**CHEMICAL ENGINEERING TRANSACTIONS**, Volume 16, 2008
Guest Editor Eliseo Ranzi
 ISBN 978-88-95608-03-7 ISSN 1974-9791


# Number concentrations of nano-, ultrafine and fine particles in Milan

Lonati G.[1], Crippa M.[1], Ozgen S.[1], Gianelle V.[2]
[1]DIIAR Environmental section, Politecnico di Milano; [2] ARPA Lombardia
[1]P.zza L. da Vinci, 32 – Milano; [2] Viale Restelli, 3/1 – Milano

This work analyses seasonal weekly and daily pattern of particles' number concentrations measured at an urban background site in Milan by means of a Differential Mobility Particle Sizer (DMPS) and of an Optical Particle Counter (OPC). The investigated size range for particles' number concentration is within 10 nm - 20000 nm, but the main focus of the work is on the submicron size range, where almost 100% of the particles fall. The daily pattern of total particle (TP) number concentrations and those of the relative contribution given by nanoparticles (NP, diameter less than 50 nm), ultrafine (UFP, diameter less than 100 nm) and submicron particles (SMP, range 100-1000 nm) are interpreted to identify the role of the emission sources and of the main atmospheric processes and factors related with the dispersion of atmospheric pollutants.

## 1. Introduction

Though it is not completely clear which fraction of particulate matter (PM) is responsible for the observed adverse effects on human health, the association between ambient PM and both respiratory and cardiovascular disorder has been long recognized (Dockery & Pope, 1994; Pope, 2000). Health-related concerns recently focused on ultrafine particles (UFP) and on nanoparticles (NP), based on the hypothesis that they might be most toxic (Oberdorster, 2001). Whereas a general agreement about the definition of UFP and NP has still to be reached, the atmospheric science community adopts these terms for indicating particles with diameter $D_p$ less than 100 nm and less than 50 nm, respectively. Epidemiological studies show that UFPs can deposit in the lungs or penetrate into the interstitial sites and access blood circulatory system, moving from the lungs to other organs, thus producing pathologies in organs not directly exposed (Wichmann et al., 2000). Toxicological studies also indicate that UFPs are more potent than larger particles in inducing cellular damage. Despite the still small number of studies and though it is still controversial whether the stronger health effects are related to UFPs or to larger submicron particles (Osunsanya et al., 2001), suggestions are that the exposure to UFPs is associated with both respiratory and cardiovascular effects and that fine and ultrafine particles are responsible for comparable and independent health effects. However, according to World Health Organization the body of epidemiological evidence is currently not sufficient in order to provide guideline concentrations for UFP (WHO, 2006). In ambient air UFPs are present in very high numbers, on average in the order of $10^4$-$10^5$ particles $cm^{-3}$ in urban

Please cite this article as: Lonati G., Crippa M., Ozgen S. and Gianelle V., (2008), Number concentrations of nano-, ultrafine and fine particles in milan, Chemical Engineering Transactions, 16, 105-112

areas, but contribute to the overall PM mass by only a few percents. Therefore, UFPs concentration is usually expressed as number concentration, with additional information provided by the size distribution of the particles. UFPs are both of primary and of secondary origin, associated with both nucleation events caused by the dilution and cooling of exhaust combustion gases in the atmosphere and with chemical-physical transformations and reactions involving gaseous precursors. In urban areas day-time concentration levels are influenced by vehicles' exhaust emissions, by photochemical nucleation and evaporation of semivolatile compounds from the particles' surface; at night-time the main factors influencing concentration levels are physical processes, such as coagulation and condensation of semivolatile species onto existing particles.
In this work NPs, UFPs and fine particles' number concentration levels observed at an urban background site in Milan are presented. Concentrations levels are analyzed both on a seasonal basis (cold and warm season) and on a weekly basis, comparing weekends' (Saturdays and Sundays) to weekdays' concentrations. Moreover, daily patterns for particles' concentrations are evaluated and interpreted in the light of the daily patterns of the emission sources and of the evolution of the main factors affecting the dispersion of atmospheric pollutants.

## 2. Materials and Methods

Monitoring campaigns of particle number concentration were performed from November 2003 to August 2004 at a monitoring site in downtown Milan. The monitoring site, located in a walled yard in a residential area far from major roads, is not directly exposed to traffic emissions and can be considered as an urban background site representative of the urban environment. In order to capture concentration data simultaneously at the smaller and larger tails of the particle size distribution (from 10 nm up to 20000 nm) a Differential Mobility Particle Sizer (DMPS) and an Optical Particle Counter (OPC) have been used during monitoring campaigns; the whole dataset of concurrent measurements with both instruments consists of the 1-hour averaged particles' number concentrations in 45 size bins between 10-20000 nm for 29 cold season days (November to March) and 22 warm season days (April to August). The DMPS is formed by a Differential Mobility Analyzer (DMA - TSI model 3071), that classifies particles according to their electrical mobility (Hinds, 1999), followed by a Condensation Particle Counter (CPC - TSI model 3022) that counts the number of size-classified particles, since they are grown to optically detectable size by condensing n-butanol vapour on them (Stolzenburg & McMurry, 1991). Based on data recorded at 6 minutes time resolution, 1-h average particles' number concentrations have been calculated for 35 size bins between 10 nm and 800 nm. The OPC (Grimm Model 1107) measures particles' number concentrations for 15 size bins within the 300-20000 nm range at 1 minute time resolution by means of laser light-scattering technology for single-particle counts. The scattered signal from the particle passing through the laser beam is collected by a mirror, transferred to a recipient photo diode and passed thorough a multi-channel signal analyser for particle classification in the corresponding size range. Though based on different measurement principles the two instruments provide comparable and correlated data, as resulting from the data comparison in the overlapping range of measure (300–800 nm). However, for this latter range DMPS

concentrations have been considered for the following reasons: i) the greater measurement resolution of this instrument in this dimensional range; ii) the greater uniformity and continuity given to the dataset since the most of particles number is included in the size spectrum below 1000 nm.

## 3. Results and discussion

### 3.1 Concentration levels

Summary statistics for the distribution of 24-hour average weekdays concentration for total (TP), nano (NP), ultrafine (UFP) and submicron (SMP) particles are reported in Table 1. In both seasons TP number concentrations are in the orders of $10^4$ $cm^{-3}$, in agreement with data reported in literature for urban areas. Cold season's concentration range is within 1.1-4.4·$10^4$ $cm^{-3}$, with an average of 2.57·$10^4$ $cm^{-3}$, whereas warm season's range is 1.4-1.6·$10^4$ $cm^{-3}$, with an average of 1.51·$10^4$ $cm^{-3}$ statistically lower ($\alpha$ = 5% significance level) than in the cold season. NPs and UFPs average concentrations are respectively 1.31·$10^4$ $cm^{-3}$ (range: 0.5-2.5·$10^4$ $cm^{-3}$) and 1.99·$10^4$ $cm^{-3}$ (range: 0.8-3.4·$10^4$ $cm^{-3}$) in the cold season; corresponding figures for the warm season are 0.73·$10^4$ $cm^{-3}$ (range: 0.6-0.8·$10^4$ $cm^{-3}$) and 1.21·$10^4$ $cm^{-3}$ (range: 1.1-1.3·$10^4$ $cm^{-3}$). SMPs average levels are 5.8·$10^3$ $cm^{-3}$ (range: 2.6-11.9·$10^3$ $cm^{-3}$) and 3.0·$10^3$ $cm^{-3}$ (range: 2.1-3.4·$10^3$ $cm^{-3}$) in the cold and warm season, respectively. In both seasons number concentrations of supermicron fine particles (1000-2500 nm range) are 3 orders of magnitude lower than those of SMPs, with average values of only a few particles $cm^{-3}$ resulting in a negligible contribution to TP number (less than 0.005%). Relative contributions of NPs, UFPs and SMPs to TP concentration are almost insensitive to the season: NPs, UFPs and SMPs respectively account for 51±11%, 77±9% and 23±9% (average±standard deviation) of TP in the cold season and for 50±9%, 78±6% and 21±6% in the warm season. For all the 4 size fractions warm season's 24-h concentrations data are very concentrated around the respective averages, whilst cold season's data display a large scatter: coefficient of variation (CV) values (std. deviation to average ratio) are in the order of 0.08 and of 0.40 for the warm and cold season, respectively; in both seasons, however, SMPs are characterised by a slightly larger scatter (CV = 0.13 and CV = 0.49), compared to NPs and UFPs. Seasonal comparison of daily average concentrations points out that warm season's values are significantly lower than those of the cold season: 44% less for NP, 39% less for UFP, 48% less for SMP and 41% less for TP. The higher cold season's concentrations are a consequence of the stronger emissions (space heating joins to traffic emissions in winter) and of the different evolution of the boundary layer. In fact, during summer the boundary layer is higher than in winter because of the convective turbulence induced by the solar radiation, resulting in more effective vertical dilution of the pollutants. Besides, the highest values of particle concentration levels observed in Milan can be related with the great atmospheric stability typical in Milan area in the cold season, which prevents their dilution causing atmospheric pollutants stagnation and concentration build-up.

Seasonal comparison between weekdays' and weekends' (Saturdays and Sundays) daily average concentrations is represented in Figure 1 for TP and the 3 size fractions considered. As already observed for weekdays, both Saturdays' and Sundays' cold

season concentrations are higher than those of the warm season, though it is not possible to provide statistical strength to the observed seasonal, due to the limited dataset.

Table 1 - Summary statistics for weekdays' 24-hour average number concentration ($10^3$ $cm^{-3}$) of nano (NP), ultrafine (UFP), submicron (SMP) and total (TP) particles.

| Parameter | Cold season (24 days) | | | | Warm season (16 days) | | | |
|---|---|---|---|---|---|---|---|---|
| | NP | UFP | SMP | TP | NP | UFP | SMP | TP |
| Average | 13,1 | 19,9 | 5,8 | 25,7 | 7,3 | 12,1 | 3,0 | 15,1 |
| Standard Deviation | 5,0 | 7,3 | 2,8 | 9,3 | 0,6 | 0,8 | 0,4 | 0,7 |
| Minimum | 5,1 | 8,2 | 2,6 | 11,4 | 6,2 | 10,7 | 2,1 | 14,1 |
| Maximum | 25,2 | 35,0 | 12,0 | 44,0 | 7,9 | 13,0 | 3,4 | 16,0 |
| 1st quartile | 9,7 | 14,4 | 4,0 | 18,9 | 6,7 | 11,4 | 2,8 | 14,5 |
| Median | 12,8 | 18,1 | 4,6 | 22,8 | 7,5 | 12,4 | 3,2 | 15,2 |
| 3rd quartile | 15,4 | 24,8 | 7,3 | 34,0 | 7,8 | 12,9 | 3,3 | 15,8 |
| 5th percentile | 8,1 | 11,7 | 2,6 | 14,4 | 6,3 | 10,8 | 2,3 | 14,2 |
| 95th percentile | 23,9 | 33,9 | 11,4 | 39,6 | 7,9 | 13,0 | 3,4 | 16,0 |

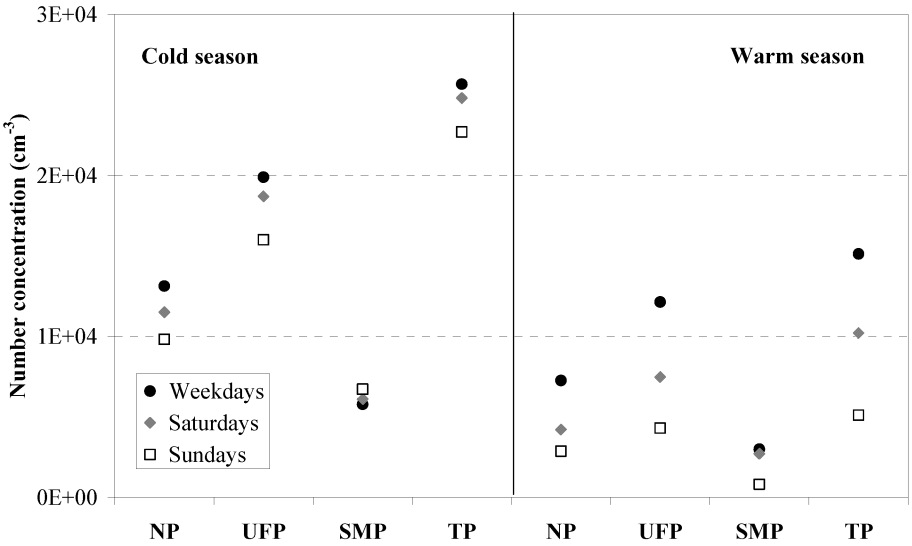


Figure 1 – Weekdays' and weekends' daily average number concentrations of TP, NP, UFP, and SMP in Milan.

In the cold season concentration levels show a slight decrease already observed on Saturdays then leading to the lowest weekly levels recorded on Sundays. Sunday' traffic in Milan is roughly estimated 30% less than on weekdays since commuters and duty vehicles are not circulating. Saturdays' and Sundays' average TP, NP, UFP and SMP concentrations are $2.48 \cdot 10^4$ $cm^{-3}$, $1.15 \cdot 10^4$ $cm^{-3}$, $1.87 \cdot 10^4$ $cm^{-3}$ and $6.1 \cdot 10^3$, and $2.27 \cdot 10^4$ $cm^{-3}$, $9.8 \cdot 10^3$ $cm^{-3}$, $1.6 \cdot 10^4$ $cm^{-3}$ and $6.7 \cdot 10^3$. Compared to weekdays, Saturdays' and Sundays' TP concentration are only 3.4% and 11.6% less, resulting from actual

reductions for NP and UFP concentration (12.4% and 6.0% on Saturdays, 25.2% and 19.6% on Sundays) and an increase for SMP concentration (5.6% and 16.3%, respectively). In the warm season, the observed decrease of concentration levels on weekends is more striking: Saturdays' average concentrations are $1.02 \cdot 10^4$ $cm^{-3}$, $4.2 \cdot 10^3$ $cm^{-3}$, $7.5 \cdot 10^3$ $cm^{-3}$ and $2.7 \cdot 10^3$ $cm^{-3}$ and Sundays' average concentrations are $5.1 \cdot 10^3$ $cm^{-3}$, $2.9 \cdot 10^3$ $cm^{-3}$, $4.3 \cdot 10^3$ $cm^{-3}$ and $0.8 \cdot 10^3$ $cm^{-3}$ for TP, NP, UFP and SMP, respectively. Compared to weekdays, the reduction of TP concentration is 32.6% on Saturdays and 66.2% on Sundays, both resulting from large actual reductions of NP (42.0% and 60.5%), UFP (38.5% and 64.6%) and SMP (9.3% and 72.9%). Though weekends' concentration levels are lower than weekdays' levels, relative contributions of the 3 size fractions to TP concentrations observed on Saturdays and Sundays are comparable with the weekdays' ones, except for NP, whose average contribution (around 47%) is a few percentage points lower than on weekdays.

**3.2 Daily patterns**

Seasonal daily patterns of weekdays' TP, NP, UFP and SMP concentration are plotted in Figure 2 and 3 for the cold and warm season, respectively. The patterns' structure is rather similar for the four size fractions in both seasons, with two main peaks tuned with the morning and evening traffic rush hours and the lowest concentrations observed during the late night hours. In the warm season, however, the evening peak tends to be delayed and concentrations are relevant also in the early night hours. In the cold season average levels of 1-hour TP concentration are within the $1.1\text{-}4.4 \cdot 10^4$ $cm^{-3}$ range, with an average 1h-peak to daily average ratio of 1.71. The highest TP concentrations observed during the morning rush hour (8-9 AM, average: $4.35 \cdot 10^4$ $cm^{-3}$) are significantly greater than in the rest of the day; moreover, in these hours extreme concentration values in the order of $8\text{-}9 \cdot 10^4$ $cm^{-3}$ are also observed ($95^{th}$ percentile: $8.2 \cdot 10^4$ $cm^{-3}$). On the evening rush hour (6-8 PM) TP concentrations are lower than in the morning (average: $2.85 \cdot 10^4$ $cm^{-3}$) but values as high as $5.7 \cdot 10^4$ $cm^{-3}$ can still be observed ($95^{th}$ percentile: $5.1 \cdot 10^4$ $cm^{-3}$). In the warm season average 1-hour TP concentrations are in the range of $1.4\text{-}1.6 \cdot 10^4$ $cm^{-3}$, with a peak to daily average ratio of 1.1. As for the cold season, during the morning rush hour TP concentrations are significantly higher than in the rest of the day, but the average concentration ($2.09 \cdot 10^4$ $cm^{-3}$) and the extreme values ($95^{th}$ percentile: $3.3 \cdot 10^4$ $cm^{-3}$; maximum $5.2 \cdot 10^4$ $cm^{-3}$) are about half the corresponding cold season's levels. The evening peak is always characterised by TP concentrations lower than in the morning (average: $1.99 \cdot 10^4$ $cm^{-3}$, $95^{th}$ percentile: $2.6 \cdot 10^4$ $cm^{-3}$); TP concentration of this evening peak is about 70% of the cold season's one and is observed a couple of hours later (9-11 PM). Traffic emissions not only affect TP concentrations levels but also the size distribution of the particles, as shown in Figure 4, where the daily patterns of the average relative contribution to TP number concentration for size-segregated particles are plotted. In both seasons on day-time hours NP and UFP relative contributions to TP are around 50% and 80% respectively, but their daily patterns display different seasonal behaviours. For the cold season maximum contribution of NPs (about 57%) and UFPs (about 82%) to TPs are registered early in the morning (at 8-9 AM) resulting from a progressive increase from their minimum values (42%-68%) observed around 4-5 AM. These increases become particularly sharp in correspondence of the beginning of weekdays' traffic circulation (6-7 AM).

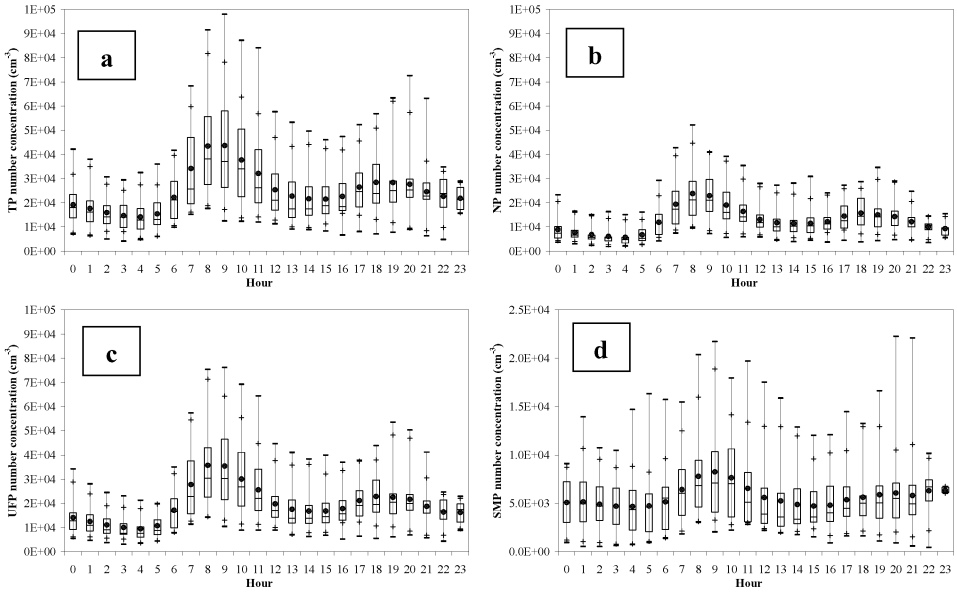


Figure 2 – Daily pattern of TP (a), NP (b), UFP (c), SMP (d) number concentrations during cold season weekdays in Milan. Average (dot), maximum and minimum value, median (line), 5$^{th}$ and 95$^{th}$ percentile (dash), interquartile range (box plot).

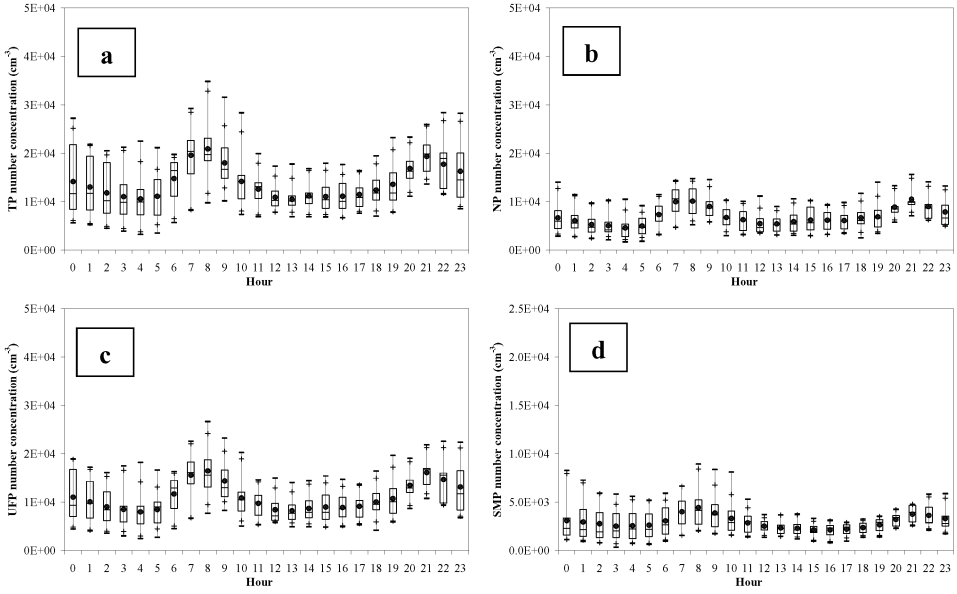


Figure 3 – Daily pattern of TP (a), NP (b), UFP (c), SMP (d) number concentrations during warm season workdays in Milan. Average (dot), maximum and minimum value, median (line), 5$^{th}$ and 95$^{th}$ percentile (dash), interquartile range (box plot).

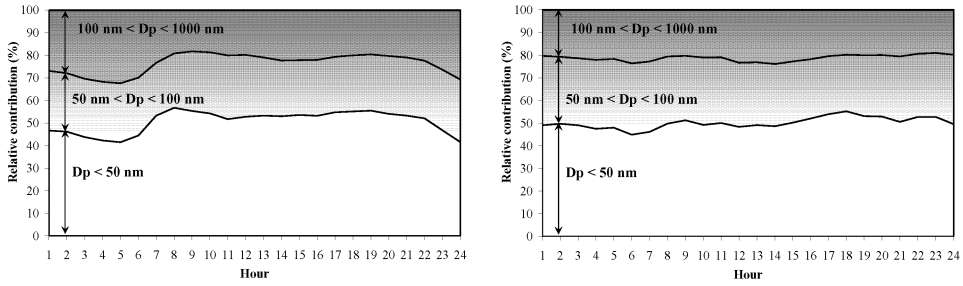


Figure 4 – Seasonal daily patterns (cold season: left; warm season: right) of the relative contribution to TP number concentration for size-segregated particles

Minimum NPs and UFPs contributions are observed at night time hours, specifically in the hours before sunrise when they fall down to 44% and 71%, concurrently with the maximum contribution from SMP. These observed smaller contributions of NP and UFP at late night is coherent with the reduced emissions of primary particles and with the condensation processes of semivolatile species onto existing particles favoured by the low temperature, resulting in particle growth and in a greater concentration of SMPs. In the warm period, daily patterns are more uniform: the morning rise of NP and UFP is less evident and leads to maximum values (52% and 79% respectively) observed in the late afternoon and early evening hours, likely for the build-up of NP and UFP photo chemically produced thanks to the stronger solar radiation of warm season daytime. The effect of night time condensation processes, which result in SMP increased contribution during the cold season, is almost absent since atmospheric cooling is less significant; therefore SMP relative contribution pattern presents only small variations around its average the daily value (20%).

Daily patterns for weekends' concentrations are quite different from weekdays', thus assessing once again the role of traffic emissions on ambient number concentration of particles. In the cold season the main differences between weekdays' and Sundays' TP patterns are: i) the much less pronounced peak ($3.09 \cdot 10^4$ $cm^{-3}$) on morning rush hour; ii) nocturnal (12 PM-2 AM) concentration levels as high as those of the morning rush hour, as a consequence of the enhanced Saturday night traffic. In the warm season, the differences are more outstanding, with the highest Sundays' concentrations at early and mid-night (both about $1.2 \cdot 10^4$ $cm^{-3}$) and almost constant values around $9.9 \cdot 10^3$ $cm^{-3}$ in the other hours of the day. Though reduced, traffic emissions affect the particles' size distribution on weekends too: in fact, NP and UFP relative contributions to TP concentration levels are still higher on day-time (59%-81%) compared to night-time (around 33%-64%) during the cold season. In the warm season NP and UFP contributions are at their highest levels, ranging from 45% up to 63% for NPs and from 74% up to 88% for UFPs. In particular, the maximum contribution is recorded at 2-4 PM, confirming the role of photochemical formation on NP and UFP ambient concentrations, already observed for weekdays.

## 4. Conclusions

Particles' number concentrations data collected at an urban background site in Milan have been analysed for their weekly and daily pattern on seasonal basis. Concentration data are in the 10-20000 nm size range but the analyses are mainly focused on the submicron particles, since almost 100% of the observed number concentrations is given by particles within this size range. Total particles' concentration levels are in the same order of magnitude reported for urban areas ($1\text{-}2\cdot10^4$ $cm^{-3}$), with daily average number concentration higher (almost twice as high) in winter than in summer. On the average, nanoparticles and ultrafine particles account for about 50% and 78% respectively of the total number concentration, the remaining 22% consisting of submicron particles in the 100-1000 nm range. In both seasons daily average weekends' levels are lower than weekdays': a progressive decrease of the concentrations starting on Saturdays and leading to the lowest weekly values on Sundays (about 11% and 66% in the cold and warm season respectively) is observed. Moreover, because of the reduced primary and precursors emissions from traffic, weekends' size distribution is less dominated by the finest fractions, with an average contribution of nanoparticles percentage points lower than on weekdays. The analyses of the time series of both total and size-segregated particle number concentrations point out a cyclic daily pattern, essentially regulated by the emission pattern of traffic and by ambient conditions that influence atmospheric dispersion and secondary formation processes. In particular, the daily pattern shows a major concentration peak (up to $10^5$ $cm^{-3}$) at morning traffic rush hour twice as high as in the evening rush hour, as a consequence of both the stronger traffic emissions and of the lower boundary layer typical of the morning hours. Minimum concentrations are usually observed at the end of night, also characterised by a greater contribution of larger particles resulting by accumulation and condensation processes, favoured by nocturnal ambient temperature cooling.

## 5. References

Dockery, D.W., Pope, C.A., 1994, Acute respiratory effects of particulate air pollution. Annual Review of Public Health, 15, 107-132.

Hinds, W.C., 1999, Aerosol technology: properties, behaviour and measurements of airborne particles. John Wiley & Sons.

Oberdorster, G., 2001, Pulmonary effects of inhaled ultrafine particles. International Archives of Occupational and Environmental Health, 74, 1-8.

Osunsanya, T. et al., 2001, Acute respiratory effects of particles: mass or number? Occupational and Environmental Medicine, 58, 154-159.

Pope, C.A., 2000, Epidemiology of Fine Particulate and Human Health: biological mechanisms and who's at risk?, Environmental Health Perspective, 108, 713-723.

Stolzenburg, M.R., McMurry, P.H., 1991, An ultrafine aerosol condensation nucleus counter. Aerosol Science and Technology, 14, 48- 65.

Wichmann, H.E., et al., 2000, Daily mortality and fine and ultrafine particles in Erfurt, Germany part I: role of particle number and particle mass. Research report, 98, 5-86.

WHO, 2006, WHO air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulphur dioxide. Global update 2005.