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Supplement of

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

Junchen Guo et al.

Correspondence to: Shengzhen Zhou (zhoushzh3@mail.sysu.edu.cn) and Jun Zhao (zhaojun23@mail.sysu.edu.cn)

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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$_1$ ($\mu$g 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 ($\mu$g 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%), LVOOA (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%), LVOOA (18.8%)</td>
</tr>
<tr>
<td>Kaiping</td>
<td>Winter 2008</td>
<td>11.92</td>
<td>BBOA (24.5%), SVOOA (35.8%), LVOOA (39.6%)</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>Winter 2017</td>
<td>17.3</td>
<td>HOA (13%), COA (18%), SVOOA (30%), LVOOA (40%)</td>
</tr>
</tbody>
</table>

### Table S3. P-value, T-value, number of points (n), and Pearson Correlations between SOA and RO$_2^*$ for different NR-PM$_1$ concentration intervals.

<table>
<thead>
<tr>
<th>NR-PM$_1$ ($\mu$g m$^{-3}$)</th>
<th>r</th>
<th>n</th>
<th>T</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 30</td>
<td>0.31</td>
<td>47</td>
<td>5.07</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>30-40</td>
<td>0.50</td>
<td>60</td>
<td>4.40</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>40-50</td>
<td>0.53</td>
<td>35</td>
<td>3.56</td>
<td>0.0012</td>
</tr>
<tr>
<td>50-60</td>
<td>0.49</td>
<td>41</td>
<td>3.51</td>
<td>0.0011</td>
</tr>
<tr>
<td>60-70</td>
<td>0.62</td>
<td>40</td>
<td>4.93</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>&gt;70</td>
<td>0.59</td>
<td>30</td>
<td>3.85</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>
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. Dependence of $O_x$ and O3 on RO$_2^*$ for different scenarios (non-pollution daytime period, pollution daytime EPs, non-pollution nighttime period, and pollution nighttime EPs). All the regressions are orthogonally linear.
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 (Canaco 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:

$$f_{j,\text{solution}} = f_{j,\text{external}} \pm a \cdot f_{j,\text{external}}$$  \hspace{1cm} (1)  
$$g_{i,\text{solution}} = g_{i,\text{external}} \pm a \cdot g_{i,\text{external}}$$  \hspace{1cm} (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 $Q/Q_{\text{expected}}$, 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 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, and Figures S16-S17.
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)
Figure S12. The diurnal fractions of 4 OA components for pollution EPs.
**Figure S13.** Dependence of SOA on RO$_2$ concentration for the same short period of every day (i.e., every 2 hours) during non-pollution periods. Note that all the correlations are statistically significant (p-value < 0.01).
Figure S14. Daytime dependence of O$_x$ on RO$_2^*$ (a, b) and dependence of SOA on O$_x$ (c,d) for pollution EPs and non-pollution period.

Figure S15. Scatter plots between RO$_2^*$ and SVOOA/LVOOA for non-pollution period and pollution EPs.
Figure S16. Scatter plots between SOA and $f_{44}$ for different scenarios (non-pollution daytime, non-pollution nighttime, pollution daytime and pollution night time).

Figure S17. Comparison between combined ME-2 and separate ME-2, along with their correlation.
References


