

We thank the referees' valuable comments and suggestions on the improving the scientific significance of this work. Here, we attempt to further explore this research topic by discussing the impact of emission uncertainty on aerosol and aerosol radiative effect (ADRE) over eastern China in the last decade, missing sources of aerosol mass in the winter, and the observed seasonality of sulfate aerosol concentration. Here are some discussions:

**Responds to Referee #1's comments:**

**Referee: "China SO<sub>2</sub> emission has been declined since 2006 while NO<sub>x</sub> and NH<sub>3</sub> have been increasing. What's the change in aerosol radiative forcing over China in the decade as the change in emission structure? Is it significantly different from the simulation uncertainty as using the different emissions of MEIC and IPCC AR5?"**

The referee raised an important question. We rely on climate models to estimate the historical and future changes of ADRE. However, the uncertainty of aerosol emissions used in the climate models could add another dimension of uncertainty in simulating the change of aerosol radiative effect. As mentioned by the referee, the emission structure changed in China during the last decade (2006-2015). The emission of SO<sub>2</sub> decreased by 9.2% from 34.0 Tg in 2006 to 30.8 Tg in 2010 (-2.4% annual growth rate) (Lu et al., 2011). The NH<sub>3</sub> emission decreased slightly from 10.5 Tg in 2006 to 9.7 Tg in 2012 with an annual rate of 1.4% (Kang et al., 2016). Meanwhile, some researches show that the emissions of BC, OC, and NO<sub>x</sub> have been increasing since 2006. The BC/OC emissions increase from 1.6 Tg/3.6Tg in 2004 to 1.9 Tg/4.0 Tg in 2010, with an annual growth rate of 2.8%/1.7%. The MEIC developer team estimates that the emission of BC/OC decreased from 2006 to 2010 due to reduced emissions in the domestic and transportation sectors. The NO<sub>x</sub> emission grew by 113.9% from 12.2 Tg in 2000 to 26.1 Tg in 2010, with an annual growth rate of 7.9% from 2000-2010 (Zhao et al., 2010).

To examine the change in the ADRE as the change in the emission structure, we carry out a simulation using MEIC emission from 2002 to 2012. We choose these 11

years because China's economy recovered from a depression in 2002, and since then the SO<sub>2</sub> emission has started to grow dramatically and has been decreasing after 2006 due to the application of desulfurization equipment. After 2012 the annual emission rates do not change as dramatically as the previous years. To separate from the impact of decadal variation of meteorological variations, we use the reanalysis wind in 2009 to nudge the model meteorological fields (winds, temperature, and etc.) towards the "constrained meteorology" for this simulation. In this way, the change of aerosol concentration is controlled by the change of emission alone since the meteorological fields are identical among the years.

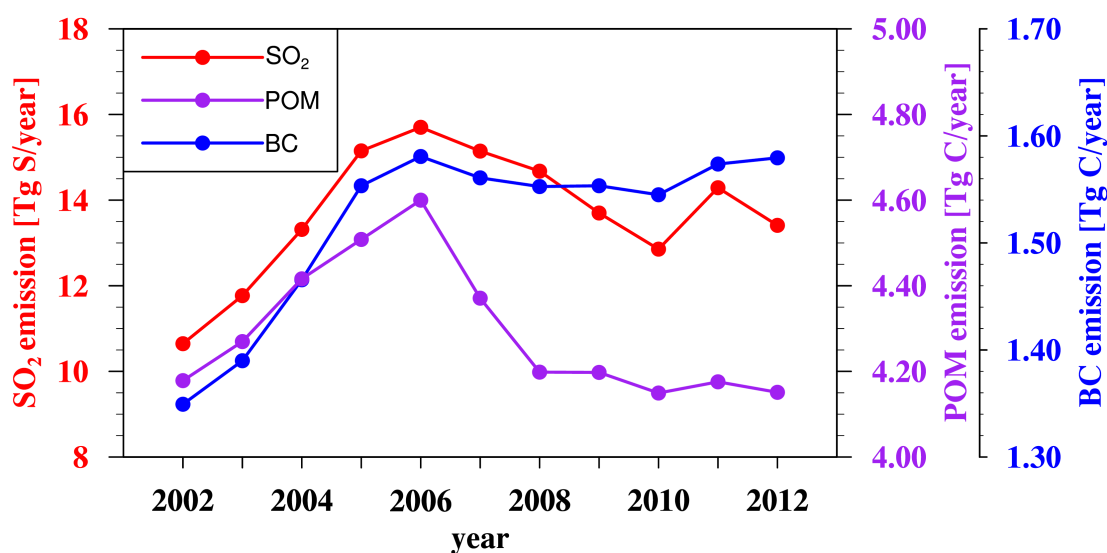


Figure S1. The change of emission rates of SO<sub>2</sub>, BC, and OC from year 2002 to 2012 in eastern China.

Figure S1 shows the MEIC 's SO<sub>2</sub>, BC, and OC emission trends from 2002 to 2012 in eastern China. Since the spatially-gridded MEIC emission data are only available for 2008, 2010, and 2012, we scale the spatial distribution and seasonal variation of other years during the period to the 2008 gridded emission with the annual emissions. Each species in different sectors (power, energy, residential, and transportation) has a different scaling factor. The annual emission rates are estimated by the MEIC developer team. The annual trends are consistent with other researches (Lu et al., 2011; Lei et al., 2009) although the absolute values are different. We use

the MEIC estimations because their fuel usage is based on China Energy Statistical Yearbook (CESY) as this dataset is based on the same algorithm as the gridded MEIC emission data that we used for 2009.

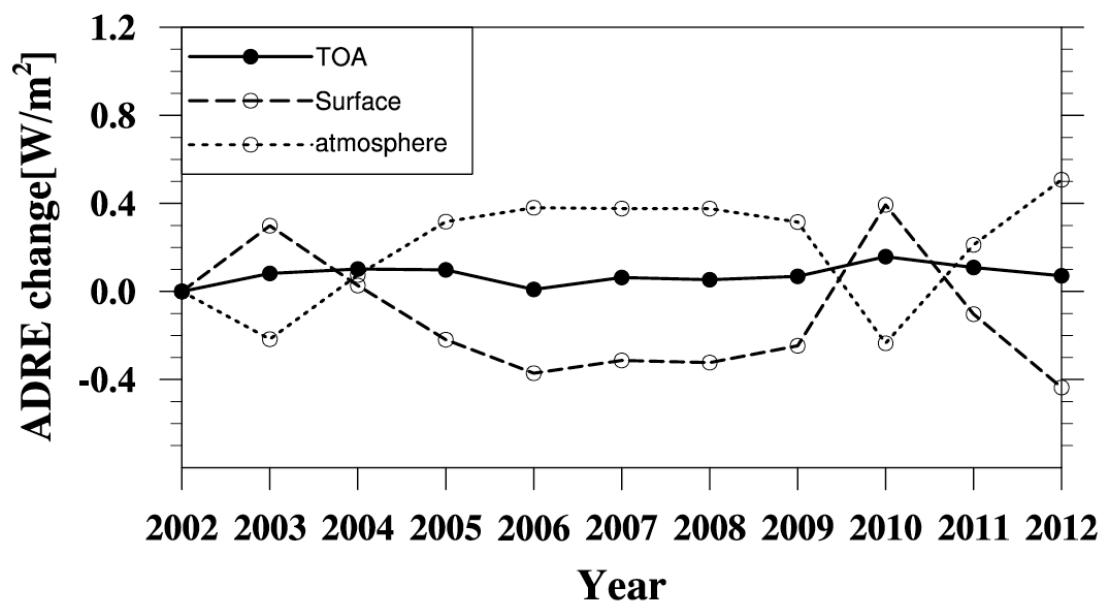


Figure S2. The change of ADREs at TOA, surface and in the atmosphere relative to year 2002 with MEIC emission in eastern China.

Figure S2 shows that the change of the ADREs from 2002 to 2012 relative to those in 2002 are 0.01~0.16 W/m<sup>2</sup>, -0.44~0.39 W/m<sup>2</sup>, and -0.23~0.51 W/m<sup>2</sup> at TOA, surface and in the atmosphere, respectively. The decadal trend of ADRE agrees with the trend of emissions as shown in Figure S1. The warming in the atmosphere and the cooling at the surface enhanced with the increase of emissions of SO<sub>2</sub>, BC, and POM from 2003 to 2006. The ADRE at TOA increases slightly indicating more energy retains in the atmosphere-earth system. From 2006 to 2009, the changes of ADREs are not significant due to the stabilized emission of BC. Since 2010, the warming in the atmosphere and the cooling at the surface increases due to the increase emission of SO<sub>2</sub> and BC. The changes of ADREs at surface and in the atmosphere from 2002 to 2003 may reflect the complicated interactions between sulfate and BC/OC in East China, enhancing the BC/OC wet scavenging due to sulfate coating.

Compare with the difference between the ADREs simulated by MEIC and AR5

emission inventories in 2009, which is  $-0.19 \text{ W/m}^2$ ,  $-2.42 \text{ W/m}^2$ ,  $2.23 \text{ W/m}^2$  at TOA, surface and in the atmosphere, respectively, the decadal change of ADRE at TOA is comparable to the uncertainty range introduced by the emission inventories. The decadal changes of ADRE at surface and in the atmosphere are smaller than the uncertainties by using the two different emissions. So as to answer the question by the referee, the change of ADRE at TOA in eastern China due to the change of emission structure is not significantly different than the difference estimation of the emission, although the magnitude of changes at surface and in the atmosphere is smaller. It highlights the uncertainty of the emission inventories and the need of constraining the emission inventories of aerosol and precursors by in-situ and satellite observations.

**Referee: “Secondly, there are large model biases in winter which cannot be explained by emissions alone and the author has no discussion. ... The model bias should be further discussed, and the implications to the conclusion should be mentioned.**

**Thirdly, the observations in Figure 9 are susceptible. The observations show minimum winter sulfate in northern China cities, which is totally opposite to the general recognition that aerosols are higher in winter than in summer. An explanation is required.”**

The second and the third comments are about the seasonal variations of simulated aerosol concentrations, so we respond to the two comments together. As shown in Figure S3, the emission of  $\text{SO}_2$  peaks in the winter in northern Chinese cities (Harbin, Chengde, Shangdianzi, Beijing, Tianjin, Shijiazhuang, and Zhengzhou) due to heating in the domestic sector. However, the modeled sulfate aerosol concentrations show their minimum in the winter (Figure 9), which is commonly seen for many climate models (personal communication with Prof. Liao Hong from Nanjing University of Information Science & Technology). Obviously, as mentioned by the referee, the surface concentration cannot be explained by emissions alone, and atmospheric physical and chemical processes are more responsible for the low bias. We examine the processes that determine the sulfate aerosol concentration in the model, including

gas-phase and aqueous-phase production, the dry removal and wet scavenging, as well as the controlling meteorological variables (Figure S3).

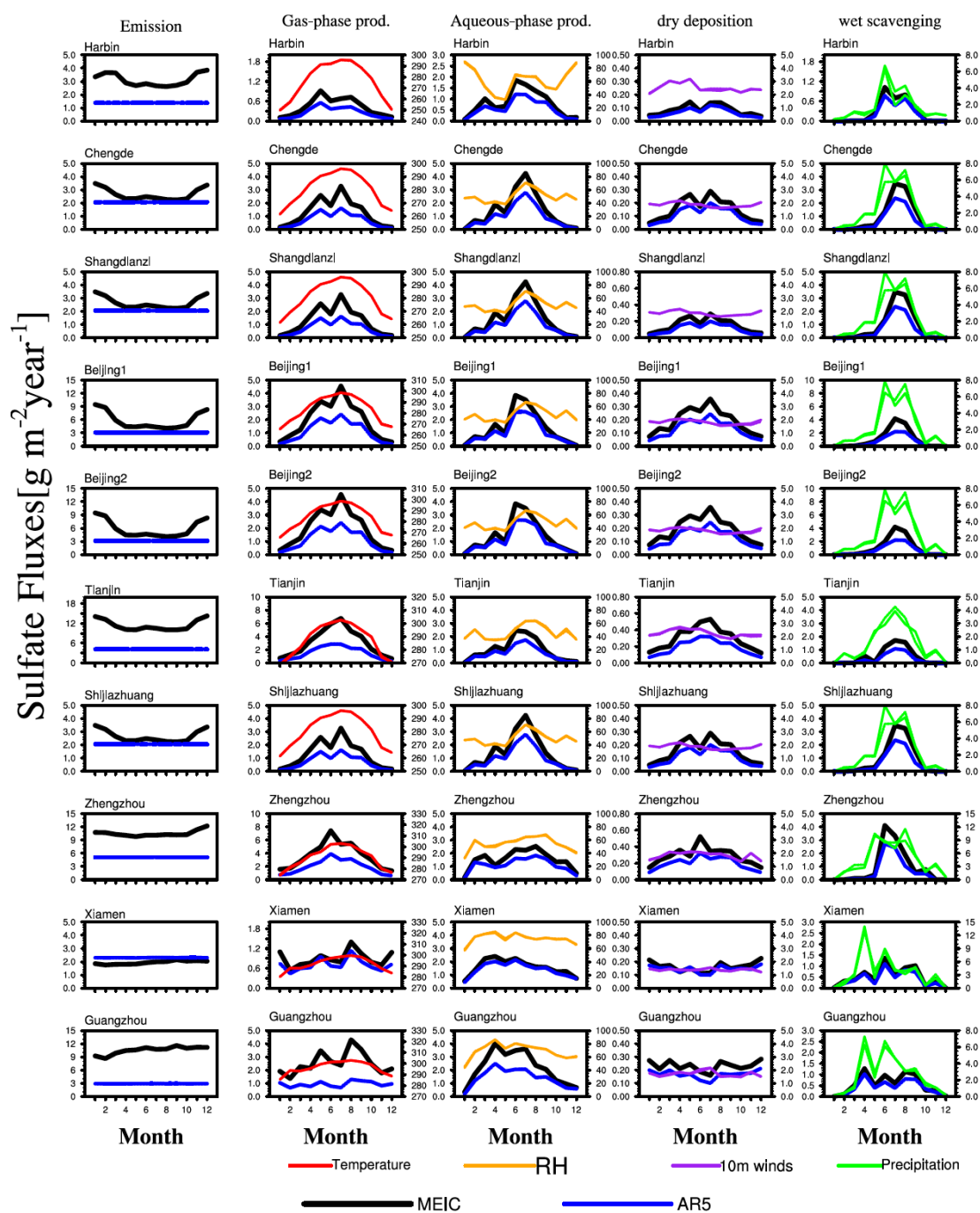


Figure S3. (From left to right columns): (1) SO<sub>2</sub> emission rates from MEIC (black) and AR5 (blue) inventories, (2) gas-phase chemistry production in the simulations by MEIC (black) and AR5 (blue) and the surface temperature (red), (3) aqueous-phase production rates (black and blue) and the relative humidity at surface (yellow), (4) dry

deposition rate (black and blue) and the 10-meter wind speed (purple), and (5) wet scavenging rate (black and blue) and the precipitation rate (green).

Figure S3 shows that the simulated seasonal variations of surface concentrations of sulfate aerosol are controlled by the gas-phase and aqueous-phase production processes, as opposed to the emission of SO<sub>2</sub>. Gas-phase chemistry is most active in the summer due to the temperature-dependence of the reaction rate in the photochemical oxidation of SO<sub>2</sub> by OH. The aqueous-phase formation of sulfate aerosol also peaks in the summer due to high relative humidity. Although the MEIC emission of SO<sub>2</sub> peak in the winter, both gas-phase and aqueous-phase oxidations are inefficient in the winter, which results in lower concentrations of sulfate aerosol than in the summer. The seasonal variation of modeled sulfate aerosol concentration is verified by some observations (Zhao et al., 2013; Zhang et al., 2013; Geng et al., 2013). However, observations from CAWNET (Zhang et al., 2012) show that sulfate aerosol in northern Chinese cities (Gucheng and Zhengzhou in Figure S4) peaks in the winter as opposed to summer in spite of a minor maximum in the summer.

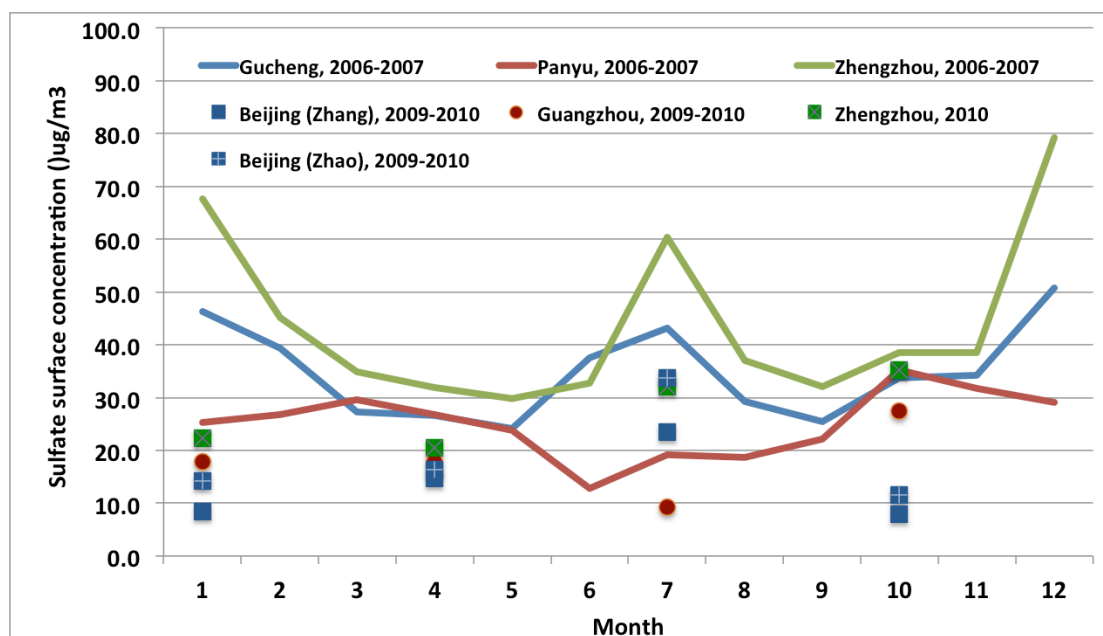


Figure S4. Seasonal variations of surface sulfate concentration at three locations (Gucheng, Panyu, and Zhengzhou) from CAWNET from 2006 to 2007. For

comparison, the observations near the three locations used in our study (Beijing, Guangzhou, Zhengzhou) from 2009 to 2010 are also shown in dots.

The contrasting result in observations could be due to different location and time. The difference between the simulated and the observed seasonal variations by the CAWNET may reveal that some mechanisms of sulfate aerosol formation in the winter over China are missing in the model. As indicated by the referee, “the importance of sulfate production through heterogeneous reactions of  $\text{SO}_2$  on deliquescence preexisting particles catalyzed by transition metal ions, which can increase  $\text{PM}_{2.5}$  concentrations and the mass fractions of secondary inorganic aerosols in the wintertime hazes of northern China (Wang et al. 2014; Huang et al., 2014; Zheng et al, 2015; Chen et al., 2016; Dong et al., 2016). The coexistence of  $\text{NO}_2$  and  $\text{SO}_2$  also promotes sulfate production (He et al., 2014; Wang et al., 2014)”. The aqueous-phase oxidation of  $\text{SO}_2$  by  $\text{NO}_2$  (Wang et al., 2016) or  $\text{O}_3$  (Palout et al., 2016) is efficient to form sulfate aerosol under high relative humidity and  $\text{NH}_3$  neutralization conditions.

Following the referee’s comments, we have added the above discussion in the revised manuscript, including the missing of sulfate production mechanisms in CAM5 model.

### **Specific comments**

**Line 113-115, What are the emission amounts in sectors of shipping, agricultural waste burning, waste treatment and natural biomass burnings? Are they high comparing to MEIC emissions?**

The emission amounts in sectors of shipping, agricultural waste burning, waste treatment and natural biomass burning are not included in the MEIC emission.

Therefore we keep them the same as the AR5 emission.

**Line 130-140, I don’t fully understand this paragraph. Did the model use BVOC from MEGAN model in MOZART-4 and use anthropogenic VOC from MEIC?**

Yes, the referee's understanding is correct. We rewrite the description in line as follows:

“Since the IPCC AR5 dataset does not provide emissions of biogenic VOCs, the SOAG emission is derived from the emission fluxes of five primary VOC categories (isoprene, monoterpenes, big alkanes, big alkenes, toluene) that are prescribed from the Model for OZone And Related chemical Tracers version 4 (MOZART-4) dataset (Emmons et al., 2010), in which the biogenic emissions of isoprene and monoterpenes are based on the Model for Emissions of Gases and Aerosols Emissions from Nature (MEGAN) (Guenther et al., 2006). The MEIC emission provides anthropogenic sources of the five VOC categories and the mapping table for lumping the MEIC VOC species to MOZART refers to Li et al. (2014). Since the MEIC does not provide the biogenic sources of isoprene and monoterpenes, which are much larger than their natural counterparts, we make their total emissions from anthropogenic and natural sources the same as those in the AR5 emission.

**Line 140-142, Did the factor of 1.4 also apply to the natural biomass burning emissions to derive SOAG?**

Yes, it does. When deriving SOAG emission, all anthropogenic and biomass burning sectors are added up and multiplied by 1.4 to convert OC (carbon mass) to POM (organic mass).

**Line 147, Is there particle number emissions in the AR5 emission inventories?**

No, the AR5 emission inventory only provides aerosol mass emissions. The number emission in both AR5 and MEIC emissions are calculated from the mass concentration as described in the text. To be clearer, the paragraph is rewritten as



follows:

“The number emission fluxes in both AR5 and MEIC are calculated from the mass fluxes in a consistent way. The mass to number conversion is based on  $E_{number} = E_{mass} / \left( \frac{\pi}{6} \rho D_v^3 \right)$ , where  $D_v$  is the volume-mean emitted diameter and  $\rho$  is the aerosol particle density (Liu et al., 2012). Since the MEIC emission does not provide mass emissions from agricultural waste burning, waste treatment, forest fire, grass fire and continuous volcanoes, we use the number fluxes from the AR5 emission for these sectors.”

**Line 170, The simulated ADRE is a “all-sky” value while the observation-deriving ADRE in Line 187 is “clear-sky”. Need to state the discrepancy.**

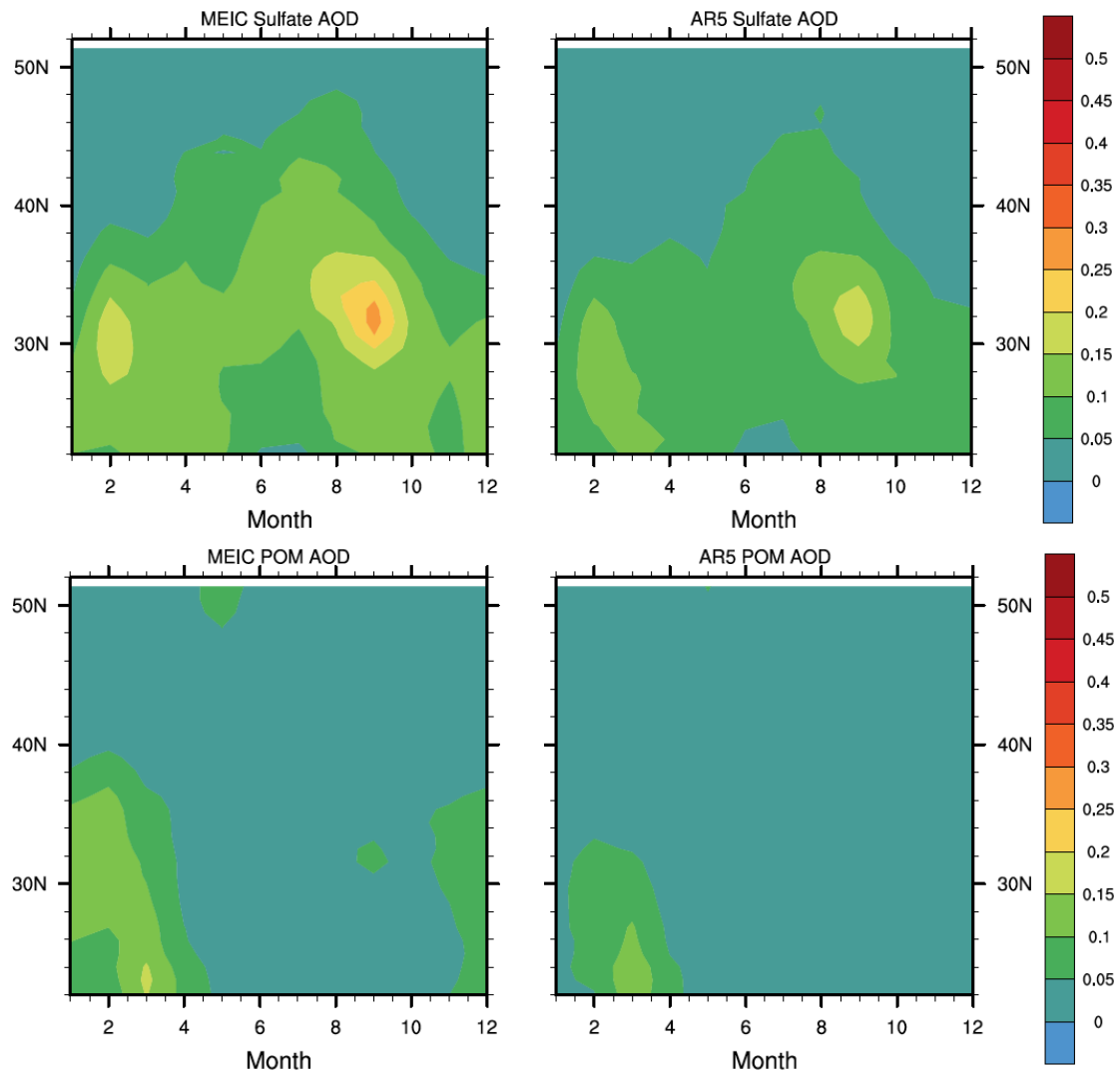
The cloud-screening method (clear-sky) in observations neglects the effect of aerosol above and below clouds. Absorption of reflected solar radiation by absorbing aerosol above clouds should result in larger radiative warming effect. The radiative cooling by scattering aerosol below clouds is not as strong as in clear sky due to less sunlight penetrating the clouds. Both of the two factors will results in lower (more negative at TOA) radiative effect in clear-sky than that in all-sky. Therefore, the observation-derived ADRE in clear-sky provides an upper-limit of the model-estimated all-sky ADRE at TOA.

**Line 211, It might be more appropriate to show concentration results (Section 3.2) before AOD results (Section 3.3).**

Thank you for the suggestion. It is more conventional to show surface concentration before AOD. Nevertheless, we show AOD first since we would like to address the question of whether the underestimated AOD by models is improved by using MEIC emission. Also, since satellite retrieved AOD provides the spatial distribution to be compared with the model results, we think it might be acceptable to show AOD before concentration results.

**Line 240, why not show the results by aerosol components?**

Following the referee's comment, we added the AOD by aerosol components (in the appendix). See the following figure.



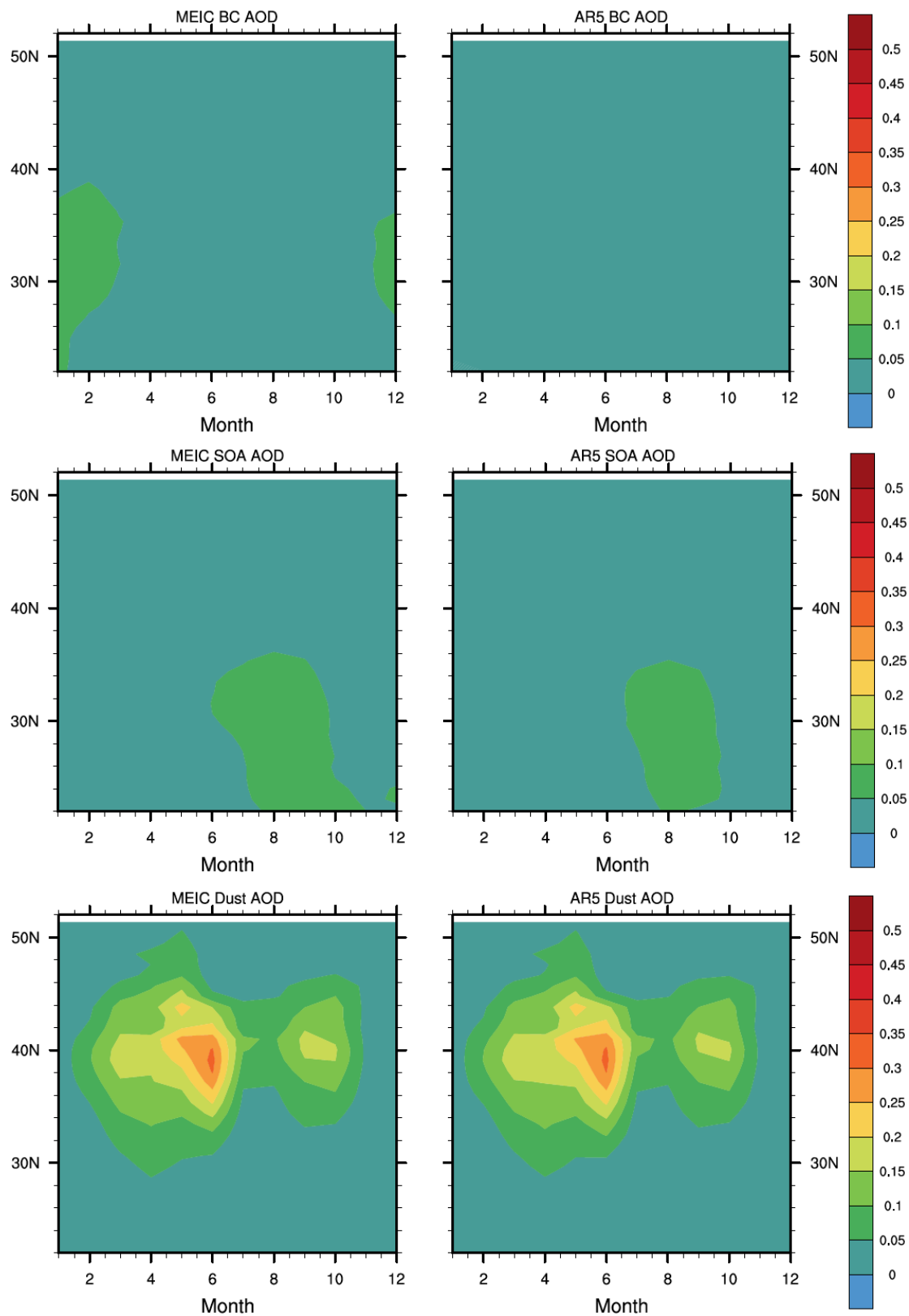


Figure S5. The seasonal variation of longitudinal averaged ( $100^{\circ}\text{E}$ - $124^{\circ}\text{E}$ ) AOD at 550 nm by aerosol components (dust, sulphate, BC, POM, and SOA from top to bottom) simulated by CAM5-MAM3 using the MEIC emission (left column) and the AR5 emission (the right column).

**Line 249, “while the observed maximum extends further north” According to Figure 5, it seems that the observed AOD maximum is in the south of the simulated maximum. Please rewrite this sentence. Line 250-251 have the same problem.**

Following the referee’s comment, we rewrite the sentences as “The model simulates a maximum between 35°N and 40°N in early summer (from May to July) which is to the north of the observed AOD maximum.”.

**Line 249, “This model maximum is mostly due to dust aerosol ...” It seems that the maximum AOD in the earlier summer is about half less than the observation, and the maximum AOD is from dust. Thus, the anthropogenic AOD is quiet low comparing with MODIS. That is, CAM5 model heavily underestimates AOD in China and this cannot be explained by emissions alone. Besides to the emissions, the author need to mention other causes (e.g. missing nitrate, particle size distribution, aerosol hygroscopic growth, etc.) that account for the large AOD bias.**

We agree with the referee that other causes beside emission also account for the large AOD bias. We mentioned the plausible causes and future effort to be made in Line 258-262 and the summary section (Line 443-449). We rewrite the sentences as “This model maximum is mostly due to dust aerosol transported from the west, while the satellite retrievals do not show such strong dust emission and transport. Since the dust emissions are the same in the simulations using the MEIC and AR5 emissions, the difference of the modeled AOD maxima between 35°N and 40°N is mainly due to anthropogenic aerosols. We notice that the maximum AOD in the satellite retrieval occurs around 30°N in early summer (May to July), as oppose to 35°N to 40°N as simulated by the model. The observed AOD maximum complies with the SO<sub>2</sub> emission maximum in early summer around 30°N (Figure S6). Therefore, this AOD maximum is heavily underestimated by the model. Since the uncertainty of

SO<sub>2</sub> emission is relative low ( $\pm 12\%$ ), this underestimation cannot be explained by emission alone. Other causes (e.g. missing nitrate, particle size distribution, aerosol hygroscopic growth, etc.) in the model are more responsible.” ”

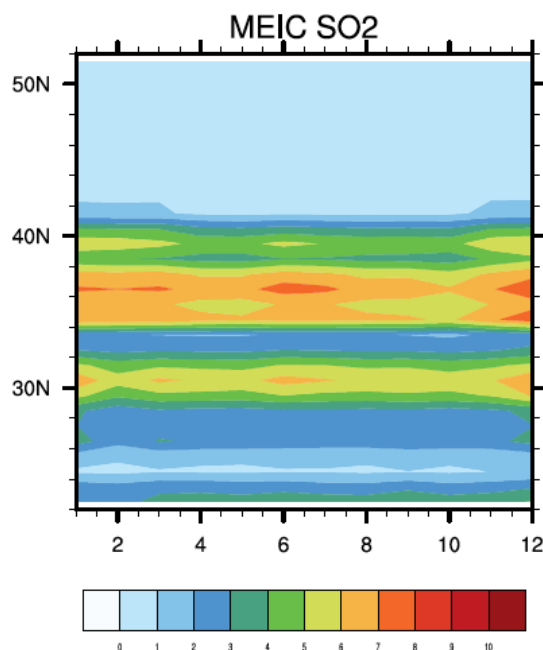


Figure S6. The seasonal variation of longitudinal averaged SO<sub>2</sub> emission from MEIC [g S/m<sup>2</sup>/year].

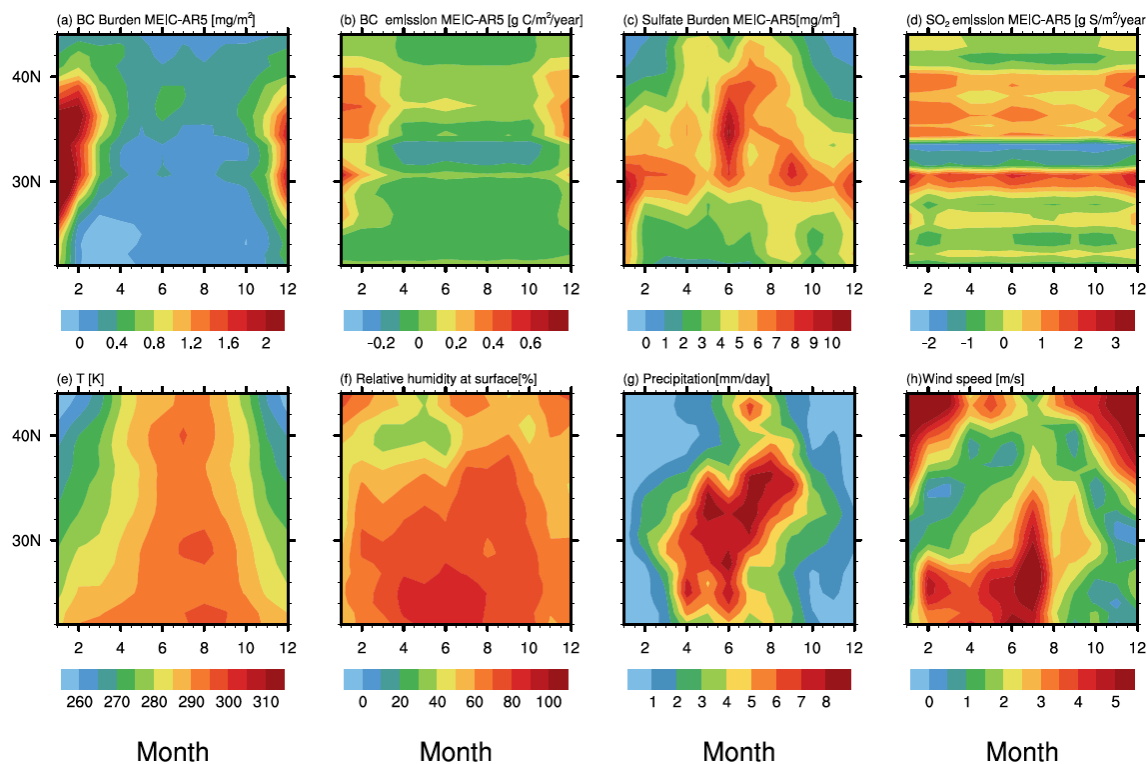
**Line 329-330, “The sulfate concentrations in northern China are characterized by the summer maximums” In Figure 9, at northern cities, the minimum wintertime sulfate in observations are susceptible. As the observations were collected from literature measurements that were carried out in different periods, the observations in summer and winter may not be comparable. The comparison uncertainty should be admitted.**

The summer maximums of the surface concentration of sulfate at northern cities in 2009 and 2010 were observed by some independent researches (Zhao et al., 2013; Zhang et al., 2013; Geng et al., 2015). It is possible that SO<sub>2</sub> to sulfate conversion is efficient in the summer due to high temperature and relative humidity. However, there were also observations showing opposite seasonal variations with sulfate concentration peaking in the winter during other periods (Zhang et al., 2012). The contrasting results in the observations could be due to that the observations were

carried out in different periods, as suggested by the referee. We have added this comparison uncertainty in the revised manuscript.

**Line 343-349, in my opinion, gas-phase oxidation of SO<sub>2</sub> is not the main pathway for sulfate production. Aqueous oxidation in droplet/cloud water should be more important. At 35°-40°N, the maximum sulfate difference between MEIC and AR5 in summer is also due to the high ambient humidity. Besides, if CAM5 can capture the wintertime high concentrations, the largest sulfate burden difference could be in winter than in summer.**

We totally agree with the referee. We added the seasonal variation of relative humidity in Figure 11(f). One thing to notice is that aqueous-phase oxidation occurs only in cloud droplets in the model. The aqueous-phase oxidation of SO<sub>2</sub> by NO<sub>2</sub> on solution aerosols is not modeled by CAM5-MAM3, which is important in China (Wang et al., 2016). If we consider the oxidation by NO<sub>2</sub> on solution aerosols in CAM5, the contribution of aqueous-phase chemistry could be more important.

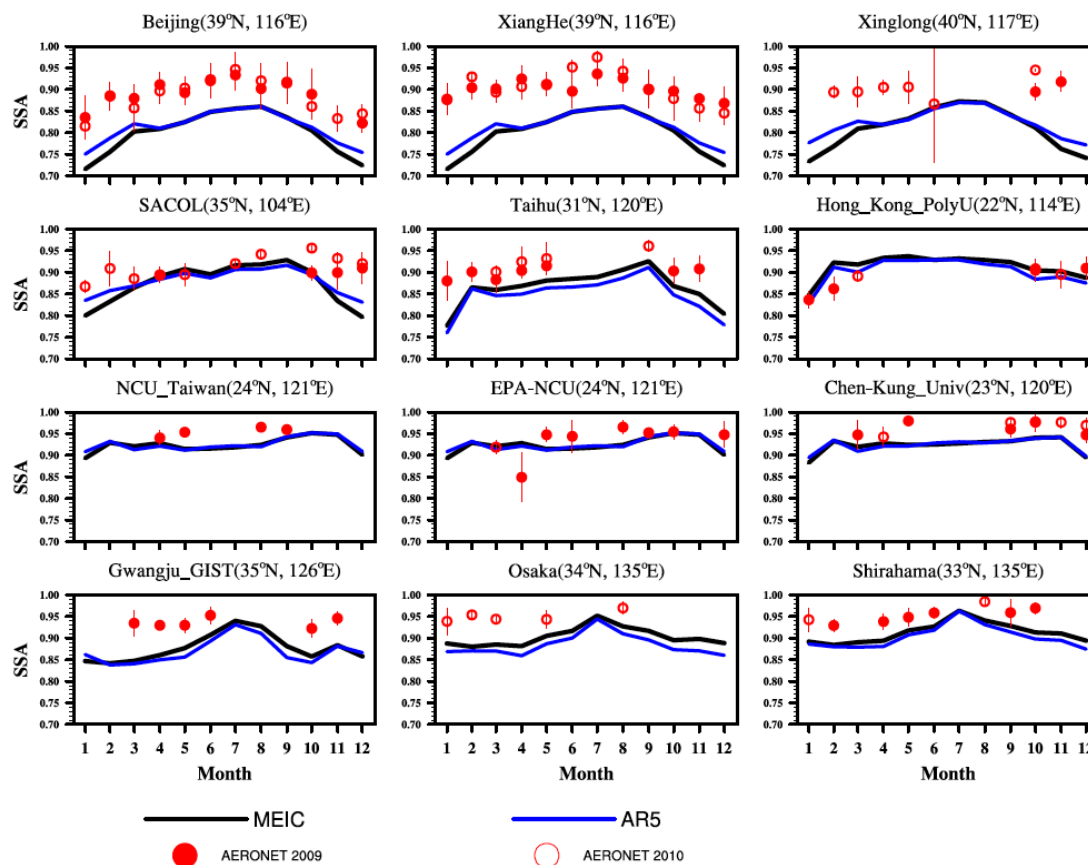


**Revised Figure 11.**

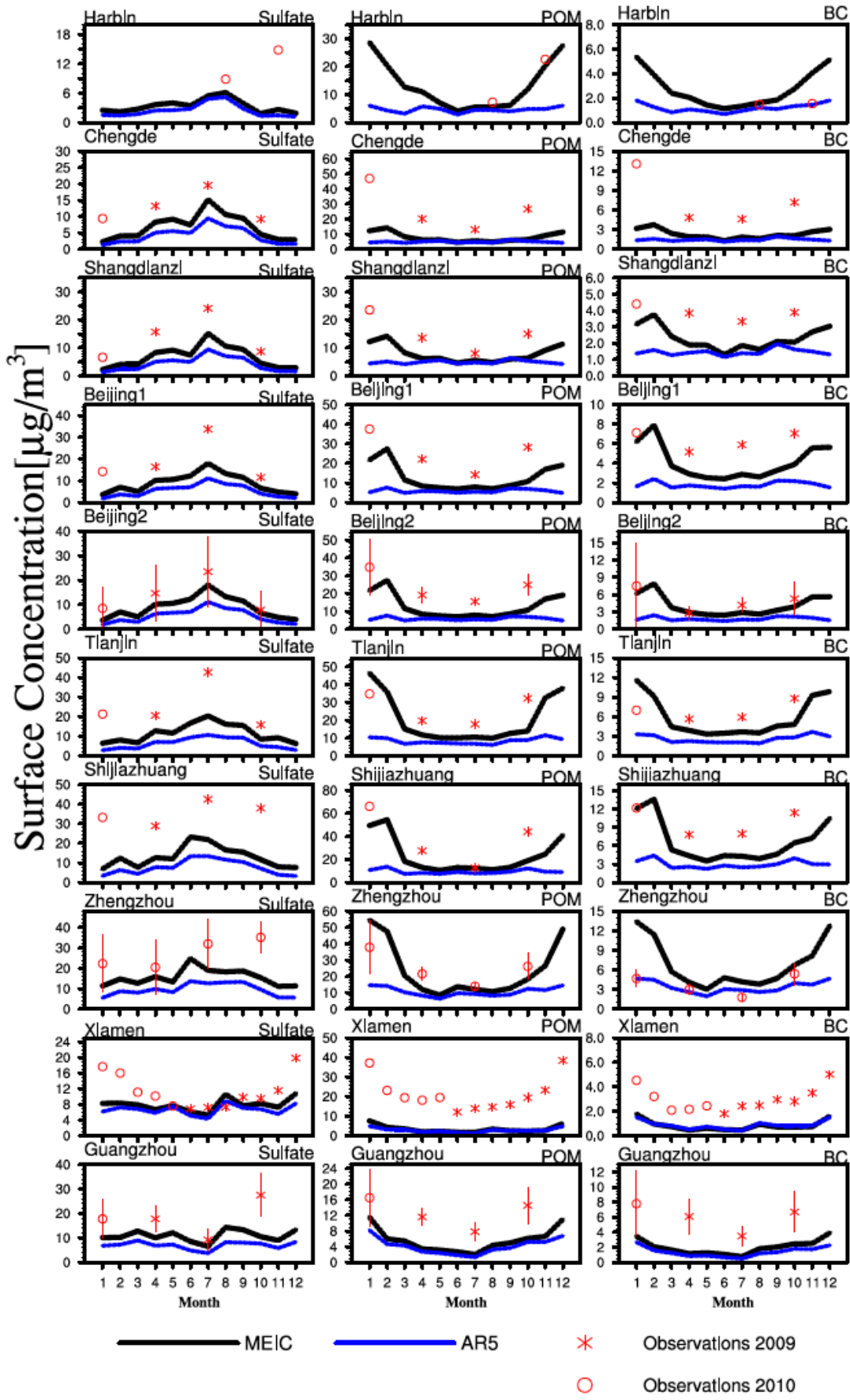
## Technical notes

If possible, mark the data range (i.e. Min, Max) in Figure 7 and 9.

Data range (one standard deviation) in Figure 7 and Figure 9 are marked. The standard deviations of the surface concentrations are provided in only three locations (Beijing, Zhengzhou, and Guangzhou) by the literatures. We add them to Figure 9.



Revised Figure 7. Error bars stand for one standard deviations of the observations.





**Revised Figure 9.** Error bars stand for one standard deviations of the observations.

References:

- Bhawar, R. L., Lee, W.-S., and Pahu, P.R.C.: Aerosol types and radiative forcing estimates over East Asia, *Atmos. Environ.*, 141, 532-541, doi: 10.1016/j.atmosenv.2016.07.028, 2016.
- Chen, D., Liu, Z., Fast, J., and Ban, J.: Simulations of sulfate-nitrate-ammonium (SNA) aerosols during the extreme haze events over northern China in October 2014. *Atmos. Chem. Phys.*, 16, 10707-10724, doi:10.5194/acp-16-10707-2016, 2016.
- Dong, X., Fu, J. S., Huang, K., Tong, D., and Zhuang, G.: Model development of dust emission and heterogeneous chemistry within the Community Multiscale Air Quality modeling system and its application over East Asia. *Atmos. Chem. Phys.*, 16, 8157-8180, doi:10.5194/acp-16-8157-2016, 2016.
- Geng, N., Wang, J., Xu, Y., Zhang, W., Chen, C., and Zhang, R.: PM<sub>2.5</sub> in an industrial district of Zhengzhou, China: chemical composition and source apportionment, *Particuology*, 11(1), 99-109, 2013.
- He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C. Zhang, H., and Hao, J.: Mineral dust and NO<sub>x</sub> promote the conversion of SO<sub>2</sub> to sulfate in heavy pollution days. *Sci. Rep.*, 4, 4172, doi:10.1038/srep04172, 2014.
- Huang, X., Song, Y., Zhao, C., Li, M., Zhu, T., Zhang, Q., and Zhang, X.: Pathways of sulfate enhancement by natural and anthropogenic mineral aerosols in China. *J. Geophys. Res.*, 119, 14165-14179, doi:10.1002/2014JD022301, 2014.
- Lu, Z., Zhang Q., and Streets D. G.: Sulfur dioxide and primary carbonaceous aerosol emissions in China and India, 1996–2010 *Atmos. Chem. Phys.*, 11, 9839–9864, doi:10.5194/acp-11-9839-2011, 2011.
- Li, Jiandong, Wei-Chyung Wang, Zhian Sun, Guoxiong Wu, Hong Liao, Yimin Liu, Decadal variation of East Asian radiative forcing due to anthropogenic aerosols during 1850–2100, and the role of atmospheric moisture, *Clim Res*, Vol. 61: 241–257, doi: 10.3354/cr01236, 2014.

- Paulot F, Fan S, Horowitz L W.: Contrasting seasonal responses of sulfate aerosols to declining SO<sub>2</sub> emissions in the Eastern US: implications for the efficacy of SO<sub>2</sub> emission controls, *Geophys. Res. Lett.*, 2016.
- Streets, D. G., Bond, T. C., Carmichael, G. R., Fernandes, S. D., Fu, Q., He, D., Klimont, Z., Nelson, S. M., Tsai, N. Y., Wang, M. Q., Woo, J.-H., and Yarber, K. F.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, *J. Geophys. Res.*, 108, 8809, doi:10.1029/2002JD003093, 2003.
- Wang, Y., Zhang, Q., Jiang, J., Zhou, W.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models. *J. Geophys. Res.*, 119, 10,425-10,440, doi:10.1002/2013JD021426, 2014.
- Wang, Y. S., Yao, L., Wang, L., Liu, Z., et al.: Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China." *Science China-Earth Sciences*, 57(1): 14-25, 2014.
- Wang G, Zhang R, Gomez M E, et al. :Persistent sulfate formation from London Fog to Chinese haze., *Proceedings of the Nat. Acad. of Sci.*, 201616540, 2016.
- Westervelt, D. M., Horowitz, L.W., Naik. V., et al: Radiative forcing and climate response to projected 21st century aerosol decreases. *Atmos. Chem. and Phys.*, 15(22): 12681-12703, 2015.
- Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C. S. L., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of PM<sub>2.5</sub> in Beijing: seasonal perspective, *Atmos. Chem. Phys.*, 13(14), 7053-7074, 2013.
- Zhao, P. S., Dong, F., He, D., Zhao, X. J., Zhang, X. L., Zhang, W. Z., Yao, Q., and Liu, H. Y.: Characteristics of concentrations and chemical compositions for PM<sub>2.5</sub> in the region of Beijing, Tianjin, and Hebei, China, *Atmos. Chem. Phys.*, 13, 4631-4644, 2013.
- Zheng, B., Zhang, Q., Zhang, Y., He, K. and et al.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China. *Atmos. Chem. Phys.*, 15, 2031-2049, doi:10.5194/acp-15-2031-2015, 2015.