

Supplementary Information for manuscript

Chemical mass balance of refractory particles (T = 300°C) at the tropospheric research site Melpitz, Germany

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SI-1 Source apportionment results

The application of positive matrix factorization (Lanz et al., 2007) to the AMS Melpitz datasets allowed the discrimination of only oxygenated organic aerosol components (LV-OOA and SV-OOA). Therefore the multi-linear engine algorithm (Canonaco et al., 2013) was used in order to identify both the primary and secondary organic aerosol sources. The adopted procedure was to fix a traffic related mass spectrum and allow the algorithm to separate 2 or 3 additional factors. The reference HOA mass spectrum was taken from the AMS spectral database (Paris, winter 2010 campaign, (Crippa et al., 2013b) and was allowed to vary of a certain percentage (a-value). To validate the chosen solutions, the time series of the retrieved sources were correlated with independent data (e.g. HOA with NO_x, SV-OOA with NO₃, LV-OOA with SO₄ and BBOA with levoglucosan). Further details about this approach and data analysis can be found in Crippa et al., 2013a. Briefly, for the late spring 2008 dataset, the ME-2 algorithm was run selecting a 3-factors solution and fixing the hydrocarbon-like OA factor (with an a-value of 5%). The solution consisted of HOA as primary source and SV- and LV-OOA as secondary components, as shown in Figure SI-1a.

For the early spring 2009 campaign, a 4-factors solution is chosen, fixing the HOA mass spectrum with a-value of 5%. The solution consisted of two primary sources (HOA and BBOA) and two secondary oxygenated fractions (SV-OOA and LV-OOA), as shown in Figure SI-1b.

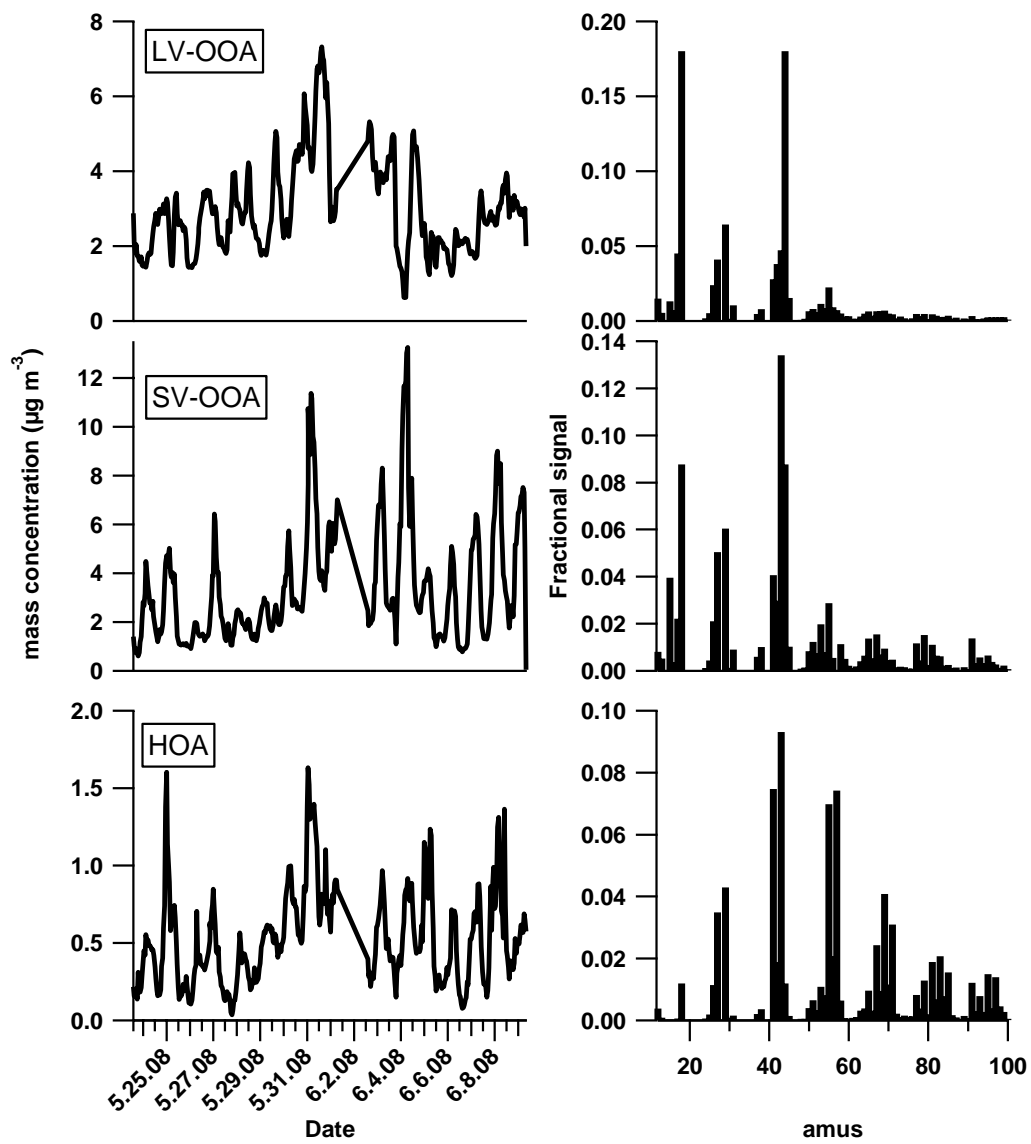


Figure SI-1a: 3-factors solution for the late spring 2008 campaign. The HOA mass spectrum was constrained with an α -value of 5%.

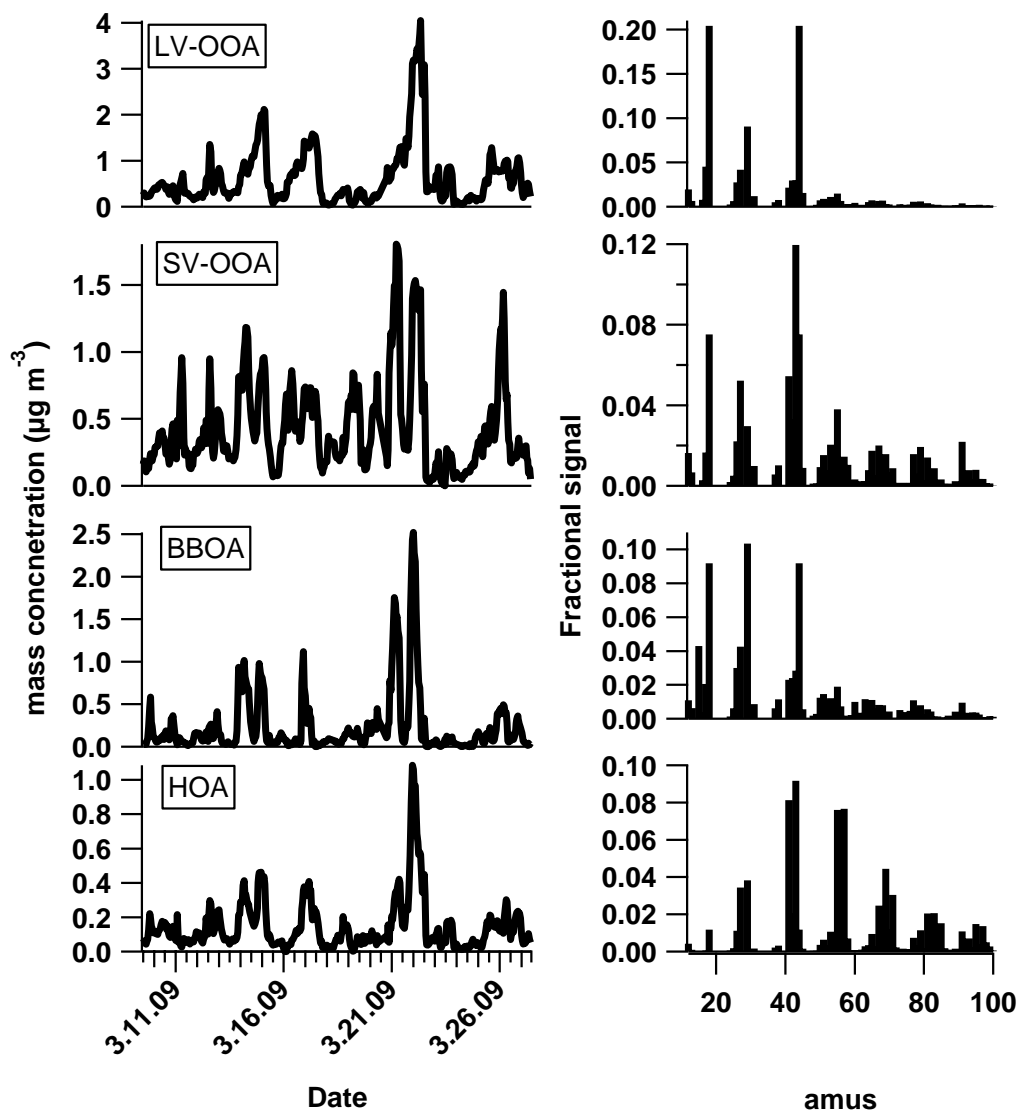


Figure SI-1b: 4-factors solution for the early spring 2009 campaign. The HOA mass spectrum was constrained with an a -value of 5%.

SI-2 Contribution of the estimated refractory organic aerosol (ROA) to the measured refractory mass

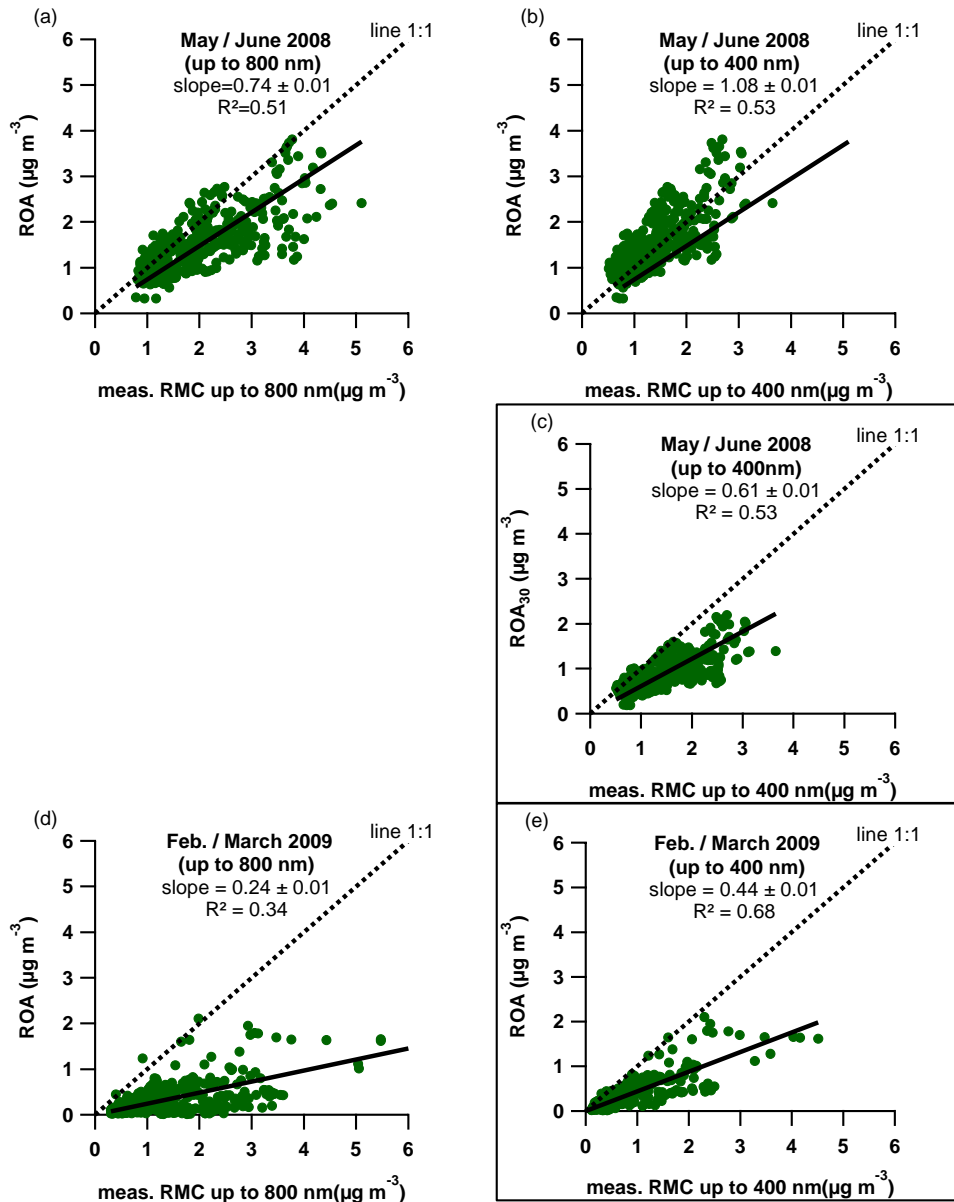


Figure SI-2: Estimated refractory organic aerosol (ROA) vs. measured refractory mass concentration for May/June 2008 (a-c) and February/March 2009 (d,e) periods. Correlation curves were calculated using the least orthogonal distance fit method. Two different upper size cutting were used for the V-TDMPS: up to 800nm and up to 400 nm. ROA was estimated to represent 52% of LVOOA excepted for ROA₃₀ which represents only 30% of LV-OOA. Encased scatter plots correspond to the best estimation for each period.

SI-3 Back trajectories analysis

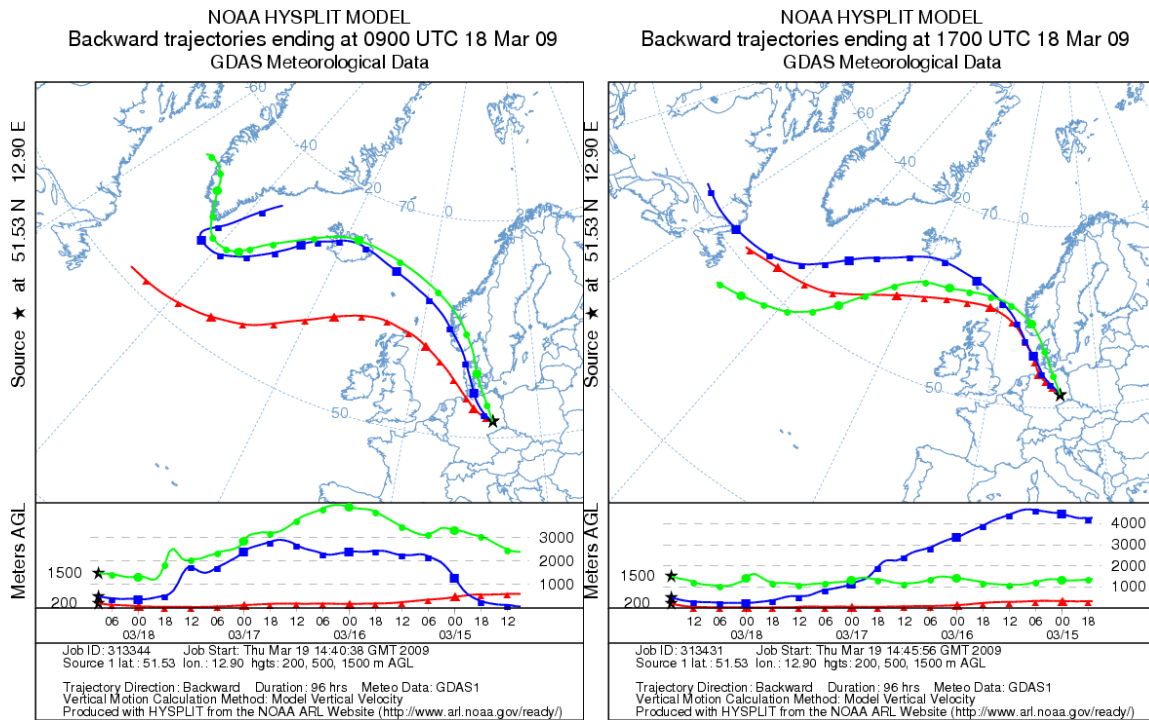


Figure SI-3: The 96h backward air mass trajectories calculated for March 18, 2009 at 09:00 (left) and 17:00 UTC (right).

SI-4 Chemical resolved particle size distribution during early spring 2009

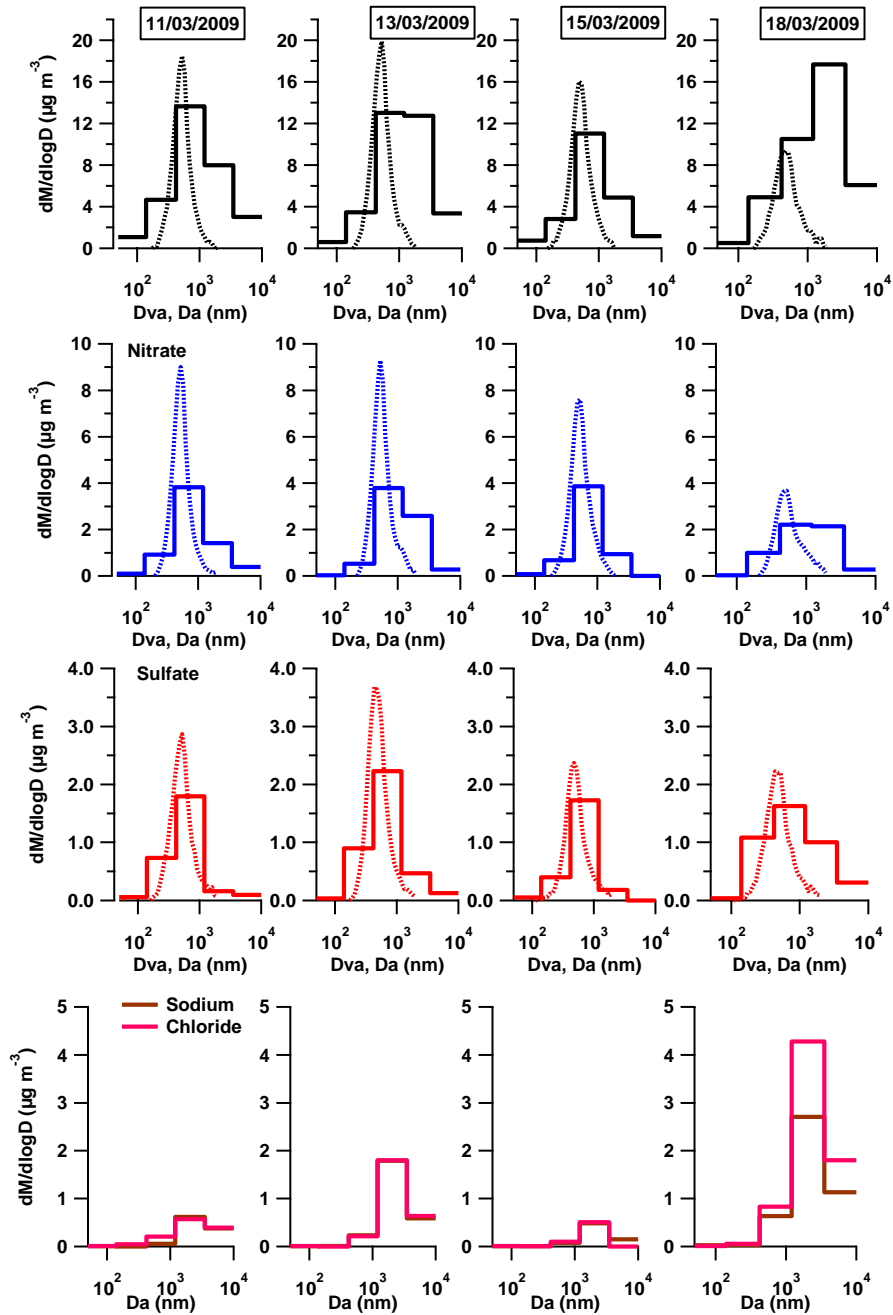


Figure SI-4: Comparison of the particle mass size distribution measured by AMS (dotted lines) and the 5-stages Berner impactor (solid lines) for the total mass (top), nitrate and sulfate during 4 different days. The Berner impactor results for sodium and chloride are also included at the

bottom. The AMS data were averaged in order to fit the sampling time and particle mass size distribution of the impactor (from midnight to midnight).

References

Canonaco, F., Crippa, M., Slowik, J. G., Prévôt, A. S. H., and Baltensperger, U.: SoFi, an Igor based interface for the efficient use of the generalized multiline engine (ME-2) for source apportionment: application to aerosol mass spectrometer data, *Atmos. Meas. Tech. Discuss.*, 6, 6409 - 6443, doi: 10.5194/amtd-6-6409-2013, 2013.

Crippa, M., Canonaco, F., Lanz, V. A., Äijälä, M., Allan, J., Carbone, S., Capes, G., Dall'Osto, M., Day, D. A., DeCarlo, P., Ehn, M., Eriksson, A., Freney, E., Hildebrandt Ruiz, L., Hillamo, R., Jimenez, J.-L., Junninen, H., Kiendler-Scharr, A., Kortelainen, A.-M., Kulmala, M., Mensah, A. A., Mohr, C., Nemitz, E., O'Dowd, C., Ovadnevaite, J., Pandis, S. N., Petäjä, T., Poulain, L., Saarikoski, S. K., Sellegri, K., Swietlicki, E., Tiitta, P., Worsnop, D., Baltensperger, U., and Prévôt, A. S. H.: Compilation of organic aerosol components for 25 AMS datasets across Europe using a newly developed ME-2 based source apportionment strategy, *Atmos. Chem. Phys. Discuss.*, 2013a submitted.

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., Nicolas, J. B., 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, doi 10.5194/acp-13-961-2013, 2013b.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, *Atmos. Chem. Phys.*, 7, 1503-1522, 2007.