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

<table>
<thead>
<tr>
<th>Location</th>
<th>time</th>
<th>NR-PM$_1$ (μg m$^{-3}$)</th>
<th>OA (%)</th>
<th>SO$_4^{2-}$ (%)</th>
<th>NO$_3^-$ (%)</th>
<th>NH$_4^+$ (%)</th>
<th>Cl (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panyu</td>
<td>winter.2014</td>
<td>55.4</td>
<td>50.5</td>
<td>25.2</td>
<td>12.2</td>
<td>9.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Shenzhen</td>
<td>winter.2009</td>
<td>44.5</td>
<td>46.2</td>
<td>28.5</td>
<td>11.6</td>
<td>11.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Kaiping</td>
<td>winter.2008</td>
<td>33.1</td>
<td>36.3</td>
<td>36.0</td>
<td>11.5</td>
<td>15.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>winter.2017</td>
<td>35.3</td>
<td>49.0</td>
<td>20.0</td>
<td>17.0</td>
<td>13.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**Table S2.** OA compositions in the PRD region

<table>
<thead>
<tr>
<th>Location</th>
<th>time</th>
<th>OA (μg m$^{-3}$)</th>
<th>OA compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panyu</td>
<td>Winter 2014</td>
<td>25.6</td>
<td>HOA (26%), COA (8%), BBOA (4%), SVOOA (32%), LVVOA (29%)</td>
</tr>
<tr>
<td>Shenzhen</td>
<td>Winter 2009</td>
<td>20.47</td>
<td>HOA (29.5%), BBOA (24.1%), SVOOA (27.6%), LVVOA (18.8%)</td>
</tr>
<tr>
<td>Kaiping</td>
<td>Winter 2008</td>
<td>11.92</td>
<td>BBOA (24.5%), SVOOA (35.8%), LVVOA (39.6%)</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>Winter 2017</td>
<td>17.3</td>
<td>HOA (13%), COA (18%), SVOOA (30%), LVVOA (40%)</td>
</tr>
</tbody>
</table>
**Figures**

![Graphs](image-url)

**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:

\[
\begin{align*}
    f_{j,\text{solution}} &= f_{j,\text{external}} \pm a \cdot f_{j,\text{external}} \\
    g_{i,\text{solution}} &= g_{i,\text{external}} \pm a \cdot g_{i,\text{external}}
\end{align*}
\]  

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\text{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\text{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 \( \geq 5 \) 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 instance, 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 remedie 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)
References


