

We thank the referees for the helpful comments. We have revised the manuscript according to the suggestions and responded to their concerns below.

**Comments from referee (1)** l. 35: Remove ‘these changes would affect regional radiation and climate’ as these consequences are not discussed in the manuscript.

**Response:** Accepted. We will delete it.

**Changes in the manuscript:** The sentence will be deleted. Please refer to Page 2 Line 34-35.

**Comments from referee (2)** l. 95-97: ‘The heterogeneous reaction parameters are rarely related to the key parameters such as mixing state and aerosol water contents in previous studies.’ - This sentence is not clear. Do you mean that there is not much data available that describe the parameters for heterogeneous reactions as a function of aerosol composition and water content? Please add a reference that shows these dependencies and lack of data.

I suggest rewording ‘For many heterogeneous reactions, comprehensive data sets for the reaction parameters as a function of aerosol composition and water content are not available.’

**Response:** Accepted. Studies found that uptake coefficients ( $\gamma$ ) were dynamically related to aerosol liquid water and aerosol mix states (coating thickness) (Riemer et al., 2009; Morgan et al., 2015). Although these parameters are obtained in some observation studies (Bian et al., 2014; Zhang et al., 2016). The parameterization of heterogeneous has rarely been linked to these parameters (Morgan et al., 2015; Zheng et al., 2015; Li et al., 2018).

**Changes in the manuscript:**

Please refer to Page 4 Line 91-97.

**Comments from referee (3)** l. 132: Please specify the aqueous processes that are included. Is it only the oxidation reactions of S(IV) by  $O_3$ ,  $H_2O_2$ , methyl hydroperoxide and peroxyacetic acid? Or does it also include additional reactions, e.g. the redox

chemistry of metal ions - as your response to my previous review implies?

**Response:** Accepted. Aqueous chemistry reactions include the oxidation reactions of S(IV) by  $O_3$ ,  $H_2O_2$ , methyl hydroperoxide, peroxyacetic acid and redox chemistry of metal ions,  $Fe^{3+}$  and  $Mn^{2+}$ .

**Changes in the manuscript:**

In the model, aqueous chemistry happens only in cloud water, including the oxidation reactions of S(IV) by  $O_3$ ,  $H_2O_2$ , methyl hydroperoxide, peroxyacetic acid and oxidation catalysis of transition metal ions ( $Fe^{3+}$  and  $Mn^{2+}$ ).

Please refer to Page 5 Line 129-132.

**Comments from referee (4)** l. 134: ‘are related with aerosol water’. I suggest adding some more details of the calculation of  $\gamma_{SO_2}$  as it is not intuitive that an uptake coefficient depends on the aerosol water content. For example:

‘Assuming that the upper limit of  $\gamma_{SO_2}$  does not exceed the uptake coefficient on dust surfaces, the upper limit of  $\gamma_{SO_2}$  is  $10^{-4}$  for  $AWC > 300 \mu g m^{-3}$  and its lower limit is  $10^{-6}$  if  $AWC < 10 \mu g m^{-3}$ . More details can be found in Li et al., (2018).’

**Response:** Accepted.

**Changes in the manuscript:**

Heterogeneous chemistry reactions happen on aerosol’s surface with aqueous layer and are related with aerosol liquid water. For sulfate, assuming that the upper limit of  $\gamma_{SO_2}$  does not exceed the uptake coefficient on dust surfaces, the upper limit of  $\gamma_{SO_2}$  is  $10^{-4}$  for aerosol water content (AWC)  $> 300 \mu g m^{-3}$  and its lower limit is  $10^{-6}$  if  $AWC < 10 \mu g m^{-3}$ . More details can be found in Li et al. (2018).

Please refer to Page 5 Line 133-136

**Comments from referee (5)** l. 217: ‘heterogeneous chemistry to sulfate’ - do you mean ‘heterogeneous formation of sulfate’?

**Response:** Yes. We will change it.

**Changes in the manuscript:**

To quantitatively assess the contribution of primary emissions, traditional chemistry

reactions (gas-phase and aqueous chemistry reactions), and heterogeneous formation of sulfate, three sensitivity simulations were conducted.

Please refer to Page 8 Line 219.

**Comments from referee (6)** l. 329: How is ‘aging degree’ quantified? There might be several measures that can be used to describe how aged a particle is, such as the coating thickness of BC or the oxidation degree of OA. However, to my knowledge, there is no universal model parameter that describes the ‘aging degree’.

**Response:** Yes, there is no universal model parameter that describe the aging degree. In this study, the mass ratio of coating to BC ( $R_{BC}$ ) was used as an indicator of aging degree. And  $R_{BC}$  is a surrogate for coating thickness (Wang et al., 2018).

**Changes in the manuscript:**

Herein, the mass ratio of coating to BC ( $R_{BC}$ ) was used as an indicator of aging degree, which has been widely used in previous studies (Oshima et al., 2009; Collier et al., 2018). Please refer to Page 12 Line 321-322.

**Comments from referee (7)** l. 368: ‘mechanisms of PA...formation’. ‘Formation’ implies that these aerosols are chemically formed; however, PA (primary aerosols) are directly emitted and do not undergo any formation processes.

**Response:** Accepted.

**Changes in the manuscript:** The difference in source apportionment between PA and SIA was related to the emission of PA and formation mechanisms of SIA. Please refer to Page 13 Line 366-367.

**Comments from referee (8)** l. 393: I had already asked in my previous review about the classification of PA and OM. It should be clarified that PA only includes primary inorganic aerosol (perhaps name it PIA) as you clarified now that OM includes both primary and secondary organic aerosol.

**Response:** Accepted. We change all PA to PIA in the manuscript. And PIA was explained in detail, when first appeared in Page 13 Line 354.

**Changes in the manuscript:** We change all PA to PIA in the manuscript, such as, Page 13 line 359, 364, 366-369 and Figure 6 and 7.

**Comments from referee (9)** l. 407 and l. 409: Specify: ...contributing up to 30% and 19% to total PM<sub>2.5</sub> levels?

**Response:** Accepted. It is contribution to SIA levels, and we will specify it.

**Changes in the manuscript:** When Beijing is controlled by strong northerly wind, NHB and SX are the main source regions, contributing up to 30% and 19% to SIA, resulting in clean conditions ( $SIA < 50 \mu g m^{-3}$ ). When Beijing is mainly affected by southerly wind (southeast, south and southwest), WHB, EHB and SD become the main source regions, contributing up to 27%, 13% and 15% to SIA, respectively.

Please refer to Page 15 Line 403 and 405.

**Comments from referee (10)** l. 613: This sentence is hard to understand now. Do you mean the following?

- 'R<sub>BC</sub> in Beijing during the episodes was higher than that of OTHER urban regions (Collier et al., 2018)'?

- At high pollution levels, R<sub>BC</sub> was close to that in remote regions (Wang et al., 2017a)

**Response:** Accepted.

**Changes in the manuscript:** R<sub>BC</sub> in Beijing during the episodes was higher than that of other urban regions (Collier et al., 2018). At high pollution levels, R<sub>BC</sub> was close to that in remote regions (Wang et al., 2017a). Please refer to Page 22 Line 603 and 604.

**Comments from referee (11)** l. 617-621: This text seems contradictory: 'In episodes with high humidity (Ep1), the average contributions of gas and aqueous chemistry, heterogeneous chemistry, and primary sulfate were comparable.'

'...heterogeneous chemistry played a relatively crucial role under high pollution levels during Ep1.'

**Response:** Accepted. The average contributions' magnitude of gas and aqueous

chemistry, heterogeneous chemistry, and primary sulfate was comparable during episodes with high humidity (Ep1). But their relative contributions varied with pollution levels. Primary emissions mostly had an effect under light to moderate pollution levels, whereas heterogeneous chemistry played a relatively crucial role under high pollution levels during Ep1.

**Changes in the manuscript:** In episodes with high humidity (Ep1), the average contributions of gas and aqueous chemistry, heterogeneous chemistry, and primary sulfate were comparable. But their relative contributions varied with pollution levels. Under light to moderate pollution levels, primary emissions mostly had an effect. But under high pollution levels during Ep1, heterogeneous chemistry played a relatively crucial role. Please refer to Page 22 Line 606 and 610.

Also seen in Page 2 line 37.

#### **Technical comments**

l. 28: ‘...was the major form of  $\text{SO}_4^{2-}$  regional transport’ is unclear. Do you mean ‘was the major source of  $\text{SO}_4^{2-}$ ’?

**Response:** Accepted. Yes.

**Changes in the manuscript:** The chemical transformation of  $\text{SO}_2$  in the transport pathway from source regions to Beijing was the major source of  $\text{SO}_4^{2-}$ . Please refer to Page 1 Line 27-28.

l. 44/45: ‘has been experiencing’ or ‘has experienced’

**Response:** Accepted.

**Changes in the manuscript:** In past decades, a megacity cluster in China that is centered on Beijing and includes 28 cities (272,500  $\text{km}^2$ , a population of 191.7 million people) has experienced frequent severe and persistent haze episodes (Zhao et al., 2013; Sun et al., 2014; Sun et al., 2016). Please refer to Page 2 Line 44.

l. 114: Detailed analysis of...

**Response:** Accepted.

**Changes in the manuscript:** Detailed analysis of the transport of precursors or secondary products, and heterogeneous reactions was mainly focused on sulfate, as recent studies indicated that sulfate is a key driver for severe haze events (Huang et al., 2014; Zheng et al., 2015). Please refer to Page 4 Line 111.

l. 356: 'non-organic' should be 'inorganic'

**Response:** Accepted.

**Changes in the manuscript:** Figure 6 shows the contributions of regional transport and local emissions to average PM<sub>2.5</sub>, primary inorganic aerosol (PIA, BC and inorganic primary PM<sub>2.5</sub>), and SIA levels in different cities during the study period. Please refer to Page 13 Line 354.

l. 443: 'convinced' seems to be a wrong word here; 'supported' might fit better.

**Response:** Accepted.

**Changes in the manuscript:** And recirculation of air masses can be supported by HYSPLIT trajectories (Fig. S6). Please refer to Page 16 Line 433.

l. 505: '...had undergone a greater degree of aging' sounds awkward. It should be, for example, 'had undergone more ageing' or 'had reached a higher degree of ageing'

**Response:** Accepted.

**Changes in the manuscript:** Higher R<sub>BC</sub> indicates that BC had undergone more ageing. Please refer to Page 18 Line 494-495.

## **References:**

- Bian, Y. X., Zhao, C. S., Ma, N., Chen, J., and Xu, W. Y.: A study of aerosol liquid water content based on hygroscopicity measurements at high relative humidity in the North China Plain, *Atmospheric Chemistry and Physics*, 14, 6417-6426, 10.5194/acp-14-6417-2014, 2014.
- Collier, S., Williams, L. R., Onasch, T. B., Cappa, C. D., Zhang, X., & Russell, L. M., et al: Influence of emissions and aqueous processing on particles containing black carbon in a polluted urban

- environment: insights from a soot particle-aerosol mass spectrometer, *Journal of Geophysical Research Atmospheres*, 123(12), 6648-6666, <https://doi.org/10.1002/2017jd027851>, 2018.
- Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N<sub>2</sub>O<sub>5</sub> uptake: airborne regional measurements in northwestern Europe, *Atmospheric Chemistry and Physics*, 15, 973-990, 10.5194/acp-15-973-2015, 2015.
- Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler-Scharr, A., and Mentel, T. F.: Relative importance of organic coatings for the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> during summer in Europe, *Journal of Geophysical Research-Atmospheres*, 114(D17), 10.1029/2008jd011369, 2009.
- Wang, J., Liu, D., Ge, X., Wu, Y., Shen, F., Chen, M., . . . Sun, Y.: Characterization of black carbon-containing fine particles in Beijing during wintertime, *Atmospheric Chemistry and Physics Discussions*, 1-25, <https://doi.org/10.5194/acp-2018-800>, 2018.
- Wang, J., Zhang, Q., Chen, M. D., Collier, S., Zhou, S., & Ge, X., et al.: First chemical characterization of refractory black carbon aerosols and associated coatings over the Tibetan plateau (4730 m a.s.l), *Environmental Science & Technology*, 51(24), 14072-14082, <https://doi.org/10.1021/acs.est.7b03973>, 2017a.
- Zhang, S. L., Ma, N., Kecorius, S., Wang, P. C., Hu, M., Wang, Z. B., Gross, J., Wu, Z. J., and Wiedensohler, A.: Mixing state of atmospheric particles over the North China Plain, *Atmospheric Environment*, 125, 152-164, 10.1016/j.atmosenv.2015.10.053, 2016.

**And we carefully edited the language and expression.**

- 1) Delete “representing”. Please refer to Page 15 line 424.
- 2) Rewrite the sentence to “were contributed by emissions from other regions”.  
Please refer to Page 21 line 579-580.

# Modeling of aerosol property evolution during winter haze episodes over a megacity cluster in northern China: Roles of regional transport and heterogeneous reactions of SO<sub>2</sub>

Huiyun Du<sup>1,2</sup>, Jie Li<sup>1,2,3\*</sup>, Xueshun Chen<sup>1</sup>, Zifa Wang<sup>1,2,3</sup>, Yele Sun<sup>1,2,3</sup>, Pingqing Fu<sup>1</sup>,  
Jianjun Li<sup>4</sup>, Jian Gao<sup>5</sup>, Ying Wei<sup>1,2</sup>

<sup>1</sup> LAPC, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

<sup>2</sup> College of Earth Sciences, University of Chinese Academy of Sciences, Beijing 100029, China

<sup>3</sup> Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China

<sup>4</sup> China National Environmental Monitoring Center, Beijing, China

<sup>5</sup> Chinese Research Academy of Environmental Sciences

**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 in mass concentrations of PM<sub>2.5</sub> and its components in Beijing but also in the number concentration, size distribution, and aging degree. We revealed that regional transport played a nonnegligible role in haze episodes, with contributions of 14%–31% to the surface PM<sub>2.5</sub> mass concentration. The contribution of regional transport to secondary inorganic aerosols was larger than that to primary aerosols (30%–63% vs. 3%–12%). The chemical transformation of SO<sub>2</sub> in the transport pathway from source regions to Beijing was the major ~~form~~-source of SO<sub>4</sub><sup>2-</sup>-~~regional transport~~. We also found that sulfate formed outside Beijing from SO<sub>2</sub> emitted in Beijing; this sulfate was then blown back to Beijing and considerably influenced haze formation. In the transport pathway, aerosols 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 emission to sulfate were comparable. But their relative contributions varied with pollution levels. 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<sup>2</sup>, a population of 191.7 million people) has ~~been~~ experienced frequent severe and persistent haze episodes (Zhao et al., 2013; Sun et al., 2014; Sun et al., 2016). PM<sub>2.5</sub> levels exceeding 500  $\mu\text{g m}^{-3}$  have often been reported. The adverse effects of PM<sub>2.5</sub> 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<sub>2.5</sub> concentration in Beijing has decreased by 35% in the recent 5 years (2013–2017) benefiting from implementation of the Atmospheric Pollution Prevention and Control Action Plan, the PM<sub>2.5</sub> level in 2017 still reached 58  $\mu\text{g m}^{-3}$ , which is 1.7 times the World Health Organization-recommended safe level of 35  $\mu\text{g m}^{-3}$  (<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

SIA mass fraction in PM<sub>2.5</sub> can be up to 55% on severe pollution days, which is 2.5 times that on clear days (Ma et al., 2017). Tang et al. (2016a) proposed that local chemical transformation associated with humidity dominated the rapid formation of SIA in Beijing. Yang et al. (2015) argued that local chemical conversion would not be fully able to explain 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 of modeling studies (Timmermans et al., 2017; Li and Han, 2016; Li et al., 2017), in which regional transport was identified as the dominant factor during haze episodes in the megacity cluster. Comprehensive observations of the physicochemical properties (e.g., mixing state, number concentration, and size distribution) of aerosols can provide more insights into 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 higher fractal dimension (Wang et al., 2017b), larger coating fraction (ratio of variation in BC mass equivalent diameter to initial BC diameter,  $\Delta D_{me}/D_{me,0}$ ) (Peng et al., 2016) and the higher mass ratio of coating to BC ( $R_{BC}$ ) (Wang et al., 2018a). 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<sub>2.5</sub> 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 was twice that under clean conditions (Ma et al., 2017). Investigating the evolution of aerosol properties other than mass concentration during regional transport is thus useful for assessing the roles of regional and local chemistry. Such investigations are rarely conducted using the current three-dimensional chemical transport models. The current models generally account for only a part of the observed  $SO_4^{2-}$

concentrations (Wang et al., 2014a). Heterogeneous chemistry is considered critical to improving model performance (Zheng et al., 2015; Cheng et al., 2016; Li et al., 2018). The treatment of heterogeneous chemistry is likely another source of modeling uncertainty. Studies found that uptake coefficients ( $\gamma$ ) were dynamically related to aerosol liquid water and aerosol mix states (coating thickness) (Riemer et al., 2009; Morgan et al., 2015). Although these parameters are obtained in some observation studies (Bian et al., 2014; Zhang et al., 2016). The parameterization of heterogeneous has rarely been linked to these parameters in previous studies (Morgan et al., 2015; Zheng et al., 2015; Li et al., 2018). The heterogeneous reaction parameters are rarely related to the key parameters such as mixing state and aerosol water contents in previous studies.

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. Details can be seen in Shi et al. (2018). Aerosol properties such as the size distribution, number concentration, and mixing states were simultaneously measured in China. APHH-Beijing aimed to explore the sources and processes affecting urban atmospheric pollution in Beijing. In this study, we used the NAQPMS to simulate aerosol properties in the campaign period as a part of the APHH research. To improve model performance, the NAQPMS was updated by incorporating an advanced particle microphysics (APM) module that explicitly accounts for the microphysical process (Chen et al., 2014) and a new heterogeneous chemistry scheme (Li et al., 2018). The hybrid single-particle Lagrangian integrated trajectory model (HYSPLIT) was also employed to explicate the evolution of aerosol properties (e.g., mixing state, number concentration, and size distribution). Detailed analysis ~~about~~of the transport of precursors or secondary products, and heterogeneous reactions was mainly focused on sulfate, as recent studies indicated that sulfate is a key driver for severe haze events (Huang et al., 2014; Zheng et al., 2015). Crucially, the effects of regional transport and heterogeneous chemistry of SO<sub>2</sub> on aerosol properties were quantified. To our knowledge, this is the first study to distinguish the contributions of transport of SIA

itself and its precursors to PM<sub>2.5</sub> in Beijing, and combine trajectories with microphysical properties evolution. 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). In the model, aqueous chemistry happens only in cloud water, including the oxidation reactions of S(IV) by O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, methyl hydroperoxide, peroxyacetic acid and oxidation catalysis of transition metal ions (Fe<sup>3+</sup> and Mn<sup>2+</sup>). Heterogeneous chemistry reactions happen on aerosol's surface with aqueous layer and are related with aerosol liquid water. For sulfate, assuming that the upper limit of  $\gamma_{SO_2}$  does not exceed the uptake coefficient on dust surfaces, the upper limit of  $\gamma_{SO_2}$  is  $10^{-4}$  for aerosol water content (AWC)  $> 300 \mu\text{g m}^{-3}$  and its lower limit is  $10^{-6}$  if  $\text{AWC} < 10 \mu\text{g m}^{-3}$ . More details can be found in 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., 2014b). The Carbon Bond Mechanism version-Z (CBMZ) is used for gas-phase chemistry mechanisms. The thermodynamic model ISORROPIA1.7 is used to calculate the composition and phase state of an NH<sub>4</sub><sup>+</sup>–SO<sub>4</sub><sup>2-</sup>–NO<sub>3</sub><sup>-</sup>–Cl<sup>-</sup>–Na<sup>+</sup>–H<sub>2</sub>O inorganic aerosol system (Nenes et al., 1998). Six secondary organic aerosols (SOA) 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  $\mu\text{m}$  were used to represent secondary particle distribution ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , 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. Mixing state is assumed to be semi-external. Primary particles coated with SIA or SOA are considered as core-shell mixing while nucleated secondary particle is internally mixed (Chen et al., 2014). 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 can be less than 2 hours in winter. This is much less 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 aerosol surface, which largely altered the sizes and hygroscopicity of particles. Heterogeneous chemistry includes oxidation of S(IV) on aqueous layer of aerosols and it is parameterized according to the scheme of Li et al. (2018). 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., 2017b, 2018; Chen et al., 2014, 2017).

Distinguishing the contributions of the transport of SIA itself and its precursors to PM<sub>2.5</sub> 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  $i^{\text{th}}$  receptor region into four parts: 1) SIA locally produced from the  $i^{\text{th}}$  region locally emitted precursors (LC); 2) SIA chemically formed in other regions from the  $i^{\text{th}}$  region locally emitted precursors (LTC); 3) SIA chemically formed in the transport pathway to the  $i^{\text{th}}$  receptor region from precursors emitted in the  $j^{\text{th}}$  source region (RTC); and 4) SIA produced in the  $j^{\text{th}}$  region from precursors emitted in the  $j^{\text{th}}$  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  $i$  means region,  $n$  is the total number of regions, and  $n$  is 10 in this study.  $C_{1i}$  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 parts 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 configuration

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 ~~formation of 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 primary sulfate emissions. Compared with Base, Control 2 (C2) excluded the heterogeneous reactions of SO<sub>2</sub>. Base–C2 represents the effect of heterogeneous reactions on sulfate. Base–C1 represents contribution of primary sulfate emissions.

The HYSPLIT model was used to analyze the trajectories of air masses (Draxler 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  $0.25^\circ \times 0.25^\circ$  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  $\text{SO}_2$  emissions in the original MEIC inventory. Cao et al. (2014), Wang et al. (2009), Zheng et al. (2013), and Ma et al. (2015) discovered that primary sulfate comprised large amounts of primary  $\text{PM}_{2.5}$  from industrial, power, and residential emissions in the main form of  $(\text{NH}_4)_2\text{SO}_4$  through in situ measurement of source profiles. Thus, we took 40%, 6% and 15% of primary  $\text{PM}_{2.5}$  from industrial, power and residential emissions, respectively, as primary sulfate emissions in the inventory. Figure 1b displays the hourly primary  $\text{PM}_{2.5}$  emission rate.

### 2.4 Observations

The surface meteorological parameters were obtained from the China Meteorological Administration, whereas the vertical profiles of meteorological parameters were obtained from the University of Wyoming (<http://weather.uwyo.edu/upperair/sounding.html>). Observations of  $\text{PM}_{2.5}$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{O}_3$  concentrations were obtained from the China National Environmental Monitoring Center (<http://www.cnemc.cn/>). Aerosol components (including organic matters [OM], sulfate, nitrate, and ammonium) were measured in situ at Beijing 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). A seven-wavelength



Aethalometer (AE33, Magee Scientific Corp.) was used to measure BC at Beijing (Xie et al., 2018). The OC/EC in aerosol was measured by a field semi-online OC/EC analyzer from Sunset Laboratory Inc. (USA) with a PM<sub>2.5</sub> cyclone inlet at Tianjin and Lang Fang (Gao et al., 2016). Two same ambient ion monitors (AIM; Model URG 9000D, URG Corporation) were used to measure hourly concentrations of water-soluble ions in PM<sub>2.5</sub>, including NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> at TJ and LF (Gao et al., 2016). The particle number size distributions at ground level were 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<sub>2.5</sub> mass and number concentrations and aging degrees

The time series of simulated and observed PM<sub>2.5</sub> in different cities of BTH from November 15 to December 15, 2016, are illustrated in Fig. 2. During 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<sub>2.5</sub> mass concentration frequently exceeded 200 µg m<sup>-3</sup> and the average concentration reached 120 µg m<sup>-3</sup> during episodes. Haze usually formed in several hours; for example, the increasing rate of PM<sub>2.5</sub> reached 200 µg m<sup>-3</sup> h<sup>-1</sup> 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<sub>2.5</sub> in Beijing and Baoding for Ep2. This was caused by the failure of the mineral 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  $\mu\text{m}$  for Ep2 in Beijing. The concentrations of  $\text{Ca}^{2+}$  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  $\text{SO}_2$  into sulfate in the form of  $\text{CaSO}_4$  or  $\text{MgSO}_4$  (Wang et al., 2018b; Wang et al., 2017c). 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  $\text{PM}_{2.5}$  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  $\mu\text{g m}^{-3}$ , which is much less than that in Beijing (45  $\mu\text{g m}^{-3}$ ). The monthly emissions employed in this study made it difficult to capture these short-term local-scale emission changes. The simulated  $\text{SO}_2$  concentrations are compared with the observations in Fig. S2, and the normalized mean bias (NMBs) 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 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  $1.8 \times 10^4 \text{ cm}^{-3}$  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 ( $R_{BC}$ ) was used as an indicator of aging degree, 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, respectively, which are extremely close to the observations (~5.0 and 5.1) (Wang et al., 2018a). The high performance of the model in terms of mass and number concentrations, compositions, and the aging degree 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 moments when 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. In sum, the high performance of the meteorological

simulation gave us confidence for PM<sub>2.5</sub> simulation.

## 4 Results and discussion

### 4.1 Source apportionment of surface PM<sub>2.5</sub>

The simulated spatial distribution of average surface PM<sub>2.5</sub> levels and the wind vector during the six haze episodes are shown in Fig. 5. In general, two types of patterns were observed. The first pattern corresponded to Ep1, Ep4, and Ep6 and reflected that a highly polluted belt with PM<sub>2.5</sub> over 200  $\mu\text{g m}^{-3}$  extended from the southwest to the northeast along the Taihang mountain range. In the second pattern (Ep2, Ep3, and Ep5), the PM<sub>2.5</sub> level of 150–200  $\mu\text{g m}^{-3}$  was concentrated in three northern cities (Beijing, Tianjin, and Tangshan). In the other cities, the PM<sub>2.5</sub> mass concentrations ranged from 75  $\mu\text{g m}^{-3}$  to 115  $\mu\text{g m}^{-3}$ , indicating a light pollution level according to the Technical Regulation on Ambient Air Quality Index (on trial).

Figure 6 shows the contributions of regional transport and local emissions to average PM<sub>2.5</sub>, primary inorganic aerosol (PIA, including BC and inorganic primary PM<sub>2.5</sub>), and SIA levels in different cities during the study period. The contribution of local emissions was more than that of regional transport to the PM<sub>2.5</sub> mass concentration in all cities, except Heng Shui, Cangzhou, Langfang, and Qinhuangdao; the magnitude of local emission contributions was 49%–80%. The principle reason for this was the accumulation of local PIA emissions. In most cities, 64%–93% of PIA originated from local emissions (Fig. 6c). In contrast to PIA, the SIA contribution was dominated by regional transport of emissions in other cities (50%–87%). Even the emissions of cities outside the city cluster (e.g., Henan, Shanxi and Shandong) were transported to the megacity cluster, travelling 500–1,000 km. In Beijing, the local contribution to total PM<sub>2.5</sub> and PIA was 74% and 94%, respectively, whereas regional transport from other cities was the major source of SIA, contributing 51%. The difference in source apportionment between PIA and SIA was related to the mechanisms-emission of PIA and formation mechanisms of SIA-formation. Regarding PIA, the inversion layer and

weak winds during stable weather conditions prevented  $\text{PIA}$  transport and resulted in local-scale accumulation of  $\text{PIA}$  emissions. The regional transport provided sufficient time (1–3 days) and aerosol surface for chemical transformation of precursors to SIA (Li et al., 2015; Li et al., 2017b). This also indicates that regional controls on precursors 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  $\text{PIA}$  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  $\text{PM}_{2.5}$  mass concentration during the six episodes. The highest contribution of regional transport occurred in Ep1 and Ep5 (29% and 31% of the total  $\text{PM}_{2.5}$ , 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  $\text{PM}_{2.5}$  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., 2017b). 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  $\text{PM}_{2.5}$ ,  $\text{PIA}$ , OM (organic matters, sum of primary organic aerosols [POA] and secondary organic aerosols [SOA]), and SIA mass concentrations were in the range 14%–23%, 3%–12%, 3%–14%, and 30%–51%, respectively. Back trajectories and emissions source regions can be connected (Fig. S5). Taking Ep6 for example, air mass mainly came from Shandong, through SHB, WHB and finally arrived at Beijing. What's more, the height of trajectory within WHB is low, so contribution of WHB should be big, which agreed with results

of Figure 7b, and source apportionment results showed that WHB contributed 24% to SIA at Beijing during Ep6.

Figure 8 presents the relative contribution of regionally transported SIA and variation of wind direction under different pollution levels in Beijing. The source regions varied considerably under different pollution levels. When Beijing is controlled by strong northerly wind, NHB and SX are the main source regions, contributing up to 30% and 19% to SIA, resulting in clean conditions ( $\text{SIA} < 50 \mu\text{g m}^{-3}$ ). When Beijing is mainly affected by southerly wind (southeast, south and southwest), WHB, EHB and SD become the main source regions, contributing 27%, 13% and 15% to SIA, respectively. Strong emissions of source regions lead to heavier pollution level in Beijing. When Beijing is dominated by weak southeast wind, contribution from far regions like HN and SD increases. Continuous transport and accumulation lead to severe pollution ( $\text{SIA} > 150 \mu\text{g m}^{-3}$ ). 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 75% 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  $\text{LTC} + \text{RLC} + \text{RTC}$ , whereas in the studies by Li et al. (2017) and Timmermans et al. (2017), it was  $\text{RLC} + \text{RTC}$ . In this study, we employed  $\text{RLC} + \text{RTC}$  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<sub>2</sub> were critical to haze formation. Notably, the LTC contribution was comparable with that of LC in Ep3, Ep4, and Ep6. This suggests that the SO<sub>2</sub> emitted in Beijing was blown away and formed sulfate outside Beijing. And recirculation of air masses can be ~~convined~~supported by HYSPLIT trajectories (Fig. S6). Take trajectories at 23:00 on December 12 [LST] for example, air masses were blown away Beijing by southwesterly, through Chengde, Tianjin and Langfang, and finally travelled back to 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 increase rate 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 contribution 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<sub>2</sub> 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., 2017b). This feature is also reflected in Fig. 9b. Under clear conditions (sulfate < 20  $\mu\text{g m}^{-3}$ ), 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  $\mu\text{g m}^{-3}$  < sulfate < 35  $\mu\text{g m}^{-3}$ ), the local contribution was lower—particularly the LTC—leading to a ratio of LC to LTC of approximately 8. Contribution of sulfate formed in the regional transport pathway (RTC) significantly increased from 40% to 65%. Under heavy pollution levels (> 35  $\mu\text{g m}^{-3}$ ), the LC contributed up to 50% due to extremely stable boundary layers. Our results are consistent with those of Ma et al. (2017), in which regional transport and local heterogeneous chemistry were qualitatively discovered to make high contributions to initial and subsequent pollution stages.

### 4.3 Evolution of aerosol properties in Beijing during haze episodes

Aerosol properties such as the particle size and aging degree can change dramatically on haze days because of fresh emissions, subsequent chemical conversions, and regional transport, which strongly affect regional radiation and climate (Cappa et al., 2012). As illustrated in Fig. 4b, the GMD of aerosols in Beijing increased remarkably to approximately 120 nm during the six haze episodes, compared with 50 nm under clean conditions. Two stages were identified: an initial rising stage and a sustained increase stage. In the initial stage, the GMD of aerosols increased by 50–60 nm within several hours, and the GMD then remained at 100–120 nm for several days in the subsequent elevated pollution stage. This GMD increase during the initial stage was mainly caused by the increase of accumulation-mode particles with diameters of 100–1,000 nm and Aitken-mode particles (Fig. 10). Under clean conditions (SIA < 50  $\mu\text{g m}^{-3}$ ), the average contributions of the three modes (nucleation, Aitken, and accumulation modes) to the number concentration were comparable, although the number of nucleation-mode particles decreased with SIA concentration. Under light-



moderate pollution conditions ( $50 < \text{SIA} < 150 \mu\text{g m}^{-3}$ ), the proportion of accumulation-mode particles significantly increased from 35% to 60%, whereas the proportion of Aitken-mode particles slowly decreased. As discussed in previous sections, regional transport played a dominant role during the initial stage. This indicates that condensation, coagulation, and chemical transformation in the transport pathway increased the number of particles with a diameter range of 100–1,000 nm. Finally, the contributions of Aitken-mode and accumulation-mode particles remained stable under the heavy-pollution conditions ( $\text{SIA} > 150 \mu\text{g m}^{-3}$ ).

Aging processes play a critical role in the growth of particles during haze episodes. According to observations, a significant coating of secondary components on BC was found in the study period (Wang et al., 2018a). Figure 11 presents a time series of the simulated  $R_{\text{BC}}$ , which is a favorable indicator of the aging degree (Oshima et al., 2009; Collier et al., 2018). Higher  $R_{\text{BC}}$  indicates that BC had undergone ~~a greater degree of~~ more ageing. In this study, the simulated  $R_{\text{BC}}$  was 2–10, with an average value of 4.5. Under pollution conditions,  $R_{\text{BC}}$  was higher than that under clean conditions, with an average value of 5.0.  $R_{\text{BC}}$  in Beijing even exceeded 10.0 in some extremely severe pollution events, which is close to observations of remote sites (Wang et al., 2017a; Massoli et al., 2015) and aged particles (Cappa et al., 2012). Urban aerosols usually have a lower  $R_{\text{BC}}$  because of fresh emissions and high  $R_{\text{BC}}$  in this study indicates that Beijing aerosol particles were more aged during the haze episodes. On clean days,  $R_{\text{BC}}$  ranged from 2 to 5, with an average of 2.8. This is similar to the  $R_{\text{BC}}$  of vehicle emissions ( $< 3$ ) (Liu et al., 2017), indicating that Beijing is affected by local emission. 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  $R_{\text{BC}}$ , GMD, and region source of BC along the transport pathway from the source region to Beijing during the six haze episodes. Aerosol properties including number concentration along transport per six hours are shown in Table S2. 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. 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. 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 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., 2014a). 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., 2017a; Tang et al., 2016b). 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 PIA. Researchers also found that household coal burning can emit certain amounts of sulfate (Zhang et al., 2018).

In this study, we examined the contributions of gas ( $\text{SO}_2 + \text{OH}$ ) 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  $< 20 \mu\text{g m}^{-3}$ ), whereas heterogeneous chemistry played a crucial role under high pollution levels (sulfate  $> 30 \mu\text{g m}^{-3}$ ). The contributions of gas and aqueous chemistry were largely consistent under all pollution conditions ( $\sim 30\%$ ). This indicates that high relative humidity and aerosol loading accelerated the  $\text{SO}_2$  chemical transformation. Interestingly, the contribution of heterogeneous chemistry was markedly higher when the sulfate mass concentration exceeded the threshold of  $20 \mu\text{g m}^{-3}$ . Under high relative humidity and mass concentration conditions, a higher aerosol surface area resulting from hygroscopic growth and haze particles under high RH (60–80%) with aqueous shell due to phase transition provided a favorable media for heterogeneous reactions (Tie et al., 2017; Sun et al., 2018). 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  $\text{SO}_2$  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  $\text{PM}_{2.5}$  mass concentration in Beijing during the six episodes, with a monthly average contribution of 26%. Regarding aerosol components, 30%–62% of the SIA in Beijing were regionally transported, whereas few PIAs ( $< 10\%$ ) were contributed ~~by~~ ~~from~~ emissions ~~from~~ other regions. Source regions differed between episodes. During high-pollution periods, WHB, SD, and EHB were the main source regions of SIA regionally transported to Beijing, whereas NHB and SX made greater contributions under clean and light pollution conditions. This indicates the complexity of regional transport in this megacity cluster.

The chemical transformation of  $\text{SO}_2$  along the transport pathway from source regions except Beijing to Beijing (RTC) was the major source of  $\text{SO}_4^{2-}$  regional transport and was more critical than the transport of sulfate formed in source regions except Beijing (RLC). Compared with sulfate that was chemically transformed from Beijing-emitted  $\text{SO}_2$  and then blown back to Beijing (LTC), contribution of sulfate produced in Beijing from Beijing-emitted  $\text{SO}_2$  (LC) was generally greater. However, RTC markedly increased in some episodes, and it explained the rapid formation of sulfate in Beijing. This suggests that the joint control of local and regional  $\text{SO}_2$

emissions is essential for reducing the rapid formation of haze in this region.

Aerosols became considerably aged during transport in haze episodes, which altered  $R_{BC}$  and the size distribution of number concentrations. During haze episodes, the 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. The number of accumulation-mode particles with a diameter range of 100–1,000 nm increased considerably more than the number of particles of different modes.  $R_{BC}$  in Beijing during the episodes was higher than that of other urban regions (Collier et al., 2018) At high pollution levels, and  $R_{BC}$  under pollution levels was close to that in remote regions (Wang et al., 2017a), which indicates that BC in Beijing under pollution conditions was more aged and thus more likely to affect radiation and circulation.

Contributions from different pathways to sulfate in Beijing were also examined. In episodes with high humidity (Ep1), the average contributions of gas and aqueous chemistry, heterogeneous chemistry, and primary sulfate were comparable. But their relative contributions varied with pollution levels. Under light to moderate pollution levels, Primary primary emissions mostly had an effect. under light to moderate pollution levels, But under high pollution levels during Ep1, whereas heterogeneous chemistry played a relatively crucial role. under high pollution levels during Ep1. In other episodes (Ep2, Ep3, Ep4, Ep5, and Ep6), gas and aqueous chemistry and primary emissions contributed 35%–40% and 58%–61%, respectively.

## Acknowledgements:

Many thanks to the anonymous reviewers for their helpful comments to improve our manuscript. This work was supported by the Natural Science Foundation of China (41571130034; 91544227; 91744203; 41225019; 41705108) and the Chinese Ministry of Science and Technology (2018YFC0213205 and 2017YFC0212402).

## References

Anderson, H. R., Atkinson, R., Balbus, J., Brauer, M., Chapman, R., Chowdhury, Z.: Outdoor Air

Pollution and Health in the Developing Countries of Asia: A Comprehensive Review, Special Report 18, Health Effects Institute, Boston, Massachusetts, 2010.

Bian, Y. X., Zhao, C. S., Ma, N., Chen, J., and Xu, W. Y.: A study of aerosol liquid water content based on hygroscopicity measurements at high relative humidity in the North China Plain, Atmospheric Chemistry and Physics, 14, 6417-6426, 10.5194/acp-14-6417-2014, 2014.

Boylan, J. W., & Russell, A. G.: PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models, Atmospheric Environment, 40(26), 4946-4959, <https://doi.org/10.1016/j.atmosenv.2005.09.087>, 2006.

Cao J.: PM<sub>2.5</sub> and environment. Science Press, 2014.

Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., ... Zaveri, R. A.: Radiative Absorption Enhancements Due to the Mixing State of Atmospheric Black Carbon, Science, 337(6098), 1078–1081, <https://doi.org/10.1126/science.1223447>, 2012.

Chen, X., Li, X., Yuan, X., Zeng, G., Liang, J., Li, X., ... Chen, G.: Effects of human activities and climate change on the reduction of visibility in Beijing over the past 36 years, Environ Int, 116, 92-100, <https://doi.org/10.1016/j.envint.2018.04.009>, 2018.

Chen, X., Wang, Z., Li, J., & Yu, F.: Development of a regional chemical transport model with size-resolved aerosol microphysics and its application on aerosol number concentration simulation over china, Scientific Online Letters on the Atmosphere Sola, 10, 83-87, <https://doi.org/10.2151/sola.2014-017>, 2014.

Chen, X., Wang, Z., Yu, F., Pan, X., Li, J., & Ge, B., et al.: Estimation of atmospheric aging time of black carbon particles in the polluted atmosphere over central-eastern china using microphysical process analysis in regional chemical transport model. Atmospheric Environment, 163, 44-56, <https://doi.org/10.1016/j.atmosenv.2017.05.016>, 2017.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., & Wang, Z., et al: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in china, Science Advances, 2(12), <https://doi.org/10.1126/sciadv.1601530>, 2016.

Collier, S., Williams, L. R., Onasch, T. B., Cappa, C. D., Zhang, X., & Russell, L. M., et al: Influence of emissions and aqueous processing on particles containing black carbon in a polluted urban environment: insights from a soot particle-aerosol mass spectrometer, Journal of Geophysical Research Atmospheres, 123(12), 6648-6666, <https://doi.org/10.1002/2017jd027851>, 2018.

Draxler, R. R., & Hess, G. D: An overview of the HYSPLIT 4 modeling system for trajectories, dispersion, and deposition, Australian Meteorological Magazine, 47(4), 295-308, 1998.

Du, W., Zhao, J., Wang, Y., Zhang, Y., Wang, Q., & Xu, W., et al: Simultaneous measurements of particle number size distributions at ground level and 260 m on a meteorological tower in urban Beijing, china, Atmospheric Chemistry & Physics, 17(11), 6797-6811, <https://doi.org/10.5194/acp-17-6797-2017>, 2017.

Gao, J., Peng, X., Chen, G., Xu, J., Shi, G. L., Zhang, Y. C., and Feng, Y. C.: Insights into the chemical characterization and sources of PM<sub>2.5</sub> in Beijing at a 1-h time resolution, The Science

658 of the total environment, 542, 162-171, 10.1016/j.scitotenv.2015.10.082, 2016.

659 Han, B., Zhang, R., Yang, W., Bai, Z., Ma, Z., & Zhang, W: Heavy haze episodes in Beijing during  
660 January 2013: inorganic ion chemistry and source analysis using highly time-resolved  
661 measurements from an urban site, *Science of the Total Environment*, 544, 319-329,  
662 <https://doi.org/10.1016/j.scitotenv.2015.10.053>, 2016.

663 Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., . . . Prevot, A. S: High secondary  
664 aerosol contribution to particulate pollution during haze events in China, *Nature*, 514(7521),  
665 218-222, <https://doi.org/10.1038/nature13774>, 2014.

666 Hyslop, N. P.: Impaired visibility: the air pollution people see, *Atmospheric Environment*, 43(1),  
667 182-195, <https://doi.org/10.1016/j.atmosenv.2008.09.067>, 2009.

668 Lee, A. K. Y., Chen, C. L., Liu, J., Price, D. J., Betha, R., Russell, L. M., Zhang, X., and Cappa, C.  
669 D.: Formation of secondary organic aerosol coating on black carbon particles near vehicular  
670 emissions, *Atmos. Chem. Phys.*, 17(24), 15055-15067, [https://doi.org/10.5194/acp-17-15055-](https://doi.org/10.5194/acp-17-15055-2017)  
671 2017, 2017.

672 Li, G., Bei, N., Cao, J., Huang, R., Wu, J., & Feng, T., et al.: A possible pathway for rapid growth  
673 of sulfate during haze days in china, *Atmospheric Chemistry & Physics*, 17(5), 3301-3316,  
674 <https://doi.org/10.5194/acp-17-3301-2017>, 2017a.

675 Li, J., Chen, X., Wang, Z., Du, H., Yang, W., & Sun, Y., et al.: Radiative and heterogeneous chemical  
676 effects of aerosols on ozone and inorganic aerosols over east Asia, *Science of the Total*  
677 *Environment*, 622-623, 1327, <https://doi.org/10.1016/j.scitotenv.2017.12.041>, 2018.

678 Li, J., Du, H., Wang, Z., Sun, Y., Yang, W., & Li, J., et al.: Rapid formation of a severe regional  
679 winter haze episode over a mega-city cluster on the North China Plain, *Environmental*  
680 *Pollution*, 223, 605-615, <https://doi.org/10.1016/j.envpol.2017.01.063>, 2017b.

681 Li, J., Han, Z.: A modeling study of severe winter haze events in Beijing and its neighboring regions,  
682 *Atmospheric Research*, 170, 87-97, <https://doi.org/10.1016/j.atmosres.2015.11.009>, 2016.

683 Li, J., Wang, Z., Huang, H., Min, H. U., Meng, F., & Sun, Y., et al.: Assessing the effects of trans-  
684 boundary aerosol transport between various city clusters on regional haze episodes in spring  
685 over east china, *Tellus*, 65(1), 60-73, <https://doi.org/10.3402/tellusb.v65i0.20052>, 2013.

686 Li, J., Yang, W., Wang, Z., Chen, H., Hu, B., & Li, J., et al.: A modeling study of source–receptor  
687 relationships in atmospheric particulate matter over northeast Asia. *Atmospheric Environment*,  
688 91(7), 40-51, <https://doi.org/10.1016/j.atmosenv.2014.03.027>, 2014.

689 Li, J., Wang, Z.F., Zhuang, G., Luo, G., Sun, Y., Wang, Q.: Mixing of Asian mineral dust with  
690 anthropogenic pollutants over East Asia: a model cast study of a super-dust storm in March  
691 2010. *Atmos. Chem. Phys.* 12 (16), 7591-7607. <https://dx.doi.org/10.5194/acp-12-7591-2012>,  
692 2012.

693 Li, P., Yan, R., Yu, S., Wang, S., Liu, W., & Bao, H.: Reinstate regional transport of PM<sub>2.5</sub> as a major  
694 cause of severe haze in Beijing, *Proc Natl Acad Sci U S A*, 112(21), E2739-2740,  
695 <https://doi.org/10.1073/pnas.1502596112>, 2015.



- Liu, D., Whitehead, J., Alfarra, M. R., Reyes-villegas, E., Spracklen, D. V., & Reddington, C. L., et al.: Black-carbon absorption enhancement in the atmosphere determined by particle mixing state, *Nature Geoscience*, 10(3), 184-188, <https://doi.org/10.1038/ngeo2901>, 2017.
- Liu, X., Zhang, Y., Jung, J., Gu, J., Li, Y., & Guo, S., et al.: Research on the hygroscopic properties of aerosols by measurement and modeling during CAREBeijing-2006, *Journal of Geophysical Research Atmospheres*, 114(16), 4723-4734, <https://doi.org/10.1029/2008jd010805>, 2009.
- Ma, Q., Wu, Y., Zhang, D., Wang, X., Xia, Y., Liu, X., . . . Zhang, R.: Roles of regional transport and heterogeneous reactions in the PM<sub>2.5</sub> increase during winter haze episodes in Beijing, *Sci Total Environ*, 599-600, 246-253, <https://doi.org/10.1016/j.scitotenv.2017.04.193>, 2017.
- Ma, X., & Yu, F.: Seasonal variability of aerosol vertical profiles over east us and west Europe: GEOS-Chem/APM simulation and comparison with CALIPSO observations, *Atmospheric Research*, 140-141(31), 28-37, <https://doi.org/10.1016/j.atmosres.2014.01.001>, 2014.
- Ma, Z., Liang YP, Zhang J.: PM<sub>2.5</sub> profiles of typical sources in Beijing, *Acta Science Circumstantiae*, 35(12), 4043-4052, <https://doi.org/10.13671/j.hjkxxb.2015.0584>, 2015.
- Massoli, P., Onasch, T. B., Cappa, C. D., Nuumaan, I., Hakala, J., & Hayden, K., et al.: Characterization of black carbon containing particles from soot particle aerosol mass spectrometer measurements on the R/V Atlantis during CalNex 2010, *Journal of Geophysical Research Atmospheres*, 120(6), 2575-2593, <https://doi.org/10.1002/2014jd022834>, 2015.
- Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N<sub>2</sub>O<sub>5</sub> uptake: airborne regional measurements in northwestern Europe, *Atmospheric Chemistry and Physics*, 15, 973-990, [10.5194/acp-15-973-2015](https://doi.org/10.5194/acp-15-973-2015), 2015.
- Nenes, A., Pandis, S.N., Pilinis, C.: ISORROPIA: A new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, *Aquat. Geochem.* 4(1), 123-152. <https://dx.doi.org/10.1023/A:1009604003981>, 1998.
- Oshima, N., Koike, M., Zhang, Y., Kondo, Y., Moteki, N., & Takegawa, N., et al.: Aging of black carbon in outflow from anthropogenic sources using a mixing state resolved model: model development and evaluation, *Journal of Geophysical Research Atmospheres*, 114(D6), <https://doi.org/10.1029/2008jd010680>, 2009.
- Pan, X., Ge, B., Wang Z., Tian, Y., et al.: Synergistic effect of water-soluble species and relative humidity on morphological changes of aerosol particles in Beijing mega-city during severe pollution episodes, *Atmos. Chem. Phys. Discuss*, 1-24, <https://doi.org/10.5194/acp-2018-623>, 2018.
- Peng J, Hu M, Guo S, et al.: Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments, *Proc Natl Acad Sci USA*, 113(16), 4266-4271, <https://doi.org/10.1073/pnas.1602310113>, 2016.
- Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler-Scharr, A., and Mentel, T. F.: Relative importance of organic coatings for the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> during summer in



[Europe, Journal of Geophysical Research-Atmospheres, 114\(D17\), 10.1029/2008jd011369, 2009.](#)

Shi, Z., Vu, T., and Kotthaus, S.: Introduction to Special Issue-In-depth study of air pollution sources and processes within Beijing and its surrounding region(APHH-Beijing), Atmos. Chem. Phys. Discuss., 10.5194/acp-2018-922, 2018.

Sun, Y., Chen, C., Zhang, Y., Xu, W., Zhou, L., Cheng, X., . . . Wang, Z.: Rapid formation and evolution of an extreme haze episode in Northern China during winter 2015, Sci Rep, 6(1), 27151. <https://doi.org/10.1038/srep27151>, 2016.

Sun, Y., Du, W., Wang, Q., Zhang, Q., Chen, C., & Chen, Y., et al. Real-time characterization of aerosol particle composition above the urban canopy in Beijing: insights into the interactions between the atmospheric boundary layer and aerosol chemistry, Environmental Science & Technology, 49(19), 11340-11347, <https://doi.org/10.1021/acs.est.5b02373>, 2015.

Sun, Y., Jiang, Q., Wang, Z., Fu, P., Li, J., Yang, T., & Yin, Y.: Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013, Journal of Geophysical Research: Atmospheres, 119(7), 4380-4398, <https://doi.org/10.1002/2014jd021641>, 2014.

Tang, G., Zhang, J., Zhu, X., Song, T., Munkel, C., Hu, B., et al.: Mixing layer height and its implications for air pollution over Beijing, China, Atmos. Chem. Phys., 16(4), 2459-2475, <https://doi.org/10.5194/acp-16-2459-2016>, 2016a.

Tang, M. J., Larish, W. A., Fang, Y., Gankanda, A., and Grassian, V. H.: Heterogeneous Reactions of Acetic Acid with Oxide Minerals: Effects of Mineralogy and Relative Humidity, J. Phys. Chem. A, 120(28), 5609-5616, <https://doi.org/10.1021/acs.jpca.6b05395>, 2016b.

Tie, X., Huang, R. J., Cao, J., Zhang, Q., Cheng, Y., Su, H., . . . O'Dowd, C. D.: Severe Pollution in China Amplified by Atmospheric Moisture, Sci Rep, 7(1), <https://doi.org/10.1038/s41598-017-15909-1>, 2017.

Timmermans, R., Kranenburg, R., Manders, A., Hendriks, C., Segers, A., & Dammers, E., et al.: Source apportionment of PM<sub>2.5</sub> across china using LOTOS-EUROS, Atmospheric Environment, 164, 370-386, <https://doi.org/10.1016/j.atmosenv.2017.06.003>, 2017.

Wang, J., Liu, D., Ge, X., Wu, Y., Shen, F., Chen, M., . . . Sun, Y.: Characterization of black carbon-containing fine particles in Beijing during wintertime, Atmospheric Chemistry and Physics Discussions, 1-25, <https://doi.org/10.5194/acp-2018-800>, 2018a.

Wang, J., Zhang, Q., Chen, M. D., Collier, S., Zhou, S., & Ge, X., et al.: First chemical characterization of refractory black carbon aerosols and associated coatings over the Tibetan plateau (4730 m a.s.l), Environmental Science & Technology, 51(24), 14072-14082, <https://doi.org/10.1021/acs.est.7b03973>, 2017a.

Wang, S., Zhao, X., Li, X., Wei, W., Hao, J.: Study on fine particle emission characteristics of industrial coal-fired chain furnace. Environmental Science (Chines), 30 (4), 963-968, <https://doi.org/10.3321/j.issn:0250-3301.2009.04.004>, 2009.

Wang, Y. Y., Liu, F. S., He, C. L., Bi, L., Cheng, T. H., Wang, Z. L., Zhang, H., Zhang, X. Y., Shi,

773 Z. B., and Li, W. J.: Fractal Dimensions and Mixing Structures of Soot Particles during  
 774 Atmospheric Processing, *Environ Sci Tech Let*, 4, 487-493, 10.1021/acs.estlett.7b00418,  
 775 2017b.

776 Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B. Y., He, K. B., . . . Xie, Y. Y.: Enhanced sulfate  
 777 formation during china's severe winter haze episode in January 2013 missing from current  
 778 models, *Journal of Geophysical Research Atmospheres*, 119(17), 10425-10440,  
 779 <https://doi.org/doi: 10.1002/2013jd021426>, 2014a.

780 Wang, Z., Maeda, T., Hayashi, M., Hsiao, L.F., Liu, K.Y.: A nested air quality prediction modeling  
 781 system for urban and regional scales, application for high-ozone episode in Taiwan, *Water, Air,  
 782 Soil Pollut*, 130, 391-396, <https://dx.doi.org/10.1023/A:1013833217916>. 2001.

783 Wang, Z., Jie, L., Wang, Z., Yang, W. Y., Tang, X., & Ge, B. Z., et al.: Modeling study of regional  
 784 severe hazes over mid-eastern China in January 2013 and its implications on pollution  
 785 prevention and control, *Science China Earth Sciences*, 57(1), 3-13,  
 786 <https://dx.doi.org/10.1007/s11430-013-4793-0>, 2014b.

787 Wang, Z., Pan, X., Uno, I., Li, J., Wang, Z., Chen, X., Fu, P., Yang, T., Kobayashi, H., Shimizu, A.,  
 788 Sugimoto, N., and Yamamoto, S.: Significant impacts of heterogeneous reactions on the  
 789 chemical composition and mixing state of dust particles: A case study during dust events over  
 790 northern China, *Atmospheric Environment*, 159, 83-91,  
 791 <https://doi.org/10.1016/j.atmosenv.2017.03.044>, 2017c.

792 Wang, Z., Pan, X., Uno, I., Chen, X., Yamamoto, S., Zheng, H., Li, J., and Wang, Z.: Importance of  
 793 mineral dust and anthropogenic pollutants mixing during a long-lasting high PM event over  
 794 East Asia, *Environmental pollution*, 234, 368-378,  
 795 <https://doi.org/10.1016/j.envpol.2017.11.068>, 2018b.

796 Wiedinmyer, C., Akagi, S. K., Yokelson, R. J., & Emmons, L. K.: The fire inventory from NCAR  
 797 (FINN) – a high resolution global model to estimate the emissions from open burning,  
 798 *Geoscientific Model Development*, 4(3), 625-641, <https://doi.org/10.5194/gmd-4-625-2011>,  
 799 2011.

800 Wu, J. B., Wang, Z., Wang, Q., Li, J., Xu, J., & Chen, H., et al.: Development of an on-line source-  
 801 tagged model for sulfate, nitrate and ammonium: A modeling study for highly polluted periods  
 802 in Shanghai, China. *Environmental Pollution*, 221, 168-179,  
 803 <https://doi.org/10.1016/j.envpol.2016.11.061>, 2017.

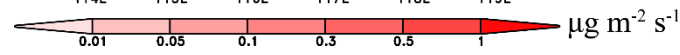
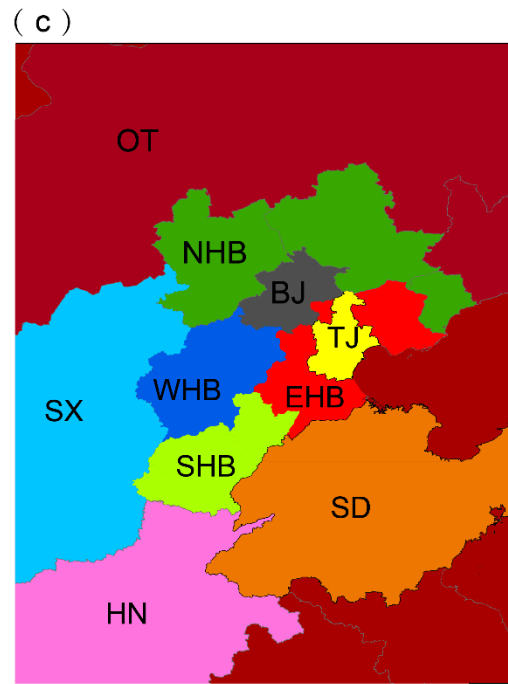
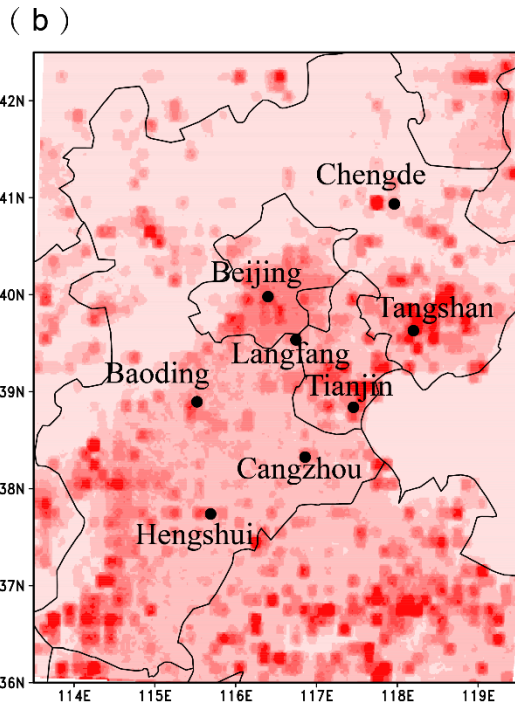
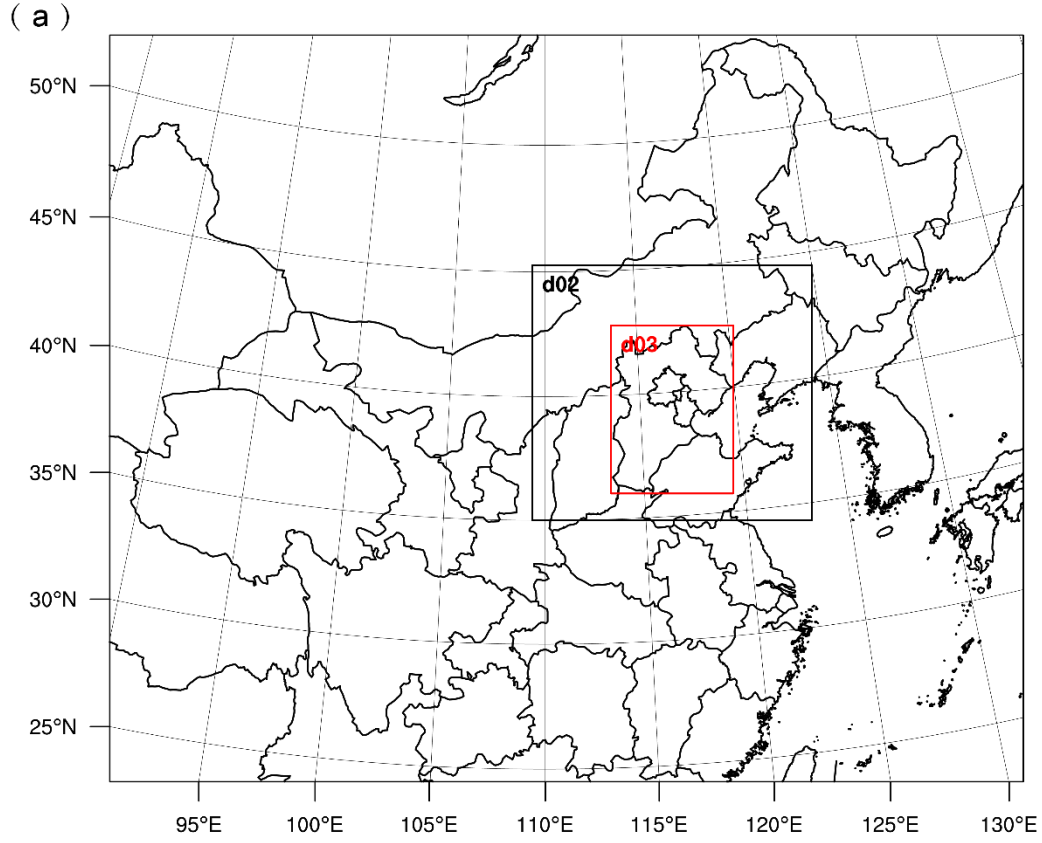
804 Xie, C., Xu, W., Wang, J., Wang, Q., Liu, D., Tang, G., Chen, P., Du, W., Zhao, J., Zhang, Y., Zhou,  
 805 W., Han, T., Bian, Q., Li, J., Fu, P., Wang, Z., Ge, X., Allan, J., Coe, H., and Sun, Y.: Vertical  
 806 characterization of aerosol optical properties and brown carbon in winter in urban Beijing,  
 807 China, *Atmospheric Chemistry and Physics Discussions*, 1-28, 10.5194/acp-2018-788, 2018.

808 Yang, H. H.: Filterable and condensable fine particulate emissions from stationary sources, *Aerosol  
 809 & Air Quality Research*, 14(7), 2010-2016, <https://doi.org/10.4209/aaqr.2014.08.0078>, 2014.

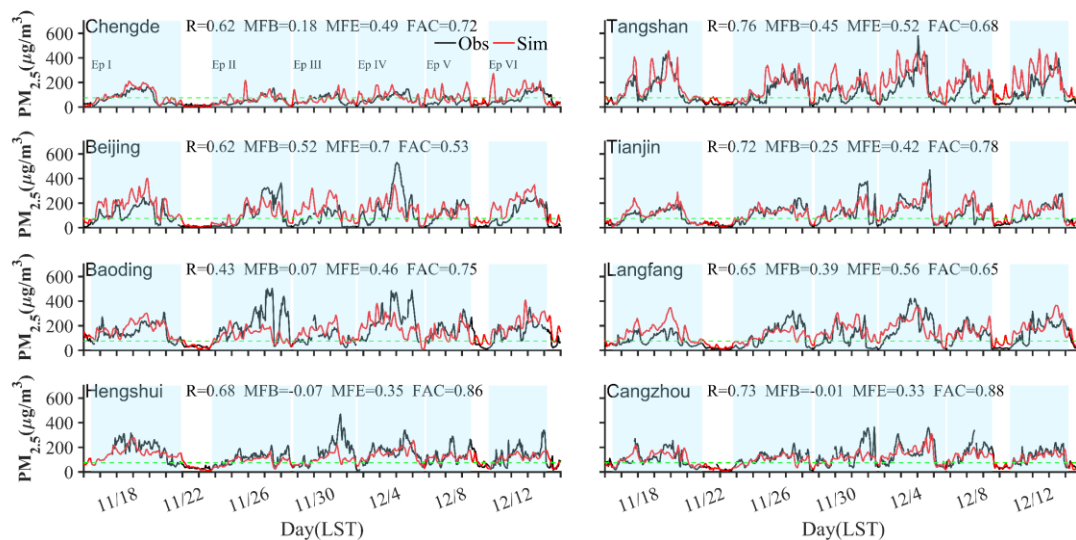
810 Yang, Y., Liu, X., Qu, Y., Wang, J., An, J., & Zhang, Y., et al.: Formation mechanism of continuous  
 811 extreme haze episodes in the megacity Beijing, China, in January 2013. *Atmospheric Research*,

- 155, 192-203, <https://doi.org/10.1016/j.atmosres.2014.11.023>, 2015.
- Yang, Y., Wang, H., Smith, S. J., Easter, R., Ma, P. L., Qian, Y., . . . Rasch, P. J.: Global source attribution of sulfate concentration and direct and indirect radiative forcing, *Atmospheric Chemistry and Physics*, 17(14), 8903-8922, <https://doi.org/10.5194/acp-17-8903-2017>, 2017a.
- Yang, Y., Wang, H., Smith, S. J., Ma, P.-L., & Rasch, P. J.: Source attribution of black carbon and its direct radiative forcing in China, *Atmospheric Chemistry and Physics*, 17(6), 4319-4336, <https://doi.org/10.5194/acp-17-4319-2017>, 2017b.
- Ying, Q. Wu, L. Zhang, H.: Local and inter-regional contributions to PM<sub>2.5</sub> nitrate and sulfate in China, *Atmos. Environ.*, 94, 582-592, <https://doi.org/10.1016/j.atmosenv.2014.05.078>, 2014.
- Yu, F., & Luo, G.: Simulation of particle size distribution with a global aerosol model: contribution of nucleation to aerosol and CCN number concentrations, *Atmospheric Chemistry & Physics*, 9(20), 7691-7710, <https://doi.org/10.5194/acp-9-7691-2009>, 2009.
- Zhang, S. L., Ma, N., Kecorius, S., Wang, P. C., Hu, M., Wang, Z. B., Gross, J., Wu, Z. J., and Wiedensohler, A.: Mixing state of atmospheric particles over the North China Plain, *Atmospheric Environment*, 125, 152-164, [10.1016/j.atmosenv.2015.10.053](https://doi.org/10.1016/j.atmosenv.2015.10.053), 2016.
- Zhang, Y., Yuan, Q., Huang, D., and Kong, S.: Direct Observations of Fine Primary Particles From Residential Coal Burning: Insights Into Their Morphology, Composition, and Hygroscopicity, *Journal of Geophysical Research*, 123, 12964–12979, 2018.
- Zhao, X. J., Zhao, P. S., Xu, J., Meng, W., Pu, W. W., Dong, F., . . . Shi, Q. F.: Analysis of a winter regional haze event and its formation mechanism in the North China Plain, *Atmospheric Chemistry and Physics*, 13(11), 5685-5696, <https://doi.org/10.5194/acp-13-5685-2013>, 2013.
- Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., . . . Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China, *Atmospheric Chemistry and Physics*, 15(4), 2031-2049, <https://doi.org/10.5194/acp-15-2031-2015>, 2015.
- Zheng M., Zhang Y., Yan C., et al.: Establishment of PM<sub>2.5</sub> industrial source profile in Shanghai, *China Environmental Science*, 33(8), 1354-1359, <https://doi.org/10.3969/j.issn.1000-6923.2013.08.002>, 2013.
- Zhu, X., Tang, G., Hu, B., Wang, L., Xin, J., & Zhang, J., et al.: Regional pollution and its formation mechanism over north China plain: a case study with ceilometer observations and model simulations, *Journal of Geophysical Research Atmospheres*, 121(24), 14574-14588, <https://doi.org/10.1002/2016jd025730>, 2016.

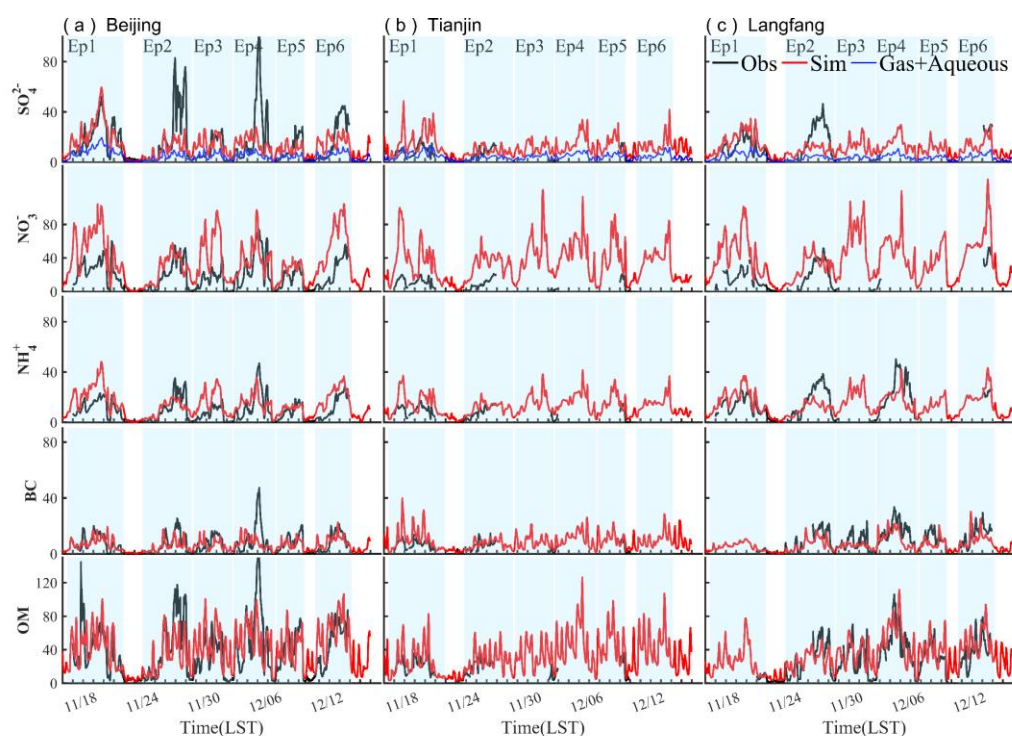
## Figures



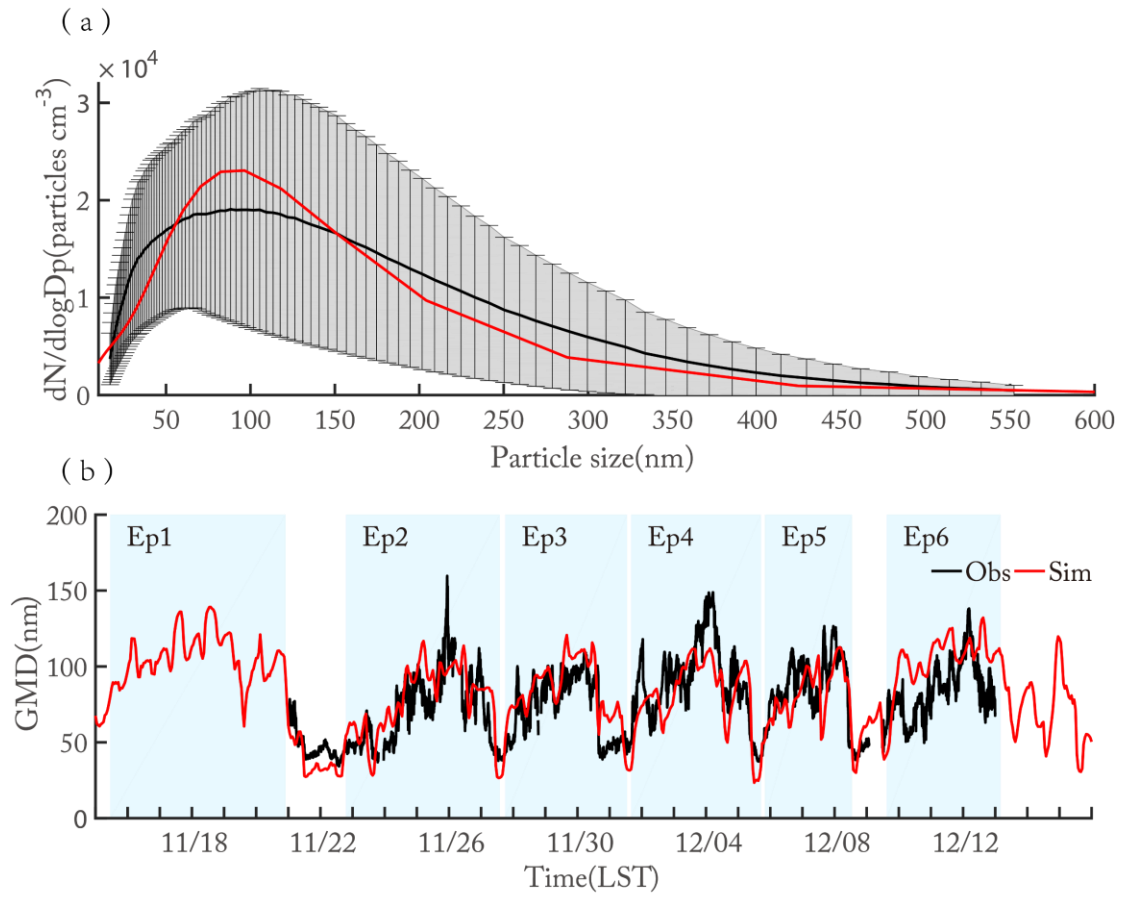
**Figure 1.** (a) Simulation domains. (b) Primary  $\text{PM}_{2.5}$  emission rates of the innermost domain and locations of observation sites (black dots). (c) tracer tagging regions which are described in Table 1.



**Figure 2.** Comparison between the simulated and observed hourly concentrations of  $PM_{2.5}$  for different sites. Black lines refer to observation and the red lines are simulation results; light blue shadows are six episodes identified; green lines mean  $75 \mu g m^{-3}$ , as a criterion judging whether pollution or not.

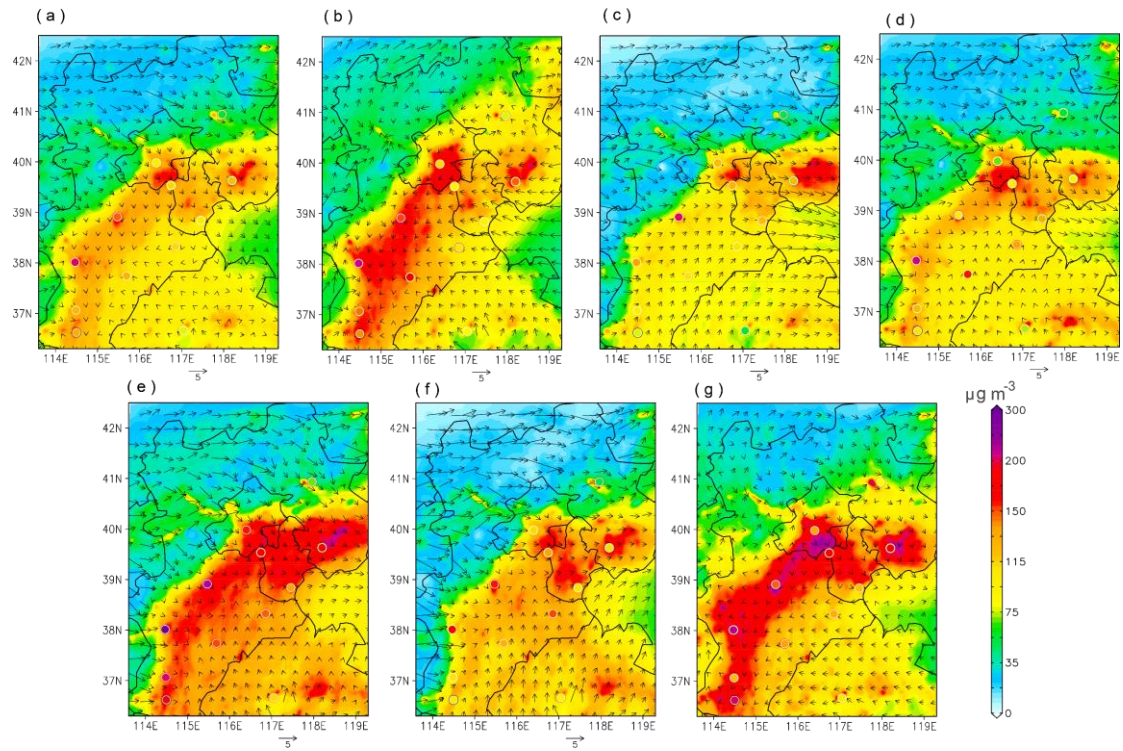


**Figure 3.** Comparison between the simulated (red) and observed (solid black) hourly components including sulfate, nitrate, ammonia, black carbon and organic aerosols at (a) Beijing, (b) Tianjin and (c) Langfang. Blue lines refer to sulfate produced by gas and aqueous chemistry reactions.

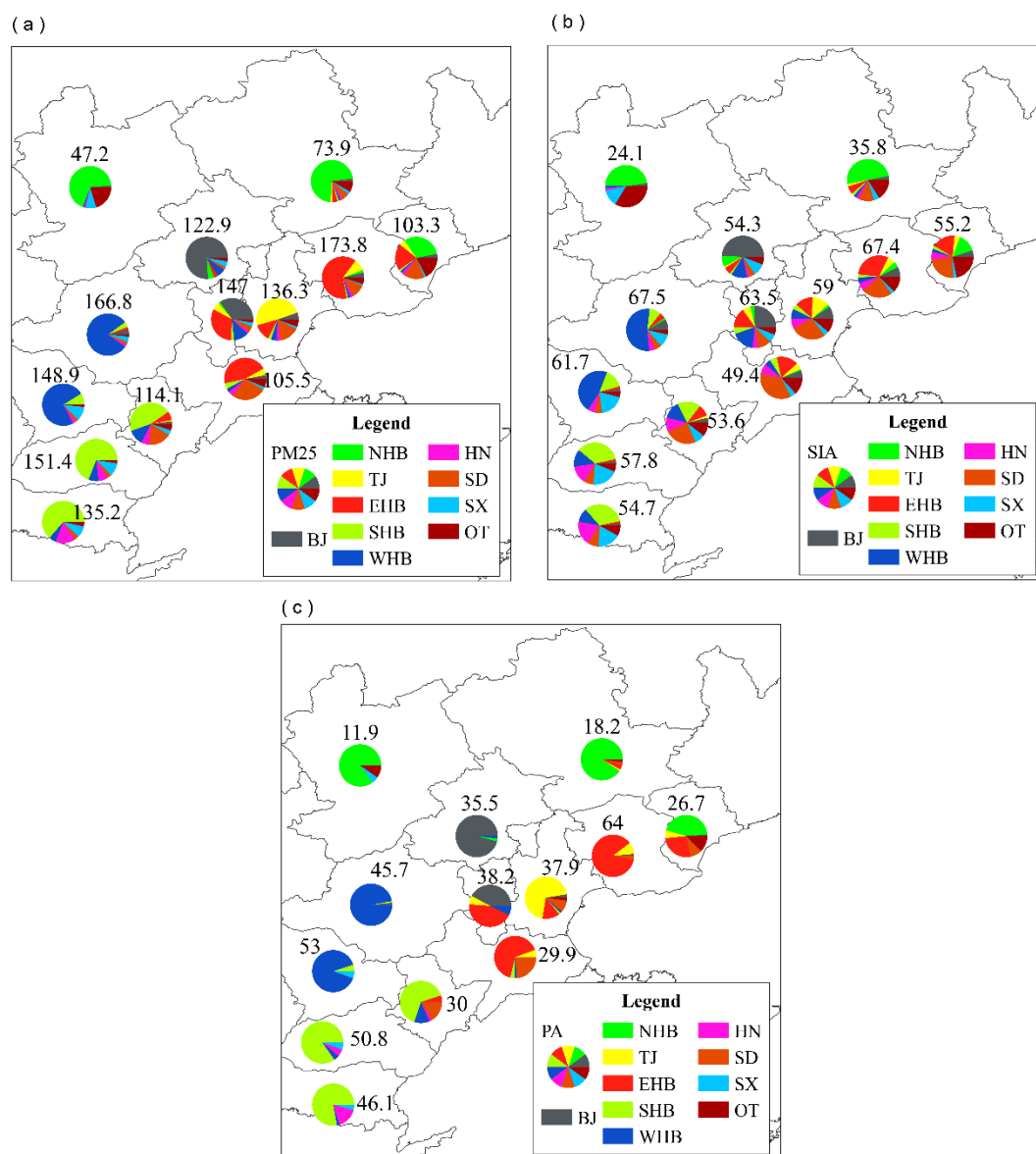


**Figure 4.** (a) Particle size distribution in Beijing at ground level. (b) Comparison of geometric mean diameter (GMD) for particles during range of 16–600nm between observation and simulation in Beijing. Black solid line and red solid line represent observation and simulation respectively.

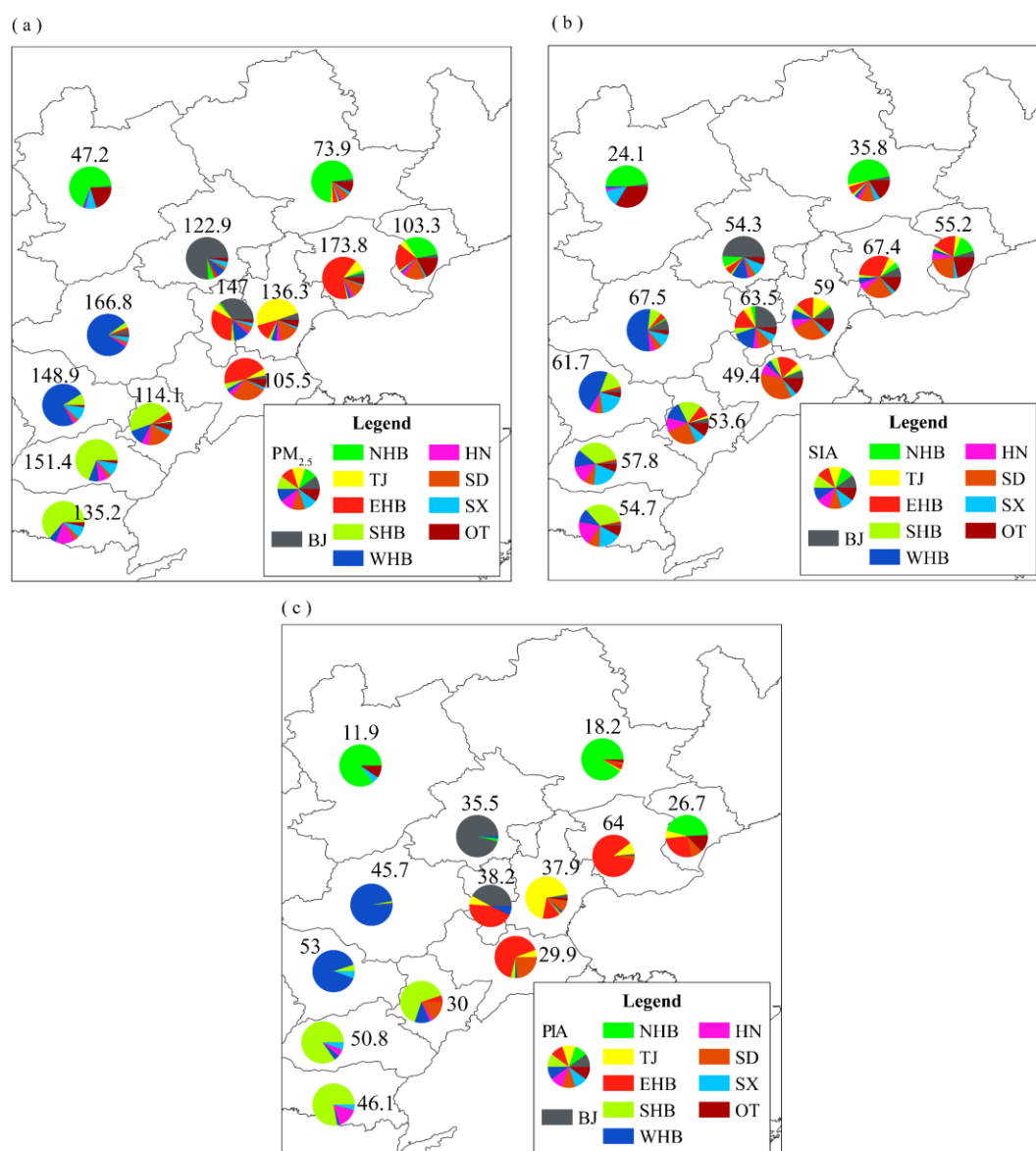




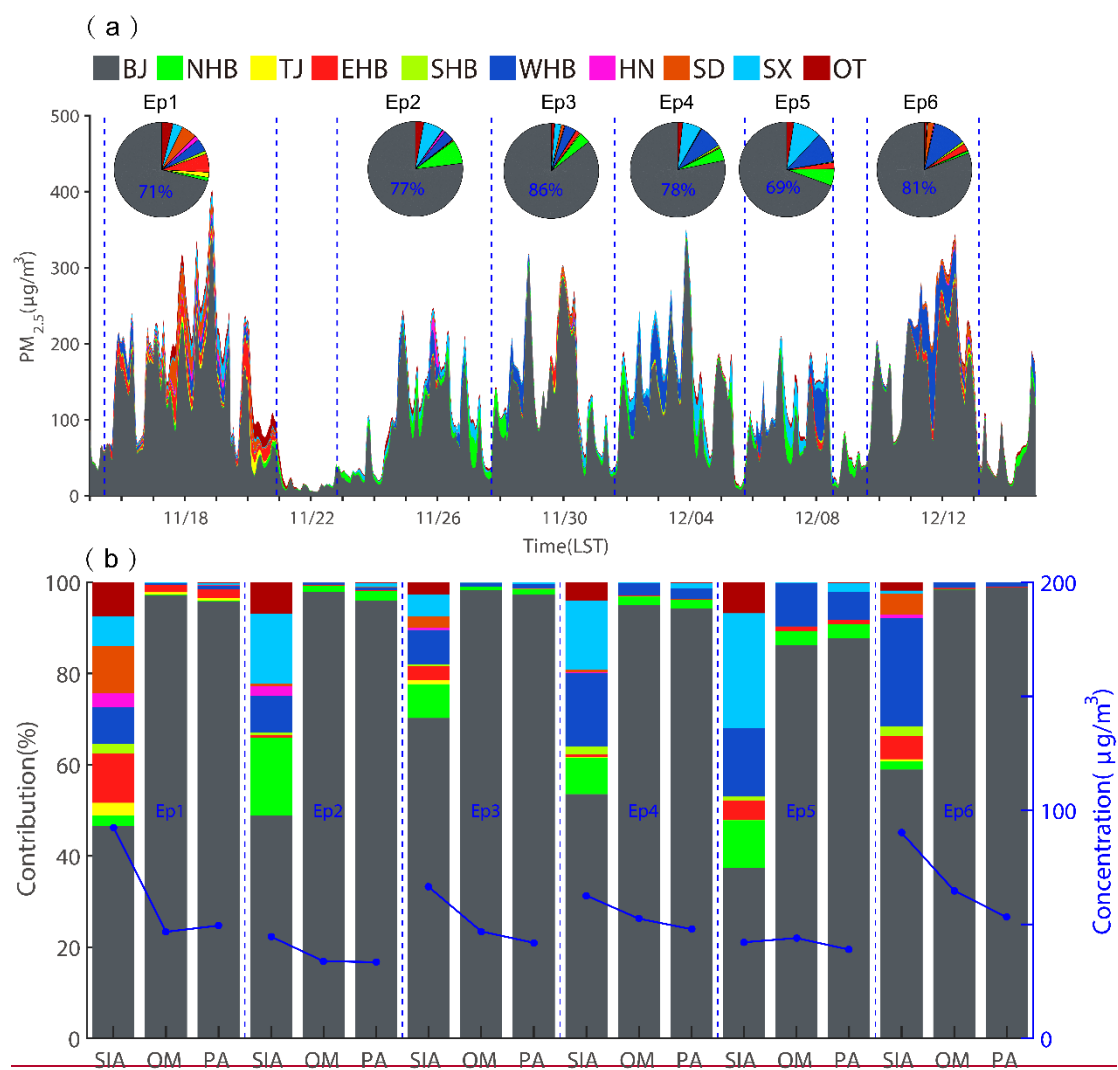
**Figure 5.** Spatial distribution of simulated average surface PM<sub>2.5</sub> ( $\mu\text{g m}^{-3}$ ) and wind ( $\text{m s}^{-1}$ ) over BTH area. (a) average of the whole study period, (b)–(g) episode average of episode1–6 identified before. Solid circles represent observations with the same color bar with simulations.



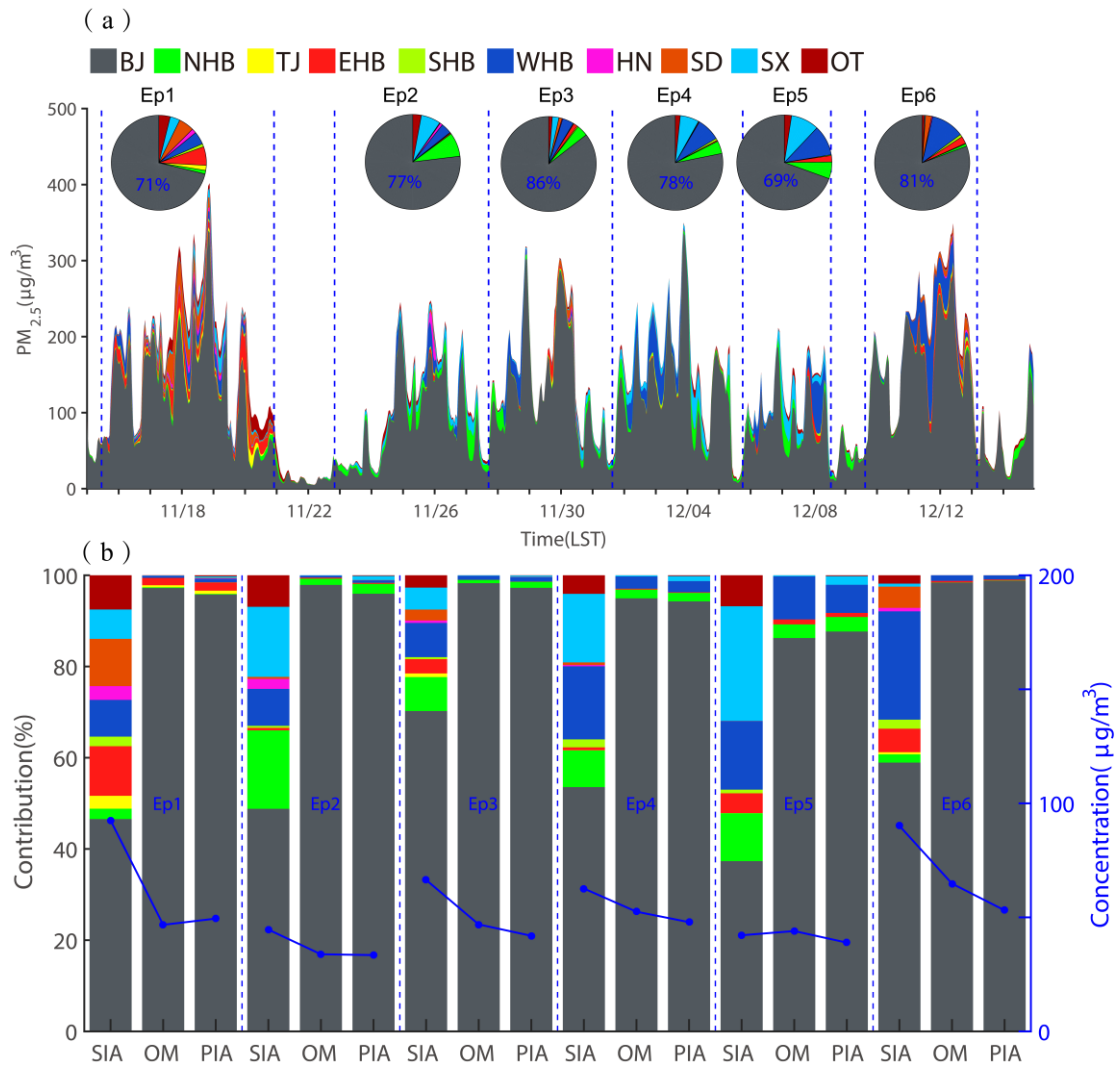




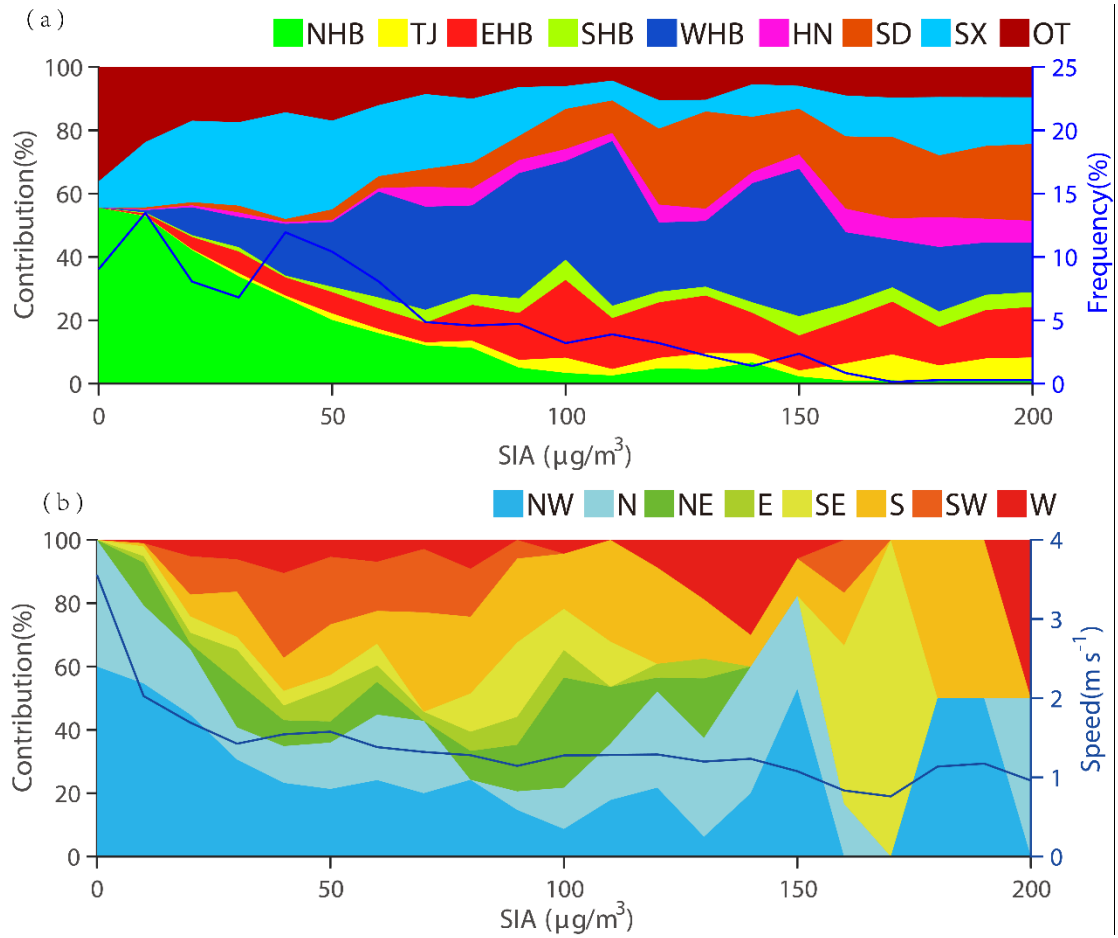
**Figure 6.** The contribution of regional transport and local emissions to the average (a) total  $\text{PM}_{2.5}$ , (b) secondary inorganic aerosols (SIA), (c) primary inorganic aerosols (PIA, including BC and primary inorganic  $\text{PM}_{2.5}$ ) over BTH area. The numbers above the pie represent average concentrations ( $\mu\text{g m}^{-3}$ ) of certain species in certain cities.



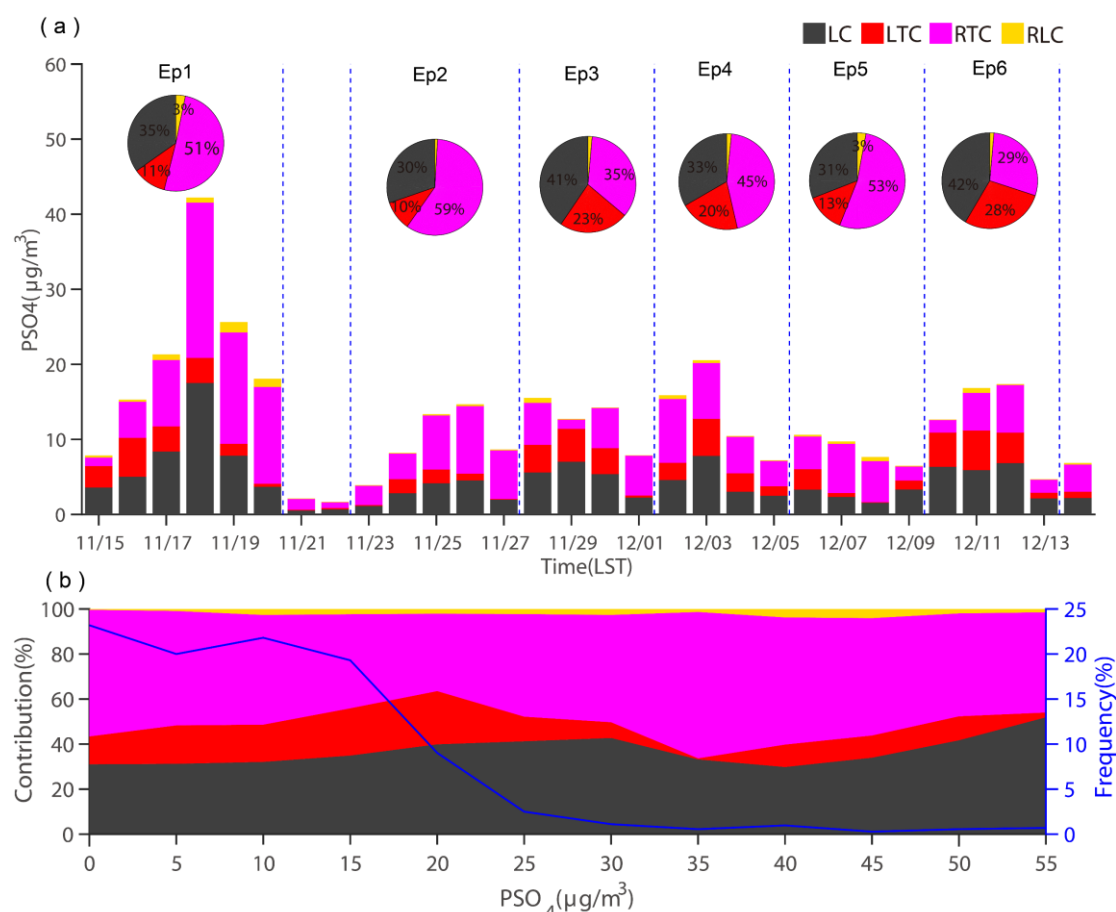
875



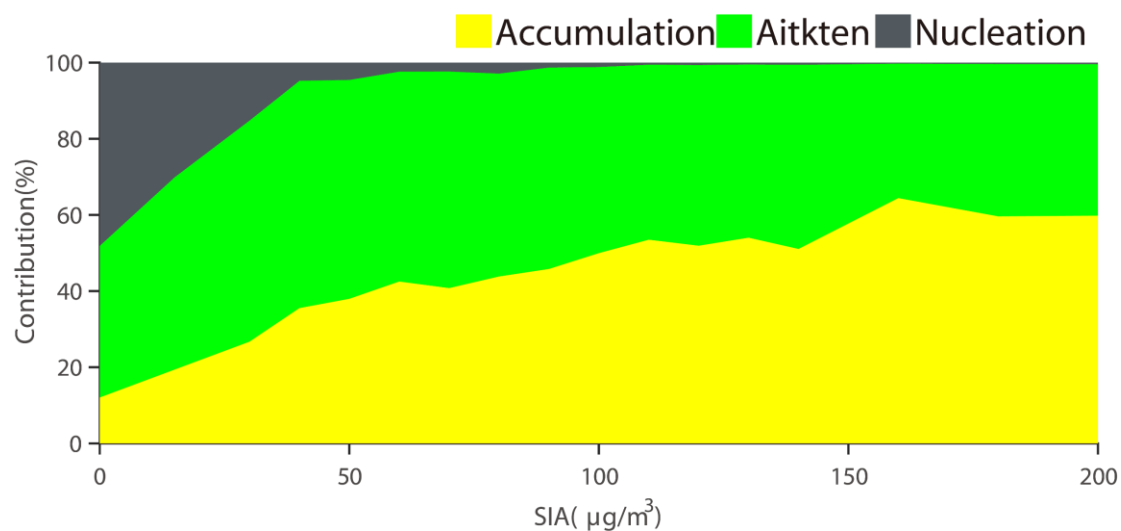
**Figure 7.** (a) Source contribution of  $PM_{2.5}$  in Beijing and pies represent average status of each episode; (b) Relative contribution of different regions to SIA, OM and PIA in Beijing at the surface layer during each episode (shaded). Concentrations are also shown (blue line).



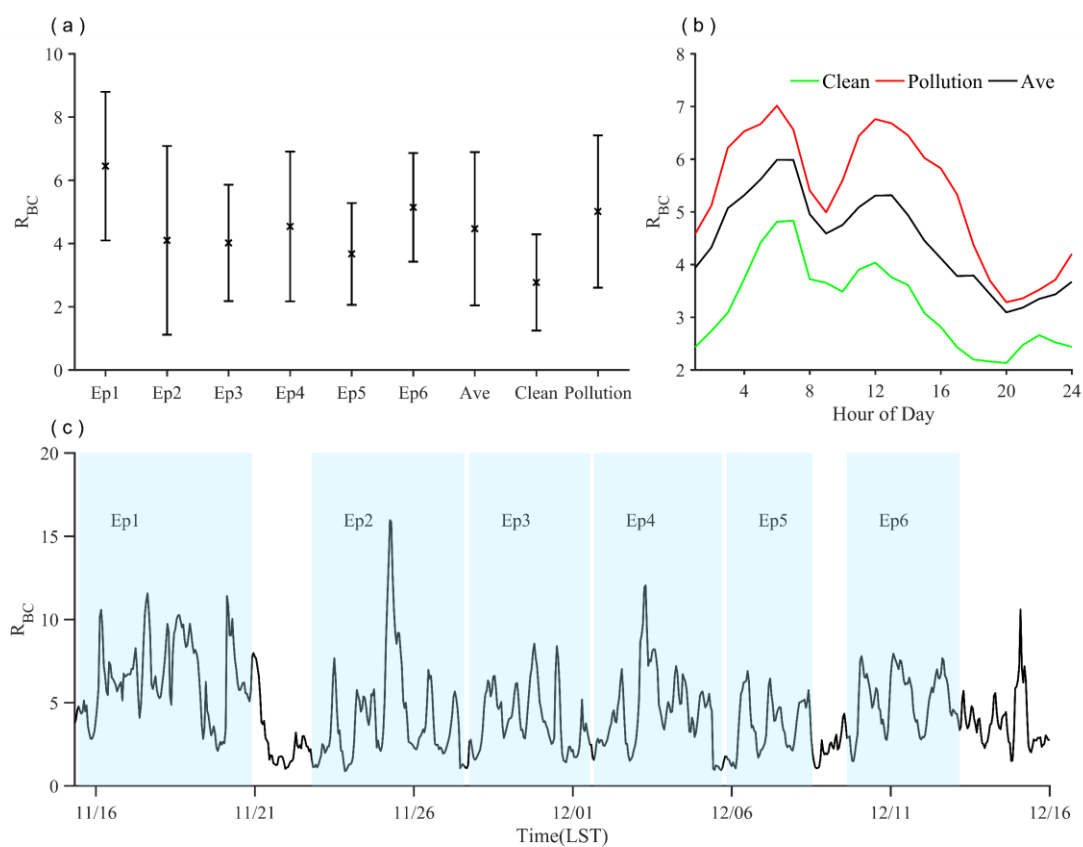
**Figure 8.** (a) Relative contribution of regionally transported SIA under different pollution levels in Beijing during the whole study period; (b) Variation of wind directions under different pollution levels in Beijing during the whole study period.



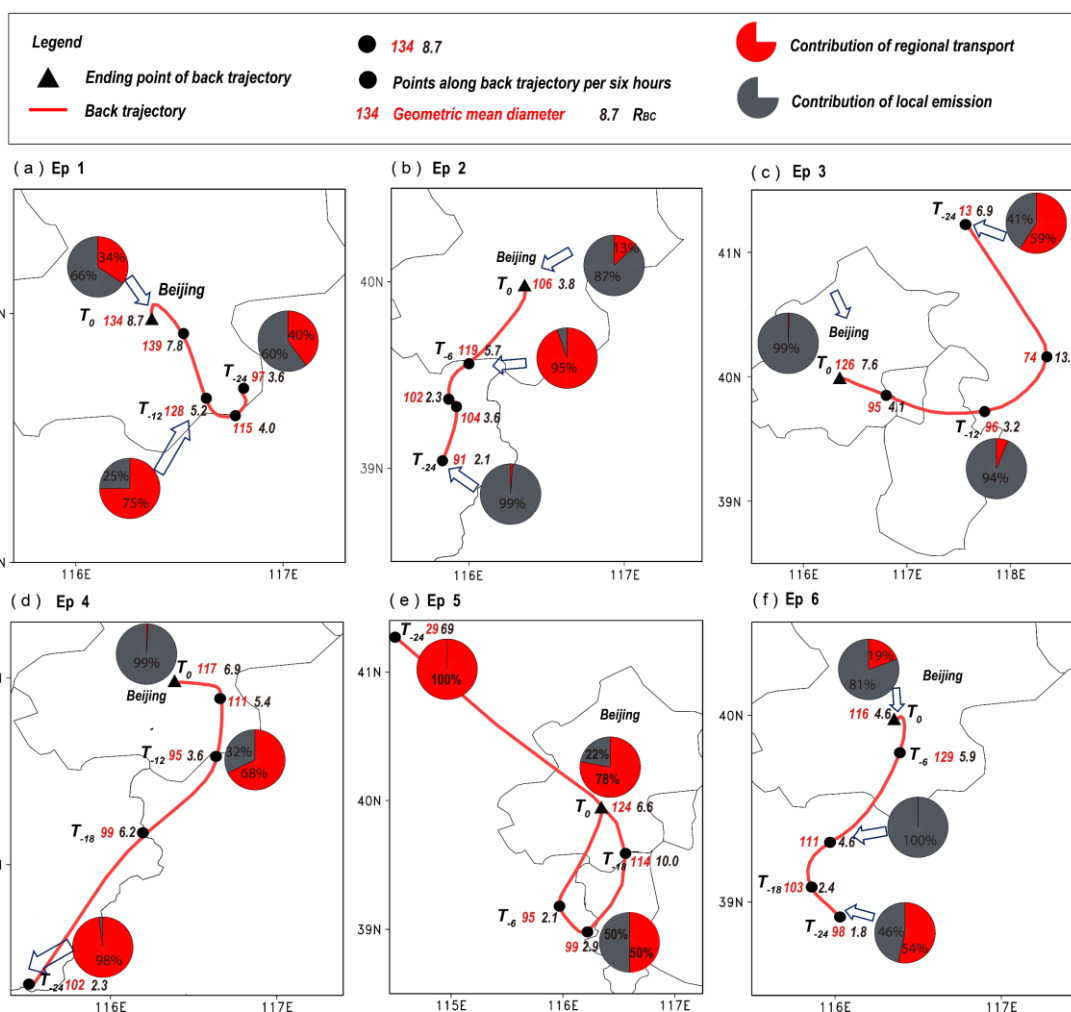
**Figure 9.** (a) Sources of secondary sulfate in Beijing. (b) Variation of secondary sulfate sources with surface sulfate concentration in Beijing for the whole study period. LC means sulfate locally produced from Beijing emitted  $\text{SO}_2$ ; LTC refers to sulfate chemically formed in regions except Beijing from the Beijing emitted  $\text{SO}_2$ ; RTC is sulfate chemically formed in the transport pathway to Beijing from  $\text{SO}_2$  emitted in source regions except Beijing; RLC is sulfate produced in regions except Beijing from locally emitted  $\text{SO}_2$  and transported to Beijing.



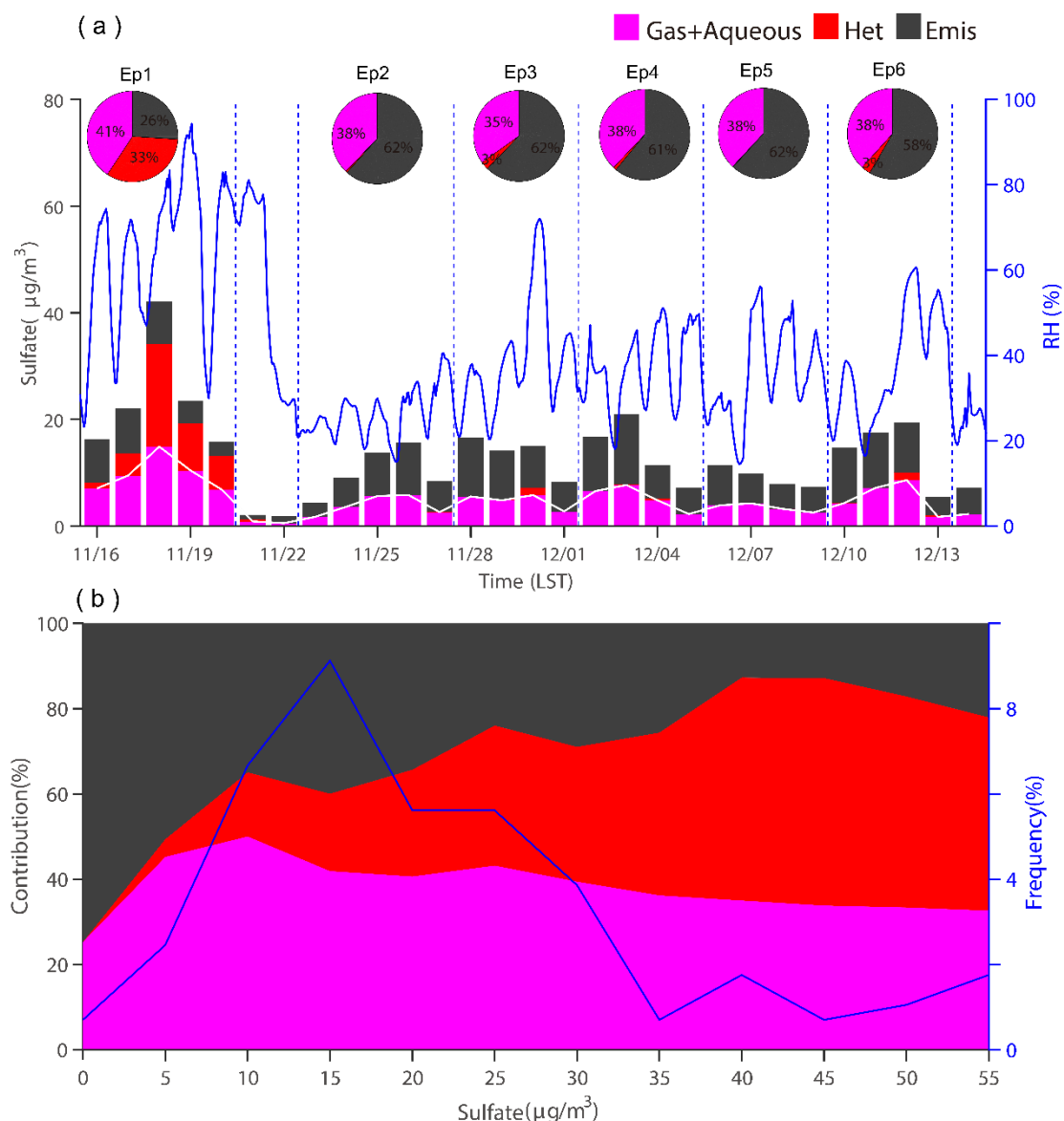
**Figure 10.** Variation of number concentration fraction of particles with SIA in Beijing during whole study period.



**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.



**Figure 12.** Variation of aerosol properties along transport. Panel a–f refers to episode 1–6. The red lines refer to 24 h backward trajectories at the altitude of 100 m. Aerosol properties include geometric mean diameter (GMD [nm], red numbers beside the solid blocks), mass ratio of coating to BC ( $R_{BC}$ , the black numbers beside the solid blocks, an indicator of aging degree), region source of BC (pies, the red represents regional transport and the gray is the local contribution). Solid black triangles are ending points of back trajectories, called  $T_0$ . Solid black circles are points along trajectories per six hours.  $T_{-6}$ ,  $T_{-12}$ ,  $T_{-18}$ ,  $T_{-24}$  mean 6, 12, 18, 24 hours before arriving at ending site. Ending times of back trajectories are before pollution peaks 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 and 22:00 on December 11 (LST), respectively.



**Figure 13.** Contribution of different formation ways to sulfate 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 formation pathways of sulphate during Ep1.

## Tables

**Table 1.** Source-tagging regions and primary PM<sub>2.5</sub> emissions during 15 November–15 December, 2016 in this study. <sup>a</sup>

Regions	Descriptions	Area 10 <sup>3</sup> km <sup>2</sup>	Population 10 <sup>6</sup>	GDP <sup>b</sup> (10 <sup>12</sup> CNY)	Emission <sup>c</sup> (10 <sup>9</sup> g)
BJ	Beijing	16.4	21.7	2.5	3.6
TJ	Tianjin	11.9	15.6	1.8	3.9



	NHB	Chengde, Zhangjiakou and Qinhuangdao	84.1	11.6	0.4	3.6
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				

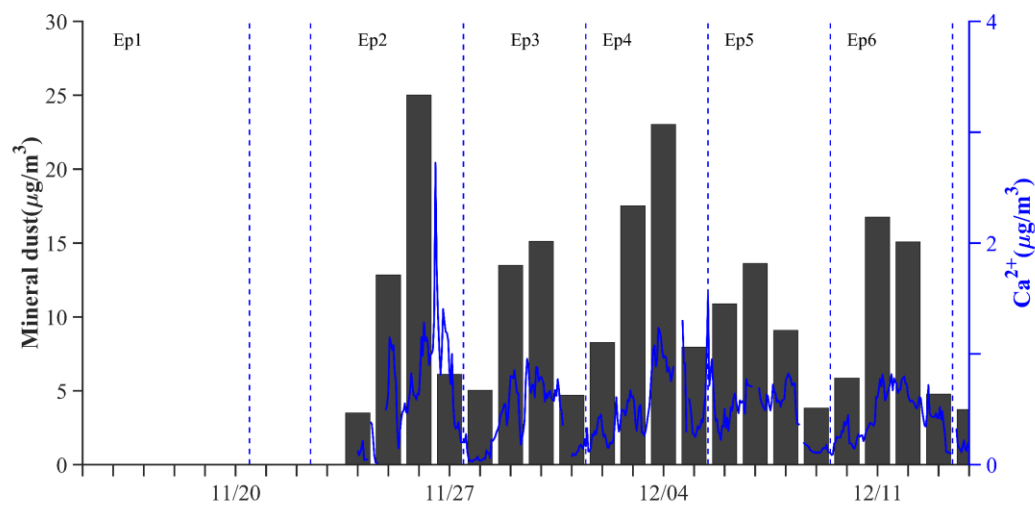
923 <sup>a</sup> Regions are shown in Fig. 1c.

924 <sup>b</sup> GDP unit in 2016 is Chinese Yuan (CNY) (<http://www.tjcn.org/tjgb/>).

925 <sup>c</sup> PM<sub>2.5</sub> emissions data are obtained from the 2016 Multi-resolution Emission Inventory for China

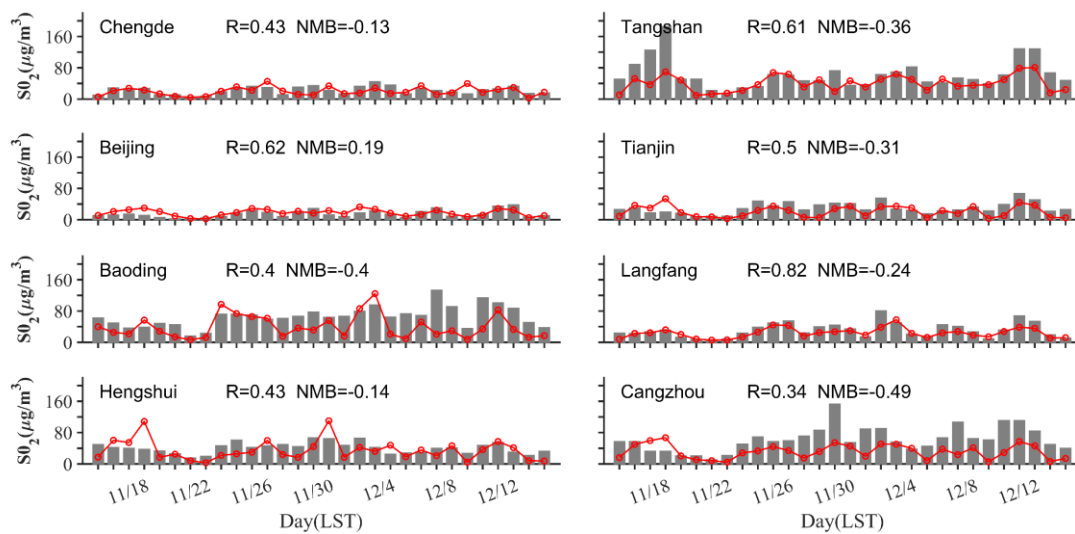
926 (MEIC) with 0.25° × 0.25° resolution.

# 1 Supplements

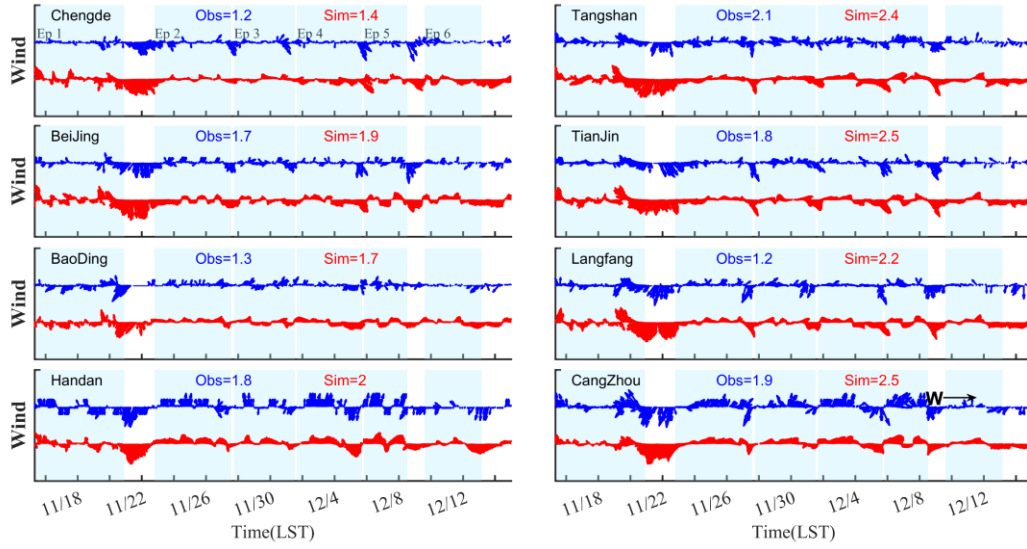


**Figure S1.** Concentration of mineral dust and  $\text{Ca}^{2+}$  in  $\text{PM}_{2.5}$  during the study period.

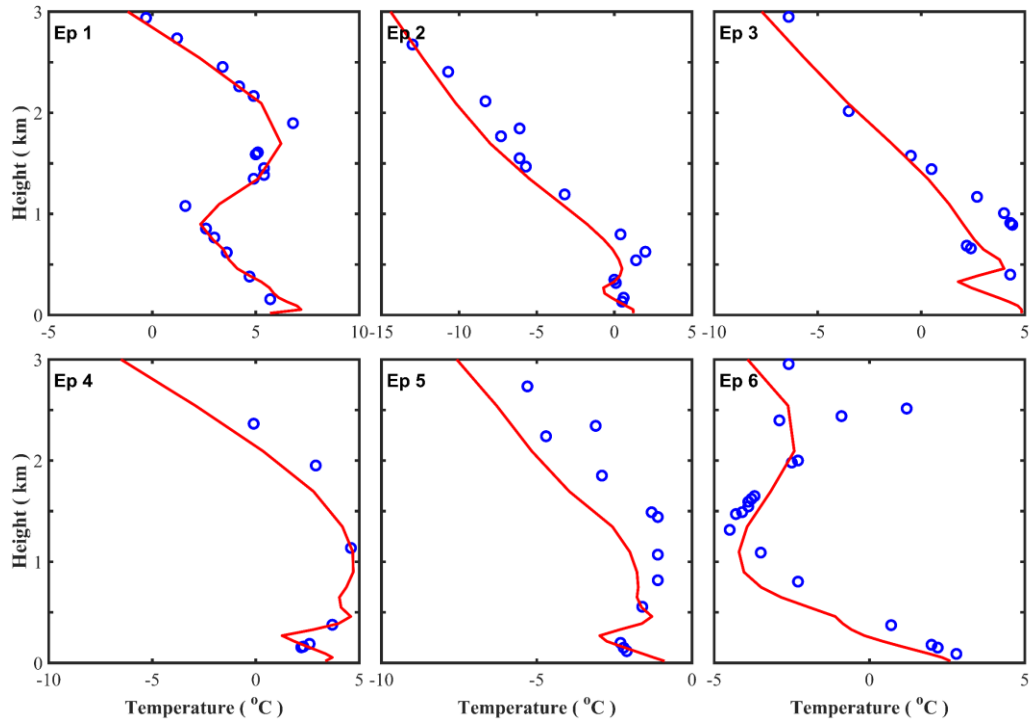
And  $\text{Mineral} = 2.2 \times [\text{Al}] + 2.49 \times [\text{Si}] + 1.63 \times [\text{Ca}] + 2.42 \times [\text{Fe}] + 1.94 \times [\text{Ti}]$ .



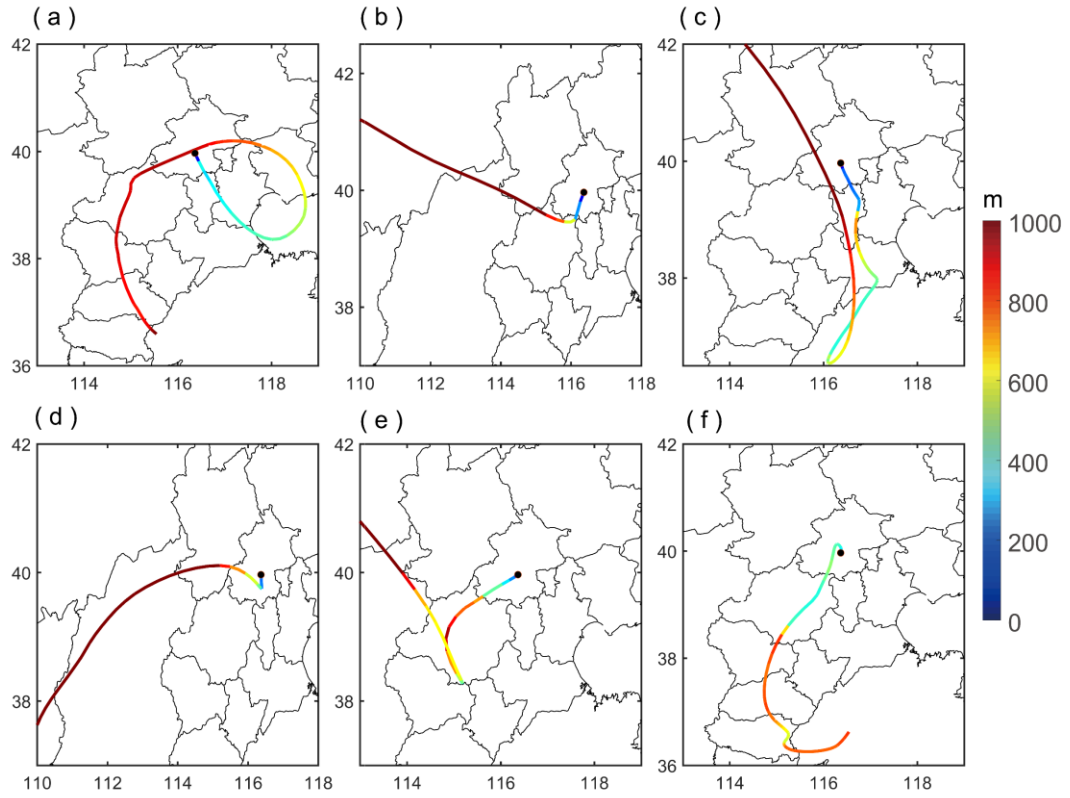
**Figure S2.** Comparison between the simulated (red) and observed (gray bars) daily concentrations of  $\text{SO}_2$ .



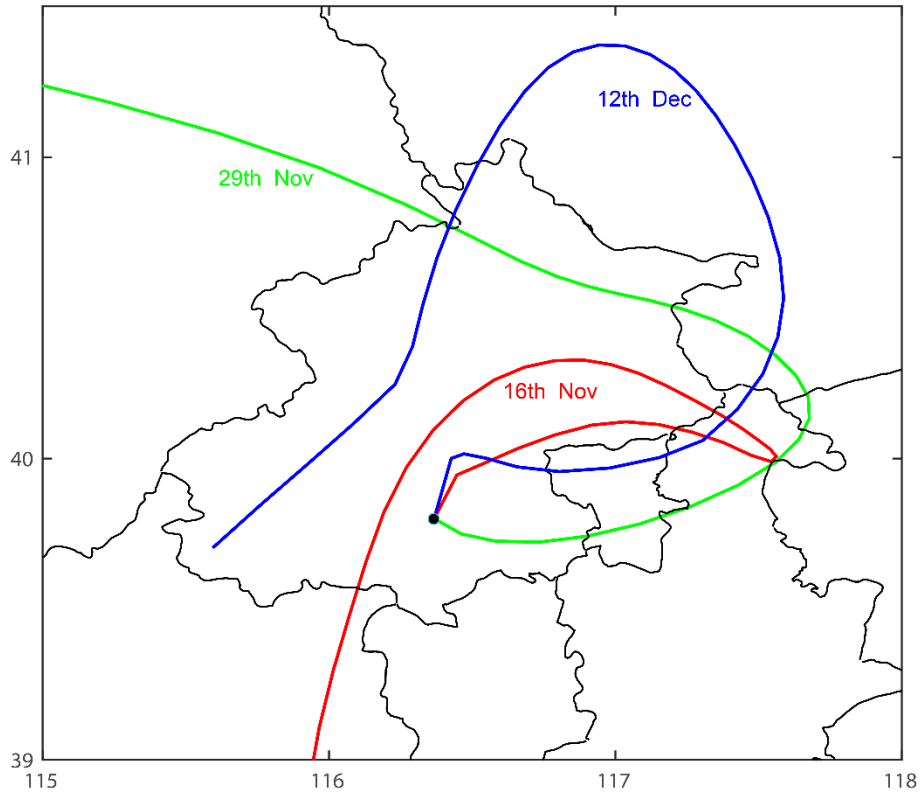
**Figure S3.** Comparison between simulated (red) and observed (blue) wind vector and wind speeds (data) at cities of BTH.



**Figure S4.** Comparison between simulated (red solid line) and observed (blue dot) temperature profiles during episodes in Beijing.



**Figure S5.** 72 h backward trajectories during different episodes (05:00 on November 20, 18:00 on November 26, 23:00 on November 29, 20:00 on December 03, 05:00 on December 08 and 11:00 on December 12 [LST]) at Beijing at 100m. Line color represents height of trajectories. a-f refer to Ep1-6.



**Figure S6.** 36 h backward trajectories at different start time (02:00 on November 17, 11:00 on November 29, and 23:00 on December 12 [LST]) at Beijing.

**Table S1.** Statistics performances of meteorological simulations, including temperature and relative humidity at 2 m, and wind speed at 10 m. Statistical parameters include correlation coefficient (R), Normalized Mean Bias (NMB) and Root Mean Squared Error (RMSE).

		Obs	Sim	NMB	R	RMSE
<b>T2(K)</b>	Beijing	2.42	3.31	0.37	0.88	2.11
	Tianjin	4.05	3.73	-0.08	0.93	1.48
	Langfang	2.13	3.06	0.44	0.89	2.13
	Chengde	-3.39	-1.66	-0.51	0.89	3.31
<b>RH2(%)</b>	Beijing	53.93	39.53	-0.27	0.69	21.87
	Tianjin	56.95	47.58	-0.16	0.73	18.09
	Langfang	60.39	46.54	-0.23	0.71	21.54

<b>WS10(m/s)</b>	Chengde	61.56	55.96	-0.09	0.47	20.26
	Beijing	1.68	1.93	0.15	0.65	1.30
	Tianjin	1.76	2.46	0.39	0.70	1.50
	Langfang	1.23	2.15	0.74	0.57	1.56
	Chengde	1.16	1.41	0.21	0.63	1.22

26

27 **Table S2.** Aerosol properties along transport, including geometric mean diameter  
28 (GMD [nm]), mass ratio of coating to BC ( $R_{BC}$ ), number concentration (N) and  
29 contribution of region source to BC (Cr [%]).  $T_0$  means ending points of back  
30 trajectories and  $T_n$  means n hours before arriving at the ending point.

Period	Property	$T_{-24}$	$T_{-18}$	$T_{-12}$	$T_{-6}$	$T_0$
<b>Ep1</b>	$R_{BC}$	3.6	4.0	5.2	7.8	8.7
	GMD	97	115	128	139	134
	N	28994	15494	15204	15592	19242
	Cr	40	93	75	7	34
<b>Ep2</b>	$R_{BC}$	2.1	3.6	2.3	5.7	3.8
	GMD	91	104	102	119	106
	N	23909	15189	17961	10994	20121
	Cr	1.2	0.14	0.01	95	13
<b>Ep3</b>	$R_{BC}$	6.9	13.2	3.2	4.1	7.6
	GMD	13	74	96	95	126
	N	22234	11880	13481	14241	12945
	Cr	59	81.4	6.2	8.8	1
<b>Ep4</b>	$R_{BC}$	2.3	6.2	3.6	5.4	6.9
	GMD	102	98	95	111	117
	N	19754	12805	21116	10536	17199
	Cr	98	56	68	25	1
<b>Ep5</b>	$R_{BC}$	69	10.0	2.9	2.1	6.6
	GMD	29	114	99	95	124
	N	8617	8086	16494	28211	13696
	Cr	100	100	50	4	78
<b>Ep6</b>	$R_{BC}$	1.8	2.4	4.6	5.9	4.6
	GMD	98	103	111	129	116
	N	31691	23691	17885	12897	21955
	Cr	54	0.17	0.01	65	19

31