Supplement of Atmos. Chem. Phys., 17, 8939–8958, 2017
https://doi.org/10.5194/acp-17-8939-2017-supplement

Supplement of

Speciation of organic aerosols in the Saharan Air Layer and in the free troposphere westerlies

M. Isabel García et al.

Correspondence to: Sergio Rodríguez (srodriguezg@aemet.es)

S1. Organic compounds

Organic species were identified by their GC retention time and characteristic ions in the mass spectrometer. Retention time was compared to those of the standards or with literature and NIST library and literature data (Claeys et al., 2007; Kourtchev et al., 2005; Clements and Seinfeld, 2007; Medeiros and Simoneit 2007; Fontal et al. 2015). The organic species analyzed and their characteristic ions are: succinic acid (*m/z* 247), glutaric acid (*m/z* 261), adipic acid (*m/z* 275), pimelic acid (*m/z* 289), suberic acid (*m/z* 303), azelaic acid (*m/z* 317), malic acid (*m/z* 233), phthalic acid (*m/z* 295), cis-pinonic acid (*m/z* 171), 3-hydroxyglutaric acid (3-HGA; *m/z* 349), 3- methyl-1,2,3-butanetricarboxylic acid (MBTCA; *m/z* 405), 2-methylglyceric acid (2-MGA; *m/z* 219), 2-methylthreitol (2-MT1) and 2-methylerythritol (2-MT2; *m/z* 219); levoglucosan (*m/z* 204), α- and β-glucose (*m/z* 204), mannitol (*m/z* 319), fructose (*m/z* 361) and sucrose (*m/z* 361); benz[a]anthracene (*m/z* 228), chrysene (*m/z* 228), benzo[b+k]fluoranthene (*m/z* 252), benzo[e]pyrene (*m/z* 252), benzo[a]pyrene (*m/z* 252), indeno[1,2,3-cd]pyrene (*m/z* 276), benzo[ghi]perylene (*m/z* 276); 17(H)α,21(H)β-29-Norhopane and 17(H)α,21(H)β-hopane (*m/z* 191); n-alkanes (*m/z* 71). The limits of quantification (LOQ) in the applied methodologies were 0.02 ng·m^{-3} for the saccharides, 0.01 ng·m^{-3} for the acids and 0.002 ng·m^{-3} for PAHs, hopanes and n-alkanes. The concentrations were corrected by the recoveries of the above mentioned surrogates. The recoveries of the surrogate standards were higher than 60 %. The field blanks concentrations of the reported compounds were between 1 and 30 % of the sample concentration. Organic compounds, such as carboxylic acids are not reported due to higher blank concentrations. No corrections for the blank concentrations were applied on the sample concentrations.

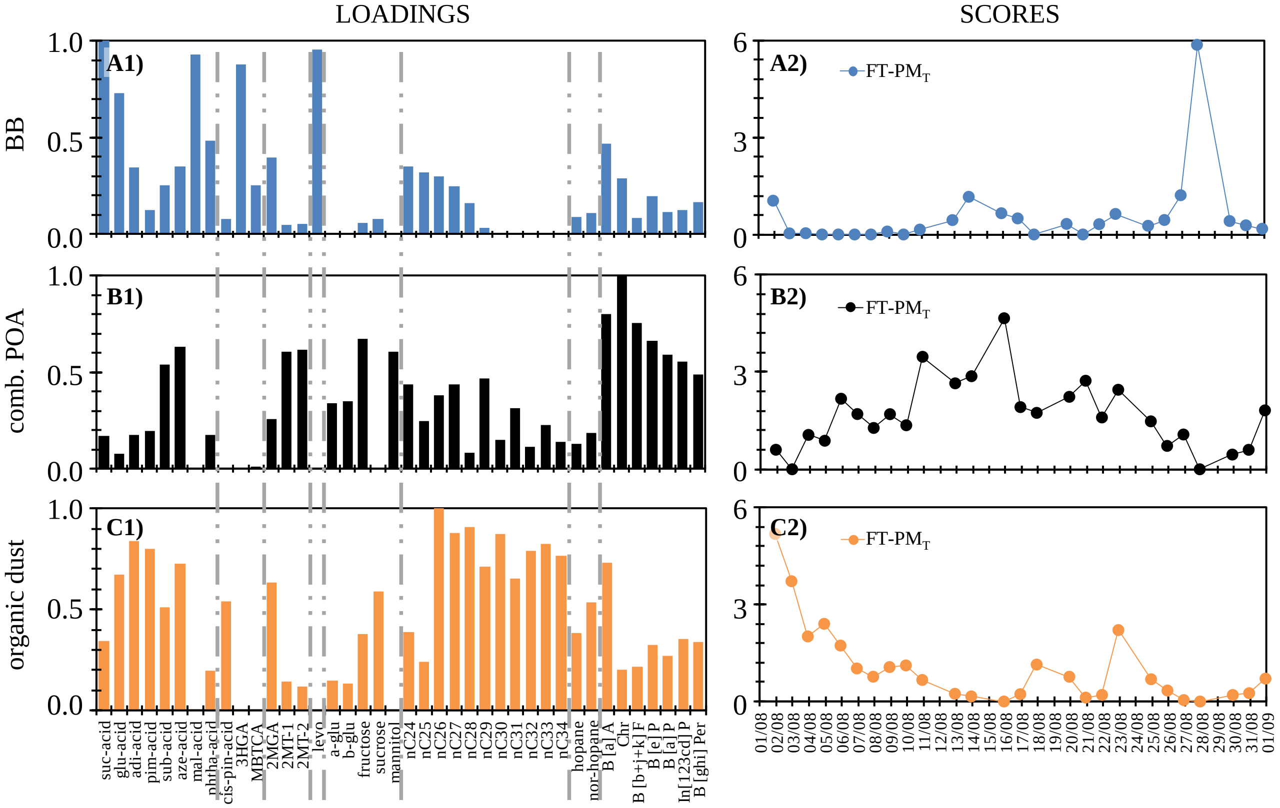

Figure S1: PM_T samples loadings and scores of the three components from MCR-ALS resolved profiles. Grey lines separate the compounds belonging to the different organic groups: dicarboxylic acids, SOA PIN, SOA ISO, levoglucosan, saccharides, n-alkanes, hopanes and PAHs (from left to right). FT-PMT samples were collected during the night (22 to 06 GMT). **BB**: biomass burning; **comb. POA**: Primary organic aerosol from combustion.

S2. Sources of organic aerosol

Multivariate Curve Resolution (MCR-ALS) was applied to identify potential contribution sources to the OM. In order to evaluate possible changes in the sources profiles whether the method was applied to the free troposphere (FT-PMT) and boundary layer (BL-PM$_{2.5}$) samples separately, we performed MCR-ALS only for the FT-PMT samples. Figure S1 shows the sources profiles, which did not vary greatly from those obtain when taking both sample sets (FT-PMT and BL-PM$_{2.5}$) into account. The main differences are seen in the n-alkanes and saccharides distributions, between combustion POA (Fig. S1B1) and organic dust (Fig. S1C1), as combustion POA is not affected by BL-PM$_{2.5}$.

S3. Evaluation of the MCR-ALS results

Table S1. Pearson correlation coefficients of the components scores and organic matter, elemental carbon and dust. Statistically significant correlations (p-value < 0.05) are highlighted. FT-PMT samples were collected during the night (22 to 06 GMT) and BL-PM$_{2.5}$ samples were collected during the day (10 to 16 GMT).

	BB	Com. POA	Organic dust	Σ SS
All				
dust	0.05	-0.27	0.84	0.53
OM	0.20	-0.28	0.64	0.44
EC	0.57	0.36	-0.38	0.51
FT-PM$_T$				
dust	0.14	-0.13	0.84	0.63
OM	0.40	-0.12	0.55	0.63
EC	0.65	0.24	-0.38	0.49
BL-PM$_{2.5}$				
dust	-0.08	-0.08	0.73	0.10
OM	-0.56	0.36	0.75	0.33
EC	-0.10	0.71	-0.50	0.67

BB: biomass burning; **comb. POA**: Primary organic aerosol from combustion; Σ **SS**: sum scores of the three components; **OM**: organic matter; **EC**: elemental carbon.

Scores obtained from the Multivariate Curve Resolution (MCR-ALS) applying non-negativity constraints, for both FT-PMT and BL-PM$_{2.5}$, were correlated with dust, organic matter (OM) and elemental carbon (EC). The correlation was done for all-samples, FT-samples and BL-samples, to verify there was a statistical relationship between the selected sources and the above mentioned variables. Overall, the correlation of the components sum with the total OM (r-All = 0.44, $p < 0.01$; Table 1S) and EC (r-All = 0.51, $p < 0.01$; Table 1S) concentrations is significant for all samples. The correlation holds for the FT (OM r-FT = 0.63 and EC r-FT = 0.49, $p < 0.05$; Table 1S) and BL (EC r-BL = 0.67, $p < 0.05$; Table S1) separately, revealing that the identified sources might describe, not only the fraction determined of the OM but also the total OM.

S4. Sources contribution

To evaluate the contribution of each source to the OM determined, a multilinear regression analysis (r2 = 0.84) was performed with the scores – obtained in the MCR-ALS – as independent variables and the sum of the organic tracer compounds as the dependent variable. Average source contribution to the OM determined was calculated for the four studied air masses. The biomass burning event is enclosed in the free troposphere under the Westerlies influence (FT-WES).

Table S2. Contribution of the three identified sources to the OM fraction for the studied air masses: free troposphere under the SAL (FT-SAL) and WES (FT-WES) influence and BL under the SAL (BL-SAL) and the WES (BL-WES) influence. FT-PMT samples were collected during the night (22 to 06 GMT) and BL-PM$_{2.5}$ samples were collected during the day (10 to 16 GMT).

	BB, %	Com. POA, %	Organic dust, %	Undetermined, %
FT-SAL	1.1	6.1	8.2	84.6
FT-WES	22.5	19.4	22.2	35.8
BL-SAL	2.3	6.1	0.8	90.8
BL-WES	35.7	40.8	0.2	23.4

BB: biomass burning; **comb. POA**: Primary organic aerosol from combustion.

Supporting References

Kourtchev, I., Ruuskanen, T., Maenhaut, W., Kulmala, M. and Claeys, M.: Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytil, Finland, Atmos. Chem. Phys. Discuss., 5(3), 29472971, doi:10.5194/acpd-5-2947-2005, 2005.

Clements, A. L. and Seinfeld, J. H.: Detection and quantification of 2-methyltetrols in ambient aerosol in the southeastern United States, Atmos. Environ., 41(9), 18251830, doi:10.1016/j.atmosenv.2006.10.056, 2007.