
CHEMOMETRIC DETERMINATION OF CHEMICAL AND PHYSICAL ASSORTMENT OF TOTAL HYDROCARBONS WITHIN CRUDE OIL SPILLED SOIL

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Abstract: *Soil and water contamination resulting from petroleum spill is a regular environmental concern in recent times. The level of penetration and movement of C₅-C₉, C₁₀-C₂₆ and C₂₆-C₄₀ hydrocarbons through the soil layers were assessed to determine the distribution and the chemical similarity of these compounds over the contaminated area. A suppllicated Chemometric technique was employed in this analysis whereby Principal Component Analysis (PCA) was adopted to interpret and classify chemical characteristics of the samples by Cluster analysis. Samples were analysed using gas chromatography equipped with a flame ionisation detector (GC-FID). It was also found that total petroleum hydrocarbon concentrations varied from 11-402 mg kg⁻¹ topsoil, 9-337 mg kg⁻¹ subsoil and 13-184 mg kg⁻¹ at the greatest depth measured. The results indicated high levels of total hydrocarbon contents when compared with the controlled samples. This work provides informative strategy to control further spills and choose the type of remediation processes to adopt.*

Key words: petroleum spill, total hydrocarbon, chemometric analysis and GC-FID.

INTRODUCTION

Public awareness of environmental issues has increased in recent years, particularly when contamination of soil, water and air is involved (Okop et al (2012); Edward and Paul (1993); Jose et al (2006); Bosco et al (2005). Recently, oil spillages (Jorge et al (2012); ITOPF (2012) accompanied by its devastating effects (Tamburlini et al (2002); Freitag et al (1985); Spoon (ed), (1998), instead of being controlled is sometimes not abated. Till today, no one has fully known the impact of the damaging and cumulative effects of petroleum contamination and pollution on the plants, animals and human beings as a result of crude oil spills on soils.

The frequency, magnitude and seriousness of environmental health problems caused by petroleum contamination is enormous. Therefore, the major task facing the Niger Delta region lies on identification, assessment, evaluation (Alain et al (2006); Hendrik et al (2006) and remediation (Perfumo et al (2007); Hinchee et al (1995) of the petroleum contaminated sites and a follow-up of the health-related actions and observations. The public health risk associated with constant exposure to these types of contaminants calls for evaluated data and information on: (a) Types of contaminants in the environmental media (b) Detected levels of concentrations of the contaminants (c) Location and migration of these contaminants within the impacted soil (d) Effect on the ecosystem, human and plant lives (e) Preventive measures and remediation action.

This paper describes the development, optimization and analysis of extracts from petroleum-contaminated soil samples using Gas Chromatography fitted with a flame ionization detector (GC-FID). This study sought to establish the concentration of the contaminants, assess the penetration and migration of C₁₀-C₂₆ and C₂₆-C₃₄ hydrocarbons through the soil layers and apply cluster observation analysis to characterize chemically similar hydrocarbons and to determine the spatial distribution of these compounds over the contaminated area. This information would be usefully employed in actions taken to ensure that cleanup is effectively carried out and to combat the contaminants through bioremediation process monitored by licensed site remediation professionals. Bioremediation provides a good cleanup strategy for some types of pollution involving hydrocarbons in petroleum spilled soils.

MATREIALS AND METHODS

Materials and Methods:

Certified reference standards used were BTEX Mix (benzene, toluene, ethylbenzene and xylene) for Gasoline Range Organics (GRO), catalog No. 47993 supplied by Supelco analytical, Bellefonte, PA, USA; Kit for the chromatographic determination of hydrocarbon content in soil according to DIN ISO 16703 and in waste according to EN 14039 comprising of the following: Standard solution for the determination of the retention time window (RTW), cat. No. 67583; Mineral Oil standard mixture type A and B for DIN EN 14039 and ISO 16703 (cat. No. 69246); Alkane standard mixture (cat. No. 68281) for the assay of the system efficiency of GC's (C₁₀-C₄₀); Heptane, Puriss. p.a (cat. No. 51745) and Dual layer Florisil[®]/Na₂SO₄ SPE Tube, 2g/2g/6mL (Cat. No 40080-1ea-F) all supplied by Fluka Analytical, Sigma Aldrich.

Diesel Range Organics (DRO) Mix (Tennessee/Mississippi), catalog No. 31214, Lot No. AO62141 was supplied by Restek, PA, USA. Hydrocarbon verification standards (C₁₀, C₁₁, C₁₄, C₁₅ and TCD) prepared in the laboratory were all HPLC and of analytical reference grades.

Sample Collection:

The most crucial step in the procedure of analysis of organic contaminants in soils and sediments of our environment starts with sampling (IUPAC (1990); Alain et al (2006). A sampling site was located in Ikot Ada Udo, Ikot Abasi in Akwa Ibom State, South-South Niger Delta, Nigeria. At this site, soil and water have been repeatedly subjected to petroleum spillages and crude oil leakages from the Shell marginal oil pipeline. Three sub-samples were collected at each sampling point at the designated depths. 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 top soil, 15 to 30 cm at middle (sub-surface) and bottom level of 30 to 60 cm. About 500g of labeled petroleum contaminated soil samples were collected into zipped plastic bags and put into a glass jar sealed with Teflon lined cap. Control samples taken on the same day prior to actual field samples were obtained to determine the background levels of petroleum hydrocarbons in the unaffected soil for comparison with the contaminated site(s). The auger was cleaned with de-ionized water and rinsed with methanol (99.9%) after each sampling point.

Sample Preparation, Preservation and Transportation:

The entire sampling exercise was carried out in one day. All the real and control samples were placed in icebox and transported to the laboratory. The samples transported to United Kingdom for analysis by the chemical shipping agent with full special shipping procedures (ASTM (2005) for transporting and handling these types of samples. Storage was done at 4°C until analysis was completed in two weeks. The average ambient temperature was 28°C. The soil samples were homogenised using mortar and pestle to obtain finer texture and to remove sticks, pebbles and rock particles.

Sample Extraction:

Soxhlet extraction using a Brinkmann Büchi 461 automated extraction apparatus was used in this work. Soxhlet extraction is a U. S. EPA (USEPA (1996) and ASTM (Annual Book of ASTM Standard (2005) approved method for semivolatile and non-volatile organic contaminants from solid materials such as soil. This procedure involves extraction of the petroleum contaminants from about 10g weight of dry oil-spilled soil with a suitable solvent. Soxhlet extraction really ensures intimate contact of the sample matrix with the extraction solvent and a reasonably large amount of 2-20g 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 (Draft (1995); Berst et al (1991) as a method of choice for extraction of non-polar organic contaminants. In this work, dichloromethane (DCM, 99.8%) used as the extracting solvent was supplied by Sigma Aldrich.

The choice of this extraction method amidst other recent extraction techniques includes its peculiar application, availability in the laboratory and the ease of setting up with minimal or no cost. Its drawbacks include delayed extraction period and use of appreciable volume of solvent.

Optimum extraction time of about 2.5 hours was established using dichloromethane DCM after comparing with other solvents such as methanol, hexane, acetone, toluene and ethyl benzene or the mixture. DCM proved to be the most suitable solvent over hexane, acetone, toluene and ethyl benzene for this extraction due to its consistency, efficiency and ability of not interfering with BTEX retention time window (RTW) - C₅-C₉. This was indicative that Tropical soil in south-south Niger Delta favoured efficient extraction with DCM as solvent.

Sample Clean-up:

Sample clean-up was done 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 Florisil[®]/Na₂SO₄ SPE Tube 2g/2g. The aim is to remove colour interferences, moisture, impurities and polar hydrocarbons. The clean-up procedure effectively removed hydrocarbons of natural origin and did not have any significant effect on the amounts of petroleum hydrocarbons present.

RESULTS AND DISCUSSION

Data Analysis

All data generated from the GC instrument were recorded into the proprietary Varian Star™ software that automatically saved the experimental information into the Microsoft Excel File format. Microsoft Excel software was subsequently used to process the data shown in this work. Basically, the information needed from the experimental data was, sample identity, retention time and sample concentration (expressed as the peak area counts). Replicate analysis was necessary to establish reproducibility and ensure good precision of the analysis.

Multivariate Analysis

The chemical information generated from this work was inherently multivariate meaning that more than one measurement or variable were made on a single sample. Statistical evaluation was done to determine the chemical similarity of the petroleum hydrocarbon contaminants by pattern recognition using cluster analysis. Cluster analysis of observations was the powerful and useful tool adopted to establish the existence of closely related classes. Cluster analysis of petroleum hydrocarbons was carried out by considering correlated variables ranging from the concentration of the samples to actual identity of the samples.

Cluster observation analysis was applied to all the sample levels using Total petroleum Hydrocarbon (TPH) as a parameter to assess the chemical similarities and or otherwise of the contaminants. Minitab software -Eigen value (**Scree**) plot displayed Eigen value profiles associated with a principal component versus the number of components as seen in figure 1. The aim was to fuse the huge chromatographic data into a simple line or plane graph projection, thereby reducing the amount of data or number of dimensions without losing the integrity and relevant information of the samples (Miller and Miller (2005)). Principal Component Analysis (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 parameter. Average sample peak areas were normalized and transposed using Minitab software. PCA was used to compute the correlation and covariance matrices to establish the principle components of all samples.

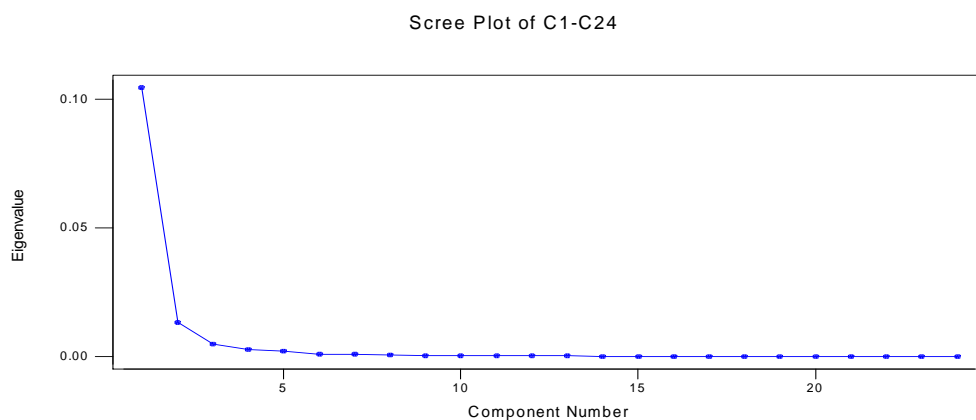


Figure 1: PCA Scree plots of the Eigen value and the principal components

Clustering of observations was applied with the complete linkage method, squared Euclidean distance, and standardization to bring out the different clusters.

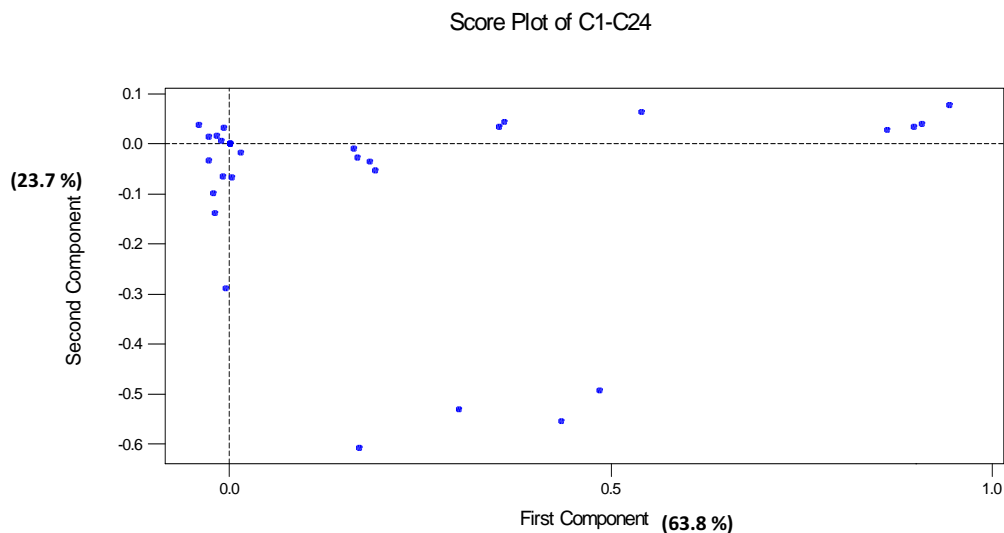
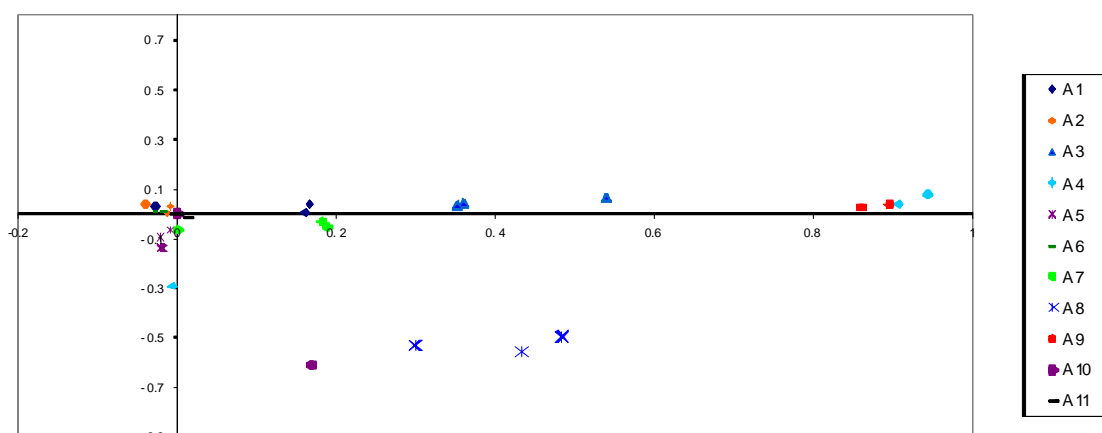


Figure 2 : Score plot of PC1 (96 % variance) and PC2 (36 % variance) of all samples.

Cluster analysis was achieved by using sample information in PC1 and PC2 and plotted in excel. A **score** plot was carried out to check the scores for the second principal component (**y-axis**) versus the scores for the first principal component (**x-axis**) and values for all samples. 11 samples had 33 dots for the three depths of top, middle and bottom levels (figure 2). The aim was to identify the hydrocarbons with similar chemical characteristics which were initially unknown. The data was transposed into excel to bring out the individual sample and their depths (figure 3).



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Figure 3: Score plot data transposed into excel format to bring out the individual sample points.

The samples close or similar to each other were successfully clustered together when they were initially unknown. The choice of final grouping (Figure 4) was made viewing from the above clustering statistics.

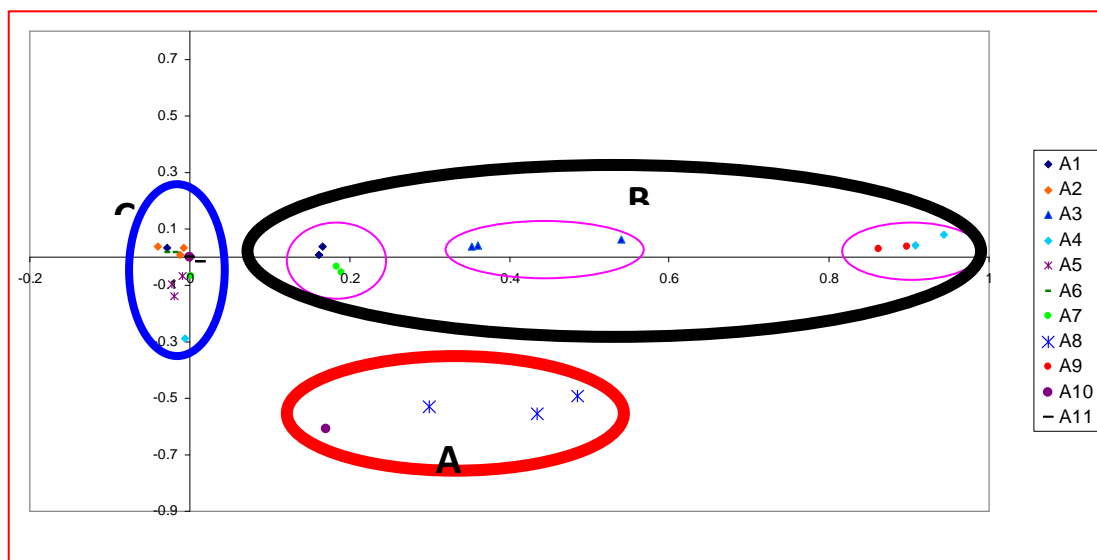


Figure 4: Cluster pattern for samples. Three main clusters were identified as represented with red (A), black (B) and blue (C) circles.

In figure 4, three main clusters were identified; namely, the clusters marked, **A** (red), **B** (black) and **C** (blue) circles. The clusters attempted to classify the samples into similar chemical characteristics without losing their integrity. Samples A8 and A10 in the red circle were classified as being chemically similar. The black circle formed close clusters of sample A1 and A3 similar in characteristics. Samples A2, A4 and A7 are similarly collected together in group 3 to form similar hydrocarbons present in that soil depths. The cluster observation of chemically similar samples was also displayed by group C, the blue circle. In this group, sample A5 & A11 were patterned alike as sample A6 and A9 formed the same cluster.

A dendrogram with cluster observations and cluster variables were produced to confirm the similarity groupings of the sample. The dendrogram cluster analysis of the oil-spilled soils was analyzed using TPH variables to characterize the samples into groups of chemical similarity. This high resolution dendrogram graph also identified three similar clusters inherent in the samples as seen in figure 5.

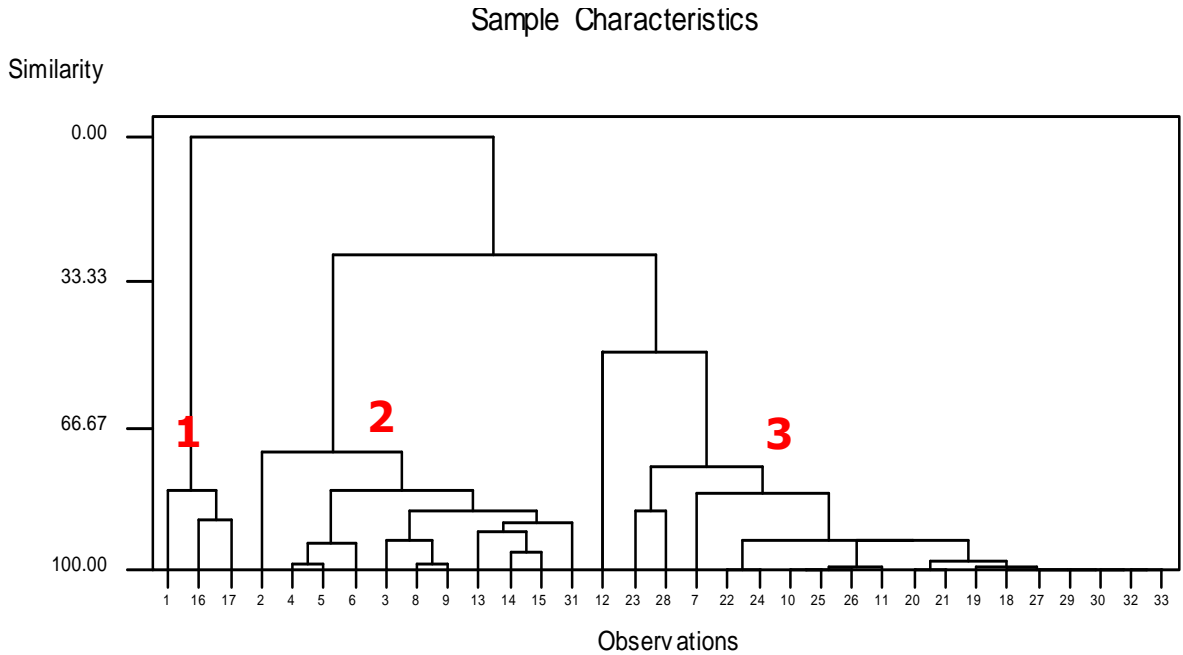


Figure 5: Dendrogram analyses of TPH cluster observations and variables in the spilled soil confirms the similarity groupings of the sample .

A dendrogram with cluster observations and cluster variables were also produced to show distance observation distribution of the individual samples and plotted using Minitab software (Figure 6). The distribution of samples relative to the distance from the sampling reference point also portrays similar hydrocarbon groupings displayed as a tree diagram below

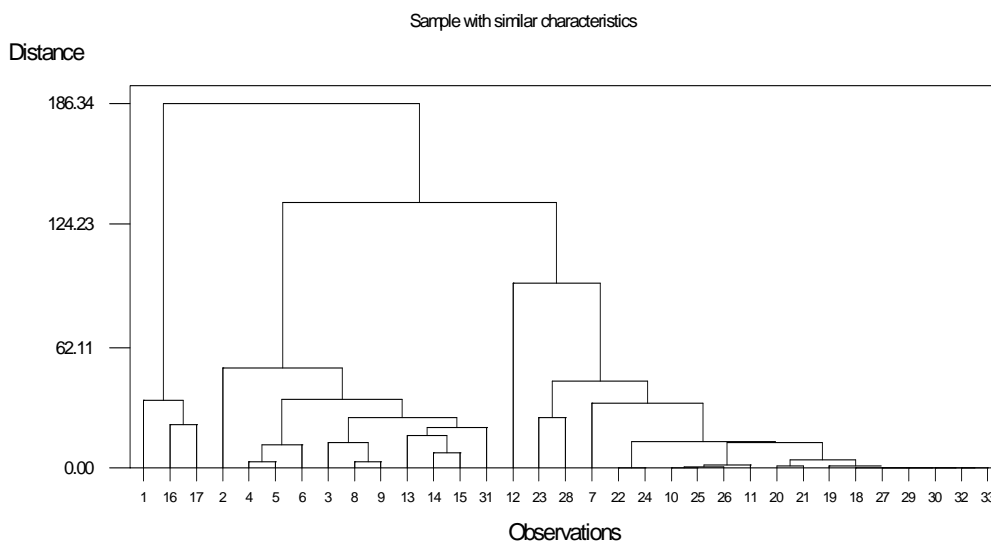


Figure 6: Distance - dendrogram analyses of TPH cluster observations in the site confirms the similarity distribution of the samples relatively.

Elevated levels of petroleum Hydrocarbons were recorded in all the depths measured. The top soil (TS) had ($402 \pm 3 \text{ mg kg}^{-1}$), mid soil recorded ($337 \pm 5 \text{ mg kg}^{-1}$) and ($184 \pm 9 \text{ mg kg}^{-1}$) was found in the deepest level measured (BL).

Table 1: Samples concentrations (mg kg^{-1}) levels of Petroleum Hydrocarbons at the site.

Sample Location	No of depths	Average Peak Area (mV*sec)			Hydrocarbon Concentration (mg kg^{-1})		
		TS	MS	BL	TS	MS	BL
1	3	422	562	306	97 ± 10	113 ± 2	86 ± 11
2	3	581	607	512	114 ± 3	104 ± 5	99 ± 9
3	3	773	332	264	139 ± 7	76 ± 12	55 ± 9
4	3	81	311	58	33 ± 8	75 ± 6	14 ± 12
5	3	211	174	202	59 ± 5	44 ± 4	54 ± 11
6	3	2223	1842	987	402 ± 3	215 ± 5	184 ± 9
7	3	44	53	47	11 ± 6	9 ± 13	13 ± 7
8	3	881	1643	695	137 ± 4	206 ± 2	117 ± 8
9	3	795	381	432	142 ± 27	64 ± 16	75 ± 29
10	3	204	219	187	41 ± 14	52 ± 12	37 ± 2
11	3	339	269	972	59 ± 5 173 ± 10		64 ± 8
12	3	101	232	98	17 ± 21 15 ± 19		26 ± 21
13	3	653	2081	583	132 ± 12 121 ± 17		337 ± 5
14	3	247	231	342	55 ± 11 76 ± 21		52 ± 13
Control Samples							
15 0.0	3	0.0	0.0	0.0		0.0	0.0
16 0.0	3	0.0	0.0	0.0		0.0	0.0
17	3	0.0	0.0	0.0		0.0	0.0

0.0

TS = Top Soil; MS = Mid Soil; BL = Bottom Level

Total Petroleum Hydrocarbon (TPH) concentration for the top soils (15 cm depth) ranges from 11 ± 6 to 402 ± 3 mg kg^{-1} . The middle or sub-soils (30 cm depth) had a concentration range of 9 ± 13 to 337 ± 5 mg kg^{-1} and a range of 13 ± 7 to 184 ± 9 mg kg^{-1} recorded for the 60 cm depths measured. No significant level of TPH was recorded for the control soil samples taken from similar geographical non-spilled soil. These levels are comparable to levels obtained by (Okop and Okorie (2013); Onianwa (1995) and study (Okop (2010); Iturbe et al (2004) The high levels of total petroleum hydrocarbon contamination observed in this study for the spilled soils far exceeded the fifty parts per million (50 mg kg^{-1}) compliance baseline limit (DPR (1991) set for petroleum industries in Nigeria.

This work attempted to group together the hydrocarbons with similar characteristics and indicated their penetration pattern within the spilled site. This provides useful information to the Oil companies and the Federal Government to plan suitable clean up method and choose type of remediation action.

CONCLUSION

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. This work showed types, distribution, migration pattern and penetration levels of the petroleum hydrocarbon contaminants in the study area.

This research has shown that it was possible to use the validated GC-FID method to qualitatively and quantitatively assess the TPH content in the crude oil spilled soils and also exploit the use of Chemometric cluster analysis to group the hydrocarbons with similar chemical characteristics. The results could not provide conclusive evidence of either the presence or absence of contamination by liquid hydrocarbons beyond C_{34} (tetratriacontane) due to the limitation of the instrument parameters.

A physicochemical study of all the sites is recommended to identify the remediation measures that could be implemented based on the type and extent of contamination reported in this work.

The unacceptable risks (Marianna (2006); Hrvoje (2006); Environmental agency (2003) to human health and the environment resulting from the release of petroleum hydrocarbons to the soil, ecosystem, water resources, property and other environmental receptors should be urgently addressed and appropriately managed.

Despite limited information on the migration and depth penetration of hydrocarbons in soils, data from this study showed hydrocarbon concentrations and their penetration capability. There is scarcity of data on Chemometric cluster classification of TPHs, data recorded in this work attempted to classify the hydrocarbons penetration in the soil depths according to their chemical similarities thereby providing vital informative guidelines to the State Government (Ministry of Environment and Natural Resources) and the oil Industries for monitoring further spills and largely to plan for a suitable clean up and remediation activity.

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