



1 Disentangling Mechanistic Controls on Ultrafine Particle 2 Number and Growth Across Seasons in an Urban Street 3 Canyon

4 Yanxia Li¹, Hengheng Zhang^{1,a}, Xuefeng Shi¹, Yaowei Li^{2,b}, Sophie Abou-Rizk², Jessica B. Smith², Zhaojin An^{2,c},
5 Adrian Wenzel³, Junwei Song⁴, Thomas Leisner^{1,5}, Frank Keutsch², Jia Chen³, and Harald Saathoff¹

6 ¹Institute of Meteorology and Climate Research Atmospheric Aerosol Research, Karlsruhe Institute of
7 Technology, 76344 Eggenstein-Leopoldshafen, Germany

8 ²Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

9 ³Environmental Sensing and Modeling, Technical University of Munich (TUM), Munich, Germany

10 ⁴School of Marine Sciences, Sun Yat-sen University, Zhuhai 519082, China

11 ⁵Institute of Environmental Physics, Heidelberg University, 69120 Heidelberg, Germany

12 ^anow at: Research Institute for Applied Mechanics, Kyushu University, Fukuoka, Japan

13 ^bnow at: Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology,
14 Cambridge, MA 02139, USA

15 ^cnow at: School of Environment, Tsinghua University, 10084, Beijing China

16

17 *Corresponding authors: Yanxia Li (yanxia.li@kit.edu) and Harald Saathoff (Harald.Saathoff@kit.edu)*

18 Abstract: Ultrafine particles (UFP; <100 nm diameter) play a disproportionate role in human health and
19 atmospheric processes, yet their sources and growth mechanisms in urban environments in different seasons
20 remain poorly constrained. This study presents a comprehensive characterization of UFP number concentrations,
21 size distributions, chemical drivers, and meteorological influences in downtown Munich across summer, winter,
22 and spring. We combine high resolution particle number size measurements with source characterization of
23 organic aerosol (OA), semi-volatile organic aerosol (SVOA) and volatile organic compounds (VOC) to
24 disentangle primary emissions from secondary processes. Results show that UFP number concentrations are
25 driven by traffic- and cooking-related emissions, consistently peaking during nighttime boundary layer collapse
26 due to accumulation. In contrast, ultrafine particle growth (from 40 to 80 nm) arises predominantly from
27 condensation of semi-volatile or low-volatility organic vapours, with distinct seasonal pathways: biogenic and
28 biomass burning OA at night, and photochemically oxidized low-volatility vapours during daytime in summer;
29 biomass-burning and combustion-related SVOA in winter; and a mixed regime involving both primary emissions
30 and moderate photochemistry in spring. No evidence of classical new particle formation appears in these non-
31 nucleation UFP growth events. These findings demonstrate that UFP evolution in Munich is governed by the
32 interplay between boundary-layer dynamics and seasonally varying organic vapour sources, highlighting the need
33 for season-specific mitigation strategies.

34 1. Introduction

35 Ultrafine particles (UFP), defined as airborne particles with diameters below 100 nm, have received increasing
36 attention due to their potential to penetrate deeply into the human respiratory tract and translocate into the
37 circulatory system (Zhang et al., 2015; Schraufnagel, 2020; Bousiotis et al., 2021a; Flood-Garibay et al., 2023;
38 Folwarczny et al., 2025). A recent White Paper identified the lack of harmonized measurement protocols and
39 emphasized that UFP composition and sources vary substantially across urban, industrial, and rural environments,



40 resulting in pronounced spatial and temporal heterogeneity (Morawska et al., 2023; Rattigan et al., 2024; Kecorius
41 et al., 2025). In response, the World Health Organization (WHO) and European Union (EU) have prioritized UFP
42 assessment within its air quality policy framework to better understand their distribution, sources, and health
43 implications across different places (Avl, 2024). The EU has established the EU Air Quality Directive 2024/2881
44 which, for the first time, requires the monitoring of UFP across the EU as part of national monitoring strategies.
45 However, no limit values have been established so far. The WHO defines UFP number concentrations exceeding
46 10^4 cm^{-3} (24-hour mean) as high concentrations (Damayanti et al., 2023), a threshold associated with increased
47 health risks including respiratory and cardiovascular effects; however, despite growing regulatory interest, the
48 mechanistic understanding of UFP sources and seasonal growth processes in specific urban environments remains
49 insufficient to inform targeted mitigation strategies.

50 UFP constitute a major fraction of atmospheric particle number but contribute negligibly to total mass,
51 necessitating particle number concentration (PNC) and size distribution as primary characterization metrics.
52 Urban UFP number concentration and $\text{PM}_{2.5}$ mass concentration are poorly correlated ($r = 0.09 - 0.64$) but strongly
53 correlated with NO and benzene, indicating motor vehicle emissions as the dominant urban source accounting for
54 50 - 60% of UFP number concentrations at roadside locations (Varotsos et al., 2012; Kumar et al., 2014; De Jesus
55 et al., 2019; Abdillah et al., 2024; Wang et al., 2024). Multiple studies reveal consistent spatial UFP number
56 concentration gradients across urban environments (Giemsa et al., 2021). A Switzerland study across 80 residential
57 sites reported median UFP number concentrations ranging from 6900 - 14700 particles cm^{-3} between urban and
58 rural areas (Meier et al., 2015). Similar spatial patterns have also been observed in other metropolitan regions. A
59 Boston metropolitan study further demonstrated a clear spatial trend: concentrations were highest on-road (32,000
60 - 64,000 particles cm^{-3}), intermediate at central sites (19,000 - 23,000 particles cm^{-3}), and lowest in residential
61 areas (14,000 - 15,000 particles cm^{-3}), with traffic-related peaks observed during rush hours (Simon et al., 2017).
62 PNC follows traffic > urban > suburban patterns, increasing from Northern/Western to Southern/Eastern Europe.
63 Environmental conditions, particularly temperature ($R = 0.814$) and relative humidity ($R = 0.787$), drive
64 nucleation processes alongside traffic emissions as dual urban UFP sources. The sources of UFP vary by site type:
65 at traffic-dominated sites, UFP number concentrations are primarily driven by direct vehicle emissions, as
66 reflected by strong positive correlations between PNC and equivalent black carbon (eBC); whereas in cities with
67 high solar radiation, photochemical particle formation becomes a significant secondary source, evidenced by
68 midday UFP peaks and seasonal anti-correlation between PNC and eBC. Some sites exhibit contributions from
69 both sources (Li et al., 2023a; Trechera et al., 2023). UFP size distributions measured via Scanning Mobility
70 Particle Sizer (SMPS)/Mobility Particle Size Spectrometer (MPSS) reveal distinct patterns across geographic
71 locations and seasons. A Paris urban background study (2019 - 2022) measured mean PNC of $8,100 \pm 4,800$
72 particles cm^{-3} (8 - 100 nm), with predominant 20 - 30 nm particles linked to vehicular emissions (Abbou et al.,
73 2024). Nucleation mode particles (< 25 nm) constitute significant proportions due to ineffective Diesel Particle
74 Filters and inadequate semi-volatile organic compound controls, substantially influencing overall UFP trends
75 (Chen et al., 2023; Garcia-Marles et al., 2024a). A 2022 Delhi study found nucleation mode particles (10 -30 nm)
76 contributed ~50% during summer daytime from fresh traffic emissions, with size modes shifting from nucleation
77 and Aitken (30-100 nm) during daytime to Aitken and accumulation modes (100 - 1000 nm) at night (Mohan et
78 al., 2024; Teinilä et al., 2025). In contrast, a Helsinki winter study reported high sub-10 nm particle concentrations
79 across all locations, indicating pronounced seasonal and geographic variations in UFP size distributions (Lepisto



80 et al., 2023). Nevertheless, most of these studies rely mainly on particle number and size distribution
81 measurements, without sufficient means to distinguish between primary emissions and secondary particle
82 formation and growth.

83 In recent years, multiple complementary methodologies have enabled comprehensive source identification and
84 composition analysis of UFP. Particle number size distribution (PNSD) measurements via SMPS form the
85 foundation for UFP source identification, revealing that traffic emissions contributed 29 - 39% of particle number
86 while secondary formation accounted for 61-71% (Dall'osto et al., 2013). At Leipzig urban roadside sites, traffic
87 was the dominant primary source (52%), while the remaining contributions arose from secondary or non-local
88 processes: diffuse urban sources (20%), reflecting city-wide oxidation of volatile organics and minor combustion
89 emissions; regional background (21%), representing long-range transport of photochemically aged aerosols; and
90 new particle formation (7%), driven by gas-to-particle conversion of sulfuric acid and organic vapours during
91 low-condensation-sink conditions (Ma and Birmili, 2015). Multiple cities using k-means clustering identified
92 traffic (44 - 65%), nucleation (14 - 19%), and background (7 - 22%) as major UFP sources, with nucleation
93 potentially increasing as traffic emissions decrease due to reduced condensation sinks (Brines et al., 2015; Ahn et
94 al., 2021; Zhao et al., 2021). Positive matrix factorization (PMF) applied to PNSD combined with chemical
95 tracers (eBC, NO_x, O₃) successfully partitioned UFP sources into primary traffic (56 - 95% at traffic and urban
96 background sites), photochemical nucleation, and secondary formation processes (Garcia-Marles et al., 2024b;
97 Tao et al., 2023). Quantitative relationships between PNC and source-apportioned eBC enabled traffic, solid fuel
98 burning, and secondary formation contributions to be distinguished across diverse environments (Hama et al.,
99 2017; Xiang et al., 2023). Chemical composition analysis reveals organic components dominate urban UFP (68-
100 81%), with seasonal variations: CHO organics peak in summer while sulfur- and nitrogen-containing organics,
101 nitrate, and chloride dominate winter, with contributions from cooking, vehicle emissions, photooxidation, and
102 aqueous/heterogeneous processes (Li et al., 2023b). Lintusaari et al. (2023) using a volatility condensation
103 particle counter battery (CPCB) with cutoff sizes combined with thermal treatment to identify non-volatile
104 particles, sub-23 nm non-volatile particles were found to dominate traffic emissions, with sub-10 nm particles
105 showing 3 times higher emission factors than larger particles. Hybrid PMF analysis incorporating both size-driven
106 and composition-driven factors revealed that daytime nucleation involved ammonium sulphate and moderately
107 oxygenated organic aerosol, while growth was facilitated by hydrocarbon-like and low-oxygenated organic
108 aerosols and nitrate (Ajith et al., 2024). Mechanistically, traffic-derived organics, sulfuric acid, and amines
109 (especially C₂-amines) drive urban UFP nucleation and growth rather than NO_x levels, with organically-
110 oxygenated molecules critical for particle formation and survival at roadsides despite high condensation sinks
111 (Saarikoski et al., 2023; Guo et al., 2020; Brean et al., 2024; Brean et al., 2025). Additionally, cooking emissions
112 represent a significant UFP source dominated by organic aerosol with reduced-nitrogen species (amine/imide
113 functionalities) comprising 15-50% of organic mass, indicating both traffic and cooking as important
114 anthropogenic UFP precursor sources (Kim et al., 2024). However, few studies have simultaneously integrated
115 gas-phase VOC, particle-phase OA/SVOA source apportionment, and size distribution measurements across
116 multiple seasons in a single urban street canyon. Therefore, leaving the seasonal chemical drivers of UFP growth
117 poorly constrained.



118 In contrast to previous studies that have primarily relied on particle number size distributions combined with
119 limited chemical tracers such as eBC and NO_x for UFP source apportionment, this investigation uniquely
120 integrates gas- and particle-phase chemical composition measurements. We employed a Condensation Particle
121 Counter (CPC), a Scanning Mobility Particle Sizer (SMPS), a High-Resolution Time-of-Flight Aerosol Mass
122 Spectrometer (HR-TOF-AMS), and a Chemical Analysis of Aerosol Online coupled with Proton Transfer
123 Reaction Mass Spectrometry (CHARON-PTR-MS) to characterize seasonal particle number concentrations, size
124 distributions, new particle formation and growth events in an urban street canyon in Munich, Germany. This
125 approach enables, for the first time in a European street canyon, a distinction between primary emission-driven
126 UFP number concentration peaks and secondary organic vapour condensation-driven UFP growth across three
127 seasons. This is going well beyond explanations reported in the literature focusing on traffic emissions and
128 nucleation. Our measurements elucidate how the seasonal variability of organic vapour sources governs UFP
129 growth, and number concentrations in an urban street canyon environment, ranging from primary traffic and
130 cooking emissions in winter to photochemically oxidized biogenic and biomass-burning compounds in summer.

131 **2. Methods**

132 **2.1 Measurement location**

133 Field observations were conducted at the same location in urban Munich (11°57'E, 48°15'N; elevation 520 m a.s.l.)
134 during three seasons: summer (August 3-29, 2023), late winter (March 1-8, 2024), and spring (March 9-27, 2024).
135 The sampling site is located at Theresienstrasse 39 within an urban street canyon adjacent to a 30 m tall building
136 of Ludwig-Maximilians-Universität München (LMU). The surrounding area comprises restaurants, residential
137 buildings, museums, and university workshops and laboratories, with substantial vehicular traffic. Due to the
138 street-canyon configuration and the building-induced flow, wind direction at street level predominantly originates
139 from the south and southeast, reflecting a vortex effect on the lee side of the LMU building where the measurement
140 site is located. In contrast, winds at the rooftop level (30 m) mainly originate from the west and east. More details
141 on the site characteristics during the measurement campaigns are provided in Li et al. (2026).

142 **2.2 Instrumentation**

143 All instruments were placed in the measurement container (Figure S1). A total suspended particle (TSP) inlet was
144 used for sampling of particles and gases, while a PM_{2.5} aerodynamic inlet (16.7 L min⁻¹) was employed to restrict
145 particle sampling to those with aerodynamic diameters below 2.5 μm. The TSP and PM_{2.5} inlets were mounted on
146 the roof of the measurement container and connected to the instruments inside via stainless steel sampling lines
147 of 2 m and 1.5 m, respectively. The TSP inlet supplied sample air to the CPC, U-SMPS, and FIDAS 200. The
148 PM_{2.5} inlet split at its downstream end into three separate lines: the HR-TOF-AMS inlet was located 0.5 m from
149 the splitting point via a stainless-steel line, the CHARON-PTR-MS inlet was located 1 m away via a stainless-
150 steel line, and the fiber laser-induced fluorescence (FILIF) inlet was connected via a 1 m PFA line following a
151 stainless-steel-to-PFA connector at the splitting point. Gas-phase measurements (O₃, NO₂, NH₃, and VOCs via
152 PTR-MS) were conducted through a dedicated 2 m PFA line mounted alongside the TSP inlet. A schematic of the
153 sampling setup is provided in Figure S1. Particle number concentrations were measured using condensation
154 particle counters (CPC): a CPC 3776 (TSI Inc.) detecting particles >2.5 nm throughout the study period with 1 s



155 time resolution, a CPC 3756 (TSI Inc.) for particles >2.5 nm in August 2023 (1 s resolution), and a CPC 3022
156 (TSI Inc.) for particles >7 nm in March 2024 (1 s resolution). Particle size distributions were measured using two
157 different systems: a Universal Scanning Mobility Particle Sizer (U-SMPS 2050, Palas GmbH) covering 7-763.5
158 nm (4 min time resolution, August 2023) and an SMPS (DMA 3081, TSI Inc.) covering 14-763.5 nm (6 min time
159 resolution, March 2024). Mass concentrations of PM₁, PM_{2.5}, PM₄ and PM₁₀ were calculated based on size
160 distributions measured using a FIDAS 200 (Palas GmbH) with 1 s time resolution. Equivalent black carbon (eBC)
161 was measured by an AE33 (Magee Scientific) with 1 min resolution. Meteorological parameters (WS700, Lufft
162 GmbH) were recorded at 1 s resolution. Trace gases were monitored at 1 min time resolution: NO₂ (AS32M,
163 Environment SA) and O₃ (O341M, Environment SA), while NH₃ (G2103, Picarro) was measured at 2 min
164 resolution. Volatile organic compounds (VOCs) in the gas phase and semi-volatile organic compounds in the
165 particle phase were measured using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS
166 4000X2, Ionicon Analytik GmbH) equipped with a particle inlet (Chemical Analysis of aeRosol ONline,
167 CHARON), with 10 s time resolution. Non-refractory PM_{2.5} (NR-PM_{2.5}) components were quantified using a high-
168 resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS, Aerodyne Research Inc.) equipped with a
169 PM_{2.5} aerodynamic lens at 1 min time resolution. The HR-TOF-AMS provides reliable chemical composition
170 measurements for particles in the 70 - 600 nm size range, and therefore the composition data reported here
171 primarily reflect the larger UFP fraction, with limited sensitivity to sub-60 nm particles (Aktypis et al., 2024).
172 Similarly, the CHARON-PTR-MS detects particles in the 60 - 600 nm size range, but shows reduced particle
173 enrichment efficiency for particles in the 60 - 150 nm size range, meaning that the semi-volatile organic
174 composition data reported here are most representative of particles larger than 150 nm (Muller et al., 2017).
175 However, source factors derived from larger particles can be correlated with UFP size evolution, and gas-phase
176 VOC source factors from PTR-MS provide additional constraints on UFP formation and growth processes across
177 all size ranges. Therefore, while the chemical composition data should be interpreted with these size-dependent
178 limitations in mind, the combined OA/SVOA and VOC source apportionment approach adopted here remains
179 valid for identifying the dominant chemical drivers of UFP dynamics. Formaldehyde was detected using FILIF
180 with ± 27 pptv precision at 10 Hz sampling frequency. CHARON-PTR-MS raw data were processed using
181 IONICON Data Analyzer software (IDA 2.2.0) following established protocols, while AMS data were processed
182 using SQUIRREL 1.65G and PIKA 1.25G. VOC and SVOA from CHARON-PTR-MS were analysed using SoFi
183 Pro 9.0 for exploratory factor analysis, while organic aerosols from AMS underwent source apportionment via
184 PMF Evaluation Tool (v3.08C) in IGOR Pro (v8.04). More details on the instrumentation during the measurement
185 campaigns are provided in Li et al. (2026).

186 To investigate the influence of air mass origins on atmospheric pollutants, 72 - hour backward trajectories arriving
187 at the measurement site at an altitude of 500 m a.g.l. were computed hourly using MeteoInfoMap (Wang, 2019),
188 an open-source trajectory tool referenced on the Hybrid Single-Particle Lagrangian Integrated Trajectory
189 (HYSPPLIT) model website (Cohen et al., 2015), driven by Global Data Assimilation System (GDAS)
190 meteorological fields.



191 **3. Results and Discussion**

192 **3.1 Overview of Ultrafine Particles in Munich**

193 In this section the ultrafine particle number concentrations as well as the variations of particle size distributions
194 during the different seasons will be discussed.

195 **3.1.1 Seasonal Variations in Particle Number Size Distributions**

196 The Particle Number Size Distributions (PNSD) of ultrafine aerosols in the Munich urban area exhibit pronounced
197 seasonal variability, strongly correlated with ambient temperature and atmospheric processes. Similar seasonal
198 variability in ultrafine particle size distributions has also been reported in other urban environments, particularly
199 in European cities such as Helsinki and Leipzig, where particle number concentrations are strongly influenced by
200 temperature-dependent photochemistry and boundary-layer dynamics (Ma and Birmili, 2015; Rose et al., 2021).
201 High average summer temperatures (21.9 ± 5.8 °C) promoted the dominance of the organic aerosol fraction (Org)
202 (Figure 1d, h) and facilitated UFP growth events, particularly during nocturnal periods (Figure 1c, g). These
203 nighttime UFP growth events are likely driven by the condensational growth of semi-volatile organic compounds
204 (SVOCs) onto the particle phase provided by traffic primary particles. Li et al. (2023b) also identified oxidized
205 organic species as dominant contributors to nighttime UFP growth in urban Beijing, suggesting that condensation
206 of secondary organic vapours onto primary traffic particles is a common nocturnal growth mechanism across
207 diverse urban environments. Conversely, the significantly colder winter/spring period (8.4 ± 3.0 °C / 10.2 ± 3.8 °C)
208 presented a more dynamic composition: nitrate dominated in early March (1st - 8th) due to its stability at lower
209 temperatures, before shifting to organic dominance later in that month (9th - 27th) as solar radiation and
210 temperature increased. The nitrate-dominated winter composition observed in Munich aligns with observations in
211 northern France and Helsinki, where low temperatures favour nitrate partitioning onto larger particles, suppressing
212 UFP formation (Roig Rodelas et al., 2019; Lepisto et al., 2023). This seasonal change is also reflected in the UFP
213 number concentration fraction, which was significantly lower in winter ($70.4 \pm 9.2\%$) compared to summer and
214 spring ($82.0 \pm 7.9\%$ and $82.0 \pm 6.7\%$, respectively), potentially due to a lower frequency of new particle formation
215 and enhanced condensational sink during the colder season. Rose et al. (2021) reported higher UFP fractions
216 during warmer months across multiple GAW network sites, attributing this pattern to enhanced photochemical
217 nucleation and growth.

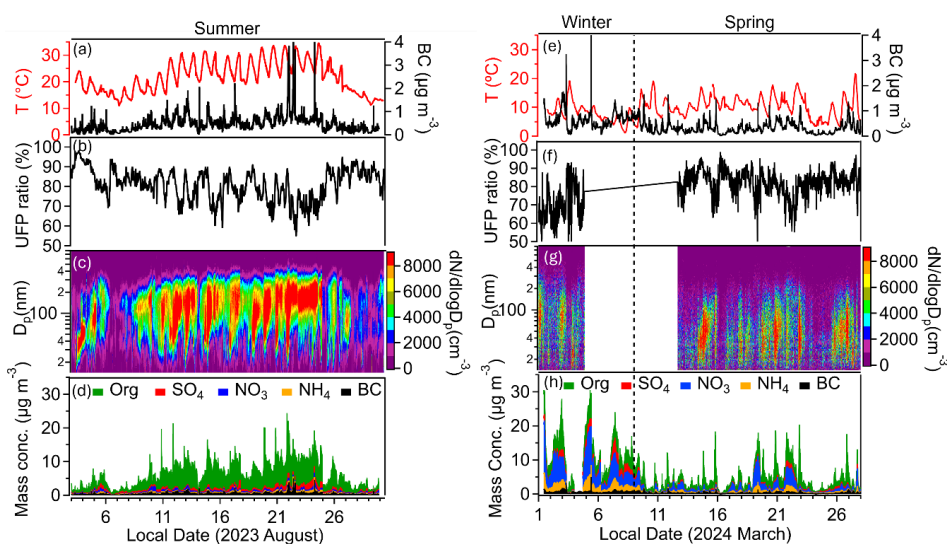


Figure 1. Seasonal characteristics of temperature (T) and equivalent black carbon (eBC) concentrations (a,e); UFP number concentration (Percentage of $D_p < 100$ nm compared to total particle number concentration) (b,f); time-resolved particle number size distributions ($dN/d\log D_p$) (c, g); and mass concentrations of major non-refractory aerosol species measured by the AMS (organic aerosol, sulfate, nitrate, ammonium) along with eBC (d, h) measured in Munich during summer (August 2023) and winter-spring (March 2024).

218 3.1.2 Seasonal Variations in UFP Number Concentrations

219 The pronounced and size-dependent seasonal variability in ultrafine PNC in the Munich urban area, are reflecting
 220 distinct atmospheric production and removal mechanisms across seasons. Focusing first on the smaller size
 221 fraction ($14 \text{ nm} < D_p < 25 \text{ nm}$), which captures recently formed particles in the nucleation and lower Aitken
 222 mode and is most sensitive to new particle formation (NPF) events. The highest median and mean concentrations
 223 are recorded in summer, accompanied by the widest variability (Figure 2a). This pattern strongly suggests that
 224 summer is characterized by frequent and rapid UFP growth events, driven by enhanced night-time oxidation and
 225 photochemical activities (higher OH, O₃), elevated biogenic volatile organic compound (BVOC) emissions, and
 226 favourable meteorological conditions that promote UFP growth (Sun et al., 2024). Winter registers the lowest
 227 concentrations, approximately half the summer values, indicating fewer dynamic atmospheric processes. This is
 228 attributed to suppressed photochemistry, reduced BVOC emissions, and potentially a stable boundary layer that
 229 limits nucleation. Stable boundary layers suppress atmospheric new particle formation (NPF) by reducing
 230 turbulent mixing and precursor transport, while simultaneously increasing the condensation sink as primary
 231 emissions accumulate near the surface, thereby favouring condensation onto pre-existing particles over new
 232 particle nucleation (Hao et al., 2018; Carrillo-Cardenas et al., 2025).

233 The seasonality in the UFP numbers is significantly attenuated in the size range ($25 \text{ nm} < D_p < 100 \text{ nm}$),
 234 suggesting that these particles are influenced more by growth processes and primary emissions than by nucleation
 235 bursts (Figure 2b). Unlike the nucleation mode fraction ($14 \text{ nm} < D_p < 25 \text{ nm}$) discussed above, they show much
 236 smaller differences across seasons compared to the nucleation mode particles, with variability remaining
 237 consistent (Rose et al., 2021). Notably, winter concentrations in this size range are slightly elevated relative to the
 238 other seasons, in contrast to the nucleation mode where summer dominates. This suggests a potential influence



239 from stable primary combustion sources (e.g., traffic and heating) which contribute consistently to this size bin
 240 (Okuljar et al., 2021; Sun et al., 2024).

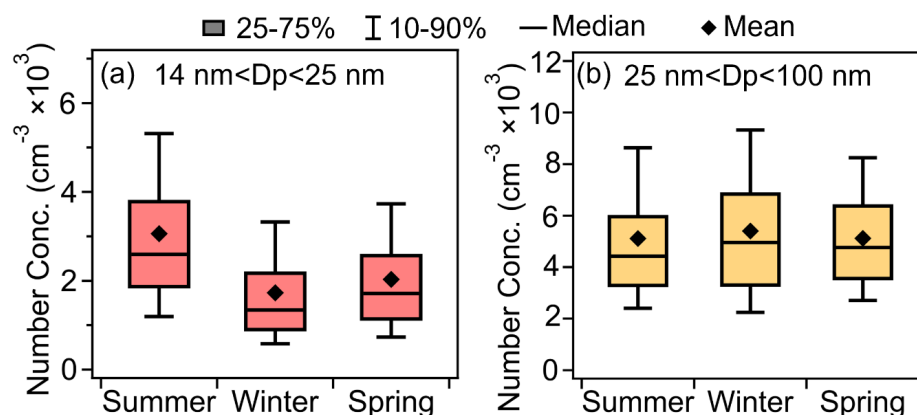


Figure 2. Seasonal variations of particle number concentrations for (a) 14-25 nm and (b) 25-100 nm diameter size ranges in summer, winter, and spring. Box plots show the median, mean, 25-75th percentiles, and 10-90th percentiles. *Please note that winter UFP data were limited to three days (1st - 3rd March) due to a power outage, and the following seasonal comparisons should be interpreted with this limitation in mind.

241 **3.1.3 Diurnal variation of particle size distributions in different seasons**

242 Seasonal differences in particle size distributions in Munich reflect the influence of particle composition on
 243 ultrafine particle behaviour. Figure 3 illustrates that the smaller particles (14nm < D_p < 25nm) show the most
 244 drastic change, with PNC in summer being significantly higher than in spring and winter. This is attributed to the
 245 dominance of secondary photochemical processes at high summer temperatures and intense solar radiation
 246 (Birmili et al., 2010). The summer aerosol mass is dominated by the organic fraction (Org), which exhibits a
 247 strong late-evening peak (21:00 - 22:00) accompanied by shrinking planetary boundary layer (PBL) heights
 248 (Figures 4, 5 and 6) and the enhanced condensation of semi-volatile organic compounds (SVOCs) like oxidized
 249 biogenic compounds (Li et al., 2017; Liaskoni et al., 2024). This high concentration of low-volatility organic
 250 material drives the observed UFP growth events (Haefelin et al., 2024), particularly those occurring nocturnally,
 251 efficiently growing particles into the Aitken mode. Conversely, the significantly colder winter/spring period
 252 suppresses photochemical production and shows much lower UFP ratios due to a combination of reduced NPF
 253 and increased condensational sink by pre-existing particles (Rose et al., 2021). Furthermore, the cold season shifts
 254 the chemical regime: Nitrate dominates in winter, particularly in early March, due to its stability in the particle
 255 phase at lower temperatures (Roig Rodelas et al., 2019). Since nitrate primarily condenses onto larger particles, it
 256 inhibits NPF and UFP growth, resulting in a noisy PNSD lacking a clear nucleation signal. Spring is a transitional
 257 period, where the midday nucleation mode partially recovers alongside an evening increase in organic aerosol,
 258 indicating the revival of photochemical activity; however, remaining nitrate-rich particles enhance the
 259 condensation sink and favour the partitioning of condensable vapours onto larger particles (Roig Rodelas et al.,
 260 2019; Lepisto et al., 2023), which limits the growth efficiency of newly formed ultrafine particles compared with
 261 summer. These seasonal differences are also reflected in the diurnal variations of the geometric mean diameter
 262 (GMD) shown in Fig. 3(g). The mean GMD values are consistently larger than 30 nm across all seasons. The
 263 smallest GMD values occur in summer, indicating a higher abundance of smaller particles associated with active



264 particle formation and growth processes. In contrast, winter exhibits the largest GMD values, reflecting the
 265 stronger influence of aged and larger particles under conditions of suppressed photochemical activity. Spring
 266 shows intermediate behaviour, consistent with its transitional atmospheric conditions.

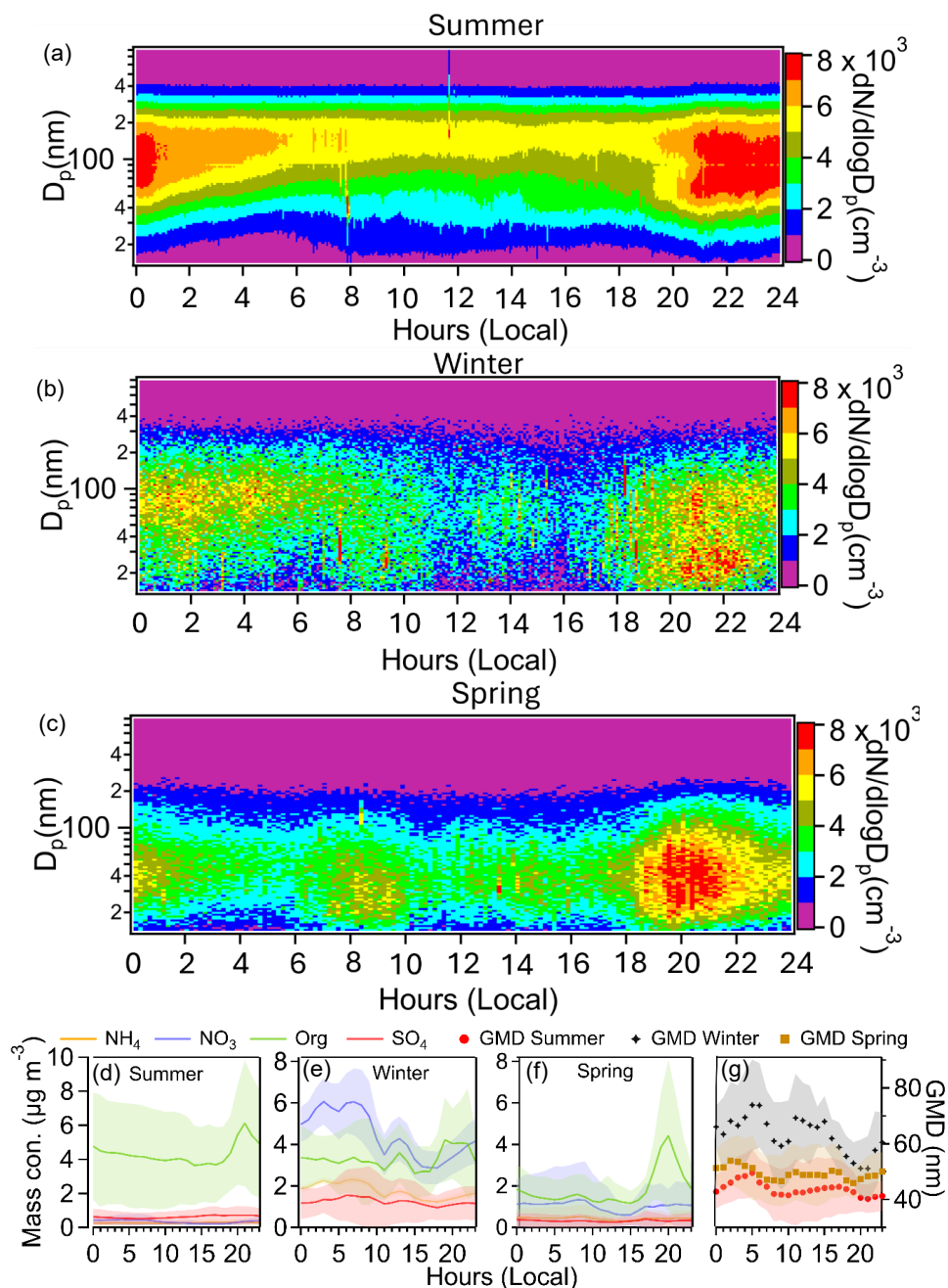


Figure 3. Diurnal variations of particle number size distributions (a–c) and major non-refractory aerosol components measured by the HR-ToF-AMS (organic aerosol, nitrate, ammonium, and sulfate) (d–f) during

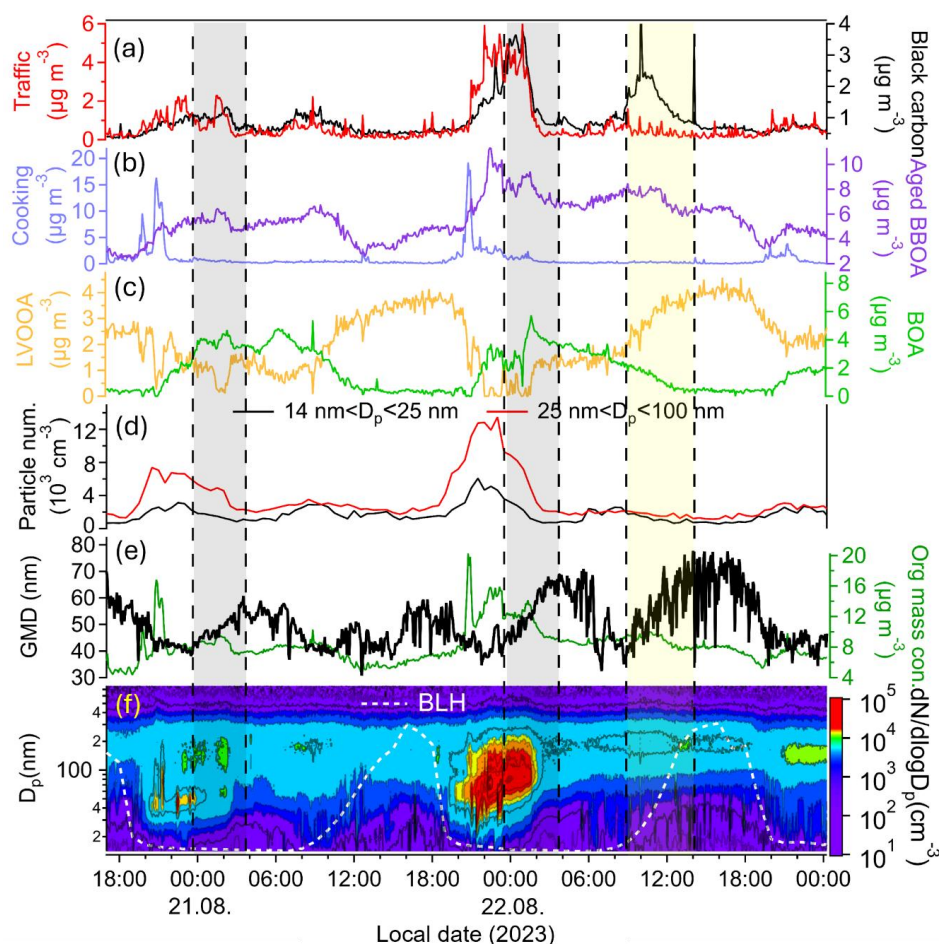


summer, winter, and spring. Lines show the diurnal mean values, and shaded areas represent the seasonal variability. Panel (g) shows the diurnal variations of particle geometric mean diameter (GMD).

267 **3.2 Seasonality of chemical drivers of ultrafine particle growth**

268 To illustrate the chemical drivers of seasonal UFP growth in detail, we focus on representative 48-hour observation
269 windows selected from each season of the two measurement campaigns (summer 2023 and winter/spring 2024).
270 These periods were chosen because they capture multiple recurring growth events with consistent temporal
271 patterns, including nighttime number concentration peaks followed by gradual size increases, that are
272 representative of the broader seasonal behaviour documented in the full dataset. Similar growth sequences were
273 observed repeatedly throughout each season, confirming that the selected periods are not isolated anomalies but
274 reflect systematic and recurring atmospheric processes.

275 Investigating the chemical factors governing seasonal UFP growth, Figure 4 provides a detailed characterization
276 of representative UFP growth events, defined here as increases in geometric mean diameter (GMD) without
277 concurrent new particle formation or sub-25 nm particle bursts, by linking UFP dynamics with organic aerosol
278 (OA) source factors derived through PMF, organic mass, boundary layer height (BLH), and particle size
279 distributions in summer. The data collectively demonstrate that the summer UFP population is fundamentally
280 regulated by an interplay between primary emissions and subsequent secondary organic vapor condensation.
281 These UFP growth events occurred frequently at night, particularly between 00:00 and 04:00, during which the
282 geometric mean diameter (GMD) particle sizes increased from about 40 nm to 60 nm. Importantly, each growth
283 event was preceded by strong particle number peaks associated with evening traffic emissions and shrinking BLH,
284 which trapped primary particles from traffic and cooking within the shallow nocturnal boundary layer. The strong
285 correlations between UFP concentrations and traffic- and cooking-related OA ($R = 0.74$ and 0.49 , respectively;
286 Table S1), together with the significant correlation with traffic VOCs ($R = 0.55$; Table S1), confirm the dominant
287 role of primary emissions during these pre-growth periods. After these sources stabilized or declined, particle
288 growth proceeded. Source apportionment indicates that the subsequent size increase was driven by the
289 condensation and coagulation of semi-volatile and low-volatility organics, particularly biogenic organic aerosol
290 (BOA) and biomass burning organic aerosol (BBOA), while cooking OA became negligible. This interpretation
291 is supported by Figure 4, which shows nighttime peaks in LV-OOA, BOA, and BBOA coincident with UFP growth,
292 and by Figure S3, which illustrates concurrent increases in BBOA, isoprene-oxidized OA & BBOA, regional
293 background OA, weakly oxidized BOA, more oxidized BOA, and black carbon. New particle formation played
294 little or no role, as OA concentrations and precursor VOCs generally peaked before growth initiation. A distinct
295 midday growth event was also observed, characterized by strong increases in BBOA, low volatile oxygenated
296 organic aerosol (LV-OOA), and black carbon while other primary sources and total particle numbers remained
297 low, indicating that photochemical oxidation of biomass-burning and low-volatility organic vapors dominated this
298 daytime growth. Consistent with this interpretation, Figure S2 shows midday increases in biomass-burning and
299 aged VOCs, and Figure S3 shows corresponding peaks in BBOA and isoprene-oxidized OA & BBOA. Early-
300 morning growth is supported by several secondary OA components except cooking OA, whereas midday growth
301 is predominantly linked to photochemically oxidized biomass-burning emissions.



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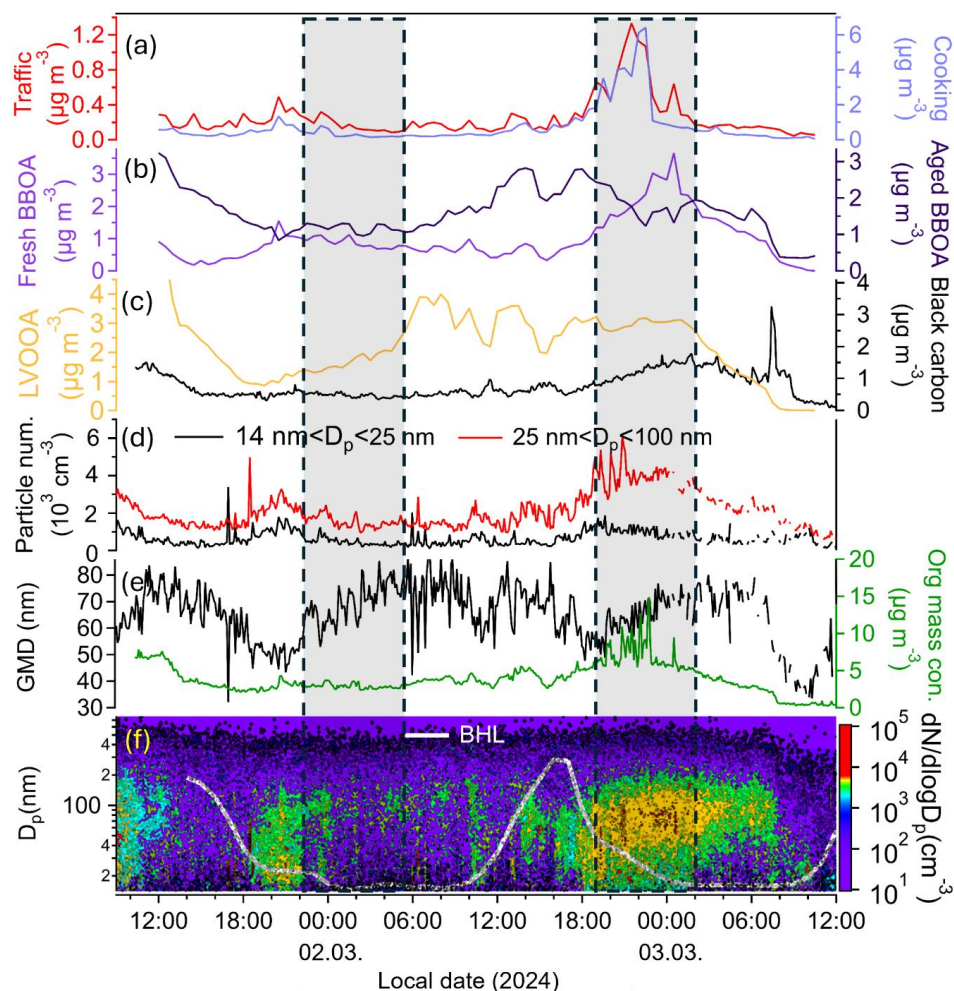
303 **Figure 4.** Representative evolution of organic aerosol source factors derived through AMS-PMF and UFP size
 304 distribution properties during the summer period. Panels show (a) Traffic OA and black carbon, (b) Cooking OA
 305 and Aged BBOA, (c) major secondary OA components (LVOOA, BOA), (d) number concentrations of 14-25 nm
 306 and 25-100 nm particles, (e) geometric mean diameter (GMD) and total organic mass concentration, and (f)
 307 particle number size distribution ($dN/d\log D_p$) with boundary layer height (BLH). Grey shaded regions denote
 308 night time non-nucleation UFP growth periods; the yellow shaded region denotes daytime UFP growth periods.

309 Winter UFP behaviour shows a similar temporal pattern compared to summer in terms of peak number
 310 concentrations, with UFP number concentration increases occurring almost exclusively during nighttime and early
 311 morning when the BLH decreases and remains very shallow, allowing primary emissions to accumulate near the
 312 surface. However, the chemical drivers differ substantially from those in summer. Due to a power outage, winter
 313 UFP data were only available for 1st - 3rd March. Although this limits the generalisability of the winter results,
 314 these observations suggest that UFP growth during this period is primarily governed by primary combustion
 315 emissions and the trapping of semi-volatile species within a shallow boundary layer, rather than photochemical
 316 SOA formation. This pattern is broadly consistent with wintertime UFP behaviour reported in comparable
 317 European urban environments (Roig Rodelas et al., 2019; Lepisto et al., 2023). Strong correlations between UFP



318 concentrations and organic aerosol from traffic ($R = 0.75$) and cooking ($R = 0.69$) (Table S2) confirm that primary
319 anthropogenic emissions dominate the initial number concentration peaks (Figure 5). In addition, SVOA factors,
320 especially nighttime-aged BBOA, which shows the highest correlation with UFP ($R = 0.86$), exhibits temporal
321 behaviour closely aligned with UFP growth periods (Fig. S5), indicating that condensation of semi-volatile
322 biomass-burning emissions strongly enhances wintertime particle growth. UFP growth from ~ 40 nm to ~ 80 nm
323 occurs during periods of elevated SVOA concentrations, particularly nighttime-aged ($R = 0.86$) and daytime-aged
324 BBOA ($R = 0.53$), regional background SVOA ($R = 0.79$), and cooking-related organics ($R = 0.61$). These
325 components rise during the same intervals in which the mean particle size (GMD) increases, while total particle
326 number remains steady or declines, consistent with condensation-driven growth and mild coagulation, rather than
327 new particle formation. VOC factor behaviour further supports this primary-emission-driven mechanism: traffic
328 related VOC correlate positively with UFP (Traffic 1: $R = 0.47$), and background VOC show even stronger
329 associations ($R = 0.73$), reflecting the accumulation of semi-volatile vapours in a stable nocturnal boundary layer
330 (Fig. S4). Overall, the winter results show that UFP dynamics are governed by primary sources (traffic, cooking,
331 biomass burning) and secondary processing of semi-volatile organics at lower temperatures. Shallow boundary
332 layer heights (BLH) amplify these effects by promoting accumulation and enhancing vapor condensation onto
333 existing particles.

334



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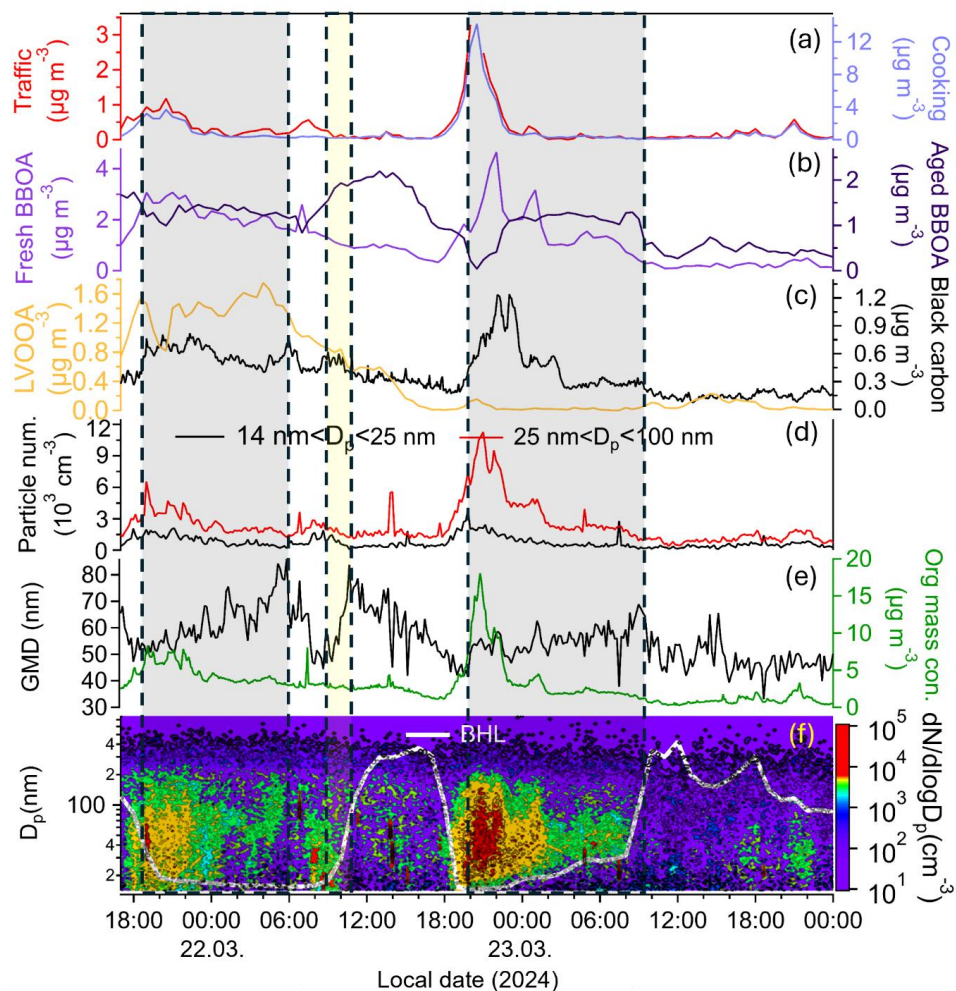
336 **Figure 5.** The evolution of organic aerosol source factors and UFP size distribution properties during the winter
 337 period (1st – 3rd March). Panels show (a) Traffic and Cooking OA, (b) Fresh BBOA and Aged BBOA, (c) LVOOA
 338 and Black carbon, (d) number concentrations of 14-25 nm and 25-100 nm particles, (e) geometric mean diameter
 339 (GMD) and total organic mass concentration, and (f) particle number size distribution ($dN/d\log D_p$) with boundary
 340 layer height (BLH). Grey shaded regions denote night time non-nucleation UFP growth periods.

341 Spring UFP behaviour again shows pronounced nighttime and early-morning increases with decreasing and
 342 shallow boundary layer heights (BLH), but with a more complex mixture of primary and secondary sources
 343 compared to winter. During 9th – 27th March, 2024, representative non-nucleation growth events (Fig. 6) reveal
 344 that UFP number peaks occur when traffic and cooking emissions accumulate in a shallow boundary layer,
 345 followed by periods of particle growth from ~ 40 nm to ~70 - 80 nm. Strong correlations between UFP
 346 concentrations and organic aerosol from traffic and cooking ($R = 0.74$ and 0.70 , respectively; Table S3) confirm
 347 the dominant role of primary anthropogenic sources in setting the initial number concentration levels. At the same



348 time, fresh and aged BBOA also correlates relatively well with UFP ($R \approx 0.64 - 0.66$; Table S3), and their time
349 series in Fig. 6 and Fig. S7 show clear enhancements during both night-time and daytime UFP growth periods,
350 indicating that biomass-burning emissions provide an important reservoir of semi-volatile compounds for
351 subsequent condensation. SVOA factors, particularly night-time-aged BBOA ($R = 0.59$), combustion OA and
352 regional SVOA (Fig. S7), rise concurrently with increases in mean particle size (GMD) while total particle number
353 remains nearly constant or decreases, which is consistent with condensation-driven growth and some coagulation
354 rather than new particle formation. The behaviour of VOC source factors further supports this interpretation:
355 Traffic 1 and Traffic 2 VOC (Fig. S6) exhibit strong positive correlations with UFP ($R = 0.73$ and 0.75), while
356 monoterpenes and biomass-burning VOC show weaker correlations ($R \approx 0.4$ and 0.36 ; Table S3). In contrast,
357 LVOOA shows almost no correlation with UFP, implying that highly aged regional SOA plays only a minor role
358 in the short-term growth episodes observed here. Overall, the spring results indicate that UFP dynamics are
359 controlled by a combination of traffic and cooking emissions, biomass-burning OA and their semi-volatile vapours,
360 with an emerging contribution from photochemically oxidized VOCs.

361



362

363 **Figure 6.** Representative evolution of organic aerosol source factors and UFP size distribution properties during the spring period. Panels show (a) Traffic OA and Cooking OA, (b) Fresh BBOA and Aged BBOA, (c) LVOOA
 364 and Black carbon, (d) number concentrations of 14 - 25 nm and 25 - 100 nm particles, (e) geometric mean diameter
 365 (GMD) and total organic mass concentration, and (f) particle number size distribution ($dN/d\log D_p$) with boundary
 366 layer height (BLH). Grey shaded regions denote night time non-nucleation UFP growth periods; the yellow shaded
 367 region denotes a daytime UFP growth period.
 368

369 Across summer, winter, and spring, UFP number concentrations consistently peaked during nighttime and early
 370 morning when the BLH decreased or remained shallow. This similarity highlights the universal importance of
 371 BLH-driven accumulation of primary emissions, mainly traffic and cooking, in setting the initial UFP number
 372 levels. In all seasons, UFP growth occurred mainly without new particle formation: increases in geometric mean
 373 diameter were accompanied by stable or decreasing particle numbers, indicating that growth proceeded through
 374 condensation onto pre-existing particles or coagulation at high particle numbers.



375 Despite these common features, the chemical drivers of UFP growth differed markedly among seasons. In summer,
376 UFP evolution was strongly influenced by secondary organic aerosol formation. Low-volatility oxygenated OA,
377 biogenic OA, and biomass-burning OA increased during growth periods, and daytime growth was linked to
378 photochemical oxidation of biomass burning organic aerosol. In winter, UFP number and growth are governed
379 primarily by traffic, cooking, and biomass-burning emissions. Strong correlations with nighttime-aged BBOA and
380 other semi-volatile OA components indicate that growth was dominated by condensation of semi-volatile vapours
381 at lower temperatures, with minimal photochemical contribution. In spring, UFP behaviour reflected a transitional
382 regime. Nighttime growth resembled winter, driven by primary emissions and biomass-burning SVOA, while
383 emerging photochemical activity supported daytime growth associated with oxidized VOCs and semi-volatile
384 organics. Overall, while BLH-driven accumulation controls UFP number peaks in all seasons, the dominant
385 growth mechanisms shift from photochemical SOA in summer to semi-volatile primary and biomass-burning
386 organics in winter, with spring exhibiting mixed characteristics.

387 **3.3 Atmospheric drivers of seasonal UFP variability**

388 Besides dynamics of emissions, chemical processes, and the urban boundary layer which have been discussed
389 above additional potential drivers of UFP like air mass origin and urban meteorology will be addressed in the
390 following.

391 **3.3.1 Influence of Air Mass Origin**

392 Across the three seasons, clear differences emerge in how regional air mass origins shape UFP size distributions.
393 In summer, four dominant air mass clusters could be identified, including local (C_1), continental (C_2 , C_4), and
394 maritime (C_3) air masses as shown in Figure 7 (a-c). Maritime air masses typically transport relatively clean
395 background air with low condensation sinks, favouring both local photochemical formation of ultrafine particles
396 during daytime and nocturnal condensation-driven UFP growth, as the reduced aerosol loading allows semi-
397 volatile organic vapours to partition more efficiently onto pre-existing particles (Salimi et al., 2017; Bousiotis et
398 al., 2021b). In contrast, continental air masses carry more aged regional aerosols with higher condensation sinks,
399 suppressing new particle formation while enhancing accumulation-mode particle fractions (Andreae et al., 2022).
400 In winter, five air mass clusters appear, with strong contributions from northwest and central European pathways
401 (C_1 , C_2). These air masses are generally aged and relatively polluted, consistent with the dominance of
402 accumulation-mode particles and limited presence of freshly formed ultrafine particles, reflecting weaker winter
403 photochemistry. Spring exhibits a transitional pattern, with a pronounced contrast between clean maritime inflow
404 (C_3), which supports higher proportions of < 25 nm particles, and continental clusters (C_4 , C_5), which transport
405 aged or biomass-burning-influenced aerosols and thus suppress the smallest size fractions. This seasonal contrast
406 is also reflected in the prevailing air mass directions: during summer and spring, air masses are predominantly
407 transported from the westerly marine sector, bringing relatively clean air to Munich, whereas in winter air masses
408 more frequently originate from the easterly continental sector, transporting more polluted and aged aerosols from
409 inland Europe. As a result, summer and spring generally exhibit lower condensation sinks and more favourable
410 conditions for ultrafine particle formation and growth, whereas winter conditions tend to suppress the smallest
411 particle fractions (Giemsas et al., 2021; Hirshorn et al., 2022).

412 Seasonal wind patterns further reinforce these behaviours: summer winds are stronger and more variable,
413 enhancing dispersion; winter winds are calmer and more stagnant, promoting accumulation of primary UFP; and



414 spring winds exhibit intermediate characteristics, with episodic easterly flow bringing polluted continental air in
 415 as shown in Figure 7(d-f). These meteorological conditions regulate dilution, residence time, and the background
 416 concentrations of ultrafine particles available for subsequent growth. Consistent with these patterns, the size-
 417 resolved particle number fractions show that, across all clusters, summer exhibits the highest fractions of 14-25
 418 nm particles, while winter shows the lowest, reflecting the suppression of new ultrafine particles under cold and
 419 stagnant conditions. Similarly, the combined 14-100 nm particle fraction is smallest in winter, whereas summer
 420 and spring both maintain high ultrafine particle fractions (~80%) as shown in Figure 7(g-i), indicating more active
 421 photochemical or semi-volatile condensation processes during these seasons.

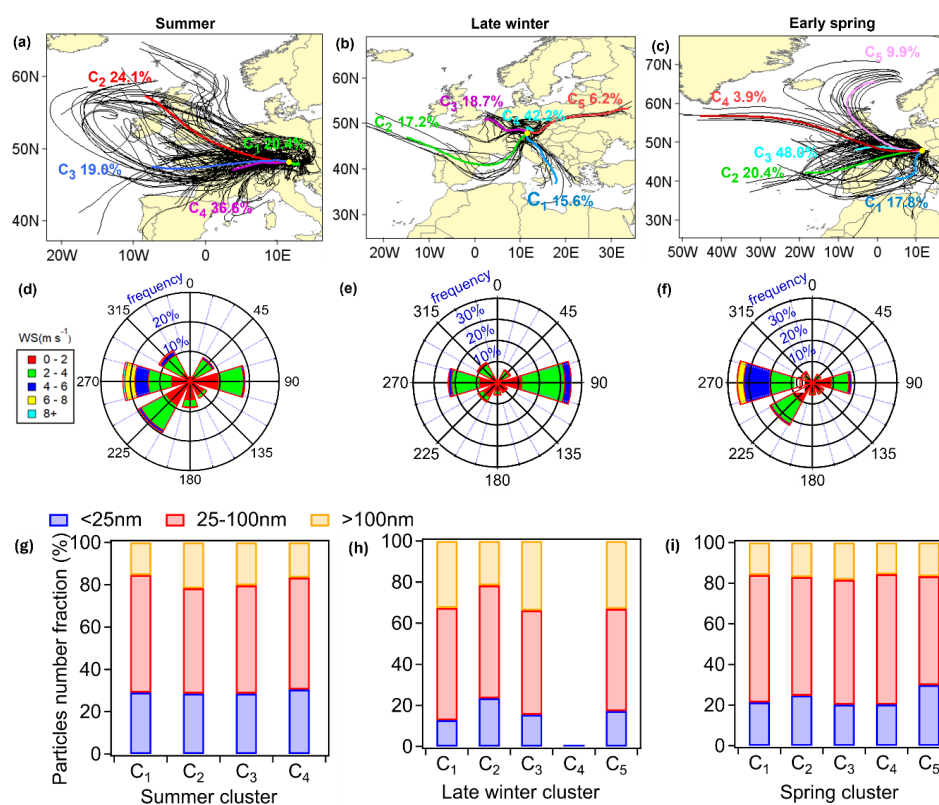


Figure 7. Seasonal air mass origins, local wind conditions (30 m above street level), and size-resolved particle number fractions for summer, late winter, and early spring. Panels (a-c) show 72-h back-trajectory air mass clusters, illustrating distinct source regions and transport pathways for each season (Wang, 2019). Panels (d-f) display wind roses of wind speed and direction measured at 30 m above street level during the respective periods, indicating seasonal differences in prevailing winds and dispersion conditions. Panels (g-i) present the fraction of particle numbers in three size ranges (14–25 nm, 25–100 nm, and 100–800 nm) for each trajectory cluster (no cluster 4 in winter due to limited SMPS data).

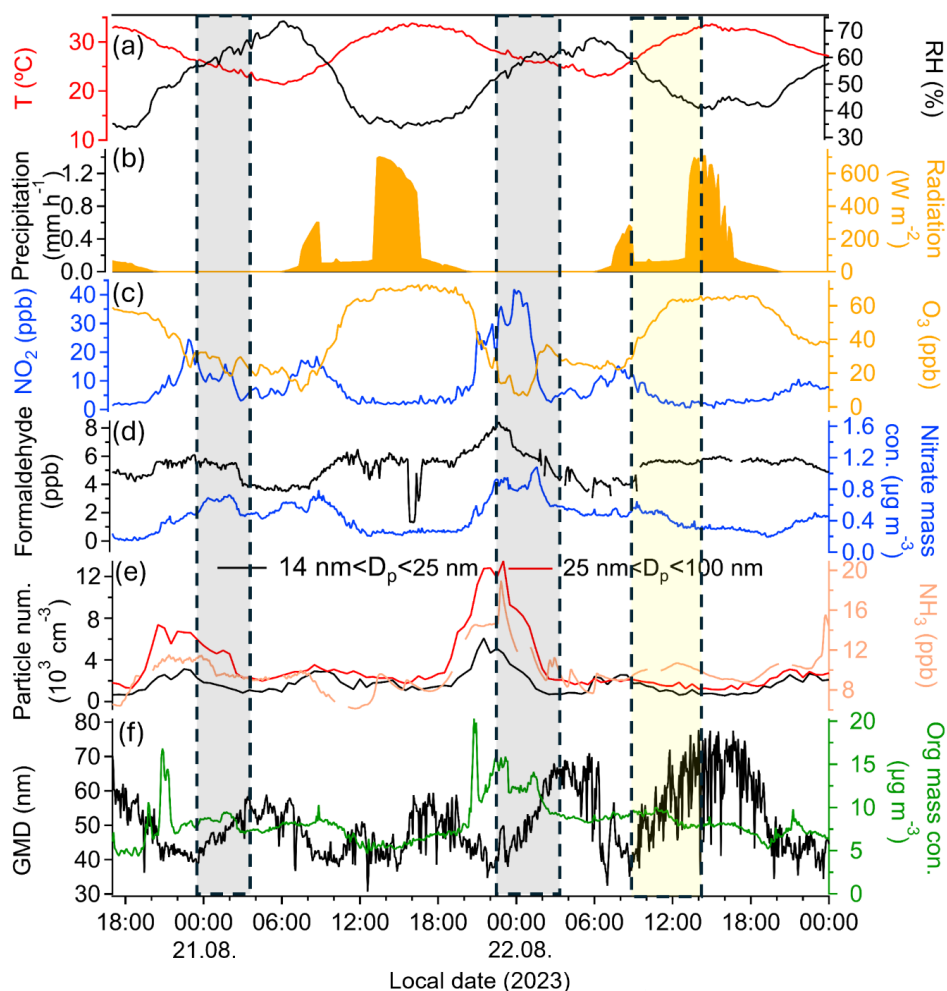
422 3.3.2 Effects of local meteorology on seasonal UFP growth

423 During two nighttime growth events in summer, Figure 8 shows conditions of lower temperature, high relative
 424 humidity, and the absence of solar radiation, under which NO₂-rich traffic-related emissions accumulate. These
 425 conditions lead to elevated UFP number concentrations and correspond to traffic- and cooking-dominated periods



426 (see Figure 4). Following these pre-growth peaks in UFP number concentrations from primary emission, the mean
427 particle size (GMD) increases while particle number declines, indicating particle growth through condensation
428 and coagulation processes. Figure 4 shows that this size growth corresponds to enhanced contributions from LV-
429 OOA, BOA and BBOA, confirming that condensation of semi-volatile and low-volatility organic vapours drives
430 nighttime growth. These conditions favour the accumulation of traffic-related emissions and condensable vapours
431 within the shallow nocturnal boundary layer. During the growth periods, particulate nitrate concentrations remain
432 relatively stable and do not show a concurrent increase, indicating that condensation of inorganic nitrate is unlikely
433 to be the dominant driver of the observed particle growth. Although NH_3 concentrations increase during the
434 preceding emission peaks (Figure 8e), they do not show a clear relationship with the particle growth phase itself,
435 suggesting that NH_3 -driven inorganic growth processes likely play only a minor role. The relatively steady levels
436 of formaldehyde and organic aerosol mass further suggest that growth is supported by condensable organic
437 vapours already present in the air mass. However, additional nighttime production of low-volatility vapours
438 through oxidation processes, such as NO_3 radical chemistry, cannot be excluded. Such nighttime particle growth
439 driven by condensation of semi-volatile organic vapours under traffic-influenced urban conditions has been
440 reported in several European field studies (Man et al., 2015; Carnerero et al., 2018). Similar growth behaviour,
441 characterised by increasing GMD following primary emission peaks and decreasing particle number
442 concentrations due to condensation and coagulation, has also been observed in traffic-influenced urban
443 environments (Straaten et al., 2022).

444 For the daytime growth event, Figure 8 shows relatively high solar radiation, elevated O_3 and reduced NO_2 ,
445 indicating active photochemistry and somewhat weaker traffic influence. Although formaldehyde and organic
446 mass do not spike sharply, mean particle size (GMD) increases while the 25 - 100 nm mode strengthens, mirroring
447 the particle size evolution shown in Figure 4. The chemical factors shown in Figure 4, especially LV-OOA, BBOA
448 and oxidized VOC-derived SOA can explain this growth, indicating that daytime oxidation processes supply
449 enough low-volatile compounds for efficient condensation even when gas-phase precursor signals vary smoothly.
450 Across European sites, daytime photochemistry supplies oxidized VOCs for growth despite variable emissions,
451 boundary-layer dilution controlling particle number concentrations (Carnerero et al., 2018).



452

453

Figure 8. Meteorological parameters and gas-phase tracers during representative summer UFP growth events. Panels show (a) temperature (T) and relative humidity (RH), (b) precipitation and solar radiation*, (c) NO₂ and O₃, (d) formaldehyde and nitrate mass concentration, (e) number concentrations of 14-25 nm, 25-100 nm particles, and ammonia (f) geometric mean diameter (GMD) and total organic mass concentration. Grey shaded regions denote nighttime non-nucleation UFP growth events; the yellow shaded region indicates a daytime growth event. *Please note that the global radiation plotted here is affected by the shadow of the nearby buildings and is thus not representative for the whole street canyon of Theresienstrasse.

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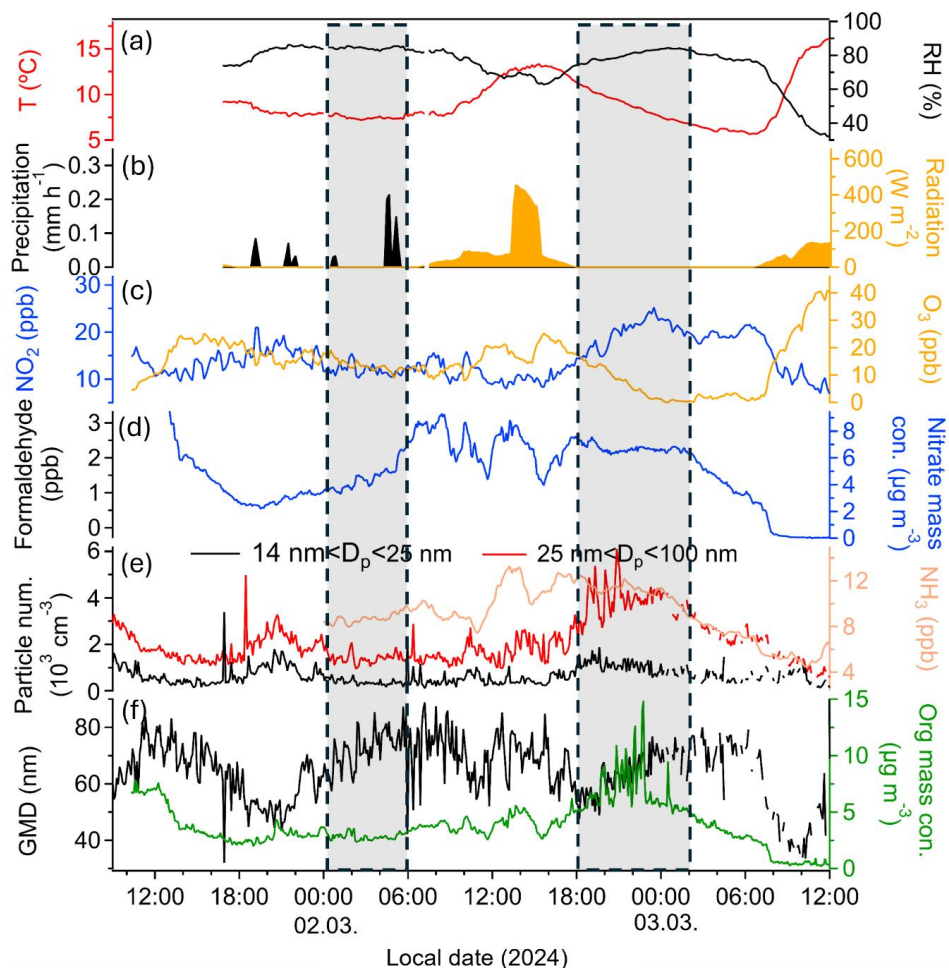
466

Winter UFP evolution is tightly controlled by meteorological conditions that favour the accumulation and condensation of primary combustion-related vapours. All UFP growth periods occur during nighttime and early morning, when solar radiation is absent, temperatures drop, and RH increases (Fig. 9a-b). These conditions coincide with a shallow boundary layer (Fig. 5f), which allows primary pollutants to build up rapidly near the surface. Correspondingly, NO₂ concentrations rise sharply while O₃ remains low (Fig. 9c), indicating intense traffic and residential combustion emissions coupled with minimal photochemical activity. This meteorological pattern aligns closely with the chemical composition shown in Figure 5, which reveals that winter UFP number



467 peaks correlate strongly with organic aerosol from traffic ($R = 0.75$), cooking ($R = 0.69$), and particularly
468 nighttime-aged BBOA ($R = 0.86$). These correlations suggest that combustion-related emissions provide both the
469 primary ultrafine particles and the semi-volatile organic vapours that contribute to subsequent particle growth.
470 Multi-city analyses across urban Europe have shown that road traffic is the dominant source of urban UFP number
471 concentrations, with additional contributions from residential combustion and, in some settings, cooking-related
472 emissions, especially during stagnant conditions and reduced dilution (Ma et al., 2023; Garcia-Marles et al., 2024b;
473 Rowell et al., 2024).

474 Figure 9 further clarifies the growth mechanism. Following the peaks in UFP number concentrations, the mean
475 particle size increases while particle number concentrations decrease, indicating particle growth through
476 condensation and coagulation processes. During these periods, neither formaldehyde nor total organic mass shows
477 sharp increases (Fig. 9d, f), suggesting that growth is not driven by fresh photochemical SOA production but
478 rather by the condensation of semi-volatile vapours already present in the air mass and accumulated within the
479 shallow nocturnal boundary layer. Likewise, nitrate concentrations (Fig. 9d) show no coherent enhancement with
480 mean particle size growth, indicating that inorganic pathways play a minor role. Similarly, NH_3 concentrations
481 increase during the preceding emission accumulation periods but do not exhibit a clear relationship with the
482 particle growth phase itself (Fig. 9e), suggesting that NH_3 -driven ammonium nitrate formation is unlikely to be
483 the dominant driver of the observed particle growth.



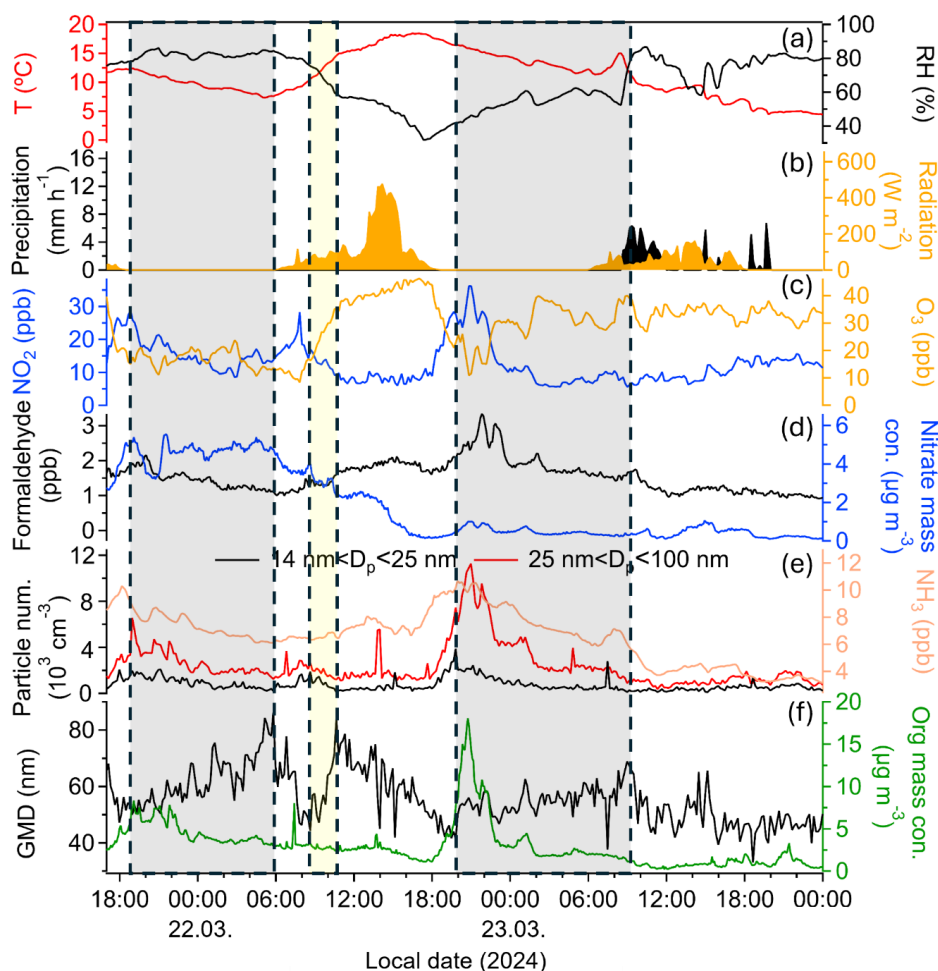
484

485 **Figure 9.** Meteorological parameters and gas-phase tracers during short-time winter UFP growth events. Panels
 486 show (a) temperature (T) and relative humidity (RH), (b) precipitation and solar radiation, (c) NO₂ and O₃, (d)
 487 formaldehyde and nitrate mass concentration, (e) number concentrations of 14-25 nm, 25-100 nm particles and
 488 ammonia (f) geometric mean diameter (GMD) and total organic mass concentration. Grey shaded regions denote
 489 nighttime non-nucleation UFP growth events.

490 Spring UFP evolution is shaped by a combination of nighttime boundary-layer stagnation and moderate daytime
 491 photochemical activity. As in other seasons, the largest UFP number peaks occur during nighttime and early
 492 morning (grey shading in Figure 10), when temperature decreases, RH increases, and solar radiation is zero (Fig.
 493 10a-b). During these periods the boundary layer is shallow (Fig. 6f), allowing NO₂ to accumulate and O₃ to remain
 494 relatively low (Fig. 10c). Correspondingly, UFP numbers rise sharply (Fig. 10e), consistent with the primary-
 495 emission correlations in spring (traffic OA R = 0.74; cooking OA R = 0.70; Table S3) and the temporal patterns
 496 in Figure 6. Following these nighttime number peaks, the mean particle size increases while particle number
 497 concentration declines, indicating particle growth through condensation and coagulation processes, similar to the
 498 nocturnal growth pattern observed in summer and winter. Unlike winter, spring also exhibits distinct daytime



499 growth episodes (yellow shading in figure 10), marked by rising solar radiation and increasing O_3 accompanied
500 by decreasing NO_2 (Fig. 10a-c). During these intervals the UFP number concentration does not show an increase,
501 but the mean particle size rises sharply (Fig. 10e-f). This behaviour indicates efficient growth of pre-existing
502 particles due to enhanced photochemical activity. The corresponding midday increase in aged BBOA in Figure 6
503 demonstrates that spring has a measurable contribution from photochemically oxidized organic vapours, although
504 less intense than in summer. At the same time, nitrate concentrations remain relatively stable during both nighttime
505 and daytime growth periods and do not show a clear concurrent increase with particle size growth, suggesting that
506 inorganic nitrate condensation is unlikely to be the dominant driver. Similarly, NH_3 concentrations increase
507 mainly during the preceding accumulation periods but show no clear relationship with the subsequent particle
508 growth phase itself, indicating that NH_3 -driven inorganic growth likely plays only a minor role. Overall, spring
509 displays a mixed seasonal growth regime, combining summer and winter nighttime accumulation of primary
510 emissions under a shallow boundary layer with summer-like daytime photochemical growth driven by oxidized
511 organic vapours. This transitional behaviour suggests that spring UFP evolution reflects the coexistence of
512 combustion-related nocturnal growth and photochemistry-enhanced daytime growth. Urban observations in
513 Beijing show that spring UFP concentrations are influenced by both primary emissions and secondary formation,
514 reflecting the transition from wintertime particle growth to the increasing occurrence of new particle formation
515 events typical of summer (Li et al., 2023b). This parallel seasonal transition, observed despite the large differences
516 in emission magnitude, suggests that the shift from combustion-dominated nocturnal growth in winter to
517 photochemically enhanced daytime growth in spring may be a general feature of mid-latitude urban environments
518 rather than a city-specific phenomenon.



519

520 **Figure 10.** Meteorological parameters and gas-phase tracers during representative spring UFP growth events.
 521 Panels show (a) temperature (T) and relative humidity (RH), (b) precipitation and solar radiation, (c) NO₂ and O₃,
 522 (d) formaldehyde and nitrate mass concentration, (e) number concentrations of 14-25 nm, 25-100 nm particles
 523 and ammonia (f) geometric mean diameter (GMD) and total organic mass concentration. Grey shaded regions
 524 denote nighttime non-nucleation UFP growth events; the yellow shaded region indicates a daytime growth event.

525 Taking together the seasonal analyses above, a consistent mechanistic picture emerges. UFP number
 526 concentrations peak primarily under shallow boundary-layer conditions that trap traffic- and cooking-related
 527 emissions, with elevated NO₂ and reduced O₃. Such accumulation under stagnant nocturnal boundary layers has
 528 also been widely reported in urban environments, where suppressed mixing enhances the influence of primary
 529 emissions on ultrafine particle number concentrations (Mohan et al., 2024). These stagnant nighttime periods
 530 produce strong pre-growth number peaks in summer, winter, and spring. In contrast, mean particle size (GMD)
 531 growth is consistently decoupled from number concentration and is driven by the availability of condensable
 532 organic vapours, consistent with previous studies showing that particle growth is primarily controlled by
 533 condensable vapours rather than by primary particle emissions themselves (Mohr et al., 2019; Li et al., 2022). In



534 summer, growth arises from LV-OOA, BOA, and BBOA at night and from photochemically oxidized vapours
535 during daytime, reflecting the strong role of photochemical oxidation and secondary organic aerosol formation
536 under high radiation conditions reported for many urban atmospheres (Gu et al., 2023; Song et al., 2024). Winter
537 growth relies almost entirely on condensation of semi-volatile biomass-burning and combustion organics
538 accumulated in the very shallow nocturnal boundary layer, with negligible photochemical contribution, similar to
539 observations in polluted wintertime urban environments where limited photochemistry shifts particle growth
540 toward condensation of primary or semi-volatile combustion emissions (Sun et al., 2013; Li et al., 2023b). Spring
541 exhibits a hybrid behaviour: nighttime growth resembles winter, while moderate daytime photochemistry enables
542 additional oxidation-driven growth. Such transitional behaviour between winter accumulation regimes and
543 summer photochemical regimes has also been observed in other mid-latitude urban environments (Li et al., 2023b).
544 These results highlight that UFP numbers are controlled primarily by boundary-layer dynamics and primary
545 emissions, whereas growth of mean particle size reflects seasonally varying sources of condensable organic
546 vapours.

547 **4 Conclusions**

548 This study addressed key gaps regarding the sources, seasonal drivers, and atmospheric processes governing UFP
549 in urban environments. Previous work has highlighted the diversity of UFP sources and the large spatial and
550 temporal variability of particle number concentrations across cities (Kumar et al., 2014; Brines et al., 2015).
551 However, limited chemical resolution and inconsistent measurement protocols have hindered a mechanistic
552 understanding of how primary emissions, atmospheric oxidation, and meteorology jointly shape UFP number
553 concentrations and size evolution. By combining particle number and size distribution measurements with aerosol
554 particle and VOC composition, this work provides an integrated, high-resolution characterization of UFP
555 dynamics across seasons in a street canyon of a typical European city, directly responding to the WHO/EU
556 emphasis on improved UFP assessment.

557 Our results reveal a consistent two-step mechanism across all seasons: (1) reduce nighttime boundary-layer
558 heights drive increasing UFP number concentrations through the accumulation of traffic, cooking and combustion
559 related emissions (Ma et al., 2023; Garcia-Marles et al., 2024b; Rowell et al., 2024), and (2) subsequent particle
560 growth from ~ 40 to 60 - 80 nm is governed by condensation of seasonally varying organic vapours, with new
561 particle formation playing a negligible role across all seasons as evidenced by stable or declining particle number
562 concentrations during growth periods. This finding extends previous observations of urban UFP variability by
563 showing that particle number concentrations and particle growth processes are mechanistically decoupled,
564 consistent with recent studies highlighting the dominant role of condensable organic vapours in particle growth
565 (Man et al., 2015; Carnerero et al., 2018).

566 These results establish a unified mechanistic framework in which UFP dynamics in urban street canyons are
567 governed by two independent controls: boundary layer modulated emission accumulation sets the number
568 concentration, while the volatility and availability of organic vapours determines the extent and pathway of size
569 growth. Seasonal differences in growth pathways further refine the conceptual understanding of UFP processes.
570 In summer, growth is driven by both semi-volatile organics at night and photochemically oxidized vapours during
571 daytime. In winter, growth is almost entirely controlled by biomass-burning and combustion-derived semi-volatile



572 organics accumulated in a very shallow nocturnal boundary layer, with negligible photochemical influence. Spring
573 represents a transitional regime in which nighttime behaviour resembles winter while moderate daytime oxidation
574 introduces an additional, weaker photochemical growth pathway. Such seasonal transitions between winter
575 accumulation regimes and summer photochemical regimes have also been reported in other urban environments,
576 including Beijing (Li et al., 2023b), and help explain the strong seasonal heterogeneity in urban UFP
577 characteristics reported across Europe (Giemsa et al., 2021; Garcia-Marles et al., 2024b).

578 By directly linking UFP size evolution with chemically resolved OA/SVOA/VOC factors and meteorological
579 drivers, this study demonstrates that UFP number concentrations are primarily determined by emission strength
580 and boundary-layer dynamics, whereas UFP growth is dominated by the availability and volatility of organic
581 vapours rather than by nucleation events. This mechanistic decoupling between number concentration and size
582 growth has not been explicitly demonstrated across three seasons in a European street canyon before. While
583 Garcia-Marles et al. (2024b) identified traffic and photonucleation as dominant UFP sources across European
584 cities, our results show that condensation of semi-volatile organics rather than nucleation governs size growth in
585 Munich across all seasons, extending the current understanding of UFP processes in urban street canyons.
586 Furthermore, the absence of classical new particle formation in all observed growth events contrasts with studies
587 in more polluted Asian megacities such as Beijing, where NPF contributed substantially to UFP number
588 concentrations across seasons (Tao et al., 2023; Li et al., 2023b), highlighting the importance of city-specific
589 emission profiles and condensation sink conditions in shaping UFP dynamics.

590 Several caveats should be considered when interpreting these results. The aerosol composition measurements
591 primarily reflect the accumulation mode, and future work combining single-particle mass spectrometry with high-
592 time-resolution volatility measurements would further constrain the role of individual organic compounds in UFP
593 growth. From a modelling perspective, the mechanistic decoupling demonstrated here suggests that separate
594 treatment of boundary-layer-driven accumulation and organics-driven condensational growth is necessary for
595 accurate representation of UFP in urban street canyons, rather than treating number concentration and size as co-
596 varying quantities. The dominance of condensational growth over new particle formation across all seasons also
597 implies that the condensation sink is a key variable for UFP modelling in European cities, in contrast to the NPF-
598 dominated regimes reported in Asian megacities.

599 These findings have direct implications for mitigation strategies targeting urban UFP exposure. First, since UFP
600 number concentrations are primarily driven by traffic and cooking emissions accumulating under shallow
601 boundary layers, measures targeting these primary emission sources are most effective for reducing peak UFP
602 exposure. Stricter vehicle emission standards targeting sub-23 nm non-volatile particles, which dominate traffic
603 emissions as shown by Lintusaari et al. (2023), and the adoption of advanced diesel particle filters represent critical
604 near-term interventions, though their effectiveness in reducing nucleation-mode UFPs remains limited
605 (Damayanti et al., 2023). Emission controls on commercial cooking, such as improved ventilation and filtration
606 systems in restaurant-dense urban areas, should also be considered given the consistently strong correlation
607 between cooking OA and UFP number concentrations observed across all seasons. Second, since UFP growth in
608 summer is strongly driven by condensable organic vapours from biomass burning and photochemical oxidation,
609 reducing open biomass burning and controlling VOC emissions from both traffic and biomass burning sources
610 would limit the availability of condensable material for particle growth. In winter, when biomass-burning SVOA



611 dominates UFP growth, targeted restrictions on residential wood burning, as already implemented in several
612 European cities, would be particularly effective (Roig Rodelas et al., 2019). Third, the strong seasonal dependence
613 of UFP drivers identified here underscores that a one-size-fits-all approach to UFP mitigation is insufficient.
614 Season-specific strategies are needed: summer interventions should prioritize VOC emission controls and
615 photochemical oxidant reduction, while winter measures should focus on combustion emission restrictions and
616 boundary-layer ventilation through urban planning. These results directly support the WHO and EU policy
617 framework calling for improved UFP monitoring and source-specific exposure reduction, and provide a seasonally
618 resolved mechanistic basis for designing targeted urban air quality interventions.

619

620 **Data availability**

621 Data corresponding to this manuscript will be available at the data repository KITopen (DOI:10.35097/bs139dd72
622 d5s0r6a). The authors are willing to provide additional information for data that may be of interest to readers upon
623 request.

624 **Supplement**

625 The supplement related to this article is available online at Atmospheric Chemistry and Physics (ACP).

626 **Author contributions**

627 FK, JC, and HS conceived the concept, planned, and organized the campaign. YXL did the AMS and PTR-MS
628 measurements, analyzed most of the data and wrote the manuscript with contributions from all co-authors. HS
629 planned and organized the measurements, took care of the particle number, size and additional trace gas
630 measurements. HZ, SA, AW, JC and FK supported instrument set up and conducted lidar measurements. XS, YWL
631 and FK checked and calibrated the instruments during the measurements. JBS, ZA, and JS contributed to data
632 analysis. TL contributed to planning of the measurement campaign and reviewed the manuscript.

633 **Competing interests**

634 Two co-authors are co-editors of ACP but the authors declare that there is no conflict of interests.

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