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Mass Concentration and Size-Distribution of Atmospheric Particulate Matter in an Urban Environment

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ABSTRACT

To investigate the ambient mass concentration, size-distribution and temporal variability of atmospheric particulate matter (PM), a long-term monitoring campaign was undertaken at an urban background site in Como, Northern Italy, from May 2015 to March 2016. A 13-stage Low Pressure Impactor (DLPI) was used for the collection of size-segregated particulates in the 0.028–10 μm size range. The results revealed a good level of agreement between DLPI and a co-located Harvard-type $PM_{2.5}$ Impactor, allowing them to be classified as comparable and characterized by a reciprocal predictability. The PM concentration levels varied greatly between the different 5-days monitoring sessions, with higher mean mass concentrations during the heating season. Appreciable seasonal differences were found for particles between 0.15 and 1.60 μm that, on average, registered concentration levels 3.5 times higher during the heating season (mean: 28.2 μg m^{-3}; median: 24.4 μg m^{-3}) compared to the non-heating season (mean: 8.3 μg m^{-3}; median: 7.6 μg m^{-3}). No relevant and significant differences were detected for the coarser ranges (> 1.60 μm). Temporal variabilities were influenced by typical PM urban sources (e.g., household heating, traffic), that significantly affected fine and submicrometer particles, and were related to meteorological factors. Ambient air particles exhibited a trimodal distribution: a first and sharp peak more pronounced during the heating season was identified between 0.3 and 0.5 μm and two other slight peaks in the coarse mode were centered on approximately 3 and 8 μm. No relevant differences were found in the shape of the size-distribution between the two investigated seasons. The mean $PM_{2.5}$ (22.4 μg m^{-3}) and PM_{10} (27.7 μg m^{-3}) concentrations monitored in the study area exceeded the annual Air Quality Guideline Values (respectively equal to 10 μg m^{-3} and 20 μg m^{-3}) established by the World Health Organization.

Keywords: Size-segregated particles; DLPI performance; Temporal variability; Mass size-distribution; Heating and non-heating season.

INTRODUCTION

Numerous epidemiological and toxicological studies have documented strong correlations between measured particulate matter (PM) levels and adverse health outcomes (Erdinger *et al.*, 2005; Schwarze *et al.*, 2006; Brook *et al.*, 2010; Stafoggia *et al.*, 2013; Raaschou-Nielsen *et al.*, 2016). Although current International Guidelines are focused on PM_{10} and $PM_{2.5}$ (WHO, 2006), increasing toxicological and epidemiological evidences have suggested consistent associations between health endpoints and particles characterized by smaller aerodynamic diameters (D*p*) (Ibald-Mulli *et al.*, 2002; Oberdörster *et al.*, 2005; Karakoti *et al.*, 2006; Ostro *et al.*, 2015).

The relationships between PM concentrations, chemical characteristics and the potential hazardous effects on human health are related to the penetration, deposition and clearance of particles into the human respiratory tract (Lippmann *et al.*, 1980). The transfer and deposition in lung airways are in turn dependent mainly on particle size and shape (Donaldson *et al.*, 2002). As extensively documented in the literature (Lippmann *et al.*, 1980; Heyder *et al.*, 1986; Donaldson *et al.*, 2002), particles > 10 μm are only deposited in the extrathoracic region by inertial impaction and they are not able to reach the nonciliated tract of the respiratory system. Particles in the 1–10 μm size range are deposited due to impaction in the extrathoracic and upper bronchial airways, while sedimentation governs their deposition in the lower bronchial and alveolar region. The impaction deposition increases with increasing particle size whereas sedimentation

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is higher around 3 μm. For particles having D*p* between 0.1 μm and 1 μm, the deposition in the conducting airways is generally very small. Indeed, these particles are mainly deposited by gravitational and diffusional transport in the alveolar tract and their total deposition therefore approximates the alveolar deposition. Finally, particles < 0.1 μm deposit by diffusion mainly in the lower bronchial and alveolar region. Their total deposition probability tends to increase with decreasing particle size and these particles are more difficult to be eliminated by mucociliary clearance and physiological leaching mechanisms (Lippmann *et al.*, 1980).

Therefore, information about the size-distribution of airborne PM, from coarse particles to the smallest particulate ranges, represent an important knowledge in terms of health concern. Moreover, unlike PM_{10} or $PM_{2.5}$ for which there are lots of continuous or time-integrated mass data (Ye *et al.*, 2003; Vecchi *et al.*, 2004; Gerasopoulos *et al.*, 2006; Zhao *et al.*, 2009), significantly less is known about the spatial and seasonal variation of size-fractionated particles.

Multistage cascade impactors at low pressure are generally used in this type of studies (Cass *et al.*, 2000; Pakkanen *et al.*, 2001; Fang *et al.*, 2005; Lin *et al.*, 2005; Mbengue *et al.*, 2014) because size cut-points can be reduced at these operating conditions, allowing the additional collection of smaller fractions (Chow and Watson, 2007).

Different researches were carried out in the last decade in the United States (Sardar *et al.*, 2005; Ning *et al.*, 2007; Ntziachristos *et al.*, 2007), Asia (Deshmukh *et al.*, 2012; Fang *et al.*, 2014; Liu *et al.*, 2015) and Europe (Mbengue *et al.*, 2014). In Italy, similar investigations were undertaken in Turin (Malandrino *et al.*, 2016), Genoa (Cuccia *et al.*, 2010) and Rome (Canepari *et al.*, 2008). However, such information is even more scarce and limited at a local scale. Moreover, most of these researches were focused on restricted time periods or low sample numbers, which makes it difficult to estimate seasonal and temporal variations in the mass concentration and size-distribution. Therefore, to improve this knowledge and provide further insights on the topic, a long-term monitoring campaign was performed at an urban background site in Como, Northern Italy.

The aims of this paper are to i) evaluate the performance of a multistage cascade impactor for a typical urban aerosol by comparison with a co-located Harvard-type Impactor; ii) assess ambient mass concentration and size-distribution of atmospheric PM in the 0.028–10 μm size range; iii) assess temporal and seasonal variations; and iv) evaluate the influence of meteorological and environmental conditions on the measured PM concentration levels.

EXPERIMENTAL METHODS

Sampling Area Description and Sampling Strategy

In this study, a long-term monitoring campaign investigating the ambient PM mass concentration and size-distribution in the 0.028–10 μm range was undertaken in the urban area of Como, a medium-sized provincial town (85,000 inhabitants; 873 inhabitants km^{-2}; 97 km^2 of surface area) located in the Lombardy region of Northern Italy.

Data from the Regional Air Emissions Inventory (INEMAR, 2012) showed that the main PM_{10} and $PM_{2.5}$ sources in the study area during the year 2012 were characterized by non-industrial combustion processes (domestic heating, wood combustion in residential structures or commercial activities), followed by road transport (especially from cars and heavy vehicles) and other sources.

The collection site was selected on the basis of the Guidelines for the Air Quality Monitoring Network (EEA, *Criteria for EUROAIRNET*, 1999). According to the Guidelines Criteria, the monitoring location could be considered an URban Background (URB) station used to assess the average urban background concentrations resulting from transport of air pollutants from outside the urban area and from emissions in the city itself, without dominant or prevailing emission sources. Verification of background concentration levels of air pollutants is a key point for the exposure assessment of the general population living in the study area in terms of the representativeness of the average levels of air pollution.

As shown in Fig. 1, atmospheric particulate samples were collected at ground level inside the area of the University of Insubria (coordinates: latitude 45°48′05″N, longitude 9°05′42″E, altitude 214 m above the mean sea level). Residential structures and commercial activities surround the sampling location. Different types of industries (textile, printing, mechanical and wood plants) mainly cover the SW sectors within a radius of approximately 2–30 km. A municipal solid waste incinerator is also located approximately 3.5 km SW of the sampling site (Fig. 1). The two main roads close to the URB location are Via Castelnuovo and Via Valleggio (Fig. 1). Via Castelnuovo is a part of the principal road network of the city and is located at approximately 215 m from the collection site. Via Valleggio is classified as a secondary street with a primary role of distribution and penetration towards the city center, especially from southern locations. It is characterized by a traffic volume of approximately 1,600 vehicles day^{-1} and a speed limit of 50 km h^{-1} and is 25 m from the selected site.

Because of the size, weight and sensitivity of the instrumentation used for particle collection, the sampling equipment was located in a dedicated sampling box, and sampling lines were placed with air inlets at 1.7 m above the ground, which approximately corresponds to the breathing zone of humans. In accordance with the Guidelines Criteria (EEA, *Criteria for EUROAIRNET*, 1999), any type of obstructions, walls or tall trees were not present in the immediate vicinity (< 10 m) of the monitoring devices. The nearest building was located at approximately 25 m from the sampling box.

The duration of the sampling campaign was 10 months in order to integrate different meteorological and environmental conditions that could potentially influence the PM mass concentration and composition in the urban environment. Atmospheric sampling started at the end of May 2015 and was stopped at the end of March 2016 to obtain a large number of samples that could be used to characterize the study area and investigate temporal variations in the measured PM concentration levels. Measurements generally started between 09:00–10:30 on Monday mornings and lasted

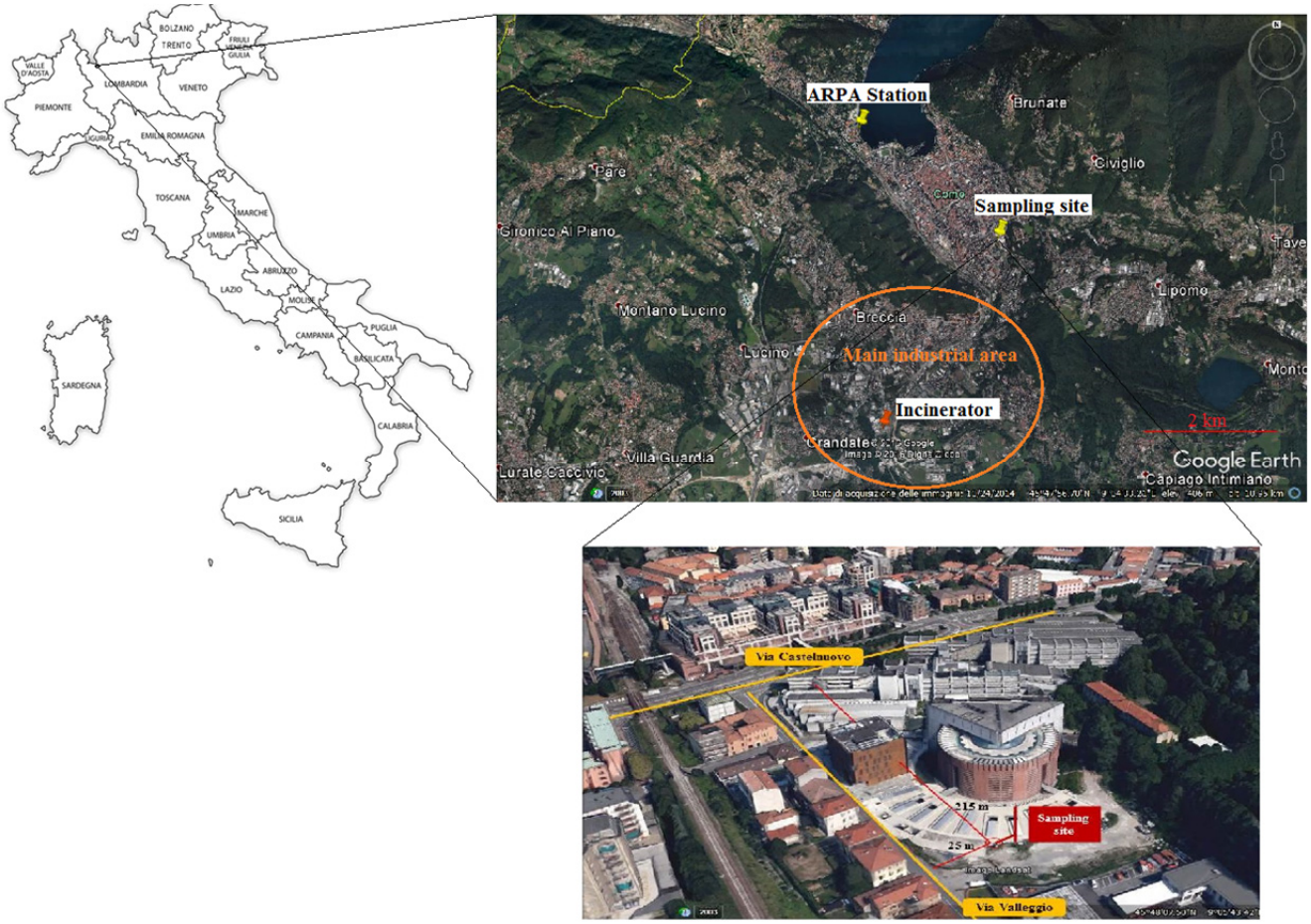

Fig. 1. Sampling site location. The main industrial area (including mainly textile, printing, mechanical and wood plants) and the minimum distances from the nearest streets are shown.

until Friday mornings, using a 96-h sampling duration every sampling week. For convenience, the mean concentrations obtained each sampling week with a sampling period of 96-h will be indicated in the text as 5-days (5-d) mean concentrations.

Sampling Equipment

The sampling equipment consisted of different monitoring devices. A 13-stage Low Pressure Impactor (Dekati Low Pressure Impactor, DLPI, DEKATI Ltd., Tampere, Finland) designed for deposition of particles in the 0.028–10 µm size range according to their aerodynamic diameter (12 real stages plus one stage for separating particles > 10 µm) was used for the collection of size-segregated PM. The nominal values for the equivalent aerodynamic 50% cut-off diameters (D50) of the impactor stages are: 0.0283; 0.0559; 0.0944; 0.157; 0.262; 0.383; 0.614; 0.950; 1.60; 2.40; 4.00; 6.60 and 9.97 µm.

The device operates at a flow rate of 30 L min^{-1} and aerosol particles were deposited on high-purity polycarbonate filters (PC, 25-mm, no-holes; Fisher Scientific, S.A.S., Illkirch, France) coated with a thin layer of Apiezon-L grease (DEKATI DS-515 Collection Substrate Spray, DEKATI Ltd., Tampere, Finland) to improve the impactor collection efficiency and prevent bounce- and blow-off effects during separation.

To evaluate DLPI performance, during 34 of the total 38 5-d samplings, $PM_{2.5}$ was also monitored by a Harvard-type Impactor (HI; MS&T Area Sampler Air Diagnostic and Engineering, Inc., Harrison, ME, USA) (Marple *et al.*, 1987), that was selected in this study as a gold standard for the $PM_{2.5}$ fraction because of its common use in the scientific literature (Cyrys *et al.*, 2001) and its documented agreement with $PM_{2.5}$ Federal Reference Methods (FRMs) (Babich *et al.*, 2000; Yanosky and Maclntosh, 2001). Fine particles were collected on 37-mm, 2.0-µm polytetrafluoro-ethylene filters (PTFE) with polymethylpentene (PMP) support rings (Pall Life Sciences, New York, NY, USA). The particle mass collected on PC and PTFE filters was determined gravimetrically following a standard operating procedure (UNI EN 14907; UNI EN 12341). See the Supplementary Material for detailed information about the weighing procedure.

An external weather station (BABUC-ABC, LSI Lastem, Milan, Italy) was also used to characterize and record on-line meteorological conditions (temperature (T), relative humidity (RH), atmospheric pressure (AtP), wind speed (WS) and wind direction (WD)) during the study period at the sampling site. WS and WD data were measured at a height of 3 m above the street level whereas T, RH and AtP sensors were placed at

a height of 1.5 m. For each parameter, the weather station was programmed with an acquisition rate of 1 min and an elaboration rate of 60 mins. The acquired data points were thus processed every hour using the programmed statistical mode to provide hourly averages, standard deviations, maximum and minimum values, time of maximum and time of minimum.

Rainfall data were obtained by the nearest monitoring station of the Regional Agency for Prevention and Environment (Agenzia Regionale Protezione Ambiente, ARPA) of Lombardy, located approximately 2.5 km NW of the sampling point. Planetary boundary layer (PBL) data related to the sampling location were recovered from the ARPA of Emilia-Romagna.

Statistical Analysis and Data Treatment

Statistical data analysis was performed using the SPSS software package (SPSS Inc., Chicago, IL, USA). For each 5-d sampling session, PM concentration levels were normalized to the specific conditions (T, RH and AtP) monitored at the sampling site.

For data treatment and analysis, results were differentiated into two main periods: the non-heating season (May 2015–October 15th 2015) and the heating season (October 19th 2015–March 2016), as is often performed in studies on atmospheric pollution (Tecer *et al.*, 2008; Schwarz *et al.*, 2012). For convenience, the separation between these periods was made in accordance with the switching on of the household heating systems during October 2015, as programmed by the Regional Directive of Lombardy.

During some of the sampling days, data from the external weather station were not available because of technical problems. In this case, due to the good correlation and the low relative error between BABUC-data and ARPA-data for T ($r = 0.997$, $p < 0.001$; 2.4%) and RH ($r = 0.963$, $p < 0.001$; 11%), hourly T and RH values from ARPA were used at the sampling site. On the contrary, WS was on average 78% lower at the URB location compared with the ARPA monitoring station and the replacement with ARPA-data was not possible.

Descriptive statistics were carried out on size-fractionated PM and meteorological parameters, including histograms of PM fraction contributions. Correlations among variables and differences between DLPI and HI-$PM_{2.5}$ data were assessed by Pearson's correlation coefficients and Paired *t*-test, respectively, on *log*-transformed data since data showed a *log*-normal distribution (Kolmogorov-Smirnov test). The Independent-Samples *t*-test was used to explore differences between groups. Finally, multiple linear regression analysis were performed. In every model, the different DLPI stages were included as dependent variables and the on-situ meteorological (T, RH, AtP, WS and PBL) and environmental (average traffic volume on the closest road) factors as predictors. Only the variables that were found to be statistically significant in bivariate correlation analysis were included in each model. In all tests, a *p*-value lower than 0.05 was considered to be statistically significant.

To assess DLPI performance, DLPI-$PM_{2.5}$ concentrations were compared with the corresponding average levels monitored by HI according to the indications summarized by Watson *et al.* (1998). Briefly, the agreement between the two methods was defined by linear regression analysis between the y-dependent variable (DLPI-$PM_{2.5}$) and the x-independent variable (HI-$PM_{2.5}$). Comparability and predictability were evaluated as a function of slope (1 ± 3 standard error (s.e.)), intercept (0 ± 3 s.e.) and Pearson correlation coefficient (r) (> 0.9). When r is > 0.9 but slope and intercept criteria are not met, the investigated method can be classified as comparable, but only the dependent variable is predictable from the independent variable. Data with $r < 0.9$ are classified as not comparable. In addition, $PM_{2.5}$ samplers were also compared by the Bland-Altman plots method (Altman and Bland, 1983; Bland and Altman, 1986).

WS and WD data were analyzed by using the WRPLOT View™ Software (Lakes Environmental Software, ver.7.0.0).

RESULTS

Sampling Information and Meteorological Conditions

Table S1 summarizes the sampling information (sampling number and sampling period) and the meteorological conditions during the two monitoring seasons.

The study period was characterized by a variety of meteorological conditions. As shown in Table S1, the highest T were reached during the central warm weeks, between July and August, when RH dropped to the lowest summer value (53.5%). The non-heating season was generally characterized by high AtP and high T from the beginning of July. These high T values unfortunately caused problems with the sampling pump operation and the sampling campaign was forcedly interrupted until the normal operating conditions were restored. Rainfall was characterized by sporadic rains that increased from late August.

The heating season began with high atmospheric stability, characterized by low PBL heights, high AtP, low WS and absence of rainfall from the beginning of November until the end of December. The lowest mean T was reached during the third week of January (–0.9°C). Then, T increased and sporadic rain events occurred in February and March.

The sampling site was characterized by generally low WS, with 5-d mean values always < 1 m s^{-1} (Table S1), probably due to the specific sampling location, far from the banks of Lake Como (approximately 1.8 km) and surrounded by moraine hills on the NE sector. The non-heating season was characterized by an average WS of 0.47 m s^{-1}, with hourly averages < 0.5 m s^{-1} for 59% of the cases. The lowest 5-d means were measured during the first half of the heating season (with 83% of hourly values < 0.5 m s^{-1}), whereas the second half registered higher values, also because of the occurrence of Föhn episodes (e.g., sampling n° 34) accompanied by decreased RH and increased T (Table S1). In general, hourly WS during the heating season were < 0.5 m s^{-1} for 75% of the cases and the average intensity was 0.36 m s^{-1}. The WD was predominantly from the S/SE sector during the entire study period and it did not change significantly between the heating and the non-heating season. Also for winds characterized by higher intensities, the prevalent WD was from SE, with some rare events from the

SW sector (Table S1 and Fig. S1). In this context, it is necessary to underline that the area of Como is characterized by a complex topographic scenario. The presence of the lake, moraine conformations and valleys favour the formation of different meteorological conditions in different areas of the city, with great differences (especially for winds) between urban areas close to the banks of the lake and urban areas located further inland. This could be the main reason of the aforementioned difference between ARPA and BABUC wind data. As shown in Fig. 1, the ARPA monitoring station is located on the SW bank of the lake and it is consequently exposed to winds that blow at higher intensities from the NE sector. Contrariwise, the sampling site was located far from the banks of the lake and winds from N/NE were shielded by the moraine hills located in that direction.

Comparison between DLPI and HI-$PM_{2.5}$ Mass Concentration

To assess DLPI performance, DLPI-$PM_{2.5}$ concentrations were compared with the corresponding average levels monitored by HI. The $PM_{2.5}$ levels measured by DLPI were generally lower than those obtained by HI, with statistically significant differences (Paired *t*-test; $p < 0.001$). The 5-d DLPI/HI ratios were mostly below 1 (71% of the cases) and ranged from 0.79 to 1.13 with an overall mean ratio of 0.95 (± 0.08) (Fig. 2).

Agreement between the two sampling methods was first evaluated according to the indications summarized by Watson *et al*. (1998). HI and DLPI-$PM_{2.5}$ concentrations were analyzed by regression analysis of 34 data pairs (Fig. 2). As previously explained, the level of agreement was defined as a function of slope, intercept and Pearson correlation coefficient. In this study, the $PM_{2.5}$ regression line presented slope = 0.906 (s.e. = 0.013), intercept = 0.816 μg m^{-3} (s.e. = 0.406 μg m^{-3}) and r = 0.997 (Fig. 2).

Additionally, to better assess possible error trends, HI and DLPI-$PM_{2.5}$ concentrations were examined using the Bland-Altman plot (Fig. 3). As shown in Fig. 3, the 95% limit of agreement, calculated as the average difference ± 1.96 × standard deviation of the difference, was ± 4.2 μg m^{-3}. The

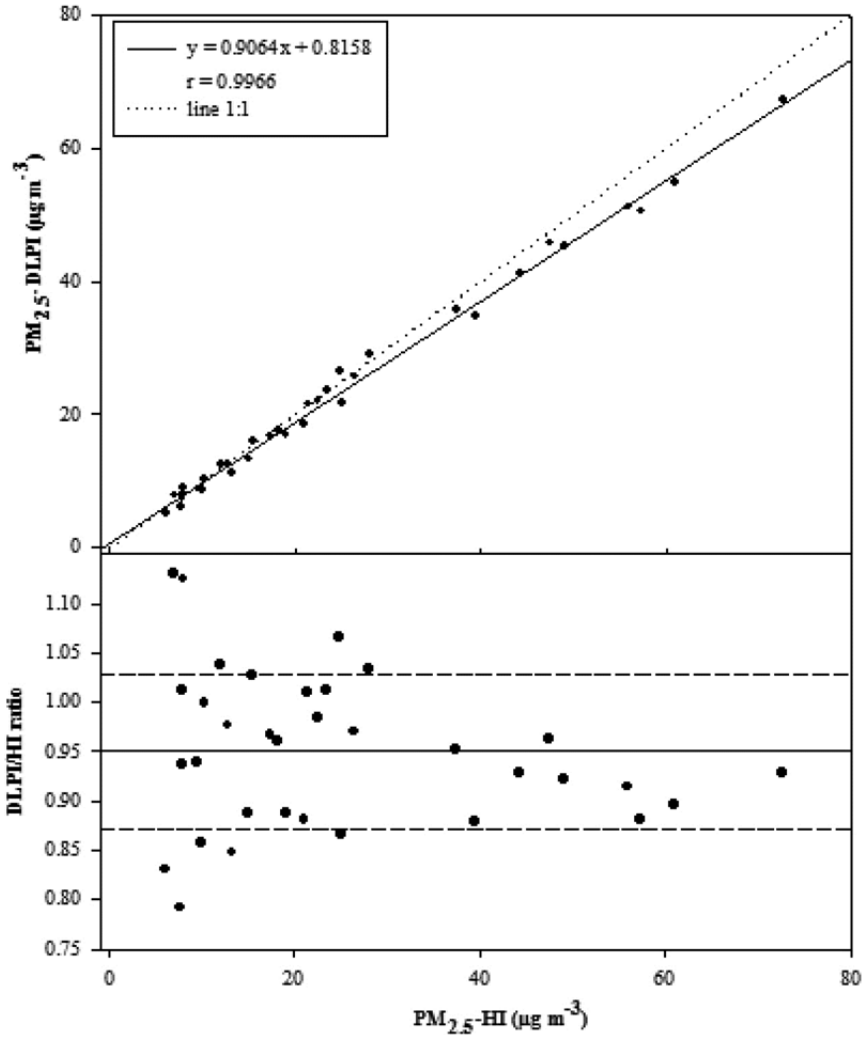

Fig. 2. Linear regression between $PM_{2.5}$ concentrations (n = 34) determined via HI and DLPI. In the bottom panel, the DLPI/HI ratios as a function of $PM_{2.5}$-HI concentrations are shown. The mean ratio and its standard deviation (0.95 ± 0.08) are indicated by the solid and dashed lines, respectively.

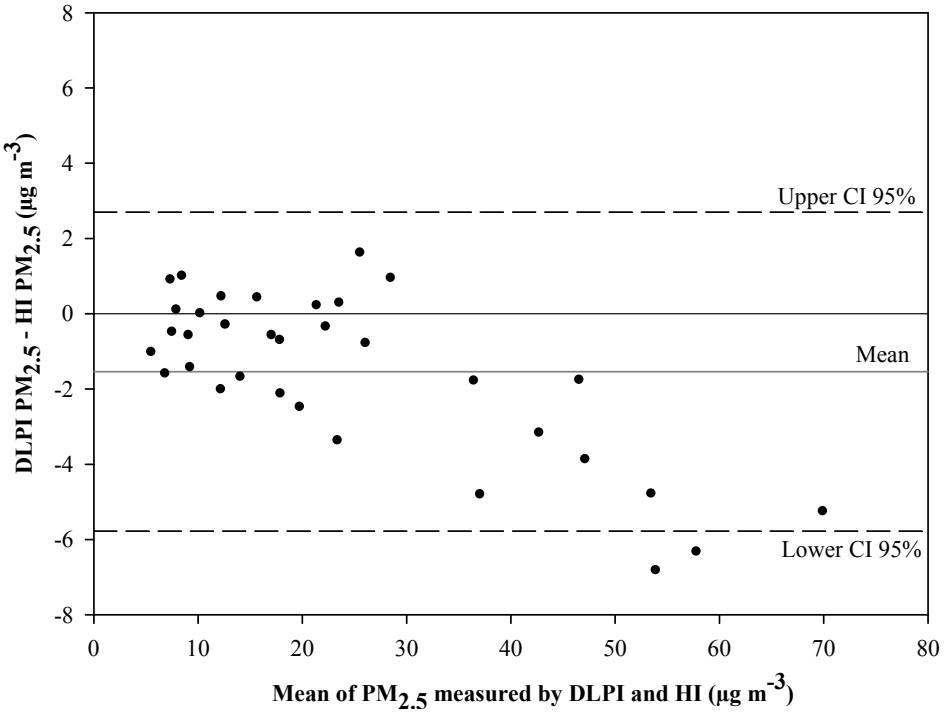

Fig. 3. Comparison of $PM_{2.5}$ sampled with DLPI and HI using the Bland-Altman plot. The solid black line represents the perfect agreement between the two methods, the solid grey line represents the observed average, whereas broken lines correspond to the upper and lower 95% limits of agreement.

maximum difference between single measurements was up to –6.8 µg m^{-3} and the average difference was –1.5 µg m^{-3}. A significant correlation (r = –0.78; $p < 0.001$) was found between $PM_{2.5}$ and DLPI-HI differences, that showed higher (negative) values at the highest concentration levels.

Ambient PM Mass Concentration and Temporal Trends

During the entire campaign, 38 5-d sampling sessions were performed at the URB station in Como and a total of 221 and 273 DLPI samples were collected for the non-heating and the heating season, respectively. Because of the good agreement between DLPI and HI sampling methods (see below), only the DLPI particle mass concentrations were subsequently used for data treatment and analysis.

Descriptive statistics of mass concentrations obtained for each DLPI collection plate and for the principal PM sizes during the two monitoring seasons and the whole campaign are reported in Table 1. For the standard PM fractions, concentration levels were obtained summing up the particulate masses collected on filter substrates, with respect to the aerodynamic diameter of particles (stages 1–12 for PM_{10}; stages 1–9 for $PM_{2.5}$; stages 1–7 for PM_1). DLPI stages 1 and 2 were considered as the ultrafine fraction, because of the absence of a backup filter stage for the collection of particles < 0.028 µm.

A great variability can be observed in the dataset and mean mass concentrations for all size ranges were higher during the heating season, as expected (Table 1 and Fig. S2). Statistically significant differences between the two investigated seasons were found for all DLPI stages (Independent-Samples *t*-test, $p < 0.01$) except for stages 1, 10, 11 and 12, namely for the finest particle fraction ($PM_{0.028–0.055}$) and for the coarse size range ($PM_{2.5–10}$). The greatest increase effect was found for particles whose D*p* was between 0.15 and 1.60 µm (collected on DLPI-stages 4, 5, 6, 7 and 8) that, on average, registered concentration levels 3.5 times higher during the heating season (mean: 28.2 µg m^{-3}; median: 24.4 µg m^{-3}) compared with the non-heating season (mean: 8.3 µg m^{-3}; median: 7.6 µg m^{-3}). For the $PM_{2.5–10}$ fraction, the main differences, although not statistically significant and almost negligible with respect to the finest fractions, were noticed in the 2.4–4.0 and 6.6–9.9 µm size ranges, whereas the ultrafine component showed a significant increase only in $PM_{0.055–0.094}$ (Table 1).

On average, 75% of the PM_{10} mass consisted of $PM_{2.5}$, with a minor contribution of the $PM_{2.5–10}$ fraction (33% and 16% during the non-heating and the heating season, respectively). PM_1 was the major component of $PM_{2.5}$ (83% and 87% during the non-heating and the heating season, respectively), with a primary contribution of the accumulation mode ($PM_{0.1–1}$) during both periods (77% and 84%, respectively). $PM_{0.1–1}$ accounted for more than 50% of the PM_{10} mass and all of the size fractions included in this mode were mutually and significantly correlated (Table S2). Lower correlation coefficients, although statistically significant, were found with coarser particles, especially with $PM_{2.5–10}$. $PM_{0.1}$ played only a minor role in the particulate mass concentration, accounting for 7%, 6% and 4% of PM_1, $PM_{2.5}$ and PM_{10}, respectively, during the non-heating season and for 3.0%, 2.7% and 2.3% in the same PM fractions during the heating season. The contribution of $PM_{0.028–0.055}$ was even lower and less relevant (30.0 %, 2.4%, 1.9% and

Table 1. Descriptive statistics on mass concentrations (μg m^{-3}) for the 12 DLPI-size ranges and for the principal PM fractions during the non-heating season (May 2015–October 15th 2015), the heating season (October 19th 2015–March 2016) and the whole campaign.

DLPI collection plate (particle size range [μm])	Non-heating season (n = 17) Mean ± SD[a] (Median; Min.–Max.)	Heating season (n = 21) Mean ± SD[a] (Median; Min.–Max.)	Total data (n = 38) Mean ± SD[a] (Median; Min.–Max.)	Ratio[b]
1 (0.0283– 0.559)	0.2 ± 0.1 (0.2; 0.1–0.3)	0.2 ± 0.2 (0.2; 0.1–1.2)	0.2 ± 0.2 (0.2; 0.1–1.2)	1.2
2 (0.0559– 0.944)	0.4 ± 0.1 (0.4; 0.3–0.6)	0.6 ± 0.2 (0.6; 0.2–1.0)	0.5 ± 0.2 (0.4; 0.2–1.0)	1.6[c]
3 (0.0944–0.157)	0.7 ± 0.2 (0.7; 0.5–1.2)	1.4 ± 0.5 (1.4; 0.7–2.0)	1.1 ± 0.5 (0.9; 0.5–2.0)	1.9[c]
4 (0.157–0.262)	1.3 ± 0.4 (1.2; 0.6–2.3)	3.9 ± 1.7 (3.8; 1.2–6.8)	2.8 ± 1.8 (2.2; 0.6–6.8)	3.1[c]
5 (0.262–0.383)	2.0 ± 0.8 (2.1; 0.7–3.7)	6.3 ± 3.1 (5.7; 1.6–11.7)	4.4 ± 3.2 (3.4; 0.7–11.7)	3.1[c]
6 (0.383–0.614)	3.0 ± 1.5 (2.6; 0.6–5.6)	10.2 ± 5.6 (8.8; 2.5–24.3)	7.0 ± 5.6 (5.3; 0.6–24.3)	3.4[c]
7 (0.614–0.950)	1.2 ± 0.7 (1.0; 0.4–3.4)	5.1 ± 3.4 (4.0; 0.9–14.3)	3.3 ± 3.2 (2.3; 0.4–14.3)	4.2[c]
8 (0.950–1.60)	0.8 ± 0.4 (0.7; 0.3–1.9)	2.6 ± 1.8 (2.1; 0.5–7.2)	1.8 ± 1.6 (1.1; 0.3–7.2)	3.3[c]
9 (1.60–2.40)	1.0 ± 0.3 (0.9; 0.6–1.6)	1.5 ± 0.7 (1.5; 0.7–2.8)	1.3 ± 0.6 (1.0; 0.6–2.8)	1.6[c]
10 (2.40–4.00)	1.9 ± 0.6 (1.8; 1.1–3.1)	2.2 ± 0.8 (2.1; 1.0–3.6)	2.0 ± 0.7 (2.0; 1.0–3.6)	1.2
11 (4.00–6.60)	1.5 ± 0.3 (1.4; 1.1–2.5)	1.6 ± 0.5 (1.6; 0.7–2.3)	1.6 ± 0.5 (1.6; 0.7–2.5)	1.1
12 (6.60–9.97)	1.5 ± 0.4 (1.5; 0.9–2.4)	1.8 ± 0.5 (1.9; 0.9–2.4)	1.7 ± 0.5 (1.6; 0.9–2.4)	1.2
Particle size fraction				
$PM_{0.028–0.1}$	0.6 ± 0.1 (0.5; 0.3–0.8)	0.8 ± 0.4 (0.7; 0.2–2.1)	0.7 ± 0.3 (0.6; 0.2–2.1)	1.5[c]
$PM_{0.1–1}$	8.3 ± 3.1 (7.7; 3.0–14.2)	27.0 ± 13.3 (22.4; 7.3–56.1)	18.6 ± 13.7 (14.3; 3.0–56.1)	3.3[c]
PM_1	8.8 ± 3.2 (8.5; 3.5–14.9)	27.8 ± 13.6 (23.2; 7.8–57.3)	19.3 ± 14.0 (14.9; 3.5–57.3)	3.2[c]
$PM_{1–2.5}$	1.8 ± 0.5 (1.5; 0.9–3.0)	4.1 ± 2.4 (3.6; 1.2–10.0)	3.1 ± 2.2 (2.2; 0.9–10.0)	2.4[c]
$PM_{2.5}$	10.6 ± 3.4 (10.2; 5.0–16.9)	31.9 ± 15.7 (26.4; 9.0–67.3)	22.4 ± 15.9 (16.8; 5.0–67.3)	3.0[c]
$PM_{2.5–10}$	4.9 ± 1.1 (4.8; 3.4–8.0)	5.6 ± 1.7 (5.6; 2.7–8.2)	5.3 ± 1.5 (5.1; 2.7–8.2)	1.1
PM_{10}	15.5 ± 3.7 (15.5; 8.4–21.4)	37.5 ± 17.0 (31.2; 12.4–75.5)	27.6 ± 16.9 (21.1; 8.4–75.5)	2.4[c]

[a]: standard deviation.
[b]: ratio between the heating and the non-heating average levels.
[c]: significant difference ($p < 0.01$) in heating vs non-heating levels by Independent-Samples *t*-test on *log*-normal parameters.

1.3% for $PM_{0.1}$, PM_1, $PM_{2.5}$ and PM_{10}, respectively, during the non-heating season and 23.1%, 0.8%, 0.7% and 0.6% during the heating season).

The measured levels of outdoor $PM_{2.5}$ and PM_{10} are not strictly comparable with the 1-y WHO Guidelines (WHO, 2006) because of the absence of weekends and some sampling weeks. However, it is reasonable to consider the $PM_{2.5}$ and PM_{10} average concentrations as cautionary surrogates of the annual means in the study area (Table 1). Therefore, considering this assumption, it could be said that the 1-y WHO Guidelines of 10 μg m^{-3} and 20 μg m^{-3} established for $PM_{2.5}$ and PM_{10} were exceeded by approximately 124% and 38.5%, respectively, on average and during the monitoring campaign.

To explain the great variability of size-fractionated PM levels, the influence of local meteorological conditions was analyzed and a bivariate correlation analysis between PM concentrations and meteorological parameters was performed (Table S3).

Significant and negative correlations were found with PBL and WS for most of the DLPI size fractions. T was negatively correlated, especially with particles between 0.055 and 0.95 μm. Negative correlations were also found with rainfall. Finally, positive correlations were found for all size ranges with AtP and, to a lesser extent, with RH (Table S3).

Moreover, despite the relatively low number of samples, the structure of the dataset and the number of independent variables, multiple linear regression analyses were performed, to more deeply investigate the complex relationship between PM concentrations and meteorological and environmental factors that could potentially influence the atmospheric concentration levels. This preliminary analysis found the PBL as the most important predictor of ambient concentrations, at least for particles between 0.094 and 0.95 μm and between 1.6 and 2.4 μm, followed in certain cases by rainfall, that, on the contrary, seemed to be the main determinant for the coarser range ($PM_{6.6–9.9}$) (Table S4).

Particle Mass Size-Distribution

The median mass size-distributions between 0.028 and 10 μm obtained with the multistage impactor during the non-heating and the heating season are depicted in Fig. 4.

During the non-heating season, ambient air particles exhibited a trimodal distribution, with a first peak clearly identified in the accumulation mode between 0.3 and 0.5 μm and two other slight and less-marked peaks centered on approximately 3 and 8 μm in the coarse mode. The accumulation mode-peak greatly increased during the heating season, whereas, at the same time, the two peaks in the coarse range remained roughly unchanged. No relevant differences were found in the shape of the particle size-distribution between the two investigated periods.

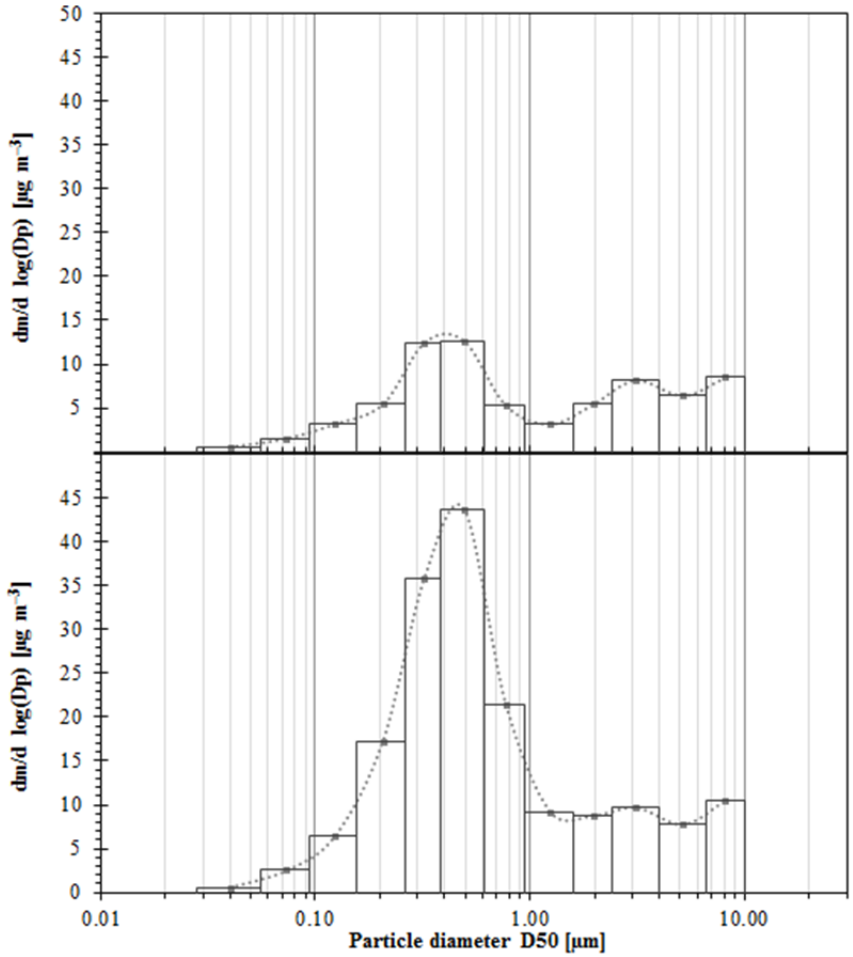

Fig. 4. Median mass size-distributions at the URB station during the non-heating (upper panel) and the heating (lower panel) season for particles between 0.028 and 10 µm.

DISCUSSION

Comparison between DLPI and HI-$PM_{2.5}$ Mass Concentration

To evaluate the performance of the multistage impactor, a comparison between DLPI- and HI-$PM_{2.5}$ mass concentrations was performed. DLPI-$PM_{2.5}$ concentration levels were, on average, lower than those simultaneously monitored by HI, with DLPI-HI disagreements that increased with increasing ambient concentration levels (Fig. 3). If considering the entire data-set, the Bland-Altman plot showed a clear negative trend for concentration levels > 30 µg m^{-3} (Fig. 3). According to the inter-comparison criteria set forth by Watson *et al.* (1998) and based on a first evaluation, DLPI and HI seemed to be classified as comparable, although not characterized by a reciprocal predictability, because of non-compliance with the slope-criterion. The absence of the DLPI backup filter stage could hardly explain the discrepancy with the HI method, because particles less than 0.028 µm are known to have a negligible role in the total PM mass concentration (Tuch *et al.*, 1997). Additionally, the approximation of DLPI-$PM_{2.4}$ to DLPI-$PM_{2.5}$ is equally negligible because the $PM_{2.4–2.5}$ fraction accounted, on average, for 0.8 and 0.5% of PM_{10} during the non-heating and the heating season, respectively. One possible explanation could be the particle deposition effect on the internal impactor walls (particle wall loss) following an excessive loading of filters. As explained by Fujitani *et al.* (2006), this effect is mainly because of particles that rebound from previously collected particulates and may be i) carried away by the air stream on subsequent stages, with a consequent distortion of the mass size-distribution towards smaller mode diameters (not observed in this study, as roughly visible in Fig. 4) or ii) deposited on the impactor's interior walls. The wall loss effect is expected to increase with increasing particle loading on the impactor collection substrates because the magnitude of particle-bounce increases under these conditions. To prevent particle-bounce and ensure the DLPI collection efficiency, a maximum mass per stage of approximately one milligram is recommended by the manufacturer. During some winter sampling weeks this recommended value was exceeded on stages 5, 6 and 7 because of the long sampling time used for particle collection (96-h) and the elevated ambient PM concentrations. Therefore, to evaluate the DLPI performance at the recommended operating conditions, the method comparison was also performed excluding those data that did not respect the manufacturer recommendations (Figs. S3 and

S4). In this case, the regression line presented slope = 0.993 (s.e. = 0.028), intercept = –0.367 μg m^{-3} (s.e. = 0.508 μg m^{-3}) and r = 0.99 (Fig. S3). The 95% limit of agreement was ± 2.1 μg m^{-3}, with an average difference between DLPI and HI equal to –0.5 μg m^{-3} (Fig. S4). These results showed that, on average, the multistage impactor still seemed to slightly underestimate the $PM_{2.5}$ concentrations under the operating conditions provided by the manufacturer, with a mean DLPI/HI ratio of 0.96 ± 0.09 (Fig. S3). Most of the ratio values were around 1 and fell within the considered range of ± 1 standard deviation. The higher relative errors, although acceptable, were found for $PM_{2.5}$ concentrations < 15 μg m^{-3} probably because of an increased difficulty and inaccuracy in the gravimetric determination of impactor stages with very low particles mass loadings. However, the strong correlation (r = 0.991; $p < 0.01$) and the good level of agreement between the two methods allowed them to be classified as comparable and characterized by reciprocal predictability, at least in the $PM_{2.5}$ concentration range under investigation (5–40 μg m^{-3}).

In light of these results, further experiments covering a wider range of ambient concentrations (> 40 μg m^{-3}) are suggested to confirm the impactor predictability and comparability and verify the potential equivalence with EN or EPA Reference Standards.

Ambient PM Mass Concentration, Size-Distribution and Temporal Trends

As was previously mentioned, large temporal differences can be observed in the dataset, with higher mean mass concentrations for all size ranges during the heating season. This behavior was expected and could be mainly explained by a combined effect of meteorological factors, thermodynamic conditions of the atmosphere and variations in type and/or number of emission sources. Other studies close to Como reported strong seasonal variations in the air pollutant levels because of differences in the atmospheric dispersion conditions between summer and winter time (Vecchi *et al.*, 2004).

The most critical scenario was registered at the beginning of the heating season when a sharp increase in the concentration levels was clearly identified (Fig. S2) and maximum levels of 75.5, 67.3 and 57.3 μg m^{-3} were reached for PM_{10}, $PM_{2.5}$ and PM_1, respectively. From the first week of November (20^{th} sample) until the end of December (27^{th} sample), the study area was characterized by extraordinary meteorological conditions (total absence of rainfall, high atmospheric stability and low PBL height; Centro Meteorologico Lombardo, 2016), that promoted the accumulation of air pollutants in the lower atmosphere. Only at the beginning of the last week of November (23^{rd} sample) the high atmospheric stability was interrupted by cold air masses that decreased ambient T and AtP and increased WS and PBL height (Table S1), with a clear reduction in PM concentration levels (Fig. S2), before the previous atmospheric conditions were restored (Centro Meteorologico Lombardo, 2016). The same episode was also registered at the beginning of January (28^{th} sample) and during the last weeks of the heating season, that were characterized by a condition of higher atmospheric dispersion (Table S1).

Bivariate correlation analysis with meteorological factors confirmed the previously mentioned qualitative evaluation. Negative correlations were found with the PBL height, which seemed to more greatly affect the fine particulate fractions (Table S3). Different studies documented that the evolution of the PBL has a significant effect on the concentration levels of air pollutants (Baumbach and Vogt, 2003; Velasco *et al.*, 2008), also because of a positive feedback loop between PBL height and aerosol loadings. As well described by Quan *et al.* (2013), the enhancement of atmospheric aerosol tends to decrease the solar radiation, thus reducing the development of PBL. At the same time, the repressed structure of PBL will in turn decrease the diffusion of surface air pollutants, with a consequent increase of aerosol concentrations at the lowest layers of the atmosphere.

Although the sampling site was characterized by very low WS, often < 0.5 m s^{-1}, the PM concentrations were found to considerably decrease when the WS increased as a result of dilution effects. No obvious relationship was shown for particles ranging from 6.6 to 9.9 μm, probably because of low WS that could not promote the transport and dilution of coarser particles (Kim *et al.*, 1997).

Additionally, T was negatively correlated with PM concentrations. Correlations were statistically significant only for the finest fractions (0.055–0.95 μm), while insignificant associations were showed with particles > 1.6 μm (Table S3). This could be because cold T favor the formation of secondary aerosols in the aerosol particle phase (Putaud *et al.*, 2004) and promote the formation of ultrafine particles (mainly particles > 0.05 μm) (Bukowiecki *et al.*, 2003; Charron and Harrison, 2003). Indeed, it has been shown that the mixing of two air parcels with different temperatures (e.g., the mixing of hot exhaust vapors with cool air) increases significantly the nucleation rates (Nilsson and Kulmala, 1998), with the formation of new particles during the cooling and dilution of the vehicle exhausts (Charron and Harrison, 2003). Ultrafine aged particles can subsequently evolve towards larger size fractions (> 0.1 μm) through condensation and aggregation phenomena which enhanced under these T conditions.

RH was unexpectedly found to positively affect the PM concentration levels. A possible explanation may be that high RH conditions, together with low T and low WS, can promote the formation of lower PBL heights, which hamper the dispersion of air pollutants, as occurred in this study at the beginning of the heating season. Similar findings were showed by Deshmukh *et al.* (2012) and Elminir (2005), that noticed the highest PM_{10} average concentrations at RH values > 80%.

Results from the multiple linear regression analysis have to be interpreted with caution, mainly because of the dataset structure and the low number of samples incorporated in the analysis (n = 25). Among all of the aforementioned meteorological factors, the PBL height seemed to exert the main influence on PM concentrations, which further confirmed the strong correlation found in the bivariate analysis. As already explained, it is known that the seasonal

effect on PM mass concentrations is mainly due to differences in the atmospheric dispersion conditions, mostly related to the atmospheric PBL height. At the same time, the PBL height is in turn dependent on different meteorological factors, including T, RH and WS, that could explain the reason for which these variables disappeared in the multivariate analysis. Furthermore, the effect of PBL seemed to be relevant for smaller particles, whereas the coarser fraction ($PM_{6.6–9.9}$) appeared to be mainly influenced by rainfall (Table S4). In any event, the quality of this evaluation does not permit definitive conclusions and it would be necessary to include more samples to develop a more robust analysis to support and improve these preliminary findings.

Large and statistically significant differences on mass concentration levels were registered for particles having D*p* values between 0.15 and 1.60 μm (Table 1 and Fig. S2), as is also shown in the particle mass size-distribution (Fig. 4), where a first and sharp peak was clearly identified in the accumulation mode between 0.3 and 0.5 μm. Similar findings were found at an urban site in Vienna, where a marked peak was equally identified in the accumulation mode at 0.5 μm (Horvath *et al.*, 1996).

In a typical urban environment, fine, submicrometer and ultrafine particles may partially result from traffic emissions, because of incomplete combustion processes of gasoline, diesel and other fuels (Knibbs and Morawska, 2012). Although the monitoring location was not a traffic sampling site close to a heavily traffic road, positive correlations were found between the average traffic volume on the closest trafficked road (via Valleggio) and particles ranging from 0.055 to 0.95 μm ($r = 0.5$; $p < 0.05$).

The large and marked peak registered in the accumulation mode may be associated with a combined influence of the aforementioned emission source together with household heating emissions that led to a sharp growth of the peak during the heating season when the heating system was switched on and the traffic intensity increased. Indeed, as explained by Vecchi *et al.* (2004), domestic heating is an additional source for particles < 1 μm and it contributes to primary PM as well as secondary aerosol because of its high emissions of gaseous precursors during winter time.

On the other hand, traffic related re-suspension phenomena, soil re-suspension phenomena and the presence of industrial activities, such as the mechanical and wood plants upwind of the sampling site, may have led to the formation of larger particles, that could otherwise explain the presence of peaks in the coarse mode fraction (Fig. 4). Mbengue *et al.* (2014) identified a bimodal distribution for an urban-traffic site, with peaks centered on 0.5 and 2.5 μm, whereas a trimodal distribution with a third maximum at 8 μm was only observed downwind of industrial emissions. Also Tecer *et al.* (2008) attributed the most important anthropogenic $PM_{2.5–10}$ sources to the coal processing and mining industries located close and upwind to the sampling location.

Comparison of Ambient PM Concentrations with Literature Data

For a comparison of our findings with the scientific literature, it must be noticed that the PM concentration levels shown in this study are not always strictly comparable with other similar investigations carried out in Europe and all over the world. Indeed, these researches are often performed at different sampling sites (under urban, traffic or industrial influences), that could determine different PM concentration levels because of different distances from various emission sources. Moreover, the comparability between other studies might be hampered and impaired because of differences in sampling periods, collection intervals and type of monitoring devices used, which may be characterized by different particle cut-off diameters. Only one survey was recently carried out in the Como urban area (Spinazzè *et al.*, 2015). In the aforementioned study, the quasi-ultrafine particles (QUFPs, referred as $PM_{0.25}$) mass concentrations were measured in different urban microenvironments along a fixed route. The results found in our survey at the URB station for $PM_{0.26}$ (2.6 ± 0.6 and 6.1 ± 2.4 μg m^{-3} during the non-heating and the heating season, respectively) were from 2 to 3 times lower than the corresponding $PM_{0.25}$ concentrations measured along urban traffic routes by Spinazzè *et al.* (2015), mainly because of the specific monitoring protocol that was properly designed to include road and transit microenvironments.

The $PM_{0.1}$ annual average shown in our survey can be compared with the average concentration of 0.5 μg m^{-3} found between April 1996 and June 1997 at an urban and rural site in Helsinki (Pakkanen *et al.*, 2001), whereas the heating mean of 0.8 μg m^{-3} is in line with the winter urban levels found in the past in Pasadena (Hughes *et al.*, 1998). Lower concentration levels were found by Ntziachristos *et al.* (2007) during winter/spring time for PM_{10}, $PM_{2.5}$ and $PM_{0.18}$ at an urban sampling site in Los Angeles and by Mbengue *et al.* (2014) for winter levels of PM_{10}, PM_1 and QUFPs both at an industrial and an urban-traffic sector in Northern France. Comparable values were shown by Sardar *et al.* (2005) for an urban mix of industrial and traffic sources in Los Angeles. In the investigation carried out by Salma *et al.* (2005), higher median PM_{10} and $PM_{2.0}$ values (50 and 20 μg m^{-3}, respectively) were found between April and May 2002 at a kerbside compared to our median concentrations monitored during the non-heating season (15.5 and 10.2 μg m^{-3} for PM_{10} and $PM_{2.5}$, respectively). Ramgolam *et al.* (2008) found in Paris PM_{10} concentration values typically observed at European urban background sites.

On the contrary, research studies carried out in some Asian countries showed, as expected, generally higher concentration levels than those measured in this study. Gugamsetty *et al.* (2012) registered summer/fall PM_{10}, $PM_{2.5}$ and $PM_{0.1}$ average concentrations more than two times higher than our non-heating results at an urban area under industrial and traffic influence in New Taipei City. The winter $PM_{0.1}$ mean level reported by Lin *et al.* (2005) for a traffic site in Taiwan was two orders of magnitude higher than our value of 0.8 μg m^{-3}. However, in this case it must be noticed that UFPs emitted from motor vehicles were more efficiently collected because the sampling site was a near-ground sampling (0.6 m above the road surface) close to the intersection of a major road with a high vehicle flow per day (approximately 72,000 vehicles day^{-1}). Moreover, Liu

et al. (2015) found relatively high concentrations, with the dominant fraction in the size range < 2.1 μm, that accounted for almost 60% of the total PM mass. Similar findings were also obtained by Duarte *et al.* (2008) and Gnauk *et al.* (2008). Only Chen *et al.* (2013) reported lower PM_{10}, $PM_{2.5}$ and $PM_{0.1}$ concentrations for a rural background station in East Asia. See Table S5 for detailed information about the PM mass concentration values reported in the previously mentioned studies.

Strengths and Limitations of the Study

One of the main limitations of this study is the long sampling period used for particle collection (approximately 96-h per week) that did not allow the identification of day-to-day or daytime-to-nighttime variability. Nonetheless, this choice was motivated by the possibility of obtaining sufficient material at each DLPI collection stage for trace element analysis. A pilot study on test samples confirmed the need for a sampling interval of 96-h for chemical characterization purposes.

Weekend days and the months of April and May were not included in the sampling protocol, mainly because of technical and/or logistical problems. Therefore, the average PM concentration levels were not expected to provide an accurate evaluation of the annual mean in the study area.

Finally, the experimental design was carried out at one urban sampling site, which did not permit the assessment of possible spatial variations in the monitored area. Moreover, because of the complex topographic scenario previously described, the meteorological conditions monitored at the URB station were representative of the sampling site but how large may be the actual area of representativeness could not be accurately defined.

Despite these limitations, this study has important strengths. To our knowledge, this is one of the first investigations in which a reasonable number of size-segregated samples were collected by a long-term monitoring campaign. Indeed, in these types of studies where multistage cascade impactors at low pressure are used, the monitoring protocol is often limited to one season (Hughes *et al.*, 1998; Lin *et al.*, 2005; Fang *et al.*, 2014), or few weeks per site (Sardar *et al.*, 2005) or per season (Chen *et al.*, 2013; Malandrino *et al.*, 2016), or one week per month (Pakkanen *et al.*, 2001). Sometimes, multistage impactors such as DLPI or nano-MOUDI are only used once during the entire sampling campaign (Canepari *et al.*, 2008; Mbengue *et al.*, 2014), likely due to their laborious and time-consuming management. Moreover, in some studies the mass concentration and size-distribution of the lowest particle fractions (e.g., UFPs) are obtained by integration of optical analyzer data using an assumed particle density (Hughes *et al.*, 1998), which could result in loss of accuracy.

In the present investigation, size-fractionated samples were collected every week for 10 consecutive months, unless there were technical or instrumental problems. Obtained findings were used to better characterize the study area in terms of: i) temporal variability; ii) identification of significant differences between, at least, the two selected seasonal periods for each of the 12 size ranges of PM_{10}; and iii) discrimination between meteorological factors that really affect PM concentration levels, although more robust statistical analysis will be needed to better confirm our findings.

Moreover, the collected DLPI and HI paired data allowed the evaluation of DLPI performance for $PM_{2.5}$ that, to our knowledge, has never been assessed before on this type of multistage low pressure impactor.

Finally, DLPI stages 1–9 are currently being analyzed for some potentially toxic trace metals (data not presented in this paper) to: i) assess their concentrations and size-distributions; ii) evaluate their potential risk for human health; and iii) evaluate the influence of in-situ meteorological conditions on the measured concentration levels. Moreover, data received from chemical analysis will gain further insights and contribute to the identification of possible emission sources in the study area.

CONCLUSIONS

In this study, the ambient PM mass concentrations and size-distributions in the range of 0.028–10 μm were assessed at an urban background site during a long-term investigation. Temporal variations, from ultrafine to coarse particles, were shown. As expected, the highest PM concentration levels were found during the heating season because of a joint effect of meteorological factors and variations in type and/or number of emission sources. One of the most interesting findings of this study is that the greatest increasing effect was registered on particles having D*p* values between 0.15 and 1.60 μm (and mainly for particles having D*p* values between 0.4 and 0.9 μm), which are more related to the presence of additional sources of submicrometer particles during winter time. No relevant and significant differences were found for particles > 1.60 μm. The average $PM_{2.5}$ and PM_{10} values measured in the study area suggested that during the monitoring campaign the general population living in the area may have been exposed to PM levels potentially harmful for human health, mainly because of the high concentrations of fine particles reached at the beginning of the heating season.

Results obtained from this investigation could be used as a valid support in epidemiological studies, as an innovative and alternative target with respect to the typical PM fractions on which these types of research are generally focused (PM_{10} or $PM_{2.5}$). Because of the type of sampling site used for particle collection (URB) and the extended time series of size-segregated particle mass concentrations, these data could be used to better assess if the known and documented PM effects exerted on the general population (e.g., increased mortality or morbidity) could be related to specific size fractions of $PM_{2.5}$ and if these effects are really greater than or independent from the effects induced by larger size particulates.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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