Multiyear chemical composition of the fine aerosol fraction in Athens, Greece, with emphasis on the contribution of residential heating in winter-time

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Abstract. In an attempt to take effective action towards mitigating pollution episodes in Athens, precise knowledge of $PM_{2.5}$ composition and their sources is a prerequisite. Thus, a two year chemical composition data set from aerosol samples collected in an urban-background site of central Athens, from December 2013 till March 2016, has been obtained and Positive Matrix Factorization (PMF) was applied in order to identify and apportion fine aerosols to their sources. A total of 850 aerosol samples, were collected on a 12 to 24h basis and analyzed for major ions, trace elements, organic and elemental carbon, allowing us to further assess the impact of residential heating as a source of air pollution over Athens.

The ionic and carbonaceous components were found to constitute the major fraction of the $PM_{2.5}$ aerosol mass. The annual contribution of the Ion Mass (IM), Particulate Organic Mass (POM), dust, Elemental Carbon (EC) and Sea Salt (SS) were calculated at 31%, 38%, 18%, 8% and 3%, respectively and exhibited considerable seasonal variation. In winter, the share of IM was estimated down to 23%, with POM + EC being the dominant component accounting for 52% of the $PM_{2.5}$ mass, while in summer IM (42%) and carbonaceous aerosols (41%) contributed almost equally.

Results from samples collected on a 12h basis (day and night) during the 3 intensive winter campaigns indicated the impact of heating on the levels of a series of compounds. Indeed, $PM_{2.5}$, EC, POM, NO_3^-, $C_2O_4^{2-}$, $nssK^+$ and selected trace metals including Cd and Pb were increased by up to a factor of 4 during night compared to day, highlighting the importance of heating on air quality in Athens. Furthermore, in order to better characterize winter-time aerosol sources and quantify the impact of biomass burning on $PM_{2.5}$ levels, source apportionment was performed. The data can be interpreted on the basis of six sources namely biomass burning (31%), vehicular emissions (19%), heavy oil combustion (7%), regional secondary (21%), marine aerosol (9%) and dust particles (8%). Regarding night to day patterns their contributions shifted from 19, 19, 8, 31, 12 and 10% of the $PM_{2.5}$ mass during day to 39, 19, 6, 14, 7 and 7% during night, underlining the significance of biomass burning as the main contributor to fine particle levels during night-time in winter.

1 Introduction

The scientific interest in aerosols has widely increased during the last decades due to their impact on air quality, human health and climate change (e.g., Seinfeld and Pandis, 1998). Legislation regarding atmospheric particulate matter is gradually becoming more stringent, as a result of the frequent episodes encountered on regional or even continental scales, associated also with synoptic and mesoscale meteorological conditions (Querol et al., 2009). Hence, significant efforts are targeted towards improving air quality through emission reduction measures (Daskalakis et al., 2016).

Particles with diameter of 2.5 μm or less are of particular interest due to the fact that they contribute significantly to detrimental health effects (Dockery and Pope, 1994; Ostro et al., 2006), penetrating more efficiently the cell membranes (Salma et al., 2002; Li et al., 2003; Bell et al., 2009) and acting as carriers of toxic and carcinogenic components (Beddows et al., 2004). Recent epidemiological studies have highlighted the risk of exposure to enhanced levels of carbonaceous aerosols, revealing notable associations with cardiovascular mortality and morbidity (Ostro et al., 2010; Lipsett et al., 2011; Krall et al., 2013). Trace metals are also related to chronic and acute health problems due to their toxicity (Pope et al., 2002; Stiebet et al., 2002).

In Greece, air quality has improved since the advent of the global economic recession in 2008, due to the abrupt cut down of anthropogenic sources such as traffic and industrial activities (Vrekoussis et al., 2013; Gratsea et al., 2017). However, since the winter 2011-2012, the extensive use of wood as fuel for residential heating appears to have changed this decreasing trend, at least for the winter period (e.g., Gratsea et al., 2017). Burning wood in residential stoves (and fireplaces) is an important source of directly emitted fine particulate matter ($PM_{2.5}$), EC and polycyclic aromatic hydrocarbons (PAH), with great impact on air quality (EEA, 2013; 2014). Paraskevopoulou et al. (2015) have shown that at a suburban site (Penteli) in the Greater Athens Area, the contribution of Particulate Organic Matter (POM) to the additional local aerosol mass, increased by 30% between winter 2012 and winter 2013. Fourtziou et al. (2017) have reported on several wood burning tracers monitored during winter 2013-2014, linking them to the presence of severe smog events due to wood combustion for residential heating.

Informed decision-making towards improving air quality, demands precise knowledge of PM chemical speciation and source attribution. Based on the effect of finer particles on health and their association with urban sources, in contrast to natural aerosols, it is even more important to focus such analyses on fine aerosol fractions. In this study, $PM_{2.5}$ was chemically characterized for inorganic species, such as trace elements and watersoluble ions, as well as for carbonaceous components, such as organic and elemental carbon. To our knowledge, this is the first time that such a long-term, uninterrupted estimation of the chemical composition of $PM_{2.5}$, a chemical mass closure exercise and source identification of particulate matter, took place in parallel, at an environment in Southeastern Europe offering challenging conditions in terms of pollution contributors and timing (recession period). Given the intensive use of wood as fuel for residential heating since winter 2012 in Athens, the current work was focused on winter periods. In order to highlight the impact of night-time winter PM sources air quality

of urban Athens, aerosol sampling was intensified from routine 24h time resolution to 12h resolution during the three consecutive winters (2013-2014 to 2015-2016).

2 Experimental

2.1 Sampling site

Aerosol sampling was conducted at the central premises of the National Observatory of Athens situated on a small hill (110m a.s.l), in downtown Athens (Thissio, 38° 0.00′ N, 23° 43.48′ E). This urban background site is not directly impacted by local human activities as it is surrounded mostly by a pedestrian zone and moderately-populated neighbourhoods. Therefore, the site could be considered as representative of the exposure of the majority of population in the Greek capital, as demonstrated by Gratsea et al. (2017).

2.2 Sampling and chemical analyses

$PM_{2.5}$ aerosol was collected on Quartz fiber filters (Flex Tissuquartz, 2500QAT-UP 47mm, Pall) with a Dichotomous Partisol Sampler 2025 (Rupprecht & Patashnick, 16.7 L min^{-1}), on a daily basis during a period of more than two years (December 2013 - March 2016). During the three winter periods (from December to February), the sampling frequency was changed to 12h, in an attempt to study in depth the characteristics of emissions from heating activities, resulting in a collection of 447 filters out of the total of 848. The $PM_{2.5}$ aerosol mass was gravimetrically determined (samples were conditioned pre- and post-sampling at 20 ± 3 °C and 45 ± 5% RH for 48h) using a microbalance (Fourtziou et al. 2017; Paraskevopoulou et al., 2014), and filters were stored until the chemical analysis. Filter blanks and blank field samples were also prepared and analyzed. All $PM_{2.5}$ samples were analyzed for organic (OC) and elemental carbon (EC), watersoluble ions (Cl^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}), elements of crustal origin (Al, Fe, Ca) and trace elements (Zn, Pb, Cu, Ni, V, Cr, Mn, Cd, As). All reported concentrations were corrected for blanks. The chemical speciation data were utilized to perform a chemical mass closure exercise and chemometric receptor modelling for source apportionment.

Filters were analyzed for the carbonaceous components, with the Thermal-Optical Transmission (TOT) technique (Birch and Cary, 1996), using a Sunset Laboratory OC/EC Analyzer, as described in detail by Theodosi et al. (2010a) and Paraskevopoulou et al. (2014), applying the EUSAAR-2 protocol (Cavalli et al., 2010).

Filter parts were analyzed by ion chromatography (IC) for the determination of the main ionic species mentioned above, as described by Paraskevopoulou et al. (2014).

An acid microwave digestion procedure, followed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Thermo Electron ICAP 6000 Series), was applied for the determination of major and trace metal concentrations during this long-term sampling period (n=848) following the procedure described in detail by Theodosi et al. (2010b). All 12 elements, were also determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer, NexION 300X)

for all winter (December-February) and summer (June-August) samples (n=592). Results reported hereafter for Al, Ca, Mn, Fe, V, Cr, Ni, Cu, Zn correspond to ICP-OES analysis, while for Cd, As and Pb to ICP-MS.

Hourly meteorological data on horizontal wind velocity and direction from NOA's station at Thissio were additionally retrieved.

2.3 Source apportionment

In order to identify major winter-time sources of $PM_{2.5}$ and their day-night patterns, Positive Matrix Factorization (PMF) receptor modelling was performed on the 12-h winter chemical composition data.

In the PMF factor analytic model, speciated sample data are decomposed into matrices of factor contributions and factor profiles. The matrix elements are obtained through the minimization of weighted decomposition residuals (object function - Q) in an iterative process. Uncertainties associated with the analysis of individual species are used for weighting. In the present case, the multilinear engine (ME-2) program was used for solving the PMF problem in the setting of the EPA PMF5.0 software.

Uncertainties per species and sample were calculated (Reff et al., 2007) based on the error fraction of the measurement and the method detection limit for each component.

Values equal to $5/6^{th}$ of the detection limit were assigned as uncertainty to samples below detection limits (BDL). Missing data points were substituted by the geometric mean of the respective species concentrations and given four times this value as uncertainty.

In total, 22 analyzed species were considered. Additionally, the insoluble fraction of Ca (Ca-ins) was also incorporated in the PMF analysis through subtraction of ionic Ca^{2+} from the ICP-OES-determined Ca (Beuck et al., 2011; Yubero et al., 2011).

$PM_{2.5}$ was set as a total variable and had its uncertainty tripled so that it would not overly influence solutions. The PMF analysis was performed on the day/night dataset to obtain the source profiles and the day and night contributions to $PM_{2.5}$ were calculated separately (Bernardoni et al., 2011; Canha et al., 2014). Supplementary PMF source apportionment was conducted for the two-year period 03/2014-02/2016, using daily mean concentration and uncertainty data.

Solutions involving 4-10 sources were examined and the ratios of actual (robust) to expected values of Q (Q_R/Q_{EXP}) were recorded. The selected solution, which was obtained for six factors, was physically interpretable, and the reduction of the Q_R/Q_{EXP} for solutions with a greater number of factors was small, indicating that new factors were not introducing additional information (Brown et al., 2015). The impact of small-medium scale atmospheric circulation has also been taken into account, by examining associations between source contributions and wind direction and velocity. Bivariate conditional probability function (CPF) calculations and graphical interpolation in polar coordinates have been performed according to the methodology developed by Uria-Tellaitxe and Carslaw (2014). The stability of the obtained solution against random sampling errors and rotational ambiguity was assessed using the BS-DISP procedure of the EPA PMF 5.0 (Paatero et al., 2014). More details on PMF model parameters and BS-DISP results are reported in the supplementary material.

3 Results and discussion

3.1 PM$_{2.5}$ levels

The daily PM$_{2.5}$ mass concentration at the urban background site of Thissio, from all 12-h and 24-h samples, varied significantly from 1 to 144 µg m^{-3}, with higher concentrations occurring in the winter (mean: 27.4±8.7 µg m^{-3}; median: 27.5

5 µg m^{-3}) and lower in the summer (mean: 14.7±1.2 µg m^{-3}; median: 15.0 µg m^{-3}) (Figure 1).

The annual mean PM$_{2.5}$ concentrations of the two complete years of the study period (2014 and 2015), based on daily values, were equal to 22.7±16.4 (median: 18.0 µg m^{-3}) and 19.3±16.1 µg m^{-3} (median: 15.2 µg m^{-3}), respectively, both being lower than the annual PM$_{2.5}$ limit imposed by the EU Ambient Air Quality Directive (2008/50/EC), which is set at 25 µg m^{-3}.

The PM$_{2.5}$ values reported here are in good agreement with those reported in other urban environment studies, for Athens

10 (18-26 µg m^{-3}, Theodosi et al., 2011; Mantas et al., 2014, Paraskevopoulou et al., 2015) or other European cities (15-30 µg m^{-3}, Putaud et al., 2010; Amato et al., 2016).

3.2 PM$_{2.5}$ chemical composition

3.2.1 Carbonaceous components

Figure 2a represents the time series of the daily concentration levels of OC, which ranged from below DL to 49.5 µg m^{-3}

15 (mean: 4.0±2.0 µg m^{-3}; median: 3.1 µg m^{-3}; Table 1), and of EC, from below DL to 19.3 µg m^{-3} (mean: 1.5±1.0 µg m^{-3}; median: 1.1 µg m^{-3}). Both carbonaceous components, exhibited a distinct seasonal variability, with lower mean concentrations during summer, in the order of 2.9±0.1 µg m^{-3} (median: 2.9 µg m^{-3}) and 0.7±0.1 µg m^{-3} (median: 0.8 µg m^{-3}) for OC and EC, respectively. Mean winter values were higher and equal to 6.3±2.9 µg m^{-3} (median: 5.8 µg m^{-3}) and 2.8±1.2 µg m^{-3} (median: 2.6 µg m^{-3}), respectively.

20 OC and EC concentrations fall within the range reported for background urban sites across Europe (Barcelona, Florence, Milan; Amato et al., 2016, OC=2.4-6.5 µg m^{-3} and EC=0.9-1.8 µg m^{-3}). Their levels are higher than those reported for a remote background site in Crete, Greece (Koulouri et al., 2008; OC=1.8±1.4 µg m^{-3} and EC=0.27±0.18 µg m^{-3}) and a suburban site in Athens (Remoundaki et al., 2013; OC=2.4 µg m^{-3} and EC=1.0 µg m^{-3}), while significantly lower than those previously reported for megacities such as Istanbul (Theodosi et al., 2010a; OC=6.6 µg m^{-3} and EC=2.9 µg m^{-3}).

25 ### 3.2.2 Ionic Composition

SO_4^{2-} was the main ion contributor to the fine aerosol mass accounting for 16% (mean: 3.0±0.8 µg m^{-3}; median: 2.9 µg m^{-3}), while NH_4^+ and NO_3^- followed with contributions of 7% (mean: 1.4±0.7 µg m^{-3}; median: 1.1 µg m^{-3}) and 2% (mean: 0.5±0.4 µg m^{-3}; median: 0.3 µg m^{-3}), respectively. Figure 2b represents the daily variation of SO_4^{2-} and NO_3^-, while Table 1 provides the annual levels of all the examined ions.

30 The mean SO_4^{-2} concentration for the whole study period (December 2013-March 2016) is in close agreement with the value (3.1±0.8 µg m^{-3}) reported from the 5-year (May 2008 – April 2013) study of Paraskevopoulou et al. (2015) for the suburban

station of Penteli and also with other recent studies performed in Athens (e.g Mantas et al., 2014). Notably, a substantial decrease is apparent in comparison to the levels recorded during the previous decade in the area (Karageorgos and Rapsomanikis, 2010; Theodosi et al., 2011). The annual measured levels of NO_3^- at Thissio are significantly higher from those reported for suburban and background locations in Greece, while for NH_4^+ they are comparable (e.g Mantas et al., 2014; Paraskevopoulou et al., 2015), highlighting the respective roles of local (NO_3^-) and regional (NH_4^+; see below) contributing sources.

Several other watersoluble ions were also identified such as Cl^-, Br^-, HPO_4^{2-}, $C_2O_4^{2-}$, Na^+, K^+, Mg^{2+} and Ca^{2+}. Annual means (Table 1) ranged between 19.4 ng m^{-3} for Br^- (median: 14.2 ng m^{-3}) to 307±196 ng m^{-3} for Na^+ (median: 369 ng m^{-3}). All annual mean concentrations of these ions are in the same range as those reported for PM$_{2.5}$ in Athens (Theodosi et al., 2011; Pateraki et al., 2012; Remoundaki et al., 2013; Paraskevopoulou et al., 2015).

3.2.3 Trace metals

Table 1 summarizes the mean annual concentrations of elements and trace metals during the sampling period and Figures 2c-f represent the daily variation of several representative metals. The mean annual concentrations of elements of crustal origin such as Al, and elements of mixed origin, still with a significant crustal component, such as Fe and Ca, vary from 0.26 to 0.75 µg m^{-3} (Table 1). The mean annual values for elements of major anthropogenic origin (Mn, V, Cr, Cd, Ni, Cu, As, Pb) are generally very low, varying from 1.7 to 27.1 ng m^{-3}. On a monthly basis, the concentrations of toxic metals originating from human activities, such as As, Cd, and Ni, which are mainly confined in the PM$_{2.5}$ fraction (Koulouri et al., 2008), do not exceed a few ng m^{-3}.

Compared to values reported in earlier studies for other locations in Athens during approximately the last decade, the trace element concentrations have remained within the same order of magnitude (Karanasiou et al., 2009; Theodosi et al., 2011; Pateraki et al., 2012; Mantas et al., 2014; Paraskevopoulou et al., 2015). As expected, the values are higher than those reported for several other rural background locations around Europe and Greece (Salvador et al., 2007; Koulouri et al., 2008; Viana et al., 2008; Pey et al., 2009; Alastuey et al., 2016).

3.3 Chemical mass closure

From the aerosol chemical components measured here -Ion Mass (IM), Particulate Organic Mass (POM), dust, EC and Sea Salt (SS)- the mass closure of the PM$_{2.5}$ aerosol samples can be undertaken. IM was calculated as the sum of the non sea salt (nss) constituents (NH_4^+, NO_3^-, K^+, SO_4^{-2}, Br^-, HPO_4^{2-} and $C_2O_4^{-2}$), estimated for the compounds having a sea-salt component by using Na^+ as a reference and the equation described by Sciare et al. (2005).

Dust was estimated using Al (Ho et al., 2006) assuming an upper crust concentration of 7.1% (Wedepohl, 1995). POM was estimated by multiplying the measured OC with a conversion factor (CF) of 1.8, derived from ACSM measurements in Athens (Stavroulas et al., 2018) aimed at the characterization of submicron organic aerosol sources. SS originating species were calculated from the sum of the measured ions: Na^+, Cl^-, Mg^{2+}, ssK^+, $ssCa^{2+}$ and $ssSO_4^{2-}$ (Sciare et al., 2005; Pio et al.,

2007). The results of the mass closure exercise on a mean monthly basis are shown in Figure 3 (results on a mean seasonal basis are reported in the supplementary material - Figure S1).

The corresponding chemical mass closure can explain about 99% of the measured fine aerosol mass, leaving out a considerably low proportion of the unaccounted mass, which is usually water (Ohta and Okita, 1990). By comparing the PM$_{2.5}$ mass (determined from the filter weighting of all 12 and 24h samples) and the sum of individual chemical aerosol components, a significant correlation is revealed, with a slope equal to 0.98 (r=0.88, n=780; not shown).

On an annual basis, POM contributes 38% to the total PM$_{2.5}$ mass, while EC comprises the 8%. IM accounts also for a significant part of the PM$_{2.5}$ mass (31%), with SO$_4^{2-}$ (16%) and NH$_4^+$ (7%) being the dominant ions. The annual contribution of dust and SS is 18% and 3%, respectively.

POM and IM present considerable seasonal variation. In winter, IM is reduced (down to 23%), the dominant component being POM (42%), and the rest is shared by dust (18%), EC (10%) and SS (4%). In summer, IM is the main component (42%), followed by POM (36%), dust (24%), EC (5%) and SS (4%).

3.4 Temporal variability of winter mass and aerosol chemical composition: the role of residential heating

3.4.1 PM$_{2.5}$ mass

The significant increase in fine aerosol mass in Athens during winter compared to summer, points towards an important additional PM source (Figures 4a, b). During winter-time, residential heating using fossil fuel, wood and coal are important sources of directly emitted PM$_{2.5}$ (EEA, 2013; 2014). The winter stable atmospheric conditions in conjunction with the seasonal decrease of the boundary-layer height (low wind speeds, temperature inversions and low-intensity solar radiation) could further limit dispersion of pollutants. High levels of PM mass during winter due to wood burning have also been observed in prior studies in the two largest urban metropolitan cities in Greece, Athens and Thessaloniki (e.g Saffari et al., 2013; Florou et al., 2017; Gratsea et al., 2017).

It is noteworthy that during winter, PM$_{2.5}$ concentrations during night-time (mean 32.9 μg m^{-3}; median 30.5 μg m^{-3}) are almost twice as high (80% increase; Table 2) as during day-time (mean 19.1 μg m^{-3}; median 19.2 μg m^{-3}), which constitutes additional evidence for the role of domestic heating. Using the approach introduced by Fourtziou et al. (2017), i.e., by selecting periods with wind speed lower than 3 m s^{-1} and an absence of precipitation, 289 days with smog conditions (hereafter named SP; Smog Period) associated with increased levels of air pollutants (NO, CO, BC) have been identified during the 3 examined winters. By further studying the PM$_{2.5}$ concentrations during these smog events, a 96% increase during night-time compared to day-time was observed (Table 2, statistically significant at 99.9% level; p<0.001).

3.4.2 Carbonaceous components

Primary OC and EC from residential heating, can explain the net seasonal trend with higher values during winter as presented in Figures 4c-f. Indeed their levels during winter-time are higher by 55% for OC and 74% for EC, emphasizing the intensity and the sporadic nature of the residential heating source.

5 This is further evidenced by the seasonal variation of Black Carbon (BC) and its wood burning fraction (BC_{wb}), obtained with the use of an aethalometer (AE33) during the period 2015-2016 (Figure 5). BC measurements on total particulate matter (no cut-off inlet) were conducted by means of the new generation seven wavelength Magee Scientific AE33 aethalometer, at one-minute resolution. The wood burning and fossil fuel fractions (BCwb and BCff, respectively) were derived by the on-line application of the two-component model in combination with the dual-spot compensation technology provided by the

10 instrument (Drinovec et al., 2015). Further details on the daily evolution of BC_{wb} and BC_{ff} fractions at the present site can be found at Gratsea et al. (2017) and Fourtziou et al. (2017).

To highlight the impact of heating on carbonaceous levels, Figures 6b and c present their day and night-time variability in winter. The average OC and EC concentrations increased 3 and 2 times during night compared to day, respectively (Table 2). A similar tendency is observed during smog events (SP, Table 2). More specifically, the average OC and EC concentrations

15 during the night for all three winter campaigns are equal to 9.4 µg m^{-3} and 3.8 µg m^{-3} (12.6 µg m^{-3} and 5.1 µg m^{-3} for SP), respectively, with corresponding mean day-time values of 2.7 µg m^{-3} and 1.6 µg m^{-3} (3.4 µg m^{-3} and 2.0 µg m^{-3} for SP). Consequently, the contribution of POM to the total mass of PM$_{2.5}$ in winter is higher during the night (52±4%, median 50%) than in the day (27±10%, median 23%; Figure 6b, c). Similarly, for EC in winter, a smaller but yet evident average increase was also observed during night (12±1%, median 12%) compared to day (8±3%, median 9%).

20 The significant correlation between OC and EC in Athens during winter (slope=2.36; r=0.94; n=472), more enhanced during night-time (slope=2.49; r=0.96; n=226) compared to day-time (1.62; r=0.85; n=221), indicates that they originate from the same sources. Notably, the higher OC to EC ratio during summer (3.21; r=-0.59; n=114), as well as their negative correlation, could be explained by the enhanced photochemical organic aerosol formation in the atmosphere, from low-volatility compounds produced by the oxidation of gas-phase anthropogenic and biogenic precursors (Paraskevopoulou et al.,

25 2014).

3.4.3 Ionic composition

SO_4^{2-} concentration in the PM$_{2.5}$ fraction of aerosol didn't present a pronounced seasonality, with a slightly increasing trend from spring to summer (Figure 2b). During the dry season (spring and summer), the absence of precipitation, and the increased photochemistry lead to secondary aerosol formation and increased lifetime in the area (Mihalopoulos et al., 1997),

30 resulting in the appearance of higher concentrations. In winter, SO_4^{2-} accounts for 8% of the PM$_{2.5}$ mass, while in summer for 26%. During winter, SO_4^{2-} did not show any significant day to night variability (about 11% increase during SP; Table 2), indicating that heating is not the major source of SO_4^{2-}. In addition, the summer maxima suggest that the majority of SO_4^{2-}

originates from long-range transport and thus it can be considered as an indicator of regional sources (Mihalopoulos et al., 1997; Theodosi et al., 2011).

The concentration of **NH_4^+** presents a less pronounced seasonal trend, with a similar monthly distribution pattern as that of SO_4^{2-}, in agreement to previous observations in Athens (Mantas et al., 2014; Paraskevopoulou et al., 2015). As in the case of SO_4^{2-}, NH_4^+ did not present a day to night increase (less than 10% during SP; Table 2). NH_4^+ vs SO_4^{2-} and consequently nss SO_4^{2-}, were significantly correlated (r=0.64) for the entire sampling period (December 2013-March 2016), with a slope on an equivalent basis ($NH_4^+/nssSO_4^{2-}$) smaller than unity (0.62), indicating partial neutralisation of $nssSO_4^{2-}$ by NH_4^+. This suggests that a mixture of NH_4HSO_4 and $(NH_4)_2SO_4$ is formed in the area. Previous studies in Athens and the Eastern Mediterranean have reached the same conclusion (Siskos et al., 2001; Bardouki et al., 2003; Koulouri et al., 2008). NH_4^+ is significantly correlated to NO_3^- only in winter (r=0.73; p<0.001), indicative of NH_4NO_3 formation, as previously suggested for the Greater Athens Area (GAA) (Karageorgos and Rapsomanikis, 2007; Remoundaki et al., 2013; Paraskevopoulou et al., 2015).

NO_3^- levels present higher concentrations in the winter (Figures 2b, 4g). This pattern is related to the formation of NH_4NO_3 stabilized under the low temperatures prevailing during winter (Park et al., 2005; Mariani and de Mello, 2007). NO_3^- could originate from local pollution sources, such as vehicular traffic and combustion for heating purposes. NO_3^- levels are considerably reduced in summer (Figure 4h), due to the thermal instability and volatilization of the NH_4NO_3 (Harrison and Pio, 1983, Querol et al., 2004). A similar seasonal pattern for NO_3^- has been reported previously in Athens (Sillanpää et al., 2006; Paraskevopoulou et al., 2015). During winter months, NO_3^- levels were found to be significantly higher by 53% (53% also if SP is considered; p<0.001 in both cases) during night-time compared to day, indicating probable contribution from heating mainly from more effective partitioning in the particle phase during the colder and humid night time conditions (Figure 6d, Table 2). A significant correlation of NO_3^- with OC, EC and $PM_{2.5}$ was also observed during winter (r=0.58, 0.60 and 0.56 respectively; p<0.001), further supporting their common origin. In summer no statistical significant correlation between these compounds was found.

For the rest of the ions analyzed, their seasonal distribution depends on their main sources which can be classified into marine, mineral or mixed. **Cl^-, Na^+ and Mg^{2+}** controlled by sea spray emissions are expected to have the same seasonal variability, which is related to the prevailing wind speed and direction. However, the temporal variation of Mg^{2+} in Athens revealed higher levels during the warm season (spring-summer), most probably from local dust resuspension and/or regional dust transport, while Cl^- and Na^+ present high levels during winter, most probably due to stronger southern winds prevailing during this period. Cl^- and Mg^{2+} didn't present an increase (even recording a slight decrease) during night compared to day. On the other hand, Na^+ increased by about 21% (Table 2) indicating a small contribution from heating and especially biomass burning, as previously reported by Fourtziou et al. (2017).

$nssCa^{+2}$, considered as an effective tracer of crustal sources in the area (Sciare et al., 2005), is distinctly higher in the warm season due to dust transport from the Sahara and/or regional dust resuspension, the latter due to the absence of precipitation. Regarding **$nssK^+$** a bimodal distribution is observed with peaks in spring and winter. The first peak is associated with

Saharan dust outbreaks and the second as a result of biomass burning emissions. The latter corroborates previous reports for online fine mode K^+ measured at the same site (Fourtziou et al., 2017). In order to discriminate between the influences of Saharan dust and biomass burning on $nssK^+$ levels, we have used Ca^{2+} as a tracer of crustal origin. During the period from March to October, with limited emissions from local biomass burning sources, $nssK^+$ and Ca^{2+} exhibit a significant correlation (r=0.83), confirming their crustal origin. Thus, by using the $nssK^+/Ca^{2+}$ slope from their linear regression (y=0.82x+0.08), the $nssK^+$ of crustal origin (K^+_{dust}) can be identified allowing to further estimate $nssK^+$ of biomass origin (K^+_{bb}) from the following equation:

$$K^+_{bb} = nssK^+ - K^+_{dust} ,$$

K^+_{bb} levels during the winter period account for 70% of the total $nssK^+$ levels and present a well-defined day-night contrast. Mean night-time K^+_{bb} concentrations of 0.5 µg m^{-3} are by 57% increased relative to day-time (Figure 6e; Table 2; p<0.001), highlighting the role of $nssK^+$ as a tracer of wood burning in agreement with Fourtziou et al. (2017). During all three winter campaigns (n>400), the estimated K^+_{bb} correlates significantly with OC, EC and NO_3^-, especially during night-time (r=0.58, 0.57 and 0.46, respectively) compared to day-time (r=0.15 to 0.23).

$C_2O_4^{2-}$ exhibits peaks during winter due to biomass burning emissions (Kawamura et al., 1996; Kawamura and Ikushima, 1993) and during summer linked to enhanced photochemistry, along with increased emissions of biogenic volatile organic compounds (Theodosi et al., 2011). $C_2O_4^{2-}$ presents strong correlations with OC and EC during summer (r=0.42-0.63) due to common emission processes such as photochemical and/or heterogeneous reactions (Myriokefalitakis et al., 2011). SO_4^{2-} presents a significant correlation with $C_2O_4^{2-}$ independent of season (r>0.54; p<0.001). Such correlations have generally been observed in many different sampling locations around the world (Pakkanen et al., 2001; Yao et al., 2003), and can be attributed to heterogeneous reactions during both seasons as proposed by Myriokefalitakis et al. (2011). During winter, from the compounds impacted by heating sources and examined so far, $C_2O_4^{2-}$ correlates significantly only with NO_3^- (r=0.41). In addition, higher concentrations during night (about 30%) compared to day (Table 2) have been also observed, indicating local biomass-burning emissions as possible contributors of $C_2O_4^{2-}$. However, the significant correlations with both SO_4^{2-} and tracers of biomass burning clearly indicate that $C_2O_4^{2-}$ have mixed sources of both local and regional origin and significant precaution is required when $C_2O_4^{2-}$ is used as exclusive tracer of biomass burning.

3.4.4 Trace metals

3.4.4a Crustal – related elements

Al is typically associated with soil dust resuspension and thus mainly linked to natural sources. It presents higher concentrations and larger variations during the transitional (spring and autumn) periods when the air mass trajectories originate predominantly from North Africa and are often associated with intense sporadic peaks of mineral dust (Figure 2c). Mn and Fe, which are affected by diverse natural and anthropogenic sources, present the same seasonal variation (Figures

2c, f) and especially Mn reveals a statistically significant correlation with Al (r=0.59). However, the moderate correlation of Al with Fe (r=0.44), suggests the existence of additional sources for Fe most probably anthropogenic.

Regarding the diurnal pattern of Al, it is higher by about 30% during day-time compared to night (Table 2), most probably due to traffic related dust resuspension. A different behavior was observed for the other two "crustal" elements, with Mn presenting no difference between day and night-time (Table 2), whereas for Fe slightly higher levels were observed during night compared to day by about 10% (Table 2). The above described diurnal variation corroborates our hypothesis for mixed sources, natural and anthropogenic for both Mn and Fe, most probably from combustion emissions in addition to dust (local or regional).

3.4.4b Elements of anthropogenic origin

The measured trace metals originating from human activities (V, Cr, Cd, Ni, Cu, Cd and Pb) relate to a variety of sources. As presented in Figures 2d-f, the elements of anthropogenic origin exhibit well defined seasonal trends with peak values during winter, as a result of additional sources, especially heating, but also of meteorology. When their diurnal distribution was examined during winter-time, only Cd and Pb presented a significant increase (at 95% confidence level) during night-time compared to day, in the range of 11 to 16% (up to about 40% when SP periods are considered; 99.9% confidence level). The above tendency indicates emissions from heating and especially wood burning, in agreement with Maenhaut et al. (2016). The other elements either present an insignificant increase in their levels during night (case of V, Ni) or even a decrease compared to day (case of traffic-related Cu).

Significant correlations of As with Pb and Cd (r=0.39 and 0.66, respectively) were observed during the whole period. When considering the three intensive winter campaigns, higher correlations were obtained between As and Cd (r=0.74) and moderate for Pb (r=0.38), suggesting that heating using coal and wood could be a source of the aforementioned heavy metals (Nava et al., 2015; Maenhaut et al, 2016). In fact, As has been associated with wood combustion, where copper chrome arsenate (CCA) treated timber is being used for residential heating purposes (Fine et al., 2002; Khalil and Rasmussen, 2003; Alastuey et al., 2016). Strong correlations of Pb with $PM_{2.5}$, OC, EC, nssK^+, NO_3^- during winter further reinforce the link with wood combustion sources at our site. Indeed, winter-time Pb concentrations present a significant correlation with $PM_{2.5}$ mass during night-time (r=0.84), as compared to day-time (r=0.14). On the contrary, during summer, Pb significantly correlates with Cd (r=0.68), indicating the prevalence of regional sources for both elements during the non-heating season. Finally, As, Pb and Cd present no pronounced overall or season-specific associations to elements such as Cu and Zn, which are considered as effective brake and tire wear tracers, generally (Weckwerth, 2001; Amato et al., 2009) and in the area (Manalis et al., 2005; Grivas et al., 2018).

During summer relatively high correlation coefficients were calculated between SO_4^{2-} and the typical heavy oil combustion tracers V and Ni, (r=0.69 and 0.60), respectively. This indicates common emission patterns and source types such as shipping. The V/Ni ratio during that period was equal to 1.2, slightly lower than the range of 2 to 4 reported by Viana et al. (2008) to identify shipping emissions, pointing to additional fuel combustion sources. During winter the poorer correlation of

V with Ni (r=0.16) can be explained by a decrease in shipping activities and thus Ni could be related to petrochemical and metallurgical activities (see below).

3.5 Winter-time PM$_{2.5}$ source apportionment

3.5.1 PMF modeling

The model identified six unique factors, characterized as biomass burning, vehicular emissions, regional secondary, heavy oil combustion, dust particles and sea salt. Factor contributions to modelled concentrations of species and source profiles are presented in Figure 7. Average contributions of factors to PM$_{2.5}$ concentrations, separately for day-time and night-time sampling periods are shown in Table 3. PM$_{2.5}$ concentrations were adequately reproduced by the model with high correlation coefficient and slope in modeled vs. observed values regression ($r = 0.92$; slope=0.94; intercept: not significantly different from 0). Results of the BS-DISP error estimation process, with over 95% accurate bootstrap mapping, small change of the Q value and minimal factor swaps indicated the stability of the solution. Details are provided in Table S1 according to recommendations of Brown et al. (2015). Additional PMF results for the full two-year period of March 2014-February 2016 are shown in supplementary Figures S2 and S3.

3.5.2 Source profiles and contributions

- Biomass burning (BB)

The factor is identified by the strong presence of K$^+$ and elevated OC/EC ratios (3.7 on average), suggestive of non-fossil fuel primary emissions. Small amounts of Cl$^-$, C$_2$O$_4^{2-}$, Fe and Pb were also included (Maenhaut et al., 2016), once again indicating wood-burning associations which have been suggested in section 3.4.4b (Table 2). Ratios of SO$_4^{2-}$ to K$^+$ below unity likely indicate relatively fresh biomass-burning emissions (Viana et al., 2013). Source contributions correlated highly to aethalometer-determined BC$_{wb}$ (r=0.88). Strong correlations (r=0.93) were also observed for the winter of 2015-2016 with the mass fragment of m/z 60, quantified by an aerosol chemical speciation monitor (ACSM) concurrently operating at the same site (Stavroulas et al., 2018). The m/z 60 fragment is considered a good tracer for biomass burning emissions (Alfarra et al., 2007) and its levels are closely associated with levoglucosan concentrations. Approximately 35% of EC concentrations are attributed to biomass burning, close to the average winter-time BC$_{wb}$ fraction, which is equal to 32% for the winter period 2015-2016 (Figure 5) and 44% during 2013-2014 (Fourtziou et al., 2017). Comparably elevated BC$_{wb}$ contributions to BC (29-32%) have been reported for the winter of 2014-2015 at two background locations in the Greater Athens Area (Kalogridis et al., 2018). Similarly, for OC, the PMF-calculated BB contribution of 2.6 μg m^{-3} to fine OC is comparable to the 2.3 μg m^{-3} of biomass-burning organic aerosol estimated to be present in submicron non-refractory OM in Thissio, during the winter of 2013 (Florou et al., 2017).

The average contribution of the BB factor in PM$_{2.5}$ during night-time is estimated at 3.4 times the day-time value, double the respective increase (1.7 times) in fine aerosol mass (Table 2). Overall, biomass burning was found to be the source with the largest input to winter-time PM$_{2.5}$ concentrations in the urban-background setting of central Athens. Biomass burning has been recognized as an important contributor to fine particle levels in post-recession Athens, with mean annual contributions varying between 7-10% (Paraskevopoulou et al., 2015; Amato et al., 2016). In the present case, for the confined winter-time period, the average share of the BB factor was found to be much higher (31%). Such large winter-time contributions are increasingly being reported for urban background locations in Southern Europe (Nava et al., 2016; Squizzato et al., 2016; Diapouli et al., 2017; Cesari et al., 2018). Florou et al (2017) have attributed 25% of winter-time (2013) non-refractory submicron aerosol to biomass burning organics at the same site, a result compatible with the presently estimated contribution.

Comparing the BB factor contributions between the two winter periods (2014-15 and 2015-16), a decrease of 33% in the mean concentrations attributed to BB was found. A comparable difference (41%) was observed for mean BC$_{wb}$ concentrations determined by aethalometer measurements. Both were found statistically significant at the 0.01 level. Variation of meteorological parameters factored in the observed difference. Cold conditions were relatively harsher during the first winter, with the mean minimum daily temperature being lower by 1.5°C and more frequent northern synoptic-scale winds transporting cold air masses. Moreover, according to data from the Hellenic Statistical Authority, the amount of heating oil sold in Greece in 2015 increased by 51% compared to the previous year (reaching 0.4 million metric tons as opposed to 0.9 million before the recession), mostly because of lower prices (up to 20% between 2014 and 2015, due to declining crude oil values). Thus, the use of biomass burning for space heating during the second winter is reasonably expected to have decreased.

Although estimated contributions during winter-time are severe, on a year-round basis they are largely curbed. Results from the full-period PMF analysis (Figure S3) indicate a year round average (03/2014-02/2016) contribution of the BB factor amounting to 2.3μg m^{-3}, with a share of 13% to PM$_{2.5}$ mass. The result is justified taking into account that biomass burning for residential heating extends as a source also into November and March which have not been included in the winter-only analysis, and also given the documented summertime long-range transport of agricultural burning emissions to Southern Greece (Bougiatioti et al., 2014). The estimated mean annual fractional contribution of 13% is elevated compared to those reported by Grivas et al. (2018) at an urban background location in central Athens (8%) during 2011-2012 and by Amato et al., (2016) at a suburban background site (10%) during 2013.

Due to the fact that only watersoluble K^{+} was included as a tracer for biomass burning in the PMF analysis, it is possible that some uncertainty is associated with estimated contributions (Pachon et al., 2013). In order to provide an indication of such an uncertainty, and in the absence of levoglucosan measurements, we have repeated the PMF analysis, for the winter of 2015-2016, adding data on the *m/z* 60 and *m/z* 73 mass fragments, from collocated ACSM measurements. These have been validated as important BB tracers at the present site, displaying strong correlations with levoglucosan, as detailed in

Fourtziou et al. (2017). Combination of data from chemical analysis and aerosol mass spectrometry in the same receptor model has been occasionally reported in the literature (Li et al., 2004; Dall' Osto et al., 2014).

A similar 6-factor solution was again obtained and -based on the comparison of resulting BB explained variances and contributions with those of the original dataset (supplementary Figures S4 and S5)- differences were find to be small. The source profiles closely agree and a mean absolute difference of 2.2% (0-10.5%) was calculated for explained variances of species. The average difference in the factor contribution to $PM_{2.5}$ for the winter of 2015-2016 was +0.60 μg m^{-3} (higher in the original solution). The latter is analyzed in +0.61 μg m^{-3} in day-time and +0.57 μg m^{-3} in night-time average contributions. The mean difference of the fractional contribution to $PM_{2.5}$ is 3.3%.

NO_3^- was predominantly classified in the biomass burning factor. NO_3^- in central Athens is formed as a product of fast chemical processes involving fresh NO_x emissions at a local level (Theodosi et al., 2011). In cold-weather conditions, nitrate condensation of semi-volatile ammonium nitrate in the particle phase is enhanced. Especially during the night, when temperatures drop significantly and fresh wood-burning NO_x is abundant, nitrate concentrations rise significantly (53%; section 3.4.3), establishing a pattern of temporal covariance with biomass burning indicators (Xie et al., 2008; Amato et al., 2016). Moreover, associations between biomass burning aerosols and nitrate that are observed in Southern Greece (Bougiatioti et al., 2014), have been attributed to reduced acidity, which facilitates NO_3^- partitioning in the particle phase (Guo et al., 2016). Higher night-time pH values are anticipated both due to the ionic content of wood-burning emissions and because of increased water content during the nocturnal hours (Bougiatioti et al., 2016), especially in humid conditions favourable for the occurrence of winter-time smog events.

While a separate secondary nitrate factor has been occasionally identified in PMF studies in Athens (Amato et al., 2016), in this winter fine particle dataset, it was not possible to obtain a stable solution with more than six factors. The absence of a nitrate factor in PMF results for PM in Athens has also been reported by Paraskevopoulou et al. (2015) and Diapouli et al. (2017). The latter, at two urban and suburban background sites in Athens, presented a nitrate mass fraction in the BB factor similar to the one presently reported (around 0.1 μg μg^{-1}), with the factor being the main contributor to fine nitrate. Since the possibility that the secondary nitrate included in the BB factor might be inflating its contribution can't be completely ruled out, the total nitrate attributed to the factor (as NH_4NO_3) has been considered as an upper bound of overestimation. In this case, the overestimation during day-time and night-time would be 0.44 and 1.46 μg m^{-3}, respectively. The contributions of the factor to the $PM_{2.5}$ would still be 17% and 35% during the two day periods (2% and 4% less than calculated). For comparison, Amato et al. (2016) have reported an annual secondary nitrate contribution of 0.7 μg m^{-3} for $PM_{2.5}$ in suburban Athens.

- Fossil fuel sources (VEH and OIL)

The vehicular emissions factor (VEH) is characterized by an abundance in EC, OC, Cu and to a lesser extent Zn, Pb and insoluble Ca, which is most probably related to traffic-induced resuspension of dust (Kassomenos et al., 2012) in the calcite rich Attica region (Silanpaa et al., 2005). Factor contributions correlate well with the fossil fuel fraction of BC (BC_{ff},

r=0.87). The factor also correlates much better than the biomass burning factor with NO_x (r=0.94) and CO (r=0.91) concentrations, measured at a nearby roadside traffic site (0.9 km to the NE) and used as indicators of local traffic variability (respective correlations with BB factor: r-NO_x=0.60, r-CO=0.61). Moreover, the factor is significantly anti-correlated with the CO/NO_x concentration ratio (r = -0.60), which has been used to discern between traffic and BB emissions, since the latter contain more CO in comparison with combustion in engines where, due to higher temperatures, a larger amount of NO_x is produced (Sandradewi et al., 2008). The EC/OC ratio in the factor equals 0.62, suggestive of vehicular exhaust emissions (Pio et al., 2011). The overall contribution of 19% to $PM_{2.5}$ is reasonable for urban background locations in Europe (Belis et al., 2013) and comparable to previous results in Athens (Paraskevopoulou et al., 2015). While an interference of fuel emissions from domestic heating in the factor can't be completely excluded, it is believed that it wouldn't be significant, given the low share of heating oil combustion to total PM emissions from domestic heating in Greece (Fameli and Assimakopoulos, 2016). Average night-time contributions are slightly higher (by a factor of 1.5); however, the difference was not statistically significant at the 0.05 level.

The oil combustion factor (OIL) is dominated by the presence of V and Ni, at ratios indicative of residual oil combustion (V/Ni: 1.8). Sulfate is present at the source profile with a contribution of 0.07µg µg^{-1} and an explained variance of 4.4%, values that are relatively small, but within the range of those reported for oil combustion factors in other cities in the Mediterranean (Amato et al., 2016; Kocak et al., 2011; Reche et al.,2012). The observed V/Ni ratio appears to fall short from the typical values reported for shipping emissions (Pandolfi et al., 2011). In Athens, a major part of shipping emissions that affect the inner parts of the basin derive from passenger and cruise ship activity, which during the winter months diminishes. Karageorgos and Rapsomanikis (2010) have reported winter-time V/Ni ratios of 1.5-1.9 for sites in central Athens for fine particles deriving from mixed harbour and industrial emissions in the S-SW part of Athens. As it can be seen in Figures S6a, b, moderately high contributions are associated with westerly advections from the industrialized Thriassion plain, while exceedances of the 75th percentile are more probable with winds from the harbour zone to the south. No pronounced day-night contrasts were observed, indicating that oil combustion for residential heating should not influence the source profile. The average contribution of the factor in $PM_{2.5}$ (7%, 1.5 µg m^{-3}) is within the range reported for Mediterranean areas affected by harbour emissions (Perez et al., 2016).

- Secondary sources (SEC)

The factor is characterized mainly by the presence of sulfate. The observed SO_4^{2-}/NH_4^+ ratio in the source profile (2.2) is close to the stoichiometric, modified by the presence of NH_4NO_3. $C_2O_4^{2-}$ is predominantly associated with this factor, its close correlation to SO_4^{2-} having been attributed to common in-cloud processing mechanisms (Yu et al, 2005), in agreement with the results in section 3.4.3. The OC/EC ratio exceeds the value of two (2.2). In comparison to year-round observations, reduced OC/EC ratios (Grivas et al., 2012) and regional contributions (Paraskevopoulou et al., 2015) have been documented in the area during winter months, due to limited formation of secondary organics from photo-oxidation processes. Higher contributions were observed during day-time, most probably due to increased photochemical activity. Grivas et al. (2018),

estimated 5.5 μg m^{-3} of secondary regional contribution for the cold period of 2011-2012 (extending from mid-October to mid-April), at an urban background location in Central Athens, consistent with values presently reported. When the analysis was conducted for the full period, this sulfate- and OC- rich factor arises as the key contributor in PM$_{2.5}$ (38%), owing to increased regional photochemical production (Hasheminassab et al., 2014). Its share is comparable with results reported for

5   fine particles at background locations in Athens, which indicate a contribution range of 27-54% (Paraskevopoulou et al., 2015; Mantas et al., 2014).

- Natural sources (DUST and SS)

The factor identified as dust is characterized by the presence of Al, Fe, Ca (soluble and insoluble) and Mn. The observed

10   ratio of Fe/Al (1.9) is higher than the values reported for local top-soil (Argyraki and Kelepertzis, 2014) or for Saharan dust (Formenti et al., 2003). It appears that road dust -rich in trace elements deriving from mechanical wear - is incorporated in the dust factor as indicated above in section 3.4.4a. A further indication of the participation of road dust is the abundance of Cr in the factor, which is largely enriched (enrichment factor EF>100, using Al as the reference element), with respect to the upper crust composition (Wedepohl, 1995). Dust contributions do not present significant day-night variability and overall

15   they account for 8% of the PM$_{2.5}$ concentrations, in line with contributions to PM$_{2.5}$ reported for the urban background of central Athens during 2011-2012 (Grivas et al., 2018).

High contributions to Cl$^-$ and Na$^+$ are characteristic for the marine aerosol factor, which records higher-than-median contributions mainly during moderate flows from the sea, five km to the S of the site (Figure S6c). Ca^{2+} ions participate at a fraction of Cl$^-$ representative of the composition of seawater, while insoluble Ca does not participate in the factor (Tan et al.,

20   2016). Cl$^-$ depletion is limited during the winter months, allowing for a more realistic quantification of the input of marine aerosols to the fine particle fraction. A relatively higher contribution of the factor to particle mass (9% in winter, 7% on a year-round basis), in comparison to past studies in Athens is noted (Paraskevopoulou et al., 2015; Amato et al., 2016), probably related to the closer vicinity of the site to the sea.

4 Conclusions

25   This study reports detailed measurements of PM$_{2.5}$ chemical composition at central Athens, from December 2013 to March 2016, including 3 intensive winter campaigns. Approximately 850 daily PM$_{2.5}$ samples were collected and analyzed for the main ions, trace metals, OC and EC, quantifying a range of useful tracers for monitoring the contribution of the different sources to the aerosol load in Athens.

From the results, it appears that in spite of reductions in anthropogenic emissions during the past years, mean annual PM$_{2.5}$

30   levels persist in the vicinity of 20 μg m^{-3}, a value of relevance for increased population exposure in urban background areas, as evidenced by its selection in the EU Average Exposure Indicator of the 2008/50/EC directive.

Levels of both POM and EC considerably increased during winter (POM 11.6 μg m^{-3}; EC, 2.8 μg m^{-3}) compared to summer (POM 5.2 μg m^{-3}; EC 0.7 μg m^{-3}), underlining the major role of heating-related emissions during winter in Athens. It is noteworthy that winter EC levels exceed mean winter EC concentration measured in PM$_{10}$ at a roadside location in central Athens, 10 years prior to this study (Grivas et al., 2012), indicating the recent intensification of winter-time emissions of

5   carbonaceous compounds.

Ionic concentrations exhibit a summer maximum, with SO$_4^{2-}$ and NH$_4^+$ concentrations up to 3.8 and 1.7 μg m^{-3}, respectively. This is related to the significant contribution from photochemistry during that period, combined with less precipitation and higher regional transport as both compounds are related to regional rather than local sources. Overall, the long-term sulfate measurements indicate that levels in the area have progressively declined during the last two decades, reflecting the

10   reductions of regional emissions of sulfur oxides from energy production in Greece.

The importance of residential heating was highlighted by examining the diurnal variation of measured species during winter-time. During the heating period, from November to February, PM$_{2.5}$, POM, EC, NO$_3^-$, nssK$^+$ and C$_2$O$_4^{2-}$ significantly increased during night compared to day-time, due to the intensive use of fossil fuel and wood for heating purposes. Heavy metals such as As, Cd and Pb were also found to be associated to heating activities in winter. However, the present results

15   from long-term measurements, indicate that violations of the EU target values for As, Cd, Ni, as defined in the 2004/107/EC directive, are unlikely at urban background locations in the area.

In order to further quantify the importance of residential heating during winter in the city centre of Athens, PMF source apportionment was performed with specific emphasis on day-night patterns. Biomass burning was found to be the source with the largest input to winter-time PM$_{2.5}$ concentrations (32%) in the urban-background site of central Athens, with a

20   higher night-time contribution (39%) to the PM$_{2.5}$ compared to day-time (19%). The vehicular emissions and oil combustion factors contributed almost equally between night and day (19% and 7 % for the two factors, respectively). The factors representing natural emissions (crustal and marine) presented slightly higher contributions during day-time (9% dust and 11% SS) compared to night-time (6% dust and 7% SS). Regional secondary sources were found to be the source with the largest input to winter day-time PM$_{2.5}$ concentrations equal to 30%, higher by a factor of almost 2 compared to night-time

25   contributions.

Based on these source apportionment results, one can infer that biomass burning, can account for a large part of the observed increase in PM$_{2.5}$ levels in winter night-time. Moreover, the smog events are likely to inflate the number of exceedances of the 24-h limit value for PM$_{10}$ samples at the station. It is noteworthy that the contribution of the biomass burning factor was estimated over 10 μg m^{-3} on 31% of the analyzed days. In spite of severe levels during winter-time, the results of the

30   extended two-year PMF analysis, indicated a much lower mean contribution to PM$_{2.5}$ on an annual basis.

An important effect of winter-time biomass burning emissions is the reversal of the long-established seasonal pattern of PM concentrations at urban background sites in Athens. Whereas, prior to the recession, the monthly variation of PM$_{10}$ and PM$_{2.5}$ concentrations at urban and suburban background sites produced an enhancement during the summer period, attributed to

secondary particles (Kassomenos et al., 2014), the results from this long-term study indicated that winter-time levels at the urban background of Athens are now significantly higher during winter.

It has been demonstrated that the contribution of the BB factor triples during the evening and night hours in winter-time. Such an increase is notable, even though its direct impact for population exposure might be moderated by the fact that the majority of the population stays mostly indoors during this time frame. On the other hand, this specific source type, has been also linked to significant indoor exposure from fireplaces and wood-stoves, so it's effects are adding up.

Given the apparent importance of biomass burning as a major pollution source in Athens -escalating since the winter of 2012- chemical composition measurements should continue in order to track its year-to-year variability. Additionally, estimation of the biomass burning-related sources using other approaches such as high resolution measurements of the organic submicron fraction (i.e the work by Stavroulas et al., 2018), should be helpful to elucidate not only the potential impacts of this environmental issue, but also the related dynamic processes in the atmospheric chemistry of urban areas.

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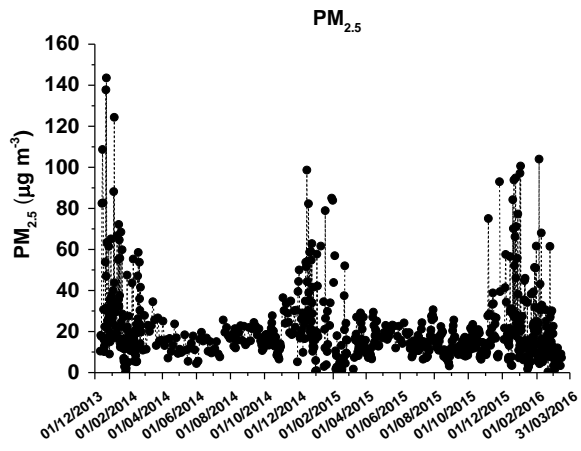


Figure 1: Daily PM₂.₅ mass concentrations (µg m⁻³) at Thissio station for the studied period December 2013 to March 2016.

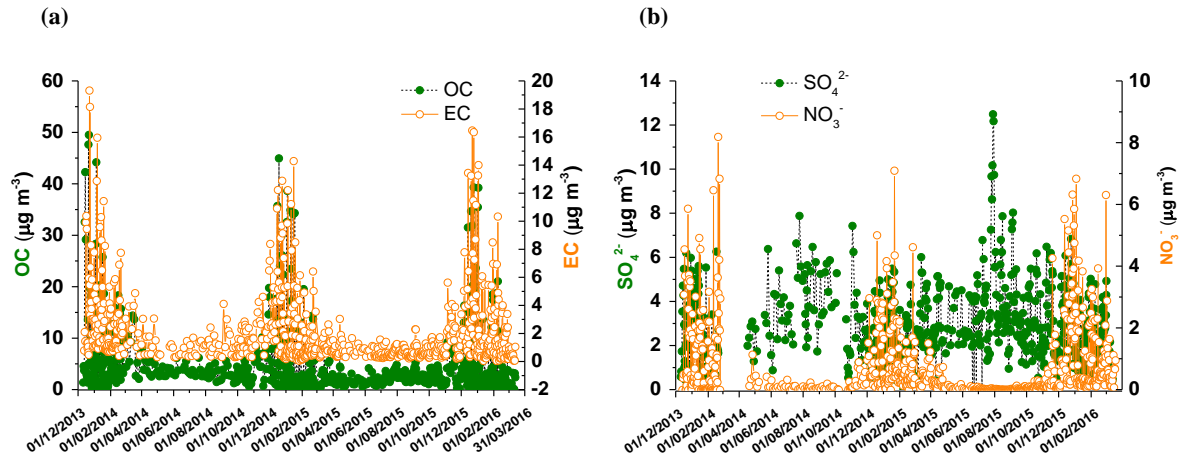
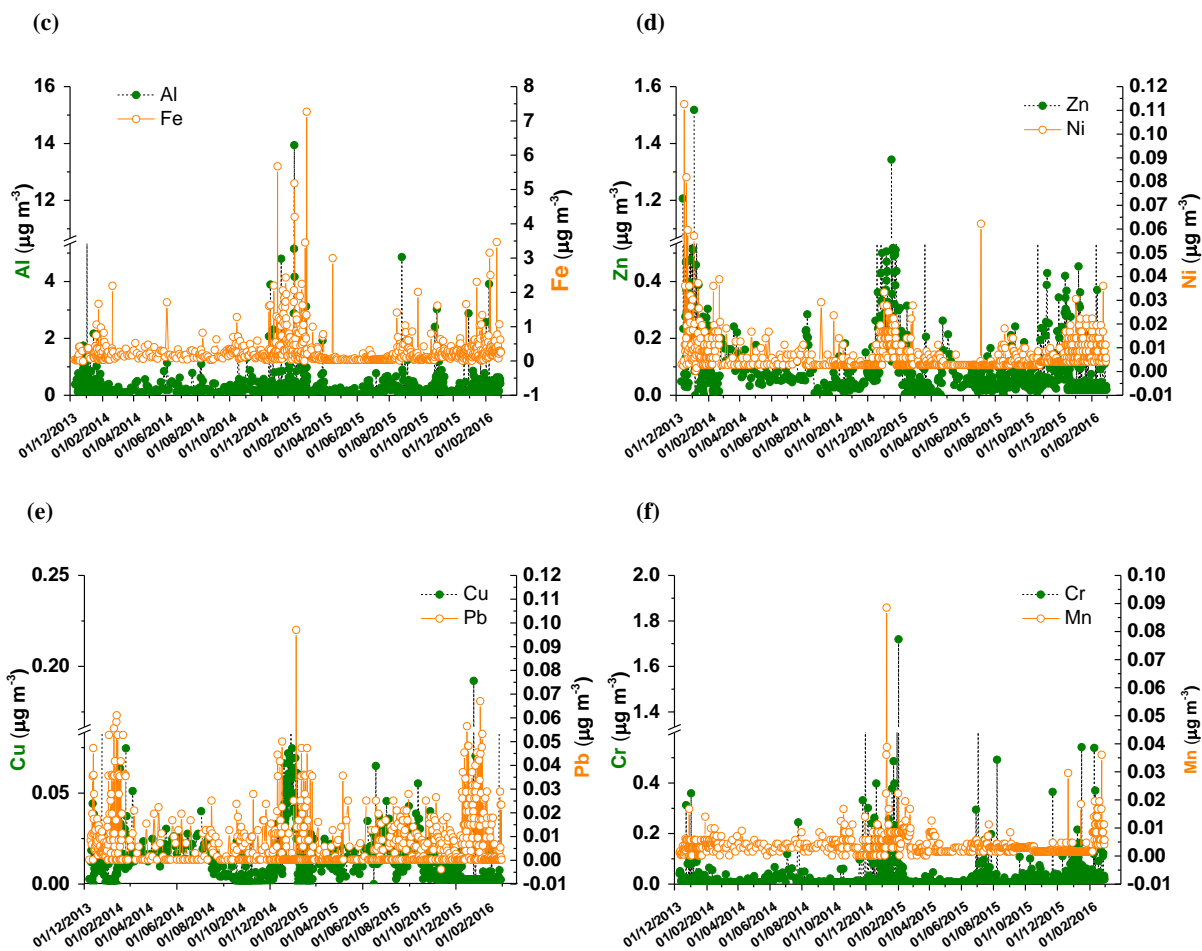



Figure 2: Daily variation of (a) OC, EC, (b) SO$_4^{2-}$, NO$_3^-$, (c) Al, Fe, (d) Zn, Ni, (e) Cu, Pb and (f) Cr, Mn for PM$_{2.5}$ samples collected at Thissio for the sampling period December 2013–March 2016.

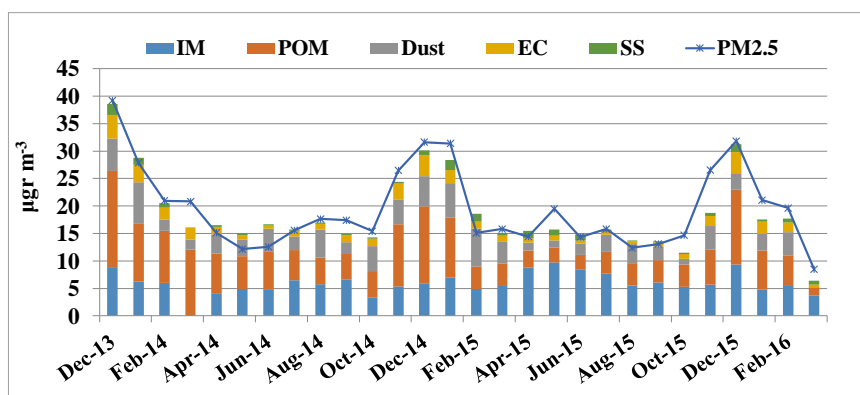
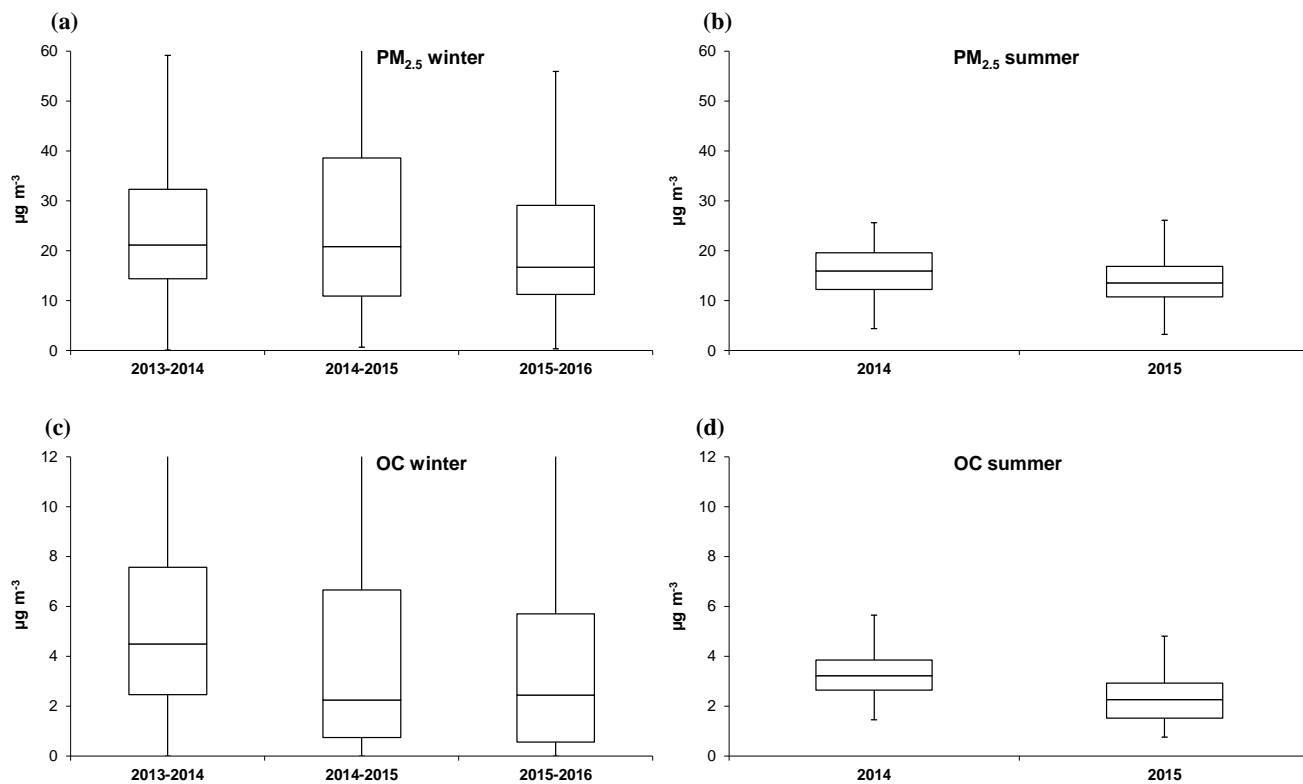
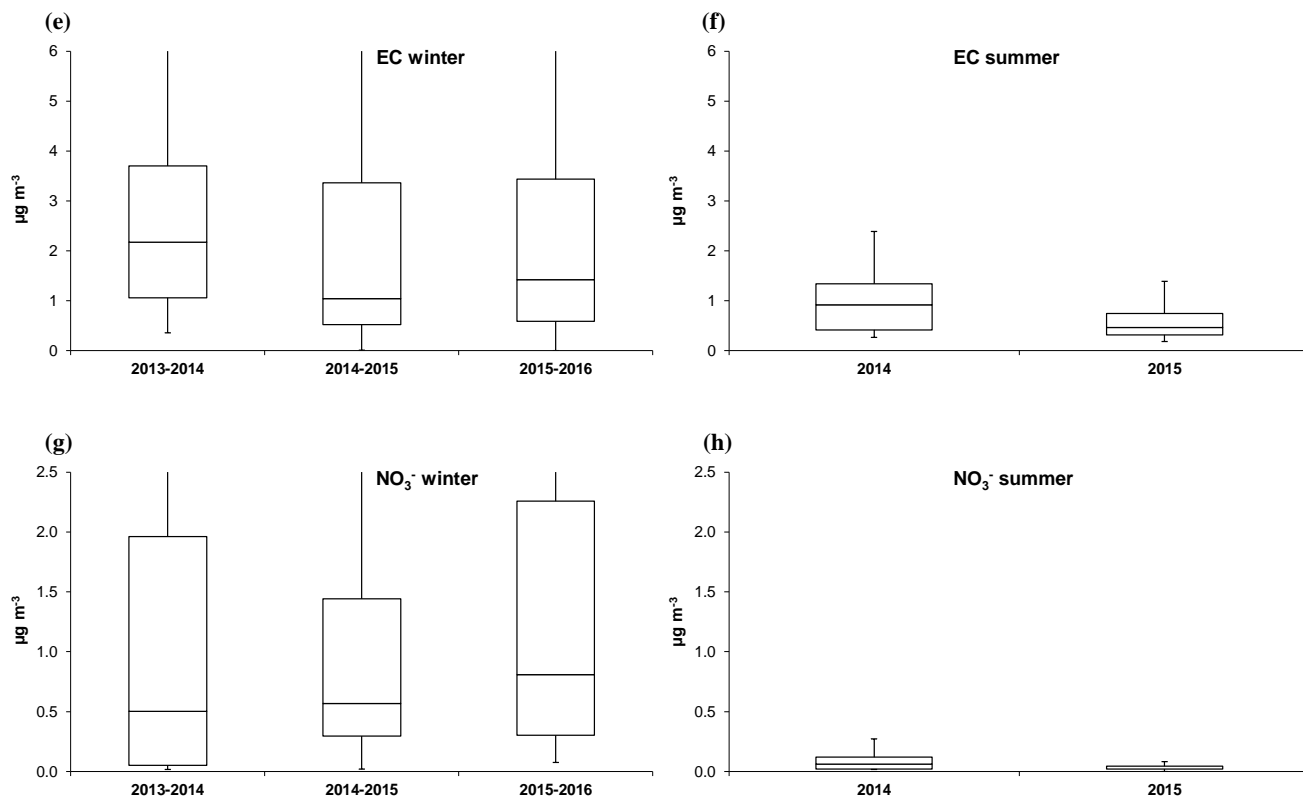
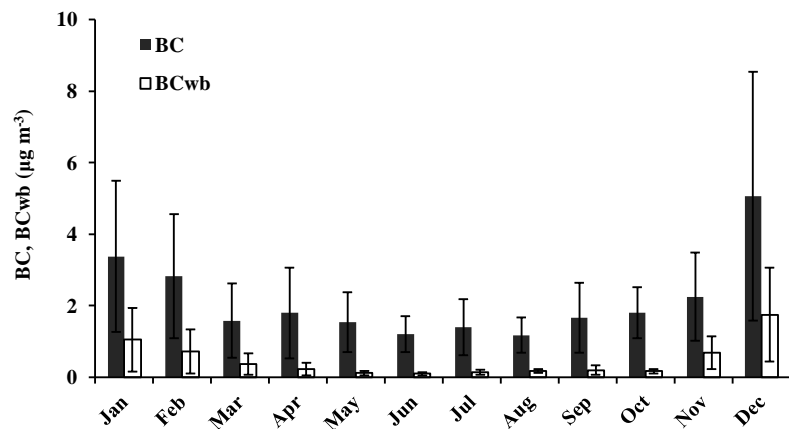



Figure 3: Annual seasonal chemical mass closure of each aerosol species for PM$_{2.5}$ samples collected at Thissio for the studied period.

(e) EC winter

(f) EC summer

(g) NO$_3^-$ winter

(h) NO$_3^-$ summer

5   **Figure 4: Winter and summer interquartile range (µg m^{-3}) for PM$_{2.5}$ mass, OC, EC and NO$_3^-$ concentrations in the urban site of Thissio for the studied period December 2013 to March 2016. The ends of the whisker are set at 1.5*IQR above the third quartile (Q3) and 1.5*IQR below the first quartile (Q1).**

10   **Figure 5: Seasonal variation of BC and BC$_{wb}$ at Thissio during May 2015-May 2016. The November point corresponds to black carbon measurements during fall of 2016. Posterior data are used in order to depict a non interrupted annual pattern.**

(g)

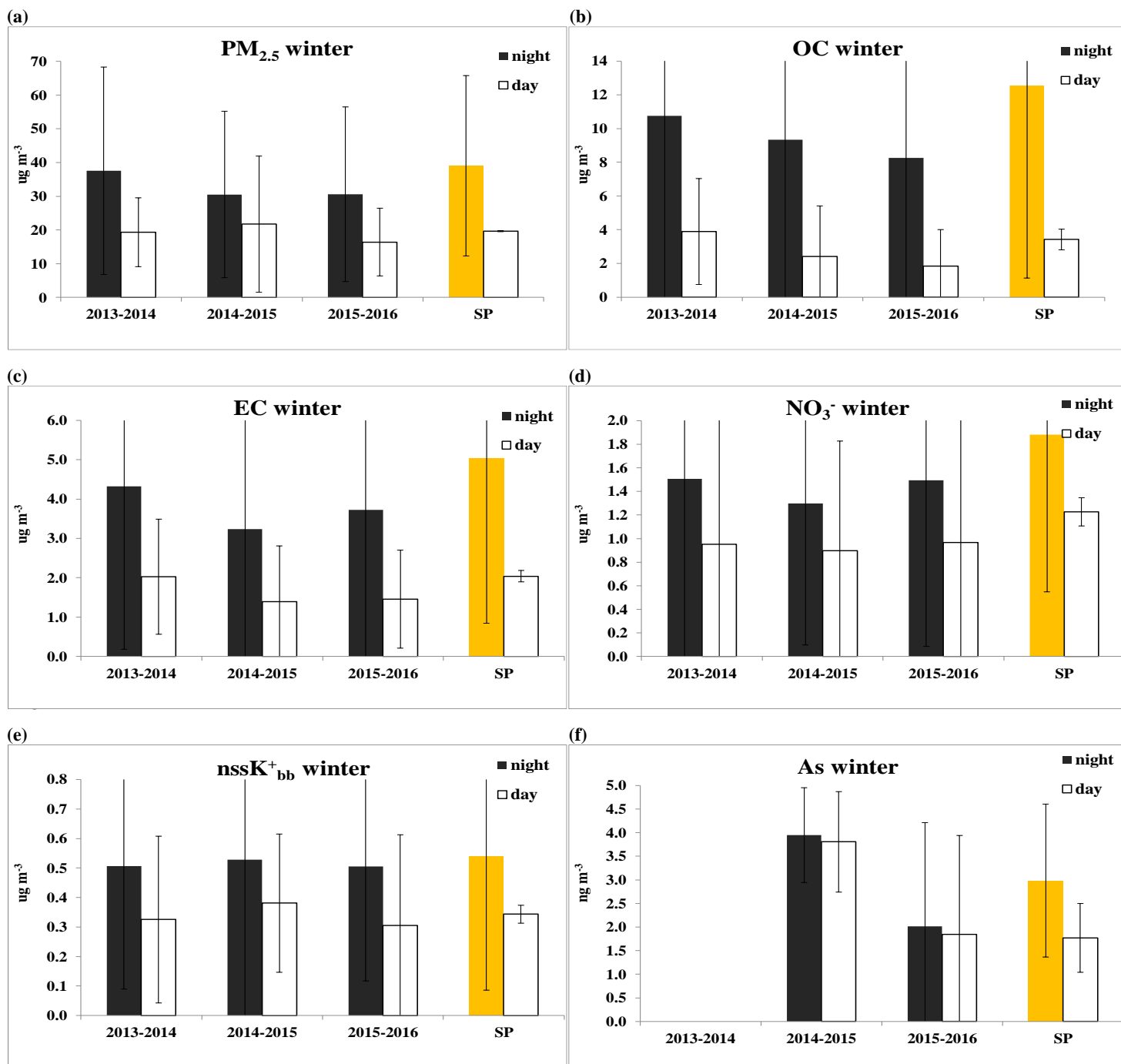
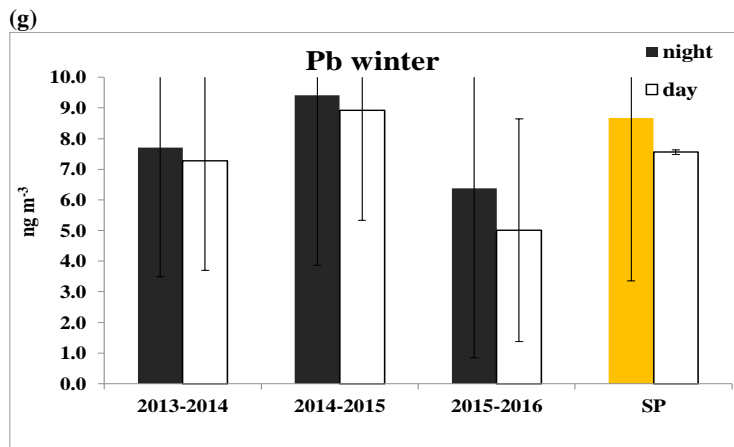



Figure 6: Winter $PM_{2.5}$ mass, OC, EC, NO_3^-, $nssK^+_{bb}$, As and Pb values (µg m^{-3}) divided into day-time and night-time samples. SP
refers to concentrations when only smog events occurred.

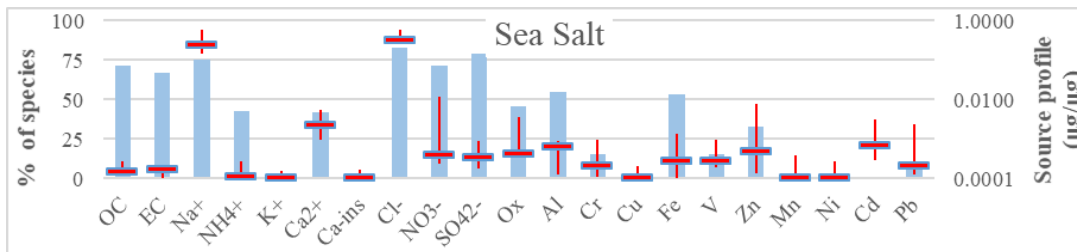
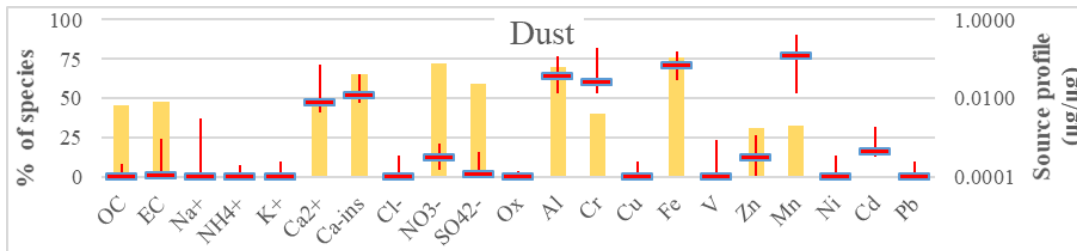
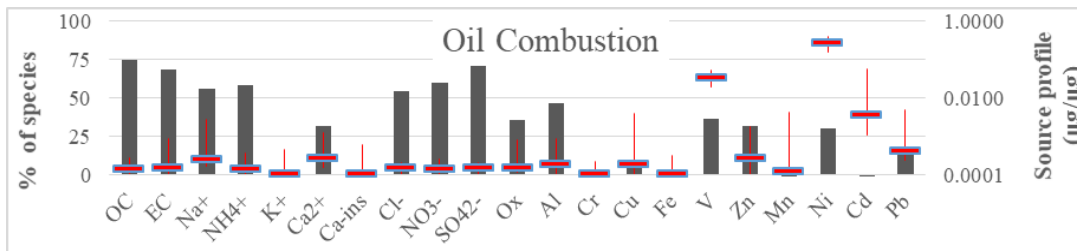
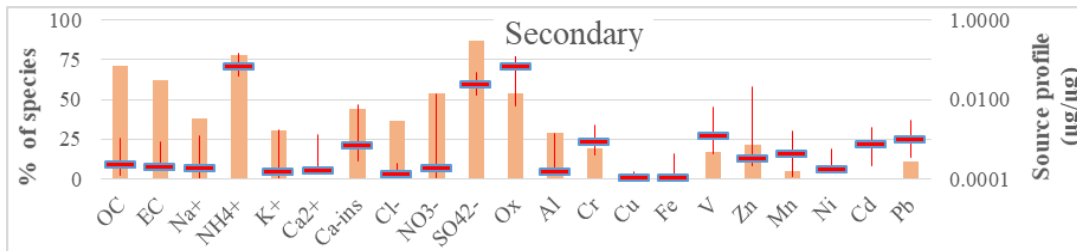
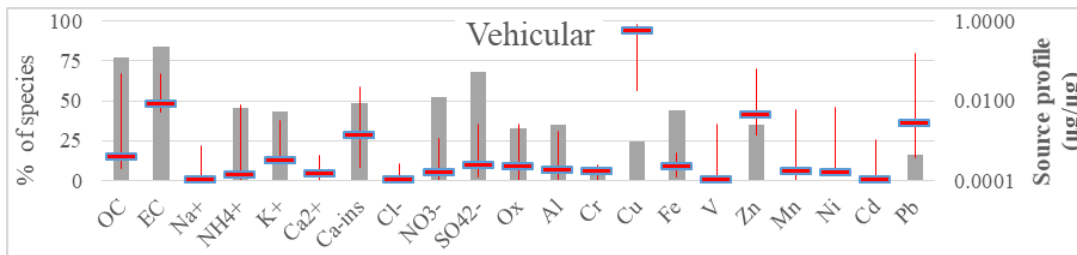
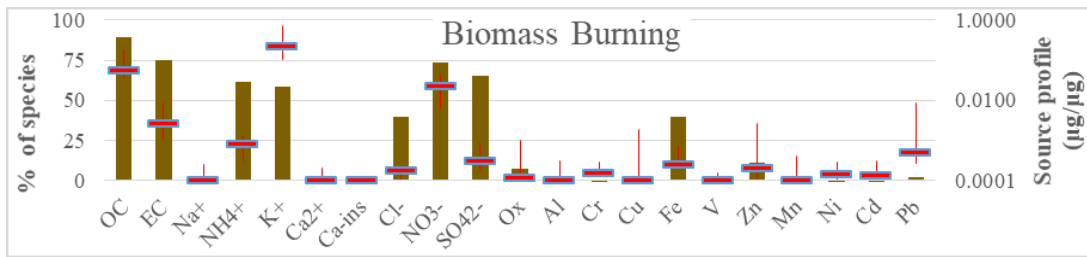



Figure 7: Average contributions to the component mass (%, red markers) and source profiles (µg mg⁻¹, colored vertical bars) of PMF-resolved sources. Error bars providing the interquartile range from bootstrap resamples.

Table 1: Mean, standard deviation, median and range of measured concentrations for PM$_{2.5}$ aerosol samples, collected at Thissio and other urban sites in Athens. Values for PM$_{2,5}$, OC and EC are in µg m^{-3}, whereas for the rest of the species in ng m^{-3}.

ng m^{-3}	PM$_{2.5}$		PM$_{2.5}$		PM$_{2.5}$	PM$_{2.5}$	PM$_{2.5}$
	Mean	Median	Mean	range	Summer/Winter Mean	Mean±stdev	Mean±stdev
Sampling	Dec 2013-March 2016 (n=850)		Summer 1987 (n=27)		Summer 1982 /winter 1982-1983 (n=29)	Sep 2005-Aug 2006 (n=109)	4 short- term seasonal campaigns Jun 2011-Feb 2013 (n=211)
Location	Athens urban		Athens urban		Athens urban	Athens urban	Athens urban
Reference	This study		Scheff and Valiozis, 1990		Valaoras et al. (1988)	Theodosi et al. (2011)	Paraskevopoulou et al. (2015)
PM$_{2.5}$	19.1±7.1	15.5	80.7	27-127		29.4±10.3	33±12
OC	4.0±2.0	3.12	16.9	5.7-43.4	25.7/16.1	-	5.55±2.01
EC	1.5±1.0	1.12	4.2	1.2-18.6	8.20/11.0	-	2.06±0.78
Cl$^-$	272±197	155	350	0-1300	75/440	490	182±80.2
Br$^-$	19.4±10.7	14.2	130	0-589	140/380	-	-
NO$_3^-$	476±377	278	2000	500-5100	-	1090	896±634
HPO$_4^{2-}$	54.3±37.4	46.4	-	-	-	-	72.9±73.6
SO$_4^{2-}$	3033±835	2933	10400	4100-23700	-	5790	3293±1473
C$_2$O$_4^{2-}$	143±56	123	-	-	-	320	203±50.4
Na$^+$	307±196	369	369	0-1890	-	830	255±78.7
NH$_4^+$	1422±685	1112	-	-	-	920	843±433
K$^+$	273±109	268	428	24.2-833	160/380**	460	150±76.7
Mg^{2+}	64.0±31.6	60.7	132	0-653	-	50	8.84±10.9
Ca^{2+}	160±127	113	-	-	-	320	219±246
Al	293±106	263	408	-	130/850	-	494±95.3
As	1.9±0.2	1.83	-	-	34/13	-	4.35±5.56
Ca	745±522	501	2610	776-4970	-	-	898±254
Cd	1.7±0.7	1.75	220	0-1141	-	-	1.16±0.60
Cr	27.1±20.4	19.6	-	-	-	-	18.8±6.29
Cu	14.8±5.2	16.2	50.6	0-143	35/260	-	17.4±5.75
Fe	264±125	234	1100	293-1990	490/300	-	304±110
V	6.9±2.4	6.61	-	-	-/6.60	-	7.79±3.86
Zn	93.0±50.1	73.1	273	46.8-615	130/210	-	94.9±34.8
Mn	4.6±1.4	5.06	21.6	0-70.3	-/14.0	-	5.68±1.23
Ni	6.0±2.6	4.86	11.6	0-37.4	21.0/8.60	-	5.16±2.41
Pb	4.1±3.4	3.68	699	162-2273	610/1100	-	12.5±2.46

Table 2: % increase in the diurnal distribution of all studied elements and species during night-time compared to day in winter for all winter samples (n=447) and smog pollution events (SP, n=289).

%	Full winter period			Only SP		
	mean	stdev	median	mean	stdev	median
$PM_{2.5}$	80%****	120%	55%	96%****	158%	80%
OC	254%****	278%	200%	278%****	285%	232%
EC	134%****	189%	113%	148%****	207%	115%
Cl^-	-6%	2%	-6%	-1%	11%	-10%
NO_3^-	53%****	32%	90%	53%****	17%	111%
SO_4^{2-}	9%	15%	3%	11%****	14%	7%
$C_2O_4^{2-}$	29%***	18%	33%	28%*	22%	35%
Na^+	36%	219%	6%	21%	46%	13%
NH_4^+	13%****	7%	13%	9%****	5%	12%
$nssK^+_{bb}$	54%****	68%	34%	57%***	53%	39%
Mg^{2+}	-11%	16%	0%	0%	13%	0%
Ca^{2+}	-57%	65%	0%	-70%	90%	0%
Al	-26%	53%	-19%	-11%	40%	-19%
As	11%	2%	26%	22%	4%	70%
Cd	16%*	6%	0%	37%****	12%	0%
Cr	-2%	20%	-13%	21%	15%	33%
Cu	-24%	66%	-50%	-23%	70%	-50%
Fe	9%	10%	13%	31%*	5%	29%
V	1%	3%	0%	5%	4%	17%
Zn	18%	34%	9%	9%	4%	30%
Mn	-5%	27%	0%	1%	14%	0%
Ni	-3%	17%	0%	5%	7%	33%
Pb	12%*	35%	10%	20%****	34%	19%

****$p<0.001$ (99.9%) *** $p<0.01$ (99%), ** $p<0.025$ (97.5%), * $p<0.05$ (95%)

Table 3: Average day/night contributions of identified sources to PM$_{2.5}$ (µg m^{-3}). Respective percentages in parentheses. Statistical significance (p) refers to differences for day-night pairwise comparison assessed with Wilcoxon signed-rank non-parametric tests.

Source	Day	Night	Significance (p)
Biomass Burning	3.3 (19)	11.3 (39)	0.00*
Vehicular	3.4 (19)	5.4 (19)	0.10
Secondary	5.4 (31)	4.2 (14)	0.00*
Oil Combustion	1.4 (8)	1.6 (6)	0.55
Dust	1.7 (10)	1.9 (7)	0.48
Sea Salt	2.2 (12)	2.1 (7)	0.17
Unaccounted	0.2 (1)	2.4 (8)	

*significant at the 0.05 level