Original Research Article

Geochemical and statistical approach to assessing trace metal accumulations in Lagos Lagoon Sediments

ABSTRACT

The study areas is located in Lagos Lagoon, longitude 3° 22' 27.97" to 3° 28' 58.60"East and latitude 6° 27' 41.44" to 6° 35' 42.60" North. Sediment samples were collected from bottom sediments in twelve sampling stations that cut across; the Southern, central and the North eastern part of the Lagos Lagoon with the aid of van-veen grab from May to July 2014, on a monthly basis. Sediment samples were air dried, disaggregated and sieved (<125μm). The sieved sediments were leached with Nitric/Hydrochloric acid (1:3), aqua regia and its trace metal contents analysed with Argillent 200 A model, Atomic Absorption Spectrophotometer (AAS).The analysed concentrations in mg/kg showed; Ni ranges from Nd-17.55, Mn ranges from 12.50-1180.25, Pb ranges from Nd-15.37, Zn ranges from 51.68-659.55, Cu ranges from Nd-35.55 and Cr ranges from Nd-53.00.The major element(Fe) used as the normalizer ranges from 832.64-25206.00. 70 grams each of sediment samples were further oven dried, and its grain size fractions determined. The result of the grain size analysis range from; coarse to very fine sand, moderate to well sorted, finely skewed to mesokurtic, while the visually described major clay fractions range from; sandy, plastic, whitish brown clay to brownish, shaly, plastic clay with occasional silt. The bi-modal peaks on the particle size plots suggest multiple source of sediment contaminants in; Unilag waterfront, Ijora and Ibeshe, and a unimodal peaks; single source of contaminant to the sediments of; Atlascove, Apapa and Ikorodu. Potential contamination benchmarks; contamination factor (CF), enrichment factor (EF), geoaccumulation factor (Lgeo) and pollution load index (PLI), were used to assess whether, the observed concentrations represent background or contaminated levels. The result affirmed the elevation of Zn, Pb and Mn and moderate contamination of zinc metals at; Iddo, Okobaba, Majidun and Ijora stations and the crustal influence in the deposition of; Cu, Cr and Ni. Multivariate statistical analysis employed also affirmed these potential contamination benchmarks. Based on the results it can be concluded that zinc metal represented a contaminated level, but, the overall toxicity level of the Lagos Lagoon sediments to the aquatic ecosystem is low.

Keywords: Lagos Lagoon, bottom Sediment samples, Atomic Absorption Spectrophotometer, grain size fractions, Potential contamination benchmarks, multivariate statistical methods, aquatic ecosystem.

1 INTRODUCTION

Assessing the concentrations of potentially harmful trace metals in sediments is crucial; it evaluates the potential risk of their contamination and toxicity. Most trace metals are toxic environmental pollutants, with well-identified adverse effect on aquatic ecosystems [1].These pollutants could be transferred to humans via ingestions, dermal contact or breathing [2].

The origin of metals that accumulate in sediments is partly from natural sources through the weathering of rocks and partly arising from a variety of human activities including; sand mining, smelting, electroplating, chemical manufacturing plants, as well as domestic discharges, shipping and boating activities, wood logging, saw dust input and marine debris. All these human induced effluents are predominant in Lagos Lagoon [3, 4, 5, 6]. Since several anthropogenic induced activities may cause trace elements contamination, many researchers have indicated the need for a better understanding of sediment contamination [7].

This paper presents trace metal contaminations on selected stations in Lagos Lagoons. The major objectives of this study are; to access potential contamination and identify the different sources that contribute to trace element concentrations in bottom sediments of the selected stations in Lagos Lagoon, to evaluate the extent of trace metal contaminations and the degree to which trace metals are influenced by anthropogenic and lithogenic factors by providing information for the background levels of metals in the sediments of the selected stations, to identify different causes of enrichment and trace metals associations via the application multivariate statistics on the studied elements, including correlations, principal component analysis and hierarchical cluster analysis and to determine the variation in grain size distributions with trace metal concentrations across the stations with a view to understanding the pattern of sediment transport in the bottom sediments of Lagos Lagoon, to compare the present results with similar studies undertaken in .the Lagos metropolis and adjourning environment.

2 Material and methods

2.1 Study area

The study areas are located between longitude 3° 22' 27.97" to 3° 28' 58.60"East and latitude 6° 27' 41.44" to 6° 35' 42.60" North. It traverses the south Eastern part of the Lagos Lagoon (Atlascove, Apapa stations), to the central part of the Lagoon and Northwestern part of the Lagos Lagoon (Ikorodu and Egbin stations figure1). Geologically, it falls within the eastern part of the Dahomey Basin, bounded to the north by then Precambrian Basement complex of southwestern

Nigeria. It is bounded by the Gulf of Guinea to the south and eastward by the Okitipupa ridge. The area is dominated by a continuous and monotonous repetition of clayey and sandy horizons. These horizons show some lateral continuation in some places but in most parts, these lithology pinches out [8]

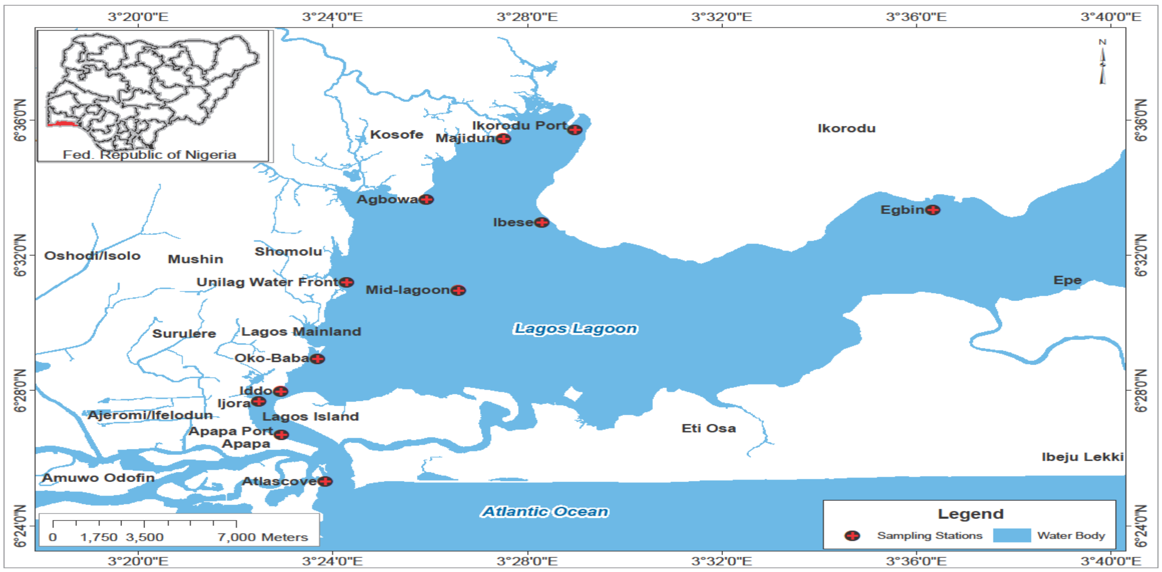

Figure1: Map of the study area showing the 12 stations

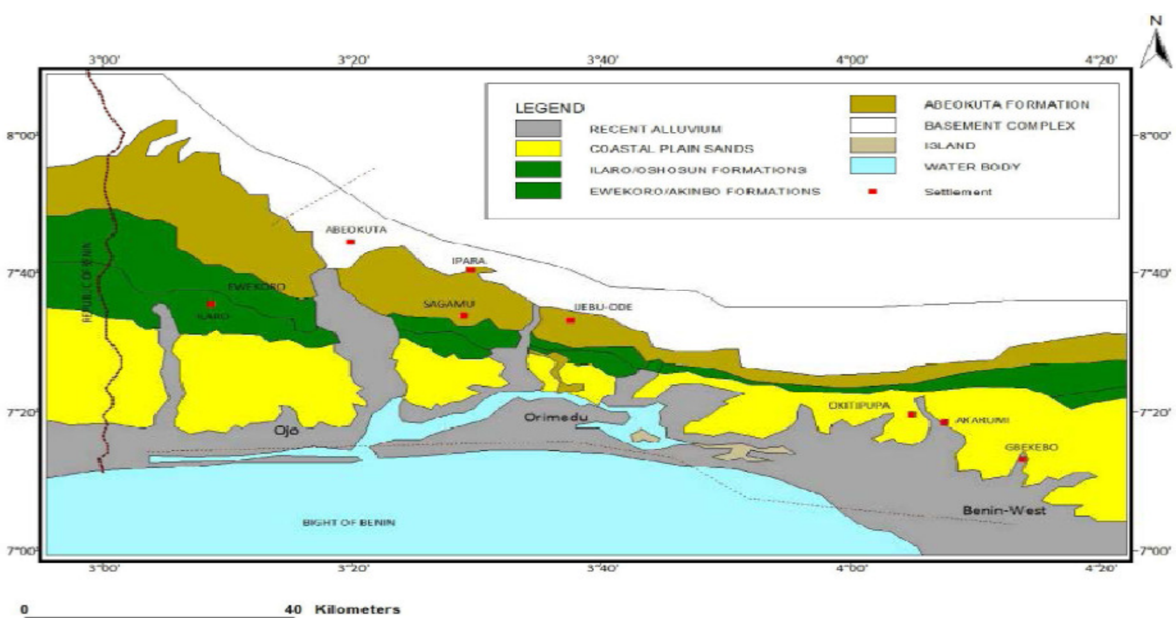

Figure2: Geological Map of the Eastern Dahomey Basin [9]

2.2 Data collection and analysis

Sediment samples were collected from twelve sampling stations with the aid of van-veen grab. from May to July 2014, on a monthly basis and kept in black polythene bags, air dried, disaggregated to remove large debris and shell fragments, pulverized in agate mortar and sieved (<125 μm). The sieved sediments were leached with Nitric/Hydrochloric acid (1:3), aqua regia using standard digestion procedure [10]. Trace metal contents were analysed with Argillent 200A model, Atomic Absorption Spectrophotometer (AAS). For grain size determination, 70 grams of each sample was oven dried at 50ºC in order to remove their moisture content. The dried and weighed sediments were transferred carefully to the uppermost (coarsest) of a stacked series of graded sand sieves, sieves were gently brushed of all material from the container. A 62 μm sieve was placed at the bottom of the stack of sieves and care was taken by using a pan below the finest sieve to catch the last of any fine material which may still pass. The stacked column of sieves was now transferred to a Rotap sieve shaker for a period 10-15minutes. When the finality of sieving was checked, the fraction of samples retained on each sieve was emptied on to a sheet of glazed paper and grains lodged in the sieve were removed with a sieve brush. The fractions were then transferred to a pre weighed dish for weighing. The analysis continues sieve by sieve through the series until, finally, the material passing through the last (62 μm) sieve and retained in the pan was also recorded.

3 Results and Discussion

3.1 Sediment transportation patterns

The statistical parameters of grain size distribution have been a major parameter in delineating the depositional processes influence [11]. Skewness and standard deviation are considered environmentally sensitive indicators while the mean value is a reflection of the competence of the mechanism of transportation. The result of the granulometric analysis of representative samples from the bottom sediment of Lagos Lagoon is presented in figure 7-12. The cumulative curve and individual particle size of each sample from which grain size parameters were calculated. The sediment distributions of ; Unilag water front, Atlas cove, Ijora, Ikorodu port, Apapa port and Ibeshe stations range; from coarse to very fine sand, moderate to well sorted, finely skewed with mesokurtic. The mean, which is a reflection of the overall size of the sediment, has values ranging from (0.58 Φ to 2.01 Φ) which represents a coarse grained – very fine sand while, the standard deviation which is a measure of the sorting has values ranging from 0.51 Φ to 1.39 Φ (moderately to poorly sorted). Skewness values range from -0.19Φ to 0.38Φ (coarse skewed to strongly skewed), while kurtosis value lies between 0.81Φ and 1.09 Φ (platykurtic to Mesokurtic). The bottom sediments of Ibeshe and Ijora are majorly very fine grained-fine grained sand; these attributes attracted incessant sand mining in the area. However, other sediment samples from the central part of the Lagos Lagoon (mid Lagoon), Agboyin, Majidun, Iddo, Egbin and Okobaba range from; sandy, plastic, whitish brown clay to brownish, shaly, plastic clay with occasional silt.

3.2 Trace element geochemistry

The concentration in mg/kg of some trace metals in the Lagos Lagoon sediments showed Ni range from Nd-17.55, Mn ranges from 12.50-1180.25, Pb ranges from Nd-15.37, Zn ranges from 51.68-659.55, Cu ranges from Nd-35.55, Cr ranges from Nd-53.00. Comparing the observed concentration with the Average Shale Concentration (ASC) as proposed by [12,13], Zn, Pb and Mn, were observed to contain elevated concentration in reference to the average shale concentration(ASC) in the Lagos Lagoon, in stations such as: Iddo, Okobaba, Majidun, Ijora, and Egbin; an indication of human-induced effluents accumulations. These accumulations might not be unconnected with; population increase, commercial centers and industrial activities known for the generation of huge volume of liquid and solid wastes' sink to the adjourning sediments in Lagos Lagoon. This is in agreement with the work of [14] on sediment quality ratios of six industrial sites in Lagos metropolis that eventually drain into the Lagos Lagoon. However metals such as Cu, Cr and Ni were observed to have elevated concentrations relative to their corresponding ASC at stations such as; Ijora, Majidun, Iddo, Agboyin, Okobaba, Egbin and the central part of the lagoon. These might be connected to the binding nature of the dominant clay and colloidal particles in these stations; thereby making the trace metals to be non-bioavailable The average concentration of the trace elements in all the stations is in the descending order of: Mn >Zn >Cr >Cu >Pb > Ni).

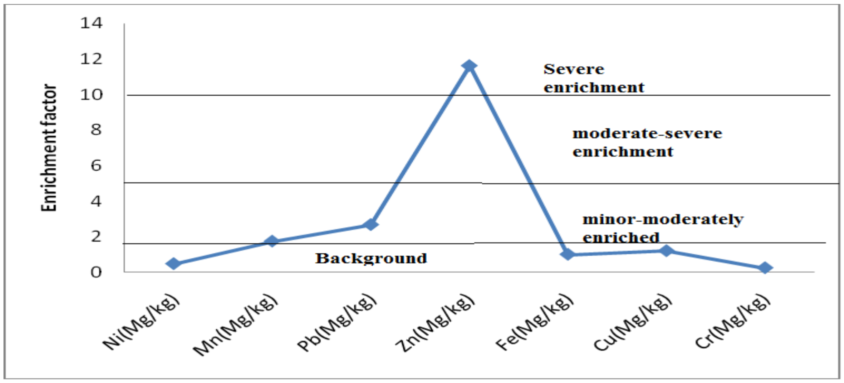

Figure 3: Trace metal enrichment showing zinc, manganese and Pb as enriched metals (anthropogenic source)

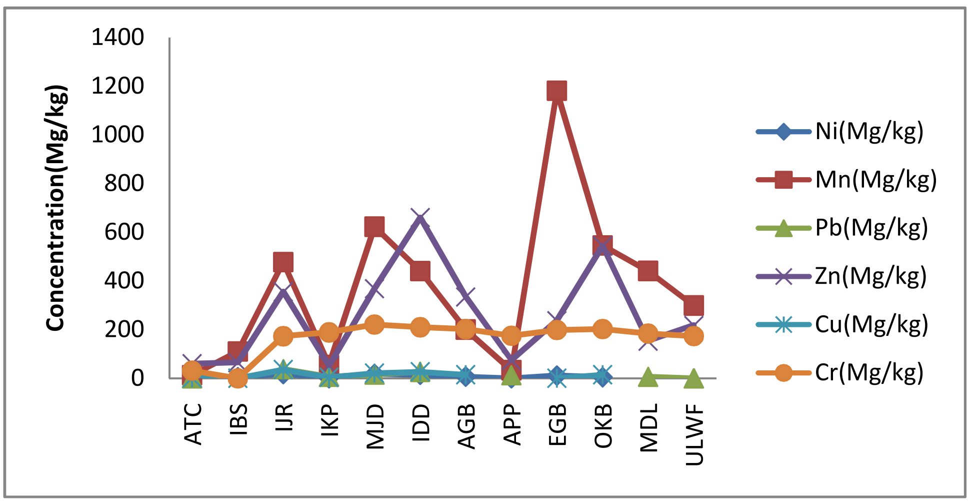

Figure 4: Showing the mean concentration of trace metals in the study area

3.3 Quality of Lagos Lagoon Sediments

The quality and potential environmental implication(s) of trace metals were evaluated using contamination indices such as; contamination factor, geo-accumulation indices, pollution load indices and contamination degrees. These methods have been used successfully by various workers to determine the quality of various environmental media [15, 16, 8].

3.3.1 Contamination Factor (CF) is calculated as the ratio between the sediment metal content at a given station and the normal concentration levels. Concentration factor, $CF = C / Cn$ (1) CF = contamination factor; C = mean concentration of each metal in the sediments; Cn=background value. The contamination factor modified by [15] showed the following classes:

CF<1, low contamination, 1<CF<3, moderate contamination and 3<CF<6, considerable contamination. Zinc metal falls within the moderate contamination ratio (figure5).

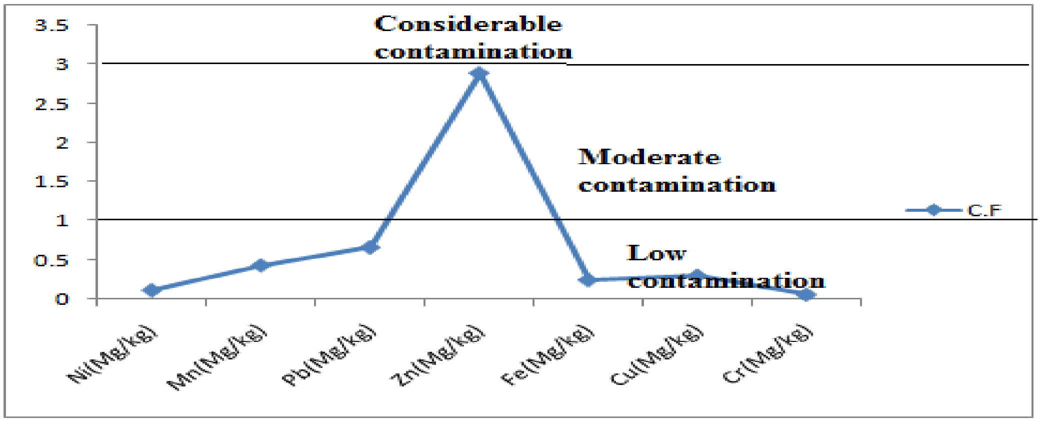

Figure 5 : showing the contamination factor plot of the Lagos Lagoon sediments

3.3.2 Geoaccumulation Index (lgeo). The lgeo is used to understand the current environmental status and trace metal pollution extent with respect to natural environment. It is distinct from EF because the factor 1.5 is introduced to include possible variations of the background values that are due to lithogenic variations [16]. The lgeo (equation2) classes are:

$$I_{geo} = \log_2\left(\frac{C_{HM}}{1.5 \times B_{HM}}\right) \qquad (2)$$

C_{HM} = concentration of metals, B_{HM} =background level of metals.

0 ≤lgeo≤1, unpolluted to moderately polluted, 1≤lgeo≤3, moderately to strongly polluted and 3≤lgeo≤5, strongly to very strongly polluted. The six metals examined all fall within the geochemical benchmarks for unpolluted to moderately polluted ratio, this affirmed that the pollution arising from trace metals/inorganic metals have not undergone a progressive state in all the stations (figure6).

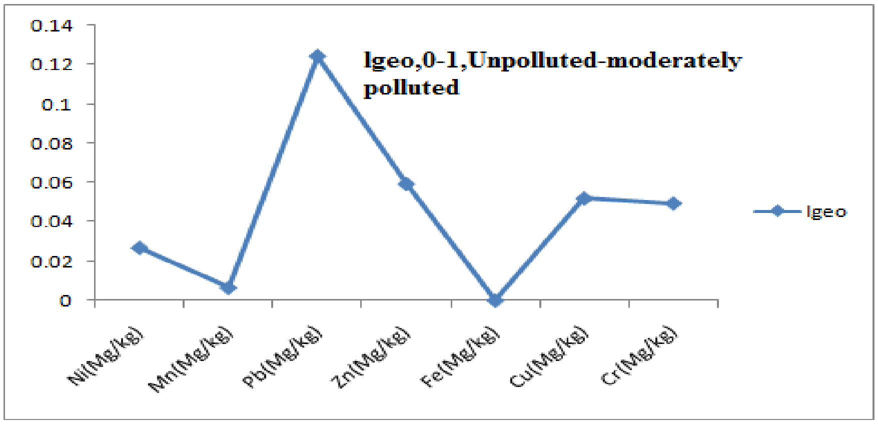

Figure 6: showing the geoaccumulation factor of the study area

3.4 Integrated Pollution indices. Degree of contamination (DC) and average pollution index (PLI) were utilized as the integrated pollution indices in the selected stations. According to [15, 8, 17]., DC is calculated as; (equation3)

$$DC = \Sigma\, Cf\,. \qquad (3)$$

Summation of the contamination factors of the trace metals

DC values of ≤ 8, represent a low degree contamination, while, 8≤DC≤16, represent a moderate contamination.

$$PLI = \sqrt[6]{cfNi * cfCr * cfMn * cfCu * cfZn * cfPb} \qquad (4)$$

CF =Contamination factor of each metals

However, PLI (the assessment of the overall toxicity of the study area) ≤1, represent close to background concentration, while, PLI.>1, represent a progressive pollution. The degree of contamination values for the study area is lower than 8; while the pollution load index values is less than 1(figure7).This fall within a low degree of contamination and close to background value (non-bioavailable state).

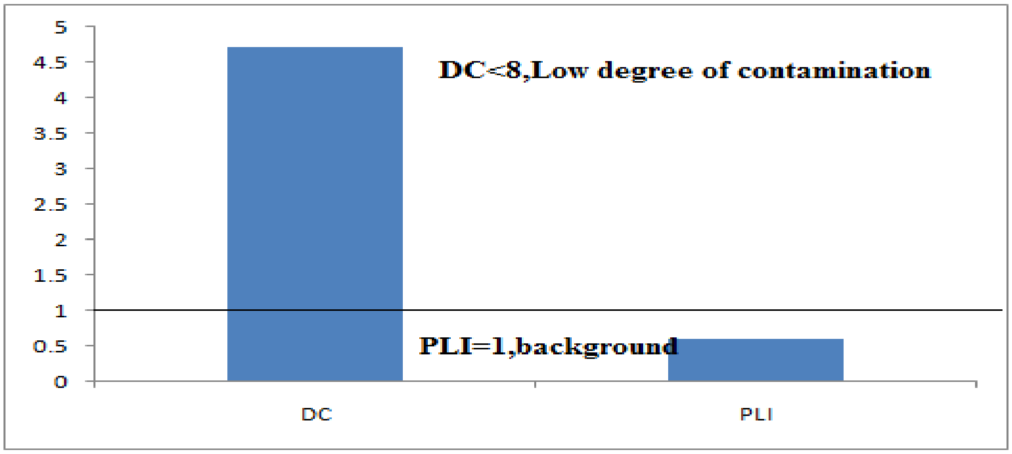

Fig7: Showing the pollution load index and degree of contamination

3.5 Multivariate statistical methods

A graph of cumulative weight percent against sieve size was plotted on the grain size results. And from the cumulative frequency curve obtained, grain size parameters such as; average size (mean), spread of the sizes about the average (standard deviation) symmetry of preferential spread to one size of the average (skewness) and kurtosis or degree of concentration of the grains to the central size were determined with matlab applications(fig8-12).Pearson correlation analysis(table1-3), Principal Component Analysis (PCA,table4), and Cluster Analysis (CA, fig 14) were carried out using; matlab, Microsoft excel descriptive tools and software statistical 7, to identify the association of metals and geochemical parameters [18,19].A correlation matrix was used to understand the relationship among the metals. Principal component analysis was applied to transform the correlation matrix, with an aim of explaining the relationships between the different factors. The resulting factors were then rotated using varimax method, for deriving more significant information on the distribution of the weights of the variables on the factors [20]. The factors are presented as factor 1 (F1) and factor 2 (F2) for 12 sediment samples. Hierarchical Cluster Analysis (HCA) was performed to create the data into groups, based on pattern and closeness.

3.5.1 Particle size plots

The plot of individual particle size against phi size for the various samples shows bi-modal peaks in bottom sediments of Unilag water front, Ijora and Ibeshe .This suggests multiple source of sediment contamination source, however, the bottom sediments of Atlascove, Apapa and Ikorodu exhibited a uni-modal peaks an evidence of a single pollution source. The low trace metal concentration in the coarse sand texture of Apapa and Ikorodu Port, coupled with the medium sand texture at the Unilag water front and Atlascove sediments affirmed low affinity of coarse fractions with trace metals. However, the high concentration of Mn in Ibeshe station confirmed the great affinity of trace metals to fine sand fractions [21,22].

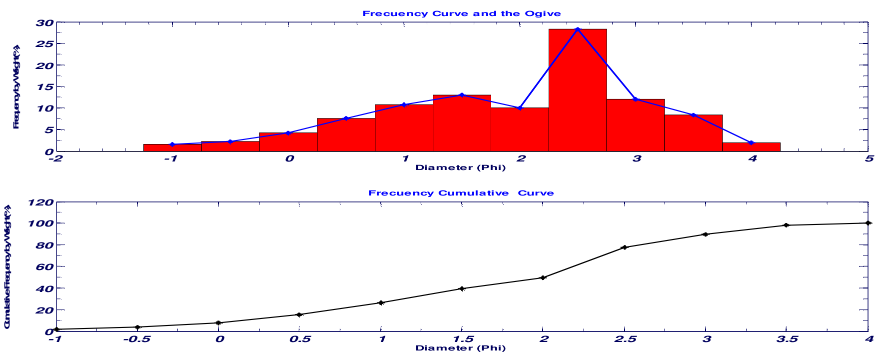

Fig8 : The plot of sediments particle size at Unilag station against phi

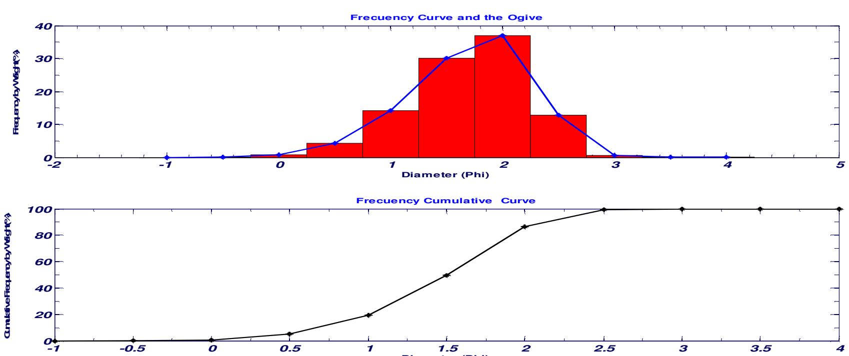

Fig9 : The plot of sediments particle size at Atlas cove station against phi

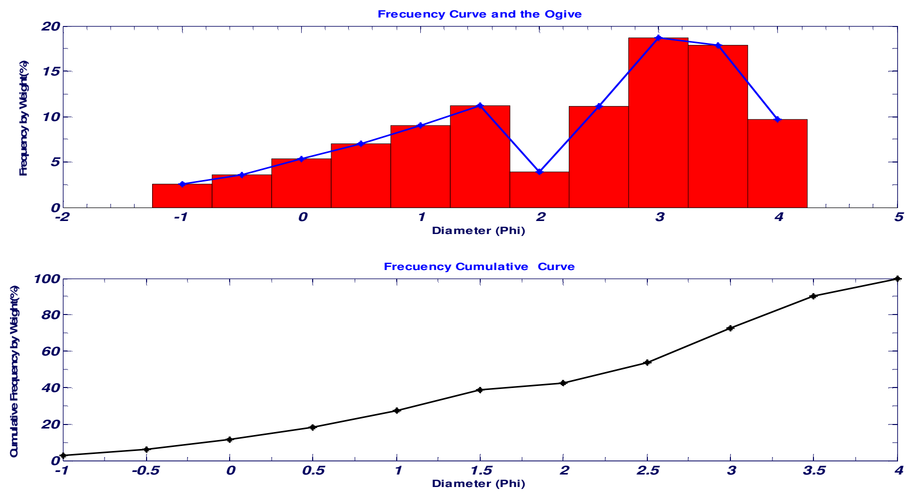

Fig10 : The plot of sediments particle size at Ijora stations against phi

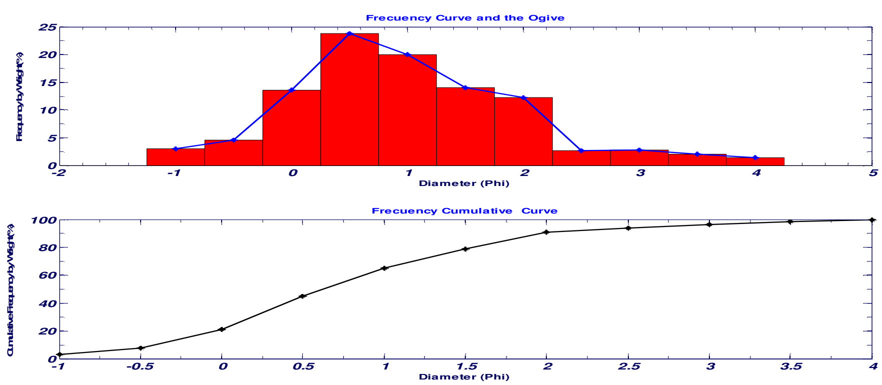

Fig11 : The plot of sediments particle size at Ikorodu port stations against phi

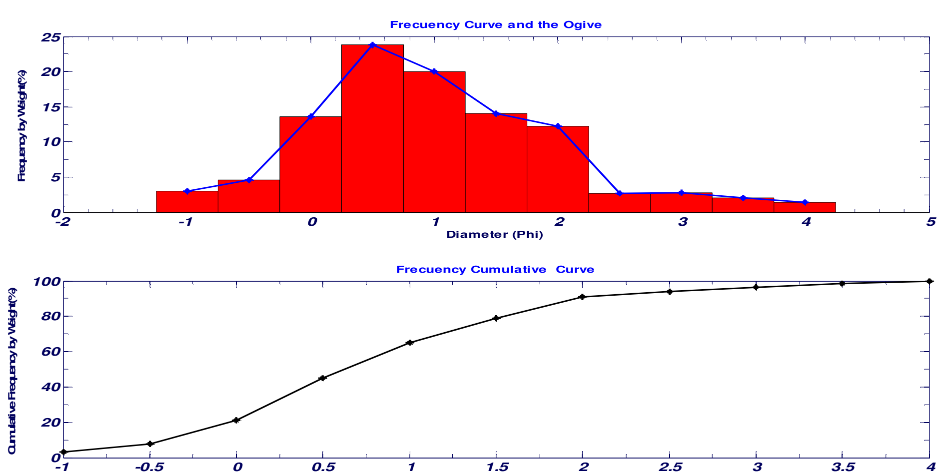

Fig12 : A: The plot of sediments particle size at Apapa port stations against phi

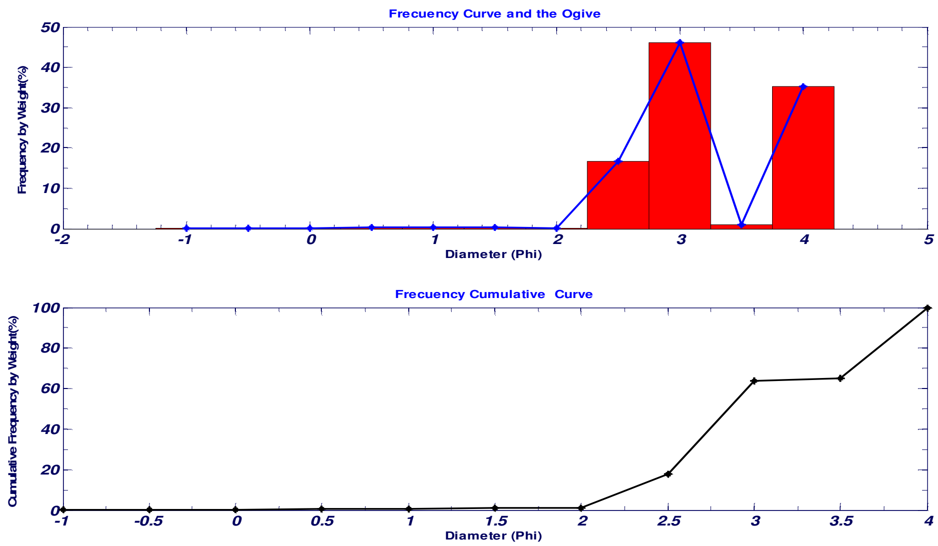

Fig 12: B: The plot of sediments particle size at Ibeshe stations against phi

3.5.2 Pearson correlation analysis

All the metal pairs in the sediments exhibit positive relations and some of them were significant at the 95% confidence levels. The Pearson correlation coefficient shows the existence of similar geochemical association for these metals; Fe–Mn, Fe–Cr-Zn, Fe–Ni-Pb-Zn and Pb–Zn-Cu pairs. Pb and Zn are significantly positively correlated with each other, which may suggest a common pollution sources or a similar geochemical behaviour for these metals [23], this is also in agreement with the enrichment factor geochemical benchmarks of the Lagos Lagoon sediments [24]. Fe-Cr and Fe-Mn are significantly correlated; this correlation may suggest a similar terrigenous source or a result of similar mechanisms of transport and accumulation within the sediments. They are Ferro-allied metals and are associated with mafic-ultramafic rock provenance [25]. However, Cr-Zn and Fe-Ni-Pb-Zn are none significantly correlated. Positive correlation between all metal studied with Fe confirmed that Fe has a higher affinity with most elements.

Table1 :Pearson Correlation coefficient result Table

R	Ni	Mn	Pb	Zn	Fe	Cu	Cr
Ni	1						
Mn	0.4804	1					

Pb	0.6107	0.0891	1				
Zn	0.5484	0.4539	0.4266	1			
Fe	0.5489	0.884	0.2974	0.5229	1		
Cu	0.7651	0.2175	0.8038	0.755	0.4363	1	
Cr	0.1302	0.5021	0.2536	0.5603	0.6364	0.3878	1

Table 2 : Statistical Test at 5% significant figure (P-value)

P-VAL	**Ni**	**Mn**	**Pb**	**Zn**	**Fe**	**Cu**	**Cr**
Ni	1						
Mn	0.1139	1					
Pb	0.0349	0.783	1				
Zn	0.0649	0.1383	0.1666	1			
Fe	0.0645	0.0001	0.3479	0.0811	1		
Cu	0.0037	0.497	0.0016	0.0045	0.1562	1	
Cr	0.6868	0.0962	0.4265	0.0581	0.0261	0.2129	1

Table3: Percentage of data utilized (R^2) IN PERCENTAGE

R^2	**Ni**	**Mn**	**Pb**	**Zn**	**Fe**	**Cu**	**Cr**
Ni	1						
Mn	0.2308	1					
Pb	0.3729	0.0079	1				
Zn	0.3007	0.206	0.182	1			
Fe	0.3013	0.7815	0.0884	0.2734	1		
Cu	0.5855	0.0473	0.6461	0.5701	0.1904	1	
Cr	0.0169	0.2521	0.0643	0.3139	0.405	0.1504	1

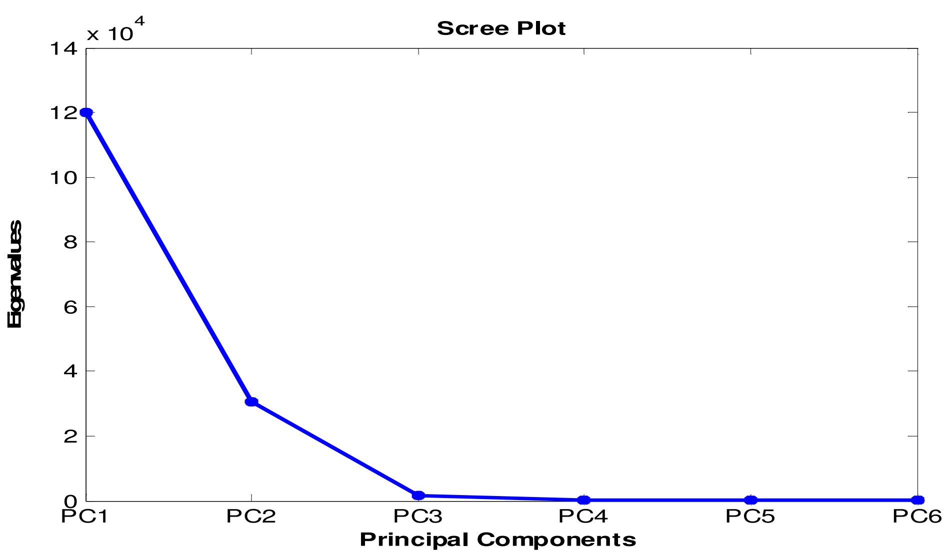

Figure 13: Scree plot for the principal component1 and 2 loading

Table4: Summary of Principal component analysis of some trace metals in Lagos Lagoon sediments

	PC1	PC2
Ni	0.009	0.01
Mn	**0.94**	-0.33
Pb	0.005	0.031
Zn	0.33	**0.937**
Cu	0.003	0.043
Cr	0.08	0.093
Eigen value	12.01	3.063
% variance	78.71	20.07
Cumulative %	78.71	98.77

Bold values: loadings > 0.5

All the Eigen values constitutes less than 10% of the total variance were eliminated

3.5.3 Principal component analysis

The statistical analysis revealed that the trace metals can be grouped into two identities. The first group identity is Zn and this account for 79% of the total variance of the variables with Eigen value of 12.05. This metal is believed to be majorly contributed from anthropogenic source (industrial effluents from electroplating, paints, fertilizers, vehicular emissions and others); the enrichment factor, contamination factor and Pearson correlation relationship corroborate this (figure 3, 5 and 6).The second identity Mn account for approximately 21% of the total variance with an Eigen value of 3.06. Mn is believed to have been contributed to the sediments of the Lagos Lagoon from washed down automobile aerosols, worn-out vulcanized products such as tyres, brake linings as well as expended paints and paint products. It is used as additives and alloys in chemical and metallurgical industries and is believed to have been contributed to the sediments from the leaching of industrial, chemical and domestic wastes. This is also in agreement with the enrichment factor, contamination factor and Pearson correlation relationship.

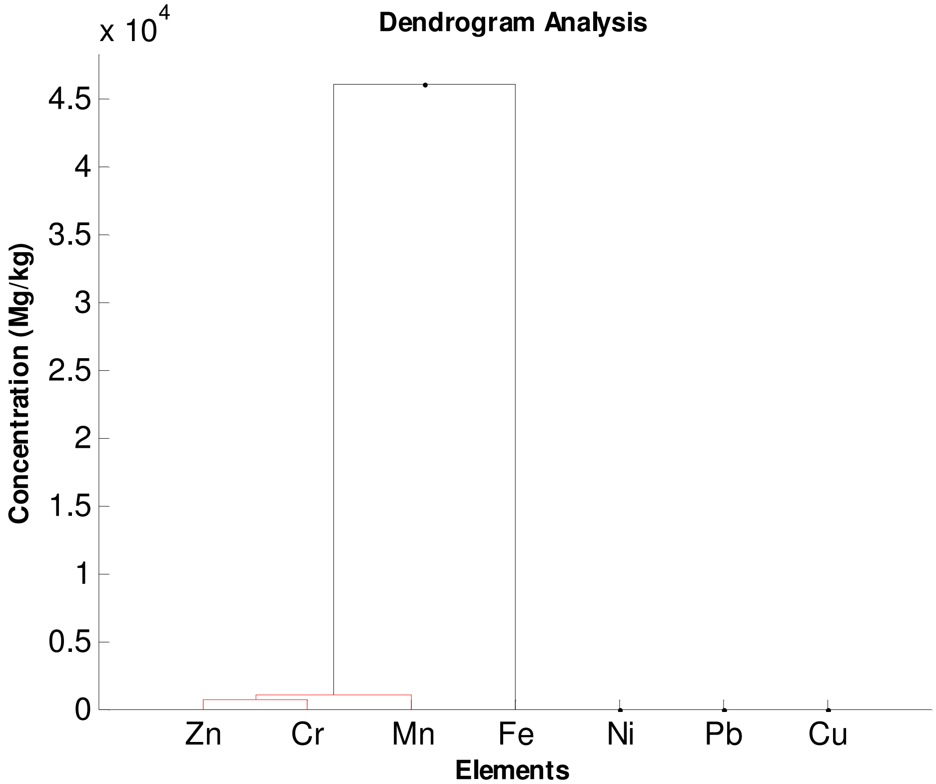

Figure 14: Cluster Relationship of the Metals

3.5.4 Hierarchical Cluster Analysis (HCA)

This is the most important cluster analysis method most commonly used for environmental analysis. It identifies groups of samples according to their similarities. The results obtained were presented in a two-dimensional plot called dendrogram. The dendrogram based on the linear pair coefficient of correlation between the variables indicate different clusters for the bottom sediments of Lagos Lagoon (Fig.14). Three groups were distinguished in the dendrogram, performed using the Ward method, which used the squared Euclidean distance as a similarity measure. The domination of Zn, Cr, Mn with Fe indicates their association with the Fe oxides. These corroborate the significant geochemical relationship as described in the Pearson correlation analysis (table 1-3).

4 CONCLUSION

The study highlights the; importance of evaluating environmental quality and trace metals' contamination in sediments, spatial elemental distributions using Iron to normalize, trace metals vis-à-vis background levels utilization. Evidently, trace metal distributions in the Lagos Lagoon sediments have been affected by various changes such as; chemical alterations, crustal weathering and post-depositional sediments mixing. Moreover, it is observed that; Zn, Mn and Pb distributions are significantly enriched from anthropogenic source, mostly prevalent at; Ijora, Iddo, Okobaba, Majidun and Egbin sediments. This enrichment might not be unconnected to the prevalent, domestic and industrial effluents from the adjourning communities around the stations. On the basis of the calculated contamination risk assessment; it can be affirmed that the analysed sediments of the Lagos Lagoon stations are; unpolluted to moderately polluted by trace metals (Pb, ,Zn, Cu Cr, Ni, Mn and Fe),moderately contaminated by Zn (especially at Ijora, Iddo, Okobaba, Majidun and Egbin stations). Nonetheless, the integrated toxicity assessment of the study area (PLI and DC) falls within background geochemical benchmarks, therefore exhibited a synthetic low toxic effect on the aquatic ecosystem.

The pearson correlation coefficient exhibit positive relations in all the metals, the trace metals geochemical associations suggest a similar; terrigenous source or mechanisms of transport and accumulation within the sediments. Hierarchical Cluster Analysis (HCA), Pearson correlation analysis and the Principal component analysis all corroborate zinc and manganese as an anthropogenically enriched metals and Ni, Fe and Cu as a background metals in the Lagos Lagoon sediments.Cr however,exhibit a mix source of deposition in the Lagos Lagoon sediments.

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