



## Spatial Distribution and Contamination Assessment of Heavy Metals in Surface Sediments of Badagry Creek, southwest Nigeria

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### ABSTRACT

Heavy metals in surface sediments from Badagry Creek in southwest Nigeria were studied to evaluate their spatial distributions, degree of contamination and possible ecological risk. Aqua regia technique was used for digestion of the pulverized sediments (< 63 µm) and, inductively coupled plasma-optical emission spectrometer (ICP-OES) was used for quantification of the heavy metals. Contamination indices including modified degree of contamination (*mCd*), pollution load index (PLI), geoaccumulation index (*Igeo*) and enrichment factor (EF) were used to assess the extent of contamination of the creek sediments. The results showed that the overall average concentrations (ppm) of heavy metals of concern are 14.6 (Cu), 9.8 (Pb), 49.9 (Zn), 19.3 (Ni), 18.9 (Co), 702.5 (Mn), 1.8 (As) and 0.7 (Cd). The decreasing order of heavy metal enrichment in sediments is Cd > As > Co > Zn > Pb > Cu ≥ Ni. The resulting Pearson's correlation matrix and dendrograms from cluster analysis identified aluminium as a conservative tracer to differentiate natural (lithogenic) and anthropogenic components. Also, the values of threshold effect level (TEL) and probable effect level (PEL) were used to assess the ecotoxicological potential of heavy metal concentrations in sediments. Results indicated that metal concentrations are below the threshold effect level (TEL), except, cadmium in all stations and; Ni, in western segment and 33.3 % of stations in eastern segment of the creek. Interestingly, Cd and Ni are not near the probable effect level (PEL), therefore, all the heavy metals examined are not likely to produce harmful effects on sediment-dwelling organisms.

**Keywords:** Heavy metals, Contamination indices, Cadmium, Cluster analysis, Aluminium

### INTRODUCTION

In response to the growing population of Lagos State, the government has initiated infrastructural development project that would accommodate the needs of the people. This necessitated the Badagry free trade zone proposed as the Africa's maritime economic city expected to be the largest in Nigeria. The free trade zone was granted license in January, 2017 by the Nigeria Export Processing Zones Authority (NEPZA). The Maritime Africa Economic City (MAEC) will be developed on 1,100 hectares of land with over six kilometres of quay wall, including a container terminal, roll-on-roll-off (RORO) terminal, general cargo terminals, oil service centre and refined products import terminals. Also, a power plant, an oil refinery, industrial park, warehousing and inland container depot functions will be included. The fact that rapid industrialization and urbanization have caused contamination of the environment by heavy metals, and their rates of mobilization and transport in the environment have greatly accelerated is not nebulous (Khan *et al.*, 2004; Ali *et al.*, 2019). These activities will definitely contribute anthropogenic chemicals to the aquatic environments in the region. It is therefore necessary to establish a baseline of comparison for future environmental investigation through the present study. Since low level contamination may not be unexpected in the resident Badagry Creek, identifying stations and assessing local processes become essential.

Heavy metal exposure has been linked to several human diseases such as development retardation, malformation, kidney damage, cancer and even death (Saha and Hossain, 2011). According to statistics, more than 99 % of heavy metals entering aquatic systems are stored in sediments in

different ways (Salomons *et al.*, 1995; Peng *et al.*, 2009; Fang *et al.*, 2019). Coastal sediments are important repositories, sinks and carriers for heavy metals (Adams *et al.*, 1992; Ikem *et al.*, 2003). Therefore, sediment analysis offers significant advantages over water analysis for the assessment and monitoring of metal contamination in coastal environments, assuming that those metals are substantially not mobilized following the deposition (Forstner and Wittman, 1983; Luoma, 1990; Belzile *et al.*, 2004). It is thus believed, that metal concentrations and distributions in sediments can provide the best information about spatial extent as well as magnitude of natural and human-induced chemical changes in this creek.

Scanty information exists on the environmental aspect of this area as the occurrence of trace metals associated with sediments has not been given wide publicity. Though, this may largely be attributable to the fact that this area is not industrialized and has low overall human population. Hence, the occurrence of metals may likely be natural and metal distribution primarily controlled by natural processes. Badagry Creek is the longest and probably the widest in southwest Nigeria (Phillips *et al.*, 2017). The major environmental pressures are from boat transportation and repairs, indiscriminate dumping of refuse and domestic sewage which are all restricted to a small segment of the creek near settlements. There is no gainsay on the fact that an increase in economic activities will contribute to a deterioration of the environment through accumulation of contaminants in street dust. Subsequently, the contaminated dust is transported as aqueous emissions during storm runoff or even dispersed as wind-blown dust. Trace elements such as Cd, Cu, Ni, Pb, Zn, Hg, As, Cr

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among others may be transferred from the water column to the bottom sediment which acts as a sink of these pollutants (Rodríguez-Barroso *et al.*, 2009). This study was therefore undertaken to document the heavy metal content and distribution in sediments of Badagry Creek along the southwest Nigeria coast, and establish baseline concentrations for future reference. Also, the degree of contamination will be assessed by using various indices of pollution and sediment quality guidelines.

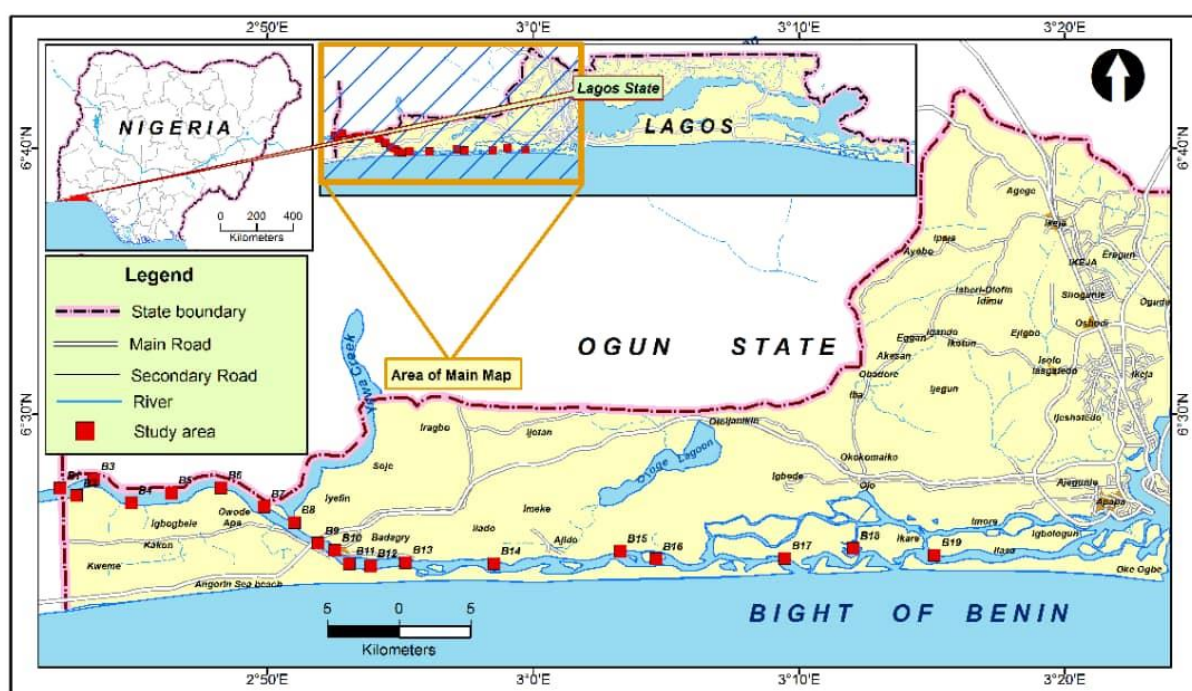
## MATERIAL AND METHODS

### Study Area

The western segment of Badagry creek connects the Porto-Novo creek at the west and Yewa creek at the north running into Ogun State, and the eastern segment run into Lagos Harbour connecting it to the Gulf of Guinea. Badagry creek flows across the boundaries of Federal

Republic of Nigeria and Bénin Republic between longitudes  $2^{\circ}42'E$  and  $3^{\circ}29'E$  and latitudes  $6^{\circ}23'N$  and  $6^{\circ}28'N$  (Fig. 1). The creek is shallow with average water depth of 3.5 m in addition to irregular topography being displayed (Phillips *et al.*, 2017). According to Ibe (1988), the barrier beach-lagoon complex extends eastward for about 200 km from the border between Nigeria and Benin republics to the western limit of the Transgressive mud coast. It was further stated that the morphology has largely been determined by coastal dynamics and drainage.

The Coastal area of Lagos such as the Badagry are situated in flat coastal plains and most areas in the state do not rise above 700 meters above sea level. Approximately one-third of this creek towards eastern boundary is usually very busy as it receives Cargo ships from Tin Can Island and Apapa ports, oil tankers from various jetties and ferries from Mile 2 suburbs in Lagos State, Nigeria.



**Fig. 1:** The map of sampled stations in Badagry Creek, southwest Nigeria Coast.

### Methods

In order to obtain the actual status of the most recently deposited sediment, samples were collected from the top 20 cm of the sediment using Ekman grab sampler. The samples might however, represent different time spans due to the differences in sedimentation rates along 19 stations where a sample each was collected. The appropriately labelled samples were dried to constant weight in an oven at  $85^{\circ}C$  for 14 hours and later made into two portions for particle size and chemical analyses. The sand size fractions were separated from mud fractions by wet sieving through a stainless steel  $63\ \mu m$  aperture sieve; and silt and clay fractions separated by using standard pipette method of Gale and Hoare, 1991. Bottom water was collected and samples were kept in labelled plastic bottles indicating the various stations, and measurements of temperature and pH were done. The pH was measured with pH meter (Hanna H 19625, Precision 0.01); temperature with a mercury thermometer; and salinity was determined in the laboratory with a Conductivity

Salinometer (WTWLF 325, Probe WTW Tetracon 325, Precision 0.1g/l). The depth was measured using a calibrated rope to the end of which a lead weight was attached.

The sample for chemical analysis was pulverized using agate mortar and pestle, and the dried homogenized samples were sieved through  $63\ \mu m$  screen. One gram each from the  $< 63\ \mu m$  sample fraction was digested using aqua regia technique (1 HNO<sub>3</sub>: 3 HCl) following a procedure described by Loring and Rantala (1992). The sample digestion, and inductively coupled plasma-optical emission spectrometric (ICP-OES) analysis for metal quantification were made in the Acme Analytical Laboratory (Vancouver), Canada, and report submitted with certificate number VAN 13002288.1. The entrance of the Porto-Novo creek from the Republic of Bénin into Badagry Creek, to the confluence of Yewa and Badagry creeks forms the western segment (B1-B7) of the study area (Fig. 1). The eastern

segment is thus represented by the much longer arm from Owode-Apa to Ibese area near Lagos Harbour (B8-B19). The difference in the hydrographic nature and the existence of the confluence informed the decision of the author to group the creek into two segments.

**Statistical Analysis**

The software of multivariate statistical technique of Hammer *et al.* (2007) was employed in the hierarchical clustering with the purpose of classifying samples across

$$D(A,B) = \min\{d(y_i, y_j, \text{ for } y_i \text{ in } A \text{ and } y_j \text{ in } B)\} \dots\dots\dots \text{Eq. 1}$$

Where  $d(y_i, y_j)$  is the Euclidean distance in equation 1. At each step, the distance is found for every pair of clusters and the two clusters with the smallest distance i.e. largest similarities are merged and the procedure is repeated to produce a dendrogram showing steps in the Hierarchical procedure (Alvin, 2002).

**Contamination Assessment**

Contamination factor (CF), pollution load index (PLI), geoaccumulation index (I<sub>geo</sub>) and enrichment

$$CF = C_s/C_{ref} \dots\dots\dots \text{Eq. 2}$$

Where CF is contamination factor, C<sub>s</sub> is concentration of element of interest in sample and C<sub>ref</sub> is the concentration of sample element in reference sample or background value.

The categories and descriptive terminologies suggested by Hakanson, 1980 are CF < 1 indicates low

$$C_d = \sum_{i=1}^N CF_i \dots\dots\dots \text{Eq. 3a}$$

This formula (Eq. 3a) where CF<sub>i</sub> represents contamination factor for a specific element, expresses the sum of the contamination values for all the heavy metals involved. Results may not represent the true nature of pollution activity in the study area, hence the need for modified

$$mC_d = \frac{\sum_{i=1}^n C_f^i}{n} \dots\dots\dots \text{Eq. 3b}$$

The modified degree of contamination is denoted as mCd, where C<sub>f</sub><sup>i</sup> is the contamination factor for element of interest (i), and n is the number of elements involved.

$$PLI = (CF_1 \times CF_2 \times \dots \times CF_n)^{1/n} \dots\dots\dots \text{Eq. 4}$$

CF<sub>1</sub>, CF<sub>2</sub>,..., CF<sub>n</sub> are contamination factors of the sediment sample with respect to element 1, 2, and n, respectively; n is the number of metals investigated. This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. When PLI > 1, it means that a pollution exists; otherwise, if PLI < 1, there is no metal pollution (Tomlinson *et al.*, 1980; Chakravarty and Patgiri, 2009).

the study area based on similarities in their specific metal concentrations. The most similar stations based on concentrations of metal under consideration are first grouped and this initial groups are merged according to their similarities. All subgroups are fused into a single cluster as the similarity decreases. Single linkage method of cluster analysis (CA) was adopted where the distances or similarities between clusters A and B is defined as the minimum distances between a point in A and a point in B:

factor (EF) were considered in the assessment of heavy metal contamination in sediments.

**Contamination Factor (CF)**

The CF is the ratio obtained by dividing the concentration of each metal in the sediment by the baseline or background value (Hakanson, 1980; Syakti *et al.*, 2015). Contamination factor is calculated using equation 2.

contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 is very high contamination.

The degree of contamination (Cd) is calculated with the formula proposed by Hakanson (*Op. Cit.*):

degree of contamination index (mCd). Modified degree of contamination (mCd) is the generalized value for contamination as indicated in equation 3b.

**Pollution Load Index (PLI)**

The level of heavy metal pollution for every sampled station is defined by PLI, which has been determined as the nth root of the product of the nCF (Ahmed *et al.*, 2016):

**Geoaccumulation Index (I<sub>geo</sub>)**

The degree of contamination from the trace metals could be assessed by determining the geoaccumulation index (I<sub>geo</sub>). The index of geoaccumulation (I<sub>geo</sub>) has been widely applied to the assessment of sediment contamination (Islam *et al.*, 2015). In order to characterize the level of pollution in the sediment, I<sub>geo</sub> values were calculated using the equation,

$$I_{geo} = \log_2 [C_n / (1.5b_n)] \dots \dots \dots \text{Eq. 5}$$

$C_n$  is the total content of the individual element  $n$  and  $b_n$  is its geochemical background concentration, and 1.5 is used because of possible variation in background values for a given metal in the environment, as well as very small anthropogenic influences. The geoaccumulation index consists of seven classes. The geoaccumulation index was distinguished into seven classes by Muller (1969). Class 0 (practically uncontaminated):  $I_{geo} \leq 0$ ; Class 1 (uncontaminated to moderately uncontaminated):  $0 < I_{geo} < 1$ ; Class 2 (moderately contaminated):  $1 < I_{geo} < 2$ ; Class 3 (moderately to heavily contaminated):  $2 < I_{geo} < 3$ ; Class 4 (heavily contaminated):  $3 < I_{geo} < 4$ ; Class 5 (heavily to extremely contaminated):  $4 < I_{geo} < 5$ ; Class 6 (extremely contaminated):  $5 > I_{geo} < 6$ .

**Enrichment Factor (EF)**

This factor evaluates the normalized concentration of an element of interest with respect to a reference similarly normalized standard. Values are obtained from formula (eq. 6) suggested by Buat-Menard (1979), while classification of values is based on Faiz *et al.* (2009).

$$EF = C_i / C_{ie} (S) / B_i / B_{ie} (RS) \quad \text{Eq. 6}$$

Where  $C_i$  is the content of element in the sample of interest and  $C_{ie}$  is content of immobile element in the sample (S) while  $B_i$  is the content of element in the selected reference sample and  $B_{ie}$  is content of immobile element in the selected reference sample (RS). The selected reference data is adopted from Li (2000) upper continental values. In this study, Al was used as the reference element for geochemical normalization, because it represents the quantity of aluminosilicates which are generally the predominant carrier phase for metals in coastal sediments and its natural concentration tends to be uniform (Alexander *et al.*, 1993). In this study, aluminium is also used as a conservative tracer to differentiate natural from anthropogenic components.

**RESULTS AND DISCUSSION**

**Sediment and Water characteristics**

Sediments description and water characteristics are shown in Table 1. The samples collected from all stations at the western segment of Badagry Creek are constituted by > 90 % clay size fraction except in two stations. The silt size fraction gained latent relevance where it overwhelmed the clay fraction at stations near Lagos harbour (B16-B19). The water depth ranges from the shallowest 1.1 m at the entrance of Porto-Novo Creek into western Badagry Creek to the deepest 5.1 m and 5.2 m around Ago-Hausa (B9 and B10) close to the “topographic low” end of the confluence. Salinity at the western segment is between 0.00 ‰ and 1.00 ‰, whereas, wide variation from 0.00 ‰ to 11.00 ‰ was obtained for the eastern segment of the creek (Table 1). The pH values recorded for the eastern Badagry Creek (7.80-8.10) are similar to that of coastal water (Riley and Chester, 1971) whereas, 7.00-7.30 were documented for western segment. Consequentially, the western segment is dominated by fluvial influx, while a remarkable reach of back-water from saline west-mole area through the harbour may have defined the eastern segment of the creek. Approximately 21 % of the stations, all at the extreme eastern end near Lagos Harbour have salinity range from 5 ‰-11 ‰, whereas, other stations are as low as 0 ‰ with the highest being 2 ‰. It is therefore apparent that the creek is more of a freshwater than brackish water environment. Upon this, comparison of sediment quality will be made on Consensus-Based Sediment Quality Guidelines (CBSQG) for Freshwater Systems, also named as International sediment quality guidelines (Macdonald *et al.*, 2000). There is slightly consistent temperature at the western Badagry Creek (25.5 °C – 25.8 °C); and slightly variable temperature (26.2 °C-28.8 °C) at the eastern portion.

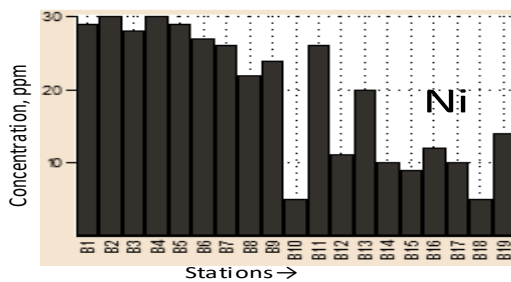


Fig. 2A. Lead distribution in sediments

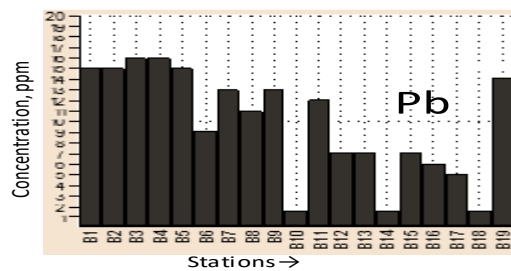


Fig. 2B. Zinc distribution in sediments

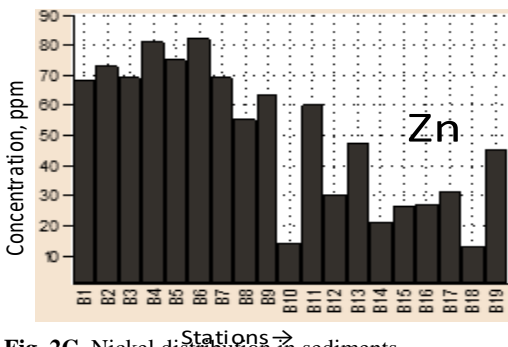


Fig. 2C. Nickel distribution in sediments

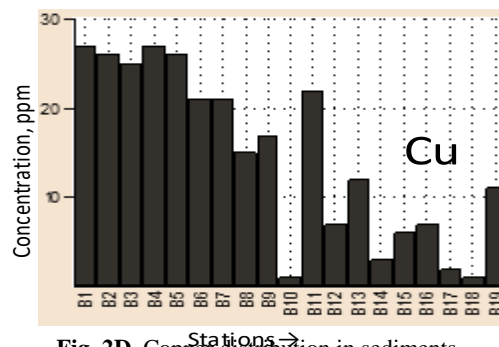
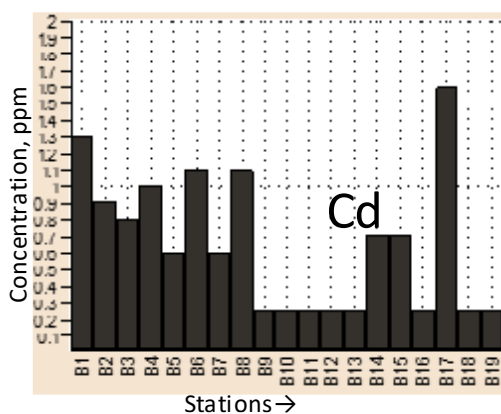


Fig. 2D. Copper distribution in sediments

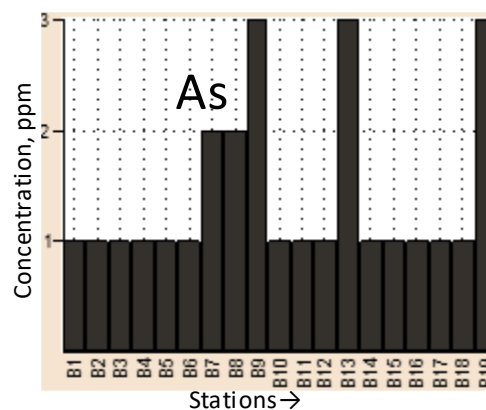


**Table 1:** Sediments' description and water characteristics for Badagry Creek, Southwest Nigeria

Serial number	Sampled stations	Depth, m (sediment-water surface)	pH	Salinity, ‰	Temperature, °C	Sediment description			Remark(s)
						Sand (%)	Silt (%)	Clay (%)	
1	B1	1.1	7.00	0.00	25.5	13.08	7.92	79.00	Sample from the boundary between Nigeria and Republic of Benin
2	B2	2.8	7.10	1.00	25.5	5.90	4.05	90.05	Sample from western segment
3	B3	2.0	7.30	1.00	25.8	8.60	1.33	90.07	Sample from western segment
4	B4	2.7	7.20	1.00	25.6	4.88	2.02	93.10	Sample from western segment
5	B5	3.6	7.00	1.00	25.5	1.59	3.40	95.01	Sample from western segment
6	B6	2.3	7.00	0.00	25.5	49.84	1.28	50.90	Sample from western segment
7	B7	1.9	7.10	0.00	25.5	28.80	5.37	65.83	Sample from western segment
8	B8	1.6	7.90	0.00	26.7	80.85	9.50	10.15	Sample from eastern segment
9	B9	5.2	7.80	0.00	26.5	72.95	11.05	16.00	Sample from eastern segment
10	B10	5.1	7.90	0.00	27.6	88.03	9.07	2.90	Sample from eastern segment
11	B11	3.6	7.90	1.00	27.5	59.91	10.36	29.73	Sample from eastern segment
12	B12	4.7	7.80	1.00	27.2	83.07	2.98	13.95	Sample from eastern segment
13	B13	3.1	7.80	1.00	28.3	20.50	10.10	69.40	Sample from eastern segment
14	B14	2.5	8.00	2.00	28.8	79.00	2.95	18.05	Sample from eastern segment
15	B15	3.1	7.90	0.00	26.8	96.02	1.68	2.30	Sample from eastern segment
16	B16	4.1	8.10	5.00	26.5	91.28	6.50	2.22	Sample from eastern segment
17	B17	4.0	8.10	6.00	26.5	97.08	1.99	0.93	Sample from eastern segment
18	B18	2.7	8.10	3.00	26.4	96.52	2.35	1.13	Sample from eastern segment
19	B19	2.3	7.90	11.00	26.2	89.04	7.07	3.89	Sample from eastern segment



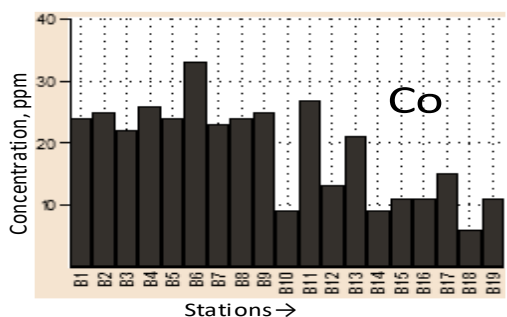
**Fig. 2E.** Arsenic distribution in sediments



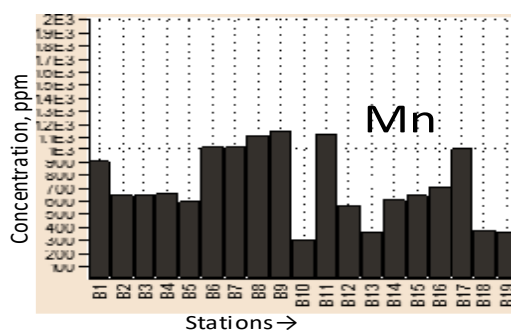
**Fig. 2F.** Cadmium distribution in sediments

**Table 2.** Heavy metals (ppm) and minor elements (%) in sediments of Badagry Creek and sediment quality guideline (SQG) from Buchman (2008).

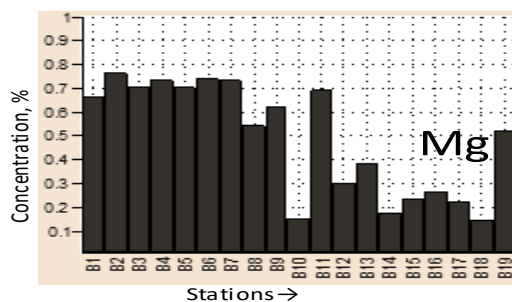
Sampled stations	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	Mg, %	Al, %	Fe, %
B1	27	15	68	29	24	903	<2	1.3	0.66	3.14	4.37
B2	26	15	73	30	25	639	<2	0.9	0.76	3.48	5.05
B3	25	16	69	28	22	644	<2	0.8	0.70	3.25	4.72
B4	27	16	81	30	26	653	<2	1.0	0.73	3.43	5.03
B5	26	15	75	29	24	592	<2	0.6	0.70	3.22	4.94
B6	21	9	82	27	33	1008	<2	1.1	0.74	3.06	7.63
B7	21	13	69	26	23	1011	2	0.6	0.73	2.91	4.92
B8	15	11	55	22	24	1109	2	1.1	0.54	2.00	5.22
B9	17	13	63	24	25	1143	3	<0.5	0.62	2.19	5.00
B10	1	<3	14	5	9	297	<2	<0.5	0.15	0.46	2.38
B11	22	12	60	26	27	1118	<2	<0.5	0.69	2.39	4.67
B12	7	7	30	11	13	555	<2	<0.5	0.30	0.90	2.07
B13	12	7	47	20	21	353	3	<0.5	0.38	1.87	7.17
B14	3	<3	21	10	9	606	<2	0.7	0.17	0.53	1.86
B15	6	7	26	9	11	647	<2	0.7	0.23	0.89	2.24
B16	7	6	27	12	11	701	<2	<0.5	0.26	0.95	2.34
B17	2	5	31	10	15	1001	<2	1.6	0.22	0.61	3.65
B18	1	<3	13	5	6	365	<2	<0.5	0.14	0.37	1.58
B19	11	14	45	14	11	363	3	<0.5	0.52	1.44	2.92
Average concentration for Study area	14.6	9.8	49.9	19.3	18.9	702.5	1.8	0.7	0.49	1.95	4.10
Background (Buchman, 1999)	10-25	4-17	7-38	9.9	10	400	1.1	0.1-0.3	-	0.26	0.99-1.8
TEL: McDonald <i>et al.</i> 2000 (Canadian ISQs and PELs, 2000)	35.7	35	123	18	-	-	5.9	0.6	-	-	-
PEL: McDonald <i>et al.</i> 2000 (Canadian ISQs and PELs, 2000)	197	91.3	315	36	-	-	17.0	3.5	-	-	-



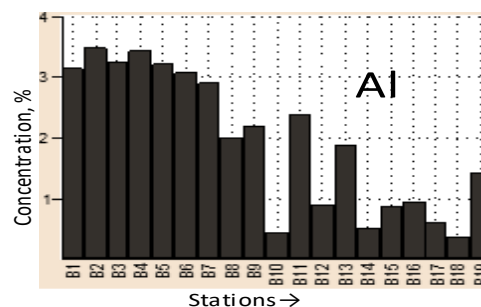
**Fig. 2G.** Cobalt distribution in sediments



**Fig. 2H.** Manganese distribution in sediments



**Fig. 2I.** Magnesium distribution in sediments



**Fig. 2J.** Aluminium distribution in sediments

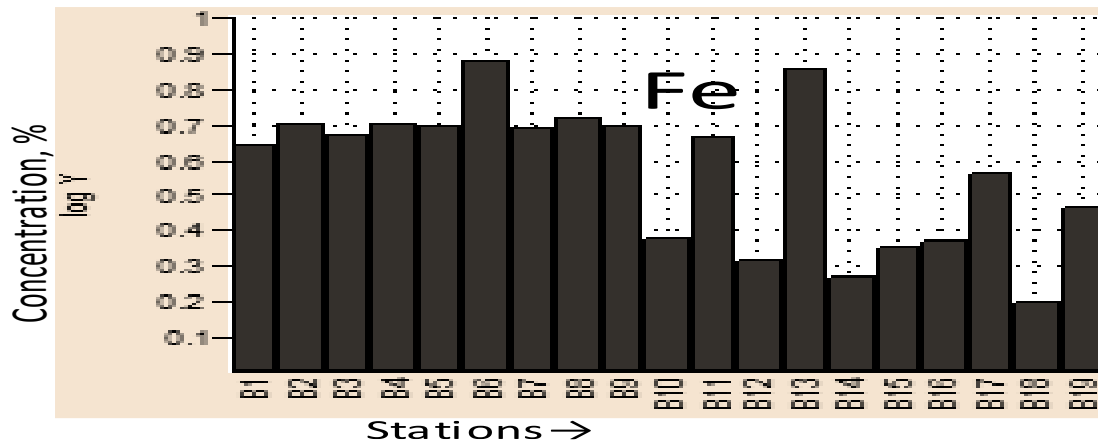


Fig. 2K. Iron distribution in sediments

The Bar charts showing the distribution of heavy metals and minor elements in sediments of Badagry Creek, southwest Nigeria Coast.

The cluster analysis yielded dendrograms as shown in Figs. 3A-3J, grouping all 19 sampled stations into two major significant clusters on the basis of

concentrations of individual metal in sediments. Exemption to this, is the dendrogram derived on the basis of Fe-concentrations in sediments (Fig. 3K) where significant outlier of B6 and B13 formed the third cluster. The third cluster being an outlier, could infer metal contribution from different sources (lithogenic and anthropogenic).

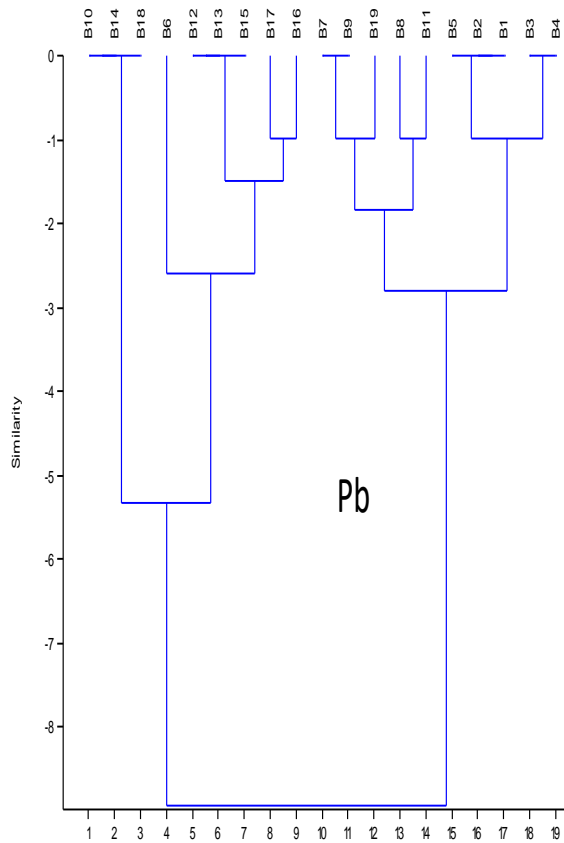


Fig. 3A. Cluster showing similarities in Pb concentrations.

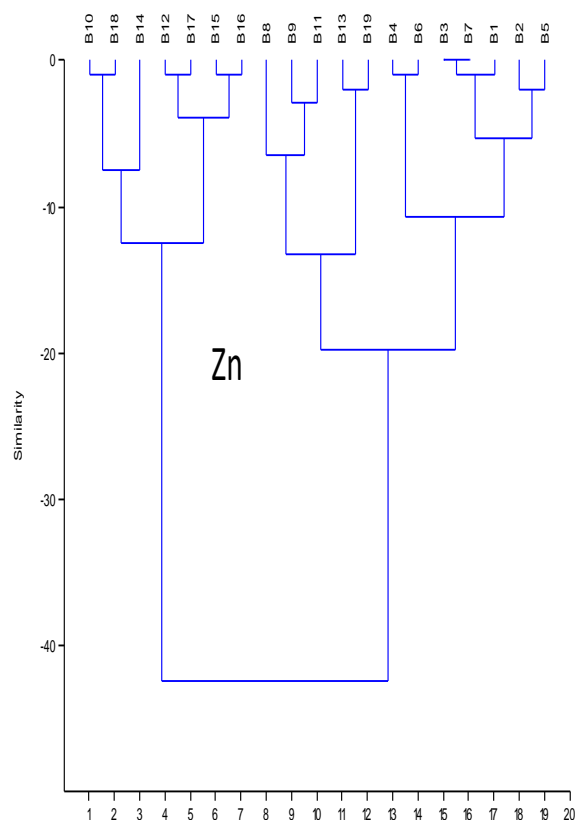
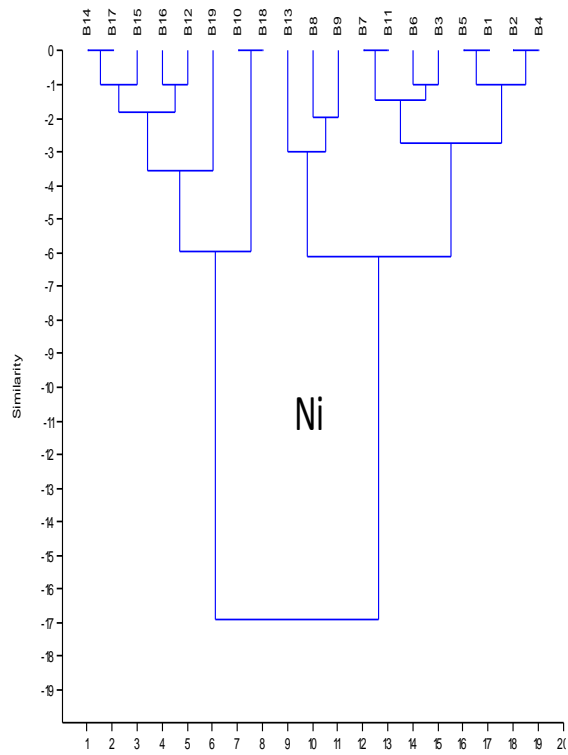
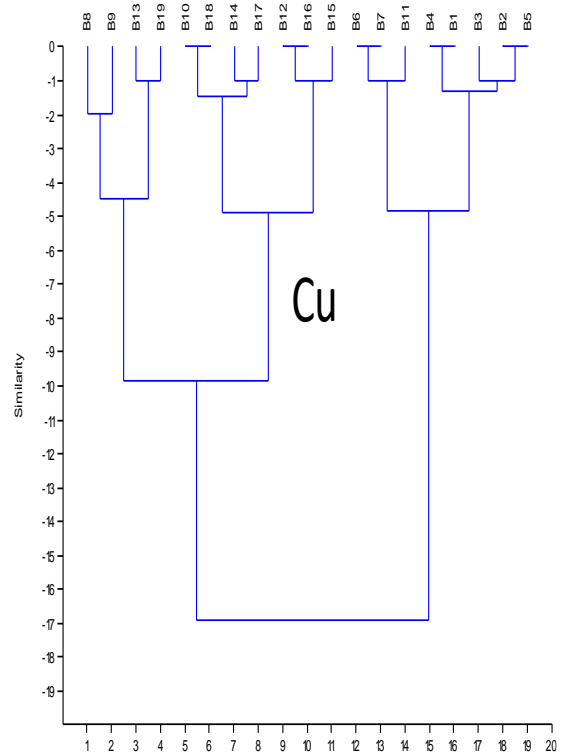


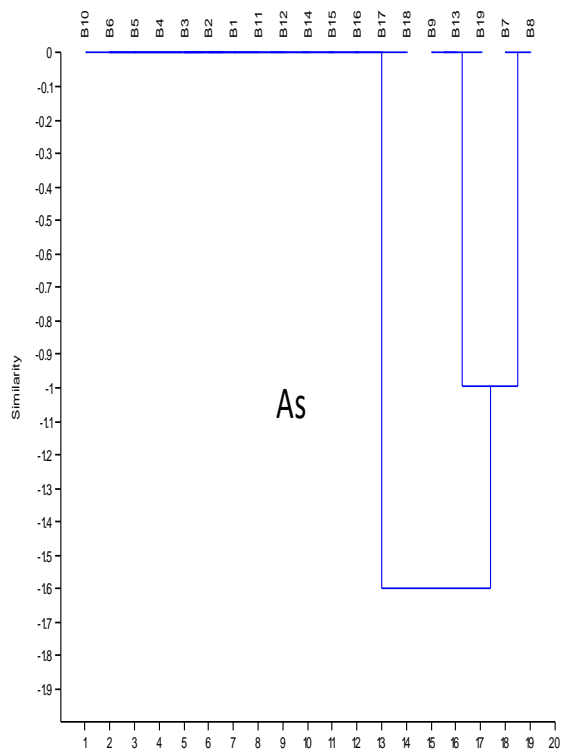
Fig. 3B. Cluster showing similarities in Zn concentrations.



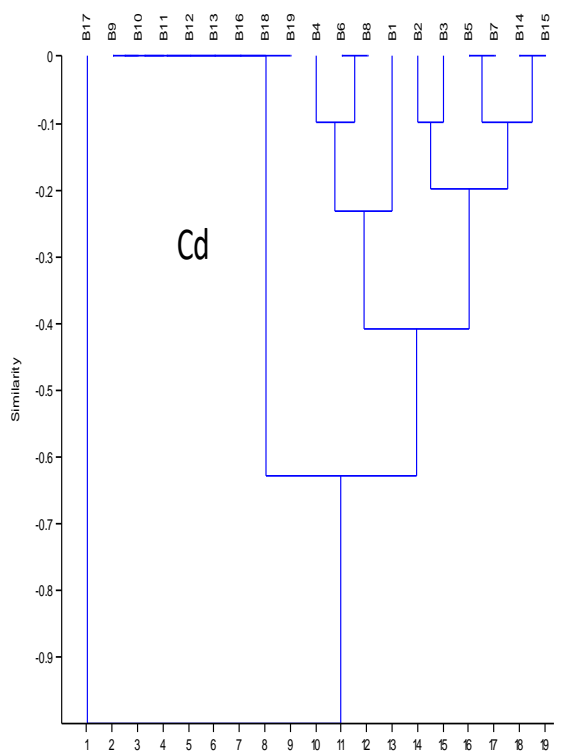
**Fig. 3C.** Cluster showing similarities in Ni concentrations.



**Fig. 3D.** Cluster showing similarities in Cu

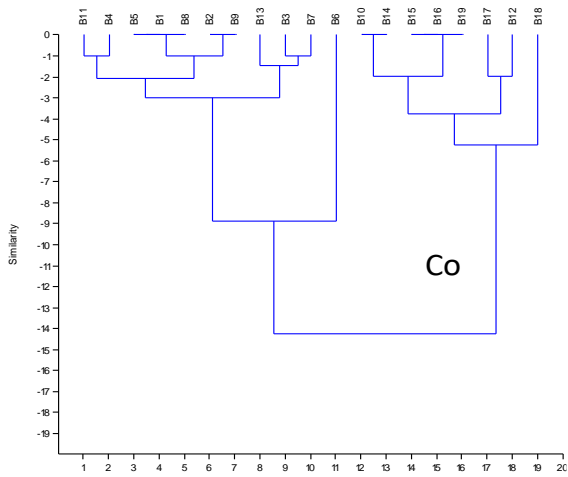


**Fig. 3E.** Cluster showing similarities in As concentrations.

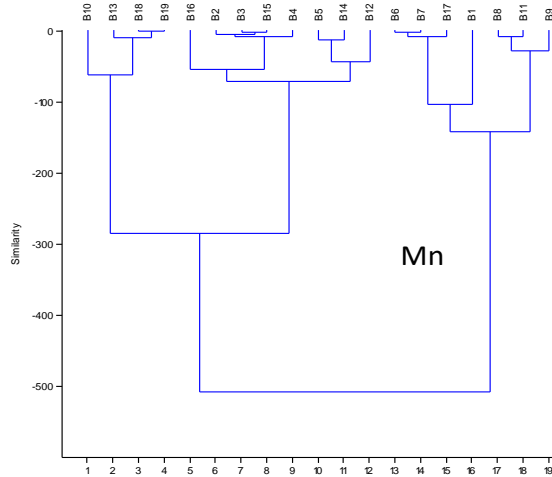


**Fig. 3F.** Cluster showing similarities in Cd

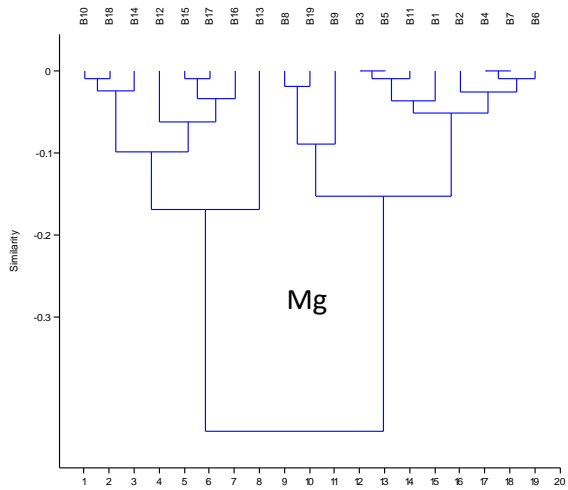




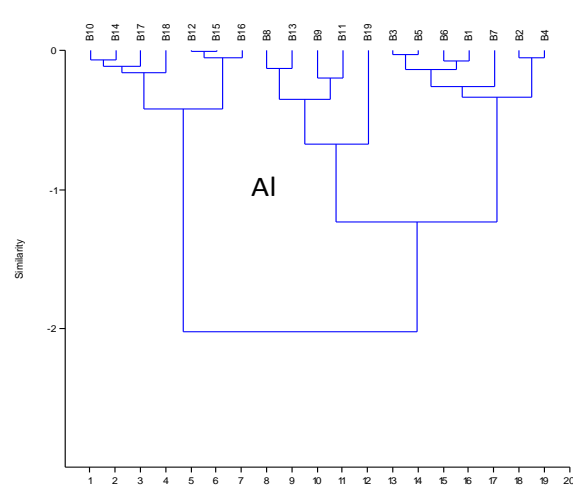
**Fig. 3G.** Cluster showing similarities in Co concentrations.



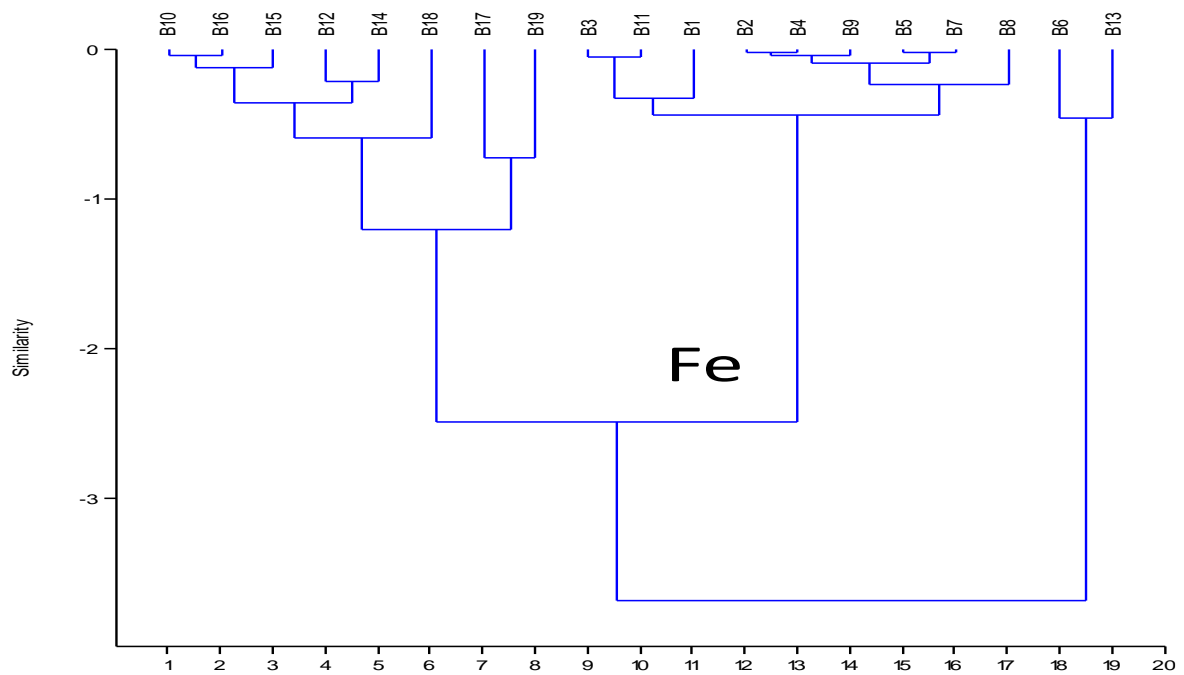
**Fig. 3H.** Cluster showing similarities in Mn concentrations.



**Fig. 3I.** Cluster showing similarities in Mg concentrations.



**Fig. 3J.** Cluster showing similarities in Al concentrations.



**Fig. 3K.** Cluster showing similarities in Fe concentrations.

Dendrograms showing similarities in samples based on concentrations of various elements.

Correlation analyses have been widely used in environmental studies. They provide an effective way of revealing the relationships between multiple variables and parameters by which the factors as well as sources of chemical components could be better understood (Varol, 2011; Zhao *et al.*, 2012; Yu *et al.* 2013; Zhuang and Gao, 2013). Pearson's correlation coefficient matrix

produced (Table 3), has shown that significant correlations exist between Cu and Zn ( $r=0.982$ ); Al and Ni ( $r=0.982$ ); Mg and Zn ( $r=0.976$ ); and Fe and Co ( $r=0.894$ ). Strong positive correlations exist among all these metals except Mn which shows fairly strong correlation with only Co ( $r=0.626$ ) and; Cd and As showing unapparent correlation. The highly significant positive correlation among metals may indicate similar or even same source input.

**Table 3.** Pearson's correlation coefficient matrix for the heavy metals and minor elements in sediments of Badagry Creek, southwest Nigeria

Metal	Cu	Pb	Zn	Ni	As	Cd	Co	Mn	Mg	Al	Fe
Cu	1										
Pb	<b>0.912</b>	1									
Zn	<b>0.957</b>	<b>0.878</b>	1								
Ni	<b>0.982</b>	<b>0.878</b>	<b>0.976</b>	1							
As	-0.005	0.196	0.106	0.075	1						
Cd	0.291	0.231	0.366	0.330	-0.345	1					
Co	<b>0.862</b>	<b>0.714</b>	<b>0.932</b>	<b>0.921</b>	0.091	0.381	1				
Mn	0.383	0.337	0.470	0.468	0.017	0.451	<b>0.626</b>	1			
Mg	<b>0.963</b>	<b>0.913</b>	<b>0.976</b>	<b>0.964</b>	0.128	0.257	<b>0.893</b>	0.468	1		
Al	<b>0.987</b>	<b>0.885</b>	<b>0.974</b>	<b>0.982</b>	0.018	0.331	<b>0.881</b>	0.360	<b>0.964</b>	1	
Fe	<b>0.681</b>	<b>0.534</b>	<b>0.805</b>	<b>0.777</b>	0.315	0.307	<b>0.894</b>	0.410	<b>0.729</b>	<b>0.746</b>	1

### Contamination Assessment

The eastern Badagry Creek presents the most and least contaminated samples, B17 with the highest value of modified degree of contamination (21); and B10, B18 with the lowest value (3). Pollution load index was at its maximum in station B1 at the boundary between the Republic of Bénin and Federal Republic of Nigeria (western segment), whereas, the least value was obtained for station B18 at the eastern end of the creek (Table 4A). According to Hakanson (1980), most stations of western Badagry Creek are moderately contaminated with Cu, Zn, Mn, Co; whereas, contamination is nil to very low at the eastern segment except arsenic in few places and Cd which produced significant contamination in all stations of the creek (Tables 4A and 4B).

Inferring from table 4B, the stations from western Badagry Creek have very high contamination to extremely contaminated samples, while, samples are either characterized by moderate, high, very high or extremely high contamination at the eastern segment. The pollution load index (PLI) is above the threshold in all stations of western Badagry creek and approximately 41.67 % of the stations at the eastern segment (*Cf.* Tomlinson *et al.*, 1980). The quantitative measurement of the contamination index in sediments (*Igeo*) showed that there is practically no contamination except Cd indicating heavy to extreme contamination levels (Table 5). The enrichment factor has also corroborated the very high Cd contents in sediments where others are indicating mostly moderate to very few minimum enrichments (Fig. 4A). This is complemented in the cluster of metal enrichment impact, where all clusters are fused together because of closeness in their Euclidean similarity measure, and Cd far apart as an outlier,

reflecting significant dissimilarity with others (Fig. 4B). Of the heavy metals considered in this study, only Cd poses threat because of the heavy to extreme contamination level. Cadmium can be derived from differing sources. According to Boehm and Schaefers (1994), primary materials containing Cd are concentrates of zinc, lead, copper, iron and phosphate ores; and hard coal and heavy oil. Surprisingly, there is no visible area near the creek that these ores are being treated. Cadmium has been linked to two zinc containing products i.e. automobile tyres and galvanized metals (Boehm and Schaefers, *Op cit.*). The presence of Cd in sewage sludge, Ni-Cd batteries, plating, pigments and plastics is also known (Thornton, 1992). The possibility of abuse of pesticides and phosphate fertilizer in agriculture and indiscriminate discharge of sewage sludge, battery scraps and plastics may have caused elevated concentration of cadmium in these sediments (Green-Ruiz and Paez-Osuna, 2001). Worthy of note, is the fact that Cd showed no correlation with any of these ores mentioned (Table 3), and no similarity in the enrichment factor based on cluster analysis (Fig. 4B). There is therefore, no contention that cadmium must have evolved from various anthropogenic activities.

Figure 4A gives decreasing order of metal enrichment in sediments as follow  $Cd > Mn > As > Co > Fe > Zn > Pb > Cu = Ni > Mg$ . Aluminium shows no visible enrichment, but exhibit significant positive correlation with Cu ( $r=0.987$ ), Ni ( $r=0.982$ ), Zn ( $r=0.974$ ), Mg ( $r=0.964$ ), Pb ( $r=0.885$ ) and Co ( $r=0.881$ ), inferring geogenic source (Table 3). Noteworthy, is the significant enrichment recorded for Mn in almost all samples of the eastern Badagry Creek (Table 6).

**Table 4A.** Contamination Factor and Pollution Load Index for the trace metals and sediments.

Sample stations	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	<i>Cd</i>	<i>mCd</i>	<i>PLI</i>
B1	1.08	0.88	0.96	0.66	1.41	1.51	0.67	6.50	13.67	17	1.81
B2	1.04	0.88	1.03	0.68	1.47	1.07	0.67	4.50	11.34	12	1.67
B3	1.00	0.94	0.97	0.64	1.29	1.07	0.67	4.00	10.58	11	1.6
B4	1.08	0.94	1.14	0.68	1.53	1.09	0.67	5.00	12.13	14	1.75
B5	1.04	0.88	1.06	0.66	1.41	0.99	0.67	3.00	9.71	8	1.57
B6	0.84	0.53	1.15	0.61	1.94	1.68	0.67	5.50	12.92	15	1.72
B7	0.84	0.76	0.97	0.59	1.35	1.69	1.33	3.00	10.53	9	1.69
B8	0.6	0.65	0.77	0.50	1.41	1.85	1.33	5.50	12.61	15	1.66
B9	0.68	0.76	0.89	0.55	1.47	1.91	2.00	1.25	9.51	4	1.56
B10	0.04	0.09	0.20	0.11	0.53	0.50	0.67	1.25	3.39	3	0.37
B 11	0.88	0.71	0.85	0.59	1.59	1.86	0.67	1.25	8.40	4	1.41
B12	0.28	0.41	0.42	0.25	0.76	0.93	0.67	1.25	4.97	4	0.79
B13	0.48	0.41	0.66	0.45	1.24	0.59	2.00	1.25	7.08	4	1.1
B14	0.12	0.09	0.30	0.23	0.53	1.01	0.67	3.50	6.45	9	0.61
B15	0.24	0.41	0.37	0.20	0.65	1.08	0.67	3.50	7.12	9	0.84
B16	0.28	0.35	0.38	0.27	0.65	1.17	0.67	1.25	5.02	4	0.77
B17	0.08	0.29	0.44	0.23	0.88	1.67	0.67	8.00	12.26	21	0.88
B18	0.04	0.09	0.18	0.11	0.35	0.61	0.67	1.25	3.30	3	0.36
B19	0.44	0.82	0.63	0.32	0.65	0.61	2.00	1.25	6.72	4	1.05

**Table 5.** Geoaccumulation index for the various trace metals in sediments

Sampled stations	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	Mg	Al	Fe
B1	0	-1	-1	-1	0	0	-1	6	-2	-2	-1
B2	-1	-1	-1	-1	0	0	-1	6	-2	-2	0
B3	-1	-1	-1	-1	0	0	-1	6	-2	-2	0
B4	0	-1	0	-1	0	0	-1	6	-2	-2	0
B5	-1	-1	-1	-1	0	-1	-1	5	-2	-2	0
B6	-1	-2	0	-1	0	0	-1	6	-2	-2	0
B7	-1	-1	-1	-1	0	0	0	5	-2	-2	0
B8	-1	-1	-1	-2	0	0	0	6	-2	-3	0
B9	-1	-1	-1	-1	0	0	0	4	-2	-2	0
B10	-5	-4	-3	-4	-2	-2	-1	4	-4	-5	-1
B 11	-1	-1	-1	-1	0	0	-1	4	-2	-2	0
B12	-2	-2	-2	-3	-1	-1	-1	4	-3	-4	-2
B13	-2	-2	-1	-2	0	-1	0	4	-3	-3	0
B14	-4	-4	-2	-3	-2	-1	-1	6	-4	-4	-2
B15	-3	-2	-2	-3	-1	0	-1	6	-3	-4	-1
B16	-2	-2	-2	-2	-1	0	-1	4	-3	-4	-1
B17	-4	-2	-2	-3	-1	0	-1	7	-3	-4	0
B18	-5	-4	-3	-4	-2	-1	-1	4	-4	-5	-2
B19	-2	-1	-1	-2	-1	-1	0	4	-2	-3	-1

**Table 4B.** Classification of modified degree of contamination and description (Hakanson, 1980)

<i>mCd</i> classes	Modified degree of contamination: interpretation
<1.5	Nil to very low degree of contamination
$2 \leq mCd < 4$	Moderate degree of contamination
$4 \leq mCd < 8$	High degree of contamination
$8 \leq mCd < 16$	Very high degree of contamination
$16 \leq mCd < 32$	Extremely Very high degree of contamination
$mCd \geq 32$	Ultra high degree of contamination

**Table 6.** Enrichment Factor of heavy metals in sediments

Sampled stations	Cu	Pb	Zn	Ni	Co	Mn	As	Cd	Mg	Al	Fe
B1	3	2	2	2	3	4	2	315	1	1	3
B2	2	2	2	2	3	2	1	200	1	1	3
B3	2	2	2	2	3	3	2	192	1	1	3
B4	2	2	3	2	3	2	1	223	1	1	3
B5	3	2	3	2	3	2	2	146	1	1	3
B6	2	1	3	2	5	4	2	277	1	1	5
B7	2	2	3	2	4	5	3	162	1	1	3
B8	2	3	3	2	5	7	5	423	1	1	5
B9	2	3	3	2	5	7	7	85	1	1	5
B10	1	1	3	2	9	8	11	415	2	1	10
B 11	3	2	3	2	5	6	2	77	1	1	4
B12	2	4	4	2	7	8	6	215	2	1	5
B13	2	2	3	2	5	2	8	100	1	1	8
B14	2	1	4	3	8	15	9	1015	2	1	7
B15	2	4	3	2	6	9	6	608	1	1	5
B16	2	3	3	2	5	10	5	200	1	1	5
B17	1	4	6	3	11	21	8	2015	2	1	3
B18	1	2	4	2	7	13	14	523	2	1	9
B19	2	4	3	2	3	3	10	131	2	1	4

### Sediment Quality Guidelines

The determination of contamination level based on comparison of concentration of a chemical in sampled sediments with background or reference values is believed to be inadequate. This is because the approach does not account for the types of biological resources in an aquatic environment or the concentration at which an adverse response would be observed in these organisms. To improve on this method, sediment quality guidelines (SQGs) has since been developed for use in assessing sediment quality and the average contaminant concentrations that cause adverse effects (Thompson and Wasserman, 2015). Threshold effect level and probable effect level values were used to assess the ecotoxicological potential of heavy metal concentrations in sediments. It is assumed that sediment contamination concentrations below the threshold effect limit (TEL) are acceptable and above the probable effect limit (PEL) are unacceptable. Low range values (TEL) include concentrations below which adverse effects on sediment dwelling fauna are uncommon, whereas, PEL denotes chemical concentrations above which adverse effects may occur. The Consensus-Based Empirical SQGs approach was not considered for this study since concentrations are below

TEL, except Cd and Ni that are above but far below PEL. The inconsequentiality becomes paramount as the values of threshold effect (TEC) and probable effect concentrations (PEC) are much higher than the TEL and PEL in relative order. The sediment quality guidelines (SQGs) of Buchman (2008) interpreted the concentrations of Cd in Badagry Creek to be above the threshold effect range though below the probable effect level (Table 2). The entire western Badagry Creek and 33.3 % of the stations at the eastern segment are characterized by high concentrations of Ni which are above threshold effect level. The concentrations of other heavy metals, Cu, Zn, As and Pb are all below the probable effect level, hence no toxic sediment in Badagry Creek as at the time of this investigation.

### CONCLUSIONS

This study has revealed that the average concentrations of heavy metals in sediments of Badagry Creek is largely enhanced at the western segment for Cu, Zn and Ni. The overall average concentrations (ppm) of heavy metals of concern are 14.6 (Cu), 9.8 (Pb), 49.9 (Zn), 19.3 (Ni), 18.9 (Co), 702.5 (Mn), 1.8 (As) and 0.7

(Cd). The spatial distribution of these metals is site-specific, exhibiting remarkably high relative concentration in sampling stations where certain commercial activities take place. For example, the eastern end of the creek receives Cargo ships from Tin Can Island and Apapa ports, oil tankers from various jetties and ferries from Mile 2 suburbs in Lagos, Nigeria. This may account for the relatively higher concentrations of Cd and As. The decreasing order of heavy metal enrichment in sediments is Cd > As > Co > Zn > Pb > Cu ≥ Ni. Pearson's correlation and cluster analysis identified similar or same source for Cu, Ni, Zn, Pb, Co, Mg and Al (lithogenic) whereas, As, Cd and Mn indicated lithogenic and anthropogenic sources. Considering the ecotoxicological potential of the heavy metals, cadmium with the highest enrichment factor in all stations exceeds the threshold effect range (TEL) but falls below the probable effect level (PEL). Also, the concentrations of other heavy metals Ni, Cu, Zn, As, and Pb are below PEL, hence are not likely to produce harmful effects on sediment-dwelling organisms.

## REFERENCES

- Adams, W.J., Kimerle, R.A. and Barnett J.W., Jr. (1992). Sediment quality and aquatic life assessment. *Environmental Science and Technology*, 26: 1864–1875.
- Ahmed, F., Fakhruddin, A.N.M., Imam, M.T., Khan, N., Khan, T.A., Rahman, M.M. and Abdullah, A.T.M. (2016). Spatial Distribution and Source Identification of Heavy Metal Pollution in Roadside Surface Soil: A Study of Dhaka Aricha Highway, Bangladesh. *Ecological Processes*, 5: 2.
- Alexander, C.R., Smith, R.G., Calder, F.D., Schropp, S.J. and Windom, H.L. (1993). The historical record of metal enrichments in two Florida estuaries. *Estuaries*, 16: 627–637.
- Ali, H., Khan, E. and Ilahi, I. (2019). Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity and bioaccumulation. *Hindawi Journal of Chemistry*, Article ID 6730305: 1-15.
- Alvin, C. R. (2002). *Methods of Multivariate Analysis*. John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012, (212): 850-6011.
- Belzile, N. Y., Gunn, C.J. and Dixit, S. (2004). "Sediment trace metal profiles in lakes of Killarney Park, Canada: from regional to continental influence," *Environmental Pollution*, 130(2): 239–248.
- Boehm, E. and Schaefer, K. (1994). "Massnahmen zur Minderung des cadmiums in der Umwelt". Prepared by Fraunhofer-Institut für Systemtechnik (BLAU). Industrial metabolism: restructuring for sustainable development, Tokyo, Japan, The United Nations Press, Pp. 330.
- Buat-Menard, P. (1979). "Variable influence of the atmospheric flux on the trace metal Chemistry of oceanic suspended matter." *Earth and Planetary Science letters*, 1979, 42 (3):99-411.
- Buchman, M.F. (1999). NOAA Screening Quick Reference Tables, NOAA HAZMAT Report 99-1, Seattle WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, Pp. 12.
- Buchman, M.F. (2008). NOAA Screening Quick Reference Tables, NOAA OR&OR Report S 08-1, Seattle WA, Office of Response and Restoration Division, National Oceanic and Atmospheric Administration, Pp. 34.
- Chakravarty, I. M. and Patgiri, A. D. (2009). "Metal Pollution Assessment in Sediments of the Dikrong River, N.E. India". *J Hum Ecol*, 27(1): 63-67.
- Faiz, Y., Tufail, M., Javed, M.T., Chaudhary, M.T. and Siddique, N. (2009). "Road dust pollution of Cd, Cu, Ni, Pb and Zn along Islamabad Expressway, Pakistan", *Micro Chem. J.* 92: 186- 192.
- Fang, S., Longjiang, M., Runxia, S., Jiling, D., Zhihai, T. and Min, D. (2019). Contamination evaluation and source identification of heavy metals in the sediments from the Lishui River Watershed, Southern China. *International Journal of environmental Research and Public Health*, 16(3): 336.
- Forstner, U. and Wittman, G. T. W. (1983). *Metal Pollution in the Aquatic Environment*, Springer, Heidelberg, Germany, Pp. 1-2.
- Gale J.G. and Hoare P.G. (1991). The physical composition and analysis of regolith materials. In *Quaternary Sediments: Petrographic Methods for the Study of Unlithified Rocks*, *Belhaven Press*, New York, Pp. 87-94.
- Green-Ruiz C. and Paez-Osuna F. (2001). Heavy metal anomalies in lagoon sediments related to intensive agriculture in Altata-Ensenada del Pabellon coastal system (SE Gulf of California) *Environ. Int.* 26: 265–273.
- Hakanson, L. (1980). An Ecological Risk Index for Aquatic Pollution Control. A Sedimentological Approach. *Water Research*, 14: 975-1001.
- Hammer, Ø., Harper, D.A.T. and Ryan, P.D. (2007): Paleontological Statistics Software Package (PAST) for education and data analysis. Version 1.67, Pp. 83.
- Ibe, A.C. (1988). *Coastline erosion in Nigeria*. Ibadan University Press, Ibadan, Nigeria, Pp. 217.
- Ikem, A., Egiebor, N.O. and Nyavor, K. (2003). Trace Elements in Water, Fish and Sediment from Tuskegee Lake, Southeastern USA. *Water Air Soil Pollution*. 149: 51–75.
- Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Habibullah-Al-Mamun, M. and Islam, M.K. (2015). Heavy Metal Pollution in Surface Water and Sediment: A Preliminary Assessment of an Urban River in a Developing Country. *Ecological Indicators*, 48: 282-291.
- Khan, F. U., Rahman, A. U., Jan, A. and Riach, M. (2004). "Toxic and trace metals (Pb, Cd, Zn, Cu, Mn, Ni, Co and Cr) in dust, dustfall /soil, *Journal of the Chemical Society of Pakistan*, 26(4): 453–456.
- Li, Y. H. (2000). *A Compendium of Geochemistry: from Solar Nebula to the Human Brain*. Princeton University Press, Princeton, NJ., Pp. 475.

- Loring, D.H. and Rantala, R.T.T. (1992). Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth Sci. Rev.* 32: 235-283.
- Luoma, S. N. (1990). "Processes affecting metal concentrations in estuarine and coastal marine sediments," in *Heavy Metal in the Marine Environment*, CRC Press, Boca Raton, Fla, USA, Pp. 51–66.
- Macdonald, D.D., Ingersoll, C.G. and Berger, T.A. (2000). Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Systems. *Archives of Environmental Contamination and Toxicology*, 39(1): 20-31.
- Muller G. (1969). Index of geoaccumulation in sediments of the Rhine River. *Geol. J.* 2(3): 108–118.
- Peng, J., Song, Y., Yuan, P., Cui, X. and Qiu, G. (2009). The remediation of heavy metals contaminated sediment. *Journal of Hazardous Materials*, 161(2-3): 633-640.
- Phillips, O.A., Falana, A.O. and Adebayo, A.J. (2017). The geochemical composition of sediment as a proxy of provenance and weathering intensity: a case study of southwest Nigeria's coastal creeks. *Geology, Geophysics and environment*, 43 (3): 229-248.
- Riley, J.P. and Chester, R. (1971). *Introduction to Marine Chemistry*. Academic Press, London, Pp. 465.
- Rodríguez-Barroso, M.R., García-Morales, J.L., Coello, M.D. and Quiroga, J.M. (2009). An assessment of heavy metal contamination in surface sediment using statistical analysis. *Environmental Monitoring and Assessment* 163(1-4): 489-501.
- Saha, P.K. and Hossain, M.D. (2011). Assessment of heavy metal contamination and sediment quality in the Buriganga River, Bangladesh. Second international conference on environmental science and technology, *IPCBE*, 6: 384-388.
- Salomons W., Stigliani W.M. (1995). *Biogeodynamics of Pollutants in Soils and Sediments*. Springer; Berlin, Germany, Pp. 30.
- Syakti, A.D., Demelas, C., Hidayati, N.V., Rakasiwi, G., Vassalo, L., Kumar, N. and Doumenq, P. (2015). Heavy Metal Concentrations in Natural and Human-Impacted Sediments of Segara Anakan Lagoon, Indonesia. *Environmental Monitoring and Assessment*, 187: 1-15.
- Thompson, R. and Wasserman, H. (2015). Sediment quality guidelines (SQGs): A review and their use in practice. *Geoenvironmental Engineering*, Pp. 11.
- Thornton, I. (1992). Sources and pathways of cadmium in the environment. In: *Cadmium in the human environment: toxicity and carcinogenicity*. Lyon, International Agency for Research on Cancer, (IARC Scientific Publications, No. 118: 149–162.
- Tomlinson, D.L., Wilson, J.G., Harris, C.R. and Jeffrey, D.W. (1980). Problems in the Assessment of Heavy-Metal Levels in Estuaries and the Formation of a Pollution Index. *Helv. Geol. Bundesanstalt Mitteilungen*, 33: 566-575.
- Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous Materials*. 195: 355–364.
- Yu, Y., Song, J.M., Li, X.G., Yuan, H.M. and Li, N. (2013). Fractionation, sources and budgets of potential harmful elements in surface sediments of the East China Sea. *Mar Pollut.* 68: 157–167.
- Zhao, S., Feng, C.H., Yang, Y.R., Niu, J.F. and Shen, Z.Y. (2012). Risk assessment of sedimentary metals in the Yangtze Estuary: New evidence of the relationships between two typical index methods. *Journal of Hazardous Materials*. 241–242: 164–172.
- Zhuang, W. and Gao, X.L. (2013). Acid-volatile sulfide and simultaneously extracted metals in surface sediments of the southwestern coastal Laizhou Bay, Bohai Sea: Concentrations, spatial distributions and the indication of heavy metal pollution status. *Mar Pollut Bull* 76: 128–138.