Source Evaluation and Trace Metal Contamination in Benthic Sediments from Imo River, South-East, Nigeria Using Multivariate Statistical Techniques

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Abstract: Studies on Source Evaluation and Trace Metal Contamination in Benthic Sediments from Imo River, South-East, Nigeria using multivariate statistical techniques was conducted between May 2016 and April 2017 with the aim of understanding the current sources of trace metal concentrations in the system. Sediment samples were collected monthly in four stations along the river and analyzed using Atomic Absorption Spectrophotometer. Mean values of trace metals in sediment for wet and dry seasons were as follows: 0.32 ± 0.05 and 0.37 ± 0.06 for cadmium, 3.33± 0.28 and 3.69 ± 0.38 for copper, 6.43 ± 0.36 and 6.72 ± 0.36 for iron, 1.00 ± 0.09 and 1.25 ± 0.11 for lead, 1.08 ± 0.18 and 2.2 ± 0.31 for zinc, 0.45 ± 0.03 and 0.40 ± 0.03 for manganese and 0.08 ± 0.03 and 0.13 ± 0.03 for chromium respectively. Trace metals concentrations in sediments were below the DPR target / intervention limit with the exception of iron. Analysis of variance and paired sample t-test revealed significant ($p = 0.05$) seasonal variations respectively. Correlation analysis revealed strong positive relationships amongst metal pairs which portends that an increase in one metal pair mandates a corresponding increase in another metal pair. Multivariate analytical technique (HCA) imprinted that the river is swayed by multiple contamination sources. However, the series of anthropogenic activities evident, coupled with the findings of this study further vindicate the need for constant monitoring of our indigenous water bodies.

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1. Introduction

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.

Metals have a number of common properties. These include; their high electrical and thermal conductance, luster, ductility (plasticity), high reflecting power and opacity. All metals are characterized by a comparative readiness to give up their valence electrons and form positive ions. The ability of metals to give up their valence electron and form other metal compounds with different oxidation state calls for concern, hence, the essence of constant monitoring of aquatic system for trace metal contamination.

The negative impacts on the natural environment due to various coastal activities are becoming an increasing concern among stakeholders and the public at large. Coastal activities includes; fishing, farming, dredging, oil exploration and seismic activities, gas flaring, indiscriminate disposal of sewage and industrial wastes. Today the environment has become fouled, undesirable, and therefore harmful to the health of living organisms, including man due to the negative impacts of coastal activities (George and Efiom, 2017). Rapid industrialization has direct and indirect adverse effects on our environment (Nasrullah *et. al.,* 2006). This has led to an increase in generation of industrial effluents which when discharged and left untreated, would result in water, sediment and seafood contamination (Wakawa *et. al.,* 2008). Environmental degradation, deterioration and underdevelopment are top public issues both at national and international levels (Ekweozor and Agbozu, 2001).

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 sediment bed (Moses, *et. al,* 2015). Trace metals can be present in amounts several times higher than their natural background levels and pollute aquatic sediments in coastal regions near industrial areas (Bowen, 1979). 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). Information on trace metal distribution and enrichment in sediment is important in detecting, tracing and monitoring pollution sources in an aquatic system (Obasahan, 2008).

It is therefore the aim of this study to evaluate the condition of the environment and examine the linkages between anthropogenic activities and the observed levels of trace metal concentration in aquatic sediment of Imo River using multivariate statistical tool in the determination of source of contaminants, which will help policy makers in the proper planning and monitoring in the event of pollution.

2.0 Materials and Methods

2.1 Study Area

The study was carried out in Imo River (Fig 1) which is one of the essential rivers in the Niger Delta region. It is situated on the South-East coast of Nigeria. The river originates from Imo State (hill region) and flows through Imo, Abia and Rivers State before empting into the Atlantic Ocean. The river is located between Latitude 4°32'30"N and Longitude 7°32'30"E. It is a tidal River with extensive mangrove swamps, intertidal mud flats and influenced by semi-diurnal tidal regime. Industrial activities are also predominant (e.g. NNPC Power Station) added with illegal petroleum refineries and bunkering activities. The River is a source of drinking water and livelihood of the people of the area. The major occupation is fishing, lumbering and farming activities (Ogbuagu *et. al*., 2012).

2.2 Samples Collection

Sediments samples were collected monthly for a one year period (May 2016 to April 2017) 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 sub-samples and 60 composite samples were collected, dried, ground and sieved.

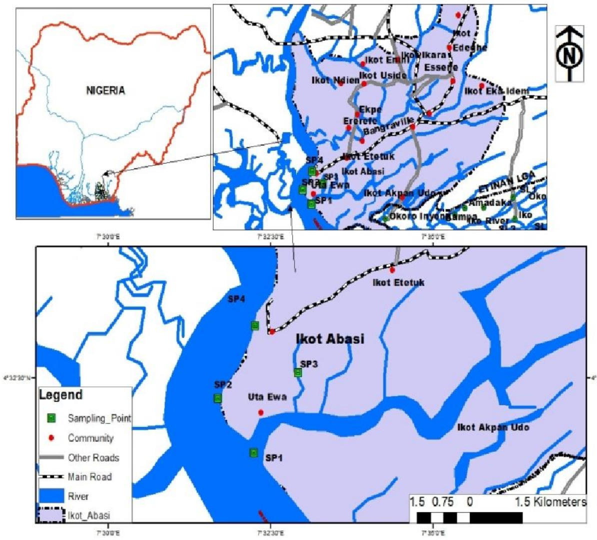

Fig 1: Map of the Study

2.3 Laboratory Analysis

2.3.1 Determination of Trace Metals

1 g of air - dried sediment was weighed accurately and passed through (a 2 mm sieve) 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 were transferred 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 stopped 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 the calibration mark with distilled water and then transferred to a 100 ml plastic can for AAS analysis. Heavy metals were determined using Atomic Absorption Spectrophotometer (model GBC scientific AASGF 3000) according to APHA, (1998).

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.

Hierarchical cluster analysis was used for stations classification and source apportionment.

3. 0 Results

3.1 Trace Metal Concentrations in Sediments

Seasonal range, mean and standard error of wet and dry season concentrations of trace metal observed in Imo River during the study period is presented in Table 1. The mean values of trace metal concentrations in wet and dry season are as follows; 0.32 ± 0.05 and 0.37 ± 0.06 for cadmium, 3.33± 0.28 and 3.69 ± 0.38 for copper, 6.43 ± 0.36 and 6.72 ± 0.36 for iron, 1.00 ± 0.09 and 1.25 ± 0.11 for lead, 1.08 ± 0.18 and 2.2 ± 0.31 for zinc, 0.45 ± 0.03 and 0.40 ± 0.03 for manganese and 0.08 ± 0.03 and 0.13 ± 0.03 for chromium respectively. Seasonal variation between the dry and wet season shows significant difference at p = 0.05 for Cu, Fe, Pb, Zn, Mn and Cr while spatial variation between the dry and wet season shows significant difference at p = 0.05 for Cd, Cu, Fe, Pb and Mn.

3.2 Correlation matrix and hierarchical cluster dendrogram based on heavy metals in sediment

3.2.1 Correlation matrix and hierarchical cluster dendrogram based on heavy metals in sediment (wet season)

Significant positive correlation was observed during the wet season between the following trace metal pairs: Cadmium – Lead (0. 554), Cadmium - Chromium (0.375), Copper – Iron (0.430), Copper – Lead (0.623), Copper – Manganese (0.633), Iron – Zinc (0.447), Zinc – Manganese (0.389) and Zinc – Chromium (0. 411) (Table 2). Hierarchical cluster analysis (HCA) was adopted for classification of trace metals based on source apportionment. Figure 2 represents a cluster dendrogram which reflects source apportionment for different trace metals in the study area. Three (3) cluster groups were identified during the wet season; group 1 (Cd, Pb, Cu), group 2 (Fe, Mn) and group 3 (Zn, Cr).

3.2.2 Correlation and hierarchical cluster dendrogram based on heavy metals in sediment (dry season)

During the dry season significant positive correlation was observed between the following metal pairs: Cadmium – iron (0.443), cadmium – lead (0.488), copper – iron (0.690) and copper – lead (0.695) (Table 3). Hierarchical cluster analysis (HCA) was used in the classification of the trace metals based on source apportionment. The cluster dendrogram shows source apportionment of individual trace metals. Two (2) cluster groups were identified during the dry season; group 1 (Cd, Pb, Mn), group 2 (Cu, Pb, Zn, Cr) (Fig. 3).

Table 1: Seasonal range, mean variation, standard error of contaminants (mg/kg) measured in sediment of Imo River for wet and dry season (May, 2016 - April, 2017)

Parameters	Units	Range Wet Season	Range Dry Season	Mean ± S.E Wet season	Mean± S.E Dry season	DPR Target limit (mg / kg)	DPR Intervention limit (mg / kg)
Cadmium	mg/kg	0.03 – 0.90	0.01 – 0.90	0.32 ± 0.05	0.37 ± 0.06	0.8	12
Copper	mg/kg	1.82 – 5.97	1.31 – 7.77	3.33± 0.28	3.69 ± 0.38	36	190
Iron	mg/kg	3.44 – 8.70	3.76 – 8.96	6.43 ± 0.36	6.72 ± 0.36	4.7	-
Lead	mg/kg	0.33 – 1.76	0.55 – 2.80	1.00 ± 0.09	1.25 ± 0.11	85	530
Zinc	mg/kg	0.06 – 2.80	0.08 – 6.20	1.08 ± 0.18	2.2 ± 0.31	140	720
Manganese	mg/kg	0.03 – 0.80	0.04 – 0.80	0.45 ± 0.03	0.40 ± 0.03	-	-
Chromium	mg/kg	0.00 – 0.43	0.01 – 0.44	0.08 ± 0.03	0.13 ± 0.03	100	380

Where: S.E = Standard Error, DPR = Department of Petroleum Resources, BDL = Below Detectable Limit

Table 2: Pearson's correlation matrix of trace metals in sediment from Qua Iboe River Estuary (Wet Season)

	Cd	Cu	Fe	Pb	Zn	Mn	Cr
Cd	1						
Cu	.334	1					
Fe	.072	-.430*	1				
Pb	.554**	.623**	.102	1			
Zn	.030	-.175	.447*	.039	1		
Mn	.044	-.633**	.195	-.179	.389*	1	
Cr	.375*	.069	.111	.289	.411*	.337	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

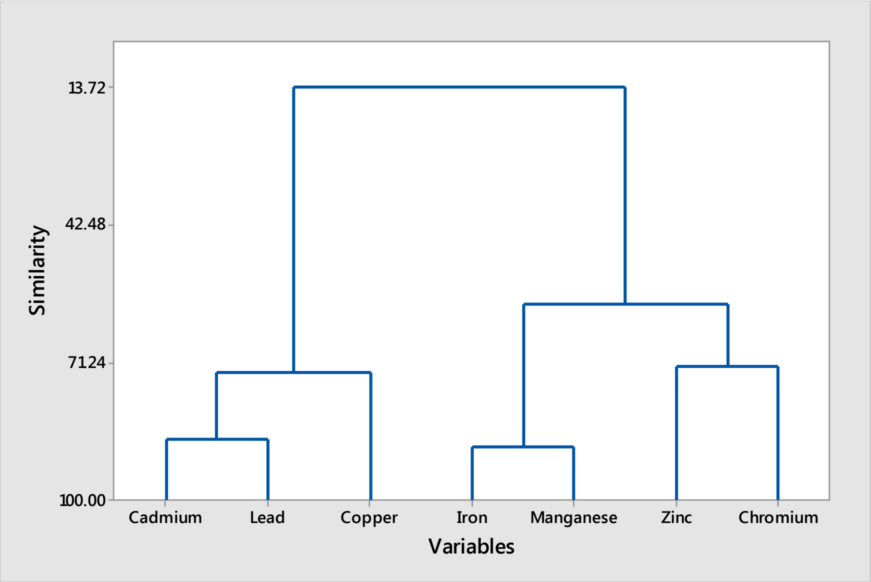

Fig 2: Dendrogram showing source apportionment in sediment of Imo River (Wet season)

Table 3: Pearson's correlation matrix of trace metals in sediment from Qua Iboe River Estuary (Dry Season)

	Cd	Cu	Fe	Pb	Zn	Mn	Cr
Cd	1						
Cu	.109	1					
Fe	.443*	-.690**	1				
Pb	.488**	.695**	-.201	1			
Zn	.084	.216	-.043	.286	1		
Mn	-.079	-.296	.254	-.311	.261	1	
Cr	-.074	.097	-.051	.076	.195	.253	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

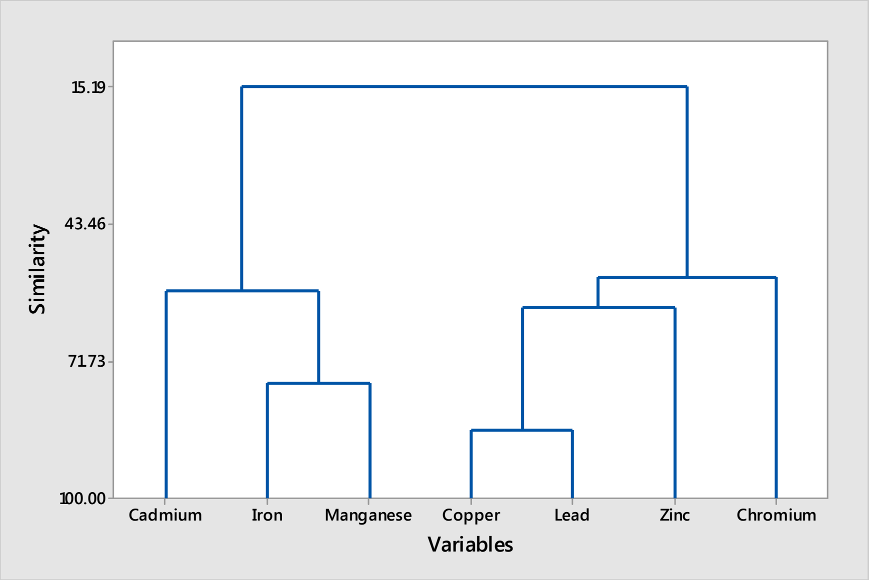

Fig 3: Dendrogram showing source apportionment in sediment of Imo River (Dry season)

4.0 Discussion

4.1 Seasonal and Spatial Variation in Trace Metal Concentration in Sediments

Trace metal concentrations were observed to be generally higher in the dry season than wet season during the study duration. 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 (Obasahan, 2008) or metal dissolution as a result of low water pH (Tomilson *et. al*. 1980). This observation clearly shows that there is a link between human activities and the observed status of sediment of Imo River. All the metals investigated in both seasons were below the Department of Petroleum Resources (DPR) target / intervention limits for sediment quality guideline except iron which was above the DPR target limit (DPR, 2002).

The results from this study inveterate earlier assertion reported by (Olatunji and Osibanjo, 2012, Ideriah, *et. al*. 2013; Chinda *et. al*. 2009; Ikpee, *et. al*. 2009; George and Efiom, 2017) from related studies. The high concentrations of iron in sediments of this study area are consistent with studies conducted by other authors (Udosen, *et. al*. 2007; Issa, *et. al*. 2011; Opaluwa, *et. al*. 2012; George and Efiom, 2017). Elevated concentrations of iron in the study area may be attributed to the use of pipelines made up of iron, ferrochromium materials and alloys of zinc and iron in conveying oil from the platform to the treatment sites. The exposure of these pipelines to environmental conditions over time can result in corrosion and possibly the release of these metals into the aquatic ecosystem. Moreover, the concentration of Fe in sediment may be due to the nature of the sediment along the aquatic ecosystem and high levels of iron in Nigerian soils have been reported by (Oluwu, *et.al*. 2010).

Generally, trace metal concentrations of sediments depends not only on anthropogenic and lithogenic sources but also on the textural characteristics such as organic matter content of the sediment, mineralogical composition and depositional environment of the sediments (Pourang, *et.al*. 2005, George and Efiom, 2017). This assertion was supported by (Saeed and Shaker, 2008) who stated that the concentration of metals in sediment depends on the amount of organic compounds 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 (Yi, *et.al*. 2011). The low values of trace metals recorded during the wet season may be attributed to dilution effects through direct precipitation and runoff from land.

4.2 Multivariate Analysis and Source Apportionment

The use of correlation analyses in establishing relationships within and between variables, locations and organisms is well established in literature (Benson *et. al.* 2016). Positive correlations between metal pairs (Cadmium, Chromium, Copper, Iron, Lead and Zinc) denote that an increase in one of these parameters leads to a corresponding increase in the other. Significant correlation coefficient between metal pairs interprets that they may have same accumulation potentials, unitary anthropogenic pollution or natural pollution source and chemical association between the trace metals within a particular area (Moses *et. al.* 2015). The agglomeration patterns observed in the cluster dendrogram representing source apportionment in both wet and dry season assorts trace metal contamination in Imo River into two and three primary cluster groups respectively. This implies that trace metals within the same cluster group had similar source of contamination. This assertion agrees with the findings of (Benson and Essien, 2012) in a related study.

5.0 Conclusion

This study was designed to assess the seasonal and spatial variation in trace metal contamination in Imo River and evaluates the sources of these trace metals. Only iron was above the sediment quality guideline stipulated by Department of Petroleum Resources while the results for other contaminants such as Cd, Cr, Cu, Pb and Zn revealed low level of concentrations but if the trend continues without checkmating the level of anthropogenic activities may result in potential ecological risk to sediment dwelling organism. This calls for the need to create awareness and educate the rural dwellers on proper management and disposal of waste generated from their homes and also industries should adhere to modern waste disposal techniques in the discharge of industrial waste which has been identified as one of the major sources of trace metals in aquatic environment.

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