Estimating Brown Carbon concentrations by Multi-wavelength Thermal-Optical Analysis

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Methods to Calculate Aerosol Radiation Absorption

\[ ATN_\lambda = \ln \left( \frac{FT_{\lambda,f}}{FT_{\lambda,i}} \right) \]  
\[ (1) \]

\[ b_{ATN}(\lambda) = ATN_\lambda \times \left( \frac{A}{V} \right) \]  
\[ (2) \]

\[ \frac{b_{ATN}(\lambda_1)}{b_{ATN}(\lambda_2)} = \left( \frac{\lambda_1}{\lambda_2} \right)^{-AAE} \]  
\[ (3) \]

\[ ATN_\lambda = q_{BC} \times \lambda^{-AAE_{BC}} + q_{BrC} \times \lambda^{-AAE_{BrC}} \]  
\[ (4) \]

Where:

- \( ATN \) is the radiation attenuation
- \( FT_{\lambda,i} \) and \( FT_{\lambda,f} \) represent the filter transmittance before and after thermal carbon analysis, respectively
- \( b_{ATN} \) is the attenuation coefficient
- \( A \) is the filter deposit area (3.53 cm\(^2\))
- \( V \) is the 25 mm IMPROVE sample volume (33.12 m\(^2\))
- \( AAE \) is the absorption Angström exponent
- \( q_{BC} \) and \( q_{BrC} \) represent the fitting coefficients
Enhanced light attenuation by BrC is found at shorter wavelengths
(average attenuation due to BrC_{405} is 6.7% for CSN and 21.9% for IMPROVE in 2016)

The wavelength ratios at 405 and 635 nm are used to derive the power-law fit of \( b_{ATN} \)

\[
y = 9.5 \times 10^8 \lambda^{-3.71}
\]

\[
y = 2.2 \times 10^{11} \lambda^{-4.81}
\]
Attenuation coefficient ($b_{\text{ATN}}$) is not easily related to BrC mass

- **Challenge:**
  -- BrC is not a single compound and $MAC_{BrC(\lambda)}$ varies with compound

- **Solution:**
  -- Measure MAC for several BrC surrogate compounds, and express BrC as surrogate-equivalent mass concentrations ($BrC_e$)

\[ *BrC(\lambda) = b_{\text{ATN}} / MAC_{BrC(\lambda)}; \quad b_{\text{ATN}}(\lambda) = ATN_{\lambda} \times \left( \frac{A}{V} \right); \quad ATN_{\lambda} = \ln \left( \frac{FT_{\lambda,f}}{FT_{\lambda,i}} \right) \]
Properties that should be considered to select BrC standards

- Atmospheric aerosol relevant
- Light absorbing OC
- Low volatility and chemically stable
- Low toxicity
- Easy to nebulize (for laboratory testing)
- Commercially available with reasonable cost
Approximately 20 BrC compounds were considered

<table>
<thead>
<tr>
<th>BrC Compound</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Humic-Like Substances (HULIS)</strong></td>
<td></td>
</tr>
<tr>
<td>Fulvic Acid</td>
<td>C_{14}H_{12}O_{8}</td>
</tr>
<tr>
<td>Humic Acid (Suwannee River, GA)</td>
<td>C_{187}H_{186}O_{89}N_{9}S_{1}</td>
</tr>
<tr>
<td>Humic Acid Sodium Salt</td>
<td>C_{9}H_{8}Na_{2}O_{4}</td>
</tr>
<tr>
<td><strong>Nitro-aromatics - Aged Smoke (SOA)</strong></td>
<td></td>
</tr>
<tr>
<td>2-nitrophenol</td>
<td>C_{6}H_{4}NO_{3}</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>C_{6}H_{4}NO_{3}</td>
</tr>
<tr>
<td>2,4-dinitrophenol</td>
<td>C_{6}H_{4}N_{2}O_{5}</td>
</tr>
<tr>
<td>3-methyl-4-nitrophenol</td>
<td>C_{7}H_{7}NO_{3}</td>
</tr>
<tr>
<td>4-nitrocatechol</td>
<td>C_{6}H_{5}NO_{4}</td>
</tr>
<tr>
<td>3-methyl-5-nitrocatechol</td>
<td>C_{7}H_{7}NO_{4}</td>
</tr>
<tr>
<td>3-methyl-6-nitrocatechol</td>
<td>C_{7}H_{7}NO_{4}</td>
</tr>
<tr>
<td>4-methyl-5-nitrocatechol</td>
<td>C_{7}H_{7}NO_{4}</td>
</tr>
<tr>
<td><strong>PAHs - Fresh Smoke</strong></td>
<td></td>
</tr>
<tr>
<td>Fluoranthene (C16)</td>
<td>C_{16}H_{10}</td>
</tr>
<tr>
<td>Pyrene (C16)</td>
<td>C_{16}H_{10}</td>
</tr>
<tr>
<td>Chrysene (C18)</td>
<td>C_{18}H_{12}</td>
</tr>
<tr>
<td>Retene (C18)</td>
<td>C_{18}H_{18}</td>
</tr>
<tr>
<td>Perylene (C20)</td>
<td>C_{20}H_{12}</td>
</tr>
<tr>
<td>Bbenzo[a]pyrene (C20)</td>
<td>C_{20}H_{12}</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene (C22)</td>
<td>C_{22}H_{12}</td>
</tr>
<tr>
<td>Anthanthrene (C22)</td>
<td>C_{22}H_{12}</td>
</tr>
<tr>
<td>Coronene (C24)</td>
<td>C_{24}H_{12}</td>
</tr>
</tbody>
</table>
BrC solutions are nebulized and sampled onto filter substrates (loadings of 1 to 1024 µm/filter)

Sampling flow rates and time are adjusted to collect different loadings (i.e., 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, and 1024 µg/filter)
BrC standards exhibit different “brownness”

Filter samples with increasing loading

BrC in Solution

Fulvic Acid

Humic Acid (Suwanee River, GA)

Humic Acid Sodium Salt

3-Methyl 4-Nitrophenol

3-Methyl 5-Nitrocatechol

Pyrene
### Large variations found for MACs and AAEs in tested brown carbon surrogates

<table>
<thead>
<tr>
<th>Brown Carbon Compound (formula)</th>
<th>Molecular Structure</th>
<th>405 nm MAC (m²/g)</th>
<th>AAE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Humic-like Substance (HULIS)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fulvic acid</strong> ((C_{14}H_{12}O_8))</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>4.5</td>
<td>5.4</td>
</tr>
<tr>
<td><strong>Humic acid (Suwannee River, GA)</strong> ((C_{187}H_{186}O_{89}N_9S_1))</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>3.9</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Humic acid sodium salt (HASS)</strong> ((C_9H_8Na_2O_4))</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>15.4</td>
<td>4.3</td>
</tr>
<tr>
<td><strong>Nitro-aeromatics- Aged Smoke (SOA)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3-methyl-4-nitrophenol</strong> ((C_7H_7NO_3))</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>2.2</td>
<td>9.7</td>
</tr>
<tr>
<td><strong>3-methyl-5-nitrocatechol</strong> PAHs- Fresh Smoke ((C_7H_7NO_4))</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>15.1</td>
<td>8.4</td>
</tr>
<tr>
<td><strong>PAHs- Fresh Smoke</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pyrene</strong> ((C_{16}H_{10}))</td>
<td><img src="image" alt="Molecular Structure" /></td>
<td>0.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*MAC: Mass absorption coefficient; AAE: Absorption Ångström Exponent; \(b_{\text{ATN}(405)}/b_{\text{ATN}(635)} = \left(\frac{405}{635}\right)^{-\text{AAE}}\)
MAC$_{405}$ of fulvic acid (4.5 m$^2$/g) are wavelength dependent (AAE = ~5.4)
Humic acid sodium salt (HASS) yield larger MAC\textsubscript{405} (15.4 m\textsuperscript{2}/g) and lower AAE (~4.3) than fulvic acid.

Used as standard to calibrate Integrated Plate Method by the Europeans
BrC_e concentrations were estimated, assuming fulvic acid or humic acid sodium salt (2016 and 2017 IMPROVE and CSN data sets)

IMPROVE 2017 OC higher than 2016 for every month, especially in summer

Average BrC concentrations about the same between 2016 and 2017
BrC_e accounts for ~5-30% of monthly average OC depending on the assumption on MAC_{405} (156 sites)

Attributing BrC_e light absorption to fulvic acid (MAC_{405}=4.5 m^2/g), BrC_e averages 20-30% of OC.

Attributing BrC_e light absorption to humic acid sodium salt (MAC_{405}=15.4 m^2/g), BrC averages 5-10% of OC.
BrC\textsubscript{e} concentrations may be lower or higher than EC depending on BrC composition

Depending upon composition of BrC, BrC concentrations are comparable in magnitude to EC concentrations.

With BrC\textsubscript{e} assumed to be fulvic acid, BrC\textsubscript{e} on average is greater than EC; if humic acid sodium salt is assumed, BrC\textsubscript{e} about half EC on average.
No specific spatial distributions were found for the 10 highest BrC\textsubscript{e} sites

(Assumes BrC\textsubscript{e} is fulvic acid for 2016 IMPROVE data)

STIL=Stillwater, OK
LIGO= Linville Gorge, NC
GRSM= Great Smoky Mtns, NC
CABA=Casco Bay, ME
PENO= Penobscot, ME
HEGL=Hercules Glade, MO
VILA= Viking Lake, IO
Egbert, Ontario
Mingo, MO
James River, VA

Low BrC concentrations tend to be western sites
TRCR= Trapper Creek-Denali, AK
GUMO= Guadalupe Mountains, TX
SAGU=Saguaro, AZ
DENA= Denali, AK
WHRI=White River, CO
SYCA= Sycamore Canyon, AZ
ORPI=Organ Pipe, AZ
SIME=Simeonof, AK
HACR=Haleakala Crater, HI
VIIS= Virgin Islands
BrCₐ accounts for ~50-100% of OC at the 10 highest sites
(Assumes BrCₐ is fulvic acid for the 2016 IMPROVE data)

HAVO= Hawaii Volcanoes, HI
FCPC=Forest County Potawatami, WI
KALM= Kalmiopsis, OR
VILA=Viking Lake, IA
KPBO=Kenai Peninsula Burough, AK
CABA=Casco Bay, ME
PENO=Penobscot, ME
EGBE=Egbert, Ontario
GRBA=Great Basin, NV
PACK=Pack Monadnock Summit, NH

Urban Areas tend to have low BrC/OC ratios
PUSO= Puget Sound, WA
SAGA=San Gabriel, CA
BYIS=South Korea
SIME=Simeonof, AK
ATLA= Atlanta, GA
BIRM= Birmingham, AL
SYCA=Sycamore Canyon, AZ
PHOE=Phoenix, AZ
NOGA=Nogales, AZ
VIIS= Virgin Islands
Monthly average $\text{BrC}_e$ ranged ~0.2 to 0.5 $\mu$g/m$^3$ for IMPROVE and 0.06 to 0.5 $\mu$g/m$^3$ for CSN.

(Assumes $\text{BrC}_e$ is fulvic acid for 2016 dates)

Not surprisingly, CSN has significantly higher OC than IMPROVE.

But- IMPROVE has on average higher BrC than CSN (less in winter, more in summer)
BrC\(_e\) concentration exceeding 7 µg/m\(^3\) was found during the 2016 Everglade fire (Florida, USA)

BrC and OC track well during Everglade area fires in spring 2016 (Assumes BrC\(_e\) is fulvic acid)
Equivalent BrC varied in source samples

**Fulvic Acid Equivalent BrC**

- Diesel
- Peat
- Tahoe Wood
- Rim Fire
- Smoldering Pine Cone
- Flaming Pine Needle

**Humic Acid Sodium Salt Equivalent BrC**

- Diesel
- Peat
- Tahoe Wood
- Rim Fire
- Smoldering Pine Cone
- Flaming Pine Needle

Peat combustion
Summary/Conclusions

• Selected BrC compounds can be used to estimate wavelength dependent Mass Absorption Coefficients (MACs) based on filter transmission

• MACs and attenuation coefficients can be used to estimate BrC mass concentration for ambient IMPROVE and CSN samples

• Calculated BrC<sub>e</sub> mass highly dependent upon MAC used, which can vary greatly from compound to compound

• Fulvic acid and humic acid sodium salt produced repeatable results

• Total light absorption from BrC is a more defensible estimate than the estimated BrC equivalent mass concentration