Source Apportionment of Inhalable Particulate Matter (PM_{10}) in a Background Coastal Site Near Venice (Italy) - Preliminary Results

M. Masiol[1], G. Rampazzo[1], D. Ceccato[2], B. Pavoni[1], F. Gonella[3], E. Molinaroli[1], L. Menegazzo Vitturi[1], F. Visin[1], M. Pistolato[1], S. Squizzato[1], G. Valotto[1]

1 Dip. Scienze Ambientali, Università Ca' Foscari Venezia, Italy
2 Dip. Chimica Fisica, Università Ca'Foscari Venezia, Italy

INTRODUCTION

Venice is located in the north-eastern part of Italy between the Adriatic Sea and the Po Valley. Atmospheric pollution of this area deserves particular care, due to the heavy industrial, urban and traffic emissions, and to peculiar weather conditions, with the tendency to trap the pollutants [1,2]. Moreover, proximity to the Adriatic Sea and the Lagoon of Venice also probably affects the atmospheric chemistry as sources of marine aerosol.

Inhalable particulate matter with an aerodynamic diameter less than 10 μm (PM_{10}) is considered a dangerous airborne pollutant [3], causing several adverse health effects [4]. Recently, there is increasing interest in the PM_{10} levels of Venice area due to the tendency to exceed the limit values fixed by the European directives.

Our study mainly focuses on elemental characterization of PM_{10} in Venice, in order to detect and quantify both natural and anthropogenic sources. In particular, we quantify the marine aerosol contribution to the total PM_{10}. We present the preliminary results for the Summer period [5].

EXPERIMENTAL SET-UP

A total of 291 PM_{10} samples were collected daily with a low-volume automatic sequential sampling station (according to US-EPA standards) between May 2007 and April 2008. Sampling station was placed in the Punta Sabbioni lighthouse (Lat. 45°25'21 N, Long. 12°26'12 E). Polycarbonate Nuclepore filters (porosity 0.4 μm) were utilized. Multi-elemental analysis were carried out with the Particle Induced X-ray Emission (PIXE) at the AN2000 Van de Graaff accelerator of Laboratori Nazionali di Legnaro. The PIXE set-up is described elsewhere [6], involving a homogenous 1.8 MeV H^+ beam and a low-energy germanium detector Canberra AP1.3. X-ray spectra were fitted to calculate the concentrations for 16 elements with Z> 10 (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu and Zn) with the GUPIX software package [7]. The quality and accuracy of quantitative analyses were checked with the NIST SRM 2783 Air Particulate on Filter Media thin film standard.

RESULTS AND DISCUSSIONS

We present the preliminary results of 75 samples collected between May and July, 2007. The highest average elemental concentrations were obtained for sulfur, major elements, and chloride: S>Na>Ca>Cl>Si>Fe>Al>K>Mg >Zn>Ti>Mn>V>Cu>Ni>Cr. High sulfur concentrations are probably due to various emission sources, i.e., crustal and marine contribution, biogenic production of dimethyl-sulfide, and several anthropogenic emissions. The sea-salt markers (Na and Cl) show high concentrations reflecting the natural contribution of Adriatic Sea. Relatively low concentrations of minor and trace elements were found, compared with other data collected in the area by our group study in the 2000s [1,2].

In order to detect and quantify the main PM_{10} sources, a source apportionment study was carried out using a receptor model [8,9]. A Varimax rotated factor analysis was applied to standardized dataset. Four factors with eigenvalues>1 were extracted, identifying four sources according to their loadings, and explaining about 85% of total variance. The first factor mainly links Si, Ti, Al, Ca, Mg, Fe, K and, secondarily, Mn, identifying crustal component, due to the resuspension of rock and soil by wind and convective processes. The second factor is made up of V, Ni and sulfur, identifying the fuel-oil burning and transformation processes [10–12]. The third factor represents the marine aerosol, mainly linking typical sea-salt elements Na, Cl, and, secondarily, Mg. The fourth factor represents a pollution source, mainly linking Zn, Cu, Mn, Cr and, secondarily, Fe and K. According to other data collected in the study area [1], we agree that this elemental association is due to local anthropogenic emissions, i.e., road dust by vehicular traffic and industrial emissions.

A multi-linear regression analysis was then performed to estimate the quantitative contribution of the four identified sources to the daily levels of particulate matter [8,9]. This operation was carried-out by regressing the PM_{10} concentrations on the absolute factor scores obtained by the factor analysis. The results are summarized in figure 1.

On the average, the two anthropogenic sources (local anthropogenic emissions and fossil fuel combustion) contributed most to PM_{10} concentration, accounting for 23% and 13%, respectively. Natural sources (crustal and marine) contributed most to PM_{10} concentration, accounting for 35% and 3%, respectively. Unfortunately, the mass contribution of non-identified sources was 26%. This high unaccounted value could be attributed to water and non-determined elements, such as the carbonaceous constituents [13]. The single daily apportion results were shownonthe time series of PM_{10} source contributions expressed as percentages in figure 2.

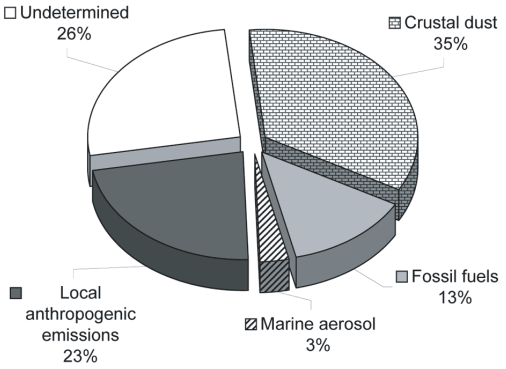

FIG. 1. *Results of source apportionment analysis expressed as percentages of PM_{10} concentration.*

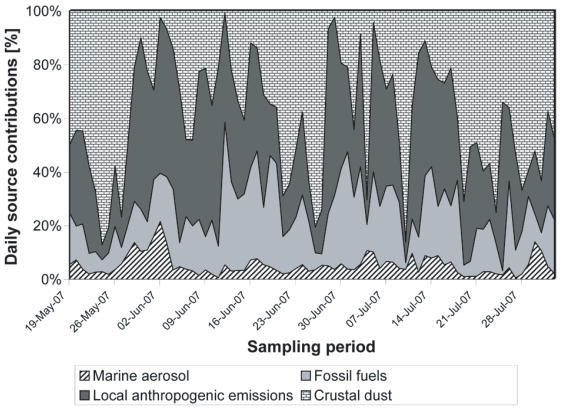

FIG. 2. *Time series of recorded PM_{10} daily source contributions, expressed as percentages. Unaccounted PM_{10} mass are not reported.*

These results are not only unexpected, but also worrying. The sampling site was chosen for the proximity to the sea and the relative distance from direct anthropogenic emission sources, such as traffic routes, large urban agglomerates, and major industrial areas. Therefore, this source apportionment study shows the importance of anthropogenic emission sources, accounting for 36% of PM_{10}, whereas natural sources (mineral dust and marine aerosol) contribute to 38%. Low values for marine aerosol are unexpected and probably due to the micro-meteorological factors influencing the sea-salt generation processes.

This work describes the preliminary results of F-GAP experiment at AN2000 accelerator. The results demonstrate the suitability of PIXE for airborne particulate matter studies, overcoming several analytical problem (e.g. avoiding the introduction of contaminations and errors associated with the filter manipulations), performing rapid multi-elemental analysis and preserving the samples, being a non-destructive technique.

ACKNOWLEDGMENTS

This work was carried out with the aid and collaboration of Ente Zona Industriale di Porto Marghera. The authors gratefully acknowledge the support of this work by Prof. P. Mittner (FISAMB-PD). The authors would like to thank the Comando Zona Fari e dei Segnalamenti Marittimi Venezia for logistics.

[1] G. Rampazzo et al., Water Air Soil Poll. 195 (2008) 161.
[2] G. Rampazzo et al., Chemosphere 71 (2008) 2068.
[3] World Health Organization, WHO Regional Publications, European Series 91 (2000).
[4] S. Medina et al., J. Epidemiol. Community Health 58 (2004) 831.
[5] M. Masiol et al., European Aerosol Conference 2008, Thessaloniki, abstract T06A075P (2008).
[6] P. Mittner et al., Nucl. Instr. and Meth., B109/110 (1996).
[7] J.A. Maxwell et al., Nucl. Instr. and Meth., B95 (1995) 407.
[8] G.D. Thurston and J.D. Spengler, Atmos. Environ., 19 (1985) 9.
[9] P. Salvador et al., Atmos. Environ., 38 (2004) 435.
[10] R.M. Harrison et al., Atmos. Environ., 31 (1997) 3309.
[11] J. Isakson et al., Atmos. Environ., 35 (2001) 3659.
[12] M.L. Bosco et al., Environ. Res., 99 (2005) 18.
[13] E. Andrews et al., J. Air Waste Manage. Assoc., 50 (2000) 648.