Supplementary Material 1 1

2 Weighting *m/z* 29 for PMF analysis 1.1

Since it was not clear whether the signal at m/z 29 was partly an artefact due to a leakage in 3 4 the vacuum chamber, this mass to charge ratio was downweighted. Given the case of a 5 leakage, more air molecules would be available to produce a signal predominantly at m/z 28 (N_2^+) . This would result in an elevated baseline influencing the neighbor m/z 29 which in turn 6 7 would be overestimated.

8 When not downweighting m/z 29 a six factor PMF solution seemed to best meet the criteria of 9 a minimum Q/Q_{exp} . However, one factor mainly consisting of m/z 29 (62.3 %) and m/z 44 (9.5 10 %) was derived. This factor, based on only two mass to charge ratios and based to more than 11 50 % on m/z 29 was not trusted, due to steps in the signal intensity occurring in the time series 12 (see Fig. S1). To test whether this factor might be an artefact, m/z 29 was downweighted by a 13 factor 100 and 1000. The factor profile disappeared when downweighting by either factor. 14 Table S1 shows the relative differences between downweighting by a factor 100 or 1000 in 15 the time series and mass spectra for the five factor solution at fpeak = 0 and seed = 0. For the 16 final analysis m/z 29 was downweighted by a factor of 1000.

Fig. S1: Time series and mass spectrum of the m/z 29 dominated factor 17



Factor	relative difference 100/1000 in mass spectra (%)	relative difference 100/1000 in time series (%)
MSA-OA	2.15	0.36
AA	1.68	0.71
M-OOA	1.04	1.30
Sea Salt	4.06	2.59
HOA	3.02	3.19

20 Table S1: Relative difference between downweighting m/z 29 by a factor 100 or 1000

23 **1.2** Key diagnostic plots for the PMF 5 factor solution

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25 The change in slope of the Q/Q_{exp} vs. the number of PMF solutions curve between factors 4 26 and 5 (see Fig. S2 a) indicates that at least 5 factors should be considered. The Q value or 27 "PMF quality of fit parameter" (Zhang et al., 2011) refers to the sum of weighed square 28 residuals. Five factors were chosen, because factor splitting was identified in the solutions 29 using 6 or more factors (see Fig. S3). For example, factor 1 (count upwards from bottom) in 30 the 5-factor solution is split into factors 1 and 2 in the 6-factor solution, as the time series clearly show (cf. Figs. S3c and S3e). Also, the correlation between the two mass spectra is 31 32 very high at 99 % (not shown). In the 5-factor solution, factor 1 contributes 23.5 % of the 33 mass, while factors 1 and 2 contribute 17.8 and 12.2 % in the 6 factor solution. The 7-factor 34 solution yields factors that do not represent meaningful OA aerosol mass spectra, where e.g., m/z 28 and 44 make up 50 % of the mass. Choosing only 4 factors results in factors 3 and 5 35 36 from the five factor solution being merged. Factor 5 in the 5-factor solution was identified as hydrocarbon-like OA (HOA), based on the high correlation ($R^2 = 0.92$) with the reference 37 mass spectrum (A-DEC-Q-015) of the AMS UMR database, based on Ng et al. (2011). When 38 39 only 4 factors are chosen, the correlation to the HOA reference spectrum decreases to $R^2 = 0.76$. The additional profile in the 5-factor solution, which was identified as marine 40 oxygenated OA (M-OOA), has a low correlation with the HOA reference spectrum (R^2 = 41 42 0.10), so that the separation of the factors is meaningful. Also, the time series of factors M-OOA and HOA have a correlation coefficient of $R^2 = 0.12$ (see Fig. S2 d), so that a 5-factor 43 44 solution is plausible. All time series' correlation coefficients are in the range between -0.25 and 0.34 (R² between 0.06 and 0.12), while the mass spectrum R ranges between 0.14 and 45 $0.59 (R^2$ between 0.02 and 0.35). The relatively high correlations in the mass spectra between 46 47 factors 1 and 2 as well as 2 and 3 (see Fig. S2 d) are based on the relatively high contributions 48 of m/z 28, 29 and 44 to the signals. Other marker fragments, however, do not coincide.

The chosen final *fpeak* is 0, where Q/Q_{exp} is at a minimum (see Fig. S2c). All other values of *fpeak* between -1 and 0.2 show only rotational ambiguity in the 5-factor solution, while *fpeak* > 0.2 introduces a factor consisting to 80 % of m/z 29, which does not represent a meaningful chemical mass spectrum. Fig. S2 f) shows that this factor starts to dominate the contributions to the total reconstructed mass of OA. The Q/Q_{exp} value < 1 at *fpeak* = 0 indicates that the error matrix was somewhat overestimated which is consistent with downweighting m/z 29 by a factor of 1000. *Seed* 0 has been chosen to represent the final 5-factor solution, as Q/Q_{exp} is very stable over the whole range of tested *seeds*. Also, the contribution of each factor to the total organic mass when varying *seeds* does not vary significantly (see Fig. S2b).

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Fig. S2: a) Q/Q_{exp} as a function of the number of factors (*P*) used in the PMF analysis; the yellow circle denotes the best solution presented in this work b) Q/Q_{exp} as a function of seeds between 0 and 50 in steps of two, c) Q/Q_{exp} as a function of *fpeaks* between -1 and 1 in steps of 0.2, d) Pearson's correlation coefficient for time series and mass spectra for the 5 factor solution, e) variation of factor contributions to total OA as a function of *seeds*, f) variation of factor contributions to total OA as a function of *fpeaks*.



- 67 Fig S3: Comparison between the time series and mass spectra of the 4 (a,b), 5 (c,d) and 6 (e,f)
- 68 factor PMF solutions







Fig. S4: **a**) scaled residuals for each m/z, the horizontal bars indicate the median while the boxes represent the interquartile, **b**) comparison time series of the reconstructed OA (sum of the five factors) and the measured OA, **c**) sum of the residuals (measured – reconstructed) of the fit, **d**) Q/Q_{exp} for each time step, and **e**) Q/Q_{exp} for each mass to charge ratio



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1.3 Estimation of uncertainty of PMF results as a function of *fpeak* and *seeds* 80 variations

For the mass spectrum averages only m/z between 12 and 130 were considered as heavier ion fragments were not significant contributors to the factors. All mass concentrations (at each m/z and at each point in time) that were smaller than 0.0001 µg m⁻³ or greater than 1 µg / m³ were excluded from the calculations. The low values add high uncertainties to the factors while the large values reflect peaks that may bias the results of the statistical analysis.

86 Table S2 shows the relative standard deviation from the mean for each factor in mass 87 spectrum and time space for varied *fpeaks* and *seeds*. The *seed* variation has very little 88 influence on the uncertainty of each individual factor. Factor 2 MS seed variation experiences 89 the largest variability with 4.67 %. The *fpeak* variation however has larger influence on the stability of the factors for both time series and mass spectra. The variability ranges between 90 91 17 and 38 % with two extreme cases for factor 1 mass spectra (75.9 %) and factor 3 time 92 series (130.17 %). The deviations in the factor 1 mass spectrum are mainly due to the 93 variability in m/z 29 and 15 that make up 65 % of the total variability in this spectrum. The M-OOA factor is dominated by masses m/z 28 and 44 and 29 which can lead to high 94 95 variability as these fragments contribute to all factors. In addition, for fpeaks greater than or equal to 0.4 M-OOA becomes the dominating factor (see Fig. S3 f) while for example, the 96 97 MSA factor nearly disappears which is not a physically meaningful solution. This explains the 98 large variability in the time series of different *fpeak* calculations.

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100 Table S2: Relative standard deviations for each factor profile mass spectrum and time series

101 based on the variations of *seeds* and *fpeaks* and based on the statistical variations through the

102 bootstrapping method	(all numbers in %).
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Factor	seeds _{MS}	seeds _{TS}	fpeak _{MS}	fpeak _{TS}	$Bootstrap_{MS}$	$Bootstrap_{TS}$
MSA-OA	1.61	0.52	75.9	29.1	2.51	2.37
AA	4.67	0.80	28.2	31.9	3.56	2.59
M-OOA	0.54	0.69	37.4	130.2	7.92	4.26
Sea Salt	1.15	0.40	29.1	15.3	16.1	7.26
HOA	0.19	0.90	16.5	14.5	13.5	9.19