

Response to Reviewer #1

General comments:

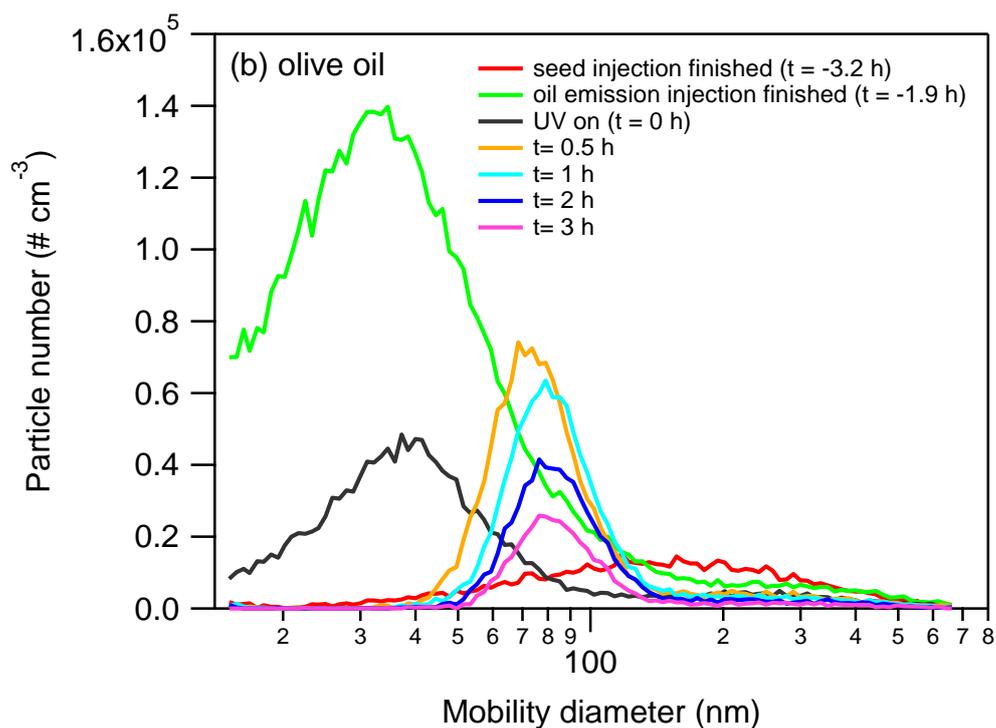
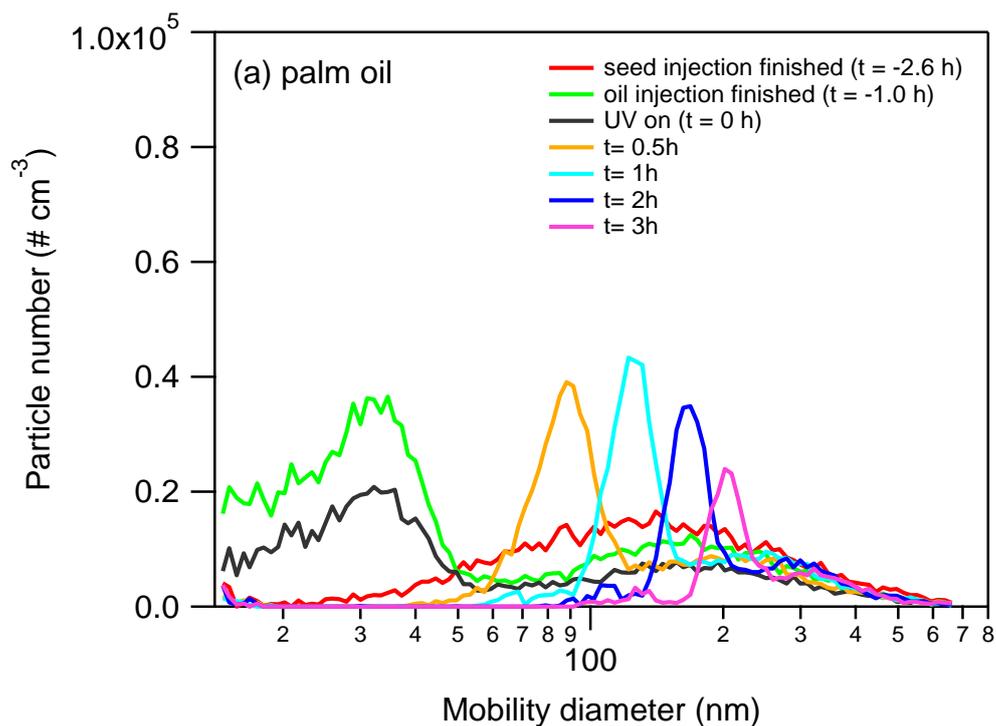
Generally, this manuscript is well-written and contain good scientific content. I would like to recommend for publication if the authors could address some comments as the following:

Specific comments:

Q1: Line 142-144. The author mention about the use of SMPS, but I have seen any results from these instrument. It is maybe better if the authors could show the evolution of particle number size distribution during the experiment.

R1: The evolution of particle number size distribution for the palm and olive oil experiments is shown in the following figure (now Fig. S4 in the Supplement). It is clear that the particle numbers decreased rapidly due to wall loss before the lights were switched on and a rapid growth of particles was observed after SOA formation. It should be noted that this work focused on the separation and characterization of POA and SOA from heated cooking oils, hence the evolution of particle number size distribution was not discussed in details and only provided in the Supplement now. The following sentence was added to the revised manuscript.

“Similarly, the particle numbers decreased rapidly due to wall loss before the lights were switched on and the mode particle diameters grew rapidly after SOA formation (Fig. S4).” (Line 195-197).



Q2: Smog chamber experiments: I think the author should describe in more details about the experiment: How many experiments the authors conducted for each oil cooking? The time resolution of each instruments?

R2: One experiment was conducted for each oil. The time resolution of each instrument was added to the revised manuscript.

Q3: What about the uncertainty of the number H:C, O:C for SOA that the author

presented in the Fig.8?

R3: According to Canagaratna et al. (2015), the uncertainty in determining O:C and H:C elemental ratios using improved-ambient method was 28% and 13%, respectively.

The following sentence was added to the revised manuscript:

“The uncertainty in determining O:C and H:C ratios was 28% and 13%, respectively (Canagaratna et al., 2015).” (Line 377-378).

References:

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem. Phys.*, 15, 253-272, <https://doi.org/10.5194/acp-15-253-2015>, 2015.

Response to Reviewer #2

General comments:

It has been well recognized that cooking emissions substantially contribute to atmospheric organic aerosols (OA), but studies on their characterization are scarce. Hence, investigation on primary and secondary OA contributions from such emissions is highly needed. This study focused on the characterization of POA and SOA produced from heated cooking oils in laboratory experiments, based on the obtained mass spectra via PMF analysis. The residual spectrum method has also been applied to separate the POA and SOA using different tracer ion signals. The authors have successfully separated the POA and SOA produced from heated palm and olive oil by PMF analysis. Further they found that residual spectrum method is not valid to calculate POA for photochemical aging of cooking oils. The results obtained from this study are interesting and the paper is written very well. Therefore, this paper is worthy to publish in ACP, after addressing the following specific comments:

Specific comments:

Q1: It has been noted (in Section 2.1; lines 142-144) that particle number concentrations and size distributions were measured using SMPS, but did not presented the obtained data in the paper. It is important to show the particle number concentrations and size distributions during the total period of the experiments, particularly during the period before the start of photochemical aging to understand the impact of gases absorption on to seed particles on the POA loading.

R1: [See response to Q1 of Reviewer #1.](#)

Q2: Surprisingly, the concentrations of POA emitted from heated palm oil and olive oil were gradually reduced starting from ~1 h and 2 h, respectively, before the start of photochemical aging and reached to almost negligible level in 4~2 h period of the aging, which has been attributed to the wall loss. However, it is not so clear whether the reduction of POA occurred due to wall loss (and/or) due to the (heterogeneous) transformations of the POA to SOA? In fact, the enhanced reduction of the olive oil POA after start of photochemical aging has been interpreted for heterogeneous

oxidation of the POA, but how about the very rapid reduction of POA before the start of the aging (Figure 1)?

R2: In the original manuscript (Line 193-194), we have mentioned that the rapid reduction of POA before the start of the aging was due to the wall loss. Heterogeneous reactions were not expected during this period because of the absence of oxidants (O_3 and/or OH radicals). After the start of photochemical aging, we have clearly shown that the reduction of POA in palm oil experiment was solely due to the wall loss while both the wall loss and heterogeneous oxidation played a role in POA reduction for olive oil experiment (Line 214-231).

A list of relevant changes

Line 119–add “One experiment was conducted for each oil.”

Line 136–add “every 1 min”

Line 145–Add “every 135 s”

Line 196-198–Add “Similarly, the particle numbers decreased rapidly due to wall loss before the lights were switched on and the mode particle diameters grew rapidly after SOA formation (Fig. S4).”

Line 208–Change “Fig. S4” to “Fig. S5”

Line 289–Change “Fig. S5” to “Fig. S6”

Line 295–Change “Fig. S6” to “Fig. S7”

Line 300–Change “Fig. S5” to “Fig. S6”

Line 315–Change “Fig. S5” to “Fig. S6”

Line 377-378–Add “The uncertainty in determining O:C and H:C ratios was 28% and 13%, respectively (Canagaratna et al., 2015).”

1 **Primary and secondary organic aerosol from heated cooking**
2 **oil emissions**

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23 **Abstract**

24 Cooking emissions have been identified as a source of both primary organic aerosol
25 (POA) and secondary organic aerosol (SOA). To examine the characteristics of SOA
26 from cooking emissions, emissions from seven vegetable oils (sunflower, olive, peanut,
27 corn, canola (rapeseed), soybean, and palm oils) heated at 200 °C were photooxidized
28 under high-NO_x conditions in a smog chamber. OA was characterized using a high-
29 resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS). Sunflower,
30 peanut, corn, canola, and soybean oil generated relatively low concentrations of POA
31 ($\leq 0.5 \mu\text{g m}^{-3}$) in the chamber. For palm and olive oil, positive matrix factorization
32 (PMF) analysis separated POA and SOA better than the residual spectrum method.
33 Temporal trends in concentrations of POA from heated palm oil were accurately
34 predicted assuming first-order POA wall loss. However, this assumption overestimated
35 POA concentrations from heated olive oil, which was attributed to the heterogeneous
36 oxidation of POA. The mass spectra of the PMF resolved POA factor for palm oil, and
37 the average POA from sunflower, peanut, corn, and canola oils were in better agreement
38 ($\theta = 8\text{--}12^\circ$) with ambient cooking organic aerosol (COA) factors resolved in select
39 Chinese megacities than those found in given European cities in the literature. The mass
40 spectra of SOA formed from heated cooking oils had high abundances of m/z s 27, 28,
41 29, 39, 41, 44, and 55 and displayed limited similarity ($\theta > 20^\circ$) with ambient semi-
42 volatile oxygenated OA (SV-OOA) factors. The entire OA data set measured herein
43 follows a linear trend with a slope of approximately -0.4 in the Van Krevelen diagram,
44 which may indicate oxidation mechanisms involving the addition of both carboxylic

- 45 acid and alcohol/peroxide functional groups without fragmentation and/or the addition
- 46 of carboxylic acid functional groups with fragmentation.

47 **1 Introduction**

48 Organic aerosol (OA) contributes greatly to atmospheric particulate matter (PM)
49 (Kanakidou et al., 2005), which influences air quality, climate, and human health
50 (Hallquist et al., 2009). OA commonly comprises primary organic aerosol (POA)
51 emitted directly from sources and secondary organic aerosol (SOA) formed via the
52 oxidation of organic gases (Donahue et al., 2009). Cooking is an important source of
53 both POA (Abdullahi et al., 2013) and SOA (Liu et al., 2018). In aerosol mass
54 spectrometer (AMS, Aerodyne Research Incorporated, USA) measurements, cooking
55 OA (COA) has been found to contribute 10–35% of OA in urban areas (Allan et al.,
56 2010; Sun et al., 2011, 2012; Ge et al., 2012; Mohr et al., 2012; Crippa et al., 2013a, b;
57 Xu et al., 2014; Lee et al., 2015), although the AMS may overestimate COA due to the
58 COA relative ionization efficiency (1.56–3.06), which is higher than the typical value
59 of 1.4 used for organics (Reyes-Villegas et al., 2018). In particular, Lee et al. (2015)
60 found that the average contribution of COA to OA (35%) was even higher than that of
61 traffic-related hydrocarbon-like OA (HOA, 26%) at a roadside site in Mongkok in Hong
62 Kong. Xu et al. (2014) also observed higher contributions of COA (24%) than HOA
63 (16%) to OA in Lanzhou, China.

64 Although most of the COA mass spectra resolved by positive matrix factorization
65 (PMF) analysis (Paatero, 1997; Paatero and Tapper, 1994; Ulbrich et al., 2009; Zhang
66 et al., 2011) in the wider AMS dataset have the same basic characteristics, including
67 predominant peaks at m/z s 41, 43, 55, and 57 and high m/z 55/57 ratios, the specific
68 COA mass spectra vary among studies (Mohr et al., 2009; Allan et al., 2010; Sun et al.,

69 2011; 2012; Ge et al., 2012; Mohr et al., 2012; Crippa et al., 2013a, b; Lee et al., 2015;
70 Elser et al., 2016; Struchmeier et al., 2016; Ajjala et al., 2017). Differing cooking styles
71 may be among the factors that induce this variability in COA mass spectra. For instance,
72 the fraction of m/z 41 was higher than that of m/z 43 in COA mass spectra for Chinese
73 cooking (He et al., 2010), while the reverse was found for meat cooking (Mohr et al.,
74 2009). Atmospheric aging may also diversify the COA mass spectra. Significantly
75 different COA mass spectra have been resolved during summer and winter in Greece
76 despite the fact that cooking activities are similar during the two seasons (Florou et al.,
77 2017; Kaltsonoudis et al., 2017). In addition, the COA factors resolved by PMF analysis
78 may include emissions from other sources (Dall'Osto et al., 2015) and sometimes
79 cannot be separated from the other factors (Kostenidou et al., 2015; Qin et al., 2017).
80 The multilinear engine (ME-2) is a relatively newly developed tool that can use mass
81 spectra input from the literature to constrain the OA source apportionment solutions
82 (Canonaco et al., 2013). Qin et al. (2017) found that inputting different COA profiles
83 resulted in proportions of COA (to total OA) that differed by factors of up to 2.
84 Comparing laboratory-generated COA mass spectra with ambient PMF factors can help
85 to improve COA source apportionment. Previous studies have been focused on
86 investigating mass spectra of POA from cooking (Mohr et al., 2009; Allan et al., 2010;
87 He et al., 2010; Reyes-Villegas et al., 2018); however, studies exploring mass spectra
88 of SOA from cooking remain scarce.

89 Recent smog chamber studies have demonstrated that cooking emissions can form
90 large amounts of SOA via photochemical aging (Kaltsonoudis et al., 2017; Liu et al.,

91 2017, 2018). Kaltsonoudis et al. (2017) observed similarities between aged COA mass
92 spectra from meat charbroiling and corresponding POA mass spectra. Liu et al. (2017)
93 also reported extensive similarities (R^2 of 0.83–0.96) between mass spectra of POA and
94 SOA from heated cooking oils. These mass spectral similarities make it difficult to
95 separate POA and SOA from cooking in smog chamber experiments in terms of both
96 abundance and mass spectral signatures.

97 PMF has been used widely to deconvolve ambient AMS datasets, but relatively
98 less to analyze smog chamber data. Presto et al. (2014) used PMF to analyze POA and
99 SOA from vehicle exhaust. Kaltsonoudis et al. (2017) performed PMF analysis on fresh
100 and aged OA from meat charbroiling. However, PMF analysis has not been applied to
101 POA and SOA from heated cooking oils.

102 Sage et al. (2008) developed a residual spectrum method to separate POA and SOA
103 in diesel exhaust; this residual spectrum method assumes that all signal at m/z s 57 and
104 44 is associated with POA and SOA, respectively. Chirico et al. (2010) and Miracolo et
105 al. (2010) further improved the residual method, using the reduced $C_4H_9^+$ ion as a POA
106 tracer. Chirico et al. (2010) suggested that the appropriate POA tracer ion may differ
107 for different sources. The optimal tracer ions for cooking emissions remain unknown.

108 This study aims to characterize POA and SOA from heated cooking oils emissions,
109 obtain POA and SOA mass spectra via PMF analysis, and compare the resolved mass
110 spectra with those for ambient COA-related factors from PMF. We will also explore the
111 heterogeneous oxidation of POA from palm and olive oils.

112 **2 Materials and methods**

113 2.1 Smog chamber experiments

114 Seven photochemical aging experiments were conducted in a 30 m³ indoor smog
115 chamber at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences
116 (Wang et al., 2014; Liu et al., 2015, 2016; Deng et al., 2017) (Table 1). The cooking
117 oils tested include sunflower, olive, peanut, corn, canola (rapeseed), soybean, and palm
118 oils, which together constitute over 90% of the vegetable oil consumed globally (USDA,
119 2017). One experiment was conducted for each oil. All experiments were conducted at
120 25 °C and a relative humidity (RH) of less than 5%. Prior to each experiment, the
121 chamber was continuously flushed with purified dry air for at least 48 h. The
122 experimental procedures have been described in detail elsewhere (Liu et al., 2018).
123 Briefly, ammonium sulfate seed particles were introduced first into the chamber to
124 serve as condensation sinks to reduce organic vapor wall losses (Zhang et al., 2014).
125 Then, emissions from heated vegetable oils were introduced into the chamber for 1–1.5
126 h by an air stream through a 2 m heated (70 °C) Teflon tube. The emissions were
127 generated by heating 250 mL of the target oil at approximately 200 °C in a 500 mL
128 flask in a dimethyl silicone oil bath. Nitrous acid (HONO) was then introduced into the
129 chamber as a source of hydroxyl radical (OH). The initial ratio of non-methane organic
130 gases (NMOGs) to NO_x (NMOG:NO_x) fell largely between 2.6 and 5.4 ppbC:ppb,
131 except for the palm oil experiment, in which it was 18.9 ppbC:ppb. These ratios were
132 larger than the typical urban ratio of ~3 (Gordon et al., 2014). After the primary
133 emissions had been characterized for at least 1 h, photochemical aging was initiated by

134 exposing the emissions to black lights (60 W Philips/10R BL365, Royal Dutch Philips
135 Electronics Ltd., the Netherlands) for 2–4.5 h.

136 Gas monitors were used to measure the concentrations of NO_x and O₃ every 1 min
137 (EC9810, 9841T, Ecotech, Australia). NMOGs were characterized using a commercial
138 proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, Model 2000,
139 H₃O⁺ reagent ion, Ionicon Analytik GmbH, Austria) (Lindinger et al., 1998; Jordan et
140 al., 2009). Detailed descriptions of operating conditions, calibrations, and
141 fragmentation corrections can be found elsewhere (Liu et al., 2018). The decay of
142 acrolein or heptadienal was used to determine the OH concentration in the chamber.

143 A scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier
144 model 3080, CPC model 3775) was used to measure particle number concentrations
145 and size distributions every 135 s. The chemical composition of submicron non-
146 refractory particulate matter (NR-PM₁) was characterized using a high-resolution time-
147 of-flight aerosol mass spectrometer (hereafter AMS, Aerodyne Research Incorporated,
148 USA) (DeCarlo et al., 2006). The instrument alternated between the high-sensitivity V-
149 mode and the high-resolution W-mode every 1 min. The Squirrel 1.57I and Pika 1.16I
150 toolkits were used in IGOR (Wavemetrics Inc., USA) to analyze the AMS data; the
151 Aiken et al. (2008) fragmentation table was adopted. Elemental ratios, such as the
152 hydrogen-to-carbon ratio (H:C) and oxygen-to-carbon ratio (O:C), were determined
153 using the improved-ambient method (Canagaratna et al., 2015). HEPA-filtered particle-
154 free air from the chamber was measured for at least 20 min before and after each

155 experiment to determine the major gas signals. The ionization efficiency was calibrated
156 using 300 nm ammonium nitrate particles.

157 **2.2 Separating POA and SOA**

158 The experiments in this study were classified into two groups (Table 1). Sunflower,
159 peanut, corn, canola, and soybean oil emissions produced low POA concentrations (<
160 $0.5 \mu\text{g m}^{-3}$) in the smog chamber. Due to wall losses, the POA concentration was close
161 to the AMS detection limit when the lights were turned on (e.g., the sunflower oil
162 experiment in Supplementary Fig. S1). These experiments were therefore assumed to
163 involve only SOA. POA and SOA mixtures were present in the palm and olive oil
164 experiments, which produced maximum POA concentrations of 14 and $39 \mu\text{g m}^{-3}$,
165 respectively. PMF analysis (Paatero, 1997; Paatero and Tapper, 1994) was performed
166 on the high-resolution mass spectra (m/z s 12–160) to deconvolve the POA and SOA
167 factors following the procedure of Ulbrich et al. (2009). PMF solutions were examined
168 for 1 to 5 factors with fPeak values varying from -1 to 1. Diagnostic plots are shown
169 for all datasets in Figs. S2 and S3. After examining the PMF residuals, time series for
170 different numbers of factors, and mass spectral similarity between PMF POA and
171 observed POA spectra, 2-factor solutions with fPeak values of -0.2 and 0 were chosen
172 for the palm and olive oil experiments, respectively.

173 The residual spectrum method (Sage et al., 2008; Chirico et al., 2010; Miracolo et
174 al., 2010; Presto et al., 2014) was used in addition to PMF analysis to separate the POA
175 and SOA. The residual method assumes that all tracer ion signal (e.g., C_4H_9^+) is
176 associated with POA and that the chemical composition of POA remains constant

177 throughout the entire experiment. The mass concentration of POA at time t can then be
178 calculated using the following equation:

$$179 \quad POA_t = Ion_t / Ion_{t_0} \times OM_{t_0}, \quad (1)$$

180 where OM_{t_0} is the total organic matter concentration at time $t = 0$, and Ion_t and Ion_{t_0} are
181 the organic mass signals of a specific POA tracer ion at time t and time $t = 0$ (lights on),
182 respectively. $C_4H_9^+$ is typically chosen as the POA tracer for combustion sources (Sage
183 et al., 2008; Chirico et al., 2010; Miracolo et al., 2010; Presto et al., 2014); the optimal
184 tracer ion for cooking emissions remain unclear. The tracer ions tested in this study
185 include $C_4H_7^+$, $C_4H_9^+$, $C_5H_8^+$, $C_5H_9^+$, $C_6H_9^+$, and $C_7H_9^+$.

186 **3 Results and discussion**

187 **3.1 POA-SOA split**

188 Figure 1 shows measured OA time series for the palm and olive oil experiments; the
189 OA concentrations were not corrected for particle wall loss. The experiments typically
190 involved introduction of the cooking emissions to the chamber (~1–1.5 h),
191 characterization of primary emissions (~1–2 h), and photochemical aging (2–4.5 h). In
192 the palm oil experiment, the POA concentration increased rapidly during the first ~1.6
193 h of the emission introduction period, reaching approximately $14 \mu\text{g m}^{-3}$. The POA
194 concentration then decreased to $\sim 9 \mu\text{g m}^{-3}$ due to wall losses. SOA was quickly formed
195 after photochemical aging was initiated at $t = 0$, and the OA concentration increased by
196 a factor of 5 in less than 1 h. Similarly, the particle numbers decreased rapidly due to
197 wall loss before the lights were switched on and the mode particle diameters grew
198 rapidly after SOA formation (Fig. S4). The maximum POA concentration in the olive

199 oil experiment was approximately two times higher than that in the palm oil experiment,
200 and the maximum OA concentration was ~50% of that in the palm oil experiment via
201 SOA formation. Palm oil produced SOA more efficiently than did olive oil; this is
202 consistent with our previous study, which found that the SOA production rate of palm
203 oil was 4 times that of olive oil, likely due to the higher abundance of SOA precursors
204 in palm oil emissions (Liu et al., 2018).

205 Figure 1 also shows time series of measured OA, resolved PMF factors, and POA
206 concentrations assuming first-order loss of POA to the walls. Two factors, namely POA
207 and SOA, were identified. Solutions with three or more factors introduced physically
208 inexplicable factors and did not improve the PMF performance (Fig. S4S5). Overall,
209 the OA reconstructed by PMF accurately captured the trends in measured OA
210 throughout the experiment. The sum of the residual was generally less than $2 \mu\text{g m}^{-3}$,
211 resulting in ratios of total residual concentration ($\Sigma\text{Residual}$) to total OA concentration
212 (ΣOA) of less than 5% (Figs. S2 and S3). The separation of POA and SOA factors was
213 reasonable and interpretable. During the introduction and characterization of cooking
214 emissions ($t < 0$), the concentrations of SOA should be, by definition, exactly zero. The
215 concentrations of the resolved SOA factors were approximately $0.3 \mu\text{g m}^{-3}$, capturing
216 the expected behavior.

217 In previous smog chamber studies of dilute emissions from combustion sources
218 (Weitkamp et al., 2007; Gordon et al., 2014; Liu et al., 2015, 2016), POA was typically
219 assumed to be inert, and POA concentrations followed first-order wall loss equations.
220 Figure 1 shows POA concentrations after the onset of photooxidation assuming first-

221 order wall loss. The wall loss rate constants were determined from the decay of POA
222 during the primary emissions characterization period. For palm oil, the predicted POA
223 concentrations agreed well with the PMF POA factor, suggesting that the assumption
224 of POA inertness was reasonable. However, for olive oil, the concentration of the PMF
225 POA factor was significantly lower after the onset of photooxidation ($t = 0$) than the
226 POA concentration predicted assuming first-order wall losses. The PMF POA factor
227 decreased rapidly in the first hour after $t = 0$, which may have been due to the
228 heterogeneous oxidation of POA. Kaltsonoudis et al. (2016) observed similar changes
229 in POA concentrations when emissions from meat charbroiling were exposed to OH
230 levels similar to those used in this experiment. Nah et al. (2013) also observed rapid
231 heterogeneous OH oxidation of select cooking POA components such as oleic acid and
232 linoleic acid. The differences in POA behavior may have arisen from the different
233 chemical compositions, and corresponding differences in reactivity, of POA from olive
234 and palm oils.

235 To validate the differences in heterogeneous oxidation reactivity between POA
236 from palm and olive oils, two additional ozonolysis experiments were conducted
237 separately using an oxidation flow reactor. Emissions generated in the flask were first
238 passed continuously through the reactor for at least 30 min and then exposed to 500–
239 600 ppb of ozone (O_3) for another 17 min. The total flow rate and residence time in the
240 flow reactor were 6 L min^{-1} and 75 s, respectively. OH radicals were not present in these
241 experiments. Previous work has demonstrated that exposing gas-phase emissions from
242 heated cooking oils to O_3 does not lead to SOA formation (Liu et al., 2017). Therefore,

243 any changes in OA chemical composition during these ozonolysis experiments were
244 attributed to heterogeneous oxidation. Figure 2 shows time series of O:C ratios and O₃
245 concentrations during the ozonolysis experiments. The olive oil O:C ratio increased
246 from 0.11 to 0.17 after the emissions were exposed to O₃ for 17 min; no obvious
247 changes were observed in the palm oil O:C ratio. These results demonstrate that POA
248 from olive oil undergoes heterogeneous ozone oxidation more readily than POA from
249 palm oil. The olive oil POA may contain more abundant unsaturated organic species,
250 which are expected to react quickly with OH radicals (Atkinson and Arey, 2003).

251 Figure 3 shows POA concentrations obtained using the residual method with
252 different POA tracer ions, along with the PMF-derived POA factors. For the palm oil
253 experiment, the residual method overestimated the POA concentrations (compared with
254 PMF) using all of the different tracer ions. For the olive oil experiment, the residual
255 method accurately predicted the POA concentrations before the lights were turned on
256 using different tracer ions. However, after photochemical aging began, the residual
257 method did not agree with the PMF results. Using C₅H₉⁺ as a POA tracer, the residual
258 method captured the changes in POA during the first 1 h, but overestimated the POA
259 concentrations by as much as a factor of 2 for the remainder of the experiment; use of
260 the other ions led to significant POA concentration overestimation in comparison with
261 the PMF-resolved POA concentrations. The POA concentrations determined using
262 C₄H₇⁺, C₄H₉⁺, and C₇H₉⁺ were higher even than those estimated for first-order POA
263 loss; this may be attributed to the presence of these ions in SOA, which is then
264 incorrectly allocated to POA by the residual method. These observations indicate that

265 the use of associated tracer ions to calculate POA is not valid for the photochemical
266 aging of cooking oil emissions.

267 Overall, PMF analysis effectively separated POA and SOA from heated cooking
268 oils. The traditional method, which assumes first-order POA wall loss, worked well
269 when the POA was inert, as in the palm oil experiment, but greatly overestimated the
270 POA concentration in the olive oil experiment, which was attributed to the occurrence
271 of heterogeneous oxidation. The residual method failed to capture the POA
272 concentrations using any of the different POA tracer ions due to the presence of these
273 ions in the SOA mass spectrum.

274 **3.2 Mass spectra of PMF-resolved factors**

275 Figure 4 shows mass spectra of POA emissions and PMF-derived POA factors from the
276 olive and palm oils. These were also compared to the average mass spectrum of POA
277 emitted from heated sunflower, peanut, corn, and canola oils obtained from Liu et al.
278 (2017). Overall, for both oils, the POA factor mass spectra agreed very well with the
279 directly measured POA spectra. For both oil types, the θ angles between the factor and
280 measured mass spectra were less than 5° ; generally, θ angles of $0\text{--}5^\circ$, $5\text{--}10^\circ$, $10\text{--}15^\circ$,
281 $15\text{--}30^\circ$, and $> 30^\circ$ indicate excellent agreement, good agreement, many similarities,
282 limited similarities, and poor agreement, respectively, between two mass spectra
283 (Kostenidou et al., 2009; Kaltsonoudis et al., 2017). The PMF analysis slightly
284 underestimated the mass fraction at m/z 28 and slightly overestimated the mass fractions
285 at m/z s 41 and 55 in both experiments.

286 The olive oil POA factor was dominated by m/z 41 ($f_{41} = 0.105$), followed by m/z s
287 69 ($f_{69} = 0.088$), 55 ($f_{55} = 0.075$), and 43 ($f_{43} = 0.050$). In the high-resolution mass
288 spectra, the most abundant ions in these unit masses were $C_3H_5^+$, $C_5H_9^+$, $C_4H_7^+$, and
289 $C_3H_7^+$, respectively (Fig. S5S6). The olive oil POA factor mass spectrum showed
290 limited similarity ($\theta = 26^\circ$) to the average POA mass spectrum for the other cooking
291 oils. The m/z 69 abundance in the POA factor was significantly higher than those
292 (average $f_{69} = 0.026$) in POA from other oils, while the mass fractions of m/z s 29, 43,
293 and 55 were generally lower. The mass spectrum of olive oil POA measured directly in
294 this study also exhibited poor agreement ($\theta = 31^\circ$) with olive oil POA mass spectra
295 measured in an oxidation flow reactor (Liu et al., 2017) (Fig. S6S7). The mass spectral
296 differences between this study and Liu et al. (2017) may have arisen from the different
297 oil heating temperatures and dilution conditions.

298 The palm oil POA factor was dominated by m/z 55 ($f_{55} = 0.092$), followed by m/z s
299 41 ($f_{41} = 0.089$) and 43 ($f_{43} = 0.069$); the most abundant ions in these unit masses were
300 $C_4H_7^+$, $C_3H_5^+$, and $C_3H_7^+$, respectively (Fig. S5S6). The high abundances of m/z s 41
301 and 55 are similar to previous studies showing POA emissions from heated peanut,
302 canola, and sunflower oils (Allan et al., 2010), Chinese cooking (He et al., 2010), and
303 meat charbroiling (Kaltsonoudis et al., 2017). The POA factor mass spectrum exhibited
304 good agreement ($\theta = 9^\circ$) with the average mass spectrum of POA from other cooking
305 oils, although the POA factor had relatively higher mass fractions of m/z s 67 and 69
306 and lower abundances of m/z s 28 and 29. The palm oil POA factor had higher
307 abundances of oxygen-containing ions such as CO^+ , CHO^+ , CO_2^+ , and $C_3H_3O^+$ than did

308 the olive oil POA factor, resulting in a relatively higher O:C ratio (palm O:C = 0.15;
309 olive O:C = 0.09).

310 Figure 5 shows PMF-derived SOA factor mass spectra of palm and olive oil and
311 the average mass spectrum of SOA formed from sunflower, peanut, corn, canola, and
312 soybean oils, which was obtained over a 10 min period after the OA concentration
313 reached its maximum for each oil. The SOA factors were dominated by m/z s 27, 28, 29,
314 41, 43, 44, and 55; the most abundant ions in these unit masses were $C_2H_3^+$, CO^+ , CHO^+ ,
315 $C_3H_5^+$, $C_2H_3O^+$, CO_2^+ , and $C_4H_7^+$, respectively (Fig. [S5S6](#)). The abundances of oxygen-
316 containing ions were generally higher than those in the corresponding POA factors. The
317 mass fraction at m/z 43 ($f_{43} = 0.087$) was higher than f_{44} (0.059) in the olive oil SOA
318 factor, while f_{44} (0.074) dominated f_{43} (0.067) in the palm oil SOA factor. Despite these
319 differences, the mass spectra of the two SOA factors exhibited good agreement ($\theta = 8^\circ$).
320 Although the olive oil and palm oil had different NMOG compositions (Liu et al., 2018)
321 and POA mass spectra, the SOA produced by the two oils had highly similar mass
322 spectra. The SOA factor mass spectra were also highly similar ($\theta = 15^\circ$ for olive oil, 7°
323 for palm oil) to the average mass spectrum of SOA from five other cooking oils, which
324 contained a higher mass fraction of m/z 44 (average $f_{44} = 0.080$). $C_4H_7^+$, $C_4H_9^+$, $C_5H_8^+$,
325 $C_5H_9^+$, $C_6H_9^+$, and $C_7H_9^+$ ions were present in both SOA factors, which led to the
326 incorrect separation of the POA and SOA by the residual method, as discussed above.

327 **3.3 Comparison of PMF-resolved factors with ambient factors**

328 Comparisons of mass spectra from laboratory-generated cooking OA with ambient
329 PMF-resolved COA factors can help to constrain COA source apportionment. Figure

330 6a summarizes θ angles between ambient COA factors from other studies and the palm
331 oil PMF POA spectrum, average PMF SOA spectrum, and average POA and SOA
332 spectra from cooking oils. The olive oil POA mass spectrum was not included in the
333 comparison as it can vary greatly under different experimental conditions. The
334 reference mass spectra from other studies were obtained from the AMS spectral
335 database (Ulbrich, I.M., Handschy, A., Lechner, M., and Jimenez, J.L., High-Resolution
336 AMS Spectral Database. URL: <http://cires.colorado.edu/jimenez-group/HRAMSsd/>)
337 (Ulbrich et al., 2009). The agreement between ambient COA factors and the palm PMF
338 POA and average POA mass spectra decreased from 8–12° for ambient COA factors
339 from the commercial and shopping area of Mongkok in Hong Kong (Lee et al., 2015)
340 to 25–28° for ambient COA factors from a suburban area in Pasadena (Hayes et al.,
341 2013). Cooking style may be among the factors that drives this variability in θ . Mass
342 spectral agreement was better for urban areas in Hong Kong, Beijing, and Xi'an, where
343 stir-frying foods with vegetable oils is popular, than in urban European cities, where
344 grilling and broiling are prevalent (Abdullahi et al., 2013). Atmospheric oxidation may
345 also influence the correlations between the POA factor mass spectra found herein and
346 the ambient COA factors. For example, the mass spectrum of a cooking-influenced
347 organic aerosol (CIOA) factor identified in Pasadena (Hayes et al., 2013) displayed
348 better agreement with the SOA factor and average SOA mass spectra than with the POA
349 factor and average POA spectra. Kaltsonoudis et al. (2017) also found that this CIOA
350 factor correlated well with mass spectra of aged OA from meat charbroiling. The
351 average PMF SOA factor and average SOA spectrum derived herein were poorly

352 correlated (θ generally $> 30^\circ$) with other ambient COA factors (Mohr et al., 2009;
353 Crippa et al., 2013a, b; Lee et al., 2015; Elser et al., 2016; Struchmeier et al., 2016;
354 Aijala et al., 2017). Our results suggest that one should consider the cooking style and
355 atmospheric oxidation conditions when constraining COA factors with the default COA
356 mass spectral inputs.

357 Figure 7 compares the average PMF SOA factor mass spectrum and average
358 ambient semi-volatile oxygenated organic aerosol (SV-OOA) factor (Ng et al., 2011a).
359 SV-OOA is ubiquitous in the atmosphere and generally associated with SOA (Ng et al.,
360 2010). The SV-OOA factor mass spectrum was recalculated following the Aiken et al.
361 (2008) fragmentation table, assuming that the OA mass at m/z 28 was equal to that at
362 m/z 44 and that m/z 18 was equal to 22.5% of m/z 44. The average mass spectrum of
363 the PMF SOA factors exhibited poor agreement with the SV-OOA average mass
364 spectrum ($\theta = 25^\circ$). The average PMF SOA factor for cooking oils had higher
365 abundances of m/z s 27, 28, 29, 39, 41, 44, and 55 than did the SV-OOA factor and lower
366 mass fractions of m/z s 15 and 43. In particular, the SV-OOA spectrum had no signal at
367 m/z 39, while the PMF SOA factor f_{39} was 0.048. The average mass spectra of the PMF
368 SOA factors and SOA from other cooking oils were also unlike other ambient SV-OOA
369 factors ($\theta > 20^\circ$) (Mohr et al., 2009; Crippa et al., 2013a; Hayes et al., 2013;
370 Struchmeier et al., 2016; Aijala et al., 2017) (Fig. 6b). The poor correlations between
371 cooking SOA and SV-OOA were not unexpected, as ambient SV-OOA may contain a
372 mixture of SOA from numerous sources, such as vehicle exhaust, biomass burning, and
373 industrial and biogenic emissions.

374 3.4 OA oxidation state and chemical evolution

375 Figure 8 shows the H:C and O:C ratios of PMF-resolved POA and SOA factors, SOA
376 from heated cooking oils, and ambient COA and SV-OOA factors in a Van Krevelen
377 diagram. The uncertainty in determining O:C and H:C ratios was 28% and 13%,
378 respectively (Canagaratna et al., 2015). The O:C ratio and estimated average carbon
379 oxidation state (OS_C) ($OS_C \approx 219 \times O:C - H:C$) (Kroll et al., 2011) generally increase
380 with increasing atmospheric OA aging. The O:C ratios for the olive and palm PMF POA
381 were 0.09 and 0.15, respectively, comparable to those found for Chinese cooking (0.08–
382 0.13) and meat charbroiling (0.10) (Kaltsonoudis et al., 2017). The O:C ratios for the
383 olive and palm PMF SOA and SOA from other cooking oils ranged from 0.40 to 0.50,
384 slightly lower than that of SV-OOA (0.53), which indicates that the SOA formed from
385 cooking oils herein was less oxidized than ambient SV-OOA. In Van Krevelen space,
386 the entire dataset features a linear trend with a slope of approximately -0.4, which may
387 indicate oxidation mechanisms involving the addition of both carboxylic acid and
388 alcohol/peroxide functional groups without fragmentation and/or the addition of
389 carboxylic acid functional groups with fragmentation (Heald et al., 2010; Ng et al.,
390 2011b). This slope is consistent with the aging of ambient OOA (Ng et al., 2011b) and
391 lower than the -0.8 slope noted in evolving ambient OA data corrected using the
392 improved-ambient method (Heald et al., 2010). The O:C ratios of these ambient COA
393 factors ranged from 0.11 to 0.34, consistent with the oxidation trends determined for
394 cooking OA in this study. Some of the COA factors had O:C ratios higher than those
395 noted for POA from cooking emissions in laboratory studies (e.g., O:C = 0.27 for CIOA

396 in Pasadena (Hayes et al., 2013) and O:C = 0.34 for COA in Atlanta (Xu et al., 2018));
397 it is possible that these COA factors contained aged OA and/or SOA formed from
398 cooking emissions.

399 **4 Conclusions**

400 SOA formation from heated cooking oil emissions was investigated in a smog chamber
401 under high-NO_x conditions. For experiments with mixtures of POA and SOA, the POA
402 and SOA factors were separated using PMF, the traditional method, and the residual
403 method; PMF outperformed the other techniques in resolving accurate POA and SOA
404 factors. Although the traditional method, which assumes first-order POA wall losses,
405 worked well when the POA was inert, it greatly overestimated the POA concentration
406 when heterogeneous oxidation occurred. The residual method, which uses different ions
407 as POA tracers, failed to capture the POA concentrations due to the presence of these
408 ions in the SOA mass spectrum.

409 Mass spectra of palm oil PMF POA and average POA from other cooking oils
410 exhibited good agreement ($\theta = 8\text{--}14^\circ$) with ambient COA factors resolved in select
411 Chinese megacities such as Hong Kong, Beijing, and Xi'an and less similarity ($\theta = 11\text{--}$
412 23°) with ambient COA factors determined in select European cities. The mass
413 spectrum of a CIOA factor determined in Pasadena was more consistent with the
414 average PMF SOA factor mass spectrum ($\theta = 17^\circ$) than with the POA factors ($\theta = 25\text{--}$
415 28°). Our results suggest that one should consider the cooking style and atmospheric
416 oxidation conditions when performing deconvolution analyses with the default COA
417 mass spectral inputs.

418 The average mass spectra of PMF SOA factors and SOA from other cooking oils
419 exhibited little similarity ($\theta > 20^\circ$) to ambient SV-OOA factors, which is not unexpected
420 given that SV-OOA may contain a mixture of SOA from many sources. In the Van
421 Krevelen diagram, the entire data set in this study yielded a linear trend with a slope of
422 approximately -0.4, which may indicate oxidation mechanisms involving the addition
423 of both carboxylic acid and alcohol/peroxide functional groups without fragmentation
424 and/or the addition of carboxylic acid functional groups with fragmentation.

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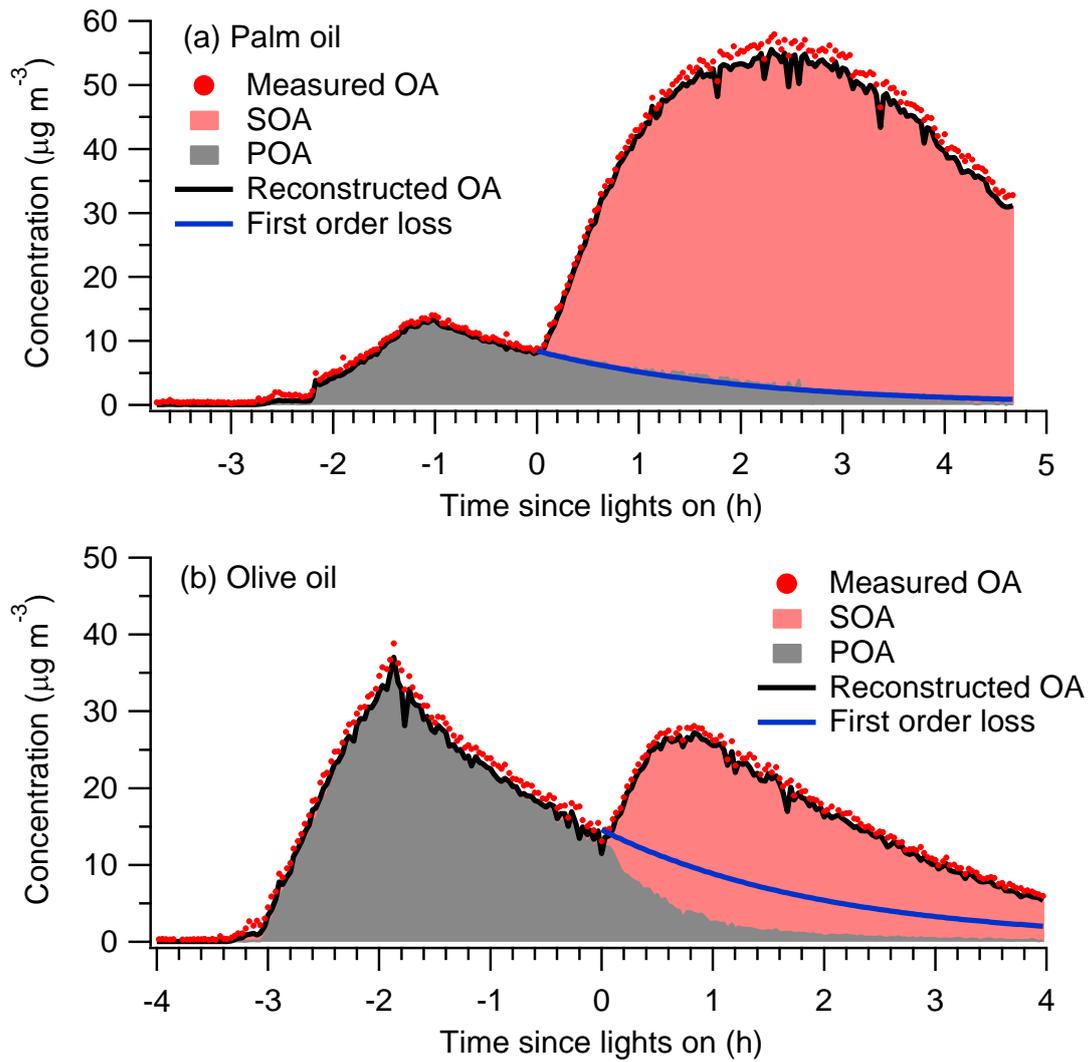
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681 **Table 1.** Experimental conditions in the photochemical aging experiments.

Cooking oil	Dilution ratio	[NMOG]:[NO _x] (ppbC:ppb)	OH exposure molec cm ⁻³ s	Category	PMF
sunflower	63	4.9	1.0×10 ¹⁰	Pure SOA	NA ^a
olive	107	4.0	1.3×10 ¹⁰	POA+SOA	2 factors
peanut	67	2.6	2.1×10 ¹⁰	Pure SOA	NA
corn	67	3.2	1.8×10 ¹⁰	Pure SOA	NA
canola	67	5.4	3.5×10 ¹⁰	Pure SOA	NA
soybean	67	3.4	1.7×10 ¹⁰	Pure SOA	NA
palm	100	18.9	1.3×10 ¹⁰	POA+SOA	2 factors

682 ^a not applicable.

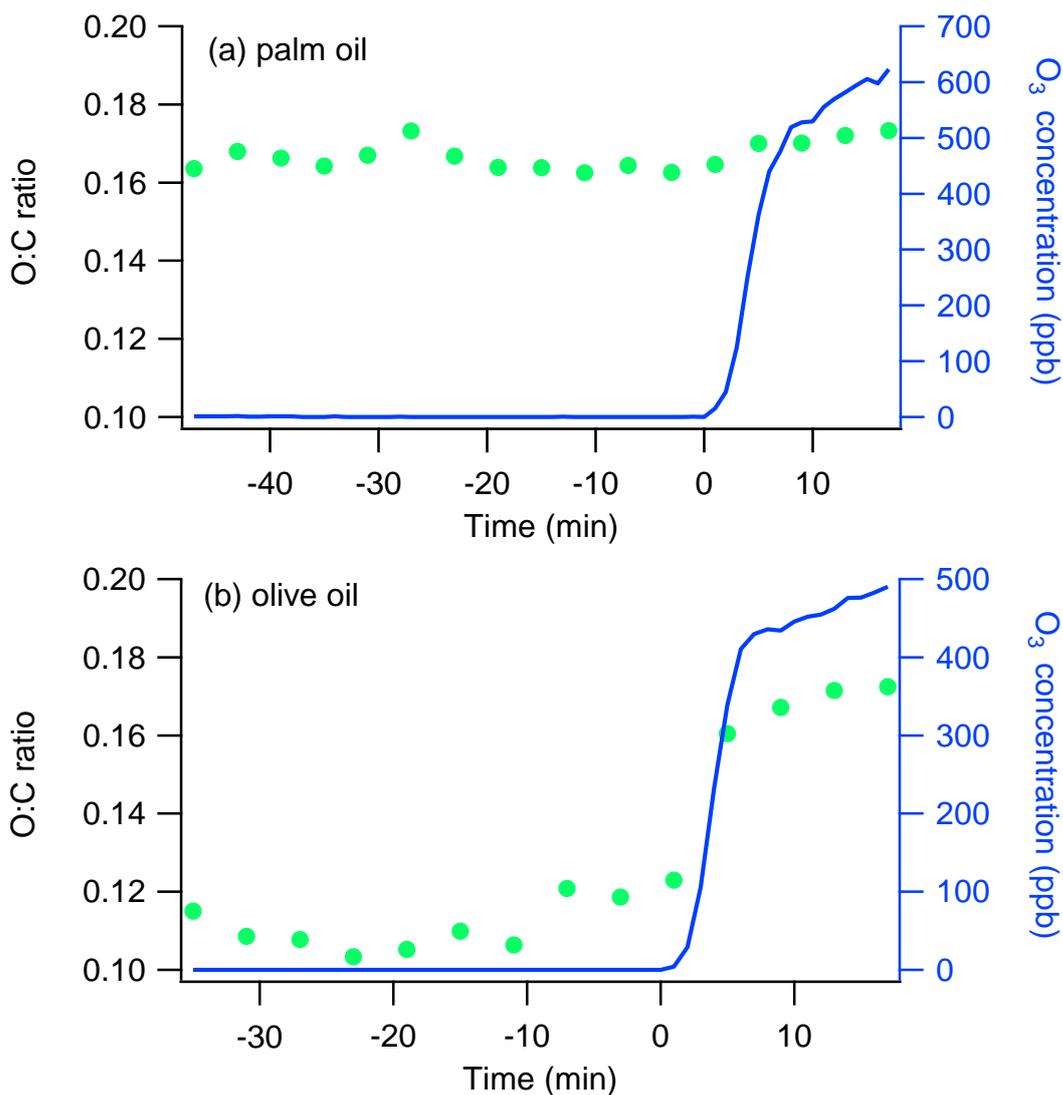


683

684 **Figure 1.** Time series of measured OA, PMF factors, and POA concentrations assuming

685 first-order loss of POA to the walls for (a) palm and (b) olive oil experiments.

686 Concentrations were not corrected for particle wall loss.



687

688 **Figure 2.** Time series of O:C ratios and O₃ concentrations for oxidation flow reactor

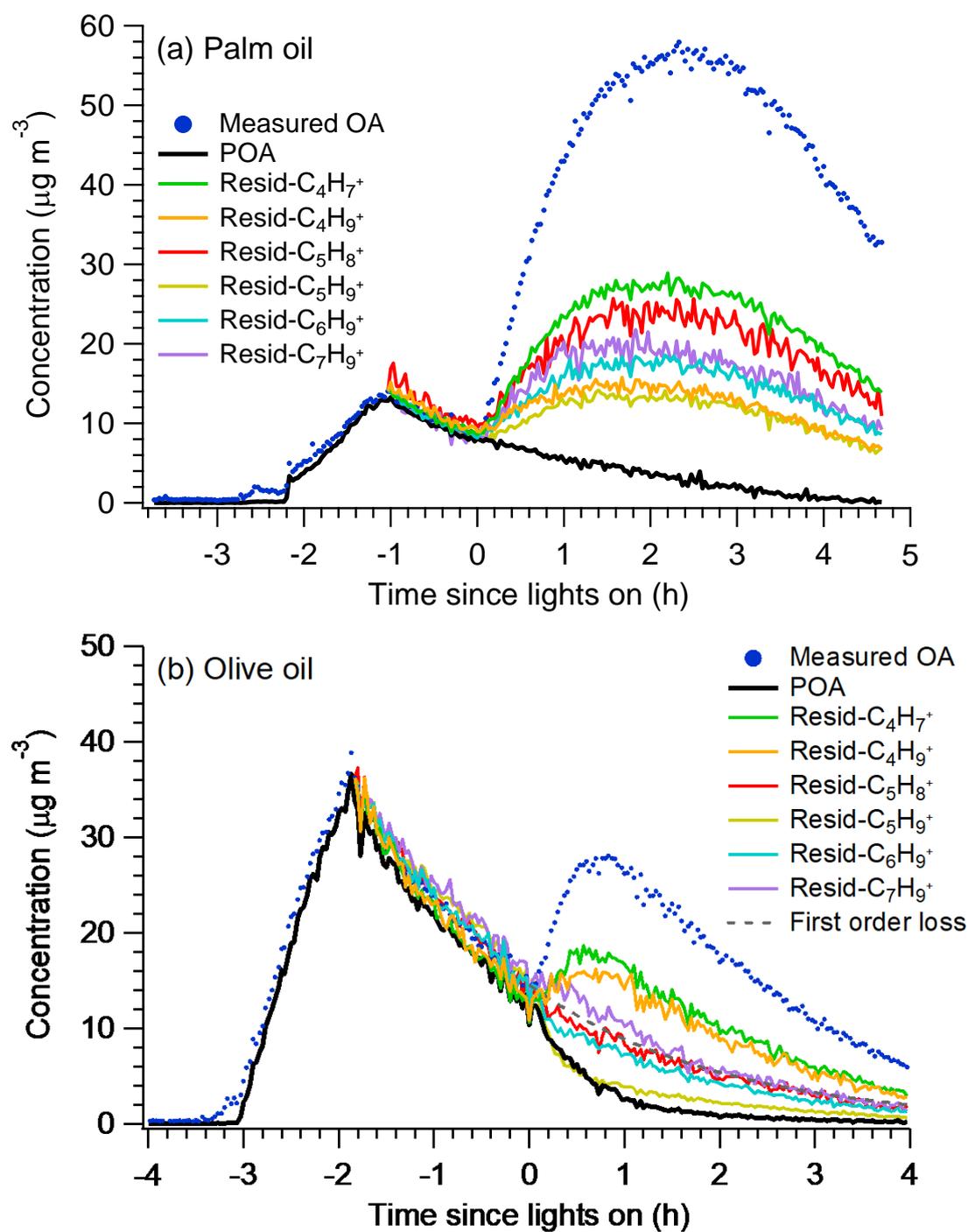
689 ozonolysis experiments with (a) palm and (b) olive oil. The ozonolysis experiments

690 involved exposing emissions from palm or olive oil to high concentrations of O₃ in an

691 oxidation flow reactor. The emissions first passed continuously through the reactor for

692 at least 30 min and then were exposed to 500–600 ppb ozone for another 17 min. Ozone

693 was introduced at time $t = 0$.

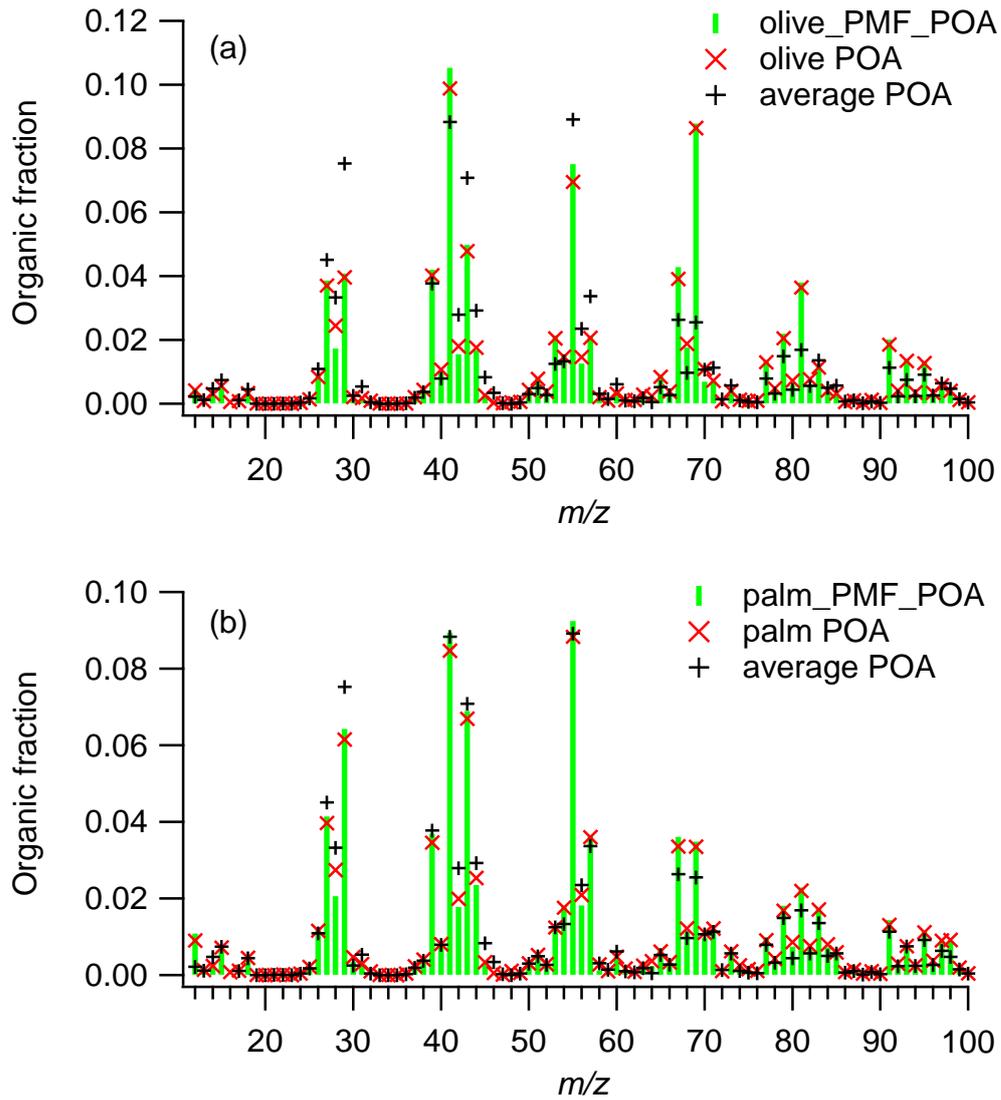


694

695 **Figure 3.** Time series of measured OA, PMF-derived POA factors, and POA

696 determined using the residual method for (a) palm and (b) olive oil experiments.

697

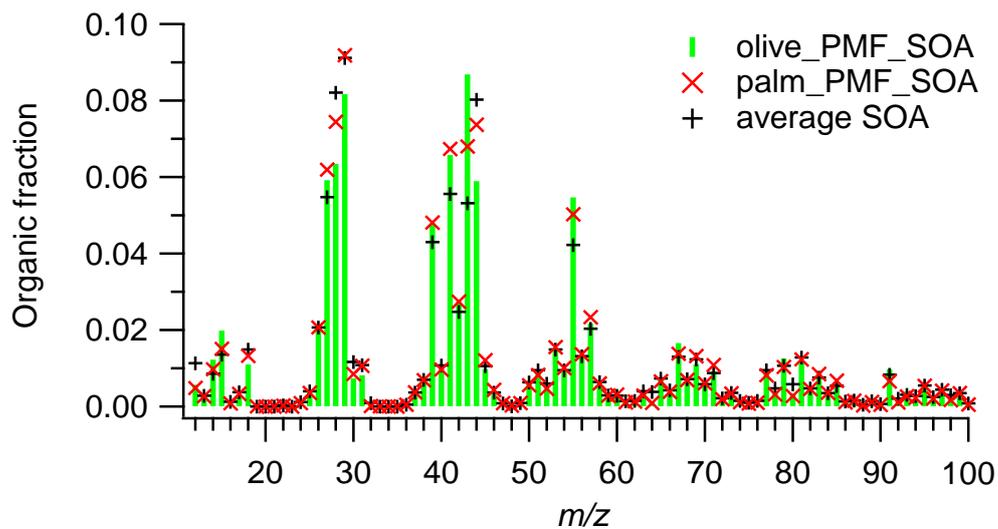


698

699 **Figure 4.** Mass spectra of POA emissions and PMF-derived POA factors for (a) olive

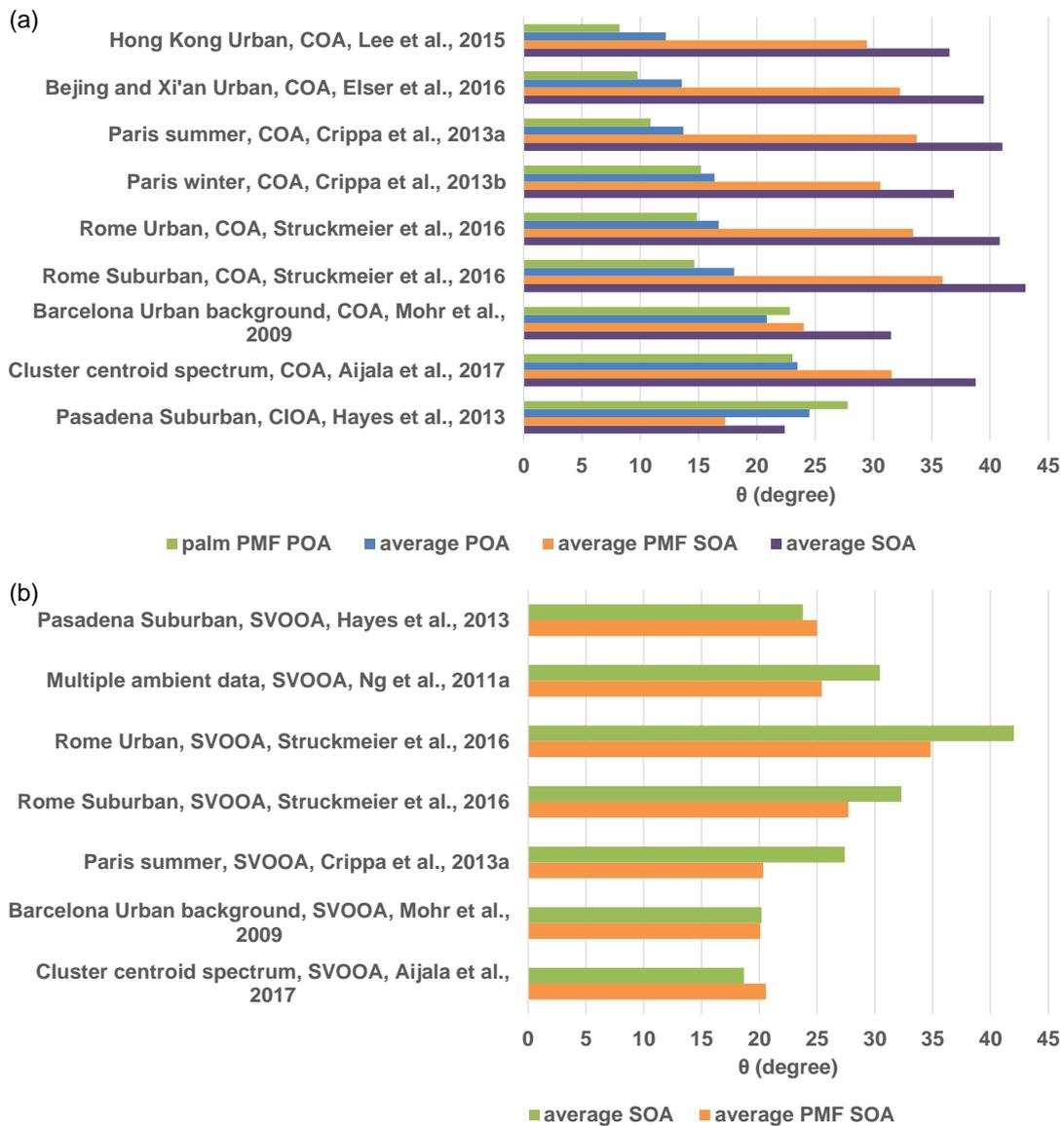
700 and (b) palm oil and, for comparison, the average mass spectrum of POA emissions

701 from sunflower, peanut, corn, and canola oils obtained from Liu et al. (2017).



702

703 **Figure 5.** Mass spectra of PMF-derived SOA factors for (a) olive and (b) palm oil and,
 704 for comparison, the average mass spectrum of SOA formed from sunflower, peanut,
 705 corn, canola, and soybean oils. The SOA mass spectra were averaged over a 10 min
 706 period after the OA concentration reached its maximum.



707

708 **Figure 6.** (a) Angles (θ) between ambient COA factor mass spectra and the palm PMF

709 POA mass spectrum, average POA mass spectrum, average PMF SOA factor mass

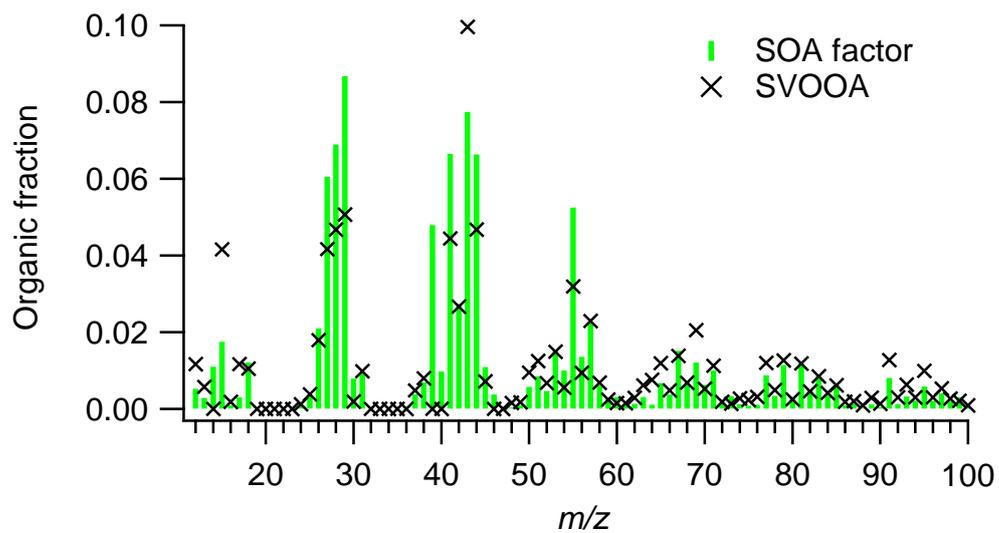
710 spectrum, and average SOA mass spectrum. (b) Angles (θ) between ambient SVOOA

711 factor mass spectra and the average PMF-derived SOA factor and average SOA mass

712 spectra. The average POA mass spectra were averaged for sunflower, peanut, corn, and

713 canola oils (Liu et al., 2017). The average SOA mass spectra were averaged for

714 sunflower, peanut, corn, canola, and soybean oils in this study.

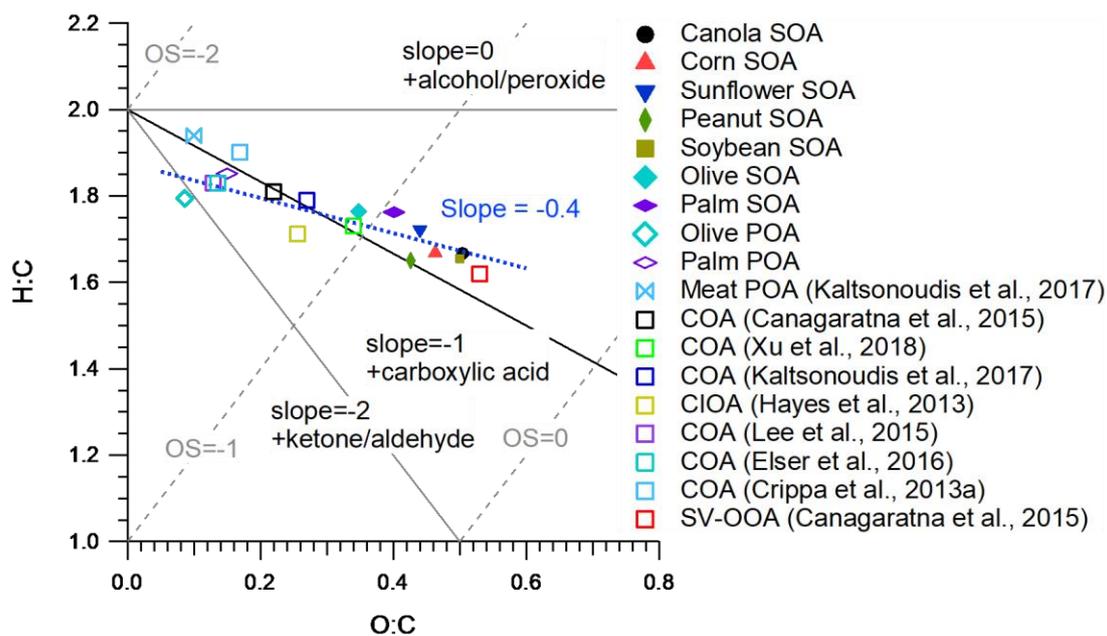


715

716 **Figure 7.** Average PMF SOA factor mass spectrum and ambient SV-OOA factor mass

717 spectrum (Ng et al., 2011a).

718



719

720 **Figure 8.** Van Krevelen diagram of POA and SOA from different cooking oils, as well

721 as ambient PMF factors. Average carbon oxidation states from Kroll et al. (2011) and

722 functionalization slopes from Heald et al. (2010) are shown for reference.