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FULL LENGTH ARTICLE

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

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KEYWORDS

Fingerprinting; PAHs; Isoprenoids; Diagnostic ratios; Gas chromatography **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.

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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].

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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.

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