Levoglucosan and Water Soluble Organic Carbon from PM2.5 Teflon Filters

Preliminary Review of 3 Studies

Neil Frank
USEPA/OAQPS

For Presentation at the NAMC
Nashville, TN
Nov 2-5, 2009
Background

Biomass combustion is large contributor to PM2.5
- From residential fireplaces and woodstoves
- Episodically from wildfires and prescribed burns

Potassium and Levoglucosan are “the” biomass markers
- LG is typically measured by organic extraction and GC-MS and emission factors quantify monthly average impacts (using composites of quartz filters)

Previous studies
- U Wisc/STI Urban Organics Study (2006):
  - 15-25% of the OC due to biomass burning at five MW sites
- Zheng, Schauer et al. (2002):
  - 25-66% of OC in the SE from wood combustion
- Sheesley, Schauer, Zheng et. al. (2007)
  - 30-50% of OC from biomass burning at 4 sites in NC
3 Pilot Studies using Archived FRM Teflon Filters to Analyze Levoglucosan and…..

- **Puget Sound Study (2004-2007 filters)**
  - 300 filters at 2 urban and 3 suburban/rural sites
  - Ethylacetate extraction procedure coupled with derivatization and GC/MS analysis using selected ion monitoring (SIM)

- **Midwest Study (2004-05 filters)**
  - 500 filters at 6 urban and 3 rural sites
  - Water extraction with IC (HPLC-PAD)
  - Also analyzed WSOC and K+

- **Southeast Study (2007 filters)**
  - 900 filters at 8 urban and 7 rural sites
  - Also analyzed WSOC, K+, Oxalate, other sugars, SO4²⁻, NO3⁻, UV absorption, other
Study Goals

- To investigate the spatial and temporal variation among various biomass related species.
- Use archived FRM teflon filters to assess impacts of biomass burning to OC and PM2.5
  - for NAAQS Implementation and EE
- Examine value of these additional PM species
  - Say, for routine network analysis
Acknowledgements

Investigators
- Chris Simpson and Gretchen Onstad (Univ. Washington)
- Jeff Collett and Amy Sullivan (Colorado State Univ.)
- Rodney Weber, Xiaolu Zhang, Arsineh Hecobian, Mei Zheng (Georgia Tech.)

State, Local and other Supporters
- Mike Gilroy & Walter Zylowski (Puget Sound Clean Air Agency); Mike Ragan (Washington State Department of Ecology)
- Donna Kenski (LADCO), Terry Sweitzer (Illinois Environmental Protection Agency); Anna Kelley (Hamilton County Department of Environmental Services); MaryAnn Heindorf (Michigan Department of Environmental Quality); Lisa Herschberger, (Minnesota Pollution Control Agency); Steve Lengerich (Indiana Department of Environmental Management)
- Susan Zimmer-Dauphine (GA), Randy Dillard (Jefferson Co., AL); Tracey Anderson and Mike Mailer (ADEM); Scott Reynolds (SC); Artra Cooper (EPA Reg4)

Funded with approval of the NACAA monitoring steering committee
Puget Sound Study
80 miles north of Seattle
Darrington, WA (population ~1200) is our “Levoglucosan Laboratory”

Max 24-hr PM2.5 > 90 ug/m3

PM2.5 has high correlation with light scattering

Study Period
Darrington, WA: “a one match community”
LG to PM2.5 ratio is highest in Darrington

Figure 7: Associations between levoglucosan and PM mass at five monitoring sites in the Puget Sound Airshed.

From Onstad and Simpson (2008)
Empirical LG Scaling Factors

% levoglucosan varies in accordance with biomass contribution

Table 4: Empirically derived scaling factors indicating the relationship between levoglucosan and PM$_{2.5}$ mass for woodsmoke dominated periods and locations in the Puget Sound Airshed.

<table>
<thead>
<tr>
<th>Location</th>
<th>Average % levoglucosan per µg PM$_{2.5}$</th>
<th>95% confidence interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darrington</td>
<td>13.9</td>
<td>12.7-15.2</td>
</tr>
<tr>
<td>South Tacoma</td>
<td>9.6</td>
<td>8.6-10.5</td>
</tr>
<tr>
<td>Marysville</td>
<td>10.0</td>
<td>9.1-10.7</td>
</tr>
</tbody>
</table>

It is notable that these values are also in agreement with the scaling factor of 9.3% determined from the PMF analysis at Beacon Hill

From Onstad and Simpson (2008)
Levoglucosan as Percent PM2.5 (2008)

*When concentrations are high, there may be SOA from multi-day accumulation in Darrington*

CSU measurements on FRM teflon
LG yield varies by wood and combustion types
Relatively higher % OC with stoves

0.4 $L_G \approx 40\%$ OM (stove) and 13% OM (fireplace)

From Fine (2004)
Figure 9: A comparison of scaling factors indicating the relationship between levoglucosan and woodsmoke derived PM$_{2.5}$ mass. The scaling factors highlighted inside the yellow box were determined from ambient measurements at the four Puget Sound sites. Error bars represent ± 1 SD.

LG/OC ratio for the combustion of leaves and twigs can be lower: 0.023 µg C/µg C)

From Onstad and Simpson (2008)
The Midwest Study
6 urban and 3 rural sites

Houghton Lake, MI
Mille Lacs, MN
Minneapolis, MN
East St. Louis, IL
Braidwood, IL
Northbrook, IL
Detroit, MI
Indiana, Indianapolis
Mechanicsburg, IN
Cincinnati, OH

Latitude (degrees)
Longitude (degrees)
“Levoglucosan peaks in fall/early winter in the more southern cities.”
Sullivan and Collett’s data have similar seasonal pattern, however the levels are 50-70% lower.
CSU concludes that BB accounts for 5-15 percent of OC

From Sullivan and Collett (2009)
Something was clearly different about July 20
July 20, 2004 also had high OCM
A regional OC event is evident

WSOC among all 15 MW sites

~2 ug/m3 excess OC

July 20

Compare to OC across the sites with speciation
Using LG concentration & “wildfire factor,” the estimated biomass contribution to PM2.5 = 22 x LG = 1.5 ug/m3. The WSOC seems to confirm excess OC.
WSOC vs. “Bulk” OC in the MidWest
Does it give us clues about OC sampling artifacts?

Figure 14. Correlations of WSOC vs. (a) the uncorrected STN OC data and (b) corrected STN OC data for all co-located FRM and STN sites. The correction applied is 1 µg C/m3 for the 2004 data and 1.1 µg C/m3 for the 2005 data.
WSOC vs $OC_{adj}$ for Indianapolis

OC artifact adjustment of 1 ug/m3 may be OK for average concentrations but seems to be too high for individual low 24-hr data

July 20, 2004
The Southeast Study

15 sites from FRM monitoring network (AL, GA and SC)
- 8 urban sites (shown in blue) and 7 rural sites (shown in red)
- 900 47mm teflon filters collected once every six days

From Xiaolu Zhang, et.al. (AAAR)
The Southeast Study

**Much higher levoglucosan concentrations in winter and spring.**

Figure 3. Seasonal-averaged (Winter, Spring, Summer, Fall) levoglucosan concentrations at each site.

From Xiaolu Zhang, et.al. (AAAR)
Figure 5. Monthly averaged Aqua MODIS fire counts (red dots) in 2007 over 7 states in southeastern U.S. Sampling sites are shown as square blue symbols.
Fire counts monthly variation more closely matches the levoglucosan pattern compared with potassium.
In the SE, WSOC (on Teflon) = ~ 43-50% of OC

Regression Equation:
\[ \text{wsoc} = 0 + 0.431199 \times \text{stn_OC_adj} \]

WSOC vs “NIOSH-type” OC

Regression Equation:
\[ \text{wsoc} = 0 + 0.519171 \times \text{stn_oc_tor} \]

WSOC vs “IMPROVE” OC

OC is measured on quartz and is adjusted for sampling artifact by subtracting 1 ug/m3 for NIOSH-type TOT method and 0.4 ug/m3 for IMPROVE_A TOR method.
Winter WSOC is correlated with LG (Biomass Combustion)

LG / WSOC = 1/3 to 1/8    LG/WSOM=1/6-1/16= 0.16 – 0.06
In the SE, oxalate is ~ 5-10% of WSOC. It appears to also correlate with Biomass Burning.
In the Southeast, biomass burning showed significant enhancement in winter, contributing 24% of the total PM$_{2.5}$ mass.

From PMF analysis, Xiaolu Zhang, et.al. (AAAR)
Levoglucosan Method Comparisons

**IC-PAD vs. GC-MS**

**Using paired Teflon**

**Using paired Quartz**

Need to do teflon vs quartz
Conclusions & Next Steps

- **FRM Teflon filters continue to be useful**
  - Water extraction can provide many OC components

- **LG and WSOC are helpful BB and SOA indicators**
  - For better source apportionment
  - To assist with more complete characterization of mass
  - K$^+$ is less important

- **More analyses needed of these rich data sets**
  - E.g. urban-rural contrasts
  - Value of oxalate?

- **Must study effects of archival and LG aging**
  - To understand CSU vs UWisc differences
  - To better distinguish local from transported smoke
We can't do this without YOU!

I WANT YOUR TEFILON FILTERS