

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 SO₂ 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 #2:

In this study the isoprene aqueous SOA chemistry is considered and incorporated into the chemical transport model GEOS-Chem. The detailed formation pathways are successfully reproduced and their relative contributions to isoprene SOA are evaluated. The results of the sensitivity of isoprene SOA to the changes of SO₂ emissions will help make countermeasures against air pollution. I found that the study was conducted very well and the manuscript is written clearly. I have below specific comments that the authors should consider and implement in the revised manuscript.

Specific comments

1. *Following IUPAC recommendations, I would suggest terming Gamma as “reactive uptake coefficients”, rather than using “reactive uptake probabilities”.*

All instances of “reactive uptake probabilities” are replaced with “reactive uptake coefficients”.

2. *SOA particles are assumed as aqueous droplets in this study. Under low humidity of below ~50% RH, isoprene SOA were shown to be semi-solid or solid (Saukko et al., ACP, 12, 7517, 2012; Song et al., ACP, 2015), and in that case there will be strong kinetic limitations of gas-particle partitioning (e.g., Perraud et al., PNAS, 109, 2836, 2012; Shiraiwa & Seinfeld, GRL, 39, L24801, 2012). This study compared the simulated results with aircraft observations within the boundary layer. While as the altitude increases to the top of the boundary layer, particles might become semi-solid or solid upon decrease of temperature (e.g., Koop et al., PCCP, 13, 19238, 2011). Although investigation of particle phase is not a priority of this research, it would be very helpful to add some discussion, justification and potential bias of assumed liquid phase state for simulation uncertainties.*

The focus of this study is on isoprene SOA formation within the boundary layer (aloft OA formation is not significant; Wagner et al., 2015). Relatively humidity is sufficiently high in the boundary layer that it is reasonable to assume aerosols are liquid. We clarify this on pages 12-13, lines 276-281.

3. *Regarding eq (1): Gas-phase diffusion seems to be neglected, as gas diffusivity is not explicitly treated in eq (1). If this is true, this should be explicitly mentioned. Several studies have clearly shown that gas diffusion can play an important role in SOA growth (e.g., Tang et al., ACP, 14, 9233, 2014; Riipinen et al., ACP, 11, 3865, 2011). Please clarify and discuss.*

Gas phase diffusion is not neglected, but included in the gas uptake rate constant calculation (equation (3)). We clarify this on p. 13, lines 288-289.

4. *It would also be helpful to show the comparison of observed and simulated meteorological parameters (e.g., T and RH). They are related to particle phase determination; RH impacts the sulfate aerosol size distribution as shown in Section 3 and IEPOX sulfate formation (Liao et al., 2015); T impacts the isoprene emission as shown on Line 8, Page 32020, and meteorological parameters impact the prediction of chemical fields.*

We now compare average GEOS-Chem (GEOS-FP) and SEAC⁴RS values of relative humidity (page 13, lines 279-280). GEOS-FP temperature is 1.6 K higher than the observations, contributing to an overestimate in MEGAN isoprene emissions. Our interpretation of isoprene SOA yields from the relationship between OA and HCHO is independent of this overestimate (page 17, lines 371-377).

5. *In the Sect. 2, I suggest including discussion on uncertainties of k_{aq} and the potential impacts on the following simulated results.*

We now provide in Section 2 (page 10, lines 227-232) a discussion of the variability in reported values of k_{H^+} and k_{nuc} used to estimate k_{aq} and point the reader to Section 4 where we show that our choice of k_{H^+} and k_{nuc} is constrained with observations of total IEPOX SOA and IEPOX organosulfates.

6. *How much uncertainties are expected in column HCHO measured by OMI? (first paragraph of Section 4).*

We now provide an estimate on the error of satellite HCHO observations from the North America error analysis study by Millet et al., 2006 (page 16, lines 360-361).

7. *Line 19, Page 32020 says that the H⁺-catalyzed channel is a larger contributor compared to the sulfate channels. Is this result applicable to all of the simulated areas? How about the results for higher altitudes? As shown in Fig. 2, this study seems not to consider the reactions involving SO₄²⁻- leading to organosulfate formation. Will this impact the result that a direct role of sulfate in IEPOX SOA is not important? It is not clear for me whether the term of $k_{nuc}[nuc][H^+]$ in eq(2) already include organosulfate formation. Please clarify.*

We now clarify in the text that the 90% contribution applies throughout the Southeast US boundary layer (page 18, line 396).

We now state that the reactions in equation (2) lead to formation of methyltetrols in the case of H⁺-catalyzed reactions and organosulfates or organonitrates for the nucleophile channels (p. 9, lines 200-203). All reactions are included in GEOS-Chem, but IEPOX and sulfate are transported separately, due to their separate treatment downstream, e.g., optical properties for estimating AOD and photolysis.

8. *Aerosol pH seems to be very critical in simulating SOA mass due to an importance of acid-catalyzed reactions. pH is modeled based on ISOROPPIA. Do you have field measurements of aerosol pH and could it be compared with modeled pH? How much uncertainty would you expect in the modeled pH?*

Aerosol pH cannot be directly measured. A publication by Guo et al. (2015) that we reference in our work (page 12, lines 274-275) validated ISORROPIA prediction of pH indirectly using observations of ammonia, as its partitioning is sensitive to model prediction of aerosol pH.

9. *Page 32021, Line 5: will nitrate take similar effects as sulfate to increase aqueous volume and acidity?*

The Southeast US summertime aerosol comprises an order of magnitude lower nitrate than sulfate mass (page 12, lines 270, and Kim et al., 2015), so a change in aerosol nitrate mass concentration has little impact on aerosol volume. Our GEOS-Chem simulation of NO_x emission reductions illustrates that a 34% decrease in NO_x emissions, leading to a 32% decrease in aerosol nitrate mass concentration, has no impact on aerosol pH (Figure 7) and only a 6% reduction in aerosol volume that is in part due to the effect of NO_x on sulfate (Figure 7).

Technical Corrections

Technical corrections: - P32019, Line 4, Abad et al., 2015 is missing in the section of References.

The correct in-text citation, consistent with the reference list, is now provided (Gonzalez Abad as opposed to Abad).

References:

- Guo, H., L. Xu, A. Bougiatioti, K. M. Cerully, S. L. Capps, J. R. Hite Jr. et al., Fine-particle water and pH in the southeastern United States, *Atmos. Chem. Phys.*, 15, 5211–5228, 2015.
- 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.
- Millet, D. B., D. J. Jacob, S. Turquety, R. C. Hudman, S. Wu et al., Formaldehyde distribution over North America: Implications for satellite retrievals of formaldehyde columns and isoprene emission, *J. Geophys. Res.*, 111, D24S02, 2006.
- 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.