

Characteristic Level of Total Petroleum Hydrocarbon in Soil and Groundwater of Oil Impacted Area in the Niger Delta Region, Nigeria.

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Abstract

Total petroleum hydrocarbon (TPH) is of environmental interest because they are toxic to human system and animals. Some of the TPH compounds are carcinogenic and poses health hazards. The communities in Niger Delta region of Nigeria where crude oil is being exploited are predominantly agricultural farmers and fishermen. The harvested crops and fishes obtained from these communities are usually contaminated with TPH. In view of health implication of crops and fishes contaminated with TPH this study was carried out to ascertain the level of total petroleum hydrocarbon in soil and groundwater of crude oil impacted area of five communities in Niger Delta region of Nigeria. The analysis were carried out with Gas Chromatography – Flame Ionization Detector (GC-FID) instrument. The result of the analysis indicates that soil samples obtained from Station I at various depths 0 - 0.5, 0.5 – 1.00 and 2.0 – 3.00 were contaminated with mean TPH concentrations 5199.52, 2341.00 and 2066.83 mg/kg, respectively. Station III recorded mean TPH concentrations 1678.25, 1366.00 and 1242.33 mg/kg at depths 1.00 – 2.00, 2.00 – 3.00 and 3.00 – 4.00, respectively. The result of the analysis indicates mean TPH 1341.00 mg/kg at topsoil of Station V. This study shows that water samples obtained from all the stations were contaminated with TPH. At depth 0 – 0.5m the mean TPH concentrations at Stations I, II, III, IV and V of water sample were 8186.67, 12110.00, 1351.67, 4137.00 and 9020.67 µg/L, respectively.

Key words: Soil and water sample contamination, total petroleum hydrocarbon, associated health hazards.

1.Introduction

Soil and groundwater are usually contaminated during crude oil production, especially in Niger Delta regions of Nigeria. The contamination of soil and groundwater occur through oil spillage and pipeline vandalization which affect aquatic plants and animals. Some compounds of crude oil are carcinogenic and cultivated plant in the soil will absorb it and this is transferred to man through food chain. Total petroleum hydrocarbon (TPH) is a mixture of hydrocarbons found in crude oil. Some of the chemicals found in TPH are hexane, benzene toluene, xylene, naphthalene etc (ATSDR, 1999). It has been reported that petroleum products from crude oil contaminate the environment during production and this poses health hazards (Gustafson, 2007).

TPH may enter the environment through accidents, from industrial releases or as by – products from commercial or private uses. Also TPH may be released directly into river and water bodies through oil spillage, leakages or vandalization of oil pipe lines. Some of the TPH fractions may float on the water and form surface films and other TPH fractions will sink to the bottom sediments. However, bacteria and microorganisms in the water may break down some of the TPH fractions.

Iturbe et al (2004) reported soil contamination of coastal Mexican refinery by hydrocarbons. They reported that main source of contamination of soil is from pipe lines, and old storage tanks besides the land disposal of untreated hydrocarbon sediments derived from the cleaning of storage tanks. Cortes et al (2012) reported determination of TPH in water and soil /sediment samples in Colombian oil Exploration and Production industry. Crude oil spillage contamination of soil samples from Ikot Ada Udo, Ikot Abasi in Akwa Ibom State of Niger Delta region of Nigeria were investigated (Okop and Ekpo, 2012). The investigation of level of TPH contamination of soil were carried out after three months of extensive oil spillage. The high level of TPH contamination of soil samples were reported after oil spillage.

Miguel and Salvador (1998); Akinlua and Ajayi (2008) have reported characterization of organic pollutants in contaminated soils. Okop et al (2012) reported crude oil spillage contamination of soil after 38 days of extensive oil spillage in South-South Niger Delta of Nigeria. They reported that TPH concentration levels varied from topsoil to subsoil. Crude oil spillage from pipe lines, leakages from storage (surface and underground) tanks, and similar discharges associated with petroleum products have been reported by Bosco et al (2005) and Abrahams (2002). Li et al (2012) reported TPH contamination of agricultural soils near a petrochemical complex. Their investigation revealed high level of TPH in top soils.

The economy of Nigeria is largely dependent on crude oil tapped from the Niger Delta region. The presence of these liquid hydrocarbon contaminants in the environment will adversely affect the plants, animals and human beings that feed on them. In view of harmful effect of TPH in soil and groundwater, the oil spill should be treated to prevent harm to the environment. Some of the remediation techniques is the decontamination of soil

containing TPH using surfactant (Torres et al 2003; Iturbe et al, 2004). Onwuka et al (2012) have reported the remediation of soil contaminated with crude oil using plant known as Bermuda grass. Bioremediation of the oil sludge have been reported to be an efficient and economic alternative for remediation of soil contaminated with TPH (Jackson et al, 1996; Venosa et al, 1996, Yudono et al, 2009). Indigenous microorganisms can utilize the total petroleum hydrocarbons of crude oil as source of carbon and energy and H₂O. But bioremediation takes a long time as the degradation efficiency of the bacteria is considerably low under natural conditions (Del' Arco and de France, 1999; Chaineau et al; 2003).

2.0 Materials and Method

2.1 Site Selection

Soil and groundwater samples were collected from five communities in Rivers state of Nigeria as shown in Fig. 1. Rivers State is one of the Niger Delta states of Nigeria where crude oil is being produced. The communities where soil and groundwater samples were collected are Baranyonwa Dere /Gio (N: 04° 43' 18.7 E: 007° 16' 27.6) (Station I), Bera (N: 04° 41' 007 E: 007° 16' 38.4) (Station II), Sibari – Gbe (N:04° 38' 27.1 E: 007° 17' 37.2) (Station III), Wileborsi Kpean (N: 04° 43' 18.6 E: 007° 24') (Station IV) and Kwawa (N: 04° 43' 18.7 E: 007° 16') (Station V)

2.2 Collection of Soil Sample

Soil samples were collected with auger at various depths in the range 0-0.5m, 0.5-1.0m, 1.0 – 2.0m, 2.0 – 3.0m, 3.0 – 4.0m and 4.0 – 5.0m. After collection the soil sample was homogenized in clean plastic container that was previously washed. The homogenized portion of soil sample was taken into a clean amber bottle and stored in ice – chest until use.

2.3 Collection of Groundwater Sample

Groundwater samples were collected from different boreholes at various depths ranging from 0-0.5m, 0.5 – 1.0m, 1.0 – 2.0m, 2.0 – 3.0m, 3.0 – 4.0m and 4.0 – 5.0m. The groundwater samples were collected into a previously washed 500ml bottles and stored in ice-chest until use.

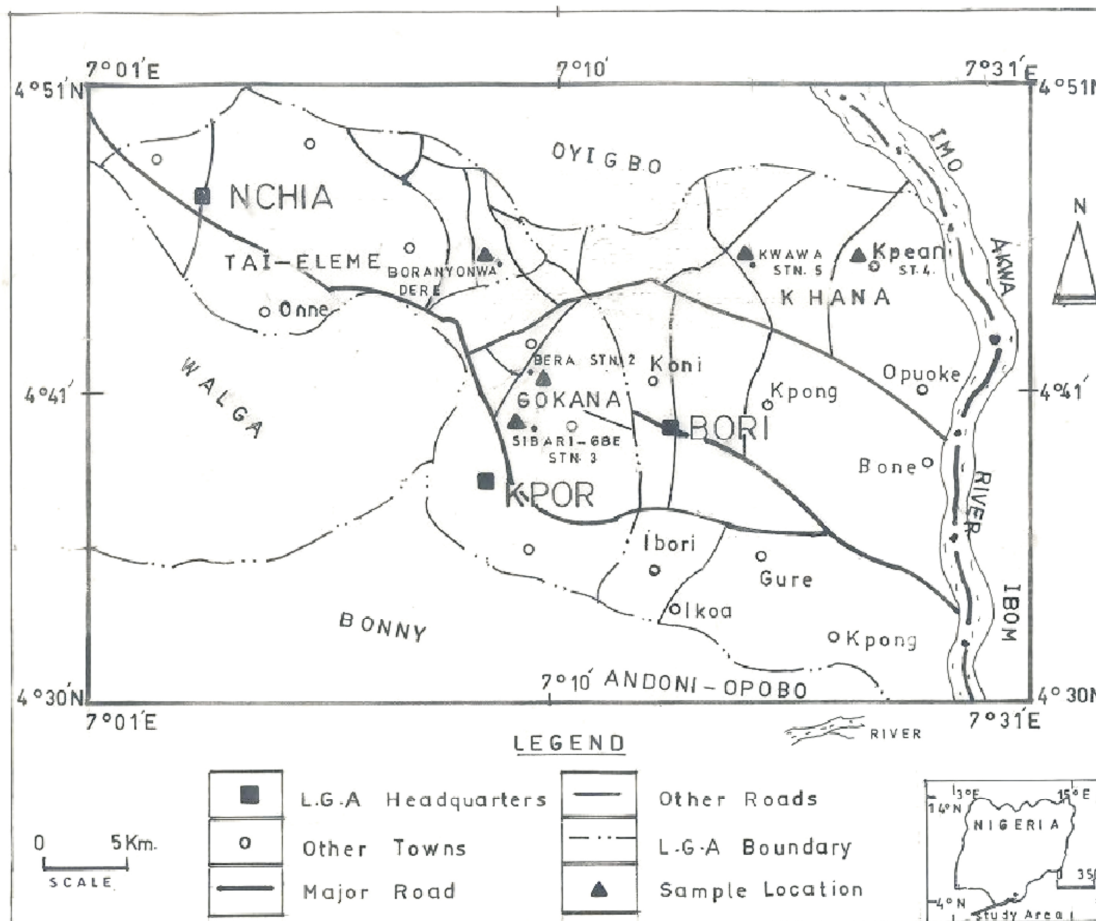


Fig : Location map of the study area

Fig: 1 Map of Study area

2.4 Soil Sample Extraction

The extraction of soil sample was carried out by weighing 10g of soil sample in an analytical weighing balance. The weighed soil sample was transferred into amber bottle with spatula. Then 5g of anhydrous sodium sulphate (Na_2SO_4) was added into the amber glass bottle containing the soil sample. After the addition of Na_2SO_4 the soil sample was stirred for proper mixing. The addition of Na_2SO_4 was to remove moisture from soil sample. 300 $\mu\text{g/ml}$ of 1-chlorooctadecane (surrogate) standard was added to soil sample after mixing and 30ml of dichloromethane (DCM) was also added to soil sample as extracting solvent.

After the addition of DCM into the amber bottle containing the soil sample. The amber bottle was corked very tight and transferred to mechanical shaker. The mechanical shaker was agitated between 5-6 hrs at room temperature. The sample was allowed to settle for 1hr after agitation and then filtered through 110mm filter paper into a clean beaker previously washed. Then the filtrate of the sample in beaker was allowed to concentrate to 1ml by evaporation at room temperature in a fume cupboard (LAWI,2011).

2.5 Water Sample Extraction

500ml of water samples were collected from different boreholes with water container. After collection of water sample it was transferred into 1000ml separating flask. 30 $\mu\text{g/ml}$ of 1-chlorooctadecane in 1ml of DCM was added into the flask containing water sample. Then 20ml of DCM was added into the flask. After addition of DCM into separating flask it was shaken and pressure released at interval. The shaking and releasing of pressure was done severally. Then the water sample was allowed to stand for few minutes. Two layers were formed in the separating flask. The lower layer (extract) was filtered through 110m filter paper into a beaker. The filtrate was concentrated to 1ml by allowing it to evaporate at room temperature in a fume cupboard (LAWI,2011).

2.6 Sample Clean – up

Preparation of column was performed by introducing a glass - wool into a previously washed chromatographic column. Silica gel was weighed and introduced into a beaker. Then dichloromethane was added to make it slurry. The slurry was then introduced into a chromatographic column. Anhydrous Na_2SO_4 was added into the column followed by addition of pentane. The concentrated sample was mixed with cyclohexane in a beaker and introduced into a prepared column. The sample was eluted with pentane and eluted sample collected in a beaker below the column. Further elution of the sample was carried out by introduction of more pentane. The column was rinsed with dichloromethane after elution. The eluted sample was allowed to stand in a fume cupboard at room temperature for evaporation to take place (LAWI, 2011).

2.7 Sample Separation and Detection

The detection of TPH in soil and water samples at different stations of study area were carried out using Agilent 6890N Gas Chromatography - Flame Ionization Detector (GC – FID) (Cortes, 2012). 3 μl of concentrated sample was injected into GC vial. The blank dichloromethane was injected into micro – syringe of GC for cleaning of syringe. The cleaning of syringe was done 3 times before sample analysis. The micro – syringe was later rinsed with the sample. Then the sample was injected into the GC column with micro – syringe for separation of different compounds of the sample. After separation, the FID detects various compounds in the sample. The amount of TPH resolved at a particular chromatogram was measured in mg/kg for soil sample and $\mu\text{g/L}$ for water sample.

3.0 Results and Discussion

The results of the analysis as shown in Table 1 illustrates the level of TPH at various depths of contaminated soil samples. At Station I the mean TPH concentration decreases as depth increases at 0-0.5, 0.5 – 1.0 and 1.0 – 2.0m, of mean TPH concentrations 5199.52, 2341.00 and 1116.96mg/kg, respectively. At depth 2.0 – 3.0m the mean TPH concentration increases to 2066.83mg/kg and then decreases as depth increases. The soil samples obtained at Station II shows a different pattern of accumulation of TPH in soil. The highest TPH concentration was recorded at depth 4.0 – 5.0m of mean TPH value 353.42mg/kg. Other TPH values recorded at various depths at Station II were fluctuating. Okop and Ekpo (2012) reported that total petroleum hydrocarbon varied from 9-289mg/kg for topsoil and 8-318mg/kg for subsoil in soil samples obtained from Ikot Ada, Akwa Ibom State, Niger Delta region of Nigeria. The high level of total petroleum hydrocarbon contamination recorded in this study are comparable to TPH contamination of soil samples obtained by (Chukwujindu et al, 2008; Onianwa, 1995). The TPH values obtained in this study exceeded 50mg/kg recommended by Department of Petroleum Resources (DPR). The TPH concentration between 100 to 500mg/kg have been reported by (Adeniyi and Afolabi, 2002; Li et al, 2005). The result presented in Table 1 Station III shows that mean TPH concentration of topsoil was 222.09mg/kg, however, the mean TPH value decreases at depth 0.5-1.0m of concentration 142.09mg/kg. At depth 1.0-2.0m the mean TPH concentration of soil samples decreases from 1678.25 to 710.67mg/kg as depth increases. Okop et al (2012) working on soil samples contaminated with petroleum spillage reported total petroleum hydrocarbon variation of 289mg/kg for topsoil, 417mg/kg for subsoil and 178mg/kg for greatest depth measured. Ibezue (2013) working on oil spillage of soil samples in Gokana area of Niger Delta region in Rivers State of Nigeria recorded high concentrations of total petroleum hydrocarbon in soil samples. The soil samples recorded have high mean TPH concentrations 13949.42 and 8279.35mg/kg for

Biara soil and Bodo soil in Gokana area, respectively. These values were higher than the concentration of TPH in soil samples obtained in this study.

Table 1 shows the level of TPH in Station IV. The mean TPH concentration decreases as depth increases from 0-0.5m to 1.0 – 2.0m. The mean TPH values obtained were 200.00, 151.82 and 62.90mg/kg for 0-0.5m, 0.5-1.0m and 1.0 – 2.0m, respectively. At depth 2.0 – 3.0m the mean TPH concentration of the soil sample increases rapidly to 605.00mg/kg, then decrease to 432.67 and 203.59mg/kg at 3.0 – 4.0 and 4.0 – 5.0m, respectively. Station IV has the same pattern of accumulation of TPH in soil as Station I. This indicates that the two stations have similar soil characteristics. The result of the analysis indicates that Station V recorded high mean TPH concentration 1341.00mg/kg at the topsoil and then decreases to 894.33mg/kg at 0.5 – 1.0m. At depth 1.0 – 2.0m the mean TPH concentration recorded was 1009.67mg/kg. However, as depth increases the mean TPH level decreases as shown in Station V.

Table 1: Level of total petroleum hydrocarbon in soil profile at various stations (mg/kg)

Depth (m)		Station I	Station II	Station III	Station IV	Station V
0-0.50	Mean	5199.52	337.52	222.09	200.00	1341.00
	Max	5560.01	362.01	242.34	217.00	1376.00
	Min	4726.33	304.21	209.41	183.00	1303.00
	SD	428.11	29.89	17.72	17.00	36.59
0.50-1.00	Mean	2341.00	74.26	142.09	151.82	894.33
	Max	2602.13	85.21	153.42	167.31	979.00
	Min	2175.32	67.13	131.73	134.42	813.00
	SD	228.84	9.63	10.88	16.53	83.05
1.0-2.00	Mean	1116.96	88.34	1678.25	62.90	1009.67
	Max	1187.41	93.46	1710.41	73.90	1053.00
	Min	1042.10	81.21	1653.32	53.39	963.00
	SD	72.76	6.37	29.22	10.34	45.09
2.0-3.00	Mean	2066.83	137.91	1366.00	605.00	363.00
	Max	2182.41	141.22	1434.00	678.00	413.00
	Min	2004.75	134.50	1301.00	536.00	312.00
	SD	100.19	3.36	66.55	71.08	50.51
3.0-4.00	Mean	1699.39	108.54	1242.33	432.67	67.10
	Max	1841.11	110.34	1278.00	507.00	70.24
	Min	1531.75	106.72	1203.00	360.00	63.91
	SD	156.30	3.28	37.79	73.51	3.17
4.0 -5.0	Mean	665.86	353.42	710.67	203.59	75.47
	Max	703.34	395.61	814.00	213.17	81.41
	Min	623.10	302.23	615.00	193.46	68.67
	SD	40.38	47.33	99.72	9.87	6.41

SD = Standard deviation

Table 2: Level of total petroleum hydrocarbon in groundwater profile at various stations ($\mu\text{g/L}$)

Depth (m)		Station I	Station II	Station III	Station IV	Station V
0-0.50	Mean	8186.67	121104.00	1351.67	4137.00	9020.67
	Max	9013.00	124000.00	1413.00	4361.00	9513.00
	Min	7401.00	119312.00	1301.00	4003.00	8415.00
	SD	806.77	2531.49	56.76	195.23	557.70
0.50-1.00	Mean	1381.67	21446.67	1242.00	3473.00	1331.00
	Max	1403.00	24123.00	1280.00	3824.00	1402.00
	Min	1345.00	19872.00	1205.00	3041.00	1290.00
	SD	31.90	2329.81	37.51	397.73	61.73
1.00-2.0	Mean	1158.00	2425.00	1101.67	2101.67	1079.33
	Max	1263.00	2513.00	1145.00	2167.00	1134.00
	Min	1006.00	2361.00	1039.00	2033.00	1041.00
	SD	134.80	78.79	55.58	67.06	48.60
2.00-3.00	Mean	878.67	25762.00	820.67	1290.00	925.67
	Max	905.00	27103.00	834.00	1305.00	934.00
	Min	834.00	24812.00	805.00	1267.00	915.00
	SD	38.89	1194.50	15.44	20.00	9.71
3.00-4.00	Mean	718.67	12933.00	755.00	736.33	776.67
	Max	732.00	13456.00	793.00	961.00	812.00
	Min	703.00	12362.00	701.00	605.00	715.00
	SD	14.64	548.58	48.04	195.49	53.59
4.00-5.00	Mean	667.00	9022.67	682.00	756.67	640.00
	Max	703.00	9613.00	712.00	784.00	681.00
	Min	640.00	8421.00	651.00	725.00	603.00
	SD	32.00	596.08	30.51	29.74	39.15

SD = Standard deviation

The result of the analysis as shown in Table 1 indicates variation of accumulation of TPH at different depths of soil samples. The variation might be attributed to textural and physical nature of the soil. The amount of TPH that are water soluble and the hydrology of the area might as well account for the variation of TPH at different depths at a particular station studied. As oil infiltrate into the soil, it has a considerable effect on the structure and wetting ability of soil. Also surface runoff may probably form the major dispersing mechanism of TPH at the stations studied. The more volatile or soluble hydrocarbons will be the most susceptible to change by volatilization, reaction, leaching or biodegradation.

Table 2 shows the level of TPH in groundwater at different stations studied. At station I the mean TPH concentration of groundwater decreases as depth increases. At depths 0-0.50, 0.5-1.00 and 1.00 – 2.00m the mean TPH concentrations of groundwater recorded were 8186.67, 1381.67 and 1158.00 $\mu\text{g/L}$, respectively. The result of the analysis indicates that station II recorded highest mean TPH concentration of 121104.00 $\mu\text{g/L}$ at topsoil. As depth increases the mean TPH concentration decreases of mean values 21446.67 and 2425.00 $\mu\text{g/L}$ at depth 0.5 – 1.00 and 1.00 – 2.00m, respectively. At 2.00 – 3.00m the mean TPH concentration rapidly increases to 25762.00 $\mu\text{g/L}$ and then decreases as soil depth increases. Ibezue (2013) working on oil spillage on marine water at Gokana area of Niger Delta region recorded mean TPH concentrations 272.68mg/L and 48.51mg/L for Biara and Bodo water samples, respectively. The result of the analysis shows that mean TPH concentration of groundwater at stations III and V decreases as depth increases. The two stations recorded high TPH concentration of mean values 1351.67 and 9020.67 $\mu\text{g/L}$ at depth 0-0.5m, respectively. At station IV the TPH concentration decreases as depth increases. Station IV recorded high TPH concentration 4137.00 $\mu\text{g/L}$ at depth 0-0.50m. However, at depth 4.0 – 5.0m the mean TPH concentration of groundwater was 756.67 $\mu\text{g/L}$.

The recommended Department of Petroleum Resources (DPR) intervention limit for groundwater is 600 $\mu\text{g/L}$. The result of the analysis indicates that all the stations of groundwater studied were contaminated with TPH in view of high concentrations of TPH obtained at various stations when compared to DPR recommended limit. It has been reported that TPH compounds such as benzene, benzo [a] pyrene and gasoline are carcinogenic to humans (ATSDR, 1999).

4.0 Conclusion

This study indicates that soil samples obtained from different stations of Niger Delta region of Nigeria were

contaminated with TPH in view of oil production activities that were carried out in the region for a very long time. The result shows that TPH obtained from different stations were high when compared to DPR acceptable limit. These communities are predominantly farmers and the crops harvested from the TPH contaminated soil poses health hazards. Some of the compounds of TPH are known to be carcinogenic and some essential organs of the body such as kidney, liver etc are at risk of being affected by TPH.

The result of the analysis have shown that water samples obtained from various stations were contaminated with TPH. These communities living in the study area have water boreholes sunk for them by oil prospecting industries and Non-Governmental Organization (NGO). These communities depend on these boreholes for their domestic activities and the boreholes also serve as a source of drinking water. Drinking water from these boreholes poses health hazards because of TPH contamination of boreholes.

Remediation measures should be carried out by oil companies immediately after oil spillage or stoppage of oil production. This will go a long way for the reduction of TPH in the environment.

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