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Origin and source regions of PM₁₀ in the Eastern Mediterranean atmosphere

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ABSTRACT

A set of daily PM_{10} (n = 281) samples collected from April 2001 to April 2002 at a rural site (Erdemli), located on the coast of the Eastern Mediterranean, were analyzed applying Mass Closure (MC), absolute principal factor analysis (APFA) and Positive Matrix Factorization (PMF) to determine source contributions. The results from the three techniques were compared to identify the similarities and differences in the sources and source contributions. Source apportionment analysis indicated that PM_{10} were mainly originated from natural sources (sea salt + crustal $\approx 60\%$) whilst secondary aerosols and residual oil burning accounted for approximately 20% and 10% of the total PM_{10} mass, respectively. Calculations for sulfate showed that on average 8% and 12% of its total concentration were originated from sea salt and biogenic emissions, respectively. However, the contribution by biogenic emissions may reach up to a maximum of ~40% in the summer. Potential Source Contribution Function (PSCF) analysis for identification of source regions showed that the Saharan desert was the main source area for crustal components. For secondary aerosol components the analysis revealed one source region, (i.e. the south-Eastern Black Sea), whereas for residual oil, Western Europe and the western Balkans areas were found to be the main source regions.

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1. Introduction

Atmospheric aerosols (or particulate matter, PM) have the potential to play an important role in modifying and/or altering climate, hydrological cycles, chemistry of the atmosphere, biogeochemical cycles and public health (Mamane and Gottlieb, 1992; Lelieveld et al., 2002; Markaki et al., 2003; Carbo et al., 2005; Griffin et al., 2007). The PM₁₀ fraction of aerosols is defined as particles with diameters smaller than 10 µm. Owing to the potential adverse health and environmental impacts, legislation of the PM concentration limits has been established in many regions of the world including the European Union. The annual and daily $\ensuremath{\text{PM}_{10}}\xspace$ values have been limited to 40 $\mu g~m^{-3}$ and 50 $\mu g~m^{-3}$ (which may only be exceeded for 35 days), respectively while annual PM_{2.5} value has been limited to 17 $\mu g m^{-3}$ as addressed by Directive 2008/50/EC of the European Parliament and the Council of 21 May 2008 on ambient air quality and cleaner Europe.

Identification of the concentration, composition, origin, transport and geographical distribution of PM in Mediterranean atmosphere has been the subject of research activities since the last two decades as it is heavily affected by two contrasting sources; namely mineral dust (mainly from Sahara Desert) and various anthropogenic (from industrialized/semi-industrialized countries) emissions (Dulac et al., 1987; Kubilay and Saydam, 1995; Avila et al., 1998; Moulin et al., 1998). In recent years there has been an increasing number of studies published on PM₁₀ concentrations in the western Mediterranean (Artinano et al., 2001; Rodriguez et al., 2002; Querol et al., 2004; Salvador et al., 2004; Viana et al., 2008). These studies have evaluated the natural and anthropogenic contributions to ambient PM₁₀ in western Mediterranean atmosphere. The general findings may be summarized as follows: (a) PM₁₀ concentrations in the western Mediterranean atmosphere increase from rural to kerbside, (b) the contribution to PM₁₀ of anthropogenic sources decreases from urban/industrialized/kerbside sites towards rural sites, and (c) PM₁₀ levels observed both in rural and urban sites are considerably affected by high mineral dust

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concentrations during African dust outbreaks. However, only a limited number of studies have been conducted on PM_{10} concentrations in the Eastern Mediterranean atmosphere (Andreae et al., 2002; Kouyoumdjian and Saliba, 2005; Gerasopoulos et al., 2006; Koçak et al., 2007a,b). These studies indicate that PM_{10} levels at regional background sites within the boundary layer in the Eastern Mediterranean are mainly related to the proximity of sampling sites to arid regions (e.g. the Sahara Desert and the Middle East).

A number of approaches have been adopted including; Mass Closure, chemical mass balance, absolute principal factor analysis and Positive Matrix Factorization (Thurston and Spengler, 1985; Paatero and Tapper, 1994; Bardouki et al., 2003; Viana et al., 2008) to identify sources and their contributions to a complex mixture of soluble and insoluble species associated with aerosols. Coupled with source apportionment techniques air mass back trajectories have been used to deduce potential source regions of aerosols. For instance clustering of trajectories, residence time analysis and Potential Source Contribution Function techniques have been successfully applied in the field of atmospheric studies (Ashbaugh et al., 1985; Dorling et al., 1992; Brankov et al., 1998; Cape et al., 2000; Salvador et al., 2004; Güllü et al., 2005). However, in the Mediterranean region relatively limited research has been carried out on the identification of potential source regions of aerosol components in particulate matter and few comparisons between the various source apportionment techniques have been performed.

To understand the origin of aerosols in the north Eastern Mediterranean, for the current study, source apportionment has been performed by applying Mass Closure, absolute principal factor analysis and Positive Matrix Factorization. The results from the three techniques have been compared to determine similarities and differences in sources and source contributions. In addition, potential source regions of detected sources will be identified by using the Potential Source Contribution Function.

2. Materials and methods

2.1. Aerosol sampling and analytical measurements

Daily two-stage aerosol filters were collected from a rural site located on the coastline of the Eastern Mediterranean, Erdemli (36° 33′ 54″N and 34° 15′ 18″E, at about 22 m above sea level and 10 m away from sea), Turkey (for more details see Kubilay and Saydam, 1995; Kubilay et al., 2002; Koçak et al., 2004a,b) between April 2001 and April 2002. A total of 281 PM_{10} (coarse + fine) aerosol samples were collected on 8.0 μ m and 0.4 µm apiezon coated Nuclepore polycarbonate filters, respectively, using a low volume sampler (Gent type PM_{10}) stack filter unit). After collection of aerosol filters, $PM_{10-2.5}$ and PM_{2.5} concentrations were determined gravimetrically. Water-soluble ions were measured by ion chromatography (IC) at Environmental Chemical Processes Laboratory (ECPL), University of Crete, following the method described in details by Bardouki et al. (2003). Concentrations of the elements (Fe, Ti, Ca, Mn, K, Cr, V, Zn) were obtained using 2 cm² of the filter sample applying proton-induced X-ray emission (PIXE) at ATOMKI (Institute of Nuclear Research of the Hungarian Academy of Sciences, Debrecen, Hungary) as described by Borbely-Kiss et al. (1999). Details on sampling and analysis of aerosols filters are given in Koçak et al. (2007a,b).

2.2. Air mass back trajectories

Air masses back trajectories arriving at the sampling site were computed by the Hysplit Dispersion Model (Hybrid Single Particle Langrangian Integrated Trajectory; Draxler and Hess, 1998) and were illustrated by one-hour endpoint locations in term of latitude and longitude. Daily back trajectories were evaluated for 3 days for four different heights above the starting point at ground level (1000, 2000, 3000 and 4000 m AGL). However, in order to calculate residence times of air mass back trajectories only the 1000 m and 4000 m altitudes were used.

2.3. Source apportionment techniques

Various apportionment techniques such as Mass Closure (MC), absolute principal factor analysis (APFA) and Positive Matrix Factorization (PMF) have been applied by various researchers to identify sources of aerosol (Thurston and Spengler, 1985; Paatero and Tapper, 1994; Huang et al., 1999; Bardouki et al., 2003; Song et al., 2008; Viana et al., 2008). Below a short description of these techniques is given.

- (a) MC: Is the easiest and simplest from all apportionment techniques since calculations are obtained directly from measured species. However, this technique is not able to provide information on how does aerosol species co-vary as well as their underlying sources.
- (b) APFA: It can be directly run from a spreadsheet which makes it easy. There are also options for selecting elements, handling missing data and extracting various numbers of factors. The main disadvantage is that loadings and factor scores may have negative values which are not desirable for quantitative analysis.
- (c) PMF: It constrains factor loadings and factor scores to nonnegative values and it separates sources better than APFA. The major disadvantage is that missing values and limits should be eliminated of filled by user, becoming time consuming compared to APFA.

Although MC, APFA and PMF have their own advantages and drawbacks, the simultaneous use of these techniques can provide valuable info to the researchers.

For Mass Closure (MC): (a) the total amount of mineral dust was estimated using Fe concentrations assuming a relative ratio to the upper crust of 3.089% (Wedepohl, 1995), (b) the sea salt contribution was calculated from Na⁺ concentrations assuming that Na⁺ has a pure marine origin, (c) ionic mass is the sum of $nssSO_4^{2-}$; NO_3^{-} , $C_2O_4^{2-}$, NH_4^{+} , $nssK^{+}$ and $nssMg^{2+}$. Non-sea salt levels of the species were calculated using Na⁺ as the tracer and the standard sea water composition (Turekian, 1976).

Factor analysis is commonly used in environmental studies to deduce sources from data (Thurston and Spengler, 1985; Salvador et al., 2004; Güllü et al., 2005). The principal application of factor analysis is to reduce the number of variables. Therefore, factor analysis can be applied as a data reduction method. Hence, for each PM₁₀ aerosol component identified the factor score can be computed for each sample.

Mass loadings for the samples can then be regressed on the AFCS (Absolute Factor Component Scores) to estimate the mass contributions (for more details see Thurston and Spengler, 1985).

The Positive Matrix Factorization model was described in detail by Paatero and Tapper (1994) and Paatero (2007). In PMF any data matrix **X** having *n* rows (number of samples) and *m* columns (number of species) can be factorized into two matrices, namely $G(n \times p)$ and $F(p \times m)$ and the residual part *E*, where *p* denotes the number of factors extracted.

$$\mathbf{X} = GF + E \tag{1}$$

G is the source contribution matrix with extracted factors (sources) and *F* is a source profile matrix. The details of the algorithm for PMF are provided by Paatero (2007).

The PMF has ability to handle missing and below detection limits data adjusting the corresponding error estimates. However during this study, missing data were removed from the data spreadsheet and uncertainties in the data were calculated using an ad hoc formula (Anttila et al., 1995) since the concentrations of each species were found to be higher than their detection limits. Therefore, in order to calculate uncertainties square root of the 5% of the measured species plus the detection limit was applied. In the concurrent analysis *n* (days) = 265 and *m* (chemical species) = 18 (identical matrix was used for MC and APFA analysis). The robust mode of PMF2 has been applied for analyzing the dataset. It can avoid excessively large values in the dataset, which can disproportionally affect the results. The parameter α is referred to as the outlier distance. Data values lying more than α standard deviations above or below the fitted value will be treated as outliers and receive a decreased weight in PMF2. Values of 2.0, 4.0 and 8.0 were suggested by Paatero (2007) for outlier distance to achieve easier comparison of results obtained by different researchers. During the application of PMF2 the vales $\alpha = 2.0$ was used in the study. Error model -14 and $C_3 = 0.1$ have been applied during this study (Lee et al., 1999; Paatero, 2007). The PMF program allows one to repeat the analysis from random starting points to test if global minimum solution is achieved. For this purpose, the analysis was allowed to repeat ten times from ten pseudorandom starting points and the Q values were not very different from each other.

There is no mathematical criterion to extract the correct number of factors. However, the observed Q and scaled species residuals can be helpful. The observed Q should not be less than the theoretical Q since this would mean that the model predicted the observed data better than it could be based on the uncertainty (Rizzo and Scheff, 2007). Expected Q value can be calculated by formula $[Q_{expected} = nm - p(n + m)]$ m)] given by Paatero et al. (2002). Scaled residuals did not indicate a tendency to mainly positive, negative and/or very small values and showed a random pattern of positive and negative values, most of them being between -2.0 and 2.0(more than 95%). Therefore, six factors were found to give the most reasonable results ($Q = 3379 > Q_{expected} = 3072$). An increase in the number of factors resulted in less meaningful sources and the Q value (2702) was less than expected (2789). The decrease being caused by a combination of distinct sources. After the number of factors was determined, PMF was run with different F_{peak} values to explore the rotational freedom. A rotational matrix (Rotmat) in PMF is utilized to reveal if factors have rotational freedom. Choosing the largest element in Rotmat can show the worst case in the rotational freedom (Lee et al., 1999). Taking into account the variation in the Q value and the largest element in Rotmat, the F_{peak} value was adjusted to 0.1 during the application of PMF.

2.4. Potential Source Contribution Function (PSCF)

A 2° longitude \times 2° latitude cells grid has been superimposed over the region defined by 10° N–76°N and 20°W–50°E. The residence time and special residence time analysis then were calculated using the formula given below by Ashbaugh et al. (1985)

$$P[A_{ij}] = \frac{n_{ij}}{N} \tag{2}$$

$$P[B_{ij}] = \frac{m_{ij}}{N} \tag{3}$$

where n_{ij} is the number of trajectory segment endpoints that fall in the *ij*th cell during a time interval *T*, m_{ij} is the number of segment points in the *ij*th cell for those trajectories which arrive at the receptor site when the aerosol species concentration is higher than the threshold values, *N* is the total number of endpoints computed for the time interval and $P[A_{ij}]$ and $P[B_{ij}]$ represent the residence time probability of the randomly selected air parcel in the *ij*th cell relative to the total time interval T and special residence time probability, respectively. Subsequently Potential Source Contribution Functions were evaluated by dividing $P[B_{ij}]$ with $P[A_{ij}]$.

3. Results and discussion

3.1. Source apportionment for PM₁₀

The Mediterranean atmosphere can be influenced by three strong, but distinct aerosol sources: (a) crustal dust, (b) sea salts and (c) anthropogenic emissions. Therefore, identification of the sources and estimation of the contribution made by each source to the particulate matter is of importance. In order to achieve this and compare results from different approaches, Mass Closure (MC), Absolute Principle Factor Analysis (APFA) and Positive Matrix Factorization (PMF) were applied.

3.1.1. Mass Closure (MC)

Fig. 1 presents daily contributions of the each source to PM₁₀. Ionic mass (Fig. 1a) exhibited higher contributions particularly in the summer owning to enhanced production of secondary aerosols under the conditions prevailing over the Eastern Mediterranean region during the summer (Mihalopoulos et al., 1997; Koçak et al., 2004b). Contribution of sea salt (Fig. 1b) was found to be higher in winter. Storms are more frequent and more intense during the winter period due to thermal gradient between warm sea and intrusions of cold continental air masses. Therefore, in winter unsettled weather conditions enhanced the concentrations of sea salt ions throughout severe sea spray generation (Koçak et al.,



Fig. 1. Daily contributions of each source to ionic mass (a), sea salt (b), PM_{10} crustal (c).

2004b). The winter minimum of crustal load could be attributed to the frequent removal of atmospheric particles via wet deposition and damp soil on both the local and surrounding landmasses due to precipitation. Even though substantial rain events were detected in the transitional periods, crustal (Fig. 1c) contribution was highest in March, April and May months due to the well documented transport from North Africa and rarely from the Middle East (Kubilay and Saydam, 1995; Kubilay et al., 2000; Koçak et al., 2004a) which is often associated with intense sporadic peaks of mineral dust. Aerosol Fe concentrations higher than 500 ng m^{-3} (as threshold values), corresponding air mass back trajectories and satellite images obtained from TOMS (Total Ozone Mapping Spectrometer) were utilized in order to refine mineral dust events at Erdemli during sampling period. During this period 34 dust days were identified by an abrupt increase in the concentrations of Fe, Ti, Mn, and Ca. It should be noted that Fe, Ti and Mn for dust and non-dust events show strong correlation between each other ($R^2 > 0.90$) whereas these species indicate weak correlation coefficients with pollutants such as Zn, V and Ni ($R^2 < 0.28$). Therefore, these relationships suggest that Fe, Ti and Mn are mainly originated from crustal source during dust and non-dust events. The highest mineral dust concentration was observed on the 13th of May 2001 with a value of more than 220 µg m⁻³ when air masses reaching the Erdemli originated from North Africa. Fig. 2 shows crustal, sea salt and ionic mass contributions for dust and non-dust events. Contribution of crustal component was found approximately 5 times higher during mineral dust transport from North Africa than during non-dust events (Crustal_{Dust} \approx 40 µg m⁻³; Crustal_{Non-Dust} \approx 8 µg m⁻³). On the other hand there was no difference for sea salt and ionic mass contributions during dust and nondust events. As a result, chemical composition is predominantly affected by crustal load due to mineral dust transport from North Africa.

3.1.2. Absolute Principle Factor Analysis (APFA)

The result of varimax-rotated factor analysis is presented in Fig. 3a for aerosol species in PM₁₀. The data for PM₁₀ can be interpreted on the basis of four common factors. The first factor can be characterized as a being representative of a crustal source since it is heavily influenced by the concentrations of Ti, Fe, Mn, Ca²⁺ and K⁺. The second factor can be identified as representing the marine source, since it consists of high loadings of Na⁺, Cl⁻, Mg²⁺ and Br⁻. The third factor has high loadings of SO²₄⁻, NH⁴₄, MS⁻, C₂O²₄⁻, NO⁻₃ and Zn. This factor, therefore, maybe ascribed to secondary aerosols as it has high loadings of sulfate, ammonium, methanesulfonate, nitrate and oxalate. The fourth has high loadings of V and Ni (moderate loadings of Zn and Cr) and hence may be attributed to residual oil combustion.

3.1.3. Positive Matrix Factorization (PMF)

The result of identified sources using PMF2 (version 4.2) is shown in Fig. 3b. The first factor analysis consists of mainly Fe, Ti, Mn, Ca and K which are typical of crustal dust. The second factor is mainly formed by Na⁺, Cl⁻, Mg²⁺ and Br⁻. Based on these species the assigned source would be sea salts. The third factor explains more than 70% of the total nitrate concentration. This factor was also related to the first and second factors which characterize reactions between acidic nitrate and sea salt/crustal sources. The fourth factor consists of principally ammonium and sulfate. This source represents around 98% of the total ammonium concentration. The calculated equivalent ratio of NH_4^+ and SO_4^{2-} is ~0.8 which shows that sulfate is not sufficiently neutralized by ammonium (for more details see Koçak et al., 2007b). The fifth factor is predominantly influenced by methanesulfonate. It is worth mentioning that sulfate found in this source accounts for ~9% of the total



Fig. 2. Contributions of crustal, sea salt and ionic mass to PM_{10} for dust and non-dust events.



Fig. 3. Source profiles for PM₁₀ from APFA (a) and PMF (b).

sulfate concentration which is consistent with results presented in Section 3.2. The sixth factor might be attributed to residual oil burning since this source can be characterized by high explained variation values of V and Ni (~70%).

3.1.4. Comparison of three techniques and source apportionment Estimated PM₁₀ concentrations from MC, APFA and PMF against measured concentrations of PM₁₀ are presented in Fig. 4a, b and c, respectively. The slope of the regression lines for three estimates (Fig. 4) showed values close to unity. Although there is no statistical difference between techniques, from regression analysis, the best estimated values is õobserved for PMF with an intercept around 2 (Unknown = 5%) and R^2 = 0.96. The results observed for APFA were similar; however a higher value was calculated for the intercept, being around 3 (Unknown = 8%). The MC technique is clearly able to identify sea salt and crustal sources but not the others. In addition, APFA was able to determine only 4 sources whilst PMF was able to identify 6 sources. The main difference between APFA and PMF was the identification of secondary aerosols. PMF was clearly able to define secondary aerosols into three distinct groups namely: ammonium bisulfate, nitrate and biogenic.

The relative estimated contributions from each of the identified sources to the PM₁₀ according to the different techniques are shown in Fig. 5. Considering the three estimation techniques, the largest portion of PM₁₀ is attributable to the sea salt and crustal related sources. MC exhibited the largest unidentified fraction (15%) of the PM₁₀, since it depends upon a simple mathematical calculation and hence resulted in the lack of ability to extract additional sources such as residual oil. For example, on 20th of February 2002 $(PM_{10} = 37.6 \ \mu g \ m^{-3})$, unidentified fraction calculated from MC reached up to ~30% when residual oil contribution was found ~28%. In general, MC, APFA and PMF produced almost identical contributions of sea salts (31–33%), crustal (28–31%) and secondary aerosols (22-24%) (ionic mass for MC) in PM₁₀. Whilst PMF indicated a lower crustal contribution (28%) and a higher contribution of residual oil (10%) to PM₁₀ compared to APFA (31% and 7%, respectively). This variation might be attributed to differences in source profiles extracted from PMF and APFA. Although quantitatively it is not possible to compare contributions of residual oil and crustal sources to



Fig. 4. Comparison of observed daily levels and estimated form MC (a), APFA (b) and PMF (c) for PM_{10} .

total species concentrations due to the different units, it is evident from extracted sources that Ca demonstrated different portionings between two profiles in PMF and APFA. For example, whilst Ca had a very high loading (0.88) in crustal sources in APFA, only 47% of the Ca originated from crustal sources in PMF. Overall, results from three techniques showed the dominance of natural sources (crustal and sea salt sources; 61–63% of the total) in PM₁₀, whereas secondary aerosols accounted for 22–24% of the total PM₁₀.



Fig. 5. Source apportionment from Mass Closure and Absolute Principle Factor Analysis and Positive Matrix Factorization for PM_{10} .

3.2. Source apportionment for sulfate

Non-sea-salt sulfate shows strong seasonal cycles with a winter minimum and a summer maximum (Fig. 6a). The lowest concentrations were found during winter when $nssSO_4^{2-}$ averaged around 2 μ g m⁻³. Monthly mean concentrations of this anion in January and February were observed, similar to those observed for March and April. Elevated concentrations were found during the summer (particularly from June to August) when $nssSO_4^{2-}$ averaged more than 6 μ g m⁻³.

The considerable increase in the concentration of $nssSO_4^{2-}$ from winter to summer may be a result of several different processes: photochemistry, wet precipitation, biogenic sulfur and change in atmospheric transport. During summer, homogeneous conversion of SO_2 to particulate SO_4^{2-} has been suggested as the main oxidation mechanism under conditions prevailing over the Eastern Mediterranean region (Luria et al., 1996; Mihalopoulos et al., 2007). Moreover, conversion rates of SO₂ to sulfate indicate a strong seasonal cycle with a winter minimum and a summer maximum in the Eastern Mediterranean (Erduran and Tuncel, 2001). These authors suggest that the observed low conversion rates during winter occur because of low solar flux. In addition, in summer, particles are accumulated in the atmosphere as a consequence of the low frequency of rain events. High sulfate levels during the summer have been attributed to biogenic sulfur emissions (Ganor et al., 2000; Kubilay et al., 2002). Additionally, Mihalopoulos et al. (1997), applying air mass back trajectories, indicated that the highest $nssSO_4^{2-}$ concentrations are associated with transport from Eastern and Central Europe in summer when dry deposition is the main removal mechanism for aerosol particles.

In order to calculate the biogenic fraction of $nssSO_4^{-}$ the formula suggested by Bates et al. (1992) was used since it is principally dependent upon temperature. The formula reflects a simple linear relationship between temperature and $[MS^-]/[nssSO_4^{2-}]$ which Bates et al. (1992) found to be a good approximation for the observed values in unpolluted marine sites in the Southern Hemisphere. The formula proposed by Bates et al. (1992) is given as fallows:

$$R = -1.5 \times T(^{\circ}C) + 42.2$$

where *R* is the $[MS^-]/[nssSO_4^{2-}]$ ratio, *T* (°C) is temperature.

However, it should be noted that application of above formula for Eastern Mediterranean is still under debate since Bates et al. (1992) equation was derived for lower temperatures and lower nitrate concentrations than those observed during summer over Eastern Mediterranean. Therefore, one should keep in mind that prevailing summer conditions and high nitrate levels may cause over estimated biogenic sulfur contribution and this formula should be tested by approaches like use of sulfur isotopes. On the other hand, biogenic contribution from this formula has been compared for Eastern Mediterranean by an alternative calculation based on DMS data (Ganor et al., 2000; Kouvarakis and Mihalopoulos, 2002). Two assumptions yielded similar biogenic contribution on observed $nssSO_4^{2-}$. Mihalopoulos et al. (1997) calculating that the biogenic emission contributions ranged from 0.6 to 28.3% of the total nssSO₄²⁻ at Finokalia, Crete (Central Mediterranean).



Fig. 6. Monthly average non-sea salt sulfate concentrations (a) and monthly biogenic sulfate contribution to non-sea salt sulfate.

Similar results were found by Kouvarakis and Mihalopoulos (2002) for the same station. Ganor et al. (2000) determined that 11% (ranged from 5.6% to 22%) of the $nssSO_4^{2-}$ from biogenic origin in aerosol samples collected from the Israeli coast.

Monthly biogenic contributions to non-sea salt sulfate are represented in Fig. 6b. During the winter months (January, February and December) the mean biogenic contributions were found to be negligible with a value around 1%. In March the biogenic contribution was also very low. However, from April to May the biogenic contribution increased gradually and the mean contribution ranged from 4% in April to 8% during May. The highest mean biogenic contributions were found in the summer and ranged from 17% in June to 38% in July and August. On average about 12% of the non-sea salt sulfate was evaluated as biogenic sulfate. Based on this calculation, unlike remote marine sites the Mediterranean



Fig. 7. Distribution of PSCF values for factor scores higher than 1 of crustal (1000 m, a), crustal (4000 m, b), secondary (c) and residual oil (d). Only statistically significant PSCF values at the 95% confidence level are shown.

site is heavily influenced by anthropogenic sulfate emissions. Moreover, calculated values indicated that even during the summer period anthropogenic sulfur sources are the predominant source in Mediterranean atmosphere. In Turkey, approximately 30% of the power generation is obtained by high sulfur containing coal burning (Say, 2006). Therefore, high conversion rates of SO₂ to SO₄²⁻ coupled with high SO₂ emissions from this source might be suggested as one of the reasons of anthropogenic origin of sulfate.

3.3. Potential Source Contribution Function (PSCF) Analysis

The PSCF analysis has been applied to sources identified in the PM_{10} (see Fig. 3a) by factor analysis: crustal, secondary and residual oil. Sea spray is produced by bubble bursting which commences at a wind speed of about 3–4 ms⁻¹

(O'Dowd et al., 1997) and hence related highly with local meteorological parameters. Indeed, Sellegri et al. (2001), did not find significant changes in Na⁺ concentrations between short and long fetch samples collected on board the R/V L'Atalante and they suggested that the production of new sea salts takes place rapidly during the first 25 km. Therefore, PSCF for sea salt was not evaluated. Since the data have been previously normalized (for more details see Thurston and Spengler, 1985), this means that means and standard deviations are equal to values of 0 and 1, respectively. In order to obtain a special case, residence time probability maps, representing $P[B_{ii}]$, were constructed by trajectories which ended at Erdemli when factor scores of each source were higher than 1 (higher than the standard deviation). Calculated PSCF values were subdivided into five categories: (a) very weak (0.0-0.20), (b) weak (0.20-0.40), (c) intermediate (0.40-0.60) and (d) strong (0.60-1.0). Calculated PSCF values in some areas occur by chance. Therefore, it is essential to check the statistical significance of every grid cell PSCF value. Two statistical tests to check significance were adopted; bootstrap technique and binomial distribution (Vasconcelos et al., 1996; Salvador et al., 2004). The binomial distribution technique was applied since it has an easier computation compared to the bootstrap method. Therefore, only PSCF values statistically significant at the 95% confidence interval have been considered in the analysis.

3.3.1. Crustal source

The PSCF map for the lower pressure level (1000 m above the sea level; see Fig. 7a) indicated that the strong potential probabilities are located at North Africa particularly the Eastern Sahara desert. From the map for the lower pressure level it might be suggested that the Eastern Sahara (particularly the central Libyan Desert fourth strongest source in the world with average AI > 1.5; Washington et al., 2003) is one of the important source of the mineral dust transported into the Eastern Mediterranean region. In addition, with strong PSCF values northern Algeria appeared as another source for crustal material. The PSCF map for the higher pressure level (4000 m; see Fig. 7b) is more representative of the Sahara desert since dust transport mainly takes place at high altitudes (Kubilay et al., 2000, 2005; Kalivitis et al., 2007). In contrast to the lower layer PSCF map, the higher level layer PSCF map showed various source areas in the Sahara desert primarily including a large area 22°-30°N and 10°W to 20°E covering patches of central/southern Algeria, northern Mali/ Mauritania and Western Sahara. The Bodele depression appeared to be an additional source region. Interestingly, these findings are similar to recent results of Engelstaedter and Washington (2007) who, applying long term mean of the satellite derived TOMS Aerosol Index, have highlighted major dust producing areas in North Africa; region in Central Chad known as the Bodele depression and a large region in West Africa covering of Mauritania, Mali and Algeria.

3.3.2. Secondary aerosol source

The PSCF map obtained for the secondary aerosol source (see Fig. 7c) does not clearly indicate any source regions, except the south-Eastern Black Sea. Recently, Kubilay et al. (2002) have observed higher $nssSO_4^{2-}$ and MS⁻ concentrations for air masses originating from the Black Sea and

proposed medium range transport of these water soluble ions due to DMS-producing phytoplankton species such as coccolithophorids, flagellates, etc. Hence, high PSCF values for this source over the south-Eastern Black Sea imply that biogenic activities taking place in the Black Sea is an important source for this group. Biomass burning from regions surrounding Black Sea might be suggested as an additional source for secondary aerosol (Sciare et al., 2008). Recently, for Erdemli site it has been shown that excess-K/BC presented two distinct ratios for winter (0.06) and summer (0.34), indicating two different sources: fossil fuel burning in winter and biomass burning in summer (Kocak et al., 2007b). Nevertheless, the lack of relationship between BC and this ratio with secondary aerosol suggests that this component is not significantly affected by biomass burning. However, lack of high PSCF values for secondary aerosol sources suggests that this class of particles is strongly influenced by local sources mainly under the prevailing summer conditions.

3.3.3. Residual oil source

The PSCF map derived for the residual oil source (see Fig. 7d) denoted that the sampling site was under the influence of several possible source regions. The main source areas are Southern Germany, Northern Italy, Eastern France, Central Poland, the former Republic of Yugoslavia and Albania. In order to compare results from the PSCF map for the residual oil source, EPER (www.eper.cec.eu.int) emissions for Ni-compounds in Europe for 2001 were used. The obtained data were divided into $2 \times 2^{\circ}$ grid cells and Ni emissions were calculated for each grid cell. Fig. 8 shows the emissions for Europe and from the map it is clear that there are no available emission data for Eastern Europe. As can be deduced from the map Spain, Italy, Germany, Holland and Belgium are the important emitters of the Ni into the atmosphere. The highest emission source regions do not exactly match the source regions obtained from the PSCF map however; there is a good match for Northern Italy and Southern France. This discrepancy



Fig. 8. Emissions of Ni-compounds into the atmosphere in Europe. Derived from EPER data for $2 \times 2^{\circ}$ grid cell.

might be attributed to the applied technique which assumes that chemical species emitted within a grid cell is swept into the air parcel and transported to the receptor site without loss due to atmospheric deposition particularly through wet scavenging.

4. Conclusions

In this study, statistical techniques were successfully applied to identify sources and source regions of PM₁₀ in the Eastern Mediterranean atmosphere. Inspection of measured and estimated concentrations using three techniques (Mass Closure, absolute principal factor analysis and Positive Matrix Factorization) showed good agreement considering regression analysis. Amongst the techniques, Mass Closure was found the least successful since it demonstrated the highest unknown (scatter as well) and was not able to define minor sources such as residual oil. PMF was found more efficient than APFA since it had the ability to classify secondary aerosols into three distinct groups (Ammonium bisulfate, nitrate and biogenic). Results from all applied techniques highlighted the dominance of natural sources (sea salt and crustal; 61-63%). Calculations for sulfate indicated that on average 8% and 12% of its total concentration are originated from sea salt and biogenic emissions. However, the contribution from biogenic emissions can reach up to ~40% during the summer months.

Potential Source Contribution Function analysis highlighted that the Saharan desert is the main source area for crustal components. Secondary aerosol components could only be associated with the south-Eastern Black Sea, whereas, Southern Germany, Northern Italy, Eastern France, Central Poland, the former Republic of Yugoslavia and Albania was identified as the main source regions for residual oil.

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References

- Andreae, T.W., Andreae, M.O., Ichoku, C., Maenhaut, W., Cafmayer, J., Karnieli, A., Orlovsky, L., 2002. Lightscattering by dust and anthropogenic aerosol at a remote site in the Negev Desert, Israel. Journal of Geophysical Research 107 (D2). doi:10.1029/2001JD00252.
- Anttila, P., Paatero, P., Tapper, U., Jarvinen, O., 1995. Source identification of bulk wet deposition in Finland by positive matrix factorization. Atmospheric Environment 29, 1705–1718.
- Artinano, B., Querol, X., Salvador, P., Rodriguez, S., Alonso, D.G., Alastuey, A., 2001. Assessment of airborne particulate levels in Spain in relation to the new EU-directive. Atmospheric Environment 35, 43–53.
- Ashbaugh, L., Malm, W., Sadeh, W., 1985. A residence time probability analysis of sulfur concentrations at Grand Canyon National Park. Atmospheric Environment 19, 1263–1270.

- Avila, A., Alarcon, M., Queralt-Mitjans, I., 1998. The chemical composition of dust transported in red rains its contribution to the biogeochemical cycle of a Holm oak forest in Catalonia, Spain. Atmospheric Environment 32, 179–191.
- Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smolik, J., Zdimal, V., Eleftheriadis, K., Lazaridis, M., Dye, C., Mihalopoulos, N., 2003. Chemical composition of size resolved atmospheric aerosols in the Eastern Mediterranean during summer and winter. Atmospheric Environment 37, 195–208.
- Bates, T.S., Calhoun, J.A., Quinn, P.K., 1992. Variations in the methanesulfonate to sulfate molar ratio in submicrometer marine aerosol particles over the South Pacific Ocean. Journal of Geophysical Research 97, 9859–9865.
- Borbely-Kiss, I., Koltay, E., Szabo, Gy., Bozo, L., Tar, K., 1999. Composition and sources of urban and rural atmospheric aerosol in Eastern Hungary. Journal of Aerosol Science 30, 369–391.
- Brankov, E., Rao, S.T., Porter, P.S., 1998. A trajectory-clustering-correlation methodology for examining the long-range transport of air pollutants. Atmospheric Environment 32, 1525–1534.
- Cape, J.N., Methven, J., Hudson, L.E., 2000. The use of trajectory cluster analysis to interpret trace gas measurements at Mace Head, Ireland. Atmospheric Environment 34, 3651–3663.
- Carbo, P., Krom, Homoky, W.B., Benning, L.G., Herut, B., 2005. Impact of atmospheric deposition on N and P geochemistry in the south Eastern Levantine basin. Deep-Sea Research 52, 2041–3053.
- Dorling, S.R., Davies, T.D., Pierce, C.E., 1992. Cluster analysis: a technique for estimating the synoptic meteorological controls on air and precipitation chemistry—method and applications. Atmospheric Environment 26A, 2575–2581.
- Dulac, F., Buat-Menard, P., Arnold, M., Ezat, U., Martin, D., 1987. Atmospheric input of trace metals to the western Mediterranean Sea: 1. factors controlling the variability of atmospheric concentrations. Journal of Geophysical Research 92, 8437–8453.
- Draxler, R.R., Hess, G.D., 1998. An overview of the HYSPLIT 4 modeling system for trajectories, dispersion and deposition. Australian Meteorological Magazine 47, 295–308.
- Engelstaedter, S., Washington, R., 2007. Atmospheric controls on the annual cycle of North African dust. Journal of Geophysical Research 112, D03103. doi:10.1029/2006JD007195.
- Erduran, S.M., Tuncel, S.G., 2001. Gaseous and particulate air pollutants in the Northeastern Mediterranean Coast. Science of the Total Environment 281, 205–215.
- Ganor, E., Foner, H.A., Bingemer, H.G., Uditsi, R., Setter, I., 2000. Biogenic sulphate generation in the Mediterranean Sea and its contribution to the sulphate anomaly in the aerosol over Israel and the Eastern Mediterranean. Atmospheric Environment 34, 3453–3462.
- Griffin, D.W., Kubilay, N., Koçak, M., Gray, M.A., Borden, T.C., Shinn, E.A., 2007. Airborne desert dust and aeromicrobiology over the Turkish Mediterranean coastline. Atmospheric Environment 41, 4050–4062.
- Gerasopoulos, E., Kouvarakis, G., Babasakalis, P., Vrekoussis, M., Putaud, J.P., Mihalapoulos, N., 2006. Origin and variability of particulate matter (PM10) mass concentrations over the Eastern Mediterranean. Atmospheric Environment 40, 4679–4690.
- Güllü, G., Güray, D., Tuncel, G., 2005. Atmospheric trace element and major ion concentrations over the Eastern Mediterranean Sea: identification of anthropogenic source regions. Atmospheric Environment 39, 6376–6387.
- Huang, S., Rahn, K.A., Arimoto, R., 1999. Testing and optimizing two factoranalysis techniques on aerosol at Narragansett, Rhode Island. Atmospheric Environment 33, 2169–2185.
- Kalivitis, N., Gerasopoulos, E., Vrekoussis, M., Kouvarakis, G., Kubilay, N., Hatzianastassiou, N., Vardavas, I., Mihalopoulos, N., 2007. Dust transport over the Eastern Mediterranean derived from Total Ozone Mapping Spectrometer, Aerosol Robotic Network, and surface measurements. Journal of Geophysical Research 112, D03202. doi:10.1029/2006JD007510.
- Koçak, M., Nimmo, M., Kubilay, N., Herut, B., 2004a. Spatio-temporal aerosol trace metal concentrations and sources in the Levantine Basin of the Eastern Mediterranean. Atmospheric Environment 38, 2133–2144.
- Koçak, M., Kubilay, N., Mihalopoulos, N., 2004b. Ionic composition of lower tropospheric aerosols at a North Eastern Mediterranean site: implications regarding sources and long-range transport. Atmospheric Environment 38, 2067–2077.
- Koçak, M., Mihalopoulos, N., Kubilay, N., 2007a. Contributions of natural sources to high PM₁₀ and PM_{2.5} events in the Eastern Mediterranean. Atmospheric Environment 41, 3806–3818.
- Koçak, M., Mihalopoulos, N., Kubilay, N., 2007b. Chemical composition of the fine and coarse fraction of aerosols in the north Eastern Mediterranean. Atmospheric Environment 41, 7351–7368.
- Kouvarakis, G., Mihalopoulos, N., 2002. Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosols phase in the Eastern Mediterranean atmosphere. Atmospheric Environment 36, 929–938.
- Kouyoumdjian, H., Saliba, N.A., 2005. Ion concentrations of PM_{10-2.5} and PM_{2.5} aerosols over the Eastern Mediterranean region: seasonal variation

and source identification. Atmospheric Chemistry and Physics Discussions 5, 13053–13073.

- Kubilay, N., Saydam, C., 1995. Trace elements in atmospheric particulates over the Eastern Mediterranean: concentration, sources and temporal variability. Atmospheric Environment 29, 2289–2300.
- Kubilay, N., Nickovic, S., Moulin, C., Dulac, F., 2000. An illustration of the transport and deposition of mineral dust onto the Eastern Mediterranean. Atmospheric Environment 34, 1293–1303.
- Kubilay, N., Koçak, M., Çokacar, T., Oğuz, T., 2002. Influence of Black Sea and local biogenic activity on the seasonal variation of aerosol sulfur species in the Eastern Mediterranean atmosphere. Global Biogeochemical Cycles 16 (4), 1079. doi:10.1029/2002GB001880.
- Kubilay, N., Oğuz, T., Koçak, M., Torres, O., 2005. Ground-based assessment of Total Ozone Mapping Spectrometer (TOMS) data for dust transport over the north Eastern Mediterranean. Global Biogeochemical Cycles 19, GB1022. doi:10.1029/2004GB002370.
- Lee, E., Chan, C.K., Paatero, P, 1999. Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong. Atmospheric Environment 33, 3201–3212.
- Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, J., Dentener, F.J., Fischer, H., Feichter, J., Flatau, P.J., Heland, J., Holzinger, R., Korrmann, R., Lawrence, M.G., Levin, Z., Markowicz, K.M., Mihalopoulos, N., Minikin, A., Ramanathan, V., de Reus, M., Roelofs, G.J., Scheeren, H.A., Sciare, J., Schlager, H., Schultz, M., Siegmund, P., Steil, B., Stephanou, E.G., Stier, P., Traub, M., Warneke, C., Williams, J., Ziereis, H., 2002. Global air pollution crossroads over the Mediterranean. Science 298, 794–798.
- Luria, M., Peleg, M., Sharf, G., Tov-Alper, D.S., Spitz, N., Ben Ami, Y., Gawii, Z., Lifschitz, B., Yitzchaki, A., Seter, I., 1996. Atmospheric sulfur over the east Mediterranean region. Journal of Geophysical Research 101, 25917–25930.
- Mamane, Y., Gottlieb, J., 1992. Nitrate formation on sea-salt and mineral particles—a single particle approach. Atmospheric Environment 26A, 1763–1769.
- Markaki, Z., Oikonomou, K., Koçak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., Mihalopoulos, N., 2003. Atmospheric deposition of inorganic phosphorus in the Levantine Basin, Eastern Mediterranean: spatial and temporal variability and its role in seawater productivity. Limnology and Oceanography 48, 1557–1568.
- Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., Bousquet, P., 1997. Tropospheric aerosol ionic composition in the E. Mediterranean region. Tellus 49B, 1–13.
- Mihalopoulos, N., Kerminen, V.M., Kanakidou, M., Berresheim, H., Sciare, J., 2007. Formation of particulate sulfur species (sulfate and methanesulfonate) during summer over the Eastern Mediterranean: a modelling approach. Atmospheric Environment 41, 6860–6871.
- Moulin, C., Lambert, E., Dayan, U., Masson, V., Ramonet, M., Bousquet, P., Legrand, M., Balkanski, Y.J., Guelle, W., Marticorena, B., Bergametti, G., Dulac, F., 1998. Satellite climatology of African dust transport in the Mediterranean atmosphere. Journal of Geophysical Research 103, 13137–13144.
- O'Dowd, C.D., Smith, M.H., Consterdine, I.E., Lowe, J.A., 1997. Marine aerosol, seasalt, and the marine sulfur cycle: a short review. Atmospheric Environment 31, 73–80.
- Paatero, P., 2007. User's Guide for Positive Matrix Factorization Programs PMF2 and PMF3, Part 1–2: tutorial. University of Helsinki, Helsinki, Finland.

- Paatero, P., Tapper, U., 1994. Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data value. Environmetrics 5, 111–126.
- Paatero, P., Hopke, P.H., Song, X.H., Ramadan, Z., 2002. Understanding and controlling rotations in factor analytic models. Chemometrics and Intelligent Laboratory Systems 60, 253–264.
- Rizzo, M.J., Scheff, P.A., 2007. Fine particulate source apportionment using data from the USEPA speciation trends network in Chicago, Illinois: comparison of two source apportionment models. Atmospheric Environment 41, 6276–6288.
- Rodriguez, S., Querol, X., Alastuey, A., Plana, F., 2002. Sources and processes affecting levels and composition of atmospheric aerosol in the western Mediterranean. Journal of Geophysical Research 107 (D24), 4777. doi:10.1029/ 2001 [D001488.
- Querol, X., Alastuey, A., Rodriquez, S., Viana, M.M., Artinano, B., Salvador, P., Mantilla, E., Garcia dos Santos, S., Patier, R.F., de Las Rosa, J., Sanchez de la Campa, A., Menendez, M., Gil, J.J., 2004. Levels of particulate matter in rural urban and industrial sites in Spain. Science of the Total Environment 334–335, 359–376.
- Salvador, P., Artinano, B., Alonso, D.G., Querol, X., Alastuey, A., 2004. Identification and characterization of sources of PM₁₀ in Madrid (Spain) by statistical methods. Atmospheric Environment 38, 435–447.
- Say, N.P., 2006. Lignite-fired thermal power plants and SO₂ pollution in Turkey. Energy Policy 34, 2690–2701.
- Sellegri, K., Gourdeau, J., Putaud, J.P., Despiau, S., 2001. Chemical composition of marine aerosol in a Mediterranean coastal zone during the FETCH experiment. Journal of Geophysical Research 106 (D11), 12,023–12,037.
- Sciare, J., Oikonomou, K., Favez, O., Markaki, Z., Liakakou, E., Cachier, H., Mihalopoulos, N., 2008. Long-term measurements of carbonaceous aerosols in the Eastern Mediterranean: evidence of long-range transport of biomass burning. Atmospheric Chemistry and Physics 8, 5551–5563.
- Song, Y., Dai, W., Shao, M., Liu, Y., Lu, S., Kuster, W., Goldan, P., 2008. Comparison of receptor models for source apportionment of volatile organic compounds in Beijing, China. Environmental Pollution 156, 174–183.
- Thurston, G.D., Spengler, J.D., 1985. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. Atmospheric Environment 19, 9–25.
- Turekian, K.K., 1976. Oceanography. Prince-Hall, Englewood Cliffs, N.J.
- Vasconcelos, L., Kahl, J., Liu, D., Macias, E., White, W., 1996. A tracer calibration of back trajectory analysis at the Grand Canyon. Journal of Geophysical Research 101 (D14), 19329–19335.
- Viana, M., Pandolfi, M., Minguillon, M.C., Querol, X., Alastuey, A., Monfort, E., Celades, I., 2008. Inter-comparison of receptor models for PM sources apportionment: case study in an industrial area. Atmospheric Environment 42, 3820–3832.
- Washington, R., Todd, M., Middleton, N.J., Andrew, S., Goudie, A.S., 2003. Dust-storm source areas determined by the Total Ozone Monitoring Spectrometer and surface observations. Annals of the Association of American Geographers 93 (2), 297–313.
- Wedepohl, K.H., 1995. The composition of the continental crust. Geochemica Cosmochimica Acta 59, 1217–1232.