Size-resolved aerosol chemical compositions and qualification of particle secondary formation pathways in northern and southern mega-cities of China

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Why size-resolved aerosols?

- Radiation budget
- Absorb and scatter
- CCN

Global

- Mortality, cardiopathy
- toxicity: PAHs
- Adsorb other toxins

Health

Regional

- Air quality
- Visibility
- Haze

Aerosol

- size
- composition

transformation
transport
reaction
fate
Motivation

• To investigate size resolved characteristics of particle mass and chemical compositions in two important megacities in China.
• To quantify the contributions of particle secondary formation pathways.
Sampling sites


2001 summer, winter
2003 summer, 2004 fall
2006 summer
Instrument

MOUDI-110 (10 stages)
MOUDI-100 (8 stages)
Filter: Teflon

PM$_{1.8}$ and PM$_{1.8-10}$ as fine and coarse particles

MOUDI cut points: $\mu$m

<table>
<thead>
<tr>
<th></th>
<th>10-stage</th>
<th>8-stage</th>
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<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>3.2</td>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
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<td>1.0</td>
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<tr>
<td>6</td>
<td>0.56</td>
<td>0.56</td>
</tr>
<tr>
<td>7</td>
<td>0.32</td>
<td>0.32</td>
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<tr>
<td>8</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.056</td>
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</table>

• Mass
• Anion (11): F$^-$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, formate, acetate, propionate, oxalate, malonate, succinate, MSA
• Cation (5): Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$
Outline

Motivations

Experiment description

Size resolved PM$_{10}$ concentration

Quantification of particle secondary formation pathways

Summary
Size resolved particle mass

- Beijing > PRD; Urban > rural
- \( \text{PM}_{1.8}, \text{PM}_{10}, \text{PM}_{1.8}/\text{PM}_{10} \) increased. Fine particle pollution more important.
- Both megacities: bimodal distributions
- Different fine mode peaks (GZ 0.32-0.56 µm, SZ, YF 0.56-1 µm)
- Peak “shifts” indicating hygroscopic growth (XK) and transport (PKU) (Guo et al., 2010)
Outline

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Summary
Quantification of secondary formation pathways by PMF model

A PMF-based method is introduced to Quantification of secondary formation pathways

\[ x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \]

Basic idea:

• PMF model can be applied to the resolution of different particle modes

• For the case of secondary compounds: different formation pathways

Suitable condition

1. Secondary origin of the selected compounds
2. Formation pathways are clear

(Guo, S., Hu, M. et al. ACP 2010)
Resolved particle modes by PMF model (case: Beijing summer)

Three modes (Sources) Yufa
Four modes (Sources) PKU
Quantification of secondary formation pathways

- **Photochemical**
  - \( \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \)
  - \( \text{NH}_3 \rightarrow \text{CaCO}_3 \)

- **Aqueous phase reaction**
  - \( \text{SO}_2 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 \)

- **Heterogeneous reaction**
  - \( \text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3 \)
  - \( \text{CaCO}_3 + \text{HNO}_3 \rightarrow \text{Ca(NO}_3)_2 \)

**Formation pathway**

- Condensation
- In-cloud

**Model results**

- Summer Beijing
  - Condensation: 22%
  - In-cloud: 70%
  - Heterogeneous: 8%
PMF results to explain regional transport

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<tr>
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<th>Yufa</th>
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<tr>
<td>Mass-A</td>
<td>13.88</td>
<td>81.77</td>
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<tr>
<td>Mass-P</td>
<td>6.57</td>
<td>103.79</td>
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<tr>
<td>Mass-N</td>
<td>7.53</td>
<td>54.74</td>
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<tr>
<td>SO$_4^{2-}$-A</td>
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<td>SO$_4^{2-}$-P</td>
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<td>SO$_4^{2-}$-N</td>
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<td>NO$_3^-$-A</td>
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<td>NO$_3^-$-P</td>
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<tr>
<td>NO$_3^-$-N</td>
<td>0.35</td>
<td>5.89</td>
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- Aqueous-phase production Anlauf et al., [2006]
- Hygroscopic growth Liu, et al., [2008]
- No diurnal variation
- Correlation south wind days
- Aqueous-phase production, but from transport
- Droplet 2 vs. wind speed
- Droplet 2 (PKU) vs. Droplet 1 (YF)
- Mountain valley breeze (Chen et al., 2009)
Related on-going work on health study

Particles concentrations → Exposure → Risk assessment

Source apportionment
Formation quantification

Source & precursor → Source control strategy
Conclusion

• High concentration of particles at both megacities, fine particle and secondary pollution became important.
• Mass and main secondary compounds showed bimodal distribution. Different fine mode peaks at different sites.
• A PMF-based method was introduced to quantify the contributions of particle secondary formation pathways. In-cloud or droplet process was important (70%). Gas to particle condensation cannot be neglected (22%).
• The PMF model results help to explain the transport.
Thanks

Sunset at Yufa