Supporting Information to

Characterization of Chemical Aerosol Composition with Aerosol Mass Spectrometry in Central Europe: An Overview

V. A. Lanz[1], A. S. H. Prévôt[1], M. R. Alfarra[1,2], C. Mohr[1], P. F. DeCarlo[1], S. Weimer[3], M. F. D. Gianini[4], C. Hüglin[4], J. Schneider[5], O. Favez[6], B. D'Anna[6], C. George[6] and U. Baltensperger[1]

[1]Paul Scherrer Institut, Laboratory of Atmospheric Chemistry, CH-5232 Villigen PSI, Switzerland
[2]Centre for Atmospheric Sciences, School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M60 1QD, UK
[3]Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Internal Combustion Engines, CH-8600 Duebendorf, Switzerland
[4]Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Air Pollution and Environmental Technology, CH-8600 Duebendorf, Switzerland
[5]Particle Chemistry Dept., Max Planck Institute for Chemistry, Mainz, Germany
[6]Université Lyon 1, Lyon, F-69626, France; CNRS, UMR5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Villeurbanne, F-69626, France

Table S1:

(a.) FA settings: method (PMF or ME based approach), number of factors (*p*), *fpeaks* used to induce rotations of the solution, robust mode (T) versus non-robust mode (F), degree of relaxation (*a*) for the *a priori* fixed HOA-profile (in ME approach). As *a priori* profiles in the ME-2 program, usually the diesel MS from a dynamometer test bench was input (Schneider et al., 2006), which reflects passenger car emissions (EURO-3). As exceptions in ROV NOV_2005 the HOA-profile found with PMF2 (*p*=3) for ROV MAR_2005 was input and in the first ME-2 application on AMS data (ZUE JAN_2006; Lanz et al., 2008), an HOA-profile measured by Canagaratna et al. (2004) was used. In the supporting information to Lanz et al. (2008) evidence is provided that the initial *a priori* HOA-profile (Schneider et al. *vs.* Canagaratna et al. *vs.* HOA from PMF) in such an approach was non-critical.

(b.) OA components identified by FA-AMS: OOA (oxygenated organic aerosol), HOA (hydrocarbon-like organic aerosol), and P-BBOA (primary biomass burning organic aerosol). ‘XX’ indicates where OOA could be separated into a low-volatility, LV-OOA, and a semi-volatile, SV-OOA, fraction. Local organic aerosols sources (LOA; charbroiling and potentially food cooking; Lanz et al., 2007) were identified only in ZUE JUL_2005 and are not listed detailed here.

(c.) Correlations of factor time series with external markers (i.e., these latter quantities were not included in the data matrix, X (see Eq. 4), for PMF/ME analyses). The reported R^2‘s (coefficients of determination) serve as a rough measure of similarity between two time series (OA component retrieved by FA-AMS *vs.* external marker). However, non-linear relationships can not be reflected in this way. As an example, the time series of semi-volatile OOA (SV-OOA) vs. time series of particulate nitrate within a campaign frequently showed different populations characterized by different slopes (due to episodical shifts in nitrate or SV-OOA concentration levels that can be explained by their different processes of formation and removal, which may also be the reason for lower overall-R^2’s when time series of gases, CO and NO_x, and aerosols are compared). It is therefore possible that the overall-R^2 is rather low, while the R^2’s for all (certain) periods of the campaign are high (e.g., 0.55 for four fifths of ZUE JUL_2005 or 0.67 for the last third of PAY JUN_2006). n.r. = OA component not retrieved by FA-AMS, n.m. = auxiliary species not measured.

Campaign	**RHI FEB_2007**	**ZUE JUL_2005**	**ZUE JAN_2006**	**GRE JAN_2009**	**MAS DEC_2006**	**HAE MAY_2005**	**REI FEB_2006**	**ROV MAR_2005**	**ROV DEC_2005**	**PAY JUN_2006**	**PAY JAN_2007**	**MOHp MAY_2002**	**JFJ MAY_2008**
a. FA settings													
Method	PMF	PMF	ME	PMF	ME	PMF	ME	PMF	ME	ME	PMF	ME	ME
Factors (*p*)	3	6	3	3	3	3	3	3	3	3	4	2	2
Fpeak	-0.6	0.0	0.0	-0.2	0.0	0.0	0.0	0.0	0.0	0.0	-0.5	0.0	0.0
Robust mode	T	F	T	T	T	F	T	T	T	T	T	T	T
HOA prior (*a*)	-	-	0.6	-	0.4	-	0.4	-	0.0	0.0	-	0.0	0.2
b. OA Components													
OOA	X	XX	X	X	X	XX	X	X	X	XX	XX	X	X
HOA	X	X	X	X	X	X	X	X	X	X	X	X	X
P-BBOA	X	X	X	X	X	-	X	X	X	-	X	-	-
c. Correlation, R^2 (number of samples)													
OOA vs. NH_4^+	**0.85** 5202		**0.72** 4212	**0.86** 7698	**0.51** 2875		**0.85** 4551	**0.69** 9504	**0.55** 5504			**0.75** 2296	**0.75** 1077
OOA vs. NO_3^-	**0.85** 5202	n.r.	**0.61** 4212	**0.86** 7698	**0.56** 2875	n.r.	**0.83** 4551	**0.63** 9504	**0.64** 5504	n.r.	n.r.	**0.69** 2296	**0.69** 1077
OOA vs. SO_4^{2-}	**0.63** 5202		**0.53** 4212	**0.59** 7698	**0.56** 2875		**0.80** 4551	**0.20** 9504	**0.32** 5504			**0.72** 2296	**0.76** 1077
LV-OOA vs. SO_4^{2-}	n.r.	**0.52** 14914	n.r.	n.r.	n.r.	**0.41** 10016	n.r.	n.r.	n.r.	**0.54** 3953	**0.44** 3702	n.r.	n.r.
SV-OOA vs. NO_3^-		**0.55** 10200				**0.33** 2669				**0.67** 1207	**0.12** 1053		
HOA vs. NOx	CO, NO_X not measured (n.m.)	**0.74** 2776	**0.70** 2099	**0.69** 1403	**0.57** 959	**0.40** 2380	**0.45** 757	**0.37** 313	**0.31** 466	**0.07** 3845	**0.31** 3598	**0.03** 1231	**0.09** 933
HOA vs. CO		**0.81** 2776	**0.63** 2099	CO n.m.	**0.55** 932	**0.20** 2433	CO n.m.	**0.68** 313	**0.65** 466	**0.00** 3939	**0.35** 3669	**0.31** 1231	**0.15** 1059
P-BBOA vs. NOx		**0.48** 2800	**0.72** 2099	**0.46** 1403	**0.42** 959	n.r.	**0.31** 757	**0.11** 313	**0.14** 466	n.r.	**0.15** 3606	n.r.	n.r.
P-BBOA vs. CO		**0.70** 2793	**0.78** 2099	CO n.m.	**0.63** 932		CO n.m.	**0.56** 313	**0.66** 466		**0.38** 3677		

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