Anonymous Referee #1

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SOA is an important but the least understood component of atmospheric aerosols. Generally, the existing models still underestimate the observed organic aerosol concentrations. The SOA formation through aqueous reactions of dicarbonyls is one of potential candidates that can reduce the model-observation gap and thus has attracted many attentions in recent SOA studies. Li et al. 2018 manuscript attempts to implement the aqueous uptake of dicarbonyls in the regional atmospheric chemistry model RAMS-CMAQ and further to estimate the contribution of the uptake of dicarbonyls to the SOA formation in China. The manuscript also tries to quantify the effect of the underestimation of gas-phase glyoxal in the model on the SOA formation. Overall, I think the manuscript would benefit the SOA community after the authors address my comments below.

General comments

1. The model accounts for the SOA formation both from the in-cloud oxidation of glyoxal and methylglyoxal and through the aqueous irreversible uptake of glyoxal and methylglyoxal as presented in equation (1). However, the SOA formation pathway through the equation (1) already includes the in-cloud reactions of dicarbonyls. So the model is double-counting the loss of dicarbonyls through the aqueous process and thus the SOA formation from the dicarbonyls.

Thanks a lot for your positive comments on this study. You are right that the model has double-counted the loss of dicarbonyls through the in-cloud oxidation and thus the corresponding SOA formation. Therefore, we have re-performed case 1 and 2 with the in-cloud reactions of dicarbonyls turned off. The corresponding descriptions have also been revised as “To avoid double-counting the loss of dicarbonyls through the in-cloud oxidation and the following formed SOA, the default aqueous formation pathway is turned off when run case 1 with the pathway M incorporated.” in Line 277-279.

2. The model does not consider the uptake of dicarbonyls on the aqueous aerosol, but only the uptake on the cloud droplets. Can the authors explain the reason for neglecting the uptake by the aqueous aerosol? Many studies (both lab and model studies) (Lim et al. 2010; Ervens and Volkamer, 2010; Stavrakou et al. 2009; Lin et al., 2014) have shown that the SOA formation from the uptake on the aqueous aerosol can be as large as or even larger than that from the cloud processing.

Thanks a lot for the comments. In fact, we have considered the uptake by aqueous aerosols, but only in the cloud processing. We use the collision limitation ($v\gamma A/4$) to account for the uptake loss of dicarbonyls by aqueous aerosols, and allocate 15% of glyoxal and 9% of methylglyoxal uptake on aqueous aerosols according to Fu et al. (2008). As a result, the contribution to SOA from the aqueous aerosol in clouds is small compared to that from the cloud droplets. But as you said, the uptake of dicarbonyls by aqueous aerosols taking place in aerosol processing are significant. Thus, referred to previous studies (e.g. Lin et al., 2014;Ying et al., 2015;Hu et al., 2017), we decide to add the pathway in the aerosol processing with the description of collision limitation. Besides, the uptake on aqueous aerosols contributes few to SOA in clouds, and the allocation of dicarbonyls between the uptake by cloud droplets and aqueous aerosols have large uncertainties, thus we use equation (1) only to account for the uptake on the cloud droplets in cloud processing. Similar to Fu et al. (2008) and Li et al. (2013), we also assume effective droplet radii of 10 μm for maritime clouds and 6 μm for continental clouds. The detailed illustration is shown in Line 150-162 as follows:

We implement the aqueous uptake of dicarbonyls by cloud droplets following the standard equation (1). In a similar manner to Fu et al. (2008) and Li et al. (2013), the cloud droplet surface area is calculated from the LWC in the cloudy fraction of the model grid by assuming an effective droplet radius of 6 μm for continental clouds and 10 μm for maritime clouds. D_g is calculated according to Perry and Green (1999) following Dentener and Crutzen (1993). Similar to previous studies (e.g. Lin et al., 2014b;Ying et al., 2015;Hu et al., 2017), the uptake of gas-phase dicarbonyls on aqueous aerosols is simply parameterized using the collision limitation ($v\gamma A/4$) of equation (1). The value of $\gamma = 2.9\times10^{-3}$ for glyoxal from Liggio et al. (2005) is used in both cloud and aerosol processing. While the uptake coefficient adopted for methylglyoxal is from De Haan et al. (2018): the average value of $\gamma = 5.7\times10^{-3}$ measured on cloud-processed glycine aerosols is used to account for the uptake by cloud droplets; the average value of $\gamma = 3.0\times10^{-3}$ used in aerosol processing is derived from the uptake coefficients measured on deliquesced ammonium sulfate aerosols (3.7×10^{-3}) and on deliquesced glycine aerosols (2.3×10^{-3}, median value).

Certainly, case 1 and 2 have been re-preformed and the corresponding descriptions as well as results have been revised.

3. The authors only used one station data to evaluate the modeled SOA concentrations. How representative is this station data? Can this single-station data evaluation draw a meaningful and robust conclusion on the model performance?

Thank you for the comments. So far, the observation of secondary organic aerosol concentration is still very limited in China. It is difficult to collect the hourly concentration of SOA measured during the same period at several stations. Since SOA measurement is usually conducted in urban areas and the air pollution event appears frequently over the North China Plain, to perform SOA studies over Beijing is an appropriate choice. In order to make our studies more persuasive, based on the data that we can collect, two long simulated periods, during which there are continuously observed hourly SOA concentrations, have been selected. To some extent, the results in our studies have certain representations.

Specific comments

Line 51-52. The references list only include the paper previous to 2008. There are many SOA modeling papers published since 2008. The authors should at least include some of them.

Thanks for your suggestion. The SOA modeling papers published after 2008 as follows have been added in Line (55-56):

Farina, S. C., Adams, P. J., and Pandis, S. N.: Modeling global secondary organic aerosol formation and processing with the volatility basis set: Implications for anthropogenic secondary organic aerosol, J. Geophys. Res.-Atmos., 115, 10.1029/2009jd013046, **2010**.

Fu, T. M., Jacob, D. J., and Heald, C. L.: Aqueous-phase reactive uptake of dicarbonyls as a source of organic aerosol over eastern North America, Atmos. Environ., 43, 1814-1822, **2009**.

Jiang, F., Liu, Q., Huang, X., Wang, T., Zhuang, B., and Xie, M.: Regional modeling of secondary organic aerosol over China using WRF/Chem, J. Aerosol Sci, 43, 57-73, 10.1016/j.jaerosci.2011.09.003, **2012**.

Jo, D. S., Park, R. J., Kim, M. J., and Spracklen, D. V.: Effects of chemical aging on global secondary organic aerosol using the volatility basis set approach, Atmos. Environ., 81, 230-244, 10.1016/j.atmosenv.2013.08.055, **2013**.

Lin, J., An, J., Qu, Y., Chen, Y., Li, Y., Tang, Y., Wang, F., and Xiang, W.: Local and distant source contributions to secondary organic aerosol in the Beijing urban area in summer, Atmos. Environ., 124, Part B, 176-185, http://dx.doi.org/10.1016/j.atmosenv.2015.08.098, **2016**.

Zhang, H., and Ying, Q.: Secondary organic aerosol from polycyclic aromatic hydrocarbons in Southeast Texas, Atmos. Environ., 55, 279-287, 10.1016/j.atmosenv.2012.03.043, **2012**.

Line 53-54. The one-to-two-order-of-magnitude underestimation applies to only the SOA modeling paper before 2007. Recent SOA modeling efforts have closed the gap to some degree, although there are still large uncertainties there (e.g. Tsigaridis et al. 2014). Again, the authors need to clarify this.

Thanks for your comments. The descriptionthe—one-to-two-order-of-magnitude underestimation in SOA simulations—used here is to explain why more and more model studies have begun to concentrate on the studies of SOA sources since the time. Then the following context in our manuscript has listed several important researches about potential SOA sources after that.

Line 70. Again, there are few other recent papers that have made efforts on modeling aqueous SOA formation. To name a few here, Lin et al. 2012; Lin et al. 2014; Woo and McNeill, 2015.

Thanks for your suggestion. We have added the corresponding references as follows in Line 75:

Lin, G., Penner, J. E., Sillman, S., Taraborrelli, D., and Lelieveld, J.: Global modeling of SOA formation from dicarbonyls, epoxides, organic nitrates and peroxides, Atmos. Chem. Phys., 12, 4743-4774, 10.5194/acp-12-4743-2012, 2012.

Lin, G., Sillman, S., Penner, J. E., and Ito, A.: Global modeling of SOA: the use of different mechanisms for aqueous-phase formation, Atmos. Chem. Phys., 14, 5451-5475, 10.5194/acp-14-5451-2014, 2014.

Woo, J. L., and McNeill, V. F.: simpleGAMMA v1.0-a reduced model of secondary organic aerosol formation in the aqueous aerosol phase (aaSOA), Geosci. Model Dev., 8, 1821-1829, 10.5194/gmd-8-1821-2015, 2015.

Line 108-110. How about the lateral boundary conditions?

Thanks for your reminder. Now the descriptions of the lateral boundary conditions have been added in Line 112-114 as follows:

The National Centers for Environmental Prediction reanalysis datasets are served as the initial and lateral boundary meteorological conditions input into RAMS.

Line 138. Does the model include the uptake by both aqueous aerosols and cloud droplets? Because according to the result section, the model seems to include the

uptake by the cloud droplets only, excluding the aqueous aerosol uptake?

Thanks a lot for the comments. In fact, we have considered the uptake by aqueous aerosols, but only in the cloud processing. We use the collision limitation ($v\gamma A/4$) to account for the uptake loss of dicarbonyls by aqueous aerosols, and allocate 15% of glyoxal and 9% of methylglyoxal uptake on aqueous aerosols according to Fu et al. (2008). However, for the significant contributions of the uptake by aqueous aerosols in aerosol processing, we have included the pathway in the aerosol processing already.

Line 150. The assumption of the same value of gamma glyoxal and methylglyoxal is not well-grounded. First, Liggio et al. (2005) only gave the value of glyoxal rather than the value of methylglyoxal. Second, the value of glyoxal was derived from the uptake on aqueous aerosols, not on the cloud water. Third, the glyoxal and methylglyoxal uptake by cloud water correlates with their water solubility. So I think scaling of methylglyoxal to that of glyoxal by the ratio of their effective Henry's law constants is a more reasonable assumption.

Thanks for your good suggestion. We have intended to compute the effective Henry's law constants of methylglyoxal and glyoxal follow the work of Fu et al. (2008), and then to scale the gamma methylglyoxal to that of glyoxal by the ratio of their effective Henry's law constants. At the moment, we find that a new work of De Haan et al. (2018) presents the uptake coefficient of methylglyoxal (γ) on aqueous aerosol surfaces from chamber studies. They have measured methylglyoxal uptake coefficient by involving ammonium sulfate (AS) and glycine seed aerosol over a broad range of relative humidity (RH). Since there is saturation and even supersaturation in clouds, we use the average uptake coefficient (5.7×10^{-3}) for cloud-processed glycine aerosol at 99 ± 1% RH to describe the uptake of methylglyoxal by cloud droplets. According to De Haan et al. (2018), methylglyoxal uptake coefficient on pre-reacted glycine aerosol particles has a strong dependence on RH while the uptake on AS aerosol particles varies a little over a broad range of RH. To take both the uptake on inorganic and organic aqueous aerosols into consideration, we choose the average value (3.0×10^{-3}) of uptake coefficient on deliquesced AS aerosol (3.7×10^{-3}, measured at 95 ± 2% RH) and median value of uptake coefficient on deliquesced glycine aerosol (2.3×10^{-3}, measured at 89 ± 2% RH) to describe the uptake of methylglyoxal by aqueous aerosols. The corresponding descriptions have been added in Line 158-162 as follows:

While the uptake coefficient adopted for methylglyoxal is from De Haan et al. (2018): the average value of $\gamma = 5.7\times10^{-3}$ measured on cloud-processed glycine aerosols is used to account for the uptake by cloud droplets; the average value of $\gamma = 3.0\times10^{-3}$ used in aerosol processing is derived from the uptake coefficients measured on deliquesced ammonium sulfate aerosols (3.7×10^{-3}) and on deliquesced glycine aerosols (2.3×10^{-3}, median value).

Line 172-173. Which two episodes?

Thanks for your question. The two episodes are from June 3 to July 11, 2014 and October 14 to November 14, 2014, respectively. We have added the detailed descriptions in Line 168 as follows:

Samples were taken from June 3 to July 11, 2014 (episode 1) and October 14 to November 14, 2014 (episode 2) at the Institute of Atmospheric Physics.

Section 3.1 Model evaluation. Can the authors compare to surface cloud water content measurements, instead of the vertically integrated water content (CWP)? Because the surface cloud water content is more relevant to the surface SOA concentrations than the CWP.

Thanks for your suggestion. There is no measured surface cloud water content that we can obtained. Thus, we decide to use the vertically integrated water content (CWP) instead.

Line 249-250. The underestimation of aromatics concentrations doesn't necessarily mean that the model underestimates the aromatic emission. The

alternate reason could be the chemical consumption rates of aromatics are too fast in the model.

Thanks for your reminders. As you said, the faster chemical consumption rates of aromatics can result in the underestimations of aromatics concentrations. However, the causes of underestimations of the aromatic emissions also cannot be excluded, since there are some researches (e.g. Zhang and Ying, 2011;Liu et al., 2012) have clarified the possibility of the underestimations. Thus, in this paper, we have concentrated on the underestimations of aromatic emissions. As a result, there are still many uncertainties probably due to the faster chemical consumption rates as you said, and we can discuss the problem in further work.

Line 332-334. Why do the authors neglect the aqueous SOA formation in the aqueous aerosols?

Thanks for the comments. In fact, we have considered the uptake by aqueous aerosols, but only in the cloud processing. We use the collision limitation ($v\gamma A/4$) to account for the uptake loss of dicarbonyls by aqueous aerosols, and allocate 15% of glyoxal and 9% of methylglyoxal uptake on aqueous aerosols according to Fu et al. (2008). However, for the significant contributions of the uptake by aqueous aerosols in aerosol processing, we have included the pathway in the aerosol processing already and the corresponding descriptions "This study considers … but does not include … from aqueous aerosols to SOA formation" have been deleted.

Line 338. Distinguish the contribution: : : from what? Please clarify this.

Thanks. We have modified the description "To distinguish the contribution of dicarbonyls to the concentration of SOA over China" as "To distinguish the contribution of dicarbonyls to the concentration of SOA in case 2 over China from that in case 0" (shown in Line 353-354). Besides, after we add the uptake of dicarbonyls by the aqueous aerosols in aerosol processing, dicarbonyls contribute a lot to SOA concentration in episode 2, thus we add the discussions about the distributions of dicarbonyl-derived SOAs and their contributions to SOAs over China in case 0 and 2 during episode 2.

Fig.4. The red line in (a) is different from the one in (c) and (e). So the red line in different panels represent different case result? Really confusing.

Thanks for your comments. All the red line in (a), (c) and (e) represent the results of case 0 in episode 1. There is a large bias between the observed and simulated SOA. In order to show the numerical value and the variable tendency of SOA concentration more clearly, we have used another Y-axis (the right one in all the panels of Figure 4) to show the results of simulated SOA. As modeled SOA concentrations increase after the improvement of SOA simulations step by step, the scales on the right Y-axis are different in (a), (c) and (e). As a result, the red line drawn in Figure 4(a, c, e) are different though the values are not changed. In order not to cause the misunderstanding again, we decide to combine the subplots in one panel as shown in Figure 4 now.

References cited in the response to Referee #1

De Haan, D. O., Jimenez, N. G., de Loera, A., Cazaunau, M., Gratien, A., Pangui, E., and Doussin, J.-F.: Methylglyoxal Uptake Coefficients on Aqueous Aerosol Surfaces, The Journal of Physical Chemistry A, 122, 4854-4860, 10.1021/acs.jpca.8b00533, 2018.

Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res.-Atmos., 113, 10.1029/2007jd009505, 2008.

Hu, J., Wang, P., Ying, Q., Zhang, H., Chen, J., Ge, X., Li, X., Jiang, J., Wang, S., Zhang, J., Zhao, Y., and Zhang, Y.: Modeling biogenic and anthropogenic secondary organic aerosol in China, Atmos. Chem. Phys., 17, 77-92, 10.5194/acp-17-77-2017, 2017.

Li, N., Fu, T.-M., Cao, J., Lee, S., Huang, X.-F., He, L.-Y., Ho, K.-F., Fu, J. S., and Lam, Y.-F.: Sources of secondary organic aerosols in the Pearl River Delta region in fall: Contributions from the aqueous reactive uptake of dicarbonyls, Atmos. Environ., 76, 200-207, 10.1016/j.atmosenv.2012.12.005, 2013.

Lin, G., Penner, J. E., Flanner, M. G., Sillman, S., Xu, L., and Zhou, C.: Radiative forcing of organic aerosol in the atmosphere and on snow: Effects of SOA and brown carbon, J. Geophys. Res.-Atmos., 119, 7453-7476, 10.1002/2013jd021186, 2014a.

Liu, Z., Wang, Y., Vrekoussis, M., Richter, A., Wittrock, F., Burrows, J. P., Shao, M., Chang, C.-C., Liu, S.-C., Wang, H., and Chen, C.: Exploring the missing source of glyoxal (CHOCHO) over China, Geophys. Res. Lett., 39, 10.1029/2012gl051645, 2012.

Ying, Q., Li, J., and Kota, S. H.: Significant Contributions of Isoprene to Summertime Secondary Organic Aerosol in Eastern United States, Environ. Sci. Technol., 49, 7834-7842, 10.1021/acs.est.5b02514, 2015.

Zhang, H., and Ying, Q.: Secondary organic aerosol formation and source apportionment in Southeast Texas, Atmos. Environ., 45, 3217-3227, 10.1016/j.atmosenv.2011.03.046, 2011.

Anonymous Referee #2

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This manuscript simulated the SOA production by the aqueous uptake of dicarbonyls on cloud droplets (pathway M) and evaluated the impact on overall SOA concentrations over China. The authors also explored the impacts of increased aromatic emission and glyoxal yields from isoprene on the SOA production from pathway M.

While the subject is of interest to the community, the present paper is confusing in its methodology and conclusions. For example, the authors went to great length to prove that aromatic emissions may be underestimated, which certainly would have an impact on the simulated glyoxal concentration. But then the authors simulated Case 2 by tripling the aromatic emissions AND increasing the glyoxal yield from isoprene by a factor of 5, without giving any rationale for the latter change. It is true that many models may have underestimated glyoxal yields from isoprene (Galloway et al. 2011), but the reader was under the impression that that

was not the focus of the paper. Why then, did the author mix-up the two potential cause of glyoxal-underestimation in their study? Why not evaluate the impact of aromatic emissions first and then move on to the impact glyoxal yields from isoprene? I strongly suspect that the improvements in Case 2 relative to Case 1 was mostly due to the change in glyoxal yields. If the authors want to focus on this effect, they need to make the rationale clear from the introduction and methodology.

Also, many statements were not supported by the figures. For example, the authors stated that the simulated SOA in Case 2 increased by a factor of 2 relative to that in Case 1. This was not seen in Figure 4. Also, Case 0 (base case) in the subplots of Figure 4 were all different!

Overall, I recommend that the paper undergo major revision to clarify the confusing points.

Thanks a lot for your comments and we will clarify your confusing points one by one in the following:

(1) The authors simulated Case 2 by tripling the aromatic emissions AND increasing the glyoxal yield from isoprene by a factor of 5, without giving any rationale for the latter change. It is true that many models may have underestimated glyoxal yields from isoprene (Galloway et al. 2011), but the reader was under the impression that that was not the focus of the paper.

Sorry for our unclear descriptions related to the reasons to increase the glyoxal yield from isoprene by a factor of 5 before we discuss the impacts of glyoxal-underestimation on SOA production. Thank you for pointing this out. The 5-fold increase of glyoxal yield from isoprene is based on the previous studies by Li et al. (2018). In that paper, we have discussed the possible reasons of glyoxal-underestimation in the model. Through the comparisons of both formaldehyde vertical column densities (VCDs) and the ratio of averaged glyoxal to formaldehyde VCDs between observations and simulations, we have concluded that glyoxal derived from biogenic precursors is underestimated and very likely results from the underestimated yields of glyoxal from biogenic precursors. Combined with previous studies (e.g. Lelieveld et al., 2008; Peeters et al., 2009; Stavrakou et al., 2009; Stavrakou et al., 2010; Li et al., 2016), we considered the underestimation possibility in glyoxal yields from isoprene degradations. However, there is no research about the special modifications of glyoxal yield in the mechanism. In order to evaluate the impacts of underestimated glyoxal yields from isoprene on glyoxal simulation, we decided to simply increase the product stoichiometric coefficient of glyoxal in SAPRC99. As shown in Fig. 2 of Li et al. (2018), the initial modeled glyoxal vertical column densities (VCDs) were generally underestimated by a factor between 2 and 10, we then boldly increased the stoichiometric coefficients of glyoxal from isoprene by a factor of 5 (a half of 10). Since the glyoxal is not the first but secondary degradation product of isoprene in the mechanisms, a 5-fold change may not be too large. As shown in Fig. 5c and d of Li et al. (2018), the better agreement between the observed and simulated glyoxal indicate the reasonable improvement on some level. Thus, in this manuscript, we directly follow the design in Li et al. (2018) (a 5-fold increase of glyoxal yield from isoprene) without no more analyses, and only simply illustrate by "By combining our results with those of Li et al. (2018)". Now, we add more detailed description as follows in Line 280-288:

According to previous studies (e.g. Stavrakou et al., 2009; Stavrakou et al., 2010; Li et al., 2016), the yields of glyoxal from isoprene are very likely to be underestimated. Li et al. (2018) has run a simple sensitivity case to evaluate the impacts of underestimated glyoxal yields from isoprene on glyoxal simulation. From their results, a better agreement has achieved between the observed and simulated glyoxal after a five-fold increase of glyoxal yields from isoprene. More detailed analyses can be found in Li et al. (2018). Thus, to take the effects of the underestimations of glyoxal concentrations into considerations, case 2 was designed with a three-fold increase in the emissions of aromatic compounds and a five-fold increase in the molar yield of glyoxal from isoprene based on the results of case 1.

Besides, we have also revised several other lines to avoid the repeated descriptions as follows:

Both Liu et al. (2012) and Li et al. (2018) have suggested that the underestimation of glyoxal concentrations in simulations is related to the underpredicted emission of aromatic compounds. (Line 176-177)

As described in Section 2.3 and with reference to previous research, the underestimation of glyoxal concentrations may partly result from the underprediction of the emissions of aromatic compounds. (Line 247-248)

Even though, we have to admit that the changes (a 5-fold increase of glyoxal yield from isoprene) exist large uncertainties and problems, especially the carbon balance. More work needs to be done in the future, but here, we just simply make an exploring test.

(2) Why then, did the author mix-up the two potential cause of glyoxal-underestimation in their study? Why not evaluate the impact of aromatic emissions first and then move on to the impact glyoxal yields from isoprene? I strongly suspect that the improvements in Case 2 relative to Case 1 was mostly due to the change in glyoxal yields. If the authors want to focus on this effect, they need to make the rationale clear from the introduction and methodology.

It is a good suggestion that we evaluate the impact of aromatic emissions first and then the yields of glyoxal from isoprene. However, since glyoxal is a trace gas, the contribution of glyoxal-underestimation is not significant to dicarbonyl-derived SOA (AAQ) without the aqueous uptake of dicarbonyls (pathway M) included. Though the pathway M is included, the improvement of AAQ is still not significant if we consider the two potential impacts separately. As the impacts of glyoxal-underestimation on AAQ are not small enough to be ignored, we decide to mix the two potential cause up. As shown in Figure 5, the concentration of AAQ in case 2 is higher than double that of case 1 during the two analyzed episodes.

(3) Many statements were not supported by the figures. For example, the authors stated that the simulated SOA in Case 2 increased by a factor of 2 relative to that

in Case 1. This was not seen in Figure 4.

There may be some misunderstandings. For the large bias between the observed and simulated SOA, we have used another Y-axis (the right one in all the panels of Figure 4) to show the numerical value and the variable tendency of simulated SOA concentration more clearly. As modeled SOA concentrations increase after the improvement of SOA source descriptions (i.e. include pathway M and improve glyoxal simulation), the scales on the right Y-axis are different in three cases during the same episode. For example, one scale represents 2 $\mu g/m^3$, 3 $\mu g/m^3$ and 6 $\mu g/m^3$ in Fig. 4(a), Fig. 4(c) and Fig. 4(e), respectively. There is no significant difference among the red line (case 0) in Fig. 4(a), the blue line (case 1) in Fig. 4(c) and the purple line (case 2) in Fig 4(e). Thus, SOA concentration of case 2 is nearly doubled that of case 1 and triple that of case 0 during episode 1. In order not to cause the misunderstanding again, we have combined the subplots of each episode in one panel as shown in Figure 4 now. Besides, we have taken the uptake of dicarbonyls by aqueous aerosols into considerations according to the comments of another reviewer, thus the results have changed.

(4) Case 0 (base case) in the subplots of Figure 4 were all different!

Thanks for your comments. The red lines in Figure 4(a, c, e) represent the results of case 0 during the episode 1 (June 3 to July 11, 2014), while the red lines in Figure 4(b, d, f) show the results of case 0 in episode 2 (October 14 to November 14, 2014). As we explained before, there is a large bias between the observed and simulated SOA. In order to show the numerical value and the variable tendency of SOA concentration more clearly, we have used another Y-axis (the right one in all the panels) to show the results from the model. Due to the improvements of SOA simulations step by step, SOA concentrations during the same episode are different in three cases, resulting in the different scales on the right Y-axis in the panels. As a result, the red line drawn in Figure 4(a, c, e) are different though the values are not changed, so are the red lines in Figure

4(b, d, f).

Other major comments:

lines 107-108: Is NCEP data not used as boundary condition to the RAMS model?

Thanks for your reminder. Now the descriptions of the lateral boundary conditions have been added in Line 112-114 as follows:

The National Centers for Environmental Prediction reanalysis datasets are served as the initial and lateral boundary meteorological conditions input into RAMS.

lines 246-247: "The O/P ratios are more concentrated for ARO1 than for ARO2, with both the mean and median O/P values being close to 2." Not sure what the authors meant by ’the O/P ratios’ being more ’concentrated’. Did the authors mean that the O/P ratios for ARO1 were less variable than those for ARO2? Also, what does the variation refer to? Is it the hourly/diurnal variation? Or is it the day-to-day variation? Please also clarify in the caption of Figure 3.

Thanks for your comments. As you said, “the O/P ratios are more concentrated” mean that the O/P ratios for ARO1 are less variable than those for ARO2. The observed aromatic concentration data were collected at 14:00 local standard time every Thursday by gas chromatography–mass spectrometer at Beijing, Xinglong and Yucheng. Thus, the O/P ratios are also the observed to predicted ratios of aromatic compound concentrations at 14:00 LST every Thursday during the two analyzed episodes. We have added the detailed description in the caption of Figure 3 now.

Lines 253-254: Again, what did the authors mean by ’the ratios of ARO1 and ARO2 in episode 1 are more concentrated’? In general, ’concentrated’ appears to not be the appropriate word in this context.

Thanks for your comments. We have modified the description “more concentrated” as “less variable” in both Line 257 and 265.

Lines 265-266: ’Case 0 is the base example’. Please clarify what this means? Do the authors mean that Case 0 was the simulation with only the three default SOA formation pathways in CMAQ (i.e., without the aqueous uptake production)?

Thanks for your comments. As you said, “Case 0 is the base example” means that Case 0 is the simulation with the default SOA formation pathways in CMAQ. We have modified the description “Case 0 is the base example and was performed with the standard model” as “Case 0 is run with the three default SOA formation pathways included in the standard model” in Line 276-277.

Lines 269-270: What is the rationale for increasing the glyoxal yield from isoprene by 5? The authors did not mention this in the text up to this point. What was the original yield?

Thanks for your comments. As we explained before, the 5-fold increase of glyoxal yield from isoprene is based on the previous studies by Li et al. (2018). In that paper, we have discussed the possible reasons of glyoxal-underestimation in the model. Through the comparisons of both formaldehyde vertical column densities (VCDs) and the ratio of averaged glyoxal to formaldehyde VCDs between observation and simulations, we have concluded that glyoxal derived from biogenic precursors is underestimated and very likely results from the underestimated yields of glyoxal from biogenic precursors. Combined with previous studies (e.g. Lelieveld et al., 2008; Peeters et al., 2009; Stavrakou et al., 2009; Stavrakou et al., 2010; Li et al., 2016), we considered the underestimation possibility in glyoxal yields from isoprene degradations. However, there is no research about the special modifications of glyoxal yield in the mechanism. In order to evaluate the impacts of underestimated glyoxal yields from isoprene on glyoxal simulation, we decided to simply increase the product stoichiometric coefficient of glyoxal in SAPRC99. As shown in Fig. 2 of Li et al. (2018), the initial modeled glyoxal vertical column densities (VCDs) were generally underestimated by a factor between 2 and 10, we then boldly increased the stoichiometric coefficients of glyoxal from isoprene by a factor of 5 (a half of 10). Since the glyoxal is not the first but secondary degradation product of isoprene in the mechanisms, a 5-fold change may not be too large. As shown in Fig. 5c and d of Li et al. (2018), the better agreement between the observed and simulated glyoxal indicate the reasonable improvement on some level. Thus, in this manuscript, we directly follow the design in Li et al. (2018) (a 5-fold increase of glyoxal yield from isoprene) without no more analyses, and only simply illustrate by "By combining our results with those of Li et al. (2018)". Now, we add more detailed description in the manuscript. Even though, we have to admit that the changes exist large uncertainties and problems, especially the carbon balance. More work needs to be done in the future, but here, we just simply make an exploring test.

Lines 273-274: "The observed PM1/PM2.5 ratio of 0.77 (Xu et al., 2015) was used to convert the observed concentrations for comparison with the simulated results for PM2.5." Is this assumption appropriate for SOA? What are the evidences?

Thanks for your comments. The measured SOA concentration we can collect are from PM_1. In order to compare with the modeled results (in $PM_{2.5}$), we have to do some conversion to the observations. According to the advices of observed data providers, we use the observed $PM_1/PM_{2.5}$ ratio of 0.77 (Xu et al., 2015) , which is also measured by them during episode 2 (October 14 to November 14, 2014), to convert the observed SOA concentration in PM_1 to $PM_{2.5}$. It is a pity that they have no observed $PM_1/PM_{2.5}$ ratio for episode 1. We have to use the same ratio though there exist uncertainties

Lines 275-298 and Figure 4: The discussion here is confusing! The authors said that Case 0 (red lines in Fig 4) is the base case, which I assume is the simulated SOA from CMAQ from the simulation using the original emissions and using the standard SOA formation pathways. Why is it then, that the red lines in (a)(b) are different than those in (c)(d) and those in (e)(f)? Clearly there are some

misunderstandings. Please clarify. Also, if the red lines should be the same in (a)(c)(e) and in (b)(d)(f), the subplots should be combined to make comparison easier.

Thanks for your comments. The red lines in Figure 4(a, c, e) represent the results of case 0 during the episode 1 (June 3 to July 11, 2014), while the red lines in Figure 4(b, d, f) show the results of case 0 in episode 2 (October 14 to November 14, 2014). As we said before, there is a large bias between the observed and simulated SOA. In order to show the numerical value and the variable tendency of SOA concentration more clearly, we have used another Y-axis (the right one in all the panels) to show the results from the model. Due to the improvements of SOA simulations step by step, SOA concentrations during the same episode are different in three cases, resulting in the different scales on the right Y-axis in the panels. As a result, the red line drawn in Figure 4(a, c, e) are different though the values are not changed, so are the red lines in Figure 4(b, d, f). Besides, if we draw SOA concentration of case 0, case 1 and case 2 in the same panel, the variation tendency of SOA in case 0 and 1 will be not clear. Thus we decide to draw them separately. But now in order not to cause the misunderstanding again, we decide to combine the subplots in one panel as shown in Figure 4.

lines 310-312: "When the impact of the underestimation of glyoxal is taken into consideration in case 2, the mean concentration of AORGCJ in both episodes increases by nearly a factor of 2 relative to case 1" I do not see this in Figure 5. Please clarify.

Thanks for your comments. Figure 5 shows the mean fractional contributions of each constituent to the total SOA in the three sensitivity cases during episode 1 and 2. As shown in Figure 5, the fraction of dicarbonyl-derived SOA (AORGCJ) to SOA in case 1 and case 2 are comparable during both two episodes. However, the averaged SOA concentration is nearly doubled in case 2 relative to case 1, which is shown in Figure 4(c and e) and Figure (d and f). Thus, we conclude that “When the impact of the underestimation of glyoxal is taken into consideration in case 2, the mean concentration of AORGCJ in both episodes increases by nearly a factor of 2 relative to case 1." Now we have taken the uptake of dicarbonyls by aqueous aerosols into considerations, and the results have changed as "When the impact of the underestimation of glyoxal is taken into consideration in case 2, the mean concentration of AAQ in both episodes are higher than double that of case 1" (Line 327-329). AAQ has been used to represent dicarbonyl-derived SOA instead of AORGCJ.

Table 2, Figure 4 and the related text: This tables shows that the simulated SOA is nearly doubled in Case 2 relative to Case 1 during episode 1. However this is not at all obvious in Figure 4. Please revise or explain why?

Thanks for your comments. As we explained before, we have used another Y-axis (the right one in all the panels of Figure 4) to show the results of simulated SOA. As modeled SOA concentrations in case 2 is larger than that in case 1, the scales on the right Y-axis are different in case 1 and 2 during episode 1. One scale represents 3 μg/m^3 in Fig. 4(c) and 6 μg/m^3 in Fig. 4(e). There is no significant difference between the blue line (case 1) in Fig. 4(c) and the purple line (case 2) in Fig 4(e). Thus, SOA concentration of case 2 is nearly double that of case 1 during episode 1. Now we have taken the uptake of dicarbonyls by aqueous aerosols into considerations, and the results have correspondingly changed.

Figure 4: Missing the subplot labels (a), (b), ...(f). Also the colors of the lines in (c) and (d) are inconsistent and different from that in the legend.

Thanks for your reminder. We have added the subplot labels and uniformed the line colors as well as that in the legend now.

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Assessment of dicarbonyl contributions to secondary organic aerosols over China using RAMS-CMAQ

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Abstract

The concentration of secondary organic aerosol (SOA) is underestimated in current model studies. Recent research suggests that the aqueous uptake of dicarbonyls contributes to the production of SOA, although few models have included this pathway. Glyoxal, an important representative component of dicarbonyls in models, is significantly underestimated. We therefore incorporated the aqueous uptake of dicarbonyls into the regional air quality modeling system RAMS-CMAQ (the Regional Atmospheric Modeling System-Community Multiscale Air Quality) to evaluate the contribution of dicardonyls to SOA, and we then assess the impact of the underestimation of glyoxal on the production of SOA in China during two time periods: June 3 to July 11, 2014 (episode 1) and October 14 to November 14, 2014 (episode 2). When the aqueous uptake process was added, the modeled mean concentration of SOA in episode 1 increased by 3.65 μg/m^3, which explained 34.8% of the unaccounted source of SOA. Whereas the increase in the concentration of SOA in episode 2 was 1.82 μg/m^3 as a result of the lower liquid water content and the lower amount of dicarbonyls produced from biogenic precursors in the fall. On this basis, when the glyoxal simulation was improved, the modeled mean dicarbonyl-derived SOA (AAQ) increased by more than a factor of 2 in both episodes relative to case 1. AAQ in episode 1 contributed, on average, 61.0% of the total concentration of SOA and the increase in this contribution represented 70.0% of the unaccounted concentration of SOA, whereas the mean AAQ in episode 2 accounted for 64.5% of total concentration of SOA. Based on the results, the mean AAQ over China was generally higher in the east than in the west during the two episodes. The highest value (10–15 μg/m^3) of episode 1 appeared in the areas around the lower reaches of the Yellow River. Whereas the highest value of 5–10 μg/m^3 in episode 2 was concentrated over regions from south of the lower reaches of the Yellow River to the south of Guangzhou Province as well as the Sichuan Basin. The contribution of AAQ to the concentration of SOA in episode 1 varied from 10 to 90% throughout China, with the highest contributions (70–90%) in the coastal regions and offshore along the East China Sea to the South China Sea and in the southwestern regions. Whereas the fraction of AAQ to SOA in episode 2 was in the range of 10–80% over China, with the fraction up to 80% in a small portion of northeastern China.

Keywords: secondary organic aerosol, aqueous uptake, glyoxal, China, RAMS-CAMQ

1. Introduction

The fine particle fraction of aerosols ($PM_{2.5}$, i.e., particulate matter with an aerodynamic diameter ≤ 2.5 μm) not only absorbs and scatters sunlight in the atmosphere, resulting in a reduction in visibility and effects on the global climate (IPCC, 2007), but also has adverse effects on human health (Harrison and Yin, 2000;Poschl, 2005). Organic aerosol (OA) is a major component of fine particulate matter globally (Murphy et al., 2006;Zhang et al., 2007), typically making up 20–90% of the fine particle fraction (Roberts et al., 2001;Kanakidou et al., 2005;Zhang et al., 2007), suggesting that it has a significant effect on the characteristics and properties of fine particulate matter. Organic aerosols are formed from both primary (direct emissions) and secondary sources. Secondary organic aerosols (SOAs) are formed from precursors of volatile organic compounds (VOCs), which can be either natural or anthropogenic. However, the underestimation of organic aerosol has become a major issue in almost all current atmospheric models due to the incomplete representation of SOA (Heald et al., 2005;Morris et al., 2005;Morris et al., 2006;Goldstein and Galbally, 2007;Yu et al., 2008;Fu et al., 2009;Farina et al., 2010;Jiang et al., 2012;Zhang and Ying, 2012;Jo et al., 2013;Lin et al., 2016).

It has been reported that the concentration of SOA in the models is underestimated by one to two orders of magnitude (de Gouw et al., 2005;Volkamer et al., 2006). These results have motivated researchers to investigate why these models are predicting SOA concentrations so poorly. Traditionally, improvements in models have mainly concentrated on the gas-phase and derived heterogeneous formation processes, such as the formation of SOA from aromatic compounds under low- and high-NO_x conditions (Ng et al., 2007), the production of SOA from the oxidation of isoprene and its subsequent growth through acid catalysis (Kroll et al., 2005, 2006;Surratt et al., 2007), the use of volatile bias set method to depict the formation of SOA instead of the two-product model (Lane et al., 2008;Murphy and Pandis, 2009;Han et al., 2016;Lin et al., 2016), and the formation of SOA through the uptake of isoprene epoxides on the surface of aerosols (Ying et al., 2015;Hu et al., 2017). The gap has been closed to some degree through the SOA modeling efforts, but there are still large uncertainties (Tsigaridis et al., 2014).

Many studies have suggested that glyoxal and methylglyoxal can form SOAs through chemical reactions in cloud or fog water (e.g. Warneck, 2003;Ervens et al., 2004;Lim and Ziemann, 2005;Carlton et al., 2006;Loeffler et al., 2006), or by irreversible uptake on the surface of cloud droplets and aqueous aerosols (e.g. Liggio et al., 2005;Corrigan et al., 2008;Galloway et al., 2009;Ervens and Volkamer, 2010;Lim et al., 2010), which is probably a significant source of SOA (Ervens et al., 2014;Curry et al., 2018). A few studies (e.g. Carlton et al., 2008;Fu et al., 2009;Carlton et al., 2010;Lin et al., 2012;Li et al., 2013;Lin et al., 2014;Woo and McNeill, 2015) have incorporated aqueous SOA formation pathways into atmospheric models. Several of these studies have shown that chemical reactions in cloud or fog water make negligible contribution to near-surface SOA relative to irreversible uptake on the surface of cloud droplets and aqueous aerosols, and that the aqueous formation of SOA cannot completely explain the gaps between the observations and simulations. There are still considerable uncertainties in our knowledge of the formation of SOA.

A series of studies (Fu et al., 2008;Myriokefalitakis et al., 2008;Liu et al., 2012;Li et al., 2018) has shown that there is a substantial underestimation in the modeled vertical column densities (VCDs) of glyoxal, but few studies have considered the impact of this underestimation on simulations of SOA concentrations. Xu et al. (2017) and Ervens et al. (2011) showed that the aqueous formation of SOA depends on the liquid water content (LWC), which varies between seasons. Previous studies, such as those of Fu et al. (2009) and Li et al. (2013), have only considered the contribution from SOA derived from the aqueous uptake of dicarbonyls (pathway M) in the summer period or over evergreen areas. In this study, we not only incorporated pathway M into the RAMS-CMAQ (the Regional Atmospheric Modeling System-Community Multiscale Air Quality) modeling system to evaluate the corresponding contribution of dicarbonyls to SOA, but also improved the simulation of glyoxal concentrations by investigating the reasons for its underestimation and assessing its impacts on the concentration of SOA during the two episodes in the summer and fall of China.

2. Model and data

2.1 Base model description

Li et al. (2017a) used the RAMS-CMAQ modeling system to investigate the effects of underestimated aromatic VOC emissions and yields of SOAs from different gas precursors on the concentration of SOAs. Similarly, we used Version 4.7.1 of the CMAQ, which is coupled with the gas-phase photochemical mechanism SAPRC99 (1999 Statewide Air Pollutant Research Center (Carter, 2000) and Version 5 of the aerosol module (AERO5) (Byun and Schere, 2006;Foley et al., 2010). There are three major formation pathways for SOAs in this version, which is based on the two-product approach. The first pathway is the equilibrium partition of semi-volatile products formed from the oxidation of seven VOC precursors: long-chain alkanes, benzene (BNZ), high-yield aromatics (mainly toluene, ARO1), low-yield aromatics (mainly xylene, ARO2), isoprene (ISOP), monoterpene (TRP) and sesquiterpenes (SESQ). The second pathway is the oligomerization of semi-volatile SOAs formed through the first pathway (Kalberer et al., 2004), namely aging process. The third pathway is the formation of SOA via the in-cloud oxidation of glyoxal (GLY) and methylglyoxal (MGLY) (Carlton et al., 2008), both of which represent dicarbonyls in the model. The details of these formation pathways are given in Carlton et al. (2010).

The meteorological fields used to drive CMAQ are obtained from RAMS, which has been described in detail by Cotton et al. (2003). The National Centers for Environmental Prediction reanalysis datasets are served as the initial and lateral boundary meteorological conditions input into RAMS. The boundary conditions used for the RAMS computations include the weekly average sea surface temperature and the monthly measured snow cover. The final modeled results are output through the four-dimensional data assimilation mode using nudging analysis.

The emission sources are derived from several different inventories. Anthropogenic emissions (Li et al., 2017b)—including SO_2, NO_x, CO, black carbon, non-methane VOCs, organic carbon, NH_3 and other particulate matter—are obtained from the monthly emissions inventory of 2012. There are five emission sectors (the power, industrial, residential, transportation and agricultural sectors) in the inventory with a spatial resolution of 0.25° × 0.25° (see www.meicmodel.org). The Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2012) provides the biogenic emissions. The emissions from open biomass burning are derived from the Global Fire Emissions Database, Version 4 (Randerson et al., 2015), whereas the information of monthly lightning NO_x is obtained from the Global Emissions Inventory Activity with a spatial resolution of 1° × 1° (Benkovitz et al., 1996). The emissions of NO_x from the soil are derived from the Regional Emission inventory in ASia, Version 2.1, with a spatial resolution of 0.25° × 0.25° (Kurokawa et al., 2013). The online dust and sea salt emissions are calculated using the empirical model developed by Han et al. (2004) and the scheme of Gong (2003), respectively. The calculation of the model boundary conditions is supported by the Model of Ozone and Related Tracers, Version 4 (MOZART-4) (Emmons et al., 2010).

The model domain is divided into 105 × 86 grid cells with the center located at (35° N, 110° E) (Fig. 1). The map projection is rotated polar-stereographic with a horizontal resolution of 64 km. The vertical simulation region is unequally spaced from the ground surface to ~23 km. There are 25 layers in the σ_z coordinate system in RAMS, with nine layers located in the lowest 2 km to resolve the planetary boundary layer. The vertical dimension of CMAQ is divided into 15 layers, with the lowest seven layers the same as those in RAMS. We focused on the area outlined by the blue box in Fig. 1.

2.2 Adding the aqueous uptake process

There is a standard reaction probability formulation for reactive uptake of gases by aerosols and clouds in Jacob (2000). In this formulation, the first-order rate constant k for the chemical loss of a gas-phase species to the aerosols or cloud droplets through molecular diffusion and free collision is given by

$$k=\left(\frac{a}{D_g}+\frac{4}{v\gamma}\right)^{-1}A \qquad (1)$$

where D_g is the gas-phase molecular diffusion coefficient, a is the radius of the aerosol particle or cloud droplet, v is the mean molecular speed, γ is the reaction uptake coefficient when a collision occurs between a gas-phase molecule and the aqueous surface, and A is the aqueous particle surface area per unit volume of air.

We implement the aqueous uptake of dicarbonyls by cloud droplets following the standard equation (1). In a similar manner to Fu et al. (2008) and Li et al. (2013), the cloud droplet surface area is calculated from the LWC in the cloudy fraction of the model grid by assuming an effective droplet radius of 6 μm for continental clouds and 10 μm for maritime clouds. D_g is calculated according to Perry and Green (1999) following Dentener and Crutzen (1993). Similar to previous studies (e.g. Lin et al., 2014;Ying et al., 2015;Hu et al., 2017), the uptake of gas-phase dicarbonyls on aqueous aerosols is simply parameterized using the collision limitation ($v\gamma A/4$) of equation (1). The value of $\gamma = 2.9\times10^{-3}$ for glyoxal from Liggio et al. (2005) is used in both cloud and aerosol processing. While the uptake coefficient adopted for methylglyoxal is from De Haan et al. (2018): the average value of $\gamma = 5.7\times10^{-3}$ measured on cloud-processed glycine aerosols is used to account for the uptake by cloud droplets; the average value of $\gamma = 3.0\times10^{-3}$ used in aerosol processing is derived from the uptake coefficients measured on deliquesced ammonium sulfate aerosols (3.7×10^{-3}) and on deliquesced glycine aerosols (2.3×10^{-3}, median value).

2.3 Observational data

To assess the contribution of dicarbonyl species to the concentration of SOA, we used the observed hourly concentration of SOA in Beijing during the summer and fall of 2014 measured by Xu et al. (2017) with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer. Samples were taken from June 3 to July 11, 2014 (episode 1) and October 14 to November 14, 2014 (episode 2) at the Institute of Atmospheric Physics. More detailed information about the data has been reported by Xu et al. (2017). The simulation periods are from May 22 to July 11 and from October 1 to November 14, with the first 12 days as the spin-up time. To evaluate the reasonability in simulating the formation processes of SOAs in the aqueous phase, the corresponding cloud water path (CWP) data measured by the MODerate Resolution Imaging Spectroradiometer (MODIS) was also obtained from the website http://ladsweb.modaps.eosdis.nasa.gov/api/v1/productPage/product=MYDATML2.

Both Liu et al. (2012) and Li et al. (2018) have suggested that the underestimation of glyoxal concentrations in simulations is related to the underpredicted emission of aromatic compounds. Therefore, the biases in the emission of aromatic compounds needs to be evaluated through a comparison of the observed and simulated concentrations of aromatic compounds. The observed data were collected at 14:00 local standard time every Thursday by gas chromatography–mass spectrometer at Beijing, Xinglong and Yucheng (Fig. 1). Sun et al. (2016) and Wu et al. (2016) have presented the detailed information.

To evaluate the performance of our model, we also compared the simulated $PM_{2.5}$ concentrations and several meteorological factors with the results measured over 12 stations (Fig. 1) during the two episodes. The observed meteorological data were derived from the Meteorological Information Comprehensive Analysis and Process System (MICAPS) dataset, whereas the Chinese National Environmental Monitoring Center provided the measured concentrations of $PM_{2.5}$.

3. Results and discussions

3.1 Model evaluation

Table 1 shows statistical results of the meteorological parameters (i.e. temperature, relative humidity, wind speed and wind direction) and $PM_{2.5}$ concentrations in the two analyzed episodes, where: N is the total number of samples; IOA is the index of agreement, which can synthetically reflect the combination of the modeled value and variable tendency being good or bad (Willmott, 1981); C_{mod} and C_{obs} are the average values of modeled and observed results, respectively; MB and FB are the mean and fractional bias, respectively; RMSE and FE are the root-mean-square and fractional error, respectively; and R is the correlation coefficient between the observed and simulated results. The calculations of these statistical parameters can be found in Juda-Rezler et al. (2012). $P_{22.5^\circ}$ and P_{45° represent the proportions of compared results that the absolute biases between the simulated and measured wind directions are within 22.5° and 45°, respectively (Li et al., 2017a).

There are inevitably some biases in the simulated meteorological parameters relative to the observations due to the limited model resolution and system errors. Nevertheless, the model reproduces the magnitude and variation trend of the temperature and relative humidity fairly well (Figs. S1 and S2), with IOAs for temperature of 0.91 and 0.95 in the two episodes and IOAs of 0.91 and 0.88 for the relative humidity, comparable with the results of Li et al. (2012) and Wang et al. (2014). The mean biases of temperature (–0.83°C, –0.68°C) and relative humidity (1.53%, –0.05%) are small in the two episodes. The RMSEs of temperature and relative humidity are comparable with the results of Gao et al. (2016) and Zhang et al. (2012), implying a reasonable performance of the simulation. Although the capture of the variable tendency of wind speed (Fig. S3) by the model is rather poor, the small values for the mean bias (–0.40 and –0.22 m/s) and the high IOAs (0.61 and 0.69) indicate a better performance than that reported by Feng et al. (2016) and Wang et al. (2014) in simulating the wind speed. The RMSE of wind speed shows that the simulated results achieve the criteria for a good performance ($|\mathrm{RMSE}| \leq 2$ m/s) given by Emery et al. (2001). For the wind direction (Fig. S4), $P_{22.5^{\circ}}$ and $P_{45^{\circ}}$ are 32.12 and 54.52% in episode 1 and 34.01 and 57.41% in episode 2, indicating the reasonable simulation of wind direction. Therefore the model provides a reasonable meteorological field for the subsequent simulations.

The modeled $PM_{2.5}$ concentrations are generally higher than the observed values in the two episodes over the 12 stations (Fig. S5). Except for the limited resolution of the model, the uncertainties of the emission inventory and the effects of the background transport may also contribute to the overestimation. However, the correlation coefficients of $PM_{2.5}$ are 0.50 and 0.56 in the two episodes, respectively, and the IOAs are 0.64 and 0.70 in the two episodes, respectively, indicating good capture of the variable tendency and magnitude by the model. Both the fractional error and the fractional bias for $PM_{2.5}$ in the two episodes fulfill the performance criteria ($\mathrm{FE} \leq 75\%$, $|\mathrm{FB}| \leq 60\%$) given by Boylan and Russell (2006), implying a good performance in simulating $PM_{2.5}$. These results show that the model gives a reasonable simulation of the chemical species.

As described in Section 2.2, pathway M is related to the cloud water content. Thus the modeled and satellite-observed mean CWP were compared during the two analyzed episodes to evaluate the reasonability of the simulation results. Fig. 2a and 2b show that in episode 1, during one summer period, the highest observed CWP (400–500 g/m^2) mainly appears over the Yellow Sea and Bohai Sea and in parts of southeastern and southern China, whereas the observed second highest values (200–300 g/m^2) are concentrated in from the Qinghai–Tibetan Plateau to the North China Plain along the Yellow River Basin. The modeled high CWP (100–400 g/m^2) appears in the same regions as in the observational dataset. In episode 2, during one fall period (Fig. 2c and 2d), the observed highest (300–500 g/m^2) and second highest (200–300 g/m^2) CWP values are mainly concentrated in the Hetao area and the regions including the northeastern China and Inner Mongolia, respectively. The modeled values (50–150 g/m^2) are also high over these regions.

Overall, there are obvious biases in the numerical values between the observed and simulated CWP. This is a result of the large uncertainties in both the model simulations and the satellite retrievals of clouds, which lead to uncertainties in the simulations of the concentrations of SOAs.

However, the mean distribution patterns of the simulated CWP during the two episodes are similar to the observational results, indicating few impacts on the simulated distribution of SOA. Both the simulated and observed CWP in episode 1 are higher than in episode 2, also implying differences in the simulation of SOA between the two episodes.

3.2 Model results and analyses

As described in Section 2.3 and with reference to previous research, the underestimation of glyoxal concentrations may partly result from the underprediction of the emissions of aromatic compounds. It is therefore necessary to evaluate the emissions of aromatic compounds during the analyzed episodes before designing and implementing the model case studies. For this purpose, comparisons were made between the simulated and observed concentrations of aromatic compounds in a similar manner to the work of Zhang and Ying (2011).

Fig. 3 presents the ratio of the observed to predicted (O/P ratio) concentrations of aromatic compounds for the original emissions (Fig. 3a and 3c) and a three-fold increase in the emissions of aromatic compounds (Fig. 3b and 3d) during the two episodes. Fig. 3a shows that there are biases between the observed and simulated concentrations of aromatic compounds in episode 1 at the original emission rates of the aromatic compounds. The O/P ratios are less variable for ARO1 than for ARO2, with both the mean and median O/P values being close to 2. The range of O/P values is large for ARO2 and there is an order of magnitude difference between the lowest and highest ratios. Both the mean and median O/P ratios of ARO2 are about 20. These results show that there are underestimations in the emissions of ARO1 and ARO2. In view of the limitations of the amount of observed data and the nonlinear relationship between emissions and the concentrations (Li et al., 2018), the underestimation in the emission rates has been conservatively estimated to be a factor of three. As a result, when the emission rates of aromatic compounds are increased (Fig. 3b), the ratios of ARO1 and ARO2 in episode 1 are less variable, especially ARO2. The mean and median ratios of ARO1 are both around 1, whereas the two ratios for ARO2 decrease from 20 to 6. The results for episode 2 are similar to those in episode 1. Fig. 3c shows that the original O/P ratio of ARO1 varies between 1 and 3.5, with a mean value close to 2, whereas the ratio of ARO2 ranges from 1 to 5, with a mean ratio of about 4, both of which indicate unaccounted emissions of aromatic compounds. Fig. 3d shows a clear decrease in the biases of the observed and simulated concentrations of aromatic compounds. The O/P ratios of ARO1 and ARO2 are concentrated and vary between 1 and 2, with a mean ratio close to 1. However, it is difficult to determine whether the factor of 3 is the actual underestimation in the emission of aromatic compounds as a result of its dependence on space and time. For convenience, a factor of 3 is chosen here as a uniform scale with which to assess the unaccounted emissions of aromatic compounds.

Three sensitivity simulation case studies are designed based on these results. Case 0 is run with the three default SOA formation pathways included in the standard model. To avoid double-counting the loss of dicarbonyls through the in-cloud oxidation and the following formed SOA, the default aqueous formation pathway is turned off when run case 1 with the pathway M incorporated. According to previous studies (e.g. Stavrakou et al., 2009;Stavrakou et al., 2010;Li et al., 2016), the yields of glyoxal from isoprene are very likely to be underestimated. Li et al. (2018) has run a simple sensitivity case to evaluate the impacts of underestimated glyoxal yields from isoprene on glyoxal simulation. From their results, a better agreement has achieved between the observed and simulated glyoxal after a five-fold increase of glyoxal yields from isoprene. More detailed analyses can be found in Li et al. (2018). Thus, to take the effects of the underestimations of glyoxal concentrations into considerations, case 2 is designed with a three-fold increase in the emissions of aromatic compounds and a five-fold increase in the molar yield of glyoxal from isoprene based on the results of case 1.

Fig. 4 compares the hourly concentrations of the simulated and observed SOAs during the two analyzed episodes; the corresponding statistical parameters are listed in Table 2. The concentrations of SOAs are measured from PM_1. The observed $PM_1/PM_{2.5}$ ratio of 0.77 (Xu et al., 2015) was used to convert the observed concentrations for comparison with the simulated results for $PM_{2.5}$.

In case 0, the SOA concentrations in episode 1 (Fig. 4a) are significantly underestimated by an average factor of 5.7, with the differences being as high as a multiple of ≥ 60. As a result of the impacts of uncertainties in the meteorological fields and emissions, the variation trend of the concentration of SOA is not well captured by the model ($R = 0.21$). Similarly, although the variation of SOA is reproduced well in episode 2 ($R = 0.83$) (Fig. 4b), the concentration of SOA is still underpredicted by an order of magnitude. The biases between the observed and simulated concentrations of SOAs decrease in case 1 when pathway M is added to the model, especially in episode 1. It shows that the mean concentration of SOA in case 1 increases by 3.65 $\mu g/m^3$ during episode 1, explaining 34.8% of the unaccounted sources of SOAs. The decreased mean bias and RMSE and the slightly increased IOA also indicate the more reasonable descriptions of the formations of SOAs. In episode 2, the SOA formed through pathway M contributes less to the total concentration of SOA. The mean SOA concentration during episode 2 reaches 2.87 μg/m^3, increased by 1.82 μg/m^3. However, the decreased bias statistical parameters (e.g. RMSE and MB) also indicate the more realistic description of contributions of dicarbonyls to SOA in this episode. The larger contribution of dicarbonyls from pathway M to the concentration of SOA in episode 1 is attributed to the higher LWC and the larger amount of dicarbonyls produced from biogenic precursors in the summer than in the fall. When the impact of the underestimation of glyoxal on the concentration of SOA is taken into consideration, the concentration of SOA clearly increases in case 2. Compared to case 0, the mean concentration of SOA in episode 1 is significantly improved by a factor of 5.4 and comparable to the observations, whereas the increase in episode 2 is a factor of 6.2. The statistical parameters (e.g. IOA and RMSE) also show the better performance of case 2, indicating a more realistic and reasonable representation of the formation of SOA. Aromatic compounds are not only the precursors of glyoxal, but are also the precursors of SOA in the gas phase. A compositional analysis is therefore required to evaluate the individual contributions from dicarbonyls in case 2.

Fig. 5 shows the mean contributions from different sources of SOAs in the three sensitivity case studies during the two analyzed episodes. AAQ, dicarbonyl-derived SOAs, contributes little in case 0 during the two episodes. The mean contribution of AAQ to the total concentration of SOAs in episode 1 is 2.39%, larger than in episode 2 (0.89%). As a result of the greater amount of emissions from biogenic sources in summer, SOAs formed from biogenic precursors (AISOP+ATRP+ASQT) contribute more (26.3%) in episode 1 than that in episode 2 (13.5%), whereas the contributions from anthropogenic precursors (AALK+ATOL+AXYL+ABNZ) are comparable between the two episodes. When pathway M is included in the model, the contribution from AAQ to SOA in case 1 clearly increases and reaches 57.5% in episode 1 and 63.7% in episode 2. The significant contributions from AAQ in the two episodes indicate the major contributions from dicarbonyls through pathway M to the formations of SOAs in summer and fall. When the impact of the underestimation of glyoxal is taken into consideration in case 2, the mean concentration of AAQ in both episodes are higher than double that of case 1. In episode 1, AAQ (7.39 μg/m^3) accounts for 61.0% of the total SOA, exceeding the sum of the contributions from ARO1 (ATOL) and ARO2

(AXYL) (15.7%), and indicating the dominant contribution of aqueous-phase process to the concentration of SOA in summer. The increase in AAQ relative to case 0 compensates for about 70.0% of the unaccounted sources of SOAs. In episode 2, AAQ (4.17 μg/m^3) contributes 64.5% to the total concentration of SOA, which is also higher than the sum of ATOL and AXYL (15.3%), implying the dominant contributions of dicarbonyls to the concentrations of SOAs. The different contribution of AAQ in case 2 during the two episodes can be attributed to the different LWC and different amount of dicarbonyls produced from biogenic precursors.

It is clear that the biases between the observed and simulated concentrations of SOAs decrease when the contributions of unaccounted dicarbonyls to the concentrations of SOAs are considered, especially in summer. However, the sources of unaccounted SOAs cannot be explained completely. As a result of uncertainties in the description of known SOA formation processes and missing pathways that are not included in the model—for example, there are many uncertainties in glyoxal simulations (Li et al. (2018)). There are also many uncertainties in incorporating pathway M into the model, such as the effective radius of cloud droplets (the empirical values used instead of the actual values), the reaction uptake coefficient (updated values over disparate land surfaces are discussed in Curry et al. (2018)), and the liquid water content in clouds (the most uncertain parameter shown in Fig. 2). Other pathways for the formations of SOAs, such as the uptake of isoprene epoxides on the surface of aerosols (Lal et al., 2012;Lin et al., 2013), the aging mechanism of semi-volatile primary organic aerosols (Shrivastava et al., 2008) and the oxidation of primary semi- and intermediate VOCs, are not considered in this model. Besides, recent studies (e.g. Galloway et al., 2009;De Haan et al., 2018) have presented that the reactive uptake of glyoxal and methylglyoxal can be reversible, especially methylglyoxal, but we do not consider in this study.

To distinguish the contribution of dicarbonyls to the concentration of SOA over China in case 2 from that in case 0, the distributions of dicarbonyl-derived SOAs and their contributions to SOAs (AAQ/SOA) over China in cases 0 and 2 are analyzed.

Fig. 6(a, b) and 6(c, d) show the mean concentration of AAQ in cases 0 and 2, respectively, during the two episodes. For the base case, in episode 1 (Fig. 6a), the concentration of AAQ over China is ≤ 0.2 μg/m^3. The higher concentration of AAQ (0.1–0.2 μg/m^3) is in the areas between the lower reaches of the Yellow and Yangtze rivers and in the Sichuan Basin, probably due to the higher LWC and a greater number of sources of dicarbonyls over these areas, as discussed in Section 3.1 and by

Li et al. (2018). While in episode 2 (Fig. 6b), the concentration of AAQ is ≤ 0.1 μg/m^3 over the regions for the lower LWC and less sources of dicarbonyls from biogenic precursors. It is clear that the concentration of AAQ is improved in case 2, when pathway M is added and the impact of the underestimation of glyoxal is considered. Overall, the concentration of AAQ is higher in eastern China than in the west during the two episodes. In episode 1 (Fig. 6c), the concentrations of AAQ mostly vary from 2 to 15 μg/m^3 over central and eastern China, with the highest value (10–15 μg/m^3) concentrated in the areas over the lower reaches of the Yangtze river. The concentration of AAQ in western China is ≤ 1 μg/m^3, with the lowest value (≤ 0.1 μg/m^3) in the Qinghai-Tibet Plateau, probably because there are few sources of dicarbonyls. In episode 2 (Fig. 6d), the concentrations of AAQ is mostly in a range of 2–10 μg/m^3 over central and eastern China, with the highest value (5–10 μg/m^3) concentrated over regions from south of the lower reaches of the Yellow River to the south of Guangzhou Province as well as the Sichuan Basin. The concentration of AAQ in western China is also ≤ 1 μg/m^3, with the lowest value (≤ 0.1 μg/m^3) in the Qinghai-Tibet Plateau. Outside China, the highest concentration of AAQ (15-20) appears in the northeastern India due to more primary sources of dicarbonyls from the large scale of postharvest paddy residue burnings (Chandra and Sinha, 2016) and the barrier of precursor gases diffusions from Himalayan orogen as well as the low wind speed.

Fig. 6(e, f) and 6(g, h) show the spatial distribution of the mean AAQ/SOA in cases 0 and 2 during the two episodes, respectively. Fig. 6e shows that the AAQ fraction over China in episode 1 is ≤ 10%, except in Yunnan Province and some parts of the South China Sea, where AAQ/SOA reaches 10–20%. In episode 2 (Fig. 6f), the mean AAQ/SOA is ≤ 10% over the whole regions. When the contributions of dicarbonyls from pathway M and improved glyoxal to SOA are considered, there is a large increase in AAQ/SOA over these regions in two episodes. As shown in Fig. 6g, in episode 1, the contribution of AAQ to SOA varies from 10 to 90% throughout China. In central and eastern areas, the fraction of AAQ is generally in the range of 50–70% and up to 70–90% in the coastal regions and offshore from the East China Sea to the South China Sea. The fraction of AAQ in the west is relatively low and usually ≤ 50%. However, the contribution of AAQ to SOA is up to 80% in southwestern regions (e.g. Yunnan Province and parts of Sichuan Province). In episode 2 (Fig. 6h), the contribution of AAQ to SOA is in the range of 10–80% throughout China. In central and eastern areas, the fraction of AAQ is generally in the range of 50–70% and up 80% in a small portion of northeastern China. The fraction of AAQ in the west is also lower and usually ≤ 50%. However, the contribution of AAQ to SOA is up to 60-70% in a small part of Sinkiang Province.

4. Conclusions

The RAMS-CMAQ modeling system was used to assess the contributions of dicarbonyls from the aqueous uptake process and unaccounted sources of glyoxal to the concentrations of SOAs during the two episodes from June 3 to July 11, 2014 and October 14 to November 14, 2014. Comparisons between the observed and simulated concentrations of SOAs from three sensitivity groups showed different improvements in the SOA simulations with the inclusion of pathway M and consideration of the underestimation of glyoxal in the two episodes. Due to the high LWC and large amount of dicarbonyls produced from biogenic precursors in summer, the contributions of dicarbonyls were greater in episode 1 than that in episode 2. When pathway M was added in case 1, the modeled mean concentration of SOA in episode 1 increased by 3.65 μg/m^3, explaining about 34.8% of the unaccounted SOA sources, while there was a 1.82 μg/m^3 increase in the mean result during episode 2. When the impacts of glyoxal underestimation were taken into consideration in case 2, the modeled mean AAQ in episode 1 was improved to 7.39 μg/m^3 and contributed 61.0% of the total concentration of SOA. The increase due to AAQ relative to case 0 is equivalent to 70.0% of the unaccounted source of SOA. Whereas the mean concentration of AAQ in episode 2 was 4.17 μg/m^3 and accounted for 64.5% of total concentration of SOA. Although the contributions of dicarbonyls to SOAs are different in the two episodes, the simulated SOA results are both improved and close to the observations, indicating a more realistic description of aqueous formation of SOA.

The mean AAQ in case 2 during the two episodes was clearly improved over China relative to case 0 and was generally higher in the east than in the west. In episode 1, the highest value (10–15 μg/m^3) was seen in the areas around the lower reaches of the Yellow River. While the highest value (5–10 μg/m^3) in episode 2 was concentrated over regions from south of the lower reaches of the Yellow River to the south of Guangzhou Province as well as the Sichuan Basin. As a result, the contribution of AAQ to the concentration of SOA in two episodes was also improved in case 2. In episode 1, the fraction varied from 10 to 90% throughout China, with the highest contribution (70–90%) in the coastal regions and offshore along the East China Sea to the South China Sea in addition to the southwestern regions (e.g. Yunnan Province and parts of Sichuan Province). While in episode 2, the contribution of AAQ to SOA was in the range of 10–80% throughout China, with the highest fraction (up to 80%) seen in a small portion of northeastern China.

It is clear that the contributions of dicarbonyls from pathway M and the unaccounted sources of glyoxal make a significant contribution to the concentration of SOA, especially in summer. However, there are still many uncertainties in the depictions of aqueous uptake processes and sources of glyoxal. More work is needed on the parameters used in pathway M (e.g. the effective radius of cloud droplets and the reaction uptake coefficient), and to improve the accuracy of the modeled liquid water content in clouds.

Author contribution. In this study, J. Li designed the sensitivity experiments, developed the model code, and performed the corresponding simulations. M. Zhang co-designed the experiments and provided valuable advices about the model operations. Y. Sun carried out the measurements of SOA and provided the corresponding data for evaluating the modeled results. G. Tang and F. Wu carried out the measurements of aromatic compound concentrations and provided the corresponding data for evaluating the simulated results. Y. Xu provided valuable advice on model result analysis.

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Table 1. Statistics for the meteorological variables and PM$_{2.5}$ between the simulated and observed data during the two episodes.

Table 1-1

Variables	Episode	*N*	C_{mod}	C_{obs}	MB	RMSE	*R*	IOA
Temperature	1	10770	23.76	24.59	–0.83	2.58	0.86	0.91
(°C)	2	8391	12.68	13.36	–0.68	3.13	0.92	0.95
Relative humidity	1	10770	69.42	67.90	1.52	13.68	0.83	0.91
(%)	2	8389	62.81	62.86	–0.05	14.73	0.77	0.88
Wind speed	1	10770	1.78	2.18	–0.40	1.64	0.35	0.61
(m/s)	2	8391	2.05	2.27	–0.22	1.75	0.50	0.69

Table 1-2

Variables	Episode	*N*	C_{mod}	C_{obs}	FB (%)	FE (%)	*R*	IOA
PM$_{2.5}$	1	8091	64.04	47.90	13.35	64.61	0.50	0.64
(μg/m^3)	2	7649	86.25	61.67	36.00	62.27	0.56	0.70

Table 1-3

Variables	Episode	*N*	$P_{22.5^\circ}$ (%)	P_{45° (%)
Wind direction	1	10770	32.12	54.52
(°)	2	8391	34.01	57.41

N is the total number of samples; C_{mod} and C_{obs} are the average value of modeled and observed results, respectively; MB and FB are the mean and fractional bias, respectively; RMSE and FE are the root-mean-square and fractional error, respectively; IOA is the index of agreement; *R* is the correlation coefficient between the observed and simulated results; $P_{22.5^\circ}$ and P_{45° represent the proportions of compared results that the absolute biases between the simulated and measured wind directions are within 22.5° and 45°, respectively.

Table 2. Performance statistics of the modeled and observed SOA concentrations (μg/m^3).

Case	Episode	*N*	C_{model}	C_{obs}	MB	RMSE	*R*	IOA
0	1	822	2.21	12.69	–10.48	13.48	0.21	0.46
	2	737	1.05	17.69	–16.64	23.52	0.83	0.45
1	1	822	5.86	12.69	–6.83	10.86	0.25	0.49
	2	737	2.87	17.69	–14.82	21.21	0.84	0.50
2	1	822	12.03	12.69	–0.66	10.19	0.21	0.52
	2	737	6.53	17.69	–11.16	16.56	0.83	0.64

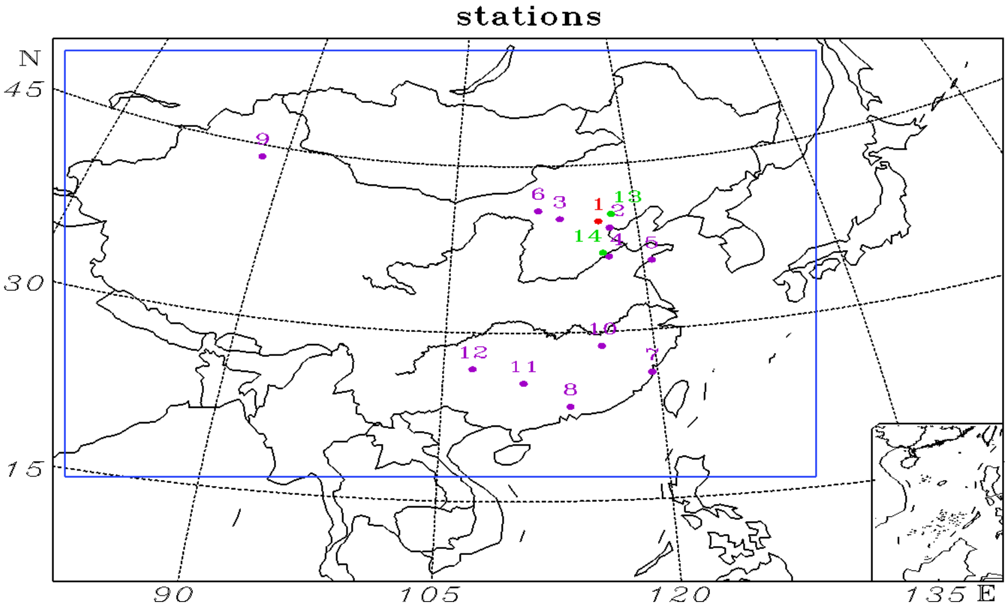


Fig. 1. Geographical locations of the measurement stations in the model domain. 1: Beijing; 2: Tianjin; 3: Datong; 4: Jinan; 5: Qingdao; 6: Hohhot; 7: Fuzhou; 8: Guangzhou; 9: Urumqi; 10: Nanchang; 11: Guilin; 12: Guiyang; 13: Xinglong; 14: Yucheng. The different colors denote which variables are compared at each station: purple: meteorological parameters; green: concentrations of aromatics; red: both meteorological parameters and aromatic compound concentrations.

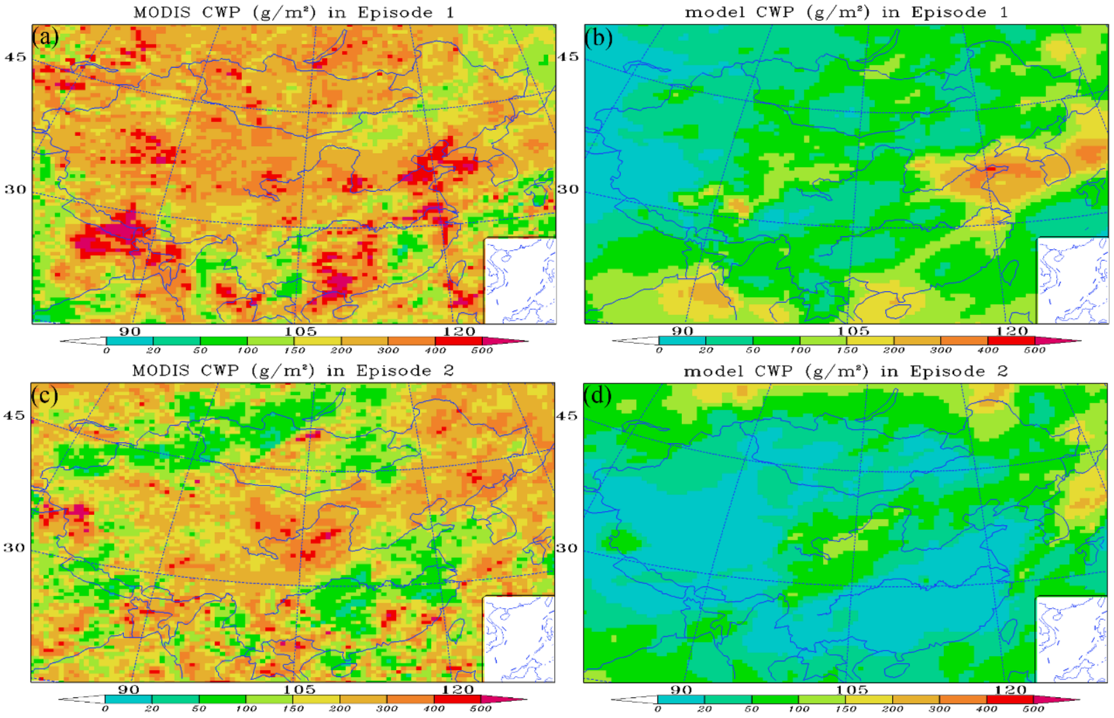


Fig. 2. Observed and simulated distributions of the mean cloud water path (CWP) during the two episodes (left-hand panels: MODIS observation; right-hand panels: results of simulations).

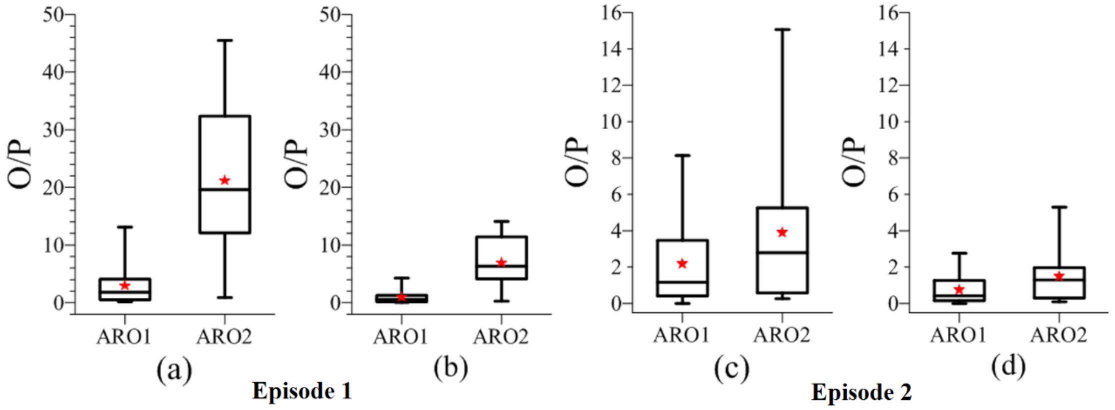
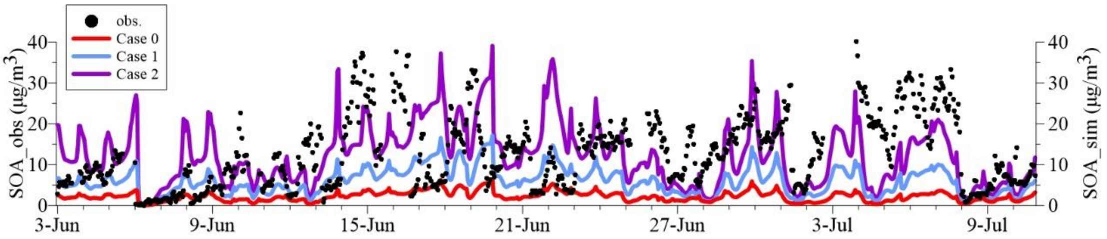
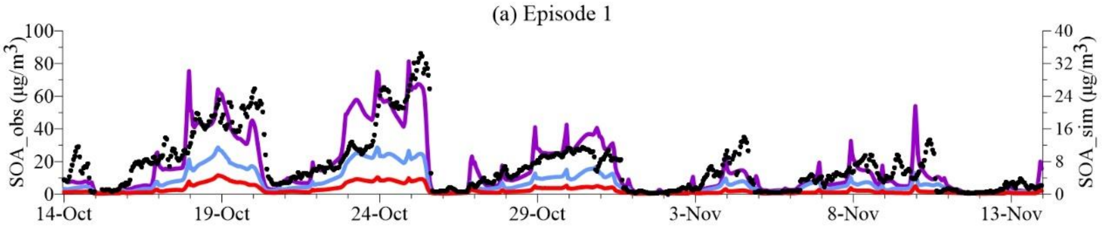


Fig. 3. Box-whisker plot of the observed to predicted (O/P) ratios of aromatic compounds during the two analyzed episodes. The observed data were measured at 14:00 LST every Thursday by gas chromatography-mass spectrometer at three sites (Beijing, Xinglong and Yucheng). (a, c): Original emissions of aromatic compounds; and (b, d): a three-fold increase in the emissions of aromatic compounds. The red stars show the mean O/P ratios.



(a) Episode 1



(b) Episode 2

Fig. 4. Hourly concentrations of the observed and simulated near-surface SOA concentrations in episode 1 (a) and 2 (b). Case 0 is base run; case 1 is run with the incorporation of the aqueous uptake of dicarbonyls (excluding the default in-cloud dicarbonyl oxidations); and case 2 is run with the glyoxal underestimation taken into consideration based on case 1.

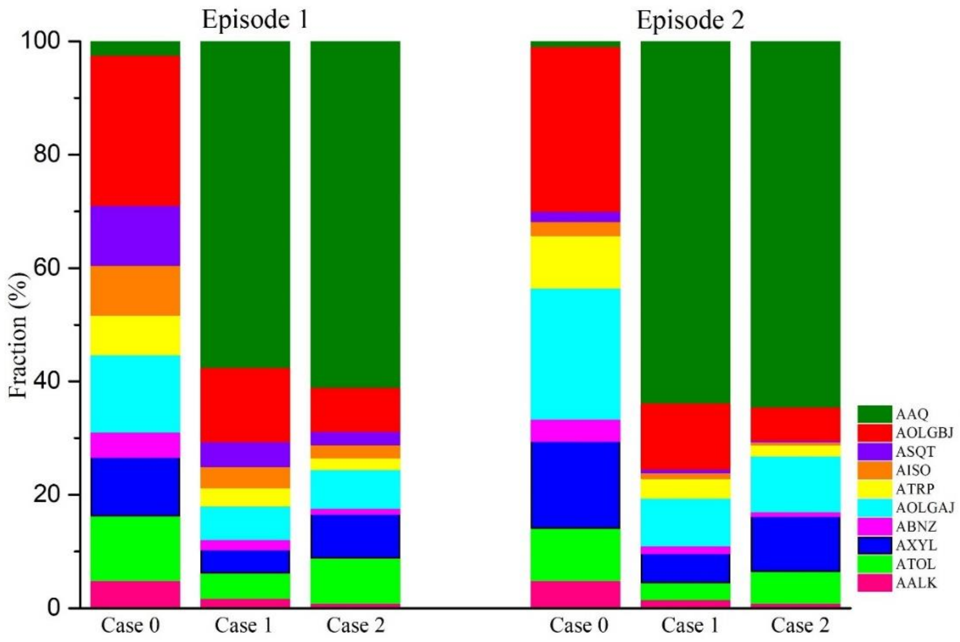


Fig. 5. Mean contributions from different sources of SOAs in the three sensitivity case studies during the two analyzed episodes. The compositions represent the SOA formed from long-chain alkanes (AALK), high-yield aromatic compounds (ATOL), low-yield aromatic compounds (AXYL), benzene (ABNZ), monoterpenes (ATRP), isoprene (AISO) and dicarbonyls (AAQ), as well as aged anthropogenic (AOLGAJ) and biogenic SOA (AOLGBJ). Case 0 is the base run; case 1 is run with the incorporation of the aqueous uptake of dicarbonyls (excluding the default in-cloud dicarbonyl oxidations); and case 2 is based on case 1, but taking into consideration the underestimation of glyoxal.

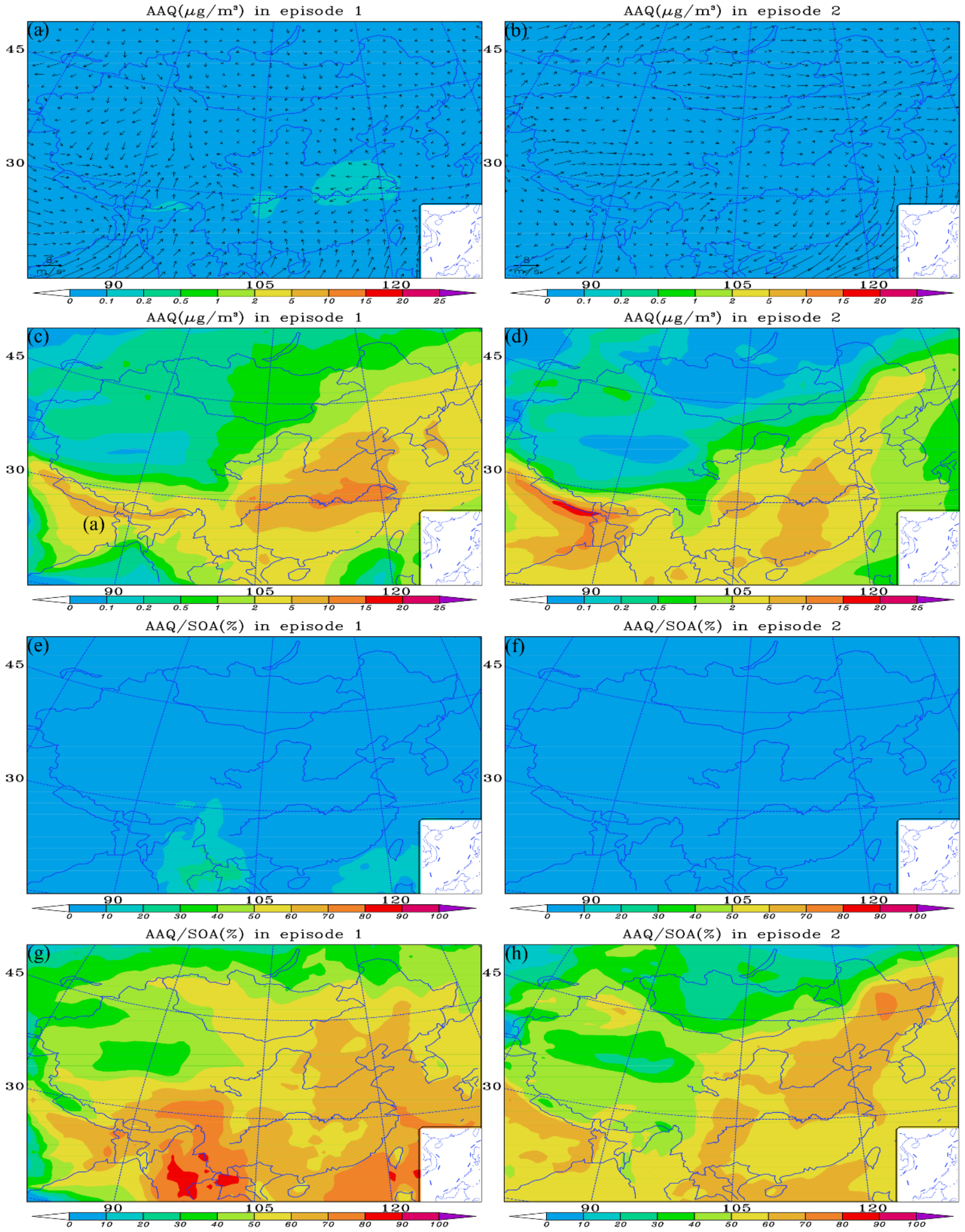


Fig. 6. Modeled distributions of the mean (a, b) wind field with SOA formed from dicarbonyls (AAQ) in case 0, (c, d) AAQ in case 2, (e, f) AAQ/SOA in case 0, (g, h) AAQ/SOA in case 2, over the regions during two episodes. Case 0 is the base run; case 2 is run taking into consideration the incorporation of the aqueous uptake of dicarbonyls (excluding the default in-cloud dicarbonyl oxidations) and the underestimation of glyoxal.