

Supplementary information for manuscript

## **Organic aerosol components derived from 25 AMS datasets across Europe using a newly developed ME-2 based source apportionment strategy**

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## SI-1 Average chemical composition

Table SI-1: Mean concentrations (in  $\mu\text{g}/\text{m}^3$ ) of AMS chemical components for the EMEP/EUCAARI campaigns.

Site	Spring 2008					Fall 2008					Spring 2009				
	Org	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	Org	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	Org	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>
<b>Barcelona</b>											8.20	3.60	2.70	1.60	0.24
<b>Cabauw</b>	4.20	2.50	1.50	1.70	0.06						1.20	2.20	1.00	1.00	0.15
<b>Finokalia</b>	2.60	0.08	5.00	1.50	0.01						1.40	0.05	1.40	0.40	0.01
<b>Helsinki</b>											2.90	0.90	2.90	0.80	0.04
<b>Hyytiälä</b>						0.80	0.10	0.50	0.20	0.01	1.40	0.20	1.40	0.40	0.01
<b>Jungfraujoch</b>	0.66	0.27	0.41	0.21	0.01										
<b>K-Puszt</b>						5.30	2.00	2.70	1.60	0.10					
<b>Mace Head</b>	0.90	0.20	0.80	0.30	0.02						0.80	0.60	0.40	0.30	0.05
<b>Melpitz</b>	6.90	0.70	2.40	0.90	0.02	3.90	3.00	1.70	1.40	0.10	1.40	3.10	1.10	1.40	0.12
<b>Montseny</b>											3.50	3.80	1.50	2.00	0.11
<b>Payerne</b>						5.40	2.70	1.70	1.60	0.03	4.10	3.90	1.10	1.70	0.08
<b>Puijo</b>						0.90	0.10	0.30	0.10	0.01					
<b>Puy de Dome</b>						1.76	0.82	1.73	1.52	0.02	0.57	0.74	0.32	0.56	0.03
<b>San Pietro Capofiume</b>	3.80	2.90	1.40	1.40	0.16										
<b>Vavihill</b>						3.70	3.20	1.60	1.60	0.16	2.60	1.80	0.90	0.80	0.09
<b>Chilbolton</b>											2.50	3.00	1.50	1.50	0.29
<b>Harwell</b>						3.21	3.12	1.72	1.57	0.11					

## SI-2 Source apportionment results

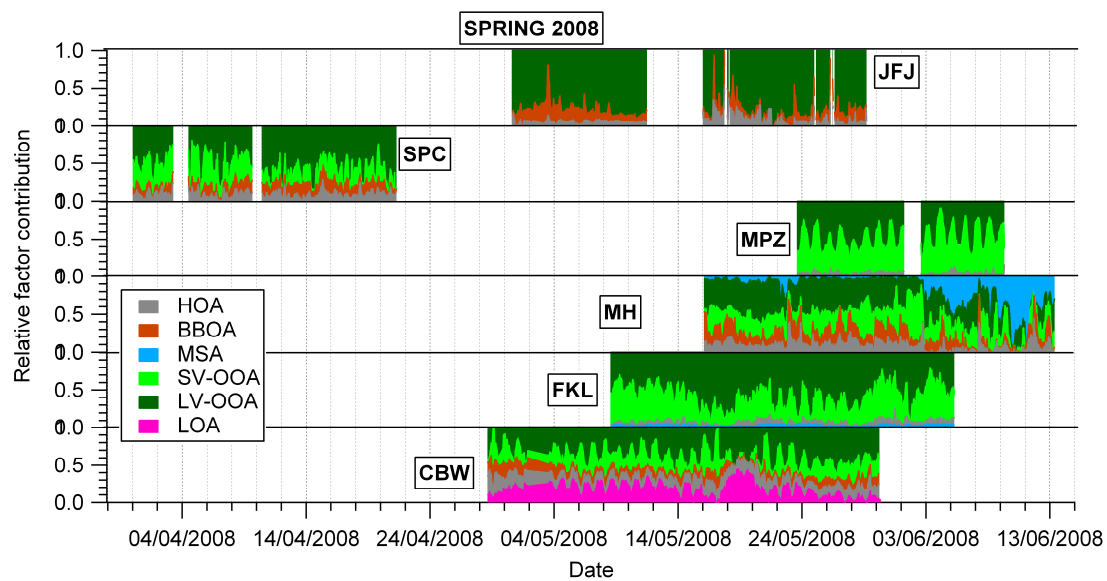
Table SI-2: Comparison of PMF and ME-2 results. Constrained factors in ME-2 are highlighted in red. The reference spectra were taken from Crippa et al. (2013) for the HOA and COA sources ( $\alpha$ -value=0.05), and from Ng et al. (2011) for the BBOA component ( $\alpha$ -value=0.3). For the PMF solutions of Barcelona, San Pietro Capofiume, Cabauw and Finokalia refer to Mohr et al. (2012), Saarikoski et al. (2012), Paglione et al. (2013), and Hildebrandt et al., (2010;2011), respectively.

Site		April/May 2008		Sep/Oct 2008		Feb/Mar 2009	
		PMF	ME2	PMF	ME2	PMF	ME2
Barcelona	ES					HR-PMF:LV-OOA, SV-OOA, HOA, BBOA, COA	HOA,BBOA,COA,SV-OOA, LV-OOA
Cabauw	NL	LV-OOA, SV-OOA,Hulis, HOA	HOA, BBOA,SV-OOA, LV-OOA			LV-OOA, SV-OOA, HOA, BBOA	HOA, BBOA, SV-OOA, LV-OOA
Finokalia	GR	LV-OOA, SV-OOA	SV-OOA, LV-OOA, HOA,MSA			OOA, LOA (OB-OA), AOA	-
Helsinki	FI					HOA, BBOA, SV-OOA, LV-OOA	HOA,BBOA, SV-OOA, LV-OOA
Hyytiälä	FI			LV-OOA, SV-OOA	HOA,BBOA,SV-OOA, LV-OOA	LV-OOA, SV-OOA	HOA,BBOA, SV-OOA, LV-OOA
Jungfrauoch	CH	LV-OOA, OOA*, POA	HOA,BBOA, LV-OOA				
K-Pusztá	HU			SV-OOA, LV-OOA, HOA, BBOA like	HOA,BBOA, SV-OOA, LV-OOA		
Mace Head	IR	HOA,MSA,SV-OOA, LV-OOA	HOA,BBOA,MSA, SV-OOA, LV-OOA			HOA, BBOA like, MSA like, LV-OOA	HOA,BBOA,MSA, LV-OOA
Melpitz	DE	LV-OOA, SV-OOA	HOA,SV-OOA, LV-OOA	HOA like, LV-OOA, SV-OOA	HOA,BBOA,SV-OOA, LV-OOA	POA, LV-OOA, SV-OOA	HOA, BBOA, SV-OOA, LV-OOA
Montseny	ES					POA, SV-OOA, LV-OOA (HR-PMF: HOA, BBOA, OOA)	HOA,BBOA, LV-OOA
Payerne	CH			OOA, POA	HOA,BBOA, SV-OOA, LV-OOA	POA, SV-OOA, LV-OOA	HOA,BBOA, SV-OOA, LV-OOA
Puijo	FI			OOA	HOA, OOA		
Puy de Dome	FR			SV-OOA, LV-OOA	HOA,BBOA,SV-OOA, LV-OOA	LV-OOA, SV-OOA	HOA, BBOA, SV-OOA, LV-OOA
San Pietro Capofiume	IT	LV-OOA, SV-OOA (HR PMF: HOA, BBOA, N-OA, OOA-a, OOA-b, OOA-c)	HOA,BBOA,SV-OOA, LV-OOA				
Vavihill	SE			HOA, BBOA, LV-OOA	HOA,BBOA, LV-OOA	HOA, SV-OOA, LV-OOA	HOA,BBOA, SV-OOA, LV-OOA
Chilbolton	UK					HOA, BBOA, SV-OOA, LV-OOA	HOA, BBOA, SV-OOA, LV-OOA
Harwell	UK					POA, LV-OOA	HOA,BBOA, SV-OOA, LV-OOA

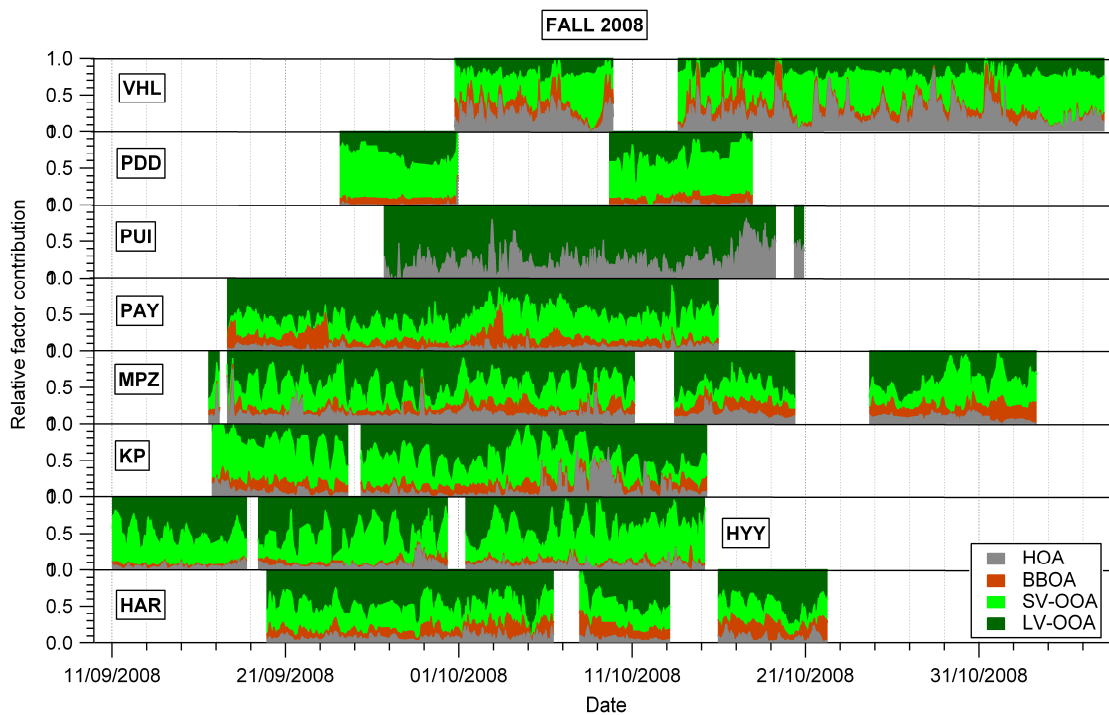
**Table SI-3: Correlation matrix of the OA factors and their tracers**

Table SI-3 reports the correlation ( $R^2$ ) between the time series of the OA sources and available tracers. HOA correlates with black carbon measurements, BBOA with the fraction of organic at mass 60, while SV-OOA and LV-OOA are compared with  $\text{NO}_3$  and  $\text{SO}_4$ , respectively.

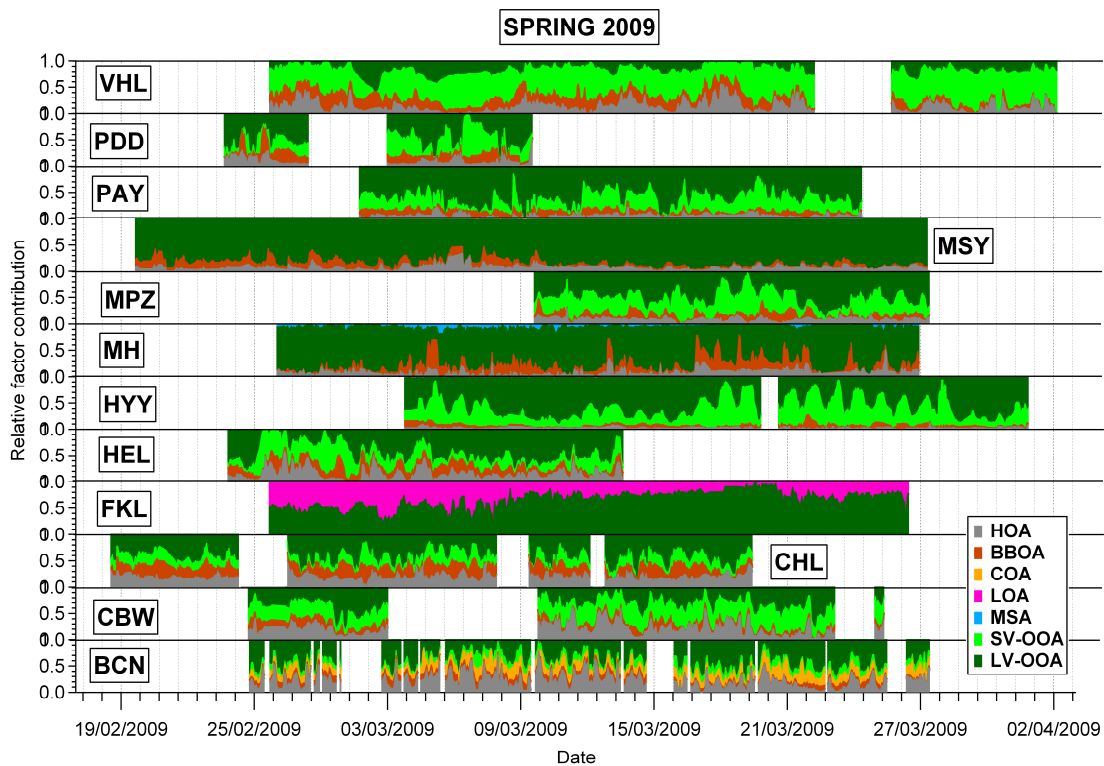
$R^2$	HOA vs. BC	BBOA vs. org60	SV-OOA vs. NO3	LV-OOA vs. SO4
<b>Barcelona</b>	0.7	0.42	0.37	0.61
<b>Cabauw 2008</b>	0.68	0.81	0.27	0.5
<b>Cabauw 2009</b>	0.43	0.82	0.75	0.67
<b>Chilbolton spring 2009</b>	0.82	0.79	0.22	0.24
<b>Finokalia 2008</b>	-	-	0.11	0.74
<b>Helsinki 2009</b>	-	0.76	0.07	0.58
<b>Hyytiälä 2008</b>	0.72	0.9	0.29	0.36
<b>Hyytiälä 2009</b>	0.66	0.65	0.11	0.74
<b>Jungfrauoch 2008</b>	-	0.71	0.79	-
<b>K-Pusztá 2008</b>	-	0.87	0.19	0.64
<b>Mace Head 2008</b>	-	0.74	-	-
<b>Mace Head 2009</b>	-	0.98	0.6	0.81
<b>Melpitz spring 2008</b>	-	-	0.22	0.58
<b>Melpitz fall 2008</b>	0.33	0.8	-	0.5
<b>Melpitz spring 2009</b>	0.74	0.8	0.27	0.34
<b>Montseny</b>	-	0.64	-	0.74
<b>Payerne fall 2008</b>	-	0.4	0.14	0.57
<b>Payerne spring 2009</b>	-	0.87	0.12	0.54
<b>Puijo</b>	-	-	-	0.5
<b>Puy de Dome fall 2008</b>	0.77	0.41	0.57	0.54
<b>Puy de Dome spring 2009</b>	-	0.97	0.93	0.11
<b>San Pietro Capofiume</b>	-	0.81	0.49	0.11
<b>Vavihill fall 2008</b>	-	0.23	-	0.58
<b>Vavihill spring 2009</b>	-	0.54	0.14	0.41



**Fig. SI-2.1: Temporal variation of the relative contributions of organic aerosol sources during the spring 2008 campaigns.**



**Fig. SI-2.2: Temporal variation of the relative contributions of organic aerosol sources during the fall 2008 campaigns.**



**Fig. SI-2.3: Temporal variation of the relative contributions of organic aerosol sources during the spring 2009 campaigns.**



### SI-3 Comparison of results from different source apportionment methods

In this section the comparison between source apportionment solutions retrieved with our standardized method and UMR/HR-PMF results available for some field campaigns is reported. This analysis shows that our source apportionment procedure produces quite comparable results with UMR/HR-PMF in the cases of Montseny and Barcelona (Figs. SI-3.1 and SI-3.2). Bigger discrepancies are indeed observed for the Cabauw case (Fig. SI-3.3) because our solution additionally includes a BBOA factor compared to the work of Paglione et al. (2013).

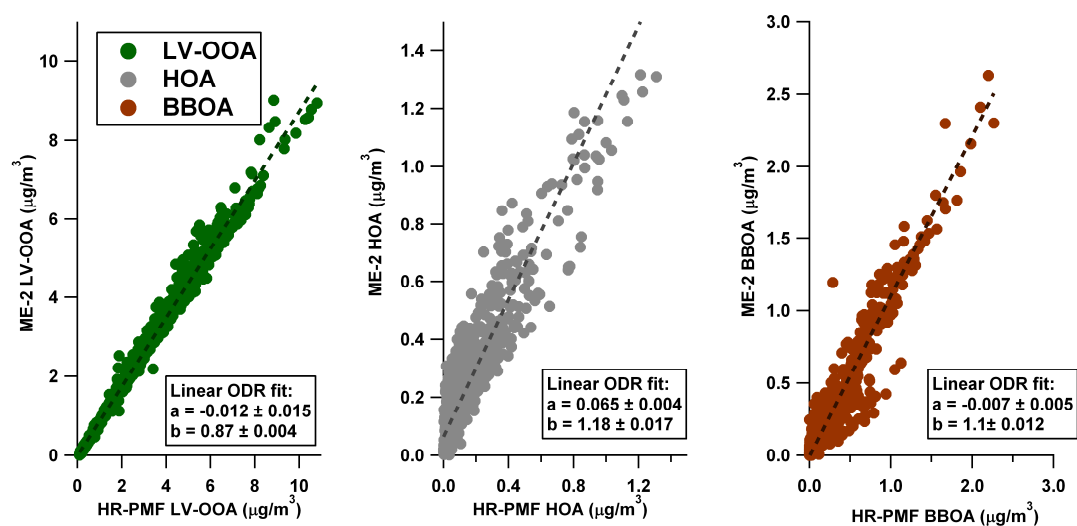
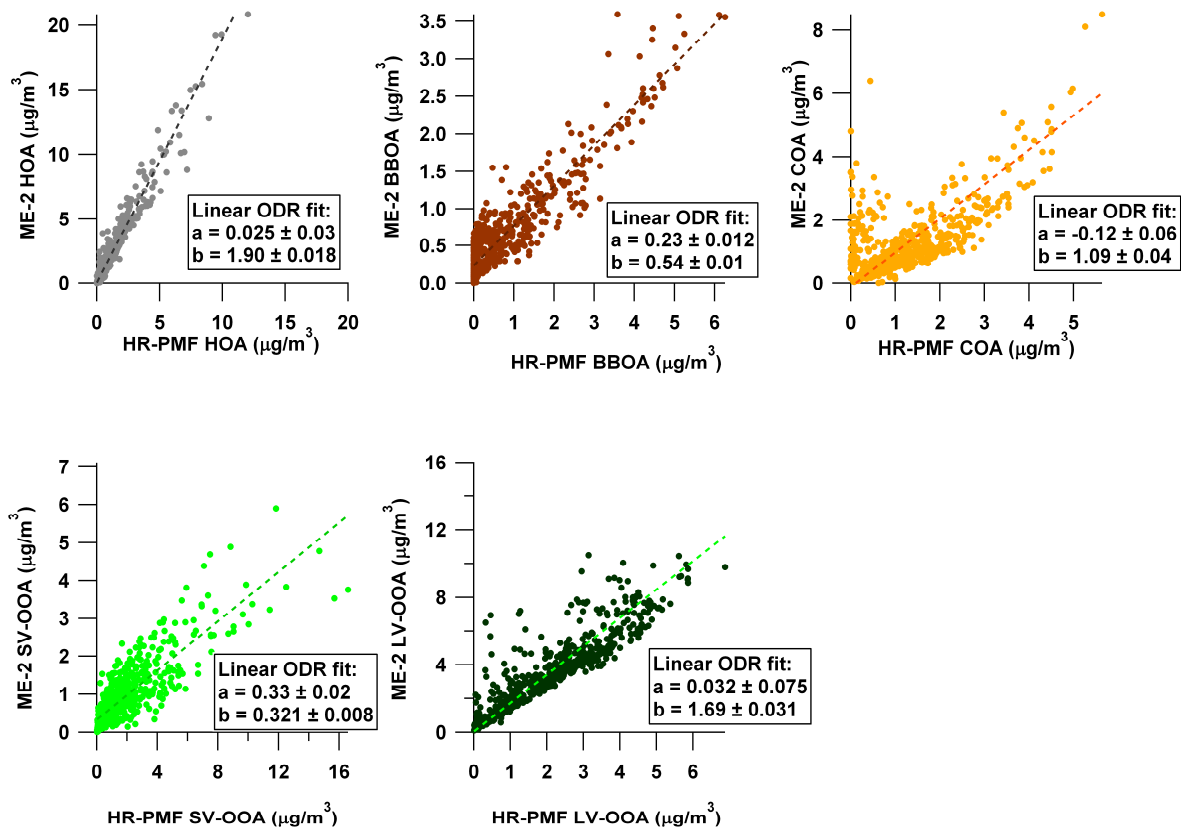
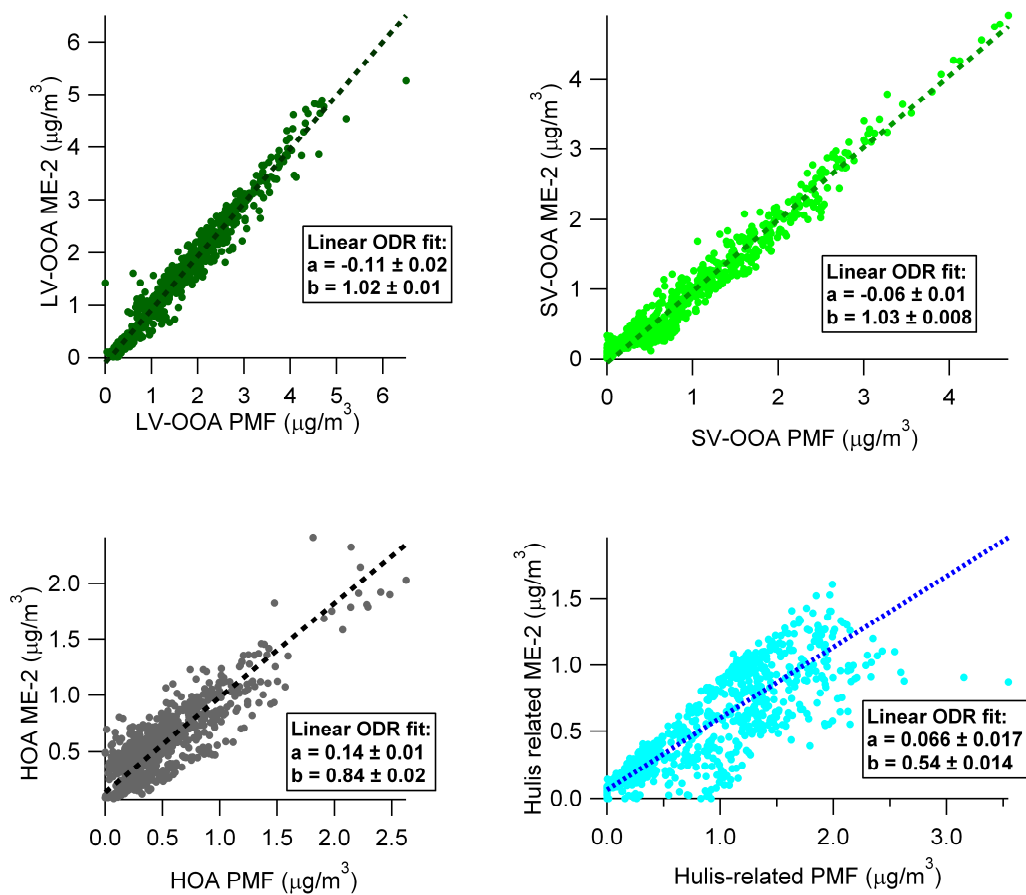


Fig. SI-3.1: Time series comparison of OA sources between the ME-2 solution and the HR-PMF solution for the Montseny spring 2009 campaign.



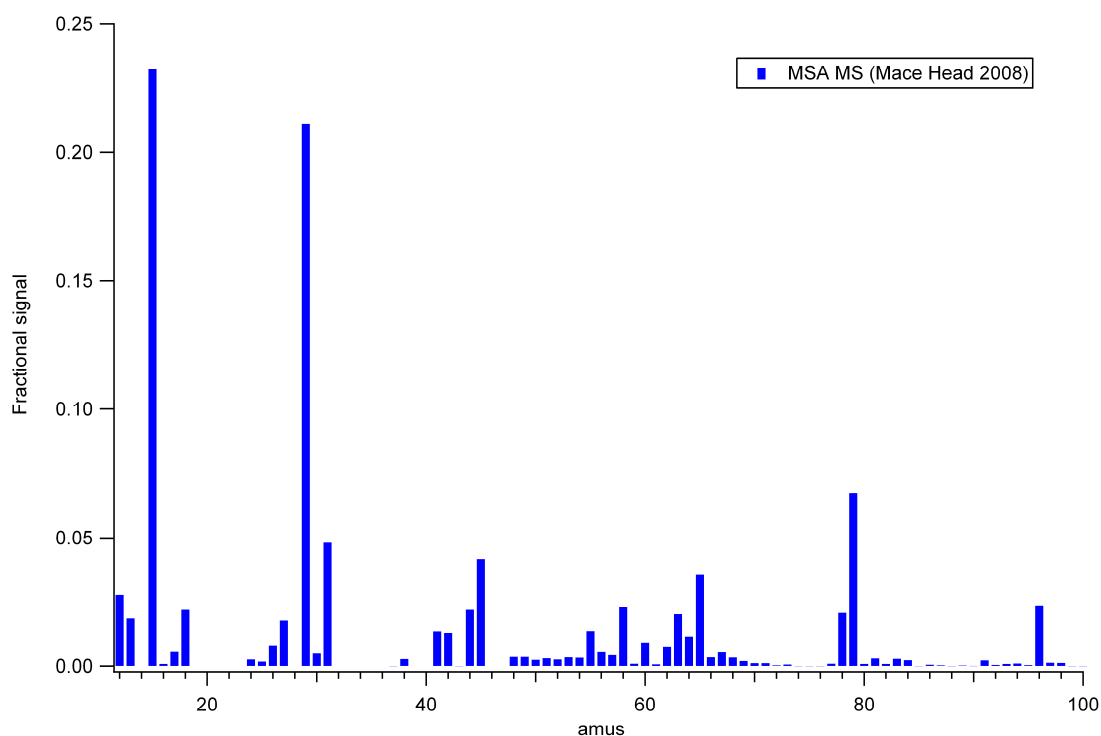
**Fig. SI-3.2:** Time series comparison of OA sources between the ME-2 solution and the HR-PMF solution for the Barcelona spring 2009 campaign (Mohr et al., 2012).



**Fig. SI-3.3: Time series comparison of OA sources between the ME-2 solution and the PMF solution for the Cabauw spring 2008 campaign (Paglione et al., 2013).**

## SI-4 Reference mass spectra

Figure SI-4 represents the MSA mass spectrum obtained for the Mace Head spring 2008 data, which was then chosen as reference spectrum to be constrained in the ME-2 approach for the Finokalia 2008 and Mace Head 2009 campaigns (Ovadnevaite et al., in prep). Typical peaks of MSA fragmentation in the AMS contribute to this spectrum, such as  $m/z$  15, 45, 65, 78, 79, 96 (Zorn et al., 2008). However this MS contains some interferences from sea salt at  $m/z$  58 and 60.



**Figure SI-4: MSA MS obtained for the Mace Head 2008 campaign, chosen as reference MSA MS for all the marine sites.**

## References

- Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., José, N., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, *Atmos. Chem. Phys.*, 13, 961-981, 2013.
- Hildebrandt, L., Engelhart, G. J., Mohr, C., Kostenidou, E., Lanz, V. A., Bougiatioti, A., DeCarlo, P. F., Prevot, A. S. H., Baltensperger, U., Mihalopoulos, N., Donahue, N. M., and Pandis, S. N.: Aged organic aerosol in the Eastern Mediterranean: the Finokalia Aerosol Measurement Experiment-2008, *Atmos. Chem. Phys.*, 10, 4167-4186, 2010.
- Hildebrandt, L., Kostenidou, E., Lanz, V. A., Prevot, A. S. H., Baltensperger, U., Mihalopoulos, N., Laaksonen, A., Donahue, N. M., and Pandis, S. N.: Sources and atmospheric processing of organic aerosol in the Mediterranean: insights from aerosol mass spectrometer factor analysis, *Atmos. Chem. Phys.*, 11, 12499-12515, 2011.
- Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., and Prévôt, A. S. H.: Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data, *Atmos. Chem. Phys.*, 12, 1649-1665, 2012.
- Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Zhang, Q., Ulbrich, I. M., and Worsnop, D. R.: Real-time methods for estimating organic component mass concentrations from aerosol mass spectrometer data, *Environ. Sci. Technol.*, 45, 910-916, 2011.
- Paglione, M., Kiendler-Scharr, A., Mensah, A. A., Finessi, E., Giulianelli, L., Sandrini, S., Facchini, M. C., Fuzzi, S., Schlag, P., Piazzalunga, A., Tagliavini, E., Henzing, J. S., and Decesari, S.: Identification of humic-like substances (HULIS) in oxygenated organic aerosols using NMR and AMS factor analyses and liquid chromatographic techniques, *Atmos. Chem. Phys. Discuss.*, 13, 17197-17252, 2013.
- Saarikoski, S., Carbone, S., Decesari, S., Giulianelli, L., Angelini, F., Canagaratna, M., Ng, N. L., Trimborn, A., Facchini, M. C., Fuzzi, S., Hillamo, R., and Worsnop, D.: Chemical characterization of springtime submicrometer aerosol in Po Valley, Italy, *Atmos. Chem. Phys.*, 12, 8401-8421, 2012.
- Zorn, S. R., Drewnick, F., Schott, M., Hoffmann, T., and Borrmann, S.: Characterization of the South Atlantic marine boundary layer aerosol using an aerodyne aerosol mass spectrometer, *Atmos. Chem. Phys.*, 8, 4711-4728, 2008.