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"

Comments from the reviewers:

Reviewer 1

This paper describes the development of a new way to perform source apportionment looking into SOA formation from traffic related and cooking -like emissions, looking into laboratory experiments and testing the results with ME2 analysis of ambient data.

The topic of this paper is interesting to the community and will help on improving future source apportionment studies. I recommend this paper for publication after the authors address the following comments.

- We appreciate the comments from the reviewer on this manuscript. According to the points mentioned by the reviewer, we supplemented the corresponding descriptions of the vehicle and cooking experiments in the materials and methods section. We also added the detailed description of source apportionment by using PMF and ME-2. The texts in bold black are the comments from the reviewer, followed by our responses in blue and/or red. All the changes are marked in the revised manuscript.

1. I think the conditions of the two experiments should be mentioned into detail, perhaps with a table in the supplement, to identify similarities/differences. For instance, line 84 mentions cooking emissions were diluted 8 times, was this the same for the vehicle experiments?

- We appreciate the comments from the reviewer. Combined with comment 6, we have added the detailed description of the experiments in the materials and methods section to make it more decent. The related modification has been added in the revised manuscript (line 86-118 in the marked revised manuscript) and supplement (Table S1-S3) as follows:

"For cooking, we prepared four dishes including deep-frying chicken, shallow-frying tofu, stir-frying cabbage, and Kung Pao chicken. The total cooking time for each experiment ranged from 40 to 66 min, which was almost related to the features of each dish (**Table S1**). Each dish was continuously carried out 8 times in parallel during the cooking process until the closed kitchen was full of fumes. The fumes produced by cooking were introduced through the pipeline from the kitchen into the Gothenburg Potential Aerosol Mass (Go: PAM) reactor (Li et al., 2019) in the laboratory after being diluted 8 times by a Dekati Dilutor (e-Diluter, Dekati Ltd., Finland). Heat insulation cotton was wrapped around the sampling pipelines to prevent fumes from condensing on the wall of the pipe. We considered the emissions sampled after Go: PAM without OH radical as primary emissions, and those monitoring after Go: PAM with given OH radicals as secondary formation. The sampling time ranged from 58 to 90 min. Each sampling was in parallel three times. The relative standard deviations were small, which were under 10% in most cases. In addition, the background blank groups and the dilution gas blank groups were separately completed using boiling water and dilution gas, according to the same steps as experimental groups. More information on the experimental setup of cooking simulations has been given in Zhang et al., 2020.

For vehicle, experiments were performed by using Gasoline direct engine (GDI)with a commercial China V gasoline fuel (Emission: 998cc; Maximum power: 100KW 6000rpm; Peak torque: 205Nm 2000-3000rpm). 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. Five running conditions covering different speeds and torques, including 1500rpm_16Nm, 1750rpm_16Nm, 2000rpm_32Nm, and 2000rpm_40Nm, were used to characterize their POA and SOA mass spectra in this study. Once the engine warmed up, it continued to work under one running condition system for the cooking experiment. Then the diluted exhaust entered the GO: PAM through the stainless pipe wrapped by heat insulation cotton. For each running condition, five parallel experiments were conducted (**Table S2**). The sampling time with collecting three parallel data groups was about 60 min for each experiment.

Go: PAM reactor consists of quartz tube that is 100 cm long and 9.6 cm in diameter, as described in Watne et al., 2018. The OH radicals in Go: PAM reactor is generated by the photolysis of ozone and the reaction in the presence of water vapor. We adjusted input ozone concentrations ranging from ~0 to ~6.5 ppm and ~0 to ~4.0 ppm to change the OH radicals in the Go: PAM for vehicle and cooking experiments, respectively. The temperature, relative humidity, and the sampling residence time in Go: PAM for vehicle and cooking experiments were documented in the supplement material (**Table S3**)."

Watne, A. K., Psichoudaki, M., Ljungstrom, E., Le Breton, M., Hallquist, M., Jerksjo, M., Fallgren, H., Jutterstrom, S., and Hallquist, A. M.: Fresh and Oxidized Emissions from In-Use Transit Buses Running on Diesel, Biodiesel, and CNG, Environmental science & technology, 52, 7720-7728, 10.1021/acs.est.8b01394, 2018.

Cooking Dish	Cooking	Oil	Cooking	Numbers for	Sampling	Fuel	Sampling
	Material	Temperature	Time	Each Dish	Time		Temperate
Deep-fried	170g chicken,	145~155°C	66 min	8	90 min		
chicken	500ml corn oil						
Shallow-frying	500g tofu,	100~110°C	64 min	8	60 min	Liquefied	
tofu	200ml corn oil					petroleum	20~25°C
Stir-frying	300g cabbage,	95~105°C	47 min	8	58 min	gas	
cabbage	40ml corn oil					Iron work	
Kung Pao	150g chicken,	90~105°C	40 min	8	60 min		
chicken	50g peanut,						
	50g cucumber,						
	40ml corn oil						

Table S2. Details of vehicle and sampling procedures.

Running C	Running Condition		Parallels	Fuel	Sampling
Rotating speed	Torque				Temperate
1500 rpm	16 Nm	60 min	5		
1750 rpm	16 Nm	60 min	5	Commercial	20~25°C
2000 rpm	16 Nm	60 min	5	China V gasoline	
2000 rpm	32 Nm	60 min	5		
2000 rpm	40 Nm	60 min	5		

	C	ooking experime	ent		Vehicle experiment				
O_3	RH (%)	Description	OH exposure	Photochemical	O_3	RH (%)	Description of	OH exposure	Photochemical
concentration	& Temperature	of Go: PAM	(molecules	Age	concentration	& Temperature	Go: PAM	(molecules	Age
(ppbv)	(°C)		$cm^{-3} s$)	(day)	(ppbv)	(°)		$cm^{-3} s$)	(day)
0		Sample flow	0	0	0		Sample flow	0	0
310		(7 L/min)	4.3E+10	0.3	624		(4 L/min) and	7.8E+10	0.6
1183	18~23%	and oxidant	9.6E+10	0.7	2367	44~49%	oxidant flow	2.1E+11	1.7
2217	&16~19°C	flow (3	1.4E+11	1.1	4433	&19~22°C	(1 L/min);	3.7E+11	2.9
4025		L/min);	2.7E+11	2.1	6533		Residence	5.4E+11	4.2
		Residence					time: 110 s		
		time: 55 s							

Table S3. The OH exposure and photochemical age for all conditions in cooking and vehicle experiments

2. Also, I could not find a description of the ambient measurements used to test the mass spec generated in the lab experiments. It would be interesting to know about the ambient measurements season, location and type of the site among other details. At the moment the paper seems to go straight into the analysis of the various θ values without giving enough details about the lab experiments and ambient measurements.

Thanks for the reviewer's comment. The specific details about laboratory experiments have been
added to the methods and materials section, as shown in the reply to the first comment.

The source characteristics of POA were uncertain due to the low concentration of particulate matter 7 emitted from the engine in this study. Therefore, we used the average HOA spectrum identified from OA 8 datasets by PMF analysis based on the ambient observations of Shanghai, Beijing, Dezhou, and Shenzhen in 9 China as an alternative to the mass spectrum of vehicle POA. Aerosol particle measurements in Shanghai 10 (Zhu et al., 2018) were taken in situ at the same location as Zhu et al. (2018), i.e., Shanghai Academy of 11 Environmental Sciences (31.10 N,121.25 E), a typical urban site in the Yangtze River Delta region, from 2 12 September to 8 October 2016, from November 2016 to 13 January 2017, and from 18 May to 4 June 2017 13 with an High-Resolution Time-of-Flight Aerosol Mass spectrometer (HR-ToF-AMS; Aerodyne Research 14 Inc., USA) of 4 min time resolution. The Dezhou and Shenzhen observations were conducted from 2 15 November 2017 to 22 January 2018 in Dezhou and from 30 September to 20 October 2019 in Shenzhen, 16 respectively. The Dezhou sampling site (37.13 N,116.45 E) was located in the Meteorological Bureau in 17 Pingyuan country, which was surrounded by large farmland. The land-use situation was relatively stable and 18 no tall buildings were blocked. The Dezhou site can be considered as a rural site in North China Plain. The 19 Shenzhen measurements were operated inside an air condition room on the top floor (4th) of Shenzhen 20 Eco-Environmental Monitoring Station. The station as a background site in the Pearl River Delta region was 21 located at a peninsula surrounded by mountains and sea, far away from the urban area. During the periods 22 23 from March 2012 to March 2013, four intensive campaigns were carried out at the Peking University Urban Atmosphere Environment MonitoRing Station (PKUERS; 39.99° N, 116.31° E), which is located on the roof 24 of a building (approximately 20 m above ground level) on the campus. Except for the main road about 150 25 m away to the east, no significant pollution sources exist near the sampling site. 26

We have added a description of the ambient measurements in the revised manuscript (for example, line
205-213, and line 329-332 in the marked revised manuscript) as follows:

29 "It was worth noting that the source characteristics of vehicle POA were uncertain due to its low 30 concentration emitted from the engine in this study. A related study has found that the POA factor from 31 vehicle emissions is similar to the HOA factor derived from environmental datasets (<u>Presto et al., 2014</u>). 32 Therefore, we used the average HOA spectrum derived from unconstrained PMF analysis based on the 33 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."

38 "The ambient measurements in Shanghai were taken in situ at the same location as Zhu et al., 2021, i.e.,
39 Shanghai Academy of Environmental Sciences (31.10 N, 121.25 °E), a typical urban site in the Yangtze River
40 Delta region from 23 August to 5 September 2016, and from 28 November 2016 to 12 December 2017 with
41 HR-ToF-AMS at 4 min time resolution."

42

3. My main concern in this work is the fact that HOA changes drastically from POA to OOA in 0.6 days (Fig. S4), while COA does not change largely over the OH exposure experiments, maybe the higher RH in the vehicle experiments influenced the SOA formation. At the moment I find difficult to follow the comparison of cooking and vehicle experiments. Were the experiments repetitive/reproducible or it was only one test per experiment?

- Thanks for the reviewer. The temperature of vehicle exhaust from the tailpipe is very high, and the 48 reviewer may think that condensation is causing high humidity. In this experiment, vehicle exhaust from 49 tailpipe was first diluted by a gradient heated dilution system (6 fold) and then diluted by an unheated 50 dilution system (5 fold). The temperature of sample flow was near indoor temperature after secondary 51 dilution systems. The dilution air was ambient air (clean period), which was firstly filtered by a particle filter 52 system (including a dryer, a filter, and an ultrafilter, SMC Inc.) to remove the particles and water. Heat 53 insulation cotton with temperature controlling was wrapped around the sampling pipelines, preventing 54 freshly warm gas from condensing on the wall of the pipe. Then the fumes were injected into the Go: PAM 55 where aerosols and gases reacted at a stable temperature (16-19°C) and relative humidity (18-20%) in 56 cooking experiments, and temperature (19-22°C) and relative humidity (44-49%). The relative humidity of 57 the two experiments before entering the PAM is comparable. Relative humidity should not influence the 58 SOA formation in the vehicle experiment, which is not quite different from the cooking experiment. 59

We have added the information about the vehicle and cooking experiments in detail in the revised manuscript, such as the description of experiments repetitive (line 86-118 in the marked revised manuscript) as follows:

"For cooking, we prepared four dishes including deep-frying chicken, shallow-frying tofu, stir-frying cabbage, and Kung Pao chicken. The total cooking time for each experiment ranged from 40 to 66 min, which was almost related to the features of each dish (Table S1). Each dish was continuously carried out 8 times in parallel during the cooking process until the closed kitchen was full of fumes. The fumes produced

by cooking were introduced through the pipeline from the kitchen into the Gothenburg Potential Aerosol 67 Mass (Go: PAM) reactor (Li et al., 2019) in the laboratory after being diluted 8 times by a Dekati Dilutor 68 (e-Diluter, Dekati Ltd., Finland). Heat insulation cotton was wrapped around the sampling pipelines to 69 prevent fumes from condensing on the wall of the pipe. We considered the emissions sampled after Go: PAM 70 without OH radical as primary emissions, and those monitoring after Go: PAM with given OH radicals as 71 72 secondary formation. The sampling time ranged from 58 to 90 min. Each sampling was in parallel three times. The relative standard deviations were small, which were under 10% in most cases. In addition, the 73 background blank groups and the dilution gas blank groups were separately completed using boiling water 74 and dilution gas, according to the same steps as experimental groups. More information on the experimental 75 76 setup of cooking simulations has been given in Zhang et al., 2020.

For vehicle, experiments were performed by using Gasoline direct engine (GDI)with a commercial 77 China V gasoline fuel (Emission: 998cc; Maximum power: 100KW 6000rpm; Peak torque: 205Nm 78 2000-3000rpm). Vehicle operating under real-life conditions were dynamic rotating speed-torque 79 combination. For example, the combination of 1500 rpm rotating speed and 16Nm torque, 2000rpm, and 80 16Nm torque for the engine in this study reflect the realistic vehicle speed of 20km/h and 40km/h, 81 respectively. Five running conditions covering different speeds and torques, including 1500rpm_16Nm, 82 1750rpm_16Nm, 2000rpm_16Nm, 2000rpm_32Nm, and 2000rpm_40Nm, were used to characterize their 83 POA and SOA mass spectra in this study. Once the engine warmed up, it continued to work under one 84 running condition. After the three-way catalytic system, the exhaust from the engine tailpipe was diluted 30 85 times by the same dilution system for the cooking experiment. Then the diluted exhaust entered the GO: PAM 86 through the stainless pipe wrapped by heat insulation cotton. For each running condition, five parallel 87 experiments were conducted (Table S2). The sampling time with collecting three parallel data groups was 88 about 60 min for each experiment. 89

Go: PAM reactor consists of quartz tube that is 100 cm long and 9.6 cm in diameter, as described in Watne et al., 2018. The OH radicals in Go: PAM reactor is generated by the photolysis of ozone and the reaction in the presence of water vapor. We adjusted input ozone concentrations ranging from ~0 to ~6.5 ppm and ~0 to ~4.0 ppm to change the OH radicals in the Go: PAM for vehicle and cooking experiments, respectively. The temperature, relative humidity, and the sampling residence time in Go: PAM for vehicle and cooking experiments were documented in the supplement material (**Table S3**)."

Watne, A. K., Psichoudaki, M., Ljungstrom, E., Le Breton, M., Hallquist, M., Jerksjo, M., Fallgren, H.,
Jutterstrom, S., and Hallquist, A. M.: Fresh and Oxidized Emissions from In-Use Transit Buses Running on
Diesel, Biodiesel, and CNG, Environmental science & technology, 52, 7720-7728, 10.1021/acs.est.8b01394,
2018.

104 Table S1. Details of cooking and sampling procedures.

Cooking Dish	Cooking	Oil	Cooking Numbers for		Sampling	Fuel	Sampling
	Material	Temperature	Time	Each Dish	Time		Temperate
Deep-fried	170g chicken,	145~155°C	66 min	8	90 min		
chicken	500ml corn oil						
Shallow-frying	500g tofu,	100~110°C	64 min	8	60 min	Liquefied	
tofu	200ml corn oil					petroleum	20~25°C
Stir-frying	300g cabbage,	95~105°C	47 min	8	58 min	gas	
cabbage	40ml corn oil					Iron work	
Kung Pao	150g chicken,	90~105°C	40 min	8	60 min		
chicken	50g peanut,						
	50g cucumber,						
	40ml corn oil						

107 Table S2. Details of vehicle and sampling procedures.

Running Co	Running Condition		Parallels	Fuel	Sampling
Rotating speed	Torque				Temperate
1500 rpm	16 Nm	60 min	5		
1750 rpm	16 Nm	60 min	5	Commercial	20~25°C
2000 rpm	16 Nm	60 min	5	China V gasoline	
2000 rpm	32 Nm	60 min	5		
2000 rpm	40 Nm	60 min	5		

	С	ooking experime	ent		Vehicle experiment				
O_3	RH (%)	Description	OH exposure	Photochemical	O ₃	RH (%)	Description of	OH exposure	Photochemical
concentration	& Temperature	of Go: PAM	(molecules	Age	concentration	& Temperature	Go: PAM	(molecules	Age
(ppbv)	(°C)		$cm^{-3} s$)	(day)	(ppbv)	(°)		$cm^{-3}s$)	(day)
0		Sample flow	0	0	0		Sample flow	0	0
310		(7 L/min)	4.3E+10	0.3	624		(4 L/min) and	7.8E+10	0.6
1183	18~23%	and oxidant	9.6E+10	0.7	2367	44~49%	oxidant flow	2.1E+11	1.7
2217	&16~19°C	flow (3	1.4E+11	1.1	4433	&19~22°C	(1 L/min);	3.7E+11	2.9
4025		L/min);	2.7E+11	2.1	6533		Residence	5.4E+11	4.2
		Residence					time: 110 s		
		time: 55 s							

Table S3. The OH exposure and photochemical age for all conditions in cooking and vehicle experiments

4. The OA source apportionment community tend to not constrain SOA as the SOA of one site is different to another site or even different to the SOA from one season to another one. There should be some caveats mentioned in the discussion/conclusion. What is the message here? For example, to recommend doing this type of experiments with local cooking in order to obtain the ME2 constrains and then do the OA source apportionment? Or to use the mass spec generated in this study as target profiles in future studies?

- Thanks for the reviewer's comment. Combined with the second reviewer's comments, we have added the section on "limitations and future work", including the limitations of the SOA spectra profiles as constraints in the revised manuscript (line 411-445 in the marked revised manuscript) as follows:.

"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 NOx 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."

It is worth mentioning that one of the limitations PMF/ME2 have is the fact that the time series generated from the OA deconvolution are average factors over the analysis period and doesn't involve chemical/physical evolution over time, thus constraining SOA is challenging and the user might be producing mixing factors or manipulating the constrains in a subjective manner. It would be also interesting to see how the Q/Qexp and residuals vary in this study.

- Thanks for the reviewer's comment. The choice for the optimal solution for PMF model was presented in the supporting information (take the wintertime as example; Figure S14-16 and Table S19-20) in the supplement.



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.

Pearson r	Sulfate	$\mathrm{CO_2}^+$	C	$C_2H_4O_2^+$	$C_{10}H_8^{+}$
MO-OOA_PMF	0.89	0.96		0.67	0.61
Pearson r	Nitrate	$C_2H_3O^+$	$C_6H_{10}O^+$	$C_{2}H_{4}O_{2}^{+}$	$C_{10}H_8^{+}$
LO-OOA_PMF	0.04	0.31	0.44	0.51	0.59
Pearson r	COA_PMF				
$C_6H_{10}O^+$	0.81				
Pearson r	HOA_PMF				
NO _x	0.73				

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.



(**d**)

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







Fig.S16. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the winter observation. (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	Fpeak	Seed	Q/Q _{exp}	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 extend based on the time series and spectra.
3	0	0	1.91	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.
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. Line 44. When the authors mention: POA includes vehicle exhaust, this sounds like HOA is only related to vehicles. However, HOA is attributed to fresh emissions from fossil fuel, manly related, but not only, to vehicle emissions. In ambient studies HOA is referred as hydrocarbon like OA rather than vehicle exhaust OA.

- We appreciate the comments from the reviewer. We have corrected the descriptions in the revised manuscript (line 45-51 in the marked revised manuscript) as follows:

"POA includes a kind of hydrocarbon-like OA, (HOA), cooking (COA) and biomass burning (BBOA), which SOA includes low oxygenated OA (LO-OOA) and more oxygenated OA (MO-OOA)(Canonaco et al., 2013; Elser et al., 2016; Qin et al., 2017; Zhang et al., 2017a; Zhou et al., 2018). Many previous studies have been found that HOA is mainly associated with vehicle-related emissions in the urban atmosphere (Hu et al., 2017; Xu et al., 2016; Zhang et al., 2017a). Hereinafter, HOA will be referred to as the abbreviation for organic aerosol emitted by urban vehicles."

6. In section 2.1. I think it needs more explanation about the experiments. How much food was being cooked? It was cooking all the time while the experiment in the PAM reactor was going on or the reactor was locked? Were the cooking emissions isolated from the laboratory air? Or it could be potential mixing? About engine experiment, How long the engine was running for? Where the experiments carried out continuously or did you leave the engine to cool down between runs? It was only one test by experiments or how many repeats did you do? Also, maybe the size of the PAM reactor. I guess this info is in one of the

references but it would be good to understand the details of the experiments without going to other publications, maybe add more details either in section 2.1 or the supplement.

- Thanks for the reviewer's constructive comment. We have supplemented the detailed description of vehicle and cooking experiments in the revised manuscript (line 86-118 in the marked revised manuscript) and the supplement (Table S1 - S3) as follows:

"For cooking, we prepared four dishes including deep-frying chicken, shallow-frying tofu, stir-frying cabbage, and Kung Pao chicken. The total cooking time for each experiment ranged from 40 to 66 min, which was almost related to the features of each dish (**Table S1**). Each dish was continuously carried out 8 times in parallel during the cooking process until the closed kitchen was full of fumes. The fumes produced by cooking were introduced through the pipeline from the kitchen into the Gothenburg Potential Aerosol Mass (Go: PAM) reactor (<u>Li et al., 2019</u>) in the laboratory after being diluted 8 times by a Dekati Dilutor (e-Diluter, Dekati Ltd., Finland). Heat insulation cotton was wrapped around the sampling pipelines to prevent fumes from condensing on the wall of the pipe. We considered the emissions sampled after Go: PAM without OH radical as primary emissions, and those monitoring after Go: PAM with given OH radicals as secondary formation. The sampling time ranged from 58 to 90 min. Each sampling was in parallel three times. The relative standard deviations were small, which were under 10% in most cases. In addition, the background blank groups and the dilution gas blank groups were separately completed using boiling water and dilution gas, according to the same steps as experimental groups. More information on the experimental setup of cooking simulations has been given in Zhang et al., 2020.

For vehicle, experiments were performed by using Gasoline direct engine (GDI)with a commercial China V gasoline fuel (Emission: 998cc; Maximum power: 100KW 6000rpm; Peak torque: 205Nm 2000-3000rpm). 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. Five running conditions covering different speeds and torques, including 1500rpm_16Nm, 1750rpm_16Nm, 2000rpm_32Nm, and 2000rpm_40Nm, were used to characterize their POA and SOA mass spectra in this study. Once the engine warmed up, it continued to work under one running condition system for the cooking experiment. Then the diluted exhaust entered the GO: PAM through the stainless pipe wrapped by heat insulation cotton. For each running condition, five parallel experiments were conducted (**Table S2**). The sampling time with collecting three parallel data groups was about 60 min for each experiment.

Go: PAM reactor consists of quartz tube that is 100 cm long and 9.6 cm in diameter, as described in Watne et al., 2018. The OH radicals in Go: PAM reactor is generated by the photolysis of ozone and the reaction in the presence of water vapor. We adjusted input ozone concentrations ranging from ~0 to ~6.5 ppm and ~0 to ~4.0 ppm to change the OH radicals in the Go: PAM for vehicle and cooking experiments, respectively. The temperature, relative humidity, and the sampling residence time in Go: PAM for vehicle and cooking experiments were documented in the supplement material (**Table S3**)."

Watne, A. K., Psichoudaki, M., Ljungstrom, E., Le Breton, M., Hallquist, M., Jerksjo, M., Fallgren, H., Jutterstrom, S., and Hallquist, A. M.: Fresh and Oxidized Emissions from In-Use Transit Buses Running on Diesel, Biodiesel, and CNG, Environmental science & technology, 52, 7720-7728, 10.1021/acs.est.8b01394, 2018.

Sampling Cooking Dish Cooking Oil Cooking Numbers for Sampling Fuel Material Temperature Time Each Dish Time Temperate Deep-fried 170g chicken, 145~155°C 66 min 8 90 min chicken 500ml corn oil Shallow-frying 500g tofu, 100~110°C 64 min 8 60 min Liquefied 200ml corn oil tofu petroleum 20~25°C 300g cabbage, 95~105°C 47 min 8 Stir-frying 58 min gas cabbage 40ml corn oil Iron work Kung Pao 150g chicken, 90~105°C 40 min 8 60 min chicken 50g peanut, 50g cucumber, 40ml corn oil

Table S1. Details of cooking and sampling procedures.

Table S2. Details of vehicle and sampling procedures.

Running Co	Running Condition		Parallels	Fuel	Sampling
Rotating speed	Torque				Temperate
1500 rpm	16 Nm	60 min	5		
1750 rpm	16 Nm	60 min	5	Commercial	20~25°C
2000 rpm	16 Nm	60 min	5	China V gasoline	
2000 rpm	32 Nm	60 min	5		
2000 rpm	40 Nm	60 min	5		

	С	ooking experime	ent		Vehicle experiment				
O ₃	RH (%)	Description	OH exposure	Photochemical	O_3	RH (%)	Description of	OH exposure	Photochemical
concentration	& Temperature	of Go: PAM	(molecules	Age	concentration	& Temperature	Go: PAM	(molecules	Age
(ppbv)	(°C)		$cm^{-3} s$)	(day)	(ppbv)	(°)		$cm^{-3}s$)	(day)
0		Sample flow	0	0	0		Sample flow	0	0
310		(7 L/min)	4.3E+10	0.3	624		(4 L/min) and	7.8E+10	0.6
1183	18~23%	and oxidant	9.6E+10	0.7	2367	44~49%	oxidant flow	2.1E+11	1.7
2217	&16~19°C	flow (3	1.4E+11	1.1	4433	&19~22°C	(1 L/min);	3.7E+11	2.9
4025		L/min);	2.7E+11	2.1	6533		Residence	5.4E+11	4.2
		Residence					time: 110 s		
		time: 55 s							

Table S3. The OH exposure and photochemical age for all conditions in cooking and vehicle experiments

7. Figure 1. I'm confused with the colours chosen for the experiments and the family groups, for example the sticks on grey refer to the CxHy family or to the 1500rpm_16Nm experiment?

- Thanks for the reviewer's comment. Both CxHy family and 1500rpm_16Nm experiment are gray, which really confuses readers. We have checked the figures in the manuscript carefully. The gray of CxHy remains unchanged. We replaced the colors of engine operating conditions, dishes, POA, and SOA with black in the revised manuscript (Figure 1 and Figure 2), and supplement material (Figure S2-S5), such as:



Fig.1. (a) The mass spectra of aged HOA emission from different vehicle running conditions at EPA 0.6 day; (b) The mass spectra of aged COA from four Chinese dishes at EPA 0.7 day. Five running conditions cover different speeds and torques, including 1500rpm_16Nm, 1750rpm_16Nm, 2000rpm_16Nm, 2000rpm_32Nm, and 2000rpm_40Nm. Four dishes include deep-frying chicken, shallow-frying tofu, stir-frying cabbage, and Kung Pao chicken.



Fig.2. (a) The mass spectra of HOA and aged HOA oxidation under different OH exposure at the same running condition (2000rpm, 16Nm). (b) The mass spectra of primary COA and aged COA oxidation of different OH exposure for shallow-frying tofu. The EPA was obtained from off-line methods according to SO_2 decay shown in Table S1. The elemental compositions were estimated by the "improved-ambient" updated method (Canagaratna et al., 2015).

8. Line 203. m/z 41, 55 and 57 are traditional markers of COA. If the authors want to identify mixing of POA and SOA should look into the increments of signals in m/z 28 and 44 for example.

- We appreciate the comments from the reviewer. The m/z 41, 55, and 57 are traditional markers of primary cooking organic aerosol (COA). The aged COA, that is organic aerosol after oxidation, should have fragments such as m/z44 with higher abundance, and ion fragments with lower abundance of m/z41, m/z55, and m/z57. If it has a higher abundance of CxHy fragments, it should be more indicative that it is mixed with POA. To express more clearly, we have added increments of f44 and f43 in the revised manuscript (line 257-259 in the marked revised manuscript) as follows:

"Although the f44 (proportion of m/z 44 in OA) of aged COA raised from 0.03 to 0.08 with oxidation increasing (**Fig.2b; Fig.S5**), the high abundance of m/z 41, 55, and 57 in aged COA mass spectra for four dishes may be a sign that aged OA identified in this study is a mixture of POA and SOA."

9. Figure 3. Why for COA there is one primary and one secondary OA and for Vehicle both are SOA? Why there is no vehicle POA?

- 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."

10. I know PMF has been widely applied to deconvolve OA factors/sources and the chosen strategy to select the 'optimal solution has been reported in previous publications. However, there is no mention on this work how the PMF/ME2 analysis was performed.

- Thanks for the reviewer's constructive comment. First, we have added the source apportionment by using PMF and ME-2 in the materials and methods section. Second, 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). Third, the optimal solution for ambient atmosphere by using the PMF model and ME-2 model has been described in the manuscript. All the changes are documented in the revised manuscript and supplement information (line 337-343; Figure S13-S16 and Table S19-S20) 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 (<u>Huang et al., 2020</u>; <u>Wang et al., 2017</u>; <u>Zhu et al., 2018</u>). In this study, we used the Igor-based PMF model with PMF2.exe algorithm (<u>Paatero and Hopke, 2003</u>) and the PMF Evaluation Toolkit version 2.08D (<u>Ulbrich et al., 2009</u>) 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 (<u>Hu et al., 2016a</u>; <u>Zhang et al., 2011</u>), 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 a-value approach to perform organic HR-AMS datasets collected in Shanghai. The a-value can vary between 0 and 1, which is the extent to which the output profiles can vary from the model inputs. The a-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

"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**). Source apportionment on OA datasets by using the unconstrained PMF model was also examined to compare with ME-2 analysis. The choice for the optimal solution for the PMF model was presented in the supporting information (**Fig.S14-S16** and **Table S19-S20**)."



Fig.S7. Diagnostic plots of the PMF analysis on OA mass spectral matrix for stir-frying cabbage. (a) Q/Qexp as a function of number of factors (P) selected for PMF modeling. For the four-factor solution (i.e., the best P), (b) Q/Qexp as a function of fPeak, (c) The fractions of OA factors vs. fPeak, (d) The Q/Qexp 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.

Factor				
number	Fpeak	Seed	Q/Q _{exp}	Solution Description
1	0	0	1.62	Too few factors, large residuals at time series and key m/z
2	0	0	0.85	Optimum choices for PMF factors (POA and SOA). Time series, mass spectra and diurnal variations of PMF factors are reasonable.
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.

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



Fig.S9. Diagnostic plots of the PMF analysis on aged HOA mass spectral matrix for 2000rpm_32Nm. (a) Q/Qexp as a function of number of factors (P) selected for PMF modeling. For the four-factor solution (i.e., the best P), (b) Q/Qexp as a function of fPeak, (c) The fractions of OA factors vs. fPeak, (d) The Q/Qexp 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.

Factor number	Fpeak	Seed	Q/Q _{exp}	Solution Description
1	0	0	15.44	Too few factors, large residuals at time series and key m/z
2	0	0	2.87	Optimum choices for PMF factors (LO-SOA and MO-SOA). Time series, mass spectra and diurnal variations of PMF factors are reasonable.
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.

Table S9. The optimum choices for PMF factors in 2000rpm_32Nm aged HOA analysis.



Fig.S13. (a) 5-factor solution performed by ME-2 on organic mass spectra; (b) 7-factor solution performed by ME-2 on organic mass spectra during the wintertime in Shanghai.



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.

Pearson r	Sulfate	$\mathrm{CO_2}^+$	C ₂	$H_4O_2^+$	$C_{10}H_8^{+}$
MO-OOA_PMF	0.89	0.96	0.96 0.67		0.61
Pearson r	Nitrate	$C_2H_3O^+$	$C_6H_{10}O^+$	$C_{2}H_{4}O_{2}^{+}$	$C_{10}H_8^{\ +}$
LO-OOA_PMF	0.04	0.31	0.44	0.51	0.59
Pearson r	COA_PMF				
$C_6H_{10}O^+$	0.81				
Pearson r	HOA_PMF				
NO _x	0.73				

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.



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







Fig.S16. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the winter observation. (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	Fpeak	Seed	Q/Q _{exp}	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 extend based on the time series and spectra.
3	0	0	1.91	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.
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.

11. Figure 5. What does other-POA refer to? And how its diurnal look like? It seems that the evening peak from the diurnal concentrations that is lost from cooking and vehicle ME2 might be in this factor and might have OA concentrations from cooking and vehicles apart from biomass burning and coal combustion.

- 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 in the marked revised manuscript) 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**)."





12. Line 308, the paragraph says that using parameter assumptions of vehicle exhaust, it is estimated that cooking SOA, accounts for 35% of the SOA in downtown Los Angeles through the model. This paragraph is not that clear and it doesn't fit well as part of the conclusions, please elaborate, move it maybe to discussions or delete it.

- We appreciate the comments from the reviewer. We have deleted the sentence from the manuscript.

13. Figure 5. The figure on the top left shows two LO-OOA for the PMF analysis, were there two LO-OOA factors?

- Thanks for the reviewer's constructive comment. We have added the explanation in the Figure 5 caption to make the reader clear.



Fig.5. The comparison of the mass spectra, the diurnal variation, and fraction between ME-2 and PMF resolved factors during the wintertime in Shanghai. The black lines in the spectra and diurnal pattern are the results of PMF analysis of the actual atmosphere in Shanghai winter. The others correspond to the ME-2 source analysis results by using two primary OA factors (the cooking PMF POA, ambient HOA) 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 winter observations of Shanghai. Note that in the mass spectra and daily patterns, the OOA_PMF factors which compared with vehicle LO-SOA and Cooking SOA respectively are the same, rather than the two resolved factors.

14. Line 155, remove one of the references.

- Thanks for the reviewer's constructive comment. We have removed one of the references in the revised manuscript (line 196-198 in the marked 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."

15. Figure 2.a The detail on the caption is extensive. Maybe add the description of Fig. S4 somewhere either in the main text or the supplement.

- We appreciate the comments from the reviewer. Figure 2 and Figure 4 are combined together to be analyzed in the revised manuscript (line 213-221 in the marked revised manuscript) 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 (**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 <u>Ng et al., 2011</u> and <u>Zhu et al., 2021b</u>. 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**) (<u>Hu et al., 2017; Zhu et al., 2021b</u>)."

16. Paragraph lines 213-215, please rephrase, it is not clear in the way is written.

- Thanks for the reviewer's constructive comment. We read the manuscript carefully and found that this sentence (line 213-215) was unnecessary. Combined with the comments of the second reviewer, we deleted this sentence in the revised manuscript (line 273-274 in the marked revised manuscript).