A summertime investigation on urban PM fine and coarse fractions using hourly elemental concentration data series

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Summary. — The summertime composition of particulate matter in the atmosphere of some Italian towns (Florence, Genoa and Milan) has been studied by means of Ion Beam Analysis (IBA) techniques. The aerosol has been collected simultaneously 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. Absolute Principal Component Factor Analysis (APCFA) has been used to obtain the apportionment of the sources of particulate matter.

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1. – Introduction

Nowadays particulate matter (PM) is the pollutant of major concern in Italian urban areas [1]. Attention is devoted mainly to PM fine fractions because of their adverse health effects [2,3] and of the presence of hazardous elements attached to smaller particles.

In the frame of a research project funded by the Italian Ministry of Education, University and Research we planned a monitoring campaign with the aim of characterizing atmospheric particulate matter in four major Italian towns. The measurement campaigns were carried out in Milan, Genoa, Florence and Naples —very different towns located along the Italian peninsula— using the same experimental methodology for sampling and elemental analysis.

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To have a general indication on PM at the four sites, two measurement campaigns were planned: one during wintertime (whose results can be found in D'Alessandro *et al.* [4]) and another during summertime, whose results will be presented here together with a comparison between the two data-sets.

The interest for a summertime campaign resides in the peculiar meteo-climatic conditions of this season in Italy that are very different from the wintertime ones and that influence the dispersive power of the atmosphere. Results of the summertime campaign compared to wintertime ones allow the evaluation of seasonal differences at the monitored sites and of the influence of other factors, such as the photochemical activity, on the elemental concentrations.

The adopted experimental methods evidenced the effectiveness of an approach that couples PM sampling with hourly resolution and the PIXE technique, which is a multielemental analysis with high sensitivity also for small amounts of matter. The assessment of the detailed elemental composition on a wide data-set allows the application of receptor models and leads to the identification of main sources and their contribution.

Moreover, the hourly concentration temporal trends for a large number of elements are very effective in singling out the contribution of fugitive sources, the hourly variability of different sources, source profiles and transport events.

2. – Material and methods

The summertime campaign was performed in the period July 2nd-14th, 2001 that was characterised by anti-cyclonic stable meteorological conditions typical of the summer season in Italy. Only in Genoa it was not possible to perform measurements in the same days because of the concurrence of the "G8 international summit". The preparation and realization of this meeting strongly modified the normal activities of the city. For these reasons the summertime campaign in Genoa was delayed to the period July 30th - August 5th, 2001, a week with meteorological conditions representative of the season and comparable with those registered at the other towns during the campaign.

Only a brief description of the experimental methods, as well as of the characteristics of the towns, is given here, as a more detailed description can be found in the previous paper on the wintertime campaign [4] and in the thereby cited literature.

The samplers were installed at the same sites used for the wintertime campaign, *i.e.* on the roof of air quality network cabins, located in proximity of main roads characterized by medium-heavy traffic conditions. The streaker samplers collect with hourly resolution the coarse and the fine fraction of particulate matter, as described in full details elsewhere [5, 6]. The particulate deposits, collected on a Kapton (coarse fraction) and on a Nuclepore (fine fraction) filter, were measured by PIXE and PIGE at the external beam facility in Florence based on a van de Graaff accelerator [7].

PIXE analysis allowed the determination of Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Pb with Minimum Detection Limits (MDL) of the order of few (1–10) ng m^{-3} for most elements. Contemporary to PIXE also PIGE analysis was carried out for a better quantification of sodium concentration. Some correction factors were applied to the coarse-fraction concentration values of Na, Mg and Al to correct for single particle's self-absorption effects, following the procedure described in a previous work [4].

Also optical analysis of Nuclepore deposits was carried out on samples with the same methodology used for the analysis of the wintertime campaign [4].
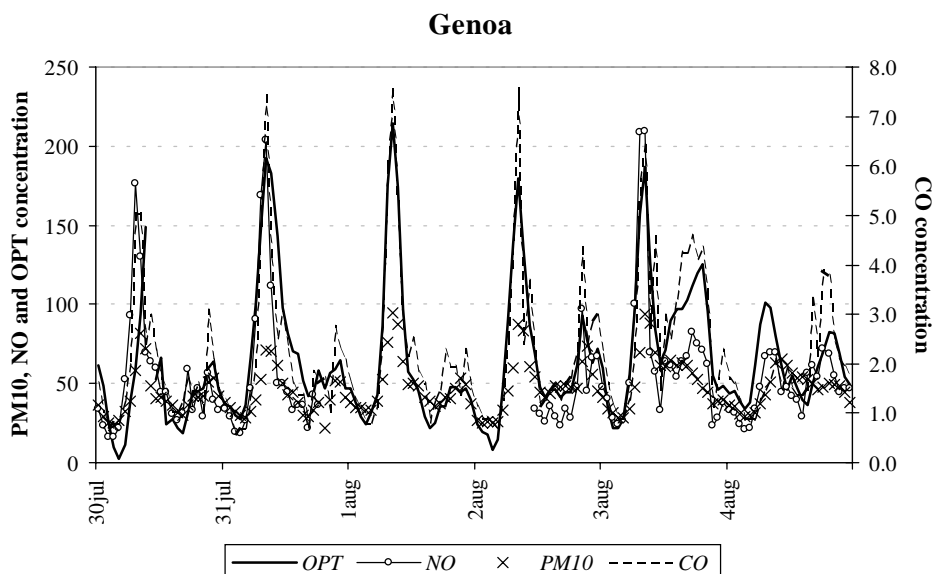
Genoa

Fig. 1. – The light attenuation of the fine fraction, OPT, in arbitrary units (left axis), NO and PM10 concentration in μg m^{-3} (left axis) and CO in mg m^{-3} (right axis) measured in Genoa-Brignole between July 30th and August 4th. Data on gaseous pollutants have been provided by the local authorities, PM10 values have been measured by TEOM$^{®}$.

Due to operation problems at the streaker sampler located in Naples these data were not validated and thus, excluded from the summertime analysis.

3. – Results

3˙1. *Optical analysis of Nuclepore deposits*. – The light attenuation has been measured on all the exposed Nuclepore filters to obtain the hourly time sequences (OPT) as in the example of fig. 1 concerning the period July, 30th - August 4th, 2001 at the Genoa-Brignole station. Due to the choice of the sampling sites, we consider traffic to be the main source of both elemental carbon (which is the main light absorber in aerosols) and total particulate matter. In this case the measured attenuation describes, with good approximation, the time behaviour of elemental carbon and, in first approximation, the total deposited particulate [4].

At all sites the OPT temporal series are highly correlated (see for example fig. 1) with CO and NO ones (tracers of traffic emissions) while there is no significant correlation with SO$_2$ (tracer of several combustion processes). During working days at all towns a typical daily pattern with a sharp peak at 8-9 a.m. and a second wider peak beginning around 19 p.m. and lasting till late evening can be observed.

This temporal behaviour is mainly related to the urban traffic during rush hours. The very similar average value of OPT at the three towns may indicate that the traffic along main roads is more or less the same in all these large urban areas.

3˙2. *PIXE elemental analysis*. – Time-series of hourly elemental concentrations have been obtained for each town from the analysis of PIXE spectra both in the coarse and in
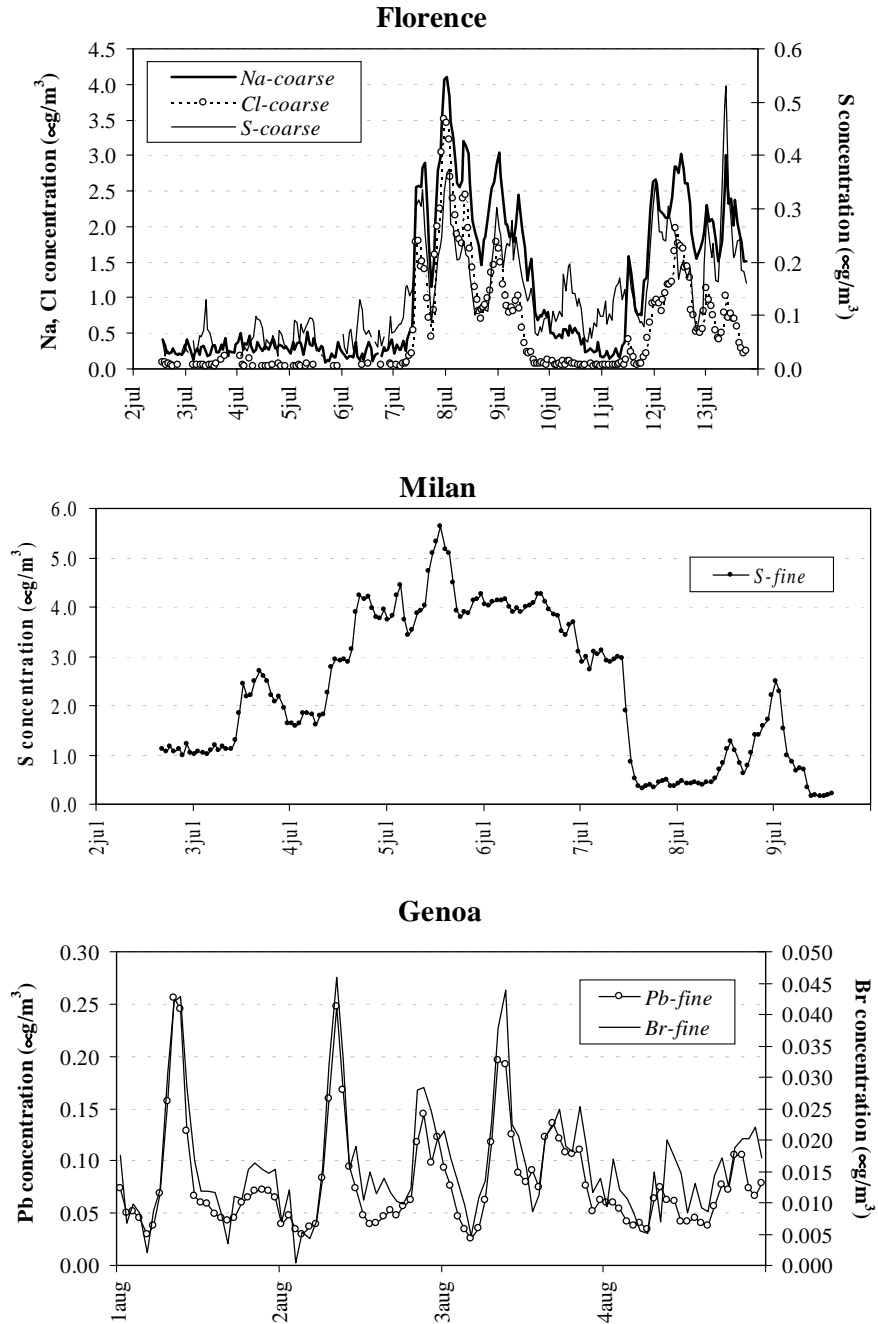
Florence

Milan

Genoa

Fig. 2. – Na, Cl and S concentrations in the coarse fraction during a "marine aerosol" transport episode detected in Florence between July 2nd and 13th (top); sulphur concentration in the fine fraction registered in Milan between July 2nd and 9th (centre); Br (right axis) and Pb (left axis) fine-fraction concentrations measured in Genoa between August 1st and 4th (bottom).

TABLE I. – *Average elemental concentrations ($\mu g\ m^{-3}$) analysed by PIXE: fine (top) and coarse (bottom) fraction. For elements marked with * the MDL (Minimum Detection Level) only is given.*

Fine fraction						
	Florence		Genoa		Milan	
Element	conc.	std. dev.	conc.	std. dev.	conc.	std. dev.
Na	0.352	0.186	0.520	0.462	0.341	0.114
Mg	0.141	0.049	0.155	0.084	0.141	0.048
Al	0.132	0.078	0.146	0.095	0.152	0.065
Si	0.324	0.166	0.252	0.210	0.446	0.222
P	0.063	0.006	0.050	0.004	0.062	0.015
S	1.372	0.462	3.212	1.349	2.335	1.459
Cl	0.139	0.031	0.165	0.143	0.109	0.010
K	0.217	0.089	0.192	0.058	0.212	0.068
Ca	0.425	0.181	0.424	0.152	0.447	0.199
Ti	0.027	0.004	0.029	0.007	0.028	0.004
V	0.017	0.003	0.027	0.016	0.018	0.003
Cr	0.012	0.004	0.014	0.004	0.014	0.005
Mn	0.009	0.002	0.010	0.008	0.013	0.007
Fe	0.370	0.205	0.422	0.217	0.395	0.165
Ni	0.004	0.002	0.009	0.006	0.005	0.002
Cu	0.022	0.012	0.019	0.012	0.022	0.010
Zn	0.020	0.011	0.030	0.016	0.057	0.067
As*	0.007		0.007		0.007	
Se	0.002	0.001	0.004	0.003	0.003	0.001
Br	0.015	0.008	0.015	0.009	0.014	0.007
Sr	0.007	0.002	0.007	0.002	0.007	0.002
Zr	0.008	0.002	0.006	0.001	0.006	0.001
Pb	0.066	0.035	0.070	0.045	0.065	0.032

Coarse fraction						
	Florence		Genoa		Milan	
Element	conc.	std. dev.	conc.	std. dev.	conc.	std. dev.
Na	0.960	1.048	0.509	0.572	0.218	0.116
Mg	0.210	0.129	0.139	0.080	0.116	0.051
Al	0.147	0.099	0.071	0.039	0.130	0.127
Si	0.295	0.196	0.104	0.060	0.236	0.218
P	0.028	0.008	0.028	0.008	0.026	0.006
S	0.114	0.0850.	0.056	0.032	0.045	0.017
Cl	0.736	0.884	0.382	0.442	0.074	0.045
K	0.102	0.049	0.063	0.013	0.073	0.023
Ca	0.582	0.305	0.156	0.046	0.305	0.261
Ti	0.018	0.009	0.011	0.002	0.015	0.006
V*	0.005		0.005		0.005	
Cr	0.007	0.003	0.005	0.006	0.005	0.001
Mn	0.007	0.003	0.003	0.001	0.005	0.002
Fe	0.642	0.390	0.066	0.041	0.175	0.180
Ni	0.002	0.001	0.002	0.002	0.002	0.001
Cu	0.038	0.023	0.003	0.002	0.010	0.009
Zn	0.017	0.011	0.002	0.003	0.009	0.013
As*	0.001		0.001		0.001	
Se*	0.001		0.001		0.001	
Br	0.003	0.002	0.002	0.001	0.001	0.001
Sr	0.004	0.002	0.003	0.001	0.003	0.001
Zr	0.005	0.002	0.003	0.001	0.003	0.001
Pb	0.011	0.006	0.004	0.001	0.007	0.003

the fine stage. Some examples are shown in fig. 2 and the average values of the complete data set are reported in table I.

Time plots for different elements display peculiar features singling out episodes due to atmospheric transport processes (fig. 2, top), meteorological conditions determining

build-up (fig. 2, centre) and variations in sources strength as the quasi-periodic daily time trends of elements emitted by traffic exhausts (fig. 2, bottom).

Lead and bromine in the fine fraction show correlated time series related to the daily variations of the traffic flow (an example is given in fig. 2, bottom); the correlation coefficient R is 0.91, 0.89, 0.81 in Genoa, Florence and Milan, respectively. Also the mean ratio Pb/Br is similar at the three sites: 4.7 in Genoa, 4.4 in Florence and 4.6 in Milan. This ratio is higher than the one registered during wintertime (about 3.7) [4], but it is well known that bromine can be lost during summer months as a consequence of volatilization.

Looking at the temporal trends of sulphur in the fine stage a long (some days) and a short (some hours) variation can be observed (see for example fig. 2, centre). Thus, the S 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 and modulated by synoptic-scale meteorology. All the Fourier components with a period greater than 48 hours have been summed to give the regional background [4]. Sulphur is mainly in the form of sulphates due to gas-to-particle conversion of SO_2. In the period July 4th-7th a stable anti-cyclonic condition was registered over the Po valley and favoured the build-up of sulphur concentration. On July 7th the arrival of cleaner air masses coming from North-North West lowered abruptly the S concentration registered in Milan.

In fig. 2 (top) the pattern of Na, Cl and S concentrations in the coarse fraction clearly indicate the occurrence of two strong episodes due to marine aerosol transported from the Tyrrhenian coastal area to Florence during the investigated period.

The elemental concentration time series were averaged separately for fine and coarse fractions (table I) to have a qualitative comparison among air quality in the three towns.

In the fine fraction sulphur is the element with the highest concentration but with absolute values quite different at the three sites. The sulphur concentration is very high in Genoa and Milan and lower in Florence. Also V, Ni, and Se concentrations (elements that are tracers of the combustion source) show the highest levels in Genoa followed by Milan and Florence even if V/S, Ni/S and Se/S concentration ratios are not the same at the three towns. It is worth noting that in the Genoa area there are a steel plant and a power plant both located inside the town. Milan has many industries (including power plants, refineries, chemical and metallurgical factories,...) in its outskirts, too. Pb, Br, Cu, Fe, Mn, Ca, K, Si, Al, Mg —all elements emitted directly or indirectly (*e.g.*, re-suspension of paved road dust) by the traffic source— show quite similar concentrations (within 10% for the greatest part of the elements, except Si and Mn) at the three locations.

In Genoa, Na and Cl (that are major elements in marine aerosol) have higher concentrations than in Milan and Florence as there a continuous source of marine aerosol is always active. This marine aerosol source gives a contribution of Na and Cl to the fine fraction as it also contains aged sea-salt aerosols which have typically smaller dimensions [8].

In the coarse fraction Na, Cl, Mg, S, Ca, K, Br concentrations are higher in Florence than in Genoa. This is an indication that in Florence the concentrations of these elements has been strongly influenced by the marine aerosol's transport events which occurred for many days during the investigated period (see fig. 2, top). It is worth noting that marine aerosol is typically concentrated (about 95 % of its mass) in the coarse-particle mode and the sea-salt composition is mainly characterized by Na, Cl, Mg, S, Ca, K, Br [9].

As already found during the wintertime campaign Fe, Cu, Zn, Pb —and to a lower extent Al, Si, Ti— show the highest concentrations in Florence, while they reach the

TABLE II. – *PCFA results for the concentrations time series of the three towns: fine (top) and coarse (bottom) fraction. Only elements with factors loadings ⩾ 0.5 have been reported. In the last row the percentage of variance associated to each factor is shown.*

Fine fraction										
Florence			Genoa				Milan			
URBAN	DUST	COMB	URBAN	DUST	COMB	SEA	URBAN	DUST	COMB	INDUS
OPT (0.9)	Mg (0.7)	Na (0.5)	OPT (0.9)	Mg (0.6)	S (0.6)	Na (0.7)	OPT (0.8)	Na (0.6)	S (0.8)	Cr (0.5)
K (0.5)	Al (0.9)	S (0.8)	Ca (0.8)	Al (0.9)	V (0.9)	Mg (0.6)	Fe (0.8)	Mg (0.8)	K (0.7)	Mn (0.8)
Ca (0.7)	Si (0.8)	Ni (0.8)	Cr (0.7)	Si (0.9)	Ni (0.9)	Cl (0.8)	Cu (0.9)	Al (0.8)	Ni (0.8)	Zn (0.9)
Fe (0.9)			Mn (0.6)	K (0.7)	Se (0.5)		Br (0.9)	Si (0.8)		
Cu (0.9)			Fe (0.9)				Pb (0.9)	Ca (0.7)		
Zn (0.8)			Cu (1.0)							
Br (0.8)			Zn (0.8)							
Pb (0.9)			Br (0.9)							
			Pb (1.0)							
36 %	*17 %*	*11 %*	*34 %*	*15 %*	*15 %*	*11 %*	*24 %*	*20 %*	*14 %*	*13 %*

Coarse fraction									
Florence			Genoa			Milan			
URBAN	DUST	SEA	SEA	DUST	URBAN	DUST+INDUS	URBAN	Na-Mg	
Ca (0.5)	Al (0.9)	Na (1.0)	Na (0.9)	Al (0.8)	Fe (0.6)	Al (0.7)	Cr (0.5)	Na (0.9)	
Ti (0.5)	Si (0.9)	Mg (0.9)	Mg (0.8)	Si (0.9)	Ni (0.7)	Si (0.8)	Fe (0.7)	Mg(0.8)	
Cr (0.9)	K (0.7)	S (0.8)	S (0.9)	Ca (0.7)	Cu (0.7)	S (0.6)	Ni (0.5)	S (0.5)	
Mn (0.8)	Ca (0.8)	Cl (0.9)	Cl (1.0)	Fe (0.6)	Zn (0.7)	K (0.8)	Cu (0.8)		
Fe (0.9)	Ti (0.7)	K (0.5)	Br (0.9)	Pb (0.5)		Ca (0.8)	Br (0.8)		
Ni (0.6)	Mn (0.5)	Br (0.5)				Ti (0.8)	Pb (0.7)		
Cu (0.9)	Sr (0.6)	Sr (0.5)				Cr (0.5)			
Zn (0.8)						Mn (0.8)			
Br (0.6)						Fe (0.6)			
Pb (0.9)						Cu (0.5)			
						Zn (0.6)			
						Sr (0.5)			
						Pb (0.5)			
34 %	*26 %*	*23 %*	*30 %*	*21 %*	*15 %*	*36 %*	*20 %*	*16 %*	

lowest concentration in Genoa; this behaviour is still under investigation.

As for the remaining elements, no significant differences between the locations can be pointed out during the summer period.

3`3. *Principal Component Factor Analysis.* – The major particulate matter sources have been individuated by the application of Principal Component Factor Analysis (PCFA) with VARIMAX rotation [10, 11] on the elemental concentration data set both for fine and coarse fraction.

Some elements (P, V, As, Se, Zr) were not included in the PCFA as they resulted to be below their MDL in 60% of sampling hours. Other elements were below MDL in fewer instances: in these cases a random value between zero and the MDL was attributed to the elemental concentration [12]. Outlier elemental concentrations due to the occurrence of few hours with concentration peaks in groups of elements have been identified by cluster analysis and excluded in order to focus the analysis on the average particulate matter composition. In the fine-fraction analysis we included OPT (see subsect. **3`1**) as a further element.

Only components with eigenvalues greater than 1 have been retained and in all cases a percentage of the global variance ranging from 64% to 83% has been accounted for. The results for each site and PM fraction are shown in table II and can be summarised as follows:

– In the fine fraction PCFA identified three factors in Florence and four in Milan and Genoa. At all sites a factor labelled as "urban" explained the greatest percentage of the

variance. It was characterised by high loadings for Pb-Br (elements used as additives in leaded gasoline, which has been in use in Italy till the end of the year 2001), for Fe-Zn-Cu (mainly derived from wear and tear of brakes and tyres as well as from impurities in fuels and lubricating oils) and for OPT (a tracer for black carbon). Thus, the "urban" factor has to be considered mainly due to direct and indirect traffic emissions as outlined also by the wintertime results. PCFA identified a second factor with high loading for Mg, Al and Si, soil-related elements which suggested a "dust" source. The third factor, labelled as "comb", was characterised by high loading for S, Ni at all sites and V, Se only in Genoa suggesting a generic "combustion" source owing to fossil fuel combustion. In Genoa a fourth factor (labelled as "sea") came out: it had a high loading for Na, Mg, Cl and identified the sea source. In Milan the presence of Cr-Mn-Zn in the fourth factor led to the identification of a generic "industrial" source.

– In the coarse fraction PCFA found three factors at all towns. Two factors were identified through elements with the highest loading; they were labelled as "urban" and "dust" at all towns. However, in Milan the factor analysis did not single out, as happened for the wintertime data-set, an "industry" source whose tracer elements can be found in the source "dust". The third factor identified in Genoa and Florence a "sea" source. In Milan the third factor was named "Na-Mg" and it is probably due to a dust transport not yet identified completely.

$3^{.}4$. *Source apportionment.* – The quantification of the source apportionment to PM elemental concentrations has been obtained by Absolute Principal Component Factor Analysis [13, 14]. The procedure is the same used for winter data analysis as reported in detail in D'Alessandro *et al.* [4]. In figs. 3a-b in bar plots the calculated source contributions to the various elements and to OPT are shown, separately for fine and coarse fraction. The percentages of the measured elemental concentrations reconstructed by the model range between 80–130% (with extreme values at 30 and 170% found for a few elements present in low concentration). An evaluation of the standard deviation on factor loadings was carried out [10] and it was used to estimate the uncertainties on elemental concentration calculated by APCA (15–20% on elements with factor loading higher than 0.50). Moreover, the correlation coefficients between measured and calculated concentrations time series are generally good.

Similarly to wintertime results, "urban" is the main source of OPT and anthropogenic elements but "dust" and "combustion" are of relevance for Al-Si-Ca-Fe and S-K-Ni-V, respectively. The "sea" source has an importance in Genoa, of course, but also in Florence, unexpectedly. This behaviour has to be ascribed to marine air transport phenomena occurred for many days during the sampling period. Both the frequency of these events and their relative weight will be studied further on longer sampling periods. In Milan the presence of the "industry" source is confirmed and it is evident in the fine fraction while not in the coarse one.

$3^{.}5$. *Comparison between winter and summer PM characterization.* – During the summertime campaign at all sites approximately the same particulate matter sources identified during wintertime have been found in both fractions. The apportionment of the elements and OPT to the different sources resulted to be fairly similar to the wintertime one, even if it should be taken into account that apportionment lower than 20% have a low degree of significance and the associated error (see subsect. $3^{.}4$) is quite high.

Nevertheless, the elemental concentrations exhibit evident differences in the two seasons. For the sake of simplicity we have considered the sum of fine and coarse fractions

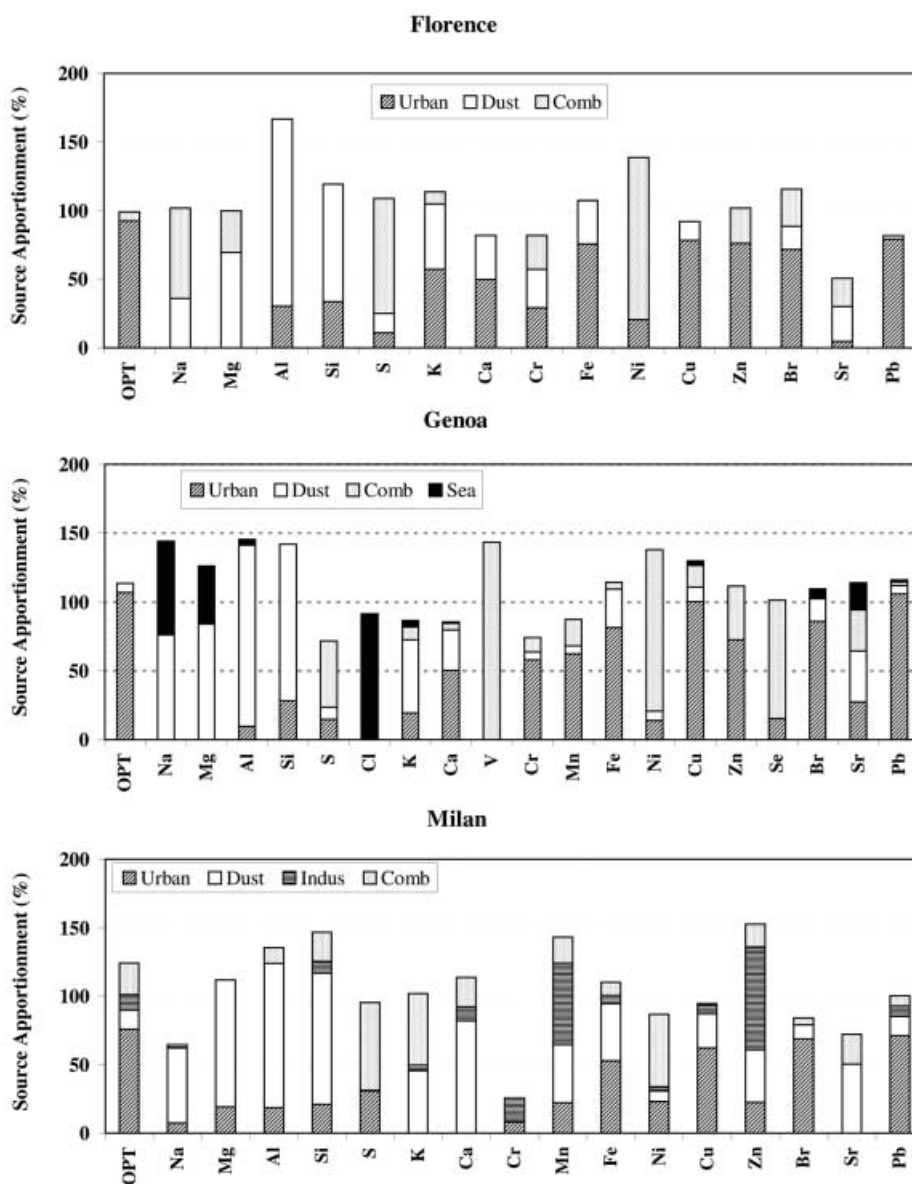**Florence**

Genoa

Milan

Fig. 3a. – Apportionment of OPT and of elements detected by PIXE in the fine fraction.

of elemental concentrations. In fig. 4 the wintertime/summertime ratio of the elemental concentrations is represented. Almost all elements are characterised by lower concentrations during summertime with seasonal differences larger in Milan and Florence than in Genoa, where many elements (Na, Mg, Al, Ca, Ni, Cu, Br, Sr, Pb) show only a slight variation (about 10%) in their concentration. In Milan and Florence significant differences in the wintertime/summertime ratio can be observed for some elements; in particular, those with a prevailing anthropogenic origin (Mn, Fe, Br, Pb) show a higher

Florence

Genova

Milan
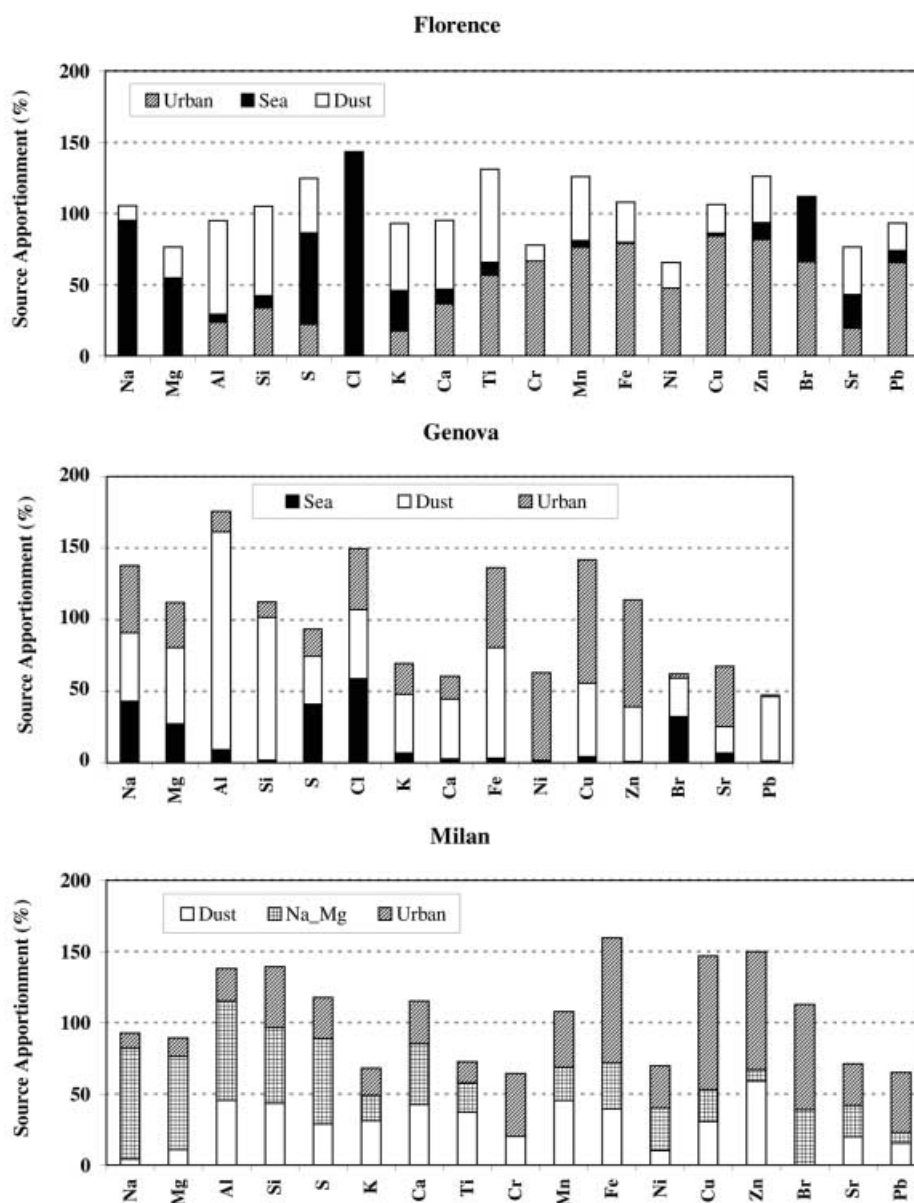
Fig. 3b. – Apportionment of the elements detected by PIXE in the coarse fraction.

ratio in comparison with soil-related elements (Al, Si, Ca, Ti). It is worth noting that the soil-related elements during the summer experience an easier re-suspension due to the dryness of soils. Also Zn and K show a high wintertime/summertime ratio as they have an additional source during the winter season due to the wood combustion for domestic heating.

An exception is sulphur, which has summer concentrations higher than wintertime ones at all sites. The increase of sulphur concentrations during the summer is due to
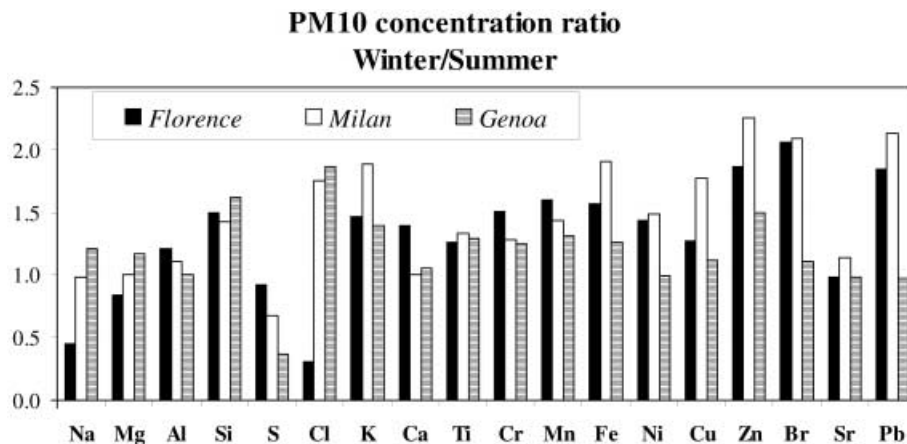
Fig. 4. – Winter/Summer ratio of element concentration in PM10 (fine + coarse fraction) at the three locations.

the fact that it is mainly present in the form of secondary sulphates whose production is favoured by the enhanced photochemical activity typical of the warm season. Of great relevance are oxidation reactions initiated by radicals such as OH produced photochemically by the action of solar radiation on ozone [15].

Also Na, Mg, Cl have high summer values in Florence due to the influence of two marine aerosol transport events in the investigated period.

In Milan and Florence the seasonal effect was observed also in previous researches [16-18]. It has been explained considering the differences in the average mixing layer height registered during the two seasons (in summer the mixing layer is on average 2-3 times higher than the wintertime one) and the stronger anemological regime during the summer. On the contrary, in Genoa during summertime frequent stagnant conditions occur and the wind speed during summertime is lower than during wintertime.

4. – Conclusions

The summertime campaign completes the results of the wintertime large-scale monitoring of the air particulate matter in Italy with continuous fractionated sampling and Ion Beam Analysis technique.

The summertime results confirm the presence of the same acting sources identified during the winter, point out a strong seasonal effect in the elemental concentrations in Florence and Milan (characterized by lower concentrations during the summer) and evidence the contribution of marine aerosol transport events in Florence. The higher sulphur concentration during summertime at all towns, also in those with better dispersion conditions, clearly indicates the importance of photochemical processes in the production of secondary aerosols.

High-resolution time series of elemental concentrations are very effective for evidencing the impact and allowing the separation of "episodic sources" (*e.g.*, transport of marine aerosols), "quasi-periodical sources" (*e.g.*, traffic), regional contributions and variations of elemental concentration on different time-scales.

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