

The authors thank the reviewers for their insightful comments. The response to each comment is in blue with corresponding changes in the manuscript italicized.

Anonymous Referee #1

The manuscript presents some interesting measurements of cooking SOA by TDGC/MS. The authors adopt a new method to achieve molecular speciation of the SOA, where SOA complex mixture was deconvoluted using mass spectral fragmentation patterns to extract useful information about functional groups and carbon numbers. They also derived the parameterizations for aldehyde oxidation and used the derived parameters to predict SOA mass. The model results generally well captured the amount of SOA formed and its chemical characteristics, e.g., O/C. Overall, this paper makes a valuable contribution to current cooking SOA understanding.

Q1. Hydroxyl radicals as major oxidants are produced through the ozone photolysis in the flow tube. However, ozone concentration would be high in the flow tube. What is the influence of ozone oxidation of aldehydes in the experiments?

We agree that ozone concentration would be high in the flow tube. However, we did not observe any particle formation during ozonolysis of heated cooking oil where OH radicals were not present. Since aldehydes are major contributors of gas-phase emissions from cooking oils, we believe that during photooxidation of aldehyde precursors ozone chemistry would have negligible effect on particle formation. Furthermore, gas-phase reaction rate constant of aldehydes with ozone is of the order of 10^{-17} - 10^{-18} (Atkinson and Arey, 2003; Atkinson and Carter, 1984) much lower than that of hydroxyl radicals, so the timescale for ozonolysis of aldehydes would likely be longer than the residence time in the flow tube reactor.

To understand the reactivity of C=C in unsaturated aldehydes, methacrolein is used as an example calculation to provide insights into the reaction timescales as its reaction rate constant with both OH and ozone is readily available. Following calculations shows that timescale of reaction with ozone is much slower than the residence time in the flow tube suggesting that the ozonolysis of unsaturated aldehydes play a negligible role in the formation of SOA from aldehydes or cooking emissions.

The reaction rate constant of methacrolein is obtained from Atkinson and Arey, 2003.

k_{OH} is $2.9E-11 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

k_{O_3} is $1.2E-18 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

For the lowest OH exposure, OH conc = $2.88E8 \text{ molec cm}^{-3}$ and ozone conc is 0.5 ppm. At these conditions, methacrolein reaction timescale with OH is $1/k_{OH}*[OH] = \sim 120 \text{ s}$, while reaction timescale with ozone is 1129 min.

For the highest OH exposure, OH conc = $1.1E9 \text{ molec cm}^{-3}$ and ozone conc is 12.6 ppm. At these conditions, methacrolein reaction timescale with OH is 31 s, while reaction timescale with ozone is $\sim 45 \text{ min}$.

To clarify this, following text have been added to the manuscript in L91-94, as well as above sample calculation have been added to SI in Sect. 1 in L60-73:

“...The effect of ozone on the SOA formation was found to be negligible as the reaction timescales of aldehydes with ozone were calculated to be at least 100 times longer than those with OH. A

sample calculation for methacrolein reaction timescales with OH and ozone is shown in SI in Sect. 1.”

Q2. What are the criteria in selecting the model compounds (Table S2) in each functional group class (e.g., different carbon number range used for different classes)?

Based on the carbon number range of VOC precursors emitted from cooking emissions, the resulting SOA products will have a similar or lower carbon # assuming oligomerization reactions are not dominant in the system. We also expect that photooxidation reactions will lead to addition of -OH and =O groups based on knowledge about gas-phase oxidation chemistry. Based on these different combinations of functional groups we selected the model compounds in Table S2 to characterize the composition of cooking SOA.

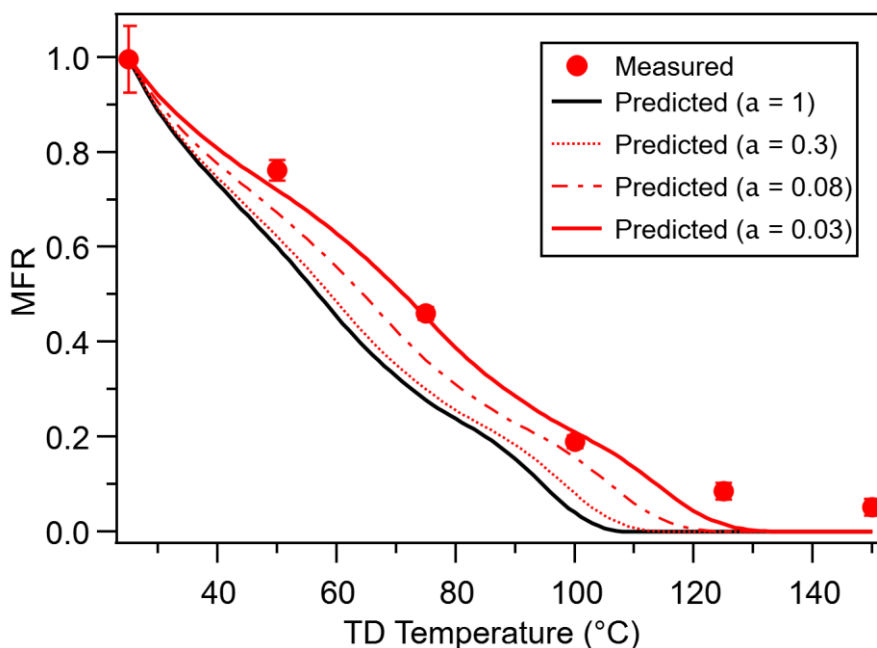
Q3. Figure 3: The author mentioned there is an increase in the average oxidation state (from -0.6 to -0.24) and a decrease in the average carbon number (from 5.2 to 4.9) with increasing photochemical aging (line 15 and line 188-193 and Fig.3 caption). The decrease in carbon is not so significant, and from the figure, the mole fraction of carbon 7-9 compounds is even higher in the 1.7d photochemical aging condition than those in 10.7h condition. The conclusion of dominant fragmentation should be better elaborated. The SOA concentration actually increased with further oxidation (TableS1).

We agree that the decrease in average carbon # is not significant in this study. However, the effect of fragmentation is evident from an increasing fraction of smaller and more oxygenated compounds formed during photooxidation. For instance, the total fraction of C2-C7 SOA products increased from 81% in 10.7h SOA to 89% in 1.7d SOA. Of this fraction, the smaller carbon # compounds (C2-C4) which are indicative of fragmentation processes increased from 42% in 10.7h SOA to ~49% in 1.7d SOA. On the other hand, total fraction of >C7 (C8-C10) products declined from ~19% to ~11% as SOA aged. An increase in smaller and more oxygenated compounds, along with decrease in larger and less oxygenated products from 10.7h SOA to 1.7d SOA suggests that fragmentation reactions are responsible for the shift towards formation of smaller oxygenated compounds. We also use the term fragmentation to refer strictly to the decrease in carbon number, and not decrease in SOA concentration. Therefore, increase in SOA concentration is not strictly inconsistent with fragmentation, since the effect of increased \overline{OSC} on volatility can exceed that of decreased carbon number. To clarify this, the following edits have been made to the manuscript in L193-198:

“...comprised of ~~long chain hydroxy acids~~ ~19% larger (C8–C10) and less oxygenated compounds, this fraction declined to ~11% at higher OH exposures. Furthermore, the total fraction of C2-C7 products increased from 81% to 89% when OH exposure increased from 10.7 h to 1.7 d. Of this fraction, the smaller carbon # compounds (C2-C4) which are indicative of fragmentation processes increased from 42% at 10.7 h to ~49% at 1.7 d. An increase in smaller and more oxygenated compounds, along with decrease in larger and less oxygenated products suggests that fragmentation reactions are responsible for the shift towards formation of smaller oxygenated compounds.”

Q4. Figure 5 compares the measured and modeled mass thermograms for canola oil SOA. A mass accommodation coefficient of 0.03 was used in the model prediction. How sensitive is the predicted results to the accommodation coefficient? When using different accommodation coefficients of 1 and 0.03, the differences between MFR are only around 30% (at the same TD temperature). Maybe be better to add some thermograms using middle accommodation coefficient values between 1 and 0.03.

Thanks for the suggestion. We have modified Fig. 5 in the manuscript with different accommodation coefficients in the range 1-0.03.



Q5. Line 291-294: Other unidentified I/SVOCs may also play a role in the unexplained SOA mass.

Thanks for the suggestion. It is likely that other unidentified precursors such as IVOCs or SVOCs can contribute to the unexplained SOA. However, IVOCs from cooking emissions have not yet been positively identified. Based on the reviewer suggestion, the following changes have been made to the manuscript in L342-347:

“...model predictions. Furthermore, the unexplained SOA can likely arise from other unidentified S/IVOCs as hypothesized by Liu et al. (2017c). However, unlike traffic emissions (Zhao et al., 2014), S/IVOCs from cooking has not been positively identified. In addition, small VOC precursors like acrolein and malondialdehyde which have been measured in large quantities from cooking emissions (Klein et al., 2016a), may form SOA products having higher O/C ratios, which may better explain the O/C ratios observed in our experiments.”

In addition, please also refer to response to Q7, Reviewer #2.

Q6. Line 314-321: When deriving the parameters for aldehyde oxidation, six tunable parameters were used to fit the measured SOA concentration. Compared with other systems, a lower mfrag was used in this study. The author attributed this to the greater fragmentation in this SOA system. However, the relative strength of these six parameters used to fit SOA concentrations is different for heptanal, 2-heptenal and 2,4- heptadienal oxidation experiments (Fig. S10). For example, mfrag used in heptanal experiment data is one order of magnitude lower than that used for the other two aldehydes. In addition to mfrag, what are the corresponding processes of the other five parameters? Are those related to gas-particle partitioning, functionalization, reactions with oxidants, or condensed-phase chemistry mentioned earlier (line 308-309)? It would be interesting to discuss the relationship between these parameters and their corresponding chemical or physical processes and how they behave in this system.

The six tunable parameters in SOM are: mfrag- which describes fragmentation reactions, ΔLVP - is decrease in logarithm of volatility upon addition of oxygen atom. Pox1, Pox2, Pox3, Pox4- describes addition of 1, 2, 3, and 4 oxygen atoms per reaction with OH, respectively.

The probability of a reaction with OH leading to fragmentation is calculated as $P_{\text{frag}} = (\text{O:C})^{\text{mfrag}}$, where mfrag is the fitting parameter. The corresponding functionalization probability can be estimated as $P_{\text{func}} = 1 - P_{\text{frag}}$. Instantaneous gas/particle partitioning equilibrium is inherently assumed at every timestep in the model. Addition of oxygen atoms upon reaction with OH will govern the reaction with oxidants. Condensed-phase chemistry was not considered in the model.

To answer reviewer's question, as the # of oxygen atom addition increases on carbon backbone, it will likely result in the higher fragmentation probability. Therefore, as shown in Fig. S10, Pox4 is much higher for heptanal than 2-heptenal or 2,4-heptadienal, thereby having much lower mfrag value than 2-heptenal or 2,4-heptadienal.

Q7. In real cooking emissions, POA are also emitted with the aldehydes and other gasphase precursors. It would be useful if the authors can project how the inclusion of POA in the system would affect their results of O/C, etc.

Inclusion of POA during oxidation of cooking vapors will likely decrease the overall O:C (or $\overline{\text{O:C}}$) of the system as POA is less functionalized than SOA due to higher contributions from long chain fatty acids, such as C16, C18 thereby giving rise to $\overline{\text{O:C}}$ of POA from heated cooking oils ~ -1.7 (Takhar et al., 2019) which is much lower compared to $\overline{\text{O:C}}$ of cooking SOA measured in this study. Therefore, inclusion of POA would likely lead to an overall decrease in the average $\overline{\text{O:C}}$ or O:C of the system. However, it should be noted that POA can itself undergo heterogenous oxidation reactions in the atmosphere resulting in an increase in O:C. On the other hand, other gas phase precursors that can potentially contribute to total vapor emissions from cooking could be S/IVOCs which have not been positively identified from cooking emissions, but have been shown to contribute to SOA from other sources e.g. traffic (Zhao et al., 2014). A similar projection for cooking emissions can likely be made. Furthermore, depending on the cooking conditions, it has been shown that cooking can emit large amounts of terpenes upon addition of condiments or spices to heated cooking oils. Emissions of terpenes have been shown to significantly contribute to total SOA production (Klein et al., 2016b; Liu et al., 2017a). Based on the reviewer suggestion, the following edits have been made to the manuscript in L384-391:

“...Formation of SOA from cooking emissions in the atmosphere is likely influenced by emissions of POA, and other gas-phase precursors. Therefore, inclusion of POA during atmospheric processing of cooking emissions will likely influence the physicochemical properties of cooking SOA. For instance, with cooking POA being much less functionalized than SOA, inclusion of POA will likely decrease the system O:C (or \overline{OSc}). However, POA from cooking emissions can undergo heterogeneous reactions in the atmosphere, thereby increasing O:C (or \overline{OSc}). On the other hand, there could potentially be contributions from other gas-phase precursors or S/IVOCs emitted from cooking vapors that can result in SOA formation. These precursors can potentially contribute to SOA formation from cooking emissions, but their oxidative evolution in the atmosphere is not well understood.”

References

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Anonymous Referee #2

The manuscript by Takhar et al. reported the SOA formation from OH oxidation of heated cooking oil and characterized the SOA composition and volatility using TD-GC/MS. A new method was used to analyze the composition of the complex product mixtures. The authors have found that an increase in OSc and a decrease in carbon number upon oxidation, which was attributed to fragmentation reactions during OH aging. In addition, by comparing product yields from individual precursors and applying an oxidation model, they conclude that aldehyde precursors are the main contributors of SOA formed from heated cooking oil. Overall, this is a well-written manuscript and the results can be a useful addition to better understanding the formation, composition and volatility of cooking SOA. I would recommend publication after a minor revision.

Specific Comments

1. The authors stated the increase in OSc and decrease in nC with oxidation. However, it is not very clear from Figure 3. Could the authors add the average OSc and nC in every panel of Figure 3?

Please refer to response to Q3, Reviewer #1.

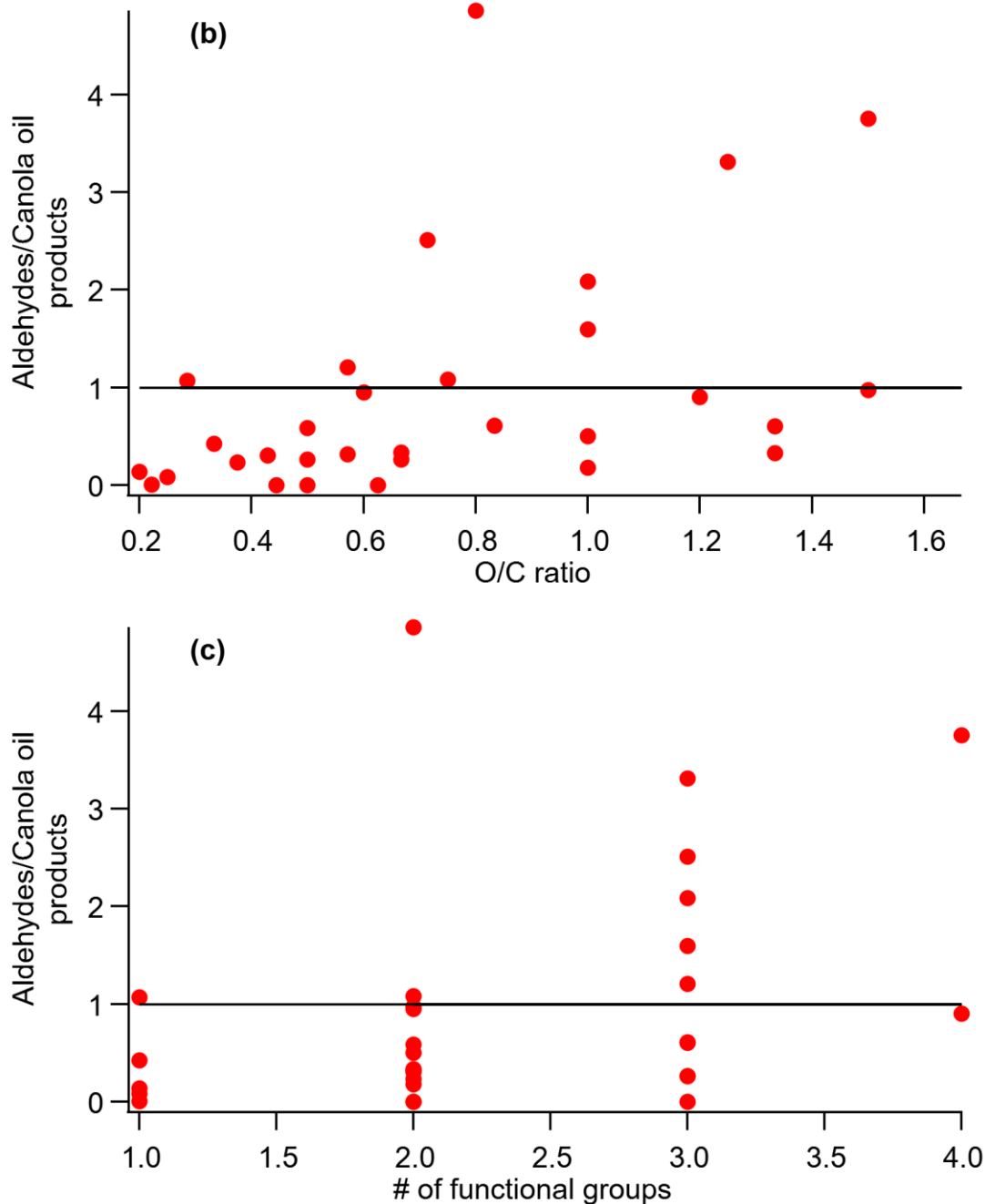
2. L193-197, the authors did not compare the same thing here. In Lambe et al. (2012, 2015), they found the evidence of fragmentation because of the decrease in SOA yield upon oxidation. However, in this study, the evidence of fragmentation is from the decrease in average carbon number. If the authors also look at the SOA yield, it never decrease with increasing photochemical age (Figure 7 and Table S1). Therefore, the authors could not state that fragmentation reactions happen earlier for cooking oil than other precursors (e.g., alkanes and isoprene).

We agree that fragmentation reactions in this study are because of decrease in carbon # and not due to decrease in SOA yield. As suggested by the reviewer, L193-197 (now updated as L200-204) have been removed from the manuscript.

3. L293-295, I do not see any O/C or number of functional group dependence in Figure S9. The authors might need to change their way to present these data.

Figure S9(b) and (c) have been replaced with following figures, where y-axis is replotted as the ratio of aldehydes products to canola oil products instead of aldehydes products only. Since most of the products ratio lies below y-axis = 1 line suggesting that more oxygenated products partitions readily in canola oil SOA than individual aldehydes SOA. Please note that L293-295 is updated as L306-308.

Furthermore, Fig. S9(a) and (d) have also been updated with the similar y-axis against vapor pressure and carbon #.



4. Figure 6 looks very interesting, but the authors did not discuss much about it. It seems that for higher-carbon-number products and 1-COOH products, the agreement is worse than others compounds. Any explanation for that?

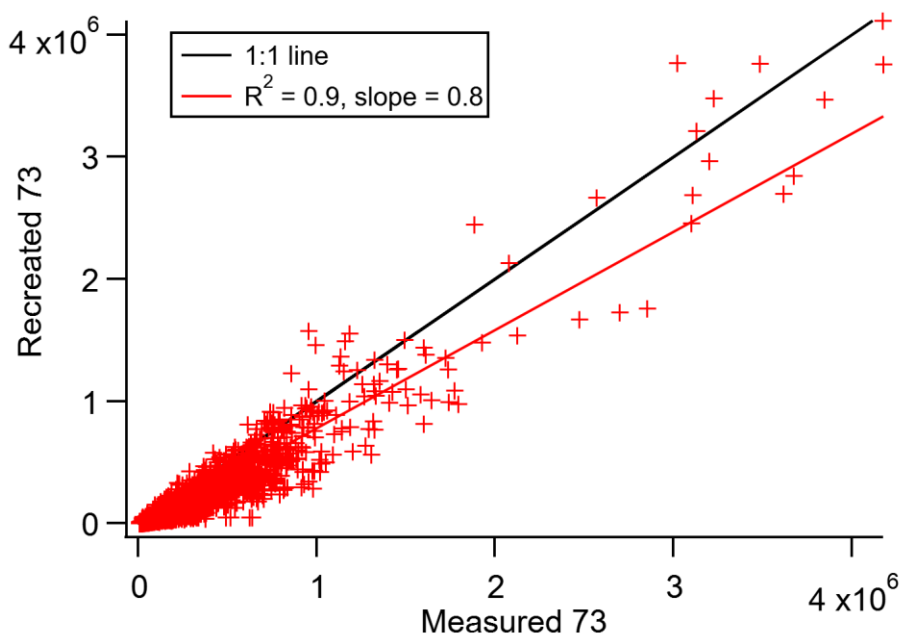
The formation of higher carbon number products from the precursors photo-oxidized in this study were not observed likely due to negligible oligomerization reactions or reactions occurring in the particle-phase that can form SOA products with higher carbon # than the smaller carbon # parent VOCs photo-oxidized in this study. In addition, 1-COOH compounds are likely to be present as

primary vapors in the gas-phase which can subsequently partition to the condensed phase upon SOA formation. Based on the reviewer comment, the following edits have been made to the manuscript in L302-305:

“...canola oil photooxidation. As shown in Fig. 6, the formation of higher carbon # products cannot be explained from the photooxidation of aldehydes used to predict oil oxidation products likely due to the assumption of negligible particle-phase or oligomerization reactions occurring in the condensed phase. In addition, higher carbon # acids are likely present as primary vapors in the gas phase which can then partition to the condensed phase upon SOA formation.”

5. In Figure 2, the recreated m/z 73 seems agree well with the measured signal. Could the authors provide a scatter plot as well? Maybe it can replace Figure S4c.

Thanks for the suggestion. Fig. S4(c) is replaced with a scatter plot in the SI as shown below. However, it should be noted that a better assessment of recreated signal should be done by plotting chromatograms to evaluate any under/overestimation of the peaks or model compounds.



6. L201, what are the O/C ratios in previous studies? The author should put them here for comparison.

The O/C ratios reported in previous studies ranged between 0.24 to 0.46. The following edits have been made to the manuscript in L207-209:

“...The O:C ratios measured using an AMS (Kaltsonoudis et al., 2017; Liu et al., 2017b) ranged between 0.24-0.46 which are within a factor of 2 measured in this study.”

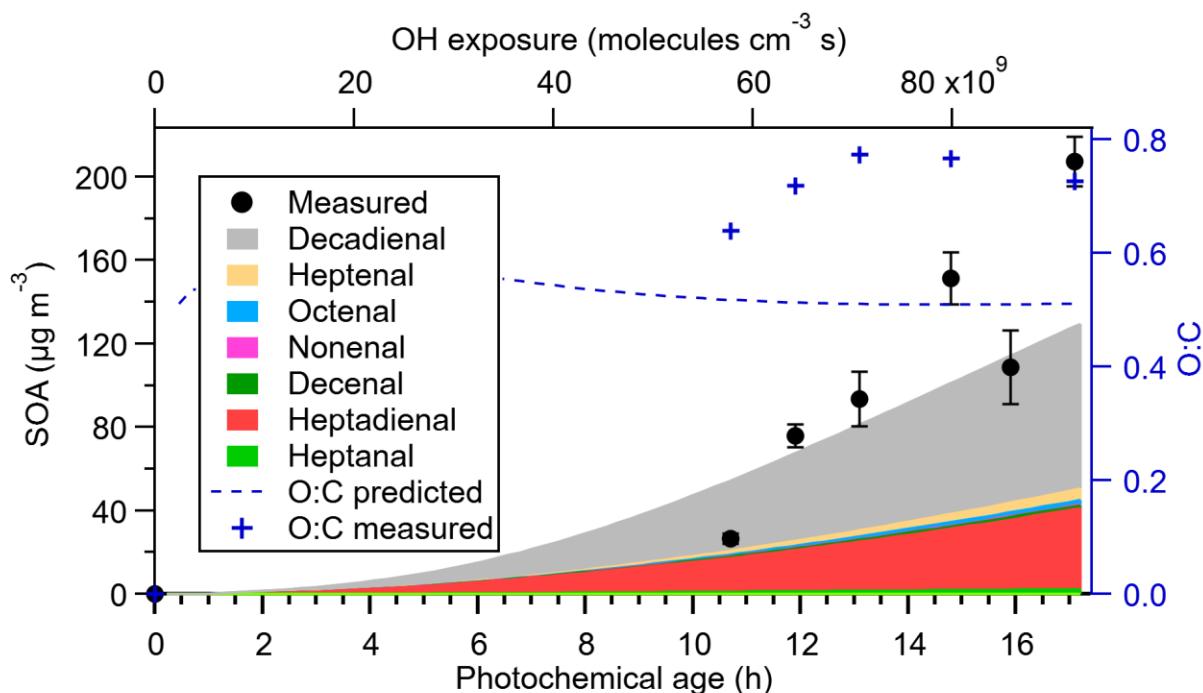
7. Exp. 7 (photochemical age = 40.7 h) is not included in Figure 7. The authors should mention that somewhere.

Thanks for pointing this out. The model simulations were run with OH exposure in the range similar to that of aldehyde photooxidation (Fig. S10). Upon further examination, we discovered that the OH exposure in the model results were incorrectly plotted in Fig. 7. In addition, we found that in earlier experiments we were unable to measure decadienal, but upon further examination, we found decadienal can be captured on Tenax tubes by measuring for longer duration, and so we have now included decadienal as one of the SOA precursors and estimated the formation of speciated products and total SOA using SOM. We have made corresponding changes to Figs. 6, 7 and S8. After correcting this error, the following corrections have been made to the manuscript with Fig. 7 revised as shown below. Our updated SOM estimate of heptadienal SOA contribution is now ~19% (down from 35% in our previous estimate, which corresponded to SOA at higher OH exposure). At the same time, decadienal accounts for 38% of the SOA. The total estimated contribution from aldehydes to canola oil SOA is 62%. Furthermore, it should be noted the modeled O:C estimate declined from 0.7 to 0.51 with the inclusion of decadienal.

In L334, "...aging conditions in the OH exposure range similar to that of aldehyde photooxidation."

In L338, "...Fig. 7, the model generally captures the amount of SOA formed to up to ~~within~~ 5062%, but..."

In L341-347 "...SOM predicts an O:C around 0.517, which ~~lies~~ is within $\pm 5020\%$ of the measured O:C likely suggesting that the changes in chemical composition of cooking SOA is in ~~good~~ a reasonable agreement with the model predictions. Furthermore, the unexplained SOA can likely arise from other unidentified S/IVOCs as hypothesized by Liu et al. (2017c). However, unlike traffic emissions (Zhao et al., 2014), S/IVOCs from cooking has not been positively identified. In addition, small VOC precursors like acrolein and malondialdehyde which have been measured in large quantities from cooking emissions (Klein et al., 2016a), may form SOA products having higher O/C ratios, which may better explain the O/C ratios observed in our experiments."



Technical Corrections

L470-475, same references.

Thanks for pointing this out. Reference in line 473-475 (updated as L499-501) have been removed.

There is an incorrect number (1:2:1) in Figure S5.

Thanks for pointing this out. 1:2:1 has been corrected to 1.2:1.

References

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1 Characterization of secondary organic aerosol from heated- 2 cooking oil emissions: evolution in composition and volatility

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7 **Abstract.** Cooking emissions account for a major fraction of urban organic aerosol. It is therefore important to
8 understand the atmospheric evolution in the physical and chemical properties of organic compounds emitted from
9 cooking activities. In this work, we investigate the formation of secondary organic aerosol (SOA) from oxidation of
10 gas-phase organic compounds from heated cooking oil. The chemical composition of cooking SOA is analyzed using
11 thermal desorption-gas chromatography-mass spectrometry (TD-GC/MS). While the particle-phase composition of
12 SOA is a highly complex mixture, we adopt a new method to achieve molecular speciation of the SOA. All the GC
13 elutable material is classified by the constituent functional groups, allowing us to provide a molecular description of
14 its chemical evolution upon oxidative aging. Our results demonstrate an increase in average oxidation state (from -0.6
15 to -0.24), and decrease in average carbon number (from 5.2 to 4.9) with increasing photochemical aging of cooking
16 oil, suggesting that fragmentation reactions are key processes in the oxidative aging of cooking emissions within 2
17 days equivalent of ambient oxidant exposure. Moreover, we estimate that aldehyde precursors from cooking emissions
18 account for a majority of the SOA formation and oxidation products. Overall, our results provide insights into the
19 atmospheric evolution of cooking SOA, a majority of which is derived from gas-phase oxidation of aldehydes.

21 1 Introduction

22 Organic aerosol (OA) has important impacts on air quality, climate and human health (Hallquist et al., 2009). OA is
23 often composed of thousands of organic compounds formed from a variety of sources. In urban areas, particulate
24 emissions from food cooking account for a significant fraction of OA (Allan et al., 2010; Crippa et al., 2013; Florou
25 et al., 2017; Kostenidou et al., 2015; Lee et al., 2015; Mohr et al., 2012; Sun et al., 2011). Furthermore, volatile organic
26 compounds (VOCs) are also emitted, and they can undergo oxidation and form secondary organic aerosol (SOA).
27 Recent studies have reported the formation of SOA from meat charbroiling (Kaltsonoudis et al., 2017[†]) and heated
28 cooking oils (Liu et al., 2017b, 2017c, 2018). Therefore, food cooking activities have substantial impacts on air quality
29 in and downwind of urban areas.

30 The emission of VOCs from cooking is highly variable and depends on a number of factors such as cooking style,
31 food, ingredients, and temperature (Fullana et al., 2004a, 2004b; Klein et al., 2016a, 2016b; Liu et al., 2017c; Schauer
32 et al., 1999, 2002). Of the different classes of VOCs characterized in these studies, aldehydes have been shown to be

33 the major group of VOCs emitted from cooking oils. These VOCs are chemically produced upon heating via peroxy
34 radical reactions of the fatty acids (Choe and Min, 2007; Gardner, 1989). Klein et al. (2016a) investigated the
35 composition of nonmethane organic gas (NMOG) emissions from boiling, charbroiling, shallow and deep frying of
36 various vegetables, meats, and cooking oils heated under different temperature conditions. The authors reported that
37 emissions from shallow frying, deep frying and charbroiling are dominated by aldehydes, and the relative amounts
38 depend on the type of oil used during cooking (Klein et al., 2016a). C7 aldehydes are the major species in emissions
39 from canola oil, whereas C9 aldehydes are dominant from olive oil (Klein et al., 2016a). These differences in emission
40 patterns of oils vary with composition of triglycerides present in the oil (Choe and Min, 2006). Katragadda et al.
41 (2010) demonstrated up to an order of magnitude increase in emissions upon reaching the smoke point of cooking
42 oils. In addition to emissions from cooking oil, the addition of condiments (herbs and peppers) to cooking leads to
43 significant emissions of mono-, sesqui- and diterpenes in the gas phase (Klein et al., 2016b). Liu et al. (2017a) showed
44 an order of magnitude increase in the emissions of VOCs when stir-frying with spices. Therefore, factors like cooking
45 style, food, cooking temperature, and ingredients play a significant role in the chemical profile of cooking emissions
46 (Fullana et al., 2004a, 2004b; Klein et al., 2016a, 2016b; Liu et al., 2017a, 2017c).

47 The VOCs emitted from cooking have been shown to produce significant amount of SOA rapidly in recent flow tube
48 (Liu et al., 2017b) and smog chamber studies (Kaltsonoudis et al., 2017a; Liu et al., 2017c, 2018). Kaltsonoudis et al.
49 (2017a) and Liu et al. (2017b, 2018) showed an increase in O/C ratio upon a few hours of atmospheric aging suggesting
50 lightly oxidized cooking SOA. Furthermore, Liu et al. (2017b) showed significant production of SOA with increasing
51 OH exposure for different cooking oils. Thus far studies have only focused on formation potential of SOA from
52 cooking emissions. Despite high emission rates of VOCs from cooking, the understanding of SOA composition from
53 these emissions remains limited.

54 Source apportionment using aerosol mass spectrometry (AMS) data in urban areas has often revealed a Cooking
55 Organic Aerosol (COA) factor, but it is unclear how this factor is related to cooking emissions. Many studies reported
56 that the mass spectra associated with this factor resemble that of hydrocarbon-like organic aerosol (HOA) factor from
57 other non-cooking sources (Dall'Osto et al., 2015; Hayes et al., 2013; Huang et al., 2010; Mohr et al., 2009, 2012). In
58 addition, it is often unclear whether ambient COA represents primary or secondary organic aerosol from cooking
59 emissions (Dall'Osto et al., 2015; Florou et al., 2017; Kaltsonoudis et al., 2017b; Kostenidou et al., 2015). Laboratory
60 studies (Liu et al., 2017b, 2018) showed that the mass spectra for primary cooking organic aerosol exhibited strong
61 correlation with ambient COA factor (Lee et al., 2015), but the cooking SOA mass spectra showed some similarities
62 to ambient semi-volatile oxygenated OA (SV-OOA) factor. These measurements highlight the challenges in assigning
63 COA factor without understanding the changes in chemical composition occurring during oxidation of cooking
64 emissions.

65 In general, there is a need to better understand the molecular composition contributing to aged COA. In this study, we
66 investigate detailed chemical composition of cooking SOA at the molecular level. The objectives of this study are to:
67 (i) understand the detailed chemical speciation of cooking SOA using TD-GC/MS, (ii) describe chemical evolution in
68 SOA upon atmospheric aging, and (iii) attribute formation of SOA to different VOCs emitted from food cooking

69 emissions. In this work we use heated cooking oil as a model for food cooking emissions. We show that the majority
70 of the SOA is derived from oxidation of aldehydes, and the oxidation mechanisms are dominated by fragmentation
71 reactions. Overall, our results provide useful insights into the evolution of cooking SOA, which may be incorporated
72 into chemical transport models for better predicting OA formation from cooking emissions in the atmosphere.

73

74 **2 Experimental methods**

75 **2.1 Flow tube experiments**

76 The experimental setup is shown in Fig. 1, and experimental conditions are listed in Table S1. For each experiment,
77 30-40 mL of canola oil was heated at 250 °C on an electric heating plate in a Pyrex bottle resulting in an average
78 cooking oil temperature of 180 °C, as measured by a thermocouple in direct contact with the heated oil. Purified air
79 flowed over the headspace of the heated oil at a rate of 0.2 L min⁻¹ and then diluted by a factor of 50. 0.2 L min⁻¹ of
80 the total diluted flow was passed through a Teflon filter to remove particles, and the oil vapors were introduced into a
81 custom-built 10 L quartz flow tube reactor. A separate flow of oxygen (99.6%) was irradiated in a UV ozone generator
82 (UVP 97006601) to produce ozone and was also introduced into the flow tube reactor. In parallel, purified air was
83 flowed through a water bubbler into the reactor to provide water vapor. The combined flow rate through the flow tube
84 was set at 3 L min⁻¹, resulting in an average residence time of approximately 200 s.

85 In the flow tube, hydroxyl radicals were produced through the photolysis of ozone irradiated by a UV lamp ($\lambda = 254$
86 nm) in the presence of water vapor. The integrated OH exposure was measured indirectly from the loss of cyclopentane
87 which was monitored by a gas chromatography-flame ionization detector (GC-FID, model 8610C, SRI Instruments
88 Inc.) equipped with a Tenax TA trap sampling downstream of the flow tube at a rate of 0.15 L min⁻¹. In this study, the
89 experiments were conducted at different OH exposures ranging from 5.77×10^{10} to 2.2×10^{11} molecules cm⁻³ s. OH
90 exposure in this range is equivalent to ~11 to 41 h of atmospheric oxidation, respectively, assuming a 24-h average
91 atmospheric OH concentration of 1.5×10^6 molecules cm⁻³ (Mao et al., 2009). The effect of ozone on the SOA
92 formation was found to be negligible as the reaction timescales of aldehydes with ozone were calculated to be at least
93 100 times longer than those with OH. A sample calculation for methacrolein reaction timescales with OH and ozone
94 is shown in SI in Sect. 1.

95 Downstream of the flow tube, pre-baked quartz fiber filter and Tenax tube samples were collected for offline chemical
96 analysis. The changes in the particle size distribution and volume concentration were monitored using a scanning
97 mobility particle sizer (SMPS) with a differential mobility analyzer (TSI 3081), and a condensation particle counter
98 (TSI 3781). A constant density of 1.4 g cm⁻³ was assumed to convert particle volume concentration into mass
99 concentration (Chan et al., 2010). Relative humidity and temperature were monitored by an Omega HX94C RH/T
100 transmitter and were maintained at 65-70%, and 19-20 °C, respectively for all experiments. A fast stepping/scanning
101 thermodenuder (TD, Aerodyne Inc. Billerica, USA) was also placed downstream of the flow tube to measure SOA
102 evaporation rates. Details about TD operating conditions and analysis can be found in Takhar et al. (2019). The TD

103 was only operated during one experiment in which the OH exposure was 9.23×10^{10} molecules cm^{-3} s. The SOA was
104 systematically heated in a TD from 25 °C to 175 °C, and changes in particle volume concentrations and corresponding
105 mass fraction remaining (MFR) were measured using a SMPS. The SOA size distribution during TD operation and
106 volatility distribution are shown in Fig. S1 and S2, respectively. A kinetic mass transfer model developed by Riipinen
107 et al. (2010) was used to interpret the TD data. The inputs to the model are volatility distribution of OA, enthalpy of
108 vaporization, mass accommodation coefficients. Compound groups are translated into volatility distributions by
109 binning components according to their saturation concentrations (Donahue et al., 2006). Parameterization for enthalpy
110 of vaporization was similar to that of Takhar et al. (2019). We assume a surface tension of 0.05 N m^{-1} , gas-phase
111 diffusion coefficients of $5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ for all simulations similar to that reported in Riipinen et al. (2010).

112

113 2.2 Chemical characterization of SOA

114 Tenax tube and quartz filter samples were analyzed separately by thermal desorption gas chromatography mass
115 spectrometry (TD-GC/MS) for detailed chemical speciation of gas- and particle-phase organic compounds. The
116 analyses were performed using a thermal desorption system (TDS 3, Gerstel) combined with a gas chromatography
117 (7890B, Agilent)-mass spectrometer (5977A, Agilent). For gas-phase analysis, concentrations of aldehydes (C7 to
118 C10 *n*-alkanals, alkenals and alkadienals) collected on Tenax tube samples before photooxidation (downstream of the
119 flow tube, with lights off) were quantified. For particle-phase analysis, thermal desorption of quartz filters was
120 performed with *in situ* derivatization using *N*-trimethylsilyl-*N*-methyl trifluoroacetamide (MSTFA). A known amount
121 of deuterated 3-hydroxy-1,5-pentanedioic-2,2,3,4,4- d_5 acid, and *n*-pentadecane- d_{32} (CDN isotopes) was injected,
122 respectively, onto quartz filter punches, and Tenax tubes as internal standards before the samples were desorbed in
123 the TDS. All GC/MS analysis was performed using a non-polar DB5 column (Rxi-5Sil MS, Restek). Details of the
124 operating parameters (GC column, GC and TDS temperature ramps, MS parameters) can be found in Sect. 4.2 of SI.

125 With *in situ* derivatization, polar organic compounds react rapidly with MSTFA at elevated temperatures during
126 thermal desorption, and functional groups with acidic hydrogen atoms (such as –OH) are replaced by a less polar
127 trimethylsilyl (TMS, [–OSi(CH₃)₃]) group. This reduction in polarity allows the derivatized analyte to elute from a
128 non-polar column and analyzed by subsequent electron impact (EI) at 70 eV. Derivatized compounds produce a
129 signature fragment ion at mass-to-charge (m/z) 73 (–Si(CH₃)₃⁺) arising from the scission of O–Si bond in R–
130 [Si(CH₃)₃]. In other words, all derivatized compounds produce ions with m/z 73 during analysis. Therefore, the total
131 signal at m/z 73 can be taken as the total concentration of organic compounds with at least one hydroxyl group
132 (including both –OH and –C(O)OH) present in cooking SOA, much like how m/z 57 represents total concentration of
133 aliphatic compounds in hydrocarbon mixtures (Zhao et al., 2014, 2015). It should be noted that organic peroxides (R–
134 OOH) were also found to be derivatized, but the major reaction product formed is R–O–[Si(CH₃)₃] (which is also
135 formed from R–OH derivatization) as shown in Fig. S3. Here we assume alcohols and acids are the major components,
136 but will explore the potential role of ROOH on the overall chemical composition in Sect. 3.1.

137 As shown in Fig. 2, many compounds in cooking SOA contain at least one –OH group and the chromatogram of m/z
 138 73 is typical of that for a highly complex mixture or unresolved complex mixture (UCM). Using traditional analytical
 139 techniques like GC/MS it is difficult to deconvolute the UCM. However, knowledge about mass spectral
 140 fragmentation of TMS derivatives can be used to understand the compounds contributing to the UCM. Table S2 shows
 141 a list of compounds containing multiple functional groups e.g. –COOH, –OH resulting in different combinations of
 142 compound classes like dicarboxylic acids, hydroxy acids, hydroxy dicarboxylic acids, and dihydroxy dicarboxylic
 143 acids with different carbon numbers. As mentioned earlier, we acknowledge the potential contribution from ROOH,
 144 but will first assume the functional groups shown in Table S2 here, and consider ROOH in more detail in a later
 145 section. The compound groups shown in Table S2 are expected to be formed from oxidation of aldehydes and be
 146 derivatized by MSTFA. The TMS derivatives of these compounds share common ion fragments in their EI mass
 147 spectra: m/z 73 $[\text{Si}(\text{CH}_3)_3]^+$, 75, 147 $[(\text{CH}_3)_2\text{Si}=\text{O}(\text{CH}_3)_3]^+$, M-15 $[\text{M}-\text{CH}_3]^+$ (Jaoui et al., 2004, 2005; Yu et al., 1998).
 148 Most importantly, all TMS derivatives exhibit quantifiable peaks at m/z 73 (ubiquitous ion for all derivatives) and M-
 149 15 (ion specific to each compound group, hereby referred to as the pseudo-parent ion). We also obtained the
 150 characteristic ratio of these two ions for each compound group ($f_{M-15/73}$) from NIST mass spectral libraries and from
 151 analyzing authentic standards. To verify the validity of this method, we calculate the total m/z 73 ion signal that is
 152 attributable to these compound groups by taking the chromatograms of the pseudo-parent ion for each compound
 153 group, dividing by its characteristic ratio $f_{M-15/73}$ and then summing across all compound groups as shown in Eq.
 154 (1).

$$155 \quad S_{73,t}^{sum} = \sum_i \frac{S_{M-15,i,t}}{f_{M-15/73,i}} \quad (1)$$

156 where $S_{73,t}^{sum}$ is the m/z 73 ion signal at retention time t that is attributable to all compound groups listed in Table S2,
 157 $S_{M-15,i,t}$ is the signal of the pseudo-parent ion for compound group i at retention time t , $f_{M-15/73,i}$ is the characteristic
 158 ratio of pseudo-parent ion to m/z 73. This approach is similar to that described in Isaacman-VanWertz et al. (2020).
 159 As shown in Fig. 2, $S_{73,t}^{sum}$ shows excellent agreement with the measured m/z 73 ion signal, suggesting that the m/z 73
 160 signal, which is representative of all TMS derivatives, is almost entirely comprised of contributions from the
 161 compound groups listed in Table S2. This agreement between our bottom-up approach and measured signal provides
 162 confidence that our method is able to provide information about the chemical composition of highly complex mixture.

163 With the signals from all the pseudo parent ions for all compound groups, the total mass of each compound group was
 164 then calculated using Eq. (2).

$$165 \quad M_i = \frac{TA_i}{RF_i} \times \frac{1}{f_{M-15/73,i}} \quad (2)$$

166 where, M_i is the mass of compound group i , TA_i is the total integrated signal of pseudo-parent ion for compound
 167 group i (normalized by the signal of deuterated internal standard), RF is the response factor (calculated from
 168 calibration curves of fatty acids and dicarboxylic acids authentic standards) of compound group i , and $f_{M-15/73,i}$ is
 169 the characteristic ratio of pseudo-parent ion to m/z 73 for compound group i . A more detailed, step-by-step description

170 of the procedure can be found in the SI in Sect. 23, and illustrated in Fig. S4 with corresponding uncertainties in the
171 fitting procedure shown in Fig. S5.

172

173 3 Results and discussion

174 3.1 Chemical evolution of SOA

175 As described in Sect. 2.2, components in cooking SOA were classified by functional groups and carbon number. To
176 describe the overall changes in SOA composition with increasing OH exposure, we use the average carbon oxidation
177 state ($\overline{\text{OSc}}$) as a metric for the evolving composition of a complex mixture undergoing oxidation (Kroll et al., 2011).
178 Both $\overline{\text{OSc}}$ and number of carbon atoms (nc) for each compound group are calculated from the GC-derived chemical
179 composition. The total mole fraction of C, H and O was calculated for each sample which was then used to calculate
180 the bulk $\overline{\text{OSc}}$ using the Eq. $2 \times O:C - H:C$ (Kroll et al., 2011). The evolution in this framework for canola oil SOA
181 is shown in Fig. 3. The bulk $\overline{\text{OSc}}$ was observed to increase from -0.6 to -0.24 when OH exposure increased from 5.77
182 to 22.0×10^{10} molecules cm^{-3} s for canola oil SOA. For comparison, Liu et al. (2017b) showed an initial decrease in
183 $\overline{\text{OSc}}$ and O:C, but gradually stabilized at OH exposure greater than 9×10^{10} molecules cm^{-3} s. For the $\overline{\text{OSc}}$ range reported
184 here, the $\overline{\text{OSc}}$ of cooking SOA falls in the range of SV-OOA as determined from factor analysis of AMS data
185 (Canagaratna et al., 2015). This degree of oxygenation is greater than that of the COA factor measured by AMS, which
186 is reported to be around -1.37 (Canagaratna et al., 2015). This difference suggests that the COA factor resolved using
187 PMF analysis is likely of primary origin and does not represent SOA formed from atmospheric oxidation of cooking
188 emissions. Furthermore, previous GC/MS analysis showed for POA from cooking oils, an $\overline{\text{OSc}}$ of -1.66 (canola oil)
189 and -1.7 (beef tallow, olive oil) was calculated (Takhar et al., 2019). These observations again suggest that COA factor
190 measured by AMS is derived of primary cooking emissions.

191 In addition to carbon oxidation state, knowledge about molecular composition provides further insights into the
192 oxidation mechanisms. Canola oil SOA at an OH exposure of 5.77×10^{10} molecules cm^{-3} s is comprised of ~~long-chain~~
193 ~~hydroxy acids ~19% larger (C8-C10) and less oxygenated compounds, this fraction declined to ~11% at higher OH~~
194 ~~exposures. Furthermore, the total fraction of C2-C7 products increased from 81% to 89% when OH exposure increased~~
195 ~~from 10.7 h to 1.7 d. Of this fraction, the smaller carbon # compounds (C2-C4) which are indicative of fragmentation~~
196 ~~processes increased from 42% at 10.7 h to ~49% at 1.7 d. An increase in smaller and more oxygenated compounds,~~
197 ~~along with decrease in larger and less oxygenated products suggests that fragmentation reactions are responsible for~~
198 ~~the shift towards formation of smaller oxygenated compounds.~~ As a result, oxidation simultaneously leads to higher
199 $\overline{\text{OSc}}$ and lower carbon number on average. Based on the compounds observable by our technique, this trend suggests
200 that fragmentation reactions are key processes in the oxidative evolution of cooking emissions. ~~These findings suggest~~
201 ~~an early onset of fragmentation reactions upon atmospheric aging of cooking emissions contrary to other SOA systems,~~
202 ~~such as alkanes and isoprene (Lambe et al., 2012, 2015), in which fragmentation reactions dominate at later OH~~

203 exposures ($>5 \times 10^{11}$ molecules cm^{-3} s). Therefore, predicting OA concentrations from cooking emissions would require
204 earlier fragmentation of SOA in climate and air quality models.

205 The compounds observed here can also be compared to previously measured bulk composition using elemental ratios,
206 such as those presented in a Van Krevelen (VK) diagram (Heald et al., 2010). As shown in Fig. 4, the O:C ratio in our
207 study ranged between 0.64 and 0.79 when OH exposure increased from 5.77×10^{10} to 22.0×10^{10} molecules cm^{-3} s. The
208 O:C ratios measured using an AMS (Kaltsonoudis et al., 2017a; Liu et al., 2017b) ranged between 0.24-0.46 which
209 are within a factor of 2 measured in this study. These ratios are within a factor of 2 than previously reported AMS
210 measurements of cooking oil SOA (Kaltsonoudis et al., 2017a; Liu et al., 2017b). Furthermore, the H:C versus O:C
211 trend is linear with a slope of -0.19, which lies between the slope of 0 measured for low- NO_x oxidation reported by
212 Liu et al. (2017b) and -0.4 for high- NO_x conditions (Liu et al., 2018). Therefore, based on elemental ratios, the
213 evolution in SOA composition measured in this study is comparable to that in bulk average properties estimated by
214 AMS. Furthermore, we use 2D-VBS framework developed by Donahue et al. (2012) to investigate OA chemistry, and
215 understand the evolution of cooking SOA through changes in the volatility of SOA system. The vapor pressures of
216 the identified compounds are calculated using group contribution method (Pankow and Asher, 2008) where
217 experimentally determined vapor pressures were unavailable, and reported in Table S2. The observed compounds in
218 SOA have a broad range of volatilities, since they were formed from oxidation of a complex ensemble of VOC
219 precursors. As shown in Fig. S6, there is minor decrease in overall volatility of the mixture (change lies within one
220 decade in C^*) irrespective of the presence of peroxides, while $\overline{\text{O}:\text{C}}$ is increasing with oxidation. This increase in
221 oxidation state is coincident with increasing fragmentation upon oxidation, and, as a result, the overall change in the
222 bulk volatility of canola oil SOA is relatively small.

223 As mentioned earlier in Sect. 2.2, there is a potential to misclassify ROOH as ROH using our current GC/MS method.
224 Here we further examine the chemical composition by assuming that each $-\text{O}[\text{Si}(\text{CH}_3)_3]$ group observed originates
225 from an $-\text{OOH}$ group in the SOA, and to support this argument we show that derivatization of cumene hydroperoxide
226 (Sigma Aldrich Co.) is observed as TMS of hydroxy-cumene in our system as shown in Fig. S3. It should be noted
227 that replacing $-\text{OH}$ with $-\text{OOH}$ results in a higher estimate of O:C (and $\overline{\text{O}:\text{C}}$) but does not change H:C or carbon #.
228 Furthermore, since pseudo molecular ion fraction ($f_{M-15/73}$) for organic peroxides (needed for quantification) is
229 unknown, we assume that it is similar to those presented in Table S2. As shown in Fig. S7, if all observed $-\text{OH}$ groups
230 are $-\text{OOH}$ groups, the VK-slope is -0.15 which is similar to -0.19 calculated based on the no-peroxide assumption.
231 Similarly, Fig. S6 shows that this uncertainty in hydroxyl group identification has negligible effect on estimation of
232 vapor pressure or volatility in the 2D-VBS framework. Therefore, this potential misclassification of peroxide groups
233 may lead to an underestimation in O:C and $\overline{\text{O}:\text{C}}$, but is not expected to affect estimates of volatility and our general
234 conclusions about the importance of fragmentation reactions. In the future, analytical techniques such as extractive
235 electrospray ionization time-of-flight mass spectrometry (Lopez-Hilfiker et al., 2019) may be useful to better
236 understand the composition of peroxides from cooking SOA. While the misclassification of peroxides may have little
237 impact on the bulk properties such as average O:C ratios, there may be important implications on understanding the
238 reactivity of the SOA.

239

240 3.2 Evaporation rates of SOA

241 The volatility of the SOA is also probed by measuring the evaporation rates in a heated thermobalance and compared
242 to the rates expected from the measured composition. In order to derive the evaporation rates from the measured
243 chemical composition of cooking SOA, we use the kinetic mass transfer model developed by Riipinen et al. (2010).
244 Among the inputs into the model, the mass accommodation coefficient is a critical but uncertain parameter that
245 accounts for the mass transfer limitations in the system.

246 Figure 5 shows both measured and modeled mass thermograms for canola oil SOA. We observe that for canola oil
247 SOA, mass accommodation coefficient of 0.03 is needed to predict the experimentally determined mass thermograms.
248 An accommodation coefficient of <1 suggests that mass transfer limitations in the system likely occurring in the
249 condensed-phase. Formation of multifunctional organic compounds such as those observed in this study is likely
250 responsible for an increase in viscosity through increasing hydrogen bonding and other polar interactions (Rothfuss
251 and Petters, 2016). It should be noted that Takhar et al. (2019) reported similar magnitudes of mass accommodation
252 coefficients for heterogeneous oxidation of cooking oil particles. Due to similarity in the type of functional groups
253 present in both aging pathways, we believe the decrease in mass accommodation coefficients for both systems undergo
254 similar changes in phase and/or viscosity.

255 These measurements of evaporation rates are consistent with the volatilities expected from our measured composition
256 of SOA containing small oxygenated compounds. Although mass accommodation coefficients are highly uncertain,
257 the mass accommodation coefficients for other SOA systems have been measured to be even lower on the order of 10^{-4}
258 (Cappa and Wilson, 2011), which would require the volatilities to be even higher to explain the measured evaporation
259 rates. Therefore, the TD measurements support the conclusion that smaller oxygenated compounds are produced from
260 oxidation of cooking oil vapors, and that fragmentation reactions are dominant. Furthermore, these measurements
261 provide useful inputs into chemical transport models for predicting SOA formation and gas-particle partitioning. Our
262 previous work (Takhar et al., 2019) showed that even at $\alpha = 10^{-2}$, gas-particle partitioning timescales are short (within
263 hours) and the assumption of equilibrium partitioning still holds for regional scale SOA formation. Further work is
264 needed to directly measure the viscosity of cooking SOA, and corresponding mixing timescales to better constrain the
265 physicochemical properties of cooking SOA.

266

267 3.3 Contribution of aldehydes to observed oxidation products and total SOA

268 Since cooking oil vapors are comprised of a number of reactive aldehydes that can lead to SOA formation, we conduct
269 further experiments of SOA formation from these precursors and identify the relative contributions to observed
270 oxidation products and to total SOA. These results are applied to the heated cooking oil experiments to understand the
271 role of aldehydes in the overall production and evolution of cooking oil SOA.

272 3.3.1 Formation of particle-phase oxidation products

273 As described in the earlier sections, we are able to quantify the mass concentrations of different compound groups (6
274 different combinations of functional groups, from C2 to C9¹⁰, summarized in Table S2) in the particle phase for all
275 experiments. We denote the observed mass concentrations of compound group i in SOA from canola oil
276 photooxidation as M_i^{oil} . The expected precursors to these oxidation products are likely aldehydes, since aldehydes are
277 emitted in significant amounts and are highly reactive. To examine this hypothesis, here we calculate the formation
278 of these observed compound groups from oxidation of aldehydes. For this calculation, heptanal, *trans*-2-heptenal,
279 *trans*-2-octenal, ~~and *trans,trans*-2,4-heptadienal, and *trans,trans*-2,4-decadienal~~ (Sigma Aldrich Co.) were considered
280 because these aldehydes are the dominant VOC precursors emitted from heated canola oil in our experiments as shown
281 in Fig. S8. ~~Unlike previous work by Fullana et al. (2004b) and Klein et al. (2016a), gas phase concentrations of~~
282 ~~decadienals were minimal in our experiments.~~ More volatile aldehydes, such as acrolein and methacrolein, were likely
283 present but could not be captured and analyzed by our techniques. The molar amount reacted for each aldehyde j in
284 the canola oil oxidation experiments is denoted as ΔVOC_j^{oil} , and was calculated based on the measured OH exposure.

285 In order to estimate the contribution from oxidation of an aldehyde j in the gas-phase mix to the formation of each
286 compound group i , we conducted a series of experiments in which a representative aldehyde was oxidized, and the
287 molar yields of the various compounds were measured:

$$288 \gamma_{ij} = \frac{M_{ij}^{ind}/MW_i}{\Delta VOC_j^{ind}} \quad (3)$$

289 where γ_{ij} represents the molar yield of compound group i from precursor j , M_{ij}^{ind} denotes the mass concentration of
290 compound i observed in photooxidation experiments in which aldehyde j was the sole precursor, MW_i is the molecular
291 weight of compound i , and ΔVOC_j^{ind} is the amount of precursor j reacted in each experiment. γ_{ij} is then applied to the
292 heated cooking oil experiments to estimate the amount of oxidation products that would form from each precursor:

$$293 M_i^{sum} = \sum_j \gamma_{ij} \Delta VOC_j^{oil} MW_i \quad (4)$$

294 A sample calculation for this analysis is presented in Sect. 3-4 of SI. The comparison between M_i^{sum} (contribution of
295 aldehyde oxidation to formation of compound i) and M_i^{oil} (observed concentrations of compound i) is shown in Fig.
296 6. Based on this methodology, oxidation of aldehydes accounts for ~~563~~ $\mu\text{g m}^{-3}$ (M_i^{sum}) of the observed $75 \mu\text{g m}^{-3}$
297 (M_i^{oil}) (or ~~8475~~%) particle-phase oxidation products measured at an OH exposure of 6.43×10^{10} molecules cm^{-3} s. The
298 contributions of alkanals (heptanal), alkenals (heptenal + octenal) and alkadienals (heptadienal + decadienal) are 7%,
299 ~31% and ~~4637~~%, respectively.

300 While the amount of oxidation products expected from aldehydes is somewhat lower than that observed in canola oil
301 SOA, this difference may arise from differences in gas-particle partitioning between single aldehyde photooxidation
302 and canola oil photooxidation. As shown in Fig. 6, the formation of higher carbon # products cannot be explained
303 from the photooxidation of aldehydes used to predict oil oxidation products likely due to the assumption of negligible

304 particle-phase or oligomerization reactions occurring in the condensed phase. In addition, higher carbon # acids are
305 likely present as primary vapors in the gas phase which can then partition to the condensed phase upon SOA formation.

306 As shown in Fig. S9, more oxygenated compounds (higher O:C and greater number of functional groups) tend to be
307 more abundant in the canola oil SOA than expected from aldehyde photooxidation, suggesting that canola oil SOA is
308 more favorable for oxygenated compounds to partition than SOA from individual aldehydes. On the other hand, there
309 is no clear trend in partitioning with respect to vapor pressures and carbon number. It should be noted that uncertainties
310 in the fitting procedure or estimation in the pseudo molecular ion (refer to Table S2 and Fig. S5) can also result in
311 uncertainties between -40% and +20%. Therefore, in summary, the quantified oxidation products from canola oil SOA
312 are generally consistent with those from aldehyde photooxidation, and the relative amounts may be subject to further
313 changes due to gas-particle partitioning.

314

315 3.3.2 Using the statistical oxidation model (SOM) framework

316 To further explore the evolution of canola oil SOA, we applied our results to the statistical oxidation model (SOM)
317 framework developed by Cappa and Wilson (Cappa et al., 2013; Cappa and Wilson, 2012). SOM describes the
318 oxidation chemistry of a VOC precursor through multi-generational space defined by the number of carbon and
319 oxygen atoms present in the precursor and its possible SOA product molecules. The SOM does not specifically track
320 the product composition in terms of functional groups, but provides adequate details to represent key atmospheric
321 processes such as gas-particle partitioning, fragmentation, functionalization, reactions with oxidants, condensed-phase
322 chemistry. The model has been applied to chamber experiments to derive parameterizations by fitting experimental
323 data to both SOA mass concentration and the bulk aerosol O/C ratio. Eluri et al. (2018) used the chamber derived
324 parameterizations to predict the properties of SOA generated from diesel exhaust in an oxidation flow tube reactor.

325 To the best of the authors' knowledge, there are no parameterizations for the oxidation of aldehydes. Therefore, in
326 this study we first derived the parameterizations for aldehyde oxidation, and then use these parameters to predict the
327 SOA mass concentrations. In order to obtain the parameters, we fit the measured SOA concentration from oxidation
328 of heptanal, *trans*-2-heptenal, *trans,trans*-2,4-heptadienal at different OH exposures to optimize the six tunable
329 parameters under low-NO_x conditions (shown in Fig. S10). Best fit SOM parameters indicate that photooxidation
330 leads to fragmentation per reaction with OH, as shown by a lower *mfrag* than compared to other systems e.g. alkanes
331 (≥ 2 for branched, cyclic or *n*-alkane under low-NO_x conditions (Eluri et al., 2018)). Since a lower value for *mfrag*
332 represents greater fragmentation (Cappa and Wilson, 2012), this again reflects the higher propensity for fragmentation
333 in this SOA system. The optimized parameters were then used to predict the SOA concentration for canola oil
334 photooxidation under different aging conditions in the OH exposure range similar to that of aldehyde photooxidation.

335 Based on these established parameterizations for different aldehydes, model simulations were conducted for canola
336 oil having a mixture of aldehydes under different photochemical aging conditions. It should be noted that we used
337 parameterizations of heptanal for all alkanals, heptenal for all alkenals, and heptadienal for alkadienals. As shown in

338 Fig. 7, the model generally captures the amount of SOA formed to ~~up to within 5062%~~, but overpredicts SOA
339 formation at lower photochemical ages and underpredicts SOA concentrations at higher photochemical ages. In
340 addition, SOM also tracks atomic O/C ratio which were further compared with the measured O/C ratio. SOM predicts
341 an O:C around 0.517, which ~~lies is~~ within ~~±5020%~~ of the measured O:C likely suggesting that the changes in chemical
342 composition of cooking SOA is in ~~good~~ reasonable agreement with the model predictions. Furthermore, the
343 unexplained SOA can likely arise from other unidentified S/IVOCs as hypothesized by Liu et al. (2017c). However,
344 unlike traffic emissions (Zhao et al., 2014), S/IVOCs from cooking has not been positively identified. In addition,
345 small VOC precursors like acrolein and malondialdehyde which have been measured in large quantities from cooking
346 emissions (Klein et al., 2016a), may form SOA products having higher O/C ratios, which may better explain the O/C
347 ratios observed in our experiments.

348 One inconsistency between the model and measurements is the slope at which SOA is being formed. The experimental
349 data suggest a steeper trend of SOA formation while the model predicts a more gradual increase in SOA formation. A
350 potential explanation for this discrepancy is the contribution from other unmeasured VOCs. These VOCs are less
351 reactive than those considered in the model, such that they contribute to higher SOA at higher OH exposures.
352 Alternatively, these missing VOCs are more volatile such that more of their SOA is formed at later generations of
353 oxidation. For example, acrolein forms SOA with measurable yields (Chan et al., 2010) and is emitted at large amounts
354 from heated cooking oils (Klein et al., 2016a). Despite these limitations, these parameterizations generally capture the
355 amount of SOA formed and its degree of oxidation (O/C) on oxidation timescales relevant to urban areas (within 2
356 days) and are useful for representing cooking oil emissions in the chemical transport models. Overall, the amount of
357 SOA formed and the evolution upon oxidation can be well described by photooxidation of aldehydes.

358

359 4 Conclusions and implications

360 In this work, we characterized the detailed chemical composition of SOA generated from cooking oil vapors. We
361 showed that cooking SOA occurring as highly complex mixture can be deconvoluted using mass spectral
362 fragmentation pattern to extract useful information about the chemical identities of organic compounds, such as
363 functional groups and carbon number. Using this detailed chemical composition of cooking SOA, we showed that
364 fragmentation is an important pathway for oxidative processing of cooking emissions in the atmosphere even within
365 short timescales of oxidation. Furthermore, we showed that aldehydes can reasonably explain the formation of SOA
366 generated from cooking oil vapors and the oxidative evolution as described using a multi-generational oxidation
367 model. Our study, therefore, highlights the importance of molecular composition in constraining the chemical
368 properties of cooking SOA, as well as understanding the contribution of aldehydes in formation of SOA from cooking
369 emissions.

370 Consistent with other studies, our work has shown that aldehydes are an important class of VOC precursors emitted
371 from cooking emissions, and substantial efforts have been made to measure their emission factors depending on
372 different cooking settings (heating temperature, cooking style, food, ingredients) (Klein et al., 2016a, 2016b).

373 However, the contribution of aldehydes from cooking emissions is underrepresented in chemical transport models.
374 Recently, McDonald et al. (2018) showed that the ambient concentrations of OA were underpredicted when aldehydes
375 were not included in the box model calculations, suggesting that aldehydes, likely from food cooking, play an
376 important role in atmospheric oxidation chemistry. Furthermore, Klein et al. (2019) showed that heavy pollutants like
377 restaurants play a significant role in contributing to the ambient cooking organic aerosol concentrations. In this study,
378 we showed a large fraction of the SOA is derived from aldehyde precursors, with strong similarities in chemical
379 composition. Therefore, it is important to consider the contribution of aldehyde chemistry in atmospheric models
380 towards total OA budget. Furthermore, we demonstrated the importance of fragmentation reactions and their influence
381 on OA properties such as volatility and chemical composition. Future work should therefore focus on measuring not
382 only the SOA formation, but also the oxygenated VOCs formed due to fragmentation upon aging to provide insights
383 into aging of cooking emissions.

384 Formation of SOA from cooking emissions in the atmosphere is likely influenced by emissions of POA, and other
385 gas-phase precursors. Therefore, inclusion of POA during atmospheric processing of cooking emissions will likely
386 influence the physicochemical properties of cooking SOA. For instance, with cooking POA being much less
387 functionalized than SOA, inclusion of POA will likely decrease the system O:C (or $\overline{O\overline{S}c}$). However, POA from
388 cooking emissions can undergo heterogeneous reactions in the atmosphere, thereby increasing O:C (or $\overline{O\overline{S}c}$). On the
389 other hand, there could potentially be contributions from other gas-phase precursors or S/IVOCs emitted from cooking
390 vapors that can result in SOA formation. These precursors can potentially contribute to SOA formation from cooking
391 emissions, but their oxidative evolution in the atmosphere is not well understood.

392 Gas-particle partitioning of SOA can be further affected by non-ideal mixing, as well as morphology of the particles
393 (Shiraiwa et al., 2013; Zuend and Seinfeld, 2012). Future work should investigate the effect of these parameters on
394 cooking SOA properties and formation potential. To account for thermodynamic mixing favourability of the particles,
395 Hansen solubility framework developed by Ye et al. (2016) can be implemented to provide insights into SOA mixing
396 and yield enhancement. As shown in Ye et al. (2018) primary meat-cooking emissions can enhance SOA yield from
397 α -pinene due to similarity in Hansen solubility parameters suggesting that primary meat cooking particles are miscible
398 with α -pinene SOA. It should be noted that present study did not investigate the effect of atmospherically relevant
399 seed particles as well as NO_x levels which are representative of typical urban environments. Since emissions upon
400 entering the atmosphere gets mixed with background air, other source emissions, and diluted upon mixing thereby
401 altering the gas-particle partitioning, and thus the total OA loading. Therefore, it is important to understand the changes
402 in partitioning and miscibility of cooking emissions as the composition continually evolves with atmospheric
403 processing. Additionally, as mentioned earlier cooking SOA undergoes large mass transfer limitations due to changes
404 in the phase state of the SOA particles, making it more so important to experimentally determine the corresponding
405 viscosity of cooking SOA. Therefore, future work should focus on measuring both the viscosity and miscibility of
406 SOA derived from cooking emissions.

407

408 *Data availability.* The data are available upon request to the corresponding author.

409

410 *Author Contributions.* MT and AWHC designed research. MT collected and analyzed data. MT, YL and AWHC
411 *interpreted results. MT and AWHC wrote the manuscript with inputs from YL.*

412

413 *Competing interests.* The authors declare that they have no conflict of interests.

414

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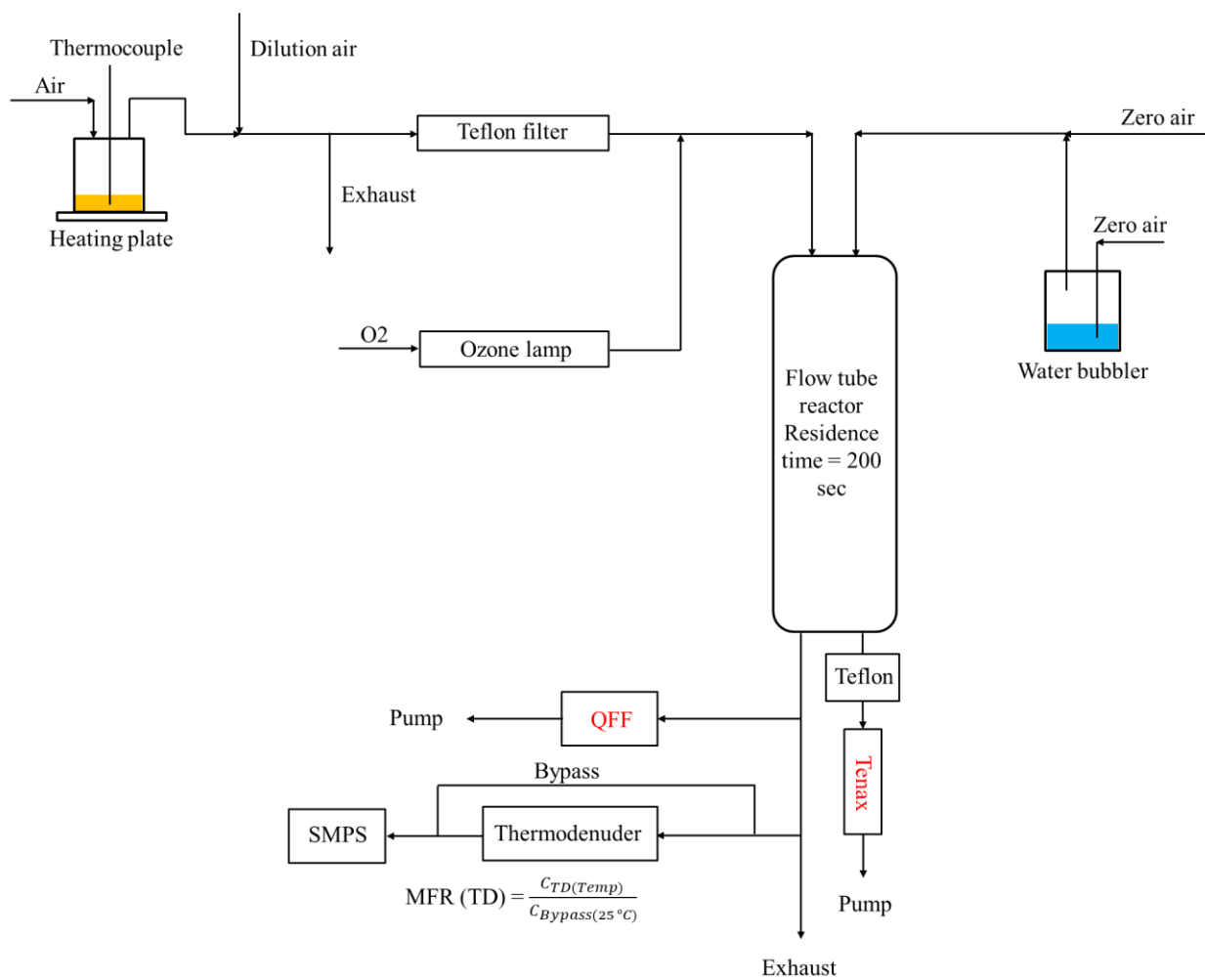
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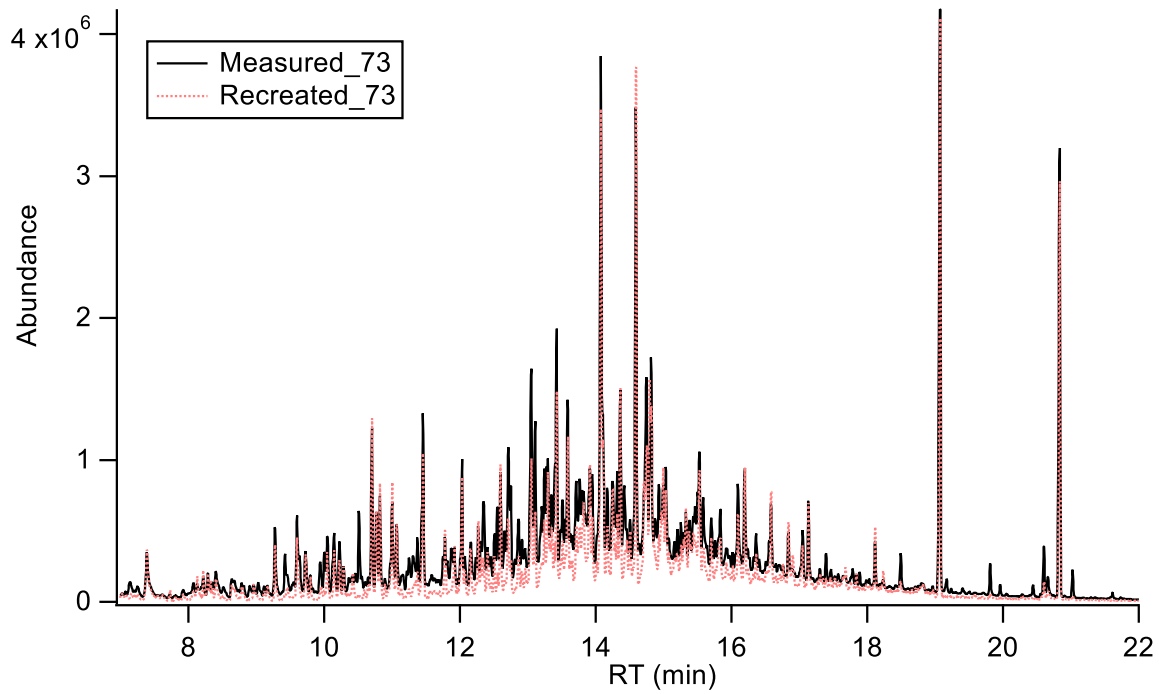
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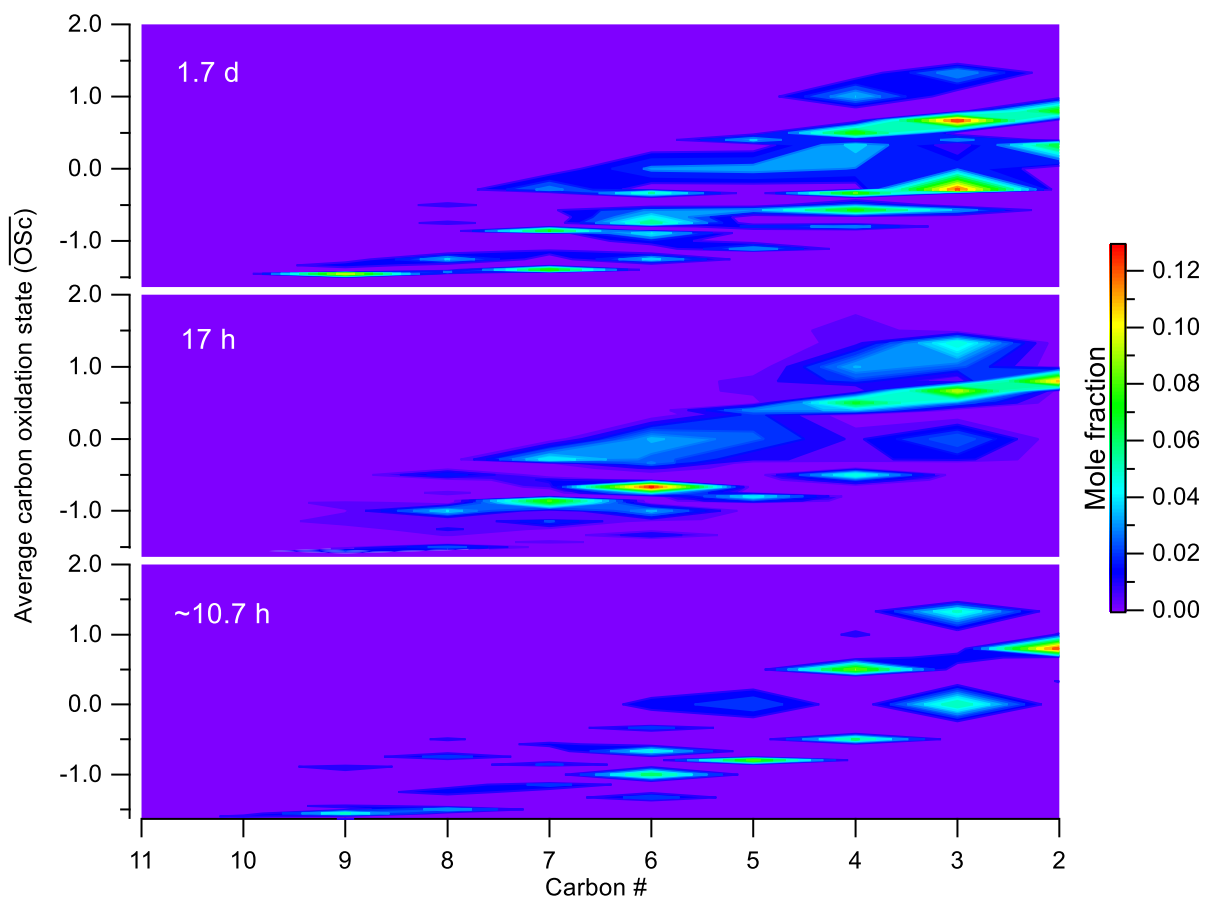
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609 **Figure 1.** Experimental setup for oxidation of heated cooking oil emissions.



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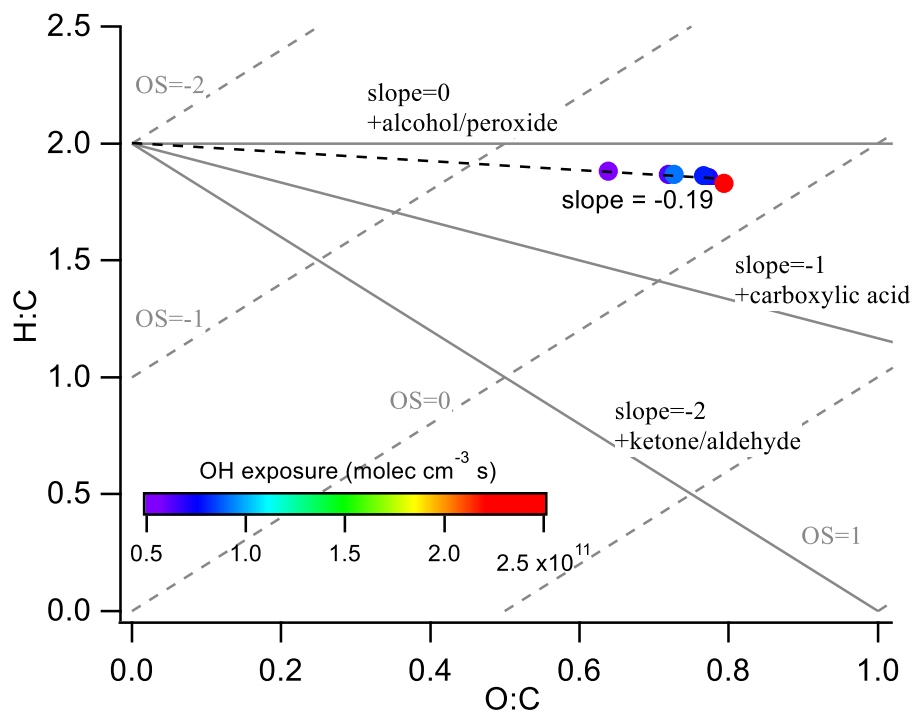
611 **Figure 2.** Highly complex mixture of canola oil SOA generated upon photooxidation. With known signal and mass fragmentation,
612 signal of m/z 73 can be recreated based on pseudo parent ions (e.g. M-15 used in this study).



613

614 **Figure 3.** Evolution in $\overline{\text{OSc}}\text{-nc}$ space for canola oil SOA under different conditions of photochemical aging. As the oxidation
 615 progresses in the atmosphere, more compounds are formed with smaller nc and higher $\overline{\text{OSc}}$ suggesting fragmentation to be a
 616 dominant pathway of oxidation for cooking emissions in the atmosphere.

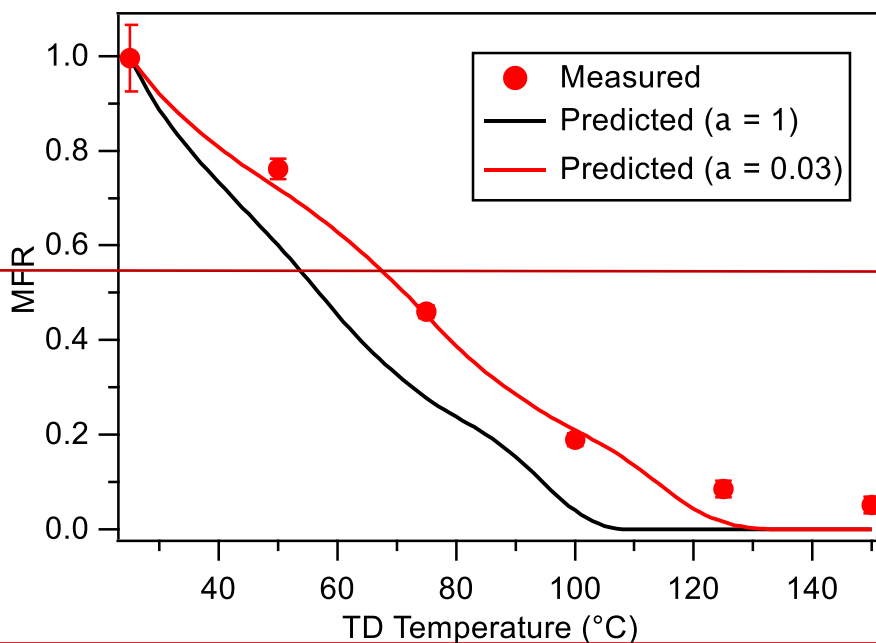
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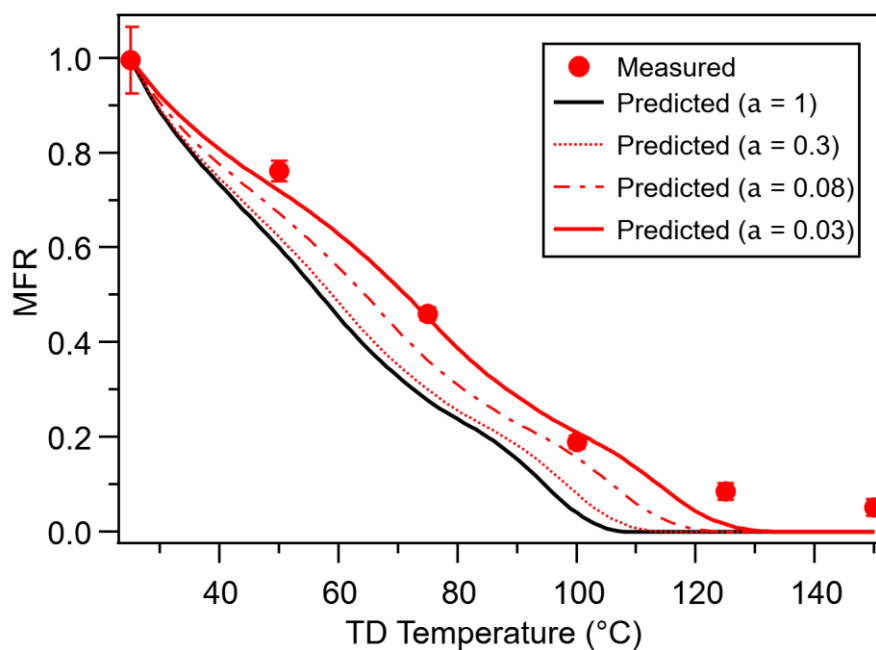
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619 **Figure 4.** Van Krevelen diagram of canola oil SOA coloured by different OH exposure. In the background, average carbon
 620 oxidation state (\overline{OS}_C) and functionalization slopes are shown for reference. The slope of -0.19 for canola oil SOA corresponds to
 621 formation of both alcohol and carboxylic acid consistent with the chemical composition obtained from TD-GC/MS.

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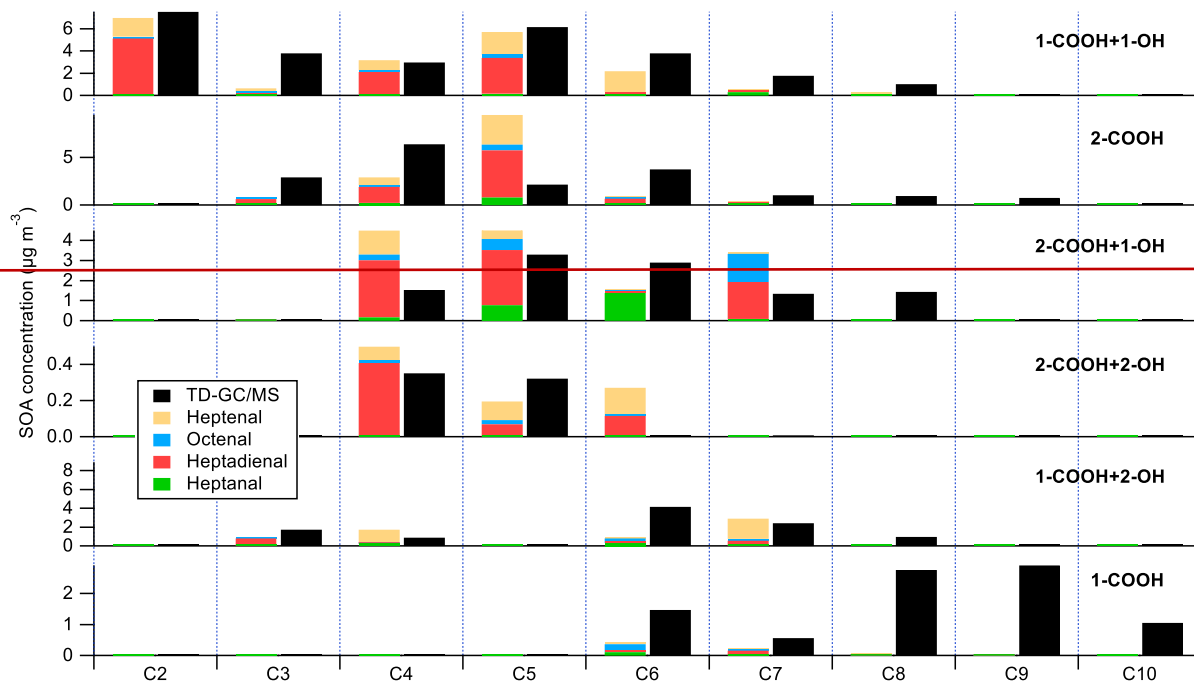
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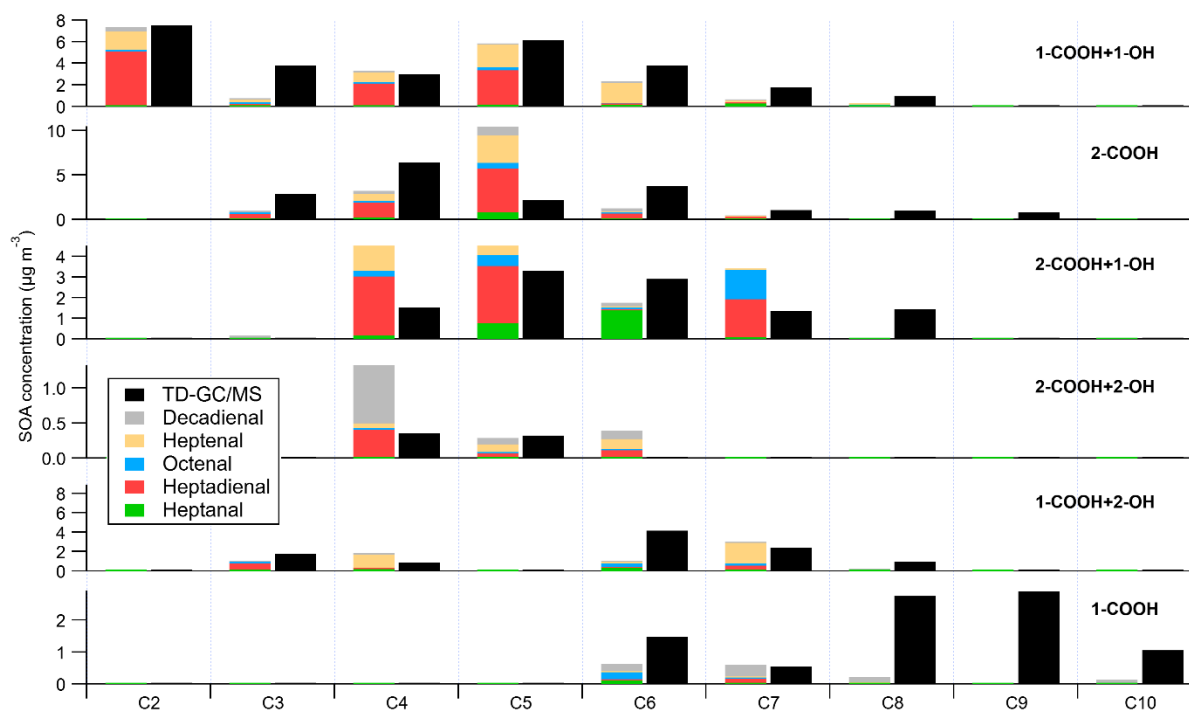
624

625 **Figure 5.** Mass thermogram of canola oil SOA at an OH exposure of 9.23×10^{10} molecules cm^{-3} s. The black line represents model
626 simulations using $\alpha = 1$ underpredicting the measured MFR. The red line corresponds to model simulations using $\alpha = 0.03$ predicting
627 the measurements reasonably well, therefore implying kinetic limitations in the system. The error bars represent $\pm 1\sigma$.

628



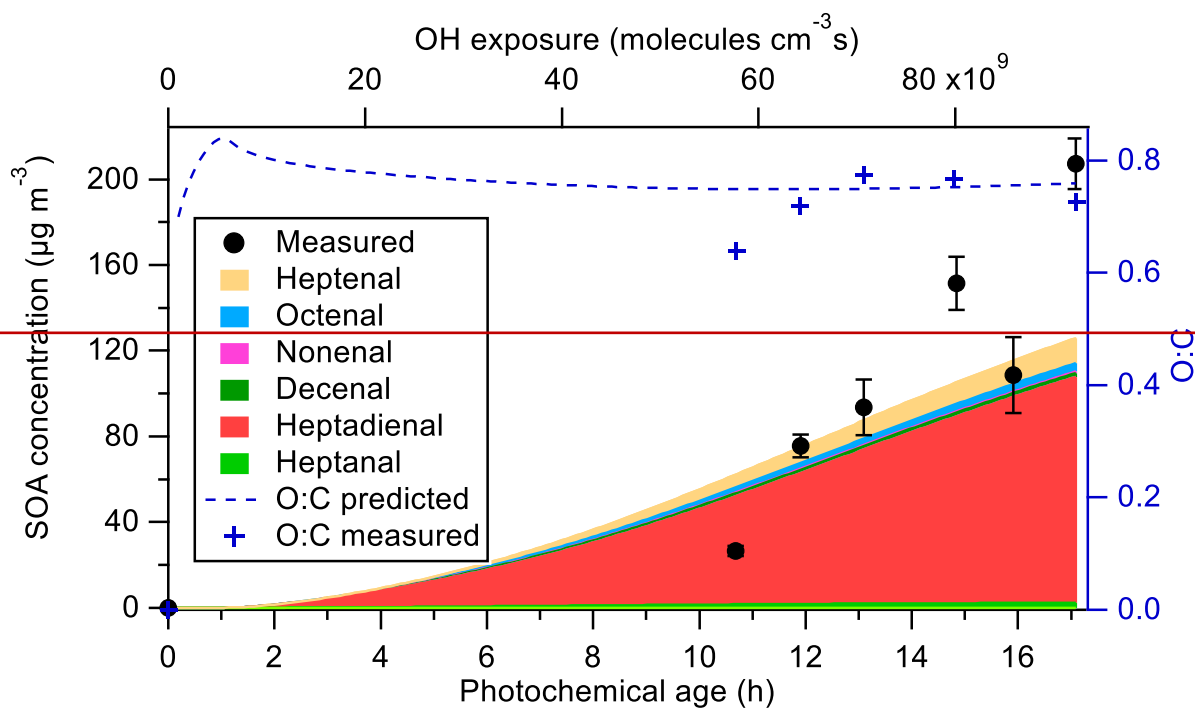
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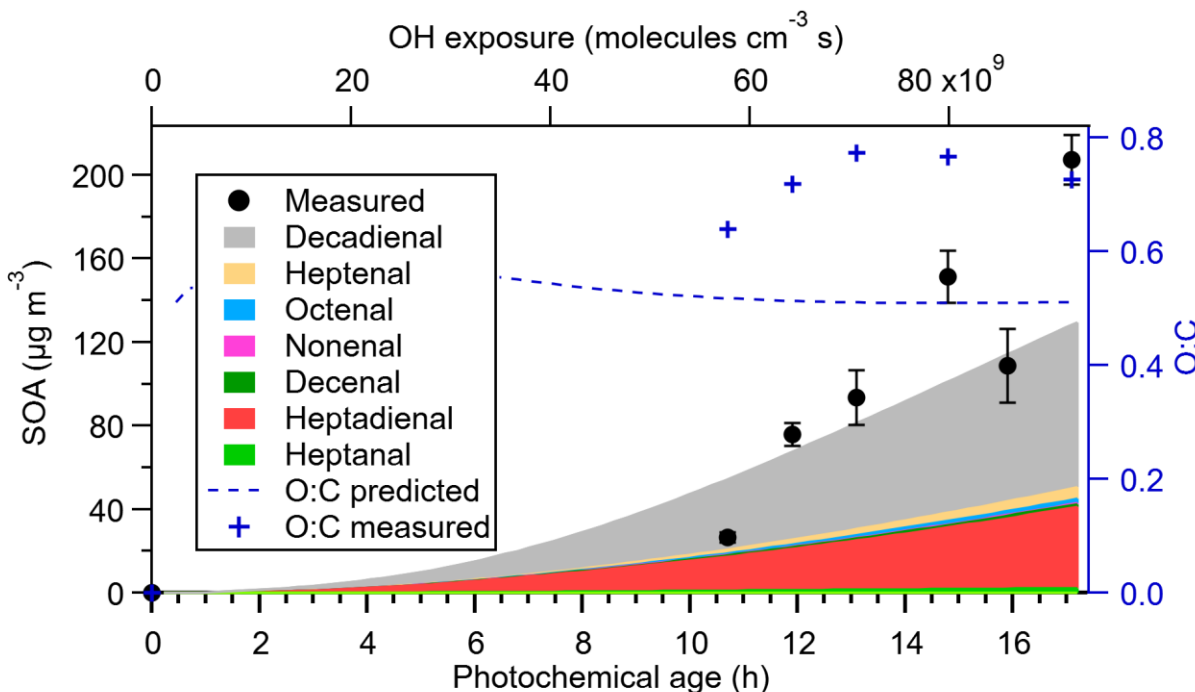
630

631 **Figure 6.** Prediction of different compounds formed at an OH exposure of 6.43×10^{10} molecules cm^{-3} s using product molar yields
 632 of heptanal, heptenal, octenal, ~~and heptadienal~~, ~~and decadienal~~. The total aldehydes products can explain the observed oil SOA
 633 products within a factor of half, while the inconsistency in prediction of some SOA products is likely caused by differences in gas-
 634 particle partitioning in both photooxidation systems.

635



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637

638 **Figure 7.** SOM prediction of SOA produced from different aldehydes with increasing photochemical age. The model overpredicts
 639 SOA formation at lower photochemical age, while underpredicts SOA formation by ~40% at higher photochemical age, suggesting
 640 that traditional VOC precursors cannot fully explain the SOA formation, and other gas-phase precursors maybe needed to better

641 constrain the formation of SOA at higher aging conditions. In addition, the SOM predicted O:C is within $\pm 50\%$ of the measured
642 O:C suggesting that the overall change in chemical composition of cooking SOA is predicted reasonably well.

1 **Characterization of secondary organic aerosol from heated-**
2 **cooking oil emissions: evolution in composition and volatility**

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30 **Table S1:** Description of the experiments conducted in this study.

Exp.	Canola oil SOA ($\mu\text{g m}^{-3}$)	OH exposure (molecules cm^{-3} s)	Photochemical age (h) ^a
1	26.57±2.32	5.77×10^{10}	10.7
2	75.67±5.33	6.43×10^{10}	11.9
3	93.48±13.1	7.07×10^{10}	13.1
4	151.46±12.45	8.01×10^{10}	14.8
5	108.74±17.6	8.60×10^{10}	15.9
6	207.2±11.91	9.23×10^{10}	17.1
7	2670.4±170.85	2.20×10^{11}	40.7

31 a: calculated by assuming an average atmospheric OH concentration of 1.5×10^6 molecules cm^{-3} (Mao et al., 2009).

32

33 **Table S2:** List of all the model compounds used in this study to recreate 73 along with its $f_{M-15/73}$. SIMPOL.1 (Pankow
34 and Asher, 2008) vapor pressure and its corresponding saturation concentrations are also listed for the compounds
35 quantified in this study.

#	Carbon #	Molecular weight (MW)	Derivatized MW (M)	M-15	$f_{M-15/73}$ (NIST)	$f_{M-15/73}$ (MS detector response)	Vapor pressure (atm)	Saturation concentration ($\mu\text{g m}^{-3}$)
2-COOH								
1	3	104	248	233	0.147	0.128±0.03	3.5E-07	29.5
2	4	118	262	247	0.24	0.273±0.06	1.3E-07	3.2 ^a
3	5	132	276	261	0.67	0.254±0.1	4.9E-08	54.8 ^a
4	6	146	290	275	0.198	0.143±0.04	1.9E-08	0.8 ^a
5	7	160	304	289	0.187	0.198±0.07	7.0E-09	4.2 ^a
6	8	174	318	303	0.147	0.182±0.08	2.6E-09	0.09 ^a
7	9	188	332	317	0.268	0.313±0.22	9.9E-10	0.5 ^a
2-COOH + 1-OH								
8	3	120	336	321	0.029	0.062±0.014	2.3E-09	0.19
9	4	134	350	335	0.067	0.051±0.03	8.6E-10	0.02
10	5	148	364	349	0.146	0.141±0.05	3.2E-10	0.36
11	6	162	378	363	0.106 ^{a1}	0.072±0.03	1.2E-10	5.3E-03
12	6	162	378	363	0.178 ^{a2}	0.272±0.11	1.2E-10	5.3E-03
13	7	176	392	377	0.012	0.034±0.02	4.6E-11	2.7E-02

14	8	190	406	391	0.002	n/a	6.5E-12	6.4E-04
15	9	204	420	405	n/a	n/a	2.4E-12	3.2E-03
1-COOH + 2-OH								
16	3	106	322	307	0.04	0.058±0.01	4.9E-08	400.2
17	4	120	336	321	0.116	0.052±0.04	1.8E-08	150.6
18	5	134	350	335	n/a	n/a	6.9E-09	56.7
19	6	148	364	349	n/a	0.125±0.05	2.6E-09	21.3
20	7	162	378	363	n/a	0.019±0.01	9.8E-10	8.02
21	7	162	378	363	n/a	0.026±0.01	9.8E-10	8.02
22	7	162	378	363	n/a	0.068±0.01	9.8E-10	8.02
23	7	162	378	363	n/a	0.056±0.01	9.8E-10	8.02
24	8	176	392	377	n/a	0.023±0.02	3.7E-10	3.01
25	8	176	392	377	n/a	0.026±0.01	3.7E-10	3.01
26	9	190	406	391	n/a	0.033±0.02	1.4E-10	1.1
27	9	190	406	391	n/a	0.021±0.02	1.4E-10	1.1
2-COOH + 2-OH								
28	4	150	438	423	0.07	0.029±0.002	5.7E-12	1.4E-04
29	5	164	452	437	0.059	0.057±0.01	2.1E-12	2.4E-03
30	6	178	466	451	0.05	n/a	8.0E-13	3.5E-05
1-COOH + 1-OH								
31	2	76	220	205	0.123	0.11±0.01	1.9E-05	162375.7
32	3	90	234	219	0.479	0.48±0.15	7.5E-06	61085.0
33	4	104	248	233	0.024 ^{b1}	0.053±0.02	2.8E-06	22979.9
34	4	104	248	233	0.226 ^{b2}	0.099±0.05	2.8E-06	22979.9
35	4	104	248	233	0.179 ^{b3}	0.147±0.06	2.8E-06	22979.9
36	5	118	262	247	0.043 ^{c1}	0.034±0.01	1.1E-06	8644.9
37	5	118	262	247	0.06 ^{c2}	0.064±0.01	1.1E-06	8644.9
38	5	118	262	247	0.341 ^{c3}	0.245±0.12	1.1E-06	8644.9
39	6	132	276	261	0.04 ^{d1}	0.043±0.01	3.9E-07	3252.2
40	6	132	276	261	0.089 ^{d2}	0.068±0.02	3.9E-07	3252.2
41	6	132	276	261	0.215 ^{d3}	0.106±0.06	3.9E-07	3252.2

42	7	146	290	275	0.06	0.071±0.01	1.5E-07	1223.5
43	8	160	304	289	0.109	0.05±0.008	5.6E-08	460.3
44	9	174	318	303	0.074	n/a	2.1E-08	173.1
1-COOH								
45	6	116	188	173	0.69	0.604±0.05	6.1E-05	5.7
46	7	130	202	187	1.18	0.656±0.02	2.3E-05	5.3
47	8	144	216	201	1.14	0.769±0.06	8.6E-06	4.8
48	9	158	230	215	1.24	0.815±0.04	3.2E-06	4.4
49	10	172	244	229	1.02	0.947±0.11	1.2E-06	3.9

36 a: Bilde et al. (2003).

37 a1: positional isomers

38 a2: positional isomers

39 b1: α -hydroxyisobutyric acid

40 b2: β -hydroxybutyric acid

41 b3: 3-hydroxybutyric acid

42 c1: α -hydroxyvaleric acid

43 c2: β -hydroxy-n-valeric acid

44 c3: 4-hydroxyvaleric acid

45 d1: 4-methyl 2-keto pentanoic acid

46 d2: 3-hydroxycaproic acid

47 d3: 5-hydroxyhexanoic acid

48

49

50 **Table S3:** List of all the model compounds used in this study to recreate 73 for single precursor oxidation experiments
51 along with corresponding product molar yields.

M-15	Heptanal + OH	2-heptenal + OH	2-octenal + OH	2,4-heptadienal + OH	<u>2,4-decadienal + OH</u>
OH exposure (molec cm⁻³ s)^a	7.71×10^{10}	6.2×10^{10}	6.02×10^{10}	5.34×10^{10}	<u>5.72×10^{10}</u>
OH reaction rate constant (cm³ molec⁻¹ s⁻¹)	3.0×10^{-11b}	4.4×10^{-11c}	4.1×10^{-11d}	4.6×10^{-10e}	<u>4.6×10^{-10e}</u>
1-COOH + 1-OH					
205	1.87E-07	7.38E-05	4.44E-05	9.40E-05	<u>1.94E-05</u>
219	6.85E-08	1.26E-05	1.29E-05	3.84E-06	<u>1.74E-06</u>
233	3.67E-06	2.97E-05	2.45E-05	2.66E-05	<u>2.24E-06</u>
247	4.49E-06	5.82E-05	5.03E-05	3.77E-05	<u>4.52E-06</u>
261	3.73E-06	4.78E-05	2.22E-05	0	<u>9.07E-07</u>

275	6.69E-06	4.35E-06	6.46E-06	0	<u>0</u>
289	0	5.70E-07	2.27E-05	0	<u>7.30E-07</u>
303	0	0	0	0	<u>0</u>
317	0	0	0	0	<u>0</u>

2-COOH

233	1.96E-06	5.32E-06	9.26E-06	7.44E-06	<u>4.05E-06</u>
247	5.56E-06	2.35E-05	3.02E-05	1.98E-05	<u>1.02E-05</u>
261	1.82E-05	7.85E-05	9.24E-05	5.26E-05	<u>3.0E-05</u>
275	2.87E-06	5.00E-06	3.62E-06	5.20E-06	<u>9.31E-06</u>
289	3.19E-06	9.94E-07	1.34E-05	0	<u>5.92E-07</u>
303	0	0	0	0	<u>0</u>
317	0	0	0	0	<u>0</u>

2-COOH + 1-OH

321	0	0	0	0	<u>5.45E-06</u>
335	3.11E-06	0	0	2.96E-05	<u>1.76E-05</u>
349	1.33E-05	3.02E-05	4.20E-05	2.61E-05	<u>1.07E-05</u>
363	2.29E-05	1.80E-05	7.28E-05	0	<u>4.29E-06</u>
377	1.63E-06	1.38E-06	1.72E-05	1.45E-05	<u>1.46E-06</u>
391	0	0	0.00016	0	<u>0</u>

2-COOH + 2-OH

423	0	1.69E-06	1.90E-06	3.81E-06	<u>2.18E-05</u>
437	0	2.15E-06	2.73E-06	5.97E-07	<u>2.28E-06</u>
451	0	2.93E-06	0	9.19E-07	<u>2.72E-06</u>

1-COOH + 2-OH

307	3.41E-07	3.32E-06	0	1.06E-05	<u>4.95E-06</u>
321	4.27E-06	3.82E-05	2.31E-05	0	<u>5.09E-06</u>
335	0	0	0	0	<u>0</u>
349	5.50E-06	0	6.69E-05	0	<u>7.46E-06</u>
363	0	4.42E-05	2.68E-05	4.86E-06	<u>0</u>
377	0	0	0	0	<u>5.71E-06</u>
391	0	0	0	0	<u>0</u>

1-COOH

173	3.70E-06	0	4.53E-05	0	<u>8.99E-06</u>
187	0	1.65E-06	2.64E-06	1.73E-06	<u>1.09E-05</u>
201	0	0	1.05E-06	0	<u>6.0E-06</u>
215	0	0	0	0	<u>4.37E-07</u>
<u>229</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>0</u>	<u>3.33E-06</u>

- 52 a: as calculated from the decay of cyclopentane in each set of experiment.
53 b: Atkinson and Arey (2003).
54 c: Davis et al. (2007).
55 d: Gao et al. (2009).
56 e: calculated by multiplying 2-heptenal OH reaction rate constant by a factor of 105 as obtained from Kwok &
57 Atkinson (1995).
58 f: assumed same as 2,4-heptadienal.

59

60 Section 1. Sample calculation for aldehyde reaction timescales

61 The reaction rate constant of methacrolein is obtained from Atkinson and Arey (2003) and is as follows:

62 $k_{OH} = 2.9E-11 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

63 $k_{O_3} = 1.2E-18 \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

64 For lowest OH exposure at 5.77×10^{10} molecules cm^{-3} s, OH conc = 2.88×10^8 molecules cm^{-3} , and ozone concentration
65 was measured ~0.5 ppm which corresponds to 1.23×10^{13} molecules cm^{-3} assuming 1ppb $O_3 = 2.46 \times 10^{10}$ molecules
66 cm^{-3} . At these photooxidation conditions, methacrolein reaction timescale is calculated as follows:

67 $\tau_{OH} = \frac{1}{k_{OH}[OH]} = \sim 120 \text{ s}$

68 $\tau_{O_3} = \frac{1}{k_{O_3}[O_3]} = 1129 \text{ min}$

69 For highest OH exposure at 2.2×10^{11} molecules cm^{-3} s, OH conc = 1.1×10^9 molecules cm^{-3} , and ozone concentration
70 was measured ~12.6 ppm which corresponds to 3.1×10^{14} molecules cm^{-3} . At these photooxidation conditions,
71 methacrolein reaction timescale is calculated as:

72 $\tau_{OH} = 31 \text{ s}$

73 $\tau_{O_3} = \sim 45 \text{ min}$

74

75 Section 12. Chemical characterization using TD-GC/MS

76 Gas-phase analysis: Tenax tubes were desorbed in the thermal desorption system (TDS) for thermal desorption with
77 initial temperature at 50 °C held for 2 minutes followed by a ramp of 60 °C min^{-1} to 320 °C and held for 4 minutes.
78 The analytes were transferred to the cooling injection system (CIS4, Gerstel) via a transfer line maintained at 300 °C
79 during the run. The CIS4 was embedded with quartz wool filled quartz liner maintained at -40 °C during thermal

80 desorption, and was heated to 320 °C at 12 °C s⁻¹, and held for 5 minutes at 320 °C. The GC column was held for 2
81 minutes at 40 °C and heated to 250 °C at a rate of 7 °C min⁻¹ and held for additional 5 minutes at 250 °C.

82 Particle-phase analysis: 4 mm diameter filter punches were inserted into glass tubes (6 mm OD × 178 mm length,
83 Gerstel) and placed in the TDS for thermal desorption. The temperature ramping program for thermal desorption was
84 from 40 °C initial temperature held for 2 minutes followed by a ramp of 60 °C min⁻¹ to 320 °C and held for 5 minutes
85 at 320 °C. After the analytes were desorbed in the TDS, they were transferred to the cooling injection system (CIS4,
86 Gerstel) via a transfer line maintained at 300 °C during the run. The CIS4 was embedded with quartz wool filled quartz
87 liner maintained at 10 °C during thermal desorption to preconcentrate the desorbed analytes. The CIS was heated from
88 10 °C to 320 °C at 12 °C s⁻¹, and held for an additional 7 minutes at 320 °C. The GC column was heated from 40 °C
89 to 300 °C at a ramp of 10 °C min⁻¹ and held for 5 minutes at 300 °C. All samples were analyzed under electron impact
90 at 70 eV using a standard tungsten filament with a source temperature at 230 °C. The MS was operated at 3.1 scans s⁻¹
91 with an acquisition range from mass-to-charge (*m/z*) ratio 35 to 500.

92

93 **Section ~~23~~. Procedure to recreate *m/z* 73**

94 **Step 1:** Extract all model M-15 ions from the total ion chromatogram.

95 **Step 2:** Divide each M-15 ion with its corresponding $f_{M-15,73}$. Wherever, NIST $f_{M-15,73}$ was not available, $f_{M-15,73}$
96 was calculated from the instrument detector response.

97 **Step 3:** Since higher *m/z* ions are susceptible to fragmentation under high electron ionization efficiency (70 eV in our
98 study), therefore caution must be taken in recreating M-15 ions so as to avoid double counting of actual (or real) peaks.
99 An example of this scenario is shown in Fig. S4 (a), using an example chromatogram of *m/z* 233, 335 and 349. As
100 shown in Fig. S4 (a), *m/z* 233 has large number of fragments from higher *m/z* ions, and some of these fragments belong
101 to actual *m/z*. Peaks at retention time (RT) = 13.059 min corresponds to *m/z* 335 while at RT = 14.599 min belongs to
102 *m/z* 349. Therefore, in order not to overestimate these peaks, fragments of higher *m/z* should be set to zero when
103 recreating smaller *m/z*.

104 **Step 4:** Repeat step 3 iteratively for remaining M-15 ions to minimize the effect of double counting, and only
105 accounting for signal from actual or real peaks as shown in Fig. S4 (b).

106 **Step 5:** Add all M-15 together to recreate 73 as shown in [Fig. 2 \(main text\) with scatter plot shown in Fig. S4 \(c\)](#).
107

108 **Section ~~34~~. Sample calculation for Sect. 3.3.1 (formation of particle-phase oxidation products)**

109 Estimation of SOA formation potential using product yields of VOC precursor oxidation products were done as
110 follows:

111 M-15 ion = 219 corresponds to 3-hydroxypropanoic acid has a yield of 1.26E-05 upon photooxidation of 2-heptenal
112 which is used to estimate SOA formation for canola oil photooxidation using Eq. (4) in main text.

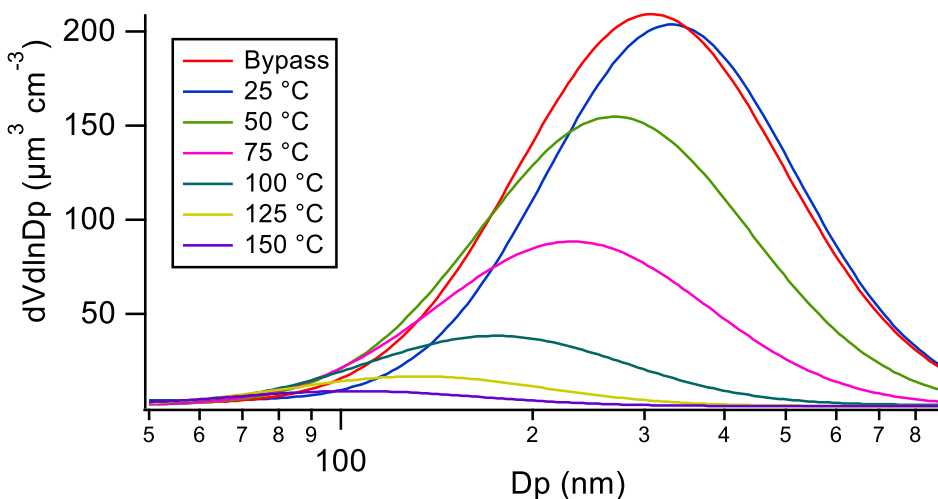
113 Where, γ_{ij} represents yields of products (i) from photooxidation of 2-heptenal (j) (obtained from Table S3), and ΔVOC_j
114 represents the decay in concentration of 2-heptenal during photooxidation of canola oil vapors, and was calculated
115 based on the measured OH exposure.

116 Therefore, for 3-hydroxypropanoic acid (or M-15 = 219) the SOA formation can be predicted as:

$$117 \quad SOA_{pred} = 1.26E - 05 * 299 * 90 = 0.339 \mu\text{g m}^{-3}.$$

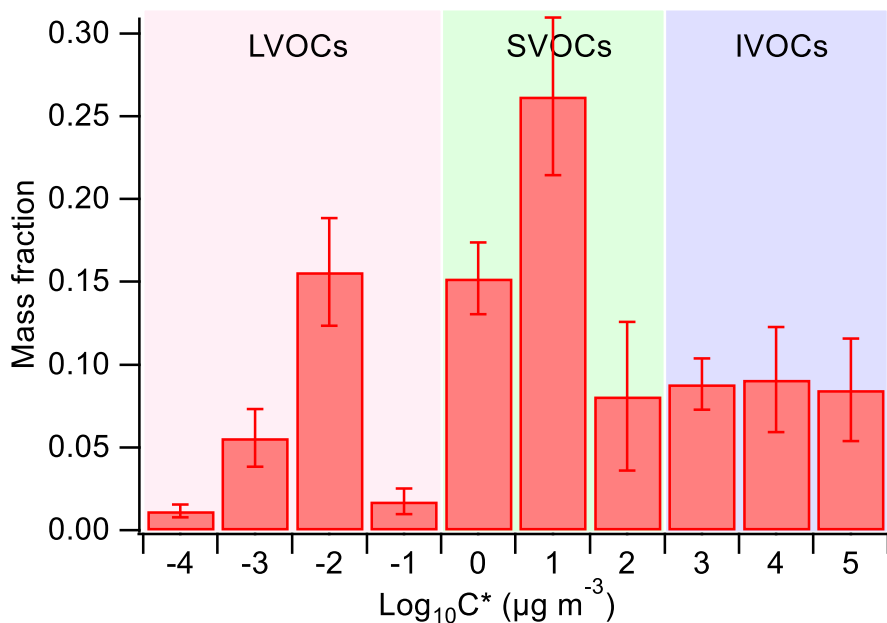
118 Similarly, using above methodology SOA formation can be estimated from other VOC precursors such as heptanal,
119 2-octenal, and 2,4-heptadienal.

120



121
122 **Figure S1.** Particle volume distribution of canola oil SOA at an OH exposure of 9.23×10^{10} molecules cm^{-3} s measured by SMPS
123 when subject to heating in a thermodenuder. The volume mode diameter shifts from 332 nm at 25 °C to 106 nm at 150 °C
124 corresponding to a decrease in volume concentration of ~96%.

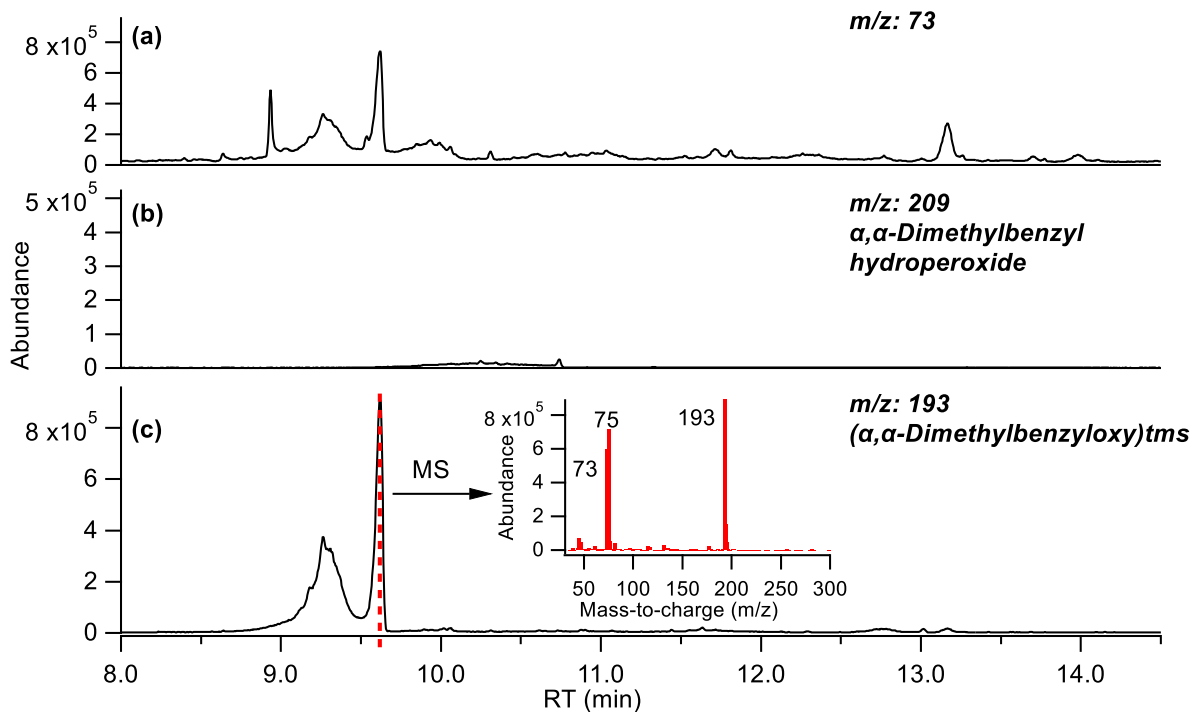
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126

127 **Figure S2.** Volatility distribution of canola oil SOA at an OH exposure of 9.23×10^{10} molecules cm^{-3} s. The volatility distribution
 128 corresponds to 24% mass in LVOCs, ~50% in SVOCs, and 26% in IVOCs. The error bars represent $\pm 1\sigma$.

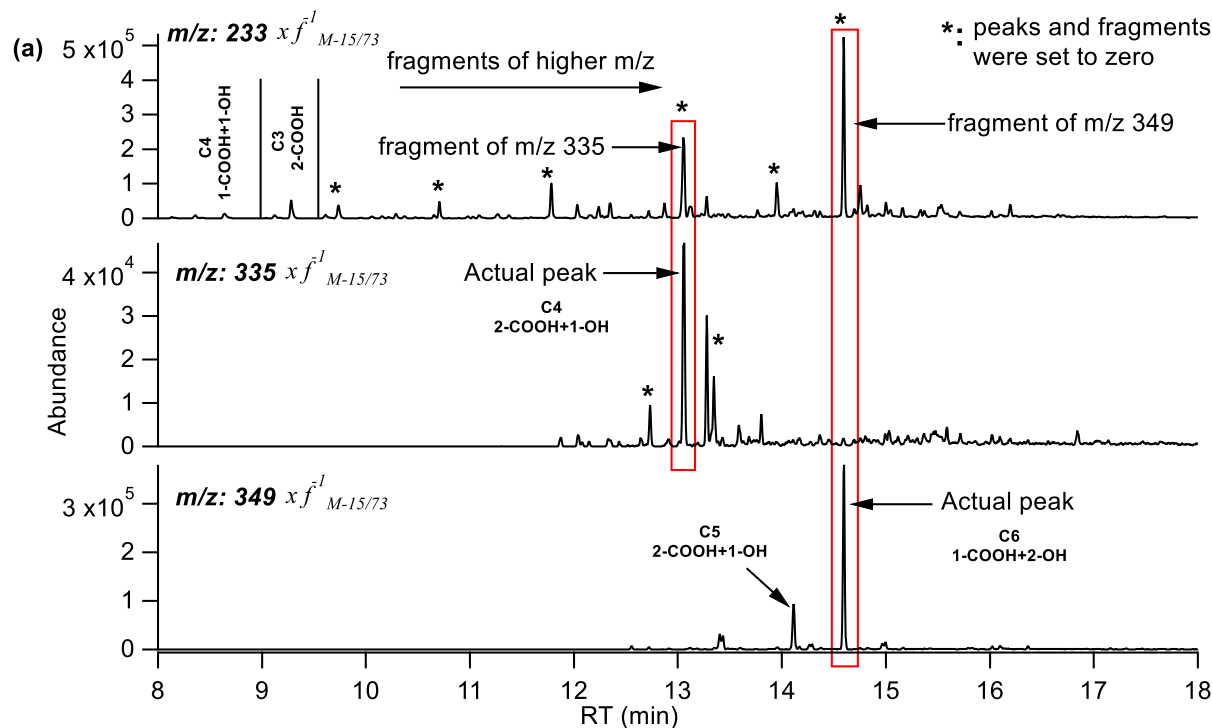
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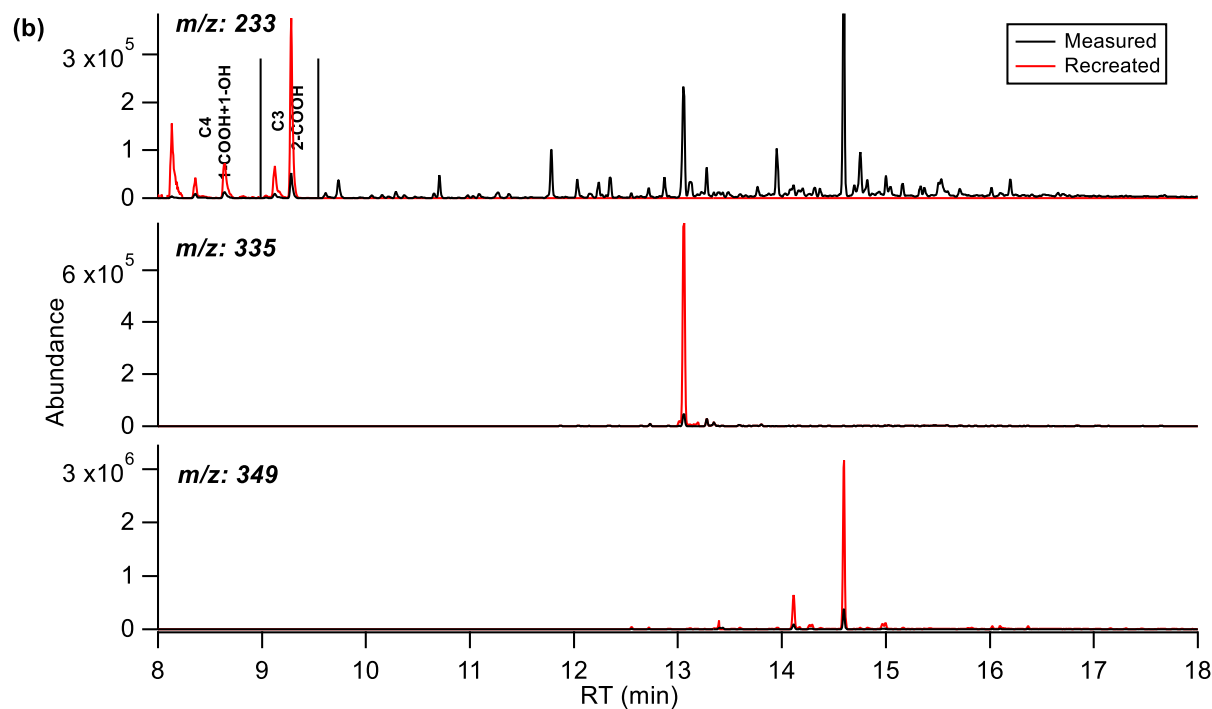
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131 **Figure S3.** Chromatogram of cumene hydroperoxide upon *in situ* derivatization (a). Based on the analytical technique discussed in
 132 main text, extracted M-15 ($m/z = 209$) chromatogram of cumene hydroperoxide contains no peaks as shown in panel (b), instead
 133 the derivatized form of R-OH is observed as shown in panel (c) along with its mass spectrum shown in the inset.

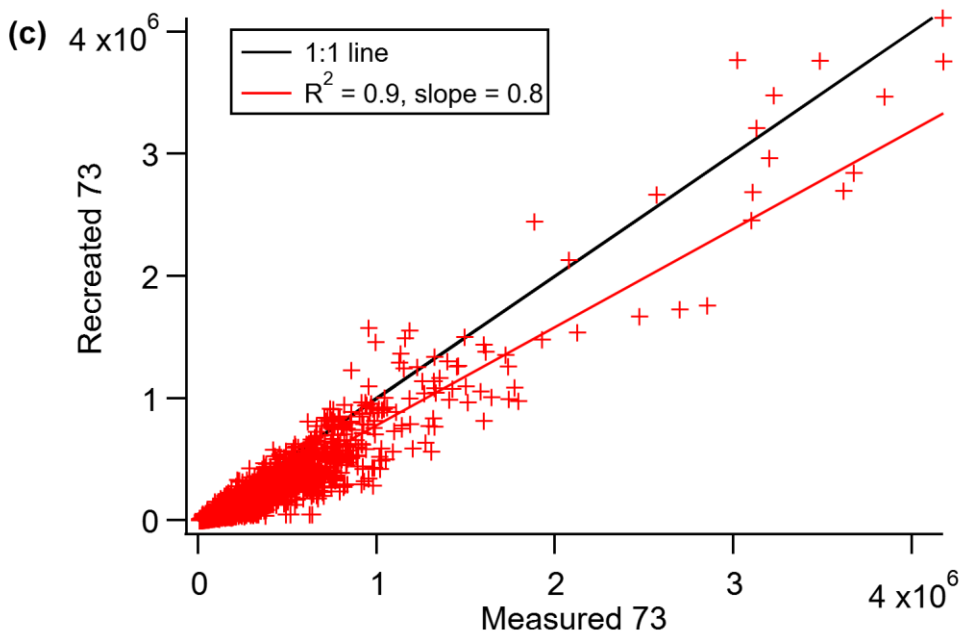
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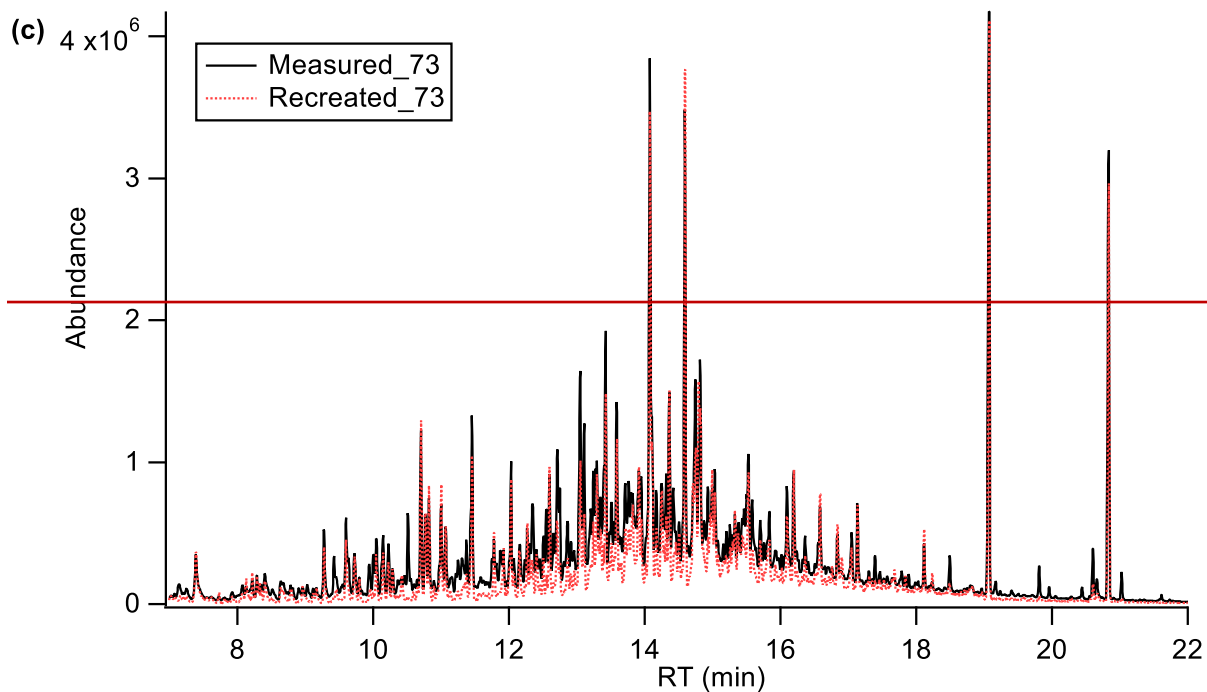
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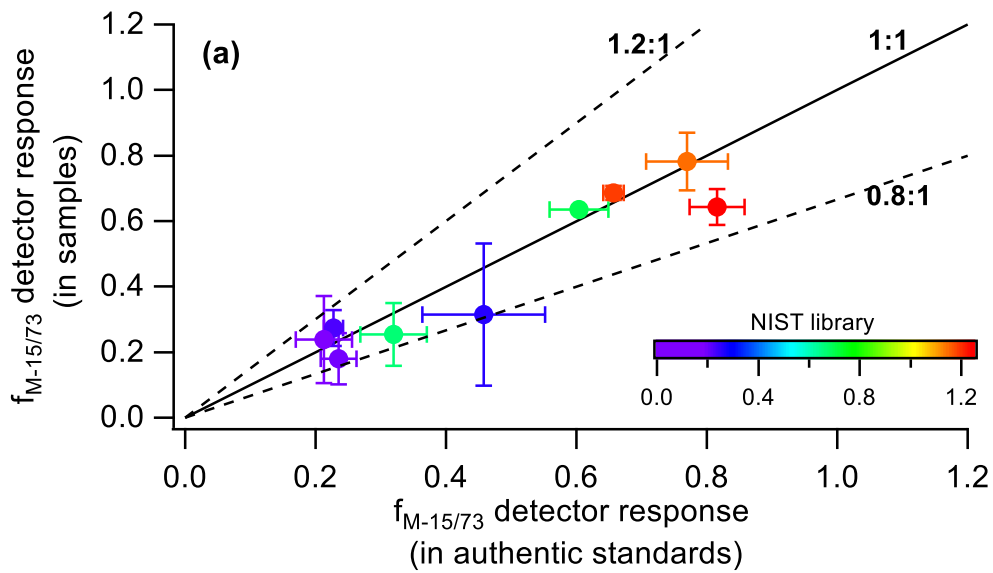
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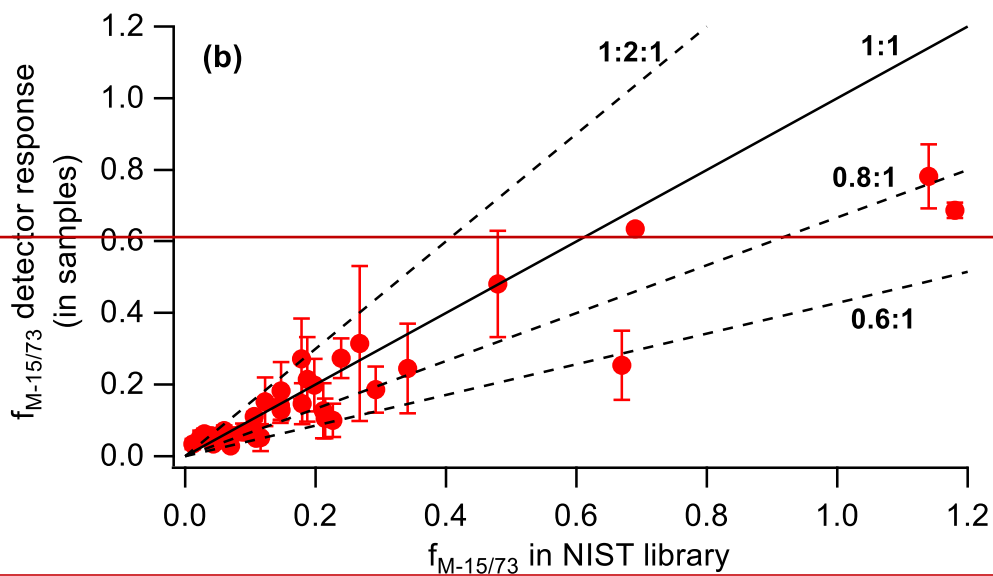
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139 **Figure S4.** Illustration to recreate m/z 73. (a) shows the unprocessed M-15 chromatograms obtained from canola oil photooxidation
 140 highlighting that lower m/z ions are susceptible to interference from higher m/z , therefore appropriate processing (refer to Sect. 23,
 141 step 3) of chromatograms should be carried out to account for these interferences. (b) chromatograms obtained after cleaning of
 142 fragments from each model m/z . (c) total ion chromatogram of measured and recreated 73.

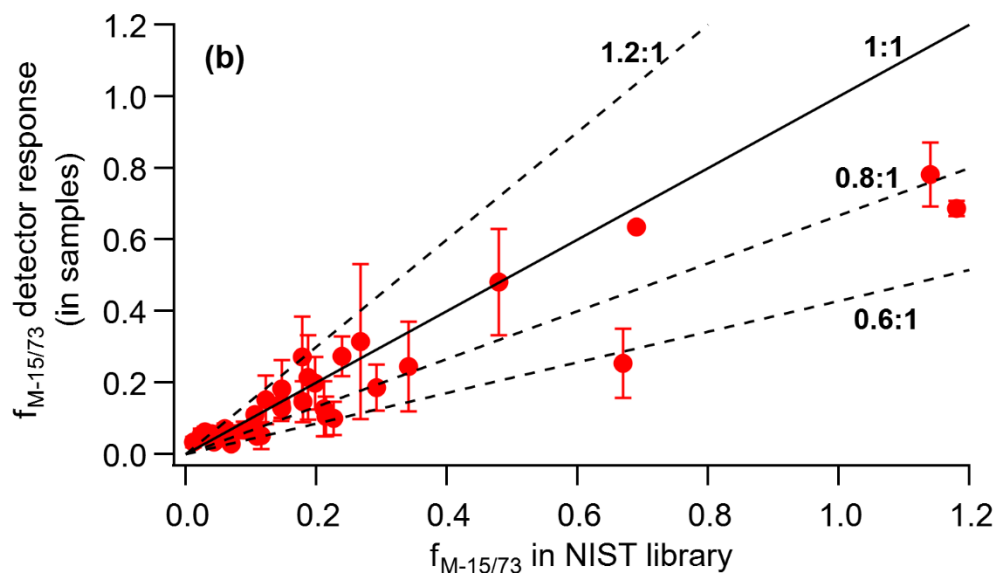
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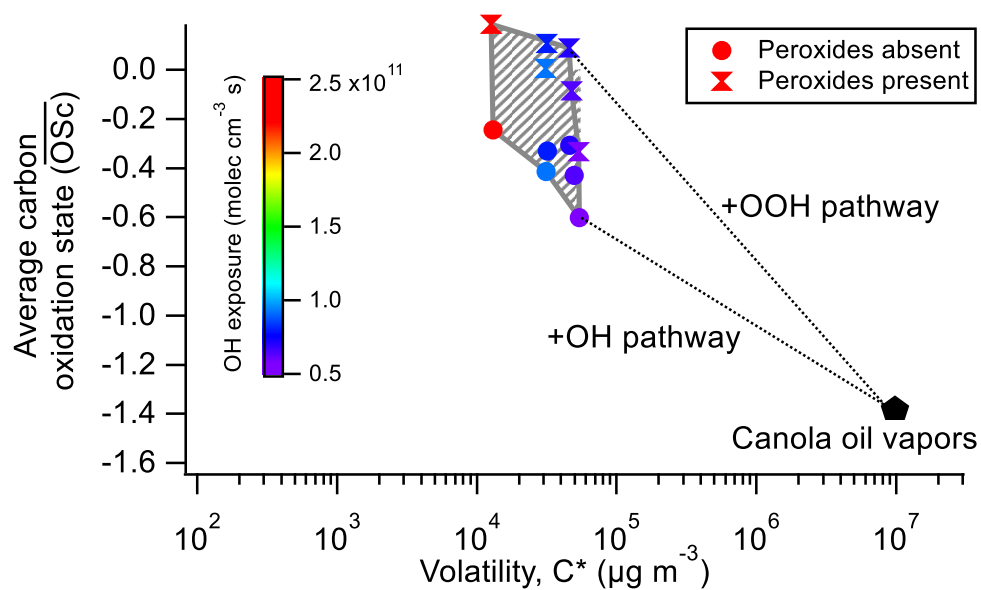
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147 **Figure S5.** Calculated uncertainties in pseudo molecular ion fraction of model components. (a) compares $f_{M-15/73}$ from instrument
 148 detector response in samples vs that in authentic standards colour coded with $f_{M-15/73}$ available in NIST library. (b) shows the
 149 comparison of $f_{M-15/73}$ obtained from instrument detector response to that available in NIST library. Both comparisons show that
 150 the uncertainty in measurement of $f_{M-15/73}$ is within 20% for measured compounds except for tartaric acid which is within 40%
 151 uncertainty.

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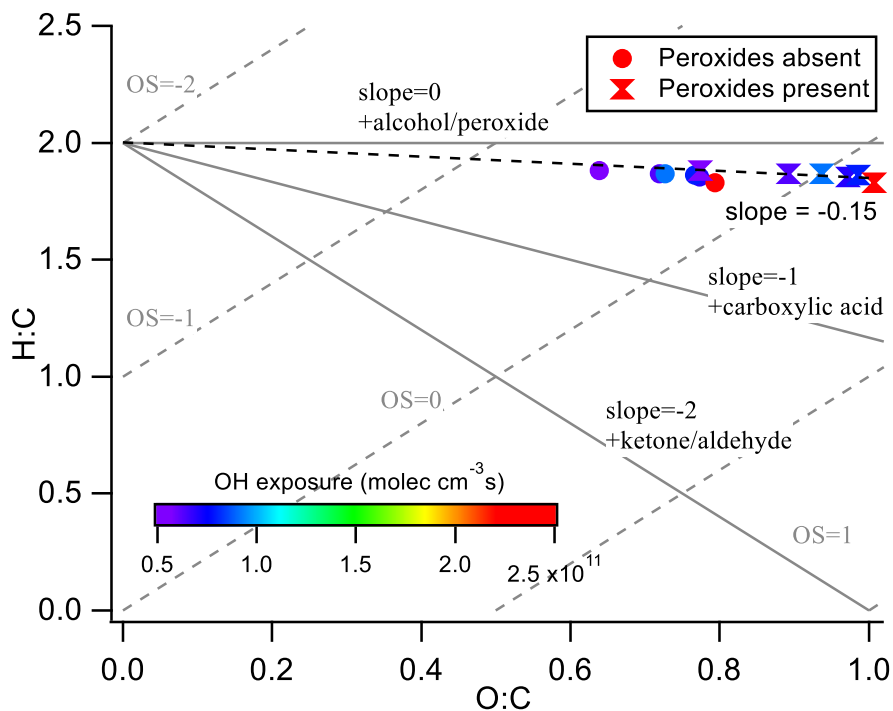


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154 **Figure S6.** 2D-VBS for canola oil SOA upon photochemical aging in the atmosphere. The coloured markers represent bulk
 155 volatility of SOA under different photochemical aging conditions, while the black marker represents properties of canola oil vapors
 156 before oxidation. The shaded area corresponds to formation of SOA products with the uncertainty associated in identifying hydroxyl

157 and peroxide groups. If all hydroxyl groups were instead classified as peroxide groups, the \overline{OS}_c increases but the bulk volatility of
158 SOA shows a minor decrease suggesting that classification of peroxide groups as hydroxyl groups has little effect on estimation of
159 volatility.

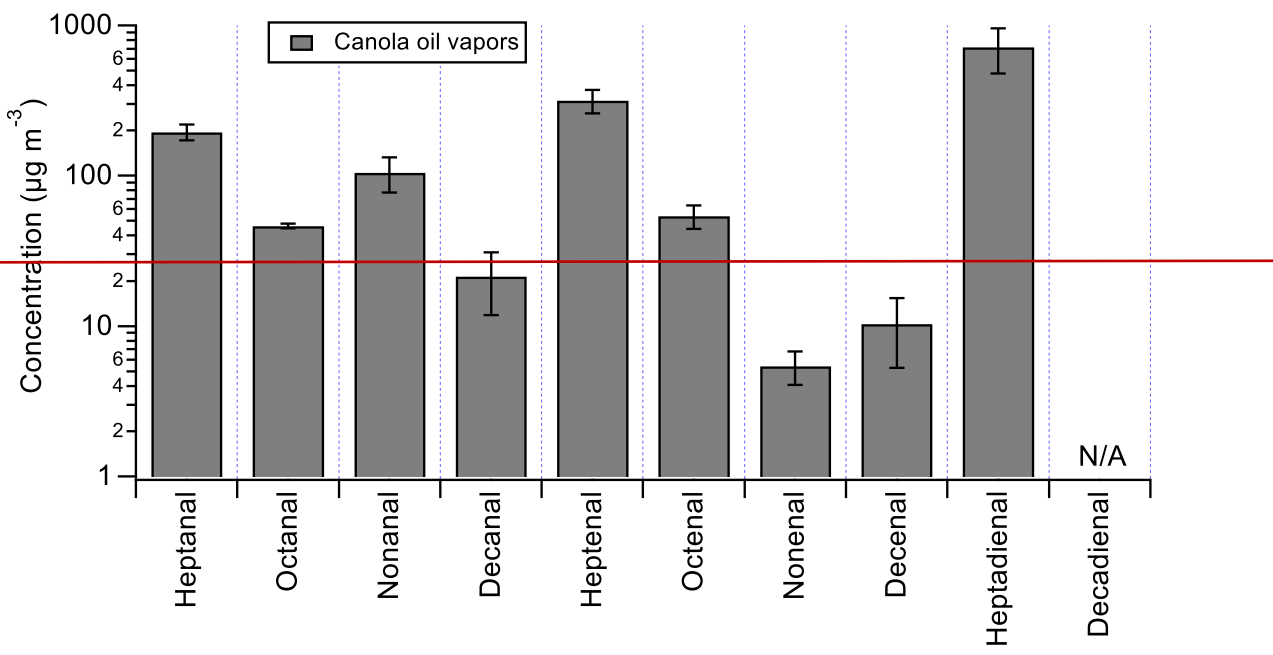
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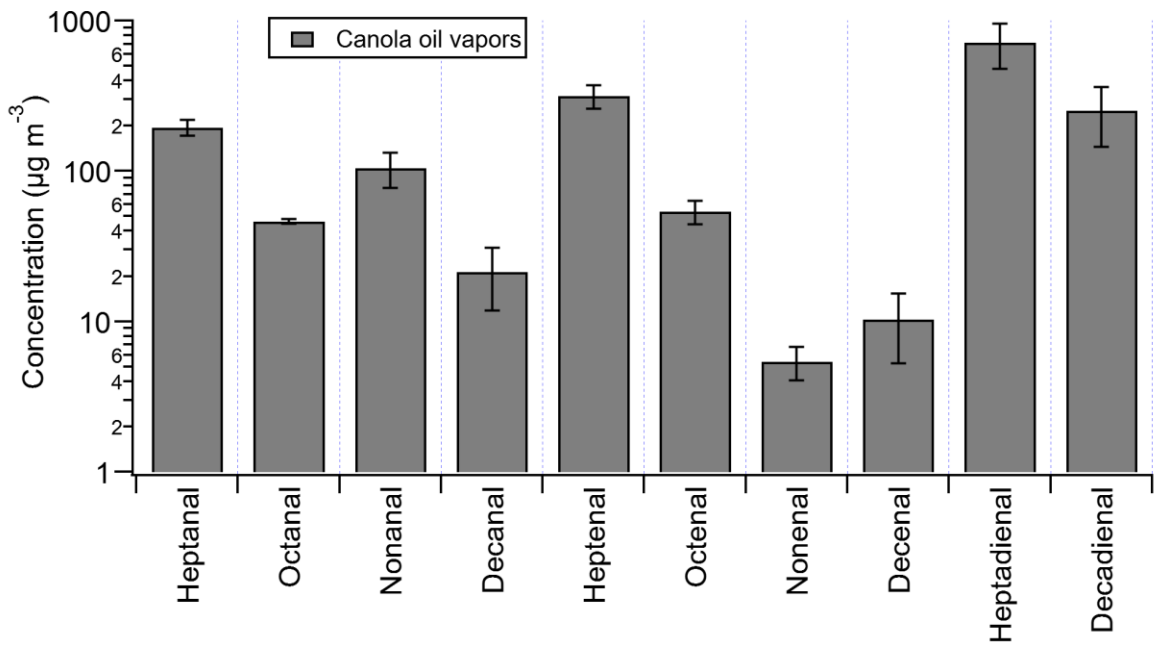
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162 **Figure S7.** Van Krevelen diagram of canola oil SOA coloured by different OH exposure considering the presence of peroxides.
163 The slope of -0.15 is observed when the formation of peroxides is considered in canola oil SOA similar to that of no-peroxides
164 assumption (Fig. 4, main text).

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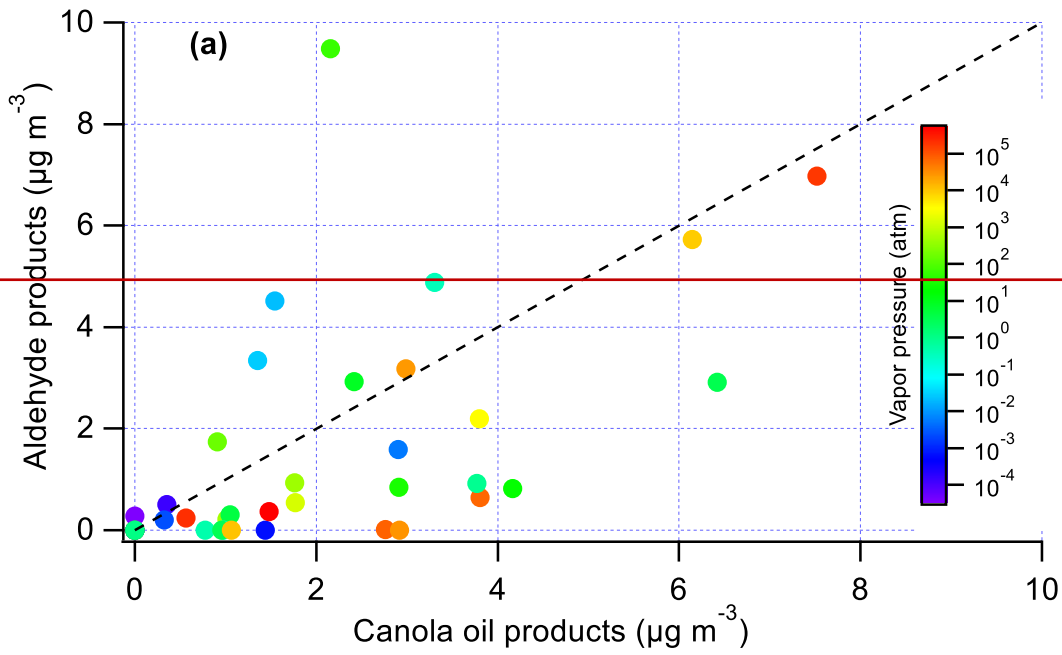


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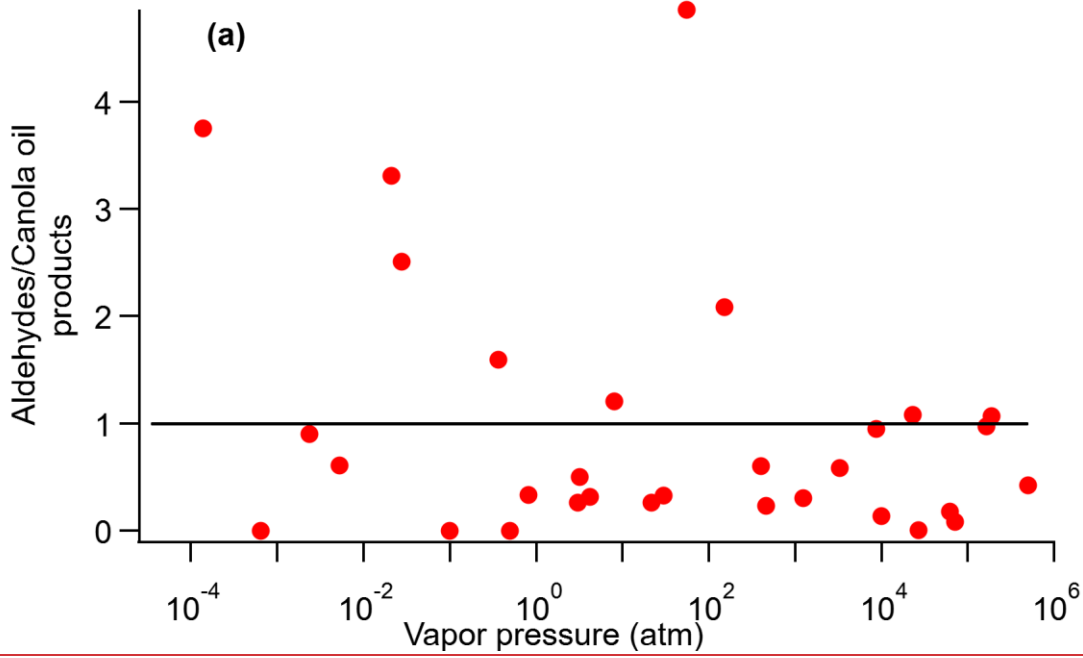
168 **Figure S8.** Concentration of different aldehydes quantified in this study.

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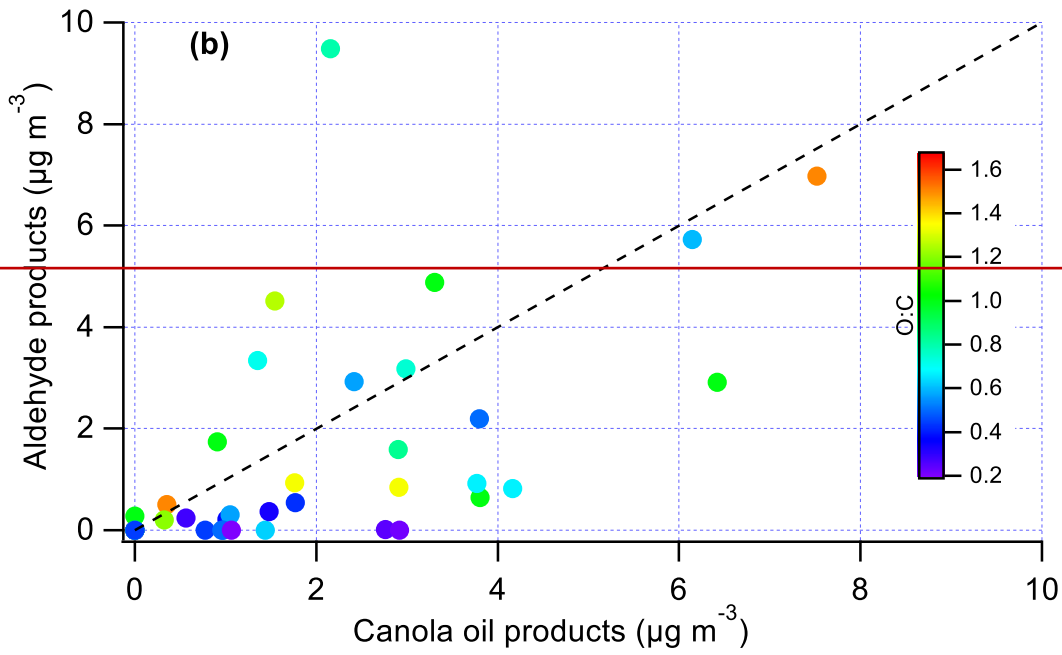
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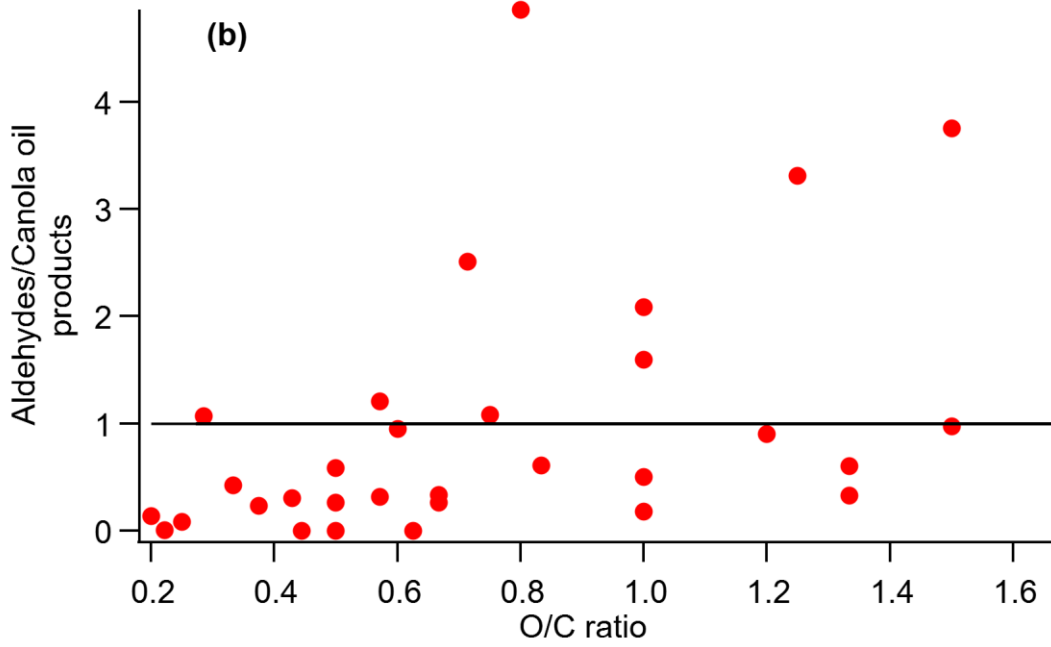
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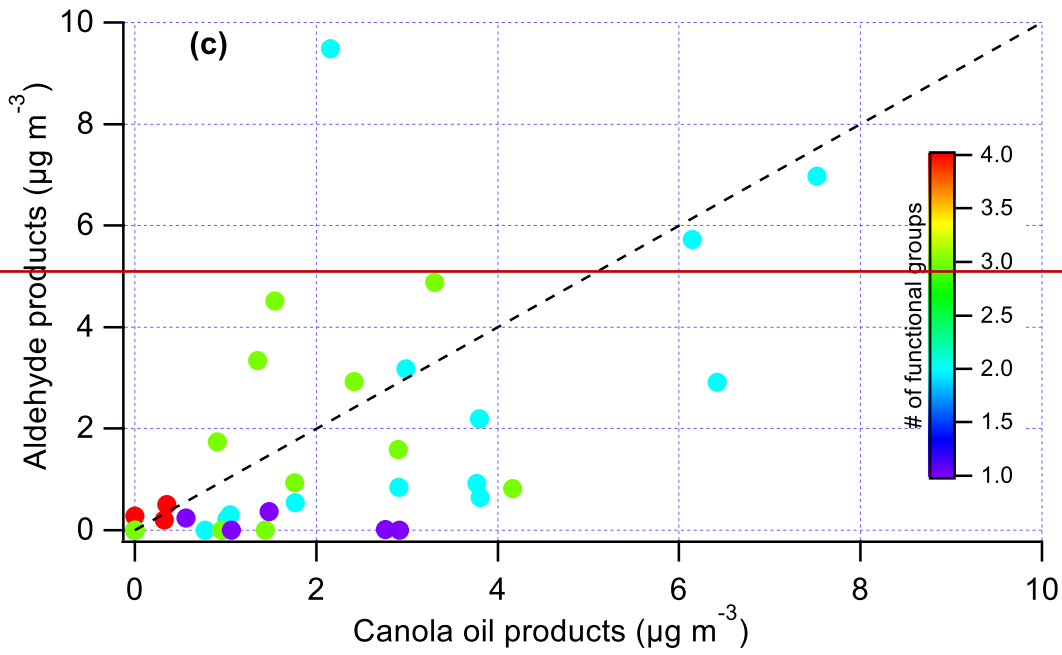


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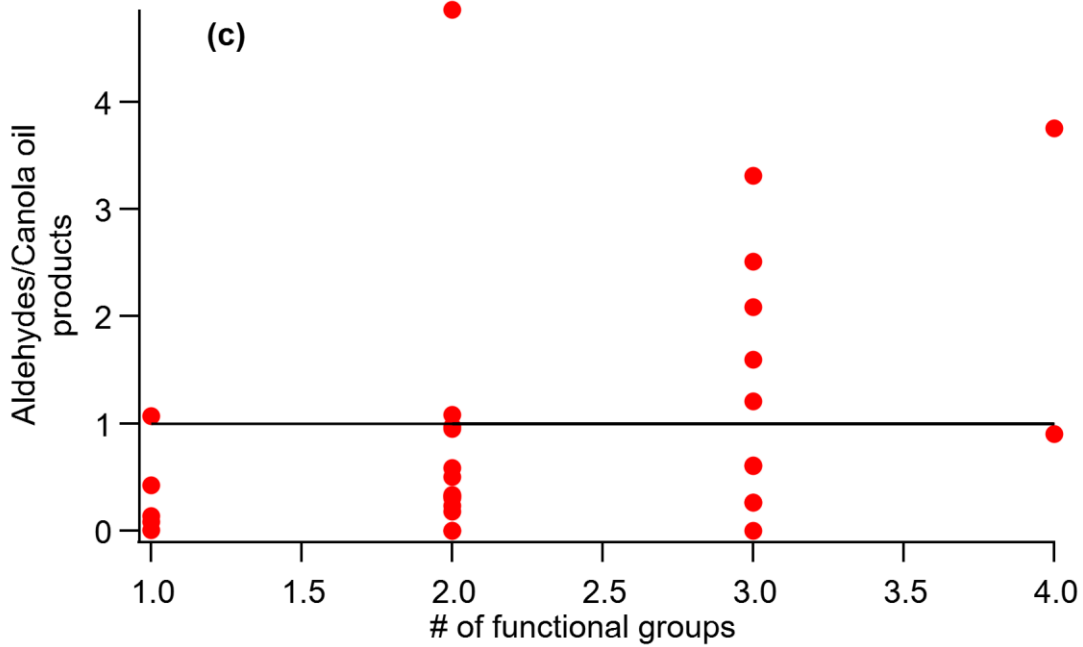


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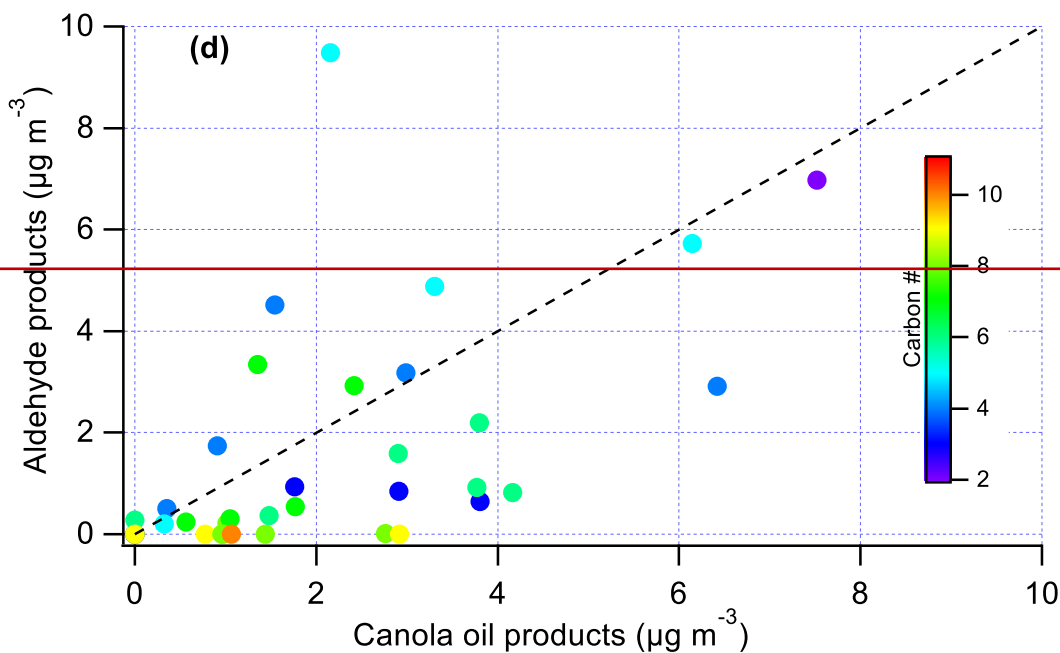


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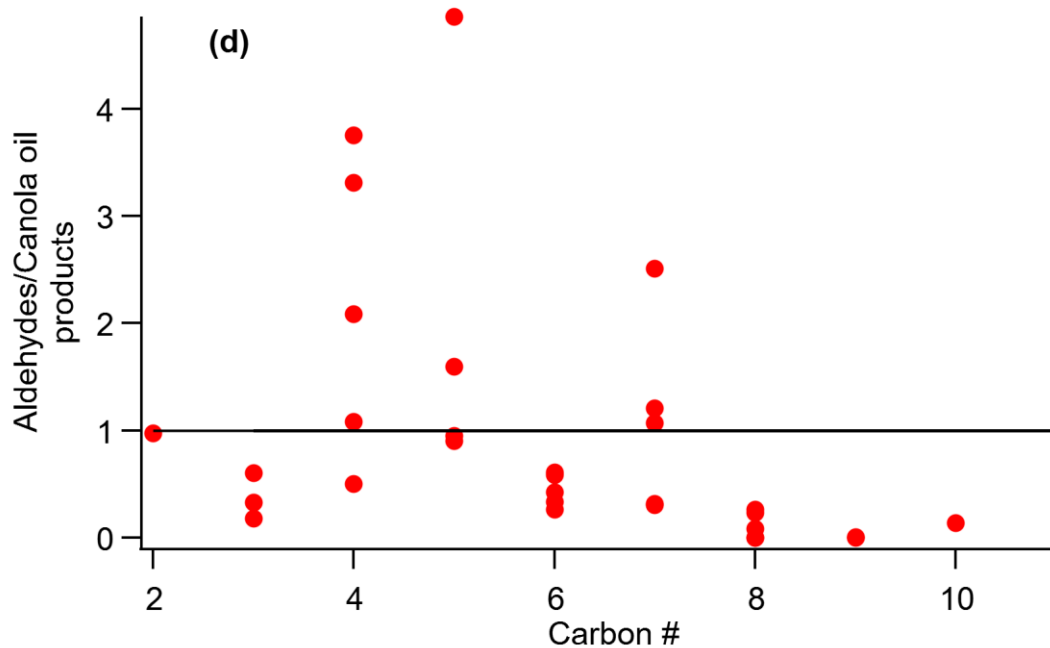


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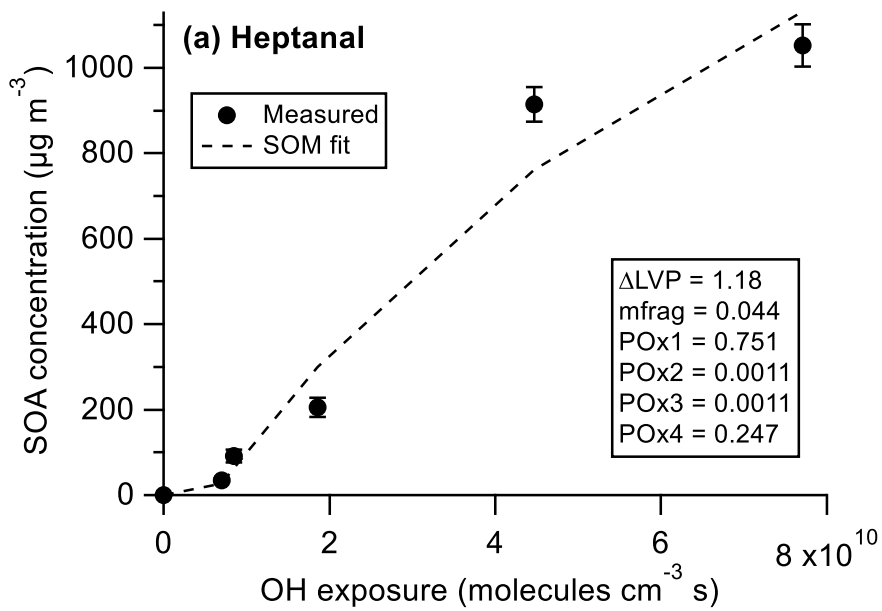
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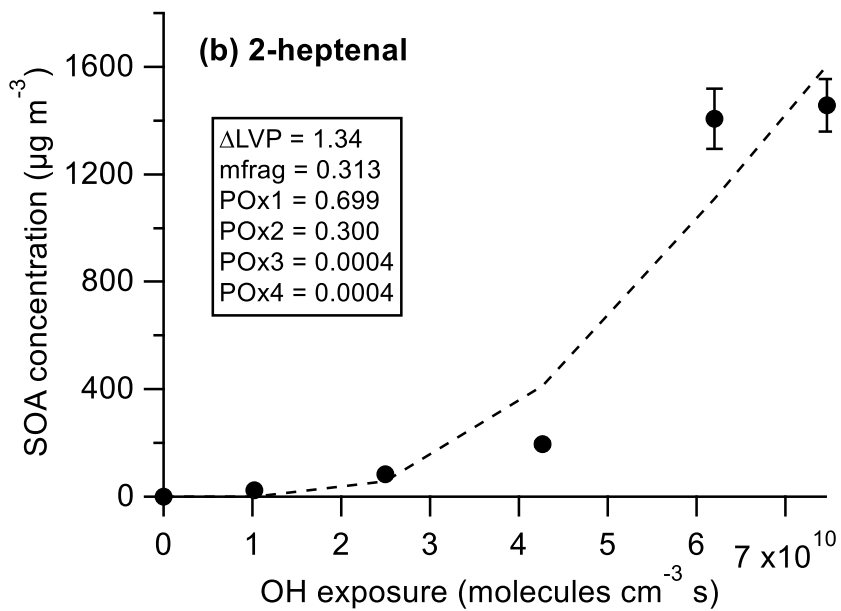
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181 **Figure S9.** Comparison of the ratio of GC measured products from aldehydes photooxidation to canola oil photooxidation and
 182 aldehydes photooxidation by vapor pressure (a), O/C ratios (b), # of functional groups (c), and carbon # (d). In general, aldehydes
 183 SOA products are underestimated for lower O/C ratios and number of functional groups, suggesting that canola oil SOA favors
 184 partitioning of more oxygenated compounds than SOA formed from aldehydes.

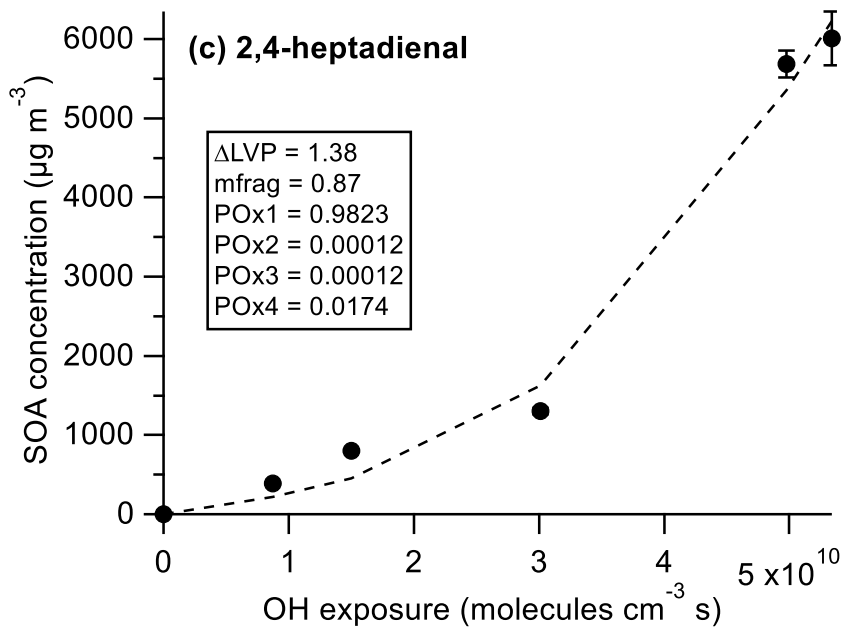
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189 **Figure S10.** Estimation of SOM parameters by fitting SOA concentrations against OH exposure for heptanal (a), *trans*-2-heptenal
 190 (b), and *trans,trans*-2,4-heptadienal (c) photooxidation.

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