



SOURCE DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS OF AN OIL SPILL IMPACTED SITE IN NIGER DELTA, NIGERIA

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Keywords: Polycyclic aromatic hydrocarbons; Petrogenic; Bodo city; oil spillage and distribution ratios

Soil samples were collected from an oil spilled polluted site in the Niger Delta, Nigeria. The polycyclic aromatic hydrocarbon content was determined using gas chromatography. Results indicated that 1,2-benzanthracene was the most abundant with concentration of 11.90 mg kg⁻¹ for surface and 8.10 mg kg⁻¹ for subsurface. Benzo[*b*]fluoranthene followed closely with concentrations of 2.15 mg kg⁻¹ for surface and 2.02 mg kg⁻¹ for subsurface. There was low concentration of phenanthrene in the samples (0.01 mg kg⁻¹) which indicate that the samples suffered from mild evaporation caused by weather. Various ratios such as the Σ3-6 ringed PAHs/Σ5-alkylated PAHs of 2.77; fluoranthene/pyrene of 7.89; benz[*a*]anthracene/chrysene of 9.79 were far greater than unity (>1) indicating petrogenic source; phenanthrene/anthracene ratio is 0.10 depicted that the area under study was unexposed to bush burning.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of compounds with two or more fused aromatic rings that occur either naturally in fossil fuels (coal and petroleum) or released from combustion of fossil fuels and degradation of manufactured materials such as lubricating oils, dyes, detergents and plastics.¹ Terrestrial PAHs are predominantly formed via pyrolysis, dehydrogenation and incomplete combustion of biogenic materials, and constituted a class of organic compounds that include potent mutagenic and carcinogenic compounds. They are often associated with combustion processes and exist under ambient environmental conditions as gases, volatile liquids, semi volatile substances and solids.²

PAHs are made of condensed aryl rings with hydrocarbons of very low molecular masses including methane which may act as precursors for the polycyclic aromatic compounds.³ PAHs can be classified into two major groups consisting of alkylated homologous PAHs (naphthalene, phenanthrene, dibenzothiophenes, fluorene and chrysene) and EPA priority (Fig. 1) PAHs (acenaphthalene, acenaphthene, anthracene and pyrene etc). The high molecular weight PAHs (three–six ringed) are known as pyrolytic (product of pyrolysis) PAHs while the low molecular weight PAHs (two–ringed) are known as fossil PAHs.⁴

Polycyclic aromatic hydrocarbons that are environmental contaminants are mainly derived from incomplete

combustion of organic matter, emissions of non-combustion related petrogenic (from petroleum) process and crude oil spillages.⁵ These compounds can be point source pollutants (e.g. oil spill) or non-point source pollutants (e.g. atmospheric deposition) and are part of the most widely spread organic pollutants.⁶

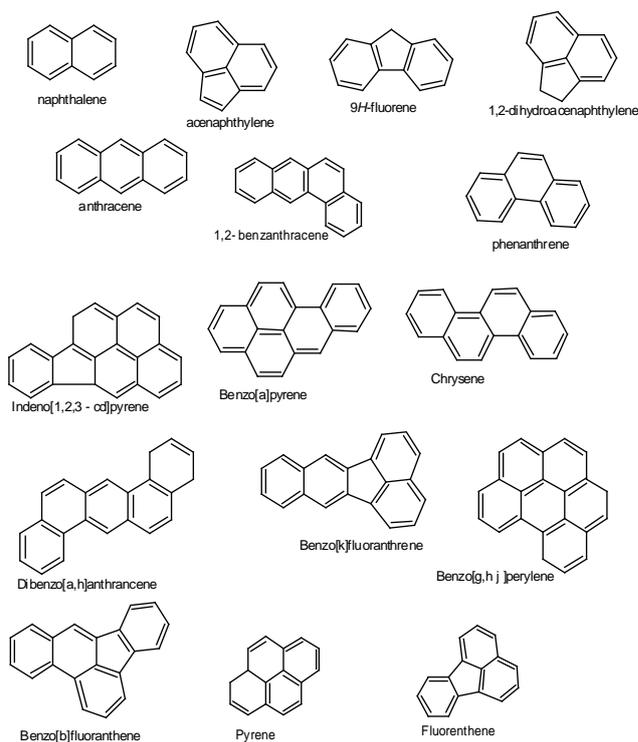


Figure 1. Chemical structures of sixteen (16) EPA PAHs.

They gain access into the environment through a number of pathways such as leakages from crude oil pipelines, sabotage, and accidental discharges such as blowouts, petroleum refining, cracking of crude oil, incineration of industrial and domestic wastes and chemical

manufacturing.⁷⁻⁹ Since they are classified as carcinogenic compounds, these are monitored worldwide in a wide range of environmental substances including drinking water, waste water, furnace emissions, soil, hazardous waste leachates and in air over major cities.¹⁰ Contamination of our environment by PAHs and how they reach our ecosystem is receiving a serious attention in society because of their impact on human health.¹¹ High molecular mass PAHs are mainly adsorbed into particulate matter and reach the hydrosphere and geosphere by dry and wet deposition.^{5,12}

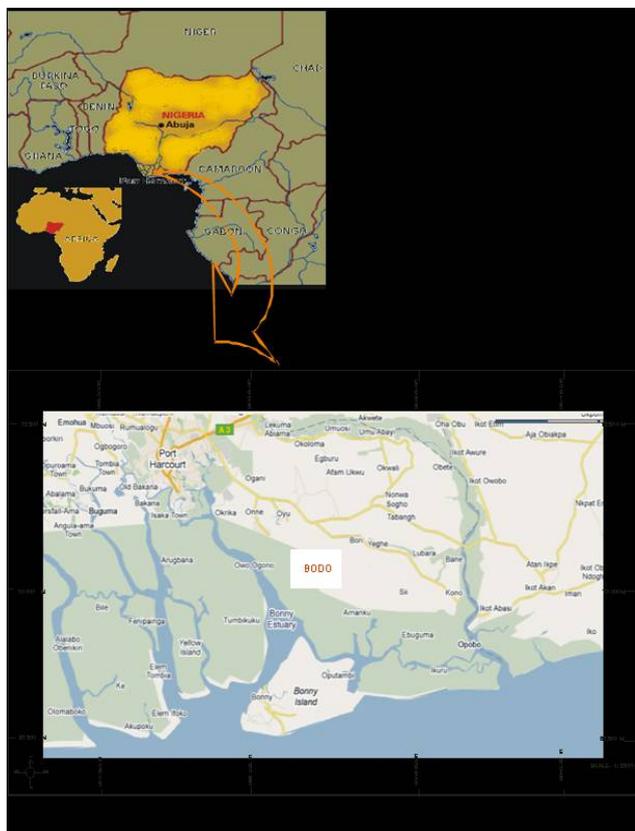


Figure 2. Map of study area showing Bodo city in Niger Delta, Nigeria.

The fate of PAHs and how they reach our ecosystem is receiving serious attention because of their impact on human health. Some of these compounds have carcinogenic, mutagenic and teratogenic effects on organisms and humans who consume these organisms.^{6,13}

The incessant oil spillage, which led to the contamination of the environment in the area under investigation, initiated the interest in determining and quantifying the source of PAHs in the environment.

Experimentals

Description of study site

The Bodo city (Fig. 1) is within latitude $6^{\circ} 73' N$ and longitude $5^{\circ} 32' - 5^{\circ}34' E$ in Gokana local Government Area of Rivers State, Nigeria. Bodo creek complexes are vulnerable to crude oil pollution due to the network of oil pipelines in the area (Fig.3).



Figure 3. A section of the oil spill site showing superficial patches on the vegetation

Chromatographic Analysis

Soil samples from surface and sub surface at the depth of 0 to 15 cm and 15 to 30 cm were collected from the oil spilled area, air dried, crushed and sieved to obtain a uniform particle size. 5g of the homogenized sample was weighed into clean and dry beakers. 10 ml of hexane/dichloromethane mixture was added and thoroughly mixed with the soil sample, and filtered. The extracts were injected into a capillary gas chromatograph, HP 6890 series GC system equipped with a flame ionization detector (FID). The column used was a HP-5, $30m \times 0.25mm \times 0.25\mu m$ (HP Part No. 19091S -433). Hydrogen (10.2 psi) was used as carrier gas at $1.5 ml min^{-1}$. The column was kept at $80^{\circ}C$ for 1 min. It was programmed to first reach $280^{\circ}C$ at the rate of $20^{\circ}C min^{-1}$, and then to $300^{\circ}C$ at the rate of $2.5^{\circ}C min^{-1}$. Temperature of the FID was kept at $325^{\circ}C$. The GC recorder was interfaced to a Hewlett (HP) Computer software (6207AA Kayak XA PIT/350) for recording the chromatographic output.

Results and Discussion

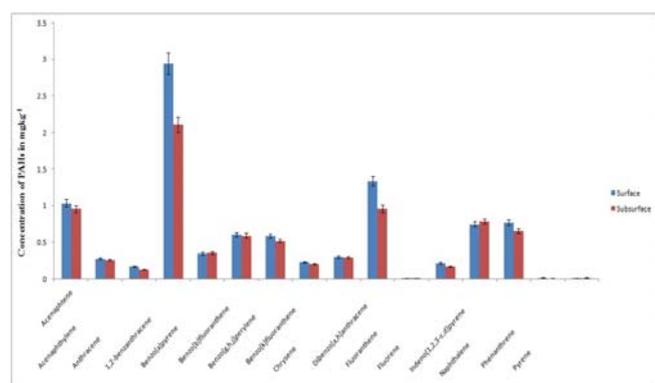
The results of the concentration of PAHs are shown in Table 1. The mean of the results is also graphically represented in Fig 4. The results show that the concentration of PAHs is more on the surface samples indicating their petrogenic origin.

Table 1. Concentration of PAHs in mg kg^{-1} of an oil spill polluted soil in Niger Delta Nigeria.

Compound	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	surface	subsurface								
Acenaphthene	0.63	0.35	3.57	3.68	0.42	0.11	0.03	0.22	0.13	0.42
Acenaphthylene	0.04	0.02	0.56	0.62	0.32	0.26	0.19	0.12	0.20	0.30
Anthracene	0.06	0.06	0.17	0.17	0.15	0.14	0.24	0.15	0.23	0.10
1,2-Benzanthracene	11.90	8.10	0.91	0.91	1.00	1.00	0.27	0.20	0.63	0.34
Benzo[a]pyrene	0.71	0.71	0.24	0.32	0.41	0.23	0.01	0.01	0.38	0.52
Benzo[b]fluoranthene	2.15	2.02	0.02	0.01	0.29	0.29	0.03	0.02	0.54	0.63
Benzo[g,h,j]perylene	2.07	1.68	0.03	0.04	0.36	0.32	0.30	0.36	0.19	0.21
Benzo[k]fluoranthene	0.52	0.48	0.28	0.22	0.12	0.12	0.11	0.11	0.12	0.10
Chrysene	0.03	0.03	0.02	0.13	0.46	0.39	0.38	0.40	0.22	0.52
Dibenzo[a,h]anthracene	2.00	1.98	0.27	0.32	1.14	1.23	2.04	1.04	1.23	0.25
Fluoranthene	0.01	0.01	0.03	0.03	0.01	0.01	0.01	0.01	0.01	0.01
Fluorene	0.11	0.13	0.08	0.12	0.15	0.41	0.03	0.05	0.21	0.13
Indeno[1,2,3-c,d]pyrene	2.29	2.31	0.30	0.30	1.04	0.97	0.07	0.04	0.04	0.31
Naphthalene	0.14	0.11	2.66	2.12	0.53	0.53	0.23	0.30	0.31	0.23
Phenanthrene	0.01	0.01	0.06	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pyrene	0.01	0.01	0.01	0.04	0.04	0.03	0.01	0.01	0.01	0.01

Crude oils and refined products from different sources can have different PAH distribution. PAHs are resistant to weathering than their saturated hydrocarbon counterparts (n-alkanes and isoprenoids) and volatile alkylbenzene compounds, thus making them one of the most valuable classes of hydrocarbons for oil spill identification.^{14,15} The distribution patterns of PAHs in the early stages of oil spillage can be used to identify sources of crude oils and petroleum products. Table 1 shows clearly the concentrations for the various PAHs in Bodo city oil spillage. The low molecular weight PAHs such as naphthalene and phenanthrene are susceptible to biodegradation and are not reliable indices for oil spill source analysis. The high molecular weight PAH containing 4, 5, and 6 rings are more stable and are therefore useful as diagnostic constituents of petroleum.⁷

The concentrations of the high molecular weight PAHs (three–six ringed PAHs) are also low. These low values indicated that the area of the oil spillage was not exposed to bush burning after the spill incidence since high values of PAHs is an indication of bush burning and combustion.¹⁶ Numerous quantitative diagnostic ratios have been defined to differentiate pyrogenic PAHs from other hydrocarbon sources including phenanthrene/anthracene (Ph/An), fluoranthene/pyrene (Fl/Py), benz[a]anthracene /chrysene (BaA/Ch), etc The ratio of the sum of the three to six ringed PAHs to the sum of five alkylated PAHs is 2.77.¹⁷ The ratio greater than unity (>1) depicted petrogenic source of PAHs.¹⁵ The higher value of the ratio shows that though the spilled oil is from a petrogenic source, the surface of the land would have been exposed to combustion or bush burning prior to the oil spilling incidence.¹⁶

**Figure 4.** Graphical representation of mean of PAHs for surface and subsurface \pm S. E

1,2-Benzanthracene is the most abundant with concentration of 11.90 mg kg^{-1} for surface and 8.10 mg kg^{-1} for subsurface (Table 1). Benzo[b]fluoranthene closely follows with concentrations of 2.15 mg kg^{-1} surface and 2.02 mg kg^{-1} for subsurface. The concentration of Phenanthrene in the samples is low (0.01 mg kg^{-1}) which further indicated that the samples suffered from mild evaporation from the weather.

Benlachen reported a method using the ratio of phenanthrene/anthracene <10 and fluoranthene/pyrene >1 to identify contamination sources of PAHs.¹⁸ Result also showed that phenanthrene/anthracene ratio is 0.10 and fluoranthene/pyrene ratio is 7.89 for soil samples. These values also support that combustion process had taken place just before the spill.

On the other hand, the ratio of benz[a]anthracene to chrysene, 9.79, also affirmed the initial argument that there was combustion/bush burning before the spilling incident.

Fig. 4 is a graphical representation of the mean concentrations of the PAHs for surface and subsurface soil samples. The higher concentrations of PAHs at surface depth may be attributable to the fact that PAHs are resistant to biodegradation and may remain at the surface depth for years.

Conclusion

Studying PAHs distribution has made it possible to identify the probable sources of these hydrocarbons in the environment. The diagnostic ratios can equally be used to

distinguish between pyrolytic and petrogenic sources. The PAHs from Bodo city oil spillage were more of petrogenic source. It was also confirmed that the area was exposed to combustion prior to the spill incident and that there was no bush burning after the spill.

Acknowledgements

The authors are sincerely grateful to Professor Leo C. Osuji for proofreading this article and his constructive criticism that brought this research article to fruition.

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Received: 01.12.2013.

Accepted: 27.12.2013.