PETROLEUM HYDROCARBON POLLUTION OF SEDIMENTS OF THE BENIN-ETHIOPE FLUVIAL SYSTEM AROUND THE OGHARA INDUSTRIAL AREA, DELTA STATE, NIGERIA

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ABSTRACT

Activities in the petroleum industry downstream sector have been known to pollute the environment. It is necessary to ascertain the effect of these activities on the sediments of the Benin-Ethiope Fluvial System where much of such activities take place. Sediment samples were collected from five sampling stations in the study area and two control (upstream) sampling stations twice in a season for two years. Sediment samples were analyzed for trace metals by method of flame atomic absorption spectrometry after wet digestion with 2M HNO_3. Analysis for sediment physicochemical parameters including total petroleum hydrocarbons (TPH) were carried out by standard methods. Results obtained are, pH (5.17 ± 0.86), total organic carbon (TOC) (0.20 ± 0.13 %), total organic extracts (TOE)+ (4090 ± 4100 $mgkg^{-1}$), TPH (3180 ± 3000 $mgkg^{-1}$), Cu (1.4 ± 2.9 $mgkg^{-1}$), Pb (0.83 ± 1.1 $mgkg^{-1}$), Zn (22 ± 26 $mgkg^{-1}$), Cd (0.15 ± 0.23 $mgkg^{-1}$), Ni (1.4 ± 1.4 $mgkg^{-1}$). The concentrations of the two oil parameters (i.e. TPH and TOE) in the study area are found to be very much higher than their concentrations in the control area. The average concentration of TPH in the study area very much exceeded guideline value. The sediments of the area is polluted with petroleum hydrocarbons in addition to the sediments having high acidity. The sediments of the study area are therefore of low quality.

Keywords: *Petroleum industry downstream sector; Benin-Ethiope Fluvial System; Oghara Town; Flame atomic absorption spectrometry, total petroleum hydrocarbon; trace metals*

INTRODUCTION

Oil pollution is a topical issue which attracts much attention in the Niger Delta region. Oil pollution in the region which is almost entirely derived from oil spillages is known to be brought about by many factors which include equipment failure as a result of non replacement of dysfunctional equipment and leakages from pipes conveying oil from oil fields to port terminals or to other collection centres such as refineries and quality control centres. Oil sabotage is another factor that has become very important of recent (Nwilo and Badejo, 2007). Crises over oil pollution as a result of oil spillages have received much attention and thishas been directed mainly at the upstream sector of the petroleum industry (which consist mainly of petroleum prospecting and processing activities) and less attention has been directed at the downstream sector of the petroleum industry (which consist mainly of petroleum refining, production of lubricating oils and general distribution of petroleum products). The main types of pollutants released to the environment by both sectors of the petroleum industry are similar and consist of petroleum residues (petroleum hydrocarbons), trace metals and polycyclic aromatic hydrocarbons (PAHs). Release of large quantities of these pollutants to the environment (e.g. through oil spillages) has been observed to result in in loss of and damage to biodiversity, depletion of arable land, depletion of available potable water, and blockages of water ways (GESAMP, 1993: Luiselli et al., 2006: UNEP, 2011: Almeida et al., 2013). Soil and sediment particles and organic matter has been observed to be primary reservoirs for hydrocarbon since hydrocarbons rapidly sorbed on the two materials (Monaco et al., 2015). Petroleum is observed to be toxic to biological processes catalyze4d by soil micro organisms, they are also known to inhibit organic matter mineralization and cause root mycorrhhizal infection (Mathe et al., 2012: Monaco et al., 2015). Health effect of trace metals are cellularly based and involve binding of trace metals to critical functional groups of enzymes and other molecular structures that are important in the physiological functions of the organism. These processes of binding usually occur by chelation, ion-exchange, ion replacement and others (Onianwa, 2016). Individual ailments caused by trace metals are well documented in literature (Gola et al., 2016). The presence of high concentrations of trace metals in oil spillage sites impedes biodegradation of petroleum hydrocarbons since trace metals are toxic to the microorganisms involed in the biodegradation (Almeida et al., 2013). It has also been observed that the health of people close to oil spillage sites and personnel involved in clean-up exercise are adversely affected (Gwack et al., 2012). Studiescarried out on the effect of the activities in the downstream sectors of the petroleum industry in the Niger Delta has shown that these activities release significant amount of pollutants into the environment (Nduka and Orisakwe, 2011: Akporido and Kadiri, 2014: Akporido et al., 2015).

The Benin-Ethiope Fluvial Systemconsist mainly of two rivers i.e. the Benin river and the Ethiope river (Fig, 1). Akporido and Kadiri (2014) and Akporido et al. (2015) have shown that water and sediments of the fluvial system around Sapele Town are polluted by the activities taking place in the downstream sector of the petroleum industries in the area.

The present study area Islocated around Oghara Town about six kilometers from Sapele and activities in these downstream sector involve offloading of petroleum products and lubricating base oils into depots, production of lubricating oil and the lifting of these products from the depots for redistribution to filling station indifferent parts of the country. All these activities brings about oil spillages into the water of the fluvial system and the surrounding soils.

The hypothesis of this study is that the sediment of the fluvial system should be polluted by oil spillages from these petroleum downstream sector companies and petroleum residues and trace metals should be the main pollutants, also the physicochemical parameters of sediment should also be affected as a result. There is currently a paucity in information on the effect of these petroleum downstream sector companies on the water, sediment and soils around Oghara area. The study examined the effects of the activities in the petroleum downstream sector companies/factories in and around Oghara town on the quality of sediment of the Benin- Ethiope Fluvial system in area around Oghara Town. This was done by determining the concentrations of petroleum hydrocarbons and selected trace metals (Cu, Pb, Zn, Cd, Ni, Fe) in the sediments of the Benin-Ethiope Fluvial System and also determining selected physicochemical parameters of sediments, pH, total organic carbon (TOC), total organic matter (TOM), and sediment texture (clay, silt and sand) by particle size analysis.

MATERIALS AND METHODS

Description of Study Area:

The present study area lies within the following coordinates, latitudes 5^0 00^1 N, 6^0 30^1 N and longitudes $5^0 00^1$ E, $6^0 45^1$ E. The study area is also shown in Figure 1 (Map of study area showing the sampling stations). Five sampling stations were established in the study area. These sampling stations and their geographical coordinates are given as follows: Rain Oil (5^0 56.5^1 N and 5^0 38.9^1 E), Nepal (5^0 32'N and 5^0 39'), Othniel Brooks (5^0 55.586'N and 5^0 38.74^1 E), Prudent Energy (5^0 54.122^1 N and 5^0 41.884'E), and Cybernetics (5^0 57.210'N and 5^0 59.025' E).Two sampling stations were established upstream to the study area which constituted the control area and they are, the First Upstream station (5^0 56.213'N and 5^0 39.176'E), and the Second Upstream Station (5^0 55.510'N and 5^0 39.085'E).

Design of Study, Collection and Preservation of Samples:

Samples were collected twice in each season (i.e. once in every quarter of a year) for two years from April, 2014 to March, 2016. Surface sediment samples were collected using a Van Vean sediment grab sampler from the bottom bed sediments and from the inter-tidal zone of the river (i.e. area between high tide and low tide). Sediment samples were collected for the following analytical parameters: trace metals (Cu, Pb, Zn, Cd, Ni and Fe), total organic extract

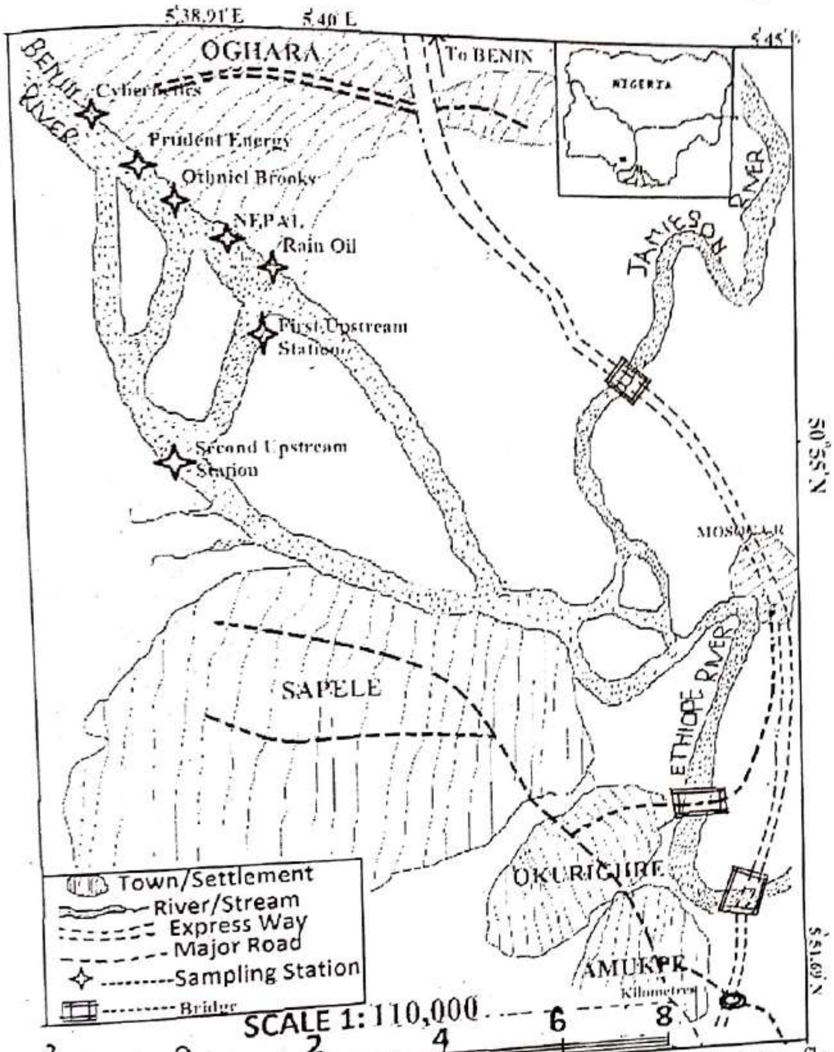

Figure 1: Map of study area showing the sampling stations

(TOE), and total petroleum hydrocarbons (TPH), total organic carbon (TOC) (or percentage organic carbon), and sediment texture (clay, silt and sand) by particle size analysis. Samples for TOE and TPH were first wrapped in aluminium foil sheets before being kept in polythene bags. Samples for these two parameters were kept in iced chest for transfer to the laboratory. At the laboratory the samples were kept in a deep freezer at below -10 ^{0}C before analysis.

Samples for trace metal analysis were kept in polythene bags for transfer to the laboratory where they were air-dried before analysis.

Analytical Procedures:

The pH of sediment samples was determined by dipping the electrode of a pH-meter in the supernatant liquid of a mixture of sediment and distilled water in a ratio of 2:1 of water to sediment in which the sediment particles have completely settled out leaving a clear supernatant liquid on top of the settled sediment particles. The pH-meter was earlier standardized against two pH buffer solutions, pH = 4 and pH = 7. TOC was determined by a modification of the Walkley-Black method (American Society of Agronomy-Soil Science Society of America, 1986)). The particle size analysis was carried out using the hydrometer method. The soil texture which consists of clay, silt and sand were determined using this method (Allens, 1989). The TOE was determined using a modification of method employed by Oudot et al. (1981) in which the Reflux method was used. Partially thawed sediment samples (200 g.) was placed in a round bottom flask, analar grade methanol (150 mL), 15 mL of 0.07 M KOH and 30 mL of pre-extracted distilled water were added. A double surface Liebig condenser was attached to the flask and the content of the flask was refluxed for one and half hours. The liquid extract from this procedure was re-extracted with three portions of 30 mL analar n-hexane.The combined organic (hexane) extract was distilled (to remove Solvent) and dried to constant weight. TOE was calculated from this weight of extract using eqüation 1

$$TOE\ \left({}^{mg}/_{kg}\right) = \frac{(A-B)x\ 10^{6}}{Dry\ weight\ of\ experimental\ sample}$$

---Equation 1

Where:

A = weight of TOE extract obtained forsample (g.)

B = weight of TOE extract obtained for blank (g.)

TPH was obtained from the TOE extract by re-dissolving TOE extract in hexane in a 250-mL glass beaker and 3 g. of partially activated silica gel (i.e. silica gel for column chromatography) was added. The content of the beaker was stirred with a magnetic stirrer for 5 min. The silica gel (with the fats it had adsorbed) was filtered out and filtrate solution collected in a clean dry round bottom glass flask. The solvent was distilled off and TPH extract dried to constant weight as done for TOE extract. TPH was obtained from the weight of this extract using equation 1.1.

Trace metals were determined by adding 50 mL of 2 M HNO_3 to 5 g. of dried sediment sample in a 250-mL glass beaker placed in a boiling water bath for 2 h. with stirring at 15 min interval. The digest resulting from this was analyzed using an atomic absorption spectrophotometer (Perkin Elmer 200 USA) (Anderson and Morel, 1978; Allens, 1989).

Indexes Used:

The indexes used included the following, enrichment ratio (ER), contamination/pollution (C/P) index and contamination factor (CF)

1) Enrichment Ratio

Enrichment ratio gives an indication of level of anthropogenic input of a trace metal into an environment (sediment or soil). The enrichment ratio of each metal in each sampling station was calculated using the average concentration of the metal in the four seasons (i.e. two wet and two dry seasons) for each sampling station and employing equation 2 (Simex and Helz, 1981)

$$ER = \frac{CxMs/CrMs}{CxMb/CrMb}$$ ------------------Equation 2

Where

CxMs = concentration of trace metal in study area

CrMs = concentration of reference trace metal in study area

CxMb = concentration of trace metal in reference matrix or background value

CrMb = concentration of reference trace metal in reference matrix or background value

The background values of metals are the world surface average (shale values) (Turkian and Wepohl, 1961) and the values are Cu = 45, Pb = 20, Zn = 95, Cd = 0.3, Ni = 68, Fe = 47200. Fe was chosen as the conservative or reference metal, this is because Fe is a ubiquitous element in most environments. The status of each sampling station with respect to each of the trace metal is given in accordance to that used in Loska et al. (2004) and they are as follows; ER < 2 shows "deficiency to minimal enrichment", ER = 2 – 5 shows "moderate enrichment", ER = 5 – 20 shows "significant enrichment", ER = 20 – 40 shows "very high enrichment" and ER > 40 shows "extremely high enrichment".0

2) Contamination/Pollution (C/P) Index

The C/P index of each sampling station with respect to a trace metal was calculated using the average concentration of the trace metal in the four seasons studied (i.e. two wet seasons and two dry seasons) and equation 3 was used in the calculation of the C/P index.

$$C/P = \frac{\text{Concentration of trace metal in sampling station}}{\text{Tolerable value of trace metal}}$$
---Equation 3

The tolerable level of trace 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).

The Lacatusu (1998) significance of interval was used in the interpretation of the results of the calculations and gave the pollution statuses of the sampling stations with respect to the trace metals. These are given as follows; C/P index < 0.1 shows "very slight contamination", C/P index = 0.10 – 0.25 shows "slight contamination", C/P index = 0.26 – 0.50 shows "moderate contamination", C/P index = 0.51 – 0.75 shows "severe contamination", C/P index = 0.76 – 1.0 shows "very severe contamination", C/P index = 1.1 – 2.0 shows "slight pollution", C/P index = 2.1 – 4.0 shows "moderate pollution", C/P index = 4.1 – 8.0 shows "severe pollution", C/P index = 8.1 – 16.0 shows "very severe pollution", and C/P index > 16.0 shows "excess pollution".

Statistical Procedures and Packages Employed:

A Comparison of the mean of each parameter in the different sampling stations and in the four seasons studied was carried out using analysis of variance (ANOVA-single Factor) from the Microsoft Excel package (Microsoft Corporation, 2007 Version). The mean of concentrations of each parameter in the study area was compared with the mean of concentration of corresponding parameter in the control area using t-test (two samples, assuming unequal variances). This was used from the Microsoft Excel package (Microsoft Corporation, 2007 Version). A Pearson (2-tailed) correlation of all parameters determined (with the exception of pH) employing the statistical package of the social sciences (SPSS) (SPSS Chicago, version 16) was also carried out.

RESULTS AND DISCUSSION

Comparison of Levels of Parameters in Study Area With Control Area:

The average concentrations of TOE and TPH were very much higher in the study area than in the control area Table 1). The average concentration of TOE in Study was found to be 10.4 time the average concentration of TOE in the control area. The average concentration of TPH in study area was also found to be 12.1 times the average concentration of TPH in the control area. The average values of these two parameters in the study area, TOE (4090±4100 $mgkg^{-1}$) and TPH (3180±3000 $mgkg^{-1}$) shows that there is oil pollution in the sediments of the study area. A comparison of the means of both parameters in the study area with their means in the control area using t-test (two samples, assuming equal variances) shows that the differences in their means are significant with p [2-tailed] values of 0.000677 and 0.000283 for TOE and TPH respectively. The presence of much oil on the surface of sediment can impede the diffusion of oxygen into the sediment and this can bring about deficiency of oxygen in the sediment core resulting in anaerobic conditions within the sediment core. This situation gives rise to increase in population of petroleum hydrocarbon utilizing microorganisms and other heterotrophic microorganism which can break down hydrocarbons and release energy for themselves and also build new cells under anaerobic conditions. This increase in population of these microorganisms (i.e petroleum utilizing microorganisms) is done at the expense of the more beneficial aerobic microorganisms which then decrease in population. This situation result in damage to and/or loss of biodiversity (Luisseli et al., 2006; Almeida. 2013). This effect is in addition to other effect of organic substances in sediment and soil already stated.

The source of this oil pollution in the sediments of the study area is most likely to be in the oil spillages from these petroleum industry downstream sector companies. The major activities in the area involve movement of large quantities of oil and spilled oil are visible on the surfaces of water of the fluvial system in this area. The pH of study area sediment varied between 4.1 and 6.6 with an average of 5.17±0.86 and that of control area varied between 4.8 and 6.6 with an average of 5.63±0.52 (Table 1). Thus the acidity of study area sediment was much higher than acidity of control area sediment. This high acidity has been probably brought about by the decomposition of organic matter and spilled oil into humic acid and other acid related compounds. These may have led to high acidity as years increased. The concentrations of trace metals were generally higher in the study area than in the control area with the exception of Cd which had an average concentration of 0.15±0.23 $mgkg^{-1}$ in the study area and 0.22±0.26 $mgkg^{-1}$ in the control area. A comparison of the mean of the concentrations of each metal in study area with the corresponding parameter in the control area has shown that the differences in their means were significant only in Zn and Fe with p[2-tailed] value of 1.11E-08 and 0.00564 for Fe and Zn respectively. The average value of silt and clay were generally lower in study compared with control area (and invariably higher percentage of sand). This indicates that the sediments of study have poor retention ability for pollutants and nutrients.

Spatial Variation of Levels of Parameters with Sampling Stations in the Study Area:

The results did not exhibit any definite pattern in the variation of levels of parameters from upstream to downstream. The average concentrations of the two oil parameters were higher in Nepal (TOE = 4900±4100 $mgkg^{-1}$ and TPH = 3180±2900 $mgkg^{-1}$) and Othniel Brooks (TOE = 4760±5100 $mgkg^{-1}$ and TPH = 3770±4100 $mgkg^{-1}$) sampling stations (Table 1). The average value of TOE was lowest at the Rain oil sampling station (3300±3400 $mgkg^{-1}$) and the average value of TPH was lowest at the Cybernetics sampling station (2550±2600 $mgkg^{-1}$). No explanation is suggested for these observations. The average concentrations of the trace metals were generally higher at the Rain oil and Prudent Energy sampling stations. A comparison of the mean of the two oil parameters and the six trace metals in the five sampling stations of study area using analysis of variance (ANOVA-single factor) shows that the differences in their means are statistically significant only in Fe with p[2-tailed] value = 6.23E-05.

Seasonal Variations of Sediment Physicochemical Parameters, Trace Metals and the Two Oil Parameters:

The average concentrations of the two oil parameters were extremely high in the first dry season. They were however much lower in the second dry season. The very high concentrations of these two oil parameters in the first dry season made the dry season average of their concentrations to be higher than the average concentrations of the two parameters in the two wet seasons. A comparison of the means of these two parameters in the four seasons using analysis of variance (ANOVA-single factor) shows that the differences in their means are significant with p[2-tailed] values of 3.33E-11 and 7.09E-18 for TOE and TPH respectively.

The average concentrations of Cd, Zn Pb and Cu were higher in the wet seasons compared with the dry seasons and the differences in their means when compared using analysis of variance (ANOVA-single factor) are significant with p [2-tailed] values of 0.000118, 5.33E-09, 0.00159 and 0.035125 for Cd, Zn, Pb and Cu respectively. pH levels were also lower in the wet seasons (i.e higher acidity) and the differences in its mean in the four seasons are also significant with p[2-tailed] value of 4.32E-07. This therefore means that rainfall played a significant role in arriving at these levels of pollutants and physicochemical parameters in the study area.

Results of Correlation of Concentrations of Parameters:

Results of Pearson [2-tailed] correlation of the concentrations of all parameters determined (with the exception of pH) shows that the following pair of parameters are very strongly correlated and their correlation coefficient (in parenthesis) are significant at 0.01 confidence level.: TOE and TPH (0.884), TOE and clay (0.826), TPH and clay (0.897), TOE and silt (0.864), TPH and silt (0.898), clay and silt (0.962), sand and Zn (0.456), Cu and Pb (0.805), Cu and Zn (0.486), Pb and Zn (0.532), Pb and Cd (0.431), Pb and Ni (0.701), Zn and Cd (0.675), Zn and Ni (0.785), and Cd and Ni (0.718). One other pair correlated strongly with the correlation coefficient being significant at 0.05 confidence level, that is Pb and Fe (0.361). Two important observations are here made from these results of the correlation of the parameters. The first is that the two oil parameters correlated strongly with clay and silt which shows that these two components of sediments retained them more. It can also be safely said that they are anthropogenic inputs in the sediment and the only process in the area that can bring about such input of these oil parameters into the sediment is oil spillages from the activities of petroleum industry downstream sector companies and their factories. The second observation is that five of the trace metals (Cu, Pb, Zn, Cd and Ni) correlated strongly with one another, showing that they have identical source. These five trace metals are trace components of petroleum which invariably means that they may be trace components of petroleum products. Although the concentrations of the five trace metals did not correlate strongly with the two oil parameters, there is the chance that the trace metals have the same source as the oil parameters.

Table 1: Results of determination of parameters (in mean±standard deviation) for study area and control area, all sampling stations in study area and control area

Parameters	Study Area	Control Area	Rain Oil	Nepal	Othniel Brooks	Prudent Energy	Cybernetics	First Upstream Station	Second Upstream Station
pH	5.17±0.86	5.63±0.52	5.35±0.98	5.10±0.79	4.93±0.92	5.20±0.80	5.25±0.93	5.89±0.39	5.38±0.53
TOC (%)	0.20±0.13	0.33±0.25	0.25±0.17	0.15±0.08	0.17±0.09	0.27±0.18	0.14±0.06	0.35±0.26	0.31±0.25
TOM (%)	0.34±0.23	0.57±0.43	0.43±0.30	0.25±0.14	0.30±0.15	0.47±0.33	0.25±0.11	0.61±0.44	0.53±0.43
TOE ($mgkg^{-1}$)	4090±4100	395±250	3300±3400	4900±4900	4760±5100	4140±3700	3330±3700	330±220	460±270
TPH ($mgkg^{-1}$)	3180±3000	263±180	3180±3400	3180±2900	3770±4100	3250±2400	2550±2600	230±160	300±200
Clay (%)	2.2±1.2	5.5±3.3	2.3±1.4	2.1±1.3	2.0±1.2	2.1±1.2	2.4±1.4	4.8±3.0	6.2±3.6
Silt (%)	0.73±1.3	2.9±3.4	0.59±1.0	0.65±1.2	0.75±1.4	0.82±1.5	0.82±1.5	1.7±2.0	4.0±4.3
Sand (%)	97.1±2.5	91.4±6.6	97.1±2.4	97.2±2.5	97.3±2.6	97.1±2.7	97.0±3.0	93.0±5.2	89.8±7.8
Cu ($mgkg^{-1}$)	1.4±2.9	1.3±1.9	2.6±4.4	0.11±0.24	1.3±3.3	2.4±3.1	0.54±0.70	0.73±0.50	1.8±2.6
Pb ($mgkg^{-1}$)	0.83±1.1	0.67±0.12	1.2±1.6	0.66±0.68	0.90±0.80	1.1±1.5	0.30±0.47	0.57±0.43	0.78±0.61
Zn ($mgkg^{-1}$)	22±26	2.5±3.1	15±23	12±15	21±22	26±29	33±38	4.3±3.6	0.81±0.70
Cd ($mgkg^{-1}$)	0.15±0.23	0.22±0.26	0.09±0.18	0.13±0.23	0.19±0.26	0.19±0.28	0.14±0.23	0.25±0.27	0.19±0.26
Ni ($mgkg^{-1}$)	1.4±1.4	1.02±0.73	1.7±1.6	1.0±1.1	1.3±1.5	1.8±1.9	1.1±1.2	1.00±0.65	1.04±0.84
Fe ($mgkg^{-1}$)	149±67	34.8±8.1	204±70	203±70	139±42	110±30	90±17	30.7±4.4	38.9±9.2

One other thing to note here is the strong correlation between Fe and Zn. This appear to indicate that Zn and Fe also have their sources in property development as observed by Akporido et al. (2015) in study carried out on sediments of the Benin-Ethiope Fluvial system in the sapele area. Zn and Fe are components of roofing sheets. Oghara town is a rapidly developing urban area so that the effect of urbanization can be seen in the moderately high concentration of Zn and Fe in the sediment.

Comparison of Average Concentration of Pollutant Parameters with Sediment Quality Guidelines (SQGs):

The average concentrations of the pollutant parameters were compared with three sediment quality guidelines (SQGs) (Table 2). The SQGs used are those of the National Oceanic atmospheric Administration (NOAA) of USA (NOAA, 1999), the Canadian Environmental Quality Guidelines (CEQG) by the Canadian Council of Ministers of the Environment (CCME, 1999) and the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) by the Department of Petroleum Resources (DPR) (DPR, 2002)(Table 4). The results showed that the average concentrations of the five trace metals ranked (Cu, Pb, Zn, Cd, and Ni) fell below the lower limit of the three SQGs used (i.e. the effect range low [ERL] of the NOAA SQGS, the target values of EGASPIN, and the Interim sediment quality guidelines (ISQG) of the CEQG). These lower limits of the sediment quality guidelines are values below which adverse effects of pollutants are unlikely to occur, in other words, are conditions most desired for the sediment in terms good and healthy environment. Based on these comparisons, the concentrations of the five trace metals do not therefore pose any serious threat as pollutants. The average concentration of TPH (3180±3000 $mgkg^{-1}$) however exceeded the target value of EGASPIN for mineral oil (petroleum hydrocarbon) (50 $mgkg^{-1}$) although it did not exceed the intervention value of 5000 $mgkg^{-1}$. An environment with concentration of TPH less than the Target value is an environment that is not polluted with petroleum hydrocarbon and a most desired condition for sediment in relation to good health for organism living in sediment. Exceeding the target value therefore means that there is some threat to the health of the organisms and plants in the sediment. As already stated oil pollution in sediment can affect living organisms adversely and can even lead to damage to and loss of biodiversity among other effects.

Results of Calculations of Indexes:

Results of calculations of indexes showed the following: values of enrichment ratios (ER) for all sampling stations were generally high with respect to Cu, Pb, Cd and Nickel. Based on the interpretation by Sutherland (2000) and Loska et al.(2004), Rain Oil (12.0), Othniel Brooks (9.00), and Cybernetics sampling stations have "significant enrichment" with copper while Prudent Energy Sampling Station (22.0) has "very high enrichment" with Cu. Four of the sampling stations, Rain Oil (15.0), Nepal (7.50), Othniel Brooks (15.0) and Cybernetics (7.50) have "significant enrichment" with Pb while the Prudent Energy station has "very high enrichment" with Pb. All the sampling stations, Rain Oil (66.2), Nepal (100), Othniel Brooks (233), Prudent Energy (283) and Cybernetics (267) have "extremely high enrichment" with Cd. Four sampling stations have "significant enrichment" with Ni. They are Rain Oil (5.93), Othniel Brooks (6.71); Prudent Energy (11.7 and Cybernetics (8.57). The result shows that These Four metals (Cu, Pb, Cd and Ni) have been enriched in the sediments of the study area by anthropogenic input of the trace metals.

Values obtained for the calculations of Contamination/pollution index were generally low and no meaningful deduction could be made from them.

The results of pH, TPH and each of the trace metals obtained in the study area were compared with results obtained for corresponding parameters in other countries and elsewhere in Nigeria (Table 3). pH values for study area varied from 4.1 to 6.6 (or average of 5.17±0.81) and this is moderately lower than results obtained for sediments of the Benin-Ethiope Fluvial system around sapele Town (5.8±1.0). This means that the acidity of study area sediment is high in most parts of the study area. High acidity which is brought about by decomposition of organic matter or breakdown of petroleum hydrocarbons to form products such as Humic acid and or H_2S can affect adversely the health of living organisms and plants in sediment (fauna and flora) The average value of TPH for study area, 3180±3000 $mgkg^{-1}$ (174.5 – 10745 $mgkg^{-1}$) was found to be comparable with average value obtained for the sediments of the Benin-Ethiope Fluvial system around sapele Town. The sediments of the Benin-Ethiope Fluvial System around Sapele Town had been observed to be polluted with petroleum hydrocarbons (Akporido et al., 2015). This has confirmed the fact that these petroleum downstream oil companies and their factories are capable of polluting a water body with petroleum residues from their activities which include offloading of petroleum products and lubricating base oil into depots and release of effluents from lubricating oil production factories.

The average concentration of Cd of study area, 0.15±0.23 $mgkg^{-1}$ (0.0 – 0.7 $mgkg^{-1}$0) was found to be comparable with result obtained for Bietri Bay and Ebrie Lagoon in Cote D'ivoire by Koffi et al. (2014). Bietri Bay and Ebrie Lagoon are known to receive effluent from multiple industrial concerns and their water and sediment have been observed to be polluted (Koffi et al., 2014). The average concentrations of the other trace metals were observed to be lower than concentrations obtained for corresponding trace metals in the other studies listed in Table 6. This has also confirmed observation made when the average concentrations of trace metals of study area were compared with Sediment Quality Guidelines (SQGs) that, the concentrations of most of the trace metals have not reach levels where they can pose threats to the health of sediment organisms and plants.

CONCLUSION

In this study sediment physicochemical parameters (pH, TOC, TOM, Soil texture [i.e. clay, silt and sand]), trace metals (Cu, Pb, Zn, Cd, Ni and Fe) and two oil parameters (TOE and TPH) were analyzed in the sediment of study area and the control area. Result has shown that pH of study is generally low (between 4.1 and 6.6) which means that acidity of sediment is high. High acidity is not good for the health of sediment dwelling organisms and plants. The average values of total organic extract (TOE) ant total petroleum hydrocarbon (TPH) were high (they are higher than sediment quality guidelines). The sediments of the study area is polluted with petroleum hydrocarbon. The presence of high concentrations of petroleum hydrocarbon in sediment can be toxic to biological processes and so can affect animal and plant life. Environmental authorities should monitor the activities of these petroleum industry downstream sector companies and their factories to ensure compliance with guidelines and regulations governing such activities.

Table 2: Comparison of results of Heavy metal and Total petroleum hydrocarbons with three Sediment Quality Guidelines (SQGs)

Parameter	Average Concentr-ations In Study Area ($mgkg^{-1}$)	Guideline Values ($mgkg^{-1}$)						Percent Incidence Biological Effect			Inferred Contami- nation Level
		NOAA ERL Values	NOAA ERM Values	EGASPIN Target Value	EGASPIN Intervent-ion Values	ISOQ Values	PEL Values	<ERL	ERL <% < ERM	> ERM	
Cu	1.4±2.9	34	270	36	190	35.7	197	9.4	29*	83.7	Low or no contamination
Pb	0.83±1.1	46.7	218	85	530	35	91.3	8.0*	35.8	90.2	Low or no contamination
Zn	22±26	150	410	140	720	123	315	6.1	47.0*	69.8	Low or no contamination
Cd	0.15±0.23	1.2	9.6	0.80	12	0.60	3.5	6.6	36.7	65.7	Low or no contaminated
Ni	1.4±1.4	20.9	51.6	35	210	-	-	1.9*	16.7	16.9	Low or no contamination
Fe	149±67	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline	Not ranked
TPH	3180±3000	-	-	50	5000	-	-	-	-	-	Intermediate contamination

*applicable % biological incidence effect for the specific parameter. NOAA = National Oceanic Atmospheric Administration sediment quality guidelines (SQGs) (NOAA, 1999)

EGASPIN = Environmental Guidelines and Standards for the petroleum Industry in Nigeria SQGs by Department of Petroleum Resources (DPR) (DPR, 2002), TPH = total petroleum hydrocarbon

Table 3: Average results of pH, TPH and the six trace metals for study area and results obtained in other studied in other countries and elsewhere in Nigeria

Country	Water Body	Major Activity in Area	pH	TPH ($mgkg^{-1}$)	Cu ($mgkg^{-1}$)	Pb ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Cd ($mgkg^{-1}$)	Ni ($mgkg^{-1}$)	Fe ($mgkg^{-1}$)	References
India	Haldi River (West Bengal)	Industrial Area	-	-	17.0	13.9	48.7	13.0	22.4	20100	Kumar et al., 2011
India	Rupnarayan River	Industrial Area	-	-	15.1	14.3	49.5	16.0	22.4	17200	Kumar et al., 2011
Cote D'Ivoire	Bietri Bay and Ebrie Lagoon	Industrial Area	-	-	21.12	26.53	106.32 – 509.75	0.11 – 1.25			Koffi et al., 2014
Nigeria	Benin-Ethiope Fluvial System (around Sapele)	Industrial and Urban Area	5.8±1.0	2800±1900	12±16	38±35	63±56	7.10±20	12±15	-	Akporido et al., 2015
United Kingdom	Irwell and Upper Mersey Catchment of Manchester Fluvial System	Industrial Area	-	-	53.1 – 383	80.4 – 442	282 - 1020	-	-	-	Hurley et al., 2017
Vietnam	South China Sea;: Vietnamese Waters	Industrial Area. First period(April, 2009)	-	-	53±61	96±129	305±425	0.69±1.2	37±28	30366± 17600	Kara et al., 2015
Slovenia	Sava River	Industrial area	-	-	-	-	-	-	250	-	Vidmar et al., 2016
Nigeria	Benin-Ethiope Fluvial system (around Oghara Town)	Industrial Area	5.17± 0.86 (4.1 – 6.6)	3180±3000 (174.3 – 10745)	1.4±2.9 (0 – 9.5)	0.83±1.1 (0 – 3.77)	22±26 (0 – 89.5)	0.15±0.23 (0 – 0.7)	1.4±1.4 (0 – 4.25)	149±67 (64.3 – 308)	Present study

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