SIZE AND CHEMICAL COMPOSITION OF THE FINE PARTICULATE IN THE URBAN AREA OF MILAN

Giovanni Lonati, Michele Giugliano, Ruggero Tardivo

Dipartimento di Ingegneria Idraulica, Ambientale, Infrastrutture viarie, Rilevamento
Politecnico di Milano - P.zza L. da Vinci, 32 - 20133 Milano, Italy. giovanni.lonati@polimi.it

ABSTRACT

Fine particulate presence at urban sites in the city of Milan (Italy) is characterised in terms of particles' size distribution and PM10, PM2.5, PM1 mass concentration for the cold and warm season. Workdays' and weekends' data from a low-volume particle size laser analyser are analysed for assessing the effect of the reduced traffic circulation on Sundays. Results of chemical speciation of the major chemical components, performed on PM2.5 samples collected during specific campaigns are presented. PM2.5-loaded filters are analysed for the elemental mass composition, for the main ionic components (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+) and for elemental carbon and particulate organic matter. Information obtained by size distribution and chemical composition analyses allow for the assessment of the source contribution to the observed concentration levels, with particular respect to the secondary source.

INTRODUCTION

Atmospheric pollution due to airborne fine particles is an environmental issue of increasing concern in the metropolitan area of Milan, the main city of Lombardy, Italy's most industrialised and populated region. In the area, both long-term and short-term standards for PM_{10} are largely not attained and restrictions of the circulation for some categories of vehicles are frequently enforced during the winter period, in order to control the acute episodes of pollution. But the strategies oriented to standard attainment require the understanding of the principal pathways leading to high concentration of the fine particulate in atmosphere, the role of the primary emission, as mobile sources and domestic heating, and the extent of the nucleation and condensation processes leading to formation of secondary fine particulate from primary pollutants [1, 2]. The aim of this work is to provide information on the fine particulate presence in the city of Milan, not only in terms of mass concentration but also in terms of particles' size distribution. By analysing the systematic differences observed between Sundays' and weekdays' concentrations and size distributions, the role of the traffic as primary source affecting the presence of fine particulate in the area is evaluated. Results of chemical speciation of the major chemical components, performed on PM2.5 samples collected during specific campaigns at a urban background site and at a tunnel site in Milan are also presented. Sampling campaigns have been carried out by means of a high-volume gravimetric automatic sequential sampler. PM2.5 mass composition is analysed in terms of the main ionic components (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+) and of the carbon species, elemental carbon and organic carbon. Whereas the speciation of PM2.5 samples collected at the urban background site can provide useful information about all the sources active in the area, including the secondary formation processes in the atmosphere, the samples collected in the tunnel are mainly affected by primary traffic emissions. Information obtained by size distribution and chemical

composition analyses allow to assess the source contribution to the observed concentration levels, with particular respect to the secondary source.

MATERIAL AND METHODS

Monitoring sites

Monitoring and sampling campaigns have been performed between August 2002 and February 2004 at 2 sites in the city of Milan characterised by a different exposure to the traffic source. The first site is representative of a urban background site (UB site) in the city centre, not directly exposed to traffic emission since located in a walled yard; the second site (TU site) is directly exposed to the traffic emissions, since the monitor was located in the kerbside position in the middle of a 250 m-long tunnel of the city centre. At both sites, the sampling campaigns were focused either on the measurements of particles' size distribution and on the collection of PM2.5 sample for their chemical speciation.

Instruments - Laser analyser

Simultaneous monitoring of fine particles' presence (0.3 µm up to 20 µm of diameter) has been performed by a Grimm model 1107 particle size analyser [3]. Particles' counts are then converted to mass distribution, and in particular into the mass cuts of PM10, PM2.5 and PM1, based on an empirical density-factor suitable for the urban suspended particulate. The ambient air to be analysed is drawn into the measurement cell by means of an inhalable sampling head at a flowrate of 1.2 liters per minute. During the monitoring campaigns, 1-minute averaged particles' counts have been recorded on a data storage card: 1-hour and daily averaged size distributions, as well as PM10, PM2.5 and PM1 mass concentrations, have been subsequently calculated based on the recorded data.

Instruments - Gravimetric sampler

Sampling of PM2.5 has been carried out by means of a high-volume (30 m^3 h^{-1} flow rate) gravimetric sampler DIGITEL DA-80H, equipped with PM2.5 cut-off inlet and 150 mm quartz filters (www.digitel-ag.com). The procedure for the preparation of the blank filters consists of 2-hours preheating at 550 °C, 48-hours equilibration of the filters in an air-conditioned weighing room at (20 ± 1)°C and (50 ± 5)% relative humidity, triple weighing by means of a balance with 1 µg resolution; the filters are then wrapped in aluminium foil and stored in a freezer until field sampling. Except for filters preheating, the same procedure of equilibration and weighing is applied after the sampling, according to the European Standard EN 12341 for PM10 [4].

Chemical characterisation

The PM2.5-loaded filters obtained by the high-volume sampler have been punched in three portions for separate analytical determination of the ionic, carbon and elemental species. Previous analyses of the filter portions have pointed out a distribution rather uniform of the species on the filter surface. The ionic components (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+) have been determined by means of the high pressure liquid chromatography technique (HPLC) after ultrasonic extraction from the filter sample with deionised water. The carbon species, elemental carbon (EC) and organic carbon (OC), have been determined by thermal evolution technique using transmission method (TOT) for correction [5] at the Sunset Laboratory (www.sunset.com). Organic carbon concentration was corrected by a factor of 1.4 in order to

assess the particulate organic matter. Elemental composition was determined by X-Ray Fluorescence (XRF) with SPECTRO X-LAB2000 spectrometer (www.spectro.com), which allows for the simultaneous determination of all elements.

RESULTS

Particles' size distributions have been separately analysed for the warm (April to September) and cold season (October to March), also distinguishing between workdays and weekends. In fact, previous work on fine PM weekly behaviours for the area [6] pointed out that in both seasons the highest concentrations are observed on Wednesdays and that, on average, Sundays' concentration levels are about 25% lower than those of the working days, as a consequence of the reduced circulating traffic volume. Diurnal average number of particles has been computed based on 1-minute data collected during Wednesdays and Sundays in 23 weeks (15 in the cold season, 8 in the warm season). In both seasons particles' size distributions present similar behaviours, with 99.8% of the total number of particles characterised by a diameter smaller than 1 µm and with Sundays' distributions shifted towards lower values compared to Wednesdays'. The difference between the size distributions is more relevant for the larger granulometric cuts, whereas for particles below 0.4 µm the distributions tend to be closer. In the cold season (Figure 1), however, the total number of particles is 40% greater than in the warm period: the increase in the total number of particles mostly derives from a larger presence of the smallest particles (below 0.65 µm) of secondary origin, while for the coarse fractions comparable counts are observed. According to these findings, the reduced traffic circulation on Sundays mainly affects the presence of particles exceeding 0.5 µm of diameter, while it has only a limited influence on the finest size fractions, characterised by a large and diffused background presence, deriving from secondary formation processes in the atmosphere. This is also confirmed by the size distribution observed at the TU site during measurements performed on weekdays, also plotted in Figure 1. Compared to ambient air observation at the UB site, a huge increase in particles' counts is observed, especially in the size range between 0.5 and 5 µm, as a consequence of the primary particulate traffic emissions and of the resuspension of soil dust deriving from traffic flow in the confined volume of the tunnel, whereas below 0.5 µm the particle counts are closer to those measured in the ambient air. Average 24-hour PM10, PM2.5 and PM1 mass concentrations derived from particle counts are reported in Table 1; the corresponding distributions of PM2.5/PM10 and PM1/PM10 mass ratios are represented in Figure 2, in terms of the minimum, mean, maximum value and of the interquartile range, separately for Sundays and Wednesdays of the two seasons. On Sundays, when concentration levels are at their lowest values, the percentage contribution of the finest fractions to PM10 mass is larger than on Wednesdays: in the cold season, on average PM2.5 and PM1 respectively account for 77% and 70% of the total PM10 mass; corresponding figures for the warm season are 59% and 52%. On Wednesdays, all the distributions are shifted towards lower values: PM2.5 contribution to the PM10 mass is about 69% (cold period) and 47% (warm period), while PM1 respectively accounts for 63% and 40%. These highest Sundays' ratios are the result of a larger reduction of coarse particle (PM10–PM2.5) concentration compared to the reduction observed for the finest PM fractions: in fact, while on Sundays the coarse particles' concentration is about 55% less than on Wednesdays, the presence of the finest PM fractions is reduced of about 25% only. As for particles' number, also in terms of mass the reduced traffic circulation on Sundays mainly affects the concentration of the coarse fraction of the fine particulate.

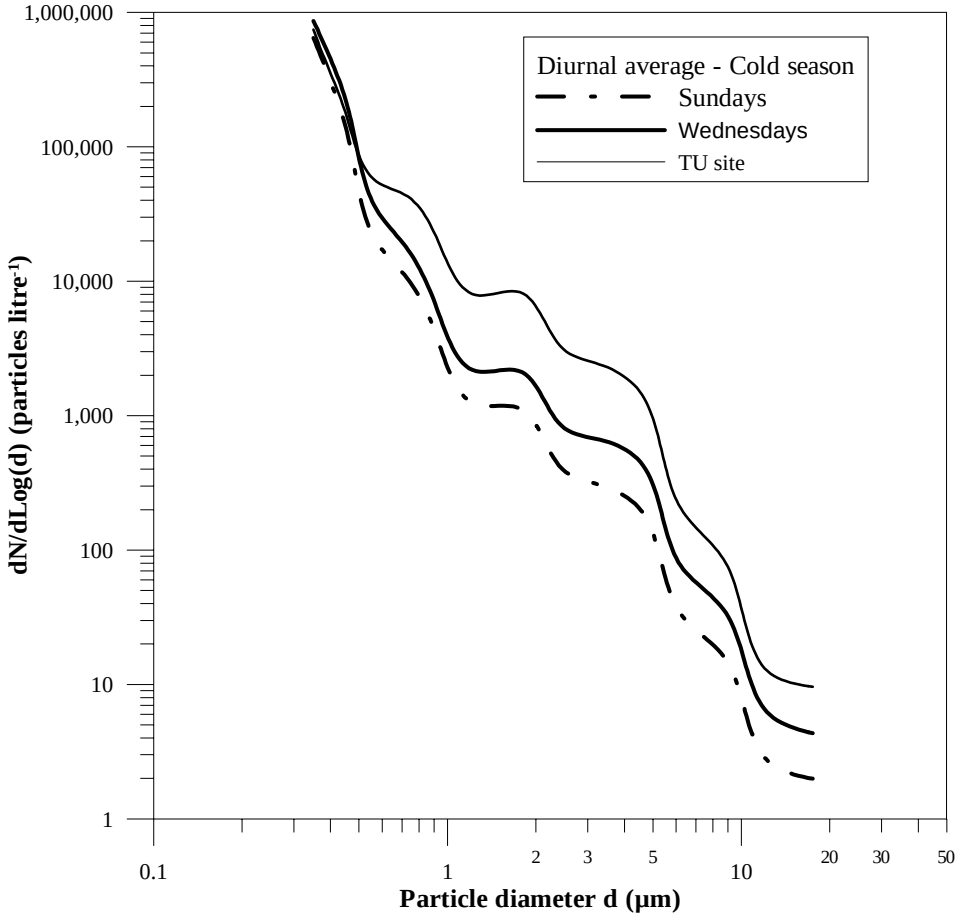

Figure 1 – Particle size distributions: UB site cold period and TU site

PM cut size	Cold season		Warm season	
	Wednesdays	Sundays	Wednesdays	Sundays
PM10	66.0	47.6	54.2	42.1
PM2.5	47.8	37.6	25.3	23.4
PM1	43.9	34.7	21.7	20.6

Table 1 - PM10, PM2.5 and PM1 average daily concentrations (µg m^{-3} @ 20 °C, 101,3 kPa)

Analytical results of the chemical speciation of PM2.5 samples collected at at the UB site (109 samples) and at the TU site (20 samples) are reported in Table 2, in terms of the average mass contribution and mass percentage contribution of the different chemical species. At the UB site, the species analysed account for about the 90% of the total PM2.5 mass regardless to the season, with organic matter largely prevailing and with the secondary component (ionic substances and part of the organic carbon) giving the largest contribution to the total mass. In fact, ionic components as a whole account for about 50% of the PM2.5 mass, with a slight seasonal difference (46.5% in the warm period and 50.3% in the cold period): on average, 26.9 µg m^{-3} (cold semester) and 9.5 µg m^{-3} (warm semester) of the PM2.5 derive from secondary formation, without considering the secondary component of particulate organic matter. The contributions of the primary and secondary PM2.5 source so identified are consistent with the shares estimated by the area emission inventory of primary PM2.5 [7] and

by the ratio of conversion into fine particulate of the precursors (NO_X, SO_2 and NH_3) emitted in the area [8]. As mass contribution is concerned, the seasonal data comparison points out similar average presence of EC in PM2.5 samples: since EC is a tracer of primary emissions, which in the warm season derive only from traffic, this result suggests a reduced contribution of the stationary emissions sources to PM2.5 in the cold season. For all the other chemical species the measured mass is greater in the cold season: a significant mass increase is observed for sulphate and ammonium, respectively about 1.5 and 2.5 times the corresponding quantities for the warm period, while even more relevant increases come out for organic compounds (three times), nitrate (five times) and chloride mass (six times).

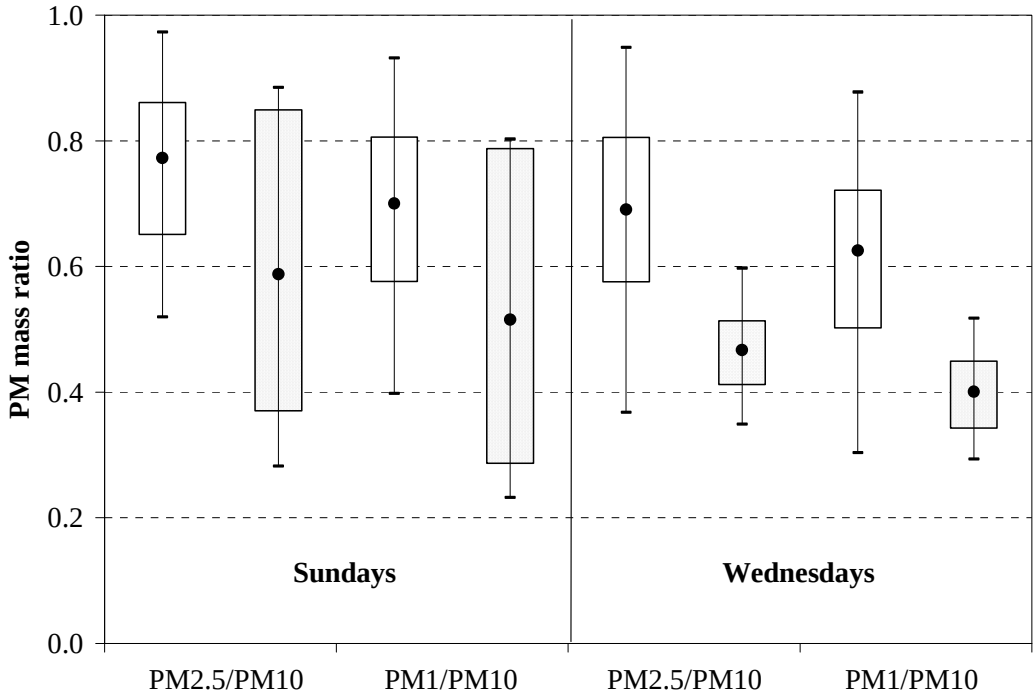

Figure 2 - Distribution of PM mass concentration ratios: mean (black dot), minimum, maximum value and interquartile range (white box for cold season, grey for warm season)

At the TU site, EC and particulate organic matter (both about 70 µg m^{-3}) are largely prevailing over the crustal fraction (47.9 µg m^{-3}), the ionic components, nitrate being the highest ionic contributor with 13.8 µg m^{-3}, and metal oxides (2.8 µg m^{-3}), respectively accounting for 23.4%, 6.7% and 1.4%. While the carbon species are largely higher than those observed at the UB site, the ionic mass presence in the tunnel samples is comparable to the corresponding data observed on annual basis at the UB site. The relevant presence of crustal elements stands for a high resuspension of soil dust deriving from traffic flow in the confined volume of the tunnel. The mass closure points out that the average contribution of the analysed species results in a slight overestimation (5%) of the total PM2.5 mass.

CONCLUSIONS

Concerning the particles' size, the distributions appear quite similar in both seasons, even though in the cold period a larger overall number of particles is observed. The analyses,

focused on the difference between workdays and Sundays, point out size distributions shifted towards lower particles' numbers on Sundays. These findings can be explained by the enhanced strength of the processes leading to the formation of the secondary component (< 1 µm) of atmospheric particulate in winter and by the cut of the coarse fraction due to the reduced emissions and resuspension from traffic flows. Concerning the PM2.5 speciation, the whole secondary component, encompassing ionic substances and part of the organic carbon, accounts for more than 50% of the total mass. Thus, short-term interventions (as occasional traffic restrictions) aimed to control acute episodes of fine particulate pollution appear poorly effective, while long-term actions, suitable for controlling also the precursors of the secondary components of the fine atmospheric particulate, as primary pollutants NO_X, SO_2 and volatile organic compounds, should be undertaken.

Parameter	UB site Cold season		UB site Warm season		UB site Year		Tunnel site	
	µg m^{-3}	*%*	µg m^{-3}	*%*	µg m^{-3}	*%*	µg m^{-3}	*%*
Total mass	53.7	-	20.2	-	32.8	-	204.5	-
Elemental carbon	1.6	*3.1*	1.2	*6.0*	1.4	*4.2*	70.9	*34.6*
Particulate organic matter	18.8	*34.9*	7.1	*35.2*	11.5	*35.1*	66.7	*32.6*
Chloride	0.5	*1.0*	0.1	*0.4*	0.3	*0.8*	1.3	*0.6*
Nitrate	17.1	*31.9*	4.0	*19.6*	9.1	*27.7*	13.8	*6.7*
Sulphate	4.9	*9.2*	3.5	*17.2*	3.9	*11.9*	6.7	*3.3*
Ammonium	4.4	*8.2*	1.9	*9.3*	2.8	*8.6*	4.8	*2.3*
Crustal elements	n.d.	-	n.d.	-	n.d	-	47.9	*23.4*
Metals	n.d.	-	n.d.	-	n.d	-	2.8	*1.4*
Undefined	6.3	*11.7*	2.5	*12.4*	3.8	*11.7*	-	-

Table 2 - Average mass composition of PM2.5 samples (n.d. = not determined)

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