

Effects of Crude oil spills on Surface water in Niger-Delta Region of Nigeria

Nkechi E. Ibisi*¹, Mercy O. Ojo¹, and Anthony O. Ano²

¹. Department of Chemistry, College of Physical and Applied Sciences, Michael Okpara University of Agriculture Umudike. P. M. B. 7267 Umuahia. Abia-State. Nigeria.

². Central Laboratory, National Root Crop Research Institute Umudike, P.M.B 7006 Umuahia, Abia-State. Nigeria.

ABSTRACT: Water pollution from crude oil spills at Obunku in Oyibo Local Government Area of Rivers State, located in Niger-Delta region Nigeria, was investigated by determining the physiochemical properties of surface water in the area. Water samples were collected from four different locations (source of pollution, 100m away from source, 200m away from source and a control) for analysis. Results from the study showed that these water samples were polluted as regards to pH, total dissolved solids, total suspended solids, total petroleum hydrocarbons, NO_3^- and NH_4^+ . Regression analysis carried out between pH, total suspended solid, total dissolved solids and total petroleum hydrocarbon respectively with ions in the water samples showed positive relationship. Among the ions, Na^+ ($r = 1.6256$) and NH_4^+ ($r = 0.9895$) have the highest correlation coefficient in the relationship between pH and all the ions. Also there is a significant and positive relation between the ions and the total dissolved solid with Mg^+ ($r = 0.9834$) and NH_4^+ ($r = 0.9924$) having the highest correlation coefficient.

Keywords: water pollution, oil spillage, total dissolved solid, total suspended solid, pH

I. INTRODUCTION

Before the advent of crude oil, Nigeria's economy used to be centered on agriculture, which its activities has little or no adverse effect on the ecosystem. However since 1970s till date oil industry has remained almost the sole source of revenue to Nigerian government, yet little attention has been paid to the oil extraction impacts on the environment and the wellbeing of people within the environs. When oil spill occurs, it results in the pollution of surface ground water as well as the destruction of biotic organisms. It also poses serious problems to socio-economic activities, sustainable development and ecological balance.

Experiences over the years show that oil spillage has some serious consequences on both man and environment. According to report from the federal environmental protection agency (FEPA), ^[1] oil spills and leaks occur hundreds of time annually thus resulting in both chronic and acute environmental degradation. ^[2]

In the Niger Delta region of Nigeria where so many oil companies are sited and their operations give little or no regards to the environment. As such, oil operations have entailed recurrent oil spillages and massive gas flaring. The impunity of oil operations in the Niger Delta is exemplified by the fact that Shell operations in Nigeria that accounts for just 14% of its oil production worldwide, accounts for a staggering 40% of its oil spills worldwide. ^[3] Oil spills records obtained from the Department of Petroleum Resources (DPR) showed that between 1976 and 2005, 3,121,909.80 barrels of oil was spilled into the Niger Delta environment in about 9,107 incidents. ^[4] Independent researchers have however argued that the volume and incidents of oil spills are underreported. ^[5, 6, 7]

The effects of oil spills have only been widely recognized but cannot be measured. Whenever oil spill occurs, its effects can be seen, people dying of cancer and respiratory diseases, defaced buildings and movement, decimated animals and plants, rivers depleted with fish death and drying forest, destruction of economic trees and crops etc. The effects of oil spills on water results in water pollution which is a word wide phenomenon

Pollution of aquatic environment as reported by GESAMP (1988) occurs when human introduce either directly or indirectly discharge to water, substance or energy that results in deleterious effect such as hazards to human health, harm to living resources, hindrance to aquatic activities or reduction of amenity value. These occurrences are common in Niger-Delta region of Nigeria where fishing is a traditional source of livelihood. This study investigates the effect of crude oil spills on surface water in Niger-Delta region of Nigeria, a case study of Obunku River in Oyigbo local government of Rivers state Nigeria.

II.

MATERIALS AND METHOD

2.1 COLLECTION OF SAMPLE

Sampling was done by collecting sub-samples at various points following standard procedures. ^[9] Each sample was properly labeled and the sampling locations were also noted.

2.1.1 Water Samples

Water samples were collected in plastics containers, which were properly labeled. The samples were collected at 3 points with a 4th point as control. Sampling was carried out at interval of 100m between sampling points. Water samples were collected below the surface using one litre polyethene bottles, which had a covering lid. Each of the containers was rinsed with water to be sampled, before the collection of the sample. Sufficient air spaces were left in the entire bottles to allow for expansion of water at increased temperature. In all cases, the sampling bottles were used directly by holding the bottles horizontally and allowing the water flow in gently. The bottles were covered, labeled and transported to the laboratory for analysis.

2.2 DETERMINATION OF PHYSICO-CHEMICAL PARAMETERS IN WATER SAMPLES

The analysis of various physico-chemical parameters analyzed namely pH, ammonium, total petroleum hydrocarbon, total nitrogen, nitrate, total hardness, calcium, magnesium, sodium, total dissolved solids and total suspended solids were carried out as per methods described in GESAMP (1988), APHA (1998), (WHO (1992), and APHA (1992)). ^[8, 9, 10, 11]

- 1) **pH:-** The pH meter was used to determine the level of acidity or basicity of the sample. It was determined by using Jenway 3310 pH meter. The pH electrode was inserted into water sample and the pH read off.
- 2) **Total Suspended Solids (TSS):-** 50ml of water sample was measured after the sample was shaken. The water sample was thereafter passed through quantitative ash free filter paper. Platinum crucible was weighed, and the filter paper was placed in the crucible, which was later placed in the ruffle furnace at 500°C. After ashing, the crucible was weighed again.
- 3) Increase in weight of the crucible = the weight of the suspended solids.
- 4) **Total dissolved solids (TDS):-** 50ml of filtered water was measured into a weighed beaker. This was evaporated to dryness and the beaker was thereafter weighed again. Increase in weight of the beaker = weight of dissolved solids.
- 5) **Total petroleum hydrocarbon (TPH):-** 20ml of the water sample was measured after the sample was shaken. A 20 ml of the organic solvent (toluene) was measured and both the water and the solvent were poured into a separating funnel which was shaken for 2 - 5 minutes. And the separating funnel was mounded on the restart stand and allowed to settle down for few minutes. Two layers were noticed. The organic solvent on the upper layer followed by the aqueous solution. A beaker was used to collect the aqueous solution and also a film container was used to collect the organic solvent which is needed for determination. Absorbance was measured at 420nm.

2.3 DETERMINATION OF TRACE METALS (Zn, Cd, Pb)

Each of the water sample containers were brought out and placed on the laboratory table for 2 hours so that the water will assume the laboratory temperature. The sample was thoroughly mixed by shaking and 50 ml of it was transferred into a 250 ml glass beaker, 5ml of concentrated HNO₃ was added. The acidified water sample was heated to boiling on a hot plate and the heating continued until the volume of the water was reduced to about 20 ml. A 5 ml of concentrated HNO₃ was thereafter added and the volume of water was further reduced to 10 ml. The water was allowed to cool and then quantitatively transferred to 100 ml volumetric flask and the volume made up to mark with distilled deionized water. Portions of these solutions were transferred into polyethylene bottles and labeled. Trace metals Zn, Cd, Pb in the solutions were determined by Atomic Absorption Spectrometer (AAS) solar 32AA model.

2.4 ANALYSIS OF MINERAL NUTRIENTS COMPOSITION

Nitrogen, Ammonia: 20 ml of water sample was collected and one tablet of kjeldahl catalyst copper and 10ml of Concentrated H₂SO₄ was added to the sample. The mixture was digested by digestion system 40, 1016 digester. The digestion was carried out about 3 hours. After digestion, the sample was allowed to cool and then quantitatively transferred to 100ml volumetric flask and the volume made to mark with distilled deionized water. 10 ml of phosphate buffer was added to the water. Distilling process was carried out gently and a 50 ml portion of the distillate was collected by means of volumetric flasks. After distillation process, the distilled liquid was 150 ml, and biomocresol green methyl red indicator was added to the solution and ammonia was titrated with 0.01N acid. The mill equivalent nitrogen and the concentration is calculated using equation 2.1.

$$\text{Concentration of nitrogen} = \frac{10T}{V} \quad (2.1)$$

Where V is the volume in ml of sample distilled, and T is the volume in ml of 0.01N acid needed to titrate the ammonia distilled.

ii) **Nitrate (NO₃⁻):** Sodium oxide (2 ml) solution and phenol di- sulphuric acid solutions (2 ml) was added to each water samples (40ml) in evaporating dish. It was stirred and the solution evaporated on a hot plate to reduce the volume to 10 ml. This was later cooled and was diluted to 200 ml with distilled water and sodium hydroxide (10 ml) was added. The absorbance was read at 401 nm against a blank solution. This was done in triplicate and the concentration of nitrate in the water sample was obtained from a KNO₃ standard solution,

iii) **Calcium and magnesium:** 20 ml of the water sample was measured into a 250 ml volumetric flask and the volume was made to 50 ml with water. Few crystals of hydroxylamine hydrochloride and 5ml of ammonia chloride buffer were added to the water sample. The mixture was warm to about 60°C, and titration was carried out with 0.020N EDTA (ethylenediaminetetraacetic acid). Two titre values were recorded for calcium and magnesium respectively. The amount of calcium and magnesium were calculated using equation 2.2 and (2.3) respectively.^[12]

$$\text{Calcium (mg/l)} = (A \times \frac{B}{D}) \times 40100 \quad (2.2)$$

$$\text{Magnesium (mg/l)} = (C \times \frac{B}{E}) - (A \times \frac{B}{D}) \times 24300 \quad (2.3)$$

Where A is standard solution required to titrate calcium minus the blank correction determined, B is morality of EDTA standard solution, C is EDTA standard solution required to titrate calcium plus magnesium minus blank correction determined, while D and E are samples taken at different time intervals.

iv) **Sodium and Potassium:** 50 ml of the water was collected and deionized water is added to made up to 100ml. 2.5 ml of standard sodium solution was added to the water. Flame emission photometry was used to determine trace amount of sodium at wavelength of 589 nm. The water sample was sprayed into a gas flame and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters. Potassium followed the same procedure at the wavelength of 766.5 nm using 2.5 ml standard potassium solution.

III. RESULT

The values for the physico-chemical parameters of the water in the four sampling sources studied are presented in Table 1, and 2. Table 3, 4, 5, and 6.0 show the relationship between pH, total suspended solid (TSS), total dissolved solid (TDS) and total petroleum hydrocarbon (TPH) respectively and concentrations of ions in solution. Figures 1, 2, 3 and 4 are graphical representations of the correlation analysis between the physico-chemical parameters of test samples and the ions present in them.

Table 1.0: Results of the physico-chemical properties of the sampling sources

Sample	pH	TSS (PPM)	TDS (PPM)	TPH (PPM)	Total nitrogen (mg/l)
Source of pollution	6.02±0.20	3833.3±288.68	3500±500	221.05±65	793.30±345.30
100m away from Source	5.93±0.75	2000±0.00	2833.3±288.67	102.7±1282	490±280
200m away from Source	5.81±0.78	1500±0.00	2000±0.00	85.63±440	385±445.48
Control source	5.62±0.35	1000±0.00	1266.7±251.66	73.38±7.69	910±572.97
Grand mean	5.85±0.29	2083.33±144.34	2400±205.01	120.69±28.56	644.58±127.67

Table 2: Results of ions in the water samples studied

Sample	NH ₄ ⁺ (mg/l)	NO ₃ ⁻ (mg/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	K ⁺ (mg/l)	Na ⁺ (mg/l)	Zn ²⁺ (mg/l)	Cd (mg/l)	Pb (mg/l)
Source of pollution	10.7±6.90	7.0±6.10	11.4±7.60	2.8±1.40	2.4±0.70	5.4±3.6	0.9±0.12	-	-
100m away from Source	9.8±1.40	6.5±2.14	9.4±1.16	2.4±1.22	2.7±0.31	5.9±3.83	1.1±0.01	-	-
200m away from source	7.5±1.52	5.6±0.66	5.4±1.27	1.8±0.86	1.0±0.07	2.2±0.07	1.0±0.02	-	-
Control source	5.6±3.70	4.4±0.15	5.0±1.00	1.6±0.70	0.3±0.15	4.3±2.51	1.0±0.11	-	-
Grand mean	8.4±2.57	5.9±2.69	7.8±3.23	2.2±0.32	1.6±0.28	4.4±1.72	1.0±0.06	-	-

3.1 DISCUSSION

pH is a unit that states the strength of a solution based on its acidic or basic properties.^[1] In this study the pH of the test samples ranged from 5.81 to 6.02 showing that the water is acidic. The highest pH value was observed at the main source of pollution 6.02 and, this decreases with the sampling distance, having the lower value at 200m away from pollution site 5.81. Sample 4 which served as control was observed to be 5.62. Since

the largest variety of aquatic animals prefer 6.5 - 8.5, it thus mean that when the pH is outside this range, diversity within the water body may decrease due to physiological stresses and reduced reproduction. The pH of the water can be attributed to the presence of dissolved salts of some metals in the water. The range for pH of the water was below the range expected for unpolluted water 6.5 - 8.5, hence the water is polluted with regards to pH. ^[13, 14 15] The pH of the water correlates positively with all the ions in the test samples, with ammonium ion and sodium ion having the highest correlation coefficient (r) values of 0.9895 and 1.9744 respectively as shown in Table 3. It can be observed from the table 3 that sodium has greater influence on pH than the other ions in the studied samples. A graphical representation of the regression analysis as shown in figure 1 supports the results in table 3.

Table 3: Correlation coefficients of pH against ions

IONS	pH CORRELATION COEFFICIENT (r)	REGRESSION EQUATION
NH ₄ ⁺	0.9895	Y=-40+125X
NO ₃ ⁻	0.7469	Y=-2.25+7.58X
Ca ²⁺	0.9115	Y=-7.25+15.0X
Mg ²⁺	0.9474	Y=-2.5+9.75X
K ⁺	0.9744	Y=-7.75+9.78X
Na ⁺	1.6256	Y=1.25+3.5X

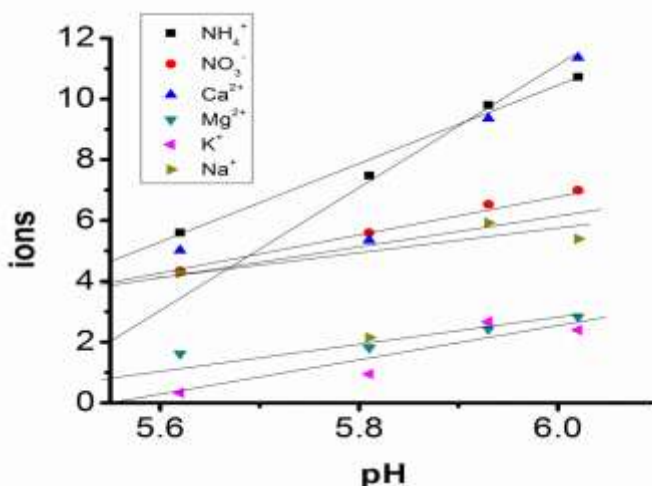


Figure 1: graphical relationship between pH and ions in the sample

Total suspended solid (TSS) expresses the suspended matter in the river. The results in table 1 revealed that TSS has highest value at the main source of pollution 3833.3ppm and decreases with the distance of sampling with the lowest at 200m away from pollution site 1500ppm. TSS is highest at source of pollution because of the nature of the soil. The control was observed to be within the range expected for potable water 1000ppm. ^[16] Observations from the TSS range, indicates the degree of pollution. High levels of solids decrease the passage of light through water, thereby slowing photosynthesis of aquatic plants, clogging fish gills and visibility in recreational waters. The measurement of total solids can be useful as an indicator of the effects of runoff from urban and agricultural areas. The observed range for the TSS of water was above the permissible limits of unpolluted water 1000ppm. ^[16] Observations from table 4 show that TSS has positive correlation with the ion in the test samples with Mg²⁺ and NH₄⁺ having the highest correlation coefficients of 0.9758 and 0.9106 respectively. From the results it can be deduced that the high TSS values of the sample are mostly affected by magnesium ion. Observations from the graphical representation of the correlation in figure 2 affirms this fact

Table 4: Correlation coefficients of TSS against ions

IONS	TSS CORRELATION COEFFICIENT (r)	REGRESSION EQUATION
NH ₄ ⁺	0.91056	Y=0.00+5.8x10 ³ X
NO ₃ ⁻	0.8489	Y=15+27x10 ³ X
Ca ²⁺	0.9526	Y=1.75+2.2x10 ³ X
Mg ²⁺	0.9758	Y=1.25+6.82x10 ⁴ X
K ⁺	0.8062	Y=0.25+6.94x10 ⁴ X
Na ⁺	0.5146	Y=1.0+5.0x10 ⁴ X

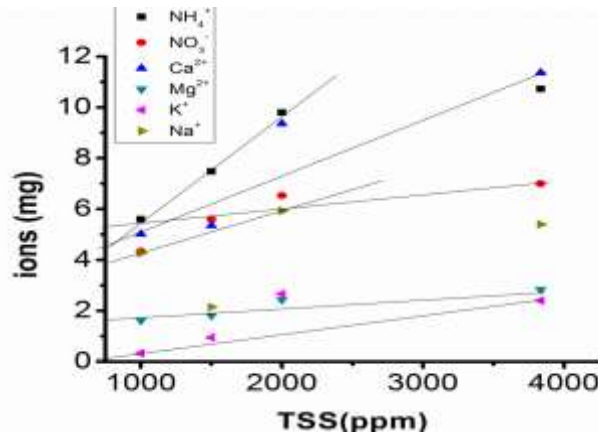


Figure 2 graphical relationships between TSS and ions in test samples

Total dissolved solid expresses the salinity of the water. The results in table 1 show that TDS was highest at the main source of pollution 3500ppm and decreases with the distance of sampling with the lowest at 200m away from pollution site 2000ppm. Control was observed to be 1266.7ppm which is above the acceptable limits, this indicates that the river flow at a low rate and the dissolved solids accumulate on the control. This could also depends on the nature of the soil or because the sampling was done during the rainy season. Samples taken from source of pollution, 100m away, and control are moderately saline and sample from 200m away from pollution source is slightly saline.

Drinking water with high dissolved solids (dissolved minerals, salts and humic acid) may not taste good and may have a laxative effect. High TDS indicate hardness and cause staining. The high level of TDS is caused by certain metals present, particularly Magnesium, Potassium, Copper and Zinc. Water with a TDS < 1200mg/l generally has an acceptable taste. For water to be treated for domestic potable supply, a TDS < 650mg/l is preferred.^[17] The observed range for TDS was above the permissible limits of unpolluted water 25.0ppm.^[18]

The total dissolved solids of the water were found to correlate positively with all ions in solution, with magnesium and ammonium having the highest correlation coefficient (r) values of 0.9834 and 0.9924 respectively. Ammonium has the greatest influence on the TDS than other ions as shown in Table 5, and graphically represented in figure 3

Table 5: Correlation coefficients between TDS and ion

IONS	TDS CORRELATION COEFFICIENT (r)	REGRESSION EQUATION
NH4+	0.9924	$Y = 325 + 2.22 \times 10^{-3} X$
NO3-	0.8024	$Y = 25 + 1.3 \times 10^{-3} X$
Ca2+	0.9594	$Y = -15 + 3.61 \times 10^{-3} X$
Mg2+	0.9834	$Y = -0.5 + 1.36 \times 10^{-3} X$
K+	0.9774	$Y = -10 + 9.75 \times 10^{-4} X$
Na+	0.5660	$Y = 3.75 + 6.25 \times 10^{-4} X$

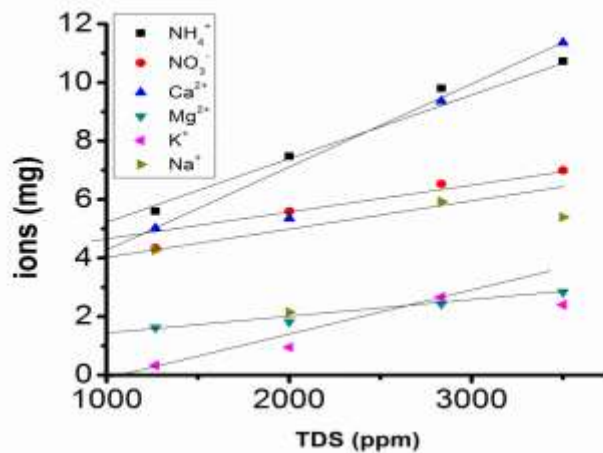
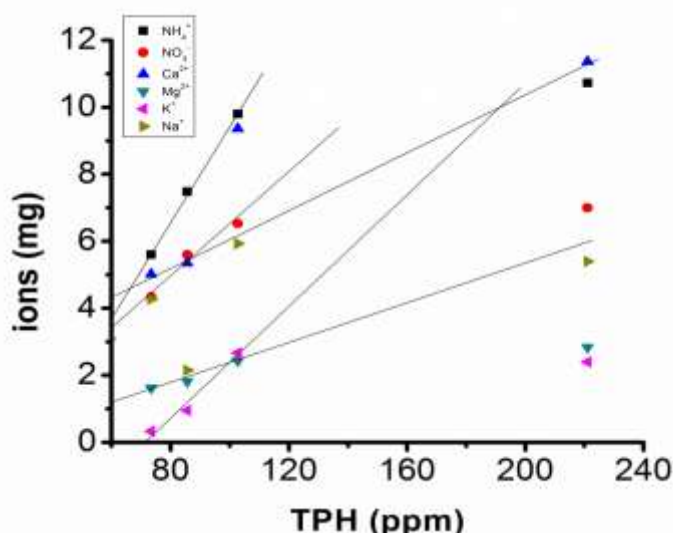


Figure 3: Graphical relationships between TDS and ions in the test samples

The results in table 1 revealed that the total petroleum hydrocarbon (TPH) has the highest value at the main source of pollution 221.05ppm and decreases with the sampling distance, the lowest shown at 200m away from pollution site 85.63ppm. Control was observed to contain high TPH 73.38ppm. The high level of TPH in water means that the spillage was massive and also due to environmental hazards such as erosion. Oil destroys much of the aquatic life of oceans, including the food of fishes and shellfish. The observed range was above the permissible limits for unpolluted water 0.05ppm. [18] Observations from table 6 show positive correlation values of TPH with ion in the test solutions, and a study of figure 4 confirms the positive correlation coefficients observed in table 6.

Table 6: Correlation coefficients of TPH against ions

IONS	TPH CORRELATION COEFFICIENT (r)	REGRESSION EQUATION
NH ₄ ⁺	0.7998	Y = 4.25 + 1.04 x 10 ⁻¹ X
NO ₃ ⁻	0.9219	Y = -3.75 + 8.10 x 10 ⁻² X
Ca ²⁺	0.8743	Y = 1.25 + 4.10 x 10 ⁻² X
Mg ²⁺	0.8928	Y = 2.25 + 3.90 x 10 ⁻² X
K ⁺	0.6689	Y = -3.25 + 3.9 x 10 ⁻² X
Na ⁺	0.4674	Y = 3.25 + 8.42 x 10 ⁻³ X



3.2 IONS IN THE WATER

The observed mean concentration of ammonium ion (8.40mg/l) in the water was above maximum admissible concentration of 0.5mg/l. [18]. The control was observed to be 5.60mg/l. It is assumed that nitrogen containing waste might have been introduced into the river by anthropogenic activities. The high level can also be due to the crude oil spillage. Dara (1993) stated that domestic waste is capable of increasing the concentration of ammonium in water in that during their decay, ammonia is liberated. [19]. The observed concentration of ammonium in control was above the permissible limits expected for unpolluted water. This observation shows that the water is polluted with regards to ammonia.

The mean concentration of nitrate in the water (5.87mg/l) was less than the maximum permissible limit 10.0mg/l. [18]. Control (4.35mg/l) was observed to be less than acceptable limit. The water is deficient as regards to nitrate. According to FEPA (1991), excessive concentration of magnesium in water will lead to a change in taste of the water and could even cause gastrointestinal irritation and scale formation. The positive correlation between pH (r = 0.9474) and TDS (r = 0.9834) confirms that magnesium is mostly found in water (especially hard water) in form of MgSO₄. The control was observed to be 1.621mg/l. Magnesium in water is an indication of hardness of water. [20] Magnesium is often associated with calcium in all kinds of water. Magnesium is essential for chlorophyll growth and acts as a limiting factor for the growth of phytoplankton. Therefore, depletion of magnesium reduces the number of phytoplankton's population. [21]. The quantities of Calcium in natural water depend upon the type of rocks. Small concentration of calcium is beneficial in reducing the corrosion in water pipes. Magnesium hardness particularly associated with sulphate ion has laxative effect on persons unaccustomed to it. In the present study, Calcium and Magnesium contents are within the recommended standards. [22]

The heavy metals as reflected on table 2.0 shows the mean concentration of zinc 0.98mg/l. The observed concentration of Zn was below the permissible limits of 5.0mg/l. [16]. Hence, the river is not polluted with respect to zinc.

Ademoroti (1993), states that although zinc is essential to life, an excess amount of it could lead to system dysfunction which may result in impairment of growth and reproduction. [23]

Cadmium and Lead has been documented to be one of the most toxic heavy metals in an aquatic environment. [19]. The permissible limits for the concentration of lead and cadmium in potable water are 0.01mg/l and 0.05mg/l respectively. However, Cadmium and Lead were not detected from the sampling sources. Hence, the river is not polluted with respect to Cadmium and Lead.

IV. CONCLUSION

From the results of the study it can be concluded that Obunkun River in Oyigbo local government of Rivers state Nigeria is polluted as regards to pH values, total suspended solids, total dissolved solids, and total petroleum hydrocarbons. The pollution is as a result of oil spillage, and the ion in solution (NO_3^- , NH_4^+ , Ca^{2+} , K^+ , Na^+ and Mg^{2+}) decreased with distance from the source of pollution. Regression analysis carried out between the physico-chemical parameter of the river water like pH, total suspended solid, total dissolved solid and total petroleum hydrocarbons respectively, and ions in the water showed positive relationship between the physico-chemical parameters and the ions. Nevertheless the results of the study showed no trace of heavy metal and as such the water is not polluted in aspect of toxic metals.

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