



Spatial attribution of sulfate and dust aerosol sources in an urban area using receptor modeling coupled with Lagrangian trajectories

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ABSTRACT

PM₁₀ and PM_{2.5} (particles with diameter less than 10 µm and 2.5 µm, respectively) aerosol samples were collected from 2002 to 2004 in Athens, Greece and analyzed for elements ranging from Na to Pb using X–ray fluorescence. Positive matrix factorization (PMF) was applied to identify and quantify the types of PM₁₀ and PM_{2.5} sources. The agreement between calculated and measured particle mass concentrations was very good for both aerosol fractions. Mineral soil, road dust and sea salt particles were the most significant types of coarse particles (PM_{10–2.5}) while their contributions to PM_{2.5} fraction were minimal. Secondary sulfate, diesel particles from shipping and other oil combustion activities and primary traffic exhausts were determined as the most important types of PM_{2.5} sources. The analysis of normalized average air mass residence times showed weak seasonal patterns on the pathways of air masses prior to their arrival in Athens. Using trajectory regression analysis, the four adjacent regions (less than 500 km) accounted for the largest fraction of fine sulfate and diesel particles. On the contrary, shipping emissions and neutralization by sea salt may explain the high contributions of the regions covering the Mediterranean Sea and Dardanelle straights. The four adjacent regions and central Europe accounted for most of road and mineral dust particles. The transport from northern Africa over Mediterranean Sea also appeared to influence the mineral dust particles.

Keywords: Road dust, sea salt, shipping emissions, trajectories, Mediterranean Sea



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1. Introduction

Exposure to particulate matter has been linked to cardiovascular and respiratory morbidity and mortality (Katsouyanni et al., 2001; Pope et al., 2002; Lippmann et al., 2006); however, particle mass cannot fully account for the observed effects. In a recent study, Zhou et al. (2011) found that wintertime biomass burning, traffic and oil residues particulate components were associated with increased cardiovascular mortality in Seattle, while summertime secondary aerosol and traffic were the most important determinants in Detroit. For comparison, the annual mean PM_{2.5} mass in Detroit was 35% higher than that measured in Seattle and above the national ambient air quality standard. In the RUIOH (Relationship between Ultrafine and fine Particulate matter in Indoor and Outdoor air and respiratory Health) study, the relationships among ambient, residential outdoor and indoor PM₁₀ mass, PM_{2.5} mass, particle number concentrations and the respiratory health (i.e. respiratory symptoms, activities, spirometry, exhaled breath condensate) of asthmatic and chronic obstructive pulmonary disease (COPD) patients in four European urban areas (Amsterdam, Athens, Birmingham and Helsinki) representing different mixtures and sources of aerosol were examined. The exhaled breath condensate nitrate levels (an indicator of oxidative stress) were highly correlated with coarse particle mass rather than fine or ultrafine particles (Manney et al., 2012). In addition, an increase of 10 µg m⁻³ of PM_{10–2.5} mass concentrations was associated with an increase of up to 0.7% in shortness of breath, wheezing, cough and limitation in walking (Karakatsani et al.,

2012). The effects were stronger in Athens, Greece than those computed for Amsterdam, Birmingham and Helsinki.

PM₁₀ particles in Athens, Greece are almost equally composed of coarse and fine particles with elemental carbon (a tracer of traffic exhausts), secondary sulfate and nitrate being the most important components of PM_{2.5} aerosol (Lianou et al., 2011; Theodosi et al., 2011). Traffic and the location of the residence (center/suburban) were the most important determinants of the measured outdoor and indoor particulate matter (Lianou et al., 2007; Hoek et al., 2008). Evaporative fugitive emissions and traffic were also the most important sources of particulate polycyclic aromatic hydrocarbons (PAHs) (Chalbot et al., 2012; Gini et al., 2013). The high content of coarse particle was primarily attributed to soil dust (Karanasiou et al., 2009). Sea salt particles were also observed in Eastern Mediterranean Sea (Im et al., 2011). Despite that the emissions of particulate matter precursors decreased by 10% for NH₃, 26% for NO_x and 54% for SO₂ between 2001 and 2010, PM₁₀ levels decreased by less than 3% (1 µg m⁻³) and PM_{2.5} (2005–2010) levels did not change at all. This discrepancy (between emissions reductions and ambient levels) was attributed to inter–annual changes of atmospheric conditions and transport patterns as well as incomplete understanding and high uncertainties of the primary emissions of particles (EEA, 2012). The highest PM₁₀ and PM_{2.5} concentrations over the 2001–2010 period were measured in southern/east and central Europe with daily levels being regularly above the daily limit values for the protection of public health. The observed trends were comparable to those observed in four European urban areas including Athens,

Amsterdam, Birmingham and Helsinki during the 2002–2004 period (Lianou et al., 2011). In a recent study, we showed that sources within Greece were the most significant determinants of PM_{2.5} levels, while a mixture and local sources and transport from Africa explained the majority of coarse particles (Kavouras et al., 2013).

The source apportionment of PM₁₀ and PM_{2.5} in Athens, Greece based on chemical speciation analysis of a subset of samples collected during the RUIOH study is presented here. The specific objectives were: (i) to identify and estimate the contributions of sources to PM₁₀ and PM_{2.5} in Athens, Greece using positive matrix factorization (PMF); and (ii) to assess the impacts of specific regions to PM₁₀ and PM_{2.5} source contributions using the Tracer Mass Balance (TrMB) model (Ashbaugh et al., 1985; Pitchford and Pitchford, 1985). The TrMB model was used to examine the regional contributions to particle mass and specific chemical components in urban, continental background and remote environments (Gebhart et al., 2001; Gebhart et al., 2006; Xu et al., 2006; Huang et al., 2010; Chalbot et al., 2013). While, the TrMB model was applied only for the days in which PM₁₀ and PM_{2.5} chemical speciation data were obtained, this analysis examined the influences of geographic regions to specific sources of particulate matter. The spatial extend and characteristics of the regions were identical to those reported in Kavouras et al. (2013) to enable comparison between regional contributions to particle mass and specific types of aerosol and sources.

2. Methods

The number of sources and their contributions on daily PM₁₀ and PM_{2.5} mass were obtained in the source apportionment part of this study. During the second part (i.e. trajectories regression analysis), the influences of specific geographic regions on daily PM₁₀ and PM_{2.5} source contributions were determined. The details of each method are presented below.

2.1. Source apportionment

PM₁₀ and PM_{2.5} aerosol samples were collected at an urban background site in Athens, Greece (Latitude: 37°59'04", Longitude: 23°46'04") from October 2002 to September 2004 (Lianou et al., 2007; Lianou et al., 2011). Sampling was done daily (noon to noon) using Harvard impactors operating at 10 L min⁻¹ on Teflon filters (Marple et al., 1987). Particle mass was determined gravimetrically. The absorbance of PM_{2.5} samples (surrogate of elemental carbon, a tracer of traffic) was measured using smoke-stain reflectometers (Puustinen et al., 2007). In addition, particle number concentration (PNC) was measured using condensation particle counters (TSI 3022A, TSI, St. Paul, MN, USA). A subset of 97 paired PM₁₀ and PM_{2.5} samples was analyzed for elements (from Na to U) by X-ray fluorescence and included in the PMF analysis. Only elements with more than 50% of valid measurements (i.e. above the limit of detection) were included in the source apportionment analysis.

We performed source apportionment analysis for both PM₁₀ and PM_{2.5} samples using the U.S. Environmental Protection Agency's (EPA) Positive Matrix Factorization (PMF) model (Version 3.0). Missing concentration and uncertainty values are not allowed in PMF analysis. For these elements, missing concentration data were replaced by the geometric mean of the measured concentrations. The uncertainties of missing values were substituted by four times the geometric mean of measured uncertainties to reduce the effect of the individual data points on the PMF model (Polissar et al., 1996). The concentrations of *m*-aerosol species for *n*-sampling days were analyzed by a least-squares method by considering that factor contributions $[G(nxp)]$ and profiles $[F(pxm)]$ were not negative [Equation (1)] during the minimization of the objective function $[Q$ in Equation (2)] (where *p* was the number of factors) (Paatero and Tapper, 1994; Paatero, 1997).

$$X(nxm) = G(nxp)xF(pxm) + E(nxm) \quad (1)$$

and

$$Q = \sum_i^n \sum_{k=1}^m \left[\frac{x_{ik} - \sum_{k=1}^n (g_{ik}x_{f_{kj}})}{\sigma_{ij}} \right] \quad (2)$$

where $E(nxm)$ was the residual component, x_{ij} and σ_{ij} were the concentration and associated uncertainty of *j*-species in *i*-sample, g_{ik} was the contribution of the *k*-factor to particle mass in *i*-sample and f_{kj} was the mass fraction of *j*-species on *k*-factor. The F_{peak} parameter introduced rotation to the resolved factors and removed the remaining ambiguity of the unrotated solution. The optimum number of factors and the rotation was evaluated by a set of statistical tools (Paatero et al., 2002; Paatero et al., 2005). It was selected on trial and error analysis of the solutions by the user and by comparison of the factor profiles with previous profiles of particle sources. Based on these similarities, factors were attributed to aerosol sources and/or types. We run the model in the robust method for factors varying from 2 to 20 with an $\alpha=4.0$ using the error model “-12” (that uses observed values) and 25 runs per configuration. Bootstrapping configuration included 500 bootstrap runs using a minimum *R* of 0.75 and block size of 6. The residuals of individual chemical species followed a normal distribution between -3 and +3. More than 95% of bootstrapped factors were mapped into the base factors, with no clear pattern for the unmapped factors. The Q_{robust} (runs without the outliers) was within 10% of Q_{true} (runs with outliers) and comparable to $Q_{theoretical}$, which was related to the size of the datasets (97x23=2 231), indicating that the selected PMF models fitted the outliers. A six factor model with a rotation with $F_{peak}=-0.1$ was selected for PM₁₀ and a four factor model with a rotation with $F_{peak}=-0.1$ was selected for PM_{2.5}.

2.2. Trajectories regression analysis

Air mass backward trajectories at starting height of 500 m with a resolution of one hour and going back five days were generated every hour from September 2002 to December 2004 using the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model and hemispheric Global Data Assimilation System (GDAS) meteorological fields as inputs (Draxler, 2007). The starting point of 500 m was within the boundary layer in Athens (Kallos et al., 2007). For each day, 2 880 trajectory points were generated (24 back trajectories per day x 5 days backward in time x 24 hours per day).

The residence time ($t_{(0,i)}$, in hours) defined as the time that an air mass spent over 0.5°x 0.5° cells (i.e. number of hourly trajectory points) was computed and summed over fifteen pre-defined regions (Figure 1) for each measurement day from noon to noon to overlap with aerosol sampling, in ArcInfo (ESRI Inc. Version 10.0) (Poirot and Wishinski, 1986). The regions were: (1) North Atlantic Ocean including Iceland and Ireland; (2) Nordic countries and northern Baltic Sea; (3) Russia; (4) Western Europe; (5) Central Europe including Ukraine; (6) Atlantic ocean; (7) Western Mediterranean sea including central/south Italy, Iberian Peninsula and northern parts of Tunisia and Algeria; (9) Northwest (NW: central and western Greece, Albania and Skopje); (10) Turkey including Black Sea; Northeast (NE: northern Aegean sea, Macedonia, Thrace, Bulgaria and Dardanelle straits); (11) Southeast (SE: southern Aegean sea); (12) Southwest (SW: Peloponnesus); (13) Western Africa; (14) Libya and Egypt; and (15) Middle East.

The relationship between the PM₁₀ and PM_{2.5} source contributions and the residence time over the pre-defined regions were assessed using the Tracer Mass Balance regression model (Pitchford and Pitchford, 1985; Xu et al., 2006; Chalbot et al., 2013; Kavouras et al., 2013). The percent attributions using the TrMB model of perfluorocarbon tracers released from specific regions

and monitored were within 5 percent of the total measured concentrations in 24 receptor sites during the Big Bend study (Green et al., 2003).

$$[Y]_j = \sum_{i=1}^n ((t_{0,i})_{ij} \cdot \beta_i) + \varepsilon_j \quad (3)$$

where $[Y]_j$ are the source contributions to PM_{10} and $PM_{2.5}$ mass at the receptor site on j -day (obtained from source apportionment analysis), $t_{(0,i)}$ is the residence time for all air parcels arriving at the receptor site over region i on j -day, β_i is the regression coefficient of region i (output of the regression analysis), and ε_j is the residual on j -day. The regression coefficient is related to the product of the emissions from the geographical region (Q), the transformation (i.e. chemical aging), diffusion and deposition factor during transport from the geographical region to the receptor site (T), and the entrainment factor to describe for disassociation between the back trajectories and the transport of particles (E) ($\beta_i = QTE$). The TrMB model sets the intercept at zero, forcing all identified source regions to account for the measured concentrations at the receptor site (Xu et al., 2006; Chalbot et al., 2013).

Because of the possible inter-variable relationships, variable screening methods (VSM), including stepwise (both forward and backward), procedures were used. Stepwise regression proceeds through all-possible one-variable models for selected independent variables using the t -test to examine the null hypothesis for specified significance levels. The variance inflation factor (VIR) (with threshold value for inclusion <10) was also used to identify the correlation between two or more independent variables by increasing the probability of rounding errors in the calculation of

regression coefficients and by affecting the signs of the regression coefficients. The percentage of the root mean square error (%RMSE) was used to measure the residual differences between measured values and predicted values by the TrMB model. Regression analysis was done using SPSS (IBM Inc., Version 20.0) and OriginPro (Version 8.6.0).

3. Results and Discussion

3.1. Source apportionment of PM_{10} and $PM_{2.5}$

This section presents the outcomes of the source apportionment using PMF. A total of six and four factors were retained for PM_{10} and $PM_{2.5}$, respectively, and attributed to specific sources of particulate matter based on the loadings of individual chemical species. We used Al, Si and Ca as tracers of soil particles, Na and Cl for primary sea salt particles, Ni and V for oil combustion, S for secondary sulfate, and fine particle absorbance and bromine for vehicular emissions (Kavouras et al., 2001; Karanasiou et al., 2009). Leaded gasoline is not currently used; however, six of the remaining eleven countries that still use leaded gasoline (Skopje, Serbia, Montenegro, Libya, Egypt and Iraq) are located within the geographical domain of the study. In addition, lead may be emitted from oil and coal combustion sources. Table 1 shows the mean contribution (in $\mu\text{g m}^{-3}$) for each source to PM_{10} , $PM_{2.5}$ and particle number concentration. Figure 2 shows the profiles of the four factors for both PM_{10} and $PM_{2.5}$ (a–d) and the two remaining PM_{10} factors (e). More than 95% of measured PM_{10} and $PM_{2.5}$ mass were explained by these factors (Table 1). Table 2 shows the elemental ratios calculated for PM_{10} aerosol sources based on the profiles of resolved factors.

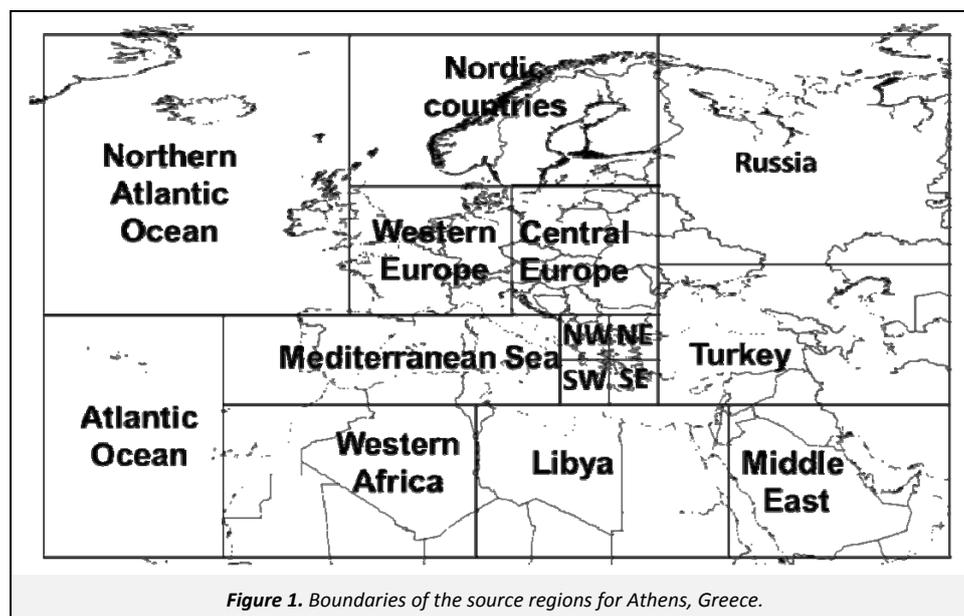


Table 1. Source contributions (mean±standard error) to PM_{10} , $PM_{2.5}$ and particle number concentration

Source	PM_{10} ($\mu\text{g m}^{-3}$)	$PM_{2.5}$ ($\mu\text{g m}^{-3}$)	Particle number (part cm^{-3})
Traffic emissions	5.9±0.5	6.4±0.6	16 001±4 120
Secondary sulfate	12.1±0.9	8.5±1.0	1 075±253
Diesel emissions	7.6±0.8	5.8±0.7	3 913±127
Mineral dust	10.2±1.1	1.8±0.2	321±126
Ca-rich dust	13.9±1.4		
Sea salt	3.9±0.7		
Reconstructed mass	53.7±2.1	22.6±1.4	21 500±4 138
Measured mass	54.3±2.3	24.4±1.3	22 700±1 325
% RMSE	0.9±1.4	3.7±4.5	5.0±1.7

Table 2. Elemental ratios (mean±standard error) of PM₁₀ aerosol sources

Source	Mineral dust	Road dust	Diesel emissions	Secondary sulfate	Traffic emissions
Ca/Al	4.07±1.49	15.17±2.17			
Fe/Ca	0.23±0.06	0.23±0.08			
K/Ca	0.08±0.01	0.04±0.01			
Si/Al	2.09±0.80	2.11±0.75			
Ni/V			0.30±0.03	0.40±0.04	0.34±0.06
Br/Pb				0.04±0.04	0.34±0.05

There were significant similarities between the profiles of four factors for PM₁₀ and the four retained factors for PM_{2.5} especially for factors 1 and 2. The differences for factors 3 and 4 were associated with elements of natural origin (Al, Si, Ca, Mg and Cl) that are typically accumulated in the coarse fraction. Factor 1 showed strong associations with fine particle absorbance (a surrogate of elemental carbon), S and heavy metals (Cu and Zn), typically found in automobile exhausts and was attributed to traffic emissions (Lough et al., 2005). Minor quantities of soil elements (Al, Si, Ca and Fe) were also observed in the profile of PM_{2.5} particles suggesting a small fraction of road dust. It accounted for 5.9±0.5 μg m⁻³ of PM₁₀ mass and 6.4±0.6 μg m⁻³ of PM_{2.5} mass.

The third factor showed strong contributions from S, Ni, V, Fe and other heavy metals and was attributed to diesel particulate emissions. Shipping emissions may be included and exceeded contributions from other industrial sources because of the use of low-quality oil, containing high amounts of sulfur and Ni/V-rich porphyrins (Viana et al., 2009; Pandolfi et al., 2011). The contributions to PM₁₀ and PM_{2.5} were 7.6±0.8 and 5.8±0.7 μg m⁻³, respectively. The high concentrations of Al, Si, Ca, Fe and Ti on the fourth factor indicated the presence of mineral dust. Soil particles typically concentrate into the coarse fraction and only a fraction of them (5–10%) may be present in PM_{2.5}. The contributions of soil minerals were 10.2±1.1 μg m⁻³ for PM₁₀ and only 1.8±0.2 μg m⁻³ for PM_{2.5}.

The fifth factor for PM₁₀ showed strong contributions from Ca and soil minerals as well as heavy metals (Mg, Mn, Cr, Cu, Zn, Ba and Pb). The values of elemental concentration ratios (Ca/Al=15.17±2.17, K/Ca=0.04±0.01; Table 2) were comparable to those observed for roadway dust in Palermo, Italy (Ca/Al=15.28, K/Ca=0.02), a region with similar geological characteristics to Athens, Greece (Varrica et al., 2003). For comparison, the values of these ratios for the mineral dust factor were 4.07±1.49 and 0.08±0.01 (Table 2). For Sahara dust, Ca/Al ratio varied from 0.20 to 0.37 and the K/Ca from 0.73 to 1.50 (Blanco et al., 2003). As a result, this factor was assigned to calcium-rich road dust. It was the largest source of PM₁₀ mass accounting for 13.9 μg m⁻³. The sixth factor demonstrated high loading of Na, Cl and Mg and it was assigned to sea salt particles. This source contributed 3.9±0.7 μg m⁻³ on PM₁₀ mass.

In this study, we did not measure elemental carbon (EC) and organic carbon (OC) because the filter medium (i.e. Teflon) was not compatible with the thermal analysis. However, filter absorbance was used as a surrogate of elemental carbon. Lianou et al. (2011) estimated that the mean EC concentration in Athens during the measurement period was 2.8 μg m⁻³, which was comparable to those measured in Athens downtown sites (Grivas et al., 2012). Assuming an OC/EC ratio of 2.92 (Remoundaki et al., 2013), OC may be accounted for 8.2 μg m⁻³, representing approximately 30% of PM_{2.5} mass. The absence of OC measurements had a negligible (if any) effect on the outcomes of PMF analysis, because of the excellent agreement between measured and estimated PM_{2.5} mass. This was due to the fact that OC is typically emitted from many sources along with other chemical species, with some of them being specific tracers (e.g. Ni and V) of particle sources.

The results of PMF analysis were further evaluated against the concentrations of major aerosol types for secondary sulfate, mineral dust and sea salt using the Interagency Monitoring of Protected Visual Environments (IMPROVE) PM_{2.5} mass reconstruction schemes (Sisler, 2000; White, 2008). For PM_{2.5}, the IMPROVE-reconstructed sulfate concentration was 7.9 μg m⁻³ (assuming neutralization by NH₄⁺), as compared to 8.5 μg m⁻³ using the PMF model. For mineral dust, the IMPROVE reconstructed mass was comparable (1.8 μg m⁻³) to that computed in the PMF analysis. In the PM₁₀ fraction, secondary sulfate and sea-salt mass using the IMPROVE reconstruction schemes were 12.3 and 2.3 μg m⁻³ indicating a very good agreement with the PMF results. For mineral particles, the IMPROVE-reconstructed mass was 16.9 μg m⁻³ as

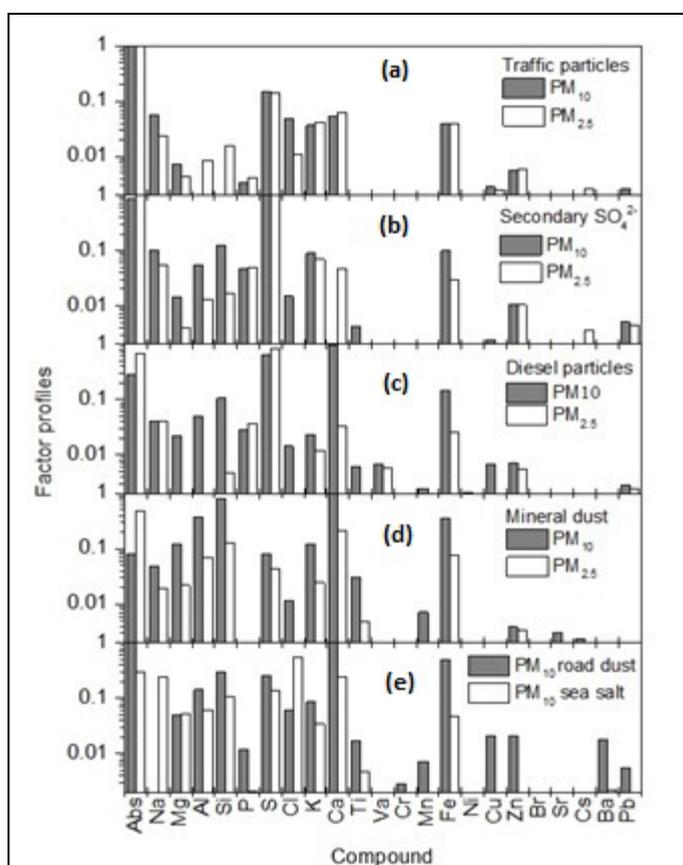


Figure 2. Profiles of (a) traffic particles; (b) secondary sulfate; (c) diesel particles; (d) mineral dust; (e) Ca-rich road dust and sea salt in Athens, Greece.

The second factor was attributed to secondary sulfate aerosol. Sulfate aerosols were typically associated with the oxidation of SO₂ emissions from oil processing and combustion and coal-fired power plants and accumulate in the PM_{2.5} fraction (Karamchandani and Seigneur, 1999). This source accounted for 12.1±0.9 μg m⁻³ of PM₁₀ mass and 8.5±1.0 μg m⁻³ of PM_{2.5} mass. The difference in the contributions may be attributed to the neutralization of sulfuric acid by minerals (Ca, Mg, Na) present in the coarse mode during transport (Im et al., 2011).

compared to $10.2 \mu\text{g m}^{-3}$ computed using the PMF analysis. This discrepancy may be due to increase calcium levels from road dust.

The four retained $\text{PM}_{2.5}$ factors also reconstructed about 95% of measured particle number concentration (PNC) (Table 1). Traffic was the predominant contributor of ultrafine particles accounting for $16\,001 \pm 4\,120 \text{ part cm}^{-3}$ (two thirds of measured PNC). Diesel emissions contributed $3\,913 \pm 127 \text{ part cm}^{-3}$ followed by secondary sulfate ($1\,075 \pm 253 \text{ part cm}^{-3}$). Lianou et al. (2007; 2011) indicated the significance of traffic on PNC in Athens (and other European urban areas) based on the daily patterns of PNC in multiple locations. The observed strong contributions of traffic and diesel emissions on PNC confirmed the primary origin of ultrafine particles as compared to secondary particles in urban areas.

3.2. Regional contributions

Kavouras et al. (2013) showed that up to 40% of fine and particle mass originated from regions more than 500 km away from Athens. Here, we examined the regional inputs to the most important sources of PM_{10} and $\text{PM}_{2.5}$ using the same approach. Initially, we computed the residence time of air masses for different seasons to determine the role of weather synoptic patterns. Figure 3 shows the normalized residence time of air mass trajectories arriving in Athens in spring (a), summer (b), fall (c), and winter (d). In all cases, air masses spent most of their time over the Balkans and the Aegean Sea. They arrived from the northeast through the Dardanelles Straits, northwest Italy and the Adriatic Sea and from the south. In spring, fall and winter, air masses also originated from northern Africa. These similar patterns indicated the influence of the same source regions throughout the year.

Secondly, we calculated the mean (\pm standard error) contributions of source regions (see Figure 1) to fine and coarse (sulfate+diesel) particles and mineral and road dust particles (Figure 4a and 4b). The areas with the highest five contributions to fine sulfate were northwest Greece including Albania and Skopje, the two adjacent sectors to the south (SE and SW), the North Atlantic Ocean and western Europe. Local regions contributed $6.2 \mu\text{g m}^{-3}$ (44.8%) of fine sulfate and diesel particles. The 2007 SO_2 emissions in Greece were 543.1 Gg, the 6th highest among European Union. The increase of 10% of SO_2 emissions since 1990 indicated that there were no important changes during the 2002–2004 monitoring period. More than 90% of these emissions were from the electric power plants using lignite [7 with a total capacity of more

than 3 500 MW (more than 80% of total capacity)] and oil (6 plants). Minor quantities were from Turkey and Russia. The influence of western Europe and the Atlantic ocean was consistent with previous studies showing the transport of secondary sulfate from industrialized centers in western Europe and eastern US (Sciare et al., 2003). Interestingly, the contributions of the five aforementioned regions to coarse sulfate and diesel particles were negligible. The four regions with statistically significant contributions to coarse sulfate included the two marine regions with high density of marine traffic, northeast Greece (Dardanelle Straits) and the Mediterranean Sea, central Europe and Turkey. The two adjacent northern regions added $3.0 \mu\text{g m}^{-3}$ (52%) of coarse sulfate and diesel particles. The high loadings of crustal elements and Mg to sulfate and diesel particles (Figure 2) indicated the neutralization of sulfuric acid by mineral and sea salts. These results are consistent with those observed for $\text{PM}_{2.5}$ and $\text{PM}_{10-2.5}$ particle mass concentrations (Kavouras et al., 2013).

For calcium-rich road dust, the three adjacent regions (NE, NW and SW covering continental Greece), Turkey added $9.0 \mu\text{g m}^{-3}$ (~67%) of contaminated road dust particles. These areas encompassed several large urban areas in countries with prolonged periods of dry conditions (Greece and Turkey), extended networks of busy unpaved roads (Albania, Skopje). Central Europe added $2.4 \mu\text{g m}^{-3}$, which may be due to the intense use of sand and salt to mitigate the effects of road icing and winter storms (central Europe) (Meanhaut et al., 2005; Arsene et al., 2011). The possible influence of coarse particles emitted from sources in central and eastern Europe at receptor sites in southern Europe was identified in previous studies (Ladstaetter–Weissenmayer et al., 2007; Sprovieri et al., 2011; Masiol et al., 2012; Kavouras et al., 2013). About $1.5 \mu\text{g m}^{-3}$ of Ca-rich dust was also associated with eastern Libya (Benghazi) and the north of Atlantic Ocean.

The dominant source regions for mineral soil dust particles $8.3 \mu\text{g m}^{-3}$ (81.3%) were the Mediterranean Sea, including Tunisia and northern Algeria; Turkey; central Europe and north of Atlantic Ocean. The influence of the four adjacent sectors on mineral dust particles was reduced to $1.7 \mu\text{g m}^{-3}$ (16.5%). The net positive contributions of the northern Atlantic Ocean to dust particles cannot be attributed to any known sources. However, Prospero et al. (2012) recently observed that large quantities of dust events with concentrations as high as $20 \mu\text{g m}^{-3}$ may be released from Icelandic proglacial regions during the same monitoring period (2002–2004).

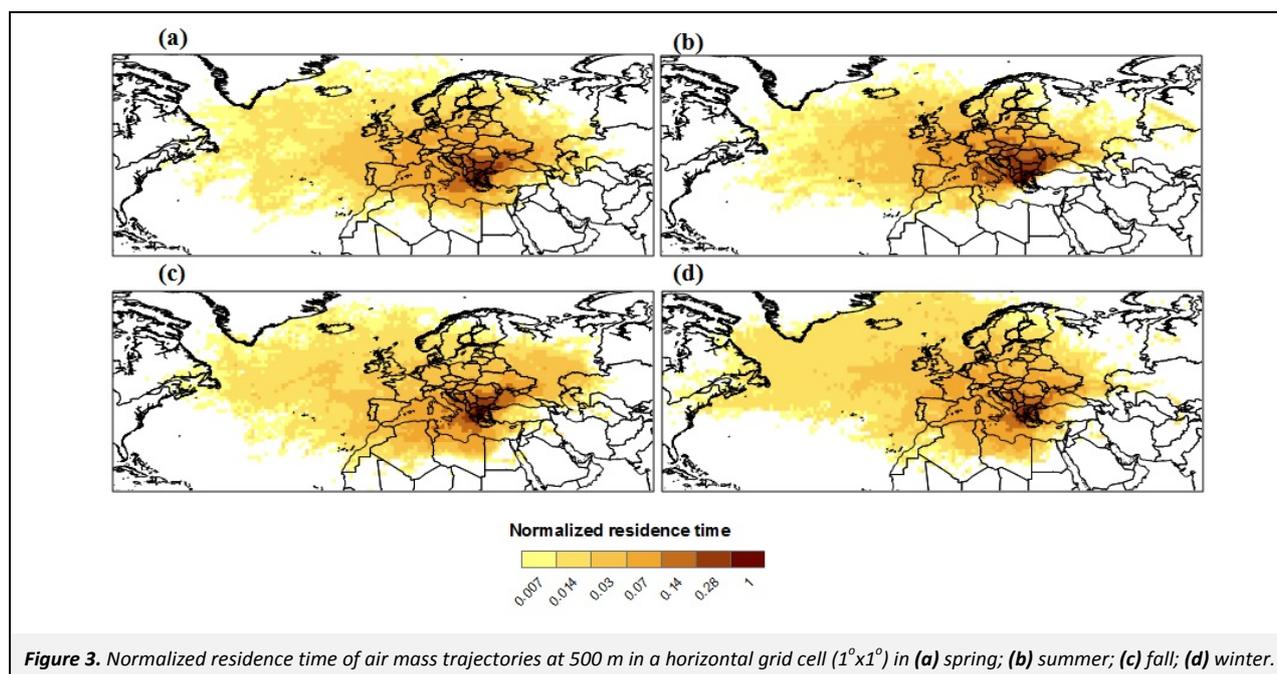
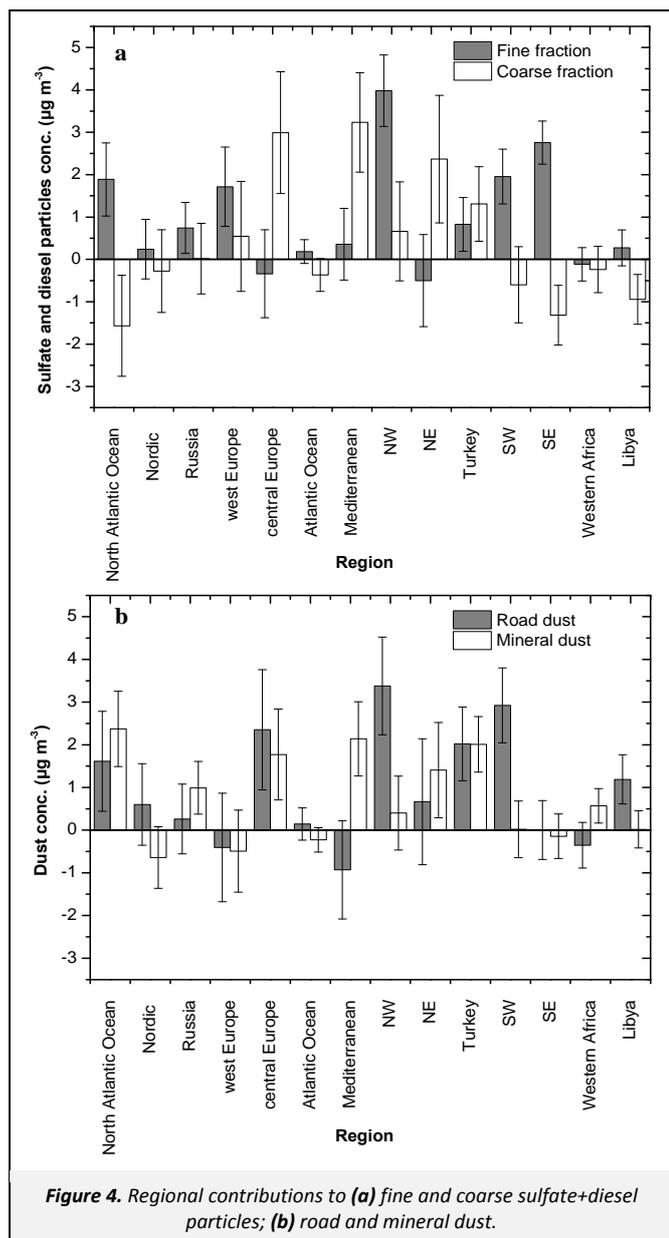


Figure 3. Normalized residence time of air mass trajectories at 500 m in a horizontal grid cell ($1^\circ \times 1^\circ$) in (a) spring; (b) summer; (c) fall; (d) winter.



4. Conclusions

The types of sources of PM_{10} and $PM_{2.5}$ particles in Athens, Greece were apportioned using positive matrix factorization. Secondary sulfate (37%), traffic exhausts (28%), shipping and oil combustion (25%) were the predominant sources of fine particles in Athens, Greece. Coarse particles were associated with mineral soil (32%), Ca-rich dust (44%) and sea spray (12%) aerosol. The contributions of geographical regions to sulfate, diesel, mineral dust and road dust particles were assessed by regression of the contributions of major sources against the residence time of air mass in nineteen pre-defined regions. The four regions adjacent to the receptor site accounted for the majority of fine sulfate and diesel particles. The two marine sectors covering the Mediterranean Sea with elevated marine traffic were responsible for most of the coarse secondary sulfate and diesel particles. Road dust was associated with the four adjacent sectors as well as Turkey and central Europe.

Through this analysis that incorporated positive matrix factorization and trajectory regression, the influence of local (i.e. traffic, road dust, power plants) and regional sources (i.e. shipping

emissions, transport from central/western Europe) on PM_{10} and $PM_{2.5}$ mass concentrations was identified and quantified. These results further underscore the immediate need to precisely characterize emissions of primary particles from fugitive sources such as road and windblown dust. This information is essential in future efforts to reduce levels of atmospheric aerosol and the overall burden of air pollution on diseases.

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