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POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS WITHIN THE COALITE PLANT IN BOLSOVER, NORTH DERBYSHIRE

Ivwurie W., Emelife S.C., Sun C. and Snape C.
Department of Chemistry,
Federal University of Petroleum Resources, Effurun
Email: wivwurie@yahoo.co.uk

Abstract: *Five soil samples collected at varying distances from the Coalite plant in Bolsover, North Derbyshire were analyzed for Polycyclic Aromatic Hydrocarbons using GC-MS. The concentrations of the PAHs ranged from 0.03-2mgg^{-1} with a mean concentration of 4.50mgg^{-1} ± 1.51mgg^{-1}. The PAH diagnostic ratio (Flu / (Flu + Py)) showed a predominant contribution from liquid fossil fuel combustion and coal combustion with a least contribution from petroleum source.*

Keywords: Polycyclic Aromatic Hydrocarbons, Soils, Coal Combustion
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INTRODUCTION

The conversion of coal and petroleum to utilizable products like gasoline, diesel and petrochemicals; which are further processed to give secondary products like plastics, dyes, drugs or served as direct source of energy to plants and automobiles has brought about the emission of toxic inorganic species such as NOx, SOx, CO, CO_2 as well as large quantities of organic effluents into the environment. Some of these materials are not readily biodegradable and can therefore find their way in food chains, through diverse routes, endangering the life of living organisms and the ecosystem at large [3,7,12]. Hydrocarbons are a widespread class of contaminants in recent environments due to the multiplicity of their sources [10, 11]. These hydrocarbons can be synthesized by living organisms (biogenic origin), produced during the degradation of the organic matter (diagenic origin), formed during incomplete organic matter combustion (pyrolytic origin) and introduced in the modern environment via natural and anthrogenic release of fossil fuel combustibles (petrogenic origin) [10].

Amongst the organic species that find their way into the environment as a result of diverse industrial and domestic operations are the polycyclic aromatic hydrocarbons (PAHs). These originate from the incomplete combustion of organic materials or directly from fossils fuels, as well as from direct biogenic precursors [1]. The fate of PAHs in the environment has drawn attention from various researchers. This is because PAHs come from different sources, coupled with the diverse pathways that they follow when they are discharged into the environment. It is therefore the objectives of this work to determine the concentrations and the distributions of the PAHs in some selected soils at varying distances from the Coalite plant in Bolsover and their possible sources.

DESCRIPTION OF STUDY AREA AND SOIL SAMPLING

The studied areas are situated around the Coalite low temperature carbonization plant in Bolsover. Bolsover is a small town near Chesterfield, Derbyshire in England. It is 233 km from London and 42 km from Nottingham. The area is known for Coal mining. A schematic sketch showing the sample collection points is given in Figure 1.

The following 5 samples were collected according to their distance from the Coalite plant:

a. 350 g of soil, 20-30 metres from the plant designated as Bolsv.1
b. 370 g of soil, 50 metres from the plant designated as Bolsv.2
c. 300 g of soil, 500 metres from the plant designated as Bolsv.3
d. 400 g of M1 motorway roadside dust designated as Bolsv.4
e. 450 g of farm field soil designated as Bolsv.5

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.

MATERIALS AND METHOD

Sample Extraction and Purification

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 N_2. 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.

PAH Analysis

The extract were analyzed for Naphthalene, 2,4-dimethylnaphthalene, 1,2,4-trimethylnaphthalene, 2-methyl biphenyl, Fluorene, Phen/Anthr, Fluoranthene, Pyrene, Benz (a) Anthr/Chrysene, Benz (b)/(k) fluoranthene, Benz (a) pyrene, Dibenz (a, h) anthr/Inden (1,2,3-cd) py and Benzo (ghi) perylene using GC-MS at the School of Chemical, Environmental and Mining Engineering, University of Nottingham. The GC-MS analysis was performed on a Fisons instruments 8000 gas chromatograph interfaced to a MD 800 mass spectrometer with a quadrupole mass analyzer (ionizing energy 70eV, source temperature 280° C). The gas chromatograph capillary column is 50 m long; i.d. is 0.32 mm and a film thickness of 0.25μm, stationary phase is polyphenylmethylsiloxane. Lab base software written by VG was used for data acquisition and Mass lynx for interpretation. The determinations were at selected ion monitoring (SIM) mode. Concentrations of the various PAHs were determined using internal standard injection. Identification of the various PAHs was achieved by comparison with authentic standards.

RESULTS AND DISCUSSIONS

PAH Concentration and Distribution

The individual PAH concentrations of the soils ranged from 0.03 –2 mgg^{-1} dry weight (Table 1) with a mean concentration of 4.50 $mgg^{-1} \pm$ 1.51 mgg^{-1} dry weight. This range is by far, higher than the range (1-10 μgg^{-1}) reported in Zhang *et al*., 2006, associated with endogenous soils resulting from plant synthesis and natural fires. The PAH concentration was highest in the Bolsv.1 (6.7 mgg^{-1}) sample which is the sample collected about 30 m from the Coalite plant. This high concentration must have been as a result of its closest proximity to the Coalite plant than the other samples collected. Bolsv.1 also had the highest concentration of 2-3 ring PAHs and also 4-6 ring PAHs. This implies that the area has been contaminated by the Coalite plant emissions and as such, the soil has a great tendency to be toxic and carcinogenic. Generally, the 2-3 ring PAHs constituted 65% of the total PAH concentration and the 4-6 ring PAHs constituted the remaining 35% (Fig. 2). As reported by Chadwick *et al.* (1987) and Homann *et al.* (1994); molecular structure of PAH dictates their level of carcinogenicity, mutagenicity and toxicity. Low molecular weight PAH (≤ 3 rings), often display acute toxicity and low carcinogenicity, while high molecular weight PAH (> 3 rings), show low toxicity, but outstanding carcinogenicity and or mutagenicity.

Sources of PAHs

To evaluate the risks of PAHs to the environment, it is very important to find out their origin and sources. A number of studies have demonstrated the usefulness of PAH isomer ratios in source apportionment [4, 8, 15]. One of the frequently used isomer ratios is the Ant/ (Ant + Phe) ratio. According to this isomer ratio, the ratio < 0.1 indicates petroleum input and the ratio > 0.1 indicates pyrogenic input [2]. However, there are limitations to the use of this isomer ratio as demonstrated by Fraser *et al.* (1998). They demonstrated that Anthracene undergoes more rapid photochemical reaction in the atmosphere than Phenanthrene. The implication is that during atmospheric transport, the original composition information will not be preserved. Therefore, in order to carry out an accurate PAH source apportionment in soils, isomer ratios where the isomer pairs degrade photolytically at comparable rates have to be adopted. From CCME (2008), the isomer ratio Flu / (Flu + Py) is a more accurate ratio as it meets with the condition. The Flu and Py isomer pair degrades photolytically at comparable rates. The ratio < 0.4 indicates petroleum input; ratio between 0.4-0.5 indicates liquid fossil fuel (vehicle and crude oil) combustion input and ratio > 0.5 indicates grass, wood or coal combustion input [13]. In this study, the PAH diagnostic ratios of Flu / (Flu + Py) ranged from 0.33-0.6 (Table. 2). 20% of the soil samples had Flu / (Flu + Py) ratio < 0.4; 40% had ratio between 0.4-0.5 and another 40% had ratio >0.5. The diagnostic ratio showed predominance and an equal input from both liquid fossil fuels combustion and coal combustion. This result is as expected as the soil samples were collected from areas around the Coalite plant. Petroleum on the other hand, showed the least contribution (20%) to the PAH accumulation in the areas.

CONCLUSION

The PAH concentrations of the study area ranged from 0.03-2mgg^{-1}. There was a predominance of the low molecular weight PAHs and the PAH diagnostic ratio showed an equal input from liquid fossil fuel combustion and coal combustion. There was a low contribution from petroleum source.

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REFERENCES

[1] Arzayus, K.M., Dickhut, R.M. and Canuel, E.A. (2002) Effects of Physical Mixing on the Attenuation of PAH's in Estuarine Sediments. Organic Geochemistry. 33, 1759-1769.

[2] Behymer, T.D. and Hites, R.A. (1998) Photolysis of Polycyclic Aromatic Hydrocarbons Adsorbed on Fly Ash. Environ. Sci. Technol. 22, 1311-1319.

[3] Bjorseth, A.G. and Becher, G. (1985) PAHs in Work Atmospheres: Occurrence and Determination. CRC Press, Inc., Boca Raton, Florida, U.S.A. pp 9-13.

[4] Budzinski, H., Jones, I., Bellocq, J., Pierard, C. and Garrigues P. (1997) Evaluation of Sediment Contamination by Polycyclic Aromatic Hydrocarbons in the Gironde Estuary. Marine Chem. 58, 85-97.

[5] CCME (2008) Canadian Soil Quality Guidelines for the Protection of the Environment and Human Health: Carcinogenic and other PAHs. In: Canadian Environmental Quality Guidelines. pp 1-11.

[6] Chadwick, M.J., Highton, N.H. and Lindman, N. (1987) The Environmental Significance of Coal-derived carbon compounds. Environmental Impacts of Coal Mining and Utilization. Pergamon Press, Oxford, U.K. pp 10-19.

[7] Collier, A.R., Rhead, M.M., Trier, C. J. and Bell, M.A. (1995) PAC Profiles from a Light-Duty Direct–Injection Diesel Engine. Fuel.74, 362.

[8] Fraser, M.P., Grass, G.R., Simoneit, B.R. and Rasmussen, R.A. (1998) Air Quality Model Evaluation Data for Organics C_6-C_{22} Non-polar and Semipolar Aromatic Compounds. Environ. Sci. Technol. 32, 1760-1770.

[9] Homann, K.H., Loffler, S., Loffler, P.H. and Weilmunsler, P. (1994) Soot Formation in Combustion. Bockhorn, Springer Series in Chemical Physics. Springer-Verlag, Berlin. pp 59-165.

[10] Mazeas, L., Budzinski, H. and Raymond, N. (2002). Absence of Stable Carbon Isotope Fractionation of Saturated and Polycyclic Aromatic Hydrocarbons during Aerobic Bacterial Biodegradation. Organic Geochemistry. 33, 1259-1272.

[11] McElroy, A.E., Farrington, J.W. and Teal, J.M., (1989) Bioavailability of PAH in the Aquatic Environment. *In*: Varanasi, U. (*Ed*.) Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. CRC Press, Boca Raton, USA. pp 41-68.

[12] Smith, K.E.C., Green, M., Thomas, G.O. and Jones, K.C. (2001a) Behavior of Sewage Sludge-Derived PAHs on Pasture. Environ. Sc. and Technol. 35, 2141-2148.

[13] Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchel, R.H., Goyette, D. and Sylvestre, S. (2002) PAHs in the Fraser River Basin: A Critical Appraisal of PAH Ratios as Indicators of PAH Sources and Composition. Organic Geochem. 33, 489-515.

[14] Zhang, H.B., Luo, Y.M., Wong, M.H., Zhao, Q.G. and Zhang, G.L. (2006) Distributions and Concentrations of PAH in Hong Kong Soils. Environ. Pollut. 141, 107-114.

[15] Zheng, G.J., Man, B.K.W., Lam, J.C.W., Lam, M.H.W. and Lam, P.K.S. (2002) Distributions and Sources of Polycyclic Aromatic Hydrocarbons in the Sediment of a Sub-tropical Coastal Wetland. Water Res. 36, 1457-1468.

Tables and Figures

Table1: Individual PAH Concentrations (mgg^{-1})

PAH	Bolsv1	Bolsv2	Bolsv3	Bolsv4	Bolsv5
Naphthalene	0.6	0.3	0.2	0.1	0.5
2,4-Dimethylnaphthalene	0.5	0.4	0.4	0.03	0.4
1,2,4-Trimethylnaphthalene	0.3	0.2	0.1	0.1	0.1
2-Methyl Biphenyl	0.2	0.1	0.1	0.1	0.1
Fluorene	1	1	1	0.5	0.1
Phen/Anthr	1.5	1.2	1.0	0.5	2
Fluoranthene	0.4	0.4	0.3	0.3	0.1
Pyrene	0.6	0.3	0.2	0.4	0.2
Benz (a) Anthr/Chrysene	0.4	0.2	0.2	0.1	0.3
Benz (b)/(k) Fluoranthene	0.3	0.1	0.1	0.08	0.2
Benz (a) Pyrene	0.2	0.1	0.1	0.1	0.1
Dibenz (a, h) Anthr/Inden (1,2,3-cd) py	0.4	0.3	0.2	0.1	0.1
Benzo (ghi) Perylene	0.3	0.3	0.2	0.1	0.1

Note: PAHs quantification was carried out using internal standard injection (2-ethylanthracene, 100ng/μl)

Table 2: PAH Diagnostic Ratio (Flu/ Flu + Py)

Study area	Bolsv1	Bolsv2	Bolsv3	Bolsv4	Bolsv5
Ratio	0.40	0.57	0.60	0.43	0.33

Figure 1: Schematic Diagram Showing Study Areas

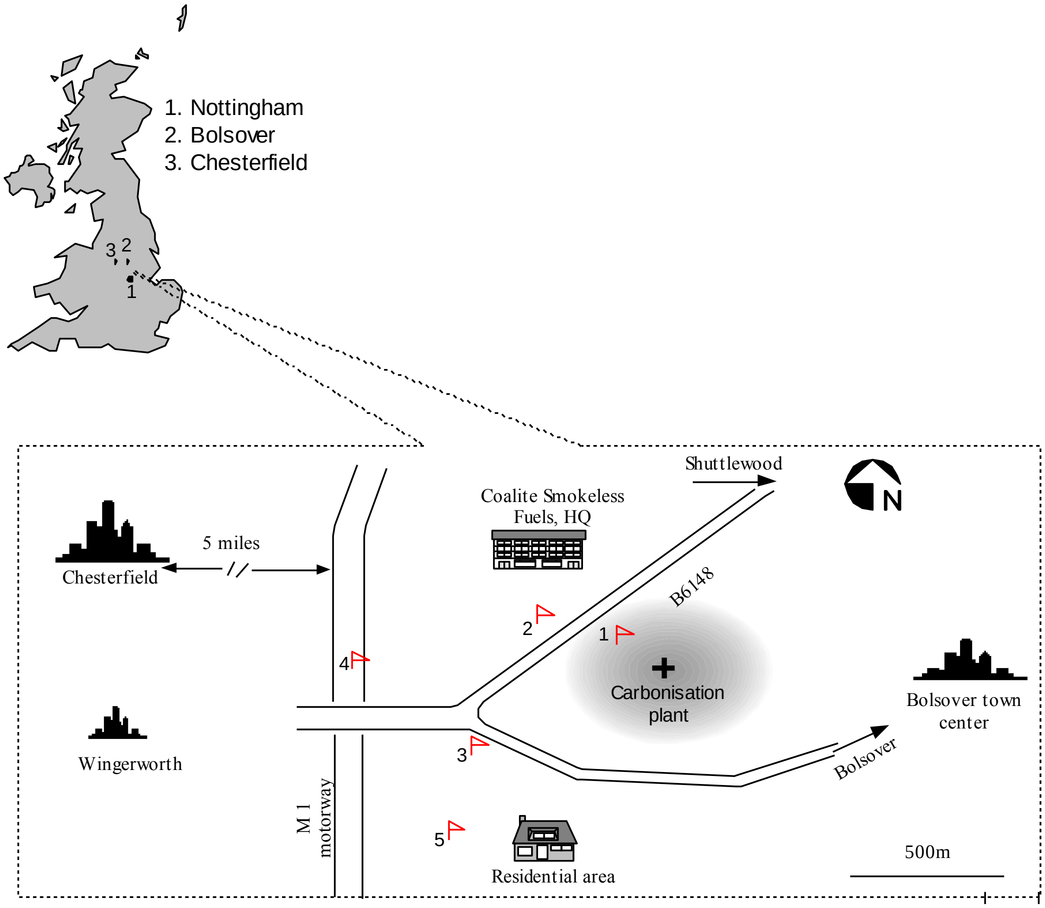
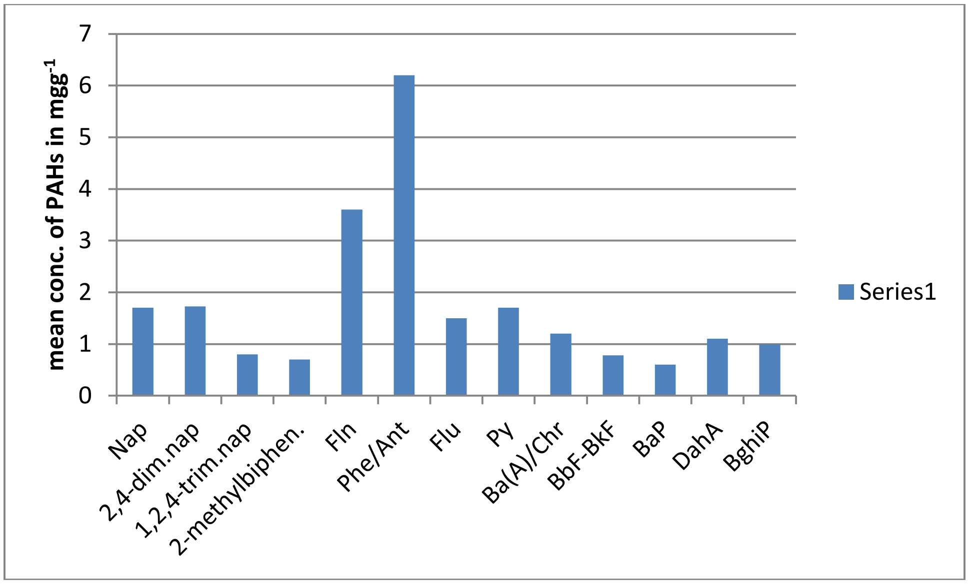


Figure 2: Distribution of PAHs in the Study Area



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BIOGRAPHY

Dr. Wisdom Ivwurie is a senior lecturer at the department of chemistry, Federal University of Petroleum Resources, Effurun. He is involved both in teaching and research. He is a member of various research groups in the university, amongst are Small Scale Refinery Research team, Power plant research team. He is also the current Ag. Head of Department of Chemistry of the Federal University of Petroleum Resources, Effurun.

Prof. Colin Snape (RSE) is the Director of Engineering Doctorate Centre in efficient fossil energy technologies and faculty of engineering, University of Nottingham. He is also the director of midlands energy graduate school. He is a fellow of the Royal Society of Edinburgh. He has been involved in fuel science and related disciplines for over 30 years and has contributed to the chemical engineering course at Nottingham by developing and delivering basic chemistry and thermodynamic modules.

Dr. Cheng-Gong Sun is an assistant professor of clean fossil energy technologies, Faculty of Engineering, University of Nottingham. He has worked in the general field of clean fuel and energy technologies for nearly 20 years, with comprehensive research expertise on clean fossil and biomass fuel technologies, fluidized beds, catalysis and adsorption materials.

Miss Emelife Stella Chinelo is a first class graduate of applied chemistry from Usmanu Danfodiyo University Sokoto. She is a much focused young girl who has a deep flair for research and acquiring knowledge. She won the vice chancellor’s award for the overall best graduating student of Usmanu Danfodiyo University Sokoto 2012/2013 academic session. She is planning on resuming her MSc programme sometime this year (2016) abroad.