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DETERMINATION OF CONTAMINATION BY POLYCYCLIC AROMATIC HYDROCARBONS, AND THEIR MODE OF ORIGIN, IN URBAN SOILS FROM LEEDS (UK)

Heiam Hamed, William Hale, Ben Stern

School of Archaeological and Forensic Sciences, University of Bradford, UK.

Email: h.a.m.hamed@bradford.ac.uk, w.h.g.hale@bradford.ac.uk, b.stern@bradford.ac.uk

Abstract: This study aims to determine the concentration of 16 Polycyclic Aromatic Hydrocarbons (PAHs) in urban soils from Leeds in order to determine what the factors are controlling their distribution and abundances. Soil samples were collected across an area from Leeds. Gas chromatography with mass spectrometry (GC-MS) using selected ion monitoring (SIM) was used to identify and quantify PAHs in the soil samples with the aid of PAH external standards. The results showed the highest concentrations of total PAHs in sample L8 (1344 ng/g) taken from an area located near a parking site and road in Leeds and the lowest total concentration of the 16 PAHs in sample L16 (87 ng/g) taken from a private garden. The ratio of anthracene to anthracene plus phenanthrene AN/(AN + PH), fluoranthene to fluoranthene plus pyrene FLU/(PY+FLU) and benzo[a]anthracene to 228 (BaA/228) implied that the PAHs pollution originated from pyrogenic, biomass and petroleum combustion in the samples which were collected from Leeds city.

Keywords: Urban soil, PAHs, soil pollution PAHs source.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds containing carbon and hydrogen with two or more fused aromatic rings [1]. Sixteen PAHs have been listed by the United States Environmental Protection Agency as priority pollutants due to their toxicity and carcinogenic behaviour [2]. PAHs are found individually or as a complex mixture. These compounds originate from anthropogenic and natural processes [3]. Most anthropogenic PAHs are produced through the incomplete combustion of carbonaceous materials for example coal, diesel and petrol [4]. The main sources of natural PAHs are volcanic eruptions and natural fires. It is noteworthy that background concentrations of PAHs in soils were reported to be 1 - 10 ng/g without anthropogenic input [5]. PAHs in the atmosphere deposit in soil through wet or dry deposition processes. In wet sediments, PAHs dissolve in precipitation, while dry sediment deposition occurs when the compounds are deposited on the soil as dry particles or gases [6]. Soil contamination of PAH could have a direct impact on public health [7]. Soil pollution with PAHs can easily be delivered to humans from direct contact or suspended dust [8][9]. The soil is one of the most important sources of storage and re-emission of PAHs. According to Wang, PAH concentrations dropped considerably from urban to suburban to countryside soils [10]. The aim of this study is to determine the concentration of 16 PAHs from urban soils in Leeds (UK) as part of a broader study to determine what the factors are controlling their distribution and abundance in the area. The samples will be analysed by using gas chromatography with mass spectrometry (GC-MS).

2. MATERIAL AND METHODS

2.1. Sample locations

Sixteen soil samples were collected across an area from Leeds in the United Kingdom. A 1 km grid was used to select approximate sampling locations. At each, a precise location was determined by the availability of surface soil and a minimum 2 m distance from the road, to ensure that road-distance is not a complicating factor. Exact locations for each sample were recorded using a GPS. Approximately 5 g of soil was taken from each site using a stainless steel spatula, the soil samples were put directly into individual aluminum bags to avoid cross contamination. Table 1 shows the coordinates for the sampling locations and Fig.1 shows a map of these locations.

Sources: Esri, HERE, DeLorme, USGS, Intermap, INCREMENT P, NRCan, Esri Japan, METI, Esri China (Hong Kong), Esri Korea, Esri (Thailand), MapmyIndia, NGCC, © OpenStreetMap contributors, and the GIS User Community

Fig 1: Map of the sampling locations

Coordinates (British National Grid)		Samples Code
East	North	
428122	435937	L1
428888	435905	L2
428094	435082	L3
428856	435903	L4
429075	435905	L5
429869	435877	L6
429089	435122	L7
429773	435108	L8
428091	434900	L9
428884	434910	L10
428076	434064	L11
428909	434060	L12
429103	434882	L13
429872	434868	L14
429103	434078	L15
429869	434074	L16

Table 1: Coordinates of the soil sample locations from Leeds based on the British National Grid.

2.2. Sample preparation

Immediately after arrival into the laboratory, the samples were air dried at room temperature for one day to remove excess water. Approximately 2 g of each sample was accurately weighed. The samples were put into glass vials, which had been solvent washed three times with dichloromethane/methanol 2:1 (v/v) before use. 4 mL of this solvent was added to cover the soil. The sample and solvent were mixed before being placed in a sonic bath for 10 minutes to aid extraction. After sonication the sample was separated into solid and liquid phases with the aid of a centrifuge for 5 minutes at 2000 rpm (~650 g relative centrifugal force); any samples which were not adequately separated by this process were centrifuged again. The liquid was transferred by Pasteur pipette into auto sampler vials for GC-MS. If necessary these extracts were stored in a fridge in order to retain the volatile PAHs.

2.3. GC-MS Method

An Agilent technologies 7890A GC system with 5975c mass selective detector (MSD) was used to separate, identify and determine the concentrations of PAHs in the soil extracts. 1 µL of each sample extract was injected into a splitless injector at a temperature of 300 °C. The samples were separated with a HP5 capillary column (30 mm × 0.25 mm × 0.25 µm film). The initial oven temperature was at

40 °C for 1 min, raising to 120 °C at 25 °C/min, then to 160 °C at 10 °C/min, and finally to 300 °C at 5° C/min, this final temperature was held for 15 min. The interface temperature was kept at 280 °C. Helium was the carrier gas used at a constant flow rate of 1 mL/min. The 16 PAHs were analysed with a Selected Ion Monitoring (SIM) mode.

2.4. SIM method

Initially a Scan method was used (*m/z* 50 to 800) to confirm the identity and retention times of the PAHs. Once these were determined, a SIM (Selected Ion Monitoring) method was developed with different masses detected for different retention times. These are shown in Table 2 (after Dong *et al.* 2012). This was carried out in order to increase the sensitivity to the PAHs and to avoid the detection of other extracted components.

2.5. Quantification

The quantification was achieved by external calibration. A standard solution of 16 PAH's (~10 ng/ul of each PAH, Sigma Aldrich) was prepared as follows; undiluted and then dilution in hexane 80:80, 60:100, 40:120 and 20:140 (uL v/v PAH standard to hexane respectively). Before each batch of ~16 samples a fresh set of calibration standards was prepared and determined by GC-MS to produce linear regression for every PAH. Peak areas were measured manually for each component from the mass chromatogram as can be seen in Fig2.

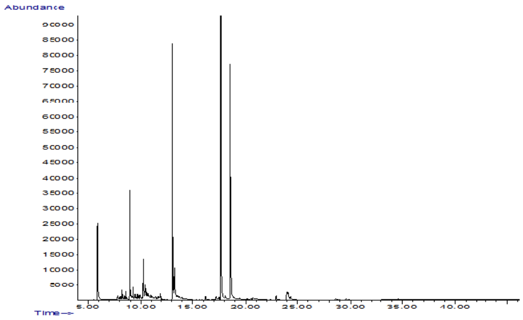

Fig .2. Example mass chromatogram of the BS NQ30MPAH SIM M method on sample number L8 from Leeds

3. RESULT AND DISCUSSION:

The peak areas, resulting calibration line and calculated limits of detection (LOD) and limits of quantification (LOQ) obtained from the 5 PAHs standard solutions are shown in Table 3. Initially, the retention time was determined with the assistance of Scan measurement of the undiluted standard. Next, the peak areas for each of the 5 PAHs standard solutions were measured by using GC-MS (using SIM). Then the concentrations for each diluted standard, the parameters of linear regression, the y-intercept and the gradient were determined. The concentration of each compound in each location can be seen in Table 4. Almost the soil samples had higher concentrations than LOQ. However, the CH value in sample L5 is lower than the LOQ, some others are very near.

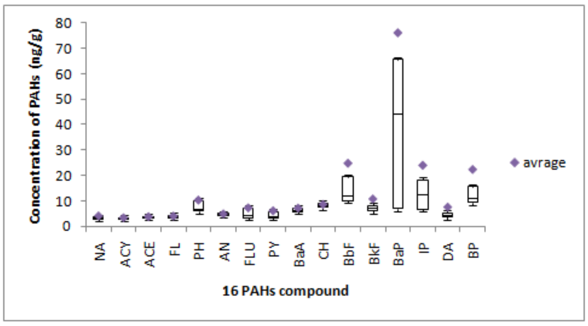

Fig. 3. Box and whisker diagram showing minimum (lower whisker), median (the line in the middle of the box) and maximum (top whisker) concentrations (ng/g) of each PAH compound in soil samples from each site in Leeds.

The lowest concentration of the 16 PAH compounds was in compound acenaphthylene at 2.8 ng/g, whilst the value of benzo[a]pyrene ranged between 4 ng/g to 585 ng/g. Benzo[a]pyrene gave the highest compound average of 75 ng/g and median 44 ng/g (Fig. 3).

Compound	Abbreviated name	Rings	Certificated Concentration (ng/ul)	m/z (M+)	RT order	RT (min)
naphthalene	NA	2	10.5	128	1	5.9
acenaphthylene	ACY	3	8.4	152	2	8.6
acenaphthene	ACE	3	8.7	154	3	9.0
fluorene	FL	3	9.4	166	4	1.3
phenanthrene	PH	3	10.8	178	5	13.2
anthracene	AN	3	9.3	178	6	13.4
fluoranthene	FLU	4	9.6	202	7	17.8
Pyrene	PY	4	9.3	202	8	18.7
benzo[a]anthracene	BaA	4	9.6	228	9	24.1
Chrysene	CH	4	9.0	228	10	24.2
benzo[b]fluoranthene	BbF	5	9.5	252	11	28.7
benzo[k]fluoranthene	BkF	5	9.1	252	12	28.8
benzo[a]pyrene	BaP	5	8.2	252	13	29.9
indeno[1,2,3-cd]pyrene	IP	6	9.5	276	14	33.9
dibenzo[a,h]anthracene	DA	5	9.6	278	15	34.1
benzo[ghi]perylene	BP	6	9.4	276	16	34.7

Table 2: 16 PAH compound analysis by mass spectrometry

	RT min	peak area	peak area	peak area	peak area	peak area	Intercept (y-axis)	Gradient	R^2	LOD (ng/ul)	LOQ (ng/ul)
NA	5.9	9323615	4898830	3515521	1880555	901477	-275351	926847	0.9951	0.9	2.9
ACY	8.6	8449266	4431761	3151380	1557176	719684	-369159	1066405	0.9933	0.8	2.7
ACE	9.0	11100608	6054030	4414590	2259075	1076734	-221918	1328972	0.9905	1.0	3.3
FL	1.3	9907871	5175044	3718212	1847747	839631	-423512	1116126	0.9937	0.9	2.9
PH	13	7014622	3951698	2738267	1324634	594985	-220654	688373	0.9849	1.6	5.2
AN	13	6982704	3696307	2493720	1151792	476031	-445790	813835	0.9907	1.1	3.5
FLU	18	7053075	3453900	2239837	1031148	435809	-644838	807313	0.9951	0.8	2.6
PY	19	6671293	3347005	2120783	982015	417595	-591816	788424	0.9937	0.9	2.9
BaA	24	347246	144586	93516	25426	25279	-48252	40616	0.9825	1.5	5.0
CH	24	350387	198784	97318	32228	6692	-47093	45475	0.9688	1.9	6.3
BbF	29	27662	17905	10261	3990	1629	-1531	3233	0.9469	2.6	8.8
BkF	29	24854	13457	8402	2526	1496	-2400	3064	0.9765	1.7	5.5
BaP	30	7750	4782	3411	2960	1530	1255	797	0.9885	1.2	3.9
IP	34	31600	13779	12679	6414	146.05	-2648	3642	0.9839	1.4	4.7
DA	34	37271	19194	13301	9698	6120	811	3775	0.9967	0.6	2.1
BP	35	41478	28168	18724	10297	5640	2196	4413	0.95	2.5	8.4

Table 3: Peak areas, resulting calibration line and calculated LOD and LOQs obtained from the standard PAH solutions measurements.

Compound	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12	L13	L14	L15	L16
NA	3.4	3.4	3.1	3.4	3.2	4.8	3.2	13.2	5.2	3.3	3.2	3.1	3.6	3.1	3.3	3.2
ACY	4.0	3.3	3.2	4.2	3.2	3.3	3.3	4.0	2.9	2.9	2.8	3.0	3.3	3.8	2.8	4.3
ACE	3.8	3.8	3.5	3.4	3.5	3.6	3.6	6.9	3.8	3.7	3.8	3.4	3.5	3.6	3.7	3.5
FL	3.7	4.2	3.8	3.3	4.3	3.0	3.1	7.2	3	4.6	4.2	4.1	4.6	4.4	3.7	3.8
PH	6.6	6.1	6.2	6.9	6.2	15.6	10.1	47.4	9.6	10.4	5.3	8.1	9.9	6.2	5.2	5.7
AN	5.4	4.4	4.6	5.0	4.8	3.9	3.7	8.5	4.5	4.0	5.0	4.7	5.1	5.5	4.5	5.3
FLU	3.5	3.0	3.7	4.3	4.4	16.0	7.6	32.1	7.3	9.0	3.6	6.6	6.6	2.9	3.4	2.7
PY	3.8	3.0	3.1	3.7	3.2	12.6	5.4	26.8	5.8	6.4	3.8	4.7	4.7	3.8	4.0	3.2
BaA	7.0	5.2	6.1	7.4	5.4	5.9	5.2	19.0	7.8	7.4	5.5	6.3	6.3	7.1	6.9	6.2
CH	7.7	7.9	6.9	8.0	6.2	7.9	6.8	18	8.3	9.2	7.1	8.1	9.2	9.6	8.0	9.1
BbF	11.3	9.5	12.6	9.9	11.4	46.3	17.8	159.9	17.8	26.1	9.1	17.7	15.4	11.5	10.2	9.4
BkF	20.3	7.1	6.0	5.9	6.9	13.0	5.6	50.1	6.7	8.3	7.8	5.6	8.2	6.3	7.5	7.4
BaP	55.6	4.4	7.3	4.7	38.9	159.3	53.8	585.3	49.2	90.2	31.2	62.2	50.4	11.6	6.5	4.1
IP	31.5	6.6	6.9	7.7	11.3	38.9	16.8	169.7	16.4	23.2	7.2	15.9	13.3	6.0	6.4	5.9
DA	5.5	3.3	5.1	4.5	3.0	9.9	3.8	52.5	4.2	6.0	4.4	3.9	3.7	4.6	2.8	4.2
BP	32.6	9.0	9.4	9.4	10.2	33.2	14.4	143.5	13.3	19.3	9.4	14	11.5	9.3	9.6	9.0

Table 4: Concentration of 16 PAH in soil samples from each site in Leeds

3.1. Total concentration of PAHs in samples from Leeds

Location	Total concentration of PAH's (ng/g soil)	Total description
L1	206	Moderate
L2	84	Low
L3	91	Low
L4	92	Low
L5	126	Moderate
L6	377	Moderate
L7	164	Moderate
L8	1344	High
L9	166	Moderate
L10	234	Moderate
L11	113	Moderate
L12	171	Moderate
L13	159	Moderate
L14	99	Low
L15	88	Low
L16	87	Low

Table 5: Total concentration of 16 PAH in soil samples from Leeds

Table 5 summarizes the overall level of contamination by PAHs in the 16 samples, these values have been classified according to Dong *et al*. [11] into these with high, medium and low contamination. Dong et al. define high values as being between 1000 and 5000 ng/g. Similarly moderate concentrations are between 100 and 1000 ng/g [11]. This shows how anomalously high sample L8 is compared to all the others, nine of which are moderate and six of which are low contaminations according to this classification.

3.2.Identification of PAHs sources in samples from Leeds.

As can be seen in Figure 4 the ratio of anthracene to anthracene plus phenanthrene AN/(AN+PH) was in the range between 0.2 to 0.5. As this ratio is more than 0.1 it indicates the dominance of pyrogenic and biomass sources. According to [12], fluoranthene to fluoranthene plus pyrene Flu/(Py+Flu) ratios of 0.2 to 0.58 imply vehicle emissions, which was the case for all these samples from Leeds. The ratio of benzo[a]anthracene to 228 (BA/228) in all the soil samples from Leeds of more than 0.35, and indicates that PAH contributions originated from combustion sources. Since for almost all the samples from Leeds the ratio of indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[ghi]perylene IP(IP+BP) was between 0.2 to 0.5 these indicate that the PAHs primarily derived from a liquid fossil fuel. The exceptions were in L6, where the ratio of more than 0.5 suggested grass, wood and coal combustion, and the ratio in L1 of less than 0.2 which implies petroleum sources [13] (see Figure 5).

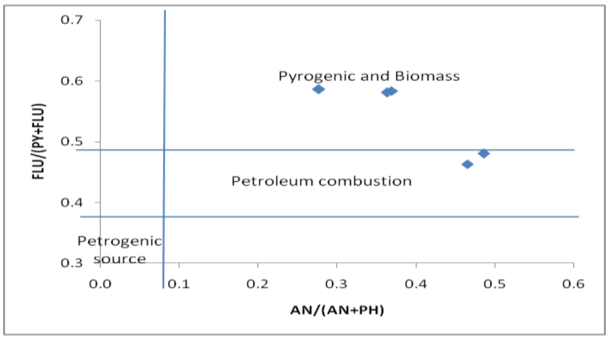

Fig.4. Plots of PAH ratios FLU/(PY+FLU) versus AN/(PH + AN) in sample sites (L1 to L16) from Leeds; not all points are separately visible because of superposition of multiple results.

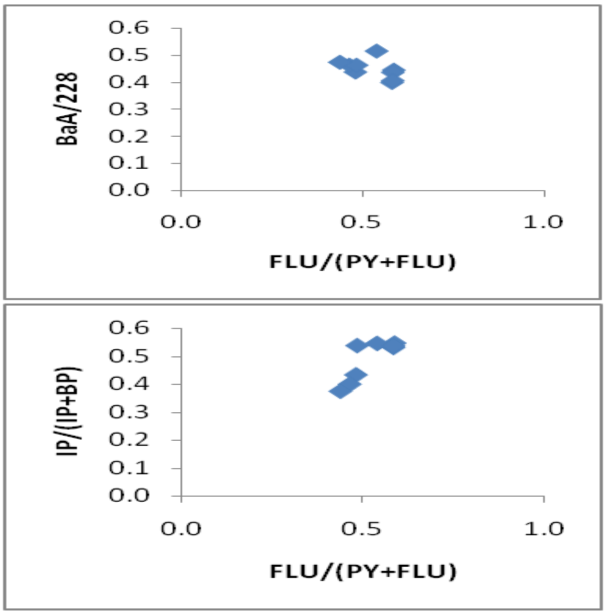

Fig. 5. Plots of PAH ratios (BaA/228) versus FLU/(PY+FLU), (IP/ (IP+BP)) versus FLU/(PY+FLU) in sample sites (L1 to L16) from Leeds; not all points are separately visible.

Fig. 6 shows that for all samples the high molecular weight compounds had higher concentrations than low and medium molecular weight ones, but that low molecular weight compounds had higher concentrations than medium molecular weight compounds in samples L1, L2, L3, L5, L11 and L16.

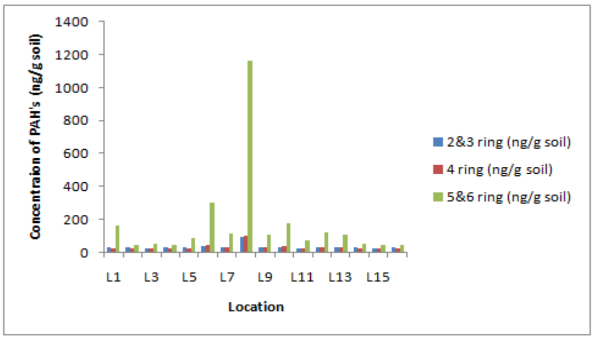

Fig.6. Bar chart shows the total concentration of PAHs containing 2&3 aromatic rings, 4 rings and 5&6 rings in samples from Leeds.

CONCLUSION

PAHs were determined in soil samples using gas chromatography with mass spectrometry; to the best of our knowledge this work is the first such study of urban soils in the UK. The results show one site with high concentrations of total PAHs while all other sites were moderate to low concentrations, with a preponderance of high-molecular weight in all sites, but particularly in the more contaminated sites. The ratio of anthracene to anthracene plus phenanthrene AN/(AN+PH), fluoranthene to fluoranthene plus pyrene FLU/(PY+FLU) and benzo[a]anthracene to 228 (BaA/228) implied that the PAHs pollution originated from pyrogenic, biomass and petroleum combustion in the samples which originated from Leeds city. This highlights the possibility that PAHs may pose a health hazard to humans not only through aerial transmission but also indirectly through soil contamination in urban areas.

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