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Aliphatic Hydrocarbon Fingerprints of Some Crude Oil Polluted Soils from Niger Delta, Nigeria

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Abstract Crude oil-polluted soil samples were collected from five different oil polluted sites at Etche, Ahoada, Bodo, Ebocha and Bille in Niger Delta. The samples were analyzed using Gas chromatography with Flame ionization detector (GC-FID) for the Total Petroleum Hydrocarbon (TPH) to determine the different oil fractions and thus provide evidence of hydrocarbon contamination at the affected sites. The Pristane/Phytane ratios of the samples indicated that the released oil had both oxidizing and reducing source input. Similarly, the n-alkane distribution gave carbon preference index (CPI) values that pointed to both marine and terrestrial source input. The similarities in pattern from the star diagram also points to the marine and terrestrial source inputs to the oils. Depletions of nC_{21}-nC_{23} hydrocarbon fractions and disappearance of nC_8-nC_{21} fractions from gas chromatogram showed serious degradation on the sites.

Keywords: *gas chromatography, fingerprinting, total petroleum hydrocarbon, carbon preference index, pristane, phytane*

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1. Introduction

Petroleum is a mixture of gaseous, liquid and solid hydrocarbons that occurs naturally beneath the earth's surface and exists as crude oil, natural gas or condensates [1]. Crude oil consists of hydrocarbons and non-hydrocarbons; the hydrocarbons consist of alkanes (paraffins), alkenes (olefins) and the aromatics [1]. With the increased rate of crude oil spillage into the environment through various oil exploration activities, soil pollution in the Niger Delta region has greatly increased. These oil releases can be as a result of equipment failures, improper system of operations or can even be caused by saboteurs damaging the oil facilities [4]. These activities can lead to pollution of aquatic environments when through the action of wind and wave, oil spreads across the water leading to soil pollution, thus agricultural activities are affected adversely [5]. The hydrocarbons in these spillages can be analyzed through a number of instrumental techniques. These techniques include but not limited to; Gas Chromatography, Gas Chromatography-Mass Spectroscopy, High Pressure Liquid Chromatography. These techniques determine the source of oil, chemical composition and degree of weathering of crude oil. GC technique is used extensively to determine hydrocarbons and other organic compounds by determining their composition, molecular specie and their concentrations in the sample [2].

Total petroleum hydrocarbons (TPH) refers to the measurable amount of petroleum-based hydrocarbons in an environmental matrix [8]. TPH is generally used to describe a large family of several hundred of chemical compounds that originally come from crude oil as each chemical in any environmental matrix (soil or water) is measured [9]. Fingerprinting of petroleum hydrocarbons from C_8 to C_{40} is used to analyze the characteristics of oil in order to evaluate among others the hydrocarbon range in the crude. Fingerprinting evaluation using gas chromatography helps to determine the maturity, source and biodegradation of the entire crude oil by determining the hydrocarbon range in a gas chromatograph and certain hydrocarbon ratios are employed [2]. Biomarker diagnostic ratios are parameters used for oil correlation, determination of organic input and precursors, depositional environment, assessment of maturity and evaluation of in-reservoir oil degradation [10]. Frequently used biomarkers for diagnostic ratios are pristine/phytane, pristine/n-C_{17}, phytane /n-C_{18}, C_{21}/C_{23} tricyclicterpanes etc. [6].

2. Materials and Methods

Soil sample were collected manually from five oil affected sites in Ahoada, Etche ,Bille, Bodo and Ebocha all in Niger Delta and wrapped in an aluminum foil and taken to the laboratory for analysis. The soil samples were extracted using static method. 10grams of homogenized soil samples were weighed and added to 100ml of an equal mixture of acetone and dichloromethane. The sample mixture was filtered through Whatman 41 filter paper. The sample extract was re-concentrated to 2ml and transferred using pipette into the injection vial for GC analysis.

3. Results and Discussions

The chemical fingerprints of oils from the five polluted sites at Etche, Ahoada, Bodo, Ebocha and Bille were assessed using GC-FID analysis of the different oil fractions. Five parameters used for this purpose include: Pristane/phytane, pristane/n-C_{17}, CPI, Pr + nC_{17}/ph + n-C_{18} and degree of waxiness ($\sum C_{21}$-$C_{32}/\sum$ C_{15}-C_{20}) as shown in Table 1 below.

Table 1. Some diagnostic ratios for the five soil samples

TPH RATIOS	Pr/ph	Pr/n-C_{17}	CPI	$\sum C_{21}$-$C_{32}/\sum$ C_{15}-C_{20}	Pr+n-C_{17}/ph+n-C_{18}
ETCHE	0.97	3.13	1.41	0.06	1.16
AHOADA	0.69	0.3	0.96	0.58	1.32
BODO	0	0	6.97	0	0
EBOCHA	4.69	0.33	3.39	0.23	7.12
BILLE	0.48	0.46	2.28	0.66	0.68

The mode of distribution of n-paraffins in the crude oil extract of Etche, Ahoada, Ebocha and Bille showed a hydrocarbon predominance of n-C_{15} to n-C_{20} reflecting marine origin [3]. Also, there was a total disappearance of n-C_{18} to n-C_{21} in the crude oil extracts from Bodo and n-C_{32} to n-C_{30} in all the five sites especially Etche suggesting serious biodegradation on these sites. The ratios of pristane to pyhtane (pr/ph) can be used as a source index of the spilled oils depositional environment. Since pristane represent a product of decarboxylation, the ratio of the Pr/Ph tends to be high in more oxidizing environment and low in reducing environment [2]. The crude oil samples of Ebocha oilfields had high Pr/Ph ratio of 4.69 suggesting terrestrial input while those from Etche, Ahoada and Bille had low Pr/Ph ratios of 0.97, 0.69 and 0.48 respectively. These ratios below unity could be an indication of petroleum origin and/or highly reducing depositional environment [2]. The Pr/n-C_{17} ratios of the oil extracts were 0.30, 0.33 and 0.46 in samples from Ahoada, Ebocha and Bille respectively indicating these ratios below unity could be an indication that serious weathering activities has taken place while Pr/n-C_{17} ratio for Etche was 3.13 indicating less weathering activities on Etche oilfield, as the pristine to its neighboring n-alkane C_{17} decreases as weathering proceeded [6]. The degree of waxiness in spilled oil samples from Ahoada, Etche, Ebocha and Bille was less than 1 revealing low waxy nature suggesting marine organic source input under reducing conditions [3].

Carbon preference index (CPI) can be used for evaluating both the source and maturity of crude oils [7] [1]. The pattern of distribution of n-alkanes in samples from Etche, Ebocha and Bille showed that the odd carbon-numbered alkanes were more abundant than the even numbered alkanes in the lower range of n-C_{13} to n-C_{22} resulting in high CPI of approximately 1.41, 3.39 and 2.28 respectively for the n-C_{13} to n-C_{22} at Etche, Ebocha and Bille respectively suggesting that the lower n-alkanes of the spilled oil, might have been derived from plants/terrestrial sources. On the other hand, n-C_{13} to n-C_{22} in oil spilled samples from Ahoada has a CPI of 0.96 close to unity indicating mature samples and marine input from nC_{13} to nC_{22}. The CPI values for the ranges indicated that oils may have been sourced from both marine and terrestrial environments.

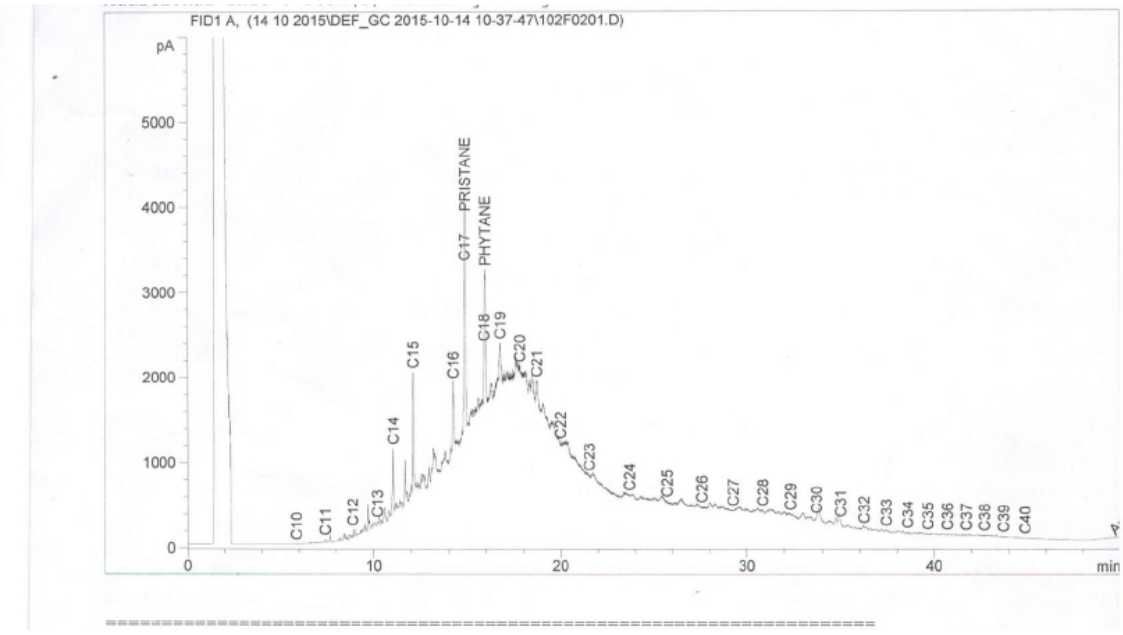

Figure 1. TPH (n-alkanes) chromatogram of oil from Etche soil sample

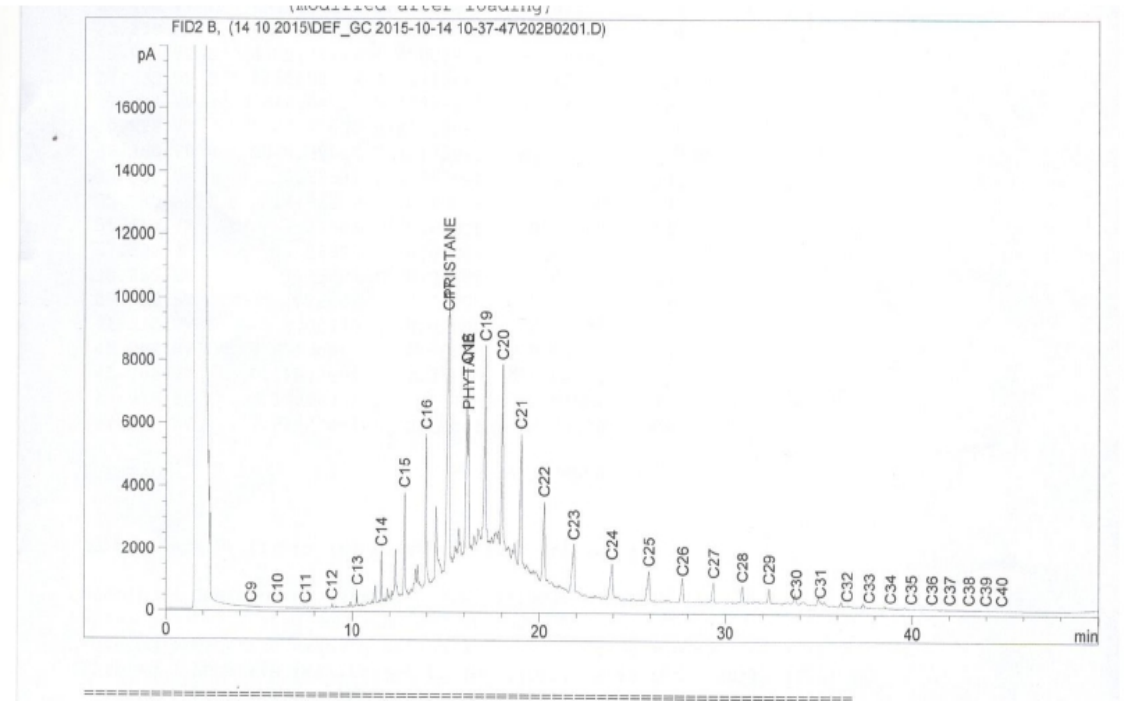

Figure 2. TPH (n-alkanes) chromatogram of oil from Ahoada soil sample

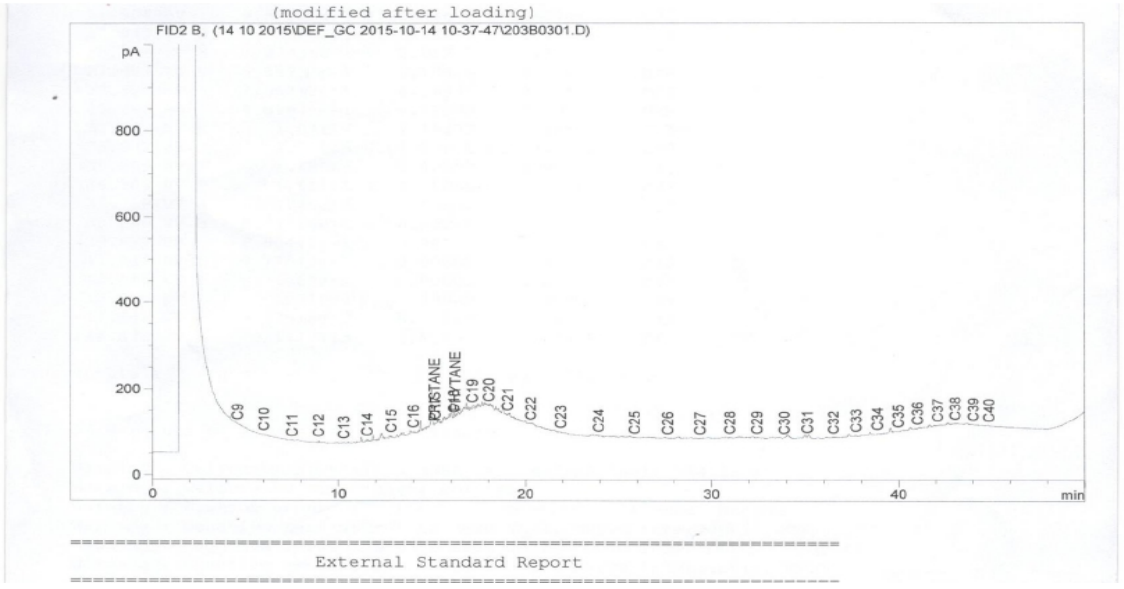

Figure 3. TPH (n-alkanes) chromatogram of oil from Bodo soil sample

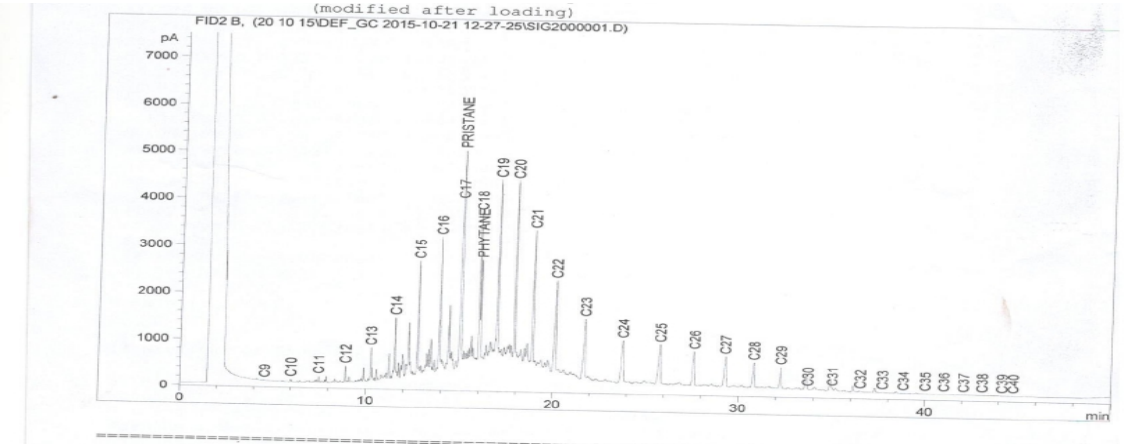

Figure 4. TPH (n-alkanes) chromatogram of oil from Ebocha soil samples

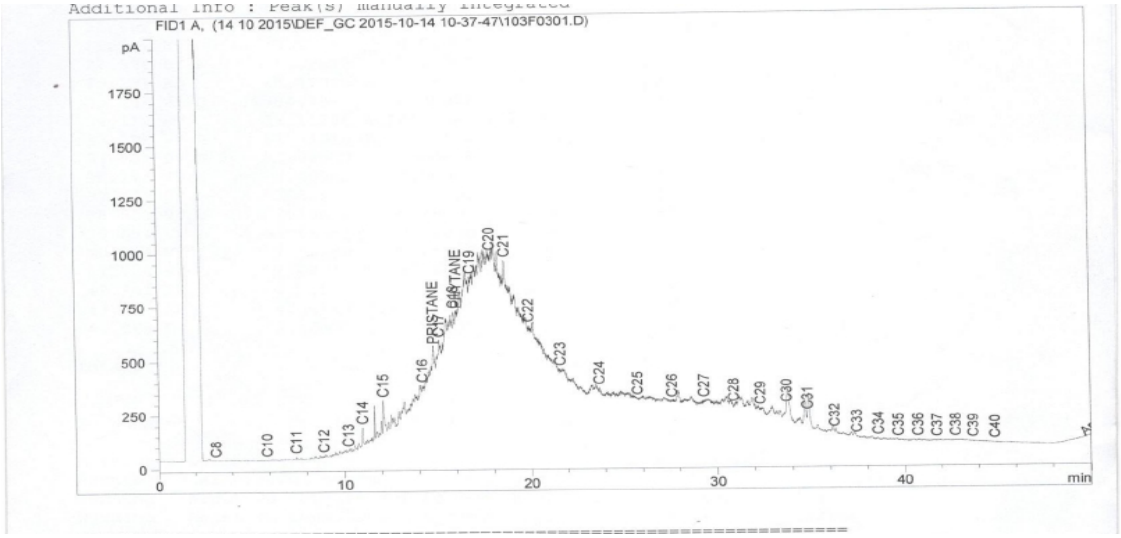

Figure 5. TPH (n-alkanes) chromatogram of oil from Bille soil sample

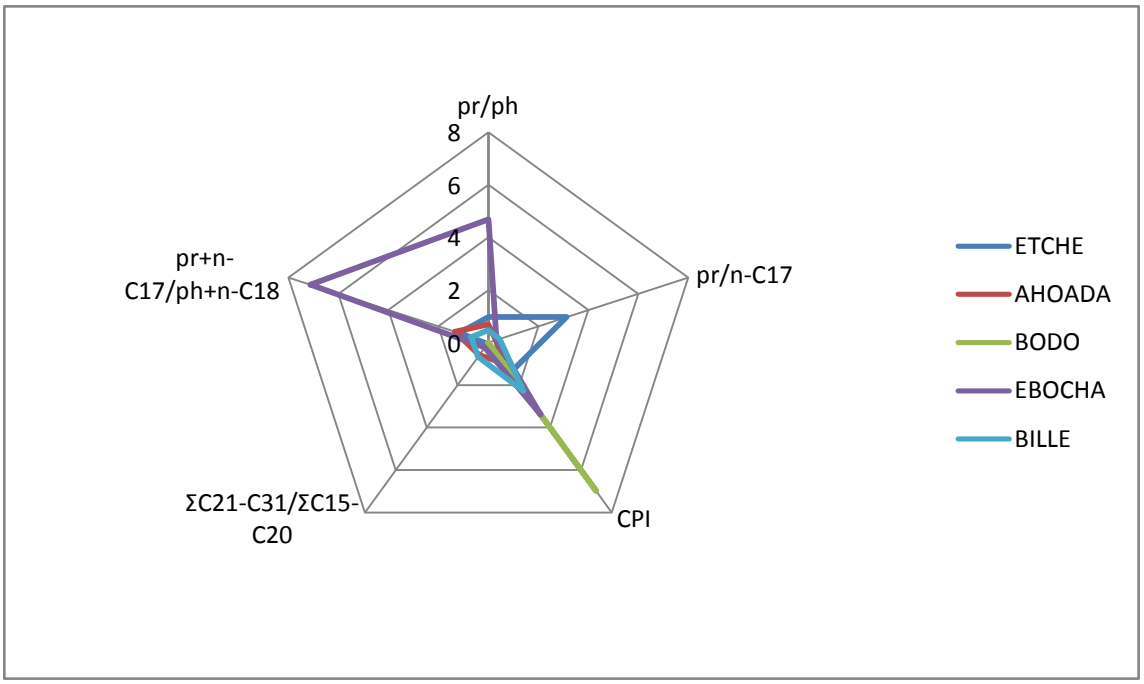

Figure 6. Star Plot depicting TPH ratios for the five sample locations

A star plot consisting of a series of ratios from the five parameters was used to make correlation of the different oilfield extracts.

4. Conclusion

Analysis of crude oil polluted soils from Ahoada, Ebocha, Bodo, Bille and Etche oil spillage sites shows that the soils were highly polluted. The CPI values reveal mature oil from marine and terrestrial source input. The star diagram shows that oils from Ahoada, Bille and Etche were closely matched suggesting a close grouping among the oils and is reflective of oil generation from a common source (marine source). Oils from Ebocha show fairly close pattern with Bille and Etche suggesting common source (terrestrial source). These similarities in pattern of oil are in line with the marine and terrestrial source rocks of the oils. However, Bodo was observed in the star plot to follow pattern different from the other oils. This difference in path followed by the oil is in line with different source rock between the oils.

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