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THE EFFECTS OF THE ROCK STRATIGRAPHY ON TPH/PAH ABSORPTION AND TRANSMISSION IN SOME SECTIONS OF THE GOKANA AND KHANA LOCAL GOVERNMENT AREAS

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ABSTRACT

Concentration of TPH/PAH in soils in parts of Gokana and Khana local government areas of Rivers state were examined using samples from 30 shallow wells drilled with hand auger. The core intervals penetrated, ranged between 0 on the surface to 100cm at total depth and was composited into two sections corresponding to upper 0 – 0.5m and lower 0.51 – 0.1m sections respectively. The samples were described to determine their sedimentological characteristics and effect on absorption and transmission of fluids. The total hydrocarbon content in samples of the study area were determined following the EPA 1664 Hexane Method (Method No: EPA 418.1/413.2 & EPA 1664). Individual concentrations of identified PAH congeners were noted and combined to generate the PAH concentrations in each of the two composited sections of the 30 sampled locations. The sedimentology of the logged sections consists mostly of peaty clay, clayey sands and organic clay in the upper section and clayey silt and clayey sand in the lower section. TPH in the study area ranged between 20612mg/kg at Location 15 to 37.09mg/kg at Location 11 for the upper (0 – 0.5m) sections and 14731mg/kg at Location 12 to 14.67mg/kg at Location 17 for the lower (0.51 – 1m) section. PAH ranged from 9.55mg/kg at Location 12 to <0.01mg/kg at several other Locations for the upper (0 – 0.5m) sections and 5.71mg/kg at Location 11 to <0.01mg/kg at several other Locations for the lower (0.51 – 1m) section. Correlation of sedimentology descriptions with the geochemical analysis indicates high concentrations of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbon (PAH) within the upper (0 – 0.5m) sections than in the lower (0.51 – 0.1m) sections in consonant with the stratigraphy of the logged section.

Keywords: Polycyclic aromatic hydrocarbon, Total petroleum hydrocarbon, sedimentology, hydrocarbon, crude oil.

INTRODUCTION

In the Niger Delta, degradation of the environment by crude oil is very common. Crude oil in its natural state is a combination of plethora of substances commonly referred to as 'hydrocarbons' and comprising of complex mixture of carbon and hydrogen linearly arranged either as aliphatic or in rings as aromatic and asphaltene fractions with oxygen (Osuji, 2011), Andersen et al., 2001), sulphur and nitrogen containing compounds. These complex mixtures of carbon and hydrogen and accompanying compounds are generally very toxic to animal, plants, aquatic

and micro-organisms as well as human, and are capable of causing alteration on the physico-chemical parameters of the soil and water, thereby damaging the environment and every form of life dependent on it. The toxic compound from the hydrocarbons occur in the form of polycyclic aromatic hydrocarbons (PAH's).

The term "Hydrocarbon" is referred to organic rich chemical compound, it is chiefly composed of carbon and hydrogen atoms with the carbon atoms arranged in straight chain, branched chains to non-aromatic rings known as aliphatic hydrocarbon and one or more ring-like carbon to carbon atom structures known as aromatic hydrocarbons. Hydrocarbon is the chief constituent of crude oil, coal, natural gas and other sources of natural energy.

The study was carried out with shallow well samples obtained from 30 sampled locations, sampled at 0.5m (50 cm) and comprising of 0m, 0.5m and 0.10m samples per sampled

The Niger Delta stratigraphy is made up of three stratigraphic units and has been extensively worked on by many authors such as Short and Stauble (1967), Reijers (2011), Doust and Omatsola (1990), Avbovbo, (1978), Reijers et al. (1997) and a host of others. The three stratigraphic units that make up the Niger Delta have been shown by well sections drilled. The formations indicate an overall coarsening-upward progradational clastic wedge (Short and Stauble, 1967), deposited in marine (Akata Formation), deltaic (Agbada Formation) and fluvial (Benin Formation) environments (Weber, 1967; Weber and Daukoru, 1975).

Stacher (1995) reported that the Niger Delta lithostratigraphic units are strongly

point. The study area lies within the transitional waters of the Niger Delta estuaries in the heavily hydrocarbon polluted Gokana and Khana Local Governments Areas of Rivers State, Nigeria. It lies within Longitudes 07º 17' 00" E to 07º 22' 00" E and Latitudes 04º 33' 00" N to 04º 37' 00" N (Fig. 1). The sampling points are indicated as Red dots. The boundary areas included Bonny, Andoni and Opobo/Nkoro Local Government Areas (Rivers state) in the south; Ogu-Bolo and Tai Local Government Areas (Rivers state) in the west; Oyigbo Local Government Area (Rivers state) and Ukwa East Local Government Area (Abia state) in the North; Oruk-Anam and Ikot-Abasi Local Government Areas (Akwa Ibom state) in the east.

This study aimed at determining the rock stratigraphy of parts of Gokana and Khana local government areas of Rivers state and how it affect the TPH/PAH absorption and transmission within the rock profile in the study area.

diachronous. These lithostratigraphic units include the Benin, Agbada and Akata Formations (Fig. 2; Table 1) in order of increasing age.

Hydrocarbon spills has been identified by Peterson (2001) to have a wide range of negative impacts on marine environment at varying scale. These negative impacts included some dire consequences on the survival of marine micro-organisms, their productivity, development, feeding and ecology as indicated by Lamont et al. (2012), Incardona et al. (2014), Gonzalez-Doncel et al. (2008), Romero et al. (2012) and Aguilera et al. (2010).

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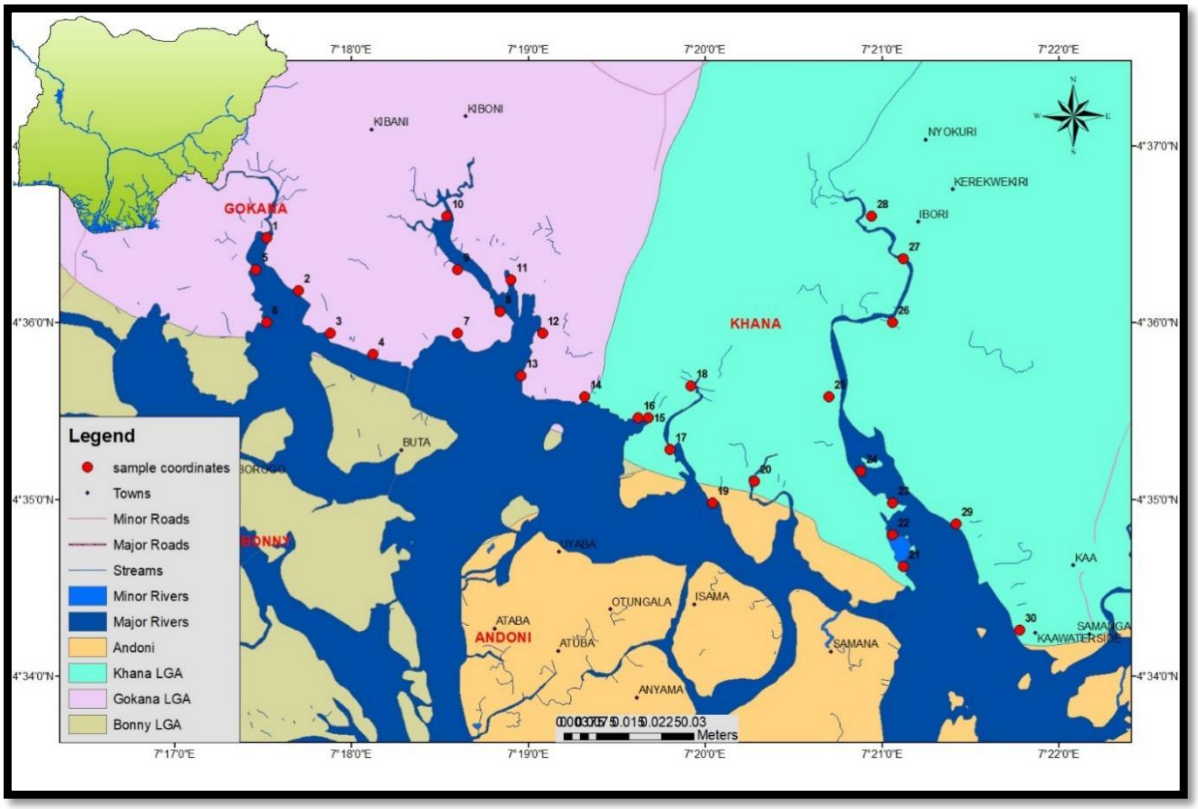

Figure1: Location map of the study area showing sampling points with red dots.

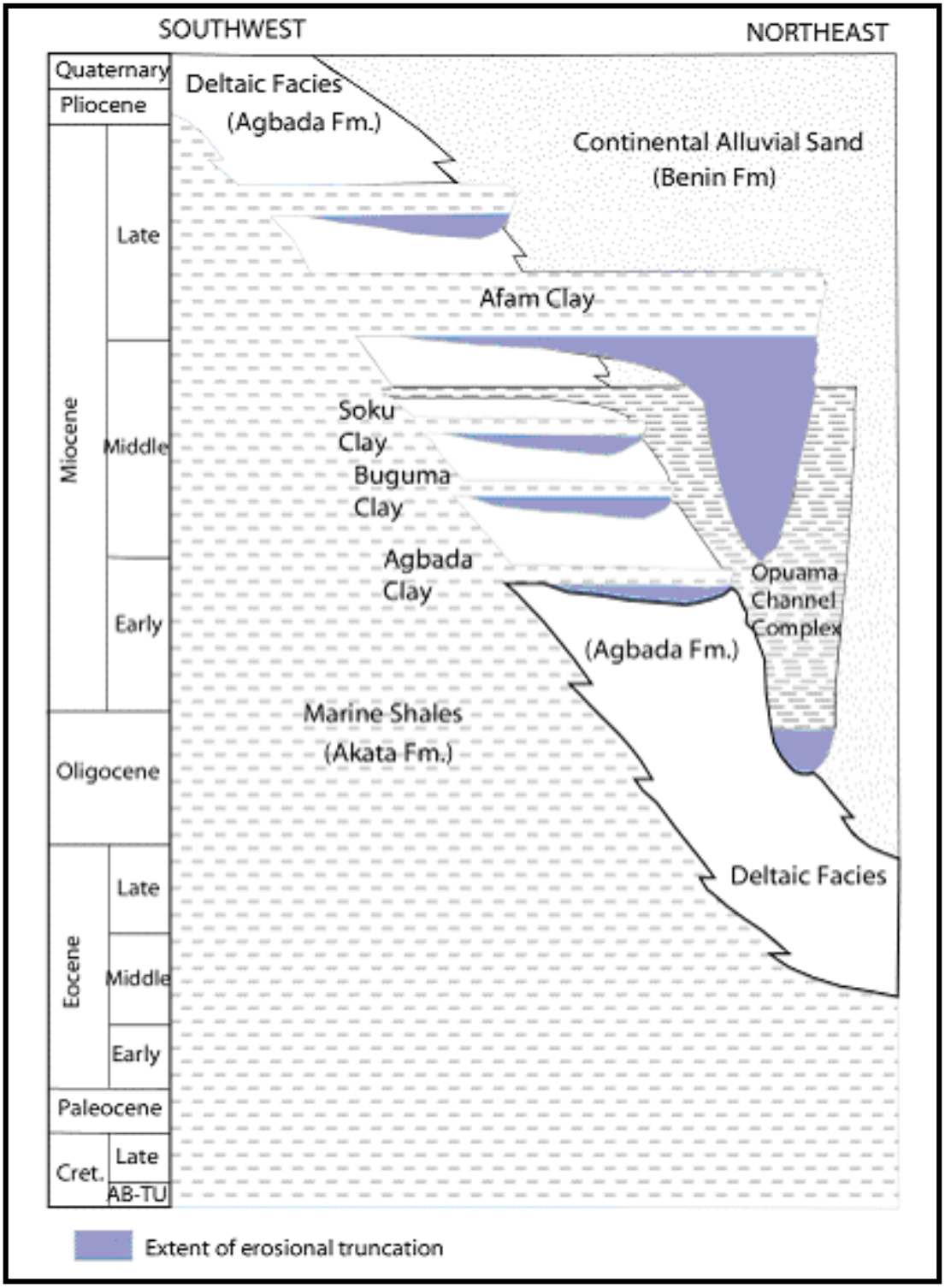

Figure 2: Lithostratigraphy of the Niger Delta (after Doust and Omatsola, 1990).

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Table 1: Stratigraphic table of the Niger Delta, showing the Formations and their lateral equivalents (modified from Short and Stauble, 1967).

Subsurface			Surface Outcrops		
Youngest Known Age		Oldest Known Age	Youngest Known Age		Oldest Known Age
Recent	Benin Formation (Afam clay member)	Oligocene	Plio/Pleistocene	Benin Formation	
			Miocene	Ogwashi-Asaba	Oligocene
Recent	Agbada Formation	Eocene	Eocene	Formation Ameki Formation	Eocene
Recent	Akata Formation	Eocene	Lower Eocene	Imo shale Formation	Paleocene
Unknown			Paleocene	Nsukka Formation	
			Maastrichtian		
			Maastrichtian	Ajali Formation	
			Maastrichtian		
			Campanian	Mamu Formation	
			Campanian		
			Campanian/Maastrictian	Nkporo Shale	
			Santonian		
			Coniacian/Santonian	Awgu Shale	
			Turonian		
			Turonian	Eze-Aku	
			Turonian		
			Albian	Asu River Group	
			Albian		

In "Characteristic level of Total Petroleum Hydrocarbon in Soil and Groundwater of Oil Impacted Area in the Niger Delta Region," Alinnor *et al*. (2014) found that the mean Total Petroleum Hydrocarbon (TPH) concentrations for soils in the studied area ranged between 5199.52, 2341.00, and 2066.83mg/kg while the mean concentrations for water were 8186.67, 12120.00, 1351.67, 4137.00, and 9020.

MATERIALS AND METHODS

Thirty locations were sampled and used for the study. The sampling points were first identified through reconnaissance survey based on observable hydrocarbon pollutions (films) on the surface. The samples were cored using hand auger. The hydrocarbons were seen filling up the wellbore surfaces (Fig.3) and draining in the hand auger after sample retrieval.

The core intervals penetrated ranged between 0 on the surface to 100cm at total depth. The samples were retrieved and composited into two sections corresponding to 0 – 50cm and 51 – 100cm respectively. The samples were bagged and labelled. All safety protocols were observed such as the use of life jackets, safety rain boots and hand gloves etc.

Figure 3: Core hole filled up with hydrocarbons.

The cores recovered from hand auger coring were taken to the laboratory for sedimentological sample descriptions. The samples were described based on grain-size, shape, colour, odour, presence or absence of hydrocarbon films, presence or absence of rootlet, and were treated with hydrochloric acid to check for the presence of carbonaceous materials. The grain-sizes were determined through processes of both wet and dry sieve analysis. The wet sieve analysis was done using 63 µm mesh sieve size and with 30 g weight of samples. The sample weight loss after wet sieve analysis represented the clay fractions. The sample weight retained after the wet sieve analysis were dried and used for dry sieve analysis with a set of sieves to obtain the percentage of samples retained at the various sieve sizes. These descriptive properties of the rocks according to BGS (British Geological Surveys) Rock Classification Scheme, were used in classifying the rock types.

Concentration of total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbon (PAH) were determined for the study samples from the 30 studied locations.

PAH, unlike TPH were measured independently to determine concentrations of identified PAH congeners. PAH congeners identified and measured in the samples from the 30 study locations included Naphthalene, Acenaphthylene, Acenaphthene, Fluorine, Anthracene, Phenanthrene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Dibenz(a,h)anthracene, Indeno(1,2,3-cd)pyrene and Benzo (g,h,i) perylene.

Individual concentrations of these identified PAH congeners were noted and combined to generate the PAH concentrations in each of the two composited sections of the 30 sampled locations.

The total hydrocarbon content in samples of the study area were determined following the EPA 1664 Hexane Method (Method No: EPA 418.1/413.2 & EPA 1664).

RESULTS

Two different types of data sets were generated from the field hand auger samples obtained from 30 sampled locations and composited into upper and lower sections. The data sets included sample sedimentology descriptions and geochemical analysis (consisting of total petroleum hydrocarbon

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(TPH) and polycyclic aromatic hydrocarbon (PAH)).

The result from the sedimentology analysis were presented as lithological logs. It showed the stratigraphy of the logged section, indicating the rock physical characteristics such as texture. The rock texture indicates the percentage of different grain sizes such as sand, silt and clay sizes which consists of the rock mineral fractions, other physical characteristics of the rock included organic components such as rootlets and other plant remains.

The sedimentology of the logged sections consists mostly of peaty clay (comprising of partly decomposed mosses), clayey sands and organic clay in the upper composited section and clayey silt and clayey sand in the lower composited section. An example of the logs is presented in Figs. 4 and 5 representing locations 5 and 12.

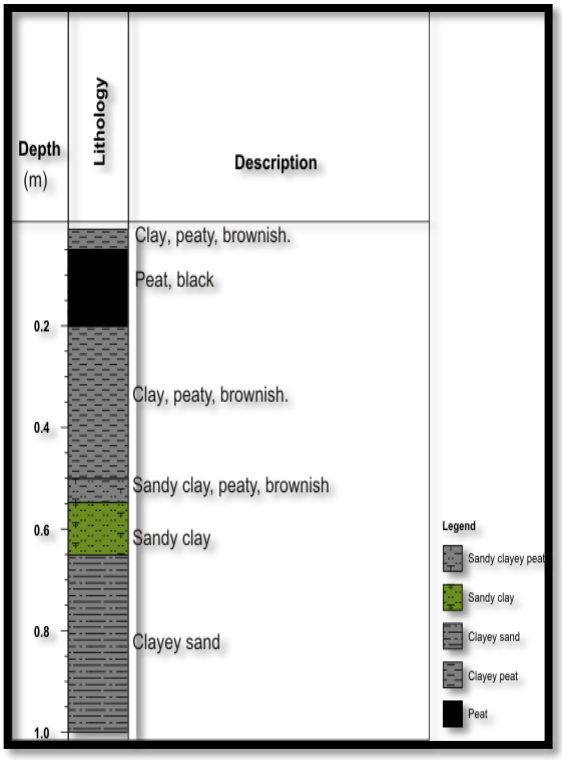

Figure 4: Lithology log for location 5

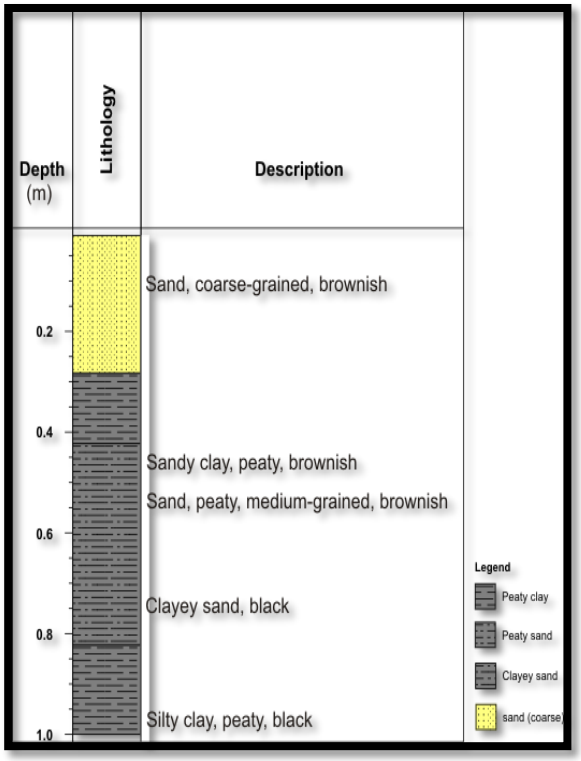

Figure 5: Lithology log for location 12

The geochemical analysis show concentrations of TPH and PAH from the study sample. PAH congeners identified in the study samples include Naphthalene; Acenaphthylene; Acenapthene; Fluorene; Anthracene; Phenanthrene; Fluoranthene; Pyrene; Benz (a) anthracene; Chrysene; Benzo (b) fluoranthene; Benzo (k) fluoranthene; Benzo (a) pyrene; Dibenz (a, h) anthracene; Indeno (1, 2, 3 - c, d) pyrene and Benzo (g, h, i) pyrylene. Many of these congeners are very toxic to terrestrial and aquatic life. They are transformed to mutagenic, carcinogenic and teratogenic substances when metabolized by terrestrial and aquatic organisms which in turn causes adverse effect on the organisms. According to (IARC, 2006), benzo(a)pyrene; benzoflouranthenes; benzo(a)anthracene; indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene are the most carcinogenic.

TPH in the study area ranged between 20612mg/kg at Location 15 to 37.09mg/kg at Location 11 for the upper (0 – 0.5m) composited sections and 14731mg/kg at Location 12 to 14.67mg/kg at Location 17 for the lower (0.51 – 1m) composited sections in the study area (Table 2). PAH in the studied samples ranged from 9.55mg/kg at Location 12 to <0.01mg/kg at several other Locations for the upper (0 – 0.5m) composited sections and 5.71mg/kg at Location 11 to <0.01mg/kg at several other Locations for the lower (0.51 – 1m) composited sections. Concentrations of TPH in the logged interval is generally higher in the upper composited section than in the lower composited sections except for Locations 11, 12, 14 and 18 where concentrations of TPH in upper composited section is lower than in lower composited sections. Concentrations of PAH is also higher in upper composited sections than in lower composited sections except for Locations 11, 16 and 26.

Table 2: Concentrations of TPH and PAH with percentage of PAH within TPH.

location / Depth (m)	TPH (mg/kg)	PAH (mg/kg)	TPH (%)	PAH (%)
1 (0 - 0.5)	1050	0.34	99.97	0.03
1 (0.51 - 1)	34.66	<0.01	99.97	0.03
2 (0 - 0.5)	129.33	0.04	99.97	0.03
2 (0.51 - 1)	32.32	<0.01	99.97	0.03
3 (0 - 0.5)	13210	1.99	99.98	0.02
3 (0.51 - 1)	100.72	<0.01	99.99	0.01
4 (0 - 0.5)	14728	4.28	99.97	0.03
4 (0.51 - 1)	65.77	<0.01	99.98	0.02
5 (0 - 0.5)	515.92	0.07	99.99	0.01
5 (0.51 - 1)	15.52	<0.01	99.94	0.06
6 (0 - 0.5)	15869	4.95	99.97	0.03
6 (0.51 - 1)	67.53	0.04	99.94	0.06
7 (0 - 0.5)	20601	5.69	99.97	0.03
7 (0.51 - 1)	729	0.46	99.94	0.06
8 (0 - 0.5)	9501	6.29	99.93	0.07
8 (0.51 - 1)	353.53	0.12	99.97	0.03
9 (0 - 0.5)	2018	0.32	99.98	0.02
9 (0.51 - 1)	43.74	0.01	99.98	0.02
10 (0 - 0.5)	7420	2.93	99.96	0.04
10 (0.51 - 1)	35.59	<0.01	99.97	0.03
11 (0 - 0.5)	37.09	<0.01	99.97	0.03
11 (0.51 - 1)	13743	5.71	99.96	0.04
12 (0 - 0.5)	967.82	9.55	99.00	0.10
12 (0.51 - 1)	14731	4.99	99.97	0.03
13 (0 - 0.5)	2079	0.47	99.98	0.02
13 (0.51 - 1)	41.35	<0.01	99.98	0.02
14 (0 - 0.5)	210.39	<0.01	100.00	0.00
14 (0.51 - 1)	985.47	<0.01	100.00	0.00

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15 (0 - 0.5)	20612	5.27	99.97	0.03
15 (0.51 - 1)	110.11	<0.01	99.99	0.01
16 (0 - 0.5)	77.35	0.02	99.97	0.03
16 (0.51 - 1)	65.57	0.1	99.85	0.15
17 (0 - 0.5)	515.85	0.07	99.99	0.01
17 (0.51 - 1)	14.67	0.02	99.86	0.14
18 (0 - 0.5)	1049.4	0.38	99.96	0.04
18 (0.51 - 1)	176.06	0.1	99.94	0.06
19 (0 - 0.5)	13208	1.9	99.99	0.01
19 (0.51 - 1)	727	0.43	99.94	0.06
20 (0 - 0.5)	9505	6.27	99.93	0.07
20 (0.51 - 1)	352.78	0.11	99.97	0.03
21 (0 - 0.5)	2015	0.33	99.98	0.02
21 (0.51 - 1)	43.54	0.04	99.91	0.09
22 (0 - 0.5)	7720	3.15	99.96	0.04
22 (0.51 - 1)	32.59	0.4	99.88	0.12
23 (0 - 0.5)	2023	0.29	99.99	0.01
23 (0.51 - 1)	53.03	0.04	99.92	0.08
24 (0 - 0.5)	6523	3.11	99.95	0.05
24 (0.51 - 1)	37.95	<0.01	99.97	0.03
25 (0 - 0.5)	14763	5.59	99.96	0.04
25 (0.51 - 1)	35.07	<0.01	99.97	0.03
26 (0 - 0.5)	213.34	<0.01	100.00	0.00
26 (0.51 - 1)	174.06	0.09	99.95	0.05
27 (0 - 0.5)	2087	0.49	99.98	0.02
27 (0.51 - 1)	42.36	0.02	99.95	0.05
28 (0 - 0.5)	958.79	9.4	99.02	0.98
28 (0.51 - 1)	987.38	0.01	100.00	0.00
29 (0 - 0.5)	20609	5.44	99.97	0.03
29 (0.51 - 1)	108.76	<0.01	99.99	0.01
30 (0 - 0.5)	14638	4.8	99.97	0.03
30 (0.51 - 1)	67.43	0.1	99.85	0.15

DISCUSSION

Generally, concentrations of TPH and PAH are higher in the upper composited sections than in the lower composited sections. These high concentrations in the upper sections of the logged interval is an indication of poor infiltration of hydrocarbon pollutants resulting from very fine grained clayey rock type with low permeability but very high absorption and retention rate in the upper composited sections of the study area. The percentage of PAH in the total crude oil rarely exceeds 15% but concentrates more in lubricating oil, gas oil and residuum generally referred to as heavy fractions of petroleum (Osuji, 2011). Concentrations in percentage of PAH in TPH ranged from 0.98% at Location 28 to 0.00% at Locations 14 and 26 for the upper (0 – 0.5m) composited sections; 0.15% at Locations 16 and 30 to 0.00% at Locations 14 and 28 for the lower (0.51 – 0.1m) composited sections (Table 2). This indicated that the source of hydrocarbon pollutants in the study area does not include heavy fractions of petroleum but essentially, were from light oil consisting of benzene, toluene and xylenes as chief constituents.

Correlation of sedimentology descriptions with the geochemical analysis indicates high concentrations of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbon (PAH) within the upper (0 – 0.5m) composited sections than in the lower (0.51 – 0.1m) composited sections. This is because of the texture (porosity and permeability) of the rocks of the study area except for locations 11 and 12 which has more permeable sand in the upper (0 – 0.5m) composited sections than in the lower (0.51 – 0.1m) composited sections (figs. 6 and 7).

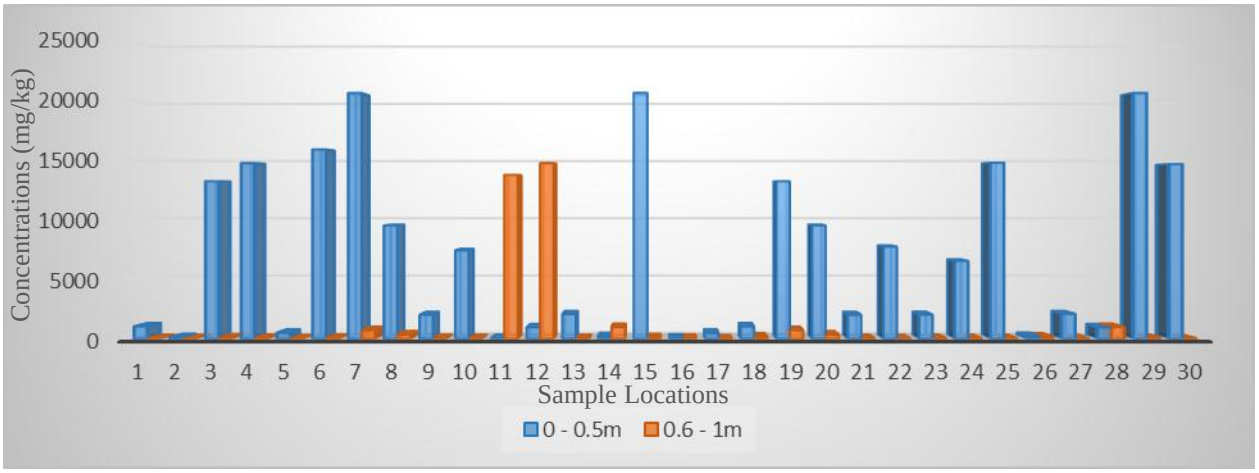

Figure 6: Histogram plot of concentrations of total petroleum hydrocarbon (TPH) in the study area for the upper (0.0 – 0.5m) and lower (0.51 – 1m) composited section.

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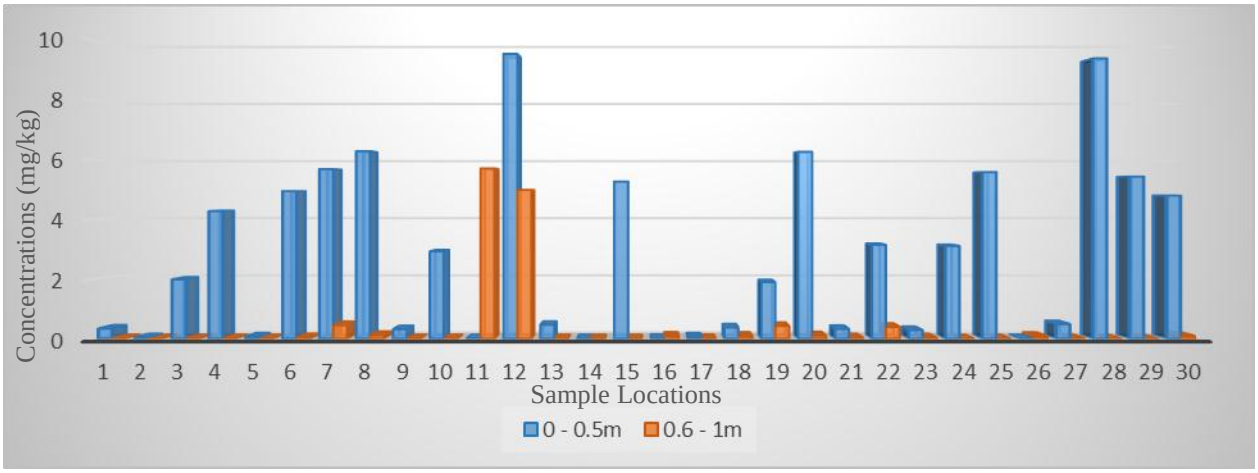

Figure 7: Histogram plot of concentrations of polycyclic aromatic hydrocarbon (PAH) in the study area for the upper (0.0 – 0.5m) and lower (0.51 – 1m) composited section.

CONCLUSION

The upper composited (0 – 0.5m) samples in the study area is mostly made up of peaty clay, while the lower composited (0.51 – 100cm) samples consists of clayey sand with sand and silty sand. This inhibits easy free flow of hydrocarbon pollutants into the lower section of the sampled locations.

Concentrations of TPH and PAH in the logged interval is generally higher in the upper composited section than in the lower composited sections in consonant with the stratigraphy of the logged section.

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