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4 Long-Range Atmospheric Transport and Local Pollution 5 Sources on PAH Concentrations in a South European 6 Urban Area. Fulfilling of the European Directive

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13 **Abstract** A 12 months study on urban atmospheric
14 concentrations of polycyclic aromatic hydrocarbons
15 (PAH) contained in the particulate matter with an
16 aerodynamic diameter less than or equal to 10 microns
17 (PM10) was carried out in Zaragoza (Spain) from July
18 12th, 2001 to July 26th, 2002 by using a high-volume
19 air sampler able to collect the PAH supported on a
20 Teflon-coated fibre glass filter. Samples were analysed
21 by using Gas Chromatography Mass Spectrometry
22 (GC-MS/MS). PAH of high molecular weight, indeno
23 [1,2,3-cd]pyrene (IcdP), benzo[g,h,i]perylene (BghiP)
24 and coronene (Co) were the most abundant com-
25 pounds. The concentrations of benz[a]pyrene equiva-
26 lent carcinogenic power (BaP-eq) showed a mean
27 value of 0.7 ng/m³ with 22.5% of the samples
28 exceeding the 1.0 ng/m³ guide value established by
29 the European Directive. These episodes were mainly
30 produced during cold season. Regarding meteorolog-
31 ical variables, a positive effect of the prevalent wind
32 “cierzo” (NW direction) over the Zaragoza city was
33 confirmed from the environmental point of view. The
34 NE, E and S directions, corresponding to highway
35 and industrial areas were the directions showing the
36 high PAH atmospheric concentrations. Despite the

proximity of a high-level traffic highway, stationary 37
sources related to industry were the dominant source 38
of PAH in the sampled area. Vehicular emissions and 39
natural gas home heating also contributed to PAH 40
concentrations. The predominance of local pollution 41
sources versus long-range transport on PAH concen- 42
trations was shown. However, the contribution of 43
long-range transport of anthropogenic origin from 44
other European areas was reflected for specific dates 45
on PAH concentrations and PM10 levels. 46

Keywords Air pollution · 47
Long-range atmospheric transport · PAH · PM10 · 48
Pollution sources 49

1 Introduction 50

The presence of atmospheric Polycyclic Aromatic 51
Hydrocarbons (PAH) are mainly due to human activities 52
(Mastral and Callén 2000). However, in South Euro- 53
pean countries due to their dry and hot climatology, the 54
natural sources, e.g. higher forest fires incidence, can 55
increase the atmospheric PAH levels. 56

The vapour pressure of some PAH makes them 57
highly mobile throughout the environment. Further- 58
more, deposition and re-volatilisation allow distribu- 59
tion between air, soil and water bodies. In this way, a 60
proportion of PAH is subject to long-range atmo- 61
spheric transport making them a transboundary envi- 62
ronmental problem (Halsall et al. 2001; Prevedouros 63

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et al. 2004). In particular, the South European countries, mainly affected by the transport of mineral dust from the African continent, could be also affected by the long-range transport of PAH. In order to distinguish local emission sources from long-range aerosol transport, several methods have been used. Among other methods, calculated backward air trajectories as well as aerosol index maps provided information of the transport paths (Borbély-Kiss et al. 2004). Naturally, the history of the transported air masses along the selected trajectory will be fundamentally affected by transport time, meteorological conditions and by the nature of emission sources touched along the transport path.

PAH compounds include some of the best studied substances known to produce cancer in experimental animals and many authors have reviewed the links between exposure to chemicals and the development of cancer (Pott 1962; Schulte et al. 1994; Constantino et al. 1995). The International Agency for Research in Cancer (IARC) has classified a number of individual PAH compounds as probable human carcinogens and a number of “common mixtures of substances” that include PAH compounds as carcinogenic to humans (Ambient air pollution by PAH. Position Paper 2001). Despite this possible carcinogenic character of PAH, only recently it was established a Directive relative PAH in air. The target value for PAH in air shall be assessed for the level of BaP: 1 ng/m³, for the total content in the PM10 fraction averaged over a calendar year (Directive 2004/107/EC). With this Directive, it is expected that each Member State shall take all necessary measures to ensure that, as from 31 December 2012, the concentration BaP do not exceed this target value. In addition, each Member State shall monitor other relevant PAH at a limited number of measurement sites to assess the contribution of BaP in ambient air. These compounds shall include at least: benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), IcdP and dibenzo[a,h]anthracene (DahA).

Nevertheless and in addition to the establishment of legislation regarding PAH, other important issue is to know the sources producing these pollutants and how these PAH behave in the atmosphere once they are released, so that it is possible to act to control them when necessary.

In this paper, PAH concentrations in an urban atmosphere of Zaragoza city were determined paying

special attention to the most carcinogenic PAH, the fulfilling of the present Directive regarding PAH and the pollution sources producing these compounds.

2 Experimental

2.1 Sampling Program

The study was performed in the city of Zaragoza (650,592 habitants) located in the Northeast of Spain (41°39'49.38"N; 0°53'16.68"W) and previously described in another article (López et al. 2005). This city is also characterized by a special kind of wind called “cierzo” which comes from the Moncayo Mountain, North–West direction.

The sampling was performed in an urban area where sources of anthropogenic emissions surrounding the sampling site included a high level traffic highway (A-2; 38695 vehicles/day in 2006) and several industrial parks related to medium and small enterprises (Cogullada: 130 enterprises (28% metal sector; 30% distribution sector); Malpica: 300 enterprises (33% metal sector; chemical, plastic, commerce); Argualas: 34 enterprises (37% commerce and distribution); Miguel Servet: (varied industry; 36% commerce and distribution; footwear, wood, textil, metal); S. Valero: 80 enterprises (50% iron and steel industry; wood, distribution); El Pilar: 26 enterprises (35% commerce and distribution); Molino El Pilar: 117 enterprises (13% metal; 39% commerce and distribution); La Cartuja: 25 enterprises (45% metal sector; 25% electronic; chemistry, plastic, paper, etc); Mercazaragoza: 112 enterprises (agroalimentary industry, slaughterhouse)), two paper fabrics and two water-treatment systems (see Fig. 1).

Samples were collected every 2 weeks from July 12th, 2001 to July 26th, 2002 on weekdays. More intensive sampling dates: 11, 12, 13, 14 and 15th March 2002, 18, 19, 20 and 21st June 2002, 22, 23, 24 and 26th July 2002 corresponding to winter, spring and summer seasons were carried out collecting a total of 41 samples. A GUV-15H Graseby Andersen High-Volume sampler with volumetric flow controlled system provided with a PM10 cut off inlet at 10 µm and located 3.5 m from the ground was used to collect particulate phase in a PTFE-coated, glass-fibre filters (0.6 µm pore size; 20.5×25.5 cm, Pall GelmanSciences). Sampling time was 24 h, yielding

Fig. 1 Localization of the sampling place in Zaragoza city

158 sample volumes among 1,200 and 1,700 m³. Before
159 the sampling, filters were cleaned by Soxhlet extrac-
160 tion for 24 h with dichloromethane (DCM) and kept
161 in desiccators before and after sampling. Filters were
162 also weighted before and after the sampling using a
163 microbalance to obtain the particulate mass. After
164 sampling, filters were wrapped in aluminium foil
165 previously rinsed with hexane and stored in a freezer
166 at -20°C until analysis.

167 2.2 Extraction and Analyses

168 Particulate matter contained in the filters was
169 extracted by Soxhlet during 18 h with DCM after
170 the addition of deuterated-PAH surrogate standards
171 containing the following PAH: acenaphthene-d₁₀
172 (Ace-d₁₀), anthracene-d₁₀ (An-d₁₀), benzo[a]pyrene-
173 d₁₂ (BaP-d₁₂) and benzo[g,h,i]perylene-d₁₂ (BghiP-
174 d₁₂). Extracts were then concentrated in a rotary
175 evaporator followed by re-concentration under a
176 gentle stream of nitrogen, solvent exchanged into
177 hexane and cleaned using solid-liquid chromatogra-
178 phy on silica gel prior to PAH analysis. A known
179 amount of p-terphenyl was added to the sample
180 previous to the analysis by gas chromatography in
181 order to calculate the deuterated PAH's recovery.

PAH quantification was performed using the
internal standard method relative to the closest eluting
PAH surrogate.

All analyses were carried out on a Varian GC 3800
gas chromatograph coupled to a Saturn 2200 mass
spectrometer detector (electron ionization mode and
ion-trap analyser with mass/mass option) with GC
capillary column (60 m×0.25 mm×0.25 μm) working
in MS-MS mode. 1 microlitre of sample was injected
in splitless-mode.

The oven temperature was programmed as follows:
60°C isotherm for 1 min, 10°/min till 300°C and
isotherm for 20 min. The injector was kept at the
following conditions: 60°C for 0.5 min, 100°C/min till
300°C and isotherm for 15 min. Helium was used as
carrier gas at a constant flow of 1 ml/min and transfer
line was heated at 280°C. In all cases, 1 μl of sample
was injected in splitless mode (1/50, split valve closed
for 3.5 min). The ion trap mass spectrometer was
operated in electron ionization (EI) mode and the
filament emission current was 80–90 μA. The mass
conditions were as follows: electron impact ionization
voltage 70 eV; scan time 0.5 s/scan; scanned mass
range: 40–650 m/z. The MS-MS process was con-
ducted by collision induced dissociation (CID) with
resonant excitation.

The compounds quantified during sampling, according to their elution orders, were: naphthalene (Np, m/z 102), acenaphthylene (Acy, m/z 150), acenaphthene (Ace, m/z 151), fluorene (Fl, m/z 163), phenanthrene (Phe, m/z 152), anthracene (An, m/z 152), 2+2/4-methylphenanthrene (2+2/4MePhe, m/z 189), 9-methylphenanthrene (9MePhe, m/z 189), 1-methylphenanthrene (1MePhe, m/z 189), 2,5-/2,7-/4,5-dimethylphenanthrene (Dimephe, m/z 191), fluoranthene (Fth, m/z 200), pyrene (Py, m/z 200), benz[a]anthracene (BaA, m/z 226), chrysene (Chry, m/z 226), benzo[b]fluoranthene (BbF, m/z 250), benzo[k]fluoranthene (BkF, m/z 250), benzo[e]pyrene (BeP, m/z 250), benzo[a]pyrene (BaP, m/z 250), indeno[1,2,3-cd]pyrene (IcdP, m/z 274), dibenzo[a,h]anthracene (DahA, m/z 276), benzo[g,h,i]perylene (BghiP, m/z 274) and coronene (Co, m/z 298).

The meteorological parameters of the sampling place for each sampling date including temperature, relative humidity, rainfall, irradiation, wind direction and speed were provided by the Spanish National Institute of Meteorology.

2.3 Quality Control and Quality Assurance

Analyte losses during the analytical procedure were evaluated by adding a known amount of deuterated PAH surrogate standards, above mentioned, before the Soxhlet

extraction. According to the results obtained, the concentrations regarding the most volatile PAH, Np, Acy, Ace and Fl could not be accurately identified by this method due to the low recovery, poor reproducibility of their results and for staying below the quantification limit. In this way, these four PAH were not considered in the interpretation of results. IcdP and DahA were quantified together due to the problem of discerning both peaks in some samples with the majority contribution of IcdP. Regarding the rest of PAH, no corrections were applied.

Limits of detection for individual compounds were defined by multiplying by 3 and 10 the standard deviation of the blank filters, respectively, with the lowest detection limit for BkF: 0.001 ng/m³ and the highest for IcdP: 0.036 ng/m³ (Table 1).

In order to check the analytical accuracy and precision, analyses of an appropriate standard reference material (SRM 1944, Waterway sediment) of National Institute of Standards and Technology (NIST) were analysed. Measured values were comparable to certified values with a precision between 0.2% (for BkF) and 22% (for BaA) for all compounds.

2.4 Statistical Tools

All statistical analyses, including Pearson correlation coefficients and Principal Component Analysis (PCA), were conducted using SPSS for Windows

Table 1 Detection limit (ng/m³), minimum, maximum, mean concentration and standard deviation (ng/m³) of the different PAH sampled in Zaragoza during July 2001–July 2002

	Detection limit	Minimum concentration	Maximum concentration	Mean concentration	Standard deviation	
Phe	0.034	N.D	2.67	0.32	0.56	t1.1
An	0.021	N.D	0.68	0.09	0.17	t1.2
2+2/4MePhe	0.012	N.D	1.33	0.19	0.27	t1.3
9MePhe	0.003	N.D	0.45	0.06	0.10	t1.4
1MePhe	0.011	N.D	0.66	0.10	0.16	t1.5
Dimephe	0.009	N.D	2.25	0.21	0.39	t1.6
Fth	0.015	N.D	6.10	0.71	1.08	t1.7
Py	0.013	0.05	6.35	0.72	1.09	t1.8
BaA	0.002	0.02	4.33	0.59	0.79	t1.9
Chry	0.002	0.03	4.35	0.83	0.99	t1.10
BbF	0.004	0.06	4.51	0.68	0.89	t1.11
BkF	0.001	N.D	1.54	0.26	0.34	t1.12
BeP	0.002	0.05	2.71	0.50	0.58	t1.13
BaP	0.002	0.03	2.11	0.45	0.51	t1.14
IcdP+DahA	0.036	N.D	3.38	0.99	1.00	t1.15
BghiP	0.003	0.05	3.32	0.97	0.86	t1.16
Co	0.002	0.05	4.81	1.09	1.15	t1.17
Total PAH		0.40	30.22	8.77	7.90	t1.18
						t1.19

N.D Not detected

version 12.0. These statistical tools were applied to the PAH variables (Phe, An, 2+2/4MePhe, 9MePhe, 1MePhe, Dimephe, Fth, Py, BaA, Chry, BbF, BkF, BeP, BaP, IcdP + DahA, BghiP, Co), total PAH, PM10 and the meteorological data (average temperature, relative humidity, rainfall, irradiation, wind direction and wind speed) for all the air samples.

2.5 Long-Range Transport

The long-range atmospheric transport was deduced by determining isentropic backward air trajectories using the HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) model with FNL meteorological input (HYSPLIT 4, 1997). In addition, Earth Probe TOMS (Total Ozone Mapping Spectrometer) aerosol index maps from Earth Probe NASA (http://toms.gsfc.nasa.gov/eptoms/ep_v8.html), which measure the relative amount of aerosols, solid or liquid particles suspended in the atmosphere, SeaWiFS-NASA satellite images (<http://www.nrlmry.navy.mil/aerosol/>) to detect dust plumes and synoptic charts of pressure at sea level (<http://www.arl.noaa.gov/ready/amet.html>), which show the weather conditions of different areas at a particular time, were also useful to support the interpretations from the NOAA Air Data Resources Laboratory.

3 Results and Discussion

3.1 PAH Concentration Levels

Daily PM10 levels and total PAH concentrations for each sampling date are shown in Fig. 2. It is observed

that there are 34% of the samples in which the PM10 exceeded the daily air quality ($50 \mu\text{g}/\text{m}^3$). In addition, the average ($43.2 \mu\text{g}/\text{m}^3$) also exceeded the yearly average ($40 \mu\text{g}/\text{m}^3$) allowed by the European legislation (Directive 1999/30/EC).

Minimum, maximum and mean concentrations for each PAH identified in the PM10 are shown in Table 1 obtaining a mean total PAH concentration for the 18 PAH in Zaragoza of $8.77 \text{ ng}/\text{m}^3$. The concentrations of the studied PAH at this sampling site were compared with results obtained in studies conducted at various urban centres.

Similar mean total PAH values were found for sampling performed in Athens, in particular in an urban localization characterized by dense vehicular traffic and commercial activity ($8.54 \text{ ng}/\text{m}^3$) and in a mixed urban-industrial location in a highly industrialized area close to a highway ($7.93 \text{ ng}/\text{m}^3$) during May 2001–June 2002 (Mantis et al. 2005).

Slightly lower particulate phase PAH concentrations, with the exception of Co, were also obtained at an urban site in Birmingham, UK, during 1992–1993 (Smith et al. 1996). Also in Birmingham, similar mean values were found for Ph, Co and BaA during a campaign performed in 1997 at a heavily trafficked city centre (Lim et al. 1999).

Regarding sampling performed in this work, the highest contribution to the total of PAH corresponded to PAH with four or more aromatic rings, the most toxic and carcinogenic PAH. The total mass was dominated by PAH like BghiP, IcdP and Co (11.1, 11.3 and 12.4%) revealing the importance of traffic to PAH concentrations (Nielsen 1996).

Fig. 2 Levels of PM10 ($\mu\text{g}/\text{m}^3$) and PAH (ng/m^3) for the different sampling dates

One of the most interesting PAH to study due to its carcinogenic character and to the target value of 1.0 ng/m³ established by the Directive 2004/107/CE is the BaP. The BaP, showed variations between 0.03 ng/m³, the lowest value and 2.11 ng/m³, the highest value with 14.6% of the samples exceeding 1.0 ng/m³ and with a mean value of 0.45 ng/m³ (Table 1). Comparing with other studies performed in other European countries, this mean value was slightly lower than the one found in a urban location in Atenas, 0.56 ng/m³ (Mantis et al. 2005), and very similar to the one found in Birmingham, 0.48 ng/m³ (Smith et al. 1996) during 1992. Other samplings performed in Italy in previous years showed values of BaP of 1.56 and 1.72 ng/m³ respectively, in traffic areas of Rome and Naples in 1994 and 1996–1997 (Cecinato et al. 1999; Caricchia et al. 1999). Considering results obtained in no European countries, similar BaP values were found in another sampling station with heavy traffic in Porto Alegre, Brazil, 0.52 ng/m³ (Dallarosa et al. 2005a).

Comparing with other Spanish cities, mean BaP values of 0.547 ng/m³ were found in the PM₁₀ during 2000–2001 in Seville (Gutiérrez-Dabán et al. 2005). However, the comparisons should be done with caution due to the unique characteristics of each sampling site, the different time of the year to conduct the sampling and differing procedures for sample collection, clean-up and analysis.

Due to not only BaP is carcinogenic and because the Directive 2004/107/CE also considers other

relevant PAH (BaA, BfF, BjF, BkF, IcdP, DahA) in addition to BaP, it was also interesting to know the BaP equivalent (BaP-eq) (Fig. 3). BaPE is calculated according to the following formula:

$$\text{BaP} - \text{eq}(\text{ng}/\text{m}^3) = \sum \text{FTE}_i \text{PAH}_i \quad (1)$$

Where PAH_i is the concentration of each individual PAH (Phe, An, Fth, Chry, BaA, BbF, BkF, BeP, BaP, IcdP + DahA, BghiP) and FTE_i the toxic equivalent factor for each PAH. In this work, it has been used the FTE proposed by Larsen and Larsen (1998) as they are the last ones published and reviewed.

It is worth saying that as IcdP was quantified together with DahA it is possible that the BaP-eq values are underestimated. Nevertheless, in most of the samples the DahA was negligible.

In this way, a better carcinogenicity parameter related to the whole PAH fraction instead of the BaP was achieved, especially if it is taken into account that BaP can easily photodegrade with light or oxidants and considering that with the Directive 2004/107/EC, not only BaP will be submitted to legislation.

The mean value of BaP-eq was 0.7 ng/m³ with BaP-eq exceeding 1 ng/m³ in nine cases which represents the 22.5% of the samples. This mean value was lower than the ones found for downtown Athens in 1996 (1.6 ng/m³) (Marino et al. 2000) and downtown Algiers (3.4 ng/m³) (Yassaa et al. 2001).

Fig. 3 BaP-eq and average BaP concentrations (ng/m³) for the different sampling dates in Zaragoza (1 ng/m³ target value for BaP according to Directive 2004/107/EC)

394 3.2 Correlation of PAH with Meteorological Variables

395 In this section, the possible influence of the local
396 meteorological variables during the sampling dates on
397 the total and individual PAH concentration was carried
398 out by using statistical tools.

399 The Pearson correlation coefficients between the
400 total of PAH, the PM10, the individual PAH (Phe, An,
401 2+2/4MePhe, 9MePhe, 1MePhe, Dimephe, Fth, Py,
402 BaA, Chry, BbF, BkF, BeP, BaP, IcdP, BghiP and Co)
403 and the meteorological parameters including rainfall,
404 temperature, humidity, radiation, wind velocity and
405 wind direction (Table 2) were calculated.

406 It is observed that with regard to the temperature,
407 the most volatile PAH, Phe, An, 2+2/4MePhe,
408 9MePhe, 1MePhe, Dimephe, Fth and Py did not show
409 correlation with the temperature indicating that these
410 PAH did not show seasonal behaviour. This indicated
411 that the pollution sources producing these compounds
412 were mainly not seasonal. On the other hand,, a sig-
413 nificant negative correlation was observed for BaA,
414 Chry, BbF, BkF, BeP, BaP, IcdP + DahA, BghiP and
415 Co with the temperature indicating that these PAH
416 showed seasonality, it means the pollution sources,
417 which produced these pollutants were seasonal. Sev-
418 eral studies have indicated the seasonal behaviour of
419 atmospheric PAH (Barrero Mazquiarán and Cantón
420 Ortiz de Pinedo 2007; Dimashki et al. 2001; Mastral
421 et al. 2003). Seasonal activities such as the use of
422 fossil fuels for heating in winter, and pho-decay
423 reactions of ambient PAH in the summer are believed
424 to be the main causes of seasonal variations. How-
425 ever, the total PAH did not show any significant
426 negative correlation with the temperature indicating
427 that the major sources of PAH were no seasonal. Traffic
428 and industry have been associated to no seasonal sources
429 although from these correlations nothing could be
430 deduced with regard to which pollution sources were.

431 A significant positive correlation was found be-
432 tween the PM10 and the average *temperature*,
433 favouring the high temperatures the accumulation of
434 particulate matter. Van der Wal and Janssen (2000)
435 also confirmed this correlation during summer under
436 the conditions of high temperatures and dry weather.

437 A positive significant correlation at the level of
438 99% was found between the total of PAH and the
439 *relative humidity*. This positive correlation was also
440 found in a previous article published by these authors
441 (Mastral et al. 2003) and could be due to a deposi-

442 tional effect of the PAH in gas phase as consequence
443 of the environmental humidity (Dickhut and Gustafson
444 1997). Harrison et al. (1996) also showed that com-
445 bustion sources such as vehicular, incineration, coal
446 and metalliferous processes were positively correlated
447 with relative humidity. BaA, Chry, BbF, BkF, BeP,
448 BaP, IcdP+DahA, BghiP and Co also showed a posi-
449 tive correlation with the relative humidity.

450 A significant negative correlation was found
451 between the total of PAH and the *radiation*, *the wind*
452 *direction* and *the wind speed*. Regarding the solar
453 radiation, this parameter is implicated in the degrada-
454 tion of reactive PAH on particles decreasing the total
455 of PAH especially in seasons with more solar
456 radiation. Concerning the wind speed and wind
457 direction, the negative correlation with the total of
458 PAH shows the influence of local sources as pollution
459 sources (Karar and Gupta 2006). Both parameters
460 play an important role in dispersing contaminants
461 with the accumulation of particles during low wind
462 periods and less degrees in the wind direction (N, NE,
463 E) and the removal during strong winds and more
464 degrees in the wind direction (W, NW). For the
465 individual PAH, it was observed that the volatile
466 PAH, Phe An, 2+2/4Mephe, 9Mephe, 1Mephe and
467 Dimephe were the compounds more affected by the
468 wind speed. It means that volatile PAH were more
469 probably swept by strong winds. Regarding the wind
470 direction, most of the individual PAH showed a
471 significant negative correlation with the wind direc-
472 tion. The higher the degrees in the wind direction, the
473 lower the PAH concentrations showing the prevalence
474 of local pollution sources coming from the N, NE and
475 E direction, direction in which most of the industrial
476 parks were located. These negative correlations were
477 also found between the PM10 and the wind speed
478 (Karar and Gupta 2006) and the wind direction.

479 Considering the localization of Zaragoza, in Ebro
480 valley and affected by a special kind of *wind*, “cierzo”
481 (NW direction), coming from the Moncayo Mountain,
482 it was also interesting to represent the mean total PAH
483 concentrations with the wind direction (Fig. 4) in order
484 to know which wind direction showed the highest
485 PAH concentrations and to which source it could be
486 attributed. It is observed that the highest PAH concen-
487 trations were obtained in the NE and SE direction.
488 Taking into account the localization of the sampling
489 place, according to Fig. 1, the NE and SE directions
490 correspond to different industrial parks and paper

Table 2 Pearson correlation coefficients between the individual PAH, the total PAH, the PM10 and the meteorological variables (rainfall, temperature, relative humidity, irradiation, wind velocity and wind direction)

	Ph	An	MePhe24	MePhe9	MePhe1	Dimephe	Fth	Py	BaA	Chry	BbF	BkF
Ph	1											
An	0.925 ^a	1										
MePhe24	0.963 ^a	0.882 ^a	1									
MePhe9	0.933 ^a	0.908 ^a	0.931 ^a	1								
MePhe1	0.945 ^a	0.957 ^a	0.916 ^a	0.956 ^a	1							
Dimephe	0.807 ^a	0.886 ^a	0.726 ^a	0.866 ^a	0.913 ^a	1						
Fth	0.894 ^a	0.803 ^a	0.879 ^a	0.860 ^a	0.843 ^a	0.764 ^a	1					
Py	0.898 ^a	0.805 ^a	0.892 ^a	0.893 ^a	0.842 ^a	0.748 ^a	0.974 ^a	1				
BaA	0.124	0.123	0.138	0.172	0.164	0.213	0.228	0.204	1			
Chry	0.248	0.328 ^b	0.238	0.296	0.322 ^b	0.402 ^a	0.372 ^b	0.345 ^b	0.908 ^a	1		
BbF	0.061	0.212	0.084	0.097	0.129	0.172	0.223	0.189	0.680 ^a	0.780 ^a	1	
BkF	-0.091	0.008	-0.049	-0.053	-0.020	0.015	0.086	0.051	0.746 ^a	0.760 ^a	0.939 ^a	1
BeP	0.131	0.296	0.136	0.204	0.251	0.342 ^b	0.295	0.263	0.672 ^a	0.813 ^a	0.952 ^a	0.905 ^a
BaP	-0.048	0.030	0.007	0.009	0.039	0.064	0.150	0.124	0.731 ^a	0.768 ^a	0.892 ^a	0.962 ^a
IcdP + DahA	0.179	0.151	0.302	0.298	0.260	0.174	0.305	0.273	0.701 ^a	0.628 ^a	0.438 ^a	0.536 ^a
BghiP	0.243	0.265	0.375 ^b	0.354 ^b	0.315 ^b	0.233	0.423 ^a	0.413 ^a	0.577 ^a	0.640 ^a	0.515 ^a	0.538 ^a
Co	0.265	0.327 ^b	0.428 ^a	0.415 ^a	0.375 ^b	0.230	0.377 ^b	0.380 ^b	0.388 ^b	0.450 ^a	0.431 ^a	0.420 ^a
Total PAH	0.583 ^a	0.611 ^a	0.635 ^a	0.650 ^a	0.643 ^a	0.591 ^a	0.718 ^a	0.699 ^a	0.720 ^a	0.824 ^a	0.703 ^a	0.648 ^a
PM10	0.083	-0.018	0.133	0.064	0.024	-0.035	0.072	0.074	0.337 ^b	0.220	0.218	0.303
Rainfall	0.090	0.198	0.162	0.252	0.193	0.233	0.127	0.145	0.121	0.077	-0.016	-0.036
T average	0.268	0.208	0.229	0.161	0.127	0.058	0.053	0.108	-0.315 ^b	-0.319 ^b	-0.312 ^b	-0.406 ^a
R humid	0.028	0.135	0.060	0.182	0.218	0.282	0.113	0.114	0.433 ^a	0.496 ^a	0.439 ^a	0.482 ^a
Irradiation	0.046	-0.034	-0.003	-0.055	-0.103	-0.134	-0.096	-0.068	-0.394 ^b	-0.443 ^a	-0.372 ^b	-0.434 ^a
Wind speed	-0.347 ^b	-0.360 ^b	-0.383 ^b	-0.362 ^b	-0.372 ^b	-0.313 ^b	-0.286	-0.298	-0.143	-0.209	-0.249	-0.198
Wind direction	-0.349 ^b	-0.410 ^a	-0.428 ^a	-0.461 ^a	-0.425 ^a	-0.408 ^a	-0.291	-0.363 ^b	-0.409 ^a	-0.458 ^a	-0.368 ^b	-0.302

^aCorrelation is significant at the 0.01 level (two-tailed).

^bCorrelation is significant at the 0.05 level (two-tailed).

industries close to the sampling place, suggesting influence from the several industrial activities taking place in the area. At high scale, this NE direction corresponds to Catalonia, a very industrialized area, from which pollutants could be coming as a function of the meteorological variables. The S direction also showed contribution to the total of PAH and was mainly associated to a highway very close to the sampling place and located in this direction.

The NW direction was the prevailing wind direction, with a 36% of frequency and with low concentration of PAH. Precisely, this NW direction is associated to the cierzo wind, which predominates in Zaragoza city. In fact, the average wind speed for the NW direction was 4 m/s reaching values until 8 m/s. The low PAH concentrations showed at this direction seem to indicate the important role that cierzo performs in Zaragoza regarding pollution transport (Mastral et al. 2003). In this way, the cierzo acts like sweeping the pollutants, avoiding in this case the possible pollution, which could be originated and accumulated in Zaragoza due to its location in the

Ebro valley. On the other hand, the directions associated to high PAH concentrations, NE and SE directions, where the main industrial activities were located in Zaragoza, showed a frequency of 2% and 15%, respectively with calm conditions and average wind speeds of 0.4 and 1.7 m/s, which prevented the dispersion of pollutants. The S direction also prevented this dispersion showing a frequency of 10% with low average wind speed of 1.8 m/s.

3.3 Principal Component Analysis

Principal Component Analysis (PCA) was used in this work as a tool, in order to identify the main pollution sources in the atmosphere and to statistically select source fingerprints. PCA with Varimax rotation was applied to the data corresponding to each individual PAH and three factors were obtained explaining 89.8% of the total variance (Table 3).

The first factor, PC1 explained 50.6% of the variance with high loadings (>0.85) for Phe, An, DiMePhe, 2+2/4MePhe, 1MePhe, 9MePhe, Fth and

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BeP	BaP	IcdP + DahA	BghiP	Co	Total PAH	PM10	Rainfall	T average	R humid	Irradiation	Wind speed	Wind direction
1												
0.910 ^a	1											
0.449 ^a	0.586 ^a	1										
0.549 ^a	0.632 ^a	0.879 ^a	1									
0.446 ^a	0.505 ^a	0.782 ^a	0.895 ^a	1								
0.753 ^a	0.701 ^a	0.753 ^a	0.826 ^a	0.740 ^a	1							
0.162	0.277	0.247	0.103	0.062	0.211	1						
0.041	-0.023	0.361 ^b	0.423 ^a	0.431 ^a	0.247	-0.025	1					
-0.377 ^b	-0.503 ^a	-0.470 ^a	-0.488 ^a	-0.398 ^a	-0.295	0.342 ^b	-0.131	1				
0.551 ^a	0.592 ^a	0.467 ^a	0.512 ^a	0.470 ^a	0.498 ^a	0.098	0.264	-0.641 ^a	1			
-0.456 ^a	-0.541 ^a	-0.575 ^a	-0.615 ^a	-0.502 ^a	-0.467 ^a	0.173	-0.273	0.836 ^a	-0.794 ^a	1		
-0.278	-0.254	-0.175	-0.217	-0.242	-0.349 ^b	-0.553 ^a	-0.051	-0.216	-0.304	0.097	1	
-0.423 ^a	-0.345 ^b	-0.303	-0.356 ^b	-0.337 ^b	-0.506 ^a	-0.435 ^a	-0.243	-0.120	-0.436 ^a	0.137	0.581 ^a	1

1												
0.910 ^a	1											
0.449 ^a	0.586 ^a	1										
0.549 ^a	0.632 ^a	0.879 ^a	1									
0.446 ^a	0.505 ^a	0.782 ^a	0.895 ^a	1								
0.753 ^a	0.701 ^a	0.753 ^a	0.826 ^a	0.740 ^a	1							
0.162	0.277	0.247	0.103	0.062	0.211	1						
0.041	-0.023	0.361 ^b	0.423 ^a	0.431 ^a	0.247	-0.025	1					
-0.377 ^b	-0.503 ^a	-0.470 ^a	-0.488 ^a	-0.398 ^a	-0.295	0.342 ^b	-0.131	1				
0.551 ^a	0.592 ^a	0.467 ^a	0.512 ^a	0.470 ^a	0.498 ^a	0.098	0.264	-0.641 ^a	1			
-0.456 ^a	-0.541 ^a	-0.575 ^a	-0.615 ^a	-0.502 ^a	-0.467 ^a	0.173	-0.273	0.836 ^a	-0.794 ^a	1		
-0.278	-0.254	-0.175	-0.217	-0.242	-0.349 ^b	-0.553 ^a	-0.051	-0.216	-0.304	0.097	1	
-0.423 ^a	-0.345 ^b	-0.303	-0.356 ^b	-0.337 ^b	-0.506 ^a	-0.435 ^a	-0.243	-0.120	-0.436 ^a	0.137	0.581 ^a	1

Py. According to bibliography, emissions from coal combustion exhibit higher relative amounts of alkyl PAH than other combustion sources (Lee et al. 1977; Simo et al. 1997; Simcik et al. 1999). This first factor is also highly loaded on Phe, Fth, Py and An, all of which are predominant in coal combustion signals (Harrison et al. 1996; Masclet et al. 1987). Diesel emissions also produce relatively high concentrations of alkyl PAH (Nielsen 1996). However, Factor 1 lacks any significant loading on IcdP, another tracer of diesel emissions (Li et al. 1993).

Other authors like Park et al. (2002) related the presence of Phe, Fth, Py and An with the industrial combustion of oil, incineration and biomass burning. Khalili et al. (1995) and Duval and Friedlander (1981) identified these four PAH as tracers for wood combustion sources.

In this way, Factor 1 was selected to represent a mixture of sources related to stationary sources including combustion of fossil fuels and/or biomass for generating power and industrial activities. On the one hand, the combustion of fossil fuels is used in power generation and iron and steel processes. In addition, the paper fabrics and water treatments systems would also be represented on this factor as they burn biomass, residues and mud to produce the necessary heat in the process. Therefore, the contribution of different types of industries existing in the sampling area is reflected on this factor and it was considered as the dominant pollution source in the sampled area.

Considering this factor as representative of pollution sources related to industry and because these PAH did not show correlation with the temperature, as mentioned in Section 3.2, this indicated that industries were a no seasonal pollution source in Zaragoza.

The second factor, PC2 explained 30.9% of the variance with high loadings for BaA, Chry, BbF, BkF, BeP and BaP. This factor was related to PAH with four and five aromatic rings.

Previous studies have reported that BaA, Chry, BbF, BkF, BaP and DahA are compounds originated mainly from vehicular emissions (Dallarosa et al. 2005b). In particular, BaP and BaA are important tracers in gasoline and diesel emissions (Harkov and Greenberg 1985; Daisey et al. 1979). With regard to

Fig. 4 Distribution of **a** the mean total PAH concentrations (ng/m³) and **b** the PAH concentration for each sampling date (ng/m³) with the wind direction

the city traffic, and on the other hand, because it is a residential area where gas natural is used as residential heating, the domestic heating as PAH pollution source.

The third factor, PC3 explained 8% of the variance with high loadings for IcdP, BghiP and Co, PAH with 6 and 7 aromatic rings. This factor can be mainly attributed to vehicle emissions because BghiP is considered as a typical molecular marker of vehicle emission (Harrison et al. 1996; Daisey et al. 1986) and also IcdP (Kulkarni et al. 2000) and Co (Venkataraman and Friedlander 1994). Therefore, this factor was selected to represent vehicular emissions and it showed the importance of the local pollution sources in Zaragoza, mainly due to the presence of the highway.

Taking into account the information obtained with the PCA and the one obtained with the meteorological variables, in particular with the temperature, it could be deduced that residential heating was a seasonal pollution source, as the PAH representing these factors were negatively correlated to temperature. The cold

Table 3 Principal component analysis obtained with rotation method, Varimax with Kaiser normalization, applied to the individual PAH compounds concentrations

	Component		
	1	2	3
Ph	0.976		
An	0.952		
2 + 2/4MePhe	0.929		
9MePhe	0.956		
1MePhe	0.967		
Dimephe	0.895		
Fth	0.900		
Py	0.907		
BaA		0.774	
Chry		0.842	
BbF		0.947	
BkF		0.947	
BeP		0.947	
BaP		0.912	
IcdP			0.851
BghiP			0.849
Co			0.854
Total variance (%)	50.6	30.9	8.3

Only factors loading higher than 0.7 were considered.

BeP, this compound indicated contribution from oil burning (Mantis et al. 2005). Rogge et al. (1993) identified BeP and benzo[fluoranthenes like prevalent PAH in particle-phase natural gas home heating emissions.

According to this, Factor 2 could be mainly attributed to motor vehicles emissions, without distinguishing between diesel and gasoline emissions and with the contribution of natural gas home heating. Considering the sampling point, it is reflected on the one hand, the proximity of a highway in addition to

Table 4 Average total PAH concentration, frequency and average PM10 concentration as a function of the air masses origin according to the backward air trajectories, TOMs aerosol index maps, SeaWiFS satellite images and synoptic charts of pressure at sea level

Scenario type	Average total PAH ng/m ³	Frequency (%) <i>n</i> =41	Average PM10 µg/m ³
REG	25.4	17.1	50.3
MED	9.7	7.3	43.2
EUR	14.6	7.3	42.9
AW	8.1	2.4	51.9
ASW	7.4	2.4	24.6
ANW	9.6	12.2	27.0
AN	7.9	12.2	30.6
AFR	7.4	39.0	48.9

REG Regional corresponding to the Iberian Peninsula, *MED* Mediterranean, *EUR* Europe, *AW* Atlantic West, *ASW* Southwest Atlantic, *ANW* Northwest Atlantic, *AN* North Atlantic, and *AFR* North Africa (Salvador 2004).

weather in Zaragoza would also influence on vehicle increase and city traffic emissions could undergo a possible seasonal behaviour in Zaragoza.

3.4 Long-Range Transport and Local Sources

In order to determine the influence of transport over the PAH concentration, it was calculated the average total PAH concentrations as a function of the origin of air masses considering as possible sectors the ones established by Salvador (2004) (Table 4) and taking into account the 120 h backward air trajectories of each sampling date performed at 9:00 a.m., arriving at 100, 500 and 1,000 m above sea level, the TOMS aerosol index maps, the SeaWiFS satellite images and the synoptic charts of pressure at sea level. The

frequency of each scenario type and the average PM10 concentration were also shown in Table 4.

The highest PAH concentrations were obtained under regional recirculation scenarios favouring pollutant accumulation. Also high PAH concentrations were obtained when air masses were coming from the Central and Oriental Europe. These areas corresponded to very industrialized areas. The lowest PAH concentrations corresponded to air masses coming from the Atlantic and North Africa.

The more detected scenario for the dates sampled in Zaragoza was the long-range transport from North Africa with a frequency of 39% followed by regional scenarios which predominated in the 17% of the dates. It was observed that the main processes of natural and anthropogenic origin influencing on the particulate matter levels were: advection processes of West Atlantic air, circulations of air masses at regional level, intrusions of African air masses and advections of air masses coming from the Mediterranean Sea and Europe. While the natural ones were related to low PAH concentrations, the ones with anthropogenic origin reflected higher PAH concentrations.

It was also interesting to study the ageing air mass through the photochemical degradation in order to know whether the local pollution sources or the long-range transport influenced on the pollutant levels. BaA and BaP degrade in the atmosphere more easily than their isomers Chry and BeP due to their higher reactivity during transportation. Gogou et al. (1996) and Tolosa et al. (1996) showed in Mediterranean aerosols that the concentrations of these compounds decreased during their transport from urban areas to other more isolated. This could be used to assess the impact of local sources against long-range transport over the PAH concentrations. In this way, BaA/Chry

Table 5 BaP (ng/m³), total PAH (ng/m³), ratios BaA/Chry and BaP/BeP, air mass origins and PM10 for the dates exceeding 1 ng/m³ of BaP-eq

	BaP eq	BaP	Total PAH	BaA/Chry	BaP/BeP	Scenario type	PM10	
26/07/2001	1.1	0.4	30	0.6	0.6	REG	57.4	t5.1
30/10/2001	3.0	2.1	26	1.0	1.0	AFR	104.3	t5.2
13/12/2001	1.8	1.3	16	0.6	0.9	EUR	59.6	t5.3
27/12/2001	2.0	1.4	20	0.7	1.3	AN	42.7	t5.4
10/01/2002	1.5	1.2	15	0.8	1.4	MED	51.7	t5.5
24/01/2002	1.1	0.7	11	1.1	1.1	ANW	34.0	t5.6
07/02/2002	1.5	0.9	19	0.8	1.1	ANW	23.0	t5.7
14/03/2002	2.7	1.9	25	0.9	0.7	ASW	24.6	t5.8
16/05/2002	1.7	1.3	11	0.9	0.9	AFR	53.1	t5.9
								t5.10

and BaP/BeP close to 1 would indicate negligible photochemical degradation and major impact from local emission sources. Lower ratios would indicate more aged PAH.

In this work, both ratios showed average values of 0.74 and 0.95 indicating that the air masses were relatively fresh and not aged. The Pearson correlation values were significant at 99% level (0.91 in both cases) indicating that both compounds of each one were originated by the same sources. The correlation between both ratios was significant at 99% level with a Pearson coefficient of 0.5 showing that these compounds might share a similar transport pathway (Ding et al. 1997).

The seasonal values of BaA/Chry and BaP/BeP for the sampling dates were also calculated with mean values of 0.81 and 1.1 for the cold season and 0.68 and 0.86 for the warm season. No significant seasonal variations were obtained showing the influence of local emission sources during all the year.

3.5 Episodes of High PAH Concentration

Table 5 shows the dates in which the value of 1 ng/m^3 for the BaP-eq was exceeded and also the scenario type by considering the air mass origin interpreted with the backward air trajectories, the TOMS aerosol index maps, the SeaWiFS satellite images and the synoptic charts of pressure at sea level. Only two of these episodes took place during warm season and the

rest during cold period in which pollutant dispersion and photochemical degradation were lower due to the lower sun radiation and mixture layer height.

For each sampling date, the contribution percentage of each PC obtained by principal component analysis was represented (Fig. 5). It is remarkable that for the dates with high BaP-eq concentrations the PC2 and PC3 contributions, identified with vehicular emissions and residential heating, mainly associated to local pollution sources, were majority.

In general, the ratios BaA/Chry and BaP/BeP are quite high, showing that air masses are relatively fresh and there is no significative photochemical degradation. In these cases, the high BaP-eq concentration would be due to local sources typical from urban areas. Nevertheless, for some dates there is evidence of long-range transport. This is the case of 13/12/2001. This date, classified as European according to the air mass origin, was considered as episode of high PM10 concentration. The photochemical tracer ratios, BaA/Cr=0.62 and BaP/BeP=0.92 seem to indicate that while for more volatile PAH there was photochemical degradation during their transport from Europe, the heavy PAH were mainly emitted from local pollution sources.

The 26/07/2001 was classified as regional recirculation episode with high PM10 concentration. Although the BaP concentration was not very high (0.30 ng/m^3), the BaP-eq concentration was higher than 1 ng/m^3 . The BaA/Chry=0.67 and BaP/BeP=

Fig. 5 Percentage of each PC obtained by principal component analysis for each sampling date. The shown dates correspond to exceedances in the BaP-eq concentration ($>1.0 \text{ ng/m}^3$)

0.64 indicated aged air masses during recirculation and degradation due to the high solar radiation for this date (304.80 W/m²). The dates corresponding to African scenarios, 30/10/01 and 16/05/02, where long-range transport processes took place, showed no photochemical degradation according to the BaA/Chry and BaP/BeP ratios. This indicated the main contribution of local pollution sources to PAH concentrations rather than the transport of PAH on dust particles. However, these episodes of African transport had a remarkable impact on the particulate matter levels.

4 Conclusions

Despite Zaragoza city has got great advantages from an air pollution point of view with regard to other European cities because a predominant wind “cierzo” sweeps pollutants, the limit value established by the 2004/107/EC Directive concerning PAH in air, 1 ng/m³ of BaP, is exceeded in 14.6% of the samples taken in a yearly sampling during 2001–2002.

Taking into account other carcinogenic compounds in addition to BaP, 22.5% of the samples showed values of BaP-eq higher than 1 ng/m³.

Influence of the local meteorological variables on the total PAH concentrations were explained and PCA analysis showed that stationary sources related to industry were the dominant pollution sources. Vehicular emissions and natural gas home heating also significantly contribute to the PAH levels in the sampled area. The main PAH pollution sources were related to local sources associated to regional air masses rather than long-range transport. The influence of long-range transport of anthropogenic origin also contributed to PAH concentrations but for specific dates. The most frequent scenarios, air masses coming from Africa with natural origin, did not show high average PAH concentrations but high particulate matter levels.

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AUTHOR PLEASE ANSWER ALL QUERIES.

- Q1. Li et al. (1993), Kulkarni et al. (2000) and Ding et al. (1997) were cited in the text but were not found in the reference list.
- Q2. Please provide complete bibliographic information for Daisey et al. 1979 and Karar and Gupta 2006.

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