Changes in PM_{10} Composition in Venice Area During Clean and Polluted Periods: a Source Apportionment Study Coupled with SEM-EDS Individual Particle Analysis

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INTRODUCTION

The individual particle analysis is a fundamental tool in aerosol science, widely used to providing important and detailed information on composition, size, morphology and mixing state of airborne particles. Over the last years, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) have been used in numerous individual particle studies to characterize both physical and chemical properties of airborne particles [1–3].

In this study we discuss the preliminary results of an individual particle analysis on PM_{10} samples with very different particulate matter masses, elemental compositions and source contributions.

MATERIALS AND METHODS

Fifty PM_{10} samples were collected according to US EPA standards on Summer 2007 in a background coastal site near Venice (Italy). Polycarbonate membranes (⌀ 47 mm; pore size 0.4 μm) were used as the best suited for SEM [2].

The concentrations for 13 elements (Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn) were measured by Particle Induced X-ray Emission (PIXE) at AN2000 accelerator, LNL. PIXE set-up: the filter deposit is bombarded with high-energy protons beam (1.8 MeV) to remove inner shell electrons [4], and the resulting X-ray spectra are detected by a germanium iper-pure detector, and are fitted with GUPIX [5]. A subsequent dissolution of 3/4 of each filter using ultrasonic method [6] was performed to determine the concentration of 5 water-soluble ions (2 cations: Na^+, NH_4^+; 3 anions: Cl^-, NO_3^-, SO_4^{2-}) by a Dionex LC20 ion chromatography system.

SEM-EDS analyses were carried out at LNL on the remaining 1/4 of each sample using a Philips XL-30 equipped with secondary electron and back-scattered electron detectors and an EDAX EDS microanalysis system. SEM set-up: samples were coated with a thin gold film by cathodic sputtering, accelerating voltage was 15 kV and the beam spot size was 2. A number of ~200 particles was recognized for each selected filter.

Analysis limitation and probable errors: In this study we collect PM_{10} on 24-h samples, resulting on a high particle density on membranes. To reduce this problem, only particles with a geometric diameter ≥ 250 nm are analyzed.

A compositional classification of individual particles was performed according to both EDS spectra and particle morphologies [1,7]. Six different classes of particles were identified: (i) crustal particles, such as silicates and carbonates, showing a relative abundance of crustal elements Si, Al, Fe, Ca; (ii) chlorides, mainly halite; (iii) sulphates, mainly Ca and Na sulphates; (iv) Elemental and Organic Carbon Compounds (EOCC), mainly composed by soot aggregates and carbonaceous spherical particles; (v) metals and metal oxides/hydroxides, mainly as Fe-rich particles and (vi) biological particles, such as bacteria, fungi, pollens, fragments of organisms, etc. In figure 1 we present some examples of different particles identified and classified in this study.

RESULT AND DISCUSSION

The source apportionment analysis is carried out using the Positive Matrix Factorization (PMF) with the US EPA PMF v. 1.1 software package [8]. Five independent sources were identified and quantified: (i) mineral dust (Si, Al, Fe, Ca, K, Mg, Ti and Mn) [9]; (ii) Local Anthropogenic Emissions (LAE) (Cr, Mn, Cu and Zn), mainly due to traffic [10]; (iii) the Secondary Inorganic Aerosol (SIA) generated by the nucleation of $H_{2S}O_4$,NH_3,and H_2O in the atmosphere [11], linking NH^+_4 and SO_4^{2-}; (iv) fossil fuels (V and Ni) [12]; (v) sea-salt (Na^+, Cl^- and NO_3^-)[9].

A total of two samples were selected on the basis of analytical and source contribution results: (i) sample 1 was selected for the low PM_{10} concentration (6.2 μgm^{-3}) and shows low contributions of anthropogenic sources (LAE and fossil fuels) calculated by the PMF, revealing a prevalent natural composition; (ii) sample 2 has a relatively high concentration of PM_{10} (19 μgm^{-3}) and show high concentrations for the elements linked to the anthropogenic emissions. Source apportionment results show that this sample is mainly made up by LAE, whereas the other source contributions are very low. In this way, the first sample is selected as representative for clean periods, whereas second sample exhibits very high contributions for anthropogenic sources, and is taken as representative for heavily polluted periods.

Table I exhibits the results of this study, showing the relative abundance of six compositional classes expressed as percentage. The sample 1 (clean) is mainly composed by crustal particles (39%), EOCC (21%) and sulphates (21%), mainly as calcium sulphates with the typical crystalline structure of gypsum and particles with geometric diameters usually larger than 1 μm. A moderate percentage of biological particles (15%) is present, whereas low percentages of chlorides (3%) and metals (1%) were found.

Sample 2 (polluted) is mainly composed of EOCC (43%), followed by sulphates (22%). Sulphates are present mainly

as mixed Na-Ca-K-sulphates with fine sizes (diameter less than 1 μm). This sample has the highest percentage of metals (14%), especially spheres of Fe, Ti and Cu. The crustal and biological particles represent only 13% and 8%, respectively. No chlorides were found. These results can be considered comparable with source contributions calculated from the PMF receptor model.

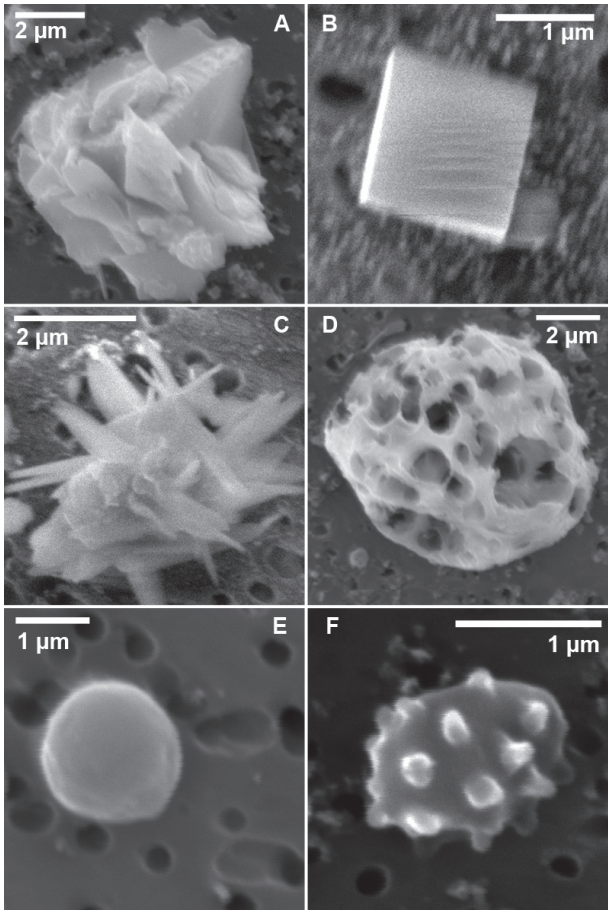

FIG. 1. *Examples of particles classified in this study. A) Crustal particle: A silicate mainly composed by Si and Al; B) Chloride: halite; C) Sulphate: Ca-sulphate with the typical mineralogical structure ofgypsum; D) EOCC: Particle probably emitted by combustion processes; E) Metal: Fe-rich spherical particle; F) Biological particle.*

TABLE 1. *The results of individual particle analysis expressed as percentage.*

	Sample 1 (clean) %	Sample 2 (polluted) %
Crustal	39	13
Chlorides	3	0
Sulphates	21	22
EOCC	21	43
Metals	1	14
Biological	15	8

CONCLUSIONS

This work describes the preliminary results of F-GAP experiment at AN2000 accelerator by Geo-mineralogical Section of Università Ca' Foscari Venezia with the collaboration of FISAMB-PD research group. The results reveal marked differences among the individual particle composition on samples collected in days with very different source contributions. This study demonstrates the effectiveness to couple source apportionment with individual particle analysis results, allowing to extract further information on PM_{10} composition and source contributions. Sample 1 shows high percentages of natural-made particulate matter, as crustal particles, whereas sample 2 exhibits high percentages of anthropic-made particles, as carbonaceous particles linked to soot, industrial and diesel vehicle emissions, and metal particles.

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