



Quantitative Oil Source Fingerprinting and Diagnostic Ratios: Application for Identification of Soil Residual Hydrocarbon (SRH) in Waste Dump Areas within Oil Well Clusters

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Abstract

The elucidation of soil residual hydrocarbon (SRH) in oil-impacted dumpsite soils is aimed at distinguishing the principal source (municipal waste dumpsite or oil well-head clusters) of petroleum and polycyclic aromatic hydrocarbons in the mangrove environment receiving mineral oil loading from mixed anthropogenic influences. Chemical fingerprints of soil specimen were obtained on determination by gas chromatographic – flame ionization detection (GC-FID) technique using an HP 5890 series II instrument. Flt/Pyr ratios revealed the presence of petrogenic hydrocarbons while carbon preference index (CPI) showed soils composed mainly of degraded material and fossil fuels, apart from location E-2 which was loaded with non-biodegraded biological materials using Ph/nC₁₈ data. Elucidation of Pr/nC₁₇ ratios showed that the retention of non-biodegraded hydrocarbon was decimated at locations E-4 and E-6 due to reduced microbial degradation in comparison to the other field areas. Overall, the soil was insignificantly impacted by terrestrial sources, as greater magnitude came from surrounding oil well clusters. Therefore, soil toxicants are likely to be bio-accumulated in crops growing along proximate farmlands, especially nypa palm fruits which are commonly consumed. It is imperative to avoid ingesting herbage or other nutriment from this area until residual oil seepages are effectively controlled and hydrocarbons have been monitored for substantial degradation.

Keywords: Soil residual hydrocarbon, Carbon preference index, Total petroleum hydrocarbon, Polycyclic aromatic hydrocarbon, Eagle Island

1 Introduction

Like most urban cities across Nigeria, Port Harcourt metropolis is characterized by series of open waste dumpsites. These dumpsites have been known to contaminate surface waters that are within close proximity (1). They have also been known to moderately contaminate air mainly from fossil fuel burning and vehicular exhausts, especially around industrial zones (2). Soils within the vicinity of auto-mechanic work areas depicted spiked levels of petroleum hydrocarbons in relation to those from cultivated farmlands, thereby suggesting direct impact of anthropic releases (3). Most dumpsites within Port Harcourt have been observed to consist of discarded household electronics, plastic and food waste. Mechanic waste dumps have been reported to represent a potential source of hydrocarbon contamination of soils, sediment, surface and ground

water (4). Correlations have been established between PAH levels and anthropogenic input into waste dumps. PAH levels in waste dumps were often higher than in pristine soils. Also, levels of PAHs have been reported to exceed 0.02 g/g as stipulated in the guidelines of Canadian Environmental Quality (5).

The release of petroleum and aromatic hydrocarbons into the immediate and surrounding environment of the Eagle Island is not limited to the anthropogenic inputs emanating from waste dumps alone. The area is characterized by the presence of crude oil equipment (such as oil well heads). In the event of equipment failure or seepages from worn-out metal joints, the proximity of the study area to nearby creeks can make the soil and aquatic resources vulnerable to crude oil contamination, creeks receives domestic, municipal and industrial wastes due to human activities from settlements, commerce and industries within its vicinity, this in turn alters soil chemistry and decimates plants population (6-8). Crude oil is a complex mixture containing several hydrocarbon compounds (such as aliphatic, volatile and semi-volatile aromatics, as well as the organometallic heavy metal complexes) which can be fractionally separated into sub-products such as: kerosene, jet and diesel fuel, heating

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oil, etc. Crude oil transportation lines linking oil well heads are susceptible to acts of vandalism or self-rupture. The presence of hydrocarbon in soil, whether from municipal or oil wastes can result in variation of microbial population, negative physicochemical changes in the environment, release of cancer-causing aromatic complexes, consequent loss of food, herbage, water and other resources (6-14).

Total petroleum hydrocarbons (TPHs) in the form of alkanes and isoprenoids (nC_8 to nC_{40}) can be used to trace the source of an oil spill (whether emanating from source rock or secondary anthropogenic sources) (15-17). Similarly, polycyclic aromatic hydrocarbons (PAHs) can be classified as petrogenic (petroleum) or pyrogenic (combustion) origins; they can be further classified as resulting from natural and anthropogenic sources (11, 18-20). Examples of anthropogenic sources of PAHs in the environment include: burning of refuse waste dumps (5), burnt remnants and soot samples (21), indiscriminate deposition of mechanic wastes (4), urbanized municipal waste effluents (19) and from oil spillage (11, 22). PAHs tend to move across soil regions while being slow to biodegradation, especially by indigenous microorganisms (20). On the other hand, alkanes and isoprenoids showing nC_8 to nC_{40} petroleum hydrocarbon compounds have been used as diagnostic tools for the identification of oil sources in soil (16), ambient air (23), crude oil (15, 17, 24) and shellfish (25), etc.

Oil source fingerprinting is an environmental forensics technique that uses analytical chemistry to determine the origin of oil residues in environmental samples by comparing to a known or suspected source of oil (22). Even though PAHs have been major constituents of hydrocarbon contaminated environmental media, its distribution and source identification has been carried out by the application of diagnostic PAH ratios (11, 18-20, 26) which is a fingerprinting technique used for the type and source identification of hydrocarbons in the environment. For the alkanes and isoprenoids, typical diagnostic ratios are: pristane/phytane (Pr/Ph), pristane/ nC_{17} (Pr/ nC_{17}), phytane/ nC_{18} (Ph/ nC_{18}), nC_{25}/nC_{18} , carbon preference index (CPI), $(Pr + nC_{17})/(Ph + nC_{18})$, have been applied by (15-17, 24-25) to determine the extent of biodegradation (Ph/ nC_{18}), level of oil maturation (CPI), determination of oil source (Pr/Ph), etc. Whereas, PAH ratios such as: phenanthrene/anthracene (Ph/anth), benzo (a) anthracene/chrysene (BaA/Ch) and fluoranthene/pyrene (Flt/Pyr) have been applied by (17), other mixed PAH isomeric ratios such as: (Ant/Ant + Ph), (Flt/Flt + Pyr), BaA/(BaA + Ch) and benzo (a) pyrene/benzo (a) pyrene + chrysene (BaP/BaP + Ch) have been used to distinguish between petrogenic and pyrogenic sources (11, 18, 27-28).

The need to specify the prevalent source of hydrocarbons within the Eagle Island environment was necessary, this is due to the presence of various waste streams (primarily consisting of waste dumps and oil well-heads) which represent human burden within the area of study. The diagnosis of aliphatic and aromatic hydrocarbon sources is concurrently aimed at identifying the nature of residual mineral oil and its effect on biodegradability over time. Also, the scarcity of literature in chemical fingerprinting of soils receiving multiple waste streams such as is typical of this study location makes this work quite unique.

2 Materials and Methods

2.1 Study area

Eagle Island is located within the Rumueme - Oroakwo axis of Port Harcourt. Its geographical coordinates lie within the different latitudes and longitudes: E1 ($N4^{\circ} 47.223'$, $E6^{\circ} 58.134'$), E2 ($N4^{\circ} 47.223'$, $E6^{\circ} 58.134'$), E3 ($N4^{\circ} 47.327'$, $E6^{\circ} 58.573'$), E4 ($N4^{\circ} 47.326'$, $E6^{\circ} 58.574'$), E5 ($N4^{\circ} 47.327'$, $E6^{\circ} 58.574'$), E6-control ($N4^{\circ} 47.204'$, $E6^{\circ} 58.336'$) (Plate 1). The waste dump environment is located within the mangrove/nypa palm forest zones of Eagle Island in Port Harcourt city local government area. It is bound by surrounding creeks and river tributaries. The common occupation of settlement dwellers within the area is fish farming and crop production. The soil environment is susceptible to hydrocarbon (petrogenic, pyrogenic or biogenic) contamination emanating from either or both of the municipal waste dumps and oil well heads.

2.2 Field Sampling and pre-treatment

Five (5) samples of soil were randomly collected from areas most visibly impacted by waste dumps at depths of 0 – 15 cm using soil auger. One (1) was collected about 1 meter away from impacted area (as control). However, the field area was within close proximity of oil equipment and well heads. Samples were transferred into pre-cleaned aluminum foil packs and preserved with ice in cold-storage box prior to laboratory delivery.

2.3 Statistical analysis

In order to determine field sample areas of close association (or mutual dependence) and those of mutual independence, the hierarchical cluster analysis was carried out using Euclidean distance based on average linkage between groups. Only one variable (sample location) across the waste dump soil was statistically evaluated. Clustering techniques are used to separate objects related with a specific cluster; such objects should be quite alike (or homogenous). Hydrocarbons of mutual dependence show similarities or closeness in features while those of mutual independence mirror diverging attributes. Principal component analysis (PCA) is a multivariate analysis technique used in transforming original sample composition data into new, smaller and uncorrelated variables called principal components. The hypothesis is based on expressing the total variance of the variables with two factors, accounting for the maximum variance of the variables (17, 29).

2.4 Sample Preparation, Quality Control Procedure and Analytical Data Validation

Soil samples were refrigerated at $4^{\circ}C$ and analyzed within the first 3 days from time of sample collection. Glass wares were acid-washed, rinsed under tap water and, further rinsed with distilled water. Washed glass wares were oven-dried at $105^{\circ}C$ for 30 minutes and cooled in a desiccator.

2.4.1 TPH extraction

Exactly 5 grams wet-weight soil was mixed with two spatulas-full of anhydrous Sodium Sulphate (as drying agent), depending on the moisture level of the sample. Also, a volatile surrogate (2-bromobenzofluoride) was mixed with sample prior to extraction. A 16 hour soxhlet extraction was applied for TPH extraction using 95% n-hexane solvent (11). A 1:1 mix ratio of n-

hexane/dichloromethane solvents was used to extract PAHs by the cold-extraction method adopted by (11, 18). Gas chromatography with flame ionization detection was the method of analysis. Helium gas (at flow rate of 14.81 psi) was streamed as mobile phase, while an Agilent HP-5 GC capillary column, with 100% 1,3-dimethylsiloxane stationary phase material, length (30 m), internal diameter (0.320 mm), and film diameter (0.25 μm) with temperature range (-60°C to 325°C), was used for the separation of vapor constituents of different hydrocarbon fractions. Hydrogen and air (at flow rates of 30 psi) served as ignition gases (10).

2.4.2 Instrument Conditions

Table 1 shows the instrument conditions. The split and split-less injection techniques were used for this analysis. Hence, the samples were introduced into the heated injection port as solvent-dissolved extracts. The inlet vent was purged at a split ratio of 10:1 for aliphatic hydrocarbons. This is because of their typically high concentrations when compared to the aromatics (split-

less mode) which are often observed in trace amounts. When the target analyte concentrations (in this case, volatile or semi-volatile aromatics) are so low that splitting the sample in the injection port will not allow an adequate signal from the detector, the spit-less mode is usually a preferred option.

2.4.3 Instrument Calibration

A three (3) point linear calibration curve was prepared from working solutions of 25, 50 and 250 $\mu\text{g/ml}$ stock of hydrocarbon window defining standard solution of TPH (500 $\mu\text{g/ml}$). Another series of working solutions (25, 50 and 250 $\mu\text{g/ml}$) were prepared from 1,000 $\mu\text{g/ml}$ of the proposed DEP(MA) – PAH mix and used for instrument calibration of the polycyclic aromatic components. All standard solutions were purchased from AccuStandard-USA. The aliphatic and aromatic hydrocarbons were determined with an HP5890 series II Gas chromatograph-Flame ionization detector (GC-FID), manufactured in USA (10).

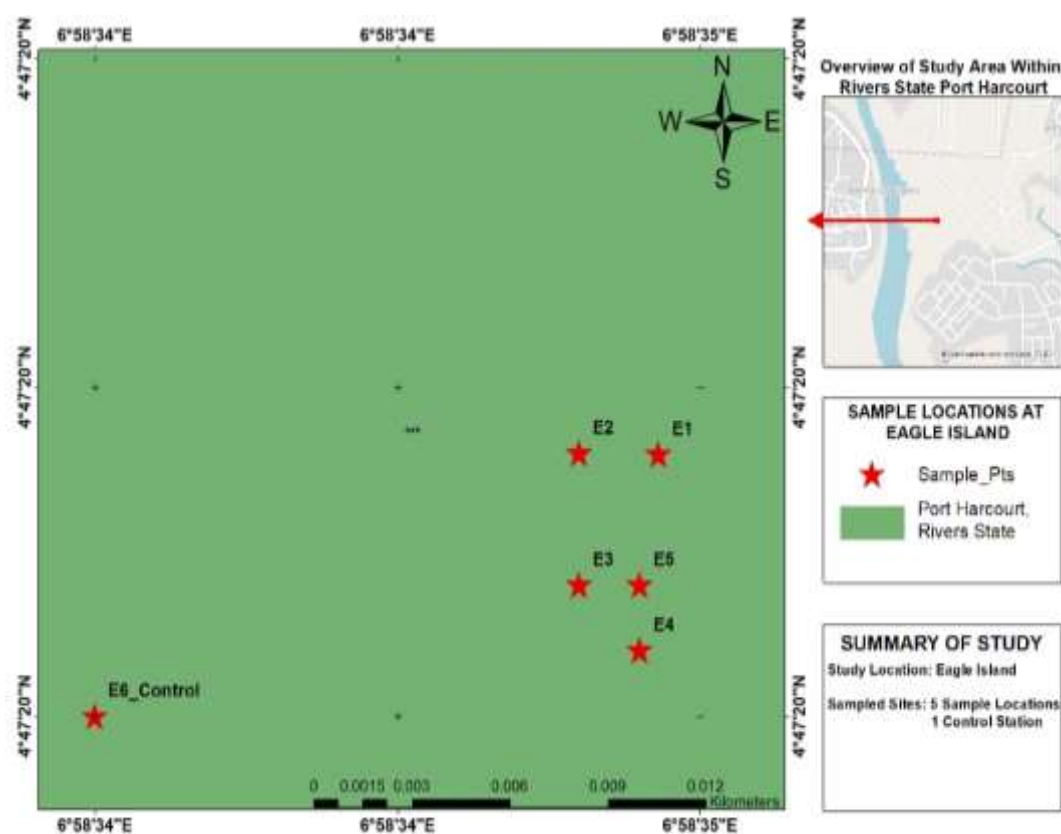


Plate 1: Map of study area

Table 1: GC-FID operating conditions

Parameters	TPH	PAH
Initial oven temperature (°C)	50	65
Final oven temperature (°C)	310	290
Column flow rate (ml/min)	0.8	1.2
Injector temperature (°C)	275	275
Detector temperature (°C)	320	310
Inlet condition	Split ratio (10:1)	Split-less

2.4.4 Instrument Blank (IB)

Immediately after instrument calibration, method blanks were analyzed as quality control at the start and end of run of each fractional species. A solvent blank was injected into the GC system using the injection solvent (95% n-hexane) to establish the chromatographic baseline and to ensure its suitability. The resulting TPH and PAH concentrations for the IB were below the reported detection limit (0.01 µg/g). The two IB concentrations generated at the start and end of sample analysis were averaged and subtracted from corresponding sample concentrations.

2.4.5 Calibration Authentication Standard (CAS)

Mid-concentration standards for TPH (100 µg/ml) and PAH (200 µg/ml) prepared from stock solution was analyzed before and after sample injection. The average concentrations, TPH (89.7 µg/ml) and PAH (192.5 µg/ml) obtained was within the acceptance criteria of ± 20% of target value.

2.4.6 Sample Duplicates

A second aliquot of one (1) of the six (6) test soil samples was weighed for each of the TPH/PAH extraction as "sample check". The duplicate sample was subjected to all sample preparation steps applied earlier.

2.4.7 Surrogate Compounds

A volatile surrogate compound (2-bromobenzofluoride) was added to each sample in 95% n-hexane solution prior to extraction. Percentage recovery was calculated as 94.2%.

2.5 Reagents and Chemicals

The following analytical grade reagents and chemicals were used: 95% n-hexane (Riedel-de Haen, Germany), dichloromethane (BDH, Poole-England), 99% sodium sulphate anhydrous, AR (JHD Guangdong Guanghua Sci-Tech Co., Ltd.). Working solutions of 25, 50 and 250 mg/l concentrations were prepared from a TPH stock solution of 500 mg/l in n-hexane. This was done by transferring aliquot volumes of 0.05, 0.10 and

0.50 ml respectively, into sample vials. Each volume was made up to the 1.0 ml mark using a 500 µl micro syringe. PAH standards were prepared in a similar manner.

3 Results and Discussion

3.1 Hydrocarbon source diagnostics in soil environment

Table 2 shows the levels of petroleum (aliphatic) and polycyclic (aromatic) hydrocarbons in soil, the amounts are compared against the regulatory limit of DPR. Apart from soils of E6 (control) all other field areas depicted TPH values exceeding stipulated limit. On the other hand, PAHs were least in the control area even though samples of E1, E2 and E3 were mostly impacted with residual oil. Results reflect a spike in contaminant levels of oil-contaminated soils in relation to the less contaminated control zones. This corroborated the findings of (10) where oil spill affected soils showed increased elevation in hydrocarbon contamination as against soils from proximate farmlands.

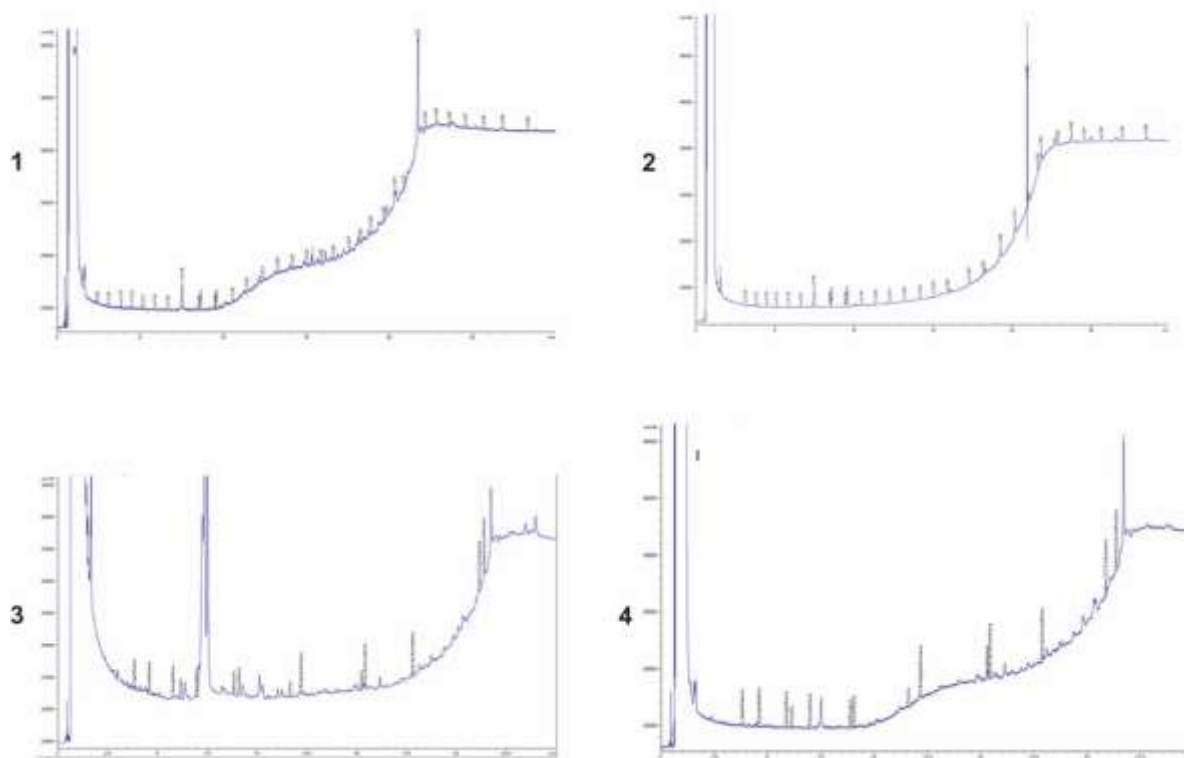
The level of total petroleum hydrocarbon in soil ranged from 26.57 to 348.08 mg/kg. Reported values were compared against the DPR limit of 50 mg/kg. Apart from samples of control location E-6 that depicted the least concentration (which was within DPR limit), residual petroleum hydrocarbon exceeded regulatory comparison for all other sample locations (E-1 to E-5) (Table 2). Similarly, the least concentration of total polycyclic aromatic hydrocarbon was observed for the control location. Overall, total PAHs ranged from 0.162 to 1.581 mg/kg. Samples of point E-4 and E-5 also depicted values slightly below DPR limit for PAHs in a standard soil (1.0 mg/kg) [30]. For this study, samples were collected during the dry season month of November, 2018. Results obtained compared with (11) that reported mean values of 148.9 mg/kg total hydrocarbon content (THC) and 0.99 mg/kg PAHs for oil spill contaminated soils of Rumuolukwu during the month of November, 2013. Results of the different isomeric ratios applied for TPH and PAH across the different field locations are recorded in Table 3.

Table 2: Concentration of total petroleum and polycyclic aromatic hydrocarbons in soil

Sample Identity	Total TPHs (mg/kg)	Total PAHs (mg/kg)
E-1	234.06	1.174
E-2	348.08	1.581
E-3	208.28	1.039
E-4	132.60	0.744
E-5	123.50	0.704
E-6	26.57	0.162
DPR Limit for standard soil	50	1

Table 3: Calculated diagnostic ratios of aliphatic and aromatic hydrocarbon fractions in soil

Diagnostic Ratios	E-1	E-2	E-3	E-4	E-5	E-6
Pr/Ph	0.81	2.45	0.91	2.11	0.35	0.92
Pr/nC17	1.26	1.54	0.68	4.70	0.62	3.82
Ph/nC18	2.21	0.93	1.71	1.44	4.33	3.48
nC25/nC18	0.40	8.57	2.06	3.43	9.11	55.80
CPI	1.16	2.74	1.29	0.79	0.67	1.33
(Pr+nC17)/(Ph+nC18)	1.00	1.95	1.42	1.51	0.80	0.91
Ph/anth	0.46	2.81	3.16	5.64	1.26	1.29
BaA/Ch	29.66	0.95	1.01	0.91	3.97	0.08
Flt/Pyr	20.87	0.04	2.33	0.86	2.82	0.16



Figures: (1) TPH fingerprint of location E-2 (point of highest CPI and lowest oil maturation), (2) TPH fingerprint of location E-5 (point of lowest CPI and highest oil maturation), (3) PAH fingerprint of location E-1 (point of highest Flt/Pyr ratio and most petrogenic source), (4) PAH fingerprint of location E-2 (point of lowest Flt/Pyr ratio and least petrogenic source).

The diagnostic ratios depicted the following ranges: Pr/Ph (0.35 - 2.45); Pr/nC₁₇ (0.62 - 4.70); Ph/nC₁₈ (0.93 - 4.33); nC₂₅/nC₁₈ (0.40 - 55.80); CPI (0.67 - 2.74); (Pr + nC₁₇)/(Ph + nC₁₈) (0.80 - 1.95); Ph/anth (0.46 - 5.64); BaA/Ch (0.08 - 29.66); Flt/Pyr (0.04 - 20.87) (Table 3). Some light hydrocarbon fractions (C₈ - C₁₀) (Figures 1 - 5) were not observed probably because of evaporative loss during sample processing and weathering of oil spill samples after the incident (15, 17).

The chemical composition of aliphatic components had not undergone significant alteration. The low Pr/Ph ratio for the soils at locations E-1 (0.81), E-3 (0.91), E-5 (0.35) and E-6 (0.92) suggests that the residual oil in soil is not derived from source rock with insignificant terrestrial contribution. On the other hand, the high Pr/Ph ratio for soils at locations E-2 (2.45) and E-4 (2.11) reflects significant terrestrial contribution and is an indication that the source of residual oil in soil is crude oil or petroleum; this may have emanated due to the presence of oil well heads in the vicinity of the waste dumpsite. [31] revealed Pr/Ph ratios of crude oil contaminated soils to decrease from 2.358 to 1.626 on amendment with oil degrading pseudomonas consortium. Also, (15) recorded Pr/Ph ratios to depict ranges from 8.78 to 32.27 for crude oils from Umutu/Bomu fields in the Niger Delta.

The application of the Pr/nC₁₇ ratio in this study reveals that soils from locations E-4 (4.70) and E-6 (3.80) are depicted by weak microbial activity and tendency for a slower rate of bio-degradation while all other sampling points may require relatively less time to be decomposed. (32) applied pristine isomerization ratio, reporting values between 0.42 and 0.97 to reflect increased thermal maturity in coal rocks of river Junggar

in China. Only soil from location E-2 reflected non-biodegradation as Ph/nC₁₈ was observed below 1.0.

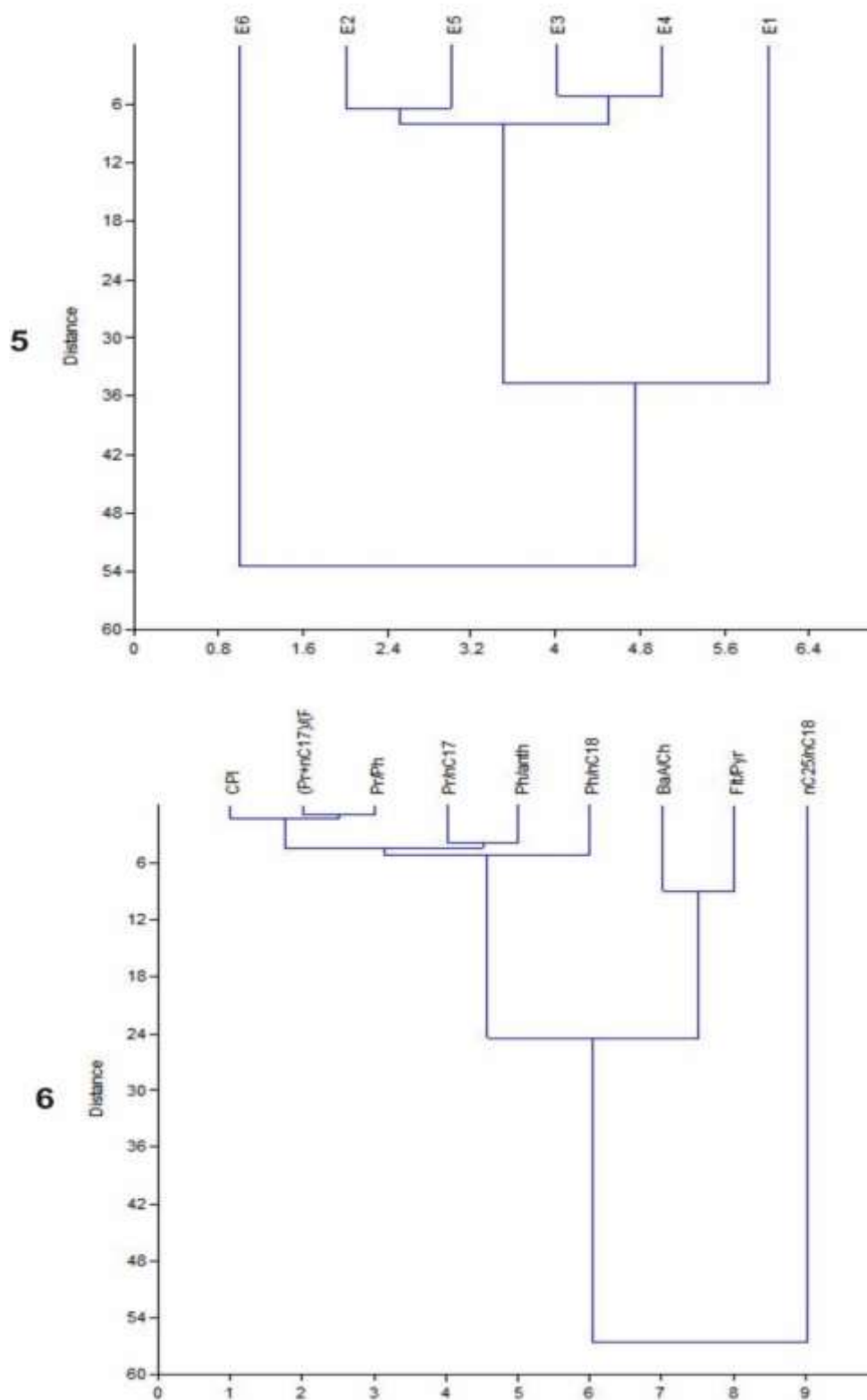
All other sample locations suggested that samples were being biodegraded. Ph/nC₁₈ ratio from this study reportedly exceeded levels reported by (17) where values ranged from 0.14 to 0.99 for Agbada-1 oil spill impacted sites in the Niger Delta. The nC₂₅/nC₁₈ ratio revealed the shortest weathering process for soil E-1 (0.40) and the longest for control soil E-6 (55.80), while (E-3 (2.06) & E-4(3.43)) with (E-2 (8.57) & E-5 (9.11)) showed similar weathering processes. Results from this study partially agreed with (17) where nC₂₅/nC₁₈ ratio reportedly ranged from 0.93 to 3.52.

Apart from location E-2 that depicted oils of low maturation with CPI value of 2.74, all other sample locations depicted CPI<1.5 thereby reflecting oils of high maturation. Crude oils from Umutu/Bomu fields in the Niger Delta had been reported to be of high maturation levels even though they lacked a specific maturity trend (15). Similarly, (17) had reported oils of high maturation in soils of Agbada-1 oil spill impacted sites in the Niger Delta. Also, (33) had reported CPI>5 to reflect significant contributions due to recent biological material while CPI≈1 reflected significant contributions from degraded material and fossil fuel compounds. Consequently, residual oil in soils of location E-2 with CPI 2.74 reflects the presence of biological materials most likely from municipal waste dump source while other locations may reflect a mixed combination of degraded biological material and fossil fuels.

Flt/Pyr ratio greater than unity (>1) is indicative of a petrogenic source of PAHs (11, 15, 17). Similar to the CPI ratios, location E-2 depicted the lowest Flt/Pyr ratio and the least petrogenicity with value of 0.04. Other points of low petrogenic inputs were locations E-4 (0.86)

and E-6 (0.16). Location E-1 (20.87) represented the area of most petrogenic contribution while E-3 (2.33) and E-5 (2.82) also indicated petrogenic sources of residual PAHs in soil. Results from this study partially compares to (17) with Flt/Pyr ratio (>1) and an indication of petrogenic

PAH sources for oil contaminated soils of Agbada-1 oil spill sites. Oil impacted soils of Rumuolukwu community had earlier been reported to consist predominantly of pyrogenic hydrocarbons (11).



Figures: (5) Hierarchical dendrograms of sample locations, (6) Hierarchical dendrograms of diagnostic TPH/PAH ratios.

Statistical analysis like the hierarchical cluster analysis (HCA) carried out across the geospatially varying sample locations revealed the closest association or mutual dependence for samples of locations E-3 and E-4. Similarly, locations E-2 and E-5 showed close association, while samples of locations E-1 and E-6 reflected the greatest mutual independence, hence, showing no similarities with other sampling points (Figure 5). The close interlink between most of the sampling points is a reflection of strong similarities between sources of residual oil in soils of the environment. Sample locations belonging to the same cluster or group are likely to have originated from a common source. The high level of similarity between interlinked sample locations is strong conformation of a common source of spilled oil and residual oil from waste dumps. In conclusion, both the aliphatic and aromatic hydrocarbons in the study area depict an anthropogenic organic source which may have emanated from the numerous human influences within the environment. Similarly, (17) had reported a common source for spilled oil in soils of Agbada-1 oil impacted field area, high levels of similarity (98%) were observed from results of cluster analysis. HCA of TPH and PAH diagnostic ratios revealed close associations for the following groups of variables (Pr/Ph and $(\text{Pr}+\text{nC}_{17})/(\text{Ph}+\text{nC}_{18})$), (Pr/nC_{17} and Ph/anth) and (BaA/Ch and Flt/Pyr) while the variable of highest mutual independence was ($\text{nC}_{25}/\text{nC}_{18}$ and CPI) (Figure 6).

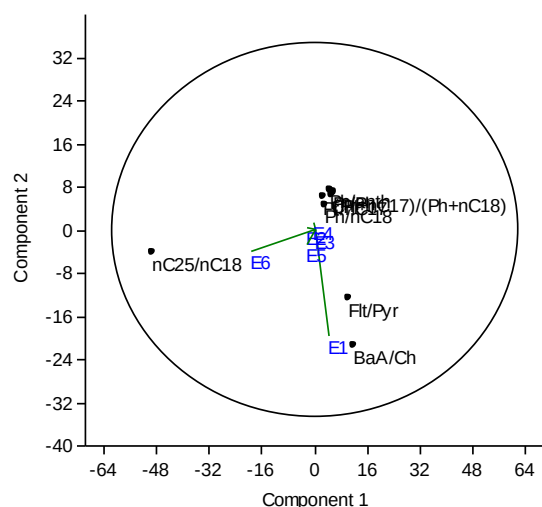


Figure 7: Scatter diagram principal component analysis

The study also found that variables such as Ph/anth , Pr/nC_{17} , Ph/nC_{18} , Pr/Ph , $(\text{Pr}+\text{nC}_{17})/(\text{Ph}+\text{nC}_{18})$ and CPI accounted for the locational separation of sites E-2, E-3, E-4 and E-5 while Flt/Pyr and BaA/Ch accounted for the distinction of location E-1. Also, $\text{nC}_{25}/\text{nC}_{18}$ accounted for the locational distinction of site E-6 in the PCA (Figure 7). The inter-relationships between locations E-2 to E-5 may have resulted due to similar characteristics of the soil and the related degradable and non-biodegradable toxicants that persist in the environment. Contrastingly, the dissimilarities in samples of E-1 and E-6 may have been due to their locational distance from the most impacted areas which are directly receiving municipal waste leachates and oil spill seepages (Plate 1). This finding reflects the soil residual hydrocarbon sources in the contaminated soils around dumpsites of the Eagle Island at the time of this study and serves as

recommendation for future studies and regulation for soils receiving hydrocarbon waste from multiple point sources. PCA relationship in this study is similar to (17) where there was observed relationship between locations PC1 and PC2, with only point PC3 depicting divergent characteristics with TPH isomeric ratios.

4 Conclusion

Typical of the study area is the availability of mixed sources of anthropogenic inputs. Results of chemical fingerprinting for soils of the area revealed an equal amount of low and high petrogenic hydrocarbons based on Flt/Pyr ratio. CPI revealed soils of location E-2 to be composed mainly of biological materials while other sample points reflected soils with residual oil resulting from degraded material and fossil fuel sources. Consequently, all other sample locations reflected biodegraded soils apart from location E-2 which composed mainly of non-biodegraded hydrocarbons based on Ph/nC_{18} ratio. Apart from soils of locations E-4 and E-6 (control) which reflected Pr/nC_{17} ratios greater than 1.0 indicating poor microbial utilization of mineral oil, all other areas showed maturation of organic material. Generally, soil residual hydrocarbons (SRH) depicted insignificant terrestrial contribution with higher levels emanating from crude oil or petroleum sources. The HCA applied to locations of sample collection showed close interlinks and strong associations except for location E-6; this indicates a common source of split oil. Using PCA, discrete locations of the sites indicated dissimilarities in the source diagnostic ratios applied due to variability in hydrocarbon sources across the study site. The numerous anthropogenic influences such as waste dumps, oil wells, amongst others are responsible for the presence of oil in soil, but oil seepages are most liable. This may impact negatively on nypa palm fruits which are found growing in this area and commonly consumed by the indigenous inhabitants who farm along the near coastal stretch of the creek.

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Competing interests

The author declares that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors Profile

Ayobami Omozemoje Aigberua is a Ph.D research student of the department of chemical sciences in the Niger Delta University, Wilberforce Island, Amassoma, Bayelsa State, Nigeria. His research interests extend across environmental topics that are relevant within sub-Saharan Africa, while partly sharing the passion to research food and herbal drugs toxicity. He is also an environmental laboratory expert, with over 12 years of experience carrying out operations and maintenance of specialized laboratory equipment such as Flame atomic absorption spectrophotometer, Gas chromatograph-flame ionization detector, Gas chromatograph-mass selective detector, amongst others. He has published several research articles in the area of oil spill pollution studies. He is currently working on the use of chemical

fingerprinting techniques to identify sources of residual hydrocarbons in environments that are prone to anthropogenic influences.

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