Inhaled Particles X, (23–25 September 2008, Manchester) IOP Publishing
Journal of Physics: Conference Series **151** (2009) 012039 doi:10.1088/1742-6596/151/1/012039

Personal exposure to airborne ultrafine particles in the urban area of Milan

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Abstract. The relevance of health effects related to ultrafine particles (UFPs; aerodynamic diameter < 100 nm) can be better evaluated using high-resolution strategies for measuring particle number concentrations. In this study, two different portable Condensation Particle Counters (CPCs) were used to measure personal exposure to UFPs in the central area of Milan for one week period during spring, with three sampling sessions per day. Experimental data were continuously collected along an established urban pathway, moving afoot or by different private and public means of transport. Correlation analysis between data measured by two CPCs was performed and general results showed a good agreement, especially at concentrations lower than 2×10^5 particles /cm^3. UFPs measures were divided on the basis of crossed environments or micro-environments, days of the week and day time (hours). The highest measured mean concentrations and data variability were observed during walking time and moving on motorized vehicles (bus and car), indicating that the highest exposure to UFPs can be reached near motorized traffic. The lowest exposures were observed in green areas and in office microenvironments. An appreciable difference between working and non-working days was observed. Concentration patterns and variation by days of the week and time periods appears related to time trends in traffic intensity.

1. Introduction

Ultrafine particles (UFPs; aerodynamic diameter < 100 nm) are generated by homogeneous nucleation of condensable gases, including photochemical production from precursors and emissions of condensable gases from high temperature combustion, or combustion processes with direct emission of soot particles. Thus, the UFPs production is often associated with high temperature phenomena occurring in natural processes such as volcanic activities or wild fires and in anthropogenic activities as industrial combustion processes, domestic activities (smoking, burning candles, cooking) and automotive mobility. As a matter of fact, combustion is the main anthropogenic source of fine particles, with the vast majority of them included in the sub-micrometer range. These particles contain a host of organic and inorganic materials [1]. Automotive traffic and in particular diesel engines are

considered the major sources of ultra-fine particles in urban environments [2]. Diesel exhausts are mainly constituted by particles in the 20-130 nm dimensional range [3], while spark ignition vehicles emit particles belonging to the 20-60 nm range [4].

Human exposure in private and public means of transport is of particular interest because many citizens and commuters spend a substantial component of their outdoor time in these microenvironments. In addition, exposures to urban atmospheric pollutants in several means of transport are often highly elevated in comparison to elsewhere so that individuals may gain a significant contribution to their daily total exposure [5].

After release into the atmosphere, UFPs are subjected to complex transformation processes, as dilution with background air, coagulation, deposition and condensation [6]. Some field data taken near freeways have shown that the size distribution of emitted particles change substantially within a few hundred meters of the emission source. Both atmospheric dispersion and coagulation appears to contribute to the rapid decrease in particle number concentration and change in particle size distribution with increasing distance from the traffic source [7]. Typical particle growth rates were determined in the range 1–20 nm per hour in mid-latitudes, depending on the temperature and the availability of condensable vapours [8].

In addition, UFPs can be also generated indoors by other combustion processes such as gas cooking [9], burning of wood and candles, tobacco smoke or gas-to-particle conversion [10].

Indoor particle concentrations can greatly differ from outdoors, even in the absence of indoor sources. Therefore, it can be important to understand the relationships between indoor and outdoor concentrations in order to assess the source and transport pathways of UFPs indoors. Some recent studies have examined this issue [11-13]. These studies show that, in absence of strong indoor sources, particles in indoor air are mainly of outdoor origin but, in the presence of significant indoor sources, the indoor/outdoor ratio can exceed unity [14].

The scientific and public interest in assessing the exposure and the risk due to UFP inhalation is growing in time, from the moment in which epidemiological studies have suggested that exposure to ultra-fine particles may cause pulmonary diseases, cardiovascular health effects and impairment of the immune system [15,16]. As a matter of facts, UFPs differ from larger particles with respect to deposition and alveolar clearance [17] and particles in the range 10-100 nm have a high probability of deposition into the deeper parts of the respiratory tract [18]. It was also found that UFPs contain higher levels of trace elements and toxins such as polycyclic aromatic hydrocarbons and some mutagenic substances [19,20]. Health effects rising from exposure to UFPs were first recognized through pulmonary toxicological studies, which have reported that UFPs can have a greater potency to cause adverse health effects than larger particles [21-25]. There are indications that particle number or surface area rather than mass may be more important factors when health implications are considered [26,27]. Currently, however, only the mass concentrations of fractions including particles with larger aerodynamic diameter (PM_{10} and $PM_{2.5}$) are regulated in Europe.

In general the study of human exposure during daily activities in different microenvironments should be conducted using high-resolution strategies, taking into account at the same time the duration, location and magnitude of exposure in order to accurately assess environmental health risks and so correctly manage and reduce the risk [28]. In the case of UFPs, the high spatial variability and the sudden variations in exposure even more suggest the use of continuous monitoring instruments.

The aim of this paper is to evaluate the personal exposure to UFPs as a function of space, investigating some microenvironments in the city Milan, and time, considering the different days of the week and periods of the day. The obtained results can be useful for future risk assessment of populations living or working in urban environments, as accurate (personal) human exposure assessment is one of the crucial steps in the risk assessment process. Until now no studies on personal exposure to UFPs in the metropolitan area of Milan (almost 3 millions inhabitants) have been reported.

2. Materials and Methods

Two hand-held Condensation Particle Counters were used to measure personal outdoor and indoor exposure to UFPs: a TSI Condensation Particle Counter model 3007 and a TSI P-Trak Ultrafine Particle Counter model 8525.

The CPC model 3007 enables number concentration measurements of particles >0.01 μm and is equipped with a continuous inlet flow rate, controlled by a pressure drop sensor which allows to minimize errors caused by flow rate variability. The P-Trak is capable of measuring particle ranging from 0.02 to > 1 μm in size. This instrument is not equipped with the flow control system present in the model CPC 3007.

It is important to underline that there is not yet a standard method or instrument for the measurement of true UFPs air concentrations in relation to health effects, particularly in the case of personal exposure, which requires the use of portable devices with reduced dimensions and less reliable performance. Among two adopted instruments, however, CPC 3007 will be considered to be the reference, owing to its wider operating particle size range and its more reliable technical features. Number concentration values reported in the following sections, then, if not differently specified, have to be considered as measured by CPC 3007.

Figure 1. The personal exposure pack used for personal monitoring**.**

Both CPCs operated with six AA batteries, at an inlet flow rate of 700 cm^3 min^{-1}. 100 cm^3 min^{-1} of the total sampled volume were automatically analyzed. Measured concentration values were recorded by internal data loggers with an acquisition time of 1 minute. Data were downloaded using the provided software. The working alcohol used for both instrument was isopropyl alcohol, with a purity grade of at least 99.5%.

The instruments were placed into a small backpack with sampling inlets on the same side (figure 1). This personal monitoring pack was carried by trained team members.

Experimental data were collected within the central area of Milan during a week in April 2005.

The city of Milan is divided into four areas of different size by two-lane, two-way concentric streets. The inner ring was chosen as sampling area for the study. The sampling strategy involved data collection whilst walking in busy and minor streets, travelling by bus (number 94, diesel), car (petrol with three-way catalyst) and metro (MM1). UFP concentrations inside car were collected while driving along a very busy street, with closed windows, ventilation system turned on and air recycling deactivated. Moreover, the car was equipped with an anti-particulate filter. Measurements were made along the route represented in figure 2, according to a sequential protocol that started and finished at the Department of Occupational Health, also used as office sampling area. The protocol comprised also the investigation of a green area and a great multi-road intersection (Cadorna square).

The sampling protocol was established in order to collect data for at least 15 minutes in each studied environment or micro-environment. Data were collected at three timings: morning (7.00 - 11.00 am), lunchtime (11 am - 3 pm) and afternoon (4 - 8 pm). A time-activity diary was completed in order to accurately separate the exposure data as a function of the different monitored environments.

The statistical analysis of collected data was performed by means of Microsoft Excel 2003 and SPSS 13.0.

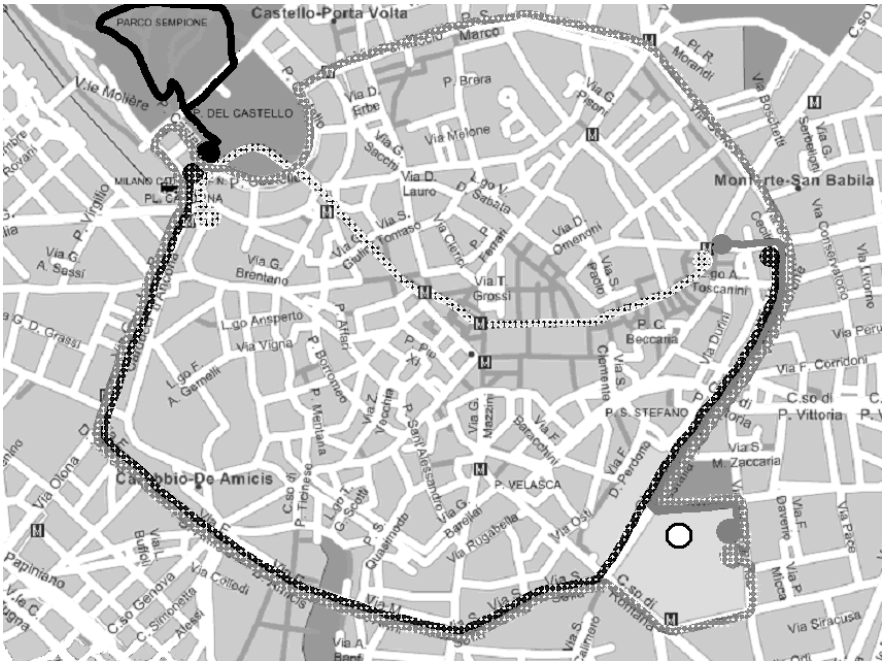

Figure 2. Sampling route map (Grey = Walking, Dotted white = Metro, Black = Park, Dotted black = Bus, Dotted grey = Car, White circle = Office).

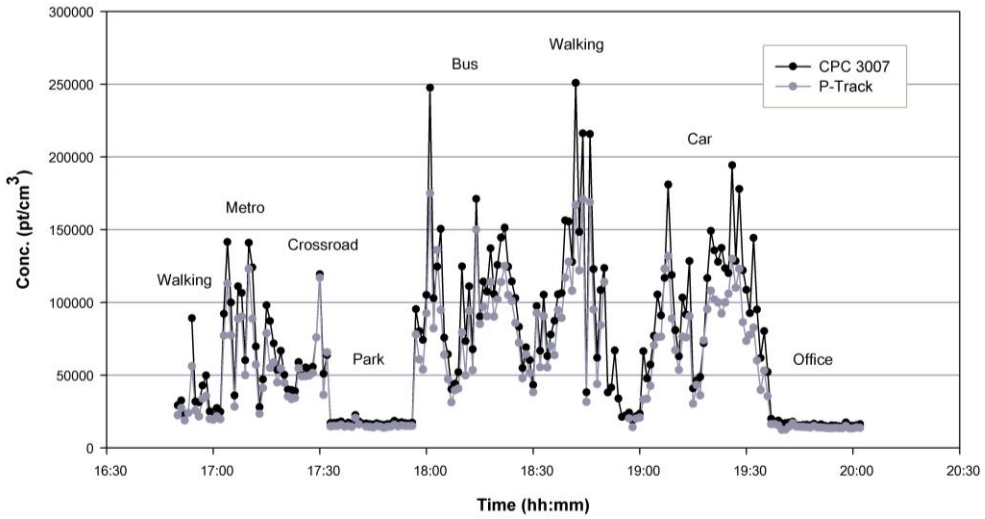

Figure 3. An example of UFP concentration trend measured by CPC 3007 and P-Trak during one sampling session.

3. Results

In total, N=4005 1-min data were collected using the two instruments of which respectively N=3728 were acceptable for CPC 3007 and N=3884 for P-Trak, since some samples were lost due to tilting errors or alcohol wick depletion. Figure 3 displays an example of particle number concentration trend detected by CPC 3007 and P-Trak during one session of measurements. Peaks corresponding to each sampled environment or micro-environment are labeled. Observed trends indicated that both CPCs are

able to detect short-time UFP variations, even if P-Trak showed a lack in detecting high concentration peaks. The best agreement between the two instruments was found for concentrations lower than 200000 particles (pt)/cm^3.

3.1. Correlation analysis between data collected by CPC 3007 and P-Trak

A linear correlation analysis was performed between time-paired concentrations measured by CPC 3007 and P-Trak (figure 4). This comparison yielded a Pearson correlation coefficient (r=0.965) close to unity (P<0.001) and the slope of the regression line was m=0.717. The relative accuracy improved (m>0.8) when considering low concentration data (< 50000 pt /cm^3).

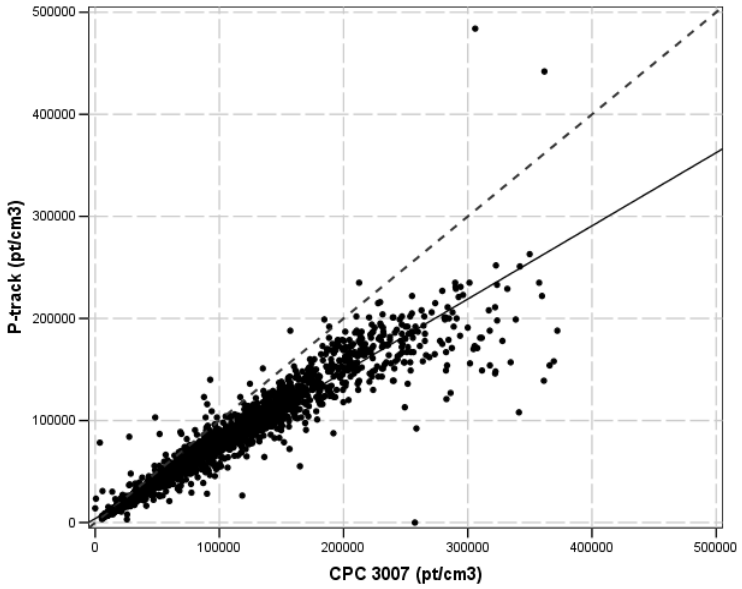

Figure 4. Linear regression plot between time-paired concentrations measured by P- Track and CPC 3007 (dotted line: y=x).

3.2. Exposure analysis

UFP personal exposure measurements were analyzed on the basis of the considered environments or micro-environments, days of the week and time (hours), and statistically significant differences were always found ($P_{ANOVA} < 0.001$). Only the statistical outputs resulted from data collected by CPC 3007 were used to quantify UFP exposure, as a consequence of the higher efficiency showed by this device in detecting the highest peak excursions (> 200000 pt/cm^3). Particle counts measured by P-Trak, however, are plotted in all graphical representations for comparison purposes.

The analysis of data showed that personal exposure magnitude and concentration variability were specific for each sampled environment or micro-environment. The highest measured mean concentrations and data variability [mean; standard deviation] were observed during walking time [100200 pt/cm^3; 80900 pt/cm^3] and moving by means of motorized vehicles like bus [117600 pt/cm^3; 59800 pt/cm^3] and car [107000 pt/cm^3; 64200 pt/cm^3]. On the contrary, the lowest exposures were observed in green areas [23400 pt/cm^3; 10800 pt/cm^3] and office [13500 pt/cm^3; 4700 pt/cm^3].

Graphical representations of data distributions according to the different considered environments and microenvironments are displayed in figure 5.

An appreciable difference between working and non-working days was observed. Concentrations measured during working days showed higher median and mean values, as well as wider data distributions, in comparison with those collected in non-working days. The highest concentrations were observed during the monitoring session of Wednesday [86000 pt/cm^3; 73200 pt/cm^3] and Thursday [87300 pt/cm^3; 73600 pt/cm^3], while lower values were measured on Saturday [40800

pt/cm^3; 37200 pt/cm^3] and Sunday [39200 pt/cm^3; 40000 pt/cm^3]. The data distribution as a function of days of the week is represented in figure 6.

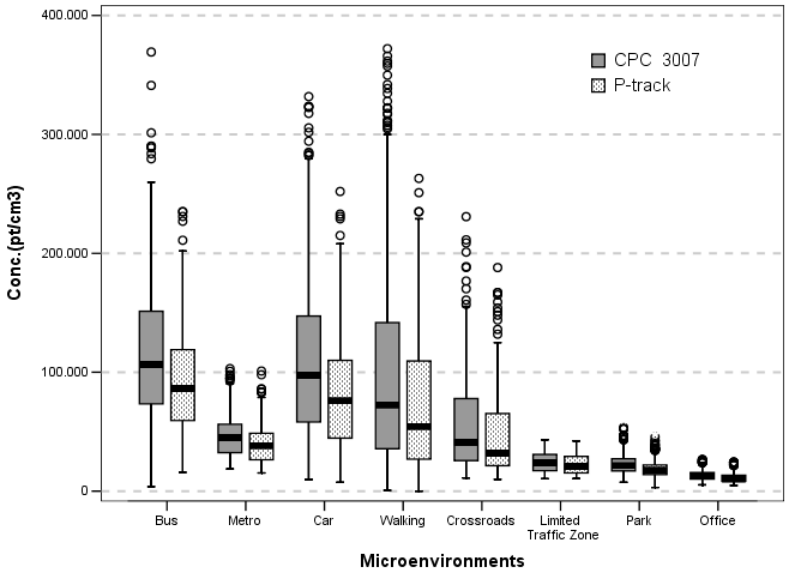

Figure 5. Box plots of data collected by CPC 3007 and P-Trak in sampled environments and micro-environments. (The central box comprises values between the 25th and 75th percentiles, the whiskers show the range of values that falls within 1.5 times the interquartile range beyond the box).

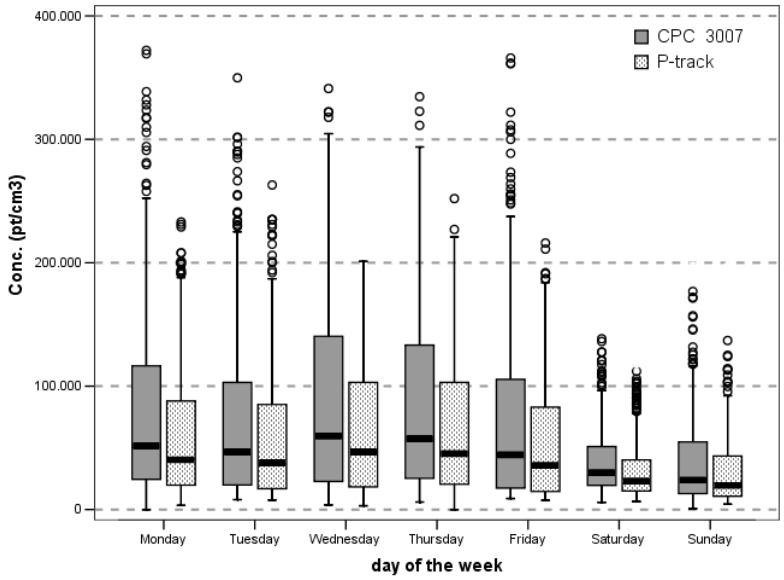

Figure 6. Box plots of data collected by CPC 3007 and P-Trak in different days of the week.

The analysis of concentrations collected in the three daily sampling sessions (7.00 - 11.00 a.m.; 11.00 a.m. - 3.00 p.m.; 4.00 - 8.00 p.m.) revealed some differences between the early morning session and the rest of the day. In fact, the most wide-spread distribution of measures and the highest mean values were obtained from 7.00 to 11.00 a.m. [82200 pt/cm^3; 77400 pt/cm^3]. The variability and mean concentrations obtained during lunchtime and afternoon were generally lower and comparable. These results are graphically displayed in figure 7.

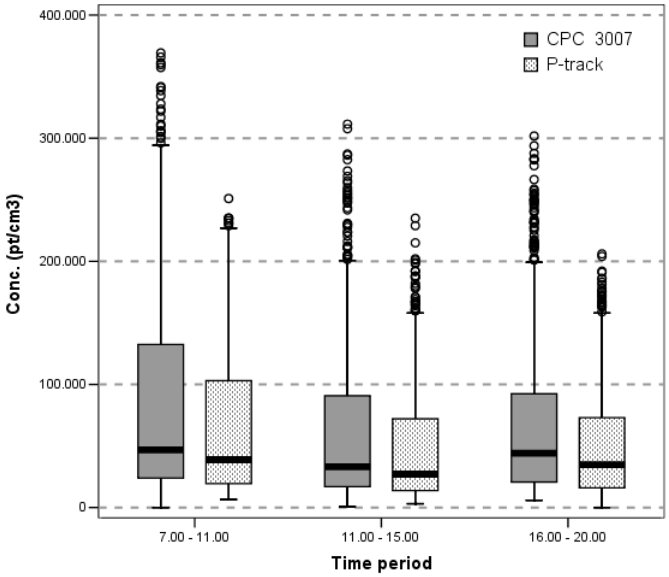

Figure 7. Box plots of particle number concentrations measured by CPC 3007 and P-Trak in three different periods of the day.

4. Discussion

The two portable instruments used in this study showed a good capacity of explaining the short time variability of UFP concentrations (R^2=0.93), even if P-Trak exhibits a lack in the detection of concentrations above 200000 pt/cm^3. Of course, a difference in readings between devices was expected owing to the lower threshold detection of CPC 3007 (> 0.01 μm) compared to P-Trak (> 0.02 μm). Nevertheless, figure 4 clearly shows a lacking of sensitivity that characterizes P-Trak respect to CPC 3007, evidenced by the displacement from the regression line when considering particle concentrations above the indicated limit. Moreover, it should be specified that, for concentration values higher than 200000 pt/cm^3, CPC 3007 also exhibits a weak loss in counting efficiency when compared with a more reliable method (electrometer TSI 3068) [29]. Therefore, P-Trak can be properly used in studies on the detection of UFP variations and in environments with low expected concentrations, whereas CPC 3007 is highly preferable in applications that require a better accuracy.

In general the highest UFP background levels were observed in southern European urban areas [30], with average values in Rome and Barcelona four times higher than those collected in Augsburg, Helsinki and Stockholm. This behaviour is confirmed in Milan, showing mean background levels (green areas) more than double than those found in northern European cities.

The personal concentrations measured in vehicles with instruments and in conditions similar to those adopted in this study (driving along a very busy street with closed windows) are comparable to the ones reported in similar international researches. A recent study in Athens [31] reported a mean value of 94000 pt/cm^3 compared with 107000 pt/cm^3 measured in Milan. These high values are related both to the meteo-climatic conditions of the considered city and to the traffic intensity along the examined streets [32]. Another study demonstrated that the highest UFP exposures occurred while driving in traffic congestions or when behind a heavy diesel-driven vehicle [33]. It is likely that higher concentrations than those observed would be expected if tunnel microenvironments were considered: here UFP concentrations higher than 10^6 pt/cm^3 have been measured [33], due to the absence of atmospheric dispersion.

Analysis of temporal variability of collected measures within the week reveals relevant differences between weekdays and the rest of the week. Sunday is characterized by lower concentration values,

while UFPs levels measured on Saturday lie in an intermediate position between Sunday and the working days. A similar behaviour have been observed for data variability: the most wide-spread distributions have been found during weekdays. The concentrations observed in different days of the week confirms a relationship with traffic trends, similarly to what described in other international research studies [30, 34]. The impact of traffic intensity on exposure is also highlighted in figure 7, where the distributions of UFP concentrations according to three different diurnal time periods are displayed. Indeed, more wide-spread distributions and higher particle number concentrations were measured during rush hours, when an increase of UFP emissions is caused by the elevated number of circulating vehicles. Similarly to other European cities [30, 31, 35], peaks of concentrations were found in the morning, between 7.00 and 11.00 a.m., while in the evening measured UFP levels are slightly higher than during the central hours of daytime.

5. Conclusions

Our observations indicate that the highest exposure to UFPs occurs while moving along busy streets or in their immediate proximities, either afoot or by motorized vehicles. Here exposure to UFPs is higher than elsewhere (7.4 to 8.8 times higher than in office micro-environments) so that individuals may gain a significant contribution to their daily total exposure, especially who spend a lot of time in these high-polluted environments. This is the case of traffic wardens, bus and taxi drivers, or those moving during rush hours (commuters), when the increase of UFP concentration is related to the elevated number of circulating vehicles.

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