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Determination of environmental reference concentration of six PAHs in urban areas (Pavia, Italy)

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Abstract

We propose a sampling strategy, using individual dosimetry to measure the daily inhaled quantity of PAHs in urban air. The method was applied to monitor 56 subjects living in an Italian town (Pavia; 80 000 inhabitants) and the Environmental Reference Concentration (E.R.C.) of six PAHs (classified as 'possible' carcinogenic agents for humans) was determined. The individual environmental samplings took place in two different seasons (winter and summer), for persons living in four different urban areas with different traffic density. Subjects were selected using a specific questionnaire designed to collect information on *indoor* and *indoor + outdoor* exposure times. The mean ± S.D. value of Benzo[*a*]pyrene [BaP] was 0.37 ± 0.15 ng m^{-3} in winter and 0.12 ± 0.07 ng m^{-3} in summer. Assuming 18 m^3 as the daily inhaled quantity the estimate of the BaP inhaled quantity was 6.66 ng/day in winter and 2.16 ng/day in summer.

1. Introduction

Italian laws (D.M. 25.11.1994) include BaP among the environmental pollutants to be monitored in urban areas fixing a quality standard of 2.5 ng m^{-3} by the 1st of January 1996 and 1.0 ng m^{-3} by the 1st of January 1999 (average yearly value) [1].

According to the *International Agency for Research on Cancer* (IARC) [2] other PAHs, together with the above mentioned BaP, are classified as 'possible' or 'probable' carcinogenic agents; these include: Benzo[*a*]anthracene [BaA], Benzo[*b*]fluoranthene [BbF], Benzo[*k*]fluoranthene [BkF], Benzo[*j*]fluoranthene [BjF], Indeno[*1,2,3-cd*]pyrene [IP] and Dibenzo[*a,h*]anthracene [DahA].

The above mentioned PAHs are routinly detectable in Italian urban areas as reported in a number of studies. The ratios between BaP and the other six PAHs are relatively constant, so that BaP can be used as a marker of environmental exposure to PAHs in urban areas, facilitating comparisons between data reported in different Italian towns [3–8].

PAHs are monitored, as other pollutants, using area samplers and high sampling flows. These samplings furnish an estimate of the *outdoor* environmental pollution. The reliability of this value depends on several factors such as the number and selection criteria of sampling sites, as well as the number and frequency of samplings.

Data thus collected is used to monitor the BaP

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concentrations in air at different traffic densities and to compare between the environmental levels of this pollutant in different seasons.

Nevertheless area samplers cannot determine the average dose of BaP (or other 'possible' carcinogenic PAHs) inhaled by the general population because information on the different *indoor/outdoor* exposure times and on the *indoor* environmental concentrations is not available.

These considerations lead to the conclusion that the reported *outdoor* PAH levels may induce an over-estimate of the general population exposure. Individual dosimetry could represent a suitable means of evaluation to be in case integrated with already existing sampling techniques in accordance with Italian law (D.M. 25.11.1994) [9].

Passive personal samplers have already been successfully used in a study on environmental exposure to benzene of three groups of primary school children (500 subjects) living in Treviglio (Lombardy), Poggibonsi (Tuscany) and Valenza (Piedmont) [10].

This study focused on a population living in Pavia (Lombardy, Italy). Individual dosimetry (active personal sampling for 24 h) was applied to the determination of the Environmental Reference Concentration (ERC) of BaP and five other 'possible' carcinogenic PAHs. The study was performed according to the guidelines fixed by the Italian Society for Reference Values (SIVR) [11]. Sampling strategy and selection criteria of the 'reference population' to be surveyed are presented. Air levels of six PAHs were determined, including BaP, to achieve a more reliable estimate of the inhaled quantity/day of the same substances in two different seasons. A comparative study of the indoor and outdoor levels of the six PAHs, applying a double individual sampling, was also performed on a weekly basis in winter.

2. Materials and methods

2.1. Study design

Fifty-six voluntary subjects (28 male and 28 female) living in Pavia (Lombardy, Italy) were divided into four subgroups:

- subjects living downtown;
- subjects living in residential areas with low traffic density;
- subjects living in areas with average traffic density;
- subjects living in areas with high traffic density

Each subgroup ($n = 14$) was formed by two primary school children, two employees, two students (high school or university), two shop assistants, two housewives and two persons in retirement. Each person involved was asked to stay in town for the whole sampling period (24 h).

Each subgroup included three subjects exposed to passive smoke, four using public transportation for at least 1 h/day and four travelling by car within town (1 h/day). Participants were trained before sampling and were guaranteed assistance by laboratory technical staff if needed. Each subject was also invited to fill in a questionnaire (see Appendix). Smokers and subjects exposed to significant *indoor* PAH sources (wood or coal stoves, fire-places) were excluded from our reference group.

2.2. Environmental samplings

Samplings (24 h from 08:00 to 08:00 the day after) were carried out in February 1996 and June 1996, meteorological and climatic data were also collected. Two subjects for each subgroups were monitored on two alternate days so that samplings were performed over a 2-week period, to ensure good representiveness of the climatic conditions of the two seasons.

The samplers (Moc. EGO or 2L/E, Zambelli Srl) were equipped with glass wool fiber filters (Ø 20 mm, Micro Filtration System, 6800 Sierra Court-Dublin, CA, USA) and ORBO-43 PAH absorption cartridges (Supelco, Bellefonte, PA, USA) and the sampling flow was 1.2 l min^{-1} (1728 l/day). During *indoor* sampling the sampler was to be put at mouth level, possibly avoiding the kitchen area.

2.3. PAH measurements in environmental particulate

Analysis of PAHs in environmental particulate samples was performed using both high resolution gas chromatography coupled with mass spectrometry (HRGC-MS) and high pressure liquid chromatography coupled with a fluorescence detector (HPLC-FLUOR) [12,13].

Considering the low sampled volumes (1.728 m^3/day) we used HPLC-FLUOR as a routine analysis technique given its higher sensitivity. On the other hand HRGC-MS was used to confirm the HPLC-FLUOR chromatografic peaks. Among the analytes we identified the seven carcinogenic PAHs: BaA, BbF, BkF, BjF, BaP, IP, DahA. Analytical separation of BjF ('possible' carcinogenic agent according to I.A.R.C.) was difficult, hence quantitation was not possible.

2.4. Apparatus

HPLC-FLUOR apparatus was equipped with a quaternary pump and an autosampler (Mod. 1050 Hewlett-Packard). An integrator (P.E. Nelson Mod.1020 Perkin Elmer) and a printer (Mod. LX-400 Perkin Elmer) were also used.

HRGC-MS analyses were performed on a Hewlett-Packard Mod. 5890 Series 2 Plus gas chomatograph equipped with a Hewlett-Packard Mod. 5972A mass detector. Spectra were processed using a Hewlett-Packard Mod. Vectra Personal Computer.

2.5. Chemicals and standard solutions

- *Milli-Ro Plus 10 + Milli-Q Plus* 185 (Millipore) ultrapure water;
- Ultrapure Acetonitrile for gradient (Merck);
- HiperSolv Methylene Chloride (BDH);
- Standard EPA 610 *Polynuclear Aromatic Hydrocarbons Mix* (Supelco Inc., Supelco Park, Bellefonte, PA, USA);
- Benzo[*j*]fluoranthene (Lab. Service Analytica Srl, Anzole E., Bologna, Italy)

2.6. Sample preparation and analysis

The glass wool filters and the ORBO43-PAH absorption media were put into 10 ml screw cap vials. Samples were extracted three times with CH_2Cl_2 in ultrasonic bath (5 min). The solvent was then evaporated either under gentle stream of nitrogen or using a rotary evaporator.

2.6.1. HPLC-FLUOR analysis

Samples were resuspended in 500 μl of acetonitrile and 20 μl were injected. Chromatography was carried out with a APEX PAH 300 5 μm, 25 cm × 4.6 ml i.d. column (Jones Chromatography, UK). The mobile phase was acetonitrile/acetonitrile/H_2O (1:1) in gradient.

2.6.2. HRGC-MS analysis

Samples were resuspended in 500 μl of CH_2Cl_2 and 1 μl was injected in splitless mode. Chromatography was carried out using a PTE 5, 30 m × 0.25 μm (Supelco, Bellefonte, PA, USA). Quantitation for the seven PAHs was carried out with Selected Ion Monitoring; the following m/z ratios were used:

PAH	m/z
Benzo[*a*]anthracene	228
Benzo[*a*]pyrene	252
Benzo[*b*]fluoranthene	252
Benzo[*k*]fluoranthene	252
Benzo[*j*]fluoranthene	252
Dibenzo[*a,h*]anthracene	278
Indeno[*1,2,3-cd*]pyrene	276

Table 1 reports the detection limits for the six PAHs, taking the sampled volume and the above mentioned operating conditions into account.

3. Results and discussion

Table 2 reports the environmental levels of six 'possible' carcinogenic PAHs reported in Pavia in

Table 1
HPLC-Fluor analysis of particulate analysis: detection limits for six 'possible' carcinogenic PAHs (sampled volume 1.728 l)

Substance	λ Excitation (nm)	λ Emission (nm)	Detection limit (ng m^{-3})
Benzo[*a*]anthracene	280	410	0.03
Benzo[*b*]fluoranthene	280	410	0.05
Benzo[*k*]fluoranthene	280	410	0.03
Benzo[*a*]pyrene	280	410	0.05
Dibenzo[*a,h*]anthracene	280	410	0.08
Indeno[*1,2,3-cd*]pyrene	305	500	0.10

February 1996 applying individual dosimetry to 56 subjects living in four areas at different traffic densities.

The data (Table 2) are expressed as mean ± standard deviation (S.D.), interval, median, 5° percentile and 95° percentile. Assuming 18 m^3 as the daily respiratory volume, the PAH daily inhaled quantity was calculated to define the 'Environmental Reference Concentration' (ERC) for these substances, as proposed by the Italian Society for Reference Values [11].

It must be pointed out that, on the basis of the data reported in Table 2, BaP represents 27.61% of the total amount of 'possible' carcinogenic inhaled PAHs (given the estimated inhaled quantity of 24.12 ng/day for the six PAHs and 6.66 ng/day for BaP).

Table 3 reports the environmental levels of the six PAHs measured in June 1996. The subjects we monitored in this period were the same as in the winter survey.

A drastic reduction of the PAH environmental concentrations was observed. The average daily inhaled quantity of BaP dropped from 6.66 to 2.16 ng during the summer. The same result was found when calculating the overall PAH inhaled quantity: it lowered from 24.12 ng/day in winter to 9.36 ng/day in summer. It must be pointed out that the summer concentrations of DahA and IP were, for most samples, below the detection limit.

A further survey was carried out in February 1996 in which eight subjects (two subjects for each of the four residential areas) underwent a double individual monitoring (*indoor and outdoor*) over a 24-h period. Each subject had two personal samplers to be switched on and off when moving from an *outdoor* environment to *indoor* and vice versa. The results are summarized in Table 4.

Higher concentrations were found for *outdoor* samplings. Table 4 shows that *outdoor* environmental levels of BaP are 10 times higher than *indoor* (21.42 ng/day vs. 1.98 ng/day).

In order to evaluate the representativeness of 24 h samplings compared to themean value reported in 7 days, a further survey was carried out on eight subjects living in four areas at different

Table 2
Environmental reference concentrations for six 'possible' carcinogenic PAHs reported in winter (Pavia, February 1996)

Substance	Environmental concentration (ng m^{-3})					
	Mean ± S.D.	Interval	Mediane	5° Perc.	95° Perc.	Inhaled quantity (ng/day)[a]
Benzo[*a*]anthracene	0.19 ± 0.11	0.05–0.76	0.16	0.11	0.58	3.42
Benzo[*b*]fluoranthene	0.38 ± 0.14	0.15–1.75	0.41	0.13	0.90	6.84
Benzo[*k*]fluoranthene	0.18 ± 0.12	0.10–0.60	0.19	0.08	0.42	3.24
Benzo[*a*]pyrene	0.37 ± 0.15	0.05–1.11	0.40	0.11	0.88	6.66
Dibenzo[*a,h*]anthracene	0.09 ± 0.07	n.d.–0.41	0.09	0.06	0.31	1.62
Indeno[*1,2,3-cd*]pyrene	0.13 ± 0.07	n.d.–0.40	0.08	0.08	0.27	2.34
						Total 24.12

n.d., below the method detection limit.
[a] Referring to a daily inhaled volume of 18 m^3; four subgroups of 14 subjects living in four areas at different traffic density were monitored.

Table 3
Environmental reference concentrations for six 'possible' carcinogenic PAHs reported during summer (Pavia, June 1996)

Substance	Environmental concentration (ng m^{-3})					
	Mean ± S.D.	Interval	Mediane	5° Perc.	95° Perc.	Inhaled quantity (ng/day)[a]
Benzo[*a*]anthracene	0.08 ± 0.07	n.d.–0.29	0.06	0.02	0.24	1.44
Benzo[*b*]fluoranthene	0.25 ± 0.11	0.06–0.66	0.24	0.09	0.42	4.50
Benzo[*k*]fluoranthene	0.07 ± 0.04	0.02–0.19	0.07	0.03	0.16	1.26
Benzo[*a*]pyrene	0.12 ± 0.07	0.03–0.33	0.11	0.04	0.27	2.16
Dibenzo[*a,h*]anthracene	—	n.d.–0.17[b]	—	—	—	—
Indeno[*1,2,3-cd*]pyrene	—	n.d.–0.54[c]	—	—	—	—
						Total 9.36

n.d., below the method detection limit.
[a] Referring to a daily inhaled volume of 18 m^3; four subgroups of 14 subjects living in four areas at different traffic density were monitored.
[b] The substance was detected in two samples.
[c] The substance was detected in 18 samples.

Table 4
Comparison between the indoor and outdoor levels of six carcinogenic PAHs (individual dosimetry; $N = 8$ subjects; two in each of the four residential areas; sampling time 7 days; February 1996)

Substance	Environmental concentration (ng m^{-3})			
	Indoor		Outdoor	
	Mean	Interval	Mean	Interval
Benzo[*a*]anthracene	0.10	0.06–0.21	0.72	0.37–2.11
Benzo[*b*]fluoranthene	0.20	0.11–0.37	1.46	0.80–3.51
Benzo[*k*]fluoranthene	0.07	0.05–0.20	0.56	0.30–1.28
Benzo[*a*]pyrene	0.11	n.d.–0.21	1.19	0.68–2.85
Dibenzo[*a,h*]anthracene	0.07	n.d.–0.10	0.37	0.37–1.15
Indeno[*1,2,3-cd*]pyrene	0.08	n.d.–0.12	0.41	0.21–0.78
	Total ERC 11.34 (ng/day)		Total ERC 82.26 (ng/day)	

n.d., below the method detection limit.

Table 5
Twenty-four hour sampling vs. 7 days sampling: a comparison between the environmental levels of six PAHs ($N = 8$ subjects; two in each of the four residential areas; February 1996)

Substance	Indoor + outdoor environmental concentration (ng m^{-3})			
	24 h		7 days	
	Mean ± S.D.	Interval	Mean ± S.D.	Interval
Benzo[*a*]anthracene	0.20 ± 0.10	0.05–0.84	0.23 ± 0.14	0.07–0.90
Benzo[*b*]fluoranthene	0.40 ± 0.32	0.14–1.78	0.42 ± 0.28	0.15–1.86
Benzo[*k*]fluoranthene	0.18 ± 0.10	0.07–0.64	0.20 ± 0.14	0.07–0.66
Benzo[*a*]pyrene	0.35 ± 0.17	0.07–1.20	0.41 ± 0.21	0.08–1.36
Dibenzo[*a,h*]anthracene	0.09 ± 0.06	n.d.–0.45	0.09 ± 0.08	n.d.–0.47
Indeno[*1,2,3-cd*]pyrene	0.15 ± 0.17	n.d.–0.40	0.18 ± 0.11	0.06–0.51

n.d., below the methoddetection limit.

traffic densities. The reported values are summarized in Table 5. An insignificant difference was noticed between the two different samplings, thus confirming the reliability of individual dosimentry and of the proposed PAH monitoring scheme to evaluate the actual exposure of the general population.

4. Conclusions

The data presented here confirm that individual dosimetry can be used as an environmental monitoring strategy together with the other routine techniques. It can determine the inhaled quantity of six 'possible' carcinogenic PAHs and differentiates between the *indoor* and *outdoor* levels of these substances (the *indoor* exposure times are much longer than the *outdoor* ones for not occupationally exposed subjects).

Higher PAH levels are found in winter since photochemical degradation due to sun irradiation occurs in summer, thus lowering the PAH concentration [14,15].

A good sampling representitiveness for a urban area can be obtained when a 'general population group' of 56 subjects is monitored, scheduling environmental samplings on alternate days (eight subjects a day for 2 weeks). Significance can be increased carrying out at least two samplings in each season; the difference between winter and summer levels of BaP must be taken into account, having a higher concentration in November–February.

The BaP concentrations reported in Pavia in February 1996 show very low levels of *indoor* pollution, ten times lower than *outdoor* levels. The course of *indoor* and *outdoor* BaP concentration in other seasons is still to be verified, nevertheless the data collected with individual dosimetry demonstrates that the actual exposure of the general population is lower than reported in studies using area samplers.

The monitoring scheme presented here can determine the E.R.C. of BaP and other PAHs in urban areas. A further application can be found in the monitoring of workers highly exposed to vehicular emissions, such as policemen. More general applications can be found whenever a non-occupational risk factor is present (i.e. a general population group living nearby a factory plant and therefore exposed to PAHs from industrial emissions).

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APPENDIX

INFORMATIVE QUESTIONNAIRE FOR A STUDY ON ENVIRONMENTAL REFERENCE VALUES OF PAH IN URBAN AREAS

(all information is confidential)

GENERAL INFORMATION

NAME	LAST NAME	AGE

SEX	M		F		Date of birth

Address	telephone

SCHOOL	CLASS

OCCUPATION:

Full time occupation		Part time occupation	

DESCRIPTION OF HOME

HOME	Urban		Suburban	

Downtown limited traffic		Downtown unlimited traffic	

N° of rooms		Floor		N° of windows	

N° of French windows		area	m^2

Garage attached to house	Y		N	

Type of heating	Methane		Fuel oil	

Air conditioning in use	Y		N	

Fireplace in the house	Y		N	

Intensity of automobile traffic near the house	High		Average		Low	

TRANSPORTATION HOME-WORKPLACE-HOME

Means of transportation used to go to work	Car		Bus		Other	

Time necessary to go to work	minutes

Returns home with the same means ?	Y		N	

Time necessary to get back from work	minutes

IMMEDIATE FAMILY

N° of Subjects	

Specify (Father, Mother, others)	

Smokers in family	Y		How many	

Cigarettes smoked/day								
	1° Subject	< 5		5-10		11-20		> 20	
	2° Subject	< 5		5-10		11-20		> 20	
	3° Subject	< 5		5-10		11-20		> 20	
	4° Subject	< 5		5-10		11-20		> 20	

Eventual NOTES, OBSERVATIONS or PROBLEMS occurring during sampling:

_____

_____

_____

_____

_____

_____

_____

Date of questionnaire completion: _____