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

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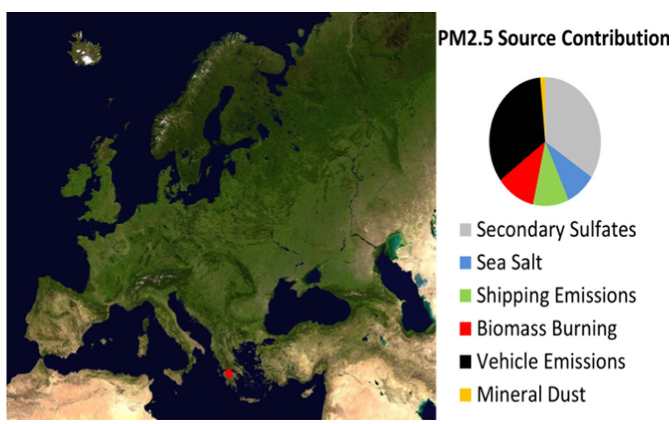
HIGHLIGHTS

- Results showed that the new tools in PMF 5.0 are very useful in the case of small datasets
- The application of the appropriate constraints may be needed to reduce the rotational ambiguity of the solution for small datasets
- The case of biomass burning revealed that sources with high seasonal variability are vulnerable to resampling techniques in small datasets
- Biomass burning (11%), shipping (10%), sea salt (9%), sulfates (34%), mineral dust (2%) and vehicle emissions (34%)

GRAPHICAL ABSTRACT



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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

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PM2.5
PMF uncertainty

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.

1. 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.

2. Experimental

2.1. Sampling

Patras is a medium size city located in Peloponnese peninsula (Fig. 1). 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.

The sampler was installed in the city center, on the roof of a high public building (>20 m) 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 24 h 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 Sartorius PB211D microbalance (readability of 0.1 μg) (Manousakas et al., 2014). Before