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Seasonal variability of $PM_{2.5}$ and PM_{10} composition and sources in an urban background site in Southern Italy

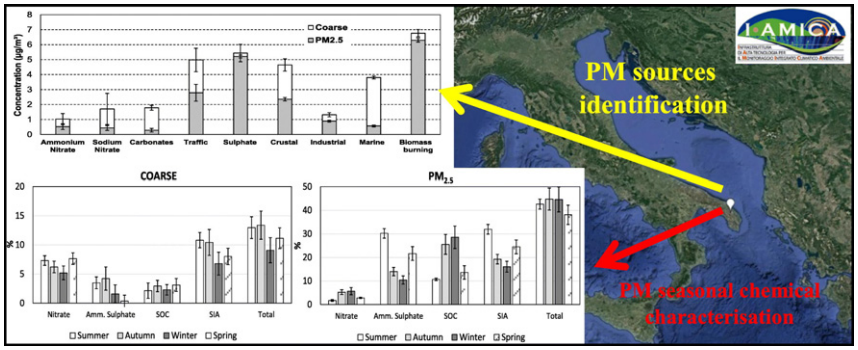
D. Cesari [a,*], G.E. De Benedetto [b], P. Bonasoni [c], M. Busetto [c], A. Dinoi [a], E. Merico [a], D. Chirizzi [b], P. Cristofanelli [c], A. Donateo [a], F.M. Grasso [a], A. Marinoni [c], A. Pennetta [b], D. Contini [a]

[a] Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, 73100 Lecce, Italy
[b] Dipartimento di Beni Culturali, Università del Salento, 73100 Lecce, Italy
[c] Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, 40129 Bologna, Italy

HIGHLIGHTS

- Composition and sources of $PM_{2.5}$ and $PM_{2.5–10}$ are investigated in Southeastern Italy.
- Secondary organic and inorganic components were 43% of $PM_{2.5}$ with opposite seasonal trends.
- Two forms of nitrate were observed: sodium nitrate and ammonium nitrate (only in winter).
- PMF and mass-closure identified two soil sources accounting for 29% of $PM_{2.5–10}$.
- Biomass burning is an important source at the urban background site even during warm seasons.

GRAPHICAL ABSTRACT



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ABSTRACT

Comparison of fine and coarse fractions in terms of sources and dynamics is scarce in southeast Mediterranean countries; differences are relevant because of the importance of natural sources like sea spray and Saharan dust advection, because most of the monitoring networks are limited to PM_{10}. In this work, the main seasonal variabilities of sources and processes involving fine and coarse PM (particulate matter) were studied at the Environmental-Climate Observatory of Lecce (Southern Italy). Simultaneous $PM_{2.5}$ and PM_{10} samples were collected between July 2013 and July 2014 and chemically analysed to determine concentrations of several species: OC (organic carbon) and EC (elemental carbon) via thermo-optical analysis, 9 major ions via IC, and 23 metals via ICP-MS. Data was processed through mass closure analysis and Positive Matrix Factorization (PMF) receptor model characterizing seasonal variabilities of nine sources contributions. Organic and inorganic secondary aerosol accounts for 43% of $PM_{2.5}$ and 12% of $PM_{2.5–10}$ with small seasonal changes. SIA (secondary inorganic aerosol) seasonal pattern is opposite to that of SOC (secondary organic carbon). SOC is larger during the cold period, sulphate (the major contributor to SIA) is larger during summer. Two forms of nitrate were identified: $NaNO_3$, correlated with chloride depletion and aging of sea-spray, mainly present in $PM_{2.5–10}$; NH_4NO_3 more abundant in $PM_{2.5}$. Biomass burning is a relevant source with larger contribution during autumn and winter because of the influence of domestic heating, however, is not negligible in spring and summer, because of the contributions of fires and agricultural practices. Mass closure analysis and PMF results identify two soil sources: crustal associated

* Corresponding author at: Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, Italy.
E-mail address: d.cesari@isac.cnr.it (D. Cesari).

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to long range transport and carbonates associated to local resuspended dust. Both sources contributes to the coarse fraction and have different dynamics with crustal source contributing mainly in high winds from SE conditions and carbonates during high winds from North direction.

1. Introduction

Particulate matter (PM) is one of the most studied atmospheric pollutant due to its potential effects on local and regional air quality, on visibility, and on global climate (Fuzzi et al., 2015). Moreover, there is a compelling evidence that exposure to PM leads to adverse health effects including respiratory and cardiovascular diseases, allergies, and premature mortality (Pope et al., 2004; Delfino et al., 2005; Dockery and Stone, 2007; Gauderman et al., 2015; Velali et al., 2016). Current studies indicate that $PM_{2.5}$ (particles with an aerodynamic diameter smaller than 2.5 μm) was responsible in 2010 of over 3 million premature deaths per year worldwide and 11.5% of these premature deaths are concentrated in Europe (Jerret, 2015; Lelieveld et al., 2015).

Atmospheric PM concentrations in Mediterranean basin are influenced by air masses coming from Europe, Eastern Countries and Africa (Lelieveld et al., 2002). Mediterranean Sea is bordered by 21 Countries accounting for >400 million inhabitants (in 2011), mostly concentrated near the coasts (Salameh et al., 2015). Being delimited at North by highly industrialised southern Europe Countries and by Africa in the South, PM concentrations are affected by a number of natural and anthropogenic sources such as road traffic, biomass burning, shipping, Saharan dust advection, and sea spray (Viana et al., 2014; Contini et al., 2014a; Salameh et al., 2015; Amato et al., 2016; Merico et al., 2017). Mediterranean region is also characterised by complex meteorology that favours aging of polluted air masses (Artíñano et al., 2001). This plays an important role in formation of secondary particles and in their successive aging with a high degree of oxidation of the organic aerosol (Hildebrandt et al., 2011).

Recent results of the AIRUSE project (Amato et al., 2016) evidenced that the spatial variability and the sources of $PM_{2.5}$ in southern Europe are less known with respect to PM_{10} because the fine fraction is not widely measured. As a consequence, there is also limited information on spatial and temporal variability of coarse fraction ($PM_{2.5–10}$), often linked to local and natural sources, being an increasing concern for health (Brunekreef and Forsberg, 2005). Therefore, further research efforts are needed to investigate long-term trends of sources of fine and coarse PM fractions in this area for air quality applications, for management of health risks, and for analysis of PM impact to climate change in Mediterranean basin.

This work analyses the first year (between summer 2013 and summer 2014) of simultaneous measurements of $PM_{2.5}$ and PM_{10} concentrations and chemical compositions collected at the Environmental-Climate Observatory, recently built in South-Est Italy (in Lecce), regional station of the Global Atmosphere Watch (GAW) network. Chemical composition is studied evaluating the concentrations of nine major water-soluble ions, of 23 metals including elements of crustal and anthropogenic origin, and evaluating the carbon content. Carbonaceous species were determined separating elemental carbon (EC) mainly of primary origin from combustion sources, and organic carbon (OC) having a primary and a secondary component. Chemical composition was used for mass closure analysis and for application of Positive Matrix Factorization (PMF) receptor model to investigate seasonal variabilities of the contributions of the main natural and anthropogenic sources to fine ($PM_{2.5}$) and coarse size fractions. Seasonal variabilities of secondary organic and inorganic aerosol concentrations were investigated, including their correlation with local meteorology, to improve the understanding of the main chemical and physical processes governing the dynamics of PM in this area.

2. Experimental

2.1. Measurement station and sampling

PM_{10} and $PM_{2.5}$ daily samples were collected at the Environmental-Climate Observatory of Lecce (Fig. S1), regional station of the GAW-WMO network (Global Atmosphere Watch, see Cristofanelli et al., 2016). The Observatory is located in south-eastern Italy (40°20′8″N–18°07′28″E) at 37 m a.s.l. inside the University Campus of Lecce. The station could be characterised as urban background because it is not strongly influenced by traffic or industrial emissions (Chirizzi et al., 2017). In this site, pollution levels are not significantly influenced by local specific sources rather by the integrated contributions of all sources upwind. The Observatory site is influenced by the activities (included traffic) inside the University Campus, and by the diffused emissions of the town of Lecce and of the other small villages located nearby the Campus. Moreover, the area is sometimes downwind of the largest industrial settlements of the Apulia Region: the area of Taranto (about 80 km in the NW direction) and the area of Brindisi (about 30 km in the NNW direction).

Samples were collected daily for a one-year period between 17/07/2013 and 14/07/2014 using a low-volume (2.3 m^3/h) dual channel (one for $PM_{2.5}$ and one for PM_{10}) sequential sampler (SWAM, Fai Instruments) with automatic detection of aerosol concentration using β-ray attenuation. Particulate matter was collected on quartz filters (Whatman Q-grade, diameter 47 mm) pre-fired for 2 h at 700 °C. Mass concentration measurements with this instrument were in very good agreement with standard reference gravimetric method and the typical uncertainty on measured mass concentration was 2% on PM_{10} and 3% on $PM_{2.5}$ (Dinoi et al., 2017).

Meteorological conditions, specifically wind velocity and direction, temperature, cumulative rain, and relative humidity were obtained from the meteorological station (Vaisala WXT520) of the Observatory.

2.2. Chemical analysis

Roughly, one sample every three days was chemically analysed for a total of 226 simultaneous samples (113 for PM_{10} and 113 for $PM_{2.5}$). Each filter was divided into four quarters, three of them used for the chemical analysis and one used for quality control: replication of specific analysis.

One quarter of the filter was used to obtain a punch (1 cm^2) for the determination of OC and EC concentrations via thermo-optical method (Sunset OC/EC Analyser), following the NIOSH 5040 protocol. To ensure the accuracy of the OC and EC analysis, the analyser was calibrated (multipoint) using as external standard a sucrose solution. Blank filters were also analysed to correct measured values, obtaining for OC an average contamination level of 2.1 μg/cm^2 (standard deviation ±0.9 μg/cm^2) and negligible contamination for EC (<0.1 μg/cm^2).

The second quarter was used for determination of water soluble ions concentrations via High Performance Ion Chromatography (Dionex DX600 IC system composed of an AS40 Autosampler, a GP50 Gradient Pump, an LC25 Chromatography Enclosure, an ED50 Conductivity detector equipped with a temperature compensated conductivity cell) with a 125 μL injection loop. The extraction was done in two steps (20 min each in ultrasonic bath) in 20 mL of ultrapure water (Milli-Q MΩ 18). Anions (Cl^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$) were separated using a Dionex AS4A-4 mm column coupled with IonPac AG14 guard column