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Factors, origin and sources affecting PM_1 concentrations and composition at an urban background site

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ABSTRACT

PM_1 is widely believed to provide better information on the anthropogenic fraction of particulate matter pollution than $PM_{2.5}$. However, data on PM_1 are still limited in Europe as well as comprehensive information about its chemical composition and source apportionment and this gap is more evident in the pollution hot-spots still remaining in Europe, such as the Po Valley (Northern Italy). Elemental and organic carbon, 7 water soluble inorganic ions and 17 elements were quantified in 117 PM_1 samples collected at an urban background site in Venice-Mestre, a large city located in the eastern Po Valley, during winter (December 2013–February 2014) and summer (May–July 2014) periods.

Results show a strong seasonality for PM_1 mass concentration (averages ranging from 6 ± 2 in summer to $34 \pm 24\ \mu g\ m^{-3}$ in winter) and for most of the analysed species. Components mainly related to road traffic, residential heating, biomass burning and secondary inorganic aerosol (ammonium nitrate) reached their highest levels in winter, while mineral dust and marine components were elevated in summer. PMF analysis revealed 7 potential sources. Secondary inorganic aerosol (33%) and biomass burning (33%) are the major contributor in winter followed by EC-primary emissions (16%), aged sulphate (6%), road traffic (7%), fossil fuel combustion (%) and marine aerosol (3%). During summer, these sources account for 12%, 14%, 20%, 22%, 8%, 14% and 10%, respectively. Some PM_1 sources are located near the sampling site (residential area, traffic road, industrial area) but a major contribution of long range transport is observed when high pollution events occur. The results give useful insights into PM_1 composition in an urban area and chemical profiles of sources helpful in the interpretation of receptor model results.

1. Introduction

In recent decades, the characterisation of airborne particulate matter (PM) has become an increasingly important topic of research since the epidemiological data have showed that PM has negative effects upon human health (Anderson et al., 2012; Rohr and Wyzga, 2012). Fine particles (with aerodynamic diameters of less than 2.5 μm, $PM_{2.5}$, and 1 μm, PM_1) may play an important role in affecting human health for a number of reasons: (i) they penetrate more effectively into the deep lung; (ii) they can penetrate more readily into indoor environments; (iii) they can remain suspended for longer periods of time in the atmosphere than coarse particles; (iv) they may be transported over long distances; (v) they tend to carry higher concentrations of the more toxic compounds, including acids, heavy metals and organic compounds; and (vi) they have a larger surface area per unit mass compared to larger particles and, thus, can absorb larger amounts of semi-volatile compounds (e.g., Pope and Dockery, 2006). Consequently, the study of levels, composition and emission sources of fine particles in densely populated areas is very important for health protection and to improve PM control strategies.

Fine particles are typically mainly composed of elemental carbon (EC), organic carbon (OC), inorganic ions and metals. Among these major components, some studies have associated carbonaceous particles with health effects (Rohr and Wyzga, 2012). These consist of compounds from combustion exhaust, soil, paved road dust, cooking and other sources (Harrison and Yin, 2008). EC comprises small (mainly sub-micrometre) graphitic particles which arise from primary

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emissions from combustion of various fuels, e.g., coal, wood, fuel oil and motor fuel, especially diesel. Organic carbon (OC) can be directly emitted into the atmosphere in the particulate phase or can originate in the atmosphere from gas-to-particle conversion processes (forming the so-called secondary organic aerosol, SOA) (Seinfeld and Pandis, 2006). Generally, EC lies in the submicrometre range, whereas OC exhibits wider size distributions (Pio et al., 2007).

Inorganic ions can be emitted from various primary sources, such as combustion, sea salt and crustal material. However, the main source of sulphate, nitrate and ammonium is the generation of secondary inorganic aerosol (SIA) through (photo-) chemical reactions of gaseous precursors (NO_x, SO_2, NH_3) and O_3 with atmospheric oxidants to form mainly ammonium nitrate (NH_4NO_3) and ammonium sulphate ($(NH_4)_2SO_4$)) (Seinfeld and Pandis, 2006).

Although metals generally represent a small fraction of PM_1 mass, their contribution to the overall toxicity of particles cannot be disregarded. The chemical and physical properties of some elemental species is size-dependent: for example, the solubility of Pb, Co and Cd increase in fine particles, making those elements more bioavailable (Birmili et al., 2006). The characterisation of elemental composition is also very important for source apportionment studies: the variable proportion of some well known elemental markers can help in the identification of potential sources using receptor modelling techniques.

Although it has been suggested that PM_1 can provide a better estimation of anthropogenic particles than $PM_{2.5}$ (Perrone et al., 2013), PM_1 source apportionment studies are still limited in Europe as well as comprehensive information about its composition (e.g. Pérez et al., 2008; Vecchi et al., 2008; Theodosi et al., 2011; Perrone et al., 2013). Moreover, PM_1 is not yet regulated in Europe and this is a major reason why there is a lack of available data and studies upon it. This is a serious gap, as some air pollution hotspots still remain in highly populated areas of Europe. Among others, the Po Valley (Northern Italy) deserves particular attention because of the frequent exceedance of guidelines and Limit Values fixed by EC Directives and international organizations such as WHO (Larsen et al., 2012). The present paper aims to investigate the composition of PM_1 in Mestre-Venice, a large city on the eastern border of the Po Valley. Here, the highest concentrations of particulate matter and nitrogen oxides ($NO + NO_2 = NO_x$) are commonly recorded in winter, while high levels of ozone are measured in summer due to photochemical processes involving precursors of natural and anthropogenic origin (Masiol et al., 2014a, 2014b).

PM_1-bound elemental and organic carbon, water soluble inorganic ions and elements, have been analysed to determine the major contributors to PM_1 mass and were then processed to (i) determine the seasonal cycles, (ii) estimate secondary inorganic and organic aerosol, (iii) assess the major components applying a mass closure model, (iv) identify and quantify the most probable sources by using a receptor modelling technique (positive matrix factorization, PMF) and (v) hypothesize their location applying a conditional probability function.

2. Material and methods

2.1. Measurement site

Venice is located between the eastern edge of the Po Valley and the Adriatic Sea. Along with the city of Mestre, they form a large coastal urban municipality hosting 270,000 inhabitants (~628 inhabitants km^{-2}) (ISTAT, 2011). The local emission scenario includes some major potential sources of PM: high density residential areas; heavily trafficked roads mostly congested during peak hours; a motorway and a motorway-link which are part of the main European routes E55 and E70; an extended industrial area (Porto Marghera) and an international airport.

The sampling site (Via Lissa-Mestre, Lat. 45.4871 N–Long. 12.2229 E) is located in a highly populated residential zone of Mestre surrounded by several heavily trafficked roads (distance ~450 m) (Fig. 1). The site was categorized as urban background by the local environmental agency (ARPAV). It lies about 200 m from an important motorway and few meters from the railway. Moreover, Via Lissa was chosen considering the background of information on $PM_{2.5}$ composition (Masiol et al., 2014b) that can help in the interpretation of PM_1 data.

2.2. Experimental

PM_1 samples were collected daily (117 samples) at an urban background site in Venice (Via Lissa-Mestre) during winter (December 2013–February 2014) and summer (May–July 2014) periods using a low volume sampler (Skypost PM, Tecora, Milan) on quartz fiber filters. Sampling time was 24 h, from 0:00 to 24:00 and the flow rate was 2.3 $m^3\ h^{-1}$. PM_1 masses were measured by gravimetric determination (microbalance with 0.1 μg sensitivity) on filters preconditioned for 48 h at constant temperature (20 °C) and relative humidity (50%).

Half of each sample was digested for elemental determination. Acid digestion was performed using 4 mL of 69% HNO_3, 1 mL H_2O_2 and 0.3 mL 48.9% HF in a microwave oven using the protocol proposed by Karthikeyan et al. (2006). An ICP-OES (Optima 5300 DV, Perkin Elmer) was used to determine the mass concentration of Mg, Al, S, K, Ca, Ti, Mn, Fe, Zn and Ba while an ICP-MS (Elan 6100, Perkin–Elmer) was used for V, Ni, Cu, As, Cd, Sb and Pb.

For the analysis of ion components an aliquot (16 mm Ø disc) was punched from the filter. Punches were extracted in vials with 10 mL MilliQ water (resistivity = 18.2 MΩ•cm at 25 °C, Millipore) and sonicated for 50 min. Extracts were pre-filtered on microporous (0.45 μm) PTFE membranes and injected in two Metrohm (Switzerland) ion chromatographic systems with conductivity detectors to quantify the concentrations of three anions (Cl^-, NO_3^-, SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). The analytical ion chromatography method is reported elsewhere (Masiol et al., 2015a). Finally, an aliquot of filter (1 cm^2) was analysed for elemental and organic carbon by using a Thermal–Optical Carbon Aerosol Analyser (Sunset Laboratory, Forest Grove, OR, USA) following the EUSAAR2 protocol (Table SI1). The carbon analyzer employs a programme of temperature and gas composition to evolve carbon species and a laser at a wavelength of 680 nm to monitor the filter transmittance (Birch and Cary, 1996).

Field blanks were prepared and analysed together with the samples and the values obtained were routinely subtracted. Limits of detection (LODs) were calculated as three times the standard deviation of field blanks (Table SI2): data below the LODs were substituted by LOD/2 for the statistical processing.

Gaseous pollutants data were provided by ARPAV (local environmental protection agency for Veneto region) whereas meteorological data refer to station 5 of the monitoring network of Ente Della Zona Industriale di Porto Marghera.

2.3. QA/QC and uncertainties

The quality of the analytical procedures was checked by blank controls, by evaluating detection limits (DLs), recoveries, accuracy, and repeatability. The accuracies of quantitative analyses were assessed by analysing certified liquid standards (TraceCERT, Fluka) for standard reference materials for elements (SRM 1648, NIST). OC and EC analyses were routinely checked by re-analysing sucrose calibration standards (relative standard deviation <4%). The recoveries of ions and elements were in the range of 80–110%. The relative standard deviation of each ion and elemental recoveries was <5%.

2.4. PMF settings

USEPA PMF 5.0 was used in this study. PMF was performed strictly following the main rules and suggestions found in the user manual (USEPA, 2014) and in Reff et al. (2007). Details of PMF settings and regression diagnostics are provided as supplementary materials (SI1 and Table SI3).