

Organic aerosol components derived from 25 AMS datasets across Europe using a consistent ME-2 based source apportionment approach

Crippa, M.^{1,*}, Canonaco, F.¹, Lanz, V. A.¹, Äijälä, M.², Allan, J. D.³, Carbone, S.⁴, Capes, G.³, Ceburnis, D.¹³, Dall'Osto, M.⁵, Day, D. A.⁶, DeCarlo, P. F.^{1,**}, Ehn, M.², Eriksson, A.⁷, Freney, E.⁸, Hildebrandt Ruiz, L.^{9,***}, Hillamo, R.⁴, Jimenez, J.-L.⁶, Junninen, H.², Kiendler-Scharr, A.¹⁰, Kortelainen, A.-M.¹¹, Kulmala, M.², Laaksonen, A.¹¹, Mensah, A. A.^{10,****}, Mohr, C.^{1,*****}, Nemitz, E.¹², O'Dowd, C.¹³, Ovadnevaite, J.¹³, Pandis, S. N.¹⁴, Petäjä, T.², Poulain, L.¹⁵, Saarikoski, S.⁴, Sellegri, K.⁸, Swietlicki, E.⁷, Tiitta, P.¹¹, Worsnop, D. R.^{2,4,11,16}, Baltensperger, U.¹, and Prévôt, A. S. H.¹.

[1]{Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, PSI Villigen, 5232, Switzerland}

[2]{Department of Physics, P.O. Box 64, 00014, University of Helsinki, Finland}

[3]{National Centre for Atmospheric Science, School of Earth, Atmospheric & Environmental Sciences, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK}

[4]{Air Quality Research, Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland}

[5]{Institute of Environmental Assessment and Water Research (IDAEA), CSIC, 08034 Barcelona, Spain}

[6]{Cooperative Institute for Research in Environmental Sciences (CIRES), USA}

[7]{Division of Nuclear Physics, University of Lund, SE-221 00 Lund, Sweden}

[8]{Laboratoire de Météorologie Physique, CNRS-Université Blaise Pascal, UMR6016, 63117, Clermont Ferrand, France}

[9]{Center for Atmospheric Particle Studies, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA, 15213, US}

[10]{Institut für Energie- und Klimaforschung: Troposphäre (IEK 8), Forschungszentrum Jülich GmbH, Jülich, Germany}

[11]{Department of Environmental Science, Univ. of Eastern Finland, P.O. Box 1627, 70211 Kuopio, Finland}

[12]{Centre for Ecology and Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK}

[13]{School of Physics & Centre for Climate & Air Pollution Studies, National University of Ireland Galway, Ireland}

[14]{Institute of Chemical Engineering Sciences (ICE-HT) Foundation for Research and Technology Hellas (FORTH), Patras, 26504, Greece}

[15]{Leibniz Institut for Tropospheric Research, Permoserstr 15, 04318, Leipzig, Germany}

[16]{Aerodyne Research, Inc. Billerica, MA, USA}

[*]{now at: European Commission, Joint Research Centre, Institute for Environment and Sustainability, Air and Climate Unit, Via Fermi, 2749, 21027 Ispra, Italy}

[**]{now at: Department of Civil, Architectural, and Environmental Engineering and Department of Chemistry, Drexel University, Philadelphia, PA, USA, 19104}

[***]{now at: The University of Texas at Austin, McKetta Department of Chemical Engineering, Austin, TX, 78712, US}

[****]{now at: ETH Zurich, Institute for Atmospheric and Climate Science, Switzerland}

[*****]{now at: Department of Atmospheric Sciences, University of Washington, Seattle WA 98195, USA}

Correspondence to: A.S.H. Prévôt (andre.prevot@psi.ch)

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_3^-	SO_4^{2-}	NH_4^+	Cl^-	Org	NO_3^-	SO_4^{2-}	NH_4^+	Cl^-	Org	NO_3^-	SO_4^{2-}	NH_4^+	Cl^-
Barcelona											8.20	3.60	2.70	1.60	0.24
Cabauw	4.20	2.50	1.50	1.70	0.06						1.20	2.20	1.00	1.00	0.15
Finokalia	2.60	0.08	5.00	1.50	0.01						1.40	0.05	1.40	0.40	0.01
Helsinki											2.90	0.90	2.90	0.80	0.04
Hyytiälä						0.80	0.10	0.50	0.20	0.01	1.40	0.20	1.40	0.40	0.01
Jungfraujoch	0.66	0.27	0.41	0.21	0.01										
K-Puszt						5.30	2.00	2.70	1.60	0.10					
Mace Head	0.90	0.20	0.80	0.30	0.02						0.80	0.60	0.40	0.30	0.05
Melpitz	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
Montseny											3.50	3.80	1.50	2.00	0.11
Payerne						5.40	2.70	1.70	1.60	0.03	4.10	3.90	1.10	1.70	0.08
Puijo						0.90	0.10	0.30	0.10	0.01					
Puy de Dome						1.76	0.82	1.73	1.52	0.02	0.57	0.74	0.32	0.56	0.03
San Pietro Capofume	3.80	2.90	1.40	1.40	0.16										
Vavihill						3.70	3.20	1.60	1.60	0.16	2.60	1.80	0.90	0.80	0.09
Chilbolton											2.50	3.00	1.50	1.50	0.29
Harwell						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 (α -value=0.05), and from Ng et al. (2011) for the BBOA component (α -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
Hyttiälä	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-Puszt	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-2 shows the comparison between OA sources retrieved with the unconstrained PMF run and with our methodology. For some datasets high resolution data were available and the PMF algorithm was able to separate the same type of sources as in our approach (see for further details section SI-3). This is the case of Barcelona, Helsinki, Mace Head, Montseny and San Pietro Capofiume. For most of the other sites, we were able to identify more primary sources and/or determine the split between OOA components following the standardized procedure here introduced (e.g. Hyttiälä, Jungfrauoch, K-Puszt, Melpitz, Puijo, Puy de Dome, Vavihill, Harwell). In the case of Chilbolton, the HOA MS was constrained to get better separation of the other

components, although both POA and SOA sources were retrieved by the unconstrained run too.

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 NO_3 and SO_4 , respectively.

R^2	HOA vs. BC	BBOA vs. org60	SV-OOA vs. NO_3	LV-OOA vs. SO_4
Barcelona	0.7	0.42	0.37	0.61
Cabauw 2008	0.68	0.81	0.27	0.5
Cabauw 2009	0.43	0.82	0.75	0.67
Chilbolton spring 2009	0.82	0.79	0.22	0.24
Finokalia 2008	-	-	0.11	0.74
Helsinki 2009	-	0.76	0.07	0.58
Hyytiälä 2008	0.72	0.9	0.29	0.36
Hyytiälä 2009	0.66	0.65	0.11	0.74
Jungfraujoch 2008	-	0.71	0.79	-
K-Pusztá 2008	-	0.87	0.19	0.64
Mace Head 2008	-	0.74	-	-
Mace Head 2009	-	0.98	0.6	0.81
Melpitz spring 2008	-	-	0.22	0.58
Melpitz fall 2008	0.33	0.8	-	0.5
Melpitz spring 2009	0.74	0.8	0.27	0.34
Montseny	-	0.64	-	0.74
Payerne fall 2008	-	0.4	0.14	0.57
Payerne spring 2009	-	0.87	0.12	0.54
Puijo	-	-	-	0.5
Puy de Dome fall 2008	0.77	0.41	0.57	0.54
Puy de Dome spring 2009	-	0.97	0.93	0.11
San Pietro Capofiume	-	0.81	0.49	0.11
Vavihill fall 2008	-	0.23	-	0.58
Vavihill spring 2009	-	0.54	0.14	0.41

Table SI-4: Measurement sites location and classification. Measurement sites are listed from North to South

Measurement site	Longitude	Latitude	Type of site
Puijo	27.6504	62.9023	Rural
Hyytiälä	24.2833	62.85	Remote
Helsinki	24.966	60.203	Urban
Vaviihill	13.15	56.0167	Rural
Mace Head	-9.6	53.333	Remote
Cabauw	4.933	51.967	Rural
Chilbolton	-1.317	51.567	Rural
Melpitz	12.9	51.533	Rural
Harwell	-1.438	51.145	Rural
K-Puszt	19.58	46.9667	Rural
Payerne	6.95	46.8	Rural
Jungfraujoch	7.9833	46.5667	High altitude
Puy de Dome	2.5	45.5	High altitude
San Pietro Capofiume	11.6489	44.6539	Rural
Montseny	2.21	41.46	Rural
Barcelona	2.116	41.39	Urban
Finokalia	25.667	35.3167	Remote

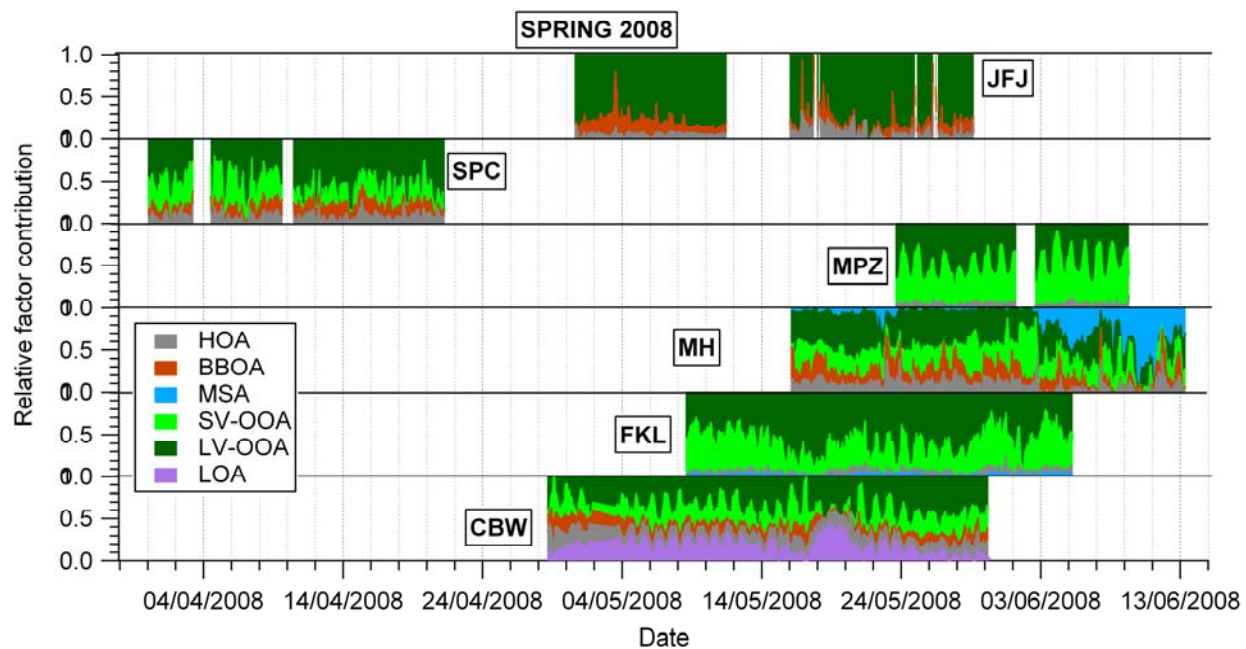


Fig. SI-2.1: Temporal variation of the relative contributions of organic aerosol sources during the spring 2008 campaigns.

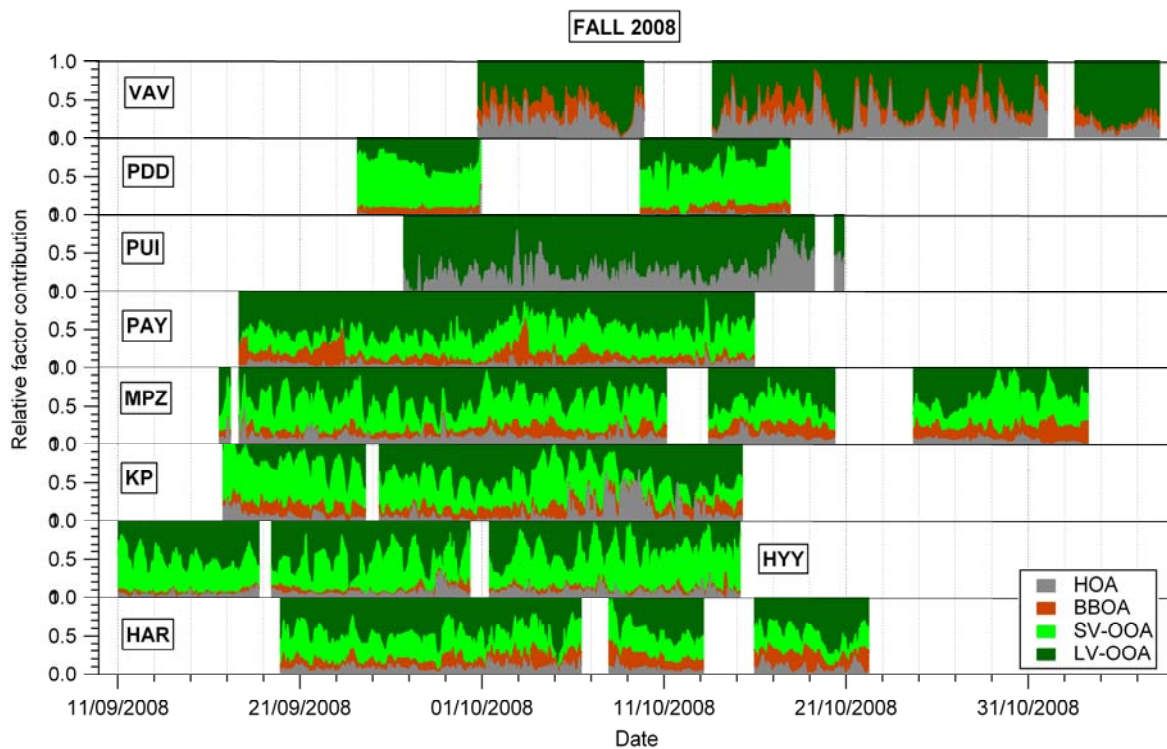


Fig. SI-2.2: Temporal variation of the relative contributions of organic aerosol sources during the fall 2008 campaigns.

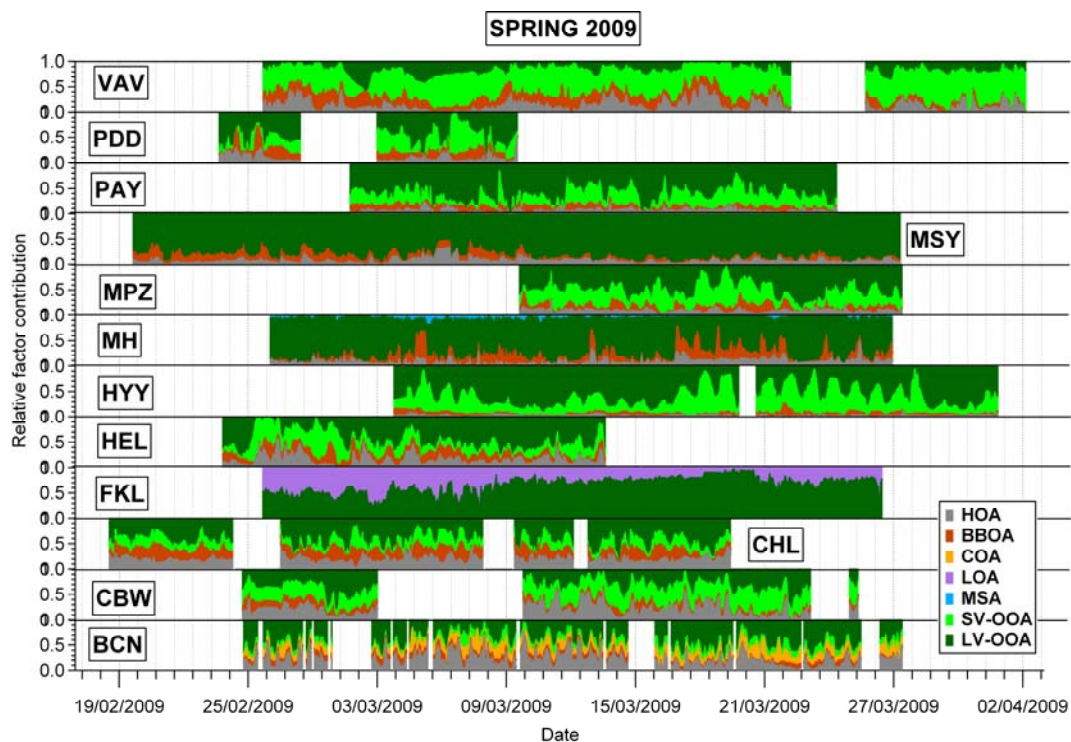


Fig. SI-2.3: Temporal variation of the relative contributions of organic aerosol sources during the spring 2009 campaigns.

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. In our work we showed the possibility to use ME-2 to extract more information from the UMR spectra that is often not otherwise possible with unconstrained UMR PMF and the comparison to more information-rich HR PMF is only meant as one assessment of how well it works. The motivation of our work is due to the fact that often HR spectra are not available (e.g. in many air quality monitoring stations ACSMs, etc. are deployed and not HR-AMS) and thus the utility/need for this method.

Comparing our ME-2 solutions with HR-PMF results shows that our source apportionment procedure produces quite similar results with UMR/HR-PMF in the case of Montseny (Figs. SI-3.1), although it was necessary to consider a 8-factor HR-PMF solution in order to get an HOA MS and merge all the OOA contributing factors into one single component. However, Fig. SI-3.2 highlights some issues with the quantification of OA sources in Barcelona, in fact despite the good agreement in terms of temporal correlations for all sources between the two methods, the slopes of the linear fit look quite different. A slope of 1.9 is found for HOA, which appears to be underestimated by our approach, while more comparable results are found for COA (slope 1.09). This is possibly due to the exact attribution of the reduced ions at mass 41, 43, 55 and 57 to the HOA MS and the oxygenated part to COA by the HR-PMF making use of the high resolution information. On the other hand, both BBOA and SV-OOA are underestimated by our methodology while LV-OOA is here overestimated. This underlines the uncertainty associated with the attribution of specific masses like m/z 43 and m/z 44 to BBOA and to the oxygenated components, which are not characterized by constant mass spectra over the world and the season. Some discrepancies are also observed for the Cabauw case (Fig. SI-3.3) since our solution additionally includes a BBOA factor compared to the work of Paglione et al. (2013).

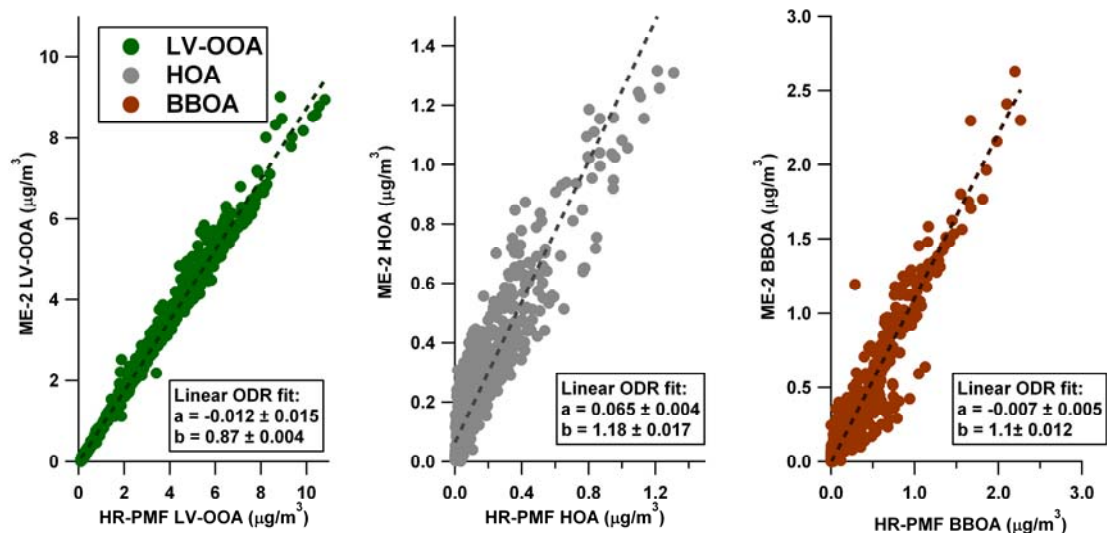


Fig. SI-3.1: Time series comparison of OA sources between the ME-2 solution and the HR-PMF solution for the Montseny spring 2009 campaign.

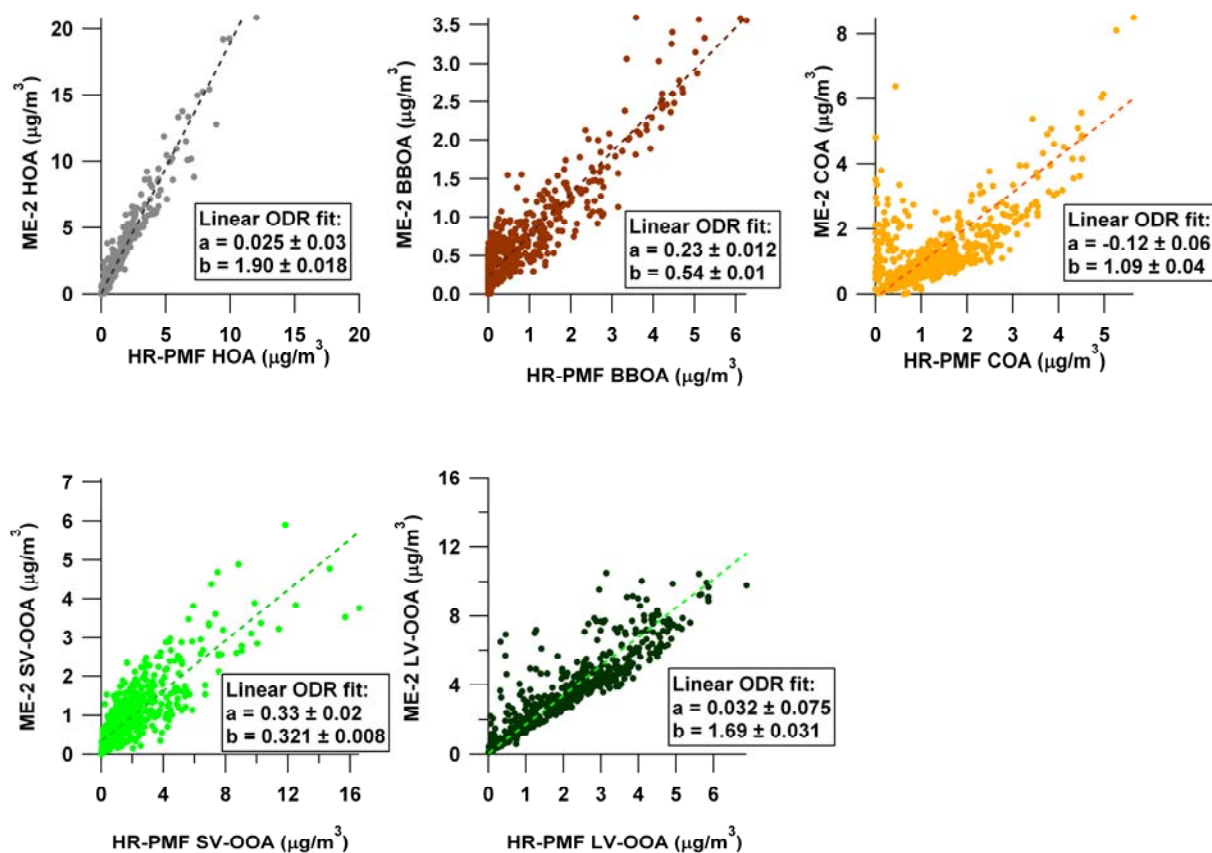


Fig. SI-3.2: Time series comparison of OA sources between the ME-2 solution and the HR-PMF solution for the Barcelona spring 2009 campaign (Mohr et al., 2012).

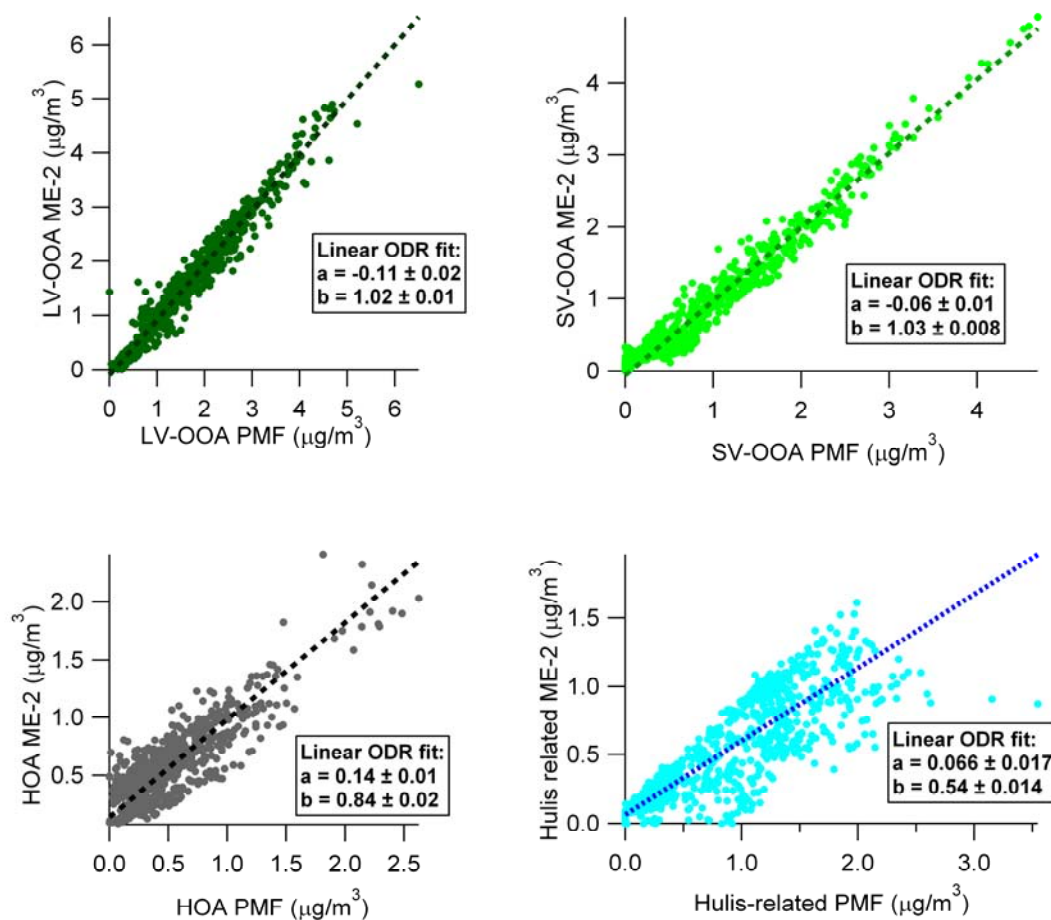


Fig. SI-3.3: Time series comparison of OA sources between the ME-2 solution and the PMF solution for the Cabauw spring 2008 campaign (Paglione et al., 2013).

SI-4 f_{44} vs. f_{43} triangular plot

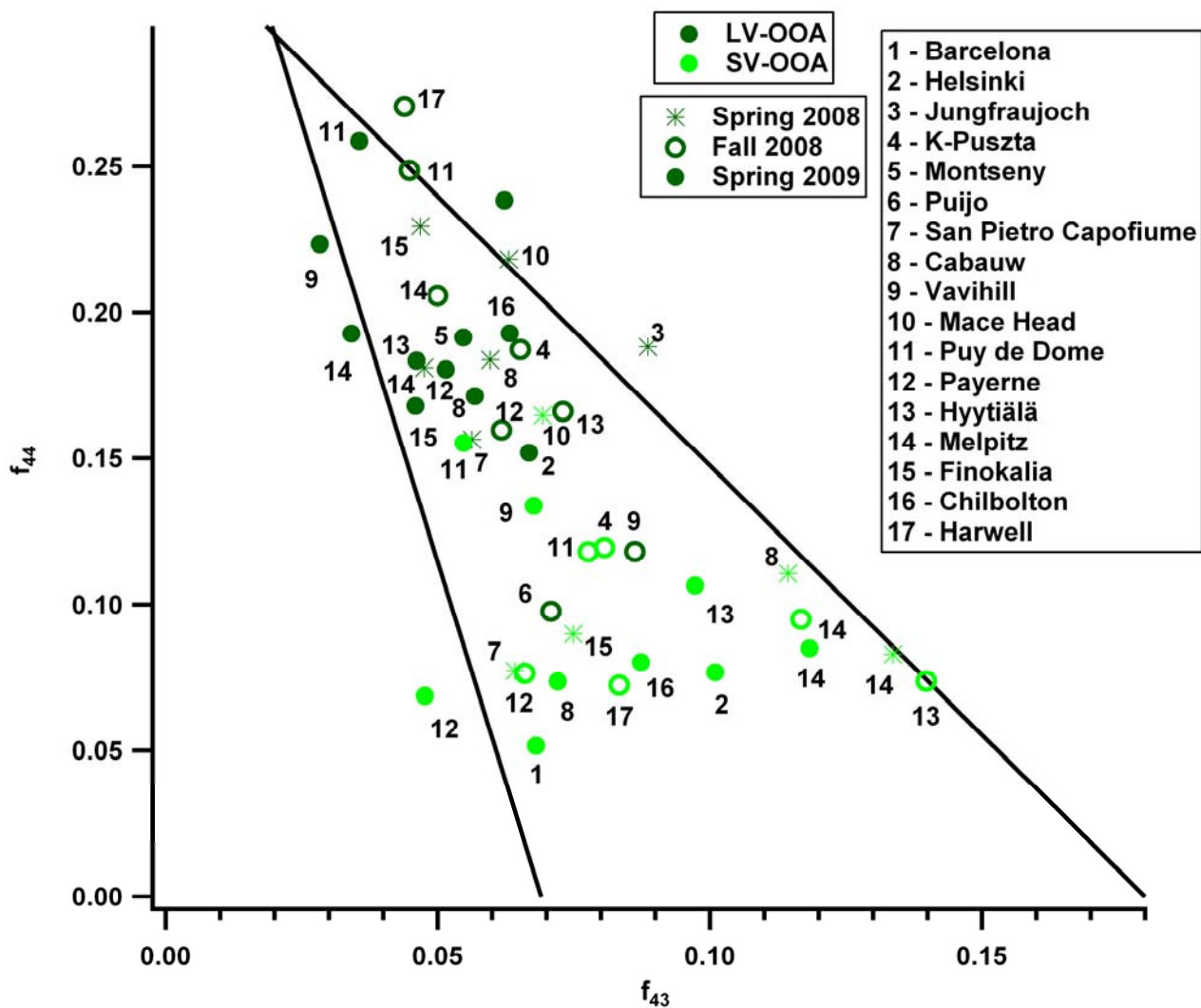


Fig. SI-4: f_{44} vs. f_{43} triangle plot.

SI-5 Reference mass spectra

Figure SI-5 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.

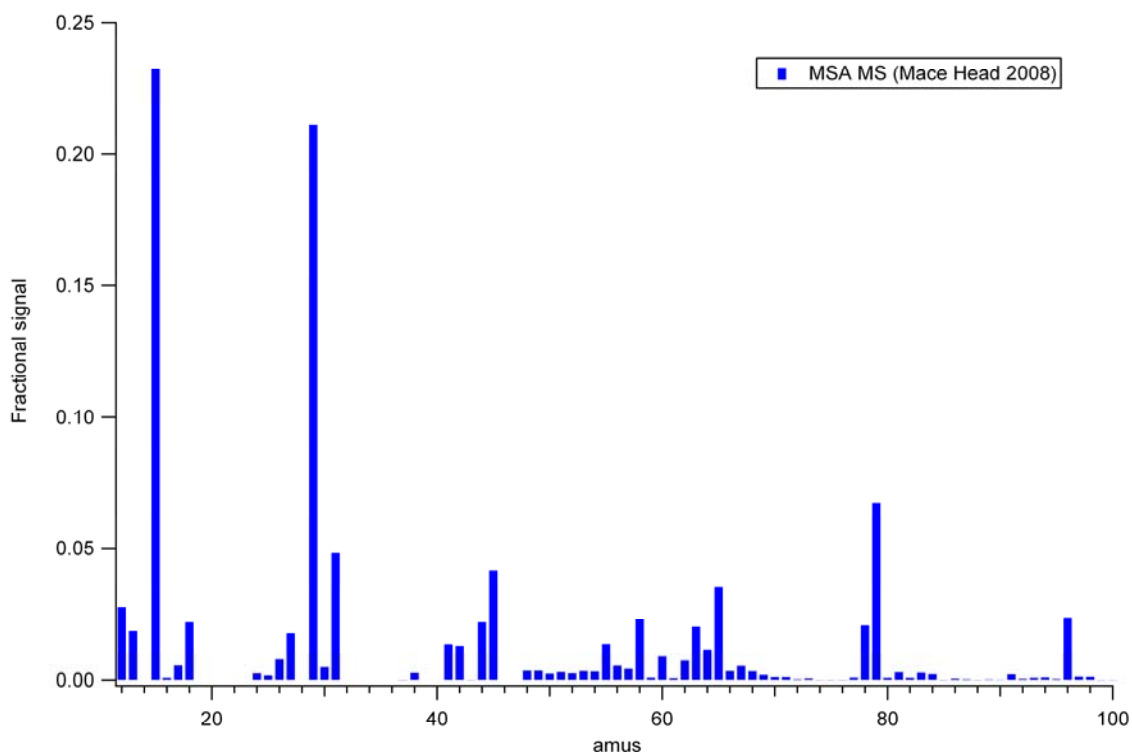


Figure SI-5: MSA MS obtained for the Mace Head 2008 campaign, chosen as reference MSA MS for all the marine sites.

SI-6 Effect of a-priori information on the ME-2 output

In this section we briefly introduce a critical aspect of our work that is the influence of a specific mass spectrum taken as reference when running ME-2 on the source apportionment output. Here we test the effect of fixing the HOA MS presented by Crippa et al. (2013) and the averaged one provided by Ng et al. (2011) for the Northern Hemisphere on the ME-2 output. Table SI-6 reports the relative contribution of OA sources to total organics varying the constrained HOA MS. We report these results for a range of a-values (0.05-0.2).

Table SI-6: Comparison of OA source apportionment results (mass fractions) constraining in ME-2 two reference HOA MS (HOA from Crippa et al., 2013 (this study) and from Ng et al., 2011). Relative contribution of OA sources to total organics is reported for 7 case studies considering an a-value range for HOA of 0.05-0.20. In the table, the first number refers to the solution obtained with an a-value of 0.05 and the second one to with a-value of 0.2.

	reference MS	HOA	BBOA	SV-OOA	LV-OOA	COA
BCN spring 09	HOA Ng et al. 2011	0.21-0.22	0.08-0.08	0.19-0.14	0.38-0.39	0.14-0.16
	HOA (this study)	0.24-0.25	0.09-0.07	0.13-0.10	0.37-0.34	0.17-0.14
MPZ spring 08	HOA Ng et al. 2011	0.04-0.07	-	0.44-0.39	0.53-0.54	-
	HOA (this study)	0.07-0.06	-	0.37-0.34	0.56-0.60	-
MPZ fall 08	HOA Ng et al. 2011	0.10-0.11	0.19-0.19	0.28-0.23	0.42-0.47	-
	HOA (this study)	0.08-0.08	0.14-0.15	0.34-0.31	0.44-0.46	-
MPZ spring 09	HOA Ng et al. 2011	0.06-0.07	0.11-0.11	0.25-0.25	0.58-0.57	-
	HOA (this study)	0.10-0.10	0.17-0.10	0.30-0.28	0.43-0.52	-
VAV fall 08	HOA Ng et al. 2011	0.16-0.17	0.19-0.16	-	0.69-0.67	-
	HOA (this study)	0.20-0.22	0.13-0.13	-	0.67-0.65	-
VAV spring 09	HOA Ng et al. 2011	0.11-0.09	0.15-0.17	0.23-0.34	0.51-0.41	-
	HOA (this study)	0.10-0.13	0.15-0.16	0.26-0.20	0.49-0.51	-

As shown in Table SI-6, varying the constrained reference HOA MS in ME-2 has an influence on the OA source attribution. For most of the cases the variation in the relative contribution of different factors is only a few percent. In order to fully address this critical topic, a more systematic study is planned using more suited datasets with more external constraints to judge which solution performs better or provide a range of results that provide similarly good performance.

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.
- Paglionie, 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.