1. Introduction

Water is undeniably the most significant and abundant natural resource in the biosphere such that it influences human and animal migration and their eventual settlement, history has it that many great civilizations sprang up along the coast (Shillington, 2013) because it manifests its uses in agriculture, household, recreation, environment, industry and transport as is obtainable in this study.

More so, all living organisms are built by tissues with over 60 percent water content and they use aqueous solutions like blood and digestive juices as media for carrying out their biological functions (Narayanan, 2007). By implication heavy, metals in water can gain entrant into the internal body system of plants and animal which poses a great risks, as well as the depletion of dissolved oxygen in water will have adverse effect on biodiversity which alters the feedback loops called homeostatic mechanisms (Rao, 2006). Water quality and effects are attributable to its physical and physicochemical properties which changes as it flows along its path collecting pollutants from natural sources, as well as anthropogenic (man-made) sources which originate from non-point and point sources, namely; domestic sewage, industrial sewage, storm sewage, agricultural sources, mining waste, atmospheric deposition (Narayanan, 2007).

All metals are relatively soluble in water (Peavey et al., 2014) and is further categorized as toxic and nontoxic metals of which nontoxic are those that are harmful in excessively high quantity while toxic metals are those metals that are harmful when found in small quantities. . As metals are non-biodegradable and can accumulate in the human body system causing damage to the nervous system and internal organs (Goel, 2006). The shipping and industrial activities at the Federal Lighter Terminal has made the Okpokiri River very busy, and as such, prone to wastewater discharge with heavy metals deposits and other pollutants and the eventual abandoned broken down boats, ships and vessels.

This paper seeks to ascertain the distribution of the heavy metals present and Dissolved Oxygen (DO) concentration along Okpokiri River Stretch as a result of the heavy industrial activity coupled with the rusting vessels. The results obtained would be compared with the Federal Ministry of Environment (FMEnv) and Department of Petroleum Resources (DPR) established standards.

2. Materials and Methods

2.1 Description of Study Area

The area of study is a river stretch of Okpokiri river which is located at the Federal Lighter Terminal, Onne, and lies between latitudes 04^{o} 41' 48" N, 007^{o} 10' 42"E to 04^{o} 41 '44" N, 007^{o} 10' 46" E. It flows from the Atlantic Ocean and meanders through Bonny Island, Sara community, where it further distributes to the federal ocean terminal at Onne,

This site is a conduit for heavy shipping, and industrial activities that discharge unwanted chemical substance into the river coupled with the decaying and rusting broken down ships or vessels.. Plates 1 and 2 is a pictorial of the study area while Table 1 shows the sampling points and location.

Plate 1: Overall view of Okpokiri River.

Plate 2: Berthed ships and fishing boats

2.2. Sample Collection

Water samples were collected from five sampling points at the disparity of 100m each both at the surface with bottles and the sediment with an eckman grab along the river stretch from bank to bank. As a standard practice ,the surface and bottom samples for heavy metals analysis specifically were acidified to pH of 2 with (1ml) concentrated nitric acid (HNO_3) per litre to prevent precipitation of metal ions. The dissolved oxygen data was obtained by the use of a hand held dissolved oxygen meter (Hanna).

TABLE 1: COORDINATES OF SAMPLE POINTS.

WATER SAMPLES	PARAMETER	NORTHING	EASTING	ACTIVITY
S.P. 1.	Surface water and Sediment.	04^{o} 41'48"	007^{o} 10'42"	Berthing area /highest region of industrial activity.
S.P. 2.	Surface water and Sediment.	04^{o} 41'47"	007^{o} 10'43"	Lower level of industrial activity.
S.P. 3.	Surface water and Sediment.	04^{o} 41'46"	007^{o} 10'44"	Transportation route with boats and vessels.
S.P. 4	Surface water and Sediment.	04^{o}41'45"	007^{o}10'45"	Some abandoned vessels.
S.P. 5	Surface water and Sediment.	04^{o}41'44"	007^{o}10'46"	Typical riverine settlement with associated activities and abandoned caravans.

2.3 Analytical Methods

The surface and bottom samples were acidified and put in a cooler full of ice so as to maintain wholesomeness.. Thereafter, the samples were allowed to attain room temperature for analysis. The Dissolved Oxygen (DO) was obtained with an oxygen meter device known as (Hanna), pH of the collected sample was obtained with a pH meter with glass electrode model PHS-25, the Nessler's comparator was used to obtain the colour values, biological oxygen demand (BOD) and chemical oxygen demand (COD) (open reflux), was determined by titrimetric according to standard methods (APHA, 1998). Heavy Metals were determined by atomic absorption spectrophotometer, Buck Scientific model 200A.

3. Results and Discussion

Table 1: Physico-Chemical Analysis of Surface Water Samples

S/N	PARAMETERS	SW1	SW2	SW3	SW4	SW5	MINIIMUM SAMPLE DATA.	MAXIMUM SAMPLE DATA	MEAN	DPR/FMEnv LIMITS
1.	**pH**	8.82	9.10	8.82	8.61	8.67	8.61	9.10	8.800	6.5-8.5
2.	**Temp (^{o}C)**	30	29	26	25	27	25	30	27.400	25
3.	**Cr(mg/l)**	0.016	<0.001	0.014	<0.001	<0.001	0.00	0.016	0.006	0.03
4.	**Salinity (mg/l)**	1,108	1,008	800	984	900	800	1108	960.000	600
5.	**DO(mg/l)**	4.1	3.1	4.1	3.71	4.1	3.1	4.1	3.822	5.0
6.	**Colour**	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
7.	**Turbidity (NTU)**	2.011	1.600	1.300	1.54	1.39	1.300	2.011	1.568	10
8	**Hg (mg/l)**	<0.0001	-	<0.0001	-	-	<0.0001	<0.0001	<0.0001	0.0005
9.	**Pb (mg/l)**	0.011	0.007	0.013	<0.001	<0.001	0.000	0.013	0.006	0.01
10.	**Cd (mg/l)**	0.004	<0.001	0.015	<0.001	0.002	0.000	0.015	0.004	0.005
11.	**Ni (mg/l)**	0.020	0.010	0.029	0.010	0.011	0.010	0.029	0.016	0.015
12.	**V (mg/l)**	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	NA
13.	**Zn (mg/l)**	1.39	0.70	1.80	1.98	1.28	0.70	1.98	1.430	1.0
14.	**Fe (mg/l)**	2.03	1.69	1.50	2.01	1.63	1.50	2.030	1.772	1.0
15.	**Cu (mg/l)**	0.039	0.02	0.03	<0.001	0.011	0.000	0.039	0.020	0.01
16.	**THC (mg/l)**	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.1
17.	**As (mg/l)**	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.05
18.	**Ag (mg/l)**	0.057	0.048	0.057	0.061	0.048	0.048	0.061	0.054	NA
19.	**BOD_5 (mg/l)**	3.870	3.011	2.870	3.490	3.753	2.870	3.870	3.399	10
20.	**COD (mg/l)**	5.305	5.017	4.307	5.373	5.730	4.307	5.730	5.146	10

Table 2: Physico-Chemical Analysis of Sediment Samples

S/N	PARAMETERS	SEDI	SED2	SED3	SED4	SED5	MINIMUM SAMPLE DATA	MAXIMUM SAMPLE DATA	MEAN	DPR/FMEnv LIMITS
1.	**pH**	4.25	4.37	4.29	4.90	5.60	4.250	5.600	4.682	6.5-8.5
2.	**Moisture (%)**	68.95	61.32	69.55	72.80	73.55	61.320	73.550	69.23	NA
3.	**Cr (mg/l)**	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.03
4.	**THC (mg/l)**	3.02	1.38	0.40	1.73	1.26	0.400	3.020	1.558	0.1
5.	**TPH (mg/l)**	4.94	0.99	0.03	0.09	<0.001	0.000	4.940	<0.001	NA
6.	**Hg (mg/l)**	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.0005
7.	**Pb (mg/l)**	4.18	2.90	0.44	2.16	<0.001	0.000	1.936	1.936	0.01
8.	**Cd (mg/l)**	0.15	0.03	<0.001	0.11	<0.001	0.000	0.058	0.058	0.005
9.	**V (mg/l)**	0.011	0.010	0.012	0.087	<0.001	0.000	0.024	0.024	1.0
10.	**As (mg/l)**	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.05
11.	**Ni (mg/l)**	0.082	0.035	0.042	0.019	0.016	0.016	0.039	0.039	0.015
12.	**Ag (mg/l)**	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	NA
13.	**Mn (mg/l)**	0.4	0.29	0.49	0.20	0.01	0.010	0.278	0.278	0.5
14.	**Zn (mg/l)**	8.83	5.63	0.91	2.16	1.09	0.910	8.830	3.724	1.0
15.	**Fe (mg/l)**	14.26	12.01	7.21	5.10	3.04	3.040	14.260	8.324	1.0
16	**Cu (mg/l)**	8.12	5.01	1.03	3.06	2.09	1.03	8.12	3.86	0.01

The results of the key surface water quality indicators presented in Tables 1 and 2 shows that the pH and temperature values are above the DPR limits. This may be attributed to the activities, the demineralization and thermal process and the rains that bring materials and water from different sources into the river. Turbidity may be due to the entrant of materials washed in by flood and flowing rivers over rocks, towns and industrial areas . Turbidity values in the study area were very low and much below the DPR limits.

. The Total Hydrocarbon Content concentrations from sample results are in trace quantities (<0.01ppm). Thus, a very minimal pollution due to leakages and seepages from vessels offloading or back loading products of the surface water; hence there is no adverse impact from the operations of the Terminal on the surface water body.

The level of dissolved oxygen is a very important factor for the survival of aquatic plants and animals. The Dissolved Oxygen (DO) values measured were 3.1 to 4.1mg/l. The measured DO levels of the surface water were within DPR and FMEnv's recommended minimum of 5mg/l. This shows that the DO levels are adequate to sustain aquatic fauna and flora and that the activities of the Terminal has no adverse impact on the surface water. The BOD values of surface water in the area ranged from 2.870 to 3.870ppm. These levels indicate very low microbial respiratory activity within the water bodies and are below the DPR limit of 10ppm for inland waters. Hence the surface waters are not in any way polluted by organic materials or the activities of the Terminal.

COD values ranged from 4.307ppm – 5.730ppm. The COD concentrations are higher than the BOD due to the fact that more compounds can be oxidized chemically than can be oxidized biologically and capacity to handle toxic substances (Rao, 2006). These COD concentrations were below the DPR limit of 10ppm. Iron (Fe), Lead(Pb0, and Zinc(Zn) loaded consistently which makes them the most prominent pollutants. However, Cd, Moisture, and pH was found to be very high at the sediment due to sunk and decaying boats, caravans and other unwanted materials . Fishing boats and vessels are made up of steels and mostly plated with Zinc. Steel is mainly a combination of iron and little fraction of carbon and trace amount of nickel and molybdenum. The rusting, demineralization processes and the saltwater nature of the river further contributed to the high salinity recorded.

Table 3: Table of parameters showing mean and descriptive statistics of the Surface Water sample.

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
pH	5	0	5	8.610	9.100	8.804	0.190
Temp (oC)	5	0	5	25.000	30.000	27.400	2.074
Cr(mg/l)	5	0	5	0.000	0.016	0.006	0.008
Salinity (mg/l)	5	0	5	800.000	1108.000	960.000	116.172
DO(mg/l)	5	0	5	3.100	4.100	3.822	0.438
Turbidity (NTU)	5	0	5	1.300	2.011	1.568	0.275
Pb (mg/l)	5	0	5	0.000	0.013	0.006	0.006
Cd (mg/l)	5	0	5	0.000	0.015	0.004	0.006
Ni (mg/l)	5	0	5	0.010	0.029	0.016	0.008
Zn (mg/l)	5	0	5	0.700	1.980	1.430	0.499
Fe (mg/l)	5	0	5	1.500	2.030	1.772	0.237
Cu (mg/l)	5	0	5	0.000	0.039	0.020	0.015
Ag (mg/l)	5	0	5	0.048	0.061	0.054	0.006
BOD (mg/l)	5	0	5	2.870	3.870	3.399	0.443
COD (mg/l)	5	0	5	4.307	5.730	5.146	0.533

Table 4: Correlation coefficient of physico-chemical parameters and heavy metals of the surface water.

Correlation matrix (Pearson (n)):

Variables	pH	Temp (oC)	Cr(mg/l)	Salinity (mg/l	DO(mg/l)	Turbidity (NTU)	Pb (mg/l)	Cd (mg/l)	Ni (mg/l)	Zn (mg/l)	Fe (mg/l)	Cu (mg/l)	Ag (mg/l)	BOD (mg/l)	COD (mg/l)
pH	1														
Temp (oC)	0.644	1													
Cr(mg/l)	0.077	0.322	1												
Salinity (mg/l)	0.198	0.677	0.033	1											
DO(mg/l)	-0.664	-0.183	0.578	-0.282	1										
Turbidity (NTU)	0.200	0.754	0.368	***0.940**	-0.043	1									
Pb (mg/l)	0.535	0.430	0.861	-0.041	0.153	0.241	1								
Cd (mg/l)	0.008	-0.220	0.717	-0.663	0.533	-0.379	0.717	1							
Ni (mg/l)	0.052	-0.014	***0.888**	-0.415	0.568	-0.092	0.840	***0.956**	1						
Zn (mg/l)	-0.786	-0.737	0.276	-0.336	0.590	-0.235	-0.061	0.407	0.387	1					
Fe (mg/l)	-0.288	0.207	0.041	0.836	-0.026	0.782	-0.222	-0.562	-0.343	0.214	1				
Cu (mg/l)	0.477	0.683	0.877	0.178	0.290	0.469	***0.912**	0.541	0.720	-0.219	-0.089	1			
Ag (mg/l)	-0.500	-0.418	0.432	0.075	0.344	0.186	0.167	0.277	0.379	0.861	0.532	0.003	1		
BOD (mg/l)	-0.538	0.268	0.009	0.566	0.454	0.560	-0.410	-0.481	-0.335	0.074	0.640	-0.050	0.064	1	
COD (mg/l)	-0.424	0.136	-0.524	0.492	0.044	0.309	-0.779	-0.808	-0.769	-0.174	0.497	-0.463	-0.253	0.842	1

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

The mean value of pH is 8.804, this implies that the surface water is slightly alkaline. Nickel has a strong correlation at $p<0.05$ which is between Ni and Cr($r=0.888$) also Ni and Cd has a very strong correlation at $p<0.01$ with Ni and Cd($r=0.956$). Now turbidity has a very strong correlation at $p<0.01$ with turbidity and salinity($r=0.940$), lastly cu has a very strong correlation at $p<0.01$ having cu and pb as($r=0.912$). These correlations at $p<0.01$ and $p<0.05$ establishes interactions that allows for extraction that will still hold the main information to fewer dimensions.

The results of the physiochemical parameters and the heavy metals of the sediment samples obtained by the XLSTAT(Excel solver) alongside their descriptive statistics as shown in the Table 5 while Table 6 is the correlation coefficient of the parameters.

Table 5: Table of parameters showing mean and descriptive statistics of the sediment sample.

Summary statistics:

Variable	Observations	Obs. with missing data	Obs. without missing data	Minimum	Maximum	Mean	Std. deviation
pH	5	0	5	4.250	5.600	4.682	0.576
Moisture (%)	5	0	5	61.320	73.550	69.234	4.852
THC (mg/l)	5	0	5	0.400	3.020	1.558	0.952
TPH (mg/l)	5	0	5	0.000	4.940	1.210	2.126
Pb (mg/l)	5	0	5	0.000	4.180	1.936	1.732
Cd (mg/l)	5	0	5	0.000	0.150	0.058	0.068
V (mg/l)	5	0	5	0.000	0.087	0.024	0.036
Ni (mg/l)	5	0	5	0.016	0.082	0.039	0.026
Mn (mg/l)	5	0	5	0.010	0.490	0.278	0.186
Zn (mg/l)	5	0	5	0.910	8.830	3.724	3.428
Fe (mg/l)	5	0	5	3.040	14.260	8.324	4.700
Cu (mg/l)	5	0	5	1.030	8.120	3.862	2.795

Table 6: Correlation coefficient of physicochemical parameters and heavy metals of sediment samples.

Correlation matrix (Pearson (n)):												
Variables	pH	Moisture (%)	THC (mg/l)	TPH (mg/l)	Pb (mg/l)	Cd (mg/l)	V (mg/l)	Ni (mg/l)	Mn (mg/l)	Zn (mg/l)	Fe (mg/l)	Cu (mg/l)
pH	**1**											
Moisture (%)	0.645	**1**										
THC (mg/l)	-0.163	-0.002	**1**									
TPH (mg/l)	-0.497	-0.216	0.868	**1**								
Pb (mg/l)	-0.604	-0.485	0.827	0.816	**1**							
Cd (mg/l)	-0.319	0.085	***0.895**	0.740	0.824	**1**						
V (mg/l)	0.078	0.336	0.113	-0.241	0.146	0.469	**1**					
Ni (mg/l)	-0.721	-0.292	0.630	***0.924**	0.699	0.579	-0.331	**1**				
Mn (mg/l)	***-0.941**	-0.416	-0.004	0.389	0.365	0.199	-0.105	0.690	**1**			
Zn (mg/l)	-0.564	-0.517	0.835	***0.922**	***0.937**	0.695	-0.194	0.814	0.345	**1**		
Fe (mg/l)	-0.815	-0.718	0.577	0.817	0.861	0.503	-0.287	0.850	0.630	***0.922**	**1**	
Cu (mg/l)	-0.448	-0.400	***0.910**	***0.926**	***0.937**	0.766	-0.114	0.766	0.227	****0.987**	0.849	**1**

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

A strong correlation of ($P<0.05$) existed between the concentration of most of the variables, from the Pearson correlation analyses most of the correlations were significantly verifiable at 95% and a single 99% significance level using the Bartlett's sphericity test.

The mean concentration value of pH is 4.682 which implies that the sediment is acidic and also shows a moderate correlation at $p<0.05$ between moisture and pH ($r=0.645$) even when moisture is standing out with a high mean value of 69.234. This value proves the presence of various external materials of industrial origin, demineralization and rusty metals at the bottom. The mean concentration of Cd ranged from 0.000 -0.150mg/l with a mean of 0.058 and having a strong correlation at $p<0.05$ between Cd and THC ($r=0.895$). Also Ni showed a mean of 0.039mg/l, a strong correlation at $p<0.05$ between Ni and TPH($r=0.924$). Mn showed a very strong correlation at $p<0.05$ between Mn and pH(0.941). There is strong correlation at $p<0.05$ between Zn and TPH($r=0.922$), Pb($r=0.937$), A strong correlation exists at $p<0.05$ between Cu and THC($r = 0.910$), TPH($r=0.926$) and Pb($r=0.937$ also there a very strong and significant correlation at $p<0.01$ between Cu and Zn($r=0.987$), in addition there exist a strong correlation at

$p<0.05$ between Fe and Zn($r=0.922$). These strongly showed the decaying process of metals from sunk fishing boats and metal containers.

4. CONCLUSION

In this paper, the industrial activities at the berthing area which is predominantly with abandoned vessels, fishing boats and smaller ships at the bank of Okpokiri River is the major source of heavy metals with associated distribution of the pollutants. The measured dissolved oxygen levels were within DPR/FMEnv recommended minimum standard. The dissolved oxygen showed that these activities at the terminal could not deplete the oxygen level of the river to. Some heavy metals such as Pb, Cd, Ni, and Zn for both surface water and sediment displayed higher level of concentrations than the DPR/FMEev acceptable limits

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