RESPONSE TO REVIEWERS

Ms. Ref. No.: Atmos. Chem. Phys. Discuss., 15, 32005-32047, 2015 (doi:10.5194/acpd-15-32005-2015).

Title: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the Southeast United States and co-benefit of SO_2 emission controls.

Journal: Atmos. Chem. Phys. Discuss.

Reviewer comments are in red. Responses are in black and include page and line numbers where changes are made to the accompanying manuscript (Marais_ACPD_2015_manuscript_with_ReviewerReponses.pdf).

Responses to Reviewer #1:

The manuscript by Marais et al. (2015) explores the SOA formation from isoprene in the Southeast using an aqueous phase SOA mechanism coupled to detailed gas chemistry. This mechanism is shown to capture measured IEPOX SOA well. SOA comprises a large fraction of total aerosol in the atmosphere. However, current models cannot fully reproduce its total mass and spatial and temporal evolutions. One potential reason for the model-observation discrepancy is that current models tend to neglect the SOA formation from aqueous phase, although both lab studies and field measurements have shown the importance of aqueous phase SOA. The manuscript is thus very useful for SOA community.

General comment

- *My major concern is that the paper seems to exclude the SOA formed from monoterpenes, one source that is comparable to the SOA formed from isoprene in Southeast USA (Xu et al., 2015). I am wondering how the missing monoterpenes SOA would affect the modeled OA and the comparison with measured OA.*

We now clarify on page 12, lines 260-266, that monoterpene and other SOA formation in GEOS-Chem is with the SOA formation scheme of Pye et al. (2010). GEOS-Chem underestimates total OA observed during SEAC^{4}RS due to too low anthropogenic and open fire SOA in the model (page 12, lines 267-268). The HCHO-OA approach to estimate isoprene SOA yields is independent of this underestimate.

- *In addition, the authors should clarify some important processes in the model (e.g., emissions of POA and aerosol depositions) that are important for the prediction of OA concentrations.*

We now point the reader to Kim et al. (2015) for a description of model treatment of aerosol wet and dry deposition and emission of POA (page 11, lines 253-254).

Specific comments

- *Page 32009, line 12-14. The references are not appropriate. Both Virtanen et al. (2010) and Song et al. (2015) showed that under dry conditions, SOA particles are semi-solid or solid phase, rather than liquid phase, which suggests that their formation processes deviate from the reversible partitioning of SVOCs, because mixing within the solid particles is very difficult.*

The text has been corrected (page 4, lines 87-89).

- *Page 32009, line 22-26. To date several models have been developed to estimate the amount of SOA formed in the aqueous phase from the regional scale to the global scale (e.g., Carlton et al., 2008; Myriokefalitakis et al., 2011; Liu et al., 2012; Lin et al., 2012; Pye et al., 2013; Lin et al., 2014). The authors should briefly discuss previous model efforts on aqueous phase SOA.*

This omission is addressed on page 4, lines 93-96.

- *Page 32011, line 6. Can the authors explain the unit of yield "7 mol%"? Why is there "mol" in the middle?*

We now clarify its use in the text (page 6, line 136).

- *Page 32011, line 24-27. Why did the authors change the yield of C5-LVOC reported by Krechmer et al. (2015)? Any scientific justification for this? Or just an arbitrary tuning?*

The yield in Krechmer et al. (2015) led to an overestimate in simulated C_5-LVOC relative to the observations. Lowering the yield improves agreement with the observations (page 7, lines 153-155).

- *Page 32014, line 14-16. Can the authors give a references for setting up the value of gamma to be 0.1? Or it is an arbitrary large number?*

Uptake of C_5-LVOC and NT-ISOPN is limited only by mass accommodation, α, set to 0.1 in this work (page 10, lines 223-224).

- *Page 32014, line 25-27. The reasoning is not convincing. First, although the aqueous phase concentrations are low in cloud water, the total amount of SOA produced in cloud is not necessary negligible, given that the cloud water content is usually larger than aerosol water content by 3-4 orders. Second, the mechanisms for aqueous phase SOA formation are different between in cloud water and aerosol water, due to the difference in aqueous-phase concentrations between them. Consequently, the major products in cloud water are carboxylic acids (e.g., oxalic acid), while major products formed from the reactions in aerosol water are oligomers (Ervens et al., 2011).*

We have amended the text to show that omission of SOA formation in clouds is supported by observations analyzed in the Wagner et al. (2015) study (page 11, lines 240-243).

- *Page 32015, line 1-2. How about the SOA formed in stratiform cloud or fogs?*

Stratiform clouds are within the "cloud layer" analyzed by Wagner et al. (2015). We have amended the text so that the statement is general to boundary layer clouds (page 11, line 243).

- *Page 32016, line 11-19. Not clear to me what aerosols were treated as aqueous particles. Did they assume only sulfate as aqueous particles? Or also included the OA (POA and/or SOA)?*

Aqueous aerosol is treated as sulfate. We have amended page 12-13, lines 276-288 for clarity.

- *Page 32013, Equation (2). How did the authors predict the concentrations of [nucl] and [HSO4-] in the model?*

GEOS-Chem uses the thermodynamic equilibrium ISORROPIA model to predict [nuc] and [HSO_4^-]. This is stated in the model description Section 3 (page 12, lines 270-272); the description of k_{aq} is general to current understanding of aqueous-phase IEPOX reactions.

- *Sec. 3 GEOS-Chem simulation and isoprene SOA yields. The authors should briefly describe how they treat the POA emissions and aerosol depositions in the model.*

Already addressed (see response to General Comments above).

- *Page 32020, line 5. "without bias" is over-stated. The model cannot capture strong IEPOX SOA peaks around June 25. The model also underestimates C5-LVOC SOA during June 18-20.*

Addressed to indicate that the model reproduces SOAS mean IEPOX SOA and C_5-LVOC SOA (page 17, line 382).

- *Sect. 5. Effect of anthropogenic emission reductions. Do the authors know the relative role of sulfate aerosol volume decrease vs. the aerosol acidity increase on the IEPOX SOA reduction? Which one is more important?*

Aerosol acidity and volume have a similar effect on IEPOX SOA, as SO_2 emission reduction reduces aerosol volume and aerosol acidity each by ~30%, and the rate of heterogeneous uptake of IEPOX to aqueous aerosol is dependent on the product of aerosol acidity ([H^+]) and aerosol volume (page 18, lines 406-409). A similar statement is now inserted in Section 5 (page 20, line 445-449).

- *Page 32023, line 9-11. This is not accurate and misleading. The traditional gas-particle partitioning model follows the Pankow (1994) absorption model, which assumes reversible partitioning to pre-existing humid OA, instead of dry OA. The problem lies in that this model was usually fit to the SOA yield data obtained from chamber studies performed under dry conditions, with very low relative humidity.*

SOA formation in GEOS-Chem using the Pankow formulation is dependent on the mass of pre-existing organic aerosol and does not account for additional mass from aerosol water (see Chung and Seinfeld, 2002; Griffin et al., 1999).

- *Figure 3. "OA mixing ratios" should be "OA mass concentrations.*

Amended.

References:

Chung, S. H., and J. H. Seinfeld, Global distribution and climate forcing of carbonaceous aerosols, J. Geophys. Res., 107, D19, 4407, 2002.

Griffin, R. J., D. R. Cocker II, and J. H. Seinfeld, D. Dabdub, Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, Geophys. Res. Lett., 26, 17, 2721-2724, 1999.

Kim, P. S., D. J. Jacob, J. A. Fisher, K. Travis, K. Yu, L. Zhu et al., Sources, seasonality, and trends of southeast US aerosol: an integrated analysis of surface, aircraft, and satellite observations with the GEOS-Chem chemical transport model, Atmos. Chem. Phys., 15, 10411–10433, 2015.

Krechmer, J. E., M. M. Coggon, P. Massoli, T. B. Nguyen, J. D. Crounse et al., Formation of low volatility organic compounds and secondary organic aerosol from isoprene hydroxyhydroperoxide low-NO oxidation, Environ. Sci. Technol., 49, 10330-10339, 2015.

Pye, H. O. T., Chan, A. W. H., Barkley, M. P., and Seinfeld, J. H.: Global modeling of organic 5 aerosol: the importance of reactive nitrogen (NO_x and NO_3), Atmos. Chem. Phys., 10, 11261–11276, 2010.

Wagner, N. L., C. A. Brock, W. M. Angevine, A. Beyersdorf, P. Campuzano-Jost et al., In situ vertical profiles of aerosol extinction, mass, and composition over the southeast United States during SENEX and SEAC4 RS: observations of a modest aerosol enhancement aloft, Atmos. Chem. Phys., 15, 7085–7102, 2015.