Supplementary material of

Seasonal variations of the highly time-resolved aerosol composition, sources, and chemical processes of background submicron particles in North China Plain

Jiayun Li[1, 4], Liming Cao[2], Wenkang Gao[1], Lingyan He[2]; Yingchao Yan[1,4], Dongsheng Ji[1], Zirui Liu[1], Yuesi Wang[1,3,4]

[1]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[2]Key Laboratory for Urban Habitat Environmental Science and Technology, Peking University Shenzhen Graduate School, Shenzhen, 518055, China

[3]Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

[4]University of Chinese Academy of Sciences, Beijing 100049, China

Correspondence: Zirui Liu (liuzirui@mail.iap.ac.cn); Lingyan He (hely@pkusz.edu.cn)

Jiayun Li and Liming Cao contributed equally to this work.
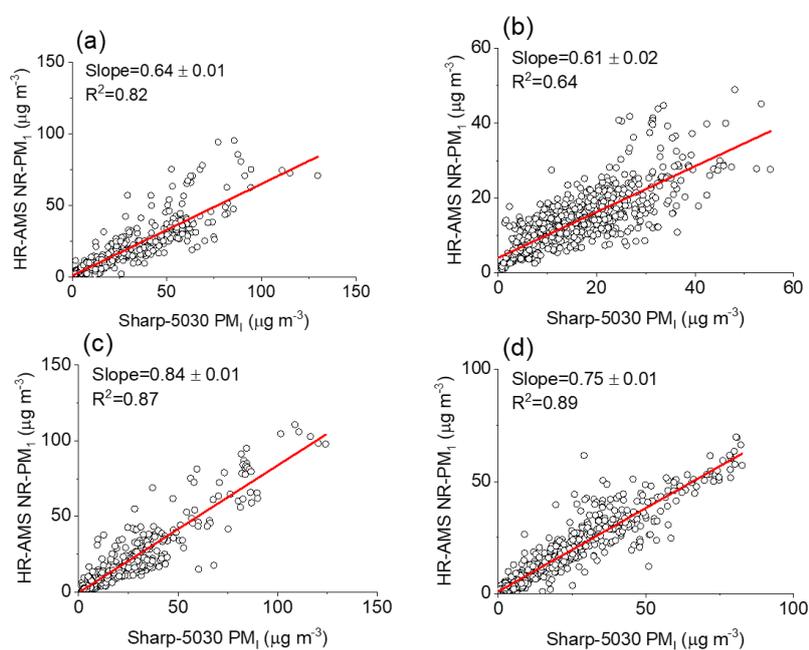
Figure S1. Scatter plots of the mass concentration of NR-PM$_1$ vs. total PM$_1$ measured by Sharp-5030 in spring (a), summer (b), autumn (c), and winter (d).

Spring：

Factor number from 1 to 8 were selected to run in the PMF model. For the spring observation, there was no POA factor appeared in the 2- to 4- factor solution. A POA factor appeared in the 5-factor solution and diagnostic plots of the PMF analysis were shown in Fig. S2. The mass spectra of the POA factor had some similarity with HOA and CCOA. The correlation coefficient between POA and NOx was 0.58, and that between POA and chloride was 0.78, suggesting a significant contribution of coal combustion and traffic-related sources to the POA factor in Xinglong. Previous studies found that HOA and CCOA showed remarkably similar mass spectrum patterns when m/z is below 120 (Sun et al., 2016; Sun et al., 2018), which was sometimes difficult to be separated by PMF analysis, so FFOA could be considered as a combined factor of HOA and CCOA (Sun et al., 2018). Therefore, the POA factor was identified as FFOA.

As shown in Fig. S4, in the 5-factor solution, factor 1, factor 2 and factor 4 had similar mass spectra, time series and O/C ratios (0.87-0.96). It was unclear if the three OOA components represent distinct sources or chemical types. Therefore, it was over split by one OOA factor. Another OOA factor (factor 5) had different mass spectra and lower O/C ratio, suggesting different formation mechanism. Therefore, we constrained the FFOA profiles separated by the 5-factor solution of PMF analysis in spring. As a result, three OA factors, including FFOA, LO-OOA and MO-OOA, were identified with ME-2 analysis in spring. The mass spectra, time series, and diurnal variations of ME-2 result were shown in Fig. S7.
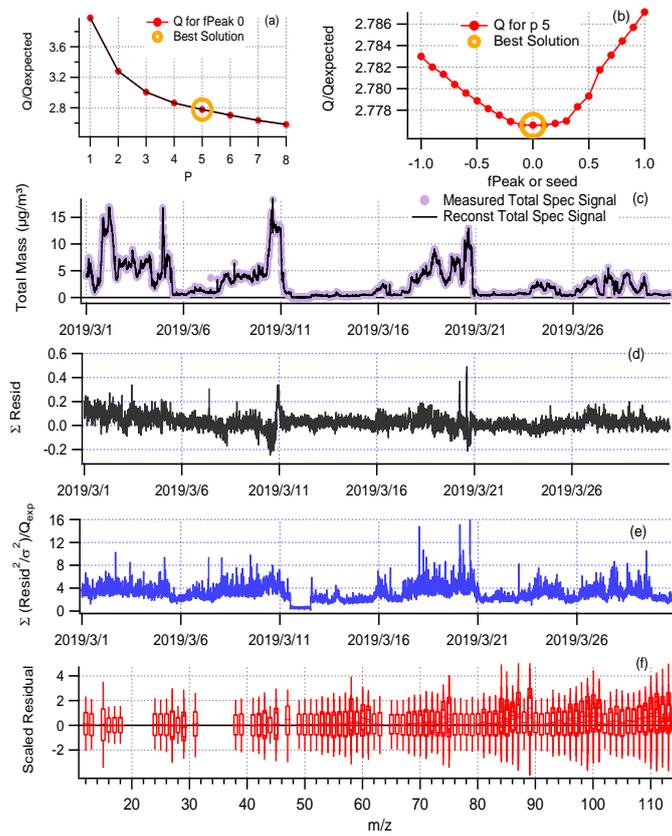
Figure S2. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the spring observation.
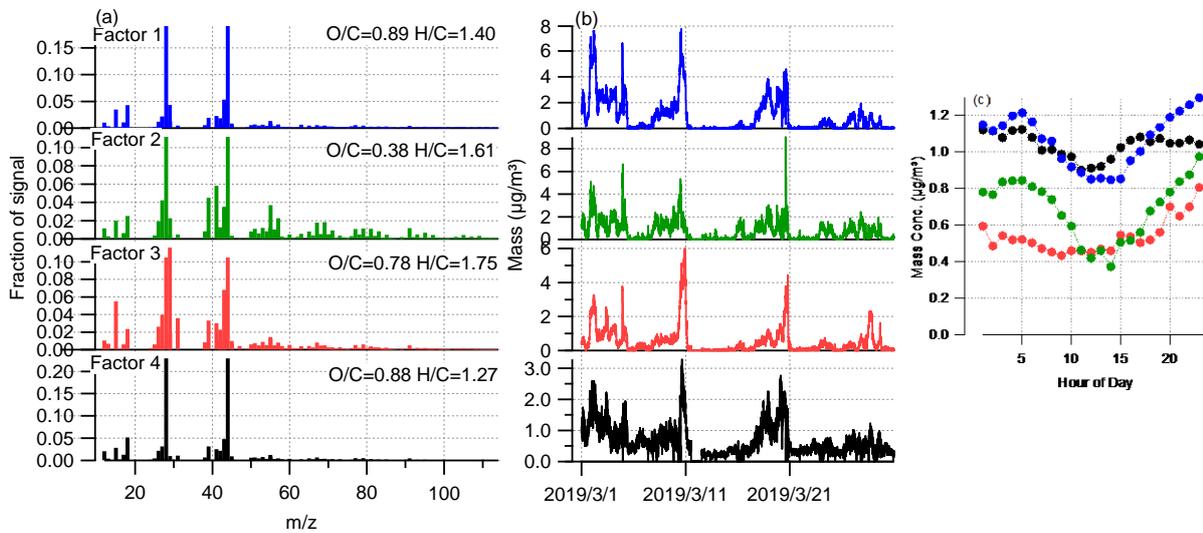
Figure S3. The mass spectra, time series, and diurnal variations of 4-factor solution of PMF analysis for the spring observation.
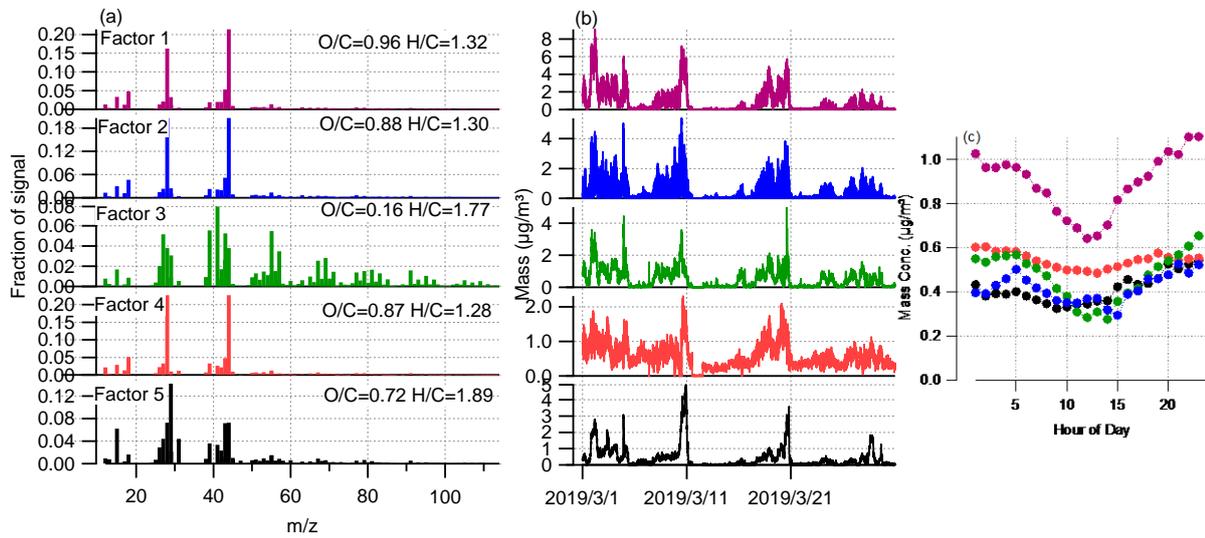
Figure S4. The mass spectra, time series, and diurnal variations of 5-factor solution of PMF analysis for the spring observation.
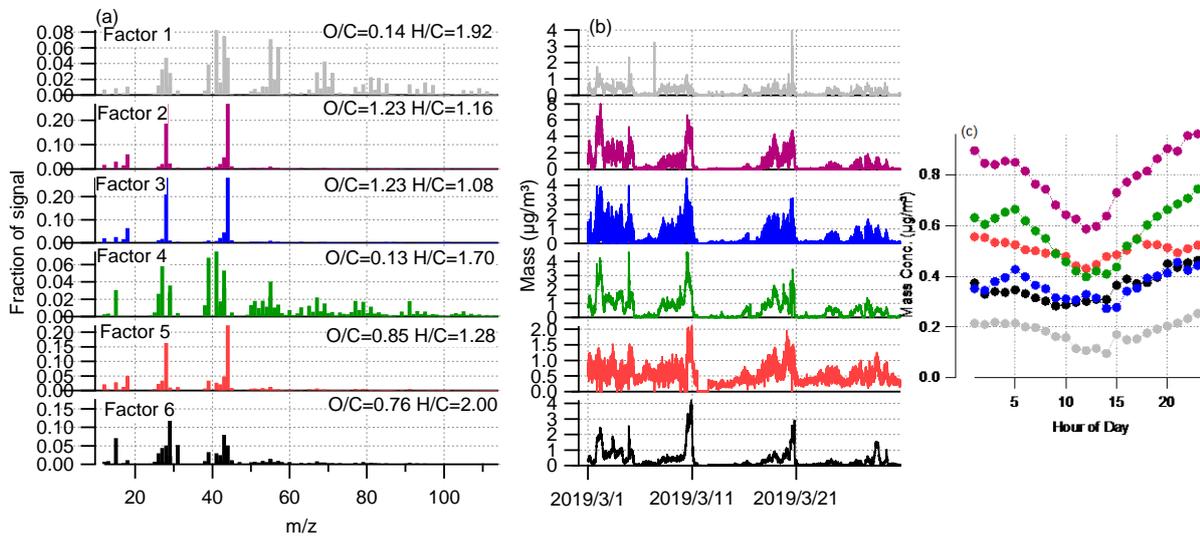
Figure S5. The mass spectra, time series, and diurnal variations of 6-factor solution of PMF analysis for the spring observation.
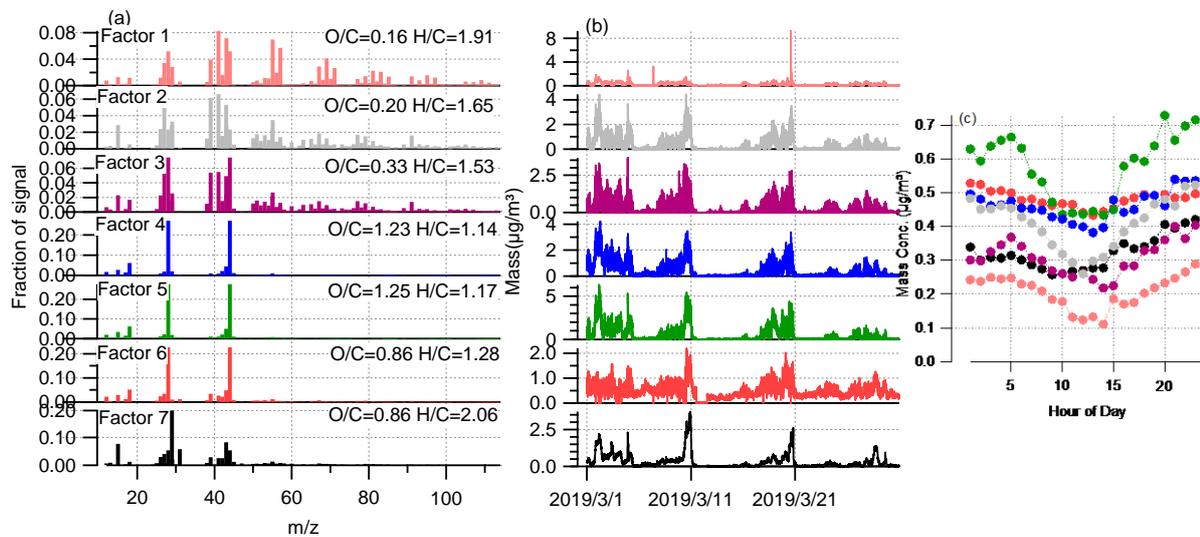
Figure S6. The mass spectra, time series, and diurnal variations of 7-factor solution of PMF analysis for the spring observation.
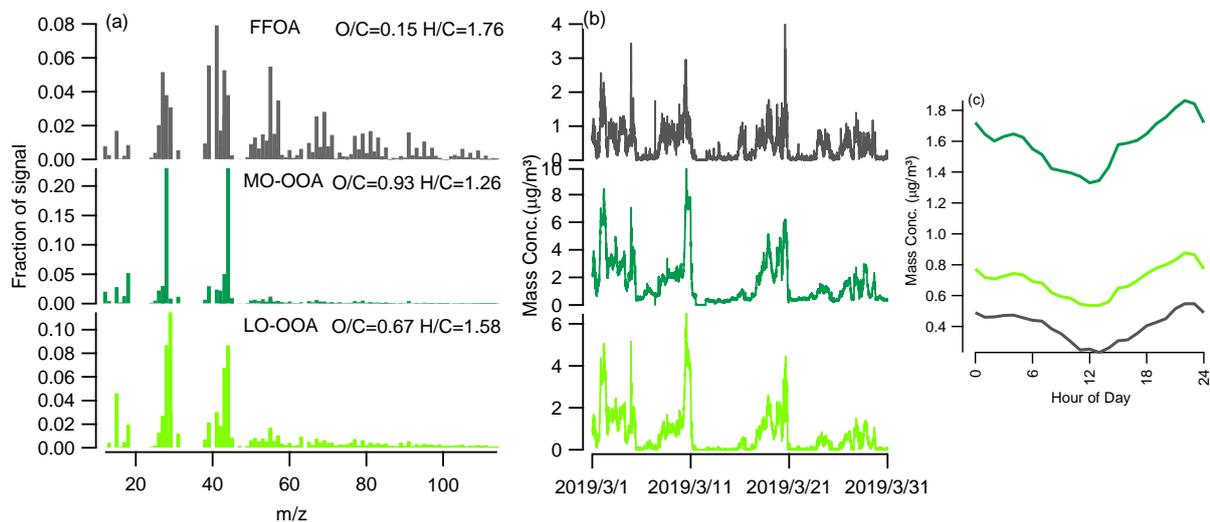
Figure S7. The mass spectra, time series, and diurnal variations of ME-2 analysis for the spring observation.

Summer:

For the summer observation, the 2-factor, fpeak=0 solution was selected as the optimum solution. The diagnostic plots of the PMF analysis were shown in Fig. S8. The two OA factors are more oxidized (MO-OOA) and less oxidized OOA (LO-OOA). The mass spectrum, time series and diurnal variations of OA factors were different. The O/C of the two factors were 0.58 and 0.93, respectively. No POA factor appeared in the 2- to 9-factor solutions. OOA was over spilt in the 3- to 9-factor solutions. The detailed information on how to select the optimum PMF solution can be found in Figure S9-S12 and Table S1.
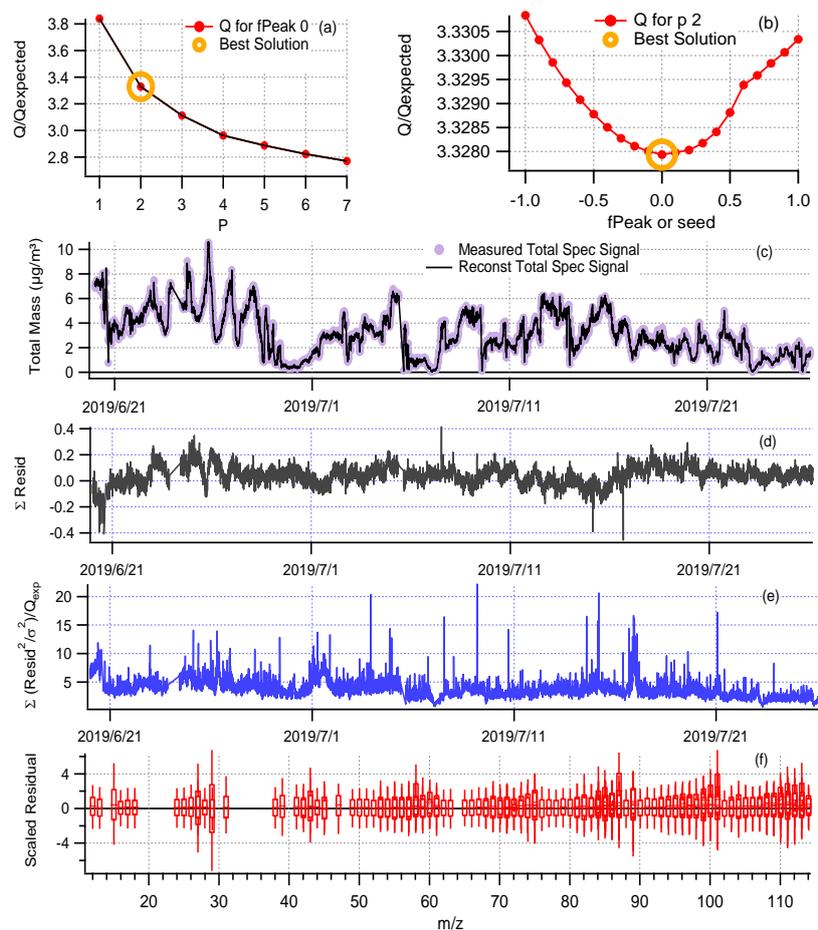
Figure S8. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the summer observation.
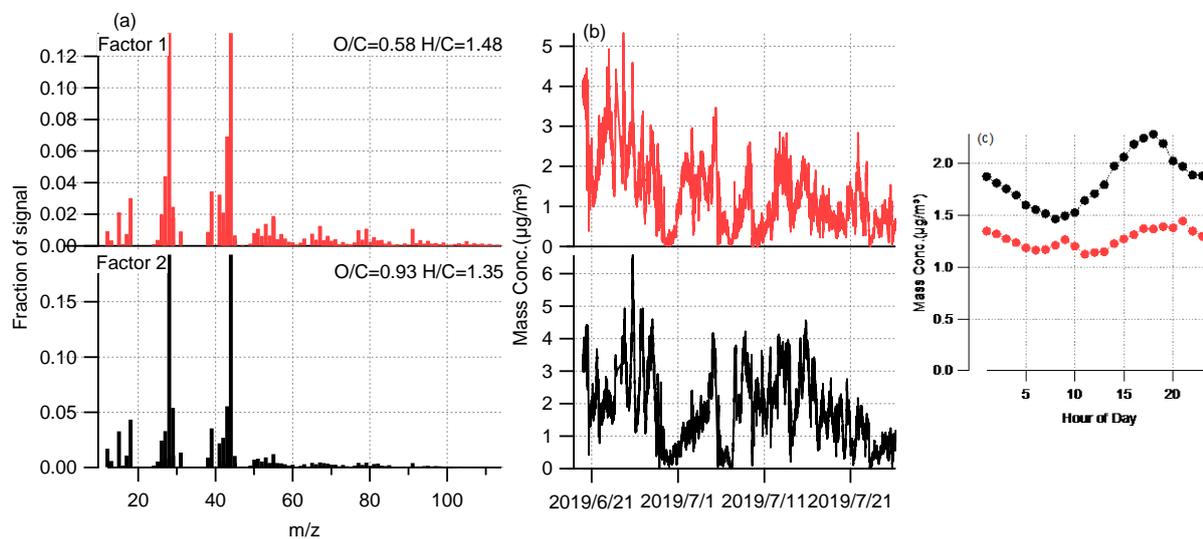
Figure S9. The mass spectra, time series, and diurnal variations of 2-factor solution of PMF analysis for the summer
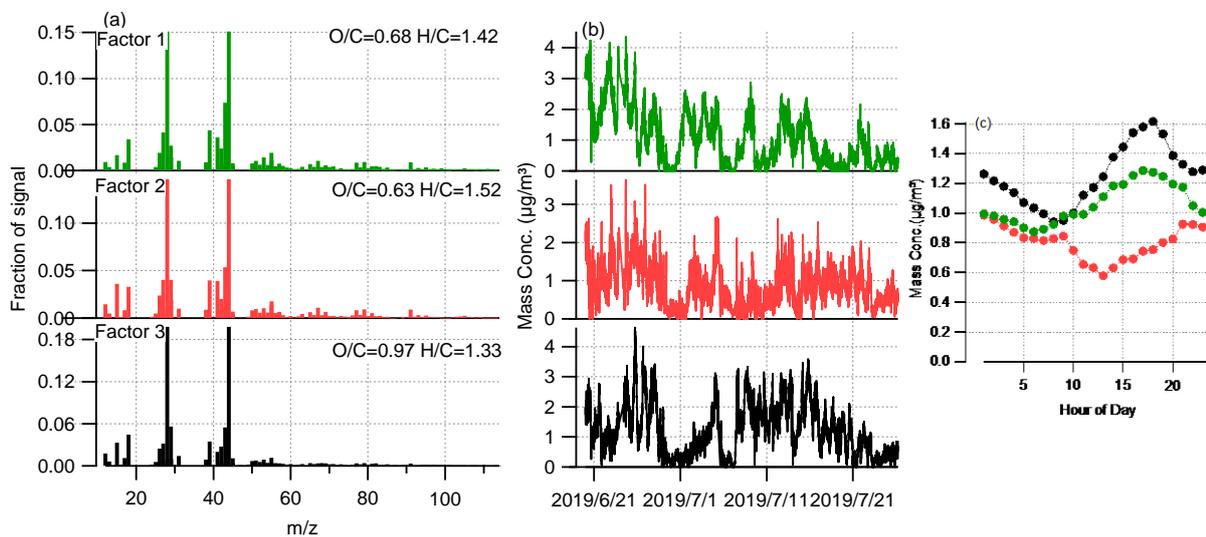
observation.

Figure S10. The mass spectra, time series, and diurnal variations of 3-factor solution of PMF analysis for the summer observation.
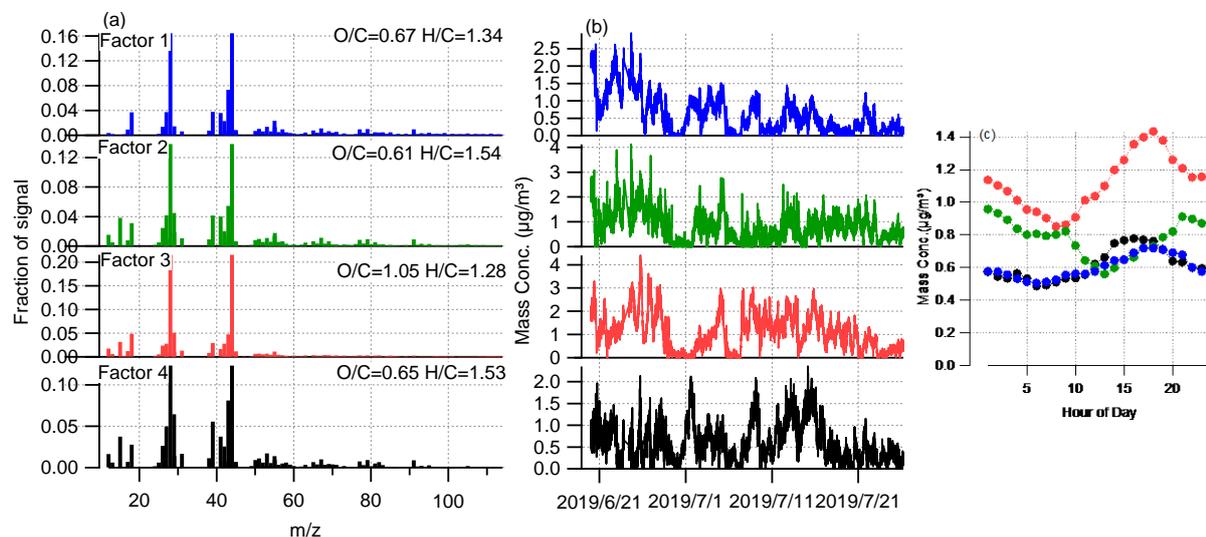
Figure S11. The mass spectra, time series, and diurnal variations of 4-factor solution of PMF analysis for the summer observation.
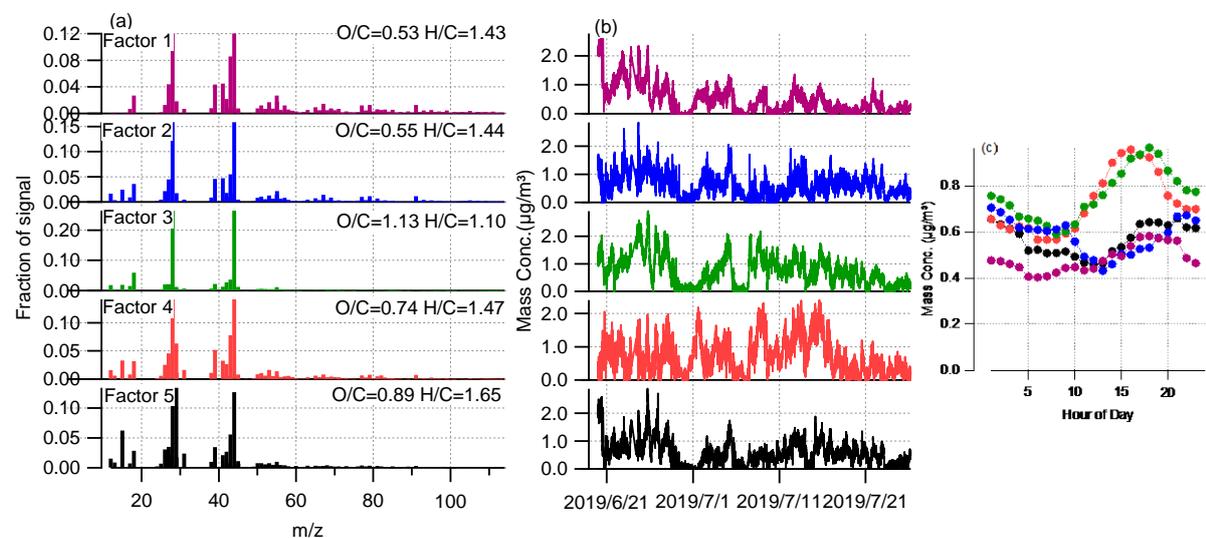
Figure S12. The mass spectra, time series, and diurnal variations of 5-factor solution of PMF analysis for the summer

observation.

Table S1 Descriptions of PMF solutions for the summer observation in Beijing.

Factor number	Fpeak	Q/Qexp	Solution Description
1	0	3.83	Too few factors, large residuals at time periods and key m/z's
2	**0**	**3.32**	**Optimum solution for the PMF analysis (MO-OOA and LO-OOA). The mass spectrum, time series and diurnal variations of OA factors were different. The O/C of the two factors were 0.58 and 0.93, respectively.**
3-9	0	3.11	Factor split. Take 3 factor number solution as an example, factor 2 was similar to the factor 2 which resolved in the 2-factor solution with similar mass spectrum, time series, diurnal variation and O/C ratios. Factor 1 and factor 3 were likely over split with similar time series and different mass spectrum. However, it was difficult to explain if they represent distinct sources or chemical types.

Autumn:

The solution of the PMF analysis for the autumn observation is similar to that for the spring observation. A POA factor appeared until the 7-factor solution and OOA was over-split. The diagnostic plots of the PMF analysis were shown in Fig. S13. The correlation coefficient of the POA vs. NOx is 0.61. The mass spectra of the POA factor is similar with the FFOA factor resolved in spring (the angle θ between the two mass spectra is 9 degree). We constrained the POA profile separated by the 7-factor solution of PMF analysis in autumn to better separate POA from OOA. As a result, three OA factors, including FFOA, LO-OOA and MO-OOA, were identified with ME-2 analysis in autumn. The mass spectra, time series, and diurnal variations of ME-2 result were shown in Fig. S16.
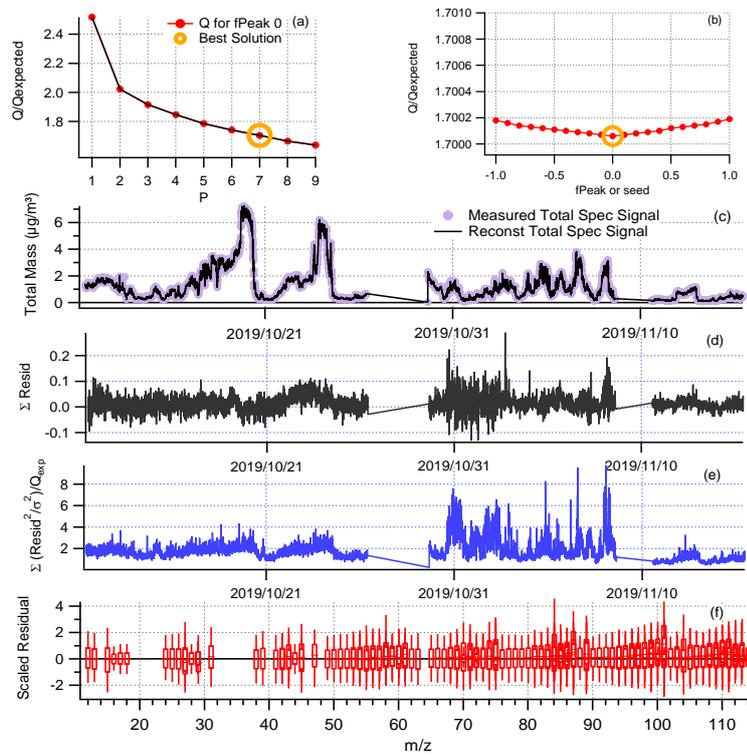
c

Figure S13. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the autumn observation.
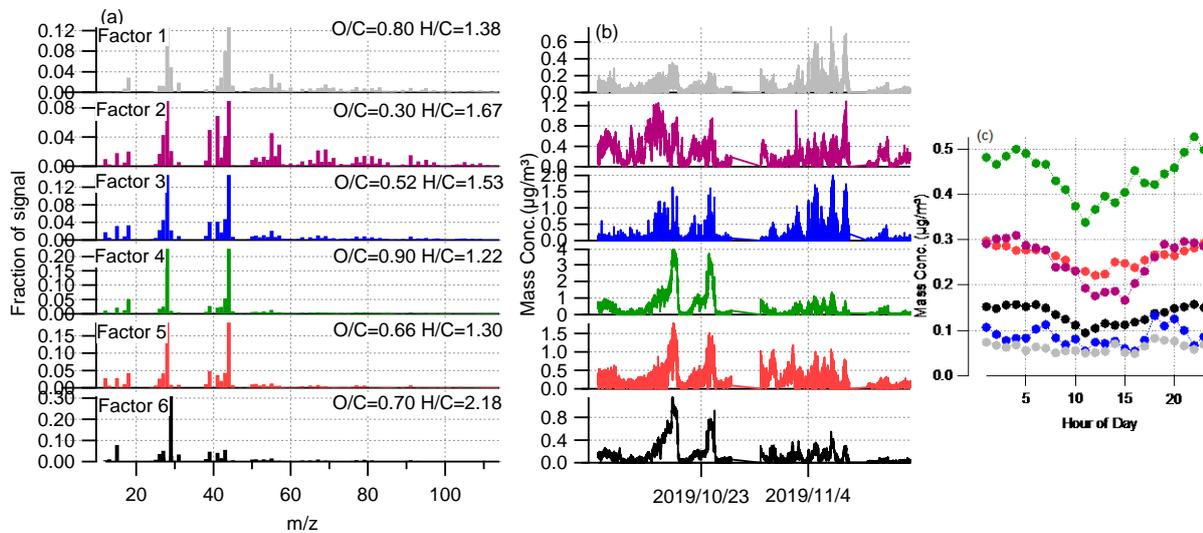
Figure S14. The mass spectra, time series, and diurnal variations of 6-factor solution of PMF analysis for the autumn observation.
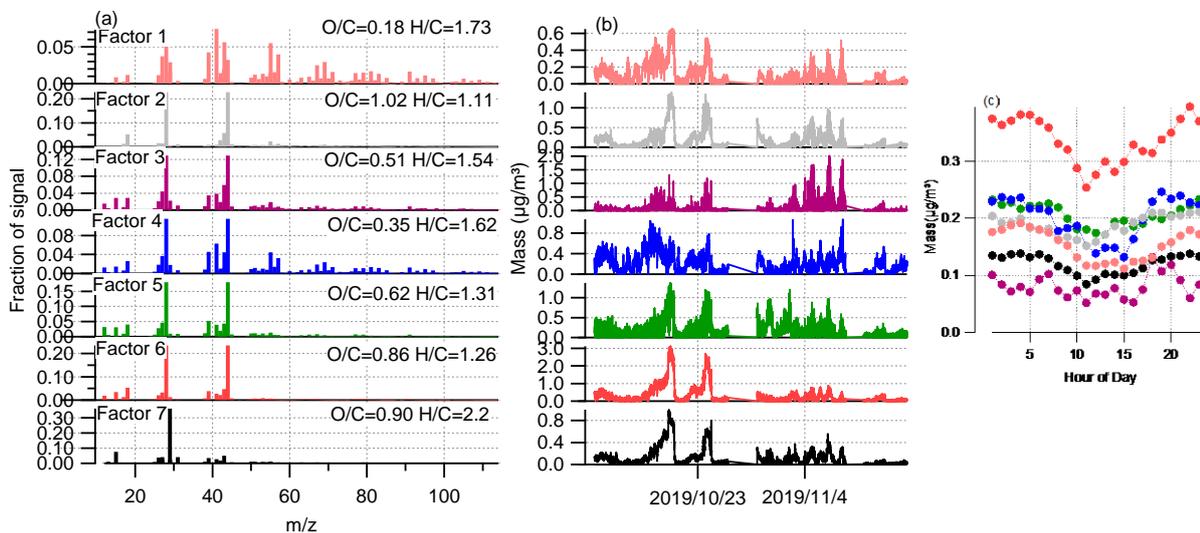
Figure S15. The mass spectra, time series, and diurnal variations of 7-factor solution of PMF analysis for the autumn observation.
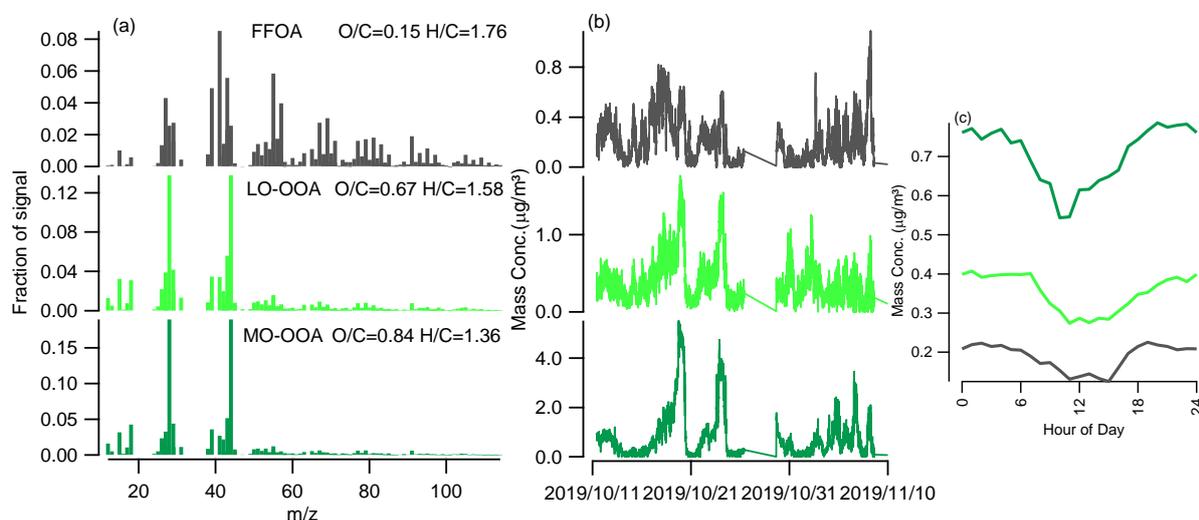
Figure S16. The mass spectra, time series, and diurnal variations of ME-2 analysis for the autumn observation.

Winter:

For the winter observation, the 3-factor, fpeak=0 solution was selected as the optimum solution. When OA was separated into four factors, OOA was also split into three factors (Fig. S19). In the 4-factor solution, factor 2 was similar to factor 2 which was resolved in the 3-factor solution with similar mass spectra, time series, diurnal variation and O/C ratios. However, factor 3 and factor 4 in the 4-factor solution had similar O/C ratios, time series and diurnal variation. It was unclear if the two OOA components represent distinct sources or chemical types. When more than 5 factors, OOA decomposed into three or more

factors. Thus, two OOA factors were combined into total OOA for further analysis. The 3-factor solution (FFOA, LO-OOA and MO-OOA) from PMF analysis was good enough, so it was not necessary to use ME-2 analysis to separate POA from OOA. The detailed information on how to select the optimum PMF solution can be found in FigureS18-S20 and Table S2.
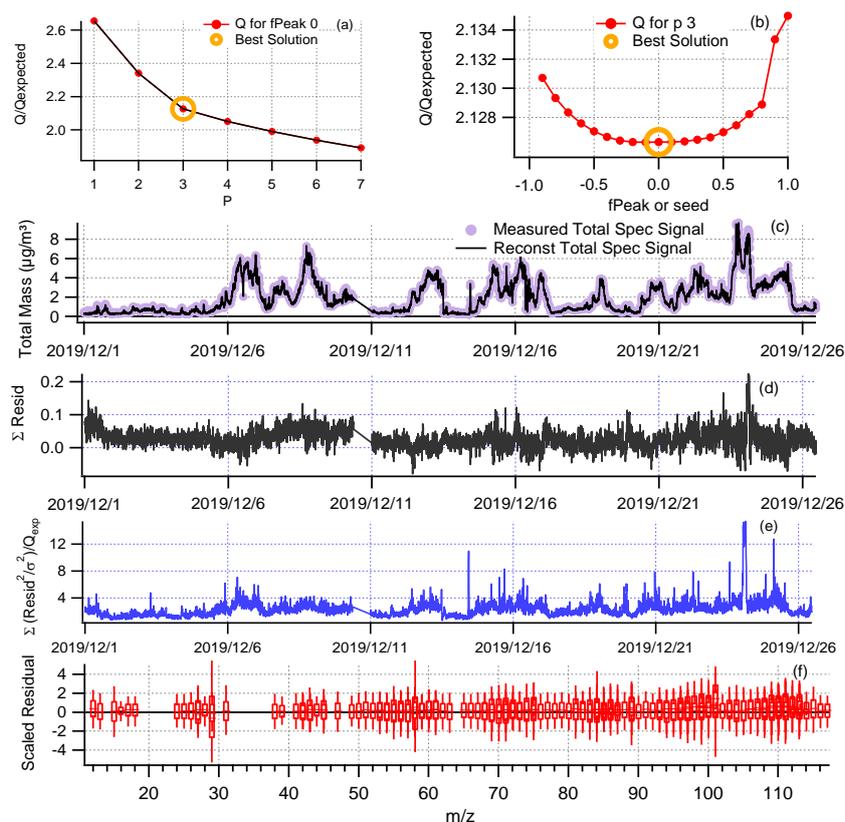
Figure S17. Diagnostic plots of the PMF analysis on OA mass spectral matrix for the winter observation.
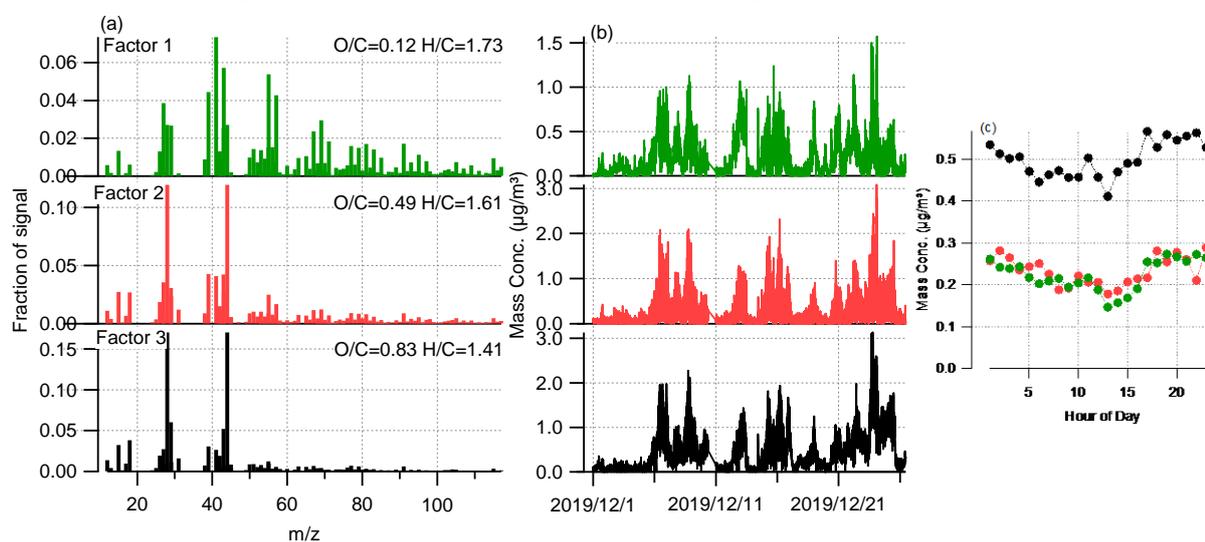
Figure S18. The mass spectra, time series, and diurnal variations of 3-factor solution of PMF analysis for the winter observation.
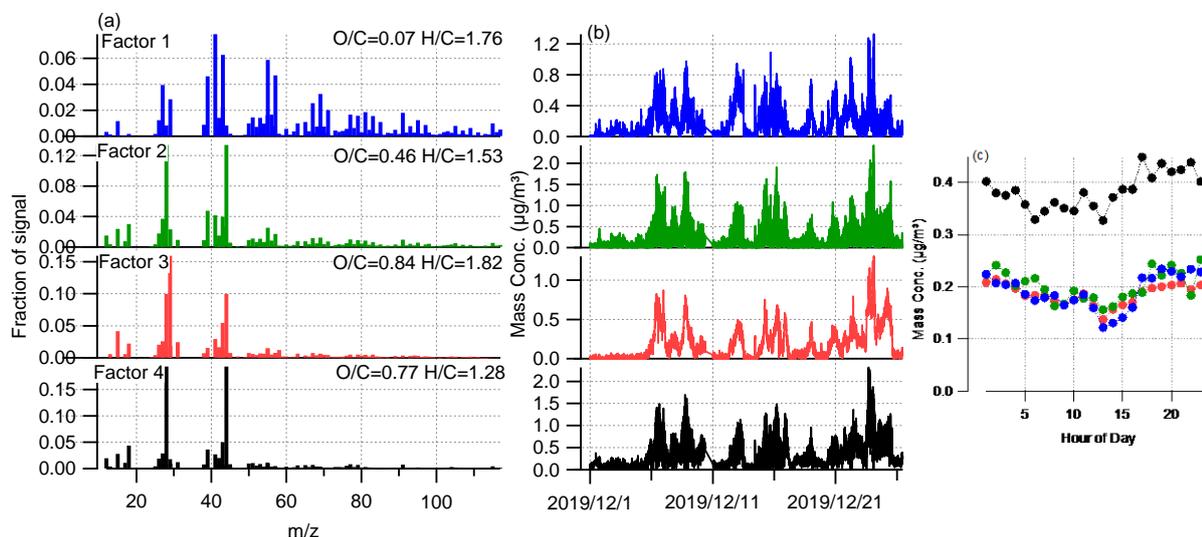
Figure S19. The mass spectra, time series, and diurnal variations of 4-factor solution of PMF analysis for the winter observation.
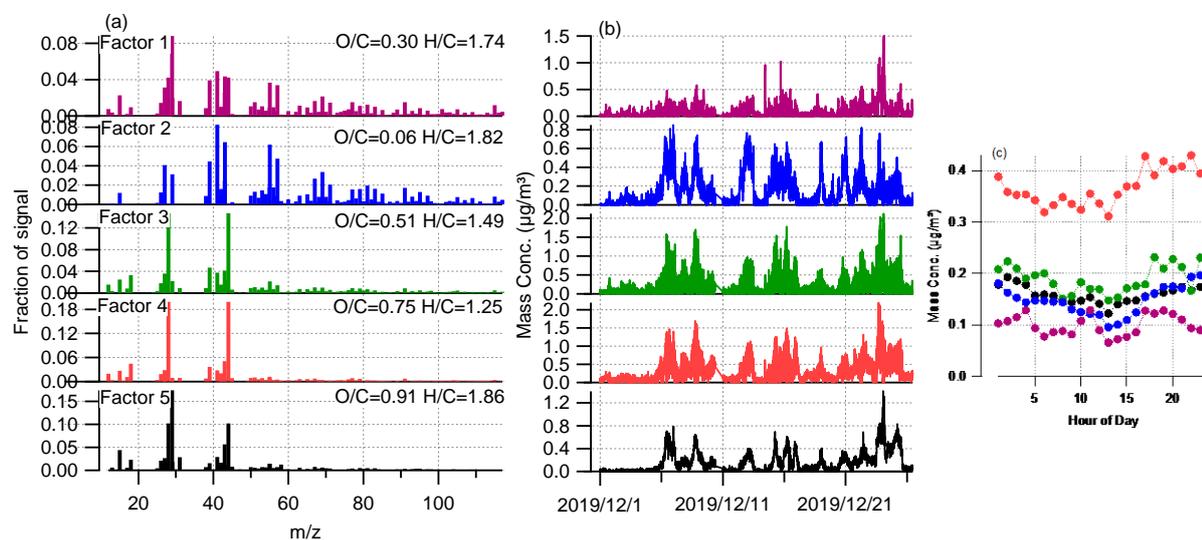
Figure S20. The mass spectra, time series, and diurnal variations of 5-factor solution of PMF analysis for the winter observation.

Table S2 Descriptions of PMF solutions for the winter observation in Beijing.

Factor number	Fpeak	Q/Qexp	Solution Description
1	0	2.65	Too few factors, large residuals at time periods and key m/z's.
2	0	2.34	Too few factors, POA was mixed with OOA.
3	**0**	**2.12**	**Optimum solution for the PMF analysis (FFOA, MO-OOA and LO-OOA). The mass spectrum and time series of the two OOA factors were different. The O/C of the two factors were 0.49 and 0.83, respectively. Thus, two OOA factors were for further analysis. The correlation coefficient between POA and NOx was 0.73, and that between POA and chloride was 0.61. Meanwhile, the mass spectra of the POA factor was similar to HOA and CCOA. Therefore, the POA factor was identified to FFOA.**

4-7	0	1.89-1.98	Factor split. Take 4 factor number solution as an example, factor 2 was similar to the factor 2 which resolved in the 2-factor solution with similar mass spectrum, time series, diurnal variation and O/C ratios. factor 1 and factor 3 were likely over split with similar time series and different mass spectrum. However, it was difficult to explain if they represent distinct sources or chemical types.