Supplementary material for:

The Effect of the Averaging Period for PMF Analysis of Aerosol Mass Spectrometer Measurements during Off-Line Applications

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Table S1: Number of samples and parameters used in PMF for the period 1 November-18 March for all the time averages.

	# of samples	# of parameters
30 min	6150	98
1 h	3035	98
2 h	1517	98
4 h	759	98
6 h	506	98
8 h	379	98
10 h	305	98
12 h	253	98
24 h	127	98

1. Four and six factor solution for the 30 min PMF solution

In the four factor solution three primary factors were identified (HOA, COA and BBOA) and one OOA.

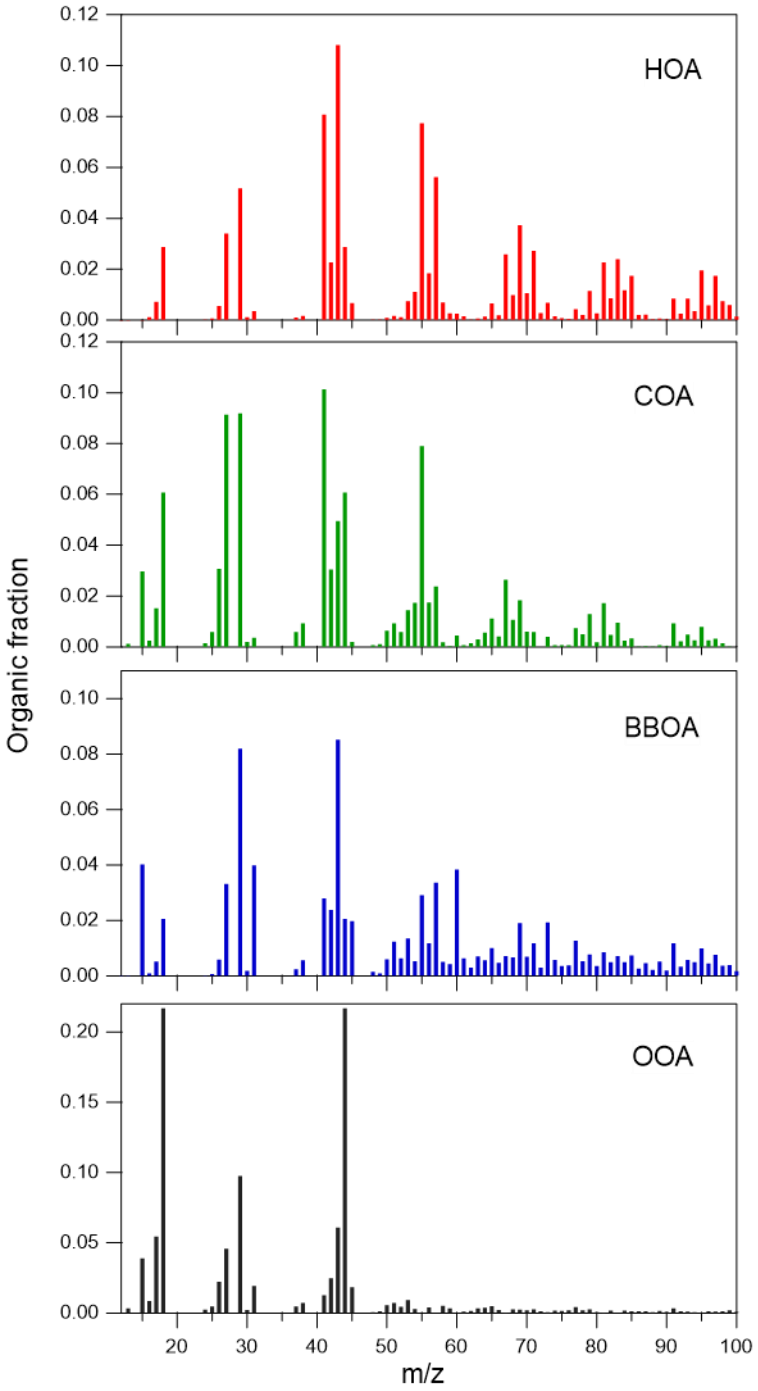

Figure S1: Organic mass spectra of the four factor PMF solution for the 30 min data resolution.

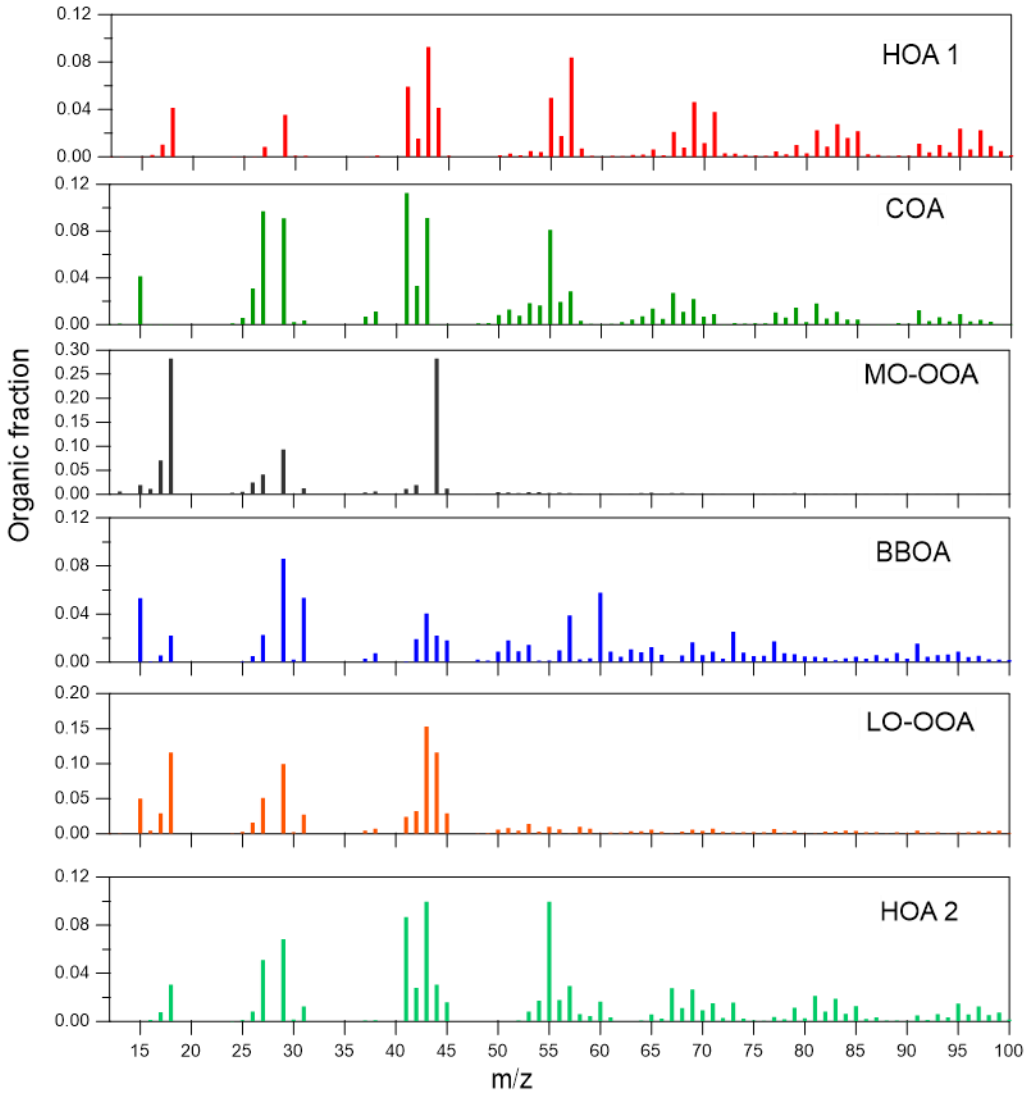

Figure S2: Organic mass spectra of the six factor PMF solution for the 30 min data resolution.

In the six factor solution an extra HOA factor was identified. The extra factor had a high *m/z* 55/57 ratio which is usually an indicator of COA emissions. However, the mass time series of the extra factor was in better agreement with HOA, than with COA so it was identified as an HOA factor. Also the *m/z* 41/43 ratio in the mass spectrum is below one which is also an aspect of HOA spectra. In COA spectra this ratio is usually above one.

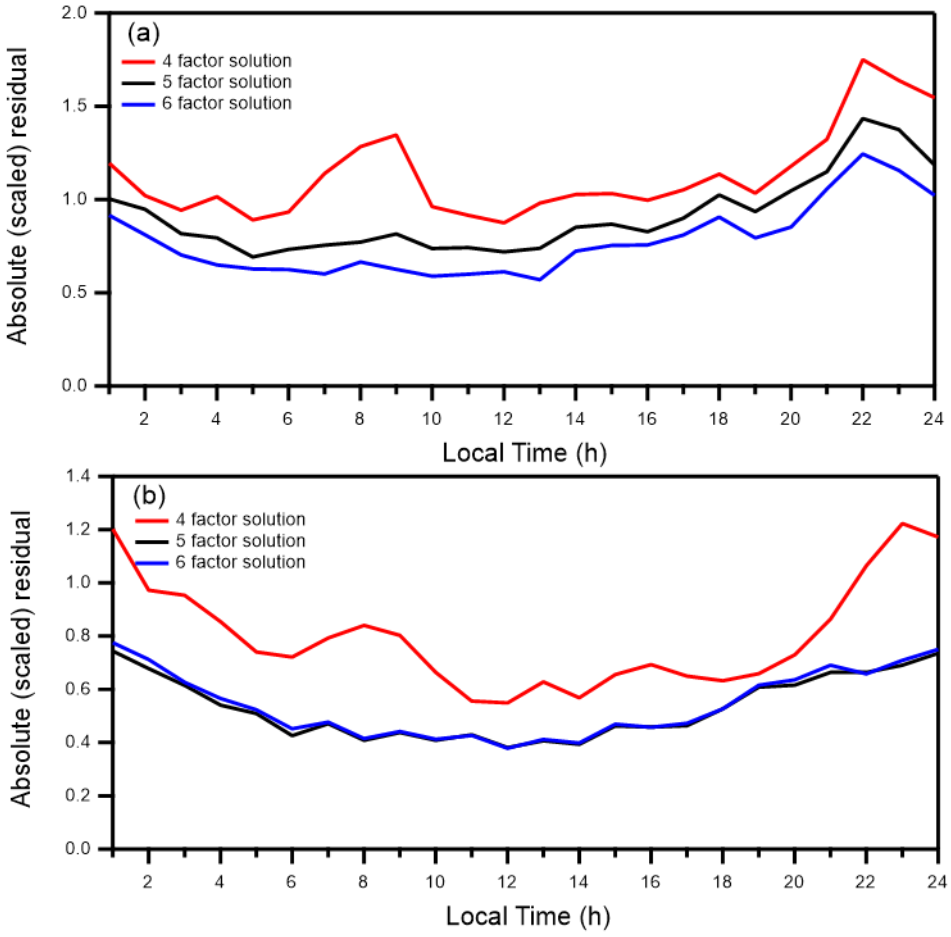

Figure S3: Diurnal profile of the absolute scaled residual of the (a) *m/z* 55 fragment (b) *m/z* 60 fragment.

The number of factors that could represent the total OA was chosen based both on the residuals and the physical meaning of the solutions. The 30 min resolution four factor solution identified an HOA, a COA, a BBOA and an OOA factor. The residuals of specific parameters (*m/z* 55, 57) showed a diurnal variation with a maximum peak at the morning rush hours. This morning peak in the residuals was not present in the five factor solution. The same behavior between the four and the five factor solution was observed in the evening hours for the *m/z* 60 residuals. For that reason the five factor solution was preferred to the four factor solution. In the five factor solution the OOA was separated into two factors, a more oxidized OA (MO-OOA) and a less oxidized OA (LO-OOA). The two oxidized factors were separated due to the different atomic Oxygen to Carbon ratio (O:C). MO-OOA had an O:C=1.09 while the LO-OOA O:C

was 0.32 (Canagaratna et al., 2015). The six factor solution did not give a significant reduction in the residuals. Also there was not identified an extra information about the origins of the OA. The additional factor was an extra HOA.

2. PMF solution for the period November 2016- March 2017 (30 min resolution)

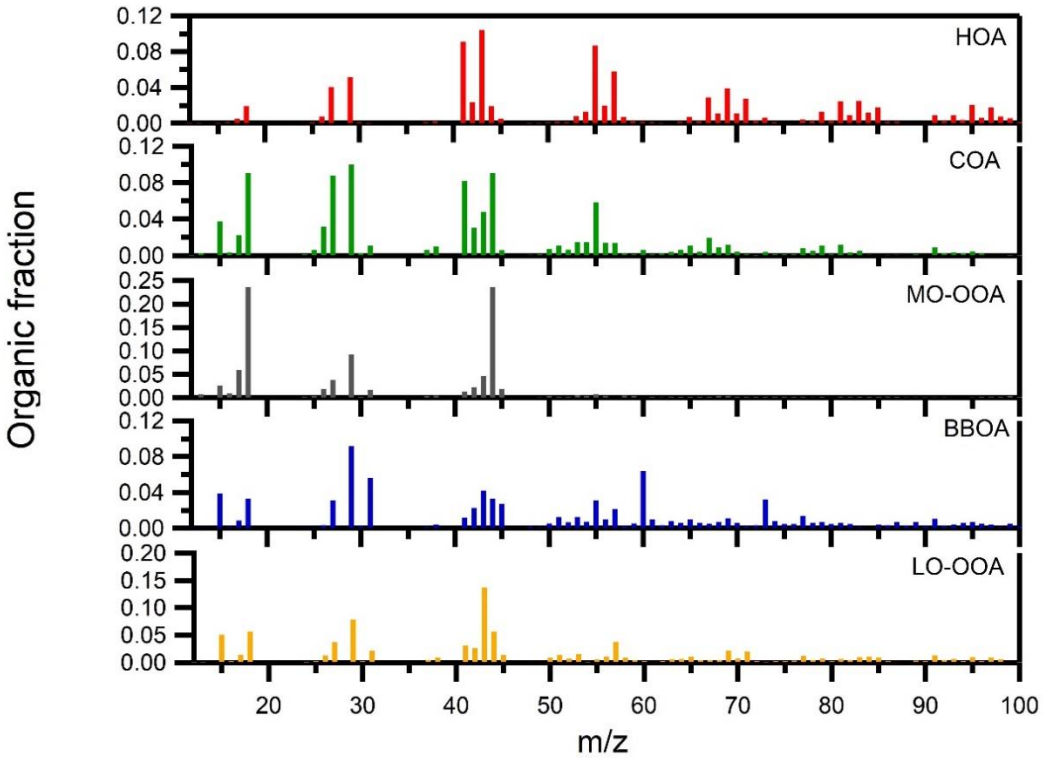

Figure S4: Organic mass spectra of the five factors for the 30 min solution.

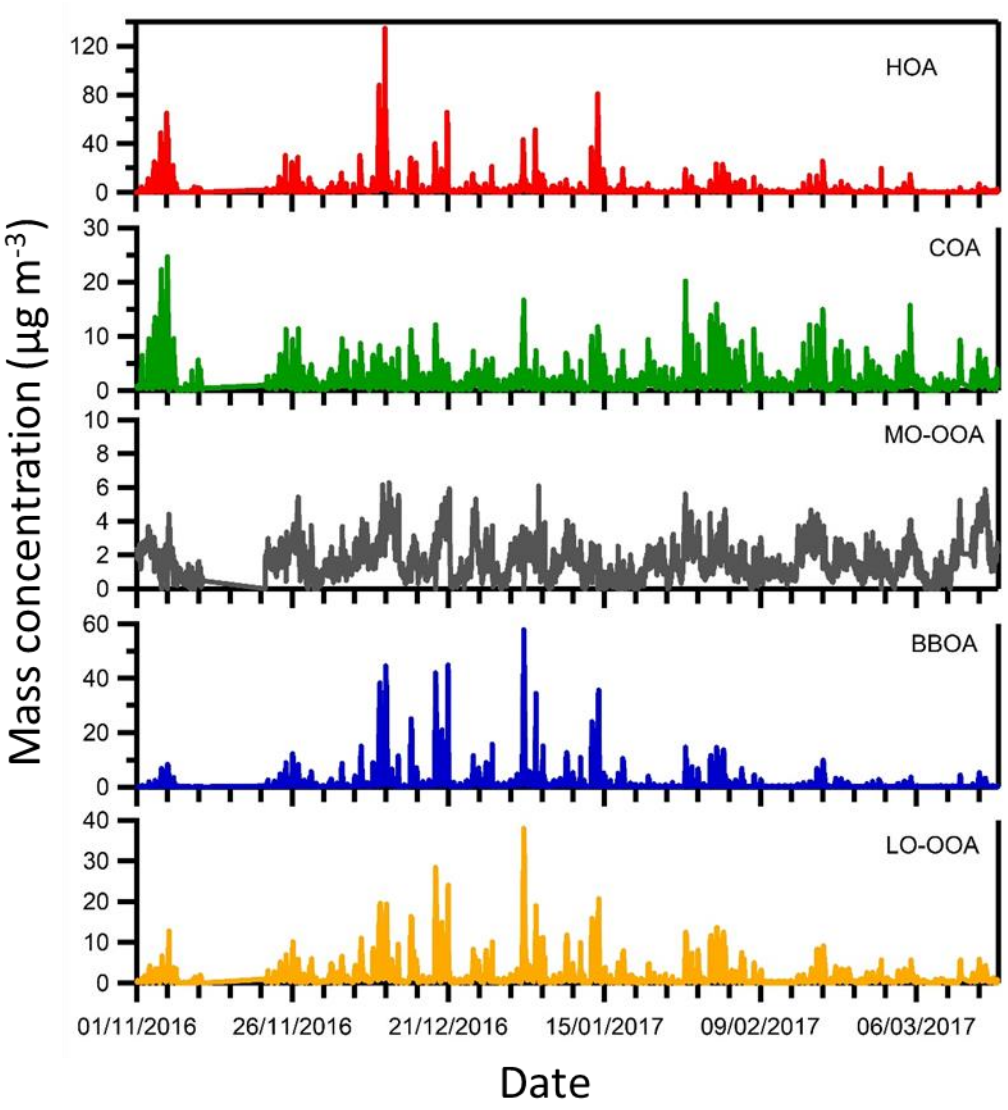

Figure S5: Mass time series of the five factors for the 30 min solution.

3. Comparisons of 30 min PMF solution with the Stavroulas et al. (2019) unconstrained solution.

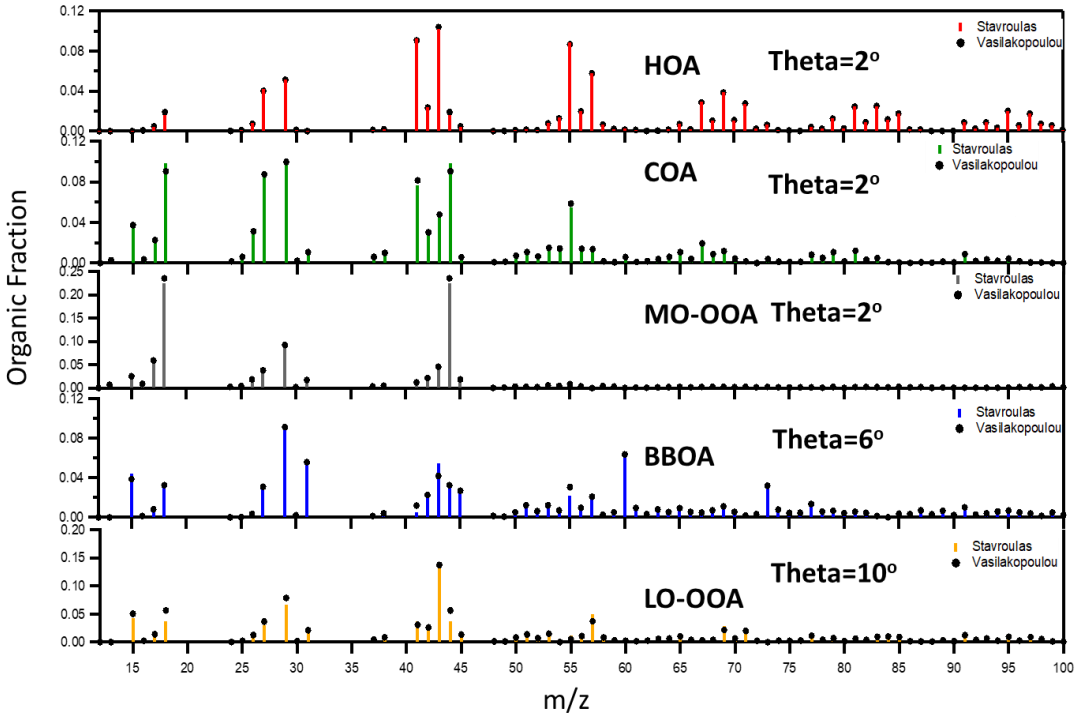

Figure S6: Comparison of the 30 min spectra with published results.

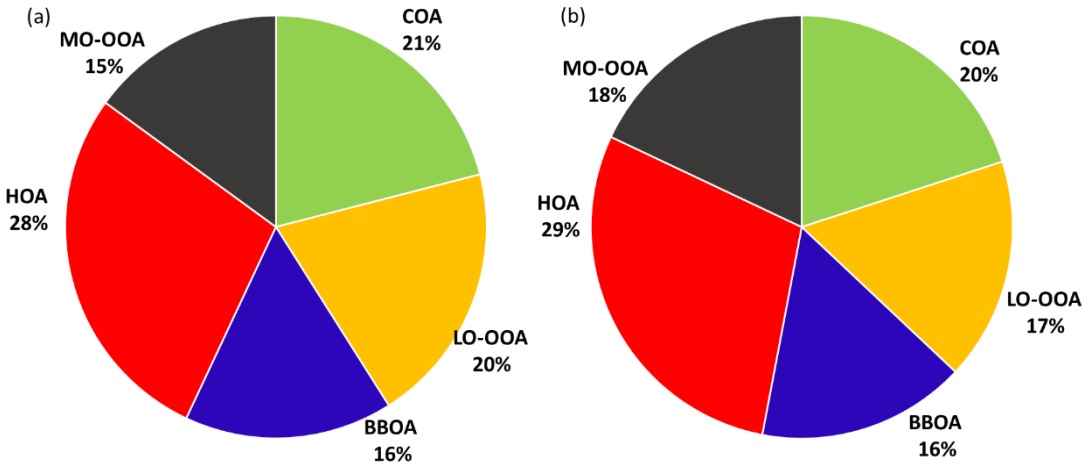

Figure S7: Contribution of each factor to the total OA for the 30 min PMF solution for the study by: (a) Stavroulas et al. (2019) and (b) the present study.

4. Spectra comparisons between different time resolution data

The highest angle calculated between the different resolution HOA spectra with the 30 min ones was 19^{o} (for the 10 h resolution). All the specific HOA markers (55, 57, 67 and 69) appeared in every averaging interval, making the identification of the HOA factor possible. For COA the highest angle was 26^{o} (for the 6 h resolution) and for BBOA 22^{o} (daily resolution). This indicates that the spectra were quite different from the 30 min spectrum in these cases. Once more the specific COA (*m/z's* 41, 43) and BBOA (*m/z's* 60, 73) markers appeared in every case, allowing the identification of these factors. The MO-OOA spectrum remained similar to the 30 min spectrum during the time averaging, with the highest angle observed being 11^{o} (for daily resolution). On the other hand the LO-OOA spectrum changed a lot, with a maximum angle of 30^{o} for the comparison between the 24 h and 30 min results. Once more the specific LO-OOA markers (*m/z's* 43, 44) appeared in every averaging interval. Noteworthy also was the fact that the m/z 44 contribution to the primary factors did not increase with the reduction of the temporal resolution. In Fig. S8 the comparisons between the 30 min and the daily resolution spectra are shown.

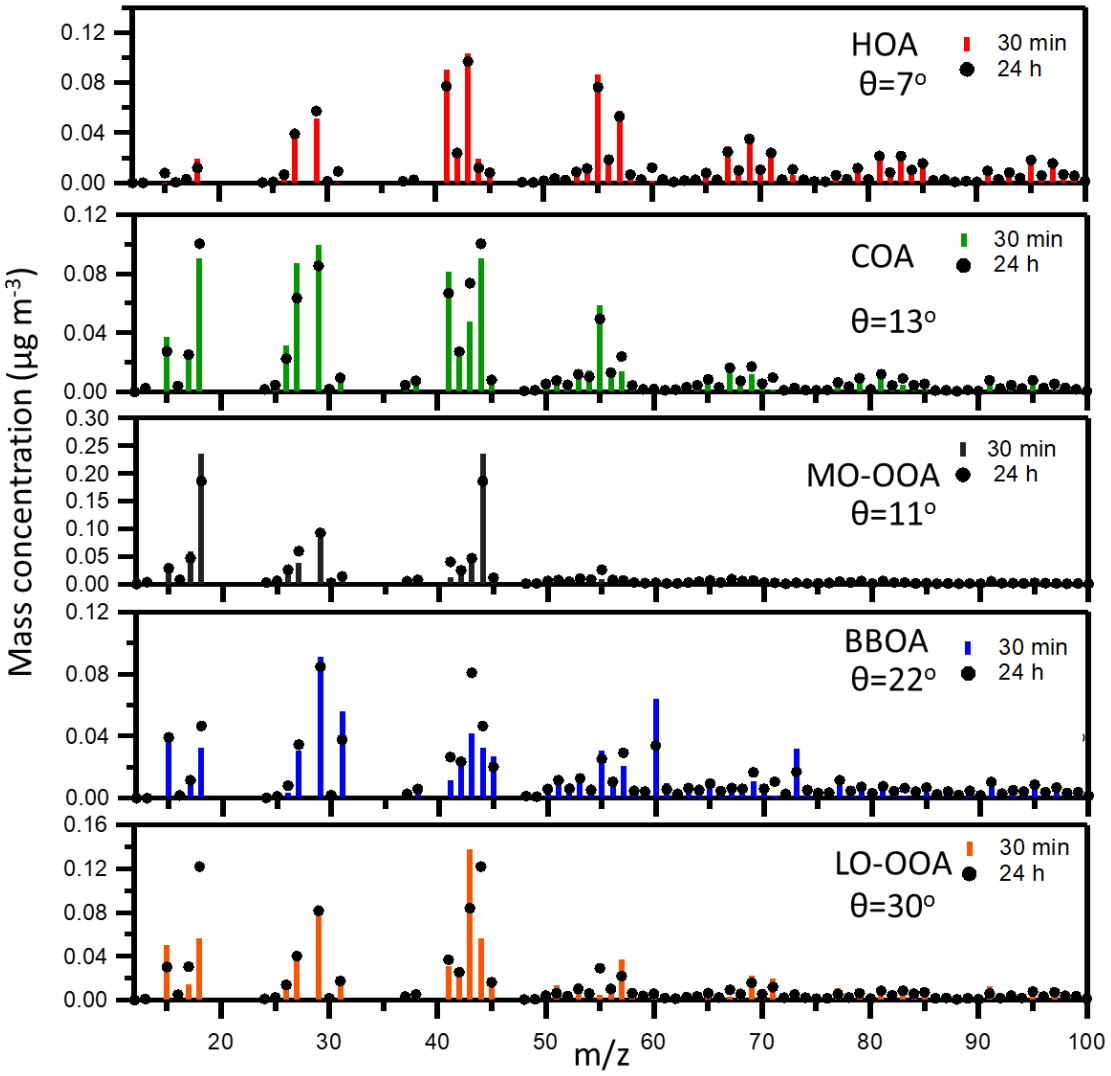

Figure S8: Spectra comparison between the 30 min and the daily resolution. The theta angle is also depicted. Different y axes are used.

5. O:C of secondary factors

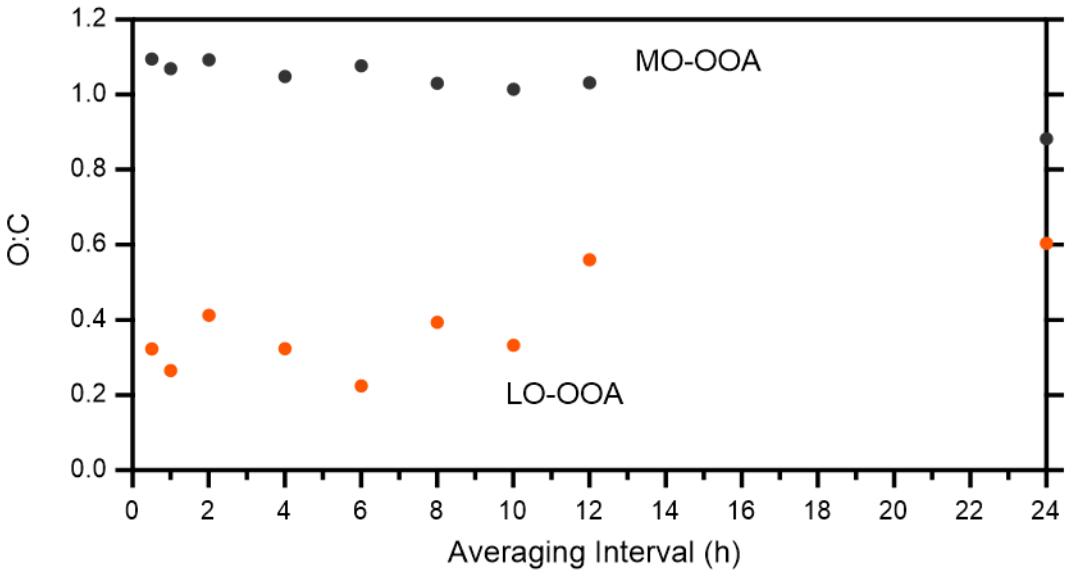

Figure S9: Atomic oxygen to carbon ratio of the two secondary factors for the different averaging intervals used in the PMF analysis.

References

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T. and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: Characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253–272, doi:10.5194/acp-15-253-2015, 2015.