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Seasonal Variation Assessment and Correlation Coefficent of Metal Pollutants in Sediments and Water from Porto Novo Lagoon Ecosystem, Benin Republic

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Abstract The study on concentrations of metal pollutants as an index of pollution in sediments and water samples of Porto-Novo Lagoon ecosystem was carried out for 12 months within two seasons (July-December 2014 and January-June 2015). Metal pollutants including Hg, Cd, Cu, Zn, Cr, Fe, Mn, Pd, Ni, Va, and Methyl mercury were investigated. This study employed the application of exploratory data analysis statistics, laboratory analysis and sampling techniques to reveal all tested metal pollutants and identify their sources. There is a significant difference in the metal pollutants in the sediments and water of Porto-Novo lagoon during rainy and dry seasons at 5% level of significance and correlation analysis showed that the mean concentration of metal pollutants in sediments and water were positive correlated values. The results proved that the sediments and water of Porto-Novo Lagoon are highly polluted with metal Pollutants, which might affect human health as well as the health of the ecosystem. National Priority List (NPL) on Porto-Novo Lagoon ecosystem is therefore, recommended for the revamping of the aquatic ecosystem.

Keywords: *porto-novo lagoon, metal pollutants, sediments, water, national priority list*

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1. Introduction

Environmental pollution has been increasing significantly over the recent years as a result of population explosion and industrial revolution that introduces lethal substances into the environment beyond the capacity the biosphere can accommodate and thus cause threat to environmental safety.

Anthropogenic and industrial activities in lacustrine areas play momentous roles in the introduction of pollutants into water bodies, causing colossal damage to aquatic ecosystems, leading to diminishing or total extinction of some economic important biota and can also pose a health risk to humans through food chains.

Contamination of aquatic ecosystems by heavy metals has been observed in sediment, water and aquatic flora and fauna [16].

Different aquatic organisms often respond to external contamination in different ways where the quantity and form of the element in water, sediment or food will determine the degree of accumulation (Langston & Spence, 1995).

Heavy metals were chosen as suitable pollutants because they are widespread environmental contaminants, from either natural or anthropogenic sources, and are widely believed to be a threat to the health and survival of many marines or aquatic animals, including crustaceans [1].

Heavy metals entering the aquatic ecosystem originate from different sources such as decay of plants and vegetation, atmospheric particulate, discharge of domestic and municipal wastes etc. [15].

The biological effect of trace metals in the lagoon ranges from beneficial stimulation to harmful retardation and death. Some trace metals including Cu, Mn, Fe and Zn are essential for good health and normal growth playing important roles in key metabolic activities in plants and animals.Such essential elements only become toxic when their concentration exceed the trace amounts required for normal metabolism [23].

Porto Novo Lagoon, an arm of Gulf of Guinea is located at the capital of Republic of Benin. The estimate terrain elevation above sea level is 0 metre. Latitude: 6°28'0.01" Longitude: 2°36'0"[38].. In Benin, the complex Porto-Novo Lagoon is one of the largest lake in West Africa with high productivities and exploitation with the sea, and run parallel to the coast behind the dune systems [38].

The biodiversity of this freshwater ecosystem is very high with large diversity of fish, mollusks, shellfishes, birds and amphibians [38].

Due to its geographical position, the complex lagoon becomes a receptacle in which all rejected water from gutter, sewage, waste water from surrounding cities such as Cotonou, Abomey-Calavi, So-Ava are emptied. Also, urban concentrations of population due to increased urbanization, anthropogenic activities and garbage deposits along the lagoon banks are the main cause of the complex pollution by trace metals and other toxic substances [38].

2. Material and Methods

2.1. Study Site

The Lagoon of Porto-Novo is a basin of up to 6meters, located in the South-East of the Republic of Benin (6º 27'N, 2º 36'E), Porto-Novo lagoon has a surface area of 17.52 km^2 and maximum length of 6km and maximum width of 4km (Figure.1). Porto-Novo lagoon is linked to Nokoue lagoon in the east through tatche where Porto-Novo lagoon receives the major inflow which characterizes the main hydrological regime of Porto-Novo lagoon seasonal tidal and salinity range.

2.2. Sampling Design and Operation

Porto-Novo Lagoon was divided into 12 sampling stations. The stations were accurately located by using Garmin GPS model 72H and in each sampling station, sediments and water samples were taken by stopping and anchoring outboard wooden boat. The sampling period was dictated by the two hydrological seasons, the first during raining season (July-December 2014) and dry season (January-June 2015) to obtain two sets of samples.

2.3. Sampling Location

Each sampling station was identified by using hand-held GPS and site selection was done based on morphological features of Porto Novo lagoon ecosystem with emphasis on all the point and non-point sources. The primary data being collected from 12 sampling stations from Porto Novo Lagoon that were carefully selected with emphasis on upstream, mid-stream and down-stream and the surrounding municipalities. Sediments and water samples were taken from each sampling stations as identified by GPS. All the chains of custody and quality assurance and quality control involve in aquatic pollution study were duly observed.

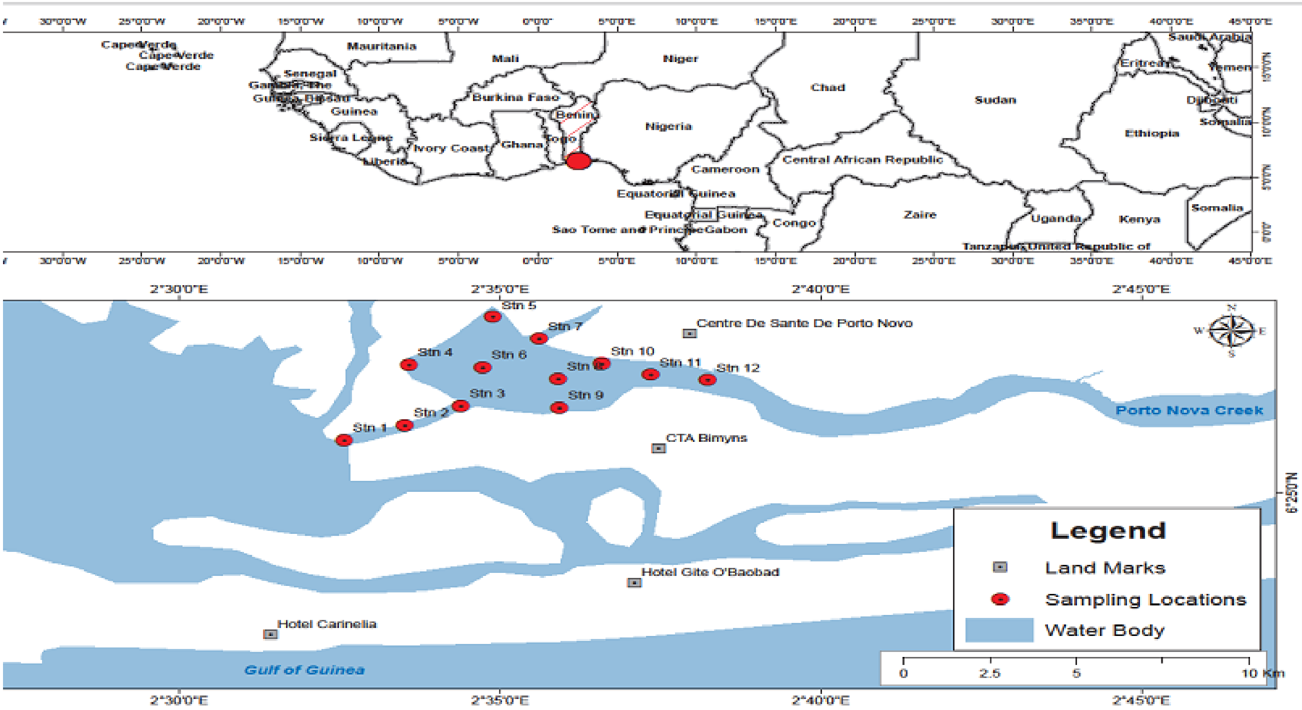

Figure 1. Goe-Referenced Points on Porto-Novo Lagoon Ecosystem

3. Collection of Water and Sediment

Collection of sediments and water samples was carried out from Porto-Novo lagoon (n=12). The sediments were hauled with the aid of Soil Grab (25tonnes) and, ¼ of sediments was removed and homogenized and kept in polythene bags. Water samples were taken with the aid of water sampler at the depth of half meter from the water surface and were poured into the plastic bucket, stirred gently and filled 1 liter sterile plastic container and fixed with 1ml of Nitric acid. This was repeated for all the n=12 by relying on geo-referenced locations of each sampling stations. All are stored in an iced cooler (<4°C) for the analyses of selected metal pollutants cited by [2]. Metal pollutants that were investigated during the period in view are: Hg, Cd, Cu, Zn, Cr, Fe, Mn, Pd, Ni, Va, and methy mercury.

4. Analytical Methods

Extraction of metal pollutants in sediments and water for metal pollutants were carried out respectively using Atomic Absorption Spectrophotometer (Model Thermo Electron Corporation, S series AA Spectrometer with Gravities furnace, UK) [4]. Extraction of closely held fraction of metal pollutants in the bottom sediments was carried out as described by [35]. Water samples that were fixed with HCl were de-fixed. 25ml of water sample was measured into a conical flask of about 250ml capacity .Heat at a temperature not more than 120°C until the sample is about 5ml and allow to cool Filter using wotman I filter paper into a 50ml standard volumetric flask. Make up to mark and set the sample for AAS (calibrated) for Trace Metals reading.

5. Statistical Analyses

To evaluate the correlation coefficient in the concentration of different metal pollutants between the sediments and water within the stations and seasons, one-way ANOVA and Duncan multiple tests were used. A probability of at level 0.05 or less was considered significant.

6. Results and Discussion

The seasonal analyses of Porto-Novo Lagoon sediments and water samples revealed that all metal pollutants detected were present in measurable concentrations and varied in between twelve sampling stations and two seasons. Three factors variance analysis were employed in the investigation (seasons, locations and metal pollutants). The results obtained are discussed based on international standards permissible limits of ([13,17,21,32,37]) as shown in the tables and also discussed from the view point of literature review.

Table 1. METAL POLLUTANTS CONCENTRATIONS (μg/g) IN SURFICIAL SEDIMENTS FROM PORTO NOVO LAGOON BETWEEN JULY-DECEMBER 2014

GEO-REF	METAL POLLUTANTS μg/g dry wt											
	Hg	Cd	Cu	Zn	Cr	Fe	Mn	Pd	Ni	Va	MH_3Hg	TOTAL
STATION 1	0.04	10.9	9.1	80.7	34.7	688.6	903.8	8.36	13.3	0.28	0.01	1749.79
STATION 2	0.13	10.4	19.1	169.9	48.7	15,126	2,135	28	20	BDL	0.032	17557.262
STATION 3	0.15	14.7	24.9	203.3	88.8	4,299.30	541.30	27.00	16.20	0.39	0.038	5216.078
STATION 4	0.11	11.9	20.3	141.4	47.8	12,991.80	24,858.30	23.50	18.80	0.32	0.028	38114.258
STATION 5	0.13	16.4	21.2	160.1	87.1	14,731.10	519.70	9.00	15.30	0.01	0.033	15560.073
STATION 6	0.05	13.7	18.6	86.9	46.6	10,589.60	119,616.68	8.20	16.80	0.05	0.013	130397.193
STATION 7	0.04	11.4	35.2	296.7	97.4	21,725.20	782.00	27.70	15.20	0.03	0.01	22990.88
STATION 8	0.04	10.9	25	104.7	50.3	27,926.50	186,099.00	27.20	20.30	0.03	0.01	214263.98
STATION 9	0.05	11.5	23.5	138.8	71.8	21,140.50	650.17	18.80	17.20	0.03	0.013	22072.363
STATION 10	0.07	6.2	20.9	90.3	64.3	17,866	157,062	37	25	BDL	0.018	175171.788
STATION 11	0.06	6.7	24	170.4	99.7	2,899.00	594.50	37.70	9.80	0.03	0.015	3841.905
STATION 12	0.04	5.9	11.8	103.4	51.6	27,183.00	30,306.00	16.70	13.80	0.01	0.01	57692.26
TOTAL	0.91	130.6	253.6	1746.6	788.8	177166.6	524068.5	269.16	201.7	1.18	0.23	704627.83
AVERAGE	**0.08 ±0.04^{b}**	**10.88 ±3.29^{b}**	**21.13 ±6.63^{b}**	**145.55 ±61.65^{b}**	**65.73 ±22.49^{b}**	**14763.88 ±9021.83^{b}**	**43672.38 ±68930.76^{a}**	**22.40 ±10.30^{b}**	**16.73 ±3.79^{b}**	**0.12 ±0.14^{b}**	**0.02 ±0.01^{b}**	
Permissible Level	****0.13**	***0.6-10.0**	***16-110**	***120-820**	****37.3**	*****5000**	***46.0-110**	***31-250**	****18**	**(0.04-220)**	****0.1**	

* According to persaud , *et,al* 1990, ** According to Friday, 1990 and 2005 (Revised), *** LASEPA, 2001, BDL; Below detectible level, (ATSDR).

Table 2. METAL POLLUTANTS CONCENTRATIONS (μg/g dry wt) IN SURFICIAL SEDIMENTS OF PORTO NOVO LAGOON BETWEEN JANUARY-JUNE 2015

GEO-REF.	METAL POLLUTANTS μg/g dry wt											
	Hg	Cd	Cu	Zn	Cr	Fe	Mn	Pd	Ni	V	MH_3Hg	TOTAL
STATION 1	0.01	1.84	12.8	129.6	5.86	610.8	594.4	1.41	2.25	0.05	0.002	1359.022
STATION 2	0.02	1.76	46.7	280.4	8.23	133,727	690	5	3	BDL	0.006	134762.116
STATION 3	0.03	2.48	35.1	326.5	15	4,785.60	174.00	4.60	2.73	0.07	0.006	5346.116
STATION 4	0.02	2.01	22.5	188.7	8.08	87,414.25	760.33	3.89	3.18	0.05	0.005	88403.015
STATION 5	0.02	2.77	29.9	257.1	14.7	16,397.19	167.80	1.52	2.59	0.00	0.006	16873.596
STATION 6	0.01	2.32	10.9	144.4	7.88	48,441.50	768.61	1.39	2.84	0.01	0.003	49379.863
STATION 7	0.01	1.93	49.6	476.5	16.5	24,182.32	252.58	4.68	2.57	0.01	0.002	24986.702
STATION 8	0.01	1.84	78.2	218.6	8.5	69,442.75	641.19	4.60	3.60	0.01	0.002	70399.302
STATION 9	0.01	1.94	33.1	222.9	12.1	23,531.50	210.00	3.18	2.91	0.01	0.002	24017.652
STATION 10	0.01	1.05	4.98	112.5	10.9	57,045	356	6	4	BDL	0.003	57540.443
STATION	0.01	1.13	33.8	273.7	16.8	3,284.86	192.02	6.37	1.66	0.01	0.003	3810.363
STATION 12	0.01	1	39.9	166.1	8.72	86,698.00	436.20	2.82	11.67	0.00	0.002	87364.422
TOTAL	0.17	22.07	397.48	2797	133.27	555560.8	5243.13	45.46	43	0.22	0.042	564242.612
AVERAGE	0.01 ±0.01^{b}	1.84 ±0.56^{a}	33.12 ±19.91^{a}	233.08 ±101.05^{a}	11.11 ±3.80^{a}	46296.67 ±41761.68^{a}	436.92 ±241.02^{a}	3.78 ±1.75^{a}	3.60 ±2.62^{a}	0.02 ±0.02^{a}	0.00 ±0.00^{a}	
Permissible Level	****0.13**	***0.6-10.0**	***16-110**	***120-820**	****37.3**	*****5000**	***460-110**	***31-250**	****18**	**(0.04-220)**	**0.1	

* According to persaud , *et,al* 1990, ** According to Friday, 1990 and 2005 (Revised), LASEPA, 2001, BDL; Below detectible level, (ATSDR)

The sequence of occurrence of metal pollutants in the sediment of Porto Novo Lagoon during rainy season as shown in Table 1 Mn> Fe> Zn> Pd> Cr> Cu> Ni> Cd> Va> Hg> MH_3Hg. And during dry season as shown in Table 2 Fe> Mn> Zn> Cu> Cr> Pd> Ni> Cd> Va> Hg> MH_3Hg. While Table 3 and Table 4 shows the sequence of occurrence of metal pollutants in the water of Porto Novo Lagoon during raining and dry seasons respectively. (Table 3) Fe> Mn> Pd> Zn> Cr> Ni> Cd> Va> Cu> Hg>

MH_3Hg. And (Table 4) Fe> Mn> Zn> Cd> Pd> Cu> Hg >.MH_3Hg.

All the metal pollutants investigated are above the permissible limits. The permissible limits in microgram/gram dry weight for all the metal pollutants investigated in sediments are as follows: Hg=0.13, Cd=0.6-10, Cu=16-110, Zn=120-820, Cr=37.3, Fe=5000, Mn=46-110, Pd=31-250, Ni=18, Va=0.04-220, MH_3Hg=0.1. The permissible limits in microgram/l for all the metal pollutants investigated in water are as follows: Hg=0.1, Cd=0.01, Ca=1.0, Zn=1.0, Cr=1.0, Fe=1.0, Mn=0.05, Pd=0.05, Ni=25-150, Va=0.04-220, MH_3Hg=0.0028. This may not be unconnected with anthropogenic, commercial and industrial activities in and around Porto-Novo lagoon ecosystem. Metal pollutants concentration in Porto-Novo Lagoon ecosystem from twelve different stations and seasons are illustrated in Table 1, Table 2, Table 3 and Table 4.

Table 3. METAL POLLUTANTS CONCENTRATIONS (mg/l)IN WATER FROM PORTO NOVO LAGOON BETWEEN JULY-DEC 2014

GEO-REF	METAL POLLUTANTS											TOTAL
	Hg	Cd	Cu	Zn	Cr	Fe	Mn	Pd	Ni	Va	MH_3Hg	TOTAL
STATION 1	0.004	0.040	0.030	0.400	0.490	9.180	0.570	0.750	0.250	0.030	0.001	11.745
STATION 2	0.005	0.230	0.050	0.330	0.500	8.000	0.500	1.000	0.500	BDL	0.001	11.116
STATION 3	0.008	0.230	0.072	1.000	0.830	11.670	1.200	1.100	0.160	BDL	0.002	16.272
STATION 4	0.005	0.230	0.020	0.600	0.500	16.000	1.000	0.330	0.160	BDL	0.001	18.846
STATION 5	0.008	0.300	0.030	0.500	0.500	25.670	1.000	0.330	0.160	BDL	0.002	28.5
STATION6	0.012	0.180	0.050	0.270	0.370	6.820	0.550	0.320	0.220	BDL	0.003	8.795
STATION 7	0.008	0.300	0.040	0.670	0.330	9.500	1.200	0.500	0.160	0.040	0.002	12.75
STATION 8	0.007	0.230	0.020	0.330	0.330	7.000	1.000	0.330	0.160	0.160	0.002	9.569
STATION 9	0.010	0.230	0.010	0.330	0.330	12.160	1.000	0.660	0.160	BDL	0.003	14.893
STATION 10	0.012	0.230	0.010	1.000	0.500	13.330	1.260	1.000	0.160	BDL	0.003	17.505
STATION 11	0.012	0.230	0.030	1.000	0.500	27.670	1.000	0.330	0.330	BDL	0.003	31.105
STATION 12	0.012	0.230	0.170	0.500	0.500	30.170	1.200	0.330	0.160	BDL	0.003	33.275
TOTAL	0.103	2.66	0.532	6.93	5.68	177.17	11.48	6.98	2.58	0.23	0.026	214.371
AVERAGE	0.01 ±0.00[b]	0.22 ±0.07[b]	0.04 ±0.04[b]	0.58 ±0.28[b]	0.47 ±0.14[b]	14.76 ±8.37[a]	0.96 ±0.27[b]	0.58 ±0.31[b]	0.22 ±0.10[b]	0.08 ±0.07[b]	0.00 ±0.00[b]	
Permissible Level	**0.1	*0.01	*1.0	*1.0	**1.0	*1.0	*0.05	*0.05	**25-150	**0.04	**0.0028	

* USEPA, 1986. **According to Friday, 1990 and 2005 (Revised). BDL: Below detectable level.

Table 4. METAL POLLUTANTS CONCENTRATIONS (mg/l) IN WATER FROM PORTO NOVO LAGOON BETWEEN JAN-JUN 2015

GEO-REF	METAL POLLUTANTS											TOTAL
	Hg	Cd	Cu	Zn	Cr	Fe	Mn	Pd	Ni	V	MH_3Hg	TOTAL
STATION 1	0.0022	0.02	ND	0.538	ND	8.51	0.3	0.02	BDL	BDL	0.00055	9.39075
STATION 2	0.002	0.15	0.116	0.837	ND	7.796	1	0	BDL	BDL	0.0005	9.9015
STATION 3	0.004	0.18	0.035	0.838	ND	10.55	0.50	0.03	BDL	BDL	0.001	12.138
STATION 4	0.003	0.17	0.0162	0.543	ND	13.867	0.70	0.14	BDL	BDL	0.00075	15.43995
STATION 5	0.004	0.15	ND	0.655	ND	20.76	0.40	0.01	BDL	BDL	0.001	21.98
STATION6	0.006	0.14	ND	0.873	ND	18.381	0.75	ND	BDL	BDL	0.0015	20.1515
STATION 7	0.005	0.13	ND	0.86	ND	8,55	0.60	ND	BDL	BDL	0.00125	1.59625
STATION 8	0.004	0.15	ND	0.854	ND	10.392	0.62	ND	BDL	BDL	0.001	12.021
STATION 9	0.001	0.155	ND	0.575	ND	10.08	0.50	ND	BDL	BDL	0.00025	11.31125
STATION 10	0.007	0.165	ND	0.567	ND	9.422	0	ND	BDL	BDL	0.00175	10.16275
STATION 11	0.005	0.19	ND	0.575	ND	22.76	0.51	ND	BDL	BDL	0.00125	24.04125
STATION 12	0.009	0.13	ND	0.625	ND	4.736	34.81	ND	BDL	BDL	0.00225	40.31225
TOTAL	**0.0522**	**1.73**	**0.1672**	**8.34**	**ND**	**137.254**	**40.69**	**0.2**	BDL	BDL	**0.01305**	**188.44645**
AVERAGE	**0.00 ±0.00[c]**	**0.14 ±0.04[c]**	**0.06 ±0.05[c]**	**0.70 ±0.14[b]**		**12.48 ±5.76[a]**	**3.40 ±9.89[b]**	**0.12 ±0.16[c]**	-	-	**0.00 +0.00[c]**	
Permissible Level	****0.1**	***0.01**	***1.0**	***1.0**	**1.0	***1.0**	***0.05**	***0.05**	****25-150**	****0.04**	****0.0028**	

*USEPA, 1986. **According to Friday, 1990 and 2005 (Revised). BDL: Below detectable level.

6.1. Metal Pollutants in the Sediment

The seasonal occurrence of metal pollutants in Porto-Novo Lagoon sediments are illustrated in Table 1 and Table 2. The metal pollutants concentration were found in the following sequence Mn> Fe> Zn> Pd> Cr> Cu> Ni> Cd> Va> Hg> MH_3Hg in raining season while in dry season, it follows this order Fe> Mn> Zn> Cu> Cr> Pd> Ni> Cd> Va> Hg> MH_3Hg.The difference among the two seasons in metal pollutants is momentous as shown in Table 1 and Table 2 above.

The inconsistency in the concentrations of metal pollutants in all the sediments collected from the twelve sampling stations can be attributed to the large area sampled and the heterogeneous nature of the sediments of which the texture and trace metals contents could vary within the scale of millimeters as elucidated by [8].

Also, attraction of some metal pollutants to the sediments texture such as clay could be responsible for the elevated concentrations of some metal pollutants such as Cu, Fe, Ni, Pb, V and Zn in the Porto-Novo lagoon complex sediments being the natural large vessel and sedimentary basin for the metal pollutants in the catchment areas and the significant influence of the sediments texture on retention and bioavailability of metal pollutants as mentioned by [20] and [24].

The lower concentrations of some metal pollutants especially water soluble metals during the raining season may be attributed to the massive dilution of fresh water brought into the lagoon from inland rivers. This is in agreement with the work of [6]. This dilution may enhance flushing of more metal pollutants to downstream via water current. While the high concentrations of other metal pollutants during raining season may be attributed to flood water which is loaded with eroded materials from the different geomorphologic zones as stated by [3], the presence of metal pollutants in Porto-Novo lagoon in high concentrations may also be due to urban concentrations of population due to increased urbanization, anthropogenic activities and garbage deposits along the lagoon banks which are the main cause of the complex pollution by trace metals and other toxic substances as mentioned by [38].

The high total value of Pb and Cd in the sediments of Porto-Novo Lagoon might be accredited to industrial and agricultural discharge from run-off and fuel spillage from fishing/navigational boats as well as from oil bunkering [34].. However, concentrations of Pd in Porto-Novo Lagoon can also be traceable to emission from petrol combustion of automobile cars from the city [19].

Table 1 and Table 2 show that Mn, Fe, Cr, Zn and Cu are the most abundant metal pollutants in the complex sediments of Porto-Novo Lagoon. This disagrees with the work of [38] which stated that Mercury, lead and Zinc are the most abundant metals in the complex sediments.

6.2. Metal Pollutants in Water

Metal pollutants concentrations in the Porto-Novo Lagoon water during the two hydrological periods from twelve sampling stations are illustrated in Table 3 and Table 4 and are present in the following order (Table 3) Fe> Mn> Pd> Zn> Cr> Ni> Cd> Va> Cu> Hg> MH_3Hg. (Table 4) Fe> Mn> Zn> Cd> Pd> Cu> Hg > MH_3Hg.

The discrepancy in the concentrations of metal pollutants in the water of Porto-Novo lagoon from twelve sampling stations during the hydrological cycle can be attributed to the large area sampled and the heterogeneous nature of the sediments of which the texture and trace metals contents could vary within the scale of millimeters as elucidated by [8]. Also, Lagoon water motion inform of surface and internal currents brought by wind and in-flow from Nouke lagoon could contribute to variations in metal pollutants in all the twelve sampling stations.

“Mouth rooting” of some benthic animals in search of food, nest building or for social gathering which causes upwelling of some sedimentary materials can be attributed to disparity in concentration of metal pollutants between the twelve stations during the study periods.

However, the trapped metal pollutants in the sediments of Porto-Novo lagoon ecosystem that are persistently leaching out as a result of solubility tendency of water and the reaction of most water soluble metals could be one of the many sources in which metal pollutants are found in lagoon water complex of Porto-Novo. This confirms the work of [35] which stated that there is a significant concentration in the biogeochemistry of trace metals from interconnected aquatic ecosystems, atmospheric deposition which may serve as an important pathway of trace metal influx to Porto-Novo lagoon ecosystem. The geochemistry and bioavailability of trace metals are strongly influenced by speciation.

Manganese and Iron are the most abundant metal pollutants in the water of Porto-Novo lagoon, their sources to lagoon water may be from underground pollution from the sediments and industrial activities and burning of gasoline in automobile from the city. Manganese is seldom found alone in water supply. It is frequently found in iron-bearing and steel manufacturing as described by [9].

Vanadium occurs naturally, but its concentrations in Porto-Novo Lagoon water is the use of it in producing rust-resistant, spring, and high-speed tool steels for in-board and outboard engine canoes use for navigation. It is an important carbide stabilizer in making steels [5].

Pb and Cd in the water of Porto-Novo Lagoon are above the threshold limit this perhaps may be due to raw sewage from shanty houses on the lagoon, industrial and agricultural discharge from run-off and fuel spillage from fishing/navigational boats as well as from oil bunkering ([25,34]) and emission from petrol combustion of automobile cars from metropolis as reiterated by [19]. However, concentrations of Pd in Porto-Novo Lagoon can also be traceable to lead (Pd) sinkers attached to fishing nets by fishermen.

Cu and zinc have an elevated concentration in Porto-Novo lagoon ecosystem. Much of the copper that enters environmental waters will be associated with particulate matter. Copper is a natural constituent of soil and will be transported into streams and waterways in runoff either due to natural weathering or anthropogenic soil disturbances [5]. Zinc and its compounds are found in the earth's crust and are present in most rocks, certain minerals, and some carbonate sediments. As a result of weathering of these materials, soluble compounds of zinc are formed and may be released to water [29].

High concentrations of Cu and Zinc could be as a result of release originated from domestic waste water, combustion processes, wood production, phosphate fertilizer production, and natural sources (e.g., windblown dust, volcanoes, decaying vegetation, forest fires, sea spray, etc.) [31]. Zinc is commonly found in the earth's crust, and natural releases to the environment can be significant. In addition, zinc is one of the most widely used metals in the world. The major industrial sources of zinc include electroplating, smelting and ore processing, and drainage from both active and inactive mining operations [27].

Total concentrations of Chromium and Nickel are respectively above the threshold in the water of Porto-Novo lagoon. On a worldwide basis, the major chromium source in aquatic ecosystems is domestic waste water effluents (32.2% of the total) [7]. The other major sources are metal manufacturing (25.6%), ocean dumping of sewage (13.2%), chemical manufacturing (9.3%), smelting and refining of nonferrous metals (8.1%), and atmospheric fallout (6.4%) [29]. Nickel is a natural constituent of soil and is transported into streams and waterways in runoff either from natural weathering or from disturbed soil. Much of this nickel is associated with particulate matter [5]. Nickel also enters bodies of water through atmospheric deposition. Emission factors have been estimated for the release of trace metals to water from various source categories and these have been used to estimate inputs of these metals into the aquatic ecosystem. The global anthropogenic input of nickel into the aquatic ecosystem for 1983 is estimated to be between 33 and 194 million kg/year with a median value of 113 million kg/year [29].

Concentration of Mercury and Methyl mercury in Porto-Novo lagoon ecosystem are above the allowable limit of [13] and [17] respectively. Atmospheric deposition of elemental mercury from both natural and anthropogenic sources has been identified as an indirect source of mercury to surface waters [37]. Surface runoff is an important mechanism for transporting mercury from soil into surface waters, particularly for soils with high humic content [26].

Mercury may also be released to surface waters in effluents from a number of industrial processes, including chloralkali production, mining operations and ore processing, metallurgy and electroplating, chemical manufacturing, ink manufacturing, pulp and paper mills, leather tanning, pharmaceutical production, and textile manufacture ([12,13]).

On the other hand, the most important transformation process in the environmental fate of mercury in surface waters is biotransformation. Photolysis of organomercurials may also occur in surface waters, but the significance of this process in relation to biotransformation is not clear [10]. Any form of mercury entering surface waters can be microbially converted to methylmercuric ions, given favorable conditions. Sulfur-reducing bacteria are responsible for most of the mercury methylation in the environment [18].

6.3. Correlation Coefficient of Metal Pollutants in Sediments and Water

In Table 5, the metal pollutants in sediments and water show that there is a positive correlation between metal pollutants in sediments in July-Dec and Jan-June but it is not significant at P=0.05. There is a significant positive correlation between metal pollutants in water in July-Dec and Jan-June at P=0.05 level of significance.

Table 5. CORRELATION OF METALS POLLUTANTS IN SEDIMENT AND WATER FROM PORTO-NOVO LAGOON ECOSYSTEM

Variables Correlated	Coefficient	P-value	Relationship Type
Metals in sediment in 2014 and 2015	0.134	0.125	Positive, not significant at 5% level
Metals in water in 2014 and 2015	0.671**	0.000	Positive, significant at 5% level
Metals in sediment and water 2014	0.130	0.139	Positive, not significant at 5% level
Metals in sediment and water in 2015	0.431**	0.000	Positive, significant at 5% level

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

There is a positive correlation between metal pollutants in sediments and water in July-Dec but it is not significant at 5% level. There is a significant positive correlation between metal pollutants in sediments and water in Jan-June at 5% level of significance. The level of significance between the two hydrological cycle explained the influence of dilution of rain water during the raining season (July-Dec) as compared to dry season (January-June).

The metal pollutants concentrations in sediment are greater than the metals concentrations in water on the average in July-December .On the other hand, the metal pollutants concentrations in sediment do not have significant correlation with the metals concentrations in water at 5% level in the period under review.

The metal pollutants concentrations in sediment are greater than the metals concentration in water on the average in January-June. This shows that the metal pollutants in sediments do not have significant correlation with the metal pollutants in water at 5% level in the period under review. However, at 10% level of significance, Zn in sediment has a positive correlation with the Zn in water. The concentrations of Hg, Cd, Cu, Zn, Cr, Fe, Mn, Pd, Ni, Va, and Methyl mercury in the sediments and water of Porto-Novo Lagoon show evidence of a seasonal and station base fluctuation.

The inconsistency in the concentration of metal pollutants in the water and sediments of Porto-Novo lagoon from twelve sampling stations during a complete hydrological cycle established inimitable seasonal pattern with highest concentration during the dry season and lowest during the wet season. This is in agreement with the studies of [28] and [14] respectively.

7. Conclusion and Recommendation

Analytical laboratory analysis using AAS and exploratory data analysis revealed that all tested metal pollutants are presents in the sediments and water of Porto-Novo lagoon ecosystem and they are above International standard permissible limits that are enough to pose health risk to the aquatic life and human being. It is therefore recommendation that Porto-Novo Lagoon should be put on National Priority List (NPL) for adequate environmental revamping and protection.

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