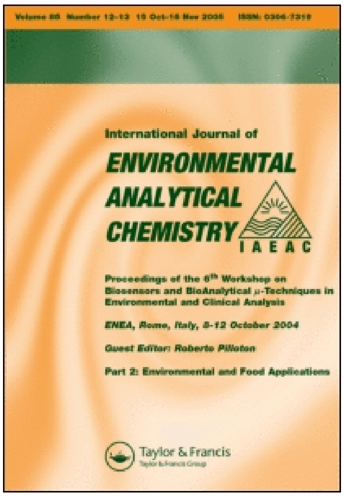

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Determination of Polycyclic Aromatic Hydrocarbons in Athens Atmosphere†

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Concentrations of total suspended particulates (TSP), benzene soluble fraction (BSF) and polycyclic aromatic hydrocarbons (PAH) have been determined in ambient air from four different sites in Athens, situated in urban, semi-industrial and industrial areas. GLC analysis has been applied for the determination of PAH, while the CGC/MS technique was used in order to confirm the obtained results. The same PAH pattern was observed for all stations. The identified PAH have been fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP) and benzo(ghi)perylene (B(ghi)P). The concentrations of individual PAH ranged from traces to 33 ng m^{-3} (e.g. same or lower comparing to other

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large cities). The higher values of PAH were found during adverse meteorological conditions.

KEY WORDS: Polycyclic aromatic hydrocarbons (PAH), gas liquid chromatography (GLC), capillary gas chromatography/mass spectrometry (CGC/MS), total suspended particulates (TSP), benzene soluble fraction (BSF).

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are components of the organic aerosols, which have both mutagenic and carcinogenic properties. These pollutants have been measured in ambient air for over 30 years and the majority of these studies have focused on the potent animal carcinogen benzo(a)pyrene.[1,2] Because of the important adverse role of these compounds on health many studies are carried out to determine their concentrations in air and also their sources.[3] The range of [BaP] in unpolluted nonurban air varied between 0.1–0.5 ng m^{-3}, while the concentration in polluted air reached 74 ng m^{-3}.[4]

The first attempt to determine the concentrations of PAH in Athens atmosphere took place during the years 1963–1966. The determined concentrations, in the order of μg m^{-3}, were not reasonable.[5] Systematic measurements of PAH concentrations in Athens have started, since the beginning of 1984, in our laboratory.[6]

The purpose of this study is to determine the mean annual PAH concentrations, the monthly variation of their concentrations, the variation of the concentrations of PAH in different areas of the city, the influence of meteorological conditions on PAH levels and finally to point out their main sources.

EXPERIMENTAL

Arrangement of collecting stations in the city

The characteristics and the location of the four sampling sites are given in Table I. Drapetsona is one of the main industrial areas of Athens including cement and fertilizer industry as well as a sulfuric acid production plant and a power plant.

The city of Athens has an open site to the sea (Saronicos gulf) and is surrounded by hills and mountains with heights ranging from 468

TABLE I

Characteristics of sampling stations

Code	Name of site	Height of sampler above ground (m)	Character of the site
A	MINISTRY	4	Commercial—Urban
B	PATISSION	21	Commercial—Urban
C	RENTIS	7	Light industrial—Urban
D	DRAPETSONA	8	Industrial

to 1413 m. During the year the prevailing winds arose from north and less from south and south-west. These winds are attributed to the sea influence and their velocity shows considerable differences from site to site. The maximum frequency of calms was observed inlands (44%), while the minimum near the sea (5%).[7]

As main sources of PAH are considered to be central heating, traffic and industry. The following data should also be taken into consideration. The fuel consumption in Athens annually is estimated to be 600,000 tn of gasoline (private cars), 1,100,000 tn of diesel oil (public traffic, heating and industry) and 570,000 tn of heavy oil (industries). It must be noted that coal is not in use in Athens either for central heating or for industrial uses.[8]

Collecting system

A Bendix 550 high volume sampler was used for TSP sampling.[9] The flow rate ($\sim 83\,m^3\,h^{-1}$) was measured at the beginning and the end of each sampling period. The mean value of the two measurements was taken as the sampling flow rate. Starting at midnight, the sampling time was 24 h. By weighing the filters on which TSP was collected, before and after exposure, it's mass was determined. The filters before and after sampling were conditioned in a descicator for at least 24 h.[9]

Samples were collected for one year started in February 1984. Sampling was usually performed twice a week at each station.

Extraction and sample preparation

The samples of TSP were analysed for benzene soluble fraction (BSF) and PAH determination. One fourth of each filter was extracted in a Soxhlet apparatus with 50 ml of benzene for 6 h in order to isolate the BSF. The extract was then evaporated in an evaporating flask at 60°C to dryness. The mass of the extracted material was measured by weighing.[10]

The same, as in Ref. 11 procedure, has been used for PAH extraction. b, b′-binaphthalene was the internal standard for quantitative determinations.[11]

GLC analysis

A Perkin-Elmer Sigma 2B chromatograph was used for chromatographic analysis. The column (2 m × 2 mm) was packed with 3% 2250 SP on supelcoport 80/100 mesh. The GLC conditions were the following: Injection temperature 280°C, FID-detector temp. 280°C, carrier gas N_2, flow rate 40 ml/min, temperature program 100°C (4 min) −280°C (8°C/min), 280°C (20 min).[12] For the identification of various peaks, PAH standards (supplied by Supelco and Jensen) have been used.

Calibration graphs were obtained by injection of standard reference mixtures after addition of the same amount of internal standard. The peak heights were plotted against the concentration of each PAH in the reference mixtures. A calibration curve was also plotted for various concentrations of internal standard. The concentration of each PAH was calculated using the formula:

$$[\mathrm{PAH}], \mathrm{ng\,m^{-3}} = \frac{a_i H_i}{a_{IS} H_{IS}} \cdot \frac{m_{IS}}{V} \cdot 4.10^3$$

where: a_i, a_{IS} the calibration factors for each PAH and the internal standard (μg ml^{-1} cm^{-1}) calculated from the corresponding calibration curves. H_i, H_{IS} the peak heights of PAH and the internal standard in the unknown sample (cm), m_{IS} the amount of internal standard added (μg), V the volume of air passed through the filter (m^3), 4 factor, since one fourth of the filter was taken, $10^3 = 10^3$ ng μg^{-1}.

No correction for blank contribution was done, since the peak heights for the blank were negligible.

CGC/MS analysis

A Finnigan mass spectrometer (Model 4021 C) with an INCOS 2000 data system was used for mass spectrometric identifications. The ion source was operated at 70 eV and a nominal temperature of 250°C. A Carlo Erba gas chromatograph (Model 4160) was connected to the mass spectrometer. The glass capillary 6C column (27 m × 0.32 mm, 3°/∞ SE-54, and 2°/∞ CP) was directly coupled to the ion source by a fused silica capillary. Aliquots of 2 μl of the methylene chloride extracts were injected without stream splitting onto the column at ambient temperature. The injector temperature was 280°C. After 30 s the split valve was opened, allowing the septum and injection port to be purged at a flow rate of approximately 10 ml/min. After the elution of the solvent the temperature program used was: 50°C (1 min), 50–280 (4°C/min) and 280°C (30 min). Helium was used for carrier gas with a back pressure of 0.8 atm.[13]

To quantify, the total surface area of each compound was integrated and then compared with the area of the internal standard (b, b'-binaphthalene).

RESULTS AND DISCUSSION

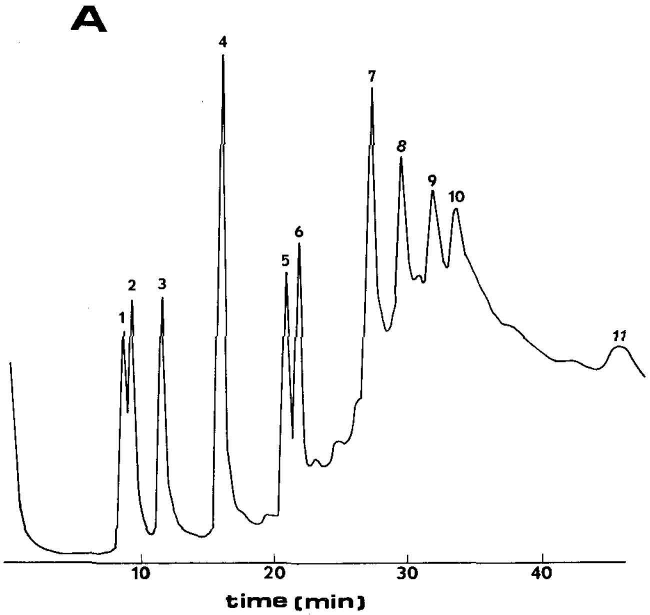
Confirmation of results obtained by GLC packed column

Trace A of Figure 1 shows the gas chromatogram obtained by GLC-packed column analysis of a reference mixture of a number of PAH, while the gas chromatogram B of the same Figure was recorded by analysing an extract from airbone particulate matter. The extensive line drifting present in both chromatograms is not due to the clean up procedure, but to the flow change of carrier gas during the temperature programming as well as to the column bleeding in temperatures above 250°C.[14]

The total ion chromatogram in Figure 2 illustrates the CGC/MS analysis of a similar extract as in Figure 1 B. The CGC/MS analysis was performed on four samples (one from each measuring site), which have also been analysed by GLC packed column method. The obtained results are presented in Table II. A comparison of the above results shows that the percent differences in the mean values of PAH concentrations vary between 5 to 38%, with the GLC packed column results being lower than the CGC/MS. The systematic lower results are probably due to the way of calculation of the results (peak height instead of peak area). Such differences are common when comparing results obtained with different analytical techniques.[15]

The ratio of [BaP]/[BeP] had a mean value of 1.5 for all samples analysed by CGC/MS. This fact indicates that extensive loss was not observed during the sampling of PAH by a high volume sampler.[16]

In addition, recovery studies were done by adding known quantities (1.0, 2.5 and 5.0 μg of each identified PAH) in 3 quarters of the same filter correspondingly. The obtained mean recoveries for the various PAH, presented in Table III, varied in the range of 80–126%, e.g. in the same order as for similar experiments.[11]



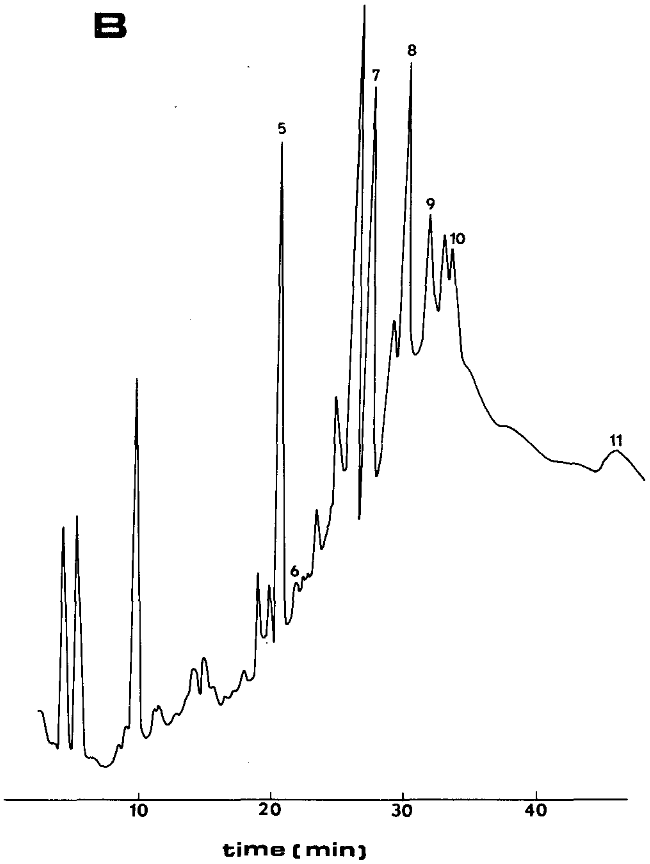


FIGURE 1 GLC packed column analysis. (A) Gas Chromatogram of a (complex) PAH-standards mixture. The peak assignment: 1: Acenaphthylene, 2: Acenaphthene, 3: Fluorene, 4: Phenanthrene + Anthracene, 5: Fluoranthene, 6: Pyrene and Benzo(a)anthracene, 7: Chrysene, 8: b,b'binapthyl, 9: Benzo(b)fluoranthene + Benzo(k)fluoranthene, 10: Benzo(a)pyrene, 11: Benzo(ghi)pyrene. (B) Gas chromatogram of PAH in airborne particulate matter. (Site: Ministry.) Peak identity as above.

TABLE II

Comparison of the results for the determination of PAH by CGC/MS and GLC/packed of the same samples. [PAH], ng m^{-3}

	[FLA]		[PYR]		[CHR]		[BbF]+[BkF]		[BaP]		[BeP]		[B(ghi)P]	
Site	CGC/MS	GLC	CGC/MS	GLC	CGC/MS	GLC	CGC/MS	GLC	CGC/MS	GLC[a]	CGC/MS	GLC	CGC/MS	GLC
A	1.0	1.7	7.0	6.0	9.1	7.1	12.6	12.3	6.0	7.6	4.2	—	4.9	4.6
B	2.1	1.5	3.3	3.0	4.7	4.1	8.8	6.2	4.7	3.7	2.9	—	3.1	3.0
C	4.1	1.6	4.9	3.0	8.3	4.6	12.9	12.5	6.3	5.9	4.3	—	6.3	3.5
D	2.5	1.3	2.5	3.0	4.6	3.7	8.1	9.6	2.1	3.8	2.1	—	1.1	1.6
Mean	2.4	1.5	4.4	3.8	6.7	4.9	10.6	10.1	4.8	5.2	3.4	—	3.9	3.2
Difference %[b]	−38		−14		−27		−5		−37		—		−18	

[a] The result is the sum of the two isomers, [BaP] and [BeP].

[b] Calculated having as basis the results of CGC/MS.

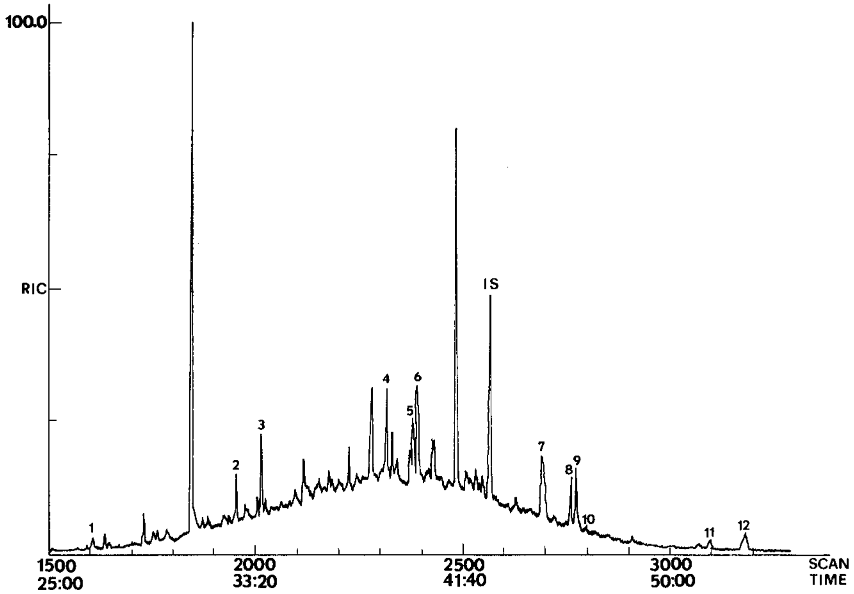


FIGURE 2 Reconstructed Ion Chromatogram (RIC) of PAH in airborne particulate matter (Site: Ministry). Peak assignment: 1: Phenanthrene, 2: Fluoranthene, 3: Pyrene, 4: Benzo(ghi)fluoranthene, 5: Benzo(a)anthracene, 6: Chrysene, IS: b,b′ binapthyl, 7: Benzo(b+j+k)fluoranthene, 8: Benzo(e)Pyrene, 9: Benzo(a)Pyrene, 10: Perylen, 11: Indeno(1, 2, 3)pyrene, 12: Benzo(ghi)perylene.

TABLE III

Recovery (%) of various PAH

Amount added, μg	1.0	2.0	5.0	Mean recovery (%)
[PAH]	Recovery (%)			
[FLA]	90	92	94	92
[PYR]+[BaA]	100	108	96	101
[CHR]	90	72	78	80
[BbF]+[BkF]	140	120	118	126
[BaP]+[BeP]	90	76	78	81
[B(ghi)P]	88	93	90	90

Mean and maximum pollution values

In Table IV the mean and maximum values of TSP, BSF, and the PAH identified in Athens atmosphere, for the various monitoring sites, are given. Due to the poor efficiency of the column some of the PAH can not be separated, since they have the same retention times. In this case the results are given as a mixture of the two PAH (1:1 mass). From this Table it can be seen that the highest mean and maximum values were observed in the Ministry site situated in the center of the city. Lower values were measured in Patission site (although in the center of city) because of the relative high altitude in which this site is situated (21 m), and therefore less influenced by traffic[17] and street dust, the latter being one of the most important sources of TSP in Athens city.[18] Similar local variation was observed, when the biological effects of TSP were examined by AMES test.[19]

Comparing the annual average [BaP] measured in Athens with the standard of $10\,\mathrm{ng\,m^{-3}}$, which has been proposed by the Federal Environmental Agency of Germany,[20] we can conclude that this standard was not exceeded for the year under study.

Monthly variations

Figure 3 shows the monthly variations of BaP concentrations measured at Ministry site. It can be seen that higher values were observed during the winter months of January, February, March, November and December. This is due to the higher emissions during the winter (Central heating operation), and to meteorological factors.[21] These factors are the temperature inversions, which are more frequent during the winter, as well as the effect of parameters such as sunlight and temperature. Also it is known that PAH can be attacked by pollutants such as O_3 and NO_2, which are present in the atmosphere in higher concentrations during the summer than during the winter.[22]

Effect of meteorological factors on PAH concentrations

Table V shows the mean BaP concentrations for various ranges of wind velocities during winter and summer period for Ministry site. It can be seen that concentrations of BaP increase as the wind velocity

TABLE IV

Mean and maximum values of [TSP], [BSF] and [PAH] measured during the period February 1984–January 1985

Site		Pollution Parameters								
		[TSP] $\mu g\,m^{-3}$	[BSF] $\mu g\,m^{-3}$	[FLA] $ng\,m^{-3}$	[PYR]+[BaA] $ng\,m^{-3a}$	[CHR] $ng\,m^{-3}$	[BaP]+[BeP] $ng\,m^{-3a}$	[BbF]+[BkF] $ng\,m^{-3a}$	[B(ghi)P] $ng\,m^{-3}$	N[b]
A	mean	191	10.5	2.0	3.6	5.6	4.0	6.6	2.4	87
	max	305	24.6	11.4	17.8	16.0	21.1	28.5	12.5	
B	mean	142	6.3	1.4	2.2	3.6	2.1	2.9	1.0	69
	max	294	24.0	6.2	12.6	10.0	8.1	12.6	8.4	
C	mean	204	6.7	1.4	2.7	4.3	3.3	4.3	1.0	75
	max	378	18.9	5.2	14.7	13.6	13.4	32.6	9.2	
D	mean	161	3.8	1.3	2.4	4.0	2.2	3.0	0.9	71
	max	358	10.8	3.5	10.2	11.1	9.1	17.0	9.9	

[a] Results calculated as a mixture of two PAH with a mass ratio 1:1.

[b] N: number of samples analysed.

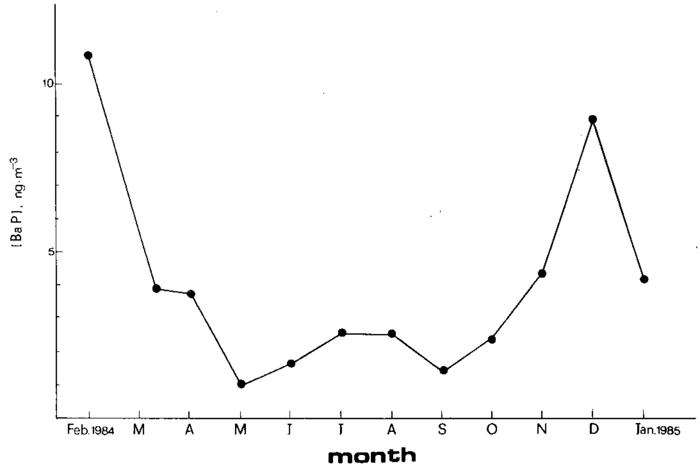


FIGURE 3 Monthly variation of [BaP] at Ministry site. Period February 1984–January 1985.

TABLE V

Mean values of [BaP] for Ministry site in relation to wind velocity range

Range of wind velocity Knt[a]	Winter mean value[b] [BaP] ng m^{-3}	Summer mean value[c] [BaP] ng m^{-3}
<3	11.3	—
3–6	7.9	2.5
6–9	5.0	2.7
>9	3.9	1.5

[a] 1 Knt $\simeq$ 0.5 m s^{-1}.

[b] Winter = January, February, March, November, December.

[c] Summer = April, May, June, July, August, September, October.

TABLE VI

Ratio of concentrations of characteristic PAH

Site / Ratio	MINISTRY		PATISSION		RENTIS		DRAPETSONA	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
[BaP]:[B(ghi)P]	1.6	1.7	1.2	2.2	3.5	3.1	1.4	1.7
[PYR]:[BaP]	0.5	1.8	0.7	1.2	0.8	1.0	0.8	1.6
[PYR]:[CHR]	0.4	1.1	0.4	1.0	0.3	1.3	0.4	1.0
[FLA]:[PYR]	0.7	0.4	0.6	0.6	0.6	0.6	0.2	0.2

Winter: January, February, March, November, December.
Summer: April, May, June, July, August, September, October.

is decreased, since higher wind velocity facilitates the pollution dispersion. Also all maximum values (Table IV) were observed during days with calms or very light winds and thermal inversions.

Allocation of PAH sources

The low linear regression coefficient between PAH and lead concentrations measured at the same site (0.32–0.38 for BaP at various sites) indicates that gasoline powered vehicles are not the main pollution source for PAH in Athens as it happens in other cities.[23] Another way to allocate the sources for PAH emissions is to examine the ratios of their concentrations which are characteristic for their sources.

The values of such characteristic ratios for all measuring sites and for the two seasons of the year are presented in Table VI. These values indicate that during winter time the main pollution source for PAH, for the examined period, was central heating as in most cities in W. Europe[24–27] while during summer the main source was the traffic. For both seasons it seems that emissions from diesel powered vehicles contributed more than those from gasoline powered vehicles to the PAH pollution.

CONCLUSIONS

The used GLC method gave reliable results.

The measured PAH concentrations during the period February 1984 to February 1985 at four different stations in Athens basin were found to be similar or lower to those found in other cities. Maximum values (i.e. $[\mathrm{BaP}]=21\,\mathrm{ng\,m^{-3}}$) were observed during pollution episodes, which occur under unfavorable meteorological conditions.

Regarding local variations, higher values of [PAH] were measured at traffic areas than in industrial areas. The PAH concentrations were higher during winter months due to more intensive urban and industrial activities, as well as to meteorological and physicochemical factors. The predominant source of PAH during winter is central heating, while during summer the diesel powered vehicles.

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