

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

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Anonymous Referee #2 This manuscript presents in detail the predicted secondary organic aerosol in China by a regional CTM model. Model performance is evaluated by comparing the predicted VOC, EC, and OC concentrations to the observations at several urban sites. In general, the paper is well-written. However, it is well known that SOA is complex and the parameterization of various pathways is highly uncertain. There are limited discussion and sensitivity tests on the uncertainty of the presented pathways as well as the potential contribution of unaccounted pathways. The results of the paper are also lack of observational constraints. I suggest the following comments to be considered for revision.

Thank you for the comments to help improve the quality of the paper. We have revised

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the manuscript to address your comments and a detailed response to each comment is provided in this file.

Specific comments: (1) Uncertainty of SOA pathways: – GLY/MGLY uptake is found to a major contributor to SOA in this study. The simulation is however based on irreversible uptake, whilst some studies have shown the process may also be reversible (Fu et al., 2009). Large uncertainties remain in the uptake mechanism (Galloway et al., 2011). A short summary of laboratory findings is needed along with the discussion about the potential impact on the model predictions.

Responses: A few sentences were included on page 5, lines 1-3 to discuss this: “The treatment of GLY and MGLY SOA formation as an irreversible process provides an upper-limit estimation of SOA formation from these two precursors, as it has been reported that reactive uptake of GLY and MGLY can be reversible (Galloway et al., 2009) and dissolved GLY and MGLY can react with oxidants to form products with volatile products (Lim et al., 2010).”

– Isoprene seems extremely important given the predictions (contributing 61% in the summertime). The predicted isoprene however doesn't match well with the observations (seems being over-predicted). The fact that better agreements were found for MACR and MVK makes the case more complicated (i.e., possibly underestimation of OH). I think it is important to confirm that the predicted isoprene peak is not due to errors in the model. Either comparison to other locations with the same model or other model predictions using the same version of MEGAN is needed.

Responses: We have examined our model results carefully and believe that the isoprene peak is not due to errors in the model (i.e. emissions and meteorological conditions are normal). As we explained in the manuscript, due to the short lifetime of isoprene (~1-2 h) but longer lifetime of MACR and MVK (5-10 h), over-prediction of isoprene at one urban location does not necessarily mean MACR and MVK in the same grid cell must be overpredicted as well – as most of the MACR and MVK are

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likely from neighboring grid cells. It would be ideal if high resolution isoprene measurements were available at another non-urban location. No changes were made regarding this comment.

– The SOA predictions are lack of observational constraints. Intensive work has been done in major cities in China for example by AMS, which provides details about various OA types and estimates of the oxidation state (Hu et al., 2016; Huang et al., 2013; Sun et al., 2016). There are also off-line filter measurements, e.g., Yang et al. (2016) and He et al. (2014) for SOA tracers in China. Direct comparisons to such observations may be difficult to make, but rough comparisons may provide constraints to tell if the model predictions make sense, and if different studies are consistent. For example, the oxidation state of the OA as well as the organosulfate concentration may not support a high contribution of oligomers as well as GLY/MGLY/IEPOX SOA.

Responses: As the reviewer pointed out, a detailed comparison of these measurements is not possible because most of them were not made at 2013, and PM1 was measured and OOA was used as a surrogate of SOA in the AMS studies. We compared our results with the major findings in these studies and found the SOA/OA fractions in summer in our studies (50-70% in urban areas) is consistent with Huang et al (2013) (~68.3%) and Hu et al. (2016) (45-67%). Also, consistent findings were found that POA is more dominant in OA in winter in our study and in three AMS studies (Hu et al., 2016; Huang et al., 2013; Sun et al., 2016), although our estimation for the SOA/OA fractions in winter is lower than theirs. We included above comparisons in Section 3.2.1 in the revised manuscript and cited the references.

While we strongly agree with the reviewer that these measurements can be applied to provide constraint on model predictions, this is better done by comparing with local scale modeling studies with higher spatial resolutions and refined local emission inventories. More effort is needed to use them to ‘constraint’ the model – as no parameters in the current model and input data can be directly adjusted based on these spatially sparse measurements. In the revised manuscript, we pointed out the existence of such

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data on page 16:

“It should be noted that the reported SOA concentrations in this study have not been compared with direct measurements of SOA. More detailed measurements of organic components within the aerosol phase, such as the oxidation state measurements from aerosol mass spectrometers (AMS) (Hu et al., 2016) and tracer species representing SOA formation from precursor species (Yang et al., 2016), are becoming available in many areas in China. Future local scale SOA modeling studies can be conducted to better utilize these data as constraints on model parameters and input data.”

– How could the unaccounted processes change the predictions? For example, the conversion between POA to SOA (Robinson et al., 2007), the gaseous (Donahue et al., 2012) and heterogeneous aging of SOA (Kroll et al., 2015).

Responses: Additional studies are obviously needed to answer how these processes will change the SOA predictions. As the reviewer #1 pointed out and we have included in the revised manuscript, Zhao et al. (2016) included IVOCs, aging of POA and SOA, and found dramatic increase of OA concentrations due to these processes. In this study, we focus on the important contributions of glyoxal, methylglyoxal and isoprene epoxydiols to SOA formation, which have also been demonstrated in many studies. We are not sure how Zhao et al. handled these processes. Nonetheless, in both studies the model-measurement discrepancies cannot be fully solved, which could indicate that there might be other precursors/processes missing and merit more studies in this area. We acknowledge the potential contributions from the processes that the reviewer pointed out, and we included a short discussion in Section 3.1 in the revised manuscript.

(2) Page 4, Line 30-32: The isoprene SOA yield does not vary much for dry or wet conditions (Carlton et al., 2009) as well as solid or liquid seed particles (Kuwata et al., 2012). Acidity is a key factor that regulate the production of SOA from isoprene (Kuwata et al., 2015). In fact, the yields from Kroll et al. (2006) along with other chamber studies

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represent both contributions of traditional partitioning and reactive uptake, although the contribution of reactive uptake might be much smaller compared to acidic conditions.

Responses: Points taken but no changes were necessary regarding this comment.

(3) Page 5, Line 7: Which version of MEIC inventory (or the base year) has been used? Isn't MEIC only for the mainland China but not for the surrounding areas in East and Southeast Asia?

Responses: We used MEIC inventory V1.0 in our study for China emissions and used Regional Emission inventory in ASia version 2 (REAS2) (Kurokawa et al., 2013) for other countries and regions rather than China in the domain. This is clarified on page 5, lines 16-17.

(4) Descriptions about the observations are needed in Section 2, particularly for unpublished data. In Sect. 3.1.1., does the VOC data come from GC-MS measurements? What is the time resolution? Have the data been processed? For the EC/OC data, what is the time resolution? Are the data from different studies obtained and processed in the same way?

Responses: The VOC data were measured by GC-MS at an hourly time resolution. As stated in the manuscript, the measured detailed 54 VOC species were further lumped into the SAPRC11 (Carter and Heo, 2012) species for model comparison. The site information was also included and a reference was cited for the PAMS method in the revised manuscript (see the responses to reviewer #1's comment # 8 and #9). We provided more description of the VOC data in Section 2. Details of the EC/OC measurements are provided in the cited reference. All EC/OC measurements were daily data analyzed using thermal-optical EC/OC analyzer.

(5) Page 6, Line 24: What kind of measurement errors? Responses: We don't have any evidence, so we are not sure whether it is a measurement error or what kind of measurement error could lead to increase in many VOC species. This statement is

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removed in the revised manuscript to avoid conjecture with no evidence.

(6) Page 8, Line 13-15: This is somewhat misleading. EC can't represent all primary emissions.

Responses: While EC cannot represent all primary emissions, it does correlate with primary OC for most combustion sources quite well. The manuscript clearly states "primary OC" instead of "all primary emissions". In fact, the primary OC/EC ratio method is a well-known and widely applied technique to estimate POA and SOA split from total OC. No changes were made regarding this comment.

(7) Page 8, Line 30-35: It is well known that POC themselves can be semi-volatile and form SOA quickly (Robinson et al., 2007). I think the data are too limited to achieve a conclusion that POC or OC is well estimated by the model. Responses: The agreement of predicted with measured OC and EC at multiple sites in a few sampling periods in different seasons build confidence that model generally reproduced the concentration levels and daily variations of OC and EC, although OC or EC was underpredicted in a few high pollution episodes. The OC agreement does not directly prove that POC or SOC were predicted correctly (it could be a compensating between POC and SOC). The process that semi-volatile POC forms SOA would change the split of OC between POC and SOC, but likely would not change much of the 'carbon' concentrations. No changes were made regarding this comment.

(8) Page 9, Line 6-7: Please clarify whether the open biomass burning emissions contribute directly more SOA precursors or more POC that causes more gas-to-particle condensation.

Responses: Our analysis shows that large contributions from GLY, MGLY and IEPOX. Thus, this is directly related with large emissions of SOA precursors. This is clarified in the revised manuscript on page 9, lines 22-23.

(9) Page 10, Line 10-15: It is also because the aging of SOA is not considered in the

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model.

Responses: Thanks for pointing out this possible reason. We have added it in the revised manuscript.

Technical Remarks: Page 10, Line 10: “sptial” should be “spatial”.

Responses: This error has been corrected.

References: Carter, W. P. L., and Heo, G.: Development of revised SAPRC aromatics mechanisms. Final Report to the California Air Resources Board, Contracts No. 07-730 and 08-326, April 12, 2012. , 2012. Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, *Atmos. Chem. Phys.*, 9, 3331-3345, 10.5194/acp-9-3331-2009, 2009. Hu, W., Hu, M., Hu, W., Jimenez, J. L., Yuan, B., Chen, W., Wang, M., Wu, Y., Chen, C., Wang, Z., Peng, J., Zeng, L., and Shao, M.: Chemical composition, sources, and aging process of submicron aerosols in Beijing: Contrast between summer and winter, *Journal of Geophysical Research: Atmospheres*, 121, 1955-1977, 10.1002/2015jd024020, 2016. Kurokawa, J., Ohara, T., Morikawa, T., Hanayama, S., Janssens-Maenhout, G., Fukui, T., Kawashima, K., and Akimoto, H.: Emissions of air pollutants and greenhouse gases over Asian regions during 2000–2008: Regional Emission inventory in ASia (REAS) version 2, *Atmos. Chem. Phys.*, 13, 11019-11058, 10.5194/acp-13-11019-2013, 2013. Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys.*, 10, 10521-10539, 10.5194/acp-10-10521-2010, 2010. Yang, F., Kawamura, K., Chen, J., Ho, K., Lee, S., Gao, Y., Cui, L., Wang, T., and Fu, P.: Anthropogenic and biogenic organic compounds in summertime fine aerosols (PM<sub>2.5</sub>) in Beijing, China, *Atmospheric Environment*, 124, Part B, 166-175, <http://dx.doi.org/10.1016/j.atmosenv.2015.08.095>, 2016.

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