



Supplement of

Understanding atmospheric aerosol particles with improved particle identification and quantification by single-particle mass spectrometry

Xiaoli Shen et al.

Correspondence to: Harald Saathoff (harald.saathoff@kit.edu)

The copyright of individual parts of the supplement might differ from the CC BY 4.0 License.

In summer time of 2016, a six-week field campaign was conducted at a rural site in the upper Rhine valley near Karlsruhe city in southwest Germany. $\sim 3.7 \times 10^5$ single particles were analysed by the laser ablation aerosol particle time-of-flight mass spectrometer (LAAPTOF). In the main manuscript we have shown an improved particle identification and quantification, and discussed the internal and external mixing state of the aerosol particles. Here is the supporting information, including tables and figures, as well as some detailed descriptions.

Table S1: Criteria for single particle identification method and the resulting correlation with fuzzy results

	class 1	class 2	class 3	class 4	class 5	class 6	class 7	total
criteria of γ_{pos} for positive spectra	≥ 0.6	≥ 0.6	≥ 0.6	≥ 0.6	≥ 0.6	≥ 0.8	≥ 0.6	—
criteria of γ_{neg} for negative spectra	≥ 0.45	≥ 0.45	≥ 0.5	≥ 0.3	≥ 0.53	≥ 0.8	≥ 0.5	—
correlation (γ) for particle number counts comparison	0.85	0.86	0.98	0.99	0.85	0.87	0.66	0.98

Note that, we have tuned both γ_{pos} and γ_{neg} in order to obtain the comparable time series of particle counts with fuzzy results.

Table S2: Four new laboratory generated aerosol particles for reference mass spectra

Aerosol particle types		Size/nm		Source	No. of Spectra
		d_{va}	width		
1	Sodium nitrate (NaNO_3)	935	230	Merck KGaA	3908
2	Secondary organic aerosol from toluene + OH radicals (A SOA) coated onto NaNO_3 seed particles	860	208	Toluene from Merck KGaA	5530
3	Secondary organic aerosol from α -pinene and toluene + OH radicals (A and B SOA) coated onto NaNO_3	838	207	(1S)-(-)- α -pinene (99%) from Aldrich	3982
4	Fly ash from coal combustion	0 to 20 μm * (sieved)		One power plant in UK	962

For aerosol generation and sampling methods: 1) Sodium nitrate particles were sampled from the 84.5 m³ simulation chamber AIDA (Aerosol Interactions and Dynamics in the Atmosphere) of KIT; 2) SOA particles coated NaNO_3 particles were formed via OH oxidation of toluene/toluene and α -pinene SOA with particle seeds in the presence of NO_x , and sampled from AIDA chamber; 3) Fly ash particles were suspended in their reservoir bottle by shaking them and sampled directly from the headspace (upper part) of these reservoir through a tube connecting it with the LAAPTOF.

For particles size information, d_{va} values represent the expected values from Gaussian fitting to the particle sizes measured by LAAPTOF. Size width represents the standard deviation from Gaussian fitting to the measured particle sizes (d_{va}).

*For fly ash particles, we give its size which was labelled in the original samples which were sieved with a 20 μm test sieve.

No. of Spectra is the number of averaged spectra.

Table S3: Corrected number fraction and mass fraction of different particle classes with different ODE*

	class 1	class 2	class 3	class 4	class 5	class 6	class 7
Corrected Number Fraction							
ODE_max	14.9%	26.0%	5.1%	4.1%	33.4%	3.5%	12.9%
ODE_mean	14.2%	24.3%	5.9%	5.0%	33.5%	4.5%	12.6%
ODE_min	13.8%	23.1%	5.5%	5.2%	34.2%	5.6%	12.6%
ODE_chemically resolved	18.2%	7.2%	3.4%	2.4%	45.0%	7.3%	16.5%
Particle Mass Fraction							
ODE_max	7.5%	9.6%	40.5%	8.8%	20.4%	3.8%	9.4%
ODE_mean	7.1%	8.0%	42.2%	9.4%	20.4%	4.7%	8.3%
ODE_min	7.6%	9.4%	33.9%	9.6%	23.6%	6.5%	9.5%
ODE_chemically resolved	10.3%	2.7%	30.1%	3.6%	31.8%	8.7%	12.9%

*see Fig. 1 for ODE_max/mean/min.

Table S4: Correlation for the comparison of non-refractory compounds measured by LAAPTOF and AMS

	Overall	Period 1	Period 2	Period 3	Period 4	Period 5	Period 6
Ammonium	0.63	0.37	0.74	0.46	0.88	0.38	0.65
Nitrate	0.32	0.65	0.70	0.67	0.47	0.55	0.43
Sulfate	0.10	-0.20	0.26	-0.14	0.69	0.07	0.15
Organic Cations	0.43	0.16	0.45	0.28	0.76	0.41	0.36
Organic Anions	0.32	-0.23	0.32	0.30	0.40	0.25	0.16
Org/(Org+Ammonium)	0.52	-0.02	0.52	0.28	0.55	0.01	0.46
Org/(Org+Nitrate)	0.62	0.78	0.85	0.81	0.68	0.76	0.35
Org/(Org+Sulfate)	0.38	-0.02	0.44	0.35	0.32	0.37	0.10

Note: The values in this table are the Pearson's correlation coefficients (γ) for the compounds measured by LAAPTOF in relative ion intensity (normalized to total ions) and AMS in mass concentration. $\gamma > 0.6$ are in bold. Periods 1 to 6 are the same time periods as in Fig. 6 and Fig. S4; LAAPTOF fragments for ammonium, nitrate, sulfate, and organics can refer to Fig. 7 and Fig. S7 captions. These two instruments show good correlations on Org/(Org+nitrate) for almost all the measurement time.

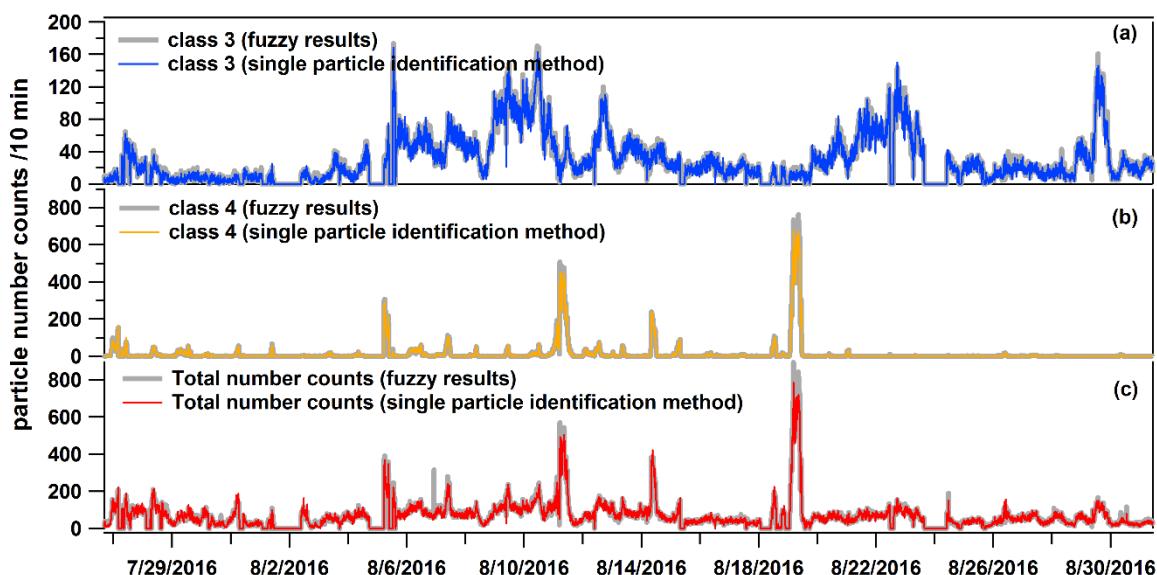


Figure S1: Time series of particle number counts obtained by fuzzy clustering and the single particle identification method using the fuzzy representative spectra as reference.

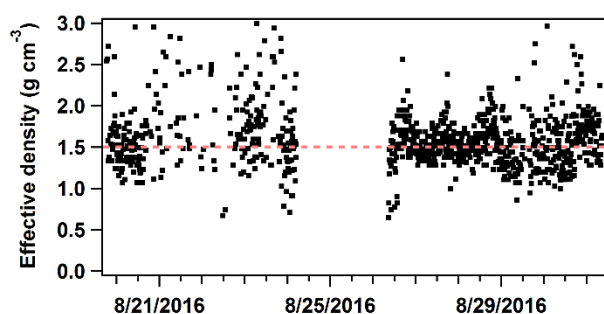


Figure S2. Time series of effective densities derived from comparison between AMS- d_{va} and SMPS- d_m .

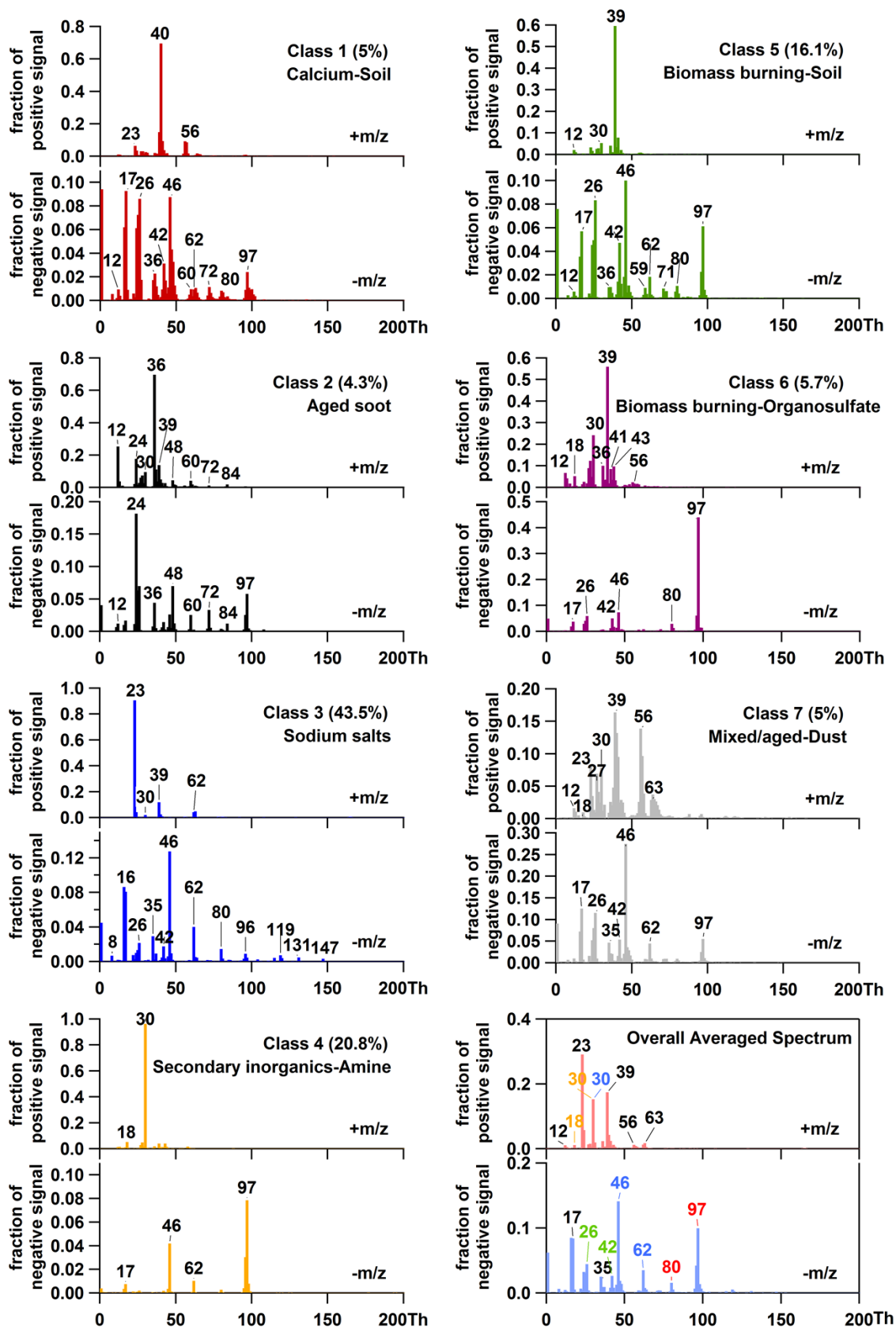


Figure S3: Representative mass spectra of seven particle classes and averaged spectrum of total $\sim 3.7 \times 10^5$ single particles measured during the field campaign TRAM01 (same as Fig. 2, except with linear mode).

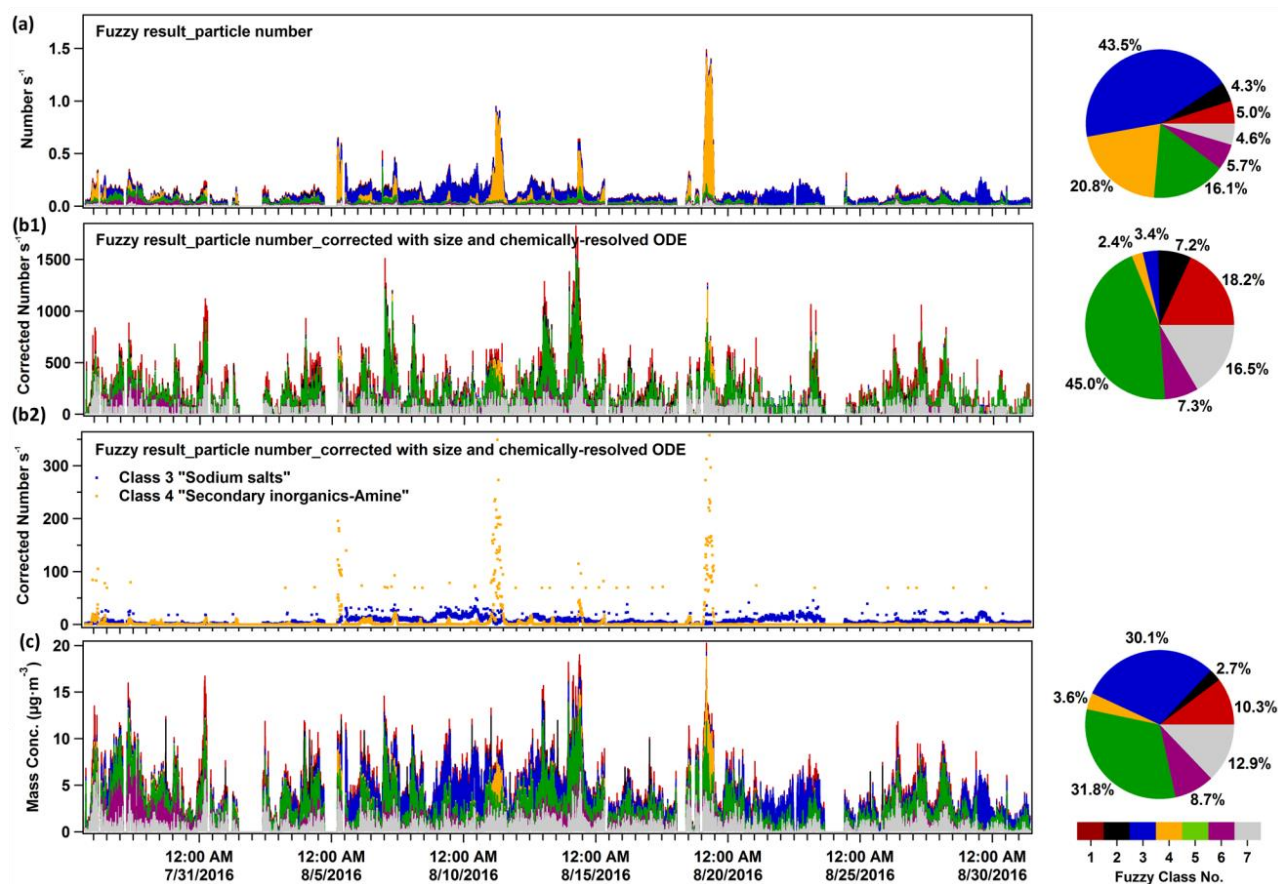


Figure S4: Time series of the particle number, corrected number, and mass concentration of seven major particle classes and the corresponding pie charts for total fractions. 7 fuzzy classes are class 1 “Calcium-Soil”; class 2 “Aged soot”; class3: “Sodium salts”; class 4 “Secondary inorganics-Amine”; class 5 “Biomass-Soil”; class 6 “Biomass-Organosulfate”; and class 7: “Mixed/aged-Dust”. This figure is similar as Fig. 4, except with the absolute values. Besides, panel (b2) is added in order to visualize the time series of class 3 and 4, since their number fraction is too small after correction.

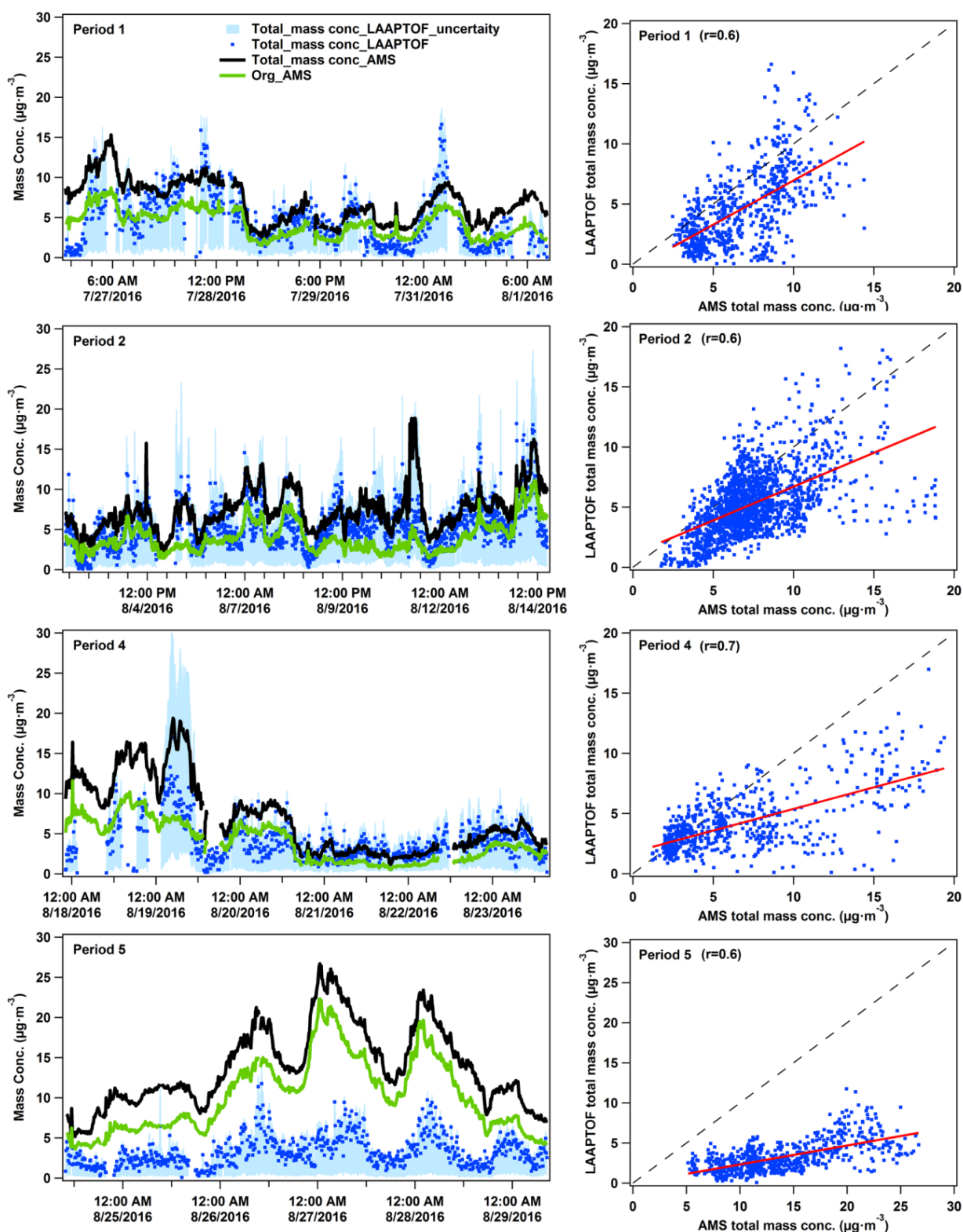


Figure S5: Comparison of mass concentration results between LAAPTOF and AMS in four periods. r represents for Pearson's correlation coefficient. Period 1 is from 7/26/2016 16:23 to 8/1/2016 11:43; P2 from 8/2/2016 09:43 to 8/14/2016 17:53; P4 from 8/17/2016 21:13:00 to 8/23/2016 15:33; P5 from 8/24/2016 15:03 to 8/29/2016 08:33.

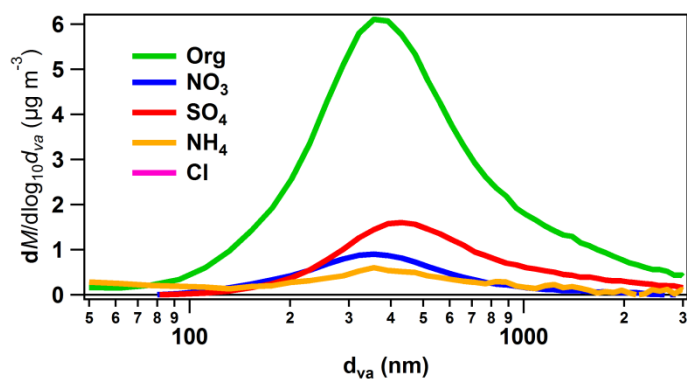


Figure S6: Chemical resolved size distributions for the particles measured by AMS during organics rich period (P5).

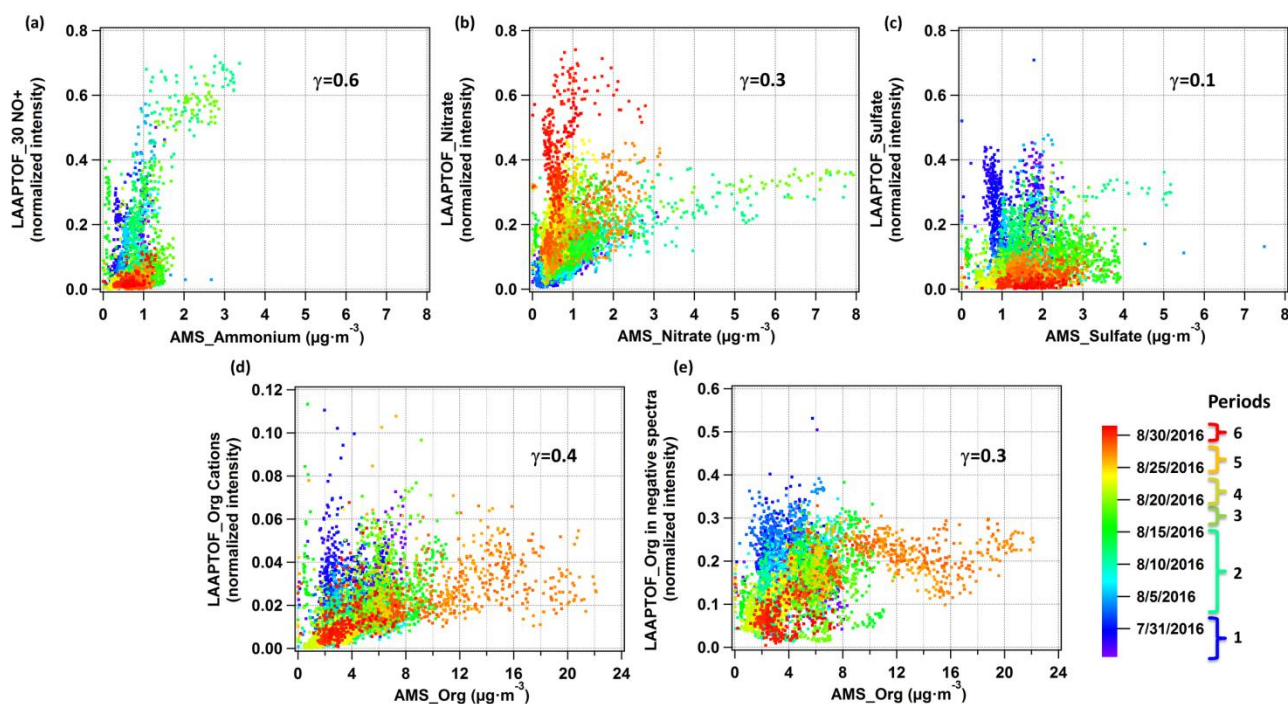


Figure S7: Comparison of non-refractory compounds measured by LAAPTOF and AMS: The normalized intensity of (a) 30 NO^+ ; (b) nitrate ($46 \text{ NO}_2^- + 62 \text{ NO}_3^-$); (c) sulfate ($32 \text{ S}^- + 64 \text{ SO}^- + 80 \text{ SO}_3^- + 81 \text{HSO}_3^- + 96 \text{ SO}_4^- + 97 \text{ HSO}_4^- + 177 \text{ SO}_3\text{HSO}_4^- + 195 \text{ H}_2\text{SO}_4\text{HSO}_4^-$); (d) sum of positive organic markers at m/z 43 $\text{C}_3\text{H}_7/\text{C}_2\text{H}_3\text{O}/\text{CHNO}^+$, 58 $\text{C}_2\text{H}_5\text{NHCH}_2^+$, 59 $(\text{CH}_3)_3\text{N}^+$, 88 $(\text{C}_2\text{H}_5)_2\text{NO}/\text{C}_3\text{H}_6\text{NO}_2^+$, 95 $\text{C}_7\text{H}_{11}^+$, 104 C_8H_8^+ , 115 C_9H_7^+ , and 129 $\text{C}_5\text{H}_7\text{NO}^+$ and (e) sum of the negative organic markers at m/z 24 C_2^- , 25 C_2H^- , 26 $\text{C}_2\text{H}_2/\text{CN}^-$, 42 $\text{C}_2\text{H}_2\text{O}/\text{CNO}^-$, 45 COOH^- , 59 CH_2COOH^- , 71 $\text{CCH}_2\text{COOH}^-$, 73 $\text{C}_2\text{H}_4\text{COOH}^-$, 85 $\text{C}_3\text{H}_4\text{COOH}^-$, and 89 $(\text{CO})_2\text{OOH}^-$ measured by LAAPTOF are plotted versus the mass concentration of ammonium, nitrate, sulfate, and organics measured by AMS, respectively. Each point is 10 min averaged data, and there are 4483 points in each scatter plot. Colour scale is related to the timeline, including periods 1 to 6.

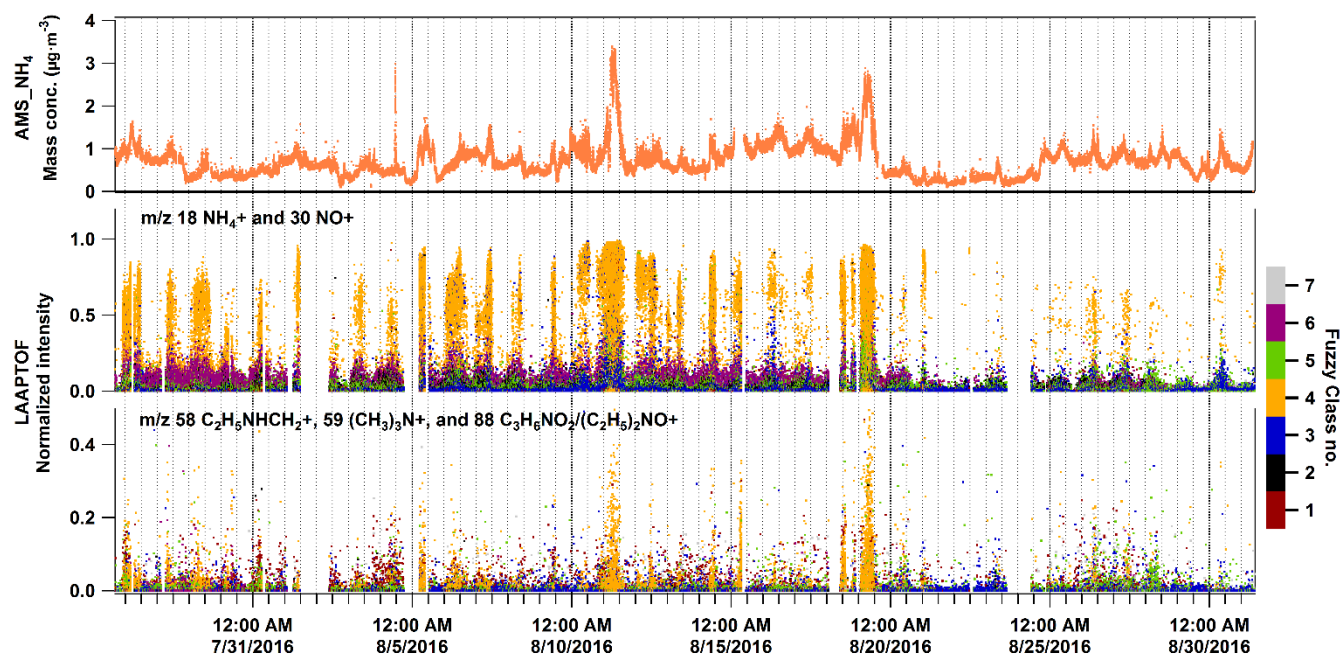


Figure S8: Time series of ammonium measured by in mass concentration and LAAPTOF in ion intensity. Normalized intensity refers to the fragment intensity divided by sum of all the ion intensities. Marker peaks for ammonium are at m/z 18 NH_4^+ and 30 NO^+ in LAAPTOF spectra, thus we use them to represent ammonium. In addition, some amine derived fragments at m/z 58 $\text{C}_2\text{H}_5\text{NHCH}_2^+$, 59 $(\text{CH}_3)_3\text{N}^+$, and 88 $(\text{C}_2\text{H}_5)_2\text{NO}/\text{C}_3\text{H}_6\text{NO}_2^+$ could also contribute to ammonium ions, therefore we also show them in this figure.