Black Carbon, Air Quality and Climate

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Sources of BC
Objectives

- Improve our understanding of the optical properties of BC-containing particles and their evolution during their lifetime
- Link emissions of BC particles with particle number concentrations over the US
- Improve the ability of the existing regional models to simulate the BC mass and number concentrations
- Quantify effects of changes in BC emissions in PM and PN over the US
1. Laboratory Studies
   - Primary emissions characterization
   - Aging of primary emissions

2. Emission inventory development
   - Source-resolved inventories
   - Inventories for number

3. Model extension
   - Particle number source attribution
   - Mixing state and optical properties

4. Black carbon number concentrations

5. Regional scale simulations - Scenarios and controls
BC Emissions, Chemical Aging, and Optical Properties
Combustion Emissions

BC particles act as condensation sites for OA

Organic Compounds + \( \cdot \text{OH} \rightarrow \) Black Carbon

Core –Shell morphology

• Brown Carbon?
• How does the condensation and chemical aging of OA affect the absorption of BC?
BrC in Biomass Burning: Chaos

Kirchstetter et al. (2004)
Chen and Bond (2010)
Saleh et al. (2013)

$k_{OA}$ vs. wavelength (nm)
BrC in Biomass Burning: More Chaos

Alexander et al. (2008)
OA and BC Formation and Aging (FLAME III and IV)

OA/BC from biomass burning

Aethalometer

SP2

PASS-3

HR-SP-AMS
Estimation of OA Optical Properties

\[ b_{\text{abs}} = f(\text{size distributions, refractive index [BC], refractive index [OA]}) \]

Bond et al. [2005]

\[ k_{OA}(\lambda) = k_{OA,550} \left( \frac{550}{\lambda} \right)^w \]

Aethalometer, PASS-3

absorption

wavelength

SMPS, SP2
Morphology and Mixing State

![Graph showing distribution of aerosol particles in terms of mass concentration and size distribution. The graph plots the number of particles per logarithmic size increment against size (nm). The curve labeled 'total' shows the overall distribution, while the curve labeled 'BC' indicates the black carbon fraction of the total distribution.]
We simulate the condensation process of OA on BC. The growing distribution cannot go beyond the SMPS distribution. We can only constrain the maximum coating thickness. This maximizes the lensing effect, thus minimizes BrC absorption. Conservative approach.
The Fit
The Fit (Absorption due to BC only-Mie calculations)
The Fit (Absorption due to BC+ Lensing)
The best fit, from which we obtain the absorptivity of OA.
Chaos Returns!

- A lot of variability across fuels, and even within the same fuel.
- Similar to previous work.
Some Order
Some Order
BrC and OA Volatility

$\kappa_{OA,all}$

$\kappa_{ELVOCs}$

~ 10% of OA
BrC and OA Volatility

Alexander et al. (2008)
CMU Smog Chamber

Ozone generator
2 ppm

Diluters

Smog Chamber 12 m³

Also:
SP2
PTR-MS

Ozone, CO, CO₂, NOₓ
gas monitors

O₂ tank

Heated Air

Air

O₂ tank

Air

Boiling water
RH=90%

HONO, H₂O₂, TME

• Pine wood
• White birch bark

Air

Air

Air

Heated Air

Diluters

RH=90%

2 PAX (blue, green)

SP-AMS

SMPS

Aethalometer
(7 wavelengths)
Coating of BC with D-toluene SOA
(fuel: White birch bark)

HONO HONO HONO

Aerosol mass (μg m⁻³)

D-toluene

CEBC = 0.4
CEorg = 1
O/C during D-toluene SOA formation
(fuel: White birch bark)
Absorption during D-toluene SOA formation
(fuel: White birch bark)

Absorption enhancement

\( \lambda = 532 \text{ nm} \)

O:C  O:C  O:C

D-toluene
Absorption Angstrom exponent during D-toluene SOA formation (fuel: White birch bark)
Aging of Monodisperse Cookstove Soot

R. Subramanian

• Absorption enhancement of mono-disperse aged BC particles.
• Three nascent BC core diameters (100, 130, 150 nm mass equivalent diameters).
• Soot was coated with α-pinene SOA in stages till a shell/core diameter ratio of ~2.5
• SP2 for BC mass; SP-AMS for organic aerosol mass; PAXs for light absorption/scattering.
Black Carbon Emissions
Organic/Elemental Carbon Emissions

OC emissions decrease with newer vehicles.

EC much less sensitive to more stringent standards.

Pre-LEV made before 1994
LEV-1 1994-2003
LEV-2 2004 and later
EC Emissions

May et al. (Atmos. Environ, 2014)
BC and Aerosol Number Concentrations
Source-Resolved Total Number Emissions (particles d^{-1} km^{-2})

- Gasoline
- Industrial
- Non-road Diesel
- On-road Diesel
- Biomass
- Dust
PMCAMx-UF base number concentration (particles cm\(^{-3}\))

[Images of map with different size ranges]
PMCAMx-UF Evaluation (Pittsburgh)
Size-resolved Aerosol Number Source Apportionment algorithm (SANSA)
Total primary particle number fractional source contributions
Primary particle number source apportionment in Pittsburgh
Sources of Measureable (>3 nm) Particle Number in Pittsburgh

PMCAMEx
- Nucleation: 38%
- Traffic: 37%
- Other: 23%
- Power Plant: 2%

Calculated from Measurements
- Nucleation: 28%
- Traffic: 42%
- Stationary Combustion: 21%
- Secondary Aerosol: 9%

Predicted: 29,000 cm⁻³
“Measured”: 26,000 cm⁻³

Zhou et al., 2005
Effects of Controls of Diesel Particulate Emissions (-50% Scenario)
Fractional Change of EC

Average PM$_{2.5}$ reduction around 3%.
Fractional Changes of $N_{0.8-3}$

Nucleation increases, creating more smaller particles due to the decrease in the condensation sink.
Fractional Changes of $N_{3-10}$

These increases also suggest that nucleation may increase and nucleated particles grow into this size range.
Fractional Changes of $N_{10-50}$

Particles in this size range are typically emitted or grown from nucleated particles, so they see increases (from nucleation) and decreases elsewhere.
Fractional changes of $N_{50-100}$
Fractional changes of $N_{100}$
Non-linear Response of CCN to Diesel PM Controls

50-100% higher reduction in N50 and N100 than the linear response
Improving Regional Scale BC Models
Relaxing the Internal Mixture Assumption

Size

Internal Mixture

External Mixture

“Type”
Simulating BC Mixing State In PMCAMx
Conclusions

- Brown carbon in emissions from biomass burning is associated mostly with organic compounds of extremely low volatility
  - Effect can be parameterized as a function of BC/OA
  - Quite sensitive to burn conditions
- This effect was not observed in diesel emissions
- Condensation and chemical aging of biogenic and anthropogenic SOA on BC was reproduced within experimental error by core-shell Mie models.
  - No effect of O:C during aging of SOA
- Estimated radiative forcing of 0.1-0.2 W m\(^{-2}\) due to biomass burning BrC.
  - Net effect of biomass burning is still cooling.
Conclusions

• New particle number source apportionment algorithm (SANSA) for TOMAS (used in PMCAMx, GISS-II’ and GEOS-CHEM)

• Diesel sources responsible for approximately 25% of particle number emissions in the Eastern US during summer
  – 30% of emissions of $N_{100}$

• Reduction of these emissions leads to increases of nucleation rates
  – Increases of very small particles predicted
  – The N50 and N100 concentrations decrease more than expected
  – This reduction in CCN could result in warming

• Development of a computationally efficient multi-distribution model to better simulate the mixing state of BC in regional models
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