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EFFECTS OF PETROLEUM PRODUCTS SPILLAGES ON THE WATER QUALITY OF BENIN –ETHIOPE FLUVIAL SYSTEM IN OGHARA, NIGERIA

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Abstract: Activities of petroleum industries downstream sector companies in and around Oghara town results in continuous spillages of petroleum products and lubricating base oil in the water of the Benin-Ethiope Fluvial System in the vicinity. The study therefore examined the effect of these spillages on the quality of water of the fluvial system in this area. Water samples were collected from the fluvial system around Oghara town twice every season for two wet and two dry seasons. The physicochemical parameters of water were determined by standard methods, heavy metals were determined by method of flame atomic absorption spectrometry after digestion of water sample with pre-concentration by heating and evaporation. The results obtained were, pH (5.48±0.39), biochemical oxygen demand (BOD) (2.2±1.2 mgL^{-1}), chemical oxygen demand (COD) (61±22 mgL^{-1}), oil and grease (O&G) (1.87±0.79 mgL^{-1}), total petroleum hydrocarbons (TPH) (1.42±0.66 mgL^{-1}), Ni (0.08±0.08 mgL^{-1}) and Cd (0.01±0.01 mgL^{-1}). The concentrations of most pollutant parameters were higher in the study area water than in the control area water (BOD [7.3±3.4 mgL^{-1}], COD [42±28 mgL^{-1}], O&G [0.65±0.50 mgL^{-1}], TPH [0.50±0.38 mgL^{-1}],Ni [0.01±0.01 mgL^{-1}], Cd [0.004±0.004 mgL^{-1}]) . The average pH value was lower than control area water (5.48±0.39) and also lower than guideline range for pH. The average Ni value of water exceeded guideline values. The results of these two parameters (pH and Ni) showed that the water was not fit for drinking. Classification of water of the five sampling stations of the study area gave them pollution status of either "slightly polluted" or "polluted." The quality of study area water was therefore found to be very low and need to be thoroughly treated before it can be used for drinking and other domestic uses.

Keywords: Benin-Ethiope, fluvial system, Oghara, petroleum products, spillages

Introduction

The Niger Delta is known for crude oil prospecting and processing, and this has brought about oil spillages in the environment. These spillages can be categorized into major and minor spillages. Major spillages which are usually accidental spillages from oil well blowout for example when there is oil well decapitation or breakage of major oil conveying pipelines caused by dysfunctional equipment. Minor oil spillages release less than 100 barrels of oil and this occurs at the oil wells and is also due to dysfunctional equipment and along smaller pipelines and release may also be caused by sabotage. The effect of these oil spillages on the environment and consequently on the economy which is estimated to cost the area and the nation a lot of funds have led to much attention being focused on the upstream sector of the petroleum industry in the Niger Delta area. The impact of crude oil spillages on the environment especially large spillages have been well documented to include, damage to and loss of biodiversity, depletion of arable land, depletion of available potable water and blockage of water ways (Forstner and Whitman, 1983; GESAMP, 1993; Luiselli *et al.*, 2006; UNEP, 2011) Recently attention of environmentalists is being attracted to the growing downstream sector of the petroleum industry in Nigeria and the effect of activities in the sector on the Niger Delta environment.

The downstream sector of the petroleum industry includes, refineries (which refines crude oil and produce petrochemicals), petroleum products depot (where imported and locally produced petroleum products are stored for distribution), transportation involving use of tankers (both boat and lorries) to bring in petroleum products obtained by importation and lifting of petroleum products for distribution locally, lubricating oil producing factories and importation of lubricating base oil, petroleum products filling stations etc.. Several studies have been carried out on the quantification of petroleum residue (petroleum hydrocarbons) and trace metals from such sources (Nduka & Orisakwe, 2011; Akporido & Kadiri, 2014; Akporido *et al.*, 2015). Spillages from petroleum products are similar to those from crude oil.

The Benin-Ethiope Fluvial system consist mainly of two rivers i.e. the Benin River and the Ethiope River. Most of the companies or their factories are located along the fluvial system. Akporido & Kadiri (2014) and Akporido *et al.* (2015) studied water and sediments respectively of the Benin-Ethiope Fluvial System in the vicinity of Sapele Town. Results from the two studies showed that these companies of the downstream sector of the petroleum industry actually polluted the waters and sediments of the fluvial system. Oghara town and area around it which constitute the present study area is located not far from Sapele Town. It is less than 6 kilometres from Sapele. Oghara town is unique in a way in that most of the companies operating in the town can be classified as part of the downstream sector of the Petroleum industry. The petroleum products depots are many and evidence for this can be seen in the number of petroleum products tanker Lorries lined up to lift gasoline, kerosene and diesel and other materials from the depot. On the river many Tanker boats can be seen offloading petroleum products into depot.

Oghara Town and Sapele Town lie in the same geographical zone. The rock type is mainly sedimentary rock. The main occupation of the people in this area is farming and fishing. Some work in these downstream oil companies and in the public sector (i.e. in government service). The arable crops include *Manihot esculenta* (cassava), *Zea mays* (maize), *Dioscoreo Sp*. (yam), *Solanum lycoperscium* (tomatoes), *Ananu comosus* (pineapple), *Telfairia occidentalis* (fluted pumpkin). The tree fruit crops include *Magnifera indica* (mango), *Elaeis guineensis* (oilpalm), *Cocus nucifera* (coconut). The river also supplies most of the fresh fish sold or eaten in the surrounding local government areas. The water of the fluvial system is used for drinking and other domestic purposes in some of the rural areas near to the town where there are no pipe borne water and sinking of boreholes cannot be afforded by the local people. Oil-like materials can be seen floating on the surface of the river in some places.

The hypothesis of this study is to assess the effect of activities involving these downstream oil companies or their factories on the levels of physicochemical parameters of water, concentrations of heavy metals and the oil contents (i.e. oil and grease and total petroleum hydrocarbons contents) of water of this fluvial system in this stretch of the river and that their levels should increase as a result of oil spillages from the activities of these petroleum downstream sector companies. There is currently a dearth in information on the effect of such activities on the water, soil and sediment of the environment in Oghara area. This study examined the effect of activities of the downstream oil companies in and around Oghara on the waters of the Benin-Ethiope Fluvial System by determining the concentrations of oil and grease (O & G), total petroleum hydrocarbons (TPH), selected heavy metals (Cd, Zn, Pb, Cu, Ni and Fe) and the following physicochemical parameters of water, pH, temperature, total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), dissolved oxygen (DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

Materials and Methods

Description of study area

Oghara Town is about 6 km from Sapele. The study area is bound by the following co-ordinates: Longitudes 5° 35' E, 5° 43' E and latitudes 5° 53' N, 5° 58' N and is shown in Fig. 1 (Map of Study area showing the sampling stations). The five sampling stations are respectively located near the following companies and so bear their names (each bearing the name of the company it is near to). The companies include, Rain Oil Company Ltd. Nepal Company Ltd, Othniel Brookes Company Ltd, Prudent Energy Ltd, and Cybernetics Ltd. The two upstream sampling stations which make up the control area, the first is located 500 m upstream from Rain oil sampling station at the confluence of the arm of the main river that did not pass near Sapele Town and a branch from the River that pass near Sapele and this was designated as "First upstream Station". The second upstream sampling station is located on the main arm of river that passed by (or near) Sapele Town at the point where tributary went to the First Upstream sampling station (i.e. at the confluence).

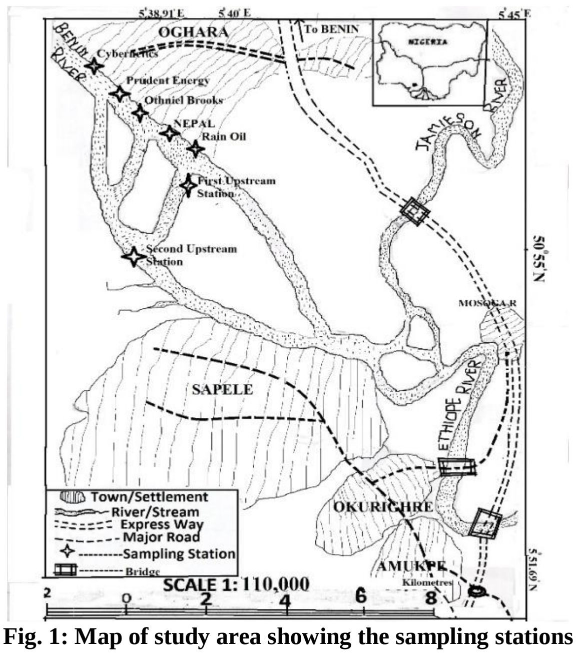

Fig. 1: Map of study area showing the sampling stations

Design of study, sample collection and sample preservation

Five sampling stations were established in the study area and two sampling stations were established upstream to the study area which constituted the control area. Grab samples were collected from each sampling station at the surface (1 metre to the surface) and at the mid-depth at the various sampling stations using Human divers who collect water samples by covering the sample bottles and opening them at the desired depth, collecting the water sample and covering the sample bottles again. Water samples were preserved as described in standard methods (APHA-AWWA-WEF, 1995). The holding period for each type of sample (parameter) was strictly adhered to. Water samples were collected for the following parameters, pH, TS, TSS, TDS, DO, BOD, COD, O & G, TPH and trace metals (Cu, Pb, Ni, Cd, Zn and Fe), Sample collection was carried out twice in each season for two years (i.e. once in each quarter of the year) from June, 2014 to March 2016.

Determination of various parameters

pH and temperature were determined at the sampling stations. These two parameters were determined as described in standard methods (APHA-AWWA-WEF, 1995). TS, TSS, TDS, Dissolved Oxygen, BOD and COD were also determined as described in standard methods (APHA-AWWA-WEF, 1995). The gravimetric method was used in the determination of O & G with hexane as the main solvent, other details are as contained in standard methods (APHA-AWWA-WEF, 1995). The TPH value was determined from the Hexane extract of the O & G by re-dissolving extract in 200 mL of hexane, adding 3.0 g of activated silica gel (for column chromatography) and stirring the contents for 5 min with a magnetic stirrer. The silica gel with the fats it had adsorbed was filtered out and the solvent distilled out. The residue was dried to constant weight in a desicator. Details and calculations are as given in standard methods (APHA-AWWA-WEF, 1995). The trace metals were determined by first digesting water sample by pre-concentrating 500 mL of water sample with heating and evaporation to below 10 mL and diluting this with distilled water to the 50 mL mark in a 50- mL volumetric flask. The digested solution was then aspirated into a flame atomic absorption spectrophotometer (Perkin Elmer AA 200, Wattham, USA).

Determination of quality assurance (control)

The quality control methods employed included the determination of blanks for all parameters determined. All determinations were also made in duplicates. The glucose-glutamic acid check for BOD determination was carried out employing method described in standard methods (APHA-AWWA-WEF, 1995). Recovery studies were also carried out. The percentage recoveries of COD, O & G, TPH and the six trace metals were determined. The determination of the % recovery of COD was carried out by determining COD on standard solutions of Potassium hydrogen Phthalate (KHP) (i.e. containing a concentration of 425 mgL^{-1}). The mean of five determinations was compared with the theoretical value of 500 mgL^{-1} (APHA-AWWA-WEF, 1995). The percentage recoveries of the remaining parameters were carried out by spiking a known volume of water sample (in which the concentration of the parameter had been determined) with a standard solution of the parameter and re-determining the parameter in the spiked sample employing the same method which was initially used for determining the parameter in the water sample. The following average results were obtained for five determinations of each parameter: COD (93.5±6.3%), O & G (92.7±4.6%), TPH (92.3±3.7%), Cu (94.7±6.5%), Pb (96.5±7.7%), Ni (94.4±5.7%), Cd (91.7±5.5%), Zn (98.7±6.8%) and Fe (99.5±7.2%).

Index used

The single index of pollution (Prati *et al.*, 1971) was used in the classification of the waters of the five sampling stations in the study area. The average COD values of the different sampling stations were used. According to this method of classification, COD values from 0 – 10 mgL^{-1} has index of quality = 1, falls into class I and has status of "excellent", COD above 10 up to 20 mgL^{-1} has index of quality -= 2, falls into class II and has a status of "acceptable". COD values from above 20 up to 40 mgL^{-1} has index of quality = 4, falls into class III and has pollution status of "slightly polluted", COD values above 40 mgL^{-1} up to 80 mgL^{-1} has index of quality = 8, falls into class IV and has a pollution status of "polluted", COD values above 80 mgL^{-1} have index of quality > 8, falls into class V and has status of "heavily polluted"..

Statistical methods used

The statistical methods and packages employed included comparison of the mean of concentrations of each parameter in the four seasons studied (i.e. two wet seasons and two dry seasons) and comparison of the mean of the concentrations of each parameter in the five sampling stations in the study area using Analysis of variance (ANOVA- Single factor) from Microsoft Excel package (Microsoft Corporation LTD) (version 2007) for both comparisons. The next is the comparison of the mean of concentrations of each parameter in the study area with the mean of concentrations of corresponding parameter in the control area using t-test (two samples, assuming unequal variance) at 0.05 confidence level with 0 hypotheses from Microsoft Excel package (Microsoft Corporation Ltd.) (Version 2007). A bivariate correlation of the parameters in the matrix (water) (with the exception of pH and the two metals, Cu and Pb which were not detected) using the Pearson (2-tailed) correlation was employed from the statistical package for the Social Sciences (version 16) (SPSS, Chicago)

Results and Discussion

A comparison of the average values of the parameters in the study area with corresponding parameters in the control area (Table 1) showed that the average pH of study area water (5.48±0.39) was lower than the average pH of the control area water (6.45±0.23) which indicated that water of the study area was more acidic than water of the control area. This may be as result of the continuous spillages of oil related materials into the water of the study area from the activities of petroleum downstream sector oil companies through the offloading of imported petroleum products and lubricating base oil into depot, lifting of petroleum products for distribution to filling stations, and to a lesser extent effluents from lubricating oil factories located in the area. The following parameters have higher average values in the study area compared with the control area as given in Table 1, COD, O & G, Ni, Zn, Cd and Fe. Cu and Pb were not detected in study area and control area. A t-test (two sample, assuming unequal variances) comparison of the mean of these parameters in the study area with corresponding parameters in the control area showed that the differences in their mean were statistically significant with P (2-tailed) values of 0.020083, 1.46E-08, 3.9E- 08, 3.77E-06, 0.00134, 0.001569 and 1.7E – 25 for COD, O & G, TPH, Ni, Cd. Zn and Fe, respectively. The variation of the concentrations of the parameters in the sampling stations will be discussed in two stages. For the purpose of this discussion the measured parameters were separated into two groups. This was done for ease of discussion since members of a particular group have similar behavior in each of the sampling stations. The first group of parameters included pH, Temperature, TS, TSS, TDS and DO and their average concentrations appeared in Table 1 and those of the second group consisted of BOD, COD, O & G, TPH, Ni, Cd, Zn and Fe which have their levels illustrated with Figs. 2 to 9. For the group 1 parameters, there was no definite pattern of variations of the concentrations of these parameters from upstream to downstream. Average values of pH were lower at Prudent Energy (5.18±0.17) and Rain Oil (5.26±0.11). The average levels of TS, TSS TDS and DO were highest at the Prudent Energy. A look at Figs. 2 – 9 showed that COD, O & G, TPH and Ni also peaked at the Prudent Energy Sampling stations for most of the seasons and did not also show any specific pattern in the variations of the concentrations from upstream to downstream. These may be as a result of the fact that most of the offloading of petroleum products and lubricating base oils occur close to this sampling station. The Rain Oil sampling station was next to the Prudent Energy station. Similar reason can be adduced as given for Prudent Energy sampling station. The Prudent Energy and the Rain oil sampling stations are thus the most polluted of the sampling stations. A comparison of the mean of these parameters in the five sampling stations using analysis of variances (ANOVA-Single factor) Showed that the differences in their means were significant in the following parameters (with the P [2-tailed] values given in parenthesis): BOD (0.000114), COD (0.010352), O & G (2.24E-10), TPH (1.33E-06), Cd (0.002487), Zn (0.000311) and Fe (8.19E- 08). The difference in the mean for Ni was not significant (P [2-tailed] = 0.557623). Seasonal changes did not appear to have any marked effect on the levels of most parameters. A comparison of the mean of the concentrations of the parameters in the four seasons studied using analysis of variance (ANOVA-single factor) showed that the differences in their means were not statistically significant.

Table 2 presents the Pearson (2-tailed) correlation of the parameters in the water matrix. The important thing to note here is that the TS, TSS, TDS and BOD correlated strongly with O & G and TPH. These showed that most of the solids and materials that are biological oxygen demanding substances are related to oil and grease or petroleum hydrocarbons or have the same source as these two oil parameters. This gives credence to the fact that the oil parameters are important pollutants in this area. They enter the water through spillages of petroleum products and lubricating base oils and these spillages occur during the offloading of these substances into the depot from oil carrying Tanker boats. They also occur during the lifting of petroleum products from the depot for re-distribution to consumers through the filling stations

The average levels of the parameters in the study area were also compared with national and international guidelines for drinking water and these are presented in Table 3. The average pH for study area water (5.48±0.39) fell below the Standard Organization of Nigeria (SON) guideline range for pH (6.5 – 8.5) (SON, 2997), the secondary drinking water regulation (SDWR) of United States Environmental Pollution Agency (USEPA) range (6.5 – 8.5) (USEPA, 2012) and the aesthetic objective (AO) pH range of Health Canada (6.5 – 8.5) Health Canada, 2012). All these indicated that the water of the study area may be too acidic for drinking purpose. This means that the rural dwellers near Oghara Town that use this water for drinking purpose may have their health adversely affected. The effect of high acidity on the environment is that it can mobilize heavy metals and make them more readily available for uptake by plants and other living organisms and this eventually reach man or higher animals through the food chain. High acidity can also have adverse effect on the growth of plants. High acidity in a river can cause loss of fish from the river (Moyle, 2006). The average value of Ni in the study area (0.08±0.08 mgL^{-1}) exceeded the SON guideline for Ni (0.02 mgL^{-1}) and the WHO guideline (0.07 mgL^{-1}) WHO, 2011). Ni is an important trace metal component of petroleum and petroleum products and this is an indication it may have entered the water of this area through the spillages of petroleum products and lubricating base oil. Nickel is a toxic metal and it can cause kidney dysfunction, heart attack, cancer, intestinal, lung, skin problems, nausea, vomiting, haemorrhage, low blood pressure, muscle tremors and paralysis (Gola *et al.,* 2016).

Table 1: Average values (mgL^{-1}) of parameters in water of study area, control area, sampling stations of study area and sampling stations of control area given in mean ±standard deviation (n^{SA} = 40, n^{CA}= 16, n^{SS}= 10, n^{CS} = 8)

Parameters	Average Levels of Parameters in Study Area	Average Levels of parameters in Control Area	Control Area Sampling Stations		Study Area Sampling Stations				
			First Upstream Station	Second Upstream Station	Rain Oil	Nepal	Othniel	Prudent Energy	Cybernetics
pH	5.48±0.39	6.45±0.23	6.36±0.28	6.54±0,14	5.26±0.11	5.41±0.24	5.85±0.32	5.18±0.17	5.61±0.61
Temp. (^{0}C)	24.8±0.60	26.6±1.0	26±0.76	27.1±1.0	24.5±0.5	25.1±0.4	24.5±0.5	25.3±0.72	24.7±0.5
TS (mgL^{-1})	0.63±0.51	0.62±0.37	0.41±0.33	0.63±0.28	0.13±0.02	0.27±0.24	1.10±0.63	1.01±0.18	0.65±0.35
TSS (mgL^{-1})	0.32±0.26	0.29±0.21	0.23±0.23	0.34±0.17	0.09±0.02	0.17±0.20	0.51±0.31	0.47±0.19	0.38±0.24
TDS (mgL^{-1})	0.33±0.29	0.42±0.26	0.31±0.30	0.53±0.15	0.07±0.02	0.16±0.13	0.61±0.36	0.53±0.21	0.30±0.18
DO (mgL^{-1})	3.6±1.2	2.65±0.98	2.7±1.0	2.7±1.0	2.72±0.36	3.80±0.80	2.28±0.83	5.15±0.38	4.0±1.1
BOD_5 (mgL^{-1})	2.2±1.2	7.3±3.4	6.2±2.2	8.5±4.1					
COD (mgL^{-1})	61±22	42±28	40±26	43±32					
O&G (mgL^{-1})	1.87±0.79	0.65±0.50	0.65±0.46	0.65±0.57					
TPH (mgL^{-1})	1.42±0.66	0.50±0.38	0.48±0.35	0.50±0.43					
Cu (mgL^{-1})	BDL	BDL	BDL	BDL					
Pb (mgL^{-1})	BDL	BDL	BDL	BDL					
Ni (mgL^{-1})	0.08±0.08	0.01±0.01	0.01±0.01	0.01±0.01					
Cd (mgL^{-1})	0.01±0.01	0.004±0.004	0.004±0.002	0.001±0.004					
Zn (mgL^{-1})	0.05±0.04	0.02±0.02	0.02±0.03	0.013±0.01					
Fe (mgL^{-1})	0.33±0.08	0.02±0.01	0.02±0.003	0.02±0.004					

N^{SA} = number of study area samples, n^{CA} = number of control area samples, n^{SS} = number of samples in study area sampling station, n^{CS} = control area station samples

Table 2: Pearson (2- tailed) correlation of concentrations of parameters in the water matrix (N = 40)

	Temp	TS	TSS	TDS	DO	BOD	COD	O & G	TPH	Ni	Cd	Zn	Fe
Temp.	1.000												
TS	0.187	1.000											
TSS	-0.021	0.873^{xx}	1.000										
TDS	0.181	0.850^{xx}	0.819^{xx}	1.000									
DO	459^{x}	0.261	0.241	0.105	1.000								
BOD	0.00	0.383^{x}	0.378^{x}	0.413^{x}	0.032	1.000							
COD	-0.133	-0.385^{x}	-0.472^{xx}	-0.225	-0.635^{xx}	-0.247	1.000						
O & G	0.291	0.688^{xx}	0.582^{xx}	0.529^{xx}	0.415^{x}	0.520^{xx}	-0.415^{xx}	1.000					
TPH	0.280	0.695^{xx}	0.595^{xx}	0.555^{xx}	0.370^{x}	0.501^{xx}	-0.408^{xx}	0.901^{xx}	1.000				
Ni	0.064	-0.242	-0.265	-0.113	-0.062	-0.172	0.230	0.250	-0.193	1.000			
Cd	0.176	-0.064	-0.074	-0.163	0.226	-0.075	0.060	-0/039	-0.025	0.222	1.000		
Zn	-0.153	-0.205	-0.289	-0.149	-0.463	-0.319	0.585^{xx}	-0.286	-0.201	0.108	0.093	1.000	
Fe	-0.219	0.335^{x}	0.315	0.361^{x}	-0.294	0.344^{x}	0.039	0.054	0.102	0.009	0.110	-0.121	1.000

^{xx}correlation significant at 0.01 (2-tailed); ^{x}Correlation significant at 0.05 (2-tailed)

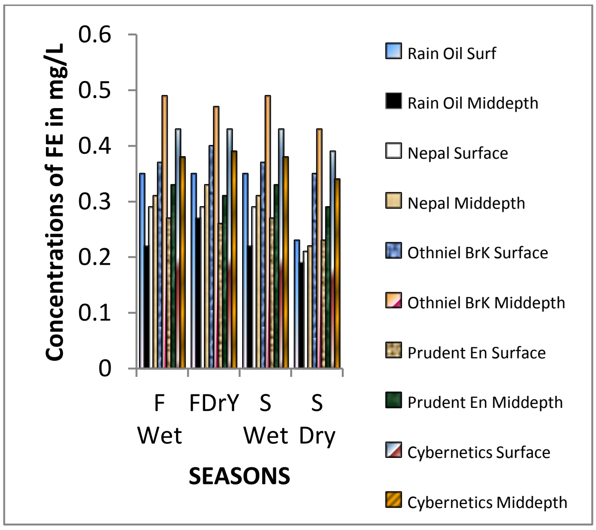

Fig. 2: BOD level of the sampling station in each of the seasons studied

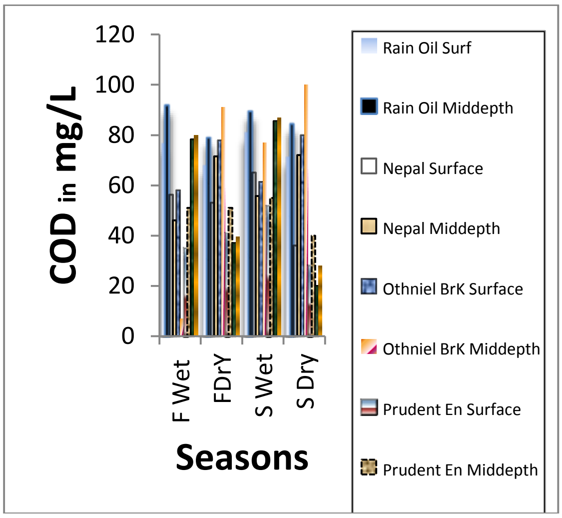

Fig. 3: COD values of the sampling stations for each season studied

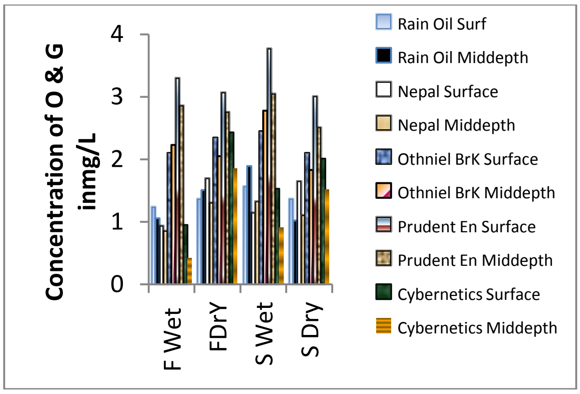

Fig. 4: O & G values of the sampling stations for each season studied

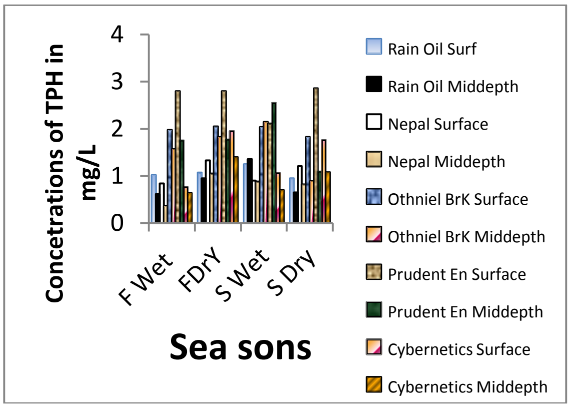

Fig. 5: TPH value of sampling stations for each season studied

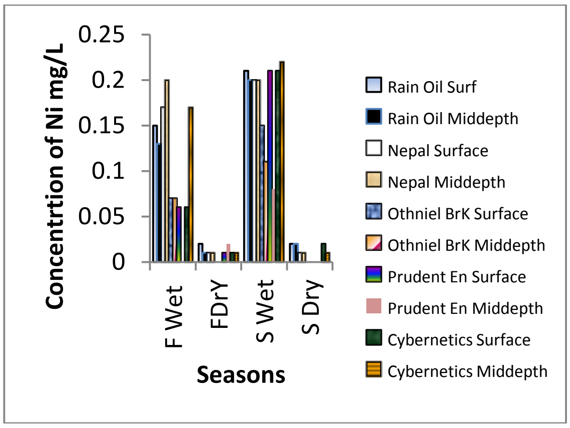

Fig. 6: Concentrations of Ni of sampling stations for each of the seasons studied

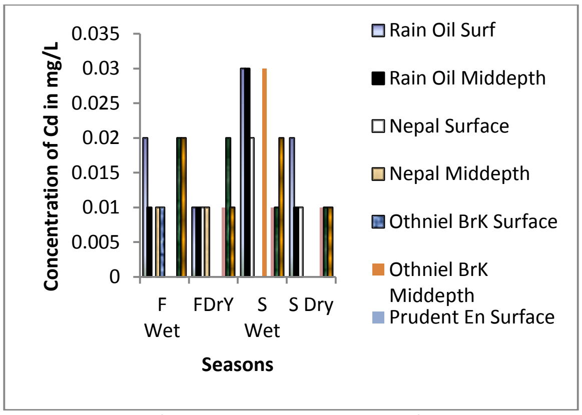

Fig 7: Cd levels of sampling stations in each of the seasons studied

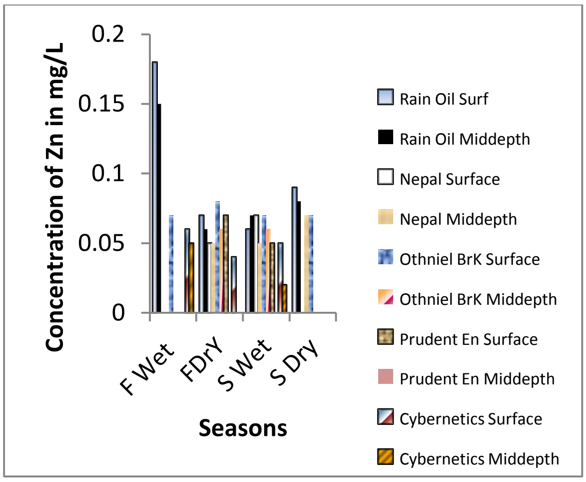

Fig. 8: Zn levels of sampling station in each of the seasons studied

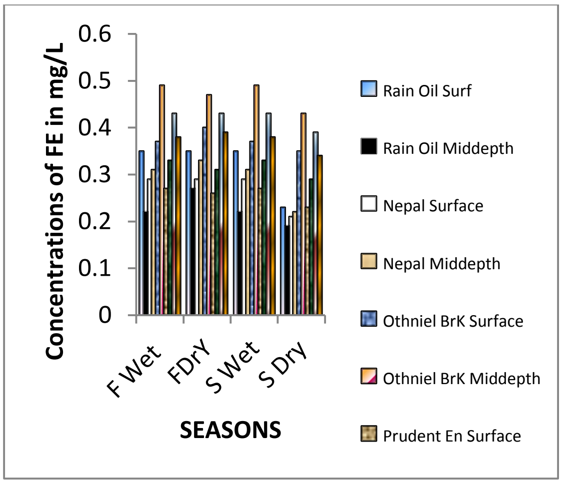

Fig. 9: Fe levels of sampling stations in each of the seasons studied

The mechanism of heavy metal toxicity is generally based in the cells of the body of organisms. It involves processes such as binding to critical functional groups of enzymes and other molecular structures that perform important physiological functions. This process of binding is done by Chelation, ion-exchange, ion replacement and others (Bryan & Langston, 1992; Onianwa, 2016). Results of classification of water of the five sampling stations of study area using the single index of pollution (Prati *et al.*, 1971) (Table 4) (using COD) showed that the Rain Oil sampling station which had an average COD of 80.2±8.4 mgL^{-1} was classified as having an index of quality = 8 and put into class IV with a pollution status of "polluted." The other four stations were given index of quality = 4 and grouped into class III and have pollution status of "slightly Polluted". Thus water of the study area can be said to be moderately polluted. The water is not fit for drinking as it is unless it undergoes rigorous treatment. The results obtained for water of the study area were also compared with guidelines for non-drinking uses of water. The results of these comparisons are presented in Table 5. The average pH of water of study area (5.48±0.39) fell below guideline ranges for all industries employing water for their production listed in Table 6 with the exception of the pulp and paper .industry which had no guideline for pH.

The implication of this is that the water of the study area was found to be too acidic for used in these industries for their production without undergoing rigorous treatment. The average TSS value of study area water (0.32±0.26 mgL^{-1}) exceeded guideline value for the power generation industry (boiler feed water) (<0.05 mgL^{-1}), The DO value for the study area (3.6±1.2 mgL^{-1}) exceeded guideline value for power generation (boiler feed water) (0.007 mgL^{-1}). The average BOD of study area water (2.2±1.2 mgL^{-1}) exceeded the Federal Ministry of Environment (Nigeria) guideline for textile industry (for dyeing process) (<1.0 mgL^{-1}).

Table 3: Average concentrations of parameters compared with national and international guideline values

Parameter	Average Values in Study Area	Nigerian Drinking Water Standards (SON, 2007)	WHO Drinking Water Guidelines (WHO, 2011)	2012 Edition USA Drinking Water Standards (USEPA, 2012	Canadian Drinking Water Standards (Health Canada, 2012)
pH at 25 °C	5.4 8±0.39	6.5 – 8.5	NS	6.5 – 8.5 (SDWR)	6.5 – 8.5 (AO)
Temp. (°C)	24.8±0.60	Ambient	NS	NS	NS
TS (mgL^{-1})	0.63±0.51	NS	NS	NS	NS
TSS	0.32±0.26	NS	NS	NS	NS
TDS (mgL^{-1})	0.33±0.29	NS	NS	500 (SDWR)	NS
DO (mgL^{-1})	3.6±1.2	NS	NS	NS	NS
BOD_5 (mgL^{-1})	2.2±1.2	NS	NS	NS	NS
COD (mgL^{-1})	61±22	NS	NS	NS	NS
O & G (μgL^{-1})	1.87±0.79	NS	NS	NS	NS
TPH (mgL^{-1})	1.42±0.66	NS	NS	NS	NS
Cu (mgL^{-1})	BDL	1.00	2.00	1.30 (MCL)	1.00 (MAC)
Pb (mgL^{-1})	BDL	0.01	0.01	0.015 (MCL)	0.01
Ni (mgL^{-1})	0.08±0.08	0.02	0.07	NS	NS
Cd (mgL^{-1})	0.01±0.01	0.003	0.003	0.005 (MCL)	0.005 (MAC)
Zn (mgL^{-1})	0.05±0.04	2.00	NS	5.00 (SDWR)	5.00 (MAC)
Fe (mgL^{-1})	0.33±0.08	NS	NS	0.30 (SDWR)	NS

SDWR = Secondary Drinking Water Regulation of USEPA; MCL = Maximum Contaminant Level of USEPA; AO = Aesthetic Objective value of Canada; MAC = Maximum Allowed Concentration of Canada, NS = not specified

Table 4: Classification of water of sampling stations using a single index of pollution (COD) (Prati *et al.*, 1971)

Sampling Station	Average value of COD (mgL^{-1})	Index of Quality	Class of Water	Pollution Status
Rain oil	80.2±8.4	8	IV	Polluted
Nepal	57±12	4	III	Slightly polluted
Othniel	69±29	4	III	Slightly polluted
Prudent Energy	44.1±9.8	4	III	Slightly polluted
Cybernetics	57±28	4	III	Slightly polluted

Table 5: Comparison of results of parameter of water with non-drinking guidelines of water

Parameters	Average value of each parameter	CEQGs Pulp and Paper Industry (Fine Paper) (CCREM, 1987)	CEQGs: Iron & Steel Industry (Manufacture) (CCREM, 1987)	FWPCA 1968 Guidelines: Petroleum Industry (Van der Leeden *et al.*, 1990)	CEQGs: Power generating industry (Boiler Feedwater) (CCREM, 1987)	CEQGs Beverage Industry (Food Canning, Freezedried) (CCREM, 1987)	FAO, 1985 Guideline: irrigation water (Limiting conc.) (Van der Leeden *et al.*, 1990)	CSWQCB 1963 Guidelines: Aquatic life protection (freshwater) (Van der Leeden *et al.*, 1990)	CEQGs Recreational Water (Water contact limiting) (CCREM, 1987)	FMEnv. guideline: Textile Industry (Dyeing Process) (FMEnv., 1991)	CSWQCB 1963 Guidelines: Livestock Water (Limiting conc.) (Van der Leeden *et al.*, 1990)
pH at 25°C	5.48±0.39	No guideline	6.8 – 7.0	6.0 – 9.0	8.8 – 9.4	6.8 – 8.5	7.0 – 8.5	6.5 – 8.5	6.0 – 10.0	7.5 – 10.0	5.6 – 9.0
Temp. °C	24.8±0.60	No guideline	<38	No guideline	No guideline	No guideline	No guideline	No guideline	50	No guideline	No guideline
TSS (mgl^{-1})	0.32±0.26	<10.0	No guideline	<10.0	<0.05	<10.0	No guideline	No guideline	No guideline	<5.00	No guideline
TDS (mgl^{-1})	0.33±0.29	<200	No guideline	<750	<0.5	<500	<1500	No guideline	No guideline	<100	No guideline
DO (mgl^{-1})	3.6±1.2	No guideline	No guideline	No guideline	<0.007	No guideline	No guideline	No guideline	No guideline	7.5 or more	No guideline
BOD_5	2.2±1.2	-	-	-	-	-	-	-	-	<1.0	-
COD(mgl^{-1})	61±22	No guideline	No guideline	No guideline	<1.0	No guideline	No guideline	No guideline	No guideline	No guideline	No guideline
O & G (mgl⁻	1.87±0.79	-	ND	-	-	-	-	ND	5000	-	-
TPH (mgl^{-1})	1.42±0.66	-	-	-	-	-	-	ND	5000	-	-
Ni (mgl^{-1})	0.08±0.08	-	-	-	-	-	200	1100	-	-	1000
Cd (mgl^{-1})	0.01±0.01	-	-	-	-	-	10.0	1160	-	-	50.0
Zn (mgl^{-1})	0.05±0.04	-	-	-	<10.0	-	2000	100	-	-	25000
Fe (mgL^{-1})	0.33±0.08	<0.10			<0.10	<0.20	5.00	0.30	-	-	-

CEQGs = Canadian Environmental Quality Guidelines; CSWQCB = California State Water Quality Control Board; FWPCA= Federal Water Pollution Control Administration CCREM = Canadian council of Resource and environment Ministers; FAO = Food and Agricultural Organization; FEPA = Federal environmental Protection Agency (Now Federal Ministry of Environment)

Table 6: Comparison of results obtained in study area with results obtained in similar studies elsewhere

Country	Water Body/ River	pH	Temp. (^{0}C)	TSS (mgL^{-1})	TDS (mgL^{-1})	DO (mgL^{-1})	BOD (mgL^{-1})	COD (mgL^{-1})	O & G (mgL^{-1})	TPH (mgL^{-1})	Ni (mgL^{-1})	Cd (mgL^{-1})	Zn (mgL^{-1})	References
India	Urban water Body	6.93	-	397	540	3.5	29.7	-	-	-	-	-	-	Yogendra & Putaiah, 2008)
Nigeria	Olosun stream Ibadan	5.9±0.4	27.0±0.8	605±250	1590±280	1.38±0.58	15.4±4.5	1010±230	-	-	-	-	-	(Ipeaiyeda and Onianwa, 2009)
Cote D'Ivoire	Bietri Bay and Ebrie Lagoon	7.46 – 8.17	-	--	-	5.10 – 6.62	-	-	-	-	-	0.02 – 0.25	12.05 – 19.87	(Koffi et al., 2014)
Nigeria	Lagos Lagoon	-	--	-	-	-	-	-	-	-	0.78 ±0.12	0.05±0.02	2.72±0.57	(Olatunji & Osibanjo, 2012)
Nigeria	Esi River	-	-	-	-	-	-	-	11.6±8.0	4.3±3.0	0.012±0.018	0.0024±0.0021	0.11±0.22	(Akporido & Onianwa, 2015)
Vietnam	Sai Gon and Dung Nai River	4.0 – 6.8	-	-	-	-	-	10 - 50	-	-	-	-	-	(Le Thi Minh et al., 2016)
Nigeria	Benin-Ethiope Fluvial System (Sapele)	5.41±0.35	27.3±1.4	8.0±6.8	7.0±4.3	3.1±1.3	9.9±2.9	65±21	910±1100	856±1100	7.7±7.0	4.9±4.1	31±39	(Akporido & Kadiri, 2014(
Nigeria	Benin-Ethiope Fluvial System (Oghara)	5.48±0.39 (4.9 – 6.5)	24.5±0.60 (24 – 26.5)	0.32±0.26 (0.01 – 0.87)	0.33±0.29 (0.02 – 0.96)	3.5±1.2 (1.18 – 5.7)	2.2±1.2 (0.25 – 4.7)	61±22 (7 – 100)	1.87±0.79 (0.91 – 3.77)	142±0.66 (0.62 – 2.86)	0.08±0.08 (0 – 0.22	0.01±0.01 (0 - 0.03)	0.05±0.04 (0 – 0.18	Present study

The average DO value obtained for the study area, 3.6±1.2 mgL^{-1} (1.18 – 5.7 mgL^{-1}) was comparable with those obtained for urban water body in Shimoga Town, India (3.5 mgL^{-1}) (Yogendra & Putaiah, 2008), and Bietri Bay and Ebrie Lagoon in Cote D'Ivoire (5.10 – 6.62 mgL^{-1}) (Koffi *et al.*, 2014). It is much higher than that for Olosun River in Ibadan Nigeria (1.38±0.5 mgL^{-1}) (Ipeaiyeda & Onianwa, 2009) The average COD of study area, 61±22 mgL^{-1} (7.0 – 100 mgL^{-1}) was comparable with those obtained for Sai Gon and Dung Nai River Basin in Vietnam (10 – 50 mgL^{-1}) (Le Thi Minh *et al.*, 2016) and Benin-Ethiope Fluvial System around Sapele Town, Nigeria (65±110 mgL^{-1}) (Akporido & Kadiri) although much lower than the average value for Olosun River in Ibadan, Nigeria (1010±230 mgL^{-1}) (Ipeaiyeda & Onianwa, 2009). Olosun River receives effluents from many industrial concerns including breweries. It also collects materials from town abattoir so that oxygen demanding materials in the waters of Olosun River is expected to be very high as shown in the results for the COD and BOD of the river. The average Cd for study area, 0.01±0.01 mgL^{-1} (0 – 0.03 mgL^{-1}) was comparable with results obtained for Bietri Bay and Ebrie Lagoon in Cote D'Ivoire (0.02 – 0.25 mgL^{-1}) (Koffi *et al.*, *2014)* and Lagos Lagoon (0.05±0.02 mgL^{-1}) (Olatunji & Osibanjo, 2012) but higher than that for Esi River in Nigeria (0.0024±0.02 mgL^{-1}) (Akporido & Onianwa, 2015). The average value for Ni in study area, 0.08±0.08 mgL^{-1} (0 – 0.22 mgL^{-1}) was comparable with results obtained for Esi River in Nigeria (0.012±0.01 mgL^{-1}) but much lower than those for Lagos Lagoon (0.78±0.12 mgL^{-1}) and the Benin-Ethiope Fluvial System around Sapele Town (7.7±7.0 mgL^{-1}). These comparisons have further shown that the study area water is polluted since results obtained from different parameters in the study area are comparable with results obtained for corresponding parameters in these other study areas which have already been observed to be polluted areas. Some Results from the present study area were in fact higher than their corresponding parameters in these other studies.

Conclusion

The results of the determination of various parameters of water of the study area have shown that, most of the parameters in the study area have higher values than corresponding parameters in the control area. These indicated lower quality of study area water compared with control area water. The average pH of study area water also fell lower than guideline ranges for pH indicating that water was too acidic for purpose of drinking. The average Ni value exceeded guideline values for drinking water, thus the results for pH and Ni showed that quality of water was too low to be used for drinking purpose. The results for various parameters also exceeded guideline values for different non-drinking uses of water, Water from this area may not also be fit for use in the industries listed. Classification of the water of the five sampling stations of the study area showed that they are moderately polluted. Use of water from this area for drinking purpose may affect the health of users adversely

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