

## Author's Response

We thank the referees for the suggestions and recommendations. Responses to all comments start on the next page. A marked-up version of the revised manuscript is attached at the end.

Responses to anonymous referee #1: Page 2-5

5 Responses to anonymous referee #2: Page 6-15

Responses to anonymous referee #3: Page 16-17

Responses to anonymous referee #4: Page 18-24

References: Page 25-31

Revised manuscript with mark-up: Page 32 and onwards

Major comments and responses.

(a) Reviewer: *p.5, line 1: The limitations of estimating O:C, H:C, and the oxidation state of carbon from  $f_{44}$  based on empirical correlations should be briefly discussed. For example, equation S-1 in section S2 may underestimate O:C values substantially in environments dominated by NO<sub>x</sub>-free isoprene chemistry (Canagaratna et al., 2015). Also, the presence of heteroatoms may introduce deviations from equation S-3 in section S2 when estimating the oxidation state of carbon (Kroll et al., 2011).*

Response: We have added a discussion of the limitations of the empirical correlation and ACSM data to the revised manuscript. We have also updated the equation labels. Equation S2 is now Eq.S10, and Eq.S3 is now Eq.S11.

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Section 2.3, Pg.6, Line 14-17: “The empirical correlations were derived using a comprehensive collection of Aerosol Mass Spectrometer datasets but may underestimate O:C values for SOA formed under low NO<sub>x</sub> conditions from isoprene or toluene (Canagaratna et al., 2015). Variability in  $f_{43}$  and  $f_{44}$  among different ACSMs have also been reported. (Crenn et al., 2015).”

15 Section S2, Pg.2, Line 8-10: “Deviation from Eq. (S11) could occur due to the presence of peroxide groups or heteroatom groups (Kroll et al., 2011), such as chloroalkyl hydroperoxide compounds identified in CIMS measurements.”

(b) Reviewer: *p.5, line 13: The separation of experiments A1-A5 and experiments H1/H2 seems to be somewhat arbitrary. In my opinion, experiment H1 should be experiment A6, and the much higher maximum yield of this experiment should be part of the discussion of section 3.3. Experiment H2 is a technical experiment to “...explore the ability of the ACSM to detect organic chloride” (supplement, section S4). I was confused to find information about H2 in Table 1, and I recommend to remove it from the table and just explain the character of this experiment in the supplement.*

25 Response: We agree with the referee’s recommendation. We have re-designated Exp. H1 as Exp. A8 and have conducted two additional initial chlorine injection experiments which are now designated as A6 and A7. Experiment H2 is now designated as Exp. S1. Experimental details for Exp. S1 are now described in-text within supplement section S4.

(c) Reviewer: *p.5, line 21: Chlorinated organic compounds have also been identified in ambient aerosol samples from Western Australia by ion cyclotron mass spectrometry (Kamilli et al., 2016), with a higher abundance of chlorinated organic compounds in daytime samples when photochemistry is active.*

30 Response: References to this work have been added to section 1 and section 3.2.

d) Reviewer: p.7, line 19: *The VOC:Cl<sub>2</sub> ratios may be expected to be much higher under atmospheric conditions than in the presented experiments. Do the authors have some insight, or could they speculate about how the yields may change for larger isoprene:Cl<sub>2</sub> ratios? Also, when presenting the highest observed SOA yields, why do the authors exclude experiment A1 for the average yield of the initial injection experiments?*

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Response: We have added discussion on a potential correlation between the VOC:Cl<sub>2</sub> ratio and SOA yields, as well as details that may be of interest to modelers. The yield calculated from experiment A1 was in fact used in calculating the average initial chlorine experiment SOA yields in the discussion paper. The text “A2-A5” was a typographical error and has now been corrected to “A1-A5.” Based on new calibration results we have also updated the relative ionization efficiency (RIE) values used in ACSM data analysis, which resulted in lower calculated yield values.

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Section 3.3, Pg.9, Line 23-32: “Under atmospheric conditions, the isoprene-chlorine ratio will usually be higher than ratios used in these experiments. Previous studies on chlorine-initiated SOA formation from toluene (Cai et al., 2008) and limonene (Cai and Griffin, 2006) suggest that SOA yields decrease with higher VOC-to-Cl ratio. While we do not observe a clear correlation between SOA yield and isoprene-to-chlorine ratios used here (0.5-1.2), such dependence could be present over a wider ratio range. For air quality models which do not explicitly account for fragmentation reactions, the use of the average continuous case yield, which is similar to recently reported OH-oxidation yields (Liu et al., 2016; Xu et al., 2014), is more appropriate because the isoprene-to-chlorine ratio is closer to atmospheric conditions and because the SOA yields from continuous injection experiments account for effects of OA aging in the atmosphere (which occur throughout the experiments). The presence of acidic aerosols and inclusion of particulate chlorine content would increase expected yields.”

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e) Reviewer: p.8, line 8: *When discussing secondary OH chemistry, the authors mention potentially unidentified HO<sub>x</sub> production pathways other than HO<sub>2</sub> production during formation of CMBO. It would be extremely interesting to have at least a semi-quantitative estimate of the contributions of chlorine-initiated secondary OH chemistry vs. OH chemistry from other sources, potentially also due to chamber wall effects.*

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Response: We have carried out some chamber box modeling and expanded the discussion of HO<sub>x</sub> chemistry. Model results show that chlorine chemistry accounts for the majority of HO<sub>2</sub> production when sufficient isoprene is present. Overall, chlorine radicals consume over 99% of the isoprene. Oxidation of isoprene by OH radical has very minor contribution in these experiments.

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Section 2.1, Pg. 3 Line 29–Pg.4 Line 2: “Background effects have been quantified using chamber characterization experiments (Carter et al., 2005) and the SAPRC chamber modeling software (<http://www.engr.ucr.edu/~carter/SAPRC/>) in combination with the Carbon Bond 6 (CB6r2) chemical mechanism, which was modified to include basic gas phase inorganic chlorine

chemistry in addition to Cl<sub>2</sub> and ClNO<sub>2</sub> photolysis (Sarwar et al., 2012; Yarwood et al., 2010). NO<sub>x</sub>-offgasing is represented within the model by a constant emission of nitrous acid (HONO) from the chamber walls on the order of 0.1 ppb min<sup>-1</sup>, which was determined separately in chamber characterization experiments (Carter et al., 2005).”

- 5 Section 3.4, Pg. 10, Line 20-21: “The formation of CMBO and MBO produces HO<sub>2</sub> radicals (Orlando et al., 2003; Ragains and Finlayson-Pitts, 1997), which serve as a source of secondary OH radicals. Other RO<sub>2</sub> + RO<sub>2</sub> reaction pathways also produce HO<sub>x</sub> radicals.”

- 10 Section 3.4, Pg.11, Line 18-24: “For chlorine-initiated oxidation of isoprene, the SAPRC chamber model results indicate that over 99% of the isoprene reacts with Cl; OH oxidation of isoprene is therefore only a very minor pathway in these experiments. Model results also show that HO<sub>2</sub> production is dominated by isoprene-chlorine chemistry when sufficient isoprene is present, whereas wall effects dominate HO<sub>2</sub> production (> 60 %) after all isoprene has been consumed. The model does not explicitly represent Cl-initiated oxidation of reaction products, which can produce additional HO<sub>x</sub> radicals, and therefore likely underestimates the importance of secondary OH chemistry.”

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#### Technical Comments and Responses

-Reviewer: in manuscript: p.2, line 16 and p.7, line.27: When referring to isomers of CMBO, these should be isomers of chloromethylbutenone, e.g. 1-chloro-3-methyl-3-butene-2-one, not "isomers of 3-methyl-3-butene-2-one".

Response: We have corrected the naming. See Pg.3, line 4.

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-Reviewer: p.3, line 23: Change "relatively ionization efficiencies" to "relative ionization efficiencies".

Response: We have corrected the typographical error. See Pg.5, Line 1.

-Reviewer: p.4, line 10: The reference should read "Odum et al., 1996".

- 25 Response: We have corrected the reference. See Pg.5, Line 21.

-Reviewer: p.9, line 4: Change "produced form" to "produced from". p.9, line 6: Change "chlorine-initiation oxidation" to "chlorine-initiated oxidation".

Response: This sentence has been removed in the revised manuscript.

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-Reviewer: p.18, Table 1: I don't understand the value of the VOC:Cl<sub>2</sub> ratio in experiment H2.

Response: Wrong precursor concentrations were reported for Exp. H2 (now Exp. S1). We have corrected the errors in the SI.

*-Reviewer: p.3, line 7: Change "number of water cluster" to "number of water clusters". p.4, line 7: Remove "greater than" before "44 % overestimation could be expected".*

Response: This sentence has been removed in the revised manuscript.

Major comments and responses

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 NO<sub>x</sub> may also be low), which is a motivating factor for this work.

Response: We have added discussions of SOA formation from marine emissions of isoprene, halogen sources and observations (e.g. reactive chlorine species within the marine boundary layer) to the introduction of the revised manuscript to motivate the work. While the model results by Gantt et al. (2010) suggest that contribution of marine isoprene emissions to coastal SOA (and O<sub>3</sub>) loadings are small, we note that the isoprene SOA yield used in the CMAQ model (3 % for low NO<sub>x</sub>) 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. We agree with the referee that the findings are also applicable to continental isoprene chemistry (and, in addition, photochemistry over salt lakes) under low NO<sub>x</sub> conditions.

Section 1, Pg.1 Line 28 - Pg.2 Line 6: “Isoprene SOA formation initiated by ozone (O<sub>3</sub>) , nitrate, and hydroxyl (OH) radicals has been studied extensively and is estimated to account for 6–30 Tg yr<sup>-1</sup> of the global aerosol budget (Brégonzio-Rozier et al., 2015; Claeys, 2004; Guenther et al., 2006; Kroll et al., 2006; Lin et al., 2012; Surratt et al., 2010, 2006; Zhao et al., 2015), but the importance of isoprene SOA formation within the marine boundary layer (MBL) remains highly disputed in literature (Arnold et al., 2009; Bikkina et al., 2014; Fu et al., 2011, 2013; Gantt et al., 2015, 2010; Hu et al., 2013; Luo and Yu, 2010; O’Dowd and de Leeuw, 2007). Although production of reactive chlorine species such as Cl<sub>2</sub>/HOCl has been observed within the MBL (Lawler et al., 2011), little is known about SOA from chlorine-initiated oxidation of isoprene.”

Section 1, Pg.2, Line 7-23: Overview of tropospheric sources and sinks for reactive halogenic species. Please refer to the responses to question (a) by referee #3 on Pg.16 in this document.

2. Reviewer: Throughout the manuscript, chlorine incorporated into organic molecules appears to be referred to as “chloride”, which chemically refers to Cl<sup>-</sup>, 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. We have clarified particle-phase chlorine quantification using ACSM

in the revised text. 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”. We have also added a discussion on the potential contribution to measured particulate chlorine contents from inorganic chlorides.

- 5 Section 3.2, Pg 8, Line 4-6: “Aerosol analytes undergo electron impact ionization in the ACSM, and chlorine-containing ion fragments are mostly expected at  $m/z$  35 and 37 as  $\text{Cl}^+$  and at  $m/z$  36 and 38 as  $\text{HCl}^+$ . Larger organochloride ion fragments may exist but cannot be separated in the unit-mass resolution spectra.”

- Section 3.2, Pg 8, Line 6-12: “A previous study on chlorine-initiated oxidation of toluene, which proceeds primarily through a hydrogen-abstraction pathway, reported particulate chlorine formation (4 % of the total aerosol mass), which was attributed to HCl uptake (Cai et al., 2008). Formation of organochloride aerosol has been observed previously for chlorine-initiated oxidation of alpha-pinene (Ofner et al., 2013), which proceeds primarily via a chlorine-addition reaction pathway. Thus, isoprene-chlorine reactions are expected to result in particulate organochloride formation. The uptake of HCl produced from Cl H-abstraction or intramolecular HCl elimination (Ragains and Finlayson-Pitts, 1997) could also contribute slightly to  
10 observed particulate chlorine.”  
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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,  
20 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  
25 and Time-of-Flight region and the resulting ion products may appear as if they were generated via proton transfer or charge transfer.

- Section 2.2, Pg.4, Line 17-27: “Reagent ions are generated by passing humidified UHP  $\text{N}_2$  over a methyl iodide permeation tube and then through a  $^{210}\text{Po}$  radioactive cartridge (NRD, 2013) at 2 LPM into the ion-molecule reaction (IMR) chamber  
30 operating at 200 mbar pressure. Analyte, “M” can undergo chemical ionization within the IMR with hydronium-water ( $[\text{H}_2\text{O}]_n[\text{H}_3\text{O}]^+$ ) or iodide-water ( $[\text{H}_2\text{O}]_n\text{I}^-$ ) ion clusters,



where the number of clusters, “n” ranges from 0 and 2 for  $[\text{H}_2\text{O}]_n[\text{H}_3\text{O}]^+$ , with  $[\text{H}_2\text{O}][\text{H}_3\text{O}]^+$  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 (Aljawhary et al., 2013). For  $[\text{H}_2\text{O}]_n\text{I}^-$  ionization, “n” ranges from 0 to 1, with  $\text{I}^-$  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  $\text{H}_3\text{O}^+$ , rather than  $(\text{H}_2\text{O})_n\text{H}_3\text{O}^+$ . What fraction of the signal was associated with  $\text{H}_3\text{O}^+$ , and how many n were observed? This would impact the resulting analyte ionization. When were  $(\text{H}_2\text{O})_n\text{H}_3\text{O}^+$  vs  $(\text{H}_2\text{O})_n\text{I}^-$  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 significant 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  $\text{H}_3\text{O}^+$  reagent ions (Yuan et al., 2016). In this work, the dominant reagent ions were  $(\text{H}_2\text{O})(\text{H}_3\text{O}^+)$  (>70% of total reagent ion signals) and  $\text{I}^-$  (>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 signal 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  $\text{Cl}_2$  concentration is high.  $(\text{H}_2\text{O})_n(\text{I}^+)$  ionization is very sensitive towards  $\text{Cl}_2$ . 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. We note that there was an error regarding the interpretation of  $f_{82}$  value in the original author response posted. We have revised our analysis. The scientific conclusion about the contribution of IEPOX-OA to observed SOA formation was not affected.

Section 3.1, Pg.7, Line 3-6: "The initial chlorine experiment (A4) exhibited similar trends, but the SOA decay was faster, where  $30 \mu\text{g m}^{-3}$  SOA decay (40% of maximum SOA mass) occurred within about 30 minutes of photo-oxidation ( $9 < T < 40$  mins), likely due to more rapid oxidation and fragmentation of reaction products."

Section 3.1, Pg.7, Line 9-11: "After extended photo-oxidation ( $T > 100$  mins), SOA concentrations achieved via initial chlorine injection (Exp. A4) and continuous chlorine injection (Exp. C2) differed by less than  $8 \mu\text{g m}^{-3}$  ( $< 20\%$  of total SOA mass at  $T = 100$  mins for Exp. C2)."

Section 3.4, Pg.12, Line 2-11: A discussion on the importance of IEPOX is provided. Please refer to responses to question (2) by referee #4 on Pg.20-21 in this document for more details.

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 pathways and expanded our gas-phase chemistry discussion. Please see the revised Section 3.4, updated Figures 6 and 7. 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.*

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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  $\text{HCl}^+$  ion appears to be a good proxy for particulate organochlorides.

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

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

Section 3.3, Pg.9 Line 13-15: “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.”

20 *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

25 *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?*

30 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 photo-oxidation 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 in section 3.4 and S7. See also Figure S13 and S14.

Section 3.4, Pg12, Line 2-11: A discussion on the importance of IEPOX is provided based on ACSM and CIMS unit mass resolution spectra comparison. Please refer to responses to question (2) by referee #4 on Pg.20-21 in this document for more details.

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. An example is provided in Section S5. The 2D-VBS model or more mechanistic frameworks are needed to describe that behavior. In this work, initial Cl<sub>2</sub> 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 formation pathways (see Section S6) that are consistent with gas-phase observations, SOA formation, and organochloride detection to provide more mechanistic information on isoprene-chlorine reactions as suggested.

Section 3.4, Pg.11, Line 3-9: “For instance, the C<sub>5</sub>H<sub>8</sub>ClO<sub>2</sub><sup>•</sup> radical produced via Cl-addition to isoprene could either undergo RO<sub>2</sub> + RO<sub>2</sub> chemistry to produce C<sub>5</sub>H<sub>7</sub>ClO (e.g. CMBO) or undergo RO<sub>2</sub> + HO<sub>2</sub> chemistry to produce C<sub>5</sub>H<sub>9</sub>ClO<sub>2</sub>, a chloroalkyl hydroperoxide. Similarly, the C<sub>5</sub>H<sub>7</sub>O<sub>2</sub><sup>•</sup> radical produced via H-abstraction from isoprene could undergo RO<sub>2</sub> + RO<sub>2</sub> chemistry to produce C<sub>5</sub>H<sub>6</sub>O (e.g. MBO) or undergo RO<sub>2</sub> + HO<sub>2</sub> chemistry to produce C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, a hydroperoxide. Ions consistent with C<sub>5</sub>H<sub>9</sub>ClO<sub>2</sub> and C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> are observed in the gas-phase, as shown in Fig 6a and 6b, where the formation of RO<sub>2</sub> + HO<sub>2</sub> reaction products appears delayed compared to their RO<sub>2</sub> + RO<sub>2</sub> pathway counterparts. This is consistent with RO<sub>2</sub> + RO<sub>2</sub> reactions being a source of HO<sub>x</sub> radicals.”

Section 4, Pg. 12: The sentence referenced by the referee has been removed, as the point has been addressed in section 3.3 and S5.

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: Similarities between chlorine-isoprene and OH-isoprene SOAs can be seen in particle-phase measurements. Gas-phase oxidation products also share some overlaps. Figure 5 shows that the chlorine-isoprene SOA yields are similar to OH-isoprene SOA yields under low NO<sub>x</sub> conditions. Figure 3 shows that the chlorine-isoprene SOA have similar  $f_{43}$  and  $f_{44}$  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 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 revised in the manuscript, in which we now also offer recommendations for modelers on what yields to use for chlorine-initiated oxidation of isoprene.

Section 4, Pg. 12, Line 19-21: “For air quality models which do not explicitly account for SOA aging, the averaged SOA yield from continuous chlorine injection experiments (8%) should be used for SOA formation from chlorine-initiated oxidation of isoprene.”

Section 4, Pg. 12, Line 30-32: “Proposed formation pathways and gas-phase measurements by the 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 NO<sub>x</sub> conditions.”

Minor comments and responses

*-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 as Eq.(5)–(8).

- 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.

10 Response: According to Orlando et al. (2002), the bimolecular rate constant of the isoprene-chlorine reaction is determined to be  $4.3 \pm 0.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , whereas the rate constants of the MVK-chlorine and MACR-chlorine reactions are  $2.2 \pm 0.3 \times 10^{-10}$  and  $2.4 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The earlier statement about high isoprene concentrations does not necessarily contradict high reactivity of chlorine with volatile organic compounds.

15 - 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.

20 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 NO<sub>x</sub> scenarios.”

Response: We have edited the sentence as suggested. See section 3.3, Pg. 9, Line 19.

25

- 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.

30

Section 3.3, Pg. 9, Line 16-17: “Complete isoprene depletion, which coincides with the maximum SOA concentration (see Fig. 1), is used as the reference condition for yield reporting in Table 1.”

- Reviewer: Page 7, Line 16: By “continuous cases”, do you mean continuous Cl<sub>2</sub> injection during an experiment? Make sure this is clear.

Response: Yes. Continuous cases refer to experiments during which Cl<sub>2</sub> is continuously injected. This has been clarified in the revised manuscript.

5

Section 3.4, Pg. 9. Line 22-23: “Observed SOA yields averaged  $20 \pm 3$  % for initial Cl<sub>2</sub> injection cases (A1–A5) and  $8 \pm 1$  % for continuous Cl<sub>2</sub> injection cases (C1–C4).”

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

10 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: This sentence has been reworked as part of the discussion on the potential IEPOX contribution to SOA.

15

- 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.

20

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 “extent of oxidation”.

25

- Reviewer: Figure 5 caption: For clarification, I suggest adding the phrase “corresponding to low and high NO<sub>x</sub> OH oxidation” at the end of the first sentence.

Response: We have clarified the caption as suggested.

30 - 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 “(C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>)H<sup>+</sup> and interfering ions, (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>)H<sup>+</sup> and (C<sub>5</sub>H<sub>11</sub>O<sub>3</sub>Cl)H<sup>+</sup>.” referring to the possibility of (C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>)H<sup>+</sup> being an adduct product (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>)(H<sub>3</sub>O)<sup>+</sup>, 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?

- 5 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.

- 10 Response: “ $k$ ” is the collision rate constant. This has been clarified in the revised S.I.

Major comments and responses

(a) Reviewer: *Introduction: The authors should add a Paragraph to the introduction about natural and anthropogenic halogen sources and sinks in the atmosphere to introduce this topic to the readers; e.g. by: Simpson et al., Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, Chem. Reviews, 2015. Roland von Glasow, Wider role for airborne chlorine, nature, 464, 2010. Finlayson-Pitts, Halogens in the Troposphere, Anal. Chem., 82, 770-776, 2010. Buxmann et al., Consumption of reactive halogen species from sea-salt aerosol by secondary organic aerosol: slowing down the bromine explosion, Environ. Chem., 12, 476-488, 2015.*

10 Response: We have added a discussion on natural and anthropogenic halogen sources and sinks to the introduction of the revised manuscript as suggested by the reviewer.

Section 1, Pg. 2, Line 7-23: “Chlorine chemistry is known to have important effects on ozone layer depletion (Crutzen, 1974; Molina and Rowland, 1974). Recent laboratory studies and field measurements also suggest an important role of halogen (X) chemistry on tropospheric composition (Faxon and Allen, 2013; Finlayson-Pitts, 2010; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Reactive halogen species in the form of  $X_2$ ,  $XO$ ,  $HOX$ ,  $XNO_2$ ,  $OXO$  are present in polar regions (Buys et al., 2013; Liao et al., 2014; Pöhler et al., 2010), the MBL (Lawler et al., 2011; Read et al., 2008), coastal and inland regions (Mielke et al., 2013; Riedel et al., 2013, 2012). Outside of MBL and polar regions, natural emissions of reactive halogen species have been observed in volcano plumes (Bobrowski et al., 2007) and over salt lakes (Kamilli et al., 2016; Stutz, 2002). Anthropogenic sources include industrial emissions (Chang and Allen, 2006; Riedel et al., 2013; Tanaka et al., 2003), oil and gas production (Edwards et al., 2014), water treatment (Chang et al., 2001), biomass burning (Lobert et al., 1999), engine exhaust (Osthoff et al., 2008; Parrish et al., 2009), and  $NO_x$ -mediated heterogeneous reactions, notably the production of  $ClNO_2$  via reactive uptake of  $N_2O_5$  onto particles containing  $Cl^-$  (Thornton et al., 2010). Recent studies have found that models underpredict the abundance of reactive halogen species, suggesting incomplete understanding of their sources (Faxon et al., 2015; Faxon and Allen, 2013; Simpson et al., 2015; Thornton et al., 2010). Photolysis of reactive halogen species produces halogen radicals that can react with  $O_3$ , hydrocarbons, SOA, and other radicals in the atmosphere. Reactions with hydrocarbons and organic aerosol serve as chlorine and bromine radical sinks (Buxmann et al., 2015; Ofner et al., 2012; Platt and Hönninger, 2003), especially in high  $NO_x$  environments where halogen recycling via  $HO_x$  and  $XO$  reaction pathways is suppressed (Edwards et al., 2013; Riedel et al., 2014; Simpson et al., 2015).”

30

(b) Reviewer: *p2 line 30: Please add the characteristics of the UVA light source: actinic flux, quantified UV/VIS spectrum.*

Response: We have included additional information on the UV light source.



Section 2.1, Pg.3, Line 22-24: “The UV spectrum is similar to other blacklight sources reported in literature (Carter et al., 2005). The NO<sub>2</sub> photolysis rate is used to characterize UV intensity and was determined to be 0.5 min<sup>-1</sup>, similar to ambient levels (e.g. 0.53 min<sup>-1</sup> at 0 degrees zenith angle, Carter et al., 2005).”

- 5 (c) Reviewer: P3 line 31 “loss of organic vapors to Teflon surfaces” Teflon films, used for aerosol smog-chambers, are known to store various gaseous species, especially NO<sub>x</sub>, which is released from the Teflon film by UV radiation and increased temperatures. Has this been observed or taken into account? Please add a related statement to the manuscript.

Response: We have added a discussion on wall emissions and conducted chamber modeling to estimate the background  
10 contribution to secondary HO<sub>x</sub> chemistry. Overall, chlorine-isoprene chemistry dominates gas-phase chemistry and secondary HO<sub>x</sub> production.

Section 2.1, Pg.3 Line 26 – Pg.4 Line 2: “Between experiments, ‘blank experiments’ were conducted in which seed particles, ozone, and chlorine gas (Cl<sub>2</sub> Airgas, 106 ppm in N<sub>2</sub>) were injected into the chamber at high concentrations and UV lights were  
15 turned on to remove any residual organics which could be released from the Teflon<sup>®</sup> chamber surface. Background effects have been quantified using chamber characterization experiments (Carter et al., 2005) and the SAPRC chamber modeling software (<http://www.engr.ucr.edu/~carter/SAPRC/>) in combination with the Carbon Bond 6 (CB6r2) chemical mechanism, which was modified to include basic gas phase inorganic chlorine chemistry in addition to Cl<sub>2</sub> and ClNO<sub>2</sub> photolysis (Sarwar et al., 2012; Yarwood et al., 2010). NO<sub>x</sub>-offgasing is represented within the model by a constant emission of nitrous acid  
20 (HONO) from the chamber walls on the order of 0.1 ppb min<sup>-1</sup>, which was determined separately in chamber characterization experiments (Carter et al., 2005).”

Section 3.4, Pg.11, Line 18-24: “For chlorine-initiated oxidation of isoprene, the SAPRC chamber model results indicate that over 99% of the isoprene reacts with Cl; OH oxidation of isoprene is therefore only a very minor pathway in these experiments.  
25 Model results also show that HO<sub>2</sub> production is dominated by isoprene-chlorine chemistry when sufficient isoprene is present, whereas wall effects dominate HO<sub>2</sub> production (> 60 %) after all isoprene has been consumed. The model does not explicitly represent Cl-initiated oxidation of reaction products, which can produce additional HO<sub>x</sub> radicals, and therefore likely underestimates the importance of secondary OH chemistry.”

Major comments and responses

1.) Reviewer: As the authors know well, acidity plays a MAJOR role for IEPOX uptake yielding isoprene SOA under low-NO<sub>x</sub> conditions. This was conclusively demonstrated with authentic IEPOX for the first time by Lin et al. (2012, ES&T); however, Wang et al. (2005, RCM), Surratt et al. (2006, JPCA), Paulot et al. (2009, Science), and Surratt et al. (2010, PNAS) were some of the first studies to propose for the existence of IEPOX even though an authentic standard did not exist at that time to study its reactive uptake. Since then, kinetic studies have demonstrated that acidity plays a key role in IEPOX producing substantial amounts of SOA (Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&T Letters; Riedel et al., ACP, 2016). If ammonium sulfate aerosol is wet, due to a high enough RH, then ammonium sulfate can take up IEPOX to yield SOA if the reaction time scales are long enough (Nguyen et al., 2014, ACP).

With this reminder above, I wonder why the authors did not consider also conducting experiments at elevated RH and increased acidities with the ammonium sulfate seed aerosol? I can imagine if the chemistry applies to remote marine locations, the aerosol may be more wet and/or acidic (especially if there are sufficient DMS emissions). Jon Abbatt's group also showed recently in Wong et al. (2015, ES&T) that deliquesced ammonium sulfate particles can yield a lot of SOA through a non-IEPOX route. So this could be something important to consider.

Response: We have conducted four additional experiments, two with initial chlorine injection (Exp. A6 and A7) and two with continuous chlorine injection (Exp. C6 and C7). We observed significant increases in SOA concentrations when acidified seeding aerosol was used as well as increases in some higher *m/z* mass fragments including *m/z* 82, which is generally associated with IEPOX-aerosol. We also observed lower gas-phase ion signals in the CIMS in acidified seed experiments compared to neutral seed experiments. Some of the changes made to the manuscript include,

Figure 1: Added time-series from Exp. C7, which used acidified seed particles for comparison with Exp. C2, which used neutral seed particles under otherwise similar experimental conditions. The figure shows that more SOA is formed in acidified seed experiments.

Table 1: Included the results from the four additional experiments. We also updated the wall loss-corrected SOA concentration and yields using updated relative ionization efficiency (RIE) values.

Section 3.1, Pg.7, Line 11-13: "The data shown in Fig. 1 and summarized in Table 1 also suggest that aerosol acidity promotes SOA formation: the SOA concentration observed in acidified seed Exp. C7 were more than twice as high as SOA concentrations observed in neutral seed Exp. C2."

Section 3.4: Added a discussion of the effect of acidified seed aerosol. Please see responses to question (2) below.

Figure S13: Additional figure showing the difference ACSM unit-mass-resolution spectra obtained from neutral (Exp. C2) and acidified seed (Exp. C7) experiments.

5

Figure S14: Additional figure comparing the CIMS unit-mass-resolution spectra obtained from neutral (C3 and C5) and acidified seed (C6 and C7) experiments.

*Reviewer: By the way, the authors don't appear to say how the ammonium sulfate aerosol were injected into the chamber?*

10 *What was the concentration of your atomizing solution? This should be added to the experimental section.*

Response: We have added additional details on our experimental protocol as follows:

Section 2.1, Pg. 4, Line 6-8: "Neutral seed particles were injected using an Aerosol Generation System (Brechtel, AGS Model  
15 9200) with a 0.01 M ammonium sulfate solution; acidic seed particles were generated using a solution containing 0.005 M ammonium sulfate and 0.0025 M sulfuric acid."

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  
20 that AMS and ACSM, respectively, datasets can resolve IEPOX-OA factor when PMF is applied. Why didn't the authors consider conducting 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  
25 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  
30 might agree with this suggestion.*

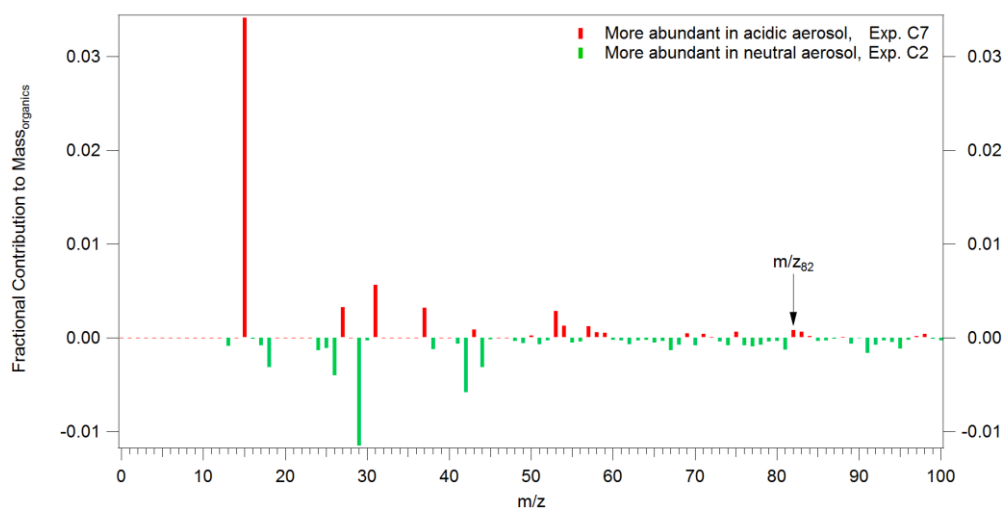
Response: We have attempted PMF analysis (without constraining factors) on these data but were unable to extract a factor related to IEPOX-OA. This is likely because the contribution of IEPOX-OA to total SOA mass from chlorine-initiated oxidation of isoprene, if present, is small. We note that an error was made in the original author response posted regarding  $f_{82}$

and the estimated contribution by IEPOX-SOA. We have revised our analysis. The conclusion remains that IEPOX-OA likely did not contribute significantly to SOA formation.

Error in the original author response: “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  $\sim 0.006$ . 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.”

By this line of logic, the maximum IEPOX-OA contribution would be 50%, which is unrealistic. We note that the observed  $f_{82}$  value ( $5.5 - 6.4 \text{ ‰}$ ) is lower than the average value observed for ambient OA that has been influenced by isoprene emissions ( $6.5 \pm 2.2 \text{ ‰}$ ) (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  $f_{82}$  values was in some cases as high as 5 ‰, which is close to observe  $f_{82}$  values for isoprene-chlorine SOAs. As shown in Figure 6 and 7,  $C_5H_8O_2$ , 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. We have included the UMR ACSM spectra comparison here, which can also be found in the updated S.I (section S6).

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 (1 ‰) 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 5 ‰. The observed  $f_{82}$  values for isoprene-chlorine SOA are below the average value observed for ambient OA influenced by isoprene emission ( $6.5 \pm 2.2 \text{ ‰}$ ) and much lower than IEPOX-derived SOA (12-40 ‰) 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.”



**Figure S13.** Comparison of ACSM unit mass spectra. Red bars indicate  $m/z$  fragments enhanced in the presence of acidic aerosols. Green bars indicate  $m/z$  fragments enhanced in the presence of neutral aerosols.

- 3.) Reviewer: Please go through carefully and make sure certain references are not missing throughout the text. I mention a few of these in my minor comments below.

Response: Additional references have been included.

- 4.) Reviewer: I know it isn't a focus in this manuscript, but it would be very powerful if molecular tracers could be identified for Cl-initiated radicals yielding SOA. The authors mention using the ACSM to try to constrain the organochlorine budget, but seemed to have trouble with this due to interference issues. This is why I suggested conducting PMF/ME-2 analyses above in # 2. However, does the CIMS data (especially the iodide reagent ion chemistry) suggest the presence of low-volatility hydroperoxides that contain chlorine in them? From OH radical studies by Krechmer et al. (2015, ES&T), Riva et al. (2016, ES&T), and Liu et al. (2016, ES&T), they all measured low-volatility multifunctional hydroperoxides that made sufficient amounts of SOA (that don't require aerosol acidity like IEPOX).

Response: Based on our CIMS measurements, multigenerational reaction pathways that could lead to hydroperoxide formation from continued oxidation of early  $C_5$  oxidation products are plausible. We show time series for some of these multifunctional chloroalkyl hydroperoxides in the updated Figure 6 and added a summary of proposed products in Figure 7. More detailed formation pathways are added as well to the S.I. (see Fig S10-12). References to previous work on hydroperoxide formation/oxidation under low  $NO_x$  are added as well.

Figure 6a and 6b: Updated with hydroperoxides, chloroalkyl hydroperoxides and additional multi-generational products observed by CIMS.

Figure 7: Observations by  $(\text{H}_2\text{O})_n\text{I}^-$  are now shown in Fig. 6b. Figure 7 now summarizes proposed reaction products, some of which are (chlorinated) hydroperoxides.

Section 3.4, Pg.11, Line 3-8: “For instance, the  $\text{C}_5\text{H}_8\text{ClO}_2^\bullet$  radical produced via Cl-addition to isoprene could either undergo  $\text{RO}_2 + \text{RO}_2$  chemistry to produce  $\text{C}_5\text{H}_7\text{ClO}$  (e.g. CMBO) or undergo  $\text{RO}_2 + \text{HO}_2$  chemistry to produce  $\text{C}_5\text{H}_9\text{ClO}_2$ , a chloroalkyl hydroperoxide. Similarly, the  $\text{C}_5\text{H}_7\text{O}_2^\bullet$  radical produced via H-abstraction from isoprene could undergo  $\text{RO}_2 + \text{RO}_2$  chemistry to produce  $\text{C}_5\text{H}_6\text{O}$  (e.g. MBO) or undergo  $\text{RO}_2 + \text{HO}_2$  chemistry to produce  $\text{C}_5\text{H}_8\text{O}_2$ , a hydroperoxide. Ions consistent with  $\text{C}_5\text{H}_9\text{ClO}_2$  and  $\text{C}_5\text{H}_8\text{O}_2$  are observed in the gas-phase, as shown in Fig 6a and 6b, where the formation of  $\text{RO}_2 + \text{HO}_2$  reaction products appears delayed compared to their  $\text{RO}_2 + \text{RO}_2$  pathway counterparts.”

Section 3.4, Pg.11, Line 11-14: “In the OH-isoprene system, multifunctional, low volatility hydroperoxides produced from non-IEPOX (“isoprene-derived epoxydiol”) reaction pathways contribute to SOA formation under low  $\text{NO}_x$  conditions (Krechmer et al., 2015; Liu et al., 2016; Riva et al., 2016). Analogously, in the Cl-isoprene system, the (chloroalkyl) hydroperoxide species identified in Fig. 6 and Fig. 7 are expected to contribute to SOA formation.”

(5). Reviewer: *When reviewing Table 1, I realized it wasn't well explained in the text why the different injection methods were used. What did these methods explicitly tell you?*

Response: The different injection methods were used to separate SOA formation from the effects of vapor wall loss. We have added some clarifying text.

Section 2.1, Pg.4, Line 10-13: “Initial  $\text{Cl}_2$  experiments were performed to achieve rapid oxidation of isoprene and to separate initial SOA formation from effects of vapor wall loss. Because chlorine radicals are not expected to regenerate, continuous  $\text{Cl}_2$  injection experiments were performed to provide more steady but lower Cl radical concentrations.”

Section 3.1, Pg.7, Line 3-6: “The initial chlorine experiment (A4) exhibited similar trends, but the SOA decay was faster, where  $30 \mu\text{g m}^{-3}$  SOA decay (40% of maximum SOA mass) occurred within about 30 minutes of photo-oxidation ( $9 < T < 40$  mins), likely due to more rapid oxidation and fragmentation of reaction products.”

Section 3.4, Pg.9, Line 20-22: “In initial chlorine injection experiments, maximum SOA concentrations were reached within 15 minutes, and the effects of vapor wall loss, oxidative fragmentation, and photolysis on reported maximum SOA yield were lower than during continuous chlorine injection experiments.”

- 5 *Reviewer: For modelers, this Table might be very difficult for them to judge which yields should be used. Also, related to my point # 1 above, modelers seeing these yields may question if these yields are accurate to remote low-NO<sub>x</sub> regions where Cl radical chemistry might matter. Can the authors offer which yield may be the most appropriate to use?*

Response: We have added the following qualifications and recommendations:

10

Section 3.3, Pg.9, Line 23-32: “Under atmospheric conditions, the isoprene-chlorine ratio will usually be higher than ratios used in these experiments. Previous studies on chlorine-initiated SOA formation from toluene (Cai et al., 2008) and limonene (Cai and Griffin, 2006) suggest that SOA yields decrease with higher VOC-to-Cl ratio. While we do not observe a clear correlation between SOA yield and isoprene-to-chlorine ratios used here (0.5-1.2), such dependence could be present over a wider ratio range. For air quality models which do not explicitly account for fragmentation reactions, the use of the average continuous case yield, which is similar to recently reported OH-oxidation yields (Liu et al., 2016; Xu et al., 2014), is more appropriate because the isoprene-to-chlorine ratio is closer to atmospheric conditions and because the SOA yields from continuous injection experiments account for effects of OA aging in the atmosphere (which occur throughout the experiments). The presence of acidic aerosols and inclusion of particulate chlorine content would increase expected yields.”

20

*Reviewer: Finally, I’m assuming these various injection methods were used to gain some insights into vapor wall losses? It remains unclear to me how exactly vapor wall losses were dealt with (if at all) in reporting the SOA yields shown in Table 1.*

- Response: The different injection methods were indeed used to separate the effects of vapor wall loss from SOA formation, as clarified above. The wall loss correction method used accounts for depositional particle loss, as well as organic vapor loss to the deposited particles. Essentially, the correction method assumes that organic aerosols lost to the chamber wall would still participate in equilibrium partitioning as if they were suspended. Loss of organic vapor to the clean Teflon® surface is not accounted for here. This was described in more concise terms in the manuscript,

- 30 Section 2.3, Pg.5, Line 11-14: “Assuming internal mixing of particles and that organic vapor can condense onto suspended and wall-deposited particles alike, we corrected for particle wall loss and the loss of organic vapors onto wall-deposited particles using the organic-to-sulfate ratio (Hildebrandt et al., 2009)”

Section 2.3, Pg.5, Line 17-18: “This correction does not account for loss of organic vapors to clean Teflon® surfaces.”

Minor comments and responses.

1.) Reviewer: Abstract, Page 1, Line 12: Remove "%" after "8." You don't need this.

Response: We have removed "%"

5

2.) Reviewer: Methods, Page 2, Line 32: Insert a space between "exceeding100"

Response: We have fixed this typographical error.

3.) Reviewer: Section 3.4, Page 7, Line 27: You write "3-methyl-3-butene-2-one (CMBO) [(C<sub>5</sub>H<sub>7</sub>OCl)H<sup>+</sup>]." This appears to  
10 be named incorrectly. Please name according to IUPAC.

Response: We have corrected the naming to 1-chloro-3-methyl-3-butene-2-one (CMBO) in Section 1, Pg.3, Line 4. The  
abbreviation "CMBO" is now used throughout section 3.4

4.) Reviewer: Section 3.4, Page 7, Line 31: I would reference Kroll et al. (2006, ES&T) and Surratt et al. (2006, JPCA) as one  
15 of the initial references to demonstrates MACR oxidation is a source of SOA.

Response: We have modified the references as suggested. See section 3.4, Pg.10, Line 6-7.

5.) Reviewer: Section 3.4, Page 8, Line 26: The authors should reference Lin et al. (2012, ES&T)

Response: We have added the suggested reference. See section 3.4, Pg.11, Line 17-18.

20

6.) Reviewer: Section 3.4, Page 8, Line 27: The authors should also reference Gaston et al. (2014, ES&T) and Riedel et al.  
(2015, ES&T Letters)

Response: We have added the suggested reference. See also section 3.4, Pg.11, Line 17-18.



## References

- Aljawhary, D., Lee, a. K.Y., Abbatt, J.P.D., 2013. High-resolution chemical ionization mass spectrometry (ToF-CIMS): Application to study SOA composition and processing. *Atmos. Meas. Tech.* 6, 3211–3224. doi:10.5194/amt-6-3211-2013
- Arnold, S.R., Spracklen, D. V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., Gros, V., Peeken, I., Lewis, a. C., Alvain, S., Moulin, C., 2009. Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol. *Atmos. Chem. Phys.* 9, 1253–1262. doi:10.5194/acpd-8-16445-2008
- Bikkina, S., Kawamura, K., Miyazaki, Y., Fu, P., 2014. High abundances of oxalic, azelaic, and glyoxylic acids and methylglyoxal in the open ocean with high biological activity: Implication for secondary OA formation from isoprene. *Geophys. Res. Lett.* 41, 3649–3657. doi:10.1002/2014GL059913
- Bobrowski, N., von Glasow, R., Aiuppa, A., Inguaggiato, S., Louban, I., Ibrahim, O.W., Platt, U., 2007. Reactive halogen chemistry in volcanic plumes. *J. Geophys. Res. Atmos.* 112, 1–17. doi:10.1029/2006JD007206
- Brégonzio-Rozier, L., Siekmann, F., Giorio, C., Pangui, E., Morales, S.B., Temime-Roussel, B., Gratien, A., Michoud, V., Ravier, S., Cazaunau, M., Tapparo, A., Monod, A., Doussin, J.F., 2015. Gaseous products and secondary organic aerosol formation during long term oxidation of isoprene and methacrolein. *Atmos. Chem. Phys.* 15, 2953–2968. doi:10.5194/acp-15-2953-2015
- 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
- Buxmann, J., Bleicher, S., Platt, U., von Glasow, R., Sommariva, R., Held, A., Zetzsch, C., Ofner, J., 2015. Consumption of reactive halogen species from sea-salt aerosol by secondary organic aerosol: slowing down the bromine explosion. *Environ. Chem.* 12, 476. doi:10.1071/EN14226
- Buys, Z., Brough, N., Huey, L.G., Tanner, D.J., Von Glasow, R., Jones, A.E., 2013. High temporal resolution Br<sub>2</sub>, BrCl and BrO observations in coastal Antarctica. *Atmos. Chem. Phys.* 13, 1329–1343. doi:10.5194/acp-13-1329-2013
- Cai, X., Griffin, R.J., 2006. Secondary aerosol formation from the oxidation of biogenic hydrocarbons by chlorine atoms. *J. Geophys. Res. Atmos.* 111, 7348–7359. doi:10.1029/2005JD006857
- Cai, X., Ziemba, L.D., Griffin, R.J., 2008. Secondary aerosol formation from the oxidation of toluene by chlorine atoms. *Atmos. Environ.* 42, 7348–7359. doi:10.1016/j.atmosenv.2008.07.014
- Canagaratna, M.R., Jimenez, J.L., Kroll, J.H., Chen, Q., Kessler, S.H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L.R., Wilson, K.R., Surratt, J.D., Donahue, N.M., Jayne, J.T., Worsnop, D.R., 2015. Elemental ratio measurements of organic compounds using aerosol mass spectrometry: Characterization, improved calibration, and implications. *Atmos. Chem. Phys.* 15, 253–272. doi:10.5194/acp-15-253-2015

- Carter, W.P.L., Cocker, D.R., Fitz, D.R., Malkina, I.L., Bumiller, K., Sauer, C.G., Pisano, J.T., Bufalino, C., Song, C., 2005. A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation. *Atmos. Environ.* 39, 7768–7788. doi:10.1016/j.atmosenv.2005.08.040
- Chang, S., Allen, D.T., 2006. Atmospheric chlorine chemistry in southeast Texas: Impacts on ozone formation and control. *Environ. Sci. Technol.* 40, 251–262. doi:10.1007/s10479-006-0033-8
- Chang, S., Tanaka, P., McDonald-buller, E., Allen, D.T., 2001. Emission inventory for atomic chlorine precursors in Southeast Texas. Rep. Contract 9880077600-18 between Univ. Texas Texas Nat. Resour. Conserv. Comm. 1–27.
- Chuang, W.K., Donahue, N.M., 2016. A two-dimensional volatility basis set &ndash; Part 3: Prognostic modeling and NO<sub>x</sub> dependence. *Atmos. Chem. Phys.* 16, 123–134. doi:10.5194/acp-16-123-2016
- 10 Claeys, M., 2004. Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene. *Science* (80-. ). 303, 1173–1176. doi:10.1126/science.1092805
- Crenn, V., Sciare, J., Croteau, P.L., Verlhac, S., Fröhlich, R., Belis, C.A., Aas, W., Äijälä, M., Alastuey, A., Artiñano, B., Baisnée, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M.J., Esser-Gietl, J.K., Green, D.C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillón, M.C., Močnik, G., O’Dowd, C.D., Ovadnevaite, J., Petit, J.E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Estève, R., Slowik, J.G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prévôt, A.S.H., Jayne, J.T., Favez, O., 2015. ACTRIS ACSM intercomparison - Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments. *Atmos. Meas. Tech.* 8, 5063–5087. doi:10.5194/amt-8-5063-2015
- 20 Crutzen, P., 1974. A Review of Upper Atmospheric Photochemistry. *Can. J. Chem.* 52, 1569–1581. doi:10.1139/v74-229
- Donahue, N.M., Epstein, S.A., Pandis, S.N., Robinson, A.L., 2011. A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics. *Atmos. Chem. Phys.* 11, 3303–3318. doi:10.5194/acp-11-3303-2011
- Donahue, N.M., Kroll, J.H., Pandis, S.N., Robinson, A.L., 2012. A two-dimensional volatility basis set-Part 2: Diagnostics of organic-aerosol evolution. *Atmos. Chem. Phys.* 12, 615–634. doi:10.5194/acp-12-615-2012
- 25 Donahue, N.M., Robinson, A.L., Stanier, C.O., Pandis, S.N., 2006. Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environ. Sci. Technol.* 40, 2635–2643. doi:10.1021/es052297c
- Edwards, P.M., Brown, S.S., Roberts, J.M., Ahmadov, R., Banta, R.M., deGouw, J.A., Dube, W.P., Field, R.A., Flynn, J.H., Gilman, J.B., Graus, M., Helmig, D., Koss, A., Langford, A.O., Lefer, B.L., Lerner, B.M., Li, R., Li, S.M., McKeen, S.A., Murphy, S.M., Parrish, D.D., Senff, C.J., Soltis, J., Stutz, J., Sweeney, C., Thompson, C.R., Trainer, M.K., Tsai, C., Veres, P.R., Washenfelder, R.A., Warneke, C., Wild, R.J., Young, C.J., Yuan, B., Zamora, R., 2014. High winter ozone pollution from carbonyl photolysis in an oil and gas basin. *Nature* 514, 351–354. doi:10.1038/nature13767
- Edwards, P.M., Young, C.J., Aikin, K., DeGouw, J., Dubé, W.P., Geiger, F., Gilman, J., Helmig, D., Holloway, J.S., Kercher, J., Lerner, B., Martin, R., McLaren, R., Parrish, D.D., Peischl, J., Roberts, J.M., Ryerson, T.B., Thornton, J., Warneke, C., Williams, E.J., Brown, S.S., 2013. Ozone photochemistry in an oil and natural gas extraction region during winter:

- Simulations of a snow-free season in the Uintah Basin, Utah. *Atmos. Chem. Phys.* 13, 8955–8971. doi:10.5194/acp-13-8955-2013
- Faxon, C., Bean, J., Ruiz, L., 2015. Inland Concentrations of Cl<sub>2</sub> and ClNO<sub>2</sub> in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity. *Atmosphere (Basel)*. 6, 1487–1506. doi:10.3390/atmos6101487
- 5 Faxon, C.B., Allen, D.T., 2013. Chlorine chemistry in urban atmospheres: A review. *Environ. Chem.* 10, 221–233. doi:10.1071/EN13026
- Finlayson-Pitts, B.J., 2010. Halogens in the troposphere. *Anal. Chem.* 82, 770–776. doi:10.1021/ac901478p
- Fu, P., Kawamura, K., Miura, K., 2011. Molecular characterization of marine organic aerosols collected during a round-the-world cruise. *J. Geophys. Res. Atmos.* 116, 1–14. doi:10.1029/2011JD015604
- 10 Fu, P.Q., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: Contributions of primary emission and secondary aerosol formation. *Biogeosciences* 10, 653–667. doi:10.5194/bg-10-653-2013
- Gantt, B., Johnson, M.S., Crippa, M., Prévôt, A.S.H., Meskhidze, N., 2015. Implementing marine organic aerosols into the GEOS-Chem model. *Geosci. Model Dev.* 8, 619–629. doi:10.5194/gmd-8-619-2015
- 15 Gantt, B., Meskhidze, N., Zhang, Y., Xu, J., 2010. The effect of marine isoprene emissions on secondary organic aerosol and ozone formation in the coastal United States. *Atmos. Environ.* 44, 115–121. doi:10.1016/j.atmosenv.2009.08.027
- 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
- Guenther, a., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.* 6, 3181–3210. doi:10.5194/acpd-6-107-2006
- 20 Hildebrandt, L., Donahue, N.M., Pandis, S.N., 2009. High formation of secondary organic aerosol from the photo-oxidation of toluene. *Atmos. Chem. Phys.* 9, 2973–2986. doi:10.5194/acp-9-2973-2009
- Hu, Q.-H., Xie, Z.-Q., Wang, X.-M., Kang, H., He, Q.-F., Zhang, P., 2013. Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic. *Sci. Rep.* 3, 2280. doi:10.1038/srep02280
- 25 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.,
- 30 Coe, H., Allan, J.D., Canagaratna, 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

- Kamilli, K.A., Ofner, J., Krause, T., Sattler, T., Schmitt-Kopplin, P., Eitenberger, E., Friedbacher, G., Lendl, B., Lohninger, H., Schöler, H.F., Held, A., 2016. How salt lakes affect atmospheric new particle formation: A case study in Western Australia. *Sci. Total Environ.* 573, submitted. doi:10.1016/j.scitotenv.2016.08.058
- Koo, B., Knipping, E., Yarwood, G., 2014. 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ. *Atmos. Environ.* 95, 158–164. doi:10.1016/j.atmosenv.2014.06.031
- Krechmer, J.E., Coggon, M.M., Massoli, P., Nguyen, T.B., Crounse, J.D., Hu, W., Day, D.A., Tyndall, G.S., Henze, D.K., Rivera-Rios, J.C., Nowak, J.B., Kimmel, J.R., Mauldin, R.L., Stark, H., Jayne, J.T., Sipila, M., Junninen, H., St. Clair, J.M., Zhang, X., Feiner, P.A., Zhang, L., Miller, D.O., Brune, W.H., Keutsch, F.N., Wennberg, P.O., Seinfeld, J.H., Worsnop, D.R., Jimenez, J.L., Canagaratna, M.R., 2015. Formation of Low Volatility Organic Compounds and Secondary Organic Aerosol from Isoprene Hydroxyhydroperoxide Low-NO Oxidation. *Environ. Sci. Technol.* 49, 10330–10339. doi:10.1021/acs.est.5b02031
- Kroll, J.H., Donahue, N.M., Jimenez, J.L., Kessler, S.H., Canagaratna, M.R., Wilson, K.R., Altieri, K.E., Mazzoleni, L.R., Wozniak, A.S., Bluhm, H., Mysak, E.R., Smith, J.D., Kolb, C.E., Worsnop, D.R., 2011. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nat. Chem.* 3, 133–139. doi:10.1038/nchem.948
- Kroll, J.H., Ng, N.L., Murphy, S.M., Flagan, R.C., Seinfeld, J.H., 2006. Secondary organic aerosol formation from isoprene photooxidation. *Environ. Sci. Technol.* 40, 1869–1877. doi:10.1021/es0524301
- Lawler, M.J., Sander, R., Carpenter, L.J., Lee, J.D., Von Glasow, R., Sommariva, R., Saltzman, E.S., 2011. HOCl and Cl<sub>2</sub> observations in marine air. *Atmos. Chem. Phys.* 11, 7617–7628. doi:10.5194/acp-11-7617-2011
- Lee, B.H., Lopez-Hilfiker, F.D., Mohr, C., Kurtén, T., Worsnop, D.R., Thornton, J.A., 2014. An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic and organic compounds. *Environ. Sci. Technol.* 48, 6309–6317. doi:10.1021/es500362a
- Liao, J., Huey, L.G., Liu, Z., Tanner, D.J., Cantrell, C. a., Orlando, J.J., Flocke, F.M., Shepson, P.B., Weinheimer, A.J., Hall, S.R., Ullmann, K., Beine, H.J., Wang, Y., Ingall, E.D., Stephens, C.R., Hornbrook, R.S., Apel, E.C., Riemer, D., Fried, A., Mauldin, R.L., Smith, J.N., Staebler, R.M., Neuman, J.A., Nowak, J.B., 2014. High levels of molecular chlorine in the Arctic atmosphere. *Nat. Geosci.* 7, 91–94. doi:10.1038/ngeo2046
- 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
- Liu, J., D'Ambro, E.L., Lee, B.H., Lopez-Hilfiker, F.D., Zaveri, R.A., Rivera-Rios, J.C., Keutsch, F.N., Iyer, S., Kurten, T., Zhang, Z., Gold, A., Surratt, J.D., Shilling, J.E., Thornton, J.A., 2016. Efficient Isoprene Secondary Organic Aerosol Formation from a Non-IEPOX Pathway. *Environ. Sci. Technol.* 50, 9872–9880. doi:10.1021/acs.est.6b01872
- Lobert, J.M., Keene, W.C., Logan, J.A., Yevich, R., 1999. Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory. *J. Geophys. Res. Atmos.* 104, 8373–8389. doi:10.1029/1998JD100077

- Luo, G., Yu, F., 2010. A numerical evaluation of global oceanic emissions of alpha-pinene and isoprene. *Atmos. Chem. Phys.* 10, 2007–2015. doi:10.5194/acp-10-2007-2010
- Mielke, L.H., Stutz, J., Tsai, C., Hurlock, S.C., Roberts, J.M., Veres, P.R., Froyd, K.D., Hayes, P.L., Cubison, M.J., Jimenez, J.L., Washenfelter, R.A., Young, C.J., Gilman, J.B., De Gouw, J.A., Flynn, J.H., Grossberg, N., Lefer, B.L., Liu, J., Weber, R.J., Osthoff, H.D., 2013. Heterogeneous formation of nitryl chloride and its role as a nocturnal NO<sub>x</sub> reservoir species during CalNex-LA 2010. *J. Geophys. Res. Atmos.* 118, 10638–10652. doi:10.1002/jgrd.50783
- Molina, M.J., Rowland, F.S., 1974. Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone. *Nature* 249, 810–812. doi:10.1038/249810a0
- Murphy, B.N., Donahue, N.M., Fountoukis, C., Dall'Osto, M., O'Dowd, C., Kiendler-Scharr, A., Pandis, S.N., 2012. Functionalization and fragmentation during ambient organic aerosol aging: Application of the 2-D volatility basis set to field studies. *Atmos. Chem. Phys.* 12, 10797–10816. doi:10.5194/acp-12-10797-2012
- O'Dowd, C.D., de Leeuw, G., 2007. Marine aerosol production: a review of the current knowledge. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 365, 1753–1774. doi:10.1098/rsta.2007.2043
- Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan Richard, C., Seinfeld John, H., 1996. Gas particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.* 30, 2580–2585. doi:10.1021/es950943+
- Ofner, J., Balzer, N., Buxmann, J., Grothe, H., Schmitt-Kopplin, P., Platt, U., Zetzsch, C., 2012. Halogenation processes of secondary organic aerosol and implications on halogen release mechanisms. *Atmos. Chem. Phys.* 12, 5787–5806. doi:10.5194/acp-12-5787-2012
- Ofner, J., Kamilli, K.A., Held, A., Lendl, B., Zetzsch, C., 2013. Halogen-induced organic aerosol (XOA): a study on ultra-fine particle formation and time-resolved chemical characterization. *Faraday Discuss.* 165, 115–135. doi:10.1039/c3fd00093a
- Orlando, J.J., Tyndall, G.S., Apel, E.C., Riemer, D.D., Paulson, S.E., 2003. Rate coefficients and mechanisms of the reaction of Cl-atoms with a series of unsaturated hydrocarbons under atmospheric conditions. *Int. J. Chem. Kinet.* 35, 334–353. doi:10.1002/kin.10135
- Osthoff, H.D., Roberts, J.M., Ravishankara, A.R., Williams, E.J., Lerner, B.M., Sommariva, R., Bates, T.S., Coffman, D., Quinn, P.K., Dibb, J.E., Stark, H., Burkholder, J.B., Talukdar, R.K., Meagher, J., Fehsenfeld, F.C., Brown, S.S., 2008. High levels of nitryl chloride in the polluted subtropical marine boundary layer. *Nat. Geosci.* 1, 324–328. doi:10.1038/ngeo177
- Parrish, D.D., Allen, D.T., Bates, T.S., Estes, M., Fehsenfeld, F.C., Feingold, G., Ferrare, R., Hardesty, R.M., Meagher, J.F., Nielsen-Gammon, J.W., Pierce, R.B., Ryerson, T.B., Seinfeld, J.H., Williams, E.J., 2009. Overview of the second texas air quality study (TexAQS II) and the Gulf of Mexico atmospheric composition and climate study (GoMACCS). *J. Geophys. Res. Atmos.* 114, 1–28. doi:10.1029/2009JD011842
- Platt, U., Hönninger, G., 2003. The role of halogen species in the troposphere. *Chemosphere* 52, 325–338. doi:10.1016/S0045-6535(03)00216-9

- Pöhler, D., Vogel, L., Friess, U., Platt, U., 2010. Observation of halogen species in the Amundsen Gulf, Arctic, by active long-path differential optical absorption spectroscopy. *Proc. Natl. Acad. Sci.* 107, 6582–6587. doi:10.1073/pnas.0912231107
- Ragains, M.L., Finlayson-Pitts, B.J., 1997. Kinetics and mechanism of the reaction of Cl atoms with 2-methyl-1,3-butadiene (isoprene) at 298 K. *J. Phys. Chem. A* 101, 1509–1517. doi:10.1021/jp962786m
- 5 Read, K.A., Mahajan, A.S., Carpenter, L.J., Evans, M.J., Faria, B.V.E., Heard, D.E., Hopkins, J.R., Lee, J.D., Moller, S.J., Lewis, A.C., Mendes, L., McQuaid, J.B., Oetjen, H., Saiz-Lopez, A., Pilling, M.J., Plane, J.M.C., 2008. Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean. *Nature* 453, 1232–1235. doi:10.1038/nature07035
- Riedel, T.P., Bertram, T.H., Crisp, T.A., Williams, E.J., Lerner, B.M., Vlasenko, A., Li, S.M., Gilman, J., De Gouw, J., Bon, D.M., Wagner, N.L., Brown, S.S., Thornton, J.A., 2012. Nitryl chloride and molecular chlorine in the coastal marine boundary layer. *Environ. Sci. Technol.* 46, 10463–10470. doi:10.1021/es204632r
- 10 Riedel, T.P., Lin, Y.H., Budisulistiorini, S.H., Gaston, C.J., Thornton, J.A., Zhang, Z., Vizuite, 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., Vizuite, 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
- 15 Riedel, T.P., Wagner, N.L., Dubé, W.P., Middlebrook, A.M., Young, C.J., Öztürk, F., Bahreini, R., Vandenboer, T.C., Wolfe, D.E., Williams, E.J., Roberts, J.M., Brown, S.S., Thornton, J.A., 2013. Chlorine activation within urban or power plant plumes: Vertically resolved  $\text{ClNO}_2$  and  $\text{Cl}_2$  measurements from a tall tower in a polluted continental setting. *J. Geophys. Res. Atmos.* 118, 8702–8715. doi:10.1002/jgrd.50637
- 20 Riedel, T.P., Wolfe, G.M., Danas, K.T., Gilman, J.B., Kuster, W.C., Bon, D.M., Vlasenko, A., Li, S.-M., Williams, E.J., Lerner, B.M., Veres, P.R., Roberts, J.M., Holloway, J.S., Lefer, B., Brown, S.S., Thornton, J. a., 2014. An MCM modeling study of nitryl chloride ( $\text{ClNO}_2$ ) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow. *Atmos. Chem. Phys.* 14, 3789–3800. doi:10.5194/acp-14-3789-2014
- 25 Riva, M., Budisulistiorini, S.H., Chen, Y., Zhang, Z., D'Ambro, E.L., Zhang, X., Gold, A., Turpin, B.J., Thornton, J.A., Canagaratna, M.R., Surratt, J.D., 2016. Chemical Characterization of Secondary Organic Aerosol from Oxidation of Isoprene Hydroxyhydroperoxides. *Environ. Sci. Technol.* 50, 9889–9899. doi:10.1021/acs.est.6b02511
- Saiz-Lopez, A., von Glasow, R., 2012. Reactive halogen chemistry in the troposphere. *Chem. Soc. Rev.* 41, 6448. doi:10.1039/c2cs35208g
- 30 Sarwar, G., Simon, H., Bhawe, P., Yarwood, G., 2012. Examining the impact of heterogeneous nitryl chloride production on air quality across the United States. *Atmos. Chem. Phys.* 12, 6455–6473. doi:10.5194/acp-12-6455-2012
- Simpson, W.R., Brown, S.S., Saiz-Lopez, A., Thornton, J.A., Von Glasow, R., 2015. Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts. *Chem. Rev.* 115, 4035–4062. doi:10.1021/cr5006638

- Stutz, J., 2002. Atmospheric reactive chlorine and bromine at the Great Salt Lake, Utah. *Geophys. Res. Lett.* 29, 18–21. doi:10.1029/2002GL014812
- Surratt, J.D., Chan, A.W., Eddingsaas, N.C., Chan, M., Loza, C.L., Kwan, A.J., Hersey, S.P., Flagan, R.C., Wennberg, P.O., Seinfeld, J.H., 2010. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proc Natl Acad Sci U S A* 107, 6640–6645. doi:10.1073/pnas.0911114107
- 5 Surratt, J.D., Murphy, S.M., Kroll, J.H., Ng, N.L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeulen, R., Maenhaut, W., Claeys, M., Flagan, R.C., Seinfeld, J.H., 2006. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. *J. Phys. Chem. A* 110, 9665–9690. doi:10.1021/jp061734m
- Tanaka, P.L., Riemer, D.D., Chang, S., Yarwood, G., McDonald-Buller, E.C., Apel, E.C., Orlando, J.J., Silva, P.J., Jimenez, J.L., Canagaratna, M.R., Neece, J.D., Mullins, C.B., Allen, D.T., 2003. Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas. *Atmos. Environ.* 37, 1393–1400. doi:10.1016/S1352-2310(02)01007-5
- 10 Thornton, J.A., Kercher, J.P., Riedel, T.P., Wagner, N.L., Cozic, J., Holloway, J.S., Dubé, W.P., Wolfe, G.M., Quinn, P.K., Middlebrook, A.M., Alexander, B., Brown, S.S., 2010. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature* 464, 271–4. doi:10.1038/nature08905
- 15 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
- 20 Xu, L., Kollman, M.S., Song, C., Shilling, J.E., Ng, N.L., 2014. Effects of NO<sub>x</sub> on the volatility of secondary organic aerosol from isoprene photooxidation. *Environ. Sci. Technol.* 48, 2253–2262. doi:10.1021/es404842g
- Yarwood, G., Jung, J., Whitten, G.Z., Heo, G., Mellberg, J., Estes, M., 2010. Updates to the Carbon Bond Mechanism for Version 6 (CB6), in: Presented at the 9th Annual CMAS Conference, Chapel Hill, NC, October 11-13. pp. 1–4.
- Yuan, B., Koss, A., Warneke, C., Gilman, J.B., Lerner, B.M., Stark, H., De Gouw, J.A., 2016. A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions (H<sub>3</sub>O<sup>+</sup> ToF-CIMS) for measurements of volatile organic compounds in the atmosphere. *Atmos. Meas. Tech.* 9, 2735–2752. doi:10.5194/amt-9-2735-2016
- 25 Zhao, B., Wang, S., Donahue, N.M., Chuang, W., Hildebrandt Ruiz, L., Ng, N.L., Wang, Y., Hao, J., 2015. Evaluation of one-dimensional and two-dimensional volatility basis sets in simulating the aging of secondary organic aerosol with smog-chamber experiments. *Environ. Sci. Technol.* 49, 2245–2254. doi:10.1021/es5048914

# Secondary organic aerosol from chlorine-initiated oxidation of isoprene

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**Abstract.** Recent studies have found ~~inland~~ concentrations of reactive chlorine species to be higher than expected, suggesting that atmospheric chlorine chemistry is more extensive than previously thought. Chlorine radicals can interact with HO<sub>x</sub> radicals and nitrogen oxides (NO<sub>x</sub>) to alter the oxidative capacity of the atmosphere. They are known to rapidly oxidize a wide range of volatile organic compounds (VOC) found in the atmosphere, yet little is known about secondary organic aerosol (SOA) formation from chlorine-initiated photo-oxidation and its atmospheric implications. Environmental chamber experiments were carried out under low-NO<sub>x</sub> conditions with isoprene and chlorine as primary VOC and oxidant sources. Upon complete isoprene consumption, observed SOA yields ranged from 8 % to 36 %, decreasing with extended photo-oxidation and SOA aging. Formation of particulate organochloride was observed. A High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer was used to determine the molecular composition of gas-phase species using iodide-water and hydronium-water cluster ionization. ~~Ions~~ Multi-generational chemistry was observed, including ions consistent with hydroperoxides, chloroalkyl hydroperoxides, isoprene-derived epoxydiol (IEPOX) and ~~other common OH isoprene oxidation products were observed, hypochlorous acid (HOCl),~~ evident of secondary OH production and resulting chemistry from Cl-initiated reactions. This is the first reported study of SOA formation from chlorine-initiated oxidation of isoprene. Results suggest that tropospheric chlorine chemistry could contribute significantly to organic aerosol loading.

## 20 1 Introduction

Studies have shown that long-term exposure to fine particulate matter (PM), also known as aerosol, is linked to increases in mortality and cardiorespiratory diseases (Dockery et al., 1993; Pope et al., 2006). Short term exposure to aerosol could also induce stress response and cytotoxicity in cells (de Bruijne et al., 2009; Ebersviller et al., 2012; Hawley et al., 2014). Equilibrium partitioning of oxidized, semi-volatile organic compounds (Pankow, 1994), collectively referred to as secondary organic aerosol (SOA), contributes 20–90 % to the global fine aerosol budget (Jimenez et al., 2009; Kanakidou et al., 2005). The majority of SOA originates from oxidation of biogenic volatile organic compounds (BVOCs), which account for ~90% of annual non-methane hydrocarbon emissions (Goldstein and Galbally, 2007; Guenther et al., 2012), among which isoprene has the highest emission rate at ~600 Tg<sub>yr</sub><sup>-1</sup> (Guenther et al., 2006). Isoprene SOA formation initiated by ozone, ~~(O<sub>3</sub>)~~, nitrate, and hydroxyl, ~~and nitrate (OH)~~ radicals has been studied extensively and is estimated to account for 6–30 Tg<sub>yr</sub><sup>-1</sup> of the global



aerosol budget (Brégonzio-Rozier et al., 2015; Claeys, 2004; Guenther et al., 2006; Kroll et al., 2006; Lin et al., 2012; Surratt et al., 2006, 2010; Zhao et al., 2015). Meanwhile, (Brégonzio-Rozier et al., 2015; Claeys, 2004; Guenther et al., 2006; Kroll et al., 2006; Lin et al., 2012; Surratt et al., 2006, 2010; Zhao et al., 2015), but the importance of isoprene SOA formation within the marine boundary layer (MBL) remains highly disputed in literature (Arnold et al., 2009; Bikkina et al., 2014; Fu et al., 2011, 2013; Gantt et al., 2010, 2015; Hu et al., 2013; Luo and Yu, 2010; O'Dowd and de Leeuw, 2007). Although production of reactive chlorine species such as  $\text{Cl}_2/\text{HOCl}$  has been observed within the MBL (Lawler et al., 2011), little is known about SOA from chlorine-initiated oxidation of isoprene.

Chlorine chemistry is known to have important effects on ozone layer depletion (Crutzen, 1974; Molina and Rowland, 1974). Recent laboratory studies and field measurements also suggest an important role of halogen (X) chemistry on tropospheric composition (Faxon and Allen, 2013; Finlayson-Pitts, 2010; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Reactive halogen species in the form of  $\text{X}_2$ ,  $\text{XO}$ ,  $\text{HOX}$ ,  $\text{XNO}_2$ ,  $\text{OXO}$  are present in polar regions (Buys et al., 2013; Liao et al., 2014; Pöhler et al., 2010), the MBL (Lawler et al., 2011; Read et al., 2008), coastal and inland regions (Mielke et al., 2013; Riedel et al., 2012, 2013). Outside of MBL and polar regions, natural emissions of reactive halogen species have been observed in volcano plumes (Bobrowski et al., 2007) and over salt lakes (Kamilli et al., 2016; Stutz, 2002). Anthropogenic sources include industrial emissions (Chang and Allen, 2006; Riedel et al., 2013; Tanaka et al., 2003), oil and gas production (Edwards et al., 2014), water treatment (Chang et al., 2001), biomass burning (Lobert et al., 1999), engine exhaust (Osthoff et al., 2008; Parrish et al., 2009), and  $\text{NO}_x$ -mediated heterogeneous reactions, notably the production of  $\text{ClNO}_2$  via reactive uptake of  $\text{N}_2\text{O}_5$  onto particles containing  $\text{Cl}^-$  (Thornton et al., 2010). Recent studies have found that models under-predict the abundance of reactive halogen species, suggesting incomplete understanding of their sources (Faxon and Allen, 2013; Faxon et al., 2015; Simpson et al., 2015; Thornton et al., 2010). Photolysis of reactive halogen species produces halogen radicals that can react with  $\text{O}_3$ , hydrocarbons, SOA, and other radicals in the atmosphere. Reactions with hydrocarbons and organic aerosol serve as chlorine and bromine radical sinks (Buxmann et al., 2015; Ofner et al., 2012; Platt and Hönninger, 2003), especially in high  $\text{NO}_x$  environments where halogen recycling via  $\text{HO}_x$  and  $\text{XO}$  reaction pathways is suppressed (Edwards et al., 2013; Riedel et al., 2014; Simpson et al., 2015).

The concentration of chlorine radicals is estimated to be on the order of  $10^2$  to  $10^5$  molecules  $\text{cm}^{-3}$  (Saiz-Lopez and von Glasow, 2012; Wingenter et al., 1999, 2005), which is one to three orders of magnitude lower compared to OH radicals under ambient conditions (Faxon and Allen, 2013; Wingenter et al., 1999), but due to its high reactivity towards numerous VOCs, chlorine radicals could contribute significantly as a primary oxidant under certain circumstances-conditions (Riedel et al., 2012; Riva et al., 2015; Young et al., 2014). Hydrogen-abstraction and chlorine-addition to alkenesVOC produce peroxy and chloroperoxy radicals, respectively, that could lead to the production of secondary  $\text{HO}_x$  radicals and the formation of semi-volatile oxidized products. Studies have shown- that chlorine-initiated oxidation of alpha-pinene (Cai and Griffin, 2006; Ofner et al., 2013), toluene (Cai et al., 2008; Huang et al., 2014; Karlsson et al., 2001), and polycyclic aromatic hydrocarbons (PAHs, Riva et al., 2015) lead to SOA formation, with close to unity SOA yield reported for select PAHs (Riva et al., 2015). Reactive chlorine species could also enhance OH-radical propagation (Young et al., 2014), nocturnal  $\text{NO}_x$  recycling (Riedel et al., 2012;

Thornton et al., 2010), and ozone production (Tanaka et al., 2003), further increasing the oxidative capacity of the atmosphere. ~~Recent studies show that air quality models severely under predict the abundance of inland reactive chlorine species (Faxon and Allen, 2013; Faxon et al., 2015; Riedel et al., 2012; Thornton et al., 2010), suggesting that chlorine chemistry may be more extensive than previously thought.~~

5 Chlorine-initiated oxidation of isoprene could either proceed via the dominant (85 %) chlorine addition pathway, ~~much like OH-isoprene reactions,~~ or ~~proceed via~~ a minor (15 %) hydrogen-abstraction pathway (Fantechi et al., 1998; Lei and Zhang, 2000; Nordmeyer et al., 1997; Orlando et al., 2003). Major gas-phase products include methyl vinyl ketone (MVK), methacrolein (MACR), chloroacetone, chloroacetaldehyde, hydrochloric acid, and isomers of 1-chloro-3-methyl-3-butene-2-one (CMBO), a unique tracer for atmospheric chlorine chemistry (Nordmeyer et al., 1997; Riemer et al., 2008; Tanaka et al.,  
10 2003). The rate constant of the isoprene-chlorine reaction at 25°C ( $2.64\text{--}5.50 \times 10^{-10}$  molecules<sup>-1</sup> cm<sup>3</sup>) (Fantechi et al., 1998; Orlando et al., 2003; Ragains and Finlayson-Pitts, 1997) is much faster than the rate constant of the isoprene-OH reaction ( $1.00 \times 10^{-10}$  molecules<sup>-1</sup> cm<sup>3</sup>) (Atkinson and Arey, 2003), suggesting that isoprene-chlorine chemistry could compete with isoprene-OH chemistry under certain conditions. Moreover, reactions between chlorine and isoprene or isoprene-derived SOA could serve as a reactive chlorine sink in the atmosphere, as has been proposed for reactions between chlorine and biogenic SOA  
15 (Ofner et al., 2012). To our knowledge, SOA formation from chlorine-initiated oxidation of isoprene has not been reported in literature. ~~To address In order to address this significant knowledge gap, we conducted~~ environmental chamber experiments were conducted using chlorine radicals as the primary oxidant source for isoprene oxidation ~~under low NO<sub>x</sub> conditions.~~ Experiments were conducted under low NO<sub>x</sub> conditions, using neutral or acidified seed aerosol to evaluate the effect of aerosol acidity on SOA formation. We report SOA composition, yields and select gas phase products. The mass yields and composition  
20 of SOA formed from chlorine-initiated oxidation of isoprene are reported for the first time. Formation of organochlorides was also observed. Gas-phase measurements provide evidence of multi-generational oxidation chemistry, secondary HO<sub>x</sub> chemistry, and multifunctional gas-phase products.

## 2 Methods

### 2.1 Environmental Chamber Experiments

25 Experiments were performed at 25° C under low relative humidity (RH < 10%) and low NO<sub>x</sub> (< 5 ppb) conditions in a 12 m<sup>3</sup> temperature-controlled Teflon® chamber lined with UVA lights. Chamber characteristics were described elsewhere (Bean and Hildebrandt Ruiz, 2016). The UV spectrum is similar to other blacklight sources reported in literature (Carter et al., 2005). The NO<sub>2</sub> photolysis rate is used to characterize UV intensity and was determined to be 0.5 min<sup>-1</sup>, similar to ambient levels (e.g. 0.53 min<sup>-1</sup> at 0 degrees zenith angle, Carter et al., 2005). Temperature, RH, and the concentrations of ozone, NO, NO<sub>2</sub>,  
30 and NO<sub>x</sub> were continuously monitored. The chamber was flushed with dry clean air generated by a clean air generator (Aadco 737R) at a flowrate exceeding 100 liters per minute (LPM) for at least 12 hours before each experiment. Between experiments, “blank experiments” were conducted in which seed particles, ozone, and chlorine gas (Cl<sub>2</sub> Airgas, 106 ppm in N<sub>2</sub>) were injected

into the chamber at high concentrations and UV lights were turned on to remove any residual organics which could be released from the Teflon® chamber surface. Background effects have been quantified using chamber characterization experiments (Carter et al., 2005) and the SAPRC chamber modeling software (<http://www.engr.ucr.edu/~carter/SAPRC/>) in combination with the Carbon Bond 6 (CB6r2) chemical mechanism, which was modified to include basic gas phase inorganic chlorine chemistry in addition to Cl<sub>2</sub> and ClNO<sub>2</sub> photolysis (Sarwar et al., 2012; Yarwood et al., 2010). NO<sub>x</sub>-offgasing is represented within the model by a constant emission of nitrous acid (HONO) from the chamber walls on the order of 0.1 ppb min<sup>-1</sup>, which was determined separately in chamber characterization experiments (Carter et al., 2005).

For each experiment, microliters of isoprene (Acros Organics, 98% stabilized) were transferred into a glass sampling tube (Kimble-Chase, 250 ml), which was then flushed with zeroclean air into the chamber. Depositional particle wall loss was constrained using dried, monomodal, and polydisperse seed particles introduced prior to photo-oxidation using an Aerosol Generation System (Brechtel, AGS Model 9200). Neutral seed particles were generated from a 0.01 M ammonium sulfate solution; acidic seed particles were generated using a solution containing 0.005 M ammonium sulfate and 0.0025 M sulfuric acid. Two Cl<sub>2</sub> injection methods were used: For “initial easeCl<sub>2</sub>” experiments, all Cl<sub>2</sub> was injected in the dark and allowed to mix with isoprene prior to photo-oxidation. For “continuous easeCl<sub>2</sub>” experiments, Cl<sub>2</sub> was injected continuously with UV lights on at 0.1 LPM with an additional 0.9 LPM clean air dilution flow, equivalent to ~0.88 ppb/min Cl<sub>2</sub> into the chamber. ~~Depositional particle wall loss was constrained using dried, monomodal, and polydisperse ammonium sulfate seed particles introduced prior to photo-oxidation.~~ Initial Cl<sub>2</sub> experiments were performed to achieve rapid oxidation of isoprene and to separate initial SOA formation from effects of vapor wall loss. Because chlorine radicals are not expected to regenerate, continuous Cl<sub>2</sub> injection experiments were performed to provide more steady but lower Cl radical concentrations.

## 2.2 Instrumentation

A High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (Aerodyne Research Inc., “CIMS”) was used to measure gas-phase organic compounds ~~via proton transfer, charge exchange, or clustering with chemical ionization (CI) reagent ions, with humidified ultra-high purity nitrogen as the carrier gas. Hydronium water cluster ([H<sub>2</sub>O]<sub>n</sub>H<sub>3</sub>O<sup>+</sup>) ionization detected isoprene and select moderately oxidized species. Iodide water cluster ([H<sub>2</sub>O]<sub>n</sub>I<sup>-</sup>) ionization detected, select highly oxidized and acidic species (Aljawhary et al., 2013; Lee et al., 2014).~~ Detailed theory and operation of the CIMS are discussed elsewhere (Aljawhary et al., 2013; Bertram et al., 2011; Lee et al., 2014; Yatavelli et al., 2012). Reagent ions are generated by passing humidified UHP N<sub>2</sub> over a methyl iodide permeation tube and then through a <sup>210</sup>Po radioactive cartridge (NRD, 2013) at 2 LPM into the ion-molecule reaction (IMR) chamber operating at 200 mbar pressure. Analyte, “M” can undergo chemical ionization within the IMR with hydronium-water ([H<sub>2</sub>O]<sub>n</sub>[H<sub>3</sub>O]<sup>+</sup>) or iodide-water ([H<sub>2</sub>O]<sub>n</sub>I<sup>-</sup>) ion clusters.



where the number of clusters, “n” ranges from 0 and 2 for  $[\text{H}_2\text{O}]_n[\text{H}_3\text{O}]^+$ , with  $[\text{H}_2\text{O}][\text{H}_3\text{O}]^+$  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 (Aljawhary et al., 2013). For  $[\text{H}_2\text{O}]_n\text{I}^-$  ionization, “n” ranges from 0 to 1, with  $\text{I}^-$  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).— An Aerosol Chemical Speciation Monitor (Aerodyne Research Inc., “ACSM”) was used to determine the bulk chemical composition of submicron, non-refractory aerosol species (Ng et al., 2011a). Analytes are flash-vaporized at 600° C, ionized via electron impact ionization (EI) (Ng et al., 2011a), and then measured by a quadrupole mass spectrometer (Ng et al., 2011a). Background-corrected (“difference”) mass spectra are obtained by subtracting filtered (“closed”) from unfiltered (“open”) measurements (Ng et al., 2011a). A standard fragmentation table is used to speciate difference mass spectra (Allan et al., 2004). Calibration is performed with 300 nm size-selected ammonium nitrate and ammonium sulfate aerosol to determine the response factor for particulate nitrate and the relatively relative ionization efficiencies (RIE) for sulfate and ammonium; these values are needed to convert ion intensities to mass concentrations (Ng et al., 2011a). Particle volume and size distributions were measured using a Scanning Electrical Mobility Spectrometer (Brechtel, SEMS Model 2002) consisting of a Differential Mobility Analyzer and a butanol Condensation Particle Counter. SEMS sheath and sample flowrates were set to 5 and 0.35 LPM, respectively, covering a 10–1000 nm sizing range.

## 2.3 Data Analysis

Suspended particles are lost to the Teflon® chamber wall over time, for which numerous correction methods have been proposed (Carter et al., 2005; Hildebrandt et al., 2009; Nah et al., 2017; Ng et al., 2007; Pathak et al., 2007; Pierce et al., 2008; Verheggen and Mozurkewich, 2006). Recent studies also report loss of organic vapors to Teflon® surfaces (Kokkola et al., 2014; Krechmer et al., 2016; Loza et al., 2010; Matsunaga and Ziemann, 2010; Zhang et al., 2015). Assuming internal mixing of particles and that organic vapor can condense onto suspended and wall-deposited particles alike, we corrected for particle wall loss and the loss of organic vapors onto wall-deposited particles using the organic-to-sulfate ratio (Hildebrandt et al., 2009),

$$C_{OA}(t) = \frac{C_{OA}^{sus}(t)}{C_{seed}^{sus}(t)} C_{seed}^{sus}(t = 0) \quad (3)$$

where  $C_{OA}^{sus}(t)$  is the suspended organic aerosol (OA) concentration, which was zero at the start of each experiment,  $C_{seed}^{sus}(t)$  is the suspended ammonium sulfate seed particle concentration,  $C_{seed}^{sus}(t = 0)$  is the suspended seed particle mass concentration at the start of photo-oxidation, and  $C_{OA}(t)$  is the corrected OA concentration. ~~Note that Eq. (1) does not account for loss of organic vapors to clean Teflon surfaces, which could be significant for SVOCs (Krechmer et al., 2016). This correction does not account for loss of organic vapors to clean Teflon® surfaces.~~

SOA yield,  $Y$ , is calculated as,

$$Y = \frac{C_{OA}}{\Delta VOC} \quad (4)$$

where  $\Delta VOC$  is the amount of VOC consumed. Based on absorptive equilibrium partitioning theory (Odum et al., 1996; Pankow, 1994), the volatility basis set (VBS) framework (Donahue et al., 2006) states that

$$Y = \xi = \sum_i \alpha_i \xi_i \quad (5)$$

$$C_i = \alpha_i \Delta VOC \quad (6)$$

$$5 \quad \xi_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad (7)$$

$$C_{OA} = \sum_i C_i \xi_i \quad (8)$$

where  $C_i^*$  is the effective saturation concentration of the surrogate compound in VBS bin  $i$  in  $\mu\text{g m}^{-3}$ ;  $\alpha_i$ ,  $C_i$ ,  $\xi_i$  are the total yield, total mass concentration, and the condensed phase mass fraction of bin  $i$ , respectively. By rearranging Eq. (3), ~~we can derive~~ (5) - (8), an expression for the minimum VOC consumption required for SOA formation can be derived (see section S1),

$$10 \quad (\Delta VOC_{min})^{-1} = \sum_1^n \frac{\alpha_i}{C_i^*} \quad (9)$$

where  $\Delta VOC_{min}$  is low if low-volatility compounds dominate the aerosol phase. When aerosol volatility is low and aerosol loading is high, such that the condensed phase mass fraction,  $\xi_i$  from Eq. (7), approaches 1, ~~where~~ the “maximum” SOA yield (Griffin et al., 1999) according to Eq. (2) and Eq. (3) is reached, where

$$Y_{max} = \sum_1^n \alpha_i \quad (10)$$

15 The extent of SOA oxidation is often depicted using  $f_{44}$  and  $f_{43}$ , which represent the fractional contribution to the total organic ion signal from ion fragments at mass-to-charge ( $m/z$ ) 44 (mostly  $\text{CO}_2^+$ , a proxy for doubly-oxidized compounds) and at  $m/z$  43 (mostly  $\text{C}_2\text{H}_3\text{O}^+$ , a proxy for singly-oxidized compounds), respectively (Chan et al., 2010; Chhabra et al., 2011; Ng et al., 2011b). Based on empirical correlations, the oxygen-to-carbon ratio (O:C), the hydrogen-to-carbon ratio (H:C), and the oxidation state of carbon ( $\overline{OS}_C$ ) can be estimated from  $f_{44}$  alone as summarized in section S2 (Canagaratna et al., 2015; Donahue et al., 2012; Heald et al., 2010; Kroll et al., 2011). The empirical correlations were derived using a comprehensive collection of Aerosol Mass Spectrometer datasets but may underestimate O:C values for SOA formed under low  $\text{NO}_x$  conditions from isoprene or toluene (Canagaratna et al., 2015). Variability in  $f_{43}$  and  $f_{44}$  among different ACSMs has also been reported (Crenn et al., 2015).

25 High resolution mass spectra fitting of CIMS data was performed using the software Tofware V2.5.7 (Tofwerk) in Igor Pro V6.37 (Wavemetrics Inc.). CIMS sensitivity correction utilized the Active Chemical Ionization Mass Spectroscopy (ACIMS) formula (de Gouw and Warneke, 2007), normalizing all product ion signals against dominant reagent ion signals,  $[\text{H}_2\text{O}]_n\text{H}_3\text{O}^+$  and  $[\text{H}_2\text{O}]_n\text{I}^-$ . For most experiments conducted, the reagent signals were at least five times greater than the summed product signals, equivalent to less than 10 % overcorrection by ACIMS compared to more rigorous methods such as Parallel-ACIMS, which accounts for reagent ion depletion (see section S3 for a more detailed discussion). Because the CIMS cannot distinguish

between isomers and because of the lack of calibration standards, gas-phase data presented here are normalized by the maximum signals for better visualization and evaluation of qualitative ~~interpretations only~~ trends.

### 3 Results and Discussion

#### 3.1 SOA Formation, Ageing, and Composition

5 Table 1 summarizes the experimental conditions and results. Figure 1 compares wall loss-corrected SOA time series from ~~two~~  
10 three experiments with similar precursor concentrations. In the continuous chlorine experiments (C2 and C7), isoprene  
gradually reacted away during chlorine injection; SOA concentration steadily increased until isoprene was depleted, at which  
point SOA concentration began to decay. The decay of SOA is likely due to ~~(Boyd et al., 2015; Krechmer et al., 2016) and~~  
15 oxidative fragmentation (Kroll et al., 2011), vapor wall loss (Boyd et al., 2015;  
Krechmer et al., 2016), and/or photolysis of, for example, peroxide species (Kroll et al., 2006; Surratt et al., 2006), which are  
observed in the gas-phase (see Section 3.4). The initial chlorine experiment (A4) exhibited similar trends, ~~though the initial~~  
SOA decay rate was very fast, but the SOA decay was faster, where 30  $\mu\text{g m}^{-3}$  SOA decay (40% of maximum SOA mass)  
20 occurred within about 30 minutes of photo-oxidation ( $9 < T < 40$  mins), likely due to more rapid oxidation and fragmentation  
of reaction products ~~and loss of early generation low volatility products that are especially susceptible towards vapor wall loss~~  
25 ~~effects (Boyd et al., 2015).~~ Under UV, the effects of oxidative fragmentation and photolysis cannot be separated from the  
effects of vapor wall loss. SOA decay was slower in the dark than under UV (see section S2 and Fig. S1). Vapor wall effects  
are expected to be more important when the concentrations of the oxidant and OA are lower, in which case oxidative  
fragmentation effects are weaker and less absorbing mass is available to compete with wall loss. After extended photo-  
oxidation ( $T > 100$  mins), SOA concentrations achieved via initial chlorine injection (Exp. A4) and continuous chlorine  
30 injection (Exp. C2) differed by less than  $8 \mu\text{g m}^{-3}$  ( $< 20\%$  of total SOA mass at  $T = 100$  mins for Exp. C2). The data shown in  
Fig. 1 and summarized in Table 1 also suggest that aerosol acidity promotes SOA formation: the SOA concentration observed  
in acidified seed Exp. C7 were more than twice as high as SOA concentrations observed in neutral seed Exp. C2. In addition,  
greater seed aerosol surface area appears to result in higher SOA concentrations, as shown in Table 1 for Exp. A6 and Exp.  
A7. ~~It should be noted that little SOA formation delay was observed in all experiments~~ The formation of SOA began shortly  
25 after UV lights were turned on in all experiments.  $\Delta VOC_{min}$  from Eq. (9) is therefore small, suggesting that the initial oxidation  
products responsible for SOA formation have very low volatility. Prompt SOA formation was also observed in previous work  
for chlorine-initiated oxidation of alpha-pinene (Cai and Griffin, 2006; Ofner et al., 2013) and toluene (Cai et al., 2008; Huang  
et al., 2014; Karlsson et al., 2001). Formation of low volatility early generation products may be a common feature of chlorine-  
initiated oxidation. ~~Outside of the initial period, some vapor wall loss was observed, although oxidative fragmentation appeared~~  
30 ~~to be the main cause of SOA mass decrease (see section S2 and Fig. S1).~~

Figure 2 shows that SOA oxidation state, represented by  $f_{447}$  and estimated  $\overline{OS}_{c,1}$  depended on the initial isoprene  
concentration and was unaffected by the oxidant injection method. Because isoprene is more reactive towards chlorine radicals



than its oxidation products, such as MVK and MACR (Orlando et al., 2003), isoprene could scavenge radicals and delay SOA aging. Additionally, increased OA mass loading could absorb less oxidized and more volatile compounds into the particle-phase, lowering the observed SOA oxidation state at higher SOA loadings resulting from higher initial isoprene concentrations. ~~Estimated~~The estimated  $\overline{OS}_c$  of chlorine-isoprene SOA increased from -0.5 to over 1 during ~~experiment~~Exp. C1, characteristic of the evolution of semi-volatile oxygenated OA (SV-OOA) to low-volatility oxygenated OA (LV-OOA) (Kroll et al., 2011). Oxidation of chlorine-isoprene SOA formed under low NO<sub>x</sub> follows a similar trajectory as OH-isoprene SOA formed in previous work under higher NO<sub>x</sub>, which is considerably more oxidized than OH-isoprene SOA formed under low NO<sub>x</sub> (Chhabra et al., 2011), as shown in ~~Figure~~Fig. 3. The oxidizing capacity of chlorine radicals has also been demonstrated for select biogenic SOA derived from ~~α~~alpha-pinene, catechol, and guaiacol, where halogenation led to significant SOA aging, formation of high molecular weight compounds, and particle growth (Ofner et al., 2012). High reactivity of chlorine radicals towards isoprene and its reaction products meant that extensive SOA processing could be easily achieved within laboratory timescales.

### 3.2 Particulate ~~Organic Chloride~~Organochloride

Chlorine addition to the double bond is the dominant (~85%) isoprene-chlorine reaction pathway (Fan and Zhang, 2004; Ragains and Finlayson-Pitts, 1997), and thus the Formation formation of semi-volatile and low-volatility chlorinated organic compounds ~~could~~ would be expected, ~~but quantification proved to be difficult.~~ Aerosol analytes undergo electron impact ionization in the ACSM, and chlorine-containing ion fragments are mostly expected at  $m/z$  35 and 37 as Cl<sup>+</sup> and at  $m/z$  36 and 38 as HCl<sup>+</sup>. Larger organochloride ion fragments may exist but cannot be separated in the unit-mass resolution spectra. A previous study on chlorine-initiated oxidation of toluene, which proceeds primarily through a hydrogen-abstraction pathway, reported particulate chlorine formation (4 % of the total aerosol mass), which was attributed to HCl uptake (Cai et al., 2008). Formation of organochloride aerosol has been observed previously for chlorine-initiated oxidation of alpha-pinene (Ofner et al., 2013), which proceeds primarily via a chlorine-addition reaction pathway. Thus, isoprene-chlorine reactions are expected to result in particulate organochloride formation. The uptake of HCl produced from Cl H-abstraction or intramolecular HCl elimination (Ragains and Finlayson-Pitts, 1997) could also contribute slightly to observed particulate chlorine. Organochloride has also been observed in biogenic SOA post-processed by halogenation (Ofner et al., 2012), in new particles formed from 1,8-cineol and limonene over simulated salt lakes (Kamilli et al., 2015), and in-situ over salt lakes (Kamilli et al., 2016). To date, this is the only reported study of organochloride measurement using an ACSM.

As shown in Fig. 4 for Exp. H1A8, significant particulate chloride the ACSM initially observed significant levels of particulate chlorine (over 9 % of the total SOA mass) ~~was initially observed~~, which then decreased to near background levels.

In other experiments, particulate ~~ehloride-chlorine~~ concentrations were near the detection limit. The low observed ~~ehloride~~ chlorine concentration was likely due to incomplete vaporization of chlorinated compounds during the sample (“open”) period, resulting in particulate matter vaporization during the filter (“closed”) period and overestimation of background signals, as explained in more detail in section S4. ~~Furthermore, our~~ Further analysis shows that while the difference signal of a faster-

desorbing chlorine ion fragment ( $\text{HCl}^+$ ) correlates well with OA, the difference signal of a slower-desorbing ion fragment ( $\text{Cl}^+$ ) anti-correlates with OA (Fig. S7). The background  $\text{Cl}^+$  signal was consistently higher than the sample  $\text{Cl}^+$  signal, except when the sample organochloride concentration increased significantly much faster than background, as was the case for Exp. H1, a high-concentration experiment, as it does during the SOA formation period in initial chlorine injection experiments. Outside the initial SOA formation period, difference  $\text{Cl}^+$  signals were negative and difference  $\text{HCl}^+$  signals were positive, the summation of which resulted in the low apparent particulate chlorine concentrations. Our results show that the particulate chloride observed was likely organic chloride. The presence of organic chloride aerosol has been observed previously in SOA from chlorine-initiated oxidation of  $\alpha$ -pinene (Ofner et al., 2013), in SOA which was post-processed by halogenation (Ofner et al., 2012), as well as in new particle formation from 1,8-cineol and limonene over simulated salt lakes (Kamilli et al., 2015) using ion cyclotron Fourier transform/mass spectroscopy. To date, this is the only reported study of organic chloride measurement using an ACSM. A more detailed discussion of organic chloride detection with the ACSM can be found in section S4.

Low abundance has been cited as the reason for highly variable measurements of ambient particulate chlorine using ACSM and similar instruments (Crenn et al., 2015). Overall, our results indicate that the standard operating procedure of the ACSM and similar instrumentation may systematically underestimate chlorideparticulate chlorine concentration. To better quantify chlorideparticulate chlorine, the filtered measurement period could be extended to better capture the true background. Higher vaporizer temperatures could be applied to desorb low-volatility species more efficiently, but doing so could also change the fragmentation profile of all aerosol components. Another idea approach would be to only use fast-desorbing chlorideions ( $\text{HCl}^+$  ions)<sup>+</sup> for quantification: For SOA from chlorine-initiated oxidation of isoprene under low  $\text{NO}_x$ , the average ( $\text{HCl}^+$ )-to-organics ratio was  $0.07 \pm 0.01$  (Fig. S8).

### 3.3 SOA Yield

It is customary to present SOA yield as a function of OA loading. From Eq. (4), when the VOC precursor has been depleted, all subsequent yield  $Y$  varies linearly with  $C_{\text{OA}}$  along a slope of  $(\Delta\text{VOC}_0)^{-1}$ , the inverse of the initial VOC concentration. Post VOC depletion, SOA mass may further increase as multi-generationgenerational oxidation products partition to the particle phase, but SOA mass will eventually decrease due to fragmentation (Kroll et al., 2011). In theory, all VOC-oxidant mixtures whose  $\Delta\text{VOC}_{\text{min}}$  is less than  $\text{VOC}_0$  eventually fall somewhere on the same, pre-defined yield “line” with a slope of  $(\Delta\text{VOC}_0)^{-1}$ , and will converge (to Cartesian origin) over time as fragmentation becomes dominantcontinues. This pre-defined yield curve is thus non-unique and depends only on  $\text{VOC}_0$ . Incorporating data collected after VOC depletion, whether from the same experiment or different experiments with similar initial  $\text{VOC}_0$  values, biases the VBS fitting parameters towards the pre-defined yield curve (see section S5). Therefore, 1-dimensional VBS fitting is not sufficient to describe SOA formation and oxidation post VOC depletion, as numerousprevious studies have also pointed outnoted (Kroll et al., 2007; Liu et al., 2016; Xu et al., 2014). A twoTwo-dimensional modelmodeling 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.



Considering the different oxidation conditions examined in this study, varying initial isoprene, chlorine concentration, and duration of oxidation, we did not perform 1-D-VBS fitting on the collective dataset. Instead, the highest observed SOA yields Complete isoprene depletion, which coincides with the maximum SOA concentration, (see Fig. 1), is used as the reference condition for yield reporting in Table 1. Due to uncertainties with organochloride quantification, the particulate chlorine content was not included in the SOA yield calculation. Only results from ~~each experiment~~ neutral seed experiments are reported in Table 1 and compared ~~used for comparison~~ with other literature values of OH-oxidation under low and high NO<sub>x</sub> scenarios (Brégonzio-Rozier et al., 2015; Koo et al., 2014; Liu et al., 2016; Xu et al., 2014) in Fig. 5. ~~Maximum SOA yields were lower for continuous cases, likely because there was less suspended absorbing mass to retain initial low volatility products or to compete with vapor wall loss. It also took longer for continuous cases to reach maximum SOA concentrations, as shown in Fig. 1; the effects of vapor wall loss and oxidative fragmentation seemed to be more pronounced. Highest SOA yields observed for initial cases (A2–A5) were on average  $23.7 \pm 3.5$  %. For continuous cases (C1–C4), the average was  $9.5 \pm 1.3$  %.~~ In initial chlorine injection experiments, maximum SOA concentrations were reached within 15 minutes, and the effects of vapor wall loss, oxidative fragmentation, and photolysis on reported maximum SOA yield were lower than during continuous chlorine injection experiments. Observed SOA yields averaged  $20 \pm 3$  % for initial Cl<sub>2</sub> injection cases (A1–A5) and  $8 \pm 1$  % for continuous Cl<sub>2</sub> injection cases (C1–C4). Under atmospheric conditions, the isoprene-chlorine ratio will usually be higher than ratios used in these experiments. Previous studies on chlorine-initiated SOA formation from toluene (Cai et al., 2008) and limonene (Cai and Griffin, 2006) suggest that SOA yields decrease with higher VOC-to-Cl ratio. While we do not observe a clear correlation between SOA yield and isoprene-to-chlorine ratios used here (0.5-1.2), such dependence could be present over a wider ratio range. For air quality models which do not explicitly account for fragmentation reactions, the use of the average continuous case yield, which is similar to recently reported OH-oxidation yields by recent publications (Liu et al., 2016; Xu et al., 2014), is more appropriate because the isoprene-to-chlorine ratio is closer to atmospheric conditions and because the SOA yields from continuous injection experiments account for effects of OA aging in the atmosphere (which occur throughout the experiments). The presence of acidic aerosols and inclusion of particulate chlorine content would increase expected yields. Recall that the  $f_{44}$ -vs- $f_{43}$ -patterns observed were also similar for chlorine isoprene and OH isoprene SOA, as shown in Fig. 3. This suggests that OH- and chlorine-initiated oxidation of isoprene may result in SOA of similar bulk-vapor pressure and oxidation state. This is also suggested by gas-phase measurements as explained below.

### 3.4 Gas-phase products: ~~Overlaps with~~ Multigenerational oxidation, organochloride formation and secondary OH chemistry

Using (H<sub>2</sub>O)<sub>n</sub>H<sub>3</sub>O<sup>+</sup> CIMS, we observed ions consistent with isoprene [C<sub>5</sub>H<sub>8</sub><sup>+</sup> and (C<sub>5</sub>H<sub>8</sub>)H<sup>+</sup>], ~~methacrolein (MACR)/methyl vinyl ketone (MVK)~~ MACR/MVK [(C<sub>4</sub>H<sub>6</sub>O)H<sup>+</sup>], isomers of ~~3-methyl-3-butene-2-one~~ CMBO [(C<sub>5</sub>H<sub>7</sub>OC)H<sup>+</sup>], 2-methyl-3-buten-2-ol (MBO) [(C<sub>5</sub>H<sub>6</sub>O)H<sup>+</sup>], chloroacetone [(C<sub>3</sub>H<sub>5</sub>ClO)H<sup>+</sup>], and other gas-phase oxidation products, as shown in Fig. 6a. CMBO, MBO, and MVK/MACR were among the earliest oxidation products, which were ~~likely~~ further oxidized to produce SOA. MVK and MACR are also key intermediary products in OH-isoprene reactions from NO + RO<sub>2</sub> and RO<sub>2</sub> + RO<sub>2</sub> reaction

pathways (Kroll et al., 2006), where MACR is a known SOA precursor (Brégonzio-Rozier et al., 2015; Kroll et al., 2006; Surratt et al., 2006; Xu et al., 2014), which could contribute to some similarities between OH-isoprene and chlorine-isoprene SOA. Multiple generations of chlorinated C<sub>5</sub> compounds were observed in the gas-phase, as shown in Fig. 6a and 6b and 7a, possibly from continued oxidation of CMBO and chlorination of 2-methyl-3-buten-2-ol (MBO), which further demonstrates that semi-volatile and low volatility organic chlorides should be present. Another gas-phase product, C<sub>5</sub>H<sub>8</sub>O also appears to act as SOA precursor, and ions resembling its oxidation products (e.g., C<sub>5</sub>H<sub>7</sub>ClO<sub>2</sub> and C<sub>5</sub>H<sub>9</sub>ClO<sub>3</sub>) were observed (see Fig. S12). The formation of C<sub>5</sub>H<sub>8</sub>O from chlorine-isoprene oxidation has been proposed in literature (Nordmeyer et al., 1997). Previous studies that observed C<sub>5</sub>H<sub>8</sub>O during OH-initiated oxidation of isoprene identified it as 2-methylbut-3-enal, but its formation mechanism remains unclear (Brégonzio-Rozier et al., 2015; Healy et al., 2008) and is beyond the scope of this work. It should be noted that CMBO has long been identified as a unique gas-phase marker for isoprene-chlorine oxidation (Chang and Allen, 2006; Nordmeyer et al., 1997; Riemer et al., 2008; Tanaka et al., 2003). Degradation of CMBO by OH is implemented in some air quality models, though only with inferred reaction rates (Tanaka and Allen, 2001). Our gas-phase measurements and proposed reaction products suggest that CMBO undergoes further oxidation reactions initiated by chlorine. The This degradation of CMBO, and its role as a potential SOA precursor, could have important implications for estimating atmospheric chlorine activity and warrants further future investigation.

The formation of CMBO and MBO also produces HO<sub>2</sub> radicals (Orlando et al., 2003; Ragains and Finlayson-Pitts, 1997), serving which serve as a source of secondary OH radicals. Other unidentified HO<sub>x</sub> production pathways could also be present. Other RO<sub>2</sub> + RO<sub>2</sub> reaction pathways also produce HO<sub>x</sub> radicals. Evidence of secondary OH radical production has been reported for NO<sub>3</sub>-oxidation of isoprene (Kwan et al., 2012; Schwantes et al., 2015), for chlorine-initiated oxidation of methylnaphthalenes and naphthalene under low-NO<sub>x</sub> (Riva et al., 2015; Wang et al., 2005) and for chlorine-initiated oxidation of toluene under high NO<sub>x</sub> (Huang et al., 2012). Figure 7a6b shows the accumulation of ClOHOC<sub>5</sub> observed using ([H<sub>2</sub>O]<sub>10</sub>)<sup>+</sup> CIMS during the SOA growth period, where HO<sub>x</sub> radicals produced from chlorine-isoprene oxidation could react with excess chlorine. Production of OH is also possible from reactions between NO and HO<sub>2</sub> radicals, which would be more pronounced under high NO<sub>x</sub> conditions. No NO<sub>x</sub> was added to our experiments, and measured concentrations were below 5 ppb, mostly in the form of NO<sub>2</sub>. Because, which may have been released from the Teflon<sup>®</sup> surface under UV. We use the SOA trend as a common reference because isoprene is not detected using ([H<sub>2</sub>O]<sub>10</sub>)<sup>+</sup> CIMS, we use the SOA trend as a common reference. It can be seen in Fig. 1 and 6a that isoprene depletion roughly coincides with the SOA concentration peak. This explains the reversal from ClOHOC<sub>5</sub> production to ClOHOC<sub>5</sub> decay following the SOA concentration peak shown in Fig. 6b, when HO<sub>x</sub> radical production from isoprene-chlorine oxidation (e.g. formation of CMBO and MBO) ceased due to isoprene depletion. Accumulated ClOHOC<sub>5</sub> was then gradually photolyzed under UV. In the absence of a primary oxidant source, such as when chlorine injection stopped in Exp. C3, ClOHOC<sub>5</sub> could provide residual OH and chlorine radicals under UV, as shown in Fig. 7a. Under dark, dry, and low-NO<sub>x</sub> conditions, ClOHOC<sub>5</sub> remains stable as a temporary radical reservoir, as shown in Fig. 6b during the period when UV lights were turned off.

Secondary OH chemistry ~~also~~ may have ~~also~~ contributed to SOA formation. For instance, the  $C_5H_8ClO_2^*$  radical produced via Cl-addition to isoprene could either undergo  $RO_2 + RO_2$  chemistry to produce  $C_5H_7ClO$  (e.g. CMBO) or undergo  $RO_2 + HO_2$  chemistry to produce  $C_5H_9ClO_2$ , a chloroalkyl hydroperoxide. Similarly, the  $C_5H_7O_2^*$  radical produced via H-abstraction from isoprene could undergo  $RO_2 + RO_2$  chemistry to produce  $C_5H_6O$  (e.g. MBO) or undergo  $RO_2 + HO_2$  chemistry to produce  $C_5H_8O_2$ , a hydroperoxide. Ions consistent with  $C_5H_9ClO_2$  and  $C_5H_8O_2$  are observed in the gas-phase, as shown in Fig 6a and 6b, where the formation of  $RO_2 + HO_2$  reaction products appears delayed compared to their  $RO_2 + RO_2$  pathway counterparts. This is consistent with  $RO_2 + RO_2$  reactions being a source of  $HO_x$  radicals. Figure 7 summarizes select observed gas-phase products whose time series are shown in Figure 6a and 6b. More detailed reaction pathways and time-series comparisons are shown in Figures S10-12 in section S6. In the OH-isoprene system, multifunctional, low volatility hydroperoxides produced from non-IEPOX (“isoprene-derived epoxydiol”) reaction pathways contribute to SOA formation under low  $NO_x$  conditions (Krechmer et al., 2015; Liu et al., 2016; Riva et al., 2016). Analogously, in the Cl-isoprene system, the (chloroalkyl) hydroperoxide species identified in Fig. 6 and Fig. 7 are expected to contribute to SOA formation.

The ion consistent with isoprene-derived hydroxyl hydroperoxides (ISOPOOH) or ~~isoprene-derived epoxydiols (IEPOX) were,  $C_5H_{10}O_3$ , was~~ observed in ~~both  $(H_2O)_nI^-$  CIMS-modes,~~ as shown in Fig. 6b ~~and 7b~~. Reactive uptake and oxidation of IEPOX has been reported to contribute significantly to SOA mass during isoprene OH-oxidation (~~Bates et al., 2014; Paulot et al., 2009; Surratt et al., 2010~~), especially under acidic or humid conditions (~~Lewandowski et al., 2015; Nguyen et al., 2014~~). (~~Bates et al., 2014; Gaston et al., 2014; Lewandowski et al., 2015; Lin et al., 2012; Nguyen et al., 2014; Paulot et al., 2009; Surratt et al., 2010~~). For chlorine-initiated oxidation of isoprene, the SAPRC chamber model results indicate that over 99% of the isoprene reacts with Cl; OH oxidation of isoprene is therefore only a very minor pathway in these experiments. Model results also show that  $HO_2$  production is dominated by isoprene-chlorine chemistry when sufficient isoprene is present, whereas wall effects dominate  $HO_2$  production ( $> 60\%$ ) after all isoprene has been consumed. The model does not explicitly represent Cl-initiated oxidation of reaction products, which can produce additional  $HO_x$  radicals, and therefore likely underestimates the importance of secondary OH chemistry. Figure 6b shows that  $(C_5H_{10}O_3)H^+$  ions correlated well with SOA growth. However, there are several ways to produce  $(C_5H_{10}O_3)H^+$  ions in addition to direct protonation, such as clustering or ligand-exchange between  $C_5H_8O_2$  (e.g. methyl methacrylate) and  $(H_2O)_nH_3O^+$  reagent ions, as well as fragmentation of  $(C_5H_{11}O_3Cl)H^+$  product ions. As seen in Fig. 6b, the qualitative  $(C_5H_{10}O_3)H^+$  trend is similar to that of both  $(C_5H_8O_2)H^+$  and  $(C_5H_{11}O_3Cl)H^+$ . Furthermore, ions that would be consistent with IEPOX oxidation products, such as  $(C_5H_8O_3)H^+$  were observed to precede the formation of  $(C_5H_{10}O_3)H^+$ . In contrast,  $(H_2O)_nI^-$  CIMS measurements show distinct trends for  $C_5H_{10}O_3$  (detected as  $[(C_5H_{10}O_3)I^-]$ ) and  $C_5H_8O_2$  (detected as  $[(C_5H_8O_2)I^-]$ ) in Fig. 7b. While  $(C_5H_8O_2)I^-$  correlated well with SOA growth and decay, as  $(C_5H_8O_2)H^+$  and  $(C_5H_{10}O_3)H^+$  did in Fig. 6a,  $(C_5H_{10}O_3)I^-$  resembled an intermediary species and a SOA precursor, consistent with the role of IEPOX during OH oxidation of isoprene. This suggests that IEPOX was observed only with  $(H_2O)_nI^-$  CIMS while its oxidation products were observed by both  $(H_2O)_nH_3O^+$  and  $(H_2O)_nI^-$  CIMS. Furthermore, we note that the observed  $(C_5H_{10}O_3)H^+$  and  $(C_5H_{10}O_3)I^-$  do not necessarily correspond to ISOPOOH or IEPOX. For instance, whereas  $(C_5H_{10}O_3)H^+$  in Fig. 6a trends with  $(C_5H_8O_2)H^+$  during SOA growth,  $(C_5H_{10}O_3)I^-$  in Fig. 6b appears early on as an SOA precursor and has a

different qualitative trend than  $(C_5H_8O_2)I^-$ . We can therefore infer that  $(C_5H_{10}O_3)H^+$  is an ion cluster in the form of  $(C_5H_8O_2)(H_3O)^+$ . Without any information on the chemical structure, it is also possible that  $(C_5H_{10}O_3)I^-$  is the fragment of some unidentified parent ion(s) or that it is an IEPOX isomer produced ~~formfrom~~ non-OH-reaction pathways. Moreover, photooxidative degradation of chlorinated organic compounds could produce products that resemble OH-oxidation products like  $C_5H_{10}O_3$ . A similar observation has been reported for chlorine-initiated oxidation of ~~alpha~~-pinene, where the SOA appeared less like halogenated organic ~~aerosolsaerosol~~ as oxidation continued (Ofner et al., 2013).

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., 2015, 2016). 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 (1 %) 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 5 %. The observed  $f_{82}$  values for isoprene-chlorine SOA are below the average value observed for ambient OA influenced by isoprene emission ( $6.5 \pm 2.2$  %) and much lower than IEPOX-derived SOA (12-40 %) 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. Regardless, it is evident Nevertheless, it is clear that SOA formation from chlorine-initiated and OH-initiated oxidation of isoprene proceeds via multi-generational oxidation chemistries involving similar, if not identical, key gas-phase products- ~~such as MACR and multifunctional hydroperoxide compounds.~~

## 4 Conclusions

Chlorine-initiated oxidation of isoprene under low  $NO_x$  was investigated inside an environmental chamber. Chlorine was injected either in bulk or continuously in low amounts to simulate fast and ~~slowslower~~ oxidation conditions; ~~prompt.~~ Prompt SOA formation was observed in both cases, indicative of ~~low volatility the~~ initial ~~product~~ formation of low volatility products. The average wall loss-corrected SOA yield was  $8 \pm 1$  % for continuous chlorine injection experiments and  $20 \pm 3$  % for initial injection experiments; the differences likely resulted from ~~loss of initial low volatility products and organic vapor to the chamber wall and from oxidative fragmentation a combination of organic vapor wall loss, oxidative fragmentation, and~~ photolysis of SOA. ~~1-D VBS fitting should not include yield data collected post VOC depletion. The effects of SOA aging must be described explicitly and separately from initial SOA formation. For air quality models which do not explicitly account for SOA aging, the averaged SOA yield from continuous chlorine injection experiments (8%) should be used for SOA~~

formation from chlorine-initiated oxidation of isoprene. The presence of acidified seed aerosol is shown to enhance SOA formation under low RH conditions.

—The extent of ~~SOA~~ oxidation of SOA from Cl-initiated oxidation of isoprene was similar to that of SOA formed from OH-oxidation of isoprene under high NO<sub>x</sub> conditions, reported in the literature. Chloride fragments at  $m/z$  35 were found to desorb  
5 slowly and to interfere with chloride quantification using standard operating and data analysis procedures. We propose  
alternative methods for improved organic chloride quantification including extended filter sampling and the use of “fast”  
desorbing chloride fragments (at  $m/z$  36) for quantifying chloride, which accounted for approximately 6.7 % of total SOA mass  
in these experiments. Measurements by HR-ToF CIMS show CIMS measurements identified several initial gas-phase  
10 oxidation products as potential SOA precursors including C<sub>5</sub>H<sub>6</sub>O (MBO), C<sub>5</sub>H<sub>8</sub>O (2-methylbut-3-enal), C<sub>5</sub>H<sub>7</sub>ClO (CMBO)  
and C<sub>4</sub>H<sub>6</sub>O (MVK/MACR). Gas-phase data provide evidence of chlorine-initiated secondary OH chemistry and ~~continued~~  
oxidation of gas phase products by chlorine and OH radicals.its potential contribution to SOA formation. Ions consistent with  
hydroperoxides and chloroalkyl hydroperoxides were observed in the CIMS and corresponding HO<sub>x</sub>-enabled formation  
pathways are proposed.

SOA formation from chlorine-initiated oxidation of isoprene is reported for the first time. The high isoprene-chlorine SOA  
15 yields suggest that, despite comparatively low ambient abundance, chlorine radicals could have a notable contribution to  
overall SOA formation. Proposed formation pathways and gas-phase measurements by the 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 NO<sub>x</sub> conditions. These may contribute to the high observed  
yields, as well as relatively fast reduction of organic aerosol under UV. The chlorine addition dominated oxidation pathway,  
20 presence of particulate chloride, and difficulties Challenges associated with ~~particulate chloride quantification~~ the detection  
and quantification of particulate organochlorides suggest that the prevalence of ambient particulate chlorine is likely  
underestimated. ~~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~~ Overall, our  
25 findings indicate that tropospheric chlorine chemistry increases the oxidative capacity of the atmosphere and directly  
contributes to SOA formation.

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## References

- Aljawhary, D., Lee, a. K. Y. and Abbatt, J. P. D.: High-resolution chemical ionization mass spectrometry (ToF-CIMS): Application to study SOA composition and processing, *Atmos. Meas. Tech.*, 6(11), 3211–3224, doi:10.5194/amt-6-3211-2013, 2013.
- 5 Allan, J. D., Delia, A. E., Coe, H., Bower, K. N., Alfarra, M. R., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T. and Worsnop, D. R.: A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, *J. Aerosol Sci.*, 35(7), 909–922, doi:10.1016/j.jaerosci.2004.02.007, 2004.
- Arnold, S. R., Spracklen, D. V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., Gros, V., Peeken, I., Lewis, a. C., Alvain,  
10 S. and Moulin, C.: Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol, *Atmos. Chem. Phys.*, 9(4), 1253–1262, doi:10.5194/acpd-8-16445-2008, 2009.
- Atkinson, R. and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, *Chem. Rev.*, 103(12), 4605–4638, doi:10.1021/cr0206420, 2003.
- Bates, K. H., Crounse, J. D., St. Clair, J. M., Bennett, N. B., Nguyen, T. B., Seinfeld, J. H., Stoltz, B. M. and Wennberg, P. O.:  
15 Gas phase production and loss of isoprene epoxydiols, *J. Phys. Chem. A*, 118(7), 1237–1246, doi:10.1021/jp4107958, 2014.
- Bean, J. K. and Hildebrandt Ruiz, L.: Gas–particle partitioning and hydrolysis of organic nitrates formed from the oxidation of  $\alpha$ -pinene in environmental chamber experiments, *Atmos. Chem. Phys.*, 16(4), 2175–2184, doi:10.5194/acp-16-2175-2016, 2016.
- 20 Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M. and Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, *Atmos. Meas. Tech.*, 4(7), 1471–1479, doi:10.5194/amt-4-1471-2011, 2011.
- Bikkina, S., Kawamura, K., Miyazaki, Y. and Fu, P.: High abundances of oxalic, azelaic, and glyoxylic acids and methylglyoxal in the open ocean with high biological activity: Implication for secondary OA formation from isoprene,  
25 *Geophys. Res. Lett.*, 41(10), 3649–3657, doi:10.1002/2014GL059913, 2014.
- Bobrowski, N., von Glasow, R., Aiuppa, A., Inguaggiato, S., Louban, I., Ibrahim, O. W. and Platt, U.: Reactive halogen chemistry in volcanic plumes, *J. Geophys. Res. Atmos.*, 112(6), 1–17, doi:10.1029/2006JD007206, 2007.
- Boyd, C. M., Sanchez, J., Xu, L., Eugene, a. J., Nah, T., Tuet, W. Y., Guzman, M. I. and Ng, N. L.: Secondary organic aerosol formation from the  $\beta$ -pinene+NO<sub>3</sub> system: effect of humidity and peroxy radical fate, *Atmos. Chem. Phys.*, 15(13), 7497–  
30 7522, doi:10.5194/acp-15-7497-2015, 2015.

- Brégonzio-Rozier, L., Siekmann, F., Giorio, C., Pangui, E., Morales, S. B., Temime-Roussel, B., Gratien, A., Michoud, V., Ravier, S., Cazaunau, M., Tapparo, A., Monod, A. and Doussin, J. F.: Gaseous products and secondary organic aerosol formation during long term oxidation of isoprene and methacrolein, *Atmos. Chem. Phys.*, 15(6), 2953–2968, doi:10.5194/acp-15-2953-2015, 2015.
- 5 de Bruijne, K., Ebersviller, S., Sexton, K. G., Lake, S., Leith, D., Goodman, R., Jetters, J., Walters, G. W., Doyle-Eisele, M., Woodside, R., Jeffries, H. E. and Jaspers, I.: Design and testing of Electrostatic Aerosol in Vitro Exposure System (EAVES): an alternative exposure system for particles., *Inhal. Toxicol.*, 21(2), 91–101, doi:10.1080/08958370802166035, 2009.
- 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. and Surratt, J. D.: 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(11), 5686–5694, doi:10.1021/es400023n, 2013.
- 10 Buxmann, J., Bleicher, S., Platt, U., von Glasow, R., Sommariva, R., Held, A., Zetzsch, C. and Ofner, J.: Consumption of reactive halogen species from sea-salt aerosol by secondary organic aerosol: slowing down the bromine explosion, *Environ. Chem.*, 12(4), 476, doi:10.1071/EN14226, 2015.
- 15 Buys, Z., Brough, N., Huey, L. G., Tanner, D. J., Von Glasow, R. and Jones, A. E.: High temporal resolution Br<sub>2</sub>, BrCl and BrO observations in coastal Antarctica, *Atmos. Chem. Phys.*, 13(3), 1329–1343, doi:10.5194/acp-13-1329-2013, 2013.
- Cai, X. and Griffin, R. J.: Secondary aerosol formation from the oxidation of biogenic hydrocarbons by chlorine atoms, *J. Geophys. Res. Atmos.*, 111(14), 7348–7359, doi:10.1029/2005JD006857, 2006.
- 20 Cai, X., Ziemba, L. D. and Griffin, R. J.: Secondary aerosol formation from the oxidation of toluene by chlorine atoms, *Atmos. Environ.*, 42(32), 7348–7359, doi:10.1016/j.atmosenv.2008.07.014, 2008.
- Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T. and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: Characterization, improved calibration, and implications, *Atmos. Chem. Phys.*, 15(1), 253–272, doi:10.5194/acp-15-253-2015, 2015.
- 25 Carter, W. P. L., Cocker, D. R., Fitz, D. R., Malkina, I. L., Bumiller, K., Sauer, C. G., Pisano, J. T., Bufalino, C. and Song, C.: A new environmental chamber for evaluation of gas-phase chemical mechanisms and secondary aerosol formation, *Atmos. Environ.*, 39(40), 7768–7788, doi:10.1016/j.atmosenv.2005.08.040, 2005.
- Chan, M. N., Surratt, J. D., Claeys, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., Eddingsaas, N. C., Wennberg, P. O. and Seinfeld, J. H.: Characterization and quantification of isoprene-derived epoxydiols in ambient aerosol in the southeastern united states, *Environ. Sci. Technol.*, 44(12), 4590–4596, doi:10.1021/es100596b, 2010.
- 30

- Chang, S. and Allen, D. T.: Atmospheric chlorine chemistry in southeast Texas: Impacts on ozone formation and control, *Environ. Sci. Technol.*, 40(1), 251–262, doi:10.1007/s10479-006-0033-8, 2006.
- Chang, S., Tanaka, P., McDonald-buller, E. and Allen, D. T.: Emission inventory for atomic chlorine precursors in Southeast Texas, Rep. Contract 9880077600-18 between Univ. Texas and Texas Nat. Resour. Conserv. Comm., 1–27, 2001.
- 5 <https://www.tceq.texas.gov/assets/public/implementation/air/am/contracts/reports/oth/EmissioninventoryForAtomicChlorinePrecursors.pdf> [Verified 13 Sep 2017]
- Chhabra, P. S., Ng, N. L., Canagaratna, M. R., Corrigan, A. L., Russell, L. M., Worsnop, D. R., Flagan, R. C. and Seinfeld, J. H.: Elemental composition and oxidation of chamber organic aerosol, *Atmos. Chem. Phys.*, 11(17), 8827–8845, doi:10.5194/acp-11-8827-2011, 2011.
- 10 Chuang, W. K. and Donahue, N. M.: A two-dimensional volatility basis set – Part 3: Prognostic modeling and NO<sub>x</sub> dependence, *Atmos. Chem. Phys.*, 16(1), 123–134, doi:10.5194/acp-16-123-2016, 2016.
- Claeys, M.: Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene, *Science* (80-. ), 303(5661), 1173–1176, doi:10.1126/science.1092805, 2004.
- Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Fröhlich, R., Belis, C. A., Aas, W., Äijälä, M., Alastuey, A., Artiñano, B.,
- 15 Baisnée, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillón, M. C., Močnik, G., O’Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Estève, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prévôt, A. S. H., Jayne, J. T. and Favez, O.: ACTRIS
- ACSM intercomparison - Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole
- 20 Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments, *Atmos. Meas. Tech.*, 8(12), 5063–5087, doi:10.5194/amt-8-5063-2015, 2015.
- Crutzen, P.: A Review of Upper Atmospheric Photochemistry, *Can. J. Chem.*, 52(8), 1569–1581, doi:10.1139/v74-229, 1974.
- Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G. and Speizer, F. E.: An Association
- 25 between Air Pollution and Mortality in Six U.S. Cities, *N. Engl. J. Med.*, 329(24), 1753–1759, doi:10.1056/NEJM199312093292401, 1993.
- Donahue, N. M., Robinson, A. L., Stanier, C. O. and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 40(8), 2635–2643, doi:10.1021/es052297c, 2006.
- Donahue, N. M., Kroll, J. H., Pandis, S. N. and Robinson, A. L.: A two-dimensional volatility basis set-Part 2: Diagnostics of organic-aerosol evolution, *Atmos. Chem. Phys.*, 12(2), 615–634, doi:10.5194/acp-12-615-2012, 2012.
- 30 Ebersviller, S., Lichtveld, K., Sexton, K. G., Zavala, J., Lin, Y.-H., Jaspers, I. and Jeffries, H. E.: Gaseous VOCs rapidly



- modify particulate matter and its biological effects - Part 1: Simple VOCs and model PM, *Atmos. Chem. Phys.*, 12(24), 12277–12292, doi:10.5194/acp-12-12277-2012, 2012.
- Edwards, P. M., Young, C. J., Aikin, K., DeGouw, J., Dubé, W. P., Geiger, F., Gilman, J., Helmig, D., Holloway, J. S., Kercher, J., Lerner, B., Martin, R., McLaren, R., Parrish, D. D., Peischl, J., Roberts, J. M., Ryerson, T. B., Thornton, J., Warneke, C., Williams, E. J. and Brown, S. S.: Ozone photochemistry in an oil and natural gas extraction region during winter: Simulations of a snow-free season in the Uintah Basin, Utah, *Atmos. Chem. Phys.*, 13(17), 8955–8971, doi:10.5194/acp-13-8955-2013, 2013.
- Edwards, P. M., Brown, S. S., Roberts, J. M., Ahmadov, R., Banta, R. M., deGouw, J. A., Dube, W. P., Field, R. A., Flynn, J. H., Gilman, J. B., Graus, M., Helmig, D., Koss, A., Langford, A. O., Lefer, B. L., Lerner, B. M., Li, R., Li, S. M., McKeen, S. A., Murphy, S. M., Parrish, D. D., Senff, C. J., Soltis, J., Stutz, J., Sweeney, C., Thompson, C. R., Trainer, M. K., Tsai, C., Veres, P. R., Washenfelder, R. A., Warneke, C., Wild, R. J., Young, C. J., Yuan, B. and Zamora, R.: High winter ozone pollution from carbonyl photolysis in an oil and gas basin, *Nature*, 514(7522), 351–354, doi:10.1038/nature13767, 2014.
- Fan, J. and Zhang, R.: Atmospheric oxidation mechanism of isoprene, *Environ. Chem.*, 1(3), 140–149, doi:10.1071/EN04045, 2004.
- Fantechi, G., Jensen, N. R., Saastad, O., Hjorth, J. and Peeters, J.: Reactions of Cl atoms with selected VOCs: Kinetics, products and mechanisms, *J. Atmos. Chem.*, 31(3), 247–267, doi:10.1023/A:1006033910014, 1998.
- Faxon, C., Bean, J. and Ruiz, L.: Inland Concentrations of Cl<sub>2</sub> and ClNO<sub>2</sub> in Southeast Texas Suggest Chlorine Chemistry Significantly Contributes to Atmospheric Reactivity, *Atmosphere (Basel)*, 6(10), 1487–1506, doi:10.3390/atmos6101487, 2015.
- Faxon, C. B. and Allen, D. T.: Chlorine chemistry in urban atmospheres: A review, *Environ. Chem.*, 10(3), 221–233, doi:10.1071/EN13026, 2013.
- Finlayson-Pitts, B. J.: Halogens in the troposphere, *Anal. Chem.*, 82(3), 770–776, doi:10.1021/ac901478p, 2010.
- Fu, P., Kawamura, K. and Miura, K.: Molecular characterization of marine organic aerosols collected during a round-the-world cruise, *J. Geophys. Res. Atmos.*, 116(13), 1–14, doi:10.1029/2011JD015604, 2011.
- Fu, P. Q., Kawamura, K., Chen, J., Charrière, B. and Sempéré, R.: Organic molecular composition of marine aerosols over the Arctic Ocean in summer: Contributions of primary emission and secondary aerosol formation, *Biogeosciences*, 10(2), 653–667, doi:10.5194/bg-10-653-2013, 2013.
- Gantt, B., Meskhidze, N., Zhang, Y. and Xu, J.: The effect of marine isoprene emissions on secondary organic aerosol and ozone formation in the coastal United States, *Atmos. Environ.*, 44(1), 115–121, doi:10.1016/j.atmosenv.2009.08.027, 2010.

2010.

- Gantt, B., Johnson, M. S., Crippa, M., Prévôt, A. S. H. and Meskhidze, N.: Implementing marine organic aerosols into the GEOS-Chem model, *Geosci. Model Dev.*, 8(3), 619–629, doi:10.5194/gmd-8-619-2015, 2015.
- Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D. and Thornton, J. A.: Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles, *Environ. Sci. Technol.*, 48(19), 11178–11186, doi:10.1021/es5034266, 2014.
- Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere, *Environ. Sci. Technol.*, 41(5), 1514–1521, doi:10.1021/es072476p, 2007.
- de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, 26(2), 223–257, doi:10.1002/mas.20119, 2007.
- Griffin, R. J., Cocker, D. R. and Seinfeld, J. H.: Incremental aerosol reactivity: Application to aromatic and biogenic hydrocarbons, *Environ. Sci. Technol.*, 33(14), 2403–2408, doi:10.1021/es981330a, 1999.
- Guenther, a., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I. and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, 6(11), 3181–3210, doi:10.5194/acpd-6-107-2006, 2006.
- Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5(6), 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.
- Hawley, B., McKenna, D., Marchese, A. and Volckens, J.: Time course of bronchial cell inflammation following exposure to diesel particulate matter using a modified EAVES, *Toxicol. Vit.*, 28(5), 829–837, doi:10.1016/j.tiv.2014.03.001, 2014.
- Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., Decarlo, P. F., Aiken, A. C., Chen, Q., Martin, S. T., Farmer, D. K. and Artaxo, P.: A simplified description of the evolution of organic aerosol composition in the atmosphere, *Geophys. Res. Lett.*, 37(8), doi:10.1029/2010GL042737, 2010.
- Healy, R. M., Wenger, J. C., Metzger, a, Duplissy, J., Kalberer, M. and Dommen, J.: Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene, *Atmos. Chem. Phys.*, 8(12), 3215–3230, doi:10.1029/2006GL026523, 2008.
- Hildebrandt, L., Donahue, N. M. and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, *Atmos. Chem. Phys.*, 9(9), 2973–2986, doi:10.5194/acp-9-2973-2009, 2009.
- Hu, Q.-H., Xie, Z.-Q., Wang, X.-M., Kang, H., He, Q.-F. and Zhang, P.: Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic, *Sci. Rep.*, 3(1), 2280, doi:10.1038/srep02280, 2013.

- 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.,  
5 Coe, H., Allan, J. D., Canagaratna, M. R., Paulot, F. and Jimenez, J. L.: Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements, *Atmos. Chem. Phys.*, 15(20), 11807–11833, doi:10.5194/acp-15-11807-2015, 2015.
- Huang, M., Zhang, W., Gu, X., Hu, C., Zhao, W., Wang, Z. and Fang, L.: Size distribution and chemical composition of secondary organic aerosol formed from Cl-initiated oxidation of toluene, *J. Environ. Sci.*, 24(5), 860–864,  
10 doi:10.1016/S1001-0742(11)60840-1, 2012.
- Huang, M., Liu, X., Hu, C., Guo, X., Gu, X., Zhao, W., Wang, Z., Fang, L. and Zhang, W.: Aerosol laser time-of-flight mass spectrometer for the on-line measurement of secondary organic aerosol in smog chamber, *Meas. J. Int. Meas. Confed.*, 55(3), 394–401, doi:10.1016/j.measurement.2014.05.038, 2014.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, a. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe,  
15 H., Ng, N. L., Aiken, a. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, a. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. a., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M.,  
20 Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, a. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U. and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, *Science* (80-. ), 326(5959), 1525–1529, doi:10.1126/science.1180353, 2009.
- Kamilli, K. A., Ofner, J., Lendl, B., Schmitt-Kopplin, P. and Held, A.: New particle formation above a simulated salt lake in aerosol chamber experiments, *Environ. Chem.*, 12(4), 489–503, doi:10.1071/EN14225, 2015.
- 25 Kamilli, K. A., Ofner, J., Krause, T., Sattler, T., Schmitt-Kopplin, P., Eitenberger, E., Friedbacher, G., Lendl, B., Lohninger, H., Schöler, H. F. and Held, A.: How salt lakes affect atmospheric new particle formation: A case study in Western Australia, *Sci. Total Environ.*, 573, submitted, doi:10.1016/j.scitotenv.2016.08.058, 2016.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R.,  
30 Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G. and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5(4), 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.

- Karlsson, R. S., Szente, J. J., Ball, J. C. and Maricq, M. M.: Homogeneous aerosol formation by the chlorine atom initiated oxidation of toluene, *J. Phys. Chem. A*, 105(1), 82–96, doi:10.1021/jp001831u, 2001.
- Kokkola, H., Yli-Pirila, P., Vesterinen, M., Korhonen, H., Keskinen, H., Romakkaniemi, S., Hao, L., Kortelainen, A., Joutsensaari, J., Worsnop, D. R., Virtanen, A. and Lehtinen, K. E. J.: The role of low volatile organics on secondary organic aerosol formation, *Atmos. Chem. Phys.*, 14(3), 1689–1700, doi:10.5194/acp-14-1689-2014, 2014.
- Koo, B., Knipping, E. and Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, *Atmos. Environ.*, 95, 158–164, doi:10.1016/j.atmosenv.2014.06.031, 2014.
- Krechmer, J. E., Coggon, M. M., Massoli, P., Nguyen, T. B., Crounse, J. D., Hu, W., Day, D. A., Tyndall, G. S., Henze, D. K., Rivera-Rios, J. C., Nowak, J. B., Kimmel, J. R., Mauldin, R. L., Stark, H., Jayne, J. T., Sipila, M., Junninen, H., St. Clair, J. M., Zhang, X., Feiner, P. A., Zhang, L., Miller, D. O., Brune, W. H., Keutsch, F. N., Wennberg, P. O., Seinfeld, J. H., Worsnop, D. R., Jimenez, J. L. and Canagaratna, M. R.: Formation of Low Volatility Organic Compounds and Secondary Organic Aerosol from Isoprene Hydroxyhydroperoxide Low-NO Oxidation, *Environ. Sci. Technol.*, 49(17), 10330–10339, doi:10.1021/acs.est.5b02031, 2015.
- Krechmer, J. E., Pagonis, D., Ziemann, P. J. and Jimenez, J. L. L.: Quantification of gas-wall partitioning in Teflon environmental chambers using rapid bursts of low-volatility oxidized species generated in-situ, *Environ. Sci. Technol.*, acs.est.6b00606, doi:10.1021/acs.est.6b00606, 2016.
- Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation., *Environ. Sci. Technol.*, 40(6), 1869–1877, doi:10.1021/es0524301, 2006.
- Kroll, J. H., Chan, A. W. H., Ng, N. L., Flagan, R. C. and Seinfeld, J. H.: Reactions of semivolatile organics and their effects on secondary organic aerosol formation, *Environ. Sci. Technol.*, 41(10), 3545–3550, doi:10.1021/es062059x, 2007.
- Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E. and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol., *Nat. Chem.*, 3(2), 133–139, doi:10.1038/nchem.948, 2011.
- Kwan, A. J., Chan, A. W. H., Ng, N. L., Kjaergaard, H. G., Seinfeld, J. H. and Wennberg, P. O.: Peroxy radical chemistry and OH radical production during the NO<sub>3</sub>-initiated oxidation of isoprene, *Atmos. Chem. Phys.*, 12(16), 7499–7515, doi:10.5194/acp-12-7499-2012, 2012.
- Lawler, M. J., Sander, R., Carpenter, L. J., Lee, J. D., Von Glasow, R., Sommariva, R. and Saltzman, E. S.: HOCl and Cl<sub>2</sub> observations in marine air, *Atmos. Chem. Phys.*, 11(15), 7617–7628, doi:10.5194/acp-11-7617-2011, 2011.
- Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R. and Thornton, J. A.: An iodide-adduct high-resolution

- time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic and organic compounds, *Environ. Sci. Technol.*, 48(11), 6309–6317, doi:10.1021/es500362a, 2014.
- Lei, W. and Zhang, R.: Chlorine atom addition reaction to isoprene: a theoretical study, *J. Chem. Phys.*, 113(1), 153–157, doi:10.1063/1.481782, 2000.
- 5 Lewandowski, M., Jaoui, M., Offenberg, J. H., Krug, J. D. and Kleindienst, T. E.: Atmospheric oxidation of isoprene and 1,3-butadiene: Influence of aerosol acidity and relative humidity on secondary organic aerosol, *Atmos. Chem. Phys.*, 15(7), 3773–3783, doi:10.5194/acp-15-3773-2015, 2015.
- Liao, J., Huey, L. G., Liu, Z., Tanner, D. J., Cantrell, C. a., Orlando, J. J., Flocke, F. M., Shepson, P. B., Weinheimer, A. J., Hall, S. R., Ullmann, K., Beine, H. J., Wang, Y., Ingall, E. D., Stephens, C. R., Hornbrook, R. S., Apel, E. C., Riemer, D.,  
 10 Fried, A., Mauldin, R. L., Smith, J. N., Staebler, R. M., Neuman, J. A. and Nowak, J. B.: High levels of molecular chlorine in the Arctic atmosphere, *Nat. Geosci.*, 7(2), 91–94, doi:10.1038/ngeo2046, 2014.
- 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. and Surratt, J. D.: Isoprene epoxydiols as precursors to secondary organic aerosol formation: Acid-catalyzed reactive uptake studies with authentic compounds, *Environ. Sci. Technol.*, 46(1), 250–  
 15 258, doi:10.1021/es202554c, 2012.
- Liu, J., D'Ambro, E. L., Lee, B. H., Lopez-Hilfiker, F. D., Zaveri, R. A., Rivera-Rios, J. C., Keutsch, F. N., Iyer, S., Kurten, T., Zhang, Z., Gold, A., Surratt, J. D., Shilling, J. E. and Thornton, J. A.: Efficient Isoprene Secondary Organic Aerosol Formation from a Non-IEPOX Pathway, *Environ. Sci. Technol.*, 50(18), 9872–9880, doi:10.1021/acs.est.6b01872, 2016.
- Lobert, J. M., Keene, W. C., Logan, J. A. and Yevich, R.: Global chlorine emissions from biomass burning: Reactive Chlorine  
 20 Emissions Inventory, *J. Geophys. Res. Atmos.*, 104(D7), 8373–8389, doi:10.1029/1998JD100077, 1999.
- Loza, C. L., Chan, A. W. H., Galloway, M. M., Keutsch, F. N., Flagan, R. C. and Seinfeld, J. H.: Characterization of vapor wall loss in laboratory chambers, *Environ. Sci. Technol.*, 44(13), 5074–5078, doi:10.1021/es100727v, 2010.
- Luo, G. and Yu, F.: A numerical evaluation of global oceanic emissions of alpha-pinene and isoprene, *Atmos. Chem. Phys.*, 10(4), 2007–2015, doi:doi:10.5194/acp-10-2007-2010, 2010.
- 25 Matsunaga, A. and Ziemann, P. J.: Yields of beta-hydroxynitrates, dihydroxynitrates, and trihydroxynitrates formed from OH radical-initiated reactions of 2-methyl-1-alkenes., *Proc. Natl. Acad. Sci.*, 107(15), 6664–6669, doi:10.1073/pnas.0910585107, 2010.
- Mielke, L. H., Stutz, J., Tsai, C., Hurlock, S. C., Roberts, J. M., Veres, P. R., Froyd, K. D., Hayes, P. L., Cubison, M. J., Jimenez, J. L., Washenfelder, R. A., Young, C. J., Gilman, J. B., De Gouw, J. A., Flynn, J. H., Grossberg, N., Lefer, B.,  
 30 L., Liu, J., Weber, R. J. and Osthoff, H. D.: Heterogeneous formation of nitryl chloride and its role as a nocturnal NO<sub>x</sub>

- reservoir species during CalNex-LA 2010, *J. Geophys. Res. Atmos.*, 118(18), 10638–10652, doi:10.1002/jgrd.50783, 2013.
- Molina, M. J. and Rowland, F. S.: Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone, *Nature*, 249(5460), 810–812, doi:10.1038/249810a0, 1974.
- 5 Murphy, B. N., Donahue, N. M., Fountoukis, C., Dall'Osto, M., O'Dowd, C., Kiendler-Scharr, A. and Pandis, S. N.: Functionalization and fragmentation during ambient organic aerosol aging: Application of the 2-D volatility basis set to field studies, *Atmos. Chem. Phys.*, 12(22), 10797–10816, doi:10.5194/acp-12-10797-2012, 2012.
- Nah, T., McVay, R. C., Pierce, J. R., Seinfeld, J. H. and Ng, N. L.: Constraining uncertainties in particle-wall deposition correction during SOA formation in chamber experiments, *Atmos. Chem. Phys.*, 17(3), 2297–2310, doi:10.5194/acp-17-2297-2017, 2017.
- 10 Ng, N. L., Kroll, J. H., Chan, a W. H., Chhabra, P. S., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos. Chem. Phys.*, 7(14), 3909–3922, doi:10.5194/acp-7-3909-2007, 2007.
- Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., Decarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y. and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, *Atmos. Chem. Phys.*, 10(10), 4625–4641, doi:10.5194/acp-10-4625-2010, 2010.
- 15 Ng, N. L., Herndon, S. C., Trimborn, a., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L. and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, *Aerosol Sci. Technol.*, 45(7), 780–794, doi:10.1080/02786826.2011.560211, 2011a.
- 20 Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H. and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, *Atmos. Chem. Phys.*, 11(13), 6465–6474, doi:10.5194/acp-11-6465-2011, 2011b.
- Nguyen, T. B., Coggon, M. M., Bates, K. H., Zhang, X., Schwantes, R. H., Schilling, K. A., Loza, C. L., Flagan, R. C., Wennberg, P. O. and Seinfeld, J. H.: Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds, *Atmos. Chem. Phys.*, 14(7), 3497–3510, doi:10.5194/acp-14-3497-2014, 2014.
- 25 Nordmeyer, T., Wang, W., Ragains, M. L., Finlayson-Pitts, B. J., Spicer, C. W. and Plastridge, R. A.: Unique products of the reaction of isoprene with atomic chlorine: Potential markers of chlorine atom chemistry, *Geophys. Res. Lett.*, 24(13), 1615–1618, doi:10.1029/97GL01547, 1997.
- 30 O'Dowd, C. D. and de Leeuw, G.: Marine aerosol production: a review of the current knowledge, *Philos. Trans. R. Soc. A*

- Math. Phys. Eng. Sci., 365(1856), 1753–1774, doi:10.1098/rsta.2007.2043, 2007.
- Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan Richard, C. and Seinfeld John, H.: Gas particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol.*, 30(8), 2580–2585, doi:10.1021/es950943+, 1996.
- Ofner, J., Balzer, N., Buxmann, J., Grothe, H., Schmitt-Kopplin, P., Platt, U. and Zetzsch, C.: Halogenation processes of secondary organic aerosol and implications on halogen release mechanisms, *Atmos. Chem. Phys.*, 12(13), 5787–5806, doi:10.5194/acp-12-5787-2012, 2012.
- Ofner, J., Kamilli, K. A., Held, A., Lendl, B. and Zetzsch, C.: Halogen-induced organic aerosol (XOA): a study on ultra-fine particle formation and time-resolved chemical characterization, *Faraday Discuss.*, 165, 115–135, doi:10.1039/c3fd00093a, 2013.
- Orlando, J. J., Tyndall, G. S., Apel, E. C., Riemer, D. D. and Paulson, S. E.: Rate coefficients and mechanisms of the reaction of Cl-atoms with a series of unsaturated hydrocarbons under atmospheric conditions, *Int. J. Chem. Kinet.*, 35(8), 334–353, doi:10.1002/kin.10135, 2003.
- Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C. and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat. Geosci.*, 1(5), 324–328, doi:10.1038/ngeo177, 2008.
- Pankow, J. F.: An absorption model of gas/particle partitioning of organic compounds in the atmosphere, *Atmos. Environ.*, 28(2), 185–188, doi:10.1016/1352-2310(94)90093-0, 1994.
- Parrish, D. D., Allen, D. T., Bates, T. S., Estes, M., Fehsenfeld, F. C., Feingold, G., Ferrare, R., Hardesty, R. M., Meagher, J. F., Nielsen-Gammon, J. W., Pierce, R. B., Ryerson, T. B., Seinfeld, J. H. and Williams, E. J.: Overview of the second texas air quality study (TexAQS II) and the Gulf of Mexico atmospheric composition and climate study (GoMACCS), *J. Geophys. Res. Atmos.*, 114(13), 1–28, doi:10.1029/2009JD011842, 2009.
- Pathak, R. K., Presto, A. A., Lane, T. E., Stanier, C. O., Donahue, N. M. and Pandis, S. N.: Ozonolysis of  $\alpha$ -pinene: parameterization of secondary organic aerosol mass fraction, *Atmos. Chem. Phys.*, 7(14), 3811–3821, doi:10.5194/acp-7-3811-2007, 2007.
- Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H. and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmos. Chem. Phys.*, 9(4), 1479–1501, doi:10.5194/acp-9-1479-2009, 2009.
- Pierce, J. R., Engelhart, G. J., Hildebrandt, L., Weitkamp, E. a., Pathak, R. K., Donahue, N. M., Robinson, a. L., Adams, P. J. and Pandis, S. N.: Constraining Particle Evolution from Wall Losses, Coagulation, and Condensation-Evaporation in

- Smog-Chamber Experiments: Optimal Estimation Based on Size Distribution Measurements, *Aerosol Sci. Technol.*, 42(12), 1001–1015, doi:10.1080/02786820802389251, 2008.
- Platt, U. and Hönninger, G.: The role of halogen species in the troposphere, *Chemosphere*, 52(2), 325–338, doi:10.1016/S0045-6535(03)00216-9, 2003.
- 5 Pöhler, D., Vogel, L., Friess, U. and Platt, U.: Observation of halogen species in the Amundsen Gulf, Arctic, by active long-path differential optical absorption spectroscopy, *Proc. Natl. Acad. Sci.*, 107(15), 6582–6587, doi:10.1073/pnas.0912231107, 2010.
- Pope, C. A., Dockery, D. W., Chow, J. C., Watson, J. G., Mauderly, J. L., Costa, D. L., Wyzga, R. E., Vedal, S., Hidy, G. M., Altshuler, S. L., Marrack, D., Heuss, J. M., Wolff, G. T. and Arden Pope III, C.: Health Effects of Fine Particulate Air  
 10 Pollution: Lines that Connect, *J. Air Waste Manage. Assoc.*, 56(6), 1368–1380, doi:10.1080/10473289.2006.10464485, 2006.
- Ragains, M. L. and Finlayson-Pitts, B. J.: Kinetics and mechanism of the reaction of Cl atoms with 2-methyl-1,3-butadiene (isoprene) at 298 K, *J. Phys. Chem. A*, 101(8), 1509–1517, doi:10.1021/jp962786m, 1997.
- Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., Hopkins, J. R., Lee, J. D., Moller, S.  
 15 J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J. and Plane, J. M. C.: Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, *Nature*, 453(7199), 1232–1235, doi:10.1038/nature07035, 2008.
- Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S. M., Gilman, J., De Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S. and Thornton, J. A.: Nitryl chloride and molecular chlorine in the coastal marine  
 20 boundary layer, *Environ. Sci. Technol.*, 46(19), 10463–10470, doi:10.1021/es204632r, 2012.
- Riedel, T. P., Wagner, N. L., Dubé, W. P., Middlebrook, A. M., Young, C. J., Öztürk, F., Bahreini, R., Vandenboer, T. C., Wolfe, D. E., Williams, E. J., Roberts, J. M., Brown, S. S. and Thornton, J. A.: Chlorine activation within urban or power plant plumes: Vertically resolved ClNO<sub>2</sub> and Cl<sub>2</sub> measurements from a tall tower in a polluted continental setting, *J. Geophys. Res. Atmos.*, 118(15), 8702–8715, doi:10.1002/jgrd.50637, 2013.
- 25 Riedel, T. P., Wolfe, G. M., Danas, K. T., Gilman, J. B., Kuster, W. C., Bon, D. M., Vlasenko, A., Li, S.-M., Williams, E. J., Lerner, B. M., Veres, P. R., Roberts, J. M., Holloway, J. S., Lefer, B., Brown, S. S. and Thornton, J. a.: An MCM modeling study of nitryl chloride (ClNO<sub>2</sub>) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow, *Atmos. Chem. Phys.*, 14(8), 3789–3800, doi:10.5194/acp-14-3789-2014, 2014.
- Riedel, T. P., Lin, Y. H., Budisulistiorini, S. H., Gaston, C. J., Thornton, J. A., Zhang, Z., Vizuete, W., Gold, A. and Surratt,  
 30 J. D.: Heterogeneous reactions of isoprene-derived epoxides: Reaction probabilities and molar secondary organic aerosol yield estimates, *Environ. Sci. Technol. Lett.*, 2(2), 38–42, doi:10.1021/ez500406f, 2015.



- Riedel, T. P., Lin, Y. H., Zhang, Z., Chu, K., Thornton, J. A., Vizuete, W., Gold, A. and Surratt, J. D.: Constraining condensed-phase formation kinetics of secondary organic aerosol components from isoprene epoxydiols, *Atmos. Chem. Phys.*, 16(3), 1245–1254, doi:10.5194/acp-16-1245-2016, 2016.
- Riemer, D. D., Apel, E. C., Orlando, J. J., Tyndall, G. S., Brune, W. H., Williams, E. J., Lonneman, W. A. and Neece, J. D.: Unique isoprene oxidation products demonstrate chlorine atom chemistry occurs in the Houston, Texas urban area, *J. Atmos. Chem.*, 61(3), 227–242, doi:10.1007/s10874-009-9134-5, 2008.
- Riva, M., Healy, R. M., Flaud, P. M., Perraudin, E., Wenger, J. C. and Villenave, E.: Gas- and Particle-Phase Products from the Chlorine-Initiated Oxidation of Polycyclic Aromatic Hydrocarbons, *J. Phys. Chem. A*, 119(45), 11170–11181, doi:10.1021/acs.jpca.5b04610, 2015.
- Riva, M., Budisulistiorini, S. H., Chen, Y., Zhang, Z., D'Ambro, E. L., Zhang, X., Gold, A., Turpin, B. J., Thornton, J. A., Canagaratna, M. R. and Surratt, J. D.: Chemical Characterization of Secondary Organic Aerosol from Oxidation of Isoprene Hydroxyhydroperoxides, *Environ. Sci. Technol.*, 50(18), 9889–9899, doi:10.1021/acs.est.6b02511, 2016.
- Saiz-Lopez, A. and von Glasow, R.: Reactive halogen chemistry in the troposphere, *Chem. Soc. Rev.*, 41(19), 6448, doi:10.1039/c2cs35208g, 2012.
- Sarwar, G., Simon, H., Bhawe, P. and Yarwood, G.: Examining the impact of heterogeneous nitryl chloride production on air quality across the United States, *Atmos. Chem. Phys.*, 12(14), 6455–6473, doi:10.5194/acp-12-6455-2012, 2012.
- Schwantes, R. H., Teng, A. P., Nguyen, T. B., Coggon, M. M., Crounse, J. D., St. Clair, J. M., Zhang, X., Schilling, K. A., Seinfeld, J. H. and Wennberg, P. O.: Isoprene NO<sub>3</sub> Oxidation Products from the RO<sub>2</sub> + HO<sub>2</sub> Pathway, *J. Phys. Chem. A*, 119(40), 10158–10171, doi:10.1021/acs.jpca.5b06355, 2015.
- Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A. and Von Glasow, R.: Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts, *Chem. Rev.*, 115(10), 4035–4062, doi:10.1021/cr5006638, 2015.
- Stutz, J.: Atmospheric reactive chlorine and bromine at the Great Salt Lake, Utah, *Geophys. Res. Lett.*, 29(10), 18–21, doi:10.1029/2002GL014812, 2002.
- Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C. and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, *J. Phys. Chem. A*, 110(31), 9665–9690, doi:10.1021/jp061734m, 2006.
- Surratt, J. D., Chan, A. W., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O. and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proc Natl Acad Sci U S A*, 107(15), 6640–6645, doi:10.1073/pnas.091114107, 2010.
- Tanaka, P. L. and Allen, D. T.: Incorporation of Chlorine Reactions into the Carbon Bond-IV Mechanism (supplement), A

2001.<https://www.tceq.texas.gov/assets/public/implementation/air/am/contracts/reports/oth/IncorporationOfChlorineReactionsIntoCB4-2.pdf> [Verified 13 Sep, 2017]

- Tanaka, P. L., Riemer, D. D., Chang, S., Yarwood, G., McDonald-Buller, E. C., Apel, E. C., Orlando, J. J., Silva, P. J., Jimenez, J. L., Canagaratna, M. R., Neece, J. D., Mullins, C. B. and Allen, D. T.: Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas, *Atmos. Environ.*, 37(9-10), 1393–1400, doi:10.1016/S1352-2310(02)01007-5, 2003.
- Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dubé, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B. and Brown, S. S.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry., *Nature*, 464(7286), 271–4, doi:10.1038/nature08905, 2010.
- Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R. and Jimenez, J. L.: 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, 2009.
- Verheggen, B. and Mozurkewich, M.: An inverse modeling procedure to determine particle growth and nucleation rates from measured aerosol size distributions, *Atmos. Chem. Phys. Discuss.*, 6(2), 1679–1723, doi:10.5194/acp-6-2927-2006, 2006.
- Wang, L., Arey, J. and Atkinson, R.: Reactions of chlorine atoms with a series of aromatic hydrocarbons, *Environ. Sci. Technol.*, 39(14), 5302–5310, doi:10.1021/es0479437, 2005.
- Wingenter, O. W., Blake, D. R., Blake, N. J., Sive, B. C., Rowland, F. S., Atlas, E. and Flocke, F.: Tropospheric hydroxyl and atomic chlorine concentrations, and mixing timescales determined from hydrocarbon and halocarbon measurements made over the Southern Ocean, *J. Geophys. Res.*, 104(D17), 21819, doi:10.1029/1999JD900203, 1999.
- Wingenter, O. W., Sive, B. C., Blake, N. J., Blake, D. R. and Rowland, F. S.: Atomic chlorine concentrations derived from ethane and hydroxyl measurements over the equatorial Pacific Ocean: Implication for dimethyl sulfide and bromine monoxide, *J. Geophys. Res. D Atmos.*, 110(20), 1–10, doi:10.1029/2005JD005875, 2005.
- Xu, L., Kollman, M. S., Song, C., Shilling, J. E. and Ng, N. L.: Effects of NO<sub>x</sub> on the volatility of secondary organic aerosol from isoprene photooxidation, *Environ. Sci. Technol.*, 48(4), 2253–2262, doi:10.1021/es404842g, 2014.
- Yarwood, G., Jung, J., Whitten, G. Z., Heo, G., Mellberg, J. and Estes, M.: Updates to the Carbon Bond Mechanism for Version 6 (CB6), in Presented at the 9th Annual CMAS Conference, Chapel Hill, NC, October 11-13, vol. 6, pp. 1–4., 2010.
- Yatavelli, R. L. N., Lopez-Hilfiker, F., Wargo, J. D., Kimmel, J. R., Cubison, M. J., Bertram, T. H., Jimenez, J. L., Gonin, M., Worsnop, D. R. and Thornton, J. a.: A Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometer Coupled to a Micro Orifice Volatilization Impactor (MOVI-HRToF-CIMS) for Analysis of Gas and Particle-Phase Organic Species, *Aerosol Sci. Technol.*, 46(February 2015), 1313–1327, doi:10.1080/02786826.2012.712236, 2012.
- Young, C. J., Washenfelder, R. A., Edwards, P. M., Parrish, D. D., Gilman, J. B., Kuster, W. C., Mielke, L. H., Osthoff, H.

D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P. R., Roberts, J. M., Griffith, S., Dusanter, S., Stevens, P. S., Flynn, J., Grossberg, N., Lefer, B., Holloway, J. S., Peischl, J., Ryerson, T. B., Atlas, E. L., Blake, D. R. and Brown, S. S.: Chlorine as a primary radical: Evaluation of methods to understand its role in initiation of oxidative cycles, *Atmos. Chem. Phys.*, 14(7), 3427–3440, doi:10.5194/acp-14-3427-2014, 2014.

- 5 Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C. and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, *Atmos. Chem. Phys.*, 15(8), 4197–4214, doi:10.5194/acp-15-4197-2015, 2015.

Zhao, B., Wang, S., Donahue, N. M., Chuang, W., Hildebrandt Ruiz, L., Ng, N. L., Wang, Y. and Hao, J.: Evaluation of one-dimensional and two-dimensional volatility basis sets in simulating the aging of secondary organic aerosol with smog-chamber experiments, *Environ. Sci. Technol.*, 49(4), 2245–2254, doi:10.1021/es5048914, 2015.

**Table 1.** Summary of Experimental Conditions and Results

Exp. <sup>a</sup>	Isoprene (ppb) <sup>b</sup>	Chlorine (ppb) <sup>c</sup>	VOC:Cl <sub>2</sub>	Cl <sub>2</sub> Inj. <sup>d</sup>	Ini Seed SA (um <sup>2</sup> cm <sup>-3</sup> ) <sup>e</sup>	Seed Acidity	Max OA (μg m <sup>-3</sup> ) <sup>f</sup>	Yield
A1	24	40	0.60	Ini	1500	Neutral	12	0.18
A2	40	88	0.45	Ini	900	Neutral	23	0.21
A3	82	120	0.68	Ini	810	Neutral	39	0.17
A4	120	180	0.67	Ini	1300	Neutral	79	0.24
A5	160	230	0.70	Ini	1800	Neutral	88	0.20
A6 <sup>i</sup>	98	100	0.98	Ini	3700	Acidic	80	0.29
A7 <sup>i</sup>	98	100	0.98	Ini	2700	Acidic	70	0.26
A8 <sup>h</sup>	180	360	0.50	Ini	780	Neutral	180	0.36
C1	40	94	0.42	Cont	950	Neutral	9	0.08
C2	120	180	0.67	Cont	880	Neutral	32	0.10
C3	240	270	0.89	Cont	770	Neutral	53	0.08
C4	300	250	1.20	Cont	1400	Neutral	60	0.07
C5 <sup>g</sup>	73	120	0.61	Cont	N/A	Neutral	N/A	N/A
C6 <sup>i</sup>	98	180	0.54	Cont	2400	Acidic	41	0.15
C7 <sup>i</sup>	120	150	0.80	Cont	3200	Acidic	70	0.21

<sup>a</sup>“A”: Initial chlorine injection experiments. “C”: Continuous chlorine injection experiments. ~~“H”: High aerosol loading (>100 μg m<sup>-3</sup>) initial chlorine injection experiments.~~

<sup>b</sup> Initial isoprene concentration

5 <sup>c</sup> Amount of chlorine injected initially (for A1–~~A5 and H1–H2A8~~) or ~~cumulative chlorine injected~~cumulatively (for C1–~~C5~~C7).

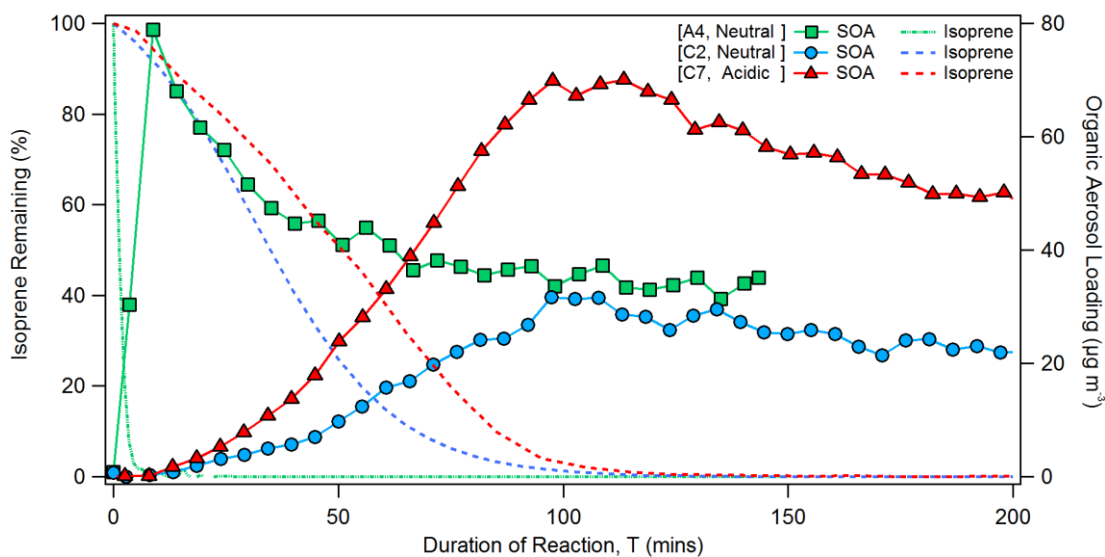
<sup>d</sup> Chlorine injection method. “Ini” for initial injection; “Cont” for continuous ~~chlorine~~ injection

<sup>e</sup> Total initial surface area of ammonium sulfate ~~or acidified~~ seed aerosol

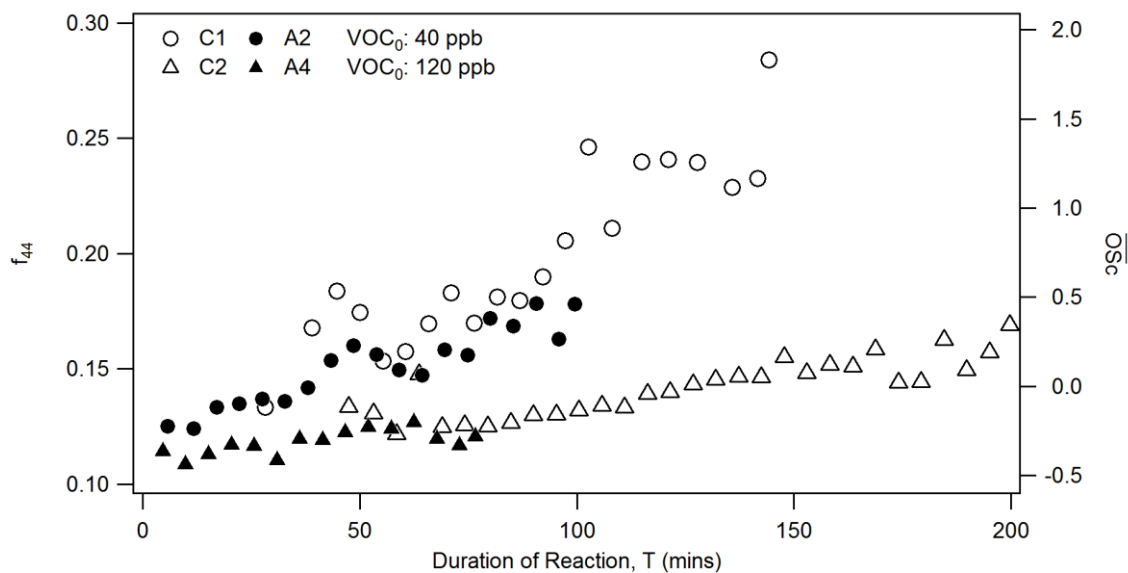
<sup>f</sup> Highest, particle wall-loss-corrected OA concentration observed

<sup>g</sup> No SEMS data available

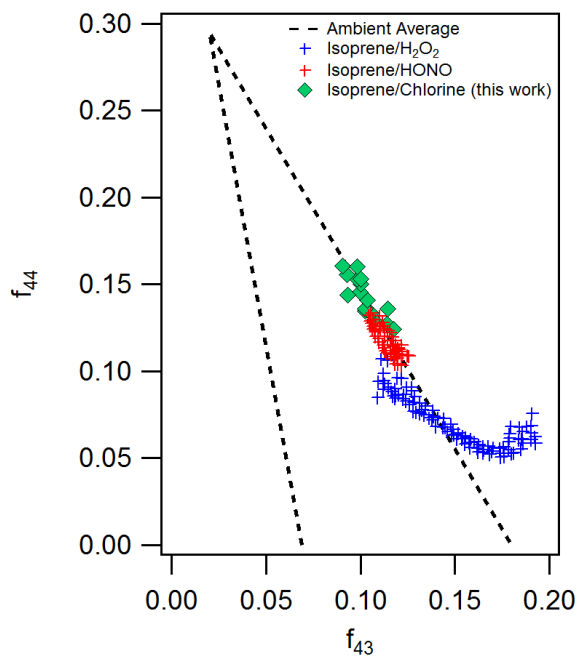
10 <sup>h</sup> ACSM scan speed for A8 (500 ms amu<sup>-1</sup>) was different from other experiments (200 ms amu<sup>-1</sup>)



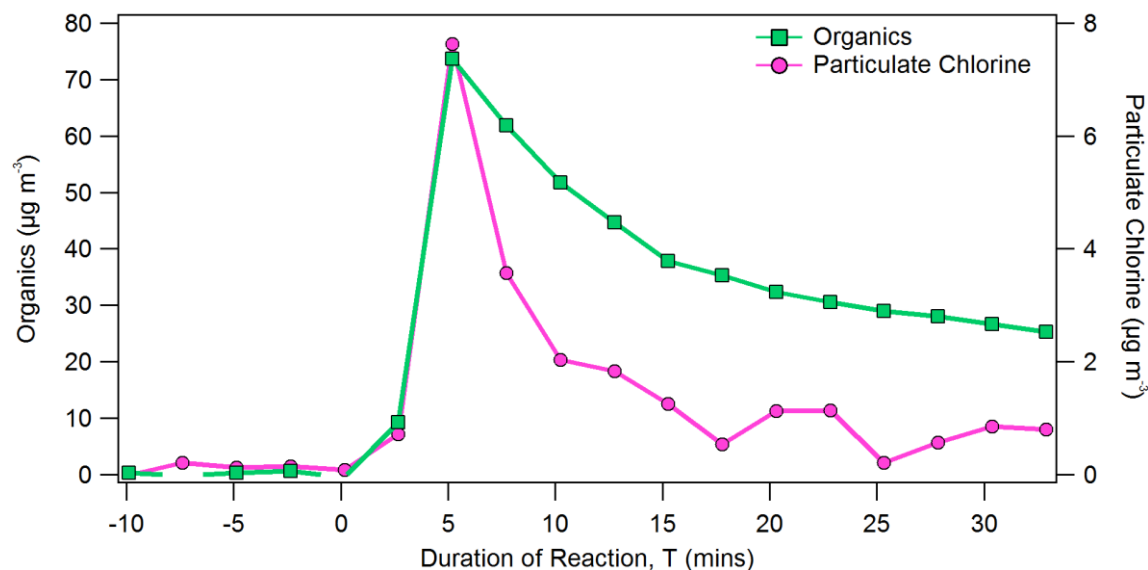
**Figure 1:** Comparison of SOA formation during continuous (C2, C7) and initial (A4) chlorine injection experiments with similar precursor concentrations- but different seed aerosol acidity (C2 vs. C7). SOA concentration is wall-loss corrected and averaged over five-minute intervals. Isoprene concentration is tracked using  $[\text{H}_2\text{O}]_n\text{H}_3\text{O}^+$  CIMS and averaged over one-minute intervals. Maximum SOA concentrations are reached when isoprene has been depleted. After extended oxidation, observed OA loadings are similar for initial chlorine and continuous chlorine experiments using neutral seed particles. Peak SOA concentration reached in the presence of acidic aerosol during Exp. C7 is much higher than peak SOA concentration reached using neutral seed during Exp. C2



**Figure 2:** Comparison of SOA aging between two pairs (C1 and A2; C2 and A4) of initial and continuous chlorine injection experiments. The trend of  $f_{44}$  is consistent for each pair, regardless of chlorine injection method used. Higher initial isoprene concentration resulted in less oxidized organic aerosol (lower  $f_{44}$ ).  $|\overline{OS}_C|$  is estimated based on  $f_{44}$  (see section S2).

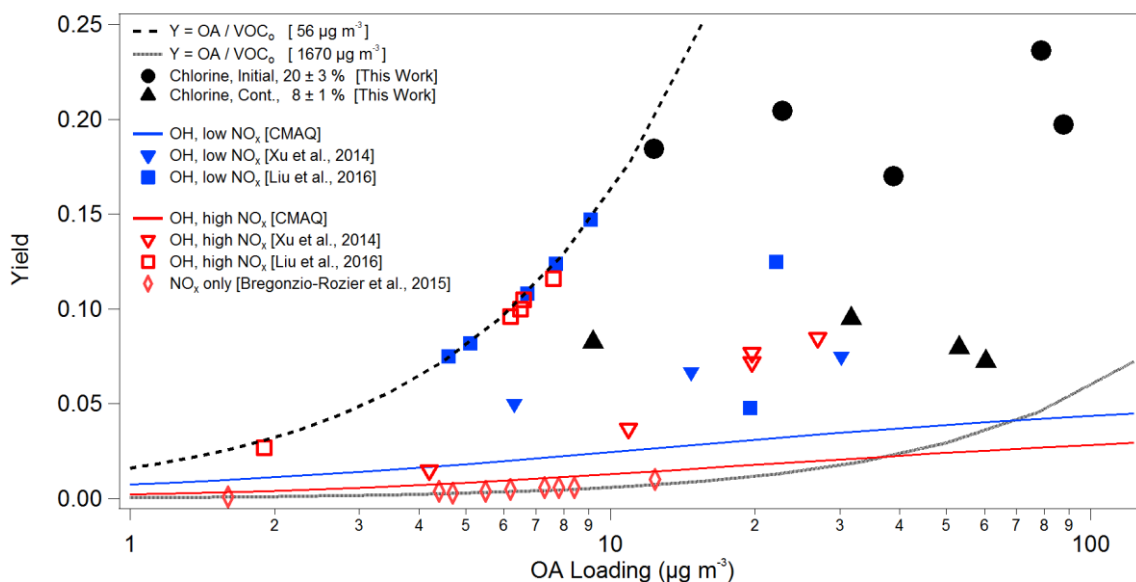


**Figure 3:** ~~Oxidation state~~-Extent of oxidation of SOA generated from chlorine-initiated ~~oxidation reactions~~ (Exp. C3, five-minute averages) compared to OH-oxidation of isoprene under low- and high- $NO_x$  (Chhabra et al., 2011). Area enclosed by the dashed lines represent typical ambient OA measurements (Ng et al., 2010).

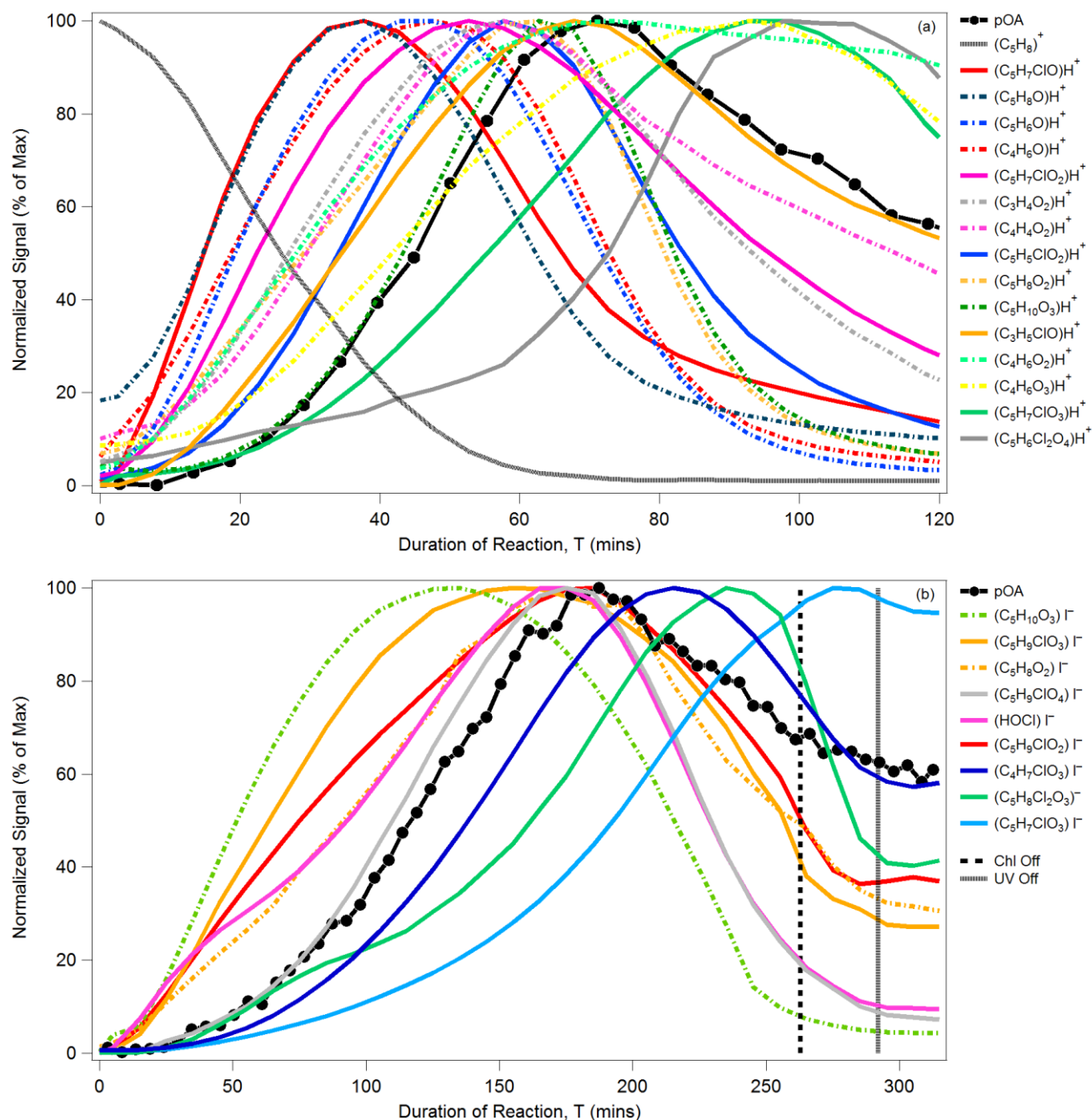


**Figure 4:** The raw measurements of particulate organics and chloride measurements for Exp. H1 from Exp. A8, not corrected for wall losses. UV was turned on at T = 0 mins. Apparent chloride concentration rapidly decreased to near-background levels while significant suspended OA mass remained. This rapid decrease is likely a measurement artifact due to build-up of chlorinated compounds on the vaporizer surface, see section 3.2 and S4.

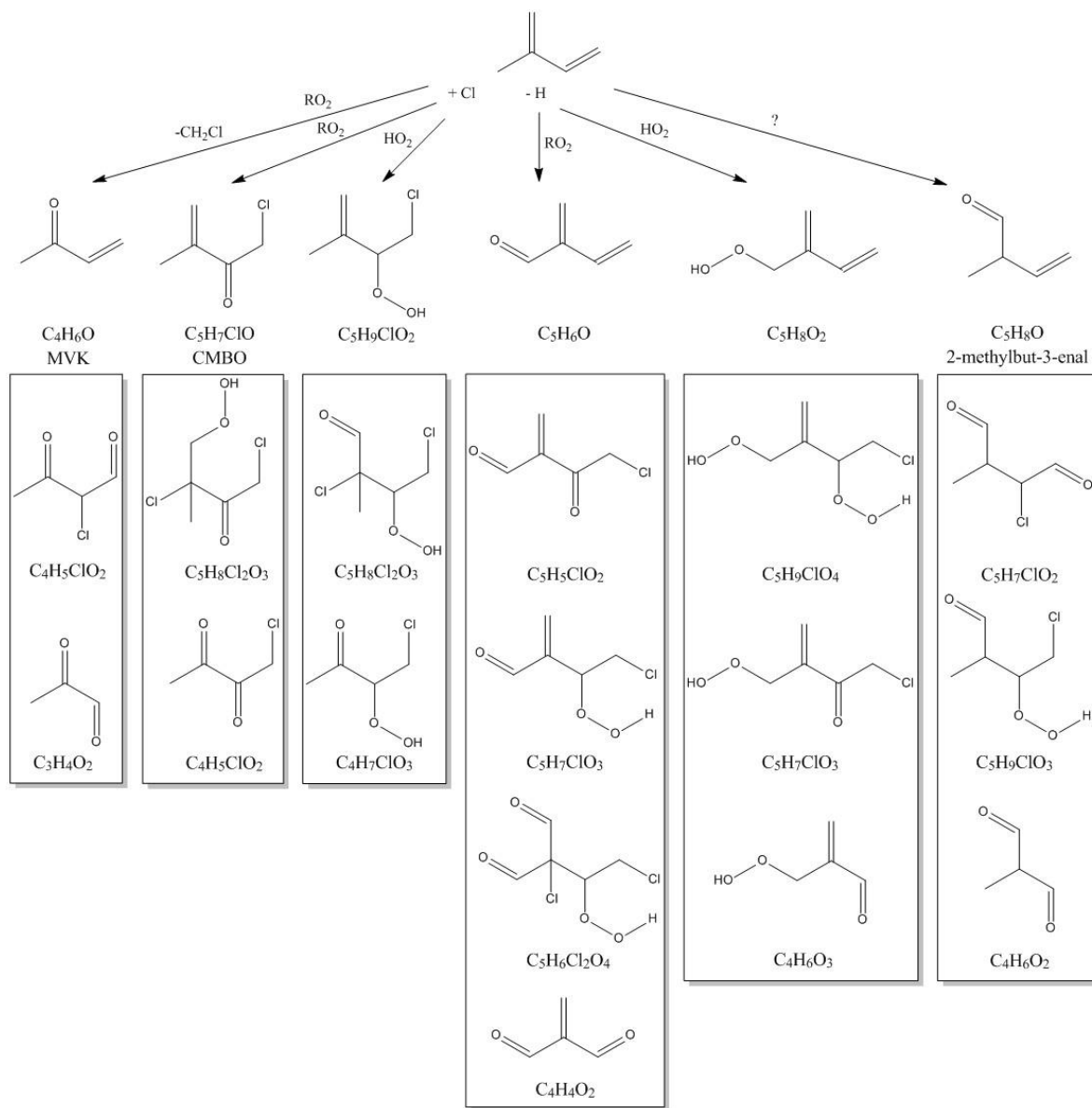




**Figure 5:** Comparison of observed isoprene-chlorine SOA yield with recent literature values (Brégonzio-Rozier et al., 2015; Liu et al., 2016; Xu et al., 2014) corresponding to low and high NO<sub>x</sub> OH-oxidation. Dashed lines illustrate the concept of a “pre-defined” yield curve as discussed in the text. The yield used in CMAQ was reproduced using cited VBS parameters (Koo et al., 2014).



**Figure 6:** Observation of ~~select~~ gas-phase species (a) using  $(H_2O)_nH_3O^+$  CIMS from Exp. C5, and (b) using  $(H_2O)_nI^-$  CIMS from Exp. C3. Suspended particle concentration from each experiment is shown. Ion signal for each individual species was normalized to its maximum value. Five-minute averages are shown. Chlorine injection stopped at T = 263 mins and UV lights were turned off at T = 292 mins during Exp. C3. Species displayed consist of previously reported products in literatures and multigenerational products proposed in Figure 7.  $(C_5H_{10}O_3)I^-$  potentially represent ISOPOOH or IEPOX, while  $(C_5H_{10}O_3)H^+$  is likely  $(C_5H_8O_2)(H_3O)^+$ , an oxidation product.  $(C_4H_7ClO_3)I^-$  may also represent  $(C_4H_5ClO_2)(H_2OI)^-$ .



**Figure 7:** Select oxidation products formed under  $\text{NO}_x$ -free conditions. More detailed individual reaction pathways are shown in Fig S10-12. For illustrative purposes, only one isomer is shown per reaction pathway type (e.g. H-abstraction vs. Cl-addition;  $\text{RO}_2 + \text{RO}_2$  vs.  $\text{RO}_2 + \text{HO}_2$ ; C-C cleavage vs. no cleavage). As explained in the text,  $\text{HO}_2$  radicals required for certain reaction pathways were produced from preceding  $\text{RO}_2 + \text{RO}_2$  chemistry; formation mechanism for  $\text{C}_5\text{H}_8\text{O}$  is unclear. Time series of all product shown can be found in either Figure 6a or 6b.