How well can we generate, characterized, and predict black carbon soot particle optical properties?

LINDSAY RENBAUM-WOLFF, James Brogan, Yatish Parmar, Andrew Lee, Paul Davidovits - BC
Timothy Onasch, Greg Magoon, Andrew Freedman, Rick Miake-Lye, Andrew Lambe, Leah Williams - ARI
Taylor Helgestad, Christopher Cappa – UC Davis
Al Fischer, Geoff Smith – University of Georgia
Noopur Sharma, Janarjan Bhandari, Swarup China, Claudio Mazzoleni – Mich Tech Univ
Arthur J. Sedlacek, Ernie Lewis – Brookhaven National Laboratory
Eleanor Browne, Gabriel Isaacman-VanWertz, Jesse Kroll - MIT

AERODYNE RESEARCH, Inc.
Atmospheric Black Carbon

- Product of incomplete combustion
- Emissions as high as 8 TgC/yr
  - ~60% fossil fuel and biofuel consumption
  - ~40% open biomass burning
- Non-spherical shape that depends on chemical processing
- Absorbs light strongly; depends upon coating material
- IPCC Fifth Assessment Report direct RF for fossil fuel
  \[ \text{BC} = +0.40 \, \text{W m}^{-2} \pm 0.05 \text{ to } 0.80 \, \text{W m}^{-2} \]
Particle mixing state

• In urban and rural environments, BC is found internally mixed to varying extents with organics (POA and SOA) and inorganics (SO$_4$ and NO$_3$).

Alex Lee et al., 2015 - U. Toronto

Radiative impact of internal mixing

Cappa et al., 2012

Liu et al., 2015

California urban summer
- Mainly urban (traffic, etc.) sources with little/no biofuels
- Measurements lower than shell-core Mie theory

UK suburban winter
- Mixed sources including solid fuel burning
- Measurements match shell-core Mie theory
BC4 experimental details

Diffusion flame

SOA coatings

Mobility size & mass selected

Optical properties measured across UV-Vis range!
Flame generated nascent soot
Methane diffusion flame – ‘mature’ soot

- Mobility selected 300 nm (DMA)
- Mass selected 3.3 fg/particle (CPMA)

- Fractal particles composed of ~30 nm spherules
- Variety of geometries, including more linear and compact

Janarjan Bhandari, Swarup China, Claudio Mazzoleni – Michigan Technical University
Mass Corrections Using SP2
Effects of $Q^+$ and $Q^{++}$

- **250 nm, 2.4 fg**
  - Two Mass Peaks
  - $Q1 = 2.1$ fg
  - $Q2 = 5.4$ fg
  - $<m> = 2.80$ fg

- **500 nm, 8.3 fg**
  - Single Valued
  - $Q1 = $ Measured Mass

**Acknowledge DOE ARM SP2**

*Arthur Sedlacek– Brookhaven National Laboratory*
MAC
Mass Absorption Coefficient (Absorption Cross Section Per Unit Mass)
Used With Soot Emission Inventories in GCMs to Calculate Radiative Forcing

\( \lambda = 630 \text{ nm} \)

- \( \text{MAC} = 6.40 \pm 0.22 \text{ m}^2 \text{ g}^{-1} \) (2\(\sigma\) precision)
- Total Uncertainty = ±10%
  (Accuracy + Precision)
- Literature
  6.5±1.0 m² g⁻¹ (Bond and Bergstrom, 2006)
  6.5±1.0 m² g⁻¹ (Petzold and Schönlinner, 2004)
Predictive optical theories

Mie theory
- assuming mass-equivalent sphere
- material density = 1.8 g cm\(^{-3}\)
- RI (1.95, -0.79) (Bond and Bergstrom, 2006)

T-Matrix theory
- assuming constant size primary spherules, no overlap of spherules, and no necking
- exact results for a given geometry
- simulated representative aggregate geometries created with cluster-cluster (CC) and diffusion limited aggregation (DLA) methods

Mie theory does not match measurements well for both absorption and scattering!
Derived complex RI’s

High Dimension Model Representation

- HDMR meta-model of T-matrix results
- One-, two-, and three-sigma confidence regions for refractive index based on the HDMR meta-model and MAC and SSA measurements

<table>
<thead>
<tr>
<th>HDMR input parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>fractal prefactor, $k_0$</td>
<td>0.68 - 1.50</td>
</tr>
<tr>
<td>fractal dimension, $D_f$</td>
<td>1.60 - 2.01</td>
</tr>
<tr>
<td>real refractive index, $n$</td>
<td>1.56 – 2.34</td>
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<tr>
<td>imaginary refractive index, $k$</td>
<td>0.632 – 1.264</td>
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<tr>
<td>primary spherule radius, $a$</td>
<td>10 - 20 nm</td>
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<tr>
<td>density, $\rho$</td>
<td>1.6 - 1.9 g/cm³</td>
</tr>
<tr>
<td>mass, $m$</td>
<td>0.11 - 16 fg</td>
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</tbody>
</table>

Bond and Bergstrom, 2006
Ångström Coefficient Determination

- AAE = 1.25 ± 0.24
- Uncertainties reflect accuracies of absorption measurements
- Uncertainties in Number Density and Mass cause points to shift up and down in concert
- Fits are Weighted by Error Bars
  Essentially Pinned to CAPS Value at 630 nm
Impacts of coatings on optical properties

- ABS increases by ~1.8 and plateaus
- EXT (really SCAT) increases more rapidly than ABS and does not plateau

\( \lambda = 630 \text{ nm} \)
Predictive core-shell Mie Theory

Core-shell Mie theory
- over predicts EXT at small mass ratios ( < 0.7 )
- over predicts ABS at small to medium mass ratios ( < 5 )
- Adequately predicts EXT and ABS high mass ratios ( > 5 )
Small mass ratios induce morphological changes which affect SCAT and ABS differently.
Conclusions

• Mie theory cannot predict both the scattering and absorption of nascent or uncoated soot particles
• Core-shell Mie theory over predicts the scattering and absorption for thinly coated soot particles, but appears to works well for thicker coatings
• Small amounts of SOA and H$_2$SO$_4$ mass condensation on fractal-like soot particles
  – Collapse the core soot structures for thin coatings, affecting the scattering more than absorption
  – Fill in interstitial regions initially, minimizing increases in cross-sections, leading to lower initial absorption enhancements
• More appropriate models, such as T-matrix or DDA, may be required for ‘freshly’ emitted and thinly coated soot particles in atmospheric models
  – HDMR may help incorporate these complex calculations into process, regional, and global models
# Acknowledgements

**DOE ASR funding – DOE ARM SP2**

## BC4 study

<table>
<thead>
<tr>
<th>Participating Institution</th>
<th>Instrumentation</th>
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<tbody>
<tr>
<td>Boston College</td>
<td>PAM, SMPS, O3 monitor, CPCs, AMS</td>
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<tr>
<td>Aerodyne Research</td>
<td>MCPC, SP-AMS, CPMA</td>
</tr>
<tr>
<td>Massachusetts Institute Of Technology</td>
<td>CAPS-SSA (630), CPMA</td>
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<tr>
<td>University of California Davis</td>
<td>CRD, PAS (405, 532nm)</td>
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<tr>
<td>University of GA</td>
<td>Broadband PAS (8 λ’s)</td>
</tr>
<tr>
<td>Michigan Technological University</td>
<td>SEM/TEM analysis</td>
</tr>
<tr>
<td>Brookhaven National Labs</td>
<td>SP2 soot photometer</td>
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