

1 Ventilation and low pollution enhancing new particle formation in 2 Milan, Italy

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21 **Abstract.** New particle formation (NPF) is a crucial process that significantly affects the number of atmospheric particles,
22 forming a substantial portion of the total aerosol population. Therefore, it has important implications for both human health
23 and climate. While extensive research has been conducted in rural areas of the Po Valley, Italy, there is a substantial lack of
24 continuous measurements with state-of-the-art instruments in Milan, one of the most industrialized and densely populated
25 cities in the region. This study aims to address this gap by analysing one year of detailed particle number size distribution
26 measurements between 1.2 and 480 nm at an urban background site in Milan. These data were used to examine the occurrence
27 and characteristics of NPF and to identify how the meteorological and air pollution conditions affect it. We show that a cleaner
28 atmosphere, meaning lower concentrations of air pollutants and lower condensation sink, and a higher ventilation promote
29 NPF. Detailed modelling of the air masses history further revealed that a longer residence time in the Po Valley and a greater
30 exposure to anthropogenic emissions inhibit NPF. Furthermore, we show that strong winds, particularly from the northwest
31 sector (e.g., Foehn winds), facilitate NPF, likely by reducing the condensation sink for precursor vapours. This locates Milan
32 among the urban sites where atmospheric cleaning enhances NPF, providing insights for urban air quality management.

33

34 **1 Introduction**

35 New particle formation (NPF) is a critical process happening in the atmosphere, consisting of the formation of molecular
36 clusters and their growth through the condensation of precursor vapors (Kulmala et al., 2013). These newly formed particles
37 play a vital role in influencing air quality (Kulmala et al., 2021). Ultrafine particles (UFP), i.e., particles smaller than 100 nm
38 in diameter, can reach the lungs, blood system, and brain, threatening human health (Schraufnagel, 2020; Vallabani et al.,
39 2023). Moreover, when newly formed particles grow in size, they can interact directly with the solar radiation or be activated
40 as cloud condensation nuclei (Gordon et al., 2017; Merikanto et al., 2009; Spracklen et al., 2008; Zhao et al., 2024), affecting
41 the radiative balance of the Earth and, therefore, the climate. WHO recommended the monitoring of UFP in 2021 (WHO,
42 2021), and, to comply with such recommendation, the European Union enforces their measurements on the member states with
43 the Ambient Air Quality Directive 2024/2881. European countries must monitor UFP at both urban and rural supersites, as
44 well as at UFP hotspots. Specifically, particle number concentration must be measured for particles larger than 10 nm, with no
45 limitation on the maximum size.

46

47 The Po Valley, in northern Italy, is a region of particular interest for studying NPF due to its unique geographical and
48 environmental characteristics. It is one of the most polluted areas in Europe (EEA, 2019), not only due to the intense and
49 diverse emissions (Kuenen et al., 2022), but also due to its enclosed position between the Alps and the Apennines, which
50 favors the accumulation of air pollutants due to the formation of a shallow boundary layer (Vecchi et al., 2004). Previous
51 research in this area has consistently highlighted the relevance of NPF events. The study by Rodríguez et al. (2005), including
52 data between June 1999 and December 2000, explored the relation between aerosol size distributions and air quality in Ispra,
53 a rural site in the Northern Po Valley, emphasizing the role of NPF in UFP number concentration. Their findings showed a
54 negative correlation between UFP number concentration and aerosol mass, underlining the weakness of the traditional air
55 quality metrics, like $PM_{2.5}$ and PM_{10} , which do not effectively capture UFP pollution. According to Rodríguez et al. (2005),
56 NPF events predominantly occurred under clean air conditions, often triggered by Foehn wind coming from the north, which
57 reduced the number of pre-existing particles and created favorable conditions for the new particles to grow. In contrast, polluted
58 conditions promoted the condensation of vapors on pre-existing particles. A study by Hamed et al. (2007) conducted over three
59 years at the rural site of San Pietro Capofiume, Po Valley, found that nucleation events occurred on 36% of the days, with the
60 highest frequency in spring and summer (peaking to $\sim 70\%$ in May and July) and the lowest in winter and autumn. Favorable
61 conditions for nucleation included higher temperature, wind speed, solar radiation, and SO_2 and O_3 concentrations, while
62 relative humidity and NO_2 levels were lower during event days. The back trajectory analysis indicated that air masses primarily
63 originated from the north and east during nucleation events, highlighting the significant impact of atmospheric circulation on
64 NPF.

65 Supporting the NPF relevance in the area, Kontkanen et al. (2016) reported frequent NPF (86% of days) during a 1-month
66 summer campaign at the same site. Focusing on sub-3 nm clusters, this study indicated high cluster concentrations also during

67 high condensation sink (CS) episodes and non-NPF events, hinting at a continuous formation of the smallest particles. During
68 NPF days, cluster formation peaked with the decrease of CS and relative humidity and the increase in boundary layer height
69 (BLH), highlighting the role of atmospheric dynamics in the process. Sulfuric acid was identified as a potentially relevant
70 precursor to the NPF process. More recent findings by Cai et al. (2024), including direct measurements of the NPF precursor
71 vapors, supported these observations, showing that NPF events occurred on approximately 66% of days during a two-month
72 spring campaign in San Pietro Capofiume, confirming favorable conditions for NPF in this region. During these events, high
73 concentrations of sulfuric acid ($8.5 \cdot 10^6 \text{ cm}^{-3}$) were detected, underlining its crucial role in NPF, alongside ammonia and
74 amines. These studies collectively suggest that NPF substantially contributes to the UFP number concentration and overall
75 pollution levels in this area, underscoring its importance for both regional air quality and climate. All the previously cited
76 studies, though, refer to rural areas, while none provide a detailed study of NPF in urban areas of the Po Valley.

77

78 Several factors differentiate rural and urban environments in regard to NPF. The higher CS in urban areas (Bae et al., 2010;
79 Cai et al., 2024) can suppress NPF, as the available precursor vapors tend to condense onto existing particles rather than
80 forming new ones (Seinfeld and Pandis, 2016). The availability, chemical composition, and temporal variation of precursor
81 vapors are also different in rural and urban areas, as they are affected by human activities and local sources, such as traffic.
82 The work by Nieminen et al. (2018), for example, showed that formation rates generally increase with an increasing
83 anthropogenic influence in the atmospheric composition, highlighting the importance of anthropogenic vapors in the NPF
84 process. Urban environments are characterized by various emission sources that release both potential precursor vapors and
85 particles across a wide size range, largely complicating the observation of NPF. Thus, in such settings, distinguishing between
86 primary and secondary particles is challenging. Therefore, studying NPF in urban areas requires a comprehensive approach
87 that accounts for the complex interplay of various processes, including emissions, atmospheric chemistry, and meteorological
88 conditions. Understanding these interactions is essential for accurately characterizing the NPF mechanism in such
89 environments. Several studies have already been conducted in urban sites across the world, such as the Chinese megacities
90 (Dai et al., 2023; Guo et al., 2014; Yao et al., 2018) and European cities (Brean et al., 2020; Salma et al., 2011), which are
91 discussed in Sect. 3.2. Within this context, the city of Milan provides a particularly complex environment for investigating
92 NPF. As a major metropolitan area within the Po Valley, Milan is characterized by high population density, intense traffic,
93 and significant industrial activities. Its geographical location further aggravates air quality challenges, as atmospheric
94 stagnation often leads to the accumulation of pollutants (Vecchi et al., 2004). This combination of factors makes Milan an
95 important hotspot for studying air quality and the processes driving NPF in urban settings.

96

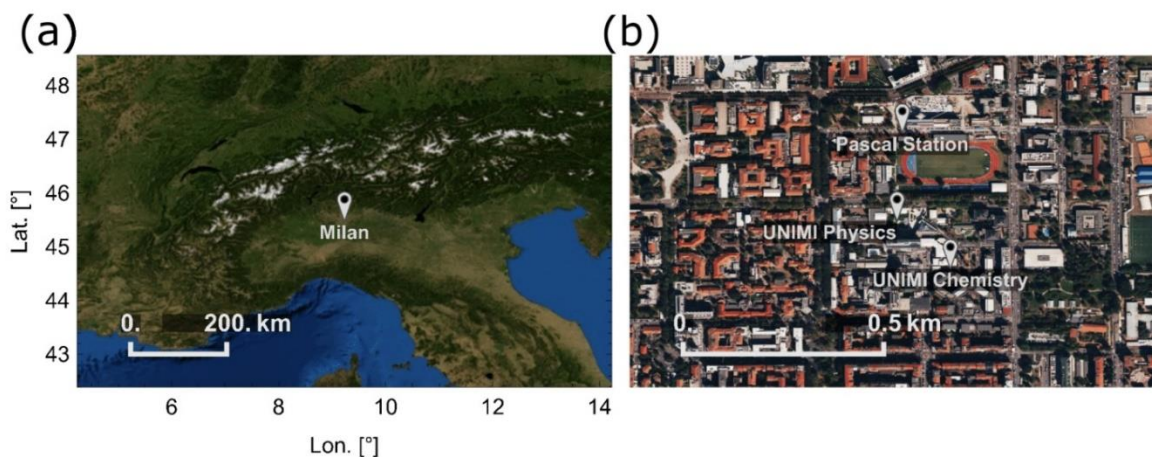
97 In this study, we present a one-year measurement campaign conducted at an urban background site in Milan between the end
98 of March 2023 and the end of March 2024, as ancillary measurements to the activities foreseen by the European project Ri-
99 Urbans (<https://riurbans.eu>). The main objective was to quantify the intensity, characteristics, and driving mechanisms of NPF.
100 By integrating measurements of particle number size distributions, air pollutant concentrations, and meteorological conditions,

101 along with outputs from the FLEXible PARTicle dispersion model (FLEXPART), we investigated the key factors governing
102 NPF. By presenting a dataset of particle number size distributions extending down to 1.2 nm, we also show the importance of
103 extending size distribution measurements below 10 nm, especially in relation to the European air quality directive 2024/2881.

104 2 Data and methods

105 2.1 Location description

106 Milan is located in the Po Valley (Fig. 1a) at the coordinates 45.47°N, 9.19°E, at an altitude of 120 m a.s.l. It is the most
107 populated city of the Po Valley with a population of ~1.4 million, reaching ~3.2 million when considering the entire
108 metropolitan area (ISTAT, 2024). Our measurements were taken in an urban background area, referred to as the Pascal area
109 (Fig. 1b) due to the presence of the Pascal air quality monitoring station of the regional environmental agency (ARPA
110 Lombardia). The area is located in the eastern part of the city of Milan, and the instruments were installed at the Physics
111 (45.4764°N, 9.2317°E) and Chemistry (45.4754°N, 9.2329°E) Departments of the University of Milan (UNIMI). This is an
112 urban background area, which is affected by several sources of pollution, such as traffic, domestic heating, and transported
113 industrial and agricultural emissions (Colombi et al., 2023).



114
115 **Figure 1:** a) Location of the Po Valley and specifically Milan, in white pin; b) focus on the Pascal area, where the measurement sites
116 (ARPA Lombardia Pascal station, Physics Department of UNIMI, and Chemistry Department of UNIMI) are located. The satellite
117 maps were generated using Mathematica 14.1 (Wolfram Research, 2025) with imagery from Bing Maps (Microsoft, last access: April
118 17th, 2025). Imagery © Microsoft Corporation, Bing Maps.

119 2.2 Size distribution data

120 Our size distribution measurements were performed with a set of three instruments: a TSI Scanning Mobility Particle Sizer
121 (SMPS), an Airedt Neutral cluster and Air Ion Spectrometer (NAIS), and an Airmodus A11 nano-Condensation Nucleus
122 Counter (nCNC) system, combining an Airmodus A10 Particle Size Magnifier (PSM) and an Airmodus A20 Condensation

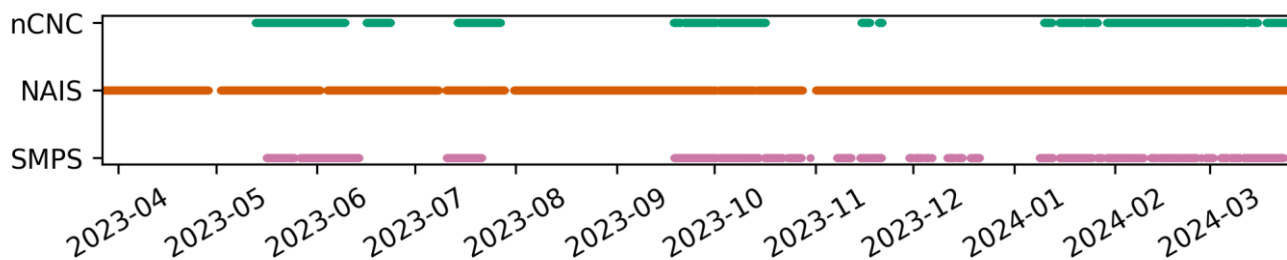
123 Particle Counter (CPC). The nCNC and the SMPS were located on the second floor of the Chemistry Department of UNIMI
124 and measured particle number size distributions between 1.2 and 3 nm (Lehtipalo et al., 2022) and between 11 and 480 nm,
125 respectively. The NAIS measured number size distributions of particles with a diameter between 2.5 and 40 nm and of positive
126 and negative ions with a diameter between 0.8 and 40 nm (Manninen et al., 2016; Mirme and Mirme, 2013). The instrument
127 was located on the first floor of the Physics Department of UNIMI, at a distance of about 160m from the nCNC and SMPS
128 measurements. While the difference in location between the NAIS and the other instruments may have introduced some
129 uncertainty, all inlets faced the interior of the University's yard, which is not constantly affected by one specific source (for
130 example, traffic), and can, therefore, be considered representative of Milan urban background. For this reason, the combination
131 of the data by these instruments was considered reasonable regardless of their different location. The NAIS measurements
132 began in March 2023 and ended in February 2025, while those of the nCNC and the SMPS started in May 2023 and ended in
133 March 2024. The particle number size distribution data between March 27th, 2023, and March 26th, 2024 were used for this
134 study.

135 Considering the high number concentration of sub-3nm particles in the city, the nCNC was equipped with an Airmodus
136 Nanoparticle Diluter (AND; Lampimäki et al., 2023) running with a dilution factor of 5 and measuring instrumental
137 background automatically three times a day for 8 minutes. The system was run with a core sampling inlet, as integrated into
138 the AND design. Using a dry flow for the dilution, the AND also acted as a dryer. The AND inlet consisted of a 40 cm stainless
139 steel tube sampling ambient air at a flow rate of about 6 L min⁻¹, while the PSM, connected to the AND through a conductive
140 tube, worked with a flow rate of 2.5 L min⁻¹. The nCNC measured in scanning mode with saturator flow scanning between 0.1
141 L min⁻¹ and 1.3 L min⁻¹. Each scan lasted 4 minutes. To guarantee the correct functioning of the instrument, several checks
142 and cleaning procedures were applied. Every week, both the PSM and the CPC were drained, and their connection was cleaned
143 with isopropanol and compressed air. The involved flows and the background were also manually checked. Flushing of the
144 PSM was performed once every two weeks, while the inlet line was cleaned once a month. The overall status of the instrument
145 was checked almost every day. The data from the nCNC were inverted using the kernel inversion method and applying the
146 corrections for the background, the detection efficiency, the dilution factor, and the inlet losses, estimated to be between 20
147 and 9.3%, depending on the particle size (Lehtipalo et al., 2022).

148 The SMPS (Wang and Flagan, 1990), consisting of a 3080 TSI classifier, a 3081 TSI DMA, and a 3772 TSI CPC, was equipped
149 with a stainless steel inlet drawing 1 L min⁻¹ of ambient air, a 4.9 kV X-ray tube to provide particles with a known charge
150 distribution, and with a silica gel dryer to reduce the relative humidity of the air sample. The DMA scanned between ~10 V
151 and ~9700 V during a cycle of 3 minutes, producing size distributions between 11 nm and 480 nm. Weekly checks of the
152 performance of the instrument included CPC draining and flow checks. The inlet line was cleaned once a month with
153 isopropanol and the silica gel was regenerated when needed. The data were inverted using the TSI Aerosol Instrument Manager
154 program. The data were corrected for counting errors due to multiple charging. For both the nCNC and the SMPS, no clear
155 step changes associated with cleaning were identified and any observed variations did not indicate clear effects of the cleaning
156 procedures.

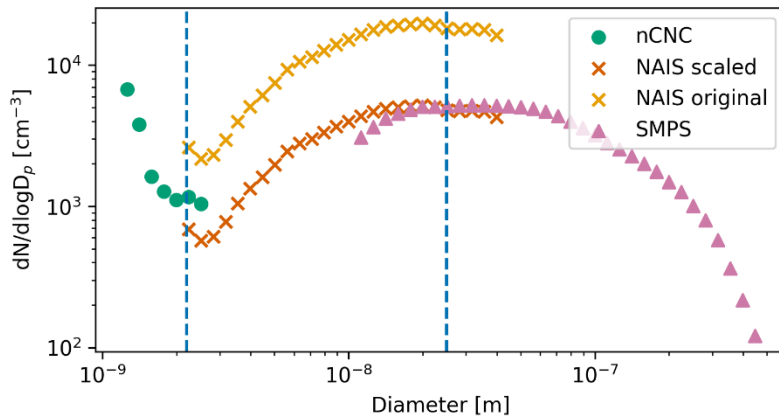
157 The NAIS was equipped with a 50 cm copper inlet followed by a downward bend to prevent rain from entering the instrument,
158 resulting in a total inlet length of approximately 60 cm. Ambient air was sampled at a flow rate of 54 L min⁻¹. The instrument
159 measured in particle, ion, and offset mode, changing mode every 90 seconds. Considering the high inlet flow rate of the NAIS,
160 drying the sample flow was not possible. Instrument cleaning was performed when needed. Concentration increases in specific
161 size bins were used as indicators of electrometer noise and to identify the need for cleaning. These artificially high
162 concentrations were manually excluded from the analysis, and no clear systematic step changes associated with cleaning were
163 observed. The measured data were inverted automatically by the Spectop software following the procedure described by Mirme
164 and Mirme (2013). The data were then corrected for inlet losses (between 15% and 0.1%, depending on the particle size;
165 Gormley and Kennedy, 1948) and ion calibration (Wagner et al., 2016). The final particle number size distributions were
166 obtained by averaging those from the positive and negative columns.

167 Figure 2 illustrates the data availability throughout the campaign. Of all the instruments, the NAIS provided the most
168 comprehensive data coverage, recording data on approximately 95% of the time. On the other hand, the nCNC and SMPS
169 recorded data for about 40% and 42% of the time, respectively. Measurement gaps mostly resulted from technical challenges,
170 including high summer temperatures, power outages, CPC flooding, and delays in equipment shipments.



171
172 **Figure 2: Particle number size distribution data availability throughout the campaign.**

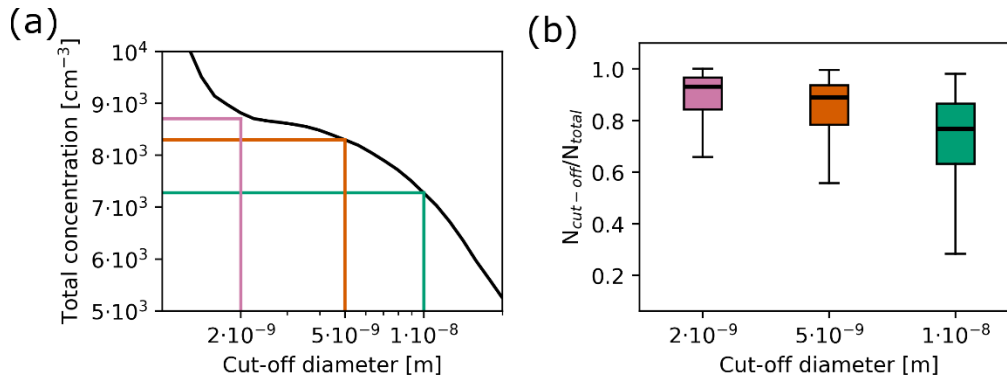
173 The total size distributions were obtained by combining the nCNC, NAIS, and SMPS data. First of all, all the data were
174 resampled to a 15-minute time resolution and rebinned to a diameter resolution of 0.05 in log₁₀ scale. Then, the median size
175 distributions of the three instruments were compared for the periods when all three instruments were operating simultaneously
176 (Fig. 3). A scaling factor of 3.8 was applied to the NAIS data, following the approach proposed by Dada et al. (2023). The
177 scaling factor was obtained by comparing the NAIS and SMPS data in the overlapping size region. Then, the number size
178 distributions from the three instruments were combined using the concentrations measured by the nCNC for the particles
179 smaller than 2.2 nm, by the NAIS for the particles in the 2.2-25 nm size range, and by the SMPS for the particles larger than
180 25 nm. Using the SMPS as a reference instrument, an artifact at the connection between the nCNC and the NAIS data was
181 created.



182

183 **Figure 3: Median particle number size distributions measured by the nCNC, the NAIS (original and scaled), and the SMPS. The**
 184 **medians were calculated using only the periods when all the instruments were measuring simultaneously. The blue vertical lines**
 185 **mark the diameters at which the size distributions were combined.**

186 The relevance of UFP has led the European Union to enforce the measurement of their number concentration. As reported in
 187 Sect. 1, a 10 nm cut-off was chosen to define UFP. In Fig. 4, the total particle number concentration for different cut-off sizes
 188 was calculated by integrating the size distribution from different lower limits (2 nm, 5 nm, and 10 nm) to the upper limit of
 189 480 nm. In our dataset, lowering the threshold from 10 nm to 5 nm would result in an average increase of 14%, whereas
 190 adopting a 2 nm cut-off would lead to a 19% increase (Fig. 4a). Fig. 4b shows the variability of the ratio between the
 191 concentration for a certain cut-off size (2, 5, 10 nm) and the total particle number concentration. These considerations highlight
 192 the potential impact of measurement thresholds on reported UFP number concentrations and emphasize the importance of
 193 detailed measurements of sub-10 nm particles. While the availability and complexity of the instrumentation pose significant
 194 challenges to measuring sub-10 nm particles, the dataset presented in this work demonstrates the value of extending the
 195 measurements below 10 nm.



196

197 **Figure 4: a) Total particle number concentration for different cut-off sizes, averaged over the entire campaign time. The green line**
 198 **marks the cut-off diameter of 10 nm, the orange one of 5 nm, and the pink one of 2 nm; b) boxplots representing the ratio between**
 199 **the concentration for different cut-off diameters ($N_{\text{cut-off}}$) and the total particle number concentration (N_{total}). In each boxplot, the**
 200 **box represents the interquartile range, between the 25th and the 75th percentile, and the median (50th percentile) is shown as a**

201 horizontal line inside the box. The whiskers of the boxplot extend from the edges of the box to the smallest and largest values within
202 1.5 times the interquartile range. Outliers are not shown in this figure.

203 2.3 Complementary data

204 The study used meteorological and air pollutant concentration data provided by ARPA Lombardia, the regional environmental
205 agency responsible for managing multiple monitoring stations across the area. For the analysis, data from the Pascal station,
206 situated approximately 250 m from the UNIMI buildings, were utilized. The meteorological dataset included variables such as
207 atmospheric temperature, wind speed and direction, radiation, and relative humidity. The pollutant concentrations included
208 PM₁₀, PM_{2.5}, NO₂, SO₂, O₃, NO_x, ammonia, and equivalent black carbon (eBC, Savadkoohi et al., 2024).

209 ARPA Lombardia also provided BLH data from the nearby station of Milano Parco Nord. The BLH was estimated using the
210 Gryning-Batchvarova model for the daytime convective boundary layer (Batchvarova and Gryning, 1991) and the Zilitinkevich
211 model for the nocturnal stable boundary layer (Zilitinkevich and Baklanov, 2002). Both models used turbulence variables that
212 were measured by ARPA Lombardia with a triaxial ultrasonic anemometer at the Milano Parco Nord station. The choice of
213 the appropriate model was based on the assessment of the boundary layer stability, determined from the sensible heat flux,
214 also measured by the ultrasonic anemometer at the same site.

215 Briefly, the Gryning-Batchvarova model describes the daytime convective boundary layer using a simplified analytical
216 approach. The profiles of the main variables are schematized considering that, throughout the boundary layer, each variable
217 assumes a constant value equal to its vertical mean, the entrainment layer is considered to be of infinitesimal thickness, and
218 that, at the entrainment layer, there is a characteristic discontinuity for each variable. For the assessment of the stable boundary
219 layer, Zilitinkevich et al. (2007) developed theoretical models considering simple equilibrium regimes in a step-by-step
220 approach. They applied Large Eddy Simulation to validate their theoretical multi-limit BLH formulation, which reduces to
221 known asymptotic limits in the neutral and nocturnal stable regime. Indeed, the stable and neutral BLH evolution is controlled
222 by factors (e.g., baroclinic shear, large-scale vertical velocity at the top of the boundary layer, non-stationarity of the boundary
223 layer and its horizontal heterogeneity) that are difficult to measure and to use for the validation of the theory.

224 All data were provided with an hourly time resolution.

225 Using these datasets, we calculated the daily ventilation index (VI), which reflects the potential of pollutants to disperse
226 efficiently through proper ventilation. For each day, this index is defined as:

$$227 VI = \text{mean}(ws) \cdot \max(BLH), \quad (1)$$

228 where ws is the wind speed, and BLH is the boundary layer height during that day.

229 In line with ARPA Lombardia guidelines, a VI value of 400 m² s⁻¹ was used as threshold to identify stagnant days.

230 2.4 Tools and parameters

231 2.4.1 Nano-particle ranking

232 The NPF occurrence was assessed through the nano-particle ranking analysis (Aliaga et al., 2023). This method provides an
233 automated, continuous, and objective way of analyzing NPF compared to the manual NPF classification based on the visual
234 inspection of the data and on the identification of a few discrete classes (Dal Maso et al., 2005). The method consists in
235 assessing the intensity and probability of NPF using the change in the concentration of 2.5-5 nm particles during each day.
236 The total concentration of 2.5-5 nm particles from the NAIS, $N_{2.5-5}$, was used to identify the NPF active and background time
237 windows as described by Aliaga et al. (2023), paying particular attention to minimize the impact of traffic rush hours from the
238 active time period, considering that Milan is an urban site. The active region was defined as between 10 and 16 Central
239 European Time (UTC+1), and the background between 23 and 5 Central European Time (UTC+1). The ranking value
240 ($\Delta N_{2.5-5}$) for day i was, then, calculated as follows:

$$241 \Delta N_{2.5-5,i} = \max(N_{2.5-5,i_{active}}) - \text{median}(N_{2.5-5,i_{background}}). \quad (2)$$

242 The ranking values were then ordered according to their magnitude to determine the percentile rank of each day. The percentile
243 rank of each day indicates the proportion of days with lower $\Delta N_{2.5-5}$ than the value of such day. Therefore, the days with a
244 lower percentile rank have lower $\Delta N_{2.5-5}$, indicating weaker NPF than those with higher percentile rank.

245 2.4.2 Model simulation

246 The Weather Research and Forecasting (WRF) model (v3.71), a regional meteorological model, was employed in this study.
247 The model was driven by data from the National Centers for Environmental Prediction (NCEP) Climate Forecast System
248 (CFSv2), with a temporal resolution of 6 hours and a horizontal resolution of 1° . For the simulation, the WRF model was
249 configured over a domain with a spatial resolution of $18 \times 18 \text{ km}^2$ (Fig. S1) centered on Milan and roughly covering Europe.
250 WRF simulations were performed using the Rapid Radiative Transfer Model radiation scheme (Mlawer et al., 1997), the
251 Thompson aerosol-aware microphysics scheme (Hong et al., 2004), the Monin-Obukhov surface-layer scheme (Janjic, 2003),
252 and the NOAA Land Surface Model scheme (Chen and Dudhia, 2001). The Mellor-Yamada-Janjic turbulent kinetic energy
253 (TKE) scheme (Janjic, 1994) was chosen to assess the boundary layer. WRF simulations were performed on 33 vertical sigma
254 layers. Annual anthropogenic emission fluxes for SO_2 and NO_x (see for example, the map of NO_x emissions in Fig. S2) were
255 retrieved from the CAMS datasets at $0.1 \times 0.1^\circ$ (around 10 km) horizontal resolution and distributed hourly over the
256 investigated period, with temporal profiles based on the EMEP MSC-W model (Simpson et al., 2012). The FLEXPART
257 (FLEXible PARTicle dispersion) model, a Lagrangian particle dispersion model, was used to simulate particle transport in the
258 backward direction. In this study, we utilized version 3.3.2 of FLEXPART (Brioude et al., 2013) for backward dispersion to
259 identify the source regions of the air masses reaching Milan. The model was driven by the meteorological data generated from
260 the WRF simulation, with input provided at a temporal resolution of 15 minutes. The FLEXPART domain was aligned with
261 the resolution and extent of the WRF domain. The vertical structure of the domain included 12 levels, spanning from ground

262 level to an altitude of 9000 meters. To conduct the simulation, 10000 particles were released every hour from Milan over the
 263 period between April 1st, 2023, and March 31st, 2024. These particles, treated as passive tracers, were emitted from an altitude
 264 between 0 to 100 meters above ground level within an $18 \times 18 \text{ km}^2$ area centered on the city. Their trajectories were traced
 265 backward in time for up to 72 hours. The backward-mode output from FLEXPART provided the source-receptor relationship
 266 (SRR), expressed in units of s, which represents the relative residence time of the particles within each grid cell, offering
 267 insights into the contribution of specific regions to the air masses arriving in Milan.

268 2.4.3 Condensation sink

269 The condensation sink (CS) refers to the rate at which vapors condense onto pre-existing particles in the atmosphere. The CS
 270 is influenced by the diffusivity of the condensing molecules, the size distribution of the particles, and the environmental
 271 conditions (Kulmala et al., 2012). It is estimated as:

$$272 \quad CS = 4\pi D \sum_{d_p'} \beta_{m,d_p'} d_p' N_{d_p'}, \quad (3)$$

273 where D is the diffusion coefficient of the condensing vapor in the air (sulfuric acid was assumed), d_p' the particle diameter,
 274 and $N_{d_p'}$ the concentration of particles with diameter d_p' . β_m was calculated using the Fuchs-Sutugin approximation (Fuchs
 275 and Sutugin, 1971). The CS was calculated only when both NAIS and SMPS data were available, using the original data
 276 without making assumptions about water. This introduces some uncertainty in the CS values as the NAIS measured a wet flow
 277 while the SMPS one was dried.

278 2.4.4 Formation rate

279 The formation rate (J) refers to the rate at which new particles appear in a given size range due to nucleation, growth into that
 280 size range, or emissions. If the selected size is small enough, it can be assumed that NPF is the main process forming new
 281 particles, although the contribution of traffic emissions cannot be excluded in urban environments (Rönkkö et al., 2017). $J_{1.5}$,
 282 J_3 , and J_7 were calculated according to the following definition (Kulmala et al., 2012) for the days with a complete size
 283 distribution:

$$284 \quad J_{d_p} = \frac{dN_{d_p}}{dt} + CoagS_{d_p} N_{d_p} + \frac{GR}{\Delta d_p} N_{d_p}, \quad (4)$$

285 where $CoagS_{d_p}$ is the coagulation sink at size d_p , GR is the growth rate and N_{d_p} is the particle number concentration at size
 286 d_p . Particle number concentrations in the 1.5-3 nm, 3-7 nm, and 7-20 nm size ranges were used to calculate $J_{1.5}$, J_3 , and J_7 ,
 287 respectively.

288 The coagulation sink is the rate at which particles are lost due to coagulation with pre-existing particles (Kulmala et al., 2012):

$$289 \quad CoagS_{d_p} = \sum_{d_p'=d_p}^{d_p'=d_{pmax}} K(d_p, d_p') N_{d_p'}, \quad (5)$$

290 where $K(d_p, d_p')$ is the coagulation coefficient between particles of diameter d_p and d_p' .

291 The growth rate (GR) indicates the rate at which particles increase in size over time. Considering the limited variability of its
 292 values (Kulmala et al., 2022), the GR was estimated using the daily median size distribution surface plot calculated over all
 293 days with NPF rank above the 80th percentile. The GR was computed for the size ranges of 3-7 nm, 7-20 nm, and 20-100 nm
 294 with the maximum concentration method (Kulmala et al., 2012) to evaluate $J_{1.5}$, J_3 , and J_7 , respectively (Kerminen et al.,
 295 2018).

296 The GR values were calculated using a size interval around the upper limit of the one used for the J calculation, in order to
 297 estimate the growth out of the size bin.

298 The uncertainty associated with this method for the estimation of GR and J is discussed in the Supplementary Materials.

299 **2.4.5 Sulfuric acid proxy calculation**

300 A proxy for sulfuric acid concentration was calculated using the approach described by Dada et al. (2020). The equation for
 301 the concentration of sulfuric acid in an urban site was used (Dada et al., 2020):

$$302 [H_2SO_4] = -\frac{CS}{2 \cdot (9.9 \cdot 10^{-9})} + \left[\left(\frac{CS}{2 \cdot (9.9 \cdot 10^{-9})} \right)^2 + \frac{[SO_2]}{9.9 \cdot 10^{-9}} (1.6 \cdot 10^{-9} \cdot GlobRad) \right]^{1/2}, \quad (6)$$

303 where $[SO_2]$ is the SO_2 concentration, $GlobRad$ is the global radiation, and CS is the condensation sink.

304 **2.4.6 Air mass exposure**

305 To investigate the impact of the air masses on NPF, we adapted the air mass exposure (AME) methodology originally proposed
 306 by Hakala et al. (2022). In their method, AME calculations combined FLEXPART output with static two-dimensional fields
 307 to identify when air masses were exposed to different pollutant emissions.

308 In this study, we modified the AME calculation by incorporating FLEXPART output with three-dimensional emissions
 309 (calculated as mentioned in section 2.4.2), including temporal variations, following the approach used by Bettineschi et al.
 310 (2025). For each particle release event, we computed the AME for a specific pollutant or substance x (denoted as AME_x) using
 311 emission data for that substance derived from the emission model (emiSURF) output. This approach allowed us to account for
 312 the temporal variability of emissions within air masses, enabling a more precise evaluation of the exposure of air masses to
 313 pollutant emissions.

314 Given a domain Ω , containing time (t), height (h), longitude (x) and latitude (y) as coordinates, and a release time (τ), the
 315 AME_x for a specific τ is calculated according to the following equation:

$$316 AME_x(\tau) = \sum_{(t,x,y) \in \Omega} \sum_{h=0}^{500m} SRR(t, x, h, y; \tau) \cdot X(t, x, y). \quad (7)$$

317 **2.4.7 Air mass trajectories description**

318 To clearly visualize the origin of the air masses, the trajectory density was defined as the absolute difference between the
 319 percentage of trajectories passing over each grid cell, regardless of their height, and arriving in Milan on days with NPF rank
 320 above the 80th percentile, and the percentage of all trajectories passing over the same area:

321 $\Delta\%T = \%T_{>80} - \%T_{tot}$. (8)

322 Specifically,

323 $\%T_{>80}(x, y) = \frac{\sum_{\tau \in T_{80}} \delta(\tau; x, y)}{N_{80}}$, (9)

324

325 $\%T_{tot}(x, y) = \frac{\sum_{\tau \in \Omega} \delta(\tau; x, y)}{N_{tot}}$, (10)

326 where T_{80} is the set of releases arriving when the percentile rank is larger than 80, N_{80} is the total number of these releases,

327 N_{tot} is the total number of releases and, $\delta(\tau; x, y)$ assumes 1 or 0 values as follows:

328 $\delta(\tau; x, y) = \begin{cases} 1 & \text{if } \sum_{(t,h) \in \Omega} SRR(t, h; x, y, \tau) > 0 \\ 0 & \text{otherwise} \end{cases}$. (11)

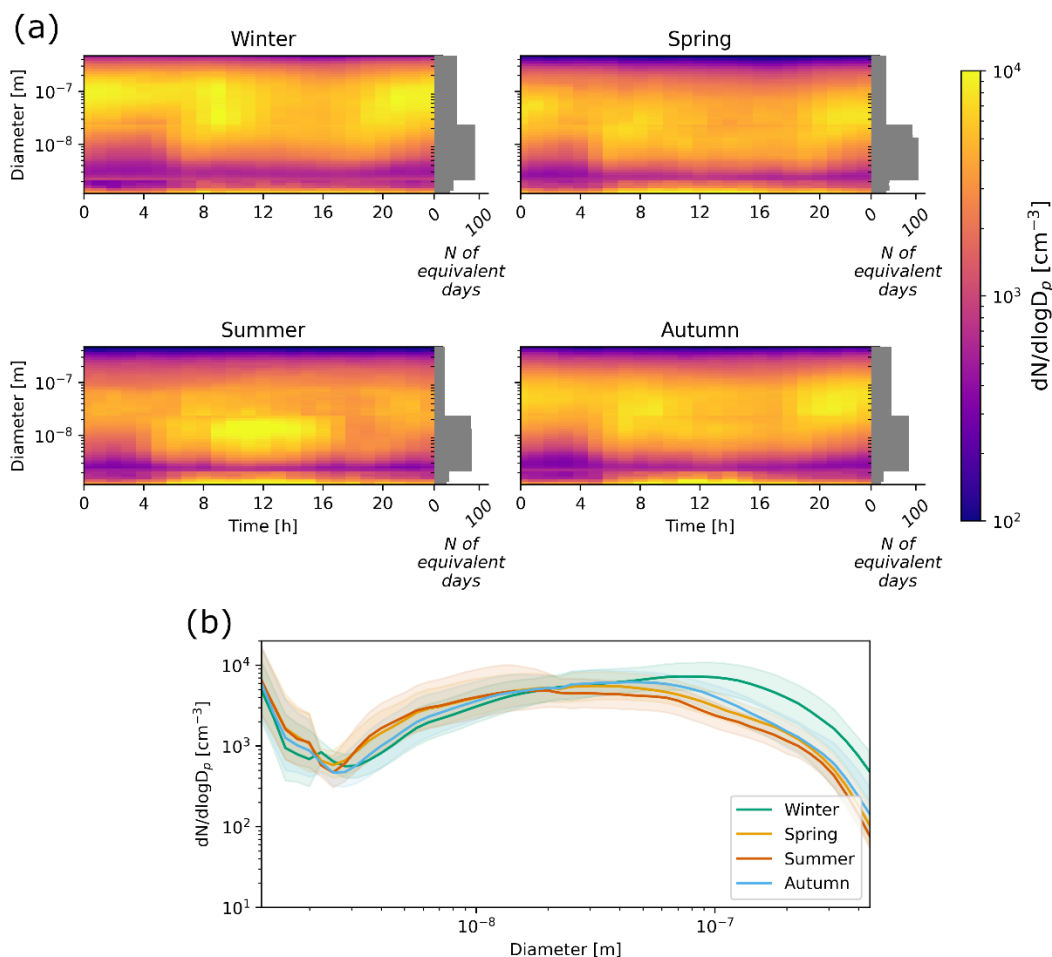
329 This means that $\delta(\tau; x, y) = 1$ if, for a given release, at least one of the 10000 released particles passed through the point
 330 (x, y) during the previous 72 hours.

331 **3 Results and discussion**

332 **3.1 Size distributions characterization**

333 The particle number size distributions in Milan exhibited a clear seasonal cycle, which is illustrated in Fig. 5a and Fig. 5b
 334 through the daily median size distribution surface plot per season and the median size distribution per season, respectively.

335 The months of December, January, and February were included in winter; March, April, and May in spring; June, July, and
 336 August in summer; September, October, and November in autumn.



337

338 **Figure 5: a) Daily median particle number size distribution surface plot per season. The bar plots report the number of equivalent**
 339 **days used to calculate the medians, computed as the total number of 15-minute data points divided by 96 (the number of 15-minute**
 340 **intervals in one day). Times are in Central European Time, UTC+1; b) median particle number size distribution per season. The**
 341 **shaded areas represent the interquartile ranges.**

342 During winter, the highest concentrations of particles larger than 50 nm were observed (Fig. 5b). This increase was probably
 343 the result of both a decrease in the BLH and an increase in biomass burning emissions (Colombi et al., 2023). Moreover, the
 344 typical traffic-related pattern was evident, with marked increases across all particle size ranges starting from 5:00 and 17:00
 345 Central European Time, UTC+1 (Fig. 5a), coinciding with the morning and evening rush hours.

346 In spring, and particularly in summer, these traffic-related peaks became less pronounced, suggesting an increase in the
 347 atmospheric mixing. Additionally, the data revealed a clear midday increase in sub-10 nm particles (Fig. 5a), which was most
 348 likely associated with NPF events. This phenomenon, which became more pronounced in the warmer months, was driven by
 349 photochemical reactions, enhanced by higher solar radiation and it was, therefore, mostly observed during spring and summer.

350 During summer, we observed the most significant increase in sub-10 nm particle number concentrations, alongside the lowest
351 levels of particles larger than 100 nm (Fig. 5b).

352 In autumn, the traffic-related peaks reappeared (Fig. 5a) due to the combined effect of the increase in traffic emissions
353 (Colombi et al., 2023) and the decrease in atmospheric dispersion and BLH, becoming again a more dominant factor
354 influencing particle number concentrations. However, the median concentrations across all particle sizes during autumn
355 remained similar to those observed in spring, indicating a seasonal transition towards winter. Overall, though, considering the
356 discontinuities in the data collection (Fig. 2) and the definition of each season, these conclusions may not be representative of
357 each entire season and their comparison has intrinsic uncertainties.

358 The shape and values of the median size distributions in Fig. 5b are in agreement with those reported for other urban
359 background sites of southern, central, and eastern Europe (Trechera et al., 2023). The comparison between the characteristics
360 of the size distribution surface plots per season (Fig. 5a) in Milan and other urban background sites (Trechera et al., 2023) also
361 does not point out any anomaly. As observed in Milan, several other urban background sites across Europe showed a more
362 pronounced increase in sub-25 nm particles at midday during the warmer months. Higher concentrations in the same size range
363 due to traffic rush hours were also recorded in all urban background sites (Trechera et al., 2023).

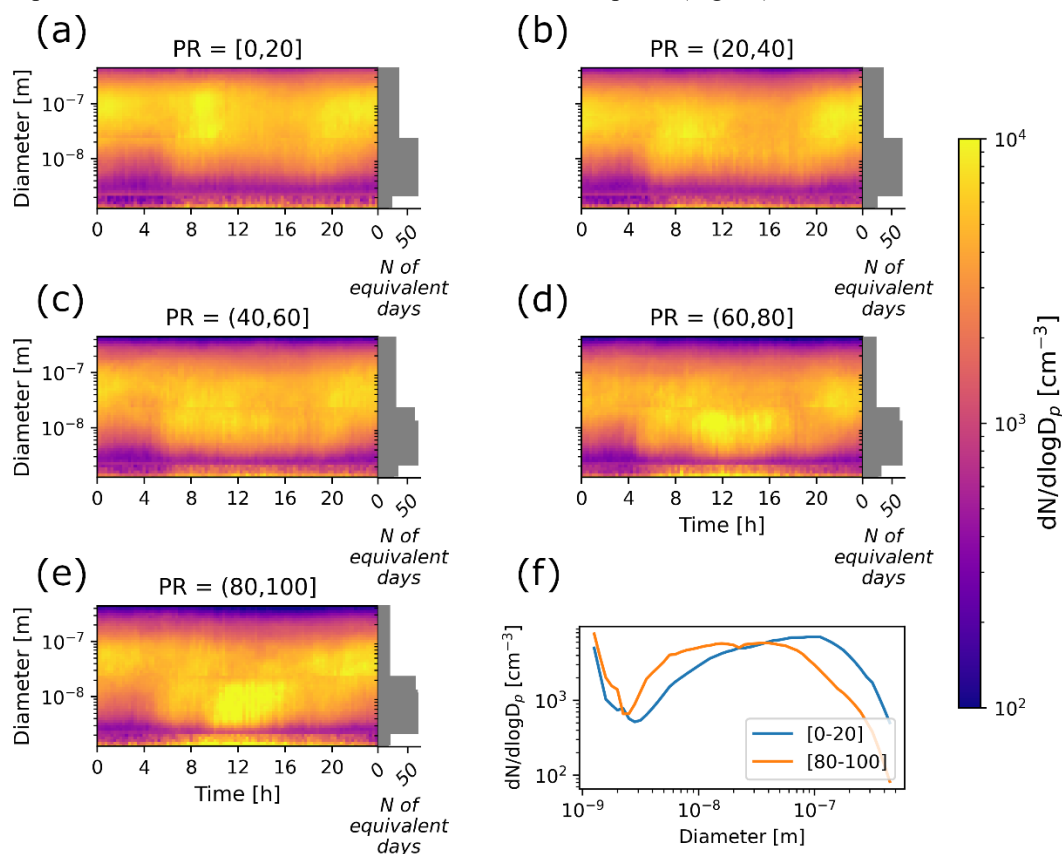
364 Other than this qualitative comparison, a quantitative one was also performed, and the concentrations in the nucleation, Aitken,
365 and accumulation modes measured in Milan were compared with the values reported for other European cities. The average
366 number concentrations for particles in the 10-25, 25-100, and 100-480 nm size ranges were 2642 cm⁻³, 4080 cm⁻³, and 1819
367 cm⁻³, respectively. Regarding the accumulation mode, Milan fell within the typical southern European cities, characterized by
368 high concentrations of particles in this size range. The Aitken mode in Milan exhibited a lower average concentration compared
369 to other southern European cities (4800-5900 cm⁻³), but lay at the upper end of the range reported for central European cities,
370 characterized by intermediate concentrations in this mode. Finally, intermediate concentration values were recorded in the
371 nucleation mode in Milan.

372 This comparison, though, should be interpreted with caution as it may be affected by several uncertainties. In fact, while the
373 data presented by Trechera et al. (2023) refer to the years 2017-2019, the data presented in this study cover a single year (2023-
374 2024), characterized by several gaps in the data availability, affecting especially the calculations in the Aitken and
375 accumulation modes. Moreover, differences in the instruments cut-off diameters may further bias this comparison.

376 The ratio between the average particle number concentration in the nucleation mode (N_{10-25}) and eBC was used to qualitatively
377 assess the relative contributions of primary and secondary emissions in Milan compared to other European urban background
378 sites. Milan exhibited an intermediate-low N_{10-25}/eBC ratio ($\sim 1444 \text{ cm}^{-3} \mu\text{g}/\text{m}^3$), within the approximate range of 900-4500
379 calculated for other cities (Trechera et al., 2023). This suggests that primary emissions (traffic) dominated the nucleation mode
380 particles in Milan, whereas in other European sites, photochemistry played a more significant role.

381 **3.2 NPF analysis**

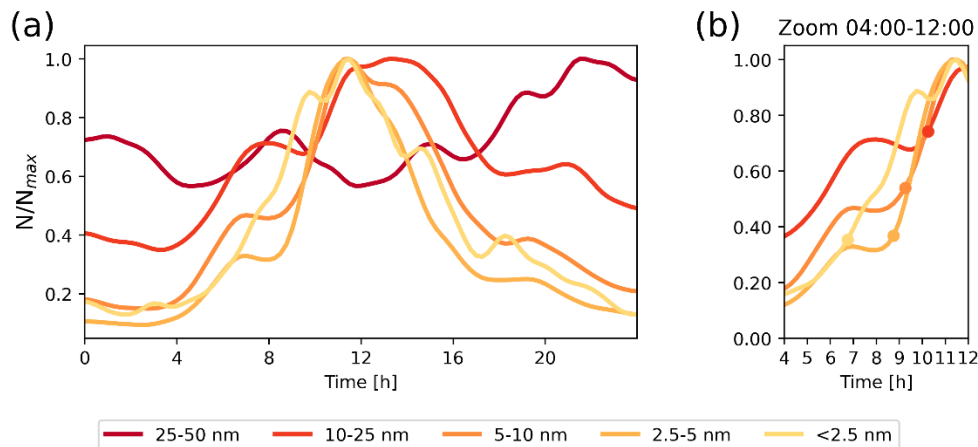
382 The Nano-particle ranking analysis was applied to characterize NPF. At higher percentile ranks, a midday increase in particle
 383 number concentration across all size ranges became clear, indicating NPF (Fig. 6). The process was marked by an initial rise
 384 in 1.2 nm particle number concentration, followed by an increase in the concentration of larger particles. This pattern indicates
 385 that NPF occurred over a wide area, including Milan itself. At lower percentile ranks, higher concentrations associated with
 386 traffic rush hours were evident, but they gradually faded at higher percentile ranks (Fig. 6, panels a to e). This pattern aligned
 387 with the seasonal variations in particle size distributions and NPF (Fig. S4, Fig. 5a). In fact, lower ranking values $\Delta N_{2.5-5}$,
 388 corresponding to weaker NPF, were more frequent during winter (December to February, Fig. S4), when traffic peaks were
 389 also more evident (Fig. 5a). Conversely, the strongest NPF events were observed in April and mid-to-high rank values
 390 (percentile ranks between 60 and 80) occurred predominantly between June and August (Fig. S4), when stronger atmospheric
 391 dispersion minimized the concentration of traffic-related peaks (Fig. 5a).



392

393 **Figure 6: Daily median particle number size distribution surface plots, grouped into 20-percentile intervals of NPF rank (PR; panels**
 394 **a-e). The bar plots indicate the number of equivalent days used to calculate the medians. For the definition of equivalent days, see**
 395 **Fig. 5. Times are in Central European Time, UTC+1. Panel f shows the median size distributions for days with NPF rank below the**
 396 **20th percentile and above the 80th percentile.**
 397

398 Our analysis demonstrates that NPF significantly contributed to the UFP number concentration through a growth process that
 399 lasted for several hours. As shown in Fig. 7, the concentration of sub-2.5 nm particles increased first around 7:00, followed
 400 sequentially by that of 2.5-5, 5-10, and 10-25 nm particles, reflecting a well-defined growth pattern in increasing size order.
 401 Accurately distinguishing the contribution of NPF from that of primary emissions is crucial for a proper interpretation of these
 402 patterns.



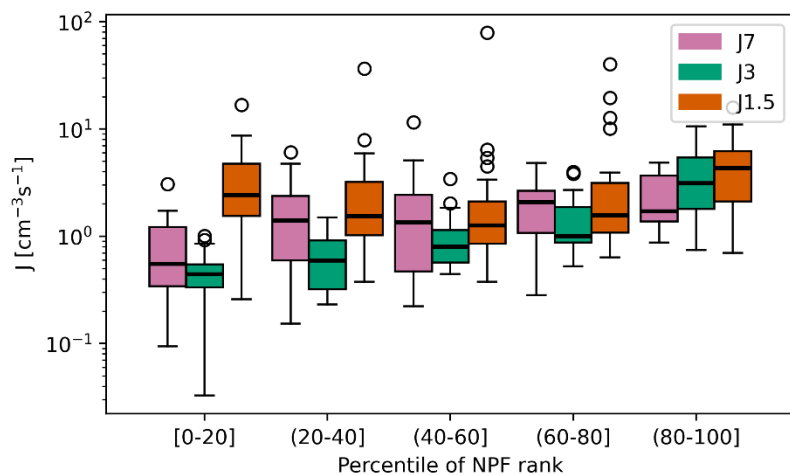
403

404 **Figure 7: a) The lines represent the median total concentration of particles in different size bins (<2.5, 2.5-5, 5-10, 10-25, 25-50 nm),**
 405 **calculated including the days above the 80th percentile of NPF rank. Each line is normalized to its own maximum value and smoothed**
 406 **through a one-dimensional Gaussian filter with a standard deviation of $\sigma = 2$ samples; b) zoom of the time interval between 4 and**
 407 **12. The dots represent the first point where the derivative of the curve was larger than 0.03 and they mark the beginning of the**
 408 **growth for each curve. The value 0.03 was chosen empirically.**

409 GR were calculated as described in Sect. 2.4.4. The values of 1.8 nm h^{-1} , 2.9 nm h^{-1} , and 9.7 nm h^{-1} were found for the GR in
 410 the size ranges of 3-7 nm, 7-20 nm, and 20-100 nm, respectively.

411 The formation rates $J_{1.5}$, J_3 , and J_7 are presented in Fig. 8. While J_3 correlated with percentile ranks - indicating higher
 412 production of 3 nm particles (higher J_3) during stronger NPF days (higher percentile rank) - $J_{1.5}$ remained relatively constant
 413 across most ranks. This suggests that clustering, which formed 1.5 nm particles, occurred at the site, but only under certain
 414 conditions the particle growth was observed (Kulmala et al., 2013). $J_{1.5}$ reached higher values only in the 80-100 rank bin,
 415 suggesting that clustering was more efficient during strong NPF days. Lastly, J_7 did not show a clear increasing trend and was
 416 often higher than J_3 , likely due to the influence of traffic in this size range. This is supported by Fig. 5a, where morning traffic
 417 peaks are clearly visible in the 5-10 nm size range. The ratio between J_7 and J_3 suggests that, for days with rank below the 80th
 418 percentile, traffic was a stronger source of particles larger than 7 nm than NPF. During high-rank days (80th -100th percentile),
 419 when NPF events were stronger, a marked increase in J_7 would have been expected as result of a dominant contribution from
 420 NPF. However, such an increase was not clearly observed, implying that traffic may have remained the dominant contributor
 421 to particles larger than 7 nm even during the most intense NPF days. This result agrees with the discussion in Sect. 3.1 about
 422 the relevant role of traffic compared to photochemistry in Milan in the 10-25 nm size range. As mentioned in Sect. 2.4.4,

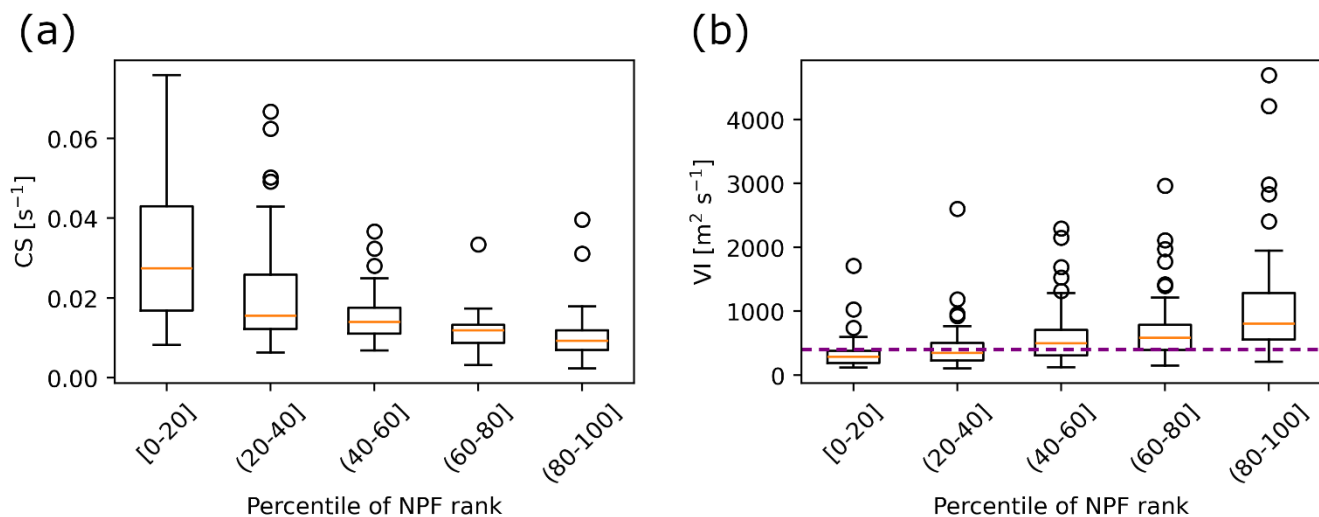
423 formation rates were calculated only for the days when all the instruments were measuring simultaneously and, therefore, the
424 data availability shown in Fig. 2 should be taken into account when interpreting Fig. 8.



425

426 **Figure 8: Maximum $J_{1.5}$, J_3 , and J_7 during the active window, per rank class. For the boxplot description, refer to Fig. 4b.**

427 The Nano-particle ranking method allows a continuous analysis of the NPF process in relation to meteorological and dispersion
428 variables and pollutant concentrations. To understand which parameters affected the process, the atmospheric conditions within
429 each bin of 20-percentile of NPF rank were compared. Figure 9 illustrates the relations between CS and ventilation index VI,
430 defined in Eq. (1), and rank as an example. Higher CS corresponded to low-rank days, while a high VI corresponded to high-
431 rank days. NO_2 , NO_x , eBC, SO_2 , PM_{10} , and $\text{PM}_{2.5}$ concentrations reported the same trend as CS, while BLH behaved as the
432 ventilation index (Fig. S5, S6, and S7). Therefore, enhanced NPF was, on average, associated with cleaner air conditions and
433 stronger atmospheric mixing. In particular, intermediate-strong NPF (percentile rank $> 60\%$) happened mostly during non-
434 stagnant days and when the CS was relatively low ($< 0.007 \text{ s}^{-1}$ on average). As reported in Sect. 2.4.3, the CS was calculated
435 only for the days when both the SMPS and NAIS provided good data availability. As a result, the CS time series contains
436 several gaps (Fig. 2), which affect Fig. 9a.



437

438 **Figure 9: a) Median CS calculated over the active time window of each day and b) daily ventilation index (VI) per rank class. The**
 439 **purple dotted line represents the threshold of VI=400 m²s⁻¹ for stagnant days. For the explanation of the boxplots, refer to Fig. 4b.**

440 Our data allowed a comparison between the environmental conditions and NPF in Milan and in other urban locations. In Milan,
 441 the CS varied between 0.01 s⁻¹ (during strong NPF events, Fig. 9a) and 0.03 s⁻¹ (during weak NPF events, Fig. 9a), which is
 442 comparable to the values observed in Shanghai (CS between 0.01 s⁻¹ and 0.02 s⁻¹ on average; Yao et al., 2018). However, while
 443 the particle formation rate at 1.5 nm ($J_{1.5}$) in Milan remained below 10² cm⁻³s⁻¹ (averaging around 10¹ cm⁻³s⁻¹), it reached up to
 444 10³ cm⁻³s⁻¹ in Shanghai (Yao et al., 2018). This is likely due to differences in the precursor vapor concentrations and
 445 atmospheric conditions. However, without precursor vapor measurements in Milan, this hypothesis remains uncertain.

446 GR also differed between the two cities. In Shanghai, the GR was approximately 6 nm h⁻¹ for 3-7 nm particles and 9 nm h⁻¹
 447 for 7-25 nm particles (Yao et al., 2018), whereas in Milan, the values were significantly lower, specifically, 1.8 nm h⁻¹ and 2.9
 448 nm h⁻¹ for 3-7 and 7-20 nm particles, respectively. A similar relation was observed in Nanjing, where both recorded GR and J
 449 were higher than in Milan. For example, the average J_3 in Nanjing ranged between 7.4 cm⁻³s⁻¹ and 13.9 cm⁻³s⁻¹, while the GR
 450 of 10 nm particles was between 13.4 nm h⁻¹ and 14.5 nm h⁻¹, depending on the type of event (Dai et al., 2023).

451 NPF has also been extensively studied in European cities. In Barcelona, for instance, Brean et al. (2020) reported an average
 452 GR of 4.69 nm h⁻¹ and 4.36 nm h⁻¹ for 4.5 and 1.9 nm particles, respectively. The CS in Barcelona was lower during NPF event
 453 days compared to non-event days, but it remained below 0.02 s⁻¹ in both cases, slightly lower than the values recorded in Milan.
 454 When comparing formation rates, Milan exhibited weaker NPF. While $J_{1.9}$ in Barcelona frequently fell between 10 cm⁻³s⁻¹ and
 455 10³ cm⁻³s⁻¹ (Brean et al., 2020), $J_{1.5}$ in Milan was mostly limited to the range of 1 cm⁻³s⁻¹ to 10 cm⁻³s⁻¹, indicating a lower
 456 particle formation intensity. In Budapest, the GR of 6 nm particles was 7.7 nm h⁻¹ on average, while J_6 was 4.2 cm⁻³s⁻¹, higher
 457 than what was observed in Milan in both cases. The CS in Budapest was lower than in Milan during non-event days but in line
 458 with Milan values during NPF event days (Salma et al., 2011). Finally, the study by Bousiotis et al. (2021) compared size
 459 distributions and NPF characteristics in several urban sites across Europe (Denmark, Germany, Spain, Finland, and Greece),

460 distinguishing urban background and roadside sites. Reported J_{10} were higher in roadside sites, but overall lower than what
461 was observed in Milan. On average, they remained below $0.1 \text{ cm}^{-3}\text{s}^{-1}$ in all sites, except for German roadside sites, where the
462 average J_{10} was higher but still below $0.2 \text{ cm}^{-3}\text{s}^{-1}$. The reasons for these differences may partially reside in the differences
463 across sites, but they are not clear. GR for 10 nm particles was, on average, between 2 nm h^{-1} and 5 nm h^{-1} , in line with the
464 value found in Milan for that of 7 nm particles (2.9 nm h^{-1}).

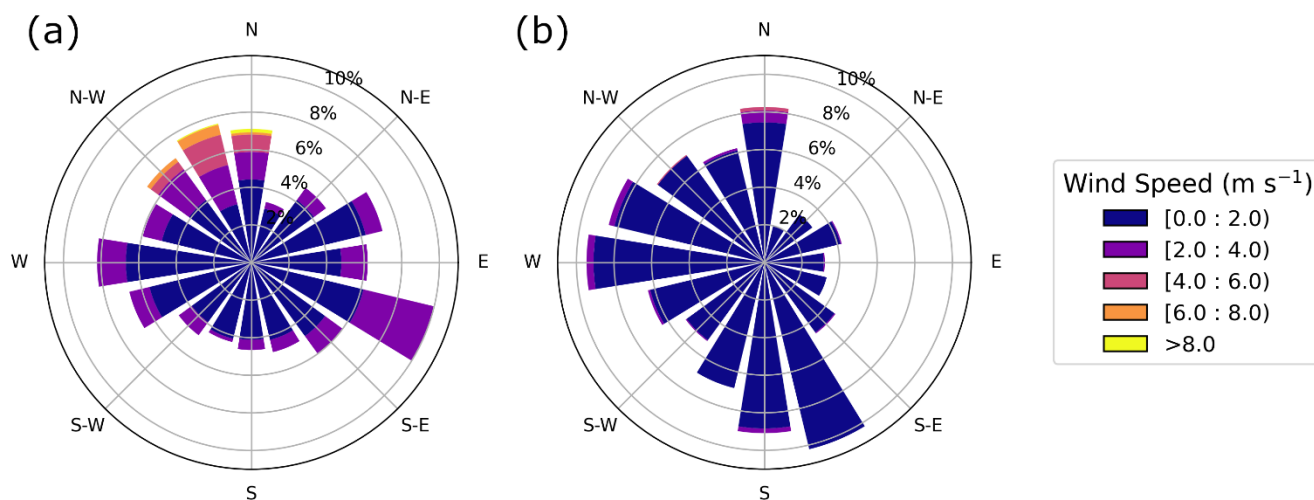
465 If we compare our results to previous studies in the rural areas of the Po Valley, it is clear that lower $J_{1.5}$ were observed in
466 Milan. Cai et al. (2024) observed an average $J_{1.7}$ of $10^2 \text{ cm}^{-3}\text{s}^{-1}$ in San Pietro Capofiume during NPF days, which was
467 significantly higher than what was found in Milano ($J_{1.5}$ was about $3 \text{ cm}^{-3}\text{s}^{-1}$). However, the values for J_3 and J_7 were more
468 similar. GR were also higher than in Milan (around 4 nm h^{-1} for 3-7 nm particles and around 5 nm h^{-1} for 7-15 nm particles).
469 The recorded CS was below 0.01 s^{-1} during both NPF and non-NPF and therefore lower than in Milan, where NPF is possibly
470 more suppressed than in the rural areas.

471 When comparing all the results, though, it is critical to take into consideration the possible differences in the methodologies
472 for estimating the formation and growth rates, including the slightly different size ranges used in different studies, which
473 contribute to the uncertainty of the comparisons.

474 3.3 Air mass analysis in relation to NPF

475 The analysis of NPF in relation to the meteorological conditions at the site pointed out that strong wind from northwest was a
476 favorable condition for NPF at this site (Fig. 10).

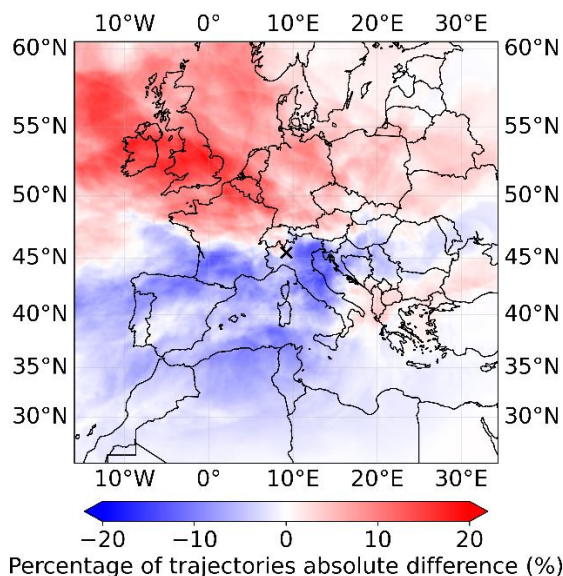
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478

479 **Figure 10: Wind rose for a) strong NPF days (percentile rank > 80) and for b) weak NPF days (percentile rank < 20).**

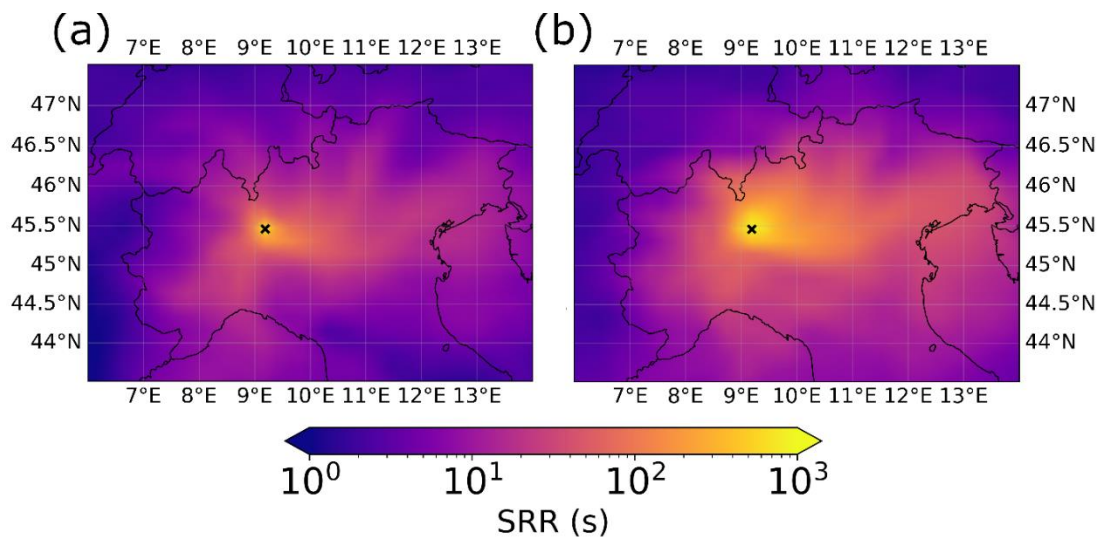
480 In order to explore further such relation and the characteristics of the air masses that favor the formation of new particles, the
481 Lagrangian particle dispersion model FLEXPART, driven by the meteorological output from WRF simulations, was applied
482 to identify the eventual preferential air mass direction for NPF and its characteristics.



484 **Figure 11: Air masses reaching the measurement site. The color scale represents the difference between the percentage of trajectories**
485 **passing over a given area and reaching Milan during a day with a percentile rank > 80 and the percentage of the total trajectories**
486 **passing over a given area. The details of the metric are reported in Sect. 2.4.7. An x marks the location of Milan on the map.**

487 The air mass trajectory density, calculated as described in Eq. (8), emphasizes that north, particularly northwest, was the
488 preferred direction for NPF (Fig. 11). An east-west axis distinctly separated the north and south sectors: air masses arriving in
489 Milan from the north promoted NPF, while those from the south hindered it.

490 Focusing on the Po Valley only (Fig. 12), it is clear that a lower air mass residence time in the area produced stronger NPF.
491 This agrees with both the anticorrelation between NPF rank and wind speed and with the anticorrelation between NPF rank
492 and pollutant concentrations, as the Po Valley is rich in emission sources. Lower exposure to anthropogenic emissions
493 enhanced NPF in this location, as shown in Fig. 13. Lower air mass exposure to NO_x and SO_2 emissions was associated with
494 higher concentration of small (sub-2.5 nm) particles, to a broader cluster band, extending to 2.5 nm, and to a smaller
495 accumulation mode. On the other hand, at higher NO_x and SO_2 air mass exposure, the cluster particles remained smaller (up
496 to ~ 1.5 nm) and had lower concentrations. Furthermore, the accumulation mode reached larger sizes. Overall, these
497 observations indicate that lower air mass exposure to anthropogenic emissions favored the formation of new particles. The air
498 mass exposure to both NO_x and SO_2 emissions anticorrelated with the median ventilation index, which decreased at increasing
499 air mass exposure, supporting the role of atmospheric ventilation (Fig. 13). Considering the data availability described in Fig.
500 2, the number of data points used in the calculation of the average concentrations shown in Fig. 13 may vary depending on the
501 diameter.

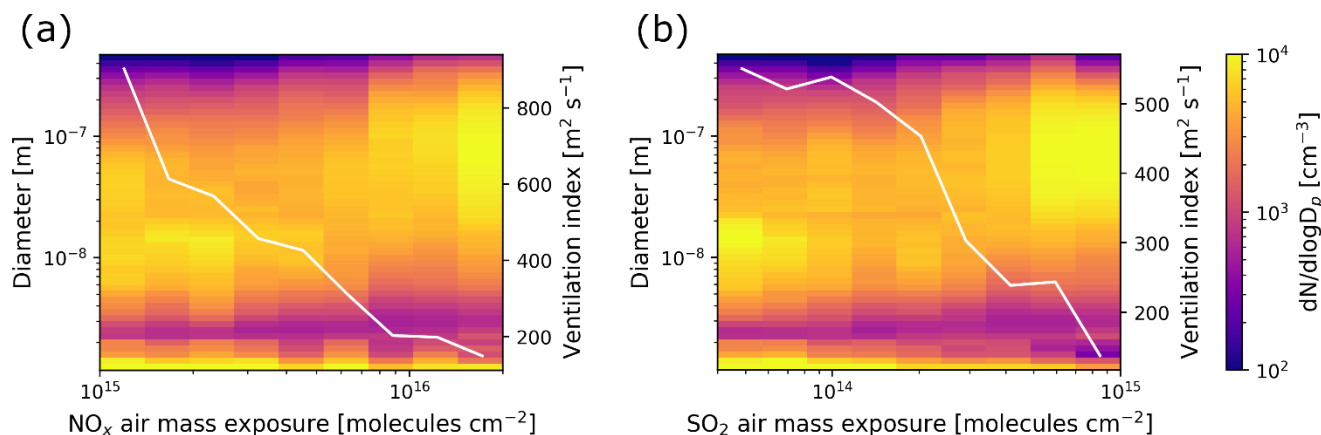


502

503 **Figure 12: Source-receptor relationship (SRR) below 500 m during a) strong NPF days (percentile rank > 80) and during b) weak**
 504 **NPF days (percentile rank < 20). The x marks indicate the study site.**

505

506

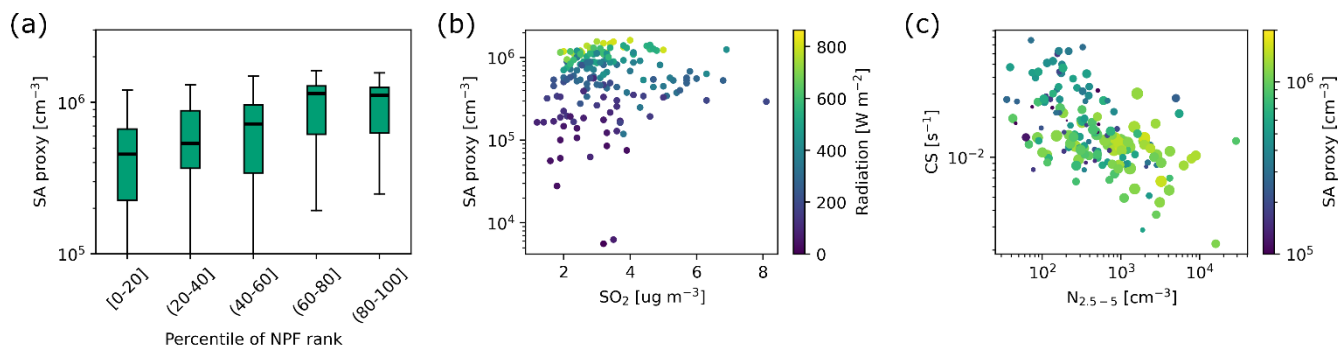


507

508 **Figure 13: Relation between a) air mass exposure to NO_x emissions and particle number size distribution and b) air mass exposure**
 509 **to SO₂ emissions and particle number size distribution. The white lines represent the median ventilation index.**

510 3.4 Sulfuric acid proxy analysis

511 The role of sulfuric acid, which has been identified in previous studies as a critical precursor vapor in the Po Valley (Cai et al.,
 512 2024), was investigated through its proxy, calculated as described in Sect. 2.4.5. The sulfuric acid proxy exhibited an increasing
 513 trend with the percentile of NPF rank (Fig. 14a), suggesting its potential contribution to the NPF process.



514

515 **Figure 14: a) Sulfuric acid (SA) proxy daily median calculated over the active time window per rank class. For the description of**
 516 **the boxplots, refer to Fig. 4b; b) relation between sulfuric acid (SA) proxy, SO_2 concentration, and radiation; c) relation between**
 517 **CS, sulfuric acid (SA) proxy, and $\text{N}_{2.5-5}$, representing NPF intensity as explained in Sect. 2.4.1. The size of the dots represents the**
 518 **radiation. For both panels b and c, each point is the daily median calculated over the active time window.**

519 No clear correlation between sulfuric acid and SO_2 concentrations was observed (Fig. 14b), indicating that SO_2 was not a
 520 limiting factor for sulfuric acid formation in Milan. On the other hand, sulfuric acid showed a clear increase with radiation
 521 (Fig. 14b and more clearly, Fig. S8), hinting at the role of photochemical processes for its formation rather than SO_2 availability
 522 or a sink effect. Indeed, while on average, a higher sulfuric acid proxy was recorded in correspondence with lower CS (Fig.
 523 S8), several cases with low CS and low sulfuric acid were observed and were linked to low radiation.

524 The relative roles of CS and sulfuric acid in NPF were then investigated using the concentration of 2.5-5 nm particles as a
 525 proxy for NPF intensity (Sect. 2.4.1). Figure 14c clearly presents an inverse correlation between $\text{N}_{2.5-5}$ and CS, indicating the
 526 relevant role of the CS in enhancing the NPF mechanism. On average, higher concentrations of sulfuric acid proxy were
 527 associated with stronger NPF (Fig. 14a and Fig. 14c). However, given the large variability in the trend, its role is less clear.
 528 The gaps in the CS time series due to the limited SMPS data coverage are reflected into the SA proxy time series and may
 529 affect Fig. 14.

530

531 3.5 NPF drivers in different atmospheric regimes

532 The results described so far were obtained using the entire dataset regardless of the environmental conditions. However,
 533 treating different atmospheric regimes, such as ventilated and stagnant conditions or different seasons together may create
 534 biases in the interpretation of the drivers of NPF and hide potentially relevant patterns.

535 To evaluate the robustness of our conclusions in different regimes, we performed an additional stratified analysis separating
 536 stagnant and non-stagnant conditions and different seasons (see Supplementary Materials) and applying the nano-particle
 537 ranking analysis on each subset. The two analyses (seasons and stagnant/non-stagnant) were performed separately, and the
 538 stratifications were not combined due to the limited amount of data.

539 Despite the differences in background conditions, the main conclusions did not change when analyzing separately stagnant
 540 and non-stagnant periods. CS values were generally higher under stagnant conditions compared to non-stagnant ones; however,

541 in both regimes, the CS decreased with increasing NPF rank, indicating that stronger NPF preferentially occurred under lower
542 CS conditions, independently of the level of stagnation (Fig. S9a). SO₂ concentrations showed a less clear behavior and did
543 not appear to limit NPF both under stagnant and non-stagnant conditions (Fig. S9b). Sulfuric acid proxy and J₃ increased with
544 NPF rank in both regimes (Fig. S9c, Fig. S9d).

545 Considering that seasonality may have still introduced some bias in the interpretation of these results (Table S1), a separate
546 study for each season was performed.

547 Seasonal stratification revealed higher CS values in winter compared to the other seasons. In winter and autumn, the CS clearly
548 decreased with increasing NPF rank, while this relation was weaker in spring and summer (Fig. S11a). J₃ was more difficult
549 to interpret on a seasonal basis, particularly in summer, due to the limited data availability. Nevertheless, J₃ generally increased
550 with NPF rank in all seasons, consistently with the results from the non-stratified dataset (Fig. S11e).

551 SO₂ concentrations were generally higher in winter than in the other seasons due to the enhanced emissions and the weaker
552 dispersion conditions. In winter, SO₂ showed a decreasing trend with increasing NPF rank (Fig. S11c), in agreement with the
553 opposite relation between NPF rank and SO₂ observed in the non-stratified analysis. In spring, summer, and autumn, SO₂
554 concentrations were lower and did not exhibit a clear trend with NPF rank. Similar SO₂ levels associated with both weak and
555 strong NPF events suggest that SO₂ availability was not a limiting factor for NPF intensity during these seasons. The sulfuric
556 acid proxy did not show a clear relation with NPF rank in most seasons, except for autumn, when an increasing trend was
557 observed (Fig. S11d).

558 The analysis of NPF after stratifying different atmospheric conditions does not contradict the results obtained with the entire
559 dataset. However, drawing conclusions may be misleading. In fact, the stratification led to a low amount of data per class,
560 reducing the reliability of the results. Furthermore, the NPF intensities in the different groups (seasons, stagnant and non-
561 stagnant) may not be comparable, considering that the nano-particle ranking was applied separately on each subset (Fig. S10).
562 To assess this, the concentration of 2.5-5 nm particles was also used as proxy for NPF intensity other than the percentile rank
563 (Fig. S11f, Fig. S11g).

564 A larger dataset would allow a more in-depth analysis of how different regimes may affect NPF and of the main drivers of this
565 process in various atmospheric conditions.

566 **3.6 Case study**

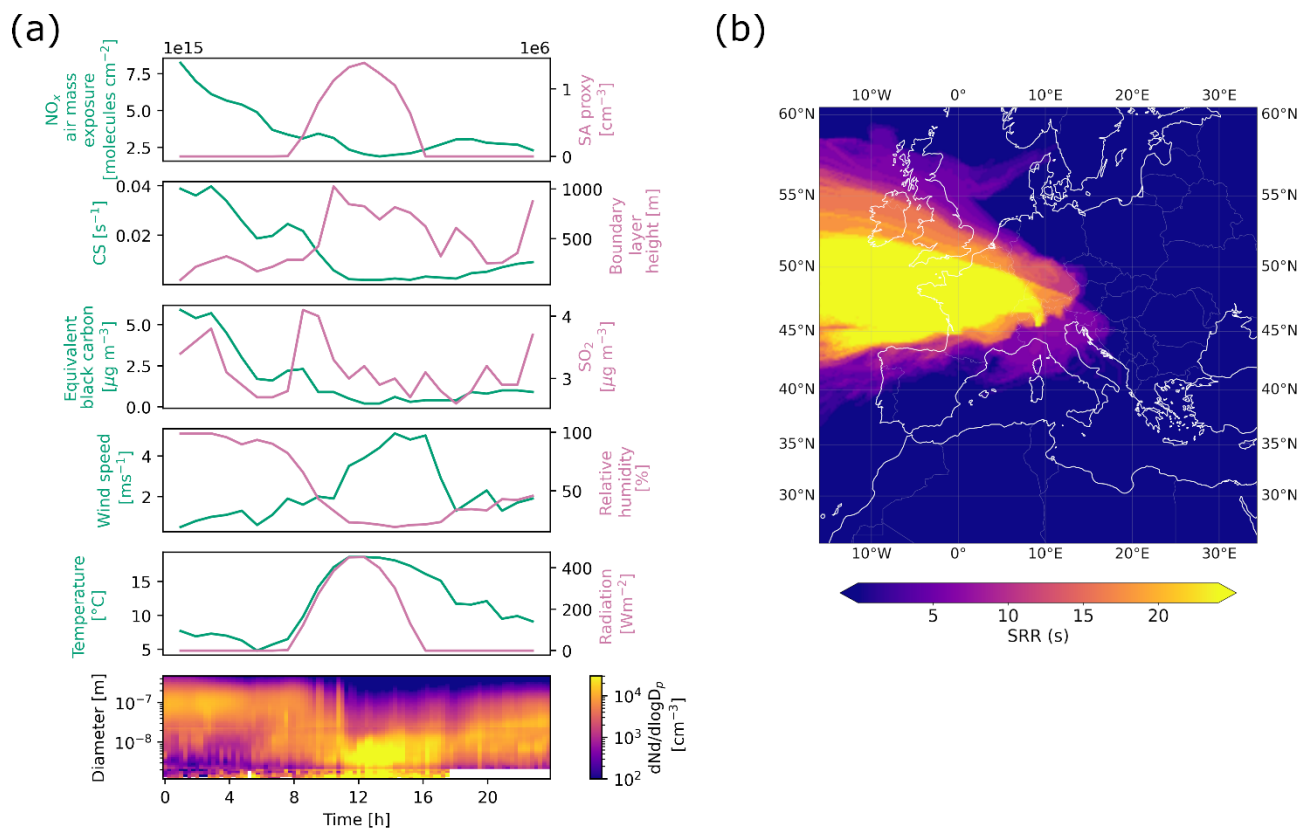
567 In this section, we present an example of NPF day, featuring the characteristics discussed so far (lower CS and eBC
568 concentration, higher BLH, and lower exposure to anthropogenic emissions). Specifically, we focus on November 17th, 2023,
569 a day that fell within the 80-100 class of percentile rank (Fig. 15). On this day, local clustering led to an increase in the
570 concentration of sub-3 nm particles starting at 8 am (UTC+1), followed by a subsequent rise in the concentration of particles
571 up to 100 nm in diameter (Fig. 15a), indicating condensational growth. These phenomena were observed in correspondence
572 with a decrease in CS, in eBC concentration, and in air mass exposure to NO_x emissions, as well as an increase in wind speed
573 and BLH (Fig. 15a), suggesting strong atmospheric mixing. Additionally, the air mass trajectory analysis revealed a dominant

574 flow from northwest (Fig. 15b). Oppositely to the average results, SO₂ concentration showed a sharp increase as the event
575 began.

576 On this day, the phenomenon driving the free tropospheric air masses advection and atmospheric clearing was the Foehn wind,
577 a warm, dry wind descending from the Alps, which brings clear skies and higher temperatures compared to seasonal averages,
578 together with exceptionally low pollutant concentrations in the Po Valley. Specifically, on November 17th, 2023, the Foehn
579 wind was identified by the decrease in relative humidity, the daytime median temperature of 17.2°C (above the daily monthly
580 average of 11.8°C), and the smooth radiation trend, indicating the absence of cloud cover. The air mass trajectory also
581 confirmed the presence of this wind pattern. The increase in SO₂, the source of which still needs to be confirmed, may have
582 further enhanced the formation of new particles, together with the decrease in CS.

583 Similar cases have been observed during the campaign but a detailed classification of Foehn wind event days would be needed
584 to further characterize them in relation to NPF. This case study is consistent with the earlier observations that Foehn wind can
585 create favorable conditions for NPF in the Po Valley (Rodríguez et al., 2005) and that it is a significant source of UFP even in
586 urban Milan.

587



588

589 **Figure 15: a) NO_x air mass exposure, sulfuric acid (SA) concentration proxy, CS, BLH, eBC and SO₂ concentrations, wind speed,**
590 **relative humidity, temperature, and radiation time series and particle number size distribution surface plot during November 17th,**
591 **2023; b) source-receptor relationship (SRR) for all the trajectories arriving during November 17th, 2023.**

592 **4 Conclusions**

593 This study examines NPF in Milan over one year, revealing that NPF was more intense during spring and summer, resulting
594 in higher concentrations of sub-10 nm particles. In contrast, winter saw higher levels of particles larger than 50 nm, mostly
595 due to the reduced BLH and increased emissions from heating sources. Traffic-related peaks during rush hours were more
596 evident in winter and autumn, but they diminished in spring and summer as atmospheric mixing increased. Our analysis shows
597 that cleaner, well-mixed conditions, particularly with strong northwesterly winds, enhanced NPF by reducing the CS, possibly
598 allowing precursor vapors to participate in the formation of new particles. Reduced air mass exposure to anthropogenic
599 emissions and shorter residence time in the Po Valley further supported stronger NPF.

600 The driving mechanisms of NPF vary by location and environmental conditions. Similar patterns have been observed in other
601 urban areas, such as Beijing, China, where Guo et al. (2014) found a higher frequency of NPF events during cleaner periods
602 characterized by lower particle number concentrations. During these periods, the reduced CS allowed nucleating vapors to
603 accumulate, facilitating NPF. Conversely, in polluted conditions with high aerosol loading, NPF was suppressed due to the
604 high CS and the abundant pre-existing particles, which provided surfaces that scavenge vapors, inhibiting the NPF process.
605 Also, in Beijing, the occurrence of both clean and polluted periods depended on the meteorology as strong winds descending
606 from the mountains in the north contributed to the cleaning of the atmosphere, while the slower winds from the south favored
607 the accumulation of pollutants (Guo et al., 2014). Our findings suggest that a similar mechanism may be happening in Milan.
608 While the absence of direct precursor vapor measurements precludes us from entirely dismissing the influence of transported
609 chemical precursors, the geographical and environmental context of Milan supports a more plausible explanation. Located in
610 a heavily industrialized, densely populated region with significant agricultural activities, it is reasonable to believe that the
611 reduction of the CS played a more prominent role in initiating NPF, rather than an eventual influx of precursors from the Alps.
612 The relation between wind speed and NPF is not uniform across all urban sites. For instance, Pushpawela et al. (2019) explored
613 this relation in Brisbane, Australia, and observed that NPF was more likely to happen on days with lower wind speed, a finding
614 opposite to that in Milan and other highly polluted environments. Their comparative analysis suggested that the impact of wind
615 speed on NPF depends on the level of pollution and the distribution of precursor vapors. In relatively cleaner urban areas like
616 Brisbane, where the accumulation of precursors can enhance NPF, a lower wind speed facilitates this process. In contrast, in
617 highly polluted cities like Beijing, a low wind speed increases the CS, suppressing NPF. At higher wind speed, the reduction
618 in CS can promote NPF in polluted areas by clearing pre-existing particles, whereas in cleaner cities, the removal of precursor
619 vapors can inhibit NPF. Our study locates Milan within this framework as a highly polluted city where the interplay between
620 wind speed, CS, and precursor vapor concentrations played a critical role in the NPF dynamics.

621

622 The findings hint at potential implications for air quality in Milan. Long-term reductions in PM₁₀ and PM_{2.5} concentrations,
623 potentially driven by regulatory measures, could lead to stronger NPF, increasing the concentrations of UFP. This highlights
624 the need for detailed studies on precursor vapors and on the chemical pathways leading to NPF to fully understand their role
625 in the NPF process, especially in relation to low CS episodes. Future research should focus on the direct measurements of
626 these precursors to clarify their contributions, whether local or transported. Comparative studies in other polluted urban
627 environments are also crucial to understand regional differences in NPF dynamics. Long-term monitoring of aerosol
628 concentrations in all size ranges and of NPF events, in relation to urban development and pollution control, would provide
629 valuable insights into the effectiveness and results of air quality strategies.

630 **Data availability**

631 The size distribution data from the nCNC, NAIS, and SMPS presented in this work are publicly available at
632 <https://doi.org/10.5281/zenodo.18130252> (Agrò, 2026).

633 **Author contribution**

634 The study was designed by FB and TP. MA, SM, IG, PF, AB, CO, AB, JS participated in the installation and the operation of
635 the instruments. MA analysed the data. MB and GC performed the model simulations and analysis. MA prepared the
636 manuscript. All the coauthors contributed to the discussion and interpretation of the results and the revision of the article.

637 **Competing interests**

638 Some authors are members of the editorial board of journal Atmospheric Chemistry and Physics.

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