## PMF source apportionment for fine and coarse PM in Athens, Greece: Evolution of source contributions over the last decade

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Particulate pollution remains a significant air environmental problem in big urban centres in Europe and around the world. The development of effective control policies calls for the identification of the main particulate matter (PM) sources, as well as the quantification of their contribution to elevated concentration levels. The city of Athens has been known to face severe air pollution problems due both to the presence of multiple particle sources and to the meteorological conditions and topography that promote pollutants build-up. The presence of significant natural sources further complicates the efforts to apply effective mitigation measures and to ensure compliance with air quality guidelines. The objective of the present work was to identify the major PM sources in the Athens area, quantify their relative contribution to coarse and fine particle concentrations and examine their evolution over the last decade.

Source apportionment by positive matrix factorization (PMF) analysis was performed on two PM<sub>10</sub>/PM<sub>25</sub> datasets from 2002 and 2012. Both datasets covered warm and cold period. The 2002 measurement campaign included 24-hr gravimetric measurements from three urban residential sites. The collected teflon filters were analysed for a number of elements by electrothermal atomic absorption spectrometry (Cd, Pb, V, Ni, Mn, Cr, Cu, Fe and Al) and flame atomic absorption spectrometry (Ca, Mg, K and Na), as well as for major anions (Cl<sup>-</sup>,  $NO_3^-$  and  $SO4^{2-}$ ) by ion chromatography. In addition, black carbon (BC) data were obtained by means of an aethalometer (AE-9, Maggee Sci). The 2012 campaign was conducted at two urban background sites. 24-hr gravimetric measurements were performed with two different filter substrates (teflon and quartz) in order to allow for a more extensive chemical characterization of the aerosol fractions. Elemental composition was again quantified by electrothermal and flame atomic absorption spectrometry. Ionic species (Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>,  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $CI^{-}$ ) were quantified by ion chromatography, while elemental (EC) and organic (OC) carbon were also measured by thermal-optical methodology.

Two-dimensional Positive Matrix Factorisation (PMF) has been applied to each dataset. Details on input data preparation are provided in Karanasiou et al. (2009). Two PMF models were used, PMF2 (Version 4.2) and EPA PMF 3.0, and the obtained results were compared. Analysis was performed for different numbers of factors

and the best solution was chosen based on goodness of fit parameters (Q value and the explained variation of the matrix F) as well as by examining the obtained factors profiles with respect to the possibility of associating them with specific source. In addition, multiple values of Fpeak (in the range -2.0 to 2.0) were examined in order to explore different rotations of the solutions.

In general the two models applied showed good agreement of results. Vehicular traffic was found the main contributor to fine particle concentrations, with marine aerosol also playing a major role. Fossil fuel combustion and traffic contributions were similar. Coarse particles concentrations seemed unaffected by all combustion-related sources and were attributed to a large extent to natural sources (sea salt, soil). (Figure 1)

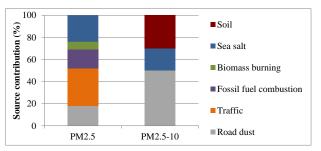


Figure 1. Relative contribution (%) of each source to PM concentration levels (Year 2002).

PMF analysis on the 2012 dataset is still in progress but initial results indicated a differentiation in PM source contributions over the last decade. This is also evident by the reduced concentration levels, attributed to a decrease in anthropogenic emissions either because of efficient mitigation measures (new-technology "cleaner" vehicles, traffic regulations etc.) and/or lower anthropogenic activity due to the financial crisis of the last two years. The final results are expected to provide an interesting insight into the present air pollution situation in the city and the potential "new" major contributors to the observed daily exceedances of air quality guidelines.

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