Hydrochemistry and levels of some heavy metals in samples of Ibeshe, Lagos Lagoon Complex, Nigeria

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ABSTRACT: The concentration of Iron, Copper, Chromium, Nickel, Lead, Manganese, Arsenic, Cadmium and Zinc were determined in the surface water, sediments and fish samples (*Chrysichthys nigrodigitatus*) of an industrial effluent receiving water in Ibeshe, Lagos Lagoon Complex between February and June, 2009. In assessing the impact of effluent discharge on the lagoon, Water and fish samples result were compared with the WHO/FEPA standard while the sediments results were compared with the results for unpolluted sediment. The average levels of heavy metals found in surface water, sediment and fish samples were as follows: surface water; 0.293mg/l for Fe, 0.177mg/l for Cu, 0.107mg/l for Pb, 0.213mg/l for Cr, 0.177mg/l for Mn, 0.233mg/l for Ni and <0.10mg/l for Cd. Sediment; 85303.33µg/g for Fe, 53.967µg/g for Cu, 38.35µg/g for Pb, 110.183µg/g for Zn, 93.88µg/g for Cr, 274.967 µg/g for Mn, 1.017 µg/g for As, 67.4 µg/g for Ni and 1.00µg/g for Cd. Fish sample; 4.263 µg/g for Fe, 8.229µg/g for Cu, 1.967µg/g for Pb, 11.338µg/g for Zn, 1.329µg/g for Cr, 1.513µg/g for Mn, 4.046µg/g for Ni and 0.458µg/g for Cd. The concentration of Pb and Ni in surface water were higher than WHO / FEPA limits, while Cd, Zn, Cr and As were found below FEPA limit. Fe, Cu, Pb, Cd and Zn were all higher in concentration when compared with the values of unpolluted sediment. Consequently, the concentration of Zn, Cr, Cd in fish were below the FEPA limit. Water quality of Ibeshe were typify of alkaline pH (8.90 - 9.00), high Dissolved Oxygen content (4.20 -7.80mg/l), Turbidity (24.8 – 156NTU) and freshwater salinity values (0‰). The findings reported in this study would be expected to serve as baseline level for future heavy metal pollution status of the Ibeshe, Lagos Lagoon area.

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1.0 Introduction:

Increase in industrial development and population of the cities have been recognized as a major sources of pollution throughout the world, most especially in the developing nation, {WHO, 1982}. The discharged of effluent by small scale industries have been equated to that of the sewage of a large city (Agarwark, 1999). Industry is recognized to be very important for economic development due to its capability to create employment for large number of people and her ability to reduce poverty.

Meanwhile, the operations or processes of some of these industries are capable of generating enormous volume of toxic waste water that could be detrimental to the environment.

Industrial untreated waste water/ effluent discharge into the environments are characterized by; foul smell and bad odour, high level of organic matter, increase in BOD, COD, TDS, TSS, and metals (Heavy metals) near point of disposal(EPA,1974). Also known to be affected is the dissolve oxygen (DO) of the water which will in turn poses a great threat to the survival of aerobic living organisms in the aquatic environment.

Aquatic environment is one of the receiving ends for these waste water components, at the same time it is also among the last destination for the effluent before some of its components such as organochlorine compounds and metals (trace metals) plough back into the food chains, through bio-accumulation in plankton to fishes and finally bio-magnified in man.

The concentration of industries at Ibeshe and the discharge of their effluents into the water body is a thing of concern, as it may cause heavy metals contamination which may have devastating effects on the ecological balance of the aquatic environment.

In light of this, assessment of levels of some heavy metals and hydrochemistry of Ibeshe, an industrial effluent receiving water body in the north of Lagos Lagoon becomes imperative, not only because of the threat of heavy metals to public water supplies, but also the damage caused to the aquatic life. This assessment therefore entails the monitoring of the aqueous phase (surface water), biota (fish

tissues) and sediments, (Benson et al., 2007, Saad Al-Sulami et al., 2002, Kakulu & Osibanjo, 1992).

2.0 Materials and Methods

Location: $6^{o}32'54.65"$ N, $3^{o}28'08.66"$ E and Elevation 0ft.

The study area characterized in this study was Ibeshe (North) Lagos Lagoon water front. The water front received the effluent from industries such as textile mills (NICHEMTEX), Foods industries and others situated at the Ibeshe community area, Ikorodu axis of Lagos state, Nigeria. Three (3) sampling points were chosen to represent the entire study area (activity points) (fig.1 above).

2.1 Sample collection

Surface water, fish and sediment samples were collected with the aids of water sampler, cast nets and van-veen grab respectively (APHA, 1995) from the three sampling stations along the Ibeshe (Ikorodu) Lagos lagoon. Samples were collected once in a month for five consecutive months, from February to June 2009, representing the late dry season and early raining season in the three sampling stations.

Water and sediment samples were kept in sterile polypropylene bottles and black polythene bags respectively. These water samples were preserved with concentrated Nitric (HNO_3) acid and stored at 4°C in an ice pack prior to the time they were analyzed.

The fish samples were kept in the ice pack from sampling station and later stored in the refrigerator (4°C) before analysis.

2.2 Physiochemical analysis:

Temperature, pH, Conductivity, turbidity, and salinity of the water samples were measured in-situ using Horiba U10 while dissolved oxygen was determined using Winkler method and alkalinity through titration in the laboratory (APHA, 1989).

2.3 Metal analysis:

The levels of Fe, Cu, Pb, Cd, Zn, Cr, As, Mn and Ni metals in different surface water, sediment and fish samples were analyzed by Atomic absorption spectrophotometer using Buck scientific 200A model Atomic Absorption Spectrophotometer (AAS).

50ml of each of the water samples were digested separately using 25ml of ratio 1:3 of concentrated HNO_3 and HCl at 105°C respectively, in a fume cupboard.

The sediment samples were air dried, grinded using mortar and pestle and sieved through 2mm mesh size to remove coarse materials Then 5g of each of the 2mm mesh size sieved sediment samples were digested separately using (Aqua regia) 25ml of ratio 1:3 of concentrated Trioxonitrate (v) acid (nitric) (HNO_3) and Hydrochloric acid (HCl) at 105°C respectively, in a fume cupboard.

The fish samples were allowed to defrost. Then 2g of each of the fish samples tissue were digested separately using 25ml of ratio 1:1 of concentrated Nitric acid (HNO_3) and Hydrogen peroxide acid (H_2O_2) at 105°C respectively, in a fume cupboard (FAO/SIDA,1983).

2.4 Bio- concentration Factor in fish:

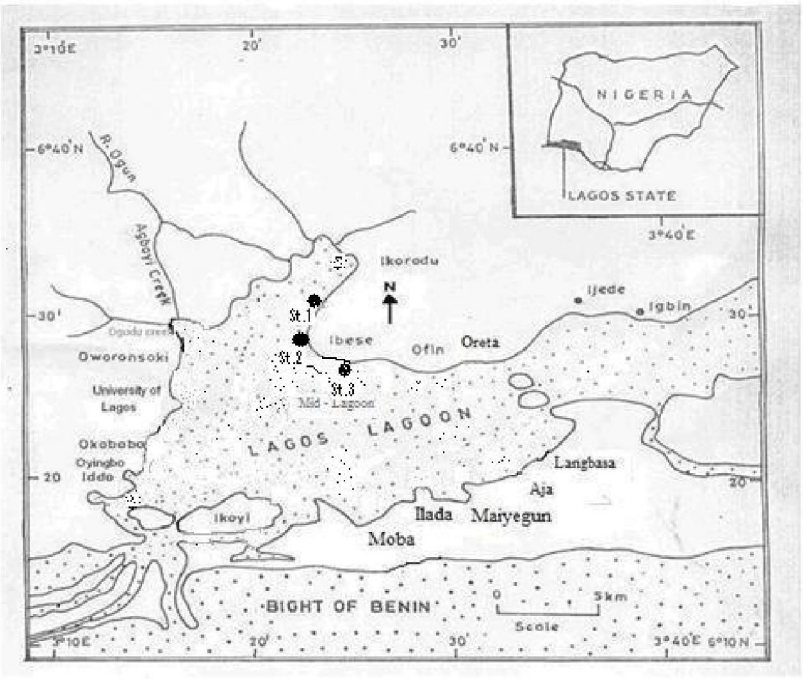
Bio concentration Factor (BCF) was determined in this study by calculating the ratio of the concentration of the metals in fish tissue to the concentration in the water (Walker et al, 1998).

3.0 RESULTS

The average of the physiochemical parameters of Ibeshe (Ikorodu) Lagos Lagoon are presented in Table 1. pH values of Ibeshe surface water ranges between 8.9 – 9.0 throughout the sampling periods. Conductivity was between 0.24 – 0.54 mS/cm. Turbidity values of between 24.8 - 156NTU. Freshwater salinity of 0‰, High Dissolved Oxygen content ranges between 4.20 – 7.80 mg/l, Alkalinity values of 10.0 – 16.0 mg/l and Water temperature ranged of 27 – 30^{0}C.

3.1 Heavy metals in water samples

The mean concentration values of studied heavy metals in water samples are presented in Table 2. The highest mean concentration value of Fe (0.330mg/l), Pb (0.120 mg/l) and Ni (0.250 mg/l) were obtained at station III. Station I and II gave the highest mean value of Cu (0.230 mg/l) and Cr (0.220 mg/l) respectively. Furthermore, highest mean concentration value of Zn (0.190 mg/l) was observed at both station I and II. In the case of Mn, station I and III recorded the highest mean concentration value of (0.120 mg/l). Consequently, the lowest mean concentration values of Fe (0.252 mg/l), Cu (0.120 mg/l) and Zn (0.148 mg/l) were obtained in the water samples from station II. Station III and I recorded the least mean concentration values of Mn (0.110 mg/l) and Ni (0.220 mg/l) respectively. Arsenic (As) was not detected in the three studied stations while Cd was below detection limits.



Map of study area showing the sampling sites ●

Table 1: The average physiochemical parameters of Ibeshe (Ikorodu) Lagos Lagoon

Parameters	pH	Conductivity (mS/cm)	Turbidity (NTU)	Salinity (‰)	DO(mg/l)	Alkalinity (mg/l)	Temperature (°C)
Range	8.9-9.0	0.24-0.54	24.8-156	0	4.2-7.8	10.0- 16.0	27-30
Mean	8.96	0.37	103.0	0	7.26	12.0	28

Table 2: The mean concentration (mg/l) of heavy metals in water of Ibeshe (Ikorodu) Lagos Lagoon at the three sampling stations (n = 5). (Range values in parentheses)
AMCS- Average means concentration of the three sampling stations
Means with the same superscript in each row are not significantly different ($p<0.05$).

Metals	Station I	Station II	Station III	AMCS	WHO/FEPA limits
Fe	0.300±0.026b (0.27-0.34)	0.252±0.011a (0.24-0.27)	0.330±0.024b (0.29-0.35)	0.293	**0.300**
Cu	0.230±0.017a (0.21-0.26)	0.120±0.012a (0.11-0.14)	0.180±0.010a (0.17-0.19)	0.177	**1.000**
Pb	0.100±0.017b (0.08-0.13)	0.100±0.007a (0.09-0.11)	0.120±0.007a (0.11-0.13)	0.107	**0.010**
Cd	ND	ND	ND	-	**0.003**
Zn	0.190±0.011a (0.18-0.21)	0.148±0.019b (0.13-0.18)	0.190±0.020b (0.17-0.22)	0.177	**3.000**
Cr	0.210±0.006a (0.20-0.22)	0.220±0.007a (0.21-0.23)	0.210±0.014b (0.19-0.23)	0.213	**2.000**
As	ND	ND	ND	-	**0.010**
Mn	0.120±0.006a (0.11-0.13)	0.120±0.010a (0.11-0.14)	0.110±0.012a (0.09-0.12)	0.117	**0.050**
Ni	0.220±0.017[a] (0.19-0.24)	0.230±0.002[a] (0.19-0.25)	0.250±0.022[b] (0.22-0.28)	0.233	**0.02**

3.2 Heavy metals in sediment samples

The mean concentration values of studied heavy metals in sediment samples are presented in Table 4. A cursory look at the Table 4 shown that the highest mean concentration values of Fe (93825.0µglg), Cu (62.75µglg), Pb (43.40µglg), Zn (122.80µglg), Cr (102.70µglg), As (1.10µglg), Mn (304.95µglg) and Ni (72.80µglg) were recorded in station III. Station I gave the highest mean value of Cd (1.08µglg). Meanwhile, the least mean concentration values of all the studied metals Fe (78371.0µglg), Cu (44.57µglg), Pb (34.95µglg), Cd (0.90µglg), Zn (94.95µglg), Cr (82.70µglg), As (0.90µglg) and Mn (256.30µglg) in sediment samples were recorded in station II except the least mean concentration value of Ni(63.85µglg) which was observed at station I.

Table 3: The mean concentration (µg/g) of heavy metals in sediment of Ibeshe (Ikorodu) Lagos Lagoon at the three sampling stations (n = 5). (Range values in parentheses).
AMCS- Average means concentration of the three sampling stations
Means with the same superscript in each row are not significantly different ($p<0.05$).

Metals	Station I	Station II	Station III	AMCS	Unpolluted Sediments (values) GESAMP, 1982.
Fe	83715.0±76.47a (83615-83830)	78371.0±325.27b (77870-78770)	93825.0±1838.5c (91225-96425)	85303.33	**41000**
Cu	52.90±1.21a (51.35-53.95)	44.57±3.00c (41.20-47.70)	62.75±1.84a (60.05-65.10)	53.967	**33**
Pb	39.80±21.51c (17.95-75.45)	34.95±16.91b (10.35-57.35)	43.40±4.39a (36.35-48.10)	38.350	**19**
Cd	1.080±0.08a (1.00-1.20)	0.90±0.08a (0.80-1.00)	1.00±0.19a (0.75-1.25)	1.000	**0.11**
Zn	112.80±7.57a (101.50-122.70)	94.95±12.67b (77.80-113.50)	122.80±21.78c (91.95-152.70)	110.183	**95**
Cr	96.25±17.11a (72.90-113.60)	82.70±34.30b (44.75-122.80)	102.70±54.60c (46.20-172.90)	93.880	
As	1.05±0.40b (0.50-1.55)	0.90±0.20a (0.60-1.10)	1.10±0.42b (0.60-1.70)	1.017	**14**
Mn	283.90±92.98b (176.40-421.70)	256.30±95.41b (117.70-342.60)	304.95±57.06a (221.20-356.10)	274.967	**770**
Ni	63.85±8.11b (56.72.60)	65.55±17.49c (48.75-94.95)	72.80±2.51a (70.25-76.10)	67.40	

3.3 Heavy metals in fish (*Chrysichthys nigrodigitatus*) samples

The mean concentration values of heavy metals in the fish tissue are presented in Table 5. The highest mean concentration value of Fe (4.313µglg) was recorded in fish samples collected at both station I and III while the lowest mean value (4.163µglg) was obtained in fish samples caught at station II. The highest mean concentration values of Cu (10.663µglg), Zn (15.713µglg) and Cr (1.663µglg) were observed in station III while the least Cu (5.975µglg), Zn (8.350µglg) and Cr (1.100µglg) were recorded at station II. Highest mean concentration values of Ni (5.725µglg) and Pb (2.225µglg) were obtained at station I while the lowest mean values of (1.650µglg) and (1.125µglg) were from the fish samples at station II. Meanwhile, fish samples from station II recorded the highest mean concentration values of Mn (1.730µglg) and Cd (1.375µglg) while the lowest Mn mean value of (1.225µglg) was obtained from fish samples caught at station II. Cd was below detection limit at station II and III while Arsenic was not detected in all the fish samples collected from all the sampling stations.

3.4 Bio-concentration factor

The mean bio-concentration factor (BCF) of heavy metals was as presented in Figure 2. Generally a relatively high BCF values were observed in this study. The highest BCF of Fe (16.5) was recorded in fish samples obtained at station II followed by 14.4 and 13.1 from stations I and III respectively. Station III fish presented the highest value for Cu (59.2) followed by stations II and I respectively. Fish samples from station II also have the highest Mn (14.4) while station I fish samples have the highest

BCF values of Pb (22.3) and Ni (26.0).The highest BCF values for Cr(7.9)and Zn (82.7) were observed at station III. The BCF values for Cd and As (Arsenic) could not be determined.

Table 4: The mean concentration (µg/g) of heavy metals in fish (*Chrysichthys nigrodigitatus*) tissues of Ibeshe(Ikorodu) Lagos Lagoon at the three sampling stations (n = 5). (Range values in parentheses).
AMCS- Average means concentration of the three sampling stations
Means with the same superscript in each row are not significantly different (p<0.05).

Metals	Station I	Station II	Station III	AMCS	WHO limits
Fe	4.313±0.953b (2.950-11.050)	4.163±0.841a (2.938-5.125)	4.313±1.204c (2.625-5.750)	4.263	**800.00**
Cu	8.050±3.137c (3.888-11.050)	5.975±1.962b (3.900-8.713)	10.663±1.391a (8.925-12.760)	8.229	**30.00**
Pb	2.225±0.463a (1.563-2.763)	1.558±0.613b (1.125-2.625)	2.113±1.353c (0.563-4.025)	1.967	**2.00**
Cd	ND	1.375±1.76a (0.25-4.38)	ND	0.458	**2.00**
Zn	9.988±1.326a (8.350-11.760)	8.350±1.606b (6.375-10.730)	15.713±1.886c (13.090-16.910)	11.338	**1000.00**
Cr	1.225±0.339a (0.638-1.500)	1.100±0.916b (0.263-2.550)	1.663±1.146c (0.138-2.513)	1.329	**150.00**
As	ND	ND	ND	ND	**3.00**
Mn	1.663±0.689c (0.813-1.888)	1.730±0.518b (1.350-2.625)	1.225±0.440a (0.563-1.688)	1.513	–
Ni	5.725±1.967c (3.513-8.300)	3.188±1.174a (1.650-4.738)	3.225±1.566b (1.313-5.438)	4.046	–

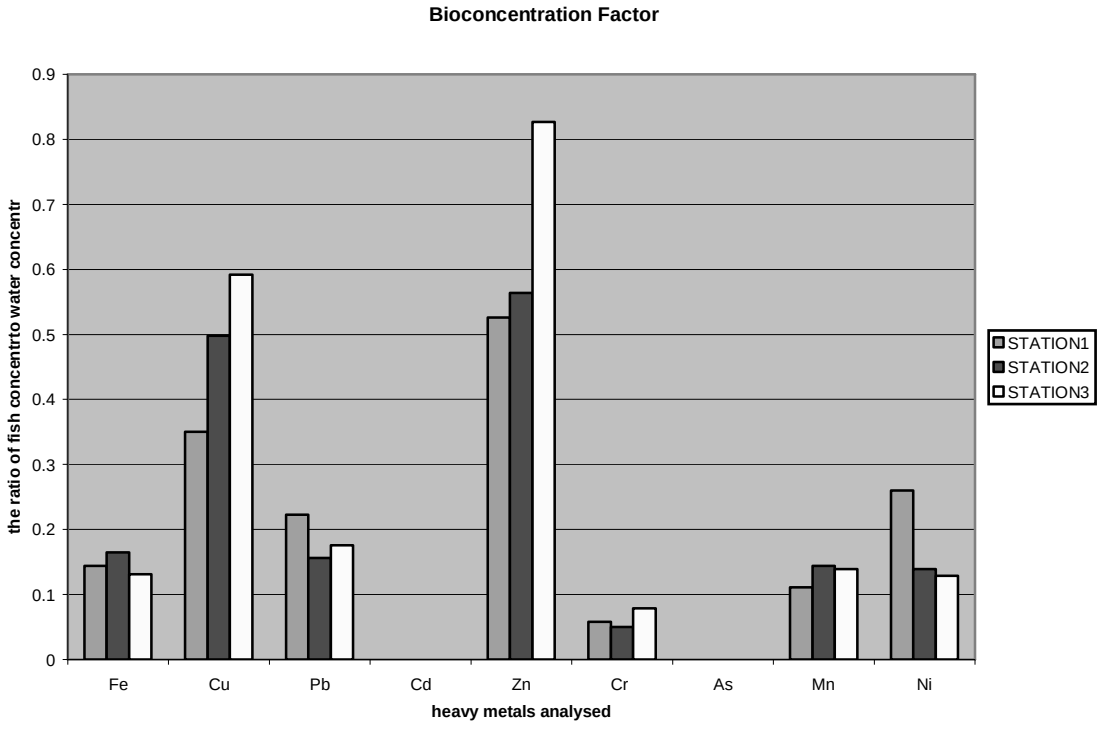


Figure 5: Bio-concentration factor (BCF) of heavy metals in fish of Ibeshe (Ikorodu) Lagos Lagoon

4.0 Discussion

Water temperatures were fairly constant throughout the study period. These temperatures have been reported by several authors in the Lagos Lagoon (Nwonkji et. al, 2010, Ajao, 1989). pH observed in Ibeshe throughout the sampling periods was alkaline. Similar findings have been reported (Nwankwo, 1996). Buffer properties of the water were responsible for this stable pH. Conductivity and Salinity have been established as associated factors (Onyema and Nwankwo 2009). Salinity recorded throughout in this study typifies freshwater condition and decrease with decline in Conductivity. High turbidity reported could be attributed to release of particulate matter brought in by rain. High Dissolved Oxygen recorded could be linked to mixing due to rainfall.

All heavy metals analyzed in this study were detected in water, sediment and fish samples (*Chrysichthys nigrodigitatus*) of Ibeshe (Ikorodu) Lagos lagoon except Cd and As that were below detection limit in all the study media (water, sediment & fish) from all the study stations.

Metals concentrations in water at all three sampling stations were below their concentration in the sediment (Table 2&3). This is similar to the findings of Amoo et al., 2005 and Sabo et al.,2008 where high concentration of metals were observed in sediment of Lake Kainji and River Gongola when compared with their surface water. The reason for this may not be unconnected with the fact that pollutant discharge into aquatic environment does not remain in aqueous phase but instead they adsorbed onto the sediment, since sediment serves as a sink for pollutants. The metals adsorbed to sediment are however remobilized back into surface water through changes in some physiochemical parameters such as temperature, pH and redox potential. The average physiochemical parameters of the study areas such as pH, Alkalinity and surface water temperature observed (Table 1) in the course of this study favour adsorption of the metals in the sediment rather than remobilization.

The mean value of Cu, Zn and Cr in water samples from the three sampling stations are below the FEPA/WHO threshold limits of 1.000mg/l, 3.000mg/l and 2.000mg/lrespectively while Pb, Mn and Ni in the water samples from the three sampling stations are above the WHO/FEPA limits of 0.01mg/l, 0.05mg/l and 0.02mg/l respectively. Fe in water samples from stations I & II are within the acceptable limit of FEPA/WHO of 0.300mg/l while the Fe mean value in water samples in station III is slightly above the threshold limit of FEPA/WHO.

The mean value of all the metals in the sediment collected at the three sampling stations exceed the GESAMP, 1982 and Solomon & Forstner, 1984 limits for unpolluted sediment except As and Mn that are below the recommended limits of 14µg/g and 770µg/g for unpolluted sediment. It is discernable from Table 4 that sediment of Ibeshe (Ikorodu) Lagos lagoon is highly polluted with all the studied heavy metals except As and Mn.

A critical look at the mean values of metal content in fish samples from all the three sampling stations (Table 4) revealed that all the studied metals are below the WHO threshold limits except Pb in station I & II that are above the threshold limits of WHO. The level of Pb observed in the studied fish poses no risk to public health but required constant monitoring.

The BCF determined for different metals revealed that bioaccumulation has occurred in the fish but not in alarming rate. This may be attributed to fact that *Crysichthys nigrodigitatus* is not a benthic fish that always have constant contact with the sediment and the average physiochemical parameters of Ibeshe; Lagos lagoon (Table 1) observed to be favourable to the adsorption of these (Fe, Cu, Pb, Cd, Zn, Cr, As, Mn and Ni) metals on to sediment rather than their remobilization. These reduce the level of heavy metals in surface water that are available for bioaccumulation in fish.

Conclusion

Although heavy metals in aquatic environment are from natural sources (soil formation), non point sources, transportation, domestic wastes, urban run-off, Agricultural practices and industries. Industrial activities such as industrial effluent discharge have been reported as a major contributing factor (Ademoroti and Sridhar, 1979, Abdel-Shafy and Abdel-Bashir, 1991, DeGregori *et al*., 1996, Agarwark, 1999 and Asia and Ademoroti, 2001).

Therefore, the appreciable level of heavy metals observed in the water, sediment, and fish (*Chrysichthys nigrodigitatus*) of Ibeshe (Ikorodu) Lagos lagoon has revealed the impact of the industrial effluent discharged on the Ibeshe in Lagos lagoon. This is a thing of concern as the presence of the following sets of metals (Pb, Mn & Ni), (Fe, Cu, Pb, Cu, Cd, Cr & Zn) & (Pb) were above their threshold limits in the studied water, sediment and fish respectively. Consequently, there is need for **NESTRA** and **Lagos Ministry of Environment** to embark on continual assessment of the effluent discharge of the industries situated at Ibeshe and other activities that could be injurious to human

health and the ecological integrity of the Ibeshe Lagos lagoon ecosystem.

The results reported in this study would also be expected to serve as baseline level for future heavy metal pollution status of the Ibeshe, Lagos Lagoon area.

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