Particulate Matter Characterization in an Industrial District Near Florence, by PIXE and PESA

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ABSTRACT

The composition of particulate matter in Montelupo Fiorentino, a little town about 20 km west of Florence characterised by the presence of a large number of ceramic and glass factories, has been studied by means of continuous and sequential sampling, Ion Beam Analysis (IBA) techniques and statistical methods. The aerosol PM_{10} fraction has been collected on a daily basis for 10 months (September 2002-June 2003). To investigate the elemental size distribution, for a shorter period (about one month) we collected PM_{10}, PM_{2.5} and PM_{1} simultaneously. A continuous Streaker sampler has also been used, which allows to study the aerosol composition with two-hour time resolution. Mass concentrations were obtained using an analytical balance. The elemental analysis was performed by the I.N.F.N. accelerator at the Physics Department of the Florence University, by PIXE and PESA techniques (the latter implemented for this campaign). The use of the two techniques allowed a complete reconstruction of the gravimetric mass. An Absolute Principal Component Analysis showed industrial sources to be, in average, the main contributors to PM_{10} mass; however the weight of the ‘soil’ source (connected to local soil re-suspension as well as to long range Saharan transport episodes) becomes dominant during some of the days in which the 50 µg/m³ limit is exceeded.

Keywords: aerosol, PIXE, PESA, light element detection, APCA.

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1. INTRODUCTION

Montelupo Fiorentino is a little town about 20 km west of Florence, characterised by the presence of a large number of ceramic and glass factories. Since the PM_{10} mean value in the area is higher than the new Air Quality Directive (1999/39/EC) recommended value and potentially harmful elements can be emitted by the local industrial activities, we decided to start an extensive investigation, whose purposes are manifold: (1) determining PM_{10} concentration and composition (by PIXE), collecting samples for a long period, (2) determining, for a certain period, the mass concentrations and the elemental composition also of the PM_{1} and PM_{2.5} fractions of the aerosol; (3) determining by Proton Elastic Scattering Analysis (PESA) the concentrations of H, C, N and O, which are important contributors to the aerosol, allowing a complete reconstruction of the mass; (4) identifying the major pollution sources and their impact, using also a streaker sampler with two-hour time resolution.

2. METHODS

The particulate matter samples were collected on 47 mm diameter Teflon filters by three sequential particle samplers. The first one is the PARTISOL 2025, which may be equipped with the EPA-standard PM_{10} and PM_{2.5} inlets and a PM_{1} inlet (flow rate 1m³/h). The other ones are two IND PNS15D sequential particulate samplers, which may be equipped with PM_{10} (CEN EN 12341 reference sampler), PM_{2.5} and PM_{1} inlets (flow rate 2.3 m³/h). The samplers were located 4 m above ground level, on the roof of an air

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The sampling campaign started on 24th September 2002 and ended on 24th June of 2003. In the first part of the campaign (till 30th October) we mounted the same inlet on all the instruments to carry out a systematic comparison between the concentrations measured by the three devices in all the granulometric fractions (about ten days for each fraction); from 1/11/2002 till 21/11/2002 we put a different inlet on each instrument to measure the granulometric fraction ratios (i.e. PM$_1$/PM$_{2.5}$ and PM$_{2.5}$/PM$_{10}$). Starting from the 23rd of November we continued the sampling with only one IND sampler with PM$_{10}$ inlet. Due to some technical problems during the campaign, we obtained PM$_{10}$ samples for about 200 days, PM$_{2.5}$ and PM$_1$ samples for about 30 days. From 13th February till 12th March we also collected the fine and coarse fraction of the aerosol with two-hour resolution by a streaker sampler.

The PM$_{10}$, PM$_{2.5}$ and PM$_1$ mass concentrations were obtained on preconditioned filters using a microbalance. The concentrations of the elements with Z>10 were measured by PIXE at the external beam facility of the KN3000 Van de Graaff accelerator in Florence [1]. To obtain a complete reconstruction of the aerosol mass, we implemented the detection of H, C, N and O by in-vacuum Particle Elastic Scattering Analysis [2].

The comparisons between the three samplers have shown generally a very good agreement both for mass and for element concentrations.

3. RESULTS AND CONCLUSIONS

The average value of PM$_{10}$ concentration over the whole sampling period was 32 µg/m$^3$ and in 21 days PM$_{10}$ concentration was above the 50 µg/m$^3$ limit. The average concentrations of the detected elements are reported in Table 1. Average As concentration is 10 ng/m$^3$, to be compared with the future limit of 5 ng/m$^3$; the concentration of this element, which is related to emissions from artistic glass manufactures, assumed very high values (with peaks up to 100 ng/m$^3$) during the first sampling months, while a sharp decrease was observed starting from December (Figure 1) and it was ascribed to changes in glass production activities.

![Figure 1](image1.png)

**FIGURE 1.** As daily concentrations.

![Figure 2](image2.png)

**FIGURE 2.** Average contributions (%) of the eight most abundant detected elements to the total PM$_{10}$ mass.

<table>
<thead>
<tr>
<th>element</th>
<th>ng/m$^3$</th>
<th>element</th>
<th>ng/m$^3$</th>
<th>element</th>
<th>ng/m$^3$</th>
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<tbody>
<tr>
<td>H</td>
<td>690</td>
<td>S</td>
<td>950</td>
<td>Ni</td>
<td>4</td>
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<td>C</td>
<td>13120</td>
<td>Cl</td>
<td>280</td>
<td>Cu</td>
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<td>K</td>
<td>340</td>
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<tr>
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<td>Ti</td>
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<td>Se</td>
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<td>Fe</td>
<td>530</td>
<td>Pb</td>
<td>19</td>
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</table>

PIXE-PESA measurements allowed a pretty good reconstruction of PM$_{10}$ gravimetric mass, as can be seen from Figure 2. C, N and O are the main aerosol components and carbon gives the most important contribution.
Considering the results from the analysis of the samples collected simultaneously in the three fractions, PM$_{2.5}$ and PM$_{1}$ turned out to be a substantial part of PM$_{10}$ (0.63 ± 0.09 and 0.46 ± 0.08 respectively). Al, Si, Ca, Fe, Sr and other typical crustal elements, and also Zr (produced by the manufacturing of tiles), are more concentrated in the PM$_{2.5-10}$ fraction, while elements like H, C, N, O, S, K, Zn, As and Pb are mainly present in the PM$_{2.5}$ and PM$_{1}$ fractions.

![Figure 3](image)

**FIGURE 3.** Percentage decomposition of the elemental concentrations in the three granulometric fractions.

The simultaneous detection of all the elements allowed us to identify several aerosol transport episodes, such as marine aerosol and Saharan dust events (see the contribution to this conference # 909). In particular on November 15$^{th}$ and 16$^{th}$ we identified a Saharan dust episode characterized by a strong increase of the concentrations of PM$_{10}$ and of all soil-related elements (e.g. Al, Si, Fe, Ti) in the PM$_{10}$ fraction (Figure 2), but not of PM$_{2.5}$ and PM$_{1}$ concentrations. Back-trajectories calculations confirm the hypothesis of the Saharan origin of the aerosol.

An Absolute Principal Component Analysis (APCA) was carried out to identify the main aerosol sources and to calculate the PM$_{10}$ mass and elemental source apportionments [3]. We identified the following sources: (1) a soil related source, connected to local soil re-suspension as well as to the above quoted Saharan transport episodes, which gives an average contribution of – 21% to the PM$_{10}$ mass, (2) a marine aerosol source connected to the above quoted sea salt transports, contributing for few percents, (3) a secondary sulfate source (high factor loading of S and V), which accounts for about – 11%, and (4) two industrial sources; the first one (characterized by Cu, Br, Ni, Cr and K) gives the higher contribution (– 41 %), the second one (with high loading of Zn, Pb) accounts for – 16 %. Some of the elements with high loadings in the industrial sources, like Cu, Zn and Cr, could be also connected with traffic; nevertheless, the analysis of the hourly concentration data-set avoided this possibility, since the time trends do not show periodic daily variations with peaks during traffic rush hours.

It is interesting to note that, although in average the anthropogenic contribution to PM$_{10}$ mass is dominant, during nearly half of the 21 days in which PM$_{10}$ mass was above 50 µg/m$^3$, the soil related source gave the main contribution.

**REFERENCES**


Proceedings of the 10th International Conference on Particle Induced X-ray Emission and its Analytical Applications, Portorož, Slovenia, June 4-8, 2004