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PM10 source apportionment applying PMF and chemical tracer analysis to ship-borne measurements in the Western Mediterranean

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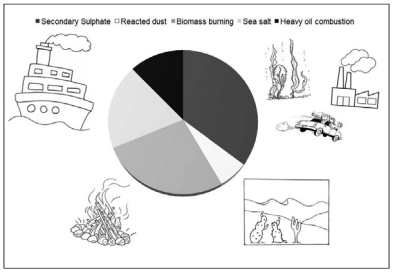
HIGHLIGHTS

- A conclusive PM10 sampling campaign on a cruise ship was performed in summer 2011.
- PMF analysis allowed evaluating the main PM10 sources met along the ship route.
- Large marine biogenic sulphur production was identified as function of strong winds.
- The study disentangles primary ship emissions and secondary sulphates.
- Primary ship emissions contributed on average to (12 ± 4)% of PM10.

GRAPHICAL ABSTRACT



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ABSTRACT

A PM10 sampling campaign was carried out on board the cruise ship Costa Concordia during three weeks in summer 2011. The ship route was Civitavecchia-Savona-Barcelona-Palma de Mallorca-Malta (Valletta)-Palermo-Civitavecchia. The PM10 composition was measured and utilized to identify and characterize the main PM10 sources along the ship route through receptor modelling, making use of the Positive Matrix Factorization (PMF) algorithm. A particular attention was given to the emissions related to heavy fuel oil combustion by ships, which is known to be also an important source of secondary sulphate aerosol. Five aerosol sources were resolved by the PMF analysis. The primary contribution of ship emissions to PM10 turned out to be (12 ± 4)%, while secondary ammonium sulphate contributed by (35 ± 5)%. Approximately, 60% of the total sulphate was identified as secondary aerosol while about 20% was attributed to heavy oil combustion in ship engines. The measured concentrations of methanesulphonic acid (MSA) indicated a relevant contribution to the observed sulphate loading by biogenic sulphate, formed by the atmospheric oxidation of dimethyl sulphide (DMS) emitted by marine phytoplankton.

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1. Introduction

The contribution of diverse anthropogenic and natural emissions sources, such as highly populated and industrial coastal areas, intense ship traffic, forest fire emissions and Sahara dust outbreaks, together with meteorological and geographical peculiarities, make the Mediterranean Basin one of the most polluted regions on Earth in terms of ozone concentrations and aerosol loading (Lelieveld et al., 2002; Velchev et al., 2011). This is caused by local emissions as well as transport of air pollution from outside the Mediterranean region. Ship emissions are an important source of pollution in this region and represent significant and growing contributors to air quality degradation in coastal areas (Van Aardenne et al., 2013). Emissions of exhaust gases and particles from the oceangoing ships affect the chemical composition of the atmosphere, climate and regional air quality (Eyring et al., 2005). In recent years, particle emissions from ships and harbour activities became a concern for air quality and object of several scientific investigations (Moreno et al., 2010; Becagli et al., 2012; Cesari et al., 2014; Bove et al., 2014). A number of studies have shown that ship exhaust particles contain V and Ni and these elements have been used as markers to investigate primary ship emissions using receptor models (Mazzei et al., 2008; Viana et al., 2009; Cuccia et al., 2010; Pandolfi et al., 2011; Salameh et al., 2015). The Joint Research Centre of the European Commission (JRC, EC) has carried out an air quality monitoring program from 2006 to 2014, based on observations from a cruise ship following a regular route in the Western Mediterranean. In the framework of a collaboration agreement between the JRC and Costa Crociere, continuous measurements of atmospheric pollutants were carried out on cruise ships from spring to autumn. During two campaigns in particular, in 2009 and 2010, a two-stage streaker sampler (Formenti et al., 1996) was installed on the ship. The elemental composition of the fine and coarse fraction of PM10, separately collected by the streaker on an hourly basis, was measured by PIXE analysis (Schembari et al., 2014). These datasets were used for an investigation of the influence of ship emissions on the composition of aerosols over the sea through a source apportionment analysis by PMF as well as by chemical marker compounds. The ship emissions were found to be an important source of aerosols in the Western Mediterranean, however a quantification of their impacts by PMF was not obtained. That experiment did not disentangle primary and secondary sources of sulphate and did not resolve the contribution of primary aerosol from ships, presumably because of the insufficient chemical speciation of PM10. A mixed combustion source, which showed evidence of a direct connection with ship emissions was found to contribute by 55%, 63% and 80% to PM10, Black Carbon and sulphate, respectively (Schembari et al., 2014). In summary, the results of the previous campaigns indicated a significant impact of ship emissions to PM levels in the explored area but were not conclusive. In this context, a new PM10 sampling campaign was organized in the summer of 2011, to complete the information of the previous studies and to get a better description of PM sources. An extensive characterisation of PM10 samples, collected using a sequential filter sampler, was addressed; the obtained data were analysed by PMF and used to identify and characterize the main PM10 sources met along the route.

2. Material and methods

2.1. Monitoring campaign

The monitoring station was placed in a cabin at the front of the top deck of the ship "Costa Concordia". It permitted to perform continuous measurements of NO_X, SO_2, O_3 and Black Carbon (BC), the last one by means of an Aethalometer (AE 21, 2 wavelengths, Magee Scientific, USA) (Schembari et al., 2014). The aerosol sampling campaigns were carried out during three weeks of summer 2011: July 18–25, August 15–22 and September 12–19. PM10 samples were collected on Quartz filters (47 mm diameter, flow rate 2.3 m^3 h^{-1}) using a Sven Leckel Ingenieurburo sequential sampler, placed on the top of the cabin where the monitoring and meteorological station were also located. The sampling was carried out on a variable time basis: the sampler was started 1 h after the departure from each harbour and stopped 1 h before the arrival in the next harbour. Each leg was then divided in periods of about 4–5 h with one filter sampled per each period. This resulted in a variable number of filters per open-sea leg and in a total number of about 20 filters per week.

2.2. Analytical methods

All filters were pre-conditioned for two days in a controlled room (temperature: 20 ± 1 °C, relative humidity: 50 ± 5%) before and after the sampling and then weighed using an analytical balance (sensitivity: 1 μg). Field blank filters were used to monitor possible artefacts. The compositional analyses were conducted using different methods. The elemental composition of filters sampled in August and September weeks, were measured by ED-XRF (Energy Dispersive – X Ray Fluorescence) using an ED-2000 spectrometer from Oxford Instruments (Ariola et al., 2006) for S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Ba, Pb. For technical reasons, the concentrations of the same elements in the samples collected during the July cruise were indeed determined by PIXE analysis at the HVEE 3 MV Tandetron accelerator, installed at the LABEC (LAboratorio BEni Culturali) laboratory of INFN in Florence (Calzolai et al., 2006; Lucarelli et al., 2013). The concentration values of S and K determined using ED-XRF were corrected for an average attenuation factor (Bove et al., 2014) to determine their mean values, whereas S, Cl, K resulted to be always below their Minimum Detection Limit when measured by PIXE. The Minimum Detection Limits obtained for both the techniques are shown in Table E1 in the electronic supplementary material. Finally, the analytical uncertainties are the sum of the systematic term on the calibration standards (5%) and of the statistical fluctuation on peak areas.

The water-soluble inorganic components of the PM10 were determined by Ion Chromatography (IC) using an ICS-1000 Ion Chromatography System (Dionex) at the University of Milan. In particular, for the extraction of the PM, a quarter of each filter was wetted previously and then three times with MilliQ water in an ultrasonic bath for 20 min (complete recovery, 98% ± 3%), renewing the water at each step (Piazzalunga et al., 2013). The extracts were analysed using IC to identify the major ionic species (i.e., Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+},Cl^-, SO_4^{2-}, NO_3^-) with an overall 10% uncertainty for the ionic concentrations. The MSA (methanesulfonic acid) concentration values were also measured by IC with the same uncertainty. The lack of quantification of low-Z elements (due to the X-ray self-absorption and the high Si concentration in the quartz filters) was partially recovered by Ionic Chromatography analysis which was finally considered more accurate for such elements.

Information on meteorological parameters (wind speed and direction, temperature, humidity from the meteorological station of the ship) and on the ships position, speed and sailing direction, were also available (in 10 min intervals) and used to identify situations where the PM sampling might be influenced by the emissions of Costa Concordia itself. When the inlets of the measurement station were downwind the ship stack within an angle of ±40°, the data were discarded to avoid any risk of contamination.

Air mass back-trajectories were calculated using the US NOAA HYSPLIT model (http://ready.arl.noaa.gov/HYSPLIT.php) with GDAS meteorological data. For each filter, five-day back trajectories