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], S. Weimer[1,3], C. Mohr[1], P. F. DeCarlo[1], 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 BBOA (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
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	**0.53** 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
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.
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		

Table S2: Relative average contributions of sulfate (SO_4^{2-}), organic matter (OM), ammonium (NH_4^+), nitrate (NO_3^-), and chloride (Cl^-) to non-refractory PM_1 (measured by aerosol mass spectrometers), as well as the fraction of PAHs relative to the total organics shown for all campaigns.

Campaign	SO_4^{2-} (%NR-PM_1)	OM (%NR-PM_1)	NH_4^+ (%NR-PM_1)	NO_3^- (%NR-PM_1)	Cl^- (%NR-PM_1)	PAH (%OM)
RHI FEB−2007	5	59	10	25	1	0.3
ZUE JUL−2005	15	68	8	8	<1	<0.05
ZUE JAN-2006	17	36	15	31	1	0.1
GRE JAN−2009	7	54	10	27	1	0.2
MAS DEC−2006	9	56	10	20	5	0.1
HAE MAY−2005	10	66	10	13	<1	0.1
REI FEB−2006	11	36	15	36	1	0.1
ROV MAR−2005	8	54	12	25	1	0.1
ROV DEC−2005	3	81	5	10	1	0.1
PAY JUN−2006	16	62	11	10	<1	<0.05
PAY JAN−2007	11	40	14	36	1	0.1
MOHp MAY−2002	19	50	11	19	1	0.1
JFJ MAY−2008	26	43	13	18	<1	<0.05

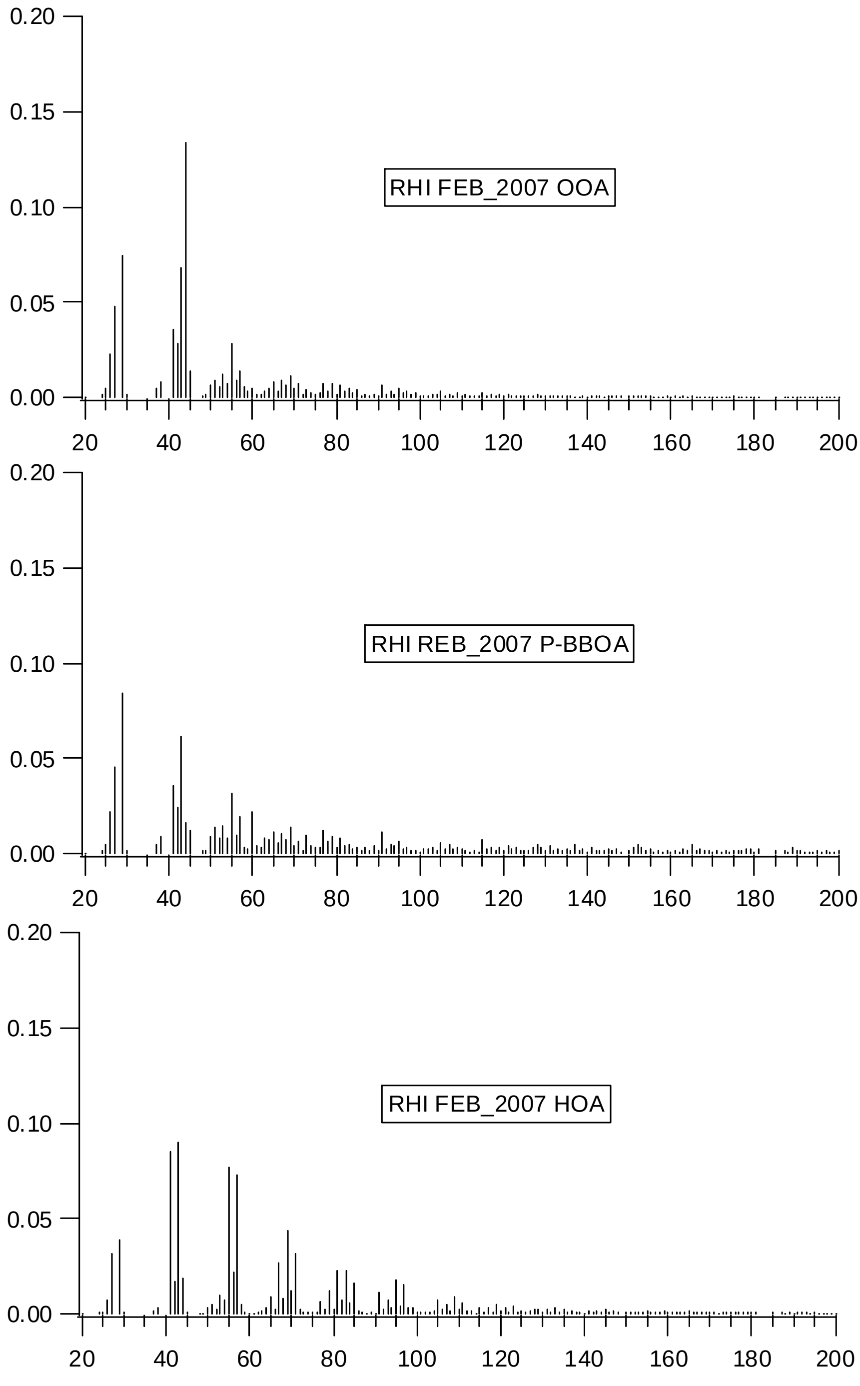

Figure S1: OOA, BBOA, and HOA spectra for the campaigns in the Rhine Valley.
(y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

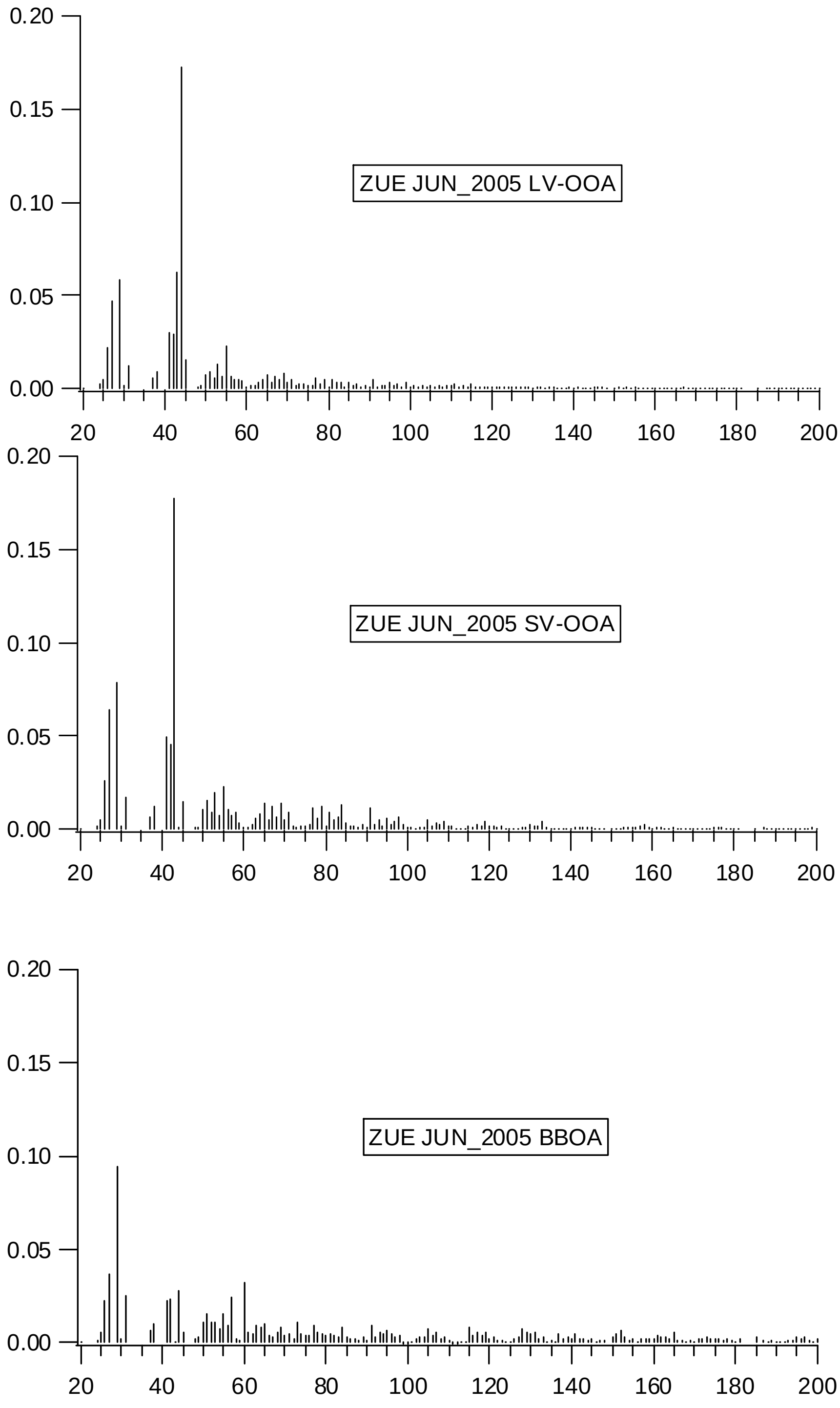

Figure S2: LV-OOA, SV-OOA, and BBOA spectra for the campaign in Zurich, July 2005. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

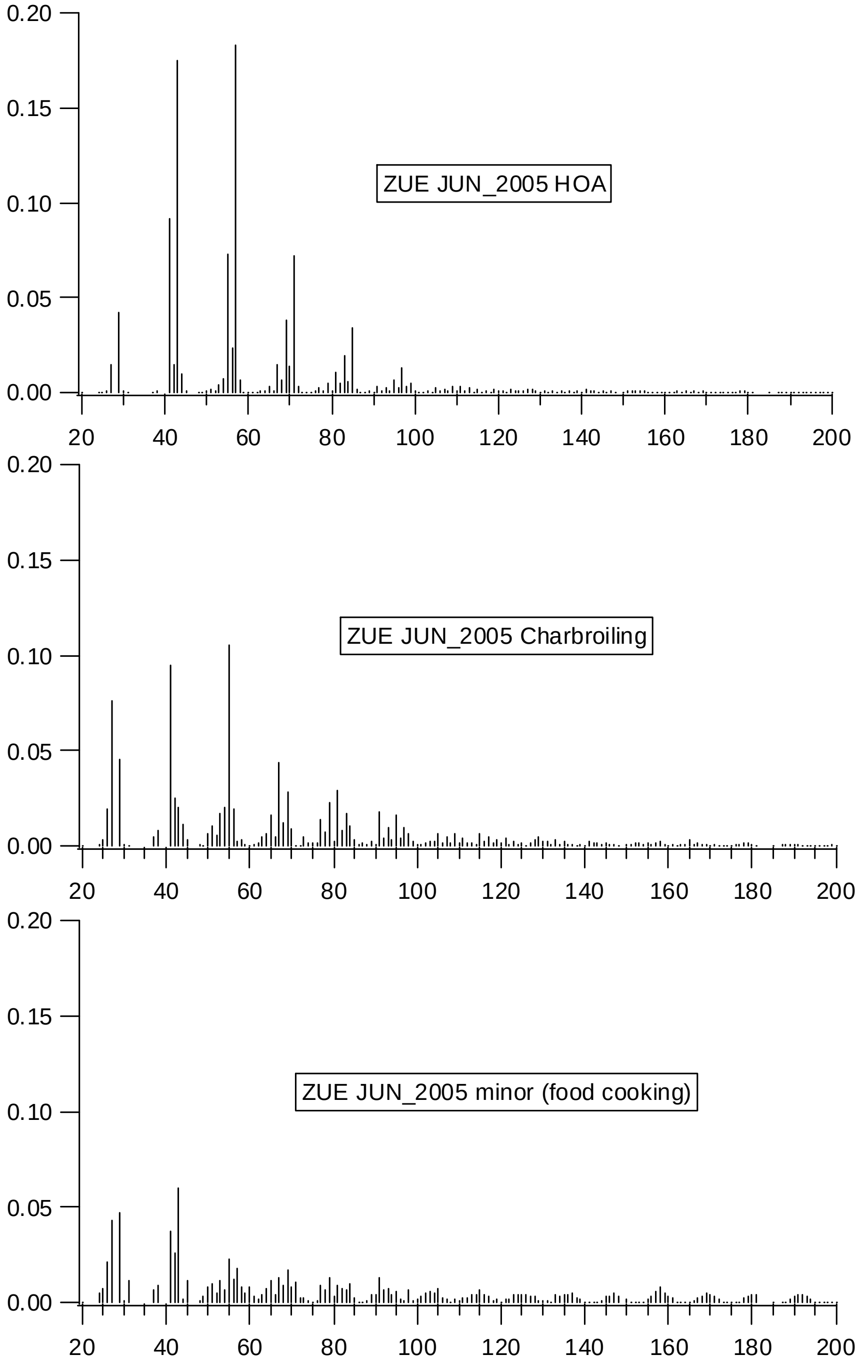

Figure S2 (cont.): HOA, charbroiling, and minor source spectra for the campaign in Zurich, July 2005. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

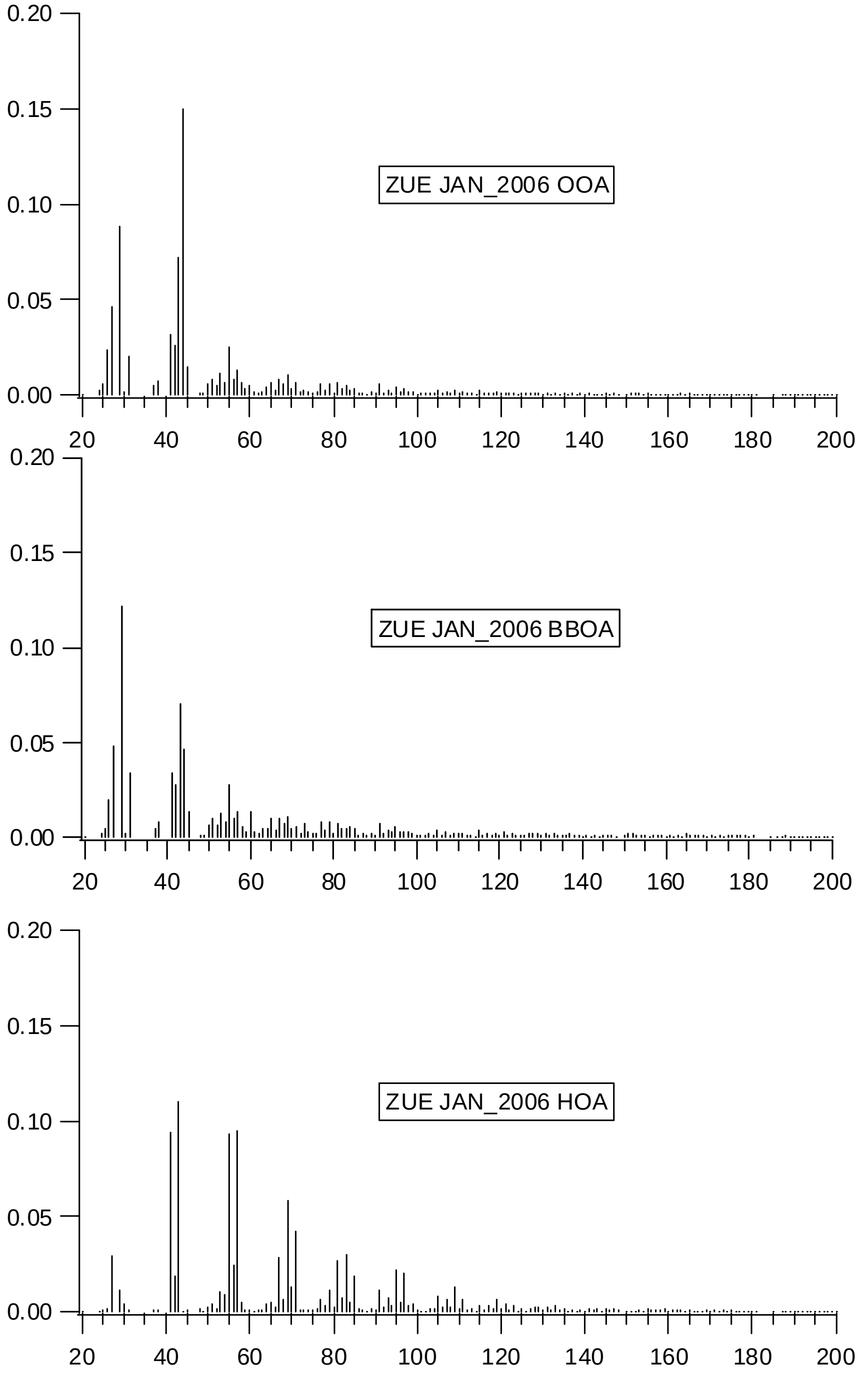

Figure S3: OOA, BBOA, and HOA spectra for the campaign in Zurich, January 2006.
(y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

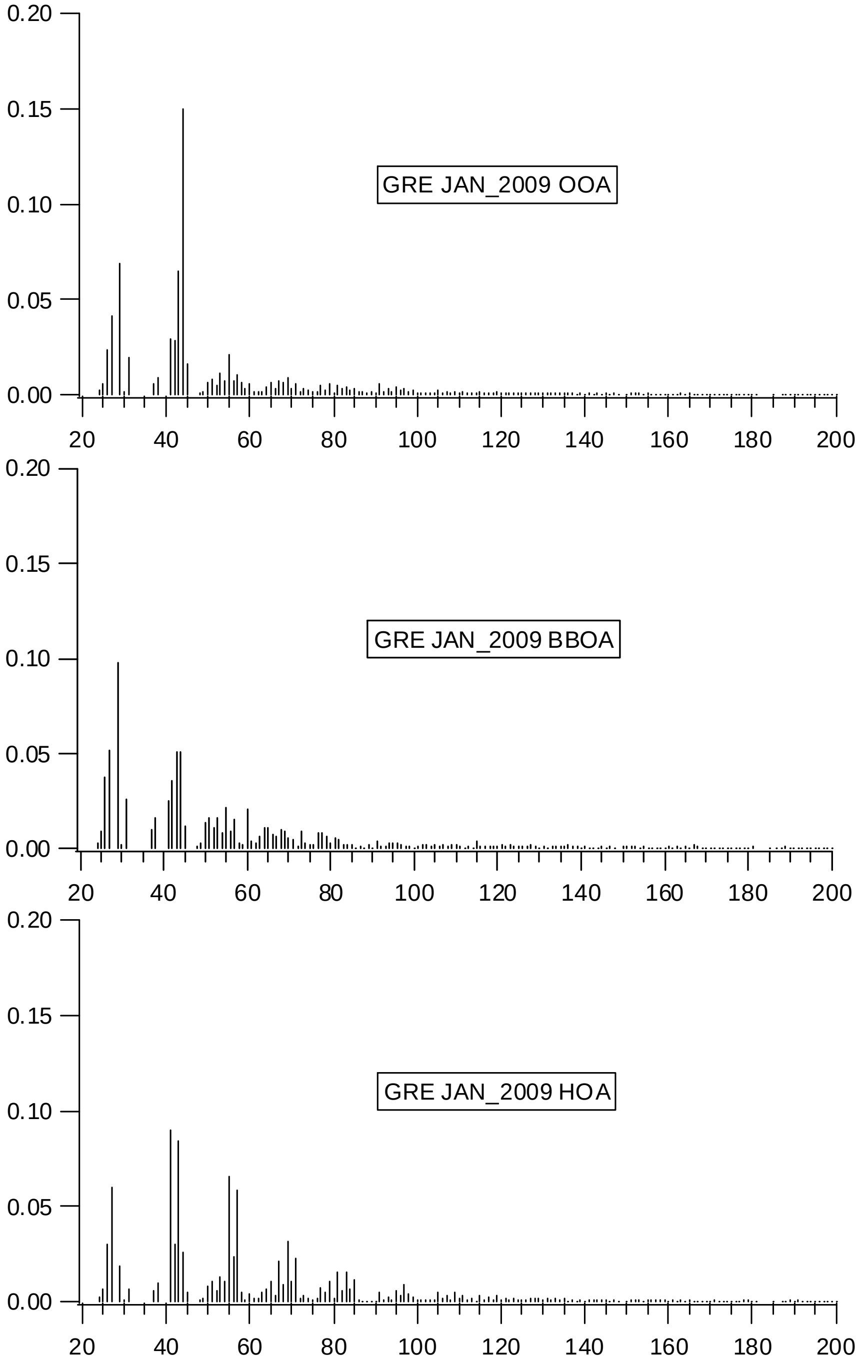

Figure S4: OOA, BBOA, and HOA spectra for the campaign in Grenoble, January 2009. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

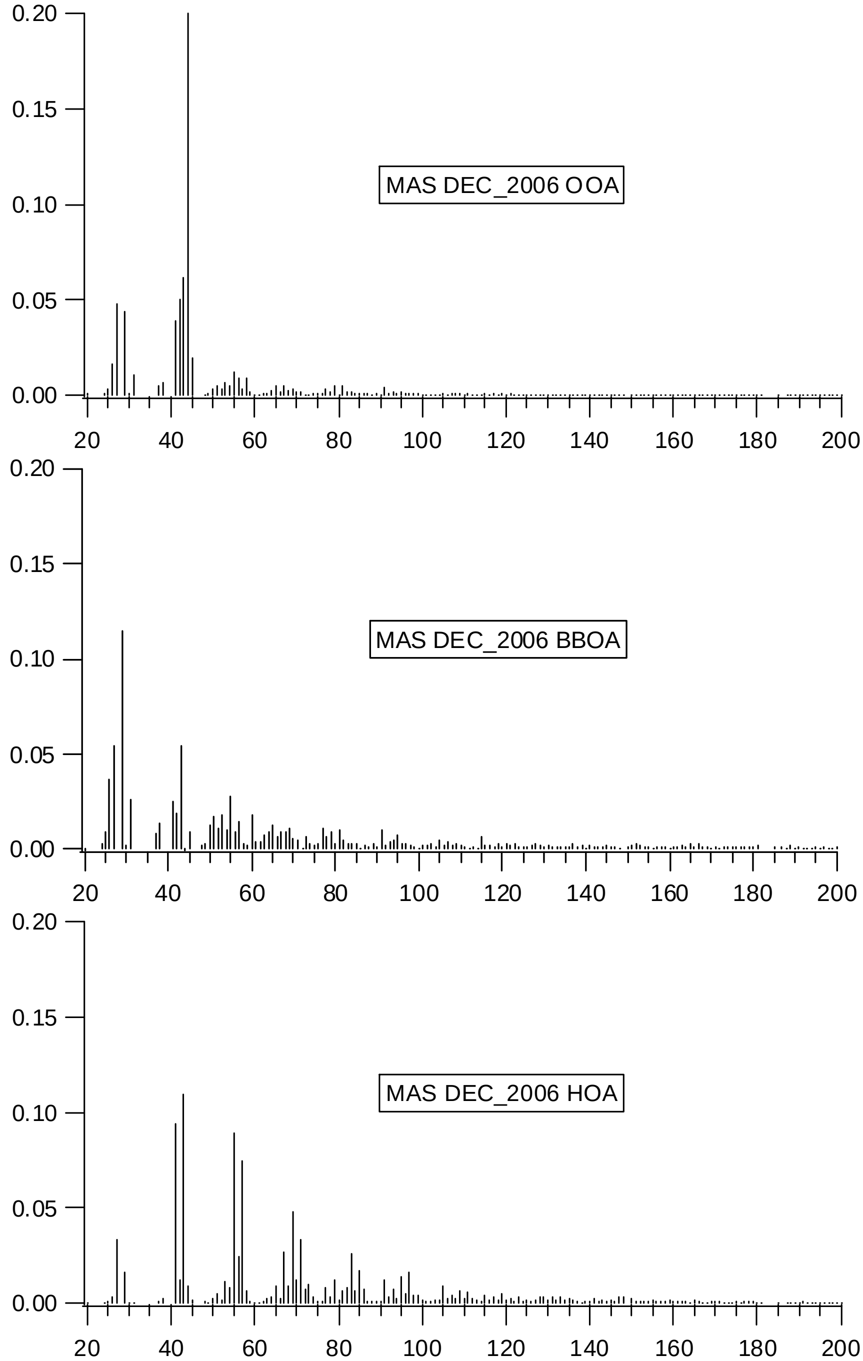

Figure S5: OOA, BBOA, and HOA spectra for the campaign in Massongex, December 2006. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

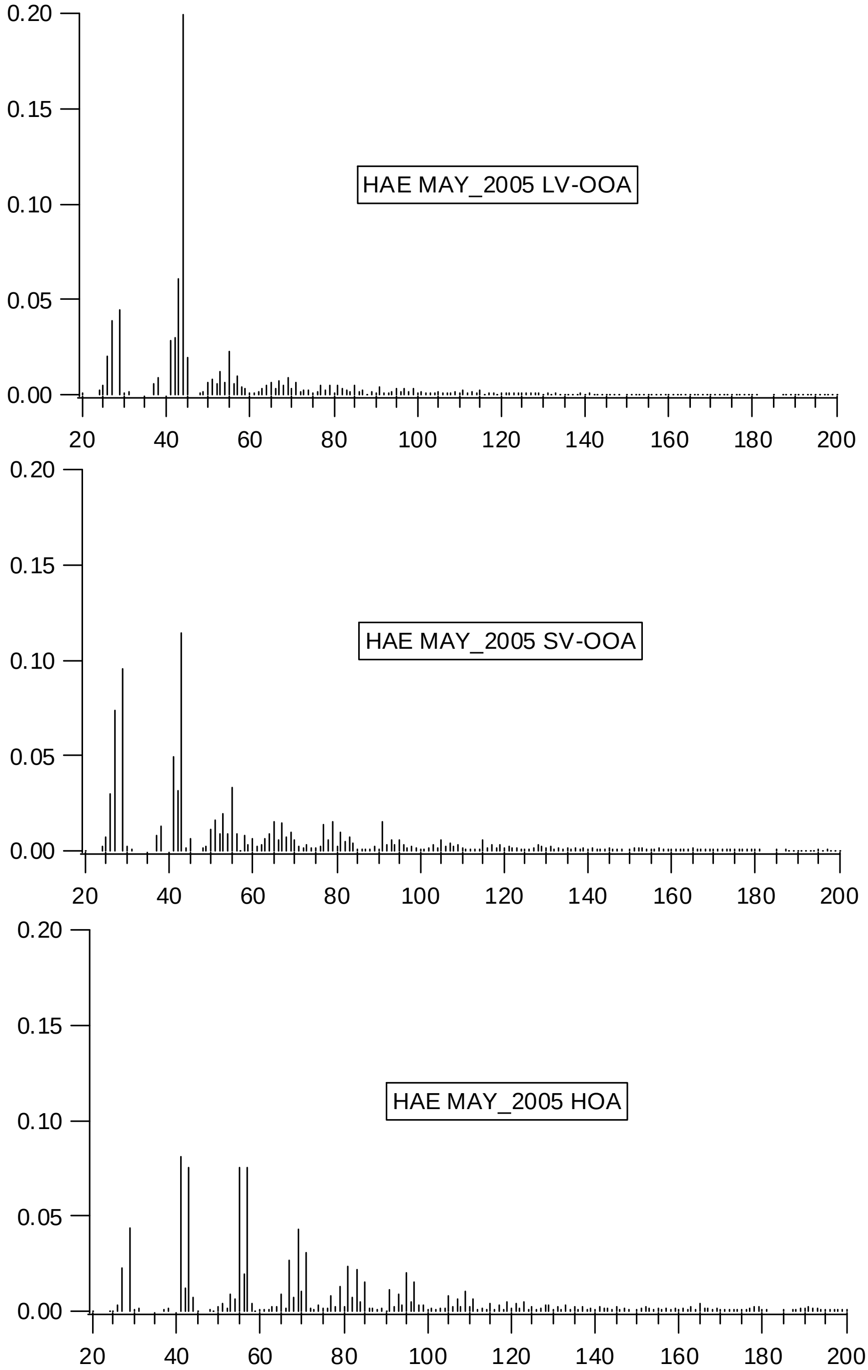

Figure S6: LV-OOA, SV-OOA, and HOA spectra for the campaign in Härkingen, May 2005. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

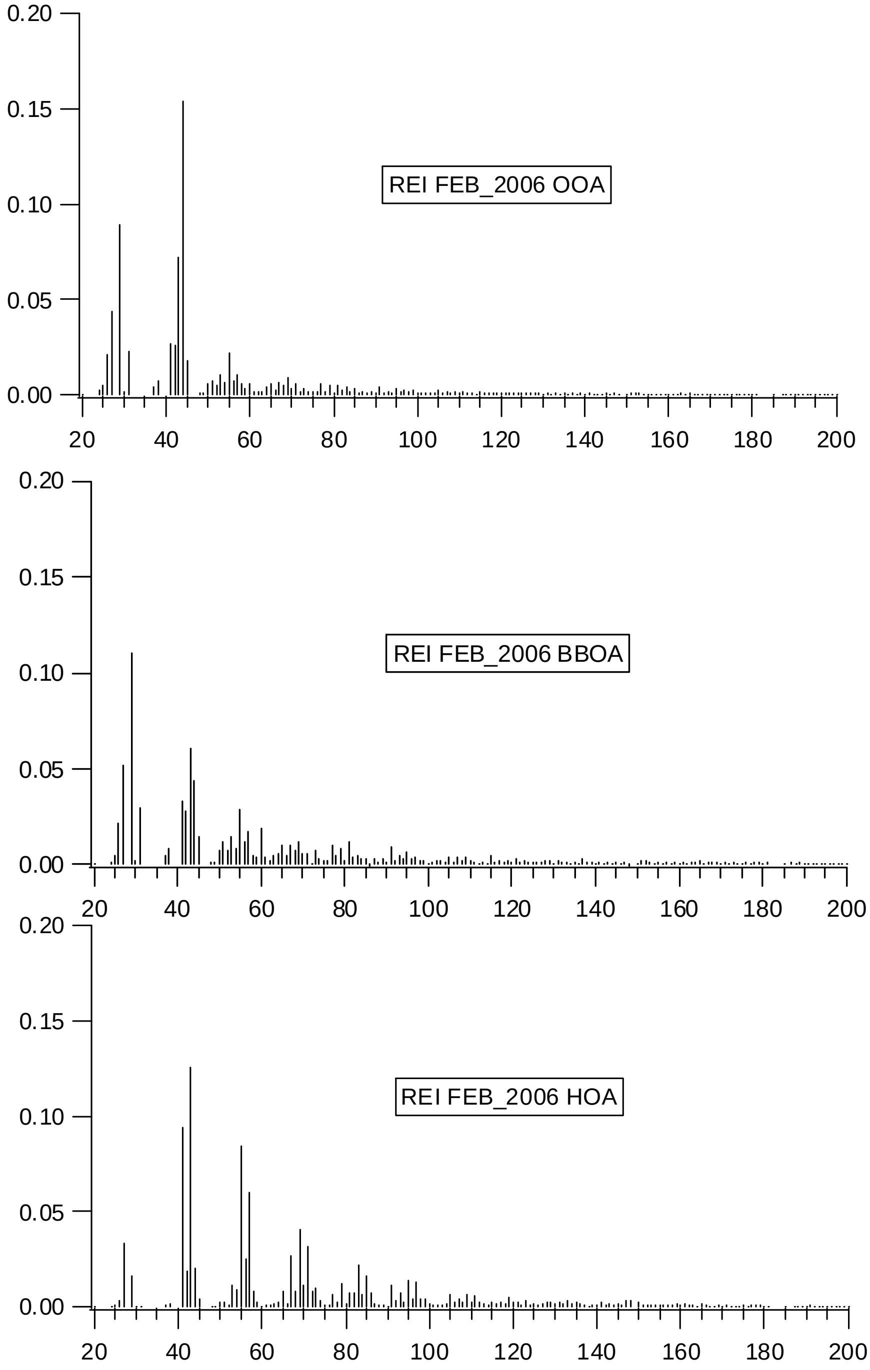

Figure S7: OOA, BBOA, and HOA spectra for the campaign in Reiden, February 2006.
(y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

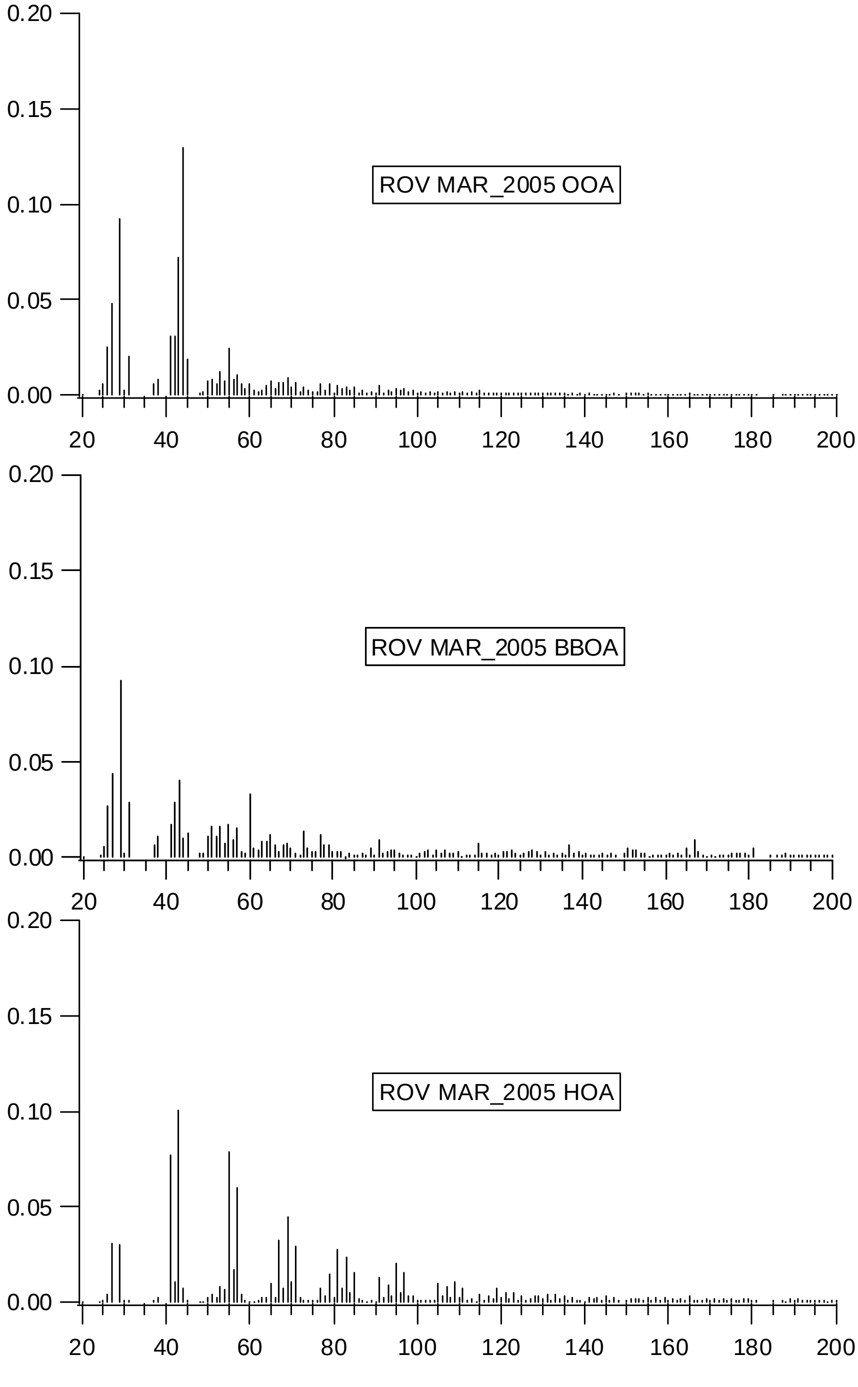

Figure S8: OOA, BBOA, and HOA spectra for the campaign in Roveredo, March 2005.
(y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

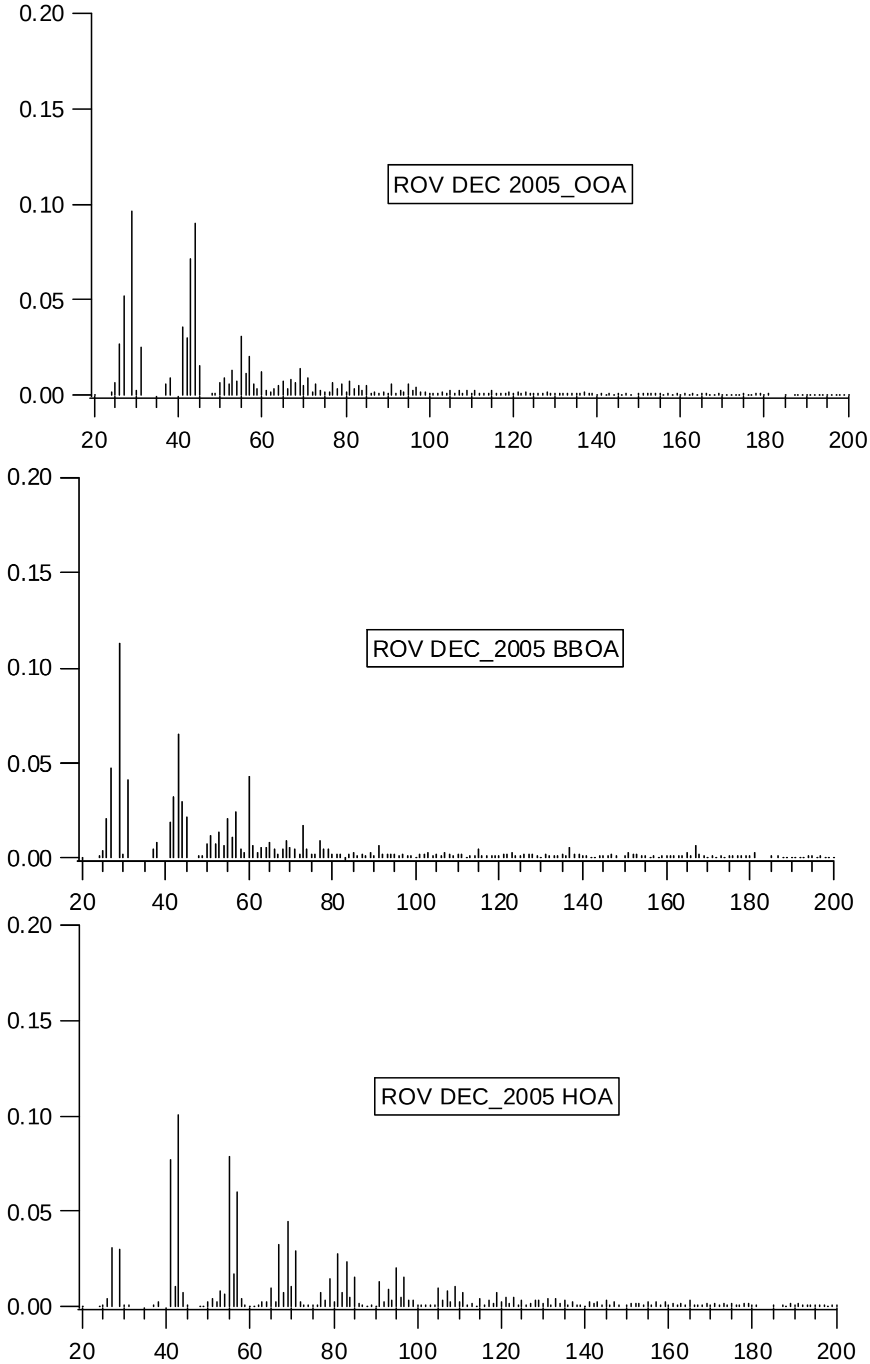

Figure S9: OOA, BBOA, and HOA spectra for the campaign in Roveredo, December 2005. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

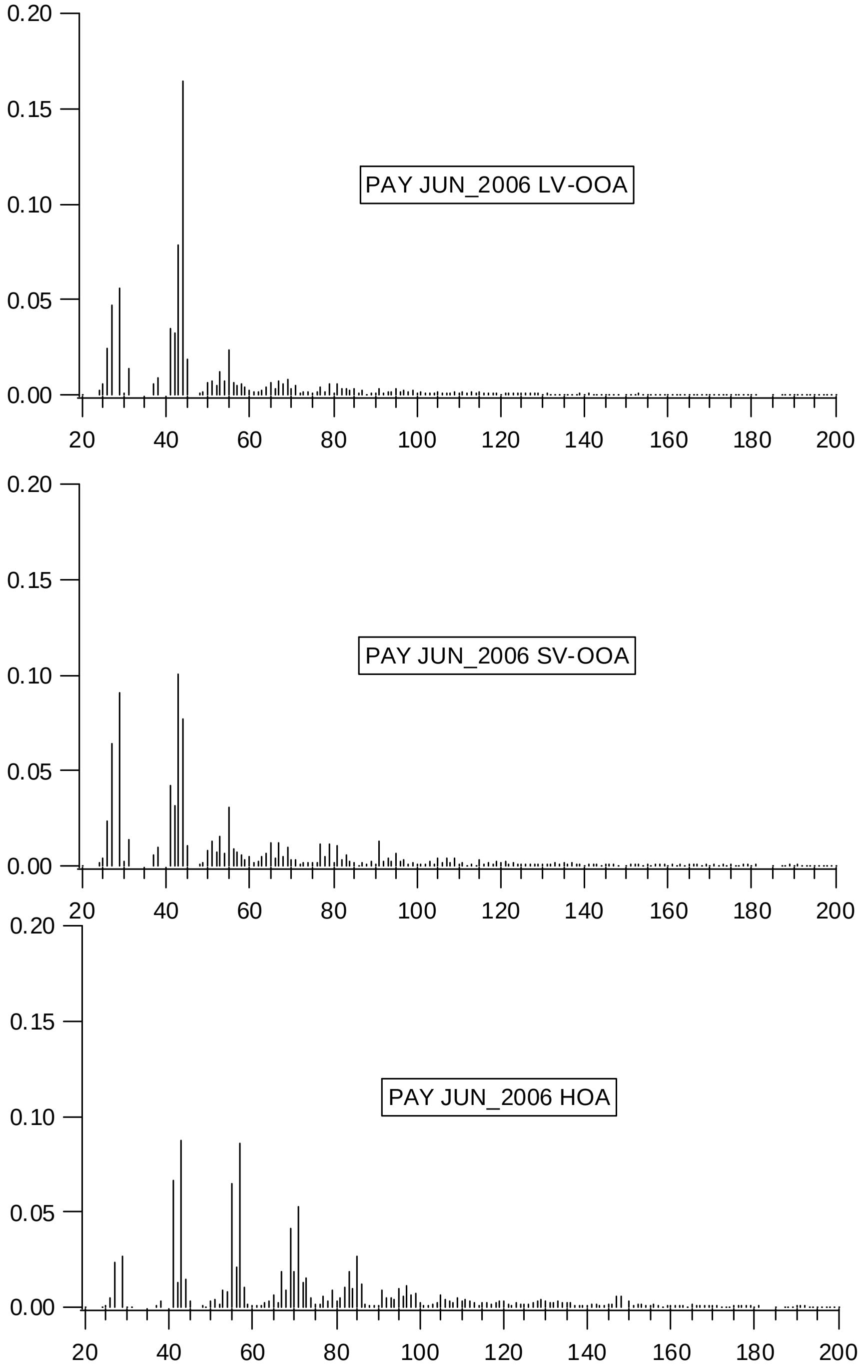

Figure S10: LV-OOA, SV-OOA, and HOA spectra for the campaign in Payerne, June 2006. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

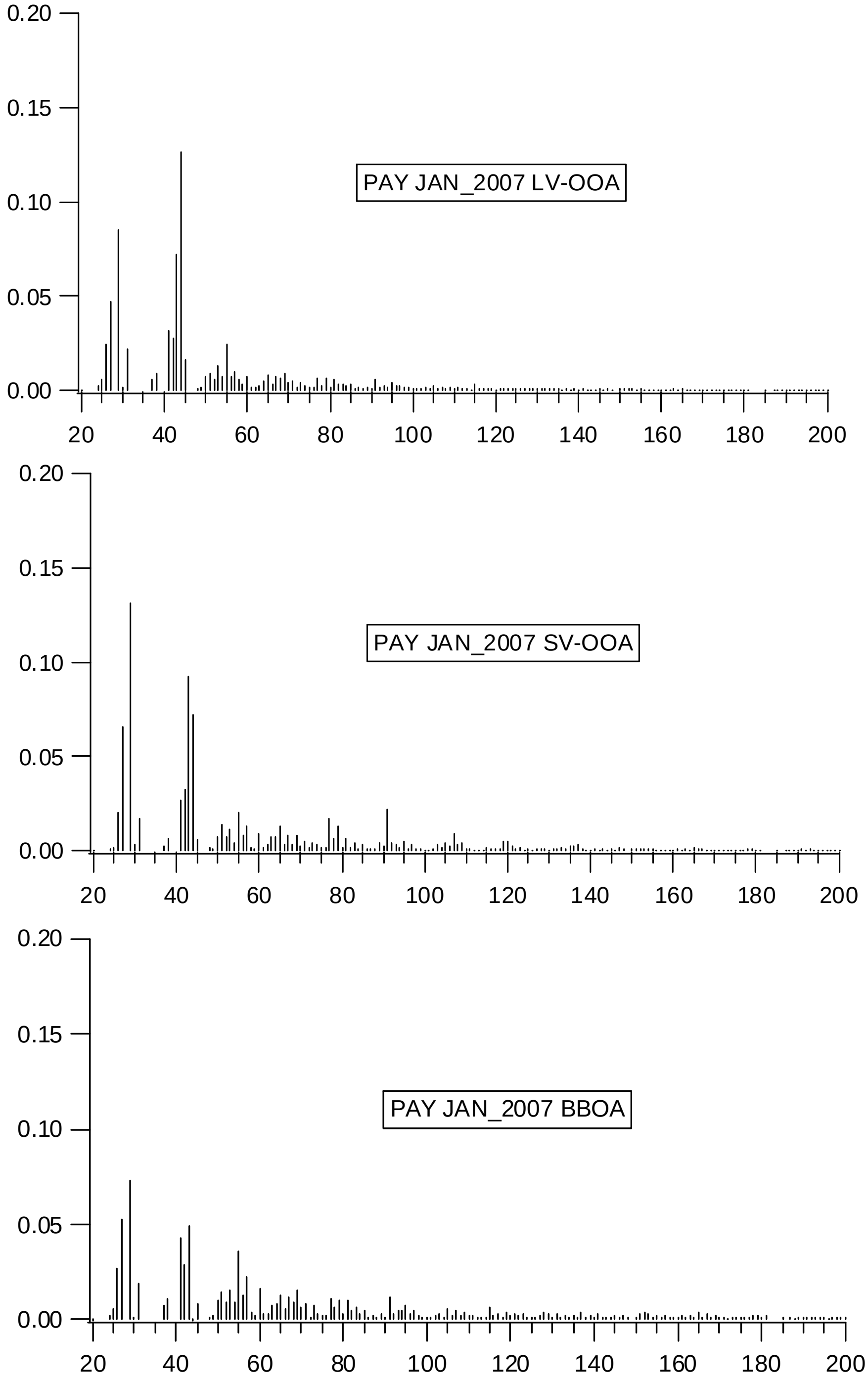

Figure S11: LV-OOA, SV-OOA, and BBOA spectra for the campaign in Payerne, January 2007. (y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

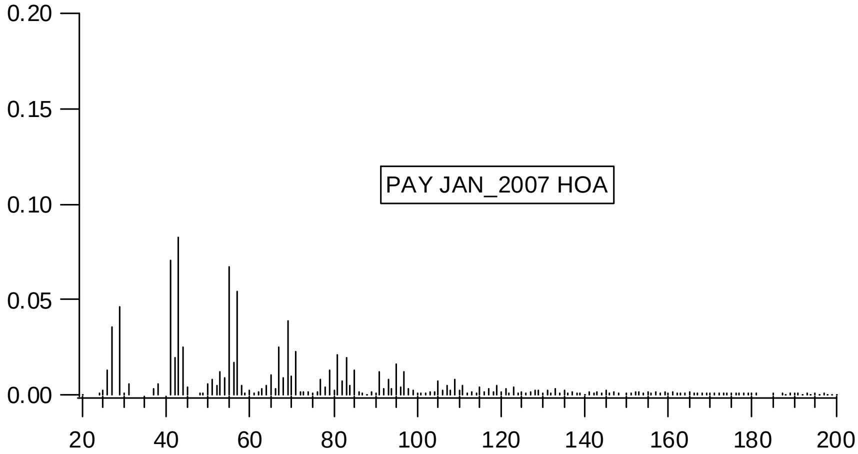

Figure S11 (cont.): HOA spectrum for the campaign in Payerne, January 2007.
(y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

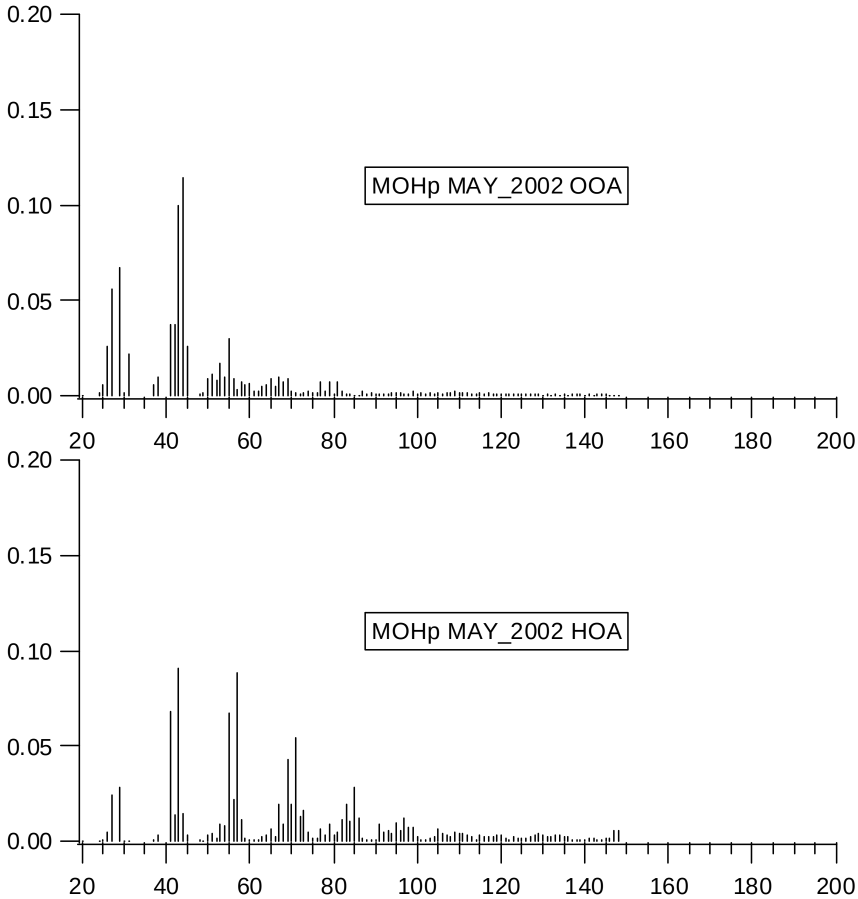

Figure S12: OOA and HOA spectra for the campaign in Hohenpeissenberg, May 2002.
(y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

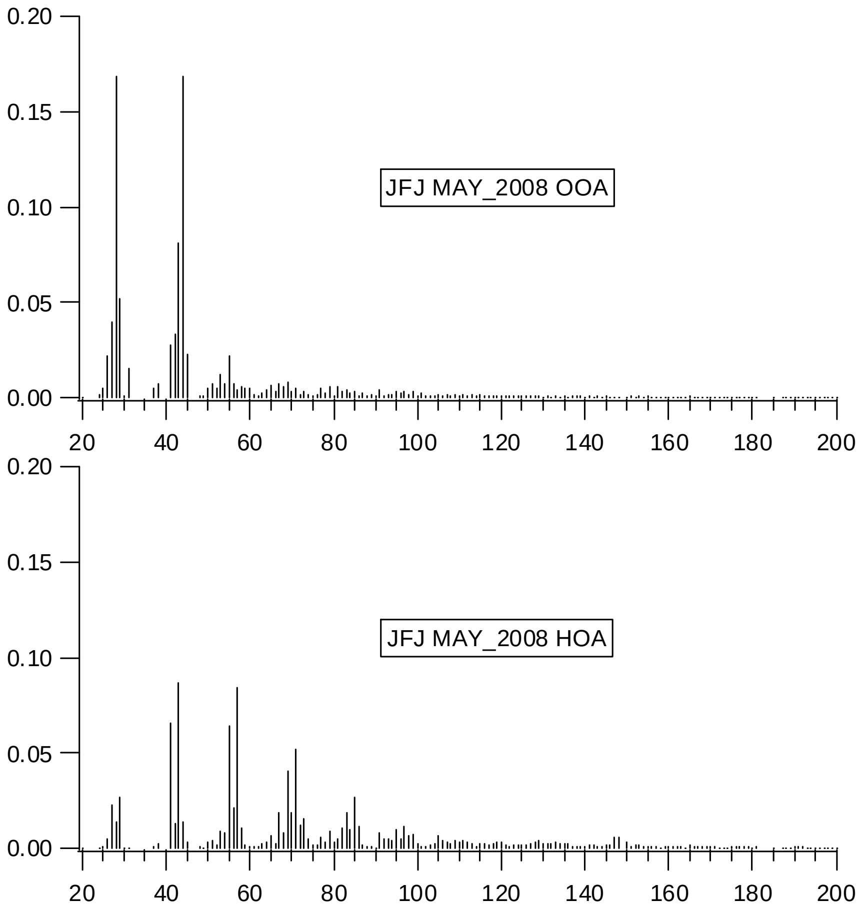

Figure S13: OOA and HOA spectra for the campaign at Jungfraujoch, May 2008.
(y-axis: intensities normalized to unity, scaled from 0.0 to 0.20; x-axis: mass fragments, *m/z*'s, 20 … 200)

References

Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q., Jimenez, J. L., Silva, P. J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L., Kolb, C. E., and Worsnop, D. R.: Chase studies of particulate emissions from in-use New York city vehicles, Aerosol Sci. Technol., 38, 555–573, doi:10.1080/02786820490465504, 2004.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prevot, 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.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., Szidat, S., Wehrli, M. N., Wacker, L., Weimer, S., Caseiro, A., Puxbaum, H., and Prevot, A. S. H.: Source attribution of submicron organic aerosols during wintertime inversions by advanced factor analysis of aerosol mass spectra, Environ. Sci. Technol., 42, 214-220, 2008.

Schneider, J., Weimer, S., Drewnick, F., Borrmann, S., Helas, G., Gwaze, P., Schmid, O., Andreae, M. O., and Kirchner, U.: Mass spectrometric analysis and aerodynamic properties of various types of combustion-related aerosol particles, Int. J. Mass. Spec., 258, 37–49, 2006.