

# Primary and secondary organic aerosol from heated cooking oil emissions

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### Introduction

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### Materials and methods



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#### 2.1 Smog chamber experiments



#### 2.1 Smog chamber experiments

- Measure the concentrations of  $NO_x$  and  $O_3$  every 1 min: Gas monitors
- NMOGs: PTR-TOF-MS
- OH concentration in the chamber: The decay of acrolein or heptadienal
- Measure particle number concentrations and size distributions/135 s: SMPS
- The chemical composition of submicron NR-PM1: AMS

#### 2.2 Separating POA and SOA

Table 1. Experimental conditions in the photochemical aging experiments.

Cooking oil	Dilution ratio	$[NMOG] : [NO_x]$ (ppbC : ppb)	OH exposure molec $\rm cm^{-3}  s$	Category	PMF
sunflower	63	4.9	$1.0  imes 10^{10}$	Pure SOA	n/a
olive	107	4.0	$1.3 \times 10^{10}$	POA + SOA	2 factors
peanut	67	2.6	$2.1 \times 10^{10}$	Pure SOA	n/a
corn	67	3.2	$1.8  imes 10^{10}$	Pure SOA	n/a
canola	67	5.4	$3.5 \times 10^{10}$	Pure SOA	n/a
soybean	67	3.4	$1.7 \times 10^{10}$	Pure SOA	n/a
palm	100	18.9	$1.3  imes 10^{10}$	POA + SOA	2 factors

n/a – not applicable.

- 1. The experiments in this study were classified into two groups.
- 2. Sunflower, peanut, corn, canola, and soybean oil emissions produced low POA concentrations (< 0.5  $\mu$ g/m<sup>3</sup>) in the smog chamber.
- 3. POA and SOA mixtures were present in the palm and olive oil experiments.



### **Results and discussion**

#### 3.1 POA–SOA split



**Figure 1.** Time series of measured OA, PMF factors, and POA concentrations assuming first-order loss of POA to the walls for **(a)** palm and **(b)** olive oil experiments. Concentrations were not corrected for particle wall loss.

- 1. The first ~ 1.6 h of the emission introduction period increased rapidly, reaching approximately  $14 \ \mu g \ m^{-3}$ .
- 2. Due to wall losses: decreased to ~ 9  $\mu$ g m<sup>-3</sup>.
- 3. Photochemical aging was initiated at t = 0: SOA was quickly formed and the OA concentration increased by a factor of 5 in less than 1 h.
- 1. The maximum POA concentration in the olive oil experiment was approximately two times higher than that in the palm oil experiment.
- 2. The maximum OA concentration was  $\sim$  50 % of that in the palm oil experiment via SOA formation.
- 3. the OA reconstructed by PMF accurately captured the trends in measured OA throughout the experiment.

#### 3.1 POA–SOA split



**Figure 2.** Time series of O:C ratios and O<sub>3</sub> concentrations for oxidation flow reactor ozonolysis experiments with (**a**) palm and (**b**) olive oil. The ozonolysis experiments involved exposing emissions from palm or olive oil to high concentrations of O<sub>3</sub> in an oxidation flow reactor. The emissions first passed continuously through the reactor for at least 30 min and then were exposed to 500–600 ppb ozone for another 17 min. Ozone was introduced at time t = 0.

- 1. No obvious changes were observed in the palm oil O : C ratio.
- 2. The olive oil O : C ratio increased from 0.11 to 0.17 after the emissions were exposed to  $O_3$  for 17 min;

#### 3.1 POA–SOA split



For the palm oil experiment, the residual method overestimated the POA concentrations (compared with PMF) using all of the different tracerions.

For the olive oil experiment, the residual method accurately predicted the POA concentrations before the lights were turned on using different tracer ions.

After photochemical aging began, the residual method did not agree with the PMF results.

Figure 3. Time series of measured OA, PMF-derived POA factors, and POA determined using the residual method for (a) palm and (b) olive oil experiments.

#### **3.2 Mass spectra of PMF resolved factors**



Figure 4. Mass spectra of POA emissions and PMF-derived POA factors for (a) olive and (b) palm oil and, for comparison, the average mass spectrum of POA emissions from sunflower, peanut, corn, and canola oils obtained from Liu et al. (2017).

 The olive oil POA factor was dominated by m/z, followed by m/zs 69, 55, and 43.
The palm oil POA factor was dominated by m/z 55, followed by m/zs 41 and 43.

- 1. For both oils, the POA factor mass spectra agreed very well with the directly measured POA spectra.
- 2. The PMF analysis slightly underestimated the mass fraction at m/z 28 and slightly overestimated the mass fractions at m/zs 41 and 55 in both experiments.

#### **3.2 Mass spectra of PMF resolved factors**



The mass fraction at m/z 43 (f43 = 0.087) was higher than f44 (0.059) in the olive oil SOA factor, while f44 (0.074) dominated f43 (0.067) in the palm oil SOA factor.

The mass spectra of the two SOA factors exhibited good agreement ( $\theta = 8^{\circ}$ ).

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

#### 3.3 Comparison of PMF-resolved factors with ambient factors







Average SOA Average PMF SOA

The agreement between ambient COA factors and the palm PMF POA and average POA mass spectra decreased from 8 to 12° for ambient COA factors from the commercial and shopping area of Mong kok in Hong Kong to 25– 28° for ambient COA factors from a suburban area in Pasadena.

**Figure 6.** (a) Angles ( $\theta$ ) between ambient COA factor mass spectra and the palm PMF POA mass spectrum, average POA mass spectrum, average PMF SOA factor mass spectrum, and average SOA mass spectrum. (b) Angles ( $\theta$ ) between ambient SVOOA factor mass spectra and the average PMF-derived SOA factor and average SOA mass spectra. The average POA mass spectra were averaged for sunflower, peanut, corn, and canola oils (Liu et al., 2017). The average SOA mass spectra were averaged for sunflower, peanut, corn, canola, and soybean oils in this study.

#### 3.3 Comparison of PMF-resolved factors with ambient factors



The average mass spectrum of the PMF SOA factors exhibited poor agreement with the SV-OOA average mass spectrum ( $\theta = 25^{\circ}$ ).

Figure 7. Average PMF SOA factor mass spectrum and ambient SV-OOA factor mass spectrum (Ng et al., 2011a).

#### 3.4 OA oxidation state and chemical evolution



**Figure 8.** Van Krevelen diagram of POA and SOA from different cooking oils, as well as ambient PMF factors. Average carbon oxidation states from Kroll et al. (2011) and functionalization slopes from Heald et al. (2010) are shown for reference.

The O : C ratios for the olive and palm PMF POA were 0.09 and 0.15.

The O : C ratios for the olive and palm PMF SOA and SOA from other cooking oils ranged from 0.40 to 0.50, slightly lower than that of SV-OOA (0.53).



### Conclusion

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#### 4. Conclusion

- 1. For experiments with mixtures of POA and SOA, the POA and SOA factors were separated using PMF, the traditional method, and the residual method; PMF outperformed the other techniques in resolving accurate POA and SOA. The residual method, which uses different ions as POA tracers, failed to capture the POA concentrations due to the presence of these ions in the SOA mass spectrum.
- 2. Our results suggest that one should consider the cooking style and atmospheric oxidation conditions when performing deconvolution analyses with the default COA mass spectral inputs.
- 3. The average mass spectra of PMF SOA factors and SOA from other cooking oils exhibited little similarity ( $\theta > 20^{\circ}$ ) to ambient SV-OOA factors. In the Van Krevelen diagram, the entire data set in this study yielded a linear trend with a slope of approximately -0.4, which may indicate oxidation mechanisms involving the addition of both carboxylic acid and alcohol or peroxide functional groups without fragmentation and/or the addition of carboxylic acid functional groups with fragmentation.



## Thank you for listening!



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