Mass spectral characterization of secondary organic aerosol from urban lifestyle sources emissions

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Abstract In the present work, we conducted experiments of secondary organic aerosol (SOA) formation from urban lifestyle sources (cooking and vehicle) to characterize the mass spectral features of primary organic aerosol (POA) and SOA using an high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Our results showed that the cooking styles have greater impact on aged COA mass spectra than oxidation condition. However, the oxidation conditions affect the aged HOA spectra more significantly than vehicle operation conditions. In our study, we use mass spectra similarity analysis and positive matrix factorization (PMF) analysis to establish the POA and SOA mass spectra of these two typical
These mass spectra are used as source constraints in a multilinear engine (ME-2) model to apportion the OA sources in the atmosphere. Comparing with the traditional ambient PMF results, the improved ME-2 model can better quantify the contribution of POA and SOA from life-style sources. Our work, for the first time, establishes the vehicle and cooking SOA source profiles, and can be further used in the OA source apportionment in the ambient atmosphere.

1. Introduction

Organic aerosol (OA) is an important component of fine particulate matter and has significant environmental and health effects, especially in the urban areas (Guo et al., 2012; Guo et al., 2014; Ying et al., 2020). Currently, real-time measurements of OA based on the aerosol mass spectrometer (AMS) has become an effective way to explore OA characteristics in the field campaigns and laboratory studies (Canagaratna et al., 2007; Ge et al., 2017; Hu et al., 2016a; Huang et al., 2011; Kim et al., 2017; Li et al., 2017; Sun et al., 2016; Zhang et al., 2011). Applying positive matrix factorization (PMF) and a multilinear engine (ME-2) (Paatero, 1999) to analyze the high-resolution mass spectrometry fragments, OA can be further identified as primary organic aerosol (POA) and secondary organic aerosol (SOA). POA includes vehicle exhaust (precisely, 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). As lifestyle sources in urban, cooking and vehicle emissions, that is COA and HOA mostly determine ambient OA loadings. For example, primary cooking OA (COA) and vehicle exhaust OA (HOA) accounted for 10-35 % and 6-26% of OA, respectively, in urban areas in China (He et al., 2011; Hu et al., 2017; Sun et al., 2010; Sun et al., 2014; Sun
et al., 2018; Wang et al., 2016; Xu et al., 2016; Zhang et al., 2014).

Besides the contribution to POA, many studies have found that these two typical urban lifestyle sources may also emit a large number of volatile organic compounds (VOCs) (Katragadda et al., 2010; Klein et al., 2016), semi-volatile organic compounds (SVOCs), and intermediate volatile organic compounds (IVOCs) (≥ C13n-alkanes and fatty acids) (Louvaris et al., 2017; Schauer et al., 2002), which may also play important roles in SOA formation. However, based on collocated AMS measurements and factor analysis results, the SOA formed by vehicle and cooking sources cannot be effectively resolved from the total SOA due to the lack of secondary mass spectral profiles. The POA mass spectral profiles based on AMS including HOA (Collier et al., 2015), BBOA (Alfarra et al., 2007; He et al., 2010; Xu et al., 2020), and COA (He et al., 2010; Liu et al., 2017; Mohr et al., 2012; Xu et al., 2020) have been fully explored in laboratory studies, and applied as constraint factors into the ME-2 model in the ambient air. Some studies have made it possible to quantify biogenic secondary aerosol products of a single precursor, such as isoprene oxidation products (IEPOX) (Budisulistiorini et al., 2013; Hu et al., 2016b), and have been extended to the urban atmosphere to obtain an IEPOX-SOA factor via PMF analysis of OA spectra (Zhang et al., 2017b). Although several studies explored the mass spectral characteristics of SOA from anthropogenic life-style sources, i.e., heated cooking oils, gasoline motors, and diesel engines (Kaltsonoudis et al., 2017; Liu et al., 2018; Presto et al., 2014), the spectral profiles of cooking SOA under actual cooking conditions and vehicle SOA under different emission conditions are still uncertain. Besides, to date, studies that used ME-2 for a better anthropogenic SOA source apportionment by inputting their SOA spectra as constraints remain scarce. Therefore, the mass spectra of SOA from abundant anthropogenic life-style sources are urgent to characterize for conducting to acquire a better source apportionment of SOA.

In this work, cooking and vehicle experiments were carried out to investigate the variation in mass spectra profiles of POA and SOA from Chinese cooking emissions under different cooking styles and
vehicle emissions under different running conditions using high-resolution time-of-flight AMS (HR-ToF-AMS). The mass spectral characterizations of POA and SOA from cooking and vehicle emissions were intercompared, and their changes in some indicated ionic fragments were elucidated. Besides, we verified the mass spectral profiles by applying mass spectra of POA and SOA to ME-2 for source apportionment of OA in the winter observation with various primary emissions and the summer observation with high oxidation conditions.

2. Materials and Methods

2.1 Simulation of POA emission and SOA formation from urban lifestyle sources.

For cooking, we prepared four dishes including deep-frying chicken, shallow-frying tofu, stir-frying cabbage, and Kung Pao chicken. The fumes produced by cooking were introduced into the Gothenburg Potential Aerosol Mass (Go: PAM) reactor (Li et al., 2019) after being diluted 8 times by a Dekati Dilutor (e-Diluter, Dekati Ltd., Finland). We considered the emissions sampled after Go: PAM without OH radical as primary emissions, and those measured after Go: PAM with the given OH exposure as secondary formation. 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 of experimental setup of cooking simulations can be found in Zhang et al., 2020 (Zhang et al., 2020). For vehicle, experiments were performed by using GDI engine with a commercial China V gasoline fuel (Emission: 998cc; Maximum power: 100KW 6000rpm; Peak torque: 205Nm 2000-3000rpm). Five running conditions covering different speeds and torques, including 1500rpm_16Nm, 1750rpm_16Nm, 2000rpm_16Nm, 2000rpm_32Nm, and 2000rpm_40Nm, were used to characterize their POA and SOA mass spectra. We adjusted input ozone concentration ranging from ~0 to ~7.7 ppm to change the OH exposure in the Go: PAM.

2.2 Instrumentation and data analysis.
Figure S1 shows the schematic of the experimental system. Two scanning mobility particle sizers (SMPS-1, Electrostatic Classifier model 3080, Condensation Particle Counter model 3778; SMPS-2, Electrostatic Classifier model 3082, Condensation Particle Counter model 3772; TSI Incorporation, USA) were set at the inlet and outlet of Go: PAM to correct the wall loss. The size distribution and number concentration of particles were scanned every 2 (cooking) - 5 min (vehicle) before and after Go: PAM for cooking and vehicle experiment, respectively. The chemical compositions and high-resolution ions fragments of OA were measured by an aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Incorporation, USA), synchronize with SMPS.

Before and after the two experiments, the ionization efficiency (IE) of HR-ToF-AMS IE calibrations were carried out by using 300 nm mono-dispersed ammonium nitrate particles combining with SMPS. The collection efficiency (CE) of HR-ToF-AMS was obtained from comparing AMS and synchronous SMPS real-time measurement of particle mass concentrations at the outlet of Go: PAM. Besides, the CO2 concentrations were simultaneously measured using a CO2 analyzer (Model 410i, Thermo Electron Corporation, USA) to reduce the CO2 interference to organic fragments in mass spectra. Other gas phase measurements included carbon monoxide (CO, Thermo, Model 48i TL), NOx (Thermo, Model 42i TL) and SO2 (Thermo, Model 42i TL).

The mass concentration, size distribution and the ion-speciated mass spectra of NR-PM1 species were analyzed using the HR-ToF-AMS standard data analysis software (SQUIRREL version 1.57 and PIKA version 1.16). 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 separate the POA and SOA from aged cooking and vehicle organic aerosol, following the procedure presented in the literatures (Hu et al., 2016a; Zhang et al., 2011). The OH exposure and equivalent photochemical age (EPA) were calculated by off-line methods according to SO2 decay shown in Zhang et al., 2020 (Zhang et al., 2020).
which were validated by a flow reactor exposure estimator using measured concentrations of reactive compounds such as VOCs, CO and NOx (Peng et al., 2016). The OH exposure and photochemical age for all conditions in cooking and vehicle experiments were listed in Table S1.

2.3 Mass spectra similarity analysis.

In this study, the angle $\theta$ was used to evaluate the correlation between the two AMS mass spectra features. The angle $\theta$ between the two AMS mass spectra (MSa, MSb) is given by:

$$\cos \theta = \frac{\text{MSa} \cdot \text{MSb}}{||\text{MSa}|| \cdot ||\text{MSb}||}$$

The $\theta$ angle between two mass spectra is 0-5, 5-10, 10-15, 15-30, and > 30, which means excellent consistency, good consistency, many similarities, limited similarities, and poor consistency, respectively, (Kaltsonoudis et al., 2017; Kostenidou et al., 2009).

3. Results and Discussion

3.1 Mass spectra of POA and aged OA from the life style sources.

Fig.1a shows the mass spectra of aged HOA under different vehicle running conditions when EPA was 0.6 days. The mass spectra of aged HOA emission from different vehicle running conditions under other various oxidation degrees are included in Fig.S2. All the aged HOA spectral profiles from different vehicle running conditions showed a similar pattern. and the $\theta$ angles among the mass spectra of aged HOA were less than 10° at EPA 0.6 days (Table 1), suggesting a little difference between the mass spectra. The mass spectra of aged HOA at 0.6 days were dominated by the ion series of $\text{C}_n\text{H}_m^-$ (m/z 29, 43, 57, 71, 85...) and $\text{C}_n\text{H}_m^+$ (m/z 41, 55, 69, 83...), resulting from less oxidized components such as saturated alkanes, alkenes. As the highest proportion of ion fragments, m/z 43 and 29 consisted of oxygen-containing ions like $\text{CHO}^+$ and $\text{C}_2\text{H}_3\text{O}^+$, respectively, whose fractions were much larger than the hydrocarbon-like ion fragments at the same mass integers. Besides, there were also abundant tracer ion fragments for SOA (m/z 28 and m/z 44).
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 covers 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.

The mass spectra of aged COA at 0.7 days of EPA are presented in Fig. 1b. Detailed mass spectra of aged COA under other various oxidation degrees are included in Fig. S3. The similarity of aged COA among different types of cooking were greater that of aged HOA among different running conditions when the EPA was at the same level. Except for the θ angles of deep-frying chicken vs stir-frying cabbage (21°), and deep-frying chicken vs shallow-frying tofu (19°), the θ angles among other aged COA at EPA 0.7 day exhibited good agreement (θ<15°) in mass spectra (Table 1). The mass spectra of cooking were dominated by the similar ion series as those of vehicle, which were mostly m/z 28, m/z 29, m/z 41, m/z 43, m/z 44, m/z 55, m/z 57, m/z 67, and m/z 69. However, the major mass spectral differences between cooking and vehicle were the abundance of m/z 41 and the ratio of oxygen-containing ions to hydrocarbon ions (C₃H₇O⁺/C₃H₇⁺).

The four Chinese dishes had prominent peaks at m/z 41, m/z 43 and m/z 55 (generated from C₃H₅⁺ and C₃H₇⁺, C₄H₇⁺) which was qualitatively consistent with mass spectra of primary COA in other studies (Xu et al., 2020). 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 are resulting from unsaturated fatty acids (He et al., 2010).

Table 1 The θ angles among the mass spectra of (a) aged HOA at EPA 0.6 day and (b) aged COA at EPA 0.7 day.
Fig. 2a shows the mass spectra of aged HOA oxidation at different OH exposures under the same vehicle running condition (2000rpm, 16Nm). The changes in mass spectra of aged HOA under different conditions are provided in Fig. S4. As the oxidation degree increased, the ion fragments varied similarly with hydrocarbon-like ion fragments decreasing. 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. When EPA was 1.65 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, similar to the spectra of the ambient LO-OOA. Oxidation degrees greatly affected the similarity of mass spectra between POA and those of aged HOA. The mass spectra profile of vehicle POA displayed poor agreement (θ > 30°) with all aged HOA spectra profiles (Tables S4-S5). 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 2.89 and 4.15 days).
Fig. 2. (a) The mass spectra of aged HOA oxidation of different OH exposure under the same vehicle emission condition (2000rpm, 16Nm). (b) The mass spectra of aged HOA oxidation of different OH exposure for shallow-frying tofu. The OH exposure and equivalent photochemical age (EPA) were calculated by off-line methods according to SO2 decay shown in Table S1.

The mass spectra of primary COA and aged COA showed great inter-correlations (θ < 15°), which were smaller than that of vehicle OA (Table S4-S5). Along with the growth of OH exposure, the f43 of aged COA increased from 0.07 to 0.10, and meanwhile its f44 increased from 0.03 to 0.08 (Fig.2b; Fig.S5), distributing in the lower region of less oxidized organic aerosol (LO-OOA). The spectra of these aged COA derived herein displayed almost the same variation with those of cooking oils OA (Liu et al., 2018). It should be noted that the fractions of m/z 28 and m/z 44 signals in aged COA were lower than those of aged HOA at the similar EPA. In addition, the aged COA had more hydrocarbon-like ions at the same mass integers than aged HOA.

All the above results imply that oxidation condition drives the variabilities in mass spectra of the vehicle OA. In contrast, cooking styles instead of oxidation conditions, significantly affected the mass spectra of cooking OA. Here we concluded some possible explanations for these results. On one hand, under the same oxidation conditions and different emission conditions, the similarity among the mass spectra of vehicles was larger than that of cooking, which may be related to their precursors. Some studies have shown that the species and the proportion of gaseous organic matter emitted by different dishes are quite different (Wang et al., 2018). As described in the literature, alkanes and O-VOCs contributed to over 97% of the total...
VOCs for fried food, and O-VOCs were the dominant contributors for Sichuan and Hunan cuisine where stir-frying is common (Wang et al., 2018). Different gaseous precursors cause distinctions in the particle phase SOA formation, which is reflected in the variations of AMS ion fragments between four dishes in our study. Compared to cooking, the precursors from vehicles are mainly hydrocarbons, and the difference in emissions under different running conditions is inapparent (Robinson et al., 2007). On the other hand, under the same emission conditions and different oxidation conditions, the similarity among the mass spectra of cooking sources is larger than that of vehicle sources, likely due to the oxidation pathway of precursors. As mentioned above, O-VOCs are important precursors of cooking sources, and their oxidation mechanisms is mostly alcohol/peroxide substitution process. This conclusion was proved by a Van Krevelen diagram, showing that the cooking data gather around the slope of approximately -0.1 (Zhang et al., 2020), in agreement with that of heated oils OA (Liu et al., 2018). However, for vehicles, with the increase of oxidation degrees, the reaction pathways of hydrocarbon precursors varied diversely. In Van Krevelen space, the vehicle data fell along a line with a slope of -0.5 (Fig.S6), indicating oxidation processes involving the addition of both carboxylic acid and alcohol or peroxide functional groups without fragmentation and/or the addition of carboxylic acid functional groups with fragmentation.

3.2 Identification of the lifestyle sources SOA mass spectra.

The high abundance of m/z 41, 55, and 57 in aged COA mass spectra may be a sign that aged OA identified in this study is a mixture of POA and SOA. PMF analysis was performed on the high-resolution mass spectra to split SOA and POA factors from aged COA. Similarly, the same PMF procedure was also applied for vehicle datasets.

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 POA of four Chinese dishes all showed obvious
hydrocarbon-like features with a large abundance of $f_{57}$, $f_{55}$, or $f_{41}$ (fraction of m/z 57, 55 and 41 in OA, respectively). For all experiments, the prominent peaks of cooking POA were m/z 41 ($f_{41}=0.051\sim0.069$), 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 ($f_{69}=0.034\sim0.049$) dominated by $C_{3}H_{7}^{+}$, $C_{4}H_{7}^{+}$, $C_{6}H_{5}^{+}$, $C_{8}H_{6}^{+}$ and $C_{3}H_{5}^{+}$ respectively. It was observed that fractions of oxygen-containing ions were rising while those of hydrocarbon-like ions were declining during the oxidation process. As for mass spectra of cooking SOA, the fractions of oxygen-containing ions were higher than those of hydrocarbon-like ions. The prominent peaks were 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 ($f_{55}=0.050\sim0.064$) and 57 ($f_{57}=0.036\sim0.067$), dominated by CO$^{+}$, CHO$^{+}$, $C_{2}H_{5}^{+}$, $C_{3}H_{5}^{+}$, $C_{2}H_{3}O^{+}$, CO$_{2}^{+}$, $C_{3}H_{5}^{+}$, $C_{4}H_{7}^{+}$, $C_{3}H_{3}O^{+}$, $C_{4}H_{5}^{+}$ and $C_{3}H_{3}O^{+}$ respectively. The evolution of m/z 43 from POA to SOA revealed a larger fraction and enhancement than those of m/z 44, suggesting that the domestic cooking SOA may generate from a less oxidized process.

Different from the cooking, two OOA factors were derived from vehicle SOA 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). As indicated in Fig.3, 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 $f_{57}=0.027$) were comparable with those of cooking SOA. The fraction of m/z 43 of LO-SOA was higher than that in cooking SOA by a factor of 2. The abundant m/z 28 and 44 (mainly generated from CO$_{2}^{+}$) are widely used as the ambient MO-OOA markers. (Sun et al., 2018; Xu et al., 2017).

We observed high fractions of m/z 28 ($f_{28}=0.110\sim0.214$) and m/z 44 ($f_{44}=0.121\sim0.224$) in MO-SOA and high O/C ratios (0.88~1.33), which were much higher than those of LO-SOA (O/C=0.37~0.53) and cooking SOA (O/C=0.29~0.41).
Fig. 3. The mass spectra of PMF-POA and SOA from vehicle and cooking. PMF analysis was performed on the high-resolution mass spectra to split two factors (cooking POA and SOA) from aged COA and two SOA factors (vehicle LO-SOA and MO-SOA) from aged HOA, respectively.

Similarly, for the resolved SOA factor, the correlation of mass spectra among cooking groups under different cooking methods ($\theta = 8$–$21^\circ$) was worse than that of vehicle groups ($\theta = 3$–$7^\circ$) under different running conditions (Table S8; Table S10). The mass spectra of the PMF POA factors for deep-frying chicken exhibited poor agreement with those of stir-frying cabbage, Kung Pao chicken, and shallow-frying tofu (Table S9). In addition, we also found that the $\theta$ angles between LO-OOA and MO-OOA under five GDI running conditions were ranged from 36° to 50° (Fig. S7), indicating that the mass spectra profiles of LO-OOA are much different from those of MO-SOA, consistent with the changes in the mass spectra characteristics of vehicles, under the same emission conditions and different oxidation conditions. Our
results suggest that it is necessary to consider the cooking styles when constraining cooking and atmospheric oxidation conditions when constraining vehicle factors.

3.3 Application of established POA and SOA profile in ambient OA source apportionment.

Based on the similarity analysis results of the four cooking groups, the mass spectra of deep-frying chicken were poorly correlated with the others. Therefore, taking into account the cooking methods of Chinese dishes, PMF model was used to identify 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. Similarly, combining different GDI running conditions, LO-SOA and MO-SOA which were resolved based on PMF model were used as the inputting mass spectra profiles of vehicles for ME-2 (Fig. S8).

The $\theta$ angles between the mass spectral profiles from urban lifestyle sources and ambient PMF-resolved factors were calculated and summarized in Fig. 4 and Table S11. The AMS mass spectra of ambient factors were obtained in Shanghai, Dezhou, Beijing, and Shenzhen in China (Hu et al., 2017; Wenfei et al., 2020). The $\theta$ angles among ambient COA, HOA, LO-OOA and MO-OOA factors and the cooking PMF POA, SOA, and the vehicle PMF LO-SOA, MO-SOA were ranged from $18^\circ$ to $52^\circ$ (Fig. 4), suggesting that the cooking PMF POA, SOA, and the vehicle PMF LO-SOA, MO-SOA can be used as source constraints for ME-2 in ambient air.
Fig. 4. The θ angles between ambient COA, HOA, LO-OOA and MO-OOA factors and the cooking PMF POA, SOA, and the vehicle PMF LO-SOA, MO-SOA. The θ 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.

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. We further demonstrated the feasibility of input primary and secondary mass spectra for OA source apportionment in two field campaigns at urban site of Shanghai in summer and winter. Ambient PMF-resolved OA factors included POA factors i.e., HOA, COA, and SOA factors i.e., LO-OOA and MO-OOA in the summer and winter observations in Shanghai. The HOA and COA identified by PMF contributed as high as 16 % and 26 % to OA in the winter observation, respectively, far exceeding expectations (Fig. 5). 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.
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 result 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, 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 observations of Shanghai.

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 during the winter observation. As expected, other POA contributions were identified in the highly polluted season, consistent with influences from biomass burning and coal combustion emissions. The diurnal patterns of PMF factors and ME-2 factors were consistent with the corresponding tracers during the winter observation. We noticed that the vehicle SOA analyzed by ME-2 exhibited more consistence with the diurnal variation of nitrate, especially the reasonable peak disappears at night, which shows that the LO-OOA mixed with POA is well separated by using ME-2 in winter. For the source apportionment in summer (Fig S8), the fraction of COA reduced
from 21% (PMF result) to 12% (ME-2 result). 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. Moreover, the diurnal patterns of ME-2 SOA factors present more reasonable than PMF SOA factors. For example, the MO-OOA obtained based on ME-2 analysis was in good agreement with the diurnal variation of $O_3$ in summer, which better reflects the characteristics of the MO-OOA factor. In general, the accurate source apportionment results have significant indicated that the reliability source profiles of the primary and secondary of cooking and vehicles obtained in our study can be used as constraint for source apportionment of OA with ME-2.

4. Conclusions and Implication

POA emissions, and SOA formation in PAM reactor from urban lifestyle sources were explored. The aged COA had higher hydrocarbon ions than aged HOA in mass spectra. Based on the mass spectra of these two urban lifestyle sources derived from the lab simulation, the ME-2 source apportionment in Shanghai suggest that the reasonable of the primary and secondary source profiles of cooking and vehicles were obtained. To our best knowledge, it’s the first time to estimate the contribution of anthropogenic sources - Chinese cooking SOA and vehicle SOA in ambient air by a multilinear engine model (ME-2), through creatively employs mass spectra of SOA factors to constrain the OA source apportionments, all which has been implemented in biogenic SOA (Hu et al., 2016b; Zhang et al., 2017b). Due to the limitation of research methods, the experiments were conducted under the oxidation conditions without other inorganic aerosol seeds. In the future, it is still necessary to take further researches, for instance, use a quasi-atmospheric aerosol evolution study (QUALITY) chamber to study the SOA formation under different actual oxidation conditions, like high/low NOx and so forth. According to previous studies, using some parameter assumptions of vehicle exhaust, it is estimated that cooking SOA accounts for 35% of the SOA in downtown Los Angeles through the model. Our research found that SOA from the urban lifestyle 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 lifestyle sources in the future.

Supporting information
Schematic depiction of the simulation and measurement system (Figure S1); Details of the mass spectra of aged HOA and aged COA (Figures S2-S5); Van Krevelen diagram of POA, aged COA and aged HOA (Figure S6); ME-2 source analysis during the summer observation in Shanghai (Figure S8); Experimental parameters (Table S1); Mass spectra similarity analysis (Table S2-S10; Figure S7).

Data availability. The data provided in this paper can be obtained from the author upon request (songguo@pku.edu.cn).

Author contribution. Wenfei Zhu, Zirui Zhang, Hui Wang, Ying Yu, Zheng Chen, Ruizhe Shen, Rui Tan, Kai Song, Kefan Liu, Rongzhi Tang, Yi Liu, Yuanju Li, Wenbin Zhang, and Zhou Zhang conducted the experiments. Wenfei Zhu, Zirui Zhang, Song Guo, and Min Hu analyzed the data. Shengrong Lou, Shijin Shuai, Hongming Xu, Shuangde Li, Yunfa Chen, Francesco Canonaco, and Andre. S. H. Prévôt reviewed and commented on the paper. Wenfei Zhu and Song Guo wrote the paper.

Competing interests. The authors declare no competing financial interest.

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