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Elemental composition and source apportionment of particulate matter near a steel plant in Genoa (Italy)

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Abstract

The composition of particulate matter near a large steel plant, located inside the town of Genoa (Italy), has been studied since July 2004. Several instruments have been used: a sequential sampler, operated on a daily basis and a two-stage continuous streaker sampler. An optical particle counter (OPC) provided the aerosol size distribution with a 1-min time resolution. PIXE and ED-XRF analysis were performed on the aerosol samples. In particular, the streaker frames were analyzed by PIXE at the new external proton beam facility of INFN-Florence whereas the daily filters were measured by ED-XRF in Genoa. We present here results obtained in a part of the campaign when all the above quoted devices have been operated simultaneously.
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1. Introduction

Genoa is the most populated coastal city in the northwest of Italy, grown during the centuries around an important harbour, with significant steelworks in the surrounding.

In the frame of a large study of the air quality in city we have placed and operated nearly continuously a sequential particulate matter sampler since July 2004 near a large steel plant located in the harbour area. This site had been object, in the past, of a similar study [1], since the plant structure is now completely changed and a renewed study was necessary. We concentrated our efforts in the characterization of PM_{10} (particulate matter with aerodynamic diameter, D_{ae}, smaller than 10 μm). Thus we collected and analyzed daily PM_{10} samples while, for a shorter period of time, we also used equipments giving information on a hourly basis on PM concentration, size distribution and elemental composition. IBA techniques, PIXE in particular, constituted a key and unique tool to analyze hourly samples collected by two-stage streaker sampler. Hourly elemental concentrations are useful to study particulate matter in industrial sites because they are unique tool for a clear identification of particulate matter sources. Samples discussed in the following were collected between 4th and 12th March 2005.

2. Methods

Daily particulate matter samples were collected on 47 mm diameter Teflon (CF_2) filters by a sequential sampler (PARTISOL 2025, by Rupprecht & Patashnick Co.); this sampler is designed for a flow rate of 1 m^3/h and may be equipped with the EPA-standard PM_{10} and $PM_{2.5}$ inlets; it can also collect PM_1 by a WINS impactor

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located before the filter. We also used a two-stage streaker sampler (by PIXE International Co.). The streaker consists of a pre-impactor that removes particles with $D_{ae} > 10$ μm from the incoming flux, a thin Kapton foil that collects particles with $2.5 < D_{ae} < 10$ μm and a Nuclepore film that intercepts all smaller particles. The sampling produces a circular continuous deposit into the two-stages. It should be noted that the performance of streaker samplers have never been certified and that differences between nominal and actual cut-off diameters are therefore possible. An optical particle counter (mod. 1.108 by Grimm) provided the particles size distribution in 15 size channels between 0.3 and 20 μm, with a 1 min time resolution.

The daily samples were analyzed by ED-XRF (ED-2000, by Oxford Instruments) at Genoa University for elements from Na to Pb, following a procedure established in the past [2]. ED-XRF spectra were fitted by AXIL software [3] and the elemental concentrations were obtained via a calibration curve from a set of thin standards of known areal density. Detection limits were about 10 ng/m^3 for low Z (atomic number) and 1 ng/m^3 (or below) for medium-high Z elements.

The elemental analysis of streaker deposits was carried out using the external beam PIXE facility [4] of the new INFN Tandem accelerator at the Physics Department of the Florence University. The samples were placed at 1 cm from the extraction window and they were perpendicular to the beam; the beam scanned the streak in steps of 1.25 mm corresponding to 1 h of aerosol sampling. Beam current was measured by a graphite Faraday cup placed behind the sample. X-rays were detected by two silicon detectors (Si1, Si2) located at a 145° angle as regards the direction of the proton beam. Si1 (10 mm^2 area, 300 μm thick, 140 eV resolution) is a silicon drift detector (SDD) and it can detect, with good efficiency, X-rays of very low energies, down to 1 keV (Na K_α line), thanks to the ultra-thin entrance window (8 μm of Be) and to the use of a helium gas flow into the volume in front of the detector. Si2 (80 mm^2 area, 5 mm thick, 190 eV resolution) is a Si (Li) detector and it can detect the medium-high energy X-rays: in front of detector's window, a Mylar absorber (425 μm) was placed to attenuate low energy X-rays. With the new set-up, we used a proton beam with current ranging from 30 to 40 nA, reducing therefore the measuring time (about 3 min). Therefore, the analysis of the entire streaker deposit requires less than 9 h of beam time.

PIXE spectra were fitted using the GUPIX software package [5] and the elemental concentrations were obtained via a calibration curve from a set of thin standard of known areal density. The detection limits were about 10 ng/m^3 for low Z elements and about 1 ng/m^3 or below for medium high elements.

3. Results

The analysis of streaker deposits produced concentration time series (fine and coarse) as those in Fig. 1 where the two most abundant elements S and Fe are shown; Fe is the tracer of steel smelter emission. Coarse is the particulate matter collected by Kapton film while fine is the aerosol intercepted by Nuclepore foil. We can observe that S is mainly concentrated in fine fraction ($S_{coarse}/S_{fine} \approx 0.05$) while the ratio between Fe_{coarse} and Fe_{fine} is about 0.6.

To identify particulate matter sources we used a principal component analysis (PCA) with Varimax rotation [6]: we also included in the datasets the particles size distribution provided by the optical counter. In the statistical analysis we used the elemental concentrations in PM_{10} fraction (obtained as the sum fine and coarse concentrations) to compare these results with those obtained by daily sample analysis. The results are reported in Table 1. Factor 1 is characterized by high loading of crustal elements (Mg, Al, Si and Ca); it is worth noting that these elements have a strong correlation with particles larger than 1 μm. Factor 2 contains S and it has high loading with fine particles (smaller than 1 μm). This result confirms that this element is mainly produced in the atmosphere by photochemical reactions, which transform SO_2 (gas emitted from fossil

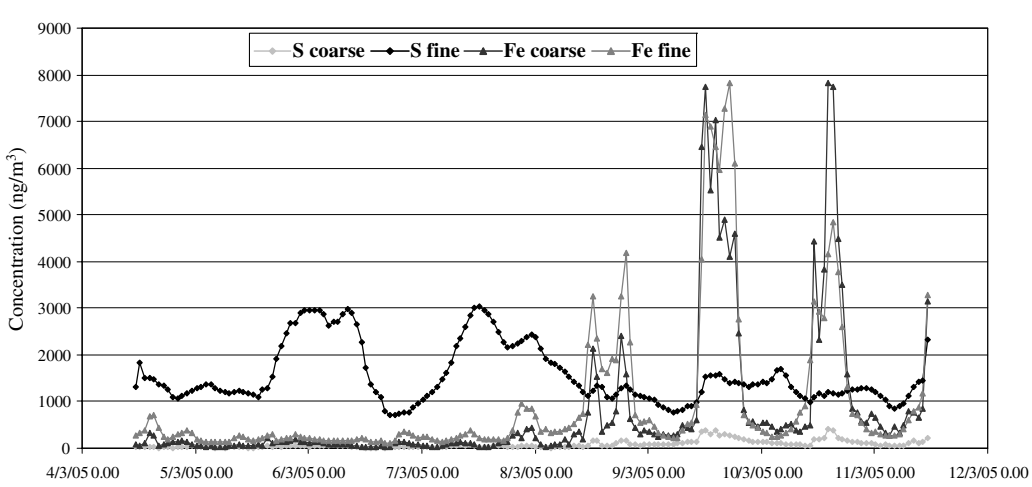

Fig. 1. Hourly concentration of S and Fe from in fine and coarse fraction.

Table 1
Varimax rotated factor loadings obtained by PCA

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
0.30 μm < x < 0.40 μm	−0.2	**−0.9**	0.0	−0.2	−0.1
0.40 μm < x < 0.50 μm	−0.1	**−1.0**	0.0	−0.2	−0.1
0.50 μm < x < 0.65 μm	0.0	**−1.0**	0.0	−0.1	−0.1
0.65 μm < x < 0.80 μm	0.2	**−0.9**	0.2	0.2	0.2
0.80 μm < x < 1 μm	**0.5**	−0.3	0.3	**0.6**	**0.5**
1 μm < x < 1.6 μm	**0.5**	0.0	0.3	**0.6**	0.4
1.6 μm < x < 2 μm	**0.5**	0.0	0.3	**0.6**	**0.5**
2 μm < x < 3 μm	**0.7**	0.0	0.2	**0.5**	**0.5**
3 μm < x < 4 μm	**0.7**	0.0	0.1	0.4	**0.5**
4 μm < x < 5 μm	**0.8**	0.0	0.1	0.4	0.4
5 μm < x < 7.5 μm	**0.9**	0.0	0.1	0.3	0.3
7.5 μm < x < 10 μm	**0.9**	0.0	0.1	0.2	0.2
10 μm < x < 15 μm	**1.0**	0.1	0.1	0.1	0.2
15 μm < x < 20 μm	**0.9**	0.0	0.1	0.1	0.2
x > 20 μm	**0.9**	0.0	0.0	0.0	0.1
Na	0.3	0.2	0.3	**0.8**	0.3
Mg	**0.6**	0.1	0.2	0.5	0.4
Al	**0.7**	0.0	0.3	0.3	0.4
Si	**0.7**	0.0	0.2	0.3	0.4
S	−0.1	**−0.9**	0.0	0.0	0.1
Cl	0.3	0.2	0.1	**0.8**	0.0
K	0.4	−0.3	0.2	0.1	**0.7**
Ca	**0.7**	0.1	0.1	0.4	**0.5**
Cr	0.3	0.1	−0.1	0.4	**0.7**
Mn	0.4	0.1	0.0	0.1	**0.8**
Fe	0.4	0.1	−0.1	0.4	**0.7**
Ni	0.2	0.0	0.4	0.1	**0.5**
Cu	0.0	0.2	**0.9**	0.2	−0.1
Zn	0.2	−0.2	**0.8**	0.2	0.3
Br	0.1	0.1	0.2	**0.7**	0.3
Pb	0.3	−0.1	**0.8**	0.1	0.0
Explained variance	30%	14%	10%	15%	17%

fuel combustion processes) in sub-micron sized sulphate particles. Factor 3 that can be connected to traffic and it does not present clear correlation with any particular dimensional class (the sampling site was about 400 m far from heavily trafficked roads), while Factor 4, which represents the sea-salt (high loading of Na, Cl and Br), is correlated with dimensional classes between 0.8 and 3 μm. Finally, Factor 5, which represents the emissions from the steel plant, shows a correlation with particles in the size range 0.8–4 μm. Note that Fe has a significant

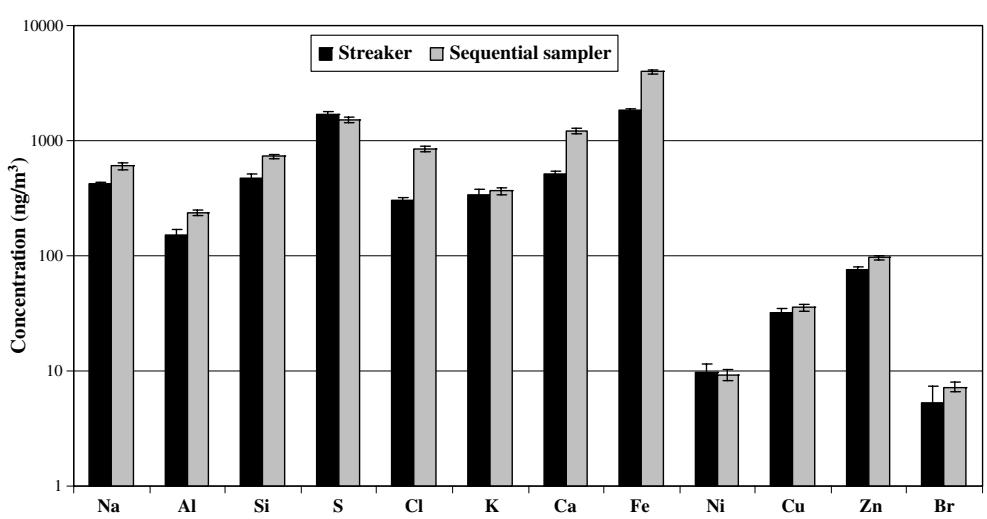

Fig. 2. Average 24-h concentration of some elements obtained by daily samples and streaker films in the PM_{10} fraction.

factor loading (0.4) in Factor 1 as well. The results obtained by using statistical analysis on streaker datasets are similar with those obtained by daily sample analysis.

Streaker and optical counter select particle diameter with different mechanisms (mechanical impaction and light scattering, respectively) and the limits of the dimensional classes in Table 1 may therefore be affected by systematic discrepancies; nevertheless, the information provided by the simultaneous use of the two equipments is valuable.

Elemental concentrations obtained by streaker sampler and PIXE analysis can be averaged and compared (Fig. 2) with results of the standard sampling by sequential sampler (analyzed by ED-XRF) in the same period. It can be noted that, while the average concentrations of S, K, Ni and Cu are in good agreement, the concentrations of Na, Al, Si, Cl, Ca and Fe show a significant discrepancy (with values from streaker lower than the counterparts from daily samples). In a different study, PIXE and ED-XRF techniques, both used to analyze a same set of daily samples, showed good agreement [7], therefore we believe that the observed discrepancy for Na, Al, Si, Ca, Cl and Fe is probably due to differences in cut-off diameters of the two samplers. This hypothesis is also confirmed by theoretical calculations [8] of the effective cut-off diameters for the streaker sampler, which actually seems to collect particles with D_{ae} of about 8 μm operating at 1 l/min, while the sequential sampler has a certified cut-off point of 10 μm.

4. Conclusion

The simultaneous use of streaker sampler and optical counter gave information on elemental size distributions for elements in particulate matter. The comparison between elemental concentration measured on daily samples and streaker deposits, showed discrepancies (for some elements) likely due to differences in cut-off diameters of the two samplers.

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