S1 Data analysis

High organic loadings during heavy biomass burning (BB) episodes interfered with sulfate detection by the AMS in unit mass resolution (UMR), resulting in negative sulfate readings and scattered data points (Fig. S1a). Adjustments in Squirrel to the fragmentation table addressed the negative data points (Fig. S1b), however significant data dispersion still remained. High resolution (HR) fitting using PIKA improved correlation among different sulfate fragments (Fig. S1c).

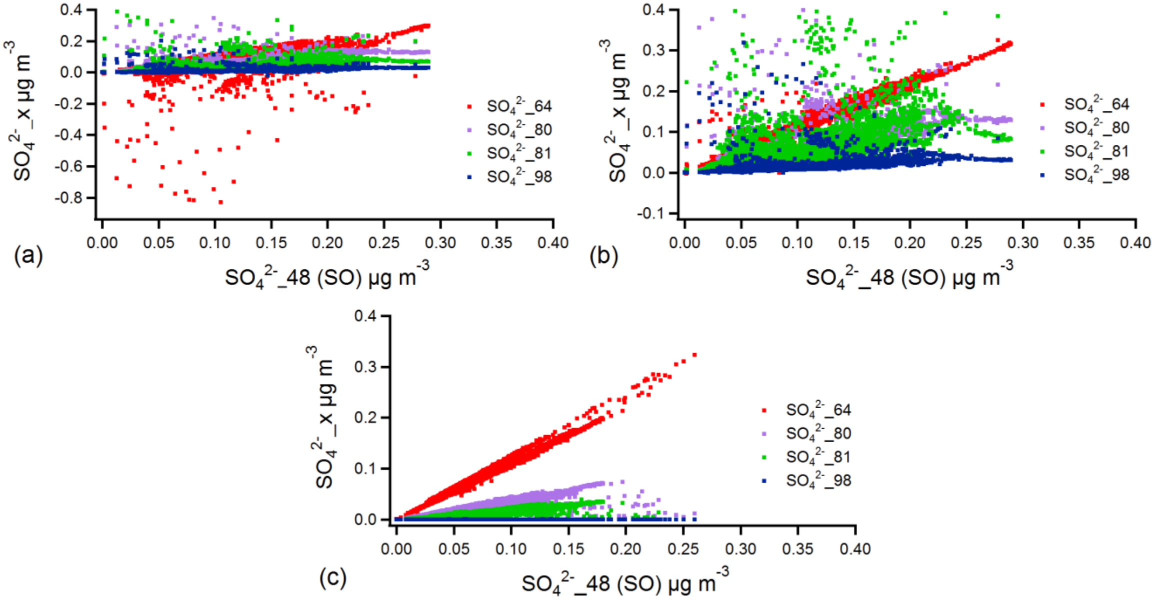

Figure S1: Sulfate fragments plots (a) before and (b) after Squirrel fragmentation table adjustments, and (c) after HR fitting in PIKA; SO_4^{2-}_x indicates sulfate fragments at m/z 64, 80, 81 and 96 plotted against the sulfate fragment at m/z 48.

PM1 soluble ions measured by ion suppressed chromatography and OM (converted from OC that was determined by the Thermal-Optical Carbon Analyser) were compared to the corresponding AMS UMR and HR data. A considerable improvement was observed in the HR analysis results for sulfate (Fig. S2b), with R changing from 0.4 to 0.8. HR fitting did not result in significant change for the other inorganic species or organics. However, improvement in the sulfate signals was significant and HR data were used in further data analysis.

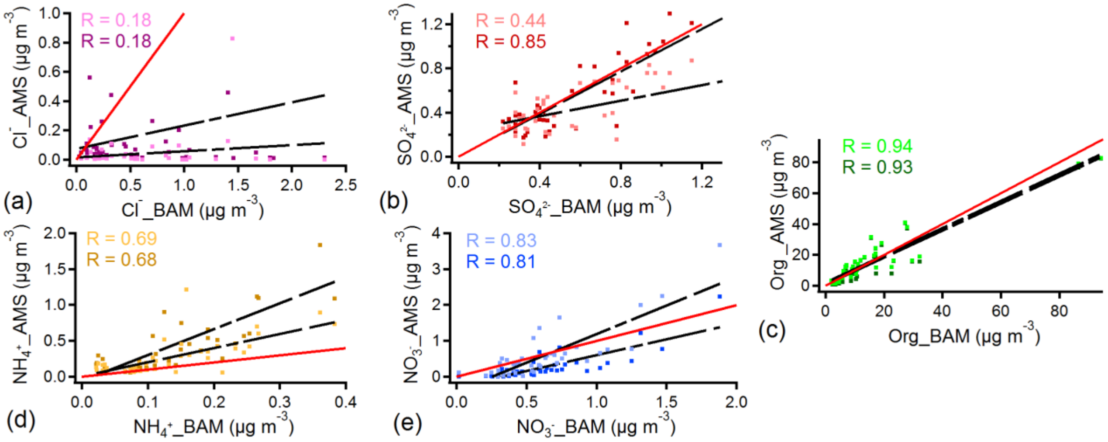

Figure S2: Correlation between BAM PM1 soluble ions and corresponding AMS species including (a) chloride, (b) sulfate, (c) organics, (d) ammonia and (e) nitrate; The lighter points and first number present correlation of BAM data with UMR AMS data, while the darker points and the second number illustrates the correlation for BAM and HR AMS data. Red line represents 1:1 line (absolute concentration between AMS and BAM). BAM organic mass (OM) was converted from OC mass using the conversion coefficient of 1.4. R refers to Pearson correlation coefficient.

Table S1: Correlation values between inorganic species and organics during the campaign, and close and distant periods separately. Inorganic species measured during the whole period (X), close BB periods (X(c)) and distant BB periods (X(d)) were compared to organics measured during the same time period (Org, Org(c), Org(d)).

	Cl^-	Cl^- (c)	Cl^- (d)	NH_4^+	NH_4^+ (c)	NH_4^+ (d)	NO_3^-	NO_3^- (c)	NO_3^- (d)	SO_4^{2-}	SO_4^{2-} (c)	SO_4^{2-} (d)
Org	0.65			0.92			0.75			0.55		
Org(c)		0.67			0.92			0.72			0.49	
Org(d)			0.47			0.73			0.77			0.48

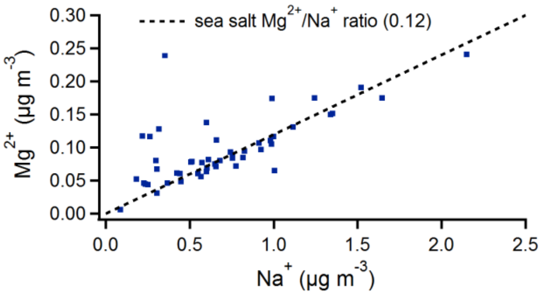

Figure S3: Filter BAM data for magnesium (Mg^{2+}) and sodium (Na^+). Black line illustrates Mg^{2+}/Na^+ ratio for the sea salt (0.12).

S2 Biomass burning aerosols and aging

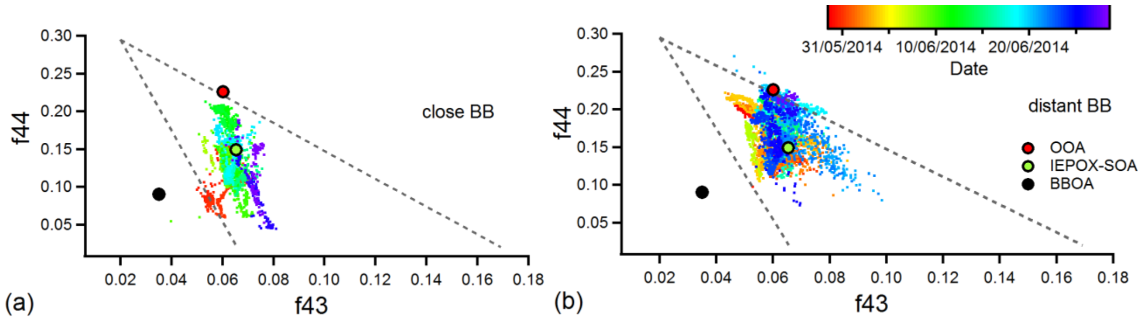

Figure S4: f44 vs. f43 coloured by date for (a) close and (b) distant BB periods. PMF-resolved factors are also indicated. The dashed lines represent boundaries for typical ambient aerosol as presented in Ng et al. (2010).

S2.1 Secondary organic aerosol (SOA) formation

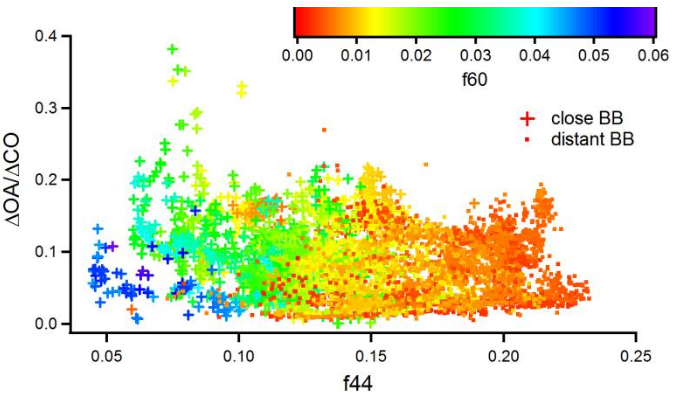

Figure S5: Change in $\Delta OA/\Delta CO$ ratio with aging (represented by f44 values) for close (crosses) and distant (dots) fires coloured by f60.

S2.2 Biomass burning events

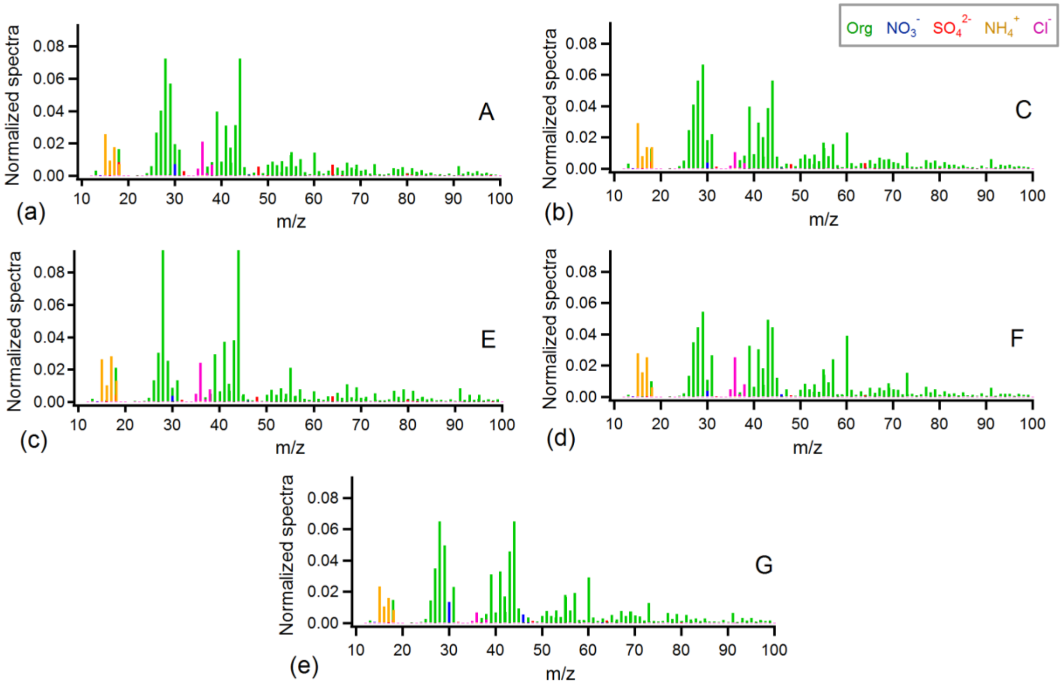

Figure S6: Mass spectra for selected BB events (A (30/05/14, 18:34-19:25), C (30/05/14, 23:41-31/05/14 00:59), E (09/06/14, 19:45-10/06/14 00:32), F (25/06/14, 12:28-16:59) and G (25/06/14, 21:40-26/06/14 03:59) are shown respectively.

Table S2: Selected BB event values for f44, f60, organic concentration, CO, MCE and $\Delta O_3/\Delta CO$ ratio, along with measurement start and end time. ND refers to no data.

	Date (start/end)	f44±SD (range)	mean f60±SD (range)	mean Org±SD* (range)	mean CO±SD* (range)	MCE	$\Delta O_3/\Delta CO$
A	30/05/14 18:34- 30/05/14 19:25	0.087±0.08 (0.079-0.105)	0.016±0.002 (0.010-0.018)	22.6±12.5 (4.6-45.2)	185.9±95.5 (90.2-370.1)	0.97±0.06	ND
C	30/05/14 23:41- 31/05/14/ 00:59	0.066±0.005 (0.060-0.079)	0.027±0.002 (0.021-0.028)	75.5±40.0 (13.7-131.2)	627.1±345.4 (185.8-1181.6)	0.98±0.11	ND
E	09/06/14 19:45- 10/06/14 00:32	0.078±0.013 (0.062-0.093)	0.032±0.002 (0.030-0.035)	175.9±105.0 (87.3-331.8)	1558.5±965.5 (671.6-3382.5)	0.91±0.05	0.024
F	25/06/14 12:28- 25/06/14 16:59	0.134±0.031 (0.073-0.178)	0.009±0.002 (0.007-0.014)	13.2±14.5 (2.4-70.8)	479.0±348.8 (139.5-1642.7	0.93±0.04	0.134
G	25/06/14 21:40- 26/06/14 03:59	0.062±0.017 (0.045-0.098)	0.046±0.004 (0.035-0.052)	144.6±104.7 (25.8-347.7)	2744.6±2299.8 (592.8-11275.7)	0.90±0.06	0.011

*unit is µg m^{-3}

S3 PMF performed on the whole dataset

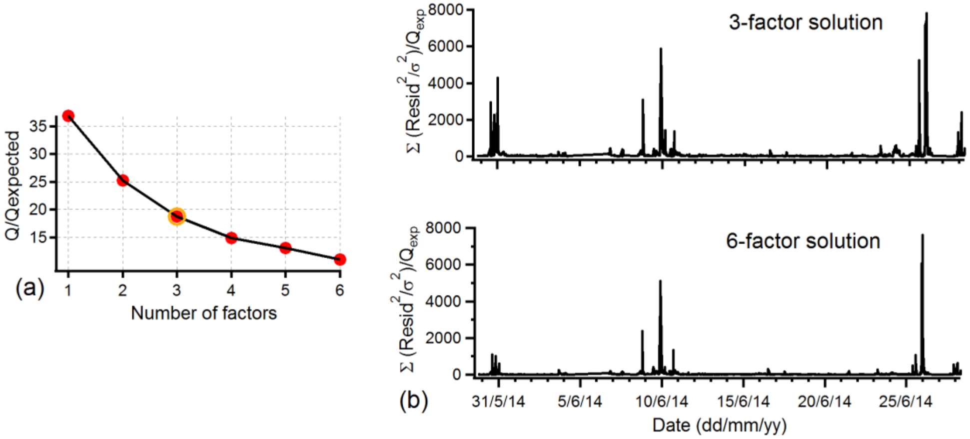

Figure S7: (a) Q/Qexpected (Q refers to the sum of squared scaled residuals over the whole dataset) vs. number of factors, illustrating high error and residual values. (b) Time series of Q/Q expected contribution for 3 and 6-factor solutions where it is clear that higher number of factors does not make the residual structure during BB events significantly lower.

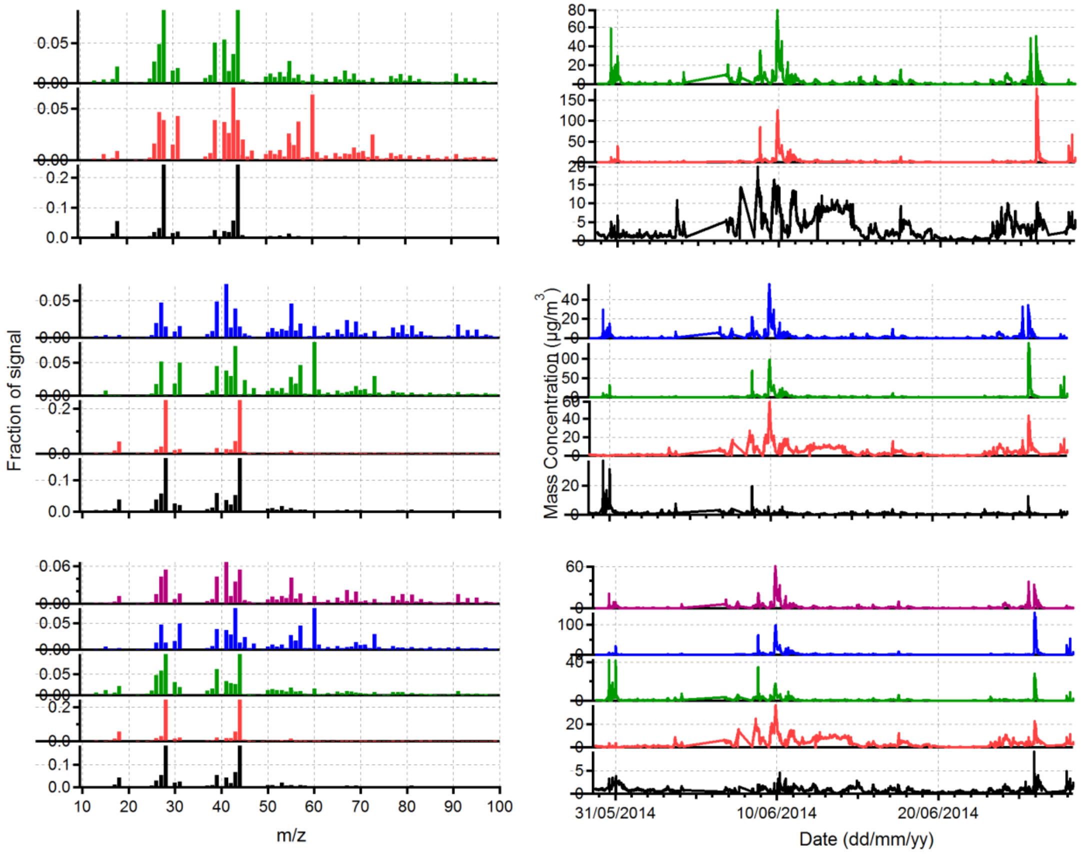

Figure S8: Factor profiles and time series for 3, 4 and 5-factor solutions showing BBOA factor splitting, suggesting that plumes are apportioned to different PMF factors.

S4 PMF performed on the background dataset

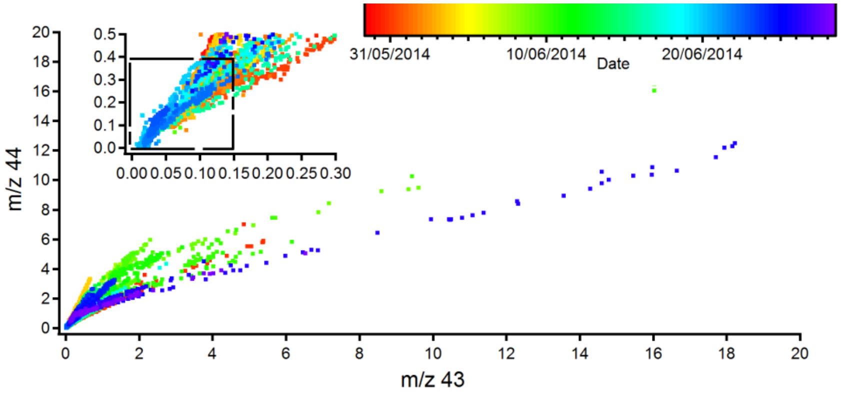

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Figure S9: m/z 44 vs. m/z 43 coloured by date for the whole dataset and for background periods (inset). Black dashed box in inset graph illustrates cut-offs of 0.15 for m/z 43 and 0.4 for m/z 44 chosen for background data.

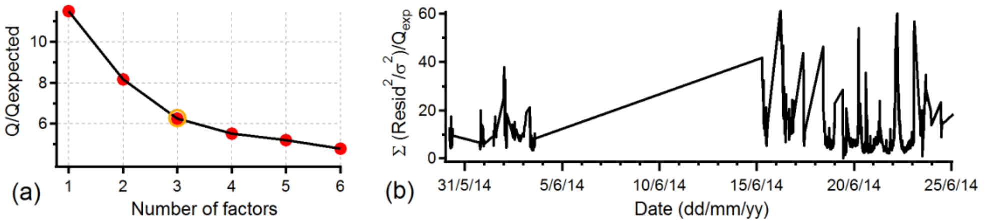

Figure S10: (a) Q/Qexpected vs. number of factors and (b) time series of Q/Q expected contribution for the 3-factor solution illustrating significantly smaller residuals in the case of the background dataset, compared to the whole dataset.

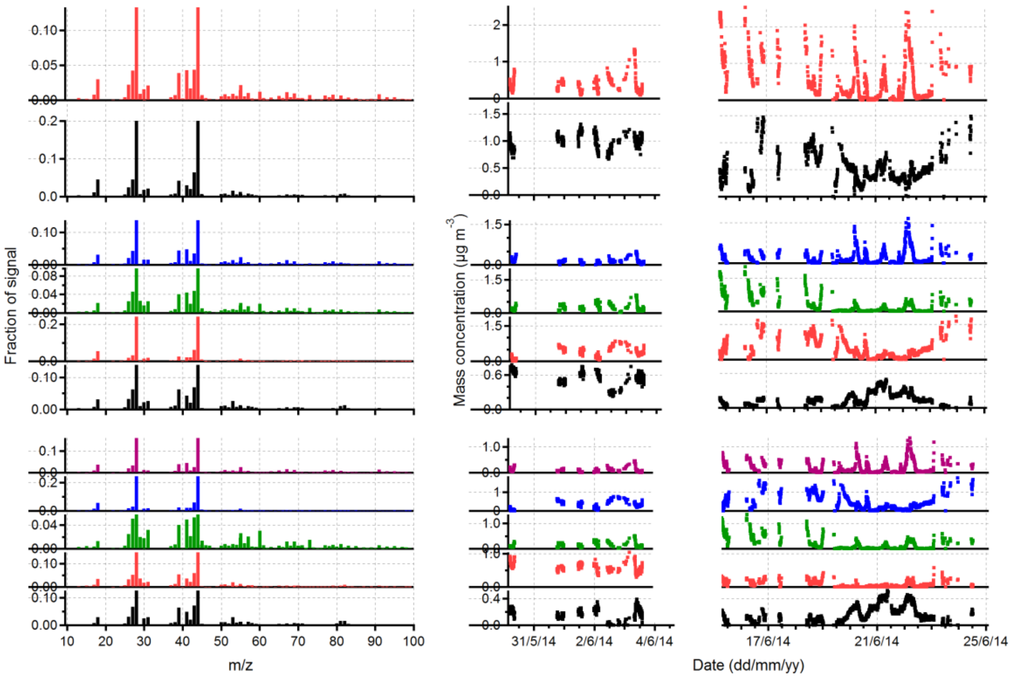

Figure S11: Factor profiles and time series for 2, 4 and 5-factor solutions for the background dataset.

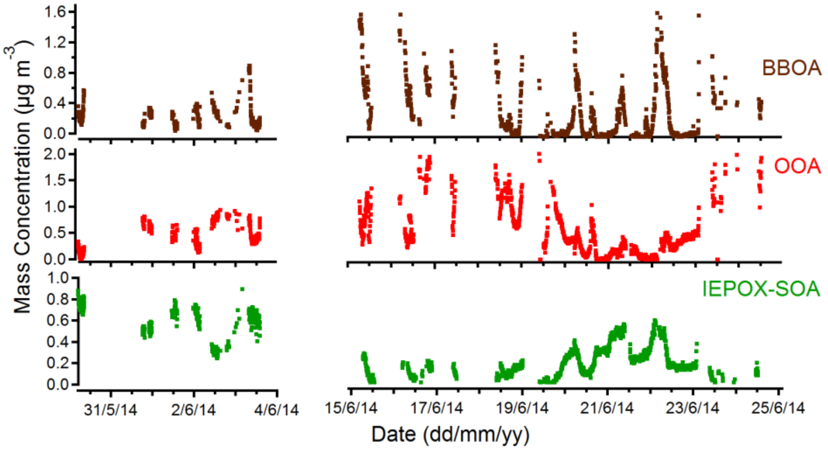

Figure S12: Time series for 3-factor solution for the background dataset.

S4.1 Isoprene epoxydiols-related secondary organic aerosol (IEPOX-SOA)

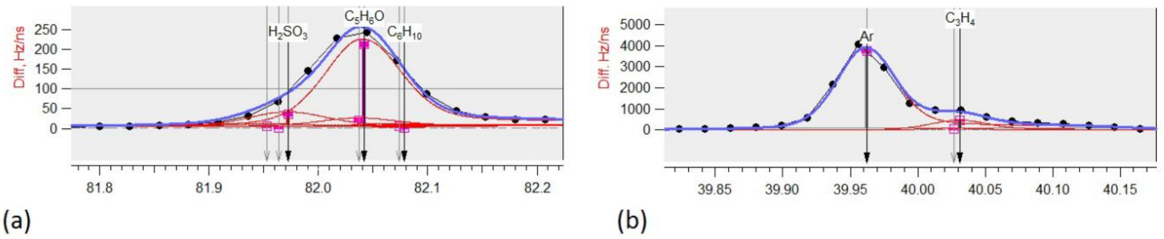

Figure S13: HR peak fitting at (a) m/z 82 showing the dominance of the $C_5H_6O^+$ fragment and (b) m/z 40 demonstrating good m/z calibration.

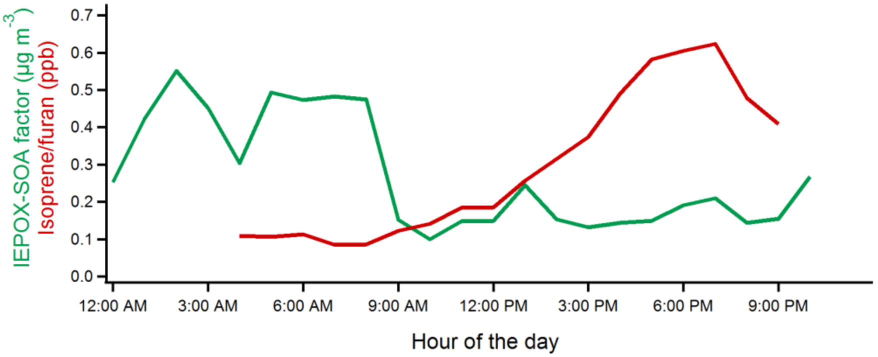

Figure S14: Diurnal trend of PMF IEPOX-SOA factor and isoprene/furan concentration measured by PTR-MS.

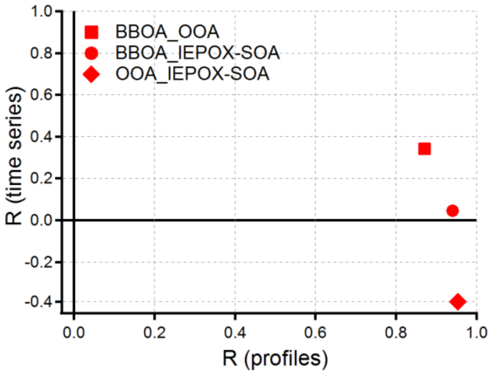

Figure S15: Time series and profile correlations between PMF factors.