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*Supplement of*

## **Chemical mass balance of 300 °C non-volatile particles at the tropospheric research site Melpitz, Germany**

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## **SI-1 estimation of the black carbon density**

Providing an estimation of the BC density is quite difficult. Here, a BC density of  $1.77 \text{ g cm}^{-3}$  was considered to determine the ambient particle density in order to convert TDMPS volume concentration into mass concentration (Equation 1, from Salcedo et al., 2006). Density of BC is not so well defined in the literature compared to the density of, for example, ammonium sulfate or ammonium nitrate. The density of the BC depends on the type of BC and the form of the particles (aggregate, linear structure, shape...). The reported density values in the literature range from more than  $2 \text{ g cm}^{-3}$  for pure graphite (Gysel et al., 2011) to lower values of  $1 \text{ g cm}^{-3}$  (Hitzenberger et al., 1999). Moreover, recent studies reported values corresponding mainly to the value used in this work. For example, Kondo et al. (2011) reported a density of  $1.72 \text{ g cm}^{-3}$  for fullerene soot, and a density of  $1.85 \text{ g cm}^{-3}$  was measured for the amorphous graphite (Kiselev et al., 2010). Park et al. (2004) demonstrated that after removing the volatile fraction, diesel soot particles have a density of  $1.77 \text{ g cm}^{-3}$  independent of the particle size in opposition to fresh diesel exhaust particles which have a size dependent density varying from  $1.27$  to  $1.78 \text{ g cm}^{-3}$  in a size range of 50 to 220 nm (mobility diameter). Based on these different values, a density of  $1.77 \text{ g cm}^{-3}$  for BC seems to be a relevant value for ambient BC.

## **SI-2 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 (LVOOA and SVOOA). 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., 2013) 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<sub>x</sub>, SV-OOA with NO<sub>3</sub>, LV-OOA with SO<sub>4</sub> and BBOA with levoglucosan). Further details about this approach and data analysis can be found in Crippa et al. (2014). 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.

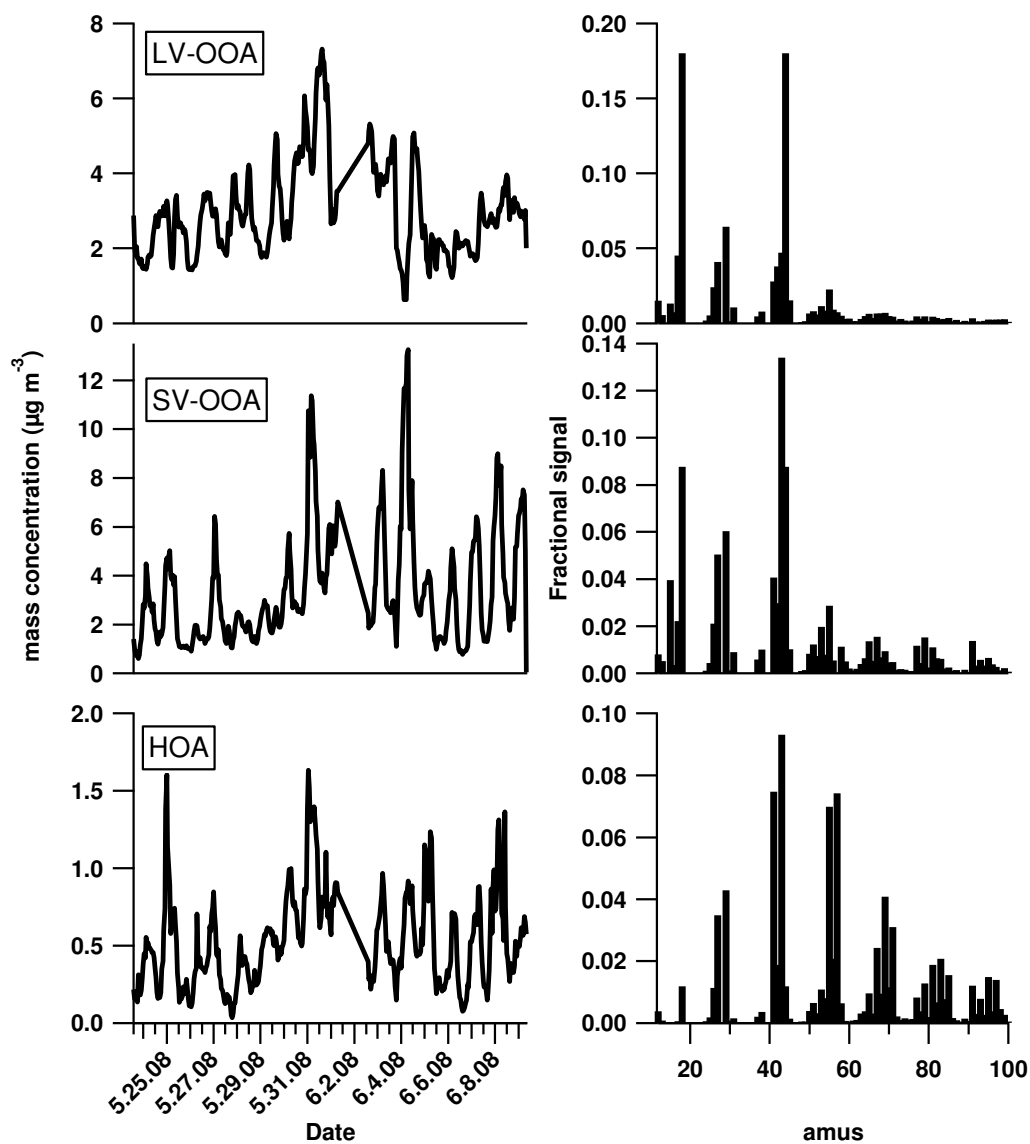


Figure SI-2a: 3-factors solution for the late spring 2008 campaign. The HOA mass spectrum was constrained with an  $\alpha$ -value of 5%.

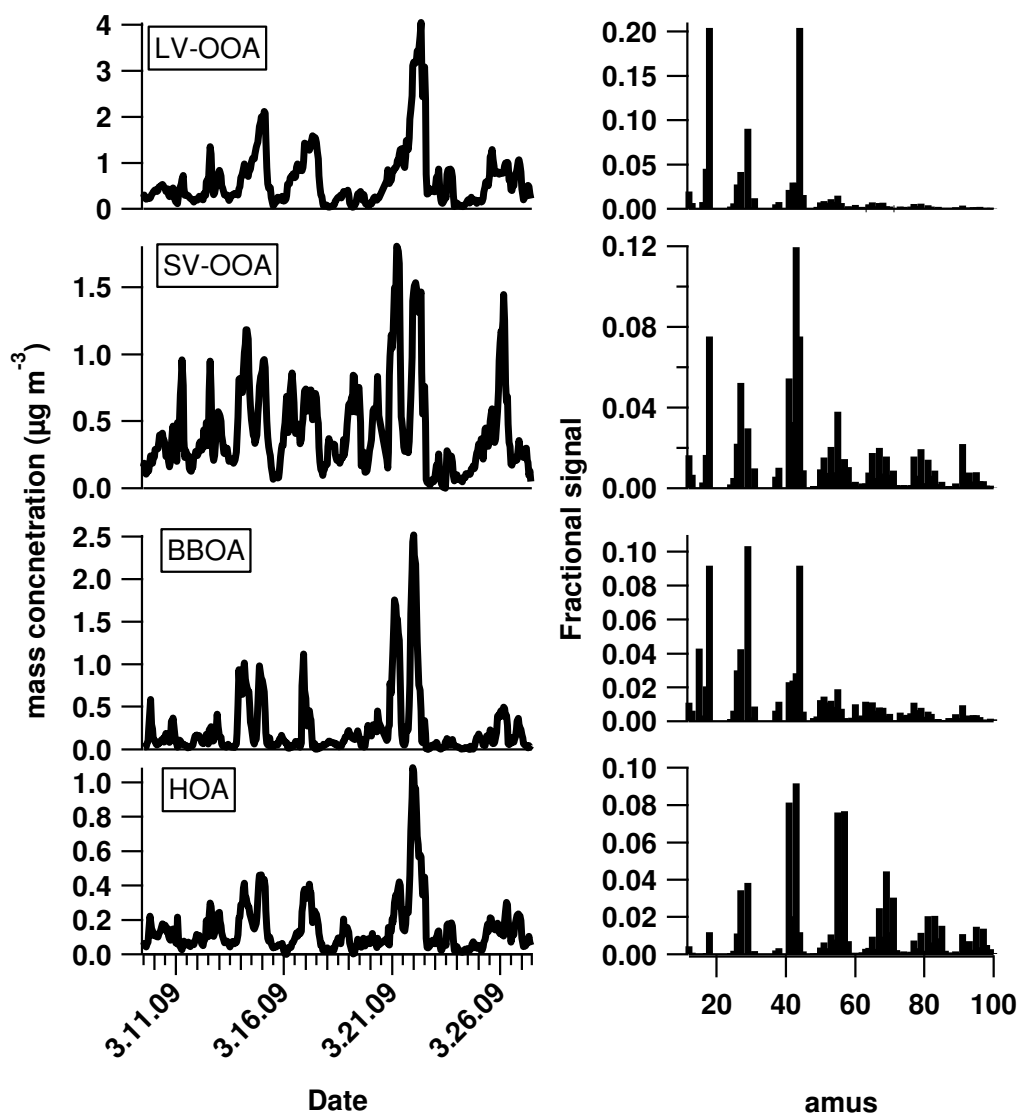


Figure SI-2b: 4-factors solution for the early spring 2009 campaign. The HOA mass spectrum was constrained with an  $a$ -value of 5%.

### SI-3 Contribution of the estimated refractory organic aerosol (ROA) to the measured refractory mass

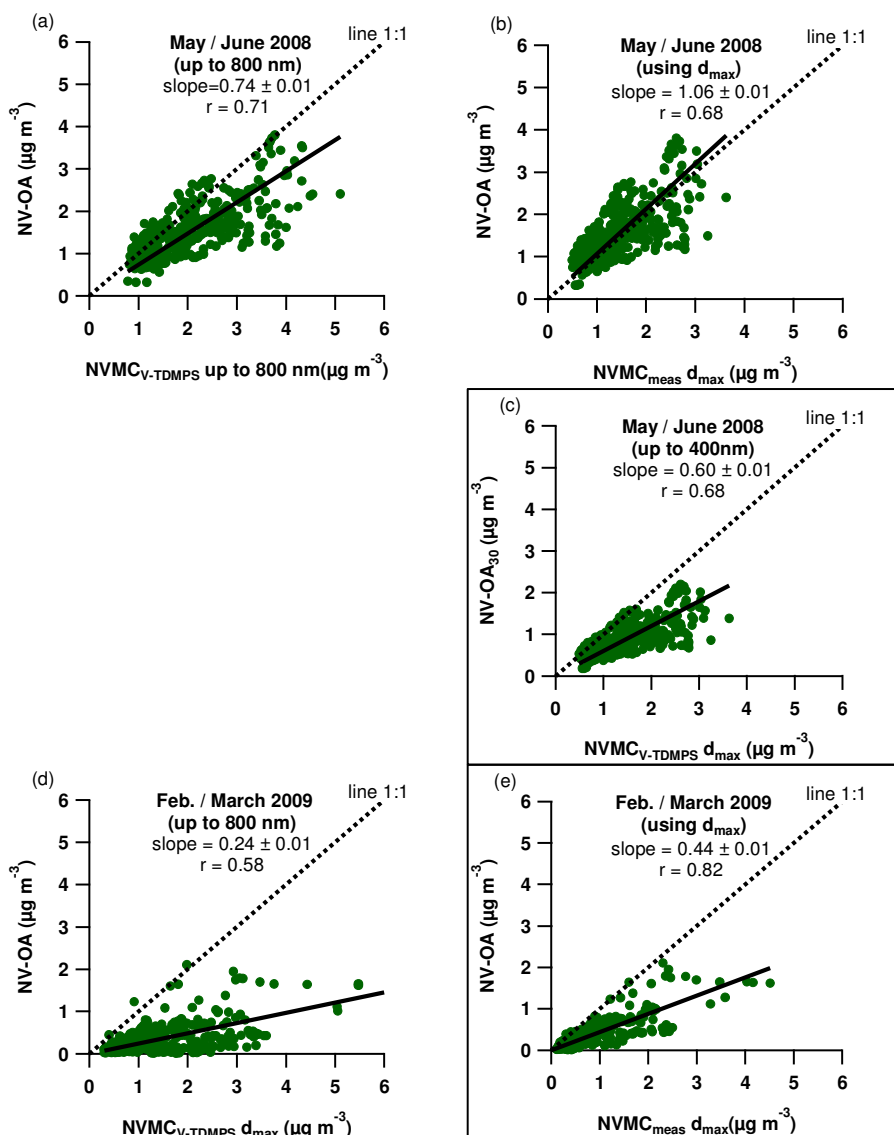


Figure SI-3: Estimated non-volatile organic aerosol (NVOA) vs. measured refractory mass concentration for May/June 2008 (a-c) and February/March 2009 (d,e) periods. Correlation curves were calculated using the least orthogonal distance fit method. Two different upper size cutting were used for the V-TDMPS: up to 800nm and using the  $d_{\text{max}}$  approach. NVOA was estimated to represent 52% of LVOOA excepted for NVOA<sub>30</sub> which represents only 30% of LV-OOA. Encased scatter plots correspond to the best estimation for each period.

## SI-4 Back trajectories analysis

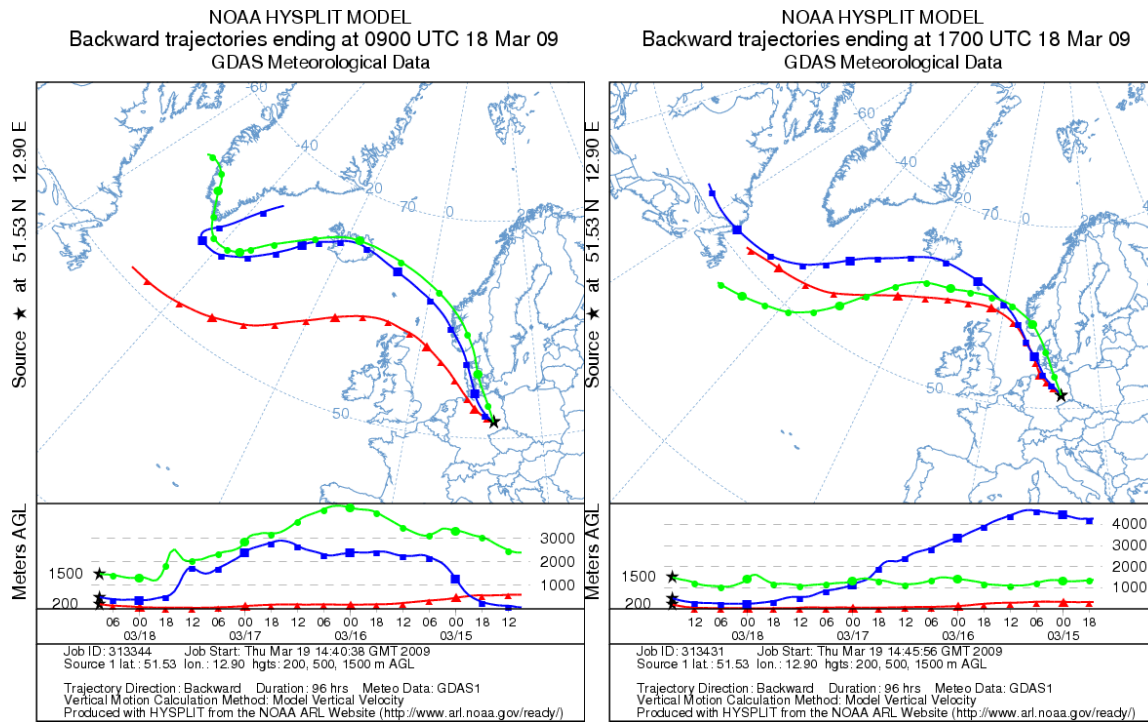


Figure SI-4: The 96h backward air mass trajectories calculated for March 18, 2009 at 09:00 (left) and 17:00 UTC (right).

## SI-5 Chemically resolved particle size distribution during early spring 2009

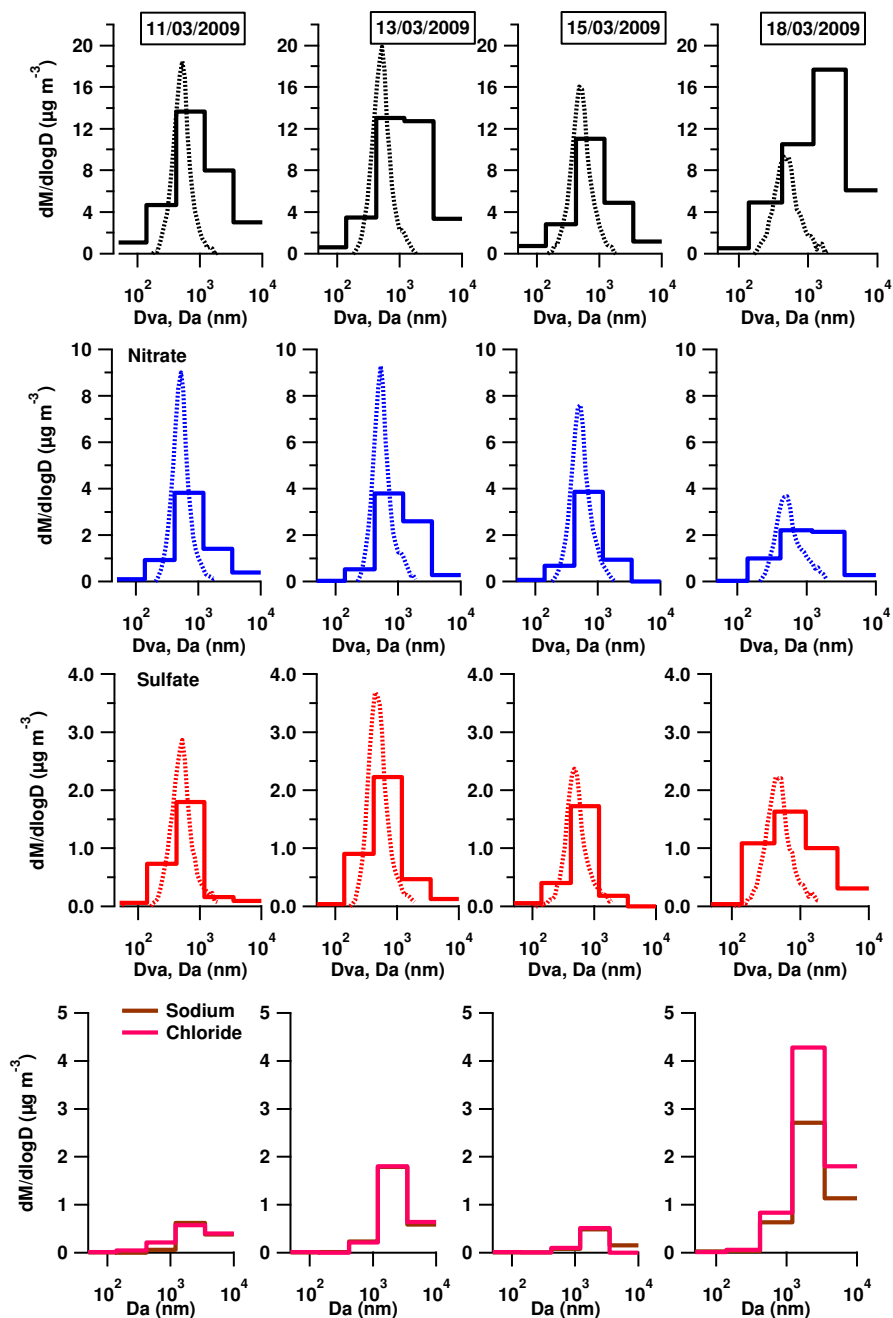


Figure SI-5: Comparison of the particle mass size distribution measured by AMS (dotted lines) and the 5-stages Berner impactor (solid lines) for the total mass (top), nitrate and sulfate during 4 different days. The Berner impactor results for sodium and chloride are also included at the bottom. The AMS data were averaged in order to fit the sampling time and particle mass size distribution of the impactor (from midnight to midnight).



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