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The size distribution of chemical elements of atmospheric aerosol at a semi-rural coastal site in Venice (Italy). The role of atmospheric circulation

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HIGHLIGHTS

- Element mass size distributions in PM were investigated in a coastal site in Venice.
- Elements accumulate in the submicrometric and intermediate modes.
- The potential sources and the relationships with air mass origin were investigated.
- The effect of meteorological conditions was discussed.
- Long distance inputs and local sources were identified.

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ABSTRACT

The concentrations of selected elemental tracers were determined in the aerosol of a semi-rural coastal site near Venice (Italy). Size-segregated aerosol samples were collected using an 8-stage cascade impactor set at 15 m above ground, during the cold season (late autumn and winter), when high levels of many pollutants are known to cause risks for human health. From the experimental data, information was extracted on potential pollutant sources by investigating the relationships between elements in the different size fractions. Moreover, an approach to highlight the importance of local atmospheric circulation and air mass origin in influencing the PM composition and fractional distribution is proposed.

Anthropogenic elements are strongly inter-correlated in the submicrometric (<1 μm) (S, K, Mn, Cu, Fe and Zn) and intermediate mode (1–4 μm) (Mn, Cu, Zn, Ni) and their relationships highlight the presence of several sources (combustions, secondary aerosol, road traffic). In the intermediate mode, associations having geochemical significance exist between marine (Na, Cl and Mg) and crustal (Si, Mg, Ca, Al, Ti and K) elements. In the coarse mode (>4 μm) Fe and Zn are well correlated and are probably linked to tire and brake wear emissions.

Regarding atmospheric circulation, results show increasing levels of elements related to pollution sources (S, K, Mn, Ni, Cu, Zn) when air masses come from Central and Eastern Europe direction and on the ground wind blows from NWN-N-NE (from mainland Venice). Low wind speed and high percentage of wind calm hours favor element accumulation in the submicrometric and intermediate modes. Furthermore, strong winds favor the formation of sea-spray and the increase of Si in the coarse mode due to the resuspension of sand fine particles.

1. Introduction

Airborne particulate matter (PM) plays direct (Yu et al., 2006) and indirect (Lohmann and Feichter, 2005) effects on climate, affects visibility (Chow et al., 2002), enters in many chemical reactions in the atmosphere (Buseck and Schwartz, 2003; Kroll and Seinfeld, 2008; George and Abbatt, 2010) and may cause a number

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of adverse effects on human health (Pope et al., 2009). The dimension of particles is directly related to their emission sources, as mechanically generated particles (e.g., wind-blown dust, sea spray) are generally larger than 1 μm, whereas combustion-generated particles (high-temperature processes, traffic exhausts, many industrial activities) are smaller than 1 μm (e.g., Lewis and Schwartz, 2004; Seinfeld and Pandis, 2006; Ning and Sioutas, 2010).

The present study has been conducted in Venice, located in the eastern part of the Po Valley (Italy), one of the most polluted areas in Europe (EEA, 2013) and it is influenced by both mainland anthropogenic emissions (automotive traffic, shipping emissions, industrial processes) (Rampazzo et al., 2008a, 2008b; Contini et al., 2011), secondary aerosol formation (Squizzato et al., 2013) and natural sources such as sea spray from the near Adriatic Sea and crustal material (Masiol et al., 2012a).

However, the air quality in Venice has also been shown to be very sensitive to local atmospheric circulation patterns (Masiol et al., 2010, 2012a). Furthermore, PM pollution was associated with external transports from the continental Europe and the Po Valley. These studies reported that PM pollution increases when air masses originate in Central Europe and secondary sulfates build up when air masses pass over the Po Valley (Squizzato et al., 2012). On the contrary, air masses coming from Northern Europe were shown to have a cleaning effect.

Recently, Toscano et al. (2011) reported the size distribution of some selected elements in the aerosol of the Venetian Lagoon. Readings were taken at three sites characterized by different anthropogenic influences and particles with aerodynamic diameter less than 3 μm were predominant. Likewise, several studies were conducted in Europe (Salma et al., 2002; Samara and Voutsa, 2005; Karanasiou et al., 2007) and Italy (Rizzio et al., 1999) to investigate the elemental size distribution on different environmental scenarios (e.g. urban background, heavy traffic, roadside, tunnel and rural residential area). However, although the weather condition and the long distance transport are considered determining factors on size distributions (Samara and Voutsa, 2005) and in changing air quality in non-polluted areas (Rizzio et al., 1999), information is still lacking about the role of atmospheric circulation and long-range transport processes on the elemental mass size distributions.

In this study the mass size distributions of some elements recognized as tracers for specific sources of PM were investigated in a semi-rural coastal site near Venice (Italy). From experimental data, information was extracted to identify the potential sources of PM and elements, by examining the relationships between elements in the different size fractions. Moreover, an approach to highlight the importance of local atmospheric circulation and air mass origin in determining the PM composition and fractional distribution is proposed. Data were processed in association with back-trajectories and local atmospheric circulation (wind speed and direction) to reveal significant links between atmospheric dynamics and aerosol elemental composition.

2. Materials and method

2.1. Sampling and analysis

A total of 112 individual sub-samples were obtained from 14 daily samples of aerosol, which were size-partitioned using an 8-stage single-orifice cascade impactor (14 daily samples × 8-stages = 112 sub-samples) (model I-1, PIXE International Co., USA) as previously reported by Salma et al. (2002). The sampling station was located on a lighthouse (45.4227 N, 12.4368 E, 15 m above ground level) at the end of a 300 m-long dam at the Lagoon of Venice port channel of the Lido (Fig. 1a). Prevalent winds during the sampling campaign flowed from N-NE (Fig. 1b), i.e. from the sea, the Lagoon and agricultural environments. The experimental data were collected during the late autumn and winter (October 2007–January 2008, non-breeze season), when the highest levels of both PM and many gaseous pollutants are generally observed (ARPAV, 2013).

The cascade impactor had 7 stages with nominal cut-points (d_{50}-values, and/or equivalent aerodynamic diameters) of 16, 8, 4, 2, 1, 0.5, 0.25 μm ahead of the backup filter (8 stages in total). The nominal flow rate was 1 L min^{-1}. Collection media were polycarbonate membranes (Prepared Ring with Nuclepore PR-1N, PIXE International Co., USA, pore size 0.4 μm, Ø27 mm) coated with Vaseline to reduce particle rebound. Air flow was frequently monitored using a flow meter and manually adjusted to be consistent with the instrument margin of tolerance (±10%). After sampling, membranes were stored at −20 °C in clean Petri slides until analyses to avoid sample contamination, degradation and losses.

Samples were analyzed for major, minor and trace elements with atomic number ⩾11 (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn) using the Particle Induced X-ray Emission (PIXE) experimental setup facility at the INFN Legnaro laboratories. The GUPIX code (Maxwell et al., 1995) was used to fit the X-ray energy spectra and to calculate the absolute elemental areal densities (ng cm^{-2}), their errors and the detection limit (DLs) values. The quality of the analytical results was assured by frequently analyzing the international reference material SRM 2783 (NIST, USA). Further details about sampling, analytical precision and limits of detection are available in Supplementary material and in Table SI1.

2.2. Weather data and back-trajectory analyses

Wind speed and direction were measured hourly at a regional environmental protection agency station (ARPAV-Centro Meteorologico di Teolo), located about 6 km East of the sampling site (Fig. 1). Moreover, daily back-trajectories were simulated and then clustered using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model version 4 (96 h backward, starting at 00:00, 6:00, 12:00 and 18:00 h local time, at 150 m above ground level, NCEP/NCAR Reanalysis data fields) (Draxler and Rolph, 2013; Rolph, 2013).

3. Results and discussion

Preliminary data evaluation and handling was carried out to clean up the dataset. Data with values below the DLs and/or with high percentage of error (>50%) were substituted by DLs/2; casual and systematic contaminations were checked by a careful evaluation of field blanks. No anomalous data were detected. The total concentration of the analyzed elements, i.e. the sum of element concentrations in all stages, which represents total suspended particulate matter (TSP), is reported as a boxplot in Fig. SI1. Basing on median values, sulfur is the most abundant element (746 μg m^{-3}), followed by Cl (491 ng m^{-3}), Ca (193 ng m^{-3}), K (183 ng m^{-3}) and Na (153 ng m^{-3}).

Each collected sample was then processed to represent the differential mass distributions with both histograms and lognormal distribution models (e.g. Majoral et al., 2006, and references therein). Fig. 2 reports the average element size distribution as differential mass concentration. In most samples, only a few membranes designed to catch particles smaller than 0.25 μm (back-up filter) contained sufficient material to be measured accurately for most of the analyzed elements. Results show that Ti, Cl, Ni, Cu and Ca are more concentrated in the intermediate mode (range 1–4 μm), whereas sulfur, potassium, vanadium and manganese