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Atmospheric Chemistry and Physics Discussions

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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We thank the referee for the suggestions and recommendations. Below are our responses to all comments.

1. Reviewer: Introduction: In motivating their laboratory study, the authors may wish to point out marine emissions of isoprene and the consideration of isoprene SOA from this source (e.g. Gantt et al 2010, Atmos. Environ.). The authors currently do not consider the potential for Cl oxidation of isoprene far from coasts (where NOx may also be low), which is a motivating factor for this work.

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Response: We have added discussions of SOA formation from marine emissions of isoprene, sources of halogen emissions, and Cl oxidation of isoprene in continental regions, to the introduction of the revised manuscript. While the model results by Gantt et al. (2010) suggest that contribution of marine isoprene emissions to coastal SOA (and O3) loadings are small, we note that the isoprene SOA yield used in the CMAQ model (3 % for low NOx) is lower than values (5∼15 %) reported in more recent literature (Krechmer et al., 2015; Liu et al., 2016; Riva et al., 2016). The inclusion of additional emissions of halogen species and findings from this work could reveal much greater contributions of coastal isoprene chemistry to total OA loading. The findings are also applicable to continental isoprene chemistry under low NOx conditions.

2. Reviewer: Throughout the manuscript, chlorine incorporated into organic molecules appears to be referred to as “chloride”, which chemically refers to Cl-, rather than chloro-organics, or organic chlorine. This reference to chloride is confusing as it makes the reader question whether the authors are indeed suggesting that inorganic chloride is present in the particle phase. This needs to be clarified throughout.

Response: In the context of chlorine-initiated oxidation of isoprene, the term (organic) “chloride” refers to the “-Cl” functional group in chloro-organics found in the condensed phase. To avoid confusion, we have changed all references to particulate organic chlorine to “organochlorides”. This is more in line with other categorizations such as “organonitrate” or “organosulfate”.

3. Reviewer: Sec 2.2, Instrumentation, should be clarified in the main text in terms of the description of the CIMS, for which additional information is needed. Perhaps material from the supplemental information should be moved here, in addition to revisions for clarity. It is stated that proton transfer, charge exchange, and clustering are all used for chemical ionization, which is confusing since typically one pathway is chosen through specific conditions within the ion molecule region of the instrument. As worded, it sounds like these reaction pathways of analyte ion formation are all occurring simultaneously.

Response: We have added some operational details about the CIMS and modified/clarified the original statement. Clustering is the chemical ionization mechanism within the ion-molecule reaction (IMR) region. Declustering can occur between the IMR and Time-of-Flight region and the resulting ion products may appear as if they were generated via proton transfer or charge transfer.

Manuscript changes in Section 2.2: "Reagent ions are generated by passing humidified UHP N2 over a methyl iodide permeation tube and then through a 210Po radioactive cartridge (NRD, 2013) at 2 LPM into the ion-molecule reaction (IMR) region operating at 200 mbar pressure. Analyte, "M" can undergo chemical ionization within the IMR:

(H2O)n(H3O+) + M → (H2O)n(MH+) + H2O (1)

(H2O)n(I-) + M → (H2O)n(MI-) (2)

depending on which ion mode is selected. The number of clusters, "n" ranges from 0 and 2 for (H2O)n(H3O+), with (H2O)(H3O+) being the most dominant reagent ion in the positive ion mode. Hydronium-water cluster CIMS was used to detect isoprene and select moderately oxidized species. For (H2O)n(I-) ionization, "n" ranges from 0 to 1, with I- being the most dominant reagent ion. Water-iodide cluster CIMS was used to detect select highly oxidized and acidic species (Aljawhary et al., 2013; Lee et al., 2014)."

Reviewer: It is also odd to me that the instrument doesn't seem to have been tuned for conditions of primarily H3O+, rather than (H2O)nH3O+. What fraction of the signal was associated with H3O+, and how many n were observed? This would impact the resulting analyte ionization. When were (H2O)nH3O+ vs (H2O)nI- reagent ions used? Did this switch back and forth during experiments, or was one ion chemistry used per experiment? Were CIMS experiments conducted during all experiments, or only during C3 and C5?

Response: The "hydronium CIMS" used here is different from PTR-MS in that signifi-

cant reagent ion clustering is still observed even after tuning. A drift tube replacement of the ion-molecule reaction region is required to decluster reagent ions and to generate primarily H3O+ (Yuan et al., 2016). In this work the dominant reagent ions were (H2O)(H3O+) (>70% of total reagent ion signals) and I- (>80%) in positive and negative ion modes, respectively. CIMS data were collected during most experiments listed in Table 1. We experimented with mode switching between negative and positive reagent ion modes, but it was ultimately impractical due to the time required for voltage discharge and signal stabilization following each mode switch.

4. Reviewer: Page 5, First Paragraph: Was a decrease in reagent ion signal observed compared to below an experiment? This might suggest a non-linear response and concern that reagent ion reactions could be limited even if still in excess. Without calibration of the signals, this would make trends more difficult to assess if in a non-linear regime. The phrasing on lines 5-6 about this is not clear.

Response: Reduction in reagent ion signal was observed in all photooxidation experiments. As described in section S3, the instrument response is still approximately linear when the reagent ion decrease is small, in which case normalization against the dominant reagent ion should correct for signal reduction. The demonstration of normalization error for large reagent ion depletion shown in section S3 was not performed for any particular set of experimental data, but rather for a simple hypothetical case.

Reviewer: Also, why wasn't at least isoprene calibrated for since each experiment started with a known mole ratio? It seems like that would be beneficial to this work and could probably even be done retroactively with knowledge of the experimental parameters. Was "significant depletion of reagent ion" (Page S3, Line 24) observed during any experiment?

Response: We have performed a few isoprene calibration experiments in positive mode, which were not reported here. A linear response was observed. Because complete isoprene depletion was achieved in every experiment and calibration experiments

showed a linear response, it was not deemed necessary to routinely calibrate for isoprene as isoprene concentrations can be calculated based on relative signal changes over the course of each experiment.

Larger reagent ion depletion was observed in negative ionization mode during some initial chlorine injection experiments, including experiments A5 and A8, where the initial Cl2 concentration is high. (H2O)n(I-) ionization is very sensitive towards Cl2. CIMS data from initial chlorine injection experiments were not used for qualitative interpretations.

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.

Response: We have added additional quantitative interpretations throughout the manuscript. For example, we have estimated the contribution of IEPOX-OA to the total OA mass: (f82 is the fractional contribution to organic aerosol mass from ions at mass-to-charge ratio 82; it is associated with IEPOX-OA factors, Budisulistiorini et al., 2013).

Manuscript changes in Section 3.4: "Lastly, considering the observed f82 value ($\sim$0.006) and that typically associated with IEPOX-OA factors (0.013$\sim$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."

6. Reviewer: Section 3.2 should either be moved after section 3.4 or moved to the supplemental information. This section does not contribute much to our understanding of Cl-SOA or precursors, as it primarily focuses on an issue with the ACSM method, which while important, doesn't seem to be the main focus of this work.

Response: During additional gas-phase CIMS data analysis we identified several chloroalkyl hydroperoxides that may be important for SOA growth. We have proposed reaction mechanisms and updated figures. Given this new context, we feel that the inclusion of section 3.2 is in line with the focus of the paper.

Reviewer: Rather than only identifying a potential issue, could a chlorinated organic standard be purchased and aerosolized for characterization so that the authors could provide a solution to the problem as well? Similarly, nearly a full paragraph in the conclusions is dedicated to this subject, which detracts from the exciting science studied. Also, use of m/z 36 here is not intuitive when referring to chloride.

Response: Issues with inorganic chloride or organochloride detection using ACSM and similar instrumentation (i.e. Aerosol Mass Spectrometer, "AMS") are well known. Our analysis presents evidence for particulate organochloride formation and suggests the cause of the quantification issue. It is beyond the scope of this paper to solve the issue. We plan to continue contributing to a resolution of this issue in future work on organochloride quantification including the use of standard compounds. While the representation may not be intuitive, the HCl+ ion appears to be a good proxy for particulate organochlorides.

7. Reviewer: Page 7, Lines 11-12: It is not clear, as written, if you then used a 2D model here.

Response: We did not run the 2-D model here. We added the following clarifying text,

Manuscript changes in Section 3.3: "Two-dimensional modeling would be more appropriate in these cases (Chuang and Donahue, 2016; Donahue et al., 2012; Murphy et al., 2012) but was not performed on this dataset."

8. Reviewer: Please review rules for significant figures for numbers and fix throughout. Please note that when reporting error only one significant figure should be used, with the same number of decimal places used for the average and the error.

Response: We have updated the significant figures and numbers

9. Reviewer: Can you compare ACSM mass spectra at different points during an experiment to examine possible evidence of oxidative fragmentation or vapor wall loss (as discussed on Page 7, Lines 18-19)? Could ACSM mass spectra be compared between experiments to examine the potential for differences in SOA composition?

Response: Most noticeable changes over the course of the experiment are observed at m/z 44 and m/z 43. The fractional contributions to the total organic mass by ions at m/z 44 ("f44") and 43 ("f43"), which are used to construct the triangle plot shown in Figure 3, can be used to estimate the oxidation state of carbon as described in section 2.3 and S2. The estimated SOA oxidation state and its trend are shown in Fig 2. Evidence of vapor wall loss is shown in Figure S1, where a decrease in SOA concentration was observed in the dark (in the absence of photooxidation effects). Additionally, we have conducted four new experiments using acidified seed particles. Comparisons of ACSM mass spectra between neutral vs. acidified seed aerosol experiments have been added to the revised manuscript/supplement (Fig. S9).

10. Reviewer: A conclusion of the study is that "The effects of SOA aging must be described explicitly and separately from initial SOA formation." (Page 9, lines 16-17) Yet, few details are given in the results and discussion for what this explicit description is. Above I suggested possible ways to provide greater mechanistic information on the Cl-isoprene oxidation and subsequent SOA formation.

Response: The purpose of the referenced statement was to reinforce the notion that a 1-D VBS framework cannot adequately describe SOA decay (due to fragmentation reactions) following SOA formation. The 2D-VBS model or more mechanistic frameworks are needed to describe that behavior. In this work, initial Cl2 injection experiments were performed to separate initial SOA formation from effects of vapor wall loss and fragmentation. We have added clarifications in the revised manuscript. As mentioned above in response to comment 6, we have proposed some reaction pathways that are

consistent with gas-phase observations, SOA formation, and organochloride detection to provide more mechanistic information on isoprene-chlorine reactions as suggested.

Manuscript changes in Section 3.4: “Multifunctional, low volatility hydroperoxides produced from non-IEPOX OH-isoprene reaction pathways under low NOx conditions have been found to contribute to SOA formation (Krechmer et al., 2015; Liu et al., 2016; Riva et al., 2016), and the same can be expected of the chloroalkyl hydroperoxide species identified in this work including C5H7ClO3 and C5H8Cl2O3.”

Manuscript changes in Section 4. “Initial chlorine injection experiment results show that initial SOA formation is followed by SOA decay, driven by oxidative fragmentation and vapor wall loss, which cannot be adequately described by a 1-D VBS model.”

11. Reviewer: Another conclusion of the study is “Similarities between chlorine-isoprene and OH-isoprene oxidation products suggest that air quality models may be able to lump the treatment of SOA produced from chlorine- and OH-initiated oxidation of isoprene.” Yet this is difficult to discern as very little discussion was dedicated to this important topic. There also appears to be no quantitative information that would indicate similar yields associated with various reaction pathways. More in-depth interpretation and discussion of the data is required to support this statement.

Response: Figure 5 shows that the chlorine-isoprene SOA yields are similar to OH-isoprene SOA yields under low NOx conditions. Figure 3 shows that the chlorine-isoprene SOA have similar f43 and f44 as OH-isoprene SOA, indicating that they are similarly oxidized. Many air quality models parameterize SOA formation using either constant yields or yields that depend on organic aerosol loading, for example, using 1-dimensional volatility basis set (VBS) parameterizations (Donahue et al., 2006) or 2-product models (Odum et al., 1996). A few models have also incorporated the OA oxidation state using 2D (or 1.5D) VBS representations (Donahue et al., 2011; Koo et al., 2014). In any case, most SOA modeling efforts focus on yields and oxidation state of OA, not the detailed chemical mechanisms. Considering that OA yields and

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oxidation state are similar for chlorine and OH-initiated oxidation of isoprene, the same 1D or 2D VBS parameterizations could be used to represent isoprene SOA formation initiated by these two oxidants. While there are some similarities in the types of product species observed (e.g. chloroalkyl hydroperoxides), detailed chemical models such as the master chemical mechanism would need to treat OH and Cl-initiated oxidation of isoprene separately considering the difference in reaction pathways. Much more work is needed to fully understand SOA formation from Cl-initiated oxidation of isoprene, and the continued atmospheric processing of OA, which is beyond the scope of this paper. This has been clarified in the revised manuscript, in which we now also offer recommendations for modelers on what yields to use for chlorine-initiated oxidation of isoprene.

Manuscript changes in section 4: "For air quality models which do not explicitly account for SOA aging and fragmentation reactions, the averaged SOA yield from continuous chlorine injection experiments should be used (8 %), which accounts for oxidative fragmentation effects in the atmosphere."

Manuscript changes in section 4: "Proposed reaction mechanisms and gas-phase measurements by CIMS show that Cl-initiated oxidation of isoprene could produce chloroalkyl hydroperoxide species, analogous to the formation of low-volatility hydroperoxides observed for OH-isoprene oxidation under low NOx conditions, which may explain the high yields observed."

Responses to minor comments

-Reviewer: Page 2, Line 11: It is unclear why Riedel et al 2012 is cited here, since that is a coastal marine study.

Response: This reference has been removed.

- Reviewer: Page 4, Line 12: It is confusing to have several equations on the same line. It would be preferable to have one equation per line and number as such.

Response: The equations are now individually numbered.

- Reviewer: Page 4, Lines 17-18: The words “low” and “high” are vague, and it would be useful to include at least approximate values in parentheses as well, for example, to aid in interpretation of these descriptors.

Response: The ratio of total organic aerosol loading to volatility bin saturation concentration is more important than the respective absolute values. When the ratio is 20, roughly 95% of the organic mass would partition to the particle phase (for that volatility bin). Further increase in the ratio would see diminishing returns in terms of SOA yield, and a maximum yield is achieved.

-Reviewer: Page 6, lines 4-5: This sentence states “high reactivity of chlorine radicals toward isoprene and its reaction products” and therefore seems to contradict the earlier sentence on page 5, lines 27-28.

Response: According to Orlando et al. (2002), the bimolecular rate constant of the isoprene-chlorine reaction is 4.3 $\pm$ 0.6 x 10-10 cm3 molecule-1 s-1, whereas the rate constants of the MVK-chlorine and MACR-chlorine reactions are 2.2 $\pm$ 0.3 x 10-10 and 2.4 $\pm$ 0.3 x 10-10 cm3 molecule-1 s-1, respectively. The earlier statement about high isoprene concentrations does not necessarily contradict high reactivity of chlorine with volatile organic compounds.

- Reviewer: Page 6, Line 10: The phrase “quantification proved to be difficult” is vague.

Response: This phrase has been removed.

- Reviewer: Page 7, Lines 13-14: I would suggest deleting this sentence, as the previous paragraph already explained this and having this information here as well could confuse the reader.

Response: This sentence has been removed.

- Reviewer: Page 7, Line 15: For clarity, I suggest adding the following to the end of

the sentence". . .literature values of OH oxidation under low and high NOx scenarios."

Response: We have edited the sentence as suggested.

- Reviewer: Page 7, Line 16: Why was the highest observed SOA yield reported, rather than an average, for example?

Response: The values reported in Table 1 are maximum wall-loss corrected SOA yield values from each experiment. These maximum values are then averaged to calculate the average yield value for all continuous chlorine injection experiments (average yield for initial chlorine experiments is calculated in a similar fashion separately from continuous experiments). The maximum SOA concentration coincides with the time of complete isoprene depletion for continuous chlorine injection experiments, which is used as a reference condition for reporting yields. This has been clarified in the revised manuscript.

- Reviewer: Page 7, Line 16: By "continuous cases", do you mean continuous Cl2 injection during an experiment? Make sure this is clear.

Response: Yes. Continuous cases refer to experiments during which Cl2 is continuously injected. This has been clarified in the revised manuscript.

- Reviewer: Hypochlorous acid is generally written as HOCl. I'm not used to ClOH, as written throughout.

Response: We have changed the representation to HOCl throughout.

- Reviewer: Page 9, Lines 1-2: This sentence is commenting on the method, more so than the science and could be moved to the methods section or supplemental.

Response: We have removed this sentence.

- Reviewer: Page 9, Line 16: It isn't clear why this sentence is needed to be highlighted in the conclusions.

Response: We have removed this sentence.

- Reviewer: Page 9, Lines 18-24: It would be useful to merge this short paragraph with the first paragraph of the conclusions section.

Response: We have merged the first and second paragraphs of section 4.

- Reviewer: Figure 3 caption: This figure does not explicitly show oxidation state as stated in the caption, which is misleading.

Response: The caption has been updated to clarify that the plotted parameters are often used as a proxy of the oxidation state.

- Reviewer: Figure 5 caption: For clarification, I suggest adding the phrase "corresponding to low and high NOx OH oxidation" at the end of the first sentence.

Response: We have clarified the caption as suggested.

- Reviewer: Figure 6 caption: It is not clear what is meant by "interfering ions" here.

Response: This figure and caption have been updated in the revised manuscript. In the discussion version of the manuscript, the figure caption should have read "(C5H10O3)H+ and interfering ions, (C5H8O2)H+ and (C5H11O3Cl)H+." referring to the possibility of (C5H10O3)H+ being a adduct product (C5H8O2)(H3O)+, or an ion fragment of another chlorinated ion.

- Reviewer: S1: Please provide references for this section of the SI.

Response: To our knowledge, the derivations shown are new. Starting equations are from works by Donahue et al. (2006)

- Reviewer: Page S3, Line 13: Why would instrument sensitivity change over time?

Response: Change in instrument sensitivity over the course of an experiment is caused by changes in the concentrations of reagent ions available for chemical ionization. Over time, instrument conditions may change, such as deterioration of the micro-channel

plate (MCP) or ToF pressures.

- Reviewer: Page S3, Line 16: k does not appear to be defined.

Response: "k" is the collision rate constant. This has been clarified in the revised manuscript.

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