

# Responses to the comments & suggestions from the reviewers

**Journal: Atmospheric Chemistry and Physics**

**Manuscript ID: acp-2021-216**

**Title: “Mass spectral characterization of secondary organic aerosol from urban lifestyle sources emissions”**

## **Reviewer 2**

This research work has been submitted for consideration as a “research article”. The authors aim to quantify atmospheric physicochemical processing of primary gas and particle-phase cooking and vehicular emissions, focusing on organic aerosols. The team uses a suite of instruments, to initially dilute (Dekati dilutor), oxidize (GO: PAM reactor), and detect (HR-ToF-AMS for organic aerosols; SMPS for particle size distributions and numbers; SO<sub>2</sub>, CO, and CO<sub>2</sub> gas phase monitors) the primary emissions from Chinese cooking (frying-based) and vehicular tests (gasoline direct injection engine used with gasoline fuel). For cooking, the authors varied the dish type (and the associated operating conditions, four types of dishes cooked) while for the engine operation, the authors varied the running speeds and torques (five combinations). The authors report data for equivalent photochemical ages (EPA) up to 2.1 days for cooking tests, and up to 4.2 days for vehicle tests. The authors note that for cooking, the type of cooking (operating condition) matters more than the EPA (extent of oxidation) for the mass spectral similarity analysis, and vice-versa for vehicular emissions. Next, the authors apply the IGOR PMF PET tool to identify primary and secondary components of the aged cooking and vehicular emissions. For cooking tests, the authors found only two PMF factors: one primary and one secondary. However, for vehicular tests, the authors found three factors: one primary and two secondary factors. Finally, the authors apply averaged mass spectra of some, and not all, obtained factors to ambient datasets collected in Shanghai. The authors show that using these lab-based primary and secondary cooking and vehicular factors in ME-2 analysis improves diurnal patterns for some factors (LO-SOA in winter, MO-OOA in summer), and allows extraction of an other-POA factor with a diurnal pattern peaking in the evening and extracted only in winter, possibly associated with biomass burning and coal combustion.

While the paper addresses a relevant and longstanding question of atmospheric chemistry (constraining secondary organic aerosols), **the present scientific and technical quality of the paper is lacking in multiple aspects. I recommend that this manuscript be reconsidered for publishing after major revisions.**

- We appreciate the comments from the reviewer on this manuscript. We supplemented the relevant figures and tables in the supplemental materials. For the source apportionment, we added the OA analysis based on ME-2 and PMF model in the section of *Materials and Methods*. Besides, detailed information about the choice for PMF and ME-2 analysis were added in the revised manuscript. In addition, we analyzed the correlation between the resolved factors of ME-2 and PMF and their tracers. Finally, we summarized the limitations of this work and supplemented the *Limitation and future work* section in the manuscript. All changes made are marked in the revised manuscript.

## Major Comments

1. The paper presents the cooking tests and results as original work of this paper, and references published work (Zhang et al., 2020) incorporating those tests and results mostly in the Methods section (exception being Line 196). However, the ACP similarity report revealed large sections of this paper discussing the cooking results (for example, Lines 172-176, 207-221) are almost verbatim from published work (Zhang et al., 2020), a clear and unfortunate case of self-plagiarism. The authors should add explicit references and paraphrasing (if taking verbatim text) to all such portions of the paper.

- We appreciate the comments from the reviewer. The repeated descriptions in the Results and discussion section have been modified in the revised manuscript (line 265-282 in the marked revised manuscript) as follows:

*“Some ions like  $m/z$  41, 55, 57, 43, 28, and 44 are typically used as tracers of OOA, COA, HOA, LO-OOA, and MO-OOA. Fig.3 shows the high-resolution mass spectra of POA and SOA from four Chinese dishes and five vehicle running conditions. The cooking PMF POA of four Chinese dishes all showed obvious hydrocarbon-like signals at  $m/z$  41, 43, 55, and 57 with ion fragments of  $C_3H_5^+$ ,  $C_3H_7^+$ ,  $C_4H_7^+$ ,  $C_4H_9^+$ ,  $C_5H_7^+$ , and  $C_5H_9^+$ . The fraction of  $m/z$  41 in cooking POA ranged from 0.051 to 0.069. The prominent fraction of  $m/z$  43 ( $f_{43}=0.068\sim0.083$ ), 55 ( $f_{55}=0.064\sim0.084$ ), 57 ( $f_{57}=0.041\sim0.097$ ), 67 ( $f_{67}=0.021\sim0.40$ ), 69 ( $f_{69}=0.034\sim0.049$ ) were observed (Table S10). For mass spectra of cooking PMF SOA, the oxygen-oxidation ion fragments had higher signals than those of hydrocarbon-like ion fragments. The dominate signals existed at  $m/z$  28 ( $f_{28}=0.045\sim0.068$ ), 29 ( $f_{29}=0.048\sim0.080$ ), 41 ( $f_{41}=0.050\sim0.068$ ), 43 ( $f_{43}=0.087\sim0.103$ ), 44 ( $f_{44}=0.058\sim0.080$ ), 55 ( $f_{55}=0.050\sim0.064$ ) (Table S11).”*

2. The authors present the use of mass spectral similarity analysis in the methods section and discuss five categorizations to be used in the rest of the paper. However, they often deviate from using the categories to describe results. For example, in lines 159-170, 176. they use phrases such as “almost resembled”, “different”, “similar”, and “almost the same variation” to describe mass spectral comparisons instead of

using the five qualitative categories introduced in the paper in Sect. 2.3. The authors should address these inconsistencies by making sure all comparisons are presented in terms of the defined categories. Otherwise, Sect. 2.3 should be removed and all references to the categories removed in the paper.

- Thanks for the reviewer's constructive comment. We modified and unified the description about mass spectral comparisons according to the similarity categorizations in the revised manuscript (line 214-225, and line 298-301 in the marked revised manuscript) as follows:

*"The mass spectra at 2.9 days and 4.1 days had very similar patterns with the most abundant signals at  $m/z$  28 and 44, respectively (**Fig.2** and **Fig.S4**), which showed good consistency with the mass spectra of MO-OOA resolved from ambient datasets( $\theta=14^\circ$  ; compared with MO-OOA obtained during the spring observations in [Ng et al., 2011](#) and [Zhu et al., 2021b](#). When EPA was 1.7 days, there were different mass spectra patterns, with dominant signals at  $m/z$  28 and  $m/z$  44, yet contained a large signal at  $m/z$  43, many similarities with the spectra of the ambient LO-OOA (**Fig.2** and **Fig.S4**) ([Hu et al., 2017](#); [Zhu et al., 2021b](#)). Oxidation degrees greatly affected the similarity of mass spectra between POA and those of aged HOA. The mass spectra profile of HOA\_ambient displayed poor agreement ( $\theta > 30^\circ$ ) with all aged HOA spectra profiles (**Tables S6**). Besides, the mass spectra under the low oxidation degree (EPA was 0.6 day) was also poorly correlated with those mass spectra under the high oxidation degree (EPA were 2.9 and 4.1 days) (**Table S6**)."*

*"In addition, we also found that the  $\theta$  angles between LO-SOA and MO-SOA under five GDI running conditions were ranged from  $36^\circ$  to  $50^\circ$  (**Fig.S11**), indicating that the mass spectra profiles of LO-SOA are poor consistency with those of MO-SOA"*

Similarly, the authors need to pick nomenclature/abbreviations for distinct factors and stick to them throughout. As an example, Fig. 3 refers to vehicle SOA factors as LO-SOA and MO-SOA, but the text below (lines 237) refers to those factors as LO-OOA and MO-OOA. Adding a nomenclature table at the end of the manuscript would also be helpful.

- Thanks for the reviewer's constructive comment. We have corrected the LO-OOA (MO-OOA) with LO-SOA (MO-SOA) in the revised manuscript (line 298-302) as follows:

*"In addition, we also found that the  $\theta$  angles between LO-SOA and MO-SOA under five GDI running conditions were ranged from  $36^\circ$  to  $50^\circ$  (**Fig.S11**), indicating that the mass spectra profiles of PMF LO-SOA are poor consistency with those of PMF MO-SOA, consistent with the changes in the mass spectra characteristics of vehicles, under the same emission conditions and different oxidation conditions."*

According to the reviewer's recommendation, a nomenclature table has been added at the end of the revised manuscript as follows:

## Nomenclature table

Abbreviations	Description
OA	organic aerosol
POA	primary organic aerosol
SOA	secondary organic aerosol
HOA	hydrocarbon-like organic aerosol; associated with vehicle-related emissions in urban
COA	cooking organic aerosol
LO-OOA	low oxygenated organic aerosol
MO-OOA	more oxygenated organic aerosol
PMF	positive matrix factorization
ME-2	a multilinear engine
HR-ToF-AMS	high-resolution time-of-flight aerosol mass spectrometer
SMPS	scanning mobility particle sizers
Go: PAM	Gothenburg Potential Aerosol Mass reactor
VOCs	volatile organic compounds
SVOCs	semi-volatile organic compounds
IVOCs	intermediate volatile organic compounds
O-VOCs	oxygenated volatile organic compounds
$f_{28, 29, 41, 43, \dots}$	fraction of $m/z$ 28, 29, 41, 43... in total organic aerosol
aged HOA	organic aerosols oxidized by Potential Aerosol Mass reactor in vehicle experiments
aged COA	organic aerosols oxidized by Potential Aerosol Mass reactor in cooking experiments
LO-SOA	low oxidized vehicle secondary organic aerosol
MO-SOA	more oxidized vehicle secondary organic aerosol

3. There is literature out there that has evaluated evolution of mass spectra of vehicle emissions such as Kroll et al., 2012. Kroll and co-workers focus on diesel emissions, a major missing gap in this study. Could the authors use mass spectra from such studies for their PMF/ME-2 analysis and quantify the effect of including/excluding such mass spectra in their work? The review by Gentner et al., 2017 might be a useful source to add relevant papers to the literature review in this paper. It is also important to note that the authors have drawn broad conclusions on vehicular emissions based on one vehicle type (one engine) and one fuel. How representative are measurements based on this combination for the entire fleet of Shanghai? This could be discussed in detail in the limitations section (see (7)).

- We appreciate the comments from the reviewer. Kroll et al., 2012 investigated the oxidative aging of diesel exhaust particles. However, the mass spectra of diesel emissions only described the signals at more than  $m/z$  40. In addition, gas-phase species were removed before oxidation to explore the oxidative chemistry of only the lowest-volatility components of the aerosol. It is difficult to directly apply the mass spectra from the work in ME-2 analysis. Some studies have been reported that although the vehicles in

China and Europe are different, e.g., the vehicle is dominated by gasoline in China and diesel in Europe, the HOA spectra from Europe and China are similar (Ng et al., 2011b; Elser et al., 2016), indicating that traffic emissions from different type of vehicles have similar primary profiles. For the secondary SOA profiles of vehicle emissions, different engines and different fuels may affect the characteristics of the SOA mass spectrum. This study only considered a limited kind of engine and one kind of fuel, but it has great limitations. We have combined the other limitations of this study pointed out by the reviewer to supplement the limitations of this study in the revised manuscript (line 411-445 in the marked revised manuscript). Some references in Gentner et al., 2017 have also been added in the literature review in our study.

#### *“4. Limitation and future work*

*POA emissions, and SOA formation in Go: PAM reactor from urban cooking and vehicular sources were explored. The aged COA had higher hydrocarbon ions than aged HOA in mass spectra. The spectra profiles of urban cooking and vehicular sources derived from the lab simulation were performed as constraints in ME-2 model. The OA source apportionment using ME-2 compared with unconstrained PMF based on the HR OA datasets in Shanghai validated the reasonable of the primary and secondary source profiles of cooking and vehicles. It is noted that the vehicle experiments were solely conducted under a single engine with gasoline, and the cooking experiment only related to limited cooking styles. The variations of VOCs in diesel and gasoline vehicle emissions may lead to differences in the SOA characteristics (Wang et al., 2020). The POA and gas-phase precursor emitted from another cooking style - meat charbroiling can also form a large amount of SOA after photochemical oxidation (Kaltsonoudis et al., 2017). More work needs to be done to explore the POA and SOA mass spectrometric characteristics of emissions from vehicles and cooking sources. In addition, SOA mass spectra were split from aged COA and aged HOA by using the PMF model, and therefore provided limited information on dynamic SOA mass spectra; we suggested that further studies control the oxidation conditions to obtain a set of dynamic pure SOA spectral profile. Due to the limitation of Go: PAM, dilution and high concentration of OH radicals without other inorganic aerosol seeds were adopted to measure and simulate atmospheric aging of aerosols. Thus, the possible atmospheric transformations and the reaction pathway are affected. In the future, it is still necessary to take further researches, for instance, use a quasi-atmospheric aerosol evolution study (QUALITY) chamber (Guo et al., 2020) to study the SOA formation under different actual oxidation conditions, like high/low NO<sub>x</sub> and so forth. Moreover, ambient datasets obtained from different sites and seasons need to be analyzed to validate the application of POA and SOA profiles of cooking and vehicles in this study, noting selecting a loose constraint via a value in SOA factors due to their high variability. Our research found that SOA from the urban cooking and vehicular sources contributed 19% and 35% of OA in*

*the wintertime and summertime of Shanghai, implying the need to develop control measures to reduce emissions from cooking and vehicular sources in the future.”*

4. The PMF/ME-2 analysis presented in this paper has multiple shortcomings, both in terms of descriptions in the methods section, as well as the analysis and presentation of results.

a. In the methods section, there is no mention of how the authors conducted ME-2 analysis on the datasets in this study. The Igor PET tool runs on PMF2.exe and does not have a ME-2 option.

- Thanks for the reviewer’s constructive comment. We have supplemented the source apportionment by using PMF and ME-2 in the Materials and Methods section in the revised manuscript (line 337-343 in the marked revised manuscript) as follows:

### ***“2.3 OA source apportionment***

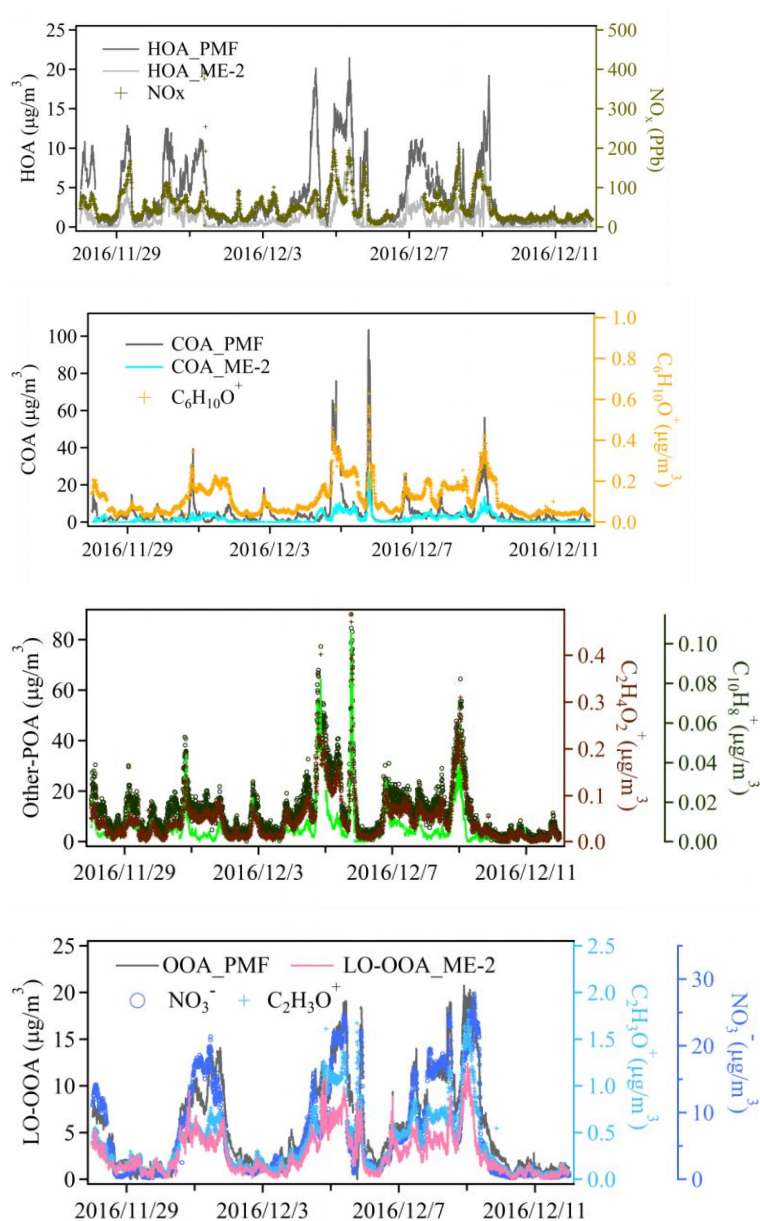
*The PMF model can describe the variability of a multivariate database as a linear combination of static factor profiles and their corresponding time series ([Huang et al., 2020](#); [Wang et al., 2017](#); [Zhu et al., 2018](#)). In this study, we used the Igor-based PMF model with PMF2.exe algorithm ([Paatero and Hopke, 2003](#)) and the PMF Evaluation Toolkit version 2.08D ([Ulbrich et al., 2009](#)) to split POA and SOA factors from cooking and vehicle aged OA. The PMF model was also used to identify the source of OA for ambient atmosphere during the summer and winter observations of Shanghai, following the procedure presented in the literature ([Hu et al., 2016a](#); [Zhang et al., 2011](#)), as described in section 3.3. In contrast to an unconstrained PMF analysis, ME-2 algorithm allows the user to add prior information (e.g., source profiles) into the model to constrain the matrix rotation and separated the mixed solution. In this study, we adopted the toolkit SoFi (Source Finder) within  $\alpha$ -value approach to perform organic HR-AMS datasets collected in Shanghai. The  $\alpha$ -value can vary between 0 and 1, which is the extent to which the output profiles can vary from the model inputs. The  $\alpha$ -value test was performed following the technical guidelines presented in [Crippa et al., 2014](#). The reference mass spectral profiles that constrained in ME-2 analysis were derived from lab-based primary and secondary cooking and vehicular factors of this study. Details of the algorithm could refer to previous studies ([Canonaco et al., 2013](#); [Huang et al., 2020](#); [Reyes-Villegas et al., 2016](#)).”*

b. PMF analysis based on mass spectral similarity analysis only has previously been shown to generate spurious factors ([Ulbrich et al., 2009](#)). Other analyses such as time-series correlations with external tracers need to be presented to justify PMF/ME-2 factors. However, such correlations have been presented only for MO-OOA factor in summer and LO-SOA factor in winter, and not for other factors. Similarly, the other-POA factor could be a mix of the HOA and the COA factors (in the same 2-D plane as defined by the



two vectors), and this should be checked using the scalar triple product. Refer to Ulbrich et al, 2009 for more details.

- We appreciate the comments from the reviewer. The time-series correlations of all factors resolved from PMF and ME-2 with external tracers have been added in the supplement information in the revised manuscript. The related descriptions have been added in the revised manuscript (line 371-389 in the marked revised manuscript).



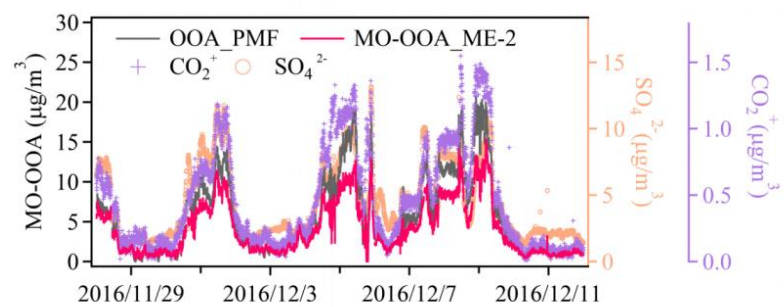


Fig.S17. The time-series correlations of all factors which resolved from PMF and ME-2 with external tracers during the wintertime observations in Shanghai.



Table S21. Pearson r between the factors identified by using PMF and ME-2 model, and the external tracers during the wintertime observations in Shanghai.

Pearson r	Sulfate	CO <sub>2</sub> <sup>+</sup>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> <sup>+</sup>	C <sub>10</sub> H <sub>8</sub> <sup>+</sup>
OOA_PMF	0.90	0.96	0.65	0.96
MO-OOA_ME-2	0.87	0.95	0.61	0.55

Pearson r	Nitrate	C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>
OOA_PMF	0.94	0.90
LO-OOA_ME-2	0.84	0.95

Pearson r	COA_PMF	COA_ME-2
C <sub>6</sub> H <sub>10</sub> O <sup>+</sup>	0.74	0.85

Pearson r	HOA_PMF	HOA_ME-2
NO <sub>x</sub>	0.70	0.64

Pearson r	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> <sup>+</sup>	C <sub>10</sub> H <sub>8</sub> <sup>+</sup>
Other POA_ME-2	0.88	0.88

*“As expected, other POA contributions were identified in the highly polluted season, correlated well with C<sub>2</sub>H<sub>4</sub>O<sub>2</sub><sup>+</sup> and C<sub>10</sub>H<sub>8</sub><sup>+</sup>, which are well-known fragments from biomass burning and coal combustion emissions (Fig.5, Fig.S17 and Table S21). The diurnal patterns of HOA\_PMF were consistent with HOA\_ME-2 during the winter observation, presenting low concentration during the daytime and high concentration at nighttime, likely due to the combined influence of boundary layer height and emissions from diesel vehicles during the nighttime. The temporal variation of two HOA factors showed a high correlation with NO<sub>x</sub> (Pearson r >0.7), suggesting two HOA factors are associated with vehicle emissions. Some variabilities existed between the diurnal cycle of COA\_PMF and COA\_ME-2. However, COA\_ME-2 correlated better with C<sub>6</sub>H<sub>10</sub>O<sup>+</sup> than COA\_PMF, which was considered a fragment tracer mainly from cooking emissions. For SOA factors, the sum of cooking SOA and vehicle LO-SOA had a high correlation with nitrate (Pearson r = 0.84; Fig.S17 and Table S21) and fragments of low-oxidizing substances (C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>; Pearson r = 0.95). In addition, we noticed that the vehicle SOA analyzed by ME-2 exhibited consistency with the diurnal variation of nitrate, especially the reasonable morning peak (~09:00) retained, implying that vehicle SOA is well separated by using ME-2 in winter. MO-OOA resolved via ME-2 was characterized by prominent signal at m/z 28 and m/z 44, consistent with those in OOA identified by using PMF and in*

other studies ([Duan et al., 2020](#); [Kim et al., 2017](#)). Meanwhile, there was a strong correlation between MO-OOA time series and sulfate (Pearson  $r = 0.93$ ), which was representative of regional aging species.”

“The Pearson  $r$  between MO-OOA\_ME-2 and  $\text{CO}_2^+$  ( $m/z$  44), a marker of SOA was 0.95, higher than that of MO-OOA\_PMF (0.79), which better reflects the characteristics of the MO-OOA factor in ME-2 ([Fig.S21](#) and [Table S22](#)).”

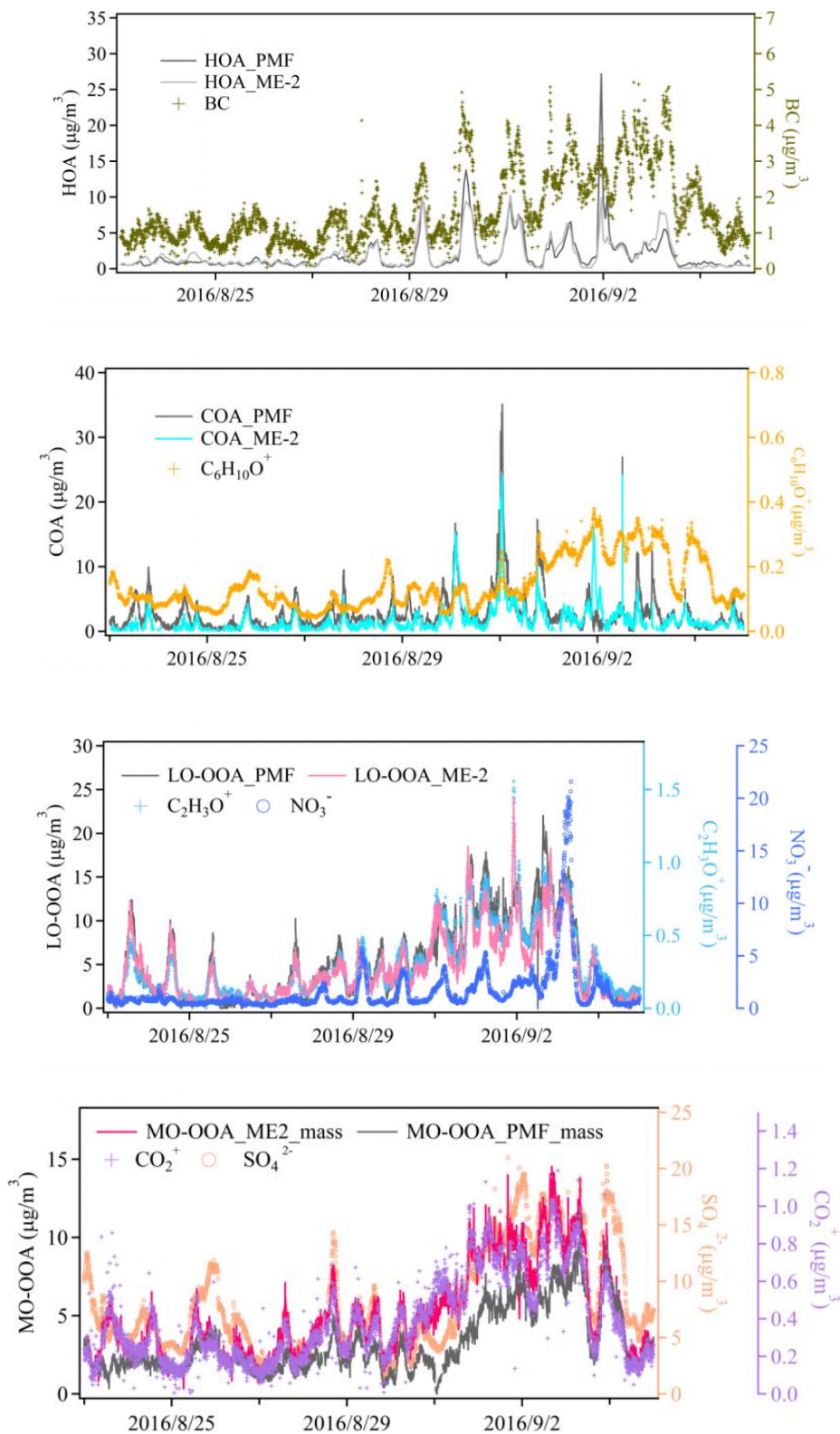


Fig. S21. The time-series correlations of all factors which resolved from PMF and ME-2 with external tracers during the summertime observations in Shanghai.

Table S22. Pearson r between the factors identified by using PMF and ME-2 model, and the external tracers during the summertime observations in Shanghai.

Pearson r	Sulfate	CO <sub>2</sub> <sup>+</sup>
MO-OOA_PMF	0.94	0.79
MO-OOA_ME-2	0.87	0.95

Pearson r	Nitrate	C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>
LO-OOA_PMF	0.53	0.94
LO-OOA_ME-2	0.60	0.96

Pearson r	COA_PMF	COA_ME-2
C <sub>6</sub> H <sub>10</sub> O <sup>+</sup>	0.23	0.36

Pearson r	HOA_PMF	HOA_ME-2
BC	0.52	0.55

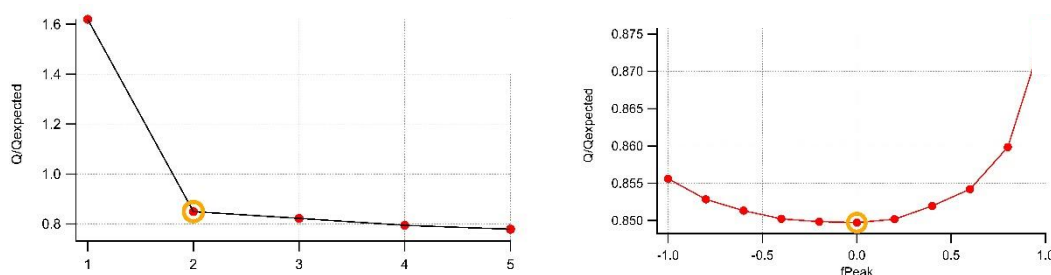
c. The authors use PMF to separate POA and SOA factors from aged HOA and COA detected in this study. However, using single MS to represent entire time series data in a test is an obvious limitation of PMF that has not been explicitly recognized. I suggest the authors recognize this as a limitation explicitly.

- We appreciate the comments from the reviewer. We have added the limitation in the Limitations and further work section in the revised manuscript (line 429-432 in the marked revised manuscript) as follows:

*“In addition, SOA mass spectra were split from aged COA and aged HOA by using PMF model, and therefore provided limited information on dynamic SOA mass spectra; we suggested that further studies control the oxidation conditions to obtain a set of dynamic pure SOA spectral profile.”*

It is also unclear how the references for the application of the PMF technique (line 118) are relevant since they are applying PMF on ambient and not lab datasets.

- We appreciate the comments from the reviewer. The choice of the PMF solution for splitting SOA and POA profiles from aged COA and aged HOA has also been added in the supplement material (Figure S7-S10 and Table S8-S9; taken stir-frying cabbage for cooking, and 2000rpm\_32Nm for vehicle as an example).



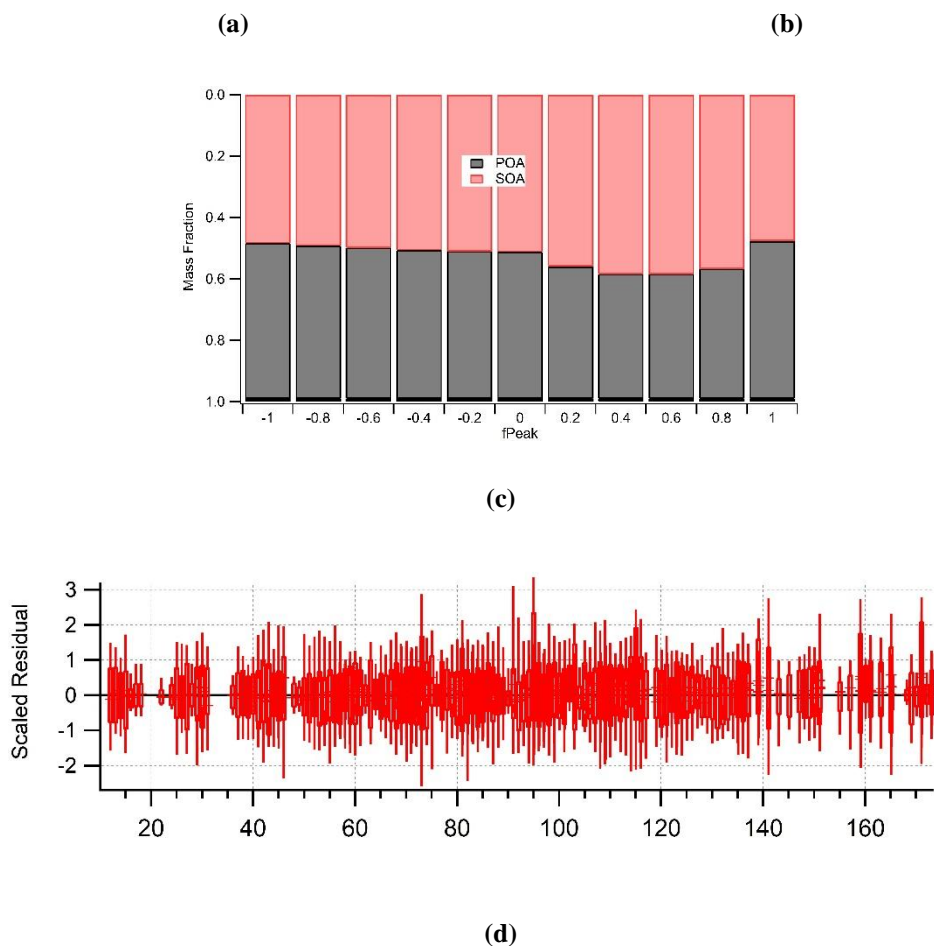
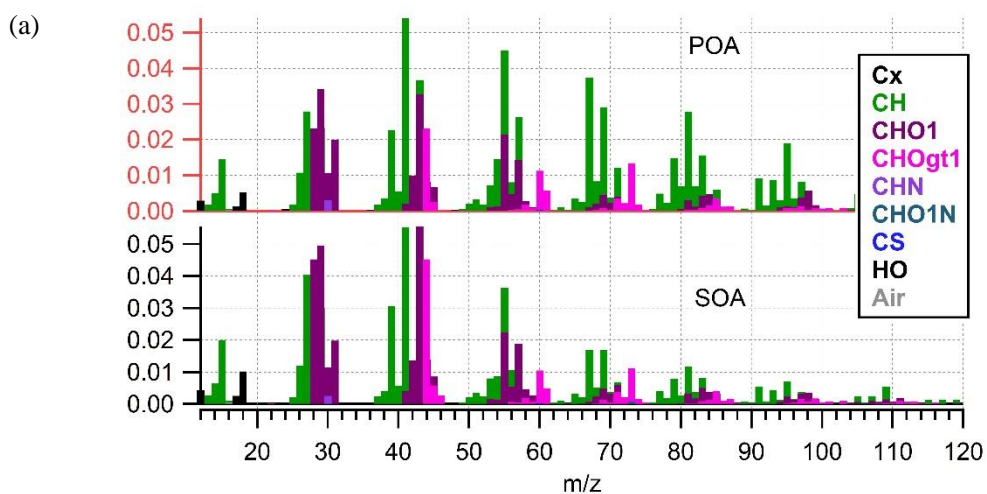


Fig.S7. Diagnostic plots of the PMF analysis on OA mass spectral matrix for stir-frying cabbage. (a)  $Q/Q_{exp}$  as a function of number of factors ( $P$ ) selected for PMF modeling. For the four-factor solution (i.e., the best  $P$ ), (b)  $Q/Q_{exp}$  as a function of  $f_{Peak}$ , (c) The fractions of OA factors vs.  $f_{Peak}$ , (d) The  $Q/Q_{exp}$  values for each  $m/z$



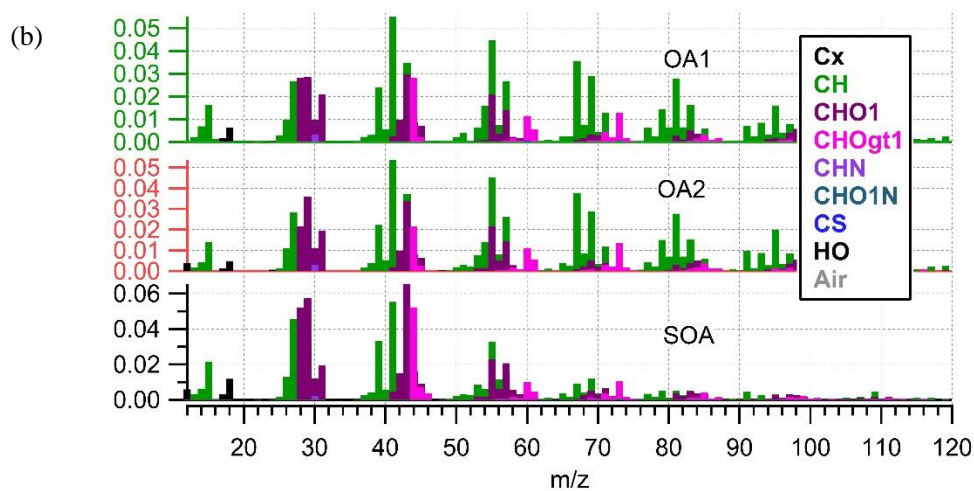


Fig.S8. Mass spectra of the (a) 2-factor, and (b) 3-factor solution using PMF method in stir-frying cabbage OA analysis.

Table S8. The optimum choices for PMF factors in stir-frying cabbage OA analysis.

Factor number	F <sub>peak</sub>	Seed	Q/Q <sub>exp</sub>	Solution Description
1	0	0	1.62	Too few factors, large residuals at time series and key m/z
2	0	0	0.85	<b>Optimum choices for PMF factors (POA and SOA). Time series, mass spectra and diurnal variations of PMF factors are reasonable.</b>
3-5	0	0	0.77-0.82	Factor split. Take 3 factor number solution as an example, POA was split into two factors with similar spectra.

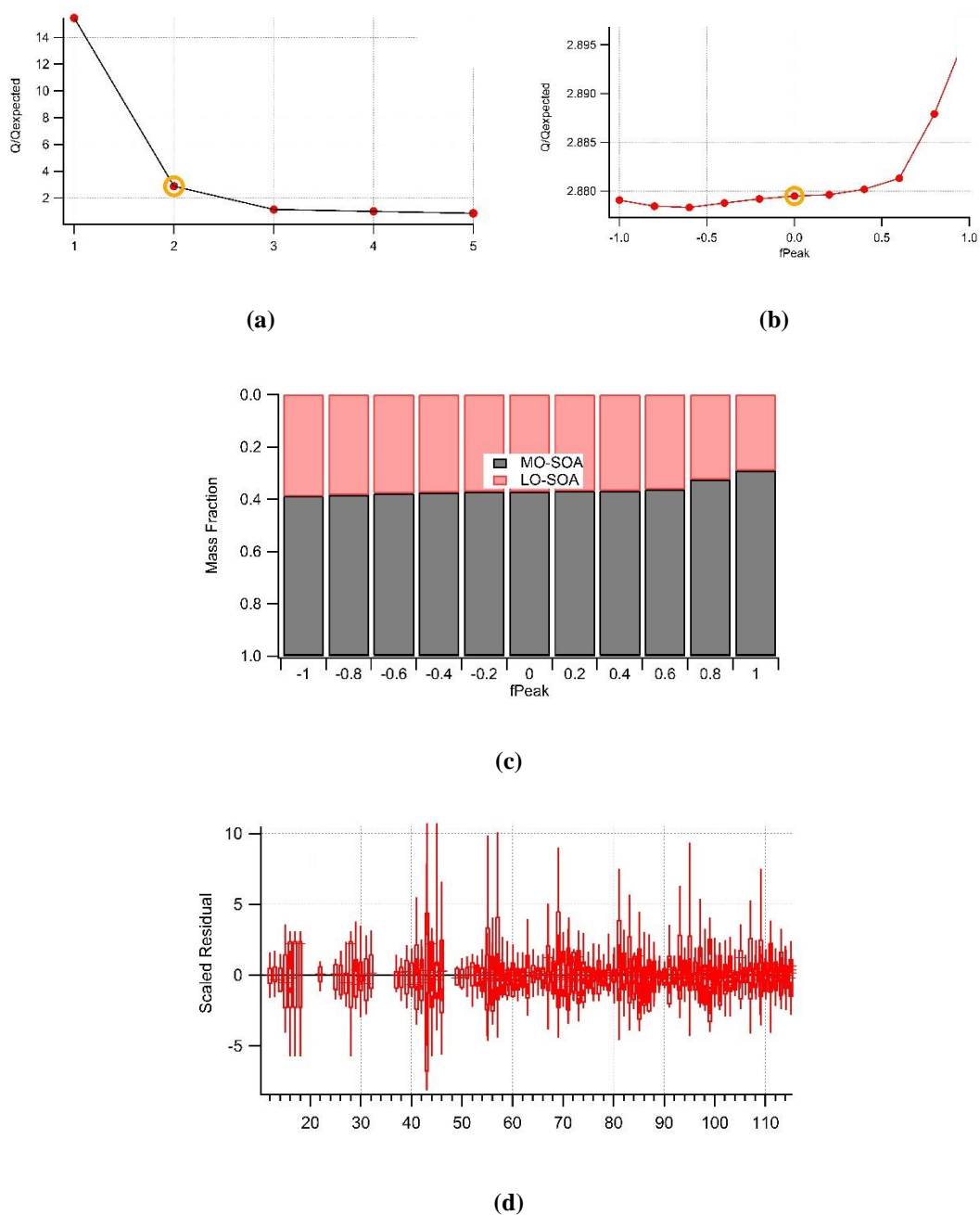


Fig.S9. Diagnostic plots of the PMF analysis on aged HOA mass spectral matrix for 2000rpm\_32Nm. (a)  $Q/Q_{exp}$  as a function of number of factors ( $P$ ) selected for PMF modeling. For the four-factor solution (i.e., the best  $P$ ), (b)  $Q/Q_{exp}$  as a function of  $f_{Peak}$ , (c) The fractions of OA factors vs.  $f_{Peak}$ , (d) The  $Q/Q_{exp}$  values for each  $m/z$



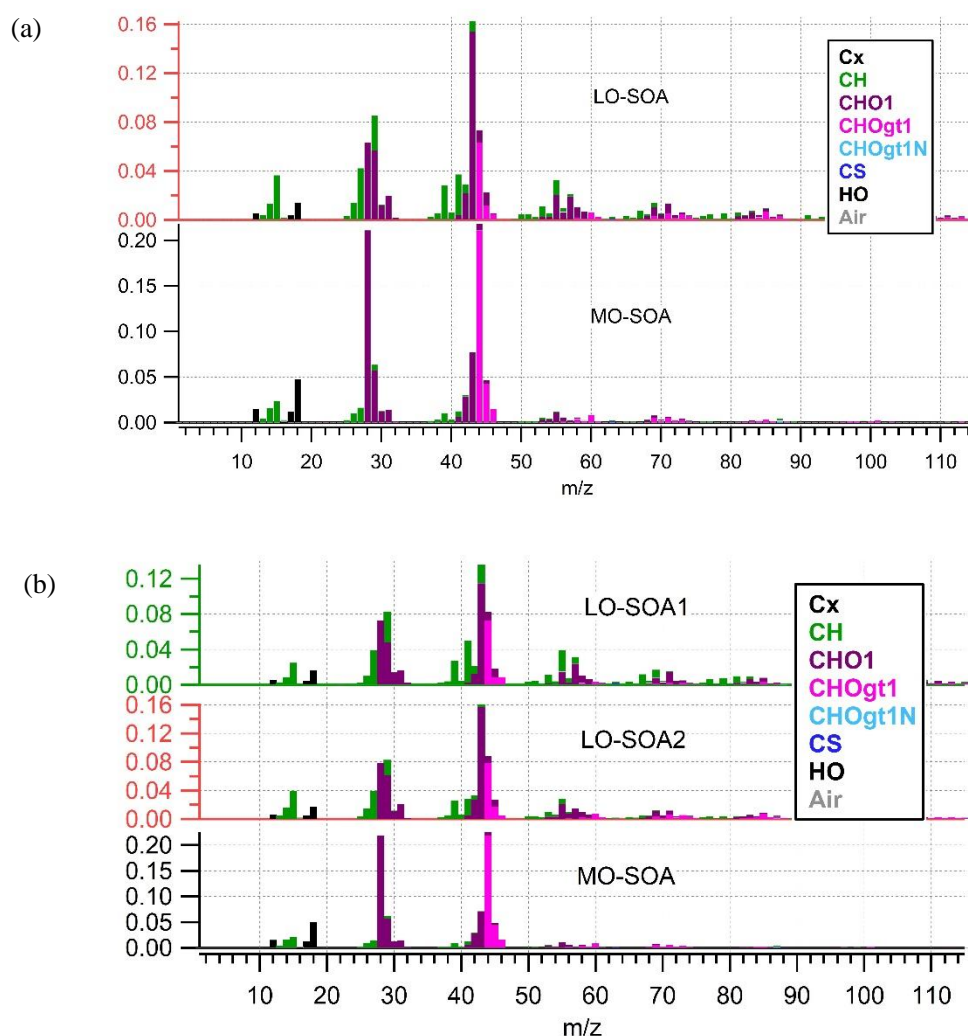


Fig.S10. Mass spectra of the (a) 2-factor, and (b) 3-factor solution using PMF method in 2000rpm\_32Nm aged HOA analysis.

Table S9. The optimum choices for PMF factors in 2000rpm\_32Nm aged HOA analysis.

Factor number	Fpeak	Seed	Q/Q <sub>exp</sub>	Solution Description
1	0	0	15.44	Too few factors, large residuals at time series and key m/z
2	0	0	2.87	<b>Optimum choices for PMF factors (LO-SOA and MO-SOA). Time series, mass spectra and diurnal variations of PMF factors are reasonable.</b>
3-5	0	0	0.85-1.14	Factor split. Take 3 factor number solution as an example, LO-SOA was split into two factors with similar spectra.



Also, it is unclear how this analysis was conducted. Were different EPA tests combined for each type (vehicle operation, food dish) and then PMF conducted? Or was PMF conducted separately for each experiment?

- Thanks for the reviewer's constructive comment. We have supplemented the corresponding description to eliminate reader confusion in the revised manuscript (line 260-262 and line 303-314 in the marked revised manuscript) as follows:

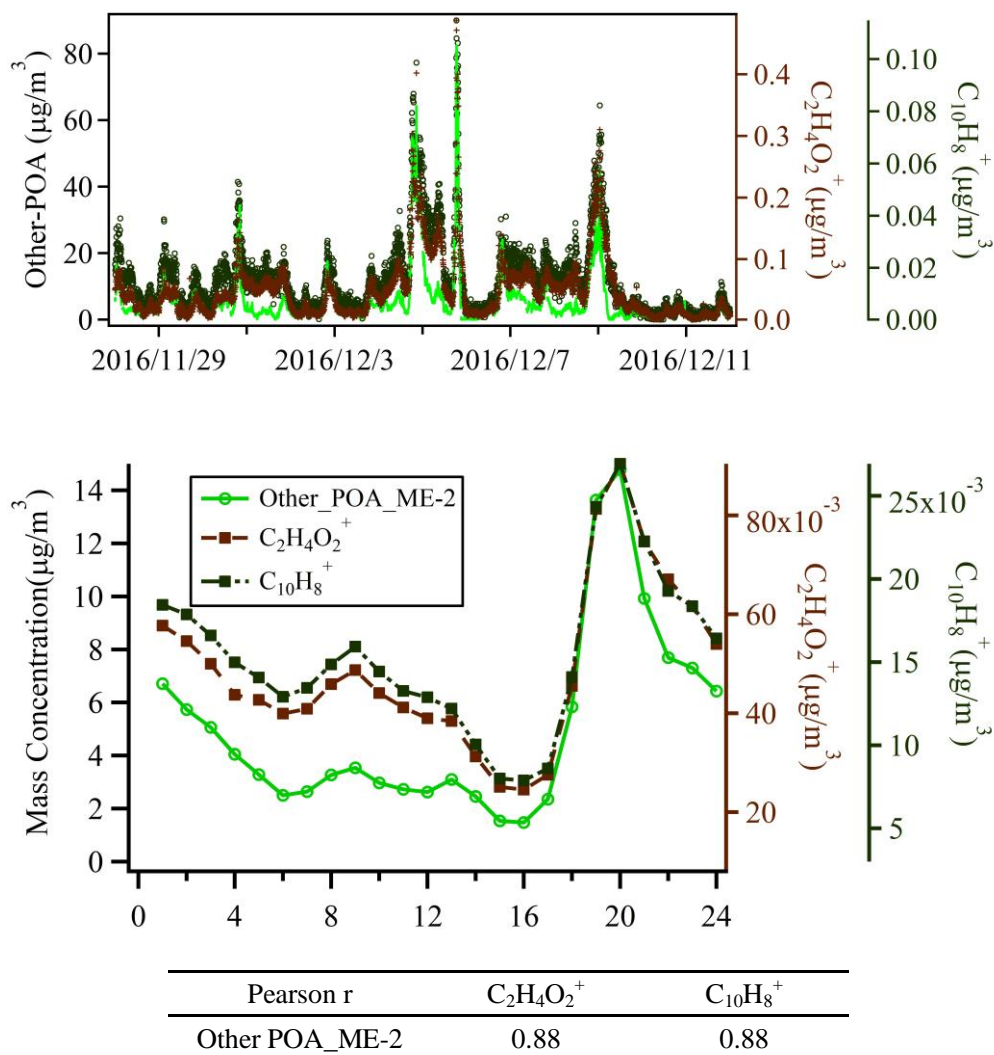
*"PMF analysis was performed on the high-resolution mass spectra to split SOA and POA factors from aged COA under each dish. Similarly, the same PMF procedure was also applied for vehicle datasets for each running condition."*

*"The POA and SOA of the cooking as the primary and secondary spectrum constraints for ME-2 were obtained by averaging the high-resolution mass spectra datasets of the four dishes, which were identified from aged COA using the PMF model. Similarly, combining different GDI running conditions, the averaged LO-SOA and MO-SOA which were resolved based on aged HOA by using the PMF model were used as the inputting mass spectra profiles of vehicles for ME-2. The mass spectral profiles for cooking and vehicle as constraints in ME-2 model are shown in **Fig.S12**."*

d. Why was other-POA in winter not identified as associated with a specific POA component such as BBOA or CCOA, given ambient source apportionment results from Chinese cities (including Shanghai) are readily available from earlier literature? The low levels of contributions at  $m/z$  60,  $m/z$  73, and  $m/z$  115, which are tracers of biomass burning and coal combustion make the argument that this other-POA factor is associated with biomass burning or coal combustion weak. What reference profile does the mass spectral similarity analysis suggest this factor resembles? What evidence do we have with respect to time series correlations?

- Thanks for the reviewer's comment. We analyzed the correlation between the time series/the diurnal of other-POA and those of ion fragments ( $C_2H_4O^+$  and  $C_{10}H_8^+$ ), which be considered as the tracer of biomass burning and coal combustion OA. The analysis has been added in the revised manuscript (line 370-373) as follows:

*"As expected, other POA contributions were identified in the highly polluted season, correlated well with  $C_2H_4O_2^+$  and  $C_{10}H_8^+$ , which are well-known fragments from biomass burning and coal combustion emissions (**Fig.5, Fig.S17 and Table S21**)."*



e. In Section 3.3, the authors compare their approach (of using constrained POA and SOA) to the completely unconstrained PMF approach. However, the improvement of ME-2 for primary factors over unconstrained PMF has already been presented in recent work such as Zhu et al., 2018. So, a more appropriate question to address would be: how much of an improvement do we observe in the ME-2 method when both primary and secondary factors are constrained (compared to when only the primary factors are constrained)? Given the PMF and ME-2 runs the team has already conducted, such a comparison should not be hard to perform, and will give much more substantial insight into the importance of the approach compared to the current presentation. Another result that could arise from this comparison is that constraining the secondary factors could be overconstraining the PMF runs, which leads to factor mixing and reduced number of factors. Interestingly, Zhu et al., 2018 were able to separate coal combustion and biomass burning cleanly in winter during heavily polluted periods using their only primary factor-constrained ME-2 approach.

- We appreciate the comments from the reviewer. The OA source apportionment using two primary (COA and HOA) profiles as constraints in ME-2 model were performed. The comparison with the ME-2

analysis by constraining four profiles has been added in the supplemental materials. The detailed descriptions have also been supplemented in the revised manuscript (line 395-401 in the marked revised manuscript) as follows:

*“In comparing the ME-2 analysis results with only two POA factors constraining to that of the four factors constraining, the diurnal variations of HOA and COA obtained by constraining two primary sources were more consistent with those of the ME-2 constraint four-factor than PMF. However, OOA and POA were weakly separated, and the diurnal patterns of OOA were correlated with the case for the peak of other-POA during the evening (20:00~21:00) (Fig.S18-S19). These phenomena imply that the SOA factor constraint can more environmental meaningful factors to a certain extent.”*

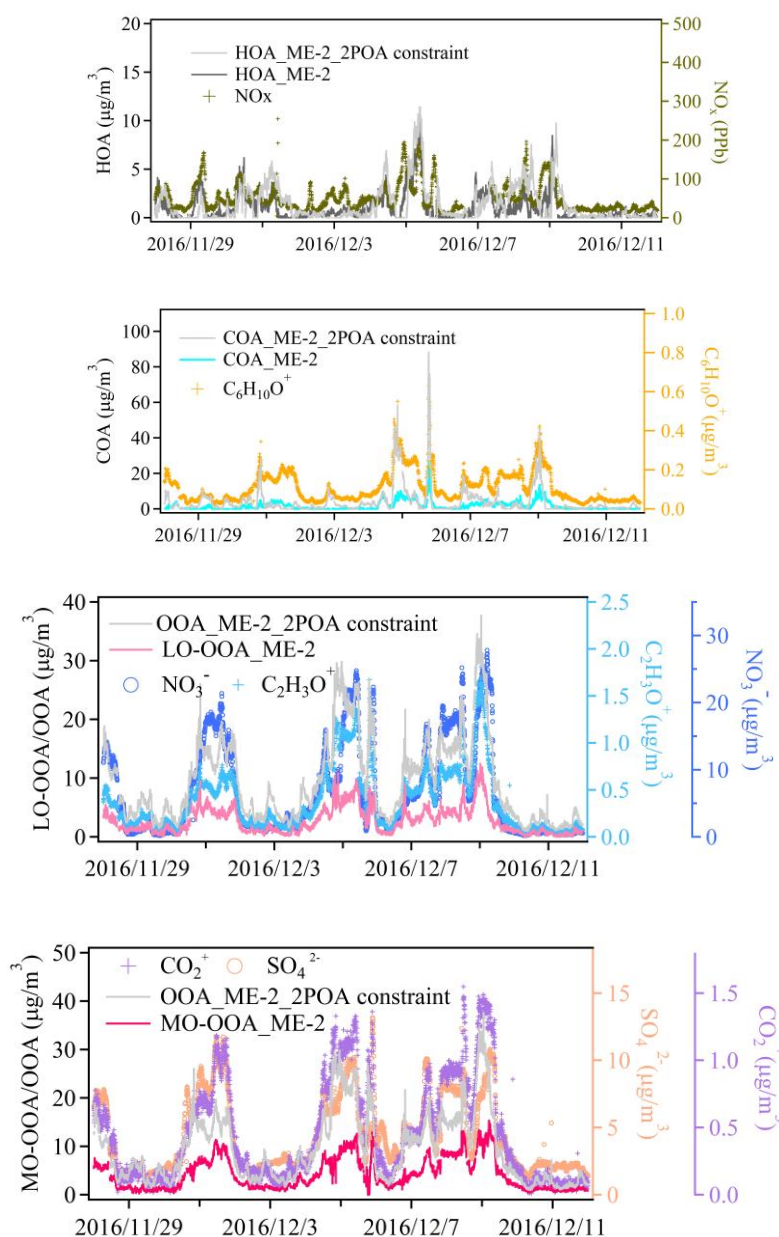


Fig. S18. The time-series correlations of all factors which resolved from ME-2 constraining two POA profiles and ME-2 constraining four factors spectral profiles with external tracers during the wintertime observations in Shanghai.

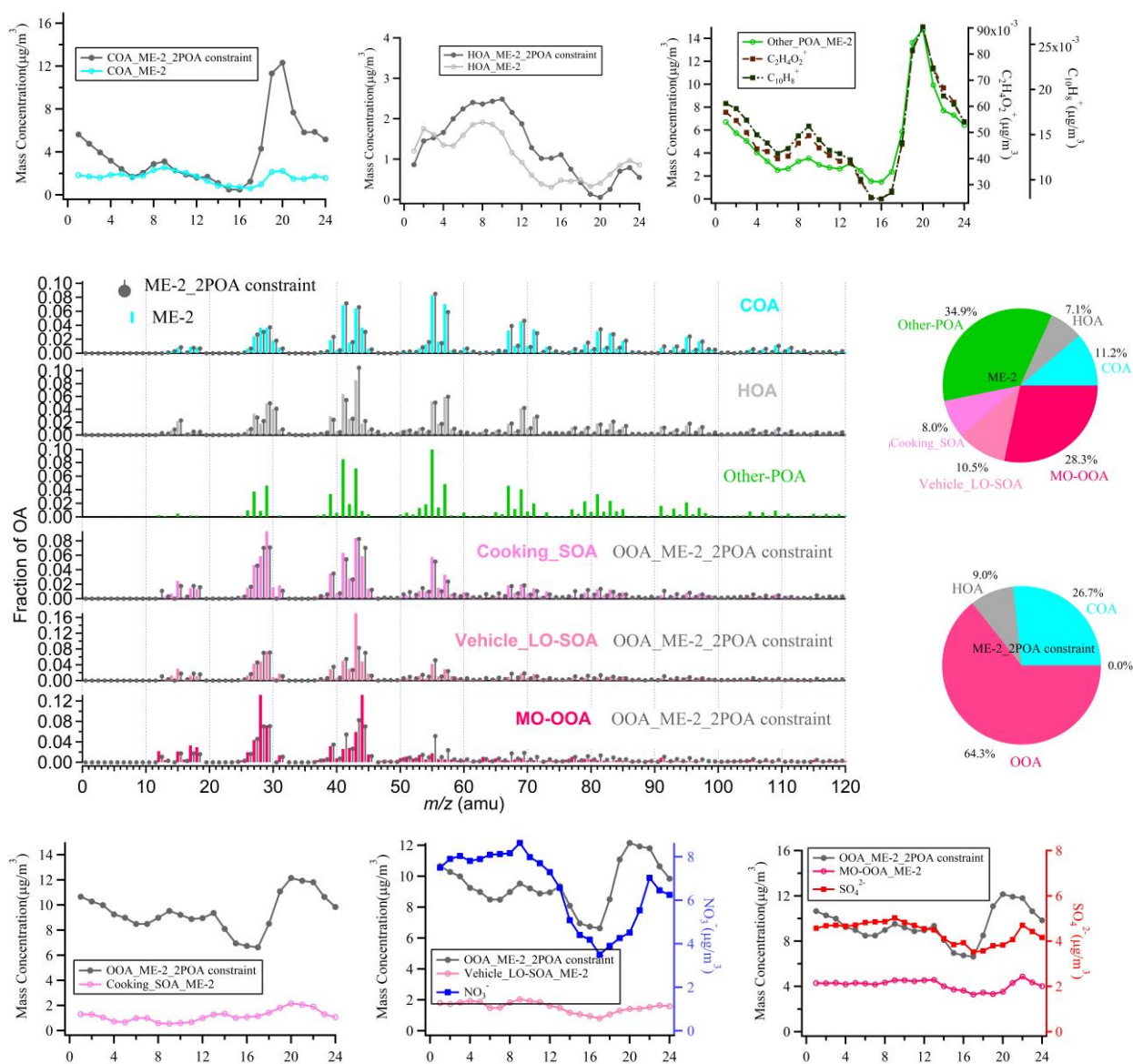


Fig.S19. The comparison of the mass spectra, the diurnal variation, and fraction between ME-2 constraining the spectral profiles of two primary factors (the cooking POA, ambient HOA) and ME-2 constraining four spectral profiles resolved factors during the wintertime in Shanghai. The black lines in the spectra and diurnal pattern are the results of ME-2 analysis by constraining two spectral profiles in the actual atmosphere in Shanghai winter. The four spectral profiles were two primary OA factors (the cooking POA, ambient HOA resolved in three cities) and two secondary OA factors (the cooking SOA, the vehicle LO-SOA).

f. The final choice of constraints using ME-2 was described in vague terms in lines 259-260 and lines 265-269. “Considering the actual oxidation conditions or the concentration of OH radicals, the cooking PMF POA, SOA, and the vehicle PMF LO-SOA was finally selected as the input source spectra of ME-2. In addition, the ME-2 source analysis was performed by using two primary OA factors (the cooking PMF POA, HOA resolved in three cities) and two secondary OA factors (the cooking PMF SOA, the vehicle PMF LO-SOA) as constraints based on the same ambient OA datasets as PMF model during the summer and winter observations of Shanghai.” This is insufficient explanation. Why were vehicle POA and vehicle MO-SOA factors from lab tests not selected? Why was HOA resolved in three cities selected? This seems an

arbitrary choice and needs to be justified further so the approach can be replicated in the future. Also, was the average of the HOA MS from three cities selected? I did not find the MS of that factor in the paper. How similar or different is it from the lab vehicle HOA MS, and why?

- We appreciate the comments from the reviewer. - Due to the low concentration of particulate matter emitted by the engine in this study, the uncertainty of the primary source mass spectrum is large. We used ambient HOA as the vehicle POA. The ambient HOA was identified by PMF model based on OA observation data of several cities. In the subsequent use of PMF to split vehicle aerosol, we only put the aged HOA (organic aerosol after oxidation) under different working conditions together, rather than the aged HOA and the primary OA together to split the mixed aerosol. We also used ambient HOA instead of vehicle POA as source constrain and input it into ME-2. To relieve confusion, we have made a supplementary explanation in the revised manuscript (line 205-213 and line 322-327 in the marked revised manuscript) as follows:

*“It was worth noting that the source characteristics of vehicle POA were uncertain due to its low concentration emitted from the engine in this study. A related study has found that the POA factor from vehicle emissions is similar to the HOA factor derived from environmental datasets ([Presto et al., 2014](#)). Therefore, we used the average HOA spectrum derived from unconstrained PMF analysis based on the ambient observations of Shanghai, Beijing, Dezhou, Shenzhen in China as an alternative to the mass spectrum of vehicle POA, as shown in **Fig.2a** and **Fig S4**. Detailed observation information of Shanghai, Dezhou, and Shenzhen referred to [Zhu et al., 2021a](#). The observations in Beijing have been given in [Hu et al., 2017](#). The HOA spectrum was similar to that reported in [Ng et al., 2011](#), which has been widely used as traffic emission profiles.”*

*“Constraining many SOA factors could be over-constraining the ME-2 runs, which leads to factor mixing and reduces the number of factors. In addition, considering the actual oxidation conditions, that is the concentration of OH radicals, and the lacking vehicle POA, the cooking POA, cooking SOA, vehicle LO-SOA, and ambient HOA (instead of vehicle POA; derived from Beijing, Shenzhen, Dezhou, Shanghai ambient measurements) was finally selected as the input source spectra of ME-2.”*

g. Factor uncertainties, residual, and total concentrations should be reported for each PMF/ME-2 analysis.

- The choice of the PMF solution for splitting SOA and POA profiles from aged COA and aged HOA has also been added in the supplement material (Figure S7-S10 and Table S8-S9; taken stir-frying cabbage for cooking, and 2000rpm\_32Nm for vehicle as an example). The optimal solution for ambient atmosphere



by using PMF model and ME-2 model has been described in the manuscript. All the changes are documented in the revised manuscript (line 338-342; Figure S13-S16 and Table S19-S20) as follows:

*“In ME-2 solutions from 1 to 7 factors, we found the solution of 6 factors (i.e., COA, HOA, Other-POA, Cooking SOA, Vehicle LO-SOA) was most interpretable for the wintertime observations. For the 5 factors solution, in addition to the constraint four factors, factor 5 appeared to be mixed primary and secondary features. However, Other-POA split into two factors with similar profiles in seven factors solution (Fig. S13).”*

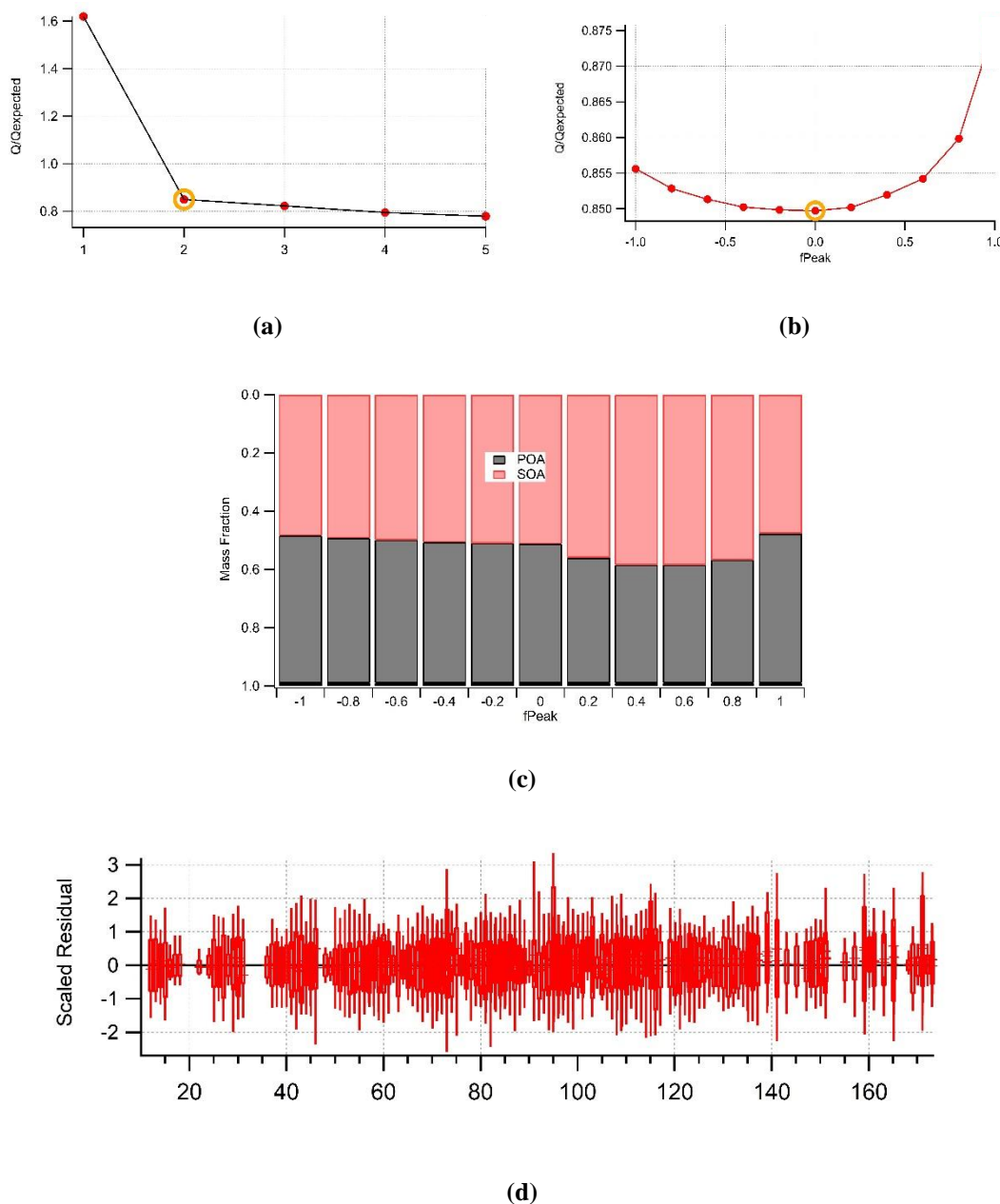


Fig.S7. Diagnostic plots of the PMF analysis on OA mass spectral matrix for stir-frying cabbage. (a)  $Q/Q_{exp}$  as a function of number of factors ( $P$ ) selected for PMF modeling. For the four-factor solution (i.e., the best  $P$ ), (b)  $Q/Q_{exp}$  as a function of  $f_{Peak}$ , (c) The fractions of OA factors vs.  $f_{Peak}$ , (d) The  $Q/Q_{exp}$  values for each  $m/z$

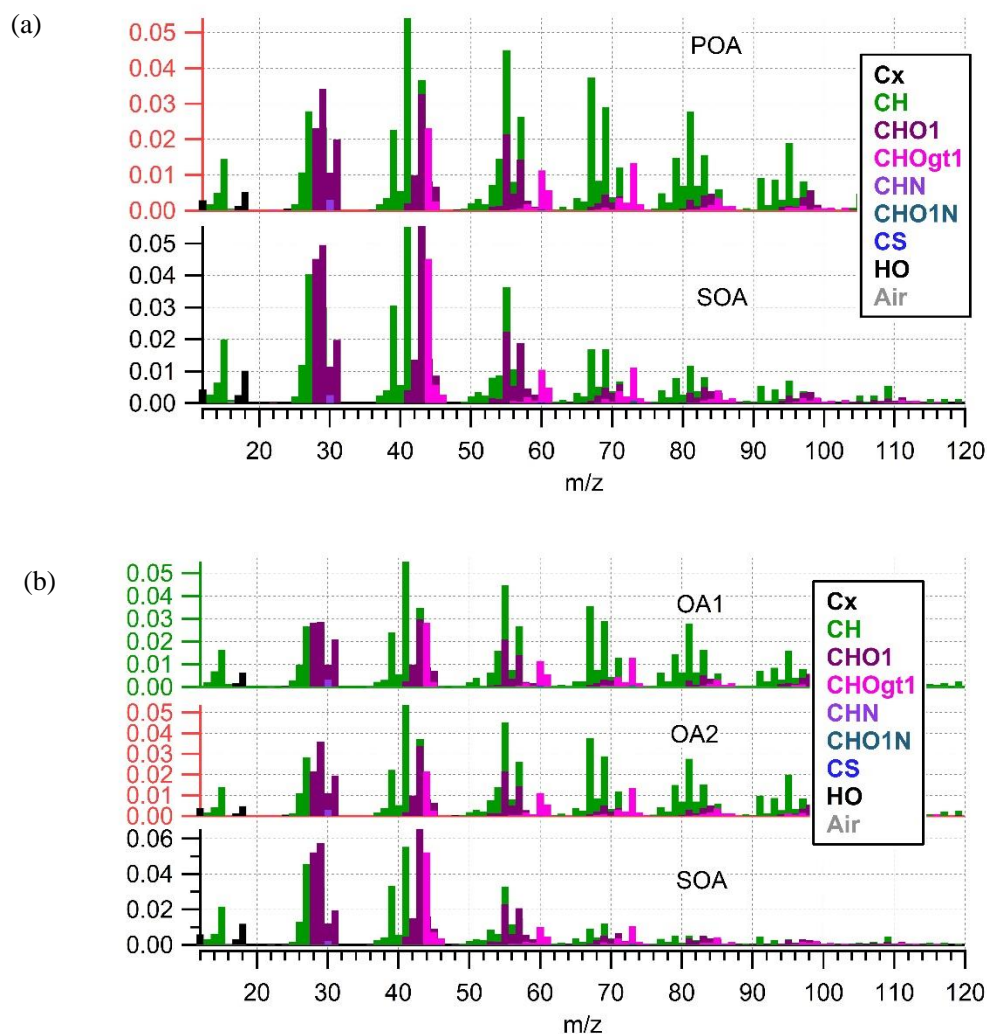


Fig.S8. Mass spectra of the (a) 2-factor, and (b) 3-factor solution using PMF method in stir-frying cabbage OA analysis.

Table S8. The optimum choices for PMF factors in stir-frying cabbage OA analysis.

Factor number	F <sub>peak</sub>	Seed	Q/Q <sub>exp</sub>	Solution Description
1	0	0	1.62	Too few factors, large residuals at time series and key m/z
2	0	0	0.85	<b>Optimum choices for PMF factors (POA and SOA). Time series, mass spectra and diurnal variations of PMF factors are reasonable.</b>
3-5	0	0	0.77-0.82	Factor split. Take 3 factor number solution as an example, POA was split into two factors with similar spectra.



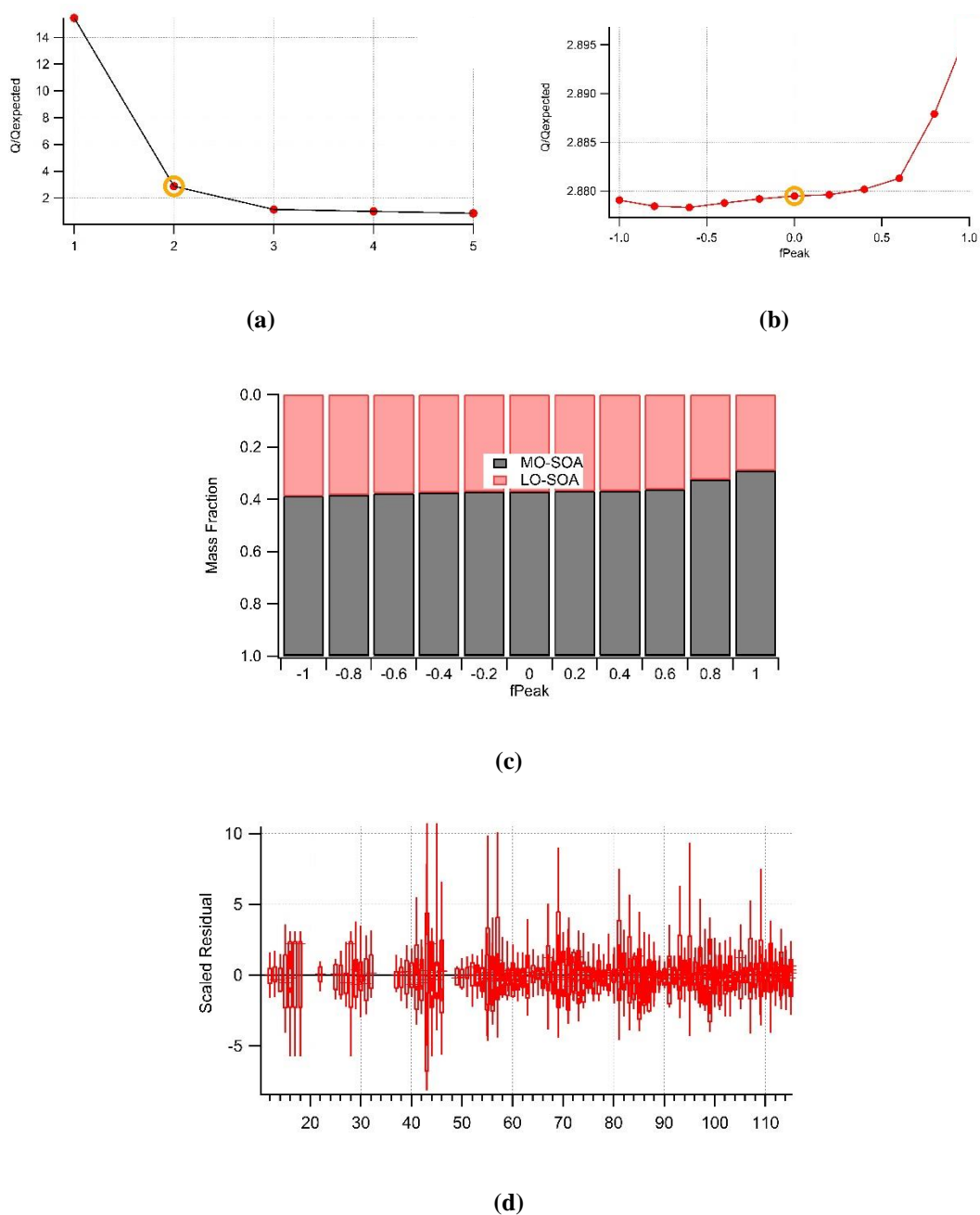


Fig.S9. Diagnostic plots of the PMF analysis on aged HOA mass spectral matrix for 2000rpm\_32Nm. (a)  $Q/Q_{exp}$  as a function of number of factors ( $P$ ) selected for PMF modeling. For the four-factor solution (i.e., the best  $P$ ), (b)  $Q/Q_{exp}$  as a function of  $f_{Peak}$ , (c) The fractions of OA factors vs.  $f_{Peak}$ , (d) The  $Q/Q_{exp}$  values for each  $m/z$

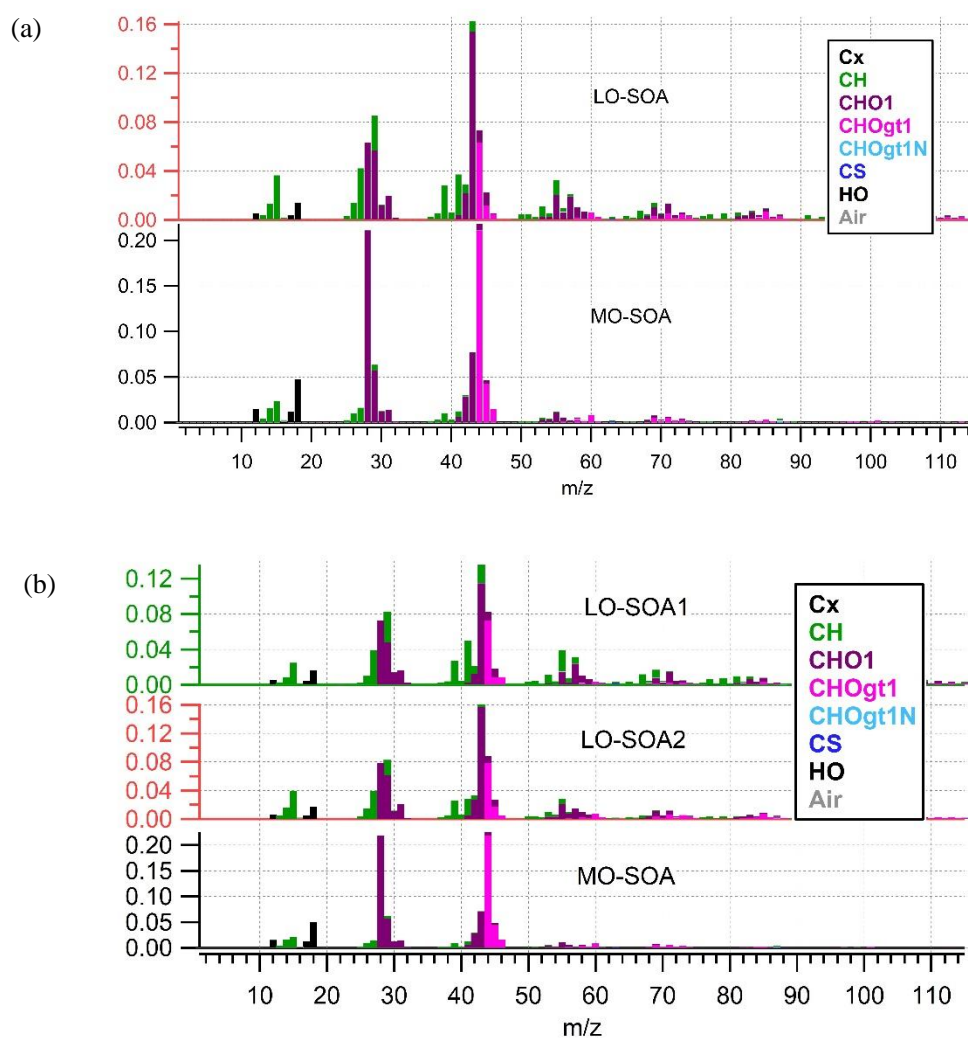
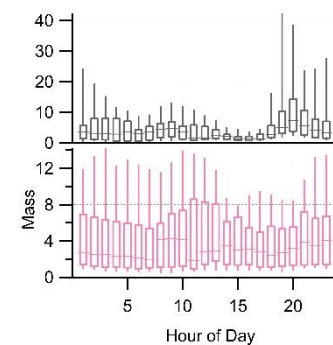
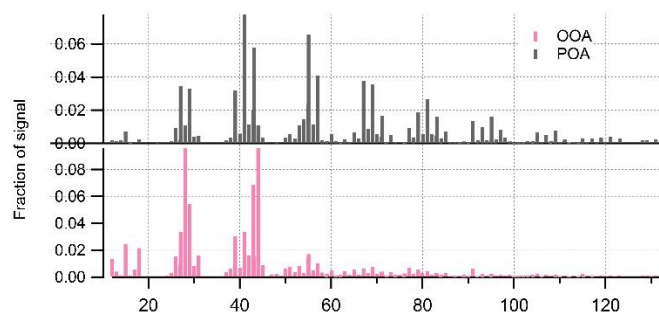
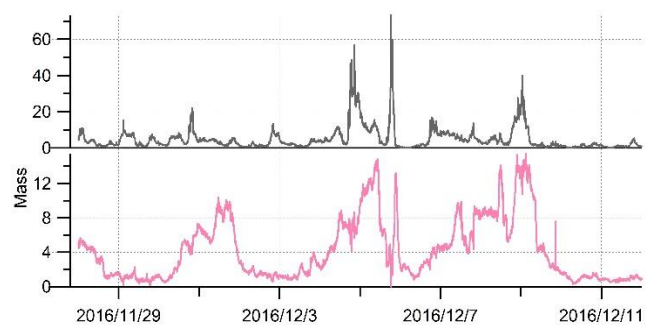


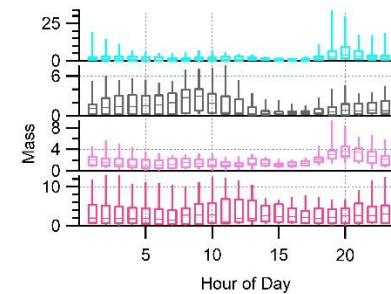
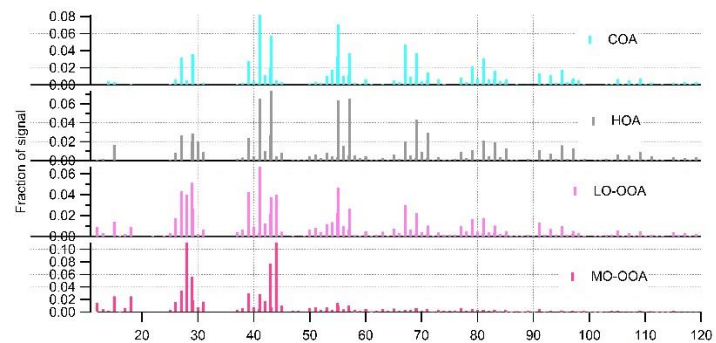
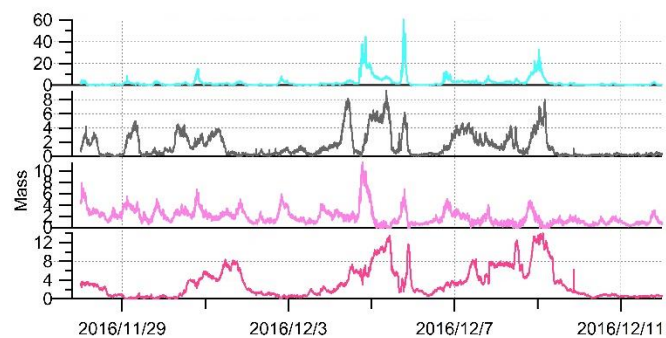
Fig.S10. Mass spectra of the (a) 2-factor, and (b) 3-factor solution using PMF method in 2000rpm\_32Nm aged HOA analysis.

Table S9. The optimum choices for PMF factors in 2000rpm\_32Nm aged HOA analysis.

Factor number	Fpeak	Seed	Q/Q <sub>exp</sub>	Solution Description
1	0	0	15.44	Too few factors, large residuals at time series and key m/z
2	0	0	2.87	<b>Optimum choices for PMF factors (LO-SOA and MO-SOA). Time series, mass spectra and diurnal variations of PMF factors are reasonable.</b>
3-5	0	0	0.85-1.14	Factor split. Take 3 factor number solution as an example, LO-SOA was split into two factors with similar spectra.



(a)



(b)

Fig.S13. (a) 2-factor solution performed by PMF on organic mass spectra during the wintertime in Shanghai; (b) 4-factor solution performed by PMF on organic mass spectra during the wintertime in Shanghai.

Table S19. Pearson r between the factors identified by using PMF model (4-factor solution), and the external tracers during the wintertime observations in Shanghai.

Pearson r	Sulfate	CO <sub>2</sub> <sup>+</sup>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> <sup>+</sup>	C <sub>10</sub> H <sub>8</sub> <sup>+</sup>
MO-OOA_PMF	0.89	0.96	0.67	0.61

Pearson r	Nitrate	C <sub>2</sub> H <sub>3</sub> O <sup>+</sup>	C <sub>6</sub> H <sub>10</sub> O <sup>+</sup>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> <sup>+</sup>	C <sub>10</sub> H <sub>8</sub> <sup>+</sup>
LO-OOA_PMF	0.04	0.31	0.44	0.51	0.59

Pearson r	COA_PMF
C <sub>6</sub> H <sub>10</sub> O <sup>+</sup>	0.81

Pearson r	HOA_PMF
NO <sub>x</sub>	0.73

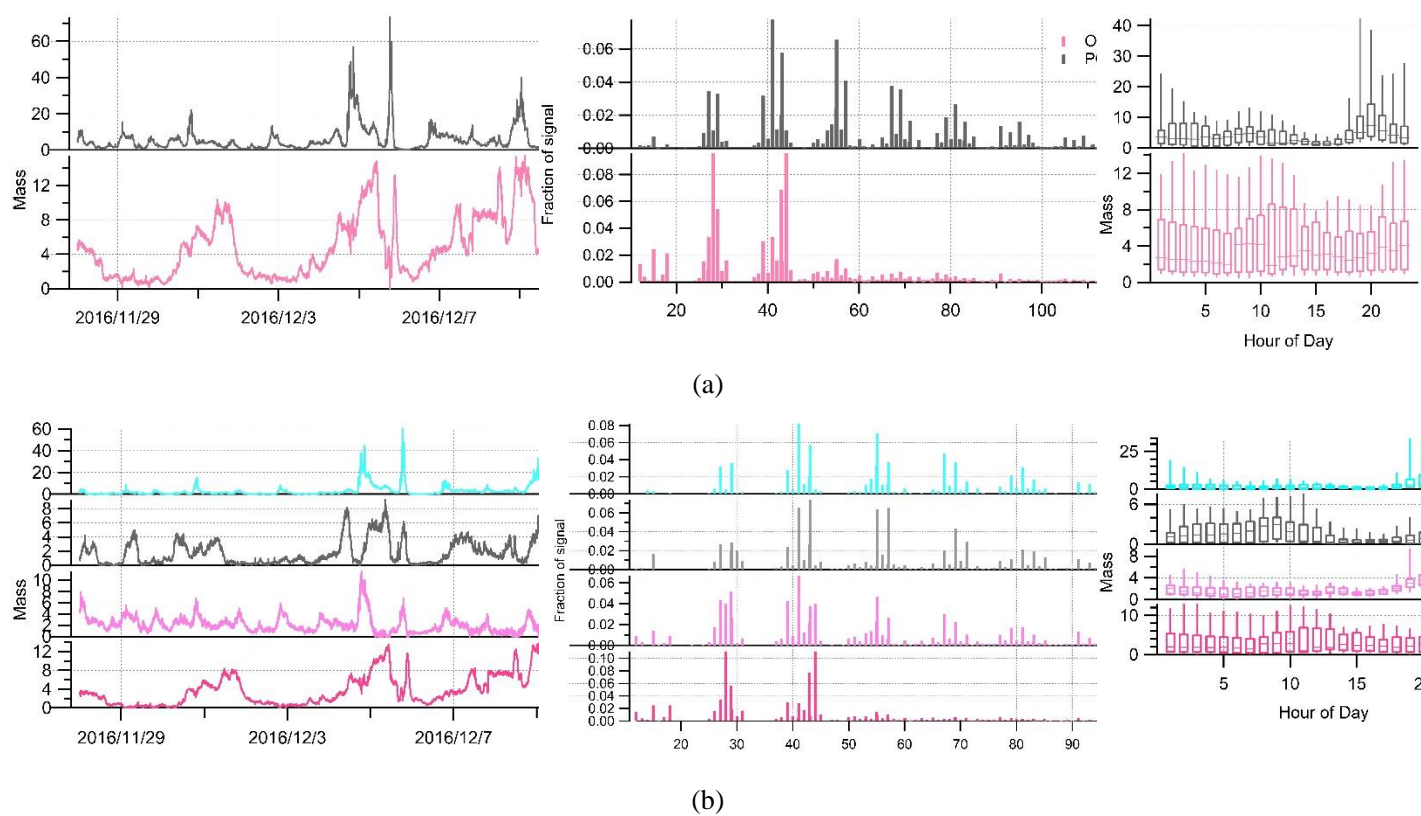


Fig.S14. (a) 2-factor solution performed by PMF on organic mass spectra during the wintertime in Shanghai; (b) 4-factor solution performed by PMF on organic mass spectra during the wintertime in Shanghai.

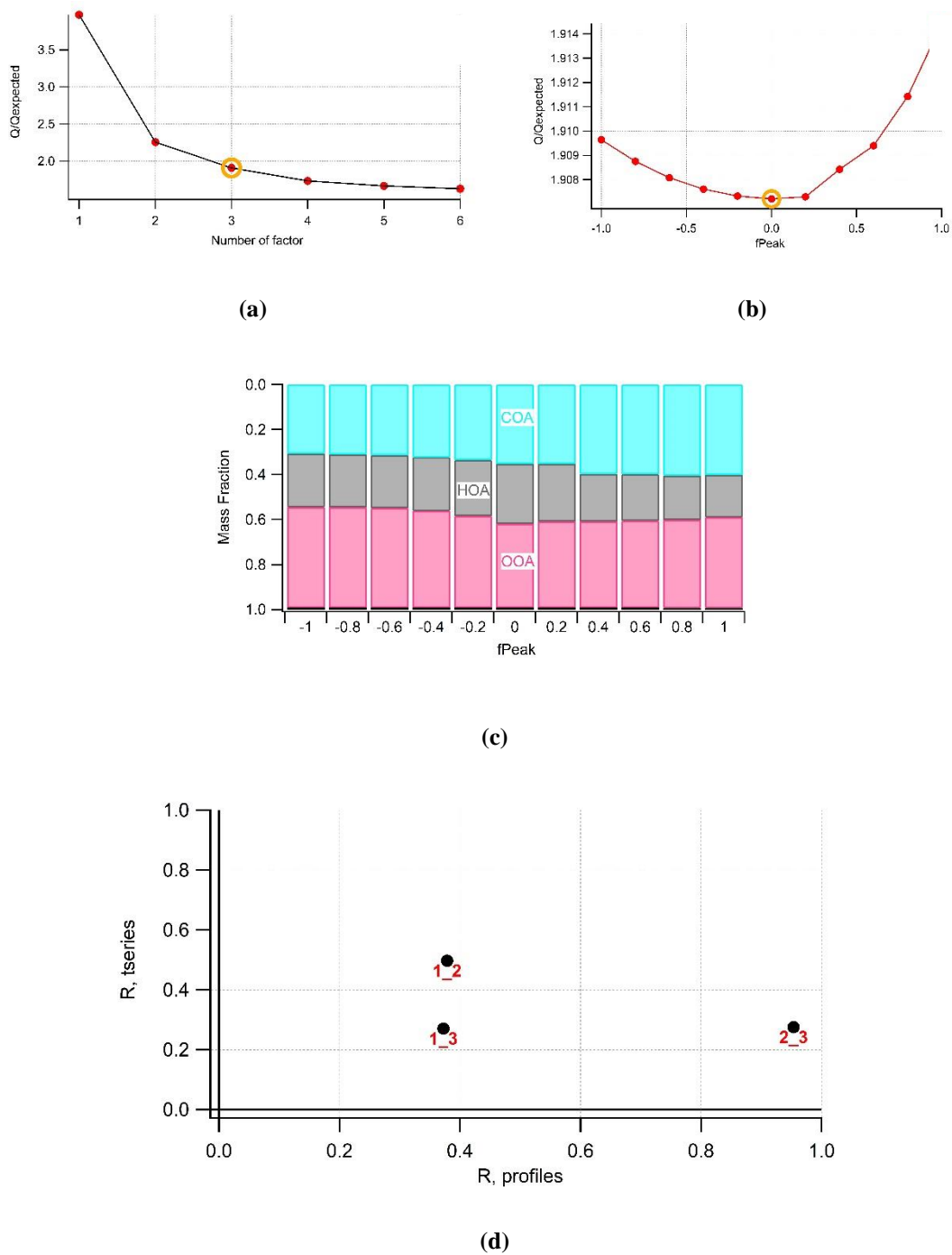


Fig.S15. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the winter observations. (a)  $Q/Q_{exp}$  as a function of number of factors ( $P$ ) selected for PMF modeling. For the four-factor solution (i.e., the best  $P$ ), (b)  $Q/Q_{exp}$  as a function of  $f_{Peak}$ , (c) The fractions of OA factors vs.  $f_{Peak}$ , (d) The correlations among PMF factors.

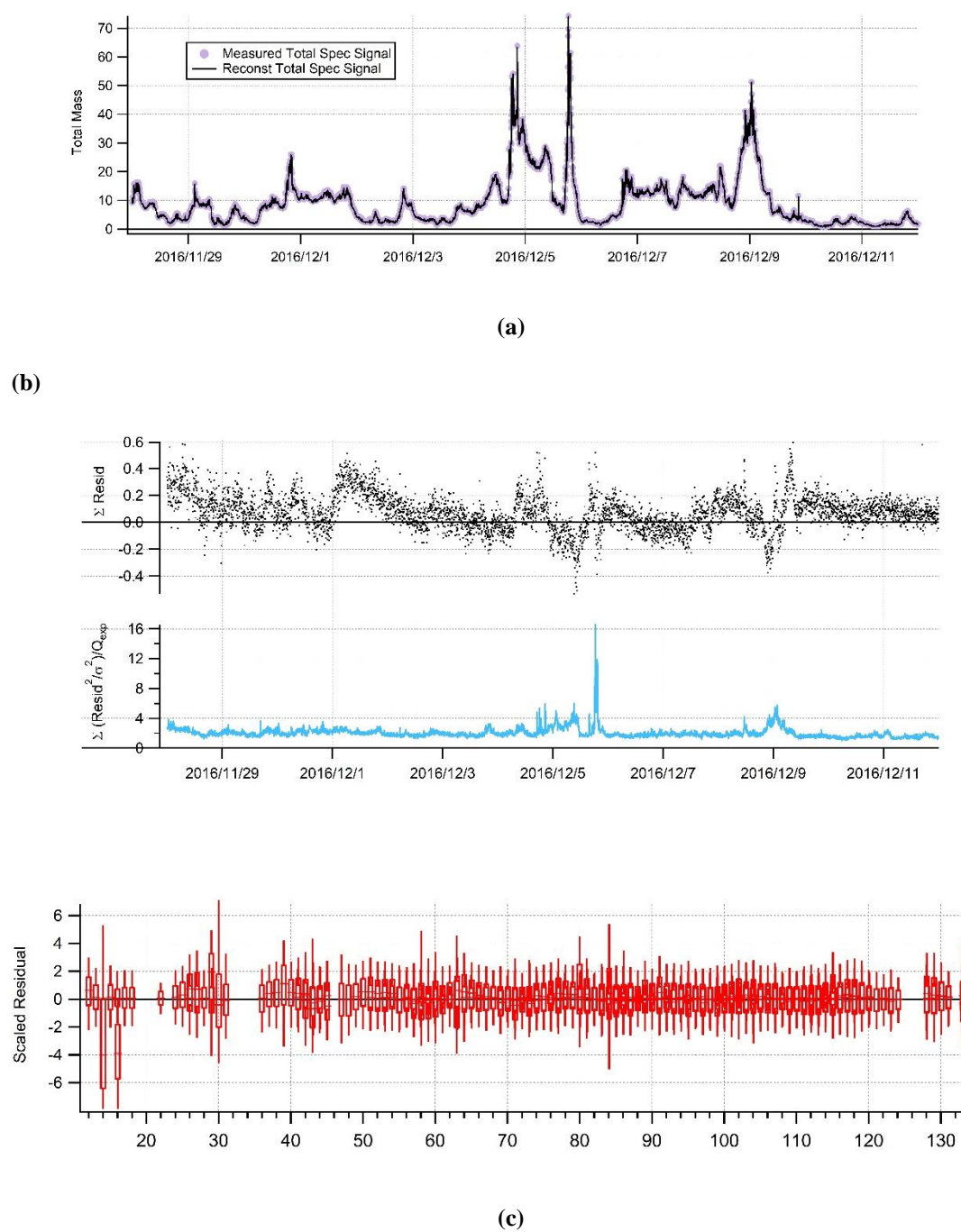


Fig.S16. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the winter observations. (a) Time series of the measured organic mass and the reconstructed organic mass, (b) Variations of the residual (= measured – reconstructed) of the fit, and the  $Q/Q_{exp}$  for each point in time, and (c) The  $Q/Q_{exp}$  values for each  $m/z$



Table S20. Descriptions of PMF solutions for organic aerosol in the winter study of Shanghai.

Factor number	F <sub>peak</sub>	Seed	Q/Q <sub>exp</sub>	Solution Description
1	0	0	3.97	Too few factors, large residuals at time series and key m/z
2	0	0	2.26	Few factors (OOA- and HOA-like), large residuals at time series and key m/z. Factors are mixed to some extent based on the time series and spectra.
3	0	0	1.91	<b>Optimum choices for PMF factors (OOA, HOA and COA). Time series and diurnal variations of PMF factors are consistent with the external tracers. The spectra of four factors are consistent with the source spectra in AMS spectra database.</b>
4-6	0	0	1.63-1.73	Factor split. Take 4 factor number solution as an example, LO-OOA was split from other factors.

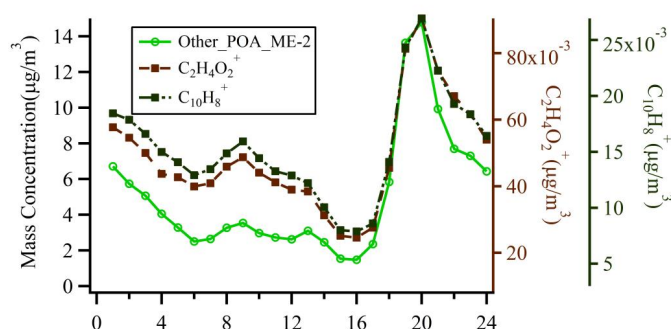
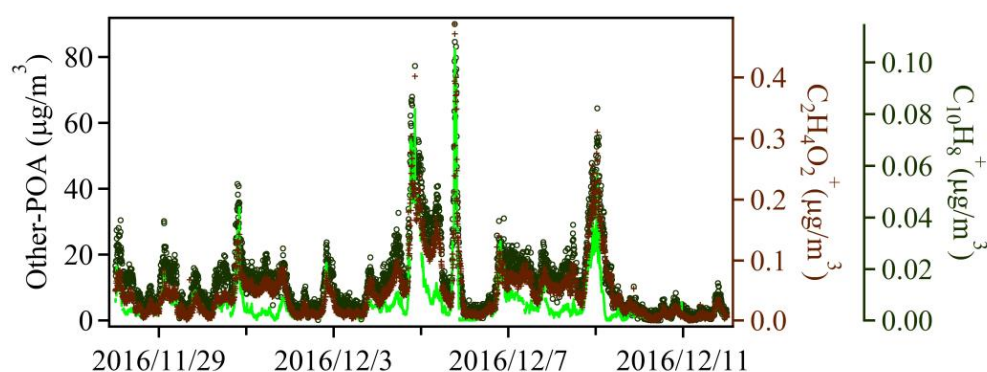
5. The conclusions of the paper are very generalized and presented as applicable to broad categories of cooking and vehicular emissions in ambient environments. However, the experiments conducted by the authors are limited in their scope: cooking experiments are all frying-based, and only one gasoline engine was assessed at a few operating conditions (combinations of vehicle speeds and torques) in this study. I have a few questions associated with this choice that questions the confidence the authors place in their PMF/ME-2-based COA and HOA concentrations and composition.

a. Could a different type of cooking be a part of other-POA and frying-related COA is what the authors are referring to as primary COA?

b. Similarly, could a different type of vehicle emission be a part of other-POA, and gasoline-related HOA is what the authors are referring to as primary HOA?

-We analyzed the correlation between the time series/the diurnal of other-POA and those of ion fragments ( $C_2H_4O_2^+$  and  $C_{10}H_8^+$ ), which be considered as the tracer of biomass burning and coal combustion OA. The analysis has been added in the revised manuscript (line 370-373) as follows:

*“As expected, other POA contributions were identified in the highly polluted season, correlated well with  $C_2H_4O_2^+$  and  $C_{10}H_8^+$ , which are well-known fragments from biomass burning and coal combustion emissions (Fig.5, Fig.S17 and Table S21).”*



Pearson r	$C_2H_4O_2^+$	$C_{10}H_8^+$
Other POA_ME-2	0.88	0.88

c. This would also complicate the secondary COA and HOA argument. Why is there no secondary component associated with the other-POA factor? How much of the MO-OOA factor is associated with other COA (non-frying) and other HOA (non-gasoline)?

- As described above, the correlation between the time series/the diurnal of other-POA and external tracers showed that other-POA factors may be derived from biomass burning and coal combustion emissions. Some studies have reported that BBOA becomes significantly oxidized through atmospheric aging, and the mass spectra of aged BBOA are similar to LO-OOA. If the spectra of aging BBOA is not constrained in ME-2 model, it is difficult to separate them from LO-OOA. Therefore, there is no secondary component associated with the other-POA factor. The corresponding description has also been added in the revised manuscript (line 389-394 in the marked revised manuscript) as follows:

*“Unfortunately, the SOA factor corresponding to other-POA (likely biomass burning OA) has not been resolved. Some studies have been found that OA emitted by biomass burning will be rapidly oxidized in the ambient atmosphere, and the BBOA in the fresh plume is mostly aged OA ([Zhou et al., 2017](#)). When the aged biomass burning OA is further oxidized, it is difficult to be identified the biomass burning SOA from mixed within OOA without constraining its SOA factor.”*

d. Finally, also drawing on (3), how influential could the choice of a single engine (GDI) and fuel (gasoline) be on the conclusions drawn? Is it possible that if four engines were evaluated, the results obtained would have suggested that vehicle type (together with operating condition) is more important than the EPA in determining the mass spectra? This would not be surprising, given that there are major differences in emission patterns from vehicle to vehicle (case in point being the fat tail phenomena in emissions). Is there evidence to support that only the quantities (of emissions) vary across vehicles under similar operating conditions, but not the mass spectral patterns? If not, please show this as a limitation of the study.

- We appreciate and accept the reviewer’s suggestion. The limitation has been added in the revised manuscript (line 424-429 in the marked revised manuscript) as follows:

*“It is noted that the vehicle experiments were solely conducted under a single engine with gasoline, and the cooking experiment only related to limited cooking styles. The variations of VOCs in diesel and gasoline vehicle emissions may lead to differences in the SOA characteristics ([Wang et al., 2020](#)). The POA and gas-phase precursor emitted from another cooking style - meat charbroiling can also form a large amount of SOA after photochemical oxidation ([Kaltsonoudis et al., 2017](#)). More work needs to be done to explore the POA and SOA mass spectrometric characteristics of emissions from vehicles and cooking sources.”*

6. The authors use dilution and high concentration of OH radicals (for brief period) to measure and simulate atmospheric aging of aerosols. However, these are both limitations since: 1) dilution changes the chemistry of aging, as also observed with volatility measurements (Cain et al., 2020), and 2) high concentrations of OH radicals could lead to changes in the reaction pathways that the aerosols undergo that are different compared to pathways on exposure to low OH concentrations for longer periods of time (but resulting in the same EPA). I suggest the authors discuss these aspects in a separate section on limitations of such work, as described in (7).

- We have supplemented the detailed description on the limitations of dilution and PAM applying for measuring and simulating atmospheric aging of aerosols (line 432-438 in the marked revised manuscript).

*“Due to the limitation of Go: PAM, dilution and high concentration of OH radicals without other inorganic aerosol seeds were adopted to measure and simulate atmospheric aging of aerosols. Thus, the possible atmospheric transformations and the reaction pathway are affected. In the future, it is still necessary to take further researches, for instance, use a quasi-atmospheric aerosol evolution study (QUALITY) chamber (Guo et al., 2020) to study the SOA formation under different actual oxidation conditions, like high/low NO<sub>x</sub> and so forth.”*

7. To address the above limitations, I suggest the authors separate the limitations briefly described in the conclusions section (Lines 304-308) and create a separate section on “limitations and future work”, where the authors can identify all the above gaps. They can also point readers to potential future work that can emanate out of this preliminary but not able effort.

- We agree and accept the reviewer’s suggestion. We have combined all the limitations, and create a separate section on “limitations and future work”. The detailed descriptions have been presented in the revised manuscript (line 411-445 in the marked revised manuscript) as follows:

#### ***“4 Limitations and future work***

*POA emissions, and SOA formation in Go: PAM reactor from urban cooking and vehicular sources were explored. The aged COA had higher hydrocarbon ions than aged HOA in mass spectra. The spectra profiles of urban cooking and vehicular sources derived from the lab simulation were performed as constraints in ME-2 model. The OA source apportionment using ME-2 compared with unconstrained PMF based on the HR OA datasets in Shanghai validated the reasonable of the primary and secondary source profiles of cooking and vehicles. It is noted that the vehicle experiments were solely conducted under a single engine with gasoline, and the cooking experiment only related to limited cooking styles. The variations of VOCs in diesel and gasoline vehicle emissions may lead to differences in the SOA characteristics (Wang et al., 2020). The POA and gas-phase precursor emitted from another cooking style -*

*meat charbroiling can also form a large amount of SOA after photochemical oxidation (Kaltsonoudis et al., 2017). More work needs to be done to explore the POA and SOA mass spectrometric characteristics of emissions from vehicles and cooking sources. In addition, SOA mass spectra were split from aged COA and aged HOA by using the PMF model, and therefore provided limited information on dynamic SOA mass spectra; we suggested that further studies control the oxidation conditions to obtain a set of dynamic pure SOA spectral profile. Due to the limitation of Go: PAM, dilution and high concentration of OH radicals without other inorganic aerosol seeds were adopted to measure and simulate atmospheric aging of aerosols. Thus, the possible atmospheric transformations and the reaction pathway are affected. In the future, it is still necessary to take further researches, for instance, use a quasi-atmospheric aerosol evolution study (QUALITY) chamber (Guo et al., 2020) to study the SOA formation under different actual oxidation conditions, like high/low NO<sub>x</sub> and so forth. Moreover, ambient datasets obtained from different sites and seasons need to be analyzed to validate the application of POA and SOA profiles of cooking and vehicles in this study, noting selecting a loose constraint via a value in SOA factors due to their high variability. Our research found that SOA from the urban cooking and vehicular sources contributed 19% and 35% of OA in the wintertime and summertime of Shanghai, implying the need to develop control measures to reduce emissions from cooking and vehicular sources in the future.”*

8. Finally, the title of the paper is misleading since “lifestyle sources emissions” would also point to volatile chemical products such as perfumes, cleaning products, and deodorants. I suggest the authors change it to “urban cooking and vehicular sources”.

- We agree and accept the reviewer’s suggestion. We have replaced “lifestyle sources emissions” with “urban cooking and vehicular sources” in the title and throughout the revised manuscript.

#### **Minor issue:**

After addressing comments for the major revision associated with the comments above, I suggest the authors address the following minor comments in the updated manuscript before resubmission.

- We appreciate the reviewer’s suggestion. We have supplemented the corresponding references, figures, and tables. We checked the manuscript carefully and corrected the errors in the revised manuscript.

1. In Sect. 2.1, lines 91-93, the authors describe vehicle operating conditions in terms of vehicle speeds and torques. However, given the goal of the paper is to use lab tests to describe and apportion real-world emissions, what do these rpm speeds and Nm torques mean in terms of real-life conditions? Would you

describe the real-life conditions in terms of vehicle speed (in mph) and rate of gain of elevation? An equivalence of each speed-torque combination would be immensely useful in understanding how relevant these combinations are to real-life conditions. Are these combinations relevant more to flat terrains in heavy traffic? Or are they more relevant to mountainous terrains with low traffic? It is hard to draw analogies to real-life conditions based on speeds and torques only.

- We appreciate the reviewer's suggestion. Indeed, it is difficult to make analogies to real-life conditions based on rotating speed and torque alone. We have combined rotating speed and torque with vehicle speed for real-life conditions. The detailed information has been added in the revised manuscript (line 102-104 in the marked revised manuscript) as follows:

*“Vehicle operating under real-life conditions were dynamic rotating speed-torque combination. For example, the combination of 1500 rpm rotating speed and 16Nm torque, 2000rpm, and 16Nm torque for the engine in this study reflect the realistic vehicle speed of 20km/h and 40km/h, respectively.”*

2. In Sect. 2.2, the authors should clearly state the type of aerosols being measured, whether they are NR-PM<sub>2.5</sub> or NR-PM<sub>1</sub>.

- The corresponding sentences have been documented in the revised manuscript (line 126-129 in the marked revised manuscript) as follows:

*“The mass concentrations of non-refractory submicron aerosol (NR-PM<sub>1</sub>), and high-resolution ions fragments of OA were recorded by HR-ToF-AMS (Aerodyne Research Incorporation, USA)”*

3. In Sect. 2.2, lines 108-110, the reference describing how CO<sub>2</sub> interference can be reduced using CO<sub>2</sub> gas phase measurements needs to be added.

- Thanks for the reviewer's comment. We have added the reference that describing how CO<sub>2</sub> interference can be reduced using CO<sub>2</sub> gas-phase measurements in the revised manuscript (line 134-137 in the marked revised manuscript) as follows:

*“Besides, the real-time measurements of CO<sub>2</sub> concentrations (Model 410i, Thermo Electron Corporation, USA) were used to correct the influence of CO<sub>2</sub> on OA ion fragments, refer to Canagaratna et al., 2015.*

*Canagaratna, M., Jimenez, J., Kroll, J., Chen, Q., Kessler, S., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L., Wilson, K., 2015. Elemental ration measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications. Atmos. Chem. Phys 15, 253-272.*

4. Lines 118-119: The method using SO<sub>2</sub> decay for OH exposure estimation is based on Zhang et al., 2020. However, Zhang and co-workers develop the method and present the assumptions as those applicable

for cooking emissions only (Refer to Supplement of Zhang et al., pg. 2). Are the same assumptions applicable on vehicular emissions?

- The OH exposure inside the Go: PAM was calibrated by an off-line method based on SO<sub>2</sub> decay before the experiments. The calculation method and calibration method of the OH exposure between the vehicle and the cooking source experiment is the same. As described in Zhang et al., 2020, in equation (1),  $K_{OH-SO_2}$  is the reaction rate constant of OH radical and SO<sub>2</sub> ( $9.0 \times 10^{-13}$  molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>). The SO<sub>2,f</sub> and SO<sub>2,i</sub> are the SO<sub>2</sub> concentrations (ppb) under the conditions of UV lamp on or off respectively. The photochemical age (days) can be calculated in equation (2) when assuming the OH concentration is  $1.5 \times 10^6$  molecules cm<sup>-3</sup> in the atmosphere.

$$OH \text{ exposure} = \frac{-1}{K_{OH-SO_2}} \times \ln \left( \frac{SO_{2,f}}{SO_{2,i}} \right) \quad (1)$$

$$Photochemical \text{ age} = \frac{OH \text{ exposure}}{24 \times 3600 \times 1.5 \times 10^6} \quad (2)$$

5. In Fig. S2 (main manuscript line 134), the evolution at the combination of 2000 rpm and 40 Nm seems to be very suspicious. In going from EPA 2.89 days to 4.15 days, f<sub>43</sub> seems to have increased and f<sub>44</sub> to have decreased, which is counterintuitive. Can the authors check the figures are correct? And if yes, using HR-ToF-AMS data, can you shed some light on what might be happening here?.

- Thanks for the reviewer's comments. We checked the figures and data carefully. The figures and data were correct. During the oxidation process, C-C cleavage may occur when the addition of an electron-withdrawing group weakens a C-C bond (Kroll et al., 2011). Reaching the oxidative end product (CO<sub>2</sub>) requires a combination of functionalization and fragmentation. With the increase of OH exposure, f<sub>44</sub> decreased at the condition of 2000 rpm and 40 Nm in our work. This similar phenomenon has also been found in other literature. Miracolo et al., 2011 observed that O/C showed a slight decrease with increasing OH exposure, and attributed this decrease to less formation of low volatility SOA under the lower OH levels (Miracolo et al., 2011). Shilling et al. reported that some chemical characteristics such as the O/C and the fraction of C<sub>x</sub>H<sub>y</sub>O<sub>z</sub><sup>+</sup>, which were determined from the measurements of the aerosol mass spectrometer, decreased with increasing concentrations of SOA mass loading (Shilling et al., 2009).

6. Lines 154-155: "Chinese cooking emissions" should be replaced by "Chinese cooking emissions associated with frying". As He et al., 2010 note, the fragments noted are associated with frying but not charboiling.



- We appreciate the reviewer's comment. The description has been modified in the revised manuscript as follows:

*"As described by He et al., 2010, the most abundant ion fragments at  $m/z$  41 and  $m/z$  55 from primary Chinese cooking emissions associated with frying are resulting from unsaturated fatty acids."*

7. Mass spectra of cooking and vehicle tests at EPA 0 (or close to zero) should be presented in the Supplement as well.

- We appreciate the reviewer's suggestion. We have added the mass spectra of cooking dishes at EPA 0 in the supplement revised material (Fig.S3 and Table S5) as follows:

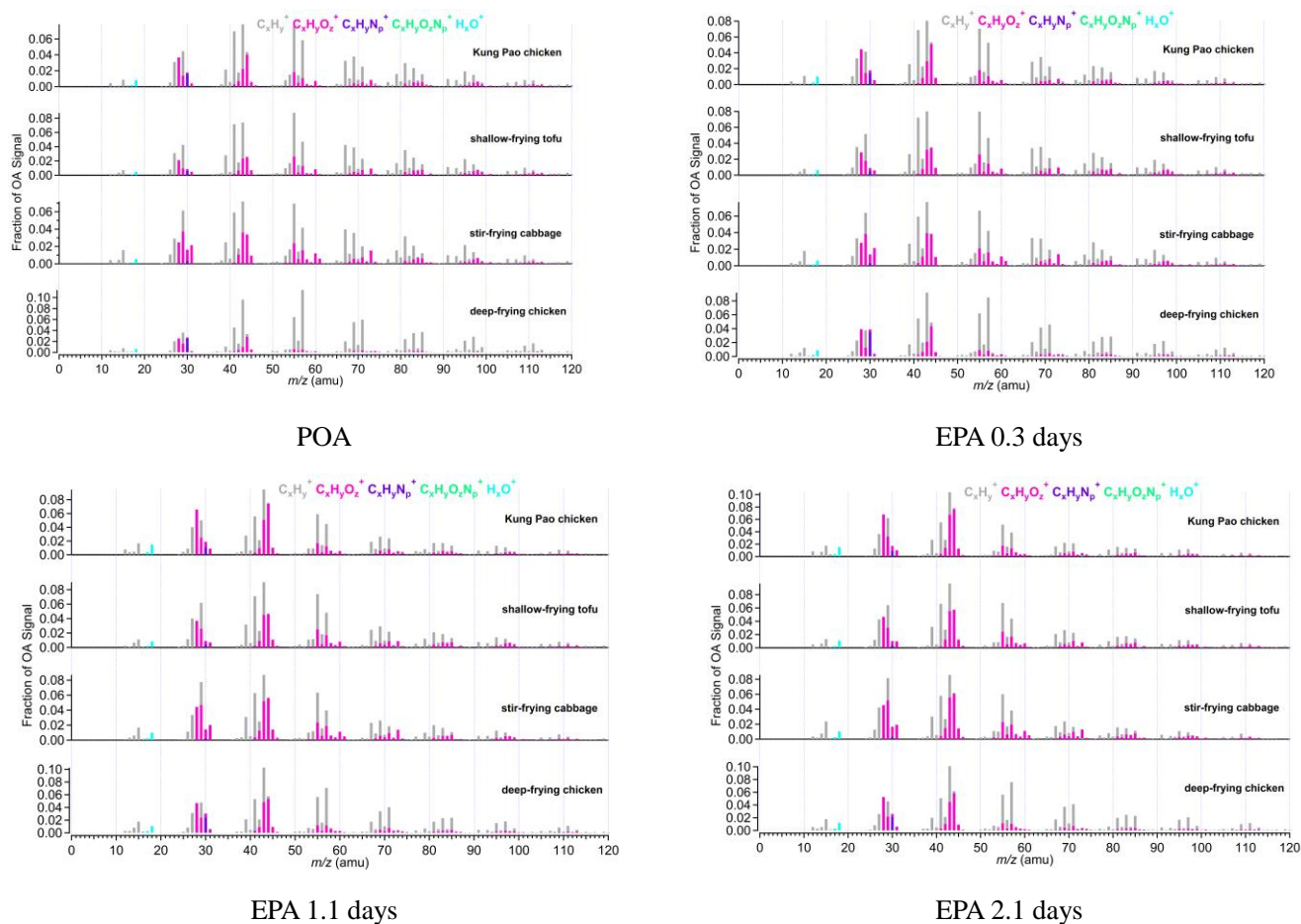


Fig.S3. The mass spectra of aged COA emission from different Chinese dishes under different EPA.

Table S5. The  $\theta$  angles among the mass spectra of POA and aged COA emission from different Chinese dishes under EPA0.3 day, 1.1 days, and 2.1 days.

POA $\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>31</b>	<b>29</b>	<b>24</b>
stir-frying cabbage		<b>0</b>	<b>12</b>	<b>13</b>
shallow-frying tofu			<b>0</b>	<b>11</b>
Kung Pao chicken				<b>0</b>

EPA0.3 day $\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>23</b>	<b>22</b>	<b>17</b>
stir-frying cabbage		<b>0</b>	<b>10</b>	<b>13</b>
shallow-frying tofu			<b>0</b>	<b>10</b>
Kung Pao chicken				<b>0</b>

EPA1.1 days $\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>20</b>	<b>17</b>	<b>15</b>
stir-frying cabbage		<b>0</b>	<b>10</b>	<b>14</b>
shallow-frying tofu			<b>0</b>	<b>16</b>
Kung Pao chicken				<b>0</b>

$\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>22</b>	<b>18</b>	<b>17</b>
stir-frying cabbage		<b>0</b>	<b>10</b>	<b>13</b>
shallow-frying tofu			<b>0</b>	<b>12</b>
Kung Pao chicken				<b>0</b>

8. Lines 162-164: “The mass spectra at 2.89 days and 4.15 days had very similar patterns with the most prominent peaks at  $m/z$  28 and 44, respectively, which almost resembled the mass spectra of MO-OOA resolved from ambient datasets.” Reference to Table S4 is missing!

- Thanks for the reviewer’s comments. We have added the information of  $\theta$  angle in this sentence as follows:

*“As the oxidation degree increased, the ion fragments varied similarly with hydrocarbon-like ion fragments decreasing. The mass spectra at 2.9 days and 4.1 days had very similar patterns with the most abundant signals at  $m/z$  28 and 44, respectively, which showed good consistency with the mass spectra of*

*MO-OOA resolved from ambient datasets(  $\theta = 14^\circ$  ; compared with MO-OOA obtained during the spring observations in [Ng et al., 2011](#); [Zhu et al., 2021b](#). ”*

9. In lines 164, 166, and elsewhere, the authors mention ambient profiles. However, the criteria used to obtain these profiles is not clear. The methods section should be updated to clarify this point.

- We have added the related references and the descriptions in the revised manuscript as follows:

*“When EPA was 1.7 days, there were different mass spectra patterns, with dominant signals at  $m/z$  28 and  $m/z$  44, yet contained a large signal at  $m/z$  43, many similarities with the spectra of the ambient LO-OOA ([Hu et al., 2017](#); [Zhu et al., 2021b](#)). ”*

*Therefore, we used the average HOA spectrum derived from unconstrained PMF analysis based on the ambient observations of Shanghai, Beijing, Dezhou, Shenzhen in China as an alternative to the mass spectrum of vehicle POA, as shown in **Fig.2a** and **Fig S4**. Detailed observation information of Shanghai, Dezhou, and Shenzhen referred to [Zhu et al., 2021a](#). The observations in Beijing have been given in [Hu et al., 2017](#).*

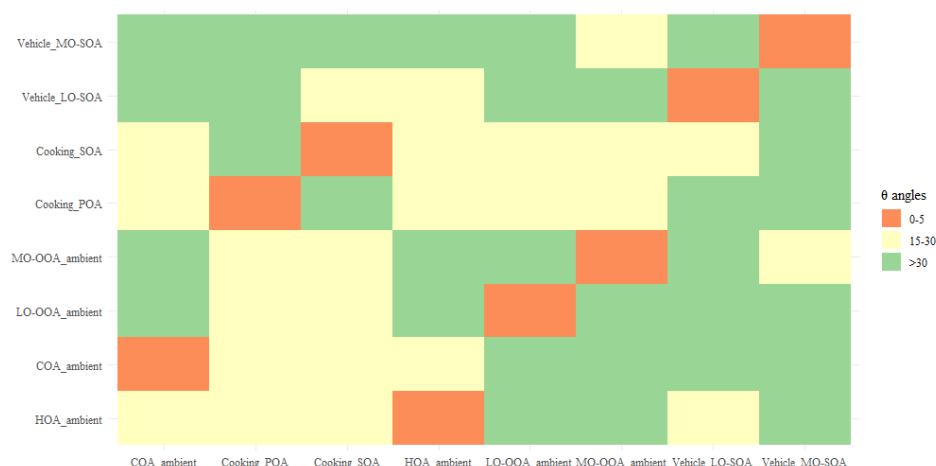


Fig.4. The  $\theta$  angles between ambient COA, HOA, LO-OOA and MO-OOA factors and the cooking PMF POA, SOA, and the vehicle LO-SOA, MO-SOA. The  $\theta$  angle between two mass spectra is 0-5, 5-10, 10-15, 15-30, and  $> 30$  indicates excellent consistency, good consistency, many similarities, limited similarities, and poor consistency, respectively. The ambient COA, HOA, LO-OOA and MO-OOA factors were averaged the resolved factors which performed on Shanghai, Dezhou, Beijing, and Shenzhen datasets ([Hu et al., 2017](#); [Zhu et al., 2021a](#)).

10. The authors supply tables Table 1 and S2-S3 in SI for MS similarity analysis for all vehicle operating conditions and for all food types at two EPAs. Similar tables should be supplied for the remaining EPAs for vehicles conditions and all food types.

- We appreciate the reviewer’s suggestion. The corresponding tables for the remaining EPAs for vehicles conditions and all food types have been added in the revised supplement material as follows:

Table S4. The  $\theta$  angles among the mass spectra of aged HOA under EPA 1.7 days, 2.9 days, and 4.1 days..

EPA1.7days $\theta$ angles	1500rpm_16Nm	1750rpm_16Nm	2000rpm_16Nm	2000rpm_32Nm	2000rpm_40Nm
1500rpm_16Nm	<b>0</b>	<b>8</b>	<b>8</b>	<b>16</b>	<b>18</b>
1750 rpm_16 Nm		<b>0</b>	<b>1</b>	<b>9</b>	<b>11</b>
2000 rpm_16 Nm			<b>0</b>	<b>9</b>	<b>11</b>
2000 rpm_32 Nm				<b>0</b>	<b>4</b>
2000 rpm_40 Nm					<b>0</b>

EPA2.9days $\theta$ angles	1500rpm_16Nm	1750rpm_16Nm	2000rpm_16Nm	2000rpm_32Nm	2000rpm_40Nm
1500rpm_16Nm	<b>0</b>	<b>14</b>	<b>14</b>	<b>29</b>	<b>19</b>
1750 rpm_16 Nm		<b>0</b>	<b>2</b>	<b>15</b>	<b>6</b>
2000 rpm_16 Nm			<b>0</b>	<b>14</b>	<b>5</b>
2000 rpm_32 Nm				<b>0</b>	<b>9</b>
2000 rpm_40 Nm					<b>0</b>

EPA4.1days $\theta$ angles	1500rpm_16Nm	1750rpm_16Nm	2000rpm_16Nm	2000rpm_32Nm	2000rpm_40Nm
1500rpm_16Nm	<b>0</b>	<b>8</b>	<b>8</b>	<b>3</b>	<b>29</b>
1750 rpm_16 Nm		<b>0</b>	<b>1</b>	<b>7</b>	<b>21</b>
2000 rpm_16 Nm			<b>0</b>	<b>7</b>	<b>21</b>
2000 rpm_32 Nm				<b>0</b>	<b>26</b>
2000 rpm_40 Nm					<b>0</b>

Table S5. The  $\theta$  angles among the mass spectra of POA and aged COA emission from different Chinese dishes under EPA 0.3 day, 1.1 days, and 2.1 days..

POA $\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>31</b>	<b>29</b>	<b>24</b>
stir-frying cabbage		<b>0</b>	<b>12</b>	<b>13</b>
shallow-frying tofu			<b>0</b>	<b>11</b>
Kung Pao chicken				<b>0</b>

EPA0.3 day $\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>23</b>	<b>22</b>	<b>17</b>
stir-frying cabbage		<b>0</b>	<b>10</b>	<b>13</b>
shallow-frying tofu			<b>0</b>	<b>10</b>
Kung Pao chicken				<b>0</b>

EPA1.1 days $\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>20</b>	<b>17</b>	<b>15</b>
stir-frying cabbage		<b>0</b>	<b>10</b>	<b>14</b>
shallow-frying tofu			<b>0</b>	<b>16</b>
Kung Pao chicken				<b>0</b>

EPA2.1 days $\theta$ angles	deep-frying chicken	stir-frying cabbage	shallow-frying tofu	Kung Pao chicken
deep-frying chicken	<b>0</b>	<b>22</b>	<b>18</b>	<b>17</b>
stir-frying cabbage		<b>0</b>	<b>10</b>	<b>13</b>
shallow-frying tofu			<b>0</b>	<b>12</b>
Kung Pao chicken				<b>0</b>

11. The authors supply four tables S4-S7 in SI for MS similarity analysis for two vehicle operating conditions and for two food types at varying EPA. Similar tables should be supplied for the remaining three vehicle conditions and for the other two food types.

- The corresponding tables for the remaining three vehicle conditions and for the other two food types have been added in the revised supplement material as follows:

Table S6. The  $\theta$  angles among the mass spectra under different EPA at one vehicle condition (1500rpm\_16Nm, 1750rpm\_16Nm, 2000rpm\_16Nm, 2000rpm\_32Nm, and 2000rpm\_40Nm, respectively).

1500rpm_16Nm $\theta$ angles	POA	0.6 day	1.7 days	2.9 days	4.1 days
POA	0	27	45	63	63
0.6 day		0	24	46	46
1.7 days			0	22	22
2.9 days				0	1
4.1 days					0

1750rpm_16Nm $\theta$ angles	POA	0.6 day	1.7 days	2.9 days	4.1 days
POA	0	29	40	51	57
0.6 day		0	14	29	35
1.7 days			0	15	21
2.9 days				0	7
4.1 days					0

2000rpm_16Nm $\theta$ angles	POA	0.6 day	1.7 days	2.9 days	4.1 days
POA	0	29	40	51	57
0.6 day		0	15	29	36
1.7 days			0	15	22
2.9 days				0	7
4.1 days					0

2000rpm_32Nm $\theta$ angles	POA	0.6 day	1.7 days	2.9 days	4.1 days
POA	0	30	35	41	62
0.6 day		0	7	13	38
1.7 days			0	10	37
2.9 days				0	28
4.1 days					0

2000rpm_40Nm $\theta$ angles	POA	0.6 day	1.7 days	2.9 days	4.1 days
POA	0	29	36	48	46
0.6 day		0	10	24	21
1.7 days			0	19	13
2.9 days				0	12
4.1 days					0



Table S7. The  $\theta$  angles among the mass spectra under different EPA for different Chinese dishes.

<b>Deep-frying chicken</b>	POA	0.3 day	0.7 day	1.1 days	2.1 days
POA	0	12	17	19	19
0.3 day		0	6	9	9
0.7 day			0	4	5
1.1 days				0	4
2.1 days					0

<b>Stir-frying cabbage</b>	POA	0.3 day	0.7 day	1.1 days	2.1 days
POA	0	5	10	15	18
0.3 day		0	6	10	14
0.7 day			0	6	9
1.1 days				0	5
2.1 days					0

<b>Shallow frying tofu</b>	POA	0.3 day	0.7 day	1.1 days	2.1 days
POA	0	7	12	15	21
0.3 day		0	6	9	14
0.7 day			0	3	9
1.1 days				0	6
2.1 days					0

<b>Kung Pao chicken</b>	POA	0.3 day	0.7 day	1.1 days	2.1 days
POA	0	7	13	19	23
0.3 day		0	8	13	17
0.7 day			0	7	10
1.1 days				0	7
2.1 days					0

12. Lines 173-175: “Along with the growth of OH exposure, the  $f_{43}$  of aged COA increased from 0.07 to 0.10, and meanwhile its  $f_{44}$  increased from 0.03 to 0.08 (**Fig.2b**; **Fig.S5**), distributing in the lower region of less oxidized organic aerosol (LO-OOA).” There is a missing reference here since the LO-OOA region is undefined. For that matter, even in Fig. S6, that region has not been defined.

- Thanks for the reviewer’s comments. Combined with the comments of the first reviewer, we moved the sentence “Along with the growth of OH exposure, the  $f_{43}$  of aged COA increased from 0.07 to 0.10, and meanwhile, its  $f_{44}$  increased from 0.03 to 0.08 (Fig.2b and Fig.S5)” to section 3.2 and deleted the sentence “distributing in the lower region of less oxidized organic aerosol (LO-OOA)”.

13. The authors discuss specifics of mass spectral contributions of different mass spectra, which are hard to decipher from the figures (e.g., lines 174, 216-218). I suggest the authors add supplementary tables of contributions at key m/zs for the different tests: vehicle/cooking type and operating condition.

- We appreciate the reviewer's suggestion. The contributions at key m/zs for the different cooking dishes and operating conditions have been supplemented in the revised supplement information as follows:

Table S10. A summary of dominant peaks among cooking PMF POA.

	Deep-frying chicken	Stir-frying cabbage	Shallow frying tofu	Kung Pao chicken
$f_{41}$	0.0508	0.0560	0.0682	0.0685
$f_{43}$	0.0802	0.0365	0.0489	0.0597
$f_{55}$	0.0641	0.0664	0.0842	0.0757
$f_{57}$	0.0966	0.0411	0.0473	0.0612
$f_{67}$	0.0211	0.0382	0.0404	0.0333
$f_{69}$	0.0486	0.0343	0.0383	0.0376

Table S11. A summary of dominant peaks among cooking PMF SOA.

	Deep-frying chicken	Stir-frying cabbage	Shallow frying tofu	Kung Pao chicken
$f_{28}$	0.0504	0.0451	0.0463	0.0682
$f_{29}$	0.0481	0.0796	0.0675	0.0644
$f_{41}$	0.0501	0.0590	0.0679	0.0547
$f_{43}$	0.1032	0.0865	0.0944	0.1023
$f_{44}$	0.0609	0.0596	0.0584	0.0800
$f_{55}$	0.0534	0.0586	0.0636	0.0495
$f_{57}$	0.0665	0.0376	0.0421	0.0364

Table S12. A summary of dominant peaks among vehicle PMF LO-SOA.

	1500rpm_16Nm	1750rpm_16Nm	2000rpm_16Nm	2000rpm_32Nm	2000rpm_40Nm
$f_{28}$	0.0579	0.0551	0.0527	0.0493	0.0081
$f_{41}$	0.0417	0.0493	0.0443	0.0386	0.0574
$f_{43}$	0.1571	0.1495	0.1523	0.1670	0.1632
$f_{44}$	0.0663	0.0653	0.0623	0.0597	0.0183
$f_{55}$	0.0384	0.0393	0.0386	0.0339	0.0447
$f_{57}$	0.0246	0.0270	0.0253	0.0226	0.0329

Table S13. A summary of dominant peaks among vehicle PMF MO-SOA.

	1500rpm_16Nm	1750rpm_16Nm	2000rpm_16Nm	2000rpm_32Nm	2000rpm_40Nm
$f_{28}$	0.2077	0.1590	0.2141	0.2049	0.1099
$f_{41}$	0.0139	0.0186	0.0124	0.0124	0.0242
$f_{43}$	0.0722	0.1063	0.0777	0.0771	0.1431
$f_{44}$	0.2190	0.1688	0.2239	0.2126	0.1208
$f_{55}$	0.0127	0.0181	0.0120	0.0120	0.0238
$f_{57}$	0.0042	0.0076	0.0026	0.0032	0.0127

14. Line 199: In Fig. S6, add and label the line with the slope of -0.5.

- Thanks for the reviewer's comment. We have added the line with the slope of -0.5 in Fig.S6 in the revised supplement material.

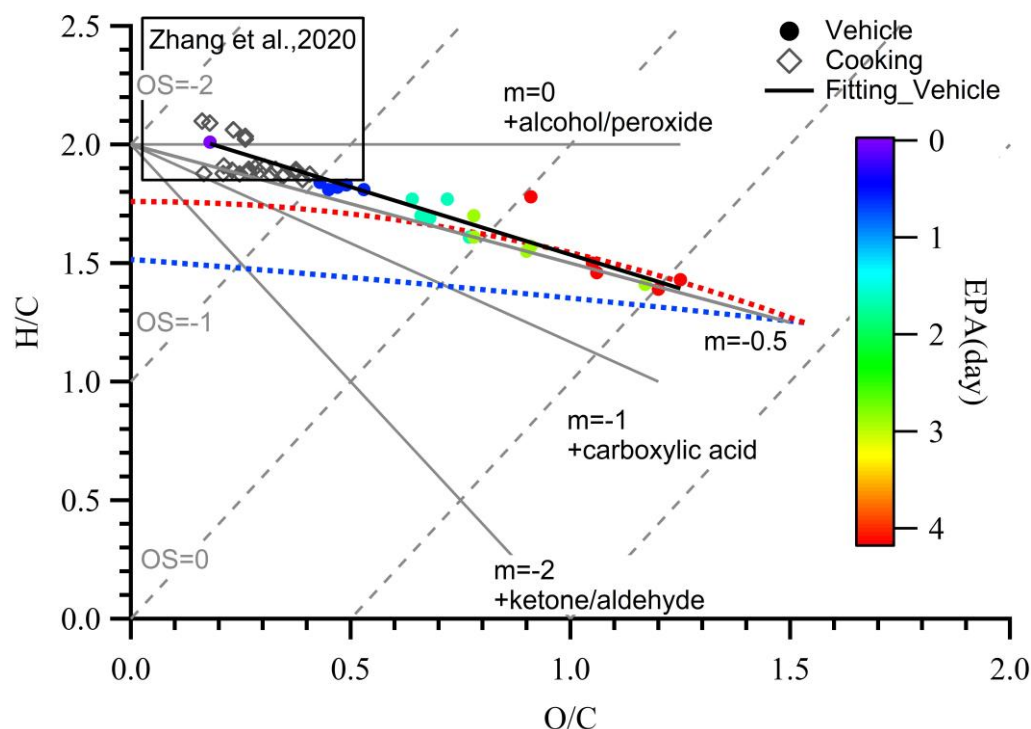


Fig.S6. Van Krevelen diagram of POA, aged COA and aged HOA from vehicle and cooking.

15. Lines 219-221: The two parts of the sentence seem disconnected, and the relevance of the sentence in this paragraph is unclear. The authors could use the oxidation state of aerosols as a quantitative metric. Refer to Kroll et al., 2015 for definition and use with HR-ToF-AMS.

- We agree with the reviewer's comment. The two parts of the sentences are indeed disconnected. We have moved the sentence from the revised manuscript.

16. Lines 224-226: It is unclear whether this sentence refers to vehicle LO-SOA or MO-SOA.

- We have added the "LO-SOA" in this sentence in the revised manuscript (line 286-288 in the marked revised manuscript).

*"As indicated in Fig.3 and Table S12, the prominent  $m/z$  28 (average  $f_{28}=0.045$ ), 41 (average  $f_{41}=0.046$ ), 43 (average  $f_{43}=0.158$ ), 44 (average  $f_{44}=0.054$ ), 55 (average  $f_{55}=0.039$ ), 57 (average  $f_{57}=0.027$ ) of PMF LO-SOA were comparable with those of cooking PMF SOA."*

17. Fig. 3: Vehicle POA MS is missing in the figure. Need to show vehicle POA mass spectral comparison.

- The vehicle POA was uncertain due to its low concentration emitted from the engine in this study. A related study has found that the POA factor from vehicle emissions is similar to the HOA factor derived from environmental datasets ([Presto et al., 2014](#)). Therefore, we used the average HOA spectrum derived from unconstrained PMF analysis based on the ambient observations of Shanghai, Beijing, Dezhou, Shenzhen in China as an alternative to the mass spectrum of vehicle POA. Different from the cooking, two-vehicle PMF SOA factors were derived from aged HOA due to higher OH exposure. According to different O/C ratios, they were considered to be low oxidized vehicle SOA (LO-SOA) and more oxidized vehicle SOA (MO-SOA).

18. Like Table S9, need to add table showing angles for vehicle PMF POA. Like Table S10, need to add table showing angles for vehicle PMF MO-SOA.

- We have added the table that showing angles for vehicle PMF MO-SOA in the revised manuscript.

The  $\theta$  angles among the mass spectra of vehicle PMF MO-SOA at different conditions

Vehicle MO-SOA $\theta$ angles	1500rpm_16Nm	1750rpm_16Nm	2000rpm_16Nm	2000rpm_32Nm	2000rpm_40Nm
1500rpm_16Nm	0	12	2	2	29
1750rpm_16Nm		0	12	11	17
2000rpm_16Nm			0	3	28
2000rpm_32Nm				0	27
2000rpm_40Nm					0

19. Lines 244-245: This sentence is missing a figure/table reference. It is also surprising that the cooking mass spectra of deep-frying chicken was excluded because it was different. Isn't diversity in MS better and wouldn't including diverse MS better allow capturing several types of cooking OA? This also means that the other-POA factor could resemble deep-frying chicken MS. Could the authors report the results of that check?

- We are sorry for our carelessness. We have checked the data and figures. We found that the mass spectra of deep-frying chicken were included in the cooking SOA in the original manuscript. At the beginning of completing the first draft, based on the similarity analysis results of the four cooking groups, we found that the mass spectra of deep-frying chicken were poorly correlated with the others. Therefore, the initial plan is to build the POA and SOA of the cooking as the primary and secondary spectrum constraints for ME-2 by combining the high-resolution mass spectra datasets of the three dishes except for deep-frying chicken. However, after careful consideration, we suggest that excluding deep-frying chicken is too arbitrary

and does not fully reflect the cooking source. Therefore, we did not exclude deep-frying chicken at the end. The figure and table have been revised in the original manuscript, but the sentence in the original manuscript has forgotten to be revised. We have removed the sentence from the revised manuscript (line 308-314 in the marked revised manuscript) as follows:

*“The POA and SOA of the cooking as the primary and secondary spectrum constraints for ME-2 were obtained by averaging the high-resolution mass spectra datasets of the four dishes, which were identified from aged COA using the PMF model. Similarly, combining different GDI running conditions, the averaged LO-SOA and MO-SOA which were resolved based on aged HOA by using the PMF model were used as the inputting mass spectra profiles of vehicles for ME-2. The mass spectral profiles for cooking and vehicle as constraints in ME-2 model are shown in **Fig.S12**.”*

20. Fig. S4, Table S11: Why is any comparison with vehicle POA MS missing in these two?

- Thanks for the reviewer's comment. the similar comments were answered (e. g., comment 17). The vehicle POA was uncertain due to its low concentration emitted from the engine in this study. A related study has found that the POA factor from vehicle emissions is similar to the HOA factor derived from environmental datasets (Presto et al., 2014). Therefore, we used the average HOA spectrum derived from unconstrained PMF analysis based on the ambient observations of Shanghai, Beijing, Dezhou, Shenzhen in China as an alternative to the mass spectrum of vehicle POA. Two vehicle PMF SOA factors were derived from aged HOA due to higher OH exposure.

21. Lines 264-265: What was the basis of deciding obtained PMF contributions of COA and HOA is “far exceeding expectations”. Such claims must be backed by proper references.

- Thanks for the reviewer's comment. Regarding section 3.3, we have revised a lot of text based on the comments of the two reviewers. This sentence has been deleted, replaced by the following sentence, with references adding in the revised manuscript (line 369-371 in the marked revised manuscript.).

*“As shown in **Fig.5**, compared with PMF results, the proportions of HOA (7%) and COA (11%) obtained by source apportionment with ME-2 have significantly decreased to the expected value during the winter observation([Huang et al., 2020](#); [Xu et al., 2020](#)).”*

22. Lines 288-289: Stable proportion % of COA across seasons does not imply it had stable contributions as volatility, dilution effects, and atmospheric chemistry, and interactions with other emissions all play a role in these stable proportions. I suggest that this sentence should be removed or edited to

consider these factors that are likely affecting COA proportion. Attribution to stable contribution would likely involve the implementation of a volatility basis set approach.

- We agree and accept the reviewer's suggestion. We have deleted the sentence "As a primary emission source with a stable contribution, COA based on ME-2 analysis accounted for the same proportion of OA in summer as in winter" in the revised manuscript.