

Article

# Long-Term Characterization of Submicron Atmospheric Particles in an Urban Background Site in Southern Italy

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**Abstract:** Continuous measurements of particle number size distributions in the size range from 10 nm to 800 nm were performed from 2015 to 2019 at the ECO Environmental-Climatology Observatory of Lecce (Global Atmosphere Watch Programme/Aerosol, Clouds and Trace Gases Research Infrastructure (GAW/ACTRIS) regional station). The main objectives of this work were to investigate the daily, weekly and seasonal trends of particle number concentrations and their dependence on meteorological parameters gathering information on potential sources. The highest total number concentrations were observed during autumn-winter with average values nearly twice as high as in summer. More than 52% of total particle number concentration consisted of Aitken mode ( $20\text{ nm} < \text{particle diameter } (D_p) < 100\text{ nm}$ ) particles followed by accumulation ( $100\text{ nm} < D_p < 800\text{ nm}$ ) and nucleation ( $10\text{ nm} < D_p < 20\text{ nm}$ ) modes representing, respectively, 27% and 21% of particles. The total number concentration was usually significantly higher during workdays than during weekends/holidays in all years, showing a trend likely correlated with local traffic activities. The number concentration of each particle mode showed a characteristic daily variation that was different in cold and warm seasons. The highest concentrations of the Aitken and accumulation particle mode were observed in the morning and the late evening, during typical rush hour traffic times, highlighting that the two-particle size ranges are related, although there was significant variation in the number concentrations. The peak in the number concentrations of the nucleation mode observed in the midday of spring and summer can be attributed to the intensive formation of new particles from gaseous precursors. Based on Pearson coefficients between particle number concentrations and meteorological parameters, temperature, and wind speed had significant negative relationships with the Aitken and accumulation particle number concentrations, whereas relative humidity was positively correlated. No significant correlations were found for the nucleation particle number concentrations.

**Keywords:** size distributions; particle number concentration; nucleation; seasonal trends

## 1. Introduction

In urban or urban-background environments, air quality could be impaired due to consistent emissions from anthropogenic activities that combined with natural sources and long-range transport of aerosols altogether contribute to producing high levels of pollution. Given the wide variability in the number and type of sources, the relative contribution to air pollution concentrations spans considerably from place to place. The number of particles with specific size present at a given site depends on many factors that include the origin of particles, atmospheric processes (condensation, nucleation, and evaporation), and chemical transformations [1]. The number concentration of submicron particles is not a metric included in European policies for air quality assessment; however, recent studies indicate

that it has adverse health effects [2]. Therefore, it becomes more and more important to investigate the concentration levels, trends, sources, and dynamics, especially in urban and urban background areas [3].

Typically, aerosol number concentrations are lower in rural areas,  $\sim 10^3\text{--}10^4\text{ cm}^{-3}$ , compared to urban agglomerations where number concentrations exceed  $10^4\text{ cm}^{-3}$  [4]. In cities, submicron particles (particle diameter  $D_p < 1\ \mu\text{m}$ ) are present in very high number concentrations, more than 80% of total number [5–7], and the major contributing sources of these particles include vehicular exhausts [8], industrial emissions [9], biomass burning, and new particle formation [10].

As observed in many studies performed in European cities [11,12], particle number concentrations and size distributions show daily and seasonal behaviors that are strongly linked to local emission sources and meteorological factors. In winter, for example, the number concentration of submicron particles is higher than in summer due to the increase of emission sources, especially from biomass burning for domestic heating, and due to more stable atmospheric conditions. On the other hand, during warmer months, a high concentration of gaseous precursors and a more intense solar radiation can trigger the process of formation of new particles [13,14]. Literature studies [15,16] suggest that the aerosol number concentration represents a better indicator of climate and health effects of particulate compared to mass concentration. Owing to their small size and chemical/physical properties, these particles are involved in toxic and carcinogenic health effects and contribute, directly and indirectly, to anthropogenic climate change.

To date, only a few studies on long-term measurements of aerosol particle number and size distributions were performed in southern Italy. Long-term observations [17–22] allow getting robust statistics to better characterize the sources that affect a measurement site, in terms of number concentration and size, and provide insights into the processes controlling aerosol dynamics.

In this work, continuous measurements of the number size distribution over five years, from 2015 to 2019, were performed in an urban background area in Southern Italy. Located in the central Mediterranean, the site is influenced by a variety of aerosol types, sources, and transport pathways that allow the study of a wide range of processes and to characterize aerosol properties of a typical coastal area. To our knowledge, this is the first long-term study done in this area, to investigate trends of both aerosol number concentration and size distribution. The seasonal and daily patterns together with the behavior of the modal structure of aerosol particles during different periods of the year were analyzed. Correlation with local meteorological parameters were also used to interpret the dynamics of particles.

## 2. Experiments

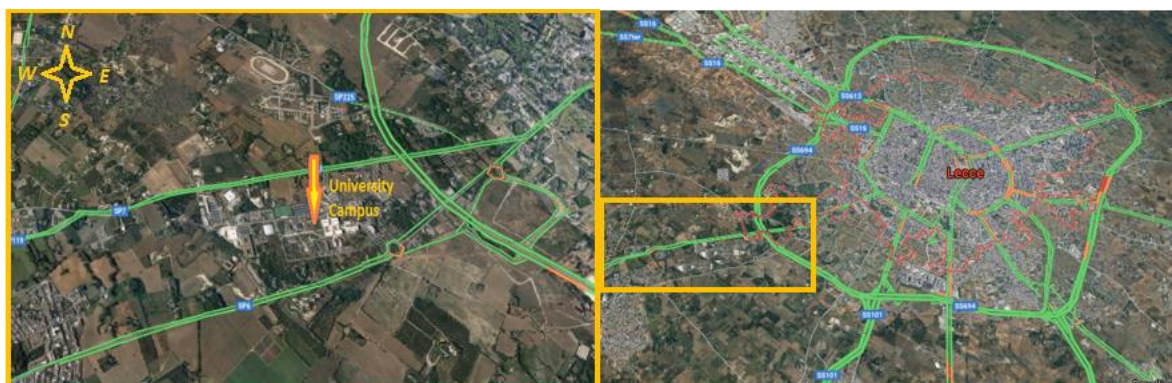
### 2.1. Measurement Site

The measurements were conducted between January 2015 and October 2019 at Environmental-Climatic Observatory of Lecce (ECO,  $40^\circ 20' 8''\text{ N}$ ,  $18^\circ 07' 28''\text{ E}$ ) that is part of GAW/ACTRIS Network. The observatory is located at the Institute of Atmospheric Sciences, Research National Council (ISAC-CNR), inside the University Campus, at about 13 m above ground level [23]. The site is at about 5 km SW of the town of Lecce,  $\sim 20$  km away from the Adriatic and the Ionian Sea, 100 km away from the Balkan coast, and 800 km away from the Northern Africa coast. There is an important road  $\sim 500$  m away from the site that, combined with on-road mobile source impact from traffic inside the campus, acts as sources of airborne particulates (Figure 1).

This area, considered an urban background site [24], is affected by the integrated contribution of local anthropogenic sources (mainly traffic and biomass burning) and by the long-range transport of natural (sea spray and desert dust) and anthropogenic dust from large industrial settlements located at distances between 30 and 80 km.

Therefore, its location in the heart of the Mediterranean is strategic to study chemical and physical characteristics of regional background conditions, and the measurements of atmospheric compounds

carried out at the ECO can be considered representative of many Mediterranean background areas located near the coast.



**Figure 1.** Location of the sampling site with respect to the city center of Lecce. The most important roads are shown in green.

## 2.2. Instrumentation

Particle number size distribution was measured by a Mobility Particle Size Spectrometer (MPSS), equipped with a differential mobility analyzer (DMA, length 28 cm) and a condensation particle counter (CPC, model: TSI 3772, TSI Inc., Rome, Italy). The instrument was designed and manufactured according to EUSAAR/ACTRIS recommendation at the Leibniz Institute for Tropospheric Research TROPOS [25]. Briefly, the system, after having aspirated air from an appositely developed  $PM_{10}$  inlet, dries the inlet flow below 40% relative humidity using a Perma Pure nafion dryer. After, the inlet flow containing aerosol passes a bipolar diffusion charger to bring the aerosol particle population into defined bipolar charge equilibrium [26]. Throughout a cylindrical differential mobility analyzer, particles are selected based on their electrical mobility and counted by a condensation particle counter that measures the resulting number concentrations in each of the selected size ranges [27]. The diffusion loss of the particles during the sample transport in the tubing and negatively charged particles were corrected according to a multiple charge correction routine proposed by [26]. Missing, incorrect, or incomplete scans were flagged using the flag list and recommendations published in [25]. Operational parameters like flows, high voltage, zero points, and size standards were checked and calibrated periodically. Each measurement was made in five minutes, covering a particle diameter range from 10 to 800 nm divided into forty channels.

During the sampling period, meteorological parameters were obtained from the continuous measurement performed at the ECO observatory. The weather data, ambient temperature, relative humidity (RH), wind speed, wind direction, and precipitation were collected simultaneously by a Vaisala WXT520 automatic weather station (Vaisala Oyj, Helsinki, Finland).

## 3. Results and Discussions

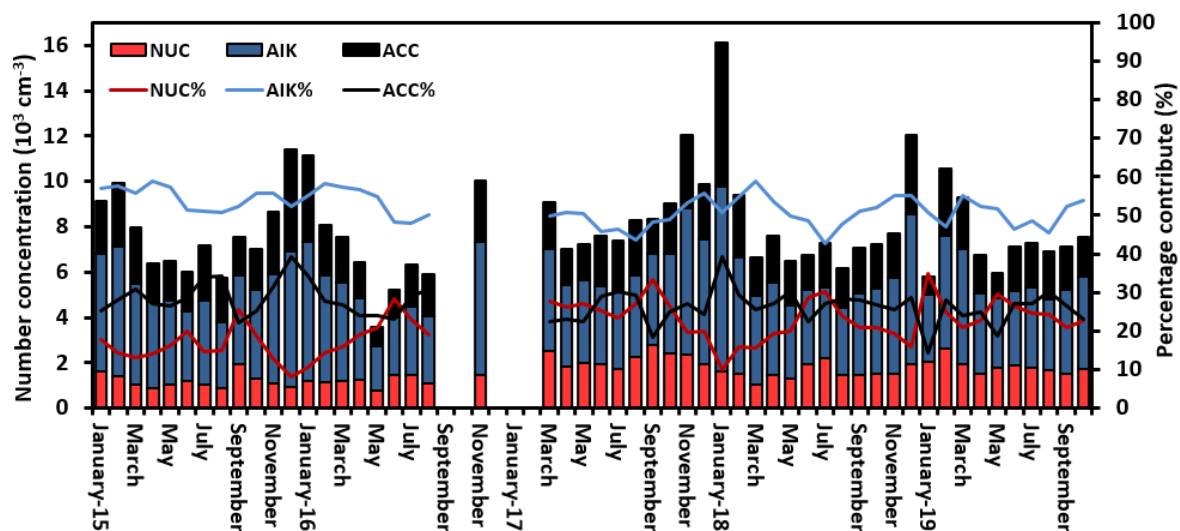
### 3.1. Overview of Particle Number Concentration

To investigate the contribution of the different size fractions, the measured particle number concentration (PNC) was divided into three classes, nucleation particle mode  $N_{NUC} < 20$  nm, Aitken particle mode  $20 < N_{AIT} < 100$  nm, and accumulation particle mode  $100 \text{ nm} < N_{ACC} < 800$  nm. The total particle number concentration,  $N_{TOT}$  (10–800 nm), is the sum of the three modes. Yearly averages  $\pm 1$  standard deviation and medians with 25th and 75th percentiles were calculated and summarized in Table 1 for each size class. The yearly average and median values of  $N_{TOT}$ ,  $N_{ACC}$ , and  $N_{AIT}$  do not show any noticeable inter-annual trend. Higher variability, about 50%, was instead observed on  $N_{NUC}$ , probably because this fraction of particles is influenced not only by the primary emissions but

also by other processes such as new particle formation when the ambient air conditions are favorable. During the study period, the number of concentrations exhibited monthly variability with several pronounced increases, as shown in Figure 2. Due to technical/maintenance problems with SMPS, measurements from late 2016 to early 2017 were not carried out, as shown in Figure 2 (missing data). The highest values of  $N_{TOT}$  were recorded during cold months where the monthly averages varied from  $12033 \pm 9017 \text{ cm}^{-3}$  to  $8068 \pm 6469 \text{ cm}^{-3}$  between December and February respectively, while lower number concentrations, between  $3577 \pm 2451 \text{ cm}^{-3}$  and  $5730 \pm 2954 \text{ cm}^{-3}$ , were measured between May and August. A similar trend was also observed in the accumulation and Aitken particle mode. Monthly averages of accumulation particles number concentrations ranged between  $828 \pm 626 \text{ cm}^{-3}$  and  $4500 \pm 4029 \text{ cm}^{-3}$  while Aitken mode number concentrations were higher than the other modes with values ranging between  $1960 \pm 1300 \text{ cm}^{-3}$  and  $8154 \pm 5330 \text{ cm}^{-3}$ . A similar behavior, but less marked was observed for the nucleation particle mode with values between  $860 \text{ cm}^{-3}$  and  $2780 \text{ cm}^{-3}$ .

**Table 1.** Yearly averages  $\pm$  1 standard deviation and medians (25th–75th) percentiles of the total, accumulation, Aitken, and nucleation number concentrations ( $\text{cm}^{-3}$ ).

	2015	2016	2017	2018	2019
$N_{ACC}$	$(2.4 \pm 2.4) \times 10^3$ 1650 (1000–2780)	$(2.0 \pm 2.3) \times 10^3$ 1190 (715–2130)	$(2.2 \pm 2.0) \times 10^3$ 1620 (963–2660)	$(2.1 \pm 2.1) \times 10^3$ 1570 (950–2500)	$(1.9 \pm 1.6) \times 10^3$ 1550 (967–2310)
$N_{AIT}$	$(4.3 \pm 3.3) \times 10^3$ 3230 (2090–5270)	$(3.8 \pm 3.2) \times 10^3$ 2760 (1740–4660)	$(4.2 \pm 3.2) \times 10^3$ 3270 (2120–5290)	$(4.1 \pm 3.3) \times 10^3$ 3020 (1990–4950)	$(3.8 \pm 2.8) \times 10^3$ 3000 (2000–4680)
$N_{NUC}$	$(1.1 \pm 1.8) \times 10^3$ 644 (324–1310)	$(1.2 \pm 2.2) \times 10^3$ 614 (313–1250)	$(2.1 \pm 3.0) \times 10^3$ 1222 (621–2470)	$(1.6 \pm 2.5) \times 10^3$ 888 (446–1780)	$(1.8 \pm 2.6) \times 10^3$ 1060 (553–2120)
$N_{TOT}$	$(7.8 \pm 5.8) \times 10^3$ 6020 (3970–9510)	$(7.0 \pm 5.9) \times 10^3$ 5010 (3160–8540)	$(8.5 \pm 6.2) \times 10^3$ 6730 (4410–10,700)	$(7.8 \pm 6.0) \times 10^3$ 5900 (3960–9400)	$(7.5 \pm 5.2) \times 10^3$ 6100 (4170–9210)



**Figure 2.** Monthly variation of particle number concentrations for the three size ranges, where the red, blue, and black lines represent the monthly percentage contribution to total particle number concentration of nucleation, Aitken, and accumulation ranges, respectively.

In general, the differences in aerosol PNCs are a consequence of the seasonal effects that could be explained by the higher emissions and lower Planetary Boundary Layer (PBL) height during autumn-winter with respect to spring-summer. In particular, the higher number concentration of particles during cold months is related to the domestic use of wood/biomass burning for home heating, which represents a significant emission source in autumn-winter as shown in recent source apportionment results at this site [24]. Along with that, the reduction of the atmospheric boundary layer

height and the greater atmospheric stability conditions, typical of the cold months, prevent the vertical dispersion of air pollutants that accumulate in the lower atmospheric layer with a consequent increase of particulate matter (PM) mass and number concentrations. The slightly higher levels of nucleation particles in warm periods are probably due to the higher frequency of new particle formation events, a feature observed in many other European sites [28]. The greater amount of biogenic precursor gases and higher photochemical activity, typical of this period of the year, together promote this process by explaining the higher frequency of events.

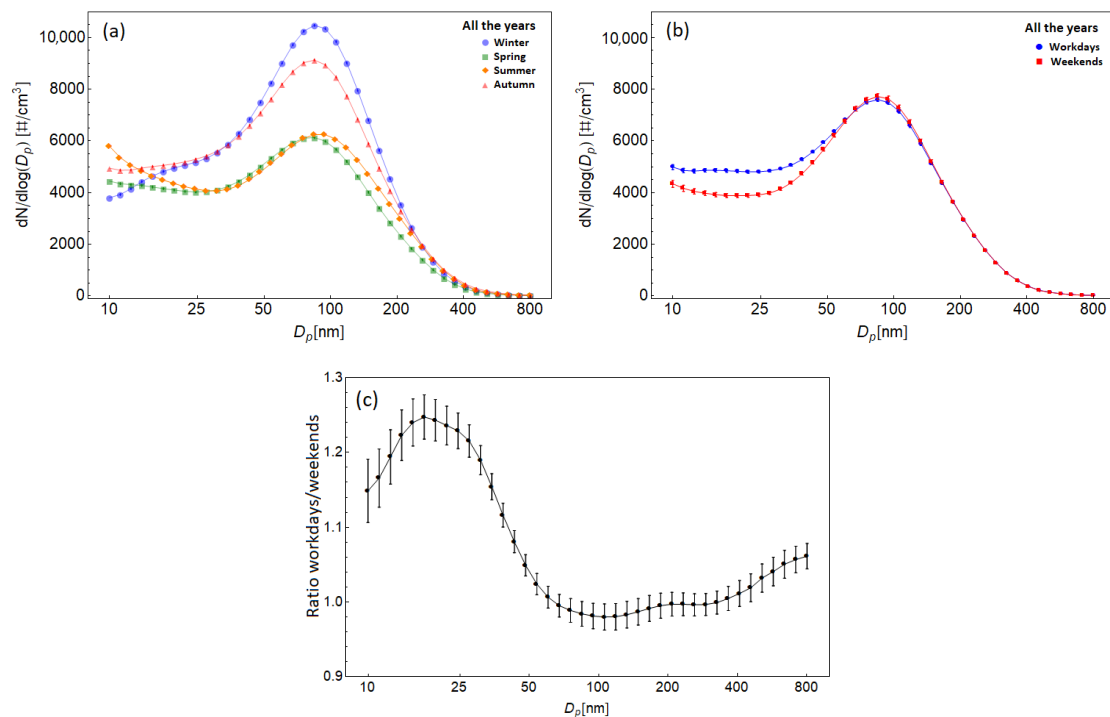
The different contributions of each size range to the total number and their different relationship offers, as a first-order approximation, some insight into the nature of particles (fresh or aged) and in the role of local sources. In this study, the Aitken particles mode were the main contributor to  $N_{TOT}$  accounting for about 52% (43–59%) of it, followed by the accumulation and nucleation modes with 27% (14–39%) and 21% (8–35%), respectively, throughout the observation period. This result is in agreement with that observed by [29,30] who found that in urban areas, influenced mainly by traffic emissions, the total particle number is dominated by the Aitken modes. This is supported by the significant correlation  $r = 0.82$  (Pearson's correlation coefficients) found between the Aitken and accumulation particles mode, pointing out that the two particle classes could be related to the same sources and processes. The observation site is influenced by direct emission of vehicular activity, inside the Campus and along the nearby roads that, as well known, is an important source of ultrafine particles from 30 nm up to some hundred nanometers [31,32]. On the contrary, the low correlation,  $r = 0.15$ , between the Aitken and nucleation particle mode is indicative of their different origin and/or atmospheric processes.

### 3.2. Variability of Particle Number Size Distribution

The size distribution of ambient particles is usually characterized by different modes (i.e., nucleation, Aitken, accumulation, and coarse mode) each of which reflects the dominant processes giving rise to levels of ambient particles [15]. In this work, the analysis of number size distributions showed the existence of two modes: one in the Aitken size range and another in the nucleation size range.

The results averaged over all years and separated for workdays, weekend and seasons, are shown in Figure 3. As can be seen, a strong seasonality is present in Figure 3a, with the lowest number concentrations in spring and summer, and highest in autumn and winter. The greatest variability in seasonal aerosol number size distribution concerns the Aitken particles mode, 20–200 nm, where each curve shows a maximum centered on median diameters around 90 nm. These seasonal differences tend to vanish for the accumulation particle, 200–800 nm, as shown by the overlapping curves. Seasonal variability was instead observed for the nucleation particle mode, 10 ÷ 20 nm, where the increase of number size distribution during the summer season is observable at very small diameters (10–15 nm) and is likely related to the larger frequency of nucleation events.

Figure 3b compares the particle number size distributions during workdays (blue dots) and weekends (red dots). In the size range between 50–800 nm, the two size distributions are similar to an intensity peak of  $7700 \text{ cm}^{-3}$  centered around 90 nm. In the size range between 10–50 nm, the number size distributions showed a different behavior, with number concentrations during weekends on average 20% lower compared to workdays, which are probably correlated to lower traffic activity during weekends. This behavior has been also confirmed by the different workdays/weekends ratio of aerosol number size distributions (Figure 3c), which varies from 0.98 to 1.25 as a function of particle size. For particles between 10 nm and 50 nm, the ratio is significantly higher than unity reaching a maximum of 1.25, highlighting a contribution of traffic source in this size range. Subsequently, in the size range between 50 nm and 400 nm, the ratio remains almost constant, around 1, but it increases again up to about 1.06 for particles larger than 400 nm. This last increase could be due to the influence of non-exhaust emissions, tires, brake wear, and resuspension of road dust [3], which are all connected to the variation of the traffic flow that is more intense on workdays than on weekends.



**Figure 3.** Particle number size distributions average over all years during different seasons (a), during workdays and weekends (b), and workdays/weekends ratio (c). Vertical bars represent the standard errors that are comparable with the size of symbols in part (a,b).

### 3.3. Daily Trends of Measured Number Concentrations

The daily evolution of total particle number concentrations was analyzed separating workdays and weekends/holidays. During different hours of the day, the particle number concentrations exhibited well-defined behavior with similar characteristics for the different years that can be directly related to human activities, in particular road traffic.

Figure 4 shows the daily trend of the size distribution averaged over the whole measurement period. It shows a larger concentration for particles around 100 nm in diameter late in the evening and during the first hours of the night. After this period there is a decrease and a successive increase starting from small particles (i.e., from 10 nm) in the morning rush hours (between 05:00 a.m. and 08:00 a.m.). A clear increase of particles in the nucleation size range is observed in the central hours of the day (between 09:00 a.m. and 02:00 p.m.). Figure 5 compares the daily trends of particle concentrations during workdays with those during weekends. Looking at Figure 5, high number of concentrations of particles were observed during the traffic rush hours, whether it was a workday or a weekend. The first peak in number concentration appeared on the morning rush hours, between 06:00 and 09:00 a.m., coincident with the beginning of the working day and school activity. In each year, the number concentrations are lower during weekends than workdays by about 20%, which could be correlated to lower traffic activity during weekends/holidays [4]. Subsequently, number concentration decreases to exhibit another peak of particles between 10:00 and 12:00 a.m., which is more visible for the years 2017 and 2019. This peak is related to new particle formation events. The differences among one year and the other arise from various combinations of factors, such as a different contribution of sources, meteorological conditions, and photochemical reactions.

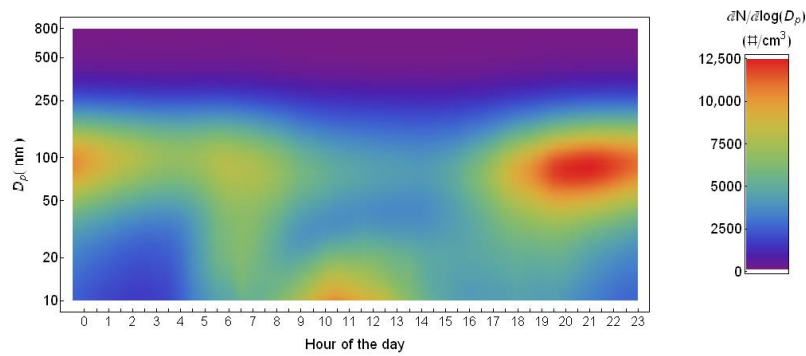


Figure 4. Average daily trend of size distribution.

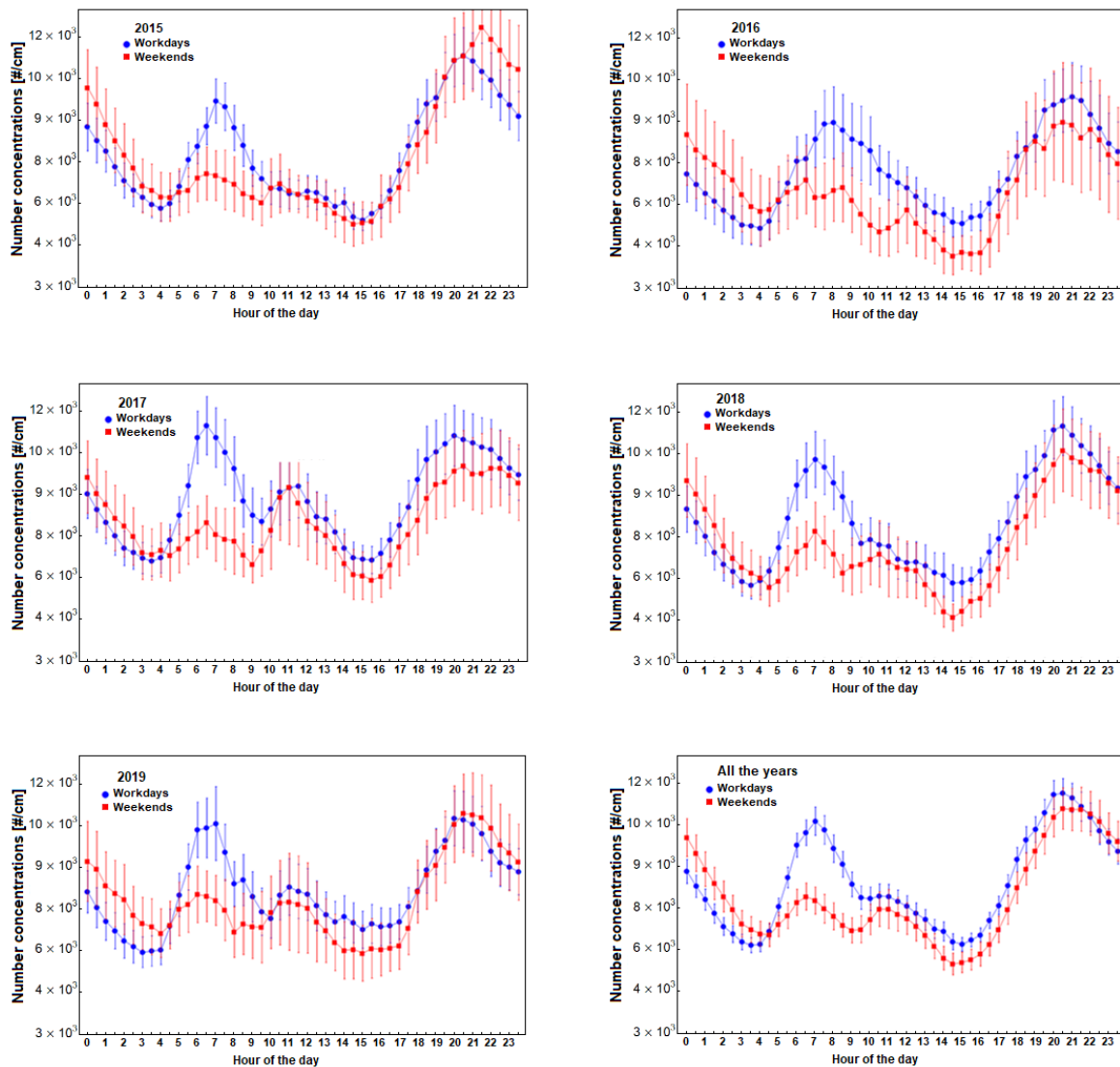


Figure 5. Temporal evolution of particle number concentrations, averaged on workdays (blue dots) and weekends (red dots), separately for each year and the whole measurement period. Vertical bars represent standard errors.

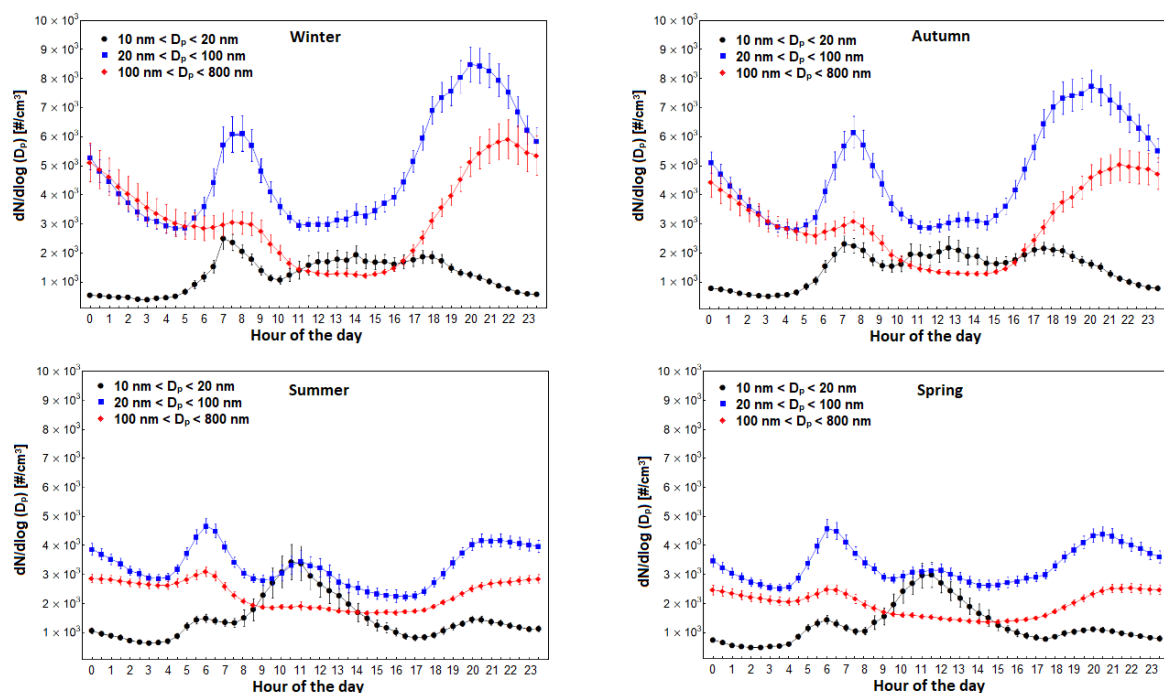
A third important peak of particles, with values higher than  $10,000 \text{ cm}^{-3}$ , appears in the evening, between 08:00 and 09:00 p.m., also attributable to the late evening rush hours traffic emissions (and to residential burning process during winter months). This peak reaches number concentrations higher than the morning peak, likely because it is also influenced by the lower height of the boundary-layer and

the stable conditions present during the late evening especially in autumn and winter. This behavior was observed also for mass concentrations at this site [23].

In all plots, the average number concentrations during weekends/holidays are lower compared to workdays with the exclusion of the night in which higher number concentrations are observed. This is due to a shift in the traffic in the area that is significantly larger late in the evening and night during weekends compared to workdays [33]. During the night, number concentrations slowly decrease until the early hours of the morning. On average, the number concentration drops by 30% between midnight and 3:00 a.m., when it reaches the minimum value. This occurs under stable atmospheric conditions, a shallower boundary layer, and smaller average wind speeds, developed during the night that are generally still present in the early hours of the day.

### 3.4. Seasonal Variation of Particle Number Concentration

The daily patterns of particle number concentrations were investigated for the different seasons. The different size ranges were averaged over the five years, considering Winter (December, January, February), Spring (March, April, May), Summer (June, July, August), and Autumn (September, October, November) seasons separately (Figure 6). Seasonal averages  $\pm 1$  standard deviation and medians with 25th and 75th percentiles were also calculated and summarized in Table 2 for each size range.



**Figure 6.** Temporal evolution of particle number concentration of  $N_{\text{NUC}}$  (black dots),  $N_{\text{AIT}}$  (blue dots), and  $N_{\text{ACC}}$  (red dots) over the four seasons, averaged over five years. Vertical bars represent standard errors.



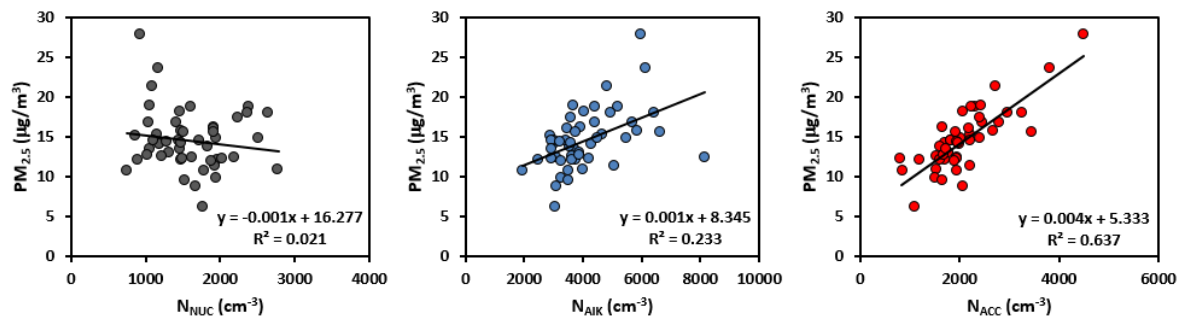
**Table 2.** Seasonal averages  $\pm 1$  standard deviation and median (25th–75th) percentiles of the accumulation, Aitken, nucleation, and total number concentrations ( $\text{cm}^{-3}$ ).

	Spring	Summer	Autumn	Winter
$N_{\text{ACC}}$	$(1.8 \pm 1.5) \times 10^3$ 1290 (793–2130)	$(2.0 \pm 1.1) \times 10^3$ 1750 (1230–2470)	$(2.1 \pm 2.0) \times 10^3$ 1570 (891–2660)	$(3.1 \pm 3.6) \times 10^3$ 1450 (764–3840)
$N_{\text{AIT}}$	$(3.7 \pm 2.7) \times 10^3$ 2980 (1940–4720)	$(3.2 \pm 2.1) \times 10^3$ 2730 (1880–4060)	$(4.3 \pm 3.4) \times 10^3$ 3270 (2080–5450)	$(5.5 \pm 4.5) \times 10^3$ 4000 (2340–7430)
$N_{\text{NUC}}$	$(1.4 \pm 2.0) \times 10^3$ 775 (387–1590)	$(1.6 \pm 2.3) \times 10^3$ 799 (403–1660)	$(1.8 \pm 2.5) \times 10^3$ 1030 (500–2100)	$(1.6 \pm 2.0) \times 10^3$ 934 (467–1850)
$N_{\text{TOT}}$	$(6.9 \pm 4.8) \times 10^3$ 5530 (3580–8700)	$(6.8 \pm 4.0) \times 10^3$ 5660 (3980–8370)	$(8.2 \pm 6.1) \times 10^3$ 6390 (4210–10,400)	$(10.2 \pm 8.0) \times 10^3$ 7370 (4260–14,000)

The particle number concentration of the Aitken mode (blue dots) shows a clear bimodal peak distribution over the autumn-winter and a triple-peak on spring-summer. The two common peaks, which are shown in all seasons, coincide with the morning and late evening traffic rush hours while midday peak, not visible in winter-autumn, may be explained by the process of the growth of particles from the nucleation mode.

The accumulation particles mode (red dots) have a pattern similar to Aitken particles mode, with the exclusion of the midday peak meaning that nucleation and growth processes have limited influence on this size range. Looking at the morning and evening peaks in the accumulation mode, it appears that they are weaker compared to Aitken size range suggesting that this size range is affected by mobile sources at a lower extent compared to smaller particles. It is instead evident that the modulation due to the daily trend of the mixing layer height can lead to higher or lower number concentrations according to the season and the hours of the day.

Each size range shows a different daily pattern with some changes between the cold and warm seasons. The particle number concentrations in the nucleation mode (black dots) are larger during diurnal hours with an increase in the morning and a decrease in the afternoon. The pattern has a peak at around 7:00 a.m. in winter-autumn and at around 6:00 a.m. in spring-summer likely due to local traffic sources. Another peak appears around 11:00–12:00 a.m. but it is relevant only in spring and summer, probably due to photochemical processes. This pattern is due to new particulate formation events and their frequency that is relatively high in spring and summer when climatic conditions and high concentrations of precursor species create suitable conditions to trigger the process [34–36]. Continuous daily measurements of  $\text{PM}_{2.5}$  is done at the observatory with a low-volume ( $2.3 \text{ m}^3/\text{h}$ ) automatic sampler [23]. The average  $\text{PM}_{2.5}$  concentration in the measurement period was  $15 \text{ g}/\text{m}^3$  presenting a clear seasonal trend with larger concentrations during the cold season autumn and winter (average  $16.6 \text{ g}/\text{m}^3$ ) compared to the warm season spring and summer (average  $13.3 \text{ g}/\text{m}^3$ ). This is in agreement with a previous source apportionment study at this site [24]. Correlations of monthly average  $\text{PM}_{2.5}$  concentrations with particle number concentrations in the three size ranges are reported in Figure 7. There is not a correlation between  $\text{PM}_{2.5}$  and  $N_{\text{NUC}}$  because these very small particles do not contribute significantly to mass concentration, the same happens for  $N_{\text{AIK}}$ . This may also be attributed to particle uptake by larger particles. Instead, there is a good correlation between  $\text{PM}_{2.5}$  and  $N_{\text{ACC}}$  suggesting that the accumulation mode particles give a contribution to mass concentrations.

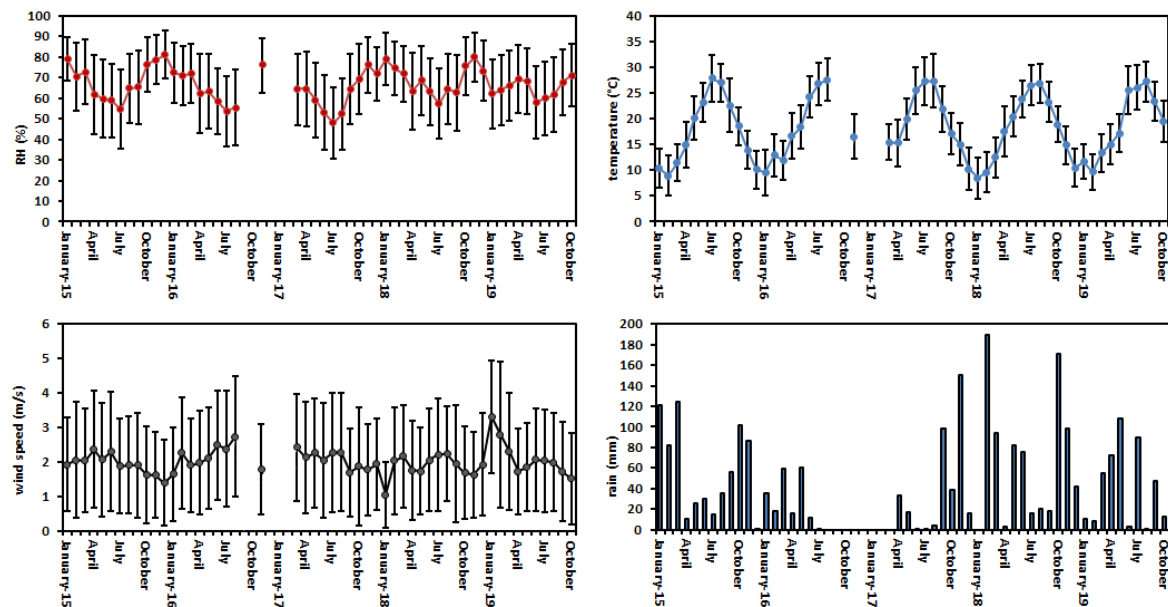


**Figure 7.** Correlation of monthly average  $PM_{2.5}$  concentration with particle number concentrations in the different size ranges (from left to right  $N_{NUC}$ ,  $N_{AIK}$ , and  $N_{ACC}$ ). The graphs include a linear fit.

The seasonal differences in number concentrations showed a clear and pronounced variability on Aitken and accumulation particles, with higher average values in winter, followed by autumn, spring, and summer. This variability was not observed in nucleation particles where the average values of particle number concentrations varied between  $1.4 \times 10^3 \text{ cm}^{-3}$  in spring and  $1.8 \times 10^3 \text{ cm}^{-3}$  in autumn.

### 3.5. Effects of Local Meteorological Conditions

In addition to the source strength and characteristics, the concentrations of aerosol particles are strongly dependent on the meteorological conditions. The observation site is characterized by the typical Mediterranean climate, with mild winters and high percentage levels of relative humidity (RH), hot summers, and low wind speed. Monthly variations in wind speed, temperature, RH, and rain accumulation during the five-year measurements are summarized in Figure 8.



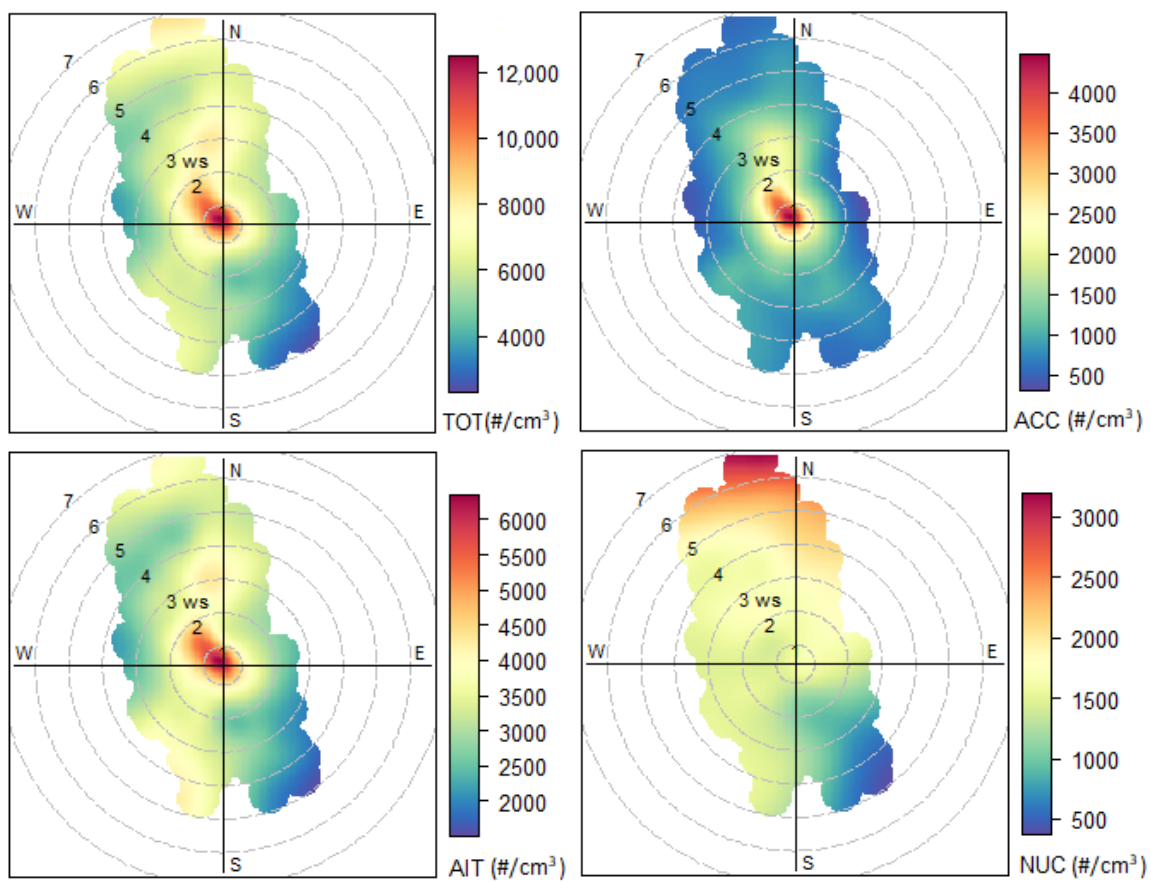
**Figure 8.** Monthly variations in temperature, relative humidity, wind speed, and rain accumulation observed in Lecce during the five-year measurements. Vertical bars represent the standard deviations.

A seasonal variation pattern was observed both for temperature and for RH. The average temperature ranged approximately from  $8 \text{ }^\circ\text{C}$  to  $28 \text{ }^\circ\text{C}$  between winter and summer, while average RH was lower in summer,  $\sim 48\%$ , than in other seasons  $\sim 81\%$ . However, no marked pattern was observed in the monthly average wind speed that ranged between  $1\text{--}3.3 \text{ m/s}$ . It rained most frequently in autumn-winter with an average of over  $70 \text{ mm}$  of precipitation, and less frequently in spring-summer with an average below  $30 \text{ mm}$ .

The correlation between the number concentration of particles, in the three modes, and meteorological parameters, both averaged by month, were calculated by Pearson coefficients, even if this approach could have some limitation in describing processes involving several meteorological parameters together, it could furnish some indications on the role of local meteorology on particle number concentrations. Considering precipitations, no correlation was observed, perhaps because of two factors: the first is that wet scavenging removes super-micrometric particles more efficiently [37] and the second is that the moderate precipitation levels of this area influenced the long-term average level of number concentrations only marginally.

It was found that particle number concentrations were negatively correlated to temperature, with Pearson coefficients of  $-0.70$  (Aitken size range) and  $-0.44$  (accumulation size range), and wind speed with Pearson coefficients of  $-0.46$  and  $-0.49$  in the Aitken, and accumulation particle modes, respectively. There was a positive correlation between RH and  $N_{AIT}$  and  $N_{ACC}$ , coefficients of  $0.66$  and  $0.45$ , respectively. No significant correlation was found between the  $N_{NUC}$  number concentration and wind speed ( $0.18$ ), temperature ( $0.04$ ), and RH ( $-0.16$ ). These results indicate that the dilution effect of wind and temperature, which promotes the dispersion of particles into the atmosphere reducing the number concentration, affects above all large particles. In addition, RH plays an important role as a catalyst in the hygroscopic growth of primary and secondary particles [38] through various processes such as nucleation, condensation, and evaporation which seems to be more relevant on  $N_{AIT}$  and  $N_{ACC}$ .

The influence of wind speed and direction on the particle number concentrations was also investigated using pollution roses. Figure 9 shows the pollution increase generated for each size range and total particle number concentration over the whole measurement period. The grey circles indicate wind speeds in  $1$  m/s intervals, while the color scales indicate particle number concentration. The analysis, related to  $N_{TOT}$ ,  $N_{ACC}$ , and  $N_{AIT}$ , revealed that the highest number concentrations were registered at very low wind speeds ( $<1$  m/s) and when weak winds ( $<2$  m/s) blew predominantly from the NW sector. This information suggests that the major sources of particle number concentrations are local and that a significant contribution comes from the NW sector where, at about  $500$  m away from the measurement site, there is a road affected by intense traffic (highlighted in green in Figure 1). The highest number concentrations of  $N_{NUC}$  were instead associated with higher wind speeds ( $6-7$  m/s) coming from the N-NNW direction, possibly indicating long-range transport and low contributions from local sources. For all size fractions, low concentrations were associated with the SSE-SE direction.



**Figure 9.** Pollution roses for each class of particle number concentrations,  $N_{TOT}$ ,  $N_{ACC}$ ,  $N_{AIT}$ , and  $N_{NUC}$  measured during the five-year period. Vertical color bars represent the number concentration.

#### 4. Conclusions

Five-years (2015–2019) continuous measurements of atmospheric particle number size distribution were conducted at the ECO Environmental-Climat Observatory of Lecce. In this study, the variability in aerosol total number concentrations as well as within specific size range was quantified for a time range from hourly to seasonal. During all period, particle number concentrations in the Aitken ( $20 < D_p < 100$  nm), accumulation ( $100 \text{ nm} < D_p < 800$  nm), and nucleation ( $D_p < 20$  nm) size ranges accounted for 52%, 27%, and 21% of total measured particle, respectively. In terms of seasonal differences, total, Aitken, and accumulation particles number concentrations showed more variability, with higher average values in winter compared to summer. The nucleation size range showed a lower seasonal variability with average values ranging between  $1.4 \times 10^3 \text{ cm}^{-3}$  in spring and  $1.8 \times 10^3 \text{ cm}^{-3}$  in autumn.

The total number concentration was usually significantly higher during workdays than during weekends/holidays in all years as also confirmed by the workday/weekend ratio, showing a strong correlation with traffic activities in the size range 10–50 nm. This correlation was also observed in daily patterns in correspondence of the morning and the late evening traffic rush hours. The peak in the number concentrations of nucleation mode observed in the midday of spring and summer was instead imputed to new particle formation events.

Pearson coefficients showed that there were distinct differences among the correlation of particle number concentrations in the three size ranges and meteorological parameters. Aitken and accumulation particles were negatively correlated to temperature (−0.70 and −0.44, respectively) and wind speed (−0.46 and −0.49, respectively) and positively correlated to RH (0.66 and 0.45, respectively), while no significant correlation was found with nucleation particles. Pollution increases

showed a similar trend for accumulation and Aitken particle number concentrations. Both size fractions had larger concentrations at low wind velocity or during wind calms, suggesting that they are dominated by local emission sources. Instead, the number concentration in the nucleation size range showed a different pattern with non-local sources, located in the NNW direction, strongly influencing concentration levels.

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