

1 **Nucleation and growth of sub-3 nm particles in the polluted urban atmosphere of a megacity in**
2 **China**

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11 **Abstract**

12 Particle size distribution down to 1.4 nm was measured in the urban atmosphere of Nanjing, China in
13 spring, summer and winter during 2014-2015. Sub-3 nm particle event, which is equivalent to
14 nucleation event, occurred on 42 out of total 90 observation days, but new particles could grow to
15 cloud condensation nuclei (CCN)-active sizes on only 9 days. In summer, infrequent nucleation was
16 limited by both unfavorable meteorological conditions (high temperature and RH) and reduced
17 anthropogenic precursor availability due to strict emission control measures during the 2014 Youth
18 Olympic Games in Nanjing. The limiting factors for nucleation in winter and spring were
19 meteorological conditions (radiation, temperature, and RH) and condensation sink, but for the further
20 growth of sub-3 nm particles to CCN-active sizes, anthropogenic precursors again became limiting
21 factors. Nucleation events were strong in the polluted urban atmosphere. Initial $J_{1.4}$ at the onset and
22 peak $J_{1.4}$ at the noontime could be up to $2.1 \times 10^2 \text{ cm}^{-3} \text{ s}^{-1}$ and $2.5 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$, respectively, during the

23 8 nucleation events selected from different seasons. Time-dependent $J_{1,4}$ usually showed good linear
24 correlations with a sulfuric acid proxy for every single event ($R^2 = 0.56 - 0.86$, excluding a day with
25 significant nocturnal nucleation), but the correlation among all the 8 events deteriorated ($R^2 = 0.17$)
26 due to temperature or season change. We observed that new particle growth rate did not increase
27 monotonically with particle size, but had a local maximum up to 25 nm h^{-1} between 1-3 nm. The
28 growth rate behavior was interpreted in this study as the solvation effect of organic activating vapor
29 in newly formed inorganic nuclei.

30

31 **1. Introduction**

32 New particle formation (NPF) is an important source of secondary aerosols in the atmosphere
33 (Kulmala et al., 2004a). Field studies and model simulations have consistently shown that NPF can
34 enhance cloud condensation nuclei (CCN) concentrations and contribute significantly to the global
35 CCN production (Wiedensohler et al., 2009; Yue et al., 2011; Spracklen et al., 2008; Pierce and
36 Adams, 2009; Merikanto, 2009; Yu and Luo, 2009; Matsui et al. 2013). NPF is a two-stage process
37 consisting of formation of clusters and subsequent growth to detectable sizes (Kulmala et al., 2000).
38 Recently, chamber experiments have made substantial progress in revealing the fundamental
39 processes involved in particle nucleation and growth (Kirkby et al., 2011; Almeida et al., 2013;
40 Schobesberger et al., 2013; Riccobono et al., 2014; Ehn et al., 2014; Kürten et al., 2014). However,
41 consistent theories are still under investigation to quantify the processes physically, chemically, and
42 dynamically (Kulmala et al., 2013, 2014). For example, the identity and physico-chemical properties
43 of assisting vapors other than sulfuric acid (H_2SO_4) are uncertain so far. It is also uncertain what
44 mechanisms allow the assisting vapors to overcome strong Kelvin effect over sub-3 nm particles.

45 Existing mechanisms include condensation of extremely low volatility organic compounds (Ehn et
46 al., 2014), nano-Köhler activation (Kulmala et al., 2004b), heterogeneous chemical reactions (Zhang
47 and Wexler, 2002), heterogeneous nucleation (Wang et al., 2013), and adsorption of organics on
48 cluster surface (Wang and Wexler, 2013). However, the relative importance of various mechanisms
49 is unknown.

50 Direct measurements of size- and time dependent nucleation rate and growth rate in sub-3 nm
51 size range are important to constrain the relative contributions from different mechanisms and
52 precursors. Such measurements are also important to evaluate the survival probability of new particle
53 to CCN-active sizes (~100 nm for soluble particles at 0.2% super saturation, Pierce and Adams, 2009)
54 and to reveal the limiting factors in the process. Recently, a series of new instruments have been
55 developed to measure sub-3 nm aerosol number concentration and chemical composition, such as
56 condensation particle counters (e.g., PSM, DEG-SMPS, Jiang et al., 2011a; Sipila et al., 2009;
57 Vanhanen et al., 2011), ion spectrometers (e.g., NAIS, Asmi et al., 2009), and mass spectrometers
58 (e.g., Cluster-CIMS, APi-TOF, CI-APi-TOF, Jokinen et al., 2012; Junninen et al., 2010; Zhao et al.,
59 2010). Kuang et al. (2012) developed a de-coupling method to measure size- and time dependent
60 growth rates of sub-5 nm particles. Their results at two urban sites in U.S.A showed that
61 size-resolved growth rates increased approximately linearly with particle size from 1 to 5 nm.
62 Similar results were also observed in the Boreal forest (Kulmala et al., 2013; Lehtipalo et al., 2014).
63 Based on growth rates measured below 2 nm, Kulmala et al. (2013) identified three separate size
64 regimes, which were dominated by different key gas to particle conversion processes.

65 The relative contribution of different precursors and mechanisms to the nucleation and growth of
66 1-3 nm particles may vary greatly with atmospheric conditions (Riipinen et al., 2012). Therefore,

67 sub-3 nm particle measurements in a variety of atmospheric conditions, e.g., remote or urban
68 atmosphere, biogenic- or anthropogenic emission dominated areas, are immensely valuable.
69 Unfortunately, such data are very sparse until now (Jiang et al., 2011b; Kuang et al., 2012; Kulmala
70 et al., 2013; Lehtipalo et al., 2009, 2010, 2011; Yu et al., 2014a, b). China is suffering from severe
71 atmospheric particulate matter pollution in recent years (Chan and Yao, 2008; Yue et al., 2011). To
72 the best of our knowledge, only two studies were conducted in China to measure the occurrence of
73 new particles down to ~1 nm. In these two studies, air ions (Herrmann et al., 2014) or neutral
74 particles (Xiao et al., 2015) were measured by AIS or PSM in two urban locations of Yangtze River
75 Delta region. Both studies were conducted in the winter season.

76 Here we reported the nucleation and growth of sub-3 nm particles in the urban atmosphere of
77 Nanjing, China on arbitrarily selected observation days in spring, summer and winter of 2014-2015.
78 Our aim was to (1) provide new information about the initial steps of NPF based on size- and time
79 resolved nucleation rate and growth rate measurements, and (2) find possible limiting factors behind
80 the seasonal and diurnal variations of nucleation events in the polluted urban atmosphere.

81 **2. Methodology**

82 **2.1 Field measurements**

83 Nanjing is the second largest megacity after Shanghai in the Yangtze River Delta (YRD) region
84 of China (Chan and Yao, 2008). The YRD city cluster, covering 2.1×10^5 km² land with 170 million
85 residents, is one of the most populated and industrialized regions in China. Field measurement was
86 conducted from the third floor (15m above the ground level) of an academic building beside a
87 Chinese national meteorology observatory facility in NUIST campus (32.20° N, 118.71° E, symbol
88 ① in Figure 1). The sampling was carried out during the months of May (May 10-30, 2014), June

89 (June 1-15, 2014), December (December 24-31, 2014), February (February 16-22, 2015), and March
90 (March 1-7, 2015). Total 58 measurement days were arbitrarily selected to represent spring, early
91 summer and winter seasons, but to avoid any rain-event.

92 As part of an intensive summer campaign (12 August-12 September 2014), the summer
93 measurement was conducted at a local governmental meteorology observatory platform (32.06°N,
94 118.70°E) that is 14km south to the NUIST site (② in Figure 1). The instruments were housed in an
95 air conditioned trailer, using exactly the same sampling inlets as the NUIST site. The main aim of the
96 summer campaign was to understand the effects of regional emission control measures during the
97 2014 Young Olympic Games (August 1-September 15) on air quality. Because the two sites locate
98 within the same urban air shed, the measurement provided an opportunity to study seasonal variation
99 of nucleation and its relationship with meteorological variables and gaseous precursors.

100 Sub-3 nm clusters/particles (hereafter referred as particles) were measured with a nano
101 condensation nucleus counter system (nCNC) consisting of a Particle Size Magnifier (PSM model
102 A10, Airmodus Oy, Finland) and a butanol Condensation Particle Counter (model A20, Airmodus
103 Oy, Finland). During the measurement, an ambient air flow of 14 standard liters per minute (slpm)
104 was drawn into building room or trailer via a 72 cm long and 1.0 cm I.D diameter stainless steel (SS)
105 tube, which was extended outside the room/trailer horizontally. PSM then sampled a split flow of 2.5
106 slpm via a SS T-union. The design of the inlet tubing (length and air flow rate) was to minimize the
107 transport loss of nano particles. The size dependent transport survival ratios of sub-3 nm particles in
108 the inlet tubing was estimated (67 %-86 % for 1.4-3.0 nm) and corrected using a particle loss
109 calculator tool (von der Weiden et al., 2009).

110 PSM was operated in a continuous scanning mode with a cycle of 240 steps between saturator

111 flow rates of 0.1 and 1.0 slpm within 240 seconds. The particle cut-off sizes of the nCNC varied with
112 saturation ratios in the saturator (Vanhanen et al., 2011). A step-wise method was used to invert raw
113 scanning data to size spectrum (time resolution: 4 minutes) of sub-3 nm particles, which were
114 classified evenly into 6 size bins, i.e. 1.4-1.6, 1.6-1.9, 1.9-2.2, 2.2-2.4, 2.4-2.7, and 2.7-3.0 nm. The
115 inverted particle number concentrations in the 6 bins were referred as $N_{1.5}$, $N_{1.8}$, $N_{2.0}$, $N_{2.3}$, $N_{2.6}$ and
116 $N_{2.8}$, using mean values of upper and lower size boundaries in each bin. The step-wise method was
117 described in detail by Lehtipalo et al. (2014).

118 Particle size distributions in the range from 3 - 750 nm were obtained by integrating two
119 scanning mobility particle spectrometers (SMPS) with a nano-SMPS (a TSI differential mobility
120 analyzer DMA3085 and a condensation particle counter CPC3776; scanning range: 3 - 64 nm) and a
121 long-SMPS (TSI DMA3081 and CPC3775; scanning range: 64 - 750 nm). During the summer
122 campaign, only the long-SMPS was operated to scan particles from 8 - 350 nm. Scanning cycles of
123 both SMPS systems were 4 minutes, in order to synchronize with the nCNC. The SMPSs sampled
124 ambient air from a separate sampling inlet. The inlet was a 129 cm long and 1.0 cm I.D
125 horizontally-oriented SS tube with an air flow of 14 slpm. The transport loss of particles in the SMPS
126 inlets was corrected using size dependent survival ratios of 85-100% for particles > 3 nm.

127 Sulfur dioxide (SO₂), ozone (O₃), carbon monoxide (CO) and nitrogen oxides (NO and NO₂)
128 concentrations were measured every 1 minute with Thermo Environmental Instruments (model
129 43i-TLE, 49i, 48i, and 42i, respectively). When gaseous SO₂, O₃, NO₂ and CO data were not
130 available, hourly SO₂, O₃, NO₂ and CO were obtained from nearby local Environmental Protection
131 Agency (EPA) monitoring station. PM_{2.5} was monitored with Thermo Scientific TEOM 1405.
132 Meteorological variables including wind speed, wind direction, relative humidity (RH), temperature

133 and solar radiation flux were recorded every 1 hour during the measurement periods. Mean
134 concentrations of PM_{2.5}, SO₂, and O₃ were 79 μ g m⁻³, 10 ppbv and 48 ppbv, respective, during the
135 whole measurement period. Therefore, we regard our measurement environment as a polluted urban
136 atmosphere.

137

138 2.2 Nucleation event and growth patterns

139 A criterion was set to determine whether the nCNC detected sub-3nm particles in the atmosphere.
140 The criterion was that total particle concentration reading followed the supersaturation scanning
141 cycle of PSM so that the highest concentrations were measured at lowest cut-off sizes (see also
142 Figure 2 in Lehtipalo et al., 2014). However, it was possible in the step-wise inversion method that
143 the number concentration fluctuation of > 3 nm particles within a 4-min scanning cycle was wrongly
144 inverted to sub-3 nm particles even when sub-3 nm particles actually did not exist according to the
145 above criterion. As a result, the step-wise inversion method always reported a background sub-3 nm
146 particle concentration (N_{sub-3} , i.e. the sum of $N_{1.5}$, $N_{1.8}$, $N_{2.0}$, $N_{2.3}$, $N_{2.6}$ and $N_{2.8}$) of $0.5 \times 10^3 - 2 \times 10^3$
147 cm⁻³ in the nighttime and $3 \times 10^3 - 8 \times 10^3$ cm⁻³ in the daytime. Similar background levels of sub-3 nm
148 particles during non-NPF periods were also reported by other studies that used the nCNC (Kulmala
149 et al., 2013; Lehtipalo et al., 2014; Xiao et al., 2015). Following their procedures, we did not attempt
150 to subtract this background from N_{sub-3} reported in this study.

151 We defined sub-3 nm particle event as sub-3 nm particle occurrence with N_{sub-3} higher than
152 background level persisting for longer than 1 h in the atmosphere. In this study, we used sub-3 nm
153 particle event as an approximate measure of nucleation event. This is because (1) there was an
154 approximately positive linear correlation between N_{sub-3} and nucleation rate ($J_{1.4}$ in this study, see

155 next section) with R^2 of 0.94 (Figure 2), and (2) N_{sub-3} calculation needs only nCNC scanning data
156 and was thus more readily available than $J_{1.4}$ calculation which needs both nCNC and SMPS
157 scanning data. Similar definition has been discussed in our previous studies (Yu et al., 2014a, b).
158 Apparently, a sub-3 nm particle event did not necessarily lead to an NPF event always, but it
159 indicated the intensity and frequency of nucleation in the atmosphere. One focus in this work was to
160 investigate the characteristics of sub-3 nm particle event.

161 Particle growth after nucleation is crucial to determine if nucleated particles could grow to
162 CCN-active sizes. We identified two growth patterns according to size spectrum characteristics in
163 sub-3 nm size range (Figure 3). In a Type A event (Figure 3a or b), size distribution $n(D_p, t)$ was
164 higher at smaller sizes (e.g., 1.4–1.6 nm) than $n(D_p, t)$ at larger sizes (e.g., 2.7–3.0 nm). The size
165 spectrum below 3 nm thus looked like a “volcano”. In a Type B event (Figure 3c or d), $n(D_p, t)$ was
166 lower at smaller sizes than $n(D_p, t)$ at larger sizes (“up-side-down volcano”). For the size range > 3
167 nm, depending on whether a banana-shape growth was seen, we further defined Type A1/A2 and
168 Type B1/B2 events: particles eventually grew to CCN-active sizes in Type A1 and B1 events, while
169 in Type A2 and B2 events banana-shape particle growth to CCN-active sizes was not seen. Therefore,
170 Type A1 and B1 events were equivalent to conventional NPF events based on either DMPS or SMPS
171 measurements.

172 Type B size distribution was more unusual since $n(D_p, t)$ of small particles were less than $n(D_p, t)$
173 of large particles in the sub-3 nm size range. We excluded the possibility of deteriorated nCNC
174 detection efficiencies for small particles due to high particle loading in the sample air. This is
175 because total number concentrations of nCNC during our measurements never approached nCNC
176 upper concentration limit $4 \times 10^5 \text{ cm}^{-3}$, especially in the early stage of nucleation when total particle

177 concentration was rather low. Our nCNC was also calibrated periodically using H₂SO₄-H₂O particles
178 in a laboratory flow tube to ensure the detection efficiency of the nCNC. The different chemical
179 composition of atmospheric particles could be another factor of lower detection efficiencies. It is
180 well known that organic substances activate less readily in diethylene glycol (e.g. Kangasluoma et al.
181 2014). However, it is accepted in general that larger particles have higher mass fraction of organics
182 than smaller particles in a NPF process. If organic substances activate less readily in DEG, it should
183 be even more difficult to activate larger particles than smaller particles. Therefore, the increasing
184 $n(D_p)$ with D_p (i.e. upside down volcano) could not be simply due to lower detection efficiency of
185 organic substances.

186 **2.3 Formation rate and growth rate calculations with a simplified GDE method**

187 Conventional appearance time method determined growth rates (hereafter, *GR*) during the initial
188 period of NPF by finding the time steps when newly-formed particles appeared at certain size bins
189 and calculating the *GR* from the time differences between successive size bins (Kulmala et al., 2012;
190 Lehtipalo et al., 2014). This method was often not applicable to the NPF event with high *GR* below 3
191 nm, e.g., 0.3 nm/4 min (i.e. 4.5 nm h⁻¹) with size intervals 0.3 nm and scanning time intervals 4
192 minutes in our measurements. Furthermore, sub-3 nm particles were often generated persistently
193 throughout the daytime period. Maximum concentrations in the sub-3 nm size bins could appear
194 around noontime, which is a few hours later than the onset of nucleation. Therefore, we were not
195 able to pinpoint correctly maximum or 50% maximum concentrations at the onset of nucleation.

196 The rapid growth of small particles in the urban atmosphere was the motivation that we used an
197 alternative method to calculate growth rate and formation rate. Here, we analyzed 8 events (listed in
198 Table 1, including both Type A1/A2 and B1/B2 events) in detail, for which complete size spectra

199 from 1.4 - 750 nm were available without distorted, broken or noisy data. Total 8 size bins were
 200 classified: 6 evenly-divided size bins in sub-3 nm and 2 size bins in 3-30 nm (3-10 and 10-30 nm).
 201 For an aerosol population that is growing through simultaneous condensation and coagulation,
 202 aerosol general dynamic equation (GDE) describes the evolution of number concentration in a size
 203 bin between particle diameters D_{p1} and D_{p2} ($D_{p2} > D_{p1}$) as:

$$204 \frac{dN(D_{p1}, D_{p2}, t)}{dt} = J(D_{p1}, t) - J(D_{p2}, t) - \text{CoagSnk}(D_{p1}, D_{p2}, t) + \text{CoagSrc}(D_{p1}, D_{p2}, t) \quad (1)$$

205
 206 where $N(D_{p1}, D_{p2}, t)$ is the number concentration from D_{p1} to D_{p2} , inverted from nCNC or SMPS
 207 scanning data. J is condensational growth flux (i.e. particle formation rate) across the lower ($D_{p,1}$) or
 208 upper ($D_{p,2}$) boundaries of a size bin. In the first size bin of 1.4-1.6 nm, $J(1.4 \text{ nm}, t)$, or simply $J_{1.4}$,
 209 is the unknown formation rate of the smallest particles that we measured.

210 $\text{CoagSnk}(D_{p1}, D_{p2}, t)$ and $\text{CoagSrc}(D_{p1}, D_{p2}, t)$ are the sink and source terms defining the
 211 coagulation out of and into the size bin between D_{p1} and D_{p2} . Assuming bin k has lower boundary
 212 $D_{p,1}$ and upper boundary $D_{p,2}$,

$$213 \text{CoagSnk}(D_{p1}, D_{p2}, t) = N(k, t) \sum_{i=1}^{98} (1 - \theta_{k,i,k}) K_{k,i} N(i, t) \quad (2)$$

$$214 \text{CoagSrc}(D_{p1}, D_{p2}, t) = \frac{1}{2} \sum_{i=1}^{k-1} \sum_{j=1}^{k-1} \theta_{i,j,k} K_{i,j} N(j, t) N(i, t) \quad (3)$$

215 Here $N(i, t)$ is number concentration of bin i . $K_{i,j}$ is coagulation kernel for a collision between
 216 particles from bins i and j . Probability coefficient $\theta_{i,j,k} = 1$, if the volume sum of two coagulating
 217 particles ($v_i + v_j$, here the volume is calculated from the center diameter of a bin) is within the
 218 volume boundaries of bin k . otherwise $\theta_{i,j,k} = 0$. The particle coagulation of total 98 bins was
 219 considered, but the coagulation terms were only needed to be calculated for the smallest 8 bins from
 220 1.4 to 30 nm. According to our calculation, $\text{CoagSrc}(D_{p1}, D_{p2}, t)$ accounted for only 0 - 0.8 % of the

221 total particle flux into a bin (i.e. $\text{CoagSrc}(D_{p1}, D_{p2}, t) + J(D_{p1}, t)$) in the sub-3 nm size range. This
222 implied that self coagulation played a negligible role and most of the production flux into a bin is due
223 to condensational growth from gas molecules.

224 The GDE here is the same as the Eq. 1 by Kuang et al. (2012). In their method, gaseous H_2SO_4
225 was measured simultaneously and a constant $GR(D_p, t) / GR_{\text{H}_2\text{SO}_4}(D_p, t)$ ratio at a given size over time
226 was assumed. Their $GR(D_p, t)$ was then solved by fitting the GDE to the measured size distributions.
227 In our study, however, we did not measure gaseous H_2SO_4 . Instead, $J(30 \text{ nm}, t)$ in the largest size
228 bin, which is the condensational growth flux out of 30 nm, was set to zero. This simplification was
229 valid in the four Type A2/B2 events when particles never grew to $> 30 \text{ nm}$ (March 4, February 19,
230 May 20 and May 16). In the rest four Type A1/B1 events (February 18, December 27, May 15, and
231 August 15), this was also valid during the early NPF period when particles did not grow out of 30 nm
232 and during the late NPF period when particles grew out of 30 nm completely. During the middle
233 period of events (usually around 11:00 AM-14:00 PM), $J(30 \text{ nm}, t)$ was underestimated and thus
234 $J_{1.4}$ could be regarded as a lower estimate. In the four Type A2/B2 events, our calculation showed
235 that J_{10} was only 0-4% of $J_{1.4}$. Xiao et al. (2015) and Kulmala et al. (2013) measured both $J_{1.5}$ and J_3
236 using appearance time method. Their J_3 was less than 7% of $J_{1.5}$. Furthermore, $J_{30}/J_{1.4}$ ratio should be
237 even smaller than $J_{10}/J_{1.4}$ or $J_3/J_{1.5}$ ratios, considering the 8 events were carefully selected to ensure
238 all sub-30 nm particles were grown from nucleation (not emitted directly from emission sources like
239 vehicular engine). All these evidences supported that even if J_{30} was set to 0, $J_{1.4}$ would not be
240 underestimated more than 7% when particles grew cross 30 nm on February 18, December 27, May
241 15, and August 15.

242 Equation 1 requires the balance of condensational growth (J), coagulation terms (CoagSnk and

243 CoagSrc) and the changing rate of particle number concentration (dN/dt). Using Eq. (1) we can
244 therefore calculate the nucleation rate $J(1.4 \text{ nm}, t)$ and formation rates $J(D_p, t)$ across all size bin
245 boundaries from 1.6 to 10 nm. After the formation rates $J(D_p, t)$ were obtained, $GR(D_p, t)$ was
246 calculated from $J(D_p, t)/n(D_p, t)$, where $n(D_p, t)$ is size distribution calculated as $n(D_p, t) = \frac{dN(t)}{dD_p}$
247 for each size bin. On the other hand, the appearance time method could still be applied to (1) the size
248 range of $> 3 \text{ nm}$ where size intervals were large (2-6 nm), and (2) the size range of $< 3 \text{ nm}$ when GR
249 was small. The results from appearance time method will also be showed in the next section.

250

251 **3. Results and discussion**

252 Section 3.1, sections 3.2-3.4 and section 3.5 were organized, respectively, to address the
253 following 3 issues: (1) seasonal variation, diurnal variation and limiting factors of nucleation event
254 (represented by sub-3 nm particle event) in the polluted urban atmosphere, (2) time- and size
255 dependent nucleation rate and growth rate of sub-3 nm particles, and their implications for nucleation
256 and growth mechanisms, (3) Inhibited particle growth to CCN-active sizes in strong nucleation
257 events of Type B2.

258 **3.1 Seasonal and diurnal variations of nucleation event**

259 As seen from Figure 2, there was an approximate linear correlation between N_{sub-3} and $J_{1.4}$ with
260 the slope of $N_{sub-3}/J_{1.4}$ equal to ~ 160 . This seemed to suggest that the average residence time of
261 new particles in the sub-3 nm size range was 160 seconds before they were scavenged due to
262 coagulation or grew out of 3 nm. The sub-3 nm particles observed at the present work were thus
263 formed in situ in the urban atmosphere and not likely to be carried-over by air transport. In this
264 section we used sub-3 nm particle event as an approximate measure of nucleation.

265 We observed significant seasonal characteristics of nucleation event (Figure 4). Nucleation was
266 rare and weak in summer, while it was commonly observed in all other seasons. During our
267 measurements from 2014 to 2015, nucleation events occurred on 81% of all spring observation days
268 (May 2014), 53% in early summer (June 2014), 10% in summer (August and September 2014), and
269 64% in winter (December 2014, February and March 2015). We compared intensity (N_{sub-3}) and
270 frequency of nucleation events, as well as meteorological variables (temperature, RH, wind speed,
271 and solar radiation flux) and gaseous pollutants (SO_2 , NO_2 , CO and O_3) for spring, summer and
272 winter seasons. June was not shown in Figure 4 for comparison, because it was a transit season from
273 spring (May) to summer (August and September). The data were first averaged over the entire event
274 period for each event; and we then used event-averaged data to create box and whistler plots for the 3
275 seasons. $PM_{2.5}$ was used here as a surrogate of condensational sink (CS), because of the more ready
276 availability of $PM_{2.5}$ data than SMPS data.

277 As shown in Figure 4, nucleation in summer was characterized by lowest frequency, lowest
278 N_{sub-3} ($2.2 \times 10^4 \text{ cm}^{-3}$), and short nucleation period (only 1-2 hours). Strict emission control measures
279 during the 2014 Youth Olympic Games resulted in relatively low $PM_{2.5}$ level ($32 \pm 8 \mu \text{g m}^{-3}$),
280 which should favor nucleation. However, relatively low SO_2 concentration ($1.4 \pm 0.6 \text{ ppbv}$), high
281 temperature ($26 \pm 2 \text{ }^\circ\text{C}$), and high RH ($74.3 \pm 4.2 \%$) might not be in favor of nucleation. A simple
282 H_2SO_4 proxy ($\text{Radiation} \times SO_2 / PM_{2.5}$) indicated that summer H_2SO_4 concentration was likely to be the
283 lowest among the 3 seasons, which could explain low nucleation intensity/frequency.

284 We further examined diurnal variations of N_{sub-3} and other variables on event and non-event days
285 in winter (Figure 5). Because nucleation in winter was characterized by Type B event
286 (“up-side-down volcano” below 3 nm), event days were further divided to Type B1 and Type B2

287 events depending on whether banana-shape particle growth was seen. The difference between Type
288 B1 and B2 will be discussed later in Section 3.5. During the non-event days, N_{sub-3} ranged from
289 $2.4 \times 10^3 \text{ cm}^{-3}$ in the night to 8.0×10^3 in the day, which was close to background levels. During the
290 event days, N_{sub-3} in the night was close to that of non-event days, but could reach $8 \times 10^4 - 20 \times 10^4$
291 cm^{-3} in the middle of the day. This was more than 10 times higher than those on the non-event days.
292 From Figure 5 we can see that non-event day had higher concentrations of anthropogenic precursors
293 (indicated by SO_2 , NO_2 , and CO), but nucleation seemed to be limited by higher pre-existing particle
294 surface area (indicated by $\text{PM}_{2.5}$), higher temperature and RH, and lower radiation flux.
295 Photochemistry indicators O_3 was also lower during non-event days.

296 Nucleation in spring was characterized by highest frequency (81%) among all seasons. Highest
297 gaseous pollutant concentration of (H_2SO_4 proxy, SO_2 , NO_2 , CO and O_3) and radiation seemed to the
298 favorable factors to explain this. However, N_{sub-3} in spring ($3.3 \times 10^4 \text{ cm}^{-3}$) was much lower than that
299 in winter ($11.2 \times 10^4 \text{ cm}^{-3}$). Unfavorable factors included high pre-existing particle surface area ($\text{PM}_{2.5}$:
300 $112 \pm 68 \mu \text{g m}^{-3}$) and high temperature ($27 \pm 4 \text{ }^\circ\text{C}$) in spring. Integrating the above seasonal and
301 diurnal variation information in Figure 4 and Figure 5, we tentatively identified that the limiting
302 factors for nucleation in our urban atmosphere were (1) radiation, temperature, RH and CS in winter
303 and spring, and (2) temperature, RH and available gaseous precursors in summer.

304 Out of total 90 measurement days, March 4, 2015 in winter was the only day that we observed
305 significant nocturnal nucleation. Sunrise and sunset were at 6:29 AM and 18:00 PM local time on
306 March 4, but nucleation were observed persistently from 4:00 AM - 20:00 PM. N_{sub-3} increased from
307 $3.5 \times 10^3 \text{ cm}^{-3}$ at 4:00 AM to $6.3 \times 10^4 \text{ cm}^{-3}$ before sunrise. During 10:00-11:00 AM, peak N_{sub-3}
308 reached $3 \times 10^4 \text{ cm}^{-3}$, 3 times higher than the average of all other event days in winter. Apparently,

309 nocturnal nucleation on March 4 could not be explained as carry-over of daytime particles nor being
310 associated with photochemistry. This implied the existence of certain dark nucleation source. There
311 are a number of observations that have also shown nighttime particle formation events in various
312 atmospheric conditions (Junninen et al., 2008; Lehtipalo et al., 2011; Lee et al., 2008; Ortega et al.,
313 2009, 2012; Russell et al., 2007; Suni et al., 2008; Svenningsson et al., 2008; Yu et al., 2014), but the
314 mechanisms behind the nocturnal nucleation are yet still highly speculative. With our instrument
315 capability in this work, we could not deduce any valuable information on the nocturnal nucleation
316 mechanism, except that we found the air mass on 04 March was relatively clean (both CS and gases,
317 mean CS: 0.15 s^{-1}), and temperature and RH (mean: 4.4°C and 33%) were favorable for nucleation.

318 319 **3.2 Size- and time dependent formation rates of sub-3 nm particles**

320 We observed 23 Type A events and 9 Type B events during the measurements. The different size
321 distribution patterns (Figure 3) were probably linked to the mechanism or intensity of nucleation and
322 growth. To address this issue, we first compared the formation rates and growth rates in two types of
323 events. Formation rates J of 1.4, 1.6, 1.9, 2.2, 2.4, 2.7 and 3.0 nm particles were shown in Figure 6
324 (upper panels) for typical Type A and Type B events. It is obvious that $J_{1.4}$ was much higher on
325 February 18 (Type B) than that on May 15 (Type A). A clear time dependence of J was observed. For
326 example, $J_{1.4}$ was $60 \text{ cm}^{-3} \text{ s}^{-1}$ at the onset of the nucleation event on May 15 and increased to 300
327 $\text{cm}^{-3} \text{ s}^{-1}$ in the middle of the day. In the type B event on February 19, the initial and peak $J_{1.4}$ were
328 2.1×10^2 and $1.2 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ respectively. Therefore, our method provided more information of
329 nucleation than conventional calculation methods that usually showed only an averaged J at the onset
330 of a nucleation event. Our method was also different from Kulmala et al. (2013). Their

331 time-dependent formation rate on an event day was equal to size distribution $n(D_{p,t})$ times a constant
332 growth rate at the onset of the event obtained with the appearance time method.

333 The diurnal variation of J implied that nucleation was probably linked to sunlight induced
334 photochemistry. We calculated the correlations between $J_{1.4}$ and an H_2SO_4 proxy for the 8 events of
335 our interest. The H_2SO_4 proxy was calculated following $[H_2SO_4] = 8.21 \times 10^{-3} k \cdot Radiation \cdot$
336 $[SO_2]^{0.62} \cdot (CS \cdot RH)^{-0.13}$ (Eq. 8 of Mikkonen et al. 2011), where k is the temperature-dependent
337 reaction-rate constant. Figure 7a show that good linear correlation was usually seen for every single
338 event with R^2 ranging from 0.72 to 0.86 for 6 out of 8 events. A moderate R^2 of 0.56 was obtained for
339 August 15. R^2 was lowest (0.34) on March 4, 2015. This is not surprising because we know March 4
340 was the only day with nocturnal nucleation during the measurement period. The H_2SO_4 proxy was
341 also calculated using the derivation of Petäjä et al. (2009), which resulted in lower R^2 of $\log J_{1.4}$ vs.
342 $\log [H_2SO_4]$ for all 8 events. Therefore, in this study we used Mikkonen H_2SO_4 proxy, as it was
343 derived with more comprehensive datasets than Petäjä et al. (2009). The slopes of $\log J_{1.4}$ vs. \log
344 $[H_2SO_4]$ were close to 1 in all events (0.82-1.17, excluding March 4), indicating activation theory
345 can explain the nucleation mechanism in our urban atmosphere.

346 If data points of all the 8 events were put together, the linear correlation between H_2SO_4 proxy
347 and $J_{1.4}$ deteriorated (slope=1.1, $R^2=0.17$, Figure 7b). In spite of considerable scattering, most of data
348 points located between $J_{1.4}=10^{-4.1} \times [H_2SO_4]$ and $J_{1.4}=10^{-6.3} \times [H_2SO_4]$. An interesting finding was
349 that the scattering of $J_{1.4}$ vs. $[H_2SO_4]$ proxy among all 8 events was probably due to temperature or
350 season change (Figure 7b). More specifically, with the same level of H_2SO_4 proxy, $J_{1.4}$ was higher in
351 winter with lower temperature than in spring/summer with higher temperature. There were two
352 possibilities behind the deteriorated linear correlation between H_2SO_4 proxy and $J_{1.4}$: (1) inaccurate

353 H₂SO₄ proxy and (2) other varying factors in nucleation mechanism. First, it was very likely that
354 H₂SO₄ concentrations in our polluted urban atmosphere were overestimated by the H₂SO₄ proxy of
355 Mikkonen et al. (2011), which was based on statistic regression of historical datasets from relatively
356 clean Europe/USA atmosphere. The extent of overestimation may vary with the levels of predictor
357 variables (e.g., SO₂, temperature, CS). Mean SO₂ mixing ratios were 10.5 and 7.3 ppbv in
358 spring/summer and winter during our measurements, respectively. These were 1 order of magnitude
359 higher than SO₂ mixing ratios at the 6 European and USA sites (mean values: 0.23-3.4 ppbv,
360 Mikkonen et al., 2011). Our CS in the 8 events was on the order of magnitude of 10⁻² s⁻¹, again higher
361 than 10⁻³ s⁻¹ in Mikkonen et al. (2011). Mikkonen et al. (2011) had already pointed out that the
362 predictive ability was lower for long term data due to atmospheric condition changes in different
363 seasons.

364 Second, organic condensing vapor concentrations in particle growth events were higher in winter
365 than those in spring/summer (Table 1, see Section 3.4). If the organics were also involved in
366 nucleation, $J_{1.4}$ should be enhanced in winter. The enhancement of nucleation by organics (most
367 likely anthropogenic organics in our urban atmosphere) could be supported by the comparison of $J_{1.4}$
368 dependences on H₂SO₄ between our study and the measurements in the Boreal forest: besides
369 possible H₂SO₄ overestimation, $J_{1.4}=10^{-4.1} \times [\text{H}_2\text{SO}_4] - 10^{-6.3} \times [\text{H}_2\text{SO}_4]$ in our sites was much higher
370 than $J_{1.5}=1.06 \times 10^{-7} [\text{H}_2\text{SO}_4]^{1.1}$ in Hyytiälä during active aerosol formation periods (Kulmala et al.,
371 2013). At last, low temperature itself might enhance nucleation in winter (Brus et al., 2011) via
372 increasing the saturation ratios of all nucleation precursors (e.g., water, H₂SO₄, organics).

373

374 **3.3 Size- and time dependent growth rates of sub-3 nm particles**

375 Particle size distribution $n(D_p)$ and corresponding $GR(D_p)$ at an instant in time during the events
376 were shown in Figure 6 middle and lower panels. A local minimum of $n(D_p)$ at 2.4 nm, followed by a
377 local maximum somewhere between 2.5 and 10 nm, was seen on May 15, 2014. Such size
378 distribution characteristics on May 15, 2014, as well as on all other Type A event days, was also
379 observed by Kulmala et al. (2013) in the Boreal forest (Figure 1A and S9A in their paper) and by
380 Jiang et al. (2011b) in the urban area of Atlanta, USA (Figure 1 in their paper). We further examined
381 the growth rates in the size range of 1-3 nm on May 15, 2014. It was shown that there was a local
382 maximum of $GR(D_p)$ at 2.4 nm. This could explain why $n(D_p)$ was increasing in 2.4-3 nm size range:
383 when particle condensational flow out of a size bin was slowed down, it was possible that particles
384 flowing into the size bin accumulated, leading to particle number increase in the bin.

385 We saw more unusual behaviors of $n(D_p)$ and $GR(D_p)$ in the Type B event on February 18
386 (Figure 6 right panels): $GR(D_p)$ decreased monotonically in the size range of 1.4 - 3 nm, and
387 accordingly $n(D_p)$ increased monotonically at the same time. A high $GR(D_p)$ of 25 nm h⁻¹ was
388 observed at 1.6 nm and $GR(D_p)$ decreased rapidly to 1.7 nm h⁻¹ at ~3 nm. If we consider that $GR(D_p)$
389 below 1.6 nm would eventually decrease due to strong Kelvin effect of all possible precursors
390 (H₂SO₄ or organics), the overall trend of $GR(D_p)$ in the Type B event was in fact the same as Type A:
391 for the smallest clusters, growth rate was small (possibly below 1 nm h⁻¹) and increased with D_p . It
392 reached a local maximum somewhere between 1-3 nm, after which $GR(D_p)$ decreased with D_p . For a
393 typical NPF event, $GR(D_p)$ would eventually increase again after a local minimum between 3-10 nm.
394 The difference between the Type A event (February 18) and Type B event (May 15) was the D_p of
395 local maximum $GR(D_p)$ (2.4 nm vs. 1.6 nm).

396 The interesting behaviors of $n(D_p)$ and $GR(D_p)$ in our urban atmosphere were different from the

397 stereotyped understanding that steady-state cluster size distribution $n(D_p)$ decreases with D_p in
398 nucleation and GR increases monotonically with D_p in an NPF event. It should be pointed out that if
399 we calculated the overall GR in 1.4-3 nm, $GR_{1.4-3}$ was 3.6 nm h⁻¹ on May 15 and 4.4 nm h⁻¹ on
400 February 18, which were still smaller than GR_{3-20} during the initial period of the events (7.7 and 6.0
401 nm h⁻¹, calculated using appearance time method). Table 1 showed that a faster GR_{3-20} than $GR_{1.4-3}$
402 were quite common, except in two events on May 16 and 20 when particles did not grow beyond 3
403 nm. Overall, GR was still increasing with increasing D_p .

404 Kuang et al. (2012) had also reported a local maximum of GR at ~2.6 nm in an NPF event
405 measured in Atlanta, USA (Figure 1b in their paper). In this study we further point out that GR could
406 decrease monotonically with D_p in 1-3 nm range in strong nucleation events. Our GR was calculated
407 from a simplified GDE method, however, the decrease of GR in 1-3 nm size range could be easily
408 inferred from the size spectra shown in Figure 3 or Figure 6 middle panels: for a D_{p2} that was larger
409 than D_{p1} , particle formation rate $J(D_{p2})$ must be smaller than $J(D_{p1})$. If we observed a higher $n(D_{p2})$
410 than $n(D_{p1})$, $GR(D_p)$ that was equal to $J(D_p)/n(D_p)$ must be smaller at D_{p2} than D_{p1} .

411 Apparently, the complicated growth rate behaviors in our polluted urban atmosphere can not be
412 explained by H₂SO₄ condensation alone, not only because H₂SO₄ condensational growth rate
413 ($GR_{H_2SO_4}$, calculated from the H₂SO₄ proxy and shown as black dashed lines in Figure 6) was smaller
414 than the measured growth rate ($GR_{measured}$), but also because $GR_{H_2SO_4}$ curve should follow a
415 monotonically decreasing trend in > 1 nm sizes assuming a collision-only condensational growth
416 without vaporization (Nieminen et al., 2010).

417

418 **3.4 Growth rate due to activating vapor on newly formed nuclei in sub-3 nm sizes**

419 Nano-Köhler theory (Anttila et al., 2004; Kulmala et al., 2004b, c) suggested that when a soluble
 420 organic vapor was dissolved in newly formed nuclei of aqueous-phase sulfate at certain size between
 421 1-3 nm, the surface organic vapor pressure was lowered and thus assisted the growth of the inorganic
 422 nuclei. Here, we continued our discussion based on the nano-Köhler theory to provide an explanation
 423 of *GR* behaviors observed in our urban atmosphere. The net uptake of gaseous molecules by a
 424 nanoparticle was driven by the difference of the condensational flux (governed by gas-phase
 425 concentration far from the particle C_∞) and the evaporation flux (governed by equilibrium surface
 426 concentration over the nuclei C_{surface}). C_{surface} was determined by the pure component saturation
 427 vapor pressure C^* , particle curvature $\exp\left(\frac{4\sigma v}{kTD_p}\right)$ and particle composition. The growth rate due to
 428 an activating organic vapor (hereafter, denoted as ELVOC, extremely low volatility organic
 429 compound) was expressed as

$$430 \quad GR_{ELVOC} = \frac{\gamma}{2\rho_v} \left(1 + \frac{D_v}{D_p}\right)^2 \left(\frac{8kT}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{m_p} + \frac{1}{m_v}\right)^{\frac{1}{2}} m_v (C_\infty - C_{\text{surface}}) \quad (4)$$

431 where $C_{\text{surface}} = C^* \exp\left(\frac{4\sigma v}{kTD_p}\right) (x_{D_p} + \exp(-\varphi(D_p/D_{p0})^3))$. The kinetic prefactor $\frac{\gamma}{2\rho_v} \left(1 + \frac{D_v}{D_p}\right)^2 \left(\frac{8kT}{\pi}\right)^{\frac{1}{2}} \left(\frac{1}{m_p} + \frac{1}{m_v}\right)^{\frac{1}{2}} m_v$ was taken from Nieminen et al. (2010). x_{D_p} is the mole fraction of
 432 water-soluble ELVOC in the pseudobinary solution consisting of ELVOC and the aqueous sulfate
 433 nuclei. Nuclei activation diameter $D_{p,act}$ is the size that ELVOC began to dilute the nuclei. $D_{p,act}$ is
 434 also the size that local maximum *GR* was measured. For $D_p > D_{p,act}$, empirical term $\exp(-\varphi(D_p/D_{p0})^3) \rightarrow 0$. Here, D_{p0} is 1 nm to cancel off the unit of D_p . Consequently, C_{surface} for $D_p > D_{p,act}$ is
 435 in effect equal to $C^* \exp\left(\frac{4\sigma v}{kTD_p}\right) x_{D_p}$ (solid black line in Figure 8a, the same as the nano Köhler
 436 curve in Figure 1 of Kulmala et al. 2004b). The pseudobinary solution was treated ideal in the Eq.
 437 (4).
 438
 439

440 In the size range of $D_p < D_{p,act}$ the empirical term $\exp(-\varphi(D_p/D_{p0})^3)$ accounts for the rapidly
 441 decreasing $C_{surface}$ with D_p (Figure 8a, dashed black line). In the traditional Köhler theory, a higher
 442 critical saturation ratio is needed to activate the nuclei with $D_p < D_{p,act}$. If this higher S is not reached,
 443 the smaller nuclei are in a stable equilibrium with gas molecules and do not grow. However, in the
 444 sub-3 nm size range, the nuclei can grow itself due to the condensation of nuclei material (i.e. H₂SO₄
 445 and H₂O vapor), opposite to the fixed mass of salt nuclei (tens to a few hundreds of nanometers) in
 446 the traditional Köhler theory. Therefore, the growing nuclei with $D_p < D_{p,act}$ have a higher mass
 447 fraction of H₂SO₄ and H₂O (organic-poor particles) than the $D_p > D_{p,act}$ particles that are diluted by a
 448 substantial amount of organics (organic-rich particles). The green line in Figure 8a represented the
 449 Kelvin curve over such an organic-poor particle (with a fixed mass fraction of organics, for
 450 simplification). The red line represented the Kelvin curve over a pure organic droplet. When
 451 H₂SO₄/H₂O inorganic fraction decreases dramatically with size in a transition zone between 1.4-3 nm,
 452 $C_{surface}$ switches from the organic-poor Kelvin curve (green line) to the organic-rich Kelvin curve
 453 (red line). This resulted in a complete equilibrium curve of $C_{surface}$ in 1-5 nm (dashed + solid black
 454 lines). In Figure 8b the blue line represented the calculated $C_{\infty} - C_{surface}$. The trend of $C_{\infty} -$
 455 $C_{surface}$ coincided with the size dependence of $GR_{measure}$.

456 We fitted GR_{ELVOC} with the measured GR in sub-3 nm sizes at an instant in time by adjusting 3
 457 free parameters in Eq. (4): C^* , C_{∞} , and φ . Other parameters like surface tension (0.02 N m⁻¹) and
 458 molar volume (135.5 cm³ mol⁻¹) of ELVOC were taken from Kulmala et al. (2004b). Molecule
 459 diameter d_v (0.8 nm) and condensed-phase density ρ_v (1.5 g cm⁻³) of ELVOC were taken from Ehn
 460 et al. (2014). Uptake coefficient γ was calculated following Nieminen et al. (2010). The fitting
 461 results in Figure 9 showed that the dependence of $GR_{GDE\ method}$ on D_p below 3 nm could be well

462 reproduced by Eq. (4) for both Type A and Type B events. Free parameter ϕ determined the slope of
463 the dashed black line. ϕ was fitted to be 0.4-1.0 for the 8 events. C_∞ determined the local maximum
464 GR at the $D_{p,act}$, for which $C_{surface}$ was lowest. C_∞ and C^* determined the local minimum GR at
465 the right side of $D_{p,act}$. Therefore, C^* and C_∞ shown in Table 1 were basically determined by the
466 measured GR (local maximum and local minimum) and not sensitive to ϕ . As shown in Table 1, the
467 activating vapor concentrations C_∞ were $2.3 \times 10^7 - 2.0 \times 10^8 \text{ cm}^{-3}$. The saturation vapor concentration
468 C^* were $2.5 \times 10^6 - 5.7 \times 10^7 \text{ cm}^{-3}$. They were within the orders of magnitude of $10^7 - 10^8 \text{ cm}^{-3}$ and
469 $10^6 - 10^7 \text{ cm}^{-3}$ suggested by Kulmala et al. (2004b), respectively.

470 For comparison, the GR calculated from appearance time method was also shown in Figure 9
471 ($GR_{AT\ method}$) for $> 3 \text{ nm}$ particles on May 15, February 18 and February 19, as well as for sub-3 nm
472 particles on May 20 when particle growth was relatively slow. It can be seen that the GR on May 20
473 calculated from the two methods agreed well with each other, leading credit to our GDE method.
474 $GR_{AT\ method}$ in $>10 \text{ nm}$ sizes was usually underestimated by GR_{ELVOC} . This could be interpreted as
475 other condensing vapors with higher volatility may contribute to particle growth in the larger
476 particles. It should be noted that the appearance time method followed the time steps when
477 newly-formed particles appeared in successive size bins and thus $GR_{AT\ method}$ was not the growth rates
478 at the same instant in time.

479 For all the 8 nucleation events, Table 1 summarizes the measured values of overall growth rate
480 in 1.4-3 nm ($GR_{1.4-3}$), maximum growth rate in 1.4-3 nm ($GR_{max,1.4-3}$), overall growth rate in 3-20 nm
481 (GR_{3-20}), nucleation rate ($J_{1.4}$), activation diameter ($D_{p,act}$), CS , and temperature (T) during the event
482 periods with maximum nucleation rates. Corresponding estimates of Mikkonen H_2SO_4 proxy, C_∞
483 and C^* were shown in the right 3 columns. It can be seen that in comparison with more

484 conventional Type A events, Type B events usually occurred with (1) higher $J_{1.4}$, $GR_{max,1.4-3}$, $GR_{1.4-3}$,
485 C_{∞} , and CS ; (2) smaller $D_{p,act}$; and (3) lower T . However, the H_2SO_4 proxy and GR_{3-20} were similar
486 in Type A and Type B events. Based on these estimations, we concluded that higher ELVOC
487 concentration C_{∞} was the key factor leading to the higher $J_{1.4}$ and $GR_{1.4-3}$, which in turn resulted in
488 the different size spectrum pattern in Type B events (“up-side-down volcano”) from in Type A
489 events (“volcano”).

490 It should be noted that the organic vapor concentrations C_{∞} referred to in this study were not
491 directly measured, but estimated based on Eq. (4). Aerosol dynamic processes, such as nucleation,
492 coagulation, and the condensation growth of H_2SO_4 and water vapors, were not considered explicitly
493 in Eq. (4). In addition, bulk thermodynamics was applied in Eq. (4) for extremely small
494 clusters/particles of sub-3 nm sizes. Therefore, although our calculation provided an possibility to
495 explain the size dependence of growth rate observed in the polluted urban atmosphere, C_{∞} in this
496 study was subject to uncertainties in (1) the growth rate derived from the GDE method, (2) the theory
497 by which the growth rate was related to the organic vapor concentration, and (3) H_2SO_4 level which
498 also contributed to the initial growth.

499

500 **3.5 Inhibited particle growth to CCN-active sizes in strong nucleation events of Type B2**

501 Type B2 was strong nucleation event that produced rather high concentrations of new particles
502 in sub-20 nm size range (Figure 3d). High concentrations of activating vapor in these events (e.g.,
503 C_{∞} : $1.4-2.0 \times 10^8 \text{ cm}^{-3}$ on February 18 and March 4) should favor a banana-shape NPF event with fast
504 growth of particles >20 nm, due to weakened Kelvin effect. However, it was puzzling to us why new
505 particles accumulated in 2-20 nm and did not grow further on Type B2 event days (see Figure 3d).

506 We first examined the air mass trajectory characteristics of Type B2 events. Compared with Type B1,
507 Type B2 was characterized by long range transport air masses from far north of China and Mongolia.
508 The lumped trajectories with insignificant wind direction change imply that the air mass in Type B2
509 event was quite uniform. In addition, meteorological and chemical variables (high solar radiation
510 flux and wind speed, low temperature, PM_{2.5}, SO₂, NO₂, CO and O₃, green lines in Figure 5)
511 collectively suggested that Type B2 was typical regional event in homogeneous cold air masses.
512 Therefore, the interrupted growth of new particles was not likely to be a result of wind direction
513 change.

514 As seen from Figure 5, meteorological variables on Type B2 days were generally more favorable
515 in aiding particle growth than on Type B1 days: lower PM_{2.5}, lower temperature, and higher solar
516 radiation flux. The unfavorable factors in Type B2 events, however, included lower concentrations of
517 SO₂, NO₂, and CO (anthropogenic emission indicators), lower secondary photochemical product
518 indicators O₃ and lower particle phase sulfate in 100-1000 nm (X. Ge, private communication, 2015,
519 X. Ge conducted simultaneous AMS measurement during our measurement periods). All these
520 evidences suggested that further particle growth in Type B2 events was limited by certain condensing
521 vapor other than ELVOC. Consequently, although there was a pool of sub-20 nm particles, they were
522 not further “activated” due to the low availability of this condensing vapor. Following the
523 terminology of Donahue et al. (2011, 2012), we called this condensing vapor LVOC (low volatility
524 organic compounds)

525 The above hypothesis was sound if we considered that the identity of LVOC for the growth of
526 particles > 20 nm could be different from ELVOC for sub-3 nm particle growth. Hirsikko et al. (2005)
527 observed that GR_{3-20} demonstrated an opposite seasonal cycle to $GR_{1.3-3}$: GR_{3-20} was higher in

528 summer, whereas $GR_{1.3-3}$ was higher in winter. This suggested that the condensing vapors were
529 different in identity for particles of different sizes. Hirsikko et al. (2005) attributed the condensing
530 vapors for GR_{3-20} to biogenetic VOCs. In our urban atmosphere, according to Figure 5, LVOC was
531 more likely to be from anthropogenic sources associated with SO_2 , NO_x and CO emissions. A picture
532 of the growth process was thus like this: ELVOC of lower volatility, lower concentration and higher
533 water solubility activated inorganic nuclei and accelerated particle growth in smaller sizes. This in
534 turn assisted in the condensation of LVOC of high volatility, low solubility, but with larger amount
535 of mass. The further growth of particles >20 nm, which means significant increment of particle mass,
536 needed continuous supply of LVOC from the anthropogenic sources. On the Type B2 days, LVOC
537 supply was not adequate (low SO_2 , CO and NO_x). As a result, continuous banana-shape particle
538 growth did not take place.

539 **4. Conclusion**

540 NPF can contribute to CCN only after going through nucleation, initial growth steps and
541 subsequent growth to CCN-active sizes. This study provided the evidences of limiting factors in
542 these processes in a polluted urban atmosphere in China. We observed atmospheric nucleation events
543 on 42 out of total 90 observation days, but particles could grow to CCN-active sizes on only 9 days,
544 which was equivalent to 9 conventional NPF events. In summer, strict emission control measures
545 during the 2014 Youth Olympic Games resulted in relatively low $PM_{2.5}$ and anthropogenic trace
546 gases (SO_2 , NO_2 , CO and O_3) levels. Infrequent nucleation was thus limited by both low
547 concentrations of gaseous precursors and high temperature and RH in summer. In more polluted
548 winter and spring atmosphere, precursor supply was not limiting anymore; nucleation occurred once
549 meteorological conditions were favorable (i.e. low CS and temperature/RH, higher solar radiation).

550 However, for the further growth of sub-3 nm particles to CCN-active sizes, anthropogenic gaseous
551 precursors again became limiting factors.

552 A simplified GDE method was used in this study to calculate particle formation rates first and
553 then growth rates. Nucleation events were strong in the polluted urban atmosphere of Nanjing. Initial
554 $J_{1.4}$ at the onset and peak $J_{1.4}$ at the noontime could be up to $2.1 \times 10^2 \text{ cm}^{-3} \text{ s}^{-1}$ and $2.5 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$,
555 respectively, during the 8 nucleation events selected from different seasons. The diurnal variation of
556 $J_{1.4}$ implied that nucleation was usually linked to sunlight induced photochemistry. Time-dependent
557 $J_{1.4}$ showed good linear correlations with the H_2SO_4 proxy for every single event, except a day with
558 significant nocturnal nucleation. However, the correlation between $J_{1.4}$ and the H_2SO_4 proxy for all 8
559 events deteriorated, which might reflect the effect of temperature or assisting vapor concentration in
560 the nucleation. The deteriorated correlation could also be due to the lower predictive ability of the
561 H_2SO_4 proxy in the polluted urban atmosphere for different seasons.

562 In all nucleation events, a local maximum growth rate was observed between 1-3 nm with GR up
563 to 25 nm h^{-1} . This means GR was not monotonically increasing with particle size. The overall $GR_{1.4-3}$,
564 however, was still smaller than GR_{3-20} , if particles could grow beyond 3 nm. The local maximum
565 growth rate was interpreted as the solvation effect of organic activating vapor in newly formed
566 inorganic nuclei. Based on our estimation, high ELVOC concentration of $2.3 \times 10^7 - 2.0 \times 10^8 \text{ cm}^{-3}$ was
567 expected to be the key factor leading to high $GR_{1.4-3}$. The varying GR of new particle in turn resulted
568 in the different particle growth patterns that we observed in Nanjing.

569 Our results call for a more robust proxy of gaseous H_2SO_4 to be developed for polluted urban
570 conditions. The study also highlighted the importance of estimating or measuring activating organic
571 vapor levels (using CI-APi-TOF, for example) in the initial growth steps of atmospheric NPF. Our

572 year-round measurement data provided valuable size evolution data of sub-3 nm clusters/particles to
573 evaluate previous aerosol dynamic models of new particle formation. A robust dynamic model was
574 needed to appropriately treat all aerosol and gas-phase processes in the initial growth steps.

575

576 **Acknowledgements**

577 This work was supported by National Science Foundation of China (41405116,
578 41275142, 41575122), Natural Science Foundation of Jiangsu Province (BK20140989), and Jiangsu
579 Specially Appointed Professor grant. The measurement campaigns were partially funded by the
580 Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). We
581 thank Dr. Vijay P. Kanawade and Dr. Xinlei Ge for valuable discussion.

582

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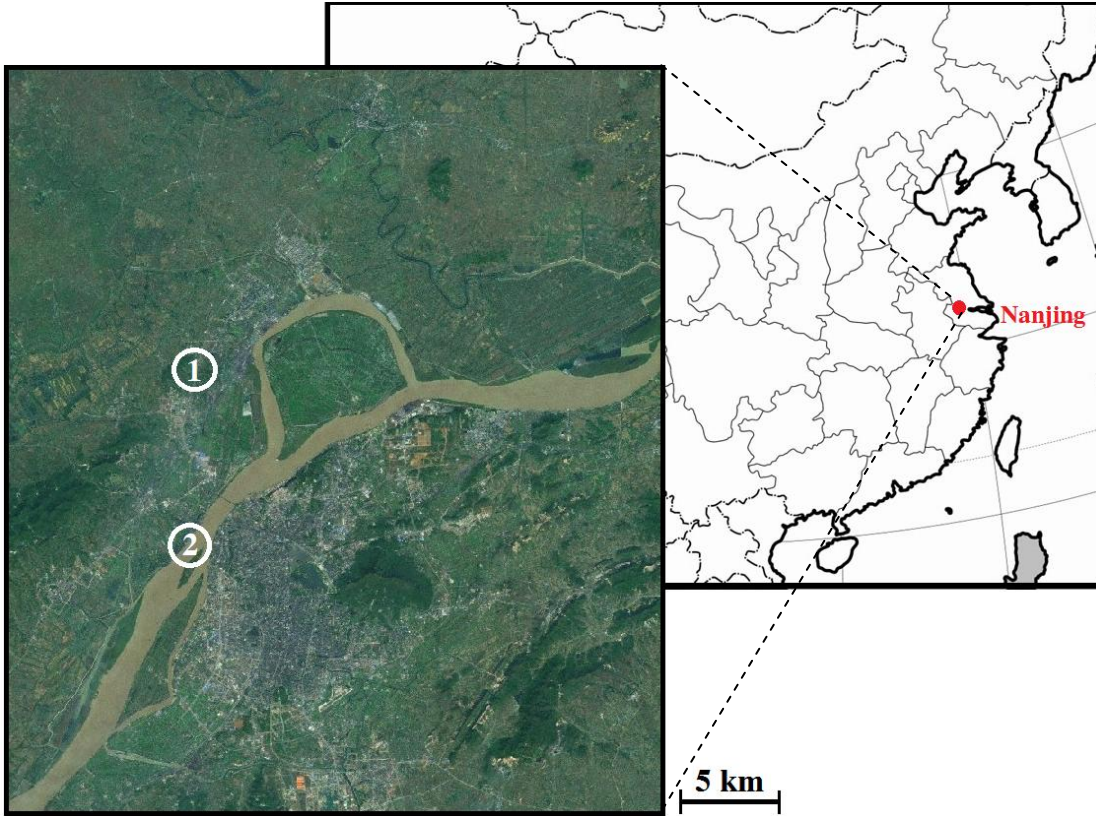
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832 spectrometric measurements of atmospheric neutral clusters using the cluster-CIMS, *J. Geophys.*
833 *Res.*, 115, D08205, doi: 10.1029/2009JD012606, 2010.

834 Table 1. Activation diameter ($D_{p,act}$), maximum growth rate in 1.4-3 nm ($GR_{max, 1.4-3}$), overall growth rate in 1.4-3 nm ($GR_{1.4-3}$), overall growth
835 rate in 3-20 nm (GR_{3-20}), nucleation rate ($J_{1.4}$), condensation sink (CS), and temperature (T) of selected nucleation events. Estimated gas-phase
836 activating vapor concentrations C_∞ , pure saturation concentration of activating vapor over flat surface C^* , and Mikkonen H_2SO_4 proxy were
837 shown in right 3 columns. All data were for the time periods with maximum nucleation rates.

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Type	Date	$D_{p,act}$ (nm)	$GR_{max,1.4-3}$ (nm h ⁻¹)	$GR_{1.4-3}$ (nm h ⁻¹)	GR_{3-20} (nm h ⁻¹)	$J_{1.4}$ (cm ⁻³ s ⁻¹)	T (°C)	CS (10 ⁻² s ⁻¹)	Mikkonen H_2SO_4 proxy (cm ⁻³)	C_∞ (cm ⁻³)	C^* (cm ⁻³)
A1	May 15, 2014	2.4	6.4	3.6	7.7	3.0×10 ²	20.8	1.6	8.7×10 ⁷	5.1×10 ⁷	6.3×10 ⁶
A1	Aug 15, 2014	2.4	14.5	7.1	7.7	2.0×10 ²	26.1	1.8	9.3×10 ⁷	1.1×10 ⁸	2.5×10 ⁷
A2	May 16, 2014	2.4	3.8	1.9	0	95	25.3	1.9	1.4×10 ⁸	3.0×10 ⁷	4.0×10 ⁶
A2	May 20, 2014	2.2	2.9	1.6	0	92	24.1	1.9	3.8×10 ⁷	2.3×10 ⁷	2.3×10 ⁶
B1	Feb 18, 2015	1.6	25.9	4.4	6.0	1.1×10 ³	8.2	3.3	3.9×10 ⁷	1.7×10 ⁸	3.5×10 ⁷
B1	Dec 27, 2014	1.6	17.7	4.2	5.5	1.9×10 ²	7.6	2.8	3.5×10 ⁷	1.2×10 ⁸	2.8×10 ⁷
B2	Feb 19, 2015	1.9	25.0	8.9	10.1	8.0×10 ²	7.4	3.2	3.7×10 ⁷	2.0×10 ⁸	5.7×10 ⁷
B2	Mar 4, 2015	1.9	18.0	5.8	8.7	2.5×10 ³	3.9	2.2	4.8×10 ⁷	1.4×10 ⁸	2.0×10 ⁷



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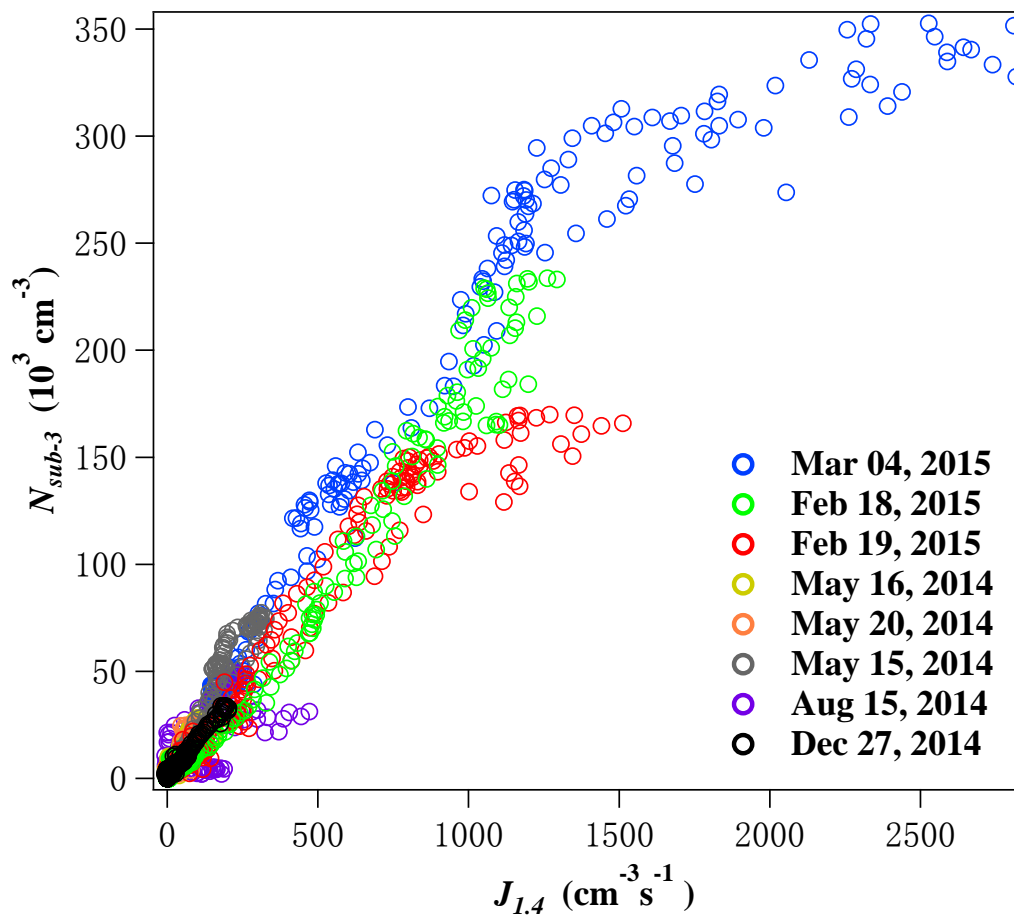
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Figure 1. Locations of two urban measurement sites in Nanjing, the second largest megacity in the Yangtze River Delta region, China. ① is the NUIST site and ② is the summer measurement site.



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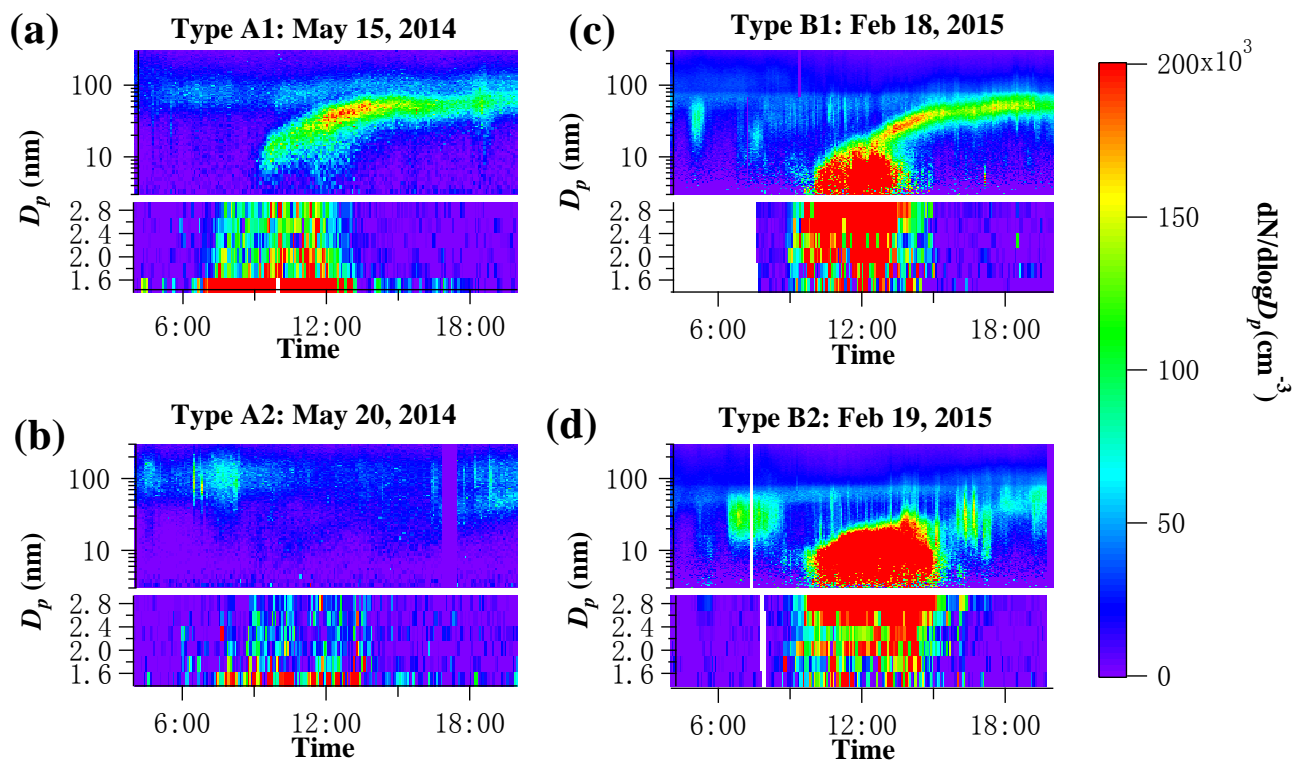
846 Figure 2. N_{sub-3} vs. $J_{1.4}$ in the 8 nucleation events in February, May, December and August during

847 2014-2015. The events were indicated by different colors (blue: March 1, 2015; green: February

848 18, 2015; red: February 19, 2015; purple: August 15, 2014; black: December 27, 2014; grey:

849 May 15, 2014; orange: May 20, 2014; yellow: May 16, 2014)

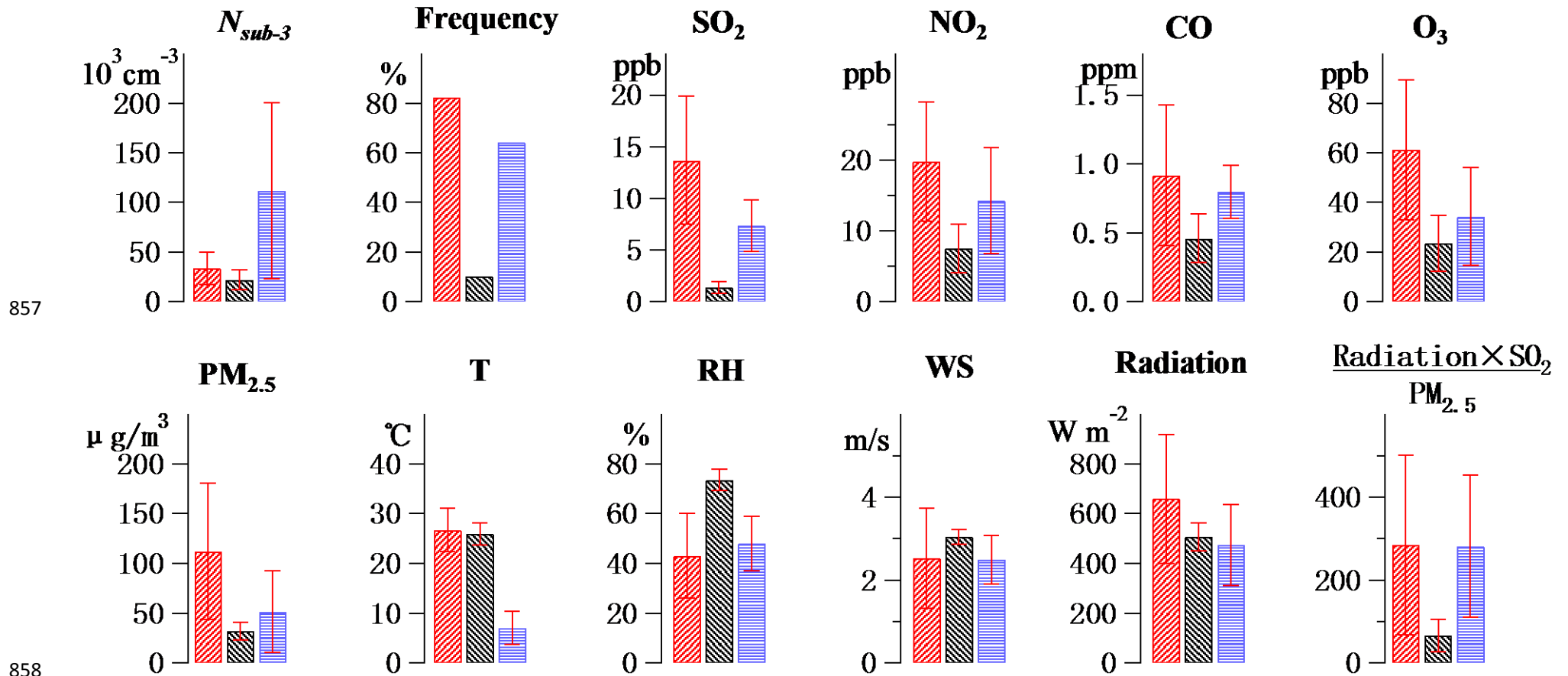
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853 Figure 3. Size spectra of typical (a) Type A1 event on May 15, 2014; (b) Type A2 event on May 20,
 854 2014; (3) Type B1 event on February 18, 2015 and (d) Type B2 event on February 19, 2015 during
 855 our measurement period. Size spectra from 3-300 nm (logarithmic scale) and 1.4-3 nm (linear scale)
 856 were obtained using SMPS and nCNC, respectively.

Spring Summer Winter

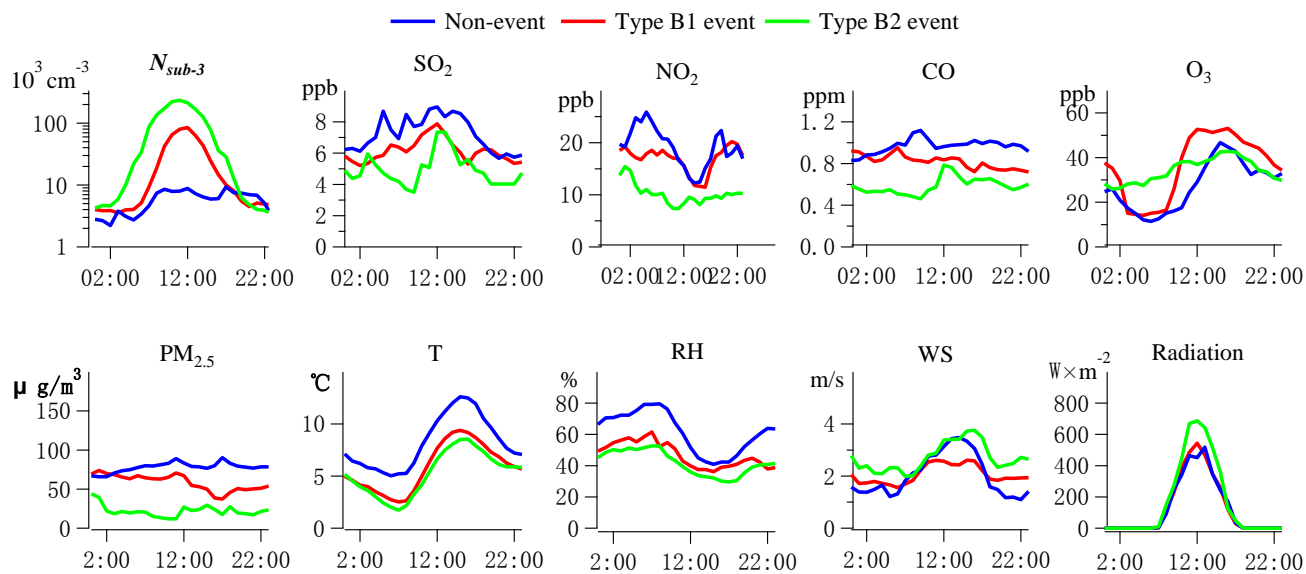


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859 Figure 4. Mean and standard deviation of event-averaged N_{sub-3} , anthropogenic trace gases (SO_2 , NO_2 , CO and O_3), $\text{PM}_{2.5}$, and meteorological
 860 variables (temperature, RH, wind speed (WS), solar radiation, and radiation \times $\text{SO}_2/\text{PM}_{2.5}$) for nucleation events in spring (n=17), summer (n=3)
 861 and winter (n=14). Nucleation frequency (the percentage of event days out of total measurement days) was also shown.

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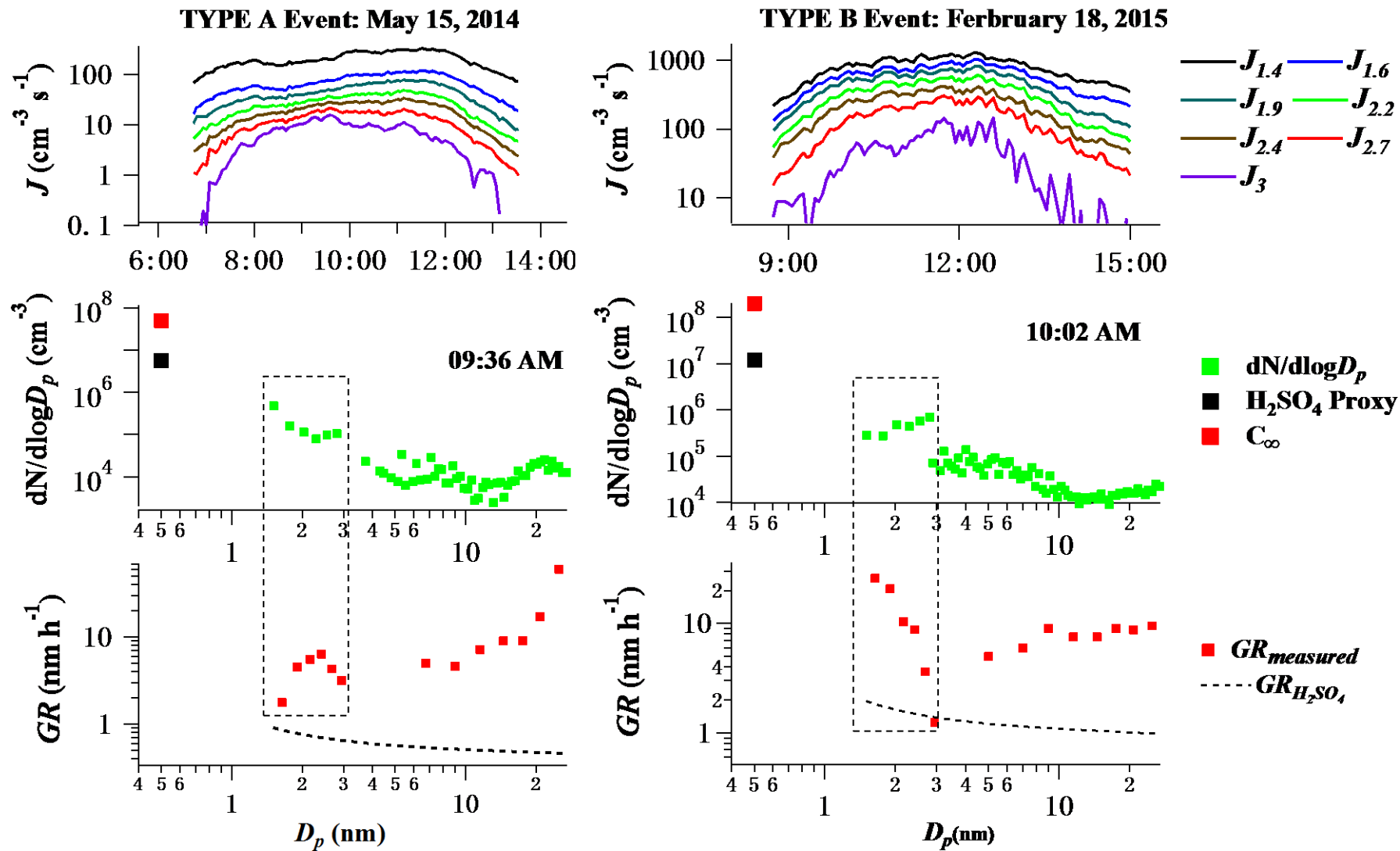
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864 Figure 5. Diurnal variations of mean N_{sub-3} , anthropogenic trace gases (SO_2 , NO_2 , CO and O_3), $\text{PM}_{2.5}$,

865 and meteorological variables (temperature, RH, wind speed, and solar radiation flux) on non-event

866 days (n=8, blue line) and event days (n=3 for Type B1 event, red line and n=6 for Type B2 event,

867 green line) during winter measurement period.

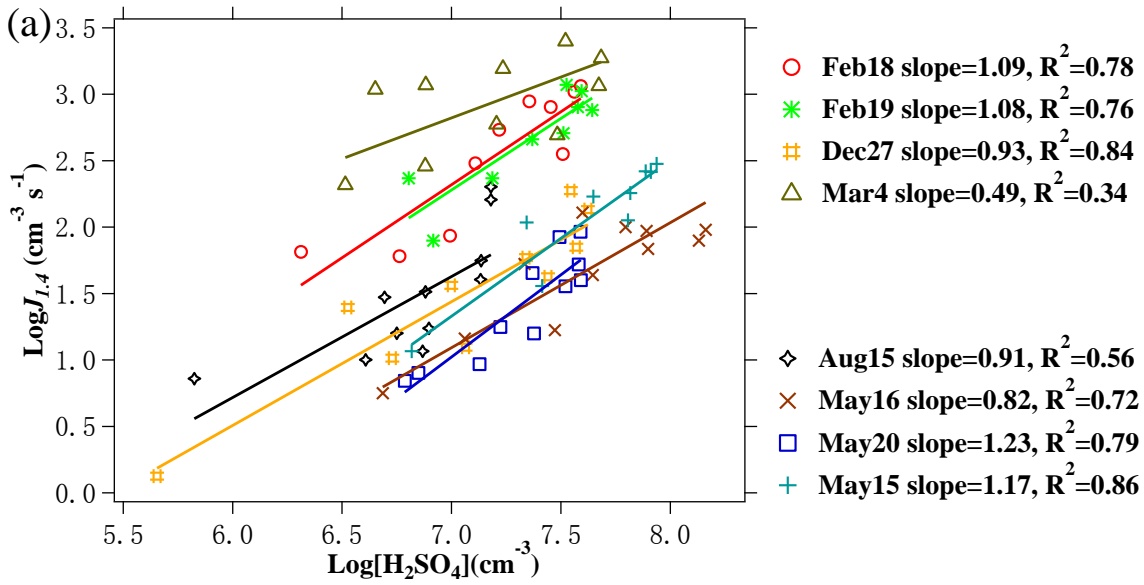


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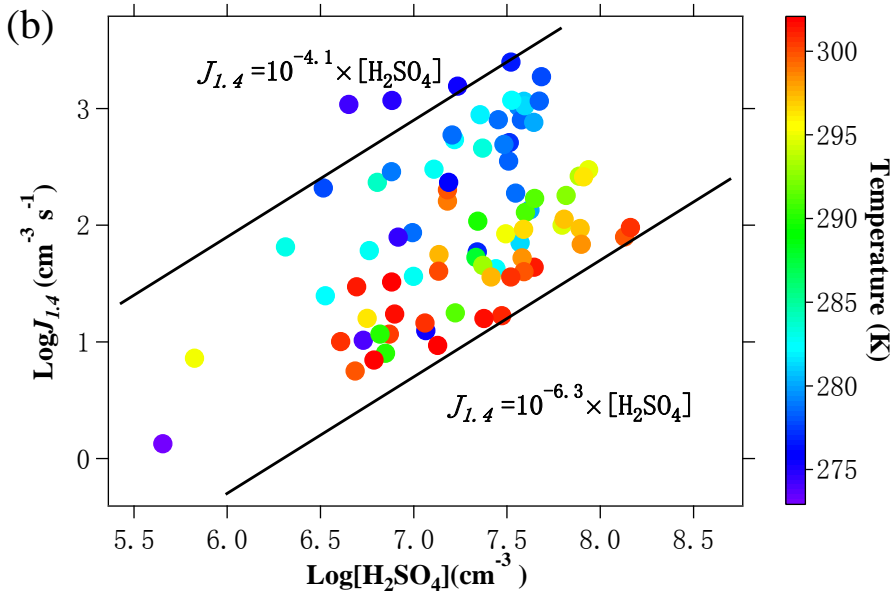
869 Figure 6. Upper: formation rates (or equivalently, particle growth fluxes) of 1.4, 1.6, 1.9, 2.2, 2.4, 2.7 and 3.0 nm cluster/particles on May 15

870 2014 (Type A1 event) and Feb 18 2015 (Type B1 event). Middle: particle size distribution ($dN/d\log D_p$, green square) selected during the two
871 events (9:36 AM and 10:02 AM). Lower: particle growth rates measured during the same time periods ($GR_{measured}$, red square). Also shown in the
872 figure were H_2SO_4 proxy (black square) and growth rates calculated from the H_2SO_4 proxy ($GR_{H_2SO_4}$, dashed black line), as well as the
873 calculated ELVOC concentration (C_∞ , red square) during the same time periods. Dashed boxes in the lower panels highlighted the size
874 distributions and growth rates between 1.4 and 3 nm measured with nCNC.

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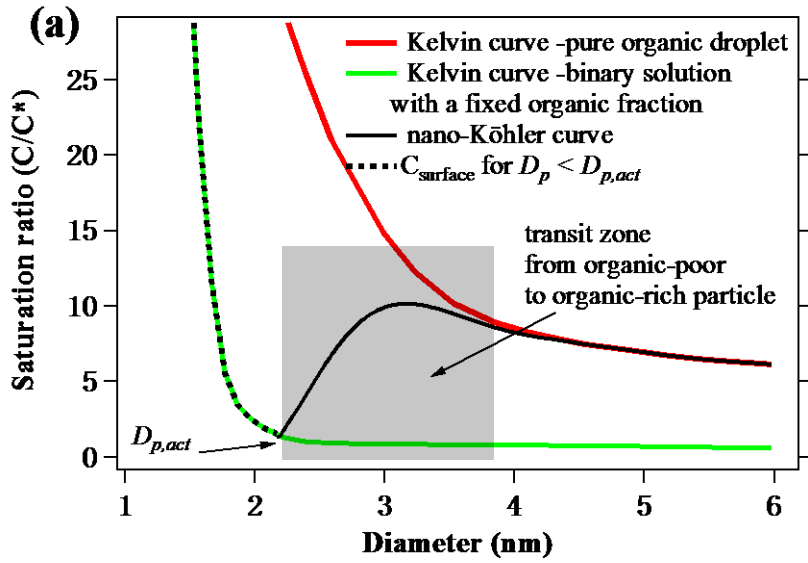


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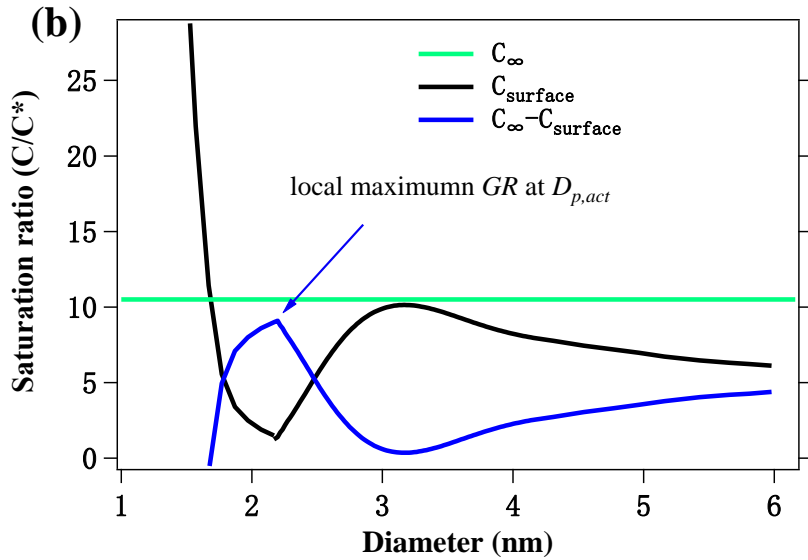


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878 Figure 7. (a) Correlations between $\log J_{1.4}$ and $\log [\text{H}_2\text{SO}_4]$ for the 8 events. H_2SO_4 proxy was
 879 calculated according to Mikkonen et al. (2011). $J_{1.4}$ and $[\text{H}_2\text{SO}_4]$ were synchronized to 1 hour that
 880 was the time resolution of solar radiation data. The colored lines showed linear fits to the data of
 881 every single event. (b) The same dataset as (a), but with symbol color to indicate ambient
 882 temperature. Two black lines showed the linear dependences of $J_{1.4}=10^{-4.1} \times [\text{H}_2\text{SO}_4]$ and $J_{1.4}=10^{-6.3} \times$
 883 $[\text{H}_2\text{SO}_4]$, between which most of data points located.



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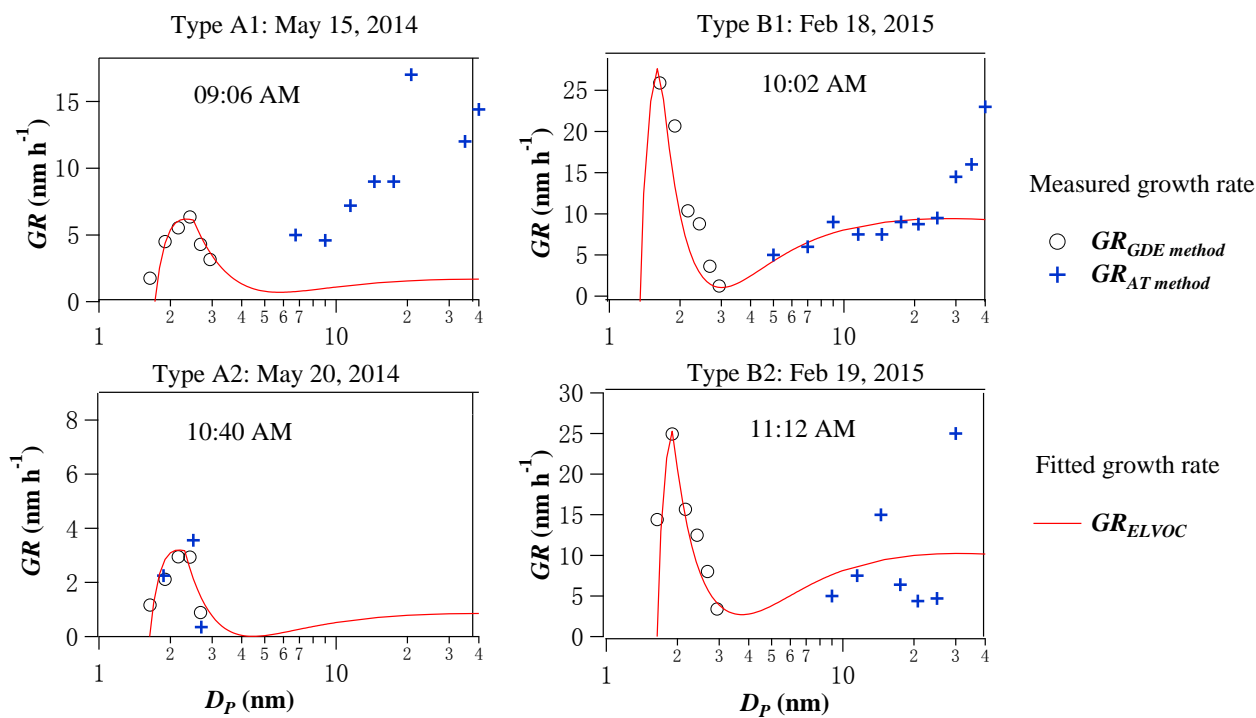
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887 Figure 8. (a) Kelvin equilibrium curves over a pure organic droplet (red line) and a binary solution
 888 with a fixed organic fraction (green line), nano Köhler curve (black solid line) and surface
 889 concentration C_{surface} curve for $D_p < D_{p,act}$ (black dashed line), (b) gas phase concentration of the
 890 organic vapor (C_∞ , light green line), surface concentration C_∞ (black line), and the resulted
 891 $C_\infty - C_{\text{surface}}$ (blue line).

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897 Figure 9. Comparisons of measured ($GR_{GDE\ method}$, black circle) and fitted (GR_{ELVOC} , red line) growth
 898 rates from Eq. (4) for typical Type A1, A2, B1, and B2 events. Also shown were growth rates
 899 calculated from appearance time method ($GR_{AT\ method}$, blue cross) for sub-3 nm particles when growth
 900 rate was relatively small or for larger particles with large size intervals.

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