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Aerosol Science 34 (2003) 243–259

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Journal of  
*Aerosol Science*

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## Hourly elemental composition and sources identification of fine and coarse PM10 particulate matter in four Italian towns

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Received 3 May 2002; accepted 15 October 2002

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### Abstract

The composition of particulate matter in the atmosphere of four major Italian towns (Florence, Genoa, Milan and Naples) has been studied with hourly resolution by means of ion beam analysis (IBA) techniques and statistical methods. The aerosol has been collected simultaneously in the four towns during the first weeks of year 2001, by two-stage continuous streaker samplers, which separate and collect the PM10 particulate matter in two fractions. The hourly concentrations in air of about 20 elements have been extracted in the fine and coarse fractions of PM10 by particle induced X-ray (and gamma-ray) emission, PIXE (and PIGE), analysis of about 2700 hourly samples. The coupled use of streaker samplers and IBA techniques made distinguishable time patterns typical of urban environments as well as fast and occasional episodes. Absolute principal component factor analysis (APCFA) and other statistical approaches have been used to obtain a synthetic apportionment of the sources of particulate matter.

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*Keywords:* Particulate matter; Urban pollution; Elemental composition; PIXE; APCFA

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### 1. Introduction

The aim of the present study was to measure the particulate matter elemental composition in four major Italian towns (Florence, Genoa, Milan, Naples) by the same methodological approach and in the same period. In the last years, the amount of data collected by the local authorities on the particulate matter concentration in Italian urban areas has been considerable but data on particulate

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matter composition are so far very few and not systematic (Decesari et al., 2001; Diociaiuti et al., 2001; Gallorini, 1995; Gallorini, Borroni, Bonandi, & Rolla, 1998; Ragosta, Caggiano, O'Emilio, & Macchiato, 2002; Rizzio et al., 1999; Rizzio, Bergamaschi, Profumo, & Gallorini, 2001). Moreover, while usually data are collected, according to regulatory laws, on a 24 h basis, a better time resolution is necessary to catch the fast events typical of urban environments and distinguish different aerosol sources. Hourly resolution and elemental analysis are not usually coupled in extended campaign due to the huge number of samples and data produced. We overcome this problem using a compact and versatile sampler which collects the 168 hourly samples of a week on a unique frame: the two-stages, continuous streaker sampler.<sup>1</sup> To exploit the compactness of the streaker, the thin particulate matter deposition on its stages must be scanned in a non-destructive and fast way. Some widely used analytical techniques, as inductively coupled plasma (ICP), cannot be applied in this case. On the contrary, the combination of continuous samplers and IBA techniques, namely PIXE and PIGE, provides elemental concentrations with hourly resolution (Annegarn, Cahill, Sellschop, & Zucchiatti, 1988) and Minimum Detection Limits (PIXE) of the order of  $\text{ng m}^{-3}$  for most elements. The analysis time is only a few minutes per sample and extended campaigns can be carried out. In our campaign we have measured and analysed about 55.000 hourly elemental concentration in the fine and coarse stage of PM10.

Lighth elements (with  $Z < 11$ ) cannot be detected by PIXE, due to X-rays self-absorption in the sample and in the detectors dead-layers. Indeed, the elements detected by PIXE contribute to a fraction of particulate matter ranging from 10% to 30% but comprises the tracers used to identify the particulate matter sources and potentially harmful elements (like As, Se, Ni, Cr, Zn, Cu). Actually, PIXE is a well established technique for aerosol studies (Lucarelli et al., 2000; Maenhaut, 1996; Marazzan et al., 1987; Prati, Zucchiatti, Lucarelli, & Mandò, 2000; Shutthanandan et al., 2002) provided that some aspects, discussed in this paper, are taken into account. Finally, a combined use of PIXE and other IBA techniques could give the possibility to detect, on streaker stages, all the elements (Cohen, 1998; Swietlicki, Martinsson, & Kristiansson, 1996a; Van Ham et al., 2002).

The four towns are different in some respect: two cities (Genoa and Naples) lie along the sea, while the other two are more than 100 km far from the nearest coast. The urban area of Milan and surroundings has more than 3 millions inhabitants, Naples and Genoa about 1 million, Florence more than half a million. Genoa and Milan are located in northern Italy, Florence near the centre of the peninsula, and Naples is the largest town in southern Italy.

Since traffic is generally a major source of atmospheric pollution in large urban areas, we selected, in each town, a sampling site in proximity of a main road characterised by similar medium-heavy traffic conditions (annual average concentration of CO between 2.5 and 3.0  $\text{mg m}^{-3}$ ). Our samplers were placed in cabins of the municipal air quality networks, which were equipped to monitor also meteorological variables and gaseous pollutants concentration (CO,  $\text{NO}_x$ ,  $\text{SO}_2$ ). The sampling lasted four weeks during winter 2001. This period of the year is particularly crucial for the north-Italy towns, in particular Florence and Milan, since long-lasting high pressure field usually produce low air re-circulation and, consequently, particularly high aerosol concentration. Starting from January 2002, leaded gasoline has been eliminated in Italy and the data collected in this campaign (year 2001) constitute a useful reference for future comparisons. A second phase of the campaign had been scheduled for a summer period.

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<sup>1</sup> Manufactured by PIXE International Corp., P.O. Box 7744, Tallahassee, FL 32316, USA.

## 2. Materials and methods

### 2.1. Particulate sampling

Sampling started on January 18, 2001 in all towns and lasted until February 16, 2001, with an effective superposition of data of about two weeks. In each town, a two-stage streaker sampler has been installed about 3 m above ground in the sites identified as: Florence—*Gramsci*, Genoa—*Brignole*, Milan—*Zavattari*, Naples—*Giulio Cesare*.

Full details of the samplers, of their cut-off diameters and of their control units can be found elsewhere (Formenti, Prati, Zucchiatti, Lucarelli, & Mandò, 1996; Prati et al., 1998). Briefly, in a streaker sampler, particles are separated on different stages by a pre-impactor and an impactor. The pre-impactor removes particulate matter with aerodynamic diameter  $D_{ae} > 10 \mu\text{m}$ . The impactor deposits the aerosol coarse fraction ( $2.5 \mu\text{m} < D_{ae} < 10 \mu\text{m}$ ) on a Kapton foil while the fine fraction ( $D_{ae} < 2.5 \mu\text{m}$ ) is collected on a Nuclepore filter having  $0.4 \mu\text{m}$  pores. The two collecting plates (Kapton and Nuclepore) are paired on a cartridge which rotates at constant speed ( $\sim 1.8^\circ/\text{h}$ ) for a week: this produces a circular continuous deposition of particular matter (“streak”) on both stages.

The cut-off diameter in working conditions was indeed just higher than the nominal  $2.5 \mu\text{m}$  since the samplers ran on average at  $0.85 \text{ l/min}$  instead of  $1.0 \text{ l/min}$  (Formenti et al., 1996). The air flow was recorded every 6-min for all the samplers.

### 2.2. PIXE and PIGE analysis of samples

The elemental composition of the streaker deposits was measured by PIXE and PIGE at the external beam facility in Florence, based on a Van de Graaff accelerator (Del Carmine et al., 1990). A 2.990 MeV proton beam has been used so that the cross section for the  $\text{Na}(p, p'\gamma)\text{Na}$  ( $E_\gamma = 441 \text{ keV}$ ) reaction, which is exploited for PIGE determination of Na (Boni, Caridi, Cereda, & Braga Marcazzan, 1990), remains sufficiently constant (Calastrini et al., 1998) even considering the moderate proton energy loss in the sample. Moreover, the beam energy is high enough to provide good sensitivity for PIXE. The beam (12 nA maximum, 10 nA average) is diffused in vacuum by an Al foil, collimated to a rectangular spot ( $1 \times 1.8 \text{ mm}^2$ ) on the thin aerosol samples and finally collected on a graphite Faraday cup. The beam moves along the streak in steps corresponding to 1 h of aerosol sampling, each step takes 5 min of beam time. Therefore, scanning the whole streaker requires about 15 h with, on average,  $3 \mu\text{C}$  collected per step.

The elemental thickness was obtained by comparing the streaker yields with a sensitivity curve [counts  $\mu\text{C}^{-1} \mu\text{g}^{-1} \text{ cm}^2$ ] measured in the same geometry on a set of thin standards certified within 5% (Micromatter Inc.). All the X-ray spectra have been fitted for 24 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Pb) using the GUPIX software package (Maxwell, Teesdale, & Campbell, 1995). Minimum detection limits (MDL), at  $3\sigma$  level, ranged between  $0.8$  and  $45 \text{ ng cm}^{-2}$ , corresponding to  $0.7$ – $40 \text{ ng m}^{-3}$  for the coarse stage and between  $1.7$  and  $100 \text{ ng m}^{-3}$  for the fine stage. The accuracy of hourly elemental concentrations is determined by a sum of independent uncertainties on: standard samples thickness (5%), aerosol deposition area (2%), air flow (2%) and X-rays counting statistics (from 2% to 20%).

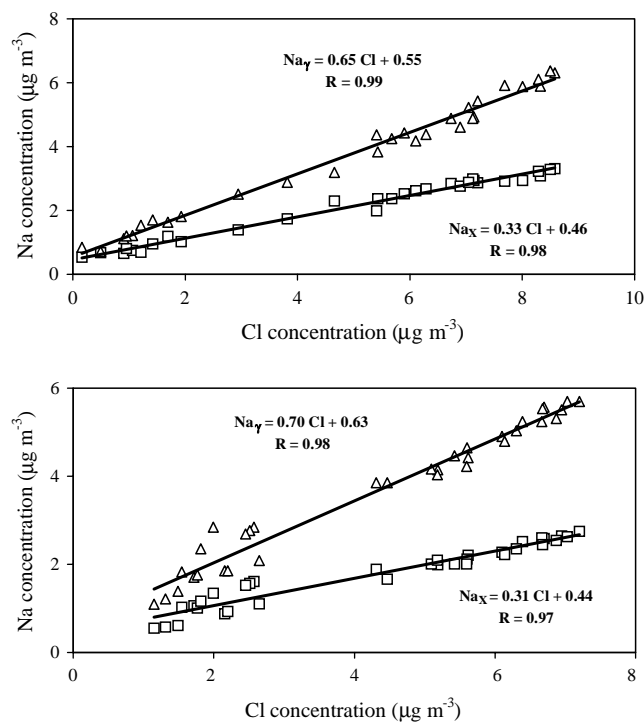


Fig. 1. Na to Cl coarse stage concentration regression curves during two “sea-salt” episodes detected in Genoa (top) and Naples (bottom) between February 7 and 10. The fitting curve equations and the regression coefficients ( $R$ ) are also shown ( $Na_{\chi}$  and  $Na_{\gamma}$  = Na concentrations deduced by PIXE, squares, and PIGE, triangles, respectively).

### 2.3. Self-attenuation of low-energy X-rays from light elements

PIXE cannot successfully cope with the detection of light elements because of the X-ray attenuation inside the target: H, N, C and O (which typically account for more than the 50% of the urban aerosol), F, Li, Be and B are generally not detectable. Moreover the quantitative analysis (obtained from direct comparison with thin standards) may underestimate the concentrations of the lightest detectable elements, like Na, Mg, and Al (Boni et al., 1990; Jex, Hill, & Mangelson, 1990); this underestimation can be relevant in the coarse fraction samples, while it should not be appreciable for the fine particles collected on Nuclepore filters.

To evaluate the attenuation experimentally, we measured the concentration of the lightest element detected by PIXE, namely Na, also by PIGE (this technique, based on the detection of gamma rays with energies above one hundred keV, does not present the problem of self-absorption). The experimental average value of  $Na_{PIXE}/Na_{PIGE}$  in the coarse fraction resulted 0.50, with low dispersion around the mean (correlation coefficient 0.98), while no appreciable attenuation resulted for the fine fraction samples. We calculated this ratio using only data when  $\gamma$  yield was at least twice higher than PIGE MDL. We performed a second check for Na, with data extracted from two high statistics episodes occurred in Genoa and Naples characterised by a high sea-salt content (Fig. 1) and most of the mass collected in the coarse stage. The average PIXE (Genoa and Naples) Na to Cl concentration

ratio in the coarse stage is 0.32 while the same ratio, using PIGE for the Na concentration, is 0.67 (average of Genoa and Naples, Fig. 1) and in NaCl molecules is 0.65. Since X-rays emitted by Cl have an energy of 2.60 keV, for which the attenuation in particles of a few microns is negligible, this confirms that PIXE gives a Na concentration around 50% of the real one. Since PIGE yield of Na is more than one order of magnitude lower than the PIXE one, we used the PIXE data for Na, but we multiplied them by the corrective factor (equal to 2) obtained experimentally.

An attenuation value between 0.5 and 0.58 (corresponding to a corrective factor between 2 and 1.7) is also obtained when the X-rays attenuation is calculated, with the usual exponential trend, for discrete values or continuous distributions of the particle diameter in specific compounds, namely NaCl (Hunter & Rhodes, 1972; Rhodes & Hunter, 1972), using tabulated attenuation coefficients (NIST, 1999). We therefore adopted calculated PIXE corrective factors also for Mg (1.7) and Al (1.4) in the coarse fraction. Very close calculated and measured values have been found in previous works (Maenhaut & Cafmeyer, 1998). Concentrations of elements with higher  $Z$  should be corrected, according to the calculations, by multiplicative factor equal or smaller than 1.3 and decreasing with  $Z$ : we did not apply any corrections to PIXE data from Si on.

#### 2.4. Optical analysis of Nuclepore deposits

Both PIXE and PIGE are not sensitive to low  $Z$  elements like C, N and O, therefore the largest part of the total particulate mass, which comes precisely from these elements cannot be measured together with that of higher  $Z$  elements. Moreover, the structure of the samples collected by streakers is such that it is impossible to obtain the total hourly aerosol mass by gravimetric measurements.

The thin deposit observed on Nuclepore filters attenuates the visible light. If the deposit composition would be constant, the light absorption would depend exponentially on the deposit thickness:  $I = I_0 e^{-\mu x}$  (Lindberg, Douglass, & Garvey, 1999). The absorption coefficient  $\mu$  is determined primarily by the aerosol black carbon content and, to a minor extent, by the rest of the aerosol (Horvath, 1993). Due to the choice of the sampling sites, we expect that traffic gives the total particulate mass a substantial contribution of which carbon is a major component. We can take the quantity  $\ln(I_0/I)$ , measured with hourly resolution along the streaks, to describe, with good approximation, the time behaviour of black carbon and, in first approximation, of the total deposited particulate. However, we cannot extract concentration values since the composition of the aerosol can have large variations during the 24 h even in the same site. Before PIXE analysis, we have determined  $\ln(I_0/I)$  on Nuclepore substrata by a simple instrument (Filippi et al., 1999) which uses a red laser at  $\lambda = 633$  nm and a stepping motor to scan the streak with hourly resolution. The results of these measurements are presented in the following in arbitrary units, with the label "OPT" to indicate the quantity  $\ln(I_0/I)$ .

### 3. Results

#### 3.1. Optical analysis of Nuclepore deposits

The light attenuation has been measured in all the exposed Nuclepore filters to obtain the time trends as in the example shown in Fig. 2, concerning the fourth week of sampling in Milan. A similar time pattern, peaked twice a day around 8 am and 6 pm of working days, has been observed in all

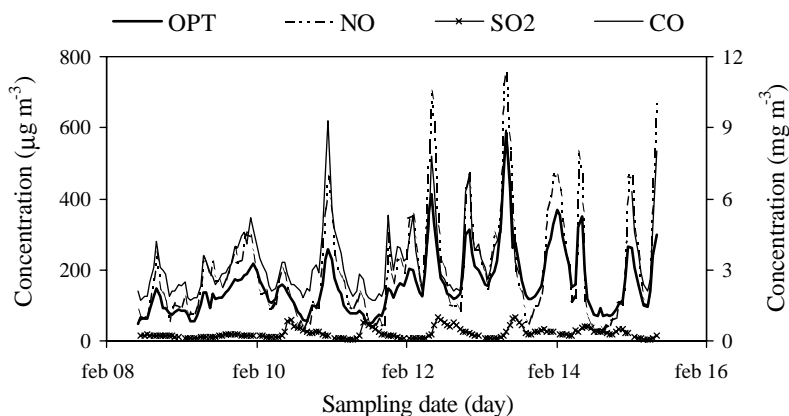


Fig. 2. The light attenuation of the fine fraction, OPT, in arbitrary units, NO, SO<sub>2</sub> concentration in  $\mu\text{g m}^{-3}$  (left axis) and CO in  $\text{mg m}^{-3}$  (right axis) measured in Milan–Zavattari between February 8 and 16. Data on gaseous pollutants have been provided by the local authorities.

four sites. This behaviour is mainly related to commuter traffic as confirmed by the high correlation observed between OPT, CO and NO while SO<sub>2</sub>, a tracer of several combustion processes, shows a different trend (Fig. 2). The same correlation is revealed by factor analysis of concentration time series (Section 3.3).

In Milan the average value of OPT over the whole sampling period is about double than in Genoa and Naples and 60% higher than in Florence.

### 3.2. PIXE analysis

Elemental concentration time series have been obtained, from PIXE spectra, for each town, both in the fine and coarse stage, covering two weeks for a total of 2688 hourly samples. Some examples are shown in Fig. 3 and the complete set of data is reported in (Ariola et al., 2002). Episodes due to meteorological conditions enhancing particular sources (Fig. 3, top) as well as the quasi-periodic time trends of elements emitted by traffic exhausts (Fig. 3, middle) could be detected. The time pattern, which we reconstruct with hourly resolution is a distinctive feature of particulate matter sources: Pb and Br in the fine fraction have high correlated time series and follow the traffic flow (Fig. 3, middle). In Florence, Genoa, and Naples the correlation coefficient ( $R$ ) is respectively 0.94, 0.94 and 0.97. The average Br/Pb concentration ratio, in the fine stage, varies in the three towns between 0.26 and 0.31, with low dispersion around the mean, in agreement with values reported in literature (Thurston & Spengler, 1985; Del Carmine et al., 1990; Lucarelli et al., 2000; Formenti et al., 1997; Prati et al., 2000; Marcazzan et al., 1987; Marcazzan, Vaccaro, Valli, & Vecchi, 2001). In Milan, the Br/Pb ratio has high fluctuations (Fig. 4) that produce a lower correlation coefficient ( $R = 0.91$ ) and bring the average value down to 0.20. This has been associated in the past to the presence of different sources of Pb (Marcazzan, 1996). When excluding from the Milan data sets the hours around midnight of February 13, the average Br/Pb in the fine stage goes to 0.27 (with  $R = 0.95$ ) in range with the other towns and in agreement with the hypothesis that, besides episodes, traffic is the major source of Pb.

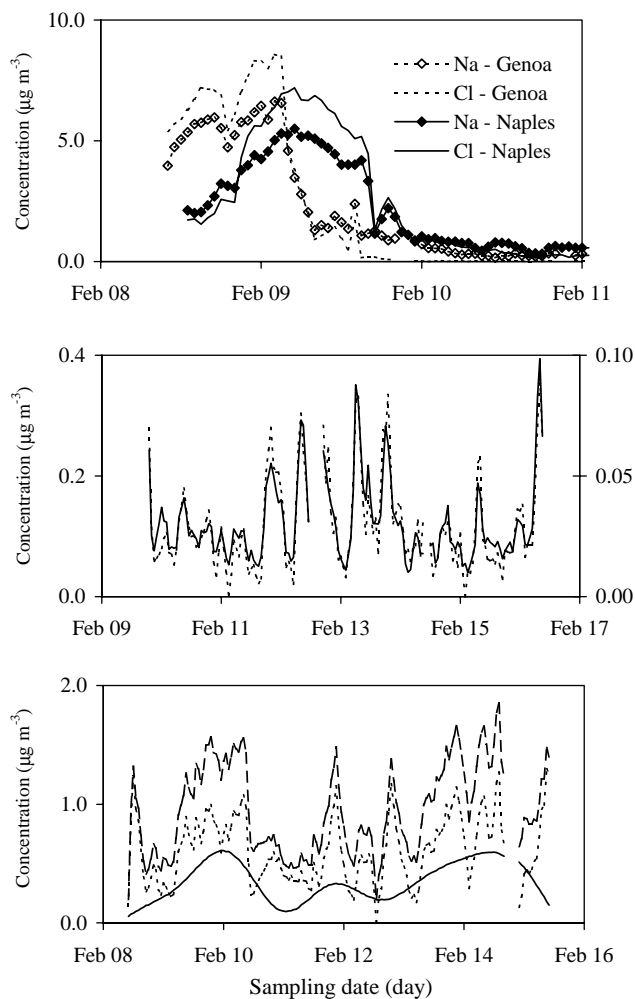


Fig. 3. Na, and Cl concentrations in the coarse fraction during a “sea-salt” episode detected in Genoa and Naples between February 7 and 10 (top); Br (dashed, right axis) and Pb (continuous, left axis) fine fraction concentrations in Florence during the fourth sampling week (middle); sulphur concentration in the fine fraction (dashed) and its decomposition in local (dotted) and regional (continuous) components in Genoa, fourth sampling week (bottom).

Sulphate particles are mainly produced by oxidation (in the atmosphere) of  $\text{SO}_2$ , which is also emitted from fossil fuel combustion process. Both fine stage sulphate particles and  $\text{SO}_2$  have a long persistency time in atmosphere; therefore it is reasonable that local sources (diesel engines, domestic heating) and slowly varying regional background both contribute to the overall sulphur concentration. The sulphur concentration in the fine stage has been decomposed, by a Fourier analysis, in a fast component, associated to local sources, and in a slow component due to regional background (Fig. 3, bottom). All the Fourier components with a period greater than 48 h have been summed to give the regional background. The fast and slow components of sulphur concentration in the fine stage are substantially similar in all four sites.



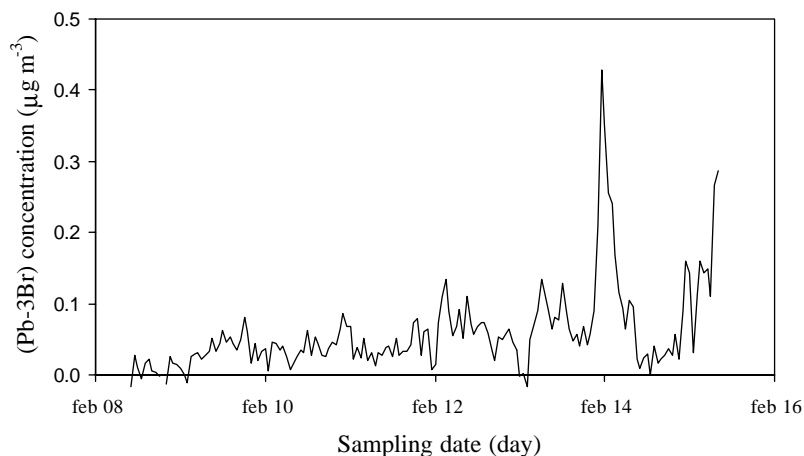
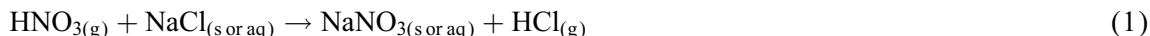


Fig. 4. Milan, February 8–15: difference between Pb and Br, (Bromine is multiplied times 3, an average Pb to Br ratio in traffic emissions), concentrations in the fine fraction.

The concentration time series can be averaged for a first comparison among the four sites (see Table 1). The sulphur concentration in Table 1 is the sum of local components and regional background (i.e. directly the measured value): it was everywhere the most abundant element detected by PIXE. In the fine fraction, Pb and Br concentrations were in Genoa about one-half than in the other sites and generally, the sum of elemental concentrations in Genoa was 40% lower than the average of the other towns. In all sites, Pb and Br concentrations are lower than in the past (Formenti et al., 1996; Lucarelli et al., 2000; Marazzan, 1996) but they are still substantially determined by traffic (Section 3.4): this depends on the high fraction (about 30%) of vehicles still fuelled with leaded gasoline in Italy until the end of 2001. Florence received a remarkably high contribution of Fe and Ca in both stages, while the high fine Zn concentration was a distinctive sign in the Milan particulate (Table 1). Fine As concentration was episodically high in the first week of sampling in Naples (January, 18–25) with maximum hourly values up to  $0.1 \mu\text{g m}^{-3}$  and values greater than  $0.05 \mu\text{g m}^{-3}$  for 11 h. The source of As is not yet identified. In the coarse fraction, Genoa and Naples show the highest concentrations due to the contribution of sea-salt aerosol (Na and Cl, in particular). The Cl concentration at the receptor site does not follow, except during episodes of fresh marine aerosol (as the example in Fig. 3, top panel), the Na/Cl ratio of sea salt since Cl is reduced due to heterogeneous reaction between airborne sea-salt particles and gaseous nitric acid, which leaves HCl in the gas phase and sodium nitrate in the particle phase (Seinfeld, 1986), particularly in the fine stage:



Another possible mechanism for Cl loss is the reaction (Singh, 1995):



Both reactions are enhanced in the fine stage, where the surface to volume ratio of particles is bigger.

Some elements (S, K, V, Ni, Zn, Pb, Br,) are present mainly in the fine fraction, while other (Mg, Al, Si, Ca, Ti, Fe) are balanced in the two components.



Table 1

Average elemental concentrations ( $\mu\text{g m}^{-3}$ ) in the two periods (January 18–25 and February 8–15) analysed by PIXE: fine (top) and coarse (bottom) fraction. For elements marked with \* the MDL only is given

Element	Florence		Genoa		Milan		Naples	
	Conc.	Std. dev.	Conc.	Std. dev.	Conc.	Std. dev.	Conc.	Std. dev.
Na	0.232	0.090	0.256	0.137	0.251	0.091	0.389	0.230
Mg	0.130	0.049	0.119	0.048	0.130	0.058	0.154	0.073
Al	0.156	0.087	0.101	0.050	0.176	0.175	0.263	0.237
Si	0.466	0.262	0.287	0.178	0.655	0.584	0.651	0.571
P	0.053	0.012	0.046	0.012	0.052	0.014	0.048	0.014
S	1.282	0.524	1.053	0.358	1.408	0.662	1.259	0.605
Cl	0.120	0.036	0.098	0.023	0.147	0.085	0.206	0.353
K	0.364	0.216	0.257	0.120	0.438	0.241	0.456	0.275
Ca	0.651	0.420	0.230	0.201	0.509	0.994	0.427	0.311
Ti	0.034	0.007	0.031	0.010	0.040	0.021	0.040	0.020
V*	0.015		0.015		0.015		0.015	
Cr	0.021	0.006	0.017	0.006	0.017	0.005	0.017	0.005
Mn	0.014	0.006	0.011	0.005	0.019	0.012	0.013	0.006
Fe	0.771	0.370	0.285	0.169	0.692	0.492	0.671	0.558
Co*	0.006		0.006		0.006		0.006	
Ni	0.007	0.004	0.008	0.005	0.008	0.003	0.005	0.003
Cu	0.039	0.020	0.013	0.007	0.038	0.025	0.029	0.029
Zn	0.050	0.035	0.035	0.023	0.124	0.108	0.039	0.031
As*	0.007		0.007		0.007		0.029	0.023
Se*	0.002		0.002		0.002		0.002	
Br	0.033	0.023	0.016	0.010	0.028	0.020	0.045	0.041
Sr	0.007	0.002	0.006	0.002	0.009	0.015	0.007	0.003
Zr	0.008	0.002	0.006	0.002	0.007	0.002	0.007	0.002
Pb	0.130	0.076	0.064	0.039	0.141	0.101	0.153	0.127
Na	0.359	0.300	0.986	1.348	0.300	0.245	1.201	1.349
Mg	0.165	0.092	0.224	0.197	0.127	0.058	0.244	0.173
Al	0.181	0.124	0.117	0.097	0.137	0.091	0.217	0.203
Si	0.457	0.308	0.289	0.277	0.317	0.248	0.394	0.368
P	0.029	0.009	0.028	0.009	0.029	0.015	0.029	0.009
S	0.081	0.051	0.147	0.155	0.193	0.275	0.120	0.099
Cl	0.145	0.196	0.923	1.875	0.173	0.292	1.060	1.611
K	0.102	0.044	0.099	0.063	0.100	0.151	0.149	0.087
Ca	0.753	0.552	0.381	0.407	0.245	0.263	0.547	0.423
Ti	0.023	0.012	0.021	0.016	0.017	0.010	0.024	0.014
V*	0.005		0.005		0.005		0.005	
Cr	0.009	0.007	0.007	0.003	0.007	0.002	0.007	0.003
Mn	0.010	0.006	0.006	0.004	0.007	0.005	0.008	0.005
Fe	0.811	0.454	0.329	0.256	0.391	0.274	0.499	0.541
Co*	0.003		0.003		0.003		0.003	
Ni	0.003	0.002	0.002	0.001	0.002	0.001	0.002	0.001
Cu	0.037	0.021	0.012	0.008	0.019	0.013	0.016	0.018
Zn	0.019	0.012	0.014	0.014	0.024	0.026	0.008	0.007
As*	0.001		0.001		0.001		0.001	

Table 1 (continued)

Element	Florence		Genoa		Milan		Naples	
	Conc.	Std. dev.	Conc.	Std. dev.	Conc.	Std. dev.	Conc.	Std. dev.
Se*		0.001		0.001		0.001		0.001
Br	0.003	0.002	0.003	0.002	0.003	0.002	0.003	0.002
Sr	0.004	0.002	0.003	0.002	0.003	0.001	0.003	0.001
Zr	0.004	0.001	0.003	0.002	0.003	0.001	0.004	0.002
Pb	0.012	0.007	0.009	0.006	0.011	0.008	0.009	0.007

### 3.3. Principal component factor analysis

In order to individualise the major particulate matter sources in each site we have performed a Principal Component Factor Analysis (PCFA) with VARIMAX rotation (Heidam, 1982; Statgraphics, 1995), separately on fine and coarse fraction data sets. Only components with eigenvalue greater than 1 (before rotation) have been retained and, in all the cases, a percentage of the global variance ranging from 70% to 85% has been accounted for. The results for each site and fraction are summarised in Table 2. We included in the fine fraction analysis, as a further element, OPT (Section 3.1) after having verified that the factor's composition does not change including this additional variable (the factor loadings remained the same within one standard deviation). Local sulphur concentration was used in PCFA: actually, the results did not change considering the total (local + regional background) concentration measured by PIXE. Some episodes (i.e. hours with particular high concentration of groups of elements as, for example, some concentration peaks of Al, Si and Ca in Milan corresponding to maintenance works in a building very near the sampler) have been identified by a cluster analysis and excluded in order to focus the analysis on the average particulate matter composition. Some elements (P, V, Co, As, Se, Zr) were below their MDL in more than 60% of sampling hours and have not been included in PCFA. Other elements were below MDL in a fewer instances: in those cases a random value between zero and MDL was attributed to the element concentration (Chan et al., 1999).

The PCFA results can be summarised as follows:

- (a) In the fine fraction, PCFA identified three or four factors (see Table 2). A factor, labelled as “urban” was everywhere associated with the highest percentage of variance and characterised by high loadings for elements typical of vehicles emissions as Pb and Br. This factor included Fe, Cu and Zn (mainly derived from wear and tear of brake and tyres rather than from combustion) but, from site to site, also elements typical of soil (e.g. Al, Si in Florence, Table 2) or industry (e.g. Cr, Mn, Ni in Naples, Table 2). In Milan high factor loadings for elements as Na, Cl and K can be noted in this factor. The OPT, always had a high loading in the “urban” factor (0.93 in Naples, 0.85 in Genoa, 0.74 in Florence and 0.59 in Milan where it showed also a high loading in the “industry” factor, see below). In all sites PCFA identified a factor, labelled as “dust”, with high loadings for crustal and soil related elements (Mg, Al, Si) connected in Florence also with the “urban” as already discussed. In Genoa and Naples it was identified a factor “sea”, with high loadings for Na, Mg and Cl. Sulphur, associated with Ni (a tracer

Table 2  
 PCFA results for the concentrations time series of the four towns: fine (top) and coarse (bottom) fraction. Elements with factors loadings  $\geq 0.5$  have been only reported. In the last row of each table the percentage of variance associated to each factor.

Florence	Genoa				Milan				Naples					
	Dust	Comb	Sea	Urban	Dust	Comb	Sea	Urban	Dust	Comb	Sea	Urban	Comb	
OPT (0.74)	Na (0.72)	Na (0.52)	OPT (0.85)	Al (0.74)	S (0.54)	Na (0.89)	OPT (0.59)	Mg (0.77)	OPT (0.52)	S (0.84)	OPT (0.93)	Mg (0.71)	Na (0.94)	S (0.92)
Al (0.60)	Mg (0.86)	S (0.81)	Ca (0.56)	Si (0.77)	K (0.77)	Mg (0.79)	Na (0.62)	Al (0.90)	Ti (0.59)	K (0.63)	Al (0.98)	Mg (0.57)	Mg (0.96)	Cl (0.87)
Si (0.67)	Al (0.65)	Ni (0.64)	Fe (0.72)	S (0.51)	Ni (0.75)		Cl (0.72)	Si (0.87)	Cr (0.74)	Cr (58)	Si (0.96)	Ca (0.80)		
K (0.60)		Br (0.52)	Cu (0.80)	Ca (0.59)			K (0.80)	Ca (0.84)	Mn (0.60)	Min (0.70)	Ca (0.80)			
Ca (0.79)			Zn (0.66)	Cr (0.57)			Cu (0.60)	Fe (0.68)	Ni (0.67)	Fe (0.89)	Ti (0.88)			
Min (0.77)			Br (0.85)	Fe (0.58)			Zn (0.78)	Cu (0.55)		Ni (0.70)				
Fe (0.92)			Pb (0.89)				Br (0.78)			Cu (0.91)				
Cu (0.91)							Pb (0.83)			Zn (0.87)				
Zn (0.69)										Br (0.96)				
Br (0.73)										Pb (0.96)				
Pb (0.86)														
40%	16%	15%	29%	21%	13%	11%	28%	25%	17%	7%	24%	12%	6%	
Urban	Dust	Sea	Sea	Urban	Urban	Dust	Dust	Urban	Indus	Na-Cl	Urban	Sea	Dust	
Al (0.57)	Mg (0.79)	Na (0.93)	Na (0.97)	Cr (0.74)	Cr (0.74)	Al (0.79)	Mg (0.73)	Cr (0.55)	S (0.82)	Na (0.88)	Ca (0.58)	Na (0.97)	Al (0.93)	
Si (0.73)	Al (0.77)	S (0.62)	Mg (0.89)	Mn (0.73)	Mn (0.73)	Si (0.85)	Al (0.91)	Fe (0.78)	Mn (0.73)	Cl (0.94)	Cr (0.80)	Mg (0.93)	Si (0.93)	
S (0.52)	Si (0.60)	Cl (0.96)	S (0.86)	Fe (0.83)	Fe (0.83)	Ca (0.80)	Si (0.92)	Ni (0.50)	Zn (0.85)		Mn (0.79)	S (0.96)	K (0.75)	
K (0.65)	Ca (0.57)		Cl (0.95)	Ni (0.54)	Ni (0.54)	Ti (0.80)	K (0.66)	Cu (0.83)	Pb (0.54)		Fe (0.91)	Cl (0.96)	Ca (0.74)	
Ca (0.76)	Ti (0.50)		K (0.81)	Cu (0.84)	Cu (0.84)	Sr (0.71)	Ca (0.85)	Br (0.72)			Ni (0.73)	Sr (0.53)	Ti (0.84)	
Ti (0.75)	Sr (0.60)		Br (0.88)	Zn (0.75)	Zn (0.75)		Ti (0.62)	Sr (0.52)			Cu (0.95)		Mn (0.51)	
Cr (0.78)				Pb (0.83)	Pb (0.83)		Fe (0.50)	Pb (0.73)			Zn (0.92)			
Mn (0.88)											Br (0.68)			
Fe (0.94)											Pb (0.87)			
Ni (0.75)														
Cu (0.94)														
Zn (0.90)														
Br (0.77)														
Sr (0.58)														
Pb (0.87)														
49%	19%	15%	30%	27%	23%	23%	25%	20%	17%	11%	36%	26%	25%	

element for oil combustion) in Florence and with K and Ni in Genoa, identified everywhere a particular factor, probably connected with fossil fuel combustion processes and labelled as “comb”. Finally, in Milan only, could be identified a factor labelled as “indus”, characterised by high loadings for Ti, Cr, Mn and Ni and with a relatively high loading (0.52) for OPT too. Actually, Milan only has, in its suburbs, large industrial plants. If the few hours with an “anomalous” Pb to Br concentration ratio (see Fig. 4) are excluded from the Milan data set, OPT gets a negligible loading in the “indus” source and a very high loading in the “urban” source, confirming the conclusions of Section 3.2.

- (b) In the coarse fraction PCFA identifies everywhere a component with high loadings for Cu, Pb and Br associated with large fractions of total variance (Table 2). This factor was marked in the different places also by high loadings for elements typical of soil dust (Al, Ca in Florence) and of industry (Cr, Mn, Ni and Zn in Florence, Genoa and Naples). We labelled this factor as “urban” since Pb concentrations in the fine and coarse fraction, as well as the time trend of the fine “urban” (see Section 3.4), were well correlated in Florence, Genoa and Naples. The situation was slightly different in Milan, where coarse Pb got associated also with another factor (Table 2 and discussion below), and in Genoa where the coarse Br had a high loading only in the “sea” source (Table 2). Natural sources as soil-dust (“dust”) and sea-salt (“sea”) were identified in Florence, Genoa and Naples. In Florence the presence of a sea source is due to transport phenomena from the neighbour coast (about 100 km). In Milan, beside dust, a source characterised by high loadings for S, Mn, Zn and Pb was labelled as “indus” (Table 2). A further source (labelled as “Na–Cl”) is characterised, in Milan, by high loadings only for Na and Cl and is therefore distinct from the “sea” components mentioned above which have high loadings also for S. A possible explanation for this factor is the use of salt to defrost the town roads during the snowfalls occurred in Milan the day before the beginning of the campaign.

### 3.4. Source apportionment

The PCFA gives only qualitative indications about the sources: to obtain quantitative results we performed also an Absolute PCFA (APCFA). This statistical model provides the *relative profiles* of the sources identified by PCFA, the *absolute scores*, i.e. the time series of the sources apart from a multiplicative coefficient, and the *source apportionment* of the measured elemental concentrations.

The *relative profile* of a source is a vector composed of the elemental fractions in the source composition multiplied by the source standard deviation. We deduced the *relative profiles*, which provide the ratios between pollutants in the various sources, from PCFA *factor loadings* and from standard deviations of elemental concentrations (Swietlicki, Puri, & Hansson, 1996b). It should be noted that these profiles are deduced at the receptor site and do not necessarily reproduce those at the emission points, because they include transformations taking place during long range transport (like oxidation of gaseous SO<sub>2</sub> to sulphates, etc.). The Br/Pb concentration ratio in the “urban” source resulted quite similar in all the sampling sites, with values in the range 0.23–0.33, in agreement with the values reported in literature for traffic emissions (Thurston & Spengler, 1985), except for Milan fine stage (0.18) and Genoa coarse stage (0.16). The Na/Cl concentration ratio in the ‘sea’ profile (in the coarse stage) resulted 0.82 and 0.88 in Genoa and Naples, quite similar to what expected for sea salt (0.67), while a higher value turn out in Florence (1.8) as a consequence of the aging

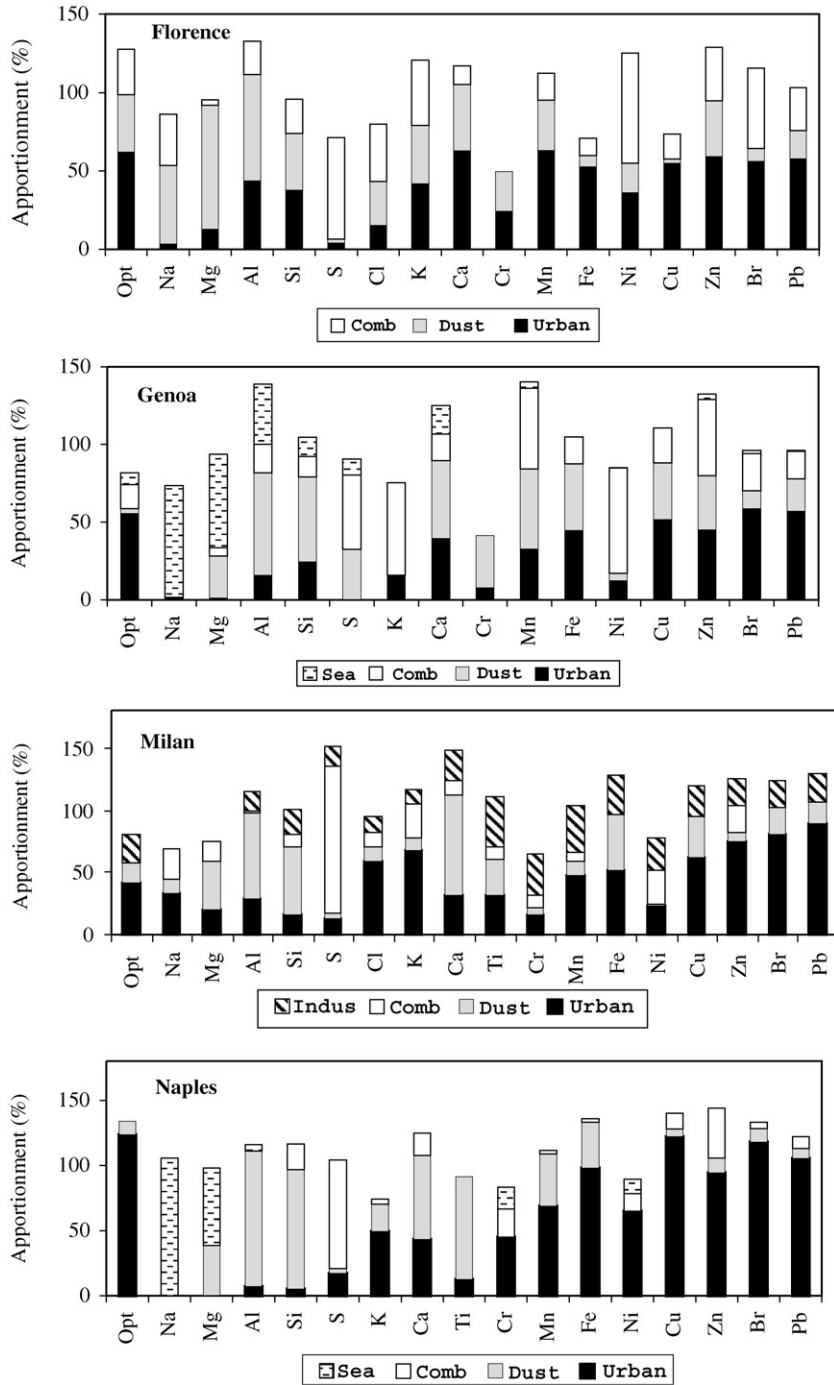


Fig. 5. Apportionment of OPT and of elements detected by PIXE in the fine fraction.

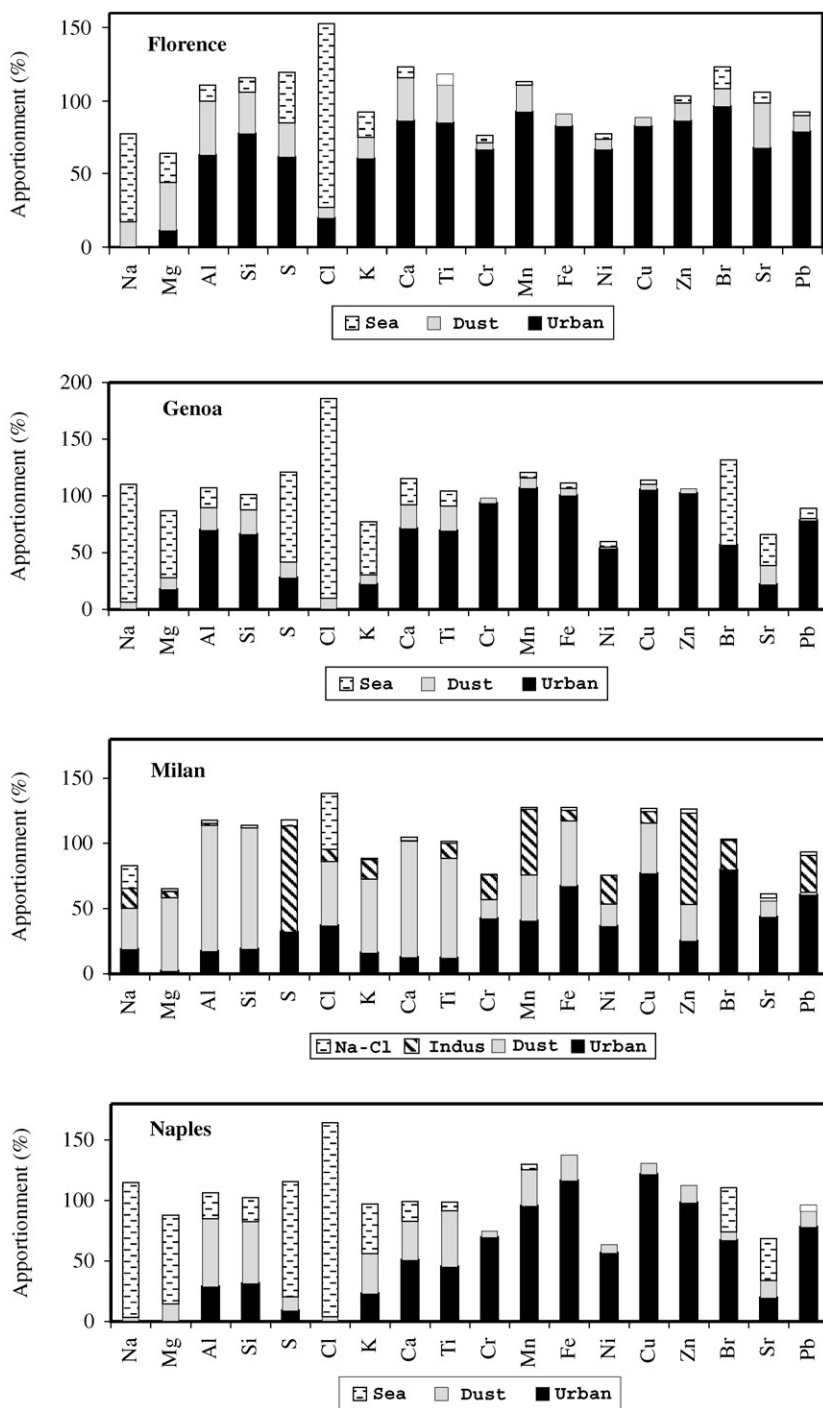


Fig. 6. Apportionment of the elements detected by PIXE in the coarse fraction.

of particles during transport. The Si/Al ratio in the ‘dust’ profiles got values in the range 1.9–3.7, compatible with what expected in typical rock composition (2.79).

The *scores* calculated by a ‘standard’ PCFA are the normalized source time series (zero mean and unitary standard deviation). The *absolute scores*, which are the source time series divided for their standard deviations, can be easily calculated if a *reference* sample, wherein all concentrations are zero, is added to the data set (Thurston & Spengler, 1985). We have already adopted and tested this approach, with concentration data sets obtained by continuous sampling, in the recent past (Nava, Prati, Zucchiatti, Lucarelli, & Mandò, 2002).

Using the *relative profiles* and the *absolute scores* we finally calculated the contributions of the sources to the concentrations of elements and OPT. In Figs. 5 and 6 we have summarised in bar plots the apportionment obtained in the two fractions. The percentage of the measured elemental concentration, reconstructed by the algorithms, range usually from 80% to 120% with extremes at 60% and 160% found only for a few, low concentration, elements. Uncertainties in the order of 15–20% affect the results in Figs. 5 and 6 and therefore elemental apportionments of this order of magnitude cannot be considered significant. The correlation coefficients between measured and calculated concentration time trends resulted quite good: greater than 0.7, with few exceptions (Sr Milan coarse stage, Cr Genoa fine stage, Ni Genoa coarse stage, Cl and Cr Florence fine and coarse stage).

“Urban” is the main contributor to the apportionment of many elements. Also the apportionment of OPT indicates that in all sites “urban” is the major source (always contributing to more than 50%) of the particulate matter light absorption: industry contributed significantly to OPT only in Milan.

#### 4. Conclusions

This study is the output of a concerted effort to perform, in Italy, a large scale monitoring of the air particulate with continuous fractionated sampling and ion beam analysis techniques. A characterisation of the air particulate in four major Italian towns has been achieved. From the time trends of the elemental concentrations in the four sites the peculiarities of the aerosol composition of each city have been put in evidence. Due to the sharp time resolution of the analysis, quasi periodical and episodic pollution sources have been traced. Source apportionment and profiling have been performed by APCFA. Urban (a mixture of traffic emission, particles created by wear of asphalt and paved roads, soil dust and industrial components), soil dust, oil combustion and sea-salt are the sources of particulate matter in all sites: in Milan only we could observe, a significant contribution from industrial activities. As expected, many elements (Cu, Pb, Br, in particular) and OPT have urban powder (i.e. traffic) as major source.

#### Acknowledgements

We thank the local authorities of Florence, Genoa, Milan and Naples for the permission to use structures and data, and for their valuable assistance during the sampling campaign. We are indebted to Prof. Renata Moro and Dr. Luigi Campajola for their help in organising the Naples sampling.



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