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Impact of vehicular traffic emissions on particulate-bound PAHs: Levels and associated health risks

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ABSTRACT

Considering vehicular transport as one of the most health-relevant emission sources of urban air, and with aim to further understand its negative impact on human health, the objective of this work was to study its influence on levels of particulate-bound PAHs and to evaluate associated health risks. The 16 PAHs considered by USEPA as priority pollutants, and dibenzo[a, l]pyrene associated with fine (PM_{2.5}) and coarse (PM_{2.5–10}) particles were determined. The samples were collected at one urban site, as well as at a reference place for comparison. The results showed that the air of the urban site was more seriously polluted than at the reference one, with total concentrations of 17 PAHs being 2240% and 640% higher for PM_{2.5} and PM_{2.5–10}, respectively; vehicular traffic was the major emission source at the urban site. PAHs were predominantly associated with PM_{2.5} (83% to 94% of Σ_{PAHs} at urban and reference site, respectively) with 5 rings PAHs being the most abundant groups of compounds at both sites. The risks associated with exposure to particulate PAHs were evaluated using the TEF approach. The estimated value of lifetime lung cancer risks exceeded the health-based guideline levels, thus demonstrating that exposure to PM_{2.5}-bound PAHs at levels found at urban site might cause potential health risks. Furthermore, the results showed that evaluation of benzo[a] pyrene (regarded as a marker of the genotoxic and carcinogenic PAHs) alone would probably underestimate the carcinogenic potential of the studied PAH mixtures.

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1. Introduction

The health and environmental impacts of vehicular transport is nowadays one of the most discussed topics (Beelen et al., 2008; Douglas et al., 2011) as its volume is growing every year (EEA, 2011a, 2011b). Consequently, various pollutants (EEA, 2011c, 2008), such as nitrogen oxides, particulate matter (PM), and polycyclic aromatic hydrocarbons (PAHs) are emitted into the atmosphere causing significant decline of air quality across Europe, which results in hundreds of thousands premature deaths every year. The European Union (EU) has made many efforts to reduce the pollution of ambient air. Implementation of legislative limits (Directive, 2008/50/EC),

other political actions devoted to improvement of air quality, and introduction of new technologies have caused significant reduction of emissions of some pollutants (EEA, 2011d; Skalska et al., 2010). These decreases, however, always did not lead to a corresponding drop in pollutant concentrations in the air, being particularly relevant for particulate matter (EEA, 2011d). Specifically regarding vehicular transport, during last two decades, progress has been made in reducing emissions from this source (EEA, 2011b). Nevertheless, many cities are still facing challenges in meeting concentration limits set in EU legislation for air pollutants – vehicular transport, in particular, makes a large contribution to urban air quality (EEA, 2011b). Currently, twenty percent of the EU urban population lives in areas where the air quality 24-hour limit for PM₁₀ concentrations (i.e. 50 µg m⁻³) is exceeded (EEA, 2011d, 2011b). Considering the more stringent annual air quality

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guideline of $20 \mu\text{g m}^{-3}$ of World Health Organisation (WHO, 2006), 80–90% of the current EU urban population is exposed to levels of PM_{10} higher than health-recommended (EEA, 2011d).

Although PM is one of the most health-hazardous pollutant and is being intensively studied (Chow et al., 2008; Khan et al., 2010; Khare and Baruah, 2010; Massoud et al., 2011; Pey et al., 2009; Xu et al., 2012), it is still not clear if it is its physical (i.e. size) or chemical parameters that are the main responsible for the health effects. However, various harmful components of PM, such as PAHs can contribute to or even enhance the respective adverse health effects (Directive, 2004/107/EC). PAHs are organic compounds that are produced during incomplete combustion of organic matter such as coal, oil and gas (Shibamoto, 1998); vehicular transport is one of their most important anthropogenic emission sources in urban area contributing as much as 60% of the total PAH emissions (Omar et al., 2002; Hanedar et al., 2011). In air PAHs are distributed between vapor and particulate phases. However, several studies have shown (Liu et al., 2001; Lu and Chen, 2008; Slezakova et al., 2011) that especially harmful PAHs with 5–6 aromatic rings are predominantly found in particulates, mostly due to their high molecular weights and low volatility. Many of the individual PAHs are cytotoxic, mutagenic, and potentially carcinogenic to humans (WHO, 1998). Out of the 16 PAHs recommend by U.S. Environmental Protection Agency (USEPA) as priority pollutants (Shibamoto, 1998; USEPA, 1986), benzo[a]pyrene is classified by International Agency for Research on Cancer (IARC) as known carcinogen to humans (IARC, 2010), whereas other PAHs are considered as probable and possible human carcinogens (IARC, 2010, 2002). Benzo[a]pyrene is probably the most known PAH carcinogen and in many studies estimating human cancer risks it is often used as a surrogate for other carcinogenic PAHs. Even current European legislation for ambient air (Directive, 2004/10/EC) uses benzo[a]pyrene as indicator for particulate carcinogenic PAHs (annual target value of 1 ng m^{-3} for the benzo[a]pyrene in PM_{10}). Nevertheless, the suitability of this approach started to be questioned (Pufulete et al., 2004) by new findings on the presence of more potent PAHs, such as dibenzo[a,l]pyrene or dibenz[a]anthracene (Okona-Mensah et al., 2005).

Considering vehicular transport among the most relevant emissions sources, this work aims to study its influence on levels of particulate-bound PAHs and to evaluate the associated health risks. The developed work included the detailed characterization of 17 PAHs (the 16 PAHs considered by U.S. EPA as priority pollutants, and dibenzo[a,l]pyrene) associated with fine ($\text{PM}_{2.5}$) and coarse ($\text{PM}_{2.5-10}$) particles collected at an urban site influenced by vehicular traffic emissions, as well as at one reference site.

2. Material and methods

2.1. Sampling

Particulate-bound PAHs were collected for a period of 54 days during December 2007 and January 2008 in north of Portugal at one urban site situated in Oporto city and one remote site (for comparison). The urban site (US; latitude $41^\circ 10' 40''$ N, longitude $8^\circ 35' 54''$ W and altitude 121 m) was located close to an access point of one of the most important high-ways connecting Lisbon and Oporto, being also the main road connection to the north of Spain. Other two major

thoroughfares that provide the traffic connection within the city as well as with surrounding towns also pass through this area; vehicular transport emissions are the main source of atmospheric pollutants in the area (Pereira et al., 2005; Slezakova et al., 2007, 2008). The reference site (RS; latitude $41^\circ 48' 13''$ N, longitude $8^\circ 41' 64''$ W and altitude 777 m) was situated in a remote area approximately 112 km north of Oporto, and about 13 km from seacoast. It was considered as rural (regional) background site (Larssen et al., 1999).

The samples were collected during 54 days daily for a period of 24 h by constant flow samplers (Bravo H2, TCR TECORA, Italy) that were combined with PM EN LVS sampling heads (in compliance with norm EN12341 for PM_{10} and EN14907 for $\text{PM}_{2.5}$); an air flow rate of $2.3 \text{ m}^3 \text{ h}^{-1}$ was used. Different fractions of particles, i.e. PM_{10} and $\text{PM}_{2.5}$, were collected on polytetrafluoroethylene (PTFE) membrane filters with polymethylpentene support ring ($2 \mu\text{m}$ porosity, $\varnothing 47 \text{ mm}$, SKC Ltd., UK).

2.2. PM masses

PM_{10} and $\text{PM}_{2.5}$ masses were determined gravimetrically by subtracting the initial average mass of the blank filter from the final average mass of the sampled filter. The $\text{PM}_{2.5-10}$ fraction (i.e. particles with aerodynamic diameter between 2.5 and $10 \mu\text{m}$) was determined as difference (by subtraction) between PM_{10} and $\text{PM}_{2.5}$.

For the gravimetric mass determination, the filters were stored in Petri dishes and the same analytical balance (Mettler Toledo AG245 analytical balance weighing with accuracy of $10 \mu\text{g}$) was always used. The steps of gravimetric mass determinations were the following: 24 h to equilibrate filters (temperature $22.5 \pm 1.0^\circ \text{C}$, relative humidity $42 \pm 6\%$) in a desiccator before weighing, followed by weighing during the following 24–48 h. The filters were repeatedly weighed until three reproducible values were obtained. Limit of detection (LOD) and limit of quantification (LOQ) were defined and determined as the minimum detectable amount of analyte with a signal-to-noise ratio of 3:1 and 10:1, respectively (Miller and Miller, 2005) and expressed as mass of particles with obtained values of $46 \mu\text{g}$ and $130 \mu\text{g}$ for LOD and LOQ, respectively. If the determined PM mass was below the LOQ, the value of LOD was used for the statistical analysis.

After sampling, filters were immediately weighed, stored in Petri dishes covered in parafilm, and kept in freezer (-18°C) until they were further analysed.

2.3. Extraction and quantification of PAHs

Dibenzo[a,l]pyrene (D[a,l]P) and more 16 PAHs identified as priority pollutants by U.S. EPA were determined in the collected particulate samples: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Acp), fluorene (Flr), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (B[a]A), chrysene (Chr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenz[a,h]anthracene (D[a,h]A), benzo[ghi]perylene (B[ghi]P), indeno[1,2,3-cd]pyrene (InP). The extraction of PAHs from particles (i.e. from PM_{10} and $\text{PM}_{2.5}$) was performed by MAE (MARS-X 1500 W Microwave Accelerated Reaction System for Extraction and Digestion, CEM, Mathews, NC, USA) for 20 min at 110°C using

30 mL of acetonitrile (Sigma–Aldrich) accordingly with Castro et al. (2009). Extracts were carefully filtered through a PTFE membrane filter (0.45 μm) and reduced to a small volume using a rotary evaporator (Buchi Rotavapor, R-200) at 20 °C. A gentle stream of nitrogen was used to dry the extracts under low temperature; the residue was then re-dissolved in 1000 μL of acetonitrile immediately before analysis.

Extracts were analysed using a Shimadzu LC system (Shimadzu Corporation, Kyoto, Japan) equipped with a LC-20AD pump, DGU-20AS degasser and photodiode array SPD-M20A (PAD) and fluorescence RF-10AXL (FLD) detectors on line. Separation of the compounds was performed in a C18 column (MP-PAH C18, 50 \times 4.0 mm; 3 μm particle size, YMC Europe GMBH, Germany); the injected volume was 15.0 μL . A mixture of water (ultra-pure grade; prepared by a Milli-Q simplicity 185 system, Millipore, Molsheim, France) and acetonitrile (Lichrosol for gradient elution, Carlo Erba, Rodano, Italy, purity > 99.9%) was used as the mobile phase. The initial composition of the mobile phase was 45% of acetonitrile and 55% ultra-pure water, and a linear gradient to 100% of acetonitrile was programmed in 15 min, with a final hold of 7 min. Initial conditions were reached in 3 min and maintained for 10 min before next run. The total run time was 35 min with a flow rate of 0.8 mL min⁻¹. Fluorescence wavelength programming was used to perform better sensitivity and minimal interference. Each compound was detected at its optimum excitation/emission wavelength pair: 260/315 nm (naphthalene, acenaphthene and fluorene), 260/366 nm (phenanthrene), 260/430 nm (anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and dibenzo[a,l]pyrene), and 290/505 nm (indeno[1,2,3-cd]pyrene). Acenaphthylene, which does not show fluorescence, was analysed at 254 nm in PAD. Each analysis was performed at least in triplicate.

2.4. Quality control

The overall analytical procedure was previously validated by systematic recovery experiments and using the standard reference material 1650b “Diesel particulate matter”. Under the microwave-assisted extraction conditions, PAHs were extracted from particulate matter with recoveries ranging from 81.4 \pm 8.8% to 112.0 \pm 1.1%, for all the compounds except for naphthalene (62.3 \pm 18.0%) and anthracene (67.3 \pm 5.7%). Regarding the reproducibility of the optimised methodology, expressed as relative standard deviation, values were lower than 9% for all the targeted contaminants except for naphthalene (18%). Limits of detection (LODs) and limits of quantification (LOQs) were calculated and expressed as PAH concentration in solution ($\mu\text{g L}^{-1}$) and in air samples (Castro et al., 2009). LODs between 0.0016 ng m⁻³ (0.090 $\mu\text{g L}^{-1}$) for benz[a]anthracene and 0.027 ng m⁻³ (1.5 $\mu\text{g L}^{-1}$) for naphthalene were obtained, with corresponding LOQs in the range 0.0054–0.089 ng m⁻³ (0.30–4.90 $\mu\text{g L}^{-1}$).

2.5. Health risk analysis of PAHs

The risks associated with inhalation exposure to all 17 PAHs were assessed by toxicity equivalency factors (TEF) using values

estimated by Muller, 1997 (Boström et al., 2002). Consequently, the lifetime lung cancer risks were estimated (WHO, 2000, 1987).

2.6. Statistical analysis

For the data treatment, the Student's *t*-test was applied to determine the statistical significance ($P < 0.05$, two tailed) of the differences between the means determined for both sites.

3. Results and discussion

3.1. PM and PAH levels

At the reference site, PM_{2.5} daily concentrations ranged from 3 to 12 $\mu\text{g m}^{-3}$ with a daily mean of $6 \pm 4 \mu\text{g m}^{-3}$. PM_{2.5–10} ranged from 1 to 6 $\mu\text{g m}^{-3}$ with a mean of $3 \pm 1 \mu\text{g m}^{-3}$. On average PM_{2.5} accounted for 67% of the total collected PM whereas it was 33% of PM_{2.5–10}. At the urban site, observed levels were significantly higher. PM_{2.5} mean concentration was $29 \pm 10 \mu\text{g m}^{-3}$ whilst it was $14 \pm 8 \mu\text{g m}^{-3}$ for PM_{2.5–10}. Fine particles accounted for 67% of PM. These levels were in agreement with those reported in other aerosol studies performed in Oporto area (Oliveira et al., 2010; Slezakova et al., 2008, 2011) and in other European urban environments with traffic emissions (Van Dingenen et al., 2004).

The means and concentration range for groups of PAHs with 2, 3, 4, 5, and 6 aromatic rings in PM_{2.5} and PM_{2.5–10} are summarized in Table 1. The results demonstrated that for both PM fractions levels of PAHs were significantly higher at the urban site. These differences were especially significant for fine particles, with total concentration of 17 PAHs (i.e. Σ_{PAHs}) at urban site being 2240% higher than at reference one; coarse fraction (i.e. PM_{2.5–10}) exhibited lower differences between both sites with Σ_{PAHs} 640% higher at urban site.

The results in Table 1 also demonstrate that PAHs associated with coarse particles accounted for 6% and 17% at the urban and reference site, respectively. Consequently, PM_{2.5}-bound PAHs accounted, respectively, for 94% and 83% of Σ_{PAHs} , thus demonstrating that particulate-bound PAHs were predominantly associated with particles of smaller sizes. Being in agreement with other studies (Castro et al., 2009; Slezakova et al., 2011) these findings are especially health-relevant as fine particles cause some of the more adverse health effects. Furthermore, at both sites compounds with 5 aromatic rings, which consists of a human carcinogen (i.e. benzo[a]pyrene; IARC, 2010), and probable and possible human carcinogens (namely benzo[b]fluoranthene, benzo[k]fluoranthene and dibenz[a,h]anthracene; IARC, 2010) were the most abundant group of particulate PAHs. They accounted for 30% and 36% of Σ_{PAHs} in PM_{2.5} at the reference and urban sites, respectively. The highest concentration (of all 17 PAHs) was observed for benzo[b]fluoranthene which in PM_{2.5} at urban site reached mean of $1.37 \pm 0.96 \text{ ng m}^{-3}$, accounting alone for 15% of Σ_{PAHs} . Considering the protection of public health it is also important to enhance that compounds with six aromatic rings were the second most abundant group of urban particulate PAHs (28% of Σ_{PAHs}). With exception to benzo[ghi]perylene, all studied 6-rings PAHs are also probable and possible human carcinogens (IARC, 2010). Finally, the least abundant compounds were PAHs with 2 rings (i.e. naphthalene), at the urban site accounting for less than 1% of Σ_{PAHs} in fine fraction.

Table 1Levels of PAHs in PM_{2.5} and PM_{2.5–10} at reference and urban site.

PAHs	Reference site (pg m ⁻³)				Urban site (ng m ⁻³)			
	PM _{2.5}		PM _{2.5–10}		PM _{2.5}		PM _{2.5–10}	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
2-rings	24.8	n.d.–83.4	6.2	n.d.–15.7	44.5 × 10 ⁻³	n.d.–0.105	33.6 × 10 ⁻³	n.d.–0.393
3-rings	77.6	0.190–194	8.6	0.119–36.8	1.08	9.79 × 10 ⁻² –3.54	0.216	0.114–0.971
4-rings	101	0.435–308	22.1	0.222–118	2.24	0.263–5.78	0.239	24.5 × 10 ⁻³ –1.48
5-rings	116	0.441–316	26.6	0.117–77.5	3.24	0.401–6.95	80.1 × 10 ⁻³	57.1 × 10 ⁻³ –0.498
6-rings	68.6	0.651–256	17.0	0.125–98.9	2.51	0.167–5.87	28.8 × 10 ⁻³	17.6 × 10 ⁻³ –0.352
Σ PAHs	389	1.99–998	80.5	0.690–211	9.11	1.56–21.3	0.598	0.239–3.21

The ratio values of individual PAH concentrations were used as diagnostic tools to identify the possible origin of the PAHs in ambient air (Guo et al., 2003; Kavouras et al., 1999; Pio et al., 2001). The diagnostic ratios were calculated for fine PM_{2.5} and PM_{2.5–10} fractions at both sites and the means and standard deviations are presented in Table 2. It is necessary to point out that the diagnostic ratios need to be used with caution as it is often difficult to distinguish between different sources (Ravindra et al., 2008). Moreover, the ratio can be altered due to the reactivity of some PAH species with other atmospheric species, such as ozone and/or oxides of nitrogen (Ravindra et al., 2008). At the urban site I[cd]P/(I[cd]P + B[ghi]P) ratio obtained within this work was 0.55 for PM_{2.5} and 0.53 and PM_{2.5–10}. Sicre et al. (1987), Rogge et al. (1993a), and Kavouras et al. (2001) used I[cd]P/(I[cd]P + B[ghi]P) ratio with range between 0.35 and 0.70 to indicate diesel emissions whereas other authors (Grimmer et al., 1983; Pio et al., 2001) used value of 0.56 to identify coal combustion. In order to further differentiate between the sources, various other ratios reported in the literature were

compared. The value of Flt/(Flt + Pyr) ratio obtained in PM_{2.5} at urban site was 0.40. Rogge et al. (1993a) reported Flt/(Flt + Pyr) ratio of 0.40 for gasoline cars; Flt/(Flt + Pyr) ratios between 0.4 and 0.5 suggest combustion of liquid fossil fuels (vehicle emissions; Kavouras et al., 1999; Yunker et al., 2002; Zencak et al., 2007). In addition the value of Flt/Pyr ratio in PM_{2.5} at the urban site (0.56) approached the range reported for vehicle emissions origin (Ravindra et al., 2008). Other ratios reported in literature were previously used to differentiate between diesel and gasoline exhausts. Flu/(Flu + Pyr) ratio higher than 0.5 indicates contribution of diesel emissions (Ravindra et al., 2008), whereas values lower than 0.5 indicates gasoline emissions (Ravindra et al., 2008; Rogge et al., 1993a). The present study shows very low values of Flu/(Flu + Pyr) ratios at urban site (0.17 for PM_{2.5} and 0.18 for PM_{2.5–10}) and indicates the presence of gasoline emissions at the urban site. Other authors (Ravindra et al., 2008) used a value of B[a]P/(B[a]P + Chr) around 0.5 for diesel emissions and 0.73 for gasoline emissions. Furthermore, B[b]F/B[k]F higher than 0.5 (Ravindra et al., 2008)

Table 2

Diagnostic ratios for PAHs at reference and urban site.

Ratio	This study				Value	Source	Reference
	Reference		Urban				
	PM _{2.5}	PM _{2.5–10}	PM _{2.5}	PM _{2.5–10}			
I[cd]P/(I[cd]P + B[ghi]P)	0.61 (0.22)	0.55 (0.23)	0.55 (0.03)	0.58 (0.07)	0.21–0.22 0.35–0.70 0.56 0.62 0.36	Gasoline cars Diesel emissions Coal combustion Wood combustion Road dust	Guo et al., 2003; Grimmer et al., 1983; Gogou et al., 1996; Kavouras et al., 2001; Khalili et al., 1995; Ravindra et al., 2008; Rogge et al., 1993a; Pio et al., 2001;
Flt/(Flt + Pyr)	1.26 (0.54)	1.13	0.40 (0.10)	0.30 (0.11)	0.40–0.5 >0.5 0.42, 0.52	Vehicular traffic Coal combustion Road dust	Kavouras et al., 1999; Yunker et al., 2002; Zencak et al., 2007; Rogge et al., 1993a; Oda et al., 2001
Flt/Pyr	0.63 (0.22)	0.69 (0.24)	0.56 (0.19)	0.43 (0.12)	0.6	Vehicular	Ravindra et al., 2008
Flu/(Flu + Pyr)	1.26 (0.24)	1.31 (0.32)	0.17 (0.05)	0.18 (0.08)	>0.5 <0.5	Diesel Gasoline	Ravindra et al., 2008
B[a]P/(B[a]P + Chr)	0.51 (0.12)	0.48 (0.07)	0.54 (0.06)	0.49 (0.10)	0.5 0.73	Diesel Gasoline	Ravindra et al., 2008
B[b]F/B[k]F	0.35 (0.13)	0.43 (0.14)	2.73 (0.17)	2.74 (0.20)	>0.5	Diesel	Ravindra et al., 2008
B[ghi]P/B[a]P	0.97 (0.21)	0.87 (0.26)	1.23 (0.20)	1.21 (0.31)	1.2–2.2 2.5–3.3 0.86, 0.91	Diesel cars Gasoline cars Road dust	Rogge et al., 1993a, 1993b Oda et al., 2001
B[a]A/(B[a]A + Chr)	0.25 (0.05)	0.20 (0.06)	0.42(0.04)	0.49 (0.10)	0.40, 0.38–0.64 0.76 0.43	Diesel Gasoline Wood combustion	Manoli et al., 2004; Sicre et al., 1987; Li and Kamens, 1993
BFs/B[ghi]P	0.79 (0.19)	0.83 (0.16)	1.69 (0.28)	2.07 (0.45)	1.60 0.33 2.18	Diesel cars Gasoline cars Wood combustion	Li and Kamens, 1993

and B[ghi]P/B[a]P between 1.2 and 2.2 indicate diesel emissions (Rogge et al., 1993a). The comparisons of the data in Table 2 with values of B[a]P/(B[a]P + Chr), B[b]F/B[k]F, B[ghi]P/B[a]P, but also with other ratios such as B[a]A/(B[a]A + Chr) and BFs/B[ghi]P show that diesel emissions also influenced particulate PAHs at the urban; in Portugal diesel is the most used car fuel – in 2008 it accounted for 76% of the total Portuguese car fuel consumption (National Institute of Statistics, 2009). Thus it was vehicle emissions that in general were a significant source that influenced the levels of PAHs at the urban site, however with some contributions from coal combustions. At the reference site, the analysis of data in Table 2 indicate some potential sources such as combustions (wood, coal vehicle diesel exhaust) or road dust. It is assumed that these contributions resulted from regional transport of anthropogenic emissions; as the observed reference PAH concentrations were very low, this site could be safely used as reference place for comparison of results at polluted places.

3.2. Health risks assessment of PAHs

In order to estimate the carcinogenic risks for humans, the benzo[a]pyrene equivalent carcinogenicity were evaluated by multiplying concentration of each PAH with their TEF value. Many studies (Bari et al., 2010; Ćwiklak et al., 2009; Fang et al., 2004; Halek et al., 2008; Mugica et al., 2010; Ohura et al., 2004) typically use TEF values estimated by Nisbet and LaGoy (1992). These authors, however do not refer TEF value for dibenzo[a,l]pyrene. As this PAH is considered relevant for the respective evaluation, in this work TEF reported by Muller, 1997 that included TEF for dibenzo[a,l]pyrene (Boström et al., 2002) were used to calculate the TEF-adjusted concentrations (based on benzo[a]pyrene) of 17 PAHs at the two sites. As acenaphthylene and acenaphthene were detected in less than 10% of samples their evaluation was not performed. The results of TEF adjusted concentration for 15 PAHs at reference and urban site are presented in Table 3. As expected the highest health risks were found for PAHs in PM_{2.5} at the urban site, where total TEF-adjusted concentration of all PAHs ($\Sigma_{\text{TEF-PAHs}}$) was 3.78 ng m^{-3} , thus showing the strong influence of anthropogenic emissions on human health. These levels were approximately twice lower than those found in Zabrze, Poland (7.94 ng m^{-3} ; Ćwiklak et al., 2009) or Teheran, Iran (7.65 ng m^{-3} ; Halek et al., 2008) but higher than those reported for urban atmospheres in European and international cities: Athens, Greece, (1.6 ng m^{-3} ; Marino et al., 2000), Dettenhausen, Germany (2.7 ng m^{-3} ; Bari et al., 2010), Curitiba, Brazil (1.12 ng m^{-3} ; Froehner et al., 2011), Mexico city, Mexico (2.17 ng m^{-3} ; Mugica et al., 2010), Algiers, Algeria, (3.4 ng m^{-3} ; Yassaa et al., 2001). In comparison with Asian countries, the values observed at this study were also lower: Shanghai, China, (5.95 ng m^{-3} ; Cheng et al., 2007), and Taiwan, Taichung (5.26 ng m^{-3} ; Fang et al., 2004). Previously, dibenzo[a,l]pyrene (that was found only in PM_{2.5} of urban site) appeared in the lowest concentration (mean of $21.8 \pm 16.7 \text{ pg m}^{-3}$, i.e. 0.2% of Σ_{PAHs}), nevertheless due to its high TEF of 100 it was the largest contributor to $\Sigma_{\text{TEF-PAHs}}$, contributing 57%. Dibenzo[a,l]pyrene is not typically determined when evaluating particulate-bound PAHs. However, the results obtained within this work show the strong relative contribution of dibenzo[a,l]pyrene to the carcinogenic potential, even at very low concentrations. These findings indicate that analysis of dibenzo[a,l]pyrene as well as benzo[a]pyrene is relevant in relation to vehicular emissions

(Bergvall and Westerholm, 2009); the common approach of using benzo[a]pyrene as an indicator might lead to underestimating the potential carcinogenic potency of PAHs in ambient air (Okona-Mensah et al., 2005).

The values of $\Sigma_{\text{TEF-PAHs}}$ at the urban and reference sites were then used to estimate the corresponding lifetime lung cancer risks. Regarding the lung cancer risk via the inhalation route, the World Health Organization suggested the unit risk of $8.7 \times 10^{-5} (\text{ng m}^{-3})^{-1}$ for lifetime (70 years) PAH exposure (Ohura et al., 2004). Taking into consideration that people spent outdoors only approximately 20% of their time, the estimated lifetime lung cancer risks at the reference site were 1.9×10^{-7} for PAHs in PM_{2.5-10}, and being about 4 times higher for fine fraction, 8.2×10^{-7} for PM_{2.5}. At the urban site, the corresponding values of lifetime lung cancer risks were higher, with figures of 3.7×10^{-6} for PAHs in PM_{2.5-10} and 6.6×10^{-5} for PM_{2.5}; PAHs in fine fraction exhibited risks about 18 times higher than in PM_{2.5-10}. It is important to point out that risks estimated for compounds in PM_{2.5} exceeded (7 times) the health-based guideline level of 10^{-5} (Boström et al., 2002). These results thus demonstrate that despite the limited time spent outdoors, particulate-bound PAHs, and especially those from traffic emissions might represent a serious risk to public health. In addition it is necessary to point out that outdoor pollution might be the potentially major pollution source to indoors, where people spend majority of their time. This is especially relevant for homes in close vicinity of major roads and highways where emissions from vehicular traffic might be significant contributor of indoor health-relevant pollutants (Castro et al., 2010); the risks associated with the elevated concentrations in confined indoor environments could be significantly higher than those calculated in this work. Therefore, in order to protect public health it is fundamental to develop strategies to reduce exposure to traffic emissions.

4. Conclusions

The concentrations of PM_{2.5} and PM_{2.5-10} at urban site were, respectively, 380% and 370% higher than at the remote (reference) place. The results showed that the air of the urban site was more seriously polluted, with total concentrations of 17 PAHs ranging from 1.56–21.3 (for PM_{2.5}) to 0.239–3.21 ng m^{-3} (for PM_{2.5-10}) being higher 2240% for PM_{2.5} and 640% for PM_{2.5-10}; vehicular emissions were the major contributor to particulate PAHs at this site. The major proportion of PAHs was present in fine fraction (94% and 83% of Σ_{PAHs} at the urban and reference sites, respectively) with 5 ringed PAHs being the most abundant groups of compounds (36% and 30% of Σ_{PAHs} at urban and reference sites, respectively).

The health risk analysis showed that estimated values of lifetime lung cancer risks for PM_{2.5}-bound PAHs exceeded at the urban site the health-based guideline level, thus demonstrating that long-term exposure to these pollutants at levels found at this site might increase the health risks. Furthermore, the results showed that evaluation of benzo[a]pyrene (regarded as a marker of the genotoxic and carcinogenic PAHs; Directive, 2004/107/EC; WHO, 1998) alone would probably underestimate the carcinogenic potential of the studied PAH mixtures. As PAHs may promote serious problems, in order to protect public health it is

Table 3TEF-adjusted mean concentrations of PAHs in PM_{2.5} and PM_{2.5–10} at reference and urban site (pg m⁻³).

	TEF ^a	Reference		Urban	
		PM _{2.5}	PM _{2.5–10}	PM _{2.5}	PM _{2.5–10}
Naphthalene	n.a	–	–	–	–
Fluorene	n.a	–	–	–	–
Phenanthrene	0.00064	2.68×10^{-2}	0.221×10^{-2}	2.68×10^{-2}	13.3×10^{-2}
Anthracene	n.a	–	–	–	–
Fluoranthene	n.a	–	–	–	–
Pyrene	0	–	–	–	–
Benz[a]anthracene	0.014	0.255	0.163×10^{-2}	9.06	0.582
Chrysene	0.026	1.18	0.194	22.9	1.63
Benzo[b]fluoranthene	0.11	6.85	1.59	151	4.61
Benzo[k]fluoranthene	0.037	0.657	0.146	18.9	0.515
Benzo[a]pyrene	1	25.7	5.45	933	20.2
Dibenz[a,h]anthracene	0.89	9.38	2.39	376	3.56
Benzo[ghi]perylene	0.012	0.322	5.03×10^{-2}	14.0	0.234
Indeno[1,2,3-cd]pyrene	0.067	2.79	0.857	91.1	0.501
Dibenzo[a,l]pyrene	100	–	–	2180	179
Σ PAHs	–	47.1	10.7	3780	211

^a TEF estimated by Muller, 1997 (Boström et al., 2002).

n.a. – not available.

fundamental to continue with efforts reducing emissions of these pollutants, mainly related to vehicular transport.

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References

- Bari, A., Baumbach, G., Kuch, B., Scheffknecht, G., 2010. Particle-phase concentrations of polycyclic aromatic hydrocarbons in ambient air of rural residential areas in southern Germany. *Air Qual. Atmos. Health* 3, 103–116.
- Beelen, R., Hoek, G., Van Den Brandt, P.A., Goldbohm, R.A., Fischer, P., Schouten, L.J., Armstrong, B., Brunekreef, B., 2008. Long-term exposure to traffic-related air pollution and lung cancer risk. *Epidemiology* 19, 702–710.
- Bergvall, C., Westerholm, R., 2009. Determination of highly carcinogenic dibenzopyrene isomers in particulate emissions from two diesel- and two gasoline-fuelled light-duty vehicles. *Atmos. Environ.* 43, 3883–3890.
- Boström, C.E., Gerde, P., Hanberg, A., Jernstrom, B., Johansson, C., Kyrklund, T., Rannug, A., Tornqvist, M., Victorin, K., Westerholm, R., 2002. Cancer risk assessments, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environ. Health Perspect.* 110 (451–488), 2002.
- Castro, D., Slezakova, K., Oliva-Teles, M.T., Delerue-Matos, C., Alvim-Ferraz, M.C., Morais, S., Pereira, M.C., 2009. Analysis of polycyclic aromatic hydrocarbons in atmospheric particulate samples by microwave-assisted extraction and liquid chromatography. *J. Sep. Sci.* 32 (501–510), 2009.
- Castro, D., Slezakova, K., Delerue-Matos, C., Alvim-Ferraz, M.C., Morais, S., Pereira, M.C., 2010. Contribution of traffic and tobacco smoke in the distribution of polycyclic aromatic hydrocarbons on outdoor and indoor PM_{2.5}. *Glob. Nest* 12, 3–11.
- Cheng, J., Yuan, T., Wu, O., Zhao, W., Xie, H., Ma, Y., et al., 2007. PM₁₀-bound polycyclic aromatic hydrocarbons (PAHs) and cancer risk estimation in the atmosphere surrounding an industrial area of Shanghai, China. *Water Air Soil Pollut.* 183, 437–446.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Magliano, K.L., 2008. Size-resolved aerosol chemical concentrations at rural and urban sites in Central California, USA. *Atmos. Res.* 90, 243–252.
- Ćwiklak, K., Pastuszka, J.S., Rogula-Kozłowska, R., 2009. Influence of traffic on particulate-matter polycyclic aromatic hydrocarbons in urban atmosphere of Zabrze, Poland. *Pol. J. Environ. Stud.* 18, 579–585.
- Directive 2004/107/EC, 2005. Directive of the European Parliament and of the Council Relating to Arsenic, Cadmium, Mercury, Nickel and Polycyclic Aromatic Hydrocarbons in Ambient Air. *Off. J. Eur. Union* L23, 3–16.
- Directive 2008/50/EC, 2008. Directive of the European Parliament and of the Council on Ambient Air Quality and Cleaner Air for Europe. *Off. J. Eur. Union* L152, 1–44.
- Douglas, M.J., Watkins, S.J., Gorman, D.R., Higgins, M., 2011. Are cars the new tobacco? *J. Public Health (Oxf.)* 33, 160–169.
- Environmental European Agency (EEA), 2008. Annual European Community LRTAP Convention Emission Inventory Report 1990–2006. EEA Technical Report No. 7/2008. Office for Official Publications of the European Union, Luxembourg, <http://dx.doi.org/10.2800/45511>.
- Environmental European Agency (EEA), 2011a. NEC Directive Status Report 2010, EEA Technical Report No. 3/2011. Publications Office of the European Union, Luxembourg, <http://dx.doi.org/10.2800/76170>.
- Environmental European Agency (EEA), 2011b. Laying the Foundations for Greener Transport: Transport Indicators Tracking Progress Towards Environmental Targets in Europe. EEA Report No. 7/2011. Office for Official Publications of the European Union, Luxembourg, <http://dx.doi.org/10.2800/82592>.
- Environmental European Agency (EEA), 2011c. European Union Emission Inventory Report 1990–2009 under the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP). EEA Technical Report No. 9/2011. Office for Official Publications of the European Union, Luxembourg, <http://dx.doi.org/10.2800/7836>.
- Environmental European Agency (EEA), 2011d. Air Quality in Europe – 2011 Report. EEA Technical Report No. 12/2011. Publications Office of the European Union, Luxembourg, <http://dx.doi.org/10.2800/83213>.
- Fang, G.-C., Chang, K.-F., Lu, C., Bai, H., 2004. Estimation of PAHs dry deposition and BaP toxic equivalency factors (TEFs) study at Urban, Industry Park and rural sampling sites in central Taiwan, Taichung. *Chemosphere* 55, 787–796.
- Froehner, S., Maceno, M., Machado, S.K., Grube, M., 2011. Health risk assessment of inhabitants exposed to PAHs particulate matter in air. *J. Environ. Sci. Health A Tox./Hazard. Subst. Environ. Eng.* 46, 817–823.
- Gogou, A., Stratigakis, N., Kanakidou, M., Stefanou, E.G., 1996. Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. *Org. Geochem.* 25, 79–96.
- Grimmer, G., Jacob, J., Naujack, K.W., Dettbarn, G., 1983. Determination of polycyclic aromatic compounds emitted from brown-coal-fired residential stoves by gas chromatography/gas spectrometry. *Anal. Chem.* 55, 892–900.
- Guo, H., Lee, S.C., Ho, K.F., Wang, X.M., Zou, C., 2003. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos. Environ.* 37, 5307–5317.
- Halek, F., Nabi, G., Kavousi, A., 2008. Polycyclic aromatic hydrocarbons study and toxic equivalency factor (TEFs) in Tehran, IRAN. *Environ. Monit. Assess.* 143, 303–311.
- Hanedar, A., Alp, K., Kaynak, B., Baek, J., Avsar, E., Odman, M.T., 2011. Concentrations and sources of PAHs at three stations in Istanbul, Turkey. *Atmos. Res.* 99, 391–399.
- International Agency for Research on Cancer (IARC), 2002. Some traditional herbal medicines, some mycotoxins, naphthalene and styrene. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 82, p. 367.

- International Agency for Research on Cancer (IARC), 2010. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 92, p. 773.
- Kavouras, I.G., Lawrence, J., Koutrakis, P., Stephanou, E.G., Oyola, P., 1999. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. *Atmos. Environ.* 33, 4977–4986.
- Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Von Baer, D., Oyola, P., 2001. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environ. Sci. Technol.* 35, 2288–2294.
- Khalili, N.R., Scheff, P.A., Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmos. Environ.* 29, 533–542.
- Khan, M.F., Shirasuna, Y., Hirano, K., Masunaga, S., 2010. Characterization of PM_{2.5}, PM_{2.5–10} and PM_{>10} in ambient air, Yokohama, Japan. *Atmos. Res.* 96, 159–172.
- Khare, P., Baruah, B.P., 2010. Elemental characterization and source identification of PM_{2.5} using multivariate analysis at the suburban site of North-East India. *Atmos. Res.* 98, 148–162.
- Larssen, S., Sluyter, R., Helms, C., 1999. Criteria for EUROAIRNET, the EEA Air Quality Monitoring and Information Network, EEA Technical Report No. 12. Environmental European Agency, Copenhagen.
- Li, C.K., Kamens, R.M., 1993. The use of polycyclic aromatic hydrocarbons as source signatures in receptor modelling. *Atmos. Environ.* 27, 523–532.
- Liu, Y., Zhu, L., Shen, X., 2001. Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China. *Environ. Sci. Technol.* 35, 840–844.
- Lu, H., Chen, S., 2008. Pollution level, phase distribution and health risk of polycyclic aromatic hydrocarbons in indoor air at public places of Hangzhou, China. *Environ. Pollut.* 152, 569–575.
- Manoli, E., Kouras, A., Samara, C., 2004. Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. *Chemosphere* 56, 867–878.
- Marino, F., Cecinato, A., Siskos, P.A., 2000. Nitro-PAH in ambient particulate matter in the atmosphere of Athens. *Chemosphere* 40, 533–537.
- Massoud, R., Shihadeh, A.L., Roumié, M., Youness, M., Gerard, J., Saliba, N., Zaarour, R., Abboud, M., Farah, W., Saliba, N.A., 2011. Intraurban variability of PM₁₀ and PM_{2.5} in an Eastern Mediterranean city. *Atmos. Res.* 101, 893–901.
- Miller, J.N., Miller, J.C., 2005. *Statistics and Chemometrics for Analytical Chemistry*, fifth ed. Pearson Education Limited, Harlow, pp. 107–149.
- Mugica, V., Hernandez, S., Torres, M., Garcia, R., 2010. Seasonal variation of polycyclic aromatic hydrocarbon exposure levels in Mexico City. *J. Air Waste Manage. Assoc.* 60, 548–555.
- Muller, P., 1997. Scientific Criteria Document for Multimedia Standards Development Polycyclic Aromatic Hydrocarbons (PAH); Part 1: Hazard Identification and Dose–response Assessment. Standard Development Branch, Ontario Ministry of Environment and Energy, Ontario, Canada.
- National Institute of Statistics, 2009. Statistical Yearbook of Portugal 2008. National Institute of Statistics, Lisbon.
- Nisbet, I.T.K., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharm.* 16, 290–300.
- Oda, J., Nomura, S., Yasuhara, A., Shibamoto, T., 2001. Mobile sources of atmospheric polycyclic aromatic hydrocarbons in a roadway tunnel. *Atmos. Environ.* 35, 4819–4827.
- Ohura, T., Amagai, T., Sugiyama, T., Fusaya, M., Matsushita, H., 2004. Characteristics of particle matter and associated polycyclic aromatic hydrocarbons in indoor and outdoor air in two cities in Shizuoka, Japan. *Atmos. Environ.* 38, 2045–2054.
- Okona-Mensah, K.W., Battershill, J., Boobis, A., Fielder, R., 2005. An approach to investigating the importance of high potency polycyclic aromatic hydrocarbons (PAHs) in the induction of lung cancer by air pollution. *Food Chem. Toxicol.* 43, 103–1116.
- Oliveira, C., Pio, C., Caseiro, A., Santos, P., Nunes, T., Mao, H., Luahana, L., Sokhi, R., 2010. Road traffic impact on urban atmospheric aerosol loading at Oporto, Portugal. *Atmos. Environ.* 44, 3147–3158.
- Omar, N.Y.M.J., Abas, M.R.B., Ketuly, K.A., Tahir, N.M., 2002. Concentrations of PAHs in atmospheric particles (PM₁₀) and roadside soil particles collected in Kuala Lumpur, Malaysia. *Atmos. Environ.* 36, 247–254.
- Pereira, M.C., Alvim Ferraz, M.C.M., Santos, R.C., 2005. Relevant aspects of air quality in Oporto (Portugal): PM₁₀ and O₃. *Environ. Monit. Assess.* 101, 203–221.
- Pey, J., Pérez, N., Castillo, S., Viana, M., Moreno, T., Pandolfi, M., López-Sebastián, J.M., Alastuey, A., Querol, X., 2009. Geochemistry of regional background aerosols in the Western Mediterranean. *Atmos. Res.* 94, 422–435.
- Pio, C.A., Alves, C.A., Duarte, A.C., 2001. Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area. *Atmos. Environ.* 35, 1365–1375.
- Pufulete, M., Battershill, J., Boobis, A., Fielder, R., 2004. Approaches to carcinogenic risk assessment for polycyclic aromatic hydrocarbon: a UK perspective. *Regul. Toxicol. Pharm.* 40, 54–56.
- Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos. Environ.* 42, 2895–2921.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993a. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 27, 636–651.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993b. Sources of fine organic aerosol. 3. Road dust, tire debris and organometallic brake lining dust: roads as sources and sinks. *Environ. Sci. Technol.* 27, 1892–1904.
- Shibamoto, T., 1998. *Chromatographic Analysis of Environmental and Food Toxicants*. Marcel Dekker, INC., New York.
- Sicre, M.A., Marty, J.C., Saliot, A., Aparicio, X., Grimalt, J., Albaiges, S., 1987. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. *Atmos. Environ.* 21, 2247–2259.
- Skalska, K., Miller, J.S., Ledakowicz, S., 2010. Trends in NO_x abatement: a review. *Sci. Total. Environ.* 408, 3976–3989.
- Slezakova, K., Pereira, M.C., Reis, M.A., Alvim-Ferraz, M.C., 2007. Influence of traffic emissions on the composition of atmospheric particles of different sizes – part 1: concentrations and elemental characterization. *J. Atmos. Chem.* 58, 55–68.
- Slezakova, K., Pereira, M.C., Pires, J.C.M., Martins, F.G., Alvim-Ferraz, M.C., 2008. Influence of traffic emissions on composition of atmospheric particles of different sizes – Part 2: SEM-EDS characterization. *Atmos. Chem.* 60, 221–236.
- Slezakova, K., Castro, D., Delerue-Matos, C., Alvim-Ferraz, M.C., Morais, S., Pereira, M.C., 2011. Air pollution from traffic emissions in Oporto, Portugal: Health and environmental implications. *Microchem. J.* 99, 51–59.
- United States Environmental Protection Agency (USEPA), 1986. Guidelines for Carcinogen Risk Assessment. Federal Register, 51(185), pp. 33992–34003. EPA/630/R-00/004, Washington, DC.
- Van Dingenen, R., Raes, F., Putaud, J.P., Baltensperger, U., Charron, A., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R.M., Hügl, C., Jones, A.M., Laj, P., Lorbeer, G., Maenhaut, W., Palmgren, F., Querol, X., Rodriguez, S., Schneider, J., Brink, H.T., Tunved, P., Tørseth, K., Wehner, B., Weingartner, E., Wiedensohler, A., Wählin, P., 2004. A European aerosol phenomenology – 1: physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos. Environ.* 38, 2561–2577.
- World Health Organization (WHO), 1987. Air Quality Guidelines for Europe. WHO Regional Publication, European Series No. 23. World Health Organization, Copenhagen.
- World Health Organization (WHO), 1998. Environmental Health Criteria 202: Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbons. World Health Organization Publication, Geneva. accessed 19.09.2011, available from <, <http://www.inchem.org/documents/ehc/ehc/ehc202.htm#SectionNumber:1.3>>.
- World Health Organization (WHO), 2000. Air Quality Guidelines for Europe, WHO Regional Publications, European Series No. 91, Second edition. World Health Organization, Copenhagen.
- World Health Organization (WHO), 2006. Air Quality Guidelines, Global Update 2005. WHO Regional Office for Europe, Copenhagen.
- Xu, L., Chen, X., Chen, J., Zhang, F., He, C., Zhao, J., Yin, L., 2012. Seasonal variations and chemical compositions of PM_{2.5} aerosol in the urban area of Fuzhou, China. *Atmos. Res.* 104–105, 264–272.
- Yassaa, N., Meklati, B.Y., Cecinato, A., Marino, F.P., 2001. Particulate n-alkanes, n-alkanoic acids and polycyclic aromatic hydrocarbons in the atmosphere of Algiers City Area. *Atmos. Environ.* 35, 1843–1851.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.
- Zencak, Z., Klanova, J., Holoubek, I., Gustafsson, Ö., 2007. Source apportionment of atmospheric PAHs in the Western Balkans by natural abundance radiocarbon analysis. *Environ. Sci. Technol.* 41, 3850–3855.