



Supplement of

The effect of the averaging period for PMF analysis of aerosol mass spectrometer measurements during offline applications

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Number of samples
6150
3035
1517
759
506
379
305
253
127

Table S1: Number of samples used in PMF^a for the period 1 November-18 March for all temporal resolutions.

^a 98 m/z values were used for the analysis at all temporal resolutions

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



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

In the six factor solution an additional HOA factor was identified. The additional factor had a high m/z 55/57 ratio which is usually an indicator of COA emissions. However, the concentration time series of the additional factor was consistent the expected behavior of HOA, than with COA so it was assumed to be another HOA factor. Also the m/z 41/43 ratio in the mass spectrum was below one which is also a characteristic 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 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 comparing 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 compared 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 O:C of the LO-OOA was 0.32

(Canagaratna et al., 2015). Moving to a six factor solution did not result in a significant reduction in the residuals. Also there was no additional information about the sources of OA. The additional factor was one more HOA factor.



S2. 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: Concentration time series of the five factors for the 30 min solution.





Figure S6: Comparison of the 30 min spectra with published results by Stavroulas et al. (2019) for the same dataset.



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

S4. Comparisons of PMF spectra using different time resolution data

The highest angle calculated between the different resolution HOA spectra with the 30 min ones was 19° (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° (for the 6 h resolution) and for BBOA 22° (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° (for daily resolution). On the other hand, the LO-OOA spectrum changed significantly, with a maximum angle of 30° 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.



Figure S8: Spectra comparison between the 30 min and the 2 h PMF results.



Figure S9: Spectra comparison between the 30 min and the 4 h PMF results.

S5. Days with high OA concentration periods ("spikes")



Figure S10: Measured OA concentration (30 min resolution) during the five-month period examined in the study. The seven highest observed 30 min OA concentrations ("spikes") are marked with the corresponding numbers.



Figure S11: Measured OA concentration (30 min resolution) during December 9, 2016 during which the OA reached a value of approximately 150 mg m⁻³ at midnight. This is day 1 in Figure S10.



Figure S12: Comparison of the estimated contribution of each source to the total OA using 30 min and 24 h temporal resolution during 9 December 2016 (day 1 in Figure S10).

S6. Constrained Solution

All three primary factors were constrained in this analysis. We adopted the anchor profiles and the a-values of Stavroulas et al. (2019). That study examined the same ACSM dataset. More specifically the HOA and BBOA factors were constrained using the reference factor profiles of Ng et al. (2011b) (a=0.1 for HOA and 0.4 for BBOA), and the COA factor was constrained using the Crippa et al. (2013) spectrum and a=0.2.

S6.1 Constrained vs Unconstrained Solution for the high temporal resolution (30 min) results



Figure S13: Comparison of constrained and unconstrained PMF analysis mass spectra derived from the 30 min PMF solutions.



Figure S14: Comparison of the contribution of each factor to the total OA between the constrained and the unconstrained 30 min PMF solution.



S6.2 Constrained versus unconstrained Solution for the low temporal resolution results (24 h)

Figure S15: Comparison of constrained and unconstrained mass spectra derived from the 24-h PMF solution.



Figure S16: Comparison of the contribution of each factor to the total OA between the constrained and the unconstrained 24 h PMF solution.



S6.3 Constrained solution (30 min vs 24 h)

Figure S17: Comparison of the constrained spectra derived from the PMF solution for the 30 min and the 24 h temporal resolution analyses.



Figure S18: Comparison of the contribution of each factor to the total OA between the 30 min and the 24 h constrained PMF solution.



S7. Bootstrap analysis for the 24 h PMF results

Figure S19: Results of the bootstrap results for the average PMF source concentrations using the 24 h data.



S8. 24-h PMF results: geometric average calculation of the error matrix

Figure S20: Comparison of the contribution of each factor to the total OA using two different averaging approaches (geometric and arithmetic average) for the error matrix calculation.



Figure S21: Comparison of the spectra of each factor estimated by PMF using the geometric (black symbols) and the arithmetic average (red bars) error.



S9. Analysis of Low and High Concentration Periods

Figure S22: Comparison between the results of the 24 h analysis and the daily averages of the 30 min analysis for each primary factor for the low and the high concentration days. The 1:1 lines are shown. Different axes are used.



Figure S23: Comparison between the results of the 24 h analysis and the daily averages of the 30 min analysis for each secondary factor for the low and the high concentration days. The 1:1 lines are shown. Different axes are used.