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Evolution of air pollution source contributions over one decade, derived by PM₁₀ and PM_{2.5} source apportionment in two metropolitan urban areas in Greece

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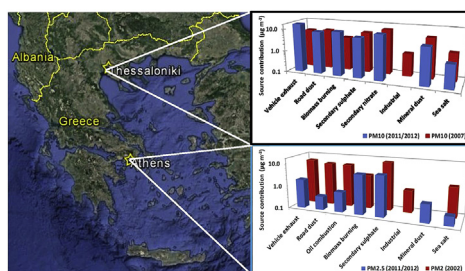
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HIGHLIGHTS

- High contributions from secondary sulphate and organics.
- NO₃⁻ is formed by the reaction of local NO_x with biomass or marine aerosol.
- Significant increase in wintertime biomass burning during recent years.
- Lower emissions due to control measures and decreased economic activities.
- The financial crisis led to more polluting practices by local populations.

GRAPHICAL ABSTRACT



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ABSTRACT

Metropolitan Urban areas in Greece have been known to suffer from poor air quality, due to variety of emission sources, topography and climatic conditions favouring the accumulation of pollution. While a number of control measures have been implemented since the 1990s, resulting in reductions of atmospheric pollution and changes in emission source contributions, the financial crisis which started in 2009 has significantly altered this picture. The present study is the first effort to assess the contribution of emission sources to PM₁₀ and PM_{2.5} concentration levels and their long-term variability (over 5–10 years), in the two largest metropolitan urban areas in Greece (Athens and Thessaloniki). Intensive measurement campaigns were conducted during 2011–2012 at suburban, urban background and urban traffic sites in these two cities. In addition, available datasets from previous measurements in Athens and Thessaloniki were used in order to assess the long-term variability of concentrations and sources. Chemical composition analysis of the 2011–2012 samples showed that carbonaceous matter was the most abundant component for both PM size fractions. Significant increase of carbonaceous particle concentrations and of OC/EC ratio during the cold period, especially in the residential urban background sites, pointed towards domestic heating and more particularly wood (biomass) burning as a significant source. PMF analysis further supported this finding. Biomass burning was the largest contributing source at the two urban background sites (with mean contributions for the two size fractions in the range of 24–46%). Secondary aerosol formation (sulphate, nitrate & organics) was also a major contributing source for both size fractions at the suburban and urban background sites. At the urban traffic site, vehicular traffic (exhaust and non-exhaust emissions) was the source with the highest contributions, accounting

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for 44% of PM₁₀ and 37% of PM_{2.5}, respectively. The long-term variability of emission sources in the two cities (over 5–10 years), assessed through a harmonized application of the PMF technique on recent and past year data, clearly demonstrates the effective reduction in emissions during the last decade due to control measures and technological development; however, it also reflects the effects of the financial crisis in Greece during these years, which has led to decreased economic activities and the adoption of more polluting practices by the local population in an effort to reduce living costs.

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1. Introduction

Particulate matter (PM) is a key atmospheric pollutant for local and regional air quality, with major implications to human health (Ostro et al., 2015; Samoli et al., 2013; Li et al., 2003), degradation of natural and built environment (Gao et al., 2002; Polissar et al., 2001) and climate change (Ramanathan and Feng, 2009; Lohmann and Feichter, 2005). Urban centres have been known to present increased PM levels due to the high degree of urbanization and dense vehicular traffic (Duh et al., 2008). According to the latest report of the European Environmental Agency (EEA), in 2014 a large fraction of European cities still displayed exceedances of the air quality standards for PM₁₀ and PM_{2.5}, with the majority of exceedances observed in Eastern Europe and the Balkan region (EEA, 2016). Apart from major concerns with respect to the impacts on public health in densely populated urban centres, these increased concentration levels may also have implications on regional pollution (Lawrence et al., 2007). The lack of progress by national or regional governments in achieving attainment of PM limit values is not always related to the absence of mitigation measures but also to the innate difficulty in controlling a pollutant with such diverse sources and formation mechanisms.

PM is a complex mixture of chemical species, originating from a variety of sources, both anthropogenic (traffic, industrial activities and combustion processes in general) and natural (wind-blown dust, sea salt, forest fires, volcanic eruptions), and may be emitted as primary pollutant or formed as a secondary product through atmospheric processes from gaseous precursors (Seinfeld and Pandis, 1998). Given the reductions in PM concentration levels already observed over the last decades, but also the evolution of the environmental legislation, with more stringent air quality standards coming into effect, it becomes apparent that future efforts need to be targeted on specific sources in order to be successful. The quantitative assessment of the contribution of the different emission sources in the observed PM levels is thus crucial for the development of effective mitigation strategies. It should also be taken into account that the origin of PM determines key properties, such as size distribution, particles' shape and chemical composition, all parameters affecting particles' toxicity and consequently human health effects. Acknowledging the strong link between particle sources and respective health impact, some researchers have attempted to associate source-apportioned PM, rather than total PM mass, and health outcomes (Ito et al., 2006 and references therein).

Source apportionment of PM concentrations has been recognized to be a powerful tool, both in terms of aerosol science and air quality management. Over the last decade, source apportionment techniques have been applied in North America, South-Eastern Asia and Europe, while, during the last years, efforts are made to include this type of modelling in EC environmental reporting protocols (Karagulian and Belis, 2012). Receptor modelling is a source apportionment method that attributes observed concentrations to

sources, through statistical interpretation of data. Positive Matrix Factorization (PMF) is a widely-used receptor modelling tool, which has been proven to effectively resolve PM sources, either of primary or secondary origin, and accurately calculate their contribution (Belis et al., 2013 and references therein).

Southern Europe, and Greece in particular, have been known to suffer from poor air quality due to emissions by natural and anthropogenic sources of local or regional origin. The Mediterranean climate (low precipitation rates and high solar radiation) which favours particle formation and accumulation (Lazaridis et al., 2006, 2005) and the complex topography and urban planning of Greek cities have further aggravated the problem, resulting in high yearly PM₁₀ and PM_{2.5} concentrations and frequent and intense air pollution episodes, documented in several studies during the last two decades (Eleftheriadis et al., 2014; Aleksandropoulou et al., 2012; Kassomenos et al., 2011; Moussiopoulos et al., 2009; Grivas et al., 2008; Chaloulakou et al., 2003; Manoli et al., 2002). A number of control measures have been implemented since the 1990s, mainly related to traffic management and vehicle emission reductions, as well as reduction in fossil fuel use due to energy efficiency improvements or interventions in favour of alternative fuels and renewable energy sources. These resulted in reductions of atmospheric pollution and changes in emission source contributions; however, the financial crisis which started on 2009 has significantly altered this picture. The present study is the first effort to assess: i) the contribution of emission sources to PM₁₀ and PM_{2.5} concentration levels in the two largest metropolitan urban areas in Greece (Athens and Thessaloniki) and ii) the long-term variability of emission sources in Greece (over 5–10 years), through a harmonized application of the PMF technique on recent and past year measurement data.

2. Methods

2.1. Sampling sites

Intensive measurement campaigns were conducted during 2011–2012, for the comprehensive characterization of PM₁₀ and PM_{2.5} chemical components, at four sites in the two largest cities in Greece, and specifically at a suburban (AMA-SUB) and an urban background (AMA-UB) site in the Athens Metropolitan Area (AMA) and at an urban background (TMA-UB) and urban traffic (TMA-UT) site in Thessaloniki Metropolitan Area (TMA). The location of all four sites is indicated in Fig. 1.

AMA, sprawling over 2928.72 km², is located within the 3808 km² Attica region that encompasses the most populated region of Greece, reaching 3,827,624 inhabitants in 2011. Athens (37°59' N, 23° 44' E), the capital and largest city of Greece, sprawls across the central plain of Attica, built around a number of hills, while it reaches to the coast of the Saronic gulf including the city of Piraeus, the largest port in the country. The climate in AMA is Mediterranean with hot dry summers and wet mild winters. A

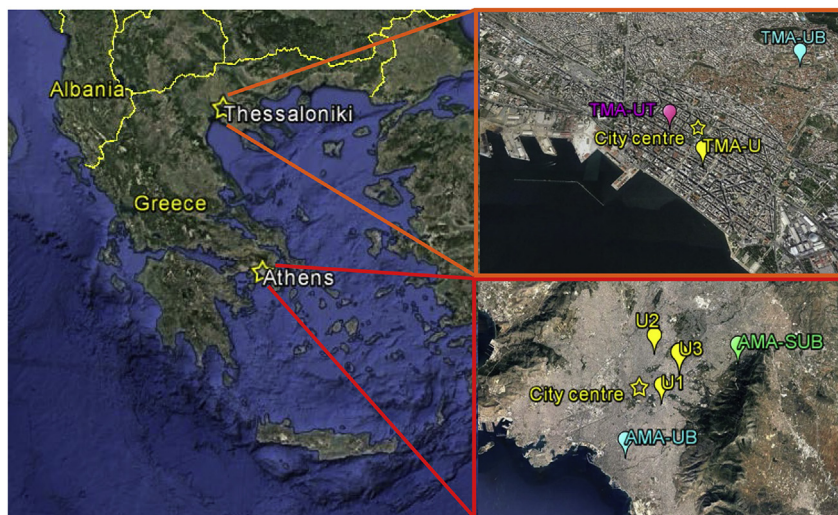


Fig. 1. Location of sampling sites in the cities of Athens (AMA-SUB, AMA-UB and U1, U2, U3) and Thessaloniki (TMA-UB, TMA-UT, TMA-U), in Greece.

complex mountainous geomorphology causes frequent temperature inversions. The sampling sites were selected to cover both the northern and southern part of AMA. The suburban site (AMA-SUB) was located at the Demokritos Monitoring Station (Triantafyllou et al., 2016) inside N.C.S.R. “Demokritos” campus (270 m asl), in a pine covered area at the north-eastern corner of AMA, on the hillside of Mount Hymettus. The urban background site (AMA-UB) was hosted at the one of the stations of the National Monitoring Network, at the south-eastern part of AMA, in a residential area (50 m asl). PM sampling at both sites was conducted at a height of around 10 m above ground.

TMA extends over an area of 1455.62 km² and its population in 2011 reached a total of 1,104,460 inhabitants. Built at the innermost point of Thermaikos Gulf (40°62'N, 22°95'E), Thessaloniki is the second largest Greek city and has the second largest commercial port. The city is characterized by intense vehicular traffic in the centre and several industrial units located in the West, North-West and North. Prevailing winds are weak (1–3 m s^{−1}) strongly influenced by the sea breeze, while frequently occurring calms result to inadequate dispersion of atmospheric pollutants and short-range transport processes. The urban traffic site (TMA-UT) is located in the commercial city centre (11.5 m asl), while the urban background (TMA-UB) site is in the upper part of the city (174 m asl). Both sites were hosted in monitoring stations of the Municipality of Thessaloniki. PM sampling was carried out from a height of around 3 m above ground.

In addition to the above-mentioned measurement campaigns, available datasets from previous measurements in Athens and Thessaloniki were used in order to assess the long-term variability of concentrations and sources. The Athens dataset consisted of PM₂ and PM₂₋₁₀ concentrations collected at three urban, residential areas (AMA-U1, U2 and U3), during the warm and cold period of 2002. The Thessaloniki dataset was collected at an urban site (TMA-U) during the cold and warm period of 2007. The location of all sites is indicated in Fig. 1.

2.2. Sampling and analysis

Information on sampling dates and number of samples for each site and season are provided in Table 1. Details on sampling and chemical analysis methods for the 2002 and 2007 datasets are provided in Karanasiou et al. (2009) and Terzi et al. (2010). During

2011–2012, PM₁₀ and PM_{2.5} sampling was carried out at all sites according to the reference method ISO/IEC EN-12341. Low volume reference samplers equipped with PM₁₀ and PM_{2.5} inlets were employed (LVS3.2, Norbent Derenda, Berlin, PM10/2.5 SEQ 47/50-CD with Peltier cooler, Sven Leckel GmbH and custom-made Demokritos EN12341 sampler). 24 h samples were concurrently collected for both size fractions, on two different filter types: Teflon filter (for the determination of mass and subsequent analysis for elements and ionic species) and binder-free pre-heated (at 800 °C) Quartz fibre filter (for the analysis of organic and elemental carbon, OC and EC). PM₁₀ and PM_{2.5} mass concentrations were determined gravimetrically. Loaded and unloaded filters were conditioned for 48 h at 20 ± 1 °C and 50 ± 5% relative humidity before weighing by the use of a microbalance (d = 0.01 mg). Filter samples were stored in a cool and dark place until analysis (for less than four weeks).

A disc of Ø 25-mm was cut from each PM₁₀ and PM_{2.5} Teflon sample and was analysed first by Energy Dispersive X-Ray Fluorescence (ED-XRF) and then by Electro Thermal Atomic Absorption Spectrometry (ET-AAS), for the determination of 18 major and trace elements (Mg, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Se, Br, Sr, Pb) and 5 trace elements (As, Cd, Co, Cr, Sb), respectively. Details on ED-XRF instrumentation, calibration method, detection limits and overall precision are provided in Grigoratos et al. (2014a). ET-AAS

Table 1

Sampling periods of the campaigns conducted in Athens and Thessaloniki and number of samples for each filter type (Teflon or Quartz fibre).

Site	Sampling period	Number of samples	
		PM ₁₀	PM _{2.5}
AMA-SUB	Warm	07/07–02/10/2011	48
	Cold	16/01–10/04/2012	47
AMA-UB	Warm	07/07–02/10/2011	40
	Cold	16/01–10/04/2012	41
AMA-U1	Cold	13/03–05/04/2002 & 29/11–18/12/2002	32
AMA-U2	Warm	12/06–10/09/2002	23
AMA-U3	Warm	14/07–01/10/2011	26
TMA-UB	Cold	10/02–06/04/2012	24
	Warm	30/06–25/09/2011	28
TMA-UT	Cold	10/02–06/04/2012	26
	Cold	10/01–31/03/2007	28
TMA-U	Warm	15/06–25/09/2007	35

^a No PM_{2.5} samples were collected during 2007 in TMA-U.

analysis was performed by a Varian 220 spectrometer equipped with a GTA 110 graphite furnace and a Varian auto sampler. Hollow cathode lamps were used as radiation source for all elements. ET-AAS conditions were carefully optimized for the compensation or elimination of interferences (Karanasiou et al., 2005). Extraction of total metal content from the filters was accomplished through microwave digestion with 2 ml of concentrated HNO_3 65% and 1 ml of HF 40%. The microwave digestion program involved 3 stages, with initial power of 300 W (4.4 min), followed by an increase at 450 W (2.0 min) and final power of 600 W (2.0 min). The analytical data were validated using the NIST 1 648 Standard Reference Material (Air particulate on filter media). The method detection limits varied from 0.04 ng m^{-3} (Cd) to 3.6 ng m^{-3} (Cu). Uncertainties were in general below 10%. The remaining portion of PM_{10} and $\text{PM}_{2.5}$ Teflon filter was analysed by Ion Chromatography (IC) for the determination of major ionic species (NO_3^- , SO_4^{2-} , Cl^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+). Details on the IC analysis of the Thessaloniki and Athens samples are provided in Voutsas et al. (2014) and Saraga et al. (2015), respectively.

PM_{10} and $\text{PM}_{2.5}$ Quartz fibre filters were analysed by the thermo-optical method (Lab OC-EC Aerosol Analyzer, Sunset Laboratory, Inc.) for the determination of elemental (EC) and organic carbon (OC) (Samara et al., 2014). The NIOSH thermal protocol was applied (NIOSH, 1999). OC concentration values were corrected for positive sampling artifacts related to the adsorption of volatile gases, through the use of field blanks and backup filters, for each sampling site and season. No correction was made for negative sampling artifacts related to the volatilization of gaseous organic species. The detection limit of analysis was $0.05 \mu\text{g cm}^{-2}$ for both OC and EC. Uncertainties were on average around 6% for OC and 18% for EC.

PM mass was reconstructed through concentrations of chemical components, by classifying species into the following categories: sea salt, mineral dust, anthropogenic elements, organic matter (OM), elemental carbon (EC), and secondary inorganic aerosol (SECONDARY). The difference between total PM mass and the sum of masses on the above classes provided the unidentified mass (UN), which corresponds to samples' water content and species not measured. Sea salt (ss) contribution was calculated assuming that soluble Cl^- in aerosol samples comes solely from sea salt. Non-sea salt sodium (nssNa^+) was calculated based on the crustal ratio Na^+/Al and total sea salt mass was calculated as the sum of Cl^- , ssNa^+ and fractions of the concentrations of Mg, K, Ca, and SO_4^{2-} based at a standard sea water concentration of these species with respect to sodium. Mineral dust was calculated as the sum of major elements: Al, Si, Ca, Ti and Fe plus non-sea salt Na^+ , Mg and K, all multiplied by factors to convert them to their common oxides. In the case Fe and K, which may also have significant anthropogenic sources, only their soil fraction was included in the above calculation. This fraction was estimated using typical crustal ratios with respect to Al ($[\text{soil}_K] = 0.32 \times [\text{Al}]$ and $[\text{soil}_\text{Fe}] = 0.62 \times [\text{Al}]$) (Diapouli et al., 2017). OC was converted to organic matter (OM), in order to include the oxygen, nitrogen and hydrogen associated with organic compounds, using a mean molecular to carbon ratio of 1.3–2.0, according to the characteristics of each site and season (Sciare et al., 2005; Turpin and Lim, 2001 and references therein). The lowest ratio was assigned to the TMA-UT site, where OM is affected mostly by fresh emissions (Grigoratos et al., 2014b); higher ratios were used for the suburban and urban background sites where aerosol is expected to be more aged and thus more oxidized. An OM/OC ratio equal to 2.0 was used for the cold season at the urban background sites, which were mainly residential areas and were considered significantly affected by wood burning during that period. Secondary inorganic aerosol was calculated as the sum of non-sea salt SO_4^{2-} , NO_3^- , and NH_4^+ .

Anthropogenic elements included all trace elements and the anthropogenic component of Fe and K.

2.3. PMF analysis

Positive Matrix Factorization (PMF) analysis was performed separately for the years 2011–2012, 2007 and 2002, by means of the PMF2 (two-way PMF) model (Paatero, 2004a). The same source apportionment tool was applied in both recent and older datasets, in order to obtain harmonized and comparable results. For each city, analysis was performed in one dataset including PM_{10} and $\text{PM}_{2.5}$ samples from all available sites. Only in the case of the 2002 Athens dataset, PMF was applied separately for the PM_2 and PM_{2-10} datasets, in order to allow a direct comparison of results with the previous PMF analysis performed in Karanasiou et al. (2009). The use of combined datasets from different sites in PMF analysis has been reported in previous research works, especially when the data collected at each site are not considered sufficient (in terms of number of observations) for PMF analysis (Belis et al., 2014 and references within). In the case of Thessaloniki, where the two sites studied in 2011–2012 represented different conditions of urbanization and traffic density, a sensitivity analysis was performed, by running the PMF model for each site separately. The obtained profiles were similar even for sources of local character (such as traffic). Nevertheless, the final result was based on the combined dataset, since larger uncertainties were associated with the site-specific PMF results, due to the limited number of observations.

Uncertainties of the concentrations of all chemical species were calculated based on the sampling and analytical uncertainties, depending on the method of analysis. Missing values in the datasets were substituted by the geometric mean of the respective time series for each site and season separately. The uncertainty was set equal to 4 times the concentration value. Below detection limit values were set equal to $1/2$ of the limit of detection and the respective uncertainty was set equal to $5/6$ of the detection limit. Signal-to-noise (S/N) ratio for each chemical specie, over all n samples, was calculated according to the following equation:

$$\left(\frac{S}{N}\right)_j = \sqrt{\frac{\sum_{i=1}^n (x_{ij} - u_{ij})^2}{\sum_{i=1}^n u_{ij}^2}} \quad (1)$$

where: x_{ij} is the concentration of species j in the day i [$\mu\text{g m}^{-3}$], and u_{ij} is the corresponding uncertainty [$\mu\text{g m}^{-3}$].

Species with S/N ratio lower than 0.2 were excluded from the analysis. When the S/N ratio was calculated between 0.2 and 2, the respective chemical species were characterized weak and their uncertainty was tripled (Paatero and Hopke, 2003). The chemical species and total number of samples included in the final datasets used for PMF source apportionment at each city are shown in Table 2.

The PMF2 model was run on the robust mode, where the uncertainties are dynamically readjusted through an iterative reweighting (Paatero, 2004b). Specifically, a measured concentration value was processed as an outlier if the residual exceeded 4 times the data point uncertainty. In that case the uncertainty was increased in order to decrease the influence of this data point. Solutions with different number of factors (ranging from 4 to 10) were examined and the best PMF solution was identified based on the possibility to relate the resulting factors to sources relevant to the studied areas, the goodness of model fit (Q value) and the Explained Variation of the matrix F . In 2-dimensional PMF (PMF2) there is always some rotational freedom though the non-negativity constraints limit the domain of possible rotations. The uniqueness of the solution may be examined through the parameter “Fpeak”,

Table 2

Chemical species and number of samples used in PMF source apportionment.

City/period	Chemical species	Number of samples
Athens/2011–2012	Al, Si, Ca, Ti, V, Mn, Fe, Ni, Co, Cr, As, Cd, Cu, Zn, Br, Sr, Sb, Ba, Pb, Na ⁺ , NH ₄ ⁺ , Mg ²⁺ , K ⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , OC, EC	357(178 PM ₁₀ + 179 PM _{2.5})
Athens/2002	Cd, Pb, V, Ni, Mn, Cr, Cu, Fe, Al, Ca, Mg, K, Na, Black carbon (BC), SO ₄ ²⁻ , NH ₄ ⁺	55 PM ₁₀ /55 PM ₂
Thessaloniki/2011–2012	Al, Si, Ti, V, Mn, Fe, Ni, As, Cu, Zn, Pb, Na ⁺ , NH ₄ ⁺ , Mg ²⁺ , Ca ²⁺ , K ⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , OC, EC	178(89 PM ₁₀ + 89 PM _{2.5})
Thessaloniki/2007	Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Cd, Sn, Sb, Te, Ba, Pb, Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Na ⁺ , NH ₄ ⁺ , OC, EC	63 PM ₁₀

assigning both positive and negative values. Positive Fpeak values mainly impact the factor profiles and negative values impact the factor contributions. The final solution for each city was tested with different Fpeak values. The goodness of fit (Q) value remained relatively stable for Fpeak values between -0.4 and 0.4, indicating that the optimal solution is found in this range. Finally, considering the physical meaning of the extracted factors, no rotation was selected in any of the cases (Fpeak = 0).

Regarding the 2002 dataset collected in Athens, a major improvement attempted in the new analysis was to resolve a secondary aerosol profile, which was not apparent in the previous PMF results, due to the absence of secondary species in the 2002 dataset, except for SO₄²⁻. Secondary aerosol formation has been identified and documented (mainly as ammonium sulphate) as a major contributor to fine particle mass in Athens (present work, as well as Amato et al., 2016; Eleftheriadis et al., 2014; Mantas et al., 2014; Diapouli et al., 2008; Eleftheriadis et al., 1998). Based on the literature reported above, it is reasonable to assume that ammonium sulphate is the major secondary aerosol specie, since ammonium nitrate in Athens is mostly unstable and nitrate rather resides in the coarse sea-salt component (Eleftheriadis et al., 2014). A modified PM₂ dataset was constructed, by adding NH₄⁺ concentration data estimated stoichiometrically to correspond to the measured nss-SO₄²⁻ concentrations. A very large uncertainty (4 times the respective concentrations) was assigned to this data, which is in line with PMF recommendations for missing data. Application of PMF2 model to the modified dataset resulted in very similar results to the original output reported in Karanasiou et al. (2009), with the main difference being the identification of a Secondary sulphate factor. Comparison of estimated contributions revealed that contributions

associated with this factor were previously apportioned to Sea salt and Traffic in the initial run. A similar observation has been reported by Manousakas et al. (2015), where the absence of inorganic ions from the input database did not allow for the identification of secondary inorganic aerosol as a separate source. In this case, the contribution of the secondary aerosol component was again apportioned to traffic. Since for all other sources and related contributions the modified database produced very similar results to Karanasiou et al. (2009), the final solution was based on the latest analysis, which provided the same source profiles, including a secondary aerosol component.

3. Results and discussion

3.1. PM mass and chemical composition

Summary statistical data for the 24 h concentrations of PM mass and related chemical components, measured during the warm and cold period of 2011–2012 for the two size fractions are provided in Tables S1 and S2, respectively. A comparison of concentration levels measured during recent (2011–2012) and previous campaigns (2002 and 2007) in Athens and Thessaloniki is provided in Tables 3 and 4. During the recent measurement campaigns, mean PM₁₀ concentration exceeded the annual limit value of the EU Air Quality Directive 2008/EC/50 (40 µg m⁻³) only at the traffic site in Thessaloniki (TMA-UT), while for PM_{2.5} both sites in Thessaloniki displayed mean concentrations above the respective annual limit value for this size fraction (25 µg m⁻³). Significant seasonal variability was observed at all sites. Wintertime is generally characterized by stable atmospheric conditions and shallow atmospheric

Table 3Mean concentrations of PM mass and major chemical components (in µg m⁻³) measured in Athens and Thessaloniki.

	Athens 2011–2012				Athens 2002		Thessaloniki 2011–2012			Thessaloniki 2007	
	Suburban		Urban background		Urban		Urban background		Urban traffic	Urban	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM ₂	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀
PM	22.8	12.4	33.5	18.0	54.0	41.0	36.1	25.9	52.6	33.3	47.2
OC	3.43	3.33	6.82	5.98	—	—	6.18	5.89	11.23	8.45	7.47
EC	0.41	0.38	1.06	0.92	—	3.63 ^a	0.93	0.69	6.69	5.24	2.27
SO ₄ ²⁻	3.18	2.45	5.97	3.70	2.04	1.38	4.38	4.50	4.36	4.12	7.74
NO ₃ ⁻	1.10	0.24	1.99	1.08	—	—	2.86	1.89	2.93	2.75	4.46
NH ₄ ⁺	0.81	0.99	1.56	1.27	—	—	1.84	3.20	1.52	2.98	2.37
Na ⁺	0.78	0.14	0.69	0.29	2.60	1.39	0.22	0.09	0.21	0.09	0.31
Ca ₂ ⁺	0.70	0.12	1.24	0.37	—	—	0.94	0.18	1.50	0.27	—
K ⁺	0.16	0.11	0.34	0.22	—	—	0.15	0.12	0.17	0.11	—
Cl ⁻	0.49	0.03	0.33	0.10	—	—	0.30	0.14	0.36	0.32	0.73
Mg ²⁺	0.09	0.03	0.10	0.05	—	—	0.03	0.02	0.03	0.01	—
S	1.06	0.95	1.09	0.78	—	—	0.78	0.82	1.26	0.98	1.35
Ca	1.29	0.19	1.49	0.37	0.51	0.17	1.67	0.17	3.96	0.44	5.67
K	0.41	0.21	0.47	0.21	0.76	0.41	0.43	0.28	0.55	0.29	0.93
Cl	0.75	0.16	0.59	0.09	—	—	0.60	0.10	1.00	0.15	1.04
Mg	0.48	0.11	0.61	0.15	0.41	0.21	0.49	0.11	1.28	0.22	0.58
Si	0.33	0.08	0.23	0.06	0.46	0.10	0.29	0.06	0.46	0.09	0.45
Fe	0.33	0.03	0.39	0.05	—	—	0.10	0.03	0.16	0.03	0.28
Al	0.13	0.04	0.13	0.04	0.18	0.06	0.12	0.03	0.22	0.04	0.20

^a This value corresponds to black carbon measurements.

Table 4Mean concentrations of trace elements (in ng m^{-3}) measured in Athens and Thessaloniki.

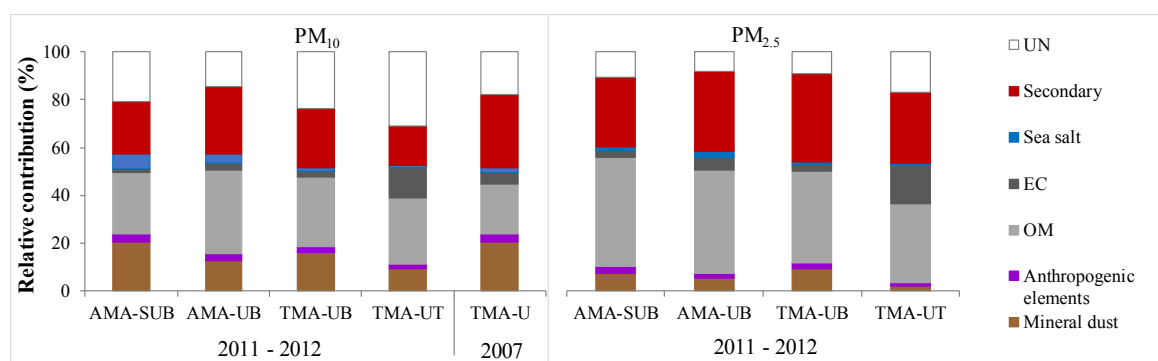
	Athens 2011–2012				Athens 2002		Thessaloniki 2011–2012				Thessaloniki 2007
	Suburban		Urban background		Urban		Urban background		Urban traffic		Urban
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM ₂	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀
Br	49	30	56	30	—	—	55	44	52	48	37
Zn	42	25	56	36	—	—	45	33	90	53	64
Ti	29	6	25	7	—	—	29	10	50	13	44
Ba	20	11	14	8	—	—	11	11	14	12	74
Cr	14	2	7	4	22	16	9	5	19	6	6
Mn	13	4	16	5	18	12	27	8	57	14	22
Cu	11	3	18	8	48	24	9	4	39	10	29
Pb	8	4	15	11	24	20	12	10	20	15	17
Sb	7	4	4	2	—	—	4	4	5	5	22
Co	6	4	6	1	—	—	3	2	6	3	3
Ni	5	3	7	4	14	8	6	3	10	4	7
V	5	5	13	9	9	7	5	5	7	6	11
Sr	4	1	11	4	—	—	8	6	11	7	7
As	2	2	1	1	—	—	1	1	2	1	3
Cd	0	0	1	0	1	1	2	1	1	1	12
Sn	—	—	—	—	—	—	—	—	—	—	24

mixing layers, which hinder dispersion of pollutants and favour air pollution episodes. Several peak events were observed during the cold period, with concentrations reaching up to more than three times the 24 h limit value for PM₁₀ ($50 \mu\text{g m}^{-3}$). This effect was more pronounced at the densely-populated AMA-UB site, pointing towards a strong PM source during the cold season such as residential heating, present also in background residential areas.

The relative contribution of the different groups of components (as calculated by mass closure analysis) are presented in Fig. 2. The Athens 2002 data are not included due to the lack of major PM chemical components (such as organic carbon and secondary inorganic species). Mass closure of PM₁₀ and PM_{2.5} separately for the warm and cold period of 2011–2012 and for each site, are presented in Fig. S1 – S4. Carbonaceous matter was the most abundant component for both PM size fractions (Pateraki et al., 2014). OC and EC concentrations were relatively low during the warm period at the Athens sites and at the Thessaloniki UB site. The background character of the sites was further demonstrated by the high OC/EC ratios (on average 10–11 at AMA-SUB, 6 at AMA-UB and 6–7 at TMA-UB) indicating relatively low contribution from traffic emissions, coupled with secondary organic formation, which enhances OC levels (Samara et al., 2014). At TMA-UT carbonaceous aerosol concentrations were significantly higher, among the highest values reported for other urban sites in European cities (Grivas et al., 2012; Viana et al., 2006). The corresponding OC/EC ratio was calculated equal to 1.1, similar to those found at kerbside sites and close to the values reported for vehicular emissions (Samara et al.,

2014). On the other hand, during the cold period, OC concentrations contributed the most to total carbon measured at all sites (OC/EC ratios on average for both size fractions equal to 9–10 at AMA-SUB, 7.0–7.5 at AMA-UB, 8–9 at TMA-UB and 3 at TMA-UT). Very high 24 h concentrations (mean 24 hr OC and EC reaching up to $45 \mu\text{g m}^{-3}$ and $6 \mu\text{g m}^{-3}$, respectively) were measured at the densely-populated area of AMA-UB during this period, again pointing towards a significant impact from residential heating. The increase in OC/EC ratios during the cold period, observed at all sites except AMA-SUB, may be associated with biomass burning aerosol and suggests intense use of fireplaces and wood stoves at the residential areas in Greece (Saffari et al., 2013). This is further supported by the increase in the concentration levels of K⁺, clearly observed during the cold period at all sites, especially in the fine fraction. This specie is commonly used as tracer for biomass burning (Popovicheva et al., 2014). For the year 2007, the calculated OC/EC ratios for Thessaloniki were similar during the cold and warm period (4.2 and 3.0, respectively), suggesting that residential biomass burning was not so pronounced in previous years, before the financial crisis.

Secondary inorganic ions, and in particular SO_4^{2-} , were the second most important contributing component in PM₁₀ and PM_{2.5} (Remoundaki et al., 2013). Even though secondary inorganic ions are generally associated with fine particles, NO_3^- displayed a significant coarse fraction at TMA-UB during the warm season and at AMA-SUB and AMA-UB during both seasons; average PM_{2.5}/PM₁₀ ratios during the warm/cold season were calculated equal to 0.12/

**Fig. 2.** Relative contribution of PM components to total PM₁₀ and PM_{2.5} mass.

0.78 at TMA-UB, 0.20/0.22 at AMA-SUB and 0.33/0.59 at AMA-UB. This result suggests neutralization of NO_3^- with Na^+ from sea salt, which is mainly found in the coarse mode (Eleftheriadis et al., 2014, 1998). Good correlation was found for the sum of NO_3^- and Cl^- against Na^+ , with Pearson coefficient equal to 0.82 and 0.88 for the AMA-SUB warm and cold period respectively, and 0.72 for TMA-UB during the warm period, further supporting the mechanism described above. The formation of NaNO_3 may be favoured in the warm rather than the cold period, when low temperatures and high relative humidity sustain the formation of NH_4NO_3 (Behera and Sharma, 2010; Chow et al., 2006). In general, NO_3^- concentrations were found to be lower during the summer months, indicating loss of particulate nitrate to the gaseous phase due to high temperatures, while SO_4^{2-} concentrations were higher during these months, due to increased photochemical formation of sulphates. An observed excess ammonium concentration found in the $\text{PM}_{2.5}$ fraction is often associated with artifact losses of species found in a different state of mixing with the coarse fraction in the PM_{10} samples, especially when ammonium can be associated with semi-volatile organic anions in case of aerosol of biomass burning origin (Akagi et al., 2012; Eleftheriadis et al., 2006).

Mineral dust contribution was significant for the PM_{10} fraction, ranging on average between 16 and 29% at the different sites. Its concentration was larger during the warm season when dry conditions favour soil dust resuspension. Sea salt contribution was larger in AMA (4–6%) with respect to TMA (1–2%). Several elements tracers of anthropogenic origin were detected in both PM fractions. The $\text{PM}_{2.5}/\text{PM}_{10}$ ratio is informative of their origin and fate. Ni, Zn, Cd, V and As had an expected higher concentration in the fine fraction although a coarse component was also visible. The latter was more pronounced for Mn, Cu and Cr, while Pb, Sb and Co had a mixed fine and coarse picture at the different sites. This variability in size may have an effect on the impact in human health, since particles' size greatly affects their transport and deposition in the respiratory tract and lungs (Zwozdziak et al., 2017).

Comparison of current and past measurements revealed a significant decrease of concentrations between 2002 and 2011–2012 in Athens, more apparent in total PM mass and primary anthropogenic pollutants, such as EC/BC, Cr, Cu, Pb, Mn and Ni. In Thessaloniki, the difference in concentrations measured in 2007 and 2011–2012 was less pronounced, suggesting that control measures implemented during the early 2000's may have already produced positive results with respect to urban air quality in 2007.

3.2. Sources and chemical profiles obtained by PMF

PMF analysis was performed separately for the years 2011–2012, 2007 and 2002. The source profiles obtained for each city for the 2011–2012 datasets are shown in Fig. 3. The species' relative mass (%) apportioned to each factor/source for Athens and Thessaloniki are shown in Figs. 4 and 5, respectively.

A total of seven factors/sources were obtained for both cities. Two traffic sources, Vehicle exhaust (VEH EXHAUST) and Vehicle non-exhaust (ROAD DUST), Secondary sulphate & organics (SEC SULPHATE), Biomass burning (BIOMASS BURNING), Mineral dust (MINERAL DUST) and Sea salt (SEA SALT) were identified at both cities. A source corresponding to Heavy oil combustion (OIL COMBUSTION) was found only in Athens, while Secondary nitrate & organics (SEC NITRATE) was identified as a separate source only in Thessaloniki.

The relative mass of species (%) apportioned to each factor/source identified for the Athens 2002 dataset and the Thessaloniki 2007 dataset is presented in Figs. 6 and 7, respectively. No significant difference was observed in the identified sources and source

profiles between the past (2002 and 2007) and recent (2011–2012) datasets. The only exception was an additional source related to industrial emissions, which was identified at both cities. In Athens, seven factors/sources were obtained for the PM_2 dataset: Two traffic sources, Vehicle exhaust and non-exhaust, Secondary sulphate, Biomass burning, Heavy oil combustion, Industrial and Sea salt. The combined PM_2 and PM_{2-10} results produced in total 8 sources for PM_{10} , including the above plus Mineral dust (Karanasidou et al., 2009). In Thessaloniki, the following eight factors/sources were identified: Vehicle exhaust and non-exhaust, Secondary sulphate, Secondary nitrate, Biomass burning, Industrial, Mineral dust and Sea salt (Argyropoulos et al., 2016).

The Vehicle exhaust profiles obtained for both cities comprised mainly of organic (OC) and elemental carbon (EC). The OC/EC ratio for the Athens profile was calculated equal to 4.1. Argyropoulos et al. (2016) report an OC/EC ratio equal to 8.9 for gasoline catalytic car exhaust source profile emissions, which indicates loss of semi-volatile organic compounds from source to receptor site. In the Thessaloniki vehicle exhaust profile, the OC/EC ratio was much lower (0.8) and similar to the ratio measured for diesel car source profile emissions (0.7–1.0) (Argyropoulos et al., 2016). This result suggests a higher contribution of diesel emissions to the vehicle exhaust profile in Thessaloniki, which may be related to the nature of the TMA sites. Both sites (UT and UB) were located at the centre of the city, where the density of traffic of the diesel vehicles (taxis, buses and commercial LDVs) is relatively higher compared to the type of traffic affecting suburban areas, like those where the AMA sites were located. Other elements contributing to the vehicle exhaust profiles were Fe, Zn and Ca, all possible tracers for traffic emissions. Fe may be related to vehicle body wear. Zn may be contributed from galvanized materials, tire wear and the use of zinc compounds in rubber production (Santoso et al., 2008). Zn and Ca may be also emitted from the combustion of lubricating oil (Viana et al., 2008).

The Vehicle non-exhaust profile, also referred to as Road dust, was traced by metals that originate from brake, tire and vehicle body wear (Cu, Fe, Zn) (Schauer et al., 2006; Sternbeck et al., 2002), while it also contained crustal species from road surface wear (Ca, Al, Si, Ti, Fe). Very similar profiles were obtained for Athens and Thessaloniki. The rather high contribution of NO_3^- in the Athens profile may be related to the background character of both AMA sites, which favours the accumulation of secondary aerosol. The SO_4^{2-} contribution was also significant for both cities, highlighting the regional origin of this specie. It should be noted that Road dust is a reservoir of particles deposited in the road surface, which are resuspended during vehicular traffic; therefore, it may contain species found in high abundance in the urban aerosol mixture of components.

The Secondary sulphate & organics profile was mainly composed of SO_4^{2-} , NH_4^+ and OC. This factor is the result of secondary aerosol formation in the atmosphere from the photochemical oxidation of emitted gaseous sulphur oxides and volatile organic compounds (VOCs), the former combined with ammonia (NH_3). A similar secondary sulphate factor containing both ammonium sulphate and organic carbon was identified by Paraskevopoulou et al. (2015) and Amato et al. (2016) through measurements in urban background and suburban sites in Athens. This secondary aerosol may be formed by local gaseous precursors and/or may be linked to long range transport of anthropogenic emissions from the Balkan region or further away. The $\text{SO}_4^{2-}/\text{NH}_4^+$ ratios for the Athens 2011–2012 and the Thessaloniki 2007 profiles were calculated equal to 2.5, very close to 2.7 which is the theoretical ratio for $(\text{NH}_4)_2\text{SO}_4$ derived from stoichiometry. The corresponding $\text{SO}_4^{2-}/\text{NH}_4^+$ ratio for the 2011–2012 Thessaloniki dataset was calculated equal to 1.9, indicating a

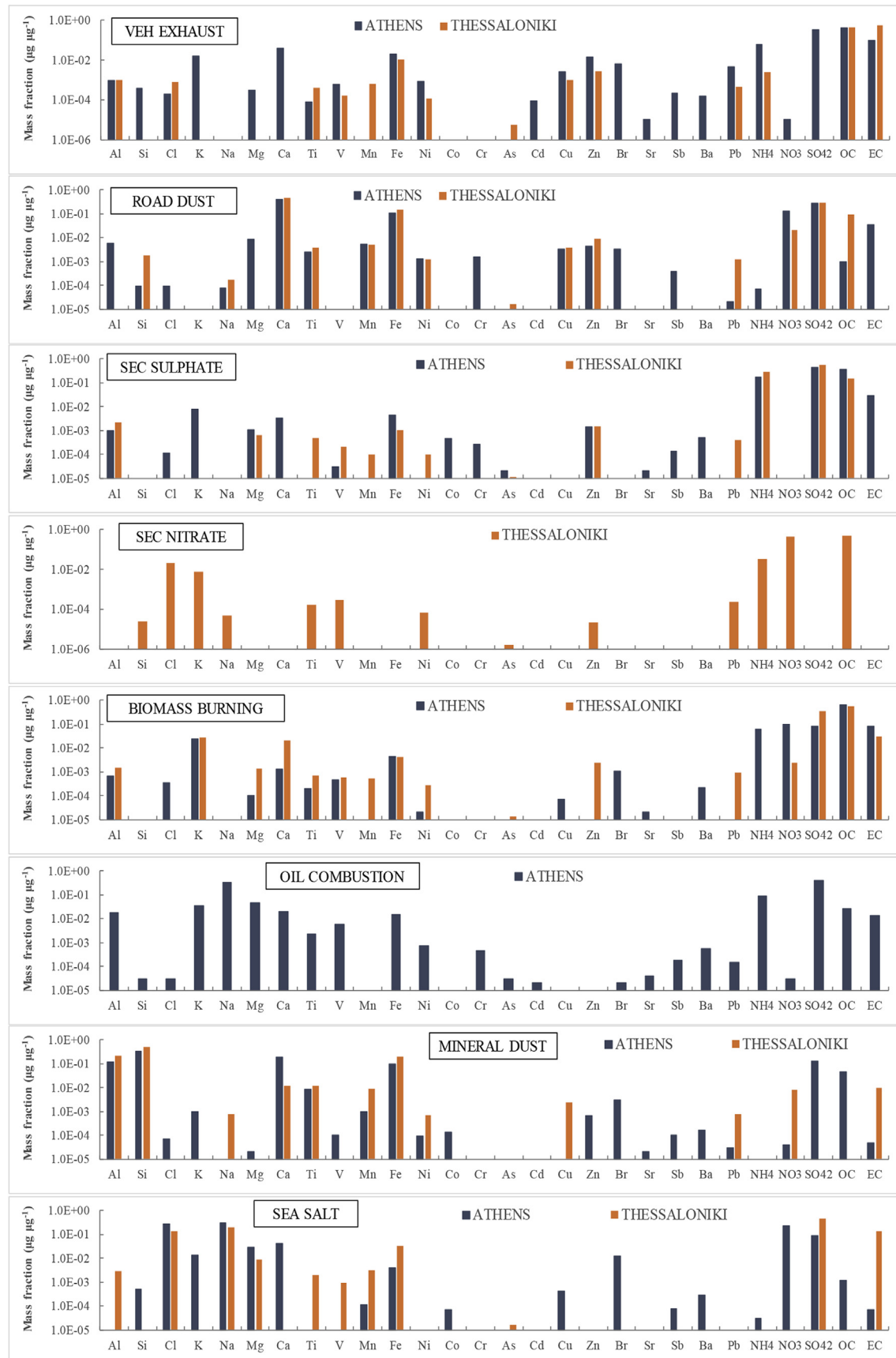


Fig. 3. Chemical profiles of sources identified for the 2011–2012 combined PM₁₀/PM_{2.5} Athens and Thessaloniki datasets.

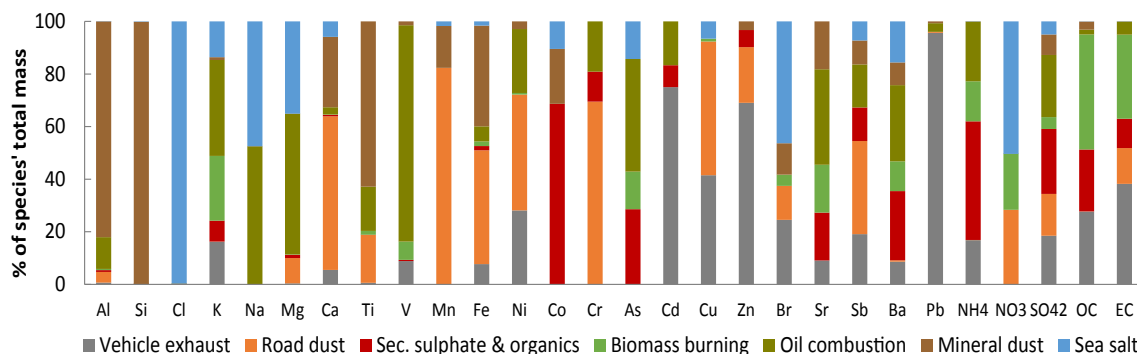


Fig. 4. Relative mass of species (%) apportioned to each factor/source identified for the AMA 2011–2012 dataset.

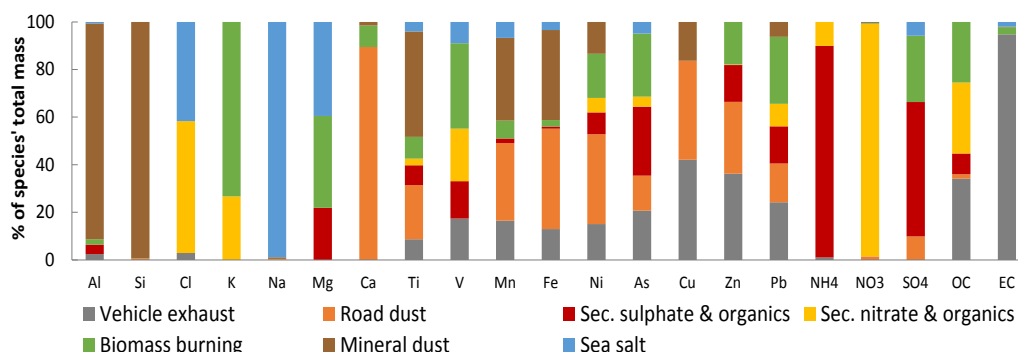


Fig. 5. Relative mass of species (%) apportioned to each factor/source identified for the TMA 2011–2012 dataset.

slight surplus of NH_4^+ as also shown in Voutsas et al. (2014).

The Secondary nitrate & organics source, obtained only for Thessaloniki, was composed of NO_3^- , NH_4^+ , OC, as well as K^+ and Cl^- . The $\text{NO}_3^-/\text{NH}_4^+$ ratio was calculated equal to 3.2 for the 2007 dataset, which is close to the stoichiometric ratio calculated for NH_4NO_3 (3.4). For the 2011–2012 dataset, this ratio was much larger, indicating that a major part of nitrate was associated with other species, such as K^+ . In Athens, the climatic conditions are dryer and warmer than Thessaloniki, it is therefore less favourable for NH_4NO_3 to exist in the aerosol phase. The result of this is the absence of a strong enough secondary nitrate factor in Athens, in contrast to the significant nitrate factor in TMA. Nitrate in Athens is included in the Sea salt factor due to the reaction with NaCl or in the biomass burning and traffic source profiles. On the other hand, in Thessaloniki, the emerging Nitrate source profile is enriched with NO_3^- from biomass burning or aged sea salt, as the source profile also contains K^+ and Cl^- . The presence of potassium nitrate is also

possible, considering that K^+ is a major constituent of fertilisers and is generally present in windblown soil (Contini et al., 2014). Secondary nitrate profiles also loaded with Na^+ , K^+ and OC were identified by PMF receptor modelling in other studies (Cesari et al., 2016a,b).

The Biomass burning profile was identified by OC, EC and K^+ (Corrigan et al., 2013; Zhang et al., 2010; Pio et al., 2008). In Athens, the OC/EC ratio was calculated equal to 7.8, being in the range of typical biomass burning values (Diapouli et al., 2014 and references therein). The corresponding ratio for Thessaloniki was equal to 18. The Biomass burning source in Thessaloniki was associated with residential heating (during the cold season) and forest fires (during the warm season), as demonstrated by the seasonal variability of the respective biomass burning concentrations, as discussed in detail below. The contribution of forest fires to the overall biomass burning source may be the reason for the much higher OC/EC ratio observed in Thessaloniki. Photo-oxidation of biomass burning

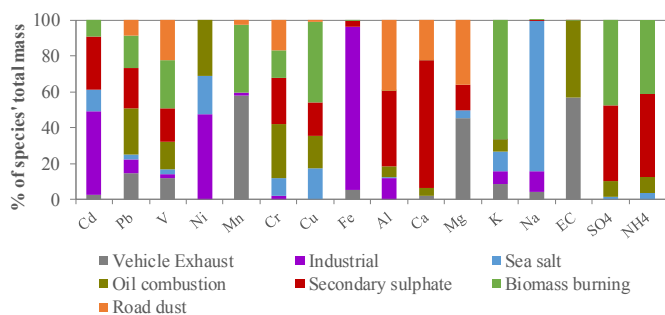


Fig. 6. Relative mass of species (%) apportioned to each factor/source identified for the Athens $\text{PM}_{2.5}$ dataset collected during warm and cold period of 2002.

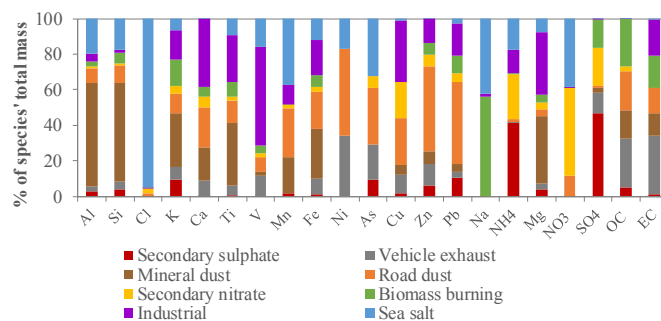


Fig. 7. Relative mass of species (%) apportioned to each factor/source identified for the Thessaloniki PM_{10} dataset collected during warm and cold period of 2007.

emissions during transport has been shown to enable production of significant amounts of secondary organic aerosol (Lee et al., 2008). Ammonium sulphate and nitrate were also present in the profiles obtained for both cities. Formation of these secondary inorganic compounds may be enhanced during biomass burning events (Popovicheva et al., 2014).

The Mineral dust profile was mainly comprised of crustal species, such as Al, Si, Ca, Fe, Ti and Mn. The enrichment factors calculated with respect to Al for the major elements (Si, Ti, Ca, Fe) were very close to the average continental crust composition reported by Mason (1966) and Rahn (1976). The only exception was the high enrichment of the Athens mineral profiles in Ca, which is compatible with the enrichment in Ca reported for the Athens soil (Argyriaki and Kelepertzis, 2014). It should be noted that the mineral dust factor may correspond to a mixture of several sources, including soil resuspension, regional mineral dust, long range transport of African dust, as well as dust generated by urban works (building/demolition etc.) (Athanasopoulou et al., 2010).

The Heavy oil combustion profiles identified in Athens were traced by V and Ni. Oil combustion may originate from local shipping emissions at the Piraeus harbour and regional emissions from the Aegean shipping routes in the area surrounding the Attica peninsula and beyond, as well as petrochemical industries west of AMA (Karanasiou et al., 2009). The high abundance of sea salt components in the 2011–2012 profile (52% of Na⁺, 54% of Mg²⁺ and 36% of K⁺) may be a further indication that this factor is partly related to shipping emissions (Öztürk et al., 2012). For the Thessaloniki dataset, a separate oil combustion source could not be identified, suggesting negligible contribution compared to other sources in the area. In the 2011–2012 dataset, a fraction of V and Ni mass was apportioned to the Biomass burning factor (36% of V and 18% of Ni) which may correspond to the combined use of oil and biomass combustion for residential heating.

The sea salt profile was traced by Na⁺ and Cl[−], while it also contained Mg²⁺ and SO₄^{2−}. The 2011–2012 profiles found for both cities were depleted in Cl[−] based on the Cl[−]/Na⁺ ratio reported for seawater (1.8) by Bowen (1979). For AMA, S/Na⁺ and Mg²⁺/Na⁺ ratios (both equal to 0.10) were similar to the literature seawater ratios (0.08 and 0.12 respectively) (Bowen, 1979), while in Thessaloniki, the sea salt profile displayed a higher enrichment in S. The low mass of Cl[−] along with the significant contribution of secondary inorganic ions in the profiles indicated ageing of sea salt. Cl depletion has been observed to occur when urban pollutants such as nitric and sulfuric acid remaining in the gaseous phase in poor NH₃ environments interact with sea-salt and other available species such as crustal minerals (Eleftheriadis et al., 2014; Lucarelli et al., 2014; Zhuang et al., 1999). The sea salt factors obtained are therefore associated with urban gaseous emissions (from traffic, fossil fuel combustion or biomass burning) heterogeneously converted to the aerosol phase and more specifically marine aerosol.

The high abundance of NO₃[−] in the Athens Sea salt profile (accounting for 50% of total NO₃[−]), further demonstrates that secondary nitrate in Athens is associated with Na⁺ (sea salt) rather than with NH₄⁺.

3.3. Source contributions to PM levels

The different source contributions (in $\mu\text{g m}^{-3}$ and as percentage of total PM mass) estimated for all four sites during 2011–2012, for PM₁₀ and PM_{2.5}, are presented in Tables 5 and 6, respectively. The uncertainty associated with each contribution to the PM mass concentration is also provided, calculated as the standard error of the coefficients of a multiple regression between the measured PM concentrations (independent variable) and the source contributions (dependent variables). The standard error was around or below 10% for individual source contributions above 2 $\mu\text{g m}^{-3}$ to the PM concentration. Higher uncertainties were associated with source contributions around 1 $\mu\text{g m}^{-3}$ (the standard error was calculated on average at 60%). For lower contributions found especially for PM_{2.5} the uncertainty was significantly higher (Table 6). For these sources with mass contributions below 1 $\mu\text{g m}^{-3}$, the result is limited at observing their very small contribution to the mass concentration, while the numerical values cannot be considered quantitative. In Athens, Secondary sulphate & organics and Biomass burning were the major contributing sources for both size fractions, while Mineral dust also contributed significantly to PM₁₀ at the AMA-SUB site. Primary anthropogenic sources (vehicle exhaust and non-exhaust emissions and oil combustion) appeared in relatively low contributions (5–13% to PM₁₀ and 1–16% to PM_{2.5}); nevertheless, an increase in absolute contributions of all anthropogenic sources was observed for the urban background site in Athens (AMA-UB), with respect to AMA-SUB, by a factor of 1.3 (for Vehicle non-exhaust) to 2.7 (for Biomass burning) in PM₁₀ and 1.9 (for Oil combustion) to 4.4 (for Vehicle non-exhaust) in PM_{2.5}. Secondary sulphate displayed comparable contributions at the two sites, indicating the regional character of this source. Biomass burning exhibited the strongest seasonal variability at AMA, with very high contributions during the winter, suggesting the use of residential fireplaces or other wood stoves for heating (Figs. S5 and S6). This effect was more pronounced in the densely populated UB area.

A very high impact of Biomass burning on PM concentration levels was also observed in the Thessaloniki urban background site, where mean contribution of this source to PM₁₀ and PM_{2.5} was found equal to 24% and 36%, respectively. Biomass burning contribution was comparable during warm and cold period (Figs. S5 and S6), due to regional and local forest fires affecting the Region of Macedonia during the summer period, in addition to the wood burning used for residential heating during winter. Increased OC/EC ratios and non-sea salt K⁺ concentrations (both indicators of

Table 5

Mean source contributions ($\mu\text{g m}^{-3}$) to PM₁₀ during the 2011–2012 measurement campaign and the respective calculated Standard Error. Mean % contribution to PM₁₀ is given in parenthesis.

FACTOR/SOURCE	AMA-SUB		AMA-UB		TMA-UB		TMA-UT	
	Mean	St. Error	Mean	St. Error	Mean	St. Error	Mean	St. Error
VEH EXHAUST	1.9 (8)	0.1	4.3 (13)	0.3	1.6 (5)	1.1	15.5 (29)	0.2
ROAD DUST	2.7 (12)	0.2	3.6 (11)	0.4	3.8 (11)	0.6	7.8 (15)	0.4
OIL COMB	1.0 (5)	0.3	1.9 (6)	0.8	^a	^a	^a	^a
BIOMASS BURNING	4.2 (19)	0.1	11.6 (36)	0.1	8.2 (24)	0.2	9.2 (17)	0.2
SEC SULPHATE	5.4 (24)	0.1	5.9 (19)	0.2	8.4 (24)	0.2	5.9 (11)	0.2
SEC NITRATE	^a	^a	^a	^a	8.9 (25)	0.2	9.8 (18)	0.2
MINERAL DUST	4.4 (20)	0.1	2.7 (8)	0.3	2.4 (7)	0.4	4.4 (8)	0.6
SEA SALT	2.7 (12)	0.1	1.9 (6)	0.6	1.5 (4)	0.6	1.0 (2)	0.9

^a This source was not identified for the specific dataset.

Table 6
Mean source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ during the 2011–2012 measurement campaign and the respective calculated Standard Error. Mean % contribution to $\text{PM}_{2.5}$ is given in parenthesis.

FACTOR/SOURCE	AMA-SUB		AMA-UB		TMA-UB		TMA-UT	
	Mean	St. Error	Mean	St. Error	Mean	St. Error	Mean	St. Error
VEH EXHAUST	1.0 (9)	0.2	2.7 (16)	0.3	1.2 (5)	1.2	10.6 (34)	0.3
ROAD DUST	0.1 (1)	1.3	0.7 (4)	0.7	0.6 (2)	2.2	1.1 (3)	1.0
OIL COMB	0.5 (4)	0.6	1.0 (6)	0.6	– ^a	– ^a	– ^a	– ^a
BIOMASS BURNING	2.6 (23)	0.1	7.9 (46)	0.1	8.7 (36)	0.2	6.7 (22)	0.2
SEC SULPHATE	6.4 (55)	0.1	4.4 (25)	0.2	8.1 (33)	0.2	5.6 (18)	0.2
SEC NITRATE	– ^a	– ^a	– ^a	– ^a	4.9 (20)	0.2	5.6 (18)	0.1
MINERAL DUST	0.8 (7)	0.2	0.3 (2)	1.6	0.4 (2)	1.6	0.7 (2)	1.6
SEA SALT	0.1 (1)	1.4	0.4 (2)	1.0	0.5 (2)	1.2	0.6 (2)	1.8

^a This source was not identified for the specific dataset.

biomass burning processes) were found to relate to transport of air masses from the Northeast during August and September (Samara et al., 2014). This period was also characterized by numerous fires in the Regions of Central and West Macedonia in Greece and the countries surrounding the Black Sea; thus, biomass smoke aerosol transported to the city of Thessaloniki from these areas may explain the relatively high contribution for the biomass burning source during the warm period. (Samara et al., 2014). Cold season concentrations were also significant (around $7\text{--}8 \mu\text{g m}^{-3}$), again pointing towards residential heating by wood burning. In addition, the presence of K^+ and Cl^- (both species found in biomass burning smoke) in the Secondary nitrate & organics profile obtained for TMA suggests that the elevated contribution of this source during the cold period may partly demonstrate a chemical interaction between biomass burning aerosol and gaseous NO_x emissions from the urban environment.

Apart from Biomass burning, Secondary aerosol formation (both Sulphate and Nitrate) were the other major contributors at TMA-UB. These two sources accounted for around 50% of total PM in TMA-UB, with average annual concentrations of $8.5\text{--}9.0 \mu\text{g m}^{-3}$ in PM_{10} and $5.0\text{--}8.0$ in $\text{PM}_{2.5}$. A large fraction of Nitrate contribution was related to the coarse particle fraction ($\text{PM}_{2.5}/\text{PM}_{10}$ contribution ratio equal to 0.6). Comparison of the two urban background sites revealed similarities in the absolute contributions of Biomass burning, Mineral and Road dusts and Sea salt. The Athens UB site seems more affected by local primary pollution (vehicle exhaust), while in Thessaloniki, secondary aerosol formation seems the major factor contributing to PM_{10} and $\text{PM}_{2.5}$ levels. The high contribution of Road dust, in comparison to vehicle exhaust emission, in TMA-UB may be related to the vicinity of the site to metro-railway construction works (Paschalidou et al., 2015).

Primary emissions had the major share at TMA-UT, for both size fractions. Vehicular traffic (exhaust and non-exhaust emissions) accounted for 44% of PM_{10} and 37% of $\text{PM}_{2.5}$, with the respective concentrations reaching to 23 and $12 \mu\text{g m}^{-3}$, respectively. Absolute contributions of Biomass burning and Secondary nitrate were similar in the two TMA sites. The nature of the secondary NO_3^- in Thessaloniki is different compared to Athens. In TMA, NO_3^- is associated with ammonium and the secondary organics, which coupled with the fact that sea salt in this area is a lesser PM component, allows secondary nitrate to appear as a separate source at this site. The marginally colder and wetter atmospheric conditions in the Region of Macedonia also favour the production and longer lifetime of NO_3^- in the area (Dassios and Pandis, 1999). This is further supported by the strong seasonal variability of the Secondary Nitrate source, especially for the fine particle fraction (Figs. S5 and S6). This source presented the largest contribution to $\text{PM}_{2.5}$ during the cold period, for both TMA sites, while its concentration dropped to below $1 \mu\text{g m}^{-3}$ during the warm period. The

effect was less pronounced in PM_{10} . Coarse nitrate may be related to more stable compounds, such as potassium or sodium nitrate, thus exhibiting less impact from meteorological conditions (Eleftheriadis et al., 2014).

Natural sources (Mineral dust and Sea salt) mainly contributed to PM_{10} , accounting for 32% at AMA-SUB, 14% at AMA-UB, and 10–11% at the TMA sites. AMA-SUB site is surrounded by non-paved open ground areas, which may explain the high mineral dust contributions (20% to PM_{10}). The contributions in the $\text{PM}_{2.5}$ fraction at all sites were minimal and 3–4 times lower than those in PM_{10} as expected from the coarse sizes of crustal material particles (Eleftheriadis and Colbeck, 2001). The mineral dust contribution at TMA-UT was also relatively high (similar to the AMA-SUB site) but may be also related to non-natural sources, such as public works near the measurement site for the construction of the Thessaloniki Metro system. Mineral dust contributed more during the warm season, probably due to drier conditions allowing for dust resuspension. Sea salt contributions were larger during cold season at AMA and during warm season at TMA, which is related to the prevailing wind directions promoting sea salt aerosol transport towards the receptor sites.

A comparison of mean source contributions during recent and past years, for the city of Athens is presented in Fig. 8. The only source displaying increased contributions during 2011–2012 in comparison to 2002 is Biomass burning. Its concentration was estimated around $3 \mu\text{g m}^{-3}$ during 2002 and in the warm period of 2011–2012, while it was dramatically increased in the cold period of 2011–2012 (average concentration of 9 and $12 \mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$ and PM_{10} , respectively). All other anthropogenic emissions (Traffic, Oil combustion, Secondary aerosol formation) were significantly lower during 2011–2012 with respect to the situation ten years before. The characteristics of the sites in the study in 2002 were closer to urban background than suburban and this may have affected this outcome but the difference in emission strengths is so large (between 53% and 95%, depending on the source and PM size fraction) that it cannot be attributed solely on the site type and should be also related to the mitigation measures, environmental policies and technological advances achieved in the past decade. Significant infrastructure, such as two lines of Underground public transport (Metro system) and a new Ring Road across the Athens Metropolitan Area has been put in operation after 2004, having among other factors contributed to a reduction in traffic congestion and corresponding traffic emissions (Fameli and Assimakopoulos, 2016). The improvements in fuel quality and European standards for exhaust emissions of new vehicles have also had a significant effect (Xiouras et al., 2012). On the other hand, this result seems to also reflect the significant decrease in economic activities during 2011–2012, which coincided with the deep financial crisis in Greece. The absence of an industrial source profile for the

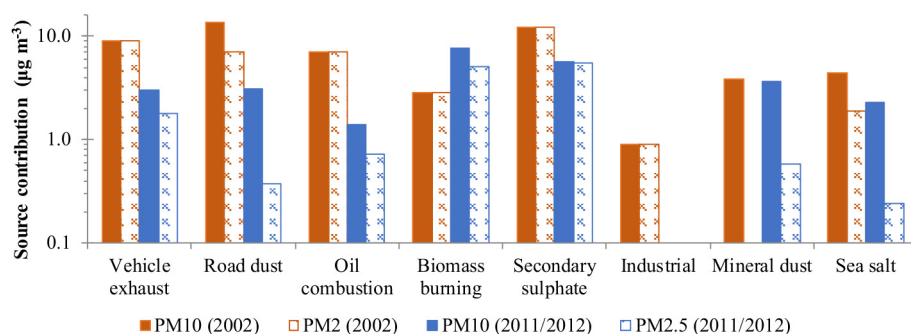


Fig. 8. Mean source contributions to PM in the city of Athens, during 2002 and 2011–2012.

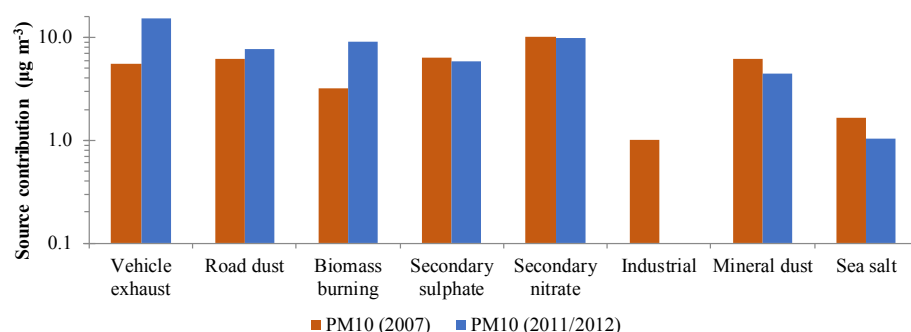


Fig. 9. Mean source contributions to PM₁₀ in urban traffic sites in Thessaloniki, during 2007 and 2011–2012.

2011–2012 dataset suggests that industrial activity contributed less than 1% during that period.

Mean source contributions to PM₁₀ concentrations estimated by PMF in Thessaloniki, at the urban traffic site (TMA-UT) during 2011–2012 and at the urban site (TMA-U) during 2007 are presented in Fig. 9. Comparison of results revealed much lower variability in source strength during this 5-year period, indicating that the positive outcome of environmental strategies of the past decade was already visible in 2007. This is also apparent by the comparable concentration levels during the two periods (average PM₁₀ concentration was measured around $53 \mu\text{g m}^{-3}$ in 2011–2012 and around $47 \mu\text{g m}^{-3}$ in 2007). Much larger PM₁₀ concentrations have been reported for central traffic sites in the city during previous years: on average $80\text{--}110 \mu\text{g m}^{-3}$, as reported by Manoli et al. (2002) for 1994–1995, by Voutsas et al. (2002) for 1997–1998 and Samara and Voutsas (2005) for 1999–2000. On the other hand, the absence of an industrial source profile in the 2011–2012 analysis highlights the effect of the financial crisis which has led to significant reductions in production or even closure of several industries in the country. In addition, a large difference was observed again for Biomass burning, which was considerably increased in 2011–2012 (from 3.0 to $3.5 \mu\text{g m}^{-3}$ in 2007, irrespective of season, to $7.0 \mu\text{g m}^{-3}$ during cold period of 2012). Vehicle exhaust emissions were also much higher during recent years, while Road dust contribution, related to the non-exhaust emissions of traffic, did not present significant difference between 2007 and 2011–2012. These results may reflect the use of improperly maintained vehicles in the city during these last years.

4. Conclusion

The present study is the first effort to assess the contribution of PM₁₀ and PM_{2.5} sources in the two largest cities of Greece in the middle of the financial crisis (in 2011 and 2012). PMF analysis

produced similar source profiles at the two cities, with respect to major sources, such as traffic (exhaust and non-exhaust emissions), secondary aerosol and biomass burning, as well as mineral dust and sea salt. Secondary nitrate was identified as a separate factor only for the Thessaloniki dataset and was comprised also of K^+ and Cl^- (27% of K^+ and 55% of Cl^- were apportioned on this factor). For the Athens dataset, a large fraction of NO_3^- (50%) was apportioned to the Sea salt factor pointing towards neutralization of nitrate with Na^+ rather than NH_4^+ . Both Athens and Thessaloniki Sea salt profiles were depleted in Cl^- . The results indicate that secondary nitrate in both cities is present mostly in the form of nitrate salts (NaNO_3 or KNO_3) and is the result of local NO_x emissions reacting with biomass or marine aerosol. Secondary sulphate was identified as a separate source in both cities. When the input data did not include most major tracers of this component such as ammonium, contributions associated with secondary sulphate were apportioned to other factors, such as Sea salt and Traffic.

Secondary aerosol formation (Sulphate, Nitrate & Organics) and Biomass burning were the major contributing sources for both size fractions at the suburban and urban background sites (accounting in total around 40–70% of PM₁₀ and 70–90% of PM_{2.5}). An increase in absolute contributions of all anthropogenic sources was observed for the urban background site in Athens, with respect to the suburban site, by a factor of 1.3 (for Vehicle non-exhaust) to 2.7 (for Biomass burning) in PM₁₀ and 1.9 (for Oil combustion) to 4.4 (for Vehicle non-exhaust) in PM_{2.5}. Only Secondary sulphate presented comparable contributions at the two sites, indicating the regional character of this source. Biomass burning was the largest contributing source at the two urban background sites, in Athens and Thessaloniki. Comparison of absolute contributions between these two sites revealed similarities in the levels of Biomass burning, Mineral and Road dust and Sea salt. At the urban traffic site, Vehicular traffic (exhaust and non-exhaust emissions) was the major contributing source, accounting for 44% of PM₁₀ and 37% of

PM_{2.5}, with the respective concentrations reaching to 23 and 12 $\mu\text{g m}^{-3}$, respectively. Biomass burning and Secondary nitrate were similar in the two TMA sites, pointing towards cold season conditions that favour the production of nitrate (high humidity and relatively low temperatures), coupled with the extensive use of wood burning for residential heating.

Assessment of the long-term variability of source contributions revealed that, in Athens, Biomass burning contribution increased from 5 to 7% in 2002 to 29–36% for 2011–2012, while all other anthropogenic emissions (Traffic, Oil combustion, Secondary aerosol formation) were significantly lower during 2011–2012 with respect to the situation ten years before (by 53%–95%, depending on the source and PM size fraction). This result reflects the mitigation strategies and technological advances achieved in the past decade, but also the dramatic changes in the Greek economy due to the financial crisis. The absence of an industrial source profile in the 2011–2012 results, for both Athens and Thessaloniki, also points towards decreased economic activity, which has led to significant reductions in industrial emissions.

Lower variability in source strengths was observed for the Thessaloniki 2007 and 2011/2012 data, indicating that the positive outcome of environmental strategies of the past decade was already visible in 2007. A large difference was observed again for Biomass burning, with was considerably increased in 2011–2012 during the cold period, while Vehicle exhaust emissions were also much higher during recent years, possibly reflecting the use of improperly maintained vehicles. This is further supported by the fact that non-exhaust emissions did not show significant change in the course of these years.

The results obtained by the application of source apportionment in recent and past year data clearly demonstrate the effective reduction in emissions during the last decade due to control measures and technological development allowing for cleaner energy and reduced emissions from traffic sources. On the other hand, they also reflect the effects of the financial crisis in Greece during these years, which has led to decreased economic activities (and consequently emissions) but also to the adoption by local population of household practices contributing to poor air quality in an effort to decrease living costs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.06.016>.

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