Particle number concentrations in the Po valley (Northern Italy) in wintertime: comparison between urban and rural sites

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Abstract. The temporal and spatial variability of particle number concentration (PNC) levels and of the related particle number size distribution (PNSD) over the Po valley in Northern Italy is investigated based on data collected during an intensive multi-site monitoring campaign conducted in February 2014. Measurements were concurrently taken at three urban sites, in the cities of Milano, Bologna, and Padova, and at two rural site, San Pietro Capofiume and Ispra, on the South-Eastern and North-Western side of the valley. PNC data have been collected by means of an Ultrafine Particle Monitor (UPM, TSI 3031), two Fast Mobility Particle Sizers (FMPS, TSI 3091), two Differential Mobility Particle Sizers (DMPS, TSI); investigated particle size ranges were 3-600 nm for both FMPS and DMPS and 20-1000 nm. Total PNC data and size-segregated PNC for 5 size bins (20-30 nm, 30-50 nm, 50-70 nm, 70-100 nm, and 100-200 nm), have been processed on hourly time resolution. Average hourly data for PNC were in the $5 \cdot 10^3$ -$1.1 \cdot 10^4$ cm^{-3} range, with the lowest values at the rural sites and the highest in the city of Milan. At the urban sites the PNC daily time pattern showed two main peaks on the morning and evening traffic rush hours; conversely, at the rural sites it was mainly driven by the boundary layer evolution and much less affected by source activity. Ultra fine particles (UFPs, 20-100 nm size range) accounted for about 75% of PNC at urban sites and for about 63% at the rural sites. On rush hours at the urban sites, PNC of the particles in the smallest size range (20-50 nm) greatly increased, thus confirming that motor vehicle emissions were the main source of UFPs, as also suggested by their correlation with NOx and CO concentrations.

Keywords: Particle number, Size distribution, Po valley, Cluster analysis.

1. Introduction

The Po valley in Northern Italy is a well-known hot-spot for atmospheric pollution, especially for particulate matter (PM), whose air quality limits are frequently exceeded at monitoring sites. However, because the current air quality standards for PM are mass based, particle number concentration (PNC) and related size distribution (PNSD) are not routinely measured and their knowledge is still scarce for this area. Some literature studies focused on the nucleation and growth of new particles in Northern Italy (Hamed et al., 2007; Rodriguez et al., 2005); Rodriguez et al., 2007 compared number size distribution of urban fine aerosols in Milan, Barcelona and London; Lonati et al., 2011 investigated the multimodal structure of the PNSD at an urban background site in Milan while Bigi and Ghermandi, 2011 focused on the PNSD at an urban background site in the central part of the Po valley. Poluzzi et al., 2015 report seasonal data for particle number concentration in the Emilia-Romagna region and Wang et at., 2016 report size resolved PNC measured at different sites within a mid-sized city in the same region. A few studies investigated exposure concentration levels to ultrafine particles in urban microenvironments in Milan (Cattaneo et al., 2009; Ozgen et al., 2016) and in other cities in the Po valley (Lonati et al., 2017).

However, all these works usually rely on monitored data from just one single site and the comparison between concentration levels concurrently measured at different sites is not addressed, thus. This work brings a piece of knowledge of the latter issue as it discusses the temporal and spatial variability of PNC levels and PNSD over the Po valley with reference to five sites where concurrent measurements were taken during a dedicated monitoring campaign conducted in February 2014 in the framework of the POAIR (PO valley atmospheric Aerosol Intensive Research) project.

2. Material and methods

2.1. Monitoring period

The monitoring campaign was performed in 2014 from February 7th to February 27th, during an intensive multi-site field campaign intended to investigate the temporal and spatial variations of particle number concentration in the Po valley area. Compared with the typical winter weather conditions in this area, February 2014 was warmer, more unstable and rainy during the first and last decade and rather warm during the central decade because of a anticylonic configuration extending its influence over the entire Po valley. Average values for the daily mean temperature, wind speed and relative humidity were respectively in the orders of 8.5 °C, 2 m s^{-1}, and 80%, with limited variations among monitoring sites. A few rain events occurred, with cumulative rainfall over the whole monitoring period ranging between 60 mm on the Eastern side and 95 mm on the Western side of the area.

2.2. Monitoring sites and instruments

Measurements were concurrently taken at five sites: three urban sites, in the cities of Bologna (BO - 400000 residents), Milano (MI - 1350000 res.), and Padova (PD - 200000 res.), and at two rural background sites, San Pietro Capofiume (SPC-R) and Ispra (ISP-R), on the South-Eastern and North-Western side of the valley (Figure 1). The urban sites in Bologna (BO-UB) and Milano (MI-UB) have the features of urban background sites, the former on the Northern outskirt of the city, nearby arterial roads and major highways, the latter in the University campus, not directly exposed to primary emission sources. The site in Padova (PD-MX) is actually in suburban area, located South-West of the city centre, with a mixture of urban, industrial and rural features. The SPC-R rural site is located in a flat area surrounded by cultivated fields; conversely, the site in Ispra shows an urban/rural mixed behaviour and recent studies identify this site as a rural background but still heavily influenced by human emissions (Henne et al., 2010; Sandrini et al., 2014).

Depending on the monitoring site PNC data have been collected by means of an Ultrafine Particle Monitor (UPM), a Fast Mobility Particle Sizer (FMPS), a Differential Mobility Particle Sizer (DMPS) and a Twin Differential Mobility Particle Sizer (T-DMPS). The instrument used at the monitoring sites, the corresponding investigated particle size range, time resolution, and number of size bins are summarized in Table 1. SMPS available at BO-UB site data were only used to correct FMPS data following Jeong and Evans, 2009. Raw PNC data have been processed in order to obtain total PNC data at actual ambient conditions on hourly time resolution and size-resolved PNC data for the same 6 size intervals (20-30 nm, 30-50 nm, 50-70 nm, 70-100 nm, 100-200 nm, and > 200 nm) at all the monitoring sites.

Table 1. Monitoring sites and instruments

Site	Size range	Time resolution	Size bins	Instrument
ISP-R	10-800 nm	10 min	45	TSI -DMPS
MI-UB	20-1000 nm	10 min	6	TSI UPM 3031
PD- MX	5.6-560 nm	1 min	32	TSI FMPS 3091
SPC-R	3-600 nm	10 min	119	TSI T-DMPS
BO-UB	5.6-560 nm	1 min	32	TSI FMPS 3091
	3-600 nm	5 min	148	TSI SMPS 3093

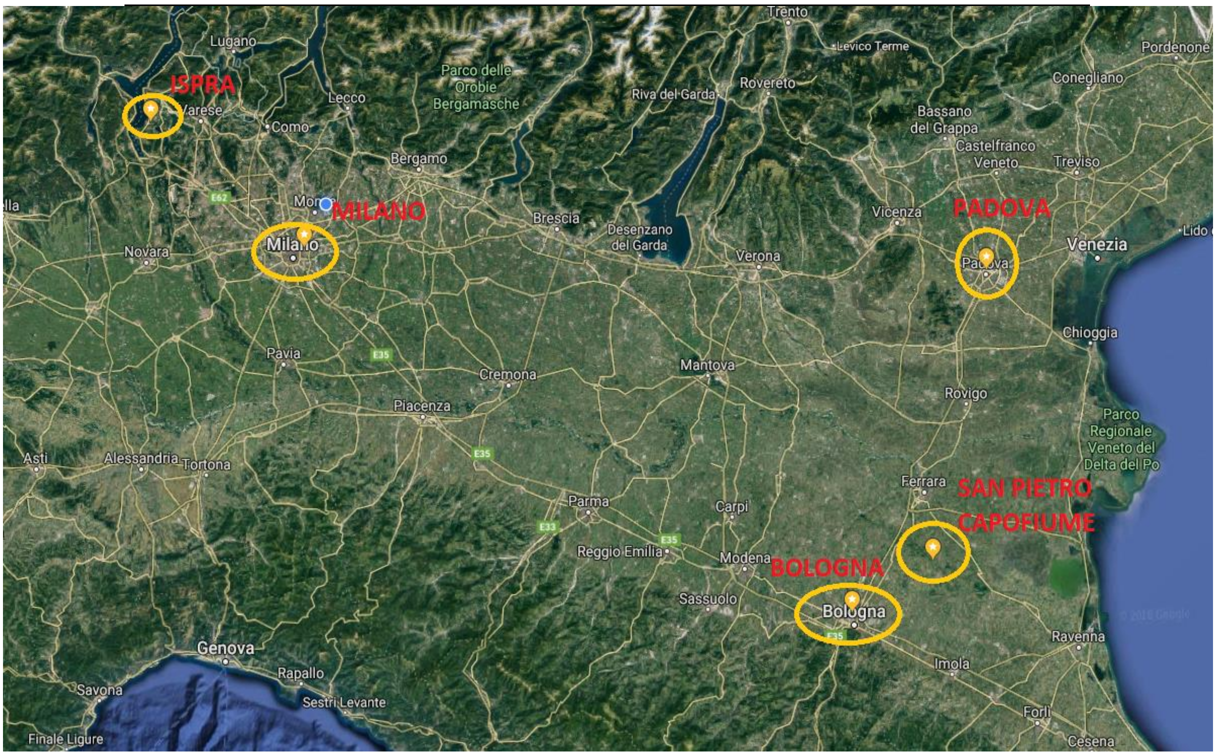


Figure 1. Location of the monitoring sites in the Po valley

3. Results

3.1. Particle number concentration

Box-plots for the hourly and daily average concentration for the total particle number are presented in Figure 2. For both the averaging times, the entire dataset from MI-UB site is shifted towards higher values than at the other sites. Hourly data for PNC are in the $3\cdot10^3$-$3.8\cdot10^4$ cm^{-3} range, with a median of $1.0\cdot10^4$ cm^{-3} and a slightly higher mean of $1.1\cdot10^4$ cm^{-3}. Data distribution is right-skewed distribution, with a number of data in excess of $2.1\cdot10^4$ cm^{-3} and up to a maximum of $3.8\cdot10^4$ cm^{-3}. Because of the longer averaging time that smooths hourly peaks, the distribution of daily data is less scattered (CV = 0.23 vs. 0.45 for 1-h data) and skewed (Pearsons' skewness = 0.35 vs. 0.65 for 1-h data), with PNC values ranging between $8.1\cdot10^3$-$1.7\cdot10^4$ cm^{-3} and almost coincident mean and median around $1.1\cdot10^4$ cm^{-3}. Among the other urban sites PD-MX is the most similar to MI-UB, though the median values of both distributions are well below 10^4 cm^{-3} ($7.5\cdot10^3$ and $8.5\cdot10^3$ cm^{-3} for 1-h and 24-h data, respectively); however, peak hourly data in excess of $2.0\cdot10^4$ cm^{-3} up to $3.4\cdot10^4$ cm^{-3} have been observed, even though less frequently than at MI-UB site. Conversely, BO-UB site is characterized by significantly lower concentration values ($8\cdot10^3$-$1.8\cdot10^4$ cm^{-3} range, $4.5\cdot10^3$ cm^{-3} as median for 1-h data) not only with respect for the urban sites but also for the SPC and ISP rural sites. In practice, PNC levels at BO-UB are similar to those of SPC-R, whereas ISP-R is actually characterized by intermediate PNC levels between the urban PD-MX site and the BO-UB and SPC-R sites. The peculiarity of PNC levels at BO-UB site compared with the other urban sites is likely due to the site location, not really in a densely built environment as on the city outskirt. Actually, the inspection of polar plots (Carslaw and Ropkins, 2012) for PNC levels in relation to wind speed and direction (Figure 3) points out that the whole urban agglomeration is the main source for airborne particles. Additionally, the similarity of BO-UB site with SPC-R site, which is only at about 30-km crow-fly distance, is also stated by the high correlation (R = 0.86) between PM2.5 daily concentrations measured during the monitoring campaign. Thus, BO-UB site has displayed rural and regional background features more than urban features, at least for the winter period of this campaign. On the other hand, PNC data collected at ISP-R site confirm its urban/rural mixed behaviour as suggested by both the concentration levels ($0.9 \cdot 10^3$-$2.2 \cdot 10^4$ cm^{-3} range, $6.6 \cdot 10^3$ cm^{-3} as median for 1-h data) and the occurrence of relatively high concentration events, already observed at urban sites.

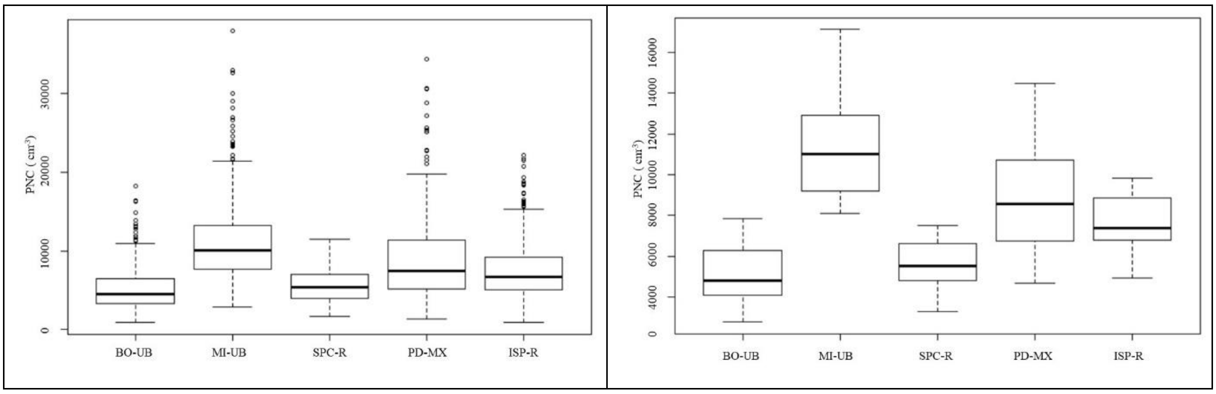
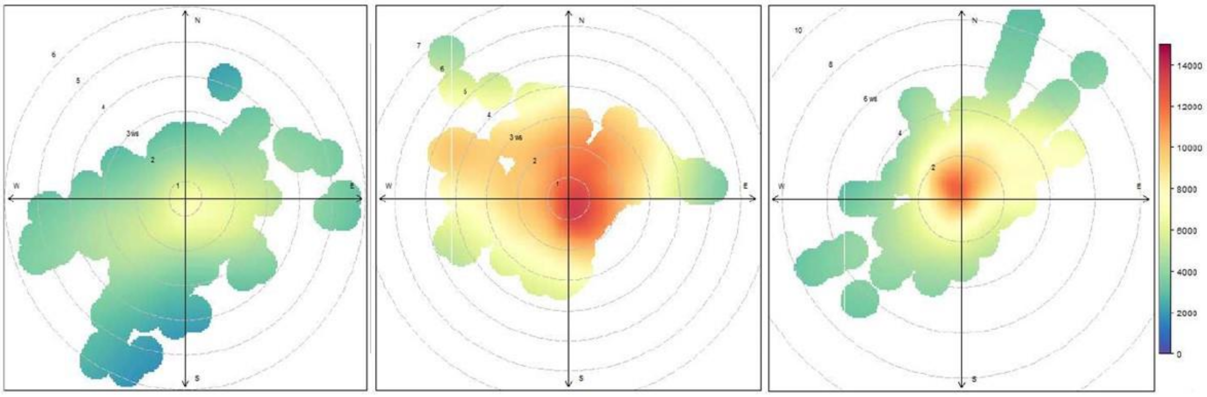


Figure 2. Hourly (left panel) and daily average total PNC (cm^{-3})



BO-UB **MI-UB** **PD-MX**

Figure 3. Polar plots for hourly total PNC (cm^{-3}) at urban sites

The measured PNC levels are in agreement with literature data for urban sites in Europe ($8 \cdot 10^3$-$4 \cdot 10^4$ cm^{-3} range) and with previous results for the Po valley area: Poluzzi et al. 2015 report a wintertime mean concentration of $1.4 \cdot 10^4$ cm^{-3} ($6.8 \cdot 10^3$-$2.2 \cdot 10^4$ cm^{-3} range); Lonati et al. 2013 report concentration levels in the $5 \cdot 10^3$-$1.1 \cdot 10^4$ cm^{-3} range at an urban background site in a mid-sized city in the centre of the Po valley and in the $6 \cdot 10^3$-$9 \cdot 10^3$ cm^{-3} range at a rural site. Based on data from the German Ultrafine Aerosol

Network for particles in the 20-800 nm size range, Sun et al., 2019 report multi-annual mean values for urban background and regional background sites of $4.9 \cdot 10^3$ cm^{-3}, and $3.3 \cdot 10^3$ cm^{-3} respectively.

3.2. Particle size distribution and cluster analyses

Particle number size distribution (PNSD) analyses are performed for the same set of six size intervals (20-30 nm, 30-50 nm, 50-70 nm, 70-100 nm, 100-200 nm, and > 200 nm) common to all the monitoring sites. In general, all the PNSDs present an Aitken mode, located in the 60-100 nm range; however, the location and the magnitude of such mode are characterized by both spatial (i.e.: site-dependent) and temporal (i.e.: day, time of the day) variability. Because of the limited size range investigated, neither the presence of a nucleation mode nor that of a coarse mode can be observed. Nevertheless, especially at the urban sites, the structure of PNSDs suggests that a first mode below 20 nm, prevailing on the observed Aitken mode, is actually present, coherently with the multimodal structure of PNSDs reported in literature for urban sites (Lonati et al., 2011). The variability of daily averaged PNSDs was investigated trough k-means cluster analysis, intended to group together days with a common pattern for the size distribution of airborne particles. Cluster analysis results are presented in Figure 4 for MI-UB site where four well-separated clusters were recognized; the four corresponding cluster-averaged PNSDs are shown in the right panel of Figure 4. Cluster #1 and cluster #4 group days with high ($1.5 \cdot 10^4$ cm^{-3} as cluster average) and low ($8 \cdot 10^3$ cm^{-3}) PNC levels; Cluster #2 and cluster #3 group days with intermediate PNC levels (both around $1.1 \cdot 10^4$ cm^{-3} as cluster average) but with a different location of the Aitken mode, shifted towards a slightly larger diameter in Cluster #3. Similar4-cluster results have been obtained for the other monitoring sites, though with site-related concentration levels and PNSDs. For each site the same k-means clustering approach was also performed based on daily averaged air pollution data (NO_x, PM_{10}, $PM_{2.5}$, SO_2, CO) and meteorological parameters (temperature, wind speed, relative humidity, solar radiation, rainfall). The comparison with the clustering results for the PNSDs shows a stronger correspondence in the cluster composition with air quality levels than weather conditions. Actually, the high-PNC days of cluster#1 are concurrently characterized by high concentration levels for criteria pollutants (for cluster#1 at MI-UB site: PM_{10} µg m^{-3} and $PM_{2.5}$ about 38 µg m^{-3}).

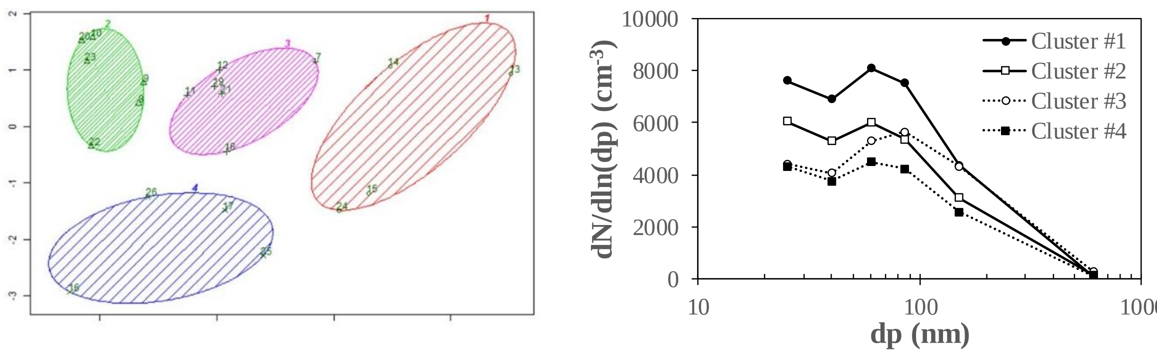


Figure 4. Principal components plot for daily averaged size distributions at MI-UB site (left); average PNC size distributions for the four identified clusters (right)

Intra-day variability of the PNSD was analysed through the investigation of the time pattern of size-resolved PNC. At the three urban sites and the ISP-R site the hourly pattern of the total PNC on weekdays displays two clear peaks on the morning and evening rush hour (Figure 5, top-left); conversely, at the SPC-R site the time pattern is quite flat, regardless for the day of the week, missing the two peaks generated by traffic emissions in the urban areas (Figure 5, top-right). The role of road traffic as a source of particles in urban areas is confirmed by the similar time patterns observed for NOx and CO concentration as well as by the lack of the morning peak on Sundays. However, the influence of the diurnal evolution of the atmospheric conditions is also highlighted by the low PNC levels on the early afternoon due to the enhanced dispersion favoured by the vertical growth of the boundary layer.

The evolution of the boundary layer appears to be the main driver for the PNC time pattern at the SPC-R rural site, where PNC levels are much less affected by the activity of anthropogenic sources. Size-resolved analysis for urban sites shows that on both peak hours the PNSD is dominated by particles in the smallest size bins (20-30 nm and 30-50 nm), also suggesting the presence of a main mode below 20 nm (Figure 5, bottom-left). On the contrary on night time hours the PNSD is more uniform, likely without a sub-20 nm mode, and with a main Aitken mode around 100 nm also driven by phenomena of particulate formation and particle growth for condensation of semi-volatile precursors favoured by the low temperature.

3.3. Inter-site comparisons

As discussed in Section 3.1, PNC levels at the monitoring sites are quite different, essentially depending on the site location. Actually, the pairwise correlation analyses for the time series of the daily averaged PNC resulted in R values usually in the order of 0.5, with a highest R = 0.64 for PD-MX and ISP-R and a lowest R = 0.08 for SPC-R and ISP-R, confirming the already mentioned particular features of this latter site. Conversely, the hourly time patterns of both concentration levels and PNSD show stronger similarities, especially for the sites located in urban environments, with a behavior clearly different for the rural SPC-R site only. In order to gain a deeper insight of the temporal and spatial variability on both PNC levels and related size distributions, cluster analysis has been performed based on the entire dataset of the daily averaged size distributions. As shown in Figure 6, four clusters were identified have been rather different composition.

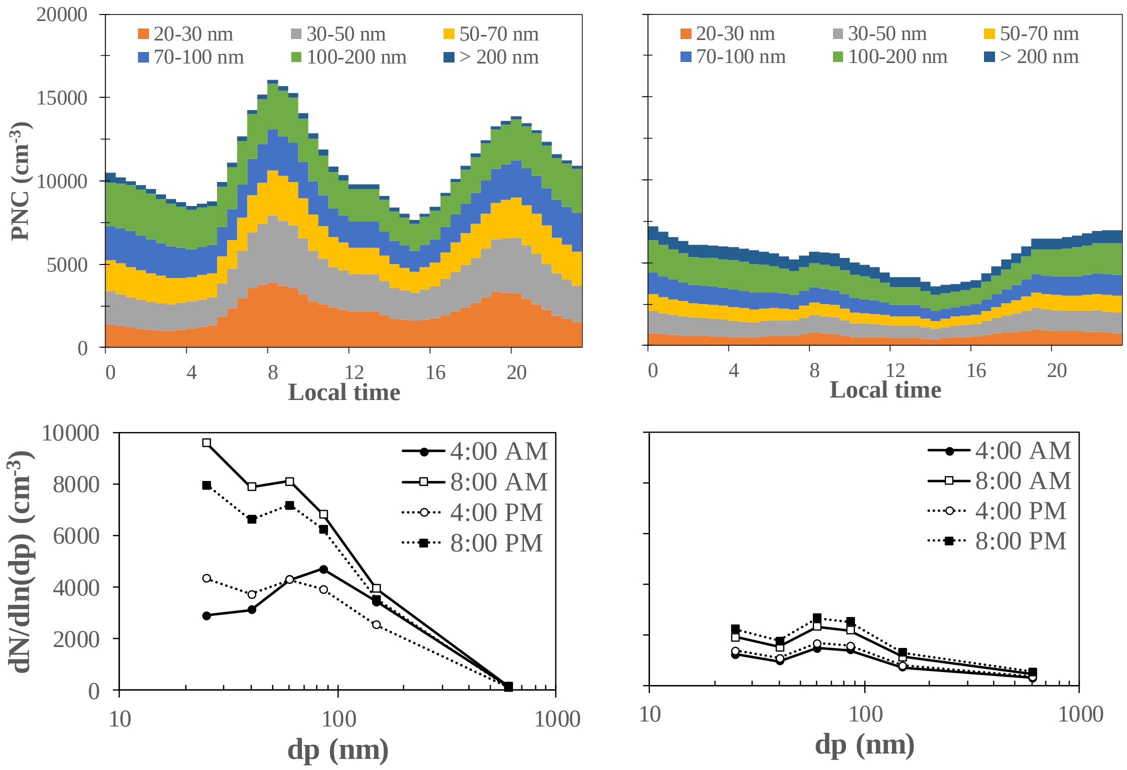


Figure 5. Hourly pattern of size-resolved PNC and related PNSDs at MI-UB site (left column) and at SPC-R site (right column)

Cluster #1 includes data only from MI-UB and PD-MX sites, corresponding to days with high PNC concentrations (cluster average: $1.2 \cdot 10^4$ cm^{-3}), but mostly (68%) from the former site in Milan. Cluster #2 and Cluster #3 group together days with intermediate PNC levels ($7.3 \cdot 10^3$ cm^{-3} and $6.9 \cdot 10^3$ cm^{-3} as cluster average, respectively) but while the former mainly includes data from the urban sites (80%

overall) the latter conversely includes data from the two rural sites (84% overall), but mostly from the ISP-R site (50%). Finally, cluster #4 ($4.2 \cdot 10^3$ cm^{-3}) is almost entirely formed by data from BO-UB and SPC-R, whose similarity in concentration levels has been already discussed in section 3.1. Figure 7 shows in details for each site the breakdown of the days of the monitoring period among the four clusters. Interestingly, we can observe that the daily data MI-UB and PD-MX sites not only fall in first two clusters mainly, but also that for 10 out of the 20 days considered in this analysis data from the two sites fall in the same cluster; the same consideration holds for the sites of BO-UB and SPC-R. Only in a few days the more than two sites fall in the same cluster (3 sites on Feb. 10th, 13th and 22nd; 4 sites on Feb. 9th) and only in one case (Sunday Feb. 16th) the PNC values and the shape of the PNSD have been such to have all the sites grouped in the same cluster. All these results indicate that the features of the site, namely its location within the urban context, have a significant influence on both the concentration levels and the particle size distribution.

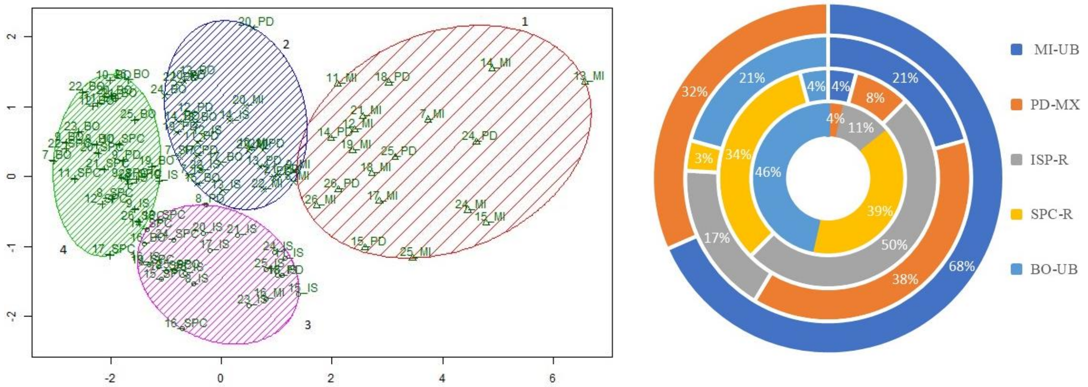


Figure 6. Principal components plot for the daily averaged size distributions (left); cluster compositions by site frequency (right: from cluster#1 on the outer to cluster#4 on the inner ring)

MI-UB	1	2	2	2	1	1	1	1	1	3	1	1	1	2	1	2	2	1	1	1
PD-MX	2	3	4	2	2	2	2	1	1	3	2	1	2	2	2	2	2	1	1	1
ISP-R	2	3	4	4	3	2	2	2	3	3	3	3	4	3	3	2	3	3	3	3
BO-UB	4	4	4	4	4	4	2	2	2	3	2	2	4	4	4	4	4	2	4	4
SPC-R	2	4	4	4	4	4	3	3	3	3	4	3	3	4	4	4	4	3	3	4
	7	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**

Calendar day

Figure 7. Breakdown by site of the days of the monitoring period among the four clusters

4. Conclusions

The results from a one-month winter campaign for particle number concentrations measurement at rural and urban sites in the Po valley show that concentration levels are in the same orders of those reported in literature for sites with similar features. At rural and urban sites average concentrations are about $5 \cdot 10^3$ cm^{-3} and $1.1 \cdot 10^4$ cm^{-3}, respectively. In spite of the background position of the urban sites, however, concentrations up to $4 \cdot 10^4$ cm^{-3} occur on traffic rush hour. Actually, the monitoring sites location within the urban area strongly influences the concentration levels: the deeper the location into the urban conurbation the higher the generalized exposure of the site to the urban emission sources and, subsequently, the higher the particle concentration. At the urban sites located on the outskirts of the city or in suburban environments concentration similar to rural sites can be observed sometimes. As a consequence of the different features of the urban sites considered in this work, the correlation between the time series of the particle number concentration is rather weak, even though the sites share a common time pattern hourly concentration, reflecting the diurnal pattern of the traffic flow in urban areas. Concentration values, size distribution and related time patterns markedly different from the urban sites are observed only at the rural site actually located in a regional background position, not directly affected by emission sources, where the levels of airborne particles are mainly driven by the daily evolution of the planetary boundary layer.

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