Characterization of particulate organic nitrates and sulfates based on high resolution aerosol mass spectrometry in urban atmosphere, Seoul.

Hwajin Kim, Qi Zhang, Sunhye Kim, Jisoo Park, Jungeun Lee, Yejin Lee
Korea Institute of Science and Technology
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Seasonal variations of PM in Seoul, Korea

- PM Concentration during summer is the lowest among four different seasons.

However,

- In terms of PM2.5, it sometimes could be problematic.
  - Intensive SOA formation occur during summer.
  - Less impact of transport, thus important to investigate the other impacts.
  - A lot of interesting aerosol chemistries occur due to different meteorological condition (strong solar radiation, high RH etc.)
Aerosol Characteristics and Sources in Seoul, Korea

- **Sampling Site**
- **National Ambient Monitoring Site**
- **National Meteorology Monitoring Site**

- **Summer : 2016 July 27- Aug.31**
**KIST HR-ToF-AMS: Real time measurement of Non-Refractory PM1 composition and Chemistry**

<table>
<thead>
<tr>
<th>Instrumentation</th>
<th>Measured Species</th>
</tr>
</thead>
</table>
| **HR-ToF-AMS**        | - Quantitative composition of PM1 (organic, nitrate, sulfate, ammonium and chloride)  
                         | - Size resolved Chemical composition of PM1                                      
                         | - Elemental composition (O/C, H/C, OM/OC)                                        
                         | - OA Source apportionment by PMF, later.                                          |
| **SMPS**              | Particle size dist. and conc. (19-948 nm)                                         |
| **MAAP (670nm)**      | Concentration of BC (± 7wl aethaolometer)                                        |
| **PAX**               | Scattering, absorption and extinction coefficient                                 |
| **VOCUS-PTR-MS**      | VOC, oxidized precursors (from 2019.10~)                                          |
### Overall characteristics of PM2.5 in Seoul

<table>
<thead>
<tr>
<th>Period</th>
<th>Winter</th>
<th>Spring (KORUS-AQ)</th>
<th>Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH(%) (Avg ±σ)</td>
<td>59 % ±12</td>
<td>62 %± 22</td>
<td>66 %± 14</td>
</tr>
<tr>
<td>Temp. (°C) (Avg ±σ)</td>
<td>-0.24°C± 3.1</td>
<td>19 °C±5.0</td>
<td>28 °C±4.1</td>
</tr>
<tr>
<td>Ave PM1 loading (µg/m³)</td>
<td>27.5 µg/m³</td>
<td>22.1 µg/m³</td>
<td>20.2 µg/m³</td>
</tr>
<tr>
<td>WS (m/s)</td>
<td>1.4</td>
<td>1.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Organic sources</td>
<td>SVOOA, LVOOA, HOA, BBOA, COA</td>
<td>SVOOA, LVOOA, COA, HOA</td>
<td>LOOOA, MOOOA, NOA, OOA, COA, HOA, NO3-OA</td>
</tr>
</tbody>
</table>


[Kim et al., ACP, 2017; Kim et al., ACP, 2018; Kim et al., Chemosphere, 2019]
Overall characteristics during summer

- There’s no significant haze episodes but ranges in composition changes are considerable
Summer

Avg PM$_1$ = 20.2 µg/m$^3$

Winter

Avg PM$_1$ = 27.5 µg/m$^3$

- Sulfate & organic fractions are higher and nitrate fraction is lower
- Summer PM is somewhat acidic whereas winter PM is well neutralized.
- Possible to have less ammonium due to high temperature
- Possibility to have organic combined sulfate and nitrate
OA Source during summer: Org+Inorg combined

- 8 organic factors were observed. (vs 5 factors during winter)
- Two of them are primarily composed of ammonium sulfate and ammonium nitrate
- Rest are probably combined with organic
OA Source during summer: Org+Inorg combined

8 factor

Inorg combined factors
Org only factors

Inorg combined factors

Org only factors

Date and Time (KST)
OA Source apportionment in Seoul Korea during summer: org+inorg combined

- ~77% of sulfate and ~80% of nitrate are in inorganic phase
- Others may exist as organic combined
Estimation of Particulate Organic nitrate
Comparisons between two methods

\( r^2 = 0.696 \)
Slope = 0.691 ± 0.005

Fraction of organic nitrates (by mass) in ambient OA (assume MW = 200 - 300 g/mole, Rollins et al., 2012)

88% 12%
92% 8%

Conc. (µg/m³)
Good Correlation between organic nitrates and SOA factors

- Organic nitrate formation might be related with secondary formation
- This is urban, thus, Anthropogenic VOC could play significant roles in particulate organic nitrate → Anthropogenic VOC + NO3 studies are needed.
Estimation of Particulate Organic Sulfate

Much more complex..& several methods to estimate particulate organic Sulfate

1. PMF method: include $SO^+$, $SO_2^+$, $SO_3^+$, $HSO_3^+$, $H_2SO_4^+$ in PMF analysis

2. Offline method : FT-IR , LC-ESI-MS/MS to measure the C-O-S functional group or organosulfur compounds → limited by the availability of authentic standards. (Stone et al., 2012; Maria et al., 2003)

3. Online particle ablation by laser mass spectrometry (PALMS) single particle MS → but quantification issues (Liao et al., 2015; Froyd et al., 2010)

4. AMS Sulfate apportionment method (Chen et al., 2019)
Estimation of Particulate Organic Sulfate

- ~18% of sulfate are organic sulfate → More validations are needed (Chen et al., 2019)
• Aerosol composition, size distribution, sources, and evolution processes were investigated using an HR-ToF-AMS.

• Found the evidence of organic combined SO4 and NO3.

• 13-23% of nitrate and 8-12% of organic are composed of organic nitrate.

• Significant of organic sulfate (18-23% of sulfate) was formed during summer, as well.

• Secondary aerosol formations are related with the formation of organic sulfate and nitrate

• Although mass conc. is lower, summer PM should be characterized.