



CHARACTERISATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN ROAD PAVING ASPHALT

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This study characterised the polycyclic aromatic hydrocarbons (PAHs) in five road paving asphalt samples randomly collected from two hot mix asphalt (HMA) plants in Port Harcourt, Nigeria. The $\Sigma 16$ PAHs of the samples ranged from 103.79 mg kg⁻¹ - 190.93 mg kg⁻¹. Naphthalene, acenaphthylene, fluorene and benzo[g,h,i]perylene were not detected in any of the samples. The characteristic isomer ratios of the asphalt samples were also calculated to serve as a reference for road runoffs and leachates studies.

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(PAHs) in road paving asphalt. The results obtained from this study will give an overview of the potential risk of contamination in case of improper use and undue exposure to both humans and the environment.

Introduction

The growing demand for road expansion in Nigeria has led to a huge increase in asphalt production. Asphalt is a primary road paving material that consists of a mixture of mineral aggregates (inert mineral materials such as sand, gravel, crushed stones, slag, rock dust or powder) and bitumen. Bitumen, a product of non-destructive distillation of crude oil during petroleum refining consists of aliphatic and cyclic alkanes, aromatic hydrocarbons, heterocyclic compounds containing oxygen, nitrogen and sulphur as well as metals like nickel, vanadium and iron.¹ It is the cement that binds the aggregate materials together. The emissions generated during the production and application of asphalt contains a large number of substances, some of which are potentially harmful to health.² Exposure to compounds contained in asphalt can occur through inhalation or even absorption through the skin during application to streets and roads.³ Asphalt can also be released to the environment through the degradation of the road surface and this may contaminate surrounding water bodies.⁴ Polycyclic aromatic hydrocarbons (PAHs) which may be generated during asphalt operations are toxic to human health. They are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms. They are ubiquitous environmental contaminants found in air, water, and soil and are always found as a mixture of individual compounds. They are mainly released during the combustion of petroleum products. PAHs comprise the largest class of chemical compounds known to be cancer-causing agents. Some (especially the 4-6 rings) are known carcinogens while the others (2-3 rings) may act as synergists.⁵ PAHs are difficult to degrade due to the complexity and stability of their molecular structures. Hence they are part of a group of adverse environmental contaminants known as persistent organic pollutants (POPs). This study, therefore, focuses on the characterisation of polycyclic aromatic hydrocarbons

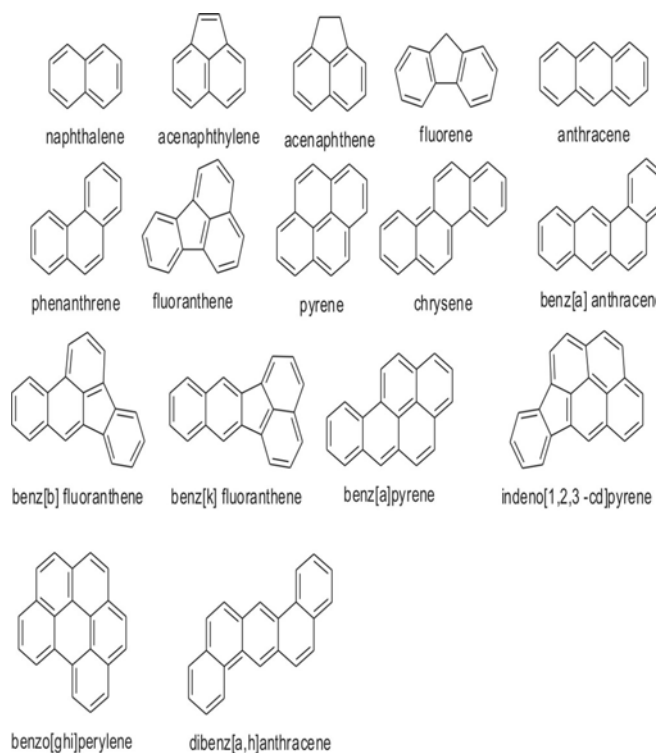


Figure 1. The chemical structure of sixteen priority PAHs

Materials and Methods

Sampling

Five asphalt samples were randomly collected from two asphalt production plants in Port Harcourt. The samples were collected immediately after production.

Extraction and Analysis by GC/FID

Extraction of hydrocarbons from the asphalt samples was done by mechanical shaking. 20 ml of dichloromethane was added to 5 g of the asphalt samples and shaken for 10 h using a bench shaker and this was repeated twice for each of the samples. The extracts were further purified in a silica gel (100 – 200 mesh) column (1 cm × 15 cm) and eluted with 30ml hexane/dichloromethane (1:1 v/v) to obtain the PAHs

fractions. The fractions were concentrated to 1 ml using a rotary evaporator and 1 µl of each of the fractions was analysed with Agilent 6890 gas chromatography equipped with flame ionization detector (FID) with the following operational conditions; flow rate (H₂: 40 ml/min, air; 450 ml/min, N₂: 30 ml/min); injection temperature (initial 60 °C, final 325 °C); detector temperature (350 °C). The chromatograms were quantified with respect to internal standards.

Table 1. PAHs content of asphalt samples

PAHs/SAMPLES	A	B	C	D	E
Naphthalene	nd	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	10.15	nd
Fluorene	nd	nd	nd	nd	nd
Phenanthrene	7.79	1.07	nd	11.67	nd
Anthracene	9.54	nd	nd	3.98	nd
Fluoranthene	5.37	2.49	5.87	14.30	3.74
Pyrene	6.46	2.38	7.68	14.55	2.35
Benz[a]anthracene	5.31	27.41	53.36	58.26	40.30
Chrysene	12.20	10.43	15.01	19.57	10.56
Benzo[b]fluoranthene	12.66	23.39	2.99	12.87	13.55
Benzo[k]fluoranthene	1.56	4.57	nd	2.79	1.20
Benzo[a]pyrene	8.05	11.98	7.74	8.06	5.11
Benzo[g,h,i]perylene	nd	nd	nd	nd	nd
Dibenz[a,h]anthracene	25.75	24.11	4.45	10.72	5.06
Indeno[1,2,3-cd]pyrene	75.98	56.74	22.21	24.01	21.92
∑16PAHs (mg kg⁻¹)	170.67	164.57	119.31	190.93	103.79
Fluoranthene/pyrene	0.83	1.05	0.76	0.98	1.59
Benz[a]anthracene/chrysene	0.44	2.63	3.55	2.98	4.61
Benzo[k]fluoranthene/benzo[b]fluoranthene	8.12	5.12	-	4.61	11.29

nd: not detected.

Results and Discussions

The result of the polyaromatic hydrocarbons (PAHs) in the asphalt samples is shown in table 1 while the chromatograms are shown in Supplementary Materials, Fig 2a-2e). The concentration of the PAHs in the samples ranges from 103.79 mg kg⁻¹ - 190.93 mg kg⁻¹ with sample D having the highest value and followed by samples A, B, C and E respectively (Table 1).

The results showed clear dominance of high molecular weight PAHs (4-6 rings PAHs). The domination of PAHs in asphalt binder by high molecular weight PAHs (4-6 rings PAHs) has been reported.² Most of the low molecular weight PAHs were not detected in the samples except for acenaphthene in sample D, phenanthrene in samples A, B, C and anthracene in samples A and D respectively. This may be attributed to the loss of low molecular weight PAHs during the refining of the parent crude oil and the combustion process that accompanies asphalt production since they are more susceptible to heat deformation than the higher molecular weight PAHs. Indeno[1,2,3-cd]pyrene was found to have the highest concentration in samples A and B while benz[a]anthracene dominated in samples C,D and E respectively. Benzo[g,h,i]perylene was not detected in any of the asphalt samples. This may be attributed to the

characteristic parent crude and an indication that the hot mix asphalt (HMA) plants might have obtained their bitumen from the same source.

Characteristic isomer ratios have been reported for PAHs from various pollution sources in road runoffs and leachate studies.⁶⁻⁹ The characteristic isomer ratios of the asphalt samples were calculated to serve as a reference point in petroleum hydrocarbon pollution studies especially in the Niger Delta area of Nigeria where such study is routine due to the vibrant oil and gas industry in the region. Flu/pyr ratio ranged from 0.76-1.59 while B[a]anth/chry ratio ranged from 0.44-3.82. B[b]fl/B[k]fl was between 4.61-11.29 (Table 1). Wang et al⁷ have reported B[b]fl/B[k]fl ratio between 1.07-1.95 for emission from vehicular exhaust.

Conclusion

This study showed the dominance of high molecular weight PAHs (4-6 rings) over the low molecular weight PAHs (2-3 rings) in the asphalt samples. Naphthalene, Acenaphthylene and fluorene were not detected in any of the samples. Asphalt exposure to both workers and the environment should be minimised to prevent the health risks and adverse environmental effects associated with polycyclic aromatic hydrocarbons.

References

- ¹National Institute for Occupational Safety and Health (NIOSH), *Hazard Review; Health Effects of Occupational Exposure to Asphalt.*, NIOSH Publication No. 2001-110. **2001**
- ²Fernandes R.N.P, Soares S. A, Nascimento R.F, Soares B. J, Cavalcante M.R., *J. Chromatogr. Sci.*, **2009**(47), 789-793.
- ³Binet S, Pfohl-Leszkwicz, A., Brandt, H., Lafontaine, M., Castegnaro, M., *Sci. Total Environ*, **2002**, 300, 37-49.
- ⁴Sadler, R., Delamont, C., White, P., Connel, D., *Toxicol Environ. Chem*, **1999**(68), 71-81
- ⁵Anyakora, C., Arbabi, M. and Coker, H., *Am. J. Env. Sci.*, **2008**, 4(2), 145-150.
- ⁶Xinag, L., Yingxia, L., Yang, Z., Shi, J., *J. Env. Sci. Health Part A*, **2010**, 45, 339-347.
- ⁷Wang, G., Zhang, Q., Peng, M. A., Rowden, J., Mielke, H. W., Gonzales, C., Powell, E., *Soil Sediment Contam.*, **2008**, 17, 1-17.
- ⁸Kose, T., Yamamoto, T., Anegawa, A., Mohri, S., Ono, Y., *Desalination*, **2008**, 226, 151-159.
- ⁹Brandt, H. C. A. and De Groot, P. C., *Aq. Wat. Res.*, **2001**, 35(17), 4200-4207.

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