

# Local and Regional Sources of Respirable Particulate Matter in Venice Preliminary Results of F-GAP(x) Experiments at the AN2000 Accelerator

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## BACKGROUND

Atmospheric particles with an aerodynamic diameter less than 10  $\mu\text{m}$  PM<sub>10</sub> are named "respirable fraction" because they can be inhaled and then enter the human respiratory tract. Whereas the largest particles are trapped in the upper respiratory tract (nose, throat and trachea), the finest ones tend to penetrate deeper down to the alveolar region. The Council Directive 1999/30/EC has recommended the monitoring of PM<sub>10</sub> in Europe, and the recently adopted 2008/50/EC has attributed great importance to the finest fraction (with an aerodynamic diameter less than 2.5  $\mu\text{m}$ , PM<sub>2.5</sub>).

## F-GAP(x) EXPERIMENTS

F-GAP (2007–2009) and F-GAP2 (2011–2012) experiments at LNL [1, 2] mainly dealt with the geochemical characterization of the PM<sub>10</sub> in the Venice area and the quantification of the main sources that caused the frequent events of PM concentrations above the EU limits. This report presents some preliminary results of an extensive sampling campaign carried out in a semi-rural coastal site near Venice. Data obtained from the AN2000 PIXE facility at LNL were processed by applying some receptor modeling techniques and other chemometric tools to detect the main emission sources having an effect on PM<sub>10</sub> levels.

## EXPERIMENTAL

About one year-long PM<sub>10</sub> sampling campaign (May 2007–February 2008) was carried out in a coastal site near Venice using a low volume sampler (TCR Tecora, Italy) and polycarbonate membranes ( $\varnothing$  47 mm, 0.4  $\mu\text{m}$  porosity, GE, USA). PM<sub>10</sub> masses were gravimetrically determined in conditioned temperature and relative humidity. Half sample was ultrasonically extracted in ultrapure water and solutions were analyzed for four anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and four cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>) using an ion chromatography system (Dionex DX500, USA), after pre-filtration.

Samples were also analyzed for quantifying 17 elements (Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb) using the AN2000 PIXE facility on the +45° beam channel. Adopted FISAMB instrumental set-up was well described in previous studies [3]. Energy resolution was 140 eV at 5.9 KeV. GUPIX code was used to fit the X-ray energy spectra.

Filter blank and fields blank were prepared in parallel with the samples and subtracted in all analyses. The quality and accuracy of quantitative analyses were checked with standard reference materials (SRMs 1648 and 2783, NIST, USA). Details of chromatography and PIXE set-up were given elsewhere [1–3].

This report shows some preliminary data of F-GAP(x) experiments. The most probable sources of respirable particulate matter were studied by applying some multivariate procedures, including some widely used receptor modeling techniques. Data were studied separately for warm and cold seasons. Warm period (May–beginning of September) shows typical atmospheric circulation patterns with sea/land breezes. This period is therefore very complex in terms of atmospheric circulation. The cold season (October–January) is characterized by a less complex atmospheric circulation, but is affected by the highest levels of PM<sub>10</sub>, and is therefore more important in terms of potential health hazard.

## FACTOR ANALYSIS AND UNMIX

Both periods were studied by applying the Varimax rotated factor analysis (FA) which is the most common and widely used approach to detect the main sources of PM<sub>10</sub> [1, 2]. In a second step, the same dataset was fed into the receptor model UNMIX version 6 to solve the general mixture problem in which data are assumed to be a linear combination of an unknown number of emission sources of unknown composition, which contribute an unknown amount to each sample. UNMIX was well described elsewhere [4]. Results are very similar to those obtained with the use of factor analysis.

Generally, four factor with eigenvalues >1 were extracted for the warm period, whereas a more complex source composition (six sources) was found in the cold season. The obtained factor loadings for both periods are shown in fig. 1.

Both periods exhibit a clear sea-salt source, which is naturally originated by the bursting of bubbles at the sea surface. This source, similar to the seawater composition, is mainly composed of chloride, sodium and magnesium. A second natural source, the mineral dust, was also found in both periods having high loadings of typical crustal markers: silicon and aluminium. However, for this latter source some differences in chemical profiles between warm and cold seasons were observed. Generally, the warm profile appears more complex, with high loadings for other crustal-like

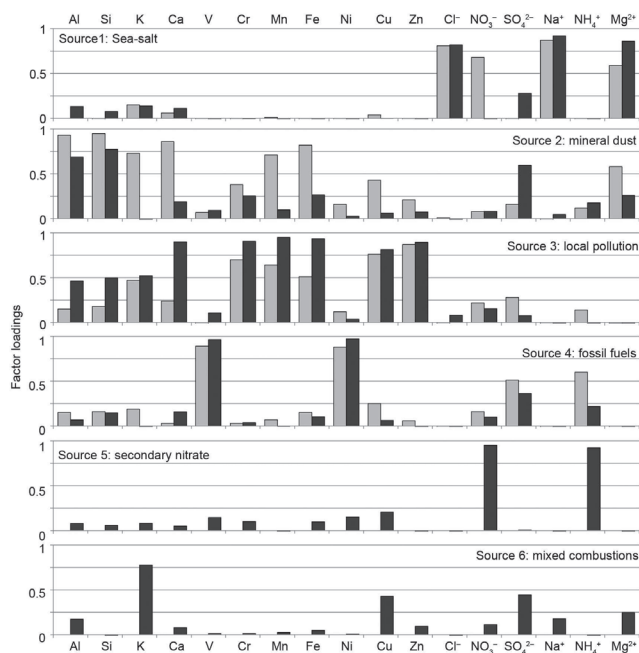


Fig. 1. Factor loading extracted by FA for warm (grey) and cold (black) seasons.

elements (K, Ca, Mn, Fe and  $Mg^{2+}$ ), whereas the cold profile shows high shares of sulfate. These differences can be mainly attributed to the higher air temperatures in summer, which may enhance the soil depletion and the road dust resuspension.

The third common factor clearly reflects an anthropogenic source, having high loadings of Cr, Mn, Fe, Cu and Zn. This association of elements has been found in other studies and interpreted as industrial or road traffic. However, since the sampling site is upwind to main industrial areas, traffic appears the most probable one [1, 2, 5, 6]. The last common source links vanadium and nickel, which are widely known tracers of fuel-oil combustion, shipping emissions, petrochemical refineries and coke production. The concurrent moderate shares of sulfate and ammonium confirm the hypothesis that this source is related to the fossil fuels burning and conversion processes [1, 2].

Two additional sources were found during the cold

season. The first source is made up of nitrate and ammonium, clearly representing the ammonium nitrate formed through the condensation and the nucleation of gaseous  $HNO_3$  and  $NH_3$  in the atmosphere [2]. The second one is mainly composed of potassium, with moderate loadings of Cu and sulfate. As potassium has been largely used as a tracer for biomass combustions, this source may identify mixed combustion processes.

## LOCAL AND REMOTE CONTRIBUTIONS

As recently reported [1, 2, 7], both local atmospheric circulation and regional-scale transport can strongly influence the air quality of Venice. Up today, many tools have been proposed to study and assess the influences of these transport processes. Recently, the authors applied a factor-cluster analysis on chemical data and cluster analyses on wind data and backward trajectories. The results revealed the important role of both local atmospheric circulation, i.e. weather conditions (air temperature, humidity, solar irradiation) and winds on the levels of  $PM_{10}$  in the study area. Moreover, also the external transports were found having a significant impact on the air pollution levels, especially in the sampling days when EU limits were exceeded.

## ACKNOWLEDGMENTS

The authors wish to thank Comando Zona Fari e Segnalamenti Marittimi di Venezia (Marina Militare Italiana) for logistics and ARPAV-Centro Meteorologico di Teolo for providing the weather data used in this study.

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