Atmospheric Environment 97 (2014) 252–261

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

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

Konstantinos Eleftheriadis [a, *], Klaus M. Ochsenkuhn [b], Theopisti Lymperopoulou [c], Angeliki Karanasiou [a, d], Panayiotis Razos [b], Maria Ochsenkuhn-Petropoulou [b, c]

[a] Institute of Nuclear & Radiological Sciences & Technology, Energy & Safety, Environmental Radioactivity Lab, N.C.S.R. "Demokritos", Agia Paraskevi, 15310 Athens, Greece
[b] National Technical University of Athens, Department of Chemical Engineering, Laboratory of Inorganic and Analytical Chemistry, Iroon Polytechniou 9, 15773 Athens, Greece
[c] National Technical University of Athens, Department of Chemical Engineering, Centre of Environment & Quality of Life, Iroon Polytechniou 9, 15773 Athens, Greece
[d] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain

HIGHLIGHTS

- $PM_{2.5}$ and PM_{10} mass concentrations at three sites of Greater Athens documented.
- The coarse aerosol fraction exhibits a spatial variability up to a factor of three.
- Size distribution of major ions show $PM_{2.5}$ includes a tale end of their coarse mode.
- SO_4^{2-} and NH_4^+ mainly peak in the fine PM, while NO_3^- also appears in coarse mode.
- Origin of $PM_{2.5}$ mass and ions do not show strong dependence on wind direction.

ARTICLE INFO

Article history:
Received 9 March 2014
Received in revised form
2 August 2014
Accepted 5 August 2014
Available online 6 August 2014

Keywords:
PM_{10}
$PM_{2.5}$
Spatial variability
Urban aerosol size distribution
Ammonium sulphate
Calcium carbonate

ABSTRACT

The variability of common aerosol species in large Metropolitan urban areas is a major air quality issue with strong health impacts of large populations. PM_{10} and $PM_{2.5}$ particulate matter samples were obtained at three sites characteristic of industrial, urban traffic and sub-urban residential areas in the Athens basin. Samples were analysed for anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+) using ion chromatography. The spatial and temporal variability for the particulate matter (PM) concentration mass and water-soluble ionic species concentrations for the investigated sites were studied. Mean PM fine concentration levels were 20% higher at the industrial and the central urban areas compared to those in the suburban area (24.2 μg/m^3). The mean values for the coarse fraction at those two sites were two to three times higher compared to those at the suburban site (12.4 μg/m^3). Comparable concentration levels of most species were observed in all areas, while SO_4^{2-} and NO_3^- differ at a significant level. Furthermore, the average size distributions of the mass and individual ions at the suburban site (NCSR Demokritos) showed a bimodal size distribution. SO_4^{2-} and NH_4^+ have their main peak in the fine fraction while NO_3^- showed equal distribution on the fine and coarse mode. . Good correlation was found for SO_4^{2-} and NO_3^- with Ca^{2+} and Na^+ with Cl^- for the coarse fraction in the industrial area. NH_4^+ was closely correlated with SO_4^{2-} in the fine particles and in all areas. For the urban site the best correlations in coarse particulates were reported between Na^+/Mg^{2+}–Cl^-, Ca^{2+}/Mg^{2+}–SO_4^{2-}, explained by neutralization of acidic aerosol by soil dust and sea salt in the coarse fraction. Moreover, time weighted concentrations roses at the industrial and urban sites, showed no significant directional dependence, indicating either uniform generation of mainly the coarse species within the metropolitan area or major influence of the regional background for the fine aerosol species.

* Corresponding author.
E-mail address: eleftheriadis@ipta.demokritos.gr (K. Eleftheriadis).

http://dx.doi.org/10.1016/j.atmosenv.2014.08.013
1352-2310/

1. Introduction

Airborne particulate matter, PM has been intensively studied mainly because of its impact on health (Katsouyanni et al., 2001), climate, visibility, ecosystems and building materials. Especially the fine particles with a diameter smaller than 2.5 μm ($PM_{2.5}$) are of great scientific interest, as they have been found to be associated with respiratory diseases and cardiovascular morbidity and mortality after long-term and short-term exposure periods (Katsouyanni et al., 2001; Anderson et al., 2012; Samoli et al., 2014). Atmospheric aerosol represents a complex mixture of inorganic substances and hundreds of different organic compounds (Seinfeld and Pandis, 1998). Aerosol properties such as the particle size and chemical composition can be used to study the sources and formation processes of atmospheric aerosols. For example, the dominance of mineral components implies the predominance of natural sources, while the high content of soot in the fine mode indicate that particles originated from combustion sources.

Sulphate, nitrate and ammonium are considered to be one of the major contributors to atmospheric aerosols whereas in European urban areas, sulphate and nitrate concentrations might reach up to 21–28% of PM_{10} and 22–37% of $PM_{2.5}$ (Putaud et al., 2010). These species are formed in the atmosphere through the oxidation of the emitted SO_2 and NO_x, as well as the direct emission of NH_3 gases. Whereas NO_3^- may be present in the gas phase as nitric acid vapour, SO_4^{2-} is nearly exclusively found in the aerosol phase (Tsitouridou et al., 2003; Danalatos and Glavas, 1999). Acidic aerosols can react with other species such as NH_3 gas and Na^+ to form neutralized ammonium and sodium salts: ammonium sulfate [$(NH_4)_2SO_4$], bisulfate (NH_4HSO_4), ammonium nitrate (NH_4NO_3), sodium nitrate ($NaNO_3$) and ammonium chloride (NH_4Cl) (Querol et al., 2001; Lazaridis et al., 2006; Kai et al., 2006). The acidic aerosols have been recognized as one of the most important pollutant with harmful impact on human health, climate and ecological system, according to the WHO guidelines (2000) and the REVIHAAP Project: WHO Technical Report (2013). Consequently, evidence is emerging that secondary constituents of PM, such as nitrate and sulphate have a negative impact on health (Reiss et al., 2007). Since inhalation is dependent on particle size, atmospheric PM fractions as well as detailed size-fractionated characterization of inorganic particles in PM is of great interest (Mitsakou et al., 2007). However, information is limited on the mass size distributions of inorganic aerosols in Europe and understanding is limited on how the mass size distributions of aerosol species, such as nitrate and sulphate, vary under different conditions, emission sources and processes (Kopanakis et al., 2012; Harrison et al., 2004).

The aim of this study was the investigation of the water-soluble chemical composition of size-fractionated aerosol samples ($PM_{10\text{-}2.5}$, $PM_{2.5}$), which had been collected from an urban area (Patission, centre of Athens) and an industrial area (Aspropyrgos, Elefsis) in the Attica basin by using a low volume sampler with a "Gent" stacked filter unit as well as the detailed size distribution of these species at suburban area (Demokritos, Ag. Paraskevi) using a Berner type low-pressure cascade impactor. Ion chromatography was used, for the determination of the anions Cl^-, NO_3^-, SO_4^{2-} and the cations Na^+, K^+, Ca^{2+} and Mg^{2+} and NH_4^+. Furthermore, the mass concentrations levels of airborne particulate matter and ionic species were studied for the three sites and the dependence on meteorological parameters of the determined anions and cations was investigated by using time weighted concentration roses.

2. Experimental

2.1. Sampling

Atmospheric aerosol samples were collected from June 2005 to September 2006 with a frequency of 1 sample/week at three ambient air quality-monitoring stations shown in Fig. 1 (Patission-urban area situated at the city centre, Elefsina-industrial area and Demokritos suburban area).

For the collection of airborne particulates from the urban and industrial area into two size fractions, $PM_{2.5}$ (fine) and $PM_{10\text{-}2.5}$ (coarse) a low volume air sampler, "Gent" stacked filter unit (sampling rate: 16.7 L min^{-1}) with two polycarbonate filters (Ø 47 mm, 0.4 μm and 8 μm pore size, Nuclepore) was used. This sampler features a PM_{10} inlet and separates the PM_{10} aerosol matter into two fractions by sequential filtration through two Nuclepore filters, the first with 8 μm pores and the second with 0.4 μm pores. The first filter collects so-called coarse particles with aerodynamic diameters between 2 and 10 μm, the second collects fine particles <2 μm (Maenhaut et al., 1994; Ochsenkuhn et al., 2008; Hopke et al., 1997). The sampler was installed at a height of 3 m above ground level. Sampling was performed on working and weekend days with duration of 24 h or 48 h starting at midnight. Additionally, size-segregated samples were collected at a suburban area (Demokritos) using a Berner type low-pressure cascade impactor (BLPI 25/0.018/2). Sampled aerosol was classified in 10 fractions with 50% cut-off sizes given at 0.026, 0.062, 0.110, 0.173, 0.262, 0.46, 0.89, 1.77, 3.4 and 6.8 μm. The impactor had an inlet providing approximately 15 μm upper cut-off particle size and operated at a flow rate of 25 L min^{-1}. Sampling was performed at intervals close to 24 h.

2.2. Analytical procedure

Loaded and unloaded polycarbonate filters were weighed after drying in a desiccator for 48 h at room temperature (25 °C). The filters were pre- and post-weighed to determine the gravimetric masses of collected materials using a 5 decimal XS205 Mettler balance placed in a controlled temperature and humidity room. One quarter of the collected polycarbonate filters was leached with 15 mL of high purity water (18.3 MΩ cm^{-1}) in an ultra-sonic apparatus for 30 min. The extracts were stored in precleaned polyethylene bottles in the refrigerator at 4 °C until analysis was carried out. Leaching solutions of blank filters were regularly checked and used for the analysis. Ion chromatography (IC) was used for the determination of the ionic constituents (K^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}). The instrumentation and the analytical conditions as well as all reagents and standard solutions used, are reported elsewhere (Ochsenkuhn et al., 2008).

3. Results and discussion

Although water soluble ionic species have been studied extensively in various localities there are certain aspects of the observed variability in their concentration levels, which are not well understood. Thorough understanding of physico-chemical aerosol processes in the micro-scale and aerosol evolution in the context of regional and global scale circulation and cycling is required. The above is a challenging task considering that tropospheric aerosol is nonlinearly dependent on the meteorological and chemical variables that govern its behaviour (Spyridaki et al., 2006; Raes et al., 2000).

The Athens Metropolitan area is an important densely populated source of anthropogenic pollutants in a climatic sensitive