Optical and physical properties of biomass burning emissions

Gavin McMeeking
Department of Atmospheric Science
Colorado State University

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Biomass burning climate effects

Focus of this work
Classifying carbon

Terms describing carbonaceous aerosol are defined from how each is measured and used.

Chemical structure controls light absorption (electrons are highly mobile in EC/BC).

<table>
<thead>
<tr>
<th>Thermochemical classification</th>
<th>Molecular structure</th>
<th>Optical classification</th>
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</thead>
<tbody>
<tr>
<td>Elemental carbon (EC)</td>
<td>Graphene layers</td>
<td>Black carbon (BC)</td>
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<tr>
<td>Refractory organics</td>
<td>Polycyclic aromatics,</td>
<td>Colored organics</td>
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<tr>
<td>Non-refractory organics (OC)</td>
<td>Humic-like substances,</td>
<td>Colorless organics (OC)</td>
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<td></td>
<td>biopolymers</td>
<td></td>
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<td></td>
<td>Low-MW hydrocarbons</td>
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</tbody>
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from Andreae and Gelencser, 2006
Evidence of visible light absorption by organic carbon

**Andreae and Gelencser, 2006 (AG06)**
Brown carbon: Light-absorbing organic matter in atmospheric aerosols of various origins – soil humics, HULIS, tarry materials from combustion, bioaerosols

**Kirchstetter et al, 2004**
Demonstrated an OC contribution to spectral light absorption for several biomass from SAFARI – same technique used in this study

**Hoffer et al., 2005, Havers et al., 1998, Gelencser et al. 2000**
Fine continental aerosol contains organic carbon with properties similar to natural humic/fulvic substances.

**Andreae and Crutzen, 1997**
Biogenic materials and their oxidation and polymerization products can absorb light
Impacts of $C_{\text{brown}}$ (AG06)

**Light absorption measurements**
Organic carbon is considered non-absorbing by most models and thermal-optical measurement techniques.

**Tropospheric photochemistry**
Downward UV irradiance can be underestimated if the light absorbing carbon has a stronger wavelength dependency than that typically assumed for light absorbing carbon.

**Cloud chemistry and cloud light absorption**
If a significant fraction of $C_{\text{brown}}$ is soluble in water it can alter cloud droplet light absorption, particularly in the UV. Could be an important process in clouds formed on/near smoke plumes.
FLAME CHAMBER
BURNS SETUP

May/June 2006 and May/June 2007

cloud micro-physics

nephelometers

size distributions

f(RH)

HTDMA extinction cell

photoacoustic (absorption)

Aerosol mass spectrometers

IMPROVE sampler

High volume sampler

~ 40 ft
Lawrence Berkeley National Lab
September/October 2006

Worked with DOE scientists Melissa Lunden and Tom Kirchstetter
Visible light attenuation measurements

Light box

Ten LED light source

Spectrometer
(Ocean Optics S2000)

400 – 1100 nm range with sub nanometer resolution
Attenuation spectral dependence (Bohren and Huffman, small particles):

\[ ATN = 100 \ln \left( \frac{1}{T} \right) \]

\[ T = \frac{I_s}{I_{s,o}} \frac{I_{r,o}}{I_r} \]

\[ ATN = K \lambda^{-\beta} \]

- \( ATN \): Attenuation
- \( T \): Transmission
- \( I_s \): Sample intensity
- \( I_{s,o} \): Sample filter intensity
- \( I_r \): Reference filter intensities
- \( I_{r,o} \): Reference intensities
- \( K \): Constant
- \( \lambda \): Wavelength
- \( \beta \): Attenuation exponent assumed = 1 for EC
Base case measurement of filter attenuation as a function of wavelength

Measured for all burns A-S on at least one 1.14 cm² punch from “B” HiVol quartz filter sample (PM$_{2.5}$)
Attenuation exponent ranged from 0.8 (chamise, lignin) to ~ 3.5 (Alaskan duff, rice straw)
smoldering-dominated

flaming-dominated

Attenuation exponent

0  1  2  3  4

alaskan duff

asian rice straw
ponderosa duff
ceanothus
puerto rican fern
puerto rican woods
lodgepole pine
wax myrtle
southern pine
ponderosa pine
palmetto
chamise 3
manzanita
lignin
chamise 1
Selected filter samples were extracted with hexane, acetone and water to determine role of organic carbon and water soluble carbon on filter attenuation.

Each organic solvent extraction was performed for ~ one hour and water extraction for 12 hours.
Puerto Rican mixed woods

No treatment

Acetone extraction
Lodgepole pine

Water extraction results in no change

Acetone extraction reduces attenuation coefficient

Attenuation (normalized)

Wavelength [nm]
**Alaskan duff**

- Hexane extraction results in increase (normalized only)
- Water extraction results in largest reduction

\[ \sigma = -1 \]
Total carbon measurements: Evolved Gas Analysis (EGA)
Total carbon measurements: Evolved Gas Analysis (EGA)
chamise
- flaming combustion
- Low OC/EC ratio

attenuation at 544 nm
longleaf pine
- mixed combustion

slight increase due to oven heat

pyrolized carbon ATN
Alaskan duff
- Smoldering combustion
- High OC/EC ratio
EGA spectrometer measurements

Puerto Rican fern - mixed combustion

Large change in ATN (EC evolving here)

‘charring’

No attenuation

oven signal
H-NMR

Performed on water-soluble material extracted from samples

Identifies functional groups

Thanks to J Hutchings and P Herckes at Arizona State
Key Results

Attenuation

Combustion phase appears to drive optical properties
There was little difference between fuels unless combustion phase changed as well. Must be accounted for in emissions inventories used by models.

Acetone/water soluble material in samples is responsible for strong attenuation wavelength-dependence
This material is classified as organic carbon by other thermal-optical methods and assumed to be non-light absorbing.
Key Results

Evolved Gas Analysis

Attenuation measurements across visible range improve optical OC/EC carbon classification
Should improve reliability of these widely used measurement methods for an important aerosol constituent, particularly for samples impacted by biomass burning
What’s next?

**Attenuation**
Additional measurements of ATN for different polarity solvent treatments
Compare smoldering and flaming phases of combustion for the same fuel (FLAME2)
Compare FLAME results to other studies (fresh vs. aged smoke)

**Evolved gas analysis**
Plan to develop a new analytical technique for quantifying pyrolized carbon in thermal-optical analysis

**Other**
Scanning Transmission X-ray Microscopy at LBNL -> single particle measurements of molecular structure
Biogenic secondary organic aerosol
Acknowledgements

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  LBNL staff
  John McLaughlin and Jeff Aguiar
Joint Fire Science Program
  National Park Service
USFS – Missoula Fire Science Laboratory
Shameless plug and questions

Come see us at AAAR in Reno
visit http://chem.atmos.colostate.edu/FLAME
for more information and talk/poster session numbers
**Burn L - Lodgepole pine**

- All solvents remove this first peak.
- Acetone removes this peak more effectively, depending on technique.
- "EC" evolves later after water soak.
- Residual acetone?

**Graph Details:**
- **$CO_2$ [ppm]** (thick lines) vs. **Temperature [°C]**
- Thin lines represent different solvent samples:
  - 20060922_burnL_1a
  - 20060926_burnL_ace_3a
  - 20060927_burnL_hex_4a
  - 20060927_burnL_w_5A
  - 20060927_burnL_acev_6a
EGA spectrometer measurements

Alaskan duff
- smoldering combustion
- very little EC

No large ATN change as seen in PR fern

‘charring’

oven signal

No attenuation
Front half vs back half ATN

Punches from selected burn samples were sliced into front and back halves and analyzed in an attempt to characterize gasses adsorbed onto the filter.
EGA measurement details

Sample heated in pure oxygen atmosphere
Only temperature and light transmission can be used to make OC/EC split.

Constant heating rate of 40 C / minute
No temperature steps as seen in the IMPROVE and NIOSH methods.

Light transmission measurement over entire visible range
Use of white light and spectrometer gives light transmission as a function of wavelength. Method may aid OC/EC split determination if OC and pyrolized OC has a different absorption wavelength than EC.

Evolved C converted to CO₂
Measured with LiCor CO₂/H₂O IR gas analyzer
Magnesium dioxide catalyst at 800 C
EGA light source upgrade

- solid quartz tube
- filter holder
- brighter light source
Light attenuation divided by total carbon mass
lodgepole pine - mixed combustion

whole filter (26 ug cm⁻²)

front half (20.5 ug cm⁻²)

back half (5.1 ug cm⁻²)
Attenuation for selected burns (log)

- Flaming
- Smoldering

Wavelength [nm]
Alaskan duff

very weak attenuation by back half of filter

σ = -1