

## POLYCYCLIC AROMATIC HYDROCARBONS IN ARCHIVAL SOIL SAMPLES FROM THE ROTHAMSTED EXPERIMENTAL STATION, HERTFORDSHIRE

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### ABSTRACT

Seven selected archival soil samples collected from the Rothamsted experimental station, Hertfordshire in the years 1881, 1927, 1937, 1956, 1966, 1980 and 1986 were collected and analyzed for Polycyclic Aromatic Hydrocarbons using GC-MS. The individual PAH concentrations ranged from 0.1-29  $\mu\text{gg}^{-1}$  with a mean concentration of  $89.55 \mu\text{gg}^{-1} \pm 37.15 \mu\text{gg}^{-1}$ . The PAH concentration showed a greater percentage of the HMW PAHs, indicating high carcinogenicity especially in the 1986 soil sample. The PAH diagnostic ratio (Flu/(Flu + Py)) showed a predominant contribution from wood and coal combustion.

**Keywords.** PAHs, Archival Soils, HMW PAHs

### 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 NO<sub>x</sub>, SO<sub>x</sub>, CO, CO<sub>2</sub> 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 [3,7,13]. Hydrocarbons are a widespread class of contaminants in recent environments due to the multiplicity of their sources [11,12]. 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 anthropogenic 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 fossil 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 times (years) from the Rothamsted Experimental station in Hertfordshire and their possible sources.

## DESCRIPTION OF STUDY AREA AND SOIL SAMPLING

This station is located at Harpenden in Hertfordshire, England. It is an agricultural research center founded over 160 years now, with an enviable international recognition for science in support of sustainable land management and environmental impact studies. Its research ranges from studies of genetics, biochemistry, cell biology and soil processes to investigation of ecosystem and landscape scale. Soil samples were collected from this Rothamsted experimental station at various times since the mid-1800s and up to 1989 were collected from the plough layer (0-23 cm) of an experimental plot for which atmospheric deposition will have been the only source of PAH input. All soils had been air-dried and ground in the same iron pestle and mortar after collection and passed through <2 mm sieves. This procedure is unlikely to contaminate the soils during processing. The samples were subsequently stored in glass jars with cork lids to the present day in a dark room at ambient temperature. For this work, 10 g of each sample from years 1881, 1927, 1937, 1956, 1966, 1980 and 1986 were taken from the archive and investigated. The soil samples are designated by their year (Jones *et al*, 1989).

## 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<sub>2</sub>. 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, Acenaphthylene, Acenaphthene, Fluorene, Phen/Anthr, fluoranthene, pyrene, Benz (a) anthr/chrysene, Benz (b)/(k) fluoranthene, Benzo (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 PAH concentration of the samples ranged from 0.1-29µgg<sup>-1</sup> dry weight with a mean concentration of 89.55µgg<sup>-1</sup> ± 37.15µgg<sup>-1</sup> dry weight. The range showed that the soil samples had PAH contributions from both endogenous and exogenous sources. As reported in Zhang *et al.*, 2006, the PAH range of 1-10µgg<sup>-1</sup> is associated with endogenous soils resulting from plant synthesis and natural fires. The PAH concentration was highest (149.3µgg<sup>-1</sup>) in the 1986 soil sample and least (50.5µgg<sup>-1</sup>) in the oldest soil sample of 1881. Generally, the PAH concentrations increased gradually from 1881 to 1986. This could be as a result of increase in industrial activities in the area as the year progressed. The 4-6 ring PAHs constituted 80% of the PAH concentration and the 2-3 ring members constituted the remaining 20% (Figure 1). This implies that the soil samples have outstanding carcinogenicity or mutagenicity. 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 [14]. In this study, the PAH diagnostic ratios of Flu / (Flu + Py) ranged from 0.51–0.58 (Table 1). This shows that all the soil samples had Flu / (Flu + Py) ratio  $> 5$ , indicating wood or coal combustion input.

### CONCLUSION

The PAH concentrations of the study area ranged from 0.1–29 $\mu\text{g g}^{-1}$ . There was a predominance of the high molecular weight PAHs especially in the 1986 soil sample, indicating high carcinogenicity of the soil samples and the PAH diagnostic ratio showed a predominant input from wood and coal combustion.

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## Tables and Figure

Figure 1. Distribution of PAHs in the Soil Samples

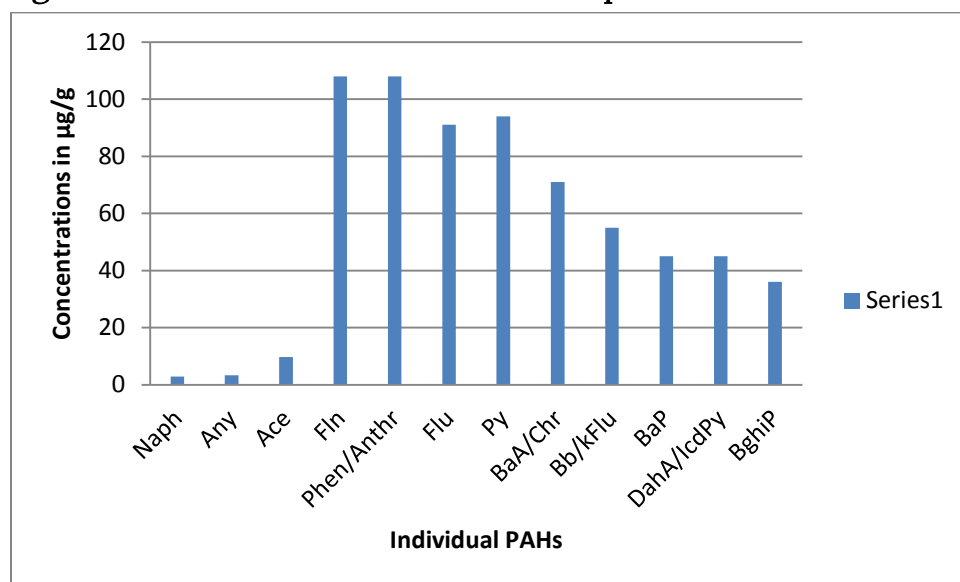


Table 1. PAH Diagnostic Ratio (Flu/ Flu + Py)

Sample	1881	1927	1937	1956	1966	'80	'86
Ratio	0.54	0.56	0.56	0.56	0.58	0.51	0.53

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## **BIOGRAPHY**

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