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# EVALUATION OF TOTAL PETROLEUM HYDROCARBON CONTENT IN CRUDE OIL EXPLORATION FIELD

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*Abstract*

***This study examined Total Petroleum Hydrocarbon contamination in Ologbo oil field in Edo state with a view to mitigate soil pollution due to incessant crude oil spill in the location. The entire study area of 1km$^2$ was divided into six (6) zones (including control region). A total of 35 soil samples (including samples from control points) were recovered from a georeferenced area of 1 km$^2$ using calibrated hand auger at depth ranging from 0-15 cm (topsoil), 15-30 cm (mid depth) and 30-60 cm (last depth). Subsurface depth of 15cm was exceeded so as to recover samples at greater depth in order to examine the maximum vertical depth of TPH contaminants in accordance with USEPA New test Methods 8015C (2003). Solvent extraction processes were used to remove moisture and other undesired substances from the soil samples before being analyzed using Gas Chromatogram (GC-FID). The result showed that TPH concentration at the subsurface ranged from 96.88±3.74 to 870.01 ±102.43 mg/kg, mid depth concentration was between 46.92±7.13 to 404.03±7.10 mg/kg while the last depth ranged from 10.74±6.62 to 106.52±23.04 mg/kg. These results indicated elevated TPH values when compare with the control points which ranged between 1.43±0.05 to 14.84±9.63 mg/kg (these values are well within the range of unpolluted sediments as prescribed by United States Environmental Protection Agency, USEPA. The results also indicated that TPH pollution was more severe at the subsurface but reduces as the depth of investigation increases. The accumulator factor in the study area was in the sequence: zone four>zone one>zone three>zone two>zone five>control. The statistical computations of TPH concentration levels in the control zones were compared against TPH concentrations at various depths in the other zones. The results showed statistically significant difference at 95% confidence level which is an indication of contamination in the site. The study concluded that there is the urgent need to carry out remediation programme at the site especially in zones four, one and three.***

***Keywords***: Pollution, Soil, Treatment, Total Petroleum Hydrocarbon (TPH), Bioremediation,

## 1.0 INTRODUCTION

Crude oil exploitation which includes drilling, refining, transportation and consumption is one of the major drivers of the Nigeria economy since it was commercially explored in the Niger Delta Region in the 19$^{th}$ century [1]. Apart from being the main source of national earning, it also accounts for over 65% of energy consumption in the country while the balance 35% is complimented by hydropower plants, coal and other energy biomass. With the increase in patronage of internal combustion engines as well as the constant demand of refined fuel in the transportation and manufacturing industries; the demand, supply, transportation and stockpiling of crude oil and its refined products have increased correspondingly [2]. The increased consumption of refined crude products has lots of implications for both the operations of the industry and the host communities which include human safety, animals, plants and the natural environment. These threats posed by crude oil pollution basically emanate from leakages or rupture of petroleum exploration, extraction refining and storage facilities.

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Recent cases of crude oil spill in the oil rich Niger Delta is not only as a result of facility rupture but from sabotage (vandalism i.e. indigenes stealing products from pipe network so as to claim compensation and cleaning up contracts) [3]. Other causative factors responsible for crude oil spill into the environment are: corrosion of pipes, aged facilities, over-flow of pipes, tankers, barges, and vessel for washing oil facilities. Incidences of spill sometimes transcends into neighboring states which are prone to the oil discharge within the network of pipes that runs across the area.

Hydrocarbons consist entirely of Hydrogen and carbon atoms which belong to the family of organic compounds. The release of hydrocarbon into the soil has negative impact on the environment such as toxicity to biological processes, reduction in bacterial biomass, imbalance in ecosystem, prevention of complete organic matters mineralization, distortion of physiochemical properties of soil, hardening of the soil structure hence preventing optimal productivity as well as loss of arable land for subsistence agriculture [4].

Before any remediation or monitoring operation in hydrocarbon spill site is considered, a post spill analysis of the soil is essential. Gas Chromatography (GC) has over time proven to be very efficient and unique in analytical capability which is also used for separating, identifying and quantification of compounds in gaseous state [5]. Previous researchers [6, 7, 8] had in time past and different locations used Inductively Coupled Plasma with Mass Spectrometry (ICP-MS) and GC-MS in quantitative assessment of soil contaminated with organic pollutant and also showed reliable results in the analysis of volatile compounds in soil samples. Gas Chromatography with Flame Ionization Detector (GC-FID) has several advantages over GC-PID and ICP-MS; hence it was deployed in the analysis of samples for this study.

The aim of this study is to ascertain the concentration levels of Total Petroleum Hydrocarbon (TPH) in Ologbo oil field in Benin City, Nigeria. This will be useful in providing baseline information (data) of the oil field and will also be resourceful in remediation measures or early warning signal by relevant environmental agencies with the aim of restoring the soil back to its useful economic state.

## 2.0 Materials and Methods

### Site Location

The Project site is located in Ologbo, Ikpoba Okha local government area of Edo state which lies between longitude 05° 38' 36.47"E to 05°4' 26.56" E and latitude 06° 4' 28.17"N to 06° 4' 33.79"Nwhich is 32 km south-west of Benin City. The location of the project is almost 18km from NPDC link road which is off Benin-Sapele Road. Within this location, soil and sometimes water are contaminated almost regular from pipes transporting products to the flow station. The sampling points in the project location are presented in figure 1.

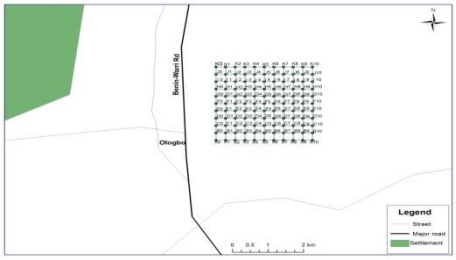


Fig. 1: Grid Lines Showing Sample Location

## 3.0 Sample Recovery

To evaluate the baseline concentration level of Total Petroleum Hydrocarbon (TPH) content available in the soil, systematic soil sampling was carried out in the field. The coordinate of the sampling positions was determined and registered with the aid of handheld global positioning system GPS) receiver (Garmin GPS 72). A reference area of 1km by 1km was gridded at 200m interval and divided into five zones where soil samples was collected from the grid intersection points with the aid of depth calibrated augers at depth of 0-15cm, 15-30cm and 30-60cm respectively. Subsurface depth of 15cm was exceeded so as to recover samples at greater depth in order to examine the maximum vertical depth of TPH contaminants in accordance with USEPA New test Methods 8015C (2003). Two additional samples were obtained as control samples within the uncontaminated region. The TPH values of these samples were compared with the contaminated samples so as to determine the extent of hydrocarbon contamination in the contaminated site. The auger used for sample recovering was washed with

water and methanol after every sampling. Recovered samples was placed in plastic bags and tightly sealed, and transported to the laboratory where the soil was characterized and analyzed. The results from the laboratory were compared with WHO standard for crude oil limit in soils.

### 3.1 Treatment of Soil Samples

This involves sample preservation, sample extraction and clean-up in order to obtain reliable values for analysis. Samples were placed in plastic bags and put into a glass jar with seal. Each sample was labeled differently and stored in a refrigerator at $4^{o}$C. Sample extraction was carried out using extraction procedure detailed in USEPA method 3540 and ASTM method D5369 with little adjustments on flask size, choice of solvent, volume of solvent and extraction time. Before extraction, samples were homogenized using mortar and pestle to obtain finer texture and to also remove pebbles and stones.

Hydrocarbons in the soil samples were then determined using Agilent 6890 Gas Chromatograph (GC-FID) fitted with a split injection auto sampler. Samples were injected and separated on a HP-5MS or DB-5MS column which is 0.25mm in diameter that is approximately 30 m long with a 0.25 μm film thickness while placed in a 2 mL chromatographic vial. Carrier gas was Nitrogen with a makeup flow of 25 mL/min while temperature throughout the chromatographic operation was $80^{0}$C for 3minutes, $20^{0}$C/minute until $280^{0}$C was obtained and hold for 20minutes and the detector flame was set at $300^{0}$C.

**3.2 Statistical Computation**: Arithmetic mean was used in determining the mean value of TPH in each zone and the values obtained were also compared with that of the control zone so as to ascertain if there is any significance difference in the contaminated zone and the control zone.

$$\text{Mean } (\bar{x}) = \frac{x_1 + x_2 + x_3 + - - - x_n}{n} \quad (1)$$

Where: $\bar{x}$ is mean, $x_1$, $x_2$, $x_3$ *and* $x_n$ are individual TPH values within a zone while $n$ is the total number of samples recovered in each zone.

$$|t| = \frac{\overline{x_1 - x_2}}{\sqrt{(\frac{1}{N_1} + \frac{1}{N_2})}} \quad (2)$$

Where /*t*/ is students' t-test, $x_1$ is mean TPH values in contaminated zone, $x_2$ is mean TPH values in control zone, $N_1$ is total number of samples in contaminated zone while $N_2$ is total number of samples in control zone.

The difference between the mean obtained in the contaminated zone and the control zone was computed using students' t-test as expressed in equation 2.

### 4.0 Results and Discussion

The summary of distribution of Total Petroleum Hydrocarbon (TPH) from each sampling depth in the study area is presented in Table 1. The mean TPH concentration levels range from 10.74± 6.62 to 870.01 ±102.43 mg/kg (Table1). TPH concentration at depth 0-15 cm ranges from 96.88±3.74to 870.01 ±102.43 mg/kg. Depth 15-30 cm had concentrations ranging from 46.92±7.13 to 404.03±7.10 mg/kg while the last depth (30-60 cm) hand concentration values ranging from 10.74±6.62 to 106.52±23.04 mg/kg. TPH concentration values recorded at the control points ranged between 1.43±0.05 to 14.84±9.63 mg/kg. These values are well within the range of unpolluted sediments (1.0-20.0 mg/kg) which was reported in [9, 10]. High TPH pollution levels were recorded at the subsurface depth (0-15 cm) in all the zones with zone four recording the highest pollution. These concentration values are little above the range reported in [11, 12, 13] for some oil exploration sites in the Niger Delta.

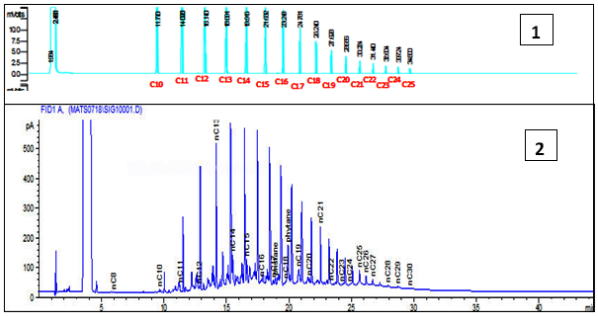


Fig 2: Sample (chromatogram 2) was compared with the reference standard (chromatograms 1) for confirmation of eluted peaks in sample.

The eluted peak of chromatogram 2 in figure 2 when compare with laboratory standard (chromatogram 1), shows that there is high presence of TPH in the sample.

**Table 1: Summary of Total Petroleum Hydrocarbon Content in the Study Area**

| zone | Location | | Number of samples | Mean Hydrocarbon Content (mg/kg) | | | Range |
|---|---|---|---|---|---|---|---|
| | Northings | Eastings | | 0-15cm | 15-30cm | 30- 60cm | 0 – 60cm |
| Zone one | $06^0$ 3' 39.06''N<br>$06^0$ 3'39.076''N<br>$06^0$ 4' 14.661''N<br>$06^0$ 4' 14.676''N | $05^0$ 39' 59.843''E<br>$05^0$ 40' 06.947''E<br>$05^0$ 39' 59.846''E<br>$05^0$ 40' 6.941''E | 5 | 510.52± 134.28 | 281.75 ± 8.47 | 59.24 ± 9.53 | 47.83 – 872.04 |
| Zone two | $06^0$ 3'39.076''N<br>$06^0$ 3'39.073''N<br>$06^0$ 4' 14.676''N<br>$06^0$ 4' 14.650''N | $05^0$ 40' 06.947''E<br>$05^0$ 40'14.056''E<br>$05^0$ 40' 6.941''E<br>$05^0$ 40'14.116''E | 5 | 112.37± 6.14 | 59.24 ± 9.53 | 26.84± 8.72 | 16.77 – 372.93 |
| Zone three | $06^0$ 3'39.073''N<br>$06^0$ 3' 39.058''N<br>$06^0$ 4' 14.650''N<br>$06^0$ 4' 14.65''N | $05^0$ 40'14.056''E<br>$05^0$ 40' 21.154''E<br>$05^0$ 40' 14.116''E<br>$05^0$ 40' 21.198''E | 5 | 225.65± 13.89 | 105.04± 10.21 | 62.04± 9.33 | 41.83 -455.61 |
| Zone four | $06^0$ 3' 39.058''N<br>$06^0$ 3' 39.058''N<br>$06^0$ 4' 14.65''N<br>$06^0$ 4' 14.659''N | $05^0$ 40' 21.154''E<br>$05^0$ 40' 28.252''E<br>$05^0$ 40'21.198''E<br>$05^0$ 40'28.25''E | 5 | 870.01 ±102.43 | 404.03± 7.10 | 106.52± 23.04 | 84.38 - 1017.45 |
| Zone five | $06^0$ 3' 39.058''N<br>$06^0$ 3' 39.067''N<br>$06^0$ 4' 14.659''N<br>$06^0$ 4' 14.656''N | $05^0$ 40' 28.252''E<br>$05^0$ 40' 35.363''E<br>$05^0$ 40' 28.25''E<br>$05^0$ 40' 35.369''E | 5 | 96.88± 3.74 | 46.92± 7.13 | 10.74± 6.62 | 03.36 - 273.11 |
| Control 1 | $06^0$ 4' 0.456''N<br>$06^0$ 4' 0.439''N<br>$06^0$ 3' 56.875''N<br>$06^0$ 3' 56.892''N | $05^0$ 40' 17.605''E<br>$05^0$ 40' 24.715''E<br>$05^0$ 40' 17.643''E<br>$05^0$ 40' 24.698''E | 5 | 05.26± 3.86 | 3.81± 1.07 | 1.43±0.05 | 0.0 – 8.73 |
| Control 2 | $06^0$ 4' 11.104''N<br>$06^0$ 4' 11.078''N<br>$06^0$ 4' 14.676''N<br>$06^0$ 4' 14.702''N | $05^0$ 40' 3.40''E<br>$05^0$ 40' 10.518''E<br>$05^0$ 40' 3.42''E<br>$05^0$ 40' 10.513''E | 5 | 14.84± 9.63 | 8.27± 6.14 | 2.03±0.04 | 0.0 -17.32 |

Lower TPH concentration values were recorded at the last depth (30-60 cm) with zone four value of 106.52±23.04 being the only exception. Zone four had the highest TPH concentration recorded (870.01 ±102.43 mg/kg at depth 0-15 cm) while zone five has the least TPH concentration (10.74±6.62 at depth 30-60 cm). The TPH concentration levels recorded in the site are comparable to those obtained in [9, 11, 12] which exceeded the baseline limits of 50 mg/kg or ppm as a result of crude oil mining, processing and transportation. However, TPH concentration in the location decreases with depth as reported in [14].

**Table 2: Accumulation Factor and t-test of TPH levels in different zones relative to control points**

| Zone | Accumulation Factor | | | t-calculated | | | t-tabulated$_{0.05, (2)\ d.f\ =8)}$ |
|---|---|---|---|---|---|---|---|
| | 0-15cm | 15-30cm | 30-60cm | 0-15cm | 15-30cm | 30-60cm | 0-60cm |
| Zone one | 34.50 | 34.07 | 29.18 | 8.682 | 3.862 | 1.307 | 2.306 |
| Zone two | 7.57 | 7.16 | 13.22 | 1.940 | 1.108 | 0.152 | 2.306 |
| Zone three | 15.21 | 12.70 | 30.56 | 3.473 | 1.063 | 1.506 | 2.306 |
| Zone four | 58.63 | 48.86 | 52.47 | 12.312 | 5.271 | 2.374 | 2.306 |
| Zone five | 6.53 | 5.67 | 5.29 | 2.014 | 0.249 | 0.081 | 2.306 |

*Control Point 2 values were used in Accumulation factor computation since it has higher values.*

The accumulation factor (contamination level in a particular zone relative to the control) presented in Table 2, was calculated using equations 1 and 2; the result indicates that the rate of contamination is in the sequence: zone four>zone one>zone three>zone two>zone five>control. The various depths of investigation in zone four shows severe pollution when compare with other zones. Table 2 also shows the statistical computations of TPH concentration levels in the control zones which were compared against TPH concentrations at various depths in the other zones. The results showed statistically significant difference at 95% confidence level which is an indication of contamination in the site. In zone four locations, as in the case of most contaminated site, the severity of the incessant spill within that region has affected plants and other smaller organisms within the region. The leakage is as a result of undetected vandalized pipe which needs repairs but have not been given required attention.

## 5.0 Conclusion

With the high concentration of Total Petroleum Hydrocarbon in the site, there is the urgent need to commence a remediation programme (preferably bioremediation) using microorganisms and plants (phytoremediation). This information can then be used by relevant ministries and agencies to provide medium and long term solutions to oil contamination challenges.

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