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### *Full Length Research Paper*

# **Effect of Urbanization and Industrialization on Waters of the Benin River- Ethiopie River System around Sapele, Nigeria**

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**Factors of industrialization and Urbanization in degrading the environment in the Niger Delta region are often undermined by researchers. Grab water samples were collected from nine sampling station in the study area and composite samples of effluents from effluents conveying conduits of two industries, all on the Benin River- Ethiopie River system around sapele for two dry and two rainy seasons. The physicochemical parameters of water, oil and grease (O&G) and total petroleum hydrocarbon (TPH) were analyzed by various standard methods and the heavy metals were determined by flame absorption spectrometry after appropriate digestion method. Important results for water samples as averages for the study area are, pH ( $5.41 \pm 0.35$ ), DO ( $3.1 \pm 1.3$  mg/L), BOD<sub>5</sub> ( $9.9 \pm 2.9$  mg/L), COD ( $65 \pm 21$  mg/L), O&G ( $910 \pm 1100$  µg/L), TPH ( $856 \pm 1100$  µg/L), Ni ( $7.7 \pm 7.0$  µg/L), Cu ( $1.2 \pm 1.8$  µg/L), Cr ( $16 \pm 25$  µg/L), Zn ( $31 \pm 39$  µg/L), Pb  $27 \pm 26$  µg/L, Cd ( $4.9 \pm 4.1$  µg/L) and Mn ( $65 \pm 14$  µg/L). The two effluents were found to have capabilities to pollute any receiving water body. The average values of some of the parameters in water exceeded national and international guideline values for drinking water and corresponding values in the control area. All the sampling station waters were r classified as either “slightly polluted” or “polluted”. The water of the Benin River- Ethiopie River system is polluted for the purpose of drinking and needs to undergo rigorous treatment before it can be used for drinking purpose.**

**Keywords:** Factors of Industrialization and Urbanization; Niger Delta region; Sapele; Benin River-Ethiopie River System; Physicochemical parameters of water, heavy metals; oil; total petroleum hydrocarbons.

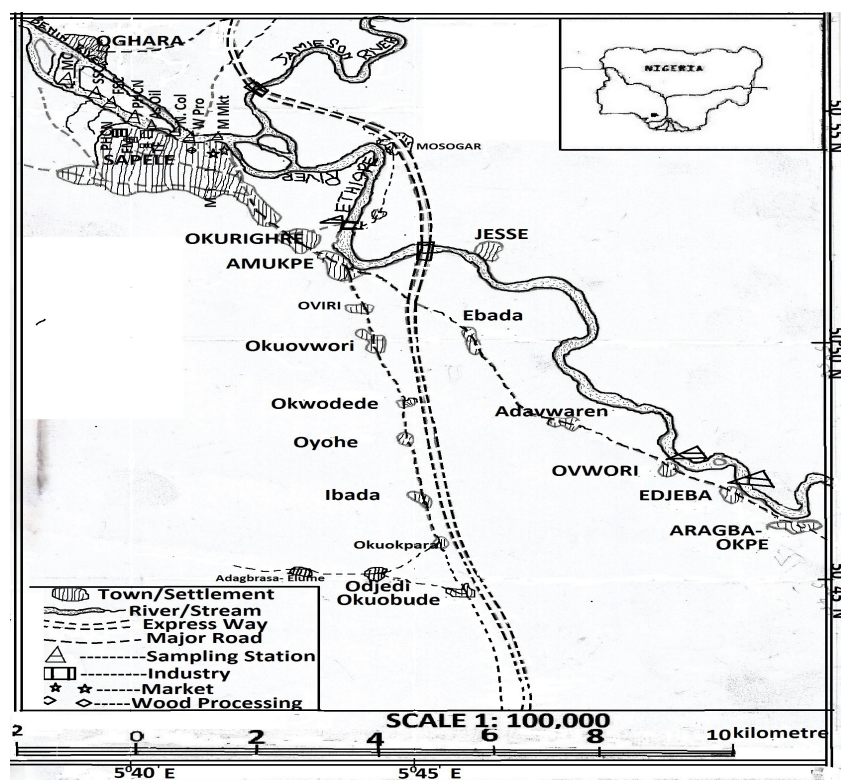
## **INTRODUCTION**

Heavy metals, petroleum hydrocarbons and other forms of contaminants often results from Urbanization and industrialization (Wang et al., 2011; Yang et al., 2007; Yang et al., 2009; Yang et al., 2012; Forstner and Witthman, 1983). The degree of contamination may be significant where rate of Urbanization and industrialization is very high or when this is coupled with

unexpected occurrences such as oil spillages as in case of petroleum prospecting and processing industries. The Niger delta region is an area that has suffered many incidences of oil spillages. The United Nation Development Programme (UNDP) report indicate that between 1976 and 2001, about 7000 spills were recorded, which accounted for a loss of about three million barrels of oil (UNDP, 2006).

The frequent oil spillages in the Niger Delta region and the consequent loss of petroleum to the Environment has

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**Figure 1** Map of study area showing the Benin River – Ethiope River System, Sapele Town and sampling stations

necessitated much research work on the effect of petroleum prospecting and processing industry (Ekundayo and Obiekwe, 2000; Sojinu et al., 2010; Osuji and Adesiyun, 2005; Ossai et al., 2010; Anyakora et al., 2011; William and Benson, 2010; UNEP, 2011), and this has led to the undermining by researchers of other important factors which may give rise to contamination of the environment with heavy metals and other contaminants. Examples of such factors are Industrialization and Urbanization. Several moderately urban areas can be identified in the Niger Delta. These include Port Harcourt, Warri, Effurun, Ughelli, Sapele, Calabar, Benin City, Agbor Asaba, Owerri and Uyo. Most of these urban centres have a number of industries in addition to oil prospecting and processing industry which the Niger delta is well known for. These other industries include: Food processing and beverage industries, Power generating industry, petroleum refining, Lubricating oil producing industry, roofing and ceiling sheet producing industry, Steel Producing industry, Iron and steel industry, Chemical industries etc. Much research work has not been carried out on the effect of these industries on host environments in this region.

A number of studies have however been carried out on the effect of non crude oil prospecting and processing industries on the environment where they are located in the Niger delta region and some other regions of Nigeria (Otukunfor and Obiuku, 2005; Nduka et al., 2009;

Ipeaiyeda and Onianwa, 2009; Umoren and Udousoro, 2009; Adeniyi and Owoade, 2010; Awomeso et al., 2010; Uzoekwe and Oghosanine, 2011; Ndimele, 2012; Akporido and Asagba, 2013; Akporido and Ipeaiyeda, 2013; Akporido et al., 2013; Akporido and Ipeaiyeda, 2014; Akporido and Agbaire, 2014). Results from these studies have confirmed that there is contamination of the environment where they are located by these industries. The amount of work done so far appear not sufficient. There therefore need more research work to be done to elucidate the effect of these industries on their host environments.

Sapele is a moderately urban area with a moderate growth rate (moderate rate of urbanization). A number of manufacturing or processing industries are located in Sapele, these include food processing industries (Flour Mill Nigeria Limited and Top Feed Ltd.), Power generating (Power Holding Company of Nigeria [PHCN] power generating Plant), ceiling and roofing Sheet Industry (Eternit PLC), Wood Processing industry (various sawmills), Rubber processing (Omatsteye Rubber factory). Effluents are released from these industries directly or indirectly into the Benin – Ethiope River system. Other activities which may increase pollutant load in the river system include presence of large market located near the river. Domestic effluent from the town also enters into the river system (the town itself i.e. Sapele is very near to the river). The presence of the

market (which consist of slaughter houses) and the closeness of the town especially residential areas can increase aggregate organics (BOD and COD) and Individual organic load in the two river system.

One industry which does not send effluents directly into the river system is the Roofing and Ceiling sheet producing industry (Eternit PLC). An investigation of the Toxic heavy metal content of soil near the waste dumpsites of the Company and waters of the semi-creeks also near the waste dumpsites revealed that the soil and water have enhanced concentrations of heavy metals (Pb, Cr, Cd, and Ni). The pH of soil and water was also found to be low (showing high acidity) Akporido and Agbaire, 2014)

The Benin river –Ethiope river System) is actually a one river system with two sections of the river having different official names (or there is controversy with respect to having a single name). From its source near to Umutu about 150 kilometres Southwest from Sapele to some point in sapele (Figure 1: Map of study area showing the Benin River – Ethiope river System, Sapele Town and sampling stations) the name of the River is Ethiope River. From this point to where it enters the Gulf of Guinea (in the Atlantic Ocean) it is known as the Benin River. Fishing and collection of Lobsters is one of the main activities that take place in the Benin River- Ethiope River System. The adjoining land which do not consist of buildings are use for crop farming. Some of the crops produced in this area are Maize, Yam, cassava, tomatoes and vegetables.

The present study examined the extent to which the waters of thre Benin River-Ethiope river system have been affected by the presence of these industries and moderately to rapidly growing urban settlement of Sapele. This was done by determining some physicochemical parameters of water, oil and grease (O&G), total petroleum hydrocarbons (TPH) and heavy metals (Ni, Cu, Cr, Zn, Pb Cd and Mn). Effluent qualities of effluents from two of these industries were also determined so as to assess their capability to pollute the receiving waters of the Benin River-Ethiope River System.

## MATERIALS AND METHODS

### Description of study area

The study area is located between latitudes  $5^{\circ} 52' \text{ N}$  and  $5^{\circ} 57' \text{ N}$  and between longitudes  $5^{\circ} 39'$  and  $5^{\circ} 45'$ . Figure 1 shows the map of study area showing the Benin River – Ethiope River system, Sapele Town and the sampling Stations. The control area is further south on the Ethiope River before Amukpe Town the first urban area near the Ethiope river when coming from the south East. The two control sampling stations are located at Edjeba (  $5^{\circ} 46' \text{ N}$  and  $5^{\circ} 48' \text{ E}$ ) and Ovwori ( $5^{\circ} 47' \text{ N}$  and  $5^{\circ} 47' \text{ E}$ ).

### Design of study

Study was carried out for two years with samples taken twice in each season (i.e. once every quarter of the year), two rainy seasons and two dry seasons. Nine sampling stations were established in the study area. The distance between successive sampling station is about 500m with the exception of the distance between the first sampling station (Okurighre Bridge) and the second sampling station (Main Market) which is up to two kilometers. The sampling stations are: Okurighre Bridge, Main market, Wood processing Depot, Naval college, Asca Oil, Power Holding Company of Nigeria (PHCN) power generating Station, First stream Confluence (FSC), Second stream confluence (SSC), and Main confluence. Most of the industries are located in the stretch of the river between the second sampling station (Main market) and PHCN sampling station The Control area is located further south in an area where the effluents from the industries in the town are not received by the river system or where the influences of Urbanization in Sapele town is not felt.

### Sample collection and preservation

Collection of effluent samples was carried out by the time-composite method, grab samples of effluent were collected every ten minutes for one hour and ten minutes (seven grab samples) these were mixed together in a sample container and the container is kept in an ice-chest for preservation and transfer to the laboratory. The effluent samples which were not collected with the others are samples for dissolved oxygen (DO) and samples for oil and grease. In the case of DO samples the time composite method was also used but in this case samples were mixed in special DO bottles before preservatives were added as described for water samples below. In the case of Oil and grease (O&G) the time composite method was also use but in this case the grab samples were mixed in wide mouth bottles before being preserved as stated for the water samples below. The water samples were collected using the discrete method (grab samples) from the surface (1 metre to the actual surface of water) and at the mid-depth of the river along the middle axis of the river. Samples were preserved in accordance with standard methods (APHA-AWWA- WEF, 1995). Samples for DO analysis were specially treated by First adding 2 mL of solution of manganous sulphate ( $\text{MnSO}_4$ .) to water sample in the brown DO bottle and inverting bottle three times; this is followed by 2 mL of alkaline potassium iodide – azide solution. The flakes are allowed to settle and sample is kept in an ice chest for transfer to the Laboratory. Samples were collected for the following parameters: temperature, pH, total suspended solids (TSS), total dissolved solid (TDS), total solids (TS), dissolve oxygen (DO), biochemical oxygen demands ( $\text{BOD}_5$ ), chemical

oxygen demand (COD), total alkalinity, Phosphate, sulphate, oil and grease (O & G), total petroleum hydrocarbon (TPH), Heavy metals (Ni, Cu, Zn, Pb, Cd, Cr, Mn).

### Analytical Procedures

Temperature of water samples was taken at the site with a mercury bulb thermometer with the bulb of thermometer well immersed in water. pH of water sample was also determined at the site with a portable pH-meter (model testr1), with the glass electrode well dipped below water surface. The TSS of sample was determined by filtering 200 mL of water sample using a gooch crucible-suction pump system and then drying the filtered solids at  $103^{\circ}\text{C}$  –  $105^{\circ}\text{C}$  to constant weight in an oven (APHA – AWWA – WEF, 1995). TDS was determined by drying filtrate from the TSS determination at  $180^{\circ}\text{C}$  in an oven to constant weight (APHA – AWWA – WEF, 1995). TS was determined by evaporating 200ml of water sample in an evaporation dish and drying the residue in the oven at  $103^{\circ}\text{C}$  –  $105^{\circ}\text{C}$  to constant weight (APHA – AWWA – WEF, 1995). DO was determined by the iodometric method (azide modification) as described in standard method (APHA-AWWA-WEF, 1995). The  $\text{BOD}_5$  of samples was determined by employing the 5-days BOD test as described in standard methods (APHA-AWWA-WEF, 1995). The COD of samples was determined by the open reflux method as described in Standard method (APHA-AWWA-WEF, 1995). Total alkalinity was determined by titrating water sample with standard hydrochloric acid (0.02 M) to the first change of colour of bromocresol green indicator solution at  $\text{pH} = 4.5$ . Details of experimentation and calculation are as described in standard method (APHA-AWWA-WEF, 1995).

Phosphate was determined in water samples by employing the Vanadomolybdophosphoric acid colorimetric method with appropriate calibration curves. Details as described in standard methods (APHA-AWWA-WEF, 1995). The turbidimetric method was used in the determination of Sulphate in samples of effluents and water as described in standard methods (APHA – AWWA – WEF, 1995). O & G of the water samples was determined by the gravimetric method as described in standard method (APHA-AWWA-WEF, 1995). The TPH of water samples was determined from the hexane extract used for the oil and grease measurement by first carrying out a clean-up procedure on the extract by the addition of 4g. of activated silica gel with stirring using a magnetic stirrer for 5 min. and then filtering off the silica gel. Solvent is removed from extract and extract dried to constant weight at a low temperature of  $40^{\circ}\text{C}$ . Calculation and other experimental details is as given in standard method (APHA-AWWA-WEF, 1995).

Heavy metals (Ni, Cu, Zn, Pb, Cd, Cr, And Mn) were determined by adding 5 mL concentrated nitric acid

into 500 mL volume of water sample in a beaker. This was pre-concentrated and digested to near dryness. The residue was dissolved with a little distilled water and made up to the mark in a 50 mL volumetric flask. Metals were determined in the digest using flame atomic absorption spectrophotometer (Perkin Elmer AA 200, Waltham, USA).

### Quality Assurance Programme for the Study

This involved mainly the determination of glucose-glutamic acid check for  $\text{BOD}_5$  determinations, determination of % recovery for COD by determining COD on standard solutions of potassium hydrogen phthalate (KHP) (i.e. solution which contains 425 mg/L of KHP) and comparing the mean of five determinations to the theoretical value of 500 mg/L (APHA-AWWA-WEF, 1995). The percentage recoveries of O&G, TPH and the seven heavy metals were also determined. The following average percentage recoveries were obtained for five determination of each parameter: COD ( $95.2 \pm 5.7\%$ ), O&G ( $91.6 \pm 5.4\%$ ), TPH ( $95.6 \pm 6.7\%$ ), Ni ( $93.4 \pm 6.1\%$ ), Cd ( $98.7 \pm 4.5\%$ ), Pb ( $99 \pm 5.5\%$ ), Cr ( $97.7 \pm 7.2\%$ ), Zn ( $101 \pm 8.5\%$ ), Cu ( $96.4 \pm 9.5\%$ ) and Mn ( $99.4 \pm 5.8\%$ ). These percentage recoveries all falls within the range 90 – 110 which means good percentage recoveries were obtained for all the parameters.

### Statistical Methods Employed

The statistical methods and packages used included the following:

I) The comparisons of the mean of concentrations of each parameter in the four seasons studied (two dry and two rainy seasons) and in the nine sampling stations were carried out using Analysis of Variance (ANOVA-single factor) from Microsoft Excel (Microsoft Corporation Ltd)

II) Comparison of the mean of concentrations of some parameters in the study with corresponding parameters in the control area were carried out using t-test (two sample, Assuming equal variance) at 0.05 confidence level Microsoft Excel (Microsoft Corporation Ltd.)

III) Bivariate correlation of parameters (pollutant parameters) in matrix with Pearson (2-tailed) correlation was employed from the statistical package of the social sciences (version 16) (SPSS, Chicago)

### RESULTS AND DISCUSSION

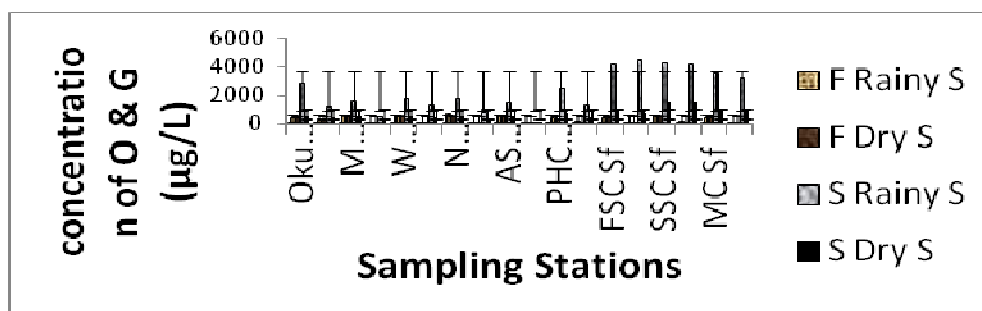
The average values of effluent parameters from Asca oil and PHCN oil for the four seasons studied (i.e. two dry season and two rainy seasons) were compared with effluent limitation guidelines for Fuel oil and sanitary

**Table 1** Results for the determination of effluent parameters in PHCN and ASCA Oil effluents (n = 4) compared with refined oil/fuel and Sanitary Effluent Limitation guideline values of EGASPIN for disposal of effluent into surface water (DPR, 2002)

Parameters	PHCN	ASCA OIL	Refined oil/Fuel Effluent Limitations Guideline values	Sanitary Effluent Limitations Guideline Values
Temp °C	27.8 ±10	28.0±2.0	NS	35.0
PH	4.90± 0.14	5.23±0.17	6.5 – 8.5	6.5 – 8.5
TSS (mg/l)	17.7± 1.0	3.18±1.1	30	30.0
TDS (mg/l)	17.1± 0.9	13.6±0.8	< 2000	2000
TS (mg/l)	35.4±2.6	32.9± 3.2	NS	NS
DO (mg/l)	4.88±6.21	5.13 ± 0.10	NS	NS
BODs	15.0±0.9	16.0±1.1	10.0	10.0
COD (mg/l)	91.3± 4.6	103±5.5	40.0	40.0
Alkalinity (mg CaCO <sub>3</sub> /L)	12.5±0.9	12.6± 1.4	NS	NS
PO <sub>4</sub> <sup>3-</sup> (mg/l)	14.9 ± 1.3	19.2± 3.1	NS	NS
SO <sub>4</sub> <sup>2-</sup> (mg/l)	14.3±1.0	15.4± 0.5	NS	NS
O& G (µg/L)	-	4090± 180	NS	10000
TPH (µg/L)	-	3980±300	10000	10000
Ni (µg/L)	16.5± 3.1	51.3± 2.9	NS	Ni
Cu (µg/L)	2.00± 0.82	5.5 ±1.3	1500	1500
Total Cr(µg/L)	10.0± 14	37± 50	300	NS
Zn (µg/L)	351±26	312±9.4	1000	1000
Pb (µg/L)	262±15	28.3±3.9	50	50.0
Cd (µg/L)	8.5± 1.3	8.75± 0.96	NS	NS
Mn (µg/L)	89.0±4.2	129± 8.7	NS	NS

**PHCN** = Power Holding Company of Nigeria, EGASPIN

**EGASPIN** = Environmental Guidelines And Standards for petroleum Industry in Nigeria



**Figure 2** Concentrations of O & G in water in all sampling stations (with error bars)

effluent (Table 1) of the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) (DPR, 2002). Results revealed that the average values of some of the parameters were higher than the guideline values. The average value of BOD<sub>5</sub> for PHCN (15.0±0.9 mg/L) and Asca Oil (16.0±1.1 mg/L) exceeded both effluent limitation guideline values of 10.0 mg/L for each. The average values of COD for both PHCN (91.3±4.6 mg/L) and Asca Oil (103±5.5 mg/L) exceeded both effluent limitation guidelines of 40.0 mg/L each. The average pH of PHCN effluent (4.90±0.14) and Asca Oil (5.23±0.17) fell below both effluent guideline

range of 6.5 – 8.5 which means that both effluent are more acidic than required. The average concentration of Pb in PHCN effluent (262±15 µg/L) exceeded both effluent limitation guideline value of 50, 0 µg/L (i.e. for both). Thus the two effluents (PHCN and Asca Oil) are polluted and are capable of polluting any receiving water body.

The variation of the concentrations of pollutant parameters (O & G, TPH, pH and the heavy metals) in the nine sampling stations of the study area are given in figures 2 – 11. **Figure 2** (O & G) and **Figure 3** (TPH) showed that the concentrations of the two parameters are

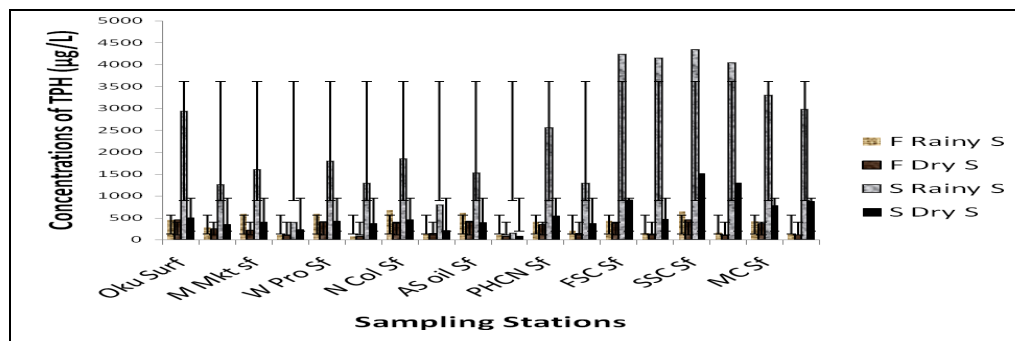


Figure 3 Concentrations of TPH in water in all sampling stations (with error bars)

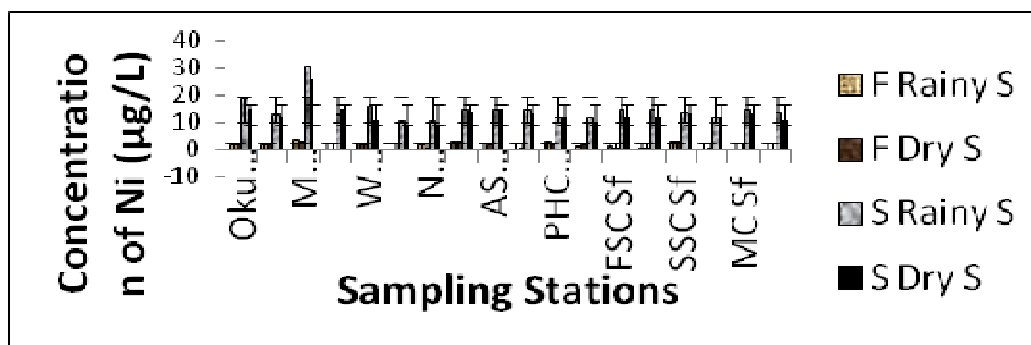


Figure 4 Concentrations of Ni in water in all sampling Stations (with error bars)

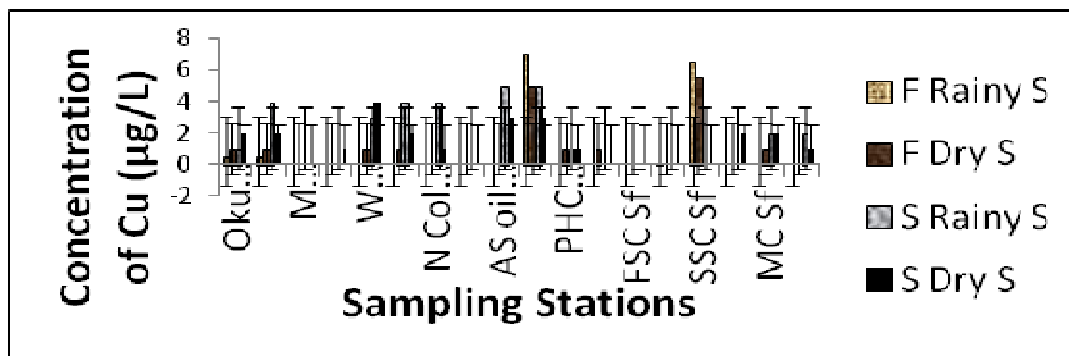


Figure 5 Concentrations of Cu in water in all sampling stations (with error bars)

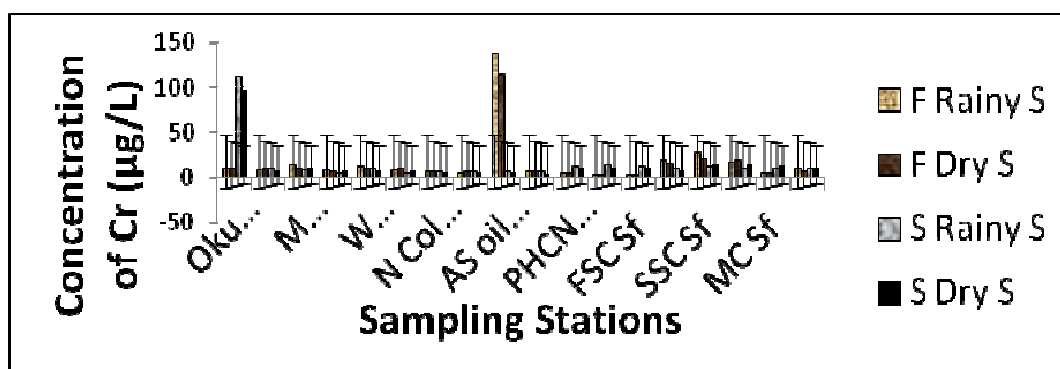


Figure 6 Concentrations of Cr in water in all sampling stations (with error bars)

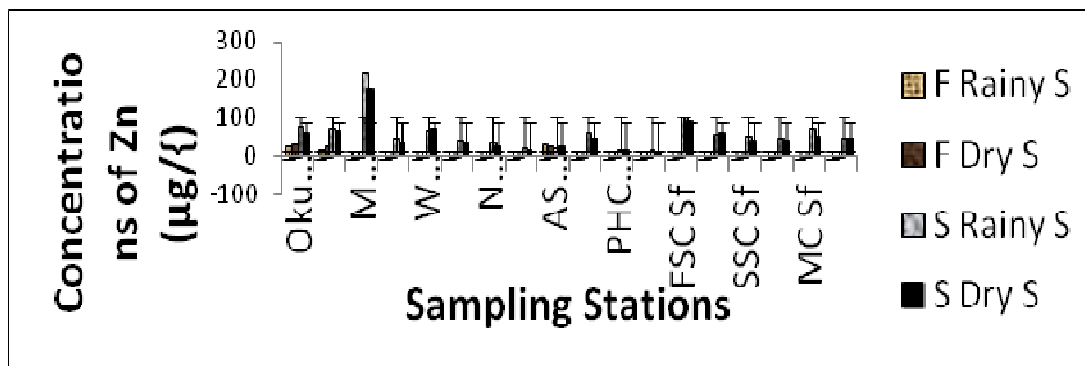


Figure 7 Concentrations of Zn in water in all sampling stations (with error bars)

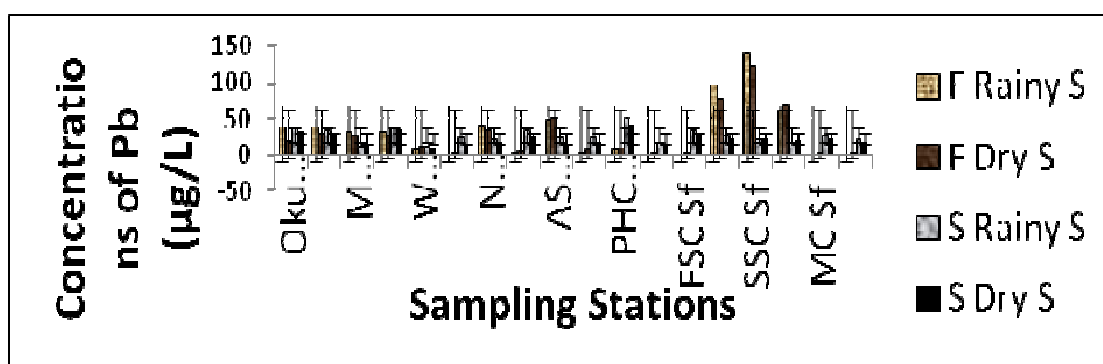


Figure 8 Concentrations of Pb in water in all sampling stations (with error bars)

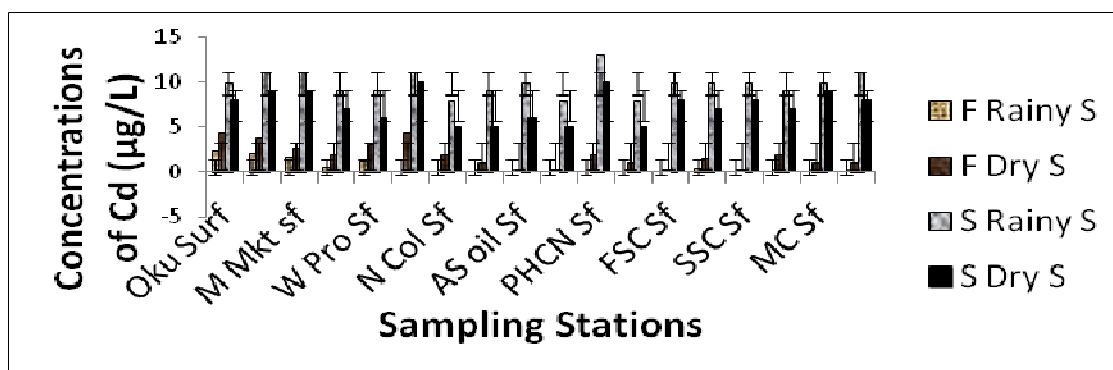


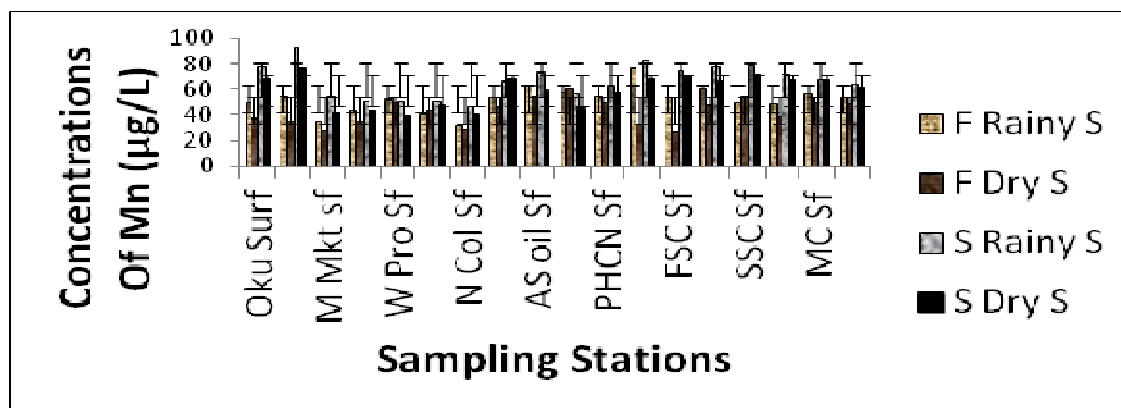
Figure 9 Concentrations of Cd in Water in all sampling Stations (with error bars)

higher at Okurighre, First Stream confluence (FSC), Second Stream Confluence (SSC) and at the main confluence (MC). The reason for this is not clear. The concentrations of both parameters are very variable in each of these sampling stations in the four seasons studied as shown by the error bars (with standard deviation). The concentrations of the two parameters were consistently higher in the second rainy season (S. rainy S.) This is as a result of the oil spillage that occurred during this season just before sampling took place in this season. The spillage may have occurred as a result of equipment failure in a flow station near to the

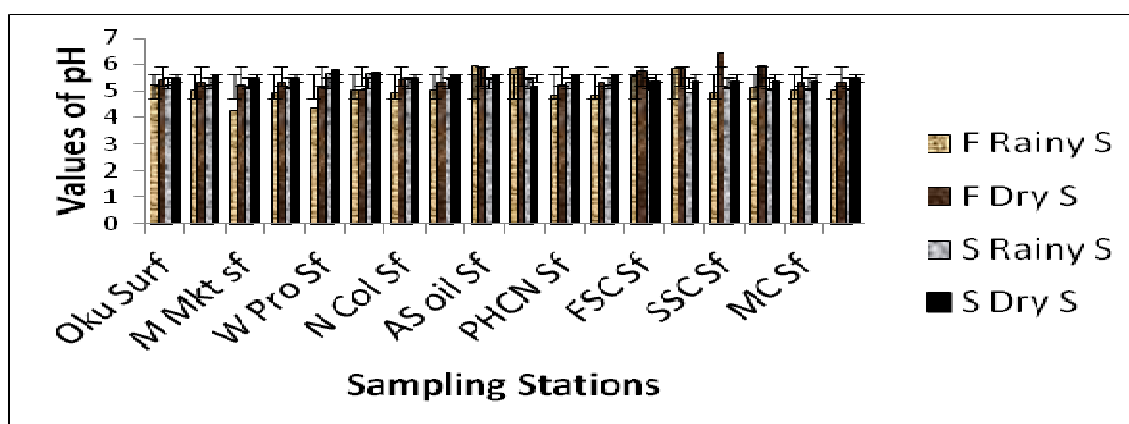
river (information about the spillage is scanty). The values of Cd (figure 9); Mn (Figure 10) and pH (Figure 11) showed no distinct variation with the sampling stations. The concentrations of Ni and Zn are highest at the Main Market (M Mkt) sampling station. No definite reason can be adduced for this. The concentrations of Cr are highest at Asca Oil sampling station followed by its concentrations at Okurighre sampling station (Figure 6). The concentrations of Pb are highest at SSC sampling station followed by those at FSC (Figure 8). No reason is also adduced for these observations.

An important observation about the heavy metals just





**Figure 10** Concentration of Mn in water in all sampling stations (with error bars)



**Figure 11** Values of pH of water in all sampling stations (with error bars)

discussed is that they are very variable in their concentrations in each station in the four seasons studied as indicated by the error bars with standard deviation. A comparison of the mean of each parameter in the nine sampling stations using analysis of variance (ANOVA-Single factor) showed that the differences in concentrations with sampling stations are statistically significant in O & G, TPH, Ni, Cr, Zn and Pb but not in Cu, Cd and Mn. The variations of the concentrations of other parameters with sampling stations are given in Table 2. All these parameters did not also show any definite pattern of variation along the course of the river from the first sampling station upstream (i.e. Okurighre) to the last sampling station downstream (Main Confluence). They peaked at different sampling stations as observed with the parameters already discussed.

Most of the parameters had higher average values in the study area compared with the control area (Table 3). The average values of DO and pH were also lower in the study area compared to the control area. When the mean of each of the parameters of the study area water was compared with the mean of the corresponding parameter in the control area using a t-test (two sample, assuming equal variances), it was found that the differences were

statistically significant in O & G, TPH, BOD<sub>5</sub>, COD TSS, TDS, Pb and Mn. This showed that the study area has a lower quality compared with the control area.

The values of the following parameters, O & G, TPH, BOD<sub>5</sub>, COD and the heavy metals were highest in the second rainy season (Table 4). This is also shown in Figures 2 – 11). This may be due to the oil spillage that occurred in that season in the study area. This occurrence appeared to have also affected the second dry season after it. This occurrence (i.e. the oil spillage) appears to have masked any seasonal variation that would have been expected.

The average values of the parameters determined in the study area were compared with national and international guideline values for drinking water (Table 5) since water from the river is used for drinking in some of the rural areas along the course of the river which are also part of the study area. The average pH,  $5.41 \pm 0.35$  is lower than the pH range specified by the Nigerian standard for drinking water quality (6.5 – 8.5) (SON, 2007), 2012 edition of USA drinking water standard (Secondary Drinking Water Regulation) (6.5 – 8.5) (USEPA, 2012), and the Canadian Drinking Water Standards (Aesthetic Objective value) (6.5 – 8.5) (Health



**Table 2** Average values of parameters in each sampling station (N=8)

Parameters	Okurighre Bridge	Main Market (Sapele)	Wood Processing Depot	Naval College	Asca Company	Oil	PHCN Power Generating Station	1 <sup>st</sup> Small Stream Confluence	2 <sup>nd</sup> Small Stream Confluence	MAIN Confluence
Temp ( <sup>o</sup> C)	27.4± 1.1	27.0± 1.8	27.1± 2.3	27.6± 1.6	26.7±1.3		27.2± 1.1	27.6±07	27.9±1.6	26.8±1.2
TSS (mg/l)	78± 5.2	9.4±8.0	7.4±6.1	9.7±9.7	8.4±8.1		10.8±6.2	5.9±64	5.9±6.2	7.1±7.2
TDS (mg/l)	8.3± 3.3	4.6±3.6	6.0± 5.9	6.2±5.1	6.6±1.8		7.3±3.1	10.9±21	6.9±5.8	6.2±5.2
TS (mg/l)	17.3±6.8	16.3±8.9	15±1.0	16.1± 9.4	9.0±8.7		19± 1.0	19.9± 5.1	16.5±8.5	16.6±9.2
DO (mg/l)	4.4±1.1	2.9±1.3	2.4±1.0	2.3±1.0	2.9±1.2		3.1±1.2	37±14	3.0±1.4	2.7±1.0
BOD5 (mg/l)	9.4±1.3	10.5±1.6	8.9±4.4	8.5±2.7	9.2±2.7		13.0±2.1	11.3±1.6	10.4±2.2	8.5±4.1
COD (mg/l)	63.0±9.7	76±12	61±35	79±23	68±15		63.1±7.4	68±12	65.0±6.0	43±32
Alkalinity (mgCaCO <sub>3</sub> /l)	9.6±1.2	15.8±2.5	12.6±2.9	8.9±1.5	8.6±1.7		8.6±1.2	13.1±3.4	9.9±1.7	9.9±1.6
PO <sub>4</sub> <sup>3-</sup> (mg/l)	13.4±3.3	14.5±2.5	15.1±2.3	12.1±2.9	11.4±3.8		13.1±3.9	14.1±3.1	11.8±2.9	12.7±2.2
SO <sub>4</sub> <sup>2-</sup> (mg/l)	9.5±2.0	9.7±1.9	9.9±2.1	15±20	9.0±3.0		7.2±3.1	7.4±1.8	9.0±1.7	8.2±2.2

**Table 3** Average values of parameters in the study and control area (n = 72 for study area, n = 16 for control area)

Parameters	Study Area	Control Area
Temp C	27.3± 1.4	28.0± 1.3
pH	5.41±0.35	5.78 ±6.08
TSS (mg/l)	8.0 ± 6.8	1.45 ±0.48
TDS (mg/l)	7.0± 4.3	2.19± 0.62
TS	17.3±8.4	3.80±0.66
DO (mg/l)	3.1 ± 1.3	5.43± 6.66
BODS (mg/l)	9.9 ± 2.9	2.90 ± 0.46
COD (mg/l)	65 ± 21	13.5 ± 3.7
Alkaline (mg CaCO <sub>3</sub> /l)	10.8 ±3.1	4.91± 0.72
PO <sub>4</sub> <sup>3-</sup> (mg/l)	13.1 ± 3.1	8.5 ± 1.3
SO <sub>4</sub> <sup>2-</sup> (mg/l)	9.5± 7.2	5.8 ± 1.3
O & G (µg/L)	910± 1100	236 ± 44
TPH (µg/L)	856 ± 1100	190 ± 41
Ni (µg/L)	7.7 ± 7.0	8.9±1.4
Cu (µg/L)	1.2 ± 1.8	1.50 ±0.63
Cr (µg/L)	16 ± 25	9.9 ± 2.5
Zn (µg/L)	31 ± 39	27.8 ± 5.5
Pb (µg/L)	27 ± 26	13.5± 2.3
Cd (µg/L)	4.9± 4.1	4.8 ± 0.96
Mn (µg/L)	65± 14	32.6± 3.2

Canada, 2012). The average concentration of Pb in the study area, 27±26 µg/L exceeded Nigerian water standards for drinking water quality (10 µg/L) (SON, 2007), WHO drinking water standards (10.0 µg/L) (WHO, 2011), the 2012 edition of USA drinking water standards (Maximum Contaminant Level) (15.0 µg/L), and the Canadian Drinking water standards (maximum acceptable concentration) (10.0µg/L) (Health Canada,2012)The average concentration of Cd in study area, 4.9±4.1 µg/L exceeded the Nigerian water quality

standards for drinking water quality (3.00 µg/L), WHO drinking water Standards (3.00 µg/L) (WHO, 2011). the 2012 edition of USA drinking water standards (Maximum Contaminant Level) ( 5.00 µg/L) (USEPA, 2012 and the Canadian Drinking water standards (maximum acceptable concentration) (5.00 µg/L) (Health Canada,2012) In view of the above, the water of the study area is of low quality and polluted for the purpose of drinking. The water needs rigorous treatment before it can be used for drinking. The use of the water for

**Table 4** Average values of parameter in the four seasons

Parameters	First Rainy season	First Dry season	Second Rainy Season	Second Dry season
Temp <sup>0</sup> C	26.0±1.7	28±10	26.9±0.50	27.8±0.9
p <sup>H</sup>	5.16± 0.41	5.57±0.31	5.32±6.21	5.51±0.14
TDS (mg/l)	1.4±2.1	2.9± 2.4	16.6± 3.2	11.1±3.5
TDS (mg/l)	3.7± 3.9	4.8±2.7	11.7±23	7.7±3.0
TS (mg/l)	11.0± 4.6	9.11±3.7	27.8±2.6	21.2±3.0
DO (mg/l)	3.73± 0.70	3.88±0.76	1.25±0.60	3.85±0.88
BOD(mg/l)	8.8 ± 2.5	7.6±2.4	13.3±1.4	10.0±1.8
COD (mg/l)	55. ± 19	47±15	84±15	74.2±8.2
Alkalinity (mg CaCO <sub>3</sub> /l)	11.6±2.1	10.0±1.9	11.1±4.4	10.4±3.2
PO <sub>4</sub> <sup>3-</sup> (mg/l)	15.1± 2.0	11.2±2.5	15.1±2.7	11.1±2.4
SO <sub>4</sub> <sup>2-</sup> (mg/l)	7.1± 2.1	13±13	9.0±3.1	8.9±1.7
O&G (µg/L)	352±40	298±170	2320±1400	666±39
TPH (µg/L)	348± 220	254±140	2550±1400	570±380
Ni (µg/L)	4.1± 1.4	1.4±1.0	14.9±4.5	13.0±3.7
Cu (µg/L)	0.8±2.2	1.0±1.6	1.7±2.0	1.3±1.2
Cr (µg/L)	18±31	16±25	15± 24	14±21
Zn (µg/L)	4.6±11	6.52±11	61±46	52±37
Pb (µg/L)	31± 39	28±33	27.3±9.9	22.5±8.2
Cd (µg/L)	0.48±0.82	1.8±1.5	9.8±1.3	7.3±1.7
Mn (µg/L)	53±10	43±10	67±13	59±12

**Table 5** Comparison of average values of parameters with National and International guideline values

Parameters	Averages of parameters obtained in the Study Area	Nigeria standards For Drinking Water (SON, 2007)	Drinking water Standards (WHO, 2011)	2012 edition USA Drinking water Standards (Health Advisory) (USEPA, 2012)	Canadian Drinking Water Standards (Health Canada, 2012)
Temp C	27.3± 1.4	ambient	NS	NS	NS
pH	5.41±0.35	6.5 – 8.5	NS	6.5 – 8.5 (SDWR)	6.5 – 8.5 (AO)
TS	17.3±8.4	NS	NS	NS	NS
TSS (mg/l)	8.0 ± 6.8	NS	NS	NS	NS
TDS (mg/l)	7.0± 4.3	NS	NS	500 (SDWR)	NS
DO (mg/l)	3.1 ± 1.3	NS	NS	NS	NS
BOD <sub>5</sub> (mg/l)	9.9 ± 2.9	NS	NS	NS	NS
COD (mg/l)	65 ± 21	NS	NS	NS	NS
Total Alkalinity (mg CaCO <sub>3</sub> /l)	10.8 ±3.1	NS	NS	NS	NS
PO <sub>4</sub> <sup>3-</sup> (mg/l)	13.1 ± 3.1	NS	NS	NS	NS
SO <sub>4</sub> <sup>2-</sup> (mg/l)	9.5± 7.2	NS	NS	250 (SDWR)	500 (AO)
O & G (µg/L)	910± 1100	NS	NS	NS	NS
TPH (µg/L)	856 ± 1100	NS	NS	NS	NS
Ni (µg/L)	7.7 ± 7.0	20	70	NS	NS
Cu (µg/L)	1.2 ± 1.8	1000	2000	1300 (MCL)	1000 (MAC)
Total Cr (µg/L)	16 ± 25	50	50	100 (MCL)	50 )MAC)
Zn (µg/L)	31 ± 39	3000	NS	5000 (SDWR)	5000 (MAC)
Pb (µg/L)	27 ± 26	10	10	15 (MCL)	10 (MAC)
Cd (µg/L)	4.9± 4.1	3.00	3.00	5.00 (MCL)	5.0 (MAC)
Mn (µg/L)	65± 14	200	400	NS	NS

**SDWR** = Secondary Drinking Water Regulation of USEPA, **MCL** = Maximum Contaminant Level of USA

**AO** = Aesthetic Objective value of Canada, **MAC** = Maximum Allowed Concentration of Canada

drinking purpose can bring about adverse health effects for the consumers.

The average values of the parameters obtained in the study area were also compared with guideline values for

**Table 6** Comparison of water characteristics of study area with quality guideline for water uses other than for drinking.

Parameters	Values from Study Area	Guidelines for Pulp and paper Industry water (Fine paper) (CCREM, 1987)	Guidelines for Iron and Steel industry water (steel manufacturing) (CCREM, 1987)	FWPCA, 1968 Guidelines for Petroleum Industry (Van der Leeden et al., 1990)	Power Generating (Boiler Feed water) (CCREM, 1987).	FAO 1985 Guideline for Irrigation water (Van der Leeden et al., 1990)	CSWQCB 1963 Water Quality Guidelines for aquatic life (freshwater) (Van der Leeden et al., 1990)	CSWQCB 1963 Water Quality guideline for Recreational Water contact: limiting Threshold) (Van der Leeden et al., 1990)	Water Quality Guidelines for livestock rearing (Ontario Ministry of Environment, 1984)
pH at 25°C	5.41±0.35	NS	6.8 – 7.0	6.0 – 9.0	8.8 – 9.4	6.0 – 9.0	6.5 – 8.5	6.0 – 10.0	NS
TSS (mg/L)	8.0±6.8	<10*	NS	<10.0	<0.05	<450	NS	100*	NS
TDS (mg/L)	7.0±4.3	<200*	NS	<750	<0.5	NS	NS	NS	NS
DO (mg/L)	3.1±1.3	NS	NS	NS	<0.007	NS	5.0	NS	NS
COD(mg/L)	65±21	NS	NS	NS	<1.0			NS	NS
Alkalinity (mgCaCO <sub>3</sub> /l)	10.8±3.1	40 - 75	NS	NS	<1.0	NS	NS	NS	NS
SO <sub>4</sub> <sup>2-</sup> (mg/L)	9.5±7.2	NS	175	NS	NS	NS	NS	NS	NS
O & G (mg/L)	910±1100	NS	ND	NS	NS	NS	0	5.0	NS
Ni (µg/L)	7.7±7.0	NS	NS	NS	NS	200	50	NS	1000
Cu (µg/L)	1.2±1.8	NS	NS	NS	NS	200	20	NS	500
Total Cr (µg/L)	16±25	NS	NS	NS	NS	100	NS	NS	1000
Zn(µg/L)	31±39	NS	NS	NS	NS	2000	100	NS	25
Pb (µg/L)	27±26	NS	NS	50	5000	NS	100	NS	100
Cd (µg/L)	4.9±4.1	NS	NS	NS		10.0	10	NS	50
Mn (µg/L)	65±14	<0.3	NS	NS	<0.01	200	NS	NS	NS

**FWPCA** = Federal Water Pollution Control Administration **CSWQCB** = California State Water Quality Control Board  
**NS** = not specified **ND** = no detected

**Table 7** Classification of water of Sampling Stations of study area using a single index of pollution (BOD<sub>5</sub>) (Prati et al., 1971)

Sampling Station	BOD <sub>5</sub> average value (mg/L)	Class of water	Pollution status
Okurighre	9.4±1.3	IV	Slightly Polluted
Main Market	10.5±1.6	IV	Slightly Polluted
Wood Processing Depot	8.9±4.4	IV	Slightly Polluted
Naval College	8.5±2.7	IV	Slightly Polluted
Asca Oil Company	9.2±2.7	IV	Slightly Polluted
PHCN (Power Generating Station)	13.0±2.1	V	Polluted
1 <sup>st</sup> Stream Confluence	11.3±1.6	IV	Slightly Polluted
2 <sup>nd</sup> Stream Confluence	10.4±2.2	IV	Slightly Polluted
Main Confluence	8.5±4.1	IV	Slightly Polluted

non-drinking water uses (Table 6). The average pH of study area water, 5.41±0.35 fell below the pH range of the Canadian guideline for the iron and steel industry (Steel manufacturing) (6.8 – 7.0) (CCREM, 1987), Federal Water Pollution control Administration (FWPCA) of USA guideline for the petroleum industry (6.0 – 9.0) (Van der Leeden et al., 1990), California State Water Quality Control Administration (CSWQCB) guidelines range for aquatic life (Freshwater) (6.5 – 8.5) (Van der Leeden et al., 1990), Canadian guideline for power generation (Boiler feed water) (8.8 – 9.4) (CCREM, 1987), CSWQCB 1963 water quality guideline for

recreational water (water contact: limiting Threshold) (6.0 – 19.0) (Van der Leeden et al., 1990), FAO 1985 guideline for Irrigation water (6.0 – 9.0) (Van der Leeden et al., 1990).

The average TSS value for study area water, 8.0±6.8 mg/L exceeded the Canadian water quality guideline for power generation (Boiler feed water) (<0.5 mg/L) (CCREM, 1987). The average TDS value 7.0±4.3 mg/L exceeded the Canadian guideline for power generation (<0.5 mg/L) (CCREM, 1987). The average of COD of study area 65±21 mg/L exceeded the Canadian water quality guideline for power generation (Boiler feed water)

**Table 8** Pearson (2-tailed) correlation of the oil parameters and heavy metals in the water matrix of study area

	O&G	TPH	Ni	Cu	Cr	Zn	Pb	Cd	Mn
O&G	1								
TPH	0.997**	1							
Ni	0.522**	0.515**	1						
Cu	-0.036	-0.034	0.114	1					
Cr	0.073	0.083	0.006	-0.054	1				
Zn	0.425**	0.422**	0.844**	0.029	0.103	1			
Pb	0.021	0.020	-0.074	0.204	0.290*	-0.086	1		
Cd	0.635**	0.627**	0.866**	0.124	-0.051	0.681**	-0.064	1	
Mn	0.528**	0.532**	0.456**	0.102	0.191	0.307**	0.018	0.506**	1

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

\*Correlation significant at the 0.05 level (2-tailed)

**Table 9** comparison of results of determination of physicochemical parameter with results obtained in similar studies elsewhere

Cou ntry	Name of River/ Water Body	Temp ( <sup>o</sup> C)	pH	TSS (mg/L)	TDS (mg/L)	DO (mg/L)	BOD <sub>5</sub> (mg/L)	COD (mg/L)	Total Alkali nity (mg CaCO <sub>3</sub> /L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	PO <sub>4</sub> <sup>3-</sup> (mg/L)	Refere nces
Cote D' Ivoire	Bays receivin g Industri al Effluent s	28.1 – 30.5	7.46 – 8.17	-	-	5.10 – 6.62	-	-	-	-	-	Koffi et al., 2014
India	Ranchi Jharkh and	24.8± 0.4 to 30.7± 0.8	6.4±0. 1 to 7.3±0. i	-	73.0± 1.0 to 1422± 0.0	3.90± 0.05 to 8.95± 0.15	2.30± 0.7 to 7.50± 0.41	-	35±1. 0 to 145±4 0	-	-	Kerkett a et al., 2013
Nige ria	Lagos Lagoon (mangr ove)	20.0 – 30.5	1.89 – 8.50	-	-	0.58 – 10.0	-	-	20.5 – 90.0	-	-	Lawso n, 2011
Nige ria	Benin River near Lubrica ting oil Factory	30.9± 1.0	6.02± 0.96	6.6±1 .7	22.4± 5.8	2.96± 0.90	6.4±2. 5	80±38	-	-	-	Akporid o and Asagba , 2013
Nige ria	Ibeshe River (Lagos) industri al Area	27.0 – 34.0	-	10 – 1513	673 – 45216	-	-	10 – 1703	-	50 – 690	1.00 – 6.02	Awome so et al., 2010
Nige ria	Olosun stream (Ibadan )	27.0± 0.8	5.9±0. 4	605± 250	1590± 280	1.38± 0.58	15.4± 4.5	1010± 230	231±8 2	30.3± 9.3	0.28± 0.17	Ipeaive da and Onianw a, 2009
Nige ria	Indusri al area Benin- Ethiope River System Industri al and urban area	27.3± 1.4 (23 – 30)	5.41± 1.4 (4.3 – 6.0)	8.0±6 .8 (0.22 – 20.9)	7.0±4. 3 (0.2 – 14.5)	3.1±1. 3 (0.71 – 5.15)	9.9±2. 9 (3.57 – 15.8)	65±21 (11 – 116)	10.8± 3.1 (6 – 20)	9.5±7 .2 (4.45 – 13.4)	13.1± 3.1 (7.1 – 20.4)	Presen t Study

(<1.0 mg/L). The average concentration of Zn in the study area 31±39 µg/L exceeded water quality guideline for

livestock rearing (25 µg/L) (Ontario Ministry of Environment, 1984). The average Cd concentration of Mn in

**Table 10** Comparison of values of oil parameters and heavy metals with results obtained in similar studies elsewhere

Coun try	Name of River/W ater Body	O & G (µg/L)	TPH (µg/L)	Ni (µg/L)	Cu (µg/L)	Total Cr (µg/L)	Zn (µg/L)	Pb (µg/L)	Cd (µg/L)	Mn (µg/L)	Refere nce
Cote D' Ivoire	Bietri Bay and Ebrie Lagoon	-	-	-	9050 - 9680	-	12050 - 19870	2400 - 4800	20 - 260	-	Koffi et al., 2014
India	Ranchi Jharkha nd	-	-	-	-	-	-	10 ±30 to 110± 30	40±10 to.110± 30	-	Kerkett a et al., 2013
Niger ia	Lagos Lagoon	-	-	780±1 20	2170± 730	2080±1 270	2720±5 70	30±2 0	50±20	3850± 930	Olatunj i and Osiban jo, 2012
Niger ia	Lagos Lagoon (mangro ve) Unilag site Benin River	-	-	-	-	116±30	1060± 210	BDL	74±50	980±1 20	Lawso n, 2011
Niger ia	near Lubricati ng oil Factory Olosun stream (Ibadan)	2270± 480	2010± 340	1880± 630	-	0.40±0. 59	62±42	146± 55	3.0±5.3	-	Akpori do and Asagb a, 2013
Niger ia	Industrial area Benin- Ethiope River System	-	-	1060± 900	360±1 4	210±80	4400±3 300	190± 90	110±90	-	Ipeaive da and Onian wa, 2009
Niger ia	Industrial and urban area	910±1 100 (90 - 4510)	856±1 100 (75 - 4350)	7.7±7. 0 (ND - 31)	1.2±1. 8 (ND - 7.1)	16±25 (3.0 - 138)	31±39 (ND - 218)	27±2 6 (ND - 142)	4.9±4.1( ND - 15)	65±14 (27 - 94)	Presen t Study

the study area 65±14 µg/L exceeded the Canadian Water quality guideline for pulp and paper industry (Fine paper) (<0.3 µg/L) (CCREM, 1987), Canadian guideline for power generation (Boiler feedwater) (<0.01 µg/L) (CCREM, 1987).

The water of the nine sampling stations of the study area were classified using the single index of pollution (Prati et al., 1971). The the average BOD<sub>5</sub> values of the different sampling stations was used (Table 7). The results of the classification showed that eight of the nine sampling station were classified into group IV with a pollution status of "slightly polluted". The only sampling station that fell into another class is the PHCN sampling station (i.e. the sampling station where power generation takes place). This sampling station was classified into group V with a pollution status of "Polluted". The waters

of the nine sampling stations in the study area are therefore of low quality, i.e the waters are polluted for the purpose of drinking. The water of the study area thus needs rigorous treatment before use for the purpose of drinking.

The Pearson (2-tailed) correlation of the main pollutant parameters (i.e. the two oil parameters and the seven heavy metals) with each other (Table 8) revealed that the correlation coefficient of the following pair of parameters are significant at the 0.01 confidence level, O&G and TPH (0.997), O&G and Ni (0.522), O&G and Zn (0.425), O&G and Cd (0.635). O&G and Mn (0.528), TPH and Ni (0.515), TPH and Zn (0.422), TPH and Cd (0.627), TPH and Mn (0.532), Ni and Zn (0.844), Ni and Cd (0.866), Ni and Mn (0.456), Zn and Cd (0.681), Zn and Mn (0.307), and Cd and Mn (0.506). The strong positive correlation of

these pairs of parameters can mean one of the following, one parameter is a component of the other as in the case of O&G and TPH, TPH is a component of O&G and the second is that both parameters have their source in the same place. The latter reason may explain the strong correlation in the remaining pairs. O&G, TPH, Ni, Zn, Cd and Mn may have arisen from the same source. The heavy metals, Ni, Zn, Cd and Mn may have their main source in the effluents from these industries in this stretch of the river especially the ones producing lubricating oil and importing refined petroleum products such as Asca oil Company Ltd and Rigardez oil Ltd, These two oil companies are located almost in the same place. Petroleum prospecting and processing industry in places around this stretch of the river system may also have aggravated the situation (especially during occurrence of oil spillages).

Two of the heavy metals (Pb and Cr) which appear not to be associated with oil in this area but which are strongly correlated with each other with correlation coefficient of 0.290 which is significant at 0.05 confidence level may have their source in other industries such as the ceiling and roofing sheet producing company (Eternit PLC) whose effluent are not disposed directly into the Benin-Ethiopia rivers system but whose effluent finally enters this river system indirectly through swampy creeks (Akporido and Agbaire, 2014).

A comparison the results obtained for the physicochemical parameters of water and the heavy metals in the study area with those obtained for other polluted sites in similar studies carried out in Nigeria, Cote D'Ivoire and India showed that the results in the present study is comparable with most of these result and in some cases are even higher (Tables 9 and 10). They were however lower in some other cases. The average pH of study area water,  $5.41 \pm 1.4$  (4.3 – 6.0) is comparable with results obtained for Ranchi Jharkhand drinking water source in India ( $6.4 \pm 0.1$  to  $7.3 \pm 0.1$ ) (Kerketta et al., 2013), Benin river water near a lubricating oil Factory ( $6.02 \pm 0.96$ ) (Akporido and Asagba, 2013), Olosun Stream which receives effluent from breweries and other industries in Ibadan, Nigeria ( $5.9 \pm 0.4$ ) (Ipeaiyeda and Onianwa, 2009) and Lagos Lagoon at Unilag (1.89 – 8.50). It is however lower than the range obtained for Bertri Bay and Ebrie lagoon in Cote D'Ivoire which receives industrial effluents (7.46 – 8.17). The implication of this is that water of this study is more acidic. Increase acidity has the effect of increasing the mobility of heavy metals and thus making them more readily available to water plants and living organisms in water including fish. The average BOD<sub>5</sub> of study area water,  $9.9 \pm 2.9$  mg/L (3.57 – 15.8 mg/L) is comparable with results obtained for Olosun Stream in Ibadan, Nigeria ( $15.4 \pm 4.5$  mg/L) (Ipeaiyeda and Onianwa, 2009), Benin River near to a lubricating oil factory ( $6.4 \pm 2.5$  mg/L) (Akporido and Asagba, 2013) and Ranchi Jharkhand drinking water source ( $2.30 \pm 0.7$  to  $7.50 \pm 0.41$

mg/L) (Kerketta et al., 2013).

The average concentration of total chromium in study area,  $16 \pm 25$  µg/L (3.0 – 138 µg/L) is higher than values obtained for Benin River near a lubricating oil factory ( $0.04 \pm 0.59$  µg/L) but is however lower than results obtained for Lagos Lagoon at Unilag ( $116 \pm 20$  µg/L) (Lawson, 2011), Lagos Lagoon ( $2080 \pm 1270$  µg/L) (Olatunji and Osibanjo, 2012). The average concentration of Cd in study area,  $4.9 \pm 4.1$  (ND – 15 µg/L) is comparable with results obtained for Benin River near to a lubricating oil factory ( $3.0 \pm 5.3$  µg/L). This value for the study area is however lower than results obtained for other sites in Table 10. The average concentration of TPH of study area,  $856 \pm 1100$  µg/L (75 – 4350 µg/L) is comparable with that obtained for Benin river near to lubricating oil factory ( $2010 \pm 340$  µg/L). Other parameters in Tables 9 and 10 showed similar trends in the relation of results obtained in the study with results obtained for these other polluted sites. The waters of the Benin-Ethiopia rivers system have definitely been affected by industrialization and the increasing Urbanization in Sapele Town.

## CONCLUSION

The study involved the determination of selected physicochemical parameters of water (which also include O&G and TPH) and selected heavy metals has revealed that the average values of some of the parameters exceeded national and international guideline values for drinking water, for example the average value of pH is lower than guideline ranges showing that water of the area are more acidic than required. The average concentration of Pb and Cd also exceeded guideline values for drinking water. The quality of water of the study area was also found to be much lower than the quality of the control area water (the control area is further upstream from the study area). The classification of water of all the sampling stations of the study area into class IV or class V by the single index classification (Prati et al., 1971) which gave them pollution status of "slightly polluted" or "polluted" indicates that the water of study area is of low quality. Industrialization and urbanization must be responsible for this since no other reason can be found; this assertion is strengthened by the low quality of effluent from two industrial concerns which were analyzed. Industries which include lubricating oil producing companies and companies involved in the importation of refined petroleum products which have oil depots situated near the river hence release oil into the river during offloading of oil into the depot storage tanks. Crude oil prospecting and processing in areas around Sapele in the stretch of the river system also aggravate the situation by the release of large volume of crude oil into the river system during oil spillage incidence. Increase urbanization results in more waste and since the

river system is the main recipient of waste in the area, this must have aggravated the pollution effect from industrialization. Environmental authorities should make sure that industries are well monitored to ensure that their effluents comply with the limitation standards set by the Government.

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