Reply to RC1

General Comments: Hygroscopicity and volatility are the key properties of atmospheric aerosols that can significantly impact the climate directly by interacting with solar radiation and indirectly by affecting cloud microphysics. Hygroscopic aerosol components can uptake substantial water under sub-saturated conditions and thus can significantly change aerosol size distribution and promote both heterogeneous and aqueous-phase reactions. Severe haze event caused by high mass loading of aerosols is one of the most critical environmental issues faced by China. Although the underlying cause is still an area of active research, it is well recognized that ever-increasing economical expansion and demands for energy have led to tremendous emissions of primary air pollutants (e.g., VOCs, NOx, SO2) in China. Many mitigation measures have been proposed to reduce air pollutant emissions but their effectiveness still needs to be verified in practice. The "Victory Day Parade" event has provided the atmospheric scientists such an opportunity to examine the aerosol properties with/without those anthropogenic emissions. Therefore, this dataset by itself is a valuable contribution. The manuscript is well written and is certainly within the scope of ACP. The measurements techniques are well established and the methodology is generally sound. Overall, the research was well planned and carefully executed. I would recommend the manuscript for publication in ACP after the authors address the following comments.

Specific Comments:

1. L231: As the authors pointed out that "Air quality has a strong correlation with local wind direction in Beijing", how did the authors manage to separate the effects of meteorological conditions from that of control measures?

Re: You are right. Separating the effects of meteorological conditions is important to analyze the impact of emission control. When selecting the comparing periods, we tried to find the periods of similar meteorological conditions, especially for Clean1 and Clean2 periods. You can refer to Figure S2 and Table S1 in the supplementary material, we have compared the wind and other meteorological variables during different periods, the meteorological parameters were similar, especially for Clean1 and Clean2 periods.

2. L259 and L294: It is interesting to note that PM mass concentration decreased by a factor of 8 between polluted and clean periods while precursors only decreased by less than 50%. Please comment on this.

Re: This is a good point. In practice, the relationship between PM_1 and precursors always is not linear. The PM_1 mass concentration is mainly determined by the larger particles (Accumulation mode particles), most of them are from condensation of fine particles and direct emission. Many control measures (such as stopping construction activities, shutting down or limiting factory production) would directly decrease the

PM_1 emission. However, the particles converted from gas precursors always are the fine particles (Aitken nuclei mode), which have a smaller contribution to PM_1.

3. L311-314: The authors may also consider the possibility that during daytime strong vertical mixing can bring down air masses transported from long distance that were more aged. However, during nighttime thermal inversion would cap the ground level, where fresh primary emissions would dominate.

Re: Yes, during nighttime the increase of hydrophobic species (like BC) from primary emissions and thermal inversion would make BC accumulation, these factors would decrease the aerosol hygroscopicity. This has been addressed as "In the evening, thermal inversion would cap the ground level and a number of low hygroscopic primary particles (like black carbon, BC) emitted from local diesel trucks and heavy-duty vehicles results in the decrease in κmean during nighttime (see L303-306).

4. L319: How did "H2O2" form during nighttime? This is more likely due to N2O5 chemistry.

Re: The heterogeneous reactions in the atmosphere are complex, the reactive material includes H_2O_2、HO_2、N_2O_5、O_3 and so on. At night the formation of NO_3 and N_2O_5 becomes important, NO_x can be oxidized to NO_3 through heterogeneous reactions. NO_3 and NO_2 can be further combined to N_2O_5. Then nitrate can be formed rapidly through NO_3 and N_2O_5. This rapid conversion enhances the available nitrate and may add significantly to the nitrate available for condensation, enhancing night-time concentrations compared to those observed in the day (Dall'Osto et al., 2009). This has been addressed as "NO_x could be transformed into hydrophilic nitrate rapidly through NO_3 and N_2O_5 (Dall'Osto et al., 2009)" in the revised version of the paper (see L310-312).

5. L324-330: "During NPF events, …condensation of VOCs". Did the authors mean that these NPF events (Clean1 case) were caused by organic precursors? If these organics were less hygroscopic, why did kappa-mean increase? Was there any possibility that these 40 nm particles were due to primary emissions, such as automobile exhaust or cooking?

Re: Yes, we think organic cursors may take some role during NPF in Clean1 case. Note that the hygroscopicity of 40-nm particles during Clean1 period had a "slight" increase, this was likely caused by the increase of OA oxidative level. The 40-nm particles can be from both growth of new formed particles and primary emissions. This has been addressed as "…40-nm particles from local sources were always hydrophobic and a very small amount of hygroscopic particles were produced through the nucleation and growth from gaseous precursors" in the revised version of the paper (see L317-319).

6. L377: "With the processes of…(i.e., SFmean increases)." Why did the aging, coagulation and growth processes cause decrease in particle volatility if the precursor gases were the same? This is more likely due to the formation of more oxidized oxygenated organic aerosols.

Re: Yes. The aging, cogulation and growth processes can enhance the oxidative level of

organics, and there are more refractory organics (like polymer-type organics) produced. This has been addressed "With the processes of particle aging, collision, and growth, they then decrease in volatility (i.e., SFmean increases). This is because these processes can enhance the oxidative level of organics and there are more refractory organics (like polymer-type organics) produced." in the revised version of the paper (see L367-370).

7. Figure 8: How was the linear fit calculated for each size? Did the authors try orthogonal distance regression (ORD), which I believe will generate more reasonable results especially for the 40 nm case?

Re: Thanks for your advice. In this paper, I used the least square fitting for each size. Here I tried to use ORD method to the linear fit (Figure 1.). The result by ORD method is similar to our linear fit results.

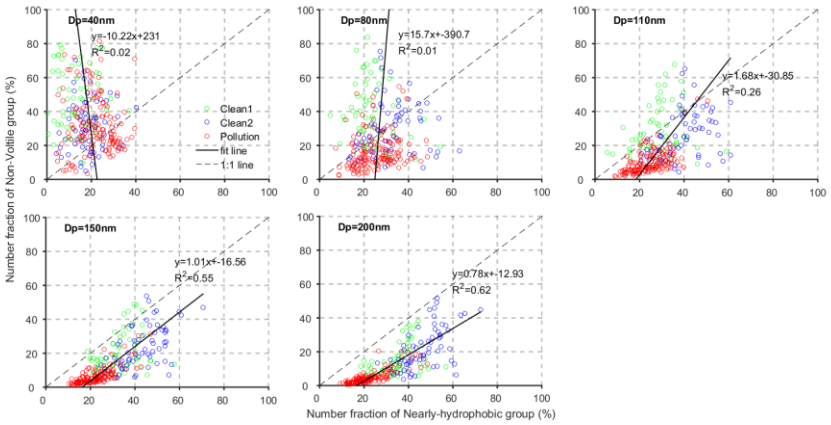

Figure 1. Comparisons between the number fractions of the nearly-hydrophobic group (NF_{NH}) and the non-volatile group (NF_{NV}) with orthogonal distance regression (ORD) fitting method.

Technical comments:

1. L138-147: remove period before semicolon;
   Re: Revised, thanks! This has been addressed in the revised version of the paper (see L138-144).
2. L248: Particle mass concentration is denoted by "" throughout the manuscript, which, however, could be misleading, since "" is commonly used to represent density. Please replace ""with "m" or "mass" or something less misleading.
   Re: Revised, thanks! This has been addressed as "$PM_{10\text{-}400\ nm}$" in the revised version of the paper (see L247)
2. L376: dominated by sulfate and "organics" not "VOCs".
   Re: Revised, thanks! This has been addressed as "Wehner et al. (2009) also showed that ~97% of newly-formed particles are volatile because they are dominated by sulfate and organics." in the revised version of the paper (see L367)

3. L459: change “corrected” to “correlated”.
Re: Revised, thanks! This has been addressed in the revised version of the paper (see L449)

References:

Dall'Osto M., Harrison R.M., Coe H., Williams P.I. and Allan J.D.: Real time chemical characterization of local and regional nitrate aerosols, Atmos. Chem. Phys., 9, 3709-3720, 2009.

Reply to RC2

Wang et al. presents their results of hygroscopicity and volatility measurements during and after the Victory Day parade period in China. Aerosol hygroscopicity describes the interaction of aerosols and water vapor, and Aerosol volatility reflect the mixing state of nonvolatile aerosol particles. In addition to their importance of climate effects, the variation of them indicates the change in primary emissions, particle aging process, and regional transport. This dataset provide us new insights into the haze formation mechanisms in Beijing. The paper is well written and organized. Overall, the manuscript is within the scope of ACP. The reviewer would recommend the manuscript for publication in ACP after some minor revisions.

Specific Comments:

Line 61-64: The authors highlight the uncertainty of aerosol on climate. However, the author discuss the aerosol chemistry indicated from hygroscopicity and volatility throughout the paper. In fact, the pollution formation mechanism remain unclear in Beijing.

Re: Revised, Thanks! This has been addressed as “the pollution formation mechanism and the climate effects of aerosols remain highly uncertain due to the highly variable physical and chemical properties of aerosols, as well as complex mechanisms that govern aerosol-climate interactions” in the revised version of the paper (see L60-63).

Line 250-251: The authors define the 40 nm and 150 nm particles as fresh and pre-existing particles, respectively. The authors should address the validity of the definition. In fact, freshly emitted refractory particles (like BC) are primarily within the 150 nm to 240 nm diameter range (Levy et al., 2013). In contrast, it takes several hours for the growth of 40 nm even during NPF events. The reviewer suggests that the 40 nm particles are from local sources whereas the 150 nm particles are influenced by long-range transport and vertical mixing.

Re: Revised, Thanks! This has been addressed as “Particles with Dp equal to 40 nm

represent local-impacted particles and particles with Dp equal to 150 nm represent regional-transport particles.” in the revised version of the paper (see L244-246).

Line 314-320: The reviewer highly suspects that the nitrate is responsible for the appearance of more hygroscopic mode in the 40 nm particles in the early morning. How can form H2O2 during the night? The presence of nitrate in Aitken mode particles is very difficult and the addition of nitrate was initially promoted by sulfate condensation (Ye et al., 2010).

Re: The heterogeneous reactions in the atmosphere are complex, the reactive material includes H_2O_2、HO_2、N_2O_5、O_3 and so on. At night the formation of NO_3 and N_2O_5 becomes important, NO_x can be oxidized to NO_3 by through heterogeneous reactions. NO_3 and NO_2 can be further combined to N_2O_5. Then nitrate can be formed rapidly through NO_3 and N_2O_5. This rapid conversion enhances the available nitrate and may add significantly to the nitrate available for condensation, enhancing night-time concentrations compared to those observed in the day (Dall'Osto et al., 2009). In addition, nitrate in locally produced aerosol was present mainly in particles smaller than 300 nm. In our study, ACSM data also suggested nitrate mass concentration increased sharply at night, especially during the non-control period (Zhao et al., 2016, Figure 8.). This has been addressed as “During the Clean2 period, there is another obvious peak at about 0300 LT in the early morning, likely related to the increase in nitrate. Because there was a large amount of NOx emitted from traffic sources in the evening during the non-control period, with the PBL height reduction and ambient temperature decrease, NOx could be transformed into hydrophilic nitrate rapidly through NO3 and N2O5 (Dall'Osto et al., 2009).” in the revised version of the paper (see L306-311).

Line 372: The vehicles emit both gas and particle pollutants, regardless of emission control conditions. However, the NPF is favored when the concentration of pre-existing particles is lower due to emission control.

Re: Revised, thanks! This has been addressed as “As stated previously, during the Clean1 period VOCs has a weaker decrease than SO2 and NOx, this would lead to more VOC-formed organic particles formed, which are normally highly volatile.” in the revised version of the paper (see L362-365).

Line 400-402: Do the authors think the emission of refractory particles at night is larger than at daytime? The increase of number fraction may be caused by the slower particle aging and weaker vertical mixing.

Re: Yes, the sampling site is located in the downtown of the city. A number of diesel vehicles and heavy trucks only can be allowed to enter the downtown at night, this made the increase of refractory particles at night. It can be reflected from the diurnal cycle of BC (Zhao et al., 2017, Section 3.5). Then the slower particle aging and weaker vertical mixing made the external-mixed BC accumulated. This has been addressed as “…and then the slower particle aging and weaker vertical mixing made the external-mixing BC accumulated” in the revised version of the paper (see L395-396).

Line 426-430: The authors should pay attention to the contradictory statements of σκ-PDF “always” exceeds 0.08, … , the mean σκ-PDF of 40-nm particles during the Clean1 period “is

equal to" 0.08.

Re: Revised, thanks! This has been addressed as "σκ-PDF always exceeds 0.08 but the 40-nm particles during the Clean1 period" in the revised version of the paper (see L418-419).

Technical comments:

Line 325: The term of hydrophilic should be replaced by "hygroscopic", because hygroscopic growth do not take place at a high RH for many hydrophilic substance.

Re: Revised, thanks! This has been addressed in the revised version of the paper (see L318).

Line 336: The condensation species are sulfate, nitrate, OA other than SO2, NOx, and VOCs.

Re: Revised, Thanks! This has been addressed in the revised version of the paper (see L329-330).

Ye, X.N., Ma, Z., Hu, D.W., Yang, X., Chen, J.M., 2010. Size-resolved hygroscopicity of submicrometer urban aerosols in Shanghai during wintertime. Atmospheric Research 99, 353-364.

References:

Dall'Osto M., Harrison R.M., Coe H., Williams P.I. and Allan J.D.: Real time chemical characterization of local and regional nitrate aerosols, Atmos. Chem. Phys., 9, 3709-3720, 2009.

Zhao J., Du W., Zhang Y., Wang Q., Chen C., Xu W., Han T., Wang Y., Fu P., Wang Z., Li Z. and Sun Y.: Insights into aerosol chemistry during the 2015 China Victory Day parade: results from simultaneous measurements at ground level and 260 m in Beijing, Atmos. Chem. Phys., 17, 3215-3232, 10.5194/acp-17-3215-2017, 2017.

Enhanced hydrophobicity and volatility of submicron aerosols under severe emission control conditions in Beijing

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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 Victory Day parade, rendering a unique opportunity to investigate anthropogenic impact of aerosol properties. Submicron aerosol hygroscopicity and volatility were measured during and after the control period using a hygroscopic and volatile tandem differential mobility analyzer (H/V-TDMA) system. Three periods, namely, the control 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 measures on aerosol hygroscopicity and volatility. Aerosol particles became more 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 period relative to the Clean2 period, while the volatile shrink factor (SF) of 40–300 nm particles decreased by 7.5%–10.5%. The emission controls also changed the diurnal variation patterns of both the probability density function of κ (κ-PDF) and the probability density function of SF (SF-PDF). During Clean1 the κ-PDF showed one 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 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 more externally-mixed state particularly for the 150 nm particles. Aerosol hygroscopicities increased as particle sizes increased, with the greatest increases seen during the Pollution period. Accordingly, the aerosol volatility became weaker (i.e., SF

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

1. Introduction

China, as the world's second largest economy, is facing severe air pollution problems due to its rapid economic growth. This has led to highly elevated aerosol concentrations, especially in urban regions such as Beijing, Shanghai, and Guangzhou (Hsu et al., 2012; Huang et al., 2014). Every year, high levels of fine particulate matter (PM) have caused many severe haze days in these regions, that may pose a great health 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 mechanism and the climate effects of aerosols ~~still~~ remain highly uncertain due to the highly 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)~~(Tao et al., 2012)~~.

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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).

The Chinese government took many drastic measures to reduce the emissions of air pollutants from industry, road traffic, and construction sites, especially during some great events such as the 2008 Summer Olympic Games, the 2014 Asia-Pacific Economic Cooperation. Swift and drastic improvement in air quality (Huang et al., 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 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 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 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 days of blue sky, vividly named "Parade Blue" (H. Li et al., 2016). During and after the parade emission control period, we conducted in situ measurements of submicron aerosol chemical and physical properties in Beijing. Size-resolved chemical compositions were also obtained (Zhao et al., 2017) ~~(Zhao et al., 2016, published)~~. The average PM less than 1 μm in diameter (PM_1) concentration was 19.3 μg m^{-3} during the parade emission control period, 57% lower than that after the control period. All chemical species decreased during the control period, but their decreasing percentages were different.

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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 hygroscopicity and volatility of submicron aerosols, which may bring some insight into how to reduce pollution in the future. Furthermore, investigating aerosol hygroscopicity and volatility with and without emission controls will help in understanding environmental and climate changes in general. This paper is structured as follows. Section 2 describes the instrumentation and data used, and section 3 introduces the methods to data analysis. Aerosol hygroscopicity and volatility during different periods were compared and discussed in section 4. Conclusions and summary are given in section 5.

2. Experimental methods

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 is located between the north 3rd and 4th ring road in northern Beijing. The sampling instruments were put into a white container at ground level and an air conditioner was used to maintain the temperature at 20–25°C inside the container. Meteorological variables, including temperature (T), relative humidity (RH), wind speed (WS), and 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 buildings on wind, we selected the 280-m wind direction and 8-m wind speed as references in this study. Simultaneously, particle number concentrations (10–600 nm) 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 (DMA, Model 3081A, TSI Inc.) and a condensation particle counter (CPC, Model 3775, TSI Inc.). In addition, the measurement of aerosol chemical composition using a High-Resolution Aerosol Mass Spectrometer (HR-AMS) and an Aerosol Chemical Speciation Monitor (ACSM) were deployed at ground level and at the 260-m level of the tower, respectively. The HR-AMS was situated in a sampling room located on the rooftop of a two-story building (~8 m), ~25 m north from the container. An analysis of the aerosol chemical composition has been done (Zhao et al., 2017) ~~(Zhao et al., 2016,~~

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published).

2.2. Instrumentation and operation

The H/V-TDMA system developed by the Guangzhou Institute of Tropical and Marine Meteorology (ITMM) was used to measure the submicron aerosol hygroscopicity and volatility. The H-TDMA system (H-mode) shown in Figure 1 consists of four main parts: (1) a nafion dryer (Model PD-70T-24ss, Perma Pure Inc., USA) and a bipolar neutralizer (Kr85, TSI Inc.). The nafion dryer ensured that the RH of the sample flow was below 20% over the entire measurement period, and the bipolar neutralizer was used to equilibrate the charge of particles (Wiedensohler, 1988).; (2) the first differential mobility analyzer (DMA_1, Model 3081L, TSI Inc.): The DMA_1 was used to select quasi-monodisperse particles of a certain diameter through a fixed electric voltage. The diameters selected were 40, 80, 110, 150, and 200 nm.; (3) a nafion humidifier (Model PD-70T-24ss, Perma Pure Inc., USA). The nafion humidifier was used to humidify the aerosol flow from the DMA_1 to a defined RH. In the study, we set RH to 90%.; (4) the second DMA (DMA_2, same model as the DMA_1) and a condensation particle counter (CPC, Model 3772, TSI Inc.). The DMA_2 and the CPC were used together to measure the number size distribution of the humidified particles. An automated valve located between the DMA_1 and the nafion humidifier directly connects the DMA_1 with the CPC. This can be used to measure the 10–400 nm particle number size distribution (PNSD) by varying the electric voltage of the DMA_1. Details about the design of the HTDMA system and its applications are given by Tan et al.

398 (2013a).

399 The design of the V-TDMA system (V-mode) is similar to that of the H-TDMA
400 system, except that the nafion humidifier in the V-TDMA system was replaced by a
401 heating tube that induces the evaporation of volatile materials. The heating tube was an
402 80-cm long stainless steel tube with an inner diameter of 8 mm. With a sample flow
403 rate of 1.0 L min^{-1}, its residence time (~ 2.4 s) in the heated section is sufficient for the
404 volatile materials to be effectively vaporized (Cheung et al., 2016). In this study, the
405 heating temperature was set to 300°C. The residual particles of volatile compounds at
406 this temperature, such as sulfates, nitrates, and most organics, are mainly refractory
407 non-volatile organic carbon (such as polymer-type organics), and sea salts (Philippin et
408 al., 2004; Wehner et al., 2009; Cheung et al., 2016; Ma et al., 2016). Particle were
409 measured at the diameters of 40, 80, 110, 150, 200 and 300 nm. The H/V-TDMA system
410 has been successfully used in previous studies (Tan et al., 2013b; Cheung et al., 2016;
411 Tan et al., 2016).

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

415 $$GF = D_p(RH)/D_{0dry}\,, \quad (1)$$

416 $$SF = D_p(T)/D_{0dry}\,. \quad (2)$$

417 Here, $D_p(RH)$ refers to the particle diameter measured at RH = 90%, $D_p(T)$ refers to the
418 particle diameter measured at T = 300°C, and D_{0dry} refers to the dry diameter set by the
419 DMA_1. The measured distribution function (MDF) versus GF or SF can be calculated

with the number concentration from CPC data downstream from the DMA_1 and the DMA_2. 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) due to the effect of the DMA diffusion transfer function (Swietlicki et al., 2008; Gysel et al., 2009). In this study, the TDMAfit algorithm (Stolzenburg et al., 1988, 2008) was used to retrieve the GF-PDF and the SF-PDF. The TDMAfit algorithm assumes that groups in the PDF following one or more lognormal distribution functions (Gaussian shape), thus allowing for the possibility that particles of a given type are not all identical.

3. Data analysis

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:

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

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, $\mathrm{D_d}$ 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

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

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

The standard deviation of κ-PDF is:

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

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

3.3. Classification of different hygroscopic and volatile groups

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 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 measurements (Figure S1), ambient aerosol particles were classified into three hygroscopic groups and three volatile groups, where κ and SF are used here to define the boundaries for each group:

Nearly-Hydrophobic, NH: $\kappa < 0.1$;

Less-Hygroscopic, LH: $0.1 \leq \kappa < 0.2$;

More-Hygroscopic, MH: $0.2 \leq \kappa$;

Non-Volatile, NV: $SF \geq 0.88$;

Slight-Volatile, SV: $0.88 > SF \geq 0.55$;

Very-Volatile, VV: $SF < 0.55$.

The number fraction (NF) for each hygroscopic group with the boundary of [a, b] is defined as:

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

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

4. Results and discussion

4.1. Overview of measurements

4.1.1. Meteorological conditions during the sampling period

Air quality has a strong correlation with local wind direction in Beijing. Previous studies have shown that high PM concentrations usually correspond to southerly winds, while low PM concentration are generally related to northerly winds, because there were more high concentration air pollutants from source locations south of the Beijing area (Wehner et al., 2008; Wang et al., 2010; Gao et al., 2011). Figure 2 displays time series of WD at 280 m, WS at 8 m, ambient T, and RH. During the emission control period, the prevailing winds were northerly, except for the period from 29 August to 30 August due to the influence of accumulated precipitation. During the non-control period, the prevailing winds changed due to the influence of weather systems. Two cold fronts

passed ~~through~~ on two different days, i.e., on the night of 9 September and in the early morning of 30 September. During these frontal passages, the prevailing winds were northerly, but on other days, the prevailing winds were southerly and the meteorological parameters showed obvious diurnal cycle patterns. Over the measurement period, the average ambient T and RH were 21.9°C and 62.4%, respectively.

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 (~~ρ10-400 nm~~$PM_{10\text{-}400\ nm}$) derived from PNSD measurements and the time series of κ-PDF and SF-PDF with 40 nm and 150 nm particles as examples. Particles with D_p equal to 40 nm represent local-impacted particles~~fresh particles~~ and particles with D_p equal to 150 nm represent regional-transport particles~~pre-existing particles~~. Several haze events during the non-control period can be seen from the time series of ~~ρ10-400 nm~~$PM_{10\text{-}400\ nm}$, which shows the rapid accumulation of particle mass concentration. Based on mass concentrations and weather conditions, we selected several clean and pollution periods to study the differences in aerosol hygroscopicity and volatility for two different cases (Figure 3). To further study the effect of emission controls, we divided the clean period into two periods: Clean1 (control clean period) and Clean2 (non-control clean period). During the Clean1, Clean2, and Pollution periods, the average ~~ρ10-400 nm~~$PM_{10\text{-}400\ nm}$ was 6.9±2.8, 6.0±4.2, and 51.0±25.6 μg m^{-3}, respectively. There was no significant precipitation during the three selected periods. The time series of κ-PDF and SF-PDF (Figure 3b-e) showed evident changes and fluctuations in the measurements. The

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505 prominent differences in κ-PDF and SF-PDF during the three periods will be discussed
506 in the following sections.

507 A wind rose diagram (Figure S2) was used to compare winds during the different
508 periods. During the Clean1 and Clean2 periods, wind directions were similar, mainly
509 from the north and northwest. During the Pollution period, the wind direction had the
510 characteristics of mountain-valley breezes where the wind direction changed routinely
511 at midnight and changed the wind direction from southerly to northerly (Figure 2). The
512 change in wind direction at night would reduce pollution in the short term (Sun et al.,
513 2016b). Even so, the prevailing wind direction was southerly during the Pollution
514 period (Figure S2), which was favorable for the transport of pollutants from the more
515 populated and more industrialized south and southeast to Beijing. The mean WS and
516 RH were similar during all periods, but the mean temperature during the Clean2 period
517 was lower than during the other periods due to the influence of cold fronts (Table S1).
518 In summary, the meteorological parameters of the Clean1 and Clean2 cases were similar
519 expect for the ambient T. This provided the opportunity to compare the differences in
520 aerosol properties between control and non-control periods. The high level of PM
521 during the Pollution case can also provide a good opportunity to compare differences
522 between clean and polluted environments.

523 **4.2.Diurnal variation**

524 **4.2.1. Diurnal variation in the aerosol size distribution**

525 Figure 4a shows the diurnal variation in total number concentration of 10–400 nm

particles ($N_{10–400\ nm}$). In general, $N_{10–400\ nm}$ 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 $N_{10–400\ nm}$ 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 $N_{10–400\ nm}$ peak was lower than that observed during the Clean2 period, and the peak in the Clean1 case appeared two hours 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 during the Clean2 period, and that it was likely related to the decrease in precursors during the Clean1 period. H. Li et al. (2016) have reported that during the parade control period, the precursors SO_2, NO_x, and volatile organic compounds (VOCs) decreased by 36.5%, 49.9%, and 32.4%, respectively. The relatively higher ambient temperature 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 particles ($PM_{10\text{-}400\ nm}$~~$\rho_{10\text{-}400\ nm}$~~) during the three periods. No clear increase in ~~$\rho_{10\text{-}400\ nm}$~~$PM_{10\text{-}400\ nm}$ is seen 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 ~~$\rho_{10\text{-}400\ nm}$~~$PM_{10\text{-}400\ nm}$. During the Clean1 and Clean2 periods, $PM_{10\text{-}400\ nm}$~~$\rho_{10\text{-}400\ nm}$~~ 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

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could partly offset the influence of the PBL.

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, BC) emitted from local diesel trucks and heavy-duty vehicles results in the decrease in κ_{mean} during nighttime (Liu et al., 2011; S. L. Zhang et al., 2016). During the Clean2 period, there is another obvious peak at about 0300 LT in the early morning, likely related to the increase in nitrate. Because there was a large amount of NO_x emitted from 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 hydrophilic nitrate rapidly through NO_3 and N_2O_5 (Dall'Osto et al., 2009). ~~through heterogeneous reactions with dissolved H_2O_2 during nighttime (Seinfeld et al., 2016).~~ This was also verified from comparisons of the nitrate diurnal cycle with and without emission controls (Zhao et al., 2017) ~~(Zhao et al., 2016, published)~~.

Figure 5b shows the diurnal variation in κ-PDF for particles with D_p equal to 40 nm (i.e., local-impacted~~newly formed~~ particles) during the three periods. During the Clean1 period, the κ-PDF has a quasi-unimodal shape (only in the hydrophobic mode). During NPF events, κ_{mean} increases slightly, indicating that 40-nm particles from local

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sources were always hydrophobic and a very small amount of hygroscopic~~hydrophilic~~ particles were produced 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 concentrations of SO_2 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 by oxidation and condensation of VOCs. By contrast, during the Clean2 period, the κ-PDF with D_p of 40 nm shows either a bimodal or quasi-trimodal distribution and 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 decreased and the hydrophilic mode increased (Figure 5b), suggesting the conversion of externally mixed particles to internally mixed particles due to the species condensation (sulfate, nitrate and organics) from the photochemical reaction of SO_2, NO_x and VOCs.~~the condensation of gas precursors (including SO_2, NO_x, as well as VOCs).~~ A similar phenomenon was also observed by Z.J. Wu et al. (2016). For 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, mainly due to substantial traffic emissions at rush hour. However, during the Pollution period, the κ-PDF shows a bimodal shape during the day. The hydrophilic mode 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 during the day.

In summary, the diurnal variations in κ-PDF for 40-nm particles were significantly

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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 SO_2 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~~pre-existing 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 pre-existing 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.

4.2.3. Diurnal variation in aerosol volatility

Figure 6a shows the diurnal variation in SF_{mean}, which shows similar trends for all three cases, with the lowest SF_{mean} in the afternoon (1200–1500 LT) and the highest SF_{mean} in the morning (0700–0900 LT) for all particles with D_p ranging from 40-300 nm. The diurnal variations illustrate that particles had a higher volatility during the day than at night. This feature is more obvious for those small particles observed during the

612 Clean1 period. During the Clean1 period, particle volatility increased dramatically (i.e.,
613 SF_{mean} decreased) along with the occurrence of NPF events, suggesting that the earliest
614 newly-formed matter (before ~1200 LT) were always volatile at 300°C. As stated
615 previously, during the Clean1 period VOCs has a weaker decrease than SO2 and NOx,
616 this would lead to more VOC-formed organic particles formed, which are normally
617 highly volatile. ~~and likely due to the dramatic reduction in soot particles, the primary~~
618 ~~emissions were VOCs from motor vehicles in urban Beijing. This would lead to more~~
619 ~~VOC-formed organic particles, which are normally highly volatile.~~ Therefore, the
620 highest volatility was observed during the Clean1 period. Wehner et al. (2009) also
621 showed that ~97% of newly-formed particles are volatile because they are dominated
622 by sulfate and organics ~~VOCs~~. With the processes of particle aging, collision, and
623 growth, they then decrease in volatility (i.e., SF_{mean} increases). This is because these
624 processes can enhance the oxidative level of organics and there are more refractory
625 organics (like polymer-type organics) produced.

626 For 40-nm particles, the lowest SF_{mean} appeared two hours later during the Clean2
627 period (~1500 LT) than during the Clean1 period (~1300 LT). This is probably because
628 NPF lasted longer during the Clean2 period. For larger particles, the coating effect of
629 condensable vapors onto pre-existing particles was the major reason behind the
630 intensification of their volatility during NPF events (Wehner et al., 2009; Cheung et al.,
631 2016). The SF_{mean} decreased little compared to that for 40-nm particles. By comparison,
632 the diurnal variation in SF_{mean} for 40-nm particles during the Pollution period changed
633 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-mixed with highly aging levels.

Figure 6b and 6c show the diurnal variation in SF-PDF for 40 nm and 150 nm particles. The SF-PDF normally has an NV mode and a SV or VV mode. The NV mode consists of non-volatile particles, like BC particles, which do not shrink when aerosols are heated. SV and VV modes suggest a mixture of volatile (e.g., organics) and non-volatile matter that shrink when aerosols are heated (Kuhn et al., 2005). The two SF-PDF modes suggest that the particles during the observed periods were mostly externally-mixed. The 40-nm and 150-nm SF-PDF show similar diurnal patterns. During daytime, active aging processes facilitated the mixing of primary particles with secondary species, leading to the transformation of externally-mixed particles to 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 reduction in emissions of soot particles during the control period. In the evening and the early morning, the number fraction of NV-mode particles increased again because a large amount of refractory particles (like BC) were emitted from traffic sources or cooking, and then the slower particle aging and weaker vertical mixing made the external-mixing BC accumulated ~~in the nocturnal boundary layer~~ (S. L. Zhang et al., 2016). The number fraction of NV-mode 150-nm particles in the Clean1 case had a stronger increase than that of 40-nm particles in the evening and early morning. This is because freshly emitted refractory particles (like BC) are primarily within the 150 nm to 240 nm diameter range (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. 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 (like SO_2, NO_x), which are usually present in extremely high concentrations during polluted days in urban Beijing (Guo et al., 2014; Sun et al., 2016a).

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

4.3. Size-resolved particle hygroscopic and volatile properties

Table 1 summarizes the size-resolved mean κ, the growth spread factor ($\sigma_{\kappa\text{-PDF}}$) of κ-PDF, size-resolved SF during different periods, and the change in percentages of κ and SF due to the emission control policy. The $\sigma_{\kappa\text{-PDF}}$, defined as the standard deviation of κ-PDF, is an indication of the mixing state of aerosol particles. A higher $\sigma_{\kappa\text{-PDF}}$ 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 $\sigma_{\kappa\text{-PDF}} = 0.08$ as the cut-off point for high external mixing and quasi-internal mixing. In this study, $\sigma_{\kappa\text{-PDF}}$ always exceeds 0.08 but the 40-nm particles during the Clean1 period, indicating that the particle population was more externally mixed in urban Beijing. THowever, the mean $\sigma_{\kappa\text{-PDF}}$ of

40-nm particles during the Clean1 period is equal to 0.08, suggesting that during the control period, 40-nm particles had a low degree of external mixing. This is also seen in the quasi-unimodal distribution of 40-nm κ-PDF (Figure 5b).

During the selected three periods, aerosol particles were more hygroscopic (i.e., κ 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 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 composed of more inorganic salts or oxidized organics, especially in a polluted environment (Swietlicki et al., 2008; Achtert et al., 2009; Fors et al., 2011; Sun et al., 2016a). Meanwhile, the increase in $\sigma_{\kappa\text{-PDF}}$ with the increase in particle size illustrates that there were more external mixing particles with larger sizes (Table 1). Accordingly, 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 during the control Clean1 period than during the non-control Clean2 period, which can also be seen from the variation in chemical composition. Based on HR-AMS measurements, secondary inorganic aerosols (SIA) had larger decreases than organic aerosols (OA) during the parade control period. The positive matrix factorization of OA further illustrates that primary OA (POA) had similar decreases as secondary OA (SOA). However, more-oxidized SOA had larger decreases than less-oxidized SOA

(Zhao et al., 2017)~~(Zhao et al., 2016, published)~~. SIA is always more hydrophilic than OA and more-oxidized SOA is also more hydrophilic than less-oxidized SOA (Jimenez et al., 2009; Chang et al., 2010; Rickards et al., 2013; Zhang et al., 2014; F. Zhang et al., 2016). Therefore, the increased fraction of POA emissions, but weakened age processing due to a sharp reduction in SO_2 and NO_x, lead to particles being less hygroscopic during the control period. Meanwhile, particles become relatively more volatile due to the high number of POA particles because OA volatility is generally inversely correlated~~corrected~~ with the O:C ratio (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)~~(Arellanes et al., 2006; Bian et al., 2014)~~, and eventually improving atmospheric visibility.

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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.

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

For submicron particles, non-volatile (NV) part particles at 300ºC 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 POA and less-oxidized SOA. Accumulation mode particles (> 100 nm) show a relatively better linear correlation between NF_{NH} and NF_{NV}, i.e., correlation coefficients (R^2) are 0.26, 0.55, and 0.62 for 110, 150, and 200 nm particles, respectively. The higher R^2 for the larger particles may arise because larger particles 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-fit regression line for the accumulation mode particles is always lower than the 1:1 line. This can be attributed not only to externally mixed SIA and volatile organics

742 (completely volatile), which are not taken into account for calculation, but also to that
743 some medium/high volatile organics are nearly-hydrophobic.

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

752

753 **5. Conclusions and Summary**

754 In this study, a H/V-TDMA system was used to measure submicron aerosol
755 hygroscopic and volatile properties in Beijing during and after the parade emission
756 control period. Three periods, namely, the control clean period (Clean1), the non-
757 control clean period (Clean2), and the non-control pollution period (Pollution), were
758 selected to study the effect of emission control on aerosol hygroscopicity and volatility.

759 When emission control measures were in place, particles became more
760 hydrophobic and volatile compared to particles in the non-control period. The κ of 40–
761 200 nm particles decreased by 32.0–8.5% during the Clean1 period relative to the
762 Clean2 period, while SF of 40–300 nm particles decreased by 7.5–10.5%. The diurnal

763 variations of κ-PDF were significantly different during the three selected periods,
764 especially for small particles. During the Clean1 period, the κ-PDF of 40-nm particles
765 always showed a quasi-unimodal distribution and had a weaker diurnal variation than
766 that observed during the Clean2 period. This demonstrates that emission control
767 measures can change the diurnal variation pattern of κ-PDF due to the reduction in gas
768 precursors like SO_2 and NO_x, which suppresses the formation of hydrophilic matter.
769 The diurnal variation in aerosol volatility was different between clean and polluted
770 periods. NPF appears to enhance aerosol volatility through the formation of volatile
771 matter and the coating effect of condensable vapors. The particles observed during the
772 control period showed two significant modes during the day, i.e., NV and VV modes,
773 and a more externally-mixed state particularly for larger particles.

774 Aerosol particles became more hygroscopic (i.e., κ increases) as the particle size
775 increased during the three periods. The trend was greatest for the Pollution case where
776 κ increased from 0.16 to 0.42 when D_p changed from 40 nm to 200 nm, but only
777 increased from 0.10 to 0.25 for the Clean1 case and from 0.14 to 0.28 for the Clean2
778 case. Meanwhile, the increase in $\sigma_{\kappa\text{-PDF}}$ (i.e., the standard deviation of κ-PDF) with the
779 increase in particle size also illustrates that there were more external mixing particles
780 with larger sizes. Accordingly, aerosol volatility became weaker (SF increased) as
781 particle size increased during the Clean1 and Clean2 periods, but no apparent trend was
782 observed for the Pollution period.

783 Our results suggest that emission control measures weaken submicron aerosol
784 hygroscopicity, and that aerosol particles are more hygroscopic in a polluted

environment. The significant decrease in aerosol hygroscopicity is favorable for suppressing the evolution of regional air pollution. In addition, because of the reduced hygroscopicity, fewer particles would be activated as could 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 from a broader perspective.

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Table 1. Summary of size-resolved mean κ, the κ-PDF growth spread factor ($\sigma_{\kappa\text{-PDF}}$), 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 period.

		40 nm	80 nm	110 nm	150 nm	200 nm	300 nm
Clean1	κ	0.10±0.05	0.11±0.06	0.15±0.07	0.20±0.10	0.25±0.12	—
	$\sigma_{\kappa\text{-PDF}}$	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
Clean2	κ	0.14±0.06	0.17±0.08	0.20±0.10	0.24±0.12	0.28±0.13	—
	$\sigma_{\kappa\text{-PDF}}$	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	—
	$\sigma_{\kappa\text{-PDF}}$	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
$\frac{(\text{Clean1}-\text{Clean2})}{\text{Clean2}}$	κ	-32.0%	-31.9%	-26.1%	-17.5%	-8.5%	—
	SF	-7.5%	-9.4%	-9.2%	-8.7%	-10.1%	-10.5%

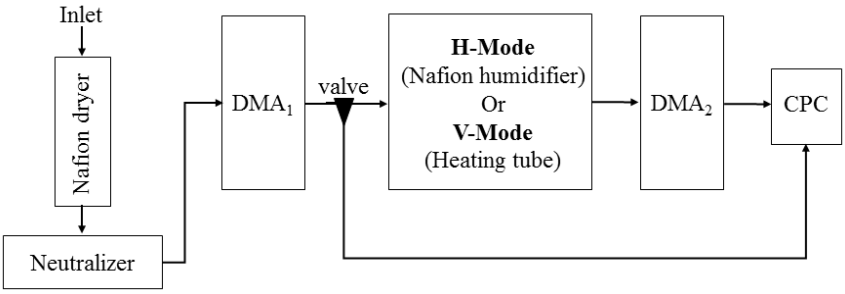

Figure 1. A schematic diagram of the hygroscopic and volatile tandem differential mobility analyzer (H/V-TDMA).

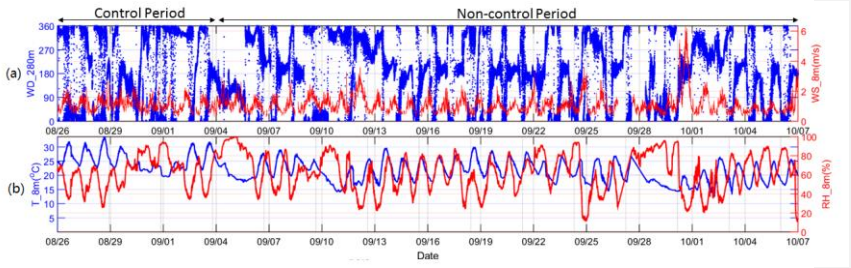

Figure 2. Time series of (a) wind direction at 280 m (in blue) and wind speed at 8 m (in red), and (b) ambient temperature at 8 m (in blue) and relative humidity at 8 m (in red) during the control and non-control periods.

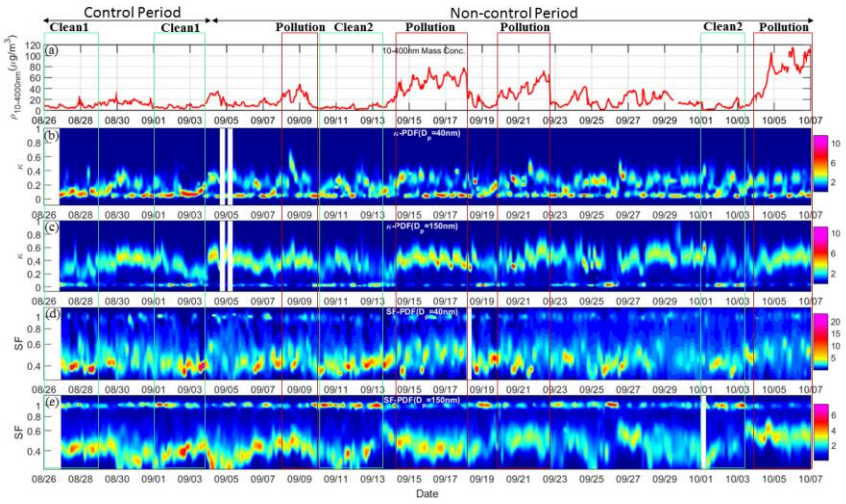

Figure 3. Time series of (a) 10-400 nm aerosol mass concentration (~~$\rho_{10\text{-}400\ nm}$~~$PM_{10\text{-}400\ nm}$) (assuming that the aerosol density is 1.6 g cm^{-3}), hygroscopicity parameter κ distributions (κ-PDF) for (b) 40-nm and (c) 150-nm particles at RH = 90%, and volatile shrink factor distributions (SF-PDF) for (d) 40-nm and (e) 150-nm particles at T = 300°C.

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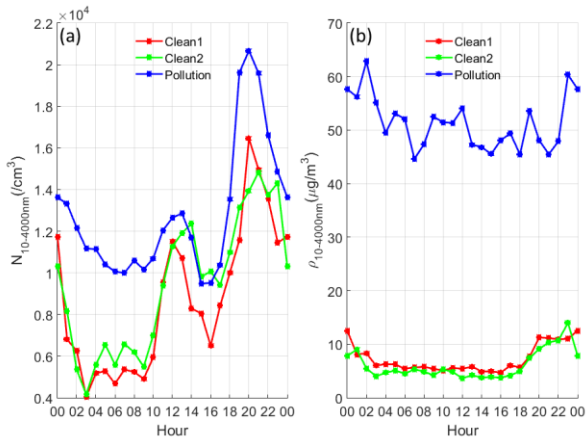

Figure 4. Diurnal variation in mobility diameter (D_p) 10-400 nm particles (a) number concentration ($N_{10\text{-}400\ nm}$) and (b) mass concentration (~~$\rho_{10\text{-}400\ nm}$~~$PM_{10\text{-}400\ nm}$) for the

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Clean1 (in red), Clean2 (in green), and Pollution (in blue) cases.

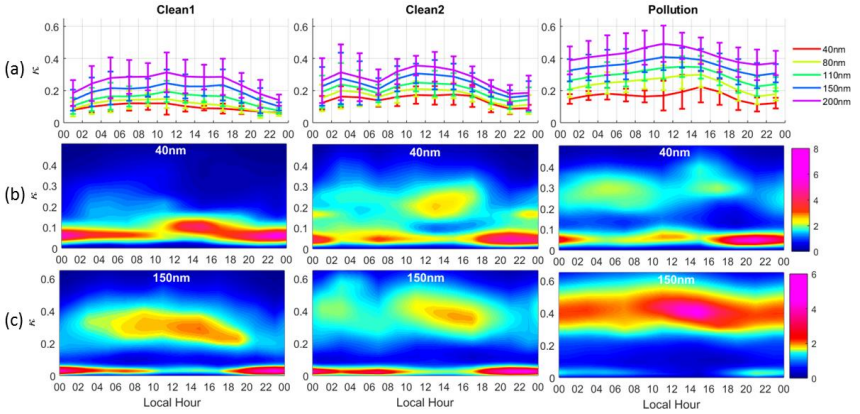

Figure 5. Diurnal variations in (a) mean κ (κ_{mean}) for different mobility diameters, (b) κ-PDF for particles with D_p equal to 40 nm, and (c) κ-PDF for particles with D_p equal to 150 nm during the Clean1, Clean2, and Pollution periods.

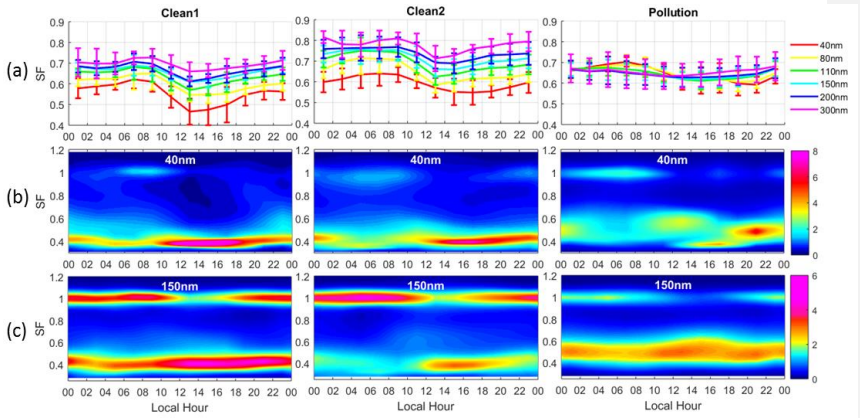

Figure 6. Diurnal variation of (a) mean SF (SF_{mean}) for different mobility diameters, (b) SF-PDF for particles with D_p equal to 40 nm, and (c) SF-PDF for particles with D_p equal to 150 nm during the Clean1, Clean2, and Pollution periods.

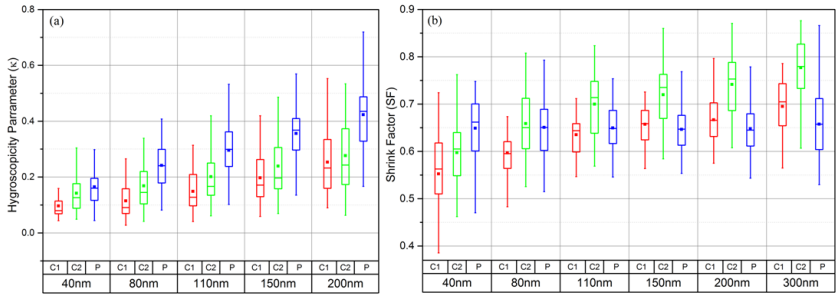

Figure 7. Size-resolved (a) κ and (b) SF during Clean1 (C1), Clean2 (C2), and Pollution (P) periods. The figure shows the mean κ or SF (solid square markers) with boxes showing the 25th, 50th, and 75th percentiles. The extremities show the 5th and 95th percentiles.

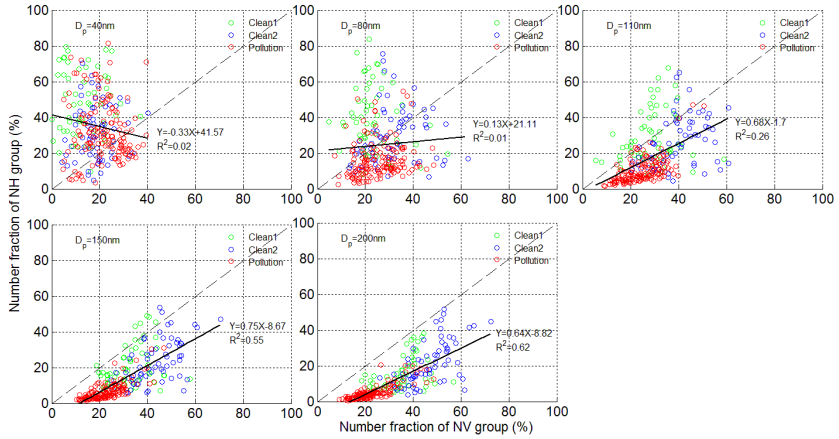

Figure 8. Comparisons between the number fractions of the nearly-hydrophobic group (NF_{NH}) and the non-volatile group (NF_{NV}) for the Clean1 (in green), Clean2 (in blue), and Pollution (in red) periods.