

SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SELECTED SOIL SAMPLES WITHIN DELTA STATE, NIGERIA USING ISOTOPE COMPOSITION

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ABSTRACT

Five soil samples from five different communities in Delta state were analyzed for their isotopic compositions using gas chromatography-isotope ratio mass spectrometry (GC-IRMS). The bulk isotope ratio ranged from -25.5 ‰ to -27.4 ‰. The bulk isotope ratio for samples from Erhiemu, Egbo-Uwherhie and Afioseri suggested that the PAHs had predominant contributions from crude oil source while that for the other two samples from Abraka (road side and farm field) showed PAH input from other sources (pyrosynthetic origin).

Keywords: Polycyclic Aromatic and Chromatography-Isotope

INTRODUCTION

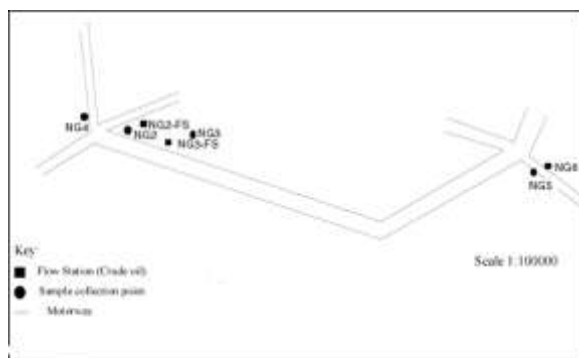
In the totality of the lithosphere, hydrosphere and atmosphere, carbon accounts for only ca.0.08% of the total mass [6]. However, it has been considered a unique element and its compound form the basis of all life. The ability of carbon to form a number of naturally occurring compounds with an equally wide range of properties makes it unique amongst other elements [6,9,10,11]. Carbon rich sedimentary deposits, which comprise diamond and graphite, calcium and magnesium carbonates and hydrocarbons like coal, oil and natural gas, are absolutely relevant to human's life and sustenance. Isotopes are defined as the atoms of the same element having the same numbers of protons and electrons but different numbers of neutrons, thus having a difference in their atomic masses. The abundance of each isotope relies on its stability. For example, carbon has three isotopes ^{12}C , ^{13}C , and ^{14}C . As a result of the relatively short half-life of the radioactive nuclide ^{14}C , natural carbon is thus a mixture of the two stable isotopes- ^{12}C and ^{13}C , with their relative abundance in geochemically undifferentiated carbonaceous materials being 98.894% and 1.106%, respectively with a ratio ($^{12}\text{C}/^{13}\text{C}$) of 89.42 [6,9,10].

The stable carbon isotope ratios of organic compounds depend on their origin and fate in the environment and have been used to elucidate the origins of hydrocarbons in ancient depositional environments [2,3,7]. Huang *et al* (1996) investigated the post-glacial variations in ^{14}C and ^{13}C profiles of individual aliphatic hydrocarbons and bulk organic matter for three stratified organic upland soils (peaty, podzol, and acid brown earth). They concluded that the rapid decreases of ^{14}C and ^{13}C profiles down the soil were mainly caused by degradation (microbial, chemical degradation and water washing) during early diagenesis. Keeling *et al* (1984) reported that fossil fuel burning has led to the depletion of atmospheric $\delta^{13}\text{C}$ by about 1 ‰, which explains the minute changes in the isotopic values of the organic matter over the last few hundred years. Farquhar *et al* (1989) explained that environmental conditions such as sunlight, nutrient levels, salinity, moisture and CO_2 concentrations can affect carbon isotopic fractionation during photosynthesis in biosphere.

The discussion so far highlights the fundamental issues in biodegradation and source apportionment studies. However a major constraint to obtaining reliable information during source apportionment is when PAHs and aliphatic hydrocarbons have been heavily biodegraded. This makes it difficult to obtain compositional and isotopic information to carry out reliable source apportionment studies. It is however the objective of this work to try to apportion sources to the PAHs present in some selected soil samples in Delta state using their isotope compositions by comparing them with the isotope compositions of a primary source (Nigerian crude oil).

DESCRIPTION OF STUDY AREA

The studied areas are Afioseri (NG2), Erhiemu (NG3) and Egbo-Uwherhie (NG4). Soil samples were collected from residential areas in the three different communities. These areas have been suspected to have been contaminated by oil spillage from oil industry operation. Two other soil samples (NG5 and NG6) were collected at a considerable distance (about 70 kilometres away) from an oil flow station, in a separate community called Abraka. All the aforementioned communities are in Delta State, which is in the South-South region of Nigeria. It is also worth mentioning that even in the Abraka community, oil prospecting by different oil companies has taken place from time to time. A schematic diagram of the study areas is given in Figure 1.



Key: NG2=Erhiemu NG3=Egbo-Uwherhie NG4=Afioseri NG5=Abraka motor way NG6=Abraka farm field

Figure 1: Schematic Diagram Showing Study Areas

Sample Preparation and Solvent Extraction

The different soils were dried at a temperature of 105°C for 3 to 4 hours and then ground to pass through a 60-mesh sieve. The samples were extracted by soxhlet extraction and refluxing techniques using redistilled dichloromethane (DCM) and dichloromethane- methanol (93:7) mixture. The weight of each sample extracted was altered to obtain sufficient amounts of PAHs analysis. 100 g of soil to 250 ml of solvent mixture was used for each extraction. When refluxing and Soxhlet extraction were completed, the slurries were filtered to obtain the extract solution. The extract of each sample was concentrated using rotary evaporator at 30°C for DCM solutions and 45°C for DCM/methanol mixtures. The extract was concentrated and dried using a stream of N₂. Open column chromatographic separation was then carried out on each extract obtained and the neutral aromatics containing the PAHs together with the aliphatics were kept for analysis.

RESULTS AND DISCUSSION

Table 1: Bulk Isotopic Data for NG Samples

Sample Name	$\delta^{13}\text{C}$ values, ‰, PDB
NG2 free aromatics	-26.1
NG2 bound aromatics	-25.9
NG3 free aromatics	-26.0
NG3 bound aromatics	-25.5
NG4 free aromatics	-25.8
NG4 bound aromatics	-26.7
NG5 free aromatics	-26.9
NG5 bound aromatics	-27.4
NG6 free aromatics	-26.0
NG6 bound aromatics	-25.5
Experimental error	-26.2±0.6

NG 2, 3, and 4 free neutral aromatics had bulk isotopic ratios of -26.1, -26.0, and -25.8‰ respectively (table 1). This close isotopic values result suggests that PAHs originate from the same source for all soil samples (crude oil source) (O`Malley *et al.*, 1994; Simcik *et al.*, 1999)). For asphaltene-derived samples, bulk isotopic ratios for NG 2, 3 and 4 was -25.9, -25.5 and -26.7‰ respectively, with isotopic ratio variation of -0.4‰ between them. These values were also very much related to crude oil as PAHs emission source [13]. For NG5 sample had lighter isotopic ratio of -26.9 and -27.4 ‰ for free and bound aromatics than other samples, suggesting that aromatics originate from petrol or diesel or generally of pyrosynthetic origin [13]. A further support comes from the fact that NG5 sample was a roadside dust. For NG6 sample, the bulk isotopic ratio was heavier than NG5 by about 1.5% (-25.5 to -26.0 ‰). This would imply that NG6 sample was from other sources, possibly biomass since this sample was a farm field sample.

CONCLUSION

The bulk isotopic data for the study area ranged from -25.5 ‰ to -26.9 ‰. This result suggested that the PAHs originate predominantly from crude oil sources with some contributions from other sources such as petrol, diesel and biomass.

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