Formation of secondary organic aerosols from gas-phase emissions of heated cooking oils

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16 Abstract

Cooking emissions can potentially contribute to secondary organic aerosol (SOA) but 17 18 remain poorly understood. In this study, formation of SOA from gas-phase emissions of five heated vegetable oils (i.e. corn, canola, sunflower, peanut and olive oils) was 19 investigated in a potential aerosol mass (PAM) chamber. Experiments were conducted 20 at 19-20 °C and 65-70% RH. The characterization instruments included a scanning 21 mobility particle sizer (SMPS) and a high-resolution time-of-flight aerosol mass 22 spectrometer (HR-TOF-AMS). The efficiency of SOA production, in ascending order, 23 24 was peanut oil, olive oil, canola oil, corn oil and sunflower oil. The major SOA precursors from heated cooking oils were related to the content of mono-unsaturated 25 fat and omega-6 fatty acids in cooking oils. The average production rate of SOA, after 26 aging at an OH exposure of 1.7×10^{11} molecules cm⁻³ s, was $1.35 \pm 0.30 \,\mu g \,\text{min}^{-1}$, three 27 orders of magnitude lower compared with emission rates of fine particulate matter 28 (PM_{2.5}) from heated cooking oils in previous studies. The mass spectra of cooking SOA 29 30 highly resemble field-derived COA (cooking-related organic aerosol) in ambient air, with R^2 ranging from 0.74 to 0.88. The average carbon oxidation state (OS_c) of SOA 31 was -1.51 - -0.81, falling in the range between ambient hydrocarbon-like organic 32 aerosol (HOA) and semi-volatile oxygenated organic aerosol (SV-OOA), indicating 33 that SOA in these experiments was lightly oxidized. 34

35 **1. Introduction**

Organic aerosol (OA) is an important component of atmospheric particulate matter 36 37 (PM), which influences air quality, climate and human health (Hallquist et al., 2009). A significant fraction of OA is secondary organic aerosol (SOA) (Zhang et al., 2007), 38 formed via the oxidation of volatile organic compounds (VOCs) (Hallquist et al., 2009). 39 However, chemical transport models generally underestimate SOA levels due to the 40 unclear sources and formation processes of SOA (de Gouw et al., 2005; Heald et al., 41 2005; Johnson et al., 2006; Volkamer et al., 2006). Recently, primary semi-volatile and 42 43 intermediate-volatility organic compounds (SVOCs and IVOCs) that can come from the evaporation of primary organic aerosol (POA) were found to form substantial SOA 44 (Robinson et al., 2007; Donahue et al., 2009). Therefore, any source of POA may be 45 46 associated with the production of SOA.

Cooking-related organic aerosol (COA), thought to be primary in origin, 47 contributed 10–34.6% of the total OA in urban areas (Allan et al., 2010; Sun et al., 2011; 48 49 2012; Ge et al., 2012; Mohr et al., 2012; Crippa et al., 2013; Lee et al., 2015). Lee et al. 50 (2015) found that COA even dominated the contribution to POA at roadside sites in the commercial and shopping area of Mongkok in Hong Kong. Cooking may be a large 51 source of SOA in urban areas, yet the formation of SOA from cooking remains poorly 52 53 understood. Kaltsonoudis et al. (2016) observed that the oxygen to carbon ratio (O:C) of OA from meat charbroiling increased from 0.09 to 0.30 after a few hours of chemical 54 55 aging. The aged aerosol mass spectra have similarities with ambient COA factors in two major Greek cities. Hayes et al. (2015) modeled that cooking emissions contributed 56

19–35% of SOA mass in downtown Los Angeles during the California Research at the
Nexus of Air Quality and Climate Change (CalNex) 2010 campaign. In their study,
primary SVOCs and IVOCs from cooking emissions were modeled using the same
parameters as those from vehicle exhaust, due to limited information about SOA
formation from cooking (Hayes et al., 2015).

Heating cooking oils, a fundamental process of frying, was found to produce large 62 amounts of fine particulate matter (PM_{2.5}) (Amouei Torkmahalleh et al, 2012; Gao et 63 al., 2013) and VOCs (Katragadda et al., 2010; Klein et al., 2016a). The PM_{2.5} emission 64 65 rate for peanut, canola, corn and olive oils heated at 197 °C was shown to be as high as 54 mg min⁻¹ (Amouei Torkmahalleh et al, 2012). Allan et al. (2010) postulated that 66 cooking oils may contribute more to PM than the meat itself in urban areas of London 67 68 and Manchester. Schauer et al. (2002) estimated that cooking seed oils might contribute a significant fraction of lighter n-alkanoic acids such as nonanoic acid in the atmosphere. 69 The VOCs emitted from heated cooking oils were dominated by aldehydes (Klein et al., 70 71 2016a), which were suggested to be potential SOA precursors (Chacon-Madrid et al., 2010). Despite these previous efforts, there are still no available data regarding SOA 72 formation from heated cooking oils. 73

The objective of this study is to characterize SOA formation from gas-phase emissions of heated cooking oils. The magnitude and composition of the SOA formed from gas-phase emissions of heated cooking oils were evaluated and have been discussed for the first time in this paper.

78 2. Materials and methods

79 **2.1 PAM chamber**

SOA formation from gas-phase emissions of five different heated cooking oils was 80 81 investigated in a potential aerosol mass (PAM) chamber, which has been described in detail elsewhere (Kang et al., 2007, 2011; Lambe et al., 2011a, 2015). Briefly, a PAM 82 chamber is a continuous flow stainless steel cylindrical reactor using high and 83 controlled levels of oxidants to oxidize precursor gases to produce SOA. The volume 84 is approximately 19 L (length 60 cm, diameter 20 cm). High OH exposures were 85 produced through the photolysis of ozone irradiated by a UV lamp ($\lambda = 254$ nm) in the 86 87 presence of water vapor. Ozone was produced by an ozone generator (1000BT-12, ENALY, Japan) via irradiation of pure O₂. The OH concentration was controlled by the 88 flow rate of ozone in the PAM chamber, which was approximately 40 ppm prior to 89 90 dilution. The ozone concentration in the PAM reactor was adjusted to five different levels, ranging from 0.4 ppm to 2.7 ppm. The total flow rate in the PAM chamber was 91 set at 3 L min⁻¹ by a mass flow controller, resulting in residence time of 380 s. The 92 corresponding upper limit of OH exposure at these operating conditions was 1.7×10^{11} 93 molecules cm⁻³ s, which is equivalent to 1.3 days of atmospheric oxidation, assuming 94 an ambient OH concentration of 1.5×10^6 molecules cm⁻³ (Mao et al., 2009). The upper 95 limit of OH exposure was determined by measuring the decay of SO₂ (Model T100, 96 TAPI Inc, USA), following previous procedures (Kang et al., 2007; Lambe et al., 2011a). 97 Peng et al. (2016) found that non-OH chemistry, especially reactions with O₃, may play 98 99 a role in the oxidation flow reactors for consumption of VOCs. According to Klein et al. (2016a), emissions of VOCs from heating cooking oils were dominated by saturated 100

and unsaturated aldehydes. In this study, the ratio of O_3 exposure to OH exposure 101 ranged from 1.5×10^5 to 1.9×10^5 , relatively lower than tropospheric values (Schmidt et 102 al., 2014). At this O_{3exp}/OH_{exp}, ozonolysis of saturated and unsaturated aldehydes was 103 negligible since the ratios of their ozonolysis rate constants to OH rate constants were 104 in the range of 10⁻⁹ to 10⁻⁷. (Grosjean et al., 1993; Atkinson and Arey, 2003). Thus 105 reactions of VOCs with O₃ played a negligible role in this study. Before and after each 106 experiment, the PAM reactor was cleaned by exposure to a high concentration of OH 107 until the mass concentration of background particles was less than 5 μ g m⁻³. 108

The PAM chamber was designed with a large radius and a small surface-to-volume ratio to minimize wall effects. The transmission efficiency for particles at a mean mobility diameter (D_m) larger than 150 nm was greater than 80% (Lambe et al., 2011a). The wall loss of particles was considered to be small, as the particles larger than 150 nm accounted for greater than 70% of the aerosol mass (Fig. 1). Transmission efficiency of gases in the PAM chamber indicates that vapor wall losses in the PAM chamber are negligible (Lambe et al., 2011a).

116 **2.2 Experimental conditions**

A schematic of the experimental setup is shown in Fig. 2. The tested vegetable oils, purchased from a local supermarket, included canola (rapeseed), corn, sunflower, peanut and olive oils. For each experiment, 30 mL vegetable oil was heated at approximately 220 °C for 20 min in a 500 mL Pyrex bottle on an electric heating plate. Note that visible smoke was observed during heating of olive oil, possibly because the temperature was above the smoke point of olive oil. This high temperature may result

in increased emissions of large aldehydes from olive oil, but may not significantly 123 change the relative composition of emissions from other oils with higher smoke points 124 125 (Klein et al., 2016a). Prior to introduction to the PAM chamber, particles from the heated oil emissions were removed using a Teflon filter. An unheated 2 m Teflon tube 126 was used as the transfer line. The residence time in the transfer line was less than 2 s, 127 resulting in wall losses of VOCs less than 5% according to Liu et al. (2015). After 10 128 min of heating, the UV lamp was turned on and the emissions were exposed to high OH 129 levels for approximately one hour. Once the UV lamp was turned off, the PAM reactor 130 131 was flushed continuously using pure N_2 and O_2 until the aerosol mass was below 3 µg m⁻³. Then the experiment was repeated at another OH level. The RH and temperature 132 of the PAM outflow were measured continuously (HMP 110, Vaisala Inc, Finland) and 133 134 stabilized at 65-70% and 19-20 °C, respectively. The adjustment of RH was achieved by passing the pure N₂ and O₂ through water bubblers. Blank experiments were 135 conducted in the absence of cooking oils under similar conditions to quantify the 136 137 amount of aerosols formed from matrix gas when exposed to different OH levels.

POA emitted from heated cooking oils was also characterized in this study. For each test, 30 mL vegetable oil was heated to 240 °C for 2 min in a pan on an induction cooker. The emissions, after passing through a mixing chamber of 36 L, were first diluted by a Dekati diluter (DI-1000, Dekati Ltd, Finland) by a factor of approximately 8. Then 0.15 L min⁻¹ of the total diluted flow was introduced to the PAM chamber, achieving a final dilution ratio of approximately 160. No ozone was introduced to the

PAM chamber during measurement, and the UV lamp was off. Temperature and RHwere similar to those of the SOA formation experiments.

A scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier 146 model 3082, CPC model 3775) was used to measure particle number concentrations 147 and size distributions. Particle size ranged from 15 nm to 661 nm. An aerosol density 148 of 1.4 g cm⁻³ was assumed to estimate the SOA mass from the particle volume 149 concentration (Zhang et al., 2005). For the SOA formation experiments, the 150 contribution from background organic aerosols was subtracted from the total organic 151 aerosols. The maximum concentration of background organic aerosols was 8.4 µg m⁻³, 152 almost negligible compared with the dozens to several hundreds of $\mu g m^{-3}$ of SOA 153 formed in this study. The organic aerosol composition was characterized by a high-154 155 resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS, abbreviated as AMS hereafter, Aerodyne Research Incorporated, USA) (DeCarlo et al., 2006). A silica 156 gel diffusion dryer was connected to the sampling line to remove water. The residence 157 158 time in the dryer was approximated 8 s, sufficient to reduce the RH to less than 30%. The instrument was operated in the high sensitivity V-mode and high resolution W-159 mode alternating every one minute. The toolkit Squirrel 1.57I and Pika 1.16I were used 160 to analyze the AMS data. The molar ratios of hydrogen to carbon (H:C) and oxygen to 161 carbon (O:C) were determined with the improved-ambient method (Canagaratna et al., 162 2015). The ionization efficiency of AMS was calibrated using 300 nm ammonium 163 nitrate particles. The particle-free matrix air, obtained by passing the air through a 164 HEPA filter, was measured for at least 20 min before each experiment to determine the 165

signals from major gases. The collection efficiency (CE) was corrected by comparing 166 AMS mass concentrations to concurrent SMPS mass concentrations, following the 167 methods of Gordon et al. (2014) and Liu et al., (2015). The value of CE varied from 168 0.38 to 0.78 in this study. Note that particles were not dried prior to SMPS 169 measurements, which might lead to an overestimate of SOA mass due to the uptake of 170 water by organics. Lambe et al. (2011b) investigated the cloud condensation nuclei 171 activity of PAM-generated SOA and found that the hygroscopicity parameter κ_{org} was 172 linearly correlated with O:C ratios. Based on their κ_{org} -to-O:C relationship, we 173 174 estimated an upper limit of κ_{org} to be 0.089 in this study. The overestimate of SOA mass due to water uptake were thus determined to be less than 18% (Petters and Kreidenweis, 175 2008; Pajunoja et al., 2015). 176

177 **2.3 SOA production rate**

The SOA production rate (PR) was expressed as micrograms (µg) of SOA produced
per minute (min), calculated using the following equation, similar to calculation of
emissions rates of primary particles from cooking (Klein et al., 2016a):

181 $PR = [SOA] \times DR \times F$ (1)

where [SOA] is the SOA concentration in μ g m⁻³; DR is the dilution ratio and F is the flow rate in m³ min⁻¹ of the carrier gas. All gas-phase emissions from heated cooking oils were assumed to be transported into the PAM chamber.

Emission rates are commonly used to normalize PM emissions from cooking activities (Amouei Torkmahalleh et al, 2012; Gao et al., 2013; Klein et al., 2016a, b). Here, the adoption of SOA PR, similar to emission rates, facilitates the normalization of SOA production from cooking and direct comparison of the amount of primary emitted and secondary formed particles. Though SOA yields were not determined due to the lack of VOC concentrations, we believe that SOA PR is a useful metric for the estimation of SOA production from cooking and can be used for comparison among different studies. Note that PR is highly related to the experimental condition, especially OH exposure and temperature of the cooking oil.

194 **3. Results and discussion**

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195 **3.1 SOA formation**

196 In Fig. 3, we plot the time series of RH, ozone and organic aerosol concentrations during the aging of gas-phase emissions from heated peanut oil. As described above, the ozone 197 concentration prior to dilution was stable at approximately 40 ppm. The pulse of RH 198 199 was caused by disconnection of the introduction line when changing the Teflon filter. During the initial 10 min of heating, the mass concentration of organics was close to 200 the detection limit of the instrument, indicating that POA emissions were thoroughly 201 202 removed by the Teflon filter. During these periods of experiments where OH radicals were not present, we found that ozone chemistry had a negligible influence on SOA 203 formation in this study. Immediately after oxidation was initiated by turning on the UV 204 lamp, substantial SOA was formed, and its concentration stabilized after about 20 min. 205

Figure 4 shows SOA concentration as a function of OH exposure and

The SOA concentration subsequently reported is the average for the steady period.

208 photochemical age in days during the aging of gas-phase emissions from different 209 heated cooking oils. The OH exposure ranged from 2.7×10^{10} molecules cm⁻³ s to

 1.7×10^{11} molecules cm⁻³ s, corresponding to 0.2–1.3 days of photochemical age, 210 assuming 24 h average ambient OH concentrations of 1.5×10^6 molecules cm⁻³ (Mao et 211 al., 2009). For all experiments, the SOA concentration almost linearly increased from 212 41–107 µg m⁻³ to 320–565 µg m⁻³ as OH exposure increased. This linear increase has 213 also been observed from vehicle exhaust at a similar range of OH exposures (Tkacik et 214 al., 2014). Typically, VOCs are oxidized through functionalization reactions to produce 215 less volatile organics that readily condense to form SOA. Upon further oxidation, 216 fragmentation reactions and cleavage of carbon bonds can occur and form more volatile 217 products that reduce SOA levels (Kroll et al., 2009). In this study, functionalization 218 reactions dominated SOA formation as reflected by the increase of SOA concentrations 219 shown in Fig. 4. 220

221 The slope of the fitted straight line to the SOA data was calculated to estimate the efficiency of different cooking oils in producing SOA (Table 1). The efficiency of SOA 222 production, in ascending order, was peanut oil, olive oil, canola oil, corn oil and 223 sunflower oil. The slope of sunflower oil was $3.82 \times 10^{-15} \,\mu g$ molecules⁻¹ s⁻¹, more than 224 two times that of peanut oil. The different slopes might be related to the emission rate 225 and composition of VOCs from various cooking oils. Table 1 presents the type of fat 226 content of the different cooking oils. It should be noted that the organic vapors studied 227 here were not the specific fats present in the raw oils, but the thermal breakdown 228 products of fat lipids. Unsaturated fat accounts for 75%-88% of the total fat content. A 229 multivariate linear regression was used to relate the SOA production efficiency to the 230 fat content of cooking oils. The intercept was set to zero. The resulting equation was Y 231

232	= $2.62 \times 10^{-17} X_1 + 4.71 \times 10^{-17} X_2$, where Y is the SOA production efficiency (µg
233	molecules ⁻¹ s ⁻¹); X_1 and X_2 represent the content of mono-unsaturated fat (%) and
234	omega-6 fatty acid (%) in cooking oil, respectively. The SOA production efficiency was
235	strongly correlated ($R^2 = 0.97$, p<0.05) with the content of mono-unsaturated fat and
236	omega-6 fatty acids. This indicated that the major SOA precursors from heated cooking
237	oils were related to the content of mono-unsaturated fat and omega-6 fatty acids in
238	cooking oils. Moreover, omega-6 fatty acids dominated the contribution to SOA
239	production. Omega-6 fatty acids are a family of poly-unsaturated fatty acids that have
240	in common a final carbon-carbon double bond in the n-6 position, counting from the
241	methyl end (Simopoulos, 2002). The peroxyl radical reactions of omega-6 fatty acids
242	might emit long-chain aldehydes (Gardner, 1989), which have been suggested as
243	potential SOA precursors (Chacon-Madrid et al., 2010).

The average SOA PR from gas-phase emissions of the five cooking oils at an OH 244 exposure of 1.7×10^{11} molecules cm⁻³ s was calculated to be $1.35 \pm 0.30 \,\mu g \,min^{-1}$. Amouei 245 Torkmahalleh et al. (2012) found that primary PM_{2.5} emission rates for peanut, canola, 246 corn and olive oils heated at 197 °C ranged from 3.7 mg min⁻¹ to 54 mg min⁻¹. He et al. 247 (2004) reported a PM_{2.5} emission rate for frying in vegetable oils of 2.68±2.18 mg min⁻ 248 ¹. The SOA PR determined in this study was negligible compared with primary $PM_{2.5}$ 249 emission rates for heated cooking oils and frying in vegetable oils. However, our results 250 may underestimate SOA production from cooking under real-world conditions. First, 251 recent studies have demonstrated that the oxidation of IVOCs and SVOCs evaporated 252 from POA could produce significant SOA (Donahue et al., 2006; Jimenez et al., 2009). 253

In this study, POA from heated cooking oils was filtered. SVOCs and IVOCs might not 254 evaporate from the filter given that they might be at saturation as the aerosol was cooled 255 256 after the emissions. Second, emissions of SOA precursors will be enhanced when cooking food compared with heating cooking oils alone. For instance, long-chain 257 aldehyde emissions from frying processes can be 10 times those of heated oil (Klein et 258 al., 2016a). Large amounts of monoterpenes will be emitted when frying vegetables or 259 cooking with herbs and black pepper (Klein et al., 2016a, b). These enhanced emitted 260 precursors may significantly enhance SOA production. Finally, laboratory and tunnel 261 262 studies indicate that SOA production from typical precursors and vehicle exhaust peak at OH exposures higher than 5.0×10^{11} molecules cm⁻³ s (Tkacik et al., 2014; Lambe et 263 al., 2015). The relatively lower OH exposures in this study compared with typical 264 265 conditions in the atmosphere may lead to the underestimation of cooking SOA.

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3.2 Mass spectra of POA and SOA

Figure 5 shows high-resolution mass spectra of POA and SOA at an OH exposure of 267 2.7×10^{10} molecules cm⁻³ s from heated canola oil. Other oils have similar mass spectra, 268 as reflected in the good correlations shown in Table 2. The mass concentration of POA 269 was approximately 35 μ g m⁻³ for canola oil. The prominent peaks in POA from canola 270 oil were m/z 41 and 55, followed by m/z 29 and 43. The m/z 41, 43 and 55 were 271 dominated by $C_3H_5^+$, $C_3H_7^+$ and $C_4H_7^+$ ion series, consistent with the previous 272 observation by Allan et al. (2010). The m/z 29 was instead dominated by ion CHO⁺, 273 which can be used as a tracer for organic compounds with alcohol and carbonyl 274 functional groups, as a result of thermal decomposition of the oils (Lee et al., 2012). 275

For the SOA mass spectra, the dominating peaks were m/z 28 and 29, followed by m/z 43 and 44. The m/z 28, 29, 43 and 44 were dominated by CO^+ , CHO^+ , $C_2H_3O^+$ and CO_2^+ , respectively. For all cooking oils, the mass fractions of m/z 28 and 44 in SOA were higher, while the mass fractions of m/z 55 and 57 in SOA were lower than those of the corresponding POA. The increase of mass fractions of the oxygen-containing ions in SOA mass spectra indicated the formation of oxidized organic aerosols.

The correlation coefficients (R²) between POA and SOA unit mass resolution 282 (UMR) spectra of heated oil and COA resolved by positive matrix factorization (PMF) 283 284 analysis (Lee et al., 2015) were calculated and summarized in Table 2 to evaluate their similarities. The POA mass spectra between different cooking oils exhibited strong 285 correlations (R^2 >0.97) and agreed well with the ambient COA factor obtained at 286 287 roadside sites in the commercial and shopping area of Mongkok in Hong Kong (Lee et al., 2015). The SOA mass spectra between different cooking oils displayed good 288 correlations (\mathbb{R}^2 >0.94), suggesting a high degree of similarity. The mass spectra of 289 290 cooking SOA also greatly resemble POA and field-derived COA in ambient air, with R^2 ranging from 0.74 to 0.88. Kaltsonoudis et al. (2016) also observed that the ambient 291 COA factor in two major Greek cities in spring and summer strongly resembled the 292 aged SOA from meat charbroiling in a smog chamber. 293

Fragments derived from the AMS data have been extensively used to explore the bulk compositions and properties of ambient organic aerosols (Zhang et al., 2005; Ng et al., 2010; Heald et al., 2010). Here, we use the approach of Ng et al. (2010) by plotting the fractions of the total organic signal at m/z 43 (f₄₃) vs. m/z 44 (f₄₄). The m/z 43 signal is abundant in $C_3H_7^+$ and $C_2H_3O^+$ ions, indicating fresh, less oxidized organic aerosols. The m/z 44 signal, usually dominated by CO_2^+ and formed from the thermal decarboxylation of organic acids, is an indicator of highly oxygenated organic aerosols (Ng et al., 2010).

In Fig. 6, we plot f₄₃ vs. f₄₄ of cooking SOA and SOA data from gasoline (Presto 302 et al., 2014; Liu et al., 2015) and diesel (Presto et al., 2014) vehicle exhaust measured 303 in a smog chamber, together with the triangle defined by Ng et al. (2010) based on the 304 analysis of ambient AMS data. The ambient low-volatility oxygenated OA (LV-OOA) 305 306 and semi-volatile OOA (SV-OOA) factors fall in the upper and lower regions of the triangle, respectively. Ng et al. (2010) proposed that aging would converge the f_{43} and 307 f_{44} toward the triangle apex ($f_{43} = 0.02$, $f_{44} = 0.30$). In this study, the f_{43} and f_{44} ranged 308 309 from 0.06 to 0.10 and from 0.05 to 0.07, respectively; they mainly lie in the lower portion of the SV-OOA region. As shown in Fig. 6, SOA from gasoline and diesel 310 vehicle exhaust at a similar range of OH exposures had f₄₄ values of 0.11–0.12. 311 312 Compared with vehicle exhaust, SOA formed from gas-phase emissions of heated cooking oils was less oxidized. The potential SOA precursors from heated cooking oils 313 might be long-chain aldehydes, which are less volatile than SOA precursors such as 314 aromatics and long-chain alkanes from vehicle exhaust. Generally, the presence of 315 additional methylene and aldehyde reduce compound vapor pressure by factors of 3 316 and 22, respectively (Pankow and Asher, 2007). For example, the vapor pressure of n-317 tridecanal is approximately 14% of that of n-tridecane at 25 °C, as predicted by the 318 group-contribution model (Pankow and Asher, 2007). A single polar moiety of first-319

generation products from long-chain aldehydes will have low enough volatility to 320 condense, while more volatile aromatics and long-chain alkanes require more 321 322 functionalization to form SOA (Donahue et al., 2012). Therefore, SOA formed from heated cooking oils was less oxidized. For each cooking oil, there was little change in 323 f_{44} and a slight increase in f_{43} as OH exposure increased. The increased SOA mass may 324 facilitate the partitioning of more volatile organics, leading to a slight increase in f_{43} 325 and little change in f_{44} . This is consistent with the observation of previous studies that 326 the f₄₄ of SOA from aromatics and monoterpenes varied little and that f₄₃ increased 327 slightly for SOA mass loadings higher than 100 µg m⁻³ (Ng et al., 2010; Kang et al., 328 2011). 329

330 **3.3 Chemical composition of SOA**

331 The O:C ratio and the estimated average carbon oxidation state (OS_c) (OSc \approx 2×O:C – H:C) (Kroll et al., 2011) can be used to evaluate the degree of oxidation of organic 332 aerosols. Fig. 7 shows the evolution of O:C ratios and OS_c of SOA from heated cooking 333 334 oils as a function of OH exposure, together with the POA data. The O:C ratios and OS_c of POA were in the range of 0.14-0.23 and -1.61 - -1.44, respectively, comparable to 335 those of POA from meat charbroiling (Kaltsonoudis et al., 2016). As shown in Fig. 7, 336 for each cooking oil, the O:C and OS_c of SOA displayed similar trends, initially 337 decreasing rapidly and then increasing slowly or leveling off (for canola oil only). In 338 this study, the increased SOA mass loadings led to the rapid decrease of the oxidation 339 degree when the OH exposure increased from 2.7×10^{10} molecules cm⁻³ s to 6.4×10^{10} 340 molecules cm⁻³ s. As OH exposure and the resulting OA mass loadings further increase, 341

even less oxidized and more volatile organics partition into the particle phase and thus 342 decrease the oxidation degree (Donahue et al., 2006). The difference in O:C for 343 different cooking oils at the same OH exposure may be attributed to the differences in 344 gas-phase SOA precursors. In general, the O:C ratios of SOA formed from gas-phase 345 emissions of heated cooking oils ranged from 0.24 to 0.46 at OH exposures of 2.7×10^{10} 346 -1.7×10^{11} molecules cm⁻³ s. The OS_c of cooking SOA was -1.51 - -0.81, falling in the 347 range between ambient hydrocarbon-like organic aerosol (HOA, $OS_c = -1.69$) and SV-348 OOA ($OS_c = -0.57$) corrected by the improved-ambient method (Canagaratna et al., 349 2015). As suggested by Canagaratna et al. (2015), the OS_c is more robust than the f_{43}/f_{44} 350 relationship for evaluating the oxidation degree of organic aerosols, as the former has 351 been estimated based on the full spectra. 352

In Fig. 8 we plot the H:C and O:C molar ratios of POA and SOA from heated cooking oils on a Van Krevelen diagram. The cooking data fell along a line with a slope of approximately 0, suggesting the chemistry of SOA formation in this study was alcohol/peroxide formation (Heald et al., 2010; Ng et al., 2011). This slope is different from ambient OA data of -0.8 determined by the improved-ambient method (Heald et al., 2010). It is also different from vehicle exhaust data with slopes ranging from -0.59 to -0.36 (Presto et al., 2014; Liu et al., 2015).

4. Conclusions

Formation of SOA from gas-phase emissions of heated cooking oils was investigated in a PAM chamber at OH exposures of 2.7×10^{10} molecules cm⁻³ s to 1.7×10^{11} molecules cm⁻³ s. The OS_c and f₄₃/f₄₄ relationship indicated that the SOA formed was lightly

oxidized. The mass spectra of SOA highly resembled POA from heated cooking oils 364 and COA factors in ambient air. The major SOA precursors from heated cooking oils 365 were related to the content of mono-unsaturated fat and omega-6 fatty acids in cooking 366 oils. Considering that animal fats such as pork and chicken fat are also abundant in 367 mono-unsaturated fat and omega-6 fatty acids, gas-phase emissions from cooking 368 animal fat might also produce SOA. It is important to note that the reported SOA data 369 only related to gas-phase emissions from heated cooking oils. The large amounts of 370 POA emitted from cooking oils may also form SOA after photochemical aging. More 371 372 work is needed to investigate SOA formation from emissions of cooking oils and food. In addition, gas-phase SOA precursors were not characterized and therefore provided 373 limited information on SOA yields from cooking; we recommend that future work 374 375 validate our results and perform similar experiments, with gas-phase SOA precursors characterized. 376

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0115.						
	Slope ^b	Saturated	Mono-	Poly-unsat	Others	
	µg molecules ⁻¹ s ⁻¹	(%)	unsaturated (%)	Omega-6	Omega-3	(%)
sunflower	3.82×10 ⁻¹⁵	10	19	64	0	7
corn	3.31×10 ⁻¹⁵	12	24	56	1	7
canola	2.68×10 ⁻¹⁵	7	59	20	9	5
olive	2.55×10 ⁻¹⁵	13	71	8	1	7
peanut	1.7×10 ⁻¹⁵	16	44	31	0	9

Table 1. SOA production efficiency and type of fat content (%) ^a of different cooking
oils.

^a The type of fat content of cooking oils was derived from skillsyouneed.com.

^bSOA production efficiency was presented as the slope of the fitted straight line to the

640 SOA concentration vs OH exposure.

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4	amblent COA resolved by FMP.											
		CA P ^a	CN P	SR P	PT P	OE P	CA S	CN S	SR S	PT S	OE S	COA ^b
	CAP	1.00	0.99	1.00	0.98	0.97	0.85	0.87	0.91	0.93	0.94	0.96
	CN P	0.99	1.00	0.99	0.99	0.99	0.89	0.90	0.94	0.96	0.96	0.95
	SR P	1.00	0.99	1.00	0.98	0.97	0.85	0.87	0.91	0.93	0.94	0.96
	PT P	0.98	0.99	0.98	1.00	0.98	0.83	0.85	0.90	0.93	0.93	0.96
	OE P	0.97	0.99	0.97	0.98	1.00	0.86	0.88	0.93	0.95	0.96	0.94
	CA S	0.85	0.89	0.85	0.83	0.86	1.00	0.95	0.98	0.96	0.94	0.74
	CN S	0.87	0.90	0.87	0.85	0.88	0.95	1.00	0.95	0.96	0.96	0.77
	SR S	0.91	0.94	0.91	0.90	0.93	0.98	0.95	1.00	0.99	0.97	0.83
	PT S	0.93	0.96	0.93	0.93	0.95	0.96	0.96	0.99	1.00	0.99	0.87
	OE S	0.94	0.96	0.94	0.93	0.96	0.94	0.96	0.97	0.99	1.00	0.88

Table 2. Correlation coefficients (\mathbb{R}^2) between POA and SOA UMR mass spectra and ambient COA resolved by PMF.

^a CA, CN, SR, PT and OE refer to canola, corn, sunflower, peanut and olive oil.

^bLee et al. (2015).





Fig. 1. Size distribution of particle volume of SOA for sunflower oil at an OH exposure

650 of 2.7×10^{10} molecules cm⁻³ s.



Fig. 2. Schematic of the experimental setup.



Fig. 3. Time series of (a) relative humidity (RH), (b) ozone and (c) organic concentrations during the aging of gas–phase emissions from heated peanut oil. The yellow and light blue regions represent the heating oil and OH exposure period, respectively. The green region is the overlap between heating oil and OH exposure period.

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Fig. 4. SOA concentration vs. OH exposure and photochemical age in days (at $[OH] = 1.5 \times 10^6$ molecules cm⁻³) during the aging of gas–phase emissions from different heated cooking oils. Error bars represent the standard deviation (1 σ).



Fig. 5. Mass spectra of POA and SOA at an OH exposure of 2.7×10¹⁰ molecules cm⁻³ s
from heated canola oil.



Fig. 6. Fractions of total organic signal at m/z 43 (f₄₃) vs. m/z (f₄₄) from SOA data in this work together with the triangle plot of Ng et al. (2010). SOA data from gasoline (Presto et al., 2014; Liu et al., 2015) and diesel (Presto et al., 2014) vehicle exhaust measured in smog chamber studies are shown. Data from this work and the literature are colored according to OH exposure. Ambient SV–OOA and LV–OOA regions are adapted from Ng et al. (2010).



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Fig. 7. Evolution of (a) oxygen to carbon (O:C) molar ratios and (b) average carbon oxidation state (OS_c) as a function of OH exposure during the aging of gas-phase emissions from heated different cooking oils, with error bars indicating standard error. Data at [OH] = 0 represent POA from cooking oils.



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Fig. 8. Van Krevelen diagram of POA and SOA from heated different cooking oils. Error bars represent the standard deviations (1σ) . SOA Data are colored by OH exposure. Average carbon oxidation states from Kroll et al. (2011) and functionalization slopes from Heald et al. (2010) are shown for reference.

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