Supplementary

Characterization of submicron particles by Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM) during wintertime: aerosol composition, sources and chemical processes in Guangzhou, China

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Table S1. Chemical composition of NR-PM_1 in the Pearl River Delta (PRD) region

Location	time	NR-PM1 (μg m^{-3})	OA (%)	SO_4^{2-} (%)	NO_3^- (%)	NH_4^+ (%)	Cl^- (%)
Panyu	winter.2014	55.4	50.5	25.2	12.2	9.9	2.1
Shenzhen	winter.2009	44.5	46.2	28.5	11.6	11.9	1.9
Kaiping	winter.2008	33.1	36.3	36.0	11.5	15.0	1.2
Guuangzhou	winter.2017	35.3	49.0	20.0	17.0	13.0	1.0

Table S2. OA compositions in the PRD region

Location	time	OA (μg m^{-3})	OA compositions
Panyu	Winter 2014	25.6	HOA (26%), COA (8%), BBOA (4%), SVOOA (32%), LVOOA (29%)
Shenzhen	Winter 2009	20.47	HOA (29.5%), BBOA (24.1%), SVOOA (27.6%), LVOOA (18.8%)
Kaiping	Winter 2008	11.92	BBOA (24.5%), SVOOA (35.8%), LVOOA (39.6%)
Guangzhou	Winter 2017	17.3	HOA (13%), COA (18%), SVOOA (30%), LVOOA (40%)

Figures

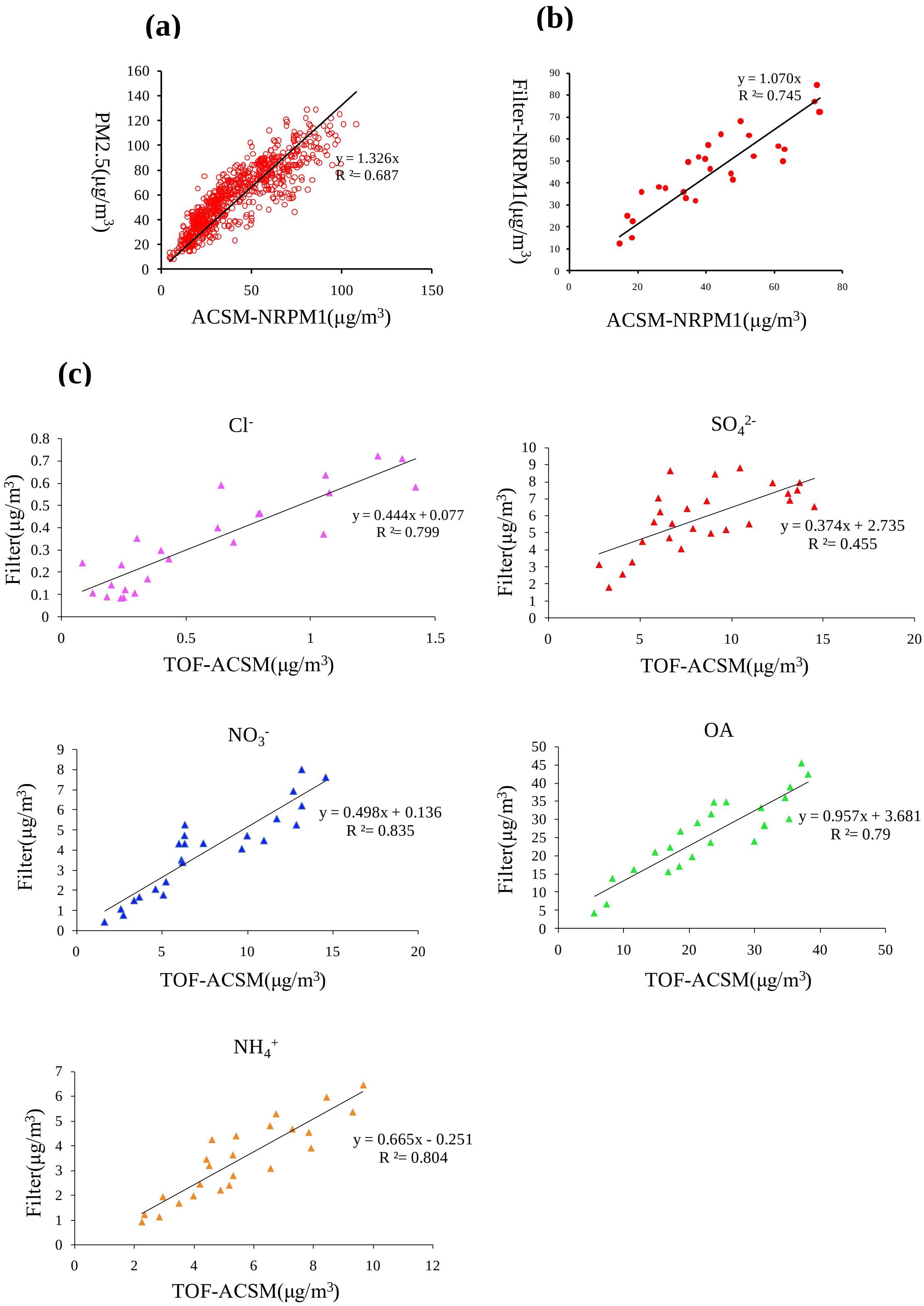

Figure S1. Comparisons between measurements by ToF-ACSM and those by BAM-1020 ($PM_{2.5}$) and filter method: (a) NR-PM_1 mass concentration measured by ToF-ACSM vs. $PM_{2.5}$ mass concentration measured by BAM-1020; (b) NR-PM_1 concentration measured by ToF-ACSM vs. NR-PM_1 concentration based on filter (sum of sulfate, nitrate, ammonium, chloride and 1.6 times of OC); (c) Comparison of filter based measurements for concentration of NR-PM_1 species (sulfate, nitrate, ammonium, chloride and OA) with the concentration of the corresponding NR-PM_1 components measured by ToF-ACSM. OA from filter data is calculated to be 1.6 times OC.

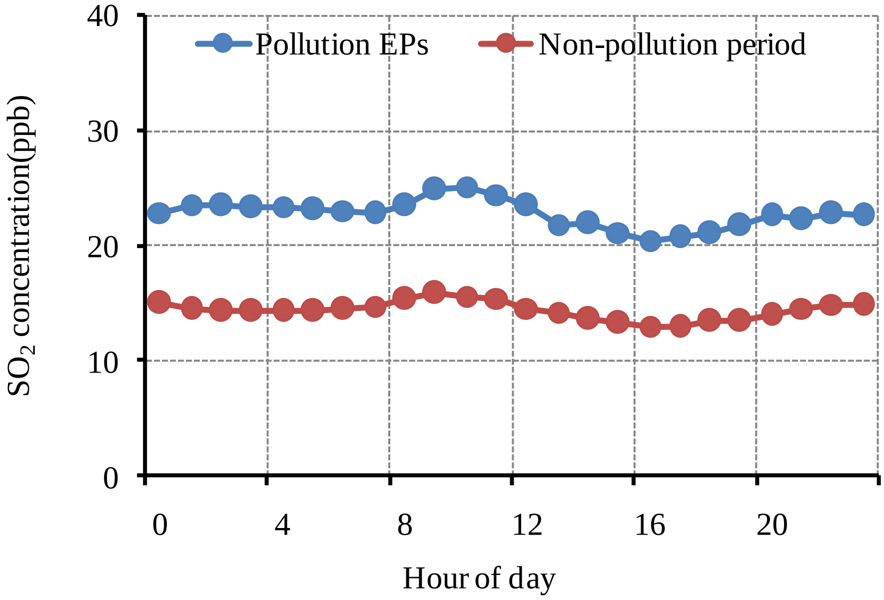

Figure S2. Diurnal profiles of SO_2 concentration for non-pollution period (red line) and pollution EPs (blue line).

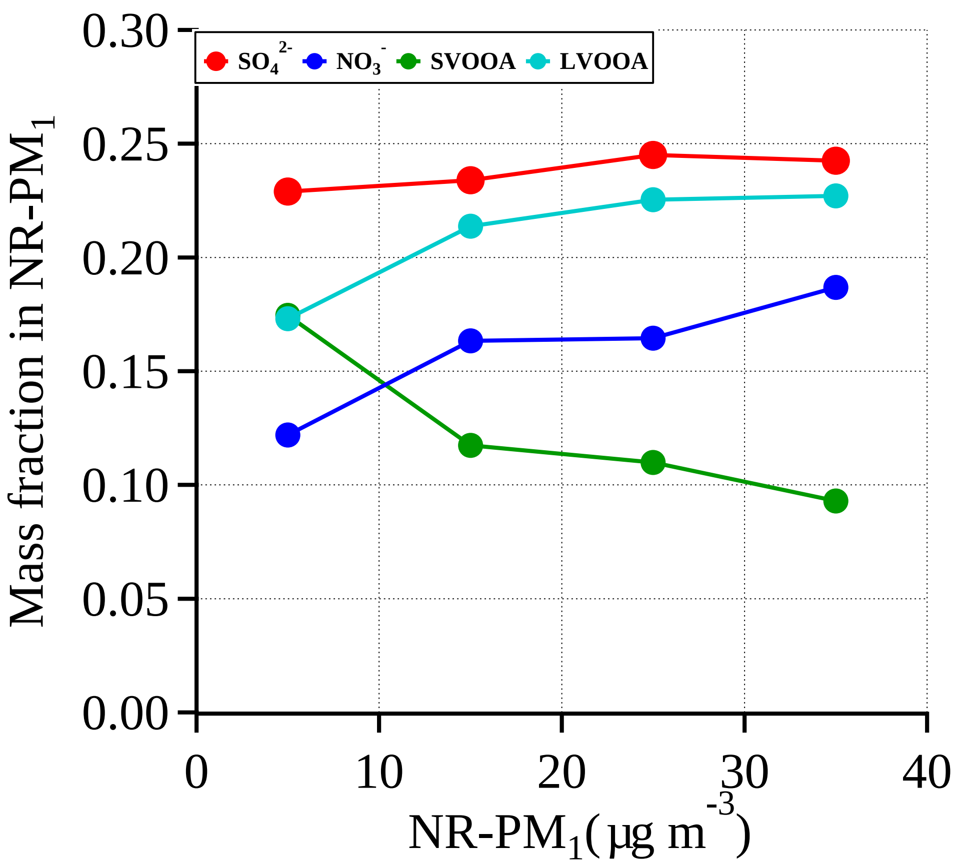

Figure S3. Evolution of SPM species fractions with concentration of NR-PM_1 for non-pollution period.

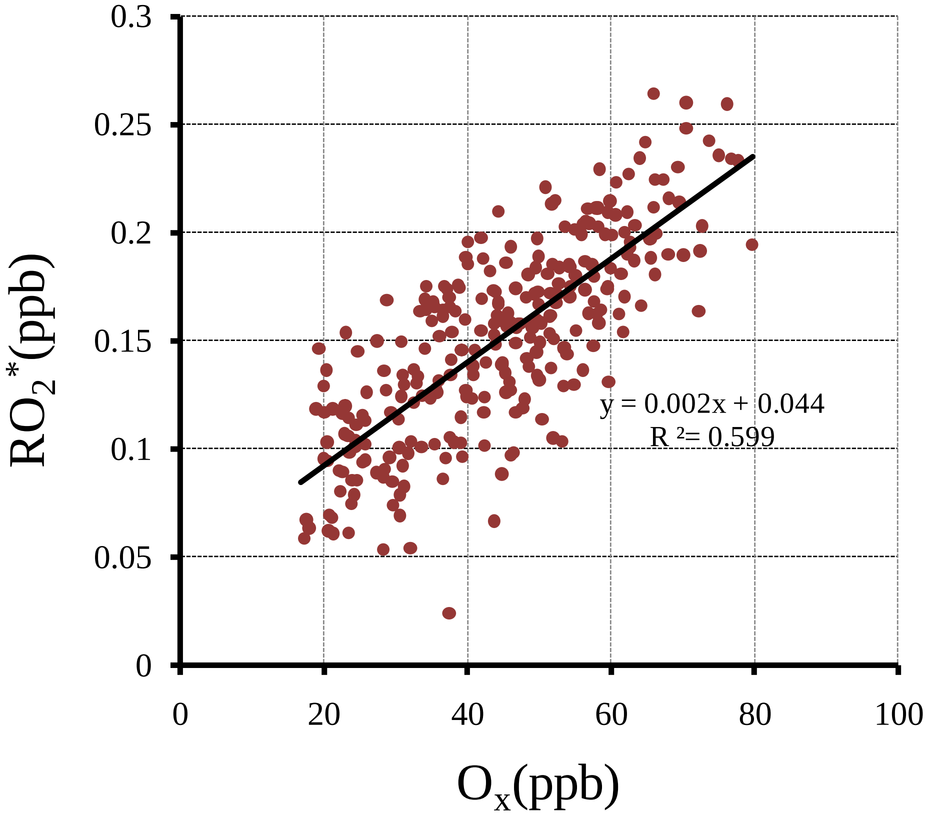

Figure S4. Correlation between O_x and RO_2* concentrations during daytime for the entire study.

Methods

OA components were deconvolved through an improved source apportionment technology called Multilinear Engine (ME-2) developed from Positive Matrix Factorization (PMF) and running on an igor-based interface (SoFi). Compared to traditional PMF, ME-2 offers a so-called a-value approach (Canonaco et al., 2013) using user defined external profiles or time series to constrain F (factor profile matrix) and G (concentration time series matrix) defined in model with a variable range (a value), which can be described as follows:

$$f_{j,solution} = f_{j,external} \pm \mathrm{a} \cdot f_{j,external} \quad (1)$$

$$g_{i,solution} = g_{i,external} \pm \mathrm{a} \cdot g_{i,external} \quad (2)$$

where f_j and g_i represent row and column of the matrices F and G, respectively. The index j varies between 0 and the number of variables and i varies between 0 and the number of measured points. Therefore, more efficient searches of solution space and a more objective choice of optimal solution are solved through the recently developed algorithm. Similar to many previous studies, ions with m/z beyond 120 were removed from ME-2 input matrix due to obviously low signal-to-noise ratios. We firstly performed totally unconstrained runs (i.e., PMF), with a possible factor number in a range of 2-10. The optimal number of factors should be chosen based on the value of $Q/Q_{expected}$, rationality of factor profile, and correlation between the time series of deconvolved factors and the corresponding external tracers (Ulbrich et al., 2009; Zhang et al., 2011). The value of $Q/Q_{expected}$ decreased with increase of factor number but this tendency was obviously damped for a factor number larger than 2, which means factor number should be larger than 2. However, we found that solutions with factor number > = 5 showed over-split factors without an explicit physical meaning while 3-factor solution was obviously mixed. Hence, it turned out that the 4-factor solution had relatively reasonable profiles and time series under a fully unconstrained condition. Although the unconstrained 4-factor solution was overall reasonable, defects existed from the uncertainty of measured data and traditional PMF algorithm. For instant, the diurnal time series of HOA and COA concentrations exhibited a slight mis-deconvolution which showed an extremely weak peak for COA and a fake peak for HOA at noon. In addition, the profile of HOA showed considerably smaller proportions of f_{55} and f_{57} than previous studies in both laboratory and field studies. Similar findings were reported in previous studies (Zhang et al., 2012; Qin et al., 2017). The a-value approach offers additional limits for rotational ambiguity through introducing user defined external factor profiles (Paatero et al., 2009; Cheng et al., 2013), which has been proven to be an efficient way to remedy these mis-deconvolution from PMF (Qin et al., 2017). Thus, we further constrained one of four factors with a standard HOA profile derived from the average PMF-resolved HOA factors from measurements carried out in 15 megacities similar to Guangzhou (Ng et al., 2011) with an a-value chosen to be 0.3, 0.5 and 0.7 respectively to explore the improved solution. The results showed that an unreasonably high proportion of m/z 44 were presented in COA profiles for solutions with an a-value of 0.5 and 0.7. We hence adopt 4 factors and an a-value of 0.3 as the optimal solution. The results from ME-2 are shown in Figures S5~S11.

PMF results

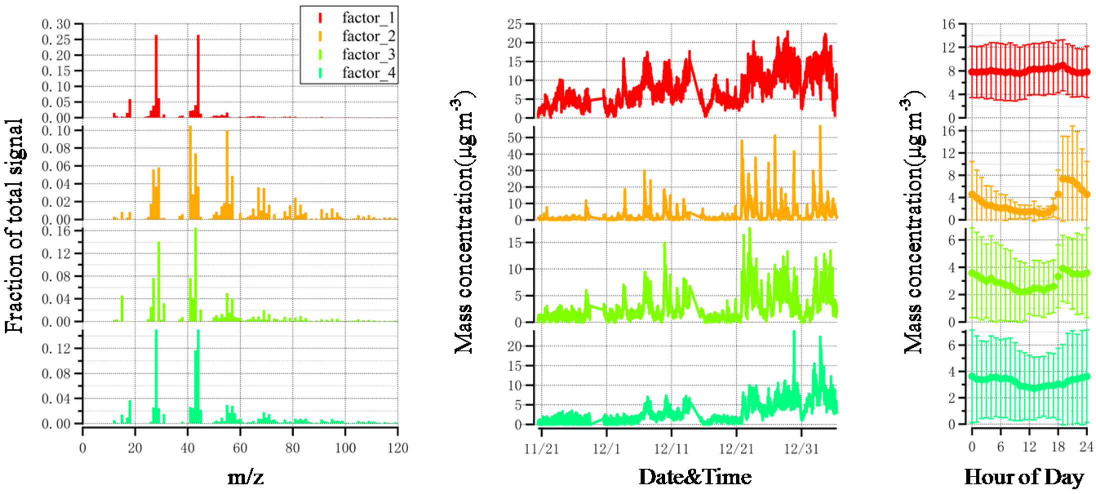

Figure S5. Results from the 4-factor solution of PMF.

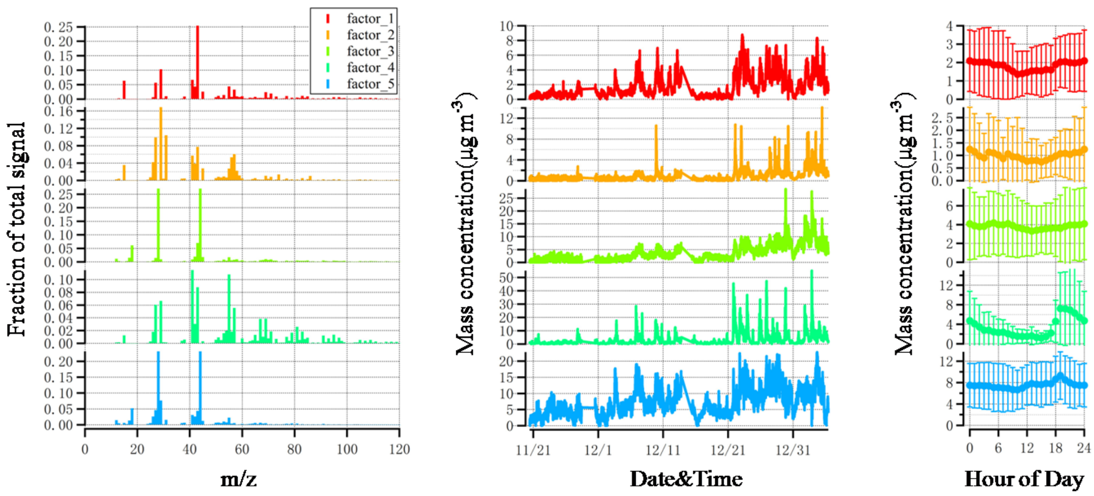

Figure S6. Results from the 5-factor solution of PMF.

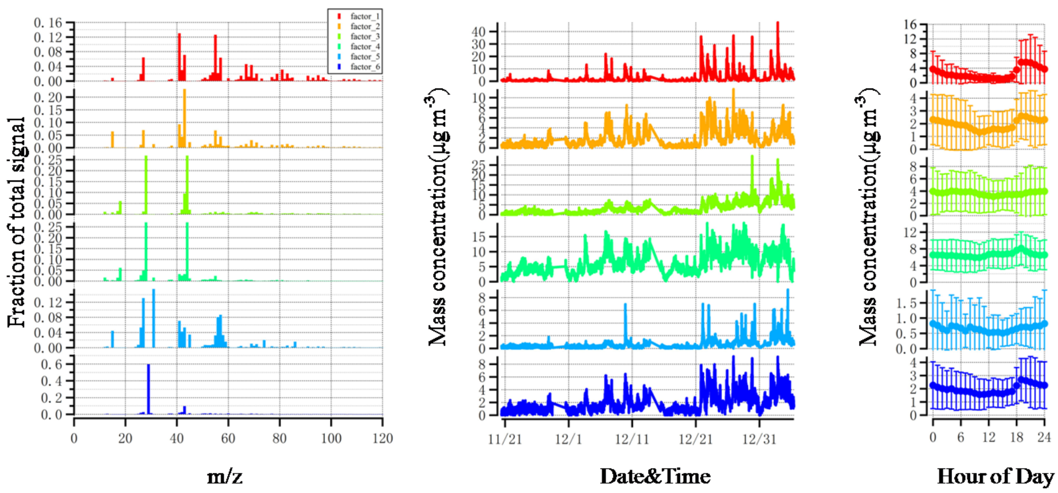

Figure S7. Results from the 6-factor solution of PMF.

a-value results (4 factors)

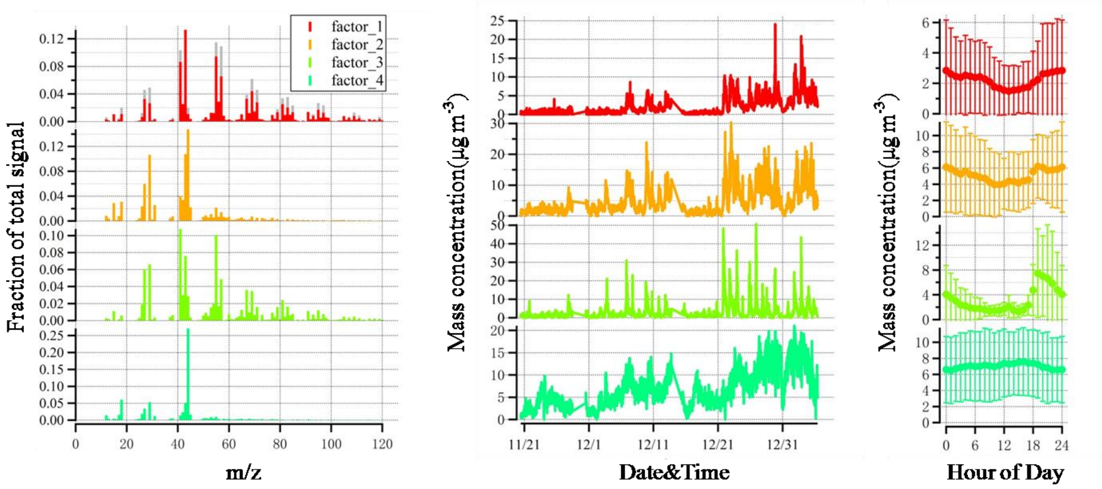

Figure S8. Results from the 4-factor solution with a-value =0.3. Gray bars represent standard HOA spectrum (Ng et al., 2011)

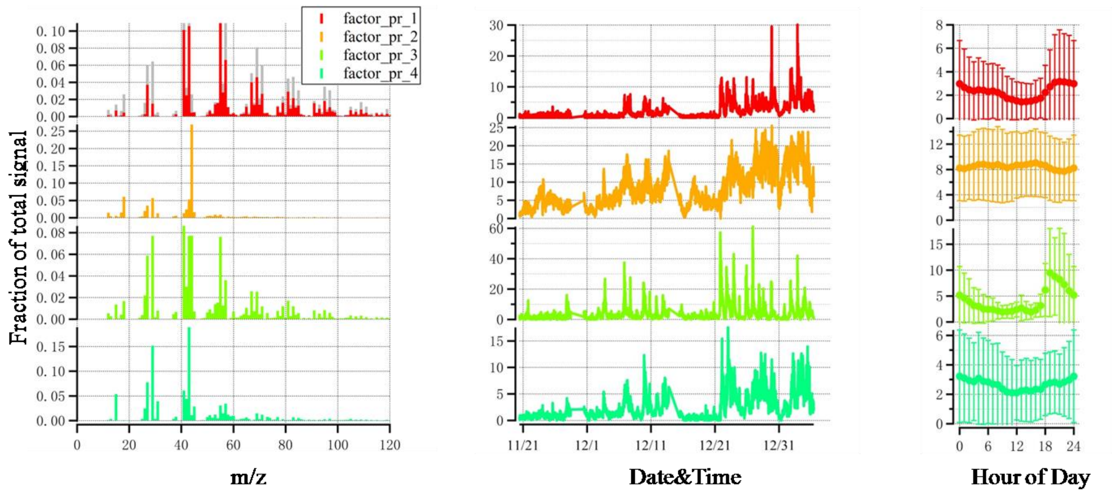

Figure S9. Results from the 4-factor solution with a-value =0.5. Gray bars represent standard HOA spectrum (Ng et al., 2011)

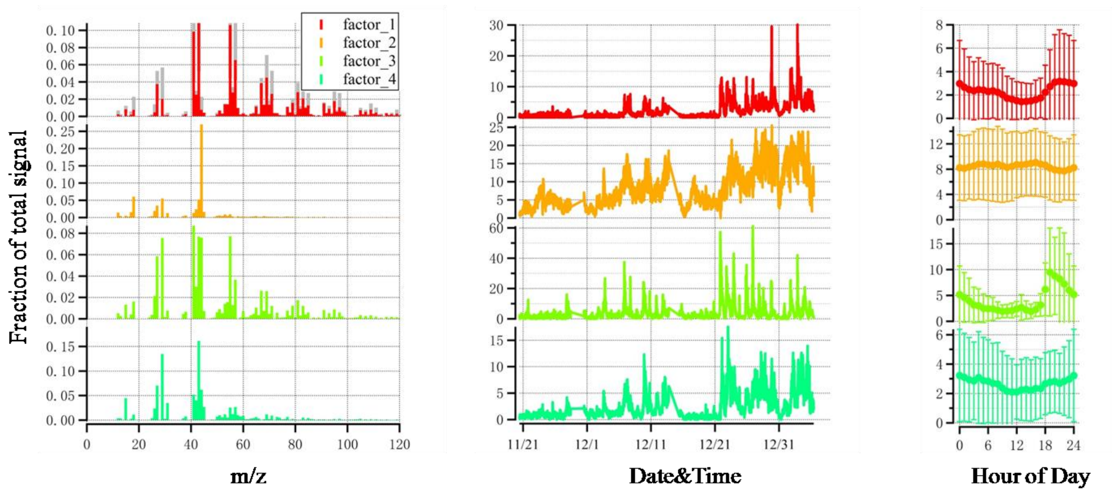

Figure S10. Results from the 4-factor solution with a-value =0.7. Gray bars represent standard HOA spectrum (Ng et al., 2011)

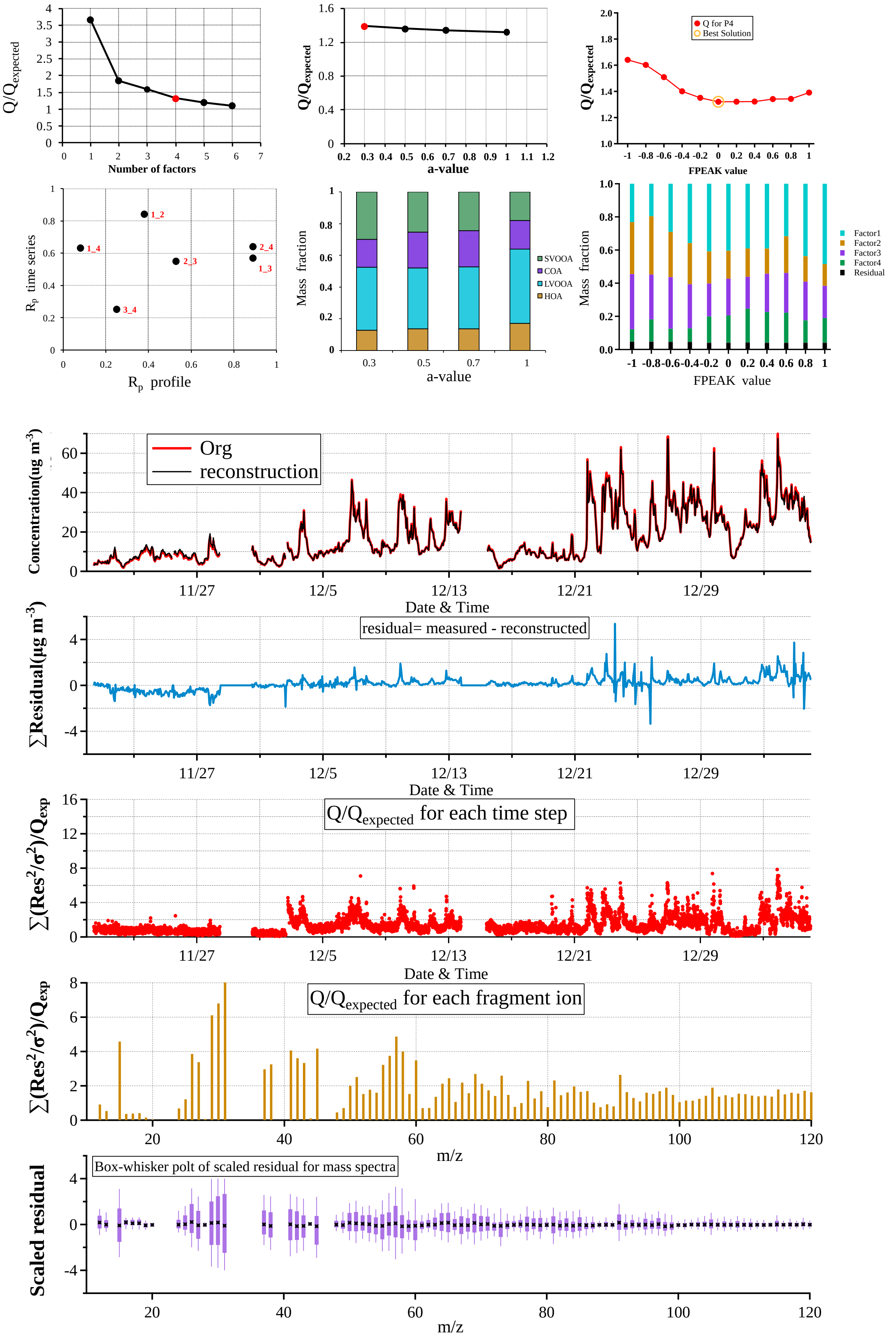

Figure S11. ME-2 diagnostics for the 4 factor solution with a-value=0.3 (the chosen optimal solution)

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