In summer time of 2016, a six weeks' field campaign was conducted at a rural site in the upper Rhine valley near Karlsruhe city in southwest Germany. ~3.7 × 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 $\gamma_{neg.}$ 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 m^3 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	9.4%	19.7%	2.7%	1.9%	47.3%	13.9%	5.2%
ODE_mean	9.3%	19.0%	3.5%	2.4%	46.5%	14.0%	5.2%
ODE_min	9.3%	18.5%	3.8%	2.7%	46.2%	14.2%	5.4%
Particle Mass Fraction							
ODE_max	6.9%	6.9%	23.2%	5.5%	38.1%	14.0%	5.4%
ODE_mean	6.8%	6.4%	25.3%	6.5%	36.0%	13.5%	5.5%
ODE_min	7.2%	6.5%	21.3%	6.6%	37.9%	14.6%	5.9%

*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**	0.36	**0.74**	-0.51	**0.88**	0.26	**0.63**
Nitrate	0.32	**0.64**	**0.70**	0.52	0.47	0.46	0.43
Sulfate	0.09	-0.22	0.25	-0.12	**0.68**	0.07	0.07
Organic Cations	0.40	0.16	0.44	-0.08	**0.76**	0.41	0.32
Organic Anions	0.33	-0.19	0.33	0.44	0.41	0.31	0.13
Org/(Org+Ammoinium)	0.51	0.00	0.52	0.27	0.54	0.00	0.45
Org/(Org+Nitrate)	**0.61**	**0.79**	**0.86**	**0.76**	**0.67**	**0.75**	0.39
Org/(Org+Sulfate)	0.37	-0.02	0.45	-0.04	0.33	0.36	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. 5 and Fig. S3; LAAPTOF fragments for ammonium, nitrate, sulfate, and organics can refer to Fig. 6 caption. These two instruments show good correlations on Org/(Org+nitrate) for almost all the measurement time. The corresponding scatter plots are in Fig. S4.

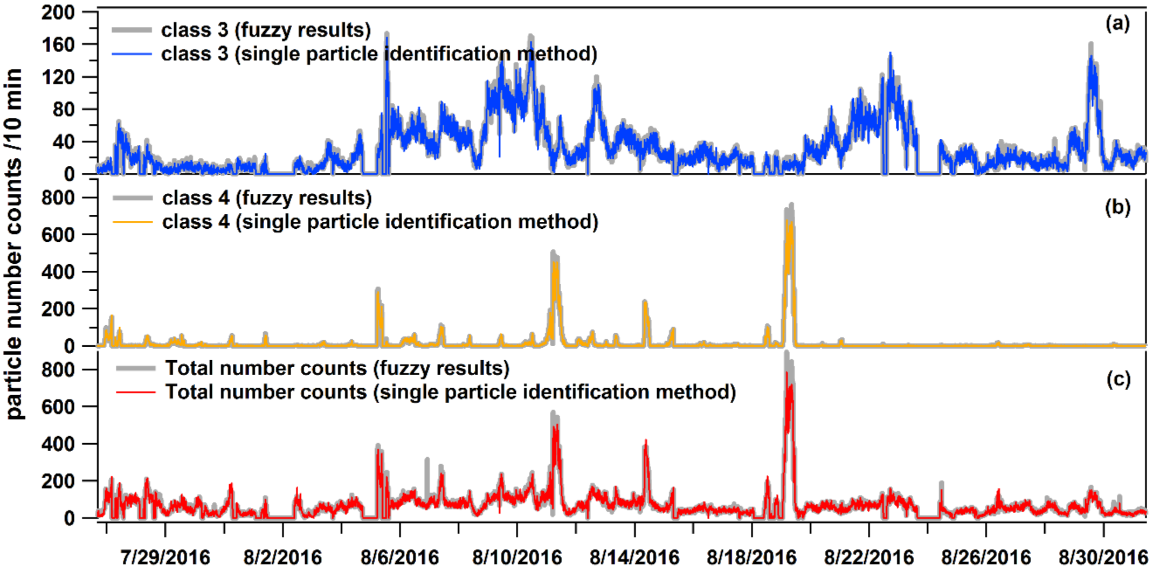

Figure S1: Time series of particle number counts obtained by fuzzy clustering and the single particle identification method using the fuzzy representative spectra as reference.

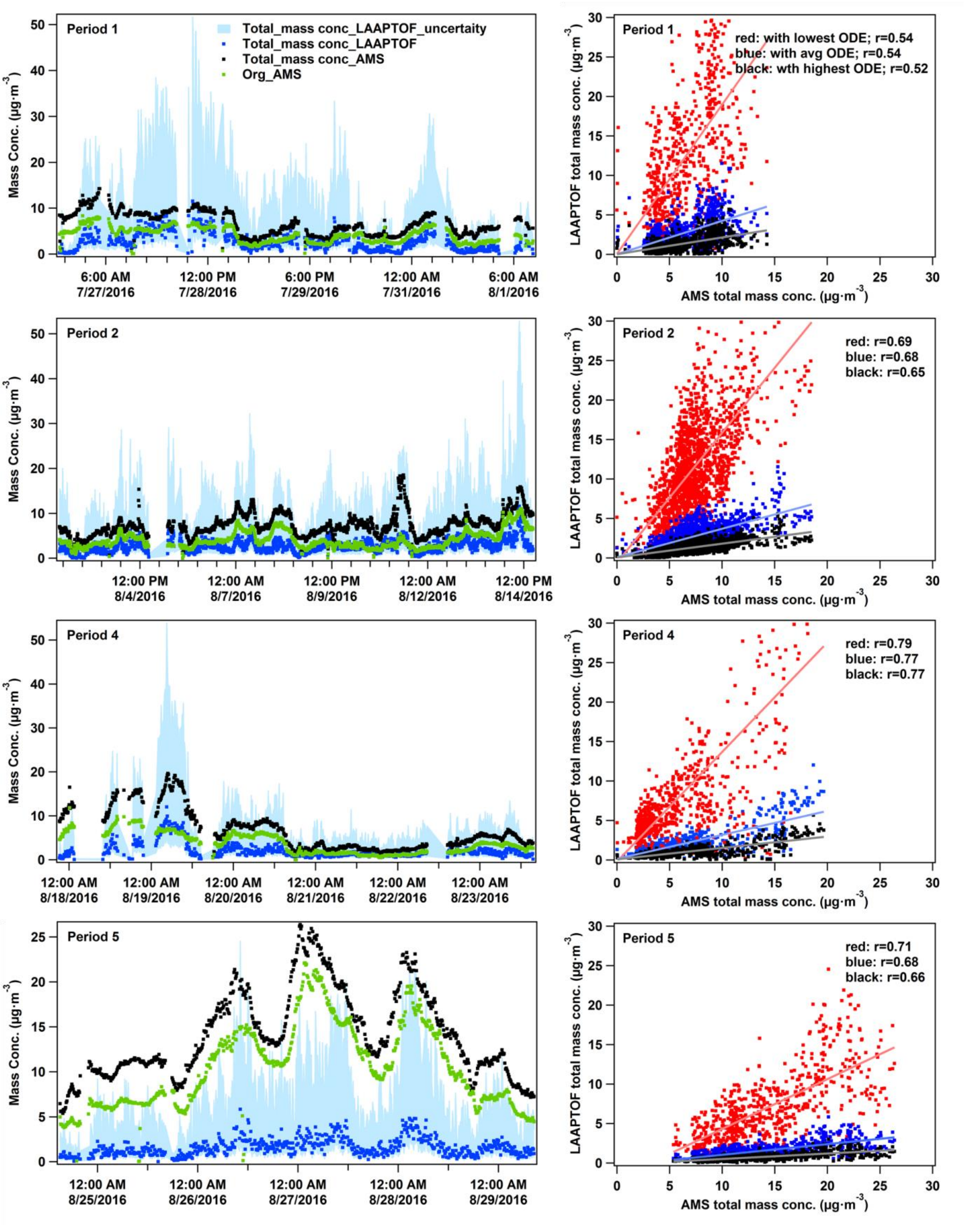

Figure S2: Comparison of mass concentration results between LAAPTOF and AMS in four periods. r represents for Pearson's correlation coefficient. Period 1 is from 7/26/2016 16:23 to 8/1/2016 11:43; P2 from 8/2/2016 09:43 to 8/14/2016 17:53; P4 from 8/17/2016 21:13:00 to 8/23/2016 15:33; P5 from 8/24/2016 15:03 to 8/29/2016 08:33.

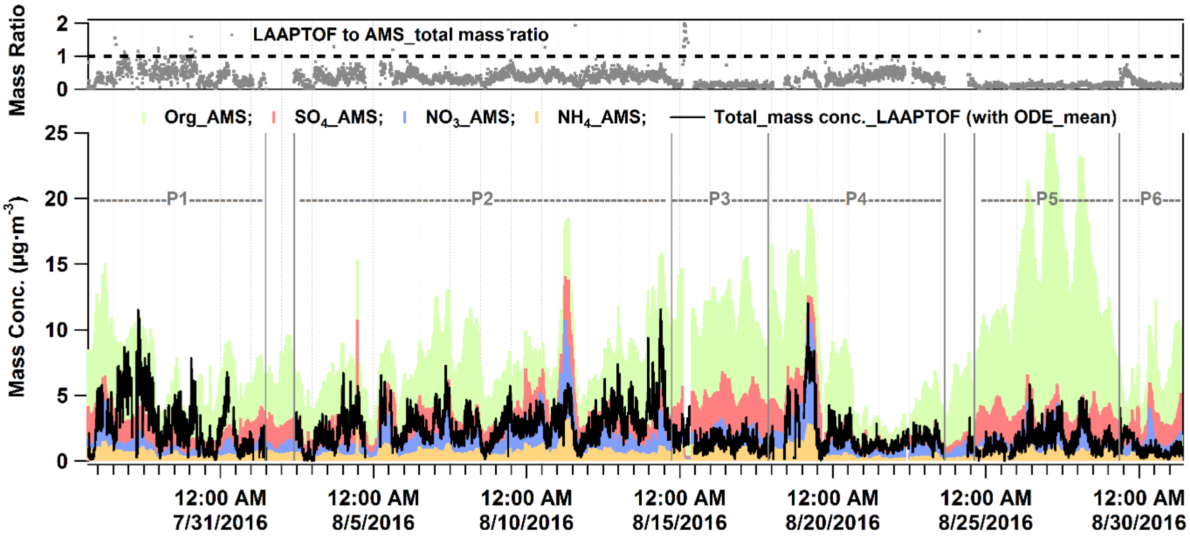

Figure S3: Time series of total mass ratio of LAAPTOF to AMS, LAAPTOF total mass concentration, and mass concentrations of organic, sulfate, nitrate, and ammonium compounds measured by AMS. Period 1 is from 7/26/2016 16:23 to 8/1/2016 11:43; P2 from 8/2/2016 09:43 to 8/14/2016 17:53; P3 from 8/14/2016; 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; P6 from 8/29/2016 08:43 to 8/31/2016 09:13.

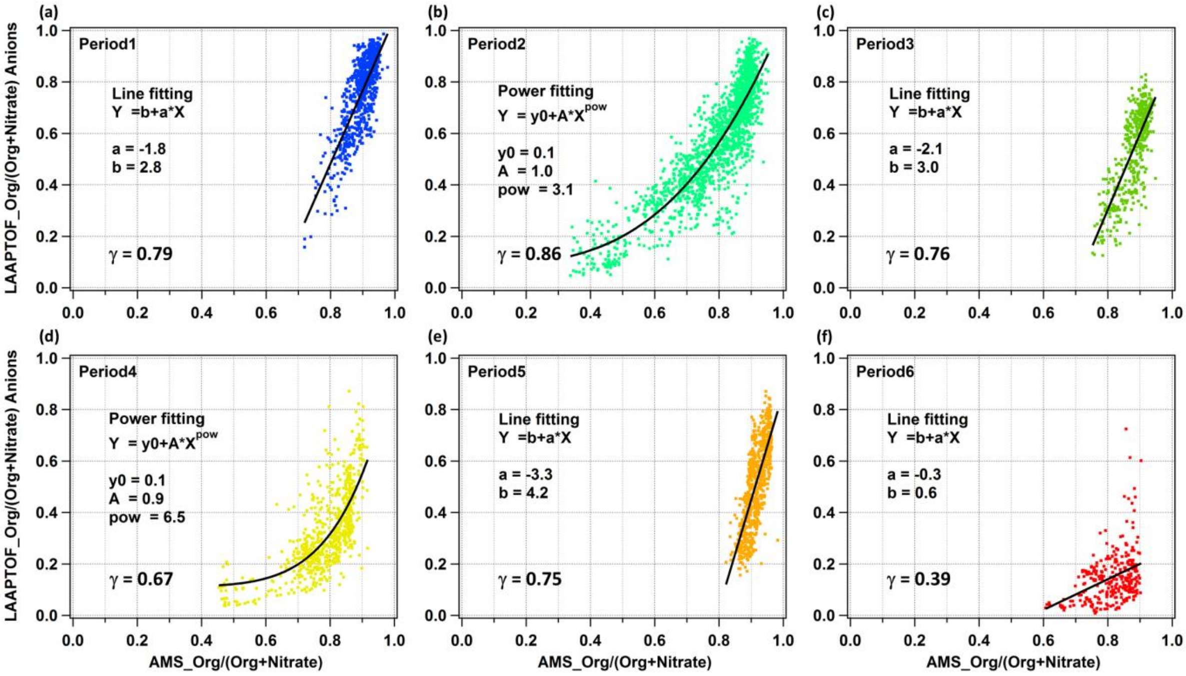

Figure S4: Comparison of LAAPTOF organic anions and nitrate fractions to the AMS mass fractions during 6 time periods of the whole campaign in the scatter plots (a) to (f), respectively. Each point is 10 min averaged data. Periods 1 to 6 correspond to the ones in Fig. 5 and Fig. S3. Different colours correspond to the colour scale in Fig. 6. LAAPTOF and AMS show good/strong correlations for almost all the measurement time periods. Pearson's correlation coefficients are > 0.6 for period 1 to 5. The suitable fittings are different for different periods: power fitting suit period 2 and 4, while line fitting suits the others.

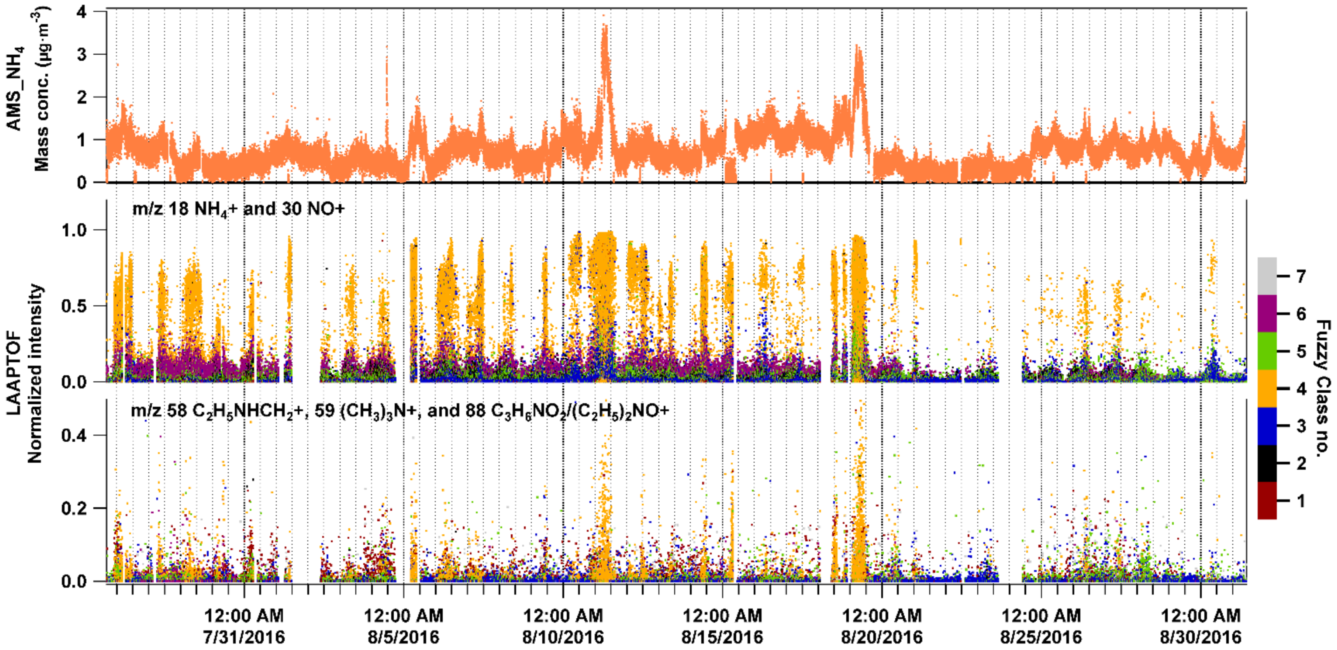

Figure S5: Time series of ammonium measured by in mass concentration and LAAPTOF in ion intensity. Normalized intensity refers to the fragment intensity divided by sum of all the ion intensities. Marker peaks for ammonium are at m/z 18 NH_4^+ and 30 60 NO^+ in LAAPTOF spectra, thus we use them to represent ammonium. In addition, some amine derived fragments at m/z 58 $C_2H_5NHCH_2^+$, 59 $(CH_3)_3N^+$, and 88 $(C_2H_5)_2NO/C_3H_6NO_2^+$ could also contribute to ammonium ions, therefore we also show them in this figure.