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

Preliminary Review of 3 Studies

Neil Frank
USEPA/OAQPS

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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, $SO4^{=}$, $NO3^{-}$, 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 $PM_{2.5}$
  - for NAAQS Implementation and EE
- Examine value of these additional PM species
  - Say, for routine network analysis

Acknowledgements

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  - Jeff Collett and Amy Sullivan (Colorado State Univ.)
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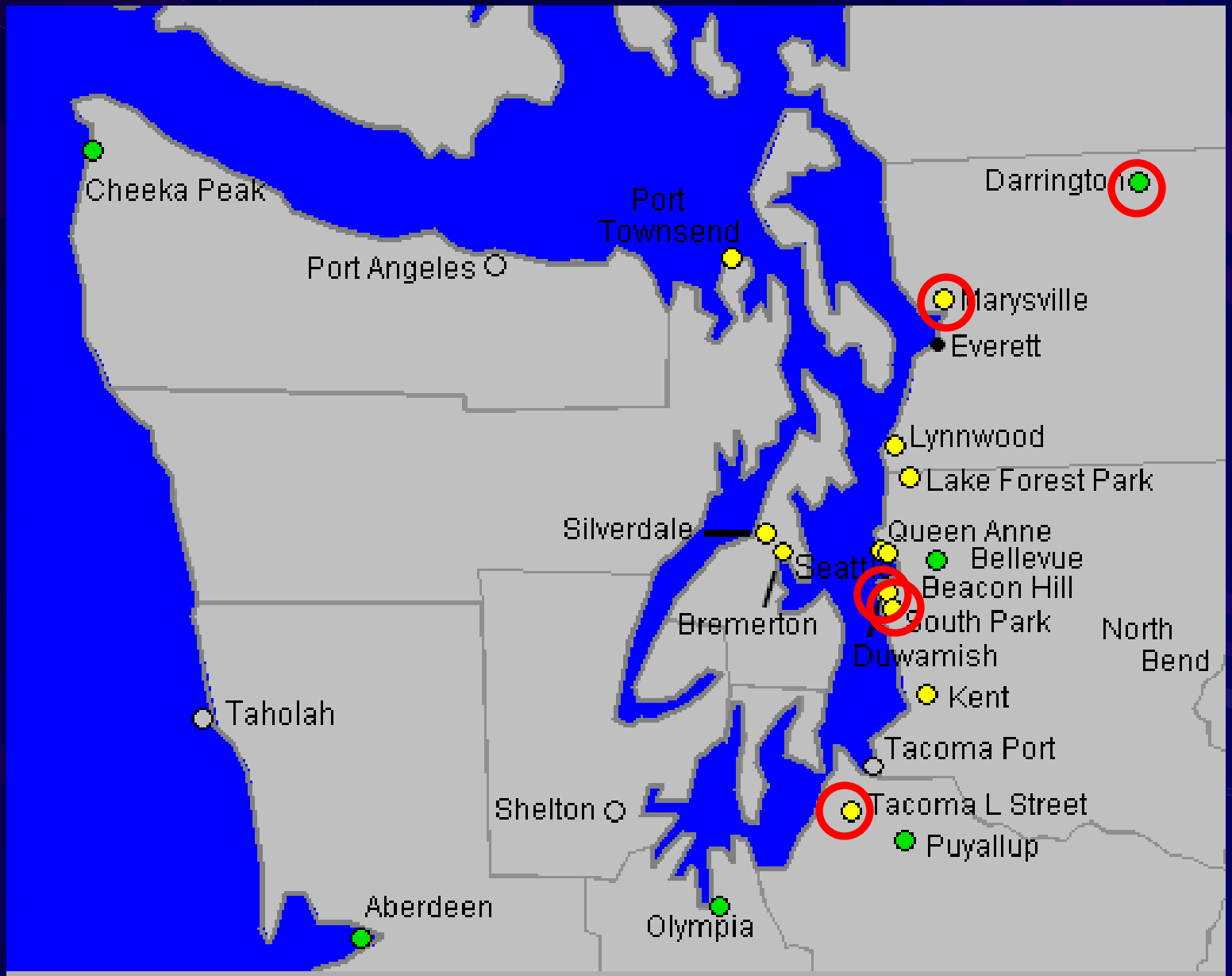
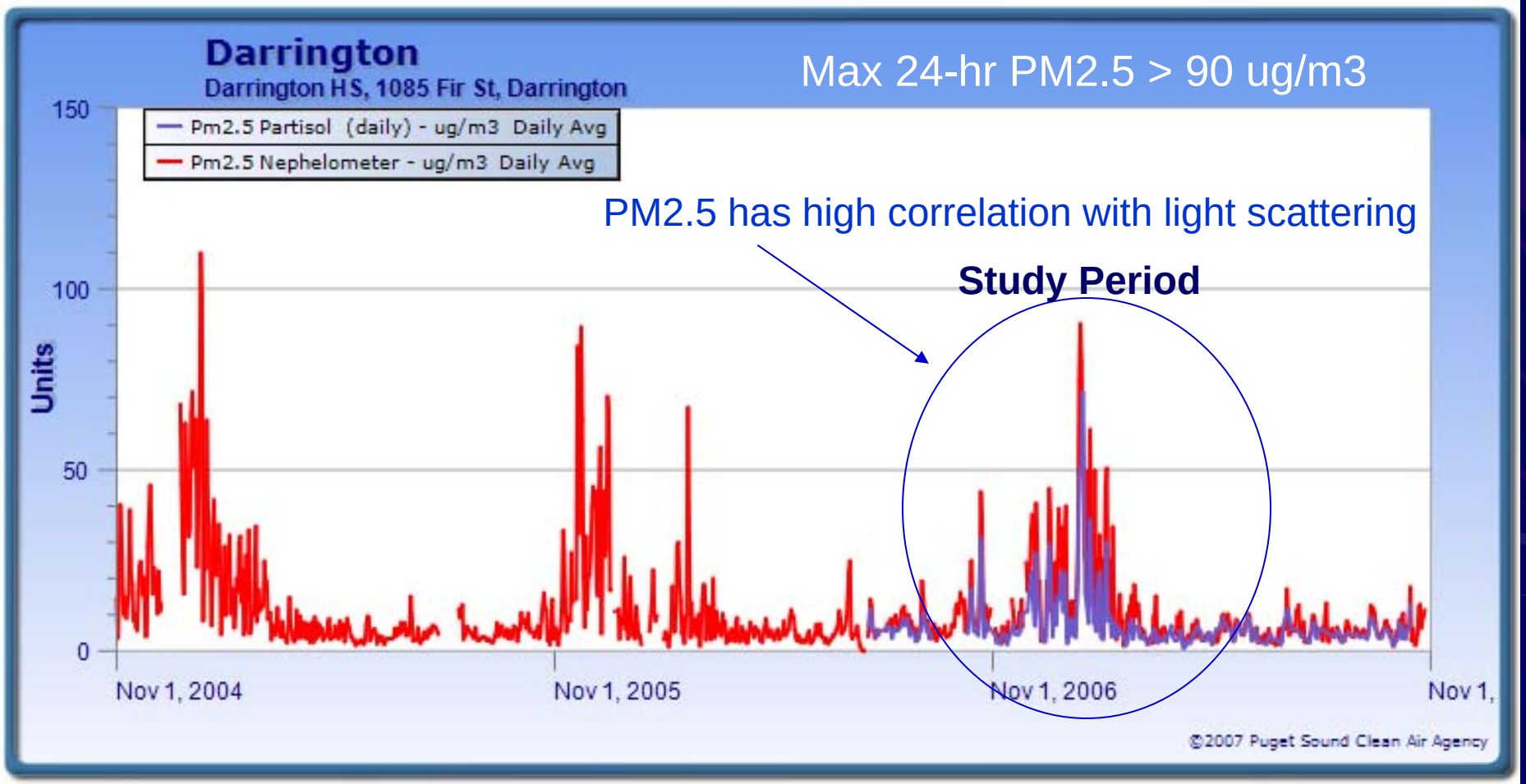
- Funded with approval of the NACAA monitoring steering committee

Puget Sound Study




80 miles north of Seattle

Darrington, WA (population ~1200) is our "Levoglucosan "Laboratory"



Darrington, WA:
"a one match community"

LG to PM2.5 ratio is highest in Darrington

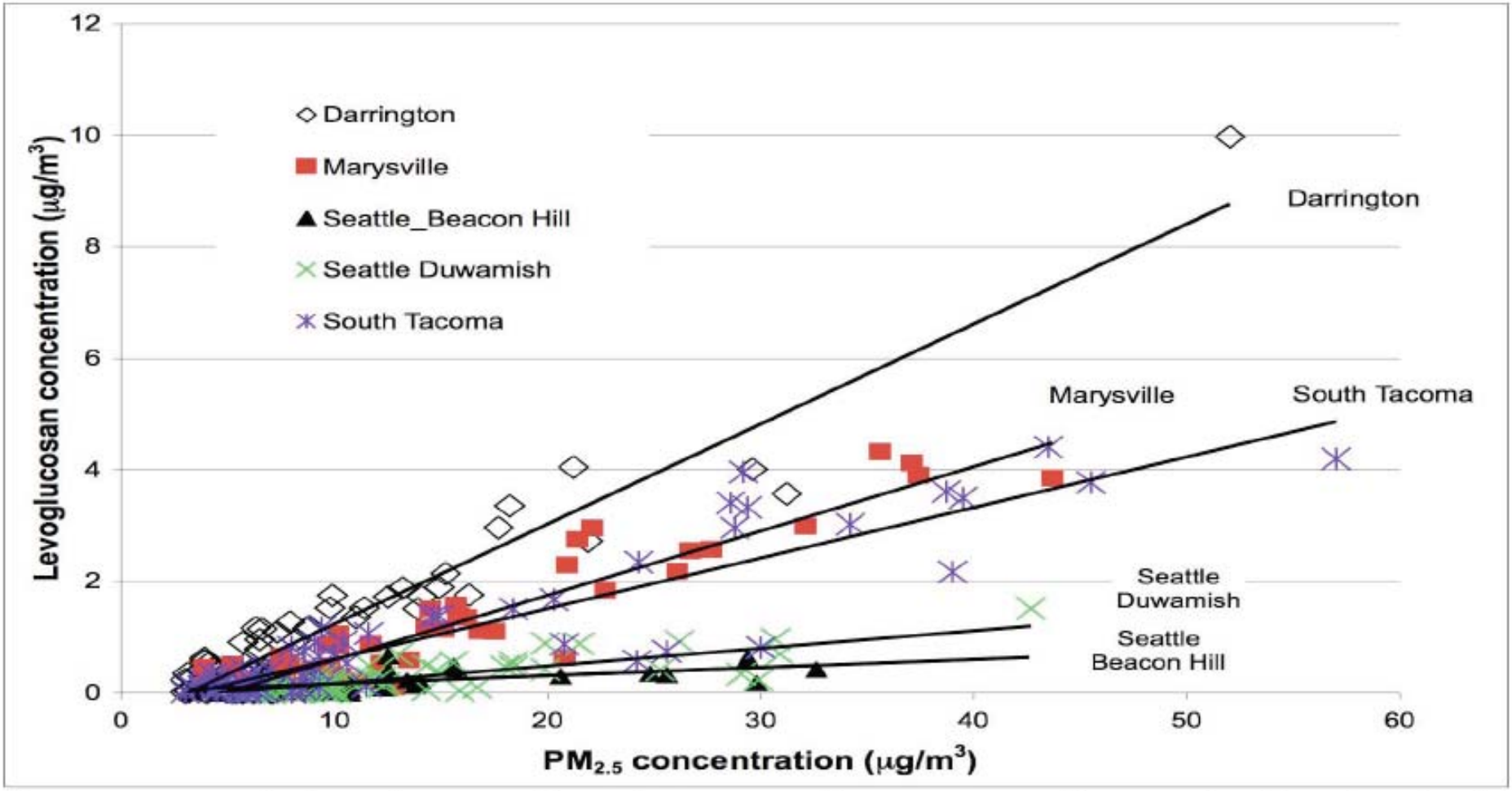


Figure 7: Associations between levoglucosan and PM mass at five monitoring sites in the Puget Sound Airshed.

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.

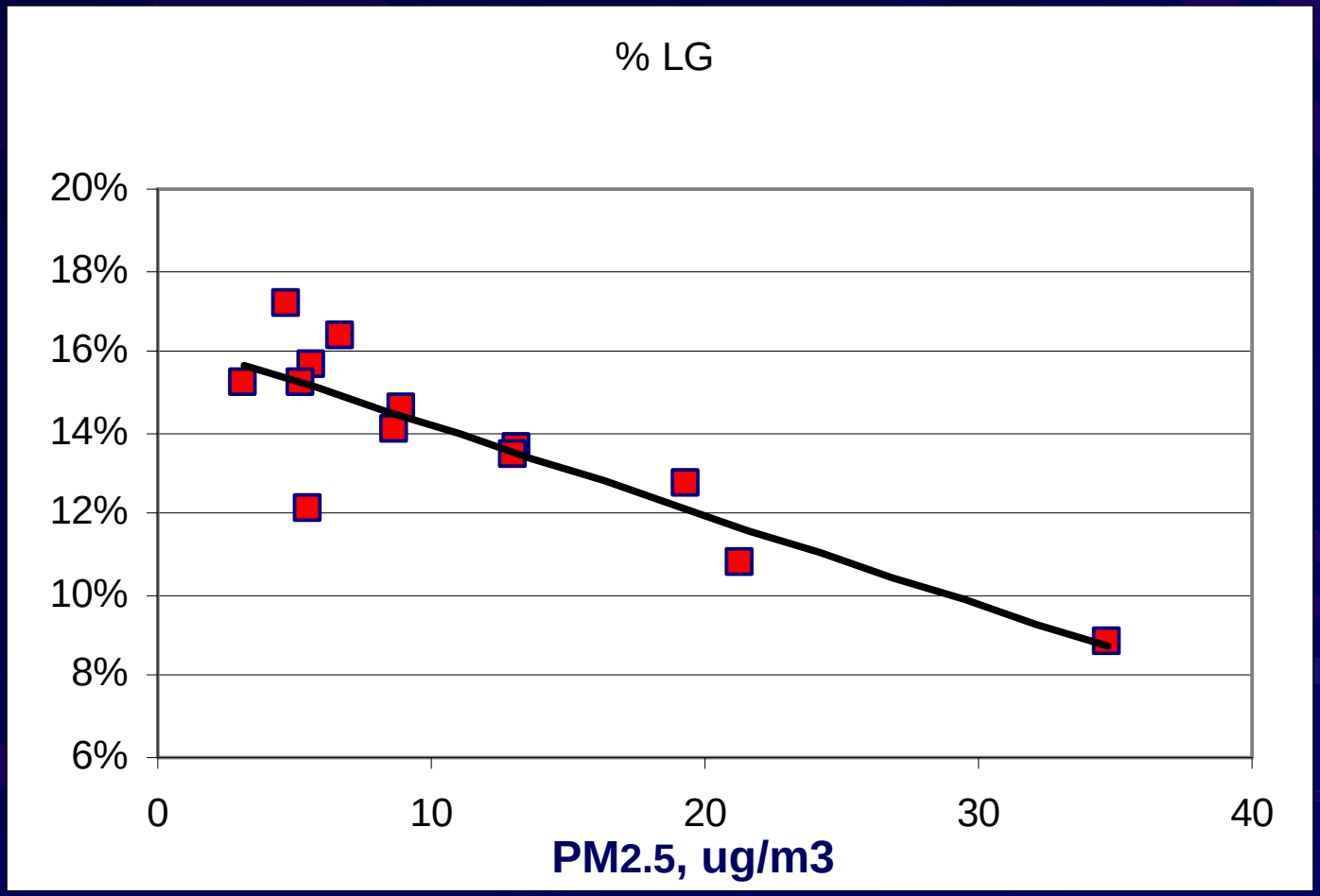
	Average % levoglucosan per µg $PM_{2.5}$	95% confidence interval
Darrington	13.9	12.7-15.2
South Tacoma	9.6	8.6-10.5
Marysville	10.0	9.1-10.7

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)
http://www.epa.gov/airtrends/specialstudies/PSCAA_biomass_subcontract_final_report.pdf

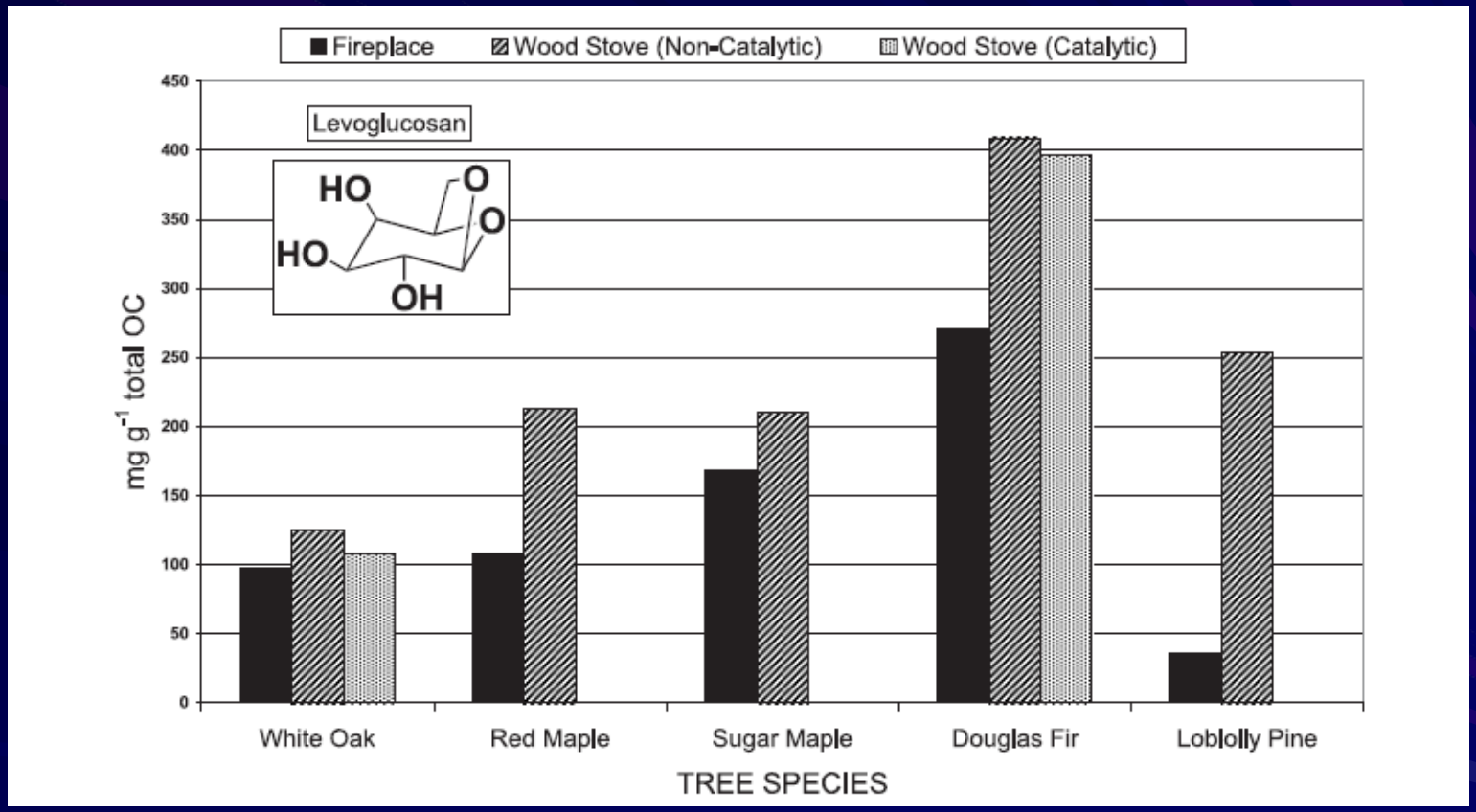
Levoglucosan as Percent PM2.5 (2008)

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 LG ~= 40% OM (stove) and 13% OM (fireplace)

From Fine (2004)

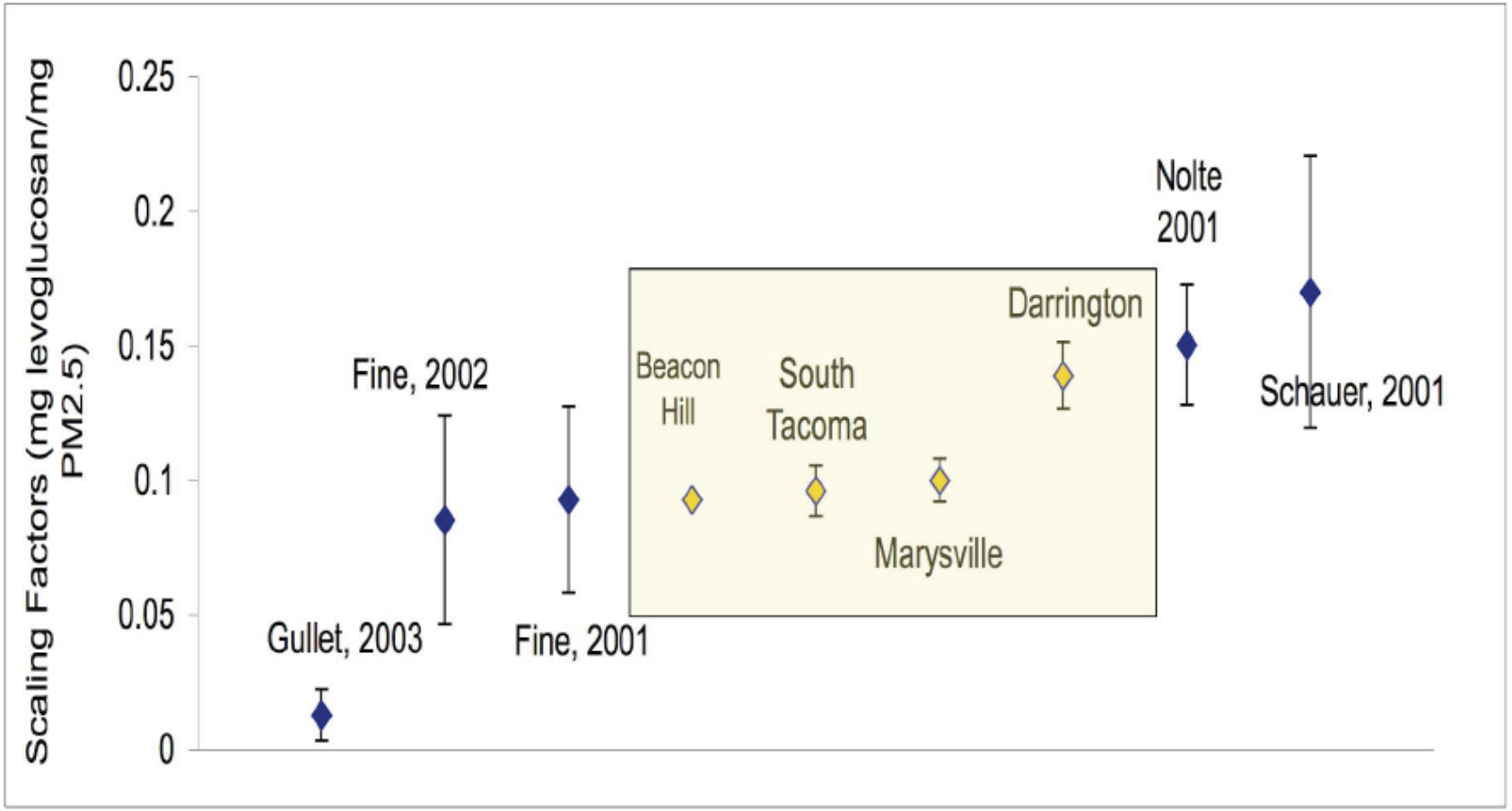


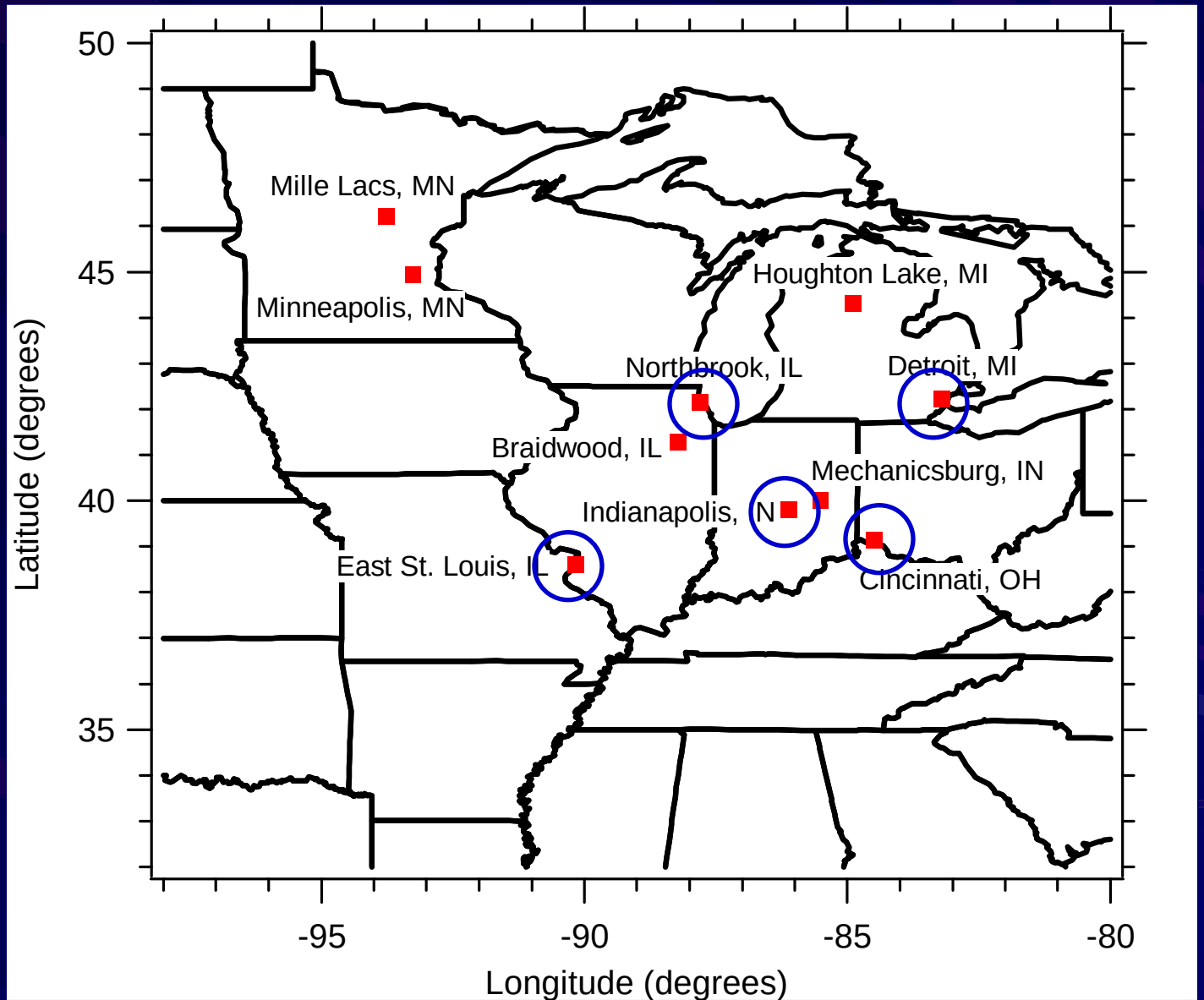
Figure 9: A comparison of scaling factors indicating the relationship between levoglucosan and woodsmoke derived $PM_{2.5}$ mass. The scaling factors highlighted inside the yellow box were determined from ambient measurements at the four Puget Sound sites. Error bars represent ± 1 SD.

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

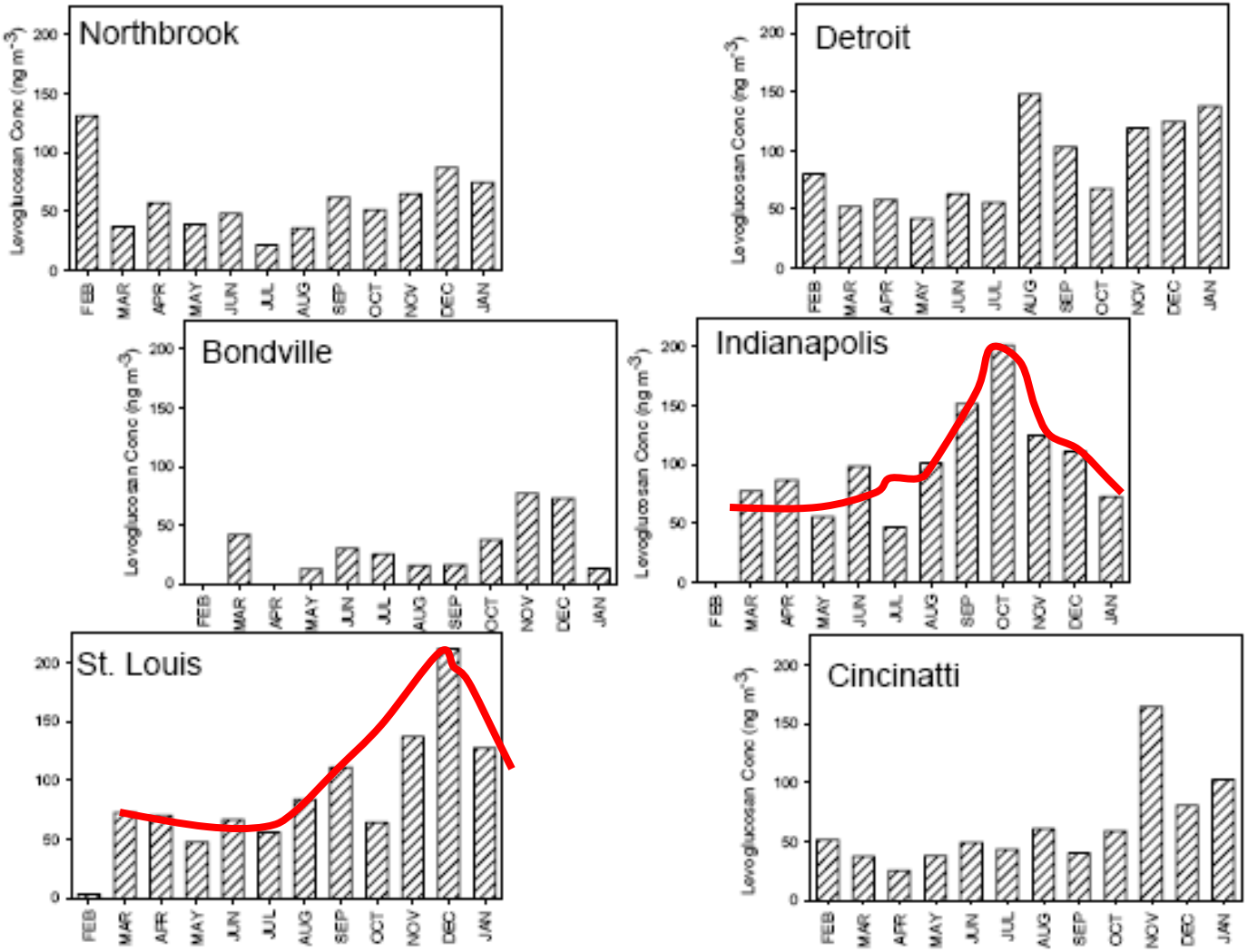
From Onstad and Simpson (2008)

The Midwest Study

6 urban and 3 rural sites

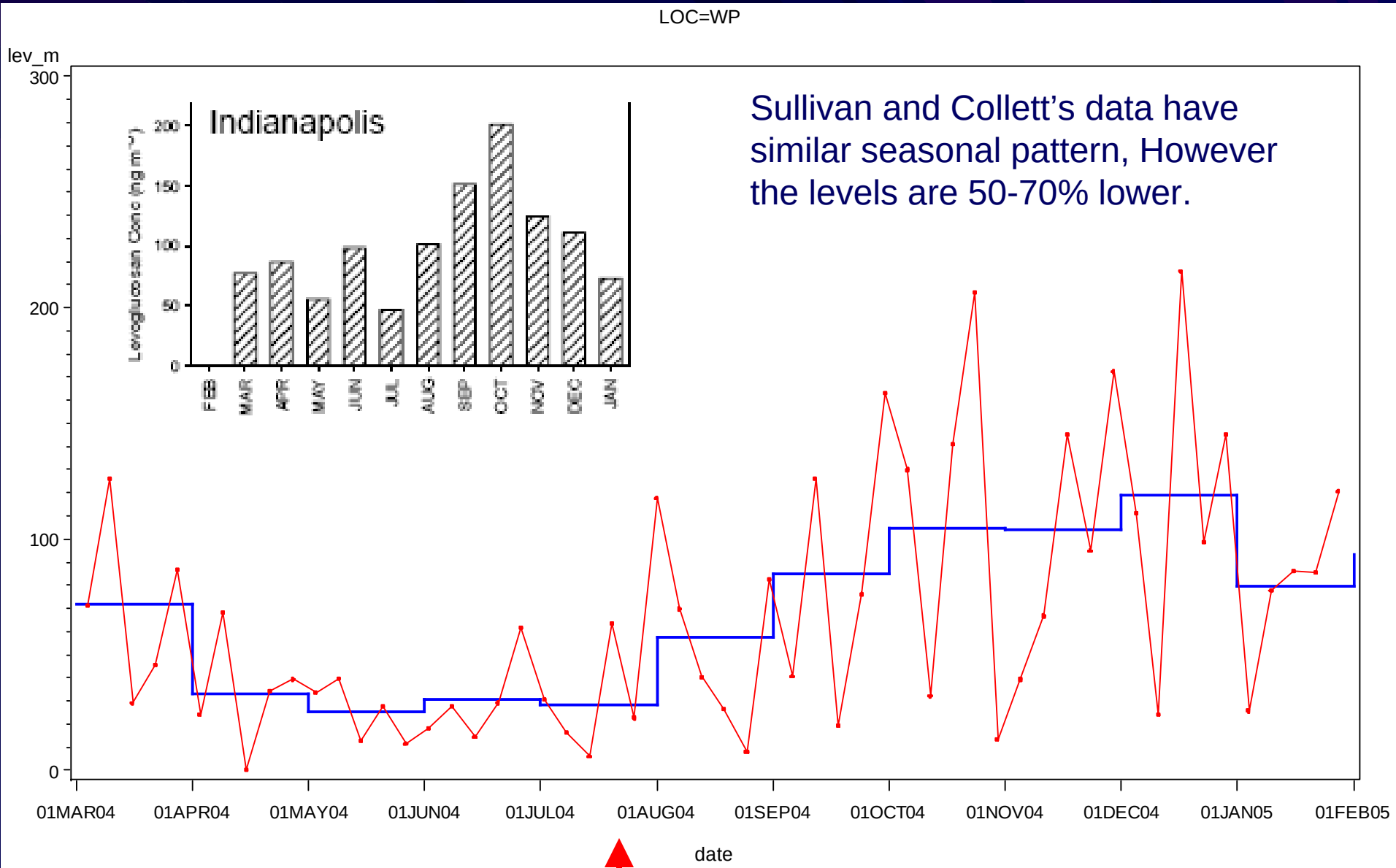


University of Wisc Urban organics study Sheesley, Schauer, et. al. (2006 LADCO Report)



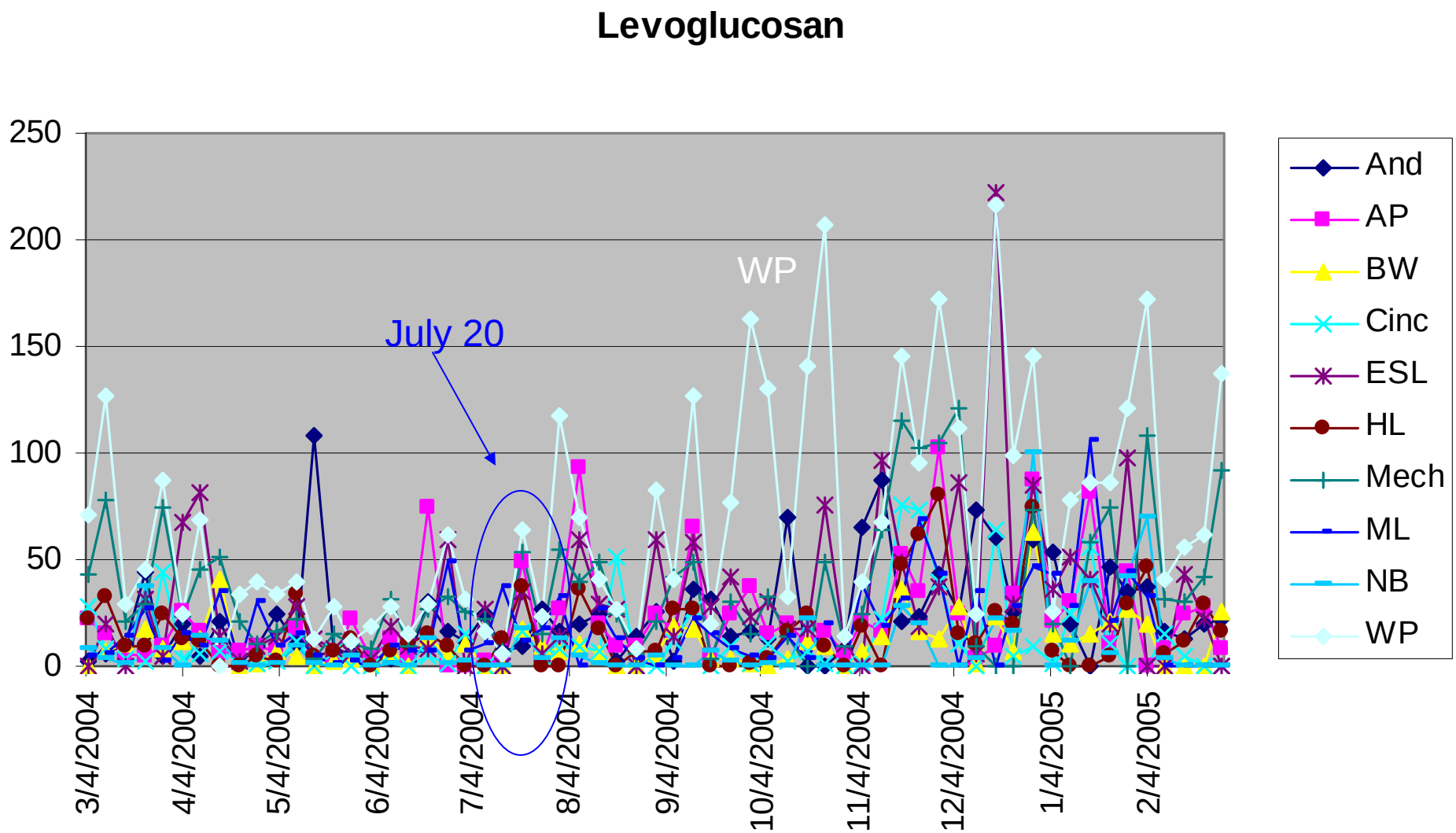
"Levoglucosan peaks in fall/early winter in the more southern cities."

Comparison of CSU (FRM Teflon) and UWisc (Quartz)



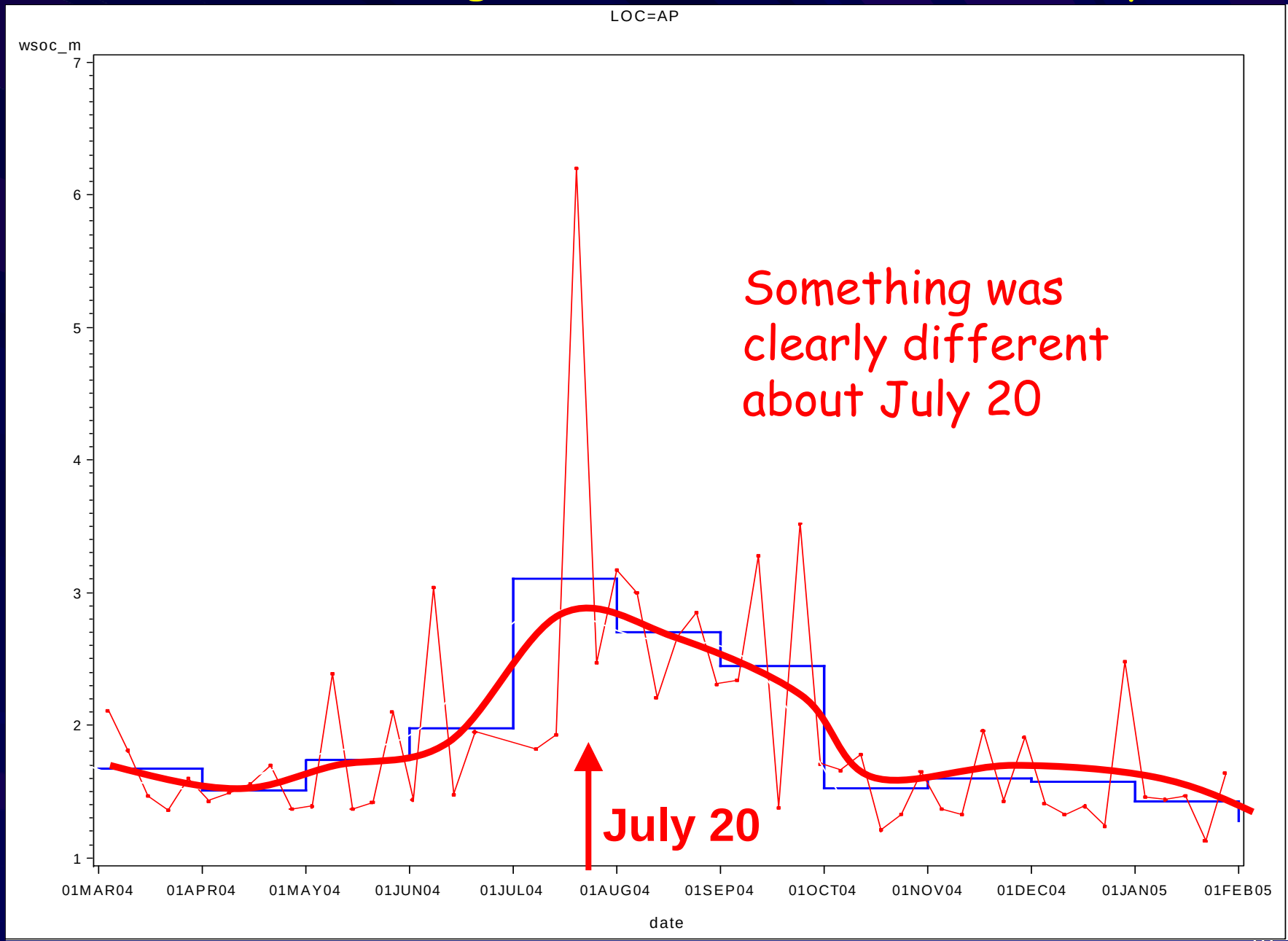
July 20

CSU concludes that BB accounts for 5-15 percent of OC

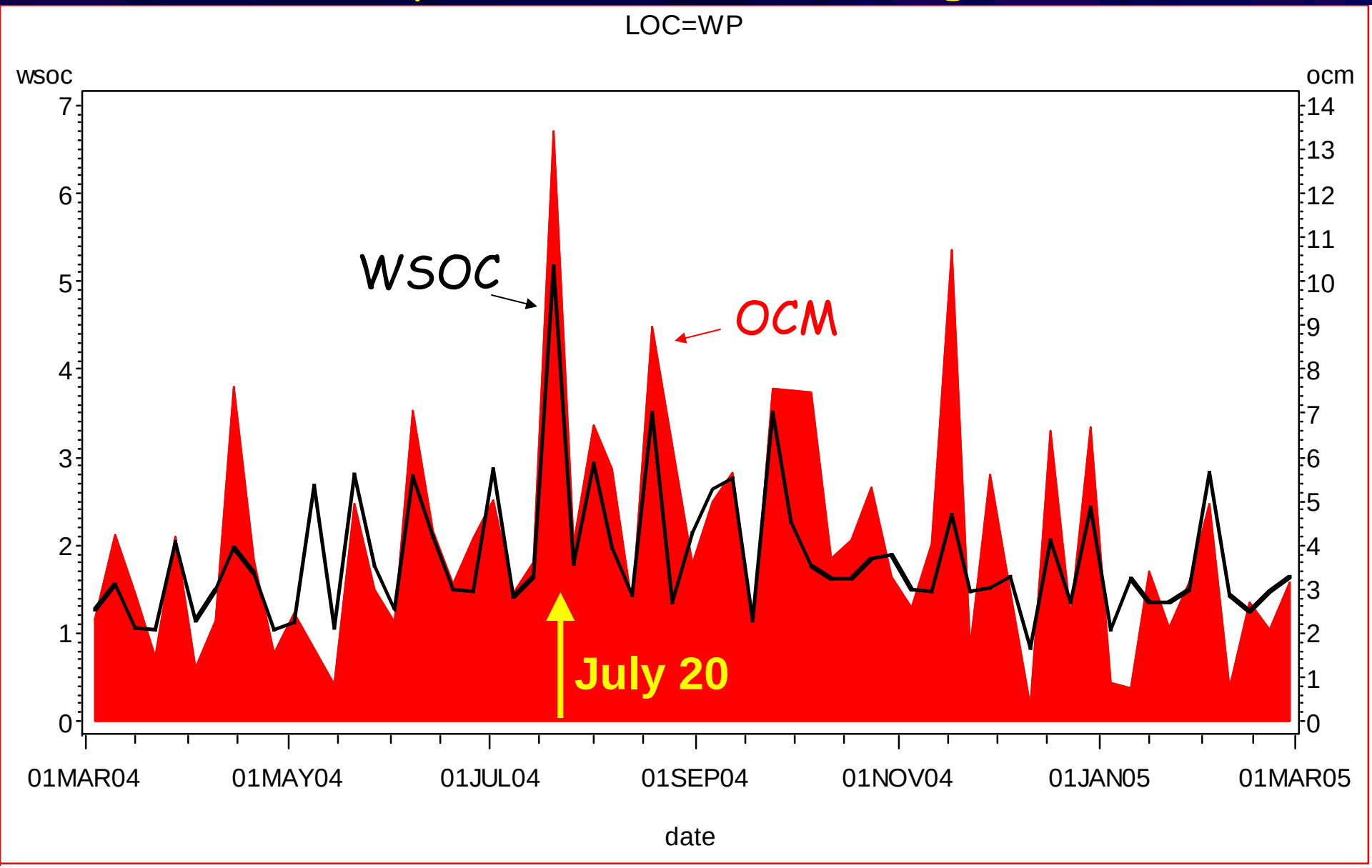


From Sullivan and Collett (2009)

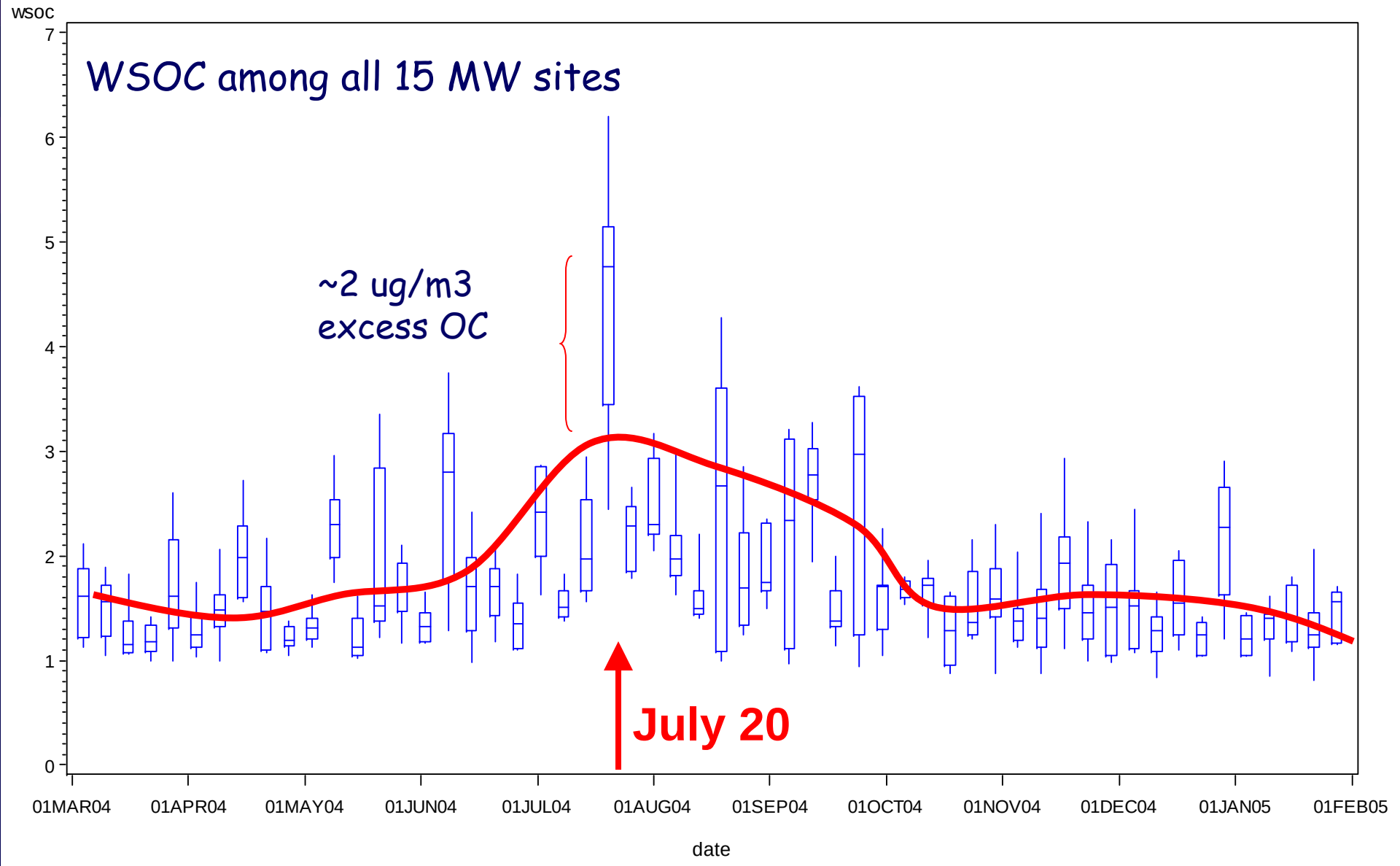
Water Soluble Organic Carbon (WSOC), Indianapolis



July 20,2004 also had high OCM

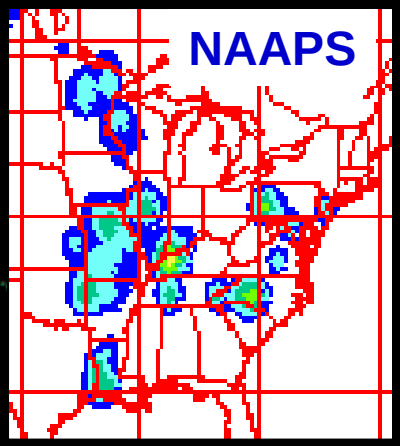


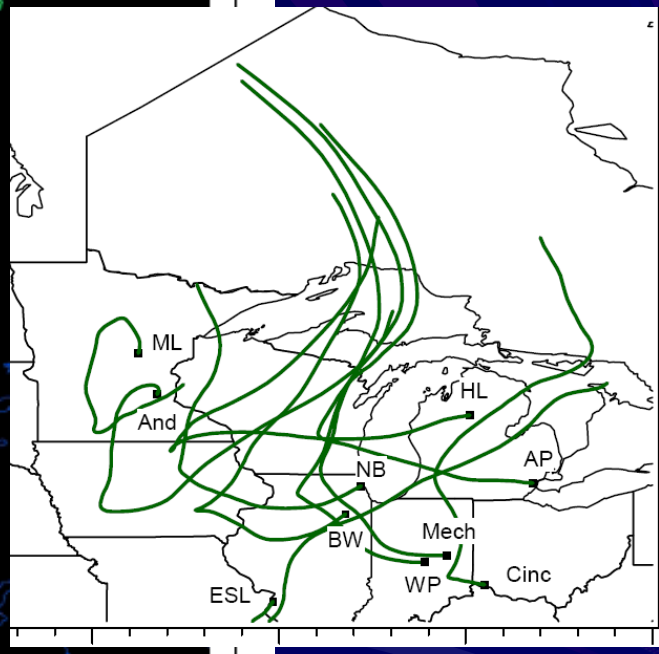
A regional OC event is evident



Compare to OC across the sites with speciation

HMS image
July 20,2004





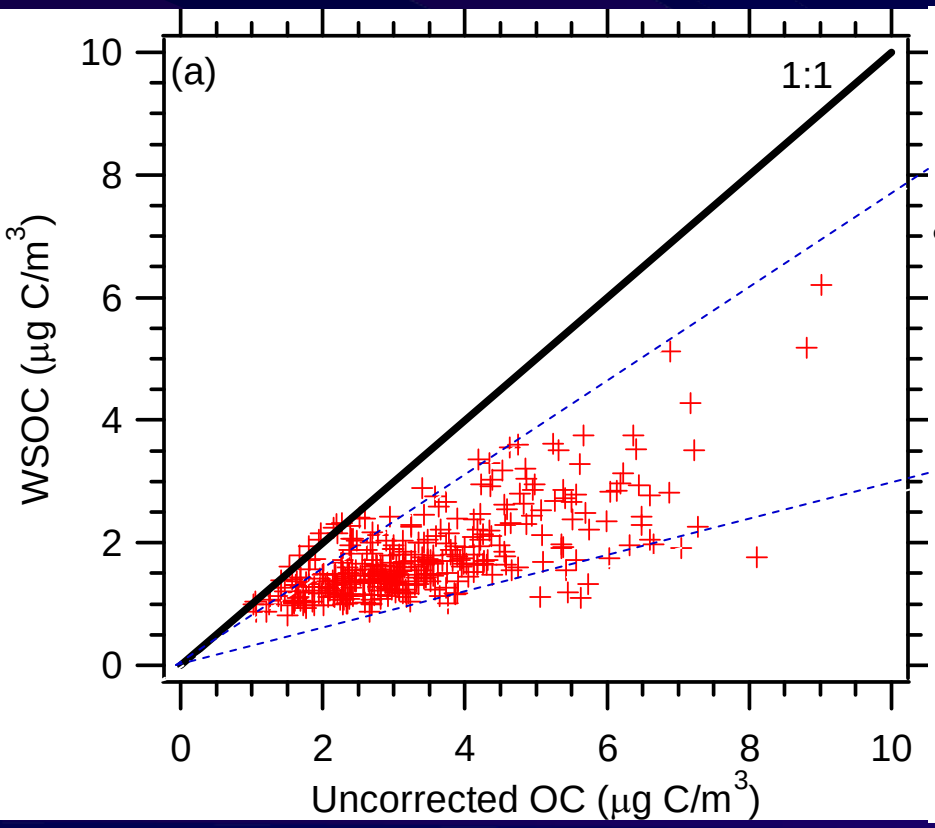
LG decay?
Low LG may be due to photo-oxidation
(Hennigan et. al, 2009 AAAR)

7-20-04

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?



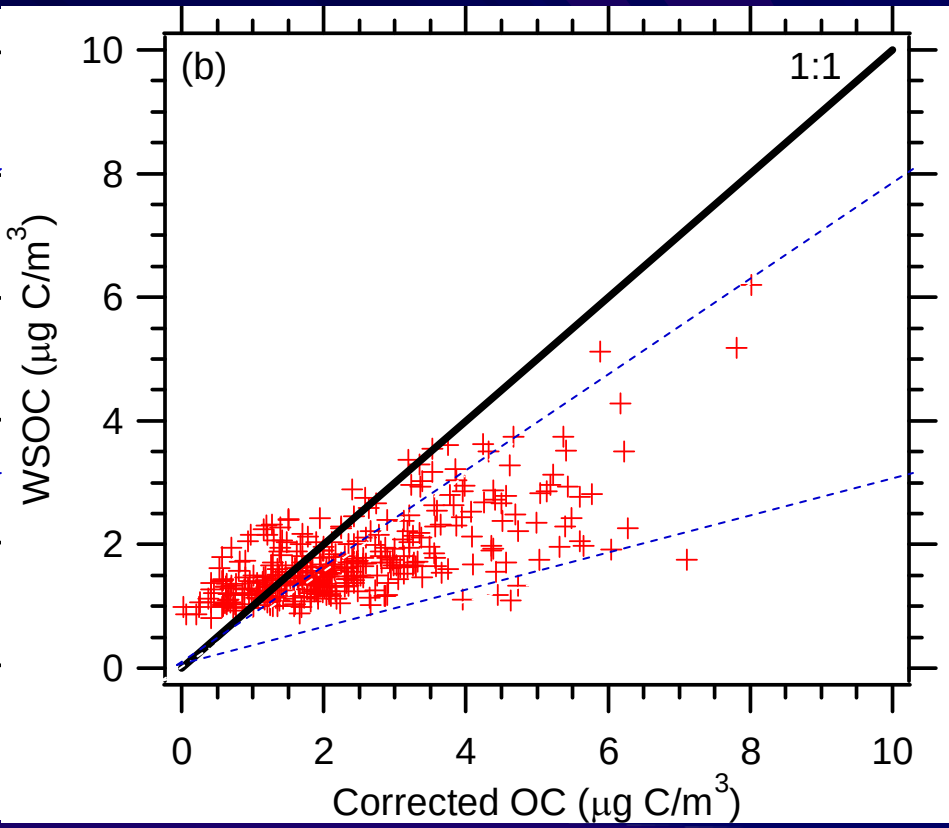
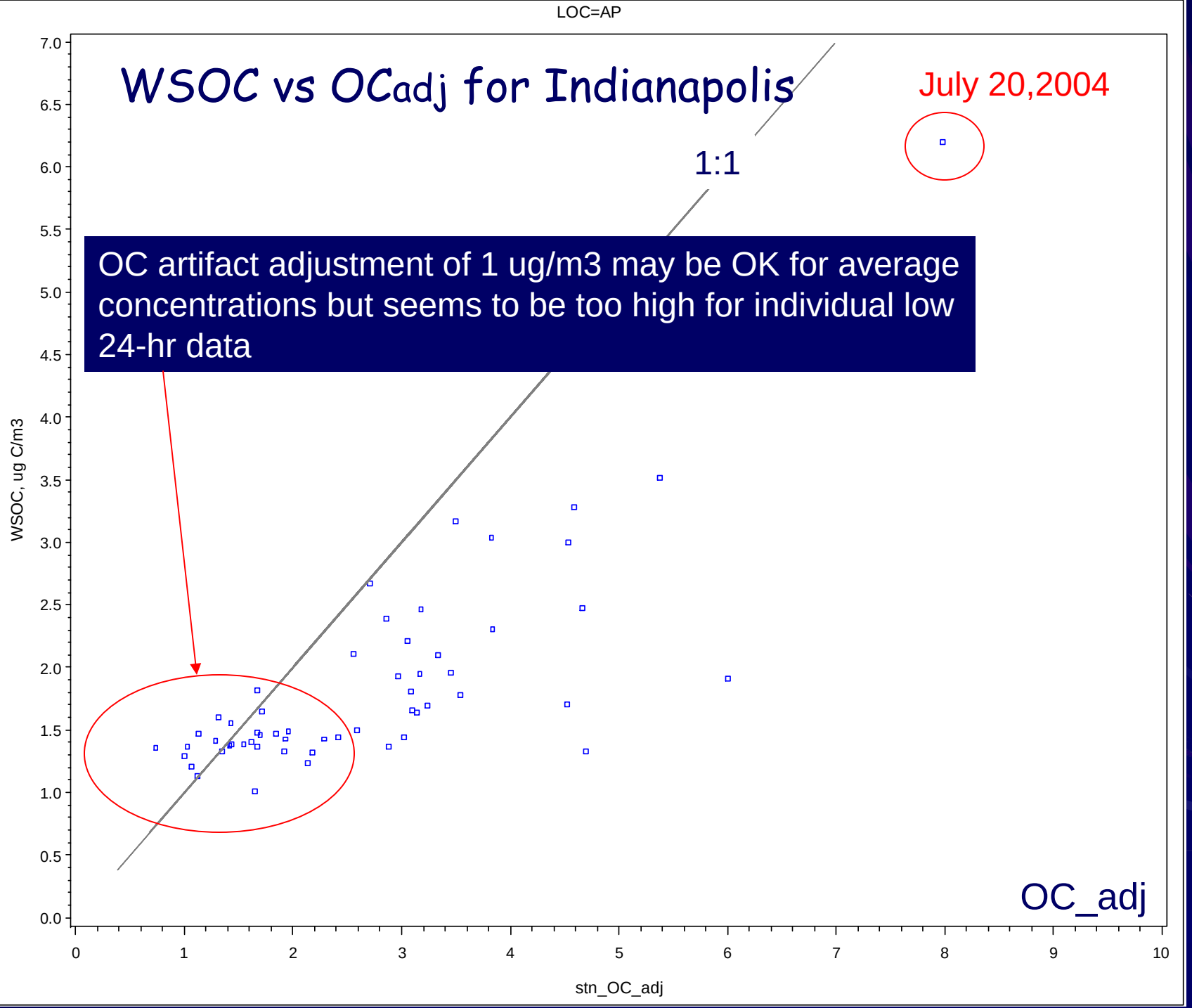


Figure 14. Correlations of WSOC vs. (a) the uncorrected STN OC data and (b) corrected STN OC data for all co-located FRM and STN sites. The correction applied is 1 µg C/m3 for the 2004 data and 1.1 µg C/m3 for the 2005 data.


LOC=AP
WSOC vs OCadj for Indianapolis
July 20,2004
1:1
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
WSOC, ug C/m3
stn_OC_adj
OC_adj
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
0
1
2
3
4
5
6
7
8
9
10

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)

Much higher levoglucosan concentrations in winter and spring.

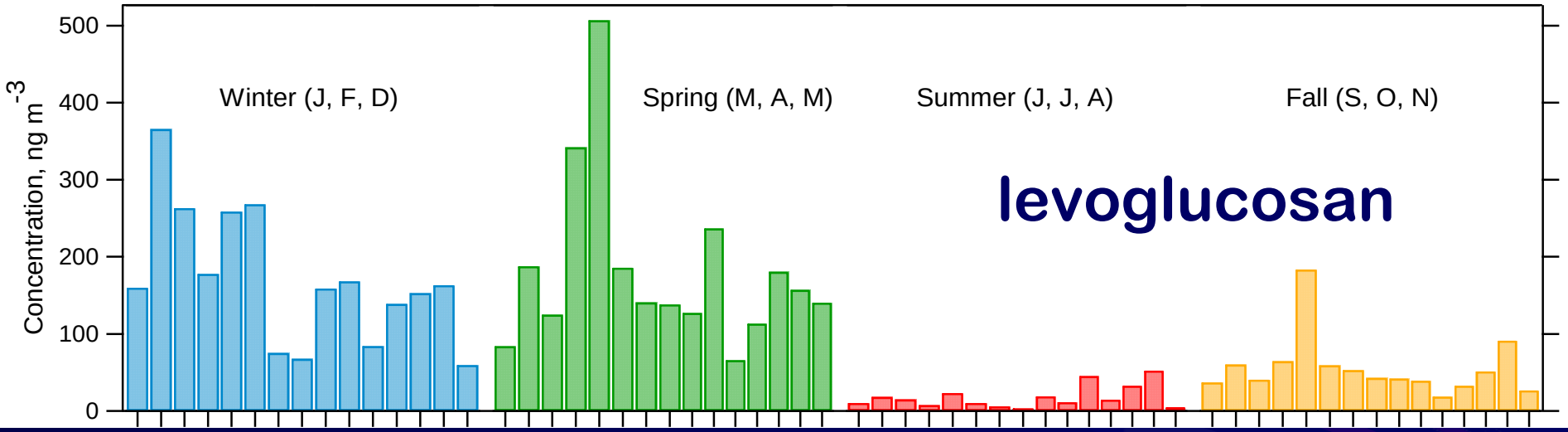


Figure 3. Seasonal-averaged (Winter, Spring, Summer, Fall) levoglucosan concentrations at each site.

From Xiaolu Zhang, et.al. .(AAAR)

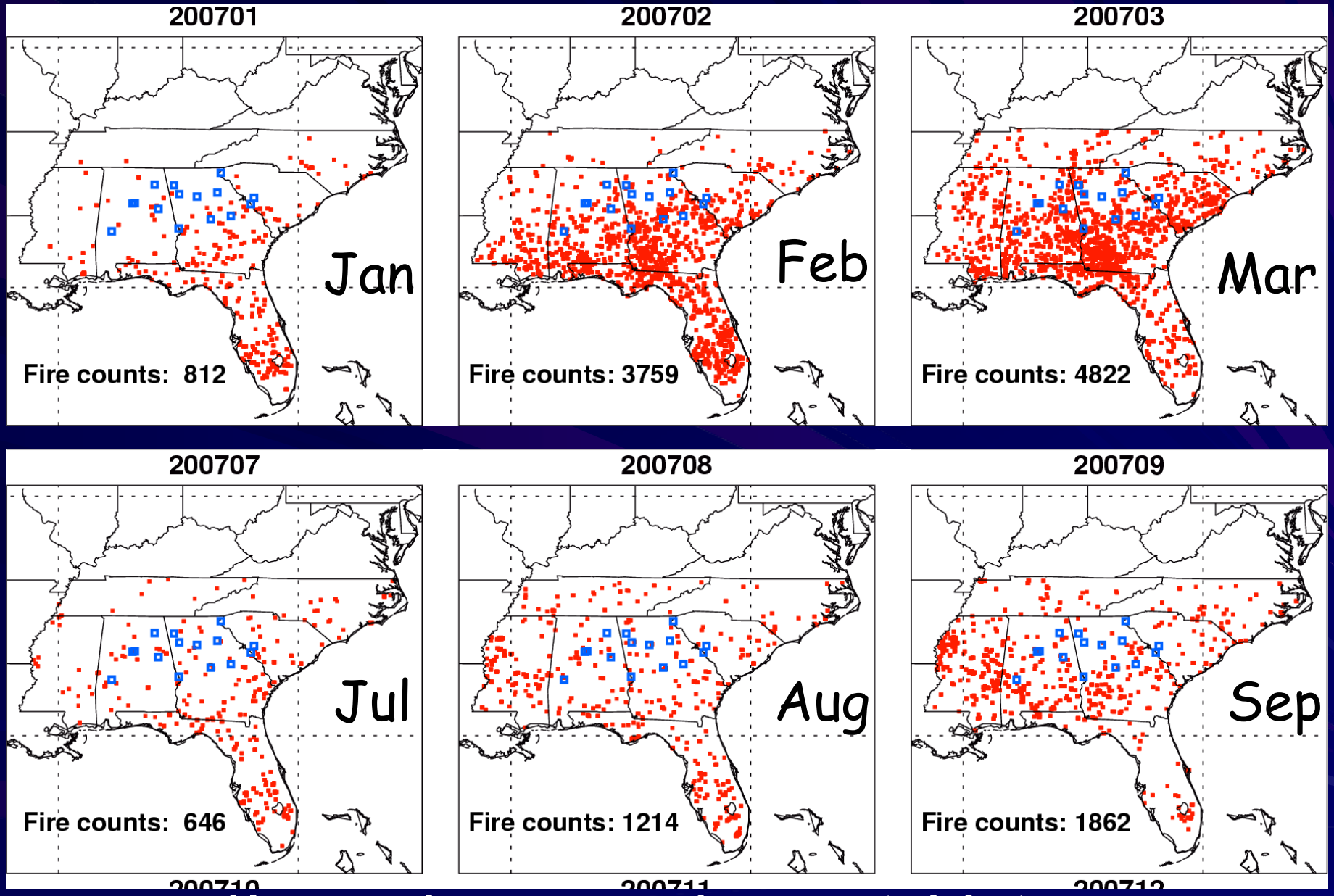
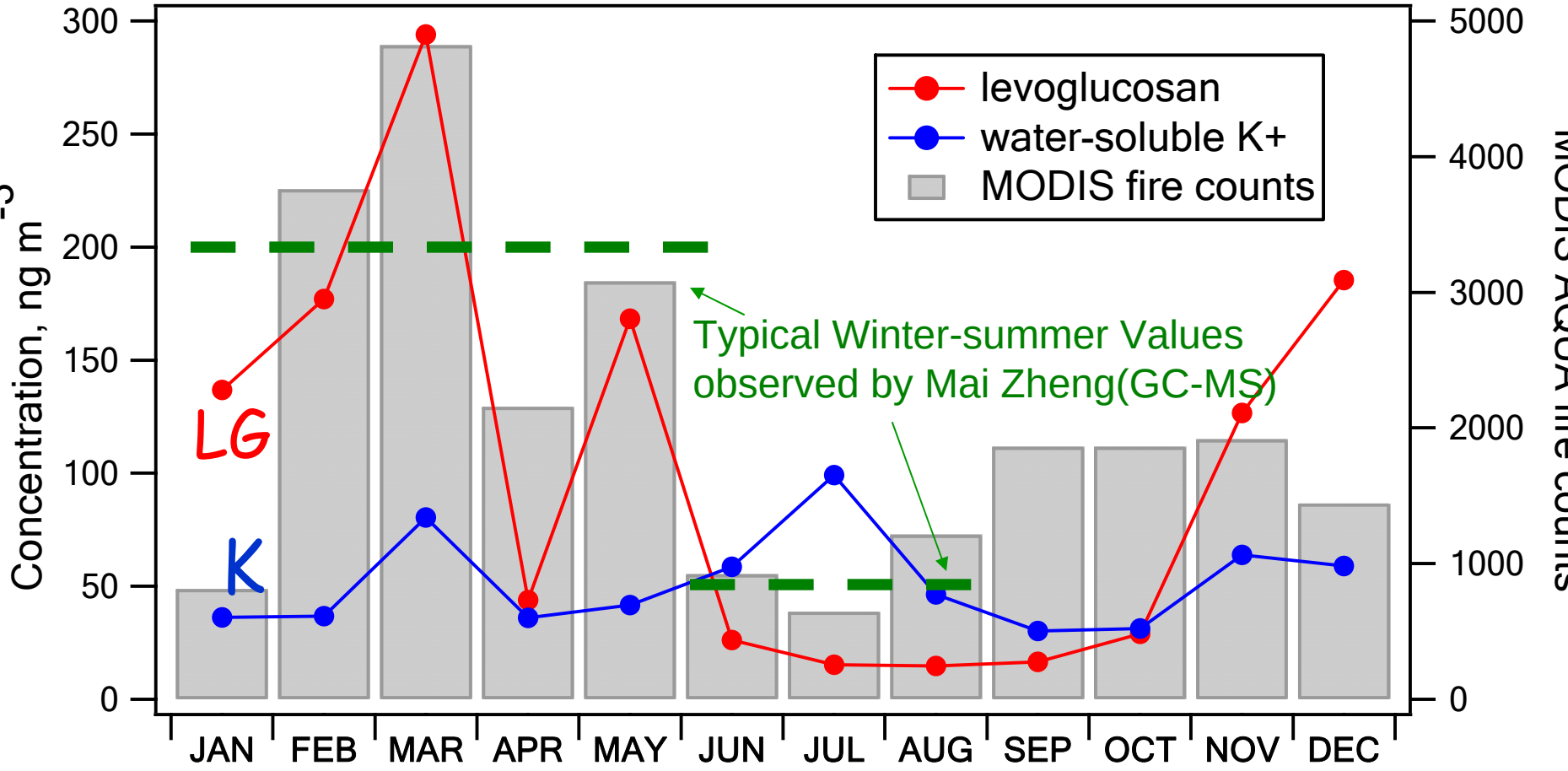


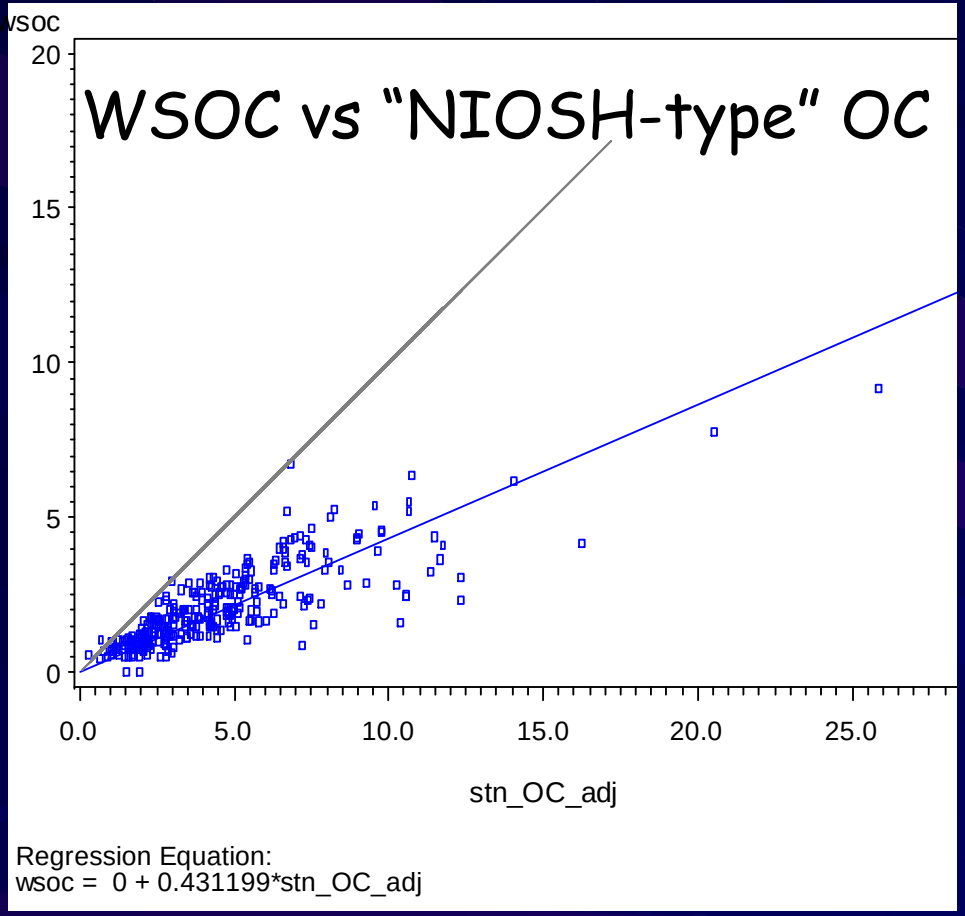
Figure 5. Monthly averaged Aqua MODIS fire counts (red dots) in 2007 over 7 states in southeastern U.S. Sampling sites are shown as square blue symbols.

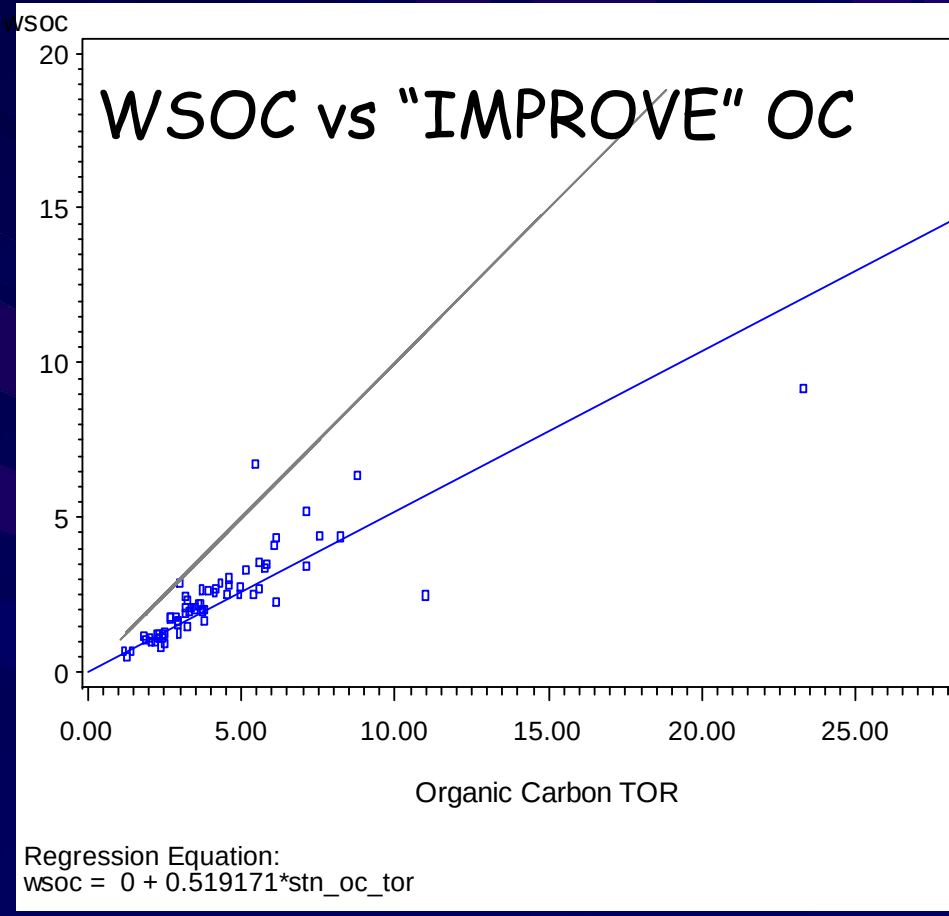
Fire counts monthly variation more closely matches the levoglucosan pattern compared with potassium



From Xiaolu Zhang, et.al. (AAAR)

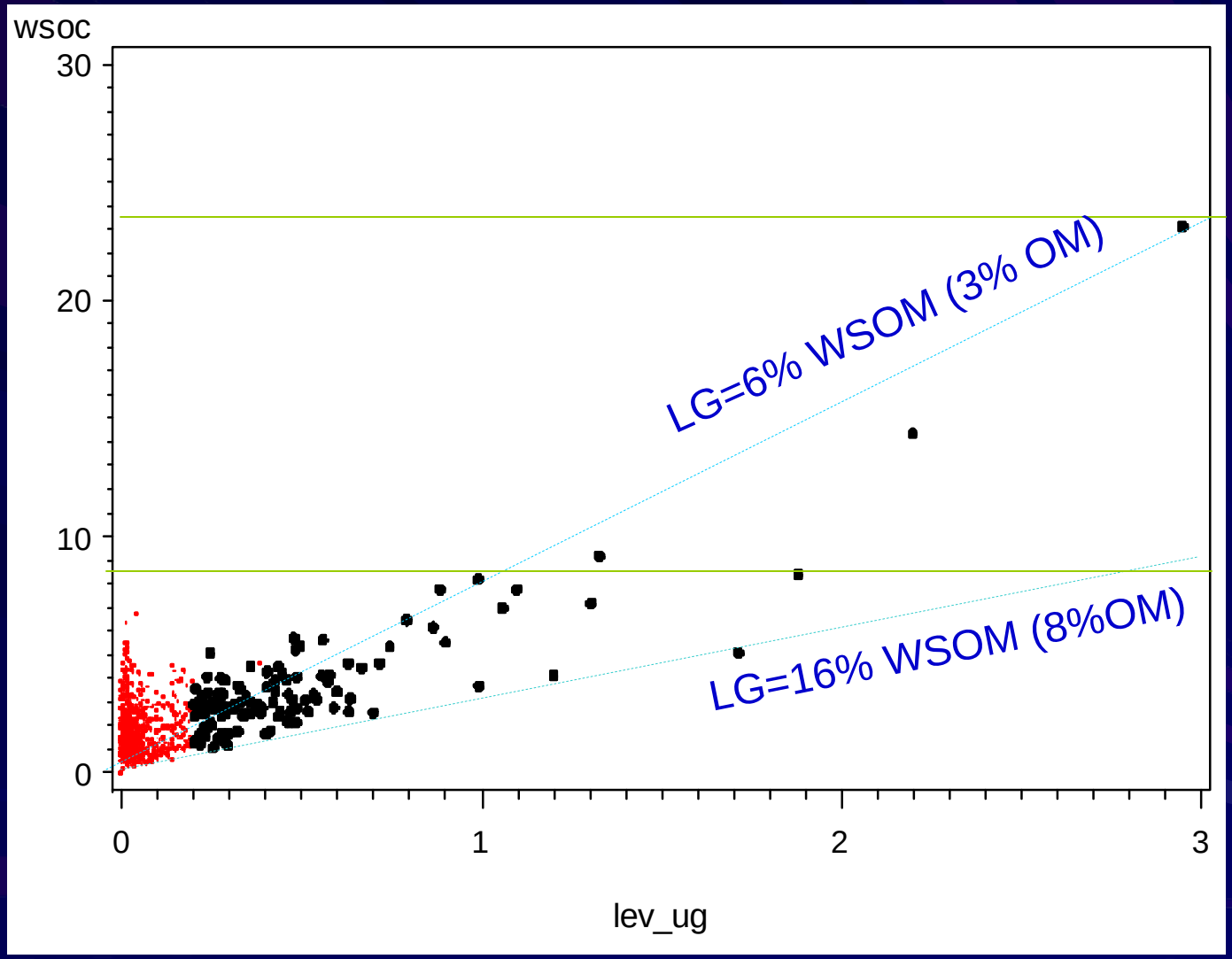
In the SE, WSOC (on Teflon) = ~ 43-50% of OC





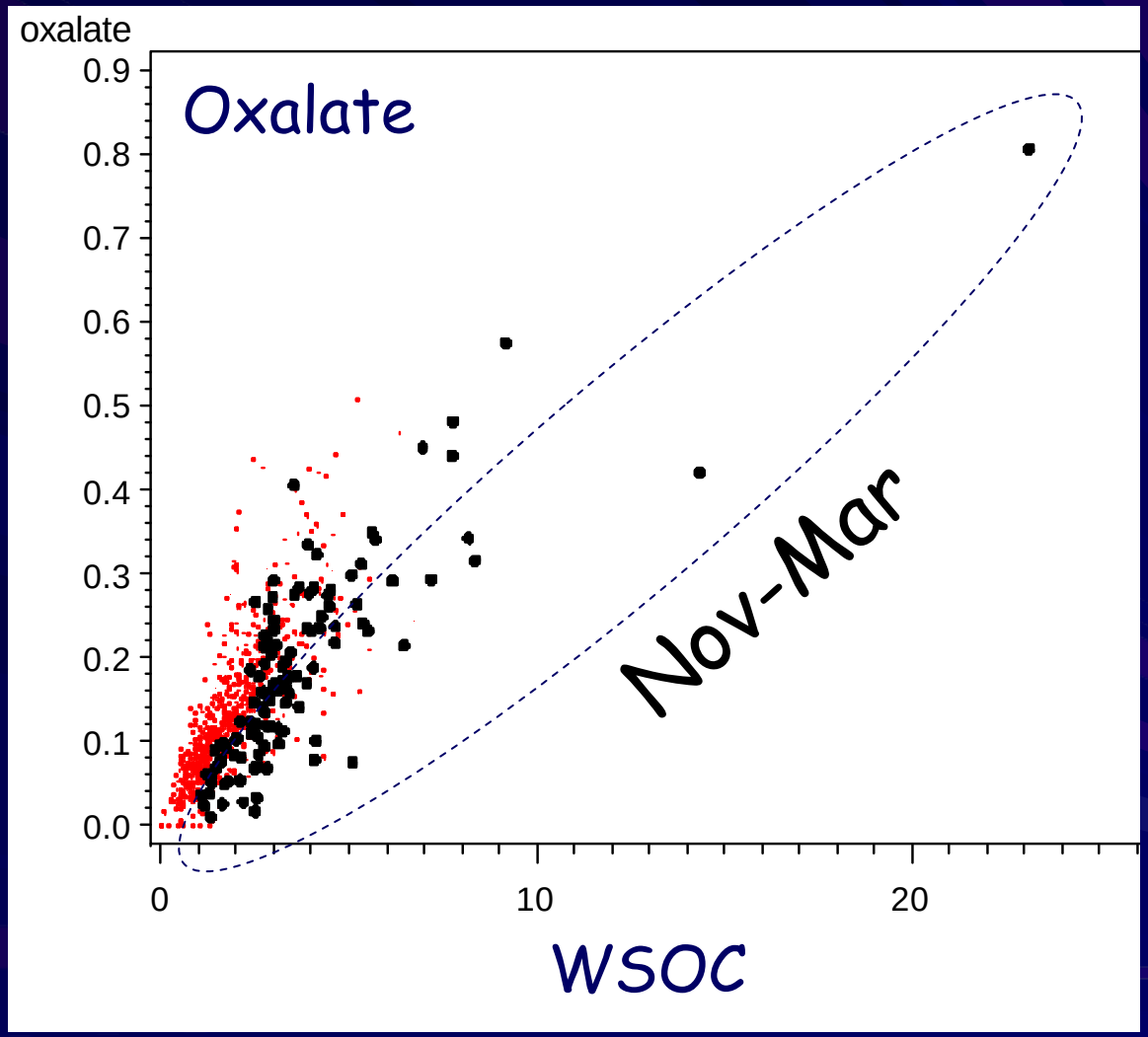
OC is measured on quartz and is adjusted for sampling artifact by subtracting 1 ug/m3 for NIOSH-type TOT method and 0.4 ug/m3 for IMPROVE_A TOR method

Winter WSOC is correlated with LG (Biomass Combustion)

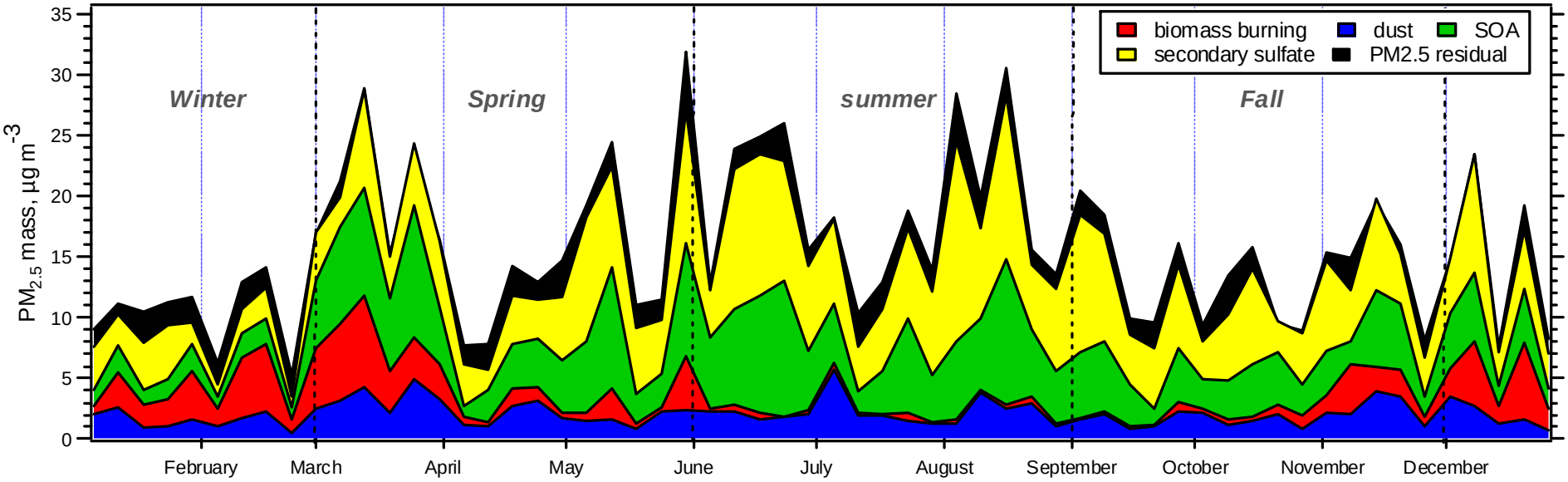


LG / WSOC = 1/3 to 1/8 LG/WSOM=1/6-1/16= 0.16 – 0.06

In the SE, oxalate is ~ 5-10% of WSOC
It appears to also correlate with Biomass Burning



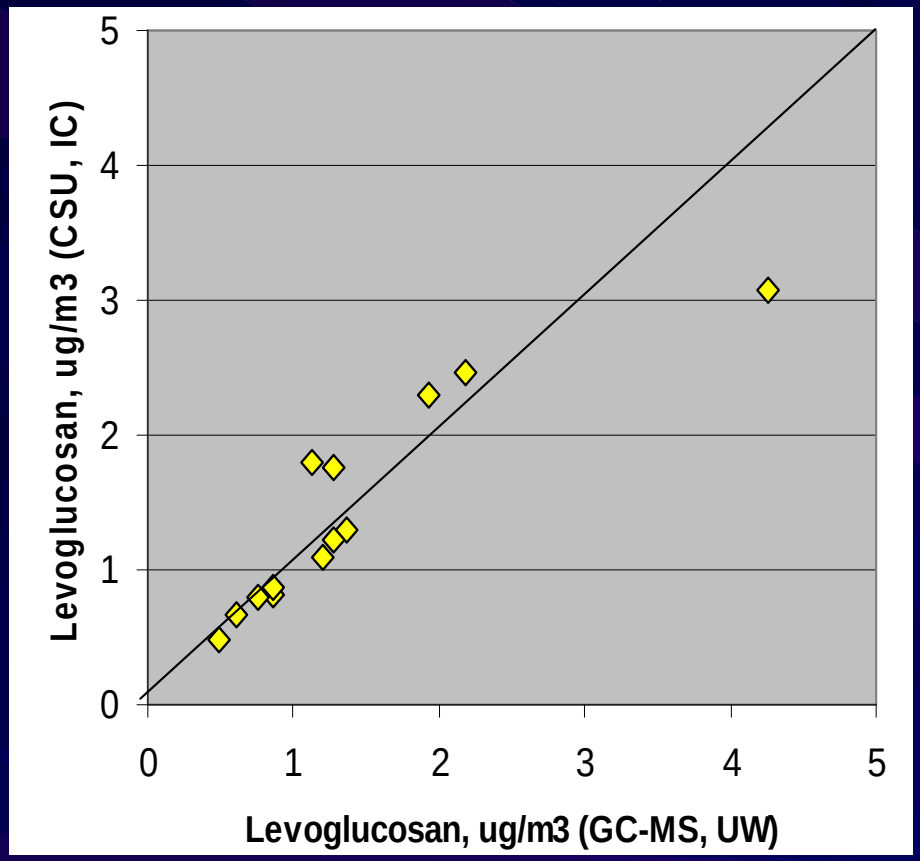
In the Southeast,
Biomass burning showed significant enhancement in winter, contributing 24% of the total $PM_{2.5}$ mass.



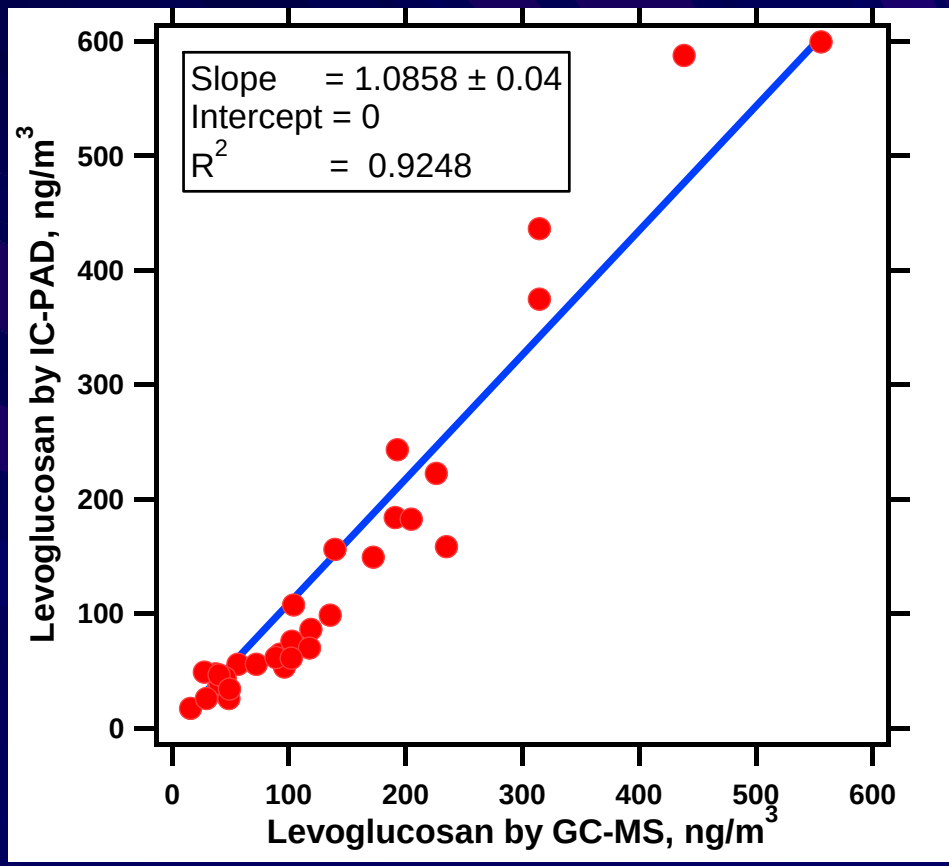
From PMF analysis, Xiaolu Zhang, et.al. .(AAAR)

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!