

Petroleum hydrocarbon variations revealed by chemical fingerprinting of oil spill soils with similar contamination source.

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Abstract: Chemical fingerprinting technique was used to determine the composition, contamination extent and significance of petroleum hydrocarbon variation in an oil spill site with similar contamination source. Soil samples were collected from an oil spill site in Ogoni area, Niger Delta, at surface (0 to 15cm) and subsurface (15 to 30cm) depths and analyzed with gas chromatography flame ionization detector (GC-FID) after extraction and fractionation of petroleum hydrocarbons. Total petroleum hydrocarbon concentrations from 3,667.1 to 4 591.9 mg/kg in surface samples and 2,206.4 to 2,949.0 mg/kg in subsurface samples revealed the Niger Delta soils were polluted. Petroleum hydrocarbons were characterized by dominance of polycyclic aromatic hydrocarbons (PAHs) with average compositions of 89.67% and 74.38% in surface and subsurface samples respectively. Diagnostic ratios of *n*-alkanes and isoprenoids suggest the oil spill hydrocarbons were altered by combustion in surface soils and by biodegradation in subsurface soils. PAH diagnostic ratios also suggested pyrogenic derived hydrocarbons in surface soils and pyrogenic input to petrogenic hydrocarbons in subsurface soils. In conclusion, the spilled crude oil polluted the Niger Delta soils at both surface and subsurface depths. As at sampling, the oil spill soils had undergone burning, which was less effective at subsurface depth.

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1. Introduction

Petroleum hydrocarbons discovered in soils and water at environmental release sites are frequently investigated to determine their source, fate and sometimes for settling disputes related to legal liability. This is mostly achieved by gas chromatography (GC) equipped with a flame ionization detector (GC-FID) or mass spectrometry (GC-MS). GC is used to facilitate the detailed composition and distribution of petroleum hydrocarbons present in contaminated samples (Wang et. al., 1999; Stout et al., 2007). Petroleum hydrocarbons studied in contaminated samples at environmental release sites are aliphatic hydrocarbons (AHCs), from C₈ to C₄₀ alkanes including pristane and phytane (Onyema et. al., 2013a), volatile benzene, toluene, ethylbenzene, xylenes (BTEX) and their alkyl homologs (Albaiges et. al., 2013), polycyclic aromatic hydrocarbons (PAHs) and in particular the petroleum specific alkyl- (C₁ – C₄) homologs (Chen et. al., 2004), and biomarker triterpanes and steranes (Mulabagal et. al., 2013). Data generated by the GC system are used as diagnostic tool to identify petroleum contamination and source, determine the extent of contamination, differentiate between hydrocarbon sources such as biogenic (biological),

petrogenic (petroleum) or pyrogenic (combustion), apportion hydrocarbon mixtures to multiple sources, and evaluate the degradation extent of released hydrocarbons (Ramsey et. al., 2014; Suneel et. al., 2013; Oros et. al., 2007; Burns et. al., 1997). Diagnostic tools widely used for chemical fingerprinting related environmental forensic investigations include ratios of AHCs such as pristane/phytane (Pr/Ph), pristane/*n*-heptadecane (Pr/*n*C₁₇), phytane/*n*-octadecane (Ph/*n*C₁₈), and carbon preference index (CPI); biomarkers such as pregnane index, tricyclic terpane index, relative distribution of C₂₇:C₂₈:C₂₉ steranes, C₂₇ 18 α,21β-trisnorhopane / C₂₇17α,21β-trisnorhopane (Ts/Tm), gammacerane / C₃₀ αβ hopane and PAHs such as low molecular weight to high molecular weight (LMW/HMW), phenanthrene/anthracene, fluoranthene/pyrene, and benz(a)anthracene/chrysene (Wang et. al., 1999).

Chemical fingerprinting of sediments from Daya Bay China, using diagnostic ratios of *n*-alkanes, isoprenoids and biomarkers, revealed petrogenic source for petroleum hydrocarbon contamination with biogenic contribution in varying proportions, which was relatively fresh (Gao and Chen, 2008). The composition as well as calculated diagnostic ratios of aliphatic and polycyclic aromatic hydrocarbon,

employed by Onyema et. al., (2013b) for chemical fingerprinting of oil spill soils in Niger Delta showed extensive degradation the residues, particularly the preferential degradation of the low molecular weight hydrocarbons, caused by weathering. Onojake et. al., (2015) using similar diagnostic ratios of *n*-alkanes, isoprenoids, PAHs and supported by statistical analyses tools, such as principal component analysis and cluster analysis, showed Agbada-1 oil spill soils in Niger delta originated from a common petrogenic source. Using PAH diagnostic ratios, Anyakora et. al., (2011) found soil contaminations in parts of Niger Delta not only emanated from petrogenic source, but from pyrogenic and biogenic sources.

Analytical chemists and geochemists have increasingly applied tiered analytical approach to chemical fingerprinting of petroleum hydrocarbon (Wang et. al., 2011). The tiered approach used may vary depending on the requirements of the environmental forensic study but usually include determination of hydrocarbon groups in environmental samples, distribution pattern recognition and comparison of diagnostic ratios. Such an approach was used in the Exxon Valdez oil spill to prove two sources for hydrocarbon contamination in Prince William (Boehm et. al., 1997), identify background contamination, confirm spill source of

stranded oils spilled along coastline, evaluate the weathering status using composition profiles of AHCs, PAHs and various weathering indices (Yim et. al., 2011), to distinguish relatively fresh unweathered oils from one another and quantitative determination of the components of a mixture of petroleum known as source allocation (Sauer and Boehm, 1991). In this study, chemical fingerprinting technique was employed to characterize aliphatic and polycyclic aromatic hydrocarbons and to determine the composition, contamination extent and significance of petroleum hydrocarbon variation in an oil spill site with similar contamination source, in Niger Delta, Nigeria.

2. Material and Methods

Sampling

Soil samples were collected from a crude oil spill site in Ogoni area of Rivers State, Niger Delta (fig. 1) in March, 2010. A total of eight soil samples were collected from four different points of the oil spill site, at surface (0 to 15cm) and subsurface (15 to 30cm) depths. The soil samples were collected with the aid of a stainless steel scoop, put in a pre-cleaned glass jar, labelled appropriately and taken to the laboratory for analyses.

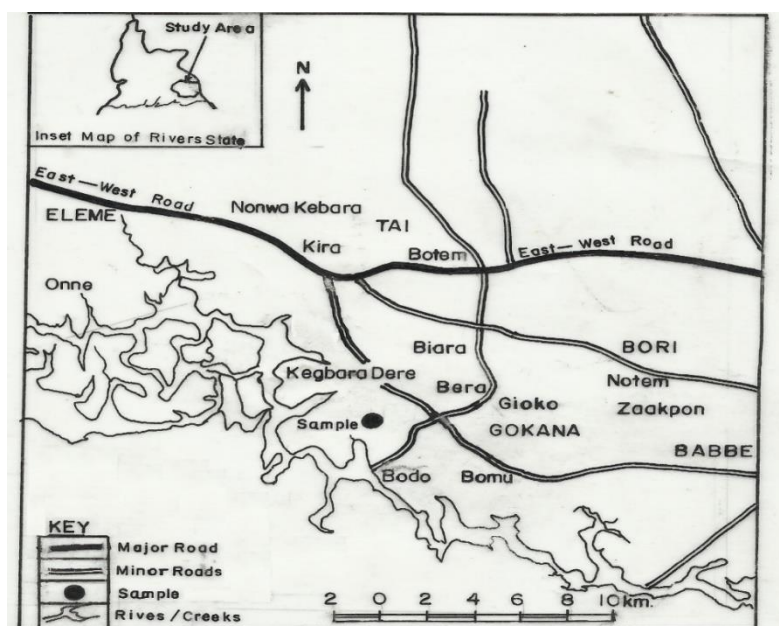


Figure 1. Map of Ogoni area showing the sample location in Gokana, Rivers State, Nigeria.

Oil hydrocarbon extraction and analysis

Soil samples were air dried at room temperature, foreign objects removed by hand picking, homogenized and sieved through a 2mm mesh to obtain uniform particle size. 50g of the homogenized samples were weighed and oil hydrocarbons extracted

with hexane and dichloromethane (v:v 1:1) in a soxhlet apparatus. The extracts were fractionated on a glass column (30 cm x 1 cm) stuffed with glass wool at the bottom and packed with activated silica gel. Hexane was used to elute the saturate fraction, which contain the aliphatic hydrocarbons, and

dichloromethane used to elute the aromatic fraction, which contain the polycyclic aromatic hydrocarbons. The fractions were concentrated under a stream of nitrogen at 40°C.

Gas chromatography (GC) analysis was performed with a Hewlett Packard (HP) 6890 series fitted to a silica capillary column (30 m x 0.25 mm) and equipped with a flame ionization detector (FID). The concentrated saturate and aromatic fractions were transferred into labelled vials and 1 μ L injected into the GC with the aid of a micro syringe. Helium was used as the carrier gas and the GC system operated in a splitless mode. Compound peaks identification were based on retention times compared to standards and

quantification acquired by Agilent's chemstation software.

3. Results and Discussion

Petroleum hydrocarbon composition

Petroleum hydrocarbons identified by gas chromatographic analysis of the oil spill soil sample extracts are aliphatic hydrocarbons (AHCs) and polycyclic aromatic hydrocarbons (PAHs). Total petroleum hydrocarbon concentration ranged from 3,667.1 to 4,591.9 mg/kg in surface samples and 2,206.4 to 2,949.0 mg/kg in subsurface samples (Fig. 2). These concentration levels were high and indicate the spilled crude oil polluted the Niger Delta soils at both surface and subsurface depths.

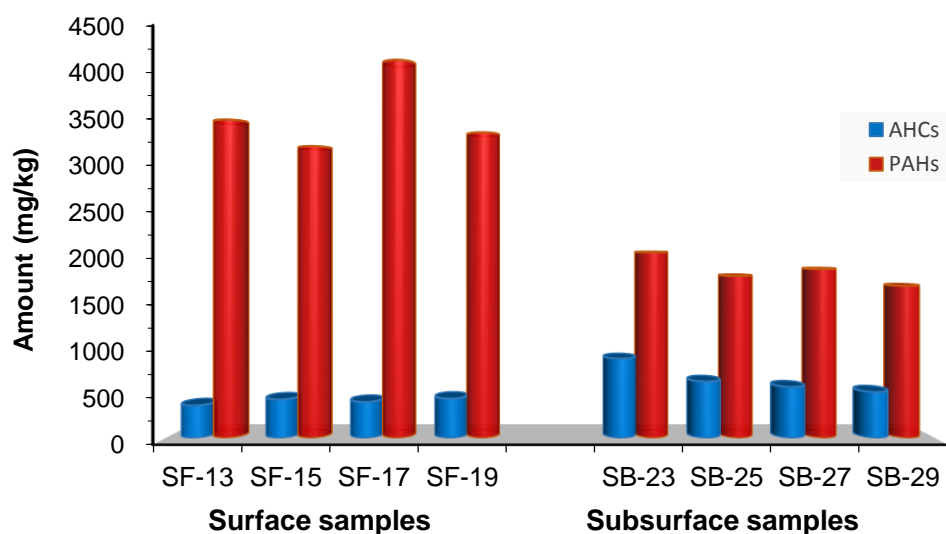


Figure 2. Distribution of total aliphatic hydrocarbons (AHCs) and polycyclic aromatic hydrocarbons (PAHs) in the Ogoni oil spill soil samples.

Petroleum hydrocarbon concentrations in the oil spill soil samples were characterized by dominance of PAHs. The PAHs concentrations were considerably higher than AHCs in all the samples at both surface and subsurface depths (fig. 2). Average AHC and PAH concentrations in surface samples was 408.8 mg/kg and 3,586.4 mg/kg and accounted for 10.33% and 89.67% of total petroleum hydrocarbon (TPH) composition respectively, while in subsurface samples, average concentrations of 649.6 mg/kg and 1,859.1 mg/kg accounted for 25.62% and 74.38% of TPH composition respectively. AHCs are the most abundant hydrocarbons in non-degraded crude oils, but they decrease as degradation proceeds, whereas PAHs are minor constituents of crude oils. PAH composition increase with degradation and they are most abundant in combustion products (Waples, 1985;

Wang et. al., 2007). The petroleum hydrocarbon concentrations in the oil spill soils indicate significant degradation of AHCs and increase in the concentrations of PAHs. Also, PAH concentrations in surface samples (3236.6 to 4190.0 mg/kg) are higher than subsurface samples (1692.9 to 2063.4 mg/kg), while AHCs concentrations in surface soil samples (363.4 to 439.6 mg/kg) were lower than subsurface samples (513.5 to 885.6 mg/kg). This indicate petroleum hydrocarbon degradation in the oil spill soils was more at surface than subsurface depth.

Distribution of Petroleum hydrocarbons

AHC distribution was obtained from the gas chromatographic analysis of saturate fraction of the oil spill soil sample extracts. The AHC distribution was from $nC_{13} - nC_{36}$ in surface samples, and $nC_{10} - nC_{36}$ in subsurface samples (fig. 3).

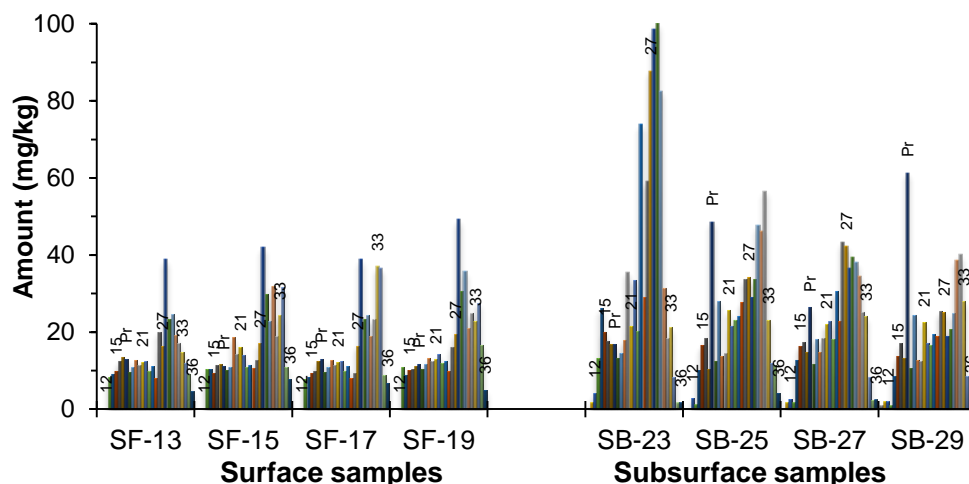
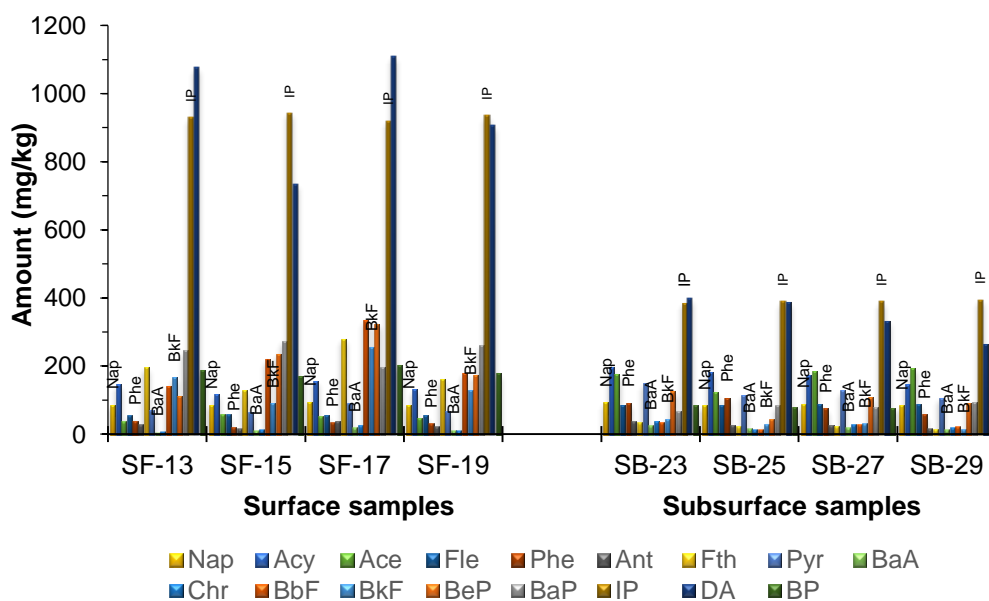


Figure 3. Aliphatic hydrocarbon distribution in the oil spill soil samples from Ogoni, Niger Delta.

Fig. 3 shows the complete absence of *n*-alkanes $\leq C_{12}$ in surface samples and $\leq C_9$ in subsurface samples. Also, *n*-alkanes with concentrations > 20 mg/kg are C_{28} - C_{34} in surface samples, and C_{20} - C_{33} in subsurface samples except for nC_{23} with a mean of 19.5 mg/kg (SB-23 20.2 mg/kg, SB-25 23.2 mg/kg, SB-27 18.2 mg/kg and SB-29 16.5 mg/kg). As weathering progresses, low molecular weight (LMW) $C_{10} - C_{22}$ *n*-alkanes are depleted more than high

molecular weight (HMW) $\geq C_{23}$ *n*-alkanes (Gao and Chen, 2008). The low concentrations of AHCs in the soils indicated degradation of the spilled oil residue. Also, the presence of LMW $nC_{10} - nC_{12}$ alkanes and the increased concentrations of HMW $nC_{20} - nC_{33}$ alkanes in subsurface samples indicated the degradation of the spilled oil residue was more in surface than subsurface soils.



Nap: naphthalene, Acy: acenaphthylene, Ace: acenaphthene, Fle: fluorene, Phe: phenanthrene, Ant: anthracene, Fth: fluoranthene, Pyr: pyrene, BaA: benzo[*a*]anthracene, Chr: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BeP: benzo[*e*]pyrene, BaP: benzo[*a*]pyrene, IP: indeno[1,2,3-*cd*]pyrene, DA: dibenzo[*a,h*]anthracene, BP: Benzo[*g,h,i*]perylene.

Figure 4. Polycyclic aromatic hydrocarbon distribution in oil spill soil samples from Ogoni, Niger Delta.

Gas chromatographic analysis identified 17 PAHs which distribute from naphthalene to benzo[*g,h,i*]perylene in the aromatic fraction of the oil

spill soil sample extracts (fig. 4). The 3-ring PAHs, Acy, Ace, Fle and Phe with mean concentrations of 137.8 mg/kg, 47.6 mg/kg, 55.4 mg/kg and 31.5 mg/kg

in surface samples were lower than 174.2 mg/kg, 168.3 mg/kg, 85.9 mg/kg, and 82.3 mg/kg in subsurface samples respectively. On the contrary, the 5-6 ring PAHs, BbF, BkF, BeP, BaP, IP, DA and BP, with mean concentrations of 218.6 mg/kg, 160.4 mg/kg, 211.3 mg/kg, 243.9 mg/kg, 931.8 mg/kg, 956.4 mg/kg and 184.8 mg/kg, in surface samples were higher than mean concentrations of 25.3 mg/kg, 30.4 mg/kg, 92.5 mg/kg, 80.7 mg/kg, 389.8 mg/kg, 345.6 mg/kg and 76.9 mg/kg in subsurface samples, respectively. This kind of PAH composition indicate generation of HMW PAHs by combustion of organic material via hydrocarbon pyrolysis and reaction between free C₂ radical species, such as olefins, and

smaller aromatic compounds (Wang, 2009). Consequently, PAH distribution in the samples suggest the oil spill soils had experienced burning. The difference in PAH concentrations, HMW enhanced in surface than subsurface samples and LMW decreased in surface than subsurface samples, indicate that burning of the oil spill soils was more efficient at surface than subsurface depth.

Diagnostic ratios of petroleum hydrocarbons

Common diagnostic ratios of AHCs employed in this environmental forensic study were calculated from gas chromatography data and presented in table 2.

Table 1. Diagnostic ratios of aliphatic hydrocarbon employed for the oil spill study.

Samples	Pr/nC ₁₇	Ph/nC ₁₈	Pr/Ph	CPI
SF-13	0.97	1.13	1.20	0.74
SF-15	0.96	1.09	1.02	0.89
SF-17	1.05	1.13	1.20	0.79
SF-19	1.05	1.12	1.00	0.69
Mean	1.01	1.12	1.11	0.78
SB-23	1.00	1.10	1.16	0.85
SB-25	4.68	2.26	1.73	0.93
SB-27	1.78	1.56	1.45	1.00
SB-29	4.65	2.32	2.51	1.08
Mean	3.03	1.81	1.71	0.96

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

Carbon preference index (CPI) shows the distribution of odd over even carbon-numbered *n*-alkanes. This parameter is frequently used in assessing the potential sources of *n*-alkane hydrocarbons in the environment (Bray and Evans, 1961). Biogenic hydrocarbons, including plant and phytoplankton, show *n*-alkanes distribution pattern of odd carbon-numbered alkanes being more abundant than even carbon-numbered alkanes with CPI values >2 (typically from 3 to 11). Crude oils characteristically have values around 1 indicating petrogenic input to source, while values close to 1 suggest *n*-alkanes from anthropogenic activities such as vehicular emissions, fossil fuel combustion and biomass combustion (Wang *et al.*, 1999; Seki *et al.*, 2006). In this study, the calculated CPI values are from 0.69 - 0.89 with mean of 0.78 in surface samples and 0.85 - 1.08 with mean of 0.96 in subsurface samples (table 1). This suggest the oil spill soils at surface depth, with CPI values below unity (< 1), had undergone combustion of the fossil fuel, while at subsurface depth, CPI values around unity (≈1) indicated the oil hydrocarbons were petrogenic.

Pristane (Pr) and Phytane (Ph) are two most abundant isoprenoid hydrocarbons found in crude oils. Their boiling points are close to *n*-heptadecane (nC₁₇)

and *n*-octadecane (nC₁₈) and they elute almost immediately after the *n*-alkanes during gas chromatography analysis, respectively (Peters and Moldowan, 1993). These hydrocarbons are diagnostic markers of petroleum source and provide valuable information on the degradation of oil hydrocarbons (Gao and Chen, 2008). In Niger Delta crude oils, pristane is usually dominant over phytane with Pr/Ph ratios characteristically > 2 (Stout *et al.*, 2007; Sonibare *et al.*, 2008), while Pr/nC₁₇ and Ph/nC₁₈ ratio values are 1.35 and 0.66 respectively (Onyema *et al.*, 2013b). But, during biodegradation *n*-alkanes are depleted faster than isoprenoids, leading to an increase in Pr/nC₁₇ and Ph/nC₁₈ ratios (Peters *et al.*, 2005). Calculated ratios of Pr/Ph, Pr/nC₁₇, and Ph/nC₁₈ for the oil spill soil samples are presented in table 1. In surface soil samples, ratios of Pr/Ph from 1.00 - 1.20 with a mean of 1.11, Pr/nC₁₇ from 0.96 - 1.05 with a mean of 1.01, and Ph/nC₁₈ from 1.09 - 1.13 with a mean of 1.12 were close to 1 (ratios ≈ 1). This indicate that these hydrocarbons, with close boiling points, were comparably depleted. In subsurface soil samples, ratios of Pr/Ph from 1.16 - 2.51 with a mean of 1.71, Pr/nC₁₇ from 1.00 - 4.68 with a mean of 3.03, and Ph/nC₁₈ from 1.10 - 2.32 with a mean of 1.81, showed pristane was dominant over phytane. Also, the

isoprenoids/*n*-alkane ratios in subsurface soil samples were higher than surface due to differential depletion. These results suggest the oil spill soils polluted by a typical Niger Delta crude oil was burnt at surface depth and biodegraded at subsurface depth.

PAHs derived from different sources have distinct compositions which are used as fingerprint to determine the most significant source in

environmental samples. PAH compositions of crude oils are usually dominated by the LMW 2-3 ring, while the HMW 4-6 ring are minor components, but dominant in products from the combustion of organic material (Chen *et al.*, 2004; Wang, 2009). Diagnostic ratios of polycyclic aromatic hydrocarbons were calculated from gas chromatography data of the oil spill soil samples and presented in table 2.

Table 2. Diagnostic ratios of polycyclic aromatic hydrocarbons employed for the oil spill study.

Samples	LMW (mg/kg)	HMW (mg/kg)	HMW/ LMW	Phe/Ant	Fth/Pyr	BaA/Chr
SF-13	389.72	3140.55	8.06	1.38	2.82	0.99
SF-15	356.15	2880.49	8.09	1.22	1.98	0.95
SF-17	430.12	3759.86	8.74	0.88	3.09	0.94
SF-19	372.93	3015.64	8.09	1.32	2.42	1.27
<i>Mean</i>	387.23	3199.14	8.24	1.20	2.57	1.04
SB-23	676.46	1386.95	2.05	2.46	0.23	0.64
SB-25	605.61	1196.48	1.98	3.85	0.21	1.17
SB-27	631.53	1246.61	1.97	2.76	0.19	0.64
SB-29	586.59	1106.26	1.89	3.42	0.15	0.65
<i>Mean</i>	625.05	1234.08	1.97	3.12	0.19	0.77

LMW PAHs = Σ 2 - 3 ring

HMW PAHs = Σ 4 - 6 ring

From table 2, HMW/LMW ratios from 8.06 - 8.74 with a mean of 8.24 in surface samples indicated that the oil spill soils at surface depth were clearly dominated by HMW PAHs. In subsurface samples, ratios from 1.89 - 2.05 with a mean of 1.97 were significantly lower than that of surface samples and attributed to increased LMW PAH concentrations. These ratios indicate generation of HMW PAHs from combustion of the oil spill soils at surface depth and mixture of pyrogenic and petrogenic PAH sources at subsurface depth.

PAH isomers suited as source diagnostic parameters are 3 ring - phenanthrene (Phe) and anthracene (Ant), and 4 ring fluoranthene (Fth), pyrene (Pyr), benzo[*a*]anthracene (BaA), and chrysene (Chr). Phenanthrene, pyrene and chrysene are petroleum characteristic compounds derived from crude oil and referred to as petrogenic PAH, while anthracene, fluoranthene and benzo[*a*]anthracene are preferentially produced during combustion (pyrolysis) of organic material and referred to as pyrogenic PAH (Peters *et al.*, 2005). Phe/Ant ratio greater than 10 (>10) suggest crude oil source for PAHs, with degraded oils having ratios <10. Similarly, Fth/Pyr ratio >1 indicate combustion processes for PAH, while ratio <1 suggest petroleum origin. BaA/Chr ratios for crude oils are < 0.02 with higher values indicating pyrogenic input from combustion of organic material (Wang *et al.*, 1999). In Niger Delta

crude oil, the composition of these PAH isomers are Phe 3.80%, Ant 0.32%, Fth 0.69%, Pyr 36.14%, BaA 0.30%, and Chr 21.83% of total PAHs (Onyema, 2012). But, their compositions are altered by degradation with Phe/Ant ratios from 4.34 - 7.18 and Fth/Pyr from 0.53 - 0.82 reported by Onyema *et al* (2013b) for natural weathered spilled oils. The calculated PAH isomer ratios for the oil spill samples are presented in table 2. Phe/Ant ratios from 0.88 - 1.38 with a mean of 1.20 in surface samples and from 2.46 - 3.85 with a mean of 3.12 in subsurface samples indicated the oil spill soils were degraded, more at surface than subsurface depth. Fth/Pyr ratios from 1.98 - 3.09 with a mean of 2.57 in surface samples and from 0.15 - 0.23 with a mean of 0.19 in subsurface samples indicated generation of pyrogenic PAHs, e.g. fluoranthene, from combustion of fossil fuels in surface soils and petrogenic source for PAHs in subsurface soils. BaA/Chr ratios from 0.94 - 1.27 with a mean of 1.04 in surface samples and from 0.64 - 1.17 with a mean of 0.77 in subsurface samples indicated pyrogenic input from combustion of process, which was more at surface than subsurface depth. From the PAH ratios, the crude oil spill soils at surface depth with high pyrogenic PAHs composition were burnt extensively and at subsurface depth, mixed pyrogenic-petrogenic PAH composition suggested the soils were burnt moderately.

Conclusion

Gas chromatographic analysis of soils spilled with crude oil from a similar source, in Niger Delta, revealed significant petroleum hydrocarbon pollution, at both surface and subsurface depths. Petroleum hydrocarbon compositions were predominantly PAHs, with the AHCs severely degraded. AHC and PAH diagnostic ratios were used as chemical fingerprinting tool. AHC ratios, CPI, Pr/Ph, Pr/nC₁₇ and Ph/nC₁₈, suggest combustion by burning of the spilled oil hydrocarbons in surface soils, and biodegradation in subsurface soils. PAH ratios, HMW/LMW, Phe/Ant, Fth/Pyr and BaA/Chr, suggest pyrogenic source for PAHs in surface soils and mixed pyrogenic and petrogenic sources for PAHs in subsurface soils. The Niger Delta oil spill, which polluted soils at both surface and subsurface depths, was burnt extensively at surface depth and moderately at subsurface depth.

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References

- Albaiges J, Jimenez N, Arcos A, Dominguez C, Bayona JM. The use of long-chain alkylbenzenes and alkyltoluenes for fingerprinting marine oil wastes. *Chemosphere* 2013; 91(3):336-343.
- Anyakora C, Coker H, Arbabi M. Application of polynuclear aromatic hydrocarbons in chemical fingerprinting: the Niger Delta case study. *Iran. J. Environ. Health. Sci. Eng.* 2011; 8(1):65-74.
- Boehm PD, Douglas GS, Burns WA, Mankiewicz PJ, Page DS, Bence AE. Application of petroleum hydrocarbon chemical fingerprinting and allocation techniques after the Exxon Valdez oil spill. *Marine Pollution Bulletin* 1997; 34(8):599-613.
- Bray EE, Evans ED. Distribution of n-Paraffins as a Clue to Recognition of Source Beds. *Geochimica et Cosmochimica Acta* 1961; 22:2-15.
- Burns WA, Mankiewicz PJ, Bence AE, Page DS, Parker KR. A principal-component and least-squares method for allocating polycyclic aromatic hydrocarbons in sediment to multiple sources. *Environmental Toxicology and Chemistry* 1997; 16:1119-1131.
- Chen B, Xuan X, Zhu L, Wang J, Gao Y, Yang K, Shen X, Lou, B. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou city, China. *Water Resource* 2004; 38:3558-3568.
- Gao X, Chen S. Petroleum pollution in surface sediments of Daya Bay, South China, revealed by chemical fingerprinting of aliphatic and alicyclic hydrocarbons. *Estuarine, Coastal and Shelf Science* 2008; 80(1):95-102.
- Mulabagal V, Yin F, John GF, Hayworth, JS, Clement TP. Chemical fingerprinting of petroleum biomarkers in Deepwater Horizon oil spill samples collected from Alabama shoreline. *Marine Pollution Bulletin* 2013; 70:147-154.
- Onojake MC, Anyanwu CO, Iwuoha GN. Chemical fingerprinting and diagnostic ratios of Agbada-1 oil spill impacted sites in Niger Delta, Nigeria. *Egyptian Journal of Petroleum* 2015; doi.org/10.1016/j.ejpe.2015.10.012 - In Press, Corrected Proof - downloaded 21/4/2016.
- Onyema MO, Osuji LC, Ofodile SE. Geochemical fingerprinting of an oil-impacted site, Niger Delta: Source and weathering profile of aliphatic hydrocarbons. *Researcher* 2013a; 5(10):16-21.
- Onyema MO, Osuji LC, Iechukwu IP. Assessment of Natural Weathered Spilled Oil, Niger Delta: Compositional Characteristics and Fate of Petroleum Hydrocarbons. *Journal of Applied Sciences in Environmental Sanitation* 2013b; 8(4):243-248.
- Onyema OM. Source determination and correlation of two oil spill sites using geochemical markers. Ph.D. Thesis, University of Port Harcourt, Nigeria 2012.
- Oros D, Collier R, Simoneit B. The extent and significance of petroleum hydrocarbon contamination in Crater Lake, Oregon. *Hydrobiologia* 2007; 574(1):85-105.
- Peters KE, Walters CC, Moldowan JW. *The Biomarker Guide* 2nd edition, Cambridge University Press, Cambridge, UK 2005.
- Ramsey E, Meyer BM, Ragoonwala A, Overton E, Jones CE, Bannister T. Oil source-fingerprinting in support of polarimetric radar mapping of Macondo-252 oil in Gulf Coast marshes. *Marine Pollution Bulletin* 2014; 89:85-95.
- Sauer TC, Boehm PD. The use of defensible analytical chemical measurements for oil spill natural resource damage assessment. *Proceedings of the 1991 Oil Spill Conference* American Petroleum Institute pp 363-370. American Petroleum Institute, Washington DC.
- Seki O, Yoshikawa C, Nakatsuka T, Kawamura K, Wakatsuchi M. Fluxes, source and transport of organic matter in the western Sea of Okhotsk: stable carbon isotopic ratios of n-alkanes and

- total organic carbon. *Deep-Sea Research I* 2006; 53:253-270.
18. Sonibare O, Alimi H, Jarvie D, Ehinola OA. Origin and occurrence of crude oil in the Niger Delta, Nigeria. *Journal of Petroleum Science and Engineering* 2008; 61:99-107.
 19. Stout SA, Liu B, Millner GC, Hamlin D, Healey E. Use of chemical fingerprinting to establish the presence of spilled crude oil in a residential area following hurricane Katrina, St. Bernard Parish, Louisiana. *Environmental Science Technology* 2007; 41:7242-7251.
 20. Suneel V, Vethamony P, Zakaria MP, Naik BG, Prasad KVS. Identification of sources of tar balls deposited along the Goa coast, India, using fingerprinting techniques. *Marine Pollution Bulletin* 2013; 70(1-2):81-89.
 21. Wang Z, Fingas M, Page DS. Oil spill identification - A Review. *Journal of Chromatography A* 1999; 843:369-411.
 22. Wang Z, Li K, Lambert P, Yang C. Identification, characterization and quantitation of pyrogenic polycyclic aromatic hydrocarbons and other organic compounds in tire fire products. *Journal of Chromatography A* 2007; 1139(1):14-26.
 23. Wang Z, Yang C, Yang Z, Sun J, Hollebne B, Brown C, Landriault M. Forensic fingerprinting and source identification of the 2009 Sarnia (Ontario) oil spill. *Journal of Environ. Monit.* 2011; 13:3004-3017.
 24. Wang Z. Oil Weathering and chemical fingerprinting of spilled or discharged petroleum in the environment. IOC/WESTPAC Workshop, Qingdao, China 2009.
 25. Waples DW. *Geochemistry in Petroleum Exploration*. International Human Resources Development Corporation, Boston 1985.
 26. Yim UH, Ha SY, An JG, Won JH, Han GM, Hong SH, Kim M, Jung JH, Shim WJ. Fingerprint and weathering characteristics of stranded oils after the Hebei Spirit oil spill. *Journal of Hazardous Materials* 2011; 197:60-69.

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