

GeoEnvironmental Implications of Heavy Metals Distribution in Parts of Lagos Lagoon, Southern Nigeria.

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Abstract: The study investigated the level of heavy metals in surface waters and sediments in the Lagos Lagoon, Lagos State. Water and sediment samples were collected in sterile plastic containers respectively from 8 sampling locations inclusive of a control. The samples were treated and digested and analyzed using the Atomic Absorption Spectrophotometer (AAS). The *t*-test, single factor ANOVA, post-hoc means plot and Principal Components Analysis (PCA) were used to analyze data. Cu, Zn, Cd, Mn, Ni, Cr and Fe varied as follows: 1.97-5.60(3.07) mg/L in water columns and 9.9-527.35 ppm in sediments, 1.58 – 6.99(3.03) mg/L in water columns and 37.69 – 875.64 ppm, 0.18–0.93 (0.62)mg/L and 0.37–11.46 ppm, 4.48–11.28 (8.51) mg/L and 184.95–547.45ppm, 9.83-20.50 (14.54)mg/L and 46.30–551.00ppm, 4.93–44.70 (23.39) mg/L and 105.17-227.77ppm and 31.60–86.17 (1.08) mg/L and 454.27-768.23ppm respectively. The pH, electrical conductivity, water temperature, salinity, total dissolved solids and dissolved oxygen varied as follows: 7.85- 8.39 (8.05), 15.60-28.20 (21.89 μ S/cm) and 28.00-30.00(29.13^oC), 8.10-14.50 (11.28^o/₀₀), 9.36 – 16.92 (13.49mg/L) and 4.40 – 7.00 (5.78mg/L) in water samples respectively. The results were compared with WHO and NESRA standards and were found to be above the limits. Results indicate lithological origin for the heavy metal presence and possible transportation of heavy metal species from the industries and domestic wastes and deposition in sediments of the proximal Lagos Lagoon.

Keywords: Surface water, Sediment, Physiochemical, Lagoon, Heavy metals, Industries, Wastes, Pollution.

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I. Introduction

Lagos city is comprised of the islands of Lagos and Victoria and the outer Lagos Mainland and parts of Lekki Peninsula (Fig. 2). Lagos is Nigeria's largest city by population; it is Nigeria's economic center. Industries in the area include railway workshop, motor vehicle assembly, food processing, and the manufacture of metal products, textiles, beverages, chemicals, pharmaceuticals, soap, and furniture. The Lagoon receives over 80% of the land-derived run-offs laden with various types of wastes and it lies within longitudes 6°25'N and 6°43'N and latitudes 3°22'E and 3°40'E [1].

II. Geology of Study Area

The Benin basin extends almost from Accra in Ghana, through the Republics of Togo and Benin to Nigeria where it separated from the Niger- Delta basin by Okitipupa ridge at the hinge of the Benin flank. The bottom of the sedimentary basin in the Benin basin consists of unfossiliferous sandstones and gravels weathered from the underlying Precambrian basement. The stratigraphy of the Benin Basin is comprised of marine shale, sandstones and limestone of Albian to Santonian ages (Fig. 1). The surface geology is made up of the Benin Formation (Miocene to Recent) and the recent littoral alluvial deposits. The Benin Formation consists of thick bodies of yellowish (ferruginous) and white sands [4]. It is friable, poorly sorted with intercalation of shale, clay lenses and sandy clay with lignite.

The Formation is overlain in many places by considerable thickness of red earth composed of iron-stained regolith formed by weathering and ferruginization of the rock [5]. The Ise Formation, the oldest, unconformable overlies the basement complex and consists of conglomerates and sandstones at base and in turn overlain by coarse to medium grained sands with inter-bedded kaolinite. Overlying the Ise Formation is the Afowo Formation. The Araromi Formation overlies the Afowo Formation and is the youngest Cretaceous sediment in the eastern Dahomey basin [10]. It is composed of fine to medium grained sandstone overlain by shale, siltstone with inter-bedded limestone, marl and lignite. The Ewekoro Formation, an extensive limestone body, overlies the Araromi Formation. The Ewekoro Formation is overlain by the Akinbo Formation, which is

made up of shale and clayey sequence [11]. Overlying the Akinbo Formation is Oshosun Formation which consists of greenish grey or beige clay and shale with inter-beds of sandstones. The Ilaro Formation overlies conformably on the Oshosun Formation and consists of massive, yellowish poorly, consolidated, cross-bedded sandstones. The Quaternary sequence in the eastern Dahomey basin is the Coastal Plain Sands and recent littoral alluvium [12], and consists of poorly sorted sands with lenses of clays. The age is from Oligocene to Recent.



Fig.1. Geology Map of Study Area

The sampling points are spread over 8 locations along the Lagos Lagoon with a control point in the middle of the Lagoon (Fig2.2).

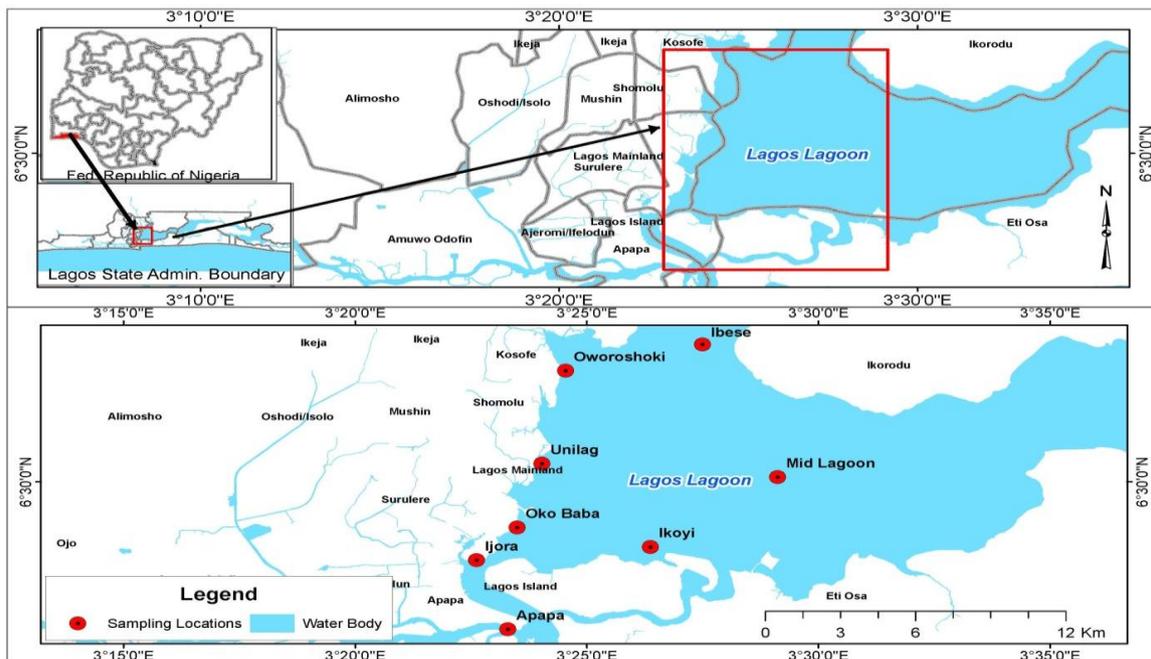


Fig. 2. Location Map of Study Area

III. Materials and Methods

3.1 Water Sample collection and Analysis

Water samples were collected randomly using a water sampling device collected below the water surface and this was done to ensure the water was collected in its natural state which were stored in sterilized plastic containers and acidified using concentrated hydrochloric acid so as to ensure that the potential respective ions remain in solution pending analysis. The sampling points were appropriately located using Global Positioning System (GPS).

The Horiba equipment was used to measure the physico-chemistry in situ. The physicochemical parameters measured in field include Temperature, Hydrogen Index (pH), Electrical Conductivity, Total Dissolve Solids (TDS), Dissolve Oxygen (DO) and Salinity while the parameters measured in the laboratory are the heavy metals such as Copper, Cadmium, Chromium, Nickel, Zinc, Manganese and Iron. The water samples were subsequently analyzed for their metal contents using Atomic Adsorption Spectrophotometer (AAS). The API-RP45 flame atomization method was used.

3.2 Sediment sample collection and Analysis

Sample bags were used to collect 6 sediment samples with the aid of a Grab device ranging from depths of 2m-12m collected along the sea port, thermal plant and the Lagoon center. There were difficulties encountered during this operation as water depths made it difficult to collect sediment samples in all the 8 sampling points. They were subsequently air-dried for three weeks under room temperature. The dried samples were disaggregated and sieved to remove materials such as wastes, animal shells and plant roots. The sieved sediments were subsequently leached with aqua regia. To achieve digestion, a 0.5g of the sieved samples was weighed into the digestion flask and digested with aqua regia (0.6ml concentrated HNO₃ and 1.8ml HCl) for two hours at 95°C. The samples were cooled and then diluted to 10ml with de-ionized water and homogenized before they were analyzed for their elemental constituents, using AAS.

3.3 Metal Speciation

Metal speciation greatly determines the behavior and toxicity of metals in the environment. Speciation refers to the occurrence of a metal in a variety of chemical forms.

These forms may include free metal ions, metal complexes dissolved in solution and sorbed on solid surfaces, and metal species that have been co precipitated in major metal solids or that occur in their own solids. The speciation of a metal affects not only its toxicity but also its volatilization, photolysis, sorption, atmospheric deposition, acid/base equilibrium, polymerization, complexation, electron-transfer reactions, solubility and precipitation equilibrium, microbial transformations, and diffusivity [13]. Speciation concerns the identification and quantization of specific forms of an element, e.g. the analysis of edible fish tissue to determine the concentrations of methyl-mercury and inorganic mercury present. As different forms of an element may exhibit differing toxicities and mobilities in the environment, it is clearly of importance to be able to distinguish between the individual species present in a particular sample. Conceptually, the solid material can be partitioned into specific fractions which can be extracted selectively by using appropriate reagents; considering the similarities between sediments and soils, extraction procedures can be borrowed or adapted from the methods of soil chemical analysis (1). Several experimental procedures, varying in manipulative complexity, have recently been proposed for determining the speciation of particulate trace metals. These procedures can be grouped into (i) methods designed to effect the separation between residual and non-residual metals only, and

(ii) More elaborate methods making use of sequential extractions. The former methods normally involve a single extraction and offer a better contrast between anomalous and background samples than does the determination of the total metal concentration. Despite their rapidity and relative simplicity, these techniques suffer from the difficulty of finding a single reagent effective in dissolving quantitatively the non-residual forms of metal without attacking the detrital forms.

3.4 Statistical Analysis

The MS Excel 2007 and SPSS[®] software were used in the analyses of data. Descriptive statistics was used to compute mean, standard error, minimum, maximum as well as range of data sets. The test of homogeneity in mean variance of accumulations across the sampling locations was conducted with the single factor analysis of variance (ANOVA). Post-hoc structures of means were detected with means plots.

IV. Results and Discussion

From the levels of the physicochemical parameters measured in the Lagos Lagoon across the sampling locations (Table 1), wide variations were recorded in Iron(Fe) ions (range =54.57 mg/L), Nickel (Ni) ions (range =10.67 mg/L), Chromium (Cr) ions (range = 39.77 mg/L) and Electrical Conductivity (range = 12.60 µS/cm). Salinity varied from 8.10-14.50 (11.28 ± 0.87 ‰), Dissolved oxygen (DO) varied

from 4.40–7.00 (5.78 ± 0.33 mg/L) and Total Dissolved Solids (TDS) varied from 9.36–16.92 (13.49 ± 0.91 mg/L). Copper (Cu) ions, Zn ions and Cadmium (Cd) ions varied from 1.97- 5.60 (3.07 ± 0.40 mg/L), 1.58 – 6.99 (3.03 ± 0.89 mg/L) and 0.18 – 0.93 (0.62 ± 0.10 mg/L) respectively. The pH limit is 6.5 – 8.5, Cu limit is 0.001mg/L and Zn limit is 0.01mg/L while Cd limit is 0.005 mg/L, Fe limit is 0.05 mg/L, Ni limit is 0.01mg/L and Cr⁶⁺ limit is 0.001 mg/L; temperature standard except in designated thermal mixing zones, temperature increase by a 7-Day Average of the Daily Maximum temperature (7-DADMax) of surface waters shall not be more than 0.3°C above background conditions [14]. The standard [15] for surface water physicochemical parameters for Cu 2.0 mg/L, Zn 3.0 mg/L, Cd 0.003 mg/L, Ni 0.02 mg/L, Cr 0.05 mg/L and Mn 0.5 mg/L.

The physicochemical parameters of the water samples exceed both the NESREA and WHO standards for surface and groundwater quality. Spatial variations were observed in the levels of the physicochemical parameters measured in the sampling locations. Minimum levels of Cu ions (1.967 mg/L), Zn ions (1.581 mg/L) and Mn ions (4.483 mg/L) were recorded at the Oworonshoki, Ikoyi and Okobaba locations respectively (Fig 3). Spatial variations in levels of Cd, Ni and Cr across the study area is shown in Fig. 4, while that of pH, Electrical Conductivity and Temperature is shown in Fig 5.

Table 1. Descriptive Statistics of the physicochemical parameters of water samples of the Lagos Lagoon.

Parameters	Minimum	Maximum	Range	Mean	SE	NESRA	WHO
pH	7.85	8.39	0.54	8.05	0.06	6.5-8.5	N/G
EC (µs/cm)	15.60	28.20	12.60	21.89	1.68	N/A	N/G
Temp(°C)	20.0	30.0	2.0	29.13	0.26	N/A	N/G
Salinity(‰)	8.10	14.50	6.40	11.28	0.87	N/A	N/G
DO(mg/l)	4.40	7.00	2.69	5.78	0.33	≥ 6.0	N/G
TDS(mg/l)	9.36	16.92	7.56	13.49	0.91	N/A	N/G
Cu(mg/l)	1.97	5.60	3.63	3.07	0.40	0.001	2.0
Zn(mg/l)	1.58	6.99	5.42	3.03	0.690	0.01	3.0
Cd(mg/l)	0.18	0.93	0.75	0.62	0.100	0.005	0.003
Fe(mg/l)	31.60	86.17	54.57	60.24	6.820	0.05	0.05
Mn(mg/l)	4.48	6.79	8.51	0.86	0.312	N/A	0.5
Ni(mg/l)	19.83	20.50	10.67	14.54	1.41	0.01	0.02
Cr(mg/l)	4.93	44.70	39.77	23.39	4.74	0.001	0.05

SE = Standard Error of Mean, DO= Dissolved Oxygen, TDS= Total Dissolved Solids, N/A= Not Available, N/G = No Guidelines, EC = Electrical Conductivity

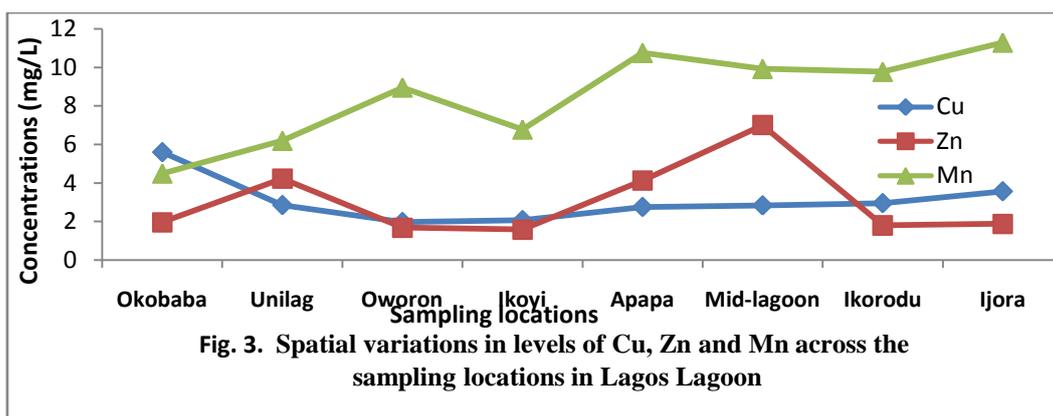


Fig. 3. Spatial variations in levels of Cu, Zn and Mn across the sampling locations in Lagos Lagoon

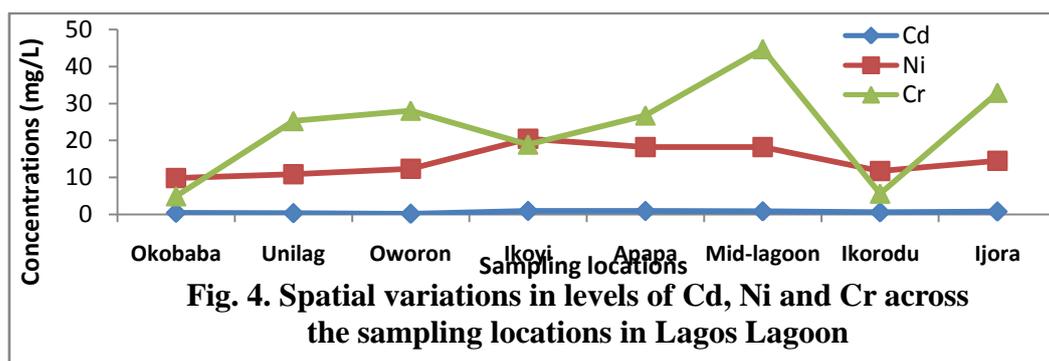


Fig. 4. Spatial variations in levels of Cd, Ni and Cr across the sampling locations in Lagos Lagoon

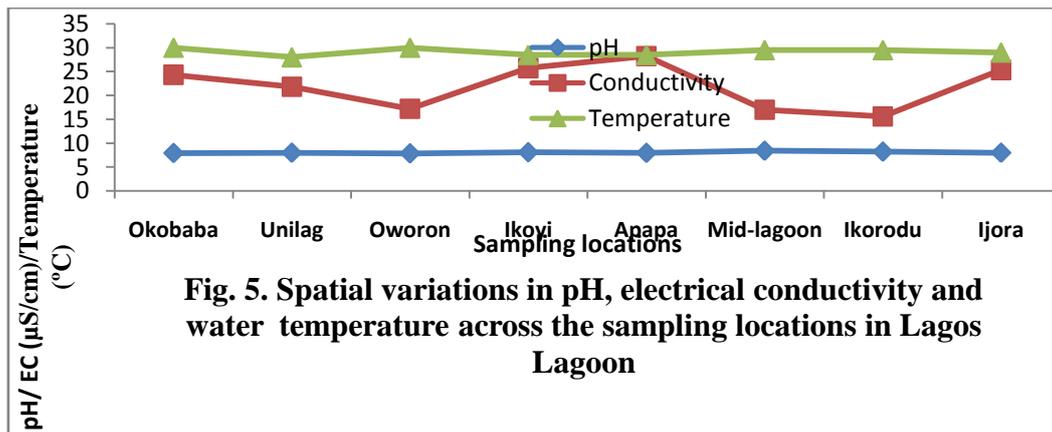


Fig. 5. Spatial variations in pH, electrical conductivity and water temperature across the sampling locations in Lagos Lagoon

4.1. Relationship between Heavy metals Concentration presence in water Column and sediment samples

Spatial variations were observed in the levels of heavy metal concentration of sediments samples and water samples measured in the sampling locations. Minimum concentration levels of Cu ions (9.3 ppm) and Fe (454.3 ppm) in sediments samples were recorded at the Okobaba and Apapa locations respectively while the minimum levels of Cu ions (1.967 mg/L) and Fe ions (45.56 mg/L) in water samples were recorded at the Oworonshoki and Oworonshoki sampling locations respectively (Fig. 6). However their maximum concentrations in sediments samples of 527.3ppm and 768.2 ppm were recorded at the Mid Lagoon and Mid Lagoon sampling locations respectively while the maximum concentrations of water samples are 5.60(mg/L) and 86.17(mg/L) were recorded at Okobaba and Apapa sampling locations respectively. Minimum concentration levels of Cd ions 0.367 ppm and Cr ions 105.2 ppm in sediment samples were recorded at the Unilag and Okobaba locations respectively (Fig. 7).

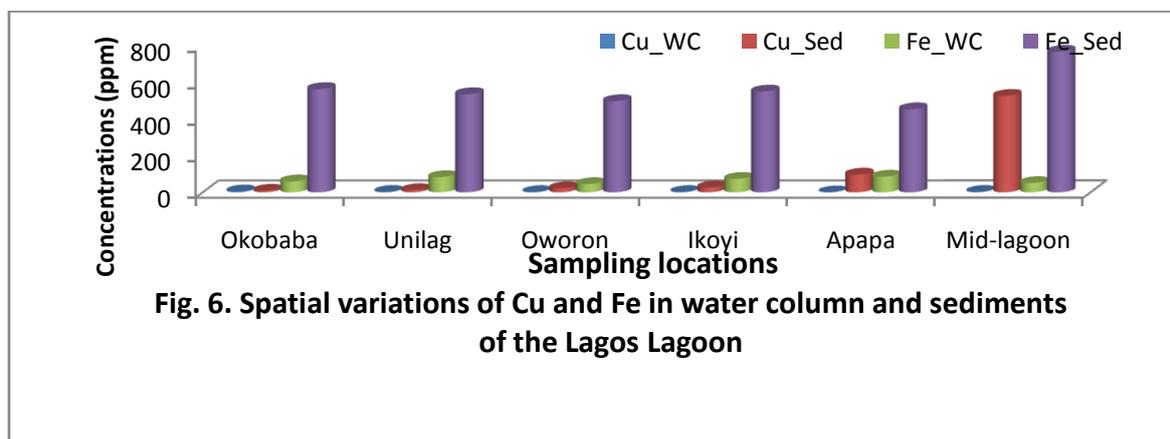


Fig. 6. Spatial variations of Cu and Fe in water column and sediments of the Lagos Lagoon

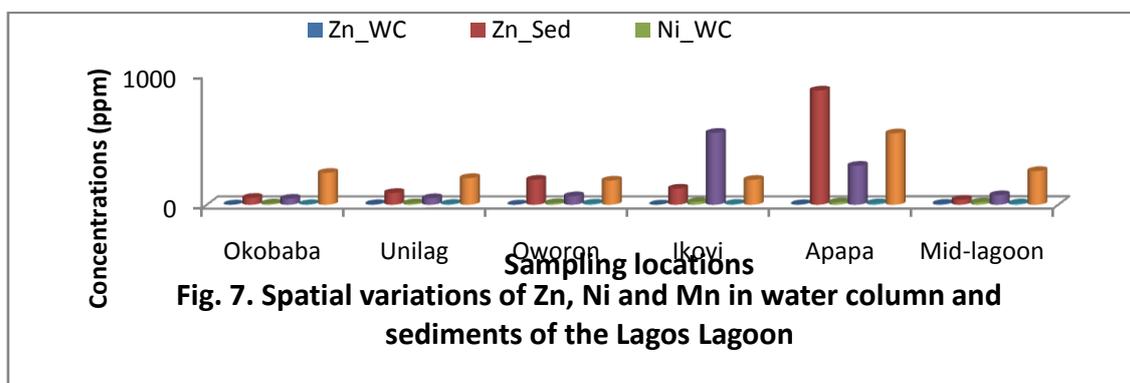


Fig. 7. Spatial variations of Zn, Ni and Mn in water column and sediments of the Lagos Lagoon

4.2. Interactions of the water column samples and sediment samples

The water column and sediment samples measured showed a significant Pearson correlation with each other. At P< 0.05, Cr ions from water column sample (r=0.890) correlated with Cr ions from sediment

sample (Table 2). This phenomenon explains that the sediment is the ultimate depository for heavy metals introduced into the water body.

Table 2. Interactions of the water column samples and sediments samples

	Cu Sed	Zn Sed	Cd Sed	Fe Sed	Mn Sed	Ni Sed	Cr Sed
Cu	-0.108	-0.201	-0.116	0.109	0.041	-0.416	-0.359
Zn	0.858*	0.052	0.841*	0.667	0.295	-0.316	0.862*
Cd	0.432	0.392	0.664	0.242	0.511	0.715	0.344
Fe	-0.369	0.531	-0.150	-0.485	0.505	0.442	-0.251
Mn	0.536	0.612	0.623	0.069	0.580	0.106	0.497
Ni	0.439	0.340	0.618	0.214	0.338	0.776	0.439
Cr	0.789	0.067	0.728	0.525	-0.139	0.109	0.890*

* = Significant at P<0.05, Sed= Sediment.

4.3. Variation of heavy metal fractions in sediments samples

The Cu ions were mostly abundant in Residual or Inert fraction in sampling locations Ikoyi (70%), Oworonshoki (49%), Apapa (78%) and Mid Lagoon (70%) while bound to carbonates fraction at Okobaba (39%) and bound to organic matter and Sulphide at Unilag (26%) were recorded at sampling locations respectively. The Cd ions were abundant in bound to carbonates fraction in sampling locations at Okobaba (35%), Unilag (40%) and Ikoyi (32%) while Apapa (34%) and Mid Lagoon (36%) recorded abundance in Residual/Inert fraction respectively. Zn ions were mostly abundant in bound to Fe and Mn oxide fraction in sampling locations Okobaba (43%), Unilag (45%), Oworonshoki (41%) and Ikoyi (61%) respectively. The record shows bound to organic matter at Apapa (37%) and Exchangeable fraction (37%) respectively.

Fe ions were mostly abundant in bound to Fe and Mn fraction in sampling locations Okobaba (34%), Unilag (28%), Oworonshoki (31%), Ikoyi (28%) and Apapa (30%) respectively. Mid Lagoon (55%) recorded abundance in Residual/Inert fraction. Ni ions were abundant in bound to carbonates fractions in sampling locations Okobaba (36%) and Unilag (42%) while Residual/Inert fractions were abundant in Oworonshoki (31%) and Mid Lagoon (43%). The record at Apapa (49%) shows bound to organic matter and Sulphide being abundant. Mn ions were mostly abundant in Residual/Inert fractions in locations Okobaba (64%), Oworonshoki (30%), Ikoyi (53%) and Apapa (47%) respectively while exchangeable fraction was recorded for Unilag (50%) and bound to organic matter and Sulphide was recorded for Mid Lagoon (41%). Cr ions were abundant in Residual/Inert fraction at sampling locations Okobaba (33%), Unilag (22%) and Apapa (26%) while bound to organic matter and Sulphide was recorded for Mid Lagoon (77%). The sampling location at Oworonshoki (24%) recorded bound to Fe and Mn oxide.

4.4 Principal Component Analysis (PCA)

The physicochemical parameters which were subjected to the PCA procedure revealed high initial and extraction communalities; indicating that the extracted components represented the variables well. The first four Principal Components (PCs) formed the extraction solution, with a cumulative percentage variability of about 88.69% in the original 13 variables (Table 3). This thus reduces the complexity of the data set using these components with only about 11.31% loss of information. The rotation maintained the cumulative percentage of variation explained by the extracted component (Table 4). The extracted components are on the steep slope, while the component on the shallow slope contributed little (11.31%) to the solution. The last big drop occurred between the fourth and fifth components. The first component (PC 1) was most highly correlated with salinity (0.958) and also had high loadings for Cd ions (0.809), Ni ions (0.590), electrical conductivity (0.859) and Total Dissolved Solids (TDS) (0.911). PC 2 was most highly correlated with Zn ions (0.934) and also had high loadings for Cr ions (0.569), pH (0.816) and Dissolved oxygen (DO) (0.758). However PC 3 was mostly high correlated with Fe ions (0.853) also had high negative loading for water temperature (-0.794) and positive loading for DO (0.528). PC 4 was most highly correlated with Cu ions (-0.863) and also had high loadings for Mn ions (0.774), Ni ions (0.599) and Cr ions (0.513). The component plot in rotated space revealed that the components were highly skewed; with all closely related on one side of the plot.

Table 3. Extraction Sums of Squared Loading of the Physicochemical Parameters of the Lagos Lagoon

Component	Total	% of Variance	Cumulative %
1	5.211	40.081	40.081
2	3.546	27.278	67.359
3	1.528	11.757	79.116
4	1.244	9.572	88.688

Table 4. Rotation Sums of Squared Loading of the Physicochemical Parameters of the Lagos Lagoon.

Component	Total	% of Variance	Cumulative %
1	3.910	30.081	30.081
2	2.862	22.018	52.098
3	2.426	18.658	70.756
4	2.331	17.931	88.688

Heavy metals have been used as indices of pollution because of their high toxicity to human and aquatic lives, [16-20] have linked the high concentrations of heavy metals in the aquatic ecosystems with effluents from industries, refuses and sewage. Fe, Ni and Cr in surface water samples of this study had wide variations. This could be attributed to mainly geologic processes and anthropological activities such as industrial and manufacturing activities in the area and some authors have associated certain heavy metals with printing and dyeing [21-24].

However, the narrow variations observed in the other metals in surface water samples could be linked to the dilution effects (heavy metal concentration 'diluted during period of storm causing flooding). Depending on the severity of the flood, during the rainy season, the dilution effect will be greater than the re-suspension of metals from sediment resulting from the flood which would normally increase metal concentration [25]. In sediment, Zn, Fe and Mn showed wide variations, this could be associated with the repositioning role of aquatic sediments, which are often linked with acidic pH that creates greater bioavailability of the heavy metals. Additionally, the quasi anaerobic conditions in the bottom zone that tends to create intensified heavy metal retention could explain these elevations [26].

Heavy metals in surface water samples were expected to be lower than their level in the sediment samples throughout the locations. This is because sediments constitute the ultimate depository for heavy element introduced into the water body [27-28]. The observed spatial variation in levels of the parameters indicates significant difference in the water sample. The presence of Fe in higher concentrations in the water sample at the control location possibly indicate a geologic origin rather than the disposal of domestic and industrial waste by inhabitants of the catchment (anthropogenic origin), which results to high concentration of these metals as rain water washes them into surface water during hydrograph events [29]. [28] made different observation in their research on factors in the migration of heavy metals in the Otamiri River system. Also, in the sediment, Fe one of the essential heavy metals [31] recorded high value in control location. This metal plays a vital role in many physiological processes, but has a toxic effect when present in higher concentration. Ni and Cr were mostly responsible for the observed significant difference in concentrations of the heavy metals in surface water samples, indicating that these metals could be associated with the operations of manufacturing and industrial activities in the vicinity [32] have also associated heavy metals with industrial activities in Southeast Regional Park in Madrid, Spain. However, Fe, Zn and Mn were mostly responsible for the observed difference in the sediment sample. This however makes the heavy metal the major pollutant species in this segment of the environment. The 1st four principal components which accounted for 88.69% variability in the original 13 parameters formed the PCA extraction solution which has high loadings for the metals factor in water samples. Cr ions in water sample had significant correlation with Cr ions in sediments; this confirms the repository role of sediments in pollutants loading in aquatic environments. This repository role has also been reported by [27-28] in the Otamiri River in Owerri, south eastern Nigeria. The significant positive correlation between the metals across the sampling locations in both surface water and sediment samples obviously imply a common source and sink in the sediment of these pollutants [30]. It could also indicate the impacts of industries and domestic wastes rain storm run-offs and their contributions into the proximal Lagos Lagoon. The observed significant correlation in levels of heavy metals between the surface water and sediment samples obviously indicates high relationship in their lithological origin in this study area. Generally from the result, the heavy metals were mostly abundant in the Residual or Inert fraction implying low mobility and bioavailability [31]. The high concentrations of Fe in the sediments have no identifiable point source discharge rather than lithological or crustal origin [32]. The heavy metals analyzed in sediment samples (Cu, Mn, Cd, and Ni) were mostly abundant in the Residual fraction. This agrees with [33] who reported that Cd, Fe, Mn, Ni and Pb were mostly associated with the Residual phase. The higher the metals present in this fraction, the lower the degree of pollution. Metals with anthropogenic origin are mainly extracted in the first steps of sequential extraction procedures while lithogenic metals are found in the last steps of the process corresponding to the residual fraction [34]. The heavy metals in the Lagos Lagoon, from the sequential extraction, were mostly lithogenic. The heavy metals Cd, Cu, Mn, Ni and Fe were highly abundant in the residual phase, implying that they were not derived from anthropogenic sources.

V. Conclusion And Recommendation

Various factors were at play in determining the input of heavy metals into the Lagos Lagoon. Anthropogenic activities in the area of study were possibly aided by flooding during the period of this study (wet season). High retention of the metals in sediment was also another important factor. The heavy metals variations in the water column and sediments were obviously related, as revealed by marked correlations. The speciation of heavy metals in the Lagos Lagoon showed that most of the heavy metals considered had high abundance in residual fraction which suggests geologic origin. This indicates that the metals were immobile and it also shows that the environment is not likely to be polluted by these metals. Cr in water sample correlated with Cr in sediment sample indicating that it could be easily released to the environment and could be of high toxicity in the environment.

This study revealed that the Lagos Lagoon is impacted most by geologic processes within the study area. The industrial activity appeared to alter the quality of the Lagos Lagoon especially at the sediment regions. Government agencies should monitor continuously the activities of industries and waste disposal companies with Lagos state with a mandate to regulate their waste disposal methods. The regulatory agencies should have regular check and evaluation of the Lagos Lagoon. The relationship between metal oxides and heavy metals occurrence should be studied further to develop the economic potential of the metal oxides in Lagos Lagoon in the future.

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