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Chemical fingerprinting and diagnostic ratios of Agbada-1 oil spill impacted sites in Niger Delta, Nigeria

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M.C. Onojake *, C.O. Anyanwu, G.N. Iwuoha

Petroleum Chemistry Research Group, Department of Pure and Industrial Chemistry, University of Port Harcourt, P.M.B 5323 Choba, Port Harcourt, Nigeria

Abstract Detailed compositional analysis by gas chromatography–flame ionization detection (GC–FID) was employed to elucidate an oil spill in the Niger delta by fingerprinting technique. Distribution patterns of normal alkanes and isoprenoids show nC_8 to nC_{40} petroleum hydrocarbons. The diagnostic ratios such as Pr/Ph ranged from 1.52 to 2.17; Pr/nC_{17} ranged from 0.31 to 0.51; Ph/nC_{18} ranged from 0.14 to 0.99; nC_{25}/nC_{18} ranged from 0.93 to 3.52; CPI ranged from 0.97 to 1.13; $(Pr + nC_{17})/(Ph + nC_{18})$ ranged from 1.10 to 2.25; Ph/anth ranged from 0.28 to 1.11; BaA/Ch ranged from 0.57 to 2.90; Fl/Py ranged from 1.24 to 2.90. The ratio Fl/Py which is greater than unity (>1) is an indication of the petrogenic source of PAHs. Statistical analyses such as principal component analysis and cluster analysis were also applied as supporting tools. PCA loadings and scores plots carried out on selected parameters obtained from the analysis of the oil spill show that PC1 and PC2 together represented 95.4% (55.8% and 39.6% respectively) of the variability. The high similarity level of the results obtained from the cluster analysis which is 98%, shows that the spilled oil originated from a common source.

1. Introduction

Oil spill has become a global problem, both in developing and industrialized countries. This is because million of gallons of oil is spilled into marine waters and onto soil by tankers, barges, vessels, and from land pipelines. The oil spill causes extensive damage to marine life, terrestrial life, human health, and natural resources [1].

Fingerprinting techniques require using a gas chromatograph in analyzing the spilled crude oil for hydrocarbon fractions which include Total Petroleum Hydrocarbon TPH, benzene, Toluene, ethyl benzene and xylene (BTEX), polycyclic aromatic hydrocarbons (PAH) present in oil [2].

* Corresponding author. Tel.: +234 8035404696.
E-mail addresses: ononed@yahoo.com, mudiaga.onojake@uniport.edu.ng (M.C. Onojake).

Chemical fingerprint represents the relative concentration of compounds present in the analyzed oil. This is usually represented in a chromatogram which is obtained on completion of the analysis with a hydrocarbon range from C_2– to –C_{45}. It shows the components of the analyzed oil and these components can be used in calculating various diagnostic ratios.

Several instrumental and non-instrumental techniques have been employed in analysis of spilled oil on the impacted site. Some of these techniques which are currently used in the analysis of crude oils, and oil spill include hydrocarbon fingerprinting or gas chromatography (GC), gas chromatography – mass spectrometry (GC–MS), high performance chromatography (HPLC), thin layer chromatography (TLC), and ultra violet (UV) spectroscopy [1,3,4].

Gas chromatographic technique has been used successfully in the determination of hundreds of hydrocarbons and other organic compounds including Total Petroleum Hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAHs). It is an ideal tool in analyzing gas and liquid samples, thus allowing the researcher to identify both the type of molecular species present, their concentrations, and also obtain information from hydrocarbon samples (free product) by determining the composition of the hydrocarbons present [5,6].

2. Materials and methods

2.1. Description of sampling site

The study site, Agbada oil field falls within latitude 6° 490′E to 7° 530′E and longitude 4° 470′N to 5° 1430′N (Fig. 1). It is a moderately populated sub-urban environment in Ikwerre Local Government Area of Rivers State, Nigeria. Agbada is vulnerable to crude oil pollution due to the network of pipelines connecting Rumuekpe and Ibaa communities located in the outskirts of Port Harcourt City in Rivers state. This is a source of crude oil leakage into the environment. At the time of the sampling, the total quantity of crude oil spill was not known.

2.2. Field reconnaissance and sampling

Field reconnaissance was carried out to delimit the area to be sampled. Sampling used the grid method reported by [7]. Six replicate soil samples were collected from the surface and subsurface at depths of 0–15 and 15–30 cm, respectively, using a hand auger. The soil samples were transferred into acid-
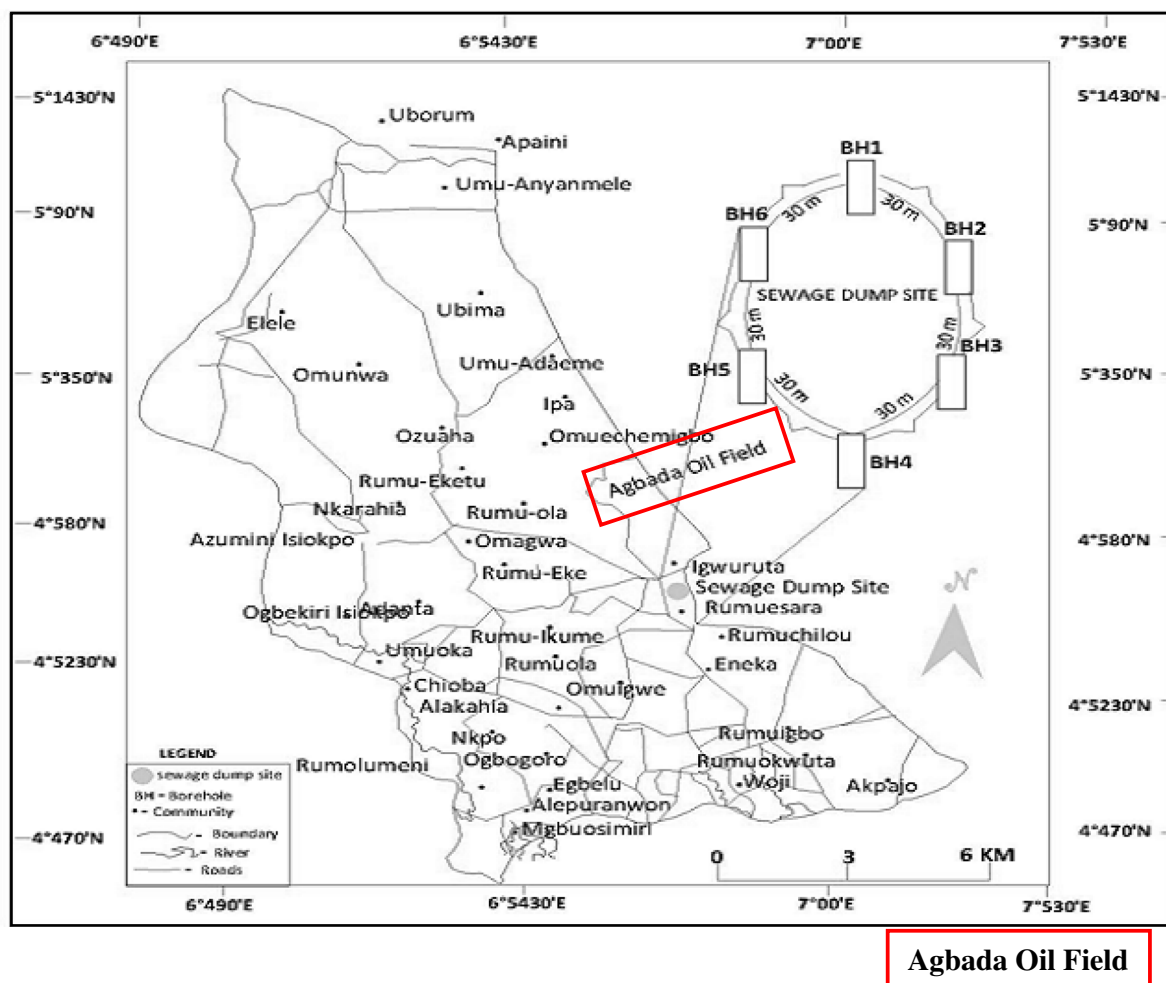

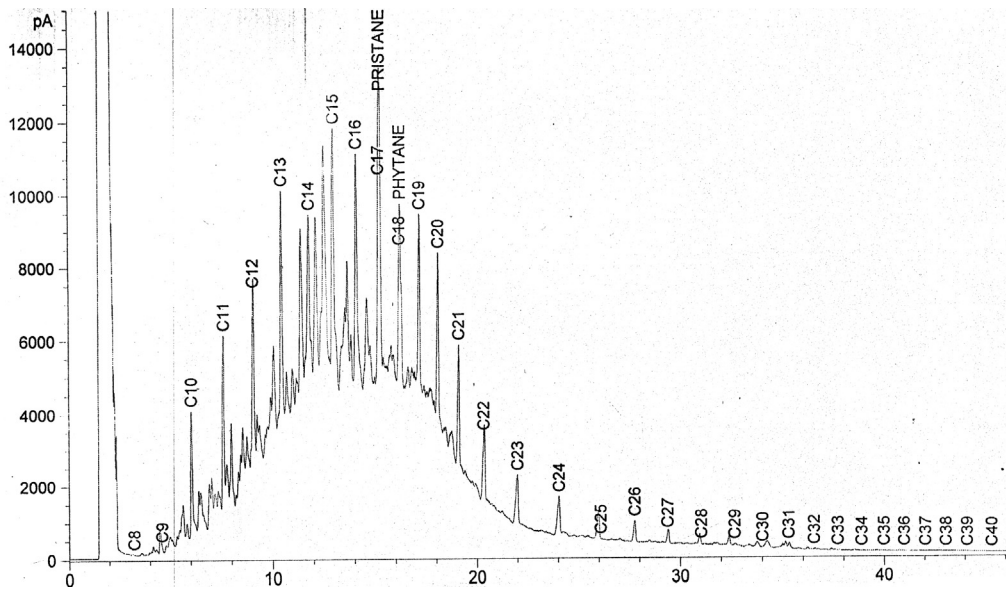**Figure 1**   Map of study area showing Agbada oil field.

Figure 2 Representative fingerprints showing TPH fractions of the samples.

washed polyethylene bags and taken to the laboratory for analysis

2.3. Sample preparation and whole – oil gas chromatographic analysis

Five grams (5 g) of oil spill soil samples were weighed into a clean dry beaker. 10 ml of hexane was used for the extraction of the soil samples. The sample was filtered with watchman filter paper and sent to the laboratory for gas chromatographic analysis.

The crude oil extract from soil samples were subjected to whole oil–gas chromatographic analysis (nC_8 through nC_{45}), TPH and PAHs. This was performed on a Hewlett–Packard (HP) 5890 gas chromatograph equipped with a flame-ionization detector (FID) and an HP 7683 autosampler. The sample (1 μL) was injected in splitless mode by means of syringe through a rubber septum into the column. Detector
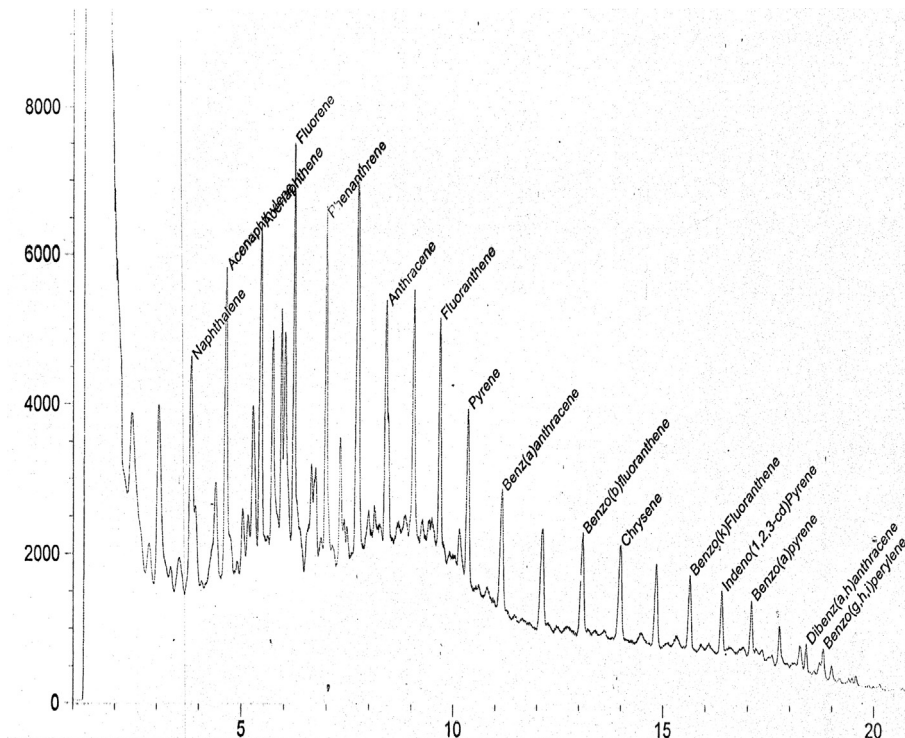

Figure 3 Representative fingerprints showing PAHs fractions of the samples.

(FID) and injector temperatures were kept at 250 and 280 °C respectively. The oven temperature was programed from 60 to 280 °C at 4 °C/min with an initial hold time of 1 min and a final hold time of 15 min. Helium at a linear velocity of 2 mL/min was used as carrier gas. The data were collected from a retention time of 0–71 min [6].

2.4. Statistical analysis of data

Multivariate statistical analysis such as Hierarchical Cluster Analysis (HCA) and principal component analysis based on factor analysis (PCA/FA) was applied in conjunction with quantitative oil analysis data to increase the precision of obtained analytical data to differentiate similar oils. Some of statistical analysis that has been used include principal components analysis, discriminant analysis and cluster analysis. The principal components analysis (PCA) is the most widely used multivariate analysis technique. It is used to transform original sample composition data into new, smaller and uncorrelated variables called principle components. For data sets with a large number of interrelated variables, PCA is a powerful tool for analyzing the structure of the data and reducing the dimensionality of the pattern vectors. The hypothesis is based on expressing the total variance of the variables with two factors, accounting for the maximum variance of the variables [1,8–10,11].

The multivariate statistical method makes it easy for the relationships between multiple samples and variables (diagnostic ratios) to be resolved and visualized using score and loading plots. It is widely employed in environmental studies for grouping different parameters in order to recognize pollution sources. HCA used in the study was calculated using Ward's method where cluster membership is assessed by calculating the total sum of squared deviation from the mean of a cluster by using square Euclidean distance formulae. Multivariate statistical methods such as Hierarchical Cluster Analysis (HCA) and principal component analysis (PCA) were used in analyses of data. HCA was also carried out using the same variables. Complete linkage method was adopted and the distance measured is Squared Euclidean, two (2) clusters were extracted and a dendrogram was derived using Minitab version 17 for the analysis data.

This paper is aimed at identifying and differentiating the hydrocarbon source, the distribution patterns of normal alkanes, isoprenoids and the PAHs in the Agbada spill impacted site using fingerprinting and multivariate statistical techniques.

3. Results and discussion

3.1. Oil spill identification

The profiles of the gas chromatogram, carbon range, and major component distribution pattern of Total Petroleum Hydrocarbon (TPH) and polycyclic aromatic hydrocarbons (PAHs) were used to identify the oil spill as shown in Figs. 2 and 3 (Tables 1 and 2). The gas chromatogram shows they are composed largely of n-alkanes and isoprenoids. The range of the distribution of the n-alkanes in analyzed oil spill samples is of nC_8 to nC_{41}. This chemical composition aligns with the characteristic hydrocarbon range for crude oils [12,13]. Low molecular weight hydrocarbons ($<nC_8$) were not observed

(Table 1), probably because of evaporative loss during sample processing or weathering of oil spill samples after the incident and the chemical composition of aliphatic components had not undergone significant alteration [12].

The ratios of isoprenoids to n-paraffin are often used for oil-source correlation, maturation and biodegradation studies.

PAHs are resistant to weathering than their saturated hydrocarbon counterparts (n-alkanes and isoprenoids) and volatile alkylbenzene compounds, thus making them one of the most valuable classes of hydrocarbons for oil spill identification [1,11,14]. The high molecular weight PAHs containing 4, 5, and 6 rings are more stable and are therefore useful as diagnostic constituents of petroleum [15].

3.2. Distinguishing pyrogenic hydrocarbons from petrogenic hydrocarbons

The distributions of the polycyclic aromatic hydrocarbons were used to distinguish the pyrogenic PAHs from the petrogenic hydrocarbons (Table 2). One of the features is the dominance of the high molecular weight (4–6 ring) PAHs over

Table 1 Total Petroleum Hydrocarbon (TPH) content of samples in mg/kg.

Hydrocarbon fraction	Samples			
	1	2	3	4
C_8	–	–	–	–
C_9	–	–	–	–
C_{10}	24.10	24.10	23.60	23.60
C_{11}	29.98	29.98	24.65	24.65
C_{12}	61.75	61.75	34.63	34.63
C_{13}	59.65	59.65	34.73	34.73
C_{14}	64.88	64.88	36.39	36.39
C_{15}	64.82	64.82	36.46	36.46
C_{16}	43.32	43.32	66.32	66.32
Pristane	87.27	87.27	45.06	45.06
C_{17}	278.05	278.05	89.04	89.04
Phytane	40.17	40.17	29.71	29.71
C_{18}	292.10	292.10	29.95	29.95
C_{19}	248.02	248.02	83.55	83.55
C_{20}	43.29	43.29	42.48	42.48
C_{21}	64.51	64.51	34.82	34.82
C_{22}	49.65	49.65	28.85	28.85
C_{23}	32.87	32.87	3.88	3.88
C_{24}	75.66	75.66	103.19	103.19
C_{25}	271.04	271.04	105.45	105.45
C_{26}	270.38	270.38	91.64	91.64
C_{27}	238.55	238.55	100.48	100.48
C_{28}	319.68	319.68	98.31	98.31
C_{29}	264.00	264.00	104.84	104.84
C_{30}	288.24	288.24	113.97	113.97
C_{31}	330.53	330.53	125.95	125.95
C_{32}	255.22	255.22	89.59	89.59
C_{33}	216.67	216.67	86.14	86.14
C_{34}	209.63	209.63	87.15	87.15
C_{35}	165.29	165.29	64.54	64.54
C_{36}	67.44	67.44	–	–
C_{37}	79.29	79.289	–	–
C_{38}	98.39	98.39	–	–
C_{39}	79.21	79.21	–	–

Table 2 Polycyclic aromatic hydrocarbon content of samples in mg/kg.

Polycyclic aromatic hydrocarbons	Samples			
	1	2	3	4
Naphthalene	14.79	1.85	2.64	3.49
Acenapthylene	71.29	55.37	18.11	16.61
2-Bromonapthalene	51.91	19.13	8.49	9.87
Acenaphthylene	56.63	45.24	23.05	13.71
Fluorene	52.43	22.02	5.68	16.13
Phenanthrene	72.92	33.50	9.82	10.70
Anthracene	65.63	60.83	34.97	14.72
Fluoranthene	43.63	40.07	17.97	4.44
Pyrene	27.55	32.44	13.22	1.53
Benzo(a)anthracene	7.83	29.79	9.00	0.90
Chrysene	13.65	14.07	3.10	0.42
Benzo (b, j, k)fluoranthene	39.09	49.45	12.56	6.20
Benzo (a) pyrene	60.76	29.75	5.09	10.44
Indeno (1, 2, 3-cd) pyrene	5.89	36.32	18.51	4.56
Dibenzo (a, h) anthracene	3.36	23.20	8.70	1.75
Benzo (g, h, i) perylene	0.82	7.10	1.40	0.69

Table 4 Unrotated factor loadings and communalities of diagnostic ratios.

Variable	Factor 1	Factor 2	Communality
Pr/Ph	−0.99	0.06	1.00
Pr/nC_{17}	0.99	−0.06	1.00
Ph/nC_{18}	0.99	−0.06	1.00
nC_{25}/nC_{18}	0.99	−0.06	1.00
CPI	0.17	0.80	0.66
(Pr + nC_{17})/(Ph + nC_{18})	0.99	−0.06	1.00
Ph/anth	−0.06	−0.99	0.98
BaA/Ch	0.06	0.99	0.98
Fl/Py	0.06	0.99	0.98
Variance	5.02	3.57	8.59
% Var	0.56	0.40	0.95

Table 5 Eigen analysis of the correlation matrix for PCA.

Eigen value	5.02	3.57	0.41	0.00	0.00	−0.00
Proportion	0.56	0.40	0.05	0.00	0.00	−0.00
Cumulative	0.56	0.95	1.00	1.00	1.00	1.00

the low molecular weight (2–3 ring) PAHs [14]. Other criteria used in differentiating petrogenic and pyrogenic PAHs from others include the use of different ratios such as phenanthrene/anthracene, fluoranthene/pyrene, benz(a) anthracene/chrysene [16,17]. The phenanthrene/anthracene, ratios are often used because phenanthrene is a common constituent of crude oil while anthracene is relatively more abundant in pyrogenics. Most crude oils usually show ratios less than 0.01.

Heavy crude oil fractions such as Bitumen and other heavy fuels show higher ratios in the range of 0.01–0.05 while soot samples show ratios in the range of 0.8–2.0 [1]. The calculated Ph/anth ratio from the impacted site ranges from 0.28 to 1.11 (Table 3). This ratio is greater than the range stipulated for crude oils. The inference is that the area under study may have

Table 3 Calculated diagnostic ratios.

Samp.	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	nC_{25}/nC_{18}	CPI	(Pr + nC_{17})/(Ph + nC_{18})	Ph/anth	BaA/Ch	Fl/Py
1	2.17	0.31	0.14	0.93	1.03	1.10	1.11	0.57	1.58
2	2.17	0.31	0.14	0.93	1.03	1.10	0.55	2.12	1.24
3	1.52	0.51	0.99	3.52	1.13	2.25	0.28	2.90	1.36
4	1.52	0.51	0.99	3.52	0.97	2.25	0.72	2.14	2.90
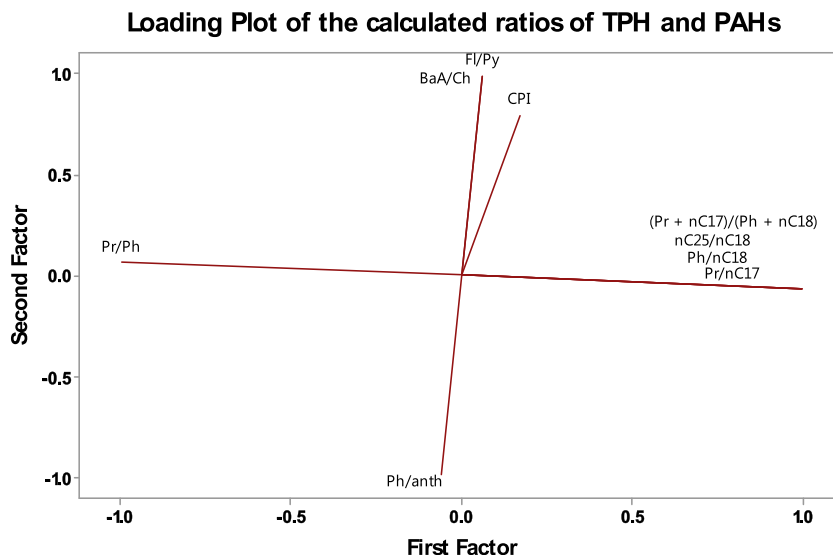
Figure 4 PCA loading plot for the calculated ratios.

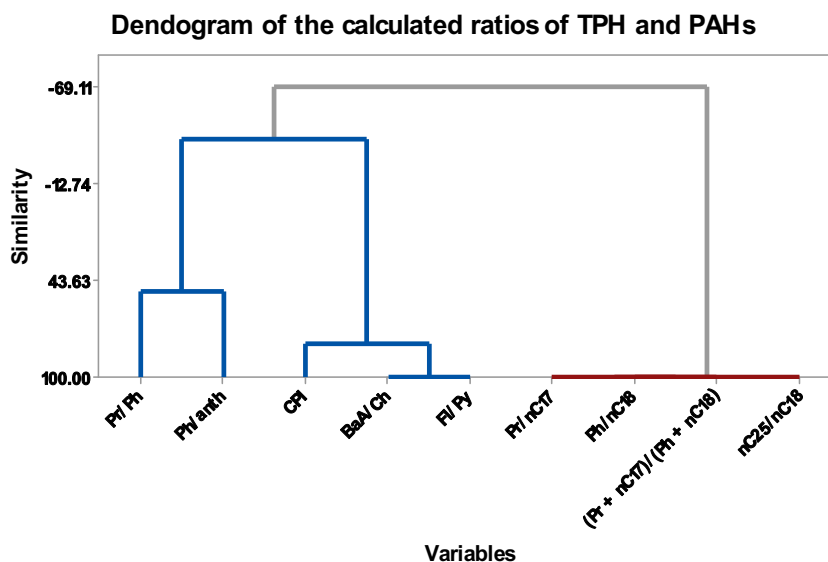## Dendogram of the calculated ratios of TPH and PAHs

Figure 5 Dendogram for Hierarchical Cluster Analysis of the calculated ratios.

been exposed to bush burning which is a common incidence in this area.

The biogenic and petrogenic hydrocarbons can be differentiated from each other. When there is a spill incident, hydrocarbons often mix with background source in the impacted area. Source of biogenic hydrocarbons are biological processes which contribute to the background hydrocarbons in the impacted area. These biogenic hydrocarbons are from land plants, phytoplankton, animals, bacteria, macroalgae and microalgae [1].

Some researchers such as [18–20] have shown some of the characteristics of these biogenic hydrocarbons which include: high carbon preference index (CPI). This value is approximately 1 for crude oils and High pristane/phytane ratios. The result in Table 3 shows CPI ranged from 0.97 to 1.03 (approximately 1) and a relatively high Pr/Ph ratio of 1.52–2.30. This depicts the source of the spill is crude oil or petroleum.

3.3. Application of multivariate statistical analysis in oil spill identification

The multivariate statistical methods make it easy for the relationships between multiple samples and variables (diagnostic ratios) to be resolved and visualized using score and loading plots. It is widely employed in environmental studies for grouping different parameters in order to recognize pollution sources [1].

Principal component analysis (PCA) loadings and scores plots were carried out on selected parameters obtained from the analysis of the oil spill soil samples (Fig. 4, Table 4). The estimated eigenvalues of the two factors of principal component (PC), PC1 to PC3 were 5.02 and 3.57 respectively (Table 5). Generally, higher eigenvalues, account for more variance that can be accounted for by the corresponding factors [21,22]. PC1 and PC2 together represented 95.4% (55.8% and 39.6% respectively) of the variability, while PC3 represented 4.6% only. Therefore, PC1 and PC2 can be used

to interpret the relationship between oil spill samples. The correlation between each variable and each principal component is very significant showing a single source of the oil spill samples.

Cluster analysis encompasses a number of different methods which organize objects (observations) into groups called clusters. Objects within the clusters are similar, whereas objects in different clusters are dissimilar [11,23]. Results of cluster analysis are shown in Fig. 5. Two groups of variable associations with eigenvalue > 1 were extracted in the analysis. The ratios were fused into clusters because of their relative similarity at each site and their coefficients. The first group comprises Pr/Ph, Ph/anth, CPI, BaA/Ch, and Fl/Py. The level of similarity of the variables is between 53% and 75%. The second group comprises of Pr/nC_{17}, Ph/nC_{18}, $(Pr + nC_{17}/Ph + nC_{18})$ and nC_{25}/nC_{18} (Fig. 5). The similarity level of these variables is about 98%. These parameters belonging to the same cluster/group are likely to have originated from a common source. The high level of similarity of the later variables is a strong conformation of common source of the spilled oil [24,25].

4. Conclusion

The results of the chemical fingerprinting obtained in this study presuppose a high level of contamination at the affected site. The calculated diagnostic PAHs ratios showed mixed sources of hydrocarbons (petrogenic and pyrogenic). The principal component analysis (FA/CA) applied to the ratios of isoprenoids to n-paraffin showed high-level similarity which indicates a common source of the oil spill. The high level of hydrocarbon in the soil may affect the occupation of the people which is predominantly farming. The presence of such levels or range of hydrocarbons at the study site might impede agricultural productivity because large amounts of hydrocarbon in soils discourage plant growth which in turn affects animals that depend on these plants for food and shelter.

Acknowledgements

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