

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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Received and published: 3 January 2019

Anonymous Referee 2 Received and published: 10 December 2018

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 sim-

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ulated 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 ra-

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tion 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

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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.

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(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 $\mu\text{g}/\text{m}^3$, 3 $\mu\text{g}/\text{m}^3$ and 6 $\mu\text{g}/\text{m}^3$ 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

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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.

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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; Stavrou et al., 2009; Stavrou 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

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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 PM1. In order to compare with the modeled results (in PM2.5), we have to do some conversion to the observations. According to the advices of observed data providers, we use the observed PM1/PM2.5 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 PM1 to PM2.5. It is a pity that they have no observed PM1/PM2.5 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

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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

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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 $\mu\text{g}/\text{m}^3$ in Fig. 4(c) and 6 $\mu\text{g}/\text{m}^3$ 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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