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Polycyclic aromatic hydrocarbons and their derivatives (nitro-PAHs, oxygenated PAHs, and azaarenes) in PM_{2.5} from Southern European cities



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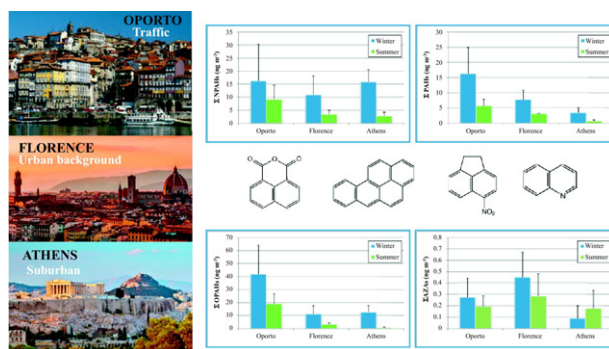
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HIGHLIGHTS

- PAHs, nitro-PAHs, oxygenated-PAHs and azaarenes were analysed in PM_{2.5} from 3 cities.
- Levels of Σ NPAHs and Σ OPAHs were higher than those of Σ PAHs.
- Most polyaromatics showed notable seasonal variation with higher levels in winter.
- Lifetime excess cancer risk for the 3 sites was higher than the WHO recommended values.
- Together with BaP, OPAHs and NPAHs are major contributors to cancer risk.

GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric particulate matter (PM_{2.5}) samples were collected over two one month periods during winter and summer in three Southern European cities (Oporto – traffic site, Florence – urban background, Athens – suburban). Concentrations of 27 polycyclic aromatic hydrocarbons (PAHs), 15 nitro-PAHs (NPAHs), 15 oxygenated-PAHs (OPAHs) and 4 azaarenes (AZAs) were determined. On average, the winter-summer concentrations of Σ PAHs were 16.3–5.60, 7.75–3.02 and 3.44–0.658 ng m⁻³ in Oporto, Florence and Athens, respectively. The corresponding concentrations of Σ NPAHs were 15.8–9.15, 10.9–3.36 and 15.9–2.73 ng m⁻³, whilst Σ OPAHs varied in the ranges 41.8–19.0, 11.3–3.10 and 12.6–0.704 ng m⁻³. Concentrations of Σ AZAs were always below 0.5 ng m⁻³. Irrespective of the city, the dominant PAHs were benzo[b + j + k]fluoranthene, retene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene. The most abundant OPAH in all cities was 1,8-naphthalic anhydride, whereas 5-nitroacenaphthene was the prevailing NPAH. The Σ OPAHs/ Σ PAHs and Σ NPAHs/ Σ PAHs were higher in summer than in winter, suggesting increasing formation of derivatives by photochemical degradation of PAHs. Molecular diagnostic ratios suggested that, after traffic, biomass burning was the dominant emission

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source. Apart from being influenced by seasonal sources, the marked differences between winter and summer may indicate that these diagnostic ratios are particularly sensitive to photodegradation, and thus should be applied and interpreted cautiously. The lifetime excess cancer risk from inhalation was, in part, attributable to PAH derivatives, acclaiming the need to include these compounds in regular monitoring programmes. On average, 206, 88 and 26 cancer cases per million people were estimated, by the World Health Organisation method, for the traffic-impacted, urban background and suburban atmospheres of Oporto, Florence and Athens, respectively.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the most widespread contaminants in the environment. The widespread occurrence of PAHs is largely due to their formation and release in all processes of incomplete combustion of organic materials. The main concern of PAHs is due to their reported carcinogenic and mutagenic characteristics (Abdel-Shafy and Mansour, 2016; Łuczynski et al., 2005; Pashin and Bakhitova, 1979). The existence of PAHs in urban air has caused particular apprehension because of the continuous nature of the exposure and the size of the population at risk.

Over the last years, attention has been redirected to PAH derivatives, such as nitrated PAHs (NPAHs), nitrogen-heterocyclic PAHs (azaarenes or AZAs) and oxygenated PAHs (OPAHs), which are emitted primarily by combustion sources. NPAHs and OPAHs are also formed by homogeneous or heterogeneous photo-oxidation reactions of PAHs with atmospheric oxidants (such as OH, NO₃ and O₃), photolysis and thermal conversions (Cochran et al., 2016; Keyte et al., 2013; Ringuet et al., 2012a). Some of these derivatives are more toxic, posing a greater threat to human health, than some PAHs, because of their direct-acting mutagenicity and carcinogenicity (EHC, 2003; IARC, 2011; Taga et al., 2005), and thus they could be significant contributors to the high toxicity of particles at extremely low concentrations (Kawanaka et al., 2008).

Hundreds of previous studies have focused on PAHs or only benzo[a]pyrene (listed as a Group 1 carcinogen by the International Agency for Research on Cancer, IARC), possibly because these are regulated by the World Health Organisation (WHO) and air quality agencies in Europe, North America, China, and several other countries (Ravindra et al., 2008). In comparison, far fewer studies have characterised the speciation and concentrations of PAH derivatives in the atmosphere. The comparative lack of data on the distribution of PAH derivatives in the atmosphere is probably because of the lack of regulatory requirements. Analytical challenges (lack of standards, low concentrations in environmental samples, lower sensitivity and degradability), the need for specialised equipment (e.g. mass spectrometer operated in chemical ionisation mode), the high cost and time required to measure them may be additional factors (Albinet et al., 2006; Bandowe and Wilcke, 2010; Bandowe et al., 2014; Walgraeve et al., 2010; Lundstedt et al., 2014). Recently, levels of particle-bound OPAHs and/or NPAHs have been reported for Chinese megacities (Bandowe et al., 2014), a rural site in the Pearl River Delta region, China (Huang et al., 2014a, 2014b), Beijing (Lin et al., 2016; Wang et al., 2011), Shanghai (Wang et al., 2014), urban and rural areas in northern China (Li et al., 2015a), Xi'an, central China (Wei et al., 2015a), Mount Bachelor Observatory and Oregon Cascade Range in the Pacific Northwest, U.S. (Lafontaine et al., 2015), Birmingham, UK (Alam et al., 2015; Delgado-Saborit et al., 2013), Weybourne in eastern England (Alam et al., 2014), Marseille, South of France (Albinet et al., 2007), French Alpine Valleys (Albinet et al., 2007), Paris (Ringuet et al., 2012b), and Madrid (Barrado et al., 2013).

The objectives of this work were: i) to determine the seasonal variation of the PM_{2.5}-bound concentrations and composition pattern of polycyclic aromatic compounds (PACs), which include PAHs, NPAHs, OPAHs and AZAs, from Southern European cities (Oporto, Florence and Athens), for which there is almost no information about these compounds; ii) to estimate the potential health impact (cancer risk) on the

inhabitants of these urban centres from inhalation of PM_{2.5}. This work was carried out in the frame of the AIRUSE project (Amato et al., 2016), whose key goal was to characterise the main contributors to particulate matter and to propose specific and non-specific abatement measures to meet the World Health Organisation Guidelines in Mediterranean countries, where the combination of multiple emission sources with the complex climatology (strong radiation, high photochemical conversion rates, low rainfall rate) have significantly contributed to exceedances of the limit values.

2. Methodology

2.1. Sampling

PM_{2.5} 24-h samples were collected at an urban background site in Florence (Italy), a suburban site in Athens (Greece), and a traffic site in Oporto (Portugal), from January 2013 to February 2014. The Italian station of Bassi (43°47'8.33"N, 11°17'13.19"E) belongs to the Environmental Protection Agency of Tuscany. In this station, samples were collected with a low volume (2.3 m³ h⁻¹) CEN sequential sampler (HYDRA Dual) onto 47 mm diameter quartz microfibre filters. The Greek suburban station was located in the NCSR "Demokritos" campus (37°99'50"N, 23°81'60"W) at the Greater Athens Metropolitan Area. It belongs to the Global Atmosphere Watch network (GAW-DEM). PM_{2.5} was also collected onto quartz microfibre filters using a high volume sampler (CAV-A/MSb, MCV, SA). The Oporto urban traffic station was located in Praça Francisco Sá Carneiro (41°09'46.10"N, 8°35'26.95"W) and is part of the Portuguese air quality monitoring network. A high volume sampler operating at a flow of 1113 L min⁻¹ with impaction plates from Sierra-Anderson was used to collect PM_{2.5} onto quartz fibre filters. PACs (PAHs, OPAHs, AZAs and NPAHs) were determined in particulate matter sampled for one-month period in the winter and in the summer seasons at each of the three sites. The three air quality monitoring sites were equipped with meteorological stations. Information on air quality and meteorological parameters is appended as supplementary material (Figs. S1 to S3).

2.2. Analytical techniques

The filters were placed in 33 mL extraction cells and spiked with a mixture of 7 deuterated-PAHs (naphthalene-D8, acenaphthene-D10, phenanthrene-D10, pyrene-D10, chrysene-D12, perylene-D12 and benzo[ghi]perylene-D12), 2 deuterated OPAHs (benzophenone-D5 and 9,10-anthraquinone-D8) and 4 deuterated NPAHs (1-nitronaphthalene-D7, 2-nitrofluorene-D9, 3-nitrofluoranthene-D9 and 6-nitrochrysene-D11) as internal standards for the PAHs, OPAHs/AZAs and NPAHs, respectively. The extra space in the extraction cells was filled with diatomaceous earth. Each filter was extracted two times by pressurised liquid extraction (PLE) with an accelerated solvent extractor (ASE 200, Dionex, Sunnyvale, CA). The first extraction was carried out with dichloromethane, followed by acetone-dichloromethane (2:1 v/v). The two extracts were then combined, filtered through sodium sulphate, spiked with hexane and concentrated to a volume lower than 1 mL using a Turbo Vap® II concentrator (Biotage, Charlotte, NC, USA). Each concentrated sample was then transferred onto silica gel

(10% deactivated) columns and fractionated using solvents of different polarity: i) 15 mL hexane-dichloromethane (5:1 v/v; PAHs) and ii) 8 mL dichloromethane followed by 5 mL acetone (NPAHs, OPAHs and AZAs). Fractions (i) and (ii) from each sample were collected in separate flasks. After elution, three drops of toluene were added to each fraction, concentrated to about 0.5 mL, spiked with fluoranthene-D10 (as recovery standard) and transferred to a 1.5 mL vial. Target PACs were analysed by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890 N gas chromatograph (GC) coupled to an Agilent 5975C inert mass selective detector (MS). The GC was equipped with a HP-5MS (30 m × 0.25 mm × 0.25 μm) column and an autosampler. During measurements of PAHs and OPAHs + AZAs, the MS was operated in the electron impact (EI) mode at 70 eV. To measure NPAHs, the MS was in negative chemical ionisation (CI) mode (at 207 eV), with CH₄ as the ionising gas. For all compound groups, the MS was operated in selected ion monitoring mode (SIM) with two ions monitored for each compound. Further details of the GC–MS instrumental parameters were described in previous papers (Alves et al., 2016; Bandowe and Wilcke, 2010; Bandowe et al., 2014, 2016). For each sample extract, the PAHs, OPAH together with AZA and NPAHs were measured in separate GC–MS injection and runs. To determine PAHs and OPAHs + AZAs, 1 μL of each sample was injected into the GC inlet in the splitless mode. The injector temperature, injector pressure, ion source temperature and quadrupole temperature of the GC–MS during the measurements of these latter compounds were 280 °C, 80 kPa, 230 °C and 150 °C, respectively. The GC oven temperature program used during the analyses of PAHs, OPAHs and AZAs has been previously described (Bandowe et al., 2014, 2016). To measure the NPAHs in samples, 1 μL of analyte was injected in the pulsed splitless mode at a pressure of 250 kPa, and injection port and transfer line temperatures of 240 °C and 280 °C, respectively. The GC oven temperature program was the same as previously described (Bandowe et al., 2014). The MS source and quadrupole temperatures were both 150 °C. A total of 27 PAHs, 15 NPAHs, 15 OPAHs and 4 AZAs were determined. The identification of target PACs in samples was done 'by comparison of their retention times and mass spectra (monitored ions, ratios of target-to-qualifier ions) with those in calibration standards that were measured together with samples in the same sequence. Target PACs were quantified by the internal standard technique. The software Agilent ChemStation was used for data recording and processing.

The accuracy and precision of the method of determination of these target compounds and their deuterated PACs (used as internal standards) have been tested and reported in previous studies (Bandowe et al., 2014, 2016; Bandowe and Wilcke, 2010; Lundstedt et al., 2014; Wei et al., 2015a, 2015b). The limits of detection (LOD) for the target PACs, defined as the amount of substance that produces a signal to noise ratio of 3:1, have also been reported in previous studies (Alves et al., 2016; Bandowe et al., 2014; Wei et al., 2015b).

2.3. Estimation of cancer risk

To estimate the lifetime excess cancer risk from inhalation (ECR) of PM_{2.5}-bound PACs in ambient air of the 3 Southern European cities the methodology described by Ramirez et al. (2011) and Bandowe et al. (2014) was followed. This methodology is based on the procedures of the Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (CalEPA). The total BaP equivalent concentrations (BaP_{eq}) were calculated from the individual PM_{2.5}-bound concentrations in each sample (C_i) and the toxicity equivalency factor (TEF) of target compounds (Ramirez et al., 2011; Wei et al., 2015b; and references therein; see Table S1):

$$\sum \text{BaP}_{\text{eq}} = \sum_i (C_i \times \text{TEF}_i) \quad (1)$$

The estimated lifetime lung cancer risk from PACs in the atmosphere based on the World Health Organisation unit risk (UR) (WHO, 2000) is

8.7 cases per 100,000 people with chronic inhalational exposure to 1 ng m⁻³ of BaP (UR_{BaP} = 8.7 × 10⁻⁵) over a lifetime of 70 years. The corresponding UR_{BaP} stipulated by CalEPA is 1.1 × 10⁻⁶ (OEHHA, 1994). The ECR from inhalation is calculated by multiplying the total BaP equivalent concentrations by the inhalation cancer unit risk factor:

$$\text{ECR} = \sum \text{BaP}_{\text{eq}} \times \text{UR}_{\text{BaP}} \quad (2)$$

3. Results and discussion

3.1. Seasonal variations in concentrations of polycyclic aromatic compounds

PAH, OPAH and NPAH levels were higher at the traffic site (Oporto) than at the urban background (Florence) and suburban (Athens) stations (Fig. 1). In general, concentrations of these PACs in the 3 European cities were substantially higher in winter than in summer. The application of the *t*-test showed that the winter means of ΣPAHs were significantly different from the summer means for the 3 cities, at the 95% confidence level (*p*-values always < 0.001, Table S2). Except for Oporto (*p* = 0.1903), there was also a significant statistical difference at the 0.05 critical level between the winter and the summer means of ΣNPAHs for the two other AIRUSE cities. However, the differences were not statistically significant for ΣOPAHs and ΣAZAs (*p*-values always > 0.1), regardless of the city. The general pattern with higher winter levels is in accordance with previous studies conducted in other regions (e.g. Alam et al., 2014; Andreou and Rapsomanikis, 2009; Bandowe et al., 2014; Tang et al., 2005; Wang et al., 2006, 2007; Zhang and Tao, 2008). The seasonal differences are explained by the greater partitioning to vapour in the warmer summer campaign, higher emissions in the winter due to increased combustion of fossil fuels and biomass for household heating, and the usual increase of primary pollutants in the colder months owing to poorer dispersion conditions and lower atmospheric mixing height. Also, the condensation of PACs on atmospheric particulate matter is favoured in winter because of lower temperature. Another reason for the higher concentrations of PACs in winter is the reduced thermal, photolytic and photochemical degradation of these compounds because of lower temperatures, less radiation and lower levels of atmospheric oxidants (Bandowe et al., 2014; and references therein).

Azaarenes have similar primary sources like the other PACs but are particularly considered to be markers for the combustion of coal (Bandowe et al., 2016; IARC, 2011; Junninen et al., 2009). The average concentrations of ΣAZAs were always < 0.5 ng m⁻³, regardless of the city and the season. Much higher levels (0.213–6.44 ng m⁻³) were determined in PM_{2.5} samples collected at an urban site of the Chinese megacity of Xi'an (Bandowe et al., 2016). Delhomme and Millet (2012) reported ΣAZA concentrations of 2.8 and 1.6 ng m⁻³ in PM₁₀ from urban areas of Strasbourg and Besancon, France, respectively. Levels of 0.120–0.60 ng m⁻³ were found in PM_{2.5} from a suburban site in Munich, Germany (Lintelmann et al., 2010). Higher concentrations of AZAs in China compared with Europe reflect a greater proportion of coal in the fossil fuel use profile of the Asiatic country (Bandowe et al., 2016). The concentration of ΣAZAs in Florence and Oporto were higher in winter than in summer, which is similar to the other PAC groups. However, in Athens, the concentration of ΣAZAs in summer was higher than that in winter (Fig. 1). Specific ambient factors (meteorology and chemistry) and source strength differences between the two seasons at this location may explain the opposite trends compared to the other PAC groups in the same site and also all other PACs in the other two sites (Bandowe et al., 2016).

On average, NPAHs accounted for 0.04, 0.05 and 0.16% of the PM_{2.5} mass during the cold season in Oporto, Florence and Athens, respectively. The corresponding mass fractions in summer were

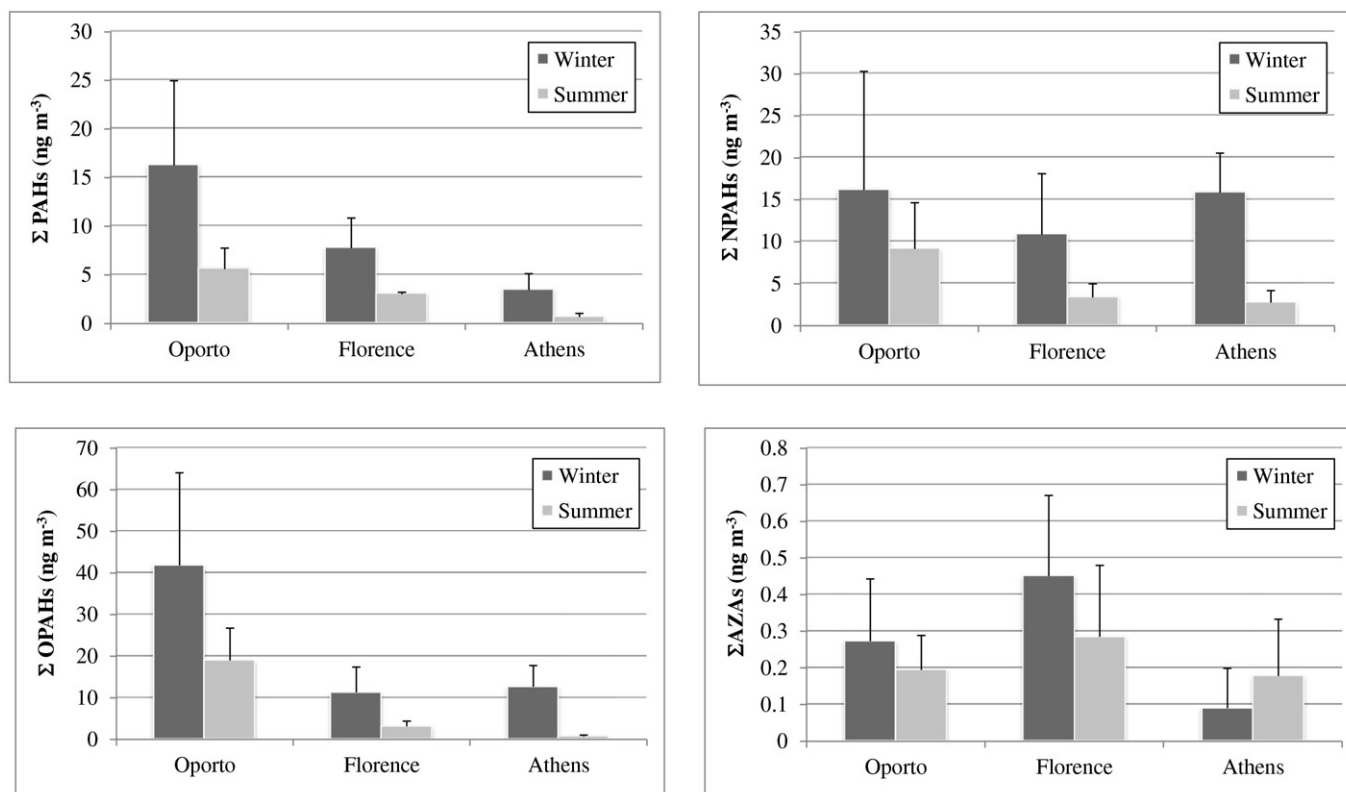


Fig. 1. Total concentrations of polycyclic aromatic compounds in PM_{2.5} from different Southern European cities.

0.02, 0.01 and 0.02%. OPAHs represented winter-summer weight percentages of 0.11–0.05, 0.09–0.03 and 0.31–0.02 in the Portuguese, Italian and Greek cities, respectively. Although the highest concentrations of ΣPAHs were observed in Oporto in the colder months ($16.3 \pm 8.71 \text{ ng m}^{-3}$), this group of PACs accounted for a lower PM_{2.5} mass fraction (0.04%) than those measured in Florence (0.07%) and Athens (0.10%).

Ambient temperature, rain and wind speed presented reasonable negative correlations (r from -0.48 to -0.87 , $p < 0.05$) with ΣPAHs, ΣOPAHs, and ΣNPAHs. Increasing household heating with decreasing temperature is partly responsible for the inverse relationship between the concentrations of PM_{2.5}-bound PAC and ambient temperature (Bandowe et al., 2014). Lower winter temperatures also favour the condensation of semi-volatile PACs onto existing atmospheric PM_{2.5}. With increasing temperatures, higher proportions of PACs redistribute into gaseous phase and coarse mode particles through the processes of evaporation and migration (i.e. evaporation from fine particulates followed by condensation on larger particle). Lighter PACs have higher vapour pressure than the heavier ones and could be shifted more quickly towards large particles (Ringuet et al., 2012b). During rainy events, particle-bound PACs are scavenged from the atmosphere by wet deposition. It is well-known that PACs are associated with small particles, which can travel longer distances with increasing wind speeds, leading to lower concentrations. The relative humidity (RH), however, showed positive relationships with total concentrations of PACs (r from 0.54 to 0.67, $p < 0.05$). This correlation could be due to a depositional effect on the particulate matter of semi-volatile PACs as a consequence of environmental humidity. The pre-existing particle population absorbs more water as RH increases and they become consequently a larger sink for condensing vapours (Anttila et al., 2004). Previous studies have reported analogous correlations between PACs and meteorological

parameters (e.g. Alam et al., 2015; Bandowe et al., 2014; Li et al., 2015b; Mastral et al., 2003; Wu et al., 2014).

3.2. Relationships between the concentrations of PAHs and their derivatives

The ΣPAHs, ΣOPAHs, and ΣNPAHs concentrations correlated significantly ($p < 0.05$) with each other throughout the year (r in the ranges 0.62–0.78, 0.69–0.94 and 0.70–0.94 for Oporto, Florence and Athens, respectively). This is a result of their similar emission sources, their co-sorption to atmospheric PM_{2.5}, inter-connections between their degradation/formation, and similar fates and mobility within the PM_{2.5} and in the atmosphere for the 3 groups of PACs.

In Oporto, the mean concentration ratio of ΣOPAHs/ΣPAHs in summer (4.8 ± 3.0) was higher than in winter (2.3 ± 0.48). The two means were significantly different ($\alpha = 0.05$; $p = 0.0185$). The ratios of some individual OPAHs to related-PAHs in the summer sampling period were higher than during the winter period (Table S3). Other individual OPAHs to parent-PAHs showed the opposite trend. Seasonal differences of PAC mixtures in primary emissions and in post emission fates of individual PACs can explain these contrasting trends. Very high concentration ratios of 1,8-naphthalic anhydride and 1,2-acenaphthenequinone to their parent-PAHs (acenaphthylene and acenaphthene) were observed. Seasonal variations in gas-particle partition and particle size redistribution of PACs, which affect these ratios, were not accounted for in the present study because PAC concentrations in the gaseous phase and other particle sizes were not quantified. Nevertheless, it has been suggested that higher ratios in summer than in winter may be an indication of increasing formation and accumulation of OPAHs from the photo(chemical) and thermal transformation of PAHs (Bandowe et al., 2014; Walgrave et al., 2010). The higher ΣOPAHs/ΣPAHs and some individual OPAH to parent PAH ratios in

summer than in winter may therefore be an indication of the accumulation of specific individual and total OPAH and the more intense dissipation of the individual and total PAHs in the summer than in winter. The processes responsible for this include enhanced photochemical and thermal degradation of PAHs to OPAHs in summer, as observed in previous studies (Walgraeve et al., 2010). Higher ratios in winter than those registered for the warmer period suggest that these individual OPAH to related PAH concentration ratios in wintertime primary emission sources may be higher than in summer time emissions. It is important to note that the relative contributions of the major sources of particulate matter vary for the two seasons (Amato et al., 2016). Residential wood combustion for household heating during winter may be an important primary source of OPAHs in atmospheric PM_{2.5} (Vicente et al., 2016). The higher temperature and more intense photochemical activity in summer, which results in enhanced post-emission transformation of individual PAHs to OPAHs (compared to the winter months), may not have been significant enough to lead to higher concentration ratios of some individual OPAHs to their related-PAHs.

The Σ NPAHs/ Σ PAHs concentration ratio in Oporto was significantly higher in summer (5.6 ± 2.2) than in winter (2.0 ± 1.2), at the 95% confidence level ($p = 0.0002$). Some of the individual NPAH to their parent-PAH ratios were higher in summer than winter, while others showed the opposite trend (Table S3). Seasonal differences in sources, differences in impacts of processes on the relative concentrations of NPAHs and PAHs (as explained above for the OPAHs) are also responsible for the observations here.

The ratios 5-nitroacenaphthene to acenaphthene and 2-nitrofluorene to fluorene for Oporto deserve particular attention because of their high values (exceeding 1000 and 5, respectively). This suggests high relative proportion of these NPAHs to parent-PAHs in primary emissions, or significant post emission atmospheric conversion of these fast reacting PAHs (fluorene and acenaphthene) to 5-nitroacenaphthene and 2-nitrofluorene at these sites. Furthermore, the vapour pressures of these NPAHs are lower than those of their parent-PAHs (Bandowe and Meusel, 2017) and, therefore, a higher proportion of these NPAHs could be partitioned into the PM_{2.5}, than their parent PAHs.

Except for quinoline to naphthalene, all other individual AZA to related-PAH ratios were higher in summer. This suggests higher AZA/related PAH ratios in summer primary emissions, enhanced volatilisation or degradation of the parent-PAHs during the more intense heat and photochemical conditions of summer in Oporto.

In Florence, the Σ OPAHs/ Σ PAHs in summer of 1.0 ± 0.42 was lower than 1.4 ± 0.26 in winter. The Σ NPAHs/ Σ PAHs of 2.2 ± 1.0 in summer was also lower than the winter value of 2.7 ± 1.5 . The Σ OPAHs/ Σ PAHs concentration ratio was found to be significantly higher in winter than in summer (p value of 0.0475). The difference between the winter and summer mean Σ NPAHs/ Σ PAHs ratios was statistically insignificant (p value of 0.4612). Mean ratios higher than 7 were obtained for 1-indanone and 9-fluorenone to their parent-PAH, fluorene (Table S4). Contrary to all other individual OPAH to parent-PAH concentration ratios, these two were higher in summer than in winter. The ratios of all individual NPAHs to their parent-PAHs were higher in winter than in summer. The trend may be due to higher ratios in winter-time primary emissions at this location and/or the effect of winter-time conditions favouring the higher levels of nitro-PAHs than of their parent-PAHs on PM_{2.5}. Higher quinoline to naphthalene and carbazole to fluorene concentration ratios in winter point out that these ratios were higher in winter primary sources at this site and perhaps relatively greater partitioning of AZAs into the particulate phase during the colder season in Florence. Additional emission sources, such as biomass burning, cannot be discarded.

In Athens, the mean Σ OPAHs/ Σ PAHs concentration ratio in summer (1.1 ± 0.48) was significantly (p values of 0.0005) lower than the winter value of 3.1 ± 1.4 . The Σ NPAHs/ Σ PAHs was 7.7 ± 4.6 in summer versus 7.5 ± 3.9 in winter. The difference between the winter and

summer means of Σ NPAHs/ Σ PAHs was statistically insignificant (p value of 0.9176). Due to the absence or very low concentrations of many compounds in summer, the individual OPAH to parent-PAH ratios were, in general, much higher or only calculable for the colder period (Table S5). As in the other two cities, very high 5-nitroacenaphthene to acenaphthene ratios were obtained in Athens. This latter and 1-nitronaphthalene to naphthalene, the only quantifiable ratios involving NPAHs, were also higher during the summer period. A much higher mean value was observed for the quinoline to naphthalene ratio in summer (146) than in winter (0.41).

The mean temperature during the summer campaign in Oporto (21.5 °C) was lower than in Florence (25.1 °C) and Athens (26.2 °C). On the contrary, the average temperature of the winter campaign in Oporto (9.5 °C) was higher than those registered in Florence (7.0 °C) and Athens (8.7 °C). Thus, the difference between the mean summer and winter temperatures, which was 18.1 °C, 17.5 °C and 12.0 °C for Florence, Athens and Oporto, respectively, could be an explanation for the observed seasonal differences in the ratios between the different cities. Ambient temperature could affect the degradation, magnitude and mechanisms of sorption of the different compound groups, their gas/particle partition, and redistribution into particulate matter of varying sizes. Distinct PAC relative proportions in emissions and differences in atmospheric composition of the various sites (Fig. S1–S3) represent additional factors. Differences between the individual PACs (e.g. molecular weight, functional groups, physical-chemical properties, photo- and thermal stability) influence their post emission fates (gas-particle partitioning, atmospheric transformation). Site specific conditions (atmospheric chemistry and meteorology) also greatly affect the fate of these PACs. These factors may explain the observed variation of either the composition or the ratios in PM_{2.5} of these PACs with seasons and at the 3 sites. The concentration of atmospheric oxidants, such as NO_x, at the traffic impacted site (Oporto) follow different patterns. On average, summer-winter NO and NO₂ levels of 24–31 and 47–32 $\mu\text{g m}^{-3}$, respectively, were registered in Oporto. In Florence, the corresponding values were 0.97–22.3 $\mu\text{g m}^{-3}$ for NO and 13.8–32.5 $\mu\text{g m}^{-3}$ for NO₂, whereas in Athens the mean levels were 3.3–4.4 $\mu\text{g m}^{-3}$ for NO and 5.7–7.4 $\mu\text{g m}^{-3}$ for NO₂ (Figs. S1–S3). The Portuguese sampling site is much more influenced by primary traffic emissions than the other two locations. Such differences in typology will also affect the profile of PACs that are emitted from the various sources.

3.3. Comparisons with other studies

Depending on the world region, very discrepant concentrations of PAHs have been described in the literature for urban atmospheres, ranging from 0.2–2 (winter) and 0.01–2 ng m^{-3} (summer) in Madrid, Spain (Barrado et al., 2013) to 701 (winter) and 104 ng m^{-3} (summer) in Xi'an, China (Wang et al., 2006). Slezakova et al. (2013) reported the sum of concentrations of 18 PAHs for samples collected at an urban site in Oporto during 40 consecutive days in November and December 2008. Levels, which included both the gas phase and PM₁₀, ranged from 16.8 to 149 ng m^{-3} , with a mean of 70 ng m^{-3} . It should be noted that 3-ring PAHs were present almost exclusively in the gas phase, accounting for 53% of the total levels, while particulate phase compounds with 5 and 6 rings represented, respectively, 14% and 6% of Σ PAHs. Specifically, the concentration of BaP ranged from 0.137 to 4.78 ng m^{-3} , with a mean of 2.02 ng m^{-3} . In the current AIRUSE winter campaign, BaP levels in Oporto varied from 0.314 to 2.25, averaging 0.979 ng m^{-3} (Table 1). However, this apparent decline could be related to a much larger number of rainfall events during the latest sampling campaign, which have certainly contributed to wet scavenging of PAHs, rather than a trend towards the fulfilment of the BaP annual limit of 1 ng m^{-3} set by the European Directive 2004/107/EC.

Martellini et al. (2012) carried out a sampling campaign from March 2009 to March 2010 at three locations in Tuscany, Italy: two urban sites

in Florence (traffic and background), and a suburban background site in Livorno. The concentrations of 16 PM_{2.5}-bound PAHs ranged between 3.5 and 24 (cold) and 1.8 and 15 (warm) ng m⁻³ at the traffic impacted site, from 0.76 and 17 (cold) to 0.46 and 10 (warm) ng m⁻³ at urban background and between 0.12 and 15 (cold) and 0.2 and 3.4 (warm) ng m⁻³ at the suburban background location. These values are consistent with those of the present study revealing that, although a decline between 2000 and 2010 had been observed due to stricter environmental legislations, update of the vehicle fleets, use of more environmental friendly fuels, etc., the increasing impact of biomass burning has attenuated the downward trend (Belis et al., 2011; Giannoni et al., 2012; Paglione et al., 2014).

Sampling of ambient PM₁₀ was conducted at four locations within the Greater Area of Athens during the period May 2001–June 2002 by Mantis et al. (2005). On average, levels of 16 PAHs were 2.84, 8.54, 7.93 and 0.656 ng m⁻³ for the urban locations of Maroussi and Aristotelous, the mixed urban-industrial location of Elefsina, and the background location of Thracomacedones, respectively. The values presently obtained for the suburban site of Demokritos (3.44 ± 1.69 ng m⁻³, winter; 0.658 ± 0.381 ng m⁻³, summer) fit those reported earlier. Concentrations of 1.12 ± 1.42 ng m⁻³ and 28.06 ± 28.91 ng m⁻³ were obtained for 15 unsubstituted PAHs in PM_{2.5} samples collected at Athinas Street, next to the City Hall of Athens, in August 2003 and March 2004, respectively (Andreou and Rapsomanikis, 2009). Higher concentrations in the city centre of Athens in comparison to those in Demokritos (suburban) are due to the fact that the sampler was placed on the ground, a few meters from the main road, which is characterised by heavy traffic.

Irrespective of the city, the dominant PAHs were BbjkF, RET, BghiP and IcdP. RET has been systematically used as a marker of softwood combustion (Ramdahl, 1983). It should be noted that the application of positive matrix factorisation to the chemically detailed annual databases of the AIRUSE project led to the conclusion that biomass burning is one of the prevailing emission sources and the major responsible for the exceedances of the European air quality thresholds (Amato et al., 2016). Despite the sampling campaign in Oporto has been carried out at a traffic station, it was observed that, after vehicle exhaust emissions, biomass burning was the second most important source of PM_{2.5}, explaining 18% of the mass concentrations. The fractional contribution from this source to PM_{2.5} doubles on exceedance days (>50 µg m⁻³). Approximately half of the exceedances was recorded in late August and early September, when intense wildfires struck the region. The other half was registered in winter months, indicating the input from residential wood combustion to the atmospheric PM_{2.5} levels. In Florence, together with traffic, biomass burning was also the dominant source contributing to the exceedances registered in the cold season. On average, the input from biomass burning to the PM_{2.5} loads was estimated to be 21%, reaching 29% during high pollution days. In Athens, this source accounted for 11% of the PM_{2.5} levels on an annual basis. Due to the economic crisis and the increased diesel oil prices, which was the most common way of residential heating in Greece, citizens of Athens have turned to alternative heating fuels, such as wood. It is important to highlight that the Greek site is considered as suburban, whereas the other AIRUSE sites (Italy and Portugal) are classified as urban background or traffic stations. This means that the levels of pollution at this site are probably lower than at other urban background sites of Athens, which are probably more comparable to the other AIRUSE locations. Despite the unequivocal association of RET with biomass burning, an additional origin in vehicle emissions cannot be put aside. In fact, corroborating previous observations in two tunnels in Sweden, Alves et al. (2016) detected RET as one of the major PAHs in particulate matter samples collected in a road underground infrastructure in Portugal.

BbjkF, BghiP and IcdP are high molecular weight compounds that have been associated with gasoline-powered vehicles, whilst diesel exhausts have been found to be enriched in lighter PAHs (Stogiannidis and Laane, 2015). Despite the higher proportion of diesel vehicles, especially

in Oporto and Florence, the lower molecular weight PAHs were not the most abundant because they are predominantly found in the gas phase. In Oporto and Florence, the total concentrations of PAHs in the winter campaign were about 3 times higher than those measured in the summer, while a 7-fold increase was observed in Athens. In this city, some compounds deserve particular attention due to their marked seasonality. On average, the PHE, PYR, RET and BghiP concentrations in the winter campaign were 257, 30, 68 and 20 times higher than those measured in the summer, respectively.

Diagnostic ratios between PAHs are commonly used as a tool for identifying and assessing pollution emission sources. A recent paper by Tobiszewski and Namieśnik (2012) lists typical values taken from the literature, reviews the applications of these ratios, comments on their use and specifies their limitations. The FLUO/(FLUO + PYR) ratio is one of the most widely used. Values < 0.5 indicate petrogenic origin, 0.4–0.5 fossil fuel combustion, and >0.5 grass, wood, or coal combustion. While in Oporto this isomeric ratio hardly varied from winter to summer, indicating an almost constant influence of petrogenic sources (Fig. 2), at the other two locations higher values were registered in the hot season. Apart from being influenced by seasonal sources, the higher summer values could suggest seasonal changes in this diagnostic ratio as a result of photodegradation, since PYR is decomposed by light faster than its isomer. The BaP/(BaP + BeP) ratio is ~0.5 close to sources, and decreases during “aging” because BaP is photodegraded faster than its isomer BeP. Thus, it would be expected to find the lowest BaP/(BaP + BeP) values in summer. Nevertheless, an inverse behaviour was observed in Florence and Athens. A few studies have indicated that biomass burning (Vicente et al., in press) and some stationary sources (Yang et al., 1998), such as steel industry, have a relatively higher emission factor for BaP compared with BeP. This suggests that the aerosol samples from these two cities were likely affected by some other sources with higher emissions of BaP than BeP. Another hypothesis, which cannot be confirmed due to the lack of additional measurements and because very little is known about the reactivity of PAHs adsorbed on carbonaceous particles, may be related to higher OH concentrations in the atmosphere of the Italian and Greek cities, since it has been observed that reactions of BaP with NO_x are more rapid, while BeP reacts faster with OH radicals (Tobiszewski and Namieśnik, 2012; and references therein). Values of 0.18, 0.37, 0.56, and 0.64 were proposed for the IcdP/(IcdP + BghiP) ratio for car, diesel, coal, and wood burning, respectively, although a broader range (0.35–0.70) was suggested by other researchers to indicate diesel emissions (Lai et al., 2013; and references therein). In the present study, the values obtained for the Portuguese city suggest that vehicle exhaust emissions were the dominant contribution source. Higher ratios in summer than in winter in the other two cities indicate enhanced photochemistry. BghiP photodegrades faster than IcdP, which suggests that particle aging shifts the IcdP/(IcdP + BghiP) ratio towards high values (Tobiszewski and Namieśnik, 2012). The BaA/(BaA + CHRY) ratio has been reported to be successful in discriminating vehicle emissions with values ~0.73 and ~0.5, respectively, for gasoline and diesel exhausts (Lai et al., 2013). While in Oporto the results were more consistent with a predominant diesel contribution, it seems that in Florence and Athens these compounds were predominantly emitted by gasoline engines. A concomitant pyrogenic origin and the fact that the BaA/(BaA + CHRY) ratio also tends to change as a result of atmospheric photoreactions may, however, mislead this interpretation.

With respect to NPAH, regardless of the city, 3-nitrobenzanthrene, 1,3-dinitropyrene, 1,6-dinitropyrene, 1,8-dinitropyrene and 6-nitrobenzo[a]pyrene were never present in the samples, whilst 5-NACEN was always the highest prevailing NPAH (Table 2). In Oporto, Florence and Athens, this constituent accounted for 84–89%, 90–100% and around 92% of the total NPAHs, respectively. 5-NACEN was also pointed out as one of the dominant NPAH in particles from both residential biomass combustion (Vicente et al., 2016) and vehicle emissions in a road tunnel (Alves et al., 2016). It was also measured as a primary

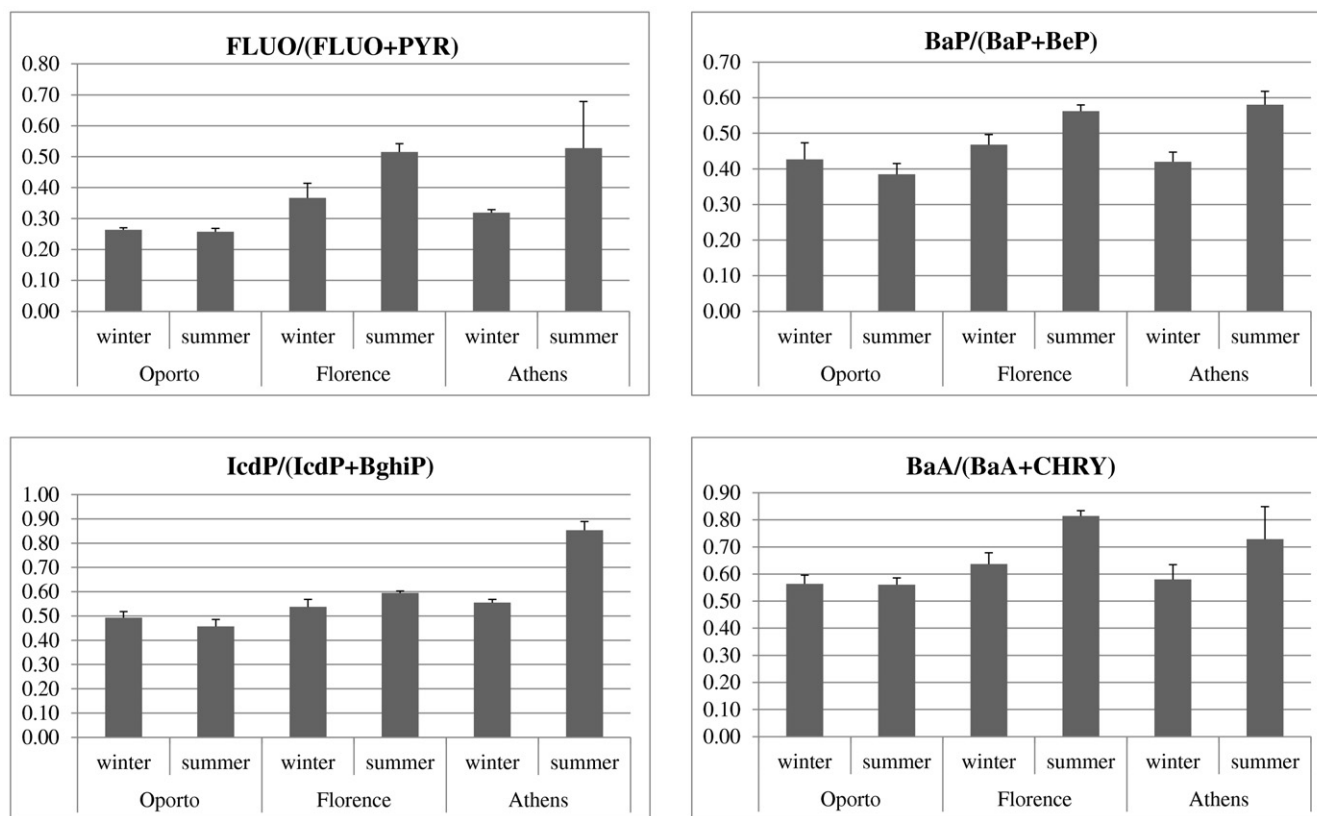


Fig. 2. Diagnostic ratios between PAHs.

compound emitted from coal combustion (Huang et al., 2014a), but also as an oxidation product of acenaphthene with OH and NO_x (Saufret-Szczepanski and Lane, 2004).

The most abundant OPAH in all cities was 1,8-NAA (Table 3). In Oporto, Florence and Athens, this compound represented about 70%, 30% and 55% of ΣOPAHs. Liu et al. (2015) detected 1,8-NAA in PM_{2.5} samples from Beijing, pointing out it as a secondary atmospheric photochemistry product. This OPAH has also been identified as a product of the reactions of ACENY and ACEN with OH and O₃ (Zhou and Wenger, 2013a, 2013b). However, its primary emission cannot be ruled out since it has been detected in aerosols collected in an urban road tunnel (Alves et al., 2016), as well in PM₁₀ from residential biomass combustion (Vicente et al., 2016).

The relative contribution of individual AZAs to their total concentrations differed considerably between seasons (in the same city) and between cities. This is probably a reflection of differences in primary emission sources between the different sampling sites (Bandowe et al., 2016). Among the AZAs analysed, QUI was the only one found in either winter or summer samples of every city. Besides having an origin in combustion sources, QUI may also derive from tyre wear, since some tyre brands use this AZA as anti-degradant to protect rubber against oxygen, ozone, and fatigue cracking (Alves et al., 2016).

3.4. Carcinogenic risk

The average BaP_{eq} for the whole sampling periods in Oporto, Florence and Athens was 2.37, 1.01 and 0.30 ng m⁻³, respectively (Fig. 3). At each location, the BaP_{eq} for winter season was higher than for summer season. Much higher BaP_{eq} concentrations, in the ranges of 2–64, 3–26 and 0.72–23 ng m⁻³, were reported for Xi'an and Beijing (both in China) and Zonguldak (Turkey), respectively (Bandowe et al., 2014; Jia et al., 2011; Akyüz and Çabuk, 2008). Based on PM_{2.5}-bound 16 priority PAHs, Martellini et al. (2012) obtained similar levels to those of the AIRUSE cities for Tuscany sites: 0.79 (Florence, traffic impacted),

0.34 (Florence, urban background) and 0.13 ng m⁻³ (Livorno, suburban background).

In Oporto, the major contributions to total BaP_{eq} came from 6-NCHRY (28%), BaP (26%) and BPYRone (17%). Compounds with the greatest contribution to BaP_{eq} in Florence were BaP (34%), DahA (33%) and BPYRone (10%). In Athens, the major proportion of BaP_{eq} was due to the contribution of four compounds: 5-NACEN (29%), BPYRone (21%), BaP (20%) and DahA (17%). Thus, without including OPAHs and NPAHs in the calculations, as is often the case, the carcinogenic risk will be almost certainly underestimated. The determination of atmospheric concentrations of PAH derivatives is quite important for risk assessment, but further investigations are needed to assess the carcinogenic potencies of NPAHs, and especially OPAHs.

In Oporto, according to the WHO method, for a lifetime of 70 years, the ECR averaged 2.06×10^{-4} (Table 4). Thus, an estimated mean excess of 206 per million people cancer cases was attributable to inhalation of PM_{2.5}-bound 20 PAHs, 3 OPAHs and 6 NPAHs. The corresponding estimated cancer cases for Florence and Athens were 88 and 26 per million people, respectively. Regardless of sampling location, the average ECRs in winter were 2 to 3 times higher than in summer. According to the American Environmental Protection Agency, 10^{-6} is the level of risk considered acceptable or inconsequential, since this compares favourably with risk levels from some 'normal' human activities, such as diagnostic X-rays, fishing, skiing, etc. An ECR $\geq 10^{-3}$ is considered very serious, and there is high priority for paying attention to such health problem (Bai et al., 2009). It is therefore concluded that the lung cancer risk due to exposure to PACs in the 3 AIRUSE cities (Athens, Florence and Oporto) is not negligible and should be taken into account for health protection in the future. It must be borne in mind that the 3 sampling sites are differently impacted by sources. While in Oporto primary traffic-related emissions dominate, the other two sites reflect urban background or suburban characteristics. Thus, in Florence and Athens the risk may be even higher in the vicinity of the numerous streets and avenues with heavy traffic. ECRs in

Table 1Minimum, maximum and average (in brackets) concentrations (ng m^{-3}) of PAHs in $\text{PM}_{2.5}$ samples collected in three Southern European cities.

Compound	Abbreviation	Oporto		Florence		Athens	
		Winter	Summer	Winter	Summer	Winter	Summer
1,2,3,4-Tetrahydronaphthalene	THNAP	0.001–0.007 (0.003)	bdl–0.007 (0.004)	0.055–0.086 (0.062)	0.058–0.084 (0.069)	0.011–0.018 (0.015)	bdl–0.004 (0.003)
Naphthalene	NAP	0.057–0.515 (0.173)	0.065–0.184 (0.134)	0.117–0.195 (0.159)	0.125–0.185 (0.146)	0.031–0.047 (0.039)	bdl–0.072 (0.011)
2-Methylnaphthalene	2-MNAP	0.017–0.127 (0.045)	0.017–0.051 (0.038)	0.052–0.081 (0.065)	0.056–0.069 (0.060)	0.013–0.018 (0.015)	bdl–0.094 (0.012)
1-Methylnaphthalene	1-MNAP	0.023–0.152 (0.049)	0.012–0.051 (0.038)	0.045–0.069 (0.056)	0.050–0.065 (0.054)	0.006–0.017 (0.014)	bdl–0.076 (0.009)
Biphenyl	BP	0.029–0.182 (0.060)	bdl–0.074 (0.035)	0.056–0.080 (0.068)	0.054–0.096 (0.066)	0.012–0.025 (0.019)	bdl–0.088 (0.013)
1,3-Dimethylnaphthalene	1,3-DMNAP	bdl–0.032 (0.006)	bdl	bdl	bdl–0.087 (0.043)	bdl–0.023 (0.002)	bdl–0.083 (0.012)
Acenaphthylene	ACENY	0.048–0.352 (0.130)	0.041–0.102 (0.074)	bdl–0.164 (0.070)	bdl–0.135 (0.019)	0.040–0.073 (0.058)	bdl–0.049 (0.014)
Acenaphthene	ACEN	bdl–0.036 (0.008)	bdl–0.011 (0.004)	0.048–0.088 (0.060)	0.054–0.073 (0.061)	0.011–0.016 (0.013)	bdl–0.005 (0.002)
Fluorene	FLU	bdl–0.081 (0.034)	bdl–0.038 (0.025)	bdl–0.119 (0.071)	0.073–0.093 (0.078)	bdl–0.043 (0.007)	bdl–0.028 (0.020)
Phenanthrene	PHEN	0.187–1.68 (0.682)	0.112–0.343 (0.262)	0.0650–0.416 (0.187)	0.064–0.098 (0.081)	0.040–0.270 (0.152)	bdl–0.006 (0.001)
Anthracene	ANTH	bdl–0.377 (0.112)	0.027–0.071 (0.052)	bdl–0.156 (0.061)	0.110–0.175 (0.124)	bdl–0.296 (0.030)	bdl–0.063 (0.016)
Cyclopenta[def]phenanthrene	CPdefP	bdl–0.283 (0.123)	bdl	bdl	bdl	bdl	bdl
2-Methylphenanthrene	2-MPHEN	0.055–0.383 (0.145)	bdl–0.102 (0.058)	bdl–0.161 (0.097)	bdl–0.099 (0.081)	0.026–0.080 (0.051)	bdl
3,6-Dimethylphenanthrene	3,6-DMPHEN	bdl–0.172 (0.055)	bdl–0.052 (0.012)	bdl–0.161 (0.043)	bdl	bdl	bdl
Fluoranthene	FLUO	0.142–1.15 (0.477)	0.068–0.214 (0.152)	0.082–0.371 (0.181)	0.070–0.090 (0.076)	0.040–0.181 (0.110)	0.004–0.038 (0.010)
Pyrene	PYR	0.383–3.29 (1.34)	0.190–0.684 (0.442)	0.090–0.731 (0.334)	0.057–0.091 (0.071)	0.088–0.382 (0.236)	0.003–0.016 (0.008)
Retene	RET	0.356–4.07 (1.79)	0.064–1.77 (0.715)	0.389–0.908 (0.633)	0.211–0.285 (0.236)	0.275–2.33 (1.09)	bdl–0.082 (0.016)
Benzo[a]anthracene	BaA	0.390–2.69 (1.15)	0.141–0.568 (0.302)	0.250–0.871 (0.553)	0.179–0.223 (0.192)	0.088–0.374 (0.218)	0.054–0.105 (0.061)
Chrysene + triphenylene	CHRY + TRY	0.340–2.13 (0.878)	0.101–0.450 (0.240)	0.103–0.593 (0.333)	0.037–0.061 (0.044)	0.060–0.291 (0.157)	0.013–0.155 (0.031)
Benzo[b + j + k]fluoranthenes	BbjkF	0.864–4.20 (2.03)	0.276–1.23 (0.650)	0.317–1.49 (0.909)	0.195–0.246 (0.222)	0.205–0.722 (0.484)	0.063–0.272 (0.091)
Benzo[e]pyrene	BeP	0.572–2.63 (1.26)	0.189–0.722 (0.424)	0.196–0.908 (0.573)	0.110–0.144 (0.126)	0.125–0.415 (0.289)	0.035–0.057 (0.041)
Benzo[a]pyrene	BaP	0.314–2.25 (0.979)	0.101–0.459 (0.269)	0.226–0.755 (0.491)	0.150–0.186 (0.162)	0.102–0.299 (0.208)	0.048–0.118 (0.059)
Perylene	PERY	0.081–0.482 (0.222)	0.031–0.105 (0.070)	0.105–0.230 (0.165)	0.094–0.106 (0.098)	0.024–0.070 (0.050)	bdl–0.029 (0.005)
Indeno[1,2,3-cd]pyrene	IcdP	0.663–3.37 (1.53)	0.205–0.790 (0.481)	0.394–1.34 (0.887)	0.271–0.331 (0.297)	0.214–0.607 (0.441)	0.087–0.180 (0.101)
Dibenzo[a,h]anthracene	DahA	0.145–0.753 (0.324)	0.063–0.211 (0.123)	0.250–0.413 (0.347)	0.233–0.289 (0.244)	0.095–0.176 (0.140)	bdl–0.245 (0.047)
Benzo[ghi]perylene	BghiP	0.821–3.62 (1.56)	0.220–0.897 (0.567)	0.292–1.31 (0.798)	0.182–0.225 (0.202)	0.151–0.490 (0.355)	0.010–0.038 (0.018)
Coronene	COR	0.430–3.00 (1.10)	0.156–0.663 (0.429)	0.215–0.900 (0.544)	0.140–0.188 (0.166)	0.141–0.350 (0.250)	0.027–0.069 (0.056)

bdl – below detection limit.

Table 2Minimum, maximum and average (in brackets) concentrations (ng m^{-3}) of NPAHs in $\text{PM}_{2.5}$ samples collected in three Southern European cities.

Compound	Abbreviation	Oporto		Florence		Athens	
		Winter	Summer	Winter	Summer	Winter	Summer
1-Nitronaphthalene	1-NNAP	bdl–0.107 (0.025)	bdl–0.084 (0.027)	bdl–0.772 (0.153)	bdl	bdl–0.104 (0.018)	0.070–0.541 (0.234)
2-Nitrobiphenyl	2-NBP	bdl–0.266 (0.064)	bdl–0.374 (0.060)	bdl–0.509 (0.133)	bdl	bdl–1.62 (0.465)	bdl
5-Nitroacenaphthene	5-NACEN	3.20–47.8 (13.6)	1.38–18.5 (8.18)	1.84–21.2 (9.83)	1.86–5.80 (3.36)	5.83–21.2 (14.6)	0.914–4.79 (2.49)
2-Nitrofluorene	2-NFLU	bdl–1.55 (0.491)	0.077–0.988 (0.385)	bdl–0.780 (0.292)	bdl	bdl–0.833 (0.470)	bdl
9-Nitroanthracene	9-NANTH	bdl–5.26 (1.32)	0.075–0.580 (0.280)	bdl–0.945 (0.377)	bdl	bdl–0.939 (0.246)	bdl
9-Nitrophenanthrene	9-NPHEN	bdl–1.18 (0.262)	bdl–0.400 (0.096)	bdl–0.616 (0.068)	bdl	bdl–0.396 (0.040)	bdl
3-Nitrofluoranthene	3-NFLUA	bdl–0.476 (0.105)	bdl–0.429 (0.064)	bdl	bdl	bdl	bdl
1-Nitropyrene	1-NPYR	bdl–0.438 (0.085)	bdl	bdl	bdl	bdl	bdl
2,7-Dinitrofluorene	2,7-DNFLUO	bdl–0.120 (0.032)	bdl–0.118 (0.012)	bdl	bdl	bdl	bdl
6-Nitrochrysene	6-NCHRY	bdl–0.881 (0.109)	bdl–0.352 (0.035)	bdl	bdl	bdl	bdl

bdl – below detection limit.

Table 3
Minimum, maximum and average (in brackets) concentrations (ng m⁻³) of OPAHs and AZAs in PM_{2.5} samples collected in three Southern European cities.

OPAHs	Abbreviation	Oporto		Florence		Athens	
		Winter	Summer	Winter	Summer	Winter	Summer
1-Indanone	1-INDA	0.303–2.71 (0.793)	bdl-0.598 (0.205)	0.689–1.54 (1.04)	bdl-1.71 (0.702)	0.009–0.804 (0.228)	bdl-0.138 (0.038)
1,4-Naphthoquinone	1,4-NQ	0.361–1.76 (0.668)	bdl-0.661 (0.352)	bdl-1.83 (0.651)	bdl	bdl-1.55 (0.594)	bdl
1-Naphthaldehyde	1-NLD	0.241–0.954 (0.383)	bdl-0.422 (0.245)	bdl-0.886 (0.098)	bdl	bdl	bdl
2-Biphenylcarboxaldehyde	2-BPCD	bdl-0.109 (0.026)	bdl-0.265 (0.087)	bdl	bdl	bdl	bdl
9-Fluorenone	9-FLO	0.500–2.80 (1.04)	bdl-0.625 (0.431)	0.812–1.70 (1.14)	0.824–1.63 (1.13)	0.448–1.93 (0.769)	bdl-0.120 (0.028)
1,2-Acenaphthylenequinone	1,2-ACQ	bdl-8.19 (1.88)	bdl-4.01 (2.32)	bdl-1.60 (0.178)	bdl	bdl-2.41 (1.06)	bdl
9,10-Anthraquinone	9,10-ANQ	bdl-3.93 (1.15)	0.172–0.488 (0.321)	bdl-1.34 (0.614)	bdl-0.715 (0.102)	0.340–0.576 (0.450)	bdl-0.048 (0.009)
1,8-Naphthalic anhydride	1,8-NAA	13.1–64.7 (29.5)	4.25–23.6 (12.7)	0.529–9.56 (2.94)	0.268–1.85 (0.973)	2.23–14.2 (7.12)	0.115–0.674 (0.381)
4H-Cyclopenta[def]phenanthrene	CPHENone	0.101–0.637 (0.259)	0.083–0.184 (0.118)	bdl-0.465 (0.181)	bdl	bdl-0.191 (0.136)	bdl
2-Methylanthracene-9,10-dione	2-MANQ	0.242–1.59 (0.585)	bdl-0.326 (0.205)	bdl-1.27 (0.643)	bdl	bdl	bdl
Benzo[a]fluorenone	BaFLUone	0.099–0.663 (0.261)	0.129–0.228 (0.161)	bdl-0.859 (0.437)	bdl	bdl-0.312 (0.210)	bdl
7H-benz[de]anthracene-7-one	BANTone	0.846–3.32 (1.85)	0.341–0.817 (0.587)	1.52–2.70 (2.07)	bdl-1.32 (0.188)	0.565–1.06 (0.834)	bdl-0.422 (0.242)
Benz[a]anthracene-7,12-dione	7,12-BaA	0.389–2.37 (0.978)	0.172–0.525 (0.331)	bdl-0.309 (0.112)	bdl	0.112–0.321 (0.227)	bdl
Naphthacene-5,12-dione	5,12-NACQ	0.220–1.26 (0.452)	0.268–0.413 (0.321)	bdl-1.85 (0.610)	bdl	bdl-0.704 (0.551)	bdl
6H-benzo[cd]pyrene-6-one	BPYRone	0.851–3.00 (1.96)	0.229–0.965 (0.579)	bdl-1.35 (0.552)	bdl	0.238–0.652 (0.463)	bdl-0.061 (0.006)
AZAs							
Quinoline	QUI	bdl-0.357 (0.119)	bdl-0.090 (0.029)	bdl-0.660 (0.405)	bdl-0.424 (0.285)	bdl-0.155 (0.016)	bdl-0.130 (0.084)
Benzo[h]quinoline	BQI	bdl-0.129 (0.051)	bdl-0.136 (0.081)	bdl	bdl	bdl	bdl-0.167 (0.031)
Acridine	ACR	bdl-0.373 (0.067)	bdl-0.102 (0.029)	bdl	bdl	bdl-0.194 (0.019)	bdl-0.216 (0.063)
Carbazole	CBZ	bdl-0.097 (0.036)	bdl-0.103 (0.056)	bdl-0.414 (0.046)	bdl	bdl-0.144 (0.055)	bdl

bdl – below detection limit.

the range from 1.4×10^{-4} to 5.6×10^{-3} , averaging 1.45×10^{-3} , were reported for a Chinese megacity, using the same PACs of the present study (Bandowe et al., 2014). Jia et al. (2011) estimated the inhalation cancer risk of 17 PAHs during different source control periods of the Beijing Olympic Games from July to October 2008. The estimated lifetime excess inhalation cancer risk ranged from 1.22×10^{-5} to 9.64×10^{-4} during the non-source control period. Cancer risks of 18 PAHs (gas + particulate phases) between 2.2×10^{-5} and 1.8×10^{-4} were estimated for a semirural and a suburban area near an industrial complex in Tarragona, Spain (Ramirez et al., 2011). Lower ECRs in European cities are likely due to cleaner energy sources, more efficient industrial technologies, and better emission control strategies.

As it can be seen from Table 4, results from different risk assessment methods varied over a large range, from the magnitude of 10^{-5} to 10^{-3}

or from 10^{-8} to 10^{-6} . This large variation is due to the adoption of diverse unit risk levels by different agencies. The assessment of inhalation cancer risk has several uncertainties and limitations: i) the BaP_{eq}-based approach is necessarily limited to a few PACs that have been measured in the experiments and may not represent the toxicity of all polyaromatic compounds to which the general population is exposed; ii) the TEF values, which were established from toxicological animal studies, and the value of BaP UR, which was extrapolated from the results of epidemiological studies with exposure to high concentrations, can be biased in some cases; iii) the sampling sites may not be representative of the entire urban areas under evaluation; iv) the point-estimate approach assumes additive cancer risk, but different isomers, in conjunction with other pollutants (including metals) may increase or decrease the toxicity of PACs, i.e., possible synergistic and/or antagonistic

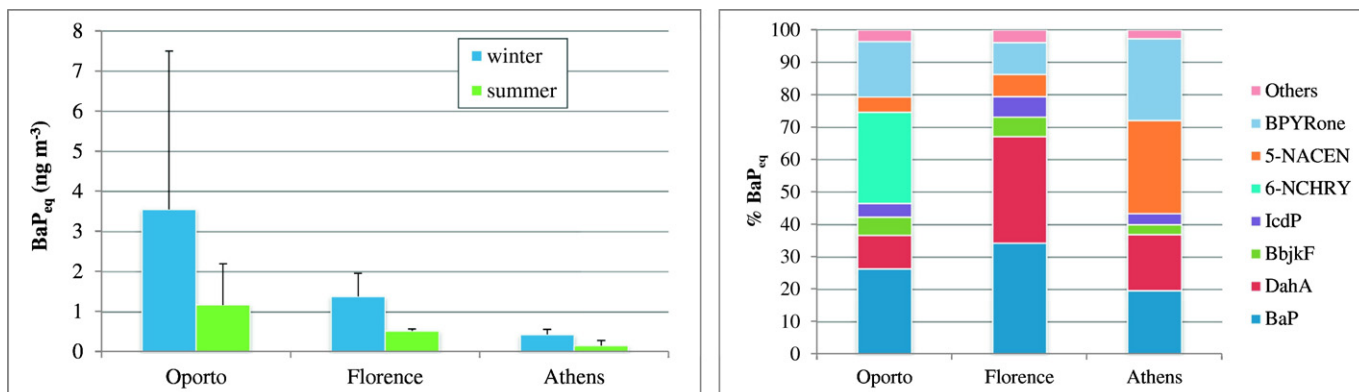


Fig. 3. Benzo[a]pyrene equivalent concentrations and percentage contributions of individual compounds to the total.

Table 4
Excess cancer risk from inhalation (ECR) of PM_{2.5}-bound PACs for the 3 cities.

	Whole period	Winter	Summer
OPORTO (CalEPA method)			
Mean	2.61×10^{-6}	3.92×10^{-6}	1.30×10^{-6}
Min	4.40×10^{-7}	1.37×10^{-6}	4.40×10^{-7}
Max	1.58×10^{-5}	1.58×10^{-5}	4.41×10^{-6}
OPORTO (WHO method)			
Mean	2.06×10^{-4}	3.10×10^{-4}	1.03×10^{-4}
Min	3.48×10^{-5}	1.08×10^{-4}	3.48×10^{-5}
Max	1.25×10^{-3}	1.25×10^{-3}	3.49×10^{-4}
FLORENCE (CalEPA method)			
Mean	1.11×10^{-6}	1.53×10^{-6}	5.82×10^{-7}
Min	5.42×10^{-7}	6.75×10^{-7}	5.42×10^{-7}
Max	2.31×10^{-6}	2.31×10^{-6}	6.76×10^{-7}
FLORENCE (WHO method)			
Mean	8.80×10^{-5}	1.21×10^{-4}	4.60×10^{-5}
Min	4.29×10^{-5}	5.34×10^{-5}	4.29×10^{-5}
Max	1.83×10^{-4}	1.83×10^{-4}	5.35×10^{-5}
ATHENS (CalEPA method)			
Mean	3.28×10^{-7}	4.80×10^{-7}	1.76×10^{-7}
Min	8.42×10^{-8}	3.35×10^{-7}	8.42×10^{-8}
Max	8.34×10^{-7}	8.34×10^{-7}	5.57×10^{-7}
ATHENS (WHO method)			
Mean	2.59×10^{-5}	3.80×10^{-5}	1.39×10^{-5}
Min	6.66×10^{-6}	2.65×10^{-5}	6.66×10^{-6}
Max	6.59×10^{-5}	6.59×10^{-5}	4.41×10^{-5}

effects with other existing compounds may take place. However, even with these uncertainties, taking into account the scarcity of data, our assessment gives a general evaluation of the inhalation cancer risk associated with exposure to PACs in atmospheres with identical characteristics.

4. Conclusions

More than 60 PM_{2.5}-borne PACs were investigated in the atmosphere of 3 Southern European cities. The detection of so many compounds in PM_{2.5} indicated that a large part of these constituents were able to reach the deepest part of the human respiratory system and highlighted the importance of studying these classes of compounds from a sanitary point of view. As expected, higher concentrations were observed at the traffic impacted site in Oporto than at the urban background station in Florence and the suburban location in Athens. Most PACs showed notable seasonal variation with higher concentrations in winter. The application of diagnostic ratios pointed out a dominant petrogenic and pyrogenic origin for PAHs, which were also found to depend on meteorological conditions. As inhalation of PACs may result in serious health and environmental problems, it is fundamental to continue with efforts at reducing the emissions, mainly related to vehicular transport and biomass burning, of these pollutants. The source identification approach based on diagnostic ratios is not conclusive and should be used with caution because the diversity of fuels and combustion conditions would produce variations in the ratios. Further, the results suggested that some ratios are sensitive to photodegradation. Therefore, the use of the different diagnostic ratios should be combined with other tools to improve the ability of discriminating the sources of PAHs.

Together with BaP, DahA, BbKf and IcdP, 6-NCHRY, 5-NACEN and BPyRone were the compounds that contributed most to the BaP_{eq} concentrations. Thus, the risk induced by PAH derivatives should not be neglected, and more research is required to better understand and control their effect on human health. The estimated lifetime lung cancer risk for the 3 sites was higher than the WHO and the U.S. EPA

recommended values but lower than the threshold value of 10^{-3} considered a priority risk level. It should, however, be borne in mind that the assessments are only based on particle-phase PACs. It would be prudent to take PAC concentrations in both gas and particle phases into account in future health-risk evaluations. The real risk values may otherwise be underestimated. Standardised methods to evaluate public health risks should be recommended to official agencies concerned with environmental quality and public health.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.03.256>.

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