Estimating the Contribution of Smoke and Its Fuel Types to Fine Particulate Carbon using a Hybrid-CMB Model

Bret A. Schichtel and William C. Malm - NPS Air Resource Division
Jeffrey L. Collett, Jr., Amy P. Sullivan, Leigh A. Patterson and Amanda S. Holden – Colorado State University

Supported by the Joint Fire Science Project (JFSP)
Urban & Rural Average Annual Organic Carbon PM2.5 Fraction
Natural and Anthropogenic Biomass Burning

[Images of Wildfire, Agricultural Fire, Prescribed Fire, Residential Wood Burning]
Hybrid Source Apportionment Model

Source-compositions (F)

Receptor model C=f(F,S)

Receptor (monitor)

Source-orientated Model
(3D Air-quality Model)
(CMAQ, CAMx)

Receptor Model
(CMB, PMF)

Chemistry

Meteorology

Air Quality

Source Impacts

Jeameen Baek et al., - Georgia Institute of Technology
Biomass burning has relatively unique and stable organic molecular marker species
- Anhydrosugars: levoglucosan, mannosan, and galactosan

\[
\text{smoke PM/TC at Receptor} = \frac{Src_{\text{smokePM}}}{Src_{\text{Marker Species}}} \times Re_{\text{Marker Species}}
\]

Issues
- Primary smoke marker species can’t apportion secondary matter
- Biomass burning source profiles vary with fires
- Can’t apportion contributions from individual fires or types of fire
CTM modeling results
- Derive fire weighted source profiles
- Apportion smoke contributions to fire types and source regions
Variation of Primary Biomass Burning Marker Species Profiles

- Profile dependence on fuel type /cellulose content (Sullivan et. al. 2008)
Levoglucosan/TC varies by a factor of 2
Mannosan/TC varies by more than a factor of 10
Each species has a unique spatial variation
“Chemical” Transport Model to Apportion TC

- Simple chemical transport model using Capita Monte Carlo model particle dispersion model and back airmass histories
- Primary and secondary contributions from fire, mobile, vegetation, point, area and other sources simulated
- Model was tuned for 4 sites using 2002 WRAP emissions

- WRAP 2002 emission
- NCAR fire emissions
- Six-day airmass histories
- Wet Removal
- Dry Removal
- First order SOA formation
- Tuned Rate Coeff.

- Kinetics
Hi-Vols samplers collecting 24-h PM2.5 samples daily
Samples analyzed for OC/EC, levoglucosan, mannosan, galactosan
Simulation of Smoke Marker Species as Upper Buffalo

- 24-hour average concentrations at Upper Buffalo, AR in March and April 2008
- Smoke marker species emissions were simulated by scaling the OC biomass burning emission rate by the spatially variable smoke source profiles
Comparisons of biomass burning TC estimated using levoglucosan, mannosan and galactosan do not display "edges" at Upper Buffalo and Monture.

The two edges at Sequia, still exist indicating errors in the source profiles.
Agricultural and Other Biomass Burning Contribution to TC

- Upper Buffalo, AR
- Sequoia, CA
- Monture, MT
Biomass Burning Air Quality Issues

- Reduced visibility
  - Regional Haze Rule – reduce haze in class I areas to natural conditions by 2064
- Adverse health effects
  - Fine particulate matter
  - Ozone
- Ecosystem effects
  - Are fires a source of reactive nitrogen?
  - Plant damage from ozone

Prescribed Fire in Grand Can
Wildfire at Glacier, MT
What is causing the haze at Big Bend, TX?
Sources of Organic Aerosol (OA)

Photochemistry
VOC + hν, O₃, OH, NO₃

Secondary Organic Aerosol

Primary Organic Aerosol

Gas Phase Emissions

Carnegie Mellon

Center for Atmospheric Particle Studies
Smoke Management Needs for Air Quality Regulations

- Develop an unambiguous routine and cost effective methodology for apportioning primary and secondary carbonaceous compounds in PM2.5 retrospectively to prescribed, wildfire, agricultural fire, and residential wood burning activities.
- Daily and long term data are needed for air quality assessments.
- Similar needs for ozone and reactive nitrogen deposition issues.
Spatial Variability in Smoke Weighted Source Profiles at IMPROVE Sites, 2008

24-hr averages at all sites

<table>
<thead>
<tr>
<th></th>
<th>Lev/TC</th>
<th>Man/TC</th>
<th>Gal/TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>0.043</td>
<td>0.001</td>
<td>0.004</td>
</tr>
<tr>
<td>Max</td>
<td>0.076</td>
<td>0.026</td>
<td>0.014</td>
</tr>
<tr>
<td>Average</td>
<td>0.059</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>Std Dev</td>
<td>0.006</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>Max/Min</td>
<td>1.8</td>
<td>19</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Average profiles at each site

<table>
<thead>
<tr>
<th></th>
<th>Lev/TC</th>
<th>Man/TC</th>
<th>Gal/TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>0.054</td>
<td>0.004</td>
<td>0.005</td>
</tr>
<tr>
<td>Max</td>
<td>0.065</td>
<td>0.018</td>
<td>0.010</td>
</tr>
<tr>
<td>Average</td>
<td>0.059</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>Std Dev</td>
<td>0.003</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>Max/Min</td>
<td>1.2</td>
<td>4.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>
“Edges” in scatter plots of smoke marker species are indications of contributions from two or more fires with different source profiles.
Measured Source Profile Variability

Upper Buffalo, AR

\[ y = 0.1311x - 2.7093 \]
\[ R^2 = 0.7702 \]

\[ y = 0.1067x \]
\[ R^2 = 0.726 \]

Monture, MT

\[ y = 0.10x + 0.84 \]
\[ R^2 = 0.95 \]

\[ y = 0.11x \]
\[ R^2 = 0.93 \]

Sequoia, CA

\[ y = 1.11x \]
\[ y = 31.26 \]
\[ R^2 = 0.80 \]

\[ y = 0.98x \]
\[ R^2 = 0.76 \]
Biomass Burning Total PM2.5 Carbon
Estimated using the Hybrid-CMB

Upper Buffalo, AR

\[
\begin{align*}
\text{Smoke - Mannosan}, & \ \mu g/m^3 \\
\gamma &= 0.78x \\
R^2 &= 0.71
\end{align*}
\]

Monture, MT

\[
\begin{align*}
\text{Smoke - Mannosan}, & \ \mu g/m^3 \\
\gamma &= 0.51x \\
R^2 &= 0.56
\end{align*}
\]

Sequoia, CA

\[
\begin{align*}
\text{Smoke - Mannosan}, & \ \mu g/m^3 \\
\gamma &= 1.62x - 0.95 \\
R^2 &= 0.81
\end{align*}
\]

\[
\begin{align*}
\text{Smoke - Galactosan}, & \ \mu g/m^3 \\
\gamma &= 0.58x \\
R^2 &= 0.92
\end{align*}
\]

\[
\begin{align*}
\text{Smoke - Galactosan}, & \ \mu g/m^3 \\
\gamma &= 0.45x + 0.04 \\
R^2 &= 0.73
\end{align*}
\]

\[
\begin{align*}
\text{Smoke - Galactosan}, & \ \mu g/m^3 \\
\gamma &= 0.50x \\
R^2 &= 0.72
\end{align*}
\]

\[
\begin{align*}
\text{Smoke - Galactosan}, & \ \mu g/m^3 \\
\gamma &= 0.41x - 0.01 \\
R^2 &= 0.94
\end{align*}
\]

\[
\begin{align*}
\text{Smoke - Galactosan}, & \ \mu g/m^3 \\
\gamma &= 0.41x \\
R^2 &= 0.94
\end{align*}
\]
Simulation of Smoke Marker Species

- 24-hour average concentrations at Upper Buffalo, AR in March and April 2008
- Smoke marker species emissions were simulated by scaling the OC biomass burning emission rate by the spatially variable smoke source profiles
Simulated vs. Measured TC, 2008

- Aggregated over all IMPROVE monitoring sites for each sample day from January – September 2008
- The model captures the temporal variability in the IMPROVE network
Simulated vs. Measured TC

Central Great Plains

Mid South East

Colorado Plateau

Death Valley

Simulated TC, micro-g/m³

Measured TC, micro-g/m³

Central Great Plains

$y = 0.69x + 0.26$

$R^2 = 0.67$

Colorado Plateau

$y = 0.76x + 0.27$

$R^2 = 0.40$

Mid South East

$y = 0.81x + 0.34$

$R^2 = 0.54$

Death Valley

$y = 0.55x + 0.53$

$R^2 = 0.44$
Simulation of Ratios of Smoke Marker Species

- 24-hour average concentrations at Upper Buffalo, AR in March and April 2008

For Lev./Man., the equation is $y = 0.5114x + 3.3498$ with $R^2 = 0.4963$.

For Lev./Gal., the equation is $y = 0.1979x + 5.2899$ with $R^2 = 0.1707$.

For Man./Gal., the equation is $y = 0.3043x + 0.4609$ with $R^2 = 0.3948$. 
Simulation of Smoke Marker Species

- 24-hour average concentrations at Monture, MT in July – September 2008

- Levoglucosan: $y = 0.5958x + 0.0132$, $R^2 = 0.3295$

- Mannosan: $y = 1.2959x + 0.0025$, $R^2 = 0.2502$

- Galactosan: $y = 2.2752x + 0.0011$, $R^2 = 0.2342$
Radiocarbon (\(^{14}\text{C}\))

Distinguishing Between Contemporary and Fossil Carbon

**Summer**
- Fraction Contemporary C
  - 80-100% - rural sites
  - 70-80% - near urban sites
  - 50% - urban sites
  - 60-75% in industrial Midwest
- Similar fraction contemporary carbon in winter and summer

**Winter**

---
Biomass Burning Emission Inventory

- Daily MODIS (Terra and Aqua) derived biomass burning emissions (Wiedinmyer et al., 2006)
- Data are aggregated to a 36 km grid
- Fires are tagged as agricultural and other
Averaged Over all Rural IMPROVE Sites – National Temporal Evaluation Model vs Model
Averaged Over all Rural IMPROVE Sites – Spatial Evaluation

Model vs Measured TC

\[ y = 1.0562x + 0.1719 \]
\[ R^2 = 0.381 \]

Model vs Measured TC

\[ y = 0.8995x + 0.0012 \]
\[ R^2 = 0.3917 \]
Spearman $r$

Model TC vs. IMPROVE TC

CMAQ 2006

Mcarlo 2006
### Smoke Source Profiles for Fuel Types (FLAME II Study)

<table>
<thead>
<tr>
<th>Biome</th>
<th>Vegetation type</th>
<th>Levoglucosan/TC</th>
<th>Mannosan/TC</th>
<th>Galactosan/TC</th>
<th>K+/TC</th>
<th>OC/TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grassland</td>
<td>Grass</td>
<td>0.12 ± 0.11</td>
<td>0.006 ± 0.004</td>
<td>0.008 ± 0.006</td>
<td>0.067 ± 0.050</td>
<td>0.94 ± 0.06</td>
</tr>
<tr>
<td>Softwood Forest</td>
<td>Branches - Fresh</td>
<td>0.07 ± 0.03</td>
<td>0.017 ± 0.006</td>
<td>0.013 ± 0.005</td>
<td>0.032 ± 0.033</td>
<td>0.98 ± 0.03</td>
</tr>
<tr>
<td>Softwood Forest</td>
<td>Branches - Dead</td>
<td>0.05 ± 0.03</td>
<td>0.013 ± 0.008</td>
<td>0.007 ± 0.006</td>
<td>0.015 ± 0.013</td>
<td>0.52 ± 0.10</td>
</tr>
<tr>
<td>Softwood Forest</td>
<td>Needles</td>
<td>0.06 ± 0.03</td>
<td><strong>0.033 ± 0.019</strong></td>
<td>0.015 ± 0.008</td>
<td>0.027 ± 0.062</td>
<td>0.97 ± 0.05</td>
</tr>
<tr>
<td>Softwood Forest</td>
<td>Duff</td>
<td>0.07 ± 0.01</td>
<td>0.050 ± 0.015</td>
<td><strong>0.022 ± 0.002</strong></td>
<td>0.004 ± 0.001</td>
<td>0.99 ± 0.00</td>
</tr>
<tr>
<td>Hardwood Forest</td>
<td>Leaves</td>
<td>0.05 ± 0.01</td>
<td>0.005 ± 0.001</td>
<td>0.010 ± 0.002</td>
<td>0.042 ± 0.014</td>
<td>0.96 ± 0.03</td>
</tr>
<tr>
<td>Scrub brush</td>
<td>Branches</td>
<td><strong>0.11 ± 0.01</strong></td>
<td>0.016 ± 0.001</td>
<td>0.013 ± 0.006</td>
<td>0.020 ± 0.005</td>
<td>1.00 ± 0.00</td>
</tr>
<tr>
<td>Scrub brush</td>
<td>Leaves</td>
<td>0.04 ± 0.02</td>
<td><strong>0.004 ± 0.002</strong></td>
<td>0.005 ± 0.003</td>
<td>0.088 ± 0.061</td>
<td>0.81 ± 0.23</td>
</tr>
<tr>
<td>Floral shrublands</td>
<td>Leaves</td>
<td>0.09</td>
<td>0.008</td>
<td>0.007</td>
<td>0.028</td>
<td>0.909</td>
</tr>
<tr>
<td>Southeaster shrublands</td>
<td>Leaves</td>
<td>0.04 ± 0.02</td>
<td>0.004 ± 0.003</td>
<td><strong>0.003 ± 0.001</strong></td>
<td><strong>0.103 ± 0.208</strong></td>
<td>0.77 ± 0.19</td>
</tr>
</tbody>
</table>
Variation of Primary Biomass Burning Marker Species Profiles

Levoglucosan source profiles

- Profile dependence on fuel/cellulose content (Sullivan et. al. 2008)
- Profile dependence on combustion temperature (Kuo et. al. 2008)
Apportionment Methods

- Chemical transport models CTM)
  - Subject to large errors in inputs
    - Current CTM model simulations estimate little to no smoke SOA
    - Results are unconstrained by measured data

- Receptor Models
  - Chemical Mass Balance
    - Can’t apportion secondary aerosols
  - Factor Analysis e.g. Positive Matrix Factorization (PMF)
  - Non-unique source factors

PMF modeling appears to have combined SOC from vegetation in with fire
• Speciated PM2.5 and PM10 mass monitoring network, > 160 sites
• Using the Mcarlo CTM 24-h PM2.5 total carbon simulated at all IMPROVE sites for 2006 - 2008
Spatial distribution of smoke source profiles

Mapping wildland fuels across the conterminous USA for coarse-scale modeling of fire effects