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Full Length Research Paper

Determination of total petroleum hydrocarbon in soil and groundwater samples in some communities in Rivers State, Nigeria

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The determinations of total petroleum hydrocarbon in soil and groundwater samples were studied at five communities in Rivers State, Nigeria. The result of the analysis indicates that soil samples obtained from Station A at various depths of 1.0 -2.0 m, 3.0 - 4.0 m and 4.0 - 5.0 m were contaminated with Total petroleum hydrocarbon (TPH) of concentrations 1320.00, 1516.66 and 1063.16 mg/kg, respectively. The result also shows that Station E of soil samples have high TPH concentrations of 1534.66, 1438.00 and 1651.00 mg/kg at different depths, respectively. The result of the analysis indicates that groundwater samples obtained from all the Stations studied were contaminated with TPH. Highest TPH concentration 33076.00 µg/L was recorded at Station D of groundwater sample at depth 0 - 0.5 m.

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

INTRODUCTION

The exploration and exploitation of crude oil in Nigeria have been in existence since 1956. In view of discovery of crude oil, oil spillages as a result of industry activities and pipe-line vandalization have been a concern in the Niger Delta area of Nigeria, were oil is being produced. The soil and groundwater of oil exploration and production zones are frequently contaminated especially in the Niger Delta area. Crude oil contains petroleum hydrocarbons which consist of three major groups of compounds. These are alkanes (paraffins), alkenes (olefins) and aromatics. Total petroleum hydrocarbon (TPH) is a term used to describe a large family of several hundreds of chemical compounds that originally come from crude oil. Crude oil is used to make petroleum products, which can contaminate the environment (Gustafson, 2007). Because there are so many different chemicals in crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of TPH at a site (ATSDR, 1999).

Some chemicals that may be found in TPH are hexane, naphthalene and fluorine, as well as other petroleum products and gasoline components. However, it is likely that samples of TPH will contain only some, or a mixture, of these chemicals. The amount and types of compounds in a petroleum hydrocarbon released into the environment differ widely depending on the product spilled and how it weathered. This variability makes it difficult to determine the toxicity and mobility of weathered petroleum products solely from TPH results. However, an analysis of soil and/or groundwater can be used to approximate risk depending on the to approximate risk depending

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on the hydrocarbon range, the release scenario, how well the site has been characterized, and the intended use of the land (ODEQ, 2010). Adeniyi and Afolabi (2002) have reported total petroleum hydrocarbon in vicinity of facilities handling refined petroleum product in Lagos metropolis, Nigeria. They determined TPH in three locations in the vicinity namely: a Petrol station, a Mechanic workshop and the Nigeria Electricity Power Authority (NEPA) station, respectively. They compared the results of the three stations with the result of the control station. The values of TPH obtained at the three stations were higher than the values obtained at control station.

Okonkwo et al. (2006) reported the level of TPH in dusts from petroleum handling facilities such as gasoline stations, selected high traffic density roads and residential areas within the Tshwane metropolitan area in South Africa. They reported high TPH values in gasoline stations than other two stations studied. It has been reported (Adeniyi and Owoade, 2010) that road side soil samples obtained along Lagos Badagry express way in Nigeria were contaminated with TPH. Two sampling stations along the express way namely Lagos State University Bus stops and Adeniran Ogunsanya College of Education Bus Stop was studied for TPH contamination of soil samples.

The aim of this study is to investigate the level of TPH in soil and groundwater samples from five communities in Rivers state of Nigeria were crude oil exploitation have stopped since 15 years ago. The communities are now farming on the land and using the groundwater for domestic activities. The associated health hazards of TPH were also examined.

MATERIALS AND METHODS

Soil and groundwater samples were collected from five communities in Rivers state of Nigeria. Rivers State is one of the Niger Delta states of Nigeria were crude oil exploration and exploitation are being carried out. The communities in Rivers State of Nigeria where soil and ground water samples were collected are shown in Figure 1. The communities are Botem (Station A), Korokoro (Station B), Kpor (Station C), Bodo (Station D) and Wiyakara (Station E).

Collection of soil sample

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

Collection of groundwater sample

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

Soil sample extraction

10 g of soil sample was added into an amber glass bottle. Anhydrous sodium sulphate (Na_2SO_4) was also added into the glass bottle containing the soil sample. The sample was stirred. The addition of Na_2SO_4 was to remove moisture from the soil sample. 300 µg/ml of surrogate (1-chlorooctadecane) standard was added to the soil sample. 30 ml of dichloromethane (DCM) was added to the sample as extracting solvent and the bottle containing soil sample was corked very tight and transferred to a mechanical shaker (LAWI, 2011).

The sample was agitated between 5 to 6 h at room temperature using a mechanical shaker. After agitation, the sample was allowed to settle for 1 h and then filtered through 110 mm filter paper into a clean beaker. The filtrate was allowed to concentrate to 1 ml by evaporation overnight in a fume cupboard.

Water sample extraction

500 ml of groundwater samples collected from different boreholes were transferred into 1000 ml separating flask. 30 µg/ml of surrogate in 1 ml of DCM was added into the flask containing groundwater sample. 20 ml of DCM was also added into the flask. The flask was shaken and pressure released at intervals. The sample was allowed to stand for few minutes and two layers were formed in the flask. The lower layer (extract) of the sample was collected into a beaker through a filter paper. The filtrate was concentrated to 1 ml by evaporation at room temperature overnight in a fume cupboard (LAWI, 2011).

Sample clean – up

Sample clean-up was performed using glass column. Column preparation was carried out by inserting glass cotton into the column. Silica gel was dissolved with DCM to form slurry, and the slurry was added into the column. Anhydrous Na_2SO_4 was added into the column followed by addition of pentane. After preparation of the column, the concentrated sample extract was mixed with cyclohexane in a beaker and transferred into prepared column. The sample extract was eluted using pentane as solvent and eluted sample collected in a beaker below the column. The sample was eluted further by adding more pentane into the column. After elution the column was rinsed with DCM. The eluted sample was allowed to stand overnight at room temperature in a fume cupboard for evaporation to take place (LAWI, 2011).

Sample separation and detection

The separation and detection of compounds in soil and groundwater samples were carried out using Agilent 6890N Gas Chromatograph - Flame Ionization Detector (GC-FID) instrument (LAWI, 2011; Cortes et al., 2012). 3 µl of concentrated sample eluted from column was injected into GC vial. The blank DCM was injected into micro-syringe of GC to clean the syringe (3 times) before taking the sample for analysis. The micro-syringe was further rinsed with the sample. Then the sample was injected into the column for separation of compounds in the sample. After separation the compounds were passed through a flame ionization detector. FID detects the compounds in the sample. The amount of TPH was resolved at a particular chromatogram in mg/kg for soil sample and µg/L for groundwater sample.

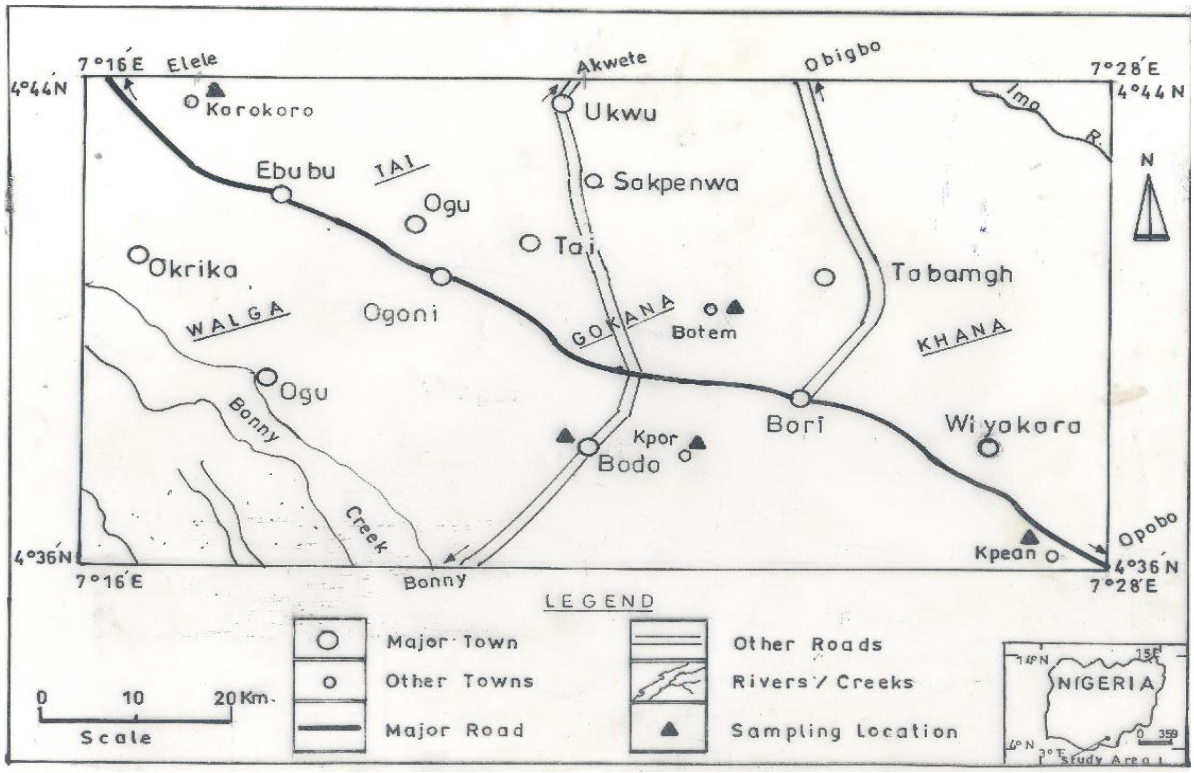

Figure 1. Location map of the study area.

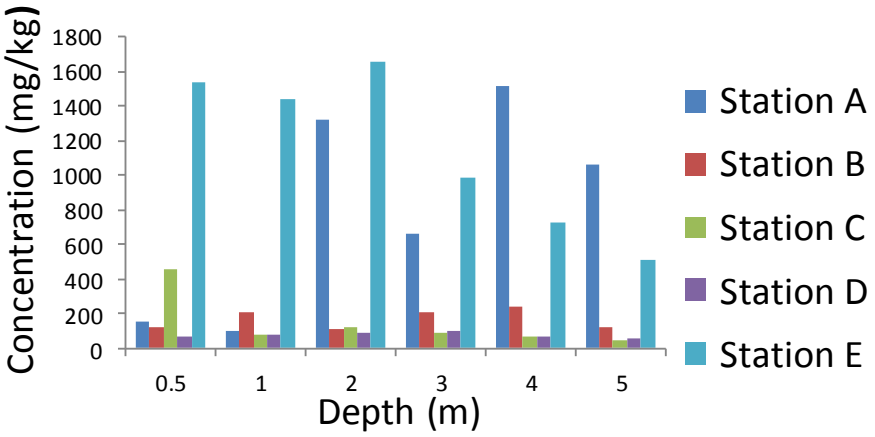

Figure 2. Soil TPH at various stations of study.

RESULTS AND DISCUSSION

The mean TPH concentrations of soil samples obtained from different stations are illustrated in Figure 2 and Table 1. The result of the analysis indicates that mean TPH concentrations (Station A) of soil samples, decreases initially as depth increases. At depth of 1.0 to 2.0 m the mean TPH concentration increased rapidly to 1320.00 mg/kg then decreased and increased again to 1519.66 mg/kg at a depth of 3.0 to 4.0m and decreased to 1063.16 mg/kg at a depth of 4.0 to 5.0 m. Iwegbue et al. (2008) working on automobile mechanic waste dumpsites at Mile 3 Diobu, Trans- Amadi and Borokiri areas of Rivers state of Nigeria reported TPH concentrations 2408.00, 4438.70 and 3618.00 mg/kg at 0-15 cm depth, respectively. The values were higher than the values obtained from this study. The high TPH value of automobile waste dump may be attributed to spent oil

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

Depth (m)		Section A	Section B	Section C	Section D	Section E
0-0.50	Mean	150.46	117.00	460.33	73.17	1534.66
	max	160.33	119.00	490.56	80.10	1600.00
	min	140.50	115.00	420.12	67.00	1484.00
	SD	9.90	2.00	36.26	6.58	59.37
0.50-1.00	mean	101.78	203.66	80.15	80.86	1438.00
	max	105.13	206.00	84.12	86.60	1450.00
	min	100.00	200.00	76.10	70.00	1420.00
	SD	2.90	3.22	4.01	9.42	15.87
1.00-2.00	mean	1320.00	112.33	117.59	90.00	1651.00
	max	1370..00	114.000	119.21	96.10	1680.00
	min	1240.00	110.00	116.34	84.60	1600.00
	SD	70.00	2.08	1.47	5.78	44.31
2.00-3.00	mean	663.33	203.57	87.62	105.93	991.00
	max	710.00	204.50	90.12	110.10	1002.00
	min	600.00	202.14	86.34	101.30	982.00
	SD	56.86	1.29	3.32	4.42	10.27
3.00-4.00	mean	1519.66	243.17	65.24	73.63	724.00
	max	1535.00	255.10	67.71	79.30	772.00
	min	1506.00	220.10	62.41	65.00	680.00
	SD	14.57.	19.98	2.67	7.60	46.13
4.00-5.00	mean	1063.16	123.26	49.87	60.17	516.00
	max	1070.24	127.50	59.31	65.10	535.00
	min	1051.12	120.10	48.20	57.00	493.00
	SD	10.48	3.81	2.16	4.33	32.72

*SD=Standard deviation.

and greases generated by the automobile mechanics working on vehicles on daily basis. The low values of TPH of soil samples (Station A) of this study, when compared to values obtained from automobile waste dump may probably be due to stoppage of crude oil exploitation in Station A for a very long time.

Crude oil staying for a long time in the soil might have been biodegraded by microbial activities. The TPH concentrations recorded in soil samples in Stations B, C and D ranges from 112.33 to 243.17 mg/kg, 49.87 to 460.33 mg/kg and 60.17 to 105.93 mg/kg, respectively. Adeniyi and Afolabi (2002) studied TPH level of soil samples of three different sites within the vicinity of facilities handling refined petroleum product in Lagos metropolis, Nigeria. The sites studied were Petrol stations, Mechanic workshop and the National Electricity Power Authority (NEPA) station and the results obtained were 399.83, 362.60 and 356.20 µg/g, respectively. Station E of this study recorded mean TPH concentration of soil samples 1534.16, 1438.00 and 1651.00 mg/kg at various depths 0-0.5 m, 0.5 - 1.0 m and 1.0 - 2.0 m, respectively.

Iturbe et al. (2004) reported that soil of coastal Mexican refinery was contaminated with hydrocarbons with detected concentration of TPH up to 130000 mg/kg. This value is high compared to TPH values obtained from this study. The main source of contamination of Mexican refinery soil as reported by the authors were from pipelines, valves and old storage tanks that were beside the land disposal of untreated hydrocarbon sediments derived from the cleaning of storage tanks. It has been reported that TPH concentrations of sediments of Koran River in Iran have values in the range 0.030 -100.00 µg/g (Hassan et al., 2013). The values are lower than values obtained from the Mexican refinery soil. Another study has shown a high concentration of TPH in the range51550 to 192130 mg/kg in soil samples of oil exploration and production zone of Tabasco State of Mexico (Torres et al., 2007).

The toxicity of petroleum hydrocarbon oil in soil has been established at concentration range greater than 1000.00 mg/kg (DPR, 2002). This study shows that soil samples at Station A, at depths 1.0-2.0 m, 3.0-4.0 m and

Table 2. level of total petroleum hydrocarbon in groundwater profile at various stations (µg/l).

Depth (m)		Section A	Section B	Section C	Section D	Section E
0-0.50	Mean	2489.00	1029.00	12424.99	33076.00	2862.00
	max	2520.00	1078.00	12500.23	33125.00	3043.00
	min	2480.00	998.00	12314.61	33000.00	2613.00
	SD	24.11	43.15	97.67	65.49	223.23
0.50-1.00	mean	1226.66	3803.33	10669.00	3783.00	1483.00
	max	1250.00	3850.00	10814.00	3840.00	1634.00
	min	1200.00	3740.00	10434.00	3710.00	1301.00
	SD	25.17	56.86	205.59	66.58	168.65
1.00-2.00	mean	1062.66	2141.30	8118.00	2714.00	1227.00
	max	1083.00	2156.00	8135.00	2932.00	1321.00
	min	1033.00	2120.00	8100.00	2401.00	1117.00
	SD	26.27	18.90	17.56	278.13	102.94
2.00-3.00	mean	821.00	1942.00	7549.00	9742.00	895.60
	max	840.00	2030.00	7715.00	10913.00	983.00
	min	789.00	1816.00	7434.00	8412.00	834.00
	SD	27.87	111.95	146.94	1258.00	77.75
3.00-4.00	mean	773.00	1576.83	5386.00	2409.00	727.00
	max	791.00	1600.32	5512.00	2512.00	741.00
	min	734.00	1560.02	5232.00	2302.00	705.00
	SD	33.81	20.97	142.18	105.06	19.51
4.00-5.00	mean	676.66	1474.52	4172.00	2304.60	694.00
	max	812.00	1483.32	4201.00	2513.00	761.00
	min	538.00	1460.12	4142.00	2134.00	593.00
	SD	137.03	12.58	29.58	192.29	89.40

*SD=Standard deviation

4.0- 5.0 m respectively, were contaminated with TPH. Also Station E shows high TPH concentrations at depths 0-0.50 m, 0.50-1.0 m and 1.00-2.0 m, respectively. It was also indicated that Stations A and E were contaminated with TPH when compared with DPR recommended limit of 1000.00 mg/kg. Some of the TPH compounds can affect the central nervous system. One compound can cause headaches and dizziness at high concentrations and another compound can cause a nerve disorder called “peripheral neuropathy” this consist of numbness in the feet and legs. Also TPH compounds can cause effects on the blood, immune system, lungs, skin and eyes (ATSDR, 1999). The high concentration of TPH at Stations A and E shows that the soil is contaminated and the crop planted in the soil may absorb these TPH compounds and these may be transferred to animals that may feed on the crop or vegetable. These TPH compounds may be transferred to man through the food chain. Therefore, effects of these TPH compounds are detrimental to health.

The concentrations of TPH increases or decreases with depth as shown in Figure 2 and Table 1 at different stations. The fluctuation of accumulation pattern of TPH in soil as shown in Table 1 and Figure 2 may probably be due to the textural and physical nature of soil, the amount of TPH that are water soluble and the hydrology of the area. Also surface runoff may probably form the major dispersing mechanism of TPH at various stations studied. The alteration of composition of hydrocarbon occurs as it gets into the soil. The hydrocarbons that are strongly sorbed onto soil organic matter will be resistant to loss or alteration by other processes. Also the more volatile or soluble hydrocarbons will be the most susceptible to change by volatilization/reaction/leaching and biodegradation.

As oil infiltrate into the soil, it has a considerable effect on the structure and welting ability of soil. It also physically displaces soil air and water. This displacement of air and water in the soil may promote anaerobic condition in the soil. The mean TPH concentrations of groundwater at different stations are illustrated in Table 2 and Figure 3, respectively. At Station A the mean TPH

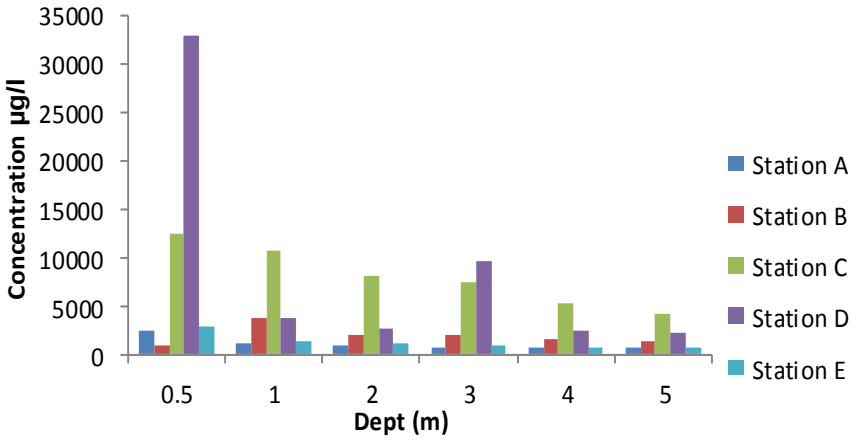

Figure 3. Groundwater TPH at various stations of study.

concentration decreases as depth increases. At depth 0-0.5 m the mean TPH concentration of groundwater was 2489.00 µg/L. As the depth increases to 0.5 - 1.0 m the mean TPH concentration decreases to 1226.66 µg/L and the decrease in TPH concentration continues up to 4.0 - 5.0 m depth of concentration 676.66 µg/L. Station C and E have the same pattern of decrease in TPH concentration as depth increases. The three stations A, C and E have the same pattern of accumulation of TPH; Station C has the highest concentration of mean TPH of the topsoil. The highest mean TPH concentration 33076.00 µg/l was recorded at Station D of the topsoil, while mean TPH concentration 1029.00 µg/L was recorded at Station B of the topsoil. After the topsoil at Station B, mean TPH concentration decreases as depth increases. The recommended DPR limit intervention value for groundwater is 600 µg/L.

The result of the analysis indicates that all the stations groundwater were contaminated with TPH in view of high concentrations of TPH obtained at various stations when compared to the recommended intervention value of DPR. It has been reported that TPH compounds such as benzene, benzo (a) pyrene and gasoline are carcinogenic to humans (ATSDR, 1999). In view of high concentrations of TPH obtained from different stations, it shows that using groundwater for domestic activities may be detrimental to human health.

Conclusion

This study shows that two soil stations A and E were contaminated with TPH. The effect of TPH will be detrimental to the health of individuals in these communities that carry out farming activities in the farm land were soil samples were collected. These TPH will be transferred to humans through the food chain. The result of this study also shows that groundwater samples obtained from Stations A, B, C, D and E were contaminated with TPH. The result indicates that making use of the groundwater for domestic activities will be hazardous to health.

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