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Full Length Research Paper

Quantitative evaluation of the spatial distribution and penetration of liquid hydrocarbons in petroleum spilled soil

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Petroleum spillage contamination of soil was investigated about 38 days after an extensive oil spillage in South –South Niger Delta. Soil samples and controls were collected at depths of 0-15 cm, 15-30 cm and 30-60 cm. Samples were analysed using gas chromatography fitted with a flame ionisation detector. Penetration and migration of C_5-C_9, C_{10}-C_{26} and C_{26}-C_{40} hydrocarbons through the soil layers were assessed to determine the spatial distribution, penetration and similarity of these compounds over the contaminated area. The results also indicated elevated levels of total hydrocarbon contents in the soil when compared with the reference sites. The total petroleum hydrocarbon concentrations levels varied from 9-289 ±3 mg kg^{-1} topsoil, 11-413±7 mg kg^{-1} subsoil and 13-178±11 mg kg^{-1} at the greatest depth measured. This paper provides informative guidelines for effective remediation processes, careful monitoring and the need to conduct more post-spill studies by competent remediation professionals.

Keywords: Petroleum spills, Total Hydrocarbon, soil contamination, remediation and gas chromatography fitted with flame ionisation detector (GC-FID).

INTRODUCTION

Contamination of soil and sediment from petroleum spills has become an environmental problem worldwide. Crude oil contamination of soil by oil exploration activities has quickly become a considerable environmental issue in a large-scale (Okop and Ekpo, 2012; (ITOPF ; Jorge et al, 2012). Petroleum spillage from pipe lines, leakage from storage (surface and underground) tanks, and similar discharges associated with petroleum bring about environmental health risk and agricultural defects (Bosco, (2005); Abrahams, (2002). The economy of Nigeria, the most populous, black African country is largely dependent on crude oil tapped from the Niger Delta region though with the attendant hazardous effects meted on the environment (Okop and Ekpo, 2012; Iwegbue et al, 2007; Chukwujindu, 2008).

The presence of these liquid hydrocarbon contaminants in the environment, will automatically incur natural weathering processes that act on the oil hydrocarbons and reducing the total concentration present as time progresses. These natural processes are often enhanced by addition of manmade fertilizers as part of the clean-up procedures (Garcia-Blanco (2007).

Not all the damaging effects of petroleum spillage are completely understood, despite effort to document such impacts on journals, scientific and other technical literature. There is continuous evidence of environmental harm though the analytical goal for each petroleum spill site is to access the level of contamination in the soil with the aim of returning the soil back to a useable form.

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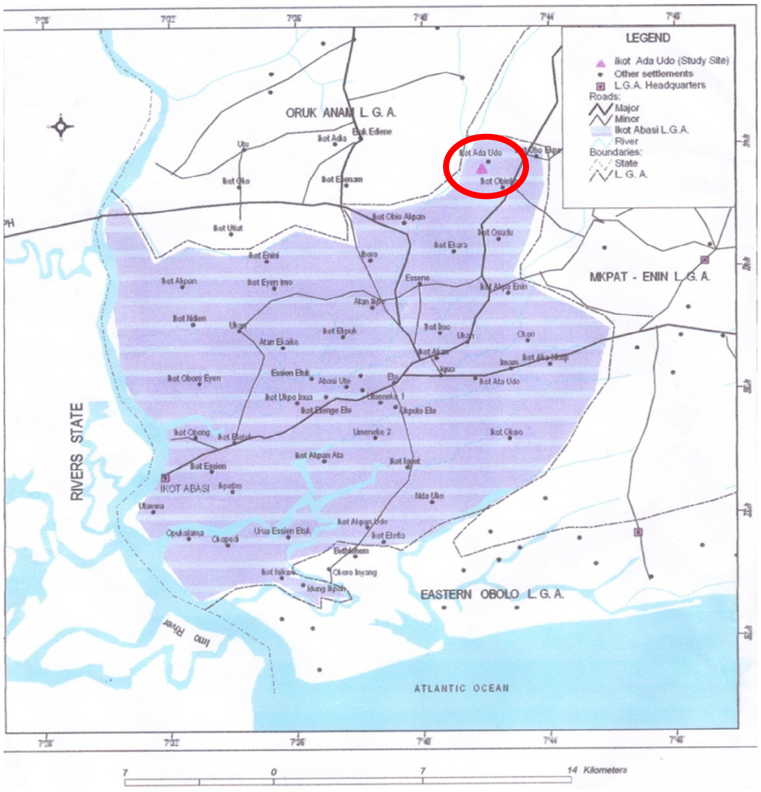

Figure 1. Ikot Abasi Local Government Area of Akwa Ibom State, South-South Niger Delta, Nigeria, showing the study site (Ikot Ada Udo) with a pink triangle in pink circle.

Attempts for complete removal may not be practically attainable either due to cost or source, but to efficiently and safely remove the spilled petroleum products from the soil. The immediate objective is to remediate the soil to the concentration levels that will be harmless to plants, fauna, human health and the entire ecosystem (USEPA, 1990; DRAFT, 1991). The way to handle, dispose or reuse non-hazardous petroleum contaminated soils has received attention (Torres et al. (2005).

In situ bioremediation proved to be an accepted mechanism to reduce the oil hydrocarbon load as it usually creates less significant disturbances than other the physical methods (Fingerman and Nagabhushanam, 2005). A reasonably large proportion of the spilled oil is ultimately taken off from the environment by biological activity although the more resistant long chain and aromatic compounds may be persistent for many years (Short, (2007).

Optimum extraction time for the soil samples was established using dichloromethane (DCM) by comparing the extraction efficiencies of other solvents. A gas chromatography equipped with flame ionisation detector (GC-FID) capable of split injection with a Varian CP-Sil-GC capillary column and Combi Pal was employed. Gas chromatography is one of the most powerful, popular, unique and readily versatile analytical techniques used for the separation, identification, and quantitative assay of compounds in the vapour state. It still remains the most important single technique for oil spill identification partly because the equipment is relatively available, easy to operate with small amount of operator time and considerable. FID limitations (Sampling protocols ..., 1990) include ability to destroy the sample, detect volatile hydrocarbons from non-petroleum matter and organic material such as methane and peat.

This work provides useful informative guidelines to oil companies and the Government to adopt in each petroleum spill site to access the level of contamination and to efficiently and safely remove the spilled petroleum products from the soil with the aim of returning the soil to its useful and natural state.

Experimental

Site selection and Sampling

The sampling site was located in Ikot Ada Udo, Ikot Abasi in Akwa Ibom State, South-South Niger Delta, Nigeria and covered about 250 x 350 m^2 and situated within longitude 7°41'-7.43'E and latitude 4°41' - 4°49' N (Figure 1). At this site, soil and water have been constantly

Figure 2. Photograph showing the researcher and the community representative standing at the spilled site near the well head (Ibibio 1).

subjected to petroleum spillages and crude oil leakages from a Shell marginal oil pipeline called “Ibibio I” - a Well head established in 1954 (Figure 2). A sample is an informative representative of a population and hence sampling is considered a vital and one of the most crucial steps in the procedure of analysis of organic pollutants in soils and sediments of our environment (Tadeusz and Jacek, 2002; Alain, et al. 2006)

An initial survey was carried out on the site to gather information about the sampling area and to establish any possible source of obstacle that may arise during sampling. The surveillance also enabled the researcher to determine the soil type, the terrain and the feasibility of using the hand soil auger for sampling as well as recognise the correct first aid kit and personal protection equipment (PPE) to use.

2.2 Sample collection and preservation

Approximately 500 g of soil was collected at each sample depth. Four control site samples were taken from the same geographically uncontaminated soil to determine the background levels of petroleum hydrocarbons for comparison with the contaminated soil. A hand soil auger (Nickel-plated carbon steel, 3´´ diameter) was used to collect soil samples from the site by taking about 5-10 auger borings at random to the depths of 0 to 15 cm at the top soil,(TS) 15 to 30 cm at middle soil (MS) and bottom layer (BL) of 30 to 60 cm. Samples were collected into zip type plastic bags and placed in a 1 L glass jar with Teflon lined cap and seal. The sampling average ambient temperature was 28℃. All the samples were carefully labelled during sampling, separated from other sampling points during storage. The samples placed in icebox and transported to the laboratory for storage at 4℃ until analysis was completed in about two weeks. Sampling took in one day. The auger was cleaned with water and rinsed with methanol after every sampling point.

Sample preparation, extraction and clean-up

The samples were prepared and shipped the same day by air to United Kingdom for analysis by the chemical shipping agent in Nigeria with adherence to full special shipping procedures for transporting and handling of the samples (ASTM, 2005). The soil samples were homogenized at ambient temperature using mortar and pestle to obtain finer texture and to remove sticks, pebbles and rock particles. Soxhlet extraction using a Brinkmann Büchi 461 automated extraction apparatus was employed in this work because it really ensures intimate contact of the sample matrix with the extraction solvent and a reasonably large amount of 5-20g could be used to allow quantitative extraction. Soxhlet technique is usually the adopted reference and most often used method for a long time (ISO/DIS,1995; Berst et al, 1999). All samples were extracted using this procedure as outlined in U.S. EPA method 3540 USAPA,1996) and ASTM method D5369 (ASTM, 2005) with slight modifications in the solvent choice and volume, extraction time and size of extraction flasks. About 2.5 hours optimum extraction time was established using dichloromethane (DCM) after comparing with other extraction solvents such as acetone, toluene, methanol, hexane, ethyl benzene and the mixtures of these solvents. DCM proved to be the most suitable solvent over hexane, acetone, toluene, ethyl benzene or the mixtures for this extraction due to its consistency,

Table 1. Overall average of the Total Hydrocarbon content (mg kg-1) in the samples and controls.

Sample Location	No of depths	Average Peak Area (mV*sec)			Hydrocarbon Concentration (mg kg^{-1})		
		TS	MS	BL	TS	MS	BL
1	3	473	678	501	76±12	108±9	91±13
2	3	561	607	517	106± 2	113±7	89±5
3	3	863	442	340	137±15	56±10	53±9
4	3	59	313	98	12±17	63±13	12±8
5	3	216	104	332	50±2	23±17	52±13
6	3	1823	1560	974	289±3	213±5	178±11
7	3	44	53	47	9±5	11±7	10±3
8	3	881	1643	695	133±4	215±6	117±8
9	3	795	381	432	132±27	64±16	75±29
10	3	204	219	187	41±14	52±12	37±2
11	3	339	288	992	53±8	44±13	172±11
12	3	66	144	99	14±24	26±21	13±19
13	3	679	2481	583	121±18	413±7	112±21
14	3	264	202	329	42±14	35±21	68±25
		Control Samples					
15	3	0.0	0.0	0.0	0.0	0.0	0.0
16	3	0.0	0.0	0.0	0.0	0.0	0.0
17	3	0.0	0.0	0.0	0.0	0.0	0.0
18	3	0.0	0.0	0.0	0.0	0.0	0.0
Total	**54**						

efficiency and ability of not interfering with BTEX retention time window (RTW) at C_5-C_9.

Each of the sample extracts were cleaned to remove moisture, polar hydrocarbons, colour interferences and any impurities before subjecting them to GC column analysis. This was achieved by filtering the extract under applied pressure through dual layer 6 mL glass, 2g/2g Florisil®/Na_2SO_4 SPE Tube supplied by Fluka Analytical, Sigma Aldrich, Switzerland. The clean-up procedure effectively removed hydrocarbons of natural origin and did not have any significant effect on the amounts of petroleum hydrocarbons present but aid in column performance.

2.4 Instrumentation

Gas chromatograph coupled to the flame ionisation detector (FID) equipped with an automatic sampler CTC Analytics CombiPAL and the 1177 split/splitless front injector was used. All samples were taken into 2 mL chromatographic vial, injected and separated on a Varian Chrompack capillary column CP 5860 with coating of 95% methyl and 5% phenyl-polysiloxane phase, (oven max tempt 350°C), WCOT fused silica, 30m long, 0.25mm inside diameter(id), 0.39mm outside diameter (od) and 0.25µm film thickness with CP-Sil 8 CB low bleeds/MS coating. Carrier gas was helium 26 cm sec^{-1}. Temperature programme during the chromatographic analysis was 50°C for 3 min; 8°C/min to 320°C hold 15 min. Detection at 320°C. The carrier gas was helium (99.99 % pure) at velocity of 26 cm sec^{-1}. Sample injection volume of 1µL, 1:25 split ratio and column flow rate of 1.0 mL min^{-1} were applied.

RESULTS AND DISCUSSION

The analysis of all the samples was carried out along with the standards. Each sampling point/hole yielded three samples taken at different depths of 0-15 cm (top soil), 15-30 cm (mid soil) and 30-60 cm bottom level). Samples were analysed and chromatograms overlaid to confirm the identity and retention times with the reference standards. The average peak values of all the samples were recorded and their standard deviation and % RSD calculated at 95% confidence level. Laboratory standards (C10, C11, C14, C15, and C16) were prepared, analyzed and overlaid with the reference standards to confirm the samples identity and retention times as parts of the validation and operational checks.

The overall concentration of total petroleum hydrocarbon (TPH) of each sample depth at the site were established and presented in table 1.

The investigation of the site revealed that the highest

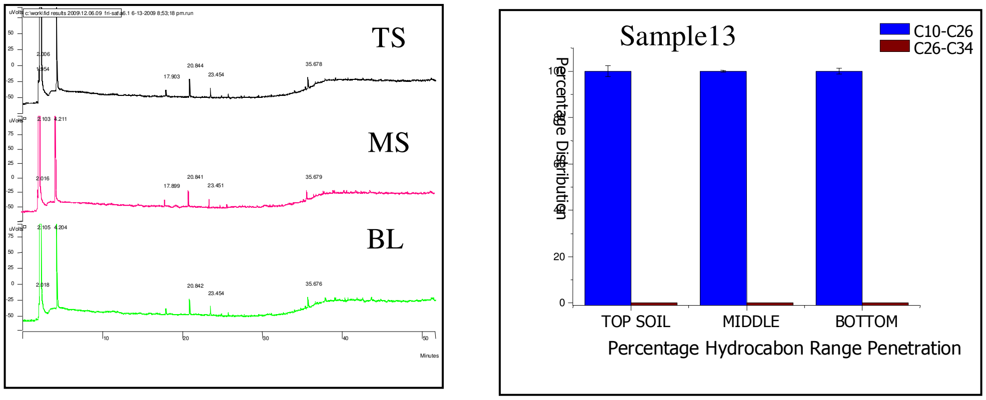

Figure 3. Chromatogram of sample 13 showing DRO penetration in TS, MS and BL on a bar graph.

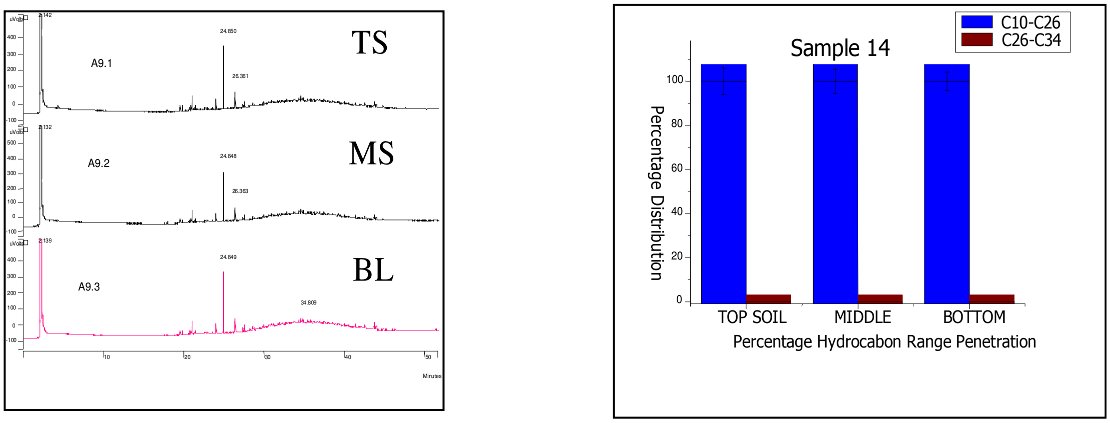

Figure 4. Chromatogram of sample 14 showing DRO penetration in TS, MS and BL on a bar graph.

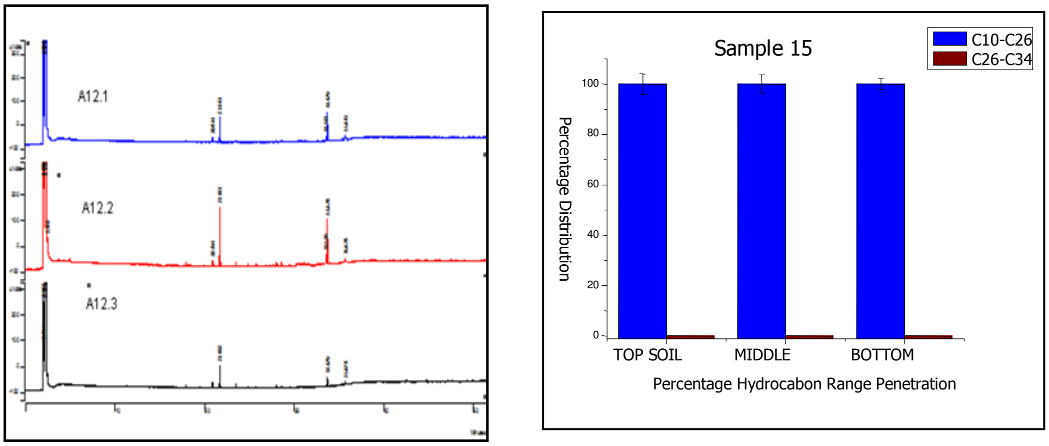

Figure 5. Chromatogram of sample 15 showing DRO penetration in TS, MS and BL on a bar graph.

concentration of 413±7 mg kg^{-1} of total hydrocarbon was recorded in the mid soil, 15-30 cm, (MS) in location 13. No significant level of concentration of total hydrocarbon was observed in the top soil (TS), 0-15 cm of location 7. The overall high concentration in a single sample point occurred in soil location 6 where TS, 0-15 cm had 289±3; MS (15-30 cm) = 213±5 and BL (60 cm) = 178±11 while the least concentration was came up in the next location 7 with TS = 9±5; MS = 11±7 and BL = 10±3. Sample points were chosen randomly and recorded serially as sampling proceeded for the purpose of sample identification.

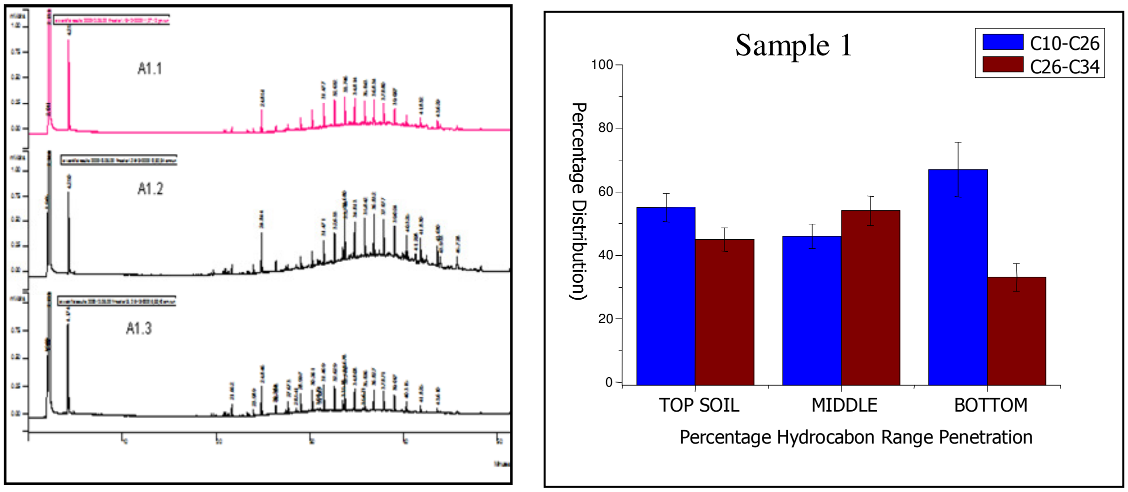

Figure 6. Chromatogram of sample 1 showing DRO and WOO penetration in TS, MS and BL on a bar graph. No presence of GRO within the measured depths.

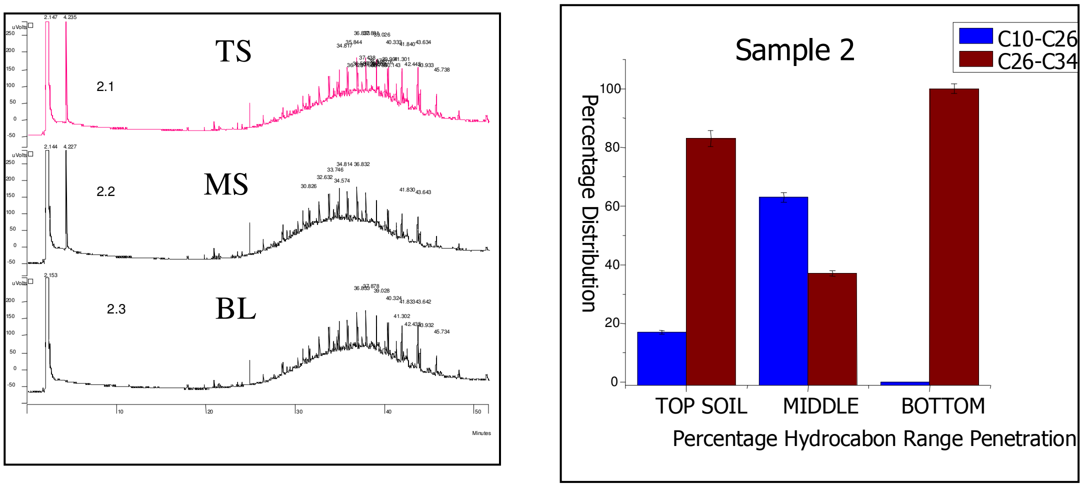

Figure 7. Chromatogram of sample 2 showing DRO and WOO penetration in TS, MS and BL on a bar graph. No presence of GRO within the measured depths.

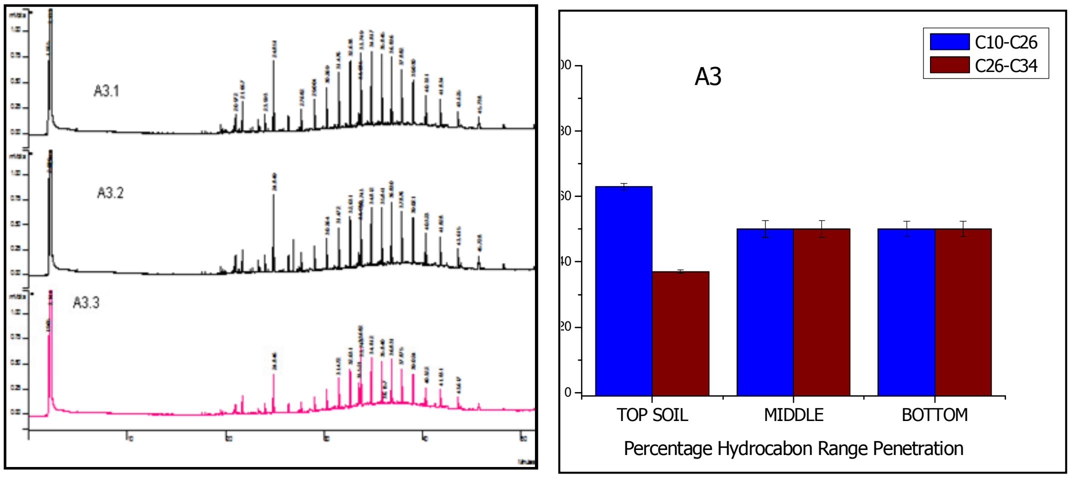

Figure 8. Chromatogram of sample 3 showing DRO and WOO penetration in TS, MS and BL on a bar graph. No presence of GRO within the measured depths.

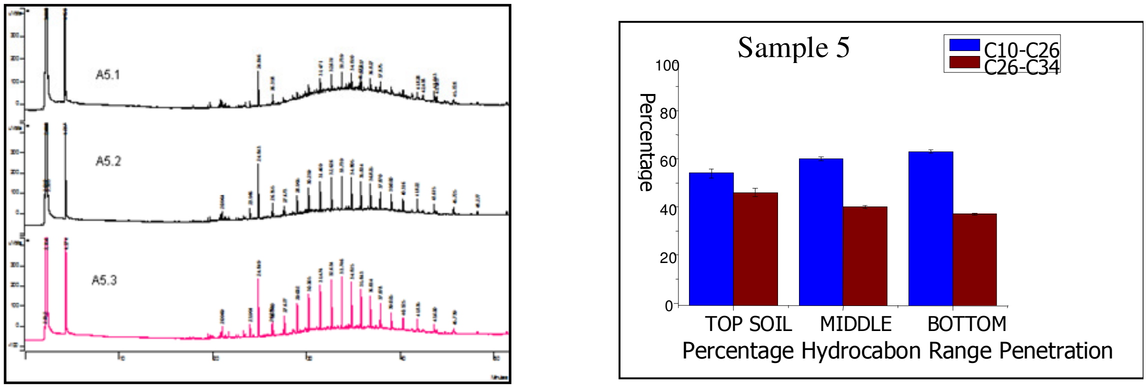

Figure 9. Chromatogram of sample 5 showing DRO and WOO penetration in TS, MS and BL on a bar graph. No presence of GRO within the measured depths.

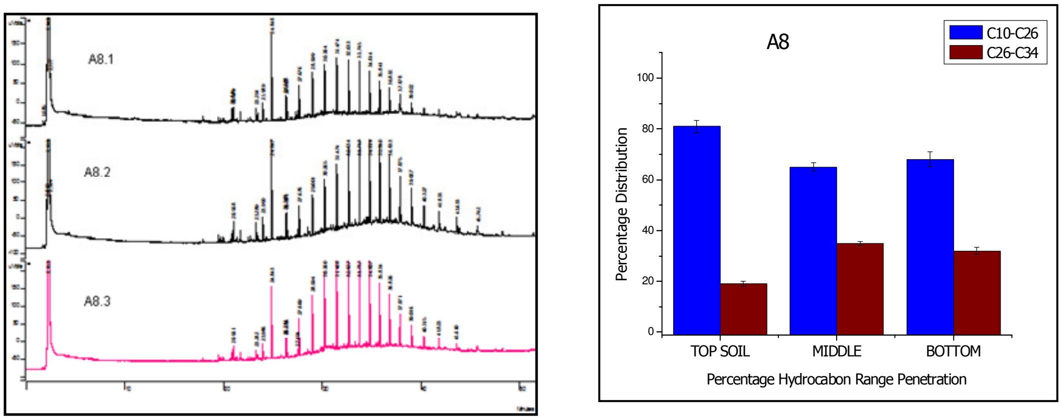

Figure 10. Chromatogram of sample 8 showing DRO and WOO penetration in TS, MS and BL on a bar graph. No presence of GRO within the measured depths.

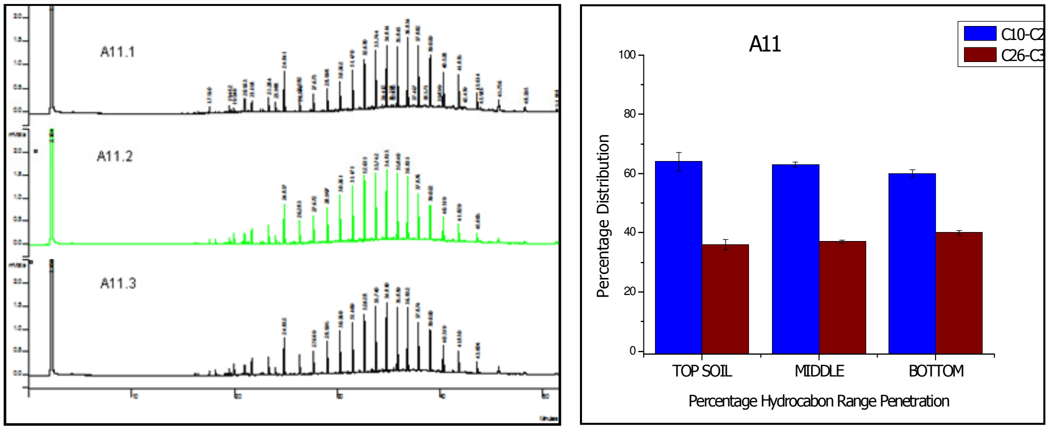

Figure 11. Chromatogram of sample 11 showing DRO and WOO penetration in TS, MS and BL on a bar graph. No presence of GRO within the measured depths.

Control samples were taken from four points with geographical similar but non-spilled areas. Trace concentration of total hydrocarbons was recorded in these areas compared to the high level of contamination recoded in the samples (table 2). High concentration levels of hydrocarbons present in contaminated sites could pose a health risk to humans, plants and animal lives and the entire ecosystem.

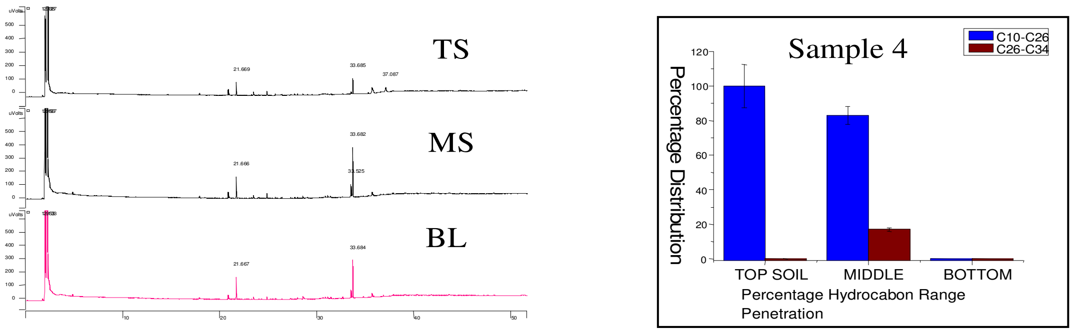

Figure 12. Chromatogram of sample 4 with the bar graph showing DRO dominating TS and MS. Small percentage (18%) of WOO penetrated MS and amount of GRO, DRO or WOO was found at the greatest depth measured.

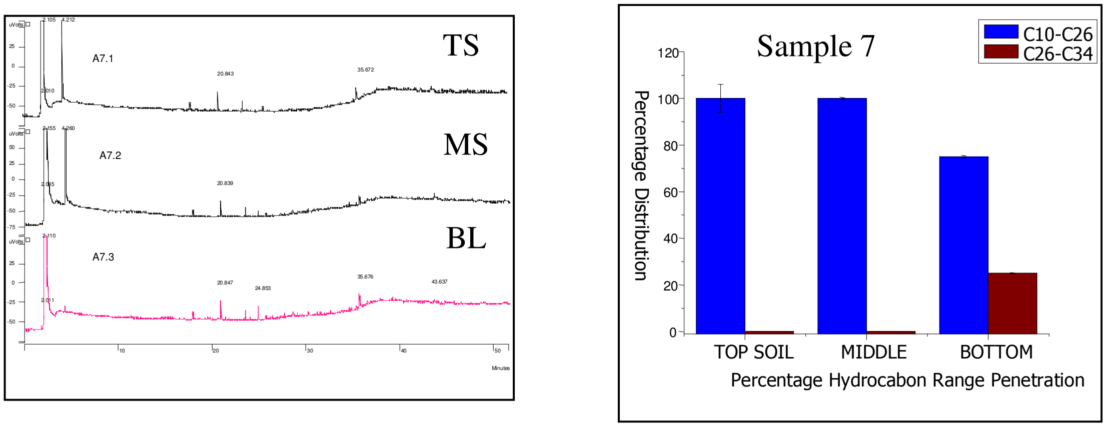

Figure 13. Chromatogram of sample 7 with the 100% presence of DRO dominating TS and MS. 80% of and 20% of WOO occurred in the BL. No significant presence of GRO in all soil levels.

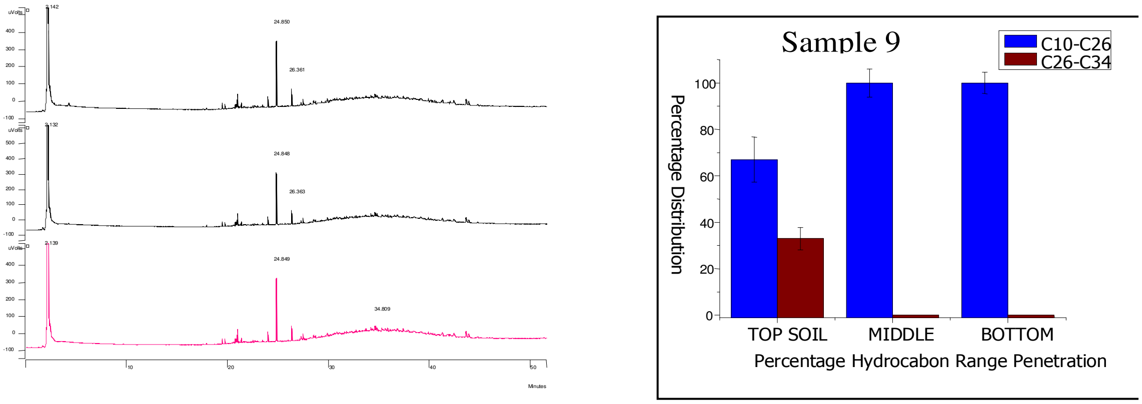

Figure 14. Chromatogram displaying sample 9 with the bar graph showing complete dominance of DRO at MS and BL. Small percentage (32%) of WOO TS and amount of GRO, DRO or WOO was found at the greatest depth measured.

The samples showed elevated concentration of TPHs when compared with control samples in all the sites. The high levels of TPH contamination observed in this study for the crude oil contaminated soils far exceeded the fifty parts per million (50 mgkg^{-1}) compliance baseline limit DPR, 1991) set for petroleum industries in Nigeria. The concentration of TPH at the mid/sub-soil (15-30 cm) depth was higher than the concentration range reported by (Okop and Ekpo, 2012; Ekundayo and Obuekwe, 2004; Iwegbue, et. al) for oil spilled soils of other parts of

Niger Delta and other areas (CCME, 2001; Zhang, et.al,. 2005). The observed inflexible standards enforced around the world are in the range of 100 – 200 mg.kg^{-1} .

The Certified Reference Standard was used in calibrating, identifying and validating the compounds in the analyzed samples. The standard with even numbers of hydrocarbons from C_{10} to C_{40} and instrument sensitivity made separation up to C_{34}.

This work showed types, distribution, migration pattern and penetration levels

of the petroleum hydrocarbon contaminants in the study area. Principal Component Analysis (PCA) using multivariate statistical package MINTAB was adopted to interpret and classify chemical characteristics of the sample. Cluster observation analysis was applied to reveal not only the nature but chemical similarity of the oil contaminants in all the levels as they penetrated the soil strata.

The aim was to fuse the huge chromatographic data into a simple plane graph projection, thereby reducing the amount of data or number of dimensions without losing the integrity and relevant information of the samples (Minitab, 2003). PCA used combined concentration and sample-discrete-identity information while related techniques like Principal Component Regression (PCR) and Partial Least Square (PLS) could only limit its quantification to concentration. Assessment of the penetration capability and distribution of the hydrocarbon contaminants were carried out. This aspect of investigation classified the hydrocarbons into groups based on their degree of penetration within the soil strata.

Basically, three major groups of petroleum hydrocarbons are known, classified and adopted in this work. These are: (i) The Gasoline Range Organics (GRO), generally eluting in window C_5-C_9.(ii) The Diesel Range Organics (DRO) elutes from C_{10}-C_{26} (iii) The Waste Oil Organics (WOO), eluting above C_{26}. The presence and the concentrations of C_5-C_9, C_{10}-C_{26}, C_{26} and above had been identified and computed. The penetration, percentage distribution and migration of these groups of hydrocarbons in the samples were considered. The sample chromatograms representing TS, MS and BL and bar graph representing the percentage penetration is shown side by side

The first group pattern was demonstrated by three (3) sample locations (13, 14 and 15), each comprising of three (3) sampling depths. This group had DRO (100%) as the major contaminant through TS (0-15 cm), MS (15-30 cm) and the greatest depth measured with no significant contribution from Gasoline range organics and Lubricating or waste oil hydrocarbon (WOO) range - C_{26} and above (Figure 3, 4 and 5).

The second group has six samples (1, 2, 3, 5, 8 and 11) exhibiting similar spatial penetration and distribution pattern. This group showed both DRO (C_{10}-C_{26}) and WOO (C_{26} and above) with competitive penetration capacity as represented in Figures 6-11 with DRO having much penetration concentration and no significant presence of GROs.

The third group consists of 3 samples (4, 7 and 9), in which DRO dominates the soil depths with little contribution from the waste oil hydrocarbon (WOO) range - C_{26} and above and the GROs - C_5-C_9, (Figures 12-14).

CONCLUSION

Quantitative assessment of petroleum contaminants in the soil of Niger Delta under the tropical weather conditions was carried out. The concentration range of these contaminants in the spilled site was established. The results in this study revealed that the TPH concentration in the all the levels of soil strata measured ranged from 9±5 to 413±7 mg kg^{-1}. The concentrations and penetration ranges for three groups of TPHs – C_5-C_9 (Gasoline Range Organics), C_{10}-C_{26} (Diesel Range Organics) and C_{26}-C_{34} (Waste Oil Organics) were recognised.

Despite limited information on the migration and depth penetration of hydrocarbons in soils, data from this study revealed the types, distribution, migration and penetration capability of the petroleum hydrocarbon contaminants in the study area.

The spatial distribution and penetration pattern of petroleum contaminants at the investigated site were established as an informative guide to the Government and oil industries during remediation process.

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