Sea-Salt Aerosol Generation Events in Venice (Italy) During the Sea/Land Breezes Season a Multivariate Statistical Approach Coupled with Wind Speed and Direction

M. Masiol[1] , D. Ceccato[2] , G. Rampazzo[1] , S. Squizzato[1]

1 Dip. Scienze Ambientali, Università Ca' Foscari Venezia, Italy, 2 Dip. Fisica "Galileo Galilei", Università di Padova, Italy

INTRODUCTION

The implementation of European directive 1999/30/EC has fixed the limit values for several airborne pollutants, such as the particulate matter with aerodynamic diameter less than 10 μm (PM_{10}). The atmosphere in Venice, like in other European cities, is influenced by complex PM_{10} multi-emission sources, with a subsequent frequent exceeding of limit. In this way, the identification and the quantification of sources have become useful tool in ambient air quality management, especially in the areas where the air quality objectives are not or are unlikely to be met [1]. Therefore, in order to characterize and manage the Venice air quality, is necessary to identify the weight of the single sources, and to understand the main local processes generating the particulate matter.

Mineral dust and sea-salt aerosol represent the worldwide main natural contributors to the particulate matter [2]. For this reason, proximity to the Adriatic Sea and the lagoon can act as sea-salt aerosol sources in Venice, but the marine contribution to PM_{10} in the area has never been investigated.

The mechanisms of sea-salt aerosol production have been well described and well investigated by several studies [3,4]. Sea-salt is mechanically generated on the sea surface by bursting bubbles as waves break due to wind stress, and their generation is heavily dependent on wind speed, direction and duration. Breaking waves create whitecaps and, subsequently, sea-spray droplets are injected in the atmosphere. Coastal areas play an important role on marine aerosol production, due to breaking waves occurring even at moderate wind speeds, e.g., the concentration of air bubbles in breaking waves was estimated four times higher in the coastal zone than in the open ocean under the same weather conditions [5].

We have evaluated the role and contribution of sea-salt generation processes in the Venetian area during the sea/land breezes season. To this purpose, a series of experimental observations were carried out in Summer 2007, and statistical tools, micro-meteorological considerations and back-trajectories are analyzed and discussed.

ANALYTICAL

A total of 50 PM_{10} samples were collected with a low-volume sampler according to US-EPA standard in a coastal site near Venice. Polycarbonate GE Water & Process Technologies Nuclepore filters (porosity 0.4 μm, φ 47 mm) were utilized. A multi-elemental analysis of PM_{10} samples was carried out by PIXE at the +45^{o} beam channel of AN2000 Van de Graaff accelerator, Laboratori Nazionali di Legnaro. The PIXE analyses were carried out utilizing a homogenous 1.8 MeV proton beam and a low-energy germanium detector Canberra AP1.3. PIXE set-up is well described elsewhere [6]. GUPIX software package [7] was used to fit X-ray spectra and to calculate the concentrations of 16 elements with $Z \geq 11$ (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu and Zn). Quality and accuracy of analysis were checked with NIST SRM 2783 Air Particulate on Filter Media thin film standard.

STATISTICAL APPROACH

A multivariate statistical approach was tested and applied to select samples by similarity on source contributions and to extract samples with high contributions of sea-salt aerosol. The methodology is well discussed in Molinaroli et al. [8]. Varimax rotated factor analysis was primarily used to identify the particulate matter sources. By applying the factor analysis to 17 variables elements and PM_{10} standardized concentrations, in this case– we extract a number of factors explaining most of variance of the original data matrix, that can be interpreted as probable emission sources [9–11].

After performing factor analysis, a number of independent sources are then identified, and the Factor Score Matrix (FSM) is calculated. The FSM matrix is composed of *n* collected samples and *m* new variables which are directly proportional to the daily source impact of each extracted factor/source [12]. This new matrix revealed the "highest" variability part of the data set, omitting the less significant part, which may be defined as "background noise" and was therefore not particularly significant for the data set [8].

The FSM is used to performing a Q-mode cluster analysis (Ward's hierarchical agglomerative method, squared Euclidean distance measure), in order to identify homogeneous subgroups of samples with compositional similarity [13,14], i.e., to organize collected samples into similar groups on the basis of similarity on the daily contribution of each source.

RESULTS AND DISCUSSION

The factor analysis extract 4 factors with eigenvalues> 1, explaining about 85% of total variance. Factors were interpreted as two natural and two anthropogenic sources: (i) mineral dust linking typical crustal elements as Al, Si, Ca, Ti, Fe; (ii) sea-salt aerosol, with high loadings for Na and Cl; (iii) industrial and/or traffic local emissions (Cr, Mn, Cu, Zn); (iv) fossil fuels combustion/transformation processes, linking typical oil markers (V, Ni) and sulfur [10,13,15].

After running factor analysis, the FSM were utilized to perform the cluster analysis. Five clusters were detected, identifying 5 groups of samples with different source contributions: group 1 exhibits high concentrations of typical crustal elements and is interpreted as representative of high mineral dust local generation or long-range transport events; group 2 has the highest values for almost all elements and particulate matter, representing severe pollution events; group 3 is composed of samples with high concentrations for fossil fuels markers and sulfur; group 4 links samples with low concentrations of all elements and PM_{10}, and was interpreted as “mixed aerosol”, representing typical local aerosol composition.

Group 5 has high contribution of sea-salt source, very high concentrations of marine elements (Na, Cl), and it is associated with sea-salt generation events. With the aim of better understanding the location, the micro-meteorological factors and the processes generating sea-salt in the area, we have studied both wind roses and back-trajectories for this group. Wind data were collected near the sampling site, whereas determinations of 5-day air mass back-trajectories were computed with the HYSPLIT model [16,17].

The wind roses are interpreted by comparing them with the full period rose, and they exhibit the prevailing wind blowing from NE, with a relative high average speed (up to 2 m s^{-1}), as reported in figure 1. Most of the back-trajectory show a north European continental air mass origin, excluding a long-range transport of sea-salt elements, e.g., from Mediterranean Sea or Atlantic Ocean.

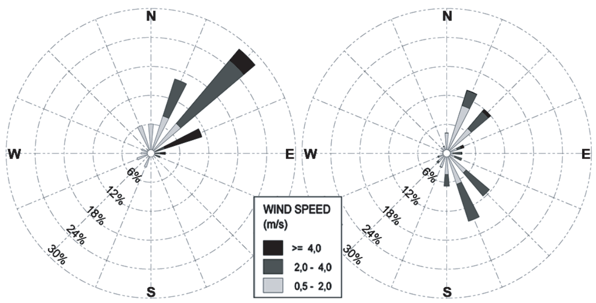

FIG. 1. *Wind roses for group 5 (left), and full sampling period (right).*

For these reasons, we hypothesize that sea-salt generation occurs locally, primarily generated by moderately intense north-east winds, passing over the surf zone. In this scenario, high levels of sea salt are primarily due to local generation processes taking place along the coastline, mainly on windy days.

In this study we verify the goodness of coupling a multivariate statistical approach and wind direction data. The combination of factor and cluster analysis results with wind direction data and back-trajectories yielded further detailed information on potential source locations and aerosol generation processes.

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