Improved source apportionment of organic aerosols in complex urban air pollution using the multilinear engine (ME-2)

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Abstract Organic aerosols (OAs), which consist of thousands of complex compounds emitted from various sources, constitute one of the major components of fine particulate matter. The traditional positive matrix factorization (PMF) method often apportions aerosol mass spectrometer (AMS) organic datasets into less meaningful or mixed factors, especially in complex urban cases. In this study, an improved source apportionment method using a bilinear model of the multilinear engine (ME-2) was applied to OAs collected during the heavily polluted season from two Chinese megacities located in the north and south with an Aerodyne high-resolution aerosol mass spectrometer (HR-ToF-AMS). We applied a rather novel procedure for utilization of prior information and selecting optimal solutions, which dose not nessesarily depend on other studies. Ultimately, six reasonable factors were clearly resolved and quantified for both sites by constraining one or more factors: hydrocarbon-like OA (HOA), cooking-related OA (COA), biomass burning OA (BBOA), coal combustion (CCOA), less-oxidized oxygenated OA (LO-OOA) and more-oxidized oxygenated OA (MO-OOA). In comparison, the traditional PMF method could not effectively resolve the appropriate factors, e.g., BBOA and CCOA, in the solutions. Moreover, coal combustion and traffic emissions were determined to be primarily responsible for the concentrations of PAHs and BC, respectively, through the regression analyses of the ME-2 results.

1 Introduction

Atmospheric aerosols are generating increasing interest due to their adverse effects on human health, visibility and the climate (IPCC, 2013; Pope and Dockery, 2006). Among different particulate compositions, many studies focus on organic aerosols (OAs) because they contribute 20-90% to the total submicron mass (Jimenez et al., 2009; Zhang et al., 2007). OAs can be either directly emitted by various sources, including anthropogenic (i.e., traffic and combustion activities) and biogenic sources, or produced via secondary formation after the oxidation of volatile organic compounds (VOCs) (Hallquist et al., 2009).

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Therefore, the reliable source identification and quantification of OAs are essential before developing effective political abatement strategies.

Aerodyne aerosol mass spectrometer (AMS) systems are the most widely adopted on-line aerosol measurement systems for acquiring aerosol chemical compositions (Canagaratna et al., 2007; Pratt and Prather, 2012). An AMS provides on-line quantitative mass spectra of non-refractory components from the submicron aerosol fraction with a high temporal resolution (i.e., seconds to minutes) (Canagaratna et al., 2007). The total mass spectra can be assigned to both several inorganic compounds and the organic fraction through mass spectral fragmentation tables (Allan et al., 2004). To further investigate the different types of organic fractions, numerous studies have exploited the positive matrix factorization (PMF) algorithm and apportioned the AMS organic mass spectra in terms of their source emissions or formation processes (Zhang et al., 2011). PMF is a standard multivariate factor analysis tool (Paatero, 1999; Paatero and Tapper, 1994) that models the time series of measured organic mass spectra as a linear combination of positive factor profiles and their respective time series. Most of the earlier PMF studies were conducted on unit-mass resolution (UMR) mass spectrometers (Lanz et al., 2007; Lanz et al., 2010; Ulbrich et al., 2009), although more have recently focused on high-resolution (HR) mass spectra PMF (Aiken et al., 2009; Docherty et al., 2008; Huang et al., 2010). The use of HR mass spectra data to constrain PMF solutions can reduce their rotational ambiguity and result in more interpretable OA factors. For example, Aiken et al. (2009) found that hydrocarbon-like OA (HOA) and biomass burning OA (BBOA) were better separated using HR-AMS data than with UMR data. However, even HR-AMS-PMF can also yield mixed factors (especially in heavily polluted areas) due to their complex emission patterns.

The abundant characteristic fragments for cooking-related OA (COA) (e.g., *m/z* 55 and 57) and coal combustion OA (CCOA) (e.g., *m/z* 51, 53, and 65) can be observed in the mass spectrum of the HOA factor (He et al., 2010; Hu et al., 2013). Elser (et al., 2016) analyzed two urban HR-AMS datasets in China, and their PMF results showed an HOA profile that contained a high concentration of $C_2H_4O_2^+$ (*m/z* 60), which is a BBOA tracer ion. In addition, CO_2^+ (*m/z* 44) contributed more to COA compared to oxygenated OA (OOA). To solve this "mixed factor" problem in PMF analysis, some researchers attempted to use the multilinear engine algorithm (ME-2) with user-provided constraints (Canonaco et al., 2013; Crippa et al., 2014; Elser et al., 2016; Reyes-Villegas et al., 2016). However, several key issues with the ME-2 in these studies, such as reliability of the user-input constraints and the criteria used to determine an optimal result, still require further investigation. Most ME-2 studies (Crippa et al., 2014; Elser et al., 2016; Reyes-Villegas et al., 2016) were based on HR-AMS datasets and utilized mass profiles of PMF results from Paris (Crippa et al., 2013; mostly due to the lack of other reliable source profiles) and did not consider the specific sampling sites, which could result in uncertainties.

In this study, a novel source apportionment technique using the multi-linear engine tool (ME-2) was successfully applied to organic mass spectra obtained with an HR-ToF-AMS at two urban sites during pollution-heavy periods during the same year. The improved OA source apportionment results are discussed and compared with an unconstrained PMF analysis.

2 Materials and methods

2.1 Sampling sites and period

Measurements at Qingdao (36.10°N, 120.47°E, 10 m above ground level, a.g.l.) were performed from 1 to 31 November 2013, while those in Dongguan were conducted from 12 December 2013 to 1 January 2014 (33.03°N, 113.75°E, 100 m a.g.l.). Qingdao is a coastal city with over 9 million inhabitants in northern China, while Dongguan has over 8 million inhabitants and is located in southern China (shown in Figure 1). Both of the sampling sites are on the tops of buildings in urban central areas, and there is no industrial emission nearby.

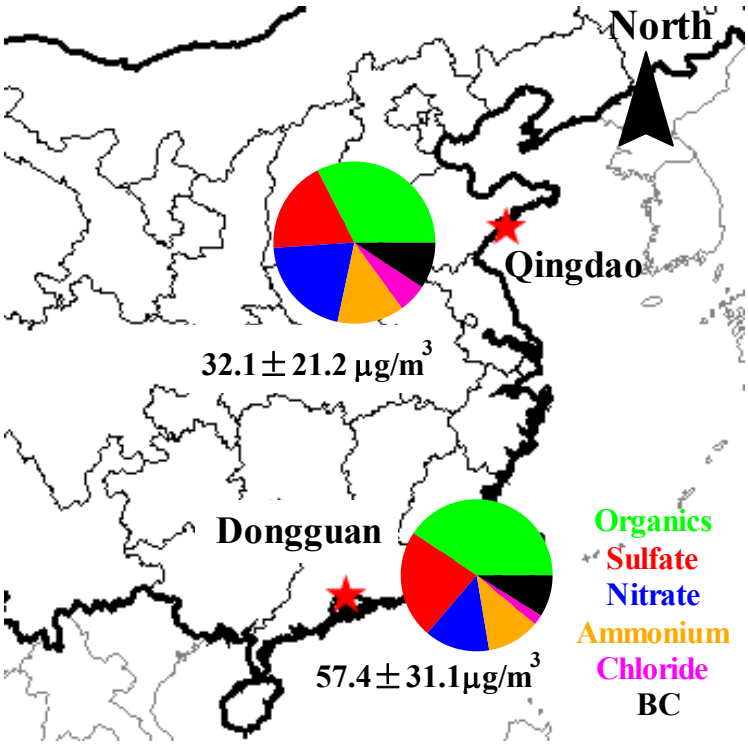

Figure 1. The locations and the average PM_1 chemical compositions of the Qingdao and Dongguan sampling sites.

2.2 Instrumentation

An HR-ToF-AMS was deployed for the on-line measurement of non-refractory PM_1 (Canagaratna et al., 2007). The setup and operation of the HR-ToF-AMS was similar to that in our previous studies (Huang et al., 2015; Huang et al., 2010). A $PM_{2.5}$ cyclone inlet was briefly placed on the roof of a building to remove coarse particles and to introduce an air stream containing the remaining particles into a room through a copper tube with a flow rate of 10 l min^{-1}. A nafion dryer (MD-070-12S-4, Perma Pure Inc.) was positioned upstream of the HR–ToF–AMS to eliminate the potential influence of relative humidity on the

particle collection (Matthew et al., 2008), after which the HR–ToF–AMS isokinetically sampled from the center of the copper tube at a flow rate of 80 ml min^{-1}. The instrument was operated at two ion optical modes with a cycle of 4 min, including 2 min for the mass-sensitive V-mode and 2 min for the high mass resolution W-mode. An aethalometer (AE-31, Magee), which also has a $PM_{2.5}$ inlet, was simultaneously used for measurements of refractory black carbon (BC) with a temporal resolution of 5 min.

A routine analysis of the HR–ToF–AMS data was performed using the software SQUIRREL (version 1.57) and PIKA (version 1.16) written in Igor Pro 6.37 (Wave Metrics Inc.)(http://cires1.colorado.edu/jimenezgroup/ToFAMSResources/ToFSoftware / index.html). The ionization efficiency (IE) was calibrated using pure ammonium nitrate particles following standard protocols (Drewnick et al., 2005; Jayne et al., 2000). The relative IEs (RIEs) for organics, nitrate and chloride were assumed to be 1.4, 1.1 and 1.3, respectively. A composition-dependent collection efficiency (CE) was applied to the data based on the method of Middlebrook et al. (2012) and an organic elemental analysis was performed using the latest approach recommended by Canagaratna et al. (2015).

2.3 PMF and ME-2 methods for OA source apportionment

PMF is a mathematical technique used to solve bilinear unmixing problems (Paatero and Tapper, 1994) that enables a description of the variability of a multivariate database as the linear combination of static factor profiles and their corresponding time series. The bilinear factor analytic model in matrix notation is defined in Eq. (1), where the measured matrix X (consisting of i rows and j columns) is approximated by the product of G (containing the factor time series) and F (the factor profiles). E denotes the model residuals. The entries in G and F are fitted using a least-squares algorithm that iteratively minimizes the quantity Q (Eq. 2), which is defined as the sum of the squared residuals (e_{ij}) weighted by their respective uncertainties (σ_{ij}).

$$X = G \times F + E \qquad (1)$$

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{\sigma_{ij}} \right)^2 \qquad (2)$$

In this study, we adopted SoFi (Canonaco et al., 2013), which is an implementation of the multilinear engine (ME-2) (Paatero, 1999), to perform the organic HR-AMS data analysis. In contrast to an unconstrained PMF analysis, ME-2 enables a more complete exploration of the rotational ambiguity of the solution space. In our case, this is achieved by directing the solution towards environmentally meaningful rotations using the *a* value approach. This method uses prior input profiles and the scalar a to constrain one or more output factor profiles such that they fall within a predetermined range. The *a* value determines the extent to which the output profiles are allowed to vary from the input profiles according to Eq. (3), where f represents the factor profile and j indicates the *m/z* of the ions.

$$f_{j,solution} = f_j \pm a \times f_j \qquad (3)$$

The number of output factors, which is selected by the user, is a key consideration for PMF analysis. Most unconstrained PMF results were chosen following the procedures detailed in Zhang et al. (2007). However, additional outputs in ME-2 can be

generated to explore more of the solution space, and more criteria should be developed to support the factor identification, which will be discussed in section 3.

2.4 Polycyclic aromatic hydrocarbons (PAHs) quantification

In this study, PAHs mass concentrations were quantitatively determined from the HR-AMS data. The steps outlined are as follows: first, the PAHs molecular ions $[M]^+$, including $[C_{10}H_8]^+$, $[C_{12}H_8]^+$, $[C_{14}H_8]^+$, $[C_{14}H_{10}]^+$, $[C_{16}H_{10}]^+$, $[C_{18}H_{10}]^+$, $[C_{18}H_{12}]^+$, $[C_{20}H_{12}]^+$, $[C_{22}H_{12}]^+$, $[C_{22}H_{14}]^+$, $[C_{24}H_{12}]^+$, $[C_{24}H_{14}]^+$, and other associated fragments, including $[M\text{-}H]^+$, $[M\text{-}2H]^+$, $[M]^{2+}$, and $[M\text{-}H]^{2+}$ were fitted in the HR spectra. Second, the fragments presented low correlation (i.e., R^2 below 0.6) with their corresponding molecular ions were not taken into account. Finally, the relative ionization efficiencie (RIE) for PAHs was assumed to be 1.4 and the dependency of the collection efficiency (CE_b) on the chemical composition of the aerosol was estimated using a composition-dependent collection efficiency (CDCE) algorithm (Middlebrook et al., 2012). More details about the method can be found in Bruns et al. (2015).

3 Interpretation of OA source apportionment using ME-2

In this section, a conventional PMF without any prior information is performed to analyze the OA source apportionment. Then, we use the ME-2 method to optimize the OA source apportionment based on the information obtained from the PMF method. The sequential steps are reported below:

1. Unconstrained PMF runs.

We performed unconstrained runs with a range from two to ten factors. Generally, PMF solutions with large numbers of factors are not considered due to possible mathematical splits of the factor profiles. However, some factors that have small contributions or that have similar mass profiles as other factors (but different time series) may only be found in solutions with large numbers of factors. We observe that most of the solutions provided via PMF include either multiply split factors or mixed factors that are not properly separated from one another. In other words, PMF does not produce an appropriate solution. The 6-factor solutions for Qingdao and Dongguan are shown in Figure S1 and S2, and three types of primary OAs (POAs) were identified for each sampling site, including HOA), coal combustion OA (CCOA) and cooking OA (COA) for Qingdao and HOA, biomass burning OA (BBOA) and COA for Dongguan. Oxygenated OA (OOA) seems to be excessively split in the 6-factor solutions for both of the sites. HOA is distinguished by alkyl fragment signatures with prominent contributions of *m/z* 55 ($C_4H_7^+$) and *m/z* 57 ($C_4H_9^+$) (Ng et al., 2011). The COA profile is similar to that of HOA but has a higher contribution from oxygenated ions at *m/z* 55 ($C_3H_3O^+$) and *m/z* 57 ($C_3H_5O^+$) (Mohr et al., 2012). BBOA is characterized by the presence of signals at *m/z* 60 ($C_2H_4O_2^+$) and *m/z* 73 ($C_3H_5O_2^+$), which are identified as fragments from anhydrous sugars present in biomass smoke (Alfarra et al., 2007). The OOA profile is characterized by a high signal at m/z 44 (CO_2^+). Note that some POA profiles in this solution indicate mixing; for example, CCOAs in Qingdao contain a high concentration of the biomass burning tracer ion (*m/z* 60, $C_2H_4O_2^+$), and HOAs in Dongguan have a higher-than-expected contribution of *m/z* 44 (CO_2^+) with a high O/C

ratio (0.26). In addition, CCOA seems to be mixed with BBOA. We then further verified the solutions with additional factors. The results show that BBOA and CCOA are separated from each other in the 7- and 8-factor solutions for Qingdao (see Figure S1) and that better signals for unmixed and stable HOA with low O/C ratios of 0.17 or 0.18 emerged in the 7- to 10-factor solutions for Dongguan (see Figure S2).

2. Investigate anchor profiles for ME-2.

Before operating ME-2, feasible and reasonable prior input profiles must be determined. To the best of our knowledge, this is the first HR-OA data set that employs anchor profiles extracted from an unconstrained PMF solution with a higher number of factors, and the same approach has been successfully applied to source apportionment efforts using UMR ME-2 (Fröhlich et al., 2015). In our case for Qingdao, the BBOA anchor profile should be investigated, and we attempted to look for it from the unconstrained PMF results based on the same dataset, and found that the BBOA factors in the 7- and 8-factor solutions might be used as the anchor profiles. They both had good correlation with the BBOA MS in Chinese biomass burning emission simulation (He et al., 2010), confirming their basic BBOA characteristics. Although these two BBOA factors are quite similar, the BBOA from the 8-factor solution is better suited to be a constraining profile due to its smaller *m/z* 44 (CO_2^+) signal and higher *m/z* 60 ($C_2H_4O_2^+$) signal (see Figure S3). In addition, the BBOA from the 8-factor solution also correlates better with the BBOA from a Chinese biomass burning simulation (R^2=0.81) than the 7-factor solution (R^2=0.79). For Dongguan, the anchor profile for HOA can be obtained from unconstrained PMF solutions. The averaged HOA profile from the 7- to 10-factor solutions was used as the anchor profile for ME-2 due to the small differences among the different solutions. Additionally, the constraining CCOA profile for Dongguan is still under consideration because the mass spectrum of BBOA was found to be very similar to that of CCOA, raising the concern that coal combustion particles might have been incorrectly apportioned to biomass burning sources (Wang et al., 2013). An appropriate CCOA anchor profile could not be obtained due to an increase in the unconstrained PMF factor number (see Figure S2). The best approach is to employ the CCOA profile from Qingdao as the constraining profile for Dongguan in ME-2, as these two campaigns were conducted using the same HR-ToF-AMS in the same year. In addition, the CCOA from Qingdao has a very good correlation (R^2=0.97) with CCOA profiles reported at other Chinese urban sites (Elser et al., 2016) (see Figure S4). Tian et al. (2012) also found that the emission compositions of coal combustion in different regions in China are quite similar. The input profiles for BBOA, HOA and CCOA prior to operating ME-2 are shown in Figure 2.

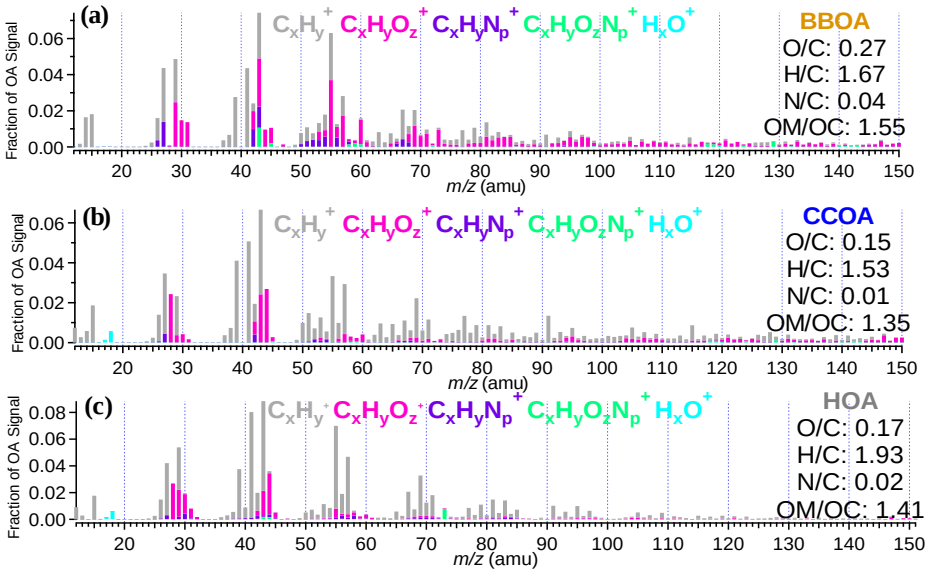

Figure 2. The anchor mass spectra for (a) BBOA, (b) CCOA and (c) HOA in the ME-2 analysis.

3. Constrain the mass spectrums of the mixed factors with different *a* values.

According to the unconstrained PMF results, the best interpretable results for both two sites are the 6-factor solutions with factors that include HOA, COA, BBOA, CCOA, less-oxidized oxygenated OA (LO-OOA) and more-oxidized oxygenated OA (MO-OOA) (Figure 3a and 3b). The *a* values set from 0 to 1 with an increment of 0.1 for BBOA in Qingdao yields 11 possible solutions, and for both HOA and CCOA in Dongguan yields 121 possible solutions.

4. Criteria for obtaining the optimal results.

In this study, we used two simple and reasonable criteria to obtain a better environmental OA source apportionment: the reasonability of the O/C ratio and the correlation between the factors and the tracers. For Qingdao, the O/C ratios for six resolved factors and the correlations between CCOA and PAHs, HOA and BC for 11 solutions with different *a* values are shown in Table S2. These results indicate that all of the O/C ratios for each factor and each factor-tracer correlation are quite similar to one another and that they agree with the range of values in the literature (Canagaratna et al., 2015). Therefore, the solutions averaged over the 11 outputs were considered the final results for Qingdao. For Dongguan, all of the O/C ratios for HOA, CCOA, COA and BBOA among the 121 possible solutions are listed in Table S3. The O/C ratio of HOA in the unconstrained PMF results remained between approximately 0.17 and 0.18, providing a filter criterion with which to assess reasonable ME-2 solutions, and only solutions with *a* values between 0 and 0.1 fell into this range (Table S1). The O/C ratios of other factors for *a* values between 0 and 0.1 are shown in Table S3. The solutions using *a* values between 0 and 0.1 for the HOA profile and an *a* value of 0.9 for the CCOA profile are considered ideal results for three reasons. First, unlike the HOA mass spectra, CCOAs from different sites show higher variability and the CCOA anchor profile is not derived from itself, and therefore, it is reasonable to restrict the constraint with small *a* values for HOA and a looser constraint should be applied for CCOA, which is consistent with the *a* values selecting rules in London ME-2 study (Reyes-Villegas et al., 2016). Second, the

POA factors in Dongguan, including HOA and CCOA, have higher O/C ratios likely as a result of a higher atmospheric oxidizing capacity and a stronger photochemical formation in Southern China (Hofzumahaus et al., 2009). Moreover, some studies reported that BBOAs undergo substantial chemical processing immediately after emission and that aged BBOAs had significant concentrations in fresh plumes (Zhou et al., 2017). Thus, CCOAs in Dongguan are very likely to demonstrate relatively higher ages than those in Qingdao (0.15) with higher O/C ratios (but with an O/C ratio of up to 1.25 when the *a* value is 1, which is unacceptable). Third, with an increase in the *a* value for CCOA, two types of OOAs become more distinctive, and the factor correlates better with the tracer (Table S1 and Table S4).

In order to prove the improvement of using the anchor profiles generated by the unconstrained PMF run with the same local datasets, we also run the ME-2 analysis using the anchor profiles available in the literature, with the results shown in Table S5 and S6. For Qingdao, the correlations between POAs and their tracers and the Q/Qexp values using the three BBOA profiles in the literature are poorer than using the BBOA obtained in this study (Table S5). For Dongguan, the results from ME-2 using the HOA profiles in the literature are also poorer than using the HOA profiles obtained in this study (Table S6). Therefore, it can be clearly seen that the method to obtain an anchor profile in this study is easier (it does not depend on the results in the literature) and more valid.

4 Results and discussion

4.1 Variations in the OA factors

Figure 1 shows the chemical compounds of PM_1, including the non-refractory (NR) components measured via HR-AMS (i.e., OA, SO_4, NO_3, NH_4 and Cl) and BC concentrations measured via the AE-31, during the sampling period in both Qingdao and Dongguan. The average PM_1 mass concentration was 32.1±21.2 $\mu g/m^3$ (mean ± standard deviation) in Qingdao and 57.4±31.1 $\mu g/m^3$ in Dongguan. The temporal variations in the PM_1 species in conjunction with meteorological parameters are shown in Figure S5. Although Dongguan is located in southern China with relatively less air pollution (Huang et al., 2012), the PM_1 mass concentration was higher. This is mainly because of stagnant meteorological conditions with low average wind speeds (i.e., 2.3 m/s) and a maximum wind speed of less than 6 m/s. Among the PM_1 compounds, OAs accounted for 32.5% of PM_1 in Qingdao and 40.6% in Dongguan. This suggests that OA constitutes a very important fraction at both urban sites. Thus, the final and detailed results of the OA source apportionment are presented in this section.

For Qingdao, the final result is the average of all of the ME-2 runs with constraints including *a* values from 0 to 1 fulfilling the criteria described in section 3.2. The mass spectra and time series of the resolved OA sources are shown in Figure 3a. The characteristics of each factor were distinct. The BBOA profile contained the highest *m/z* 60 fraction *f*60 (1.5%) compared to the other factors, and the concentrations were highly correlated with $C_2H_4O_2^+$ (R^2=0.81). The mass spectra of COA was characterized by a high *m/z* 55/57 ratio, which is consistent with previous results (He et al., 2010; Mohr et al., 2012; Sun et al.,

2016). In addition, the time series of COA showed a good correlation with its tracer ion $C_6H_{10}O^+$ in accordance with (Sun et al., 2016). HOAs were correlated well with BC (R^2=0.65), and CCOAs were highly correlated with PAHs (R^2=0.94). Among the two types of OOAs, the less-oxidized OOA (LO-OOA) had a lower CO_2^+ fraction and O/C ratio (0.62) compared with the more oxidized OOA (MO-OOA), which had a higher CO_2^+ fraction and O/C (0.91) ratio. The sum of LO-OOA and MO-OOA showed a high correlation with the sum of sulfate and nitrate (R^2=0.76). The POAs (including HOA, COA, BBOA and CCOA) contributed 53.4% to the OA concentration (Figure 3a), which was almost equal to the SOA fraction. In terms of the diurnal trends of the OA factors shown in Figure 3a, they are all partially driven both by PBL dynamics (demonstrating an increased dilution during the daytime and an accumulation of particulate matter overnight) and by the diurnal emission profile. The diurnal trend of HOA showed pronounced peaks during the morning and evening rush hours (8:00-9:00 and 19:00-21:00), which is typically the case for traffic-related pollutants. COA shows a very distinct daily trend with strong peaks during the lunch (approximately 12:00) and dinner (19:00-20:00) periods. CCOAs constituted an important and dominant source of pollutants during the wintertime in northern Chinese areas (Elser et al., 2016) due to heating activities, especially with regard to the central-heating supply that began on November 13 and continued until the end of the campaign. The diurnal variations of the four POA factors before and during the central-heating period are shown in Figure S6. In comparison with the other three POAs, the diurnal pattern of CCOA showed a clear increase during the central-heating period with concentration peaks during the morning (at approximately 9:00) and at night (starting to rise at 18:00), which seems consistent with heating emissions and atmospheric dilution. The diurnal trends of BBOA were similar to those of CCOA. The dilution of these particles within a deeper PBL during the daytime resulted in a decreasing trend in the BBOA concentration, while peaks related to residential heating were observed during the morning (between 09:00 to 10:00) and at night (starting to rise at 17:00). The main difference between the LO-OOA and MO-OOA diurnal patterns is that an increase in the MO-OOA mass concentration was observed during the daytime, implying that the formation of secondary organic aerosols was greatly enhanced during the afternoon. In addition, the diurnal cycle for LO-OOA showed a relatively smaller decrease during the daytime compared with the POA factors. These characteristics of the OOA diurnal trend confirm their secondary nature.

For Dongguan, similar to the OA source apportionment using ME-2 in Qingdao, the final result is the average of two accepted a-value solutions with six identified factors, including HOA, CCOA, COA, Aged-BBOA, LO-OOA and MO-OOA. Although the range of the O/C ratio of BBOA reported in Canagaratna et al. (2015) was from 0.25 to 0.55, fresh BBOA was found to be rapidly converted to OOA in less than 1 day (Bougiatioti et al., 2014), and the O/C ratio of aged BBOA could be up to 0.85 (Zheng et al., 2017). BBOA in Dongguan was apparently not fresh considering it is an urban site and Dongguan has a warmer winter (17 ºC in Dongguan vs. 9 ºC in Qingdao). The BBOA factor identified in Dongguan, with a strong contribution of m/z 60, had a higher O/C, indicating it was an oxygenated BBOA, therefore we name it Aged-BBOA in this study. All of the information regarding the final source results is shown in Figure 3b. Good correlations between each OA factor and their tracers indicate that the resolved ME-2 results are reasonable. A few sharp drops (which always occurred at approximately 20:00) were observed in the MO-OOA time series ranging from December 29 to January 5, which coincides with extreme organic aerosol pollution (Figure S5). The inherent mechanisms for these drops remain unexplained, although we have tried a

number of reasonable approaches (e.g., splitting the period into sub-periods to identify the sources, constraining more factors before running ME-2, and examining more factors) to address this issue. A similar problem in the MO-OOA time series was also found in a recent ME-2 application (Qin et al., 2017). In our case, we presume this might be the result of relatively worse meteorological conditions at night during the sampling period, thereby increasing the contribution of late supper emissions and leading to the overestimation of COAs offset by drops in the MO-OOA concentration. Also note that the O/C ratios of the POAs in Dongguan were higher than those in Qingdao, suggesting that POA emissions in Dongguan underwent faster chemical processing. In addition, the relatively smaller contributions of POAs further support this inference. Freshly emitted POAs may get mixed with aged OAs more easily, while ME-2 may still consider them unmixed. MO-OOAs accounted for an average of 42.8% of the total OA mass (which is much greater than the contribution of LO-OOAs), which is probably because some POA species could have been rapidly converted to very aged OOAs (Bougiatioti et al., 2014; Xu et al., 2015). As mentioned above, the characteristics of the diurnal trends of the POA factors in Dongguan were similar to those in Qingdao, and thus, we focused on the OOA factors. MO-OOAs still showed higher concentrations during the daytime but, unlike LO-OOAs in Qingdao, the diurnal patterns of LO-OOAs in Dongguan were flat, implying that secondary OA formation in the LO-OOAs basically offset the influences of PBL variations.

Meteorological conditions (especially wind) play a crucial role in the dilution and transport of air pollution. We used the relationships between the component concentrations and wind to profoundly understand the origins of the OA factors and their nature. The distributions of the OA factor concentrations versus the wind direction and speed are plotted in Figure S7. For both of the urban sites, higher mass concentrations of the POA factors were mostly accompanied by low wind speeds, denoting their local emission characteristics. Additionally, for the OOA factors, a large proportion of their higher concentrations were maintained at higher wind speeds, indicating that the OOAs were formed by transport processes. However, the small fraction of high-level OOAs that was concentrated within the low wind-speed region represents the fast formation of OOAs from some local POA.

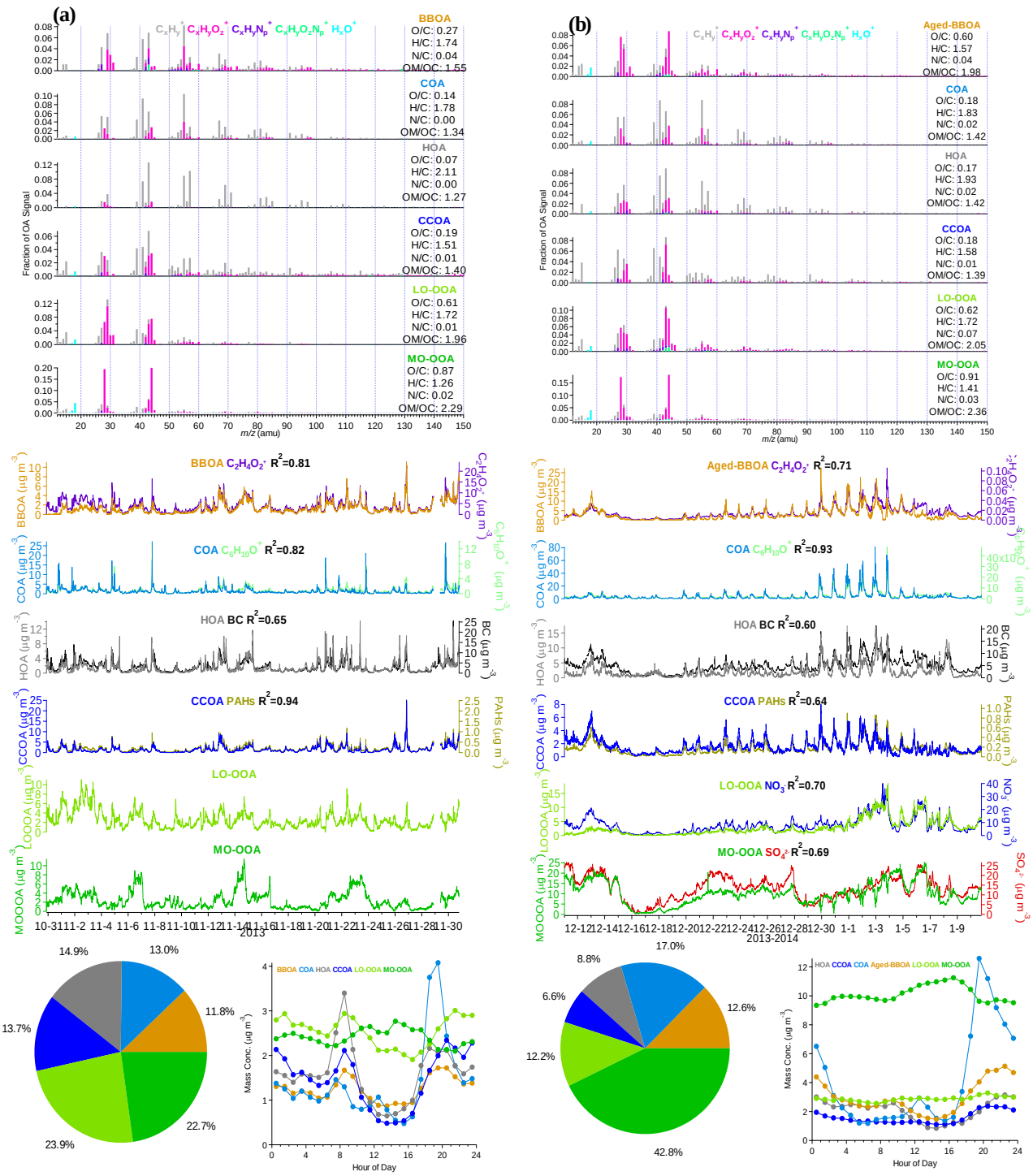

Figure 3. Mass spectra of the OA factors, average fractions of the OA factors, diurnal variations of the OA factors and time series of the OA factors identified by the ME-2 method for (a)Qingdao and (b) Dongguan.

4.2 Regression analysis for POA tracers

BC and PAHs are mainly derived from incomplete combustion processes (Schmidt and Noack, 2000; White, 1985), and thus, they were used as tracers for the POAs. In this study, the BC was directly measured by the AE-31, and the PAHs were quantified using the method developed by Bruns et al. (2015) based on AMS data. Both the BC and PAHs showed pronounced diurnal cycles similar to those of the POAs (see Figure S8). In addition, POAs are properly split into different subtypes via the ME-2 method, thereby providing the possibility to better understand the contributions of different POAs to BC and PAHs and to verify the POA source identification. In this section, we use a multi-linear regression method to analyze the POA factors for BC and PAHs.

Figure 4 shows the average contributions of OA sources to BC and PAHs in Qingdao and Dongguan. At both sites, HOAs were the dominant attribute of BC (51% for Qingdao and 40% for Dongguan) and CCOAs contributed the most to the PAHs (59% for Qingdao and 43% for Dongguan), indicating that BC mainly originates from traffic emissions and that PAHs in the Chinese urban polluted atmosphere are dominated by coal combustion during the wintertime. These findings are consistent with results reported in similar studies (Elser et al., 2016; Huang et al., 2015; Huang et al., 2010; Sun et al., 2016; Xu et al., 2014; Zhang et al., 2008). Moreover, the ratio of PAHs to OAs (1.8%) in Qingdao was similar to that in the northern Chinese urban site of Xi'an (1.9%) (Elser et al., 2016) but was higher than that in Dongguan (0.9%). This is likely because a larger fraction of coal combustion to the total OA concentration would enhance the ratio of PAHs to OAs (Elser et al., 2016). Biomass burning was the second-most important source for both BC and PAHs; it was responsible for 33% and 29% of the BC at Qingdao and Dongguan, respectively, and for 29% and 34% of the PAHs at Qingdao and Dongguan, respectively. Cooking emissions were a minor source of BC and PAHs, accounting for less than 10%. These results are also consistent with the published findings. For example, biomass burning is an important source for BC (Kondo et al., 2011; Reddy et al., 2002) and, in some regions with fewer traffic emissions, BC has the best correlation with BBOAs (Schwarz et al., 2008). In addition, in Beijing and California, PAHs are correlated well with BBOAs but are much more weakly correlated with COAs (Ge et al., 2012; Hu et al., 2016; Sun et al., 2016).

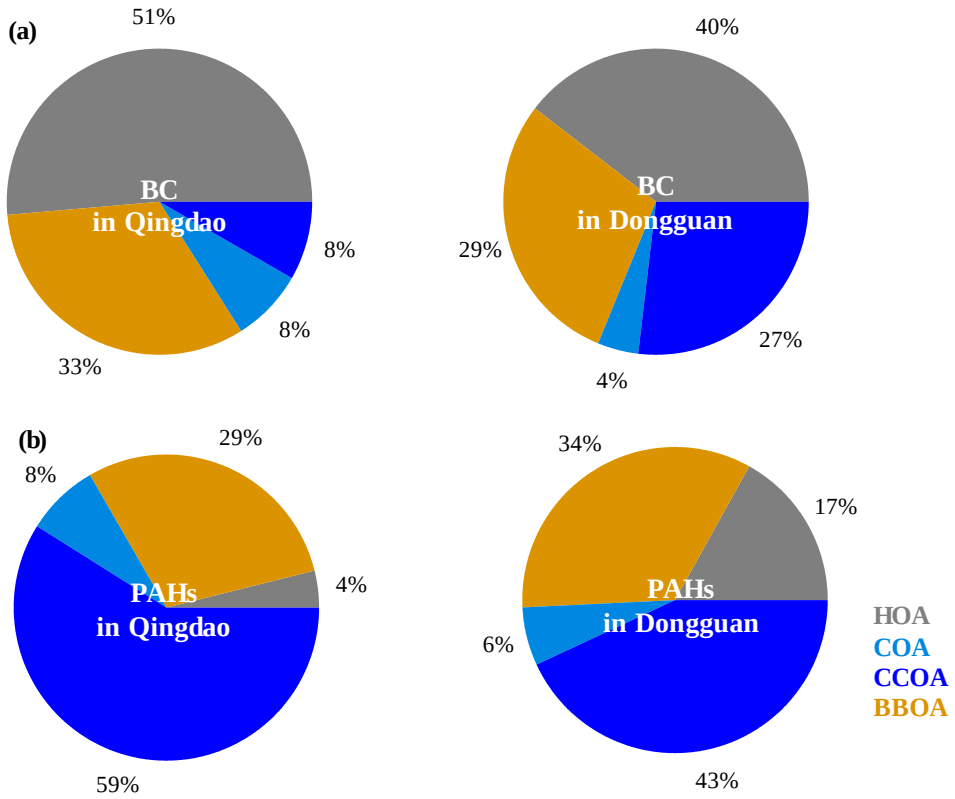

Figure 4. (a) Average contributions of POA factors to BC; (b) average contributions of POA factors to PAHs.

5 Conclusions

In this study, we used PMF to interpret the organic aerosol sources at two Chinese urban sites in winter, and found that PMF did not work properly (i.e., it did not allow for the separation of several primary sources of OAs). Therefore, we adopted the ME-2 approach, which yields more reliable solutions. Technically, there are three important steps when using the ME-2 method to interpret the sources of OAs. The first step is to investigate the mixed and unidentified factors that are constrained according to issues in the unconstrained PMF results. Generally, we constrained one or more POA factors (i.e., HOA, COA, BBOA and CCOA) for the polluted urban sites. The second step is to search for a reasonable anchor profile for each constrained factor. Two approaches were used: searching for anchor profiles via an increase in the number of unconstrained PMF factors from the same data set and using mass profiles derived from other similar studies. The third step is to choose the criteria for obtaining the optimal results. The choice of a reasonable range of O/C ratios may represent a good criterion for HR-OA apportionment since the O/C ratio is a significant and distinctive characteristic for different OA factors. In addition, correlations between the resolved OA factors and their tracers were also suggested.

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