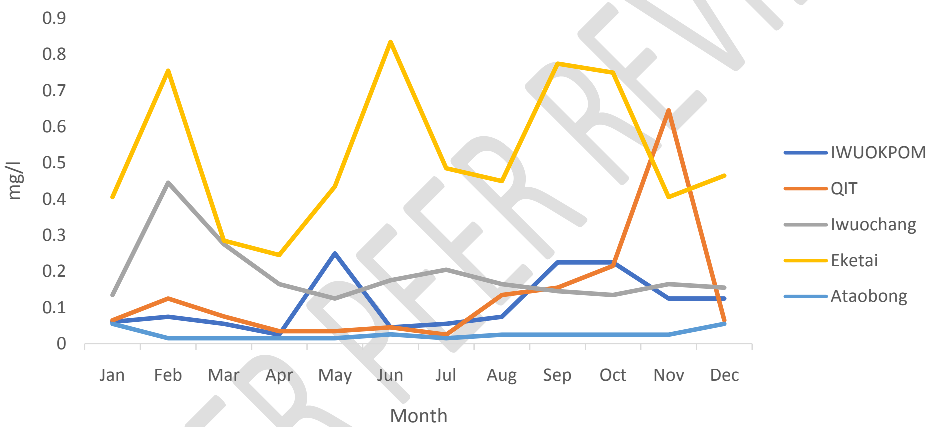

FIGURE 2: SPATIO-TEMPORAL VARIATIOINS IN CADMIUM IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022).

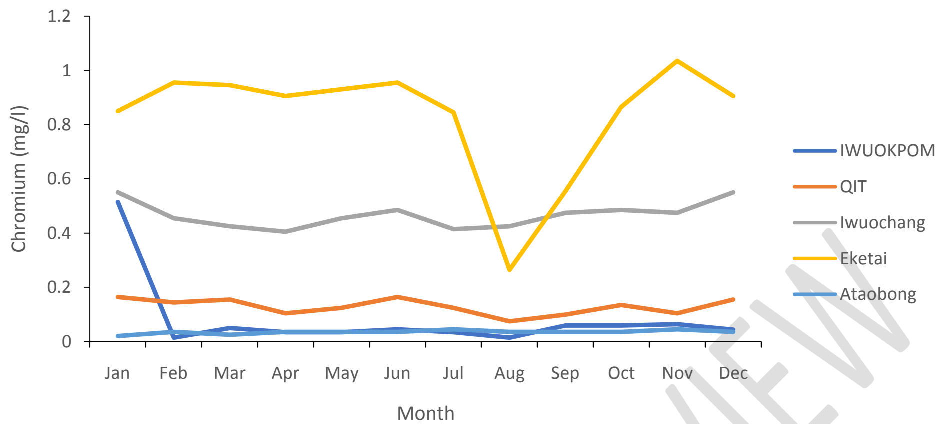

FIGURE 3: SPATIO-TEMPORAL VARIATIOINS IN CHROMIUM IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022).

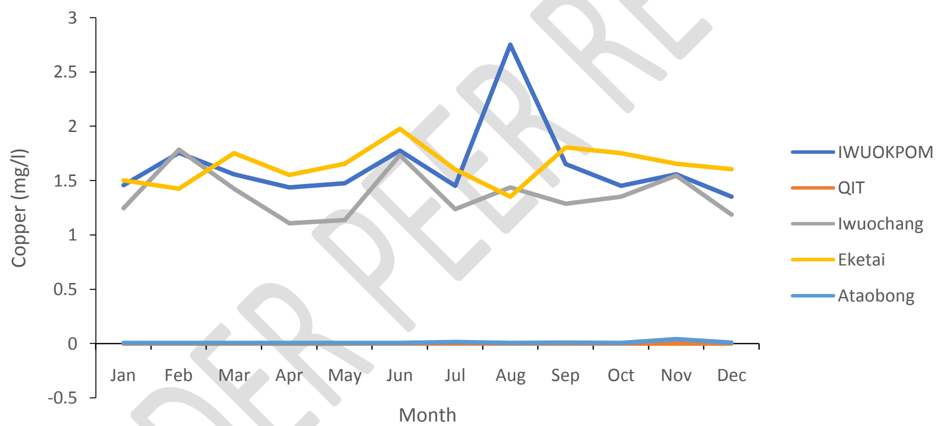

FIGURE 4: SPATIO-TEMPORAL VARIATIOINS IN COPPER IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022).

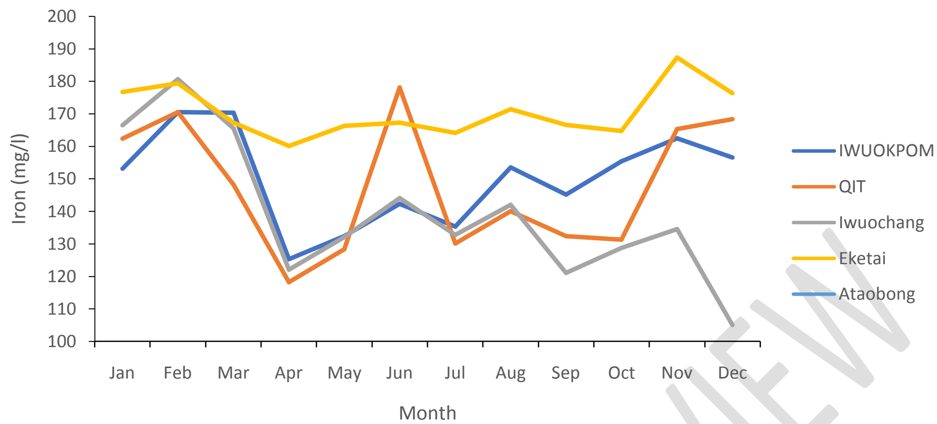

FIGURE 5: SPATIO-TEMPORAL VARIATIOINS IN IRON IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022)

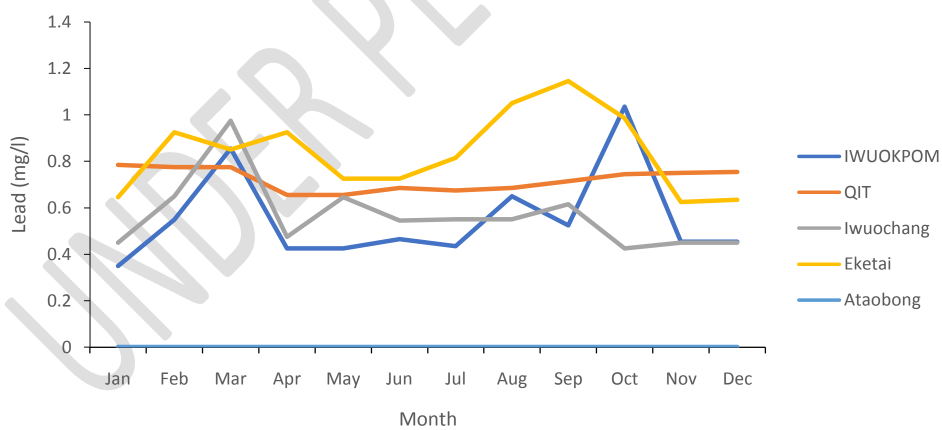

FIGURE 6: SPATIO-TEMPORAL VARIATIOINS IN LEAD IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022)

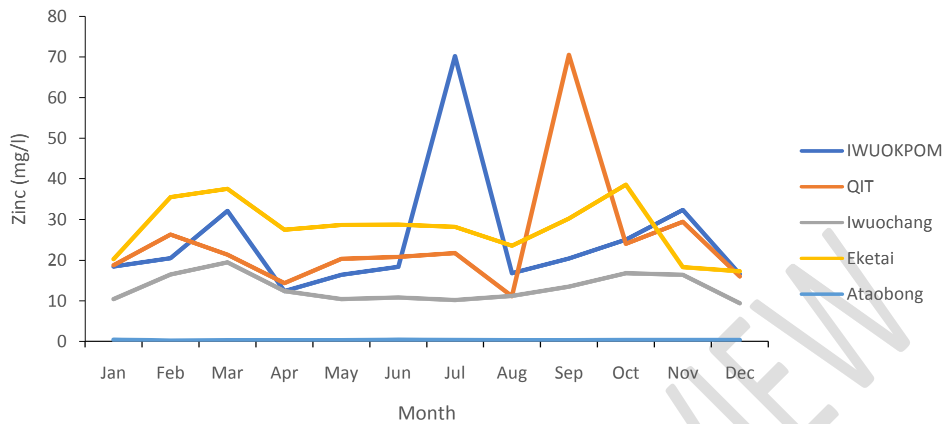

FIGURE 7: SPATIO-TEMPORAL VARIATIOINS IN ZINC IN QUA IBOE RIVER ESTUARY FOR WET AND DRY SEASON (January, 2022 -December, 2022).

4.0 Discussion

The results computed for this study shows 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 landsor reduction in human / industrial activities as a result of the rains. The concentrations of heavy metals computed for each of the stations in this study were adjudge based on the levels of human activities emanating from each of these stations. The high values of heavy metal concentration recorded at Eketai is a clear evidence of the levels of anthropogenic activities sited in this 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 theDepartment of Petroleum Resources (DPR) target / intervention limits for sediment quality guideline exception ofiron which the DPR target limit is not known (DPR, 2002). The results of this studies are consistent with related study 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 been 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 aroundthe study area. High levels of iron in Nigerian soils have been documented by (Oluwu, *et.al*. 2010).

Generally, theelemental concentrations of heavy metal in sediments is not only attributed to anthropogenic and lithogenicroutes 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 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 assessed 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 washigh 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 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

Akpan, I. O. and Thompson, E. (2013).Assessment of heavy metal contamination of sediments along the cross-river channel in Cross River state, Nigeria.*Journal of Environmental Science, Toxicology and Food Technology*; 2(5):20-28.

American Public Health Association (APHA).(1998). Standard methods for the examination of water and wastewater,20th edition. New York: American Water Resources Association, 980Pp.

Benson, N. U, Asuquo, F. E, Williams, A. B, Essien, J. P., Ekong, C. andAkpabio, O. (2016). Source evaluation and trace metal contamination in benthic sediments from Equatorial Ecosystems using multivariate statistical techniques. *PLoS ONE*; 11(6):1-19.

Chindah, A. C, Braide, S. A, Amakiri, J. andChikwendu, S. O. N.(2009).Heavy metal concentrations in sediment and periwinkle(Tympanotonusfuscastus) in the different ecologicalzones of Bonny River system, Niger Delta, Nigeria.*TheOpen Environmental Pollution & Toxicology Journal*; 1:93-106.

Department of Petroleum Resources (DPR).(2002). Environmental guidelines and standards for the petroleum industry in Nigeria (revised edition).Department of Petroleum Resources, Ministry of Petroleum and National Resources, Abuja, Nigeria, 185Pp.

Efiom, E. and George, U. (2018).Source Evaluation and Trace Metal Contamination in Benthic Sediments from Imo River, South-East, Nigeria Using Multivariate Statistical Techniques.*World Rural Observations*;10(2):66-72.

George, U. and Efiom, E. (2017).Impacts of coastal activities on benthic sediments from Qua Iboe River Estuary, South-South, Nigeria using multivariate statistical techniques.*International Journal of Applied Research*, 3(7): 39-50.

Ideriah, T., Ikpee, J. K. and Nwanjoku, F. N. (2013). Distribution and speciation of heavy metals in crude oil contaminated soils from Niger Delta, Nigeria. *World Environment*; 3(1):18-28.

Issa, B. R., Arimoro, F. O., Ibrahim, M., Birma, G. J. and Fadairo, E. A. (2011).Assessment of sediment contamination by heavy metals in River OrogodoAgbor, Delta State, Nigeria.*Current World Environment*; 6(1):29-38.

Loska, K. and Wiechula, D. (2003).Application of Principal Component Analysis for the estimation of source of Heavy Metal Contamination in Surface Sediment from Rybnik Reservoir.*Chemosphere*; 51:723-733.

Moses, E. A, Etuk, B. A, Udosen, E. D. (2015). Spatial and seasonal variation in the contamination indices of trace metals in sediment from Qua Iboe River Estuary, South-South, Nigeria. *International Journal of Science and Technology*; 4(11):506-516.

Obasohan, E.E. (2008).Heavy metals in the sediment of Ibiekuma Stream in Ekpoma, Edo State, Nigeria. African *Journal of General Agriculture*; 4:21-27.

Olatunji, O. S. and Osibanjo, O.(2012). Distribution and temporal variation of selected heavy metals in sediment of River Osara mainstream drainage in North Central Nigeria.*African Journal of Pure and Applied Chemistry*; 6(13):188-194.

Olowu, R. A., Ayejuyo, G. O, Adewuyi, I.A, Adejoro, A. A, Denloye, A. O, Ogundajo, A. I. (2010). Determination of heavy metals in fish tissues, water and sediment from Epe and Badagry Lagoons, Lagos, Nigeria.*Electronic journal of Chemistry*; 7(1):215-222.

Opaluwa, O. D., Aremu, M. O., Ogbo, L. O., Magaji, J. I., Odiba, I. E, Ekpo, E. R. (2012). Assessment of heavy metals in water, fish and sediments from Uke Stream, Nassarawa State, Nigeria.*Current World Environment*; 7(2):213- 220.

Pourang, N., Nikouyan, A. and Dennis, J. (2005).Trace element concentration of fish, surficial sediment and water fromNorthern part of the Persian Gulf. *Environmental Monitoring Assessment*; 109:293-216.

]Saeed, S. M, Shaker, I. M. (2008). Assessment of heavy metal pollution in water and sediment and their effect on*Oreochromisniloticus* in North Delta Lake. Egyptian International symposium on Tilapia in Aquaculture,490Pp.

Udosen, E. D, Benson, N. U, Essien, J. P. (2007).Trends in heavy metals and total hydrocarbon burdens in stubb Creek,Qua Iboe River Estuary, Nigeria.*Trends in Applied Science Resources*; 2(4):312-319.

Uwah, I. E., Dan, S. F., Etiuma, R. A. and Umoh, U. E. (2013).Evaluation of the status of heavy metals pollution of sediments inQua Iboe River Estuary and associated Creeks, Nigeria.*Environmental Pollution*; 2(4):110-121.