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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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64 et al. 2004). In particular, the South European
 65 countries, mainly affected by the transport of mineral
 66 dust from the African continent, could be also
 67 affected by the long-range transport of PAH. In order
 68 to distinguish local emission sources from long-range
 69 aerosol transport, several methods have been used.
 70 Among other methods, calculated backward air
 71 trajectories as well as aerosol index maps provided
 72 information of the transport paths (Borbély-Kiss et al.
 73 2004). Naturally, the history of the transported air
 74 masses along the selected trajectory will be funda-
 75 mentally affected by transport time, meteorological
 76 conditions and by the nature of emission sources
 77 touched along the transport path.

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

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

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

special attention to the most carcinogenic PAH, the 113
 fulfilling of the present Directive regarding PAH and 114
 the pollution sources producing these compounds. 115

2 Experimental 116

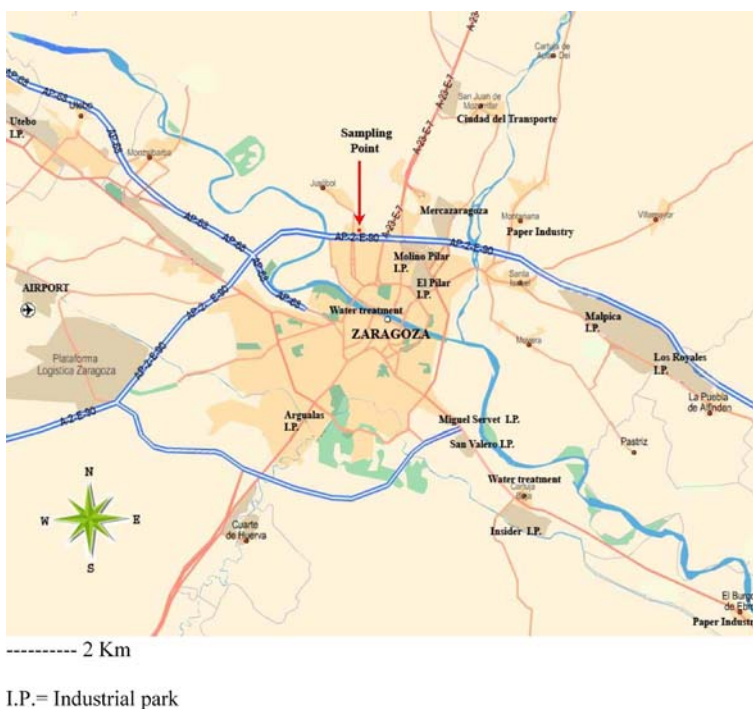
2.1 Sampling Program 117

The study was performed in the city of Zaragoza 118
 (650,592 habitants) located in the Northeast of Spain 119
 (41°39'49.38"N; 0°53'16.68"W) and previously de- 120
 scribed in another article (López et al. 2005). This city 121
 is also characterized by a special kind of wind called 122
 “cierzo” which comes from the Moncayo Mountain, 123
 North–West direction. 124

The sampling was performed in an urban area 125
 where sources of anthropogenic emissions surround- 126
 ing the sampling site included a high level traffic 127
 highway (A-2; 38695 vehicles/day in 2006) and 128
 several industrial parks related to medium and small 129
 enterprises (Cogullada: 130 enterprises (28% metal 130
 sector; 30% distribution sector); Malpica: 300 enter- 131
 prises (33% metal sector; chemical, plastic, com- 132
 merce); Argualas: 34 enterprises (37% commerce and 133
 distribution); Miguel Servet: (varied industry; 36% 134
 commerce and distribution; footwear, wood, textil, 135
 metal); S. Valero: 80 enterprises (50% iron and steel 136
 industry; wood, distribution); El Pilar: 26 enterprises 137
 (35% commerce and distribution); Molino El Pilar: 138
 117 enterprises (13% metal; 39% commerce and 139
 distribution); La Cartuja: 25 enterprises (45% metal 140
 sector; 25% electronic; chemistry, plastic, paper, etc); 141
 Mercazaragoza: 112 enterprises (agroalimentary in- 142
 dustry, slaughterhouse)), two paper fabrics and two 143
 water-treatment systems (see Fig. 1). 144

Samples were collected every 2 weeks from July 145
 12th, 2001 to July 26th, 2002 on weekdays. More 146
 intensive sampling dates: 11, 12, 13, 14 and 15th 147
 March 2002, 18, 19, 20 and 21st June 2002, 22, 23, 148
 24 and 26th July 2002 corresponding to winter, spring 149
 and summer seasons were carried out collecting a 150
 total of 41 samples. A GUV-15H Graseby Andersen 151
 High-Volume sampler with volumetric flow con- 152
 trolled system provided with a PM10 cut off inlet at 153
 10 µm and located 3.5 m from the ground was used to 154
 collect particulate phase in a PTFE-coated, glass-fibre 155
 filters (0.6 µm pore size; 20.5×25.5 cm, Pall 156
 GelmanSciences). Sampling time was 24 h, yielding 157

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.

208 The compounds quantified during sampling, ac-
 209 cording to their elution orders, were: naphthalene (Np,
 210 m/z 102), acenaphthylene (Acy, m/z 150), acenaph-
 211 thene (Ace, m/z 151), fluorene (Fl, m/z 163), phenan-
 212 threne (Phe, m/z 152), anthracene (An, m/z 152), 2+2/
 213 4-methylphenanthrene (2+2/4MePhe, m/z 189),
 214 9-methylphenanthrene (9MePhe, m/z 189), 1-meth-
 215 ylphenanthrene (1MePhe, m/z 189), 2,5-/2,7-/4,
 216 5-dimethylphenanthrene (Dimephe, m/z 191), fluo-
 217 ranthene (Fth, m/z 200), pyrene (Py, m/z 200), benz
 218 [a]anthracene (BaA, m/z 226), chrysene (Chry, m/z
 219 226), benzo[b]fluoranthene (BbF, m/z 250), benzo[k]
 220 fluoranthene (BkF, m/z 250), benzo[e]pyrene (BeP,
 221 m/z 250), benzo[a]pyrene (BaP, m/z 250), indeno
 222 [1,2,3-cd]pyrene (IcdP, m/z 274), dibenzo[a,h]anthra-
 223 cene (DahA, m/z 276), benzo[g,h,i]perylene (BghiP,
 224 m/z 274) and coronene (Co, m/z 298).

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

230 2.3 Quality Control and Quality Assurance

231 Analyte losses during the analytical procedure were eval-
 232 uated by adding a known amount of deuterated PAH
 233 surrogate standards, above mentioned, before the Soxhlet

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

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

249 In order to check the analytical accuracy and pre-
 250 cision, analyses of an appropriate standard reference
 251 material (SRM 1944, Waterway sediment) of National
 252 Institute of Standards and Technology (NIST) were
 253 analysed. Measured values were comparable to certified
 254 values with a precision between 0.2% (for BkF) and
 255 22% (for BaA) for all compounds.

256 2.4 Statistical Tools

257 All statistical analyses, including Pearson correlation
 258 coefficients and Principal Component Analysis
 259 (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

260 version 12.0. These statistical tools were applied to
 261 the PAH variables (Phe, An, 2+2/4MePhe, 9MePhe,
 262 1MePhe, Dimephe, Fth, Py, BaA, Chry, BbF, BkF,
 263 BeP, BaP, IcdP + DahA, BghiP, Co), total PAH, PM10
 264 and the meteorological data (average temperature,
 265 relative humidity, rainfall, irradiation, wind direction
 266 and wind speed) for all the air samples.

267 **2.5 Long-Range Transport**

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

284 **3 Results and Discussion**

285 **3.1 PAH Concentration Levels**

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

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

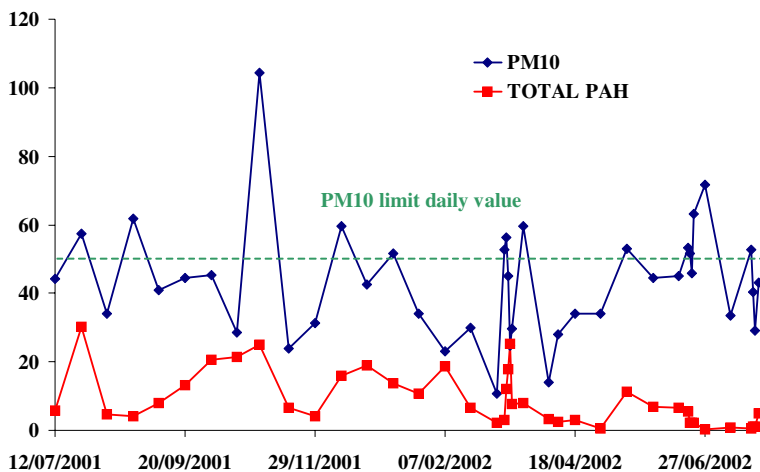
308 Minimum, maximum and mean concentrations
 309 for each PAH identified in the PM10 are shown in
 310 Table 1 obtaining a mean total PAH concentration for
 311 the 18 PAH in Zaragoza of $8.77 \text{ ng}/\text{m}^3$. The con-
 312 centrations of the studied PAH at this sampling site
 313 were compared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

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

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

329 Regarding sampling performed in this work,
 330 the highest contribution to the total of PAH cor-
 331 responded to PAH with four or more aromatic
 332 rings, the most toxic and carcinogenic PAH. The
 333 total mass was dominated by PAH like BghiP,
 334 IcdP and Co (11.1, 11.3 and 12.4%) revealing
 335 the importance of traffic to PAH concentrations
 336 (Nielsen 1996).

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



337 One of the most interesting PAH to study due to
 338 its carcinogenic character and to the target value of
 339 1.0 ng/m³ established by the Directive 2004/107/CE
 340 is the BaP. The BaP, showed variations between
 341 0.03 ng/m³, the lowest value and 2.11 ng/m³, the
 342 highest value with 14.6% of the samples exceeding
 343 1.0 ng/m³ and with a mean value of 0.45 ng/m³
 344 (Table 1). Comparing with other studies performed in
 345 other European countries, this mean value was slightly
 346 lower than the one found in a urban location in Atenas,
 347 0.56 ng/m³ (Mantis et al. 2005), and very similar to the
 348 one found in Birmingham, 0.48 ng/m³ (Smith et al.
 349 1996) during 1992. Other samplings performed in Italy
 350 in previous years showed values of BaP of 1.56 and
 351 1.72 ng/m³ respectively, in traffic areas of Rome and
 352 Naples in 1994 and 1996–1997 (Cecinato et al. 1999;
 353 Caricchia et al. 1999). Considering results obtained in
 354 no European countries, similar BaP values were found
 355 in another sampling station with heavy traffic in Porto
 356 Alegre, Brazil, 0.52 ng/m³ (Dallarosa et al. 2005a).
 357 Comparing with other Spanish cities, mean BaP
 358 values of 0.547 ng/m³ were found in the PM10 during
 359 2000–2001 in Seville (Gutiérrez-Dabán et al. 2005).
 360 However, the comparisons should be done with
 361 caution due to the unique characteristics of each
 362 sampling site, the different time of the year to conduct
 363 the sampling and differing procedures for sample
 364 collection, clean-up and analysis.
 365 Due to not only BaP is carcinogenic and because
 366 the Directive 2004/107/CE also considers other

relevant PAH (BaA, BfF, BjF, BkF, IcdP, DahA) in 367
 addition to BaP, it was also interesting to know the 368
 BaP equivalent (BaP-eq) (Fig. 3). BaPE is calculated 369
 according to the following formula:

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

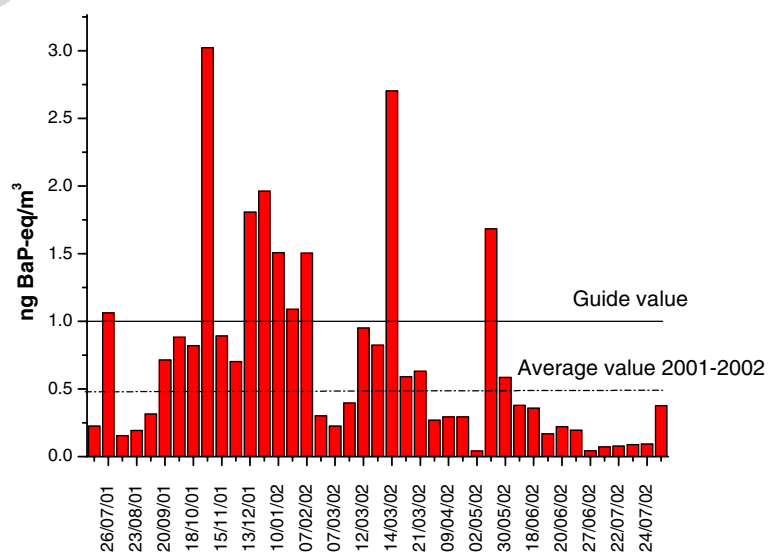
Where PAH_i is the concentration of each individual 372
 PAH (Phe, An, Fth, Chry, BaA, BbF, BkF, BeP, BaP, 373
 IcdP + DahA, BghiP) and FTE_i the toxic equivalent 374
 factor for each PAH. In this work, it has been used the 375
 FTE proposed by Larsen and Larsen (1998) as they 376
 are the last ones published and reviewed. 377

It is worth saying that as IcdP was quantified 378
 together with DahA it is possible that the BaP-eq 379
 values are underestimated. Nevertheless, in most of 380
 the samples the DahA was negligible. 381

In this way, a better carcinogenicity parameter 382
 related to the whole PAH fraction instead of the BaP 383
 was achieved, especially if it is taken into account that 384
 BaP can easily photodegrade with light or oxidants 385
 and considering that with the Directive 2004/107/EC, 386
 not only BaP will be submitted to legislation. 387

The mean value of BaP-eq was 0.7 ng/m³ with 388
 BaP-eq exceeding 1 ng/m³ in nine cases which 389
 represents the 22.5% of the samples. This mean value 390
 was lower than the ones found for downtown Athens 391
 in 1996 (1.6 ng/m³) (Marino et al. 2000) and down- 392
 town Algiers (3.4 ng/m³) (Yassaa et al. 2001). 393

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,
473 the 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).

491 industries close to the sampling place, suggesting in-
 492 fluence from the several industrial activities taking
 493 place in the area. At high scale, this NE direction cor-
 494 responds to Catalonia, a very industrialized area, from
 495 which pollutants could be coming as a function of the
 496 meteorological variables. The S direction also showed
 497 contribution to the total of PAH and was mainly
 498 associated to a highway very close to the sampling
 499 place and located in this direction.

500 The NW direction was the prevailing wind direc-
 501 tion, with a 36% of frequency and with low con-
 502 centration of PAH. Precisely, this NW direction is
 503 associated to the ciero wind, which predominates in
 504 Zaragoza city. In fact, the average wind speed for the
 505 NW direction was 4 m/s reaching values until 8 m/s.
 506 The low PAH concentrations showed at this direction
 507 seem to indicate the important role that ciero per-
 508 forms in Zaragoza regarding pollution transport
 509 (Mastral et al. 2003). In this way, the ciero acts like
 510 sweeping the pollutants, avoiding in this case the
 511 possible pollution, which could be originated and
 512 accumulated in Zaragoza due to its location in the

Ebro valley. On the other hand, the directions 513
 associated to high PAH concentrations, NE and SE 514
 directions, where the main industrial activities were 515
 located in Zaragoza, showed a frequency of 2% and 516
 15%, respectively with calm conditions and average 517
 wind speeds of 0.4 and 1.7 m/s, which prevented the 518
 dispersion of pollutants. The S direction also pre- 519
 vented this dispersion showing a frequency of 10% 520
 with low average wind speed of 1.8 m/s. 521

3.3 Principal Component Analysis 522

Principal Component Analysis (PCA) was used in this 523
 work as a tool, in order to identify the main pollution 524
 sources in the atmosphere and to statistically select 525
 source fingerprints. PCA with Varimax rotation was 526
 applied to the data corresponding to each individual 527
 PAH and three factors were obtained explaining 528
 89.8% of the total variance (Table 3). 529

The first factor, PC1 explained 50.6% of the 530
 variance with high loadings (>0.85) for Phe, An, 531
 DiMePhe, 2+2/4MePhe, 1MePhe, 9MePhe, Fth and 532

Water Air Soil Pollut

BeP	BaP	IcdP + DahA	BghiP	Co	Total PAH	PM10	Rainfall	T average	R humid	Irradiation	Wind speed	Wind direction	
1													t2.2
0.910 ^a	1												t2.3
0.449 ^a	0.586 ^a	1											t2.4
0.549 ^a	0.632 ^a	0.879 ^a	1										t2.5
0.446 ^a	0.505 ^a	0.782 ^a	0.895 ^a	1									t2.6
0.753 ^a	0.701 ^a	0.753 ^a	0.826 ^a	0.740 ^a	1								t2.7
0.162	0.277	0.247	0.103	0.062	0.211	1							t2.8
0.041	-0.023	0.361 ^b	0.423 ^a	0.431 ^a	0.247	-0.025	1						t2.9
-0.377 ^b	-0.503 ^a	-0.470 ^a	-0.488 ^a	-0.398 ^a	-0.295	0.342 ^b	-0.131	1					t2.10
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				t2.11
-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			t2.12
-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		t2.13
-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	t2.14
													t2.15
													t2.16
													t2.17
													t2.18
													t2.19
													t2.20
													t2.21
													t2.22
													t2.23
													t2.24
													t2.25
													t2.26
													t2.27

Q1

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

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

550 In this way, Factor 1 was selected to represent a
 551 mixture of sources related to stationary sources
 552 including combustion of fossil fuels and/or biomass
 553 for generating power and industrial activities. On the
 554 one hand, the combustion of fossil fuels is used in
 555 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 contri-
 bution 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 pollu-
 tion 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

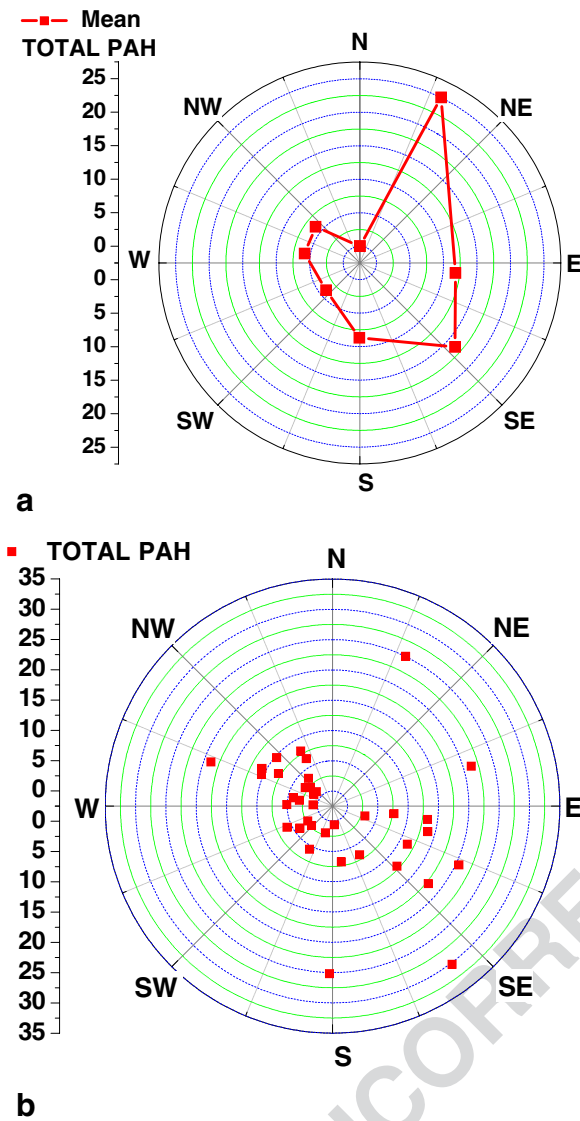


Fig. 4 Distribution of **a** the mean total PAH concentrations (ng/m³) and **b** the PAH concentration for each sampling date (ng/m³) with the wind direction

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			t3.4
An	0.952			t3.5
2 + 2/4MePhe	0.929			t3.6
9MePhe	0.956			t3.7
1MePhe	0.967			t3.8
Dimephe	0.895			t3.9
Fth	0.900			t3.10
Py	0.907			t3.11
BaA		0.774		t3.12
Chry		0.842		t3.13
BbF		0.947		t3.14
BkF		0.947		t3.15
BeP		0.947		t3.16
BaP		0.912		t3.17
IcdP			0.851	t3.18
BghiP			0.849	t3.19
Co			0.854	t3.20
Total variance (%)	50.6	30.9	8.3	t3.21

Only factors loading higher than 0.7 were considered. t3.22

579 BeP, this compound indicated contribution from
580 oil burning (Mantis et al. 2005). Rogge et al.
581 (1993) identified BeP and benzofluoranthenes like
582 prevalent PAH in particle-phase natural gas home
583 heating emissions.

584 According to this, Factor 2 could be mainly at-
585 tributed to motor vehicles emissions, without distin-
586 guishing between diesel and gasoline emissions and
587 with the contribution of natural gas home heating.
588 Considering the sampling point, it is reflected on the
589 one hand, the proximity of a highway in addition to

t4.1 **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

t4.2	Scenario type	Average total PAH ng/m ³	Frequency (%) n=41	Average PM10 µg/m ³
t4.3	REG	25.4	17.1	50.3
t4.4	MED	9.7	7.3	43.2
t4.5	EUR	14.6	7.3	42.9
t4.6	AW	8.1	2.4	51.9
t4.7	ASW	7.4	2.4	24.6
t4.8	ANW	9.6	12.2	27.0
t4.9	AN	7.9	12.2	30.6
t4.10	AFR	7.4	39.0	48.9

t4.11 *REG* Regional corresponding to the Iberian Peninsula, *MED* Mediterranean, *EUR* Europe, *AW* Atlantic West, *ASW* South-west Atlantic, *ANW* Northwest Atlantic, *AN* North Atlantic, and *AFR* North Africa (Salvador 2004).

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 advectons 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

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

615 3.4 Long-Range Transport and Local Sources

616 In order to determine the influence of transport over
617 the PAH concentration, it was calculated the average
618 total PAH concentrations as a function of the origin of
619 air masses considering as possible sectors the ones
620 established by Salvador (2004) (Table 4) and taking
621 into account the 120 h backward air trajectories of
622 each sampling date performed at 9:00 a.m., arriving at
623 100, 500 and 1,000 m above sea level, the TOMS
624 aerosol index maps, the SeaWiFS satellite images and
625 the synoptic charts of pressure at sea level. The

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

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

666 In this work, both ratios showed average values of
 667 0.74 and 0.95 indicating that the air masses were
 668 relatively fresh and not aged. The Pearson correlation
 669 values were significant at 99% level (0.91 in both
 670 cases) indicating that both compounds of each one
 671 were originated by the same sources. The correlation
 672 between both ratios was significant at 99% level with
 673 a Pearson coefficient of 0.5 showing that these
 674 compounds might share a similar transport pathway
 675 (Ding et al. 1997).

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

682 3.5 Episodes of High PAH Concentration

683 Table 5 shows the dates in which the value of 1 ng/m³
 684 for the BaP-eq was exceeded and also the scenario
 685 type by considering the air mass origin interpreted
 686 with the backward air trajectories, the TOMS aerosol
 687 index maps, the SeaWiFS satellite images and the
 688 synoptic charts of pressure at sea level. Only two of
 689 these episodes took place during warm season and the

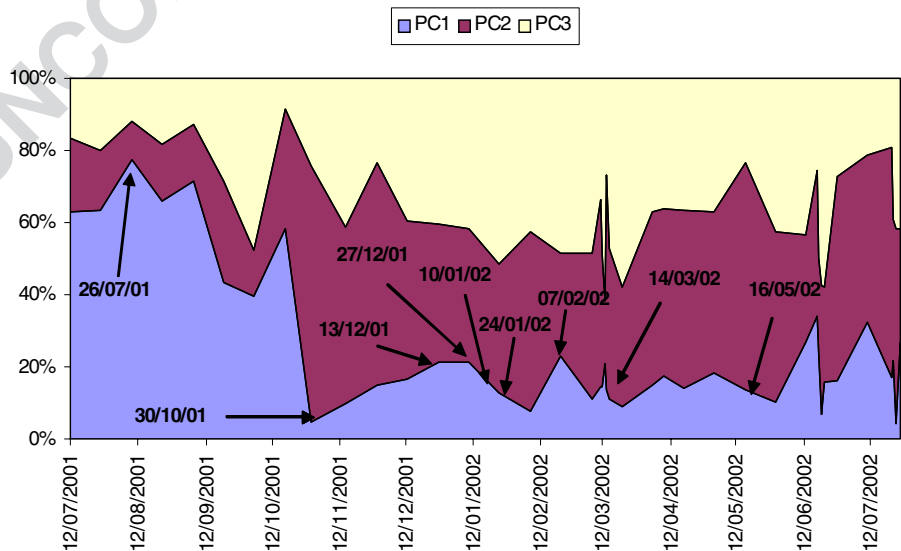
690 rest during cold period in which pollutant dispersion
 691 and photochemical degradation were lower due to the
 692 lower sun radiation and mixture layer height.

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

700 In general, the ratios BaA/Chry and BaP/BeP are
 701 quite high, showing that air masses are relatively fresh
 702 and there is no significative photochemical degrada-
 703 tion. In these cases, the high BaP-eq concentration
 704 would be due to local sources typical from urban
 705 areas. Nevertheless, for some dates there is evidence
 706 of long-range transport. This is the case of 13/12/
 707 2001. This date, classified as European according to
 708 the air mass origin, was considered as episode of high
 709 PM10 concentration. The photochemical tracer ratios,
 710 BaA/Cr=0.62 and BaP/BeP=0.92 seem to indicate
 711 that while for more volatile PAH there was photo-
 712 chemical degradation during their transport from
 713 Europe, the heavy PAH were mainly emitted from
 714 local pollution sources.

715 The 26/07/2001 was classified as regional recirculation
 716 episode with high PM10 concentration. Al-
 717 though the BaP concentration was not very high
 718 (0.30 ng/m³), the BaP-eq concentration was higher
 719 than 1 ng/m³. The BaA/Chry=0.67 and BaP/BeP=

Q1 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 ng/m³)



720 0.64 indicated aged air masses during recirculation
 721 and degradation due to the high solar radiation for this
 722 date (304.80 W/m²).
 723 The dates corresponding to African scenarios, 30/
 724 10/01 and 16/05/02, where long-range transport pro-
 725 cesses took place, showed no photochemical degrada-
 726 tion according to the BaA/Chry and BaP/BeP ratios.
 727 This indicated the main contribution of local pollution
 728 sources to PAH concentrations rather than the transport
 729 of PAH on dust particles. However, these episodes of
 730 African transport had a remarkable impact on the
 731 particulate matter levels.

732 **4 Conclusions**

733 Despite Zaragoza city has got great advantages from
 734 an air pollution point of view with regard to other
 735 European cities because a predominant wind “cierzo”
 736 sweeps pollutants, the limit value established by the
 737 2004/107/EC Directive concerning PAH in air, 1 ng/m³
 738 of BaP, is exceeded in 14.6% of the samples taken in
 739 a yearly sampling during 2001–2002.

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

743 Influence of the local meteorological variables on the
 744 total PAH concentrations were explained and PCA
 745 analysis showed that stationary sources related to
 746 industry were the dominant pollution sources. Vehicular
 747 emissions and natural gas home heating also signifi-
 748 cantly contribute to the PAH levels in the sampled area.
 749 The main PAH pollution sources were related to local
 750 sources associated to regional air masses rather than
 751 long-range transport. The influence of long-range
 752 transport of anthropogenic origin also contributed to
 753 PAH concentrations but for specific dates. The most
 754 frequent scenarios, air masses coming from Africa with
 755 natural origin, did not show high average PAH concen-
 756 trations but high particulate matter levels.

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 767 meteorological data set.

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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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