Determination of Total Hydrocarbon Content in Soil after Petroleum Spillage

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Abstract-Crude oil spillage contamination of soil from the Niger Delta region of Nigeria was investigated three months after an extensive oil spillage. 60 Soil samples (300 - 500 g) were collected at several points in the South-South region of the Niger Delta. Samples were collected at depths of 0 – 15 cm, 15 – 30 cm and 30 - 60 cm. The soil samples were prepared for analysis using solvent extraction methods, passed through a column of Florisil[®] and sodium sulphate to remove moisture, gross impurities and to aid in column performance. Samples were analysed by gas chromatography fitted with a flame ionisation detector. It was found that total petroleum hydrocarbon concentrations varied from 9 - 289 mgkg⁻¹ topsoil, 8 - 318 mgkg⁻¹ subsoil and 7 – 163 mgkg⁻¹ at the greatest depth measured. The results show elevated levels of total hydrocarbon contents when compared with the reference sites. The findings reveal the need for a holistic and sustainable monitoring and remediation of the environment.

Index Terms— GC-FID, oil spill, petroleum hydrocarbons, soil contamination.

I. INTRODUCTION

 A_{LL} over the world, scientists and environmentalists are faced with the challenge of overcoming the detrimental effects of the contamination of soil, air and water. Large-scale crude oil spills on soil, leakages from pipelines, underground and surface fuel storage tanks, indiscriminate spills and careless disposal and mismanagement of waste and other petroleum by-products of the society, constitute the major sources of petroleum contamination in our environment. It has become a topic of interest and attracted increasing attention because of the carcinogenic, mutagenic and toxic effects [1, 2, 3]. High concentration levels of hydrocarbons present in contaminated sites could pose a health risk to humans, plants and animal lives. In recent years, the release of hazardous and toxic substances into the soil, water, sediment and air in Niger Delta, Nigeria has been a widespread problem [4, 5, 6, 7]. The economy of Nigeria, the most populous, black African country is largely dependent on crude oil tapped from the Niger Delta

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region. Niger Delta has a population of about 30 million and an estimated 2.8 million barrels of crude oil per day come from this region.

Gas chromatography (GC) 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. The popularity of GC is absolutely centred on high selectivity, sensitivity, high resolution combined with good accuracy and precision in a wide dynamic concentration range [8, 19, 10].

Miguel [11] and Akinlua et al [12] have determined and characterised organic pollutants in contaminated soils in Niger Delta crude oils. Replicate digested oil samples were analysed using ICP-MS. Agadi and Al Swaidan [13] used ICP-MS to determine vanadium in crude oil. Application of comprehensive two-dimensional gas chromatography [14] was also adopted for the assessment of oil-contaminated soils. GC-MS has been shown in [15] to be a well-established approach for the analysis of volatile organic compounds in samples. A gas chromatography fitted with flame ionisation detector was employed. The choice of GC-FID over photo ionisation detector (PID) includes the following advantages: (i) FID can cope with high humidity and equally handle very wet samples than PID. (ii) In FID, the flame is capable of ionising large range of volatile organic and petroleum Hydrocarbons than PID, thereby detecting a wide range of Hydrocarbons. (iii). FID is very useful in detecting lower concentrations volatile organics because of its lower detection limits. FID limitations [16] include ability to destroy the sample, detect volatile hydrocarbons from non-petroleum matter and organic material such as methane and peat. The analytical goal for each petroleum spill site is to assess the level of contamination and to efficiently and safely remove the spilled petroleum products from the soil with the aim of returning the soil back to its normal useable form and economic value.

II. MATERIALS AND METHODS

A. Site Selection

The sampling site which covered about 200 x 300 m² was located at Ikot Ada Udo, Ikot Abasi in Akwa Ibom State, South-South of the Niger Delta region of Nigeria (within longitude 7°41'-7.43'E and latitude 4°41' - 4°49' N). At this site, soil and water have been constantly subjected to petroleum spillages and crude oil leakages from a Shell

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marginal oil pipeline called "Ibibio I" - a Well head established in 1954 (Fig. 1). Figure 1 shows the Well head after a recent spillage. All sampling points were measured in metres from the well head as a reference point.



Fig. 1. Crude Petroleum spill on farmland in Ikot Ada Udo village, Akwa Ibom State, South-South of Niger Delta, Nigeria.

B. Sample Collection

An initial survey was carried out on the site prior to sample collection in order to ensure that problems during sampling would be minimised. Soil from various depths on the sample locations were selected to represent areas of contamination resulting from the recent petroleum pipe line spillages. A hand soil auger (Nickel-plated carbon steel, 3^{''} diameter) was used to collect soil samples from the site by taking about 6-10 auger borings at random grid at sampling points to depths of 0 to 15 cm at the surface soil, 15 to 30 cm at middle (subsurface) and bottom layer of 30 to 60 cm.

Four control samples were obtained to determine the background levels of petroleum hydrocarbons in the unaffected soil for comparison with the contaminated site(s). All four control samples were taken on the same day prior to actual field samples. The auger was cleaned with water and rinsed with methanol after each sampling point.

C. Sample preservation, extraction and clean-up

Samples were collected into zip type plastic bags and placed in a 1 L wide mouth glass jars with Teflon lined cap and sealed. Each individual sample was prepared and separately stored in sealed bags. These were put into appropriate containers and stored in the laboratory fridge at 4°C. Soxhlet extraction using a Brinkmann Büchi 461 automated extraction apparatus was used in this work. All samples were extracted using the Soxhlet extraction procedures as outlined in U.S. EPA method 3540 [17] and ASTM method D5369 [18] with slight modifications in the solvent choice and volume, extraction time and size of extraction flasks. Soxhlet extraction really ensures intimate contact of the sample matrix with the extraction solvent and a reasonably large amount of 3-20g sample could be used to allow quantitative extraction. Soxhlet technique is usually the adopted reference and most often used method for a long time. It has been proposed by many agencies [19, 20] as a method of choice for extraction of non-polar organic contaminants. Prior to extraction, the soil samples were homogenised using mortar and pestle to obtain finer texture and to remove sticks, pebbles and rock particles. Approximately 10 g of homogenised dry soil was weighed into a Whatman fat-free extraction thimble and extraction commenced. Dichloromethane (DCM) proved to be the most suitable solvent over hexane, acetone and toluene for this extraction due to its consistency, efficiency and ability of not interfering with BTEX RTW, C5-C9.

Each of the sample extracts was cleaned to remove moisture, polar hydrocarbons, colour interferences and any impurities during GC column analysis. This was achieved by filtering the extract under applied pressure through dual layer 6 mL glass Florisil[®]/Na₂SO₄ SPE Tube 2g/2g. In this work, dichloromethane (99.8%) was used as the extracting solvent; it was supplied by Sigma Aldrich, Germany. Toluene (99.8%), hexane/cyclohexane, methanol (99.9%), heptanes (99%), undecane, tetradecane, pentadecane were all HPLC reagent grades.

Reference standards and calibration mixtures were used for qualitative and quantitative analyses, instrument calibration and validation such as: the kit for the chromatographic determination of hydrocarbon content in soil, mineral Oil standard mixture type A and B for DIN EN 14039 and ISO 16703, alkane standard mixture for the assay of the system efficiency of GC's (C10-C40), and dual layer Florisil[®]/Na₂SO₄ SPE Tube 2g/2g/6mL (Cat. No 40080-1ea-F) supplied by Fluka Analytical, Sigma Aldrich, Switzerland. DRO Mix (Tennessee/Mississippi) was supplied by Restek, USA and hydrocarbon internal standards C14, C15 and verification standards (C10, C11, C14, C15 and TCD) prepared in the laboratory were all HPLC and analytical reference grades.

D.Instrumentation

The determination of hydrocarbons in the soil was performed on the samples and standards using a Varian model BV CP 3800 GC-FID equipped with a split/splitless injection port and Combi PAL auto sampler. All samples were taken into 2 mL chromatographic vial, injected and separated on a Varian Chrompack capillary column CP 5860 with 95% methyl and 5% phenyl-polysiloxane phase, (oven max tempt 350°C), WCOT fused silica, 30 m x 0.25 mm id and 0.25 μ m film thickness with CP-Sil 8 CB low bleeds/MS coating. Carrier gas was helium 26 cm sec⁻¹. Temperature profile during the chromatographic analysis was 50°C for 3 minutes; 8°C/min to 320°C hold 15 minutes and detector at 320°C.

III. RESULTS AND DISCUSSION

A. Method and Validation

Identification and quantification of the samples were based on the comparison of the chromatographic data with the reference standards (alkane and Diesel Range Organics (DRO) mix) as shown in Figures 5 and 6. Quantitative analysis was computed based on [21]. The average percentage recovery was $73.7\% \pm 26$. The average peak values of all the samples were recorded and their standard deviation and % RSD calculated at 95% confidence level.

In Fig. 2, the retention times of the sample (chromatogram 2) were compared with that of the reference standards I (DRO) and 3 (Alkane standard mix, even carbon numbers).

The validation and checking of samples and standards retention times in Fig. 3 allowed the comparison and confirmation of eluted peaks in samples.

The concentrations of the total petroleum hydrocarbon (TPH) of each sample depth at the site are presented in Table 1. The overall level of TPH recorded here in the petroleum contaminated site ranges from 54 ± 7 to 345 ± 4 mgkg⁻¹ (Table 1). TPH concentration for the top soils (15 cm depth) ranges from 55 ± 13 to 302 ± 14 mgkg⁻¹. The middle or sub-soils (30 cm depth) had a concentration range of 54 ± 7 to 345 ± 4 mgkg⁻¹ and a range of 57 ± 4 to 289 ± 15 mg recorded for the 60 cm depths measured. Sample A11 and A3 had high TPH concentration with the middle soil (15-30 cm depth) and sample A11 had the highest value of TPH (345 ± 4 mgkg⁻¹) followed by 294 ± 16 mgkg⁻¹ at the same soil level.

TABLE I
A SUMMARY OF AVERAGE TOTAL HYDROCARBON CONTENT
IN ALL SAMPLES AND CONTROLS

Site	No of	f Sample Mass (g)			Hydrocarbon Content		
	Samples	-			(mgkg ⁻¹)		
	(soil layers)						
		TS	MS	LD	TS	MS	LD
A							
A1	3	10.07	10.03	10.09	104 ± 20	156±25	176±39
A2	3	10.02	10.05	10.03	133±38	66±19	79±15
A3	3	10.04	10.06	10.02	235±5	294±16	163±15
A4	3	10.01	10.02	10.03	77±44	84±18	84±14
A5	3	10.10	10.07	10.10	105±11	88±4	98±3
A6	3	10.03	10.01	10.02	73±2	68±1	57±4
A7	3	10.12	10.13	10.15	70±2	69±3	68±2
A8	3	10.20	10.25	10.23	55±13	54±7	59±12
В							
B1	3	10.30	10.25	10.26	113 ± 18	237±6	159±8
B2	3	10.08	10.09	10.05	109±5	123±13	104±7
B3	3	10.30	10.20	10.22	302 ± 14	345±4	289±9
B4	3	10.05	10.07	10.08	62±13	76±5	59±8
B5	3	10.02	10.05	10.07	125±5	116±2	103±5
B6	3	10.08	10.03	10.04	98±12	66±4	63±6
B7	3	10.14	10.16	10.18	287±4	229±6	189 ± 2
B8	3	10.02	10.02	10.	88±14	71±3	93±2
C (cor	trol samples)						
C1	3	10.02	10.05	10.03	0.0	0.0	0.0
C2	3	10.02	10.05	10.03	0.0	0.0	0.0
C3	3	10.02	10.05	10.03	0.0	0.0	0.0
C4	3	10.02	10.05	10.03	0.0	0.0	0.0

TS = top soil; MS = middle soil; LD = last depth

The lowest depths (60 cm) in most of the samples recorded had significantly low values of TPH though concentrations of total petroleum hydrocarbons did not decrease generally with depth as pointed out by [4, 5]. The concentration of TPH at the middle/sub-soil (15-30 cm) depth was higher than the concentration range reported by [4, 6, 7, 22] for oil spilled soils of other parts of the Niger Delta region. However, no significant level of TPH was recorded for the control soil samples taken from similar geographical non-spilled areas. The samples showed elevated concentrations of TPHs when compared with control samples in all the sites. The high levels of total petroleum hydrocarbon contamination observed in this study for the spilled soils are comparable to levels obtained by [5, 23, 24] and far exceeded the fifty parts per million (50 mgkg⁻¹ or ppm) compliance baseline limit [25] set for petroleum industries in Nigeria. These studies show that about 1 to 100 mgkg⁻¹ of TPH contents were found in soils [5, 26, 27, 28]. In another study [22, 23, 29, 30], the TPH concentration in soil was reported between 100 to 500 mgkg⁻¹. Some publications [4, 31, 32, 33], reported the amount of TPH in soil to vary considerably by a few thousand mgkg⁻¹.

IV. CONCLUSION

This work attempted to classify the hydrocarbons penetration in the soil depths according to their chemical similarities thereby providing informative guidelines to the type of bioremediation procedures envisaged. Methods were developed and validated for GC-FID analysis of petroleum contaminated soil. The results showed a total petroleum hydrocarbon level of about 318±4 mgkg-1. Experimental stages involved in the work were collection of soil samples (sampling), preservation, storage of samples and extracts, = extraction and clean-up of extract and GC-FID method of analysis. The instrumentation process occurred in phases. Gas _ Chromatography (GC-FID) was used. All samples were taken - into 2 mL chromatographic vial, injected and separated on a Varian Chrompack capillary column with 95% methyl and 5% phenyl-polysiloxane phase, WCOT fused silica, 30 m x 0.25 mm id x 0.25µm. Oven temperature programming for the chromatographic analysis was 50°C for 3 min; 8°C/min to 300°C hold for 15 min. Detection was at 300°C.

The findings obtained from this work revealed that the GC-FID analysis of the petroleum contaminated soil extracts using the optimised methods yielded higher concentrations of petroleum hydrocarbons than the control soil samples. The smallest concentration of hydrocarbon was recorded in the deepest level of soil measured while greatest concentration occurred in the middle soil level. The increased concentration of hydrocarbons in the middle soil is critical to plant and animal lives. This study provides vital information to the State Government (Ministry of Environment and Natural Resources) and the oil industries for monitoring further spills. Furthermore, it provides quantitative and qualitative objective data for planning a suitable remediation activity. The results obtained from this work portrayed that bioremediation would be the recommended choice of sustainable environmental remediation. Moreover, this work promises to enhance lunar mission applications where gas chromatography techniques will be applied in interplanetary missions involving deep space sample analysis.







Fig. 3. Sample (chromatogram 4) was compared with the reference standards (chromatograms 2 and 3) and other laboratory standards (chromatograms 1, 5 and 6) for confirmation of eluted peaks in samples.

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