

1 **Insight into winter haze formation mechanisms based on aerosol**

2 **hygroscopicity and effective density measurements**

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9
10 **Abstract:** We characterize a representative particulate matter (PM) episode that occurred in Shanghai
11 during winter 2014. Particle size distribution, hygroscopicity, effective density, and single particle mass
12 spectrometry were determined online, along with offline analysis of water-soluble inorganic ions. The
13 mass ratio of SNA/PM_{1.0} (sulfate, nitrate, and ammonium) fluctuated slightly around 0.28, suggesting that
14 both secondary inorganic compounds and carbonaceous aerosols contributed substantially to the haze
15 formation, regardless of pollution level. Nitrate was the most abundant ionic species during hazy periods,
16 indicating that NO_x contributed more to haze formation in Shanghai than did SO₂. During the
17 representative PM episode, the calculated PM was always consistent with the measured PM_{1.0}, indicating

that the enhanced pollution level was attributable to the elevated number of larger particles. The number fraction of the near-hydrophobic group increased as the PM episode developed, indicating the accumulation of local emissions. Three “banana-shaped” particle evolutions were consistent with the rapid increase of PM_{1.0} mass loading, indicating that the rapid size growth by the condensation of condensable materials was responsible for the severe haze formation. Both hygroscopicity and effective density of the particles increased considerably with growing particle size during the banana-shaped evolutions, indicating that the secondary transformation of NO_x and SO₂ was one of the most important contributors to the particle growth. Our results suggest that the accumulation of gas-phase and particulate pollutants under stagnant meteorological conditions and subsequent rapid particle growth by secondary processes, were primarily responsible for the haze pollution in Shanghai during wintertime.

Keywords: air pollution; size distribution; hygroscopic growth; secondary process; Shanghai.

1. Introduction

Atmospheric aerosol has significant influences on radiation balance and climate forcing of the atmosphere (Wang et al., 2011; Wang et al., 2014c; Wu et al., 2016a; IPCC, 2013). Also, atmospheric aerosol has strong impacts on visibility (Yang et al., 2012; Lin et al., 2014; Xiao et al., 2014) and public health (Heal et al., 2012). Recent studies found that short-term exposure to haze pollution could cause airway inflammation and aggravate respiratory symptoms in chronic obstructive pulmonary disease

36 patients (Wu et al., 2016b;Guan et al., 2016).

37 With the huge achievements in economic development and rapid urbanization over the past 30 years,
38 particulate pollution has become a major environmental concern in China. The most severe haze event
39 that occurred in the first quarter of 2013, spread over 1.6 million km² (Wang et al., 2014a). This event
40 motivated the release of the Action Plan on Prevention and Control of Air Pollution with the goal of
41 reducing PM_{2.5} (particulate matter smaller than 2.5 μm in aerodynamic diameter) concentration by 15–25%
42 in 2017 against 2012 in three major city clusters
43 (http://english.mep.gov.cn/News_service/infocus/201309/t20130924_260707.htm). In order to reduce
44 the PM_{2.5} concentration, extensive studies have been conducted to investigate the sources and formation
45 mechanisms of haze pollution in recent years (Ye et al., 2011;Sun et al., 2016;Qiao et al., 2016;Hu et al.,
46 2016;Li et al., 2016;Guo et al., 2014;Zheng et al., 2015;Guo et al., 2013;Wang et al., 2016;Peng et al.,
47 2016). However, the haze formation mechanisms and source appointment of fine particles remain
48 uncertain.

49 Guo et al. (2013) summarized historical reports from 2000 to 2008 in Beijing and found that the
50 origins of urban fine particles varied in different seasons: the contribution of primary emissions is
51 comparable to that of secondary formation during winter heating periods whereas secondarily produced
52 aerosols dominate the fine PM sources in other seasons. As an important type of primary emissions in
53 urban area, black carbon (BC) is primarily from incomplete fossil fuel combustion. Light absorption of

54 BC aerosols is increased after atmospheric aging by coating with secondary materials and restructuring
55 (Khalizov et al., 2009). Due to cooling effect at the surface and warming effect aloft, the enhanced light
56 absorption and scattering by aged BC particles stabilize the atmosphere, hindering vertical transport of
57 gaseous and particulate pollutants (Wang et al., 2013). BC aging occurs much more efficiently in the
58 presence of highly elevated gaseous aerosol precursors so that light absorption increases by a factor of
59 2.4 within 4.6 h under highly polluted conditions in Beijing, significantly exacerbating pollution
60 accumulation and strongly contributing to severe haze formation (Peng et al., 2016).

61 Due to the implement of several effective regulatory policies, the increasing trend of primary
62 emissions has been under control since the 11th five-year period. A growing number of studies suggested
63 that secondary production was the major contributor to the haze events in recent years (Shi et al.,
64 2014;Zhao et al., 2013;Zhang et al., 2015a;Huang et al., 2014), in contrast with the fact that primary
65 emissions were of great importance in some haze events (Niu et al., 2016). Guo et al. (2014) reported that
66 the development of PM episodes in Beijing was characterized by efficient nucleation and continuous
67 particle growth over an extend period dominated by local secondary formation. They attributed the
68 continuous growth of particle size and constant accumulation of particle mass concentration to the highly
69 elevated concentrations of gaseous precursors such as NO_x, SO₂, and volatile organic compounds (VOCs),
70 while the contribution from primary emissions and regional transport was negligible. However, the role
71 of regional transport of PM_{2.5} in haze formation remains controversial (Li et al., 2015;Zhang et al., 2015b).

72 The most important advances in the understanding of urban PM formation were reviewed by Zhang
73 et al. (2015c). The concentrations of SO₂, NO_x, and anthropogenic source VOCs in Beijing and other
74 cities of the developing world are significantly higher than those in the urban areas of developed countries,
75 resulting in large secondary production of sulfate, nitrate, and SOA. Synergetic effects among various
76 organic and inorganic compounds may exist under highly polluted conditions, indicating different PM
77 formation rates between developing and developed urban regions. Indeed, a large enhancement of
78 particulate sulfate was typically observed during regional haze events in China (Chen et al., 2016; Wang
79 et al., 2015; Fu et al., 2008; Xie et al., 2015). Currently, the highly elevated sulfate concentration during
80 haze events cannot be fully explained by model simulations (Wang et al., 2014b; Chen et al., 2016).
81 Recently, a significant breakthrough made by Wang et al. (2016) has provided a reasonable explanation
82 about the high level of sulfate during haze events. It was revealed by their laboratory experiments that the
83 aqueous oxidation of SO₂ by NO₂ proceeds more efficiently with the increase of NO₂ concentration
84 whereas the reaction is suppressed in acid conditions, because acid effect reduces the solubility of SO₂
85 and reaction rate. The enhanced sulfate formation during severe haze periods in Beijing was attributable
86 to aqueous oxidation of SO₂ by NO₂ on hygroscopic fine particles under conditions of elevated RH and
87 the concentrations of NH₃ and NO₂, as confirmed by the comparable SO₂ uptake coefficients for sulfate
88 formation from field and laboratory results.

89 The hygroscopic properties of ambient particles vary significantly depending on the origin of the air

90 masses and the atmospheric aging process. In urban air, the population of near-hydrophobic particles can
91 be assumed to consist largely of freshly emitted combustion particles containing high mass fractions of
92 soot and water-insoluble organic compounds (Swietlicki et al., 2008;Massling et al., 2009). In contrast,
93 secondary sulfate or nitrate aged particles are more-hygroscopic, and their relative abundance is primarily
94 responsible for the hygroscopic growth of ambient particles at elevated RH (Topping et al.,
95 2005;Aggarwal et al., 2007;Gysel et al., 2007). Thus, hygroscopicity can serve as a tracer of source origins,
96 mixing state, and aging mechanisms of ambient particles. For example, the temporal variation of aerosol
97 hygroscopicity has thrown some new light on haze formation mechanisms in Beijing and Shanghai (Ye
98 et al., 2011;Guo et al., 2014).

99 Density is one of the most important physicochemical properties for atmospheric aerosols. Effective
100 density has served as a tracer for new particle formation and for the aging process in previous studies (Yin
101 et al., 2015;Guo et al., 2014). The ambient particles in urban areas are mostly complex mixtures of
102 elemental carbon (EC), organics (OC), and secondary inorganic aerosols (SIA) (Hu et al., 2012). The
103 effective density of nascent traffic particles varies from approximately 0.9 g cm^{-3} to below 0.4 g cm^{-3} ,
104 decreasing with the increase of particle size, because there are more voids between primary particles in
105 relatively larger aggregates (Momenimovahed and Olfert, 2015). The effective density of OC is in
106 between those of EC and SIA, and varies with source. The effective density of combustion particles
107 increases by filling the voids in the agglomerate particles with condensed semi-volatile materials, or by

108 restructuring agglomerates with hygroscopic SIA (Momenimovahed and Olfert, 2015;Zhang et al., 2008).

109 In this study, a combined HTDMA-APM system was used to investigate the variations of
110 hygroscopicity and effective density of submicrometer aerosols during winter 2014 in urban Shanghai. In
111 addition, cascade impactor samples were collected and temporal variations of particle composition were
112 determined by a single particle mass spectrometry, which provided further insight into the hygroscopicity
113 and density variations. The primary objectives of this study were to investigate the particle growth
114 mechanisms and to identify the contribution of local emissions during the winter haze events.

115

116 **2. Experimental**

117 **2.1. Sampling site**

118 The measurements of particle hygroscopicity and effective density were conducted from December 21,
119 2014 to January 13, 2015 at the Department of Environmental Science and Engineering in the main
120 campus of Fudan University (31.30°N, 121.5°E). It can be considered as a representative urban site for
121 Shanghai. There are many dwelling quarters and commercial blocks in surrounding area. About 400 m
122 away from the measurement site, there is the Middle Ring Line, one of the busiest elevated roads in the
123 city.

124 **2.2 Measurements of air quality index and ground meteorological parameters**

125 At a supersite about 100 m away from the Environmental Building, PM_{1.0} was monitored using a

126 Thermo Scientific™ 5030 SHARP monitor. Trace gas pollutants were monitored using Thermo
127 Scientific™ i-series gas analyzers (43i for SO₂, 49i for O₃, 42i for NO/NO₂/NO_x), and meteorological
128 data were monitored using an automatic meteorological station (Model CAWS600, Huayun Inc., China)
129 (Yin et al., 2015). The datas of PM_{2.5}, PM₁₀, and CO were released by the Shanghai Environmental
130 Monitoring Center. The height of the Planet Boundary Layer (PBL) was computed online using the NCEP
131 Global Data Assimilation System (GDAS) model (<http://ready.arl.noaa.gov/READYamet.php>).

132 **2.3. HTDMA-APM system**

133 Particle size distribution, hygroscopic growth factor (GF), and effective density were measured using
134 a custom-built HTDMA-APM system (Figure 1). The custom-built HTDMA (Hygroscopic Tandem
135 Differential Mobility Analyzers) mainly consist of two long DMAs (3081L, TSI Inc.), a humidifier (PD-
136 50T-12MSS, Perma Pure Inc.) and a Condensation Particle Counter (CPC, Model 3771, TSI Inc.). A
137 detailed description of the HTDMA is available in Ye et al. (2009). In this observation, particle number
138 size distribution in the range of 14–600 nm and hygroscopic growth at 83% RH for particles with dry
139 diameters of 40, 100, 220, 300, 350, and 400 nm were determined by HTDMA in turn. The determination
140 of effective density by DMA-APM was described previously (Yin et al., 2015; Pagels et al., 2009). Briefly,
141 a combined system consisting of a compact Aerosol Particle Mass Analyzer (APM, Model 3601,
142 Kanomax Inc.) and a CPC (Model 3775, TSI Inc.) was connected to the sample tubing through a 3-way
143 electrical switch behind the upstream DMA (DMA1). The APM comprises two coaxial cylindrical

144 electrodes rotating at the same angular velocity. Charged aerosol particles of a certain diameter sized by
145 DMA1 are axially fed into the annular gap between the electrodes and experienced an outward centrifugal
146 force from the particle rotating and an inward electrostatic force from the high-voltage field between the
147 electrodes. Particles pass through the APM and are sent to the CPC when the two forces are balanced.
148 The mass of particles that pass through the APM is determined by the rotation rate and the applied voltage.
149 Effective densities for dry diameters of 40, 100, 220, and 300 nm were determined by the method of
150 DMA-APM in this study. The HTDMA-APM was operated alternatively in HTDMA mode and then
151 DMA-APM mode, for every 40 min.

152 Before the field observation, the HTDMA-APM was calibrated using 40–450 nm NIST-Traceable PSL
153 particles and ammonium sulfate. The measured HTDMA data were inversed with the $TDMA_{inv}$ algorithm
154 to obtain the actual GF distribution. This is because the raw data are only a skewed and smoothed
155 integral transform of the actual growth factor probability density function (GF-PDF) (Gysel et al., 2009).
156 The hygroscopicity parameter κ was derived from the GF data after inversion with the $TDMA_{inv}$ algorithm
157 according to the κ -Köhler theory (Petters and Kreidenweis, 2007).

158 **2.4. SPAMS**

159 A Single Particle Aerosol Mass Spectrometry (SPAMS, Hexin Analytical Instrument Co., Ltd., China)
160 installed in the same room with the HTDMA-APM system was used to obtain the chemical and size
161 information of individual particles in the range of 0.2-2 μm . Detailed information on SPAMS is available

162 in Li et al. (2011). Briefly, ambient particles are drawn into a vacuum chamber through an aerodynamic
163 focusing lens and accelerated to a size-dependent terminal velocity. Sized particles are desorbed and
164 ionized by the pulsed desorption/ionization laser (Q-switched Nd: YAG, $\lambda=266$ nm) at the ion source
165 region. Both positive and negative mass spectra for a single particle are recorded by a bipolar time-of-
166 flight spectrometer. The single particle information was imported into YAADA (version 2.11,
167 www.yaada.org). Based on the similarities of the mass-to-charge ratio and peak intensity, particles were
168 classified using the ART-2a method.

169 **2.5. Ion chromatography**

170 Cascade impactor aerosol samples for offline analysis were collected at the roof platform of the
171 Environmental Building using a 10-stage MOUDI sampler (Micro-Orifice Uniform Deposit Impactor,
172 Model 110-NR, MSP Corp., USA). Detailed description of the sampling, pretreatment, chemical analysis,
173 and quality control of this system is available in Tao et al. (2016). Briefly, cascade impactor samples were
174 collected every 24 h using the PALL7204 quartz filter as the collection substrate. Each filter was weighted
175 with a BP211D electronic balance at $25\pm1^\circ\text{C}$ and $40\pm2\%\text{RH}$. The water extract of each sample was
176 analyzed using an Ion Chromatograph (Metrohm 883 basic IC plus, Switzerland) equipped with a third-
177 party column heater (CT-100, Agela Corp., China). Seven anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^{2-} and PO_4^{3-})
178 were resolved using a Metrosep A Supp 5-250/4.0 column at 35°C with an eluent of $3.2\text{ mmol L}^{-1}\text{ Na}_2\text{CO}_3$
179 + $1.0\text{ mmol L}^{-1}\text{ NaHCO}_3$. Six cations (Li^+ , Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}) were separated by a Metrosep

180 C4-250/4.0 column at 30°C with an eluent of 1.7 mmol L⁻¹ HNO₃ + 0.7 mmol L⁻¹ 2,6-pyridine
181 dicarboxylic acid.

182

183 3. Results and discussion

184 3.1. Periodic cycle of PM episodes during the observation period

185 Figure 2 shows the temporal variations of PM mass loading during the winter observation (December
186 21, 2014 to January 13, 2015). The official data of PM_{2.5} and PM₁₀ were blank on some clean days.
187 Meteorologically, our measurement was deployed in a typical winter period. The average concentrations
188 of PM_{1.0}, PM_{2.5}, and PM₁₀ were 57 ± 37 , 87 ± 67 , and 129 ± 78 $\mu\text{g m}^{-3}$, respectively. About 62% of hourly
189 averaged PM_{2.5} concentrations exceeded 75 $\mu\text{g m}^{-3}$ of the Chinese Grade II guideline (GB 3095-2012),
190 indicating heavy particle pollution in Shanghai during wintertime. The PM episodes exhibited a clear
191 periodic cycle of ~5 days. A similar feature was previously observed in Beijing (Guo et al., 2014). At the
192 beginning of each cycle, the PM_{1.0} level was below 35 $\mu\text{g m}^{-3}$. Generally, the difference between the
193 concentrations of PM_{1.0} and PM_{2.5} during clean days was less significant than that in haze periods.
194 Occasionally the measured PM_{2.5} concentrations were larger than those of PM₁₀, possibly due to system
195 error. However, the particle mass concentration began to increase in the next few days, with PM_{1.0} and
196 PM_{2.5} peaking at over 100 and 200 $\mu\text{g m}^{-3}$, respectively. During the end of each PM episode, the change
197 in weather conditions played a key role in the decrease of particle concentration. As shown in Figure S1,

the prevailing winds on haze days were from the northwest. The prevailing winds during two clean periods (December 25-27 and January 12-14) were northeasterly, bringing clean air mass from East China Sea. Two cold fronts from the north swept Shanghai on December 31 and January 6, bringing gale and lower temperature which favored the dispersion of atmospheric pollutants.

3.2 Contributions of secondary inorganic aerosols to PM_{1.0} mass loading

Figure 3 illustrates the daily concentrations of sulfate, nitrate, and ammonium as a function of PM_{1.0} mass loading. In general, the sum of concentrations of sulfate, nitrate, and ammonium (SNA) increased linearly as the PM_{1.0} mass loading increased. It is noticeable that the SNA/PM_{1.0} ratio slightly fluctuated around 0.28, regardless of the pollution level. Because soil dust and sea salt made a negligible contribution to the fine particle mass concentration in this study, the almost constant ratio of SNA/PM_{1.0} indicates that SNA and carbonaceous aerosols (including soot and organic matter) synchronously increased during the haze events. As the PM_{1.0} concentration increased, the concentration of nitrate increased more rapidly than sulfate so that it became the most abundant ionic species at PM_{1.0} > 40 μg m⁻³. This finding indicates that NO_x contributed more to haze formation in Shanghai compared to SO₂. Generally, the visibility decreased with the increase in PM concentration, indicating photochemical activity began to weaken as the development of haze events. The large increase in nitrate concentration may be attributable to heterogeneous reaction on the preexisting particles. Nitrate formation is highly dependent on the surface area of preexisting particles and is favored under NH₃-rich conditions (Chu et al., 2016). In contrast, Han

et al. (2016) reported that the mass ratio of nitrate to sulfate decreased with the increase of $PM_{2.5}$ level and that the sources of sulfate contributed more to the haze formation in Beijing than mobile sources. This finding suggests that the haze formation mechanism in Shanghai is likely different from that in Beijing. VOCs and NO_x are exclusively from local emissions whereas regional transport is a big source of SO_2 under stagnant atmosphere, due to different atmospheric lifetimes among SO_2 , NO_x , and VOCs (Guo et al., 2014). Considering the relatively smaller contribution of sulfate, our results reveal that the accumulation and secondary transformation of local emissions likely played a dominant role in this haze formation.

3.3 Aerosol hygroscopicity and effective density during the observation period

Figure 4a displays a box chart of the mean hygroscopicity of each hygroscopic growth factor distribution for different sizes. Considering all of the growth factor distributions collectively, the hygroscopicity parameter κ increased with increase of the dry diameter, with a mean κ of 0.161 at 40 nm and 0.338 at 300 nm. Assuming a two-component system of a model salt (ammonium sulfate, $\kappa_m = 0.53$) and an insoluble species ($\kappa = 0$), the volume fraction of hygroscopic species (ϵ) can be obtained based on the Zdanovsldi-Stokes-Robinson (ZSR) mixing rule. The average ϵ was 0.3 for 40 nm particles, suggesting that the primary particles or initial growth of freshly generated particles were dominated by non-hygroscopic species. In contrast, the 300 nm particles were extremely aged, with more-hygroscopic species.

234 Generally, HTDMAs measure dry particles smaller than 300 nm due to technical limitations, and it is
235 common that particle hygroscopicity increases with the increase of particle size (Liu et al.,
236 2014;Swietlicki et al., 2008). The increase of particle hygroscopicity with particle size was attributed to
237 the addition of more-hygroscopic SNA (Swietlicki et al., 2008;Ye et al., 2010). The very few
238 measurements for dry particles larger than 300 nm showed different size dependencies. Gasparini et al.
239 (2006) reported that particle hygroscopicity first increased and then decreased with the increase of particle
240 size, peaking at the diameter of 300 nm. In contrast, Wu et al. (2016c) reported that particle hygroscopicity
241 increased with particle diameter in the range of 35-350 nm. In this study, the determination size range
242 was extended to 400 nm and the mean κ s of 300, 350, and 400 nm particles were nearly equal. We attribute
243 the different size dependencies of hygroscopicity among various measurement sites to the total emissions
244 of SO₂ and NO_x, gas precursors of hygroscopic sulfate and nitrate. It is noticeable that the 5th percentile
245 hygroscopicity decreased for dry diameter larger than 300 nm, likely due to the presence of the smallest
246 dust particles (Gasparini et al., 2006). The variability of hygroscopicity parameter κ was much greater for
247 40 nm particles. The particle population with $\kappa < 0.1$ was attributed to fresh traffic particles (Ye et al.,
248 2013). The considerable percentile of $\kappa < 0.1$ indicates that the 40 nm particle population was sometimes
249 dominated by near-hydrophobic particles.

250 Figure 4b displays a box chart of median effective density for different particle sizes. The median
251 effective density varied in the narrow range of $\rho_{\text{eff}} = 1.35\text{--}1.41 \text{ g cm}^{-3}$ for 40–300 nm particle population.

252 The size dependency of particle effective density varied in the literature. Hu et al. (2012) and Yin et al.
253 (2015) reported that effective density of the particles increased as particle size increased while a opposite
254 trend was observed by Geller et al. (2006) and Spencer et al. (2007). The different trends were attributable
255 to the variable fraction of lower density mode particles ($\rho_{\text{eff}} < 1.0 \text{ g cm}^{-3}$). The densities of the secondarily
256 produced $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and NH_4NO_3 are $\sim 1.75 \text{ g cm}^{-3}$. The effective density of organic aerosols
257 varies mostly in the range of $1.2\text{-}1.6 \text{ g cm}^{-3}$, depending on their source origins (Malloy et al., 2009; Turpin
258 and Lim, 2001; Dinar et al., 2006). The lower density particles with $\rho_{\text{eff}} < 1.0 \text{ g cm}^{-3}$ were attributable to
259 fresh or partially aged traffic-related particles, because the number fraction of the lower density group in
260 urban area was found to be consistent with the concentration of NO (indicator of traffic) (Levy et al.,
261 2013; Rissler et al., 2014). Although the dominant accumulation mode particles have an effective density
262 greater than Aitken mode ones, the presence of a lower effective density group associated with traffic
263 emissions might decrease the mean effective density to a value lower than that of Aitken mode particles
264 (Levy et al., 2014). Yin et al. (2015) reported that effective density distributions were dominated by a
265 single peak in the previous observation. In contrast, a lower density peak below 1.0 g cm^{-3} was often
266 present in this observation, decreasing the mean effective density of externally mixed aerosols.

267 **3.4 Characteristics of a representative PM episode**

268 As shown in Figure 2, the PM episode from January 7 to 12 was a representative case of severe haze
269 formation and elimination processes. It can be divided into clean (January 7), transition (January 8), haze

270 (January 9–11), and post-haze (January 12) periods. During the transition from the clean period to haze
271 period (January 7 to 8), both $\text{PM}_{1.0}$ and $\text{PM}_{2.5}$ concentrations increased slightly, with an average
272 $\text{PM}_{1.0}/\text{PM}_{2.5}$ ratio of 0.65. A sharp increase in $\text{PM}_{2.5}$ (of $125 \mu\text{g m}^{-3}$) was observed from 6:00 to 12:00
273 local time on the morning of January 9. During the haze period, the concentration of $\text{PM}_{2.5}$ exceeded 115
274 $\mu\text{g m}^{-3}$ (medially polluted level, HJ633-2012) for 63 h. On January 11, the hourly $\text{PM}_{2.5}$ concentration
275 exceeded $250 \mu\text{g m}^{-3}$, corresponding to the severely polluted level.

276 Figure 5 displays the temporal profile of particle size distribution, along with the measured $\text{PM}_{1.0}$
277 concentration during the representative PM episode. The calculated PM concentrations (PM_{cal}) were
278 obtained based on the particle size distribution and average effective density of 1.39 g m^{-3} in the range of
279 14–600 nm measured in this study. It is noticeable that the temporal trends in mass concentrations of
280 PM_{cal} and $\text{PM}_{1.0}$ are highly consistent. In contrast to the fact that particle size distribution was dominated
281 by nanoparticles during the clean period, the burst of Aitken mode particles and subsequent continuous
282 growth to approximately 200 nm in diameter was observed three times during the haze period, indicating
283 that the presence of numerous larger particles is likely responsible for the severe particle pollution (Guo
284 et al., 2014). The importance of larger particles in haze formation is also illustrated by the contour plot of
285 the particle volume size distribution. The difference of particle number concentration between transition
286 and haze periods was less significant, whereas the volume concentration increased considerably during
287 the haze period. This feature clearly demonstrates that the haze formation was closely correlated with

288 particle growth and elevated number of larger particles.

289 Interestingly, the particle mass concentration was sensitive to variations of wind speed and planetary
290 boundary layer (PBL). During the transition and haze periods, the wind speed decreased considerably
291 with insignificant change in prevailing wind (Figure S1). This finding indicates that outside transportation
292 became less and less significant. It is noteworthy that the temporal evolution of the particle mass
293 concentration was inversely correlated with the PBL height. The decreasing PBL provided a stagnant
294 atmosphere that favored the accumulation of local emissions. This finding reveals that the severe haze
295 pollution was likely triggered by the adverse meteorological conditions. The impact of decreasing PBL
296 height on haze formation can also be evidenced by the variations of trace gaseous species (Figure S2).
297 During the PM episode, the concentrations of NO₂, SO₂, and CO displayed variation trends similar to that
298 of the particle concentration. The fluctuations of trace gas concentrations were caused by primary
299 emission and secondary processes. Noticeably, the concentration of NO increased dramatically in rush
300 hours during the haze period, whereas it fluctuated slightly during the clean period; indicating that local
301 emissions were easily accumulated under stagnant atmosphere. In addition, the maximum concentration
302 of O₃ remained considerably higher during daytime, whereas it decreased significantly at night. The most
303 plausible explanation is that O₃ was consumed rapidly by the accumulated trace gases, such as NO_x, and
304 VOCs.

305 **3.5 Variations of hygroscopicity and effective density during the PM episode**

306 Figure 6 shows the averaged hygroscopicity and effective density for different pollution periods of the
307 PM episode. Regardless of the pollution period, the nearly-hydrophobic particles were externally mixed
308 with some hygroscopic particles. During the clean period, the more-hygroscopic particles dominated the
309 40 nm particle population, indicating that the near-hydrophobic primary particles were rapidly dispersed
310 due to atmospheric dilution. The number fraction of the near-hydrophobic group for different sizes
311 increased as the PM episode developed, indicative of the increasing accumulation of local emissions.
312 Notably, the increase of the near-hydrophobic particles with the evolution of the PM episode become less
313 significant as particle size increased, indicating that primary emission exerted a more significant impact
314 on smaller particles than on larger ones. The median diameter of nascent traffic particles from various
315 gasoline sources ranged between 55 and 73 nm with an average of 65 nm (Momenimovahed and Olfert,
316 2015). Therefore, the number fraction of the near-hydrophobic particles larger than 200 nm is not sensitive
317 to the accumulation of traffic emissions.

318 Interestingly, the variations of particle effective density for different sizes are in good agreement with
319 the hygroscopicity. The dominant peak of effective density distribution appeared at $\rho_{\text{eff}} = \sim 1.5 \text{ g cm}^{-3}$ for
320 40 nm particles in the clean period, indicating that they are highly aged with hygroscopic inorganic salts
321 (Yin et al., 2015). As the episode developed, the mean density shifted to lower values, indicating the
322 increasing contribution of lower density carbonaceous materials. The averaged density distribution was
323 broadened as the episode developed, suggesting that it could be deconvolved into two groups and that the

324 number fraction of the low-density group increased. This finding revealed that the lower density particles
325 are less hygroscopic whereas the larger density group corresponds to the more-hygroscopic one. In
326 addition, the variations of hygroscopicity and effective density coincided with the evolution of PBL height,
327 indicating that the increasing accumulation of local emissions due to adverse atmospheric conditions is
328 likely responsible for the enhancement of those near-hydrophobic and lower density particles.

329 Figure 7 displays the temporal profiles for contributions of EC (including bare EC and OC-coated EC),
330 OC, sulfate, and nitrate determined by SPAMS. Obviously, the relative contribution of nitrate increased
331 as the episode developed. In contrast, the relative contribution of sulfate displayed an opposite trend. This
332 feature is comparable with the aforementioned results of SNA, thus further highlighting the important
333 role of nitrate in haze formation in Shanghai. The number fraction of EC particles generally increased
334 during the haze period, peaking at midnight on January 9 and 10. It should be pointed out that the
335 measured number fraction possibly underestimated the contribution of EC particles because the dominant
336 size range of fresh traffic particles is below the detection limit of SPAMS (0.2–2.0 μm). This finding
337 provides good support for the increase of near-hydrophobic and lower density particles as the episode
338 developed. Niu et al. (2016) reported that the number ratio of secondary particles to soot in haze samples
339 was higher than that collected in the clean days in Beijing. Our finding is comparable to their results. In
340 contrast, the number fraction of pure OC decreased during the pollution event. The possible explanation
341 is that the condensation of organic matter was favored on the large amount of preexisting EC particles, or

that photo-oxidation of VOCs was minimized due to lower solar radiation.

3.6 Evolutions of hygroscopicity and effective density with particle growth

As shown in Figure 5, three “banana-shaped” evolutions of the particle size distribution were identified in the representative PM episode. The banana-type contour plot of particle size distributions is a typical characteristics of new particle formation (NPF) events and traditionally regarded as one of the most important criteria for identifying NPF (Xiao et al., 2015; Dal Maso et al., 2005; Levy et al., 2013; Zhang et al., 2012). Atmospheric NPF is often defined by the burst of nucleation mode particles and subsequent growth of the nuclei to larger particles (Zhang et al., 2012; Kulmala et al., 2012). Gas-phase sulfuric acid produced via oxidation of SO₂ by OH radical plays a dominant role in the NPF events. NPF is typically completely suppressed when preexisting particles is abundant, because gas-phase sulfuric acid is rapidly lost to the surfaces of preexisting aerosols (Zhang et al., 2012). In addition to sulfuric acid, low-volatility organic species, and interaction between sulfate and organics are important for NPF (Zhang et al., 2004; Zhao et al., 2009). However, the possibility of NPF can be ignored in this study due to the absence of the burst of nucleation mode particles and the high concentration of PM_{1.0}. The burst of Aitken mode particles in the current study may be attributable to rapid accumulation of traffic emissions during rush hours under stagnant atmospheric conditions. The “banana-shaped” particle growth in the time evolution of particle size distribution from the Aitken mode size range to accumulation mode size range was primarily due to coagulation and condensation processes. This feature provided an excellent opportunity

360 to reveal the chemical mechanism of particle growth during the PM episode.

361 The first “banana-shaped” evolution of the particle size distribution occurred from approximately
362 05:00 to 15:00 on January 9, with increase of the particle number concentration (N_{total}) from 1.7×10^4 to
363 $3.4 \times 10^4 \text{ cm}^{-3}$ followed by a decrease trend until 17:00 (Period 1). The second “banana-shaped” evolution
364 occurred from approximately 18:00 on January 9 to approximately 12:00 on January 10 (Period 2). The
365 N_{total} increased from 2.1×10^4 to $4.2 \times 10^4 \text{ cm}^{-3}$ within 3 h, followed by gradual decrease of N_{total} in contrast
366 to a continuous increase of the particle mass concentration. During the growth process, the mode diameter
367 of the particle population increased from below 40 nm to approximately 200 nm. The third “banana-
368 shaped” evolution began in the evening rush hours on January 10, with the continuous increase of PM
369 mass concentration for 12 h (Period 3). The latter two banana-shaped evolutions lasted long enough to
370 tracer the changes in hygroscopicity and effective density due to particle growth.

371 Figure 8 illustrates the evolution of particle hygroscopicity and effective density during periods 2 and
372 3. During the initial stage, the measured GF and effective density distributions were both bimodal, with
373 a dominant peak at $\text{GF} = \sim 1.0$ and $\rho_{\text{eff}} = \sim 1.0 \text{ g cm}^{-3}$, respectively. In a previous study, we found that the
374 number fraction of near-hydrophobic particles varied with the traffic exhaust (Ye et al., 2013). Moreover,
375 laboratory studies showed that the effective density of 50 nm vehicle particles was approximately 1.0 g
376 cm^{-3} (Olfert et al., 2007; Park et al., 2003; Momenimovahed and Olfert, 2015). These findings indicate that
377 the initial burst of Aitken mode particles is attributable to the presence of enhanced traffic-related

emissions. In contrast, the number fraction and GF of the more-hygroscopic group increased with the growing particle size, indicating the addition of hygroscopic inorganic species. The variation of the effective density of the particles was similar to that of the hygroscopicity, indicating the increase of high density materials. In general, inorganic sulfate and nitrate are more hygroscopic and denser than soot particles or organic aerosols (Yin et al., 2015). These findings suggest that secondary sulfate and nitrate increased with the growing particle size, indicating the importance of the conversion of SO_2 and NO_x in particle growth. This conclusion is supported by the largest SNA concentration in $\text{PM}_{1.0}$ during the PM episode ($31.3 \mu\text{g m}^{-3}$ on January 10 and $23.8 \mu\text{g m}^{-3}$ on January 11). Considering that the concentration of nitrate was much higher than that of sulfate during the haze event, the increase of hygroscopicity was dominated by the addition of nitrate.

4. Conclusions

Particle size distribution, size-resolved hygroscopic growth and effective density of sub-micrometer aerosols were determined using a HTDMA-APM system, along with measurements of cascade impactor samples and single particle mass spectrometry in urban Shanghai during winter 2014.

The PM episode exhibited a periodic cycle of ~5 days. The average concentration of $\text{PM}_{2.5}$ was $87 \pm 67 \mu\text{g m}^{-3}$, with approximately 62% of hourly $\text{PM}_{2.5}$ concentrations exceeding the Chinese Grade II guideline. Both secondary inorganic salts and carbonaceous aerosols contributed substantially to haze

396 formation, because the mass ratio of SNA/PM_{1.0} fluctuated slightly around 0.28 during the observation
397 period. Nitrate became the most abundant ionic species at PM_{1.0} >40 µg m⁻³, indicating that the sources
398 of nitrate contributed more to haze formation in Shanghai than did SO₂.

399 The severe haze pollution was likely triggered by the adverse meteorological conditions, which favored
400 the accumulation of local emissions and subsequent rapid growth to larger particles. As the PM episode
401 developed, the number fraction of nearly-hydrophobic particles of different size increased, consistent with
402 decrease of the mean effective density. Both hygroscopicity and effective density of the particles were
403 found to increase considerably with growing particle size, indicating that secondary aerosol formation
404 was one of the most important contributors to particle growth. Our results suggest that the accumulation
405 of local emissions under adverse meteorological conditions and subsequent rapid particle growth by
406 secondary processes are primarily responsible for the haze pollution in Shanghai during wintertime.

407

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412 **Reference**

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647 **Figure and Table Captions**

648 Figure 1 Schematic diagram of HTDMA-APM system.

649 Figure 2. Temporal evolutions of $PM_{1.0}$, $PM_{2.5}$, and PM_{10} concentrations during the winter observation.

650 Figure 3 Variations of sulfate, nitrate, and ammonium concentrations as a function of $PM_{1.0}$ mass loading.

651 Figure 4 Box plots showing hygroscopicity parameter and effective density at each dry diameter over the
652 whole observation. The whiskers represent the 5th and 95th percentile, the two borders of box display the
653 25th and 75th percentile, and the band in each box denotes the median.

654 Figure 5 Temporal evolutions of particle number size distribution (A), volume size distribution (B), total
655 number concentration and total volume concentration (C), and $PM_{1.0}$ concentration and calculated PM
656 (less than 600 nm in mobility diameter) concentration during the representative PM episode from 7 to 12
657 January.

658 Figure 6 Evolutions of particle hygroscopic growth factor and effective density for different sizes during
659 the representative PM episode.

660 Figure 7 Temporal evolutions of chemical compositions determined by SPAMS during the representative
661 PM episode.

662 Figure 8 Particle hygroscopicity and density during the two particle growth processes

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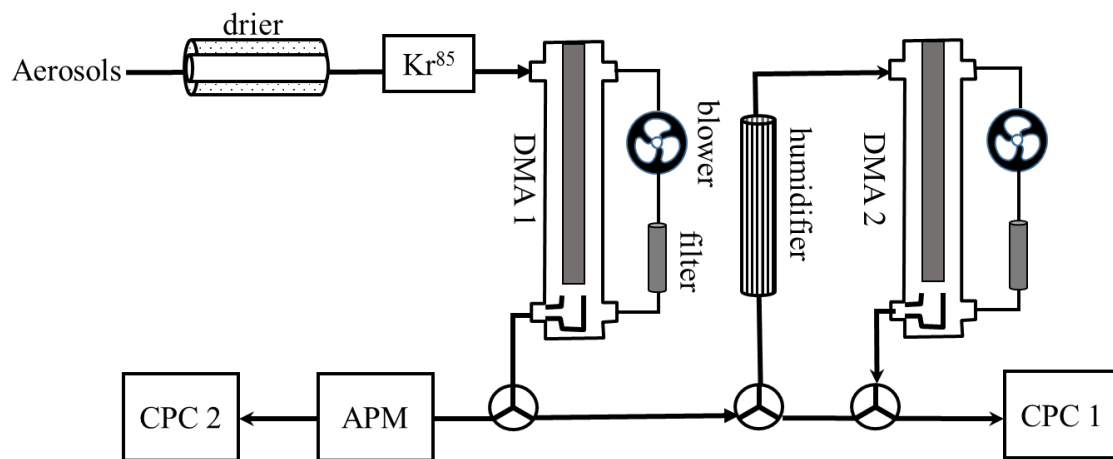
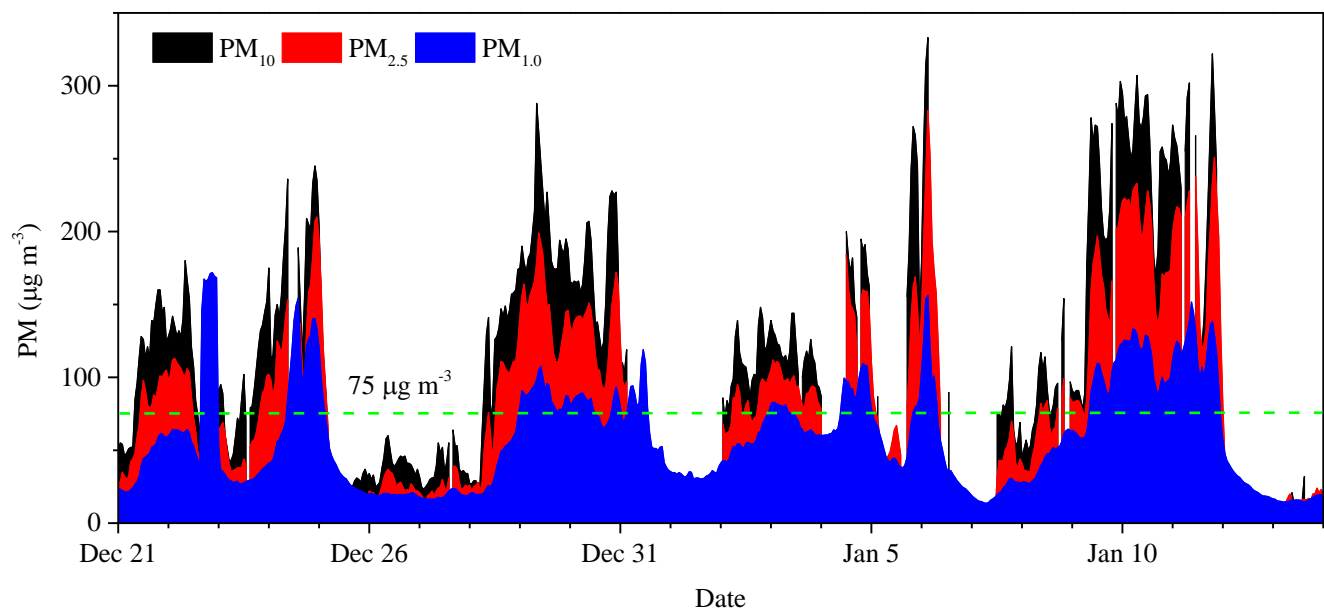


Figure 1 Schematic diagram of HTDMA-APM system.

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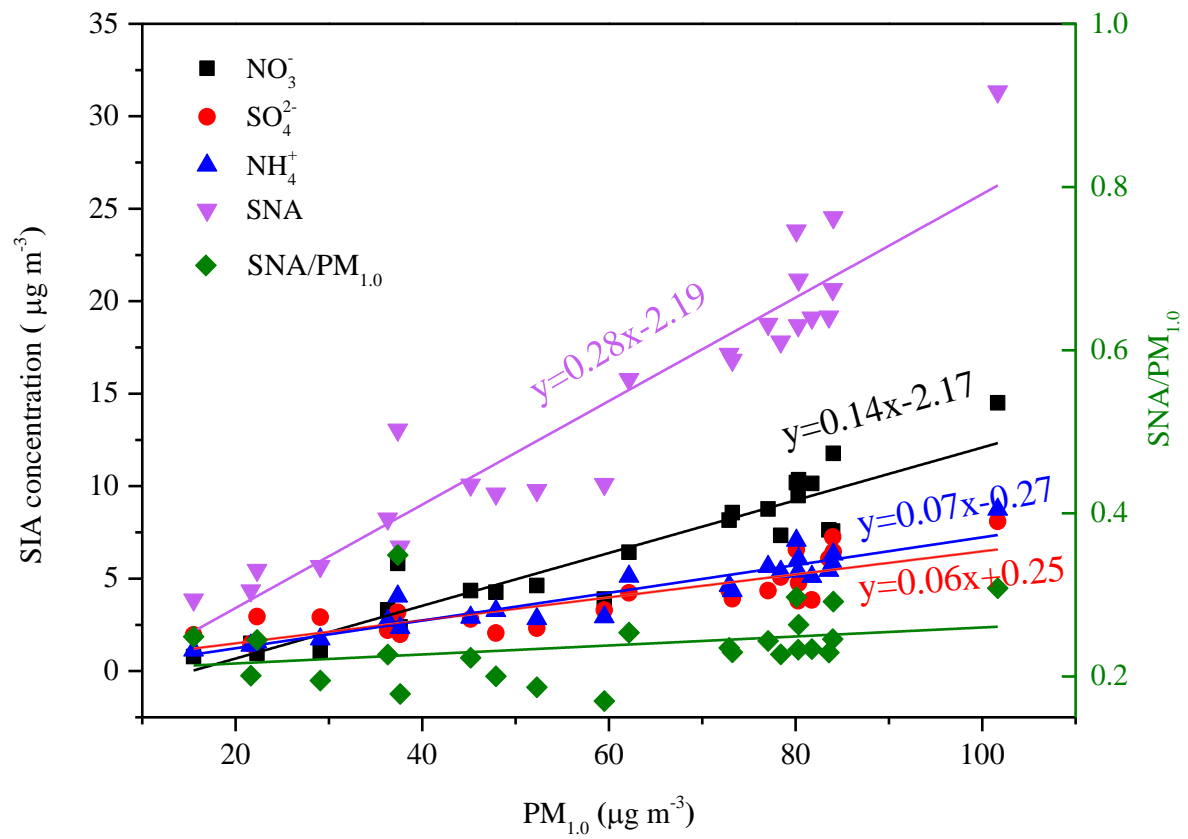


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674 Figure 2. Temporal evolutions of $\text{PM}_{1.0}$, $\text{PM}_{2.5}$, and PM_{10} concentrations during the winter observation.

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Figure 3 Variations of sulfate, nitrate, and ammonium concentrations as a function of PM_{1.0} mass loading

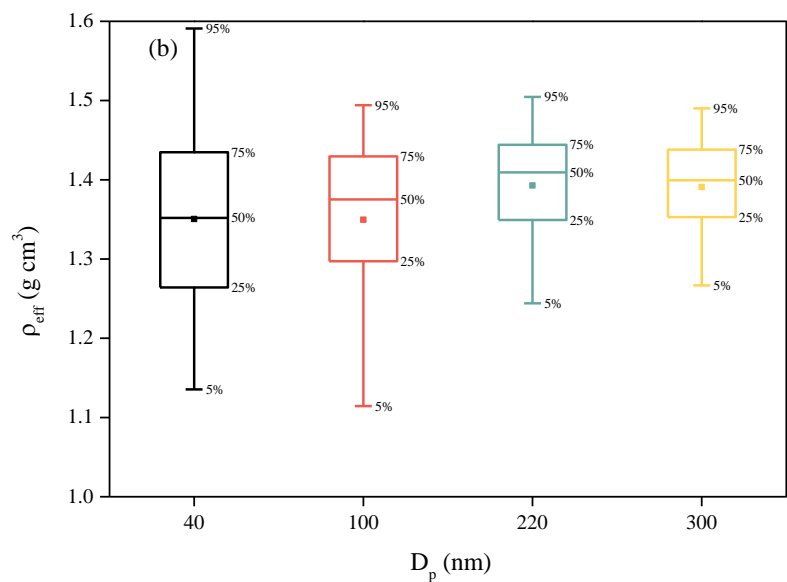
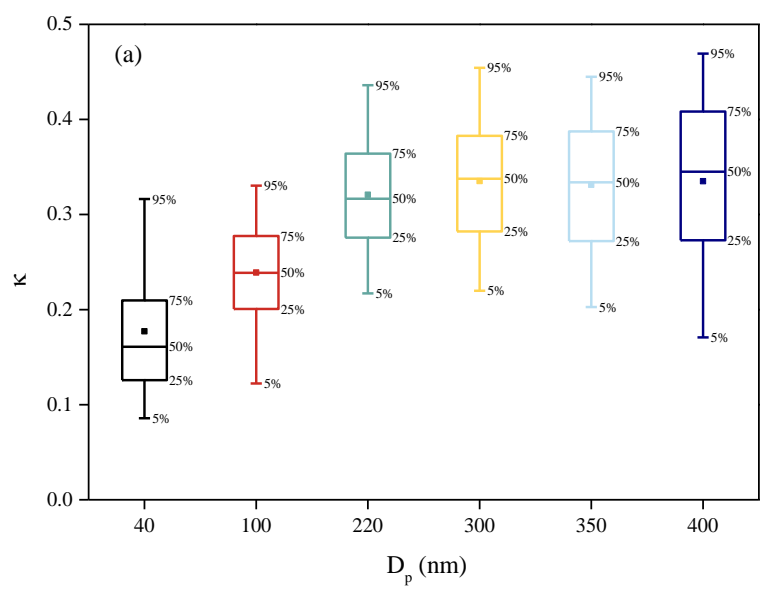
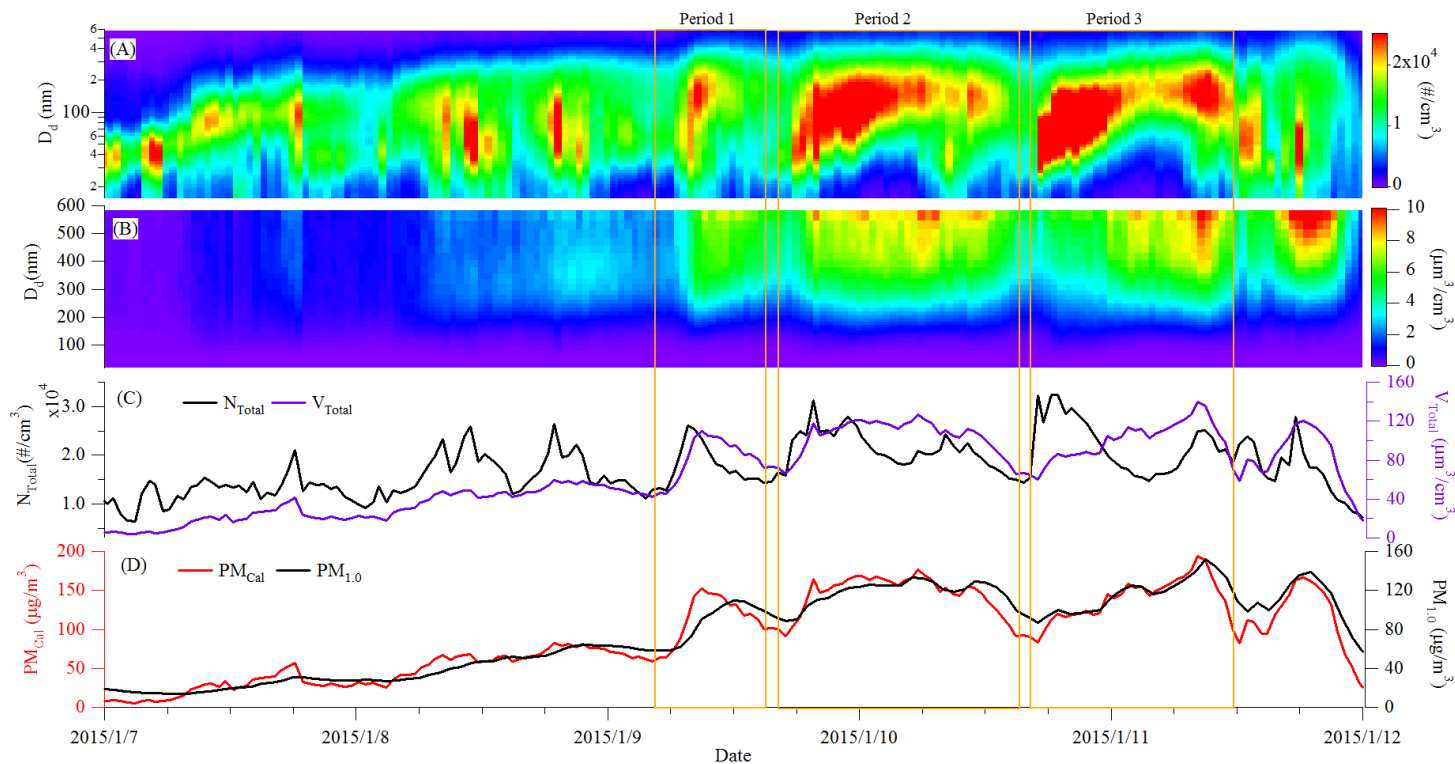


Figure 4 Box plots showing hygroscopicity parameter and effective density at each dry diameter over the whole observation. The whiskers represent the 5th and 95th percentile, the two borders of box display the 25th and 75th percentile, and the band in each box denotes the median.

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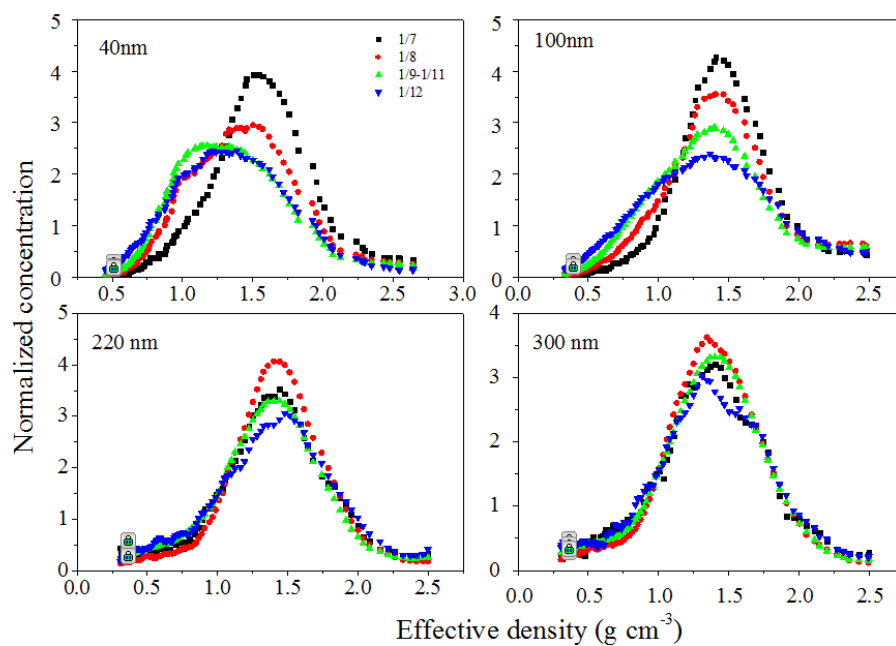
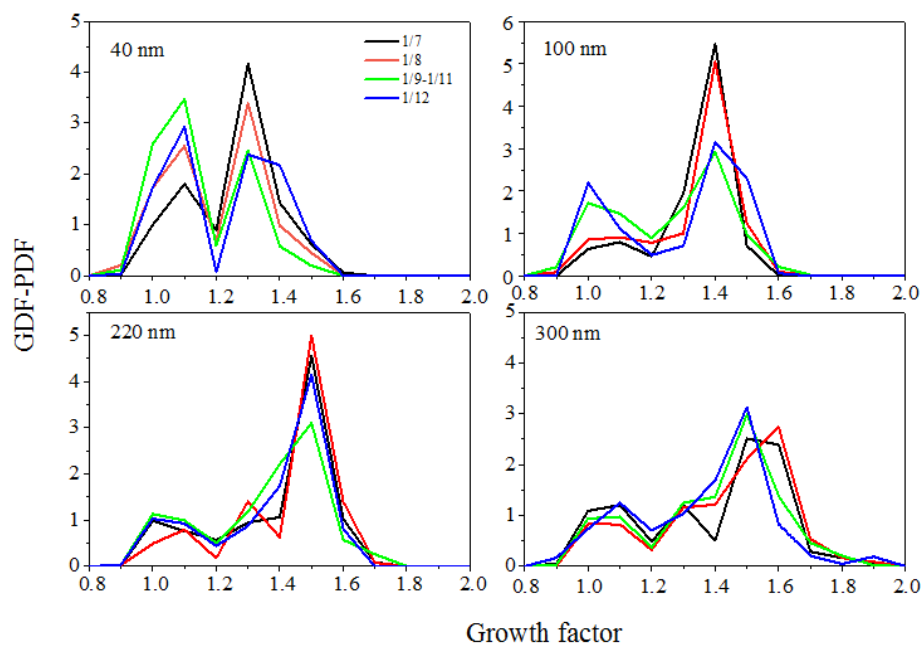


Figure 6 Evolutions of particle hygroscopic growth factor and effective density for different sizes during the representative PM episode.

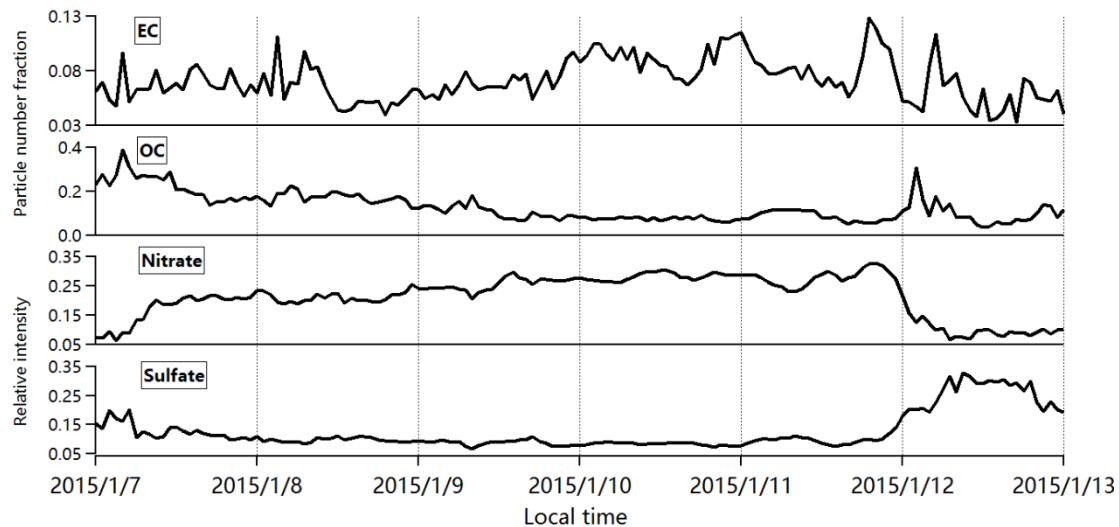


Figure 7 Temporal evolutions of chemical compositions determined by SPAMS during the representative PM episode.

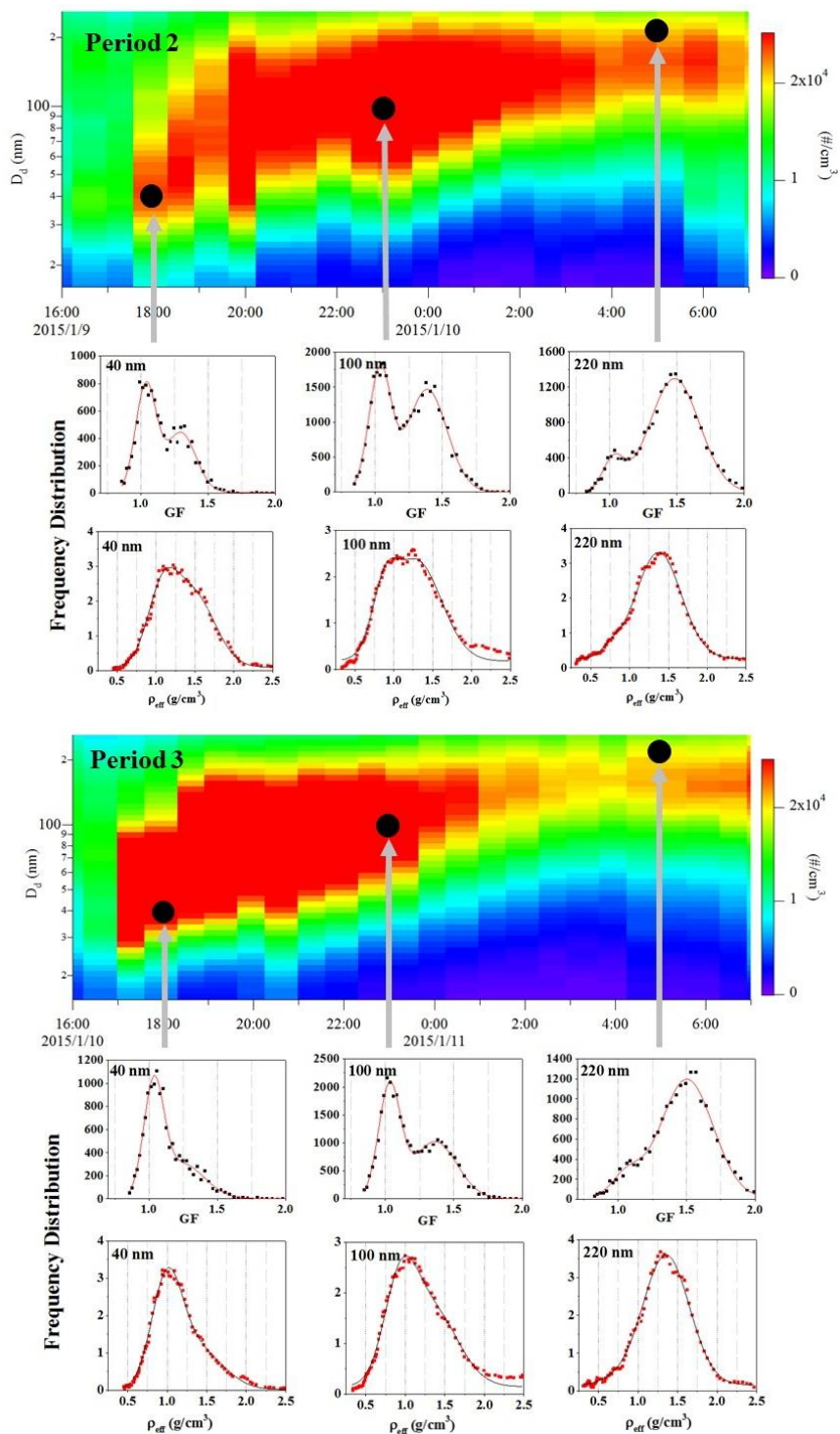


Figure 8 Particle hygroscopicity and density during the two particle growth processes.