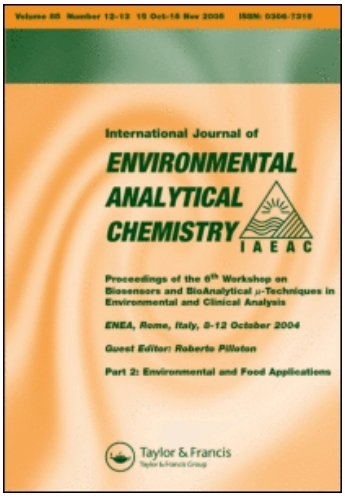

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Monitoring of carcinogenic PAHs in air under mild-warm ambient temperatures: relative importance of vapour- and particulate-phase analyses in assessing exposure and risk

Edoardo Menichini[a]; Fabio Monfredini[a]
[a] Istituto Superiore di Sanità, 00161 Rome, Italy

Online publication date: 12 May 2010

To cite this Article Menichini, Edoardo and Monfredini, Fabio(2003) 'Monitoring of carcinogenic PAHs in air under mild-warm ambient temperatures: relative importance of vapour- and particulate-phase analyses in assessing exposure and risk', International Journal of Environmental Analytical Chemistry, 83: 11, 897 — 908
To link to this Article: DOI: 10.1080/03067310310001621060
URL: http://dx.doi.org/10.1080/03067310310001621060

Intern. J. Environ. Anal. Chem., Vol. 83, No. 11, pp. 897–908

MONITORING OF CARCINOGENIC PAHs IN AIR UNDER MILD–WARM AMBIENT TEMPERATURES: RELATIVE IMPORTANCE OF VAPOUR- AND PARTICULATE-PHASE ANALYSES IN ASSESSING EXPOSURE AND RISK

EDOARDO MENICHINI* and FABIO MONFREDINI

Istituto Superiore di Sanità, viale Regina Elena 299, 00161 Rome, Italy

(Received 07 July 2003; In final form 31 July 2003)

Atmospheric polycyclic aromatic hydrocarbons (PAHs) are often determined by collecting only the particulate phase. The aim of this study was to ascertain in the field to what extent not collecting the vapour phase may affect the exposure assessment and the risk assessment for carcinogenic PAHs, under ambient temperatures typical of Southern Europe. PM_{10} 24-h samples were collected in Rome every two months throughout one year on a filter backed by two polyurethane foam sections. Daily mean temperatures during sampling reached 31°C, with hourly maximum values up to 36°C. While four-ring PAHs were found in the vapour phase to a large extent, the calculated annual means of five-ring PAHs, including benzo[*a*]pyrene, were not affected significantly by the amounts collected as vapour phase. By using the "toxicity equivalence factor" approach, the carcinogenic risk overall attributable to particle-bound PAHs accounted for at least 97% of the risk attributable to total (particulate + vapour phase) PAHs.

Keywords: Carcinogenic risk assessment; Phase distribution; Polycyclic aromatic hydrocarbons; Polyurethane foam

INTRODUCTION

Monitoring of atmospheric polycyclic aromatic hydrocarbons (PAHs) is most commonly performed by collecting air samples on filters [1,2]. According to several studies, however, the lower- and intermediate-molecular PAHs may be present in air in the vapour phase in considerable or even predominating proportions [3–10]. Factors affecting phase partition are the ambient temperature [11], the vapour pressure of the compound and its concentration in air.

As the carcinogenicity of several PAHs [12,13] is commonly the reason for monitoring this class, attention should be focussed on the partitioning of carcinogenic PAHs. For the purposes of this study, we consider the following PAHs as carcinogenic (abbreviations are given in Table I): BaA, BbFA, BjFA, BkFA, BaP, IP and

*Corresponding author. Fax: +39-06-49387083. E-mail: emenichini@iss.it

ISSN 0306-7319 print: ISSN 1029-0397 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0306731031000162106

TABLE I Target PAHs of this study

Compound[a]	*Abbreviation*	*Relative molecular mass*	*No. of rings*	*Vapour pressure*[b] (*Pa at 25°C*)	*IARC class*[c]
Fluoranthene	FA	202	4	1.2×10^{-3}	3
Pyrene	PY	202	4	6.0×10^{-4}	3
Benz[*a*]anthracene	BaA	228	4	2.8×10^{-5}	2A
Chrysene	CHR	228	4	8.4×10^{-5} (20°C)	3[d]
Triphenylene	TRI	228	4	Not available	3
Benzo[*b*]fluoranthene	BbFA	252	5	6.7×10^{-5} (20°C)	2B
Benzo[*j*]fluoranthene	BjFA	252	5	2.0×10^{-6}	2B
Benzo[*k*]fluoranthene	BkFA	252	5	1.3×10^{-8} (20°C)	2B
Benzo[*a*]pyrene	BaP	252	5	7.3×10^{-7}	2A
Indeno[1,2,3-cd]pyrene	IP	276	6	1.3×10^{-8} (20°C)	2B
Dibenz[*a,c*]anthracene	DBacA	278	5	Not available	3
Dibenz[*a,h*]anthracene	DBahA	278	5	1.3×10^{-8} (20°C)	2A
Benzo[*ghi*]perylene	BghiP	276	6	1.4×10^{-8}	3

The following PAHs are determined together as they are unresolved in GC analysis: CHR and TRI; BbFA, BjFA and BkFA (BFAs); DBacA and DBahA (DBAs).
[a]Ranked according to increasing GC retention time.
[b]From [13].
[c]Human carcinogenicity according to IARC [12]. 2A: probably carcinogenic; 2B: possibly carcinogenic; 3: not classifiable.
[d]Included by IPCS [13] among PAHs which are, or are suspected of being, carcinogenic.

DBahA (all classified as "probably" or "possibly" carcinogenic to humans by IARC [12] and commonly occurring in the atmosphere), plus CHR which was subsequently reported by IPCS [13] among PAHs which are, or are suspected of being, carcinogenic.

In the above-cited investigations [3–10], out of the carcinogenic PAHs, only four-ring BaA and CHR were found in the vapour phase in considerable proportions, the actual distribution being highly dependent on sampling temperature. The five- and six-ring PAHs were almost exclusively found in the particulate phase. This holds also for BaP which, owing to its large contribution to the overall carcinogenicity of PAH mixture in air, is often used as an indicator of PAH occurrence and carcinogenicity [2,13], and is the object of an air quality standard in various European countries (1 ng/m^3, as annual mean concentration) [2].

These findings suggest that in health-related studies the collection of particle-bound PAHs is sufficient to accurately determine BaP, as well as most carcinogenic PAHs and also most of the carcinogenic burden of air samples due to PAHs. However, under relatively high ambient temperatures, as may be common in Italy and more generally in Southern Europe, is this still valid? Is BaP air concentration still accurately determined by air sampling on filters only?

In this field study, we investigated the phase distribution of carcinogenic PAHs (and some other PAHs) in samples collected at a site in Rome throughout one year. This sampling period allowed different meteorological conditions, and in particular different sampling temperatures, to be taken into account. The aim of the work was to collect information on the efficiency of filter collection of BaP and other carcinogenic PAHs, under temperature conditions (generally mild but possibly very warm during the summer) which are typical of many areas in Southern Europe. In particular, we wanted to estimate to what extent the annual mean concentration of these species, and the consequent carcinogenic risk for the population, may be underestimated when analysis is limited to the particulate phase.

EXPERIMENTAL

Target PAHs

PAHs determined in this study are listed in Table I. In addition to the carcinogenic ones mentioned in the Introduction, three other PAHs (FA, PY and BghiP) were included as a control of the sampling module performance in partitioning PAHs. In fact, their vapour pressures are higher (FA and PY) or lower (BghiP) than those of the carcinogenic PAHs under study: hence, there is a high expectation of their almost complete recovery as, respectively, vapour or particulate phase [5,8,10].

Table I also includes TRI and DBacA because, under the analytical conditions of this study, they coelute with, respectively, CHR and DBahA. (Urban concentrations of TRI and DBacA were reported to be, respectively, 45 and 70% of those of pertinent coeluting species [14].)

Sampling

The sampling site was in Rome, in an area located between the city centre and the outskirts, along a large road with an estimated passage of 25 000 cars/day. Six air samples were collected throughout one year, one every two months. Sampling duration was 24 h. Three samples were collected during the domestic heating period (samples no. 1, 2 and 6 in Table II; fuels used in the area were gas, oil and, to a lesser extent, coal in some buildings located at a distance greater than 400 m).

Sampling was performed by a conventional high-volume air sampler (General Metal Works-Sierra Andersen, GMW-SA, model SAUV-15H) equipped with a PM_{10} size-selective inlet (GMW-SA, model SA 1200) and operating at a constant flow rate of 1.13 m^3/min. Particle-bound PAHs were collected on 20×25 cm glass fibre filters (GMW-SA, type G810), and weighed before and after sampling to determine PM_{10} concentrations according to a previously described procedure [15]. Polyurethane foam (PUF) was used to collect vapour-phase PAHs [16,17]. PUF sheets, $18 \times 23 \times 5$ cm, were of upholstery type (density: 0.026 g/cm^3) and were commercially

TABLE II PAH and PM_{10} atmospheric concentrations measured in this study

	Total (filter + PUFs) PAH concentration (ng/m^3)							
Sample no.	*1*	*2*	*3*	*4*	*5*	*6*	*All samples*	
Sampling month	*February*	*April*	*June*	*August*	*October*	*December*	*Mean*	*Median*
PAH								
FA	22.6	8.2	7.1	6.3	7.5	14.3	11.0	7.9
PY	25.4	8.3	7.5	4.4	8.7	17.3	12.0	8.5
BaA	4.0	0.5	0.4	0.4	1.0	1.7	1.3	0.8
CHR+TRI	9.0	1.3	0.8	0.6	1.2	3.0	2.7	1.3
BFAs	9.4	1.5	0.5	0.7	1.2	3.8	2.9	1.3
BaP	4.8	0.5	0.3	0.4	1.1	2.0	1.5	0.8
IP	3.5	0.6	0.5	0.6	1.1	1.8	1.3	0.8
DBAs	0.5	0.1	0.1	0.1	0.1	0.2	0.2	0.1
BghiP	6.1	1.1	1.0	0.5	2.3	3.9	2.5	1.7
PM_{10} (μg/m^3)	88	42	66	44	49	29	53	46

PAH abbreviations: see Table I.

purchased (Tecora, Milan). Before being inserted into the sampling module, each sheet was cut by a scalpel into two 2.5-cm thick sheets which were used as front and backup sections. The original filter holder was substituted by a commercially available module (GMW-SA, model G10602) consisting of a filter holder backed by a PUF holder. Ambient air temperatures were recorded during sampling.

Chemicals

All solvents used throughout the analytical procedure were HPLC grade, except diethyl ether (analytical grade). Individual PAH standards were commercially purchased as pure compounds; they were used to prepare the calibration solutions.

PUF Preparation and Handling

Front and backup PUFs were analysed separately to check for any PAH breakthrough. Sheets were handled using latex gloves or PTFE-coated tweezers.

All the extractions of PUF sheets (including initial cleanup, after-sampling extraction, after-extraction cleanup for re-use) were performed by a Soxhlet apparatus (capacity of the extractor, 1 L; o.d., 80 mm; height to the top of the siphon tube, 22 cm; capacity of the flask, 2 L). To allow handling the PUF inside the Soxhlet, a laboratory-made stainless steel rod was used, bearing a hook at one end to be grasped and a circular wire netting (diameter, 55 mm) at the other. The PUF was rolled up around the rod and, while being compressed by hand, was inserted into the extractor and pushed against the bottom of it. The rod remained inside the Soxhlet during extraction.

For the initial cleanup, each PUF sheet was extracted with 1 L acetone/*n*-hexane/diethyl ether 500 : 450 : 50 for at least 24 h. The efficiency of cleanup in removing interferences from the PUF was checked by re-extracting each cleaned sheet under the conditions of loaded samples (see below) and analysing the extract. At the end of this cleanup, the PUF (whose volume had increased due to solvent absorption) was pulled out from the Soxhlet by means of the rod. While pulling out, the PUF was compressed against the cone, so most of the absorbed solvent was allowed to drip into the extractor. Then, the PUF was leant on a laboratory-made stainless steel holder under a fume cupboard until it returned to its original size and flatness (about 30 min). Finally, it was dried in a glass vacuum desiccator connected to a water aspirator, until no solvent odour could be detected (about 4–5 h). Cleaned sheets were wrapped with hexane-rinsed aluminium foil and stored in glass jars until placed in the sampling module.

Extraction and Cleanup

Immediately after sampling, the filter was conditioned in the balance room and weighed to determine PM_{10} concentration; conditioning time was limited to 30 min to avoid any potential PAH degradation [15]. All the samples were extracted within 1 h of the end of sampling. Filters were ultrasonically extracted with cyclohexane [18]. PUFs were Soxhlet extracted with 1 L of a mixture of 10% v/v diethyl ether in *n*-hexane [16,17], by the same procedure above described for PUF preparation; amber glass flasks were used.

Each PUF sheet was used for three sampling events and then discarded. If the PUF had to be re-used, at the end of the extraction process it was left in the Soxhlet extractor and subjected to the cleanup procedure reported above. As for the initial cleanup, the actual cleanliness was checked on selected sheets by re-extraction under the conditions of loaded samples and subsequent analysis of the extract.

The extracts, from both filters and PUFs, were concentrated by rotary evaporator and then under a nitrogen stream to about 0.5 mL, and cleaned-up by thin-layer chromatography on silica-gel plates by a previously described procedure [18].

Analysis

Analysis was performed by gas chromatography with flame ionization detection (GC/FID). The instrument (Carlo Erba Instruments, HRGC 5160 Mega Series) was equipped with a cold on-column injector and a 30 m × 0.32 mm × 0.25 μm fused-silica SPB-5 column (Supelco). The following temperature programme, optimised for a rapid determination of target PAHs, was used: oven temperature held at 90°C for 1 min, raised to 190°C at 25°C/min, then to 300°C at 6°C/min, where it was held isothermally until all peaks were eluted. (Occasionally, the second ramp was programmed at a reduced rate (5 or 4°C/min) to resolve some PAH peaks from interferences.) A computer system (HP 3365 Series II ChemStation) was used for data acquisition and processing. After carefully checking the proper assignment of the baseline for each target peak, height measurements were used for quantification; only the large peak constituted by the three unresolved benzofluoranthene isomers (BFAs) was quantified by area integration. The external standard calibration procedure was used.

Quality Control

The whole procedure was subject to a strict quality control programme. PAH identification was confirmed in each sample by the standard addition method and, in selected samples, by GC with mass spectrometric detection (GC/MS; Hewlett-Packard 5971A). GC/MS was also used for some PUF samples whose analysis by GC/FID showed poor accuracy due to interferences or to concentrations near the detection limit.

A laboratory blank test was run on each sampling event by subjecting a glass fibre filter to the whole analytical procedure. The blankness of each individual PUF was checked as above described. Recovery and repeatability tests of the analysis for particle-bound PAHs were part of a previous study [19]. The separate analysis of front and backup PUFs allowed detection of significant breakthrough, if any, of vapour-phase PAHs from the PUF (see "Results and discussion").

A laboratory test was conducted to check no significant degradation of target PAHs occurs at the extraction temperature of PUFs. A *n*-hexane solution containing 1.6 μg of each PAH (the amount present in a sample collected at an air concentration of 1 ng/m^3) was refluxed for 18 h. The test was performed in duplicate, and together with a blank (i.e. *n*-hexane with no PAH added). The BeP profile (i.e. the concentration ratios of all target PAHs to BeP, the latter selected as a relatively stable compound [20,21]) was compared before and after refluxing and was found unchanged.

The stability of the PAH calibration solution was checked by including the stable hexacosane ($C_{26}H_{54}$, eluting between BaA and BFAs) in the calibration solution and regularly checking the PAH response factors relative to it.

RESULTS AND DISCUSSION

Phase Distribution of PAHs

Total (filter + PUFs) PAH concentrations measured in this study are summarised in Table II. For completeness of information, PM_{10} concentrations are also shown. The mean concentrations of PAHs and PM_{10} were at levels typically found at urban traffic-oriented sites in Europe [2,22]. Concentrations of PM_{10} were only moderately correlated ($r = ca.$ 0.6; not significant, $P > 0.05$) with those of PAHs (either BaP or the sum of all PAHs or the sum of carcinogenic PAHs), consistent with the findings of a previous study [15]. Table III presents the PAH proportions found in the individual PUFs *versus* the total (filter + PUFs) PAH found, and the ambient temperature data during sampling. Figure 1 shows the overall proportion found in the vapour phase (i.e. front + backup PUFs) as a time trend, for pertinent PAHs.

Higher-molecular compounds BaP, IP, DBAs and BghiP were not detected in the vapour phase in any sample. Vapour-phase BFAs ranged from $< 1\%$ (not detected) to 20%, the percentage increasing along with ambient temperature. The phase distribution of intermediate-molecular compounds (BaA and CHR + TRI) was highly seasonally variable: the amount found in PUFs ranged from 8% in winter up to *ca.* 70% in summer (with temperatures exceeding 30°C). As expected, the lower-molecular compounds (FA and PY) were mostly or almost totally found in the vapour phase, ranging approximately from 80 to 99%.

The yearly based phase distribution is roughly indicated by the mean distribution calculated over the six samples (Table III). As to PAHs detected in both phases, BFAs were almost totally found on the filter (93%); BaA and CHR + TRI were found in the PUF in remarkable proportions (*ca.* 40%); FA and PY were almost totally found in the PUF (*ca.* 93%).

It is worthwhile noting that PAH distribution, as calculated from filter and adsorbent analyses, does not necessarily represent the actual phase distribution existing in ambient air. In fact, artefact processes may occur during sampling: volatilisation of PAHs already trapped on the filter [5] (often referred to as the "blowing-off" effect), and adsorption of vapour-phase PAHs by the particles trapped on the filter [23] or by the filter material [24].

Our findings are in good agreement with those obtained in previous studies (Table IV). This holds in particular for BaP (previously generally not detected in vapour phase or detected within 10% of the total) and the other higher-molecular PAHs. Relative to our results, lower proportions of more volatile PAHs (FA, PY, BaA, CHR + TRI) in the vapour phase were reported in two studies performed in Oslo and in Minneapolis and Salt Lake City: this may be explained by the different ambient temperatures during sampling (not available for those studies but supposed to be somewhat lower than in Rome).

Breakthrough of PAHs

No PAH was detected in the backup PUFs, other than FA and PY whose amounts, however, were low: at most, 8% of that found in the front PUF occurred during days with maximum air temperatures (calculated from data of Table III). Hence,

TABLE III PAH proportions (%) found in front and backup PUF sections *versus* the total (filter + PUFs) PAH found

Sample no.	*1*		*2*		*3*		*4*		*5*		*6*		*All samples*	
Sampling month	*February*		*April*		*June*		*August*		*October*		*December*			
T, mean (max)[a]	12 (17)°C		19 (23)°C		31 (36)°C		28 (33)°C		19 (24)°C		11 (14)°C			
PUF section	*Front*	*Backup*	*Front*	*Backup*	*Front*	*Backup*	*Front*	*Backup*	*Front*	*Backup*	*Front*	*Backup*	*Sum of both sections*[b]	
PAH													*Range*	*Mean*[c]
FA	84	< 0.2	96	1	97	1	93	5	91	4	92	1	84–99	94
PY	80	< 0.3	95	1	97	1	91	7	88	4	90	1	80–98	93
BaA	8	< 1	41	< 2	69	< 1	47	< 1	24	≤1	18	< 1	8–69	35
CHR+TRI	8	< 1	53	< 1	70	< 1	63	≤2	32	≤2	17	< 0.5	8–70	41
BFAs	< 1	< 1	3	< 1	20	< 1	16	< 1	2	< 1	< 1	< 1	< 1–20	7
BaP	< 1	< 1	< 1	< 1	< 1	< 1	< 2	< 2	< 1	< 1	< 1	< 1	< 2–< 4	< 2
IP	< 1	< 1	< 2	< 1	< 2	< 1	< 2	< 2	< 1	< 1	< 1	< 1	< 2–< 3	< 2
DBAs	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ	NQ
BghiP	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 2	< 2

PAH abbreviations: see Table I.
< . . . : The given percentage is based on the minimum detectable concentration.
≤ . . . : The PAH is present but, owing to an interference, the given percentage is an upper-bound estimate.
NQ: percentage not quantifiable (compound not detected in PUFs and concentration on filter near the detection limit; see Table II).
[a]Ambient temperature recorded during sampling: 24-h mean and, in brackets, hourly maximum.
[b]Some small inconsistencies in the sums are due to rounding of decimal figures.
[c]Mean values may be approximate due to the presence of data " < . . . ".

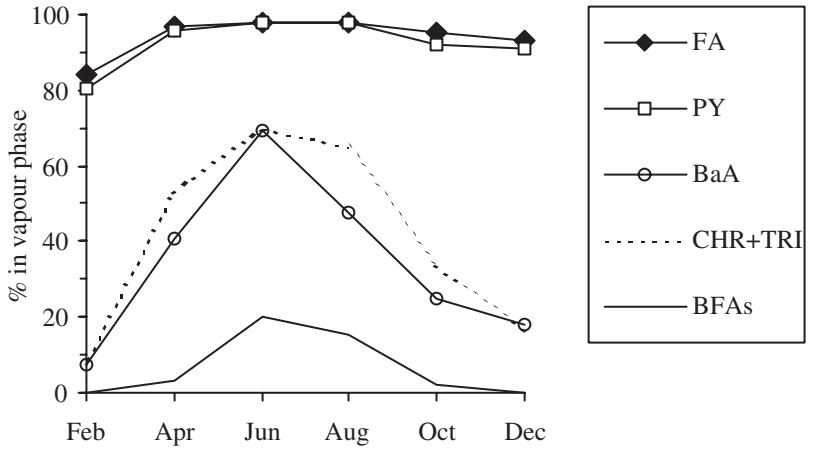

FIGURE 1 Time trend of PAH proportion found in the vapour phase, as percentage of the total (vapour + particulate phases). From data of Table III (data "<..." and "≤..." were entered as, respectively, zero and the given value). Unshown PAHs were not detected in the vapour phase in any sample. PAH abbreviations: see Table I.

there was no evidence of significant losses of target PAHs due to breakthrough from the whole PUF adsorbent.

Carcinogenic Burden of PAHs Collected in the Vapour Phase

The importance of the contribution of vapour-phase PAHs to total collected PAHs (vapour + particulate phases) was evaluated in terms of carcinogenic risk. For this purpose, the "toxicity equivalence factor" approach [13] was used. According to this, the risks attributable to individual PAHs in a mixture with given concentrations are expressed relative to that attributable to BaP, as BaP-equivalent concentrations. While this approach has a disadvantage in possibly underestimating the whole risk for a mixture by summing the equivalents of only a number of compounds, it is quite useful in comparing the estimated risks associated with selected PAHs in a mixture. Table V shows how we adopted this procedure.

For each carcinogenic PAH, we considered the range of carcinogenic potencies relative to BaP, as estimated in different studies (reviewed in [13]). The extremes of each range were multiplied by the two mean concentrations determined by the analysis of, respectively, filter + PUF and filter only: hence, the lower- and upper-bound estimates of the total BaP-equivalent concentrations were obtained for both data sets. The total BaP-equivalent concentration resulting from the analysis of particle-bound PAHs accounted for at least 97% of the one resulting from the analysis of both phases (upper-bound estimates). BaP clearly gave the highest contribution to total BaP-equivalent concentration. Even after applying this procedure to the individual June sample, which showed the highest vapour-phase proportions (Table III), the total BaP-equivalent concentration based only on filter analysis still accounted for a high 91–99% (respectively, upper- and lower-bound estimates).

TABLE IV PAH proportions (%) found in vapour phase *versus* the total (filter + PUFs) PAH found: comparison with literature data

City	*Oslo, N*		*Birmingham, UK*		*Rotterdam, NL*	*Augsburg, D*	*Jülich, D*		*Columbus, USA*	*Minneapolis and Salt Lake City, USA*	*Chicago, USA*	*Rome, I*
Month(s)	*Jan–Feb*		*Feb*	*Aug*		*Whole year*	*Jan*	*Jul–Aug*	*Summer and winter*	*Nov–Feb*	*Jun–Oct*	*Whole year*
Site location	*Street*	*Roof, 25 m*	*Roof, 15 m*		*Roof, at seaport*	*Outskirts*	*Non-urban*			*Various*	*Roof, 12 m*	
Air T, °C[a]						*0–20*	*−5–10*	*10–30*	*−5–29*		*15–30*	*11–31*
n	*17*	*9*			*3*	*8*	*4*	*4*	*13*	*22*	*12*	*6*
Adsorbent	*PUF*		*PUF*		*PUF*	*XAD-2*	*PUF*		*Denuder + PUF*	*PUF*	*PUF + XAD-2*	*PUF*
Notes			b			c, d					e, f	
Reference	*[3]*		*[8]*		*[4]*	*[9]*	*[6]*		*[5]*	*[7]*	*[10]*	*This study*
PAH												
FA	47	45	90	83	84–88	69–96	78–87	87–94	90	*ca.* 50	85	94
PY	42	44	94	83	81–90	75–92	71–84	72–92	90	*ca.* 50	83	93
BaA	4	2	74	62	15–27		17–41	33–50	39	ND	35	35
CHR+TRI	2	4	69[g]	66[g]	8–12[g]	7–45	17–34	44–67	66	ND	44	41
BFAs	1[h]	3[h]	13/7.5[i]	10/12.5[i]	ND	note d	ND or NQ	ND or NQ		ND	12/10[i]	7
BaP	ND	10[e,j]	9	8	ND	note d	ND	ND or NQ	ND	ND	5	< 2
IP			0.5	< 2	ND-1	note d	ND	ND	ND		2	< 2
DBahA	ND	ND	6	< 14		note d						ND
BghiP	ND	ND	3	< 1	ND	note d	ND	ND	ND		2	< 2

PAH abbreviations: see Table I.
Void: datum not available; *n*: number of samples; ND: not detected in vapour phase; NQ: detected but not quantified ($\leq 0.1\,ng/m^3$) in vapour phase.
Data re-elaborated from original literature. Individual values are mean (or, in Columbus, median) proportions during the whole investigation.
[a]Range of mean temperatures during each sampling event, except in the Jülich study (range over the whole sampling period).
[b]Reason for the higher percentage of lower-molecular PAHs in February unclear to the authors.
[c]Six-week samples.
[d]The concentration of five- and six-ring PAHs (species unspecified by the authors) was below the quantification limit.
[e]Approximate data estimated from a figure.
[f]Day-time samples.
[g]Only CHR.
[h]Only BbFA.
[i]BbFA/BkFA.
[j]Difference between street and roof "unexplained completely" by the authors.

TABLE V BaP-equivalent concentrations of carcinogenic PAHs estimated from the analysis of, respectively, filter + PUF and filter only (mean values from the six samples)

PAH	*Relative carcinogenic potency*[a]		*BaP-equivalent concentrations*			
			Filter + PUF[b]		*Filter only*[c]	
	min	*max*	*Lower-bound*	*Upper-bound*	*Lower-bound*	*Upper-bound*
BaA	0.01	0.1	0.013	0.13	0.011	0.11
CHR[d]	0.001	0.1	0.0027	0.27	0.0021	0.21
BFAs	0.01[e]	0.1	0.029	0.29	0.028	0.28
BaP	1.0	1.0	1.5	1.5	1.5	1.5
IP	0.1	0.1	0.13	0.13	0.13	0.13
DBahA[f]	1.0	5	0.2	1.0	0.2	1.0
Total			1.87	3.32	1.87	3.23

PAH abbreviations: see Table I.
[a]Relative to that of BaP (orders of magnitude). Range of estimates reported in literature (from [13]).
[b]From mean concentrations reported in Table II.
[c]By combining the data of Tables II (column 'mean') and III.
[d]As worst-case, CHR is assumed to account for 100% of the concentration of CHR + TRI (Table III).
[e]Assuming BkFA to account for 100% of the three isomers.
[f]As worst-case, DBahA is assumed to account for 100% of the concentration of DBAs (Table III).

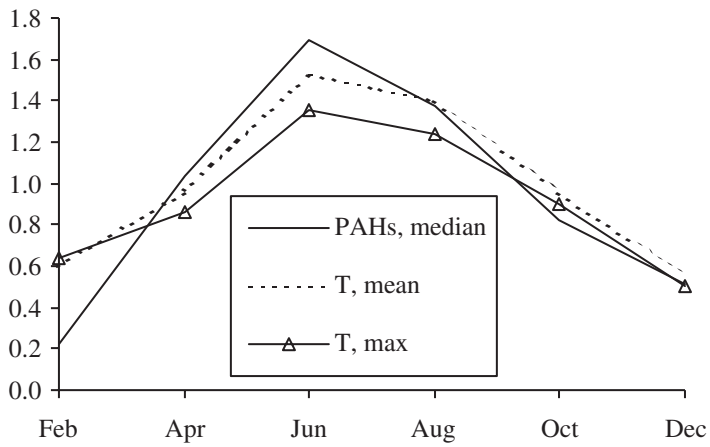

FIGURE 2 Time trends of median PAH proportions in the vapour phase and ambient temperatures during sampling. PAH proportions and temperatures are normalised to the mean value of the pertinent series. PAHs considered are the same as in Fig. 1.

Correlation between Vapour-phase Proportions and Ambient Temperatures

Figure 2 allows comparison of the seasonal trends of PAH proportions in the vapour phase, mean temperatures and maximum hourly mean temperatures during sampling. The PAHs considered are those detected in vapour phase. The median of the proportions calculated for each PAH was taken as an overall indicator of the vapour-phase proportion on each sampling event. For graphic convenience, the three data sets were preliminarily normalised to the pertinent mean value over the six samples. A visual inspection of Fig. 2 confirms the expected positive correlation between PAH proportions in the vapour phase and ambient temperatures. Figure 3 shows the regression line of the median PAH proportion in the vapour phase on the mean temperature, with

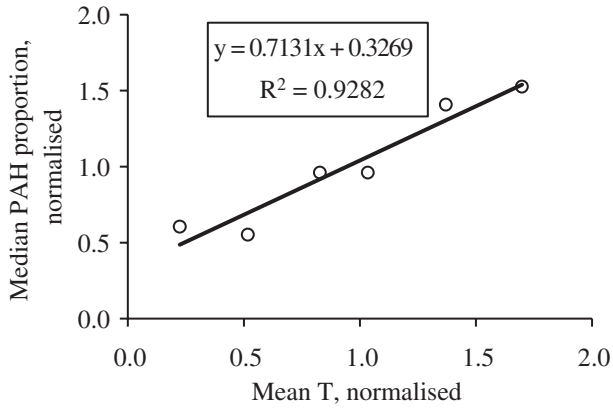

FIGURE 3 Linear regression of median PAH proportion in the vapour phase on mean ambient temperature. PAH proportions and temperatures are normalised to the mean value of the pertinent series. PAHs considered are the same as in Fig. 1.

the two parameters strongly correlated ($r = 0.96$, $P < 0.01$); a similar correlation was found with the maximum hourly mean ($r = 0.94$, $P < 0.01$; not shown).

CONCLUSIONS

BaP, IP and DBahA, out of the carcinogenic PAHs, as well as the six-ring BghiP, were not detected as vapour phase in any one sample. BFAs were found as vapour phase in summer samples in a considerable proportion (up to 20%). BaA and CHR were partially found as vapour phase in all samples, in proportions increasing with increasing temperature, up to 70% of the total collected amount. On an annual basis, the vapour-phase proportions averaged a low 7% for BFAs and *ca.* 40% for BaA and CHR.

The experimental conditions of this study included warm temperatures, with daily mean values up to 31°C and hourly maximum values up to 36°C, which are roughly typical of many areas in Southern Europe. Even under these conditions, the collection of particulate phase alone appears to be adequate to quantify the annual mean concentration of five-ring carcinogenic PAHs and, in particular, of BaP which is usually used as a surrogate for the carcinogenic PAH fraction. The study confirms that, conversely, the addition of a vapour-phase trap is required to quantify four-ring carcinogenic PAHs (otherwise, the yearly averaged concentrations of BaA and CHR are underestimated roughly by a factor of two).

Despite the losses of BaA and CHR, the collection of vapour-phase PAHs appears to be unnecessary if the annual monitoring of PAHs is aimed at a carcinogenic risk assessment, rather than an exposure assessment. In fact, the underestimate of concentrations of more volatile PAHs, resulting from sampling the particulate phase only, was shown not to significantly affect the overall carcinogenic risk of air samples attributable to PAHs. This observation has an advantageous practical implication in health-related long-term monitoring, as including a vapour-phase trap in the sampling module requires a modification to most conventional air samplers and considerably increases

the workload (pre-cleaning, preparation and extraction of the adsorbent) of a complex and time-consuming analysis.

Acknowledgements

Acknowledgements are due to Dr. F. Merli for co-operation in analysing a number of samples by GC/MS. Mr. F. Massa gave excellent technical assistance in sampling operations. This study has been carried out within the framework of Research Program PR-22/IS, Subproject 1, jointly financed by the Ministry of the Environment (Rome, Italy) and the Italian National Institute of Health (Istituto Superiore di Sanità).

References

[1] E. Menichini, *Sci. Total Environ.*, **116**, 109–135 (1992).
[2] European Commission, *Ambient Air Pollution by Polycyclic Aromatic Hydrocarbons* (*PAH*), Position Paper and Annexes. Prepared by the Working Group On Polycyclic Aromatic Hydrocarbons (Office for Official Publications of the European Communities, Luxembourg, 2001). ⟨http://europa.eu.int/comm/environment/air/pdf/pp_pah.pdf⟩ and ⟨http://europa.eu.int/comm/environment/air/pdf/annex_pah.pdf⟩
[3] K.E. Thrane and A. Mikalsen, *Atmos. Environ.*, **15**, 909–918 (1981).
[4] W.K. De Raat, F.L. Schulting, E. Burghardt and F.A. De Meijere, *Sci. Total Environ.*, **63**, 175–189 (1987).
[5] R.W. Coutant, L. Brown, J.C. Chuang, R.M. Riggin and R.G. Lewis, *Atmos. Environ.*, **22**, 403–409 (1988).
[6] R. Niehaus, B. Scheulen and H.W. Dürbeck, *Sci. Total Environ.*, **99**, 163–172 (1990).
[7] S.B. Hawthorne, D.J. Miller, J.J. Langenfeld and M.S. Krieger, *Environ. Sci. Technol.*, **26**, 2251–2262 (1992).
[8] D.J.T. Smith and R.M. Harrison, *Atmos. Environ.*, **30**, 2513–2525 (1996).
[9] H. Kaupp and M.S. McLachlan, *Chemosphere*, **38**, 3411–3421 (1999).
[10] M. Odabasi, N. Vardar, A. Sofuoglu, Y. Tasdemir and T.M. Holsen, *Sci. Total Environ.*, **227**, 57–67 (1999).
[11] H. Yamasaki, K. Kuwata and H. Miyamoto, *Environ. Sci. Technol.*, **16**, 189–194 (1982).
[12] IARC. *Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42*; IARC Monogr. Eval. Carcinog. Risks Hum., Suppl. 7. Int. Agency Res. Cancer, Lyon (1987).
[13] International Programme on Chemical Safety. *Selected Non-heterocyclic Polycyclic Aromatic Hydrocarbons*. Environmental Health Criteria 202. World Health Organization, Geneva, 1998.
[14] S.A. Wise, M.M. Schantz, M.J. Hays, B.J. Koster, K.E. Sharpless, L.C. Sander, B.A. Benner Jr and S.B. Schiller, *Polycyclic Aromatic Compounds*, **9**, 209–216 (1996).
[15] E. Menichini and F. Monfredini, *Fresenius Environ. Bull.*, **10**, 533–538 (2001).
[16] U.S. Environmental Protection Agency. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS), Compendium Method TO-13A, In: *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA/625/R-96/010b, 2nd Edn. U.S. Environ. Prot. Agency, Cincinnati, OH (1997).
[17] International Organization for Standardization. *Ambient Air – Determination of Total* (*Gas and Particle-Phase*) *Polycyclic Aromatic Hydrocarbons – Collection on Sorbent-Backed Filters with Gas Chromatographic/Mass Spectrometric Analyses*. ISO 12884:2000, ISO, Geneva (2000).
[18] E. Menichini and F. Monfredini, *Intern. J. Environ. Anal. Chem.*, **61**, 299–307 (1995).
[19] E. Menichini, F. Monfredini and F. Merli, *Atmos. Environ.*, **33**, 3739–3750 (1999).
[20] J.D. Butler and P. Crossley, *Atmos. Environ.*, **15**, 91–94 (1981).
[21] D.A. Lane, In: T. Vo-Dinh (Ed.), *Chemical Analysis of Polycyclic Aromatic Compounds*, pp. 31–58. J. Wiley & Sons, New York (1989).
[22] European Commission, *Ambient Air Pollution by Particulate Matter*, Position Paper. Prepared by the Technical Working Group On Particles, European Commission (1997). ⟨http://europa.eu.int/comm/environment/air/pdf/pp_pm.pdf⟩
[23] K.M. Hart, L.M. Isabelle and J.F. Pankow, *Environ. Sci. Technol.*, **26**, 1048–1052 (1992).
[24] K.M. Hart and J.F. Pankow, *Environ. Sci. Technol.*, **28**, 655–661 (1994).