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Interactive comment on "Assessment of dicarbonyl contributions to secondary organic aerosols over China using RAMS-CMAQ" *by* Jialin Li et al.

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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 methyl-glyoxal 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." (shown 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 ($\nu\gamma A/4$) to account for the uptake loss of dicarbonyls by aqueous aerosols, and allocate fifteen

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percent of glyoxal and nine percent 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. Dg 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 (vγA/4) of equation (1). The value of γ = 2.9×10–3 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 γ = 5.7×10-3 measured on cloud-processed glycine aerosols is used to account for the uptake by cloud droplets; the average value of γ = 3.0×10-3 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 description (the 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 ($\nu\gamma A/4$) to account for the uptake loss of dicarbonyls by aqueous aerosols, and allocate fifteen percent of glyoxal and nine percent 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 $\times$ 10-3) for cloud-processed glycine aerosol at 99 $\pm$ 1

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

ments, 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 ($\nu\gamma A/4$) to account for the uptake loss of dicarbonyls by aqueous aerosols, and allocate fifteen percent of glyoxal and nine percent 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 response to RC1

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 implica-

tions 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.