Elemental Composition and Source Apportionment of Fine and Coarse Particles at Traffic and Urban Background Locations in Athens, Greece

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ABSTRACT

Athens is one of the European cities most burdened by particle pollution; thus, characterizing the aerosol composition and sources is imperative for addressing health concerns and undertaking mitigation measures. In this study, PM10 and PM2.5 ambient samples, collected at a roadside traffic and at an urban background site throughout an annual period, were analyzed for their elemental composition and light-absorbing carbon. Positive Matrix Factorization (PMF) analysis was performed to identify sources and quantify their contributions to the PM2.5 and PM10–2.5 fractions. Above a two-fold roadside enhancement of concentrations was observed for a number of vehicle-emitted and road-dust resuspended species (BC, Cu, Zn, Fe and Ca), with increments for trace elements being more notable in the coarse fraction. Source apportionment indicated that road traffic and sulfate-rich regional aerosols were the key contributors to the fine particles, with the former being dominant at the roadside site (43%) and the latter accounting for the majority (52%) of the particle mass at the background location. Other fine particle sources included biomass burning—mainly during wintertime—, heavy oil combustion, mineral dust and sea salt. For coarse particles, the PMF-extracted factors were associated with vehicular emissions and road dust (prevailing at the roadside site, with a combined contribution of 60%), mineral dust and sea salt (52% cumulatively at the background site). Regional contributions of secondary and natural particles were comparable in level and well correlated among the sites. On the contrary, the net contributions from traffic related sources exhibited large concentration gradients; however, high spatial correlations were observed, especially in cases with favorable wind circulations from the city center towards the background site. It appears that controlling traffic related emissions, in the absence of significant point sources in the area, could have a pronounced effect on a wide spatial scale within Athens, with broad implications for the protection of public health.

Keywords: PM2.5; PM10–2.5; XRF; Spatial variability; Receptor modelling.

INTRODUCTION

The association of human exposure to atmospheric particles with a wide array of adverse health effects has long been established, leading to promulgation of air quality standards and pertinent regulatory action for their enforcement. In Europe, in spite of declining PM concentrations over the last decade (Pandolfi et al., 2016), recent results indicate the link between recorded levels in a large number of European cities to cardiorespiratory symptoms, morbidity and general mortality (Beelen et al., 2014). While exposure risks for fine particles are widely acknowledged, having led to establishing relevant limit values, coarse particle toxicity is also reported (Brunekreef and Forsberg, 2005) and especially in Southern Europe it appears enhanced in the presence of dust events (Mallone et al., 2011).

Besides size, chemical composition is a fundamental parameter driving particle toxicity, especially for constituents such as carbonaceous compounds and trace elements (Kelly and Fussel, 2010). While the multiplicity of aerosol emission sources and atmospheric processes is reflected on the various species comprising particle mass, single species may not always suffice as tracers of particular sources (Sarnat et al., 2008). Hence, chemometric receptor models (Belis et al., 2013) don’t only offer identification/quantification of source contributions—with apparent implications for the development of control strategies—but can also assist...
Several health studies have utilized source contribution data from multivariate receptor modelling (Bell et al., 2014). However, the effect of spatial variability in source profiles and in contributions within large urban agglomerations has been acknowledged early on (Ito et al., 2006) and significant discrepancies between monitoring sites within the same city are frequently reported (Kim and Hopke, 2008; Minguillon et al., 2014). Spatially representative data is a key prerequisite for lowering the risk of exposure misclassification error. Source contributions not correlated among areas of a city, due to varying source profiles, might affect community epidemiology, in case single-site data are used. Even with adequately correlated data, large within-area variability in mean contributions of sources could bias cohort studies of chronic exposure effects (Wilson et al., 2005).

The greater area of Athens has long been aggravated by particle pollution (Grivas et al., 2008). Over the last decade, PM levels have gradually decreased, yet they remain elevated in comparison to other large European cities (Eeftens et al., 2012). The onset of the economic recession in Greece has altered the mixture and intensity of primary sources (Paraskevopoulou et al., 2014; Diapouli et al., 2017); therefore, the availability of reference data on source types and contributions seems critical for understanding the evolving landscape. In the past, there have been source apportionment studies in the area (Karageorgos and Rapsomanikis, 2010; Mantas et al., 2014; Paraskevopoulou et al., 2015). However, spatial contrasts of source contributions to fine and coarse particles have not been explored, especially between sites of different characterization. This field of study emerges as salient, in view of the significant spatial heterogeneity which has been reported for particle concentrations and chemical composition in the area (Manalis et al., 2005; Theodosi et al., 2011).

The present study aims to characterize the elemental composition of fine and coarse particles, for an annual period, at two sites in Athens, Greece and perform PMF (Positive Matrix Factorization) analysis for source apportionment. Emphasis is placed on the contrasts between traffic-impacted and urban background measurement locations, in order to explore the intra-urban correlations and homogeneity in the profiles and contributions of identified sources.

**METHODOLOGY**

**Study Area**

Sampling was conducted within the Athens basin (Fig. 1), where the majority of the population (3.1 of 3.8 million) and economic activity of the Greater Athens Area is gathered. The 450 km² quadrilateral area is bound by mountainous terrain on three sides and the Saronic Gulf in the S–SW direction. The area experiences “hot dry summer” Mediterranean-type climate and winds flow mainly in the SW–NE axis. The build-up of pollution is mostly associated with sea breeze circulations, while ventilation occurs during N–NE synoptic-scale flows (Kanakidou et al., 2011).

Nearly 2.8 million vehicles are circulating in the area, the vast majority of which (2.5 million) are gasoline-fueled passenger cars. The vehicle parc includes 0.2 million LDV, HDV, buses and taxies, mostly diesel-fueled (Progiou and Zimomas, 2011). Although heating oil was predominantly used for residential heating in the area prior to 2010, due to recession-related heating fuel taxes, since the winter of 2011 wood-burning use has amplified, leading to the appearance of intense wintertime episodes (Athanasopoulou et al., 2017). Industrial activity within the basin is limited; however, heavy-industrial installations are operating in the Thriassion plain, to the west (Manalis et al., 2005). The port of Piraeus, occupying a large part of the basin’s exit to the sea, is the busiest passenger port in Europe and since 2009 has grown to be one of the largest container ports in the Mediterranean.

**Measurement Locations and Particle Sampling**

Simultaneous PM$_{10}$ and PM$_{2.5}$ 24-h samples were collected during a yearly measurement period, between May 2011 and April 2012 (with sampling frequency of 1-in-3 days on average), at a roadside traffic and at an urban background site (Fig. 1). Sites were located in the central section of the basin, at 6.5 and 9.5 km from the sea respectively, while the inter-site distance was 5.5 km.

The roadside traffic site (ARI) was located at Aristotelous Street, in the densely populated (17,050 inhabitants km$^{-2}$) center of Athens, at a station of the National Air Quality Monitoring Network. Particle pollution at this site has been reported in the past for PM concentrations and toxic metals (Chaloulakou et al., 2005, Manalis et al., 2005). Samplers were placed on the first floor (~6 m) of a building, standing at a three-road intersection with traffic lights, at the exit of a street canyon. Traffic counts within a 50 m radius from the site report a mean daily circulation of 40,000 vehicles.
per day, characterized by frequent congestion and stop-and-go driving patterns.

The urban background site (POL) was located inside the campus of the National Technical University of Athens, in the moderately populated (8,350 inhabitants km$^{-2}$) urban residential area of Zografos. Sampling was conducted at 3 m from the ground, with no obstacles within a 100 m radius. Local, in-campus, traffic is limited, with the nearest road being at 80 m. However, the site was expected to receive some influence from a motorway at 0.6 km from the site. Low PM$_{10}$ levels have been reported in the past in the area of Zografos (Grivas et al., 2008; Remoudaki et al., 2013), rendering the measurement location suitable for characterizing the urban background in the central section of the Athens Basin.

PM$_{10}$ and PM$_{2.5}$ samples were collected using Harvard Impactors (Air Diagnostics and Engineering Inc., Naples, ME, US), at a flow rate of 10 L min$^{-1}$ (Eeftens et al., 2012). Particles were collected on PTFE membrane 37-mm filters (Teflo, Pall Inc., Ann Arbor, MI, USA). Filters were conditioned for 24-h before and after weighing at controlled temperature (20 ± 1°C) and relative humidity (50 ± 5%). Measured PM$_{10}$ mass at ARI was compared to colocated PM$_{10}$ measurements from an automated monitor (beta-attenuation, mod. FH 62 I-R, Thermo Scientific Inc.), with results (Fig. S1) indicating excellent collinearity ($r^2 = 0.88$).

**Chemical Analysis**

Following the determination of PM concentrations, filters were analyzed by means of energy-dispersive X-Ray Fluorescence (XRF) spectroscopy (Epsilon 5, PANalytical B.V., Almelo, The Netherlands), to determine concentrations of 48 elements. Elemental analysis was conducted at the Harvard School of Public Health. Details on the operation of the XRF analyzer and the evaluation of its performance in terms of accuracy and precision for ambient PM samples can be found in Kang et al. (2014).

Light absorbing carbon content of particles was determined by measuring reflectance (Eeftens et al., 2012) of PM$_{10}$ and PM$_{2.5}$ filters, using a smoke stack reflectometer (EEL43D, Diffusion Systems Ltd., Ealing, UK). The light absorption coefficient (ABS) was determined according to ISO9835 and subsequently converted (dos Santos et al., 2014) to equivalent BC concentrations (eBC), by means of a linear regression equation (Fig. S2), which was obtained for pairwise comparisons between reflectance-based absorbance on sampled filters and concurrently measured EC (Grivas et al., 2012). Results of the comparison between methods, depicted in Fig. S2, demonstrate a high degree of linear interdependency ($r^2 = 0.87$).

**Ancillary Data**

Concentrations of nitrogen oxides (NO$_x$), utilized in the study as an indicator of traffic emissions (Chaloulakou et al., 2005), were acquired from the National Air Quality Monitoring Network, in situ for ARI and by the nearest sampling site for POL (Fig. 1), in the area of Agia Paraskevi (AGP). Concentrations at both sites were determined using a chemiluminescence analyzer (APNA-360, Horiba Inc.). Hourly data on wind speed and direction were retrieved from a meteorological station operated by the Hydrological Observatory of Athens, inside the campus of the National Technical University of Athens (Fig. 1). Four-day back-trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT-4, NOAA), with one-degree Global Data Assimilation System meteorological data fields (GDAS1, NCEP). Trajectories were calculated for air masses arriving at Athens four times each sampling day (00, 06, 12, 18 local times), at heights of 750 and 1500 m, in order to capture the build-up of concentrations and to avoid grounding effects, while describing transport within the boundary layer (Grivas et al., 2008).

**Data Management and Analysis**

A total of 82 days of concurrent sampling and analysis for each fraction and measurement site were included in the source apportionment analysis. Concentrations for particle mass and constituents in the coarse particle fraction (PM$_{10-2.5}$) were obtained by subtracting respective values in PM$_{2.5}$ from PM$_{10}$. Detection limits for PM mass, elemental concentrations and light absorption coefficients were determined as 3 times the standard deviation of values of field blank samples (9% of total samples) and are presented in Table S1 along with percentages of samples below detection limits (BDL). Species with over 50% BDL data were excluded from the subsequent analysis and source apportionment, which included a total of 19 elements plus eBC.

Wind direction data were utilized to identify potential origins of sources, by calculating conditional probability functions (CPF) of source contributions. The probability that the 80$^{th}$ percentile of fractional source contributions would be exceeded, depending on wind direction and speed, was plotted using the bivariate methodology developed by Uria-Tellaetxe and Carslaw (2014). The same value of calculated 24-h fractional contributions were assigned at hours of each day. Calm conditions (mean wind speed $< 1$ m s$^{-1}$) were excluded. To detect distant areas of influence for long-range transport, the Potential Source Contribution Function (PSCF) was calculated by combining estimated source contributions and calculated trajectories (Polissar et al., 1999). The threshold was set at the 80$^{th}$ percentile of fractional source contributions. PSCF values were down-weighted to reduce the effect of 1 × 1° grid cells containing a small number of endpoints, according to the weighting scheme proposed by Dimitriou et al. (2015).

**Source Apportionment Methodology**

For source apportionment, the positive matrix factorization (PMF) multivariate receptor model was applied, using the specialized software EPA PMF 5.0, which incorporates the multilinear engine (ME-2) program (Paatero, 1999). In brief, the PMF model decomposes speculated PM time-series into the product of factor contribution and factor profile matrices. The chemical mass balance equation between measured species concentrations and factor profiles is solved by minimizing the sum of squared, uncertainty-weighted,
residuals of the decomposition error matrix (objective function, $Q$), under non-negativity constraints for factor contributions.

Uncertainties for XRF-quantified elements were calculated as the sum of the analytical uncertainty and one-third the detection limit, while for the light absorption coefficients and PM concentrations they were based on detection limits and precision calculated as coefficient of variance from field duplicate measurements (Reff et al., 2007). BDL concentration values were given 5/6th the value of the detection limit as uncertainty. For coarse particles, uncertainties were propagated as the square root of the sum of PM10 and PM2.5 squared uncertainties. The uncertainties of PM, which were included in the model to obtain their source contributions, were tripled, so that they would not substantially influence solutions.

For the selection of the appropriate number of factors, the ratio of actual $Q$ to a theoretically expected value ($Q_{EXP}$) was observed while increasing their number, with a large decrease signifying an improvement in the explanatory power of the model (Brown et al., 2015). Multiple linear regression was also performed between PM concentrations and factor contributions, with the appearance of negative regression coefficients denoting the presence of redundant factors (Kim et al., 2003). Most importantly, a realistic physical reasoning was required for each resolved factor.

PMF models were separately run for the two sites and the two size fractions (Crilley et al., 2017), since focus was placed on differences among sampling locations. Random measurement/modeling errors and rotational ambiguity in solutions were assessed using FPEAK rotations and the bootstrap-displacement (BS-DISP) error estimation method included in the EPA PMF5.0 software (Paatero et al., 2014).

**RESULTS AND DISCUSSION**

**Characterization of Chemical Composition**

**Elemental Concentrations**

Descriptive statistics for speciated PM data are displayed in Table 1. Average PM concentrations at the ARI site were higher than the annual average EU limit values for both PM$_{10}$ and PM$_{2.5}$. These levels, being over two-fold in comparison to those observed at the urban background site, highlight the impact of traffic emissions. Estimated eBC concentrations in PM$_{10}$ at ARI were 1.5 times higher than average EC concentrations reported by Grivas et al. (2012) for a roadside site with lighter traffic in central Athens during 2003, while fine eBC levels were comparable to fine EC levels determined for multiple street-side locations in Athens, during the year preceding this study (Jedynska et al., 2014). Traffic-related light-absorbing carbon levels in Athens seem to persist over the years, but at moderate levels in comparison to other European cities (Eeftens et al., 2012). At POL, estimated fine eBC concentrations were comparable to the established background for EC in the area (Paraskevopoulos et al., 2014).

On the contrary, PM$_{10}$ sulfur levels (1.5–1.7 μg m$^{-3}$) appear to be on the decline since Karageorgos and Rapsomanikis (2010) reported mean levels of 3.5 μg m$^{-3}$ for central Athens during 2003–2004. However, such values place Athens at the higher tier of European cities for particle S (Tsai et al., 2015), owing to the prevalent use of sulfur-rich fuels for energy production in Greece (Manousakas et al., 2013), which however has gradually declined over the years. For

**Table 1.** Average concentrations (standard deviations) for elemental (ng m$^{-3}$), equivalent BC (eBC) and PM mass concentrations in PM$_{2.5}$ and PM$_{10,2.5}$ at the two sites.

<table>
<thead>
<tr>
<th>Component</th>
<th>ARI (Roadside Traffic)</th>
<th>POL (Urban Background)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM$_{2.5}$</td>
<td>PM$_{10,2.5}$</td>
</tr>
<tr>
<td>PM (μg m$^{-3}$)</td>
<td>30.1(19.2)</td>
<td>23.8(10.0)</td>
</tr>
<tr>
<td>eBC (μg m$^{-3}$)</td>
<td>2.6(1.2)</td>
<td>0.7(0.3)</td>
</tr>
<tr>
<td>Na</td>
<td>222.1(106.5)</td>
<td>285.2(264.5)</td>
</tr>
<tr>
<td>Mg</td>
<td>34.9(25.5)</td>
<td>131.5(69.1)</td>
</tr>
<tr>
<td>Al</td>
<td>87.7(96.1)</td>
<td>384.3(219.4)</td>
</tr>
<tr>
<td>Si</td>
<td>173(178.6)</td>
<td>858.4(477.7)</td>
</tr>
<tr>
<td>S</td>
<td>1572.5(739.9)</td>
<td>118.5(151.4)</td>
</tr>
<tr>
<td>Cl</td>
<td>43.9(91.4)</td>
<td>644.4(484.6)</td>
</tr>
<tr>
<td>K</td>
<td>240.8(157.7)</td>
<td>176.1(89.4)</td>
</tr>
<tr>
<td>Ca</td>
<td>397.3(163.0)</td>
<td>3079.3(1323.6)</td>
</tr>
<tr>
<td>Ti</td>
<td>8.1(5.2)</td>
<td>45.0(19.7)</td>
</tr>
<tr>
<td>V</td>
<td>5.8(5.4)</td>
<td>2.6(2.1)</td>
</tr>
<tr>
<td>Cr</td>
<td>1.8(1.0)</td>
<td>11.1(5.7)</td>
</tr>
<tr>
<td>Mn</td>
<td>4.8(2.9)</td>
<td>18.3(8.2)</td>
</tr>
<tr>
<td>Fe</td>
<td>320.1(142.1)</td>
<td>1548.9(718.8)</td>
</tr>
<tr>
<td>Ni</td>
<td>3.2(2.3)</td>
<td>3.5(2.5)</td>
</tr>
<tr>
<td>Cu</td>
<td>13.5(7.3)</td>
<td>55.6(30.3)</td>
</tr>
<tr>
<td>Zn</td>
<td>50.6(37.2)</td>
<td>37.5(19.6)</td>
</tr>
<tr>
<td>Br</td>
<td>5.5(3.3)</td>
<td>2.5(2.7)</td>
</tr>
<tr>
<td>Ba</td>
<td>29.5(13.2)</td>
<td>28.7(35.9)</td>
</tr>
<tr>
<td>Pb</td>
<td>14.3(8.7)</td>
<td>4.9(5.0)</td>
</tr>
</tbody>
</table>
fine potassium, an indicator of wood-burning, average year-round levels at the two sites (0.15–0.24 μg m⁻³) were comparable to those reported for urban background locations in Athens before the onset of the economic recession (Karanasiou et al., 2009). It appears that there are limits to the overall effect that biomass burning for heating can bear on annual average levels, since its use is temporally confined within wintertime and mainly during the evening hours (Athanasopoulou et al., 2017). Concentrations of Pb and Ni, were found well below the EU defined limit values of 0.5 and 0.02 μg m⁻³, respectively, indicating time-sustained compliance to the provisions of 2004/107/EC and 2008/50/EC directives (Manalis et al., 2005).

**Fine/Coarse Partitioning of Species**

Relative contributions of fine and coarse particles to PM₁₀ elemental concentrations, along with fine-coarse correlation coefficients are displayed in Fig. 2. Enrichment factors (EF) are provided in Fig. S3. At both sites, elements associated with tailpipe or energy production emissions (eBC, S and V) were preferentially categorized in PM₂.₅, while those emitted through natural processes (Mg, Cl, Al, Si and Ti), were mainly found in the coarse fraction.

Fine and coarse sulfate were uncorrelated to each other, since the former is mainly expected as ammonium sulfate originating from processed regional anthropogenic emissions and the latter found in aged marine aerosol or formed by heterogeneous reactions between sulfur dioxide and mineral dust particles (Kouyoumjian and Saliba, 2006). Potassium was not favorably partitioned in either fraction and no correlation was observed between fine and coarse K concentrations. It exhibited large enrichment in the fine fraction indicating production from biomass burning, while coarse K was closely associated with mineral dust (Masri et al., 2015).

Some trace metals (Cu, Cr and to a lesser extent Fe, Mn) were mainly classified in the coarse fraction while recording EF values indicative of anthropogenic production, suggesting their emission through local mechanical processes linked to automotive wear. Notably, copper was by 67–80% confined in the coarse mode, 75–165 times enriched and highly correlated between coarse and fine fractions, indicating the importance of brake wear as a source in the urban environment (Weckwerth et al., 2001). For Zn, an established tracer for tire wear (Harrison et al., 2012), a similar pattern was observed at the traffic site, its concentrations being nonetheless enhanced in PM₂.₅, due to its presence in additional anthropogenic emissions, including tailpipe aerosols (Lough et al., 2005).

**Seasonal Variability**

Table 2 displays cold-warm period concentration ratios for elements recording statistically significant between-period differences (p < 0.05). Correlations for inter-species pairwise comparisons are presented in Fig. S4. Increased traffic emissions during the cold period, related mainly to the seasonal variation of traffic loads observed at the two sites (Chaloulakou et al., 2005; Lianou et al., 2011), were translated into higher (33–56%) eBC average values at both sites. Fine potassium levels increased about 60–90% during the heating season, indicative of wood-burning in the area (Paraskevopoulou et al., 2014).

Increased concentrations of coarse mineral elements (Al, Si at both sites and Ti, Ca, Fe at the urban background) were observed during the warm period, due to dry conditions which favor soil and road dust resuspension (Kassomenos et al., 2012). Mean ratios higher than respective median ratios, for mineral dust elements especially in the fine fraction, should be attributed to the presence of extreme values observed during episodes of Saharan dust transport.

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**Fig. 2.** Relative contributions of coarse and fine components in PM₁₀ (stacked columns-left axis) and correlation coefficients between fine and coarse concentrations (dots-right axis), at the two sites.
Table 2. Cold/warm period ratios for average (median) values and statistical significance\(^{b}\) of cold/warm seasonal variability.

<table>
<thead>
<tr>
<th>Component</th>
<th>ARI (Roadside Traffic)</th>
<th>POL (Urban Background)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>PM(_{2.5})</td>
<td>PM(_{10-2.5})</td>
</tr>
<tr>
<td>PM</td>
<td>1.69(1.43)(^{**})</td>
<td>1.31(1.26)*</td>
</tr>
<tr>
<td>eBC</td>
<td>1.56(1.55)(^{**})</td>
<td>1.44(1.33)(^{**})</td>
</tr>
<tr>
<td>Na</td>
<td>1.26(1.18)*</td>
<td>1.75(1.70)(^{**})</td>
</tr>
<tr>
<td>Al</td>
<td>1.05(0.59)*</td>
<td>0.85(0.65)(^{**})</td>
</tr>
<tr>
<td>Si</td>
<td>1.10(0.72)*</td>
<td>0.81(0.62)(^{**})</td>
</tr>
<tr>
<td>S</td>
<td>0.89(0.81)</td>
<td>2.05(2.71)*</td>
</tr>
<tr>
<td>Cl</td>
<td>5.76(5.41)(^{**})</td>
<td>3.17(3.89)(^{**})</td>
</tr>
<tr>
<td>K</td>
<td>1.89(2.03)(^{**})</td>
<td>0.76(0.73)(^{**})</td>
</tr>
<tr>
<td>Ca</td>
<td>1.12(1.11)</td>
<td>1.18(1.13)</td>
</tr>
<tr>
<td>Ti</td>
<td>1.14(0.97)</td>
<td>0.99(0.88)</td>
</tr>
<tr>
<td>Fe</td>
<td>1.32(1.19)*</td>
<td>1.32(1.24)*</td>
</tr>
<tr>
<td>Pb</td>
<td>1.13(1.11)</td>
<td>0.58(0.27)*</td>
</tr>
</tbody>
</table>

\(^{a}\) Cold period: 16 Oct–15 Apr (n = 36), Warm period 16 Apr–15 Oct (n = 46).

\(^{b}\) Mann Whitney U-test.

* significant at the 0.05 level.

** significant at the 0.01 level.

(Remoundaki et al., 2013) that occurred during the cold period of the study.

Concentrations of fine and coarse S displayed contrasting seasonal patterns. Secondary formation of fine sulfate, which in Mediterranean climatic conditions is enhanced during summertime via photochemistry and heterogeneous cloud processing of precursors (Kalivitis et al., 2015), supports the observed cold/warm ratios below unity. Coarse S exhibited poor correlations with Na, Cl (\(r: 0.13–0.32\)) and was associated with mineral dust elements, especially at high PM\(_{10-2.5}\) concentration levels, indicating its inclusion in dust in the course of long-range transport events (Kocak et al., 2004). Though similar in seasonal pattern and well correlated to Na (\(r: 0.54–0.88\)), markedly higher cold/warm ratios were observed for Cl. Significant depletion of chloride, through evaporation after reaction of sea salt with acidic species, has been observed in warm conditions of Mediterranean cities (Terzi et al., 2010).

Roadside Enhancement of Elemental Concentrations and Inter-site Variability

Roadside enhancements of concentrations, calculated as the concentration ratio of ARI to POL, are presented in Fig.3, for elements (excluding Cl) which recorded significantly higher concentrations at the traffic site (\(p < 0.05\), Wilcoxon signed rank test). In PM\(_{2.5}\), a large increment was observed for eBC (mean ratio of 3.3), comparable to findings for EC in the area (Pateraki et al., 2012) and typical for heavy traffic-urban background site pairs (Harrison and Yin, 2008). Over two-fold levels compared to the background were measured at ARI for Cu, a part of which is emitted from brakes in the fine size-range (Thorpe and Harrison, 2008) and for Fe, known to be present in tailpipe emissions as a result of engine wear (Gertler et al., 2002). These ratios lie in the upper range for European urban areas reported by Tsai et al. (2015). A notable enhancement was apparent for fine Ca and Zn whose emission in the fine range has also been attributed to their use as additives in lubricating oil (Schauer et al., 2006). High traffic/background ratios were calculated for the coarse fraction of Cu, Zn, Fe, Cr, Pb and Ba, which are associated with brake and tire wear and known to be present in road dust (Pant et al., 2017), with mean ratios ranging between 4.4–6.8 (Harrison et al., 2012). A large roadside increment for coarse Ca, in comparison to those of Al and Si was observed, which besides road dust resuspension might indicate road surface wear due to heavy traffic conditions at the ARI site (Grigoratos et al., 2014).

Inter-site correlations are displayed in Table S2. Traffic-related elements (eBC, Cu, Fe, Zn) were moderately correlated (\(r: 0.43–0.75\)) in the fine fraction between sites, due to similar temporal traffic patterns effective over the area (Grivas et al., 2008). Nickel and vanadium, known tracers of fuel oil combustion from shipping emissions (Pandolfi et al., 2011), presented similar temporal covariance (\(r: 0.66–0.75\)), reflecting the relative absence of oil combustion point sources within the basin and the influence of external emissions, mainly from the port zone. Larger concentrations were recorded at ARI, related to its closest proximity to the port and industrial areas to the SW-W of the basin. Noteworthy inter-site correlations were observed for Al, Si and Ti in both fractions (\(r: 0.58–0.85\)), signifying the effectiveness of processes that influence mineral dust suspension at the intra-urban spatial scale. Strong temporal covariance among mineral dust elements has been observed in other urban areas of Southern Europe as well (Dall’Osto et al., 2013). Fine S concentrations were highly correlated (\(r = 0.89\)) due to their regional origin. Values of the coefficient of divergence (Grivas et al., 2008), which are also shown in Table S2, exceed 0.2, a value typically used to indicate spatial homogeneity, with the sole exception of regionally uniform fine S (Pateraki et al., 2012), while all CoD values for coarse fraction elements were higher than 0.4.

\(\text{CoD} = \frac{\text{covariance}}{\text{standard deviation of ARI} \times \text{standard deviation of POL}}\)
Source Identification and Apportionment

**PMF Results**

Solutions with six and four factors for fine and coarse particles, respectively, were resolved at both sites. The characterization of sources was the same between sites (Mazzei et al., 2008; Liu et al., 2014); however, site-dependent discrepancies were noted within the source profiles of respective factors. Figs. 4(a) and 4(b) present explained variance by factors for each species, by size fraction. The associated source profiles are provided in Figs. S5(a)–S5(d). Results from the PMF implementation are reported in Table S3, according to recommendations of Brown et al. (2015). The error indicators of the BS-DISP procedure exhibited the stability of the obtained solutions for FPEAK = 0, which was further verified by inspection of G-space plots and rotations for FPEAK values between −0.5 and 0.5, that provided matching sources and source profiles to the base solution.

**Source Apportionment for Fine Particles**

**Road Traffic:** The factor was characterized by high loadings primarily for eBC and for trace elements such as Cu, Zn, Fe and Ca. It was also highly correlated with NOx (r: 0.90, 0.81, at ARI and POL, respectively). Notable differences in source profiles were observed among sites. At the traffic site, tailpipe emitted S and to a lesser extent K appear to participate in the road traffic profile, the latter being used as an additive in lead replacement gasoline for the small number of non-catalytic vehicles still circulating in the center of Athens. The participation of Ca and Fe was largely increased as well. Road traffic was not the dominant source of eBC at POL and a series of elements included in the factor (Pb, Cr, Mn) received lower traffic contributions, in comparison to ARI. The CPF plot for the road traffic factor at the background site is shown in Fig. 5(a). It is indicated that increased traffic contributions are associated with SW-NW flows, transporting particles from the city center, or with lighter winds from the E-NE of the site, which are indicative of emissions from the nearby motorway.

**Regional:** The factor is characterized by regional S, formed through the oxidation of SO2. At both sites, factor contributions increased during the warm months (Farao et al., 2014) by 28–48%, at ARI and POL, respectively. Several trace elements, which are also found in primary emissions of large combustion plants, such as Pb and Zn, received important contributions from this source. Given the known transboundary potential of emissions from industry and energy production, long-range transport of fine particles and especially sulfate, from Balkans and Eastern Europe, has been suggested for Greece (Theodosi et al., 2011). Paschalidou et al. (2015) have identified air masses transported through the north-east sector, originating in Southern Russia, to be related to the occurrence of PM episodes recorded in the center of Athens and with generally elevated levels in the area. The results of the PSCF analysis presented in Fig. 6(a) appear to corroborate these findings, indicating the region surrounding the Black Sea as a major hotspot for anthropogenic fine particle emissions (Gerasopoulos et al., 2011).

**Biomass Burning:** Potassium dominates the factor with additional loadings of eBC, S, Cl. Increased abundances of Cl and eBC are considered indicative of freshly produced smoke from biomass burning, whereas a stronger presence

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**Fig. 3.** Roadside enhancement expressed as mean value of TR/UB ratios of 24-h concentrations measured at ARI relative to POL, for (a) PM2.5 and (b) PM10-2.5. Dots denote the median of ratios and whiskers the interquartile range.
of S signifies the substitution of chloride in aged smoke containing potassium sulfate (Viana et al., 2013). In this case higher S/K ratios were calculated at the background site (1.8 vs. 1.0), characteristic of moderate ageing of smoke and the absence of direct wood-burning emissions in its direct vicinity. The CPF plot for biomass burning (Fig. 5(b)) suggests transport to the background location mainly from the northern sector of the basin, where lower temperatures are recorded during the winter and intense wood-burning for heating has been documented (Athanasopoulou et al., 2017). Mass contributions increase by 30–43% during the cold season. Nonetheless, the factor has a presence during the remainder of the year. In Fig. S6 it can be observed that, during the warm period, increased concentrations of biomass burning particles were associated with trajectories originating in the Balkans and Eastern Europe, where agricultural waste burning has been identified as an important source of fine aerosols transported to Southern Greece in summertime (Sciare et al., 2008).

Oil Combustion: The factor is characterized by the presence of vanadium and nickel, with V/Ni ratios nearing three (2.8 and 2.5, for ARI and POL respectively), suggesting emissions from heavy oil combustion related to shipping activity (Pandolfi et al., 2011). The CPF plot (Fig. 5(c)) is indicative of transport from the port zone of Piraeus to the SW of the sites. Inclusion of additional species (Zn, Cu, Cr, Mn) is likely related to oil combustion and industrial emissions in the Thriassion plain to the west.

![Fig. 4(a). Comparison between the two sites regarding the relative mass of species attributed to each PMF source, for PM$_{2.5}$. Grey bars for the traffic site, white bars for the background site. Whiskers denote the bootstrap interquartile range.](image-url)
Fig. 4(b). Same as Fig. 4(a), for PM$_{10-2.5}$.

Fig. 5. Bivariate polar plots for conditional probabilities of threshold exceedance, for fractional source contributions estimated at the urban background site, regarding the road traffic (TRA), biomass burning (BB) and oil combustion (OIL) sources in PM$_{2.5}$.

of the basin (Manalis et al., 2005). Contributions increase during the warm period, by 27–40% at POL and ARI, respectively, relevant to the increased activity of passenger and cruise ships.

Mineral dust and Sea Salt: The factors associated with mineral dust presented characteristically high loadings of Si, Al, Fe, Ca, and Ti. Ratios of these elements were generally in agreement with average values reported for
crustal material in the geophysical region. We observed Ca/Al ratios closer to unity (1.3–1.4) in the source profiles, lower than 2.0–3.0 observed in the enrich calcite soil of Athens (Scheff and Valiozis, 1990), denoting the additional contribution of fine African dust, for which ratios of 0.45 have been reported (Formenti et al., 2003). Regarding the sea salt factor, the Cl/Na ratio (0.9) was significantly lower than in seawater indicating significant loss of sea-salt chloride in the fine fraction.

Source Apportionment for Coarse Particles

**Vehicular emissions:** The factor represents direct emissions of coarse particles associated with road traffic. The factor was correlated with NOx concentrations at both sites (r: 0.96, 0.70, at ARI and POL, respectively), and it followed the temporal pattern of the road traffic source identified in PM2.5, with contributions being significantly increased during the cold period. The factor is characterized by elements associated with automotive and road wear (Cu, Zn, Ba, Ca, Fe). Some eBC was also associated in the factor, given the light absorbing characteristics of particles originating from tire wear (Achilleos et al., 2016). Barium whose emissions have been linked to brake wear from heavy vehicles (Karageorgos and Rapsomanikis, 2010) was notably present in the ARI profile, since circulation of public transportation buses and heavy duty commercial vehicles is frequent in the center of Athens.

**Road Dust:** This factor is characterized as resuspended road dust. Contrary to the vehicular coarse fraction, its correlations to NOx were weak (r: 0.31, 0.12, at ARI and POL, respectively). To account for the difference, it is noted that traffic-related road dust resuspension is favored by continuous traffic flow at higher speeds, while direct emission of coarse particles is mostly linked to stop-and-go heavy traffic. Characteristically, Amato et al. (2017) have estimated that road dust resuspension increases with a power of 1.5 of the vehicle speed. A seasonal profile different from the vehicular factor was detected. Average contributions were higher, by 43–72% at POL and ARI, respectively, under low-moisture conditions during the warm period, which favor traffic-induced and wind-driven resuspension of road dust (Oliveira et al., 2010). Mineral dust tracers (Al, Si) are included in the road dust factor, when their presence in the vehicular factor was minimal.

**Mineral dust:** Typical source profiles for mineral dust were observed at both sites, with high loadings of tracer elements similar to the fine fraction. Factor contributions were uncorrelated to NOx. Elemental ratios involving Al, Si, Fe, Ti and K corresponded to urban soil composition in Athens, as opposed to the road dust factor where a notable enhancement of the Fe/Si factor was observed (Masri et al., 2015). A large enrichment was noted for Ca concentrations, due the abundance of calcium carbonate in local topsoil (Argyraki and Kelepetzis, 2014). Values of the Si/Al ratio approaching two are consistent to those reported by Chalbot et al. (2014) for Athens and between values for local soil and Saharan dust. It appears that LRT dust events are critical in determining mineral dust contributions, as it

![Fig. 6. PSCF values for factors associated with long-range transport in the area of Athens (for fractional contributions calculated at the urban background site).](image-url)
was evident by the PSCF values associated with the factor, displayed in Fig. 6(b). The participation of eBC in the factor is most likely linked to its indirect estimation, since light absorbing particles include mineral hematite in small quantities (Horvath, 1996).

**Sea Salt:** Contrary to the fine fraction, it was observed that chloride depletion was less severe in coarse sea salt with Cl/Na ratios near 1.6. S/Na values close to 0.15 indicate moderate ageing of sea salt in the central part of the Athens basin. Elevated contributions of sea-salt to coarse mass were recorded under transport of air masses from Western Mediterranean and Atlantic Ocean (Fig. S6).

**PM Mass Contributions and Comparisons to Other Studies**

Results for the average contribution of identified sources to PM$_{2.5}$ and PM$_{10-2.5}$ mass are given in Fig. 7. PMF models successfully reconstructed PM concentrations with $r^2$ values between modelled and actual values exceeding 0.85, with unexplained variance being attributed mainly to the absence of nitrate and organic carbon from the speciation dataset.

For PM$_{2.5}$, at the central site, the road traffic factor accounted for 43% of measured concentrations, on a yearly average. This value is comparable to those previously reported for traffic sites in Europe, marginally exceeding the range (27 ± 12%) established by the meta-analysis of Belis et al. (2013). Downtown areas in Greek cities appear to be significantly burdened by traffic emissions. Up to 37% of PM$_{2.5}$ measured at a traffic site in Thessaloniki, Greece, has been attributed to road traffic (Diapouli et al., 2017), with exhaust emissions estimated to account for nearly 30% (Argyropoulos et al., 2017). At the urban background site, the road traffic factor contributed one-fourth the respective mass at the central site and accounted for 24% of PM$_{2.5}$, a value similar to the European median for urban background sites (Belis et al., 2013) and the estimation of Mantas et al. (2014) for the urban background in the central part of the Athens basin.

The factor characterized as regional has a comparable contribution at the two sites (8.4 and 7.4 μg m$^{-3}$ corresponding to 28 and 52% of PM$_{2.5}$ mass, at ARI and POL). These concentration values are higher than the reconstructed masses of ammonium sulfate from fine S concentrations (Chow et al., 2015), which correspond to concentrations of 6.2 and 5.8 μg m$^{-3}$ at the two sites. It is likely that the source profile incorporates a significant part of secondary organic carbon. Paraskevopoulou et al. (2015) have reported the participation of organic matter in secondary sulfate PMF source profiles, while Grivas et al. (2012) have estimated that annual average secondary organic carbon concentrations of at least 1.7 μg m$^{-3}$ should be anticipated in central Athens, even at traffic sites. The factor accounts for nearly half the mass at POL, an observation in

![Image](Fig. 7. Average contribution to particle mass (μg m$^{-3}$ and % of PM), by apportioned source for the two size fractions at the two sites.

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agreement with results by Amato et al. (2016) for the contribution of secondary formed and transported particles, at Southern European urban background sites. Molnar et al. (2014) have highlighted the implications of large contributions of regional sources for personal exposure to fine particles.

Year-round contributions of biomass burning in the area of Athens during 2011–2012 accounted for 7–9% of PM$_{2.5}$ concentrations. These values are considered reasonable, since results from continuous 5-year measurements (Paraskevopoulou et al., 2015) at a suburban background site in Athens (2008–2013), covering the period before the appearance of the wood-burning trend in the area and tracking it up to its establishment as a major air pollution issue, have attributed 7% cumulatively to biomass burning. The net biomass burning contribution was higher at the ARI site, which should be attributed to the population density in the surrounding area and to the central location of the site within the basin, which enhances its function as a receptor of wood-burning emissions.

Heavy oil combustion contributed 0.6–2.0 μg m$^{-3}$ of PM$_{2.5}$ at the two sites. Results of PM$_{2.5}$ source apportionment for multiple locations in central Athens, conducted over 10 years prior to this study, had attributed almost 2 μg m$^{-3}$ of PM$_{2.5}$ to oil combustion emissions related to shipping (Iliaçqua et al., 2007). It appears that up to 2012, the gradual increase of shipping activity in the port of Piraeus had not yet manifested itself in terms of increased PM$_{2.5}$ pollution over Athens.

Vehicular direct emissions of coarse particles were estimated to account for 21–29% of average concentrations, with contributions of 2.5–7.1 μg m$^{-3}$ at the urban background and traffic sites, respectively. These particles, based on the source profile, appear to be principally non-exhaust. Up to 8% of coarse total mass has been attributed in the past to vehicular exhaust emissions for background locations in Athens (Karanasiou et al., 2009). The estimated levels for the background site are noteworthy and supported by relevant findings of Sturtz et al. (2014), who reported average contributions of non-exhaust emissions to coarse particles ranging between 1.4–2.2 μg m$^{-3}$, for multiple residential locations in US cities experiencing much lower PM$_{10,2.5}$ levels. Similar contributions of traffic to coarse particle mass have been reported for urban background locations in Europe (Amato et al., 2009). The large roadside increment of 4.6 μg m$^{-3}$ from vehicular emissions in coarse mass is in line with the roadside enhancement of non-resuspended coarse particles from tire and break wear estimated by Harrison et al. (2012).

Road dust at the background site contributes 3.1 μg m$^{-3}$, which corresponds to roughly one-fourth of PM$_{10,2.5}$. Being comparable to reported contributions of 2.6–3.0 μg m$^{-3}$ at urban/suburban background sites in Athens (Diaipouli et al., 2017), this value is considerable, given the distance of the sampling location from major roads. Along with the estimated concentration at the traffic site, where it is the primary coarse particle contributor, it is indicated that road dust resuspension is an important process for the entire study area. Kassomenos et al. (2012) have estimated the total wind-resuspended component of coarse particles in Athens and reported values of 10–14% for background and traffic locations. In view of larger contributions estimated here for the resuspended road dust factors (26–30%), it is assumed that road dust resuspension is, in a substantial part, traffic-induced.

The mineral dust factor, which represents the combined natural processes of soil resuspension and long-range dust transport, accounted for 25–33% of PM$_{10,2.5}$ at the two sites. Respective contributions for the fine fraction were considerably lower (6–7%). Estimated average concentrations, although largely contingent on the frequency and intensity of dust transport events, are in good agreement with values reported for mineral dust contribution in PM$_{10}$ in central Athens (Chalbot et al., 2014) and in coarse mass for the regional background of Southern Greece (Koulouri et al., 2008). The input of marine aerosols in annual average PM$_{10}$ in Athens appears not to exceed 5 μg m$^{-3}$, however, this is applicable only for the inner part of the basin, as for coastal Mediterranean locations expected contributions are much larger (Kocak et al., 2009).

### Spatial Variability of Source Contributions

Values of mean traffic/background ratios, squared correlation coefficients and coefficients of divergence, calculated for source contributions, are summarized in Table 3. The analysis is performed separately for days with prevalent winds, blowing from the SW–NW directions, thus arriving at the background site from the city center. Higher contributions were recorded at the traffic site for all identified sources, a result that in the case of non-traffic related sources should be mainly attributed to ventilation conditions of the measurement location (Dall’Osto et al., 2013), which at POL are largely improved. The traffic site, under northern winds, which normally have a clearing effect in the area, may come under the influence of canyon-type wind circulations and experience poor wind dilution (Chaloulakou et al., 2005).

In PM$_{2.5}$, contributions of the regional factor were highly correlated among sites and recorded the lowest CoD values among sources, indicating its effectiveness over the entire study area (Lee and Hopke, 2006). It is noted that the CoD value was higher than the one calculated for S individually, reflecting the broader characterization of the factor as representative of secondary aerosols, rather than of secondary sulfate. For road traffic particles, large roadside enhancements (Minguillon et al., 2014) and CoD values were recorded, together with strong correlations. The similarity of temporal traffic patterns has been identified as a primary cause of inter-site correlations between sites of different characterization. (Grivas et al., 2008). However, higher correlations and lower enhancements under winds from the city center towards the background site suggest small-scale transport within the area (Turner and Allen 2008). On the contrary, the biomass burning factor was largely uncorrelated among sites, with large CoD values.

Results were stable if the cold period was examined separately. It appears that during the study period, when wintertime wood-burning had not reached its current
Table 3. Squared correlation coefficients ($r^2$) and coefficients of divergence (CoD) between the two sites and traffic/background mean ratios for source contributions. Displaying values for the whole study period and separately for winds* arriving at the urban background site from the city center.

<table>
<thead>
<tr>
<th></th>
<th>Full Period ($n = 82$)</th>
<th>Days with prevailing winds from the SW–NW* ($n = 22$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>CoD</td>
</tr>
<tr>
<td>PM$_{10.2.5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Road Traffic</td>
<td>0.45</td>
<td>0.58</td>
</tr>
<tr>
<td>Regional</td>
<td>0.60</td>
<td>0.34</td>
</tr>
<tr>
<td>Biomass Burning</td>
<td>0.10</td>
<td>0.61</td>
</tr>
<tr>
<td>Oil Combustion</td>
<td>0.52</td>
<td>0.55</td>
</tr>
<tr>
<td>Mineral Dust</td>
<td>0.54</td>
<td>0.48</td>
</tr>
<tr>
<td>Sea Salt</td>
<td>0.17</td>
<td>0.79</td>
</tr>
<tr>
<td>Vehicular</td>
<td>0.32</td>
<td>0.56</td>
</tr>
<tr>
<td>Road Dust</td>
<td>0.05</td>
<td>0.58</td>
</tr>
<tr>
<td>Mineral Dust</td>
<td>0.61</td>
<td>0.50</td>
</tr>
<tr>
<td>Sea Salt</td>
<td>0.64</td>
<td>0.66</td>
</tr>
</tbody>
</table>

* excluding days with average wind speeds below 1 m s$^{-1}$.

proportions, locality of wood-smoke emissions could induce large spatial heterogeneity (Kim and Hopke, 2008).

In the coarse fraction, the vehicular factor displayed inter-site variability comparable to the road factor for PM$_{2.5}$, with the significant correlation (Hwang et al., 2008) being attributed to common driving cycles on a day-to-day basis. The road dust factor presents strong locality and was found to be spatially uncorrelated. On the other hand, mineral dust exhibited a higher degree of uniformity (Gildemeister et al., 2007), which indicated both the influence of dust transport on the entire area of Athens, as well as common soil resuspension processes. The sea salt factor exhibited increased homogeneity of levels under wind directions inclusive of the SW–W range, which is associated with transport of marine aerosols.

Overall, it is noted that, in spite of increased correlation, CoD values indicated substantial deviation from spatial uniformity (Qadir et al., 2014) and were also higher than calculated values for respective indicative species (e.g., S, V, eBC). This fact, aside from the different characterization and location characteristics of the two sites reflects also the complexity in physicochemical processes taking place between source and receptor sites. These findings regarding temporal covariance and heterogeneity of absolute levels are considered of importance for the utilization of source apportionment data in health studies and for the exposure misclassification error related to study design.

CONCLUSIONS

To identify the sources of and quantify their contributions to the fine and coarse fractions, PM$_{10}$ and PM$_{2.5}$ ambient samples were collected at a roadside traffic and an urban background site over the period of a year and analyzed for elemental composition and light-absorbing carbon.

Size-specific temporal covariance and spatial heterogeneity of elemental concentrations, characteristic of urban Mediterranean areas, present a challenge in source-apportionment studies. Moreover, the emergence of intense wood burning as a means for residential heating is introducing an additional aspect in the particle-pollution problem in the area. Wintertime biomass burning, during the past five years, has rapidly evolved into a major environmental concern for the area. The necessity of accurate identification and quantification of its impact on pollutant concentrations, characterizing specific tracers from long-term measurements with high temporal resolution, has been recognized. Automotive wear particles play an important role in the observed spatial heterogeneity, accounting for large roadside increments. This enhancement, which was detected in the fine mode as well, can be much strengthened in the street configurations of densely populated residential areas. Given the toxicity and redox activity of traffic-related abrasion species, there is an increased health risk for inner-city inhabitants.

Separate PMF models were run for the fine and coarse fractions at each site. Since factors with similar characterization were extracted for both sites, it appears that in cases similar to Athens, where point sources are relatively absent and vehicular traffic is a ubiquitous influence on air pollution, the use of combined datasets for traffic/background sites could be attempted.

Over one fifth of the particle mass was attributed to vehicular emissions in both size fractions at the urban background site. Taking into account the site location and associated low PM levels, this is considered to represent the lower threshold of vehicular contributions within the urban zone in Athens. The strong inter-site correlations for road-traffic contributions and the observed intra-urban transport of traffic-emitted particles indicate the potential effectiveness of traffic-emission control measures on an extended spatial scale. It also appears that shipping operations in the port of Piraeus remain—in view of a waning industrial sector—the principal localized productive activity of relevance for particle levels, in the inner part of the Athens basin. However, source-apportionment data in the direct
vicinity of the port and industrial zones (Kara et al., 2015) are necessary to better characterize near-source exposures.

Natural sources contribute 8–13 μg m−3 (25–32%) of combined fine and coarse mass on an annual basis, posing a major obstacle to compliance with air-quality standards. The significant additional inputs of regional and transboundary anthropogenic emissions further hinder the efficacy of local control policies. Road-dust contributions were uncorrelated among the sites, indicating the local nature of these emissions. It appears that active mitigation measures, such as street washing (Karanasiou et al., 2014), which can have a significant bearing on coarse particle concentrations, should be undertaken on an extensive scale to leave a mark, and their cost-effectiveness should be examined.

Despite the absence of organic carbon, ammonium and nitrate concentration data, the models successfully reconstructed the actual mass, with $r^2$ values over 0.85 and slopes over 0.9 in all cases. While organic matter and nitrate concentrations can be partially represented by road traffic and regional factors, it is recognized that a full speciation dataset could enable the differentiation between secondary processes evolving on local and broader spatial scales. The sample size here was deemed adequate to provide an average representation of levels on an annual basis and to facilitate PMF source apportionment; however, a better association of the sources with short-term exposure would necessitate taking into account the day-to-day and intra-day variability of source contributions.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES


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Sciare, J., Oikonomou, K., Favez, O., Liakakou, E.,


