Size Resolved Elemental Composition of Aerosol at the Rim of Po Valley, Italy. Preliminary Results: General Geochemical Characteristics and the Most Probable Sources

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BACKGROUND AND F-GAP2 EXPERIMENT

Particles in the atmosphere, showing different sizes, shapes and chemical compositions, exert direct or indirect effects on climate and visibility and cause a number of adverse effects on human health. Size distributions of particles, and their physical and chemical composition as well, are strictly related to the emission sources and to secondary formation processes that can alter the initial characteristics. Therefore, size resolved data may have a key role in the study of the aerosol properties.

Since the second half of '80s, high quality elemental analyses on size segregated aerosol samples have been performed using the Particle Induced X-ray Emission (PIXE) and micro-PIXE facilities of the AN2000 accelerator at LNL-INFN, e.g. [1–6]. Most of these samples were collected in remote regions (Antarctica or Svalbard Islands), very few in anthropized regions so far.

This report deals with the preliminary results of an experimental sampling campaign carried out in a semi-rural coastal background site near Venice (Italy) using a 8-stage cascade impactor. The general characteristics of the samples and the most probable emission sources are here presented and discussed. This study represents a part of a main research project aiming at studying the effects of micro-meteorological conditions, atmospheric circulation patterns and regional-scale transports on the air quality of Venice [7–9]. The PIXE analyses at LNL have been carried out as a part of the F-GAP and F-GAP2 experiments.

EXPERIMENTAL

About twenty samples were collected using a 8-stage single-orifice cascade impactor (model I-1, PIXE International Co., USA), for a total of 144 individual Samples in the period September, 2007-January, 2008. The sampling station was located on a lighthouse (45.4227 N, 12.4368 E) at the end of a 300 m-long dam at the Lagoon of Venice port channel of Lido.

The cascade impactor (7 stages with nominal cut-points –d_{50}-values– of 16, 8, 4, 2, 1, 0.5, 0.25 μm aerodynamic diameter, D_{ae}) was provided with a backup filter and worked with a nominal flow rate of 1 L min^{-1}. The sampling time was about 24 h; start and stop were programmed with an electronic timer. The collection media were polycarbonate membranes (Prepared Ring with Nuclepore PR-1N, PIXE International Co., USA) coated with Vaseline to reduce particle bounce-off.

In the samples 17 elements (Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb) were quantified by using the AN2000 PIXE facility on the +45° beam channel. Adopted FISAMB instrumental set-up was well described in previous studies [3]. Briefly, a 2 MeV proton beam generated by the AN2000 Van de Graaff accelerator with an average intensity of about 15 nA induced on the sample targets X-rays which were detected with an ultra-low energy germanium detector (model GUL0110, Canberra, USA) set at 135° to the beam, at a distance of 50 mm and behind a 4 μm Mylar filter and a 50 μm "Funny filter" (hole fraction 14%). Energy resolution was 140 eV at 5.9 KeV. GUPIX was used to fit the X-ray energy spectra and calculate the elemental densities, their errors and the detection limits. For each day, one filter blank sample was prepared together with the samples and was determined and subtracted in all analyses. The quality and accuracy of quantitative analyses were checked with a thin film standard for air particulate (SRM 2783, NIST, USA).

PRELIMINARY RESULTS

Experimental data have been processed using both the normalized histogram of the differential distributions and the log-normal distribution models [10].

Sea salt tracers. Sea salt aerosols typically show the original seawater composition. Most of the analyzed samples exhibited one single supermicrometric mode between 2 and 4 μm of the main sea salt tracers, chlorine and sodium, whereas magnesium was often found below the detection limits. An example of a chlorine distribution is shown in figure 1a.

Anthropogenic elements. Cr, Mn, Cu and Zn are the main tracers for pollution sources. According to the literature available for the study area, road traffic appears as the most probable source for this association of elements [7, 9, 11, 12]. When detectable, these elements show a main submicrometric mode around 0.5 and 0.9 μm, and rarely a secondary supermicrometric mode. An example of a zinc distribution is shown in figure 1b.

Sulfur. Sulfur can be primarily originated from several sources: mineral dust mainly as gypsum, sea salts and various anthropogenic sources. In addition, sulfates can be secondarily originated in the atmosphere as a consequence of the oxidation of gaseous species (mainly SO_2 and biogenic compounds) and the following ternary nucleation with ammonium and water [8]. In the analyzed

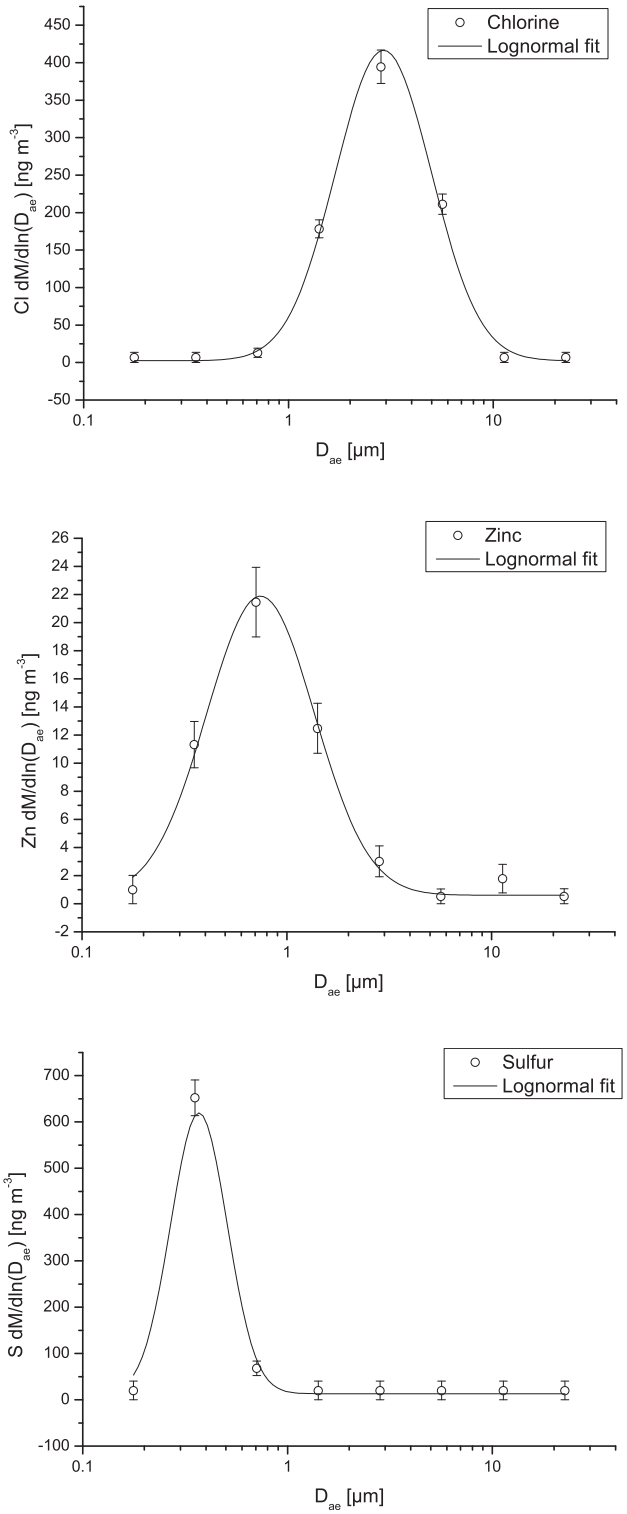

Fig. 1. Mono-modal size distributions of Chlorine (upper), zinc (middle) and sulfur (bottom).

samples, sulfur exhibited a predominant submicrometric mode (0.5–0.25 μm) due to the secondary gas-to-particle processes. In few cases, a secondary supermicrometric mode clearly reflecting the sea salt composition was also found. Figure 1c shows a mono-modal distribution of sulfur.

Crustal dust markers. Generally, Al, Si, Ca, Ti and Fe identify the mineral dust source due to the deflation of soils and rocks. However, iron can be also emitted from road traffic [7]. Figure 2 shows a size distribution of Fe, with two modes. The supermicrometric mode (1–5 μm) is related to the crustal-like iron, whereas the submicrometric one was probably emitted from the same processes as the previous examined anthropogenic tracers.

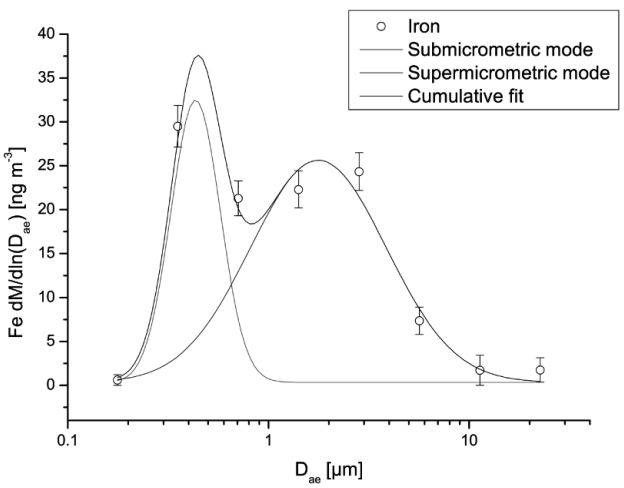

Fig. 2. Bi-modal distribution of iron.

Potassium generally exhibits a bimodal distribution with a main submicrometric mode associated to biomass burning and other combution processes. A secondary supermicrometric mode was found in few samples as a consequence of sea salt or crustal dust components.

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