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Determining the influence of different atmospheric circulation patterns on PM_{10} chemical composition in a source apportionment study

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HIGHLIGHTS

- ► Elements and ions in 193 PM_{10} samples were studied by Positive Matrix Factorization.
- ► Results were geochemically interpreted in relation to weather data.
- ► Days with similar circulation patterns were clustered on the basis of wind data.
- ► Samples with similar air mass histories were grouped using back-trajectories.
- ► The major components of PM_{10} chemistry and dynamics in NE Italy were identified.

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ABSTRACT

This study combines a set of chemometric analyses with a source apportionment model for discriminating the weather conditions, local processes and remote contributions having an impact on particulate matter levels and chemical composition. The proposed approach was tested on PM_{10} data collected in a semi-rural coastal site near Venice (Italy). The PM_{10} mass, elemental composition and the water soluble inorganic ions were quantified and seven sources were identified and apportioned using the positive matrix factorization: sea spray, aged sea salt, mineral dust, mixed combustions, road traffic, secondary sulfate and secondary nitrate. The influence of weather conditions on PM_{10} composition and its sources was investigated and the importance of air temperature and relative humidity on secondary components was evaluated. Samples collected in days with similar atmospheric circulation patterns were clustered on the basis of wind speed and direction. Significant differences in PM_{10} levels and chemical composition pointed out that the production of sea salt is strongly depending on the intensity of local winds. Differently, typical primary pollutants (i.e. from combustion and road traffic) increased during slow wind regimes. External contributions were also investigated by clustering the backward trajectories of air masses. The increase of combustion and traffic-related pollutants was observed when air masses originated from Central and Northwestern Europe and secondary sulfate was observed to rise when air masses had passed over the Po Valley. Conversely, anthropogenic contributions dropped when the origin was in the Mediterranean area and Northern Europe. The chemometric approach adopted can discriminate the role local and external sources play in determining the level and composition of airborne particulate matter and points out the weather circumstances favoring the worst pollution conditions. It may be of significant help in designing local and national air pollution control strategies.

1. Introduction

All over Europe, a large number of studies identified and apportioned the sources of PM for regulatory purposes and for developing and implementing policies for the human health and environmental protection. Most of these present a detailed knowledge of the chemical composition and the application of various receptor-modeling techniques to identify and quantify the main emission sources (e.g. Viana et al., 2008). However, the identification of the main sources should be only a starting point to characterize the space distribution and variability of PM as other factors strongly contribute to the levels of PM and influence the processes at various scales: from local, to regional, to long-distance. Among those, local

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weather conditions, atmospheric circulation patterns and transboundary or regional transports of pollutants strongly interfere with the chemistry of aerosol generation and its subsequent atmospheric evolution, through the ageing of air masses. For example, Southern European countries can be affected by the influence of African dust outbreaks (Pederzoli et al., 2010; Remoundaki et al., 2011), although other sources can also be potentially relevant under specific weather conditions. These include sea spray under high wind regimes (Lewis and Schwartz, 2004), pollutant transports from external sources (Baker, 2010) or secondary aerosol formation processes in air masses coming from polluted areas (Squizzato et al., 2012). Nevertheless, weather conditions are not adequately considered in source apportionment studies.

Recently, the authors applied a factor–cluster analysis on chemical PM_{10} data to group samples on the basis of their similar chemical composition and origin (Masiol et al., 2010, 2012). Differences in wind roses and back-trajectories between groups have been subsequently used to identify potential sources and highlight possible relationships between weather conditions and PM_{10} variations. In the present study, a novel approach was tested to assess the contributions of local and external sources of PM_{10}, based on the application of chemometric procedures to source apportionment data. A first identification of the most probable emission sources was accomplished by applying the positive matrix factorization (PMF) model. The source apportionment results were interpreted on the basis of the most relevant weather parameters (air temperature, rain, relative humidity and solar radiation). A cluster analysis (CA) on wind data was then used to identify groups of days with similar atmospheric circulation patterns. The variations in PM_{10} levels and chemistry for each identified group were then examined to extract additional information on the most probable source locations and assess the influence of wind dynamics on air quality. A second CA was carried out on the back-trajectories to merge samples with similar air mass histories. The chemical composition of each group was then analyzed to evaluate the potential impact of regional and transboundary sources.

The proposed approach, used in the framework of source apportionment studies, can discriminate the influence of meteorological conditions in the events that PM exceeds the limits, can lead to improved understanding of the aerosol generation processes and, finally, provide a more reliable basis for mitigation strategies.

2. Study area

PM_{10} data were collected in a semi-rural coastal site near Venice (Italy), where pollution limits fixed by the European Directives are frequently exceeded because of several emission sources (ARPAV, 2010; EEA, 2012): an extended urban area with ~270,000 inhabitants and the related road, maritime and airport traffic, an industrial zone including chemical and steel plants, an oil-refinery, incineration facilities, thermoelectric power plants, glass factories (Rampazzo et al., 2008a,b). Recently, it was observed that Venice is also an ideal place to study the effects of the atmospheric circulation and the long-range transports in the Po Valley as strongly influenced by local aerosol generation processes (e.g., sea spray) and regional-scale transports of primary and secondary pollutants (Masiol et al., 2010, 2012; Squizzato et al., 2012).

3. Materials and methods

3.1. Sampling, analytical procedures and QA/QC

A PM_{10} sampling campaign was carried out from May 2007 to January 2008, to be representative of all seasons, and to include different weather and atmospheric circulation patterns. About two hundred samples (24 h) were collected with a low-volume automatic sequential sampler (Skypost, TCR Tecora, Italy) on polycarbonate Nuclepore membranes (0.4 μm pore size; GE, USA). Filters were weighed in a controlled clean room (20 ± 5 °C and 50 ± 5% relative humidity) before and after sampling, by using a microbalance. Samples were then analyzed for both water-soluble inorganic ions and elemental composition. Half filter was ultrasonically extracted with ultrapure water (specific resistivity ≈ 18 MΩ cm) and filtered through prewashed Teflon membranes (pore size 0.45 μm, PALL, USA). The aqueous extracts were then analyzed by an ion chromatographic system (model DX500, Dionex, USA) to determine the concentrations of six major inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, NH_4^+). Samples were also analyzed for 16 elements with atomic number ≥13 (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br) using the Particle Induced X-ray Emission technique (PIXE) at the AN2000 Van de Graaff accelerator of INFN Legnaro laboratories (Padua, Italy). The GUPIX code was used to fit the X-ray energy spectra and calculate concentrations, errors and detection limits (DLs). More details of both analytical procedures and instrumental setup are given in Masiol et al. (2010).

Filter blanks and field blanks were used to detect sample contamination and the obtained values were routinely subtracted from those of the samples. For ion chromatography, single- and multi-ionic standards (Fluka-Riedel de-Haën, Germany) were used to test the linearity and calibrate the instrumental responses. The quality and accuracy of quantitative analyses for some ions were checked by analyzing the SRM 1648 standard for air particulate (NIST, USA). The recovery of each ion was in the range 90–110%. The relative standard deviation of each ion determination was <5%. The quality and accuracy of quantitative PIXE analyses were checked with the SRM 2783 thin film standard for air particulate (NIST, USA).

3.2. Data treatment and uncertainty assessment for PMF

USEPA PMF version 3.0 based on multilinear engine 2 program (ME 2) was used in this study. This multivariate model was widely used as a standard method for source apportionment studies (Viana et al., 2008). Details of the model and ME 2 are given elsewhere (Paatero and Tapper, 1994; Paatero, 1997; USEPA, 2008). PMF needs both species concentrations at receptor site and associated uncertainties: some methods to manage the dataset and to calculate the uncertainties are summarized in Reff et al. (2007). In this study, missing data were preliminarily treated following three approaches: i) eliminating samples for which any measurement was missing, ii) replacing missing data with the arithmetic mean or iii) the median of the remaining cases. As the approaches have not returned significantly different results, the arithmetic mean was selected and the assigned uncertainty was tripled. Uncertainties for PIXE data were handled according to Polissar et al. (1998): for data above the DLs, uncertainties were determined by compounding errors from the most uncertain components (PIXE errors, air sampled volumes and contaminations found in the field blanks) with the addition of 1/3 of the DLs. Concentrations below the DLs or with PIXE errors >50% were set as DL/2, with an uncertainty of 5/6 of the corresponding element DL. Uncertainties associated to ion determinations were estimated using the equation-based method (USEPA, 2008) with an error fraction computed by compounding the variation on four different water extraction of SRM, field blank errors and sampled air volumes. Common uncertainties were found in the range of 7–20% for SO_4^{2-} and Mg^{2+}, respectively.

3.3. Local weather conditions and cluster analysis on wind data

Common weather data including wind speed ($m\ s^{-1}$) and direction (degree), air temperature (°C), relative humidity (%), solar