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ASSESSMENT OF PETROCHEMICAL EFFLUENT AND ITS EFFECT ON EKEREKENA RIVER IN OKIRIKA *(A CASE STUDY OF PORT HARCOURT REFINERY COMPANY)*: AN EXTRACT

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ABSTRACT: *Petrochemical effluent could hamper the quality of a water body and contribute to the contamination of nearby aquifers and habitats. This study investigated the concentration of some physicochemical parameters (pH, Temperature, odour, colour, conductivity, alkalinity, TSS, TDS, BOD, iron, lead, phosphate) and TPH in a suspected petroleum hydrocarbon contaminated river in Okirika and the effluents discharged from the Port Harcourt Refinery Company (PHRC). The effluents for the analysis were collected at the point of discharge and the water samples were collected at 100m downstream, 200m downstream and 100m upstream. The samples for trace metal analysis were collected in 1liter amber bottles and fixed with concentrated‘* HNO_3 *in a ratio of 2:500; samples for other physicochemical parameters were collected in 1liter sterile containers, while those for TPH were collected in a glass container and fixed with concentrated* H_2SO_4 *in a ratio of 2:500. However, all samples collected were preserved in ice-packed cooler. The statistical package for the social science SPSS* $^{(0)}$ *version l7.0 was used to analyze the emerging data. The interaction between the physicochemical parameters was explored using the Pearson Product Moment Correlation (r) and further associations were investigated using linear regression. The one-way ANOVA was used to determine variance equality in spatial means of the physicochemical parameters, which gave a P value of 0.111823, (<0.05), thus giving criterion to the acceptance of the Ho hypothesis. From the result of the analysis, pH ranged between 5.28 and 6.39 (5.9±0.276), conductivity showed a significant variation; it ranged between 40.00 and 10,400 (2,840±2,521.9), there were no variation in the values of temperature across the sampling locations. Total dissolved solids (TDS) varied significantly between 20.00 and 7,280.00 (1,991.3 ± 1,764.46), total suspended solids (TSS) also varied between 17.00 and 41.00 (25.3±5.54), TPH varied slightly between 7 and 17 (11.8±2.136), Sulphate varied significantly with values ranging between 6.20 and 310.00 (107.1±68.68), lead (pb) varied slightly between 0.001 and 0.052 (0.00±0.013), phosphate ranged between 3.400 and 6.200 (5.2±0.628), iron (Fe) varied slightly, ranging from 0.063 and 1.22 (0.5 ± 0.25), biological oxygen demand (BOD) value ranged between 48.00 and 80.00 (62.3±6.765), alkalinity varied significantly, ranging from 20.00 and 70.00 (44.50±10.50) respectively. TPH correlated positively with BOD at (r = 0.985). The mean concentrations of all the parameters exceeded the DPR standard in the effluent, while those of BOD, pH, TPH and Phosphate exceeded the FEPA standard at 100m downstream. This confirms that Ekerekana River is contaminated, as a result of the inadequately treated effluents discharged from the Port Harcourt Refinery Company (PHRC).*

KEYWORDS: petrochemical effluents, physicochemical parameters, concentration and contamination.

INTRODUCTION

Effluent is a term used to denote all the wastewater produced from industries and municipalities during their day-to-day activities. These wastewaters are known to be “Liquid-form Waste” especially of chemicals or sewage which is used during production processes (Conway, 1990). Effluent discharge is point-source pollution. It contains contaminants such as Heavy metals, Coliform, Bacteria and Various disease-causing protozoans. These contaminants accumulate in bottom sediments and become incorporated into bottom-dwelling fish and invertebrates. Once assimilated in living plants, the contaminants move quickly through the food chain, affecting the health of both animals and human. During production processes in refineries and other petrochemical industries, a reasonable quantity of wastewater is released into the environment. This wastewater even when treated is not completely devoid of toxic substances. In view of the toxic effect often caused by effluent discharge even at very low concentrations, certain communities are re-evaluating the general practice of combining pretreated or partially pretreated industrial waste with domestic waste (Helmen *et al*., 2003).

Effluent treatment discharge is one of the problems facing Nigeria presently and several efforts are being vigorously pursued to ensure the proper and adequate treatment of effluents discharged from industries, so as to ensure the protection of the receiving water body. Water contaminated by effluent from various sources is associated with heavy disease burden (Okoh *et al.,* 2002) and this could influence the current shorter life expectancy in the developing countries compared with the developed countries (WHO 2002).

In developing country like Nigeria, people rely heavily on water sources of doubtful quality in the absent of better alternatives or due to economic and technological constraint to adequately treat the available water before use (Aina and Adedipe, 1996; Calamari and Naere, 1994). The scarcity of clean water and pollution of fresh water has therefore led to a situation in which one fifth of the urban dwellers in developing countries and three quarter of their rural dwelling population do not have access to reasonably safe water supplies (Lloyd and Helmet, 1999). The effluent discharge needs to be treated before discharging it into the receiving water channels on a flow basin from which it will circulate into several rivers surrounding the area. This treatment process is of great importance, because it will help to mitigate the environmental hazards associated with effluent discharge.

In this effect, effluent treatment discharge is a multi-stage process which is carried out at the end of every production process to de-contaminate waste water before discharging them into a body of water or reusing them? (Goldman and Paul, 2002). Effluent treatment includes oil and water separation, primary treatment to remove solids and biological treatment. These different sections of treatment remove most of the pollutants present in the waste water, though not in all cases. For instance, in 1991, approximately 144,000 pounds of oil and grease were discharged into Puget Sound by refineries through their treated effluent discharge (Beredek, 1999). Thus the toxic effect of eff1uent discharge may be due to the waste oil and other impurities which the water picks up during the production or refining process. Some of the impurities are present in the crude oil itself, they include: heavy metals, sulfide and phenols, while others may be created during the refining process and may include; phenols, dioxins and

Ammonia (Gorear, 1995). These chemicals can be toxic to aquatic life even at a very low concentration (Archer,1992).

Water pollution in Nigeria occurs both in the rural and urban areas. In the rural area, drinking water from natural sources such as rivers and stream is usually polluted by organic substances from upstream users who use water mainly for agricultural purposes. Also in the urban area, industrialization and urbanization has greatly contributed to water pollution. The most common form of stream pollution associated with forestry activities is caused by land disturbance. During such disturbance, the large soil particles sink to the bottom of the river and increase the bed load, while the small particles remain in suspension, depending on the stream velocity.
High concentration of suspended particles can obstruct the penetration of light and limit the photosynthetic zone to less than 1m dept. Suspended sediments in water courses have become a serious concern for the water supply authorities, because they increase the cost of treating water. Besides the water pollution caused by forestry and agricultural activities, we also have water pollution associated with industrial activities. Many industries in Nigeria are located close to a river bank and use the rivers as open sewers for their effluents. Such industries include: petroleum industries, mining industries, wood and pulp industries, pharmaceutical industries, textile, plastics, iron and still, brewing, distillery fermentation, and paint as well as food industries. Of all these industries, the petroleum industry poses the greatest threat to water quality especially in urban areas. From time to time, accidental oil spillage occurs which endangers local sources of water supply and fresh water living resources. The lack of adequate clean water resources in the county places the health of many citizens at risk, because the intake of unsafe water deteriorates human health and places other resources at risk such as fishes and land resources.

The 1972 version of the clean water act focused on cleaning up point sources like chemical discharges from industries and effluent from sewage treatment plant, because large discharges are easier to identify and control association.

Petrochemical industries have greatly contributed to the degradation of the environment as well as to deteriorate of human health. Effluent discharge constitutes significantly to water pollution, because they contain contaminants like suspended solids, bacteria, oxygen demanding matters and possibly toxic substances which results in water impurity.

Effluent discharge also cause the eutrophication of some rivers, a process whereby the river becomes over nourished as a result of accumulation of excess nutrients from the wastewater and agricultural runoffs. This leads to the overgrowth of algae and the depletion of the oxygen level, as well as to the increase in water temperature. To these effects, this study aims to determine the effects of the Port Harcourt Refinery Company's effluents on the Ekerakana River; which will be achieved by determining the quality of the Port Harcourt Refinery Company's effluent and comparing it with the DPR standard, by determining the level of pollution in the Ekerakana River, by determining the level of pollutants present in the effluent and in the Ekerekana River, and by analyzing the results using statistical methods such as arithmetic mean and ANOVA.

This study focused on assessing the effluents discharged from Port Harcourt Refinery and emphasizing on evaluating the water quality of the Ekerekana River, and also looks at the efficiency of the Port Harcourt Refinery Company's effluent treatment facilities.

METHODOLOGY

Study Area

The area is a mangrove habitat in Okirika Local Government Area of Rivers State. It is about 800 meters away from the Port Harcourt Refinery Company (PHRC) and the major recipients of effluents are therefore serves as impacted area. This area is located on latitude 04° 44"N and longitude 07° 05"B at the height of 18 meters above the sea level, the refinery drainage channel passes through the Kalio-Ekerekana community and empties into the mangrove wetland. This community is situated on Bonny River System above 60km (45knots) from the Atlantic Ocean. The area serves not only for fishing and other marine activities; the Port Harcourt Refinery Company's jetty is situated there.

The relief of Port Harcourt falls within the Niger Delta relief system and Ekerekana is an environment of Port Harcourt. The relief is based on land units or common land from assemblage. The Niger Delta where Ekerekana is situated extends from foreclose in the West Bonny river in the East, this area is about a distance of 360km from Apex of Aboh to the coastline which is about 50km. Ekerekana in particular has a swamp low lying undulating terrain within Eleme-Okirika-Onne axis. The study area within Niger Delta is characterized by numerous distributions high levels and meandering water channels, comprised mainly of creeks and creek lets are small rivers which drain into the Bonn river system.

The study area is best described as belonging to the earlier deposit of the marine sediments Aries of lower and upper cretaceous age. The geology of the study area are mainly of the sedimentary rock formation, comprising of the tertiary marine and recent or quarter dry marine or continental deposit. The tertiary deposits consists of the coastal plain sand, deposit of sand, fine silt and mud are found in and along the coast.

Ekerekana, the study area is located within the sub equatorial zone of the tropical climate; it has an annual rainfall of over 3000m and mean annual temperature ranging from 24°C-27°C. The tropical rainfall season lasts for about six to seven months of the year, beginning in May through October. The heaviest rainfall is normally experienced in June, July and September, while the Dry season begins November through January. The area has high rainfall and evaporation experience a relative humidity of over 50%.

There are two types of vegetation in Nigeria: 1. Forest, 2. Savanna. Each One of them has many variants affecting the floristic diversity and the structural appearance of the plant communities. This study area is dominated by coastal forest and mangroves, The mangroves are along the coastal creeks and the vegetation is dominated by varieties of the same trees species like the red mangrove (Rhozophaoa) and the Nypa Fruitcan. Other species are Aricenna Africana and legumicularia spp. In the drier outer mangrove, the trees attain heights of about 30-50m and girth up to 2.7m. But due to industrial deposits, the tree heights and girth have reduced drastically.

The study area is in Okirika Local Government Area, in East of Port Harcourt terrain and the water system flows towards bonny river system. As coastal area, they are actively in fishing occupation and a small terrestrial area is used for planting of Plantain, banana etc. They trade in different types of business within neighboring Coastal areas. They have different types of cultural dances, traditional rites like the Boatregater and Odomur.

Figure 1.

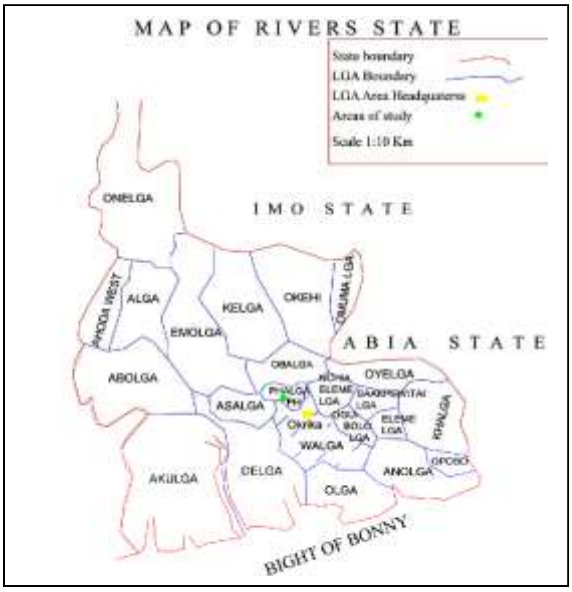

Figure 2.

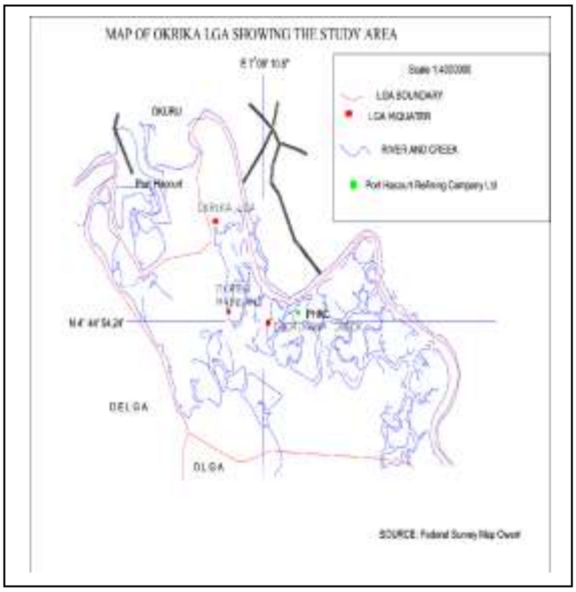

Figure 1: Map of Rivers State, showing the LGAs in the State.
Figure 2: Map of Okirika, showing PHRC Ltd, the study locations.

MATERIALS AND METHOD

Research Design
The parameters studied in this work required a lot of laboratory analysis. These analyses were all aimed at identifying the particular pollutants present in the PHRC effluent, which they discharge into Ekerekana River. To this effect, four stations were mapped out for sample collection, and each sample was subjected to laboratory analysis to identify the pollutants present in them and at what concentrations.
The following steps were taken:

i. Field Sampling
ii. Sample Collection and Preservation
iii. Sample Description
iv. Sample Analysis

- **Sources of Data**

The two main sources of data for this study are the Secondary source and the Primary source. The information from the secondary sources includes past publications from Port Harcourt Refinery Company (PHRC) and its allied industries, materials from laboratory reports, books, dictionary, regulatory standards, seminars and the internet. While the information for the primary sources were obtained from the following: Visiting of the sample stations, direct observations, sample collection, result of analysis and obtained statistical data.

- **Data Collection Techniques**

The samples were properly handled in such a way that no significant change occurred in their composition before being taken to the laboratory.

The samples used in this study were: the effluent discharged from the PHRC and water samples at different location downstream and upstream of Ekerekana River.

Four water samples were collected from four different sample locations once in September, 2010. One sample point was taken from each sample location. The four sampling locations were named as follows:

- Sample Location A coded SLA: outfall basin (point of discharge)
- Sample Location B coded SLB:
- Sample Location C coded SLC:
- Sample Location D coded SLD:

SLA is an outfall basin, also known as the point of discharge, SLB is Surface water at 100m downstream, SLC is Surface water at 200m downstream, and SLD is Surface water at 100m upstream; taken as the Control Sample.

The samples were analyzed for Colour, Odour, Temperature, Alkalinity, pH, Electrical Electricity Conductivity, Total Dissolved Solids (TDS), Biochemical Oxygen Demand (BOD), Total Petroleum Hydrocarbon (TPH), Total Suspended Solids (TSS), Sulphate (SO_4^{2-}), Phosphate (PO_4^{3-}), lead and iron.

- **Sample Collection and Preservation**

The samples were collected in 1liter rubbers; each rubber was rinsed three times with the corresponding Sample before collection. The sample bottle for each sample was submerged vertically to a depth of about 20cm below the water surface and the cock was removed under the water and replaced under the water after taking the corresponding sample. Air spaces were left in all the bottles to allow for expansion of water at elevated temperatures.

- **Sample Preservation**

The samples for the analysis were taken in the morning hours and taken to the laboratory in about 30mins. The samples for BOD was taken in a separate rubber and was kept in moderate temperature in a cooler with ice cubes, well cocked to prevent exchange of oxygen with the atmosphere and other physical, chemical or biological changes that could occur once the sample were removed from the source. On reaching the laboratory, water samples for physicochemical parameters were filtered with Whatman NO_4 filter paper to remove any suspended matter. The water for metal analysis was treated with 2ml concentrated HNO_3 to maintain the original oxidation state of the metal. It also prevents metals from adhering to the walls of the container. All the water samples were preserved in a refrigerator at 4°C to prevent microbial and bacterial activities which may affect the accuracy of the result.

- **Sample Analysis**

Colour

The colour of the different water samples were observed with the sight organ (the eyes). The observed colours for different samples were recorded.

Odour

The odour of the different water samples were also dictated with the smell organ (the nose). The odour perceived for each water sample was recorded.

pH

The water pH was determined in the laboratory by the use of a pH meter (APHA 4500-H^+B). The procedure followed the standard method for water and waste water analysis. According to this method the pH meter was calibrated using two buffer solutions at the range of pH 7.0- pH 4.0. After calibration, the electrodes were rinsed thoroughly with distilled water and blotted dry with soft tissue paper before the electrodes were inserted inside the sample and read after 120 seconds (2minutes).

Temperature

The temperature of the samples was determined in-situ by dipping a Celsius scaled thermometer (0-100^{o}C) into the water sample for five minutes until a steady temperature was reached, and the results were recorded.

Electricity Conductivity

The conductivity meter was used to determine the conductivity of the water samples. The reagent used were 0.01m potassium chloride and dissolved 0.745g of dry KCL in water, and it was made up to 1litre at 25^{o}C. The resulting solution is known as the standard reference solution and at a temperature of 25^{o}C, it has an electricity conductivity of 1413mhos/cm.

Sulphate (SO_4^{2-})

The sulphate was determined using the UV Spectroscope, and Sulfaver 4 Powder pillows were used as a reagent. According to the procedure 10ml of sample was poured into the cuvette before zeroing, 1 (one) packet of Sulfaver 4 Powder pillows was added into the cuvette and shake gently for one minute using a stop watch before reinserting the cuvette into the instrument for five minute count down before reading the result which was displayed in mg/l SO_4^{2-}.

Total Dissolved Solids (TDS)

The samples for determining the total dissolved solids were evaporated and dried in weighed dishes at 105^{o}C to constant weight. The increase in weight over the empty dish represents the total dissolved solid content. 100ml of the sample was used and evaporating dishes were left to cool in a desiccator before the weighing is done. The results obtained were expressed in mg/l.

Total Suspended Solids (TSS)

100ml of the samples were filtered through a glass filter disc and transferred to previously ignited and weighed evaporating dishes. The samples were evaporated to dryness in an oven as in the case of TDS and further dried at 105^{o}C for two hours in the oven; they were afterwards cooled and reweighed. The difference between the weights obtained gave the value of the TSS content of the samples. The results obtained were expressed in mg/l of sample.

Total Petroleum Hydrocarbon (TPH)

The Total Petroleum Hydrocarbon content of the water samples was determined using the Gas Chromatograph Analysis. The reagents used include Helium and Nitrogen (both used as carrier gases to help the hydrocarbon travel the 30meters length of the capillary column), as well as the ignition gases: Hydrogen and Air. All the Gas Chromatograph gases were set to a pressure of 30psi. The procedures require that 250ml of the water sample be measured into a separating funnel; 25ml of Dichloromethane (DCM) was added to the water sample in the separating funnel. The content was vigorously agitated to facilitate mixing and extraction of the organic materials present, the outlet/tap of the separating funnel was at the same time intermittently opened to allow for escape of built-up pressure.

The separating funnel was clipped to the retort stand and was left for about 20-30 minutes for proper extraction and settling of the organic extract. The organic phase alone was allowed to pass through a column containing cotton-wool, silica gel (used to clean up any residue that is not organic in nature) and sodium sulphate (used as a dehydrating agent, to remove any excess moisture that might have accidentally been discharged via the separating funnel outlet). The organic extract/material is concentrated by leaving it to evaporate away via the mobile Phase (organic solvent, DCM) leaving behind the stationary phase (organic material; e.g. Petroleum Hydrocarbons). 1ml of DCM was added to the extract to dissolve the organic material, after which 1ml of the organic material was injected into the Gas Chromatograph via the injection point into the capillary column for a retention time of 53.0mins and the detected aliphatic/total petroleum hydrocarbon s were laid-out in a readable format called the 'Chromatograph'. The chromatograph is a plot of signal Vs time.

Biological Oxygen Demand (BOD)
In this procedure 250ml reagent bottle was filled with the sample to determine the BOD. After which the reagent bottle was washed and filled with the sample again and tightly stopped with a stopper. It was wrapped in an aluminum foil to keep it away from light. It was incubated at a temperature of 20^oC for 5 days, and BOD was determined. The difference between the initial dissolved oxygen and final values gave the BOD_5 value of the sample.

Phosphate
Phosphate in water was determined by automation using the (ASTM-D515) Ascorbic Acid Method. According to the procedure 2ml of the clear sample was added into a test tube, followed by 5ml deionised water and 2ml ammonium molybdate solution. The content was properly mixed, and 1ml of $SnCL_2.2H_2O$ dilute solution was again added and the resulting mixture was mixed again and was allowed to stand for ten minutes. The absorbance measurement was taken on the spectrophotometer at 660nm wavelength. A standard curve was prepared within 0.5ppmp (mg/l) containing the same concentration of reagents as the sample solution. The absorbance of standard solution was plotted against the mg/l or ppmp, and the phosphate phosphorus content of the samples were calculated and recorded.

Alkalinity
The level of alkalinity in water was determined by automation using the ASTM-D1067-70. 1.060g of $NaCO_3$, NaOH distilled water, Methyl orange, 0.1ml HCL, and 2.8ml H_2SO_4 were used as the reagents. According to the procedure, 10ml of the sample was used for all the analysis, 0.1N stock acid was prepared by diluting the sample with 8.3ml concentrated HCl to 1litre. 0.02N acid solution was diluted with 200ml of the stock with CO_2 free water to 1litre. The acid solution was standardized with 0.02N sodium carbonate solution dried at 140^oC, methyl orange indicator was added drop by drop to the mixed solution. Titration was carried out and the observations were made. The yellow colored solution turned pink and the volume of the acid was read and recorded in mg/l.

Lead and Iron
The gases used to determine the concentration of lead and iron in this analysis were Acetylene at 70psi and air at 70psi. The blank solution used to zero the AAS was distilled water and the lamp used as light source was the "Hollow Cathode Lamp."The AAS was calibrated using the standard solutions of pb0.5mg/l and 1.0mg/l for lead, and Fe1.0mg/l and 4.0mg/l for Iron. A calibration graph of absorbance vs concentration was obtained, and the individual samples were presented to the instrument and the absorbance of lead and iron obtained. The concentration was also extrapolated from the calibration graph.The statistical analyses of the results obtained from the laboratory were done using Microsoft Excel and XLStat for One-way ANOVA of the results obtained. Comparisons were made with the standard of National Environmental Standards and Regulations Enforcement Agency (NESREA) an arm of the Nigerian Federal Ministry of Environment (FMEnv).

RESULTS AND ANALYSIS

This section deals with the presentation and the analysis of the results obtained from the laboratory.

Table 4.1: Variations in Physicochemical Parameters, Total Petroleum Hydrocarbon and Trace Metals.

SAMPLES	**SLA**	**SLB**	**SLC**	**SLD**	**NESREA (Limit)**
PARAMETERS	**RESULTS**				
Temperature ^{0}C	25.8	25.8	25.8	25.8	≤32
pH	5.28	5.51	6.39	6.28	6.5-8.5
Alkalinity Mg/L	70	50	38	20	≤100
EC Ms/Cm	10, 400	470	450	40	1,000
TDS Mg/L	7, 280	329	336	20	≤1000
TSS Mg/L	41	17	25	18	30
TPH	17	13	10	7	-
Sulphate Mg/L	310	52	60	6.2	≤200
Phosphate Mg/L	6.2	5.1	5.9	3.4	≤1.0
BOD_5 Mg/L	80	64	57	48	≤6.0
Lead Mg/L	0.052	≤0.001	≤0.001	≤0.001	≤0.05
Iron Mg/L	1.219	0.634	0.063	0.278	≤0.3

Source: *Researcher's Fieldwork (2010).*

Table 4.1 above shows the results obtained from fieldwork at the study locations. From the table, it was observed that variations were recorded in most of the physicochemical parameters measured. pH ranged between 5.28 and 6.39 (5.9±0.276), conductivity showed a significant variation; it ranged between 40.00 and 10,400 (2,840±2,521.9), there were no variation in the values of temperature across the sampling locations. Total dissolved solids (TDS) varied significantly between 20.00 and 7,280.00 (1,991.3±1,764.46), total suspended solids (TSS) also varied between 17.00 and 41.00 (25.3±5.54), TPH varied slightly between 7 and 17 (11.8±2.136), Sulphate varied significantly with values ranging between 6.20 and 310.00 (107.1±68.68), lead (pb) varied slightly between 0.001 and 0.052 (0.00±0.013), phosphate ranged between 3.400 and 6.200 (5.2±0.628), iron (Fe) varied slightly, ranging from 0.063 and 1.22 (0.5±0.25), biological oxygen demand (BOD) value ranged between 48.00 and 80.00 (62.3±6.765), alkalinity varied significantly, ranging from 20.00 and 70.00 (44.50±10.50).

Table 4.2: Descriptive Statistics of the Physicochemical Parameters.

PARAMETERS	**Minimum**	**Maximum**	**Mean**	**Standard Error**
Temperature ^{0}C	25.8	25.8	25.8	0.000
pH	5.28	6.39	5.9	0.276
Alkalinity Mg/L	20	70	44.5	10.500
EC Ms/Cm	40	10400	2840.0	2521.947
TDS Mg/L	20	7280	1991.3	1764.455
TSS Mg/L	17	41	25.3	5.543
TPH	7	17	11.8	2.136
Sulphate Mg/L	6.2	310	107.1	68.680
Phosphate Mg/L	3.4	6.2	5.2	0.628
BOD_5 Mg/L	48	80	62.3	6.762
Lead Mg/L	0.001	0.052	0.0	0.013
Iron Mg/L	0.278	1.219	0.5	0.253

DESCRIPTIVE GRAPHS

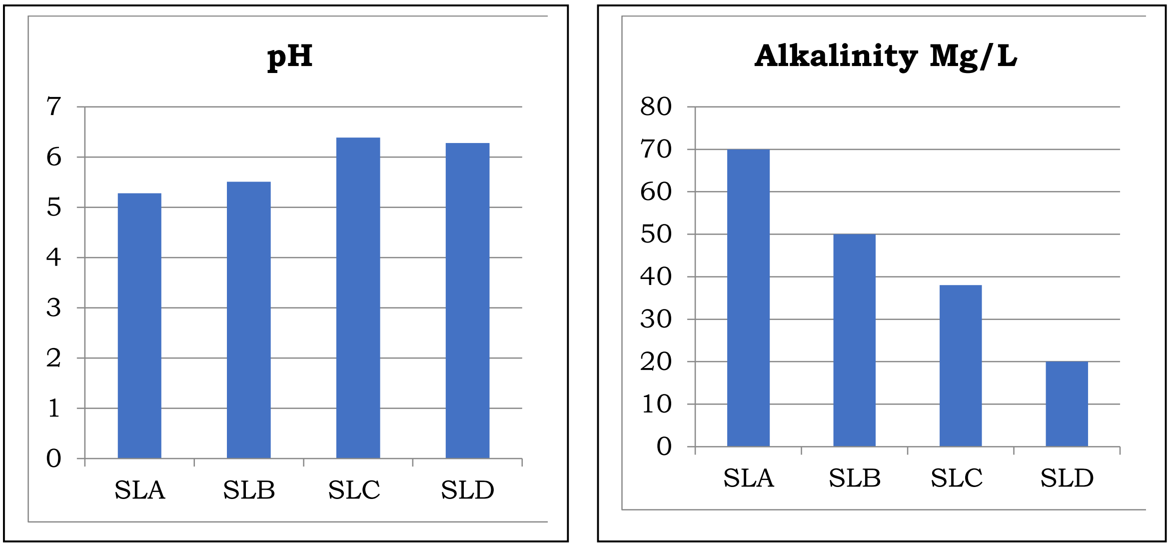

Figure 3: Spatial Variation in pH and Alkalinity of the location.

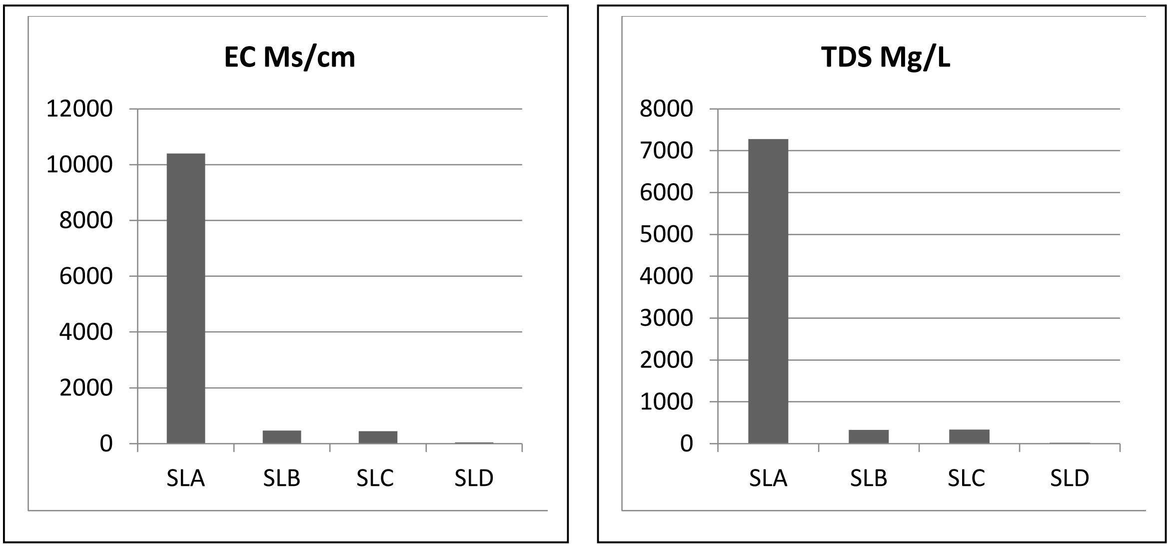

Figure 4: Spatial Variation in EC and TDS of Ekerekena Creek

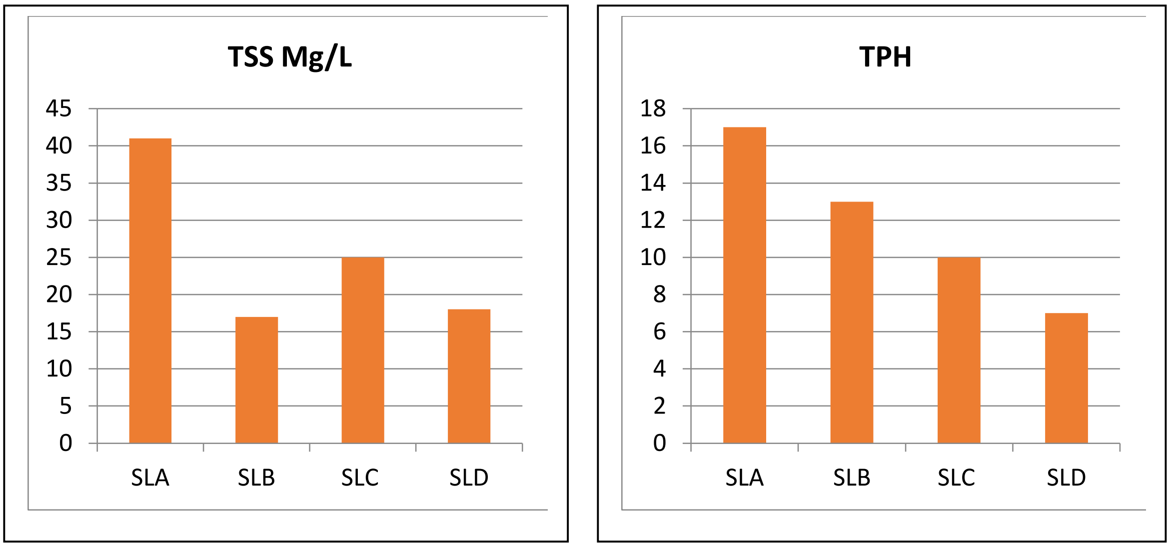

Figure 5: Spatial Variation in TSS and TPH of Ekerekena Creek

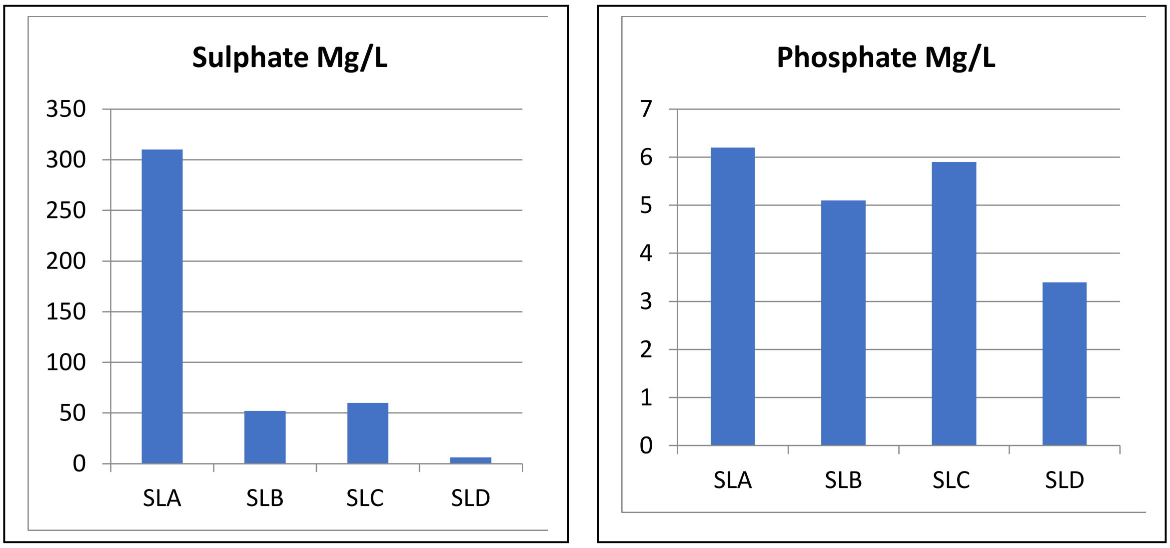

Figure 6: Spatial Variation in Sulphate and Phosphate of Ekerekena Creek

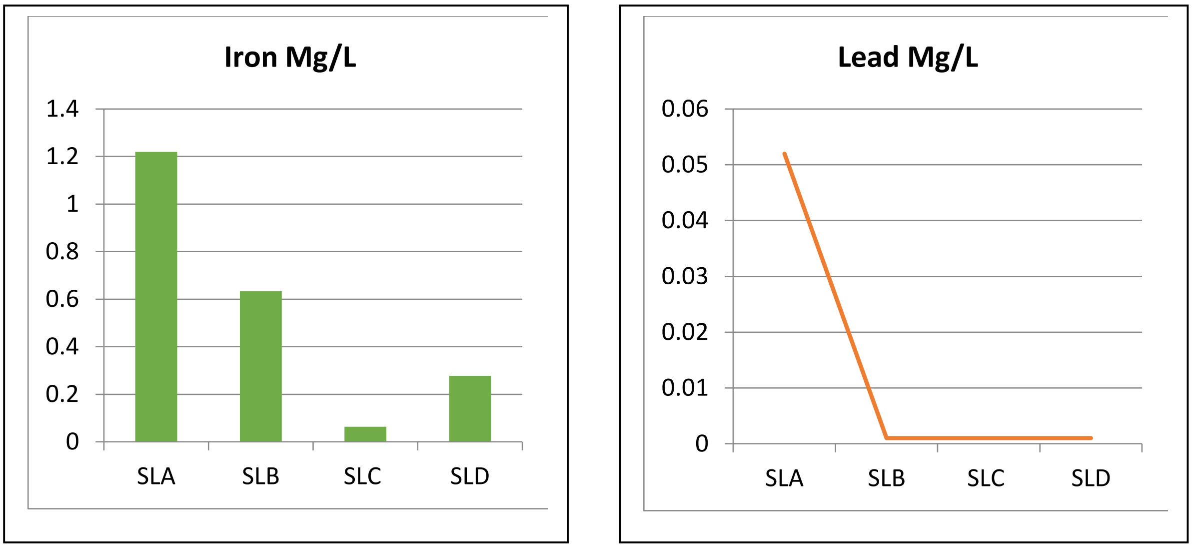

Figure 7: Spatial Variation in Trace metals of Ekerekena Creek

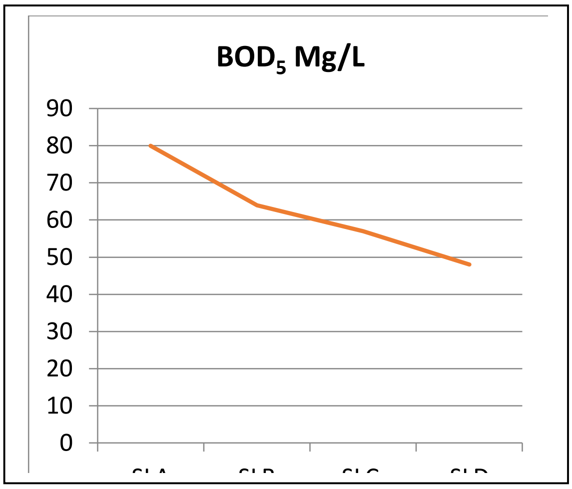

Figure 8: Spatial Variation in BOD$_5$ of Ekerekena Creek

Spatial Variation in the Physicochemical Parameters

There were wide variations recorded for pH with the highest value of (6.39) at point of discharge and a least value of (5.28) at 100m upstream (Fig 3a), while Alkalinity had the highest value (70) recorded at the effluent discharge point and the least value (20.00) recorded at 100m upstream sampling location (Fig. 3b) conductivity, total dissolved solids, total suspended solids. Total petroleum hydrocarbon, sulphate, phosphate, iron, biological oxygen demand and alkalinity. Conductivity had the highest value (10,400) recorded at the effluent discharge point and the lowest value (40.00) was recorded at 100m upstream (Fig 4a). The highest concentration (7280.00) for total dissolved solids (TDS) was recorded at the effluent discharge point, while the lowest value (20.00) was recorded at 100m upstream sampling location (Fig 4b). Total suspended solids (TSS) had the highest value (41.00) recorded at the effluent discharge point and the least value (17.00) recorded at 100m downstream sampling location (Fig 5a). Total petroleum hydrocarbon also varied, with the highest value (17.0) recorded at the effluent discharge point and the lowest value (7.0) recorded at 100m upstream sampling location (Fig 5b). The highest value (310.00) for sulphate was recorded at the effluent discharge point and the lowest value (6.20) was recorded at 100m upstream sampling location (Fig 6a). Phosphate had the highest value (6.2) recorded at the effluent discharge point and the least value (3.4) recorded at 100m upstream sampling location (Fig 6b). Iron (Fe) also varied, with the highest value (1.22) recorded at the effluent point and the least value (0.063) recorded at 200m downstream sampling location (Fig 7a). Lead (pb) had the highest value (0.052) recorded at the effluent discharge point and the least value (0.001) was recorded at the three other sampling locations (Fig 7b). Biological Oxygen Demand varied, with the highest value (20.00) recorded at the effluent discharge point and the lowest value (12.00) recorded at 100m upstream sampling location (Fig. 8).

A test of variance equality in means of the physicochemical parameters, spatially revealed equality in means. [$F_{(2.58)} < F_{crit(3.94)}$] at $P < 0.05$ (Table 4.3).

Table 4.3. ANOVA: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	48	20213.02	421.1046	3264649
Column 2	48	120	2.5	1.276596

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Group	4205515	1	4205515	2.576395	0.111823	3.942303
Within Group	1.53E+08	94	1632325			
Total	1.53E+08	95				

DISCUSSION

P^H is a measure of the intensity of acidic and alkaline reactions 0f water. Many biological and chemical processes within a water body are influenced by the p" (Chapman 1992). F0} example, the corrosiveness of water is a function of P^H. The P^H concentration at sample locations C and D falls within the FEPA interim standard for aquatic life, water quality, while the P^H concentration at the point of effluent discharge (sample location A) and at 100m sampling location (sample location B) fell below the FEPA recommended limits thus cannot support aquatic life, being acidic. This can be as a result of the effluent discharged into the Ekerekana River as well as the runoffs into the river and atmospheric depositions mainly in the form of acid rain. From the result of the analysis, it can be deduced that the effluent has potential influence on the P^H.

The concentration of conductivity at the effluent discharge point (sample location A) exceeded the WHO recommended limits, this could be as a result of the activities going on in the Port

Harcourt Refinery Company at the time of sample collection. While the concentration of conductivity at sample locations B, C and D fell within the recommended limits. Conductivity depends on the quality and quantity of dissolved salts present in the water body, which can be as a result of dissolved solids. Thus the high concentration of total dissolved solids recorded in the point of effluent discharge contributed to the high concentration of conductivity in the same sample.

High concentration of total dissolved solids (TDS) gives a water body an unobjectionable taste and may affect the ecosystem, as well as the domestic and agricultural usefulness of the water (FEPA 1991). From the result of analysis, only the concentration of total dissolved solids (TDS) at the point of effluent discharge (sample location A) exceeded the DPR recommended limits, the concentrations at sample location B, C and D falls within the recommended limit. This maybe as a result of the activities going on in the Port Harcourt Refinery Company at the time of sample collection, as well as the concentration of the Total Suspended Solids in the sample, which was recorded as the highest as indicated in the result of the analysis. Other organic sources such as; leaves, silt, plankton, industrial waste and sewage can also increase the concentration of total dissolved solids in a water sample. Increase in P^H brought about an increase in the concentration of total dissolved solids. If toxic ions constitute high concentration of total dissolved solids (TDS), it poses a serious health hazard.

Total petroleum hydrocarbon (TPH) is a term used to describe a broad family of several hundred chemical compounds that originally come from crude oil. Thus, it is a mixture of chemicals. The health effects associated with total petroleum hydrocarbon (TPH) depends on various factors such as; period of exposure, type and quantity of chemicals ingested. Some can affect the central nervous system, while others can cause fatigue, headache, nausea, drowsiness or even death in some cases. The concentration of the total petroleum hydrocarbon (TPH) at the Point of effluent discharge and at sample location B (100m downstream) exceeded the DPR recommended limits, while the concentration of the Total Petroleum Hydrocarbon at sample location C and D falls within the DPR recommended limits. This may be due to the activities going on in the Port Harcourt Refinery Company (PHRC) during the period of sample collection, as well as the natural breakdown activities going on in the water body.

Biological oxygen demand (BOD) measurement is an approximate measure of the amount of biochemical dependable organic matters present in the water sample. Activities that require oxygen declines biological oxygen demand (BOD), for example, aerobic micro organisms present in the water requires oxygen to oxidize the organic matters into a stable inorganic form. The further explains why biological oxygen demand (BOD) significantly correlated with total petroleum hydrocarbon. From the result of analysis, only the concentrations of biological oxygen demand (BOD) at the point of effluent discharge and the 100m sampling locations exceeded the recommended FEPA/DPR limits, while the sample locations C and D had concentrations within the recommended limit. This may due to increase input of domestic effluent, industrial effluent and runoff from several waste dumps.

The temperature of the water affects the aquatic life. From the result of analysis, an concentrations of temperature at all the different sampling locations falls within the FEPA interim standard for aquatic life water quality (1991) and can positively affect the aquatic life.

Despite the fact that the concentrations of the temperature falls within the recommended limit, the river is heavily polluted with many other contaminants as indicated in the result of analysis. The colour of the water samples were observed physically. From the observation, only the colour at the point of effluent discharge (sample location A) exceeded the recommended limits, while those of the sample locations B, C and D fell within the recommended limits. This may be as a result of the high concentration of the dissolve and particulate matter discharged from the effluent as well as the organic matters and micro organisms like; phyto, zooplankans (Chapman, 1992).

The odour of the water samples which were also determined physically revealed that the odour at sample locations A, B and C exceeded the WHO recommended limit. The odour of sample D (100m upstream sampling location) fell within the recommended limit, being odourless. The offensive odour recorded at sample location. A, B and C may be due to the composition of the effluent discharged from the Port Harcourt refinery Company (PHRC) during the period of sample collection, as well as runoffs from agricultural activities.

Phosphate is an essential nutrient for living organisms; it exists in water bodies as both dissolved and particulate species. It is generally the limiting nutrient for the growth of algae and thus can control the primary productivity of the water body. From the result of analysis, it was observed that the concentrations of phosphate in sample locations A, B and C exceeds the DPR/WHO recommended limits, while the concentrations of phosphate in sample location D fell within the recommended limits. The later may be due to the presence of plants along the river banks, which is known to take up a significant amount of phosphate. While the high concentrations of phosphate in the other samples may be due to the activities going on in the Port Harcourt refinery Company (PHRC), runoff from residential areas, especially areas with high laundry activities which makes use of detergents, as well as from agricultural runoff, slaughters, waste dumps and car wash. The high concentration of phosphate in a water body may lead to eutrophication of the Water body. (Otokunefor and Obiukwu, 2005).

Sulphate is another nutrient that supports aquatic life, but in excess can lead to eutrophication of the water body. The result 0f analysis revealed that only the concentration of sulphate at the point 0f effluent discharge exceeded the WHO recommended limits, but the concentrations at sample locations B, C and D falls within the recommended limits. Source of sulphate includes; runoff from residential areas, especially areas with high laundry activities which makes use of detergents, as well as from agricultural runoff, slaughters, waste dumps and car wash.

The iron concentrations in sample locations A and B were relatively high when compared with the DPR/WHO recommended limits, while the sample locations C and D had concentrations within the recommended limits. For this reason, the water cannot be recommended for domestic purpose, unless the effluent is adequately treated before being discharged into the river. High level of iron in the water stains clothes when used for laundry purposes and gives the water a bitter taste which makes it unpalatable for drinking.

The concentration of lead (Pb) in sample locations A, B and C fell within the DPR/WHO recommended limits, with the exception of the point of effluent discharge (sample location A), which slightly exceeded the recommended limits. Lead is a toxic metal and is present only in minute concentrations in a water body. Its sources include; atmospheric depositions of lead

(Pb), input from leaded petrol used in automobiles and when in high concentrations can cause adverse health impact, like affecting the central nervous system (CNS).

Alkalinity refers to the capability of water to neutralize acid. Alkalinity depends upon the P^H of the water sample and to some extent on the hardness of the water. Beyond the recommended limits, alkalinity makes the taste of the water unpleasant. Alkalinity is important for fish and aquatic life, because it protects or buffers against rapid P^H changes. Thus, we say that alkalinity is a measure of how much acid can be added to a liquid without causing a large change in P^H. The result of the analysis shows that the concentration of alkalinity for all the samples fell within the recommended limit.

Total Suspended Solids (TSS) is a measure of the suspended solids. In high concentration, it limits the ability of a water body to support a diversity of aquatic lives. It absorbs heat from the sunlight and increases the temperature of the water body, thus reducing the level of dissolved oxygen. Total suspended solids can also destroy fish habitats, because it settles at the bottom of the river and can eventually blanket the river. From the result of analysis, the concentration of total suspended solids at the point of effluent discharge exceeded the DPR recommended limit and thus affected the color of the sample. The concentration of total suspended solids in sample locations B fall within the FEPA recommended limit. Sample locations C and D also had concentration within the recommended limit.

RECOMMENDATION

There is need to monitor and place surveillance on the amount and quality of effluents/pollutants discharged into Ekerekana River. Activities such as oil exploration and exploitation, as well as agricultural and domestic activities which pollute the water bodies should be properly checked and if possible reduced.
No industry should release toxic substances into the air, water or land in Nigerian environment beyond permissible limits. The environment should be conserved appropriately to ensure that the present and future generations of both human and aquatic life can enjoy the blessings of a healthy and productive environment and that the environment as the foundation of human survival can be preserved unto the future, considering the fact that preserving the environment is indispensable for a healthy living for both human and animals.

Environmental Management System (EMS) should be developed to improve environmental performance. Also industries must employ personnel with the competent hand, instead of assigning roles to unskilled personnel who do not know the predicaments of discharging pollutants beyond the tolerable limits into the environment.

Training programs have to be organized, such as workshops and seminars with environmental management focus, in terms of practicing environmental impacts assessment (EIA), environmental pollution control, monitoring and compliance, preventive and corrective measures must be put in place and enforced for a healthy environment.

Petrochemical industries through the Federal Government should provide financial and technical support to the local communities to compensate them for the damage industries has caused their environment. Ekerekana as a community should request for adequate compensation from the PHRC fir the damages done to their environment and such compensation should be utilized to meet the needs of the community.

The Federal Environmental Protection Agency (FEPA) should try to implement the laws for the proper protection of the environment, such as the “Polluter Pays Principle”; it will help to reduce the level of environmental pollution especially in the Niger Delta Area of the country.

CONCLUSION

This study was carried out to assess the quality of effluents discharged from Port Harcourt Refinery Company (PHRC) and their impact on Ekerekana River It focused on the analysis of some physicochemical Parameters (pH, Temperature, conductivity, total suspended solids, total dissolved solids, biological oxygen demand, colour, odour and alkalinity), trace metals (Lead and Iron), nutrients (sulphate and phosphate) and total petroleum hydrocarbon. From the result of analysis and works done in the past, it is concluded that Ekerekana River is heavily polluted. All physicochemical parameters studied exceeded the DPR recommended limits at the point of effluent discharge and at some of the water sampling locations. The trace metals at the point of effluent discharge exceeded the DPR recommended limit. At some locations downstream, the concentrations also exceeded the recommended limits, thus posing a threat to the water body and the aquatic lives dwelling in it. The concentration of the Total Petroleum Hydrocarbon (TPH) was high in the effluent, and the reason may be due to the operation going on in the Port Harcourt Refinery Company (PHRC) at the time of sample collection.

This Work revealed that the effluent discharged from the Port Harcourt Refinery Company (PHRC) is not properly and adequately treated. The pollution of Ekerekana River is both as a result of the effluent discharged from the Port Harcourt Refinery Company (PHRC), as well as other agricultural and domestic activities that go on downstream.

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