Biomass Burning Contribution to Haze Episode in Winter of Nanjing

Liu Xiaoyan

2016-12-16
Outline

• Introduction
• Material and method
• Result and Discussion
• Conclusion
• Other work
1月24日，雾霾给南京“颜色”看

2015年1月24日，江苏省南京市，双休日的第一天遭遇严重雾霾天气，能见度极低的天空，给这个大都市“颜色”看。

当日，南京9个空气质量实时监测点平均数值一直处于200以上，到16点，9个监测点中，有7个严重污染，其余2个处在重度级别。仙林监测点数值一度达到316。
Introduction

- **Biomass Burning (BB)**
  - **what is BB?**
  - Biomass burning includes the combustion of biomass fuels through either natural (e.g., wildfires) or planned processes (e.g., prescribed burning and residential wood combustion in fireplaces and wood stoves).
  - **Impact:** BB emit large amounts of air pollutants, which especially exists in fine particles.
  - Fossil fuel burning has gained attention for about 2 centuries, but scientific interest in biomass burning grew when it had been suggested that for some atmospheric pollutants biomass burning could rival fossil fuel use as a source of atmospheric pollution (Seiler and Crutzen, 1980; Crutzen and Andreae, 1990). The biomass burning contribution to seasonal ambient PM$_{2.5}$ mass is much higher in China, that is, 12-27μg m$^{-3}$ (15-24%) in Beijing (Cheng et al., 2013; Song et al., 2007; Wang et al., 2009), 5.4-25.4 μg m$^{-3}$ (4-19%) in Guangzhou (Wang et al., 2007), 37% in YRD (70% to OC) (Z. Cheng et al., 2014).
  - It became evident that these emissions could affect large areas of the world as a consequence of long-range transport (Andreae, 1983; Fishman et al., 1990).
  - **Tracer:** Levoglucosan, K$^+$. 
Material and method

• Sampling site

Yale-NUIST Center on Atmospheric Environment
PM$_{2.5}$ Sampling instrument

- Sampler: KC 1000
- Sample collector: quartz filter (8×10 inch)

Sampling frequency and time:

<table>
<thead>
<tr>
<th>Time</th>
<th>Frequency</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>14$^{th}$ Jan 16:30-26$^{th}$ Jan 18:00</td>
<td>Every 3 hrs</td>
<td>Afternoon of 14$^{th}$ : after light rain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Morning of 25$^{th}$ : light rain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9 a.m. to 1 p.m. of 25$^{th}$ : power failure</td>
</tr>
<tr>
<td>26$^{th}$ Jan 18:00-29$^{th}$ Jan 00:00</td>
<td>Every 6 hrs</td>
<td>27$^{th}$ to 29$^{th}$ : rain and snow</td>
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</table>
Material and method

- Laboratory analysis of chemical species

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Instrument</th>
<th>Principle</th>
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<tbody>
<tr>
<td>Carbonaceous component</td>
<td>Sunset EC/OC analyzer</td>
<td>TOT</td>
</tr>
<tr>
<td>Water-soluble ion</td>
<td>ICS 5000+</td>
<td>Ion Chromatography + Conductive Detector</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>ICS 5000+</td>
<td>Ion Chromatography + Electrochemical Detector</td>
</tr>
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<table>
<thead>
<tr>
<th>Cation</th>
<th>Anion</th>
<th>Carbohydrate</th>
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<tbody>
<tr>
<td>Column</td>
<td>IonPac CS12A</td>
<td>MA</td>
</tr>
<tr>
<td></td>
<td>IonPac CG 12A</td>
<td>200 μL</td>
</tr>
<tr>
<td>Loop</td>
<td>25 μL</td>
<td></td>
</tr>
<tr>
<td>Elution Method</td>
<td>Flow:1mL min⁻¹ MSA:0-20min</td>
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<tr>
<td></td>
<td>30mM L⁻¹</td>
<td></td>
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<tr>
<td></td>
<td>Flow:1.5mL min⁻¹ NaOH:0-3min</td>
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<tr>
<td></td>
<td>0.5mM L⁻¹, 3-5min 0.5-5mM L⁻¹,</td>
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</tr>
<tr>
<td></td>
<td>5-15min 5-30mM L⁻¹,15.1-20min</td>
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</tr>
<tr>
<td></td>
<td>0.5mM L⁻¹</td>
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<tr>
<td></td>
<td>Flow:0.4mL min⁻¹ NaOH:15-34min</td>
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<td>300mM L⁻¹, 34-45min 480mM L⁻¹,</td>
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<td>45-60min 480-650mM L⁻¹</td>
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### QAQC

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<tr>
<th>Cation</th>
<th>Cal.Type</th>
<th>Points</th>
<th>Offset</th>
<th>Slope</th>
<th>Coeff.Det.</th>
<th>RSD</th>
<th>LOD</th>
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<td>glycerol</td>
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<td>0</td>
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<td>0.0297</td>
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<td>3.6142</td>
<td>0.80</td>
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<td>Lin</td>
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<td>0</td>
<td>0.0398</td>
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<td>2.6905</td>
<td>0.69</td>
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<td>glucose</td>
<td>Lin</td>
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<td>0</td>
<td>0.0347</td>
<td>99.953</td>
<td>2.7181</td>
<td>0.65</td>
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<td>galactose</td>
<td>Lin</td>
<td>5</td>
<td>0</td>
<td>0.0342</td>
<td>99.9592</td>
<td>2.0977</td>
<td>0.47</td>
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<tr>
<td>fructose</td>
<td>Lin</td>
<td>5</td>
<td>0</td>
<td>0.001</td>
<td>99.9779</td>
<td>1.603</td>
<td>19.94</td>
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## QAQC

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<tr>
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<th>RSD</th>
<th>recovery</th>
<th>LOD</th>
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<tr>
<td>Na⁺</td>
<td>LOff</td>
<td>10</td>
<td>0.0108</td>
<td>0.2783</td>
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<td>98.25</td>
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<td>NH₄⁺</td>
<td>Quad</td>
<td>9</td>
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<td>0.1975</td>
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<td>1.06</td>
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<tr>
<td>K⁺</td>
<td>LOff</td>
<td>9</td>
<td>0.0025</td>
<td>0.1787</td>
<td>99.9985</td>
<td>0.72</td>
<td>95.72</td>
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<tr>
<td>Mg²⁺</td>
<td>LOff</td>
<td>8</td>
<td>0.0037</td>
<td>0.5311</td>
<td>99.9984</td>
<td>1.75</td>
<td>97.25</td>
<td>0.08</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>LOff</td>
<td>10</td>
<td>0.0113</td>
<td>0.3375</td>
<td>99.9985</td>
<td>1.09</td>
<td>111.95</td>
<td>0.13</td>
</tr>
<tr>
<td>F⁻</td>
<td>LOff</td>
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<td>-0.0037</td>
<td>0.3836</td>
<td>99.921</td>
<td>0.03</td>
<td>89.59</td>
<td>0.22</td>
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<td>MSA⁻</td>
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<td>0.0691</td>
<td>99.9321</td>
<td>0.01</td>
<td>107.29</td>
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<tr>
<td>Cl⁻</td>
<td>LOff</td>
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<td>-0.0003</td>
<td>0.2241</td>
<td>99.9494</td>
<td>0.72</td>
<td>95.75</td>
<td>0.64</td>
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<tr>
<td>NO₂⁻</td>
<td>LOff</td>
<td>5</td>
<td>0</td>
<td>0.13</td>
<td>99.9298</td>
<td>0.06</td>
<td>104.48</td>
<td>1.11</td>
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<td>NO₃⁻</td>
<td>LOff</td>
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<td>-0.0254</td>
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<tr>
<td>SO₄²⁻</td>
<td>LOff</td>
<td>9</td>
<td>-0.009</td>
<td>0.1481</td>
<td>99.8518</td>
<td>0.08</td>
<td>116.15</td>
<td>1.41</td>
</tr>
</tbody>
</table>

\[
CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39.1} + \frac{2\cdot Mg^{2+}}{24.3} + \frac{2\cdot Ca^{2+}}{40}
\]

\[
AE = \frac{Cl^-}{35.45} + \frac{2\cdot SO_4^{2-}}{96} + \frac{NO_3^-}{62} + \frac{MSA^-}{95.08} + \frac{F^-}{19} + \frac{NO_2^-}{46}
\]
Result and Discussion

<table>
<thead>
<tr>
<th></th>
<th>OC</th>
<th>EC</th>
<th>SOC</th>
<th>OC/EC</th>
<th>SOC/OC</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>avg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5. Concentration distribution of inorganic ion. The box represent the 25th (lower line), 50th (middle line), 75th (top line) percentiles; the end of the vertical bars represent the 10th (below the box) and 90th (above the box) percentiles. The solid dots and stars represent abnormal value.

Table 3. The max, min and average value of inorganic ion in PM$_{2.5}$ and its ratio to PM$_{2.5}$. Ion in $\mu$g m$^{-3}$

<table>
<thead>
<tr>
<th>Ion</th>
<th>Average</th>
<th>SD</th>
<th>Max</th>
<th>Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0.64</td>
<td>0.57</td>
<td>4.49</td>
<td>0.03</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>19.79</td>
<td>11.23</td>
<td>44.73</td>
<td>2.02</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.24</td>
<td>0.71</td>
<td>3.79</td>
<td>0.19</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.14</td>
<td>0.13</td>
<td>0.67</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>2.72</td>
<td>3.45</td>
<td>16.13</td>
<td>0.11</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.08</td>
<td>0.10</td>
<td>0.46</td>
<td>0.00</td>
</tr>
<tr>
<td>MSA$^-$</td>
<td>1.33</td>
<td>1.10</td>
<td>4.58</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>4.89</td>
<td>4.22</td>
<td>18.21</td>
<td>0.45</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>0.29</td>
<td>0.22</td>
<td>1.07</td>
<td>0.00</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>32.30</td>
<td>20.05</td>
<td>84.14</td>
<td>3.98</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>23.18</td>
<td>11.37</td>
<td>52.14</td>
<td>6.86</td>
</tr>
</tbody>
</table>
Total carbohydrate level in this study is higher than the mean level in urban area of Shanghai (503.7 ng m\(^{-3}\)) and Guangzhou (206.0 ng m\(^{-3}\)) during winter time \(\text{(Ma et al., 2009, Du et al., 2015)}\).
Levoglucosan is the most dominant component in total carbohydrate with a portion of 63%, indicating the significant contribution of biomass burning. Levoglucosan to OC ratio varies from 0.08% to 3.99%, with a mean level of 1.81%.

Total carbohydrate to OC ratio ranges from 0.54% to 5.31%, with a mean value of 2.86% which is higher than that of urban area in Shanghai during winter (X. Li et al., 2016).

Levoglucosan is the most dominant component in total carbohydrate with a portion of 63%, indicating the significant contribution of biomass burning. Levoglucosan to OC ratio varies from 0.08% to 3.99%, with a mean level of 1.81%.
Good correlation between levoglucosan and $\text{K}^+$ or OC suggested the important contribution of biomass burning.

Above mean amount of levoglucosan

Second Ion: 88.28%

Below mean amount of levoglucosan

Second Ion: 85.39%
Levoglucosan is the most dominant component in total carbohydrate with a portion of 63%, indicating the significant contribution of biomass burning. Levoglucosan to OC ratio varies from 0.08% to 3.99%, with a mean level of 1.81%.

Total carbohydrate to OC ratio ranges from 0.54% to 5.31%, with a mean value of 2.86% which is higher than that of urban area in Shanghai during winter (X. Li et al., 2016).

Levoglucosan is the most dominant component in total carbohydrate with a portion of 63%, indicating the significant contribution of biomass burning. Levoglucosan to OC ratio varies from 0.08% to 3.99%, with a mean level of 1.81%. 
- **Factor 1:** Biomass burning, fossil fuel burning
- **Factor 2:** Soil dust
- **Factor 3:** Marine emission

<table>
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<th>成份</th>
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<th>2</th>
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<tbody>
<tr>
<td>OC</td>
<td>.800</td>
<td>.494</td>
<td>.026</td>
</tr>
<tr>
<td>EC</td>
<td>.728</td>
<td>.554</td>
<td>.067</td>
</tr>
<tr>
<td>Na</td>
<td>.165</td>
<td>.438</td>
<td>-.550</td>
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<td>NH4</td>
<td>.935</td>
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<td>.072</td>
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<td>.842</td>
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<td>Mg</td>
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<td>.957</td>
<td>-.017</td>
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<tr>
<td>Ca</td>
<td>-.031</td>
<td>.955</td>
<td>-.018</td>
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<tr>
<td>F</td>
<td>.078</td>
<td>.884</td>
<td>.255</td>
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<td>MSA</td>
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<tr>
<td>Cl</td>
<td>.457</td>
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<tr>
<td>NO3</td>
<td>.954</td>
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<tr>
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<td>.082</td>
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<tr>
<td>levoglucosan</td>
<td>.779</td>
<td>.199</td>
<td>.009</td>
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**旋转成份矩阵**

| 提取方法: | 主成分分析法。
旋转法: | 具有Kaiser标准化的正交旋转法。

<table>
<thead>
<tr>
<th>BB to OC_K⁺</th>
<th>BB to OC_lev</th>
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<tbody>
<tr>
<td>%</td>
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<tr>
<td>average</td>
<td>72.99%</td>
</tr>
<tr>
<td>min</td>
<td>10.75%</td>
</tr>
<tr>
<td>max</td>
<td>99.02%</td>
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</table>

- OC=12.91*K⁺+4.69
  \[ R^2=0.8432 \]
- OC=28.18*levoglucosan+9.83
  \[ R^2=0.5925 \]
Conclusion

- OC, EC mean concentration is 20.41 and 2.35 μg m\(^{-3}\), with a mean OC/EC of in the ambient environment during this winter time pollution event in Nanjing. The good relationship between OC and EC indicates the important contribution of fuel combustion.

- The total carbohydrate concentration is 508.6 ng m\(^{-3}\), including levoglucosan (375.6 ng m\(^{-3}\)) as its dominant component, with a high levoglucosan/OC (1.81) illustrating the significant contribution of biomass burning to OC, which is estimated as 53.89%.

- It is identified that Nanjing has been influenced by open biomass burning in southeast China, through air mass long-range transport.

- Through PCA, main sources of emission are divided to biomass burning, fossil fuel burning, soil dust and marine emission.
Nepal_PM_{10}
Thailand

- The 10 sugars concentrations (ng/m$^3$) on PM$_{2.5}$ in BB and NBB
The ratio of any sugars in total sugars on PM$_{2.5}$ in BB
Outlook

• Looking for method to quantify contribution of biomass burning better.
• Investigate research method for various kinds of carbohydrates.
• Continue to improve separation method for more sorts of target carbohydrate.
Thank you