

**Supplementary information for manuscript**

**Burning of Olive Tree Branches: A Major Organic Aerosol Emission Source in the  
Mediterranean**

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## 1. GC-MS analysis and extraction procedure

Levoglucosan was extracted from the filter sample with 40 mL of ethylacetate containing 3.6 mM triethylamine under sonication for 1 hour. The extract was then filtered through a PTFE 0.2  $\mu\text{m}$  filter (PALL) and condensed by rotary evaporation to a suitable volume (approximately 1 mL, weighted in order to calculate the exact amount). An aliquot (100  $\mu\text{L}$ ) of the condensed extract was derivatised with *N*-trimethylsilylimidazole (TMSI) agent (10  $\mu\text{L}$ ) for 1 hour at ambient temperature prior to GC-MS analysis.

The GC-MS system consisted of a Shimadzu QP2010 Ultra equipped with an AOC 20i autoinjector. 1  $\mu\text{L}$  of the sample was injected at split mode (1:50). The injector was set at 250°C. The temperature program for the column (Mega 5 ms, 0.25 mm I.D., 0.25  $\mu\text{m}$  film thickness, 30 m) was as follows: 1 min at 55°C, ramp up to 270°C at 20°C  $\text{min}^{-1}$ , 0.25 min at 270°C. Helium was used as carrier gas at 1 mL  $\text{min}^{-1}$ . The temperatures for the ion source for the interface between the GC and the MS were set to 170°C and 200°C respectively. The range of 35-350 atomic mass units was acquired.

Total Ion Count (TIC) was used for the quantification of levoglucosan. The calibration curve was linear in the range between 1-50  $\mu\text{g mL}^{-1}$  ( $R^2=0.999$ ). The identification of levoglucosan was based on mass spectra and retention time of the standard compound as well as comparison with mass spectra libraries. The recovery was estimated to be 91.8% for Teflon and 90.4% for Quartz filters, based on spiked filters in the range of 10  $\mu\text{g}$  per filter. The entire Teflon filter was used for each analysis, while for the high volume Quartz filters, analysis was done at a punch of 1.5  $\text{cm}^2$ , in order to compare with Sunset OC/EC results (by using punches of the same filter). If the levoglucosan concentration was low (outside the linear range of the calibration curve) a new analysis was performed for the same filter using two or more punches.

## 2. Comparison of the fresh mass spectra between the 4 source experiments

**Table S1.** Angle  $\theta$  between the organic mass spectra of the 4 burning chamber experiments.

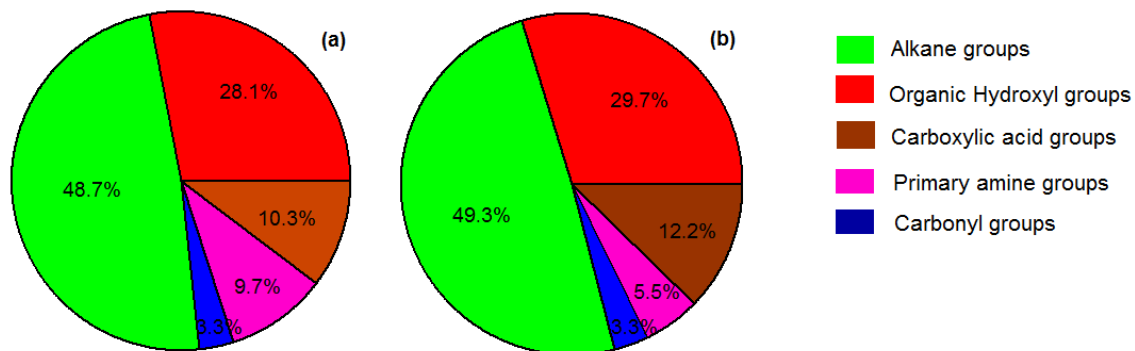
Exp Number	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
<b>1</b>	0	10.5	5.3	7.2
<b>2</b>	10.5	0	13.2	10.5
<b>3</b>	5.3	13.2	0	7.3
<b>4</b>	7.2	10.5	7.3	0

### 3. PMF Factors and their correlation with various species

**Table S2.** Correlations among PMF factors, inorganic species and selected *m/z* fragments.

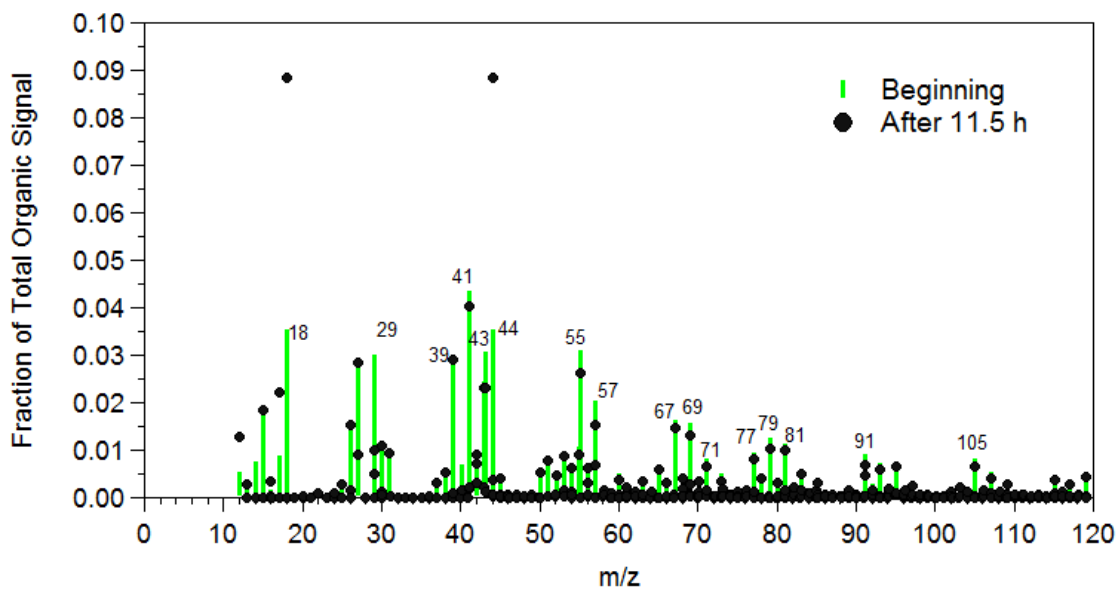
<b>R<sup>2</sup></b>	<b>OOA</b>	<b>HOA</b>	<b>otBB-OA</b>
Ammonium	0.73	0.00	0.04
Sulfate	0.58	0.00	0.00
Organics	0.32	0.29	0.63
Nitrate	0.14	0.08	0.61
Chloride	0.01	0.08	0.53
Potassium	0.16	0.07	0.34
CO <sub>2</sub> <sup>+</sup> (m/z 44)	0.87	0.02	0.19
<b>C<sub>n</sub>H<sup>+</sup><sub>2n-1</sub></b>			
C <sub>2</sub> H <sub>3</sub> (m/z 27)	0.30	0.14	0.74
C <sub>3</sub> H <sub>5</sub> (m/z 41)	0.08	0.41	0.69
C <sub>4</sub> H <sub>7</sub> (m/z 55)	0.01	0.79	0.43
C <sub>5</sub> H <sub>9</sub> (m/z 69)	0.00	0.92	0.27
<b>C<sub>n</sub>H<sup>+</sup><sub>2n+1</sub></b>			
C <sub>2</sub> H <sub>5</sub> (m/z 29)	0.09	0.40	0.70
C <sub>3</sub> H <sub>7</sub> (m/z 43)	0.01	0.88	0.33
C <sub>4</sub> H <sub>9</sub> (m/z 57)	0.00	0.97	0.18
<b>C<sub>n</sub>H<sub>2n-3</sub>O<sup>+</sup></b>			
C <sub>2</sub> HO (m/z 41)	0.19	0.02	0.01
C <sub>3</sub> H <sub>3</sub> O (m/z 55)	0.27	0.10	0.73
C <sub>4</sub> H <sub>5</sub> O (m/z 69)	0.43	0.02	0.66
<b>C<sub>n</sub>H<sub>2n-1</sub>O<sup>+</sup></b>			
CHO (m/z 29)	0.00	0.00	0.03
C <sub>2</sub> H <sub>3</sub> O (m/z 43)	0.58	0.05	0.52
C <sub>3</sub> H <sub>5</sub> O (m/z 57)	0.23	0.07	0.83
Levogluconan			
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> (m/z 60)	0.14	0.07	0.87
C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> (m/z 73)	0.14	0.08	0.87
<b>C<sub>n</sub>H<sup>+</sup><sub>n-2</sub></b>			
C <sub>3</sub> H (m/z 37)	0.43	0.07	0.65
C <sub>4</sub> H <sub>2</sub> (m/z 50)	0.38	0.08	0.70
C <sub>5</sub> H <sub>3</sub> (m/z 63)	0.28	0.09	0.78
C <sub>6</sub> H <sub>4</sub> (m/z 76)	0.33	0.09	0.70
C <sub>7</sub> H <sub>5</sub> (m/z 89)	0.23	0.08	0.81
C <sub>8</sub> H <sub>6</sub> (m/z 102)	0.16	0.08	0.79
C <sub>9</sub> H <sub>7</sub> (m/z 115)	0.12	0.17	0.88

#### 4. FTIR filter composition for experiment 2



**Figure S1.** otBB-OA organic functional group composition from FTIR analysis for experiment 2 (a) for the sample taken directly from the olive tree branches fire and (b) from the chamber the first hour of the experiment. One difference is the carboxylic acid contribution, where the fresher particles contain less carboxylic acids, 10.3%, than the 1 hour aged particles 12.2%.

## 5. Comparison of mass spectra during experiment 2



**Figure S2.** The HR mass spectra at  $t=0$  and  $t=11.5$  h for experiment 2. The  $f_{44}$  has increased while the hydrocarbon parts of the  $f_{m/z}$ 's: 29, 39, 41, 43, 55, 57, 67, 69, 71 etc. have decreased.

## 6. PMF analysis

We investigated the solutions using 1 to 5 factors. Figures S3 and S4 illustrate the model residuals for 1 to 5 factor solution. Moving from 1 to 2 and from 2 to 3 factors the reduction in the residuals is significant. For the 4-factor solution the residuals are lower only during 16 February 2012 (Figure S4a and S4c). This day was Fat Thursday in Greece characterized by wide-spread barbecuing in Patras, so one would expect additional OA sources. The angle  $\theta$  between the otBB-OA (4 solution factor) and the average otBB-OA mass spectrum from the chamber was calculated (Figure S5) and the best correlation ( $\theta < 10$  degrees) found between  $f_{peak}$  -2 and -0.6. However, in this range the mass spectra of the OOA and the fourth (probably COA) factor are becoming identical (Figure S6). This implies that the 4 factor solution splits the OOA mass spectra into 2 almost identical factors. For  $f_{peak}$  -0.4 and 2, the fourth factor has a resemblance with other COA mass spectra e.g. from SIRTAs and LHVPs, during the winter 2010 MEGAPOLI campaign in Paris, (Crippa et al., 2013) as the angle  $\theta$  is 27 degrees (Figure S7). Even more the time series of the otBB-OA and the COA factor correlate each other as the  $f_{peak}$  increases (Figure S8). This means that in the  $f_{peak}$  range between -0.4 and 2 the PMF tries to create a COA factor but “destroys” in the process the otBB-OA factor. Given the fact that both of them are primary sources PMF rather mixes them instead of deconvoluting them.

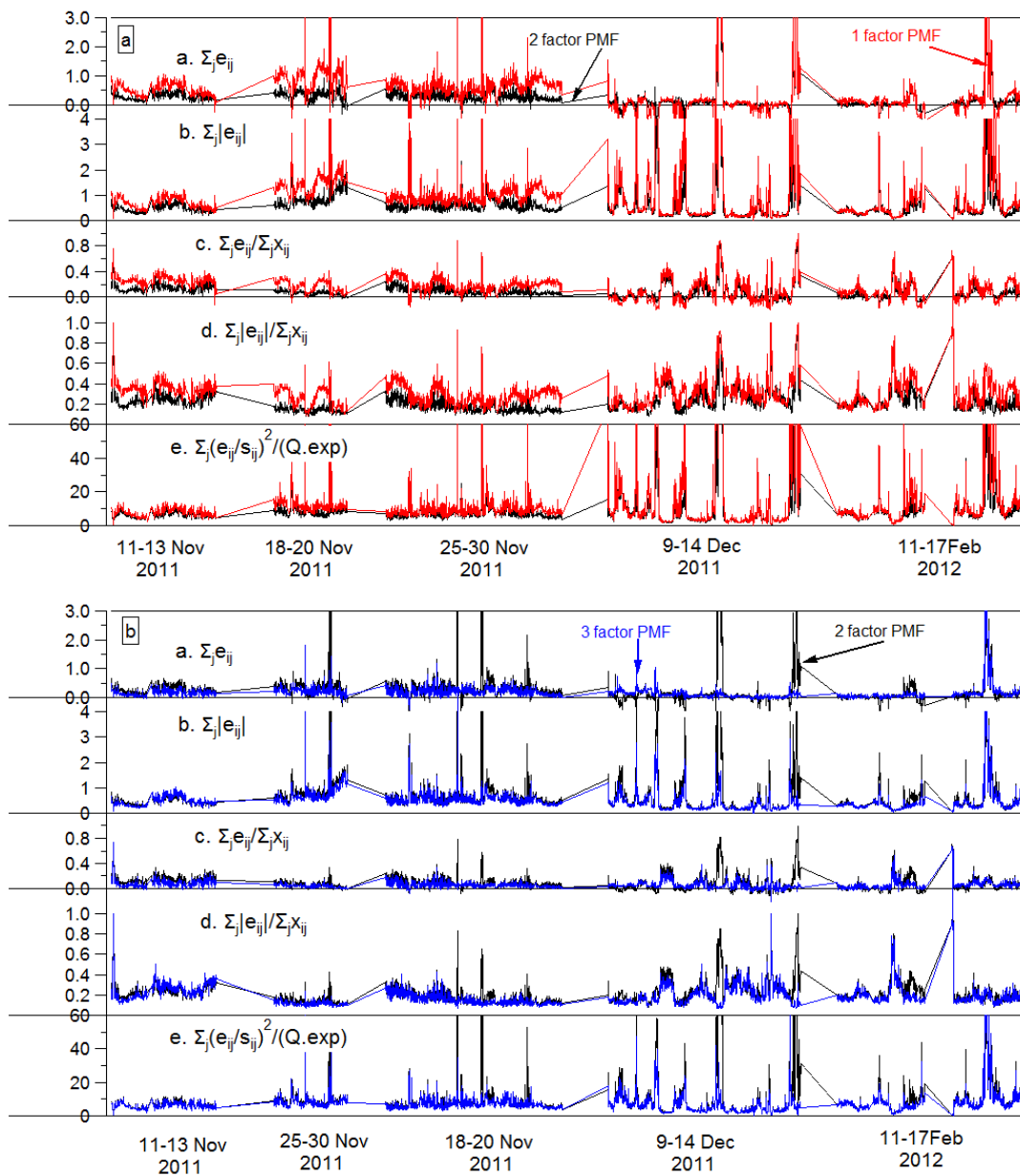
Performing the PMF analysis excluding the Fat Thursday data (12 hours out of a total of 20 days) the 3 factor solution does not practically change compared to the initial selected solution that included the Fat Thursday inputs. The 4 factor solution splits the OOA spectrum into 2 identical spectra for  $f_{peak}$  -2 to 2 (Figure S9). This implies that there is no COA factor in our data except for the day of the Fat Thursday and that the 12 hours of cooking aerosol emissions rather leads to artifacts, probably due to their small contribution in the whole data set (2.5% of to total data). The Q/Qexp including and excluding the Fat Thursday data is presented in Figure S10.

Doing the PMF analysis for the last 3 days, including the Fat Thursday, the 3 factor solution results in 3 mass spectra: OOA, otBB-OA and a mixture of HOA and COA. Moving to 4 factors we have 2 cases: (a) For  $f_{peak}$  in the range -2 to 0.6, the OOA and otBB-OA mass spectra are very close to the OOA and otBB-OA from the 3 factor solution excluding the Fat Thursday ( $R^2=0.99$  and  $0.98$  correspondingly). However, the HOA mass spectrum has changed ( $R^2=0.6$  in comparison with the HOA excluding the Fat Thursday) and the COA does not correlate well with the literature COA spectra

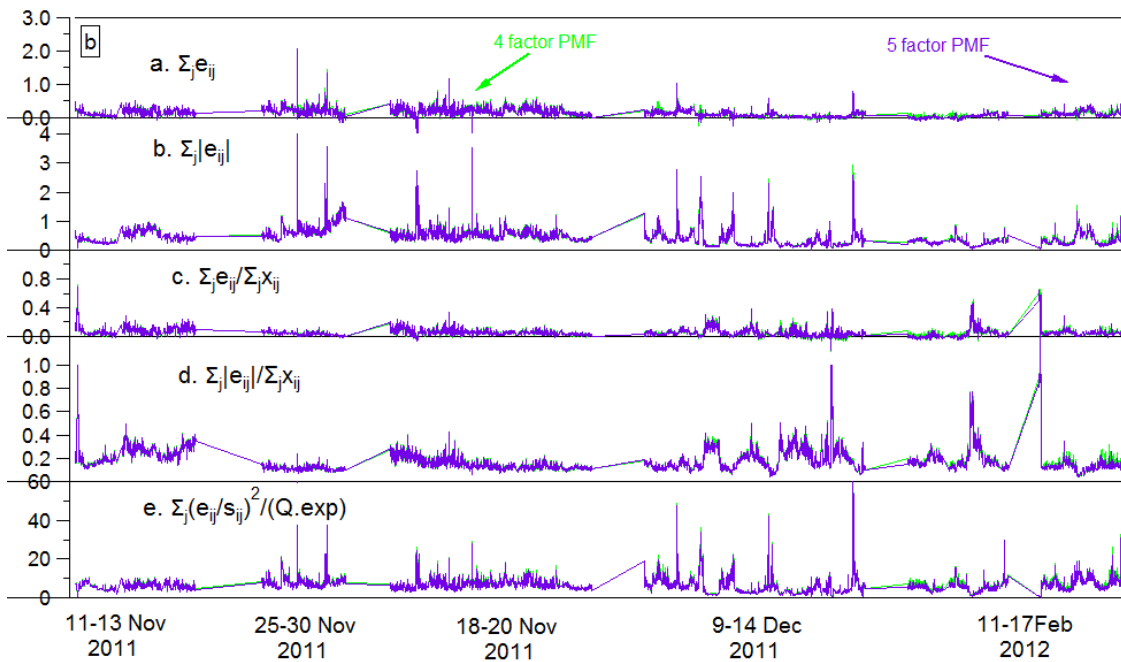
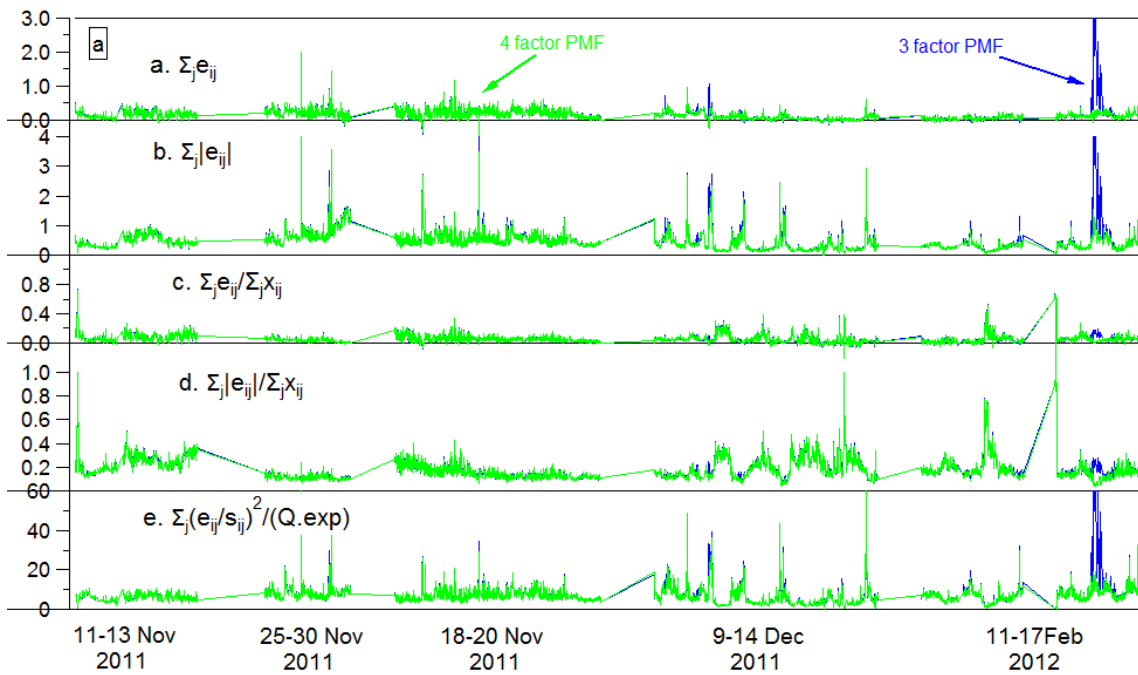
(maximum  $R^2=0.4$ ). Moreover the COA and HOA mass spectra are quite similar to each other ( $R^2=0.82$ ). (b) For  $f_{peaks}$  between 0.8 and 2 the COA and HOA mass spectra are becoming more independent ( $R^2=0.63-0.53$ ), but the otBB-OA mass spectrum differs from the chamber otBB-OA mass spectrum ( $R^2=0.78-0.73$ ) and the COA time series highly correlates the HOA time series ( $R^2=0.91$ ). This indicates that the extraction of a COA factor is leading to artifacts given the small amount of cooking emissions in our overall data set. So, we discuss the characteristics of the 3 factor solution from all the 20 days, but we will not apply this solution to the 12 hours of the Fat Thursday.

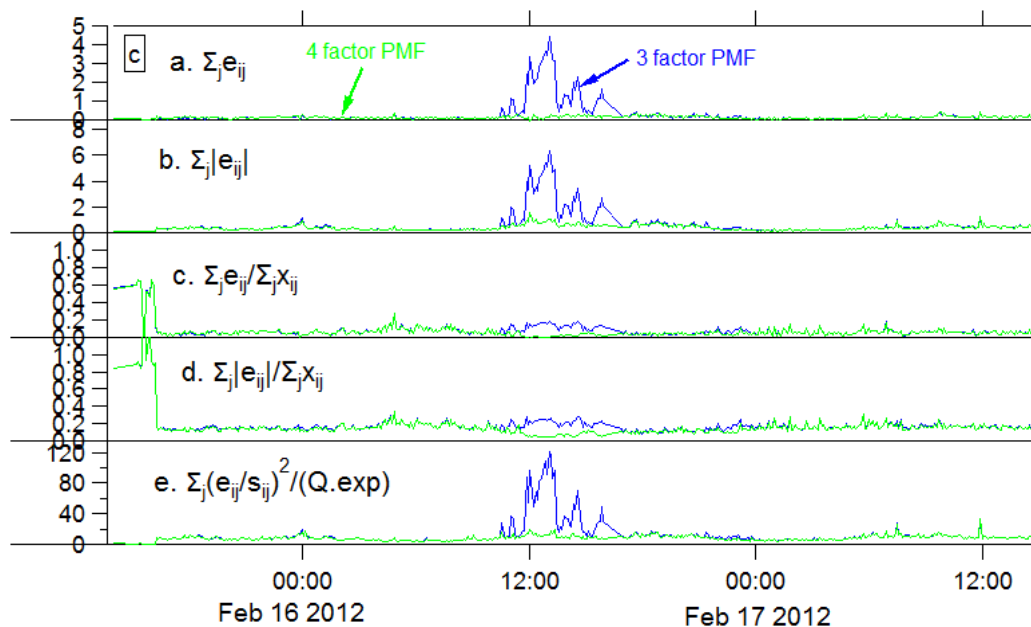
The selection of the  $f_{peak}$  was based on the structure of the deconvoluted mass spectra and correlation by comparison between the factor time series and various tracers. First we investigated the correlation  $R^2$  between the times series of the 3 factors (i.e. OOA, HOA and otBB-OA) with external tracers like sulfate, ammonium, potassium and chloride (Figure S11a). In the range of  $f_{peaks}$  -2 to 2 the  $R^2$  between OOA and sulfate, OOA and ammonium, otBB-OA and potassium and otBB-OA and chloride is very small and it is rather difficult to select an appropriate  $f_{peak}$ . We also checked the time series correlation between the 3 factors with each other (Figure S11b). All the  $R^2$  values were below 0.1. However the  $R^2$  between the times series of HOA and otBB-OA has a discontinuity at  $f_{peaks}=0$  and 0.2, with lower correlation for the negative  $f_{peaks}$  (approximately the half compared to the positive  $f_{peaks}$ ). This could be a first indication that the  $f_{peak}$  should be negative. Another criterion could be the comparison between the average otBB-OA mass spectrum (obtained from the 4 experiments) and the PMF otBB-OA mass spectrum, as shown in Figure S11c for  $f_{peaks}$  in the range -2.0 to 2.0. The angle  $\theta$  was less than 17 degrees in all cases so the spectra resembled each other for all  $f_{peak}$  choices. The 2 mass spectra become very alike in the negative  $f_{peak}$  region. Any of these  $f_{peaks}$  (-2 to 0) could be candidates for the final solution. We would not choose an  $f_{peak}=0$  because there is a discontinuity between  $f_{peak}=0$  and 0.2 and these  $f_{peaks}$  are the limits of 2 different solutions. We prefer not to select a solution on a limit but a solution right next to it. Between  $f_{peaks}=-0.6$  and 0 there is no change in the mass spectra ( $R^2=0.999$ ) and the time series between the same factors each other for the  $f_{peaks}$  above.



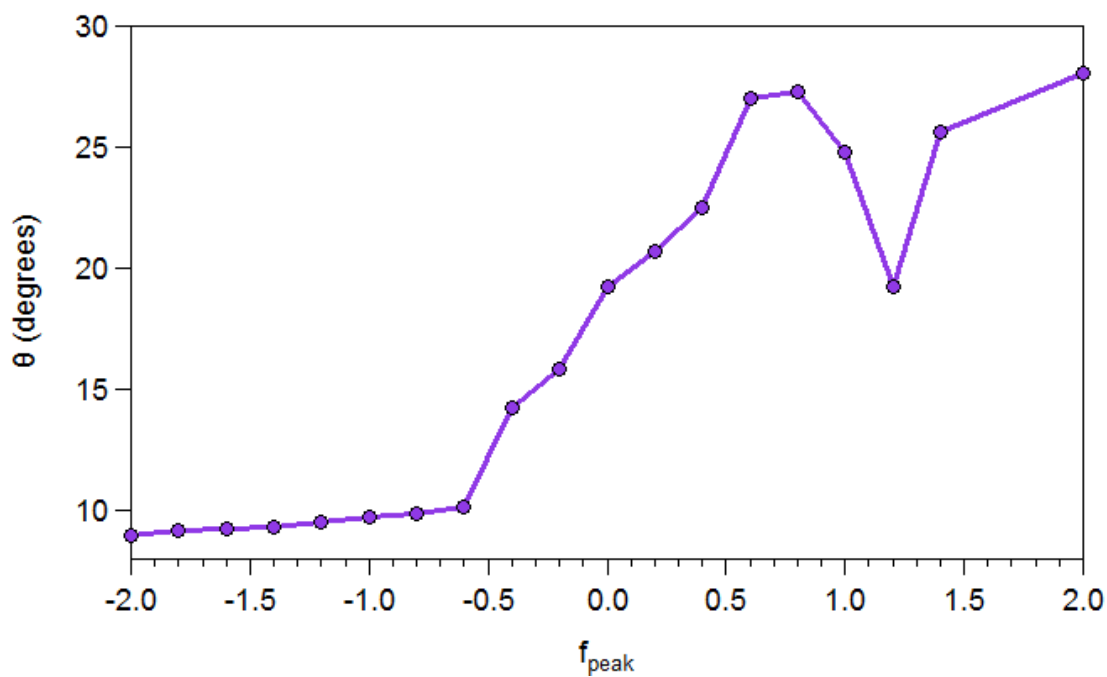


**Figure S3.** Comparison between model residuals  $\mathbf{E} = \mathbf{X} - \mathbf{GF}$  (a) for 1-factor (red lines) to 2-factors (black lines) PMF solution and (b) for 2-factors (black lines) to 3-factors (blue lines) PMF solution. The model residuals were calculated in five different ways: (1) sum of residuals, (2) sum of the absolute value of residuals, (3) sum of residuals relative to total organics, (4) sum of absolute value of residuals relative to total organics, and (5) sum of squared, uncertainty-weighted (scaled) residuals,  $Q(t) = E(t)/S(t)$ , relative to expected values,  $Q_{exp}(t)$ . The model residuals were estimated using the PMF evaluation tool, PET, by Ulbrich et al. (2009). The structure in the residuals was decreased significantly in the  $p = 2$  solution compared to the  $p = 1$  solution. Comparing the 2 and 3 factor solutions the residuals decreased significantly from  $p = 2$  to  $p = 3$  solution.

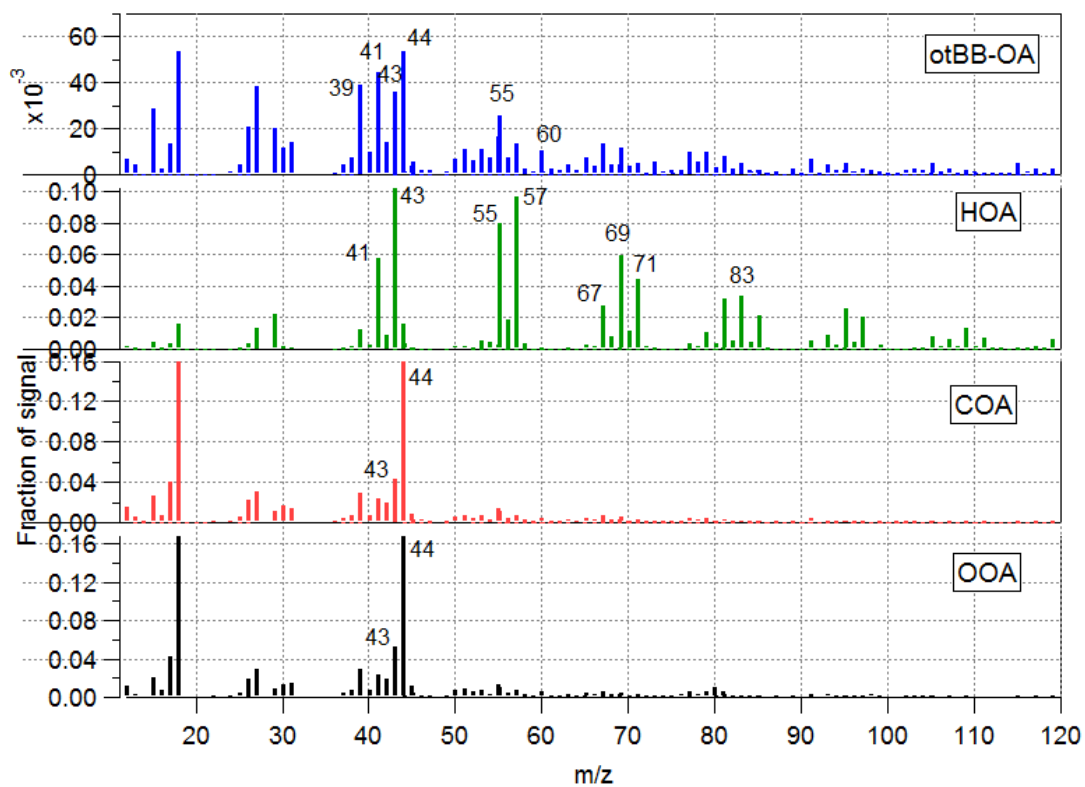




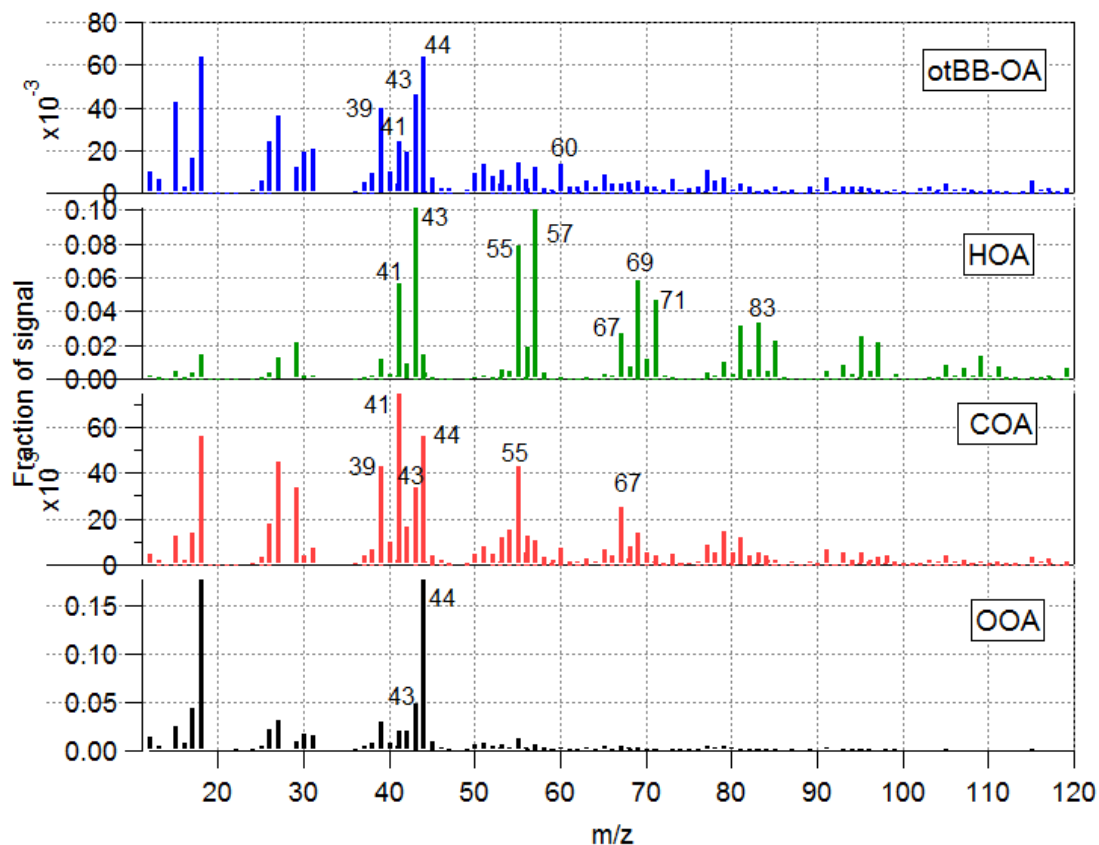
**Figure S4.** Comparison between model residuals  $\mathbf{E} = \mathbf{X} - \mathbf{GF}$  (a) for 3-factor (blue lines) to 4-factors (green lines) PMF solution and (b) for 4-factors (green lines) to 5-factors (purple lines) PMF solution. The model residuals were calculated in five different ways: (1) sum of residuals, (2) sum of the absolute value of residuals, (3) sum of residuals relative to total organics, (4) sum of absolute value of residuals relative to total organics, and (5) sum of squared, uncertainty-weighted (scaled) residuals,  $Q(t) = E(t)/S(t)$ , relative to expected values,  $Q_{exp}(t)$ . The model residuals were estimated using the PMF evaluation tool, PET, by Ulbrich et al. (2009). The structure in the residuals was decreased significantly in the  $p = 4$  solution compared to the  $p = 3$  solution only during Fat Thursday 16 February 2012. Comparing the 4 and 5 factor solutions the residuals practically did not change. (c) Detail of the comparison between 3 and 4 factor solution for the Fat Thursday period.



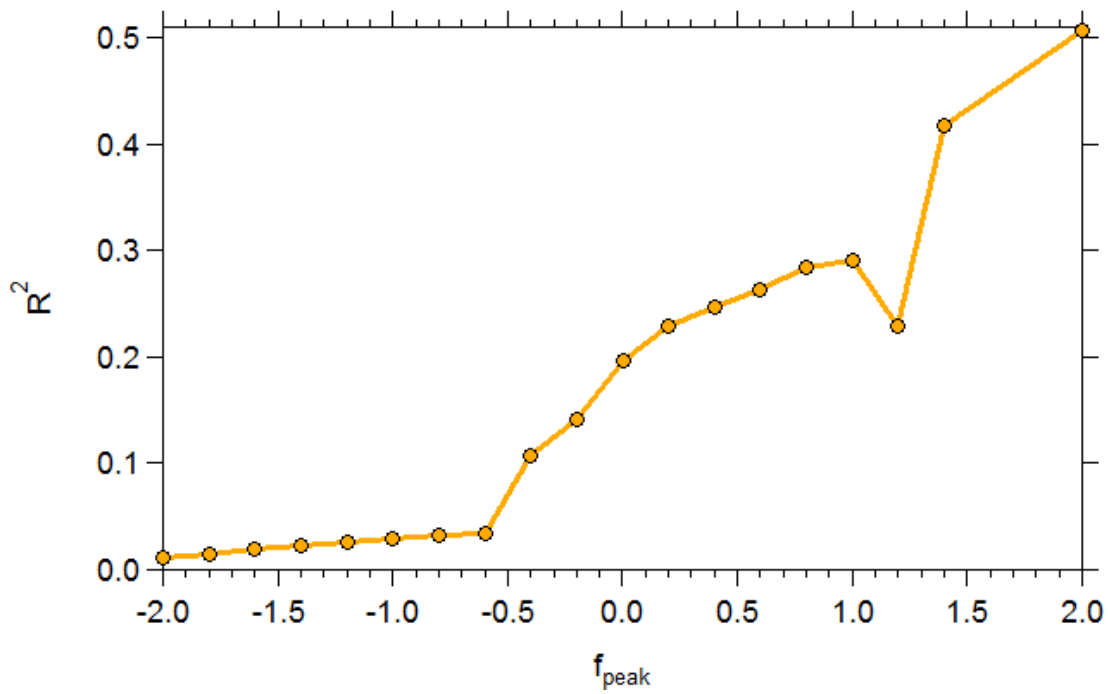
**Figure S5.** Angle  $\theta$  between the average otBB-OA chamber mass spectrum and the otBB-OA profile factor from the 4 PMF solution. The lower angle and so the greater resemblance, is in the range  $f_{peak}$  -2 to -0.6, but after  $f_{peak}=-0.4$  the two mass spectra deviate each other.



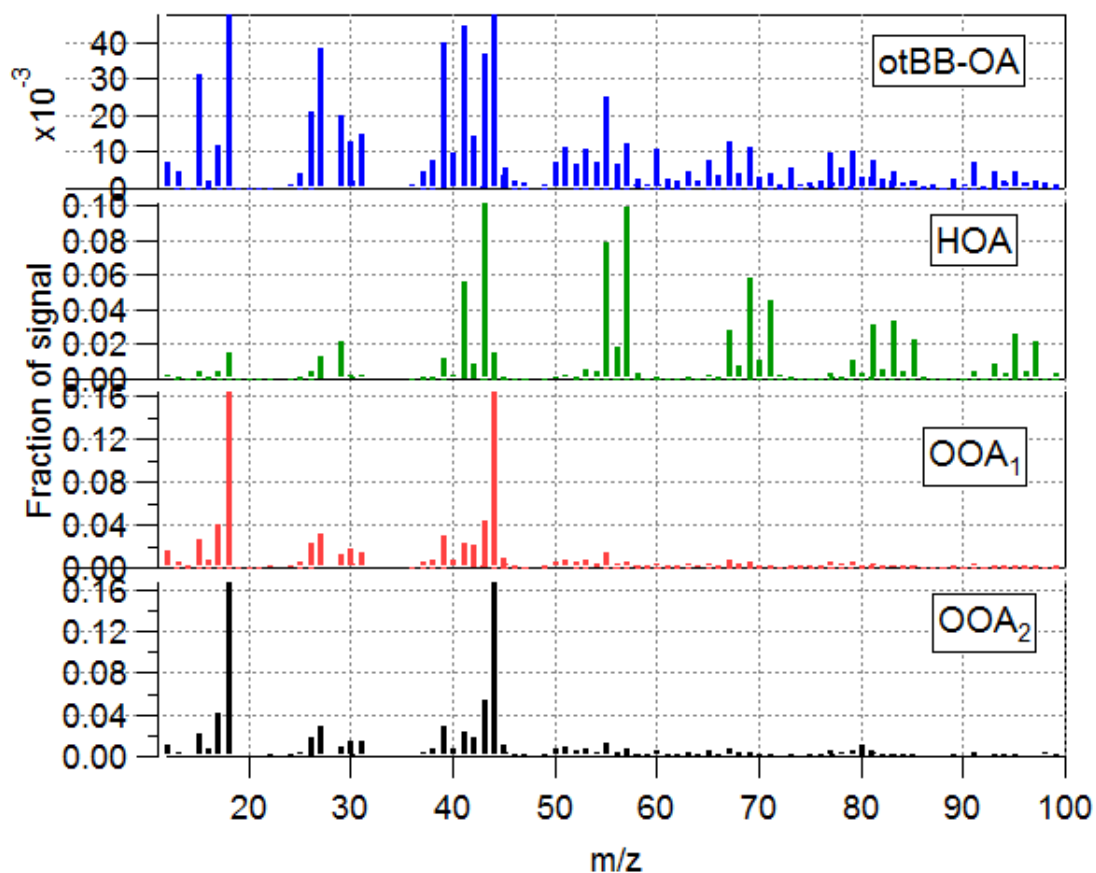
**Figure S6.** The 4 factor PMF solution for  $f_{peak}=-1.0$ . The mass spectrum of the COA factor is identical to the OOA spectrum ( $\theta=4.7$  degrees). This behavior is observed in the  $f_{peak}$  range -2 to -0.6.



**Figure S7.** The 4 factor PMF solution for  $f_{peak}=1.0$ . The mass spectrum of the COA factor resembles the COA mass spectra in the literature ( $\theta=27$  degrees between our COA mass spectrum and the COA mass spectra obtained by Crippa et al. (2013)). However the otBB-OA mass spectrum factor deviates from the otBB-OA measured in the chamber ( $\theta=25$  degrees). This behavior is typical in the  $f_{peak}$  range -0.4 to 2.

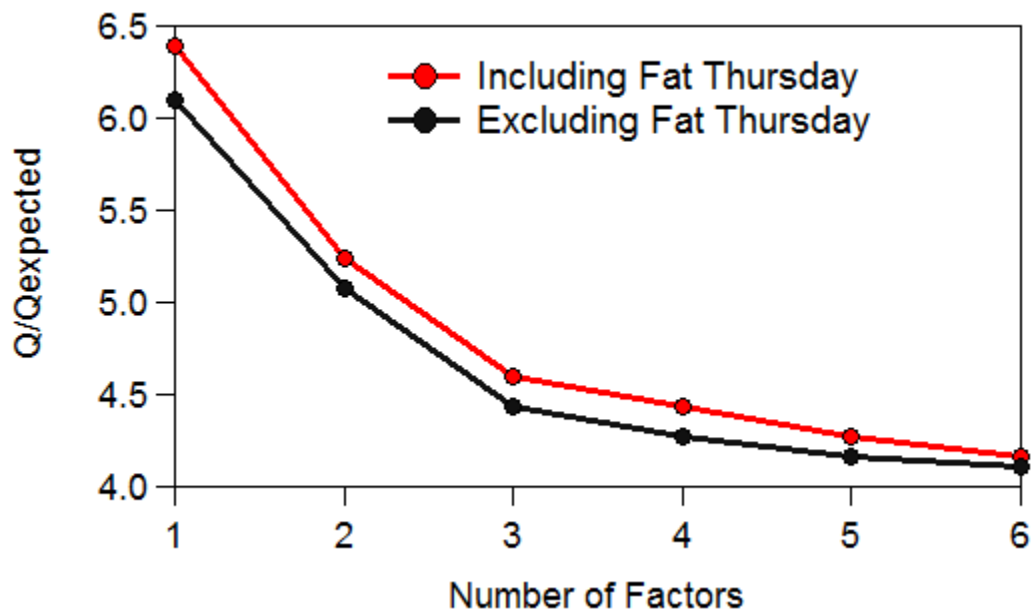


**Figure S8.** Correlation coefficient  $R^2$  between the time series of the otBB-OA and the COA. For  $f_{peak}$  -2 to -0.6 the time series are practically independent, but after -0.6 there is an increasing correlation between them, which suggests a problematic solution.

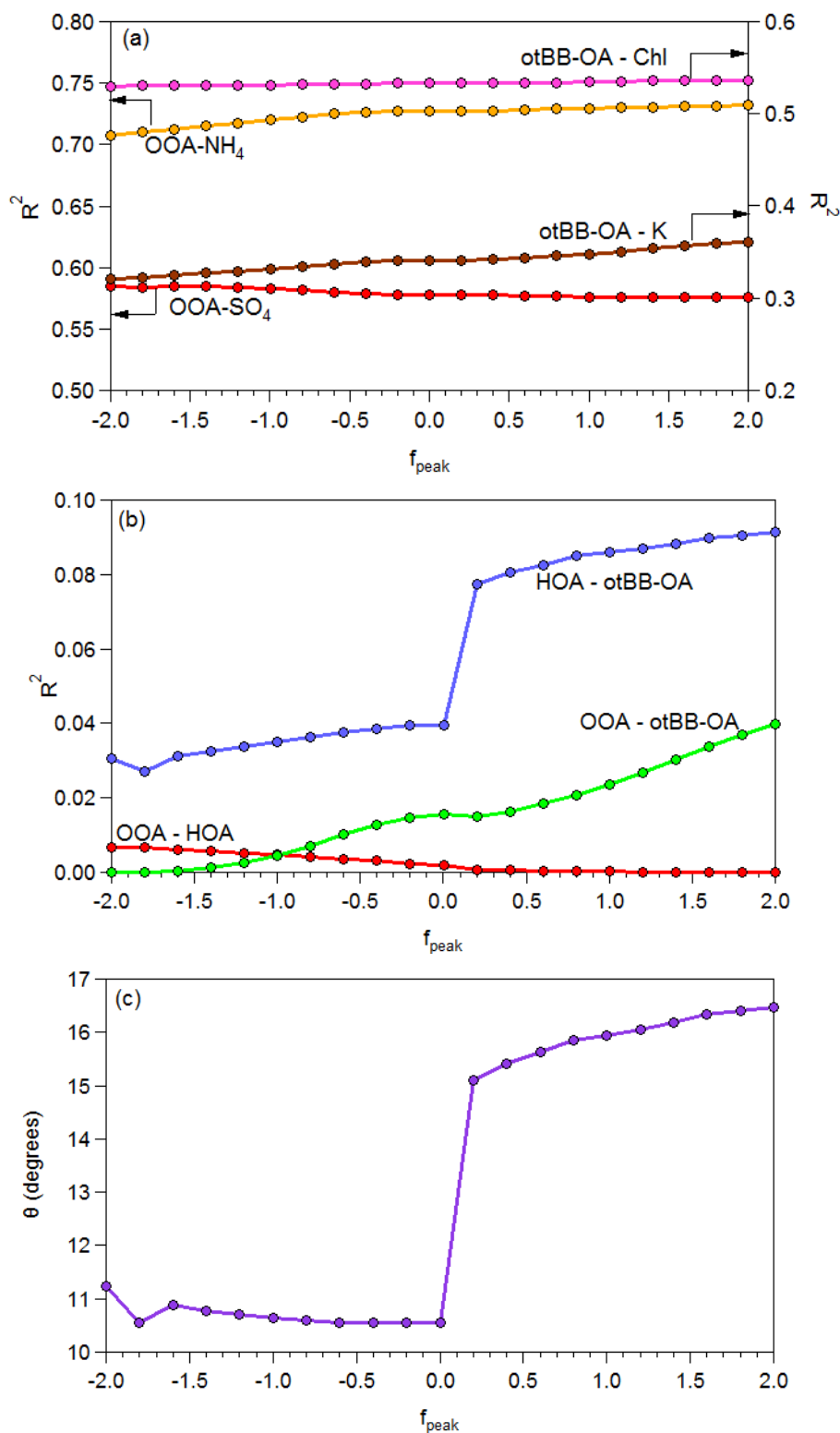


**Figure S9.** The 4 factor PMF solution for  $f_{peak}=-0.2$  excluding the 12 hours data during Fat Thursday. PMF splits the OOA factor in 2 identical OOA spectra. This is observed in the  $f_{peak}$  range -2 to 2.



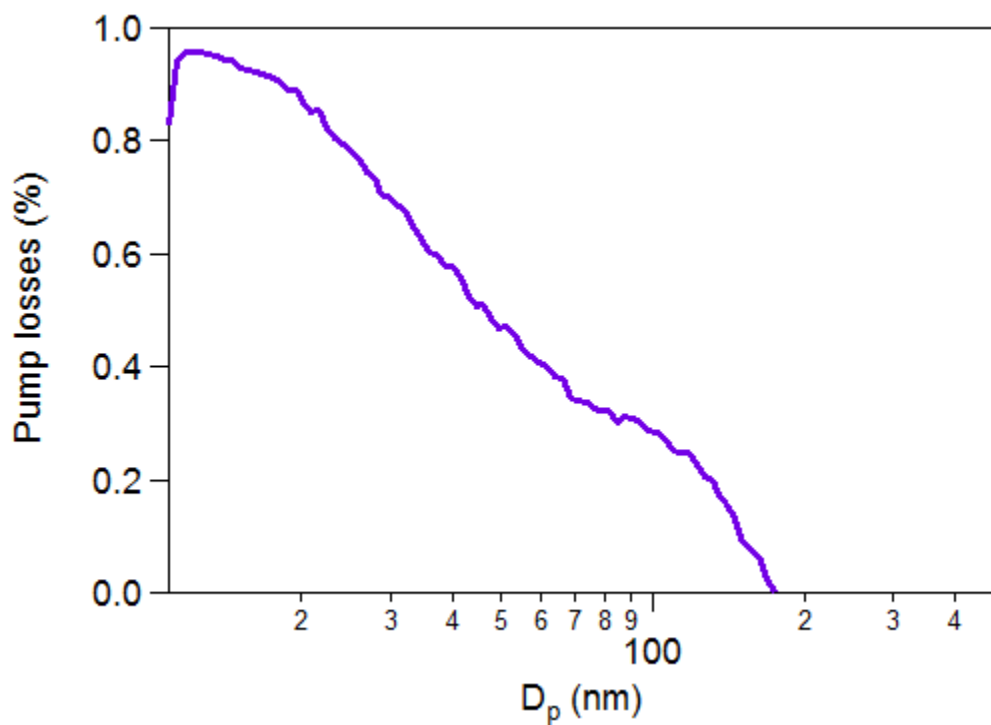


**Figure S10.**  $Q/Q_{\text{expected}}$  versus the number of the factors (for  $f_{\text{peak}}=-0.2$ ) including (red color) and excluding the Fat Thursday data.



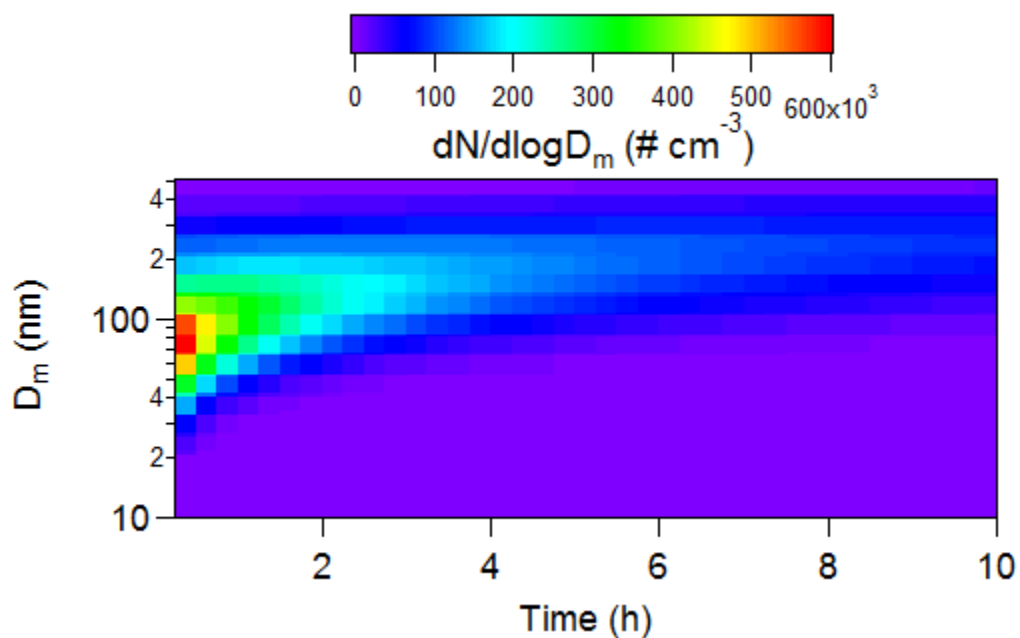
**Figure S11.** Criteria for the selection of the  $f_{peak}$ : (a) The correlation  $R^2$  between 3 factors (i.e. OOA, HOA and otBB-OA) and external tracers (i.e. sulfate, ammonium, potassium and chloride) did not indicate a favorable  $f_{peak}$ . (b) The time series correlation between the 3 factors each other may imply that a negative  $f_{peak}$  could be more appropriate, as the correlation between HOA and otBB-OA time series dropped to the half. (c) The otBB-OA factor profile is closer to the average otBB-OA chamber mass spectrum for negative  $f_{peak}$ s. We choose an  $f_{peak} = -0.2$  where the angle  $\theta$  is minimum ( $\theta = 10.55$  degrees).

## 7. Pump losses calculation



**Figure S12.** The percent pump loss versus the mobility diameter in nm, measured by 2 SMPS systems.

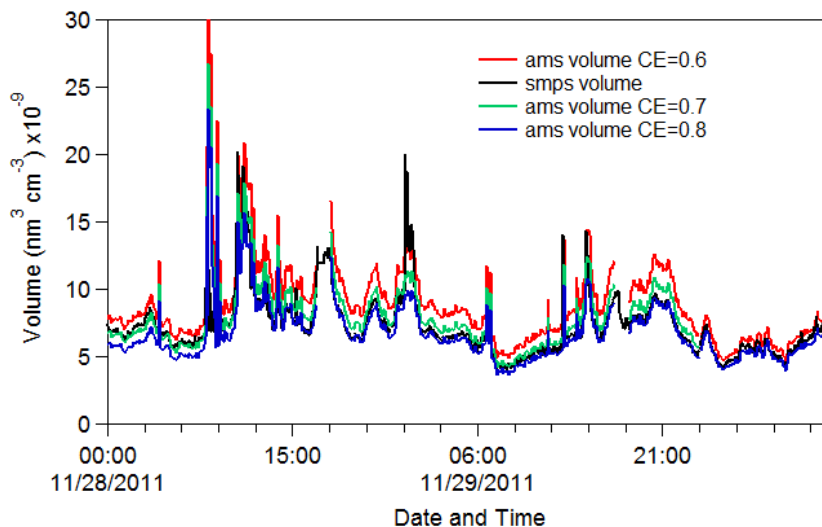
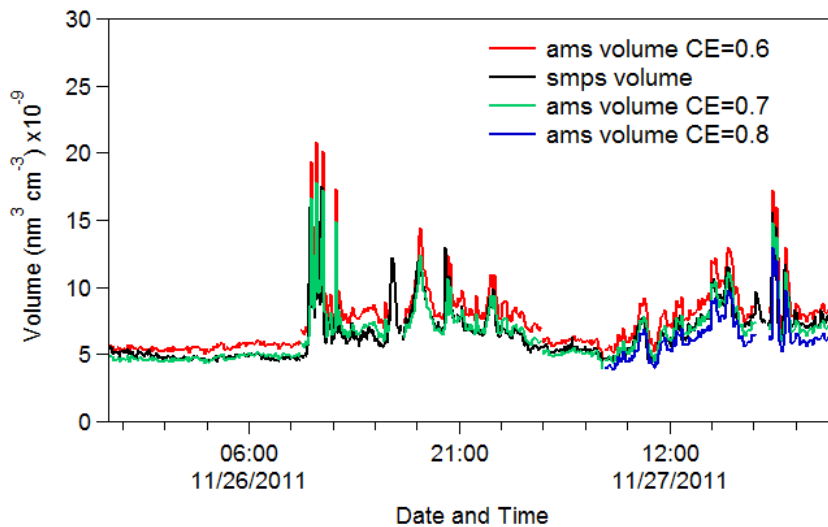
## 8. Coagulation of otBB-OA using the model TOMAS

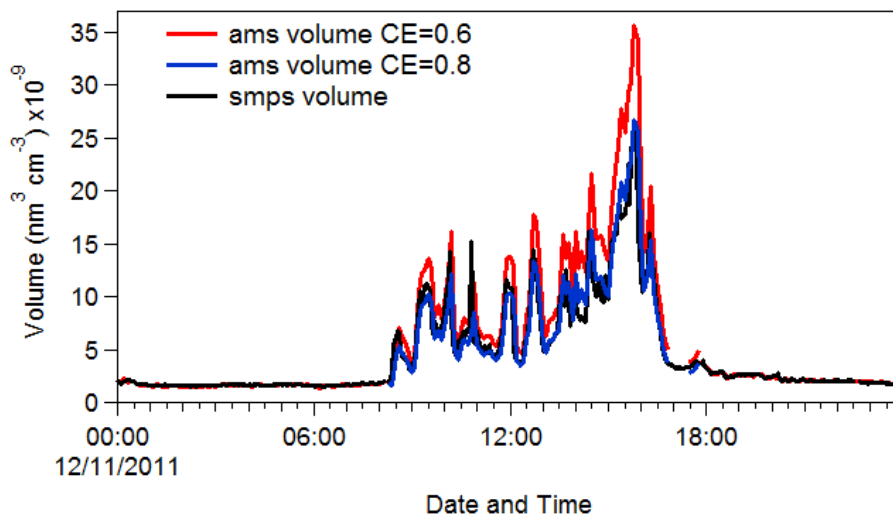


**Figure S13.** Evolution of ambient otBB-OA size distribution for 500,000 particles  $\text{cm}^{-3}$ , if there was no dilution, using the model TOMAS (Adams and Seinfeld, 2002). Within 1-2 hours the mode diameter becomes  $\sim 115$  nm.

## 9. Evaluation of the CE

In order to evaluate the uncertainties of using a constant CE=0.6 to the ambient AMS data, we applied various CE's in the range 0.5-0.9 to the ambient AMS data and we compared with the volume estimated from the SMPS. As organic densities we used  $1.4 \text{ g cm}^{-3}$  for the OOA (Kostenidou et al., 2007),  $1.0 \text{ g cm}^{-3}$  for the HOA (Canagaratna et al., 2010) and  $1.25 \text{ g cm}^{-3}$  for the otBB-OA, found for the chamber experiments. The two time series agreed better for CE's in the range 0.6 to 0.8 (3 examples are given in Figure S14).





**Figure S14:** Example of volume times series from the AMS for CE=0.6, 0.7 and 0.8 and from the SMPS for the corresponding periods.

## References

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