

# Strong Atmospheric New Particle Formation in Winter, Urban Shanghai, China

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**Abstract** Particle size distributions in the range of 1.34-615 nm were recorded from Nov. 25<sup>th</sup>, 2013 to Jan. 25<sup>th</sup>, 2014 in urban Shanghai, using a combination of one nano Condensation Nucleus Counter system (nCNC), one nano-Scanning Mobility Particle Sizer (SMPS), and one long-SMPS. Measurements of sulfur dioxide by an SO<sub>2</sub> analyzer with pulsed UV fluorescence technique allowed calculation of sulfuric acid proxy. In addition, concentrations of ammonia were recorded with a Differential Optical Absorption Spectroscopy (DOAS). During this 62-day campaign, 13 NPF events were identified with strong burst of sub-3 nm particles and subsequent fast growth of newly formed particles. The observed nucleation rate ( $J_{1.34}$ ), formation rate of 3 nm particles ( $J_3$ ), and condensation sink ( $CS$ ) were 112.4-271.0 cm<sup>-3</sup> s<sup>-1</sup>, 2.3-19.2 cm<sup>-3</sup> s<sup>-1</sup>, and 0.030-0.10 s<sup>-1</sup>, respectively. Subsequent cluster/nanoparticle growth showed a clear size dependence, with average values of  $GR_{1.35\sim 1.39}$ ,  $GR_{1.39\sim 1.46}$ ,  $GR_{1.46\sim 1.70}$ ,  $GR_{1.70\sim 2.39}$ ,  $GR_{2.39\sim 7}$ , and  $GR_{7\sim 20}$  being  $1.6\pm 1.0$ ,  $1.4\pm 2.2$ ,  $7.2\pm 7.1$ ,  $9.0\pm 11.4$ ,  $10.9\pm 9.8$ , and  $11.4\pm 9.7$  nm h<sup>-1</sup>, respectively. Correlation between nucleation rate ( $J_{1.34}$ ) and sulfuric acid proxy indicates that nucleation rate  $J_{1.34}$  was proportional to a  $0.65\pm 0.28$  power of sulfuric acid proxy, indicating that the nucleation of particles can be explained by the activation theory. Correlation between nucleation rate ( $J_{1.34}$ )

32 and gas-phase ammonia suggests that ammonia was associated with NPF events. The  
33 calculated sulfuric acid proxy was sufficient to explain the subsequent growth of 1.34-  
34 3 nm particles, but its contribution became smaller when the particle size grew.  
35 Qualitatively, NPF events in urban Shanghai likely occur on days with low levels of  
36 aerosol surface area and sulfuric acid proxy is important only when aerosol surface  
37 area is low.

38

## 39 **1 Introduction**

40 Aerosol particles can influence climate directly and indirectly (Andreae and Crutzen,  
41 1997; Haywood and Boucher, 2000; IPCC, 2013), and have adverse impact on human  
42 health (Dockery et al., 1993; Laden et al., 2006; Pope and Dockery, 2006).  
43 Atmospheric nucleation of gas-phase precursors to clusters, and then further to  
44 nanoparticles is the largest source of atmospheric aerosol particles (Kulmala et al.,  
45 2004; Zhang et al., 2012). This phenomenon has been observed in numerous locations  
46 around the world, including areas with a pristine atmosphere, e.g., coastal areas  
47 (O'Dowd et al., 2002), Antarctic/Arctic (Park et al., 2004), remote forest (Dal Maso et  
48 al., 2005), semi-rural locations with very low pollution levels such as Kent, OH  
49 (Kanawade et al., 2012), and heavily polluted cities, such as Mexico City (Dunn et al.,  
50 2004).

51

52 The exact mechanism for atmospheric nucleation is still under active investigation.  
53 Field measurements and laboratory studies have shown that sulfuric acid is a key  
54 precursor species for atmospheric nucleation (Weber et al., 1996; Sipila et al., 2010),  
55 and that atmospheric nucleation rate can be significantly promoted in presence of  
56 other precursors including ammonia (Ball et al., 1999; Benson et al., 2009), amines  
57 (Berndt et al., 2010; Zhao et al., 2011), and organic acids (Zhang et al., 2004; Zhang  
58 et al., 2009). At certain locations, ion-induced nucleation (Yu and Turco, 2001; Lee et  
59 al., 2003) or iodine species (O'Dowd et al., 2002) may also help to explain the  
60 observed new particle formation. Very recently progress has been made by the use of  
61 Particle Size Magnifier (PSM) and Chemical Ionization Atmospheric Pressure

62 interface Time-of-Flight (CI-API-ToF) mass spectrometer, by combining the Cloud  
63 (Cosmics Leaving OUtdoor Droplets) chamber experiments and ambient observations  
64 including those at Hyytiälä, Finland, showing that oxidation products of biogenic  
65 emissions, together with sulfuric acid, contribute to new particle formation in the  
66 atmosphere (Schobesberger et al., 2013; Riccobono et al., 2014).

67

68 China suffers severe air pollution, especially high atmospheric particle loadings in  
69 recent years (Chan and Yao, 2008). Among many potential sources of atmospheric  
70 particles, atmospheric nucleation has been suggested to be a significant source of  
71 particles (Matsui et al., 2011; Yue et al., 2011). Correspondingly, a number of  
72 extensive campaign or long-term observational studies have been carried out in the  
73 Beijing area (e.g., Wu et al., 2007; Yue et al., 2009; Zhang et al., 2011; Gao et al.,  
74 2012) and Pearl River Delta, including Hong Kong (e.g., Guo et al., 2012; Yue et al.,  
75 2013). As one of the most industrialized area of China, one of the most populated  
76 region in the world, and one of the hotspots for particle pollution, Yangtze River Delta  
77 (YRD) has only seen a few research activities on atmospheric nucleation (Du et al.,  
78 2012; Herrmann et al., 2014). Among the few studies, measurements at the station for  
79 Observing Regional Processes of the Earth System, Nanjing University (SORPES-  
80 NJU) offered a first insight for new particle formation in the western part of YRD  
81 (Herrmann et al., 2014). On the other hand, atmospheric nucleation research in China  
82 is still in its infant stage and the latest experimental techniques are yet to be applied in  
83 China. For example, data on freshly nucleated particles are really sparse, except for  
84 those from an air ion spectrometer employed at SORPES-NJU (Herrmann et al.,  
85 2014). To the best of our knowledge, the use of a Particle Size Magnifier (PSM),  
86 which is able to study atmospheric nucleation at the size (mobility diameter) down to  
87  $1.5 \pm 0.4$  nm (Kulmala et al., 2012), has not been reported in a Chinese location in  
88 literature. The lack of key information greatly hinders a better understanding of  
89 nucleation mechanisms in China, where concentrations of sulfuric acid and basic  
90 gases including ammonia and amines are high (Zheng et al., 2011; Zheng et al., 2015)  
91 but concentrations of extremely low volatility organic compounds formed from

92 biogenic emissions are yet to be determined.

93

94 Direct measurements of atmospheric nucleation rates down to  $1.5 \pm 0.4$  nm provide a  
95 better and more accurate characterization of atmospheric nucleation, since the indirect  
96 calculation of atmospheric nucleation rates from the formation rates of 3 nm particles  
97 leads to substantial uncertainty due to our incomplete understanding of condensational  
98 growth and coagulation scavenging of particles in the 1.5 to 3 nm range (Anttila et al.,  
99 2010; Korhonen et al., 2011). With the growing number of reports of real nucleation  
100 rates in clean atmosphere (e.g., Kulmala et al., 2012; Yu et al., 2014), it is ideal to  
101 measure nucleation rates in a polluted urban atmosphere to find out how atmospheric  
102 nucleation rates vary under different atmospheric conditions. In addition, the  
103 nucleation mechanism in a polluted urban atmosphere that is vital to understand  
104 atmospheric nucleation at a global scale and for atmospheric model development can  
105 be preliminarily investigated by examining the relationship between the measured  
106 atmospheric nucleation rates and the well-accepted precursor gases that exist in high  
107 concentrations.

108

109 In this study, we measured atmospheric nucleation from Nov. 25<sup>th</sup>, 2013 to Jan. 25<sup>th</sup>,  
110 2014 in urban Shanghai with nCNC and two sets of SMPS. Nucleation frequency,  
111 nucleation rate ( $J_{1.34}$ ), condensation sink ( $CS$ ), and growth rates ( $GR$ ) are reported  
112 and compared with previous studies with similar or dissimilar atmospheric  
113 environments. In addition, the potential nucleation mechanism was explored by  
114 correlating sulfuric acid proxy calculated from sulfur dioxide precursor and gas-phase  
115 ammonia to nucleation rate ( $J_{1.34}$ ).

116

## 117 **2 Experimental**

### 118 **2.1 Nucleation Measurements**

119 Nucleation measurements were carried out on the rooftop of a teaching building  
120 ( $31^{\circ}18'N$ ,  $121^{\circ}30'E$ ) that is about 20 m above ground on the campus of Fudan

121 University between Nov. 25<sup>th</sup>, 2013 and Jan. 25<sup>th</sup>, 2014. This monitoring site is mostly  
122 surrounded by commercial properties and residential dwellings. The Middle Ring  
123 Road, one of main overhead highways in Shanghai, lies about 100 m to the south of  
124 the site. Hence, the Fudan site can be treated as a representative urban site influenced  
125 by a wide mixture of emission sources (Wang et al., 2013; Ma et al., 2014).

126

127 Ambient particle size distributions in the range of 1.34-615 nm were measured using a  
128 combination of one nano Condensation Nucleus Counter system (model A11,  
129 Airmodus, Finland), one nano-SMPS (consisting of one DMA3085 and one  
130 CPC3776, TSI, USA), and one long-SMPS (consisting of one DMA3081 and one  
131 CPC3775, TSI, USA). The instruments were continuously running except for  
132 maintenance and minor instrument breakdown during the campaign.

133

134 Ambient air was drawn into a stainless steel manifold of 5.0 m length and 4 inch inner  
135 diameter at a flow rate of 153 CFM using a blower (Model DJT10U- 25M, NUSSUN,  
136 China). From this main manifold, 1.75 lpm ambient air was drawn through a 1/4 inch  
137 inner diameter stainless tube of 18 cm length, and diluted with a zero air flow  
138 generated by a zero air generator (Model 111, Thermo, USA) at a ratio of 1:1 to  
139 reduce the overall relative humidity (RH) and the number of particles entering PSM,  
140 since high RH and particle loading had an impact on the saturation of diethylene  
141 glycol in PSM and hence data quality. Subsequently 2.5 lpm diluted air was sampled  
142 into nCNC. In addition, 30 lpm split flow was drawn from the main manifold through  
143 a 1/4 inch inner diameter conductive silicon tubing of 50 cm length, and then 0.3 lpm  
144 and 1.5 lpm ambient air from the split flow, respectively, were drawn into nano-SMPS  
145 and long-SMPS. The calculated diffusion loss is up to 29% for 1.35 nm particles with  
146 the above setup, and has been taken into account in the entire size range during the  
147 data processing.

148

149 The nCNC system consists of one PSM (model A10, Airmodus, Finland) and one  
150 butanol Condensation Particle Counter (bCPC, model A20, Airmodus, Finland), and

151 was used to measure size distributions of 1.34-3 nm clusters/particles. Briefly, PSM  
152 activates the smallest particles using diethylene glycol as a working fluid and  
153 condensationally grows nanoparticles up to larger than 90 nm in mobility equivalent  
154 diameter, after which an external CPC is used for further growing the particles to  
155 optical sizes and counting the grown particles (Vanhanen et al., 2011). In this study,  
156 PSM was used in the scanning mode in which the saturator flow rate is changed  
157 continuously, giving an activation spectrum of the measured particles to obtain size  
158 distribution of sub-3 nm clusters/particles. A scanning cycle of 100 steps between  
159 saturator flow rates 0.1-1 lpm and a time resolution of 220 sec were chosen. Sub-3 nm  
160 clusters/particles were classified into 5 bins, i.e., 1.34-1.37, 1.37-1.41, 1.41-1.52,  
161 1.52-1.89, 1.89-3.0 nm, respectively. Geometric mean values of upper and lower  
162 limits of the five bins, i.e., 1.35, 1.39, 1.46, 1.70, and 2.39 nm, respectively, were used  
163 to refer to the five bins in the growth rate calculation.

164

165 The nano-SMPS measured particles in the size range from 3 to 64 nm and the long-  
166 SMPS recorded particles from 14 to 615 nm. For both SMPSs, 64 size bins and 5-min  
167 time resolution were chosen. The sample flow to sheath flow ratios for both SMPSs  
168 were set at 1:10. A comparison analysis on the total particle concentrations between  
169 14 and 64 nm measured by both nano-SMPS and long-SMPS showed less than 10%  
170 difference in the size range of 55-64 nm between two SMPSs. Hence, number  
171 concentrations of particles in the size range of 3-615 nm,  $N_{3-615}$ , were calculated from  
172 the sum of  $N_{3-55}$  obtained from nano-SMPS,  $N_{55-64}$  from the arithmetic average of  
173 nano-SPMS and long-SMPS, and  $N_{64-615}$  from long-SMPS.

174

175 At the same site, sulfur dioxide (SO<sub>2</sub>) was measured by an SO<sub>2</sub> analyzer with pulsed  
176 UV fluorescence technique (Model 43i, Thermo, USA) with a time resolution of 5  
177 min and calibration of this SO<sub>2</sub> analyzer was performed every month. A DOAS  
178 system was used to measure the integrated concentration of NH<sub>3</sub> along the optical  
179 path between a transmitter telescope using a 35W Deuterium lamp as the light source  
180 and a receiver telescope (53 m), and then to yield the average concentration of NH<sub>3</sub>

181 through dividing the integrated concentration by the absorption length (Platt and Stutz,  
 182 2008). In this study, the concentration of NH<sub>3</sub> was determined by fitting the reference  
 183 spectra to the atmospheric spectra in a given window (205-220 nm) using a nonlinear  
 184 least-squares method, similarly to a previous measurement of HONO and NO<sub>2</sub> (Wang  
 185 et al., 2013). Detection limit of NH<sub>3</sub> was about 1 ppb with a 3 min integration time.

186

187 Solar radiation intensity measured by a Pyranometer (Kipp & Zonen CMP6,  
 188 Netherland) was obtained from Shanghai Pudong Environmental Monitoring Centre  
 189 (31°14'N, 121°32'E, about 8.78 km from the Fudan site).

190

## 191 **2.2 Data Processing**

### 192 **2.2.1 Nucleation rate ( $J_{1.34}$ ), formation rate of 3 nm particles ( $J_3$ ), growth rate** 193 **( $GR$ ), and condensation sink ( $CS$ )**

194 In this study, PSM allowed measurements of clusters/particles down to 1.34 nm.  
 195 Hence, atmospheric nucleation rate,  $J_{1.34}$ , defined as the flux of particles growing  
 196 over 1.34 nm, can be calculated by taking into account the coagulation losses and  
 197 condensational growth out of the considered size range (Kulmala et al., 2012),

$$198 \quad J_{1.34} = \frac{dN_{1.34-3}}{dt} + CoagS_{d_p=2nm} \cdot N_{1.34-3} + \frac{1}{1.66nm} GR_{1.34-3} \cdot N_{1.34-3} \quad (1)$$

199 where  $CoagS_{d_p=2nm}$  represents coagulation sink of 2 nm particles, an approximation for  
 200 that in the size interval of 1.34-3 nm; and  $GR_{1.34-3}$  represents the apparent  
 201 clusters/particle growth rate between 1.34 and 3 nm.

202

203 Formation rate of 3nm particles was calculated in a similar way (Sihto et al., 2006;  
 204 Kulmala et al., 2012), providing a comparison with previous studies,

$$205 \quad J_3 = \frac{dN_{3-6}}{dt} + CoagS_{d_p=4nm} \cdot N_{3-6} + \frac{1}{3nm} GR_{3-6} \cdot N_{3-6} \quad (2)$$

206 where  $CoagS_{d_p=4nm}$  represents coagulation sink of 4 nm particles, an approximation  
 207 for that in the size interval of 3-6 nm.

208

209 Growth rate ( $GR$ ) is defined as the rate of change in the diameter of a growing  
210 particle population, using the maximum-concentration method (Kulmala et al., 2012),

$$211 \quad GR = \frac{dd_p}{dt} = \frac{\Delta d_p}{\Delta t} = \frac{d_{p_2} - d_{p_1}}{t_2 - t_1} \quad (3)$$

212 where  $d_{p_1}$  and  $d_{p_2}$  are the representative particle diameters at times  $t_1$  and  $t_2$ ,  
213 respectively.

214

215 Condensation sink ( $CS$ ) describes the condensing vapor sink caused by the particle  
216 population (Kulmala et al., 2012),

$$217 \quad CS = 4\pi D \int_0^{d_p \max} \beta_{m,d_p} d_p N_{d_p} dd_p = 4\pi D \sum_{d_p} \beta_{m,d_p} d_p N_{d_p} \quad (4)$$

218 where  $D$  is the diffusion coefficient of the condensing vapor, usually assumed to be  
219 sulfuric acid ( $0.104 \text{ cm}^2 \text{ s}^{-1}$  used in this study); and  $\beta_{m,d_p}$  is the transitional regime  
220 correction factor.

221

### 222 2.2.2 Sulfuric acid

223 Sulfuric acid has been accepted as a key gas-phase precursor for atmospheric  
224 nucleation and contributes to the subsequent growth of newly-formed particles  
225 (Weber et al., 1996; Sipila et al., 2010). The accurate measurement of gas-phase  
226 sulfuric acid requires application of chemical ionization mass spectrometry using  
227 nitrates as reagent ions (Eisele and Tanner, 1993), which is not possessed by this  
228 research group during this study. Instead, the sulfuric acid proxy  $[H_2SO_4]$  was  
229 estimated based on local solar radiation level  $Radiation$ ,  $SO_2$  concentration  $[SO_2]$ ,  
230 condensation sink  $CS$ , and relative humidity (Mikkonen et al., 2011),

$$231 \quad [H_2SO_4] = 8.21 \times 10^{-3} \cdot k \cdot Radiation \cdot [SO_2]^{0.62} \cdot (CS \cdot RH)^{-0.13} \quad (5)$$

232 where  $k$  is the temperature dependent reaction rate constant. The relative error  
233 between calculated sulfuric acid proxy and measured sulfuric acid concentration is  
234 estimated to be 42% (Mikkonen et al., 2011). The time resolution of calculated



235 sulfuric acid proxy was 1 hour since those of temperature and relative humidity was 1  
236 hour.

237

238 Condensation of sulfuric acid contributes to the growth of newly-formed particles.

239 The growth of clusters/particles due to condensation of sulfuric acid,  $GR_{H_2SO_4}$ , can be

240 estimated by the following equations (Nieminen et al., 2010),

$$241 \quad GR_{H_2SO_4} = \frac{\gamma}{2\rho_v} \left(1 + \frac{d_v}{d_p}\right)^2 \left(\frac{8kT}{\pi}\right)^{1/2} \left(\frac{1}{m_p} + \frac{1}{m_v}\right)^{1/2} m_v [H_2SO_4] \quad (6)$$

$$242 \quad \text{and } \gamma = \frac{4}{3} \cdot Kn \cdot \beta_{m,d_p} \quad (7)$$

243 where  $\rho_v$  and  $d_v$  are the condensed phase density and molecule diameter of  $H_2SO_4$ ,

244 respectively;  $m_p$  and  $m_v$  are particle and  $H_2SO_4$  vapor molecule masses, respectively;

245  $\gamma$  is a correction factor;  $Kn$  is the Knudsen number (Lehtinen and Kulmala, 2003).

246 For this calculation, particle density  $\rho_p = 1.83 \text{ g cm}^{-3}$  was used.

247

248 The particle growth due to the hydration of  $H_2SO_4$  is taken into account by assuming

249 that sulfuric acid is instantaneously equilibrated with gas-phase water. During our

250 campaign, daily average RH varied between 28.7%~60.0%. Hence, using the  $H_2SO_4$ -

251 hydrate distribution data given by Kurtén et al. (2007), the density and mass of the

252 average hydrated  $H_2SO_4$  molecule at 50% relative humidity is calculated and further

253 used in equation (6).

254

### 255 **3 Results and Discussion**

#### 256 **3.1 Classification of new particle formation (NPF) events**

257 Figure 1 presents a contour plot for particle size distributions of 3-615 nm and a

258 number concentration plot of sub-3 nm clusters/particles  $N_{1,34\sim 3}$  during Nov. 25<sup>th</sup>,

259 2013 - Jan. 25<sup>th</sup>, 2014. Data were occasionally missing because of maintenance and

260 minor breakdown of instruments. From the figure, frequent bursts of sub-3 nm

261 particles were evident, with concentrations up to  $8.0 \times 10^4 \text{ cm}^{-3}$  around noon time.  
262 However, similarly to previous studies (Kulmala et al., 2007; Kulmala et al., 2013; Yu  
263 et al., 2014), not all sub-3 nm particles eventually underwent a continuous growth to  
264 larger sizes. In this study, we define an observation day with appearances of sub-3 nm  
265 clusters/particles over a time span of hours and subsequent growth to larger sizes for a  
266 few hours as a NPF event day. In this case, a NPF day will present a banana-shaped  
267 contour plot of particle size distributions obtained from SMPS (Dal Maso et al.,  
268 2005). We focus on characteristics and potential mechanisms of these events.

269

270 According to the classification, there were 13 event days during the 62-day campaign,  
271 as illustrated by the shadow in Figure 1. Although nCNC data were partially  
272 unavailable on Dec. 26<sup>th</sup>, 2013 and completely unavailable on Jan. 24<sup>th</sup>, 2014, these  
273 two days are still defined as NPF days since a distinctive banana-shaped contour plot  
274 for particle distributions between 3-615 nm existed. Dec. 18<sup>th</sup>, 2013 was not regarded  
275 as a NPF day since  $N_{1.34\sim 3}$  was not recorded and the growth of 3~20 nm particles was  
276 relatively short-lived.

277

278 Among these NPF events, 5 NPF events occurred in November, 3 in December, and 5  
279 in January. The averaged frequency for NPF events was 21.0% during the 62-day  
280 campaign. Our NPF frequency at Shanghai is larger than the average value in winter  
281 1996-2003, SMEAR II station, Hyytiälä, Finland (Dal Maso et al., 2005), likely  
282 because nucleation events at Hyytiälä have recently been related to oxidation products  
283 of biogenic emissions (Kulmala et al., 1998; Schobesberger et al., 2013; Riccobono et  
284 al., 2014) and photochemistry of volatile organic compounds is less intensive in  
285 winter months. This frequency is also higher than that in winter, semi-rural Kent, OH,  
286 during which transport of sulfur dioxide from the east-southeast power plant to Kent  
287 is not favored (Kanawade et al., 2012). NPF events occurred at a frequency of around  
288 40% during Nov.-Dec. 2004 in Beijing (Wu et al., 2007), much more often than in  
289 Shanghai. On the other hand, NPF frequency in Shanghai is remarkably close to that

290 measured in winter 2012, Nanjing, which is also located in Yangtze River delta  
291 (Herrmann et al., 2014).

292

293 Number concentrations of particles in different size ranges, i.e.,  $N_{1.34\sim3}$ ,  $N_{3\sim7}$ , and  
294  $N_{7\sim30}$ , respectively, on a NPF day (Dec. 11<sup>th</sup>, 2013) and an obvious non-NPF day  
295 (Jan. 7<sup>th</sup>, 2014) are further examined to illustrate features of a NPF event, as shown  
296 in Figure 2. On the NPF day, 1.34-3 nm particles appeared as early as 7 am in the  
297 morning that was right after sunrise (6:42 am on Dec. 11<sup>th</sup>, 2013), reached its  
298 maximum just before noontime, and spanned for almost the whole daytime (sunset at  
299 4:52 pm, Dec. 11<sup>th</sup>, 2013), suggesting that photochemistry products likely contribute  
300 to formation of smallest particles. This size distribution of atmospheric neutral and  
301 charged clusters/particles by a scanning PSM is identical to that measured at  
302 Hyytiälä, Finland (Kulmala et al., 2013). On the same NPF day, 3-7 nm and 7-30 nm  
303 particles appeared much later, resembling previous findings only with SMPS  
304 measurements (e.g., Yue et al., 2010). The lag in peaking times of  $N_{1.34\sim3}$ ,  $N_{3\sim7}$ , and  
305  $N_{7\sim30}$  on the NPF day clearly indicated the continuous growth of clusters/particles,  
306 the reduction of particles due to coagulation during the growth, and the diverse  
307 sources of particles in the size range of 7-30 nm. In contrast,  $N_{1.34\sim3}$  and  $N_{3\sim7}$   
308 showed a flat profile on the non-NPF day. The minor enhancement in  $N_{7\sim30}$  between  
309 10 am and 5 pm on the non-NPF day was not due to growth of newly formed  
310 particles. Instead, direct emission of 7-30 nm particles from transportation activity  
311 likely explained their appearance.

312

### 313 **3.2 General characteristics of NPF events**

314 Table 1 summaries characteristics of each NPF event observed in this campaign,  
315 including  $J_{1.34}$ ,  $J_3$ ,  $GR_{1.35\sim2.39}$  (from the bin of 1.34-1.37 nm to the bin of 1.89-3.0  
316 nm),  $GR_{2.39\sim7}$ ,  $GR_{7\sim20}$ ,  $CS$ ,  $[H_2SO_4]$ ,  $N_{1.34\sim3}$ , and total number concentrations of

317 particles  $N_{1.34\sim 615}$ , and compares the mean values to those in selected other studies.  
318 Nucleation rate  $J_{1.34}$  and formation rate of 3 nm particles  $J_3$  were 112.4-271.0 and  
319 2.3-19.2  $\text{cm}^{-3} \text{s}^{-1}$ , respectively. Nucleation rate  $J_{1.34}$  at Shanghai is obviously  
320 significantly larger than 1.4  $\text{cm}^{-3} \text{s}^{-1}$  at Hyytiälä, Finland with a pristine atmosphere  
321 (Kulmala et al., 2012) and 1.3  $\text{cm}^{-3} \text{s}^{-1}$  at Kent, OH with relatively lower levels of  
322 pollutants (Yu et al., 2014). Direct comparison of our nucleation rate with that in a  
323 Chinese location is not feasible because no previous reports are available. However,  
324 Herrmann et al. (2014) reported a  $J_2$  of 33.2  $\text{cm}^{-3} \text{s}^{-1}$  at the SORPES-NJU station,  
325 Nanjing China. Together with their results, we conclude that strong nucleation events  
326 occur geographically widely in the YRD region.

327

328 Formation rate of 3 nm particles  $J_3$  has been more routinely reported. Similarly to  
329  $J_{1.34}$ ,  $J_3$  at Shanghai is significantly larger than 0.61  $\text{cm}^{-3} \text{s}^{-1}$  at Hyytiälä, Finland  
330 (Kulmala et al., 2012), and generally comparable to 3.3-81.4 and 1.1-22.4  $\text{cm}^{-3} \text{s}^{-1}$  at  
331 Beijing (Wu et al., 2007; Yue et al., 2009), 3.6-6.9  $\text{cm}^{-3} \text{s}^{-1}$  at Hong Kong (Guo et al.,  
332 2012), and 2.4-4.0  $\text{cm}^{-3} \text{s}^{-1}$  in a back-garden rural site of Pearl River Delta (Yue et al.,  
333 2013). The fast reduction from  $J_{1.34}$  to  $J_3$  was likely due to the presence of a large  
334 background particle number as shown in Table 1.

335

336 The large background particle number concentrations corresponded to the high  
337 condensation sink ( $CS$  of 0.030-0.10  $\text{s}^{-1}$ ) observed during the campaign. As shown in  
338 Table 1,  $CS$  at Shanghai is much larger than  $(0.05-0.35) \times 10^{-2} \text{s}^{-1}$  at Hyytiälä, Finland  
339 (Kulmala et al., 2012) and  $0.8 \times 10^{-2} \text{s}^{-1}$  at Kent, OH (Yu et al., 2014), but comparable  
340 to  $(0.58-8.4) \times 10^{-2} \text{s}^{-1}$  at Beijing (Wu et al., 2007; Yue et al., 2009; Zhang et al., 2011;  
341 Gao et al., 2012),  $(1.0-6.2) \times 10^{-2} \text{s}^{-1}$  at Hong Kong (Guo et al., 2012),  $2.4 \times 10^{-2} \text{s}^{-1}$  at  
342 Nanjing (Herrmann et al., 2014), and  $(3.5-4.6) \times 10^{-2} \text{s}^{-1}$  in an urban site of Pearl  
343 River Delta (Yue et al., 2013). High sulfuric acid proxy ( $[H_2SO_4]$  of  $(2.3-6.4) \times 10^7$

344 molecules  $\text{cm}^{-3}$ ) existed to promote the NPF events. Measurements of gas-phase  
345 sulfuric acid by a chemical ionization mass spectrometer during the CAREBeijing  
346 2008 Campaign, a time period with strict air quality control regulations, reported peak  
347 concentrations of sulfuric acid up to the order of  $10^7$  molecules  $\text{cm}^{-3}$  (Zheng et al.,  
348 2011), smaller than our sulfuric acid proxy. Uncertainty may well exist for our  
349 sulfuric acid proxy that was calculated from the concentrations of sulfur dioxide and  
350 radiation intensity. However, Judging from CS and  $[H_2SO_4]$  together, it is clear that  
351 the condensable vapor at Shanghai is likely a main impetus for observed strong new  
352 particle formation events.

353

354  $GR_{1.35\sim 2.39}$ ,  $GR_{2.39\sim 7}$ , and  $GR_{7\sim 20}$  were in the range of 0.49-8.1, 3.1-35.7, 4.5-38.3  $\text{nm h}^{-1}$ ,  
355 respectively. The arithmetic average values of  $GR_{1.35\sim 2.39}$ ,  $GR_{2.39\sim 7}$ , and  $GR_{7\sim 20}$  were  
356  $2.0\pm 2.7$  (one standard deviation),  $10.9\pm 9.8$  and  $11.4\pm 9.7$   $\text{nm h}^{-1}$ , respectively,  
357 which are comparable to 3-20  $\text{nm h}^{-1}$  for nucleation mode particles in another sulfur-  
358 rich city, Atlanta, GA (Stolzenburg et al., 2005). In addition,  $GR_{1.35\sim 2.39}$  at Shanghai is  
359 smaller than the growth rates (5.5-7.6  $\text{nm h}^{-1}$ ) for particles in 1~3 nm geometric  
360 diameter range in Atlanta (Kuang et al., 2012). A closer examination of growth rates  
361 was performed by dividing  $GR_{1.35\sim 2.39}$  into growth of clusters/particles from one bin to  
362 another, i.e.,  $GR_{1.35\sim 1.39}$  ( $1.6\pm 1.0$   $\text{nm h}^{-1}$  from the bin of 1.34-1.37 nm to the bin of  
363 1.37-1.41 nm),  $GR_{1.39\sim 1.46}$  ( $1.4\pm 2.2$   $\text{nm h}^{-1}$  from 1.37-1.41 nm to 1.41-1.52 nm),  
364  $GR_{1.46\sim 1.70}$  ( $7.2\pm 7.1$   $\text{nm h}^{-1}$  from 1.41-1.52 nm to 1.52-1.89 nm), and  $GR_{1.70\sim 2.39}$  ( $9.0\pm$   
365  $11.4$   $\text{nm h}^{-1}$  from 1.52-1.89 nm to 1.89-3.0 nm). These growth rates show a clear size-  
366 dependent particle growth (Fig.3), owing to the nano-Köhler activation that suggests a  
367 faster growth for activated nanoparticles due to a decreasing Kelvin effect and, thus,  
368 an enhanced condensation flux (Kulmala et al., 2004), Kelvin effect, and surface or  
369 volume-controlled reaction corrected for the Kelvin effect on surface or volume  
370 concentrations (Kuang et al., 2012). Similar observations have been reported in

371 previous studies using nCNC (Kulmala et al., 2013) and DEG UCPC (Kuang et al.,  
372 2012), respectively. Our  $GR_{2.39\sim7}$  is larger than  $6.3 \text{ nm h}^{-1}$  at Nanjing (Herrmann et al.,  
373 2014), and our  $GR_{7\sim20}$  is close to the upper bound of those at urban Beijing (Wu et al.,  
374 2007; Yue et al., 2009; Zhang et al., 2011; Gao et al., 2012), and generally larger than  
375  $1.5\text{-}8.4 \text{ nm h}^{-1}$  in Hong Kong (Guo et al., 2012), indicating that high concentrations of  
376 condensable vapors existed. In addition, our growth rates suggest that the smallest  
377 clusters (the bin of 1.34-1.37 nm), if not scavenged by larger particles, would grow to  
378 3 nm within  $\sim 12$  min, and to 20 nm within  $\sim 2$  hr.

379

### 380 **3.3 Potential mechanisms for NPF events**

381 As shown in Table 1, nucleation rate ( $J_{1.34}$ ) in this study is typically larger than 100  
382  $\text{cm}^{-3} \text{ s}^{-1}$ , suggesting that the ion-induced nucleation was not a main mechanism for  
383 observed fast nucleation (Hirsikko et al., 2011; Riccobono et al., 2014). The 2012  
384 winter study at the SORPES-NJU station that is also located at YRD shows that the  
385 ratio of  $J_2$  between ions and total particles (ions plus neutral particles) was 0.002,  
386 also indicating the minor role of ion-induced nucleation (Herrmann et al., 2014).  
387 Hence, it is likely that nucleation of neutral precursor molecules actually largely  
388 determined the observed NPF events.

389

390 Correlations between  $\log J_{1.34}$  and  $\log[H_2SO_4]$  (Figure 4) and between  $\log J_{1.34}$  and  
391  $\log[NH_3]$  (Figure 5) were examined to elucidate potential mechanisms for our NPF  
392 events. Since  $J_{1.34}$  could not be accurately determined on some of the NPF days, the  
393 number of data points in both figures was less than the actual number of NPF events  
394 that have been observed. Daily peak concentration of sulfuric acid proxy and daytime  
395 (6 am – 6 pm) averages of ammonia were used as approximations for their effective  
396 concentrations on a NPF day since there was no peak concentration for ammonia. The  
397 correlation ( $R^2=0.62$ ) between  $\log J_{1.34}$  and  $\log[NH_3]$  is better than that ( $R^2=0.38$ )

398 between  $\log J_{1.34}$  and  $\log [H_2SO_4]$ , and slopes are  $0.57 \pm 0.17$  and  $0.65 \pm 0.28$ ,  
399 respectively.

400

401 Most ambient studies showed that nucleation rate  $J$  is proportional to the first or  
402 second power of the concentration of gas-phase sulfuric acid, i.e.,  $J = A \cdot [H_2SO_4]^P$ ,  
403 where  $P$  is equal to 1 or 2, conventionally interpreted as the number of sulfuric acid  
404 molecules in the critical nucleus, and  $A$  is a pre-exponential factor (McMurry et al.,  
405 2005; Sihto et al., 2006; Erupe et al., 2010). Our  $P$  of  $0.65 \pm 0.28$  is of a significant  
406 uncertainty, which could come from the uncertainty during the calculation of sulfuric  
407 acid proxy  $[H_2SO_4]$  and the scarcity of our data points. The upper limit of our  $P$   
408 indicates that nucleation occurs after activation of clusters containing one molecule of  
409 sulfuric acid, with subsequent growth involving other species (Kulmala et al., 2006).  
410 The lower limit, on the other hand, suggests that a less important role of sulfuric acid  
411 in the critical nucleus during our campaign, which is unlikely to be true according to  
412 numerous previous studies (Weber et al., 1996; Sipila et al., 2010; Yu and Hallar,  
413 2014). Kupiainen-Määttä, et al. (2014) recently reported that the number of  
414 molecules in a critical cluster cannot be determined by a slope analysis in  
415 atmospherically relevant applications, underscoring the need to further explore the  
416 exact nucleation mechanism. Herrmann et al., (2014) also calculated the sulfuric acid  
417 proxy, related it to observed nucleation rates, and speculated that the sulfuric acid  
418 exponent might be well over 2, which underscores the reliability of calculation  
419 methods in a Chinese location. Hence, our preliminary result should be further tested  
420 with actual measurements of gas-phase sulfuric acid, but does indicate the key role of  
421 sulfuric acid in NPF events. On the other hand, linear correlation between  $\log J$  and  
422  $\log [NH_3]$  was observed in a previous nucleation study in Atlanta, GA, with a slope of  
423 1.17 (McMurry et al., 2005), but a clear relationship was not perceived at Kent, OH  
424 (Erupe et al., 2010). This discrepancy may come from the level of ammonia that has  
425 been predicted to have a saturation threshold (Napari et al., 2002) and/or the co-

426 existing sulfuric acid concentration (Benson et al., 2009). Nevertheless, our  
427 correlation between  $\log J$  and  $\log[NH_3]$  suggests that ammonia also participated in  
428 the nucleation. A recent CIMS study (Zheng et al., 2015) observed good correlations  
429 between  $NH_3$  and amines at an urban site of Nanjing, China. Hence, it is plausible that  
430 amines may contribute to nucleation in our site at Shanghai, too.

431

432 The subsequent growth of newly formed particles can be partially attributed to  
433 condensation of sulfuric acid. The theoretical maximum growth rate of 1.34-3 nm  
434 clusters/particles due to condensation of hydrated sulfuric acid at 50% RH  
435 ( $GR_{H_2SO_4(1.34-3)}$ ), calculated according to eq. 6 and 7, was  $3.9 \pm 1.3 \text{ nm h}^{-1}$  on average.

436 This rate is larger than the observed growth rates of clusters/particles from the bin of  
437 1.34-1.37 nm to the bin of 1.89-3.0 nm ( $GR_{1.35-2.39}$ ), being  $2.0 \pm 2.7 \text{ nm h}^{-1}$ , indicating  
438 that sulfuric acid proxy was enough to explain the observed growth for particles under  
439 3 nm. Similar calculation of  $GR_{H_2SO_4(3-7)}$  and  $GR_{H_2SO_4(7-20)}$  yielded  $2.8 \pm 0.94$  and  $2.2$   
440  $\pm 0.74 \text{ nm h}^{-1}$ , respectively. In figure 6, relative contributions of sulfuric acid to  
441 growth of particles in the range of 3-7 and 7-20 nm, respectively, on each NPF day is  
442 presented. Since 7 nm particles reached their maximum earlier than 3 nm particles on  
443 Jan. 9<sup>th</sup> and Jan. 15<sup>th</sup>, 2014, there was no calculated  $GR_{3-7}$  and hence no ratios  
444 available on these two days. In addition, condensation of hydrated sulfuric acid was  
445 more prominent for 3-7 nm particles on 6 NPF days (Nov. 25<sup>th</sup>, Nov. 26<sup>th</sup>, Nov. 30<sup>th</sup>,  
446 Dec. 10<sup>th</sup>, Dec. 11<sup>th</sup>, and Dec. 12<sup>th</sup> 2013), whereas it was more significant for 7-20 nm  
447 particles on the other 5 NPF days (Nov. 28<sup>th</sup> 2013, Nov. 29<sup>th</sup> 2013, Jan. 13<sup>th</sup> 2014, Jan.  
448 21<sup>st</sup> 2014, and Jan. 24<sup>th</sup> 2014). On average, condensation of gas-phase hydrated  
449 sulfuric acid explained 39.1% of  $GR_{2.39-7}$ , and 29.0% of  $GR_{7-20}$ , respectively. The rest  
450 of growth might be largely attributed to condensation of extremely low volatility  
451 organic compounds (Ehn et al., 2014), and potentially heterogeneous reactions of  
452 organics on nanoparticle surface (Wang et al., 2010; Wang et al., 2011).

453



### 454 3.4 NPF and Aerosol Surface Area

455 NPF events in urban environment are of special interests since the pre-existing  
456 particle surface may significantly scavenge the newly formed particles and change the  
457 probability of NPF. We plot number concentrations of 1.34-10 nm particles ( $N_{1.34-10}$ ),  
458 sulfuric acid proxy ( $[H_2SO_4]$ ), ammonia ( $[NH_3]$ ), and aerosol surface area with  
459 shadowed blocks representing NPF events in Figure 7. Note that  $N_{1.34-10}$  was used as  
460 an approximation for nucleation and subsequent growth while excluding particles  
461 from direct emission. The average daytime (6 am-6 pm)  $N_{1.34-10}$  on NPF days was  
462  $(2.7 \pm 2.1) \times 10^4 \text{ cm}^{-3}$ , much larger than  $(1.5 \pm 1.0) \times 10^4 \text{ cm}^{-3}$  on the rest days of the  
463 campaign, indicating that a stronger input of particles from nucleation processes on  
464 NPF days. However, daytime  $[H_2SO_4]$  did not show an apparent difference between  
465 on NPF days  $((3.7 \pm 1.2) \times 10^7 \text{ molecules cm}^{-3})$  and on the rest days  $((3.9 \pm 2.5) \times 10^7$   
466  $\text{molecules cm}^{-3})$ . For example, an episode with high daily sulfuric acid proxy during  
467 Dec. 19<sup>th</sup>, 2013 and Jan. 16<sup>th</sup>, 2014 did not lead to any NPF events. Instead, observed  
468 NPF events occurred on days with low aerosol surface area levels and moderate  
469  $[H_2SO_4]$ . During our campaign, NPF days were characterized with low aerosol  
470 surface area  $((7.8 \pm 3.8) \times 10^8 \text{ nm}^3 \text{ cm}^{-3})$ , whereas the average was  $(10.4 \pm 4.7) \times 10^8 \text{ nm}^3$   
471  $\text{cm}^{-3}$  on the rest days of the campaign. Ammonia varied dramatically, even within a  
472 single day. NPF events occurred on days with around 10-fold difference in ammonia  
473 concentrations. According to ammonia's profile and its positive correlation with  $J_{1.34}$ ,  
474 we speculate that ammonia was involved in nucleation but it is not the driving force.

475

476 Examination of these parameters from Jan. 12<sup>th</sup> to Jan. 14<sup>th</sup>, 2014 was performed since  
477 the three days were characterized with similar meteorological conditions. The average  
478 daytime concentration of sulfuric acid proxy was 2.8, 2.3, and  $1.0 \times 10^7 \text{ molecules cm}^{-3}$   
479 on Jan. 12<sup>th</sup>, 13<sup>th</sup> and 14<sup>th</sup>, 2014, respectively. No NPF event was observed on Jan.  
480 14<sup>th</sup> at least partially because of the low sulfuric acid proxy. Appearance of a NPF

481 event on Jan. 13<sup>th</sup> and non-appearance on Jan, 12<sup>th</sup> could be explained by the high  
482 aerosol surface area on Jan. 12<sup>th</sup>, with maximum aerosol surface area up to  $1.8 \times 10^9$   
483  $\text{nm}^3 \text{cm}^{-3}$ , although similar sulfuric acid proxies existed between the two days. Hence,  
484 we conclude that, qualitatively, NPF processes in urban Shanghai occurred with low  
485 levels of aerosol surface and that high sulfuric acid favored NPF events when aerosol  
486 surface area was low. This conclusion is identical to that drawn from a Mexico City  
487 study where NPF events observed in the city correlated with elevated concentrations  
488 of sulfur dioxide and low particulate matter mass concentrations in the afternoon  
489 hours (Dunn et al., 2004).

490

#### 491 **4 Summary and Conclusions**

492 Atmospheric new particle formation is a significant source of atmospheric aerosol  
493 particles. Understanding NPF under the current levels of air pollution in China is of  
494 special scientific interests because the exact nucleation mechanism under urban  
495 environment remains elusive. From Nov. 25<sup>th</sup>, 2013 to Jan. 25<sup>th</sup>, 2014, a combination  
496 of one nano-CNC, one nano-SPMS, and one long-SPMS has been utilized to  
497 investigate atmospheric nucleation by measuring particle size distributions in the  
498 range of 1.34-615 nm at urban Shanghai, located in the east Yangtze River Delta.  
499 During this 62-day campaign, 13 NPF events were identified with strong burst of sub-  
500 3 nm particles and subsequent fast growth of newly formed particles. Together with  
501 nucleation frequency (21%), the obtained nucleation rate  $J_{1.34}$  ( $112.4\text{-}271.0 \text{ cm}^{-3} \text{ s}^{-1}$ ),  
502 condensation sink  $CS$  ( $0.030\text{-}0.10 \text{ s}^{-1}$ ), and aerosol surface area ( $(7.8 \pm 3.8) \times 10^8 \text{ nm}^3$   
503  $\text{cm}^{-3}$ ) on NPF event days clearly indicate that strong atmospheric new particle  
504 formation occurred in winter, urban Shanghai with competition between promotion  
505 from condensable vapors and scavenging by preexisting particles. The absolute values  
506 of  $J_{1.34}$  and  $CS$  are one to two orders of magnitude larger than those at locations with a  
507 pristine atmosphere (e.g., Kulmala et al., 2012) and semi-rural locations with very low  
508 pollution levels such as Kent, OH (Yu et al., 2014), as a reflection from the  
509 significantly-altered atmospheric background.

510

511 Our preliminary exploration on nucleation mechanism indicates that nucleation rate  
512  $J_{1.34}$  was proportional to a  $0.65 \pm 0.28$  power of sulfuric acid proxy. It is hence likely  
513 that observed NPF events could be explained by the activation theory. As Herrmann et  
514 al., (2014) doubted reliability of sulfuric acid proxy, accurate measurements of gas-  
515 phase sulfuric acid instead of calculation of a proxy is necessary to achieve an  
516 unambiguous conclusion. The positive correlation between  $J_{1.34}$  and gas-phase  
517 ammonia hints the involvement of ammonia in new particle formation, but its exact  
518 role cannot be determined without measurements of nucleating clusters, either.

519

520 A size-depend particle growth in the range of 1.34-20 nm has been observed in this  
521 study, consistent with predictions from nano-Köhler theory (Kulmala et al., 2004), and  
522 Kelvin-limited diffusion, surface, and volume growth laws (Kuang et al., 2012).  
523 Sulfuric acid proxy was enough to explain the observed growth for particles under 3  
524 nm, and contributed to 39.1% of  $GR_{2.39-7}$ , and 29.0% of  $GR_{7-20}$ , respectively. The rest  
525 of growth could be largely attributed to condensation of extremely low volatility  
526 organic compounds (Ehn et al., 2014), and potentially heterogeneous reactions of  
527 organics on nanoparticle surface (Wang et al., 2010; Wang et al., 2011).

528

529 Clearly, further long term measurements with integrated state-of-the-art measurement  
530 techniques are necessary to draw a comprehensive picture of atmospheric nucleation  
531 events in China. Currently, atmospheric sub-3 nm particle measurements are still  
532 scarce in China, not mentioning measurements of gas-phase sulfuric acid, nucleating  
533 clusters, and other potential precursors. Nevertheless, our study offers a very first  
534 measurement of sub-3 nm particles in urban Shanghai, and provides some of the  
535 preliminary mechanisms for NPF events in China.

536

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543

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**Table 1. Nucleation rate ( $J_{1.34}$ ), formation rate of 3 nm particles ( $J_3$ ), particle growth rates ( $GR_{1.35-2.39}$ ,  $GR_{2.39-7}$ , and  $GR_{7-20}$ ), condensation sink ( $CS$ ), sulfuric acid proxy ( $[H_2SO_4]$ ), number concentrations of 1.34-3 nm clusters/particles ( $N_{1.34-3}$ ), and total number concentrations of particles  $N_{1.34-615}$ , of each NPF event during this campaign**

Date	$J_{1.34}$ ( $\text{cm}^{-3} \text{s}^{-1}$ )	$J_3$ ( $\text{cm}^{-3} \text{s}^{-1}$ )	$GR_{1.35-2.39}$ ( $\text{nm h}^{-1}$ )	$GR_{2.39-7}$ ( $\text{nm h}^{-1}$ )	$GR_{7-20}$ ( $\text{nm h}^{-1}$ )	$CS$ <sup>e</sup> ( $10^{-2} \text{s}^{-1}$ )	$[H_2SO_4]$ <sup>e</sup> ( $10^7 \text{cm}^{-3}$ )	$N_{1.34-3}$ <sup>f</sup> ( $10^4 \text{cm}^{-3}$ )	$N_{1.34-615}$ <sup>f</sup> ( $10^4 \text{cm}^{-3}$ )	Ref.
Nov. 25 <sup>th</sup> , 2013	n.a. <sup>a</sup>	10.6	n.a.	12.4 <sup>b</sup>	38.3	4.7	2.7	3.3 <sup>g</sup>	6.3	this study
Nov. 26 <sup>th</sup> , 2013	n.a.	2.3	n.a.	0.32 <sup>b</sup>	n.a.	5.9	2.6	n.a.	n.a.	this study
Nov. 28 <sup>th</sup> , 2013	185.1	13.4	0.94	35.7	4.6	5.7	3.6	1.6	4.2	this study
Nov. 29 <sup>th</sup> , 2013	271.0	3.9	1.7	10.6	4.5	6.3	4.3	2.1	4.5	this study
Nov. 30 <sup>th</sup> , 2013	n.a.	n.a.	0.82	3.4	10.2	n.a.	3.1	1.5	n.a.	this study
Dec. 10 <sup>th</sup> , 2013	268.4	10.0	0.49	18.6	21.0	9.9	5.5	1.4	4.6	this study
Dec. 11 <sup>th</sup> , 2013	219.0	19.2	n.a.	5.1	9.6	10.2	6.4	1.1	4.5	this study
Dec. 12 <sup>th</sup> , 2013	190.3	7.6	n.a.	3.1	12.3	8.8	4.5	1.1	4.1	this study
Jan. 9 <sup>th</sup> , 2014	136.2	n.a.	8.1	n.a.	9.5	3.7	2.3	1.6	3.8	this study
Jan. 13 <sup>th</sup> , 2014	n.a.	2.7	n.a.	6.3	1.9	3.0	2.3	1.5	3.4	this study
Jan. 15 <sup>th</sup> , 2014	121.9	n.a.	0.56	n.a.	9.7	4.2	4.1	1.5	4.3	this study
Jan. 21 <sup>st</sup> , 2014	112.4	9.2	1.5	11.9	7.5	4.9	3.7	1.1	3.9	this study
Jan. 24 <sup>th</sup> , 2014	n.a.	8.1	n.a.	12.2 <sup>b</sup>	7.8	4.7	3.4	1.7	4.2	this study
<b>Mean</b>	<b>188.0</b>	<b>8.7</b>	<b>2.0</b>	<b>10.9</b>	<b>11.4</b>	<b>6.0</b>	<b>3.7</b>	<b>1.5</b>	<b>4.4</b>	this study
<b>Finland</b>	1.4	0.61	1.4	3.9	4.9	0.05-0.35				Kulmala et al. (2012)
<b>USA<sup>b</sup></b>	1.3					0.8		0.9		Yu et al. (2014)
<b>Atlanta</b>					3-20 <sup>c</sup>					Stolzenburg et al. (2005)
<b>Atlanta</b>			5.5-7.6							Kuang et al. (2012)
<b>Beijing</b>					1.2-8.0 <sup>c</sup>	2.4-3.6				Gao et al. (2012)
<b>Beijing</b>		3.3-81.4			0.1-11.2 <sup>c</sup>	0.58-4.3				Wu et al. (2007)
<b>Beijing</b>					2.7-13.9 <sup>c</sup>	0.6-8.4				Zhang et al. (2011)
<b>Beijing</b>		1.1-22.4			1.2-5.6 <sup>c</sup>	0.9-5.3				Yue et al. (2009)
<b>Nanjing</b>	33.2 <sup>i</sup>	1.1 <sup>j</sup>		6.3	8 <sup>d</sup>	2.4				Herrmann et al. (2014)
<b>Hong Kong</b>		3.6-6.9			1.5-8.4 <sup>c</sup>	1.0-6.2				Guo et al. (2012)
<b>Pearl River Delta</b>		2.4-4.0(rural)			4.0-22.7(rural)	2.3-3.3(rural)				Yue et al. (2013)
					10.1-18.9(urban)	3.5-4.6(urban)				

<sup>a</sup> Data were not available or could not be accurately determined; <sup>b</sup> Result were calculated from nano-SMPS data; <sup>c</sup> Shown here is  $GR_{3-30}$ ; <sup>d</sup> Shown here is  $GR_{7-30}$ ; <sup>e</sup> Daytime average (from 6:00 am to 6:00 pm); <sup>f</sup> 24hr-average; <sup>g</sup> Average values between 10 am and 4 pm; <sup>h</sup> Shown here are data in Kent, OH; <sup>i</sup> Shown here is  $J_2$ ; <sup>j</sup> Shown here is  $J_6$ .

## Figure Captions

**Figure 1.** Contour plot for particle size distributions of 3-615 nm and plot of number concentrations of sub-3 nm clusters/particles ( $N_{1.34-3}$ ) during Nov. 25<sup>th</sup>, 2013 - Jan. 25<sup>th</sup>, 2014. Data were occasionally missing because of the maintenance and minor breakdown of instruments. NPF events are illustrated with shadows.

**Figure 2.** Profiles of  $N_{1.34-3}$ ,  $N_{3-7}$ , and  $N_{7-30}$  from 6 am to 6 pm on a NPF day (Dec. 11<sup>th</sup>, 2013) and a non-NPF day (Jan. 7<sup>th</sup>, 2014), respectively.

**Figure 3.** Averaged particle size evolution on NPF days. Arithmetic mean of particle growth rates are given with one standard deviation.

**Figure 4.** Correlation between  $\log J_{1.34}$  and  $\log[H_2SO_4]$ . Daily peak concentration of sulfuric acid proxy was used as an approximation for its effective concentration on a NPF day. The error bar corresponds to a 42% uncertainty of sulfuric acid proxy according to Mikkonen et al., (2011).

**Figure 5.** Correlation between  $\log J_{1.34}$  and  $\log[NH_3]$ . Daytime average of ammonia was used as an approximation for its effective concentration on a NPF day. The error bar represents the standard deviation of the daytime average concentration of ammonia.

**Figure 6.** Relative contribution of sulfuric acid to growth of particles in the range of 3-7 and 7-20 nm, respectively, on each NPF day.

**Figure 7.** Number concentrations of 1.34-10 nm particles ( $N_{1.34-10}$ ), sulfuric acid proxy ( $[H_2SO_4]$ ), concentrations of ammonia, and aerosol surface area during the campaign. NPF events are illustrated with shadows.

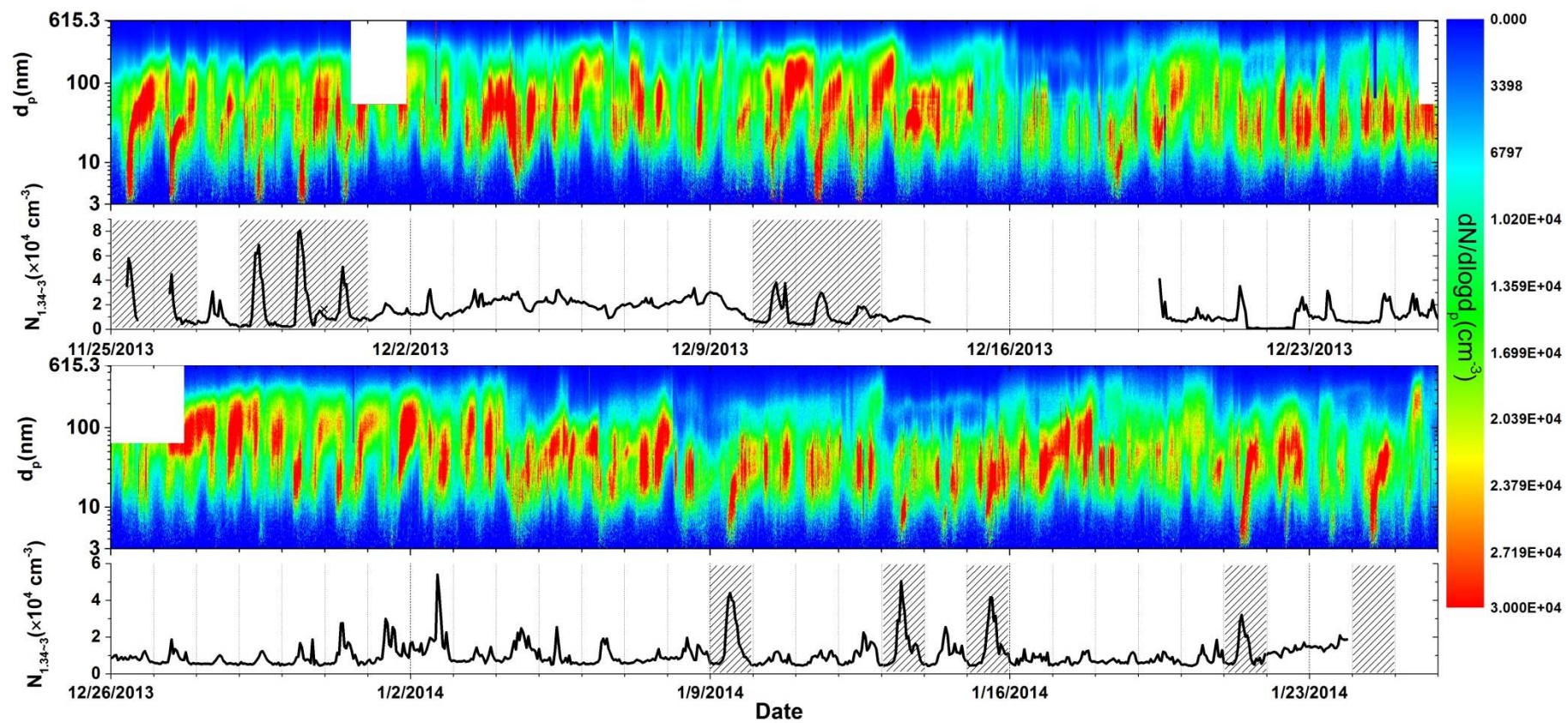
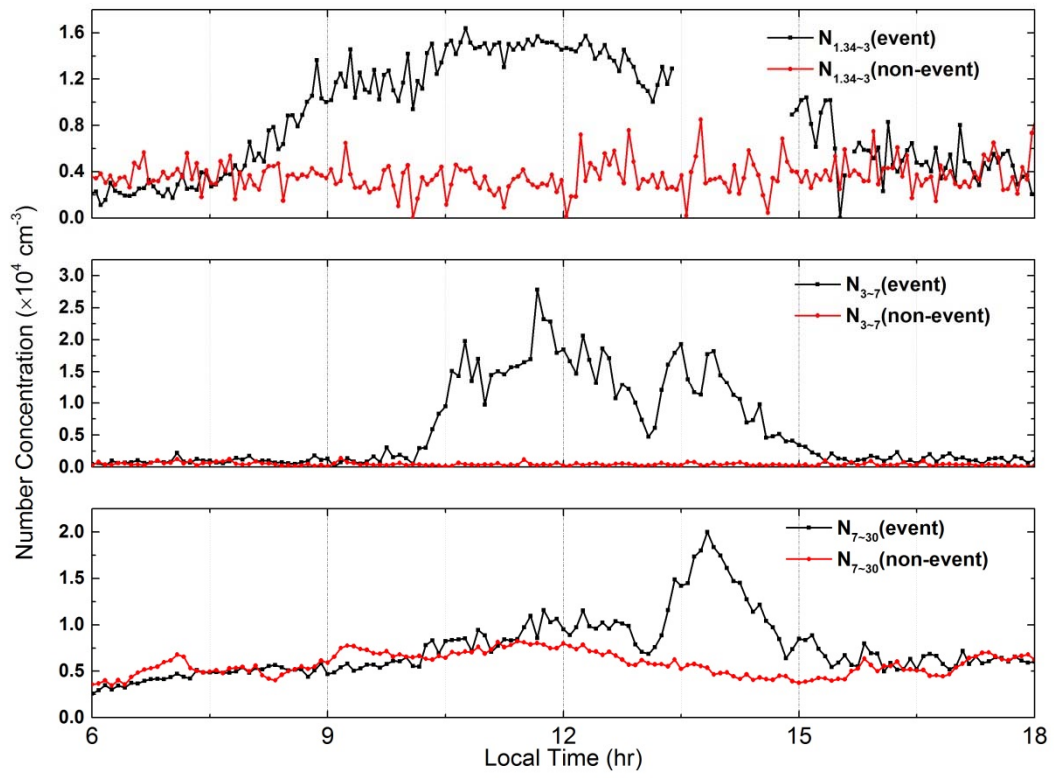


Figure 1.



**Figure 2.**

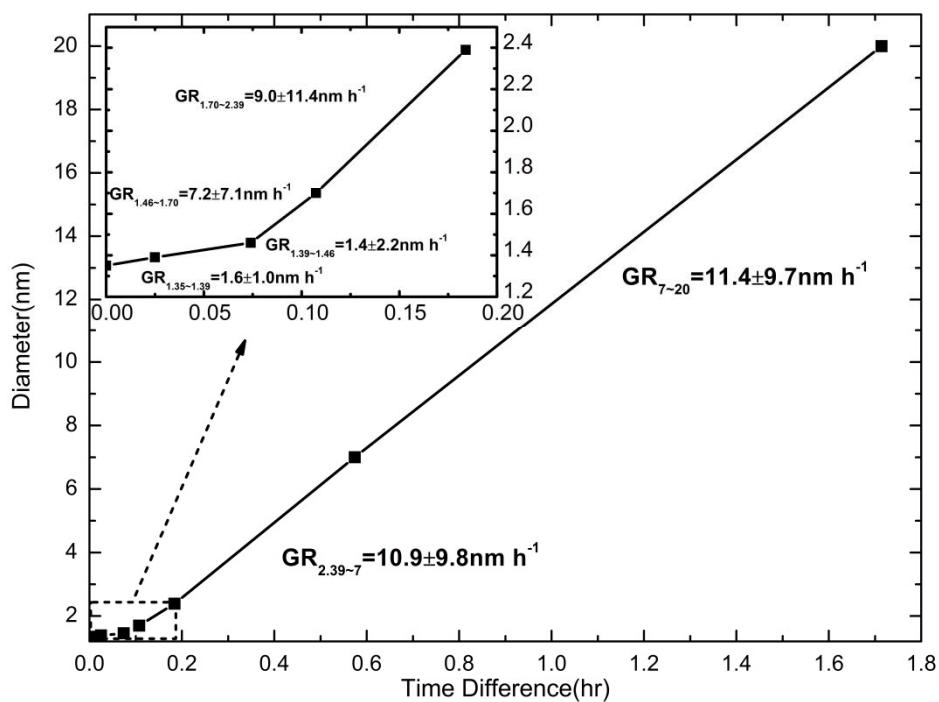


Figure 3.

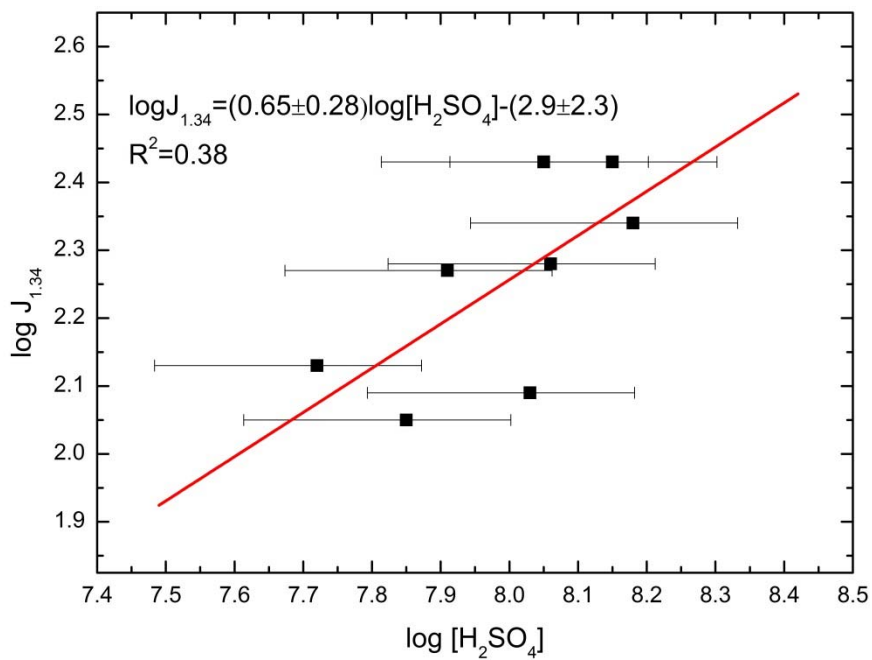
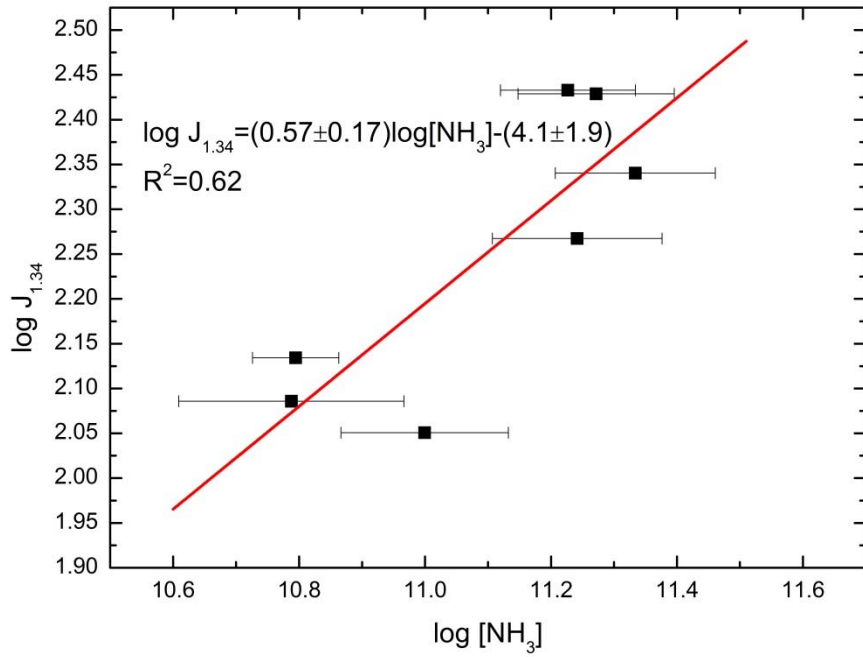
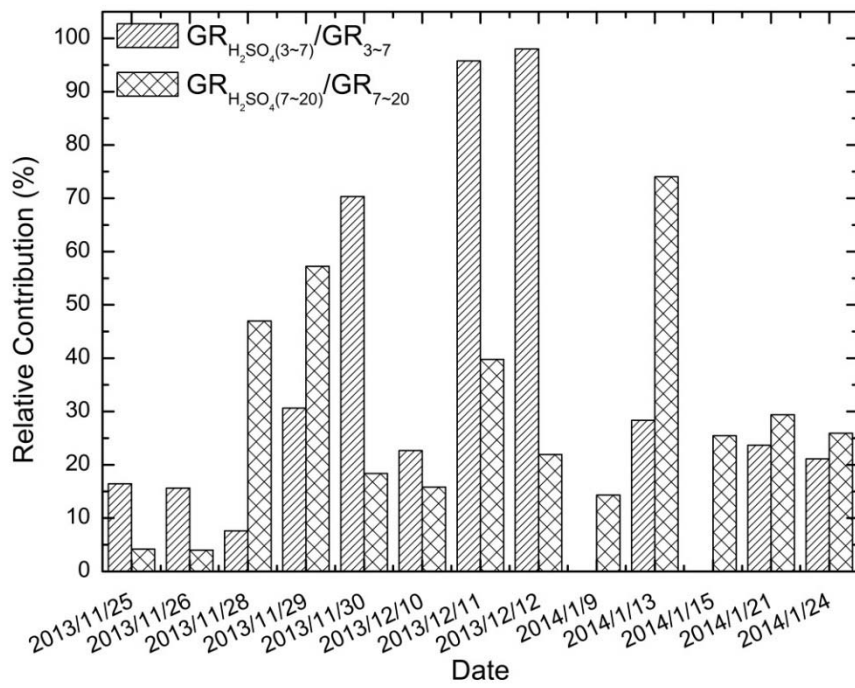


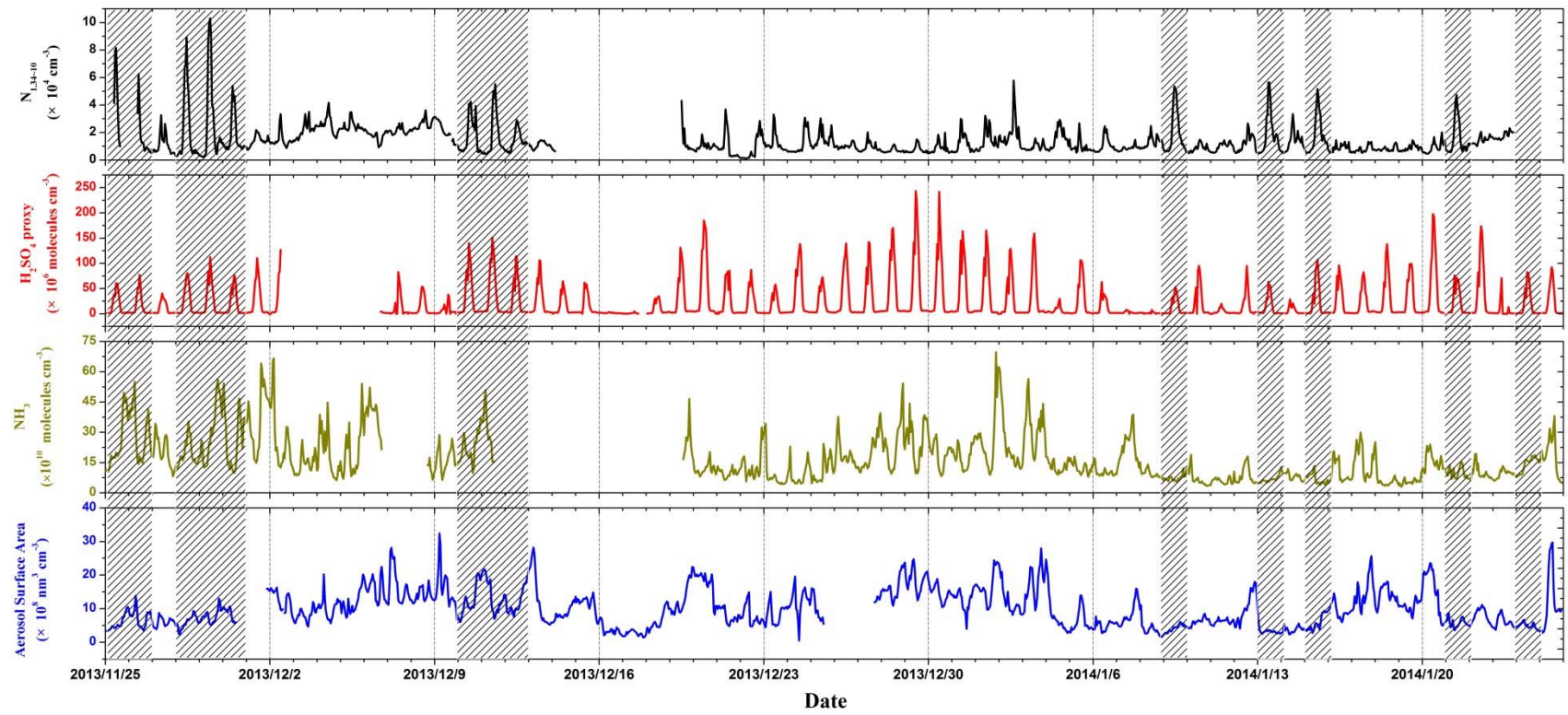
Figure 4.



**Figure 5.**



**Figure 6.**



**Figure 7**



