Light Absorption By Organic Carbon
From Wood Combustion

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Carbonaceous aerosols are a large fraction of both urban and global aerosol

- Affect global radiative balance by scattering and absorbing light
- Impacts on agriculture due to reduced sunlight
- Effect on reflectivity of clouds

Source: http://www.pmel.noaa.gov/
Carbonaceous aerosol is composed of black carbon (BC) and organic carbon (OC).

BC is the most absorbing aerosol, \textit{BUT}……

OC has complex composition, and is estimated to be ten times more abundant than BC (10-70\% of total fine aerosol mass)

OC may also have significant absorption, which is greater at near-ultraviolet and blue wavelength (around 400nm)

This absorption would affect radiative transfer.

Evidence for absorbing OC

- Summarized by \textit{Andrae and Gelencser (2006), Sun et al (2007), and Bergstrom et al. (2007)}
- Measured by \textit{Bond et al. (2001), Kirchstetter et al. (2004), Roden et al. (2006)}
WHY CHOOSE AEROSOL FROM BIOMASS BURNING

Biofuels and open vegetative burning contribute a large amount of primary, combustion-related OC (~70%).

- **Biofuels:** wood, crop residue, charcoal used for heating and cooking

- **Open vegetative burning:** forests, fields, and savannas

Source: Bond, Streets et al., JGR 109, D14203, doi:10.1029/2003JD003697, 2004

http://www.flickr.com/photos/elmada/253979357/
Motivation

- Generation type may affect optical properties of OC (fuel composition, fuel size, combustion conditions)

- Field observations:
  - Same fuel $\rightarrow$ different emission quantities & properties
  - Therefore, combustion conditions in addition to fuel composition affect emissions

- Ultimate goal: Parameterize OC emissions in terms of combustion and fuel type
Isolate **controlling variables** of wood combustion, determine key governing factors to parameterize emission models.

Provide **optical properties** of organic carbon emitted from wood combustion for use in radiative transfer models.
Generate samples in a laboratory combustor under different conditions

<table>
<thead>
<tr>
<th>Wood type</th>
<th>Pine, oak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood size</td>
<td>3/4”× 1/4”×3/4” (S), 3/4”×3/4”×3/4” (M), 9/4”×3/4”×3/4” (L)</td>
</tr>
<tr>
<td>Initial burning temperature</td>
<td>200±5 °C, 380±5 °C, 500±5 °C</td>
</tr>
<tr>
<td>Burning condition</td>
<td>Smoldering</td>
</tr>
</tbody>
</table>

OC samples were collected on quartz filters for analysis.

Extraction: polar and non-polar solvents (acetone, methanol, DI water and hexane)

UV-Vis absorption measurement of extract solutions: Shimadzu UV-2401 UV-Vis recording spectrophotometer

Total aerosol carbon: Sunset OC/EC analyzer

Real-time absorption and scattering
SAMPLING SCHEMATIC

Filter collection

Dilution air

probe

impactor

Real-time optical analysis

Vacuum pump

OC/EC

Millipore

Quartz

OC/EC backup

UV-Vis

Nephelometer

PSAP

CO₂ analyzer

OC/EC UV-Vis dilution air probe impactor Millipore Quartz OC/EC backup UV-Vis Nephelometer PSAP CO₂ analyzer
EXTRACTION

Quartz filter

A punch of original sample filter analyzed in OC/EC analyzer

Solvents
(acetone, methanol, hexane or DI water)

Sonicate for 1hr

Maintain at room temperature for 19hrs

Sonicate for 1hr

Residual filter after extraction dried & analyzed in OC/EC analyzer

Extract solution analyzed in UV-vis spectrophotometer
Extracted fraction: **methanol ≈ acetone (~95%)** > water (73%) > hexane (52%)
Average single scattering albedo (green, 530nm): High – 0.95-0.99

Light absorption by water-soluble organic carbon smaller than that of organic carbon soluble in methanol or acetone.

What is absorbing most light? – Large molecular weight PAHs with some (but not many) functional groups containing oxygen.

We consider the absorption by methanol extracts to represent the behavior of total OC
Different method: Sequential extraction

- Methanol (most of carbon)
- Water (water-soluble fraction only)
- Methanol following water (water-insoluble)

Note: total absorbance
Absorption by water-soluble vs water-insoluble

Note: absorption per C mass

Water-insoluble OC is much more absorbing than water-soluble OC!!!
What affects OC light absorption?

- Temperature at start of combustion?
- Wood size?
- Wood type?
INITIAL TEMPERATURE

Higher temperature = higher absorption per mass (polymerization of volatile matter within wood)

Especially for smaller size

Pine, Large size wood

Oak samples have the same trend

Pine, Medium size wood
WOOD SIZE

Starting temperature: 380 °C

Large (L)  Medium (M)  Small (S)

Smallest dimension governs heat transfer in

Along-grain dimension governs residence time at temperature because escaping volatile matter travels along grain
Low T: Longer residence time in the large wood allows polymerization, resulting in greater absorption per mass.

Higher T: Polymerization occurs even without increased residence time.

Oak samples and 500 °C samples have the same trend.
WOOD TYPE (Soft wood vs. hard wood)

Pine emissions have lower absorption than oak at the medium temperature (380°C).

At the higher temperature (500°C) the absorption is identical.

Medium size wood samples have the same trend.
Absorption Ångström Exponent ($\text{Åap}$)

$$\frac{\alpha(\lambda_1)}{\alpha(\lambda_2)} = (\frac{\lambda_1}{\lambda_2})^{-A_{ap}}$$

- Linear regression of $\ln(\alpha/\rho)$ against $\ln(\lambda)$, $R^2$ ranges from 0.989 to 1.000
- Higher Åap values are associated with weakly absorbing particles

Recall: Higher $T$, higher $\alpha/\rho$
Absorption Ångström Exponent (Åap)

Water extracts had much higher Åap
Weaker absorption with stronger wavelength dependence
A large fraction of light absorption is attributable to water-insoluble OC, which has some polar functional groups.

Combustion temperature is the most important factor in determining the light absorption of primary OC.

- Higher temperatures and longer residence time of volatile matter in wood create higher absorption.

Higher Åap values are associated with weakly absorbing particles.
Acknowledgements to:

- Bond’s Group members
- National Science Foundation

Thank you!
Any Questions?
Absorption per mass, $\alpha/\rho$, is the absorption per mass of carbon in bulk liquid.

$$\alpha / \rho = \frac{A}{cL} \cdot \ln(10)$$

Where: $\alpha =$ absorption coefficient, cm$^{-1}$; $\rho =$ density; $A =$ absorbance obtained from UV-vis spectrophotometer, dimensionless; $c =$ concentration of dissolved organic carbon in extract, g/mL; $L =$ light path length, cm

To get absorption for use in models:
- Multiply by $\rho$
- Calculate imaginary refractive index ($k = \alpha \lambda / 4\pi$)
- Use $k$ and same density in Mie model
Sequential extraction

- Methanol
- Water
- Water
- Methanol
Wood Pyrolysis

Complex fuel: cellulose, hemicellulose, and lignin = \((C_5H_7O_3) + \) trace elements

- 100-200 °C
  - Endothermic
  - H2O, simple gases
- 200-280 °C
  - Weakly Endothermic
  - Char production favored
- 280-450 °C
  - Exothermic reaction dominate
  - Production of flammable volatiles
  - Cellulose -> tar
- > 450 °C
  - Only Char remains
  - Converted to CO and CO2

Bryden et al., 2002
Wood combustion process

Evans and Milne, 1986
Carboxylic acid
Aromatic groups