

## ***Interactive comment on “Secondary organic aerosol from chlorine-initiated oxidation of isoprene” by Dongyu S. Wang and Lea Hildebrandt Ruiz***

**Dongyu S. Wang and Lea Hildebrandt Ruiz**

dywang05@utexas.edu

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An error was made in an example given as part of the response to question (5) by anonymous referee #2. The question, original author comment, and corrected author comment are shown below.

-Question 5, Reviewer: In the results and discussion, it would often be helpful, when possible, to give values in parentheses, rather than vague descriptors so that you don't require the reader to review and correctly interpret the graphs.

-Error in the original author response: “Lastly, considering the observed f82 value

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(~0.006) and that typically associated with IEPOX-OA factors (0.013~0.022) (Budisulistiorini et al., 2013; Krechmer et al., 2015), IEPOX-OA is estimated to contribute less than 0.5% to the total OA formed in these experiments. This suggests that the contribution of secondary OH chemistry to SOA formation initiated by chlorine radicals is minor.”

-Corrected author comment: By this line of logic, the maximum IEPOX-OA contribution to chlorine-isoprene SOA would be 50 % (not 0.5 %), which is unrealistic. We note that the observed f82 values (0.0055 to 0.0064) are lower than the average value observed for ambient OA that has been influenced by isoprene emissions ( $0.0065 \pm 0.0022$ ) (Hu et al., 2015), which would suggest that IEPOX-OA did not contribute significantly to SOA formation (Wong et al., 2015). In other chlorine-initiated SOA formation from biogenic volatile organic compounds experiments, the observed f82 values were in some cases as high as 0.005, which is close to the observed f82 values for isoprene-chlorine SOAs. Updated Figures 6 and 7 show that C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, which could produce C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> fragment within the ACSM, was observed as a gas-phase product. It is plausible that other biogenic SOA species would produce ion fragments at m/z 82 (C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> or other ions with the same integer m/z). A more detailed discussion on IEPOX and secondary OH chemistry is included in the revised manuscript.

Section 3.4, Pg.11 Line 32 – Pg.12 Line 11: “Another way to test the presence of IEPOX is to reduce aerosol pH, which should lead to increased uptake of IEPOX (Budisulistiorini et al., 2013; Gaston et al., 2014; Hu et al., 2015; Lin et al., 2012; Riedel et al., 2016, 2015). Comparison of ACSM mass spectra (see Fig. S13) suggests that the presence of acidic aerosol increases the contribution of ion mass fragments at m/z 82 (C<sub>5</sub>H<sub>6</sub>O<sup>+</sup>, “f82”) to the overall SOA mass, which is associated with IEPOX-derived OA (Budisulistiorini et al., 2013; Hu et al., 2015). However, the magnitude of change is low (0.001) and within uncertainty of the instrument. Interference by non-IEPOX-derived OA fragments and non-C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> ions at m/z 82 is also possible. Separate monoterpene-chlorine experiments observed f82 values as high as 0.005. The ob-

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served f82 values for isoprene-chlorine SOA are below the average value observed for ambient OA influenced by isoprene emission ( $0.0065 \pm 0.0022$ ) and much lower than IEPOX-derived SOA (0.0012 to 0.0040) observed in laboratory studies (Hu et al., 2015). We also attempted to but were unable to extract an IEPOX factor using positive matrix factorization (Ulbrich et al., 2009), as some studies have done (Budisulistiorini et al., 2013; Lin et al., 2012). Reduction in gas-phase products including those resembling IEPOX was also observed in the CIMS when the aerosol was acidic (see Fig. S14). These observations are consistent with increased partitioning of gas-phase products to the aerosol when the seed aerosol is acidic, resulting in the higher SOA concentrations shown in Fig. 1 and Table 1, but do not prove the presence of IEPOX-derived SOA.”

#### References

- Budisulistiorini, S.H., Canagaratna, M.R., Croteau, P.L., Marth, W.J., Baumann, K., Edgerton, E.S., Shaw, S.L., Knipping, E.M., Worsnop, D.R., Jayne, J.T., Gold, A., Surratt, J.D., 2013. Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown Atlanta, Georgia, using the aerodyne aerosol chemical speciation monitor. *Environ. Sci. Technol.* 47, 5686–5694. doi:10.1021/es400023n
- Gaston, C.J., Riedel, T.P., Zhang, Z., Gold, A., Surratt, J.D., Thornton, J.A., 2014. Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles. *Environ. Sci. Technol.* 48, 11178–11186. doi:10.1021/es5034266
- Hu, W.W., Campuzano-Jost, P., Palm, B.B., Day, D.A., Ortega, A.M., Hayes, P.L., Krechmer, J.E., Chen, Q., Kuwata, M., Liu, Y.J., De Sá, S.S., McKinney, K., Martin, S.T., Hu, M., Budisulistiorini, S.H., Riva, M., Surratt, J.D., St. Clair, J.M., Isaacman-Van Wertz, G., Yee, L.D., Goldstein, A.H., Carbone, S., Brito, J., Artaxo, P., De Gouw, J.A., Koss, A., Wisthaler, A., Mikoviny, T., Karl, T., Kaser, L., Jud, W., Hansel, A., Docherty, K.S., Alexander, M.L., Robinson, N.H., Coe, H., Allan, J.D., Canagaratna,

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- M.R., Paulot, F., Jimenez, J.L., 2015. Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements. *Atmos. Chem. Phys.* 15, 11807–11833. doi:10.5194/acp-15-11807-2015
- Lin, Y.H., Zhang, Z., Docherty, K.S., Zhang, H., Budisulistiorini, S.H., Rubitschun, C.L., Shaw, S.L., Knipping, E.M., Edgerton, E.S., Kleindienst, T.E., Gold, A., Surratt, J.D., 2012. Isoprene epoxydiols as precursors to secondary organic aerosol formation: Acid-catalyzed reactive uptake studies with authentic compounds. *Environ. Sci. Technol.* 46, 250–258. doi:10.1021/es202554c
- Riedel, T.P., Lin, Y.H., Budisulistiorini, S.H., Gaston, C.J., Thornton, J.A., Zhang, Z., Vizuete, W., Gold, A., Surratt, J.D., 2015. Heterogeneous reactions of isoprene-derived epoxides: Reaction probabilities and molar secondary organic aerosol yield estimates. *Environ. Sci. Technol. Lett.* 2, 38–42. doi:10.1021/ez500406f
- Riedel, T.P., Lin, Y.H., Zhang, Z., Chu, K., Thornton, J.A., Vizuete, W., Gold, A., Surratt, J.D., 2016. Constraining condensed-phase formation kinetics of secondary organic aerosol components from isoprene epoxydiols. *Atmos. Chem. Phys.* 16, 1245–1254. doi:10.5194/acp-16-1245-2016
- Ulbrich, I.M., Canagaratna, M.R., Zhang, Q., Worsnop, D.R., Jimenez, J.L., 2009. Interpretation of Organic Components from Positive Matrix Factorization of Aerosol Mass Spectrometric Data. *Atmos. Chem. Phys.* 9, 2891. doi:10.5194/acp-9-2891-2009
- Wong, J.P.S., Lee, A.K.Y., Abbatt, J.P.D., 2015. Impacts of Sulfate Seed Acidity and Water Content on Isoprene Secondary Organic Aerosol Formation. *Environ. Sci. Technol.* 49, 13215–13221. doi:10.1021/acs.est.5b02686

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