Study of air pollution in the proximity of a waste incinerator

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ABSTRACT

Montale is a small town in Tuscany characterised by high PM10 levels. Close to the town there is a waste incinerator plant. There are many concerns in the population and in the press about the causes of the high levels of pollution in this area. Daily PM10 samples were collected for 1 year by the FAI Hydra Dual sampler and analysed by different techniques in order to obtain a complete chemical speciation (elements by PIXE and ICP-MS, ions by Ion Chromatography, elemental and organic carbon by a thermo-optical instrument); hourly fine (<2.5 μm) and coarse (2.5–10 μm) PM samples were collected for shorter periods by the Streaker sampler and hourly elemental concentrations were obtained by PIXE analysis.

Positive Matrix Factorization identified and quantified the major aerosol sources. Biomass burning turned out to be the most important source with an average percentage contribution to PM10 of 27% of and even higher percentages during the winter period when there are the highest PM10 concentrations. The contribution of the incinerator source has been estimated as about 6% of PM10.

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1. Introduction

Particle Induced X-ray Emission (PIXE) is a suitable technique for analysing aerosol samples [1,2] due to its ability to carry out a multi-elemental analysis of the particulate deposited on the filter surface without any solubilization procedure, therefore shortening the analysis time and reducing the sample contamination risk. In particular it is unrivalled for the detection of the crustal elements. However, it provides only part of the desired information with regard to the chemical composition therefore it is mandatory to perform also at least measurements for important ionic species (e.g., ammonium, nitrate), for organic carbon (OC) and elemental carbon (EC). Finally Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Mass Spectroscopy (ICP-MS) and PIXE can be used as complementary techniques and their combined use is able to give powerful information on chemical speciation of metals in the particulate matter (PM). By using the appropriate extraction conditions (extracting solution composition, pH, temperature, pressure, contact time) the metal fraction which is more "available" for the natural systems is obtained and in this way it is possible to evaluate better the impact of heavy metals on the environment and the human health [3].

Standard daily sampling allows the study of aerosol composition for a long period covering all the seasonal changes in aerosol composition and tracing sources which may be present only in specific periods; however some particulate emissions change within a few hours and source apportionment receptor models need a series of samples containing material from the same set of sources in differing proportions. Increasing the time resolution of the measurements produces samples that have greater between-sample variability in the source contributions than samples integrated over longer time periods. Therefore time-resolved measurement can give a valuable help in source identification.

Montale is a small town in Tuscany characterised by high PM10 levels. There are many concerns in the population and in the press about the causes of the high levels of pollution in this area, mainly because close to the town there is a waste incinerator plant. However many other sources can give a relevant contribution to PM10: many fields are present in the surroundings therefore a relevant crustal contribution could be present; biomass burning is used as heating system and also open fires are often present for the combustion of pruning; traffic, too, could give a relevant contribution. Therefore a multidisciplinary approach involving different analytical techniques is necessary to obtain a complete chemical speciation which can be used as a starting point for the application of multivariate statistical methods like Positive Matrix Factorization (PMF) to identify the PM sources and their contribution to the PM mass.

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The Regional Government has promoted an extensive field campaign for the aerosol characterization in Montale, to give to policy-makers the knowledge and the tools for a significant reduction of the main anthropogenic emissions. We will present here some of the results obtained for the first period of the campaign both for the daily and the hourly resolution samples.

2. Methods

2.1. Sampling

Montale is a small town located 35 km W of Florence (Italy) with about 10,000 inhabitants. The sampling site is close to a garden and adjacent to a public car park, mainly for residential use. On a wider scale, the site can be classified as a "suburban" site, as it is in a built area but close to vast not urbanised areas.

PM10 samples were collected on a daily base (from midnight to midnight), every second day, for 1 year (from December 2013 to December 2014) by the low-volume (2.3 m^3/h, EU rule EN 12341) FAI Hydra Dual sampler equipped with two inlets so that aerosol can be simultaneously collected on Teflon and Quartz fibre filters (47 mm diameter), thus allowing the application of different analytical techniques.

During shorter periods (2 weeks in winter and 2 weeks in summer) the aerosol was also collected by a low volume (1 lpm) Streaker sampler. In this device particles are separated on two different stages: the coarse fraction (2.5 μm < Dae < 10 μm) and the fine fraction (Dae < 2.5 μm), collected on a Kimfol foil and on a Nuclepore filter respectively. The two collecting substrata are paired on a cartridge which, rotating at constant speed for 1 week, produces a circular continuous deposition of particulate matter ("streak") on both stages [4].

2.2. Measurements and data analysis

PM10 daily mass concentrations were obtained by weighing the Teflon filters by an analytical balance in controlled conditions of temperature (20 ± 1 °C) and relative humidity (50 ± 5%). Samples on Teflon filters are cut in three parts. On one half of the filter PIXE is used to measure the concentrations of all the elements with atomic number $Z > 10$. PIXE analyses were performed at the 3MV Tandetron accelerator of the INFN-LABEC laboratory, with the new external beam set-up similar to the one extensively used so far [5] but improved by the duplication of the SDD detector used for medium–high energy X-rays [6]; the measuring time was therefore reduced to only 90 s/sample with better statistics. Each sample was irradiated for ∼90 s with a 3.0 MeV proton beam (∼2 mm^2 spot, 10–150 nA intensity). A filter scanning was carried out to analyse most of the deposit area. PIXE spectra were fitted using the GUPIX code [7] and elemental concentrations were obtained by a calibration curve from a set of thin standards of known areal density (Micromatter Inc.).

The water-soluble fraction (sample extraction in ultra-pure MilliQ water in ultrasonic bath) of inorganic cations, inorganic anions and low molecular weight organic anions is measured by Ion Chromatography (IC) on one quarter of the filter [8]; ICP methods are used to determine the "soluble fraction" (in the acidic extraction conditions) of several major (ICP-AES) and trace (ICP-MS) metals on the remaining quarter of the filter [3]. 0.1% sub-boiled distilled HNO$_3$ (pH = 1.5) in an ultrasonic bath for 15 min at room temperature was used as extraction method. This fraction represents the most "available" metal fraction (including free metal, labile complexes, carbonate and bicarbonate salts), considering the pH = 1.5 as the lowest limit for "natural" pH values [3].

A 1.5 cm^2 punch of the Quartz fibre filters is used for Organic and Elemental Carbon assessment by Thermo Optical Transmission analysis (using a Sunset Lab analyser [9]) at LABEC.

Streaker samples were analysed by PIXE, with the same experimental set-up used for daily samples. A properly collimated proton beam (2.7 MeV, 50–300 nA) was used to scan the deposit in steps corresponding to 1 h of aerosol sampling, thus providing the elemental concentrations with hourly time resolution. Thanks to the improved efficiency of the experimental set-up, 90 s. of measuring time for each spot corresponding to 1 h of sampling was enough to obtain a good statistics [6].

We report here the first results obtained for the winter and spring season.

Positive Matrix Factorization (PMF) has been applied to this preliminary data set (daily and hourly samples separately) aiming at a first identification and quantification of the major aerosol sources, using the EPA PMFv5 software. PMF is an advanced factor analysis technique based on a weighted least square fit approach [10]; it uses realistic error estimates to weigh data values and imposes non-negativity constraints in the factor computational process. Briefly, the PMF factor model may be written as X = G·F + E, where X is a known n by m matrix of the m measured chemical species in n samples; G is an n by p matrix of source contributions to the samples (i.e. time variations of the p factor scores); F is a p by m matrix of factors composition (often called source profiles). G and F are factor matrices to be determined and E is defined as a residual matrix. Input data were prepared using the procedure suggested by Polissar [11] and PMF results for different number of factors and multiple values of FPEAK were systematically explored to find out the most reasonable solution.

For daily samples, to obtain absolute source profiles and contributions the aerosol mass was introduced as a variable with a 400% error. For hourly data, only elemental concentrations are measured and no information about the PM mass concentration is available: in this case, only relative source profiles (elemental ratios within the composition of the identified sources) can be obtained and source time series are in arbitrary units.

3. Results

3.1. PM10 mass

PM10 concentrations are reported in Fig. 1. Lower levels were recorded in spring, with values between 10 and 20 μg/m^3, except for a peak close to the PM10 daily limit threshold on 22 May (44.7 μg/m^3) in correspondence of an episode of Saharan dust transport (see below). In winter levels were far higher with many concentration peaks around 100 μg/m^3 (up to 174 μg/m^3 on December 20th). This is due to the typical winter weather conditions with greater atmospheric stability, with a reduced height of the boundary layer and a poor dispersion of the pollutants themselves

3.2. Chemical composition

As an example of the results obtained from the analysis of the daily samples, in Fig. 2 the Na, Si, K and S concentrations (obtained by PIXE) are reported.

Na is a typical marker of sea-salt aerosol (together with Mg and Cl). Several episodes with a strong increase of Na, always together with Mg, sometimes with sometimes without a corresponding increase in Cl concentration, are present, pointing to the transport of marine aerosol. In all the cases the Mg/Na ratio (0.14) is very similar to the one typical of bulk sea-water (Mg/Na = 0.12, [12]) but often there is a strong Cl depletion probably due to reactions