Light Absorption and Chemical Composition of Primary and Secondary Organic Aerosol

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The 1st Regional GEOS-Chem Asia Meeting
Nanjing, Jiangsu, China
May 21-23, 2018
Background

Warming Effect of BrC

- BC contributes 72% of the global atmospheric absorption
- Strong BrC contributes > 20–50% of the global atmospheric absorption over regions dominated by seasonal biomass burnings and biofuel combustion
- Overall, BrC > ¼ BC absorption on a global basis.

Feng et al., 2013 Atmos. Chem. Phys.
Background

BrC Sources

Lin et al., 2015, PCCP

Galloway et al., 2009, ACP
Background

**Particle-based VS Extract-based**

**Light Absorption Measurement**

*Photoacoustic Spectrometer (PASS-3), Aethalometer: $b_{abs}$*

*UV/Vis spectrometer: $A_{abs}$ (Solvent extraction)*

**Imaginary Part of the Refractive Index ($k_{OA}$)**

**Mie theory:**
Optimized $k_{OA}$ resulting in best theoretical fit to measured $b_{abs}$

**Inputs:**
BC, OA size distribution (SP2 and SMPS)
BC refractive index (existed measurements)
Real part of RI (existed measurements or from PASS-3 scattering coefficient measurement)

**Major Uncertainties:**
BC mass concentration and size distribution;
Assumptions on mixing state of OA and BC.

**Empirical equation:**

$$k_{OA} = \frac{\rho \times \lambda \times MAC_{\lambda}}{4 \times \pi \times OM}$$

**MAC$_{\lambda}$ calculation:**

$$Abs_{\lambda} = (A_{\lambda} - A_{700}) \times \frac{v_i}{v_a} \times \ln(10)$$

$$MAC_{\lambda} = \frac{Abs_{\lambda}}{C_{OC}}$$

**Advantage:** Reflect the absorption of pure OM, no influence from BC or EC;

**Disadvantage:** Cannot reflect BrC absorption in suspended particles.
Background

Particle-based VS Extract-based

Composition Measurement

**HR-ToF-AMS:**
- H:C ratio, primary
- O:C ratio, secondary

**PASS-3 and Aethalometer:**
- $b_{\text{abs}}$
- H:C/O:C ratio vs. $b_{\text{abs}}$

**GC-MS, LC-DAD-ToFMS:**
- Molecular composition

**UV/Vis spectrometer:**
- $A_{\text{abs}}$
- Attribute $A_{\text{abs}}$ to light-absorbing molecules.
Background

Light-absorbing Organic Molecules

PAHs
Nearly all combustion processes........
Half-life: ~20 h

Nitro aromatics
Biomass burning;
Gas-phase oxidation

Imidazole
Reactive uptake of GL
or Methyl-GL on AS
Half-life: minutes to hours
Objective

- Light-absorbing properties of organic matter from biomass burning and SOA formation
- Relationship of BrC absorption vs. burn condition
- Contribution of BrC molecules to OA mass and bulk absorption
Biomass burning

Sample information for prescribed and laboratory burns

<table>
<thead>
<tr>
<th>Location</th>
<th>Fuel type</th>
<th>Field burn sample No.</th>
<th>Lab burn sample No.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agriculture Field</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nez Perce, ID</td>
<td>Kentucky Bluegrass (“KBG”)</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Nez Perce, ID</td>
<td>Wheat stubble (“Wheat”)</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Nez Perce, ID</td>
<td>Chemically fallowed wheat stubble (“Wheat + Herbicide”)</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td><strong>Forest Field</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eglin Air Force Base, FL</td>
<td>Grass/forb/shrub/wood debris (“Forest burn”)</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Eglin Air Force Base, FL</td>
<td>Grass/forb/shrub (“Grass burn”)</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>
Biomass burning

Typical absorption spectra

The MAC at 365 nm was usually used as proxy for BrC absorption.

1. Far from short UV region, avoiding the interference from non-organic compounds in aqueous extracts;

2. High correlated with the sum of absorption over 300 – 400 nm.

## Biomass burning

Light absorbing properties of methanol extractable OC from biomass burning

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Sampling type</th>
<th>EC/OC</th>
<th>Extraction Efficiency (%)</th>
<th>MAC$_{365}$ (m$^2$ g$^{-1}$C)</th>
<th>AAE (300 - 550 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBG</td>
<td>Aerostat</td>
<td>0.036 ± 0.011</td>
<td>93.4 ± 0.84</td>
<td>1.38 ± 0.033</td>
<td>7.03 ± 0.068</td>
</tr>
<tr>
<td></td>
<td>Ground</td>
<td>0.032 ± 0.015</td>
<td>94.7 ± 1.91</td>
<td>1.32 ± 0.17</td>
<td>7.12 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>OBTF</td>
<td>0.17 ± 0.091</td>
<td>94.5 ± 2.01</td>
<td>1.80 ± 0.15</td>
<td>6.25 ± 0.26</td>
</tr>
<tr>
<td>Wheat</td>
<td>Aerostat</td>
<td>0.084</td>
<td>90.1</td>
<td>1.19</td>
<td>7.82</td>
</tr>
<tr>
<td></td>
<td>Ground</td>
<td>0.018</td>
<td>90.8</td>
<td>1.06</td>
<td>8.11</td>
</tr>
<tr>
<td></td>
<td>OBTF</td>
<td>0.33 ± 0.18</td>
<td>94.5 ± 2.97</td>
<td>1.28 ± 0.12</td>
<td>5.28 ± 0.96</td>
</tr>
<tr>
<td>Wheat + Herbicide</td>
<td>Aerostat</td>
<td>0.046 ± 0.019</td>
<td>90.8 ± 3.59</td>
<td>1.05 ± 0.059</td>
<td>7.77 ± 0.51</td>
</tr>
<tr>
<td></td>
<td>Ground</td>
<td>0.016 ± 0.0081</td>
<td>95.1 ± 1.18</td>
<td>1.00 ± 0.076</td>
<td>7.93 ± 0.64</td>
</tr>
<tr>
<td></td>
<td>OBTF</td>
<td>0.13 ± 0.022</td>
<td>91.5 ± 3.17</td>
<td>2.09 ± 0.12</td>
<td>5.83 ± 0.69</td>
</tr>
<tr>
<td>Forest burn</td>
<td>Aerostat</td>
<td>0.041</td>
<td>96.5</td>
<td>1.10</td>
<td>7.08</td>
</tr>
<tr>
<td></td>
<td>Ground</td>
<td>0.026 ± 0.0095</td>
<td>97.5 ± 1.13</td>
<td>1.04 ± 0.084</td>
<td>7.37 ± 0.078</td>
</tr>
<tr>
<td></td>
<td>OBTF</td>
<td>0.21 ± 0.16</td>
<td>97.0 ± 1.87</td>
<td>1.13 ± 0.15</td>
<td>7.36 ± 0.59</td>
</tr>
<tr>
<td>Grass burn</td>
<td>Aerostat</td>
<td>0.086</td>
<td>95.1</td>
<td>0.90</td>
<td>6.43</td>
</tr>
<tr>
<td></td>
<td>Ground</td>
<td>0.089</td>
<td>95.3</td>
<td>0.97</td>
<td>6.92</td>
</tr>
</tbody>
</table>

Biomass burning

Dependence of Light Absorption on BC-OC ratio


Biomass burning

Dependence of Light Absorption on EC-OC ratio

Biomass burning

Dependence of Light Absorption on EC-OC ratio

The light absorption of BrC from biomass burning is not only dependent on burn condition, but also fuel species.
Biomass burning

Similar fuel species burned in different seasons

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Phase</th>
<th>Fuels</th>
<th>EC/OC (m^2 g^{-1}C)</th>
<th>MAC_{365} (m^2 g^{-1}C)</th>
<th>MAC_{550} (m^2 g^{-1}C)</th>
<th>Aabs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burn 1</td>
<td>Flaming</td>
<td>hardwood/loblolly pine (N=3)</td>
<td>0.042 ± 0.014</td>
<td>1.47 ± 0.25</td>
<td>0.15 ± 0.065</td>
<td>5.68 ± 0.70</td>
</tr>
<tr>
<td></td>
<td>Smoldering</td>
<td>hardwood/loblolly pine (N=3)</td>
<td>0.0098 ± 0.0024</td>
<td>1.00 ± 0.11</td>
<td>0.054 ± 0.015</td>
<td>6.83 ± 0.52</td>
</tr>
<tr>
<td>Burn 2</td>
<td>Flaming</td>
<td>hardwood/loblolly pine (N=4)</td>
<td>0.049 ± 0.011</td>
<td>4.07 ± 0.15</td>
<td>0.17 ± 0.0051</td>
<td>7.38 ± 0.069</td>
</tr>
<tr>
<td></td>
<td>Smoldering</td>
<td>hardwood/loblolly pine (N=4)</td>
<td>0.0075 ± 0.0026</td>
<td>3.25 ± 0.35</td>
<td>0.12 ± 0.033</td>
<td>7.95 ± 0.22</td>
</tr>
</tbody>
</table>

Fuel: hardwood/loblolly pine
Burn type: Lab burn (OBTF)

Burn 1:
Date: 04/16/2016
Temp: 12 °C
RH: 49%

Burn 2:
Date: 07/14/2016
Temp: 29 °C
RH: 70%
Biomass burning

Similar fuel species burned in different seasons

Ambient temperature might also have an impact on BrC absorption of biomass burning.

Xie et al., submitted
Biomass burning

Molecular Composition of BrC

4-Nitrophenol (C₆H₅NO₃)

4-Nitrocatechol (C₆H₅NO₄)

Methyl-nitrocatechol (C₇H₇NO₄)

Biomass burning impacted atmosphere:
Cloud water, (Desyaterik et al., 2013, JGR)
Ambient aerosol, (Claeys et al., 2012; Zhang et al., 2013, EST; Teich et al., 2017, EST)
Biomass burning

Molecular composition of Nitroaromatics

Mass contribution to OA: 0.037 – 0.21%

Xie et al., submitted
Biomass burning

Contribution to bulk $\text{Abs}_{365}$

Abs$_{365}$ contribution: 0.12 – 2.44%

Mass contribution to OA: 0.037 – 0.21%

Nitroaromatics are strong BrC chromophores.
Chamber reactions

**Biogenic VOCs:** α-pinene, isoprene and β-caryophyllene;

**Aromatic VOCs:** 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, m-xylene, toluene, ethylbenzene, benzene, naphthalene and m-cresol;

**Aerosol Seed:** Neutral ammonium sulfate;

**Oxidant:** NO\textsubscript{x}; \cdot OH (H2O2)
Chamber reactions

Light absorption spectra

1. Photo-oxidation of biogenic VOCs may not generate light-absorbing SOA on neutral seed [(NH₄)₂SO₄];

2. The aromatic SOA contains BrC, for which the light-absorption is sensitive to differences in molecular structures of SOA precursors and the availability of NOₓ;

3. Reveals the potential significance of aromatic VOCs as important precursors for secondary BrC;

4. Secondary BrC should have more impacts on aerosol absorption in urban atmosphere with abundant aromatic VOCs and NOₓ.

Xie et al., 2017, EST
Chamber reactions

Molecular Composition of Nitroaromatics

1. Nitroaromatics were mostly identified in reactions with NO\textsubscript{X}, except Naphthalene/H\textsubscript{2}O\textsubscript{2} reactions.

2. The \textit{m}-cresol/NO\textsubscript{X} SOA has the highest average mass contribution from total NACs (10.4 ± 6.74%), followed by naphthalene/NO\textsubscript{X} (6.41 ± 2.08%) and benzene/NO\textsubscript{X} (5.81 ± 3.82%) SOA.

3. Formula with high mass contributions, \textit{m}-cresol/NO\textsubscript{X} SOA: C\textsubscript{7}H\textsubscript{7}NO\textsubscript{3} and C\textsubscript{7}H\textsubscript{7}NO\textsubscript{5}; naphthalene/NO\textsubscript{X}: C\textsubscript{10}H\textsubscript{7}NO\textsubscript{3} and C\textsubscript{10}H\textsubscript{7}NO\textsubscript{4}; benzene/NO\textsubscript{X}: C\textsubscript{6}H\textsubscript{5}NO\textsubscript{4} and C\textsubscript{6}H\textsubscript{5}NO\textsubscript{5}. 
Chamber reactions

Contribution to bulk Abs\textsubscript{365}

1. m-Cresol/NO\textsubscript{X}: 50.4%
2. Naphthalene/NO\textsubscript{X}: 20.3%
3. Naphthalene/H\textsubscript{2}O\textsubscript{2}: 9.58%
4. Benzene/NO\textsubscript{X}: 27.9%
5. Ethylbenezene/NO\textsubscript{X}: 7.69%
6. Toluene/NO\textsubscript{X}: 11.5%

Mass contribution: up to 10%
Chamber reactions

Uncertainties

1. Surrogates

2. Chamber reactions vs. Atmospheric photo-chemical reactions

3. For source apportionment, the impact from atmospheric processing (G/P partitioning, photo-bleaching) and other sources should be evaluated.
Future work

1. Identification of BrC chromophores in both emission and ambient aerosols;

2. HMW and highly conjugated compounds

3. ................................
Thanks!