Response to Reviewer #1

## General comments:

This paper shows the production of SOA from oil vapours associated with cooking using a PAM chamber, which is of strong relevance for the modelling and source apportionment of urban particulate matter. While questions persist regarding how atmospherically representative PAM yields are, this paper focuses on the qualitative mass spectral features, comparisons of different oils and speculations on chemical mechanisms, which will no doubt prove highly useful for further studies, so is well within scope for ACP and represents a decent contribution to the science. The paper is generally well written and I recommend publication after consideration of minor comments.

**Q1:** I find myself at odds with the conclusion that some of the ambient reported COA in other studies could be secondary in nature because the SOA spectrum shows inconsistencies with the key features normally reported. Specifically, the m/z=41 peak is relatively low compared to m/z=43 and the m/z=44 peak is much higher. By comparison, the POA spectrum is very consistent with the literature. I should note that $R^2$ is not a good metric to compare spectra in the context of discussing PMF outputs because these spectra are derived according to precision-weighted variance, so factors tend to be dictated by the 'strong' variables, i.e. a subset of peaks with the highest signal-to-noise ratios, so it is these features that should really be compared. Furthermore, previously reported diurnal profiles of COA almost universally show a maximum in late evening, which is after dusk in many cases, where oxidation through the OH pathway is not plausible (while ozone and nitrate oxidation of unsaturated bonds will occur, this is not what is investigated here). I think it far more likely that any cooking SOA contribution will be included with one of the OOA factors in a typical urban PMF study. I would recommend that the authors adjust their conclusions accordingly.

R1: We agree with the reviewer that $R^2$ is not a good metric to give a conclusion here. The relevant discussion in the manuscript has been revised accordingly. The following sentences were deleted.

"*suggesting that COA might not be entirely primary in origin*" (Line 31-32).

"*This similarity between the cooking SOA and ambient COA suggests that the COA resolved based on ambient data may be a convolution of POA and SOA, even though vegetable oil may not be the oil commonly used in commercial kitchens.*" (Line 294-297).

"*These similarities indicated that ambient COA factors identified by AMS could contain cooking SOA.*" (Line 371-372).

**Q2:** All the oils were heated to 220C. While I can recognise the value in experimental consistency, this is possibly beyond the smoke point of some of the oils used here (depending on their grade). Can the authors verify that the oils did not give off visible smoke during the experiments? If they did, this should be added as an important caveat because this would fundamentally alter the emissions profiles.

R2: Visible smoke was only observed during heating olive oil, probably due to the low smoke point of olive oil. According to Klein et al. (2016), olive oil emissions show an increase in larger aldehydes such as nonanal and 2,4-decadienal when the temperature increased from 160 to 220 °C. But for sunflower and canola oil, changing the temperature from 160 to 220 °C do not significantly change the relative composition of their emissions. The following sentences were added to the revised manuscript for clarification.

"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 change the relative composition of emissions from other oils with higher smoke points (Klein et al., 2016a)." (Line 122-126).

## Specific comments:

**Q3:** Line 67: Allan et al. (2010) did not strictly find the conclusion that cooking oils were a major contribution; this was a speculative explanation for trends within the data. More conventional marker-based studies (e.g. using chromatography) are probably more of more value to support this notion.

R3: We agree but at the same time conclusions based on marker studies cannot reveal the relative contribution of cooking oils to PM. A study by Schauer et al. (2002) was added to emphasize the large emissions of organic vapor and aerosols from heating cooking oils.

The sentence "*Allan et al. (2010) found that cooking oils may contribute more to PM than the meat itself in urban areas of London and Manchester.*" has been revised and now reads:

"Allan et al. (2010) postulated that cooking oils may contribute more to PM than the meat itself in urban areas of London 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." (Line 67-71).

**Q4:** Line 111: Was the Teflon transfer line heated? If not, some condensation onto the tube may have occurred. The authors should comment on whether they consider this to be an issue.

R4: The Teflon transfer line was not heated. However, the residence time in the transfer line was less than 2 s to minimize wall loss of VOCs. Furthermore, vapors from cooking oils were continuously introduced to the PAM chamber for 10 min to saturate the transfer lines before the UV lamp was turned on. According to Liu et al. (2015), the losses of VOCs in Teflon transfer lines with such a short residence time were less than 5%.

The sentence "*A 2 m Teflon tube was used as the transfer line to minimize wall loss of VOCs.*" has been revised and now reads:

"An unheated 2 m Teflon tube was used as the transfer line. The residence time in the transfer line was less than 2 s, resulting in wall losses of VOCs less than 5% according to Liu et al. (2015). " (Line 127-130).

**Q5:** Line 125: How were the flow rate and dilution ratio measured/estimated?

R5: The original text may have misled the reviewer. 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. The sentences "*The emissions, after passing through a mixing chamber of 36 L, were introduced to the PAM chamber by a Dekati diluter (DI-1000, Dekati Ltd, Finland) at a flow rate of 0.15 L min$^{-1}$, achieving a final dilution ratio of approximately 160.*" has been revised and now reads:

"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." (Line 142-146).

**Q6:** Line 163: PR has a number of issues, not least of which is the fact that the oxidant concentrations and simulated timescales in PAM are far in excess of those likely experienced in urban atmospheric and chamber studies. While I am not questioning its usefulness, I would put some caveats in concerning its quantitative merit.

R6: We concede that PR may be affected by a number of factors such as the OH exposure and the temperature of the cooking oil. For this study, the OH exposure ranged from 2.7×10$^{10}$ molecules cm$^{-3}$ s to 1.7×10$^{11}$ molecules cm$^{-3}$ s, equivalent to 0.2–1.3 days of atmospheric oxidation, actually comparable with those in urban atmospheric and chamber studies. As a caution, the following sentence has been added to the revised manuscript.

"Note that PR is highly related to the experimental condition, especially OH exposure and temperature of the cooking oil." (Line 195-196).

**Q7:** Line 222: It should be noted that the S- and IVOCs will most likely evaporate from the filter if they are not at gas phase saturation, although I concede that given that the aerosol is cooling, it is most likely that they are at saturation in this case. However, an experiment where filtration occurs after dilution may produce different results, so this should be noted.

R7: The following sentence has been added.

"SVOCs and IVOCs might not evaporate from the filter given that they might be at saturation as the aerosol was cooled after the emissions." (Line 257-259).

**Q8:** Line 260: The statement about vegetable oil not being used in commercial kitchens needs further explanation because the vegetable oils studied here are almost universal in many countries. Are the authors referring to Hong Kong specifically? What other oils are in use and why weren't these studied here?

R8: It is true that vegetable oils are not commonly used in commercial kitchens in Hong Kong. Vegetable oils are widely used in residential cooking. However, this statement has been removed when addressing the Q1.

**Q9:** Line 284: Statements are made concerning vapour pressures, but it is all very nonspecific and hand-waving. Some typical saturation vapour pressures (either measured or predicted) for some example compounds should be given.

R9: The following text was added to the revised manuscript.

"Generally, the presence of additional methylene and aldehyde reduce compound vapor pressure by factors of 3 and 22, respectively (Pankow and Asher, 2007). For example, the vapor pressure of n-tridecanal is approximately 14% of that of n-tridecane at 25 °C, as predicted by the group-contribution model (Pankow and Asher, 2008)." (Line 321-325).

**Q10:** Line 336: The conclusion regarding animal fat yields should be treated as a speculative inference because while a correlation with omega-6 is found here, its role as a determining factor is not conclusively proven.

R10: Softer word was used in the revised manuscript.

"*can be as efficient as vegetable oils in producing SOA*" was changed to "might also produce SOA" (Line 376).

**Q11:** Line 343: The 'gas phase' measurements referred to should be specified, e.g. GC-MS.

R11: Here, 'gas phase' mainly referred to SOA precursors, which can be characterized by GC-MS, PTR-MS and/or other instruments.

"*with gas-phase emissions measured*" was changed to "with gas-phase SOA precursors characterized" (Line 383).

**Q12:** Supplement: I would argue that both graphs in the supplementary material are of sufficient interest to warrant inclusion in the main article.

R12: Both graphs were added to the revised manuscript.

## Technical comments:

**Q13**: The term 'canola' will not be familiar to all readers worldwide. The alternative name 'rapeseed' should be offered somewhere, by way of explanation.

R13: Rapeseed was added to the revised manuscript when canola oil was mentioned for the first time.

**Q14:** Line 124: The model of the Dekati dilutor should be given.

R14: The model DI-1000 was given in the revised manuscript.

**Q15:** Line 139: More information on the diffusion drier must be given. I would note that membranes such as Naphion are known to remove OVOCs. Do the authors have a rough idea what RH the AMS sampled at?

R15: A silica gel diffusion dryer was used here. It is widely used and will not remove VOCs. The residence time in the dryer was approximated 8 s, sufficient to reduce the RH to less than 30%.

The sentence "*A diffusion dryer was connected to the sampling line to remove water.*" has been revised and now reads:

"A silica gel diffusion dryer was connected to the sampling line to remove water. The residence time in the dryer was approximated 8 s, sufficient to reduce the RH to less than 30%." (Line 159-161).

**Q16**- Line 196: It should be noted that the fatty acid vapors studied here are not the specific fats present in the raw oils, but thermal breakdown products of fat lipids.

R16: Agree. The following sentence was added to the revised manuscript.

"It should be noted that the organic vapors studied here were not the specific fats present in the raw oils, but the thermal breakdown products of fat lipids." (Line 230-232).

References:

Klein, F., Platt, S. M., Farren, N. J., Detournay, A., Bruns, E. A., Bozzetti, C., Daellenbach, K. R., Kilic, D., Kumar, N. K., Pieber, S. M., Slowik, J. G., Temime-Roussel, B., Marchand, N., Hamilton, J. F., Baltensperger, U., Prévôt, A. S. H., and El Haddad, I.: Characterization of Gas-Phase Organics Using Proton Transfer Reaction

Time-of-Flight Mass Spectrometry: Cooking Emissions, Environ Sci Technol, 50, 1243-1250, 10.1021/acs.est.5b04618, 2016.

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Pankow, J. F., and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, Atmos. Chem. Phys., 8, 2773-2796, 10.5194/acp-8-2773-2008, 2008.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 4. C1−C27 Organic Compounds from Cooking with Seed Oils, Environ Sci Technol, 36, 567-575, 10.1021/es002053m, 2002.

Response to Reviewer #2

## General comments:

This work reports secondary organic aerosol (SOA) formation by OH radical oxidation of VOCs emitted from heated cooking oil using an oxidation flow reactor approach. Cooking emissions have been recognized as one of the major primary organic aerosol (POA) sources in urban environments. However, SOA formation potential of cooking emissions are largely unknown and hence this study is of great interest to the atmospheric community. Although the observations presented in this manuscript is qualitative due to their experimental limitations, this work clearly demonstrates SOA formation from cooking emissions that provide sufficient insight into future studies. The experiments are well performed in general but some clarifications are required, in particularly the relative importance of other oxidation chemistry in the flow tube reactor. The manuscript is well written and organized. I recommended this manuscript to be published in Atmospheric Chemistry and Physics after addressing the specific comments below:

## Specific comments:

**Q1:** This manuscript focuses on discussing SOA production from OH radical oxidation chemistry. However, a recent modelling study by Peng et al. (2016) has illustrated potential significance of non-OH chemistry in oxidation flow reactors (OFR) for degradation of various SOA precursors. For example, some unsaturated VOCs such as monoterpenes might largely involve in the reaction with ozone depending on operating conditions of OFR. Since this manuscript demonstrates that mono- and poly-unsaturated fatty acids are important SOA precursors from heated cooking oils, it is necessary to comment on the relative importance of non-OH chemistry in the PAM reactor, especially for ozonolysis of unsaturated fatty acids, and how may this related to the observations reported in this manuscript. Control experiments of ozonolysis in the absence of OH radical may provide insight into this issue.

R1: As was also mentioned by Reviewer 1, it should be noted that the organic vapors studied here were not the specific fatty acids present in the raw oils, but the thermal breakdown products of these fatty acids. According to Klein et al. (2016), emissions of VOCs from heating cooking oils were dominated by saturated and unsaturated aldehydes. In this study, the ratio of $O_3$ exposure to OH exposure ranged from $1.5\times10^5$ to $1.9\times10^5$, relatively lower than tropospheric values (Schmidt et al., 2014). At this $O_{3exp}/OH_{exp}$, ozonolysis of saturated and unsaturated aldehydes was negligible since the ratios of their ozonolysis rate constants to OH rate constants were in the range of $10^{-9}$ to $10^{-7}$. (Grosjean et al., 1993; Atkinson and Arey, 2003). Thus reactions with $O_3$ played a negligible role in this study. In addition, SOA formation in the absence of OH radicals was also tested. As shown in Fig. 3 in the revised manuscript, during the initial 10 min of heating, the mass concentration of organics was close to the detection limit of the instrument. During these periods of experiments, OH radicals were not present, indicating that ozone chemistry had a negligible influence on SOA formation in this study.

The following sentence has been added to the manuscript.

"Peng et al. (2016) found that non-OH chemistry, especially reactions with $O_3$, may play 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 and unsaturated aldehydes. In this study, the ratio of $O_3$ exposure to OH exposure ranged from $1.5\times10^5$ to $1.9\times10^5$, relatively lower than tropospheric values (Schmidt et al., 2014). At this $O_{3exp}/OH_{exp}$, ozonolysis of saturated and unsaturated aldehydes was negligible since the ratios of their ozonolysis rate constants to OH rate constants were in the range of $10^{-9}$ to $10^{-7}$. (Grosjean et al., 1993; Atkinson and Arey, 2003). Thus reactions of VOCs with $O_3$ played a negligible role in this study." (Line 99-107).

"During these periods of experiments where OH radicals were not present, we found that ozone chemistry had a negligible influence on SOA formation in this study." (Line 205-207).

**Q2:** Line 88: What was the initial ozone concentration in the PAM reactor?

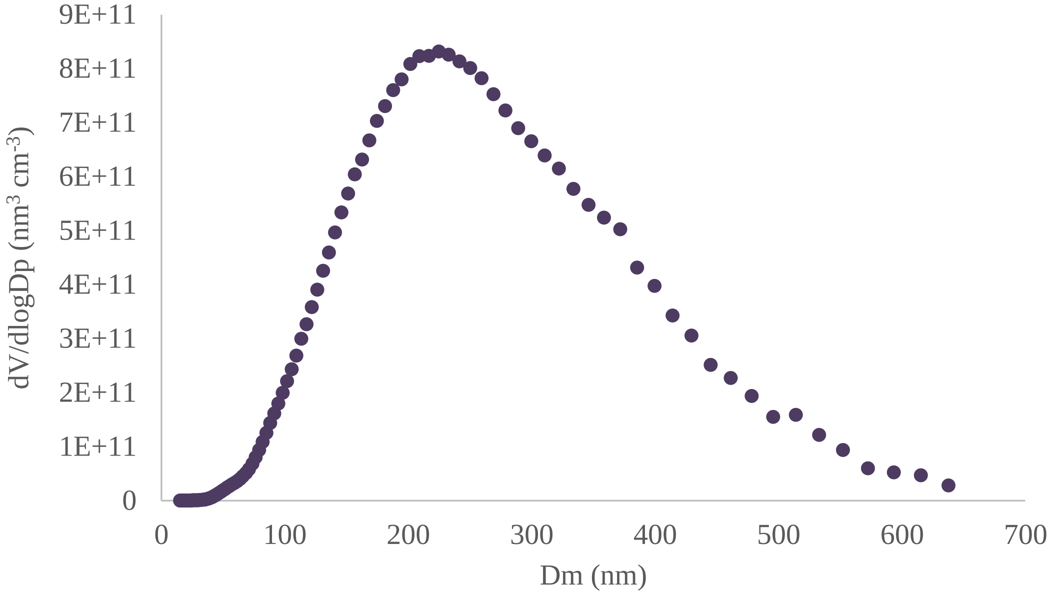
R2: The ozone concentration in the PAM reactor was adjusted to five different levels, ranging from 0.4 ppm to 2.7 ppm. This sentence has been added to the revised manuscript (Line 91-92).

**Q3:** Line 111: Was the Teflon line heated and temperature controlled to minimize wall loss of VOCs? Please clarify.

R3: This issue has been addressed in response to Q4 of Reviewer 1.

**Q4:** Particle mass determination from SMPS data: Line 131: In general, particle effective density of SOA can be estimated by comparing SMPS data and particle time-of-flight (PToF) measurements from AMS in laboratory experiments. Did the authors conduct this type of estimation to validate their assumption? Furthermore, Figure 1 illustrates that aerosol particles were not dried before SMPS measurements. Please discuss uncertainties of SOA mass calculation due to the presence of aerosol water content.

R4: The following figure shows the volume distribution of SOA measured by AMS for sunflower oil at an OH exposure of 1.7×$10^{11}$ molecules $cm^{-3}$ s. The mode diameter fell in the range of 210 nm to 230 nm. This variation of mode diameter might lead to large uncertainties in calculating the effective density. For instance, the effective density for sunflower oil SOA was estimated to be 1.55±0.28 by comparing SMPS data and PToF measurements from AMS. The density of SOA for other oils was expected to be similar with that for sunflower oil, considering their similar H:C and O:C ratios. Taking considerations of the large uncertainty, the assumption of 1.4 g $cm^{-3}$ is reasonable.



Lambe et al. (2011) investigated the cloud condensation nuclei activity of PAM-generated SOA and found that the hygroscopicity parameter $\kappa_{org}$ was linearly correlated with O:C ratios. Based on their $\kappa_{org}$-to-O:C relationship, we estimated an upper limit of $\kappa_{org}$ to be 0.089 in this study. The overestimate of SOA mass due to water uptake were thus determined to be less than 18%. The following sentences have been added to the revised manuscript.

"Note that particles were not dried prior to SMPS measurements, which might lead to an overestimate of SOA mass due to the uptake of water by organics. Lambe et al. (2011b) investigated the cloud condensation nuclei activity of PAM-generated SOA and found that the hygroscopicity parameter $\kappa_{org}$ was linearly correlated with O:C ratios. Based on their $\kappa_{org}$-to-O:C relationship, we estimated an upper limit of $\kappa_{org}$ 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, 2008; Pajunoja et al., 2015)." (Line 171-179).

**Q5:** Line 147: What was the collection efficiency (CE) for the SOA produced? Primary cooking organic aerosol is likely oil-like droplets that gives CE approximately equal to 1. Such information can provide insight into the viscosity of SOA produced from cooking emissions (i.e. particle bouncing on tungsten vaporizer increased with particle viscosity).

R5: The CE varied from 0.38 to 0.78 in this study. Given that a diffusion dryer was used to remove water, which may change the morphology of SOA, we may not speculate on the viscosity of SOA.

The following sentence has been added to the manuscript.

"The value of CE varied from 0.38 to 0.78 in this study." (Line 171).

**Q6:** SOA production rate: I agree that it is reasonable to define SOA production rate as SOA mass produced per minute due to the experimental limitations (i.e. no VOC measurements). However, considering emission rates of VOCs from oils at a given temperature can be different, an additional SOA production rate defined as SOA mass produced per volume of oil evaporated may be able to reduce one experimental variable for interpreting the data (e.g. line 195-196). It is recommended to perform such calculation if the evaporation rate of oils were measured (i.e. volume change of heated cooking oils before and after heating).

R6: The reviewer proposed a very good method to constrain the SOA production rate. But the evaporation rate of oils was not measured to perform such calculation in this study. Actually, it is difficult to measure the volume of cooking oils consumed as the oils became stickier after heating. We will adopt this method in the future study.

**Q7:** Lines 213-216: What were the emission rate of POA from heated cooking oils? Please include this information (if available) in the comparison.

R7: During the measurement of POA, the cooking oils were heated in a pan. We were not sure about the fraction of emissions introduced into the PAM reactor while all emissions were introduced to the PAM for SOA experiments. Thus, only mass spectra and elemental ratios of POA were discussed in the manuscript.

**Q8:** Lines 256-260: This argument is true if SOA is only a minor contributor to total COA mass because typical mass spectrum of COA factors have high m/z 41-to-m/z 43 ratios which are similar to the POA of heated cooking oil. Furthermore, typical diurnal patterns of COA show a strong peak during dinner time with extremely low OH radical concentration in the atmosphere. Of course, VOCs from cooking can react with other atmospheric oxidants but it is unclear if SOA produced by night time chemistry gives the similar mass spectrum.

R8: This issue has been addressed in response to Q1 of Reviewer 1.

References:

Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chem. Rev., 103, 4605-4638, doi:10.1021/cr0206420, 2003.

Grosjean, D., Grosjean, E., and Williams, E. L.: Rate constants for the gas-phase reactions of ozone with unsaturated alcohols, esters, and carbonyls, Int. J Chem. Kinet., 25, 783-794, doi:10.1002/kin.550250909, 1993.

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Lambe, A. T., Onasch, T. B., Massoli, P., Croasdale, D. R., Wright, J. P., Ahern, A. T., Williams, L. R., Worsnop, D. R., Brune, W. H., and Davidovits, P.: Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA), Atmos. Chem. Phys., 11, 8913-8928, doi:10.5194/acp-11-8913-2011, 2011.

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Petters, M. D., and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, doi:10.5194/acp-7-1961-2007, 2007.

# A list of relevant changes

**Line 31-32**–delete “suggesting that COA might not be entirely primary in origin”

**Line 67-71**–Change “Allan et al. (2010) found that cooking oils may contribute more to PM than the meat itself in urban areas of London and Manchester.” to “Allan et al. (2010) postulated that cooking oils may contribute more to PM than the meat itself in urban areas of London 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.”

**Line 83**–Change “Lambe et al., 2011” to “Lambe et al., 2011a”

**Line 91-92**–Add “The ozone concentration in the PAM reactor was adjusted to five different levels, ranging from 0.4 ppm to 2.7 ppm.” after “…prior to dilution.”

**Line 98**–Change “Lambe et al., 2011” to “Lambe et al., 2011a”

**Line 99-107**–Add “Peng et al. (2016) found that non-OH chemistry, especially reactions with $O_3$, may play 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 and unsaturated aldehydes. In this study, the ratio of $O_3$ exposure to OH exposure ranged from $1.5\times10^5$ to $1.9\times10^5$, relatively lower than tropospheric values (Schmidt et al., 2014). At this $O_{3exp}/OH_{exp}$, ozonolysis of saturated and unsaturated aldehydes was negligible since the ratios of their ozonolysis rate constants to OH rate constants were in the range of $10^{-9}$ to $10^{-7}$. (Grosjean et al., 1993; Atkinson and Arey, 2003). Thus reactions of VOCs with $O_3$ played a negligible role in this study.” before “Before and after each experiment…”

**Line 112**–Change “Lambe et al., 2011” to “Lambe et al., 2011a”

**Line 114-115**–Change “Fig. S1 in the supporting information” to “Fig. 1”

**Line 116**–Change “Lambe et al., 2011” to “Lambe et al., 2011a”

**Line 118**–Change “Fig. 1” to “Fig. 2”

**Line 119**–Add “(rapeseed)” after “canola”

**Line 122-126**–Add “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 change the relative composition of emissions from other oils with higher smoke points (Klein et al., 2016a).” after “…on an electric heating plate.”

**Line 127-130**–Change “A 2 m Teflon tube was used as the transfer line to minimize wall loss of VOCs.” to “significantly”

**Line 143-145**–Change “The emissions, after passing through a mixing chamber of 36 L, were introduced to the PAM chamber by a Dekati diluter (DI-1000, Dekati Ltd, Finland) at a flow rate of 0.15 L $min^{-1}$, achieving a final dilution ratio of approximately 160.” to “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.”

**Line 159-161**–Change “A diffusion dryer was connected to the sampling line to remove water.” to “A silica gel diffusion dryer was connected to the sampling line to remove water. The residence time in the dryer was approximated 8 s, sufficient to reduce the RH to less than 30%.”

**Line 171-178**–Add “The value of CE varied from 0.38 to 0.78 in this study. Note that particles were not dried prior to SMPS measurements, which might lead to an overestimate of SOA mass due to the uptake of water by organics. Lambe et al. (2011b) investigated the cloud condensation nuclei activity of PAM-generated SOA and found that the hygroscopicity parameter $\kappa_{org}$ was linearly correlated with O:C ratios. Based on their $\kappa_{org}$-to-O:C relationship, we estimated an upper limit of $\kappa_{org}$ to be 0.089 in this study. The overestimate of SOA mass due to water uptake were thus determined to be less than 18%.” after “…Gordon et al. (2014) and Liu et al., (2015).”

**Line 194-195**–Add “Note that PR is highly related to the experimental condition, especially OH exposure and temperature of the cooking oil.” after “…different studies.”

**Line 198**–Change “Fig. 2” to “Fig. 3”

**Line 204-205**–Add “This also suggested that non-OH chemistry played a negligible role in forming SOA in this study.” after “…by the Teflon filter.”

**Line 209**–Change “Fig. 3” to “Figure 4”

**Line 222**–Change “Fig. 3” to “Fig. 4”

**Line 229-231**–Add “It should be noted that the organic vapors studied here were not the specific fats present in the raw oils, but the thermal breakdown products of fat lipids.” after “…the different cooking oils.”

**Line 256-258**–Add “SVOCs and IVOCs might not evaporate from the filter given that they might be at saturation as the aerosol was cooled after the emissions.” after “…was filtered.”

**Line 269**–Change “Fig. 4” to “Figure 5”

**Line 293-296**–Delete “This similarity between the cooking SOA and ambient COA suggests that the COA resolved based on ambient data may be a convolution of POA and SOA, even though vegetable oil may not be the oil commonly used in commercial kitchens.”

**Line 307**–Change “Fig. 5” to “Fig. 6”

**Line 315**–Change “Fig. 5” to “Fig. 6”

**Line 320-322**–Add “For example, the vapor pressure of n-tridecanal is approximately 14% of that of n-tridecane at 25 °C, as predicted by the group-contribution model (Pankow and Asher, 2007).” after “...long-chain alkanes from vehicle exhaust.”

**Line 336**–Change “Fig. 6” to “Fig. 7”

**Line 340**–Change “Fig. 6” to “Fig. 7”

**Line 340**–Change “Fig. S2” to “Fig. 8”

**Line 368-369**–Delete “These similarities indicated that ambient COA factors identified by AMS could contain cooking SOA.”

**Line 373**–Change “can be as efficient as vegetable oils in producing SOA” to “might also produce SOA”

**Line 380**–Change “with gas-phase emissions measured” to “with gas-phase SOA precursors characterized”

**Line 398**–Add the reference “Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chem. Rev., 103, 4605-4638, doi:10.1021/cr0206420, 2003.”

**Line 450**–Add the reference “Grosjean, D., Grosjean, E., and Williams, E. L.: Rate constants for the gas-phase reactions of ozone with unsaturated alcohols, esters, and carbonyls, Int. J Chem. Kinet., 25, 783-794, doi:10.1002/kin.550250909, 1993.”

**Line 512**–Add the reference “Klein, F., Farren, N. J., Bozzetti, C., Daellenbach, K. R., Kilic, D., Kumar, N. K., Pieber, S. M., Slowik, J. G., Tuthill, R. N., Hamilton, J. F., Baltensperger, U., Prévôt, A. S. H., and El Haddad, I.: Indoor terpene emissions from cooking with herbs and pepper and their secondary organic aerosol production potential, Sci Rep-Uk, 6, 36623, doi:10.1038/srep36623, 2016b."

**Line 532**–Add the reference "Lambe, A. T., Onasch, T. B., Massoli, P., Croasdale, D. R., Wright, J. P., Ahern, A. T., Williams, L. R., Worsnop, D. R., Brune, W. H., and Davidovits, P.: Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA), Atmos. Chem. Phys., 11, 8913-8928, doi:10.5194/acp-11-8913-2011, 2011b."

**Line 568-574**–Add references "Pankow, J. F., and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, Atmos. Chem. Phys., 8, 2773-2796, doi:10.5194/acp-8-2773-2008, 2008.

Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, W., Stark, H., Li, R., Tsigaridis, K., Brune, W. H., and Jimenez, J. L.: Non-OH chemistry in oxidation flow reactors for the study of atmospheric chemistry systematically examined by modeling, Atmos. Chem. Phys., 16, 4283-4305, doi:10.5194/acp-16-4283-2016, 2016."

**Line 582-595**–Add the reference "Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 4. C1−C27 Organic Compounds from Cooking with Seed Oils, Environ. Sci. Technol., 36, 567-575, doi:10.1021/es002053m, 2002.

Schmidt, G. A., Kelley, M., Nazarenko, L., Ruedy, R., Russell, G. L., Aleinov, I., Bauer, M., Bauer, S. E., Bhat, M. K., Bleck, R., Canuto, V., Chen, Y.-H., Cheng, Y., Clune, T. L., Del Genio, A., de Fainchtein, R., Faluvegi, G., Hansen, J. E., Healy, R. J., Kiang, N. Y., Koch, D., Lacis, A. A., LeGrande, A. N., Lerner, J., Lo, K. K., Matthews, E. E., Menon, S., Miller, R. L., Oinas, V., Oloso, A. O., Perlwitz, J. P., Puma, M. J., Putman, W. M., Rind, D., Romanou, A., Sato, M., Shindell, D. T., Sun, S., Syed, R. A., Tausnev, N., Tsigaridis, K., Unger, N., Voulgarakis, A., Yao, M.-S., and Zhang, J.: Configuration and assessment of the GISS ModelE2 contributions to the CMIP5 archive, Journal of Advances in Modeling Earth Systems, 6, 141-184, doi:10.1002/2013MS000265, 2014."

The following figure was added as **Fig. 1.**

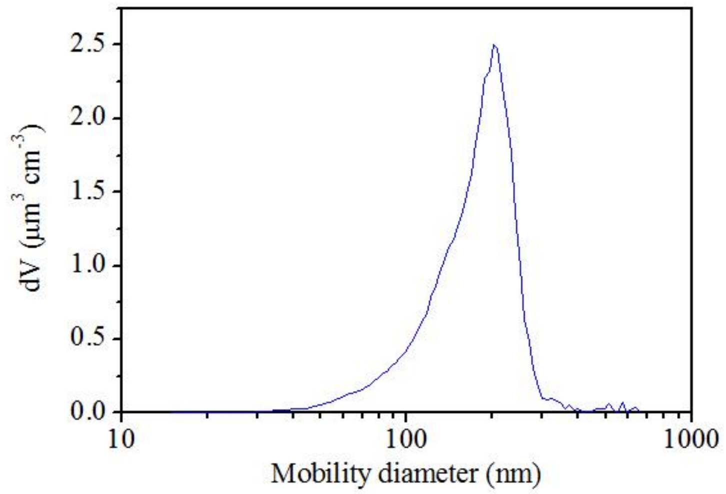

**Fig. 1.** Size distribution of particle volume of SOA for sunflower oil at an OH exposure of 2.7×$10^{10}$ molecules $cm^{-3}$ s.

**Fig. 1** was now presented as **Fig. 2**.

**Fig. 2** was now presented as **Fig. 3**.

**Fig. 3** was now presented as **Fig. 4**.

**Fig. 4** was now presented as **Fig. 5**.

**Fig. 5** was now presented as **Fig. 6**.

**Fig. 6** was now presented as **Fig. 7**.

The following figure was added as **Fig. 8.**

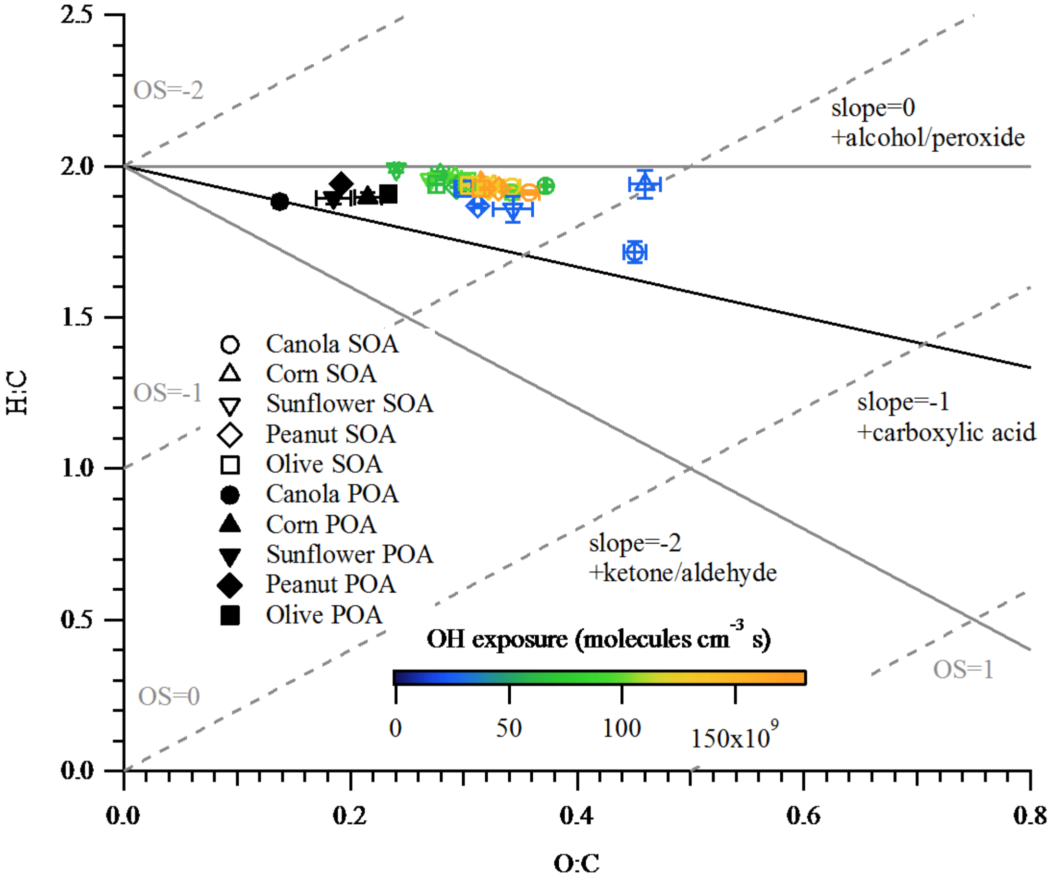

**Fig. 8.** Van Krevelen diagram of POA and SOA from heated different cooking oils. Error bars represent the standard deviations (1σ). SOA Data are colored by OH exposure. Average carbon oxidation states from Kroll et al. (2011) and functionalization slopes from Heald et al. (2010) are shown for reference.

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

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# Abstract

Cooking emissions can potentially contribute to secondary organic aerosol (SOA) but 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 investigated in a potential aerosol mass (PAM) chamber. Experiments were conducted at 19-20 ºC and 65-70% RH. The characterization instruments included a scanning mobility particle sizer (SMPS) and a high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS). The efficiency of SOA production, in ascending order, 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 fat and omega-6 fatty acids in cooking oils. The average production rate of SOA, after aging at an OH exposure of $1.7\times10^{11}$ molecules $cm^{-3}$ s, was 1.35±0.30 μg $min^{-1}$, three orders of magnitude lower compared with emission rates of fine particulate matter ($PM_{2.5}$) from heated cooking oils in previous studies. The mass spectra of cooking SOA highly resemble field-derived COA (cooking-related organic aerosol) in ambient air, with $R^2$ ranging from 0.74 to 0.88~~, suggesting that COA might not be entirely primary in origin~~. The average carbon oxidation state ($OS_c$) of SOA was -1.51 – -0.81, falling in the range between ambient hydrocarbon-like organic aerosol (HOA) and semi-volatile oxygenated organic aerosol (SV-OOA), indicating that SOA in these experiments was lightly oxidized.

# 1. Introduction

Organic aerosol (OA) is an important component of atmospheric particulate matter (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), formed via the oxidation of volatile organic compounds (VOCs) (Hallquist et al., 2009). However, chemical transport models generally underestimate SOA levels due to the unclear sources and formation processes of SOA (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006). Recently, primary semi-volatile and intermediate-volatility organic compounds (SVOCs and IVOCs) that can come from the evaporation of primary organic aerosol (POA) were found to form substantial SOA (Robinson et al., 2007; Donahue et al., 2009). Therefore, any source of POA may be associated with the production of SOA.

Cooking-related organic aerosol (COA), thought to be primary in origin, contributed 10–34.6% of the total OA in urban areas (Allan et al., 2010; Sun et al., 2011; 2012; Ge et al., 2012; Mohr et al., 2012; Crippa et al., 2013; Lee et al., 2015). Lee et al. (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 source of SOA in urban areas, yet the formation of SOA from cooking remains poorly 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 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

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 amounts of fine particulate matter ($PM_{2.5}$) (Amouei Torkmahalleh et al, 2012; Gao et al., 2013) and VOCs (Katragadda et al., 2010; Klein et al., 2016a). The $PM_{2.5}$ emission 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~~found~~ that cooking oils may contribute more to PM than the meat itself in urban areas of London 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. The VOCs emitted from heated cooking oils were dominated by aldehydes (Klein et al., 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 formation from heated cooking oils.

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.

## 2. Materials and methods

## 2.1 PAM chamber

SOA formation from gas–phase emissions of five different heated cooking oils was 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 chamber is a continuous flow stainless steel cylindrical reactor using high and controlled levels of oxidants to oxidize precursor gases to produce SOA. The volume is approximately 19 L (length 60 cm, diameter 20 cm). High OH exposures were produced through the photolysis of ozone irradiated by a UV lamp (λ = 254 nm) in the presence of water vapor. Ozone was produced by an ozone generator (1000BT-12, ENALY, Japan) via irradiation of pure $O_2$. The OH concentration was controlled by the flow rate of ozone in the PAM chamber, which was approximately 40 ppm prior to 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 set at 3 L $min^{-1}$ by a mass flow controller, resulting in residence time of 380 s. The corresponding upper limit of OH exposure at these operating conditions was $1.7\times10^{11}$ molecules $cm^{-3}$ s, which is equivalent to 1.3 days of atmospheric oxidation, assuming an ambient OH concentration of $1.5\times10^{6}$ molecules $cm^{-3}$ (Mao et al., 2009). The upper limit of OH exposure was determined by measuring the decay of $SO_2$ (Model T100, TAPI Inc, USA), following previous procedures (Kang et al., 2007; Lambe et al., 2011a). Peng et al. (2016) found that non-OH chemistry, especially reactions with $O_3$, may play 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 and unsaturated aldehydes. In this study, the ratio of $O_3$ exposure to OH exposure ranged from $1.5\times10^5$ to $1.9\times10^5$, relatively lower than tropospheric values (Schmidt et al., 2014). At this $O_{3exp}/OH_{exp}$, ozonolysis of saturated and unsaturated aldehydes was negligible since the ratios of their ozonolysis rate constants to OH rate constants were in the range of $10^{-9}$ to $10^{-7}$. (Grosjean et al., 1993; Atkinson and Arey, 2003). Thus reactions of VOCs with $O_3$ played a negligible role in this study. Before and after each experiment, the PAM reactor was cleaned by exposure to a high concentration of OH until the mass concentration of background particles was less than 5 μg $m^{-3}$.

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. ~~S~~1~~ in the supporting information~~). Transmission efficiency of gases in the PAM chamber indicates that vapor wall losses in the PAM chamber are negligible (Lambe et al., 2011a).

## 2.2 Experimental conditions

A schematic of the experimental setup is shown in Fig. ~~1~~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 ℃ 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 change the relative composition of emissions from other oils with higher smoke points (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 was used as the transfer line~~ to minimize wall loss of VOCs~~. The residence time in the transfer line was less than 2 s, resulting in wall losses of VOCs less than 5% according to Liu et al. (2015). After 10 min of heating, the UV lamp was turned on and the emissions were exposed to high OH levels for approximately one hour. Once the UV lamp was turned off, the PAM reactor 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 of the PAM outflow were measured continuously (HMP 110, Vaisala Inc, Finland) and stabilized at 65-70% and 19-20 ºC, respectively. The adjustment of RH was achieved by passing the pure $N_2$ and $O_2$ through water bubblers. Blank experiments were conducted in the absence of cooking oils under similar conditions to quantify the 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 ºC for 2 min in a pan on an induction cooker. The emissions, after passing through a mixing chamber of 36 L, were ~~introduced to the PAM chamber~~first diluted by a Dekati diluter (DI-1000, Dekati Ltd, Finland) by a factor of approximately 8. Then ~~at a flow rate of~~ 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 RH were similar to those of the SOA formation experiments.

A scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier model 3082, CPC model 3775) was used to measure particle number concentrations and size distributions. Particle size ranged from 15 nm to 661 nm. An aerosol density of 1.4 g cm$^{-3}$ was assumed to estimate the SOA mass from the particle volume concentration (Zhang et al., 2005). For the SOA formation experiments, the contribution from background organic aerosols was subtracted from the total organic aerosols. The maximum concentration of background organic aerosols was 8.4 μg m$^{-3}$, almost negligible compared with the dozens to several hundreds of μg m$^{-3}$ of SOA formed in this study. The organic aerosol composition was characterized by a high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS, abbreviated as AMS hereafter, Aerodyne Research Incorporated, USA) (DeCarlo et al., 2006). A silica gel diffusion dryer was connected to the sampling line to remove water. The residence 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-mode alternating every one minute. The toolkit Squirrel 1.57I and Pika 1.16I were used to analyze the AMS data. The molar ratios of hydrogen to carbon (H:C) and oxygen to carbon (O:C) were determined with the improved-ambient method (Canagaratna et al., 2015). The ionization efficiency of AMS was calibrated using 300 nm ammonium nitrate particles. The particle-free matrix air, obtained by passing the air through a

HEPA filter, was measured for at least 20 min before each experiment to determine the signals from major gases. The collection efficiency (CE) was corrected by comparing AMS mass concentrations to concurrent SMPS mass concentrations, following the methods of Gordon et al. (2014) and Liu et al., (2015). The value of CE varied from 0.38 to 0.78 in this study. Note that particles were not dried prior to SMPS measurements, which might lead to an overestimate of SOA mass due to the uptake of water by organics. Lambe et al. (2011b) investigated the cloud condensation nuclei activity of PAM-generated SOA and found that the hygroscopicity parameter $\kappa_{\mathrm{org}}$ was linearly correlated with O:C ratios. Based on their $\kappa_{\mathrm{org}}$-to-O:C relationship, we estimated an upper limit of $\kappa_{\mathrm{org}}$ 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, 2008; Pajunoja et al., 2015).

### 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):

$$\mathrm{PR} = [\mathrm{SOA}] \times \mathrm{DR} \times \mathrm{F} \quad (1)$$

where [SOA] is the SOA concentration in μg $m^{-3}$; DR is the dilution ratio and F is the flow rate in $m^3$ $min^{-1}$ 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.

## 3. Results and discussion

### 3.1 SOA formation

In Fig. ~~2~~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 concentration prior to dilution was stable at approximately 40 ppm. The pulse of RH 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 the detection limit of the instrument, indicating that POA emissions were thoroughly 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 formation in this study. Immediately after oxidation was initiated by turning on the UV lamp, substantial SOA was formed, and its concentration stabilized after about 20 min. The SOA concentration subsequently reported is the average for the steady period.

Fig~~. 3~~ure 4 shows SOA concentration as a function of OH exposure and photochemical age in days during the aging of gas–phase emissions from different heated cooking oils. The OH exposure ranged from $2.7\times10^{10}$ molecules cm$^{-3}$ s to $1.7\times10^{11}$ molecules cm$^{-3}$ s, corresponding to 0.2–1.3 days of photochemical age, assuming 24 h average ambient OH concentrations of $1.5\times10^{6}$ molecules cm$^{-3}$ (Mao et al., 2009). For all experiments, the SOA concentration almost linearly increased from 41–107 µg m$^{-3}$ to 320–565 µg m$^{-3}$ as OH exposure increased. This linear increase has also been observed from vehicle exhaust at a similar range of OH exposures (Tkacik et al., 2014). Typically, VOCs are oxidized through functionalization reactions to produce less volatile organics that readily condense to form SOA. Upon further oxidation, fragmentation reactions and cleavage of carbon bonds can occur and form more volatile products that reduce SOA levels (Kroll et al., 2009). In this study, functionalization reactions dominated SOA formation as reflected by the increase of SOA concentrations shown in Fig. ~~3~~4.

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 production, in ascending order, was peanut oil, olive oil, canola oil, corn oil and sunflower oil. The slope of sunflower oil was $3.82\times10^{-15}$ µg molecules$^{-1}$ s$^{-1}$, more than two times that of peanut oil. The different slopes might be related to the emission rate and composition of VOCs from various cooking oils. Table 1 presents the type of fat content of the different cooking oils. It should be noted that the organic vapors studied here were not the specific fats present in the raw oils, but the thermal breakdown products of fat lipids. Unsaturated fat accounts for 75%-88% of the total fat content. A multivariate linear regression was used to relate the SOA production efficiency to the fat content of cooking oils. The intercept was set to zero. The resulting equation was $Y = 2.62\times10^{-17}X_1 + 4.71\times10^{-17}X_2$, where Y is the SOA production efficiency (μg molecules$^{-1}$ s$^{-1}$); $X_1$ and $X_2$ represent the content of mono-unsaturated fat (%) and omega-6 fatty acid (%) in cooking oil, respectively. The SOA production efficiency was strongly correlated ($R^2 = 0.97$, $p<0.05$) with the content of mono-unsaturated fat and omega-6 fatty acids. This indicated that the major SOA precursors from heated cooking oils were related to the content of mono-unsaturated fat and omega-6 fatty acids in cooking oils. Moreover, omega-6 fatty acids dominated the contribution to SOA production. Omega-6 fatty acids are a family of poly-unsaturated fatty acids that have in common a final carbon-carbon double bond in the n-6 position, counting from the methyl end (Simopoulos, 2002). The peroxyl radical reactions of omega-6 fatty acids might emit long-chain aldehydes (Gardner, 1989), which have been suggested as potential SOA precursors (Chacon-Madrid et al., 2010).

The average SOA PR from gas–phase emissions of the five cooking oils at an OH exposure of $1.7\times10^{11}$ molecules cm$^{-3}$ s was calculated to be 1.35±0.30 μg min$^{-1}$. Amouei Torkmahalleh et al. (2012) found that primary $PM_{2.5}$ emission rates for peanut, canola, corn and olive oils heated at 197 °C ranged from 3.7 mg min$^{-1}$ to 54 mg min$^{-1}$. He et al. (2004) reported a $PM_{2.5}$ emission rate for frying in vegetable oils of 2.68±2.18 mg min$^{-1}$. The SOA PR determined in this study was negligible compared with primary $PM_{2.5}$ emission rates for heated cooking oils and frying in vegetable oils. However, our results may underestimate SOA production from cooking under real-world conditions. First, recent studies have demonstrated that the oxidation of IVOCs and SVOCs evaporated from POA could produce significant SOA (Donahue et al., 2006; Jimenez et al., 2009). In this study, POA from heated cooking oils was filtered. SVOCs and IVOCs might not evaporate from the filter given that they might be at saturation as the aerosol was cooled after the emissions. Second, emissions of SOA precursors will be enhanced when cooking food compared with heating cooking oils alone. For instance, long-chain aldehyde emissions from frying processes can be 10 times those of heated oil (Klein et al., 2016a). Large amounts of monoterpenes will be emitted when frying vegetables or cooking with herbs and black pepper (Klein et al., 2016a, b). These enhanced emitted precursors may significantly enhance SOA production. Finally, laboratory and tunnel studies indicate that SOA production from typical precursors and vehicle exhaust peak at OH exposures higher than $5.0\times10^{11}$ molecules $cm^{-3}$ s (Tkacik et al., 2014; Lambe et al., 2015). The relatively lower OH exposures in this study compared with typical conditions in the atmosphere may lead to the underestimation of cooking SOA.

### 3.2 Mass spectra of POA and SOA

Fig~~. 4~~ure 5 shows high-resolution mass spectra of POA and SOA at an OH exposure of $2.7\times10^{10}$ molecules $cm^{-3}$ s from heated canola oil. Other oils have similar mass spectra, as reflected in the good correlations shown in Table 2. The mass concentration of POA was approximately 35 µg $m^{-3}$ for canola oil. The prominent peaks in POA from canola oil were m/z 41 and 55, followed by m/z 29 and 43. The m/z 41, 43 and 55 were dominated by $C_3H_5^+$, $C_3H_7^+$ and $C_4H_7^+$ ion series, consistent with the previous observation by Allan et al. (2010). The m/z 29 was instead dominated by ion $CHO^+$, which can be used as a tracer for organic compounds with alcohol and carbonyl functional groups, as a result of thermal decomposition of the oils (Lee et al., 2012). 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 ($R^2$) between POA and SOA unit mass resolution (UMR) spectra of heated oil and COA resolved by positive matrix factorization (PMF) 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 correlations ($R^2$>0.97) and agreed well with the ambient COA factor obtained at 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 correlations ($R^2$>0.94), suggesting a high degree of similarity. The mass spectra of cooking SOA also greatly resemble POA and field-derived COA in ambient air, with $R^2$ ranging from 0.74 to 0.88. ~~This similarity between the cooking SOA and ambient COA suggests that the COA resolved based on ambient data may be a convolution of POA and SOA, even though vegetable oil may not be the oil commonly used in commercial kitchens.~~ Kaltsonoudis et al. (2016) also observed that the ambient COA factor in two major Greek cities in spring and summer strongly resembled the aged SOA from meat charbroiling in a smog chamber.

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 ($f_{43}$) vs. m/z 44 ($f_{44}$). 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. ~~5~~6, we plot $f_{43}$ vs. $f_{44}$ of cooking SOA and SOA data from gasoline (Presto et al., 2014; Liu et al., 2015) and diesel (Presto et al., 2014) vehicle exhaust measured in a smog chamber, together with the triangle defined by Ng et al. (2010) based on the analysis of ambient AMS data. The ambient low-volatility oxygenated OA (LV-OOA) 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 $f_{44}$ toward the triangle apex ($f_{43} = 0.02$, $f_{44} = 0.30$). In this study, the $f_{43}$ and $f_{44}$ ranged 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. ~~5~~6, SOA from gasoline and diesel vehicle exhaust at a similar range of OH exposures had $f_{44}$ values of 0.11–0.12. 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 might be long-chain aldehydes, which are less volatile than SOA precursors such as aromatics and long-chain alkanes from vehicle exhaust. Generally, the presence of additional methylene and aldehyde reduce compound vapor pressure by factors of 3 and 22, respectively (Pankow and Asher, 2007). For example, the vapor pressure of n-tridecanal is approximately 14% of that of n-tridecane at 25 °C, as predicted by the group-contribution model (Pankow and Asher, 2007). A single polar moiety of first-generation products from long-chain aldehydes will have low enough volatility to condense, while more volatile aromatics and long-chain alkanes require more 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 $f_{44}$ and a slight increase in $f_{43}$ as OH exposure increased. The increased SOA mass may facilitate the partitioning of more volatile organics, leading to a slight increase in $f_{43}$ and little change in $f_{44}$. This is consistent with the observation of previous studies that the $f_{44}$ of SOA from aromatics and monoterpenes varied little and that $f_{43}$ increased slightly for SOA mass loadings higher than 100 µg $m^{-3}$ (Ng et al., 2010; Kang et al., 2011).

### 3.3 Chemical composition of SOA

The O:C ratio and the estimated average carbon oxidation state ($OS_c$) ($OSc \approx 2 \times O:C - H:C$) (Kroll et al., 2011) can be used to evaluate the degree of oxidation of organic aerosols. Fig. ~~6~~ 7 shows the evolution of O:C ratios and $OS_c$ of SOA from heated cooking 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 those of POA from meat charbroiling (Kaltsonoudis et al., 2016). As shown in Fig. ~~6~~7, for each cooking oil, the O:C and $OS_c$ of SOA displayed similar trends, initially decreasing rapidly and then increasing slowly or leveling off (for canola oil only). In this study, the increased SOA mass loadings led to the rapid decrease of the oxidation degree when the OH exposure increased from $2.7\times10^{10}$ molecules $cm^{-3}$ s to $6.4\times10^{10}$ molecules $cm^{-3}$ s. As OH exposure and the resulting OA mass loadings further increase, even less oxidized and more volatile organics partition into the particle phase and thus decrease the oxidation degree (Donahue et al., 2006). The difference in O:C for different cooking oils at the same OH exposure may be attributed to the differences in gas-phase SOA precursors. In general, the O:C ratios of SOA formed from gas–phase emissions of heated cooking oils ranged from 0.24 to 0.46 at OH exposures of $2.7\times10^{10}$ – $1.7\times10^{11}$ molecules $cm^{-3}$ s. The $OS_c$ of cooking SOA was -1.51 – -0.81, falling in the range between ambient hydrocarbon-like organic aerosol (HOA, $OS_c$ = -1.69) and SV-OOA ($OS_c$ = -0.57) corrected by the improved-ambient method (Canagaratna et al., 2015)**.** As suggested by Canagaratna et al. (2015), the $OS_c$ is more robust than the $f_{43}$/$f_{44}$ relationship for evaluating the oxidation degree of organic aerosols, as the former has been estimated based on the full spectra.

In Fig. ~~S2~~ 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 $2.7\times10^{10}$ molecules $cm^{-3}$ s to $1.7\times10^{11}$ molecules $cm^{-3}$ s. The $OS_c$ and $f_{43}/f_{44}$ relationship indicated that the SOA formed was lightly oxidized. The mass spectra of SOA highly resembled POA from heated cooking oils and COA factors in ambient air. ~~These similarities indicated that ambient COA factors identified by AMS could contain cooking SOA.~~ The major SOA precursors from heated cooking oils were related to the content of mono-unsaturated fat and omega-6 fatty acids in cooking oils. Considering that animal fats such as pork and chicken fat are also abundant in mono-unsaturated fat and omega-6 fatty acids, gas-phase emissions from cooking animal fat ~~can be as efficient as vegetable oils in producing~~might also produce SOA. It is important to note that the reported SOA data only related to gas-phase emissions from heated cooking oils. The large amounts of POA emitted from cooking oils may also form SOA after photochemical aging. More 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 limited information on SOA yields from cooking; we recommend that future work validate our results and perform similar experiments, with gas-phase SOA precursors characterized~~emissions measured~~.

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

| | Slope [b] µg molecules$^{-1}$ s$^{-1}$ | Saturated (%) | Mono-unsaturated (%) | Poly-unsaturated (%) | | Others (%) |
|---|---|---|---|---|---|---|
| | | | | Omega-6 | Omega-3 | |
| sunflower | $3.82\times10^{-15}$ | 10 | 19 | 64 | 0 | 7 |
| corn | $3.31\times10^{-15}$ | 12 | 24 | 56 | 1 | 7 |
| canola | $2.68\times10^{-15}$ | 7 | 59 | 20 | 9 | 5 |
| olive | $2.55\times10^{-15}$ | 13 | 71 | 8 | 1 | 7 |
| peanut | $1.7\times10^{-15}$ | 16 | 44 | 31 | 0 | 9 |

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

[b] SOA production efficiency was presented as the slope of the fitted straight line to the SOA concentration vs OH exposure.

**Table 2.** Correlation coefficients ($R^2$) between POA and SOA UMR mass spectra and ambient COA resolved by PMF.

| | CA P[a] | CN P | SR P | PT P | OE P | CA S | CN S | SR S | PT S | OE S | COA[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CA P | 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 |

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

[b] Lee et al. (2015).

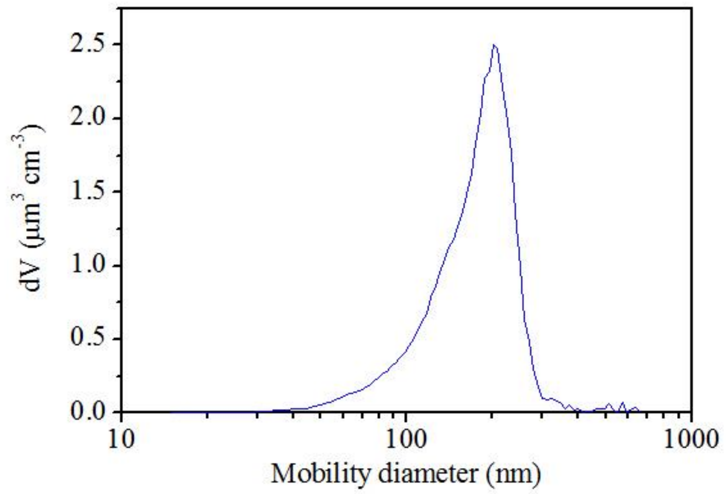

**Fig. 1.** Size distribution of particle volume of SOA for sunflower oil at an OH exposure of 2.7×$10^{10}$ molecules $cm^{-3}$ s.

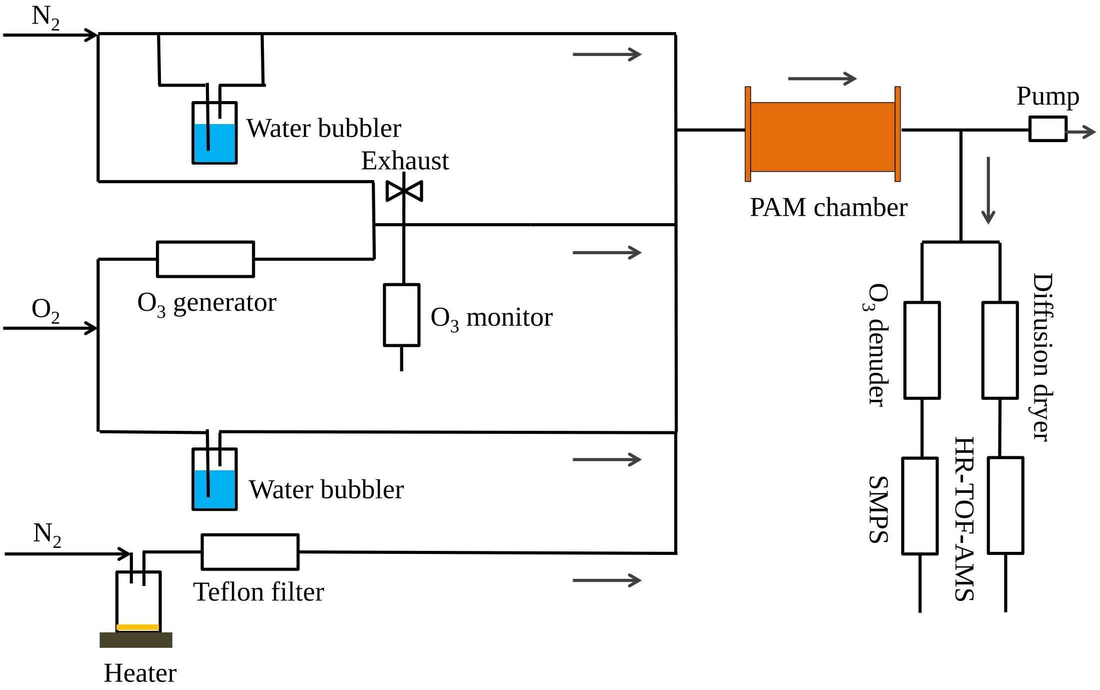

**Fig. ~~1~~2.** Schematic of the experimental setup.

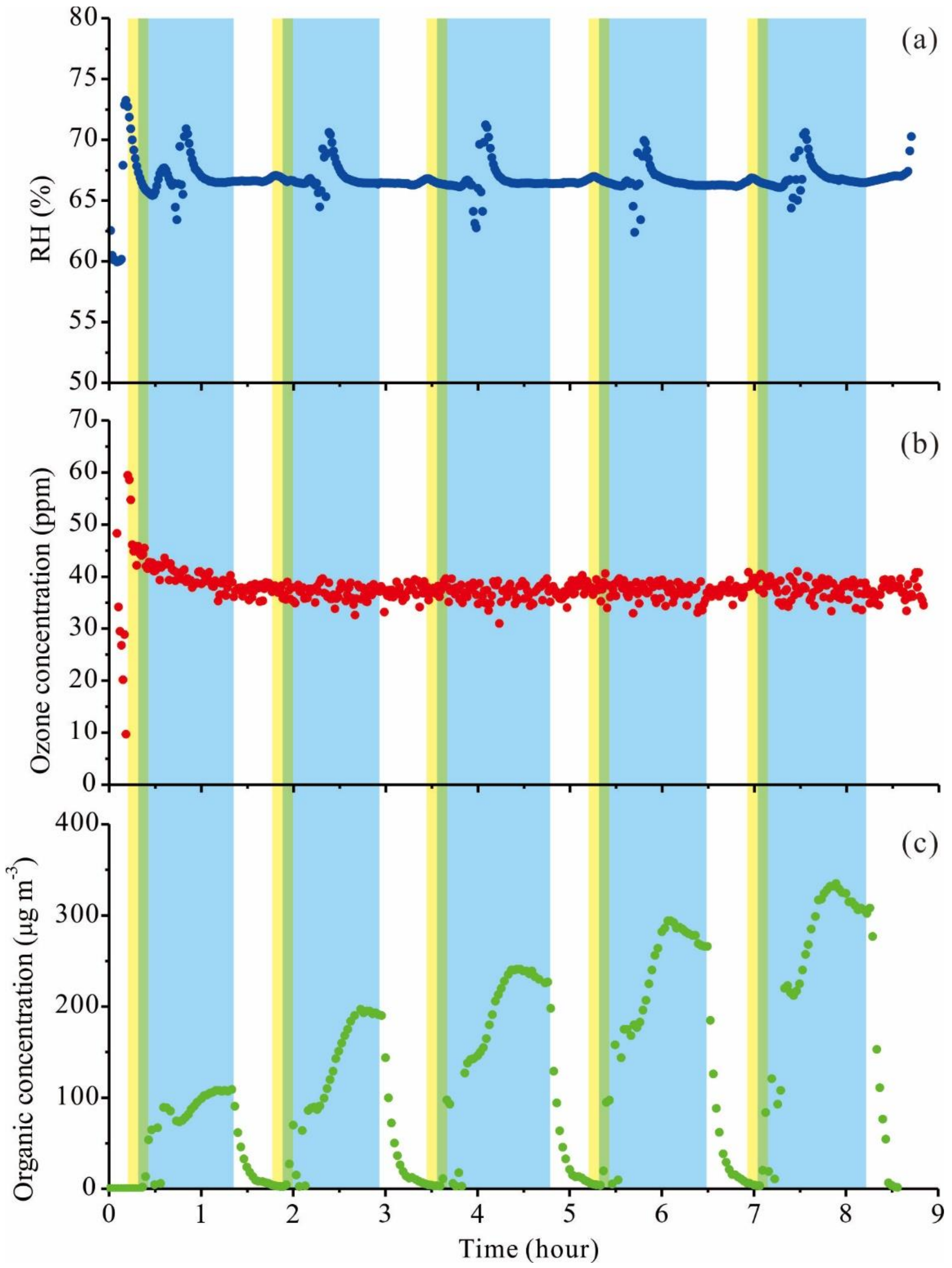

**Fig. ~~2~~3.** Time series of (a) relative humidity (RH), (b) ozone and (c) organic concentrations during the aging of gas–phase emissions from heated peanut oil. The yellow and light blue regions represent the heating oil and OH exposure period, respectively. The green region is the overlap between heating oil and OH exposure period.

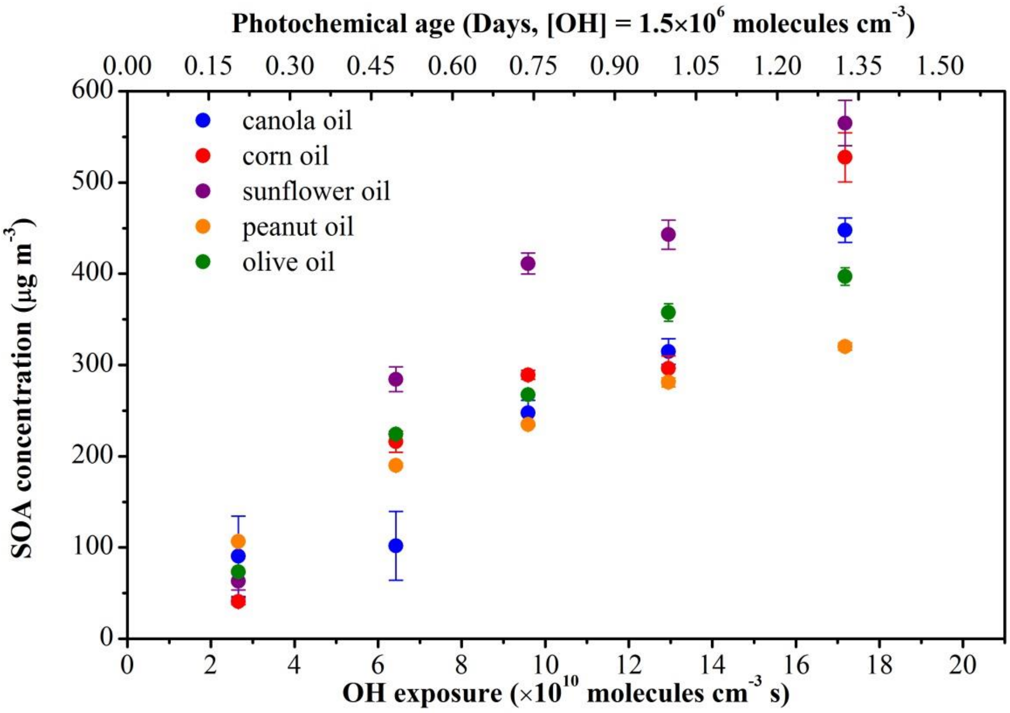

**Fig. ~~3~~4.** SOA concentration vs. OH exposure and photochemical age in days (at [OH] = 1.5×10$^6$ molecules cm$^{-3}$) during the aging of gas–phase emissions from different heated cooking oils. Error bars represent the standard deviation (1σ).

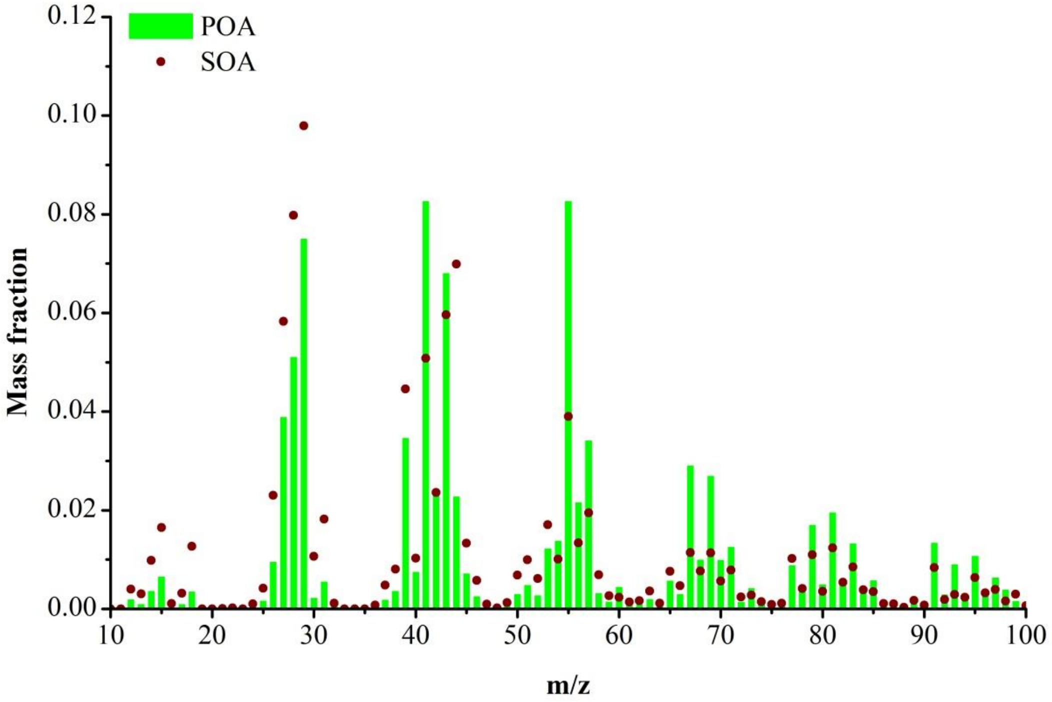

**Fig. ~~4~~5.** Mass spectra of POA and SOA at an OH exposure of 2.7×10$^{10}$ molecules cm$^{-3}$ s from heated canola oil.

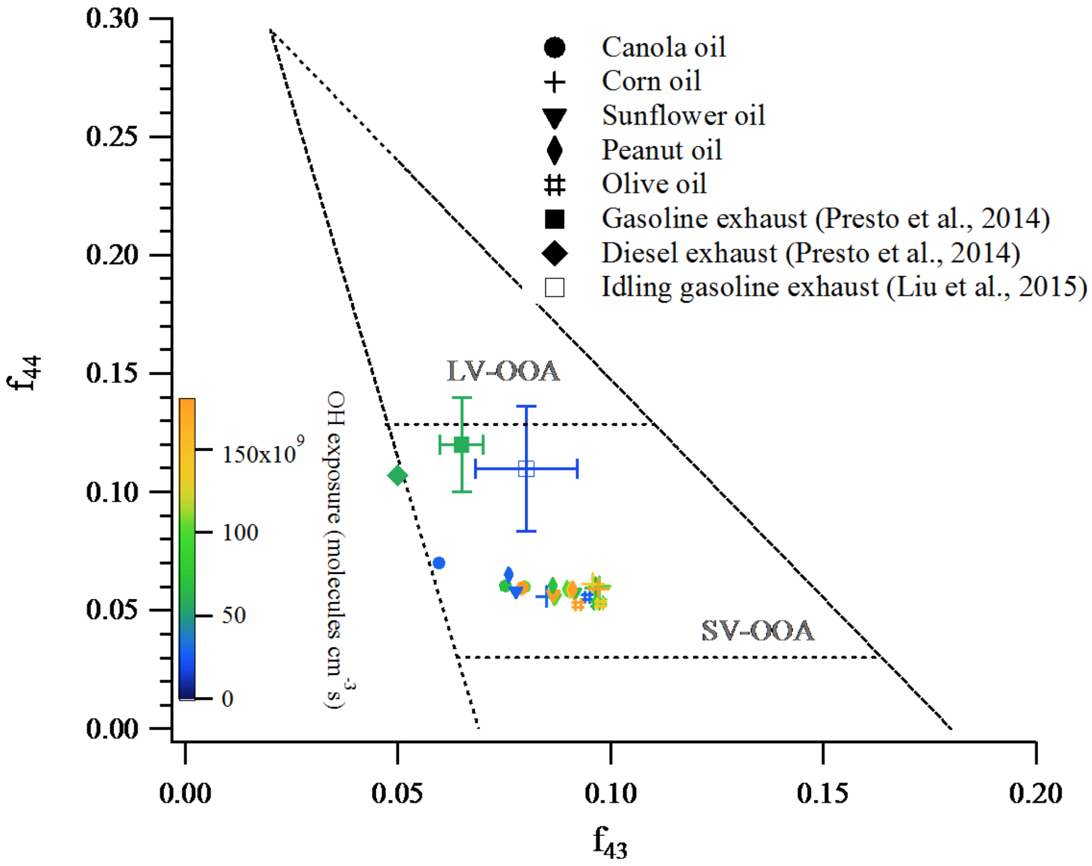

**Fig. ~~5~~6.** Fractions of total organic signal at m/z 43 ($f_{43}$) vs. m/z ($f_{44}$) from SOA data in this work together with the triangle plot of Ng et al. (2010). SOA data from gasoline (Presto et al., 2014; Liu et al., 2015) and diesel (Presto et al., 2014) vehicle exhaust measured in smog chamber 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).

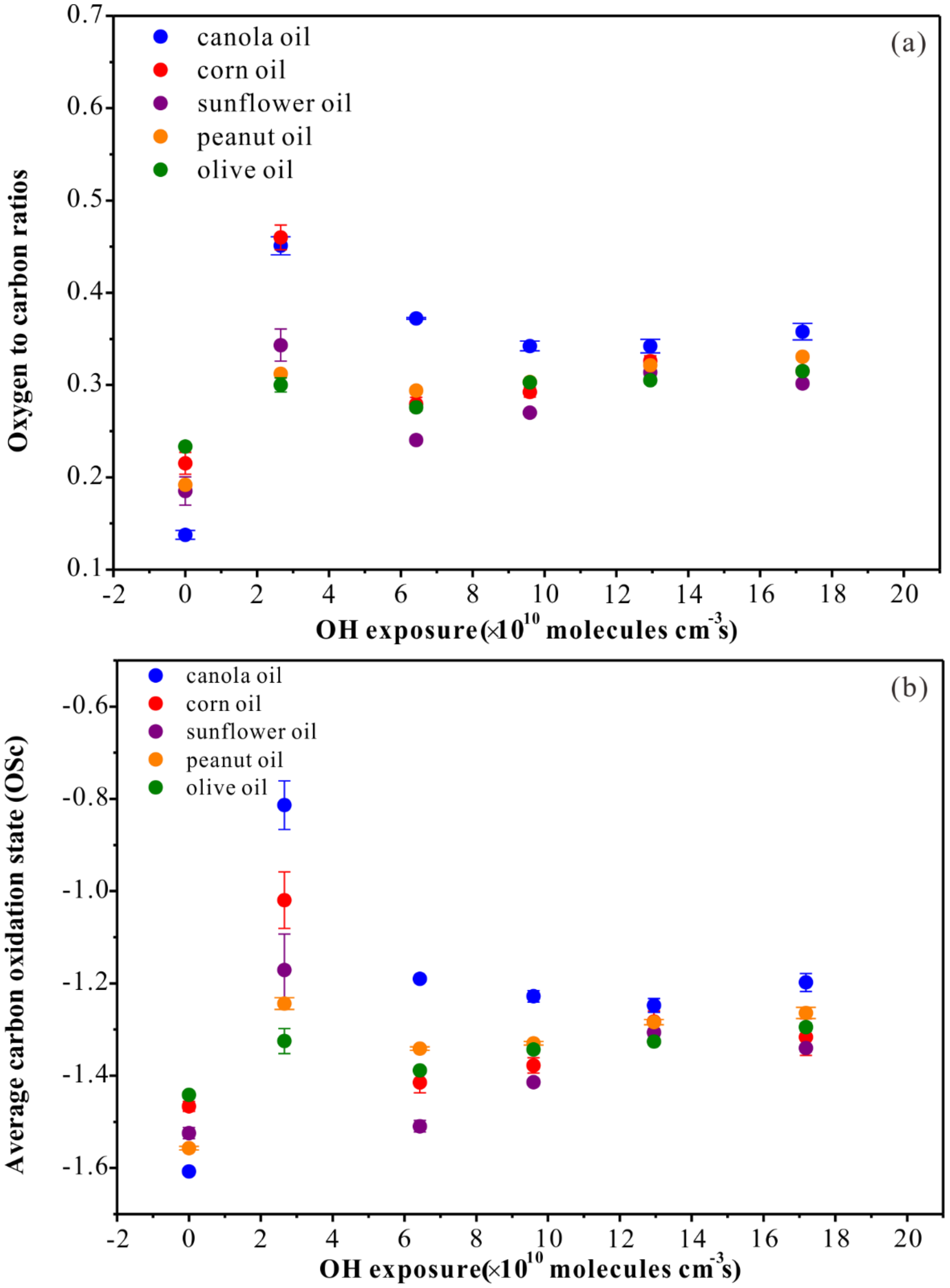

**Fig. ~~6~~7.** Evolution of (a) oxygen to carbon (O:C) molar ratios and (b) average carbon oxidation state ($OS_c$) as a function of OH exposure during the aging of gas–phase emissions from heated different cooking oils, with error bars indicating standard error. Data at [OH] = 0 represent POA from cooking oils.

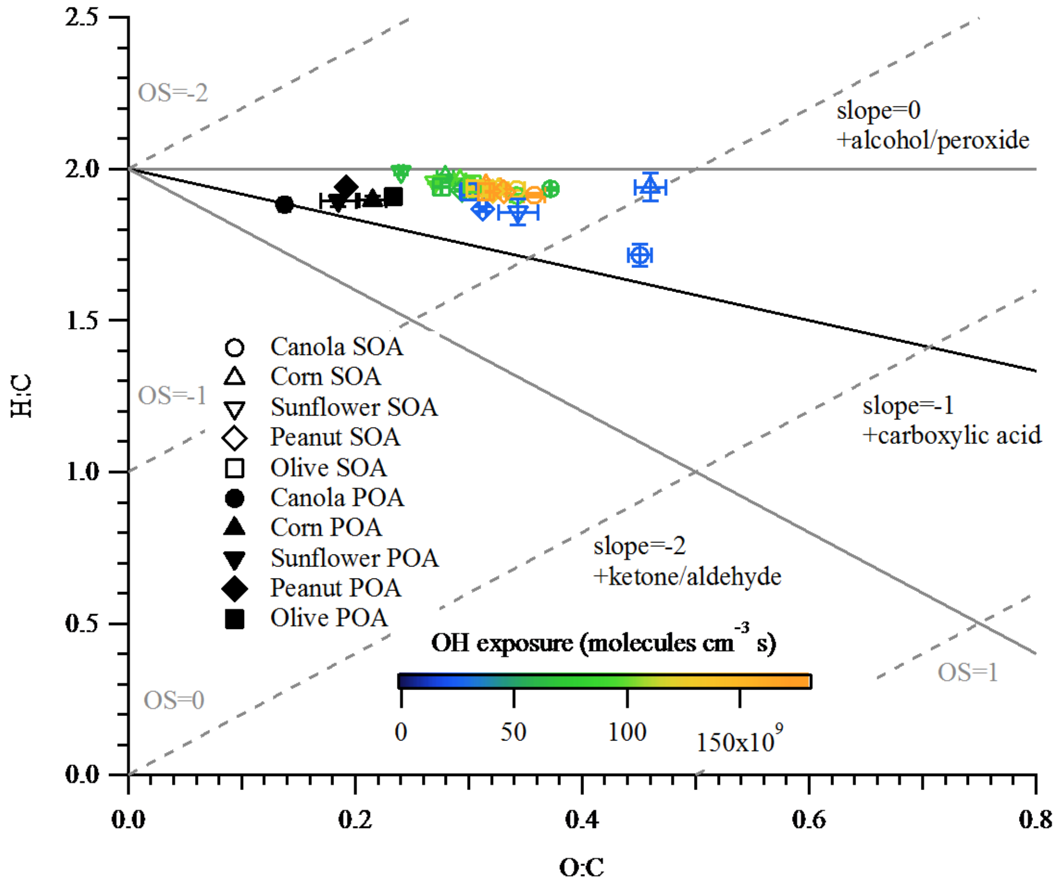

**Fig. 8.** Van Krevelen diagram of POA and SOA from heated different cooking oils. Error bars represent the standard deviations (1σ). SOA Data are colored by OH exposure. Average carbon oxidation states from Kroll et al. (2011) and functionalization slopes from Heald et al. (2010) are shown for reference.