

1 **Secondary aerosol formation alters CCN activity in the North China**
2 **Plain**

3 Jiangchuan Tao^{1, 2}, Ye Kuang^{1, 2}, Nan Ma^{1, 2}, Juan Hong^{1, 2}, Yele Sun^{3, 4, 5}, Wanyun Xu⁶, Yanyan
4 Zhang¹, Yao He³, Qingwei Luo¹, Linhong Xie^{1, 2}, Hang Su⁷, Yafang Cheng⁷

5 ¹Institute for Environmental and Climate Research, Jinan University, Guangzhou, Guangdong 511443,
6 China

7 ²Guangdong-Hongkong-Macau Joint Laboratory of Collaborative Innovation for Environmental
8 Quality, Guangzhou, China

9 ³State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute
10 of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

11 ⁴College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049,
12 China

13 ⁵Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment,
14 Chinese Academy of Sciences, Xiamen 361021, China

15 ⁶State Key Laboratory of Severe Weather, Key Laboratory for Atmospheric Chemistry, Institute of
16 Atmospheric Composition, Chinese Academy of Meteorological Sciences, Beijing, 100081, china

17 ⁷Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz 55128, Germany

18 Correspondence to: Jiangchuan Tao (taojch@jnu.edu.cn) and Nan Ma (nan.ma@jnu.edu.cn)

19

20 **Abstract:**

21 Secondary aerosols (SA, including secondary organic and inorganic aerosols, SOA and SIA) are
22 predominant components of aerosol particles in the North China Plain (NCP) and its formation has
23 significant impacts on the evolution of particle size distribution (PNSD) and hygroscopicity. Previous
24 studies have shown that distinct SA formation mechanisms can dominate under different relative
25 humidity (RH). This would lead to different influences of SA formation on the aerosol hygroscopicity
26 and PNSD under different RH conditions. Based on the measurements of size-resolved particle
27 activation ratio (SPAR), hygroscopicity distribution (GF-PDF), $PM_{2.5}$ chemical composition, PNSD,
28 meteorology and gaseous pollutants in a recent field campaign, McFAN (Multiphase chemistry
29 experiment in Fogs and Aerosols in the North China Plain), conducted during the autumn-winter
30 transition period in 2018 at a polluted rural site in the NCP, the influences of SA formation on cloud
31 condensation nuclei (CCN) activity and CCN number concentration (N_{CCN}) calculation under different
32 RH conditions were studied. Results suggest that during daytime, SA formation could lead to a
33 significant increase in N_{CCN} and a strong diurnal variation in SPAR at Super-saturations lower than
34 0.07%. During periods with daytime minimum RH exceeding 50% (high RH conditions), SA
35 formation significantly contributed to the particle mass/size changes in a broad size range of 150 nm
36 to 1000 nm, led to $N_{CCN}(0.05\%)$ increases within the size range of 200 nm to 300 nm, and mass
37 concentration growth mainly for particles larger than 300 nm. During periods with daytime minimum
38 RH below 30% (low RH conditions), SA formation mainly contributed to the particle mass/size and
39 N_{CCN} changes for particles smaller than 300 nm. As a result, under the same amount of mass increase
40 induced by SA formation, the increase of $N_{CCN}(0.05\%)$ was stronger under low RH conditions and
41 weaker under high RH conditions. Moreover, the diurnal variations of SPAR parameter (inferred from
42 CCN measurements) due to SA formation varied with RH conditions, which was one of the largest
43 uncertainties within N_{CCN} predictions. After considering the SPAR parameter (estimated through the
44 number fraction of hygroscopic particles or mass fraction of SA), the relative deviation of $N_{CCN}(0.05\%)$
45 predictions were reduced to within 30%. This study highlights the impact of SA formation on CCN
46 activity and N_{CCN} calculation, which provides guidance for future improvements of CCN predictions
47 in chemical-transport models and climate models.

48 **1. Introduction**

49 Cloud condensation nuclei (CCN) activity of aerosol particles describes its ability to activate
50 and grow into cloud droplets at given supersaturations and thus has important impacts on cloud
51 microphysics and the aerosol indirect effect on climate. CCN activity is dependent on the
52 physicochemical properties of aerosol particles, including particle size distributions, hygroscopicity
53 (determined by chemical composition) and mixing state. Thus, atmospheric processes influencing
54 these aerosol properties may exert influences on CCN activity.

55 Secondary aerosols (SA) formation contributes greatly to aerosol populations and impacts
56 CCN properties in many ways, generally increasing CCN number concentrations (N_{CCN}) and leading
57 to changes in the CCN activity (Wiedensohler et al., 2009; Kerminen et al., 2012; Wu et al., 2015;
58 Farmer et al., 2015; Ma et al., 2016; Zhang et al., 2019 and reference therein). Differences in precursor
59 and oxidant concentrations as well as SA formation mechanisms lead to particle size growth in
60 different size ranges (Dal Maso et al., 2005; Kulmala et al., 2007; Zhang et al., 2012; Farmer et al.,
61 2015; Cheng et al., 2016; Kuang et al., 2020c), thus would impact CCN activities in different ways.
62 SA formation includes both the formation and subsequent growth of new particles (New Particle
63 Formation, NPF), and the growth of existing particles. NPF can directly provide particles large enough
64 to act as CCNs (Wiedensohler et al., 2009; Kerminen et al., 2012; Farmer et al., 2015), generally
65 affecting aerosol particles smaller than 100 nm, thereby elevating N_{CCN} at higher supersaturations
66 ($SSs > 0.2\%$) (Wiedensohler et al., 2009; Kerminen et al., 2012; Ma et al., 2016; Zhang et al., 2019 and
67 reference therein). SA formation on existing particles, especially under polluted conditions,
68 significantly adds mass to and changes the chemical composition of accumulation mode particles
69 (Farmer et al., 2015), thus affecting CCN at lower $SSs (< 0.2\%)$ (Wiedensohler et al., 2009; Mei et al.,
70 2013; Yue et al., 2016; Thalman et al., 2017; Duan et al., 2018). SSs varies greatly among different
71 clouds categories. Cumulus clouds are formed under higher SSs and are thus mostly influenced by
72 Aitken mode particles formed in NPF events (Reuter et al., 2009; Gryspeerd and Stier, 2012; Fan et
73 al., 2016; Jia et al., 2019 and reference therein). Stratus clouds and fogs that exert stronger effects on
74 climate and environment, however, are generally formed at SSs lower than 0.2%, indicating that only
75 accumulation mode particles can serve as CCN (Ditas et al., 2012; Hammer et al., 2014a, b; Krüger et
76 al., 2014; Shen et al., 2018). Numerous studies have investigated the impact of NPF on CCN (Gorden
77 et al., 2016; Ma et al., 2016; Yu et al., 2020 and reference therein), however, only few studies have
78 focused on the influence of SA formation on CCN activity of accumulation mode particles, which
79 might exhibit strong climate and environment impacts and urgently requires attention.

80 SA formation affects CCN activity of accumulation mode particles not only by enlarging their
81 size, but also by changing their chemical compositions. At a specific particle size, the CCN activity is
82 determined both by the chemical composition of particles, which originally were and stayed this size,
83 and that of particles, which grew into this size via added SA mass. These two groups of particles can
84 exert different variations to CCN activity at the same particle size (Wiedensohler et al., 2009 and
85 reference therein). In general, the SA formation can increase the hygroscopicity of particles by adding
86 chemical compounds with lower volatility and higher oxidation state, which are usually more
87 hydrophilic, thereby enhancing CCN activity of accumulation mode particles (Mei et al., 2013; Yue et
88 al., 2016). However, CCN activity may also remain unchanged (Wiedensohler et al., 2009) or be
89 weakened in some cases (Thalman et al., 2017; Duan et al., 2018). In SA formation observed in central
90 Amazon forests, Thalman et al. (2017) reported enhanced CCN activity in dry season while constant
91 CCN activity in wet season. In SA formation events under polluted conditions in Guangzhou (Pearl
92 River Delta, China), Duan et al. (2018) found that bulk CCN activity can be enhanced in summer due
93 to the formation of large and inorganic-rich particles, but weakened in winter due to the formation of
94 small and organic-rich particles, where RH seemed to have been an important factor in the variations
95 of bulk CCN activity due to different particle formation pathways. Aside from variations of particle
96 chemical composition, changes in aerosol mixing states caused by SA formation can also change CCN
97 activity (Su et al., 2010; Rose et al., 2011; Cheng et al., 2012). The fast condensation of SA components
98 on accumulation mode particles led to the turnover of soot particle mixing state from externally to
99 internally mixed, which contributed mostly to enhancements of CCN activity (Cheng et al., 2012).
100 Thus, SA formation influences the CCN activity of accumulation mode particles through its integrated
101 impacts on their size, hygroscopicity and mixing state, which requires more detailed and
102 comprehensive investigations.

103 The North China Plain (NCP) frequently experiences severe aerosol pollution due to both
104 strong emissions of primary aerosol and strong SA formation caused by the abundance of gaseous
105 precursors and oxidants (Zheng et al. ACP, 2015; Liu et al., 2010; Huang et al., 2014; Xu et al., 2019).
106 In the SA formation events on the NCP, both aqueous-phase processes and gas-phase photochemical
107 processes can play important roles, depending on atmospheric conditions such as RH (Hu et al., 2016;
108 Xu et al., 2017a; Wang et al., 2019). A recent observational study on the NCP found that SA formation
109 dominantly contributed to different particle size since SA formation mechanisms varied with RH
110 conditions (Kuang et al., 2020c). Under dry conditions, SA were mainly formed through gas-phase
111 photochemical processing and mostly added mass to accumulation mode particles. While under high
112 RH conditions or super-saturated conditions, SA was also formed in aqueous phase, contributing to

113 the formation of both accumulation mode and coarse mode particles. The difference in particle size
114 where SA formation took place and the difference in SA chemical compositions could result in distinct
115 variations of CCN activity, which has not been evaluated yet. In this study, we will study the influence
116 of SA formation on Size-resolved Particle Activation Ratio (SPAR) of accumulation mode particles
117 in the NCP under different RH conditions, which fills a gap of knowledge within CCN studies in the
118 NCP and may provide guidance for the improvement of current CCN parameterization schemes in
119 chemical-transport and climate models.

120 **2. Method:**

121 2.1. Measurements

122 2.1.1. Site

123 Under the framework of McFAN (Multiphase chemistry experiment in Fogs and Aerosols in
124 the North China Plain) (Li et al., 2021), from 16th November to 16th December 2018, physical and
125 chemical properties of ambient aerosol particles as well as meteorological parameters were
126 continuously measured at the Gucheng site in Dingxing county, Hebei province, China. This site is an
127 Ecological and Agricultural Meteorology Station (39°09'N, 115°44'E) of the Chinese Academy of
128 Meteorological Sciences, which is located between Beijing (~100km) and Baoding (~40km), two
129 mega cities in the North China Plain, and surrounded by farmlands and small towns. Measurements at
130 this site can well represent the polluted background conditions of the NCP. All aerosol measurement
131 instruments were placed in a container with temperature maintained at 24 °C, while conventional trace
132 gas instruments including CO were housed in an air-conditioned room on a two-story building located
133 ~80 meters to the south of the container, with no taller buildings between them blocking the air flow.

134 2.1.2 Instrumentation

135 In this study, ambient aerosol was sampled by an inlet system consisting of a PM10 inlet
136 (Rupprecht & Patashnick Co., Inc., Thermo, 16.67 L/min), a Nafion dryer that dried relative humidity
137 to below 30% and an isokinetic flow splitter directing the air sample to each instrument.

138 A DMA-CCNC system measured SPAR at five supersaturations (SSs), 0.05%, 0.07%, 0.2%,
139 0.44% and 0.81%, with a running time of 20 min for 0.05% and 10 min for the other SSs. This system
140 consisted of a differential mobility analyzer (DMA model 3081; TSI, Inc, MN USA), a condensation
141 particle counter (CPC model 3772; TSI, Inc., MN USA) and a continuous-flow CCN counter (model
142 CCN200, Droplet Measurement Technologies, USA; Roberts and Nenes, 2005). The system was
143 operated in a size-scanning mode over the particle size range from 9 to 400 nm. SPAR can be obtained
144 by combining the measurements of CPC and CCNC at different particle size. The sample and sheath

145 flow rate of the DMA were set to 1 lpm and 5 lpm, respectively, hence the resultant measured particle
146 diameter ranged from 9 nm to 500 nm. Since the low number concentration of particles above 300 nm
147 could lead to large uncertainty in CCNC counting, the measurements for particles larger than 300 nm
148 were excluded, except for 0.05% SS. In order to characterize the variations of particles with low
149 hygroscopicity of about 0.1, SPAR measurement up to about 400 nm is used at 0.05% SS. There are
150 12 size distribution scans during a complete 1-hour cycle, with four scans for first SS and two scans
151 for each of the rest four SSs. Only the last scan for each SS is used as the CCNC needs time for SS
152 stabilization. The SSs of CCNC were calibrated with monodispersed ammonium sulphate particles
153 (Rose et al., 2008) both before and after the campaign. The flowrates were checked regularly (every
154 few days) during the campaign, as the flows (sample flow and sheath flow) of the instrument can affect
155 both the counting of droplets and the SS in the column. A modified algorithm based on Hagen and
156 Alofs (1983) and Deng et al. (2011, 2013) was used to correct the influence of multiple-charge particles
157 and DMA transfer function on SPAR. Details about the system are described in Ma et al. (2016) and
158 the description about the inversion method can be found in the supplements.

159 Non-refractory particulate matter (NR-PM) including SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- and organics with
160 dry aerodynamic diameters below $2.5 \mu\text{m}$ was measured by an Aerodyne Time-of-Flight Aerosol
161 Chemical Speciation Monitor (ToF-ACSM hereafter) equipped with a $\text{PM}_{2.5}$ aerodynamic lens
162 (Williams et al., 2010) and a capture vaporizer (Xu et al., 2017b; Hu et al., 2017a) at 2-minute time
163 resolution. The ToF-ACSM data were analyzed with the standard data analysis software (Tofware
164 v2.5.13; <https://sites.google.com/site/ariacsm/>, last access: 21 January 2020). The organic mass spectra
165 from m/z 12 to 214 were analyzed with an Igor Pro based positive matrix factorization (PMF)
166 evaluation tool (v3.04) and then evaluated following the procedures described in Zhang et al. (2011).
167 The chosen five-factor solution includes four primary factors i.e. hydrocarbon-like OA (HOA),
168 cooking OA (COA), biomass burning OA (BBOA), and coal combustion OA (CCOA), and a
169 secondary factor, i.e. oxygenated OA (OOA). More detailed descriptions on the ACSM measurements
170 and data analysis can be found in Kuang et al. (2020b) and Sun et al. (2020).

171 A Humidified Tandem differential mobility analyzer (HTDMA, Tan et al., 2013) measured the
172 size-resolved aerosol growth factor (GF) at 90% RH. The sampled particles were subsequently charged
173 by a neutralizer (Kr85, TSI Inc.) and size selected by a DMA (DMA1, model 3081L, TSI Inc.). A
174 Nafion humidifier (model PD-70T-24ss, Perma Pure Inc., USA) was used to humidify the
175 monodisperse particles with a specific diameter (D_d) at a fixed RH of $(90 \pm 0.44) \%$ and then the
176 number size distribution of the humidified particles (D_{wet}) was measured by another DMA (DMA2,

177 model 3081L, TSI Inc.) and a condensation particle counter (CPC, model 3772, TSI Inc.). Thus, GF
178 of the particles can be calculated as:

$$179 \quad GF = \frac{D_{\text{wet}}}{D_{\text{d}}} \quad (1)$$

180 During the campaign, four dry mobility diameters (60, 100, 150, and 200 nm) were selected for the
181 HTDMA measurements. A full scan takes about 1 hour in order to cover the four sizes. Regular
182 calibration by using standard polystyrene latex spheres and ammonium sulfate were performed to
183 ensure the instrument functioned normally. The tandem differential mobility analyzer (TDMA)
184 inversion algorithm (Gysel et al., 2009) was applied to calculate the Probability Density Function of
185 GF (GF-PDF). More details about this system can be found in Cai et al. (2018) and Hong et al. (2018).

186 Particle number size distributions (PNSDs) were measured by combining the measurements of
187 a scanning mobility particle sizer (SMPS, TSI model 3080) and an aerodynamic particle sizer (APS,
188 TSI Inc., Model 3321), that measured particle mobility diameter size distributions in the range of 12
189 nm to 760 nm and particle aerodynamic diameter size distribution in the range of 700 nm to 10 μm ,
190 respectively. A commercial instrument from Thermo Electronics (Model 48C) was used to measure
191 CO concentration. Besides monthly multipoint calibrations and weekly zero-span check, additional 6-
192 hourly zero checks were also performed for the CO instrument.

193 2.2. Data processing

194 2.2.1. Aerosol hygroscopicity and cloud activation: κ -Köhler theory

195 The ability of particles to act as CCN and its dependence on particle size and particle chemical
196 composition on CCN activity can be described by the Köhler theory (Köhler, 1936). A hygroscopic
197 parameter κ is calculated based on the κ -Köhler theory (Petters and Kreidenweis, 2007) to evaluate
198 the influence of particle chemical compositions:

$$199 \quad \kappa = \left(\frac{D_{\text{wet}}^3 - D_{\text{d}}^3}{D_{\text{d}}^3} \right) \left[\frac{1}{S} \exp \left(\frac{4\sigma_{\text{s/a}} M_{\text{w}}}{RT\rho_{\text{w}} D_{\text{wet}}} \right) - 1 \right], \quad (1)$$

200 where S represents the saturation ratio, ρ_{w} is the density of water, M_{w} is the molecular weight of water,
201 $\sigma_{\text{s/a}}$ is the surface tension of the solution/air interface, R is the universal gas constant, T is the
202 temperature, D_{d} is the diameter of dry particle and D_{wet} is the diameter of the humidified particle. In
203 this study, $\sigma_{\text{s/a}}$ is assumed to be the surface tension of pure water/air interface. Based on the κ -Köhler
204 theory, the surface equilibrium water vapor saturation ratio of particles with a specific κ at different
205 wet particle size can be calculated, and the maximum value of surface equilibrium saturation ratio
206 (which is generally supersaturated) is defined as the critical SS for CCN activation. As a result, the

207 variation of the critical diameter (D_a) for particles with different hygroscopicity (or GF at a specific
208 RH) at different SSs can be determined.

209 2.2.2. Aerosol growth factor and its probability density function

210 In practice, the growth factor probability density function (GF-PDF) was inverted from the
211 measured GF distribution using a TDMA_{inv} algorithm (Gysel et al., 2009). After obtaining the GF-
212 PDF, the ensemble average GF and corresponding critical diameter under a certain SS ($D_{a,GF}$) can be
213 calculated. Furthermore, the number fraction and the weighted-average GF of hygroscopic particles
214 ($\kappa > 0.1$ and $GF(90\%, 200 \text{ nm}) > 1.22$) were calculated as:

$$215 \quad NF_{\text{hygro}} = \int_{1.2}^{\infty} \text{PDF}(\text{GF}) \times d\text{GF} \quad (2)$$

$$216 \quad GF_{\text{hygro}} = \int_{1.2}^{\infty} \text{GF} \times \text{PDF}(\text{GF}) \times d\text{GF} \quad (3)$$

217 Based on the κ -Köhler theory, the hygroscopicity parameter κ and corresponding critical diameter
218 ($D_{a,\text{hygro}}$) under a certain SS for particles with GF_{hygro} can be calculated. As GF_{hygro} is higher than the
219 average GF, $D_{a,\text{hygro}}$ is smaller than $D_{a,GF}$.

220 2.2.3 Calculations of aerosol hygroscopicity from aerosol chemical-composition measurements

221 For the calculation of aerosol hygroscopicity parameter κ based on measured chemical
222 composition data (κ_{chem}), detailed information on the chemical species are needed. The ACSM can
223 only provide bulk mass concentrations of SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- ions and organic components, which
224 cannot be used to calculate size resolved hygroscopicity. However, in the North China Plain,
225 accumulation mode particles are the dominant contributors to the bulk particle mass concentration (Liu
226 et al., 2014; Xu et al., 2015; Hu et al., 2017b) and thus the bulk chemical compositions can be used as
227 a proxy for that of accumulation mode particles. For the inorganic ions, a simplified ion pairing scheme
228 was used to convert ion mass concentrations to mass concentrations of corresponding inorganic salts
229 (Gysel et al., 2007; Wu et al., 2016). Thus, mass concentrations of SO_4^{2-} , NO_3^- , NH_4^+ and Cl^- are
230 specified into ammonium sulfate (AS), ammonium nitrate (AN), ammonium chloride (AC) and
231 ammonium bisulfate (ABS), for which the κ values under super-saturated conditions were specified
232 according to Petters and Kreidenweis (2007). For a given internal mixture of different aerosol chemical
233 species, the Zdanovskii–Stokes–Robinson (ZSR) mixing rule can be applied to predict the overall κ_{chem}
234 using volume fractions of each chemical species (ε_i) (Petters and Kreidenweis, 2007):

$$235 \quad \kappa_{\text{chem}} = \sum_i \kappa_i \cdot \varepsilon_i \quad (4)$$

236 where κ_i and ε_i represent the hygroscopicity parameter κ and volume fraction of chemical component
237 i in the mixture. Based on Eq.2, κ_{chem} can be calculated as follows:

$$238 \quad \kappa_{\text{chem}} = \kappa_{\text{AS}}\varepsilon_{\text{AS}} + \kappa_{\text{AN}}\varepsilon_{\text{AN}} + \kappa_{\text{ABS}}\varepsilon_{\text{ABS}} + \kappa_{\text{AC}}\varepsilon_{\text{AC}} + \kappa_{\text{BC}}\varepsilon_{\text{BC}} + \kappa_{\text{Org}}\varepsilon_{\text{Org}} \quad (5)$$

239 where κ_{BC} is assumed to be zero as black carbon is non-hygroscopic. κ_{org} and ε_{org} represent κ and
240 volume fraction of total organics. The values of hygroscopicity parameter for inorganic compounds
241 can be found in Table 1 of Kuang et al. (2020b). Large variations in κ_{org} has been reported in former
242 studies and a linear relationship between κ_{org} and organic aerosol oxidation state (f44) was detected in
243 our campaign (Kuang et al., 2020b), which was adopted to calculate κ_{org} in this study:

$$244 \quad \kappa_{\text{Org}} = 1.04 \times f44 - 0.02 \quad (6)$$

245 It should be noted that the κ -Köhler theory is not perfect, even for inorganic compounds.
246 Numerous studies have been focusing on the performance of its application on measurements under
247 different RH conditions (Liu et al., 2011; Wang et al., 2017). And κ_{org} used in this study was
248 determined by the measurement of humidified nephelometer at RH of 85% in Petters and Kreidenweis,
249 (2007), due to the lack of κ_{org} measured under super-saturated conditions. In this study, we focus on
250 the variations of κ values derived from HTDMA and CCN measurement during the SA formation
251 events, rather than the closure between κ values derived using different techniques, which will be
252 addressed in an upcoming study.

253 2.2.4. Fitting parameterization scheme of SPAR

254 In general, the variation in CCN activity of a particle population can be attributed to the
255 variation in the number fraction of hygroscopic particles or its hygroscopicity, which can be indicated
256 by fitting parameters of SPAR curves parameterization. SPAR curves are often parameterized using a
257 sigmoidal function with three parameters. This parameterization assumes aerosols to be an external
258 mixture of apparently hygroscopic particles that can act as CCN and non-hygroscopic particles that
259 cannot be measured by CCNC within the measured particle size range below 400 nm (Rose et al.,
260 2010). SPAR ($Ra(D_p)$) at a specific SS can be described as follows (Rose et al., 2008):

$$261 \quad Ra(D_p) = \frac{\text{MAF}}{2} \left(1 + \text{erf} \left(\frac{D_p - D_a}{\sqrt{2}\pi\sigma} \right) \right) \quad (7)$$

262 where erf is the error function. MAF is the asymptote of the measured SPAR curve at large particle
263 sizes. D_a is the midpoint activation diameter and is associated with the hygroscopicity of CCNs. σ is
264 the standard deviation of the cumulative Gaussian distribution function and indicates the heterogeneity
265 of CCN hygroscopicity. As reported by Jiang et al. (2021), based on the investigation of the

266 covariations between SPAR curves and parameterized hygroscopicity distribution, it was found that
267 the MAF can be used to estimate the number fraction of hygroscopic (thus CCN-active) particles, for
268 aerosol hygroscopicity distributions generally observed in ambient atmosphere, and thus half MAF
269 can be used to represent the number fraction of CCNs to total particles at particle size around D_a .
270 Although the influence of particles whose κ is less than 0.1 on SPAR cannot be considered in this
271 parameterization scheme, significant deviation were only found under higher SSs (Tao et al., 2020)
272 and need not to be considered under the low SSs discussed in this study.

273 To be noted, the meaning of MAF can be different regard to the SS, and SPAR measurement
274 up to about 400 nm is needed for the MAF fitting for SPAR at SS of 0.05% to represent the particles
275 with κ value higher than 0.1. For SPAR at SS of 0.8%, MAF should be 1 at 400 nm diameter. However,
276 a MAF of 1 in this case can lead to overestimations of hygroscopic particle number fraction due to the
277 significant difference between SPAR curves and sigmodal fitting curves. In the former study on SPAR
278 fitting curves in the NCP, it was found that a fitting parameterization with the combination of two
279 sigmodal fitting curves was needed for SPAR fitting at SSs higher than 0.4% (Tao et al., 2020).
280 However, in this study, we investigate SA formation on accumulation mode particles and particle CCN
281 activity at SSs below 0.1%, under which condition non-hygroscopic particles smaller than 400 nm are
282 typically CCN-inactive. The MAF fitted in the particle size range below 400 nm was used to indicate
283 the variations of SPAR that was of the main focus here in this work. In addition, due to the very low
284 N_{CCN} in particle size ranges larger than 400 nm, the deviations of N_{CCN} due to the limited range of
285 measured particle size are also very small.

286

287 3. Results

288 3.1. Overview of the measurements

289 The timeseries of meteorological parameters, SPAR, N_{CCN} at SS of 0.05% and mass
290 concentration of Non-refractory particulate matter of $PM_{2.5}$ (NR- $PM_{2.5}$), $PM_{2.5}$ SA (inorganic
291 compounds and OOA) and $PM_{2.5}$ PA (primary aerosol, defined as the sum of POA) are shown in Fig.
292 1. The mass concentration of OOA and four POA were quantified by the ACSM PMF analysis (Zhang
293 et al. 2011). During the campaign, $PM_{2.5}$ PA were generally lower than $100 \mu\text{g m}^{-3}$ under both high
294 and low RH periods. Meanwhile, $PM_{2.5}$ SA can approach about $400 \mu\text{g m}^{-3}$, especially during the
295 strong SA formation events under high RH conditions, but can be lower than $100 \mu\text{g m}^{-3}$ under low
296 RH conditions. Strong diurnal variations were found in SPAR with varying meteorological parameters.
297 During the whole period, the wind speed was generally lower than 4 m s^{-1} , which is in favor of aerosol
298 particle accumulation and SA formation on existing particles. However, RH, $N_{CCN}(0.05\%)$, $PM_{2.5}$ SA
299 and NR- $PM_{2.5}$ mass concentrations revealed very distinct levels before and after 4th Dec, and thus the
300 whole campaign was divided into two stages with different RH and SA pollution conditions: higher
301 RH and stronger SA pollution before 4th Dec, and lower RH and lighter SA pollution after 4th Dec. In
302 the following discussions, the high RH stage corresponds to days before 4th Dec with daily maximum
303 and minimum RH higher than 75% and 50%, respectively. Two events that occurred during 25th Nov
304 to 27th Nov (Event 1) and 30th Nov to 2nd Dec (Event 2), respectively, displayed especially high RH
305 conditions with successive nighttime fogs (blue shaded areas). The low RH stage corresponds to the
306 period after 4th Dec with daily maximum and minimum RH below 70% and 30%, which was
307 represented by two events that occurred during 9th Dec to 11th Dec (Event 3) and 13th Dec to 15th Dec
308 (Event 4), respectively. These events were selected based on the similarity of $PM_{2.5}$ concentration and
309 evolution, while the time window was fixed to two days for the convenience of intercomparing. In
310 addition, during these events, the wind speed was generally low, the RH followed a general diurnal
311 variations and SA mass grew steadily and continuously. Thus the interference of the variations of air
312 mass and short-term local emissions can be eliminated and the influence of SA formation can be
313 highlighted. It should be noted that variations of N_{CCN} at 0.07% were similar to those at 0.05%, which
314 followed the variations of SA mass concentration. While at higher SSs, the variations of N_{CCN} differed
315 from those of SA mass concentration, especially under high RH conditions, suggesting different
316 responses of CCN activity towards distinct SA formation processes. As reported in Kuang et al.
317 (2020c), during the high RH stage aqueous phase SA formation was promoted, leading to persistent
318 increases in $N_{CCN}(0.05\%$ and $0.07\%)$, mass concentration of NR- $PM_{2.5}$ and especially mass
319 concentration of $PM_{2.5}$ SA during Event 1 and 2. During the low RH stage, the SA formation

320 dominantly occurred in the gas-phase, that generated much less SA than aqueous-phase formation
321 (Kuang et al., 2020c). Thus, the persistent increases of $N_{CCN}(0.05\%)$ and $PM_{2.5}$ during
322 Event 3 and 4 was much weaker than those in Events 1 and 2. Due to the different SA mass fractions,
323 SPAR during the high RH stage was generally higher than that during the low RH stage. However, the
324 ratios between $N_{CCN}(0.05\%)$ and mass concentration of $PM_{2.5}$ SA or NR- $PM_{2.5}$, were lower during the
325 high RH period and demonstrated strong decreases, especially in Event 1 and 2. The response of CCN
326 activity and $N_{CCN}(0.05\%)$ to the different SA formation mechanisms will be discussed
327 comprehensively in the following parts.

328 **3.2. The influence of different secondary aerosol formation on the diurnal variation of CCN** 329 **activity**

330 The diurnal averages of PNSD, SPAR at SS of 0.05%, GF-PDF for 200 nm particle and mass
331 fraction of particle chemical compositions during high RH periods before 4th Dec, low RH periods
332 after 4th Dec and the four events are shown in Fig. 2, respectively. To be noted, the “high (or low) RH
333 events” is used to refer to the SA formation events under high (or low) RH conditions for convenience,
334 and it doesn't mean that RH caused variations of CCN behavior. As can be seen in Figs. 2 (1b) and
335 (2b), different variations of SPAR due to SA formations can be found during the periods with different
336 RH conditions. The average diurnal variations of these parameters for the entire high RH stage and
337 low RH stage as shown in Figs. 2 (1a-1d) and (2a-2d) revealed similar but more smoothed variations
338 as in the four selected events. The four events are discussed and intercompared in the following to
339 magnify the differences under distinct RH conditions. For accumulation mode particles, particle
340 number concentrations were higher during daytime in high RH events, while stronger diurnal
341 variations occurred in low RH events. Simultaneous daytime increases in particle SPAR in size range
342 from 200 nm to 400 nm, GF-PDF in GF range from 1.2 to 1.8 and SA mass fraction were found in all
343 four events, suggesting that SA formation led to increasing hygroscopic particles number
344 concentration, which in turn enhanced particle CCN activity. This effect was more pronounced in
345 Events 1 and 2 than in Events 3 and 4. In Events 1 and 2, SPAR values were generally higher than 0.4
346 at 200 nm and reached the maximum of 1 during noontime at 300 nm. A hygroscopic mode with
347 $GF > 1.4$ was found throughout the day, which dominated aerosol hygroscopicity during daytime. Mass
348 fraction of SA were generally higher than 70% and reach a maximum of 80% at noon. While in Events
349 3 and 4, SPAR at 200 nm was lower than 0.4 at night and the maximum SPAR at 300 nm was lower
350 than 0.9. A particle mode with $GF < 1.1$ dominates particle hygroscopicity, and the mass fraction of SA
351 was lower than 60% and 30% at noon and at night, respectively. However, stronger daytime increase

352 of SA mass fraction and accordingly larger variation in SPAR was observed in Events 3 and 4 than in
353 Events 1 and 2.

354 Besides SS of 0.05%, variations of SPAR at SSs of 0.07% and 0.2% are also shown in Figs.
355 S1 and S2 in the supplement. And as shown in Figs. S1 and S2, the variations of SPAR and N_{CCN}/PM
356 at SS of 0.07% are similar but lighter, compared with those at SS of 0.05%. While for SS of 0.2%, the
357 difference of SPAR between different periods or events are smaller (Fig. S1), and so did the diurnal
358 variations of SPAR and GF-PDF at particle size of 100 nm (Fig. S2). Because CCN activity at SS of
359 0.2% was strong enough (indicated by SPAR value close to 1) in particle size range where the SA
360 formation dominates, and thus the different SA formations under high or low RH conditions cannot
361 lead to significant variations of CCN activity at SS of 0.2%. In summary, based on CCN measurements
362 in this study, the RH-dependent influence of SA formation on CCN activity can be found obviously at
363 SSs of 0.05% and 0.07%. As the variations of SPAR at SS of 0.07% were quite similar to those at SS
364 of 0.05%, further analysis was only based on CCN activity at SS of 0.05%.

365 In Fig. 3a, detailed comparison of particle CCN activity during SA formation events of N_{CCN}
366 enhancements at SS of 0.05% under different RH conditions are shown as the variations of SPAR
367 curves. Particle CCN activity in Events 1 and 2 were combined due to their similar diurnal variations
368 (as shown in Fig. 2). Besides SPAR curves (Fig. 3a), corresponding fitting parameters of the SPAR
369 curve including D_a and MAF were also shown in Figs. 3b and c, respectively, as enhanced SPAR for
370 particle population can be attributed to hygroscopic particle number fraction increase (MAF increase)
371 or enhancement of hygroscopic particle hygroscopicity (D_a decrease). Same as demonstrated in Fig. 2,
372 SPAR was generally higher and thus particle CCN activity(0.05%) were generally stronger in high RH
373 events than those in low RH events. However, as shown in Fig. 3a, the difference between SPAR in
374 high and low RH events at 300 nm decreased from 0.2 to 0.1 during the SA formations, indicating for
375 a stronger enhancement in low RH events, probably due to both the stronger increase of SA mass
376 fraction and the higher nighttime PA mass fraction (Fig. 2(e)). Furthermore, in high RH events, there
377 were daytime enhancements of SPAR within the 150 to 300 nm size range, as was indicated by the
378 daytime increase of MAF and decrease of D_a , which mainly resulted from number fraction and
379 hygroscopicity increases of CCN-active particles. While in low RH events, the daytime enhancement
380 of SPAR was only observed for particles larger than 200 nm. This can be attributed to the strong
381 increase of MAF and the slight decrease of D_a , which indicates significant increasing number fraction
382 yet slightly enhanced hygroscopicity of hygroscopic particles, respectively. Overall, the enhancement
383 of SPAR was weaker but occurred at a broader particle size range in high RH events than in low RH
384 events, as shown in Fig. 3a. This is in accordance with previous the results from Kuang et al. (2020c),

385 suggesting that SA formation occurred mainly in aqueous phase within a broad particle size range (up
386 to 1 μm) in high RH events, while SA formation dominantly proceeded via gas phase reactions and
387 contributed to aerosol sizes smaller than 300 nm in low RH events. At SS of 0.05% (Fig. 3(a)), the
388 variation of SPAR from 8:00-12:00 to 12:00-16:00 in particle size smaller than 200 nm was very small
389 during low RH events, suggesting a smaller CCN activity enhancement due to SA formation compared
390 with those at high RH events. In detail, the different variations of SPAR in high and low RH events
391 indicated by MAF and D_a shown in Figs. 3(b & c) suggested different variations of hygroscopicity,
392 number fraction and size of SA particles. Before SA formation, there was a significant difference
393 between the MAF in high and low RH events, which disappeared after the SA formation. The stronger
394 variations in MAF in low RH events suggested stronger enhancement of number concentration of
395 formed SA particles. As for D_a during SA formation, there were similar, little decrease in both high
396 and low RH events, suggesting similar hygroscopicity of the SA formed under low and high RH
397 conditions. Thus differences of SPAR and the resultant N_{CCN} during low and high RH events were
398 mainly due to the different variations of number fraction of formed SA particles.

399 As there were different influences of SA formation on both CCN activity at SS of 0.05% and
400 PNSD under different RH conditions, different variation of $N_{\text{CCN}}(0.05\%)$ due to SA formation can also
401 be expected. Fig. 4 displays the diurnal variation of $\text{PM}_{2.5}$ mass concentration, volume concentration
402 (V_{conc}), number concentration (N_{conc}) and $N_{\text{CCN}}(0.05\%)$ (all divided by CO to partially compensate
403 for changes in planetary boundary layer height), as well as the $N_{\text{CCN}}/\text{PM}_{2.5}$ mass concentration ratio
404 and SPAR during high and low RH events, respectively. Variables in Fig. 4 were also presented in Fig.
405 S3 averaged for the entire high RH and low RH stages, respectively. Compared with the selected case
406 events featuring significant N_{CCN} enhancement (Fig. 4(1c-2c)), the diurnal variations averaged for the
407 entire high and low RH stages were similar, with higher levels of particle mass concentration but
408 weaker enhancement of SA and N_{CCN} , indicating similar but weakened impact of SA formation on
409 CCN activity due to the interference of other aerosol processes. Hereinafter, we discuss the variations
410 in the four events to magnify the discrepancies of SA formation under high RH and low RH conditions
411 and its distinct impact on N_{CCN} . The V_{conc} size distribution variations can be used as a proxy for the
412 evolution of NR- $\text{PM}_{2.5}$ size distributions, considering the relatively small variations in particle density
413 (ranging from 1.2 to 1.8 and with relative variations within 20% (Hu et al., 2012; Zhao et al., 2019)).
414 The variations of the ratio between N_{CCN} (in different particle size range) and the mass concentration
415 of $\text{PM}_{2.5}$ SA (referred as to N_{CCN}/SA) or NR- $\text{PM}_{2.5}$ (referred as to N_{CCN}/NR) can be used to evaluate
416 the response of N_{CCN} to SA formation.

417 During high RH events, normalized $N_{CCN}(0.05\%)$ increased by $\sim 50\%$ from 8:00 to 14:00, with a
418 similar increase in normalized $PM_{2.5}$ SA mass concentration (Fig. 4(1a)). As the $PM_{2.5}$ PA mass
419 concentration decrease was much smaller than the SA increase, the NR- $PM_{2.5}$ mass concentration
420 increase can be expected to be similar to the SA increase. As reported by Kuang et al. (2020c), SA
421 during daytime were mainly formed at larger particle sizes, featuring Vconc increase in the particle
422 size range of 400 to 1000 nm. In Fig. 4(1d), significant increases of particle number concentration
423 (Nconc) in particle size range of 150 nm to 1000 nm can be observed. At larger particle size the
424 increase of Nconc led to stronger increase of Vconc, which is why there was simultaneous but much
425 weaker increases of Vconc in particle size range of 150 to 300 nm compared with increases of those
426 in particle size of larger than 300 nm (Fig. 4(1b)). This suggests that $PM_{2.5}$ SA mainly contributed to
427 particle sizes of larger than 300 nm. In addition, because the SA formation enhanced hygroscopicity
428 and number fraction of CCN-active particles in particle size range of 150 to 300 nm, simultaneous
429 enhancements of SPAR can be found throughout the measured particle size range of 180 to 300 nm
430 (Fig. 4(1e)). By combining the enhancements of Nconc and SPAR in measured particle size ranges,
431 there were increases of N_{CCN} from 200 to 500 nm (Fig. 4(1c)). Thus while SA formation processes
432 contributed to their volume (mass) and hygroscopicity increase, it had no further impact on N_{CCN} . As
433 a result, $N_{CCN} (>300 \text{ nm})/SA$, $N_{CCN} (<300 \text{ nm})/SA$, $N_{CCN} (>300 \text{ nm})/NR$ and $N_{CCN} (<300 \text{ nm})/NR$ all
434 decreased during the SA formation (Fig. 4(1f)), suggesting that weakening enhancement of
435 $N_{CCN}(0.05\%)$ in SA formation under high RH condition as SA formation mainly added mass to already
436 CCN-active particles .

437 During low RH events, weaker increases of both $N_{CCN}(0.05\%)$ and $PM_{2.5}$ SA mass
438 concentration from 8:00 to 14:00 was found (Fig. 4(2a)). At the same time, PA mass decreased by 50%
439 and the variation of total NR mass was small. Under low RH conditions, SA formation mainly
440 contributed to mass enhancements of smaller particle sizes (Kuang et al., 2020c). Vconc increased
441 mostly in the range of 150 to 300 nm (Fig. 4(2b)), while Nconc only increased within 300 nm (Fig.
442 4(2d)), suggesting that $PM_{2.5}$ SA mainly formed in particle size range below 300 nm. SA formation
443 mainly enhanced number fraction of CCN-active particles in particle size of 200 to 300 nm, as SPAR
444 only revealed evident enhancement (Fig. 4(2e)) and N_{CCN} only significantly increased (Fig. 4(2c)) in
445 that size range. As a result, although $N_{CCN} (>300 \text{ nm})/SA$ decreased similar as that under high RH
446 conditions, $N_{CCN} (<300 \text{ nm})/SA$ and $N_{CCN} (>300 \text{ nm})/NR$ generally stayed constant and N_{CCN}
447 ($<300 \text{ nm})/NR$ even increased during SA formation in daytime (Fig. 4(2f)). The ratio between bulk
448 N_{CCN} and mass concentration of NR- $PM_{2.5}$ became larger due to the SA formation, suggesting that

449 stronger enhancement of $N_{CCN}(0.05\%)$ in SA formation under low RH condition, because SA
450 formation mainly added mass to CCN-inactive particles and turned them into CCN-active particles.

451 In summary, during the campaign in this study, two kinds of SA formation events were
452 observed under different RH conditions with different variations of PM and N_{CCN} at SSs lower than
453 0.07%. Under high RH conditions, there were strong SIA dominated SA formation leading to stronger
454 enhancements of CCN-active particle number fraction and N_{CCN} . Meanwhile, under low RH conditions,
455 there were moderate SOA dominated SA formation with moderate enhancements of CCN-active
456 particle number fraction and N_{CCN} . However, for a unit amount of SA formation, the increase of N_{CCN}
457 was stronger under low RH conditions and weaker under high RH conditions. This was because SA
458 formation under low RH conditions was more concentrated on particle sizes smaller than 300 nm and
459 added more mass to CCN-inactive particles, turning them into CCN-active particles. In addition, strong
460 and distinct diurnal variations of CCN activity of particles were observed during different SA
461 formation processes, whose effects on N_{CCN} calculation need to be further evaluated.

462

463 **3.3. The influence of diurnal variation of CCN activity on N_{CCN} prediction**

464 Since PNSD measurements are generally simpler and more common than N_{CCN} measurements,
465 N_{CCN} is usually estimated from real-time PNSD combined with parameterized CCN activity. In former
466 sections, it was already manifested that SA formations under different RH conditions led to distinct
467 variations in PNSD and SPAR at SS of 0.05%, hence different variations in N_{CCN} . Thus, it is important
468 for the prediction of N_{CCN} to quantify its sensitivity towards changes in PNSD and SPAR during SA
469 formation processes under different RH conditions.

470 In this study, N_{CCN} was mostly determined by PNSD, as was generally the case in former
471 studies (Dusek et al., 2006). During SA formation events, however, the variation of CCN activity also
472 contributed significantly to the deviation of N_{CCN} calculation. In former discussions, CCN activity
473 (indicated by SPAR) at 0.05% SS revealed significant diurnal variations during this campaign, which
474 were different during SA formations under distinct RH conditions. The ratio of N_{CCN} calculated based
475 on campaign averaged SPAR (N_{CCN_cal}) to those measured at 0.05% SS (N_{CCN_meas}) before and after
476 4th Dec are shown in Fig. 5. SPAR is determined by the variation of D_a and MAF, which reflect changes
477 in hygroscopicity and number fraction of hygroscopic particles. Thus, to investigate the respective
478 influences of MAF and D_a variations on N_{CCN} predictions, N_{CCN_AvgMAF} (or N_{CCN_avgDa}) was calculated
479 based on the real-time PNSD and SPAR estimated by replacing MAF (or D_a) in Eq. 7 with the
480 campaign averaged value. During the high RH stage, underestimation of daytime N_{CCN_cal} can reach

481 up to 20%, since SPAR variations due to CCN activity enhancement were not considered. Similar
482 deviations of both N_{CCN_AvgMAF} and N_{CCN_avgDa} from N_{CCN_meas} were detected, suggesting that both
483 MAF and D_a variations contributed to N_{CCN_cal} underestimation under high RH conditions. During the
484 low RH stage, up to 50% overestimation existed in $N_{CCN_AvgSPAR}$ outside SA formation time periods.
485 Only N_{CCN_AvgMAF} displayed similar deviations from N_{CCN_meas} as $N_{CCN_AvgSPAR}$, indicating that
486 differences between N_{CCN_cal} and N_{CCN_meas} were mainly contributed by variations in MAF brought on
487 by significant CCN-active particles number fraction growth due to SA formations. To be noted,
488 $N_{CCN_AvgSPAR}$ before and after 4th Dec were both calculated based on the SPAR averaged over the entire
489 campaign (green dots in Fig. 5a), since the applicability of campaign averaged SPAR in N_{CCN}
490 calculations was confirmed by many former studies in the NCP (Deng et al., 2012; Wang et al., 2013;
491 Ma et al., 2016). During low RH periods, SPAR was generally lower than the campaign averaged
492 SPAR and the ratio between the calculated and measured N_{CCN} were systematically higher (lasting for
493 the whole night). In summary, SA formation processes can induce significant deviation to N_{CCN}
494 prediction that varied with RH conditions and mainly resulted from the variation in MAF. Thus, for
495 accurate N_{CCN} estimations, considering the variation of MAF (changes in the fraction of the
496 hygroscopic particles) is highly essential.

497 As SOA is generally considered to be more hygroscopic than POA (Frosch et al., 2011; Lambe
498 et al., 2011; Kuang et al., 2020a), the increase of hygroscopic particles or SA particles (both SIA and
499 SOA) were considered to be the cause for the increase of SPAR within 200 to 300 nm size range (Fig.
500 2). In order to account for the variations of hygroscopic particles or SA particles in N_{CCN} calculation,
501 in the following part, Number Fraction of hygroscopic particles ($GF(90\%, 200\text{ nm}) > 1.22$, $N_{F_{hygro}}$)
502 measured by HTDMA and Mass Fraction of SA particles (MF_{SA}) measured by ACSM in this campaign
503 were used to represent MAF variations and to provide calculation of N_{CCN} at SS of 0.05% with smaller
504 deviations combined with PNSD measurement. To be noted, in order to highlight the application of
505 using MF_{SA} as estimation of MAF variations on N_{CCN} calculation, the campaign averaged D_a from
506 SPAR curves was used.

507 Based on the bulk hygroscopicity derived from particle chemical compositions measurements
508 (κ_{chem}), a critical diameter for CCN activation can be calculated based on κ -Köhler theory. With this
509 critical diameter, $N_{CCN}(0.05\%)$ can be predicted incorporating measured PNSD (N_{CCN_Chem}). κ of
510 accumulation mode particles derived from chemical composition of the bulk aerosol might bear
511 significant uncertainties, which leads to significant deviations of N_{CCN} prediction. However, in practice,
512 chemical compositions measurements specifically for accumulation mode particles are not common,
513 thus bulk aerosol chemical compositions are commonly applied in CCN studies as substitute (Zhang

514 et al., 2014; Zhang et al., 2016; Che et al., 2017; Cai et al., 2018), especially when particle
515 hygroscopicity measurements were in lack. As can be seen in Fig. 6(a), N_{CCN_meas} at 0.05% SS was
516 strongly underestimated by N_{CCN_Chem} , especially at lower N_{CCN_meas} ($\sim 10^2 \# \text{ cm}^{-3}$), which is similar to
517 the results of studies that encountered high fractions of organics (Chang et al., 2010; Kawana et al.,
518 2015). This deviation between N_{CCN_meas} and N_{CCN_Chem} may have resulted from the hypothesis of
519 internal mixing state and the difference of particle hygroscopicity derived by particle chemical
520 composition measurements and CCN activity. Fig. 6(b) depicts the correlation between mass fraction
521 of SA (MF_{SA}) and MAF at 0.05% SS. MF_{SA} was generally positively correlated to MAF ($r=0.8$) with
522 slight underestimations, suggesting that externally mixed SA dominated CCN-active particles. Thus,
523 in the prediction of N_{CCN} , real-time SPAR can be calculated from campaign average D_a and MAF
524 assumed to be equal to real-time MF_{SA} (N_{CCN_MF}). As displayed in Fig. 6(c), the underestimation and
525 correlation between N_{CCN_cal} and N_{CCN_meas} was improved after introducing MF_{SA} into N_{CCN} calculation.
526 Additionally, the diurnal variations of N_{CCN_cal}/N_{CCN_meas} ratio based on different methods of N_{CCN}
527 calculation during the whole campaign were shown in Fig. 6(d). By considering real-time MF_{SA}
528 variations, the deviation of calculated N_{CCN} (Real-time MF) can be reduced throughout the day,
529 compared to N_{CCN_Chem} (Real-time Chem). Meanwhile, using an averaged MF_{SA} to estimate SPAR and
530 N_{CCN} could also reduce deviations of calculated N_{CCN} (Averaged MF), however, demonstrated a much
531 stronger diurnal variation than the deviation of N_{CCN_MF} .

532 Based on the bulk hygroscopicity derived from GF measurements (κ_{GF}) at 200 nm, D_a can be
533 calculated based on the κ -Köhler theory, which can be applied to predict N_{CCN} at 0.05% SS (N_{CCN_GF}) in
534 combination with measured PNSD. Fig. 7(a) reveals that N_{CCN_meas} were strongly underestimated by
535 N_{CCN_GF} (by more than 30%), which might have resulted from the hypothesis of internal mixing state
536 and the difference of particle hygroscopicity derived by GF and particle CCN activity measured under
537 different water vapor saturated conditions. Fig. 7(b) depicts the positive correlation between NF_{hygro}
538 and MAF at 0.05% SS, which was weaker than that between MF_{SA} and MAF. Similar as before, NF_{hygro}
539 was applied as a proxy for MAF in the N_{CCN} calculation, which also improved the underestimation and
540 correlation between N_{CCN_cal} and N_{CCN_meas} (Fig. 7(c)). Also, the campaign averaged D_a in Fig. 5a. was
541 used to calculate SPAR curves and N_{CCN} . The diurnal variations of the N_{CCN_cal}/N_{CCN_meas} ratio based
542 on different methods of N_{CCN} calculation during the whole campaign are shown in Fig. 7(d). By
543 considering the real-time variation of NF_{hygro} , the deviation of N_{CCN_NF} (Real-time NF) was mainly
544 reduced during nighttime compared to N_{CCN_GF} (Real-time GF). Meanwhile, applying an averaged
545 NF_{hygro} to estimate SPAR and N_{CCN} , reduced the deviations of calculated N_{CCN} (Averaged NF) during
546 nighttime as well, but its deviations demonstrated stronger diurnal variations than those of N_{CCN_NF} . If

547 GF-PDF were directly used to calculate N_{CCN} , N_{CCN_cal} would agree well with measured N_{CCN} (Fig.
548 S4), because in this way the mixing state of aerosol would have been accounted for. However,
549 compared to the approach using GF-PDF, $N_{F_{hygro}}$ is easier to apply in N_{CCN} calculation and can yield
550 similar accuracies.

551 In summary, MAF exhibited strong diurnal variation that varied under different RH conditions
552 due to different SA formation mechanisms, which contributed most to N_{CCN} estimation deviations if
553 unaccounted for. The diurnal variations of MAF at the five measured SSs (Fig. S5) revealed significant
554 diurnal variations at low SSs (0.05% and 0.07%) that were dependent on RH conditions, while only
555 small diurnal variations that were insensitive to the RH conditions were detected at SSs above 0.2%.
556 In general, MAF became lower at lower SSs, especially during nighttime. As the fraction of CCN-
557 active particles were generally hygroscopic and composed of secondary compounds, positive
558 correlation was found between MAF, MF_{SA} and $N_{F_{hygro}}$. Although a good prediction of $N_{CCN}(0.05\%)$
559 was achieved by applying an averaged MAF (Figs. 5, 6d and 7d), in practice, this would still require
560 CCN measurements or HTDMA/chemical composition measurements as proxies. Additionally,
561 deviations of N_{CCN_cal} based on the averaged MAF can be large under low RH conditions (Fig. 5c),
562 while time-dependent MAF can eliminate a great part of these deviations. Thus, by replacing MAF
563 with real-time MF_{SA} or $N_{F_{hygro}}$ when deriving SPAR curves, the relative deviation of $N_{CCN}(0.05\%)$
564 calculation can be reduced. The proposed N_{CCN} parameterization using MF_{SA} can also be easily
565 adopted by chemical-transport and climate models, improving their representation of N_{CCN} changes
566 due to distinct SA formation processes.

567

568 4. Conclusions

569 SA formation drives the development of haze pollution in the NCP and can result in significant
570 variations of PNSD and aerosol hygroscopicity. Studies in the NCP have shown that the mechanism
571 of SA formation can be affected by relative humidity (RH), and thus has different influences on the
572 aerosol hygroscopicity and PNSD under distinct RH conditions. The difference in particle size where
573 SA formation is taking place and the different chemical compositions of formed SA can result in
574 different variations of CCN activity. Thus, it is essential to study the influence of SA formation on
575 CCN activity of existing accumulation mode particles under different RH conditions in the NCP. As
576 N_{CCN} is often predicted based on real-time PNSD and parameterized SPAR, the influence of varying
577 SPAR in distinct SA formation processes on N_{CCN} calculation needs to be evaluated in detail.

578 Based on the measurements of CCN-activity, particle hygroscopicity, particle chemical
579 composition, PNSD during the McFAN campaign in Gucheng winter 2018, the influences of SA
580 formation on CCN activity and N_{CCN} calculation under different RH conditions were investigated
581 especially at SSs lower than 0.07%. Two kinds of SA formation events were identified under different
582 RH conditions with distinct variations in PM and N_{CCN} at 0.05% SS. Under high RH conditions, which
583 corresponds to the periods with minimum RH higher than 50% in daytime, strong SA formation and
584 $N_{CCN}(0.05\%)$ enhancements with strong hygroscopic particles and SIA dominated contribution to SA
585 (>70%) was found. While under low RH conditions, which corresponds to the periods with daytime
586 minimum RH below 30%, moderate SA formation and $N_{CCN}(0.05\%)$ enhancements with moderately
587 hygroscopic particles and SOA dominated contribution to SA was found. However, the increase of
588 N_{CCN} under the a same amount of SA formation was stronger under low RH conditions and weaker
589 under high RH conditions. This was because the formation of SA under low RH conditions was more
590 concentrated in particle size range smaller than 300 nm and added more mass to CCN-inactive particles
591 turning them into CCN-active ones after SA formation.

592 In addition, strong diurnal variations of CCN activity of particles at 0.05% SS due to the strong
593 SA formations were also observed, both varying with RH conditions. $N_{CCN}(0.05\%)$ was significantly
594 underestimated when MAF (SPAR parameter) variations were not considered. As the fraction of CCN-
595 active particles were generally hygroscopic and composed of secondary compounds, there were good
596 correlation among MAF inferred from measurements of CCN activity, particle hygroscopicity and
597 particle chemical compositions. Thus, the relative deviation of $N_{CCN}(0.05\%)$ estimation can be
598 reduced by applying measurements of particle hygroscopicity or particle chemical compositions as a
599 proxy for aerosol mixing state.

600 This study can further the understanding of the impact of SA formation on CCN activity and
601 N_{CCN} calculation, specifically for SA formations on existing particles, which can strongly affect cloud
602 microphysics properties in stratus clouds and fogs. The investigation of the influence of SA formation
603 on CCN activity of existing particles in this study is important for improving N_{CCN} parameterizations
604 in chemical-transport and climate models, so that they can account for the large variations induced by
605 SA formation processes.

606

607 **Supporting Information**

608 The supporting information is available in a separate file.

609 **Data availability.**

610 The data used in this study are available from the corresponding author upon request
611 (taojch@jnu.edu.cn and nan.ma@jnu.edu.cn)

612 **Author contributions.**

613 JT, YK and NM designed this research. JT performed the data analysis and wrote the manuscript. YC,
614 HS, NM, YK, JT, and JH planned this campaign. JT and YZ conducted the CCN measurements. YS
615 and YH conducted the ACSM measurements and the ACSM PMF analysis. JH and QL conducted the
616 HTDMA measurements. LX and YZ conducted the particle number size distribution measurements.
617 WX conducted the measurements of CO and meteorological parameters. YC, HS, YS, YK and NM
618 contributed to the revisions of this manuscript and all other coauthors have contributed to this paper in
619 different ways.

620 **Acknowledgement**

621 We acknowledge the National Key Research and Development Program of China (grant no.
622 2017YFC0210104), the National Natural Science Foundation of China (grant no. 91644218 and
623 41805110), the Guangdong Innovative and Entrepreneurial Research Team Program (Research team
624 on atmospheric environmental roles and effects of carbonaceous species: 2016ZT06N263), Special
625 Fund Project for Science and Technology Innovation Strategy of Guangdong Province
626 (2019B121205004) and the Basic Research Fund of CAMS (2020Z002)..

627 **Conflicts of interest**

628 There are no conflicts to declare.

629

630

631 Reference:

632 Cai, M., Tan, H., Chan, C. K., Qin, Y., Xu, H., Li, F., Schurman, M. I., Liu, L., and Zhao, J.: The size-
633 resolved cloud condensation nuclei (CCN) activity and its prediction based on aerosol hygroscopicity
634 and composition in the Pearl Delta River (PRD) region during wintertime 2014, *Atmos. Chem. Phys.*,
635 18, 16419–16437, <https://doi.org/10.5194/acp-18-16419-2018>, 2018.

636 Chang, R. Y.-W., Slowik, J. G., Shantz, N. C., Vlasenko, A., Liggio, J., Sjostedt, S. J., Leaitch, W. R.,
637 and Abbatt, J. P. D.: The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject
638 to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation, *Atmos. Chem.*
639 *Phys.*, 10, 5047–5064, <https://doi.org/10.5194/acp-10-5047-2010>, 2010.

640 Che, H., Zhang, X., Zhang, L., Wang, Y., Zhang, Y., Shen, X., Ma, Q., Sun, J., and Zhong, J.:
641 Prediction of size-resolved number concentration of cloud condensation nuclei and long-term
642 measurements of their activation characteristics, *Scientific reports*, 7, 1–12, 2017.

643 Cheng, Y. F., Su, H., Rose, D., Gunthe, S. S., Berghof, M., Wehner, B., Achtert, P., Nowak, A.,
644 Takegawa, N., Kondo, Y., Shiraiwa, M., Gong, Y. G., Shao, M., Hu, M., Zhu, T., Zhang, Y. H.,
645 Carmichael, G. R., Wiedensohler, A., Andreae, M. O., and Pöschl, U.: Size-resolved measurement of
646 the mixing state of soot in the megacity Beijing, China: diurnal cycle, aging and parameterization,
647 *Atmos. Chem. Phys.*, 12, 4477–4491, <https://doi.org/10.5194/acp-12-4477-2012>, 2012.

648 Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P. P., and Lehtinen, K. E. J.:
649 Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from
650 SMEAR II, Hyytiälä, Finland, 10, 323–336, 2005.

651 Deng, Z. Z., Zhao, C. S., Ma, N., Liu, P. F., Ran, L., Xu, W. Y., Chen, J., Liang, Z., Liang, S., Huang,
652 M. Y., Ma, X. C., Zhang, Q., Quan, J. N., Yan, P., Henning, S., Mildenerger, K., Sommerhage, E.,
653 Schäfer, M., Stratmann, F., and Wiedensohler, A.: Size-resolved and bulk activation properties of
654 aerosols in the North China Plain, *Atmos. Chem. Phys.*, 11, 3835–3846, [https://doi.org/10.5194/acp-](https://doi.org/10.5194/acp-11-3835-2011)
655 [11-3835-2011](https://doi.org/10.5194/acp-11-3835-2011), 2011.

656 Deng, Z. Z., Zhao, C. S., Ma, N., Ran, L., Zhou, G. Q., Lu, D. R., and Zhou, X. J.: An examination of
657 parameterizations for the CCN number concentration based on in situ measurements of aerosol
658 activation properties in the North China Plain, *Atmos. Chem. Phys.*, 13, 6227–6237,
659 <https://doi.org/10.5194/acp-13-6227-2013>, 2013.

660 Ditas, F., Shaw, R. A., Siebert, H., Simmel, M., Wehner, B., and Wiedensohler, A.: Aerosols-cloud
661 microphysics-thermodynamics-turbulence: evaluating supersaturation in a marine stratocumulus cloud,
662 *Atmos. Chem. Phys.*, 12, 2459–2468, <https://doi.org/10.5194/acp-12-2459-2012>, 2012.

663 Duan, J., Wang, Y., Xie, X., Li, M., Tao, J., Wu, Y., Cheng, T., Zhang, R., Liu, Y., Li, X., He, Q.,
664 Gao, W., and Wang, J.: Influence of pollutants on activity of aerosol cloud condensation nuclei (CCN)
665 during pollution and post-rain periods in Guangzhou, southern China, 642, 1008–1019,
666 <https://doi.org/10.1016/j.scitotenv.2018.06.053>, 2018.

667 Dusek, U., Frank, G., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F.,
668 Hings, S., and Jung, D.: Size matters more than chemistry for cloud-nucleating ability of aerosol
669 particles, *Science*, 312, 1375–1378, 2006.

670 Fan, J., Wang, Y., Rosenfeld, D., and Liu, X.: Review of Aerosol–Cloud Interactions: Mechanisms,
671 Significance, and Challenges, *Journal of the Atmospheric Sciences*, 73, 4221–4252,
672 <https://doi.org/10.1175/JAS-D-16-0037.1>, 2016.

673 Farmer, D. K., Cappa, C. D., and Kreidenweis, S. M.: Atmospheric Processes and Their Controlling
674 Influence on Cloud Condensation Nuclei Activity, 115, 4199–4217,
675 <https://doi.org/10.1021/cr5006292>, 2015.

676 Frosch, M., Bilde, M., DeCarlo, P., Jurányi, Z., Tritscher, T., Dommen, J., Donahue, N., Gysel, M.,
677 Weingartner, E., and Baltensperger, U.: Relating cloud condensation nuclei activity and oxidation
678 level of α -pinene secondary organic aerosols, *Journal of Geophysical Research: Atmospheres*, 116,
679 2011.

680 Gordon, H., Sengupta, K., Rap, A., Duplissy, J., Frege, C., Williamson, C., Heinritzi, M., Simon, M.,
681 Yan, C., Almeida, J., Trostl, J., Nieminen, T., Ortega, I. K., Wagner, R., Dunne, E. M., Adamov, A.,
682 Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X., Craven, J. S.,
683 Dias, A., Ehrhart, S., Fischer, L., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle,
684 C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Kirkby, J., Krapf, M., Kuerten, A.,
685 Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Monks, S. A., Onnela, A.,
686 Perakyla, O., Piel, F., Petaja, T., Praplan, A. P., Pringle, K. J., Richards, N. A. D., Rissanen, M. P.,
687 Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeldo, J. H., Sharma, S., Sipila, M., Steiner,
688 G., Stozhkov, Y., Stratmann, F., Tome, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E.,
689 Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue,
690 N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Curtius, J., and Carslaw, K. S.: Reduced

691 anthropogenic aerosol radiative forcing caused by biogenic new particle formation, 113, 12053–12058,
692 <https://doi.org/10.1073/pnas.1602360113>, 2016.

693 Gryspeerdt, E. and Stier, P.: Regime-based analysis of aerosol-cloud interactions, *Geophysical*
694 *Research Letters*, 39, <https://doi.org/10.1029/2012GL053221>, 2012.

695 Gysel, M., Crosier, J., Topping, D. O., Whitehead, J. D., Bower, K. N., Cubison, M. J., Williams, P.
696 I., Flynn, M. J., McFiggans, G. B., and Coe, H.: Closure study between chemical composition and
697 hygroscopic growth of aerosol particles during TORCH2, *Atmos. Chem. Phys.*, 7, 6131–6144,
698 <https://doi.org/10.5194/acp-7-6131-2007>, 2007.

699 Gysel, M., McFiggans, G. B., and Coe, H.: Inversion of tandem differential mobility analyser (TDMA)
700 measurements, 40, 134–151, <https://doi.org/10.1016/j.jaerosci.2008.07.013>, 2009.

701 Hagen, D. E. and Alofs, D. J.: Linear Inversion Method to Obtain Aerosol Size Distributions from
702 Measurements with a Differential Mobility Analyzer, *Aerosol Science and Technology*, 2, 465–475,
703 <https://doi.org/10.1080/02786828308958650>, 1983.

704 Hammer, E., Bukowiecki, N., Gysel, M., Jurányi, Z., Hoyle, C. R., Vogt, R., Baltensperger, U., and
705 Weingartner, E.: Investigation of the effective peak supersaturation for liquid-phase clouds at the high-
706 alpine site Jungfraujoch, Switzerland (3580 m a.s.l.), *Atmos. Chem. Phys.*, 14, 1123–1139,
707 <https://doi.org/10.5194/acp-14-1123-2014>, 2014a.

708 Hammer, E., Gysel, M., Roberts, G. C., Elias, T., Hofer, J., Hoyle, C. R., Bukowiecki, N., Dupont, J.-
709 C., Burnet, F., Baltensperger, U., and Weingartner, E.: Size-dependent particle activation properties in
710 fog during the ParisFog 2012/13 field campaign, *Atmos. Chem. Phys.*, 14, 10517–10533,
711 <https://doi.org/10.5194/acp-14-10517-2014>, 2014b.

712 Hong, J., Xu, H., Tan, H., Yin, C., and Kerminen, V. M.: Mixing state and particle hygroscopicity of
713 organic-dominated aerosols over the Pearl River Delta region in China, *Atmos. Chem. Phys.*, 18,
714 14079–14094, 2018.

715 Hu, M., Peng, J., Sun, K., Yue, D., Guo, S., Wiedensohler, A., and Wu, Z.: Estimation of Size-
716 Resolved Ambient Particle Density Based on the Measurement of Aerosol Number, Mass, and
717 Chemical Size Distributions in the Winter in Beijing, *Environ. Sci. Technol.*, 46, 9941–9947,
718 <https://doi.org/10.1021/es204073t>, 2012.

719 Hu, W., Hu, M., Hu, W., Jimenez, J. L., Yuan, B., Chen, W., Wang, M., Wu, Y., Chen, C., Wang, Z.,
720 Peng, J., Zeng, L., and Shao, M.: Chemical composition, sources, and aging process of submicron

721 aerosols in Beijing: Contrast between summer and winter, *Journal of Geophysical Research:*
722 *Atmospheres*, 121, 1955–1977, <https://doi.org/10.1002/2015JD024020>, 2016.

723 Hu, W., Campuzano-Jost, P., Day, D. A., Croteau, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D.
724 R., and Jimenez, J. L.: Evaluation of the new capture vapourizer for aerosol mass spectrometers (AMS)
725 through laboratory studies of inorganic species, *Atmos. Meas. Tech.*, 10, 2897–2921,
726 <https://doi.org/10.5194/amt-10-2897-2017>, 2017a.

727 Hu, W., Hu, M., Hu, W.-W., Zheng, J., Chen, C., Wu, Y., and Guo, S.: Seasonal variations in high
728 time-resolved chemical compositions, sources, and evolution of atmospheric submicron aerosols in
729 the megacity Beijing, *Atmos. Chem. Phys.*, 17, 9979–10000, [https://doi.org/10.5194/acp-17-9979-](https://doi.org/10.5194/acp-17-9979-2017)
730 2017, 2017b.

731 Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G.,
732 Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G.,
733 Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat,
734 S., Baltensperger, U., Haddad, I. E., and Prévôt, A. S. H.: High secondary aerosol contribution to
735 particulate pollution during haze events in China, *Nature*, 514, 218–222,
736 <https://doi.org/10.1038/nature13774>, 2014.

737 Jia, H., Ma, X., Yu, F., Liu, Y., and Yin, Y.: Distinct Impacts of Increased Aerosols on Cloud Droplet
738 Number Concentration of Stratus/Stratocumulus and Cumulus, *Geophysical Research Letters*, n/a,
739 <https://doi.org/10.1029/2019GL085081>, 2019.

740 Jiang, X., Tao, J., Kuang, Y., Hong, J., and Ma, N.: Mathematical derivation and physical interpretation
741 of particle size-resolved activation ratio based on particle hygroscopicity distribution: Application on
742 global characterization of CCN activity, *Atmospheric Environment*, 246, 118137,
743 <https://doi.org/10.1016/j.atmosenv.2020.118137>, 2021.

744 Kawana, K., Nakayama, T., and Mochida, M.: Hygroscopicity and CCN activity of atmospheric
745 aerosol particles and their relation to organics: Characteristics of urban aerosols in Nagoya, Japan, 121,
746 4100–4121, <https://doi.org/10.1002/2015jd023213>, 2016.

747 Kerminen, V.-M., Paramonov, M., Anttila, T., Riipinen, I., Fountoukis, C., Korhonen, H., Asmi, E.,
748 Laakso, L., Lihavainen, H., Swietlicki, E., Svenningsson, B., Asmi, A., Pandis, S. N., Kulmala, M.,
749 and Petaja, T.: Cloud condensation nuclei production associated with atmospheric nucleation: a
750 synthesis based on existing literature and new results, 12, 12037–12059, [https://doi.org/10.5194/acp-](https://doi.org/10.5194/acp-12-12037-2012)
751 12-12037-2012, 2012.

752 Köhler, H.: The nucleus in and the growth of hygroscopic droplets, 32, 1152–1161, 1936.

753 Krüger, M. L., Mertes, S., Klimach, T., Cheng, Y. F., Su, H., Schneider, J., Andreae, M. O., Pöschl,
754 U., and Rose, D.: Assessment of cloud supersaturation by size-resolved aerosol particle and cloud
755 condensation nuclei (CCN) measurements, *Atmos. Meas. Tech.*, 7, 2615–2629,
756 <https://doi.org/10.5194/amt-7-2615-2014>, 2014.

757 Kuang, Y., Xu, W., Tao, J., Ma, N., Zhao, C., and Shao, M.: A Review on Laboratory Studies and
758 Field Measurements of Atmospheric Organic Aerosol Hygroscopicity and Its Parameterization Based
759 on Oxidation Levels, *Current Pollution Reports*, 1–15, 2020a.

760 Kuang, Y., He, Y., Xu, W., Zhao, P., Cheng, Y., Zhao, G., Tao, J., Ma, N., Su, H., Zhang, Y., Sun, J.,
761 Cheng, P., Yang, W., Zhang, S., Wu, C., Sun, Y., and Zhao, C.: Distinct diurnal variation in organic
762 aerosol hygroscopicity and its relationship with oxygenated organic aerosol, *Atmos. Chem. Phys.*, 20,
763 865–880, <https://doi.org/10.5194/acp-20-865-2020>, 2020b.

764 Kuang, Y., He, Y., Xu, W., Yuan, B., Zhang, G., Ma, Z., Wu, C., Wang, C., Wang, S., Zhang, S., Tao,
765 J., Ma, N., Su, H., Cheng, Y., Shao, M., and Sun, Y.: Photochemical Aqueous-Phase Reactions Induce
766 Rapid Daytime Formation of Oxygenated Organic Aerosol on the North China Plain, 54, 3849–3860,
767 <https://doi.org/10.1021/acs.est.9b06836>, 2020c.

768 Kulmala, M., Riipinen, I., Sipila, M., Manninen, H. E., Petaja, T., Junninen, H., Dal Maso, M., Mordas,
769 G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen,
770 K. E. J., and Kerminen, V.-M.: Toward direct measurement of atmospheric nucleation, 318, 89–92,
771 <https://doi.org/10.1126/science.1144124>, 2007.

772 Lambe, A. T., Onasch, T. B., Massoli, P., Croasdale, D. R., Wright, J. P., Ahern, A. T., Williams, L.
773 R., Worsnop, D. R., Brune, W. H., and Davidovits, P.: Laboratory studies of the chemical composition
774 and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized
775 primary organic aerosol (OPOA), 11, 8913–8928, <https://doi.org/10.5194/acp-11-8913-2011>, 2011.

776 Li, G., Su, H., Ma, N., Tao, J., Kuang, Y., Wang, Q., Hong, J., Zhang, Y., Kuhn, U., and Zhang, S.:
777 Multiphase chemistry experiment in Fogs and Aerosols in the North China Plain (McFAN): integrated
778 analysis and intensive winter campaign 2018, *Faraday Discussions*, 2021.

779 Liu, H. J., Zhao, C. S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Müller,
780 K., and Herrmann, H.: Aerosol hygroscopicity derived from size-segregated chemical composition and
781 its parameterization in the North China Plain, *Atmos. Chem. Phys.*, 14, 2525–2539,
782 <https://doi.org/10.5194/acp-14-2525-2014>, 2014.

783 Liu, P. F., Zhao, C. S., Göbel, T., Hallbauer, E., Nowak, A., Ran, L., Xu, W. Y., Deng, Z. Z., Ma, N.,
784 and Mildenberger, K.: Hygroscopic properties of aerosol particles at high relative humidity and their
785 diurnal variations in the North China Plain, *11*, 3479–3494, 2011.

786 Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L. G., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L.,
787 Liu, S.-C., Chang, C.-C., Amoroso, A., and Costabile, F.: Evidence of Reactive Aromatics As a Major
788 Source of Peroxy Acetyl Nitrate over China, *Environ. Sci. Technol.*, *44*, 7017–7022,
789 <https://doi.org/10.1021/es1007966>, 2010.

790 Ma, N., Zhao, C., Tao, J., Wu, Z., Kecorius, S., Wang, Z., Größ, J., Liu, H., Bian, Y., Kuang, Y., Teich,
791 M., Spindler, G., Müller, K., van Pinxteren, D., Herrmann, H., Hu, M., and Wiedensohler, A.:
792 Variation of CCN activity during new particle formation events in the North China Plain, *Atmos.*
793 *Chem. Phys.*, *16*, 8593–8607, <https://doi.org/10.5194/acp-16-8593-2016>, 2016.

794 Mei, F., Hayes, P. L., Ortega, A., Taylor, J. W., Allan, J. D., Gilman, J., Kuster, W., de Gouw, J.,
795 Jimenez, J. L., and Wang, J.: Droplet activation properties of organic aerosols observed at an urban
796 site during CalNex-LA, *118*, 2903–2917, <https://doi.org/10.1002/jgrd.50285>, 2013.

797 Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and
798 cloud condensation nucleus activity, *Atmos. Chem. Phys.*, *7*, 1961–1971, 2007.

799 Reutter, P., Su, H., Trentmann, J., Simmel, M., Rose, D., Gunthe, S. S., Wernli, H., Andreae, M. O.,
800 and Pöschl, U.: Aerosol- and updraft-limited regimes of cloud droplet formation: influence of particle
801 number, size and hygroscopicity on the activation of cloud condensation nuclei (CCN), *Atmos. Chem.*
802 *Phys.*, *9*, 7067–7080, <https://doi.org/10.5194/acp-9-7067-2009>, 2009.

803 Roberts, G. C. and Nenes, A.: A continuous-flow streamwise thermal-gradient CCN chamber for
804 atmospheric measurements, *39*, 206–221, 2005.

805 Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Pöschl, U.:
806 Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter
807 (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory
808 and experiment, *Atmos. Chem. Phys.*, *8*, 1153–1179, 2008.

809 Rose, D., Nowak, A., Achtert, P., Wiedensohler, A., Hu, M., Shao, M., Zhang, Y., Andreae, M. O.,
810 and Pöschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-
811 city Guangzhou, China - Part 1: Size-resolved measurements and implications for the modeling of
812 aerosol particle hygroscopicity and CCN activity, *Atmos. Chem. Phys.*, *10*, 3365–3383, 2010.

813 Rose, D., Gunthe, S. S., Su, H., Garland, R. M., Yang, H., Berghof, M., Cheng, Y. F., Wehner, B.,
814 Achtert, P., Nowak, A., Wiedensohler, A., Takegawa, N., Kondo, Y., Hu, M., Zhang, Y., Andreae, M.
815 O., and Poschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the
816 mega-city Guangzhou, China -Part 2: Size-resolved aerosol chemical composition, diurnal cycles, and
817 externally mixed weakly CCN-active soot particles, *Atmos. Chem. Phys.*, 11, 2817–2836,
818 <https://doi.org/10.5194/acp-11-2817-2011>, 2011.

819 Shen, C., Zhao, C., Ma, N., Tao, J., Zhao, G., Yu, Y., and Kuang, Y.: Method to Estimate Water Vapor
820 Supersaturation in the Ambient Activation Process Using Aerosol and Droplet Measurement Data,
821 *Journal of Geophysical Research: Atmospheres*, 123, 10,606-10,619,
822 <https://doi.org/10.1029/2018JD028315>, 2018.

823 Su, H., Rose, D., Cheng, Y. F., Gunthe, S. S., Massling, A., Stock, M., Wiedensohler, A., Andreae, M.
824 O., and Poschl, U.: Hygroscopicity distribution concept for measurement data analysis and modeling
825 of aerosol particle mixing state with regard to hygroscopic growth and CCN activation, *Atmos. Chem.*
826 *Phys.*, 10, 7489–7503, <https://doi.org/10.5194/acp-10-7489-2010>, 2010.

827 Sun, Y., He, Y., Kuang, Y., Xu, W., Song, S., Ma, N., Tao, J., Cheng, P., Wu, C., Su, H., Cheng, Y.,
828 Xie, C., Chen, C., Lei, L., Qiu, Y., Fu, P., Croteau, P., and Worsnop, D. R.: Chemical Differences
829 Between PM1 and PM2.5 in Highly Polluted Environment and Implications in Air Pollution Studies,
830 47, e2019GL086288, <https://doi.org/10.1029/2019GL086288>, 2020.

831 Tan, H., Xu, H., Wan, Q., Li, F., Deng, X., Chan, P. W., Xia, D., and Yin, Y.: Design and Application
832 of an Unattended Multifunctional H-TDMA System, 30, 1136–1148, [https://doi.org/10.1175/JTECH-](https://doi.org/10.1175/JTECH-D-12-00129.1)
833 [D-12-00129.1](https://doi.org/10.1175/JTECH-D-12-00129.1), 2013.

834 Tao, J., Kuang, Y., Ma, N., Zheng, Y., Wiedensohler, A., and Zhao, C.: An improved parameterization
835 scheme for size-resolved particle activation ratio and its application on comparison study of particle
836 hygroscopicity measurements between HTDMA and DMA-CCNC, 226, 117403,
837 <https://doi.org/10.1016/j.atmosenv.2020.117403>, 2020.

838 Thalman, R., de Sa, S. S., Palm, B. B., Barbosa, H. M. J., Poehlker, M. L., Alexander, M. L., Brito, J.,
839 Carbone, S., Castillo, P., Day, D. A., Kuang, C., Manzi, A., Ng, N. L., Sedlacek, A. J., Souza, R.,
840 Springston, S., Watson, T., Poehlker, C., Poeschl, U., Andreae, M. O., Artaxo, P., Jimenez, J. L.,
841 Martin, S. T., and Wang, J.: CCN activity and organic hygroscopicity of aerosols downwind of an
842 urban region in central Amazonia: seasonal and diel variations and impact of anthropogenic emissions,
843 17, 11779–11801, <https://doi.org/10.5194/acp-17-11779-2017>, 2017.

844 Wang, Y., Chen, J., Wang, Q., Qin, Q., Ye, J., Han, Y., Li, L., Zhen, W., Zhi, Q., Zhang, Y., and Cao,
845 J.: Increased secondary aerosol contribution and possible processing on polluted winter days in China,
846 *Environment International*, 127, 78–84, <https://doi.org/10.1016/j.envint.2019.03.021>, 2019.

847 Wang, Z., Cheng, Y., Ma, N., Mikhailov, E., Pöschl, U., and Su, H.: Dependence of the hygroscopicity
848 parameter κ on particle size, humidity and solute concentration: implications for laboratory
849 experiments, field measurements and model studies, *Atmos. Chem. Phys. Discuss.*, 2017, 1–33,
850 <https://doi.org/10.5194/acp-2017-253>, 2017.

851 Wiedensohler, A., Cheng, Y. F., Nowak, A., Wehner, B., Achtert, P., Berghof, M., Birmili, W., Wu,
852 Z. J., Hu, M., Zhu, T., Takegawa, N., Kita, K., Kondo, Y., Lou, S. R., Hofzumahaus, A., Holland, F.,
853 Wahner, A., Gunthe, S. S., Rose, D., Su, H., and Poeschl, U.: Rapid aerosol particle growth and
854 increase of cloud condensation nucleus activity by secondary aerosol formation and condensation: A
855 case study for regional air pollution in northeastern China, 114, D00G08,
856 <https://doi.org/10.1029/2008JD010884>, 2009.

857 Williams, B. J., Goldstein, A. H., Kreisberg, N. M., Hering, S. V., Worsnop, D. R., Ulbrich, I. M.,
858 Docherty, K. S., and Jimenez, J. L.: Major components of atmospheric organic aerosol in southern
859 California as determined by hourly measurements of source marker compounds, *Atmos. Chem. Phys.*,
860 10, 11577–11603, <https://doi.org/10.5194/acp-10-11577-2010>, 2010.

861 Wu, Z. J., Poulain, L., Birmili, W., Groess, J., Niedermeier, N., Wang, Z. B., Herrmann, H., and
862 Wiedensohler, A.: Some insights into the condensing vapors driving new particle growth to CCN sizes
863 on the basis of hygroscopicity measurements, 15, 13071–13083, [https://doi.org/10.5194/acp-15-](https://doi.org/10.5194/acp-15-13071-2015)
864 13071-2015, 2015.

865 Wu, Z. J., Zheng, J., Shang, D. J., Du, Z. F., Wu, Y. S., Zeng, L. M., Wiedensohler, A., and Hu, M.:
866 Particle hygroscopicity and its link to chemical composition in the urban atmosphere of Beijing, China,
867 during summertime, *Atmos. Chem. Phys.*, 16, 1123–1138, <https://doi.org/10.5194/acp-16-1123-2016>,
868 2016.

869 Xu, W., Han, T., Du, W., Wang, Q., Chen, C., Zhao, J., Zhang, Y., Li, J., Fu, P., Wang, Z., Worsnop,
870 D. R., and Sun, Y.: Effects of Aqueous-Phase and Photochemical Processing on Secondary Organic
871 Aerosol Formation and Evolution in Beijing, China, *Environ. Sci. Technol.*, 51, 762–770,
872 <https://doi.org/10.1021/acs.est.6b04498>, 2017a.

873 Xu, W., Croteau, P., Williams, L., Canagaratna, M., Onasch, T., Cross, E., Zhang, X., Robinson, W.,
874 Worsnop, D., and Jayne, J.: Laboratory characterization of an aerosol chemical speciation monitor

875 with PM_{2.5} measurement capability, *Aerosol Science and Technology*, 51, 69–83,
876 <https://doi.org/10.1080/02786826.2016.1241859>, 2017b.

877 Xu, W., Sun, Y., Wang, Q., Zhao, J., Wang, J., Ge, X., Xie, C., Zhou, W., Du, W., Li, J., Fu, P., Wang,
878 Z., Worsnop, D. R., and Coe, H.: Changes in Aerosol Chemistry From 2014 to 2016 in Winter in
879 Beijing: Insights From High-Resolution Aerosol Mass Spectrometry, *Journal of Geophysical Research:*
880 *Atmospheres*, 124, 1132–1147, <https://doi.org/10.1029/2018JD029245>, 2019.

881 Xu, W. Q., Sun, Y. L., Chen, C., Du, W., Han, T. T., Wang, Q. Q., Fu, P. Q., Wang, Z. F., Zhao, X. J.,
882 Zhou, L. B., Ji, D. S., Wang, P. C., and Worsnop, D. R.: Aerosol composition, oxidation properties,
883 and sources in Beijing: results from the 2014 Asia-Pacific Economic Cooperation summit study,
884 *Atmos. Chem. Phys.*, 15, 13681–13698, <https://doi.org/10.5194/acp-15-13681-2015>, 2015.

885 Yu, F., Luo, G., Nair, A. A., Schwab, J. J., Sherman, J. P., and Zhang, Y.: Wintertime new particle
886 formation and its contribution to cloud condensation nuclei in the Northeastern United States, *Atmos.*
887 *Chem. Phys.*, 20, 2591–2601, <https://doi.org/10.5194/acp-20-2591-2020>, 2020.

888 Yue, D., Zhong, L., Zhang, T., Shen, J., Yuan, L., Ye, S., Zhou, Y., and Zeng, L.: Particle Growth and
889 Variation of Cloud Condensation Nucleus Activity on Polluted Days with New Particle Formation: A
890 Case Study for Regional Air Pollution in the PRD Region, China, 16, 323–335,
891 <https://doi.org/10.4209/aaqr.2015.06.0381>, 2016.

892 Zhang, F., Li, Y., Li, Z., Sun, L., Li, R., Zhao, C., Wang, P., Sun, Y., Liu, X., Li, J., Li, P., Ren, G.,
893 and Fan, T.: Aerosol hygroscopicity and cloud condensation nuclei activity during the AC3Exp
894 campaign: implications for cloud condensation nuclei parameterization, *Atmos. Chem. Phys.*, 14,
895 13423–13437, <https://doi.org/10.5194/acp-14-13423-2014>, 2014.

896 Zhang, F., Li, Z., Li, Y., Sun, Y., Wang, Z., Li, P., Sun, L., Wang, P., Cribb, M., Zhao, C., Fan, T.,
897 Yang, X., and Wang, Q.: Impacts of organic aerosols and its oxidation level on CCN activity from
898 measurement at a suburban site in China, 16, 5413–5425, <https://doi.org/10.5194/acp-16-5413-2016>,
899 2016.

900 Zhang, F., Ren, J., Fan, T., Chen, L., Xu, W., Sun, Y., Zhang, R., Liu, J., Jiang, S., Jin, X., Wu, H., Li,
901 S., Cribb, M. C., and Li, Z.: Significantly enhanced aerosol CCN activity and number concentrations
902 by nucleation-initiated haze events: a case study in urban Beijing, *Journal of Geophysical Research:*
903 *Atmospheres*, n/a, <https://doi.org/10.1029/2019JD031457>, 2019.

904 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Ulbrich, I. M., Ng, N. L., Worsnop, D. R., and Sun, Y.:
905 Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review,

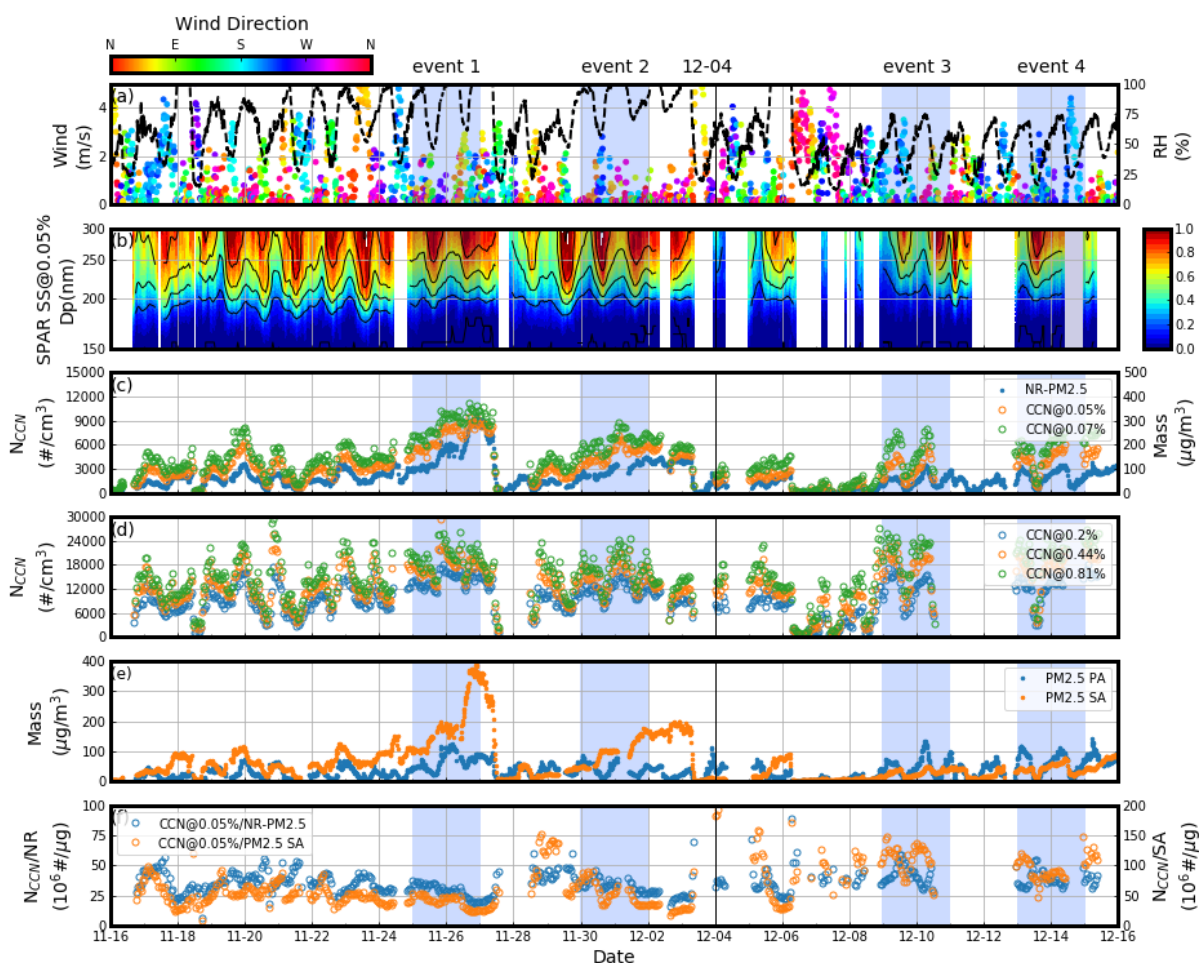
906 Analytical and Bioanalytical Chemistry, 401, 3045–3067, <https://doi.org/10.1007/s00216-011-5355->
907 y, 2011.

908 Zhang, R., Khalizov, A., Wang, L., Hu, M., and Xu, W.: Nucleation and Growth of Nanoparticles in
909 the Atmosphere, 112, 1957–2011, <https://doi.org/10.1021/cr2001756>, 2012.

910 Zhao, G., Tan, T., Zhao, W., Guo, S., Tian, P., and Zhao, C.: A new parameterization scheme for the
911 real part of the ambient urban aerosol refractive index, 19, 12875–12885, <https://doi.org/10.5194/acp->
912 19-12875-2019, 2019.

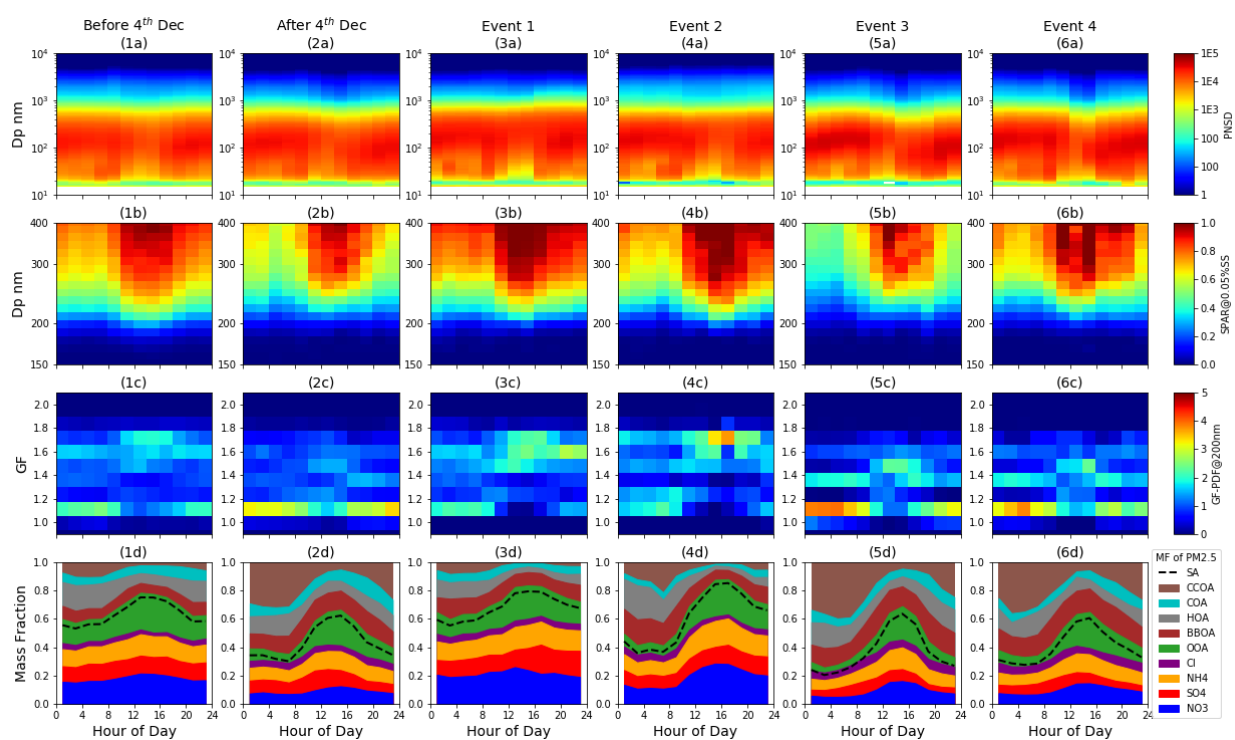
913

914 **Figures:**



915

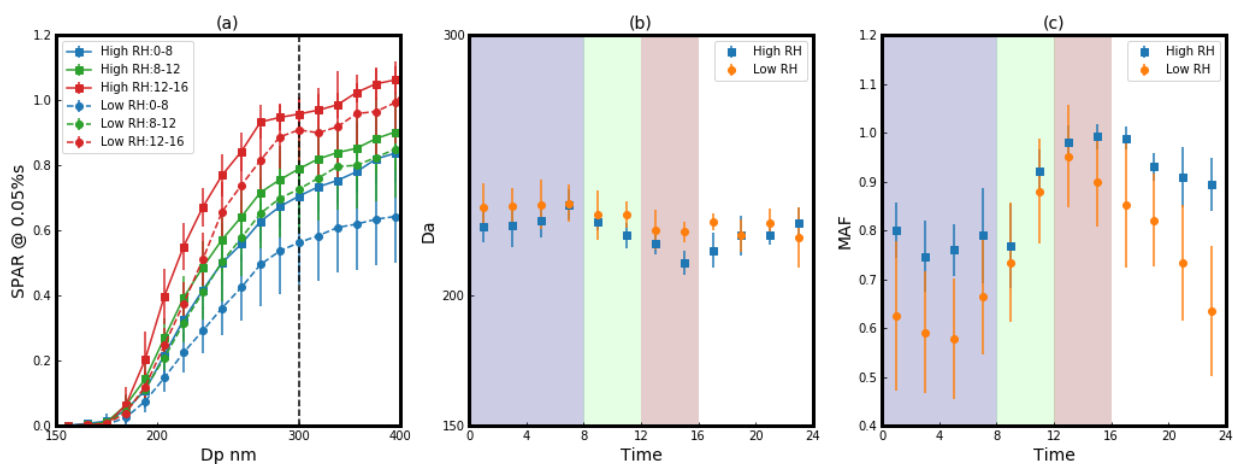
916 Fig 1. Overview of the measurements during the campaign: (a) dots represent wind speed with color
 917 indicating wind direction, and black lines represent RH; (b) SPAR under SS of 0.05%; (c) blue, green
 918 and yellow dots represent N_{CCN} under SS of 0.05% and 0.07%, and mass concentration of NR-PM_{2.5},
 919 respectively; (d) blue, green and yellow dots represent N_{CCN} under SS of 0.2%, 0.44% and 0.81%,
 920 respectively; (e) blue and yellow dots represent mass concentration of PM_{2.5} PA and PM_{2.5} SA
 921 respectively; (f) blue and yellow dots represent ratio between N_{CCN} and mass concentration of NR-
 922 PM_{2.5} and PM_{2.5} SA, respectively. There were four events with significant enhancements of N_{CCN}
 923 during the blue shaded periods.



925

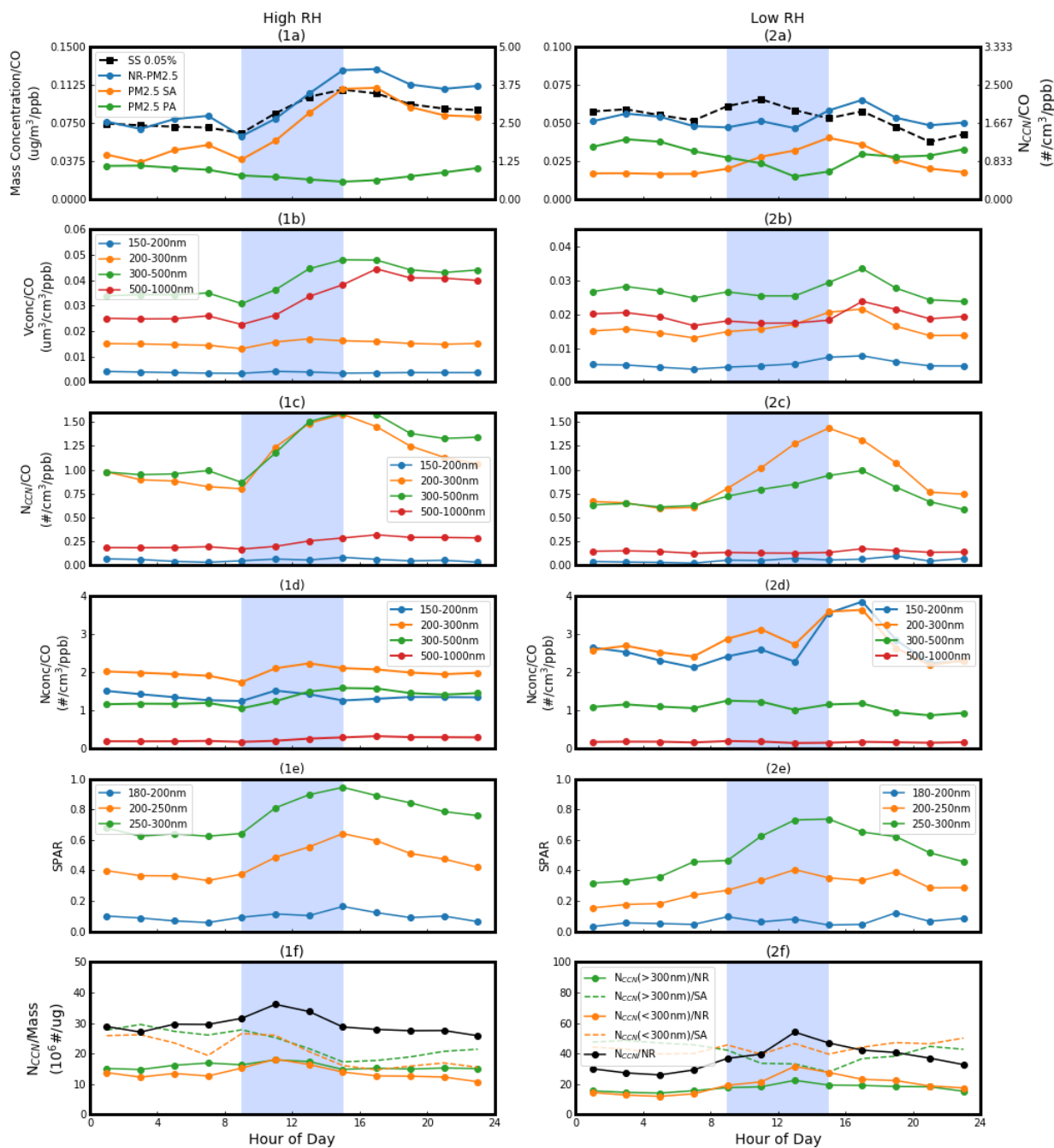
926 Fig 2. Diurnal variation of (a) PNSD, (b) SPAR at SS of 0.05%, (c) GF-PDF at 200 nm and (d) mass
 927 fraction of different PM_{2.5} chemical species during high RH periods before 4th Dec (1), low RH
 928 periods after 4th Dec (2) and the four events (3-6), including OA factors: hydrocarbon-like OA
 929 (HOA), cooking OA (COA), biomass burning OA (BBOA), coal combustion OA (CCOA), and
 930 oxygenated OA (OOA).

931



932

933 Fig 3. (a) The averages of SPAR curves at SS of 0.05% in three different time periods (blue: 0:00-
 934 8:00; green: 8:00-12:00; red: 12:00-16:00) during high (squares with solid line, event 1 and 2) and low
 935 (dots with dashed line, event 3 and 4) RH events. Diurnal variation of (b) D_a and (c) MAF under high
 936 (blue) and low (yellow) RH conditions. The blue, green and red shades correspond to with the three
 937 periods in (a & d). Error bars indicate the standard deviations of data.



938

939

940

941

942

943

944

945

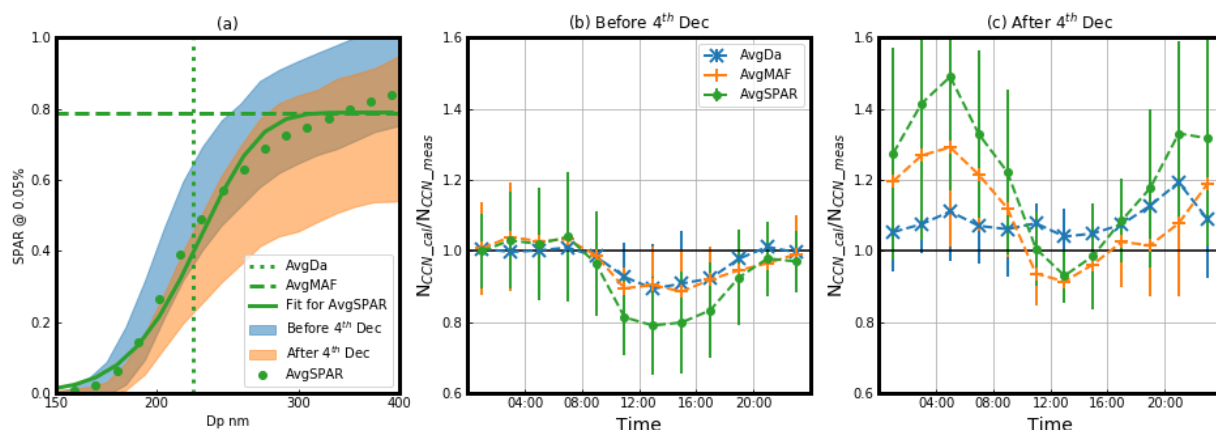
946

947

Fig 4. During different RH events, the average diurnal variation of (a) the ratios between particle mass concentration (dots with solid lines; blue: NR-PM_{2.5}; yellow: PM_{2.5} SA; green: PM_{2.5} PA) and CO concentration, and the ratio between N_{CCN} at SS of 0.05% and CO concentration (squares with solid line); (b) the ratios between particle volume concentration (Vconc) of different particle size range (indicated by colors) and CO concentration; (c) the ratios between N_{CCN} of different particle size range at SS of 0.05% (indicated by colors) and CO concentration; (d) the ratios between particle number concentration (Nconc) of different particle size range (indicated by colors) and CO concentration; (e) SPAR of different particle size range (indicated by colors); (f) the ratios between N_{CCN} at SS of 0.05% (black: bulk N_{CCN}; yellow: N_{CCN} with particle size larger than 300 nm; blue:

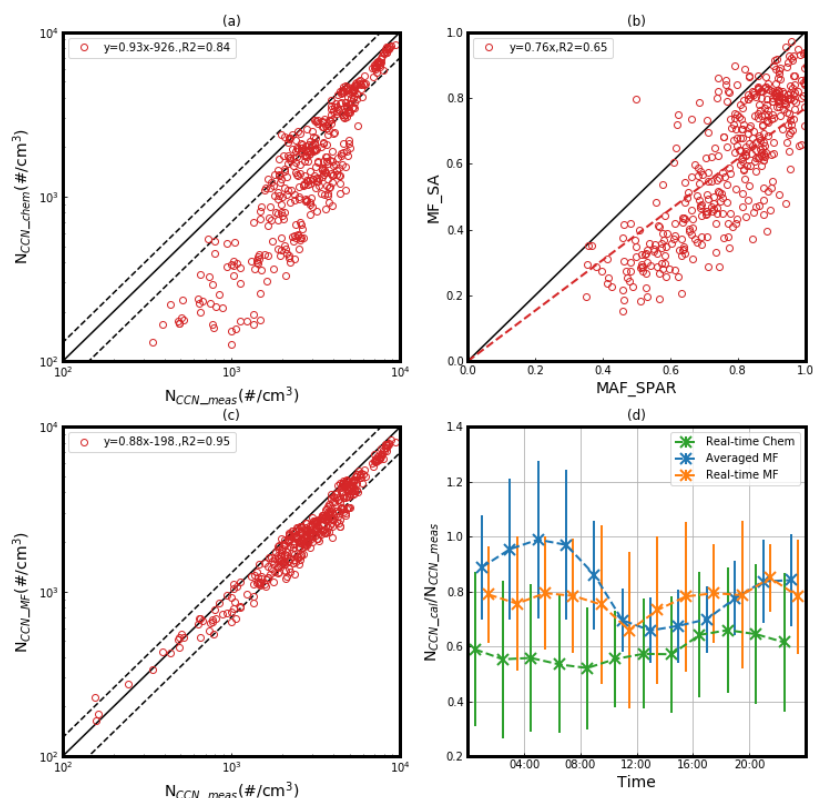
948 N_{CCN} with particle size smaller than 300 nm) and mass concentration of NR-PM_{2.5} SA and the ratios
949 between N_{CCN} and mass concentration of NR-PM_{2.5} (dashed lines).

950



951

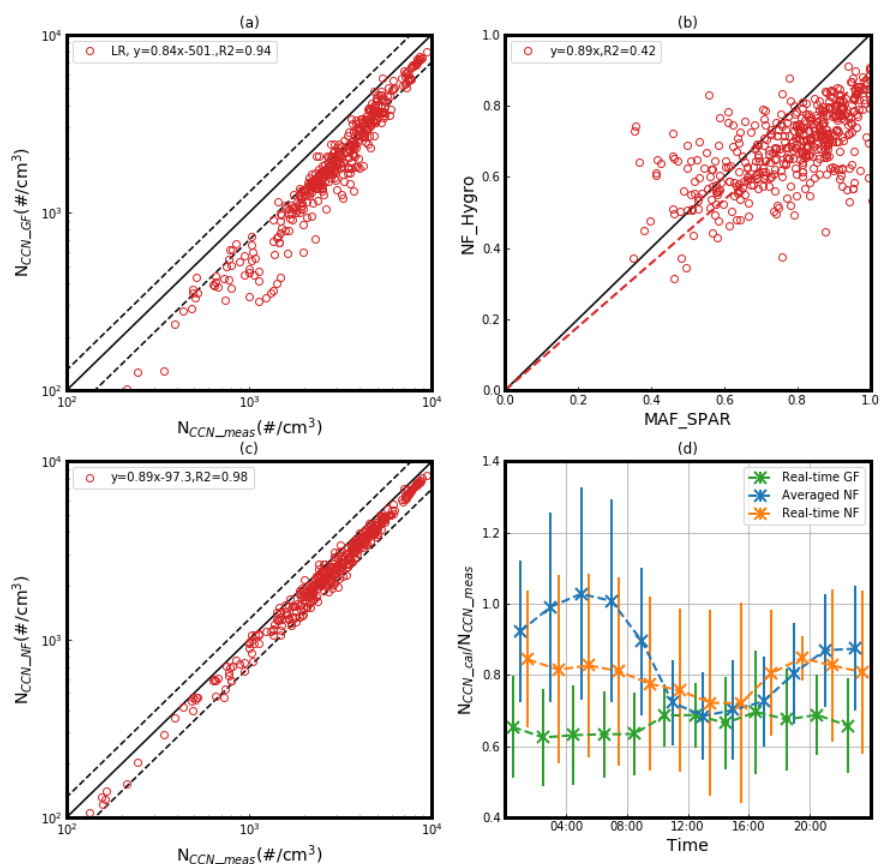
952 Fig 5. (a) The averaged SPAR at SS of 0.05% during the campaign (green scatters), the
 953 corresponding fitting curve (green line) and the averaged fitting parameters (dotted line for D_a and
 954 dashed line for MAF). The blue and yellow shaded areas represent the variations of SPAR before 4th
 955 Dec and after 4th Dec, respectively. The ratio between calculated N_{CCN} and measured N_{CCN} under (b)
 956 before and (c) after 4th Dec. Bars represent one standard deviation and colors represent different
 957 calculation of SPAR curves: green represent average SPAR during the campaign (AvgSPAR),
 958 yellow represent SPAR calculated with average D_a and real-time MAF (AvgDa) and blue represent
 959 SPAR calculated with average MAF and real-time D_a (AvgMAF).



960

961 Fig 6. (a) The comparison between calculated N_{CCN} based on κ derived from bulk particle chemical
 962 compositions (N_{CCN_chem}) and measured N_{CCN} at SS of 0.05%. (b) The correlation between MAF and
 963 mass fraction of secondary aerosol (MF_{SA}). (c) the comparison between calculated N_{CCN} based on
 964 SPAR derived from real-time MF_{SA} and average D_a (N_{CCN_MF}) and measured N_{CCN} . The black dashed
 965 lines represent the relative deviation of 30%. (d) the diurnal variations of the ratio between the
 966 calculated and measured N_{CCN} during the whole campaign based on different methods (green:
 967 N_{CCN_chem} ; blue: N_{CCN} calculated based on SPAR derived from averaged MF_{SA} and average D_a ; yellow:
 968 N_{CCN_MF}).

969



970

971 Fig 7. (a) The comparison between calculated N_{CCN} based on κ derived from bulk GF at 200 nm
 972 (N_{CCN_GF}) and measured N_{CCN} at SS of 0.05%. (b) The correlation between MAF and number fraction
 973 of hygroscopic particles (NF_{hygro} , $GF > 1.2$). (c) The comparison between calculated N_{CCN} based on
 974 SPAR derived from real-time NF_{hygro} and average D_a (N_{CCN_NF}) and measured N_{CCN} . The black dashed
 975 lines represent the relative deviation of 30%. (d) the diurnal variations of the ratio between the
 976 calculated and measured N_{CCN} during the whole campaign based on different methods (green: N_{CCN_GF} ;
 977 blue: N_{CCN} based on SPAR derived from averaged NF_{hygro} and average D_a ; yellow: N_{CCN_NF}).