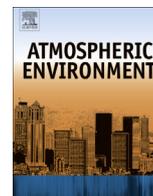




Contents lists available at ScienceDirect

# Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

## Mass closure and source apportionment of PM<sub>2.5</sub> by Positive Matrix Factorization analysis in urban Mediterranean environment



E. Mantas<sup>a</sup>, E. Remoundaki<sup>a,\*</sup>, I. Halari<sup>b</sup>, P. Kassomenos<sup>d</sup>, C. Theodosi<sup>c</sup>,  
A. Hatzikioseyan<sup>a</sup>, N. Mihalopoulos<sup>c</sup>

<sup>a</sup>Laboratory of Environmental Science and Engineering, School of Mining and Metallurgical Engineering, National Technical University of Athens, Heroon Polytechniou 9, 15780 Zografou, Greece

<sup>b</sup>Hellenic Open University, School of Science and Technology, Tsamadou 13-15, 26222 Patras, Greece

<sup>c</sup>Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, PO Box 2208, 71003 Heraklion, University of Crete, Greece

<sup>d</sup>Laboratory of Meteorology, Department of Physics, University of Ioannina, University Campus GR-45110, Ioannina, Greece

### HIGHLIGHTS

- Simultaneous determination of ionic, carbonaceous and mineral fraction of PM<sub>2.5</sub>.
- Sulfates and organic carbon are the most abundant, equally distributed in PM<sub>2.5</sub> mass.
- The sum of SIA, OM, EC, Dust, MIN and SS >80% of the PM<sub>2.5</sub> mass.
- PMF results: Six factors include both main natural and anthropogenic sources.
- Atmospheric dynamics & aerosol ageing processes play key roles in factors profiles.

### ARTICLE INFO

#### Article history:

Received 28 November 2013

Received in revised form

29 April 2014

Accepted 2 May 2014

Available online 4 May 2014

#### Keywords:

Secondary inorganic aerosol

Organic matter

Elemental carbon

Mass closure

Source apportionment

EPA PMF

### ABSTRACT

A systematic monitoring of PM<sub>2.5</sub> was carried out during a period of three years (from February 2010 to April 2013) at an urban site, at the National Technical University of Athens campus. Two types of 24-h PM<sub>2.5</sub> samples have been collected: 271 samples on PTFE and 116 samples on quartz filters. Daily PM<sub>2.5</sub> concentrations were determined for both types of samples. Total sulfur, crustal origin elements and elements of a major crustal component (Al, Si, Fe, Ca, K, Mg, Ti) trace elements (Zn, Pb, Cu, Ni, P, V, Cr, Mn) and water soluble ions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) were determined on the PTFE samples. Organic carbon (OC), elemental carbon (EC) and water soluble ions were determined on the quartz samples. For the mass closure six components were considered: Secondary Inorganic Aerosol (SIA), Organic Matter (OM), Elemental Carbon (EC), Dust, Mineral anthropogenic component (MIN) and Sea Salt (SS). SIA and OM contributed in the mass of PM<sub>2.5</sub> almost equally: 30–36% and 30% respectively. EC, SS and MIN accounted for 5, 4 and 3% respectively of the total PM<sub>2.5</sub> mass. Dust accounted for about 3–5% in absence of dust transport event and reached a much higher percentage in case of dust transport event. These contributions justify at least 80% of the PM<sub>2.5</sub> mass. Source apportionment analysis has been performed by Positive Matrix Factorization. The combination of the PMF results obtained by both data sets lead to the definition of six factors: 1. SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, OC (industrial/regional sources, secondary aerosol) 2. EC, OC, K and trace metals (traffic and heating by biomass burning, locally emitted aerosol). 3. Ca, EC, OC and trace metals (urban-resuspended road dust reflecting exhaust emissions), 4. Secondary nitrates 5. Na, Cl (marine source) 6. Si, Al, Ti, Ca, Fe (Dust transported from Sahara). These factors reflect not only main sources contributions but also underline the key role of atmospheric dynamics and aerosol ageing processes in this Mediterranean environment.

© 2014 Elsevier Ltd. All rights reserved.

### 1. Introduction

Atmospheric particulate matter in urban environments is considered one of the highest priority pollutants for which legislation is becoming more stringent: PM<sub>2.5</sub> annual target value is set

\* Corresponding author.

E-mail address: [remound@metal.ntua.gr](mailto:remound@metal.ntua.gr) (E. Remoundaki).

at 25  $\mu\text{g}/\text{m}^3$ , not to be exceeded for more than 35 days in a calendar year, EU Directive (2008/50/EC). To evaluate the risks of exposure to atmospheric aerosols and provide the necessary scientific support to elaborate abatement strategies for air quality improvement, quantitative data of fine PM composition over long time-series are necessary.

The Greater Athens Area (GAA), a region of 450  $\text{km}^2$  where half of the population of the country is accumulated (>4 million), is characterized by enhanced concentrations of locally emitted (Kanakidou et al., 2011) and long range transported (Koulouri et al., 2008; Perrone et al., 2013; Remoundaki et al., 2013b) particulate matter, absence of precipitation from spring to late autumn, favorable conditions for the formation of photochemical smog and unfavorable topography for dispersion of air pollutants. On a yearly basis the northern sector, which covers Central and Eastern Europe as well as part of the Western Turkey, is the most important, accounting for almost two thirds of the air masses arriving at GAA. Southern winds, responsible for the transport of Saharan dust during dust events, are very frequent during spring and autumn, contributing up to 25% of the prevailing air masses (Kassomenos et al., 1998; Papadopoulou et al., 2009).

For the above reasons, the urban environment of the greater Athens area presents particular interest for the quantitative monitoring, not only of the daily concentrations, but also of the composition of the fine fraction of atmospheric particulate matter.

To our knowledge, simultaneous quantitative estimation of secondary inorganic and carbonaceous components as well as of the contributions of major natural sources such as Saharan dust and sea salt in  $\text{PM}_{2.5}$  for long time series and the corresponding mass closure are not reported in literature for the greater Athens area.

Source apportionment studies of PM in the urban Mediterranean environment are scarce and recent (Carvalho and Freitas, 2011; Perrone et al., 2013; Pey et al., 2009, 2013). There is one relative study for Athens concerning a limited data set of  $\text{PM}_{2.5}$  which does not include chemical speciation for elements associated with “main factors” as those related to secondary aerosol and the contribution of dust (Karanasiou et al., 2009). Although factor analysis for the fine PM fraction by Varimax-Rotated Factor Analysis was presented in a recent paper using data sets of ionic and carbonaceous fractions, elements of crustal origin (dust tracers) and characteristic heavy metals were not determined and thus not included in the analysis (Pateraki et al., 2012).

When the PM charge is simultaneously controlled by local emission sources, long range transport, intense oxidative conditions and intricate atmospheric dynamics, it may be expected that the number of factors extracted, after a source apportionment analysis, does not reflect individual emission sources but mixtures of different sources together with the results of some atmospheric processes (Amato et al., 2009; Pey et al., 2009).

The present paper reports quantitative results of secondary inorganic and carbonaceous components content, as well as of the contributions of major natural sources such as Saharan dust and sea salt in  $\text{PM}_{2.5}$ . Twenty four hour  $\text{PM}_{2.5}$  samples have been collected over a period of three years at an urban site in Athens. Two types of 24-h samples have been collected: 271 samples on PTFE membranes and 116 samples on high purity quartz filters. In total 20 species were determined on the PTFE and 10 species on the quartz samples.

The data sets, both in terms of number of samples and in terms of species detected, are among the very few and the most complete reported in literature for  $\text{PM}_{2.5}$  in an urban Mediterranean environment. Mass closure and source apportionment results by Positive Matrix Factorization are presented and compared for both data sets.

## 2. Materials and methods

### 2.1. $\text{PM}_{2.5}$ sampling and concentrations determinations

The methodology followed is already presented in detail in previous papers (Remoundaki et al., 2011, 2013a, 2013b) and is briefly described below.

Twenty four hours aerosol samples were collected at the top of the building of the School of Mining and Metallurgical Engineering at the National Technical University of Athens campus at 14 m above ground level. Two types of samples have been collected: 271 24-h samples on PTFE membranes and 116 24-h samples on high purity quartz filters. The sampling point is fully exposed to wind and free all around of other obstacles (Remoundaki et al., 2011, 2013a, 2013b). Aerosol samples were collected on PTFE membranes ( $\text{PM}_{2.5}$  air monitoring membranes Whatman) between February 2010 and November 2012. Between February 2010 and May 2012 the sampling span was 3 samples/week. Between May 2012 and November 2012 the sampling span was 2 samples/week.

For organic carbon (OC) and elemental carbon (EC) determinations high purity quartz filters were used pre-fired at 450° for 12 h. Sampling on quartz filters was carried out between February 2011 and April 2013 with a span of 1 sample/week. Thus, for a long period, 2–3 PTFE samples and one quartz sample were collected on different dates of every week. The sampling has been interrupted for two two-month periods for sampler calibration and maintenance: from December 2010 to February 2011 and from October 2011 to November 2011.

Between May and November 2012, eighty PTFE samples of  $\text{PM}_{2.5}$  have been collected using the same sampling protocol at the ground meteorological station of NTUA in parallel to those collected at 14 m in order to compare ground level concentrations of  $\text{PM}_{2.5}$  to those monitored at 14 m above ground level.

In order to determine  $\text{PM}_{2.5}$  concentrations, the filters were weighted before and after sampling according to the procedure described in EN12341 (Annex C) using a Mettler Toledo MS105 with a resolution of 10  $\mu\text{g}$  in the air conditioned weighing room of the laboratory. Filter blanks and blank field samples were also prepared and analyzed together with samples.

### 2.2. Analytical techniques

#### 2.2.1. Elemental concentrations determinations by WDXRF

The elemental determinations for Al, Si, Fe, Ca, K, Ti and S have been carried out by WDXRF (Thermo ARL Advant XP, sequential XRF) with Rh X-ray tube at 30 kV, 30 mA. Single element standards purchased from Micromatter have been used for calibration for each element. Two NIST standard SRM 2783 have been also used as calibration points and for calibration verification. Following WDXRF analysis, one half of the filter was extracted with 10 mL of ultrapure water for ion chromatography analysis and acid digestion was performed to the second part for trace metals analysis.

#### 2.2.2. Ion chromatography

The concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  were determined by ion chromatography (IC). Ions were determined by a Metrohm 732 IC Separation Center connected to a 732 IC conductivity detector and 753 Suppressor Module for anions determination as described in Remoundaki et al. (2013a).

#### 2.2.3. ICP-MS

Trace metals: Zn, Pb, Cu, Ni, V, Cr and Mn have been determined by ICP-MS Perkin Elmer (Elan 6100), Dual Detector Mode: Pulse. The calculated detection limits were: 5  $\mu\text{g}/\text{L}$  for Zn and 1  $\mu\text{g}/\text{L}$  for the other trace elements.

Download English Version:

<https://daneshyari.com/en/article/6339539>

Download Persian Version:

<https://daneshyari.com/article/6339539>

[Daneshyari.com](https://daneshyari.com)