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Original Research Article

Sediment pollution of the Benin – Ethiope fluvial system around Sapele (Nigeria) from industrial and urban wastes

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Sediments of rivers receiving industrial and urban effluents are often polluted, and this has prompted investigation. Sediment samples were collected twice every season for two years from the Benin river-Ethiope River System around Sapele, Nigeria. Trace heavy metals were determined by flame atomic absorption spectrophotometric method. Total petroleum hydrocarbons (TPH) and other physicochemical parameters were determined too. Important results were: pH (5.8±1.0), total organic extract (3780±2600 mg/kg), TPH (2800±1900 mg/kg), Cu (12±16 mg/kg), Pb (38±35 mg/kg), Ni (12±15 mg/kg), Cd (7.10±20 mg/kg), Zn (63±42 mg/kg), Cr (25±56 mg/kg), and Mn (67±39 mg/kg). The average concentrations of some of the pollutant parameters exceeded sediment quality guideline values. The enrichment ratio values of some of the trace metals showed that most of the sampling stations suffered much enrichment with the metals. The contamination/pollution index calculations of each metal also showed that all sampling stations are polluted with one or more trace metal.

Key words: effluents, trace metals, total petroleum hydrocarbons, sediment guideline values, enrichment ratio

INTRODUCTION

Contributions to water, sediment and soil pollution from oil spillages by petroleum products, including lubricating oil from petroleum Refineries and petroleum products storage facilities (petroleum product depots) is often undermined in the Niger Delta, most of the emphasis being placed on petroleum (crude oil) spillages (Akporido and Ipeaiyeda, 2014). Other important contributors to water, sediment and soil pollution in the Niger Delta that is also undermined are industrial and urban waste. It has been observed that urbanization and industrialization are important sources of petroleum hydrocarbons, trace metals and other forms of contaminants (Forstner and Whittman, 1983; Yang et al., 2007;Yang et al., 2009; Upadhyay et al., 2006; Bai et al., 2012; Wang et al., 2011; Haapala et al., 2012; Giri et al., 2013; Akporido and Kadiri, 2014; Islam et al., 2015). The effect of pollution from these other sources (i.e. petroleum products and lubricating oil from refineries and petroleum products storage facilities, urban and industrial wastes) are equally as damaging on the environment as is crude oil spillages. This is more so because the rates of urbanization and industrialization are increasing.

Quantification of trace metals and petroleum hydrocarbons from matrices affected by effluents from petroleum refineries and lubricating oil production factories, spillages from activities at petroleum product depots and from other industrial concerns have been carried out in the Niger Delta (Horsfall and Spiff, 2002; Chindah et al., 2004; Otukunefor and Obiukwu,2005; Nduka et al., 2009; Adeniyi and Owoade, 2010; Uzoekwe and Oghosanine, 2011; Akporido and Asagba, 2013, Akporido and Ipeaiyeda, 2013, Akporido and Ipeaiyeda, 2014; Akporido and Kadiri, 2014). Most research have however been focused on the effect of petroleum prospecting and processing activities, especially oil spillages from such activities and the facilities which they make use of (Anyakora et al., 2005; Osuji et al., 2006; Davies and Abowei, 2009; Umoren and Udousoro, 2009; Anyakora and Coker, 2009; Sojinu et al., 2010, Ossai et al., 2010; UNEP, 2011; Ekpo et al., 2012; Oyetibo et al., 2013). Akporido and Kadiri (2014) has observed that much of trace metals and petroleum hydrocarbon determined in waters of the Benin -Ethiope River system actually emanated from the industries (offloading of lubricating base oil from ship and the subsequent production of lubricating oils from the base oils in the factory, agro-industrial concerns e.g. for the Production of animal feeds and flour, power generation industry and wood processing industry) and from activities in the urban area of Sapele city. The quantities of these pollutants (trace metals and petroleum hydrocarbons) are sometimes greatly enhanced when there is an oil spillage as a result of accidents in the facilities of oil prospecting and processing concerns located around Sapele Town.

The main occupation of people in this area is farming and fishing. Most of bush around the river system is used for crop farming, the arable crops grown in the area are Yam (*Diocorea sp*), cassava (*Manihot esculanta*), tomatoes (*Solanum lycoperscium*), pineapple (*Annas comosus*) and vegetables such as fluted pumpkin (*Telfera occidentalis*). Tree crops such as oil palms (*Elaeis guineensis)*, mango (*magnifera indica*) and natural rubber are also grown. Fishing and collection of lobsters is carried out at a high volume in the river system. Many of the inhabitants are also employed by Government Departments and the industries that operate in the area

As has been observed by Akporido and Kadiri (2014) Sapele is a moderate urban city with fairly high rate of urbanization. Among the industries in the town which have direct link to the Benin River-Ethiope River system are the power generating industry represented by Power Holding company of Nigeria (PHCN) power generating plant, Agro-industry (represented by Flour Mills Limited and Top feeds limited), lubricating oil producing and importer of petroleum product (represented by Asca oil Ltd and Regandez Ltd), and wood processing industries. The operating base of these industries has direct contact with the river system i.e. effluents from activities of these industries may enter the river directly. The ceiling and roofing industry is another industry whose effluents do not enter the Benin -Ethiope river system directly. The main ceiling and roofing sheet producing company is Eternit PLC. Effluents from the factory first enter into a network of swamps and small creeks but these creeks finally empty into the Benin River-Ethiope River system (Akporido and Agbaire, 2014). As has also been observed by Akporido and kadiri (2014) waste from the city enters the river system directly through drains and through stormwater runoffs. The main market (MKT) consisting of slaughter houses and many vegetable mills is located by the river system. It is obvious that the river system is the main recipient of industrial and urban wastes in Sapele town and local government area.

It is generally known that sediment of water bodies are the final sinks of most pollutants from land which enters into bodies of water such as a river (Forstner and Whittman, 1983). It will be good to test the hypothesis that if river water is polluted by certain pollutants, the fluvial sediment should also be polluted with these same pollutants just as the case with Benin River-Ethiope River system around Sapele as observed by Akporido and Kadiri (2014). These Authors found that the water of this river system is of low quality with Pb and Cd exceeding guideline values for drinking water. Also the values of oil and grease and total petroleum hydrocarbons for the water are commonly high. It will be important to know if sediment has low quality and whether these parameters are pollutants in the sediments of the river. This hypothesis can be tested by determining the concentration of seven trace metals and two oil parameters: total organic extract (TOE) ant total petroleum hydrocarbons (TPH).

This study examined the pollution status of the sediments by determining the concentration of seven trace metals (Cu, Pb, Ni, Cd, Zn Cr and Mn) and two oil parameters i.e TOE and TPH. pH, total organic carbon (TOC), total organic matter (TOM) and texture of sediments were also studied. Several pollution indices were also used to determine the pollution status of the sediments.

MATERIALS AND METHODS

Description of Study Area

The study area is located around Sapele and its satellite towns along the course of the river system, it is located between latitudes 5° 52' N and 5° 57' N and between longtitudes 5° 39′ and 5° 45′. The Benin -Ethiope River System is actually one river two different names at different location. It has one source at Umuaja town about one hundred and thirty kilometers (130 Km) North-East of Sapele. From the source to somewhere in Sapele area it is known as Ethiope River. From there to the Gulf of Guinea it is known as Benin River. The first sampling station is located at Okurighre one of the satellite towns of sapele at the bridge on Sapele to Benin road, and the last sampling station at the main confluence. These are showed in Figure 1. The two control area sampling stations are located at Edjeba (5° 46′ N and 5° 48′ E) and Ovwori (5° 47′ N and 5° 47′ E). These two control sampling stations are further upstream to the study area.

Design of Study

Seven sampling stations were established in the study: Okurighre Bridge, which is the extreme upstream sampling station; the market (MKT) about two kilometers from the Okurighre; the wood processing area located where there is active processing of timber for export or into wood for local use; the Naval college; Asca oil; Power Holding company of Nigeria (PHCN); and a sampling site located at the main confluence near Oghara town, where two arms flowed out from the river to the left and to the right. This sampling station is named main confluence (MC). Two sampling stations were located 13.9 kilometers upstream at Ovwori

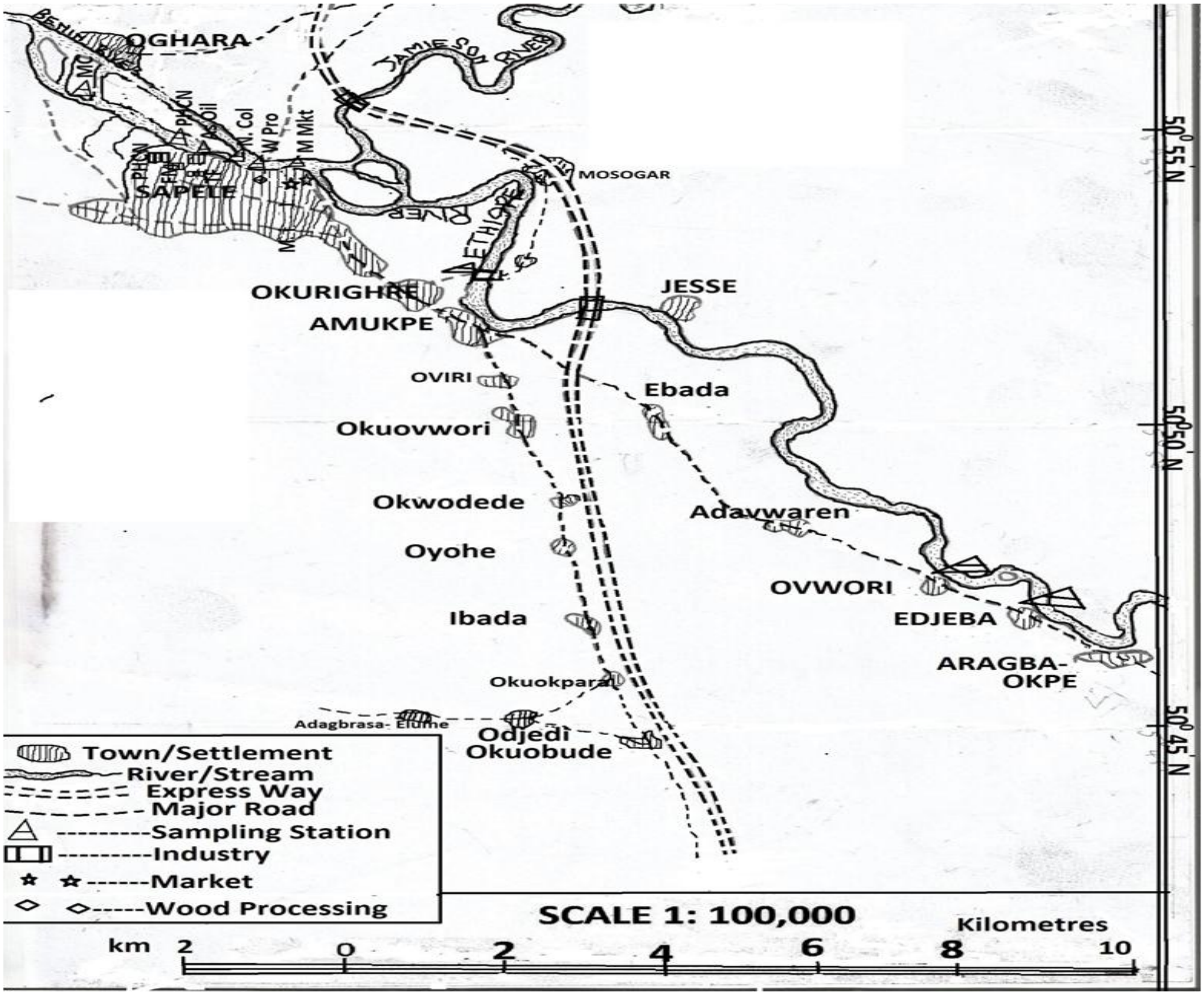

Figure 1: Map of study area showing a section of the Benin River-Ethiope river system and the sampling stations

and Edjeba as control area. These two sampling stations should not be affected by effluents from industries in Sapele or influenced by Sapele urban effluents. Samples were collected twice in every season i.e. once every quarter of the year. Sampling was carried out for a period of two years from July 2010 to May 2012.

Collection and Preservation

Sediment samples were collected from the bottom bed and Inter-tidal zones of the river using Vanveen sediment grab sampler. Grab sediment samples were collected at each site and preserved for onward transfer to the laboratory. Sediment samples for the physicochemical parameters and trace metal analysis were kept in polythene bags and kept in ice chest for onward transfer to the laboratory. Sediment samples for TOE and TPH analysis were first wrapped with aluminium foil before being kept in polythene bags and in an ice chest for transfer to the laboratory. In the laboratory the samples for oil parameters were kept in deep freezers at a temperature of -10 °C until they were analyzed. Samples for other parameters were dried in the oven at 80 °C for 2h.

Analytical Procedure

The pH of sediment samples was determined electrometrically in a 2:1water to sediment mixture in which sediment materials had settled. TOC was determined using the Walkley-Black method (Walkley and Black, 1934). TOM was evaluated by multiplying value obtained for TOC with a factor of 1.724 (Walkley and Black, 1934). The hydrometer method was used for the particle size analysis (Allen, 1989).

TOE was determined with the procedure which involved extracting 200g of partially thawed sediment in a Soxhlet extractor with 150 mL of re-distilled methanol. The filtrate from this procedure was re-extracted with three 30 mL portion of redistilled hexane (Fisher grade). The extract solution was dried of moisture with anhydrous sodium sulphate on a filter paper and funnel. The dried extract solution was subsequently evaporated by distillation and dried until constant weight at a low temperature in an oven (Oudot et al., 1981, Berthou et al. 1981; Adekambi, 1989). The residual oil was then weighed to determine TOE (equation 1).

$$\text{TOE (mg/kg)} = \frac{(A - B) \times 10^6}{\text{Dry weight of experimental sample (g)}} \quad \text{Equation 1}$$

Where:

A = weight of TOE obtained for sample (g)

B = weight of TOE obtained for blank (g)

TPH was determined from the TOE extract by subjecting it to a clean-up procedure which involved passing a solution of the extract in hexane through a short column of activated silica gel to yield effluent hydrocarbons. This was then distilled to residual petroleum hydrocarbon, which was dried and weighed. TPH was calculated from equation 1. Metals were determined by adding 50 mL of 2M HNO_3 to 5g of dried sediment placed on a boiling water bath for 2h, with stirring at 15 min. interval. The extracted material was filtered and subsequently analyzed using atomic absorption spectrophotometer (Perkin Elmer AA200) (Anderson, 1978; Allens, 1989).

Quality Assurance Programme

Blanks were determined in all analysis where it is necessary and analyses were carried out in duplicates. Percentage recoveries were determined for the seven trace metals and the two oil parameters (i.e. TOE and TPH). The results for the determination of percentage recoveries given as the mean±standard deviations of five replicate determination are as follow: Cu (95.3±4,4 %), Pb (93.7±2.9 %), Ni (97.3±6.5 %), 92.5±3.3 %), Zn (101±1.7 %), Cr (94.8±3.8 %), Mn (98.2±5.5 %), TOE (99.3±1.9 %) and TPH (99.1±1.7 %).

The enrichment ratio (enrichment factor) for each of the metals in each sampling station was also calculated using the average concentration of each of the metals in the four seasons studied (first rainy season, first dry season, second rainy season and second dry season) and employing the formula (Simex and Helz, 1981).

$$ER = \frac{CxMe/CrMe}{CxMr/CrMr}$$

Where:

CxMe = concentration of trace heavy metal in studied matrix.

CrMe = concentration of reference heavy metal in the studied matrix.

CxMr = concentration of trace heavy metal in reference matrix.

CrMr = concentration of reference trace heavy metal in the reference matrix (or background)

The background value is that of the world surface average (Martin and Meybeck, 1979) The background value of the studied heavy metals are Mn = 720, Zn = 129, Cu = 32, Cr = 97, Ni = 49, Pb = 20, Cd = 10 (value for Cd was obtained from Puyate et al., 2007). Mn was chosen as the reference or conservative trace metal since it is one of the most common elements in the area, Its concentration is always high in sediment and soil samples obtained from the area. The status of each sampling station based on the enrichment ratio was derived as follows: ER < 2 shows 'deficiency' to 'minimal enrichment', ER = 2 – 5 shows 'moderate enrichment', ER = 5 – 20 shows 'significant enrichmen't, ER = 20 – 40 shows 'very high enrichment', and ER > 40 shows 'extremely high enrichment' (Sutherland, 2000; Loska et al., 2004).

The contamination/pollution (C/P) index for each metal in each sampling station was also calculated based on the mean value of each station for four seasons using the equation:

$$\text{C/P index} = \frac{\textit{Concentration of metal}}{\textit{Tolerable level of metal in sediment}}$$

The tolerable level of metal in sediment was taken to be the target value of the metal in the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) (DPR, 2002)

$$\frac{C}{P} Index = \frac{Concentration\ of\ metal}{Target\ value\ of\ metal\ in\ sediment}$$

Statistical procedures

The statistical procedure involved a bivarate correlation of all parameters (with the exception of pH) in the matrix using a Pearson (2 – tailed) correlation from the statistical package of the social sciences (ah 0.01 and 0.05 confidence level). Analysis of variance (ANOVA – single factor) from Microsoft excel (version 2007) was used to compare the means of concentrations of parameters in the seven different sampling stations and the four seasons studied. The mean of the concentrations of each parameter in the study area was compared with the mean of the concentration of corresponding parameter in the control area using a t-test (two sample, with equal variance) from Microsoft excel (Version 2007). A comparison of a set of values (i.e. for the study area and for the control area) was carried out using a student t-test at 0.05 confidence level and at 14 degrees of freedom.

RESULTS AND DISCUSSION

Results of analyses of all parameters in the study were

Table 1. Results of determination of all parameters (mg/kg) in all the sampling stations of study area and control area given as mean±standard deviation (n = 8)

Parameters	Control Area Sampling Stations		Average for control Area	Study Area sampling Stations							Average for Study Area
	Edjeba	Ovwori		Okurighre	Main MKT	Wood Proc	Navy Coll	ASCA oil	PHCN	Main Confluence	
pH	6.64±0.11	6.69±0.06	6.66± 0.08	6.28± 0.69	6.6± 1.5	6.2± 1.3	6.1±0.7	5.2±0.8	5.2± 0.3	5.4±0.5	5.8 ± 1.0
TOC[a]	0.17±0.03	0.19±0.01	0.18±0.02	0.21± 0.04	0.32 ±0.27	0.31± 0.27	0.33±0.11	0.16±0.05	0.16±0.05	0.31±0.25	0.29±0.19
TOM[a]	0.31±0.06	0.32±0.02	0.32± 0.04	0.35±0.08	0.55± 0.47	0.53± 0.46	0.56±0.190	0.28+0.08	0.28±0.08	0.53±0.43	0.50±0.33
Silt[a]	2.40±0.63	2.50±0.66	2.5±0.6	6.4±3.0	1.2±1.3	1.4± 1.6	3.7±4.6	3.2±3.5	3.2±3.5	4.0±4.3	3.4± 3.7
Clay[a]	2.65±03.1.94	2.83±0.72	2.8±0.8	10.0±1.4	5.6 ±4.4	5.6±4.6	4.3±3.7	6.5±5.4	6.5±5.4	6.2±3.6	6.2±4.2
Sand[a]	95.0±1.5	94.6±1.2	94.8±1.3	84.0±4.2	93.5 ±5.2	93.0 ± 6.1	92.0±8.3	90.3±8.8	90.3±8.8	89.8±7.8	90.5± 7.4
TOE	275±93	231±51	253±76	4710±2700	4860± 2900	3440 ±2900	3760±2600	2120±960	2120±960	4250±3100	3780±2600
TPH	180±35	164±21	172±29	3520±2200	3870±2100	2620±2100	2700±1900	1580±760	1580±760	2970±2100	2800±1900
Cu	9.25±0.89	7.6±1.4	8.4±1.4	12.3±72	26 ±3.5	5.7±0.8	5.5±3.7	14±12	14±12	34±30	12±16
Pb	17.1±2.7	13.6±2.4	15.4±3.1	44±18	61±58	18±14	29±26	44±45	44±45	43±31	38± 35
Ni	8.6±1.7	9.00±0.76	8.5±1.4	23.7±9.3	16±28	2.6±0.9	2.4±1.5	20±20	20±20	9.1±5.1	12±15
Cd	3.1±1.2	1.1±1.1	2.1± 1.5	35±46	1.7±1.7	2.0±2.2	2.5±3.0	4.1±4.1	4.1±4.1	2.6±2.7	7.10±20
Zn	20.3±2.1	19.4±2.6	198± 2.3	46±13	67 ±52	42±21	75±50	59±49	59±49	66±44	63±42
Cr (total)	13.0±3.1	14.6±3.6	13.8±3.4	80.1± 143	14.3±4.4	13.4 ±8.2	13.5±7.1	26±11	26±11	132±4.4	25±56
Mn	15.9±2.7	18.3±4.0	17.1± 3.5	44±21	67± 11	41.7±6.9	83±65	68±21	68±21	66±18	67±39

a = %

compared with result of analyses of corresponding parameters in the control area (Table 1). The average pH of study area (5.8±1.0) is lower than pH for control area (6.66±0.08). The higher acidity can increase the mobility of heavy metals in the study area sediment making them more readily available to plants and sediment dwelling organism, which may be at the bottom of the food chain involving all biota, including humans. The four pollutants which have average values higher in the study area than in the control area were: TOE with average value of 3780±2600 mg/kg and 253±76 mg/kg, TPH with 2800±1900 mg/kg and 172±29 mg/kg, Zn with 63±42 mg/kg and 19.8±2.3 mg/kg, and Pb with 38±35 mg/kg (in study area) and 15.4±3.1 mg/kg (in control area) respectively. The student t-test applied to study area and control area showed that those areas not statistically significantly different from each other (t-calculate (1.450) < t-tabulated (2.100). The t-test two sample (assuming equal variances) applied on the results however showed that there were statistical differences between the values from study area and control area to TOE, TPH, Pb and Zn. These four parameters appears to be the ones that are increased in the study area as a result of effluents from the various industrial concerns and from urban centre activities. The average concentration of TOE in the study area is about 15 times the average concentration in the control area and the average concentration of TPH in the study area is about 16 times the concentration of TPH in the control area.

The average concentrations of the oil parameters (i.e. TOE and TPH) were highest at the Main Market, TOE (4860±2900 mg/kg), TPH (3860±2100 mg/kg) (Table 1). This is not surprising since effluents coming from this market consist of much vegetable oil, waste gasoline, diesel and lubricating oils. Effluent drains from urban centres are known to be sources of pollutant to water bodies and design and constructuction of drainage systems are impotant factors in the control of pollution of receiving water bodies (Valipour, 2012;Valipour, 2013; Valipour et al. 2013; Valipour et al., (2012). Another sampling station with high average concentrations of the two oil parameters is the Okurighre sampling station, TOE (4710±2700 mg/kg) and TPH (3520±2200 mg/kg). The reason for this may also be as a result of the location of another market near to this station and the presence of a number of auto-mobile repair workshops near to this sampling station. The average concentrations of most of the heavy metals were also higher in these two sampling stations (i.e. main market and Okirighre). A comparison of levels of each parameter in each of the sampling stations

Table 2. Result of the determination of all parameters in the four seasons given as mean ±standard deviation (n = 14)

Parameters	First Rainy Season	First dry season	Second Rainy season	Second dry season
pH	6.3 ± 1.1	6.3 ± 1.1	5.37 ±0.73	6.3 ±1.1
TOC (%)	0.3 ±0.2	0.34 ± 6.21	0.23± 0.16	0.325 ± 0.21
TOM (%)	0.6 ± 0.4	0.59±0.30	0.40±0.28	0.59 ±0.36
Silt (%)	0.6 ± 1.5	0.70± 1.8	6.1±33	0.7±1.8
Clay (%)	2.8±2.9	2.8 ± 3.0	9.5±1.8	2.8± 3.0
Sand (%)	96.7± 4.3	96 .7 ± 4.2	84.4 ±4.1	96.7± 4.2
TOE (mg/kg)	1570± 480	1550± 440	6090 ±2000	1550± 440
TPH (mg/kg)	1220±420	1200± 400	4420±1400	1200± 400
Cu (mg/kg)	11± 21	11± 21	13.7± 9.4	11±21
Pb (mg/kg)	22±39	21±39	52±23	21±39
Ni (mg/kg)	7.0± 9.3	6.9± 8.8	14±14	6.9± 8.8
Cd (mg/kg)	1.9± 4.8	1.5± 3.6	12±27	1.5 ±3.6
Zn (mg/kg)	46± 44	46±44	81±36	46± 44
Cr (mg/kg)	18.5± 5.3	17.9 ±44	43.7± 110	17.9±4.4
Mn (mg/kg)	51±12	50 ± 12	80± 52	50±12

Table 3. Results of of determination of all parameters in bottom bed sediments and inter-tidal sediments given as mean ± standard deviation (n = 28 for both types of sediments)

Parameters	Bottom bed sediment	Inter- tidal
pH	5.9± 1.2	5.8 ± 0.9
TOC (%)	0.30± 0.22	0.27± 0.16
TOM (%)	0.52+0.37	0.47 ± 0.28
Silt (%)	4.0 ± 4.5	2.8±2.8
Clay (%)	6.4 ± 3.9	6.0± 4.5
Sand (%)	89.7± 7.9	91.3 ± 7.0
TOE (mg/kg)	4120 ±3000	3440± 2300
TPH (mg/kg)	3130± 2200	2540 ± 1600
Cu (mg/kg)	16± 20	8.2 ± 7.4
Pb (mg/kg)	44± 41	31± 27
Ni (mg/kg)	12 ± 12	11± 18
Cd (mg/kg)	11± 28	3.6 ± 4.2
Zn (mg/kg)	63 ± 44	64 ± 41
Cr (mg/kg)	35 ± 79	15.7± 9.2
Mn (mg/kg)	72± 53	62± 16

showed that there was no definite pattern of variation of levels of parameters with distance of sampling station from the first sampling station Okurighre Upstream to the last sampling station downstream (Main confluence) (Table 1). The mean of each of the pollutant parameters and pH were compared in the seven sampling stations using analysis of variance. The differences in the means of the parameters were only statistically significant in four parameters i.e. pH, Cd, Ni and Cu (ANOVA-single factor).

The average concentrations of the pollutant parameters were generally higher in the rainy seasons (Table 2). The oil spillage that occurred in the second rainy season must have raised the concentrations of the oil parameters and the trace metals in that season. The effect of rains in the wet season was masked to a great extent by the effect of this oil spillage. A comparison of the mean of pH and the pollutant parameters in the four seasons studied using analysis of variance showed that the differences in their means were statistically significant in pH, Mn, Zn, Pb, TPH and TOE (ANOVA-Single factor). The effect of type of sediment (i.e bottom or inter-tidal sediments) was not very clear some were higher in bottom bed sediments while others are higher in inter-tidal sediments (Table 3).

Table 4 shows that many pairs of parameters have positive correlation coefficients that are significant at 0.01 confidence and hence very strongly correlated level and a few have positive correlation coefficient that are significant at 0.05 confidence level and hence are strongly correlated. It can be observe from Table 4 that most of the pollutant parameters are strongly or very strongly correlated with silt and clay (especially clay), clay has high cation exchange capacity thus its correlation specially with metals is high.. This strong association with these two types of texture of soil should result in high retention of the metals by these soil types. Pb and Ni are either strongly to very strongly correlated with TOE and TPH and with each other showing

Table 4. Pearson (2-tailed) correlation of parameters determined in the sediment matrix

	TOC	TOM	Silt	Clay	Sand	TOE	TPH	Cu	Pb	Ni	Cd	Zn	Cr	Mn
TOC	1													
TOM	0.521**	1												
Silt	-0.119	-0.204	1											
Clay	-0.243	-0.206	0.521**	1										
Sand	0.311*	0.294**	-0.608**	-0.693**	1									
TOE	-0.293**	-0.242**	0.529**	0.721**	-0.531**	1								
TPH	-0.237**	-0.267**	0.367**	0.608**	-0.688**	0.704**	1							
Cu	0.262	0.022	0.270*	0.250	-0.049	0.028	-0.035	1						
Pb	0.122	-0.043	0.245	0.484**	-0.362	0.403**	0.378**	0.191	1					
Ni	-0.167	-0.168	0.120	0.580**	-0.358**	0.256	0.305*	0.222	0.520**	1				
Cd	-0.189	-0.147	0.050	0.300*	-0.311*	0.328*	0.353**	0.139	0.248	0.338*	1			
Zn	0.247	-0.009	0.273*	0.357**	-0.195	0.336*	0.200	0.113	0.632**	0.251	-0.098	1		
Cr	-0.115	-0.100	0.028	0.170	-0.134	0.187	0-226	0.146	0.168	0.303*	0.738**	-0.092	1	
Mn	0.140	0.021	0.278*	0.279*	-0.327	0.224	0.244	-0.025	0.262	0.016	-0.087	0.377**	-0.204	1

*correlation coefficient significant at 0.05 confidence level
**correlation coefficient significant at 0.01 confidence level

Table 5. Comparison of the concentrations of heavy metals in sediment with NOAA sediment Quality Guidelines (NOAA, 1999**)**

parameter	Average concentration	Guideline values (mg/kg)		Percentage incidence biological effect			Inferred Contamination level
		ERL	ERM	<ERL	ERL-ERM	>ERM	
Cu (mgkg-1)	12±16	34	270	9.4 *	29	83.7	Low or no contamination
Pb (mgkg-1)	38±35	46.7	218	8.0 *	35.8	90.2	Low or no contamination
Ni (mgkg-1)	12±15	20.9	51.6	1.9 *	16.7	16.9	Low or no contamination
Cd (mgkg-1)	7.10±20	1.2	9.6	6.6	36.7 *	65.7	Intermediate
Zn (mgkg-1)	62±42	150	410	6.1*	47.0	69.8	Low or no contamination
Cr (mg/kg-1)	25±56	81	370	2.9 *	21.1	85.0	Low or no contamination
Mn	67±39	-	-	-	-	-	Not ranked

*applicable % biological incidence effect for the specific parameter ERL = effect range low ERM = effect range median
NOAA = National Oceanic and Atmospheric Administration

that they may have the same source, which may be petroleum products and lubricating oil importation and storage (or direct production of lubricating oils) activities of some of the industries. Zn is very strongly correlated with Pb, Cr and Cd are strongly correlated with Ni. No explanation is suggested for this strong correlation since Zn did not correlate positively with either Cd or Cr.

A comparison of the average concentrations of the seven heavy metals studied with the National Oceanic and Atmospheric Administration (NOAA) sediment quality guidelines (NOAA, 1999) (Table 5) showed that Cd is a very important pollutant in the study area. Cadmium's average concentration (7.10±20 mg/kg) is higher than the 'effect range low' (ERL) but lower than the 'effect range median' (ERM) and has a percentage incidence of biological effect of 36.7 %. It is ranked to have intermediate (or moderate) contamination level. Cd competes with and displaces Zn in a number of Zn-metalloenzymes by irreversibly binding to the active sites, thereby destroying normal metabolism (Langston, 1990; Bryan and Langston, 1992). A disease caused by Cd known as 'itai-itai' is rheumatic in nature and affect the bones adversely and conditions can become fatal. Sediment dwelling organisms can be affected and these may be at the bottom of the food chain involving humans and higher animals. The average concentrations of TPH and the seven heavy metals were also compared with the target and intervention values of Environmental Guidelines and standards of the petroleum industries in Nigeria (EGASPIN) by the Department of Petroleum Resources (DPR) (DPR, 2002) (Table 6). This revealed that the average concentrations of Cd (7.10±20 mg/kg) and TPH (2800±1900 mg/kg) exceeded the respective target values but did not exceed the intervention values (Table 6). "Target values indicate sediment/soil quality required for sustainability or expressed in terms of remedial policy, the soil/sediment quality required for full restoration of the soil's functionality for human, animal and plant life. The target values therefore indicate the soil quality levels ultimately aimed for" (DPR, 2002). The fact that the average concentration of these two parameters (i.e. Cd and TPH)

Table 6. comparison of sediment metals and TPH concentrations with EGASPIN soil/sediment target and intervention values (DPR, 2002)

parameters	Average Concentration ($mgkg^{-1}$)	Guidelines		Inferred Contamination Levels
		Target values ($mgkg^{-1}$)	Intervention Values ($mgkg^{-1}$)	
Cu ($mgkg^{-1}$)	12±16	36	190	No guideline value exceeded
Pb ($mgkg^{-1}$)	38±35	85	530	No guideline value exceeded
Ni ($mgkg^{-1}$)	12±15	35.0	210	No guideline value exceeded
Cd ($mgkg^{-1}$)	7.10±20	0.80	12.0	Exceeded target value
Zn ($mgkg^{-1}$)	63±42	140	720	No guideline value exceeded
Cr ($mgkg^{-1}$)	25±56	100	380	No guideline value exceeded
Mn ($mgkg^{-1}$)	67±39	-	-	Not ranked
TPH ($mgkg^{-1}$)	2800±1900	50	5000	Exceeded target values

EGASPIN = Environmental Guidelines and Standards for The Petroleum Industry in Nigeria DPR = Department of Petroleum Resources

Table 7. Enrichment Ratio of each metal in each sampling station using the average concentration of each metal for the four seasons for each sampling station

Sampling Stations	Enrichment Ratio						
	Cu	Pb	Ni	Cd	Zn	Cr	Mn
Okurighre	7.00	33.3	7.71	80.0	5.85	14	1.00
Main Market	9.75	30.3	3.42	6.00	5.56	1.62	1.00
Wood Processing	3.5	14.3	0.86	5.00	5.61	2.46	1.00
Navy college	1.75	11.7	0.38	3.00	5.00	1.23	1.00
Asca Oil	3.00	8.67	1.42	2.00	5.33	1.46	1.00
PHCN	5.25	21.7	4.14	6.00	4.83	2.92	1.00
Main Confluence	13.0	22.3	2.00	4.00	5.44	1.54	1.00

Table 8. Contamination/Pollution (C/P) index of each metal in each of of the sampling stations using the average value of each metal for the four seasons for the sampling station

Sampling Stations	C/P Index						
	Cu	Pb	Ni	Cd	Zn	Cr	Mn
Okurighre	0.34	0.52	0.68	43.8	0.33	0.80	Not ranked
Main Market	0.72	0.72	0.46	2.13	0.48	0.14	Not ranked
Wood Processing	0.16	0.21	0.07	2.5	0.30	0.13	Not ranked
Naval college	0.15	0.34	0.06	3.13	0.54	0.14	Not ranked
Asca Oil	0.33	0.29	1.2	2.25	0.65	0.18	Not ranked
PHCN	0.39	0.52	0.38	5.13	0.13	0.26	Not ranked
Main Confluence	0.94	0.51	1.19	3.25	0.68	0.13	Not ranked

exceeded the target values means that the sediments of the study area has lesser quality than expected for sediment functionality for human, animal and plant life.

It can be seen based on the classification given enrichment ratio values above that Okurighre sampling station has 'moderately' to 'extremely high enrichment' ratios for all the metals: Pb (33.3) has 'very high enrichment', Cu (7.00), Ni (7.71), Zn (5.85), Cr (14) all have 'significant enrichment', and Cd (80.0) has 'extremely high enrichment'. The second sampling station which has a fairly high enrichment of the metals is the main market sampling station: Cu (9.75), Cd (6.00) and Zn (5.56) all have 'significant enrichment' in this station with these metals. Pb (30.3) has 'very high enrichment' in this station (Table 7). Pb is the metal which have 'significant' to 'very high enrichment' in all the sampling stations (Table 7). A high proportion of most of the metals have been brought into the study area by anthropogenic input, probably from the industries already mentioned and also from petroleum prospecting and processing activities around the study area.

The results for the calculations of contamination/pollution index are given in Table 8. The pollution (or contamination) status of the metals in the sampling stations are given the significance of interval of C/p Index in Table 9 (Lacatusu,1998). It was observed that Cd is a major pollutant in the study area. All the sampling stations fell into the 'pollution' category with Cd: The

Table 9. Significance of interval of contamination/pollution (C/P) Index (Lacatusu, 1998)

C/P Index	Significance	Symbol
<0.1	Very slightly polluted	v.s.l
0.10 – 0.25	Slightly contaminated	s.l
0.26 – 0.50	Moderate contamination	m.l
0.51 – 0.75	Severe contamination	St. l
0.76 – 1.00	Very severe contamination	v.st.l
1.1 – 2.0	Slight pollution	s.p.
2.1 – 4.0	Moderate pollution	m.p.
4.1 – 8.0	Severe pollution	st.p.
8.1 – 16.0	Very severe pollution	v.st.p.
➢ 16.0	Excessive pollution	e.p.

Table 10. Results from the study compared results from similar studies elsewhere

River/water body	country	TOE (mg/kg)	TPH (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	References
Dikrong River	India	.		(182 - 194)±3.5	(31 – 47.0)±5.8	(7 – 15)±3.2	-	(19 – 35)±3.5	(41.5 – 59.5)±8.1	(4.085 – 4.755)±0.31	Chakravarty and Pattgiri, (2009)
Wembanad Lake	India	-	-	16.7 – 56.1	0.61 – 80.0	36.5 - 305	0.07 – 2.00	103 - 305	-	-	Harikumar et al., (2009)
Yangtze River	China	-	-	6.87 – 49.7	18.3 – 44.1	17.6 – 48.0	0.12 – 0.75	47.6 - 154	36.9 - 173	413 - 1112	Zhang et al., (2009)
Vembanad Lake	India	-	-	8.00 – 50.0	-	30.0 - 118	1.00 – 16.0	36.0 - 856	-	-	Priju and Narayana, (2007)
Subarnarekha River	India			69±57	75±61	42±22	-	100±31	111±74	842±335	Giri et al., (2013)
Benin River (at Koko)	Nigeria	496000± 12000	41900± 11000	-	53±57	0.14±0.17	0.08±0.09	92.1±170	4.1±2.0	-	Akporido and Ipeaiyeda, (2014)
Bietri Bay and Ebrie Lagoon	Cote D'ivoire	-	-	21.12	26.53	-	0.11 – 1.25	106.32 – 509.75	-	-	Koffi et al., (2014)
Orogodo River	Nigeria			2.50	4.39	6.71	0.49	1.26	-	-	Puyate et al., (2007)
Benin River-Ethiope River System	Nigeria	3780±2600 (945 – 8000)	2800±1900 (775 – 6540)	12±16 (ND – 81.6)	38±35 (ND – 149)	12±15 (0.9 – 40)	7.10±20 (ND – 107)	63±56 (9.95 – 154)	25±56 (2.8 – 431)	67±39 (5.00 – 189)	Present Study

following sampling stations, Main market (2.13), Naval college (3.13), Asca Oil (2.25), Wood processing (2.5) and Main Confluence (3.25) all have 'moderate pollution' status with Cd, The PHCN sampling station has C/P index value of 5.13 and thus ranked to have 'severe pollution' status and the Okurighre sampling station has C/P index value of 43.8 and thus have 'excessive pollution' status. This confirmed that the Okurighre sampling station is excessively polluted with Cd. The source of this excessive pollution by Cd has not yet been discovered. Another trace heavy metal which placed some sampling station into the pollution category is Ni: Asca oil (1.20), main Confluence (1.19) have 'slight pollution' status with Nickel. Other metals have 'slight Contamination' to 'very severe contamination' in the remaining sampling stations. The observed enrichment ratio and the C/P index values of the sampling stations of the study area has further confirmed that the sediments of the Benin River-Ethiope River system are highly polluted with these heavy metals which have been contributed into the environment by the different industries in the area and also by effluents from the urban centers of Sapele and the satellite towns. The amount of the pollutants entering the rivers system is abnormally increased when there is an oil spillage from oil prospecting and processing facilities in the surrounding areas and near to the urban centers.

The results of the parameters (especially pollutant parameters) in this study were compared with results obtained for corresponding parameters in polluted sites in similar studies elsewhere (Table 10). Most of the results were comparable with results from these other polluted sites. A few of the results were either higher or lower. The average concentration of Cu in study area, 12±16 mg/kg (ND – 81.6 mg/kg) is comparable with results obtained for Bietri Bay and Ebrie Lagoon (21.12 mg/kg), Vembanad Lake (8.00 – 50.0) (Priju and Narayana, 2007), Vembanad Lake (16.7 – 56.1 mg/kg) (Harikumar et al., 2009), These sampling sites receive industrial effluents and effluents from urban centers. The average concentration of Cu in the present study area is however lower than results obtained for Subarnarekhe River (69±57 mg/kg) and Dikrong River (182±35 – 194±35 mg/kg). It is higher than the value obtained for Orogodo River (2.50 mg/kg). The average concentration of Pb, 38±35 mg/kg (ND – 149 mg/kg) is comparable with results obtained for Dikrong River (31±5.8 – 47.0±5.8 mg/kg), Vembanad Lake (0.61 – 80.0 mg/kg) (Harikumar et al. 2009), Yangtze River (18.3 – 44.1 mg/kg), Benin River (at Koko) (53±57 mg/kg), Bietri Bay and Ebrie Lagoon (26.53 mg/kg). It is higher than results obtained for Orogodo River (4.39) and lower than results obtained for Subarnarekha River (75±61 mg/kg).

The average concentration of Zn in the study area, 63±56 mg/kg (9.95 – 154 mg/kg) is comparable with results obtained for Dikrong River (19±3.5 – 35±3.5 mg/kg), Yangtze River (47.6 – 154 mg/kg), Subarnarekha River (100±31 mg/kg) and Benin River (at Koko) (92.1±170 mg/kg. It is lower than values obtained for Wembanad lake (103 – 305 mg/kg) (Harikumar et al., 2009), Wembanad Lake (36.0 – 856 mg/kg) (Priju and Narayana, 2007) and Bietri Bay and Ebrie Lagoon (106.32 – 509.75 mg/kg). It is higher than values obtained for Orogodo River (1.26 mg/kg). It can be seen from the comparison made above that most of the results obtained in this study are comparable with results obtained for sites which are known to be polluted and which receive effluents from industries and urban centres. Some of the results are even higher than for these other sites. Akporido and kadiri (2014) had already established that effluents from PHCN and Asca oil Ltd effluent drains are capable of polluting any receiving water body. These two effluents and those from other industrial set ups in addition to domestic effluents from the urban centre must be responsible for the pollution observed in the sediments of the Benin River-Ethiope River system.

CONCLUSION

The average pH value in the study area is lower than average pH in the control area showing higher acidity in the sediments of the study area. The average concentrations of most pollutants were higher in the study area than in the control area. The differences in the mean of the concentrations of the pollutant parameters were even statistically significant in the case of some of these pollutants (TOE, TPH, Pb and Zn). This an indication that the study area is polluted with these four parameters. A comparison of the average concentrations of these pollutant parameters with guideline values also showed that some exceeded guideline values thus confirming that the study area is polluted with these pollutant parameters. An assessment of the pollution status of the sampling stations of the study area with enrichment ratio and the contamination/pollution index showed that most the sampling stations suffered enrichment with these pollutant parameters, showing that there was anthropogenic input of pollutant with trace metals into study area. These indexes also showed that some of these sampling stations are polluted (i.e. from 'moderate pollution' to 'excessive pollution') with some of the trace metals. TOE, TPH, Pb, Cd, Ni and Zn were important pollutants in the study area.

Environmental authorities such as the Department of Petroleum Resources (DPR) in Nigeria and the Federal Ministry of Environment (FMEnv) of Nigeria have put in place effluent limitation, water, soil and sediment guidelines and standards, high levels of pollution is still being observed.

This may be as a result of the ineffectiveness of the enforcement agencies. The Nigerian Environmental Standards Regulatory and Enforcement Agency (NESREA) is the main enforcement agency in Nigeria. The effectiveness of this organization and other enforcement agencies is yet to be seen. The Federal Government should ensure that these enforcement agencies carry out their duties of monitoring compliance of the various industries with established effluent limitation guidelines to achieve a cleaner environment in Nigeria.

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