RESPONSE TO REVIEWER 3

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. Text edits are indicated with green highlighting in the revised manuscript.

Responses to Reviewer #3:

In this study, the authors developed a coupled aqueous-phase and gas-phase mechanism for isoprene oxidation. The mechanism was applied to simulate observations from SEAC4RS and SOAS using GEOS-Chem. The authors found that IEPOX and glyoxal are the main SOA precursors, the fates of both are dominated by gas-phase photooxidation and their uptake to aqueous aerosol is minor. The authors further explored the effects of reduced NOx and SO2 emissions on isoprene SOA.

This manuscript is generally clearly-written and the work would be of interest to atmospheric research community. The application of the coupled framework to simulate isoprene SOA formation in the SE US can provide substantial insights into the importance of various processed involved in the multi-phase chemistry.

My main concern is that there are a large number of parameters in the model and the uncertainties in these parameters are not recognized and discussed in the manuscript. However, these uncertainties could directly affect the conclusions of the manuscript. In this work, for many parameters, the authors simply chose a particular value reported in literature. The authors need to recognize that the experimental values for many of the parameters used in their model span a wide range. With this, it is not clear if the conclusions that the authors drew regarding aerosol formation in the SE US still hold if the authors were to choose another set of values other than those employed in the current study. Without a thorough evaluation of the uncertainties in the parameters, it is difficult for the readers to evaluate the robustness of the conclusions in the manuscript.

Specific comments

1. *There are multiple possible reasons for the overestimation of gas phase IEPOX. The uncertainties in the values of the parameters used in this study will directly affect the conclusions of the paper. For instance, on p32018 line 3, the authors argued that uptake is a minor sink competing with gas phase photochemical loss. And, on p32018 line 12, the authors argued that the aerosol reactive uptake probabilities (gamma) of IEPOX is controlled by acidity, but not driven by nucleophiles. All this could be correct; however, these conclusions could also be affected by the uncertainties in k's. If different values of k (instead of the values used in this study) are used, would their conclusions still be valid?*

We now acknowledge the uncertainties in model parameters on pages 10-11; lines 231-238 and also indicate that we chose k_{nuc} and k_{H+} to reproduce observations during SOAS and SEAC^{4}RS (page 18; lines 402-403).

a. *p32011, line 20, uncertainty in the kinetics of IEPOX oxidation by OH. As the authors correctly pointed out, the IEPOX lifetime varies from 8 to 28 hours for an OH concentration of 1e6 molecules/cm3 (Jacobs et al., 2013; Bates et al., 2014). In this study, the value from Jacobs et al. (2013) was used. Why? How did the authors determine that the value from Jacobs et al. (2013) is more suitable/accurate than the value reported in Bates et al., (2014)? If the value from Bates et al. (2014) were used, how would that change the conclusions of the current study? Given the large difference in the values reported by Jacobs et al and Bates et al., the authors need to clearly justify the use the of the value from Jacobs et al. and perform a sensitivity analysis using both values. It is not clear if their conclusions still hold if the values from Bates et al. (2014) were used instead.*

We use the Jacobs et al. (2013) to address a factor of 4 overestimate in gas-phase IEPOX reported in the Nguyen et al. (2015) study. This is clarified on page 7, lines 149-153. We now state that the conclusions still hold if the Bates et al. (2014) rate constant is used (page 15, lines 332-334).

b. *Henry's law constant: the reported value for Henry's law constant of IEPOX in literature spans two orders of magnitude (Chan et al., 2010;Eddingsaas et al., 2010;Gaston et al., 2014;Nguyen et al., 2014;Pye et al., 2013). In this study, the value from Nguyen et al. was used. The value of Henry's law constant will directly affect the relative importance of reactive uptake vs. gas-phase oxidation (and the conclusions of the manuscript). What is the justification of the use of the value from Nguyen et al. (instead of the values reported in other studies)? At this point, it is not clear what the true value of Henry's law constant of IEPOX is (it is difficult to judge from these prior work and determine which value is more accurate). With this, it is not clear whether the conclusions in this manuscript regarding the isoprene SOA formation mechanism still hold if other values for the Henry's law constant were to be used in their model.*

We have amended footnote (c) of Table 1 to instead indicate that our value is chosen to reproduce the SOAS and SEAC^{4}RS IEPOX SOA observations and turns out to be consistent with Nguyen et al. (2015). Discussion of variability in reported H^* is now included on page 11; lines 232-235.

c. *p32013, line 14, uncertainties in knuc: The rate of nucleophilic addition of sulfate was obtained from Eddingsaas et al. The authors need to recognize that in Eddingsaas et al, "the kso4 was not explicitly determined due to the complex nature of the solution" but evaluated by assuming the nucleophilic strength of sulfate is the same as nitrate. However, as demonstrated in Piletic et al. (2013), sulfate has stronger nucleophilic strength than other species (nitrate, water). Therefore, there is a large uncertainty in the value for knuc of sulfate used in this study. This uncertainty directly affects the relative importance of the nucleophilic addition of sulfate. The authors need to recognize and address the uncertainty in knuc and how this might affect their conclusions.*

The uncertainty is recognized and discussed on page 15, lines 340-342 and page 18, lines 410-411.

d. *Table 2. IEPOX gamma is only 0.01 when pH is between 0 and 1. This is one order of magnitude lower than the value measured in Gaston et al., which suggests the gamma calculation in the model may be wrong. This has implications regarding the major fate of IEPOX (uptake vs OH oxidation) and the conclusions of this manuscript.*

The difference is addressed on page 11, lines 238-240.

2. *Page 32018 line 5. The authors stated that "The model boundary-layer yield of IEPOX SOA from IEPOX is 5%, consistent with average yields from chamber experiments (4-10%) for aerosols with similar acidity to aerosols in the Southeast US (Riedel et al., 2015)". This comparison is incorrect. According to the results of this study, the major fate of IEPOX is reaction with OH in the gas phase in their model. Thus, the 5% SOA yield is mainly from IEPOX+OH reactions. However, the SOA yield reported in Riedel et al. is purely from IEPOX uptake. Therefore, the authors cannot compare the 5% SOA yield in their model to the results from Riedel et al.*

This statement has been removed.

3. *Page 32020 line 7. The low values of isoprene SOA on 2-7 July, 2013 are due to rain, instead of low temperature. In general, the organic aerosol loading was low during this period (Xu et al., 2015a, PNAS; Xu et al., 2015b, ACP).*

This statement has been removed.

4. *Page 32020 line 17. The authors stated that "Xu et al. (PNAS, 2015) concluded that IEPOX SOA must form by acid-catalyzed nucleophilic addition of sulfate (sulfate channels in Eq.2) leading to organosulfates". This is not a correct interpretation of the results in Xu et al. (PNAS, 2015). Xu et al. reported a strong association between Isoprene SOA and sulfate, and hypothesized that one possible explanation for this association might be the concerted nucleophilic addition to the IEPOX ring. Xu et al. did not conclude that IEPOX SOA must form by acid-catalyzed nucleophilic addition of sulfate.*

Text amended (page 18, line 397).

5. *Page 32021 line 1-3. These sentences are confusing. Please elaborate.*

To avoid confusion this paragraph has been removed and instead we provide a mechanistic explanation for the correlation between sulfate and IEPOX SOA on page 18; lines 401-402.

6. *Page 32022 line 19. Should this be pH, instead of aerosol [H+]?*

$[H^+]$ is correct here. SO_2 reduces aerosol sulfate leading to a decrease in aerosol $[H^+]$ and so a corresponding increase in pH.

7. *Figure 4 and Figure 5: The authors should add two scatter plots to the manuscript: 1) modeled vs. measured IEPOX SOA, 2) modeled vs. measured sulfate.*

Not clear what is the utility of a scatter plot. Figure 5 shows that the model reproduces the range in IEPOX SOA and sulfate observed during SOAS and SEAC^{4}RS.

References:

Bates, K. H., Crounse, J. D., St Clair, J. M. et al., Gas phase production and loss of isoprene epoxydiols, J. Phys. Chem. A, 118, 1237-1246, 2014.

Gaston, C. J., Riedel, T. P., Zhang, Z. et al., Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles, Environ. Sci. Technol., 48, 11178-11186, 2014.

Jacobs, M. I., Darer, A. I., and Elrod, M. J., Rate constants and products of the OH reaction with isoprene-derived epoxides, Environ. Sci. Technol., 47, 12868-12876, 2013.

Nguyen, T. B., Crounse, J. D., Teng, A. P. et al., Rapid deposition of oxidized biogenic compounds to a temperate forest, P. Natl. Acad. Sci. USA, 112, E392-E401, 2015.