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Modeling of aerosol property evolution during winter haze episodes over a megacity cluster in northern China: Roles of regional transport and heterogeneous reactions

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Abstract. Regional transport and heterogeneous reactions played crucial roles in haze formation over a megacity cluster centered on Beijing. In this study, the updated Nested Air Quality Prediction Model System (NAQPMS) and the HYSPLIT Lagrangian trajectory model were employed to investigate the evolution of aerosols—in terms of the number concentration, size distribution, and aging degree—in Beijing during six haze episodes between November 15 and December 15, 2016, as part of the Air Pollution and Human Health–Beijing (APHH-Beijing) winter campaign of 2016. The model exhibited reasonable performance not only for mass concentrations of $PM_{2.5}$ and its components in Beijing but also for the number concentration, size distribution, and aging degree. We discovered that regional transport played a nonnegligible role in haze episodes, with contributions of 14%–31% to the surface $PM_{2.5}$ mass concentration. The contribution of regional transport to secondary inorganic aerosols was larger than that of regional transport to primary aerosols (30%–63% vs. 3%–12%). The chemical transformation of SO_2 in the transport pathway from source regions to Beijing was the major form of SO_4^{2-} regional transport. We also found that sulfate formed outside Beijing from SO_2 that was emitted in Beijing; this sulfate was then blown back to Beijing and considerably influenced haze formation. In the transport pathway, aerosols

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underwent aging, which altered the mass ratio of coating to black carbon (R_{BC}) and the size distribution of number concentrations. During the episodes, the geometric mean diameter (GMD) increased from less than 100 nm at the initial site to approximately 120 nm at the final site (Beijing), and R_{BC} increased from 2–4 to 4–8. These changes would affect regional radiation and climate. In haze episodes with high humidity, the average contributions of gas and aqueous chemistry, heterogeneous chemistry, and primary sulfate emission were comparable. Primary emissions had the greatest impact under light to moderate pollution levels, whereas heterogeneous chemistry had a stronger effect under high pollution levels.

Keywords: Regional transport; heterogeneous reactions; number size distribution; NAQPMS

1 Introduction

In past decades, a megacity cluster in China that is centered on Beijing and includes 28 cities (272,500 km^2, a population of 191.7 million people) has been experiencing frequent severe and persistent haze episodes (Zhao et al., 2013; Sun et al., 2014; Sun et al., 2016). $PM_{2.5}$ levels exceeding 500 μg m^{-3} have often been reported. The adverse effects of $PM_{2.5}$ on visibility, climate, and particularly human health have drawn widespread public attention (Hyslop, 2009; Chen et al., 2018; Yang et al., 2017a; Yang et al., 2017b; Anderson et al., 2010). Although the $PM_{2.5}$ concentration in Beijing has decreased by 35% in the recent 5 years (2013–2017) because of implementation of the Atmospheric Pollution Prevention and Control Action Plan, the $PM_{2.5}$ level in Beijing in 2017 still reached 58 μg m^{-3}, which is 1.7 times the World Health Organization-recommended safe level of 35 μg m^{-3} (http://www.bjepb.gov.cn/bjhrb/index/index.html). Understanding the mechanism of haze episodes in this megacity cluster is thus an urgent task for policymakers.

Observations have revealed that haze episodes in this megacity cluster are mainly caused by the rapid formation of secondary inorganic species (SIA, including sulfate, nitrate, and ammonium) (Huang et al., 2014; Zheng et al., 2015; Han et al., 2016). The

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SIA mass fraction in $PM_{2.5}$ can be up to 55% on days of severe pollution, which is 2.5 times that on clear days (Ma et al., 2017). Tang et al. (2016) proposed that local chemical transformation related to humidity dominates the rapid formation of SIA in Beijing. Yang et al. (2015) argued that local chemical conversion would not be fully able to support the observed rapid formation of SIA in a short time. Using a ceilometer and in situ observation data, Zhu et al. (2016) and Ma et al. (2017) further proposed that regional transport was the major cause of the initial haze stage and that local chemistry, particularly heterogeneous chemistry, dominated the later rise in Beijing. This result is different from the findings obtained using numerical air quality models (LOTOS-EUROS, Regional Air Quality Model System [RAQMS], and the Nested Air Quality Prediction Modeling System [NAQPMS]) (Timmermans et al., 2017; Li and Han, 2016; Li et al.,2017), in which regional transport dominated during haze episodes in the megacity cluster. Recent observations of the physiochemical properties (e.g., mixing state, number concentration, and size distribution) of aerosols can provide more information for improving the accuracy of regional transport and chemistry assessment. Black carbon (BC) is usually more thickly coated by SIA and organic aerosols in transported and aged air masses than in fresh particles, as indicated by the higher mass ratio of coating to BC (R_{BC}) (Wang et al., 2018). Massoli et al. (2015) and Wang et al. (2017) reported that R_{BC} exceeded 10 in remote sites after BC had undergone long-term transport. This value was much higher than that in an urban area with high fresh particle emissions, where R_{BC} generally was less than 1.5 (Liu et al., 2017). The geometric mean diameter (GMD) of $PM_{2.5}$ also changed significantly due to the impact of regional transport. In haze episodes in Beijing, the GMD increased to 120 nm in regionally transported air masses, which is twice that under clean conditions (Ma et al., 2017). Investigating the evolution of aerosol properties other than mass concentration during regional transport is thus essential for assessing the roles of regional and local chemistry. Such investigations are rarely conducted using the current three-dimensional chemical transport models, which mostly concentrate on mass concentrations. The treatment of heterogeneous chemistry is likely another source of modeling uncertainty. The current

models generally account for only a part of the observed SO_4^{2-} concentrations (Wang et al., 2014). Heterogeneous chemistry is considered critical to improving model performance (Zheng et al., 2015; Cheng et al., 2016; Li et al., 2018).

From November 15 to December 15, 2016, a field campaign was carried out in Beijing within the framework of the UK-China Air Pollution & Human Health (APHH) project. Nearly 30 Chinese and British institutions—including the Institute of Atmospheric Physics, Chinese Academy of Sciences, Leeds University, the University of Birmingham, the University of Reading, Tsinghua University, and Peking University—participated in this campaign. Aerosol properties such as the size distribution, number concentration, and mixing states were simultaneously measured in China. APHH-Beijing aimed to explore the sources of and processes affecting urban atmospheric pollution in Beijing. In the present study, we used the NAQPMS to simulate aerosol properties in the campaign period as a part of the APHH winter campaign. To improve model performance, the NAQPMS was updated by coupling it with an advanced particle microphysics (APM) module that explicitly accounts for the microphysical process and a new heterogeneous chemistry scheme (Chen et al., 2014; Li et al., 2018). The hybrid single-particle Lagrangian integrated trajectory model (HYSPLIT) was also employed to assess the evolution of aerosol properties (e.g., mixing state, number concentration, and size distribution). Crucially, the effects of regional transport and heterogeneous chemistry on aerosol properties were quantified. To the best of our knowledge, this is the first study to distinguish the contributions of transport of SIA itself and its precursors to $PM_{2.5}$ in Beijing. We believe that this study is helpful to understanding the causes of haze in this megacity cluster.

2 Model description and methodology

2.1 Model description

The Nested Air Quality Prediction Model System (NAQPMS) developed by the Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP/CAS) is a three-

dimensional Eulerian terrain-following chemical transport model. WRFv3.6.1, driven by Final Analysis (FNL)data from the National Centers for Environmental Prediction (NCEP), provides the meteorology field for the NAQPMS. The NAQPMS includes emission, horizontal and vertical advection and diffusion, dry and wet deposition, and chemical (including gas, aqueous, and heterogeneous) reaction processes (Wang et al., 2001; Li et al., 2012; Li et al., 2018). It also incorporates online source tagging, process analysis, an online WRF coupler, and other techniques (Wu et al., 2017; Wang et al., 2014). The Carbon Bond Mechanism version-Z (CBMZ) is used for gas-phase chemistry mechanisms. The thermodynamic model ISORROPIAI1.7 is used to calculate the composition and phase state of an NH_4^+–SO_4^{2-}–NO_3^-–Cl^-–Na^+–H_2O inorganic aerosol system (Nenes et al., 1998). Six secondary organic aerosols are managed using a two-product module. Further details of the NAQPMS can be found in the studies of Li et al. (2013, 2014, 2017), and numerous subsequent papers have been published describing recent updates.

To accurately describe aerosol properties (e.g., number concentration, size distribution, and mixing states), an advanced multitype, multicomponent, size-resolved microphysics (APM) module is coupled to the NAQPMS (Chen et al., 2014). APM explicitly describes microphysical aerosol processes, including nucleation, condensation, evaporation, coagulation, thermodynamic equilibrium with local humidity, hygroscopic growth, and dry and wet deposition (Yu and Luo, 2009), and it has already been applied in the global GEOS-Chem model (Ma et al., 2014). In the updated NAQPMS, 40 sectional bins covering 0.0012–12 μm were used to represent secondary particle distribution (SO_4^{2-}, NO_3^-, NH_4^+, and secondary organic aerosols) (Chen et al., 2014). The size distribution of BC and primary organic aerosol was represented using 28 section bins. Other primary particles such as dust and sea salt were represented using four bins. The coating of secondary species on primary particles (sea salt, BC, OC, and dust) was explicitly simulated using a scheme that dynamically calculates the aerosol aging time with an hourly resolution on the basis of aerosol microphysics. The mass concentrations of coating species were also tracked in the

model. Chen et al. (2017) employed the updated NAQPMS and revealed that the daytime aging time of BC in Beijing in winter can be less than 2 hours. This is much less time than the fixed aging time scale of 1.2 days that has been stipulated in previous studies (Liu et al. 2009) but is close to observed levels (2–4 hours) (Peng et al. 2016). Li et al. (2018) further developed a heterogeneous chemical scheme based on mixing states to reproduce the chemical transformation of gaseous precursors on an aerosol surface, which largely altered the sizes and hygroscopicity of particles. Comparison with long-term observations has proven that the updated NAQPMS can successfully estimate aerosol mass and the number concentration, size distribution, mixing states, and BC aging time in China (Li et al., 2017, 2018; Chen et al., 2014, 2017).

Distinguishing the contributions of the transport of SIA itself and its precursors to $PM_{2.5}$ is always difficult (Sun et al., 2014; Li et al., 2014, 2017; Ying et al., 2014). These contributions have generally been named regional transport in studies; this leads to ambiguity in regional transport. In this study, we divided the secondary species (e.g., SIA) in the i^{th} receptor region into four parts: 1) SIA locally produced from the i^{th} locally emitted precursors (LC); 2) SIA chemically formed in other regions from the i^{th} locally emitted precursors (LTC); 3) SIA chemically formed in the transport pathway to the i^{th} receptor region of precursors emitted in the j^{th} source region (RTC); and 4) SIA produced in the j^{th} region from precursors emitted in the j^{th} source region (RLC).

An online tracer-tagging module in the NAQPMS was used to resolve the contributions from LC, LTC, RTC, and RLC. The module is capable of tracing both the emission regions of precursors and the formation regions of secondary aerosols. First, the mass contribution from the locations in which SIA was formed, called C_2, was tagged. The mass contribution from precursors emitted in different locations, called C_1, was then tagged. More technical details can be found in the studies of Li et al. (2014) and Wu et al. (2017). The following equation can be employed to calculate the degree of chemical conversion during transport (TC):

$$TC = \sum_{i=1}^{n}(C_{1i} - C_{2i} \times CC_i) \quad (1)$$

where C_{1i} refers to the absolute mass concentration transported to the receptor site,

produced by precursors emitted in region i;

C_{2i} refers to the absolute mass concentration formed in region i and transported to receptor site;

CC_i refers to the local contribution ratio of precursors in region i;

$C_{2i} \times CC_i$ refers to the absolute mass transported to receptor site and generated at region *i* by chemical conversion of precursors released at region *i*. When $i = 1$, it refers to LC; when $i \neq 1$, $\sum_{i=2}^{n} C_{2i} \times CC_i$ refers to RLC;

$C_{1i} - C_{2i} \times CC_i$ is the mass concentration generated in all regions except *i* by chemical conversion of the precursors released at region *i* and finally transported to the receptor site. When $i = 1$, it refers to LTC; when $i \neq 1$, $\sum_{i=2}^{n}(C_{1i} - C_{2i} \times CC_i)$ refers to RTC.

In this study, 10 regions according to administrative division are selected for source tagging (Fig. 1c), six of which—Chengde, Zhangjiakou, and Qinhuangdao (NHB); Beijing (BJ); Tianjin (LT); Hengshui, Xingtai, and Handan (SHB); Baoding and Shijiazhuang (WHB); and Tangshan, Langfang, and Cangzhou (EHB)—are a part of the Beijing–Tianjin–Hebei (BTH) area. Henan (HN), Shandong (SD), Shanxi (SX), and other regions (OT) are regions outside the BTH area.

2.2 Model structure

Simulation was conducted from November 10 to December 15, 2016, and the first 5 days were set aside as a spin-up period. The three nested model domains were shown in Fig. 1a. The horizontal resolutions were 27, 9, and 3 km from the coarsest to innermost domain. The first level of the NAQPMS was approximately 20 m in height, and there were approximately 17 layers under 2 km.

To quantitatively assess the contribution of primary emissions, traditional chemistry reactions (gas-phase and aqueous chemistry reactions), and heterogeneous chemistry to sulfate, three sensitivity simulations were conducted. The baseline scenario (Base) involving all heterogeneous reactions considered primary sulfate emissions and its results were used for model verification and source apportionment analysis. Control 1 (C1) involved all heterogeneous reactions but did not consider

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primary sulfate emissions. Compared with Base, Control 2 (C2) excluded the heterogeneous reactions of SO_2. Base–C2 represents the effect of heterogeneous reactions on sulfate. Base–C1 represents primary sulfate emissions.

The HYSPLIT model was used to analyze the trajectories of air masses (Draxier and Hess, 1998). The calculated trajectories are helpful to resolving the evolution of aerosol properties in the transport pathway by extracting the simulated results by the NAQPMS along trajectories. In this study, the same meteorology data (obtained hourly data of the third domain) used in the NAQPMS were employed to perform trajectory analysis; this avoided the errors caused by inconsistency between the two models (the NAQPMS and HYSPLIT).

2.3 Emission inventory

The anthropogenic emissions were obtained from the 0.25° × 0.25° Multi–resolution Emission Inventory for China (MEIC), and the base year was 2016 for BTH (http://www.meicmodel.org/publications.html). In addition, observation data collected at sites within BTH were used to update the MEIC on the basis of their latitude and longitude information. Biomass burning emissions were taken from the Fire Inventory from NCAR (National Center for Atmospheric Research) (Wiedinmyer et al., 2011). Primary sulfate was assumed to constitute 5% of SO_2 emissions in the original MEIC inventory, but through in situ measurement of source profiles, Cao et al. (2014), Wang et al. (2009), Zheng et al. (2013), and Ma et al. (2015) discovered that primary sulfate comprised approximately 40%, 6%, and 15% of primary $PM_{2.5}$ from industrial, power, and residential emissions, respectively, in the main form of $(NH4)_2SO_4$. Thus, we modified primary sulfate emissions in this study. Figure 1b displays the hourly primary $PM_{2.5}$ emission rate.

2.4 Observations

The surface meteorological parameters were obtained from the China Meteorological Administration, whereas the vertical profiles of meteorological

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parameters were obtained from the University of Wyoming (http://weather.uwyo.edu/upperair/sounding.html). Observations of $PM_{2.5}$, SO_2, NO_2, and O_3 concentrations were obtained from the China National Environmental Monitoring Center (http://www.cnemc.cn/). Aerosol components (including BC, organic matters [OM], sulfate, nitrate, and ammonium) were measured in situ by using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer. Details of the instruments can be found in the study by Sun et al. (2015). The particle number size distributions at ground level was obtained using a scanning mobility particle sizer (SMPS) with a time resolution of 5 min. Details of the instruments can be found in the study by Du et al. (2017). All data in this study are presented in Beijing local time (UTC + 8 h).

3 Model validation

3.1 $PM_{2.5}$ mass and number concentrations and aging degrees

The time series of simulated and observed $PM_{2.5}$ in different cities of BTH from November 15 to December 15, 2016, are illustrated in Fig. 2. In the study period, six regional haze episodes were identified, namely, November 15–20 (Ep1), November 23–26 (Ep2), November 28–30 (Ep3), December 2–4 (Ep4), December 6–8 (Ep5), December 10–12 (Ep6). The $PM_{2.5}$ mass concentration frequently exceeded 200 μg m^{-3} and the average concentration reached 120 μg m^{-3} during episodes. Haze usually formed in several hours; for example, the increasing rate of $PM_{2.5}$ reached 200 μg m^{-3} h^{-1} and lasted approximately 12 hours in Tangshan. These observed haze patterns were generally reproduced by the NAQPMS. The correlation coefficient (R) between the observation and simulation in most cities was 0.6–0.8, and 60%–80% of simulation results were within a factor of 2 of the observation. The mean fractional bias (MFB) and mean fractional error (MFE) ranged from −0.07 to 0.7, meeting the criteria of MFB ≤ 0.6 and MFE ≤ 0.75 (Boylan et al., 2006). The simulation did however underestimate $PM_{2.5}$ in Beijing and Baoding for Ep2. This was caused by the failure of the mineral

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aerosol transport simulation. Compared with other cities in the cluster, Beijing and Baoding are closer to the Gobi Desert, a major dust source in East Asia, and they are thus more easily affected by dust storm transport. Pan et al. (2018) found a pronounced peak in the size distribution at 4–5 μm for Ep2 in Beijing. The concentrations of Ca^{2+} was 7 times the campaign averages (Fig. S1).

The aerosol components in Beijing, Langfang, and Baoding are compared in Fig. 3. In general, the simulation largely reproduced the variation in primary and secondary aerosols. In particular, the rapid increase in SIA during Ep1, Ep2, and Ep4 was captured by the simulation. Interestingly, the NAQPMS underestimated the sulfate concentration in Beijing during Ep2 and Ep4, but the nitrate and ammoniate concentrations during these two episodes were successfully reproduced. This was related to the transport of mineral dust (Ep2) and local emissions (Ep4). As discussed in the last paragraph, Beijing had high mineral loadings for Ep2, which provided a favorable medium for chemical transformation of anthropogenic SO_2 into sulfate in the form of $CaSO_4$ or $MgSO_4$ (Zhuang et al., 1992). Underestimation of the sulfate concentration for Ep4 may have been caused by local emissions in Beijing. As illustrated in Fig. 3, the simulation failed to reproduce the sharp increase in both sulfate and BC in Beijing during this episode. This is different from the case of Ep2, in which sulfate was underestimated but BC was favorably reproduced. Wang et al. (2009) and Ma et al. (2015) found that sulfate accounted for 40% and 6.6% of primary $PM_{2.5}$ emissions from industry and power plants, which also emit a large amount of BC. This sharp increase in BC was a local-scale episode. In Langfang, a site 50–60 km from Beijing, both the observed and simulated BC concentration increased slowly to 20 μg m^{-3}, which is much less than that in Beijing (45 μg m^{-3}). The monthly emissions employed in this study made it difficult to capture these short-term local-scale emission changes. The simulated SO_2 and NO_2 concentrations are compared with the observations in Fig. S2, and the normalized mean bias (NMBs) of these concentrations were less than 40%.

The number size distribution is critical to examining aerosol evolution during haze episodes (Ma et al., 2017). In this study, both the simulation and observation revealed

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a rapid increase in the GMD from 50 to approximately 120 nm during the initial stages of episodes in Beijing (Fig. 4). The observed mean number concentration of aerosols (dN/dlogDp) showed a unimodal distribution and was mainly concentrated in the Aitken mode (25–100 nm) and accumulation mode (100–1,000 nm). The highest concentration was approximately 1.8×10^4 cm^{-3} at a 100-nm diameter. These patterns were favorably reproduced by the simulation. The simulated number concentrations were underestimated in 10–60 nm by 20%–30% and overestimated in 80–150 nm by 20%. This indicated that the model needs to be improved regarding its treatment of new particle formation and the volatility of primary organic aerosols.

Herein, the aging degree of BC is represented by the mass ratio of coating to BC (R_{BC}), which has been widely used in previous studies (Oshima et al., 2009; Collier et al., 2018). Figure 11 shows that the mean simulated R_{BC} in Beijing was 4.5 and 5.0 in the entire study period and during pollution episodes, receptively, which are extremely close to the observations (~5.0 and 5.1) (Wang et al., 2018). The high performance of the model in terms of mass and number concentrations, compositions, and the mixing state of aerosols gives us confidence for analyzing aerosol evolution during transport in the megacity cluster centered on Beijing.

3.2 Meteorology

The simulated wind direction and speed coincided with the observations for the haze episodes. In particular, the model captured low wind speeds, and the times at which the wind shifted direction were well reproduced (Fig. S3). Regarding relative humidity and temperature, WRF performed high values of R (0.68–0.93) and low NMBs (−0.51 to 0.44) (Table S1). In particular, the high relative humidity during Ep1 was well reproduced. Inversion layers were present during the initial stage of haze formation (Fig. S4). The height of the inversion layers varied among episodes. During Ep1 and Ep6, strongly elevated inversion layers were present between 1 and 2 km, whereas the inversion layers were close to the surface during other episodes. Temperature inversion is favorable for pollution accumulation, and the model reproduced this feature favorably.

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312 In sum, the high performance of the meteorological simulation gave us confidence for
313 $PM_{2.5}$ simulation.

314 4 Results and discussion

315 4.1 Source apportionment of surface $PM_{2.5}$

316 The simulated spatial distribution of average surface $PM_{2.5}$ levels and the wind
317 vector during the six haze episodes are shown in Fig. 5. In general, two types of patterns
318 were observed. The first pattern corresponded to Ep1, Ep4, and Ep6 and reflected that
319 a highly polluted belt with >200 μg m^{-3} $PM_{2.5}$ extended from the southwest to the
320 northeast along the Taihang mountain range. In the second pattern (Ep2, Ep3, and Ep5),
321 the $PM_{2.5}$ level of 150–200 μg m^{-3} was concentrated in three northern cities (Beijing,
322 Tianjin, and Tangshan). In the other cities, the $PM_{2.5}$ mass concentrations ranged from
323 75 to 115 μg m^{-3}, indicating a light pollution level according to the Technical
324 Regulation on Ambient Air Quality Index (on trial).
325 Figure 6 shows the contributions of regional transport and local emissions to
326 average $PM_{2.5}$, primary aerosol (PA, BC and primary $PM_{2.5}$), and SIA levels in different
327 cities during the study period. The contribution of local emissions was more than that
328 of regional transport to the $PM_{2.5}$ mass concentration in all cities, except Heng Shui,
329 Cangzhou, Langfang, and Qinhuangdao; the magnitude of local emission contributions
330 was 49%–80%. The principle reason for this was the accumulation of local PA
331 emissions. In most cities, 64%–93% of PA originated from local emissions (Fig. 6c). In
332 contrast to PA, the SIA contribution was dominated by regional transport of emissions
333 in other cities (50%–87%). Even the emissions of cities outside the city cluster (e.g.,
334 Henan, Shanxi and Shandong) were transported to the megacity cluster, travelling 500–
335 1,000 km. In Beijing, the local contribution to total $PM_{2.5}$ and PA was 74% and 94%,
336 respectively, whereas regional transport from other cities was the major source of SIA,
337 contributing 51%. The difference in source apportionment between PA and SIA was
338 related to the mechanisms of PA and SIA formation. Regarding PA, the inversion layer

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and weak winds during stable weather conditions prevented PA transport and resulted in local-scale accumulation of PA emissions. SIA mostly originated from the chemical conversion of its gaseous precursors (e.g., SO_2, NO_2, and NH_3). The regional transport provided sufficient time (1–3 days) and aerosol surface for this chemical transformation (Li et al., 2015; Li et al., 2017). This also indicates that regional controls would be the most efficient way to decreasing the SIA concentration in this megacity cluster. Our results agree favorably with the observed impact of regional emission controls in Asia-Pacific Economic Cooperation China 2014. During this gathering, the SIA concentration in Beijing decreased to a greater degree than the PA concentration because of regional controls (Sun et al., 2016).

The source apportionment in haze episodes in Beijing is illustrated in Fig. 7. Regional transport contributed 14%–31% to the surface $PM_{2.5}$ mass concentration during the six episodes. The highest contribution of regional transport occurred in Ep1 and Ep5 (29% and 31% of the total $PM_{2.5}$, respectively). In Ep1 and Ep5, the contribution of the SIA originating from regional transport reached 53% and 63%, respectively. Interestingly, the regionally transported SIA had different source regions in Ep1 and Ep5. In Ep5, SX, WHB, and NHB were the dominant source regions, whereas the source regions for Ep1 were more diverse. This indicates the complexity of regional transport in this megacity cluster. Compared with the episodes in November 2015, the effects of regional transport of $PM_{2.5}$ and SIA mass concentrations were weaker in this study, which may be related to the weather system and emission controls in 2016 (Li et al., 2017). Therefore, more studies on regional transport should be conducted to further understand regional haze formation mechanisms. In other episodes (Ep2, Ep3, Ep4, and Ep6), regional transport of surface $PM_{2.5}$, PA, OM, and SIA mass concentrations were in the range 14%–23%, 3%–12%, 3%–14%, and 30%–51%, respectively. Local emissions during the episodes were more dominant than the monthly averages.

Figure 8 presents the relative contribution of regionally transported SIA under different levels of pollution in Beijing. The source regions varied considerably under

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different pollution levels. Under clean conditions (when SIA < 50 μg m^{-3}), NHB and SX were the main source regions, contributing up to 30% and 19%, respectively. With the increase of SIA concentrations, WHB, SD, and EHB became the main source regions, contributing 27%, 15%, and 13%, respectively, which is consistent with transport along the southwest and southeast corridors of BTH. Under heavy pollution, pollutants from HN and farther regions were blown to Beijing, resulting in a remarkably higher contribution of HN. This indicates that wider regional emission control is necessary to reduce severe pollution.

4.2 Impact of regional transport of sulfate and its precursors on Beijing

Quantifying the impact of regional transport of sulfate and its precursors is a crucial task. Sun et al. (2014) considered sulfate formed outside Beijing as regionally transported sulfate, and they estimated that its contribution reached 67% during winter haze episodes. By tagging emissions regions of precursors in models and ignoring where secondary aerosols were formed, Li et al. (2017) and Timmermans et al. (2017) estimated the contribution of transport to be 40%–50%. These estimated contributions of regional transport are different in physical meaning, which may confuse policymakers. In this study, we divided the sulfate mass concentration in Beijing into four parts, LC, LTC, RLC, and RTC as described in Sect. 2.1. The regional transport defined by Sun et al. (2014) was LTC + RLC + RTC, whereas in the studies by Li et al. (2017) and Timmermans et al. (2017), it was RLC + RTC. In this study, we employed RLC + RTC as representing regional transport.

Figure 9a shows the contributions of LC, LTC, RLC, and RTC to the daily average sulfate concentration in Beijing during the study period. RTC and LC were the dominant sources of sulfate, contributing 71%–89% in total. The contributions of RTC ranged from 29% in Ep6 to 59% in Ep2, and contributions of LC were 30%–42%. RTC dominated the regional transport over the whole period, which indicates that chemical conversions in the transport pathway of SO_2 were critical to haze formation. Notably,

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the LTC contribution was comparable with that of LC in Ep3, Ep4, and Ep6. This suggests that the SO_2 emitted in Beijing was blown away and formed sulfate outside of Beijing. These formed sulfates may have been blown back to Beijing under certain weather conditions and were previously considered regional transport. The contribution of LTC also largely explains the difference in estimated regional transport contributions between Sun et al. (2014) and Li et al. (2017). In the present study, LTC + RLC + RTC accounted for 58%–70% of the sulfate concentration in the six episodes, which is relatively similar to the estimation (75%) of Sun et al. (2014), which was based on the observed hourly rate of increase of local sulfate concentration.

In the initial and subsequent pollution stages, LC, LTC, and RTC showed different patterns in Beijing. In Ep1, local contributions dominated before the sulfate concentration increased rapidly (November 15 and 16). In particular, sulfate blown back to Beijing from its local emissions (LTC) made a larger contribution (35%) than RTC (25%). In the rapid rising phase of sulfate (November 17 and 18), contribution of RTC increased from 25% to 47%. LC was also significant and increased considerably from 37% to 41%. These two parts (LC and RTC) explained the rapid formation of sulfate in Beijing. This suggests that the joint control of local and regional SO_2 emissions is essential for preventing the rapid formation of haze in this region, which is receiving considerable attention and eliciting widespread interest among the researchers and policymakers (Sun et al., 2014; Ma et al., 2017; Li et al., 2017). This feature is also reflected in Fig. 9b. Under clear conditions (sulfate < 20 μg m^{-3}), the local contributions (LC and LTC) were positively correlated with the sulfate mass concentration. In total, they contributed 40%–60% of the sulfate mass concentration. The ratio of LC to LTC was approximately 2:1. Under moderate sulfate levels (20 μg m^{-3} < sulfate < 35 μg m^{-3}), the local contribution was lower—particularly the LTC—leading to a ratio of LC to LTC of approximately 8. Sulfate formed in the regional transport pathway (RTC) significantly increased from 40 to 65%. Under heavy pollution levels (> 35 μg m^{-3}), the LC was up to at 50% due to extremely stable boundary layers. Our results are consistent with those of Ma et al. (2017), in which

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425 regional transport and local heterogeneous chemistry were qualitatively discovered to
426 make high contributions to initial and subsequent pollution stages.

427 4.3 Evolution of aerosol properties in Beijing during haze
428 episodes

429 Aerosol properties such as the particle size and aging degree can change
430 dramatically on haze days because of fresh emissions, subsequent chemical conversions,
431 and regional transport, which strongly affect regional radiation and climate (Cappa et
432 al., 2012). As illustrated in Fig. 4b, the GMD of aerosols in Beijing increased
433 remarkably to approximately 120 nm during the six haze episodes, compared with the
434 GMD of 50 nm under clean conditions. Two stages were identified: an initial rising
435 stage and a sustained increase stage. In the initial stage, the GMD of aerosols increased
436 by 50–60 nm for several hours, and the GMD then remained at 100–120 nm for several
437 days in the subsequent elevated pollution stage. This GMD increase during the initial
438 stage was mainly caused by the increase of accumulation-mode particles with diameters
439 of 100–1,000 nm and Aitken-mode particles (Fig. 10). Under clean conditions (SIA <
440 50 μg m^{-3}), the average contributions of the three modes (nucleation, Aitken, and
441 accumulation modes) to the number concentration were comparable, although the
442 number of nucleation-mode particles decreased with SIA concentration. Under light-
443 moderate pollution conditions (50 < SIA < 150 μg m^{-3}), the proportion of accumulation-
444 mode particles significantly increased from 35% to 60%, whereas the proportion of
445 Aitken-mode particles slowly decreased. As discussed in previous sections, regional
446 transport played a dominant role during the initial stage. This indicates that
447 condensation, coagulation, and chemical transformation in the transport pathway
448 increased the number of particles with a diameter range of 100–1,000 nm. Finally, the
449 contributions of Aitken-mode and accumulation-mode particles remained stable under
450 the heavy-pollution conditions (SIA >150 μg m^{-3}).

451 Aging processes play a critical role in the growth of particles during haze episodes.
452 According to observations, a significant coating of secondary components on BC was

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found in the study period (Wang et al., 2018). Figure 11 presents a time series of the simulated R_{BC}, which is a favorable indicator of the aging degree (Oshima et al., 2009; Collier et al., 2018). Higher R_{BC} indicates that BC had undergone a greater degree of aging. In this study, the simulated R_{BC} was 2–10, with an average value of 4.5. This value is higher than that for fresh traffic source particles (Liu et al., 2017). Under pollution conditions, R_{BC} was higher than that under clean conditions, with an average value of 5.0. R_{BC} in Beijing even exceeded 10.0 in some extremely severe pollution events, which is close to observations of remote sites (Wang et al., 2017; Massoli et al., 2015) and aged particles (Cappa et al., 2012). Urban aerosols usually have a lower R_{BC} because of fresh emissions and high R_{BC} in this study indicates that Beijing aerosol particles were more aged during the haze episodes. On clean days, R_{BC} ranged from 2 to 5, with an average of 2.8. This is similar to the R_{BC} of vehicle emissions (<3) (Liu et al, 2017). Vehicle emissions contributed 70% of BC in downtown Beijing in 2016 after strict controls on coal burning had been implemented (Kebin He, personal communication).

Figure 12 shows the evolution of R_{BC}, the size distribution of number concentrations, and the GMD along the transport pathway from the source region to Beijing during the six haze episodes. The transport pathway was calculated using the HYSPLIT model. The figure clearly shows that the aerosol properties changed considerably along the transport pathway. In Ep1, the GMD of aerosols was only 97 nm at the initial site of the 24 h back trajectories (T_{-24}). At a larger transport distance, the diameters of aerosol particles were markedly increased to 128 nm in the middle (T_{-12}) and 134 nm at the final site (T_0) of the back trajectory. R_{BC} increased from 3.6 at T_{-24} to 8.7 at Beijing (T_0) because of BC being coated during the transport. This indicates that BC underwent considerable aging and increased in size while moving along the transport pathway; this would affect radiation and climate change (Cappa et al., 2012). Similar characteristics were discovered for Ep3–6. In Ep3, Ep4, Ep5, and Ep6, the GMD in Beijing (T_0) was 126, 117, 124, and 116 nm, respectively, compared with 96, 95, 99, and 111 nm in the middle point of transport (T_{-12}). R_{BC} also increased to 4.6–7.6.

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An exception was Ep2, in which the GMD (106 nm) and R_{BC} (3.8) at the final ending site (Beijing, T_0) were lower than those 6 h previously (T_{-6}). Regional transport contributed 95% of BC at T_{-6}, whereas local emissions accounted for 87% of BC at T_0. The number concentration was smaller at T_{-6} than that at T_0. Therefore, we conclude that regional transport of aged aerosols led to a high GMD at T_{-6}, and that the addition of locally emitted fresh air caused a high number concentration but low GMD at T_0. In clean areas, such as at T_{-24} in Ep3 and Ep5, R_{BC} was higher than 10 and the GMD was considerably smaller.

4.4 Impact of heterogeneous chemistry on sulfate mass concentration

Current models generally account for a part of the observed SO_4^{2-} concentrations in China (Wang et al., 2014). Heterogeneous chemistry on aerosol surfaces under high relative humidity has been considered a potential missing source of sulfate formation (Cheng et al., 2016; Zheng et al., 2015; Li et al., 2017; Tang et al., 2016). Li et al. (2018) developed a simple parameterization of heterogeneous chemistry and discovered that SO_2 uptake on aerosols partly closed the gap between simulation and observation. In their study, uptake coefficients were dependent on the aerosol core and shell species, shell thickness, and amount of aerosol liquid water. Zheng et al. (2013) and Yang et al. (2014) measured local source profiles, and they reported that primary sulfate from industry and power plants accounted for a large fraction of PA.

In this study, we examined the contributions of gas (SO_2 + OH) and aqueous chemistry, heterogeneous chemistry, and primary sulfate emissions to the sulfate mass concentration in Beijing (Fig. 13). In Ep1, under high relative humidity, the contribution of heterogeneous chemistry was 33%. Primary emissions exerted an effect mostly under light to moderate pollution levels (sulfate <20 μg m^{-3}), whereas heterogeneous chemistry played the largest role under high pollution levels (sulfate > 30 μg m^{-3}). The contributions of gas and aqueous chemistry were largely consistent under all pollution

conditions (~30%). This indicates that high relative humidity and aerosol loading accelerated the SO_2 chemical transformation. Interestingly, the contribution of heterogeneous chemistry was markedly higher when the sulfate mass concentration exceeded the threshold of 20 μg m^{-3}. Under high relative humidity and mass concentration conditions, a higher aerosol surface area resulting from hygroscopic growth provided a favorable media for heterogeneous reactions (Tie et al., 2017). The aforementioned threshold is relatively similar to that during the haze episodes in the winter of 2013 (Li et al, 2018). For policymakers, implementing measures to prevent the sulfate concentration from exceeding this threshold is essential. Such measures would be effective for avoiding extremely high sulfate levels. In other episodes, heterogeneous chemistry was depressed because of the low relative humidity (<70%). Gas and aqueous chemistry and primary emissions contributed 35%–40% and 58%–61%, respectively. It should be noted that failure of the model to simulate mineral dust led to underestimation of the sulfate level in Ep2. The interaction between SO_2 and alkaline dust can contribute considerably to the sulfate concentration.

5 Conclusions

The contributions of regional transport to haze episodes over a megacity cluster centered on Beijing have been under debate in recent decades. Investigating the evolution of aerosol properties along the transport pathway may provide more information on how researchers can improve the accuracy of regional transport and chemistry impact assessments. To address one of the aims of the APHH 2016 winter campaign, we employed a Eulerian chemical transport model (NAQPMS) and a Lagrangian trajectory model (HYSPLIT) to assess the evolution of aerosols—in terms of the number concentration, size distribution, and aging degree—in Beijing during six haze episodes between November 15 and December 15, 2016. The transport of sulfate and its precursors was also quantitatively investigated.

The results demonstrated that regional transport contributed 14%–31% to the surface $PM_{2.5}$ mass concentration in Beijing during the six episodes, with a monthly

537 average contribution of 26%. Regarding aerosol components, 30%–62% of the SIA in
538 Beijing were regionally transported, whereas few PAs (<10%) were contributed from
539 emissions in other regions. Source regions differed between episodes. During high-
540 pollution periods, WHB, SD, and EHB were the main source regions of SIA regionally
541 transported to Beijing, whereas NHB and SX made greater contributions under clean
542 and light pollution conditions. This indicates the complexity of regional transport in
543 this megacity cluster.

544 The chemical transformation of SO_2 along the transport pathway from source
545 regions except Beijing to Beijing (RTC) was the major form of SO_4^{2-} regional transport
546 and was more critical than the transport of sulfate formed in source regions except
547 Beijing (RTC). Compared with sulfate that was chemically transformed from Beijing-
548 emitted SO_2 and then blown back to Beijing (LTC), contribution of sulfate produced in
549 Beijing from Beijing-emitted SO_2 (LC) was generally greater. However, RTC markedly
550 increased in some episodes, and this explains the rapid formation of sulfate in Beijing.
551 This suggests that the joint control of local and regional SO_2 emissions is essential for
552 reducing the rapid formation of haze in this region.

553 Aerosols became considerably aged during transport in haze episodes, which
554 altered R_{BC} and the size distribution of number concentrations. During haze episodes,
555 the GMD increased from less than 100 nm at the initial site to approximately 120 nm
556 at the final site (Beijing), and R_{BC} increased from 2–4 to 4–8. The number of
557 accumulation-mode particles with a diameter range of 100–1,000 nm increased
558 considerably more than the number of particles of different modes. R_{BC} in Beijing
559 during the episodes was higher than that of fresh particles (<1.5), which indicates that
560 BC in Beijing was more aged and thus more likely to affect radiation and climate.

561 Contributions from different pathways to sulfate in Beijing were also examined.
562 In episodes with high humidity (Ep1), the average contributions of gas and aqueous
563 chemistry, heterogeneous chemistry, and primary sulfate were comparable. Primary
564 emissions mostly had an effect under light to moderate pollution levels, whereas

565 heterogeneous chemistry played the most crucial role under high pollution levels. In
566 other episodes (Ep2, Ep3, Ep4, Ep5, and Ep6), gas and aqueous chemistry and primary
567 emissions contributed 35%–40% and 58%–61%, respectively.

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Figures

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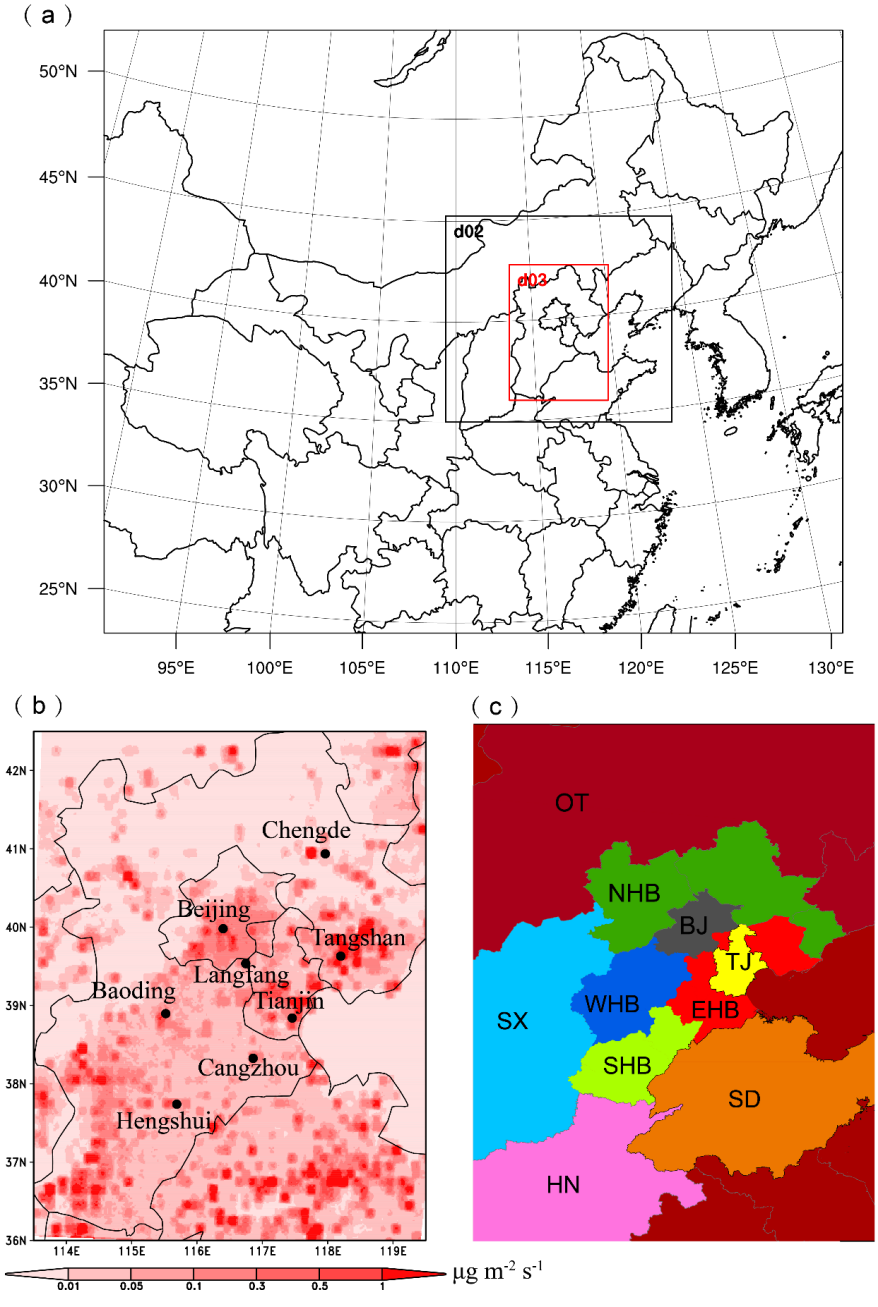

Figure 1. (a) Simulation domains. (b) Primary $PM_{2.5}$ emission rates of the innermost domain and locations of observation sites (black dots). (c) tracer tagging regions which are described in Table 1.

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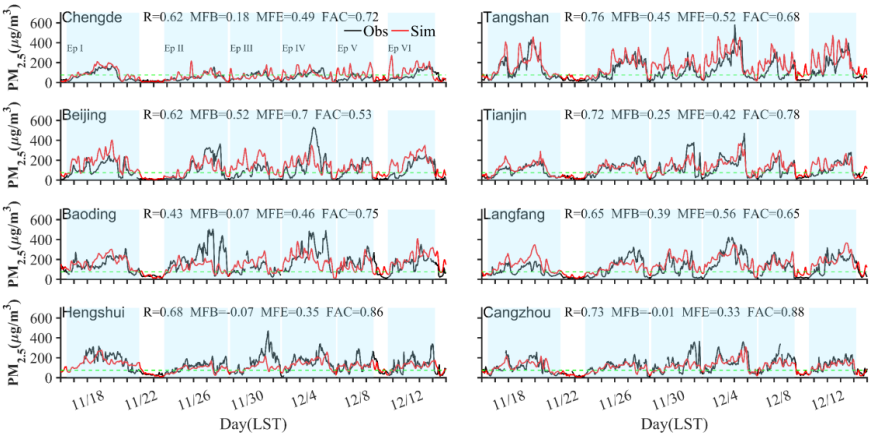
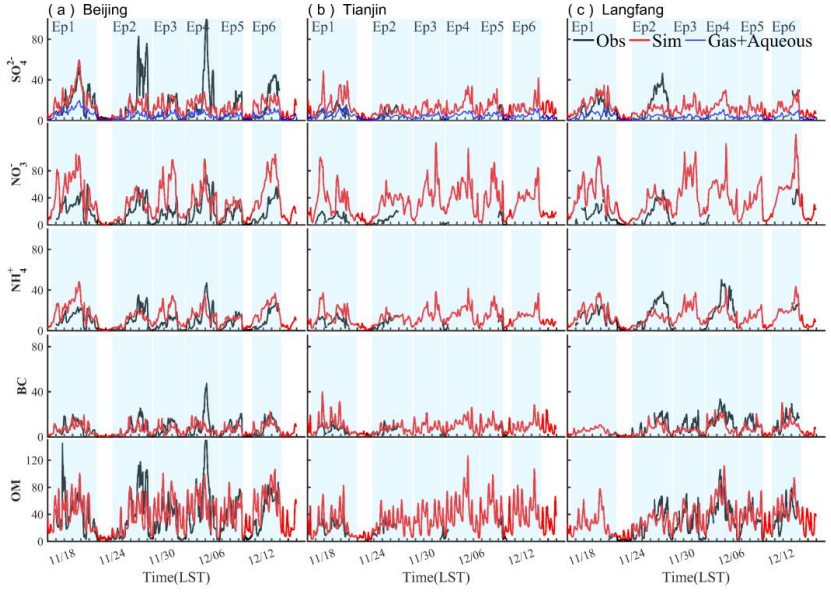


767

768 **Figure 2.** Comparison between the simulated and observed hourly concentrations of
769 $PM_{2.5}$ for different sites. Black lines refer to observation and the red lines are simulation
770 results; light blue shadows are six episodes identified.



771

772 **Figure 3.** Comparison between the simulated (red) and observed (solid black) hourly
773 components including sulfate, nitrate, ammonia, black carbon and organic aerosols at
774 (a) Beijing, (b) Tianjin and (c) Langfang. Blue lines refer to sulfate produced by gas

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and aqueous chemistry reactions.

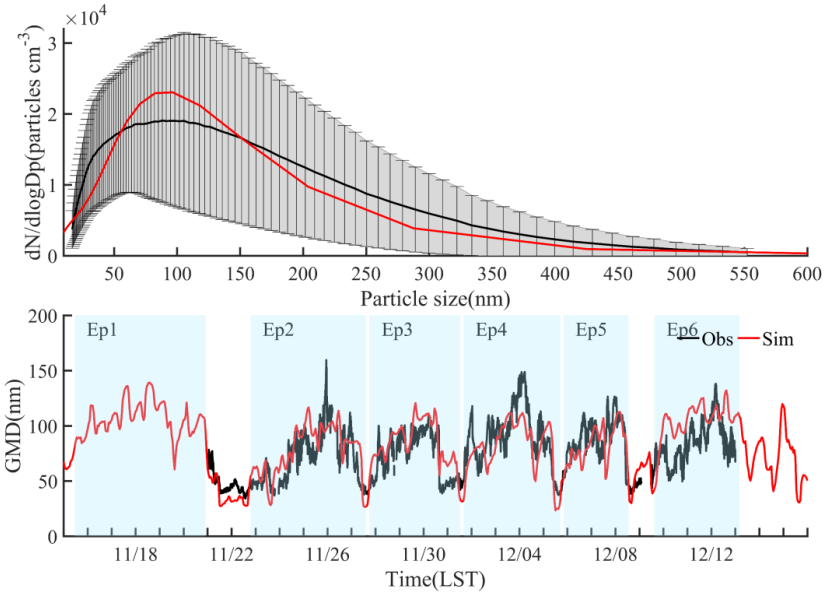

Figure 4. (a) Particle size distribution in Beijing at ground level. (b) Comparison of geometric mean diameter (GMD) for particles during range of 16–600nm between observation and simulation in Beijing. Black solid line and red solid line represent observation and simulation respectively.

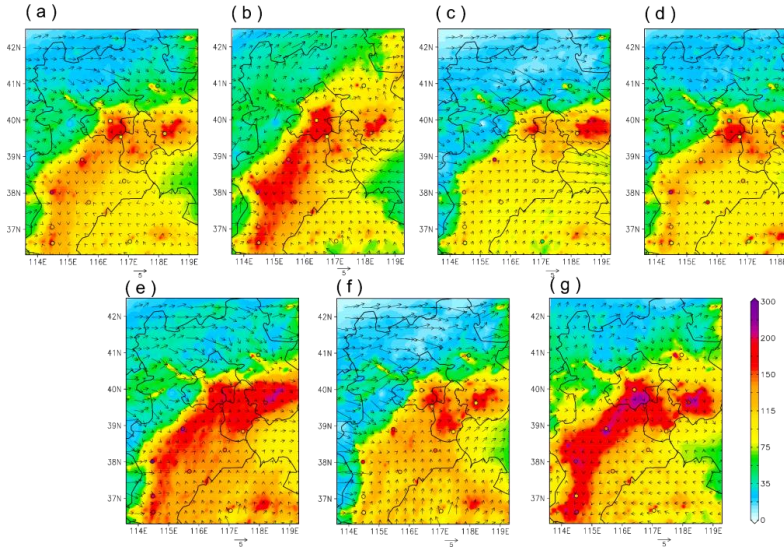

Figure 5. Spatial distribution of simulated average surface $PM_{2.5}$ (μg m^{-3}) and wind (m

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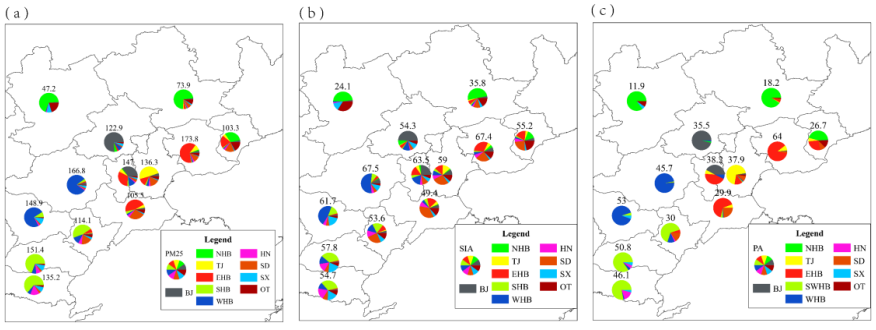
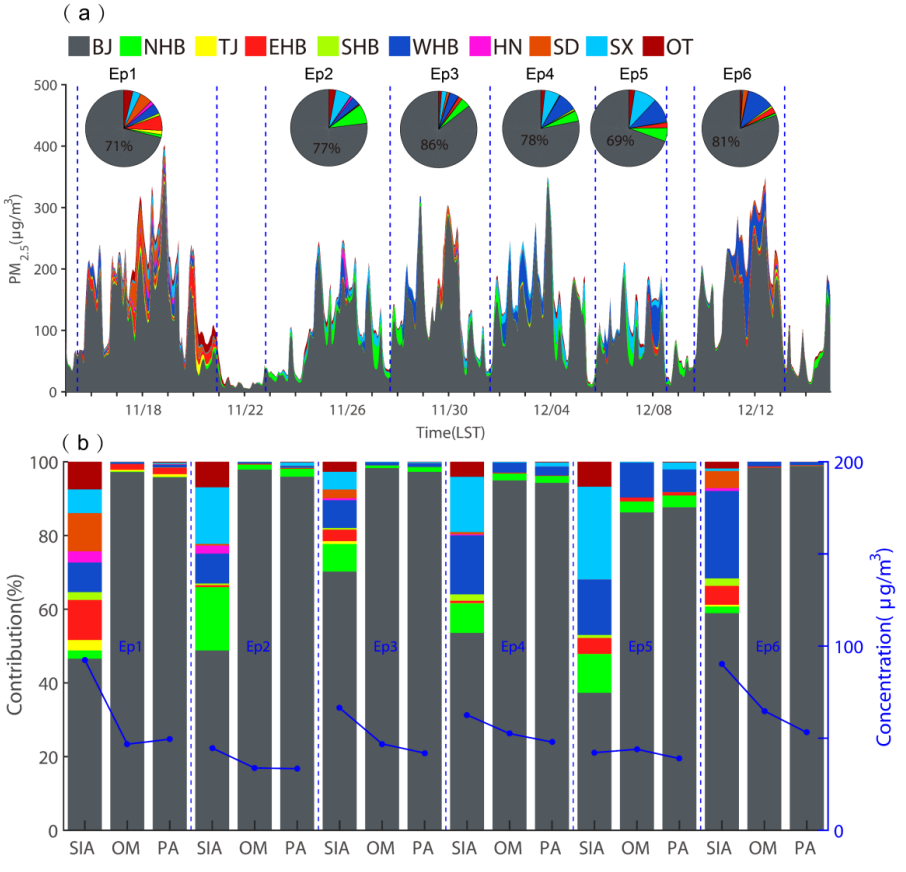
783 s^{-1}) over BTH area. (a) average of whole study period, (b)–(g) episode average of
784 episode1–6 identified before. Solid circles represent observations with the same color
785 bar with simulations.



786
787 **Figure 6.** The contribution of regional transport and local emissions to the average (a)
788 total $PM_{2.5}$, (b) secondary inorganic aerosols (SIA), (c) primary aerosols (PA, BC and
789 primary $PM_{2.5}$) over BTH area. The numbers above the pie represent average
790 concentrations (μg m^{-3}) of certain species in certain cities.



791
792 **Figure 7.** (a) Source contribution of $PM_{2.5}$ in Beijing and pies represent average status

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of each episode; (b) Relative contribution of different regions to SIA, OM and PA in Beijing at the surface layer during each episode (shaded). Concentrations are also shown (blue line).

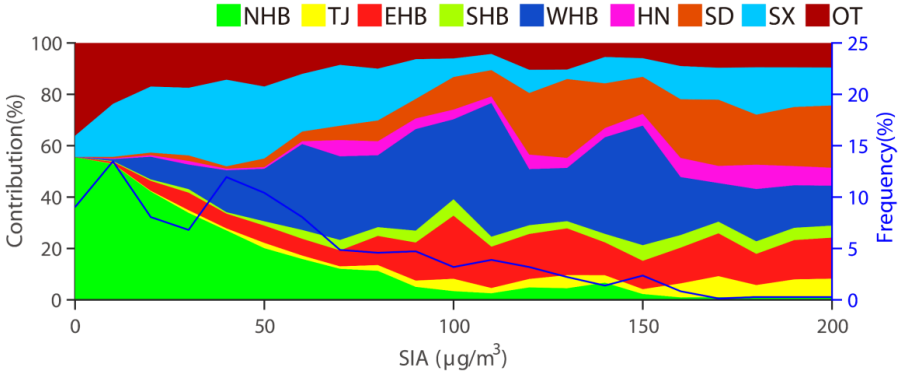

Figure 8. Relative contribution of regionally transported SIA under different levels of pollution in Beijing during whole study period.

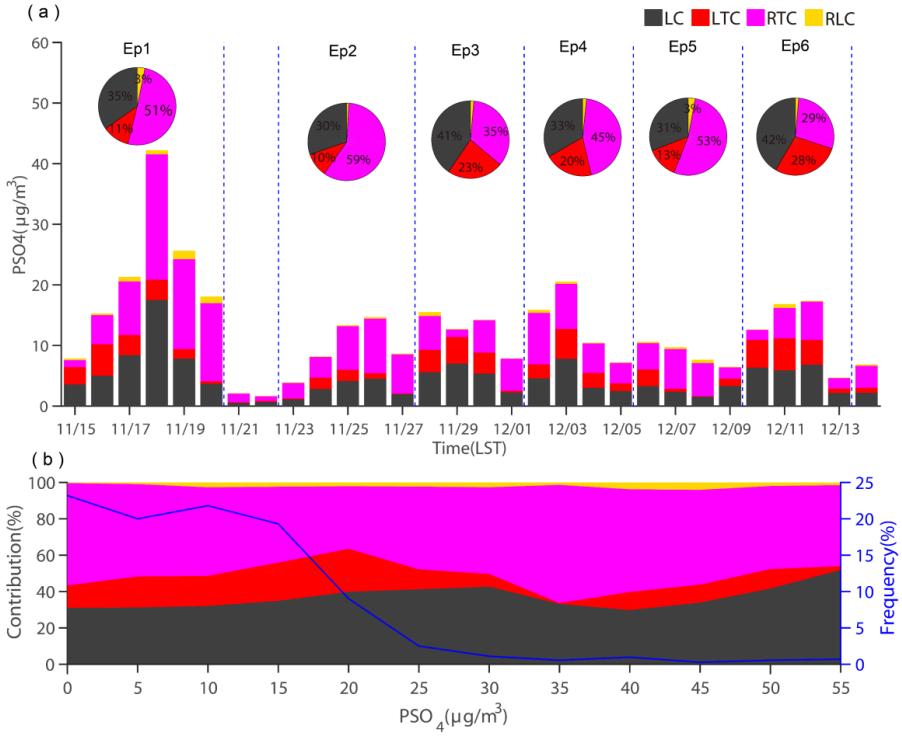

Figure 9. (a) Regional sources of chemical conversion of secondary sulfate in Beijing.

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802 (b) Variation of region source of chemical conversion of secondary sulfate with hourly
803 surface sulfate concentration level in Beijing for the whole study period. LC means
804 sulfate locally produced from Beijing emitted SO_2; LTC refers to sulfate chemically
805 formed in regions except Beijing from the Beijing emitted SO_2; RTC is sulfate
806 chemically formed in the transport pathway to Beijing from SO_2 emitted in source
807 regions except Beijing; RLC is sulfate produced in regions except Beijing from locally
808 emitted SO_2 and transported to Beijing.
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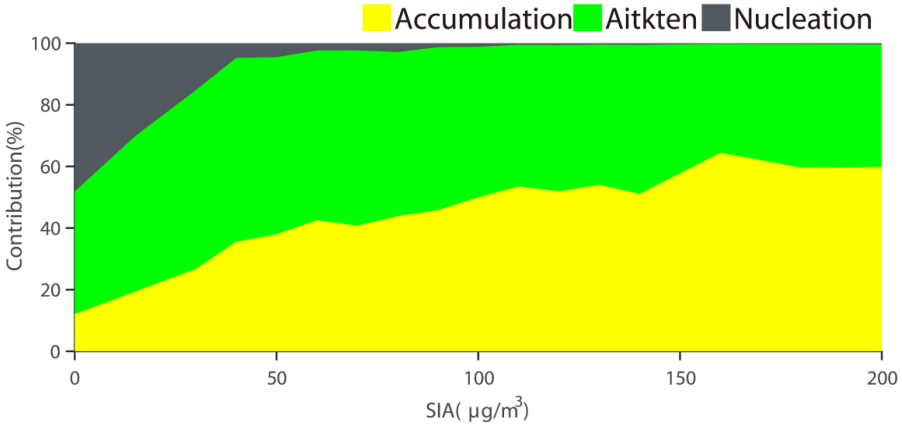

810
811 **Figure 10.** Variation of number concentration fraction of particles with SIA in Beijing
812 during whole study period.

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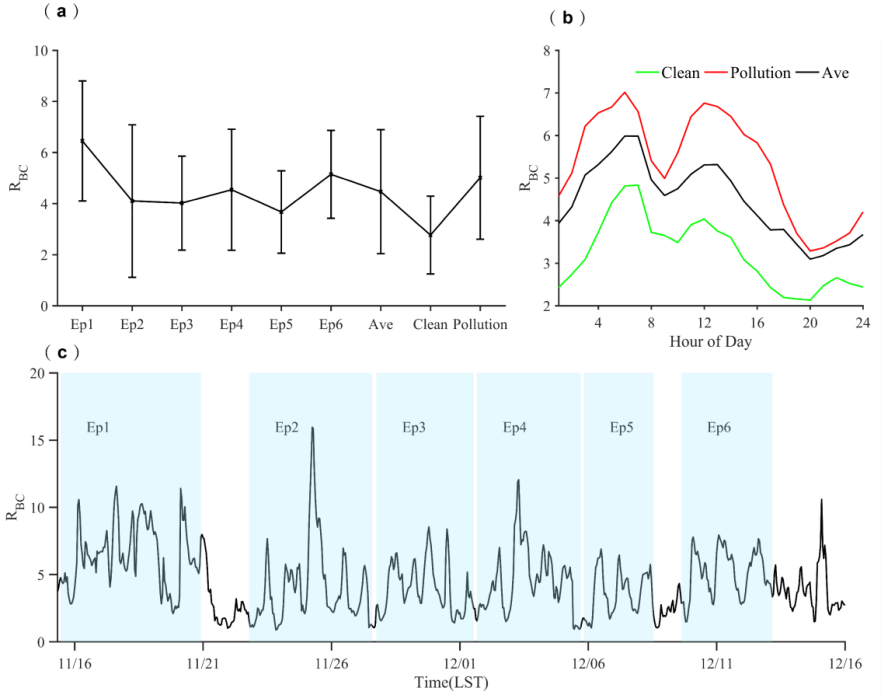

Figure 11. (a) average and standard variation of massing ratio of coating to BC (R_{BC}) during different episodes and pollution levels, (b) diurnal cycles of R_{BC} under different pollution levels, (c) temporal variation of R_{BC} during study period.

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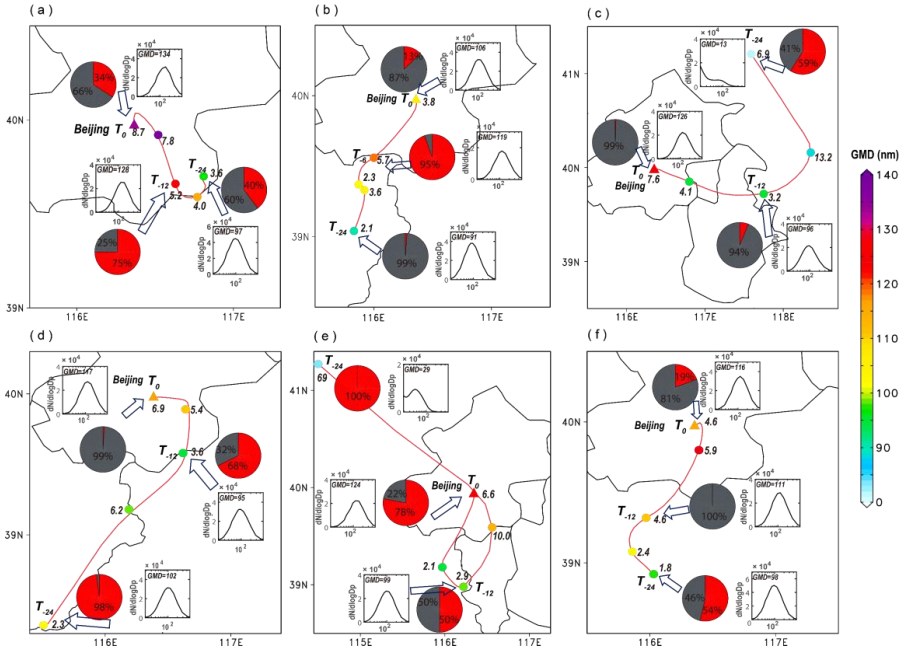

Figure 12. 24 h back trajectories for air mass at the altitude of 100 m and aerosol properties along each trajectory. Panel a–f refers to episode 1–6 at 21:00 on November 18, 22:00 on November 25, 16:00 on November 29, 22:00 on December 03, 0:00 on December 8, 22:00 on December 11 (LST). Triangles show ending site at Beijing, called T_0. T_{-6}, T_{-12}, T_{-18}, T_{-24} mean 6, 12, 18, 24 hours before arriving at ending site. The red lines refer to backward trajectories and the solid shaded circles represent the geometric mean particle size (GMD, nm) labeled in color bar on the right. The number beside the solid circle is the mass ratio of coating to BC, called R_{BC} for short. The pie chart shows the region source of BC. The gray represents the local contribution, and the red represents the contribution of regional transport. The blacklines refer to the distribution of number concentration.

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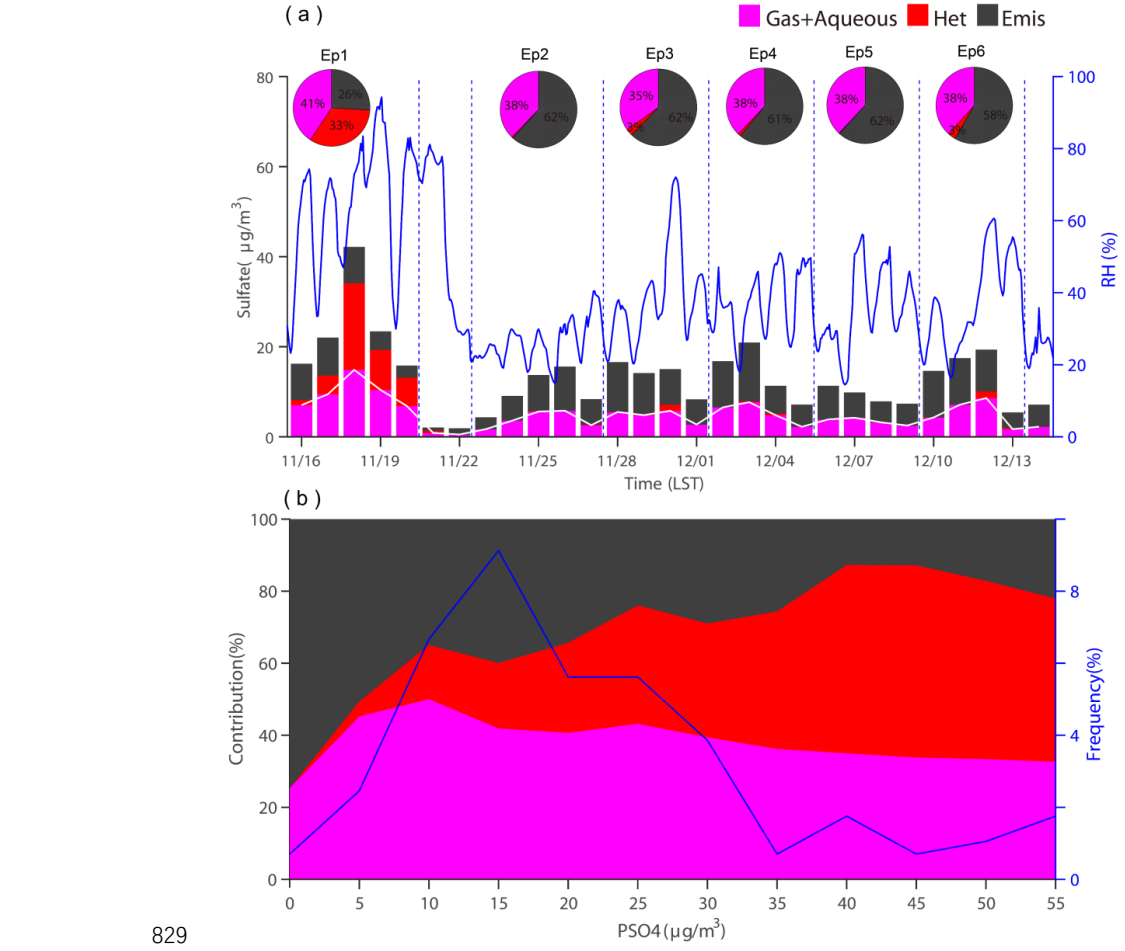

Figure 13. Contribution of different ways of sulfate formation in Beijing. (a) Daily average. Blue line shows relative humidity at Beijing. Pies show average contribution of different ways during each episode. (b) Relationship between sulphate concentration and different pathways of sulphate formation during Ep1.

Tables

Table 1. Source-tagging regions and primary $PM_{2.5}$ emissions during 15 November–15 December, 2016 in this study. [a]

Regions	Descriptions	Area 10^3 km^2	Population 10^6	GDP [b] (10^{12} CNY)	Emission [c] (10^9g)
BJ	Beijing	16.4	21.7	2.5	3.6
TJ	Tianjin	11.9	15.6	1.8	3.9
NHB	Chengde, Zhangjiakou and	84.1	11.6	0.4	3.6

		Qinhuangdao				
BTH	WHB	Baoding and Shijiazhuang	38.0	21.2	0.9	8.1
	EHB	Tangshan, Langfang and Cangzhou	33.9	20.3	1.1	10.1
	SHB	Hengshui, Xingtai and Handan	33.3	22.9	0.7	6.8
HN		Henan	167.0	95.3	4.0	26.6
SD		Shandong	155.8	99.5	6.8	38.5
SX		Shanxi	156.7	36.8	1.3	25.9
OT		Other regions				

[a] Regions are shown in Fig. 1c.

[b] GDP unit in 2016 is Chinese Yuan (CNY) (http://www.tjcn.org/tjgb/).

[c] $PM_{2.5}$ emissions data are obtained from the 2016 Multi–resolution Emission Inventory for China (MEIC) with 0.25° × 0.25° resolution.