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Sources of atmospheric aerosol from long-term measurements (5 years) of chemical composition in Athens, Greece

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HIGHLIGHTS

- First long-term continuous daily record of Athens' aerosol chemical composition.
- Study period includes years before and during the Greek economic recession.
- Identification and quantification of fine aerosol sources' contribution.
- Discrimination between regional and local emission sources.

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ABSTRACT

To identify the sources of aerosols in Greater Athens Area (GAA), a total of 1510 daily samples of fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) aerosols were collected at a suburban site (Penteli), during a five year period (May 2008–April 2013) corresponding to the period before and during the financial crisis. In addition, aerosol sampling was also conducted in parallel at an urban site (Thissio), during specific, short-term campaigns during all seasons. In all these samples mass and chemical composition measurements were performed, the latest only at the fine fraction. Particulate organic matter (POM) and ionic masses (IM) are the main contributors of aerosol mass, equally contributing by accounting for about 24% of the fine aerosol mass. In the IM, nss-SO_4^{-2} is the prevailing specie followed by NO_3^- and NH_4^+ and shows a decreasing trend during the 2008–2013 period similar to that observed for PM masses. The contribution of water in fine aerosol is equally significant (21 ± 2%), while during dust transport, the contribution of dust increases from 7 ± 2% to 31 ± 9%. Source apportionment (PCA and PMF) and mass closure exercises identified the presence of six sources of fine aerosols: secondary photochemistry, primary combustion, soil, biomass burning, sea salt and traffic. Finally, from winter 2012 to winter 2013 the contribution of POM to the urban aerosol mass is increased by almost 30%, reflecting the impact of wood combustion (dominant fuel for domestic heating) to air quality in Athens, which massively started in winter 2013.

1. Introduction

Aerosols constitute a significant component of the atmospheric system. They are emitted in the atmosphere by variable sources, through diverse formation and subsequent transformation mechanisms, resulting in a mixture of chemical characteristics. Particulate matter is of the most highlighted atmospheric pollutants, due to its effect on local and regional deterioration of air quality, visibility reduction (Kanakidou et al., 2005) and global climate system (Seinfeld and Pandis, 1998).

Aerosols aerodynamically smaller than 2.5 μm ($PM_{2.5}$) are of particular concern because of the significant contribution to detrimental health effects (Dockery and Pope, 1994; Ostro et al., 2006), since they act as carriers for toxicants and mutagenic components (Beddows et al., 2004) and, owing to their size, are able to penetrate cell membranes (Li et al., 2003), permeating easier into human organism (Salma et al., 2002; Bell et al., 2009). As a consequence, one of the major challenges in aerosol science is the knowledge of fine particle chemical properties and the identification and quantification of emission sources at local and regional scales.

The city of Athens is situated in the Mediterranean Basin, which constitutes a crossroad of three continents, being highly influenced by ambient particles with both natural and anthropogenic origin deriving from marine boundary layer, Saharan desert and European mainland (Gerasopoulos et al., 2011; Perrone et al., 2011; Bougiatioti et al.,

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2013). Several studies have focused on $PM_{2.5}$ concentration levels and composition, in Athens, during sampling periods of a few months to one year (e.g., Sillanpää et al., 2006; Karageorgos and Rapsomanikis, 2007; Theodosi et al., 2011; Pateraki et al., 2012; Remoundaki et al., 2013; Kassomenos et al., 2014); some of which included a chemical mass closure exercise. Nevertheless, the source identification and apportionment of particulate matter is more appropriately attained through a combination of source apportionment tools including Positive Matrix Factorization (PMF) (Belis et al., 2013 and references therein). This kind of source apportionment technique is rare in Athens, Greece (Karanasiou et al., 2009; Mantas et al., 2014) and relatively recent in the Eastern Mediterranean Basin, being reported by a limited number of authors (Kocak et al., 2009; Kocak et al., 2011; Ozturk et al., 2012).

The present paper uses for the first time, to our knowledge, an uninterrupted 5-year daily sampling dataset in Penteli, which constitutes a regional suburban site, in order to perform a chemical mass closure exercise, including carbonaceous materials, ionic species and, for a selected number of samples trace metals. The inter-annual trends (from 2008 to 2013) of the analyzed species are studied, in order to investigate the effects of the economic crisis on the quality of the air. Furthermore, all the acquired data are analyzed through a variety of source apportionment techniques including chemical mass closure, principal component analysis (PCA) and PMF to identify the sources of fine aerosols at the studied suburban site in Athens and determine the contribution of each source to $PM_{2.5}$ mass on a five-year basis. Additionally, four campaigns with simultaneous measurements at the suburban station (Penteli) and an urban site (Thissio) were performed. Based on the differences between the two sites, the relative contribution of regional and local aerosol sources is quantified. PMF analysis is applied for the first time on a long-term data set, while concurrent characterization of local and regional aerosol sources is performed. Additionally, in parallel with the investigation of the inter-annual variability of air pollutant levels over Athens, the acquired PMF results are compared to posterior (prior to economic crisis i.e., 2008) PMF analysis performed for the studied area, in order to reach to more secure results regarding the impacts of the economic crisis on the air quality of Athens as, during the last years (2008 and onwards), a new era characterized by intense wood burning for domestic heating has begun.

2. Methodology

2.1. Sampling sites

The implementation of this analysis is based on the operation of two ground based stations in Athens. Penteli station (38° 2.94′ N, 23° 51.78′ E, 495 m a.s.l.) is located at 17 km from the center of Athens in a suburban location, within the premises of the National Observatory of Athens at Penteli (Fig. 1). A detailed description of the sampling site is provided by Paraskevopoulou et al. (2014). The second station is at the National Observatory of Athens premises at Thissio (38° 0.00′ N, 23° 43.48′ E, 110 m a.s.l.), located on top of a hill down-town Athens, surrounded mostly by a pedestrian zone and populated neighborhoods, while to the S–SE sector it adjoins with the Filopappou and Acropolis Hills (Fig. 1). Thissio station, located in the historical center of Athens, is considered an urban station which reflects the average pollution of the city. The major sources of air pollution affecting the two sites at different degrees, are expected to be vehicular emissions and residential heating. A detailed description of the Athens' morphology, meteorology and dominant transport patterns is provided by Kanakidou et al. (2011) and Melas et al. (1998) and references therein.

2.2. Sampling and mass measurement

A total of 1510 samples of fine and separately of coarse aerosols were collected at the Penteli site, during a five year period (May 2008–April 2013), on quartz fiber filters (4.7 cm, Whatman QMA). The collection was conducted using a Dichotomous Partisol sampler (R&P Co) during most of the period (90% of the sampling time) and a Partisol FRM Model 2000 $PM_{2.5}$ & PM_{10} air samplers (R&P Co) (10% of the sampling time). A detailed overview of the sampling and the applied samplers is given by Paraskevopoulou et al. (2014).

Parallel aerosol collection was also conducted at Thissio during specific, short-term campaigns, in order to identify and discriminate between local and regional aerosol sources and contribution. Overall, four experimental campaigns were organized during different seasons of the year: from 28 June to 1 August 2011 (summer campaign), from 16 January to 17 February 2012 (winter campaign), from 9 March to 5 April 2012 (spring campaign) and from 11 January to 8 February 2013

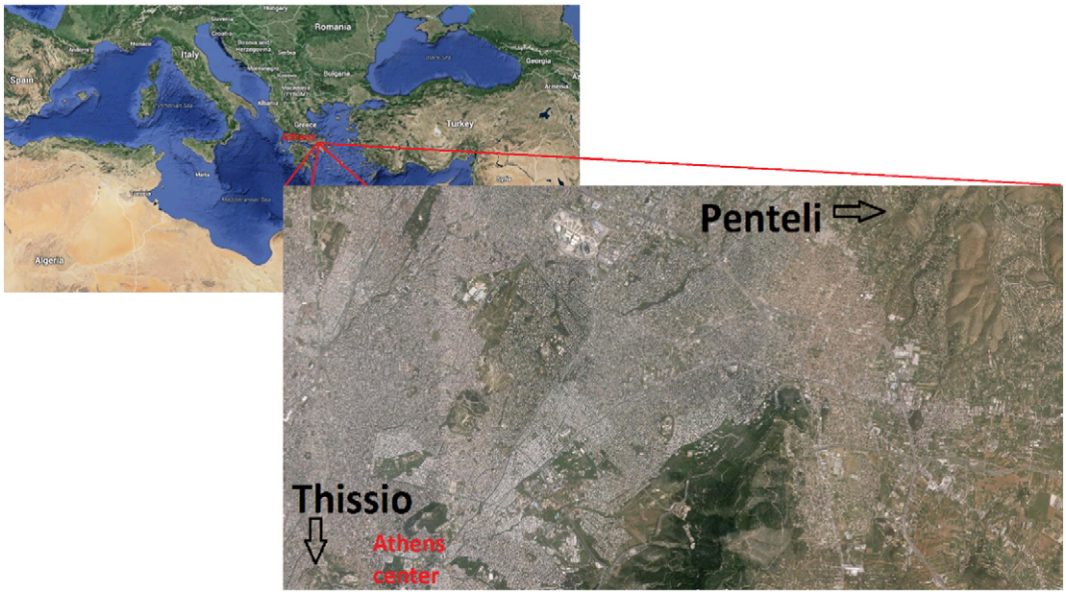

Fig. 1. Map indicating the sampling sites at Thissio (urban location) and Penteli (suburban location).