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Elemental characterization of PM₁₀, PM_{2.5} and PM₁ in the town of Genoa (Italy)

V. Ariola ^a, A. D'Alessandro ^a, F. Lucarelli ^b, G. Marcazzan ^c,
F. Mazzei ^a, S. Nava ^b, I. Garcia-Orellana ^d, P. Prati ^{a,*}, G. Valli ^c,
R. Vecchi ^c, A. Zucchiatti ^a

^a *Dipartimento di Fisica and INFN, Università degli Studi di Genova, via Dodecaneso 33, I-16146 Genova, Italy*

^b *Dipartimento di Fisica and INFN, via Sansone 1, 50019, Sesto Fiorentino, Italy*

^c *Istituto di Fisica Generale Applicata and INFN, Via Celoria 16, 20133, Milano, Italy*

^d *Universidad de Sevilla and INFN-Florence, via Sansone 1, 50019, Sesto Fiorentino, Italy*

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Abstract

The particulate matter (PM) concentration and composition, the PM₁₀, PM_{2.5}, PM₁ fractions, were studied in the urban area of Genoa, a coastal town in the northwest of Italy. Two instruments, the continuous monitor TEOM and the sequential sampler PARTISOL, were operated almost continuously on the same site from July 2001 to September 2004. Samples collected by PARTISOL were weighted to obtain PM concentration and then analysed by PIXE (particle induced X-ray emission) and by ED-XRF (energy dispersion X-ray fluorescence), obtaining concentrations for elements from Na to Pb. Some of the filters used in the TEOM microbalance were analysed by ED-XRF to calculate Pb concentration values averaged over 7–30 d periods.

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Keywords: PM₁; PM_{2.5}; PM₁₀; Elemental composition; PIXE; XRF; TEOM

1. Introduction

In accordance with the European Directive 1999/30/EC, the concentration of PM₁₀ (particulate matter with aerodynamic diameter smaller than 10 µm) in Europe should be reduced to the average annual value of 20 µg m⁻³ by year 2010. Large amount of PM₁₀ concentration data are daily collected for regulatory purposes in several countries (Manoli et al., 2004; Mantis et al.,

2005) while poor information is available on the other finer fractions (PM_{2.5} and PM₁; particulate matter with aerodynamic diameter smaller than 2.5 µm and 1 µm, respectively) and on their composition. Moreover, recent works indicate the finer fraction of PM as the most dangerous for human health and environment (Schwartz et al., 1996; Maynard and Howard, 1999; Wichmann and Peters, 2000; Chow et al., 2002a,b; Stieb et al., 2002). On the other hand, standard methods for continuous PM monitoring are still to be assessed; in such a situation the Tapered Element Oscillating Microbalance (TEOM) is widely used even if the air flux heating to 50 °C, to eliminate the effects of atmospheric humidity, is known to cause losses of volatile materials. These

* Corresponding author. Tel.: +39 010 353 6439; fax: +39 010 314 218.

E-mail address: prati@ge.infn.it (P. Prati).

possible losses constitute a problem for continuous PM measurements in particular in urban areas, where a considerable fraction of particulate matter can take form of semi-volatile species (i.e. nitrates and organics). For these reasons, a number of studies in the last years have been devoted to the assessment of TEOM performance versus standard gravimetric methods for PM₁₀ and, in a limited number of cases, for PM_{2.5} monitoring (Reponen et al., 1996; Allen et al., 1997; Soutar et al., 1999; King et al., 2000; Muir, 2000; Cyrus et al., 2001). In the past, it was suggested to apply a default correction factor of 1.3 to PM₁₀ data collected by TEOM (DETR, 1999). Nevertheless, this correction factor shows a great day-to-day variability even in the same site as it depends on the season and on the aerosol composition (Green et al., 2001) and the problem is still open.

Genoa is the most populated coastal town in the northwest of Italy, grown during the centuries around an important harbour, with significant steelworks in the surrounding, and largely influenced by Mediterranean climate. The PM₁₀ and PM_{2.5} compositions in town were object of several studies in the past (D'Alessandro et al., 2003 and references therein). The campaign described in this work was addressed to different tasks: the evaluation of PM₁₀, PM_{2.5}, PM₁ concentration levels and composition in the urban area of Genoa and to a comparison between continuous (TEOM) and standard gravimetric methods in the three quoted PM fractions. We developed as well a procedure, based on XRF analysis, to measure average Pb concentration values directly from the 16 mm Teflon-coated borosilicate glass fibre filters used by the TEOM microbalance.

2. Material and methods

We used for the campaign two samplers both manufactured by Rupprecht & Patashnick Co. Inc.: the TEOM 1400ab Ambient particulate monitor and the PARTISOL 2025 sequential particulate matter sampler. Our TEOM was not complemented with the new FDMS (Filter Dynamics Measuring System). Both the samplers can be equipped with the same inlets, the EPA-standards PM₁₀ inlet or the sharp-cut cyclones for selecting PM_{2.5} and PM₁. The sampling site was located in the urban area of Genoa, in a node of the municipal air quality network identified as “Brignole”, at the cross of three main roads and in front of a large railway station. Both TEOM and PARTISOL inlets were installed on the cabin roof, at about 3.5 m above ground and at about 4 m from the kerbsides: the distance between the two inlets was 120 cm. By collecting PM with similar inlets (i.e. with the same cut-off diameter) on both the instruments we compared samplers performance. According to EPA-standards, flow rate was fixed at 16.7 l/min

(actual flow) in both instruments. In Table 1 the sampling configurations during the campaign are listed. While PM₁₀ and PM_{2.5} were collected in different seasons, PM₁ was only sampled in summer.

The gravimetric PM concentration was determined by PARTISOL operated with 47 mm mixed cellulose esters (year 2002) and Teflon (years 2003–2004) membranes with 0.4 μm and 2 μm pore size, respectively. Sampling time was always 24 h beginning at midnight. Filters, pre-conditioned for 2 d in a controlled room (temperature: $20 \pm 1^\circ\text{C}$, relative humidity: $50 \pm 5\%$), were weighed using an analytical balance (sensitivity: 1 μg).

The elemental composition of PM collected by PARTISOL until June 2003 was studied by PIXE, at the external proton beam facility of INFN-Florence (Del Carmine et al., 1990). The beam was scanned along each filter, to average possible in-homogeneities in the deposition thickness, each filter requiring 10 min of beam time and a total charge of about 6 μC . The elemental thickness [$\mu\text{g cm}^{-2}$] was obtained by comparing the filter yields with a sensitivity curve [$\text{counts } \mu\text{C}^{-1} \mu\text{g}^{-1} \text{cm}^2$] measured in the same geometry on a set of thin standards certified within 5% (Micromatter Inc.). All X-ray spectra were fitted for 23 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr, Pb) using the GUPIX software package (Maxwell et al., 1995).

Filters sampled by PARTISOL after June 20th 2003 were analyzed at the Physics Department of Genoa by ED-XRF with the ED2000 spectrometer manufactured by Oxford Instruments. In ED2000 primary radiation is produced by a X-ray tube ($I_{\text{max}} = 1 \text{ mA}$, $V_{\text{max}} = 50 \text{ kV}$) with an Ag anode, and modified by putting appropriate filters between anode and sample. Two measuring conditions were fixed to optimise the sensitivity for groups of elements: runs with HV = 15 kV, $I = 100 \mu\text{A}$, no primary filter, live time = 1000 s, gave light elements (Na to Si) concentrations while the medium-heavy (S to Pb) elements concentrations were measured setting HV = 30 kV, $I = 500 \mu\text{A}$, thin Ag filter, live time = 3000 s. Spectra were fitted for the same 23 elements listed above by the AXIL software package (Van Espen et al., 1977). Elemental thickness were again deduced by comparison with a sensitivity curve measured in the two conditions with the same set of certified standards used for PIXE.

TEOM collected particulate matter on the Teflon-coated glass fibre filter placed on the top of the oscillating hollow element of the microbalance and continuously provided PM concentrations (twice-hourly in our set-up). Daily PM concentrations were evaluated as the average of 1-h values. In TEOM standard use, the air flow on the filter is 3 l/min: during the campaign, to increase the sampling time per filter, we reduced the flow to 2 l/min, maintaining fixed the total flow rate to 16.7 l/min. The

Table 1

Mean value (\bar{X}) and standard deviation (s) of the particulate matter concentration distributions obtained by TEOM and PARTISOL during the whole campaign

	PM1 $\bar{X} \pm s$	PM2.5 $\bar{X} \pm s$	PM10 $\bar{X} \pm s$
<i>TEOM sampling period</i>			
2001			
Jul 4–Aug 6			40 ± 16
Sep 4–Sep 14			31 ± 15
Sep 14–Sep 24		20 ± 11	
2002			
Jan 8–Mar 22		25 ± 12	
Mar 22–Apr 24	20 ± 10		
Apr 24–Jun 14			36 ± 16
Jun 14–Jul 16		29 ± 14	
Jul 16–Aug 19	20 ± 10		
Aug 19–Sep 29			36 ± 15
Oct 5–Dec 6			36 ± 18
2003			
Dec 6–Feb 7		21 ± 11	
Apr 17–Apr 30	21 ± 7		
May 1–Jun 12			45 ± 18
Jun 13–Jun 19		32 ± 9	
Jul 16–Aug 5	23 ± 10		
Aug 6–Oct 8		24 ± 11	
Oct 9–Nov 18			34 ± 17
2004			
Nov 19–Mar 21	16 ± 9		
Mar 23–Jun 16		19 ± 9	
Jun 18–Aug 11			40 ± 16
Aug 26–Sep 30			39 ± 16
All data	18 ± 9	23 ± 12	37 ± 17
<i>PARTISOL sampling period</i>			
2002			
Apr 29–May 31			40 ± 10
Jun 1–Jun 26		34 ± 11	
Jun 27–Aug 18	22 ± 6		
2003			
May 1–Jun 12			44 ± 10
Jun 13–Jul 10		23 ± 7	
Jul 11–Aug 5	22 ± 7		
Aug 6–Sep 5		24 ± 7	
Sep 27–Oct 8		22 ± 9	
Oct 9–Nov 25			36 ± 15
2004			
Mar 6–Mar 21			51 ± 19
Mar 23–Jun 11		18 ± 7	
Jun 18–Jun 30			47 ± 7
All data	22 ± 6	23 ± 9	41 ± 13

Number of PARTISOL samples corresponds to number of sampling days while TEOM provided 24 hourly concentration values per day. Concentration values were calculated using volumetric flow and are given in $\mu\text{g m}^{-3}$.

maximum loading on the filters was so reached in periods of 2–4 w, depending on PM concentration and on inlets used.

Some TEOM filters were analyzed by ED-XRF to deduce Pb concentrations averaged over 7–30 d. In this case, quantitative PIXE analysis was hampered by the relatively large and inhomogeneous thickness of the samples ($1\text{--}2\text{ mg cm}^{-2}$) which can cause changes of the PIXE cross-section along the proton beam path inside the sample. This set of ED-XRF analyses were performed at the University of Milan—Istituto di Fisica Generale Applicata where another ED2000 spectrometer is installed. Details on this facility and on the analysis technique can be found in (Marcazzan, 1998; Marcazzan et al., 2004). Unfortunately, the glass fibre filters showed, when analysed by ED-XRF, a considerable background (Fig. 1) that allowed the identification of only a few elements (S, Fe, Cu, Pb, Br). Moreover, the non-homogeneous PM deposition on TEOM filters produced large and partially unpredictable X-ray self-attenuation. A comparison with PIXE analysis of PARTISOL filter sampled in corresponding periods (see Table 1) showed that Pb peaks only could be quantitatively analyzed: for this element PIXE and ED-XRF results turned out to be in agreement within 10%.

3. Results

3.1. Particulate matter concentration

Average daily PM concentrations obtained by PARTISOL and TEOM are summarized in Table 1. On average, concentration values measured by PARTISOL appeared to be larger than those determined by TEOM, even if the sampling periods were not exactly the same. By comparing mean values (averaged on all data), the PARTISOL to TEOM PM concentration ratio was about 1.22, 1.00 and 1.11, respectively in the PM1, PM2.5 and PM10 fraction. The average PM1:PM2.5 and PM2.5:PM10 ratios, calculated separately for PARTISOL and TEOM data sets, ranged between 0.80 and 0.90 and 0.55 and 0.60, respectively. The PM10 concentration could be compared with the European limit of $50\text{ }\mu\text{g m}^{-3}$, the air quality standard beginning January 2005, not to be exceeded more than 35 days per year. Both in PARTISOL and in TEOM data, about 20% of the PM10 concentrations were greater than $50\text{ }\mu\text{g m}^{-3}$. Particulate matter concentration did not show any appreciable reduction during the time (see Table 1) and the highest values were actually measured in the winter 2004. Particulate matter concentrations were generally larger in summer when, in the area of Genoa, stable atmospheric conditions are very frequent causing an increase of all the pollutants.

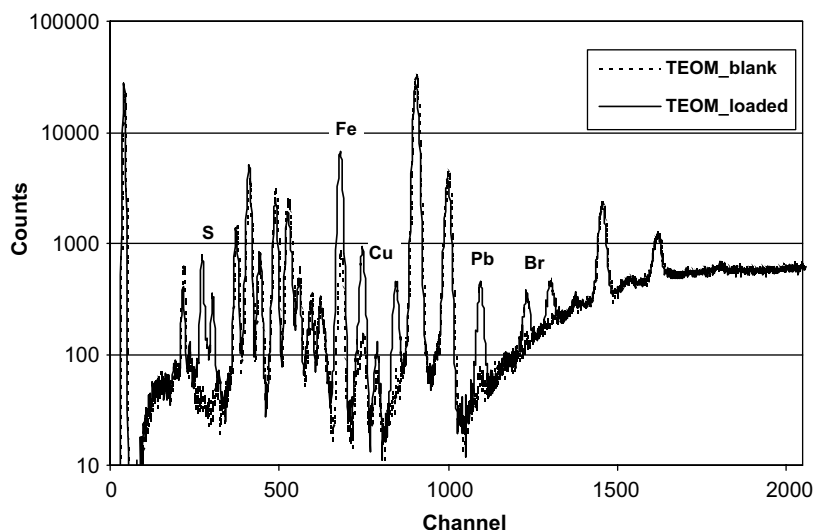


Fig. 1. XRF spectra of blank and loaded TEOM filters: the large background allows the identification of a few elements. Both the spectra have been obtained with a 30 kV–500 μ A X-ray tube and 1000 s of acquisition time. The loaded filter has been used in TEOM for 15 d in July 2001 with the PM10 inlet.

3.2. Intercomparison between TEOM and gravimetric method

Selecting data collected when PARTISOL and TEOM were operated with the same inlets (see Table 1) we directly compared the performance of the two instruments. Basically we followed the procedure established by the European Standard 12341 (European Standard EN12341, 1998; EC working group, 2001) to verify the equivalence of different samplers even if PARTISOL, designed according to EPA standards, cannot be considered a reference sampler. We must note that PARTISOL was successfully tested against reference EU samplers in a previous campaign (Chiari et al., in press). We used for PM10 the usual 50 $\mu\text{g}/\text{m}^3$ threshold and we fixed exceedence thresholds at 30 $\mu\text{g}/\text{m}^3$ and at 25 $\mu\text{g}/\text{m}^3$ for PM2.5 and PM1, respectively (according to the PM1:PM2.5 and PM2.5:PM10 ratios discussed above). The inter-comparison results are summarised in Table 2 for all the PM fractions. The two instruments turned out in good agreement

but the number of threshold exceedences is always larger for PARTISOL. Actually, the regression coefficient for PM1 data is quite low ($R^2 = 0.58$, $n = 32$), this corresponding to a ratio between light elements and PM concentration (light elements concentration = PM – sum of elemental concentrations measured by PIXE or XRF, see below) larger than 0.90 in 71% of the days. The same condition was observed in 3% and 28% of the sampling period in PM10 and PM2.5, respectively.

Following the scheme of the European procedure, we calculated a correction factor k for TEOM data (PARTISOL = $k \cdot \text{TEOM}$) forcing the regression curves between the two data series through the origin. The k factor resulted 1.03 ± 0.03 ($R^2 = 0.52$, $n = 32$), 1.00 ± 0.04 ($R^2 = 0.88$, $n = 121$) and 1.09 ± 0.05 ($R^2 = 0.79$, $n = 95$) for PM1, PM2.5 and PM10, respectively. This result differs from the suggested correction factor given in (DETR, 1999) for PM10, but $k \sim 1$ was obtained several times in the campaigns on PM10 reported in (EC working group, 2001).

Table 2
TEOM vs. PARTISOL inter-comparison summary

Fraction	TEOM average ($\mu\text{g}/\text{m}^3$)	PARTISOL average ($\mu\text{g}/\text{m}^3$)	Regression equation ^a	R^2 and number of samples	Concentration threshold ($\mu\text{g}/\text{m}^3$)	Number of exceedences TEOM	Number of exceedences PARTISOL
PM10	37.7	41.2	$T = 0.85P + 2.34$	0.81 ($n = 95$)	50	10	18
PM2.5	22.9	22.3	$T = 0.77P + 5.71$	0.90 ($n = 121$)	30	26	25
PM1	19.3	20.5	$T = 0.75P + 3.89$	0.58 ($n = 32$)	25	6	10

^a T, P = PM concentration measured by TEOM and PARTISOL, respectively.

3.3. Elemental composition

Elemental concentrations of PM deposited on PARTISOL filters were obtained by PIXE and ED-XRF for elements from Na to Pb, with a sensitivity in the order of a few ng m^{-3} similar for both the techniques. Detected elements accounted for, on average, 20%, 10% and 7% of the total PM₁₀, PM_{2.5} and PM₁ concentrations, respectively. Light elements (in particular nitrogen and carbon compounds), were thus more concentrated in the finest fraction. In Fig. 2 we compare the median elemental concentrations in the three PM

fractions. Sulphur was always the most abundant detected element accounting for about 4%, 8% and 6% of the total concentrations in PM₁₀, PM_{2.5} and PM₁, respectively. The three PM fractions were collected in different periods, nevertheless, considering the samples (57 for PM₁, 139 for PM_{2.5} and 128 for PM₁₀, see Table 1) representative of the average PM composition, we can note that elements typical of marine aerosol (Na, Cl) and of soil-related particulate matter (Al, Si, Ca, Ti, Fe) were mainly concentrated in the coarse fraction of PM₁₀ (defined as PM with aerodynamic diameter between 2.5 and 10 μm). The atmospheric concentration

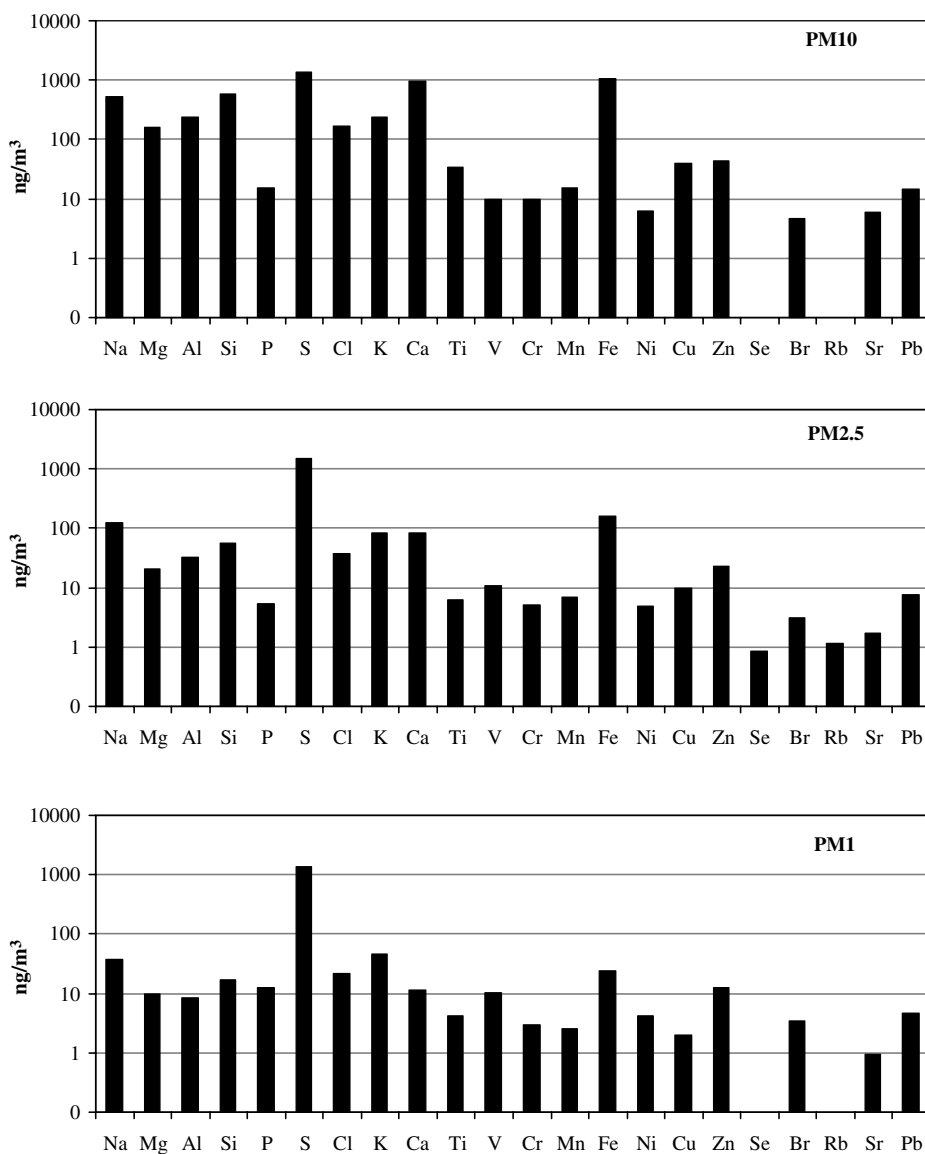


Fig. 2. Median elemental composition of PM₁₀, PM_{2.5}, PM₁ deduced by PIXE and ED-XRF analysis of PARTISOL filters. Sampling periods are listed in Table 1.

Table 3
Average Pb concentrations obtained by XRF analysis of some TEOM filters used in the campaign

Sampling period	PM fraction	Pb (ng m ⁻³)
2001		
Jul 16–Jul 30	PM10	29 ± 3
Jul 30–Aug 6	PM10	44 ± 5
Sep 4–Sep 14	PM10	38 ± 4
Sep 14–Sep 24	PM2.5	37 ± 4
2002		
Jan 15–Jan 22	PM2.5	18 ± 3
Jan 22–Jan 29	PM2.5	17 ± 3
Jan 31–Feb 8	PM2.5	9 ± 2
Feb 8–Feb 15	PM2.5	11 ± 2
Mar 22–Apr 2	PM1	8 ± 2
Apr 2–Apr 11	PM1	15 ± 2
Apr 11–Apr 24	PM1	5 ± 2
Apr 24–May 21	PM10	10 ± 2
May 21–Jun 14	PM10	9 ± 2
Jun 14–Jul 12	PM2.5	9 ± 2
Jul 16–Aug 18	PM1	15 ± 2
Sep 11–Sep 29	PM10	11 ± 2
Oct 23–Nov 15	PM10	10 ± 2
Nov 15–Dec 6	PM10	6 ± 1

For each period the Pb concentration was measured using one TEOM filter.

of crustal matter can be obtained following a standard procedure (Chan et al., 1997; Salma et al., 2001) as $CM(\text{crustal matter}) = 1.16(1.90c(\text{Al}) + 2.15c(\text{Si}) + 1.41c(\text{Ca}) + 1.67c(\text{Ti}) + 2.09c(\text{Fe}))$, where $c(i)$ is the concentration of element i . We got 17%, 4% and 1% of total PM concentration, respectively in the PM10, PM2.5 and PM1 fractions. Sulphur, V and Ni as well as Br and Pb were concentrated in the PM2.5 and PM1 fractions. Sulphates can be calculated from S elemental concentration assuming $(\text{NH}_4)_2\text{SO}_4$ as their main chemical form in the urban environment (Chan et al., 1997; Salma et al., 2001): we got 15%, 32% and 28% of total PM concentration, respectively in the PM10, PM2.5 and PM1 fractions. Atmospheric conditions were monitored during the sampling periods, but no correlations among meteorological parameters and particulate matter composition were identified with the unique exception of a strong increase of Na and Cl concentration (up to a factor 10 in PM10) with winds coming from the South (i.e. from the sea).

By comparing the present results with data collected in the same site in the recent past (D'Alessandro et al., 2003), we could observe a clear decrease of Pb concentration. Lead average concentration was about 64 ng m⁻³ in PM2.5 and 73 ng m⁻³ in PM10, during the winter 2001 (D'Alessandro et al., 2003) while values measured in this work range between 8 and 12 ng m⁻³ in both the PM fractions. Leaded fuel was legally banned in Italy in January 2002 (DPCM, 2000) and this explains the decrease of Pb concentration in the atmosphere. A

Pb concentration trend was obtained by ED-XRF analysis of the TEOM glass-fibre filters. As shown in Table 3, data confirm the decrease of Pb concentration after January 2002. Each value in Table 3 is an average over 7–30 d period: this non-standard use of TEOM allows to couple on-line continuous monitoring of PM concentration and off-line evaluation of Pb concentration on about 15–20 samples per year.

4. Conclusion

A long term sampling campaign with two instruments, PARTISOL and TEOM, installed in the same site gave a temporal trend of PM in the town of Genoa. No significant evolution in PM concentration and composition was observed. The campaign also produced the first data on PM1 concentration (about 50% of PM10) and composition in town. The TEOM continuous monitor gave PM concentration values in substantial agreement with those measured by the standard sequential sampler (PARTISOL) and gravimetric analysis. Two analytical techniques, PIXE and ED-XRF, were used to measure daily and average composition of PM, collected both on PARTISOL and on TEOM filters.

The same approach is now followed in the frame of a new study which plans to monitor the urban area of Genoa in several sites for 2 years to deduce a firmer evaluation of PM concentration and composition.

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