Annual exposure to PAHs in urban environments linked to wintertime wood-burning episodes

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants in fine particulate matter (PM) long known to have mutagenic and carcinogenic effects, but much is unknown about the importance of local and remote sources to PAH levels observed in population-dense urban environments. A year-long sampling campaign in Athens, Greece, where more than 150 samples were analyzed for 31 PAHs and a wide range of chemical markers were used in combination with Positive Matrix Factorization (PMF) to constrain the temporal variability, sources and carcinogenic risk associated with PAHs. We find that biomass burning (BB), a source mostly effective during wintertime intense pollution events (observed for 18% of measurement days in 2017), lead to wintertime PAH levels 7 times higher than in other seasons and was responsible for annual mean PAH concentrations (31%) comparable to those from diesel/oil (33%) and gasoline (29%) sources. The contribution of non-local sources, although limited on an annual basis (7%), was increased during summer, becoming comparable to that of local sources combined. The fraction of PAHs associated with BB is linked to increased health risk compared to the other sources, accounting for almost half the annual carcinogenic potential of PAHs (43%). This can result in a larger number of excess cancer cases due to BB-related high PM levels and urges immediate action to reduce residential BB emissions in urban areas facing similar issues.

Keywords:

PAHs, Biomass Burning, Air Pollution Evens, Source Apportionment, Receptor Modeling, Positive Matrix Factorization, Carcinogenic potential, Risk Assessment

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are abundant in the atmosphere and can be present in the gas or particulate phase (Finlayson-Pitts, 1997; Lin et al., 2015). Ambient PAHs originate mainly from internal combustion engines, stationary sources   power and industrial plants, residential heating (including using firewood) , as well as from regional sources (e.g. wildfires) (Finlayson-Pitts, 1997; Simoneit, 2002; Bond et al., 2013). Specifically, biomass burning (BB) emissions heavily impact air quality (Karagulian et al., 2015), ecosystems (Crutzen and Andreae, 1990) and the climate (Bond et al., 2013), and are considered of ever-increasing importance for global aerosol source characterization.

Particular PAH members are either known or potential carcinogens and mutagens (IARC,2010; Nowakowski et al., 2017). The IARC Group 1 carcinogen Benzo[*a*]pyrene (BaP) is extensively studied among PAHs and is used as a marker for PAH toxicity. The European Union has set the air quality standard for the carcinogenic risk of PAHs at an annual target value of 1 ng m^{-3} BaP.

The presence of PAHs tends to be highly enriched in large urban agglomerations (Jiang et al., 2014; Mo et al., 2019; Ringuet et al., 2012), such as Athens, Greece. Studies to date in Athens show that PAH concentrations are significantly enhanced during the cold period of the year (Mantis et al., 2005). Potential sources in the area include incomplete combustion processes, like domestic heating, road transport, fossil fuel combustion and cooking (Stavroulas et al., 2019). Since the 2010 economic crisis in Greece, fireplace and woodstove usage for domestic heating increased dramatically (Grivas et al., 2018; Paraskevopoulou et al., 2014; Theodosi et al., 2018). Moreover, the contribution of wildfires to regional background PAHs in the area could be significant, given their increased incidence as a result of climate change (McCarty et al., 2020; O'Dell et al., 2020).

The uncontrolled residential BB emissions have led to the appearance of intense pollution events (IPE), during which very high levels of organic aerosols are observed in urban centers like Athens (Florou et al., 2017), Thessaloniki (Saffari et al., 2013) , Paris (Fountoukis et al., 2016) and other cities worldwide. It is feared that excessive exposure of urban populations to ambient wood-smoke pollution can cause severe health effects (Kocbach Bølling et al., 2009; Naeher et al., 2007), especially in view of the very high concentrations of highly-oxidized organic species from nighttime chemistry, and their potential to enhance toxicity (Kodros et al., 2020).

It is worth noting that since 2013 – following the remarkable increase of biomass use for residential heating in Greece – violations of the EU limit value for BaP have started to be recorded in several Greek cities, with concentrations showing a clear wintertime enhancement (NAPMN, 2020). Greek cities, where excessive wood burning appeared as a result of the recent recession, are not a "special case", since residential BB is emerging as a major issue for urban air quality throughout Europe. Studies in Central European cities have reported BB contributions to cumulative particle PAH concentrations that even exceed 50% (Li et al., 2018; Masiol et al., 2020; Schnelle-Kreis et al., 2007) while in other Mediterranean urban areas its impact appears less profound (Callén et al., 2014).

Although much work has been done on sources of PAHs, their attribution using atmospheric samples is often pursued through highly uncertain diagnostic ratios for measured concentrations (Katsoyiannis et al., 2011). Relatively few studies exist in Europe and N. America that utilize receptor modeling (e.g. Schnelle-Kreis et al., 2007; Sofowote et al., 2008), an approach that can quantify the relative

contributions of distinct local and regional sources to PAH levels and associated carcinogenic risks that
urban populations are exposed to. The identification of carbonaceous aerosol source profiles can provide
80 useful reference for source apportionment studies that use long-term chemical speciation data in urban
areas, enabling a source-specific toxicity assessment. Here, we demonstrate this for Athens, Greece, one
of the largest urban centers in the E. Mediterranean, and characterize PAH sources associated with
biomass burning, diesel/oil burning, gasoline vehicles and non-local aerosols, while we assess the
importance of long-range transport for PAH levels observed in the region.

2. Materials and Methods

2.1 Study area

The Greater Athens Area (GAA, Figure S1), with 3.8 million inhabitants, is one of the largest
metropolitan regions in Southern Europe and a major commercial and transportation hub. Nearly 3
million private cars are registered for circulation in the GAA, along with 0.3 million trucks and buses
90 (Hellenic Statistical Authority, 2020). Up to 2011, diesel-powered private cars were banned in Athens
and while nowadays they consist the majority of new sales, they still only account for only 10% of the
fleet, approximately. Up to 2011, heating oil has been the predominantly used fuel for domestic heating
in Athens (in 76% of residences). However, between 2011-2018 its consumption in the GAA decreased
by 61% (Hellenic Statistical Authority, 2019) , with people resorting to alternative sources including
95 biomass burning in fireplaces and stoves. Industrial activity in the GAA is minor in the central basin and
mostly concentrated in the Thriassion plain, 10-20 km to the northwest of central Athens and separated
by a low altitude mountain range. The port of Piraeus, to the southwest, is the largest passenger port in
Europe and also one of the busiest container ports in the Mediterranean (Figure S1). The complex
topography of the basin favors the appearance of mesoscale flows throughout the year and the frequent
100 stagnation of air masses (Kassomenos et al., 1998).

2.2 Sampling and Analyses

Ambient $PM_{2.5}$ samples were collected between December 4, 2016 – January 31, 2018, at the urban
background site of the National Observatory of Athens (NOA) at Thissio (37.97326◦ N, 23.71836◦ E), a
location representative of urban background air quality in central Athens (Stavroulas et al., 2019;
105 Theodosi et al., 2018). During the winter months (December-February), separate daytime and nighttime
filters were collected every 12h (6:00-18:00 LST, 18:00-6:00 LST, respectively), for a total of 80
samples, while 76 24-h filters were sampled from March to November. A low-volume sampler (3.1 PNS
15, Comde Derenda GmbH, Stahnsdorf, DE) with a flow rate of 2.3 $m^3 h^{-1}$ was used to collect particles
onto quartz fiber filters of 47mm diameter (Flex Tissuquartz, Pall Corporation, Port Washington, NY,
110 USA). Field and laboratory blanks were routinely collected.
PAHs were quantified by gas chromatography-mass spectrometry (GC-MS, Agilent 6890N, Agilent
Technologies Inc., Santa Clara, CA, USA). Prior to the analysis, samples were spiked with a mixture of
deuterated internal standards for identification of PAHs and calculation of recovery efficiencies (16
members, LGC Standards, Middlesex, UK). Extraction was made following the pre-established

115   procedure of Gogou et al. (1998) with modifications (Parinos et al., 2019) (Supplement, Section S1, Table S1). Briefly, extracts were obtained using a 50:50 n-hexane-dichloromethane mixture and purified on a silica column. PAHs were eluted with a 10 mL n-hexane/ethyl acetate (9:1 v/v) mixture and placed into a glass vial for further concentration under a gentle nitrogen stream. [^{2}H$_{12}$]perylene, used as an internal standard, was spiked into the vial before sealing and storage. Limits of Detection (LODs) were

120   calculated as 3 times the standard deviation of blanks. On the day of the analysis, injections with internal standards were also run to calculate relative response factors (RRF). The identification of compounds was based on the retention time, mass fractionation and co-injection of standard mixtures.

Organic and elemental carbon (OC, EC) were determined with the thermal-optical transmission method (TOT, Sunset Laboratory Inc., Portland, OR, USA) (Cavalli et al., 2010; Paraskevopoulou et al., 2014),

125   water-soluble ions with ion chromatography (IC) (Paraskevopoulou et al., 2014) and monosaccharide anhydrides (levoglucosan, mannosan and galactosan) using High-Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD) (Iinuma et al., 2009).

The submicron organic aerosol (OA) fraction, that was monitored by an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Inc., Billerica, MA, USA)(Ng et al., 2011) during the first winter period

130   (December 2016 – February 2017), was decomposed into components representative of specific sources-processes (namely hydrocarbon-like OA, biomass burning OA, cooking OA, semi-volatile and low-volatility oxygenated OA), through Positive Matrix Factorization (PMF) using the Source Finder toolkit (SoFi) (Bougiatioti et al., 2014; Canonaco et al., 2013). Finally, equivalent Black carbon (BC) levels were monitored by a 7-wavelenth aethalometer (AE33, Magee Scientific, Berkeley, CA, USA) and

135   apportioned in two components, associated with fossil-fuel combustion (BC$_{ff}$) and wood-burning (BC$_{bb}$), respectively (Drinovec et al., 2015; Liakakou et al., 2020).

Regulatory pollutants and meteorological parameters were routinely measured at the Thissio station. Four-day air mass back trajectories, arriving at Thissio at 1000m, were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model and grouped daily using cluster analysis

140   (Kalkavouras et al., 2020).

2.3 Source apportionment

PMF analysis was performed using the EPA PMF 5.0 model (Norris et al., 2014). The 12-h samples collected during the winter intensive campaigns were appropriately combined to 24-h periods, between 6:00 LST of each day and 6:00 LST of the following. In total, 104 24-h samples were considered for the

145   analysis. The carbonaceous aerosol speciation dataset that was used consisted of OC and EC, PAHs, oxalate and levoglucosan. Total carbon (TC: sum of OC, EC) was included as a total variable in the PMF model, for a meaningful mass balance approach (Piletic et al., 2013; Valotto et al., 2017). In total, 16 species were entered in the analysis, including 12 PAH members. Rotational and random errors were assessed using the bootstrap (BS) and displacement (DISP) error estimation methods included in the EPA

150   PMF 5.0 software (Paatero et al., 2014). Details on PMF model design parameters, solution metrics, uncertainties and error indices are provided in the Supplement (Section S2, Table S2).

2.4 PAH contribution to carcinogenic risk

The "toxic equivalence factor" (TEF) approach was used to estimate the carcinogenic potency of measured PAHs, in which the toxicity of each member is expressed using BaP as reference (Taghvaee et al., 2018):

$$\sum BaP_{eq} = \sum (C_i \ TEF_i) \tag{1}$$

where C_i is the concentration (ng m^{-3}) and TEF_i is the Toxicity Equivalent Factor of each member (Bari et al., 2010; Nisbet and LaGoy, 1992). The lifetime excess cancer risk (ECR) from inhalation was estimated as follows:

$$ECR = \sum BaP_{eq} \ UR_{BaP} \tag{2}$$

where UR_{BaP} (unit risk) refers to the number of excess cancer cases in the population with chronic inhalation exposure to 1 ng m^{-3} of BaP over a lifetime of 70 years. Estimations were made using reference UR_{BaP} values of 1.1×10^{-6} (0.11 cases per 100,000 people) – according to the Office of Environmental Health Hazards Assessment (OEHHA) of the California Environmental Protection Agency (CalEPA) – and 8.7×10^{-5} (8.7 cases per 100,000 people) – according to the World Health Organization (WHO) (Alves et al., 2017; Elzein et al., 2019).

3.Results and Discussion

3.1 Temporal Variability

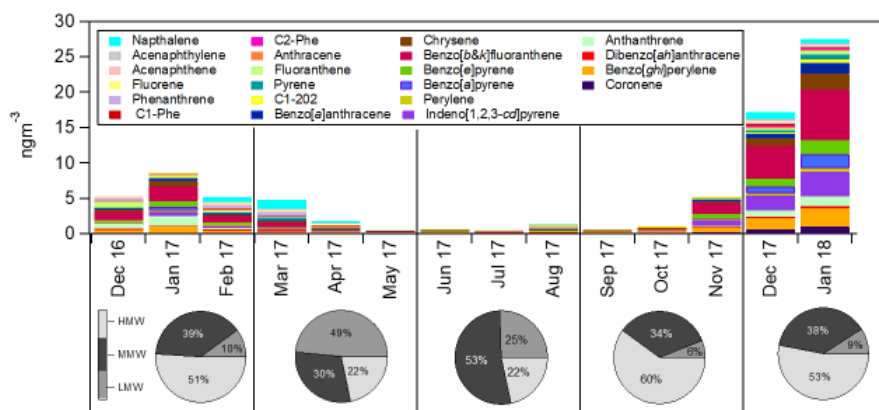
Figure 1 presents the monthly variation of total PAH concentrations, displaying a notable wintertime enhancement of concentrations relative to summer. Mean ΣPAH concentrations in winter 2016-2017, spring 2017, summer 2017, fall 2017 and winter 2017-2018 were 7.0 ± 10.1, 2.5 ± 4.1, 0.9 ± 0.9, 2.2 ± 3.2 and 22.3 ± 26.8 ng m^{-3}, respectively, indicating a clear seasonal cycle. The mean annual (2017) BaP concentration in this study (0.26 ng m^{-3} in 2017) does not exceed the EU target value, but remains above the WHO reference level (0.12 ng m^{-3}), with largely increased BaP levels being observed during episodic wintertime events. These results can be placed in context by comparison against past studies on PAHs in the GAA (Table S3), that have identified similar seasonal profiles, although not with such pronounced winter-summer differences. Moreover, this study reports the highest mean annual BaP concentrations at a background location in the GAA in over two decades (Marino et al., 2000). In the few studies in the area that have compared traffic with background sites, there appears to be an important roadside enhancement of PAH levels. Therefore, it is noteworthy that the present, urban background, BaP annual mean concentration is comparable to the mean BaP concentrations reported at 21 sites in the GAA by a study of annual duration in 2010-2011, which however included 7 high-traffic locations (Jedynska et al., 2014). This likely indicates an increase of urban background levels in Athens, with implications for the population's exposure.

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Figure 1: The color bars represent each PAH member average concentration for months December 2016 to January 2018. The grayscale pies in the lower panel show the concentration fraction of high (HMW), medium (MHW) and low (LMW) molecular weight PAHs for each season.

190   Classification of PAHs by molecular weight is thought to provide a link to their sources. For example, low molecular weight PAHs (LMW; 128-178 gmol⁻¹) and medium molecular weight PAHs (MMW; 202-228gmol⁻¹) have been linked to diesel engine emissions (Zheng et al., 2017), while MMW and high molecular weight (HMW; 252-300 gmol⁻¹) PAH concentrations can be notably influenced by BB emissions (Han et al., 2019; Masiol et al., 2020). Figure 1 displays also the ΣPAH fractions of LMW,

195   MMW and HMW PAHs, by-season of the year. During winter and autumn, HMW PAHs comprise the most abundant fraction (60% and 51%, respectively), implying a possible impact from BB. In spring there is an increase of the LMW fraction (49%), while during summer, when regional fine aerosol sources maximize their influence (Grivas et al., 2018), the higher percentage (53%) comes from MMW species. A prior study carried out during 2001-2002 (Table S3), well-before the economic recession, at a GAA

200   site not adjacent to a major road (Mantis et al., 2005), reports an LMW-MMW-HMW PAHs fractionation similar to our study (Figure S2), despite the considerably higher residential BB emissions here. However, concentrations of ΣPAHs and BaP in the present study are higher (by a factor of 1.4 and 1.8, respectively). This most likely suggests an important effect of the new BB source on an annual level, since PAHs emissions from the road transport sector in Greece remained similar between the two periods (EIONET,

205   2021). This implies that approaches based on MW alone have limitations, since many PAH members are emitted by both fossil fuel and biomass burning, and the attribution of PAH sources can be better constrained by receptor modelling.

3.2 Investigating intense pollution events: nighttime vs. daytime

   Summary statistics for 12- and 24-h ΣPAH averages are provided in Table 1. The highest PAH

210   concentrations are observed during intense pollution events (IPE) – in this work defined as periods with mean BC concentrations exceeding 2 μg m⁻³, stagnant conditions with wind speeds below 3 ms⁻¹ and a lack of precipitation (Fourtziou et al., 2017). Peak wintertime levels of BC (Figure S3) coincide with

BC$_{bb}$ maxima, indicating a predominance of biomass burning over other combustion sources (Liakakou et al., 2020). These high levels are considered to be mainly driven by emissions and not changes in
215   mixing-layer height (Liakakou et al., 2020).

Table 1: Average values ± standard deviation of PAH concentrations categorized according to their molecular weight, during wintertime intense pollution events (IPE).

	LMW (128-178 gmol^{-1}) (ng m^{-3})	MMW (202-228 gmol^{-1}) (ng m^{-3})	HMW (252-300 gmol^{-1}) (ng m^{-3})	ΣPAHs (ng m^{-3})
IPE DAY	1.79 ± 1.95	1.13 ± 0.50	4.01 ± 4.11	6.94 ± 4.27
IPE NIGHT	1.51 ± 1.28	4.97 ± 7.69	21.56 ± 20.31	28.04 ± 27.56
IPE 24-h	1.62 ± 1.57	3.44 ± 6.22	14.54 ± 18.05	19.6 ± 23.78
Non-IPE DAY	1.21 ± 1.27	0.92 ± 0.77	1.81 ± 1.59	3.93 ± 2.51
Non-IPE NIGHT	0.46 ± 0.25	0.71 ± 0.48	1.61 ± 2.24	2.78 ± 2.32
Non-IPE 24-h	0.92 ± 1.06	0.84 ± 0.67	1.73 ± 1.83	3.49 ± 2.47

220   Among the 80 winter samples, 50 met the above criteria for IPE (20 daytime and 30 nighttime samples). During IPEs, ΣPAH concentrations present a strong night-day gradient, owing to the effect of nighttime residential BB emissions. Several studies have examined the diurnal variability of PAH levels, worldwide (Yan et al., 2009). Similarly pronounced nighttime enhancements were reported mostly for megacities in E. Asia, such as Beijing and Nanjing (Elzein et al., 2019; Haque et al., 2019), where PAH levels are
225   considerably higher than in Athens, owing to the intensity and diversity of local sources that include burning of biomass, coal and plastics. During non-IPE periods, ΣPAH levels are lower by 43% in daytime and 90% in nighttime, resulting in daytime levels being higher than nighttime and indicative of substantial contributions from other combustion sources like vehicular traffic.

HMW PAHs have the highest contribution to ΣPAHs during IPEs and present the most pronounced day-
230   night differences. MMW PAHs are more abundant during nighttime, with 24-h levels more than double during IPEs. Levels of LMW PAHs are higher during daytime in both IPE and non-IPE periods, suggesting that biomass burning has a more limited effect in their particle-phase concentrations, compared to higher MW members.

To explore the various sources that drive the variability of PAHs, the correlations of ΣPAHs with specific
235   tracers is examined (Table S4). Given the very high correlations of ΣPAHs with BaP (Figure S4), especially during nighttime IPEs ($r = 0.95$, $p < 0.01$), similar associations with examined tracers can be expected for the corresponding PAH carcinogenicity. Strong correlations with biomass burning tracers such as non-sea salt K$^+$ and BC$_{bb}$ are observed, particularly during IPE nights (r: 0.81 and 0.95, respectively, $p < 0.01$). Levoglucosan, mannosan and galactosan displayed very high correlations with
240   ΣPAHs during nighttime IPE (r: 0.90-0.93, $p < 0.01$). When compared with the "fingerprint" ACSM wood-burning fragments (m/z 60 and 73) as well as with submicron organic aerosol (OA), ΣPAHs exhibit significant nighttime IPE correlations, with r values of 0.92, 0.91 and 0.89 ($p < 0.01$), respectively.

The results indicate a significant impact of BB emissions on PAH levels during nighttime IPEs. The ratio of ΣPAHs to levoglucosan during these events was 53% lower than in daytime, when biomass burning

245 and therefore levoglucosan concentrations decrease. This indicates an important activity of additional PAH sources such as vehicular traffic and is consistent with past studies in Greece (Saffari et al., 2013). The levoglucosan/(mannosan+galactosan) ratio can also indicate whether solid fuels used for heating are either "aged" (e.g. aged wood or lignite) producing more levoglucosan, or more fresh (Saffari et al., 2013). The calculated value close to 6 for both daytime and nighttime samples suggests that solid fuels

250 used for residential heating in Athens are mainly associated with fresh firewood and their type has not changed since 2013, when a similar wintertime ratio was reported in Athens (Fourtziou et al., 2017). Finally, the ratio of levoglucosan to mannosan can be indicative of wood type, with hardwood (e.g., olive, oak, beech) producing ratios around 14–15, while softwood (e.g., pine) gives lower ratios, around 4 (Schmidl et al., 2008). In our study, this ratio ranged from 7.3 to 9.7 (Table S5), indicating a balanced

255 use of both wood types, in agreement with observations at the same site during the 2013-2014 winter (Fourtziou et al., 2017), once again supporting that a similar mixture of softwood and hardwood is consistently used for residential heating over the recent years.

3.3 PMF modeling and source characterization

Solutions with 3-8 factors were examined, with the four-factor solution deemed as the most physically

260 meaningful (a more detailed presentation of the selected solution can be found in Section S5 of the supplement). The four identified factors are presented below; an extended description of their validation is provided in Section S5 of the Supplement.

The first factor was attributed to biomass burning (BB). Levoglucosan, a well-established BB signature marker, is almost exclusively associated with this factor (Figure 2). The factor is also characterized by

265 important loadings in 5-6 ring PAHs, a feature that has been reported in BB source profiles of studies in urban areas worldwide (Han et al., 2019; Masiol et al., 2020; Taghvaee et al., 2018). The strong presence of BaP in the factor is consistent with results from studies in European cities (Li et al., 2018; Srivastava et al., 2018) and also with a recent study at Thissio (Fourtziou et al., 2017) that reported direct associations between wintertime BaP levels and several BB tracers. The OC/EC ratio in the profile was

270 4.2, higher than the other local sources and characteristic of fresh BB emissions and also comparable to the value (3.7) calculated for the BB source at the same site by a long-term $PM_{2.5}$ source apportionment study (Theodosi et al., 2018). Moreover, the source contributions registered the highest, among the four factors, correlations with BB external tracers and specifically with BC_{bb} ($r = 0.93$, $p < 0.01$) and water-soluble K^+ ($r = 0.61$, $p < 0.01$). The bivariate polar wind plot (calculatated according to the methodology

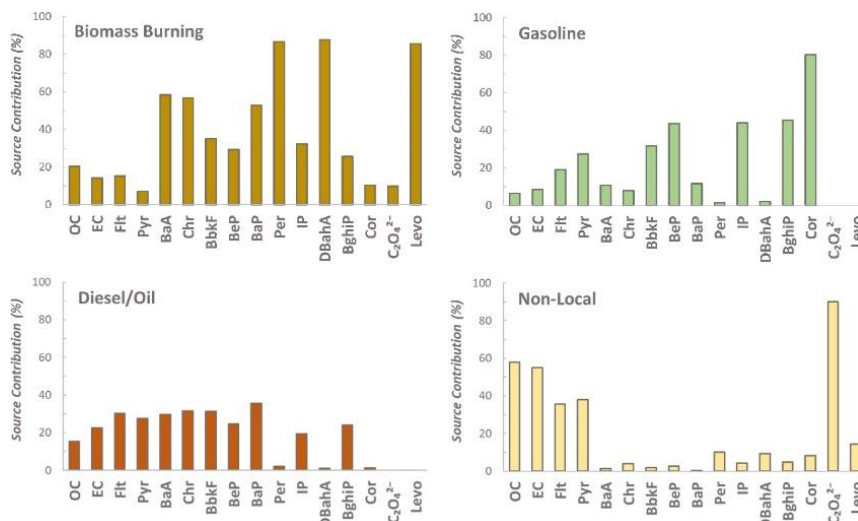
275 of Uria-Tellaetxe and Carslaw, 2014) for contributions of the BB source (Figure S5a) indicate the local character of the source, with concentrations being enhanced during low-wind conditions, as it has been observed at the same site for fresh BB aerosols emitted in central Athens (Kaskaoutis et al., 2021; Stavroulas et al., 2019). The factor was present almost exclusively during the winter months (Figure S6), when local wood-burning emissions for residential heating intensify, leading to frequent IPE.

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Figure 2: Percentage contributions of individual sources to mean modelled concentrations of PAHs and other carbonaceous species, obtained from PMF analysis for 24-h samples collected at Thissio Athens, during December 2016 – January 2018.

285 The second factor was linked to gasoline-powered vehicles, which constitute the major fraction (over 90%) of the vehicular fleet in the GAA. The factor was characterized by stronger contributions to HMW PAHs (e.g., IP, BghiP and Cor), over lower-MW members (Figure 2). This feature has been used to differentiate the gasoline source from general traffic sources in several PAH source apportionment studies (Callén et al., 2013; Javed et al., 2019; Sofowote et al., 2008; Wu et al., 2014). The OC/EC ratio

290 in the source profile was 1.9, within the range (1.7-2.3) typically reported for fresh emissions from gasoline vehicles (Grivas et al., 2012). The source contribution time series presented the highest correlations with BC_{ff} ($r = 0.79$, $p < 0.01$), which is mostly a proxy of traffic emissions impacting Thissio (Liakakou et al., 2020). It was the only factor that correlated significantly during both non-winter ($r = 0.80$, $p < 0.01$) and winter ($r = 0.66$, $p < 0.01$) periods with CO, which is emitted mainly by gasoline

295 vehicles in the GAA (Fameli and Assimakopoulos, 2016). On the contrary the BB source correlated with CO only in winter ($r = 0.83$, $p < 0.01$) due to strong CO emissions from wood burning during IPE (Gratsea et al., 2017). The wind plot for the factor's contributions (Figure S5b), again given the absence of a strong directional pattern, is suggestive of aerosols produced in the vicinity of the site (central Athens). Higher contributions were observed during the winter months (Figure S6), consistent with the increased traffic

300 in the center of Athens (especially during the December holiday period), relative to the vacation months of July-August.

The third factor was associated with emissions from diesel/oil combustion and is characterized by an increased abundance of lower MW members (Shirmohammadi et al., 2016; Zheng et al., 2017). It presented the highest contributions to Flt and Pyr among local sources and also substantial loadings in

305 BaA, Chr, BbkF and BaP, along with smaller – compared to the gasoline factor – loadings in IP and BghiP (Figure 2). Comparable patterns can be observed in source profiles of other PMF studies that

distinguish diesel and gasoline sources (Agudelo-Castañeda and Teixeira, 2014; Liu et al., 2019), where contributions in the diesel factor are found relatively increased for 4-, 5-ring PAHs and decreased for HMW members. The OC/EC ratio was 1.6, higher than typically reported values for diesel exhaust,

310 which could indicate moderate aging. Higher OC/EC ratios can be expected also in the cases of heavy-duty diesel vehicles in creeping mode (Pio et al., 2011) and non-traffic oil combustion emissions (e.g. ships in the port). Based on its wind plot, the factor, while still local, presents a relative enhancement for moderate-speed winds transporting aerosols from the S-W sectors of the GAA (Figure S5c). Primary pollution hot-spots are found in this direction, such as the port of Piraeus (at a distance of 7-11 km) and

315 the industrial/commercial hub of the Athens basin (2-4 km) that is traversed by the E75 international route, the most heavily trafficked – and frequently congested – highway in the GAA (Grivas et al., 2019). Therefore, the area to the S-W of the site is characterized by increased circulation of light- and heavy-duty diesel vehicles. As with the gasoline factor, the contribution time-series recorded statistically significant ($p < 0.01$) correlations with external combustion indicators, albeit weaker ($r = 0.66$, $p < 0.01$

320 with CO; $r = 0.39$, $p < 0.01$ with BC_{ff}).

The fourth factor was characteristic of non-local contributions to carbonaceous aerosol. It was mainly associated with high contributions to OC and EC, which at urban background locations are moderately impacted from local primary sources and mostly driven by aerosols regionally transported to the receptor site (Buzcu-Guven et al., 2007; Hasheminassab et al., 2014). The dominance of regional/secondary

325 sources at urban and suburban background sites has been identified by the majority of aerosol source apportionment studies in the GAA (Diapouli et al., 2017; Grivas et al., 2018; Paraskevopoulou et al., 2015; Theodosi et al., 2018) and other urban areas worldwide, like Mexico City (Aiken et al., 2009) and Paris (Skyllakou et al., 2014). The factor was also characterized by a high contribution of oxalate, an important secondary constituent of water-soluble organic carbon (Myriokefalitakis et al., 2011). The

330 contribution time-series was positively correlated with sulfate and ammonium (r: 0.57 and 0.51, respectively, $p < 0.01$), indicators of regionally-transported secondary aerosol. This is the only factor that showed a statistically significant ($p < 0.01$) enhancement (Figure S6) during the non-winter months, due to increased photo-oxidation for production of secondary organics under stronger insolation. The polar plot of Figure S5d displays the typically observed (Stavroulas et al., 2019) large dispersion of

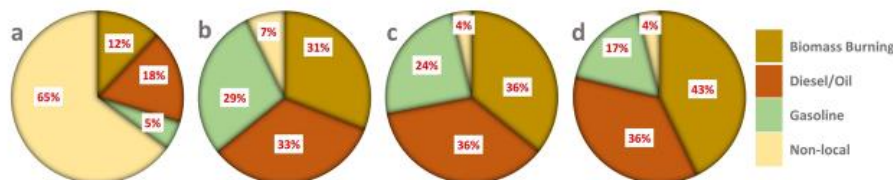
335 concentration enhancements along the SW-NE axis of the Athens basin, indicating the association of the factor with transport on a larger-than-urban spatial level. A considerable fraction of the lighter members (Flt and Pyr) were attributed to this factor. Studies performed at regional background sites that are mainly impacted by long-range transport have attributed increased contributions of Flt and Pyr to aerosols deriving from distant combustion of coal and heavy oil (Lhotka et al., 2019; Mao et al., 2018; Miura et

340 al., 2019; Wang et al., 2014). The OC/EC ratio in the source profile (2.9) was increased compared to the petroleum-related sources (1.6-1.9), but not as much as usually reported for secondary aerosol factors. Given this, and that PAHs are subject to oxidative aging and removal during atmospheric transport (Galarneau, 2008; Ravindra et al., 2008) it is likely that the non-local factor not only includes transboundary aerosols, but also partially-aged aerosol from a less extended spatial scale (e.g. from

345 energy production using fossil fuels in continental Greece or from emissions from marine oil combustion in the Aegean Sea). In support of this, we note that the centroids of all identified air mass trajectory

clusters during the study period converge to the north of the GAA before arriving in the Athens basin (see also the discussion in the following section).

3.4 Source contributions

350   Average source contributions to PAHs and TC are presented in Figure 3 for the calendar year 2017 (January to December; 93 24-h values), to achieve consistent statistical sampling of each season. Here we focus on contributions to PAHs, while contributions to TC are discussed in Section S5 of the Supplement.

355   **Figure 3: Fractional contributions of PMF-resolved sources to mean modeled concentrations of: a) TC, b) Sum of 12 PAHs included in the PMF analysis, c) Sum of 6 carcinogenic PAHs (IARC groups 1, 2A, 2B: BaP, DBahA, BaA, Chr, BbjkF, IP), d) estimated BaPeq.**

Regarding local sources, the annual contribution of biomass burning source ΣPAHs is amplified
360   compared to TC (31% vs 12%, Figures 2a, 2b), ever so more when assessing only the contributions to carcinogenic PAHs (36%, Figure 3c). The large impact of biomass burning on long- and short-term exposure becomes more evident considering that it essentially is a source active only in wintertime and manifests mostly during IPEs (18% of measurement days in 2017).

The other two local sources (diesel/oil and gasoline) accounted for a combined 62% of ΣPAHs (Figure
365   3b), highlighting the importance of urban vehicular emissions on a long-term basis – but not during IPEs. Even though the participation of diesel cars is minimal in the passenger fleet in Athens (<10%, the vast majority being Euro 5 and 6 vehicles), the contribution of the diesel/oil factor is at least comparable to the gasoline factor for ΣPAHs (and much larger for TC), indicating that it is probably emissions from older light- and heavy-duty vehicles (and to an extent stationary emissions) that should be associated
370   with the significant contributions of this source. Manoli et al. (2016), reported an even larger gap between diesel and gasoline contributions to ΣPAHs (51% vs 30% approximately), at an urban background location in Thessaloniki, Greece, during 2011-2012. Even before the lifting of the ban on private diesel cars in Athens and Thessaloniki (2011), diesel emissions were considered to be more important regarding the impact of road transport on PAH concentrations (Andreou and Rapsomanikis, 2009; Viras and Siskos,
375   1993). Comparing with these studies, a declining contribution to PAHs of diesel vehicles in Greek cities is implied.

Non-local sources were the major contributors to total carbon concentrations (65%) at the Thissio site (Figure 3a) – consistent with findings from previous studies at urban background sites in the GAA and

elsewhere. The effect of non-local sources is greatly reduced (Figure 3b) when examining contributions
380   to ΣPAHs (7%) against those of the three local sources (29-33%). Figure 4a shows that non-local daily
contributions remain lower than 20% during winter but regularly exceed 50% during summer.

Non-local contributions are intimately linked with regional transport, therefore, an air mass trajectory
cluster analysis can help understand its variability and origin. Four major air mass source regions are
identified for the GAA during the study period, using 96-h back-trajectories: The Black Sea area (with a
385   frequency of 43%), Northern Greece/Balkans (32%), Western Europe (20%) and Eastern Europe (5%).

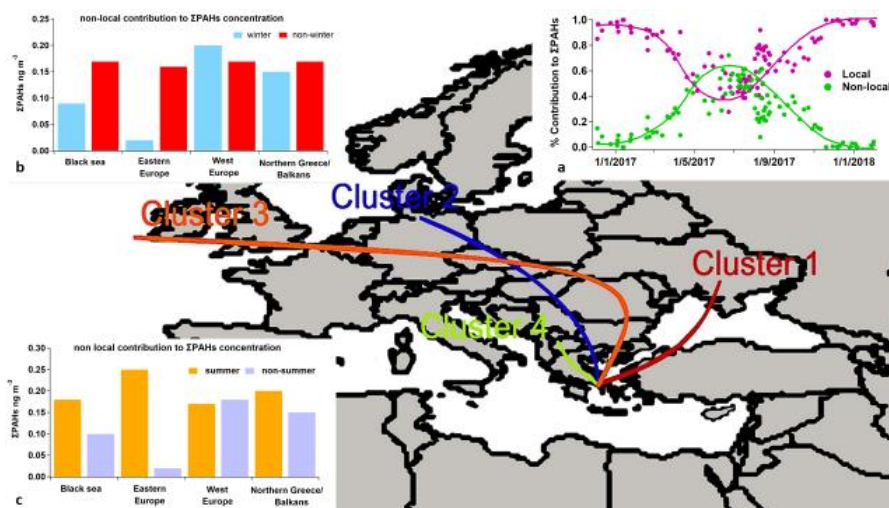



**Figure 4: The four dominant clusters of backward trajectories, Black sea (1: red), Eastern Europe
(2: blue), Western Europe (3: orange) and Northern Greece /Balkans (4: green). Panel a shows the**
390   **local & non-local relative source contributions during the study period. Panels b,c show the non-
local contribution to ΣPAHs concentration according to the respective air mass origin.**

When examining total PAH levels per trajectory cluster, associated synoptic circulation patterns can
affect the intensity of local emission sources (e.g. during wintertime cold fronts that may lead to increased
395   BB), so this impedes a fully unbiased assessment. The source apportionment results were utilized here
instead to remove the effect of local sources and associate trajectory clusters more directly with non-
local sources.

Figure 4b shows that the non-local contribution of the four clusters to ΣPAH concentrations during the
non-winter period is practically the same (differences from the mean within 10%). For the winter period
400   it is observed that the contribution from Eastern Europe is very small compared to the other clusters.
During summer (Figure 4c), the highest contributions are related to trajectories from Eastern Europe, an
area identified as a hotspot of PAH production in Europe (EEA, 2018; Guerreiro et al., 2016; Rogula-
Kozłowska et al., 2013). We note however the small frequency – 5% – of the cluster in summer. An
important summertime enhancement is also observed for non-local contributions associated with
405   trajectories from the Black Sea area, where extensive summer agricultural burning has been identified as

a significant source of carbonaceous aerosol in the Eastern Mediterranean (Amiridis et al., 2009; Sciare et al., 2005). For Western Europe and Northern Greece/Balkan clusters, the mean contributions remain effectively constant on a seasonal basis. Outside of winter, when non-local sources become much more prominent, contributions do not depend on air mass sector, possibly indicating that anthropogenic production of harmful aerosols is a continental-scale problem. Even more, PAH concentrations attributed to non-local sources show limited seasonal variability, meaning that increased atmospheric degradation during the warm period plays a minor role.

3.5 Contributions to carcinogenic potency and risk assessment

The calculated annual BaPeq value at the urban background site of Thissio for 2017 was 0.53 ng m^{-3}, higher than the one reported during 2013 for a suburban background site in the GAA, less affected by local emissions (0.3 ng m^{-3}) (Alves et al., 2017). With the exception of sites in heavily industrialized areas (Kozielska et al., 2014), studies in other European and North American cities, generally calculate BaPeq values in the same order of magnitude as Athens. However, much higher values, in the order of several ng m^{-3} BaPeq are usually reported for cities in China. (Table S6). Figure S7 shows the members that contribute the most to BaPeq during the full measurement period; 50% of the annual BaPeq is attributed to BaP, consistent with studies worldwide (Amador-Muñoz et al., 2010) and confirming its importance as an indicator of PAH carcinogenic risk. The BaPeq value displayed clear seasonal variability, with the highest levels during winter and the lowest in summer (Table S7). Especially, during nighttime IPE in the winter of 2017-2018, the mean BaP concentration and BaPeq estimate reached peak values of 2.75 ng m^{-3} and 5.18 ng m^{-3}, respectively. Comparing to the mean BaPeq from all non-IPE samples (0.21 ng m^{-3}), it appears that these short-duration wintertime events influence disproportionately mean annual BaPeq (0.53 ng m^{-3}).

The PMF-resolved concentration profiles were used to obtain BaPeq contributions of each source. The annual contributions of biomass burning, diesel/oil and gasoline to BaPeq are 43%, 36% and 17%, respectively, with the remaining 4% attributed to non-local sources (Figure 3d). These results clearly highlight BB, in spite of its seasonal and highly episodic character, as a principal driver of long-term carcinogenic risk. In the few European studies, where BB factors were apportioned and their contributions to BaPeq reported (mainly in Southern European cities) these contributions are not that pronounced, even during the winter season (Callén et al., 2014; Masiol et al., 2012). Inhalation ECR values (Table S6) estimated for the annual period were equal to 0.58 × 10^{-6} (OEHHA method) and 45.73 × 10^{-6} (WHO method). These estimates approached or exceeded 10^{-6}, thought to be a threshold above which carcinogenic risks become not acceptable (EPA, 2011). At current levels, 76% of the excess risk would be attributed to wintertime exposure, mostly during IPEs, a percentage largely superior to those of the other three seasons (4-14%). Based on the stricter WHO unit risk, an excess of 4.6 cancer cases per 100,000 people can be linked to inhalation exposure to PAHs in urban background conditions in Athens. For the 3 million living in the central Athens basin it can be projected that the number of excess cancer cases can be well over 100.

4. Conclusions

445   Domestic biomass burning is identified as a considerable source of carcinogenic PAHs in one of the most populated regions of the Mediterranean. Overutilization of wood burning for domestic heating during the economic recession in Greece, persists even today despite the improved economy, leading to a significant increase in annual urban background levels of ΣPAHs and BaP, with respect to the period preceding the recession. The local biomass burning source, that is present almost exclusively during the winter period,

450   emerges as the most important contributor to carcinogenic toxicity of ΣPAHs (43% on an annual basis). Therefore, wintertime exposure is seen as responsible for the largest part (76%) of the estimated excess lifetime cancer risk. This large wintertime enhancement in 2017 can be mostly attributed to a few nighttime episodes (19 events in 105 days with measurements), revealing a disproportional impact of residential BB emissions but also an opportunity for targeted intervention measures. Given this, and the

455   extended usage of biomass burning throughout Europe (e.g., France, Germany, Ireland and the UK), European action and policies aimed at the regulation of biomass burning emissions are immediately needed in order to achieve considerable benefits for public health.

Sources related to local road transport were found responsible for the major part of ΣPAH concentrations (62%), indicating that current EU planning to further curb vehicular emissions and promote

460   electromobility can have tangible results in the reduction of urban aerosol toxicity. There is an indication that the effects of diesel vehicles are weakening in Greek cities, consistent with the modernization of the commercial vehicle fleet in Greece over the last two decades. More research in other European cities, where diesel penetration in the passenger fleets is much higher, could be rather useful to study the relative contributions and trends of diesel and gasoline vehicle contributions.

465   Non-local sources had a relatively small contribution to ΣPAHs level and toxicity but their relative contribution during the warm period of the year becomes comparable with that of the local sources. It should be noted that oxidized PAHs products, which can be considerably more toxic than parent PAHs, may revise the relative importance of non-local to local sources, although this remains to be explored in future studies.

470   We have shown that a comprehensive observation dataset, combined with receptor modeling and back-trajectory analysis provides powerful insights on the source apportionment and contributions to the health risks from PAH exposure. Despite the large body of work to date on PAHs, similar studies are surprisingly scarce in Europe and the US, so we hope our study will motivate urgently needed follow-ups in other urban environments.

475   **Data availability**

Data are available upon request, by the corresponding authors

Author contributions

Conceptualization, NM and AN; methodology, NM and AN; formal analysis, IT and GG; investigation, IT, GG, AB, DP, MA, AG, CP, KT, PZ, MT, CO; writing—original draft preparation, IT and GG;

480   writing—review and editing, IT, GG, AB, DP,NM and AN; supervision, NM and AN; project
       administration, NM and AN; funding acquisition, NM and AN.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

485   This work has been funded by the European Research Council, CoG-2016 project PyroTRACH (726165)
       H2020-EU.1.1. – Excellent. We also acknowledge support by the "PANhellenic infrastructure for
       Atmospheric Composition and climatE change" (MIS 5021516) which is implemented under the Action
       "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme
       "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and
490   the European Union (European Regional Development Fund). The authors thank Dr. E. Liakakou for
       providing BC and BC speciation data (BC_{ff} and BC_{wb}) for Thissio, Dr. Hatzianestis of HCMR for
       providing guidance in the PAH analysis method, I. Stavroulas for the contribution in the ACSM PMF
       analysis and P. Kalkavouras for the trajectory cluster analysis.

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