Response to Reviewer 2

Overall comment: This work reported 4-season filter-based WSOC measurements including tracer measurements and group separation of the aqueous extracts into so-called hydrophobic and hydrophilic fractions by the SPE method. The sources of WSOC were speculated based on some correlations with O_3, RH, ALWC etc. The authors also conducted the PMF analysis to evaluate the source contributions. The problem is the quality of data analysis and discussion. Many of the discussions were not logically presented. Loss terms (e.g., photolysis, chemical reactions, gas-particle partitioning) were generally ignored. Conclusions about the relative contributions of photochemical vs aqueous pathways were made mainly on the basis of simple correlations with O_3 or ALWC etc., which can be largely uncertain especially for the winter-haze episodes when all components of $PM_{2.5}$ including primary species were correlated with ALWC or RH. There is also a lack of sufficient information to validate the PMF analysis in this study. The presented PMF results seem quite arbitrary.

Response: We deeply appreciate the reviewer's rigorous consideration and valuable comments, which enabled us to essentially improve the analysis and interpretation of the data. We have fully considered and carefully addressed all the comments raised by the reviewer, and have thoroughly revised the manuscript accordingly. The potential effect of photolysis, chemical reactions and gas-particle partitioning have been discussed in the revised manuscript. The relative contributions of photochemical vs aqueous pathways have been more cautiously discussed in the revised manuscript, and the correlation analysis between the ratio of SOA tracers to OC with RH or ALWC has been added to further support some of our speculations. Moreover, for the PMF analysis, we have provided detailed information on the uncertainty calculation of the input data, the selection criteria for the optimal PMF solution, the diagnostic plots and the error estimation of the PMF results in the revised manuscript. Below the comments are our responses point by point, and the revisions have been indicated in the revised manuscript.

Comment 1: Page 1, Line 14; Page 2, Line 53-57; Page 4, Line 106-112: Different SPE columns and extraction procedures (e.g., pH) result in various fractions of the WSOC (Sullivan et al., 2006). The authors used SPE (Oasis HLB) to separate the "hydrophilic and hydrophobic" fractions of WSOC. However, as described by Kiss et al. (2002), the one-step SPE on Oasis HLB column is to separate the WSOC into moderately hydrophilic (retained on the column) and strongly hydrophilic (passed through the column) fractions. I think it is wrong to simply assign the retained fraction herein as "hydrophobic" or "mainly HULIS" and the passed-through fraction as typical "hydrophilic (short-chain dicarboxylic acids and saccharides)".

Response: We deeply appreciate the reviewer's valuable comment. We used the same SPE column and separating procedure as described by Kiss et al. (2002) to separate different portions of WSOC in this study. As suggested by the reviewer, we have changed the term "hydrophobic WSOC" to "moderately hydrophilic WSOC", and "hydrophilic WSOC" to "strongly hydrophilic WSOC" throughout the revised manuscript.

To correctly identify different portions of WSOC, we have also reviewed the literature for support. As concluded by Kiss et al. (2002), the moderately hydrophilic WSOC (retained on the Oasis HLB column) is composed of humic-like substances (HULIS). This method is commonly used for the determination of atmospheric HULIS (Lin et al., 2010; Lin and Yu, 2011; Fan et al., 2016; Ma et al., 2018; Sengupta et al., 2018). Lin et al. (2010) suggested that several anhydrosugars (levoglucosan, xylose, sucrose) and short-chain organic acids (oxalic acid, succinic acid, malic acid) were present in the passed-through fraction. Therefore, we thought that it should be proper to assign the retained WSOC fraction as "mainly HULIS", and the passed-through portion as "strongly hydrophilic WSOC (short-chain dicarboxylic acids and saccharides)".

In Line 54-57, the references we cited (Verma et al., 2012, 2015; Yu et al., 2018) all used C-18 silica gel SPE columns to separate different WSOC fractions. Varga et al. (2001) compared the performance of C-18 silica gel columns and Oasis HLB columns, and suggested that Oasis HLB columns retained the same fraction of organic matter as silica-based columns. Hence, the statement that "previous studies have revealed that the moderately and strongly hydrophilic fractions of WSOC show significantly different intrinsic oxidative potential, thus would pose different effects on human health" should be proper here.

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Comment 2: Introduction: Previous understanding of the characteristics of WSOC and its separated fractions as well as their primary and secondary sources were poorly summarized in the current Introduction section.

Response: We deeply appreciate the reviewer's valuable comment. The composition and sources of WSOC and its separated fractions have been summarized and added in the Introduction section of the revised manuscript. The corresponding revision is as follows.

Based on the solid phase extraction (SPE) by the Oasis HLB column, WSOC can be divided into the moderately hydrophilic fraction and strongly hydrophilic fraction (Varga et al., 2001; Kiss et al., 2002). The moderately hydrophilic fraction of WSOC mainly consists of humic-like substances (HULIS), which are an unresolved mixture of polycyclic ring structures with substituted hydroxyl, carboxyl, carbonyl, methoxy, and ester groups (Kiss et al., 2002; Lin et al., 2010; Fan et al., 2012). In addition, some smaller molecular with well-defined structures, such as phthalic acid and suberic acid, may also constitute a minor portion of the moderately hydrophilic fraction (Lin et al., 2010). The strongly hydrophilic fraction mainly includes low-molecular-weight organic acids (such as oxalic acid, succinic acid, malic acid) and anhydrosugars (such as levoglucosan, xylose, sucrose) (Lin et al., 2010). Previous studies have revealed that the moderately and strongly hydrophilic fractions of WSOC show significantly different intrinsic oxidative potential, thus would pose different effects on human health (Verma et al., 2012, 2015; Yu et al., 2018). However, source contributions of the moderately and strongly hydrophilic WSOC were scarcely investigated and compared in previous research.

Previous studies have suggested that coal combustion (Zhang et al., 2018; Li et al., 2019c), traffic emissions (Kawamura and Kaplan, 1987; Li et al., 2019c), residual oil combustion (Kuang et al., 2015), cooking (Qiu et al., 2020), soil dust and sea salts (Huang et al., 2006) can all contribute to WSOC. Nevertheless, it is most commonly recognized that WSOC mainly derives from the direct emissions of biomass burning and secondary organic aerosols (SOA) (Ding et al., 2008; Feng et al., 2013; Du et al., 2014; Zhang et al., 2018). For example, Du et al. (2014) suggested that SOA, biomass burning and other primary combustion sources contributed about 54 %, 40 % and 6 % respectively to WSOC in Beijing during 2010-2011. Zhang et al. (2018) also indicated that the sum of biomass burning and SOA contributed more than 80 % to WSOC in Beijing, Shanghai, Guangzhou and Xi'an in the wintertime of 2013. In recent years, the adjustment of energy and industrial structures as well as the effective control of the open burning activities in the surrounding areas of Beijing have posed significant impact on the source emissions. The average $PM_{2.5}$ concentration in Beijing has been greatly reduced from 89.5 $\mu g \cdot m^{-3}$ in 2013 to 58.0 $\mu g \cdot m^{-3}$ in 2017 since the implement of the Action Plan of Air Pollution Prevention and Control in 2013 (Cheng et al., 2019). Meanwhile, it has been reported that the oxidant concentrations were enhanced accompanying the decrease of $PM_{2.5}$ level, which might promote the SOA formation (Feng et al., 2019). Consequently, the sources and composition of WSOC in Beijing may show significant changes due to the control policies and enhanced atmospheric oxidizing capacity in the surrounding areas in recent years. Therefore, it is necessary to compare the source contributions of WSOC with those in the previous studies.

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Comment 3: Page 4, Line 97 and Page 5, Line 124-125: How were the field blanks collected before and after sampling? What exactly were corrected?

Response: Thanks for the reviewer’s careful concern. We have clarified the corresponding statement as follows.

The field blanks were collected before and after each sampling period, and a total of 8 field blank samples were obtained. The blank filters were put on the filter holder of the $PM_{2.5}$ sampler without pumping for 1 min, then stored and analyzed together with the ambient samples. Since two field blanks were obtained during each sampling period, the average concentrations of the targeted compounds on these two field blanks were used to correct the measured concentrations of the ambient samples in the corresponding season. Therefore, the reported concentrations of the targeted species were the measured concentrations on each ambient sample minus the average concentration on the two field blank samples.

Comment 4: Page 5, Line 129-131: Detailed information about the PMF analysis should be provided. The authors said that "the uncertainties were calculated referring to the measured RSD data of chemical analysis and previous studies". It is unclear to me whether this is a right approach. What do "the measured RSD data of chemical analysis and previous studies" mean specifically? Also, the authors said "The PMF model was run repeatedly to obtain a clear and reasonable source profile". How? The reasons of the selection of the numbers of PMF factors as well as the PMF uncertainty estimates and diagnostics are necessary.

Response: We deeply appreciate the reviewer's thoughtful comment. We have provided detailed information on the uncertainty calculation of input data, the selection criteria for the optimal solution and diagnostic plots. Besides, we have conducted the error estimates for the selected PMF solution, and found some uncertainties involved in this solution. To improve the reliability of the selected solution, we have added some constraints on the source profiles based on the priori information of the sources. Details of the PMF analysis are as follow.

1. Uncertainties of the input data

According to the User Guide of PMF5.0 (Norris et al., 2014), the uncertainties of the target species can be calculated as follow:

$$Unc = 5/6 \times MDL \ (c \leq MDL) \qquad (1)$$

$$Unc = \sqrt{(P \times c)^2 + (0.5 \times MDL)^2} \ (c > MDL) \qquad (2)$$

where *Unc* is the data uncertainty, c is the concentration of target species, MDL is the method detection limit, and P is the error fraction. Since the User Guide did not give the calculation method for the error fraction (P), we estimated the P values referring to the measured relative standard deviations (RSD) of the target species. The RSD values were calculated by measuring six identical portions of an ambient sample. P was set as 10 % when RSD < 10 %, and 15 % or 20 % when RSD > 10 %.

2. Selection of base solutions

The chemical components input into the PMF model were selected based on our understanding of the possible WSOC sources (Norris et al., 2014). Interpretability was usually considered to be the most important factor for selecting the optimum solution (Shrivastava et al., 2007; Huang et al., 2014). Interpretable solutions are those which group tracers from different sources into distinct factors, while those solutions grouping tracers from multiple sources into one factor, distributing tracers for one source across multiple factors, or including factors with no distinct grouping of species are judged less interpretable (Shrivastava et al., 2007; Sowlat et al., 2016). In some literature, the optimal solution was defined as that with the maximum number of factors which had distinctive groupings of species, and explained at least 90 % of the total variable (Shrivastava et al., 2007).

In this study, PMF was run repeatedly by changing the number of factors and the start seed numbers. The base solution was selected based on: (1) the interpretability of the derived factor profiles and the temporal variations of source contributions; (2) the reconstruction of the total variable and R^2 of input organic tracers (R^2>0.90); (3) the scaled residuals of the input species. As presented in Figure S1, the 7-factor solution separated cholesterol (the tracer for cooking) into multiple sources. It was difficult to explain why cholesterol appeared in the factor profiles of biomass burning, dust and fresh biogenic SOC. Besides, this solution led to poor fits for cholesterol ($R^2 = 0.28$) and *cis*-pinonic acid ($R^2 = 0.32$), which were the key tracers selected in this study. Therefore, the 7-factor solution was not selected. As shown in Figure S2, the 8-factor solution also distributed cholesterol into multiple factors. This solution also resulted in a poor fit ($R^2 = 0.28$) for cholesterol. Therefore, the 8-factor solution was not chosen in this study. As shown in Figures S5-7, the solutions with 4 to 6 factors all showed poor interpretability for the derived factor profiles and poor fits for the key organic tracers. The 10-factor solution involved a factor without any tracer of high loading to indicate a specific source, thus could not be explained. By comparing the results with different factor numbers, the solution with 9 factors (Figure S3) was thought to be the most interpretable one.

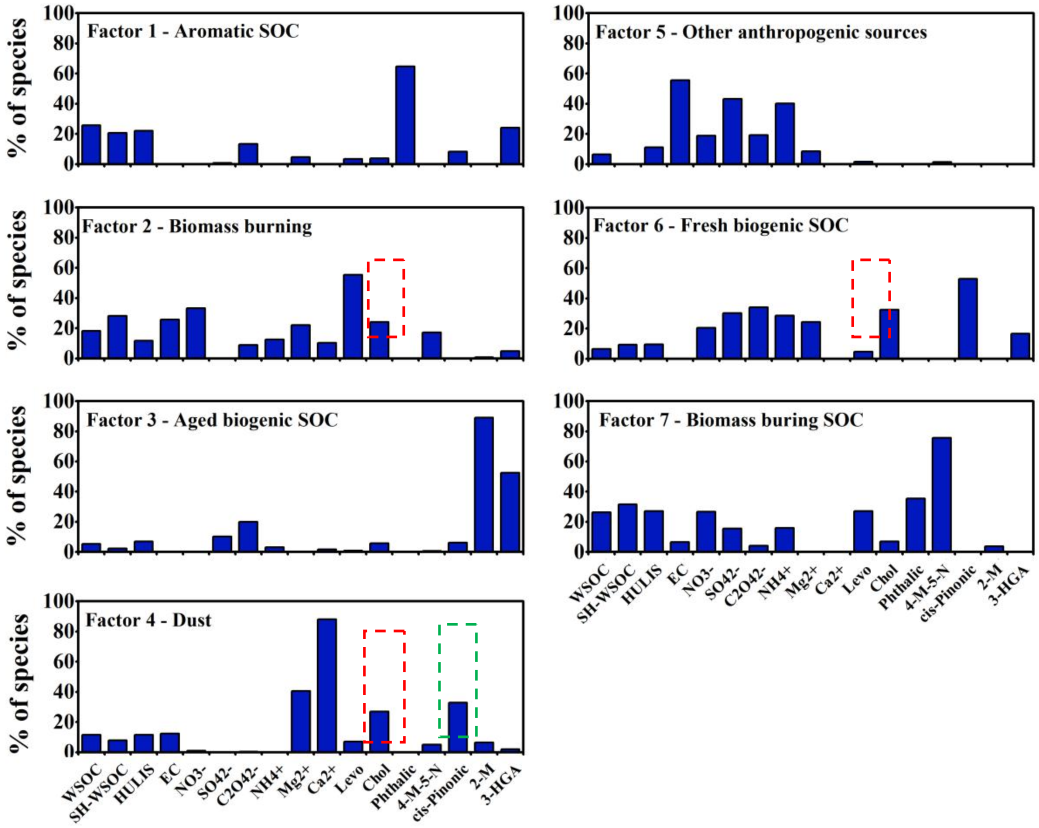

Figure S1. A 7-factor solution resolved by the PMF model.

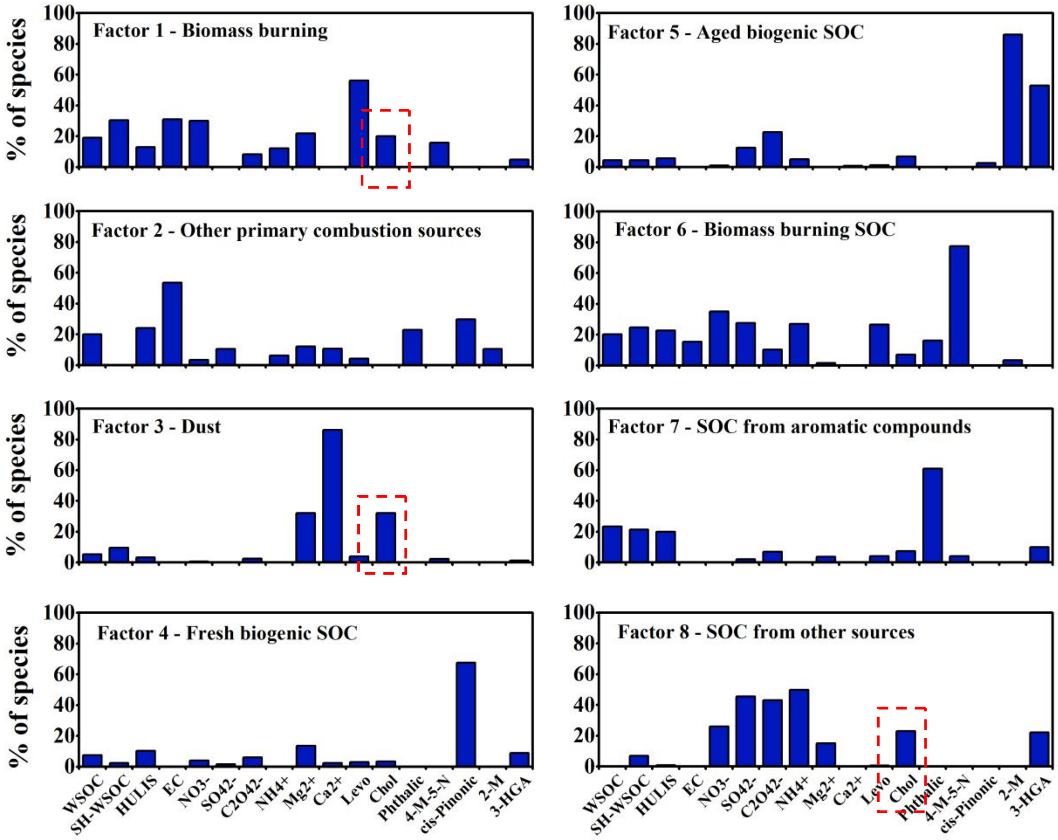

Figure S2. An 8-factor solution resolved by the PMF model.

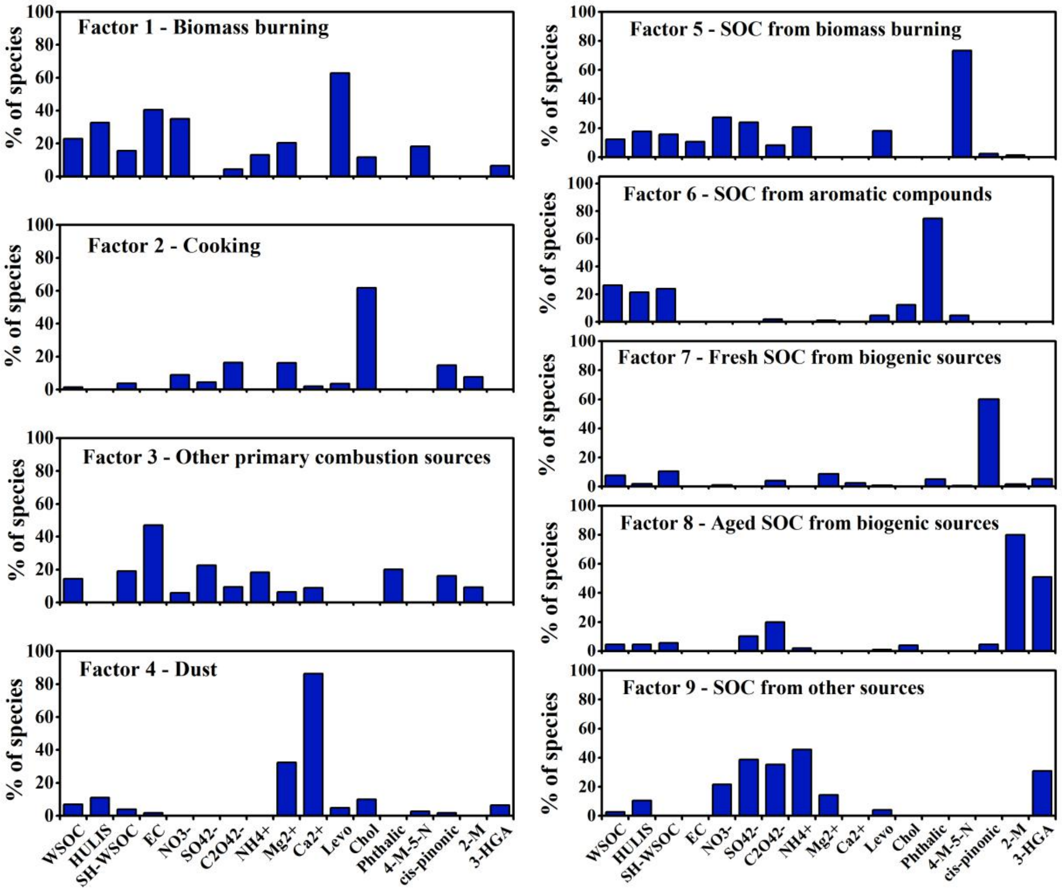

Figure S3. A 9-factor solution resolved by the PMF model.

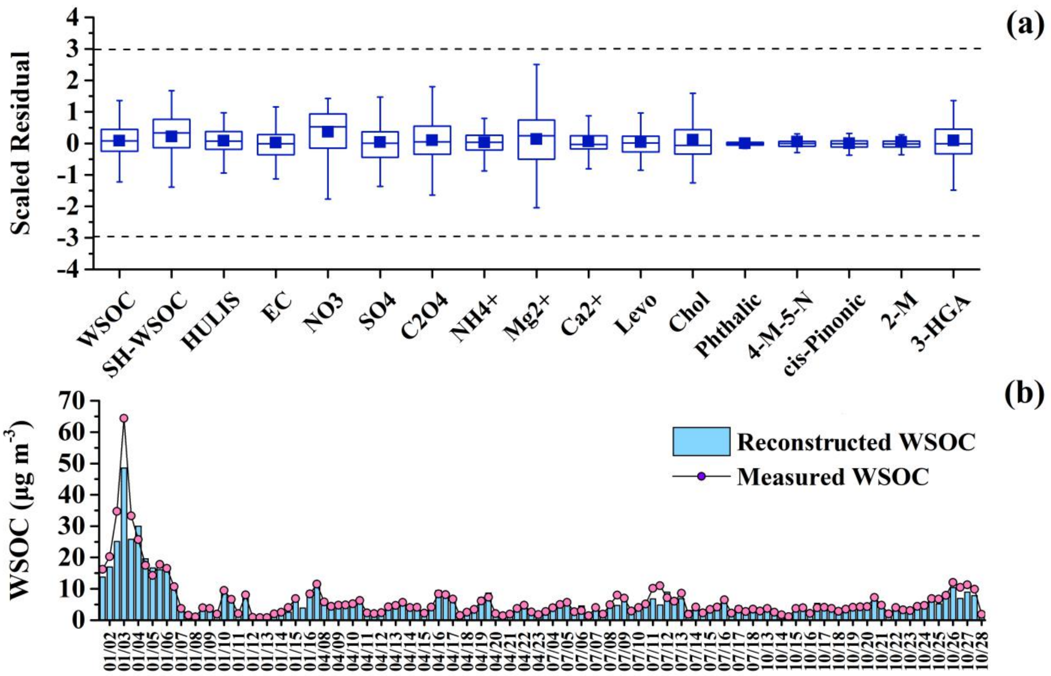

Figure S4. (a) The box plots showing the distributions of the scaled residuals for each species; (b) The time series of the measured WSOC and the reconstructed WSOC based on the 9-factor solution.

3. Diagnostics for the base model run

The selected 9-factor solution was converged, and Q(Robust) was similar to Q(True). As shown in Figure S4, most of the input species showed normally distributed residuals between -2.0 and +2.0, indicating that these species were well modeled. The R^2 of WSOC and HULIS were 0.94 and 0.93, respectively, and the R^2 for all the organic tracers were higher than 0.96, again suggesting that these species were well modeled.

4. Error estimation

The selected base solution was subjected to displacement (DISP) and bootstrap (BS) tests for error estimation. For the DISP test, the percent change in Q (%dQ) was less than 0.1 %, indicating that this solution was the global minimum (Paatero et al., 2014). No factor swapped for any value of dQ^{max}, indicating little rotational ambiguity in this solution (Paatero et al., 2014). For the BS test, the factor of “cooking” was mapped 79 % of the runs, the factor of “other primary combustion sources” was mapped 69 % of the runs, while other factors were mapped more than 91 % of the runs. The BS results indicated some uncertainties for the factors of cooking and other primary combustion sources, while the other factors were relatively stable.

Brown et al. (2015) indicated that the unstable solution might be due to too many factors involved. To investigate the effect of factor number on the stability of solutions, the BS results for solutions with different factor numbers were compared and shown in Table S3. As shown in Table S3, reducing the number of factors did not significantly increase the successful rates of BS mapping, but decreased the interpretability of the derived factor profiles. As recommended by the previous studies (Norris et al., 2014; Paatero et al., 2014), some constraints can be defined based on the priori information of the sources to reduce the variability of the solution.

Table S3 The successful rates of BS mapping for the solutions with different numbers of factors. The values no more than 85 % were shown in bold.

BS mapping	3-factor solution	4-factor solution	5-factor solution	6-factor solution	7-factor solution	8-factor solution	9-factor solution
Factor 1	93 %	93 %	95 %	95 %	**82 %**	99 %	99 %
Factor 2	**83 %**	**85 %**	99 %	98 %	88 %	95 %	**79 %**
Factor 3	100 %	95 %	**78 %**	99 %	**74 %**	100 %	100 %
Factor 4		87 %	**74 %**	**75 %**	**79 %**	98 %	**69 %**
Factor 5			94 %	91 %	92 %	92 %	96 %
Factor 6				**81 %**	99 %	**67 %**	96 %
Factor 7					98 %	100 %	100 %
Factor 8						98 %	91 %
Factor 9							99 %

5. Constrained model run

Bozzetti et al. (2017) exploited the markers' source specificity to set constraints for the profiles, so as to solve the problem of large mixtures of PMF factors associated with contributions of markers from different sources. They treated the contribution of unrelated source-specific markers as zero for each source, while non-source-specific variables were freely apportioned by the PMF algorithm. In addition, they set constraints for primary markers and combustion-related markers that can be seen as negligible in the secondary factors.

In the constrained model run, we set the constraints similar to those of Bozzetti et al. (2017), with a slight difference that we set the constraints by "soft pulling" so as to obtain a stable solution with a minimal change in the Q-value (dQ). The constraints were set as: (1) Levoglucosan was pulled up maximally with a limit of 0.25 % dQ for the factor of "primary biomass burning"; (2) Cholesterol was pulled up maximally with a limit of 0.50 % dQ for the factor of "cooking"; (3) Sulfate, *cis*-pinonic acid and 2-methylerythritol were pulled down maximally with limits of 0.25 % dQ for the factor of "other primary combustion sources"; (4) Phthalic acid was pulled up maximally with a limit of 0.25 % dQ for the factor profile of aromatic SOA. The dQ(Robust) for all the constraints were 0.93 % in the final constrained model run, which was acceptable (below 1 %) as recommended by the PMF user guide (Norris et al., 2014). As shown in Table S4, all the factors were mapped more than 94 % of the runs, suggesting that this solution was stable. Thus the constrained 9-factor solution was chosen as the final solution.

Table S4 The successful rates of BS mapping for the constrained 9-factor solution.

BS Mapping:	Base Factor 1	Base Factor 2	Base Factor 3	Base Factor 4	Base Factor 5	Base Factor 6	Base Factor 7	Base Factor 8	Base Factor 9	Unmapped
Boot Factor 1	97 %	0	0	0	3 %	0	0	0	0	0
Boot Factor 2	1 %	95 %	0	0	0	0	0	1 %	3 %	0
Boot Factor 3	0	0	100 %	0	0	0	0	0	0	0
Boot Factor 4	4 %	0	0	94 %	0	1 %	0	1 %	0	0
Boot Factor 5	3 %	0	0	0	97 %	0	0	0	0	0
Boot Factor 6	0	0	0	1 %	0	99 %	0	0	0	0
Boot Factor 7	0	0	0	0	0	0	100 %	0	0	0
Boot Factor 8	0	0	0	0	0	1 %	0	97 %	2 %	0
Boot Factor 9	0	0	0	0	0	0	0	0	100 %	0

6. Factor identification

The source profiles of the final solution are shown in Figure 4. Factor 1 showed high levels of levoglucosan and EC, thus was interpreted as the direct emissions from biomass burning. Factor 2 exhibited a high level of cholesterol, thus was regarded as cooking. Factor 3 exhibited a large fraction of EC that could not be explained by the direct emissions from biomass burning, suggesting that it was primary emissions from other combustion sources, such as coal combustion, traffic emissions and waste burning. Factor 4 was featured by high loadings of Mg^{2+} and Ca^{2+}, thus was considered as dust. No significant EC but high fractions of 4-methyl-5-nitrocatechol and phthalic acid were observed in Factor 5 and Factor 6, respectively, which were recognized as SOC from biomass burning (biomass burning SOC) and aromatic precursors (aromatic SOC), respectively. Factor 7 exhibited a high level of *cis*-pinonic acid, thus was explained as the freshly generated biogenic SOC. Factor 8 was characterized by high fractions of 2-methylerythritol and 3-hydroxyglutaric acid, which are the end products from isoprene and monoterpenes respectively, thus was identified as the aged biogenic SOC. Note that 3-hydroxyglutaric acid and *cis*-pinonic acid were not grouped into one factor though they are both SOA tracers of monoterpenes, owing to their different oxidation degree as discussed above. Factor 9 covered the secondary components (such as SO_4^{2-}, NO_3^-, NH_4^+ and $C_2O_4^{2-}$) that can not be well explained by the identified sources above, thus was considered to be SOC from other sources. More detailed discussion is provided below the next comment (Comment 14).

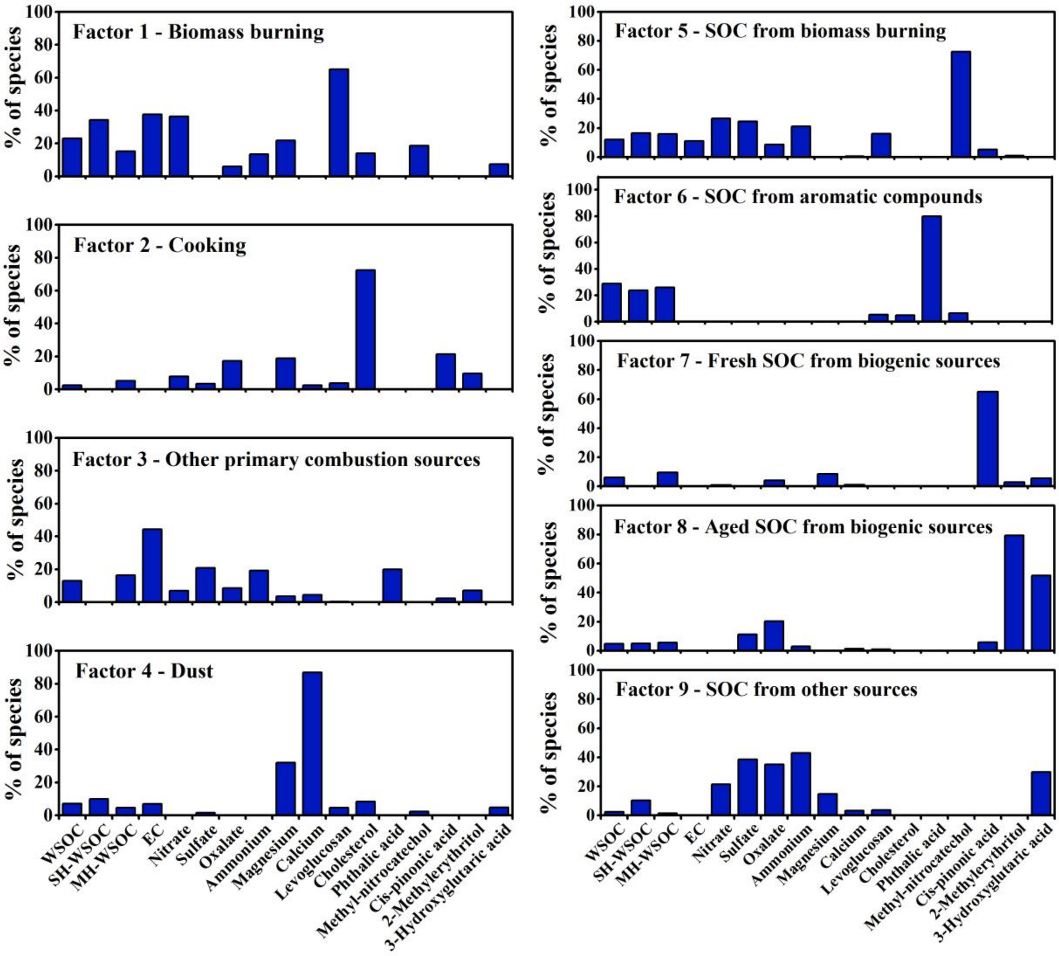

Figure 4. The constrained 9-factor solution resolved by the PMF model.

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Comment 14: Page 11, Line 314-327: The interpretation of the PMF factors is over simple here. It looks like the authors intentionally choose a PMF solution that has separate factors for individual tracers. However, how do the tracers correlate each other? (1) Previous studies found that methyl-nitrocatechol correlates with AMS BBOA and levoglucosan (Linuma et al. 2010; Mohr et al. 2013). If the two temporally correlates, the split of the biomass burning factor into two (primary and secondary) may be highly uncertain given the small sample size of this study. (2) Factor 7, 8, and 9 are all associated with biogenic SOA tracers. It was said in Page 10, Line 297-298 that 3-hydroxyglutaric acid correlated strongly with 2-methylerythritol. Then how and why to separate Factor 8 and 9. Is 3-hydroxyglutaric acid a unique tracer for monoterpene SOA? For day and night samples which did not maintain much oxidation process information (meaning first-generation vs multi-generation), I am surprised that there were two monoterpene SOA factors (one is marked by cis-pinonic acid and the other is marked by 3-hydroxyglutaric acid). (3) For Factor 3, the profile has significant contributions of secondary species, is it really primary?

Response: We deeply appreciate the reviewer’s valuable comment. We understood the reviewer’s concerns and would like to respond to the above concerns point by point.

1. The separation of primary biomass burning and secondary biomass burning SOA.

Indeed, levoglucosan correlated strongly with 4-methyl-5-nitrocatechol ($r=0.87$, $p<0.01$) in this study. However, even if we reduced the factor number from nine to five, levoglucosan and 4-methyl-5-nitrocatechol could not be merged into one source (Figure S1, 2, 5, 6). As presented in Figure S2, for the 8-factor solution, levoglucosan had a high loading in Factor 1, and 4-methyl-5-nitrocatechol showed a high loading in Factor 6. This solution distributed cholesterol into multiple sources and led to a poor fit for cholesterol ($R^2=0.28$), and the factor profile was less interpretable compared to the 9-factor solution. As shown in Figure S1, for the 7-factor solution, levoglucosan exhibited a high loading in Factor 2, and 4-methyl-5-nitrocatechol showed a high fraction in Factor 7. Cholesterol was again separated into distinct sources, leading to poor fits for both cholesterol ($R^2 = 0.28$) and *cis*-pinonic acid ($R^2 = 0.32$). As presented in Figure S5, for the 6-factor solution, levoglucosan had a high loading in Factor 4, and 4-methyl-5-nitrocatechol had a high fraction in Factor 6. Cholesterol, *cis*-pinonic acid and phthalic acid were divided into different sources, resulting in poor fits for cholesterol ($R^2 = 0.26$) and *cis*-pinonic acid ($R^2 = 0.25$). For the 5-factor solution (Figure S6), levoglucosan showed a high loading in Factor 3, and 4-methyl-5-nitrocatechol had a high fraction in Factor 5. Compared to the 6-factor solution, biomass burning SOC and aromatic SOC were merged into one factor, which was interpreted as the anthropogenic SOC. When the factor number decreased to four, levoglucosan and 4-methyl-5-nitrocatechol were merged into the same factor (Figure S8). However, this solution was less interpretable, and resulted in poorer fits for most of the species (cholesterol: $R^2=0.17$; *cis*-pinonic acid: $R^2=0.25$; Ca^{2+}: $R^2=0.67$; Mg^{2+}: $R^2=0.73$; NO_3^-: $R^2=0.75$; etc). Furthermore, the slope of the fitting equation for observed and predicted 4-methyl-5-nitrocatechol was only 0.31. And the high value of 4-methyl-5-nitrocatechol in winter was not reproduced by the 4-factor solution. Hence, the 4-factor solution was also excluded in this study.

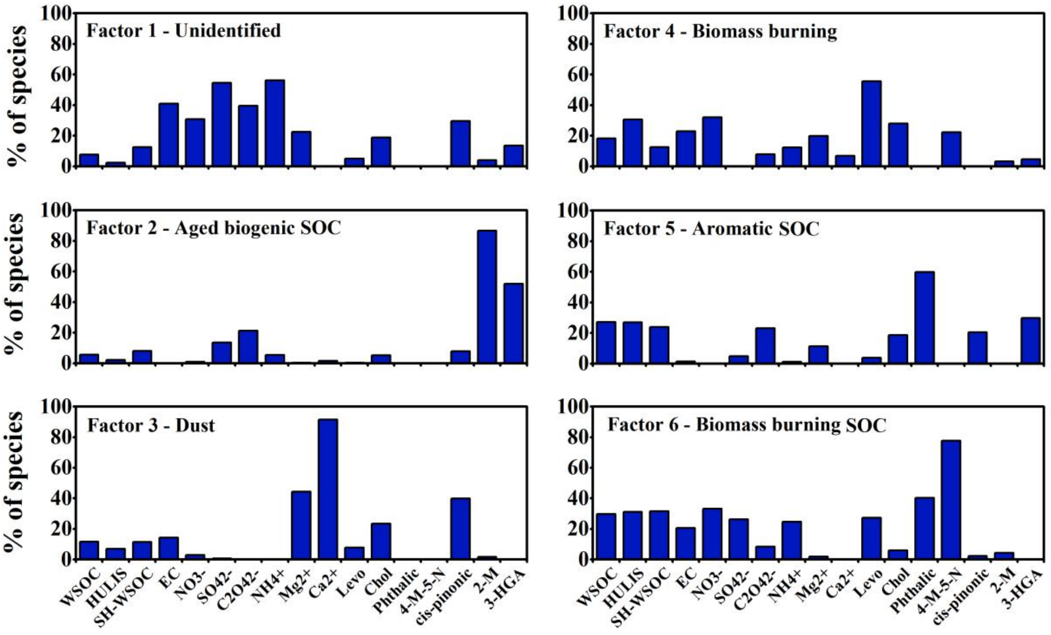

Figure S5. A 6-factor solution resolved by the PMF model.

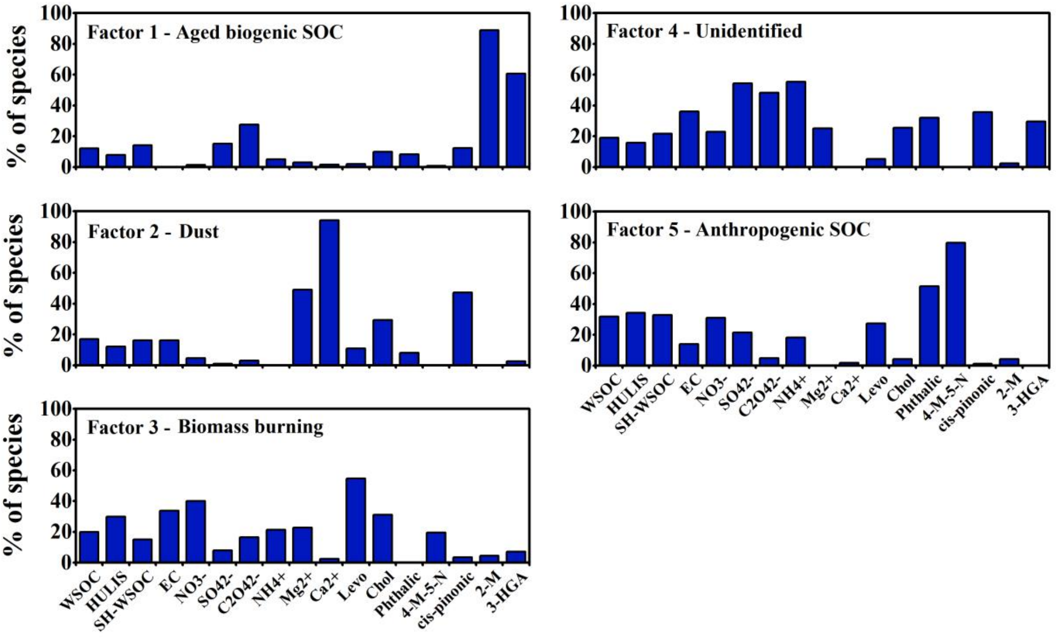

Figure S6. A 5-factor solution resolved by the PMF model.

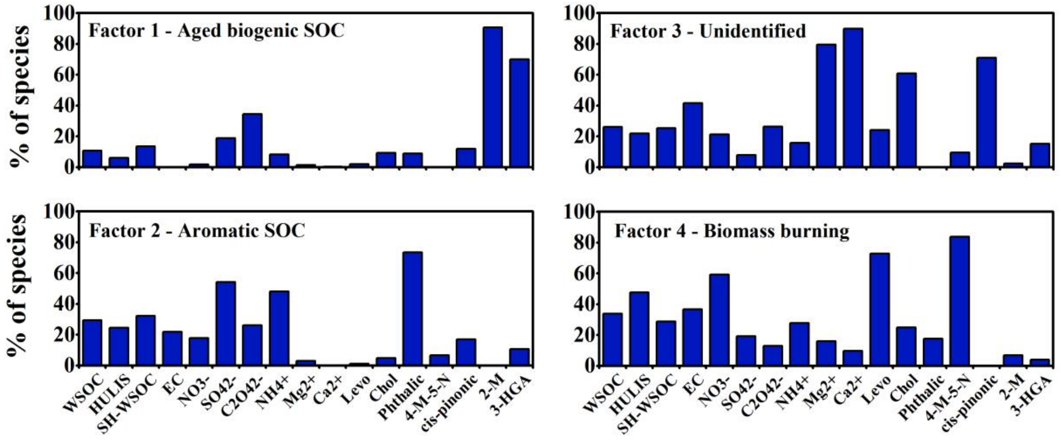

Figure S7. A 4-factor solution resolved by the PMF model.

It was indeed interesting that levoglucosan and 4-methyl-5-nitrocatechol were not distributed in the same factor, though they showed strong correlation with each other. We attempted to explain this phenomenon as follows. The ratio of 4-methyl-5-nitrocatechol to levoglucosan had significantly higher values ($p<0.01$) in winter than in other seasons (winter: 0.071 ± 0.029; other seasons: 0.010 ± 0.009), implying different types of biomass burning sources (primary and secondary). If they were merged into the same source, the ratio of 4-methyl-5-nitrocatechol to levoglucosan was supposed to be stable throughout the year, which was not the truth. As shown in Figure S8, the linear regression between levoglucosan and 4-methyl-5-nitrocatechol on the whole year scale (the blue line) was largely affected by the high values in winter. However, according to the uncertainty estimation method for the input species (Equation 2), the species with lower concentrations usually have lower uncertainties, thus may have a larger impact on the Q value. Taking the 4-factor solution (Figure S7) as an example, when the two tracers were merged into one factor, to minimize the Q value, the algorithm in the PMF model tended to assign a low value for the ratio of 4-methyl-5-nitrocatechol to levoglucosan in the factor profile of biomass burning (i.e. 0.024 in Factor 4). As presented in Figure S8, this ratio (orange line) was closer to the regression slope in other seasons (0.017), but much lower than that in winter (0.096). Consequently, the high concentration of 4-methyl-5-nitrocatechol in winter could not be reproduced at all by such PMF solution. In conclusion, the solution which merged these two tracers into the same factor might bring about large uncertainties, and fail to reproduce the peak values of 4-methyl-5-nitrocatechol over the study period in winter.

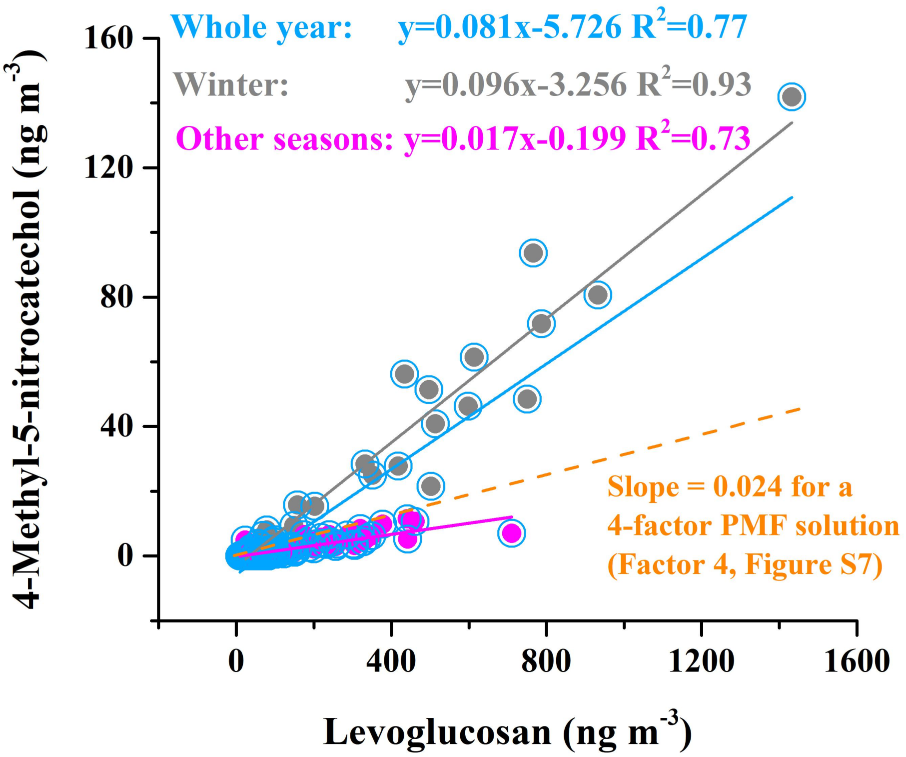

Figure S8 The relationship between levoglucosan and 4-methyl-5-nitrocatechol.

Fresh biomass burning emissions show a high fraction of anhydrosugar, such as levoglucosan. The relative intensity of anhydrosugar decreased due to the degradation or oxidation reactions (Gilardon et al., 2016; Sengupta et al., 2020). Chamber studies indicated that substantial amounts of nitrogen-containing organic compounds, such as nitrophenols and methyl-nitrocatechols, were generated during aging (Bertrand et al., 2018; Hartikainen et al., 2018). 4-Methyl-5-nitrocatechol was recommended to be the secondary tracer for aged biomass burning SOA (Bertrand et al., 2018). In the previous studies (Gilardon et al., 2016; Zhou et al., 2017; Srivastava et al., 2018), the biomass burning source was also separated into primary and secondary fractions with the PMF model. In Gilardon et al. (2016), the factor profile of primary biomass burning was featured by a high loading of anhydrosugar (signal at m/z=60) but a low level of the aged OA (signal at m/z=44), while the factor profile of biomass burning

SOA was featured by a high fraction of the aged OA (signal at m/z=44) but a low fraction of anhydrosugar (signal at m/z=60) (Gilardon et al., 2016). Srivastava et al. (2018) also used levoglucosan and 4-methyl-5-nitrocatechol as tracers to differentiate the primary biomass burning and biomass burning SOA using the PMF model (92 samples, which was less than that in our study). In this study, as shown in Figure 4, Factor 1 showed high fractions of levoglucosan and EC, but a low fraction of 4-methyl-5-nitrocatechol, thus was considered as the direct emission from biomass burning. The concentration ratio of levoglucosan to WSOC in this factor was 0.085 μg μg^{-1}, which was similar to that measured in the primary combustion of crop straws (0.097 μg μg^{-1}), wood (0.081 μg μg^{-1}) and leaves (0.095 μg μg^{-1}) in North China (Yan et al., 2018). Factor 5 had a high level of 4-methyl-5-nitrocatechol, but low levels of EC and levoglucosan, thus was identified as biomass burning SOA.

2. The interpretation of Factor 7, Factor 8, and Factor 9.

As presented in Figures S1-3 and Figures S5-7, even if we reduced the factor number from nine to four, 2-methylerythritol, 3-hydroxyglutaric acid and *cis*-pinonic acid could not be merged into the same factor. Large fractions of 3-hydroxyglutaric acid and 2-methylerythritol were usually grouped into one factor, since they strongly correlated with each other ($r=0.94$, $p<0.01$). *Cis*-pinonic acid could not be distributed in this factor since it correlated less strongly with 2-methylerythritol ($r=0.51$, $p<0.01$) and 3-hydroxyglutaric acid ($r=0.58$, $p<0.01$). As stated in Section 3.2, *cis*-pinonic acid is a lower-generation oxidative product from monoterpenes, while 2-methylerythritol and 3-hydroxyglutaric acid are more aged products from isoprene and monoterpenes, respectively (Kourtchev et al., 2009). Hence, Factor 7 with a high level of *cis*-pinonic acid was interpreted as the fresh biogenic SOC, and Factor 8 with high loadings of 2-methylerythritol and 3-hydroxyglutaric acid was interpreted as aged biogenic SOC. As shown in Figure 5, the seasonal variation of their source contributions also supported this interpretation.

Since the major fraction of 3-hydroxyglutaric acid was distributed in Factor 8, it was not proper to interpret Factor 9 as monoterpene SOC. In fact, as shown in Figure

S1-3 and Figure S5-7, a minor fraction of 3-hydroxyglutaric acid was always distributed in factors other than the biogenic SOC. It was more interpretable when this minor fraction of 3-hydroxyglutaric acid was distributed in the same factor together with SO_4^{2-}, NO_3^-, NH_4^+ and $C_2O_4^{2-}$. In this case, Factor 9 of the selected 9-factor solution could be interpreted as a mixed secondary source and explain the secondary species that were not well fitted by other identified secondary sources. Similar factor profile has also been resolved in the literature, and was usually interpreted as the "inorganic-rich SOA" (Huang et al., 2014).

3. The interpretation of Factor 3 (Other primary combustion sources).

As shown in Figure 4, for the constrained 9-factor solution, Factor 3 exhibited a significant fraction of EC from sources other than the direct emissions of biomass burning, implying that it could be associated with the primary emissions from other combustion sources, such as coal combustion, traffic emissions, and waste burning, etc. Indeed, a minor fraction of SO_4^{2-} (20.8 %), NH_4^+ (19.3 %) and phthalic acid (20.0 %) were also distributed in Factor 3. Previous studies have found that SO_4^{2-}, NO_3^-, NH_4^+ and phthalic acid can also be directly emitted from coal combustion (Zhang et al., 2008; Dai et al., 2019) and traffic emissions (Al-Naiema and Stone, 2017; Hao et al., 2019). Dai et al. (2019) suggested that primary SO_4^{2-} accounted for 38.9 % and 16.9 % to the total SO_4^{2-} in $PM_{2.5}$ during the heating and non-heating seasons respectively. Accordingly, such distribution of SO_4^{2-} (20.8 %) in Factor 3 was acceptable. Similar loadings of SO_4^{2-} and NH_4^+ were also found in the factor profile of coal combustion in the previous source apportionment study (Huang et al., 2014). To sum up, it was reasonable that a minor fraction of SO_4^{2-}, NH_4^+ and phthalic acid presented in the factor profile of Factor 3, i.e., other primary combustion sources.

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Zhou, S., Collier. S., Jaffe, D. A., Briggs, N. L., Hee, J., Sedlacek III, A. J., Kleinman, L., Onasch, T. B., and Zhang, Q.: Regional influence of wildfires on aerosol chemistry in the western US and insights into atmospheric aging of biomass burning organic aerosol, Atmos. Chem. Phys., 17, 2477-2493, doi: 10.5194/acp-17-2477-2017, 2017.

Comment 5: Page 5, Line 140-141: The equation calculates ion balance not “aerosol acidity”.

Response: We deeply appreciate the reviewer’s valuable suggestion. According to Pye et al. (2020), we changed the ratio of $R_{A/C}$ to the approximate value of aerosol pH (pH_F) to denote the aerosol acidity. The pH_F value was estimated using the ISORROPIA-II model. And the molality of H^+ (m_{H^+}), which was calculated by $m_{H^+} = 10^{-pH_F}$, was used instead for the correlation analysis in the revised manuscript.

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Comment 6: Page 6, Line 166: Why would the reduction of open biomass burning lead to decreased WSOC/OC ratios? Please clarify and cite references to support the reduction of open biomass burning.

Response: Thanks for the reviewer's valuable comment. We deleted this sentence after careful consideration. Some previous studies suggested that the ratios of WSOC/OC in biomass burning aerosols were higher than those from other primary combustion sources (Ruellan and Cachier, 2001; MayolBracero et al., 2002; Yang et al., 2020). However, the formation of SOC can also significantly influence the ratio of WSOC/OC (Jaffrezo et al., 2005; Deshmukh et al., 2016). The influencing factors of the WSOC/OC ratio are actually complex, thus we have deleted this uncertain speculation in the revised manuscript.

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Comment 7: Page 6, Line 173-176: The correlations (r = 0.44-0.58) are not strong. I think it is difficult to conclude that OA became more hygroscopic as pollution aggravated. Indeed, if primary sources make a large contribution, e.g., in winter when coal combustion was enhanced, OA might not be more hygroscopic although its concentration became greater.

Response: We deeply appreciate the reviewer's valuable suggestion. We have deleted this statement in the revised manuscript.

Comment 8: Page 6, Line 180: Perhaps remove "ideal". Levoglucosan is not chemically inert. It is also not a unique tracer for biomass burning. As the authors mentioned in Page 7, Line 199, biofuel and coal burning are also sources of levoglucosan.

Response: We agree with the reviewer's valuable suggestion and have removed "ideal" in the revised manuscript.

Comment 9: Methylnitrocatechol is not necessarily secondary. Wang X et al. (2017) showed primary emissions of methylnitrocatechol from biomass burning. Coal burning is also a source. The statement that "4-methyl-5-nitrocatechol is a good indicator for biomass burning SOA" is perhaps inappropriate.

Response: Thanks for the reviewer's valuable comment. We have removed the word "good" and revised the statement to: "4-methyl-5-nitrocatechol can be used as a tracer for biomass burning SOA (Iinuma et al., 2010; Bertrand et al., 2018; Srivastava et al., 2018)".

Iinuma et al. (2010) proposed that 4-methyl-5-nitrocatechol could be used as a tracer for biomass burning SOA. Bertrand et al. (2018) investigated the evolution of chemical fingerprint of biomass burning OA during aging, and sorted the tracers into three types: primary, non-conventional primary and secondary tracers. They also concluded that 4-methyl-5-nitrocatechol was the secondary tracer for biomass burning, and could be used as an aged biomass burning tracer in source apportionment studies. Srivastava et al. (2018) also used 4-methyl-5-nitrocatechol in the PMF model as the tracer for biomass burning SOA.

Wang et al. (2017) reported that the ratio of primary 4-methyl-5-nitrocatechol to OC varied greatly for different biomass types and burning conditions. The ratio for corncob under the flaming condition (0.87 ng μg^{-1}) was much higher than that for the other biomass types or other burning conditions (0.11 ng μg^{-1} on average). Therefore, we used the ratio of primary 4-methyl-5-nitrocatechol to OC for corncob burning (0.87 ng μg^{-1}) to roughly estimate the maximum contribution of primary biomass burning to the concentration of 4-methyl-5-nitrocatechol in the atmosphere. Recent source apportionment studies in Beijing suggested that biomass burning OA contributed at most 14 % of total OA (Sun et al., 2018; Tang et al., 2018; Duan et al., 2020). It was thus estimated that at most 16.2 % of atmospheric 4-methyl-5-nitrocatechol was from primary biomass burning. Therefore, it should be proper to use 4-methyl-5-nitrocatechol to indicate biomass burning SOA.

References

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Comment 10: Page 7, Line 200-203; Line 210-218; Page 8, Line 237-243: Errors can be propagated to the ratios in Figure 2b so that the day/night CO-scaled ratios can be discussed statistically (not just seasonal mean values). The authors said the CO-scaled concentration of cholesterol was close for the whole sampling period. However, panel a is in log scale. I think it is hard to conclude that 4 vs 7 (75% difference) is “close”.

Response: We are very thankful for the reviewer’s valuable suggestion. The error bars have been added to Figure 2b, and the results have been discussed statistically in the revised manuscript. We agree that the CO-scaled concentration of cholesterol was not that close for the whole sampling period, and we have made the corresponding revision as: “The CO-scaled concentration of cholesterol during the study periods in spring and autumn were significantly higher ($p<0.05$) than that in winter and summer.”

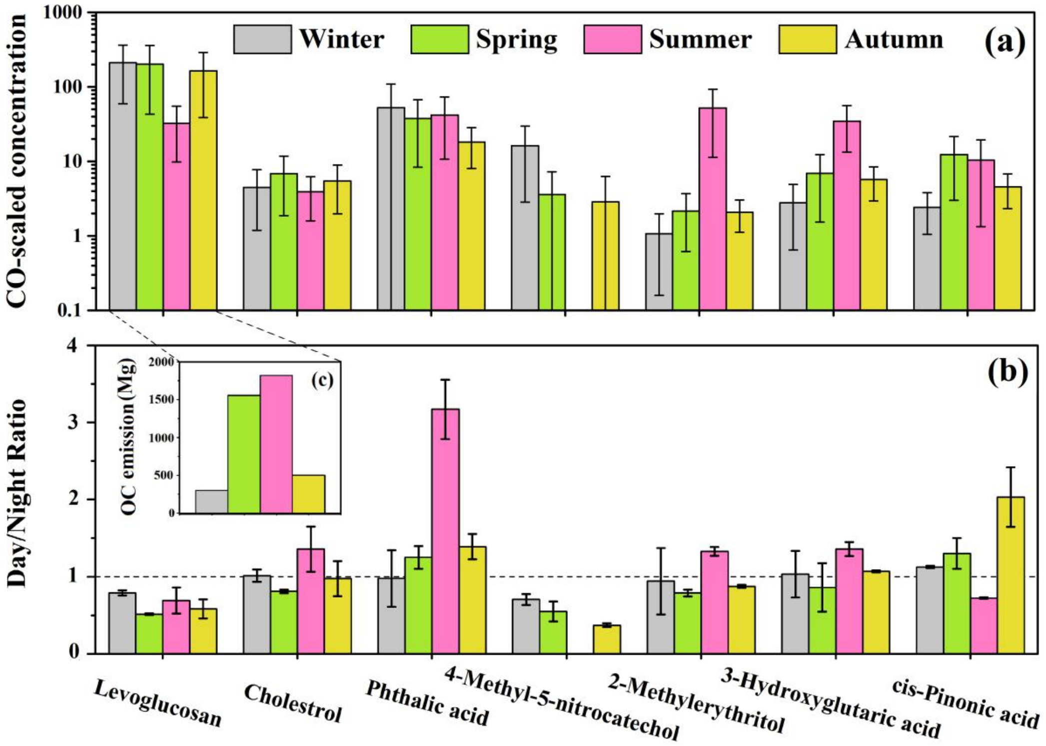

Figure 2. (a) The CO-scaled concentration of the identified organic tracers; (b) The day to night ratio of the measured concentrations of the organic tracers; (c) The OC emission amount from open biomass burning provided by the Fire Inventory (FINN) in Beijing during the sampling periods in four seasons of 2017.

Comment 11: Besides the statistical issue, other problems exist for the conclusions made on the basis of day/night ratios. First, biomass burning is not the only source of CO. The <1 day/night CO-scaled ratios of levoglucosan can be simply caused by enhanced CO emissions at night from other sources when the biomass burning contributions were constant. Similarly for cooking. Second, from emissions to concentrations, many factors are involved. Biomass burning is not a local source in Beijing. Similar strength of emissions may lead to different concentrations in Beijing because of the atmospheric aging and dilution during the regional transport process. Also, scaling secondary tracers by CO has complicated meaning, especially for biogenic-related tracers. I can't understand the logic behind Line 236-243. Not to mention that the phthalic acid concentrations may be affected by the OA concentrations due to gas-particle partitioning and the photolysis of

4-methyl-5-nitrocatechol might be significant to affect its daytime concentrations.

Response: We deeply appreciate the reviewer's valuable comment. We agree with the reviewer that there were many factors involved from emissions to atmospheric concentrations, thus it is hard to draw certain conclusions. Therefore, we focused on the result demonstration and explanation, instead of reaching certain conclusions in the revised manuscript.

As we know, the observed concentrations of organic tracers in different seasons were not only controlled by their emission strengths or secondary formation rates, but also affected by the atmospheric dilution conditions or boundary layer height. As a tracer for traffic exhaust, carbon monoxide (CO) shows relatively stable emission rates in different seasons, and is quite inertial to chemical reactions. Thus we used the CO-scaled concentration of the organic tracers (the concentration of organic tracers divided by CO concentration) to correct for different diffusion conditions in four seasons, so as to better discuss their differences in emission strengths or secondary production rates (Kleinman et al., 2008; Aiken et al., 2009).

As mentioned by the reviewer, the emission rates of CO might be different between day and night, thus it was not meaningful to compare the day/night ratios of the CO-scaled concentrations of the organic tracers. Therefore, in the revised manuscript, we demonstrated the day/night ratios of the observed concentrations of the organic tracers (not scaled by CO) instead. The planetary boundary layer (PBL) heights (derived from the WRF model) and wind speeds were shown in Table S6. The diffusion conditions were typically worse at night. Therefore, if the day/night ratio was much higher than 1, it could be attributed to stronger source emission or secondary formation during the daytime. However, if the day/night ratio was lower than 1, it cannot be concluded that the source emission strength or secondary formation rate was stronger at night. Besides, the impact of gas-particle partitioning on phthalic acid and the photolysis of 4-methyl-5-nitrocatechol were also discussed in the revised manuscript.

Table S6 The mean values and standard deviations (SD) of planetary boundary layer

(PBL) heights and wind speeds in Beijing during the study periods in four seasons.

		Winter		Spring		Summer		Autumn	
		Day	**Night**	**Day**	**Night**	**Day**	**Night**	**Day**	**Night**
PBL (m)	**Mean**	309.7	283.2	1149.4	303.9	871.6	210.5	423.2	90.9
	SD	236.7	259.1	841.1	363.2	405.6	164.3	278.9	90.4
WS (m s^{-1})	**Mean**	1.14	0.83	1.75	0.83	1.03	0.63	0.72	0.39
	SD	0.79	0.61	0.71	0.75	0.68	0.44	0.62	0.25

References:

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Comment 12: Page 7, Line 205-207: The cited reference is only for PAH. How about other aromatic precursors (e.g., single-ring aromatics)? Do those typical SOA precursors show higher concentrations in winter? Please note that oxidation conditions are also important when discussing about the secondary formation potential of SOA. In winter, the oxidant concentrations (e.g., OH) might be lower.

Response: We deeply appreciate the reviewer's valuable comments. Based on the VOC measurements in Beijing, some studies reported that single-ring aromatics (such as benzene, toluene, xylenes, ethylbenzene, etc) also exhibited higher concentrations in winter (Li et al., 2020a, b), while others reported a different result (Liu et al., 2020). Thus the related expression has been corrected to: "In winter, the enhanced emissions due to residential heating and adverse atmospheric diffusion conditions led to higher concentrations of PAHs (Feng et al., 2018; Sun et al., 2018), thus might facilitate the PAH-derived SOA formation." In fact, a significant increase of toluene-derived SOA (indicated by DHOPA) in winter has also been observed in northern cities of China due to residential heating (Ding et al., 2017).

We agree with the reviewer that the concentrations of oxidants might be lower in winter due to weak solar radiation. Discussion on the oxidation conditions in winter has also been added in the revised manuscript. A previous observation found that the ·OH concentration in Beijing was significantly higher than that in New York, Birmingham and Tokyo, and was nearly 1 order of magnitude higher than that predicted by global models in northern China in winter (Tan et al., 2018). Zhang et al. (2019) indicated that HONO, which was mainly from the heterogeneous reactions of NO_2 and traffic emissions, was the major precursor of ·OH in winter. According to the WRF-Chem model simulation, HONO resulted in a significant enhancement (5-25 μg m^{-3}) of SOA formation (most of which were from the aromatic precursors) during a haze episode in winter in the Beijing-Tianjin-Hebei region (Zhang et al., 2019). Besides, some recent studies suggested that the brown carbon-derived singlet molecular oxygen ($^1O_2^*$) in aerosol liquid water could react rapidly with the electron-rich organics such as PAHs, thus facilitate the aromatic SOA formation (Kaur et al., 2019; Manfrin et al., 2019). This process might be more significant in winter, when the concentration of HULIS was much higher than that in other seasons.

Response:

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Comment 13: Section 3.2.2 in Page 8-10: Conclusions in this section are generally arbitrary. Although correlations sometimes help diagnostics, connections between O_3, ALWC, RH, T and the tracer species as well as WSOC/OC are not simple/obvious. For example, in Line 248-251, it was said that "WSOC/OC did not correlate with O_3, suggesting that gas-phase photooxidation was not the dominant formation mechanism of SOC". Why? Do the authors assume that WSOC are SOC and gas-phase photooxidation is equivalent to O_3? What about terms other than chemical production in the mass balance (e.g., photolysis, primary contributions, and so on? Besides, the correlation isn't strong (r=0.5) when the authors sometimes said "significantly correlated". Such kind of correlations might be used as non-conflict evidence for explaining the formation pathways but definitely insufficient to make any conclusions. A common argument is that in winter Beijing all components of $PM_{2.5}$ often correlate with RH and ALWC, even for primary OA. It is not surprise that 4-methyl-5-nitrocatechol correlate with RH and ALWC. The study done by Wang L et al. (2018) suggest coal and traffic contributions to 4-methyl-5-nitrocatechol were the dominant sources in northern China.

Response: We deeply appreciate the reviewer's valuable comments. We agree with the reviewer that it was inappropriate to conclude that "gas-phase photooxidation was not the dominant formation mechanism of SOC" merely based on the result that "WSOC/OC did not show any significant positive correlation with O_3 concentration". Therefore, we have deleted the related discussion in the revised manuscript. We also agree with the reviewer that correlation analysis was insufficient to make certain conclusions. Therefore, in the revised manuscript, we focused on the result explanation instead of making certain conclusions in most cases. Besides, the potential impact of photolysis and gas-particle partitioning was also discussed in the revised manuscript.

Indeed, in the wintertime of Beijing, $PM_{2.5}$ often correlates well with RH and ALWC, which is also the case even for primary OA (Sun et al., 2013). In some previous studies, the concentration of SOA was normalized by HOA (Sun et al., 2013), CO (Kleinman et al., 2008; Aiken et al., 2009), EC (Zheng et al., 2015) or OA (Xu et al., 2017), to eliminate the diffusion effect and better evaluate their secondary production as far as possible. In this study, not only 4-methyl-5-nitrocatechol correlated strongly with RH ($r=0.69$, $p<0.01$) and ALWC ($r=0.88$, $p<0.01$), but also the ratios of 4-methyl-5-nitrocatechol/OC (RH: $r=0.73$, $p<0.01$; ALWC: $r=0.82$, $p<0.01$), 4-methyl-5-nitrocatechol/EC (RH: $r=0.57$, $p<0.01$; ALWC: $r=0.73$, $p<0.01$), 4-methyl-5-nitrocatechol/CO (RH: $r=0.64$, $p<0.01$; ALWC: $r=0.81$, $p<0.01$), all correlated significantly with RH and ALWC during the sampling period in winter. Therefore, we speculated that the aqueous-phase oxidation probably facilitated the formation of 4-methyl-5-nitrocatechol during the study period in winter, and these correlations were added in the revised manuscript.

The work done by Wang et al. (2018) did not directly measure nitrophenols of the source samples, but reached their conclusion based on the PMF result (that is, the correlations between 4-methyl-5-nitrocatechol and SO_2 or NO). Besides, levoglucosan was not measured in their study, thus we could not compare its correlations with SO_2 or NO and levoglucosan. The result of Wang et al. (2018) was different from the other studies which commonly suggested that 4-methyl-5-nitrocatechol mainly derived from secondary formation (Iinuma et al., 2010; Bertrand et al., 2018; Wang et al., 2019). In this study, correlation between 4-methyl-5-nitrocatechol and levoglucosan ($r=0.87$) was higher than those with SO_2 ($r=0.59$) or CO ($r=0.44$). Therefore, coal combustion and traffic emissions should not be the dominant sources of 4-methyl-5-nitrocatechol in Beijing during the sampling period in 2017 in this study.

References

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Comment 15: Technical remarks:

Page 7, Line 211: “secondary formation of aromatic SOA” - SOA is secondary.

Page 8, Line 239: “the diurnal patterns were close to 1” – What does this mean?

Page 9, Line 252: LWC has already defined.

Response: We are deeply thankful for the reviewer’s comments. (1) The expression “secondary formation of aromatic SOA” has been corrected to “formation of aromatic SOA”. (2) The expression “the diurnal patterns were close to 1” has been corrected to “the day to night ratios were close to 1”. (3) The “LWC” in the bracket has been deleted.