Size distribution of ultrafine particles and trends of concentration near a linear (major highway) and point source (waste incinerator)

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In the last years numerous epidemiological studies were carried out about particulate matter effects on human health. Even if there is no agreement among the epidemiological and toxicological studies about the importance of total particle concentrations in terms of number, area or mass having the major negative effects on human health, it seems that the aerosol number concentrations plays a predominant role. For this reason, international standards move the attention from PM_{10} to $PM_{2.5}$ even if the number concentration is still not considered. In industrialized areas, the highest contribution to the fine and ultrafine particles comes from anthropogenic activities, namely from emissions of industrial combustion processes and traffic-related emissions (Cass et al., 2000). For this reason it is important to estimate the total particle number emission for each anthropogenic source and to understand the evolution of the particle size distribution (PSD) near these emission points. Zhu *et al.* (2004) have characterized the PSD evolution near major highway in Los Angeles showing the PSD seasonal trends and PSD evolution at different distances from the highways. Similar analysis were conducted by Kittelson on Minnesota highways (Kittelson *et al*., 2004). Fine *et al*., 2004 have obtained an ultrafine particle source apportionment in Los Angeles' industrial area. In this study the authors evaluate the PSD spatial and temporal variations in the San Vittore del Lazio industrialized area in Italy in which there are two main sources of emission: an highway and a municipal waste incinerator (MWI) plant. The main aim is to comprehend how these two sources can influence the background aerosol PSD of the area. In particular, an experimental campaign was carried out by means of a TSI 3936 Scanning Mobility Particle Sizer® (SMPS) and a TSI 3321 Aerodynamic Particle Sizer® (APS) Spectrometers.

1. Introduction

In the last years several epidemiological studies have pointed out a tight correlation between particle number concentration and health effects (Dockery et al., 1992, 1993 and 1996). In particular, toxicologists have focused their attention on fine ($PM_{2.5}$) and ultrafine particles (UFP) but there is no consensus in the scientific community on what particles property has negative effects on human health (number, mass, surface area concentration or chemical composition). The reference method used to measure particle mass concentration is the gravimetric one (McMurry et al., 2000). It allows to guarantee the direct traceability to the International System of Measurements (Buonanno et al.,

2007). This technique is not an on-line and automatic measurement method because filtration and collection setting-up operations are required. Other on-line measurement techniques are available to measure number and mass distribution or chemical composition of particles. In particular, the tandem constituted by a SMPS (Scanning Mobility Particle Sizer®; TSI Inc.) and an APS (Aerodynamic Particle Sizer®; TSI Inc.) is able to measure particle concentration distribution, total number of particles and can also be used to estimate the particles mass concentration (Shen et al., 2002). The aerosol of the urban background is constituted of *primary* particles (directly emitted from combustion sources; Cass et al., 2000) and *secondary* particles (due to the photochemical processes in the atmosphere leading to the gas-to-particle conversion). The aerosol sampling in a generic site is influenced by transportation and diffusion phenomena of emitted particles from primary emission sources and by newly secondary particles formed in the atmosphere due to gas-to-particle conversion.
Several papers reported in the scientific literature show the influence of primary emission sources (e.g. highways or industrial areas) on the surrounding aerosol. Zhu *et al.* (2004) have shown the particle size distribution (PSD) trend as function of the distance from highways in Los Angeles. Kittelson *et al.* (2004) have conducted similar studies along Minnesota's highways, while, Fine *et al.*, 2004 have estimated the PSD in Los Angeles industrial area. These studies show a good correlation between highway traffic and UFP number concentration.
In this paper the authors have conducted an on-line UFP sampling through a TSI 3936 Scanning Mobility Particle Sizer® (SMPS) and a TSI 3321 Aerodynamic Particle Sizer® (APS) Spectrometer also monitoring the main climatic parameters in order to estimate the contribution of two emission sources on the local UFP distribution concentration: the highway traffic and the stack of a waste incinerator.

2. Experimental apparatus

The aerosol sampling has been performed by the Laboratory of Environmental Measurements of the University of Cassino (Italy) from November 2007 up to the end of February 2008. The sampling site is placed 25 km apart from the mar Tirreno in NE direction, 400 m apart the highway A1 in NE direction and about 100 m apart the stack of a Refuse Derived Fuel (RDF) incinerator in NE direction.
The experimental apparatus is constituted by:

- a Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc.) composed of a condensation particle counter (CPC 3775) and an electrostatic classifier (DMA 3080), able to detect particles with dimension between 10 and 1000 nm and particles number concentration from 2 to $1 \cdot 10^8$ part/cm^3;
- an Aerodynamic Particle Sizer (APS 3321, TSI, Inc.) able to evaluate the aerodynamic diameter of particles in the range 0.5-20 μm measuring the time of flight (TOF) with a 52 channels resolution and particle number concentration starting from 10^{-3} to 10^3 part/cm^3;
- an automatic gravimetric sampling (Zambelli 6000 Plus) to measure PM_{10} and $PM_{2.5}$ mass concentration;
- a weather station (Davis Vantage Pro) to estimate the main climatic parameters (temperature, relative humidity, atmospheric pressure, rain, wind direction and velocity, solar irradiation, …).

Using the SMPS/APS tandem the number, surface area and mass particle distribution in the 10 nm-10 μm aerodynamic diameter range can be determinated. The postprocessing analysis was performed through the Aerosol Instrument Manager and Data Merge Software TSI Inc. softwares, together with authors' self made subroutines. The measures conducted with the SMPS/APS tandem have been obtained every 20 minutes: every value represents the arithmetic average of three measurements. Mass concentration has been evaluated hypothising a constant value of the particle density equal to 1.7 g/cm^3 and on the basis of an algoritmh well described in Fine *et al*. (2004) and Sioutas *et al*. (1999). However, Park *et al*. (2004) noticed that in the measurement range below 100 nm, density value seems to diminish when the particle diamater decreases. It is mainly due to an higher contribution of volatile organic compounds emitted by diesel vehicles. Urban ultrafine atmospheric aerosol and particle emissions from combustion sources such as diesel engines are typically low fractal dimension aggregates ($D_f \leq 2$) composed of spherical primary particles with a diameter of 5-50 nm. Xiong and Friedlander (2001), in Los Angeles area, found that the fraction of aggregates was about 60% for particles with aerodynamic diameters between 50 and 75 nm and 34% for the range 75 to 120 nm. Besides, they also observed a rural aggregate concentration in the size range 50-120 nm less than 1% with respect to the concentrations at urban sites. The SMPS spectrometer uses electrical mobility to measure the particle size. This technique utilizes a bipolar charger to impart a known charge distribution on the aerosol sample. The particles are then classified according to their ability to cross an electric field. The most common method of interpreting electrical mobility analysis to obtain size is based on a spherical particle model, including an expression for the drag coefficient over a wide range of Knudsen numbers (*Kn*) and the bipolar charging efficiency of spherical particles. While this method is appropriate for sizing spherical particles, it leads to errors in the mobility size data interpretation for aerosol carrying an high aggregates percentage and subsequent calculations of its surface area and volume (and hence mass) distributions.

Lall and Friedlander, 2006 have developed a new method for analyzing mobility of nanoparticle aggregates for a limiting case of idealized aggregates ($D_f \leq 2$). The basic assumption of this method is that aggregates are composed of primary particles all of which have the same (known) diameter. Primary particles aggregates diameter have been observed in some scientific studies: a 30 nm primary particles aggregates diameter has been found by Barone *et al*. (2006). They reported results of the experimental analysis conducted in major freeway and at Los Angeles International Airport in which showed an average primary particle diameter in the range 23-36 nm. Lee *et al*. (2001) obtained an average primary particle diameter in the range 28.5-34.4 nm with a distribution similar to a gaussian distribution. Park *et al*. (2004) determined the primary particles aggregates diameter by transmission electron microscopy (TEM) obtaining an average value of 31.9 nm with a 7.2 nm standard deviation for diesel agglomerates.

The authors have corrected the measurement data using an hypothized value (equal to 30 nm) for aggregates primary particles as function of the source of the analyzed aerosol. Other corrections have been done about the diffusion loss. A common situation where deposition of small particles by diffusion to walls is of significant importance is diffusion loss of particles on the walls of tubes in which aerosol is transported. This diffusion loss causes losses of particles transported through tubes like in aerosol measurement. Due to the higher diffusion velocity of smaller particles the losses

become more significant as the particle size decreases. Diffusion is the primary transportation mechanism for particles with aerodynamic diameters less than 100 nm. Diffusion losses are expected on the measurement devices inner surfaces which leads to an underestimation in the real PSD. The acquisition data software has a diffusion correction tool created according to the algorithms reported in Chen et al., 1998, Birmili et al., 1997 and Reineking et al., 1986.

3. Results and discussion

$PM_{2.5}$, PM_{10} and PSD measurements have been obtained through the SMPS/APS tandem. The correlation factor between mass and number aerosol particles concentration is not high taking into account all the measurement data of the sampling period. But a good correlation there is on weekly basis as shown in Fig. 1.

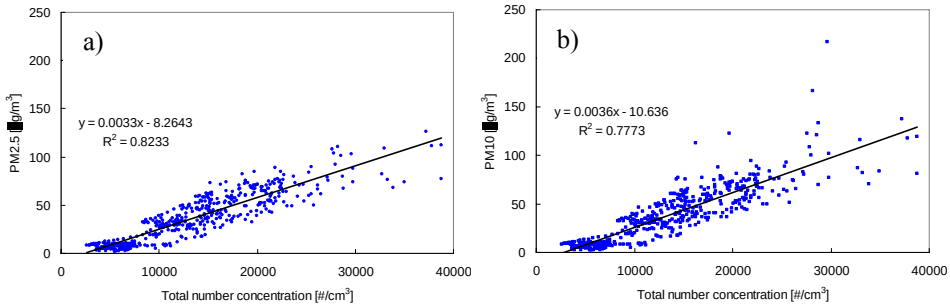

Fig. 1: Correlation between mass, a) $PM_{2.5}$ and b) PM_{10}, and particle number concentration in San Vittore del Lazio from the 7th up to 13th January

Particles number concentration is strictly related to the UFP with aerodynamic diameter less than 150 nm, so the high correlation factor between mass and number concentration implies a similar shape for mass and number particle distribution approaching a typical monodisperse curve. Fig. 2 shows the average distribution trends of the sampling period. It demonstrates that the mass concentration is strongly influenced by the unimodal distribution with a peak corresponding to a diameter less than 400 nm.
The sampling period is characterized by a thermal inversion condition of the atmosphere with an increasing mixing height in the afternoon. The mean total concentration values were $1.1 \cdot 10^4$ part./cm^3 on number basis and 41 µg/m^3 for PM_{10}.

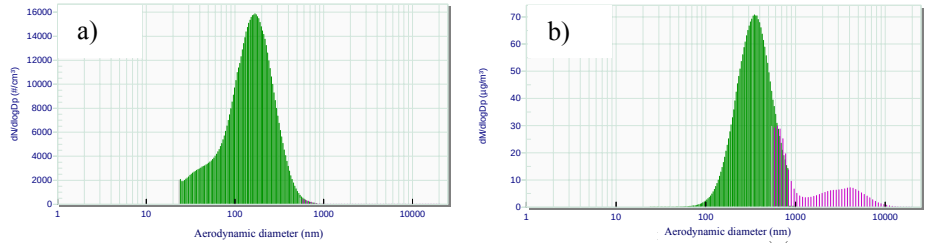

Fig. 2: a) Average mass (PM_{10}) and b) number concentration distribution in the winter period

In Fig. 3 the mass and number concentration distributions as function of the week days are reported. Both the concentrations are higher in the weekdays than the weekend. The worst situations are noticed on Monday (morning) and Friday (late afternoon) corresponding to the highest traffic density along the A1 highway.

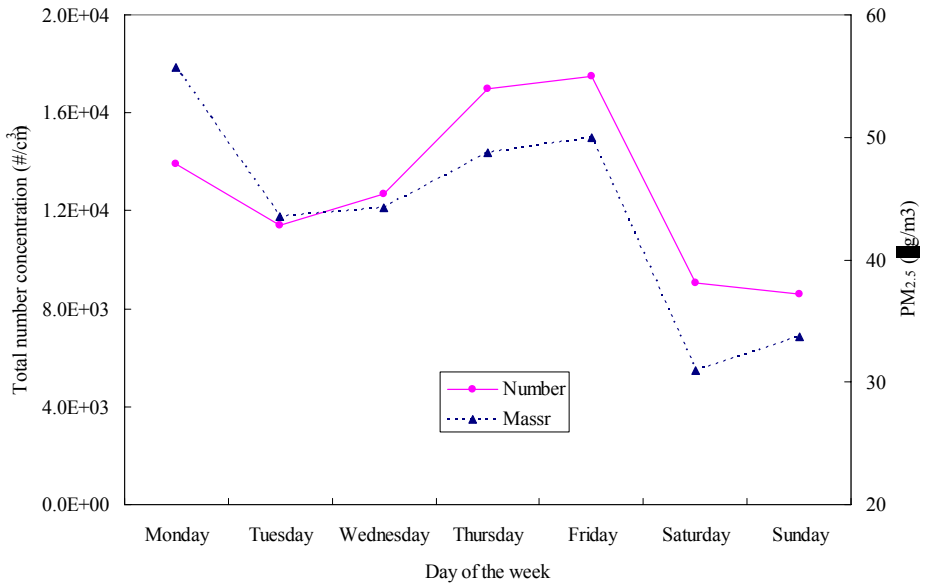

Fig. 3: Mass ($PM_{2.5}$) and number concentration during the week in the winter season

In the winter season, traffic emissions are the main sources in the morning (7:30–10.00 AM) and in the evening (6:00–8.00 PM) as shown in Fig. 4a where mass and number concentration measurements are reported. The particles number is very high showing the presence of *fresh* particles. Because of the wind velocity was not high in the sampling period, the linear source (the highway) has to be considered as a local source in respect to the sampling point. Fig. 4b shows the decrease of the mode value when *fresh* particles achieve the sampling site. Besides, Fig. 4 also shows that the number particle concentration increases during the early afternoon (3.00-5.00 PM) whilst the related mass particle concentration and mode decrease. The most probable reason of these trends is the secondary aerosol formation in the atmosphere due to nucleation events. Typical winter climatic conditions are responsible of an increasing thermal inversion height with temperature increasing. The long range transportation cannot explain the *fresh* particles presence because this phenomena only can carry *aged* particles, so the only reason of the mode decrease in the first afternoon is the formation of new *fresh* particles.

O'Dowd *et al.* (1999), O'Dowd *et al.* (2001) and Shi *et al.* (1999) report observations of nucleation events with formation of particle less than 10 nm in remote sampling sites.

The hypothesis of photochemical formation is also in agreement to the relationship between particles number and solar irradiation (with a sequent increase of photochemical phenomena) in the first afternoon.

O'Dowd et al., 1999 and 2001 also show as a lot of nucleation events are noticed in remote sites having low background values. A negligible surface area to support the supersaturate vapor condensation corresponds to these background values: consequently nucleation mechanisms are advantaged. This explanation is in agreement with values reported in Fig. 4b, where a minimum surface area value is found in the early afternoon.

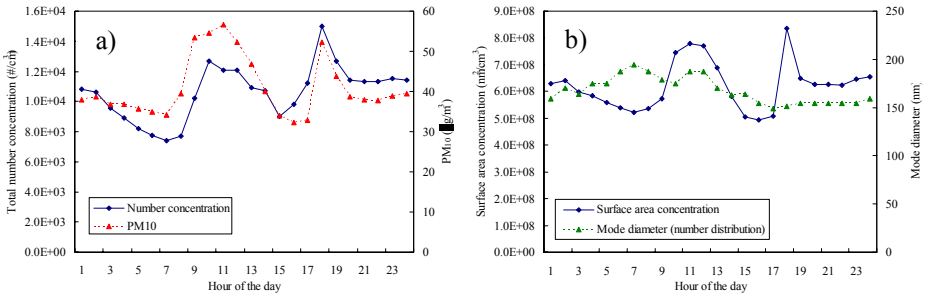

Fig. 4: Daily mass and number concentration trend (a), surface area and mode concentration trend (b) in the winter season in San Vittore del Lazio

Nucleation phenomenon is very complex and it is not yet completely clear. Well known mechanism are the binary nucleation involving sulfuric acid and water and the ternary nucleation with sulfuric acid, water and ammonia as explained in Korhonen *et al.* (1997 and 1999) and Kulmala *et al.* (1998).

In the present study, the stack of the incineration plant (100 m away) represents the main cause of the presence in the atmosphere of precursor gases able to support the gas-to-particle conversion. In particular, a 10^5 m^3/h exhaust flow rate is emitted by the stack with an average daily concentration equal to 100 mg/m^3 of NO_x emission, 10 mg/m^3 of SO_2 and ammonia which is not yet monitored. Actually there are not sufficient parameters to establish if there is a regular homogeneous nucleation phenomenon around the sampling site. More complete consideration could be carried out after a summer season sampling and a plant stop period sampling.

In Fig. 5a the PSD daily evolution on the January 25th, 2008 in the sampling site is shown. On 7:00 a.m. the PSD is unimodal with a peak at about 150 nm. On 9:00 a.m. the PSD becomes bimodal with a nucleation mode around 30 nm and another peak at 100 nm. Then, with respect to 7:00 a.m., on 9:00 a.m. there are *fresh* particles coming from the highway mainly due to diffusion processes and an increasing number of *aged* particles due to the convective transport mechanisms. On 3:00 p.m. the total concentration is diminished and the PSD presents an homogeneous nucleation mode around 10 nm and the usual peak in proximity of 100 nm. On 8:00 p.m. the PSD is unimodal with a peak around 30 nm as consequence of the high traffic density along the highway during the Friday evening. In this situation, the contribution of particles larger than 100 nm to the total number concentration is quite negligible.

Fig. 5b shows that, even if the mass concentration increases in the early morning with a corresponding increase of the particle number, it can be observed a decrease of the mass concentration as the number concentration increases during the evening (when the highway traffic is very high).

The different PSD can be explain on the basis of the weather conditions estimated through the weather station (Fig. 6). On 8:00 a.m. there was a slightly wind in W-SW direction (from the highway to the sampling point). In the afternoon the wind velocity reached 2.0 m/s in NE-E direction (from the sampling site to the highway).

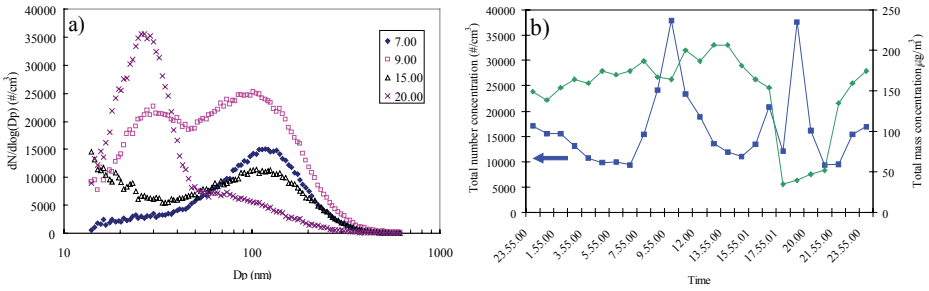

Fig. 5: PSD in different hours (a) and total mass and number aerosol concentratio (b) in San Vittore del Lazio on January 25th, 2008

During these conditions, particles with aerodynamic diameter less than 100 nm were able to reach the sampling point from the highway mainly due to diffusion mechanism transport supported by the high highway traffic of the Friday evening. Around 8:00 PM the wind direction changed becoming in the opposite direction and carrying particles with greater diameter from the highway to the sampling site (Fig. 5b).

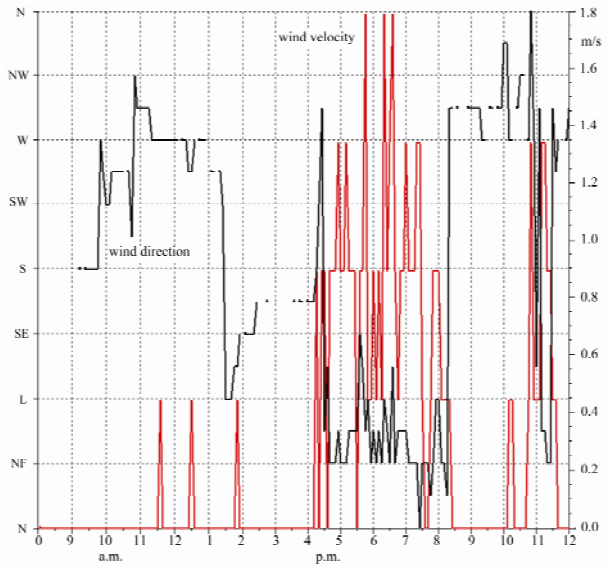

Fig. 6 – Wind velocity and direction in San Vittore del Lazio on January 25th, 2008

In order to underline the primary highway influence on the PSD in the sampling site, in Fig. 7 the PSD measured on January 25th, 2008 at 9:00 a.m. is reported and compared to the PSD obtained by other researchers (Zhu *et al.*, 2004 and Kittelson, 2004) at similar distance from the highway.

Zhu *et al.*, 2004 measured PSD at different distance from the highway in Los Angeles area. In particular they carried out measurements in the vicinity of Interstate 405 (200-270 vehicles/min passing the sampling site in both directions with approximately 5% heavy-duty diesel trucks) and Interstate 710 (180-230 vehicles/min passing the sampling site in both directions, with approximately 25–30% heavy-duty diesel trucks). Kittelson *et al*. (2004) monitored Minnesota's highways. Measurements results are strictly dependent on the traffic conditions (vehicle velocity and number) and on the heavy-duty vehicle percentage.
The A1 highway traffic between Rome and Naples on the first quarter of 2007 has been characterized by 200 000 vehicles passed on with a 22% percentage of heavy-duty diesel trucks (AISCAT report, January-June 2007).
Local monitoring on the A1 highway have showed a traffic density ranging between 50 and 100 vehicles/min with an average 22% of heavy-duty vehicles ranging between 30% and 45%.
Fig. 7 shows the similarity between the A1 highway and the Freeway 710: the PSD obtained in San Vittore del Lazio at 8:30 p.m. has only one mode around 30 nm and concentration values close to the Freeway 710 ones. San Vittore PSD has a larger value of the mode probably due to the major distance to the source with more *aged* particles; however concentration values are similar even if the traffic density is less than the Freeway 710, probably because of the larger average velocity of Italian traffic and on higher percentage of heavy-duty vehicles in respect to the Freeway analyzed in Zhu *et al.*, 2004. At 9:00 a.m. the PSD is bimodal and there is a peak on 30 nm too.

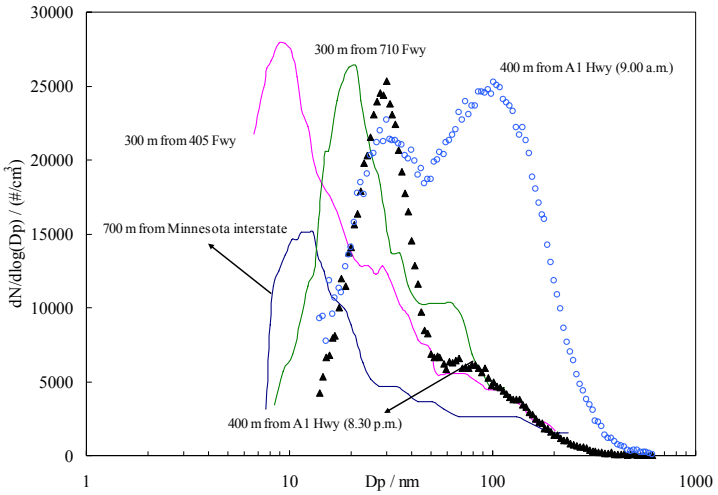

Fig. 7: San Vittore del Lazio PSD on on January 25th, 2008 compared with other experimental analysis

4. Conclusions

In the present work an experimental analysis to evaluate linear (major highway) and point source (waste incinerator) ultrafine particles emission impact has been carried out. The following conclusions can be withdrawal:

- number, surface area and mass concentrations are typical of semi-rural sites;

- the effect of the incineration plant is only restricted to the emission of precursor gases for secondary particle formation (this aspect needs for further investigations);
- the main impact is due to the highway. The obtained PSDs are similar to PSDs obtained by other researcher having similar highway traffic conditions;
- it is essential an UFP highway emission characterization.

Moreover, a tight correlation between the particle number concentration and the highway traffic density has been found. For this reason the linear source has to be considered predominant in respect to the incineration plant.

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