

Geochemical fingerprinting of an oil-impacted site, Niger Delta: Source and weathering profile of aliphatic hydrocarbons.

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Abstract: Aliphatic hydrocarbon fingerprints of oil residues extracted from oil-impacted soil samples were compared with the source crude oil in order to characterize the oil hydrocarbons and assess the extent of their degradation at surface and subsurface depths. Gas chromatographic analysis of the saturate fraction identified aliphatic hydrocarbon in the nC_8 to nC_{35} range including pristane and phytane. Reduced abundance of aliphatic hydrocarbons characterized by unresolved complex mixtures (UCM) in the chromatograms were suggestive of degraded oil hydrocarbons, which was more at surface than subsurface depth. Compositional data of aliphatic hydrocarbons such as CPI, Pr/Ph, Pr/ nC_{17} and Ph/ nC_{18} revealed the following: typical Niger Delta crude oil as source of spill, the differential depletion of spilled oil hydrocarbons and weathering by biodegradation, which varied more at surface than subsurface depth. Hierarchical cluster analysis (HCA) used to test for correlation of the aliphatic hydrocarbon components among the spill samples was based on compositional similarity with the source crude oil. The result showed the spill oil residue at surface had undergone significant alteration in its chemical composition and did not correlate with the source crude oil, the subsurface spill oil residue showed similarity with the source crude oil. This indicated extensive weathering of the surface spill oil, while the subsurface spill oil was only moderately weathered.

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1. Introduction

Spills of crude oil are common in the Niger Delta region of Nigeria. When such spills occur via equipment failure, operational mishap and /or intentional damage to oil production facilities, hydrocarbons are released into the environment. This leads to the destruction of aquatic and terrestrial flora of the Niger Delta region (Zabbey, 2008).

The alkanes constitute a large percentage of hydrocarbons found in crude oil and originate from the chemical and geological transformation of biomolecules deposited during sedimentary processes (Tissot and Welte, 1984). Within the carbon-carbon skeletons of certain geochemical compounds are embodied essential information on the fate of these hydrocarbons. Hence, they are used as indicators and/or characteristic fingerprints of the oil in which they occur (Hunt, 1996; Osuji and Antia, 2005; Martinez-Frias *et al.*, 2007). Geochemical ratios of aliphatic hydrocarbons, such as carbon preference index (CPI), pristane/ n -heptadecane (Pr/ nC_{17}), phytane/ n -octadecane (Ph/ nC_{18}) and pristane/phytane (Pr/Ph), have been used as diagnostic tool for identifying pollution sources, monitoring weathering and biological degradation processes and interpreting chemical data from oil spills (Peters *et al.*, 2005; Osuji *et al.*, 2006b; Gao and Chen, 2008). Advances in analytical methodologies in the

quantification of aliphatic hydrocarbons and enhanced understanding petroleum geochemistry, now allow investigators to characterize, differentiate and/or correlate between spilled oil and suspected source oils using chemical principles - geochemical markers (Wang *et al.*, 2000; Faksness *et al.*, 2002; Sun *et al.*, 2009).

Weathering causes changes in the composition of spilled oil by reducing the toxicity and concentration of the contaminant. Microbial degradation (biodegradation), represents one of the main mechanisms of natural weathering processes by which oil hydrocarbons are removed from contaminated (EPA, 1999). By evaluation of the aliphatic hydrocarbon content of an oil-impacted soil and in comparison with the source crude oil, the effect of weathering in the Niger delta region by hydrocarbon attenuation was studied.

2. Materials and Method

2.1 Sampling site description

The study site (fig. 1) is located at Gokana Local Government Area of Rivers State, in the oil rich Niger Delta region of southern Nigeria bordering the Atlantic Ocean. The area has two (2) flow stations -Bomu and Bodo West. The presence of oil production facilities, which includes flow stations and numerous Trans-Niger pipelines that criss-cross the land, renders the area prone to oil spills.



Figure 1: A photograph showing a section of the oil-contaminated site.

2.2 Sampling

Oil contaminated soil samples were collected from four different points at surface (0-15cm) and subsurface (15-30cm) depths each with the aid of a stainless still scoop. The spill samples were placed in a pre-cleaned glass jar, labelled appropriately and then transported to the laboratory. Crude oil of same source as the spill was also collected. The codes and identities for the oil spill soil samples collected are given as follows:

Table 1: Sampling codes for the different spill points

Sample location	Sample Codes
Surface (NW-SF)	NW-02
	NW-04
	NW-06
	NW-08
Subsurface (NW-SS)	NW-22
	NW-24
	NW-26
	NW-28
Source Crude Oil	Oil

2.3 Oil Extraction and Chromatographic Analysis

Air dried soil samples were finely grounded and homogenized with an agate pestle and mortar, soxhlet extracted with hexane/dichloromethane (1:1) mixture, while the crude oil sample was deasphalted in excess pentane and filtered. Cleanup of oil hydrocarbons was achieved on a chromatographic column (30cm x 1cm) packed with silica gel and hexane used to elute the

saturate, which contains aliphatic hydrocarbons. Analysis of the saturate fraction was performed with a Hewlett Packard (HP) 6890 gas chromatograph (GC) fused with a silica capillary column (30m, 0.25mm id) and equipped a flame ionization detector (FID). Compound peaks identification and area integration of each compound peaks was processed by the chemstation software.

3. Results and Discussion

3.1 Gas Chromatographic Analysis

Gas chromatographic analysis of aliphatic fraction of the source crude oil (fig. 2) identified *n*-alkanes in the nC_8 to nC_{35} range and the acyclic isoprenoids pristane (Pr) and phytane (Ph), which were well resolved. The chromatogram of the source crude oil showed *n*-alkane peak concentration in the nC_{12} to nC_{16} and nC_{22} to nC_{27} range.

This bimodal *n*-alkane distribution as well as the dominance of pristane over phytane indicates mixed marine and terrestrial organic matter, typical of Niger Delta crude oil (Eneogwe *et. al.*, 2003; Stout *et. al.*, 2007).

At surface depth, spill oil residues contained aliphatic hydrocarbons (AHCs) in the nC_{13} to nC_{33} range with extremely low abundance (fig. 3). The chromatogram also contained a hump of unresolved complex mixture (UCM), which consists of hydrocarbons not resolved into peaks during gas chromatography (Peters *et. al.*, 2005; Gough and Rowland, 1990).

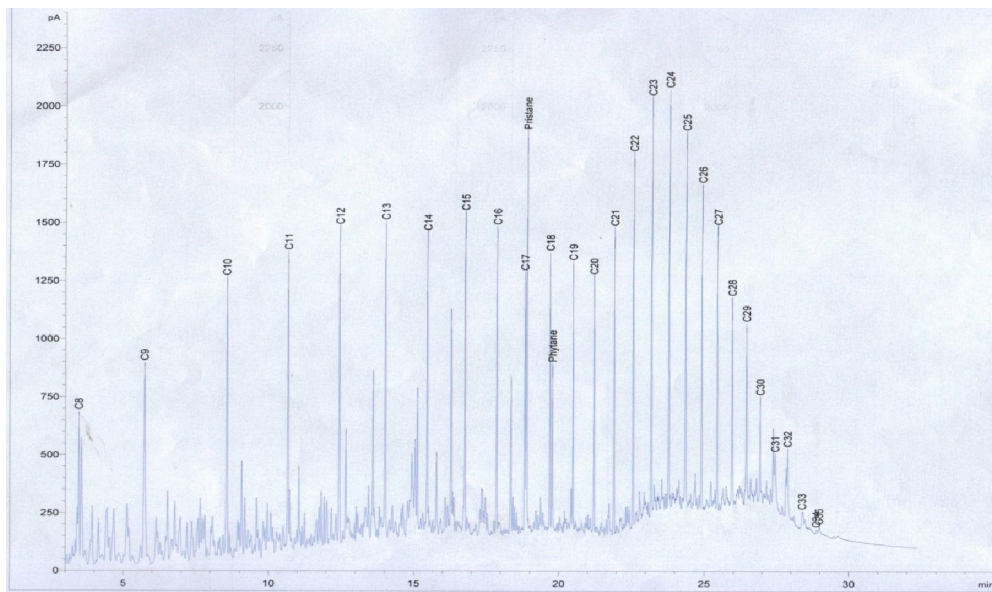


Figure 2: GC-FID chromatogram of the source crude oil showing well resolved aliphatic hydrocarbon peaks.

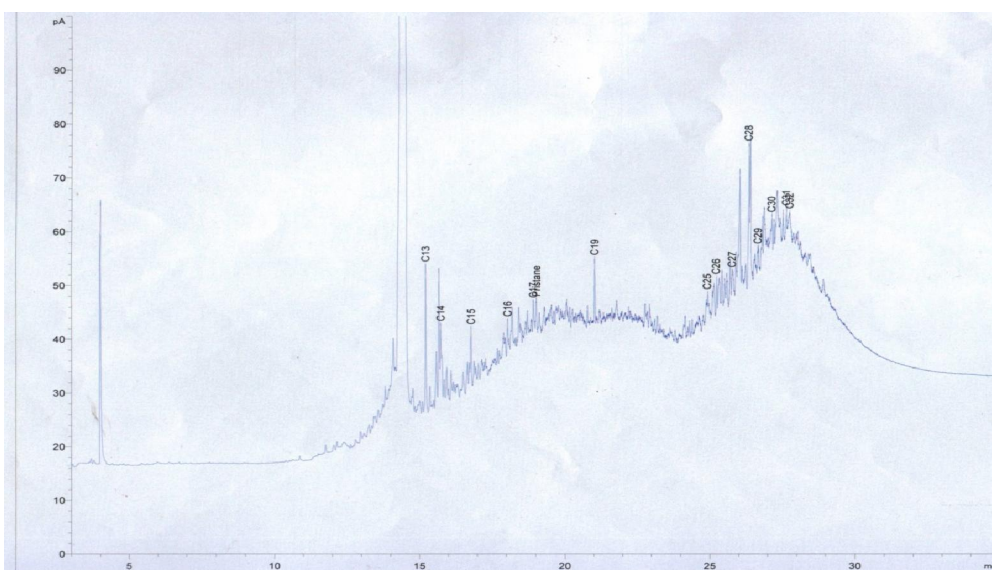


Figure 3: A representative GC-FID chromatogram of the surface spill (NW-SF) showing high rising unresolved complex mixture (UCM).

The extreme low abundance AHCs with the loss of hydrocarbons below C_{13} and high rising UCM is indicative of extensive degradation of the spilled oil residue at surface (NW-SF).

At the subsurface depth, GC analysis of the oil spill residue identified aliphatic hydrocarbons from C_8 – C_{35} , which were resolved (fig. 4). This aliphatic hydrocarbon (AHC) peak distribution is same for the source crude oil. AHC abundance, at subsurface depth, was observed to be more (about 25 times) than at surface depth (vertical axis of chromatograms), with reduced UCM height. Chromatogram peak concentration in the high molecular weight range

(nC_{19+}) for the oil spill residue at subsurface depth, showed similarities with the source crude oil, but different in the low molecular weight (LMW; nC_8 to nC_{17}) range with reduced abundance.

Similarities in aliphatic hydrocarbon distribution and high molecular weight (HMW) n -alkane peak concentrations point to a close relationship between the source oil and oil residue at subsurface depth (NW-SS). However, reduced low molecular weight (LMW) n -alkanes abundance and UCM height are suggestive of degraded spill oil residue at subsurface depth, which was moderately weathered.

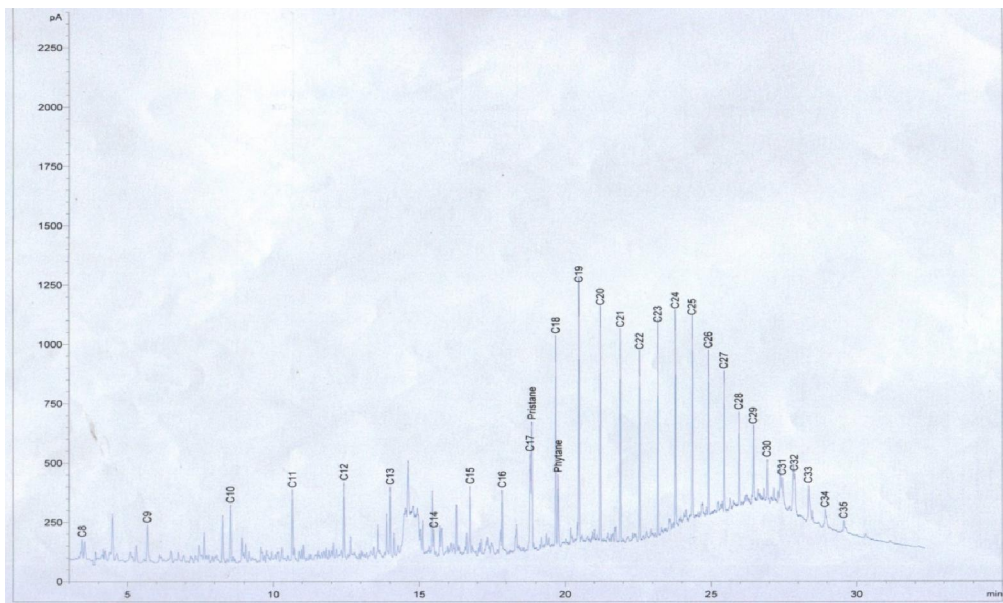


Figure 4: A representative GC-FID chromatogram of the subsurface spill (NW-SS) showing low abundance of nC_8 to nC_{17} n -alkanes and reduced UCM height.

3.2. n -Alkane Distribution

n -alkanes fingerprints of the oil spill samples in comparison with the source crude oil (table 2), were used for characterization. The carbon preference index (CPI) shows the distribution of odd/even carbon numbered n -alkanes and used as an indicator of source hydrocarbon input in the environment. Biogenic hydrocarbon input, including plant and phytoplankton, have CPI values from 3 to 11. Crude oils characteristically have values around 1 while values between 1 and 3 are reflective of an admixture of petrogenic (crude oil) with varying biogenic

contributions (Wang *et. al.*, 1999; Gao and Chen, 2008). In this study, n -alkane distribution (CPI) ranged from 0.72 to 1.07 for NW-SF samples and 1.10 to 1.27 for NW-SS samples (table 2). These values are within range and affirm crude oil as source of the spill. Deviation from mean CPI values for NW-SF (0.88 ± 0.14) and NW-SS (1.17 ± 0.07) was suggestive of variable degree of weathering. In comparison with CPI value of the source crude oil (1.10; table 2), the spill oil residue was more weathered at surface than at subsurface depth.

Table 2: Diagnostic ratios of geochemical markers for aliphatic hydrocarbon analysis

Samples	CPI	Pr/ nC_{17}	Ph/ nC_{18}	Pr/Ph
Oil	1.10	1.35	0.66	2.07
Diagnostic ratios for NW-SF samples				
NW-02	1.07	3.64	2.35	2.59
NW-04	0.88	3.78	2.45	3.05
NW-06	0.86	3.72	2.37	2.33
NW-08	0.72	3.82	2.39	2.10
Mean	0.88 ± 0.14	3.74	2.39	2.52
Diagnostic ratios for NW-SS samples				
NW-22	1.10	1.11	0.37	2.31
NW-24	1.15	1.12	0.36	1.59
NW-26	1.27	1.07	0.36	1.96
NW-28	1.16	1.12	0.37	1.93
Mean	1.17 ± 0.07	1.11	0.37	1.95

$$CPI = (C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34})$$

3.3. Isoprenoid Analysis

Pristane (Pr) and Phytane (Ph) are two

prominent isoprenoid hydrocarbons found in crude oil. Ratios of these isoprenoids obtained from gas

chromatographic analysis are expressed as Pr/nC_{17} , Ph/nC_{18} and Pr/Ph . They are used as petroleum contamination markers and provide valuable information on source and degradation extent of oil hydrocarbons (Wang *et al.*, 2000; Peters *et al.*, 2005; Osuji *et al.*, 2006a). *n*-alkanes degrade faster than isoprenoids (branched alkanes), leading to an increase in ratio values of Pr/nC_{17} and Ph/nC_{18} , especially when they are highly degraded (Wang *et al.*, 2006 and references therein). Pr/nC_{17} ratio for NW-SF, from 3.64 at NW-02 to 3.82 at NW-08, were significantly high when compared with a ratio of 1.35 for the source crude oil (table 2). These high ratios are suggestive of extensive biodegradation of aliphatic hydrocarbons at surface. Ratio values for NW-SS spill samples, from 1.07 at NW-26 to 1.12 at NW-24, were close to the source crude oil indicating only slight to moderate degradation of the aliphatic hydrocarbons since the spill incident. Ph/nC_{18} ratio from 2.35 to 2.37 for the NW-SF, compared with the source oil - 0.66, and NW-SS ratios from 0.36 to 0.37 further points to extensively weathered oil spill residue at surface, while the subsurface was only moderately weathered.

Pristane and phytane isoprenoids originate from the phytol (C_{20}) side chain of chlorophylls by decarboxylation in the presence of oxygen to give pristane (*i*- C_{19}) or reduction in the absence of oxygen to give phytane (*i*- C_{20}). Thus Pr/Ph ratio is a parameter indicative of the redox condition of the environment – oxic or anoxic. Calculated mean Pr/Ph ratio for the oil-impacted soil samples at NW-SF (2.52) and NW-SS (1.95) were compared with the source oil (2.07). These ratios also buttress the differential depletion of the aliphatic oil hydrocarbons at surface (NW-SF) and subsurface (NW-SS) depth by the biodegradation process of weathering. The NW-SF had higher ratio values due to the decarboxylation of phytane to pristane (in the presence of oxygen) and attributed to weathering by biodegradation, while the NW-SS had ratio values close to the source oil and suggestive of a lightly biodegraded spill oil. However, Pr/Ph ratios remained within range of the source oil (2.07) with the surface (NW-SF) having values from 2.10 – 2.59 and subsurface (NW-SS) from 1.59 – 2.31. These ratio values reveal the effect of biodegradation did not alter the Pr/Ph ratio of the oil spill samples appreciably and thus could still be indicative of the spill source (Wang *et al.*, 2000).

3.4. Correlation of spill samples with Source oil

Compositional data of aliphatic hydrocarbons was used to characterize the spill samples. Hierarchical cluster analysis (HCA) approach was applied to sort the data and test for correlation among the samples. This relationship was put in a pictorial form (fig. 2) to make correlation and / or differentiation between the spill oil

and source oil samples easier, and provide information on the extent of weathering and degradation. The HCA dendrogram showed similarity of 64.71% for surface (NW-02, NW-04, NW-06 and NW-08) and 83.27% for subsurface (NW-22, NW-24, NW-26 and NW-28) spill samples.

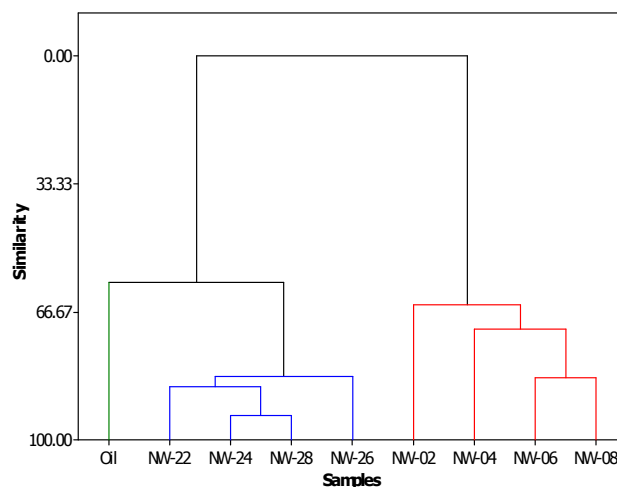


Figure 5: Hierarchical cluster analysis (HCA) dendrogram showing the relationship among aliphatic hydrocarbon composition for the samples

Greater variance – viz lesser similarity – among the NW-SF spill samples indicated the degradation of aliphatic hydrocarbons by weathering was variable more at surface than at subsurface. HCA separated the samples into three distinct groups according to their aliphatic hydrocarbon composition. Group 1 contained only the source crude oil, an unweathered oil. Group 2 contains NW-22, NW-28, NW-24 and NW-26 which are all spill samples at subsurface depth. They were 59.04% correlated with the source crude oil suggesting compositional alteration of the aliphatic hydrocarbon component of the spilled oil by degradation was moderate. The third group contained NW-02, NW-06, NW-04 and NW-08 which were spill samples at surface depth. This group did not correlate with the source crude oil suggesting that the chemical composition of the aliphatic hydrocarbon component of the spilled oil had undergone significant alteration by degradation, thus extensively weathered.

4. Conclusion

The distribution and composition of aliphatic hydrocarbon compounds was used in the assessment and fate of oil hydrocarbons in an oil-impacted site. Hydrocarbon peak range and carbon preference index (CPI) values were typical of crude oil as the source of spill. The abundance of aliphatic hydrocarbons coupled with characteristic UCM, showed the spilled oil was more degraded at surface than subsurface depth. Pr/Ph

ratios were suggestive of weathering by biodegradation, which was more active at the surface than subsurface. Isoprenoid/*n*-alkane ratios and hierarchical cluster analysis (HCA) showed compositional alteration of the aliphatic hydrocarbon component of the spilled oil by degradation. Consequently, the spilled oil at surface (NW-SF) was extensively weathered while the subsurface (NW-SS) was moderately weathered.

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