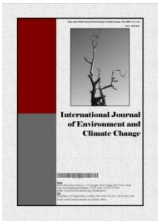

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Evaluation of the Pollution Status of Lagos Coastal Waters and Sediments, using Physicochemical Characteristics, Contamination Factor, Nemerow Pollution Index, Ecological Risk and Potential Ecological Risk Index

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Authors' contributions

This work was carried out in collaboration among all authors. Author GEA designed the Conceptualization and Methodology. Author OOO wrote the original draft preparation. Author SOP wrote the review and edited the paper. All authors read and approved the final manuscript.

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ABSTRACT

The heavy metals and physicochemical properties of Lagos coastal waters and sediments, Southwestern Nigeria were investigated in 5 stations (station 1-5), to determine their levels, distributions and pollution index. The observed ranges of physicochemical characteristics from the study area are: dissolved oxygen (DO): 2.15-11.3 mg/L; pH: 6-7.7; temperature (Temp): 28.05-29.25°C; biochemical oxygen demand (BOD): 1.6-110.1 mg/L; electrical conductivity (EC): 1.8-29.8 mS/cm; salinity (SAL): 0.02-2.05ppt; total dissolved solids (TDS): 211.8-1210.2 mg/L and total

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suspended solids (TSS): 12.13-117.95 mg/L. The analyzed physicochemical properties from all the stations are within the desired values for healthy marine ecosystems when compared with Federal ministry of environment (FMENV) Nigeria and World Health organization permissible limits (DO:>5 mg/L; pH:6.5-9; TEMP:<40°C; BOD: 50 mg/L; EC:900 mS/cm; TDS:1000mg/L and TSS:600 mg/L), with the exception of low DO at station 1 and station 5; and high BOD at; station 2 and station 3 respectively. The concentrations of heavy metals present in the water samples followed the sequence: Fe > Pb > Cu > Cr > Zn > Cd, and showed high values for Pb, Cd and Cr, relative to the standard permissible limits according to FMENV (Pb 0.001; Zn 50 mg/L; Cd < 0.0018; Cu 2-4 mg/L and Cr 0.02-2.0 mg/L). The calculated contamination factor (CF) in the sediment samples showed low-moderate contamination for the analyzed heavy metals (Cr, Zn, Cu and Pb), except for cadmium (Cd) that showed extremely severe contamination (CF > 6) values across the sampling stations. The calculated Nemerow pollution index (NPI) and ecological risk index (R_I) showed heavily polluted (NPI > 10) values and very high ecological risk (RI > 380) values at Apapa (location 1), Iddo (location 2) and Makoko (location 3). The potential ecological risk factor (Eir) confirmed Cd as the highest polluted heavy metals (Eir >320), with the greatest potential threat to the marine ecosystems in the Lagos coastal waters. The study highlights the impacts of anthropogenic pollutions on the coastal ecosystems and human health.

Keywords: Lagos coastal waters; sediments; hydrochemistry; heavy metals, ecological risk index; Southwest Nigeria.

1. INTRODUCTION

Point source anthropogenic pollutants from river discharge, atmospheric deposition, domestic and industrial waste effluents and shipping activities, has resulted to surface water pollution and devastating threat to aquatic biota (e.g., fish, crab and periwinkles) and human health [1]. Heavy metals are known to be one of the major inorganic pollution sources, with a significant negative impact on marine ecosystems [2,3]. They show increasing concentrations in sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds there-in [4,5]. They are considered a potential secondary water pollution source with changes in environmental conditions such as pH, redox potential, organic matter content and temperature [6,7]. Heavy metals are stable and persistent environmental contaminants because they are not biologically degraded like many organic pollutants; thus, they tend to accumulate, particularly in sediments in association with organic and inorganic matter [8]. Therefore, the analysis of heavy metals in sediments enables the detection of pollutants that might not be identified in water samples. Additionally, the dissolution and adsorption processes of heavy metals are influenced by several physicochemical parameters such as pH, dissolved oxygen, salinity, redox potential, organic and inorganic carbon contents and the presence of some anions and cations that can bind or co-precipitate the dissolved or suspended inorganic pollutants in the water phase [5]. The increasing needs to meet the food supply of growing population has put a lot of pressure on coastal and marine resources, therefore, the utilization of wastewater for the production of aquatic biota has created great harm to human through the food chain contamination [9,10].

Lagos Lagoon complex (Fig.1) is the largest Lagoon systems in the Gulf of Guinea coast, West Africa [11]. Over 85% of all industries are situated in Lagos metropolitan area, Southwest Nigeria [12]. In the Lagos Lagoon axis. There are reported proliferations of urban settlements that have led to the generation of industrial and domestic anthropogenic effluents which eventually find their way into the Lagos coastal waters as an ultimate sink [13].

This study aims to investigate the levels of pollution and potential ecological risk index in Lagos coastal waters using physicochemical parameters, heavy metals in surface water and sediment and calculated pollution index as an indicator.

2. MATERIALS AND METHODS

2.1 Study Area

Lagos Lagoon complex stretches from Cotonou in the Republic of Benin and extend to the fringes of the Niger Delta in Nigeria along its 257

km course [11] and empties into the Atlantic via Lagos Harbor. It lies between the longitude 3° 22' and 3° 40' E and latitude 6° 17' and 6° 28'. The study area has a typical tropical climate, which is marked by two prominent seasons. The rainy season extends generally from March to November with intermittent dry spells. This is the period when the south-westerly wind prevails. The dry season usually occurs from December and March when the area is under the influence of the northeasterly wind. The Lagoon is generally shallow with a depth of between 0.3 and 3.2m in most parts except for some dredged parts, notably in the Lagos Harbor, where depth is greater than 10m. Five sampling stations were selected along the Lagoon (Table 1) based on accessibility and proximity gradient from expected pollution sources. The locations were marked with the aid of Global Positioning System (GPS) coordinates and visual notes of permanent and semi-permanent structures were used in marking sampling locations.

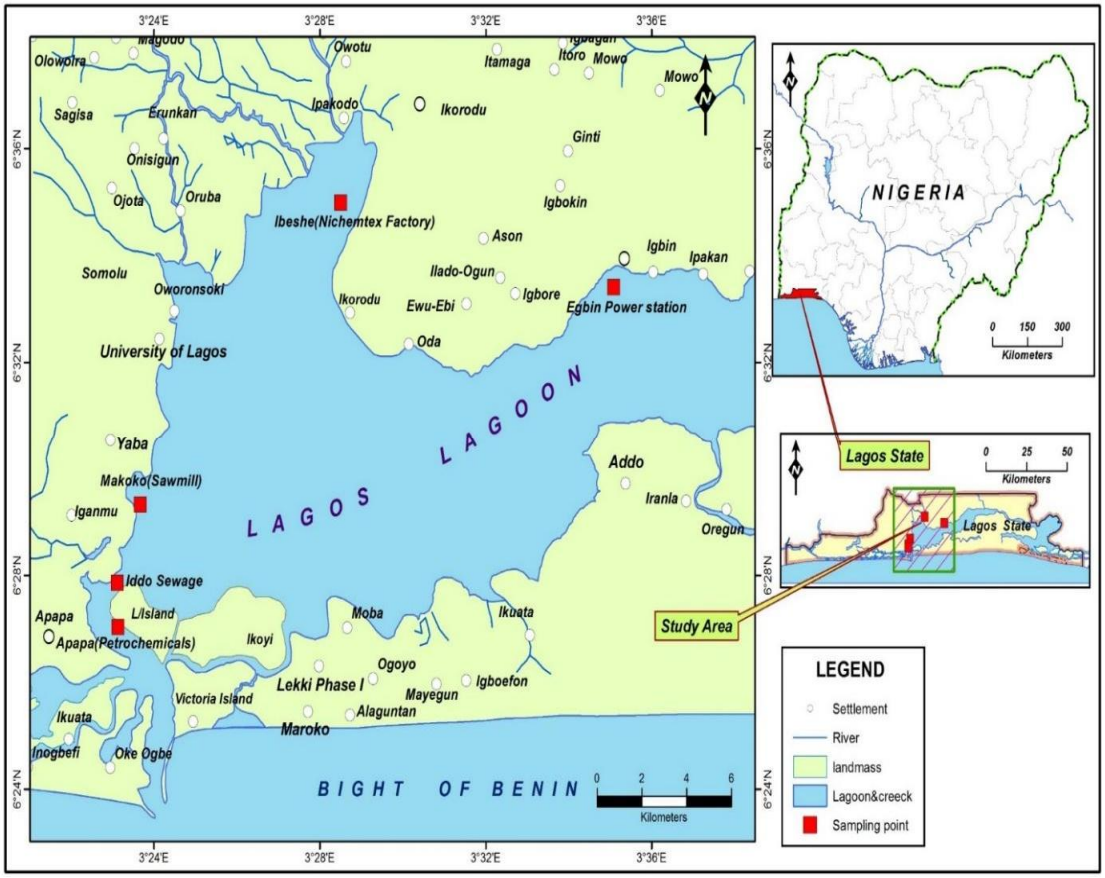

Fig. 1. Map showing sampling locations in Lagos lagoon

Table 1. The GPS locations of the study area

Stations	Name	Coordinates		Associated anthropogenic activities
1	Apapa	N06° 27' 02.3"	E003° 23' 07.7"	Dredging, oil spillages.
2	Iddo	N06° 28' 00.3"	E003° 23' 01.6"	Domestic sewage Discharges.
3	Makoko	N06° 28' 54.0"	E003° 23' 06.4"	Sewage dump, Biodegradable organic matter.
4	Ibese	N06° 34' 59.9"	E003° 28' 30.1"	Local dredging.
5	Egbin	N06° 33' 24.9"	E003° 35' 51.3"	Thermal pollution.

2.2 Collection and Analysis of Samples

2.2.1 Sample collection

Water and sediment samples were collected monthly at each study location for a period of six months (May to October, 2016), during the wet season. Physicochemical parameters such as water temperatures, dissolved oxygen (DO) and total dissolved solids (TDS), pH, biochemical oxygen demand (BOD), salinity, conductivity, total dissolved solids (TDS) and total suspended solids (TSS) were measured in-situ at every sampling location with Horiba-U10 multi water parameter. Before sampling, sample bottles were soaked overnight in 1.4 M HNO_3 solution, washed with detergents, and rinsed severally with deionized water. At the sampling site, the cleaned bottles were again rinsed with the sample water before sampling [14]. At the sampling locations, surface water samples were collected at ~0.1 m depth using in plastic containers. The bottles were opened below the water surface to avoid sampling of the surface microlayer and after, they were kept in airtight plastic ice chest at 4°C to prevent sample deterioration. Separate water samples were further collected in 250 ml amber bottles at each location and incubated in the dark for five days for biochemical oxygen demand (BOD_5). Sediment samples were collected with a 0.25 m^2 Van-Veen grab at each sampling location and were stored in an polyethylene bag and labeled accordingly. Sediments were air-dried for three weeks under room temperature, homogenized, in an agate mortar and passed through a 2 mm sieve to remove the coarse grains size.

2.2.2 Sample digestion and analysis

25 ml of each water sample was digested with 15 ml of HNO_3 in a fume cupboard at 130°C until 2–5 mL remained in the beaker. The water digests were then filtered through Whatman no. 41 filter paper and then made to 50 mL volume using deionized water. Sampling and analysis were conducted according to APHA [15].

1 g of the sieved sediment samples were weighed into a 100 ml beaker. 25 ml of freshly prepared mixture of aqua regia (HNO_3 /HCl in ratio 1:3) were added to each sample and covered with a watch glass. It was allowed to stand for 30 minutes during which initial reaction subsided. Digestion was carried out on hot plate whose temperature was allowed to rise gradually until it reached a maximum temperature of 160ºC in a fume cupboard. Heating was continued for about 2 hours, reducing the volume in the beaker to about 2 – 5 ml. The beaker and its contents were allowed to cool and the content was transferred through Whatman no. 41 filter paper 50 ml volumetric flask and made up to mark with distilled water [16]. The digested samples (both water and sediment) were analyzed for Fe, Pb, Zn, Cu, Cd and Cr by Atomic Absorption Spectrophotometer (Argillent 200 A model) to determine the metal content at the wet laboratory of the Physical and Chemical Oceanography, Nigerian Institute for Oceanography and Marine Research (NIOMR), Lagos, Nigeria. The standard for the ASS calibration was prepared by diluting standard (1000 ppm). All measured results were converted from milligram per liter and microgram per liter to milligram per kilogram for sediment. Matrix Spike recovery was in the range of 85–100%. The performance of the AAS was checked daily to ensure that the instrument is working according to the specifications. Ultrapure metal free deionized water was used for all analyses.

2.3 Pollution Assessment Methods of Heavy Metals

2.3.1 Contamination factor (CF)

Contamination factor (CF) is a single index and it is considered to be a simple and effective tool used to monitor metal contamination in the environment. It was suggested by Hakanson [17] and is given by:

$$CF = \frac{Ci}{Bi} \quad (1)$$

Ci is the measured concentration of metal i. Bi is the background value of metal i. Average shale concentration given by Turekian and Wedepohl [18] is a worldwide standard that satisfies the basics of using it as reference for unpolluted sediments. The contamination factor was classified into four groups: $CF < 1$ refers to the low contamination factor; $1 \leq CF < 3$ refers to the moderate contamination; $3 \leq CF < 6$ refers to the considerable contamination factor and $CF \geq 6$ refers to the very high contamination.

2.3.2 Nemerow's pollution index (NPI)

Nemerow's pollution index is used to evaluate the comprehensive pollution status of heavy metals. It considers the most polluting factors, in particular, can be used to assess the status of comprehensive pollution caused by all the heavy

metals in the sediments, because different heavy metals may have different impacts in the same station [19,20]. The Nemerow pollution index (NPI) is defined as

$$NPI = \frac{2\sqrt{(CFmax)^2-(CFiave)^2}}{2} \quad (2)$$

Where CF_{max} and CF_{iave} represent the maximum contaminations and average of contamination factors, respectively. The relationships between the level of water pollution and the NPI criteria are shown in Table 2 [21].

2.3.3 Potential ecological risk index

The potential ecological risk index was developed to assess the ecological risks for aquatic pollution control. The methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. It was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity of heavy metals and the response of the environment, and can be calculated with the following formula: [17,19,22].

$$R_I = \sum E^i_r \quad (3)$$

$$E^i_r = T^i_r C^i_f \quad (4)$$

$$C^i_f = C^i_o \quad (5)$$

Where R_I is the potential ecological risk for multinomial factor and is calculated as the sum of all risk factors for heavy metals in sediments. E^i_r is the monomial potential ecological risk factor. T^i_r is the toxic response factor for a given substance that accounts for the toxic requirement and the sensitivity requirement. The toxic-response factors are Pb (5), Cu (5), Cr (2), Zn (1) and Cd (30) [23]. C^i_f is the contamination factor, C^i_0 is the concentration of metals in the sediment and C^i_n is a reference value for metals. The reference values of Pb, Cu, Cr, Zn, and Cd in sediments were 20, 45, 60, 80 and 0.3 mg/kg respectively [24].

2.4 Statistical Analysis

Sigma plot 10 and SPSS 20 software were used in the analyses of data. Correlations were performed in a pairwise fashion employing Pearson correlation procedure. For all metal concentration, descriptive statistics were used to compute mean, standard deviation, minimum, maximum as well as a range of data sets. The data were compared by one- way ANOVA to determine if the difference was significant using a 95% confidence interval (P-value < 0.05).

3. RESULTS AND DISCUSSIONS

3.1 Physicochemistry

The results of the physicochemical characteristics at five sample locations are shown in Table 3. Temperature is known to be one of the important factors in coastal environment; it regulates biological activities as well as physicochemical properties [25]. The temperature of the study area varied from 28.7 ± 0.44ºC at location 1 (Apapa) to 30.36 ± 0.62ºC at location 5 (Egbin). The high value of temperature at location 5 could be as a result of heat from Egbin power plant, in agreement with the reported thermal pollution in the study area (Table 1). The temperature values recorded were within the range for a tropical climate by Federal ministry of environment effluent permissible limit of < 40ºC FMENV [26] for coastal waters. The temperature recorded in this study is in agreement with the research of Alabaster and Lloyd [27] who stated that the temperature of surface tropical water ranged from 25-35 ºC. Hydrogen ion concentration is measured in terms of pH in water and its fluctuation is linked with chemical changes, species composition and life processes [28]. Aquatic biotas are affected by pH because most of their metabolic activities are pH-dependent [29]. pH value ranged from 6.74 ± 0.47 (at location 5) to 7.37 ± 0.07 (at location 2). pH values of other sampling locations (except for location 5,) are alkaline. The pH values are in agreement with the work of Abowei and George [30] who reported a pH range of 6.68 and 7.03 at Okpoka Creek, Niger Delta. The Dissolved Oxygen (DO) is a regulator of metabolic activities of organisms and thus governs metabolisms of the biological community as a whole and also acts as an indicator of the trophic status of the water body [28]. DO affect the growth, survival, distribution, behavior and physiology of shrimps and other marine organisms [31,32]. The principal sources of oxygen in water are atmospheric air and photosynthetic planktons. Concentrations of DO above 5 mg/L are considered supportive of marine life while oxygen depletion in water leads to poor feeding of fish, starvation, reduced growth, survival and population [32,33]. The DO values of this study ranged from 5.45 ± 0.14 mg/L (at location 5, Egbin) to 8.18 ± 0.02 mg/L (at location 2, Iddo). The result also compared favorably with the

finding of Biney [34], who reported mean DO concentrations of 6-8 mg/L for brackish water samples. DO showed a positive correlations (Table 9) with pH (r = 0.894). The BOD values

Table 2. Potential ecological risk (E^i_r) for monomial factor in sediment of Lagos lagoon

E^i_r	R_I	Potential ecological risk	NPI	Nemerow's Pollution Index classes
< 40	< 95	Low ecological risk	0 ≤ NPI ≤ 1	standard/good quality
40 – 80	95 – 190	Moderate ecological risk	1 ≤ NPI ≤ 5	lightly polluted
80 – 160	190 – 380	Considerable ecological risk	5 ≤ NPI ≤ 10	moderately polluted
160 - 320		High ecological risk	NPI > 10	heavily polluted
>320	>380	Very high ecological risk		

Table 3. Physicochemical parameters of the study area

Parameter	Stations	Min	Max	Mean	SD	FMENV
Temperature (°C)	1	28.05	29.25	28.69	0.44	<40ºC
	2	28.65	29.5	29.21	0.31	
	3	29.10	29.85	29.32	0.28	
	4	29.30	30.55	29.87	0.44	
	5	29.70	31.25	30.36	0.62	
pH	1	7.1	7.4	7.2	0.11	6.5- 9
	2	7.3	7.5	7.3	0.08	
	3	7	7.7	7.2	0.26	
	4	6.3	7.7	7.2	0.5	
	5	6	7.2	6.8	0.45	
Dissolve Oxygen	1	2.6	11.3	6.73	3.45	>5 mg/L
(mg/l)	2	6.89	9.35	8.19	1.21	
	3	4.45	8.9	7.28	1.75	
	4	5.55	6.45	6	0.44	
	5	2.15	7.7	5.57	2.23	
BOD (mg/l)	1	8.75	10.57	9.6	0.68	50 mg/L
	2	7.11	52.1	15.11	18.13	
	3	7.35	110.1	25.83	41.31	
	4	4.1	31.05	12.93	12.11	
	5	1.6	14.35	6.86	5.68	
Salinity (ppt)	1	12	16.25	14.17	1.89	
	2	10.25	20.4	12.6	3.86	
	3	2.4	21.55	8.31	7.61	
	4	2.4	14.4	4.78	4.72	
	5	0.02	2.55	1.25	1.07	
	1	21.8	29.8	25.78	2.95	[b]900mS/cm
EC (mS/cm)	2	19.9	28.35	23	3.52	
	3	5.9	8.6	7.18	0.96	
	4	6.06	7.65	6.72	0.58	
	5	1.8	5.7	3.79	1.71	
TDS (mg/l)	1	450.15	1210.2	749.11	322.96	[b]1000 mg/l
	2	270.45	573.4	436.03	103.38	
	3	211.8	881.25	503.1	245.89	
	4	275.25	601.27	419.01	131.52	
	5	209.43	716.95	365.81	189.34	
TSS (mg/l)	1	16.39	17.7	16.89	0.51	600mg/L
	2	12.56	16.42	14.92	1.39	
	3	48.76	117.95	78.35	26.7	
	4	47.61	106.3	83.14	20	
	5	12.13	21.25	14.96	3.4	

SD= standard deviation. b= WHO, 1997

across the locations were below the permissible limit of 50 mg/L [26]. The recorded high value of BOD could be due to point source effluents from waste discharge from the coastal dwellers. BOD showed a significant positive correlation with pH (r = 0.592) and DO (r = 0.552).

Salinity is the measurement of the ionic composition of water and it varies depending on the mixing of relatively fresh inland waters with saline marine waters [35]. The distinction between saline and freshwater characteristics is evident in the diversity of the marine organisms there-in [36]. Other researchers suggest that salinity variation is caused by dilution and evaporation, with great influence on the fauna of the intertidal zones [37,38]. However, brackish-water, habitats (such as estuaries, backwater and mangrove) is formed due to the influx of freshwater from land runoff caused by precipitation or by tidal fluctuations [28]. Ajibare [39] further reported waters with salinity values of below 1‰ as fresh, while waters with salinity values higher than 1‰ are brackish/marine water. The salinity values of the study area varied from 1.24 ± 1.06 ‰ at Egbin (location 5) to 14.16 ± 1.88 ‰ at Apapa (location 1) which is a clear indication that our study area is a brackish-water habitat. The locations (1 and 2) with high salinity values are due to closeness and proximity to the sea.

Onyema and Nwankwo [40] reported a close association between conductivity and salinity. Similar tends was established in this study, the conductivity values followed a similar trend with salinity. Salinity showed a significant negative correlation (r = -0.971) with the temperature (Table 5), which suggest that increased temperature conditions tend to trigger reduced salinity values.

The electrical conductivity (EC) is a good measure of the total amount of salts in water and this is commonly used to determine the conditions of salinity in a study area. Natural water ions usually originate from inorganic compounds present in water. The EC values in the study area ranged from 3.79 ± 1.171 mS/cm at Egbin (location 5) to 25.78 ± 2.95 mS/cm at Apapa (location 1). The highest value of EC recorded at Apapa was probably associated with the municipal effluent discharged from the resident community, or seawater incursion, due to the closeness of the study area to the Atlantic Ocean. Although FMENV has no limit for EC values, the EC values from the study area were below the permissible limit of 900 mS/cm WHO [41]. The EC showed an expected significant positive correlation with pH (r = 0.614), DO (r = 0.637), salinity (r = 0.932) and TDS (r = 0.693).

TDS shows the general nature of water quality or salinity. In natural water, dissolved solids consist mainly of inorganic salts such as carbonates, bicarbonates, chlorides, sulfates, phosphates, and nitrates of calcium, magnesium, sodium, potassium, iron, etc., and a small amount of organic matter and dissolved gases (Jain *et al*., 2010). The TDS values from the study area varied from 365.81 ± 189.34 mg/L at Egbin (location 5) to 749.11 ± 322.96 mg/L at Apapa (location 1). Ladipo [42] also recorded that the variation in TDS followed a similar pattern as EC. The TDS values across the stations (except location 1) were below 1000 mg/l stipulated by WHO [43]. TDS showed a significant positive correlation (r = 0.75) with salinity. The TSS values of the study area ranged from 14.93 ± 1.39 mg/L (at Apapa, location 2) to 83.14 ± 19.99 mg/L (Location 4), and were within the 600mg/L standard permissible limit stipulated by FMENV [26].

3.2 Heavy Metal Concentrations

3.2.1 Water sample

Heavy metal concentrations in water samples are shown in Table 4. The values were compared with the World Health Organization [44] permissible limit. The six heavy metals displayed moderate variation, indicating that the heavy metal concentrations of the water samples varied largely within the sampling stations. The concentration of Fe varied from 759.70 ± 138.61 mg/l at Egbin (location 5) to 10515.79 ± 8434.23 at Iddo (location 2). Our results indicated that the Fe concentrations were above the permissible limit recommended by WHO [44]. Source of Fe in the surface water is often from the wet and dry deposition of atmospheric aerosols, vertical mixing and upwelling, inputs from rivers and bottom sediments, and biogenic recycling of cellular iron in surface waters [45,46]. The Pb concentrations from our samples ranged from 0.25 ± 0.16 mg/l at Makoko (location 3) to 3.43 ± 2.01 at Apapa (location 1). The minimum Pb values were above the maximum stipulated permissible limit (0.001mg/l) by FMENV [26]. Pb has been reported to be associated with effluents from electroplating, batteries storage and disposals, sewage sludge, paint and dyes, effluents from crude oil transportations, fertilizers

and vehicular emissions in Lagos lagoon [19,47]. High values of Pb at location 1 could be attributed to lead gasoline, exhaust emission from marine vessels and industrial effluents. Pb varies significantly ($P<0.05$) across the sample locations.

The Zinc (Zn) concentrations in the study area have a minimum value of 0.25 ± 0.15 mg/l at Makoko (location 3) and a maximum value of 0.60 ± 0.17 mg/l at Apapa (location 1). High Zn concentrations at location 1 could be attributed to domestic waste, shipyard, automobile, and industrial effluent. Zinc concentrations were within the maximum permissible limit of 5.0 mg/l given by FMENV [26]. Zn showed a significant difference ($p<0.05$) across the sample locations and also showed a significant positive correlation with Pb (Table 10). The significant positive correlation between Pb and Zn suggests the influence of galvanized roofing materials to Zn source, or an integrated action of weathering and pollution arising from rooftop structure materials, and its eventual erosion into the water bodies [48]. The concentrations of Cd ranged from 0.10 ± 0.04 mg/l at Egbin (location 5) to 0.53 ± 0.38 mg/l at Iddo (location 2). Cd values across the sample locations exceeded the FMENV [26] permissible limit for coastal waters (0.0018mg/l). High values of Cd could be attributed to industrial and metallurgical effluents (ship breaking), automobile and domestic sewage discharges [49].

Copper (Cu) in the study area has a minimum value of 0.25 ± 0.13 mg/l at location 1 (Apapa) and maximum value of 1.30 ± 0.77 mg/l at location 4 (Ibeshe). The Cu concentrations were within the FMENV [26] standard (2.0-4.0 mg/l), except at station 4. Human-induced anthropogenic activities such as domestic sewage and runoff, effluents from textile, sand mining may trigger the high Cu concentrations at location 4 (Ibeshe). Copper showed a significant difference ($p<0.05$) across stations.

Table 4. Heavy metal distribution in the surface water of the study area

Parameters	Stations	Min	Max	Mean	SD	FMENV, 2001
Fe (mg/L)	1	470.42	11549.14	2831.77	4284.52	
	2	800.6	19722.82	10515.79	8434.23	
	3	321.83	1500.3	833.25	471.38	
	4	806.82	4261.4	1761.78	1280.61	
	5	520.37	901.37	759.7	138.61	
Pb (mg/L)	1	1.33	5.96	3.43	2.01	0.001
	2	0.26	1.74	0.93	0.48	
	3	0.14	0.57	0.25	0.16	
	4	0.15	0.69	0.45	0.21	
	5	0.16	0.85	0.47	0.29	
Zn (mg/L)	1	0.36	0.76	0.6	0.17	50
	2	0.12	0.99	0.47	0.3	
	3	0.01	0.39	0.25	0.16	
	4	0.13	0.47	0.29	0.12	
	5	0.21	0.81	0.43	0.24	
Cd (mg/L)	1	0.01	0.77	0.32	0.3	0.0002-0.0018
	2	0.11	0.98	0.53	0.38	
	3	0.19	0.35	0.26	0.06	
	4	0.08	0.35	0.21	0.09	
	5	0.04	0.17	0.1	0.04	
Cu (mg/L)	1	0.13	0.44	0.26	0.13	2.0-4.0
	2	0.17	1.81	0.87	0.66	
	3	0.06	0.64	0.34	0.19	
	4	0.64	2.42	1.3	0.77	
	5	0.14	0.58	0.27	0.16	
Cr (mg/L)	1	0.11	0.57	0.35	0.18	0.02-2.0
	2	0.06	1.08	0.41	0.44	
	3	0.05	1.08	0.36	0.39	
	4	0.08	1.28	0.55	0.48	
	5	0.05	0.77	0.44	0.25	

Table 5. Heavy metal distribution in the surface sediment in the study area

Parameter	Stations	Min	Max	Mean	SD	USEPA 1999
Fe (mg/kg)	1	244.11	5911.24	3016.88	2272.25	30
	2	474.22	5231.41	2596.42	2055.07	
	3	130.18	3672.91	1697.45	1535.93	
	4	109.85	1238.1	662.43	470.61	
	5	419.16	5462.12	3264.99	2240.68	
Pb (mg/kg)	1	15.36	94.25	61.6	32.09	40
	2	8.76	72.11	32.34	25.99	
	3	6.1	31.35	17.5	8.53	
	4	2.01	43.31	20.3	15.45	
	5	0.06	28.72	10.7	11.57	
Zn (mg/kg)	1	10.31	92.1	59.24	33.31	110
	2	57.27	100.51	77.66	17.75	
	3	7.88	66.22	38.48	20.29	
	4	18.22	49.87	32.08	11.33	
	5	6.44	31.01	16.29	10.69	
Cd (mg/kg)	1	3.76	37.51	16.65	14.41	0.6
	2	5.02	13.14	8.3	2.93	
	3	3.21	30.12	17.37	10.66	
	4	1.14	8.91	3.4	2.93	
	5	0.03	6.42	3.47	2.66	
Cu (mg/kg)	1	1.12	57.25	25.48	22.99	16
	2	1.81	45.85	21.68	18.29	
	3	1.15	79.62	47.57	26.86	
	4	17.81	54.41	38.99	14.39	
	5	10.06	47.86	31.36	16.64	
Cr (mg/kg)	1	20.81	92.09	48.96	23.89	25
	2	7.5	75.55	43.32	25.31	
	3	19.12	132.34	58.45	43.57	
	4	34.1	168.27	90.45	57.57	
	5	3.33	80.68	43.67	29.26	

Chromium (Cr) varied from 0.35± 0.18 mg/l at location 1 (Apapa) to 0.55± 0.48 mg/l at location 4 (Ibeshe). Chromium values were below the maximum stipulated requirement of 0.02-2.0mg/l by FMENV [26].

3.2.2 Sediment samples

Spatial distributions of heavy metals in the sediment are displayed in Table 5. The analyzed metal concentrations (in mg/kg) ranged from: Cd (3.39 ± 2.92 -17.37 ± 10.66); Cu (21.67 ± 18.29 – 47.57 ± 26.85); Cr (43.66 ± 25.31 – 90.44 ± 57.56); Pb (10.69 ± 11.57 – 61.59 ± 32.09); Zn (16.28 ± 10.68 – 77.65 ± 17.74); Fe (662.43 ± 470.61 – 3264.98 ± 2240.67). These wide ranges are attributed to differential behavior of heavy metals rich urban effluents draining into the Lagos coastal waters. It was noticed that Pb at station 1 (Apapa) among the analyzed metals was below the permissible limit given by USEPA [50]. Among the analyzed heavy metals, Cu did not exhibit significant difference across sampling stations, but contributed up to ~19.08% to the total heavy metals analyzed in the sediment samples (Fig. 2), while Zn showed a significant positive correlation (r = 0.85, *p*=0.05) with lead, and contributed ~25.9% to the total heavy metals analyzed in the sediment samples (Table 10). Cu and Fe showed a significant negative correlation with zinc (r = -0.60) and chromium (r = -0.93) respectively (Table 6). The contributions of Pb, Cd and Cr to the total heavy metals analyzed in the sediment samples are ~16.5%; ~25.9% and ~19.08% respectively (Fig. 2). The trends of heavy metals in the sediment of the study area are in the order Fe > Cr > Zn > Cu > Pb > Cd. The potentially toxic trace metals (Cd and Pb) and the essential metal (Cu, Cr and Zn) contributed ~22.14% and ~77.86% respectively to the total heavy metal concentrations in the sediment samples (Fig. 3).

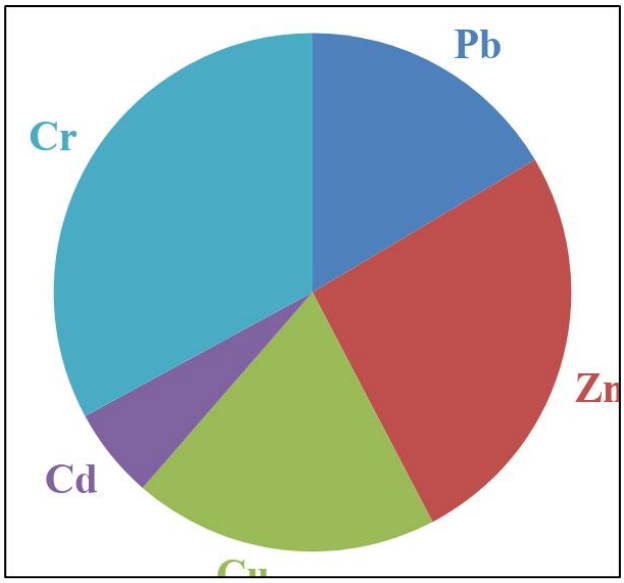

Fig. 2. Contributions (%) of Cu, Zn, Cr, Pb and Cd in sediment samples

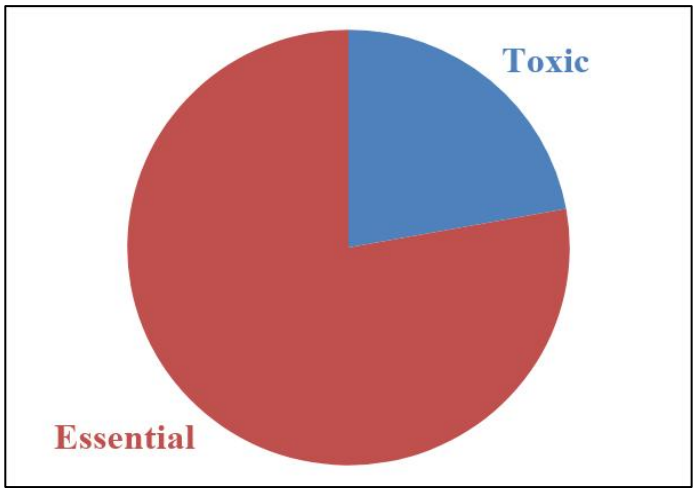

Fig. 3. Contributions (%) of toxic trace metals (Pb, Cd) and essential trace metals (Cu, Zn and Cr) in sediment sample

We compared the metal concentrations from the Lagos coastal sediments with other Lagoons and coastal sediments (Table 6). The Cd concentrations of the Lagos coastal sediments were higher than those in the Turag River, Bangladesh [51] and Benin city, south-south Nigeria [52]. The Cu range was slightly higher than the coastal sediments from the Francisco Estuary, Brazil, Al-Hawija, North of Iraq, but was lower than the Turag River, Bangladesh. The Cr range was slightly higher in our study area than the reported values from the Francisco Estuary, Brazil, Turag River, Bangladesh, but was lower than the reported values from Al-Hawija coastal sediments, North of Iraq. The Pb range was higher in our study area when compared with other data, Fe values were not reported in most of the compared stations. These comparisons further attest to the high concentration of Cd and Pb in our sediment samples.

3.3 Pollution Assessment Methods of Heavy Metals

The contamination factor (CF) of metal content in the sediment of the study area shown in Table 7.

CF values of less than 1 were calculated for Zn (at all the sample locations), Pb at sample location 3 (Makoko) and 5 (Egbin), Cu and Cr (all the sample locations, except location 3 and location 4). Cd showed a very high contamination factor (CF > 6) across all the sample locations. Pb showed moderate contamination factor (1<CF<3) at all the sample stations.

The high CF values are not unconnected to various metals and metallic compounds released from anthropogenic activities that add up to their natural background values in the study area. Leaded gasoline, vehicular emission, Ni-Cd batteries, paint, waste treatment plants, as well as agricultural fertilizer, have been identified as sources of cadmium and lead in the marine environment [53]. Effluents from these sources with allochthonous deposits and marine debris which include high and low-density polythene, empty cans of, glass bottles, disposed car tyres, food/pesticide sprays, worn clothes and many others that moved alongside Lagos coastal waters has contributed to the CF of the study area [53]. The NPI values (Fig. 4) reflected the status of comprehensive pollution caused by all the heavy metals. The NPI ranged from 8.3 at Ibeshe (location 4) to 41.8 at Makoko (location 3). The study area varied from moderately polluted at location 3 (Makoko) and location 5 (Egbin) to heavily polluted at location 1 (Apapa), location 2 (Iddo) and location 3 (Makoko). The enhance pollution status at location 1 (Apapa), location 2 (Iddo) and 3 (Makoko) were majorly triggered by the high and considerable contamination values of Cd and Pb respectively at the stations (Table 5).

The results of potential ecological risk index were shown in Table 8. The monomial potential ecological factors (E^i_r) of all the calculated heavy metals (except Cd) were less than 40 in all the sample stations, an indication of low risk of these metals (Cu, Zn, Cr, Pb) to the marine ecosystems. The monomial potential ecological

Table 6. Concentration range (in mg/Kg) of selected metals in Lagos coastal sediments (This study), for comparisons with marine sediment in different region

Regions	Cd	Cu	Cr	Pb	Zn	Fe
This study	3.39 - 17.37	21.67 - 47.57	43.66 - 90.44	10.69 - 61.59	16.28 - 77.65	662.43 - 3264.98
São Francisco estuary (Brazil)[a]	-	1.00 – 26.00	10.00 – 82.00	4.00 – 16.00	1.00 – 57.00	-
Al-Hawija, North of Iraq[b]	-	23.00 – 30.00	310.00 - 600.00	9.00 - 20.00	56.00 – 111.00	-
Benin City, Nigeria.[c]	1.80- 5.89	7.20- 10.73	1.99- 4.89	1.41- 6.36	28.38- 43.63	156.49- 329.14
Turag River, Bangladesh[d]	0.00 - 0.80	46.30 - 60.00	32.00 - 75.50	28.30 - 36.40	94.60 - 190.10	-

Table 7. Heavy metal contamination factor (CF) in sediment of Lagos lagoon

Stations	Pb	Zn	Cu	Cd	Cr
1	3.07	0.62	0.57	55.50	0.54
2	1.62	0.82	0.48	27.67	0.48
3	0.87	0.41	1.06	57.91	0.65
4	1.01	0.34	0.87	11.32	1.00
5	0.53	0.17	0.70	11.57	0.49

Table 8. Potential ecological risk (E^i_r) for monomial factor in sediment of Lagos lagoon

	E^i_r					R_I
Locations	Pb	Cu	Cr	Zn	Cd	
1	15.40	2.83	1.63	0.74	1664.72	1685.323
2	8.08	2.41	1.44	0.97	830.03	842.9374
3	4.37	5.29	1.95	0.48	1737.31	1749.399
4	5.07	4.33	3.01	0.40	339.58	352.4027
5	2.67	3.48	1.46	0.20	347.24	355.0586

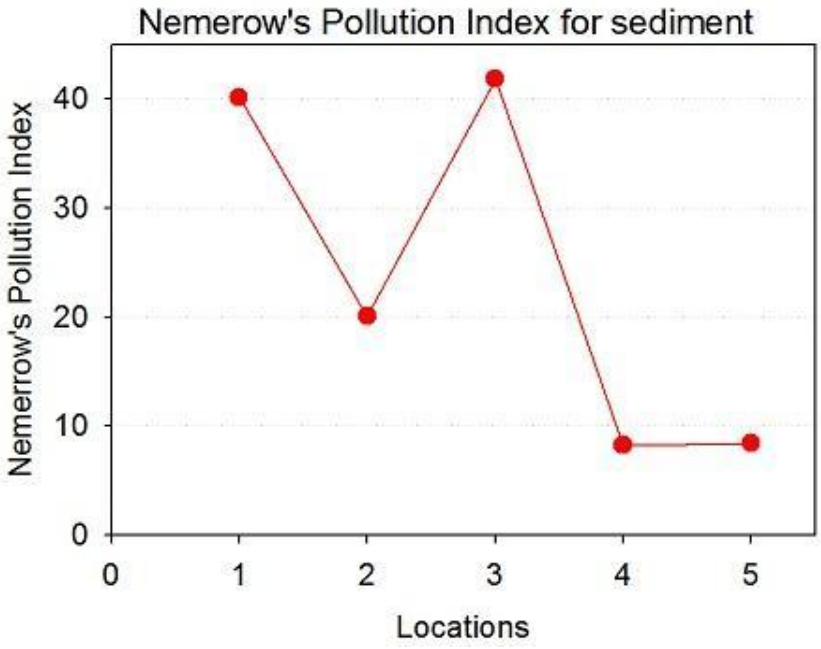

Fig. 4. Nemerow's pollution index calculated from heavy metal concentrations of sediments in the study area

factors (E_r^i) for Cd showed a very high ecological risk in all the sample stations, an indication of the high ecological risk of Cd to the marine ecosystems. Moreover, the multinomial potential ecological risk index (R_I) values for all stations varied from 352.40 at location 4 (Ibeshe) to 1685.32 at location 1 (Apapa, Table 3 and Table 4). This is an indication of a considerable to the very high ecological risk of Pb. Cd, Zn, Cu and Cr in the sediment of the studied area to the marine ecosystems.

Table 9. Pearson correlation coefficient for physicochemical parameters of Lagos lagoon

	pH	Temp	DO	BOD	Sal	TDS	TSS	EC
pH	1							
Temp	-0.754	1						
DO	.894*	-0.674	1					
BOD	0.592	-0.289	0.552	1				
Sal	0.796	-.971**	0.772	0.212	1			
TDS	0.333	-0.852	0.197	-0.019	0.749	1		
TSS	0.198	0.148	-0.115	0.633	-0.284	-0.192	1	
EC	0.614	-0.852	0.637	-0.139	.932*	0.693	-0.554	1

** Correlation is significant at the 0.05 level (2-tailed).*
** Correlation is significant at the 0.01 level (2-tailed)*

Table 10. Pearson correlation coefficient for heavy metals in surface water of Lagos lagoon

	Pb	Zn	Cu	Cr	Cd	Fe
Pb	1					
Zn	.847*	1				
Cu	-0.353	-0.372	1			
Cr	-0.488	-0.428	0.814	1		
Cd	0.268	0.339	0.235	-0.328	1	
Fe	0.11	0.376	0.331	-0.108	.918*	1

Table 11. Pearson correlation coefficient for heavy metals in sediment of Lagos lagoon

	Pb	Zn	Cu	Cr	Cd	Fe
Pb	1					
Zn	.847*	1				
Cu	-0.353	-0.372	1			
Cr	-0.488	-0.428	0.814	1		
Cd	0.268	0.339	0.235	-0.328	1	
Fe	0.11	0.376	0.331	-0.108	.918*	1

4. CONCLUSION AND RCOMMENDATION

This study was conducted to monitor and assess the distribution of the physicochemical characteristics (TEMP, SAL, DO, BOD, TDS and EC), heavy metals (Cu, Zn, Fe, Pb, Cd and Cr), contamination factor (CF), Nemerow pollution index (NPI), ecological risk (R_I) and potential ecological risk index (Eir) of the Lagos coastal waters and sediments Southwest Nigeria. Five sampling locations (location 1 (Apapa); location 2 (Iddo); location 3 (Makoko); location 4 (Ibsehe) and location 5 (Egbin) with identified anthropogenic activities such as thermal pollution, dredging, domestic and industrial waste discharges were selected. The physicochemical characteristics of water samples from all the stations were within permissible limits for healthy marine ecosystems stipulated by the Federal Ministry of Environment of Nigeria (FMNEV, 2001) and World health organization (WHO, 1997) (DO:>5 mg/L; pH:6.5-9; TEMP:<40ºC; BOD: 50mg/L; EC:900 mS/cm; TDS:1000mg/L and TSS:600mg/L), with the exception of low DO at station 1 and station 5; and high BOD at; station 2 and station 3 respectively. Heavy metal concentrations, when compared with the FMNEV (2001) standard, showed exceedingly high values for Pb, Cd and Fe above the permissible limits for coastal water bodies, while Cu and Zn concentrations were within the permissible limits. The trend of heavy metals accumulations in the water samples were in the order of Fe > Pb > Cu > Cr > Zn > Cd.

The concentration of heavy metal in the sediment was in the order of Fe > Cr > Zn > Cu > Pb > Cd. Heavy metal contamination status of the sediments was determined through various indices such as CF, NPI, R_I and Eir. Zinc and Chromium showed low (CF < 1) contamination across all the sampling stations, similar low contamination were demonstrated by Cu, except station 3 that returned a slightly high value (CF, 1.06), which fell within moderate contamination level. Lead showed moderate ($1 \leq CF \leq 3$) contamination at all stations except station 3 and 5 that fell within low contamination range. Cadmium showed extremely severe (CF > 6) contamination values across the five sampling stations. The calculated NPI and R_I showed heavily polluted (NPI >10) and a very high ecological risk characteristic ($R_I > 380$) at station 1-3, and moderately polluted ($5 \leq NPI \leq 10$) at station 4 and station 5 respectively. Finally, the calculated Eir showed a low ecological risk of Pb, Cr, Zn and Cu to the coastal ecosystems, except for Cd (Eir >320), which is an indication of a very high ecological risk to the marine ecosystems.

Our study reveals the heavy pollution of cadmium and moderate pollution of lead in the water and sediment column across the five sampling stations. Based on this study, the framework for mandatory action should be initiated for normal assessment of Lagos Lagoon to ensure the conservation of Lagos lagoon coastal resources. There should be strict regulations to regulate the dumping of chemical contaminants into the lagoon with enforcement of penalties imposed on defaulters. Enlightenment programs for the general public on the risks of Lagos lagoon pollution are very necessary.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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