Characteristics of Carbonaceous Aerosol in Guangzhou during the 2006 PRD Campaign: Optical Properties and Mixing State

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Introduction

Increases of Emissions in Asia

Global NO$_2$ map (Jan. 2003~ June 2004)

MODIS AOD (February 11 ~ 28, 2003)

[ Novakov et al., GRL, 2002 ]
Introduction

Why carbonaceous aerosol is important?

**Semi-Direct Radiative Forcing**

**BC above Cloud layer**
- increase cloud formation
- Cooling effect
  - RF = +0.1 to –0.5 W m\(^{-2}\) [IPCC, 2007]

**BC within Cloud layer**
- reduce cloud formation
- Warming effect

**BC on Snow**
- reduce albedo
- Warming effect
  - RF = +0.1W m\(^{-2}\) ± 0.3 W m\(^{-2}\)

**Direct effect**

**Scattering**

- Cooling
- Organic carbon (OC) ±0.05 W m\(^{-2}\)

**Absorption**

- Heating
- Black carbon (BC) +0.30 W m\(^{-2}\) ± 0.15 W m\(^{-2}\)
Introduction

Long-range Transport of Aerosol in Asia

Forest Fire Smoke

Asian Dust

Anthropogenic Aerosols

Korea

Japan
Long-range transport of aerosol in Asia

Introduction

[Image: Map showing the transport of aerosols over Asia during 28-30 April 2005. The map highlights Asian Dust and Carbonaceous Aerosol (Urban).]

[Source: Jung et al., 2006]
Average Vertical Column Density of NO2 Observed by GOME: 1997~2006
Program of Regional Integrated Experiment of Air Quality over Pearl River Delta (PRIDE-PRD) Campaign

► 2004 PRIDE-PRD campaign
- Period: 4 October ~ 5 November 2004
- Sites: urban (Guangzhou), non-urban (Xinken)

► 2006 PRIDE-PRD campaign
- Period: 2 ~ 31 July 2006
- Sites: urban (Guangzhou), downwind rural (Backgarden)

► 2008 PRIDE-PRD campaign
- Period: mid October ~ mid November 2008
- Sites: upwind (Conghua), downwind (Jiangmen), urban (Guangzhou)

Participants: Peking University, Chinese Universities and Institutes, RCEC (Taiwan), IFT, JRC, MPI (Germany), Univ of Tokyo & NIES (Japan), GIST (Korea), MIT (USA)
Objectives of PRIDE-PRD campaign

- Understand and quantify current complex air pollution problem in PRD.
- Understand chemical composition, size distribution, hygroscopic properties, and optical properties of aerosols.
- Quantify formation of oxidants and secondary aerosol by measurements and modeling.
- Study on interaction of aerosols and gases through measurements of precursors of aerosols and oxidants (e.g., HNO3, NH3) as well as by modeling.
- Validation of modeling of transformation and transport for oxidants and aerosol.
- Determine source-receptor relationship in PRD.
- Define the regional mitigation strategies and technical options to keep the air pollution load in PRD within sustainable limits in terms of ecological effects and human health effects.
GI ST Measurement (PRD 2006)

- Transmissometer (TX): bext
- Sunset OC/EC analyzer: thermal OC and EC, optical EC
- Aerosol spectrometer: PM mass, size distribution
- MAX-DOAS: NO₂, SO₂, HCHO

Legend:
- Regional
- Urban
- Supersite

Total: 16 sites
**Measurement site and parameters**

- **Site:** Guangzhou, China (23.13°N, 113.26°E)
- **Period:** 2 ~ 31 July 2006

### Measurement parameters

<table>
<thead>
<tr>
<th>Measurement parameters</th>
<th>Monitoring instrument</th>
<th>Diameter</th>
<th>Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light absorption coefficient ((b_{abs}))</td>
<td>Aethalometer (AE16, Magee Scientific, Berkeley, USA)</td>
<td>(D_p &lt; 2.5\mu m)</td>
<td>5 minute</td>
</tr>
<tr>
<td>(PM_{10}, PM_{2.5}, PM_{1.0}) mass concentration</td>
<td>Aerosol Spectrometer (265, Grimm Aerosol Technik, Ainring, Germany)</td>
<td>(D_p &lt; 10, 2.5, 1.0\mu m)</td>
<td>30 minute</td>
</tr>
<tr>
<td>Organic carbon/elemental carbon (OC/EC)</td>
<td>Semi-continuous OC/EC analyzer (RT3015, Sunset Laboratory, Oregon, USA)</td>
<td>(D_p &lt; 2.5\mu m)</td>
<td>1 hour</td>
</tr>
</tbody>
</table>
Guangzhou
## GIST Measurement Parameters (PRD 2006)

<table>
<thead>
<tr>
<th>Measurement parameter</th>
<th>Instrument</th>
<th>Averaging time</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$, NO$_2$, aerosol</td>
<td>GIST MAX-DOAS</td>
<td>15 min</td>
</tr>
<tr>
<td>SO$_2$, NO$_2$, aerosol</td>
<td>GIST Imaging DOAS</td>
<td>20 min</td>
</tr>
<tr>
<td>Light extinction coefficient ($b_{\text{ext}}$) (Visibility)</td>
<td>Optec Transmissometer</td>
<td>1 min</td>
</tr>
<tr>
<td>Light scattering coefficient ($b_{\text{scat}}$)</td>
<td>Ecotech Nephelometer (PKU)</td>
<td>5 min</td>
</tr>
<tr>
<td>Light absorption coefficient ($b_{\text{abs}}$)</td>
<td>Magee Aethalometer (PKU)</td>
<td>5 min</td>
</tr>
<tr>
<td>PM$_{2.5}$ OC/EC mass concentration</td>
<td>Sunset semi-continuous carbon field instrument</td>
<td>1 hr</td>
</tr>
</tbody>
</table>
Objectives of GIST Measurement at Urban Site

- The effect of aerosol chemistry and aerosol water on air quality, visibility impairment, and radiative forcing in Guangzhou
- Time-resolved measurement of carbonaceous aerosol in Guangzhou
- MAX-DOAS measurement of gaseous and particulate pollutants
- Size distribution and f(RH) of urban aerosol
Classification of Atmospheric Conditions

Results
Results

Three-day Air Mass Back-trajectories

Marine (16~18, 28~29 July)

LH (12, 22~23 July)

LRT1 (13~15 July)

LRT2 (24~26 July)
Results

**PM$_{2.5}$ Mass Budget**

- **Marine**
  - PM$_{2.5}$
  - Others 27%
  - SS 6%
  - EC 11%
  - OMC 25%
  - NHNO 5%
  - NHISO 26%

- **LH1**
  - PM$_{2.5}$ = 129.9 ± 40.0 µg m$^{-3}$
  - NHISO 38%
  - OMC 29%
  - NHNO 6%
  - SS 3%
  - EC 7%

- **LH2**
  - PM$_{2.5}$ = 115.6 ± 49.0 µg m$^{-3}$
  - NHISO 7%
  - OMC 28%
  - NHNO 7%
  - SS 3%
  - EC 2%
  - PM$_{2.5}$ others 3%

- **LRT1**
  - PM$_{2.5}$ = 92.3 ± 30.3 µg m$^{-3}$
  - NHISO 23%
  - OMC 35%
  - NHNO 3%
  - SS 2%
  - EC 8%

- **LRT2**
  - PM$_{2.5}$ = 140.2 ± 44.1 µg m$^{-3}$
  - NHISO 44%
  - OMC 28%
  - NHNO 7%
  - SS 3%
  - EC 6%
  - PM$_{2.5}$ others 12%
## Summary of Aerosol Properties

<table>
<thead>
<tr>
<th></th>
<th>PM$_{10}$</th>
<th>PM$_{2.5}$</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
<th>OC</th>
<th>EC</th>
<th>BC</th>
<th>OC/EC</th>
<th>$b_{\text{scat}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine</td>
<td>43.4 ± 14.5</td>
<td>34.0 ± 10.9</td>
<td>6.3 ± 2.8</td>
<td>2.5 ± 1.0</td>
<td>5.0 ± 2.8</td>
<td>3.6 ± 1.9</td>
<td>4.4 ± 2.2</td>
<td>1.5 ± 0.7</td>
<td>74.1 ± 30.7</td>
</tr>
<tr>
<td>LH1</td>
<td>129.9 ± 40.0</td>
<td>93.8 ± 27.3</td>
<td>26.4 ± 13.3</td>
<td>5.6 ± 2.8</td>
<td>15.9 ± 5.9</td>
<td>6.8 ± 2.5</td>
<td>9.0 ± 3.7</td>
<td>2.4 ± 0.6</td>
<td>318.8 ± 110.4</td>
</tr>
<tr>
<td>LH2</td>
<td>115.6 ± 49.0</td>
<td>86.9 ± 37.2</td>
<td>33.9 ± 17.4</td>
<td>5.1 ± 3.0</td>
<td>14.4 ± 7.3</td>
<td>6.6 ± 2.9</td>
<td>9.0 ± 4.3</td>
<td>2.1 ± 0.7</td>
<td>306.3 ± 165.7</td>
</tr>
<tr>
<td>LRT1</td>
<td>92.3 ± 30.3</td>
<td>68.2 ± 20.1</td>
<td>11.5 ± 6.0</td>
<td>3.2 ± 2.4</td>
<td>13.9 ± 5.3</td>
<td>5.4 ± 1.7</td>
<td>6.6 ± 2.3</td>
<td>2.8 ± 1.2</td>
<td>220.5 ± 72.3</td>
</tr>
<tr>
<td>LRT2</td>
<td>140.2 ± 44.1</td>
<td>108.2 ± 32.2</td>
<td>31.5 ± 11.1</td>
<td>5.1 ± 4.1</td>
<td>16.9 ± 6.4</td>
<td>6.5 ± 2.5</td>
<td>9.5 ± 4.3</td>
<td>2.8 ± 1.0</td>
<td>418.9 ± 155.0</td>
</tr>
</tbody>
</table>
Results

Average PM$_{2.5}$ OC vs. EC in Different Areas in Asia

<table>
<thead>
<tr>
<th>Area</th>
<th>Country</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guangzhou</td>
<td>China</td>
<td>Cao et al., 2004</td>
</tr>
<tr>
<td>Beijing</td>
<td>China</td>
<td>He et al., 2001</td>
</tr>
<tr>
<td>Shanghai</td>
<td>China</td>
<td>Ye et al., 2003</td>
</tr>
<tr>
<td>Shenzhen</td>
<td>China</td>
<td>Cao et al., 2004</td>
</tr>
<tr>
<td>Hong Kong</td>
<td>China</td>
<td>Cao et al., 2004</td>
</tr>
<tr>
<td>Chongju</td>
<td>Korea</td>
<td>Lee and Kang, 2001</td>
</tr>
<tr>
<td>Sapporo</td>
<td>Japan</td>
<td>Ohta et al., 1998</td>
</tr>
<tr>
<td>Uji</td>
<td>Japan</td>
<td>Holler et al., 2002</td>
</tr>
<tr>
<td>Kosan</td>
<td>Korea</td>
<td>Kim et al., 2003</td>
</tr>
<tr>
<td>Kangwha</td>
<td>Korea</td>
<td>Kim et al. 2000</td>
</tr>
<tr>
<td>Seoul</td>
<td>Korea</td>
<td>Kim et al., 2007</td>
</tr>
<tr>
<td>Guangzhou (this study)</td>
<td>China</td>
<td></td>
</tr>
</tbody>
</table>

OC = 9.8 ± 6.1 μg m$^{-3}$
EC = 4.8 ± 2.3 μg m$^{-3}$
OC/EC = 2.1 ± 1.0
Results

Correlation between OC and EC

Primary OC dominant
6~8 hr

Secondary OC dominant
12~15 hr
Minimum OC/EC ratio method (Turpin and Huntzicker, 1991; Castro et al., 1999):

\[
OC_{sec} = OC_{total} - EC \cdot (OC / EC)_{min}
\]

-Conditions:
Low photochemical processing period: 6~8 A.M.
NO>40ppb, NO2+O3<40ppb
Avg. minimum OC/EC ratio = 1.06±0.28
When SOC was compared with oxidant sum (NO$_2$+O$_3$), higher SOC was observed at the same value of oxidant sum during LRT period, which indicates the transport of secondary OC outside the measurement site.
The formation of secondary OC was highly correlated with ambient temperature as the formation rate of $1.5 \mu g \ C \ m^{-3}/C^\circ$ under the condition of ambient temperature $> 31^\circ C$. 

The equation is given by $y = 1.5034x - 43.715$ with $R^2 = 0.4091$. 

Where: 
- $y$: SOC formation rate ($\mu g \ C \ m^{-3}$) 
- $x$: Ambient temperature ($^\circ C$)
Results

Carbonaceous Aerosol Characteristics

-Highest OC/EC ratio was observed during LRT period due to the transport of OC from biomass burning and the formation secondary OC during the transport.
Loading Effect on Aethalometer BC

“Shadowing” effect due to filter loading, \( R(\text{ATN}) \)

\[
\begin{align*}
\text{“Shadowing” effect due to filter loading} & \quad \rightarrow \quad \text{Decrease the } b_{\text{ATN}} & \quad \rightarrow \quad R(\text{ATN}) < 1 \\

b_{\text{aeth}}(\lambda) &= \frac{b_{\text{ATN}}(\lambda)}{C(\lambda) \cdot R(\text{ATN})} \\
R(\text{ATN}) &= \left( \frac{1}{f} - 1 \right) \cdot \frac{\ln \text{ATN} - \ln 10}{\ln 50 - \ln 10} + 1
\end{align*}
\]

C(\(\lambda\)>1 = multiple scattering correction factor within the filter. Shadowing factor, \( f \) (when \( \omega_0(532\text{nm}) < 0.85 \))

\[
f = a(1 - \omega_0) + 1
\]

Here, \( a = 0.87 \pm 0.10 \) and \( 0.85 \pm 0.05 \) at \( \lambda = 450 \) and 660nm, respectively. [Weingartner et al., 2003]

In this study, \( f \) was determined to be \( 1.15 \) with \( \omega_{0,\text{PM2.5}}(550\text{nm}) = 0.82. \)
Results

Aethalometer BC after Loading Effect Correction

\[ BC_{corrected} = \text{Aethalometer } BC + BC, \text{loading effect} \]

Average loading effect = 12.3 ± 4.7 % of total BC.
Results

Mixing State Effect on Aerosol Absorption

We Define: BC/EC minimum method

\[
b_{abs,ext} = \sigma_{BC} \times \frac{BC}{EC_{\text{min}}} \times EC
\]

\[
b_{abs,total} = \sigma_{BC} \times BC
\]

\[
b_{abs,total} - b_{abs,ext} = \Delta b_{abs,int}
\]

Where,
EC=Sunset EC (Thermally)
BC=Aethalometer BC (Optically)
\(\sigma_{BC}\)=Mass absorption efficiency, 7.7 m²/g
BC/EC\(_{\text{min}}\)= average of lower 10 % of BC/EC ratio

![Graph showing BC/EC and SOC ratios over time]

Lower 10% of BC/EC ratio
= 1.14 ± 0.06
Total light absorption coefficient ($b_{abs\_total}$) = 54.7 ± 28.5 Mm$^{-1}$
Additional light absorption coefficient by the mixing state of EC ($\Delta b_{abs\_int}$) = 10.5 ± 8.6 Mm$^{-1}$
19.4% of total $b_{abs}$ was due to additional absorption by internal mixing of EC.
Results

Aerosol Absorption Coefficient

- Contribution of $\Delta b_{abs,\text{int}}$ to $b_{abs,\text{total}}$ shows minimum during night (11P.M.-2A.M.) and maximum in the afternoon (1P.M.-4P.M.).
- Generally high contribution of $\Delta b_{abs,\text{int}}$ to $b_{abs,\text{total}}$ was observed during LH and LRT periods.
Aerosol absorption coefficient

<table>
<thead>
<tr>
<th></th>
<th>$b_{\text{abs_total}}$</th>
<th>$\Delta b_{\text{abs_int}}$</th>
<th>Mixing effect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mm$^{-1}$</td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Marine</td>
<td>41.4±19.5</td>
<td>6.9±4.9</td>
<td>16.6±9.1</td>
</tr>
<tr>
<td>LH1</td>
<td>77.9±32.4</td>
<td>18.0±12.5</td>
<td>21.3±10.0</td>
</tr>
<tr>
<td>LH2</td>
<td>67.0±39.4</td>
<td>16.1±14.0</td>
<td>22.9±8.8</td>
</tr>
<tr>
<td>LRT1</td>
<td>57.5±20.0</td>
<td>10.7±8.3</td>
<td>18.3±9.7</td>
</tr>
<tr>
<td>LRT2</td>
<td>81.9±37.9</td>
<td>16.0±9.8</td>
<td>21.1±7.2</td>
</tr>
<tr>
<td>All</td>
<td>54.7±28.5</td>
<td>10.5±8.6</td>
<td>19.4±9.1</td>
</tr>
</tbody>
</table>

-Generally high contribution of $\Delta b_{\text{abs\_int}}$ to $b_{\text{abs\_total}}$ was observed during LH and LRT period.
- Average OC/EC ratio were determined to be 1.5±0.6, 2.4±0.6, 1.9±0.8, 2.8±1.2, and 2.8±1.0 during clean marine (CM), LH1, LH2, LRT1, and LRT2 periods, respectively.

- Minimum OC/EC ratio was determined to be 1.06±0.28 under low photochemical processing condition (6~8 A.M.). Average fraction of secondary OC to total OC was determined to be 41.6±23.8% with a minimum of 26.8±16.8% in the morning and a maximum of 64.4±8.7% at noon.

- It was found that the formation of secondary OC was highly correlated with ambient temperature as the formation rate of 1.5 μg C m⁻³/C° under the condition of ambient temperature > 31°C.

- Average shadowing effect was determined to 12.3±4.7% of total light attenuation, resulted in 12.3±4.7% underestimation of EC by aethalometer measurement.
- Diurnal variation of BC/EC ratio is very similar to that of secondary OC with low in the morning and high in the afternoon, which suggests the enhancement of light attenuation in the afternoon by the internal mixing of EC with secondary aerosols.

- Minimum BC/EC ratio method was used to determine the additional absorption due to internal mixing of EC. It is found that 19.4% of total $b_{\text{abs}}$ was due to it.

- Generally high contribution of the additional absorption by the mixing state of EC to total $b_{\text{abs}}$ was observed during LH and LRT periods.
Thank you