

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

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An error was made in the response to question (2) by anonymous referee #4. The question, original author comment, and corrected author comment are shown below.

Question 2.) Reviewer: PMF/ME-2 analyses of your SOA composition using the ACSM data:

As the authors likely know, Lin et al. (2012, ES&T), and more specifically Budisulistiorini et al. (2013, ES&T), demonstrated that AMS and ACSM, respectively, datasets can resolve IEPOX-OA factor when PMF is applied. Why didn't the authors consider con-

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ducting PMF in their analyses to constrain how much of the SOA is from IEPOX? You could run PMF with the IEPOX-OA factor constrained using the reference MS library (so this would be ME-2). Furthermore, Krechmer et al. (2015, ES&T) did this for the non-IEPOX SOA pathway. He used his reference mass spectrum for the non-IEPOX SOA to constrain its importance to field aerosol collected during the 2013 SOAS campaign! Riva et al. (2016, ES&T) also showed that authentic ISOPOOH makes SOA without needing IEPOX due to the low-volatility nature of the multifunctional hydroperoxides produced!

Since you don't use offline chemical analyses to measure molecular-level SOA components, I think it is worth while conducting PMF/ME-2 analyses to see if that can help constrain the different pathways yielding the total SOA mass. I hope the authors might agree with this suggestion.

-Error in the original author response: "We have attempted PMF analysis (without constraining factors) on these data but were unable to extract a factor related to IEPOX-OA. This is likely because the contribution of IEPOX-OA to total SOA mass from chlorine-initiated oxidation of isoprene, if present, is small. As mentioned in the revised manuscript, the observed f_{82} (the fraction of the total organic signal due to ions at m/z 82) is ~ 0.006 . Assuming that the IEPOX-OA factor would have an f_{82} value of 0.0132 based on the work of Budisulistiorini et al. (2013), the contribution of the IEPOX-OA to total OA in the present study would be at most 0.5%. It is considered infeasible to extract factors with such low contributions to total OA mass; for example, Ulbrich et al. (2009) suggest that only factors which contribute at least 5% to total OA mass can be extracted reliably using PMF."

-Corrected author comment: By this line of logic, the maximum IEPOX-OA contribution would actually be 50 % (not 0.5 %), which is unrealistic. We note that the observed f_{82} 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 ± 0.0022) (Hu et al., 2015), which would suggest that IEPOX-OA did not contribute significantly to SOA formation

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(Wong et al., 2015). In other chlorine-initiated SOA formation from biogenic volatile organic compounds experiments, the observed f_{82} values were in some cases as high as 0.005, which is close to the observed f_{82} values for isoprene-chlorine SOAs. Updated Figures 6 and 7 show that $C_5H_8O_2$, which could produce $C_5H_6O^+$ 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 ($C_5H_6O^+$ or other ions with the same integer m/z). A more detailed discussion is included in the revised manuscript.

Section 3.4, Pg.11 Line 32 – Pg.14 Line 13: “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 ($C_5H_6O^+$, “ f_{82} ”) 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- $C_5H_6O^+$ ions at m/z 82 is also possible. Separate monoterpene-chlorine experiments observed f_{82} values as high as 0.005. The observed f_{82} values for isoprene-chlorine SOA are below the average value observed for ambient OA influenced by isoprene emission (0.0065 ± 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.”

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