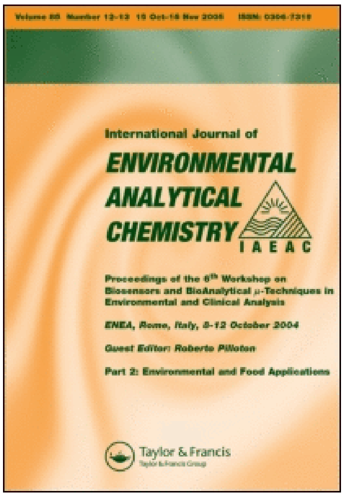

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Atmospheric levels of polycyclic aromatic hydrocarbons in gas and particulate phases from Tarragona Region (NE Spain)

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The atmospheric levels of polycyclic aromatic hydrocarbons (PAHs) in atmospheric samples taken at two urban sites and two sites near industrial areas of the Tarragona region (Catalonia, Spain), where one of the most important petrochemical complexes in the south of Europe is located, were determined. Gas and particulate phase of air were separately sampled and analysed. Concentrations of 16 PAHs studied ranged from 4.2 to 22.5 ng m^{-3}, with predominant levels of PAHs appearing in gas phase ($\sim$90% of total PAHs). In all samples, the most abundant compounds were phenanthrene, with a contribution to total PAHs between 32 and 44%, followed by naphthalene, fluorene and fluoranthene (contribution range: 10–22%). The levels of total PAHs, expressed as benzo[*a*]pyrene toxic equivalent factors (BaP$_{\mathrm{TEF}}$), were lower than 0.06 ng m^{-3}.

Keywords: gas/particle partitioning; industrial air; polycyclic aromatic hydrocarbons; Tarragona region; urban air

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of semi-volatile organic compounds composed of two or more fused aromatic rings. They are widely present in environmental media, including air, water and aquatic systems, soils and sediments, and biological samples [1–3]. Because of their physico-chemical properties, especially non-polarity and hydrophobicity, they are highly persistent in the environment [4]. Although different sources of PAHs has been described, around 90% of their emissions have been estimated to be anthropogenic [5]. These mainly include pyrolitic processes, such as the incomplete combustion of organic materials during the industrial activities, residential heating, power generation, incineration and vehicle emissions. PAHs are also emitted by petrochemical industries, during petroleum cracking and refining, as well as during chemical manufacturing [4,6]. Moreover, they can be transformed to more toxic compounds by chemical reactions such as sulfonation, nitration, photo-oxidation [7], or even photodegradation [8].

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Studies on animals have shown that PAHs can cause harmful effects on the skin, body fluids, and they can even lead to death after prolonged exposure, according to the Agency for Toxic Substances and Disease Registry [9]. Moreover, a strong historical reason to study PAHs is the evidence that some of these hydrocarbons have carcinogenic and mutagenic activity. The International Agency for Research on Cancer classified benzo[*a*]anthracene and benzo[*a*]pyrene as probable human carcinogens, and benzo[*b*]-fluoranthene, benzo[*k*]fluoranthene and indeno[1,2,3-*cd*]pyrene as possible human carcinogens [10]. Meanwhile, the United States Environment Protection Agency classified benzo[*a*]pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenzo[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene, as well as naphthalene, as possible human carcinogens, establishing a list of 16 unsubstituted PAHs as priority pollutants [11]. European Community has established the objective value in ambient air for benzo[*a*]pyrene of $1\,\mathrm{ng\,m^{-3}}$, since 31 December 2012 [12].

To date, many authors have reported PAH concentrations from urban air from various parts of the world. The results of some recent studies are summarised (Table 1). As can be seen, several studies reported PAHs on both gas and particulate phase, but others only in filters. PAH levels at highly traffic-affected urban areas [5,13–18] and industrial areas [18–21] have been reported.

The physico-chemical and toxicity properties of PAHs can vary according to their chemical structure and molecular weight. Most of the PAHs present in air which have low vapour pressure are adsorbed on particles [4]. Many studies only collected the particulate phase through an easier sampling method using filters, providing wide information about the multi-ringed heavier PAHs, which have the highest carcinogenic potential. Although the lightest PAHs, predominantly present in the vapour phase, have weaker carcinogenic and mutagenic properties, they are the most abundant in the urban atmospheres, contributing to their toxicity. Moreover, they react with other pollutants to form more toxic derivatives. In order to estimate the total PAH levels both the vapour and the particulate phases must be collected and analysed [13,22].

In Tarragona, a region in the south of Catalonia (NE Spain), one of the most important petrochemical centres in the south of Europe is located, which includes a chemical industry, an oil refinery and a large industrial port. In recent years, public concern over possible adverse health effects for the population living near this industrial complex has increased [6,23]. As a response to this concern, studies of PAHs in soil and vegetation samples has been carried out in this area [1,24]. However, to the best of our knowledge, investigations concerning the levels of atmospheric PAHs in this region have not been conducted till date. Since inhalation is a major pathway of exposure to airborne chemical substances, information obtained on the chemical composition of the urban air samples may assist the assessment of potential human health risks [25]. In this article, the results of a monitoring campaign to determine 16 PAHs in airborne samples, taken at different urban and industrial sectors in the Tarragona region, are presented.

2. Experimental

2.1 *Sampled sites*

A sampling campaign was carried out at two urban sites, and at two sites near industrial areas in the Tarragona region, which are influenced by urban traffic and petrochemical industry emissions, respectively. Figure 1 shows the location of the sampled towns and

Table 1. Summary of several studies of PAHs in various cities around the world.

			Concentration (ng m^{-3})						
City	PAHs	Studied area	Particulate	Gas	Sampling	Extraction	Solvent	Analysis	Ref.
Guangzhou, China	13	Urban 1	70.84–93.60	–	24, 48 h	Sonication (F)	DCM (P, F)	GC-MS	[5]
		Urban 2	32.47–153.74	–					
		Suburban	39.21	–					
Seoul, Korea	16	Urban	26.25 ± 29.40	63.03 ± 47.48	24 h	SFE (P^{a}) Sonication (F^{a})	DCM (P, F)	GC-MS	[13]
Athens, Greece	20	Urban	4.94 ± 1.70	25.96 ± 4.53	12, 24 h	Soxhlet (P, F)	MeOH/DCM (P, F)	GC-MS	[14]
		Coastal	1.33	22.23					
Guangzhou, China	37	Urban	298.5 at 0 metres 134.4 at 25 metres		24 h	Soxhlet (P) Sonication (F)	DCM (P, F)	GC-MS	[15]
Athens, Greece	7	Urban	33.4 ± 69.3 Flu^{b} 1.9 ± 2.1 Phen^{b}	112 ± 94.1 Flu 37.4 ± 2.07 Phen^{b}	4, 24 h	Sonication (P, F)	Acetone/cyclohexane (P), DCM (F)	GC-FID	[16]
Nova Delhi, India	16	Urban	668 ± 399 (2002) 672 ± 388 (2003)	– –	24 h	Sonication (F)	Toluene (F)	GC-FID	[17]
Bursa, Turkey	16	Urban-industrial	44 ± 39	412 ± 537	24 h	Soxhlet (P, F)	DCM/petroleum ether(P, F)	GC-MS	[18]
Prato, Italia	15	Industrial	14.0 ± 5.58	45.5 ± 23.9	12 h	Sonication (F) Soxhlet (P)	Acetone/petroleum ether (P), DCM (F)	HPLC-UVD, FD	[19]
Brisbane, Australia	16	Urban	0.458 ± 0.346	1.596 ± 0.659	2, 24 h	Sonication (X^{a}, F)	DCM/hexane DCM/acetone (X, F)	GC-MS	[20]
		Bus st.	5.955 ± 1.526	13.285 ± 9.464					
		Industrial	0.020 ± 0.001	0.421 ± 0.377					
		Suburban	1.163 ± 1.042	1.011 ± 0.278					
Flanders, Belgium	16	Rural	0.9	15.6	24 h	PLE (P, F)	DCM/acetone (P, F)	HPLC- UVD, FD	[21]
		Urban	8.7	45.7					
		Refinery	3.9	110					

Notes: ^{a}P = PUF, F = filters, X = XAD-2.
^{b}Flu = fluorene, Phen = phenanthrene.

Figure 1. Map of Tarragona region.

industrial areas in the Tarragona region. Due to the high toxicity of compounds studied, the sampling points were located at different schools in these sites. Schools from urban sampling points were located in the urban area of Tarragona city: Vidal i Barraquer (U1) and l'Estonnac – L'Ensenyança (U2). U1 is a school located in the centre of the city with high traffic intensity, in an area where the main access roads to the city meet, whereas U2 is located in the historical centre of the city, with narrow streets and low traffic intensity. On the other hand, schools near industrial points were situated in two villages of Tarragona region: High School Coll Blanc (I1), from La Canonja, and High School El Morell (I2), from El Morell. Due to their location, La Canonja and El Morell are highly influenced by industrial emissions from South and North complexes, respectively, which are the main and most extensive industrial areas of the region. The South complex groups a great variety of chemical factories, while an oil refinery and other petrochemical industry are situated in the North complex. Four samples were consecutively taken for 4 days at each sampling point, to collect a total of 16 daily samples, and all samples were taken in April and May 2007.

2.2 *Sampling procedure*

The sampling was performed by using a TE-1000 Poly-Urethane Foam (PUF) High Volume Air Sampler (Tisch Environmental, Inc., Village of Cleves, Ohio, USA), working at a flow of $\sim 0.2\,\mathrm{m^3\,min^{-1}}$, for 24 h, meeting the specifications of TO-13 Method [26]. Around $288\,\mathrm{m^3}$ of air was collected in each sample. PAHs present in the particulate phase were trapped on quartz fiber filters (QFFs) of 102 mm diameter, while PAHs present in the gas phase were collected on PUFs of 76 mm length (Long Polyurethane Vapour Collection Substrate) (Pacwill Environmental, Ontario, Canada), precleaned by Soxhlet extraction with dichloromethane for 24 h, and subsequently dried in a vacuum desiccator. Atmospheric conditions of temperature and pressure, as well as sampling flow rate and time, were taken for each sample. The sampled QFFs and PUFs were introduced in a glass amber jar with screwed top and kept at −24°C until the moment of their analysis.

2.3 *Sample treatment*

Polycyclic aromatic hydrocarbons were extracted from QFFs and PUFs by a sonication bath (J.P. Selecta, S.A., Barcelona, Spain). The PAHs contained in each PUF and QFF were initially extracted with 150 and 50 mL, respectively, of dichloromethane : hexane (3 : 1, v/v). Subsequently, a further extraction was done with the same volumes of dichloromethane : acetone (7 : 3, v/v). Each extraction lasted for 30 min. Solvents used were 99.9% pure dichloromethane pestipur, 99% pure *n*-hexane for analysis (SDS, Toulouse, France) and 99.8% pure acetone Chromasolv (Riedel de-Haën, Seelze, Germany). Both extracts were mixed, thermalised at 50°C in a water bath and their volume was reduced to about 2 mL using a R-114 rotary evaporator (Büchi, Flawil, Swiss). Preconcentrated extracts were passed through 0.45 µm porous syringe filters, and, finally, they were reduced to dryness by a gentle flow of 99.999% pure nitrogen gas. Prior to the chromatographic analysis, analytes were redissolved in 1 mL of 9 : 1 *n*-hexane to dichloromethane, with previous addition of 20 µL of internal standard solution of $50\,\mathrm{mg\,L^{-1}}$, to obtain a concentration of $1\,\mathrm{mg\,L^{-1}}$.

2.4 *Chromatographic analysis*

Compounds were chromatographically separated by injection of 1 µL of sample extracts in a gas chromatograph 6890N, and detected by a mass spectrometer 5973 inert (Agilent Technologies, Palo Alto, USA) in splitless mode, using 99.999% pure helium as carrier gas, at a flow rate of $1\,\mathrm{mL\,min^{-1}}$, in constant flow mode. The chromatographic column was a capillary column FactorFour VF-5 ms, 5% methyl-phenyl 95% dimethylpolysiloxane ($30\,\mathrm{m} \times 0.25\,\mathrm{mm} \times 0.25\,\mu\mathrm{m}$) (Varian, Palo Alto, USA). The injector was set at a temperature of 270°C, and the oven temperature of GC was initially held at 100°C for 4 min, raised to 290°C at a rate of $6^{\circ}\mathrm{C\,min^{-1}}$, and finally held for 10 min. The total chromatographic analysis time was <46 min. The mass spectrometer acquired data in scan mode with an *m*/*z* interval from 35 to 280. The compounds were quantified by a target ion and identified by retention time and two qualifier ions (Table 2).

Internal standard calibration was done by using deuterated PAHs with a similar analytical behaviour to target compounds. They were d_8-naphtalene for naphthalene, d_{10}-acenaphthene for acenaphthylene, acenaphthene, fluorene, indeno[1,2,3-*cd*]pyrene,

Table 2. Target compounds in chromatographic elution order, and their characteristics, retention times (t_R), and quantifier and qualifier ions. Recoveries and repeatability for both PUF and filter analysis.

Compound		t_R (min)	Target ion	Qualifier ions[a]		Recovery (%)		Repeat. (%)[b]	
						PUF	Filter	PUF	Filter
1	Naphthalene (Nap)	7.3	128	102 *(6)*	64 *(7)*	55	55	10	10
2	Acenaphthylene (AcPy)	13.4	152	126 *(3)*	76 *(18)*	54	72	12	12
3	Acenaphthene (AcP)	14.1	154	126 *(5)*	76 *(28)*	63	80	14	13
4	Fluorene (Flu)	16.1	166	139 *(8)*	83 *(11)*	68	84	11	18
5	Phenanthrene (PA)	19.9	178	152 *(5)*	89 *(18)*	75	92	10	13
6	Anthracene (Ant)	20.1	178	152 *(6)*	89 *(13)*	65	92	12	13
7	Fluoranthene (FluT)	24.6	202	101 *(13)*	87 *(6)*	83	93	15	13
8	Pyrene (Pyr)	25.5	202	101 *(21)*	88 *(9)*	81	100	17	13
9	Benzo[*a*]anthracene (B*a*A)	30.2	228	164 *(7)*	114 *(15)*	78	88	15	12
10	Chrysene (Chr)	30.4	228	200 *(3)*	114 *(8)*	80	78	14	13
11	Benzo[*b*]fluoranthene (B*b*F)	34.2	252	126 *(23)*	113 *(8)*	103	83	13	11
12	Benzo[*k*]fluoranthene (B*k*F)	34.3	252	126 *(37)*	112 *(14)*	104	98	16	12
13	Benzo[*a*]pyrene (B*a*P)	35.2	252	126 *(36)*	113 *(17)*	67	97	16	11
14	Indeno[*1,2,3-cd*]pyrene (Ind)	39.4	276	138 *(28)*	126 *(6)*	109	72	18	9
15	Dibenzo[*a,h*]anthracene (D*ah*A)	39.6	278	139 *(24)*	125 *(7)*	103	64	18	13
16	Benzo[*g,h,i*]perylene (B*ghi*P)	40.6	276	138 *(38)*	124 *(6)*	109	60	18	8

Notes: [a] The value in italics next to qualifier ions are percent abundances of each ion respective the target ion (100% of abundance)
[b] Repeatability expressed as relative standard deviation (RSD%) on an analysis intraday for both PUFs and filters ($n=3$)

dibenzo[*a,h*]anthracene and dibenzo[*g,h,i*]perylene, d_{10}-phenanthrene for phenanthrene, anthracene and fluoranthene, d_{12}-chrysene for pyrene, benzo[*a*]anthracene and chrysene, and d_{12}-perylene for benzo[*k*]fluoranthene and benzo[*a*]pyrene [26]. Acenaphthylene, indeno[1,2,3-*cd*]pyrene, d_8-naphtalene, d_{12}-chrysene and d_{12}-perylene were acquired from Supelco (Bellefonte, USA), while the remaining standard compounds were purchased from Sigma Aldrich (Saint Louis, Missouri, USA).

Individual standard solutions of 2000 $\mathrm{mg\,L^{-1}}$ were separately prepared for each one of the 16 PAHs and 5 internal standards, in *n*-hexane: dichloromethane (9 : 1, v/v). These solutions were used to prepare a mixed standard solution of 100 $\mathrm{mg\,L^{-1}}$ of 16 PAHs, and a mixed standard solution of 5 internal standards, in the same solvent mixture. All these solutions were kept in glass amber vials with screwed tops with septum, and stored at about 4°C. Seven calibration levels were freshly prepared at the moment of calibration, also in *n*-hexane: dichloromethane (9 : 1, v/v), from the mixed solution of 100 $\mathrm{mg\,L^{-1}}$ of 16 PAHs, at 7 different concentrations between 0.01 and 50 $\mathrm{mg\,L^{-1}}$, adding the necessary volume of mixed internal standard solution of 50 $\mathrm{mg\,L^{-1}}$, to get a concentration of 1 $\mathrm{mg\,L^{-1}}$ of internal standard in every calibration level.

2.5 *Method validation*

Calibration curves showed good linearity between the range studied, and their determination coefficients (r^2) were higher than 0.994 for all compounds. Recoveries were determined by spiking 100 µL of a mixed solution of 100 $\mathrm{mg\,L^{-1}}$ of PAHs, introduced with a syringe in QFFs and PUFs, after extraction, evaporation and analysis, as described in Sections 2.3 and 2.4. Initial proofs showed the quantitative extraction of all compounds, with recoveries higher than 87%, by one extraction with dichloromethane : hexane (3: 1, v/v), followed by one extraction with dichloromethane : acetone (7 : 3, v/v). However, losses of the most volatile compounds were detected during the extraction evaporation process (Table 2). Recoveries for all the compounds in QFFs and PUFs treatment were taken into account in sample quantification.

Method detection and quantification limits (MDL and MQL) were determined for the sampling volume, taking into account recoveries observed for each compound. For a sample volume of 300 $\mathrm{m^3}$, MDL ranged between 0.01 and 0.02 $\mathrm{ng\,m^{-3}}$, and MQL ranged from 0.02 to 0.06 $\mathrm{ng\,m^{-3}}$, for all compounds excepting for Ind, D*ah*A and B*ghi*P, which showed MDL between 0.07 and 0.10 $\mathrm{ng\,m^{-3}}$ and MQL between 0.20 and 0.30 $\mathrm{ng\,m^{-3}}$. Finally, repeatability of analytical method was determined by a triplicate spiking, treatment and chromatographic analysis of 100 µL of a mixed solution of 100 $\mathrm{mg\,L^{-1}}$ of PAHs in QFFs and PUFs. Results expressed as percentage of relative standard deviation (%RSD) are shown in Table 2.

The solvent purity was checked by the analysis of an extract obtained by preconcentrating 300 mL of dichloromethane : hexane (3 : 1, v/v) and dichloromethane : acetone (7 : 3, v/v), following the steps described in Sections 2.3 and 2.4. The chromatogram obtained did not show peaks of any target compounds.

Blanks of QFFs and PUFs were also checked by extracting of new QFFs and previously conditioned PUFs, following the same procedure described in Sections 2.3 and 2.4. Fluorene, phenanthrene, anthracene, fluoranthene and pyrene were detected in the chromatograms obtained, at levels beneath their respective instrumental quantification limits.

3. Results and discussion

Thirteen of the 16 studied PAHs were detected and quantified, phenanthrene, naphthalene, pyrene and fluorene being the most predominant compounds. All samples showed a similar qualitative composition, with contributions at four sites between 32 and 44% of phenanthrene, 11 and 22% of naphthalene, 10 and 16% of pyrene and 10 and 15% of fluorene. Indeno[1,2,3-*cd*]pyrene, dibenzo[*a,h*]anthracene and benzo[*g,h,i*]perylene were not found over the MQL, and benzo[*a*]pyrene was only quantified in the sample mostly affected by traffic (I1). Park *et al.* [13] also found that phenanthrene, pyrene and naphthalene were the predominant compounds in urban air from Seoul, Korea, while Lim *et al.* [20] found naphthalene to be the most abundant PAH, with a contribution of 36% to total PAHs at the urban centre of Brisbane, Australia. Minimum and maximum concentrations for each compound found in each sampling site at both particulate and phase gas, as well as the total PAHs, are given in Table 3.

3.1 *Urban and industrial atmospheres*

Similar average concentrations of total PAHs were found in schools situated at four sampling points. PAH levels of 12.4, 12.9 and 10.9 $\mathrm{ng\,m^{-3}}$ were observed in U1, I1 and I2 respectively, while a slightly lower concentration of 6.7 $\mathrm{ng\,m^{-3}}$ was found in U2, the sampling site less affected by traffic. These values are in the order of the average concentrations reported by several authors (Table 1). For instance, a total PAH level of 7.1 $\mathrm{ng\,m^{-3}}$ was found by Lim *et al.* [20] at urban air from Brisbane, Australia. In turn, PAH concentrations of 26.0 and 45.7 $\mathrm{ng\,m^{-3}}$ were observed in urban air from Athens (Greece) and Flanders (Belgium) [14,21]. However, much higher values of total PAHs were found in Bursa (Turkey) [18], and in Asiatic cities such as Seoul (Korea), Guangzhou (China) or Nova Delhi (India) [13,15,17,27].

Significant differences between urban and industrial atmospheres have been reported by several authors, such as both Lim *et al.* [20] and Ravindra *et al.* [21], finding major averages of PAHs levels at urban areas than at industrial areas (Table 1). Although PAH concentration might be correlated with traffic intensity [20], in the present study, the similar averages found at U1, I1 and I2 do not evidence clearly the different traffic influence in each sampling point. Furthermore, the highest levels of total PAHs were detected at industrial sites, such as the measure of 22.5 $\mathrm{ng\,m^{-3}}$ found in a sample taken at site I1, which is also affected by higher maximum levels of the most volatile compounds (Table 3).

However, different RSD (%RSD, $n = 4$) among total PAHs were observed at urban and industrial sites, and the values found at industrial sites were higher (50.7% in I1 and 24.1% in I2) than in U1 (13.5%), the urban site directly affected by traffic. This can be due to the regularity characteristics of traffic emissions, which are the main source of PAHs in urban atmospheres, while industrial emissions are dependent on production processes, which could show more variability. It can be concluded that despite the relatively low number of samples taken in this sampling campaign, an influence of industrial emissions could be observed in I1 and I2, while the influence of traffic emissions could be observed in urban levels of PAHs.

The diversity in PAH sources could also be characterised from diagnostic ratios, and many studies have developed and used a specific value of PAH diagnostic ratio for a source category. For example, the ratio of fluoranthene/pyrene is assigned to be 0.6 for

Table 3. Concentration of individual PAHs compounds (ng m^{-3}) at the four sampling sites from the Tarragona region.

Location			Nap	AcPy	AcP	Flu	PA	Ant	FluT	Pyr	B*a*A	Chr	B*b*F	B*k*F	B*a*P	Ind	D*ah*A	B*ghi*P	Total
U1	G[a]	Min	1.50	0.44	n.d.[b]	0.76	4.20	0.21	0.38	0.90	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**8.84**
		Max	2.59	1.07	0.53	1.65	6.01	0.42	0.64	1.65	0.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**13.85**
	P[a]	Min	n.d.	n.d.	0.02	n.d.	0.04	n.q.[b]	0.04	0.18	0.04	0.08	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	**0.49**
		Max	n.d.	n.d.	0.04	n.d.	0.11	n.q.	0.11	0.43	0.09	0.22	0.07	0.05	0.04	n.d.	n.d.	n.q.	**1.07**
	∑[a]	Min	**1.50**	**0.44**	**0.02**	**0.76**	**4.29**	**0.21**	**0.50**	**1.20**	**0.08**	**0.08**	**0.03**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**9.71**
		Max	**2.59**	**1.07**	**0.57**	**1.65**	**6.05**	**0.42**	**0.68**	**1.83**	**0.21**	**0.22**	**0.07**	**0.05**	**0.04**	**n.d.**	**n.d.**	**n.q.**	**14.30**
U2	G	Min	0.51	n.d.	n.d.	0.41	1.96	n.d.	0.18	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**3.60**
		Max	1.36	0.37	0.44	0.97	4.13	0.17	0.51	1.69	n.d.	0.13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**8.88**
	P	Min	n.d.	n.d.	0.02	n.d.	0.03	n.d.	0.04	0.13	0.04	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.36**
		Max	n.d.	n.d.	0.04	0.02	0.07	n.q.	0.07	0.26	0.08	0.17	0.06	0.05	n.d.	n.d.	n.d.	n.d.	**0.82**
	∑	Min	**0.51**	**n.d.**	**0.04**	**0.41**	**2.00**	**n.q.**	**0.23**	**0.26**	**0.04**	**0.10**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**4.16**
		Max	**1.36**	**0.37**	**0.46**	**0.97**	**4.20**	**0.17**	**0.58**	**1.95**	**0.08**	**0.22**	**0.06**	**0.05**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**9.63**
I1	G	Min	0.16	0.19	0.16	0.45	1.66	0.12	0.39	0.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**3.77**
		Max	8.26	1.79	0.85	3.12	5.39	0.24	0.94	1.24	0.05	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**21.38**
	P	Min	n.d.	n.d.	n.d.	n.d.	0.04	n.q.	0.06	0.21	0.06	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.q.	**0.47**
		Max	n.d.	n.d.	0.02	n.d.	0.07	n.q.	0.08	0.39	0.13	0.28	0.06	0.11	n.q.	n.q.	n.d.	n.q.	**1.20**
	∑	Min	**0.16**	**0.19**	**0.16**	**0.45**	**1.70**	**0.12**	**0.46**	**0.81**	**0.06**	**0.10**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**4.24**
		Max	**8.26**	**1.79**	**0.85**	**3.12**	**5.46**	**0.24**	**1.00**	**1.58**	**0.13**	**0.28**	**0.06**	**0.11**	**n.q.**	**n.q.**	**n.d.**	**n.q.**	**22.50**
I2	G	Min	0.53	0.45	0.31	1.20	3.16	0.20	0.51	1.07	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**8.22**
		Max	2.59	0.73	0.58	1.63	6.36	0.44	1.29	2.64	n.q.	n.q.	n.q.	n.q.	n.d.	n.d.	n.d.	n.d.	**14.51**
	P	Min	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	0.04	0.11	0.04	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.45**
		Max	n.d.	n.d.	0.03	n.d.	0.04	n.q.	0.06	0.22	0.12	0.23	0.07	0.06	n.d.	n.q.	n.d.	n.d.	**0.82**
	∑	Min	**0.53**	**0.45**	**0.31**	**1.20**	**3.19**	**0.20**	**0.55**	**1.24**	**0.04**	**0.09**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**8.90**
		Max	**2.59**	**0.73**	**0.61**	**1.63**	**6.40**	**0.44**	**1.35**	**2.85**	**0.12**	**0.23**	**0.07**	**0.06**	**n.q.**	**n.q.**	**n.d.**	**n.d.**	**15.33**

Notes: [a]G: compounds appearing at gas phase, P: compounds appearing at particle phase, and ∑ and in bold: total PAHs appearing on both, gas an particle phase.

[b]n.d.: compound not detected (value < MDL); n.q.: compound not quantified (value < MQL).

vehicular emissions, and the ratio of fluorene/fluorene + pyrene is reported to be >0.5 for diesel emissions and <0.5 for gasoline emissions [28]. In the present study, the ratios fluoranthene/pyrene were between 0.4 and 0.5, which can indicate a predominance of vehicular sources, and ratios fluorene/fluorene + pyrene were about 0.3, showing a higher influence of gasoline emissions.

3.2 *Gas/particle partitioning*

The reported average levels of total PAHs in urban and industrial areas in literature are in a wide range of concentrations. However, PAH levels found in the gas phase are higher than in the particulate phase, with averages of concentrations between 0.4 and 412 ng m^{-3} in the gas phase, and between 0.02 and 44 ng m^{-3} in the particulate phase (Table 1). In fact, gas phase concentrations have been reported to be between 55 and 91% [15], and other authors have reported that more than 80% of PAHs can be present in gas phase [21]. In the present study, the main concentrations of PAHs were also found at gas phase, and were between 91 and 94% of the total PAHs. The gas/particle partitioning and the total concentration of PAHs in each sampling point are summarised in Table 3, and the average of concentrations of each compound found in both phases, for each sampling site, are presented (Figure 2).

Depending on their distribution gas-particle, which depends on the molecular weight of compound, three groups of compounds can be distinguished. Naphthalene, acenaphthylene, acenaphthene, fluorene and anthracene appear only at the gas phase. Excepting naphthalene, all the compounds are three-ringed compounds. Phenanthrene, fluoranthene and pyrene appear distributed in both phases – gas and particle. While phenanthrene is a three-ringed compound, fluoranthene and pyrene are four-ringed compounds. The remaining quantified compounds, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]pyrene appeared only at the particulate phase. This is in accordance with the known fact that low-molecular-weight PAHs (two and three rings) occur in the atmosphere in the vapour phase, intermediate molecular weight PAHs (four rings) are partitioned between the vapour and particulate phases, depending on the atmospheric temperature, whereas multi-ringed PAHs (five rings) are bound to particles [4].

As an example, the total ion chromatograms of a sample from I1 at both gas (Figure 3a) and particle phases (Figure 3b) are shown. The differences between gas and particle phases mentioned before are clearly appreciated, with the most volatile compounds appearing in the gas phase, and the less volatile compounds appearing in the particulate phase. A higher number of peaks can also be observed in the total ion chromatogram of particulate phase. The correlation of PAHs concentration with air temperature, positive in the case of low-molecular-weight PAHs and negative in the case of higher molecular weight compounds, has been reported [15]. However, in this study, due to the similar ambient temperatures measured on almost all sampling days, ranging between 17°C and 18°C, the dependence of gas/phase partitioning with temperature could not be evaluated.

3.3 *Potential toxicity of ambient air from the Tarragona region*

The low measured levels of benzo[*a*]pyrene, which was only detected in one of the samples at 0.04 ng m^{-3}, show a low carcinogenic potential for PAHs of sampled air, if this measure

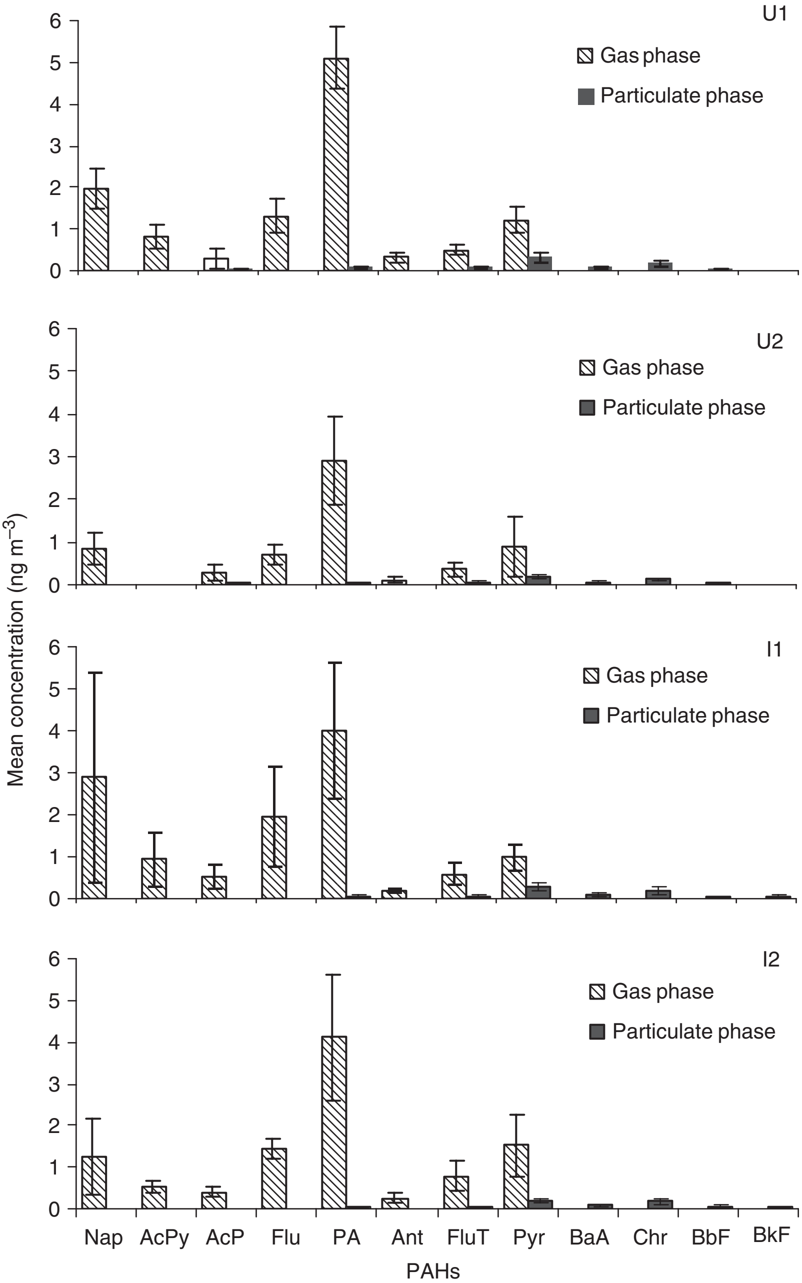

Figure 2. Mean PAH concentrations found at gas and particle phases at four sampling sites.

is compared with the objective value of 1 ng m^{-3} in PM_{10} in ambient air for benzo[*a*]pyrene for the European Union, as from 31 December 2012 [12].

Taking into account that benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene, chrysene and dibenzo[*a,h*]anthracene are verified as probable human carcinogens, the average fraction of carcinogenic PAHs found

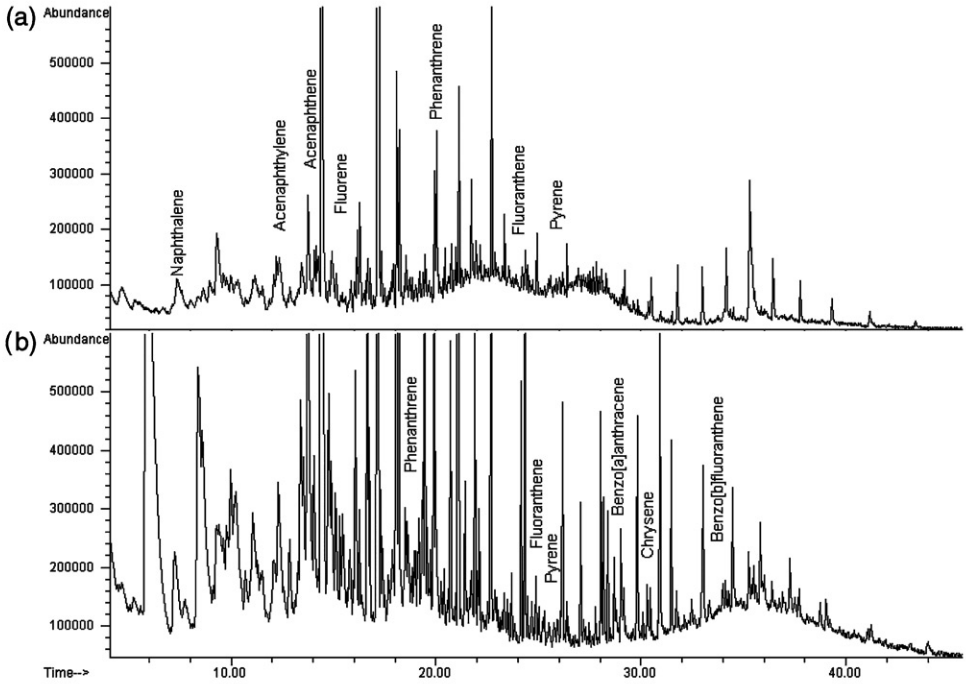

Figure 3. Example of a (a) gas phase and (b) particulate phase sample total ion chromatograms in a school sited at industrial site (I1).

in particles corresponded to the 45%, while only 2% of PAHs present in gas phase have carcinogenic effects, concluding that most of the carcinogenic potential of PAHs are associated with particulate matter in Tarragona region. However, the health risk associated with the vapour phase cannot be ignored, as the vapour phase has around 10 times higher PAHs concentration than the particulate phase. Similar results were observed by Ravindra *et al.* [21], who also found 2% of total PAHs in vapour phase and 55% in aerosols to be carcinogenic in Flanders.

Carcinogenic risks of a PAHs mixture can be estimated by multiplying individual concentrations of each PAH with the corresponding toxic equivalence factor (TEFs), and determining the concentration of total PAHs expressed as benzo[*a*]pyrene equivalents ($\mathrm{BaP_{TEF}}$) [1]. $\mathrm{BaP_{TEF}}$ were determined in the present study for each sample and, despite the industrial and highly traffic-affected monitored areas, the values were lower than $0.06\,\mathrm{ng\,m^{-3}}$ in all cases. This shows a very low value of $\mathrm{BaP_{TEF}}$, if it is compared with the values of $\mathrm{BaP_{TEF}}$ between 0.1 and $2.63\,\mathrm{ng\,m^{-3}}$ found by Lodovici *et al.* [29] in urban air of Florence (Italy).

4. Conclusions

The mean of total PAHs obtained in samples collected at schools situated at urban and industrial sites of Tarragona were similar, ranging from 6 to $13\,\mathrm{ng\,m^{-3}}$. Moreover, a similar qualitative composition in all sampling sites was observed, with phenanthrene, naphthalene and fluoranthene as predominant compounds, and a similar percentage to the total PAHs. However, a certain influence of industrial emissions was observed, with some higher levels of total PAHs, and more deviation among samples taken in the schools situated near industrial areas.

As expected, the gas phase presented higher concentrations of PAHs, while the particulate phase contained the most weighted and carcinogenic PAHs. Moreover, notably higher concentrations of PAHs were found in the gas phase (around 90% of total PAHs), suggesting that, in the PAHs atmospheric monitoring, the analysis of both gas and particulate phases, are important. Despite the high presence of industry and traffic in the monitored areas, benzo[*a*]pyrene was found to be under the European limit value for this compound, showing a poor carcinogenic potential for PAHs of sampled air.

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