1	Enhanced hydrophobicity and volatility of submicron aerosols under
2	severe emission control conditions in Beijing
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27 Abstract. A series of strict emission control measures were implemented in Beijing and the surrounding seven provinces to ensure good air quality during the 2015 China 28 Victory Day parade, rendering a unique opportunity to investigate anthropogenic 29 impact of aerosol properties. Submicron aerosol hygroscopicity and volatility were 30 measured during and after the control period using a hygroscopic and volatile tandem 31 32 differential mobility analyzer (H/V-TDMA) system. Three periods, namely, the control 33 clean period (Clean1), the non-control clean period (Clean2), and the non-control pollution period (Pollution), were selected to study the effect of the emission control 34 measures on aerosol hygroscopicity and volatility. Aerosol particles became more 35 36 hydrophobic and volatile due to the emission control measures. The hygroscopicity parameter (κ) of 40–200 nm particles decreased by 32.0%–8.5% during the Clean1 37 period relative to the Clean2 period, while the volatile shrink factor (SF) of 40-300 nm 38 particles decreased by 7.5%-10.5%. The emission controls also changed the diurnal 39 variation patterns of both the probability density function of κ (κ -PDF) and the 40 probability density function of SF (SF-PDF). During Clean1 the κ -PDF showed one 41 42 nearly-hydrophobic (NH) mode for particles in the nucleation mode, which was likely due to the dramatic reduction in industrial emissions of inorganic trace gases. Compared 43 44 to the Pollution period, particles observed during the Clean1 and Clean2 periods exhibited a more significant non-volatile (NV) mode throughout the day, suggesting a 45 more externally-mixed state particularly for the 150 nm particles. Aerosol 46 47 hygroscopicities increased as particle sizes increased, with the greatest increases seen 48 during the Pollution period. Accordingly, the aerosol volatility became weaker (i.e., SF

49 increased) as particle sizes increased during the Clean1 and Clean2 periods, but no
50 apparent trend was observed during the Pollution period. Based on a correlation
51 analysis of the number fractions of NH and NV particles, we found that a higher number
52 fraction of hydrophobic and volatile particles during the emission control period.

53 1. Introduction

54 China, as the world's second largest economy, is facing severe air pollution 55 problems due to its rapid economic growth. This has led to highly elevated aerosol 56 concentrations, especially in urban regions such as Beijing, Shanghai, and Guangzhou 57 (Hsu et al., 2012; Huang et al., 2014). Every year, high levels of fine particulate matter 58 (PM) have caused many severe haze days in these regions, that may pose a great health 59 hazard and changes in the regional climate because of aerosol direct and indirect climate effects (Z. Li et al., 2016; G. X. Wu et al., 2016). However, the pollution formation 60 61 mechanism and the climate effects of aerosols remain highly uncertain due to the highly 62 variable physical and chemical properties of aerosols, as well as complex mechanisms that govern aerosol-climate interactions (Tao et al., 2012; Wang et al., 2014). 63

Aerosol hygroscopicity and volatility are two important physical properties describing the process of haze formation and its effects on climate. Aerosol hygroscopicity describes the interaction of aerosols and water vapor under sub- and supersaturation conditions, and is a vital parameter to the aerosol life cycle, aerosol activation ability, and aerosol direct and indirect climate effects (Swietlicki et al., 2008; Tao et al., 2012; Bian et al., 2014). Aerosol volatility is a physical parameter correlated with carbonaceous aerosols, commonly used to study the aerosol mixing state and aging
level (Wehner et al., 2009; S. L. Zhang et al., 2016). To date, there are many ways to
measure aerosol hygroscopicity and volatility, but the most popular one is the
Hygroscopic and Volatile Tandem Differential Mobility Analyzer (H/V-TDMA)
system because it can measure these properties in great detail (Swietlicki et al., 2008).

75 The Chinese government took many drastic measures to reduce the emissions of air pollutants from industry, road traffic, and construction sites, especially during some 76 great events such as the 2008 Summer Olympic Games, the 2014 Asia-Pacific 77 Economic Cooperation. Swift and drastic improvement in air quality (Huang et al., 78 79 2015; Shi et al., 2016) provide unique opportunities to investigate the effects of emissions on air quality. To our knowledge, previous studies have usually focused on 80 81 aerosol chemistry, sources, and transport (Wang et al., 2010; Gao et al., 2011; Sun et al., 2016b), but not on the effects of emission controls on aerosol hygroscopicity and 82 83 volatility. Due to the importance of the two factors on describing the process of haze formation as well as the effect on climate, it is necessary to investigate the changes in 84 85 aerosol hygroscopicity and volatility when emission control measures are in place.

To guarantee good air quality in Beijing during the 2015 China Victory Day parade, the Chinese government implemented much stricter emission control measures than normally done in Beijing and the surrounding seven provinces from 20 August to 3 September. The control measures consisted of a ban on driving vehicles every other day, shutting down or limiting factory production, stopping construction activities, and so on. These emission control measures successfully ensured a continuous stretch of 15 92 days of blue sky, vividly named "Parade Blue" (H. Li et al., 2016). During and after the 93 parade emission control period, we conducted in situ measurements of submicron 94 aerosol chemical and physical properties in Beijing. Size-resolved chemical 95 compositions were also obtained (Zhao et al., 2017). The average PM less than 1 μ m in 96 diameter (PM₁) concentration was 19.3 μ g m⁻³ during the parade emission control 97 period, 57% lower than that after the control period. All chemical species decreased 98 during the control period, but their decreasing percentages were different.

99 This study period is unique for investigating aerosol properties during low PM level periods. This paper will further evaluate the impact of emission controls on the 100 101 hygroscopicity and volatility of submicron aerosols, which may bring some insight into how to reduce pollution in the future. Furthermore, investigating aerosol hygroscopicity 102 and volatility with and without emission controls will help in understanding 103 environmental and climate changes in general. This paper is structured as follows. 104 105 Section 2 describes the instrumentation and data used, and section 3 introduces the 106 methods to data analysis. Aerosol hygroscopicity and volatility during different periods 107 were compared and discussed in section 4. Conclusions and summary are given in section 5. 108

- 109 2. Experimental methods
- 110 2.1. Sampling site and meteorology

The submicron aerosol hygroscopicity and volatility were measured in situ from
26 August to 7 October 2015 using the H/VTDMA system located at the Institute of

Atmospheric Physics (IAP), Chinese Academy of Sciences (39.97°N, 116.37°E), which 113 is located between the north 3rd and 4th ring road in northern Beijing. The sampling 114 instruments were put into a white container at ground level and an air conditioner was 115 used to maintain the temperature at 20-25°C inside the container. Meteorological 116 variables, including temperature (T), relative humidity (RH), wind speed (WS), and 117 118 wind direction (WD), were measured at different heights of a 325 m meteorological tower, the tower located ~ 20 m west of the container. To eliminate the influence of 119 buildings on wind, we selected the 280-m wind direction and 8-m wind speed as 120 references in this study. Simultaneously, particle number concentrations (10–600 nm) 121 122 were also measured by a scanning mobility particle sizer (SMPS) located at the 260-m level of the tower. The SMPS is equipped with a long differential mobility analyzer 123 (DMA, Model 3081A, TSI Inc.) and a condensation particle counter (CPC, Model 3775, 124 TSI Inc.). In addition, the measurement of aerosol chemical composition using a High-125 Resolution Aerosol Mass Spectrometer (HR-AMS) and an Aerosol Chemical 126 Speciation Monitor (ACSM) were deployed at ground level and at the 260-m level of 127 the tower, respectively. The HR-AMS was situated in a sampling room located on the 128 rooftop of a two-story building (~ 8 m), ~ 25 m north from the container. An analysis of 129 130 the aerosol chemical composition has been done (Zhao et al., 2017).

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2.2. Instrumentation and operation

132 The H/V-TDMA system developed by the Guangzhou Institute of Tropical and133 Marine Meteorology (ITMM) was used to measure the submicron aerosol

134	hygroscopicity and volatility. The H-TDMA system (H-mode) shown in Figure 1
135	consists of four main parts: (1) a nafion dryer (Model PD-70T-24ss, Perma Pure Inc.,
136	USA) and a bipolar neutralizer (Kr85, TSI Inc.). The nation dryer ensured that the RH
137	of the sample flow was below 20% over the entire measurement period, and the bipolar
138	neutralizer was used to equilibrate the charge of particles (Wiedensohler, 1988); (2) the
139	first differential mobility analyzer (DMA1, Model 3081L, TSI Inc.): The DMA1 was
140	used to select quasi-monodisperse particles of a certain diameter through a fixed electric
141	voltage. The diameters selected were 40, 80, 110, 150, and 200 nm; (3) a nafion
142	humidifier (Model PD-70T-24ss, Perma Pure Inc., USA). The nation humidifier was
143	used to humidify the aerosol flow from the DMA_1 to a defined RH. In the study, we set
144	RH to 90%; (4) the second DMA (DMA ₂ , same model as the DMA ₁) and a condensation
145	particle counter (CPC, Model 3772, TSI Inc.). The DMA ₂ and the CPC were used
146	together to measure the number size distribution of the humidified particles. An
147	automated valve located between the DMA1 and the nation humidifier directly connects
148	the DMA ₁ with the CPC. This can be used to measure the $10-400$ nm particle number
149	size distribution (PNSD) by varying the electric voltage of the DMA ₁ . Details about the
150	design of the HTDMA system and its applications are given by Tan et al. (2013a).
151	The design of the V-TDMA system (V-mode) is similar to that of the H-TDMA
152	system, except that the nation humidifier in the V-TDMA system was replaced by a
153	heating tube that induces the evaporation of volatile materials. The heating tube was an
154	80-cm long stainless steel tube with an inner diameter of 8 mm. With a sample flow
155	rate of 1.0 L min ⁻¹ , its residence time (~ 2.4 s) in the heated section is sufficient for the

156 volatile materials to be effectively vaporized (Cheung et al., 2016). In this study, the heating temperature was set to 300°C. The residual particles of volatile compounds at 157 this temperature, such as sulfates, nitrates, and most organics, are mainly refractory 158 non-volatile organic carbon (such as polymer-type organics), and sea salts (Philippin et 159 al., 2004; Wehner et al., 2009; Cheung et al., 2016; Ma et al., 2016). Particle were 160 161 measured at the diameters of 40, 80, 110, 150, 200 and 300 nm. The H/V-TDMA system 162 has been successfully used in previous studies (Tan et al., 2013b; Cheung et al., 2016; Tan et al., 2016). 163

164 The hygroscopic growth factor (GF) at a given RH and the volatile shrink factor 165 (SF) at a certain temperature are defined as the ratio of the conditional diameter to the 166 dry diameter, with respect to RH and T, respectively:

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$$GF = D_p(RH)/D_{0dry}, \qquad (1)$$

168 $SF = D_p(T)/D_{0dry}$. (2)

Here, $D_p(RH)$ refers to the particle diameter measured at RH = 90%, $D_p(T)$ refers to the 169 particle diameter measured at T = 300 °C, and D_{0dry} refers to the dry diameter set by the 170 171 DMA₁. The measured distribution function (MDF) versus GF or SF can be calculated with the number concentration from CPC data downstream from the DMA₁ and the 172 173 DMA₂. However, the MDF is a skewed and smoothed integral transformation of the particles' actual growth/shrink factor probability density function (GF-PDF or SF-PDF) 174 due to the effect of the DMA diffusion transfer function (Swietlicki et al., 2008; Gysel 175 et al., 2009). In this study, the TDMAfit algorithm (Stolzenburg et al., 1988, 2008) was 176 used to retrieve the GF-PDF and the SF-PDF. The TDMAfit algorithm assumes that 177

groups in the PDF following one or more lognormal distribution functions (Gaussianshape), thus allowing for the possibility that particles of a given type are not all identical.

180 **3.** Data analysis

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3.1. Hygroscopicity parameter

According to the Köhler theory (Petters et al., 2007), the hygroscopicity parameter
κ can be used to depict the hygroscopicity of particles at different RHs. Using H-TDMA
data, κ is calculated as:

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$$\kappa(GF, D_d) = (GF^3 - 1) \cdot \left[\frac{1}{RH} \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D_d GF}\right) - 1\right] \quad , \tag{3}$$

where RH is the default value of the H-TDMA, $\sigma_{s/a}$ is the surface tension of the solution/air interface, M_w is the molecular weight of water, R is the universal gas constant, T is the temperature, ρ_w is the density of water, D_d is the diameter of the dry particles (equivalent to D_{0dry} as mentioned above), and GF from equation (1). In this study, T used in the κ calculation is 23°C (the average temperature of the inner container) and $\sigma_{s/a}$ is assumed to be the same as the surface tension of the pure water/air interface (about 0.0723 N m⁻¹ at 23°C).

3.2. Statistics of κ-PDF and SF-PDF

194 The probability distribution function of κ (κ -PDF, $c(\kappa, D_d)$) derived from the GF-195 PDF was normalized as $\int c(\kappa, D_d) d\kappa = 1$. The ensemble mean hygroscopicity 196 parameter is then defined as the number-weighted mean GF of κ -PDF over the whole κ 197 range:

$$\kappa_{\text{mean}} = \int_0^\infty \kappa c(\kappa, D_d) d\kappa \qquad . \tag{4}$$

199 The standard deviation of κ -PDF is:

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$$\sigma_{\kappa-\text{PDF}} = \left(\int_0^\infty (\kappa - \kappa_{\text{mean}})^2 c(\kappa, D_d) d\kappa\right)^{\frac{1}{2}} \quad . \tag{5}$$

The calculated statistical parameters of SF-PDF ($c(SF, D_d)$) are similar to those of κ -201 202 PDF, so SF can be used instead of κ and $c(SF, D_d)$ instead of $c(\kappa, D_d)$ in these 203 equations.

3.3. Classification of different hygroscopic and volatile groups 204

The mixing state of ambient aerosol particles is complex due to different sources, different aging processes, and so on. Different hygroscopic and volatile groups had been 206 207 used around the Beijing region using H-TDMAs and V-TDMAs (Massling et al., 2009; Liu et al., 2011; S. L. Zhang et al., 2016). Based on previous studies and our 208 209 measurements (Figure S1), ambient aerosol particles were classified into three 210 hygroscopic groups and three volatile groups, where κ and SF are used here to define

- 211 the boundaries for each group:
- Nearly-Hydrophobic, NH: $\kappa < 0.1$; 212
- 213 Less-Hygroscopic, LH: $0.1 \le \kappa < 0.2$;
- More-Hygroscopic, MH: $0.2 \le \kappa$; 214
- Non-Volatile, NV: $SF \ge 0.88$; 215
- 216 Slight-Volatile, SV: $0.88 > SF \ge 0.55$;
- Very-Volatile, VV: SF < 0.55. 217
- The number fraction (NF) for each hygroscopic group with the boundary of [a, b] 218

is defined as:

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$$NF = \int_{a}^{b} c(\kappa, Dp) d\kappa \quad . \tag{6}$$

The number fraction of each volatile group also can be calculated using a similarequation.

223 4. Results and discussion

224 4.1. Overview of measurements

225 4.1.1. Meteorological conditions during the sampling period

226 Air quality has a strong correlation with local wind direction in Beijing. Previous 227 studies have shown that high PM concentrations usually correspond to southerly winds, while low PM concentration are generally related to northerly winds, because there 228 229 were more high concentration air pollutants from source locations south of the Beijing 230 area (Wehner et al., 2008; Wang et al., 2010; Gao et al., 2011). Figure 2 displays time 231 series of WD at 280 m, WS at 8 m, ambient T, and RH. During the emission control 232 period, the prevailing winds were northerly, except for the period from 29 August to 30 233 August due to the influence of accumulated precipitation. During the non-control period, 234 the prevailing winds changed due to the influence of weather systems. Two cold fronts 235 passed on two different days, i.e., on the night of 9 September and in the early morning 236 of 30 September. During these frontal passages, the prevailing winds were northerly, but on other days, the prevailing winds were southerly and the meteorological 237 238 parameters showed obvious diurnal cycle patterns. Over the measurement period, the average ambient T and RH were 21.9°C and 62.4%, respectively. 239

4.1.2. Time series of κ-PDF and SF-PDF, and the division of clean and pollution periods

Figure 3 shows the time series of 10-400 nm particle mass concentrations (PM_{10} -242 $_{400 \text{ nm}}$) derived from PNSD measurements and the time series of κ -PDF and SF-PDF 243 with 40 nm and 150 nm particles as examples. Particles with D_p equal to 40 nm 244 245 represent local-impacted particles and particles with D_p equal to 150 nm represent regional-transport particles. Several haze events during the non-control period can be 246 247 seen from the time series of PM_{10-400 nm}, which shows the rapid accumulation of particle mass concentration. Based on mass concentrations and weather conditions, we selected 248 several clean and pollution periods to study the differences in aerosol hygroscopicity 249 250 and volatility for two different cases (Figure 3). To further study the effect of emission 251 controls, we divided the clean period into two periods: Clean1 (control clean period) 252 and Clean2 (non-control clean period). During the Clean1, Clean2, and Pollution periods, the average PM_{10-400 nm} was 6.9±2.8, 6.0±4.2, and 51.0±25.6 µg m⁻³, 253 respectively. There was no significant precipitation during the three selected periods. 254 255 The time series of κ -PDF and SF-PDF (Figure 3b-e) showed evident changes and 256 fluctuations in the measurements. The prominent differences in K-PDF and SF-PDF 257 during the three periods will be discussed in the following sections.

A wind rose diagram (Figure S2) was used to compare winds during the different periods. During the Clean1 and Clean2 periods, wind directions were similar, mainly from the north and northwest. During the Pollution period, the wind direction had the characteristics of mountain-valley breezes where the wind direction changed routinely

at midnight and changed the wind direction from southerly to northerly (Figure 2). The 262 change in wind direction at night would reduce pollution in the short term (Sun et al., 263 2016b). Even so, the prevailing wind direction was southerly during the Pollution 264 period (Figure S2), which was favorable for the transport of pollutants from the more 265 populated and more industrialized south and southeast to Beijing. The mean WS and 266 267 RH were similar during all periods, but the mean temperature during the Clean2 period 268 was lower than during the other periods due to the influence of cold fronts (Table S1). In summary, the meteorological parameters of the Clean1 and Clean2 cases were similar 269 expect for the ambient T. This provided the opportunity to compare the differences in 270 271 aerosol properties between control and non-control periods. The high level of PM during the Pollution case can also provide a good opportunity to compare differences 272 between clean and polluted environments. 273

274 4.2.Diurnal variation

4.2.1. Diurnal variation in the aerosol size distribution

Figure 4a shows the diurnal variation in total number concentration of 10–400 nm particles ($N_{10-400 \text{ nm}}$). In general, $N_{10-400 \text{ nm}}$ is higher at night and lower during the day due to the influence of changes in the planetary boundary layer (PBL). However, a significant peak in $N_{10-400 \text{ nm}}$ is also seen at noontime because of new particle formation (NPF) events (Figure S3). NPF started at about 0900 local time (LT) during the Clean1 and Clean2 periods. During the Clean1 period, the $N_{10-400 \text{ nm}}$ peak was lower than that observed during the Clean2 period, and the peak in the Clean1 case appeared two hours 283 earlier than that in the Clean2 case (1200 LT during Clean1 and 1400 LT during Clean2). This illustrates that the strength of the NPF was weaker during the Clean1 period than 284 during the Clean2 period, and that it was likely related to the decrease in precursors 285 during the Clean1 period. H. Li et al. (2016) have reported that during the parade control 286 period, the precursors SO₂, NO_x, and volatile organic compounds (VOCs) decreased by 287 36.5%, 49.9%, and 32.4%, respectively. The relatively higher ambient temperature 288 289 during the Clean1 period was also unfavorable for NPF (Kulmala et al., 2004). Figure 4b compares diurnal variations in total mass concentration of 10-400 nm 290 particles (PM_{10-400 nm}) during the three periods. No clear increase in PM_{10-400 nm} is seen 291 292 while N_{10-400 nm} sharply increases during the Clean1 and Clean2 daytime periods. This is because the D_p for most particles was less than 100 nm, which contributed little to 293

PM_{10-400 nm}. During the Clean1 and Clean2 periods, PM_{10-400 nm} had an obvious diurnal variation, which could be attributed to the evolution of the PBL. As is known, the lower PBL at night aids in the accumulation of pollutants (Achtert et al., 2009). However, this effect was weak in the pollution case because of the change in wind direction from southerly to northerly at midnight, which could partly offset the influence of the PBL.

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4.2.2. Diurnal variation in aerosol hygroscopicity

Figure 5a shows the diurnal variation in size-resolved κ_{mean} during the three periods. κ_{mean} shows a peak during daytime, and is always higher than that observed during nighttime. This is because more highly aged particles due to photochemical reactions cause the increase in κ_{mean} during daytime. In the evening, thermal inversion would cap

the ground level and a number of low hygroscopic primary particles (like black carbon, 304 BC) emitted from local diesel trucks and heavy-duty vehicles results in the decrease in 305 κ_{mean} during nighttime (Liu et al., 2011; S. L. Zhang et al., 2016). During the Clean2 306 period, there is another obvious peak at about 0300 LT in the early morning, likely 307 related to the increase in nitrate. Because there was a large amount of NO_x emitted from 308 309 traffic sources in the evening during the non-control period, with the PBL height reduction and ambient temperature decrease, NO_x could be transformed into 310 hydrophilic nitrate rapidly through NO₃ and N₂O₅ (Dall'Osto et al., 2009). This was 311 also verified from comparisons of the nitrate diurnal cycle with and without emission 312 313 controls (Zhao et al., 2017).

Figure 5b shows the diurnal variation in κ -PDF for particles with D_p equal to 40 314 nm (i.e., local-impacted particles) during the three periods. During the Clean1 period, 315 the κ -PDF has a quasi-unimodal shape (only in the hydrophobic mode). During NPF 316 events, κ_{mean} increases slightly, indicating that 40-nm particles from local sources were 317 always hydrophobic and a very small amount of hygroscopic particles were produced 318 319 through the nucleation and growth from gaseous precursors. This is likely because the secondary formation of hydrophilic sulfate and nitrate was suppressed due to low 320 321 concentrations of SO₂ and NO_X during the parade control period (H. Li et al., 2016). Most of the new particles should consist of less hygroscopic organics that are formed 322 by oxidation and condensation of VOCs. By contrast, during the Clean2 period, the ĸ-323 324 PDF with D_p of 40 nm shows either a bimodal or quasi-trimodal distribution and 325 exhibits a large diurnal variation during the day. Interestingly, when the NPF event

occurred at about 0900 LT, the number fraction of the hydrophobic mode quickly 326 decreased and the hydrophilic mode increased (Figure 5b), suggesting the conversion 327 of externally mixed particles to internally mixed particles due to the species 328 condensation (sulfate, nitrate and organics) from the photochemical reaction of SO₂, 329 NO_x and VOCs. A similar phenomenon was also observed by Z.J. Wu et al. (2016). For 330 331 the Clean1 case, much less of these gases were in the atmosphere due to the emission control. Around 1700 LT, the fraction of hydrophobic mode particles increased again, 332 mainly due to substantial traffic emissions at rush hour. However, during the Pollution 333 period, the κ -PDF shows a bimodal shape during the day. The hydrophilic mode 334 335 becomes stronger in the early morning and in the afternoon, which is attributed to the NO_x heterogeneous reactions at night, and the aging and growth of pre-existing particles 336 during the day. 337

In summary, the diurnal variations in κ -PDF for 40-nm particles were significantly different during the three periods and the emission control appeared to change the diurnal pattern of κ -PDF, mainly due to the decrease in gas precursors, like SO₂ and NO_x, the reduction of which will suppress the formation of hydrophilic matter.

However, the κ -PDF for 150-nm D_p particles (i.e., regional-transport particles) had a similar diurnal variation pattern during the three periods (Figure 5c) and showed NH and MH modes. The number fraction of the MH mode increased significantly during daytime. There are different reasons for the diurnal variations. One reason is that during daytime, strong photochemistry can produce a large number of condensable vapors, such as sulfuric acid and secondary organic species, which can condense onto preexisting particles and enhance their water absorbing capacity (Z. J. Wu et al., 2016).
Another reason is that when the sun rises, the PBL height increases and older particles
are well-mixed, making them more hydrophilic (S. L. Zhang et al., 2016). However, the
MH mode is much more evident for the Pollution case and may be related to the higher
mass fractions of inorganic salts and more internal-mixed particles during the Pollution
period.

354 **4.2.3.** Diurnal variation in aerosol volatility

Figure 6a shows the diurnal variation in SF_{mean}, which shows similar trends for all 355 three cases, with the lowest SF_{mean} in the afternoon (1200–1500 LT) and the highest 356 SF_{mean} in the morning (0700–0900 LT) for all particles with D_p ranging from 40-300 357 nm. The diurnal variations illustrate that particles had a higher volatility during the day 358 359 than at night. This feature is more obvious for those small particles observed during the 360 Clean1 period. During the Clean1 period, particle volatility increased dramatically (i.e., SF_{mean} decreased) along with the occurrence of NPF events, suggesting that the earliest 361 newly-formed matter (before ~1200 LT) were always volatile at 300°C. As stated 362 previously, during the Clean1 period VOCs has a weaker decrease than SO2 and NOx, 363 this would lead to more VOC-formed organic particles formed, which are normally 364 highly volatile. Therefore, the highest volatility was observed during the Clean1 period. 365 366 Wehner et al. (2009) also showed that ~97% of newly-formed particles are volatile because they are dominated by sulfate and organics. With the processes of particle aging, 367 collision, and growth, they then decrease in volatility (i.e., SF_{mean} increases). This is 368

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because these processes can enhance the oxidative level of organics and there are more refractory organics (like polymer-type organics) produced.

For 40-nm particles, the lowest SF_{mean} appeared two hours later during the Clean2 371 period (~1500 LT) than during the Clean1 period (~1300 LT). This is probably because 372 NPF lasted longer during the Clean2 period. For larger particles, the coating effect of 373 374 condensable vapors onto pre-existing particles was the major reason behind the intensification of their volatility during NPF events (Wehner et al., 2009; Cheung et al., 375 2016). The SF_{mean} decreased little compared to that for 40-nm particles. By comparison, 376 the diurnal variation in SF_{mean} for 40-nm particles during the Pollution period changed 377 378 more smoothly, likely because under a polluted environment, the mass fractions of all chemical species were relatively stable (Sun et al., 2016a) and the particles were well-379 mixed with highly aging levels. 380

Figure 6b and 6c show the diurnal variation in SF-PDF for 40 nm and 150 nm 381 particles. The SF-PDF normally has an NV mode and a SV or VV mode. The NV mode 382 consists of non-volatile particles, like BC particles, which do not shrink when aerosols 383 384 are heated. SV and VV modes suggest a mixture of volatile (e.g., organics) and nonvolatile matter that shrink when aerosols are heated (Kuhn et al., 2005). The two SF-385 PDF modes suggest that the particles during the observed periods were mostly 386 externally-mixed. The 40-nm and 150-nm SF-PDF show similar diurnal patterns. 387 During daytime, active aging processes facilitated the mixing of primary particles with 388 secondary species, leading to the transformation of externally-mixed particles to 389 390 internally-mixed particles, and weakening the NV mode. In particular, this effect was

stronger during the Clean1 period than during the other periods. This may be due to the 391 reduction in emissions of soot particles during the control period. In the evening and 392 the early morning, the number fraction of NV-mode particles increased again because 393 a large amount of refractory particles (like BC) were emitted from traffic sources or 394 cooking, and then the slower particle aging and weaker vertical mixing made the 395 external-mixing BC accumulated (S. L. Zhang et al., 2016). The number fraction of 396 NV-mode 150-nm particles in the Clean1 case had a stronger increase than that of 40-397 nm particles in the evening and early morning. This is because freshly emitted 398 refractory particles (like BC) are primarily within the 150 nm to 240 nm diameter range 399 400 (Levy et al., 2013). Furthermore, compared with the Pollution case, the number fraction of NV-mode 150-nm particles are much higher during the Clean1 and Clean2 cases. 401 402 This may reflect the fact that soot particles in a polluted environment can be coated and aged quickly through the heterogeneous reactions of VOCs and other precursor gases 403 (like SO₂, NO_x), which are usually present in extremely high concentrations during 404 polluted days in urban Beijing (Guo et al., 2014; Sun et al., 2016a). 405

406 Overall, the diurnal variation in aerosol volatility is different between clean and 407 polluted periods. NPF can enhance volatility through the formation of volatile matter 408 and the coating effect of condensation vapors. Particles observed during the control 409 period showed two significant NV and VV modes during the day, suggesting a more 410 externally-mixed state, particularly for the larger particles.

411 4.3. Size-resolved particle hygroscopic and volatile properties

Table 1 summarizes the size-resolved mean κ , the growth spread factor ($\sigma_{\kappa-PDF}$) of 412 κ -PDF, size-resolved SF during different periods, and the change in percentages of κ 413 and SF due to the emission control policy. The $\sigma_{\kappa-PDF}$, defined as the standard deviation 414 415 of κ -PDF, is an indication of the mixing state of aerosol particles. A higher σ_{κ -PDF 416 generally suggests a higher degree of external mixing (Sjogren et al., 2008; Liu et al., 2011; Jiang et al., 2016). Liu et al. (2011) chose $\sigma_{\kappa-PDF} = 0.08$ as the cut-off point for 417 high external mixing and quasi-internal mixing. In this study, $\sigma_{\kappa-PDF}$ always exceeds 418 419 0.08 but the 40-nm particles during the Clean1 period, indicating that the particle population was more externally mixed in urban Beijing. The mean $\sigma_{\kappa-PDF}$ of 40-nm 420 particles during the Clean1 period is equal to 0.08, suggesting that during the control 421 period, 40-nm particles had a low degree of external mixing. This is also seen in the 422 quasi-unimodal distribution of 40-nm κ -PDF (Figure 5b). 423

During the selected three periods, aerosol particles were more hygroscopic (i.e., κ 424 425 increased) with increase in particle size (Figure 7a). The most significant trend is seen in the Pollution case where κ increases from 0.16 to 0.42 when D_p changes from 40 nm 426 427 to 200 nm, but only increases from 0.10 to 0.25 for the Clean1 case and from 0.14 to 0.28 for the Clean2 case. This is because particles with a larger size are usually 428 429 composed of more inorganic salts or oxidized organics, especially in a polluted 430 environment (Swietlicki et al., 2008; Achtert et al., 2009; Fors et al., 2011; Sun et al., 2016a). Meanwhile, the increase in $\sigma_{\kappa-PDF}$ with the increase in particle size illustrates 431 that there were more external mixing particles with larger sizes (Table 1). Accordingly, 432

aerosol volatility became weaker (SF increased) as particle size increased during the
Clean1 and Clean2 periods, but no apparent trend was observed for the Pollution period
(Figure 7b). This finding is consistent with that reported by Wehner et al. (2009).

Figure 6 also shows that all particles were less hygroscopic and more volatile 436 during the control Clean1 period than during the non-control Clean2 period, which can 437 438 also be seen from the variation in chemical composition. Based on HR-AMS 439 measurements, secondary inorganic aerosols (SIA) had larger decreases than organic aerosols (OA) during the parade control period. The positive matrix factorization of OA 440 further illustrates that primary OA (POA) had similar decreases as secondary OA 441 442 (SOA). However, more-oxidized SOA had larger decreases than less-oxidized SOA (Zhao et al., 2017). SIA is always more hydrophilic than OA and more-oxidized SOA 443 is also more hydrophilic than less-oxidized SOA (Jimenez et al., 2009; Chang et al., 444 2010; Rickards et al., 2013; Zhang et al., 2014; F. Zhang et al., 2016). Therefore, the 445 increased fraction of POA emissions, but weakened age processing due to a sharp 446 reduction in SO₂ and NO_x, lead to particles being less hygroscopic during the control 447 period. Meanwhile, particles become relatively more volatile due to the high number of 448 POA particles because OA volatility is generally inversely correlated with the O:C ratio 449 450 (an indicator of oxidation state) (Jimenez et al., 2009).

To quantify the effects of emission control on aerosol hygroscopicity and volatility, Table 1 also gives the change in percentages of κ and SF during the control Clean1 period compared with that during the non-control Clean2 period. Results show that κ decreased by 32.0–8.5% from 40 nm to 200 nm during the control period, with a more significant reduction for small particles, while SF reduced by 7.5–10.5% from 40 nm
to 300 nm. The significant decrease in aerosol hygroscopicity is favorable for
decreasing the aerosol water content, thus suppressing the evolution of regional air
pollution (like liquid-phase chemical reaction processes in the atmosphere) (Arellanes
et al., 2006; Ye et al., 2011; Bian et al., 2014), and eventually improving atmospheric
visibility.

In addition, because of the reduced hygroscopicity, fewer particles would be activated as cloud condensation nuclei, which is a critical parameter in evaluating the aerosol indirect effect. Thus, our study is important for investigating environmental and climate changes, and should inspire both scientists and policy makers to think more deeply about the issue of heavy air pollution in China.

466 4.4.Relationship between nearly-hydrophobic and non-volatile particles

For submicron particles, non-volatile (NV) part particles at 300°C were normally the major nearly-hydrophobic (NH) part particles because both their main components are soot particles (Massling et al., 2009; Wehner et al., 2009). S. L. Zhang et al. (2016) compared the relationship between the number fraction of measured non-volatile particles (NF_{NV}) and nearly hydrophobic (NF_{NH}) particles and found those two groups are very likely to be dominated by the same component. In this study, we also analyze the relationship of NF_{NH} and NF_{NV} particles as shown Figure 8.

The results show that Aitken mode particles (40 nm and 80 nm) have a very weak
linear relationship between NF_{NH} and NF_{NV}, likely because Aitken mode particles are

not as aged. There are a large number of hydrophobic, but volatile, particles such as 476 POA and less-oxidized SOA. Accumulation mode particles (> 100 nm) show a 477 relatively better linear correlation between NF_{NH} and NF_{NV}, i.e., correlation 478 coefficients (R²) are 0.26, 0.55, and 0.62 for 110, 150, and 200 nm particles, 479 respectively. The higher R² for the larger particles may arise because larger particles 480 481 are highly aged particles from cloud processes. Also, freshly emitted refractory and hydrophobic matter is mostly in the accumulation mode (Levy et al., 2013). The best-482 fit regression line for the accumulation mode particles is always lower than the 1:1 line. 483 This can be attributed not only to externally mixed SIA and volatile organics 484 485 (completely volatile), which are not taken into account for calculation, but also to that some medium/high volatile organics are nearly-hydrophobic. 486

There were obvious differences in NF_{NH} and NF_{NV} during the three selected 487 periods. For the Clean1 and Clean2 cases, NF_{NH} and NF_{NV} were larger than those 488 obtained for the Pollution case, but more scatter was seen. This is likely related to the 489 influence of NPF events, during which secondary aerosol material had more complex 490 491 chemical compositions due to the different sources of precursors. A higher NF_{NH}/NF_{NV} ratio was seen during the Clean1 period than during the other two periods, illustrating 492 that a higher number fraction of hydrophobic and volatile particles during the control 493 period. 494

496 **5.** Conclusions and Summary

In this study, a H/V-TDMA system was used to measure submicron aerosol 497 498 hygroscopic and volatile properties in Beijing during and after the parade emission control period. Three periods, namely, the control clean period (Clean1), the non-499 500 control clean period (Clean2), and the non-control pollution period (Pollution), were selected to study the effect of emission control on aerosol hygroscopicity and volatility. 501 502 When emission control measures were in place, particles became more hydrophobic and volatile compared to particles in the non-control period. The κ of 40-503 504 200 nm particles decreased by 32.0-8.5% during the Clean1 period relative to the 505 Clean2 period, while SF of 40–300 nm particles decreased by 7.5–10.5%. The diurnal variations of κ -PDF were significantly different during the three selected periods, 506 especially for small particles. During the Clean1 period, the κ-PDF of 40-nm particles 507 always showed a quasi-unimodal distribution and had a weaker diurnal variation than 508 that observed during the Clean2 period. This demonstrates that emission control 509 510 measures can change the diurnal variation pattern of κ -PDF due to the reduction in gas precursors like SO₂ and NO_x, which suppresses the formation of hydrophilic matter. 511 512 The diurnal variation in aerosol volatility was different between clean and polluted 513 periods. NPF appears to enhance aerosol volatility through the formation of volatile matter and the coating effect of condensable vapors. The particles observed during the 514 515 control period showed two significant modes during the day, i.e., NV and VV modes, 516 and a more externally-mixed state particularly for larger particles.

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Aerosol particles became more hygroscopic (i.e., κ increases) as the particle size

518 increased during the three periods. The trend was greatest for the Pollution case where κ increased from 0.16 to 0.42 when D_p changed from 40 nm to 200 nm, but only 519 increased from 0.10 to 0.25 for the Clean1 case and from 0.14 to 0.28 for the Clean2 520 case. Meanwhile, the increase in $\sigma_{\kappa-PDF}$ (i.e., the standard deviation of κ -PDF) with the 521 increase in particle size also illustrates that there were more external mixing particles 522 with larger sizes. Accordingly, aerosol volatility became weaker (SF increased) as 523 524 particle size increased during the Clean1 and Clean2 periods, but no apparent trend was 525 observed for the Pollution period.

Our results suggest that emission control measures weaken submicron aerosol 526 527 hygroscopicity, and that aerosol particles are more hygroscopic in a polluted environment. The significant decrease in aerosol hygroscopicity is favorable for 528 suppressing the evolution of regional air pollution. In addition, because of the reduced 529 hygroscopicity, fewer particles would be activated as could condensation nuclei, which 530 is a critical parameter in evaluating the aerosol indirect effect. Thus, our study is 531 important for investigating environmental and climate changes, and should inspire both 532 533 scientists and policy makers to think more deeply about the issue of heavy air pollution in China from a broader perspective. 534

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Table 1. Summary of size-resolved mean κ , the κ -PDF growth spread factor (σ_{κ -PDF}), size-resolved mean SF during the selected three periods, and the change in percentage of κ and SF during the control Clean1 period compared with the non-control Clean2

692 period.

		40 nm	80 nm	110 nm	150 nm	200 nm	300 nm
	κ	0.10±0.05	0.11±0.06	0.15±0.07	0.20±0.10	0.25±0.12	
Clean1	σ_{κ} -PDF	0.08±0.03	0.10±0.03	0.12±0.03	0.14±0.03	0.15±0.04	—
	SF	0.55±0.08	0.60±0.07	0.64±0.06	0.66±0.05	0.67±0.05	0.70±0.06
	κ	0.14±0.06	0.17±0.08	0.20±0.10	0.24±0.12	0.28±0.13	_
Clean2	σ_{κ} -PDF	0.11±0.04	0.13±0.03	0.15±0.03	0.17±0.03	0.19±0.04	—
	SF	0.60±0.06	0.66±0.07	0.70±0.07	0.72±0.07	0.74±0.06	0.78±0.06

Pollution	κ	0.16±0.08	0.24±0.08	0.30±0.09	0.36±0.10	0.42±0.12	_
	σ _κ -pdf	0.12±0.02	0.13±0.02	0.14±0.02	0.14±0.0.02	0.15±0.04	
	SF	0.65±0.06	0.65±0.06	0.65±0.05	0.65±0.05	0.65±0.06	0.66±0.07
(Clean1 – Clean2)	κ	-32.0%	-31.9%	-26.1%	-17.5%	-8.5%	
Clean2	SF	-7.5%	-9.4%	-9.2%	-8.7%	-10.1%	-10.5%



Figure 2. Time series of (a) wind direction at 280 m (in blue) and wind speed at 8 m (in

red), and (b) ambient temperature at 8 m (in blue) and relative humidity at 8 m (in red)



704 during the control and non-control periods.

shrink factor distributions (SF-PDF) for (d) 40-nm and (e) 150-nm particles at T =
300°C.



Figure 4. Diurnal variation in mobility diameter (D_p) 10-400 nm particles (a) number

concentration $(N_{10-400 \text{ nm}})$ and (b) mass concentration $(PM_{10-400 \text{ nm}})$ for the Clean1 (in



red), Clean2 (in green), and Pollution (in blue) cases.



717 κ-PDF for particles with D_p equal to 40 nm, and (c) κ-PDF for particles with D_p equal







Figure 6. Diurnal variation of (a) mean SF (SF_{mean}) for different mobility diameters,

- 721 (b) SF-PDF for particles with D_p equal to 40 nm, and (c) SF-PDF for particles with D_p
- equal to 150 nm during the Clean1, Clean2, and Pollution periods.





Figure 7. Size-resolved (a) κ and (b) SF during Clean1 (C1), Clean2 (C2), and

Pollution (P) periods. The figure shows the mean κ or SF (solid square markers) with

boxes showing the 25th, 50th, and 75th percentiles. The extremities show the 5th and

727 95th percentiles.





Figure 8. Comparisons between the number fractions of the nearly-hydrophobic group



731 and Pollution (in red) periods.