Assessment of PM2.5 sources and their corresponding level of uncertainty in a coastal urban area using EPA PMF 5.0 enhanced diagnostics

M. Manousakas[(1)*], H. Papaefthymiou[(2)], E. Diapouli[(1)], A. Migliori[(3)], A.G. Karydas[(3,4)], I. Bogdanovic-Radovic[(5)] and K. Eleftheriadis[(1)]

(1) E.R.L., Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, N.C.S.R. Demokritos, 15310 Ag. Paraskevi, Attiki, Greece

(2) Department of Chemistry, University of Patras, 26500 Patras, Achaia, Greece

(3) Physics Section, International Atomic Energy Agency, Vienna International Centre, PO Box 100, A-1400 Vienna, Austria

(4) Institute of Nuclear and Particle Physics, NCSR "Demokritos" 153 10 Ag. Paraskevi, Athens, Greece

(5) Ruder Boskovic Institute, Bijenicka 54, P.O. Box 180, 10002 Zagreb, Croatia

**Corresponding author: manosman@ipta.demokritos.gr*

Abstract

Datasets that include only the PM elemental composition and no other important constituents such as ions and OC, should be treated carefully when used for source apportionment. This work is demonstrating how a source apportionment study utilizing PMF 5.0 enhanced diagnostic tools can achieve an improved solution with documented levels of uncertainty for such a dataset.The uncertainty of the solution is rarely reported in source apportionment studies or it is reported partially. Reporting the uncertainty of the solution is very important especially in the case of small datasets. PM2.5 samples collected in Patras during the year 2011 were used. The concentrations of 22 elements (Z=11-33) were determined using PIXE. Source apportionment analysis revealed that PM2.5 emission sources were biomass burning (11%), sea salt (8%), shipping emissions (10%), vehicle emissions (33%), mineral dust (2%) and secondary sulfates (33%) while unaccounted mass was 3%. Although Patras city center is located in a very close proximity to the city's harbor, the contribution of shipping originating emissions was never before quantified. As rotational stability is hard to be achieved when a small dataset is used the rotational stability of the solution was thoroughly evaluated. A number of constraints were applied to the solution in order to reduce rotational ambiguity.

Keywords: Source apportionment, PMF 5.0, PM2.5, PMF uncertainty

Introduction

Particulate air pollution has been associated with adverse effects on human health. PM is a chemically non-specific pollutant, and may originate from various emission source types. Thus, its toxicity may well vary depending on its source and chemical composition. If PM toxicity is determined with respect to source types, the regulation of PM can be implemented more effectively (Ito et al. 2006). Several factor analysis and source apportionment methods have been developed to apportion sources of ambient PM2.5. Estimates of resulting source contributions have subsequently been used in epidemiological studies to investigate the association between source-specific PM2.5 and health (Kioumourtzoglou et al. 2014). Given the impact of such air quality standards, it is very important to lower and assess the uncertainty of the results (Hopke et al. 2006; Kioumourtzoglou et al. 2014).

Greece is located at the Eastern Mediterranean basin which is characterized as air pollution hotspot, located at the crossroad of air masses coming from Asia, Europe and Africa (Karanasiou and Mihalopoulos 2013). Because of the particular characteristics of the location, PM in the area can originate from a variety of sources both local and regional. Biomass burning (Amiridis et al. 2012; Saraga et al. 2015) traffic related processes, dust resuspension (Athanasopoulou et al. 2010), industrial activities, transported Saharan dust are some of the most common sources in the area (Grigoropoulos et al. 2009; Karanasiou et al. 2009; Amato et al. 2016). In addition to those sources the climate conditions of the area (low precipitation, high solar activity) favor the accumulation of pollutants and the formation of secondary particles. For example model simulations indicate that SO_2 is transported in the Mediterranean basin where sulfate is produced due to intense photochemical activity (Pikridas et al. 2013). The aforementioned reasons coupled with the weather conditions lead to high PM background concentrations in the area, with high impact on human health in urban areas (Ostro et al. 2014).

Although Greece is a coastal country with several harbors of various sizes and shipping emissions have been already identified (Karanasiou et al. 2009; Amato et al. 2016) as a source, it still remains to be adequately quantified . This source is active when the ships are in dock, as well as when they are at sea. In particular, 70% of ship emissions are estimated to occur within 400 km of the mainland (Endresen et al. 2003). Another complexity is that ships in many cases use old engine technology and that the fuel quality used is poor. Heavy oil usually contains high level of sulfur when compared with the diesel used for passenger cars and residential heating in most European countries (Fridell et al. 2008).

Receptor modeling using aerosol chemical composition data is a reliable method that can provide information on aerosol sources (Belis et al. 2013). Positive Matrix Factorization (PMF) (Paatero and Tappert 1994), is a receptor model that has been successfully applied to many areas with different characteristics (Querol et al. 2001; Kim et al. 2003; Johnson et al. 2006a; Moon et al. 2008; Cohen et al. 2009; Amato et al. 2016; Liang et al. 2016). PMF introduces a weighting scheme taking into account errors of the data points, which are used as point-by-point weights. Adjustment of the corresponding error estimates also allows it to handle missing and below detection limit data. Moreover, non-negative constraints are implemented in order to obtain more physically meaningful factors. The latest PMF version available by USEPA, is designed to overcome some of the weak points of the previous versions of the model, providing better tools to investigate the rotational ambiguity of the factors. PMF 5.0 for the first time offers three methods for estimating uncertainty in factor analytical models: bootstrap (BS, also available on the previous versions of the model), displacement of factor elements (DISP), and bootstrap enhanced by displacement of factor elements (BS-DISP) (Paatero et al. 2014). The uncertainty of PMF analysis due to random errors and rotational ambiguity can be reduced by applying these methods.

In this study a small dataset was used to identify PM2.5 sources in a medium-sized coastal Greek city. The elements determined in the samples by PIXE were namely Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sc, P, Ga, Co, and Ge. The concentration of all the elements except from Sc, P, Ga, Co and Ge was used as a variable in the model. This dataset was used as an example of how small datasets of PM elemental composition, could be treated and more importantly how the uncertainty of the results could be evaluated and reported. The tools offered by PMF 5.0 were used in order to evaluate the rotational stability of the solution. As rotational stability is hard to be achieved when a very small dataset is used, a number of constraints were used in the solution, so that the stability is maintained as high as possible. The application of constraints reduces the rotational space (Hopke 2016). Small dataset lead to another implication. It is hard to obtain representative source profiles without an appropriate number of samples. For example, in the manual of PMF it is suggested that for atmospheric PM at least 100 samples are necessary. The application of some constraints can again improve the rotational stability and assist towards obtaining a meaningful solution.

Experimental

Sampling

Patras is a medium size city located in Peloponnese peninsula. Patras' population according to the last census (2011) was 168.034 citizens. It is a residential area with low industrial activity, which is mainly located in the industrial zone at the southeastern outskirts of the city. Two commercial ports are located in the area, the north or old port and the south or new port. The new port started operating at 11-Jun-2011, and it is used mainly by passenger and cargo ferries sailing to Italy. About 1.5 million passengers per year is estimated to travel using Patras' ports. Traffic in the city is high especially during rush hours. Public transport fleet is composed mainly of buses of very old technology. Olive groves are located in the surrounding area of the city. Scrap wood originating from agricultural activities is commonly used by households in close proximity to the city.

Figure 1. Right: Patras' location, left: sampling and potentional PM2.5 sources' location

The sampler was installed in the city center, on the roof of a high public building (>20m) located in the central city square. The sampling site at this location allowed representative sampling of urban air from any direction. The site was selected because strong influence by nearby sources such as traffic was minimal, when compared to a kerbside station. Hence, the samples collected would be representative of the greater urban area and not be overwhelmed by the contribution of only one source. The sampler used was a low volume sampler model FRM 2000 by Rupprecht Pataschnick. This sampler is designed according to USEPA directive CFR 40. PM2.5 samples were collected onto Teflon membrane filters Whatman PTFE 47 mm diameter with 1 μm pore size. The filter is a PTFE membrane (4 mg/cm^2) with polypropylene backing. The samples were collected over a 24h sampling interval (from 00:00 to 23:59). All filters were weighed before and after sampling to determine the collected PM2.5 mass using a

133 Sartorius PB211D microbalance (readability of 0.1 μg) (Manousakas et al. 2014). Before weighing, the
134 filters were equilibrated for 24h inside a custom designed chamber with automated controls designed to
135 maintain environmental conditions at a constant air temperature of 20 °C and constant RH of 50%. To
136 avoid static electricity interference the balance was equipped with a 210Po static eliminator. The filters
137 were loaded into clean polystyrene Petri dishes and transferred to the sampling site. A number of
138 samples were collected throughout 2011 and 55 of them were selected to be analyzed by PIXE. After the
139 analysis the concentration of 22 elements were determined and 17 of them was used as input on the
140 model (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and As). The samples analyzed by PIXE were
141 selected to equally represent the warm and cold season of the sampling period.

142 The concentration of black carbon (BC) in the collected filters was determined by optical analysis using a
143 Smoke Reflectrometer (Model 43 Smoke Stain Reflectometer, Diffusion Systems LTD). The method
144 followed is described in detail elsewhere (Manousakas et al. 2013).

145

146 *Elemental analysis, PIXE*

147 Particle Induced X-ray Emission (PIXE) was used for elemental analysis of the samples. PIXE has many
148 advantages for elemental analysis of Particulate Matter: it provides rapid multielemental analysis
149 capable to detect a large number of elements from Z=11 (Na) and heavier, including all the crustal and
150 important anthropogenic elements. The advantage of a single analytical technique is the lower
151 possibility for a random error. If a random error does occur in a PIXE measurement it is highly likely to
152 affect all elements in a given sample, which makes it much easier to locate and treat accordingly. Of
153 course there are drawbacks as well. It is not possible to determine all the useful PM components need in
154 source apportionment analysis such as ions, organic carbon or some specific tracers such as
155 levoglucosan (Kostenidou et al. 2015) and carbonate (Karanasiou et al. 2011) with a single analytical
156 technique. The lack of those very important PM components in the analysis is very possible to lead to a
157 solution not easily interpretable and with high levels of uncertainty. Thus, it is very important to
158 evaluate and reduce the uncertainty.

159 PIXE measurements were performed at the Laboratory for Ion Beam Interactions, Rudjer Boskovic
160 Institute, Zagreb Croatia. A mass calibration of the PIXE set-up has been performed utilizing Micromatter
161 thin standards evaporated on thin Nucleopore (polycarbonate) filters. Micromatter standards are known

to have ±5% uncertainty on areal mass concentrations (Calzolai et al. 2008). One multielemental standard (Vienna Dust Standard V98, Air particulate matter on filter media) has also been measured. PIXE set up and the calibration technique is described in detail in (Manousakas et al. 2015).

Positive Matrix Factorization (PMF)

The basic equation that refers to the solution of the mass balance problem is common for all the utilized multivariate receptor models including PMF:

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

Where X_{ij} is the concentration of species j measured on sample i, p is the number of factors contributing to the samples, f_{kj} is the concentration of species j in factor profile k, g_{ik} is the relative contribution of factor k to sample i, and e_{ij} is error of the PMF model for the j species measured on sample i. The values of g_{ik} and f_{kj} are adjusted until a minimum value of Q for a given p is found. Q is defined as:

$$Q = \sum_{j=1}^{m} \sum_{i=1}^{n} \frac{{e_{ij}}^2}{{s_{ij}}^2} \quad (2)$$

Where s_{ij} is the uncertainty of the j_{th} species concentration in sample i, n is the number of samples, and m is the number of species. In some cases other auxiliary equations can be added in order to include a priori information such as well-known chemical profiles for certain sources (Paatero and Hopke 2008; Liao et al. 2015). The auxiliary equations define the auxiliary part Q^a of object function Q:

$$Q = \sum_{v=1}^{v} Q_v^a = \sum_{v=1}^{v} \frac{{r_v}^2}{{s_v}^2} \quad (3)$$

v enumerates the auxiliary equations. The residuals of auxiliary equations are denoted by r_v while s_v denotes the 'softness' of vth auxiliary equation, which is usually provided by the user (Paatero 1999). Those auxiliary equations can be applied to the solution in the form of constraints. Constraints can allow us identify a free rotation of the solution with better physical meaning than the original solution. In addition to that a number of rotations blocking zero values can be introduced to the matrix increasing thus the rotational stability of the solution.

In the current study Sc, P, Ga, Co and Ge were set as “bad” and thus were excluded from the analysis and Cr and As as “weak”. PM2.5 concentration was set as total variable.

A range of solutions were examined with different number of factors (4-8), but 6 factors were the maximum number of factors corresponding to meaningful sources. If the factors were increased some profiles were split creating profiles with no physical meaning, while the rotational instability of the solution increased significantly.

The data uncertainty was calculated by taking into account three individual errors: analytical error, PIXE calibration error and sampling error. The final uncertainty used in the model was the total uncertainty plus 1/3 LOD (Polissar et al. 1998; Lee et al. 2002; Kim and Hopke 2004; Li et al. 2004; Johnson et al. 2006b). The modeling uncertainty was adjusted to 5%. Values that were much lower than LOD were substituted by ½ LOD and the uncertainty was set as 5/6 of the LOD value.

Small datasets (number of cases close to 50) pose an extra challenge when used for PMF because the solution is strongly affected by rotational ambiguity and the overall uncertainty is increased. Previous versions of PMF offered only “bootstrapping” as a tool to estimate the effect of random errors and to some extent the rotational ambiguity in the dataset. Fpeak was a function for estimating the lower limit of rotational uncertainty (Reff et al. 2007). The latest version gives the user more advanced tools to evaluate rotational ambiguity, namely the displacement (DISP) and the bootstrap-displacement (BS-DISP) methods. BS estimates the random errors on the matrix, while DISP explicitly explores the rotational ambiguity (Paatero et al. 2014). BS-DISP being a combination of the two methods estimates both random errors and rotational ambiguity. When the rotational ambiguity of the solution is high the identity of the resolved factors may be exchanged or swapped during DISP and BS-DISP runs. This is expressed in the diagnostic result as a number of factor swaps. In addition, the number of cases used in BS-DISP is reported, which expresses the number of accepted resamples. If all cases were accepted this number is equal to 1 (base run) plus the number of bootstraps.

As the base run revealed that the solution had high rotational ambiguity indicating no well-defined solutions, some physical and chemical constraints were applied in order to arrive at a more stable solution. Rotational ambiguity can be reduced among other ways by constraining individual factor elements, either scores and/or loadings, toward zero values, prescribing values for ratios of certain key factor elements (Paatero et al. 2002). It must be emphasized that application of these techniques must be based on some external information about acceptable or evidence based factor profiles. The base

run can be modified (constrained) by the following methods: by setting some factor elements to a fixed value, by specifying lower and/or upper limits, by pulling a factor element towards a certain value and by setting an equation such as a ratio, a mass balance equation or a custom equation. Some constraints are considered strong such as setting a variable on a fixed value because they can perturb the model results significantly. Pulling towards a value has the advantage that if the equation is incompatible with the result (Q changes too much), then the pulling will fall sort of the target value (Paatero and Hopke 2008). In other words if a free rotation is not available then the pulled factor will never reach the user defined outcome. Setting constraints in the form of equations such as a ratio is regarded as a rather strong constraint but a lesser one than setting a particular value. For all other constraints apart from setting a certain value the model offers the option to set the maximum allowed dQ % change. Giving low maximum dQ% change ensures that significant perturbation of the model results are less probable.

After constraints were applied, BS results indicated very good reproducibility with the factors being reproduced 96-100 % of the times (88-100% before the application of the constraints). The number of bootstrap runs was set to 100 and the minimum correlation remained to the default value of 0.6. For the base run (initial unconstrained run) BS-DISP and DISP results showed 6 factor swaps for the lowest dQ change, while the cases accepted were 79%, indicating the presence of rotational ambiguity. Factor swaps are observed at the extreme case that factors change identity with no significant change in Q. The species selected to be displaced in BS-DISP, namely Na, S, Cl, K, V and PM2.5, were the key species for factor identification. It is suggested that in order to speed up computation only a small number of variables is selected for BS-DIS (Norris and Brown 2014). After the application of the constraints no factor swaps were observed for %dQ 0.5, 1 and 2 and the number of accepted cases rose to 99. The BS-DISP analysis results indicate that the solution (factor profiles) is stable. The maximum decrease in Q for the constrained run was 1%.

In our case not all constraints were introduced at once. The strongest were introduced first and when it was clear that the factor identity did not change, the weaker ones were applied as well. The dQ% was kept in almost all cases at the lowest value of 0.5%. The ratios applied were not significantly different from the initial run as they were not set to alter the factors but rather to keep them more rotationally stable.

Two of the constraints added to the analysis were in the form of elemental ratios and were derived in particular from the following equations: i) for shipping emissions: $V - 3\times Ni=0$, and ii) for biomass burning $S - 0.5\times K=0$. Al, Si, Ca and Ti were pulled up maximally in the mineral dust source, BC was pulled up in

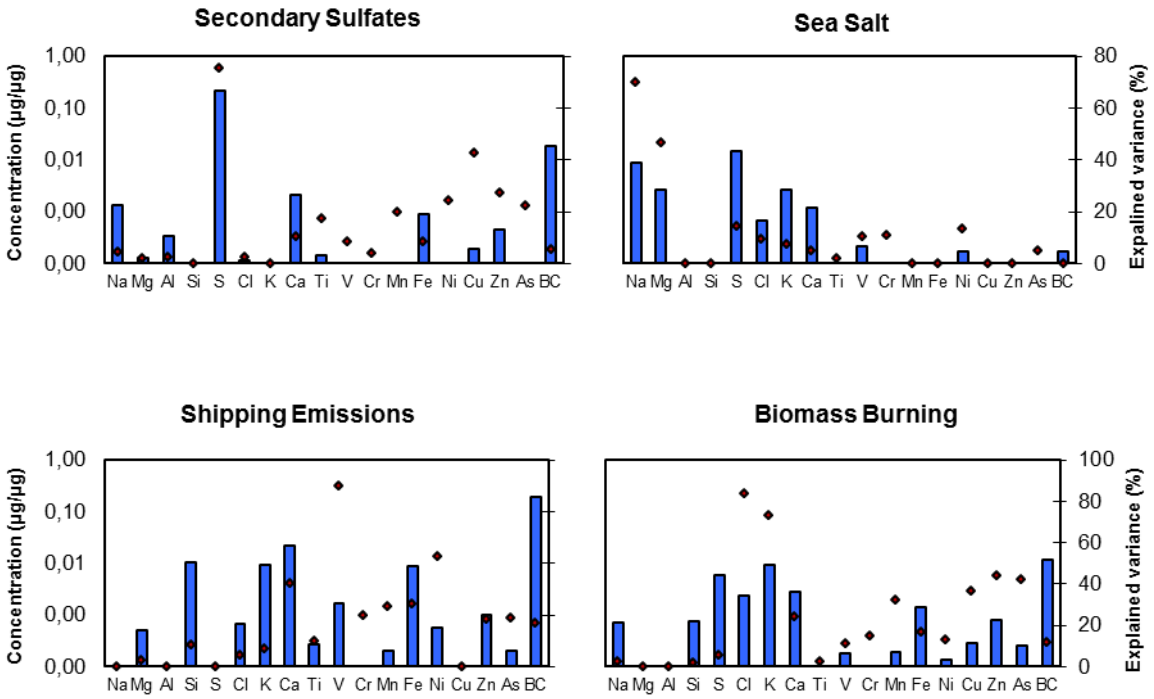
biomass burning and finally BC was set to zero in mineral dust. For shipping emissions V/Ni ratio the maximum allowed change in dQ was set to 5%. For all other constraints dQ was set to 0.5% making thus sure that no significant changes with respect to the unconstrained results would occur. V and Ni are well known tracers of crude oil (Viana et al. 2008, 2009; Karanasiou et al. 2009; Argyropoulos et al. 2013; Chuang et al. 2016), which is used mainly in shipping and industry. In Patras the most probable source of V and Ni is shipping, since industrial activity is low. For that reason V/Ni was set to 3 because that is the generally used ratio characteristic of shipping emissions in the Mediterranean region (Viana et al. 2009, 2014). As fresh biomass burning is known to take place in Patras mainly for domestic heating and scrap wood burning from farming (Kostenidou et al. 2013; Pikridas et al. 2013), the S/K ratio in the factor was set to 0.5 which is indicative of fresh biomass burning processes (Niemi et al. 2004; Viana et al. 2013). Potassium chloride (KCl) is known to occur in fresh smoke, whereas increased amounts of potassium sulfate (K_2SO_4) and nitrate (KNO_3) are present in aged smoke. The S/K ratio depends on a number of factors such as the wood type and the season of the year. It must be noted that the S/K ratio in the base run had a value close to 0.5, so even though the application of this constraint comes from a rather strong assumption is considered quite safe. Another constraint that could be used was in the Na/Cl ratio for sea salt; nevertheless, the ratio obtained in the initial run was much lower than 1.8, which is that of fresh sea salt, meaning that even though the sampling station is very close to sea, extensive Cl depletion has already taken place. Trying to set such a ratio is a good example of bad use of constraints. BC was pulled up in biomass burning factor from a value of zero in the initial run, which is not considered acceptable for any combustion source profile. BC was determined using a reflectometer with analog output (Manousakas et al. 2013). Such an instrument gives an estimate of the BC concentration but it is not capable of capturing with high precision small variations in BC concentrations. This fact can lead to a more “rough around the edges” distribution of BC in the PMF factors. The presence of other key compounds for the identification of this source like OC (Organic Carbon), would have helped in getting a clearer profile. The very low dQ change allowed ensures that no big changes were imposed on the factors. The strongest constrained applied was BC set to zero in the Mineral dust factor. That was considered necessary in order to introduce to the matrix more rotation blocking zero values. Mineral dust as a source is not expected to produce any BC so setting its concentration to zero is regarded as a rather safe option. Of course the possibility that some BC is transferred along with mineral dust cannot be excluded. This constraint might add a small subjectivity to the analysis. After all the constraints were applied, the factors prior and after their application were examined and compared to investigate the

changes that have occurred. No significant changes to either the profiles or the contributions were observed meaning that the identity of the factors remained the same in all cases.

Results and Discussion

Source apportionment Results

Six factors were found to be the maximum number of physically meaningful factors for the city of Patras. This number of fine aerosol sources is identified in a number of studies conducted in other Greek Urban environments (Mantas et al. 2014; Manousakas et al. 2015). Good correlation was observed between the model predicted and the real PM2.5 mass (R^2=0.80, y = 1,00x – 0.30). Theoretical Q and Q_{robust} displayed a 25% difference. As stated before the extra modeling uncertainty was set to 5%.



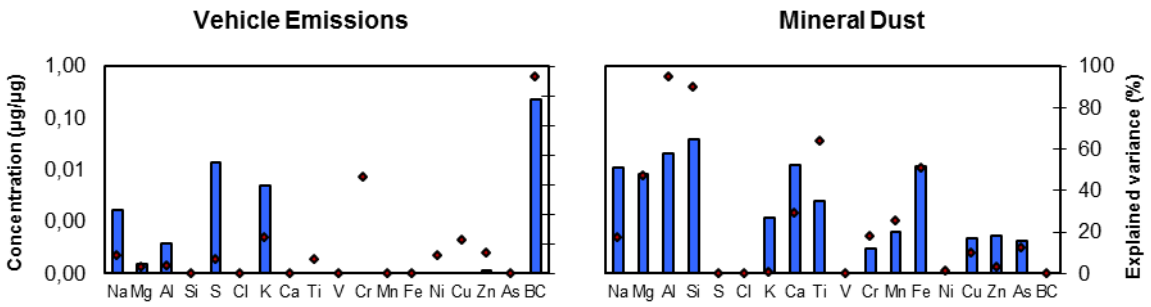


Figure 2. PMF factors profiles for the identified sources

The first factor (Figure 2) was identified as secondary sulfates because of the high abundance of S in the source profile (Figure 3). The profile also contains a substantial proportion of elements related to vehicular traffic, and in particular tire/break wear (such as Cu and Zn), indicating possible influence by non-exhaust traffic emissions as well. Secondary inorganic aerosols are formed from the reaction of H_2SO_4(g) and HNO_3(g) with NH_3, giving $(NH_4)_2SO_4$ and NH_4NO_3 accordingly (Stockwell et al. 2003; Squizzato et al. 2013). The main tracers of this source are SO_4^{2-} and NH_4^+ but NO_3^- may also be present in the source profile, when the factor represents inorganic aerosols in general rather than secondary sulfates exclusively (Yin et al. 2005; Viana et al. 2008). Since the formation of $(NH_4)_2SO_4$ and NH_4NO_3 is usually favored in different seasons, the concentrations of these two secondary species do not have high correlation and they tend to be apportioned in separate factors. Because the concentration of major ions was not available in the current dataset, S was used as the main tracer to identify this source, a practice that has been previously applied in other studies (Marcazzan et al. 2003). The absence of the major ions and especially NO_3^- can add some implications to the results because the mass of the secondary nitrates can be apportioned to others sources such as traffic or biomass burning. Secondary sulfates represent a high percentage in the mass of PM2.5 in Greek urban environments with regional origin. This result is in agreement with those reported for the Greater Athens Area (Pateraki et al. 2012; Mantas et al. 2014; Dimitriou et al. 2015). Secondary sulfates are in many cases attributed to long range transport events (Viana et al. 2008). Previous studies have stated that sulfates are ingredients of the "aged" air masses, because the oxidation of SO_2 to SO_4^{2-} is slow (Querol et al. 1998), and thus this aerosol component is more related to transported than local pollution (Eleftheriadis et al. 1998; Ricard and Jaffrezo 2002; Schaap et al. 2004; Saffari et al. 2013). High sulfate concentrations due to transport have been known to influence Greece, as documented by the high levels observed in background areas

in the Aegean (Gerasopoulos et al. 2006; Lazaridis et al. 2006). This source has the highest contribution along with vehicle emissions (7.21 μg/m^3, accounting for 33% of total PM2.5 mass on average, Figure 4).

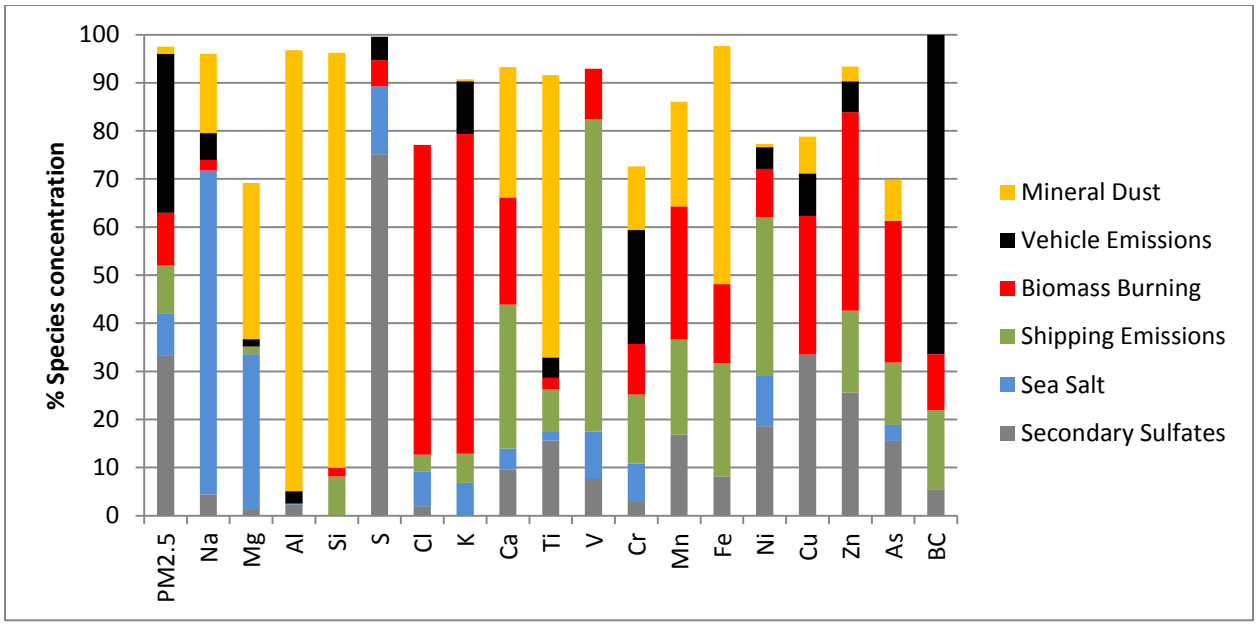


Figure 3. Source fingerprints

The factor representing sea salt has been identified by the high contribution of Na and Mg. Sea spray is commonly identified as a source of PM and especially PM10 in southern European Countries (Viana et al. 2008; Bove et al. 2016). Cl is present in the factor but in much lower concentration than expected for sea salt by stoichiometry. The Cl depletion in the factor indicates that the sea salt cannot be characterized as fresh but rather as aged. Fresh sea salt is almost exclusively found at the coarse particle fraction (Eleftheriadis et al. 2014), and that is probably the reason why fresh sea salt is not identified as a source despite that sampling in this study took place in very close proximity to the sea. Sea salt has a contribution of 8% which remains very stable throughout the seasons.

Shipping emissions are identified by the high presence of Ni and V in the factor along with the presence of Fe. All of them are common tracers of crude oil burning (Karanasiou et al. 2009; Argyropoulos et al. 2013). This source is common in the Mediterranean region (Waked et al. 2014; Amato et al. 2016). As mentioned before the ratio of V/Ni was constrained to 3 for this factor (was 2.6 in the initial base run), which is an indicative value for shipping emissions in the Mediterranean region. BC is present in the factor as expected in all combustion processes. Since there are no refineries or oil powered plants in the area it is safe to say that the contribution of this source can be attributed to shipping alone. The

contribution of this source is 10% of PM2.5 on annual basis and is higher during the warm season probably because of the higher vessel related activity that peaks during that period.

Biomass burning is resolved mainly by the presence of high K concentrations and to a lesser extent by presence of Cl in the factor (Diapouli et al. 2014). As mentioned biomass burning in the area of Patras is related mainly to farming processes, and specifically to scrap wood burning at olive groves and agricultural fires in the region. In addition to that, due to the economic crisis and the increased prices of diesel (diesel based central heating was the most common means of domestic heating in Greece), biomass burning use for domestic heating has dramatically increased in the last years (Saffari et al. 2013). K in fresh smoke is in the form of KCl which explains the high abundance of this element in the factor (Viana et al. 2013). Additionally it is quite common that plastic waste is burned in fires along with the biomass, leading to fresh particle formation with up to 21% concentration of Cl (Kostenidou et al. 2013). This source has 11% contribution and is manifested almost exclusively in the cold season (Table 1).

Table 1. Source contribution in μg/m^3 annually and for the cold and warm season of the year

	Secondary Sulfates	**Sea Salt**	**Shipping Emissions**	**Biomass Burning**	**Vehicle Emissions**	**Mineral Dust**
Annual	7.2	1.9	2.2	2.4	7.1	0.3
Warm	7.5	1.7	2.9	0.8	4.5	0.3
Cold	7.0	1.9	1.7	3.4	8.8	0.3

Vehicle exhaust emissions are traced by the high percentage of BC in the factor and the lower presence of Cu, Zn, K, and Cr. A vehicle non-exhaust factor has not been identified, probably because of the elevated position of the sampler and the small number of samples. The elevated position of the sampler made resuspension sources less influential. In addition, non-exhaust emissions generally contribute more to coarse rather than fine particles. The chemical profile obtained for this vehicle exhaust source, consists mainly of BC. The old technology buses, which are the only means of public transport in the city, as well as the many trucks that circulate in the port area, are expected to influence this source the most. The contribution of this source is 33% and it is higher on the cold period of the year probably due to the lower inversion layer, which limits the dilution of vehicular emissions during the winter season (Khillare and Sarkar 2012).

Mineral dust is a well-defined factor identified by the high concentration of the crustal elements such as Al, Si, Ca, Ti and Fe. Al, Si, Ca and Ti are expected to originate mainly from this source. The contribution of this source is very small (2%) and stable throughout the year. Even though this source is not expected to have high contribution in PM2.5(Eleftheriadis and Colbeck 2001) it is expected that it is also influenced by the high sampling location.

Generally no correlations are expected to exist between the sources, as each source contributes aerosol to the receptor independently from others. Examination of the scatter plot of secondary sulfates and shipping emissions contributions, reveals a lower edge in the data points, indicating that for high shipping emissions the secondary sulfates are also high (Figure 5). Ships can emit SO_3 which is transformed very fast to sulfates (Kim and Hopke 2008; Pandolfi et al. 2011). Combustion of residual oil will also produce particles containing vanadium (V) and nickel (Ni). Vanadium reacts with the oxygen from the combustion air surplus creating V_2O_5 that forms layers on the heat exchanger and other boiler and stack surfaces. The V_2O_5 acts as a catalyst in the temperature range of 500–800 ^{o}C, accelerating the SO_3 formation. SO_3 formed by this mechanism can exceed the amount produced in the flame by a factor of two or three (Kim and Hopke 2008). Therefore, part of secondary sulfates may be associated with shipping emissions. The absence of S from the shipping emissions might be another indication that partially shipping emissions are recognized by the model as secondary sulfates. The lack of ions in the analysis makes it hard for factors such as secondary sulfates to be very “selective”. That means that even though this source can be identified because of its high contribution, probably S originating from other processes is also accumulated in the factor.

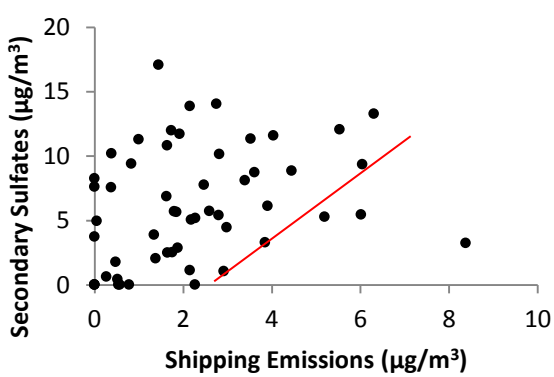


Figure 5. G space plot between secondary sulfates and shipping emissions

Result Evaluation

The constrained applied first helped "clear" the factor profile from the "noise" that is present in the form of elements that are not related to the source itself. This problem is of course more pronounced in the case of small datasets and especially when the constituents included in the analysis represent only a small fraction of total PM mass. The elements of crustal origin being pulled up in the mineral factor and BC pulled up in the biomass burning factor are examples of the first type of constraints. The second type are constraints applied for reducing the rotational ambiguity of the factors. Rotational ambiguity is decreased when a sufficient number of zero values in G and F matrixes are present (Paatero and Hopke 2008). Assigning fixed values to either F or G will have the same result as zero values but it might be a more subjective choice. Known elemental ratios fixed for certain source profiles and BC pulled to zero are examples of this type of constraints.

Table 2. Uncertainty tools' results for PM2.5 mass concentration (μg/m^3)

	Base Value	BS 5th	BS Median	BS 95th	BS-DISP 5th	BS-DISP Average	BS-DISP 95th	DISP Min	DISP Average	DISP Max
Secondary Sulfates	7.1	4.9	7.0	7.2	0.8	5.0	9.2	5.7	6.9	8.1
Sea Salt	1.8	0.0	3.0	3.4	0.0	2.1	4.1	0.9	1.8	2.6
Shipping Emissions	2.2	2.5	2.8	3.1	1.1	3.9	6.7	1.6	2.4	3.2
Biomass Burning	2.3	0.6	0.8	0.9	0.6	5.1	9.6	2.8	3.3	3.8
Vehicle Emissions	7.1	4.2	6.9	7.4	0.4	5.0	9.6	5.6	6.5	7.4
Mineral Dust	0.3	0.0	0.5	0.8	0.0	3.4	6.9	0.1	0.6	1.1

Table 3. Uncertainty tools' results for specific elements used as tracers of particular sources, where: SSU secondary sulfates, SEA sea salt, SHI shipping emissions, BIB biomass burning, VEH vehicle exhaust and MID mineral dust

	Source	Base Value	BS 5th	BS Median	BS 95th	BS-DISP 5th	BS-DISP Average	BS-DISP 95th	DISP Min	DISP Average	DISP Max
S	SSU	1.789	1.496	1.132	1.389	3.169	0.888	1.250	1.612	1.236	1.512
Na	SEA	0.200	0.141	0.162	0.234	1.084	0.104	0.145	0.186	0.130	0.165
V	SHI	0.005	0.004	0.001	0.003	0.005	0.000	0.002	0.004	0.003	0.004
K	BIB	0.271	0.217	0.025	0.068	0.103	0.148	0.210	0.273	0.217	0.244
BC	VEH	1.601	1.648	1.143	1.583	3.049	0.635	1.120	1.604	1.287	1.444
Si	MID	0.279	0.231	0.049	0.203	0.434	0.236	0.264	0.292	0.244	0.262

In Tables 2 and 3 the results from the uncertainty tools offered by PMF 5.0 are presented. The results provided in Table 2 are based on PM2.5 concentration for each source. Mineral dust has high uncertainty as expected by the low contributing mass concentration of this source. For secondary sulfates and vehicle emissions the results are quite stable as indicated by the three rotational tools. The higher uncertainty for BS and BS-DISP, indicates that a number of peak events affect these factors. Those events might not be resampled in the BS runs leading to higher uncertainty. The time series of 24h source contributions presented in Figure 4, reveals that such events do exist. A matter of discussion is whether such events should be considered as outliers and be subsequently removed from the analysis. It is noted here that after the first model run the results were evaluated in order to locate any possible outliers in the dataset. After the convergence of the PMF algorithm the program calculates the residuals and identifies the points of bad fit (Paatero and Tappert 1994). For the small number of such cases identified, their corresponding uncertainties were increased thus their significance in the fitting was decreased. Events of episodic nature such as forest fires or intense long range transport events may appear as outliers, but if they are down weighted, then a serious modeling error is made, leading to loss of critical information (Paatero et al. 2014).

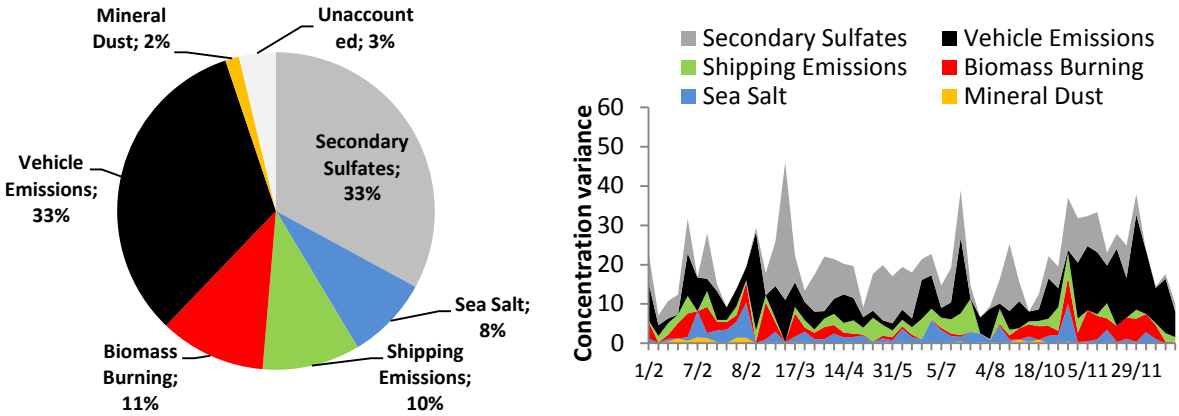


Figure 4. Source contributions and their time variability

Sea salt seems to have a similar uncertainty level as secondary sulfates and vehicle emissions, with BS tests yielding the highest uncertainty. Unlike the sources discussed so far, in the case of sea salt resampling is not assured for both low (or even zero values) and peak events instead of peak events only, affecting the uncertainty. Shipping emissions seem to be more sensitive to BS-DISP even though BS and DISP when tested separately produce similar results. Generally speaking sources identified only by a small number of elements are much more sensitive to DISP based analysis. Biomass burning has the highest uncertainty for all three tests. Biomass burning has either very high (cold season) or very low/zero (warm season) contributions and it is identified mainly by one element (K), thus it is very sensitive both to resampling and displacement. Generally speaking high uncertainties are to be expected when small datasets are used (Paatero et al. 2014).

The uncertainties provided by the rotational tools correspond to profile uncertainties. The uncertainty given on Table 2 regarding PM2.5 applies also to estimates of average PM2.5 contribution from each factor because all modeling is performed under the constraint that average G values must be normalized for each factor with respect to mass (Paatero et al. 2014). A straightforward method to calculate uncertainty for individual (24-h) contribution values does not yet exist, although intercomparison studies has given some indications towards this direction (Belis et al. 2015). An approach using regression analysis is proposed in this work. The error of the source contribution was calculated based on the standard error of the coefficients of a multiple regression between the daily PM2.5 concentration (independent variable) and the six source contributions for any given day (dependent variables). The regression approach assumes that all the factors that explain the mass are identified. However, if a significant portion of the mass that is not directly correlated with the species that are in the PMF

436 analysis is missed, the source contributions will be overestimated. This might be an important source of
437 additional uncertainty. Results are shown in Table 4. It must be noted that this method captures only
438 one part of the uncertainty, because it does not include the error arising from the profile uncertainty
439 and the rotational ambiguity. Using this method we can investigate how well the daily contributions can
440 recreate the daily PM mass. Since the correlation of the model predicted mass and the true PM mass is
441 high (R^2= 0.80) it is believed that this method could provide an estimate of this uncertainty.

442

Table 4. Sources contribution and corresponding error in μg/m^3

	Contribution	Err
Secondary Sulfates	7.2	0.1
Sea Salt	1.9	0.6
Shipping Emissions	2.2	0.6
Biomass Burning	2.4	0.5
Vehicle Emissions	7.1	0.2
Mineral Dust	0.3	0.2

443

444 The errors calculated by this method are quite low indicating a good model fit. Mineral dust because of
445 its very low contribution has a high error assigned to its contribution.

446 In Table 3 the uncertainty of the main elements used as tracers for each source are presented. Those
447 results are very useful because they are needed in order to evaluate which factors may be more reliably
448 attributed to sources, by showing which components were fitted confidently and which components
449 were too uncertain to be considered for source identification. All elements uncertainties are considered
450 reasonably low and thus the factors can be indeed identified as specific PM sources. The only element
451 that shows quite high uncertainty for BS is K probably because of the variability in concentrations it has,
452 making it very sensitive on resampling. DISP result for the same element is much more stable.

453

454 *Conclusions*

455 A small dataset of 55 samples was used in order to identify the sources of PM2.5 in Patras. The target of
456 the study, appart from source identification and characterizarion, was to evaluate the stability of the

sollution resulting from the use of a small dataset, using the tools offerd by PMF 5.0. When no constraints are applied, the results from the base run were characterized by high uncertainty, to the extent that no sources could be attributed to the factors. After the application of the constraints the solution was stable and could be interpreted in a meaningful manner.

The constraints applied were in the form of elemental ratios and in particular for shipping emissions (V - 3×Ni=0) and for biomass burning (S - 0.5×K=0). Al, Si, Ca and Ti were pulled up maximally in the mineral dust source, BC was pulled up in biomass burning and finally BC was set to zero in mineral dust. The change in Q after the application of the constraints was low (<1%).

Six sources were identified and were namely biomass burning (11%), shipping emissions (10%), sea salt (9%), secondary sulfates (34%), mineral dust (2%) and vehicle emissions (34%). This is the first time that the contribution of shipping emissions is quantified in a Greek urban area with port. This information can be used for the development of more effective measures for the improvement of the air quality of the area.

BS, DISP and BS-DISP results showed that the profile uncertainty for the elements used as tracers for factor identification was quite low, providing strong evidence for the identification of the factors. PM2.5 concentration in the profiles has high uncertainty in some cases, a fact that is attributed mainly to the small dataset and the high level of uncertainty assigned to PM2.5 when set as total variable (uncertainty is tripled in that case). The case of biomass burning revealed that sources with high seasonal variability are especially vulnerable to resampling techniques in small datasets.

Overall the results indicate that the use of the tools offered by PMF 5.0 and the consideration of appropriate constraints significantly improve the solution even for data sets of limited number of samples. It is very important to fully report the uncertainty of the solution in source apportionment studies especially if small datasets are used. In any case it should be noted that this work does not encourage the use of small datasets, and datasets with a larger number of samples should be used whenever possible.

Acknowledgements

This work has been supported by the European Community as an Integrating Activity 'Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)' under EC contract no. 227012. Financial

support from the EnTeC FP7 Capacities program (REGPOT-2012-2013-1, FP7, ID: 655 316173) and K. Karatheodori program (Grand D165) are also acknowledged.

References

Amato F, Alastuey A, Karanasiou A, Lucarelli F, Nava S, Calzolai G, et al. AIRUSE-LIFE + : a harmonized PM speciation and source apportionment in five southern European cities. Atmos Chem Phys. 2016;16:3289–309.

Amiridis V, Zerefos C, Kazadzis S, Gerasopoulos E, Eleftheratos K, Vrekoussis M, et al. Impact of the 2009 Attica wild fires on the air quality in urban Athens. Atmos Environ [Internet]. Elsevier Ltd; 2012;46:536–44. Available from: http://dx.doi.org/10.1016/j.atmosenv.2011.07.056

Argyropoulos G, Grigoratos T, Voutsinas M, Samara C. Concentrations and source apportionment of PM10 and associated elemental and ionic species in a lignite-burning power generation area of southern Greece. Environ Sci Pollut Res Int [Internet]. 2013 Oct [cited 2014 Jan 30];20(10):7214–30. Available from: http://www.ncbi.nlm.nih.gov/pubmed/23644947

Athanasopoulou E, Tombrou M, Russell AG, Karanasiou A, Eleftheriadis K, Dandou A. Implementation of road and soil dust emission parameterizations in the aerosol model CAMx: Applications over the greater Athens urban area affected by natural sources. J Geophys Res Atmos. 2010;115(17):1–21.

Belis CA, Karagulian F, Larsen BR, Hopke PK. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. Atmos Environ [Internet]. Elsevier Ltd; 2013 Apr [cited 2014 Jun 3];69:94–108. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231012010540

Belis CA, Pernigotti D, Karagulian F, Pirovano G, Larsen BR, Gerboles M, et al. A new methodology to assess the performance and uncertainty of source apportionment models in intercomparison exercises. Atmos Environ [Internet]. Elsevier Ltd; 2015;119:35–44. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231015302478

Bove MC, Brotto P, Calzolai G, Cassola F, Cavalli F, Fermo P, et al. PM10 source apportionment applying PMF and chemical tracer analysis to ship-borne measurements in the Western Mediterranean. Atmos Environ. 2016;125:140–51.

Calzolai G, Chiari M, Lucarelli F, Mazzei F, Nava S, Prati P, et al. PIXE and XRF analysis of particulate matter samples: an inter-laboratory comparison. Beam Interact with Mater Atoms [Internet]. 2008 May [cited 2013 Feb 14];266(10):2401–4. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0168583X08002772

Chuang M-T, Chen Y-C, Lee C-T, Cheng C-H, Tsai Y-J, Chang S-Y, et al. Apportionment of the sources of high fine particulate matter concentration events in a developing aerotropolis in Taoyuan, Taiwan. Environ Pollut [Internet]. Elsevier Ltd; 2016;214:273–81. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0269749116303116

Cohen DD, Stelcer E, Santos FL, Prior M, Thompson C, Pabroa PCB. Fingerprinting and source apportionment of fine particle pollution in Manila by IBA and PMF techniques: A 7-year study. X-

Ray Spectrom [Internet]. 2009 Jan [cited 2013 Feb 14];38(1):18–25. Available from: http://doi.wiley.com/10.1002/xrs.1112

Diapouli E, Popovicheva O, Kistler M, Vratolis S, Persiantseva N, Timofeev M, et al. Physicochemical characterization of aged biomass burning aerosol after long-range transport to Greece from large scale wildfires in Russia and surrounding regions, Summer 2010. Atmos Environ [Internet]. Elsevier Ltd; 2014 Oct [cited 2014 Dec 2];96:393–404. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231014005858

Dimitriou K, Remoundaki E, Mantas E, Kassomenos P. Spatial distribution of source areas of PM2.5 by Concentration Weighted Trajectory (CWT) model applied in PM2.5 concentration and composition data. Atmos Environ [Internet]. Elsevier Ltd; 2015;116:138–45. Available from: http://www.sciencedirect.com/science/article/pii/S1352231015301631

Eleftheriadis K, Balis D, Ziomas I, ColBeck I, Manalis N. Atmospheric aerosol and gaseous species in Athens, Greece. Atmos Environ [Internet]. 1998 Jun;32(12):2183–91. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231097004123

Eleftheriadis K, Colbeck I. Coarse atmospheric aerosol: Size distributions of trace elements. Atmos Environ. 2001;35(31):5321–30.

Eleftheriadis K, Ochsenkuhn KM, Lymperopoulou T, Karanasiou A, Razos P, Ochsenkuhn-Petropoulou M. Influence of local and regional sources on the observed spatial and temporal variability of size resolved atmospheric aerosol mass concentrations and water-soluble species in the Athens metropolitan area. Atmos Environ [Internet]. Elsevier Ltd; 2014 Nov [cited 2014 Dec 18];97:252–61. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231014006074

Endresen Ø, Sorgard E, Sundet JK, Dalsoren SB, Isaksen ISA, Berglen TF, et al. Emission from international sea transportation and environmental impact. J Geophys Res [Internet]. 2003 [cited 2015 Jan 14];108(D17):4560. Available from: http://doi.wiley.com/10.1029/2002JD002898

Fridell E, Steen E, Peterson K. Primary particles in ship emissions. Atmos Environ [Internet]. 2008 Feb [cited 2014 Apr 24];42(6):1160–8. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231007009648

Gerasopoulos E, Kouvarakis G, Babasakalis P, Vrekoussis M, Putaud J, Mihalopoulos N. Origin and variability of particulate matter (PM10) mass concentrations over the Eastern Mediterranean. Atmos Environ [Internet]. 2006 Aug [cited 2014 May 6];40(25):4679–90. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231006004043

Grigoropoulos KN, Nastos PT, Ferentinos G. Spatial distribution of PM 1 and PM 10 during Saharan dust episodes in Athens , Greece. Adv Sci Res. 2009;3:59–62.

Hopke PK. A Review of Receptor Modeling Methods for Source Apportionment. J Air Waste Manage Assoc [Internet]. 2016;2247(January):10962247.2016.1140693. Available from: http://www.tandfonline.com/doi/full/10.1080/10962247.2016.1140693

Hopke PK, Ito K, Mar T, Christensen WF, Eatough DJ, Henry RC, et al. PM source apportionment and health effects : 1 . Intercomparison of source apportionment results. J Expo Sci Environ Epidemiol. 2006;275–86.

Ito K, Christensen WF, Eatough DJ, Henry RC, Thurston GD. PM source apportionment and health effects : 2 . An investigation of intermethod variability in associations between source-apportioned fine particle mass and daily mortality in Washington , DC. J Expo Sci Environ Epidemiol. 2006;2000:300–10.

Johnson KS, de Foy B, Zuberi B, Molina LT, Molina MJ, Xie Y, et al. Aerosol composition and source apportionment in the Mexico City Metropolitan Area with PIXE/PESA/STIM and multivariate analysis. Atmos Chem Phys Discuss [Internet]. 2006a May 19;6(3):3997–4022. Available from: http://www.atmos-chem-phys-discuss.net/6/3997/2006/

Johnson KS, de Foy B, Zuberi B, Molina LT, Molina MJ, Xie Y, et al. Aerosol composition and source apportionment in the Mexico City Metropolitan Area with PIXE/PESA/STIM and multivariate analysis. Atmos Chem Phys Discuss [Internet]. 2006b May 19;6(3):3997–4022. Available from: http://www.atmos-chem-phys-discuss.net/6/3997/2006/

Karanasiou A, Diapouli E, Cavalli F, Eleftheriadis K, Viana M, Alastuey A, et al. On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols. Atmos Meas Tech. 2011;4(11):2409–19.

Karanasiou A, Mihalopoulos N. Air Quality in Urban Environments in the Eastern Mediterranean. In: Viana M, editor. Handb Environ Chem 26. Berlin: Springer; 2013. p. 219–38.

Karanasiou AA, Siskos PA, Eleftheriadis K. Assessment of source apportionment by Positive Matrix Factorization analysis on fine and coarse urban aerosol size fractions. Atmos Environ [Internet]. Elsevier Ltd; 2009 Jul [cited 2013 Feb 13];43(21):3385–95. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231009002854

Khillare PS, Sarkar S. Airborne inhalable metals in residential areas of Delhi, India: distribution, source apportionment and health risks. Atmos Pollut Res [Internet]. 2012 Jan 1 [cited 2014 Mar 10];3:46–54. Available from: http://www.atmospolres.com/articles/Volume3/issue1/APR-12-004.pdf

Kim E, Hopke PK. Source Apportionment of Fine Particles in Washington, DC, Utilizing Temperature-Resolved Carbon Fractions. J Air Waste Manage Assoc [Internet]. 2004 Jul [cited 2014 Apr 4];54(7):773–85. Available from: http://www.tandfonline.com/doi/abs/10.1080/10473289.2004.10470948

Kim E, Hopke PK. Source characterization of ambient fine particles at multiple sites in the Seattle area. Atmos Environ [Internet]. 2008 Aug [cited 2014 May 27];42(24):6047–56. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231008003087

Kim E, Larson T V, Hopke PK, Slaughter C, Sheppard LE, Claiborn C. Source identification of PM2.5 in an arid Northwest U.S. City by positive matrix factorization. Atmos Res [Internet]. 2003 May [cited 2013 Feb 20];66(4):291–305. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0169809503000255

Kioumourtzoglou M-A a, Coull B a, Dominici F, Koutrakis P, Schwartz J, Suh H. The impact of source contribution uncertainty on the effects of source-specific PM2.5 on hospital admissions: a case study in Boston, MA. J Expo Sci Environ Epidemiol [Internet]. Nature Publishing Group; 2014;24(4):365–71. Available from: http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=4063325&tool=pmcentrez&rendertype=abstract\nhttp://dx.doi.org/10.1038/jes.2014.7

Kostenidou E, Florou K, Kaltsonoudis C, Tsiflikiotou M, Vratolis S, Eleftheriadis K, et al. Sources and chemical characterization of organic aerosol during the summer in the eastern Mediterranean. Atmos Chem Phys. 2015;15(19):11355–71.

Kostenidou E, Kaltsonoudis C, Tsiflikiotou M, Louvaris E, Russell LM, Pandis SN. Burning of olive tree branches: a major organic aerosol source in the Mediterranean. Atmos Chem Phys Discuss [Internet]. 2013 Mar 19 [cited 2013 Mar 20];13(3):7223–66. Available from: http://www.atmos-chem-phys-discuss.net/13/7223/2013/

Lazaridis M, Eleftheriadis K, Smolik J, Colbeck I, Kallos G, Drossinos Y, et al. Dynamics of fine particles and photo-oxidants in the Eastern Mediterranean (SUB-AERO). Atmos Environ [Internet]. 2006 Oct [cited 2014 Dec 18];40:6214–28. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231005005029

Lee JH, Yoshida Y, Turpin BJ, Hopke PK, Poirot RL, Lioy PJ, et al. Identification of Sources Contributing to Mid-Atlantic Regional Aerosol. J Air Waste Manage Assoc [Internet]. 2002 Oct [cited 2014 Apr 4];52(10):1186–205. Available from: http://www.tandfonline.com/doi/abs/10.1080/10473289.2002.10470850

Li Z, Hopke PK, Husain L, Qureshi S, Dutkiewicz V a., Schwab JJ, et al. Sources of fine particle composition in New York city. Atmos Environ [Internet]. 2004 Dec [cited 2013 Feb 7];38(38):6521–9. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231004008192

Liang CS, Duan FK, He K Bin, Ma YL. Review on recent progress in observations, source identifications and countermeasures of PM2.5. Environ Int [Internet]. Elsevier Ltd; 2016;86:150–70. Available from: http://dx.doi.org/10.1016/j.envint.2015.10.016

Liao H-T, Chou CC-K, Chow JC, Watson JG, Hopke PK, Wu C-F. Source and risk apportionment of selected VOCs and PM2.5 species using partially constrained receptor models with multiple time resolution data. Environ Pollut [Internet]. Elsevier Ltd; 2015;205:121–30. Available from: http://www.sciencedirect.com/science/article/pii/S0269749115002699

Manousakas M, Diapouli E, Papaefthymiou H, Migliori a., Karydas a. G, Padilla-Alvarez R, et al. Source apportionment by PMF on elemental concentrations obtained by PIXE analysis of PM10 samples collected at the vicinity of lignite power plants and mines in Megalopolis, Greece. Nucl Instruments Methods Phys Res Sect B Beam Interact with Mater Atoms [Internet]. Elsevier B.V.; 2015;349:114–24. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0168583X15001548

Manousakas M, Eleftheriadis K, Papaefthymiou H. Characterization of PM10 Sources and Ambient Air Concentration Levels at Megalopolis City (Southern Greece) Located in the Vicinity of Lignite-Fired Plants. Aerosol Air Qual Res [Internet]. 2013 [cited 2013 Apr 19];13(3):804–17. Available from: http://www.aaqr.org/Doi.php?id=2_AAQR-12-09-OA-0239&v=13&i=3&m=6&y=2013

Manousakas M, Papaefthymiou H, Eleftheriadis K, Katsanou K. Determination of water-soluble and insoluble elements in PM2.5 by ICP-MS. Sci Total Environ [Internet]. Elsevier B.V.; 2014 Jun 30 [cited 2014 Jul 9];493C:694–700. Available from: http://www.ncbi.nlm.nih.gov/pubmed/24992462

Mantas E, Remoundaki E, Halari I, Kassomenos P, Theodosi C, Hatzikioseyian A, et al. Mass closure and source apportionment of PM2.5 by Positive Matrix Factorization analysis in urban Mediterranean environment. Atmos Environ [Internet]. Elsevier Ltd; 2014;94:154–63. Available from: http://dx.doi.org/10.1016/j.atmosenv.2014.05.002

Marcazzan GM, Ceriani M, Valli G, Vecchi R. Source apportionment of PM10 and PM2.5 in Milan (Italy) using receptor modelling. Sci Total Environ [Internet]. 2003 Dec 30 [cited 2014 Mar 14];317(1-3):137–47. Available from: http://www.ncbi.nlm.nih.gov/pubmed/14630417

Moon KJ, Han JS, Ghim YS, Kim YJ. Source apportionment of fine carbonaceous particles by positive matrix factorization at Gosan background site in East Asia. Environ Int. 2008;34(5):654–64.

Niemi J V., Tervahattu H, Vehkamäki H, Kulmala M, Koskentalo T, Sillanpää M, et al. Characterization and source identification of a fine particle episode in Finland. Atmos Environ. 2004;38:5003–12.

Norris G, Brown S. EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. EPA PMF 50 Man. 2014;

Ostro B, Tobias A, Karanasiou A, Samoli E, Querol X, Rodopoulou S, et al. The risks of acute exposure to black carbon in Southern Europe: results from the MED-PARTICLES project. Occup Environ Med [Internet]. 2014 Nov 10 [cited 2014 Dec 13];1–7. Available from: http://www.ncbi.nlm.nih.gov/pubmed/25385880

Paatero P. The Multilinear Engine—A Table-Driven, Least Squares Program for Solving Multilinear Problems, Including the n -Way Parallel Factor Analysis Model. J Comput Graph Stat [Internet]. 1999;8(October 2014):854–88. Available from: http://dx.doi.org/10.1080/10618600.1999.10474853

Paatero P, Eberly S, Brown SG, Norris G a. Methods for estimating uncertainty in factor analytic solutions. Atmos Meas Tech [Internet]. 2014 Mar 27 [cited 2014 Jun 12];7(3):781–97. Available from: http://www.atmos-meas-tech.net/7/781/2014/

Paatero P, Hopke PK. Rotational tools for factor analytic models. J Chemom [Internet]. 2008 Feb [cited 2014 Jun 15];23(2):91–100. Available from: http://doi.wiley.com/10.1002/cem.1197

Paatero P, Hopke PK, Song X-H, Ramadan Z. Understanding and controlling rotations in factor analytic models. Chemom Intell Lab Syst [Internet]. 2002 Jan;60(1-2):253–64. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0169743901002003

Paatero P, Tappert U. Positive Matrix Factorization : A non-negative factor model with optimal utilization of error stimates od data values. Environmetrics. 1994;5:111–26.

Pandolfi M, Gonzalez-Castanedo Y, Alastuey A, de la Rosa JD, Mantilla E, de la Campa a S, et al. Source apportionment of PM(10) and PM(2.5) at multiple sites in the strait of Gibraltar by PMF: impact of shipping emissions. Environ Sci Pollut Res Int [Internet]. 2011 Feb [cited 2014 Apr 24];18(2):260–9. Available from: http://www.ncbi.nlm.nih.gov/pubmed/20623340

Pateraki S, Assimakopoulos VD, Bougiatioti A, Kouvarakis G, Mihalopoulos N, Vasilakos C. Carbonaceous and ionic compositional patterns of fine particles over an urban Mediterranean area. Sci Total Environ [Internet]. Elsevier B.V.; 2012;424:251–63. Available from: http://dx.doi.org/10.1016/j.scitotenv.2012.02.046

Pikridas M, Tasoglou A, Florou K, Pandis SN. Characterization of the origin of fine particulate matter in a medium size urban area in the Mediterranean. Atmos Environ [Internet]. Elsevier Ltd; 2013 Dec [cited 2014 Jan 9];80:264–74. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231013006018

Polissar V, Hopke PK, Paatero P, Malm WC, Sisler JF. Atmospheric aerosol over Alaska 2 . Elemental composition and sources. J Geophys Res. 1998;103:19045–57.

Querol X, Alastuey A, Puicercus JA, Mantilla E, Ruiz CR, Lopez-Soler A, et al. Seasonal Evolution of Suspended Particles Around a Large Coal-Fired Power Station: Chemical Characterization. Atmos Environ. 1998;32(4):719–31.

Querol X, Alastuey A, Rodriguez S, Plana F, Ruiz CR, Cots N, et al. PM10 and PM2 . 5 source apportionment in the Barcelona Metropolitan area , Catalonia , Spain. Atmos Environ. 2001;35:6407–19.

Reff A, Eberly SI, Bhave P V. Receptor Modeling of Ambient Particulate Matter Data Using Positive Matrix Factorization: Review of Existing Methods. J Air Waste Manage Assoc [Internet]. 2007 Feb [cited 2013 Aug 1];57(2):146–54. Available from: http://www.tandfonline.com/doi/abs/10.1080/10473289.2007.10465319

Ricard V, Jaffrezo J. Two years of continuous aerosol measurements in northern Finland. J Geophys Res.

2002;107:ACH 10 1–17.

Saffari A, Daher N, Samara C, Voutsa D, Kouras A, Manoli E, et al. Increased biomass burning due to the economic crisis in Greece and its adverse impact on wintertime air quality in Thessaloniki. Environ Sci Technol [Internet]. 2013 Dec 3;47(23):13313–20. Available from: http://www.ncbi.nlm.nih.gov/pubmed/24187932

Saraga DE, Makrogkika A, Karavoltsos S, Sakellari A, Diapouli E, Eleftheriadis K, et al. A Pilot Investigation of PM Indoor/Outdoor Mass Concentration and Chemical Analysis during a Period of Extensive Fireplace Use in Athens. Aerosol Air Qual Res [Internet]. 2015;15(7):2485–95. Available from: http://www.aaqr.org/Doi.php?id=1_AAQR-15-02-SIUAHE-0100&v=15&i=7&m=12&y=2015

Schaap M, van Loon M, ten Brink HM, Dentener FJ, Builtjes PJH. Secondary inorganic aerosol simulations for Europe with special attention to nitrate. Atmos Chem Phys [Internet]. 2004 Jun 15;4(3):857–74. Available from: http://www.atmos-chem-phys.net/4/857/2004/

Squizzato S, Masiol M, Brunelli A, Pistollato S, Tarabotti E, Rampazzo G, et al. Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy). Atmos Chem Phys [Internet]. 2013 Feb 19 [cited 2014 Mar 21];13(4):1927–39. Available from: http://www.atmos-chem-phys.net/13/1927/2013/

Stockwell WR, Kuhns H, Etyemezian V, Green MC, Chow JC, Watson JG, et al. The Treasure Valley secondary aerosol study II: modeling of the formation of inorganic secondary aerosols and precursors for southwestern Idaho. Atmos Environ [Internet]. 2003 Feb [cited 2014 Apr 23];37(4):525–34. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231002008956

Viana M, Amato F, Alastuey A, Querol X, Moreno T, Dos Santos SG, et al. Chemical tracers of particulate emissions from commercial shipping. Environ Sci Technol [Internet]. 2009 Oct 1;43(19):7472–7. Available from: http://www.ncbi.nlm.nih.gov/pubmed/19848163

Viana M, Hammingh P, Colette A, Querol X, Degraeuwe B, Vlieger I De, et al. Impact of maritime transport emissions on coastal air quality in Europe. Atmos Environ [Internet]. Elsevier Ltd; 2014 Jun [cited 2014 Jun 4];90:96–105. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231014002313

Viana M, Kuhlbusch T a. J, Querol X, Alastuey A, Harrison RM, Hopke PK, et al. Source apportionment of particulate matter in Europe: A review of methods and results. J Aerosol Sci [Internet]. 2008 Oct [cited 2013 Jan 30];39(10):827–49. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0021850208001018

Viana M, Reche C, Amato F, Alastuey a., Querol X, Moreno T, et al. Evidence of biomass burning aerosols in the Barcelona urban environment during winter time. Atmos Environ [Internet]. Elsevier Ltd; 2013 Jun [cited 2014 Sep 9];72:81–8. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1352231013001325

Waked a., Favez O, Alleman LY, Piot C, Petit JE, Delaunay T, et al. Source apportionment of PM10 in a north-western Europe regional urban background site (Lens, France) using positive matrix factorization and including primary biogenic emissions. Atmos Chem Phys. 2014;14(7):3325–46.

Yin J, Allen AG, Harrison RM, Jennings SG, Wright E, Fitzpatrick M, et al. Major component composition of urban PM10 and PM2.5 in Ireland. Atmos Res [Internet]. 2005 Dec [cited 2014 Feb 21];78(3-4):149–65. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0169809505001249