

Interactive comment on “Modeling Biogenic and Anthropogenic Secondary Organic Aerosol in China” by Jianlin Hu et al.

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Response to Anonymous Referee #1

Hu et al. present a regional modeling study for China in 2013 focusing on contributions to secondary organic aerosol (SOA). They consider some more recently recognized pathways to SOA such as heterogeneous uptake of epoxides, dicarbonyls, and oligomerization in addition to traditional semi-volatile SOA. SOA is classified in terms of its parent hydrocarbon source as well as precursor in different seasons across the domain. Model predictions of OC as well as precursor gases are compared to observations in select locations at select times and the model seems to perform reasonably.

Main comments 1. MGLY SOA: This work predicts a large role for methylglyoxal (MGLY) in forming SOA (23-28% of SOA), consistent with their previous work for the

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eastern United States (Ying et al., 2015). How well is this supported by laboratory and/or field work? Is the MGLY parameterization justified given that the uptake coefficient is based on glyoxal? More recent work by Marais et al. (2016) scaled the MGLY uptake coefficient to that of glyoxal using the relative Henry's law coefficient resulting in MGLY producing less than 1% of isoprene SOA. Mechanistic modeling by Woo and McNeill (2015) also indicate MGLY is not a dominant contributor to SOA.

Responses: Measurement of uptake coefficient of methylglyoxal on acidic particles has been reported by Zhao et al. (2006). While the effective Henry's law coefficient determined from that experiment is on the same order of magnitude as cited in Marais et al. (2016), the measured uptake coefficients for methylglyoxal was on the order of 7.6×10^{-3} , which is on the same order of magnitude as those of glyoxal on acidic particles. Assuming that the uptake coefficient can be scaled by effective Henry's law alone might be an over-simplification and has not verified experimentally. In the revised manuscript in Section 4.1, we mentioned the work of Marais et al. (2016) as well as Zhao et al. (2006) to inform the readers that significant uncertainties can exist in the uptake coefficient.

2. Biogenic vs anthropogenic carbon and POA vs SOA: This work's predictions of SOA indicate a significant fraction of SOA contains modern carbon as it comes from biogenic VOCs such as isoprene and monoterpenes. Total OA in the study is however dominated by POA (SOA is ~30% of total OA, Fig S5). Other recent work such as that of Zhao et al. (2016) indicates anthropogenic VOCs (specifically semi-volatile POA and IVOCs) are the major contributors to SOA in China. Can the authors reconcile their results with Zhao et al.'s results? Can the authors provide any insight as to why their large modern carbon contribution is more (or less) accurate than the anthropogenic VOC hypothesis? This affects your control strategy and which VOCs you might target (i.e. those important for OH interactions or those with low-volatility). Are there modern/fossil carbon measurements or POA/SOA proxies that can be compared with the model?

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Responses: The significance of modern carbon to SOA varies significantly from season to season. As indicated in Table 3, contributions of BSOA to total SOA varies from 24% (in winter) to 75% (in summer) based on average concentrations throughout the country. Zhao et al. (2016), however, estimated a much lower contribution of BSOA to total SOA.

Although Zhao et al. (2016) showed that the “high-yield” VBS model led to higher SOA predictions, it is unclear to the authors how the model handles the important contributions of glyoxal, methylglyoxal and isoprene epoxydiols to SOA formation. The typical reactive uptake approach does not fit the VBS modeling framework. The enhanced yields used in the VBS approach for anthropogenic emissions and IVOCs to improve the model prediction and observation of OA might lead to an overestimation of the importance of the anthropogenic contributions to SOA. A recent study reveals that in addition to primary emissions from coal burning, traffic-related exhaust and biomass burning, secondary PM (i.e. secondary organic matter and secondary inorganic matter) is an important if not a dominant contributor in 4 Chinese megacities of Beijing, Xi’an, Shanghai and Guangzhou during winter 2013 (Zhang et al., 2015). Non-fossil source contributes to ~60% of SOA or ~50% of OA. This obviously contradicts the conclusions of Zhao et al. (2006) that fossil-fuel sources always dominate the SOA budget throughout the country.

We included a short discussion on the potential contributions of the precursors/pathways in Section 3.1 in the revised manuscript on page 9.

3. While the figures are clear and nicely presented, there could be more synthesis of information in the figures. Figure 2 for example has different dates in each panel and different vertical axis limits as well. The last figure shows some synthesis by including a pie chart along with spatial distribution. Figure S2 (locations) would be best in the main manuscript. Figure 4-5 each have 24 subplots. While the information is useful and I don’t recommend removing it, it would be nice to have synthesis plots too. As an example, do underestimates in any of the precursor species correlate with

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underestimates in OC?

Responses: 1) Different axis limits were used to better illustrate variations in the concentrations – no changes were made regarding this point. 2) We moved Figure S2 to the main manuscript as Figure 1 3) We do not think multiple panel plot is a problem. It is the best way to illustrate the spatial distribution of different precursors and chemical components to SOA at different seasons. – no changes were made regarding this comment. 4) Unfortunately, we don’t have simultaneous measurement of VOC precursors and OC at any locations.

Other comments

4. Recent work by Marais et al. (2016) and Lin et al. (2016) indicate IEPOX SOA is mainly controlled via aerosol surface area which is linked to sulfate. The author’s mechanism of IEPOX uptake may capture this phenomenon and show a relationship with sulfate. Page 15, line 5 about the model not capturing the Xu et al. relationship with sulfate should be verified.

Responses: The reviewer might have misread the statement of page 15, line 5. That sentence simply pointed out that the model does not explicitly consider the effect of sulfate and nitrate on iSOA (although the acidity dependent uptake coefficient is partially related with sulfate concentrations). We change the word “modeled” to “included” in the revised manuscript.

5. Page 1, line 26 indicates SOA is highest in summer, but this seems very spatially dependent with winter perhaps having higher concentrations in a more localized area. Clarify.

Responses: We clearly mentioned that it is “generally” higher in the original statement. In the revised manuscript, the sentence in question was modified to include “, although the relative importance varies in different regions” to make it more clear.

6. Page 4, Model description section: Are these simulations the same as used by Hu

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et al. 2016?

Responses: Yes, the simulations are the same as used by Hu et al. 2016. – no changes were made regarding this comment.

7. Page 5, line 2: What CMAQ version served as the basis for this work?

Responses: The CMAQ version is 5.0.1. We have added the version information in the manuscript.

8. Page 6, 7 and for data in general, can you provide a latitude, longitude, and sampling altitude for observations? Will observational data be made available with this manuscript for future model evaluation?

Responses: The latitude and longitude of the site are 33.205 N and 118.727 E, and the sampling altitude is about 15m above the ground. The observational data will be available with the manuscript upon written request to the corresponding author.

9. Page 6, line 13: Is there a reference for the PAMS method?

Responses: A reference (Lonneman, 1994) was added for the PAMS method. Detailed description of the PAMS program, including sampling methods can be found from the US EPA's website <https://www3.epa.gov/ttnamti1/pamsmain.html>.

10. Page 6, line 28: Which species in particular are you referring to in terms of good olefin performance? OLE2 was quite high.

Responses: The model predicted higher OLE2 on Aug. 25 and Aug. 29-30, but for other days, the model predictions were in good agreement with observations. The model predicted higher OLE1 on Aug. 2-3, Aug. 8-12, and Aug.29-30, predicted lower OLE1 on Aug. 19-21, and model predictions were in general agreement on other days. We modified "good agreement" to "general agreement" in the revised manuscript.

11. Page 7, line 7: In light of potentially large vehicle contributions to isoprene mentioned here, in your work, is isoprene attributed entirely (or mostly) to biogenic sources?

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Responses: We checked the emissions in our study. Over the entire China most isoprene emission (> 99%) is from the biogenic sources, but in urban areas, there is some isoprene emission from vehicle sources. The BSOA we mentioned in the paper includes all isoprene SOA, as we didn't track the emissions of isoprene from vehicle sources separately from biogenic sources. This could lead to some overestimation of BSOA contributions, especially in the urban areas. A future study with carbon source tracking will determine the contributions of different sources of isoprene to iSOA. No changes were made in the manuscript regarding this comment.

12. Page: 8, line 25, regarding underestimated OC, what about potential missing SOA sources (such as IVOCs, etc)? What role may they play? See also main comment number 2.

Responses: The model underpredicted both EC and OC in Beijing during the first week of March. Missing IVOC could be a potential source of underestimation of SOA in our study, but we think some primary emission sources (which emitted both EC, POA and VOC/SVOCs/IVOCs) were missing during this period. We have added the discussion on the implications of IVOCs. Also, as we discussed in the manuscript, "POA provides the medium for the partitioning of SVOCs formed from oxidation of the precursors, and correctly predicting POA is necessary for correctly predicting SOA concentrations." Therefore, missing POA sources could also contribute to underprediction of SOA. Missing other SOA precursors in the study such as PAHs (Zhang and Ying, 2012) could also contribute to the OC under-prediction. Both field observations and detailed modeling studies are needed to close the gap between predicted and observed SOA concentrations. This discussion is included in the revised manuscript on page 9, lines 11-14.

13. Page 19, Table 1: How do ARO1 and ARO2 map to benzene, toluene, and xylene and their respective yields (as used in CMAQ v4.7 and later)? C* should be provided with the alphas.

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Responses: In SAPRC11 mechanism, Aromatics with $\text{kOH} < 2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ are lumped as ARO1, and Aromatics with $\text{kOH} > 2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$ are lumped as ARO2. Their yields were described in CMAQ5.0.1. C^* values are provided in the table in the revised manuscript. Emissions of benzene were lumped into ARO1.

14. Page 19, Table 1: This table indicates the aromatic alphas were increased 13% while the monoterpene alphas were increased 30%. Isoprene alphas were increased by 2.2x. These numbers are all consistent with the biases in high-NO_x SOA yields reported by Zhang et al. (2014). As Zhang et al. reported the bias in yield, it is the yield not alpha that should be increased which involves refitting the yield vs organic aerosol concentration data to get the new alpha and C^* parameters. Scaling the alpha alone results in an upper bound correction. The wall loss corrections have also been shown to be highly chamber specific (for example, Zhang et al. report two different toluene yield factors: 2.2 (their work) and 1.13 (another study)). Are the original parameterizations and the correction values from Zhang et al. from the same group/chamber? TERP yields in the original formulation match Carlton et al. (2010) and thus were a weighted contribution from different monoterpenes in the work of Griffin et al. (1999). Zhang et al. α -pinene+OH matches work from Chhabra et al. (2011). I suspect performing the proper correction to yield curves is unlikely to significantly change conclusions, but we should avoid propagating incorrect values.

Responses: We completely agree with the reviewer that C^* values should be recalculated along with the updates on the alpha values. In the revised manuscript, as commented by the reviewer, we noted that keeping the original C^* values likely provide an upper bound of the wall loss effect. The mass yields and C^* values used in CMAQ for toluene and xylene were based on the chamber experiments reported by Ng et al. (2007). The correction factor (1.13) provided in Table 1 of Zhang et al. (2014) are also based on these experiments. Terpene and isoprene yields in CMAQ were reported by Carlton et al. (2011), which were based on experiments reported by Griffin et al. (1999). Griffin et al. (1999) performed their experiments in 20 m³ Teflon chambers in

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Seinfeld's group at Caltech. Chhabra et al. (2011) conducted their experiment in 28 m³ Teflon chambers at Caltech, which are also operated by Seinfeld's group. Considering the factor that the chambers are similar in size and construction, and are operated by the same research group, using the correction factors derived by Chhabra et al. (2011) can be justified, lacking of reliable source of information. While the values used in this study can be debated, they are based on the best information we have currently. In the revised manuscript, the following paragraph is included:

"No changes of the saturation concentrations (C^*) of the products were made although the mass yields were updated. This partial correction only represents an upper bound estimation of the wall-loss effect. It should also be noted that while the correction factors proposed for aromatic compounds by Zhang et al. (2014) were based on the same chamber experiments that the CMAQ yields were based on, the correction factors for alpha-pinene and isoprene reported by Zhang et al. (2014) were based on a different set of chamber experiments. This could lead to additional uncertainties in the yields used in this study."

15. Page 22, Table 4, Simulation 6: Clarify that anthropogenic VOC, NO_x, SO₂, etc were removed (not just VOC, NO_x) Responses: Yes, all anthropogenic emissions were removed in simulation 6. A footnote is included to clarify this.

16. What is the major driver for how anthropogenic emissions affect SOA? Is it through POA? Responses: We indicated that the major driver is due to "reduced oxidation capacity of the atmosphere (i.e. lower OH during the day and NO₃ radical at night) that leads to slower formation of semi-volatile and oligomers as well as lower acidity of the aerosols that reduces the uptake coefficient of IEPOX thus less SOA." (page 15, lines 10-13).

References

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