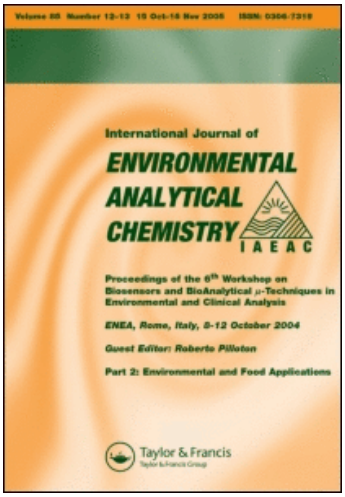

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Muel, B. and Saguem, S.(1985) 'Determination of 23 Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate Matter of the Paris Area and Photolysis by Sunlight', International Journal of Environmental Analytical Chemistry, 19: 2, 111 — 131
To link to this Article: DOI: 10.1080/03067318508077022
URL: http://dx.doi.org/10.1080/03067318508077022

Intern. J. Environ. Anal. Chem., 1985, Vol. 19, pp. 111–131
0306-7319/85/1902-0111 $18.50/0

Determination of 23 Polycyclic Aromatic Hydrocarbons in Atmospheric Particulate Matter of the Paris Area and Photolysis by Sunlight

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(*Received August 13, 1983; in final form June 30, 1984*)

Twenty-three polycyclic aromatic hydrocarbons (PAH) were determined in atmospheric particulate matter in 4 places of the Paris area at several times of the year. Fractionation was performed by reversed-phase high-pressure liquid chromatography. Determination was done by recording emission or excitation fluorescence spectra via a stopped-flow technique. Triphenylene was also extemporaneously determined by its phosphorescence spectrum at low temperature. Among the PAH determined dibenz(e,ghi)perylene has not been detected before in atmospheric particulate matter.

The 10 more abundant PAH ranged from 0.1 to 40 ng/m^3 of filtered air. Concentrations in August are from 14 to 250 times less than in January depending on the PAH. The reasons for this difference of behaviour among the PAH were investigated with regard to their photochemical and non-photochemical reactivity.

KEY WORDS: Atmospheric PAH determination, sunlight photolysis.

INTRODUCTION

Very few data are available on the atmospheric pollution by polycyclic aromatic hydrocarbons (PAH) in the Paris area.[1–3] As part of a governmental program for monitoring pollution by carcinogenic compounds, we have determined the concentration of several PAH in the atmosphere of the Parisian area. In a parallel study by the Laboratoire d'Hygiène de la Ville de Paris, the

concentration of a limited number of PAH was also investigated in different places and conditions.[4]

Our present work represents an effort of adjusting the current techniques of high-pressure liquid chromatography (HPLC)[5-7] and fluorescence detection[8-10] so as to allow the specific determination of more than 20 PAH with 3 or more rings. Different factors affecting the analytical results were studied: time and location of sampling, technique of extraction. Particular attention was paid to the photosensitivity of PAH[11,12] and to the way it may affect the amount of PAH recovered, according to the season.

MATERIALS AND METHODS

Sample collection†

Atmospheric air was passed through 17 g of teflon wool (surface area 12.5 cm^2) at a flow rate of about 1.5 m^3/hour, usually during one month. About 1000 m^3 of air were filtered and 25 to 120 mg of particulate matter were retained on the filter.

The samples were collected from three places: *Paris*, center of Paris at 15 m above ground; *Antony*, suburban residential area at a height of 4 m; *St. Denis*, an industrially polluted suburban area, at 14 m above ground.

Solvents

Chloroform analytical grade from Merck, 2-methylbutane Uvasol from Merck and acetone Normapur from Prolabo were used as such. Other solvents were distilled using a 2 m high column.

Spectra

Fluorescence and phosphorescence spectra were recorded with a Jobin–Yvon Bearn instrument modified to increase its sensitivity and stability by replacement of the IP28 RCA photomultiplier by a selected Hamamatsu R212 and directly recording the photomultiplier output with a microvoltmeter (Micrograph BD5, Kipp and Zonen).

†We thank F. Coviaux from the Laboratory of Hygiène of Paris, who furnished the samples.

Absorption spectra were recorded with a Cary 15 spectrophotometer.

Reference compounds and standard solutions

The following PAH were determined (names according to IUPAC rules): fluoranthene (FLA), pyrene (PY), triphenylene (TRI), benz(a)-anthracene (BAA), chrysene (CHR), benz(j)fluoranthene (BJF), benz(e)pyrene (BEP), benz(b)fluoranthene (BBF), perylene (PE), benz(k)fluoranthene (BKF), benz(a)pyrene (BAP), dibenz(a,c)-anthracene (DBAC), dibenz(a,j)anthracene (DBAJ), dibenz(a,h)-anthracene (DBAH), benz(b)chrysene (BBCH), picene (PIC), indeno(1,2,3-cd)pyrene (INPY), benz(ghi)perylene (BGHI), anthanthrene (ANTH), naphtho(1,2,3,4-def)chrysene (NC), benz(rst)-pentaphene (BRP), coronene (COR), dibenz(e,ghi)perylene (EGHI).

We checked the identity and purity of our reference samples of various origin by recording their absorption spectra which were found very close to the spectra given by Clar.[13]

In the case of EGHI no pure sample was available. The identification in atmospheric fractions was based on the analogy of the fluorescence spectra with that of BGHI (Figure 1) and on the presence in the absorption spectra and fluorescence excitation spectra of the 4 principal absorption bands of EGHI[13] (Figure 1).

The concentrations of the standard solutions were calculated according to the molar absorptivity of the principal band given by Clar[13] (after evaporation to dryness and change of the solvent if necessary). In the case of EGHI standard solutions were prepared from samples obtained by chromatography of atmospheric extracts.

The standard solutions, usually in ethanol, were kept in the dark at ordinary temperature in ground glass stoppered vials, without grease, entailing a slow evaporation of the solvent which necessitated re-evaluating their concentration by optical density measurement every two months. Recently, the vials were placed in a bigger tank containing ethanol-saturated air where evaporation is much reduced.

Precautions against light in the laboratory

Simple precautions were taken to avoid photolysis of the PAH during sample handling. The extractions were done in a partly darkened room. Exposure to electric light was limited to the time

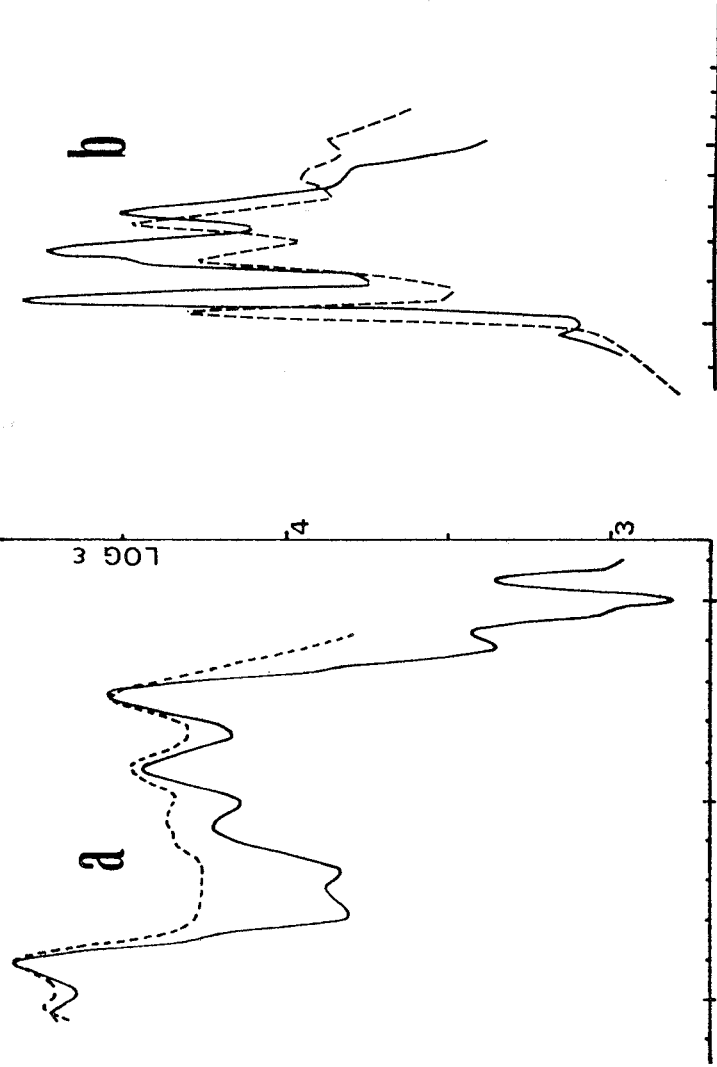

FIGURE 1a ——— Absorption spectrum of EGHI[13] (logarithm of molar adsorption coefficients), ---- corrected excitation fluorescence spectrum of an atmospheric fraction (logarithm of fluorescence intensity at 403.5 nm as function of excitation wavelength at constant photon-rate).

b) Fluorescence spectra recorded in HPLC cell, solutions in methanol–water (95:5, v/v), ——, BGHI; ----, EGHI, from an atmospheric fraction.

taken for the manipulations. Simple experiments showed that these precautions are sufficient. In particular, solutions of the highly photosensitive PAH, ANTH, PE and BAP remained essentially unchanged (absorption spectra) after 24 h exposition in the laboratory with lights on.

Extractions

The teflon pads were extracted twice in cold chloroform (3 ml chloroform per mg of matter collected with a minimum of 200 ml at a time).

The completeness of the extraction was evaluated for different periods of agitation or sonication (with 150 W Mk2 instrument from MSE) by re-extracting the treated pads with acetone and/or with boiling ether in a Kumagawa extractor. Such results are summarized in Table I. Six hours agitation plus 20 min sonication gave satisfactory results with 84% and above extracted by chloroform.

In boiling ether extractions, the yields of PE, ANTH and BAP were often very low. This is related to the instability of these compounds, particularly in the presence of atmospheric matter, as was shown in independent experiments.

Another way of evaluating the extraction procedure was as follows: two samples collected at the same time and place were analysed after one of them was supplemented by internal standards added on the teflon pad as a solution which was thoroughly dried before analysis. The pads were extracted by chloroform twice for 30 min without sonication. The per cent recovery of the standards obtained by difference of the two determinations is reported in column f of Table I. The average yield of 76%. The low yield of ANTH (43%) is probably related to the particular instability of this compound.

Prior to the chromatography, the chloroform solutions were evaporated under reduced pressure at a temperature of 30°C. The residue of evaporation was shaken 1 h with 8.5 to 10 ml of methanol. A blank experiment showed that the teflon wool, filters and solvents did not contain significant quantities of our markers.

Chromatgraphy

Apparatus. For isocratic HPLC the elution solvent was constantly

TABLE I

Percent of recovery.[a]

	(A) % by successive extractions					
	sample 1			sample 2	sample 3	(B) % recovery of
Compound	$CHCl_3$ 20+20 min a	Acetone b	Kumag. ether c	Kum. ether after 30 min $CHCl_3$+9 min sonic. d	Kum. ether after 6 h. $CHCl_3$ +20 min sonic. e	internal standard added to atmospheric material f
FLA	70	17	13	26	8.7	66
PY	54	15	31	29	11	67
TRI				29	16	75
BAA	77	12	11	27	13	78
CHR	67	16	17	32	12	80
BJF	92	2.5	5.5	21	13	
BBF	90	3.6	6.4	27	13	67
BEP	94	1.5	4.5	21	13	80
PE	98	2	<1	0	5.9	60
BKF	90	3.3	6.7	24	11	87

BAP	98	1.8	0.2	0.5	7.1	68
DBAC				9	9.8	92
DBAJ				7	8.7	104
DBAH				15	11	95
BBCH				11	11	85
PIC				12	14	
INPY	95	2	3	15	9.1	77
BGHI	95	2	3	7	12	80
ANTH	99.5	<0.5	0.5	0		43
NC	93	2	5			62
BRP					2.5	65
COR	93	2	5	2	5.5	68
EGHI	94	2	4	13	5.7	90

[a](A) with respect to the total PAH extracted:

Sample 1: Paris January, (a) agitation with cold $CHCl_3$, twice 20 min each, (b) agitation with cold acetone 20 min, (c) boiling ether 8 h.

Sample 2: St. Denis October, (d) boiling ether 15 h after agitation with cold $CHCl_3$ 30 min and sonication 9 min with new $CHCl_3$.

Sample 3: Antony January, (e) boiling ether 13 h after 6 h agitation and 20 minutes sonication with $CHCl_3$.

(B) *recovery of internal standards* added to one of two samples collected simultaneously in May in St. Denis (extraction by agitation with $CHCl_3$ twice 30 min).

$$\% = \frac{\text{amount determined in loaded sample} - \text{amount determined in unloaded sample}}{\text{amount of PAH added}}$$

degassed by boiling. The solvent passed via stainless steel tubing to a constant-flow high pressure pump (LDC, Constametric IIG). A (Valco loop injector) was used with one of two loops (0.85 and 7.6 ml) made of stainless steel 1 mm I.D. The solvent successively passed a precolumn, the analytical column and the absorption cell (optical path 3 mm, internal volume 25 μl) of the dual wavelength (254–280 nm) Model 1222 duomonitor from LDC. The exit of the absorption cell was connected by a 1 m long, 0.5 mm I.D., teflon tubing to a 25 μl fluorescence cell (176.70; Helma). This cell was positioned in the sample compartment of a spectrofluorimeter (Bearn from Jobin–Yvon) modified to increase its sensitivity and stability by replacement of the 1P28 RCA by a Hamamatsu R212 photomultiplier and direct recording of the output signal with a Micrograph BD5 microvoltmeter.

Columns. Initially a nitrile bonded phase (Partisil PAC from Whatman) with elution by heptane containing small proportions of ethanol) and a phenyl phase (from Shodex) with elution by dry heptane were tested. An ODS phase with elution by methanol–water mixtures gave better results. We used almost exclusively a 500 × 9.4 mm I.D. semi-preparative ODS column (M9, Partisil 10 μm, ODS 2 from Whatman). A 250 × 4 mm I.D. ODS column was also used (RP18, Lichrosorb 5 μm, Merck). The columns were thermostated by circulating water at 25°C through soft plastic tubing coiled around them.

HPLC. 7.6 ml of the methanol extract were injected on a semi-preparative ODS column (Whatman ODS2) and eluted with methanol at a flow rate of 10 ml/min, for an initial separation. A typical absorbance chromatogram is shown in Figure 2, together with the elution volumes of several PAH. The function of this first chromatography is to eliminate a high proportion of very polar compounds as well as high-molecular weight compounds. Some of the latter were quantitatively determined during this first chromatography.

An approximate determination of some medium-sized PAH was possible at this level so that we could adjust the volume of solvent to obtain concentrations suitable for a second HPLC run.

In routine analysis, with small samples, the first HPLC run can be omitted; the heavy PAH will then have to be eluted by a gradient up to 100% of methanol and the column should be advantageously replaced by a smaller analytical column.

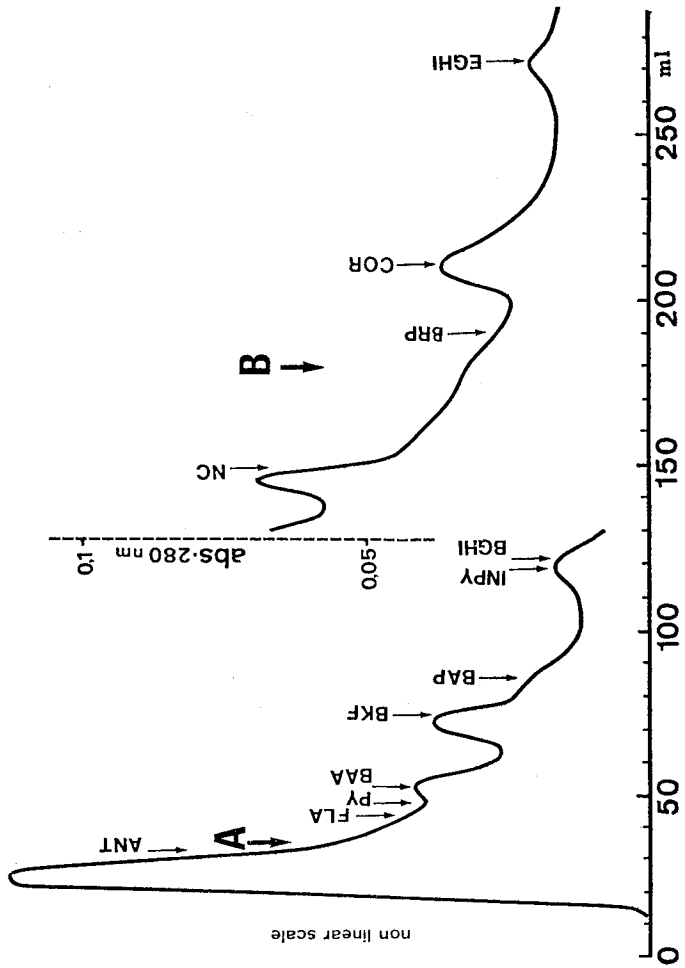

FIGURE 2 Absorbance at 280 nm as function of ml of effluent, for first chromatography on ODS of an extract from atmospheric particulate matter. Elution by methanol at 10 ml/min.

The eluates of the first HPLC run were collected after the first 35 ml (A in Figure 2), just after anthracene (ANT) up to 180 ml (B) just before the elution of BRP. This fraction was evaporated to dryness and the residue dissolved in methanol–water (90:10). The volume was adjusted so that the BKF concentration calculated after the first HPLC run, was less than 2 μg/ml. By doing so, the concentrations of all compounds were very likely (for our type of extracts) to be within the range of linearity (see below) and solubility (NC less than 1.3 μg/ml). 0.85 ml of this solution was injected on the same M9 column previously equilibrated with the eluent (methanol–water, 90:10). The elution flow rate began at 3 ml/min until the CHR maximum (Figure 3). The flow rate was then increased to 5 ml/min abd after the BGHI maximum to 10 ml/min (Figure 3).

Determination by fluorescence. Many peaks were not completely separated so that determination of concentrations from absorption peak measurement was often impossible or unreliable.

Increased selectivity was obtained by fluorescence detection with adjustment of excitation and emission wavelengths for each compound.[8,10] For many PAH, further improvement in selectivity was obtained by stopping the flow and recording a part of the fluorescence excitation of emission spectrum.[9] The flow was stopped as close as possible to the fluorescence maximum. Care has to be taken that when starting the pump, there is a sudden decrease of fluorescence intensity which recovers its normal value after the passage of less than 1.0 ml. No measurements should be taken during this period. This phenomenon may be explained by fluorescence quenching resulting from diffusion of some air in the tubing during the rest period.

In Table II the conditions for determination of each PAH are summarized. Without stopping the flow, we measured either the difference (d) between "fast" ground level and the level of maximum, or the "height" (h) of the peak above the the "average" ground level. For spectral measurements, peak heights in fluorescence emission or excitation spectra, respectively Δ_{em} or Δ_{ex}, were measured.

The concentrations of PAH were determined by comparison with a reference solution containing BBF, BEP, INPY, BGHI:2 μg/ml, FLA, PY, TRI, BAA, CHR, BJF, BKF, BAP:1 μg/ml, BBCH, PIC, NC, COR:0.5 μg/ml, PE, DBAC, DBAJ, DBAH:0.2 μg/ml, ANTH, BRP, EGHI:0.1 μg/ml, that can conveniently be diluted to obtain

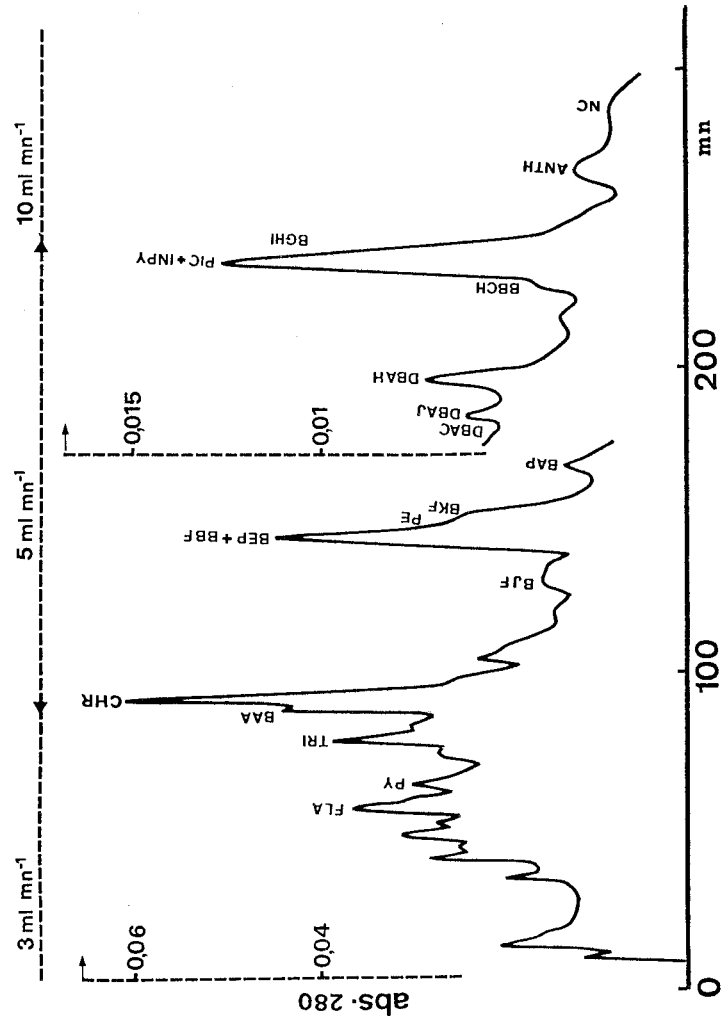

FIGURE 3 Absorbance at 280 nm as function of retention time for the second chromatography.

TABLE II

Conditions of monitoring and determination of PAHs by fluorescence spectroscopy.[a]

	Compound	Monitoring λ_{ex}	Monitoring λ_{em}	Measurements	Bandwidth ex–em	Flowrates (ml/min)
1st CHROMATOGRAPHY	PY	338	393	d	3–4	10
	BKF			d	3–4	
	BAP	382	407	h	5–4	
	BGHI			d	5–4	
	ANTH	427.5	451	d	7–5	
	BRP	392	434	em 421–434–451	11–2	
	COR	301	446	em 421–426–431	5–2	
	EGHI	373	403.5	em 396–403.5–409	9–1.5	
2nd CHROMATOGRAPHY	FLA	360	490	d	4–11	3
	PY	335	393	d	3–6	
	TRI	258.5	353.5	ex 252–258.5–265	1.5–4	
	BAA	288	387.5	em 376–387.5–401	2–3	
	CHR	268.5	362.5	em 356–362.5–371	1.5–2.5	
	BJF	383.5	530.5	ex 371–383.5–396	5–25	5
	BBF	301	471.5	ex 295–301–311	2–5	
	BEP	331	378.5	ex 321–331–345	3–3	
	PE	432.5	467.5	em 454–467.5–497	8–5	
	BKF	379.5	408	em 396–408–420	5–4	
	BAP	382.5	405	h	5–4	
	DBAC	287	376.5	ex 280–287–293	2–10	
	DBAJ	298	397	ex 291–298–309	2–12	
	DBAH	297.5	396.5	em 384–396.5–408	8–5	
	BBCH	287	396.5	em 384–396.5–408	8–5	
	PIC	326.5	377.5	em 371–377.5–389	7–5	
	INPY	431	506	ex 309–314–326	8–24	
	BGHI	381	407	em 401–407–413	10–1.5	
	ANTH	404	433	em 423–433–447	6–4	10
	NC	374	397.5	em 389–396.5–411	5–3	

[a]Wavelengths (λ) and bandwidths in nm. Bandwidths are given for excitation (ex) and emission (em) monochromators. Measurement: d and h are for peaks measured on the chromatogram (see text), em is for a peak on the fluorescence spectrum using the wavelengths indicated (excitation at monitoring wavelength) and ex is for a peak on the fluorescence excitation spectrum using the wavelengths indicated (observation at monitoring wavelength).

PAH concentrations not too far from those in the sample. Linearity of the fluorescence intensity was observed to within $\pm 10\%$ in the second HPLC run, for injected amounts of less than 2.5 μg for TRI, BAA and CHR, 5 μg for FLA, PY, DBAC, DBAJ, DBAH, BBCH and 10 μg for other PAH.

To compensate for day-to-day variations in peak width or instrument sensitivity, the system was calibrated before and after each run by recording the fluorescence peak height of an anthracene standard solution chromatographed at a flow rate of 10 ml/min. In these conditions, an accuracy of $\pm 10\%$ was obtained.

The lower limits of detection are the following, in ng:

FLA:3 – PY:0.3 – TRI:20 – BAA:10 – CHR:20 – BBF:50 – BEP:50

– PE:0.4 – BJF:10 – BKF:4 – BAP:0.6 – DBAC:10

– DBAJ:10 – DBAH:3 – BBCH:2 – INPY:30 – BGHI:10

– ANTH:0.5 – NC:10 – BRP:2 – COR:10 – EGHI:10.

With the 250 × 4 mm I.D. analytical column, the detection limits are about 20 times lower.

Determination of triphenylene by phosphorescence. The determination of TRI by the preceding technique is often difficult because of the low yield of fluorescence and the usually high content of the TRI fraction in other fluorescent compounds. Here, the concentration of TRI was determined by using its phosphorescence which gives a well defined spectrum and a high yield. This determination implies the collection of the fraction containing TRI, followed by evaporation and dissolution in a solvent suitable for 77°K measurements (EPA:diethylether—2-methylbutane—ethanol, 5:5:2). The simple comparison of the phosphorescence intensity of the fraction to be determined with the phosphorescence intensity of a standard solution of TRI, would give a very inaccurate determination because of the lack of reproducibility of the luminescence intensity measurements in frozen solutions. It is possible to compensate for most of this effect by adding to the solution to be determined and to the

standard solution the same amount of a compound, e.g., BEP chosen so as not to interfere spectrally with TRI phosphorescence. Instead of TRI phosphorescence intensity, its ratio to the added compound phosphorescence intensity was measured.[14,15]

In practice, 5 μg of BEP were added to a chromatographic fraction containing 0.01–0.2 μg of TRI and to a standard solution of TRI. The mixtures were evaporated to dryness, the residues dissolved in about 1 ml of EPA and, after freezing in a silica tube, placed in the spectrophosphorimeter. The heights h_T, h_T^0, h_B, h_B^0 of the peaks of TRI at 461 nm and of BEP at 537 nm, were measured in the solution to be analyzed and in the standard solution (superscript zero), with the same excitation wavelength, 257.5 nm. If the mass of TRI in the standard sample is M^0, the mass of TRI in the unknown sample is obtained by:

$$M = M^0 \frac{h_T/h_B}{h_T^0/h_B^0}. \tag{1}$$

With this method, the exact volume of EPA is of no consequence and there can be no problem with selfscreening of the solution, because the same excitation wavelength is used for both compounds. The validity of the relation (1) was verified experimentally to $\pm 10\%$ in the range 0.01–0.2 μg of TRI.

COMPARISON OF PAH LEVELS IN ATMOSPHERIC PARTICULATE MATTER

The analytical results for Antony and St. Denis in January, August and October are given in Table III. As the extraction procedures reported in Table III were not exactly the same in all cases the results are only comparable to about $\pm 30\%$ as shown by the control experiments related in material and methods. Variations in concentrations are, however, so large that the conclusions drawn below are unlikely to be altered by such errors.

On the average, the concentration of PAH was higher in St. Denis than in Antony by a factor of two, but the main variations are seasonal and differences are maximal between January and August. The ratios of concentrations in January and in August (average

TABLE III

Concentrations of PAH in ng/m^3 of air and average ratios of August to January concentrations.[a]

Compound	August 1979		October 1979		January 1980		ratios: January / August (average)
	Antony	St. Denis	Antony	St. Denis	Antony	St. Denis	
FLA	0.32	0.80	2.6	3.1	8.6	14.2	22.5
PY	0.13	0.34	2.0	2.2	6.7	10.4	41.5
TRI	0.11	0.15	0.95	0.8	2.9	6.9	44.5
BAA	0.028	0.10	2.0	2.7	4.8	25	210
CHR	0.22	0.56	3.6	4.3	8.9	29	46.5
BJF	—	0.17	2.6	4.0	5.5	13	76
BBF	0.46	1.03	8.6	9.7	15.7	36	34.5
BEP	0.18	0.40	4.9	6.5	8.8	27	58.5
PE	0.004	0.011	0.27	0.4	0.88	4.4	310
BKF	0.12	0.29	3.0	3.7	7.4	25	74
BAP	0.023	0.074	1.6	2.0	4.6	15	201
DBAC	0.016	0.028	0.42	0.41	0.69	2.8	71.5
DBAJ	—	0.022	0.42	0.51	0.75	1.4	64
DBAH	0.012	0.029	0.50	0.69	0.98	2.8	89.5
BBCH	0.0086	0.015	0.35	0.50	1.16	4.1	203.5
PIC	0.038	0.065	0.72	0.60	1.55	4.4	54.5
INPY	0.16	0.39	4.4	5.7	9.6	30	68.5
BGHI	0.21	0.45	6.7	7.6	11.5	31	62
ANTH	0.0013	0.003	0.21	0.16	—	0.76	253
NC	0.034	0.047	0.53	1.0	—	4.4	94
BRP	0.0046	0.007	0.089	0.096	0.18	0.62	64
COR	0.14	0.22	2.1	1.9	1.84	3.3	14
EGHI	0.046	0.095	0.97	1.4	1.35	4.5	38
$CHCl_3$ extrations							
1°	3 h	3 h	3 h	30 min	6 h	4 h	
2°	7 h	20 h	20 h	—	—	—	
sonicat.	20 min	20 min	—	9 min	20 min	20 min	

[a]Concentrations of PAH are determined from 1 month collection from about 1000 m^3 of air. No corrections are applied to take into account incomplete extraction or losses of PAH during the treatment. At the bottom of the table are indicated the duration of each extraction by $CHCl_3$.

values for St. Denis and Antony) are given in the last column of Table III. These ratios are less than 50 for COR, FLA, EGHI, PY, TRI and CHR but higher than 100 for PE, ANTH, BBCH, BAP and BAA.

Grimmer[16] recorded BAP concentrations as a function of the week of the year. Some weeks yielded about 200 times more BAP than other weeks but on an average the BAP concentration during January was only 15 times more than in August. The differences with our results may be related to differences in climate, emission of pollutants and conditions of collection (one-week instead of one-month collection). Coviaux *et al.*,[4] with one-month collection time and conditions similar to ours, found average winter to summer concentration ratios of 16 for BAP, 20 for PE and 31 for BAA, but on certain sites, the February-to-July BAP ratio was more than 100.

PHOTOLYSIS OF PAH IN SUNLIGHT

As the highly coloured PAH, e.g. PE, ANTH, dibenz(a,e)aceanthrylene and dibenz(b,def)chrysene were either not found or found in very low concentrations, particularly during the summer, we suspected that they may have been photolysed during their stay in the atmosphere.[11,12] But the quantum yield of photolysis should be taken into account and this may explain why the highly coloured INPY is present in high concentrations in the atmospheric extracts.

Photosensitivity of dibenz(a,e)aceanthrylene (DBAE) and INPY

Solutions of DBAE and INPY were prepared at a concentration of 2.5 μg per ml of distilled dry n-heptane. To compare the rate of absorption of solar photons by the two solutions in an optically thin layer, the convolutions of an average solar spectrum,[17] $S_{(\lambda)}$, and the absorbance spectrum, $A_{(\lambda)}$, of the two solutions on the same thickness are calculated:

$$\int_{300\,\mathrm{nm}}^{480\,\mathrm{nm}} S_{(\lambda)} . A_{(\lambda)} . d\lambda.$$

The integral is proportional to the number of solar photons absorbed by the solution. The solution of INPY was found to absorb twice as many solar photons as DBAE.

Two identical, ground glass stoppered, 50 ml pyrex erlenmeyer flasks were used for irradiation of 10 ml of each solution. No grease was used but the top of the vials was wrapped in parafilm foil. Any loss of the solvent was compensated after the irradiation. The liquid layers, of about 4 mm, resulted in an absorbance lower than 0.2 between 300 and 480 nm.

After 98 days of solar exposure on the roof of the laboratory during the months February to June, the INPY absorption bands had only decreased by 10% while there was only 35% of the DBAE left. The rate of photolysis of DBAE is then 10 times higher than the rate of photolysis of INPY and it is deduced from the ratios of solar photons absorbed by the two solutions calculated above that the quantum yield of photolysis of DBAE is 20 times higher than the quantum yield of photolysis of INPY.

Photolysis of a mixture of PAH

Seven ml of a solution containing per ml of n-heptane: 0.4 μg of BBF-BEP-INPY-BGHI, 0.2 μg of FLA-PY-TRI-BAA-CHR-BJF-BKF-BAP-COR, 0.1 μg of BBCH-PIC-NC, 0.04 μg of PE-DBAC-DBAJ-DBAH-EGHI-BRP, 0.02 μg of ANTH were placed in a 50 ml erlenmayer flask. The proportions are similar to those found in atmospheric extracts.

After one month of sunlight exposure (November), the PAH concentrations were determined. The PAH can be classified according to their sun photo-sensitivities as follows (between brackets, the per cent recovery after photolysis): INPY (94), BJF (93), FLA (90), BBF (80), CHR (74), DBAJ (57), DBAH (54), PIC (50), DBAC (39), BKF (28), COR (21), BEP (18), BBCH (12), EGHI (10), BAA (9,3), NC (3), PY (0,9), BAP (0), BGHI (0), PE (0), ANTH (0).

A similar experiment with only 4 days exposure (October) was done to compare the highly photosensitive PAH (from NC to ANTH). The following per cent recoveries were found: NC (43), PY (12), BGHI (2.8), PE (1.6), BAP (0.9), BRP (<0.1), ANTH (<0.1).

DISCUSSION

We determined 23 PAH and our technique can be extended to a

higher number of PAH if the reference fluorescence spectra become available. We have characterized and determined dibenz(e,ghi)perylene which to our knowledge has not been detected before in atmospheric particulate matter.

Our method of determination includes often the measurement of a spectral peak height. This is a verification of the identity of each compound detected and attenuates the perturbing influence of fluorescent compounds whose spectra can be approximated by a straight line in the region of interest. This improvement of selectivity is obtained at the expense of an increased time of determination. But the technique could be completely automated without great difficulty with a computerised chromatograph and spectrofluorimeter.

The concentrations of PAH found in the Parisian atmosphere are comparable to those found in other relatively clean cities.[18] The higher levels recorded in St. Denis are probably related to a higher level of industrialisation.

Concerning the seasonal effect, it is noticed that the five PAH giving the highest January/August concentration ratio, are among the 8 more photosensitive PAH as determined in heptane solution in sunlight. The existence of a correlation between photosensitivity and seasonal variation is confirmed by log–log plotting of the January/August concentration ratio as a function of the estimated lifetime of each PAH exposed to sunlight, from our results in solution assuming an exponential decay (Figure 4). The best fitted straight line was obtained by the least square method (correlation coefficient: -0.46; 3% chance for no correlation by Student's t test).[19] The patent exception of COR could be related to its probable automobile origin.[20, 21]

The weak correlation may be interpreted by the existence of an important photolysis[12] of some PAH during their stay in the atmosphere. Other arguments, however, do not seem to support this explanation:

(1) Korfmacher *et al.*[22] showed that photolysis of PAH adsorbed onto coal fly ash particules was less than when measured in solutions or adsorbed on alumina, so that non-photochemical oxidation may be more important under field conditions. On the other hand, Thomas *et al.*[23] found a 40 min half-life for BAP adsorbed on soot in the presence of artificial daylight and Peters and Seifert[24] showed that the presence of atmospheric particulate matter on glass filters did not influence the sensitivity of adsorbed BAP to ozone or ozone plus light.

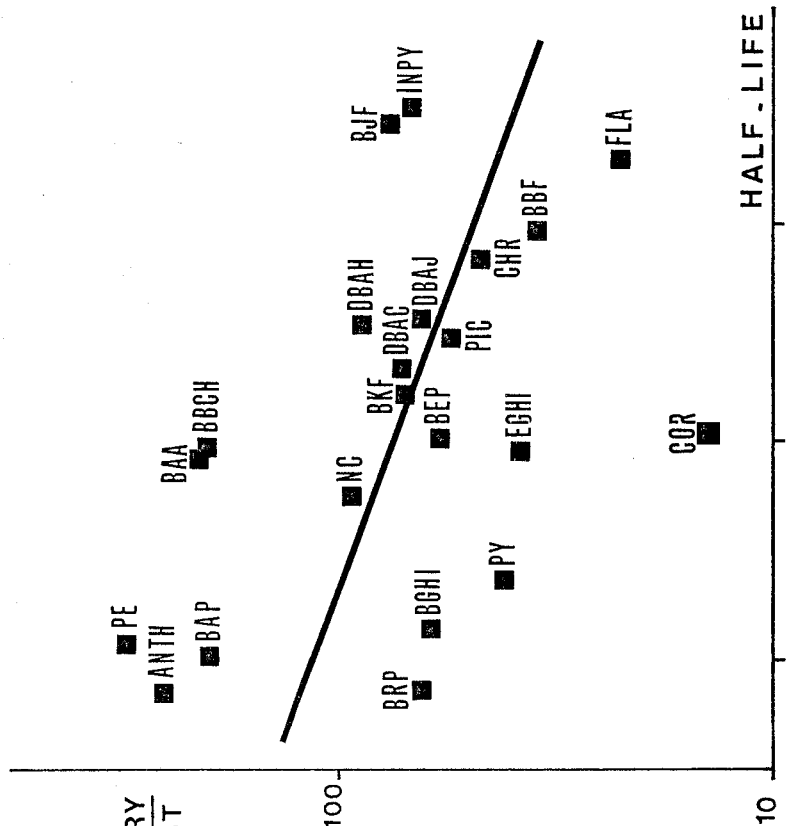

FIGURE 4 Ratios of January to August concentrations as function of the photo-chemical half-lifes determined for solution in sunlight (November).

(2) Chemical transformation of PAH occurs after collection in high-volume samplers,[24,25] under the influence of polluted air drawn through the filters.[25] Losses of pure BAP deposited on the filter of a high-volume sampler were up to 90% in 24 h and the extent of destruction was correlated with the ambient concentration of ozone.[24] However, the experiments of Konig *et al.*[25] in a real situation, show that destruction of BAP is less rapid; BAP concentrations obtained from 4 weeks collection time were only one half the concentrations obtained from 4 separate collections of one week time during the same period. Some of our concentrations of PAH determined in summer may be underestimated for this reason.

If ground state reactivity only is important, the correlation of seasonal effect with lifetime of photolysis may result from the fact that the reactivity of PAH in the excited state is somewhat correlated with ground state reactivity, as supported by the comparison of PAH reactivity with light and with different oxidizing agents.[26] Higher reaction rates in summer may then result from higher temperature and perhaps from higher ozone concentration.[27] Photolysis on the filter is also possible but unlikely because the filters were protected from direct daylight.

In conclusion, it is certain that the concentration of PAH recovered will be influenced by their photolysis in the atmosphere if photolysis lifetime is less than perhaps half a day, because the residence time of fine particles (less than 10 μm) is at least 10 hours,[28] but chemical reactivity after collection may play a still more important role.

Acknowledgment

This research was supported by a Grant from the "Ministère de l'Environnement".

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