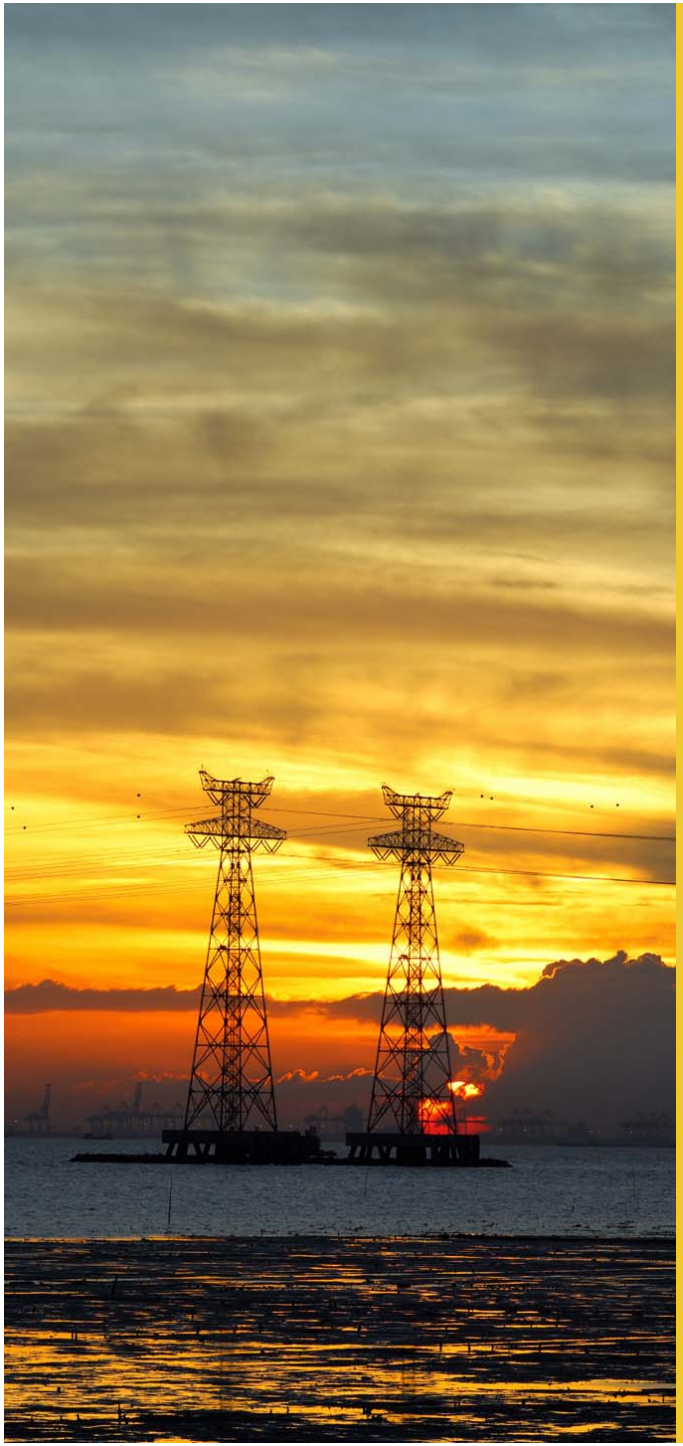


RUTGERS

Center for Advanced Infrastructure and Transportation

A U.S. Department of Transportation
University Transportation Center

Environment and Energy Program (EEP)

Urban Sources of Fine Particles >>

A Look At Biomass Smoke Emissions

MARAMA Monitoring Committee
Prof. Monica Mazurek, Civil & Environmental Engineering Department
February 24, 2009

Markers for source apportionment >>

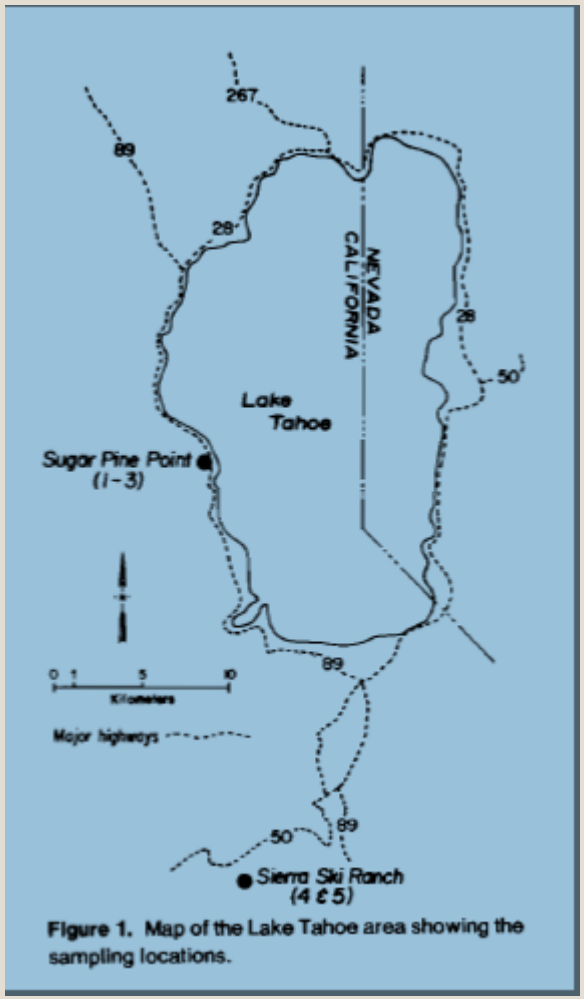


Figure 1. Map of the Lake Tahoe area showing the sampling locations.

Simoneit et al. 1980, *JAPCA 30*, 387-390

Contamination of the Lake Tahoe Air Basin by High Molecular Weight Petroleum Residues

Bernd R. T. Simoneit, M. A. Mazurek
Institute of Geophysics and Planetary Physics
University of California, Los Angeles

T. A. Cahill
Air Quality Group, Crocker Nuclear Laboratory
University of California, Davis

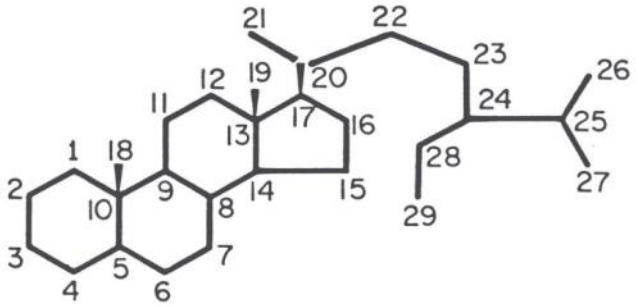
The atmosphere of the Lake Tahoe air basin is contaminated with high molecular weight ($> C_{12}$) petroleum hydrocarbons. Aerosol samples were collected by high-volume filtration and the solvent-soluble organic matter was analyzed. The relative concentrations of petroleum residues found were as follows: winter > summer and day > night. This contamination is primarily due to the poorer combustion of diesel and home heating fuels at that altitude and during periods of colder climate.

eluent mixture. Several sample extracts were saponified with NaOH in methanol prior to esterification. After development with iodine vapor, the bands corresponding to hydrocarbons and esters with ketones were scraped from the TLC plate and eluted with methylene

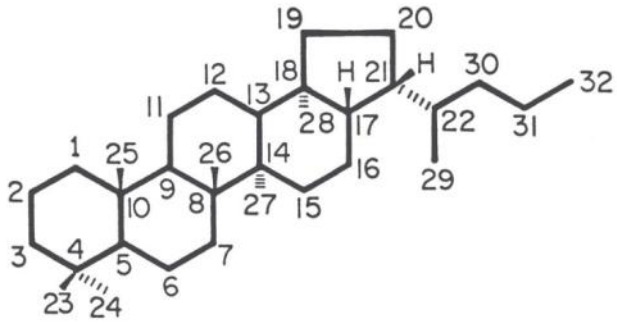
Petroleum biomarkers >>

- Characterization crude oils
- Geochemical evidence oil field evaluation
- Distribution patterns homologs large organic
- Sources.....

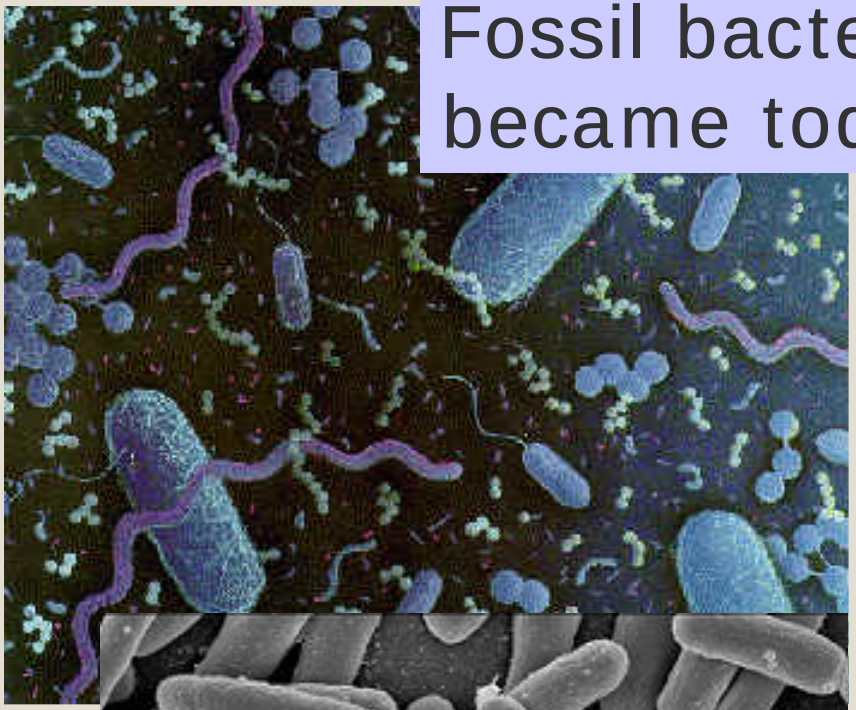
STERANES

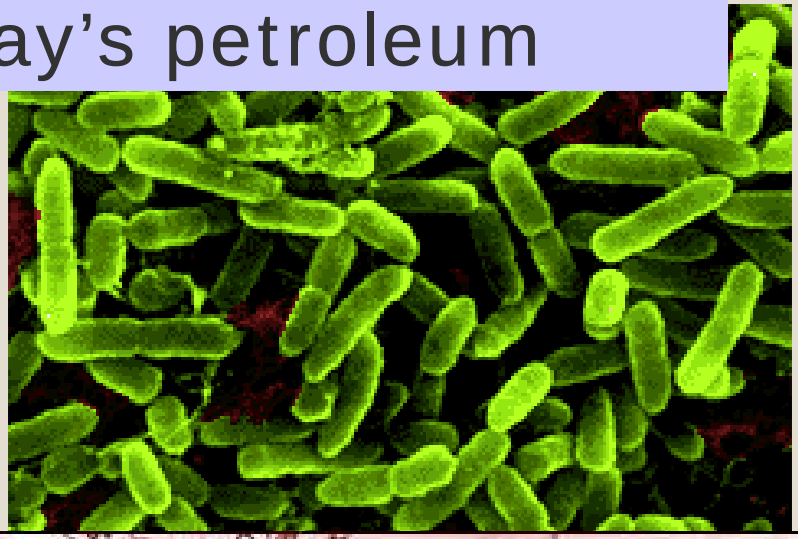


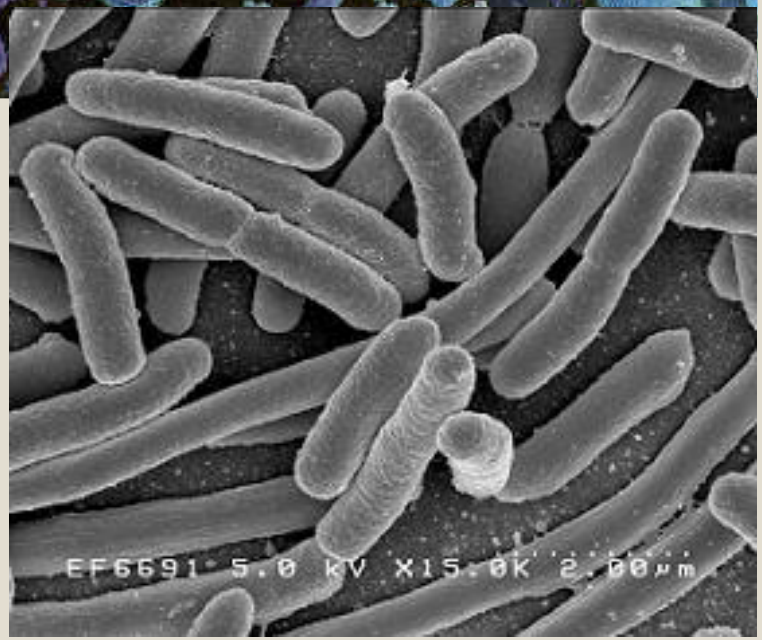
HOPANES



Fossil bacteria and microbiota became today's petroleum







PM origin from petroleum >>

Lake Tahoe winter PM
hopanes & steranes

Southern California Bight sediment
hopanes & steranes

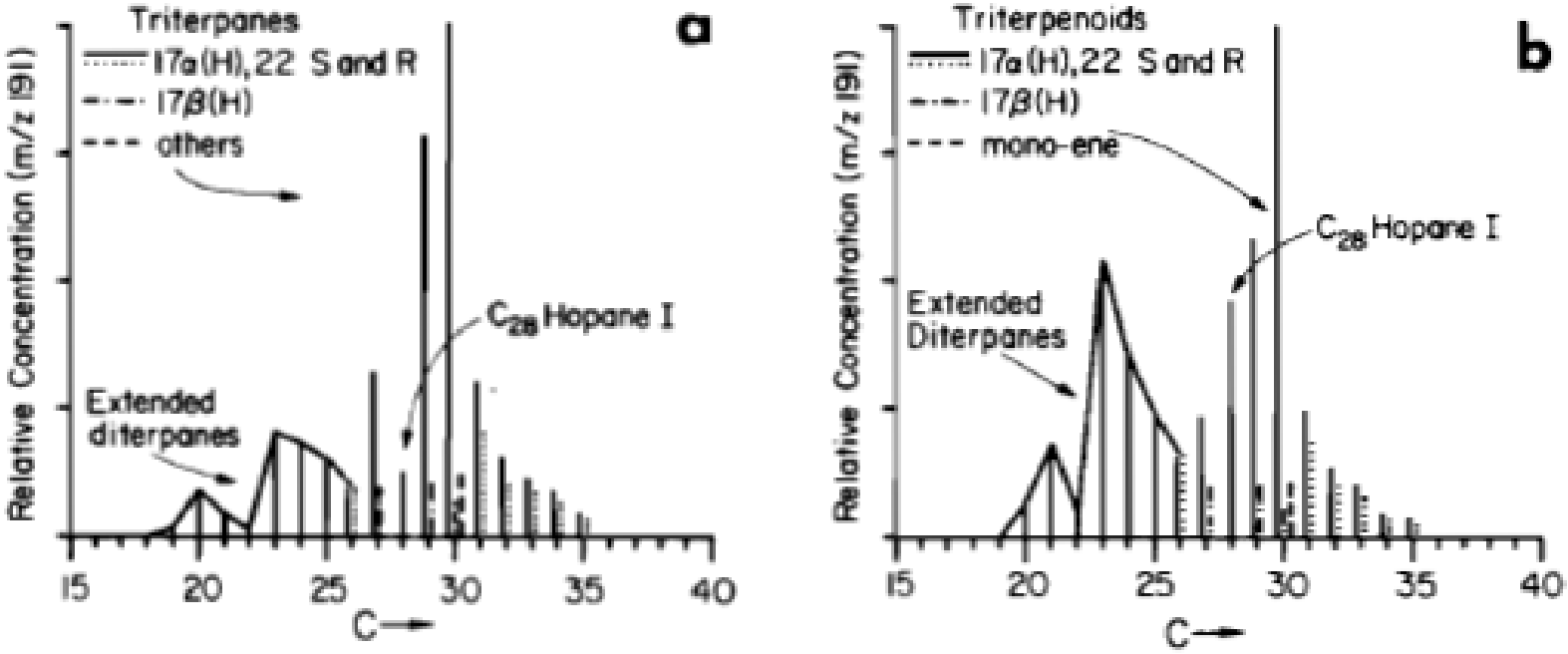


Figure 3. Relative distribution histogram for extended diterpanes and triterpanes (based on the m/z 191 mass chromatograms of the GC/MS data) for an example of Lake Tahoe aerosol and a sediment from the Southern California Bight which is contaminated by petroleum seepage. (a) Sample 3, Sugarpine Point State Park, winter; (b) Sample 193, seabed Santa Barbara Basin (reference 5). The R and S diastereomers are also indicated and C_{28} hopane I is

Simoneit et al. 1980, *JAPCA 30,* 387-390

Receptor modeling and CMB-MM >>

Professor Glen Cass

Urban sources of fine PM >>

Los Angeles, CA fine particle emissions inventory

- Oil-fired boiler
- Autos (non- and catalyst-equipped)
- Heavy-duty diesel trucks
- Home heating furnace
- Home fireplace
- Roofing tar pots

- Road dust
- Tire dust
- Brake dust
- Cigarette smoke
- Meat cooking operations
- Vegetation (cultivated, native)

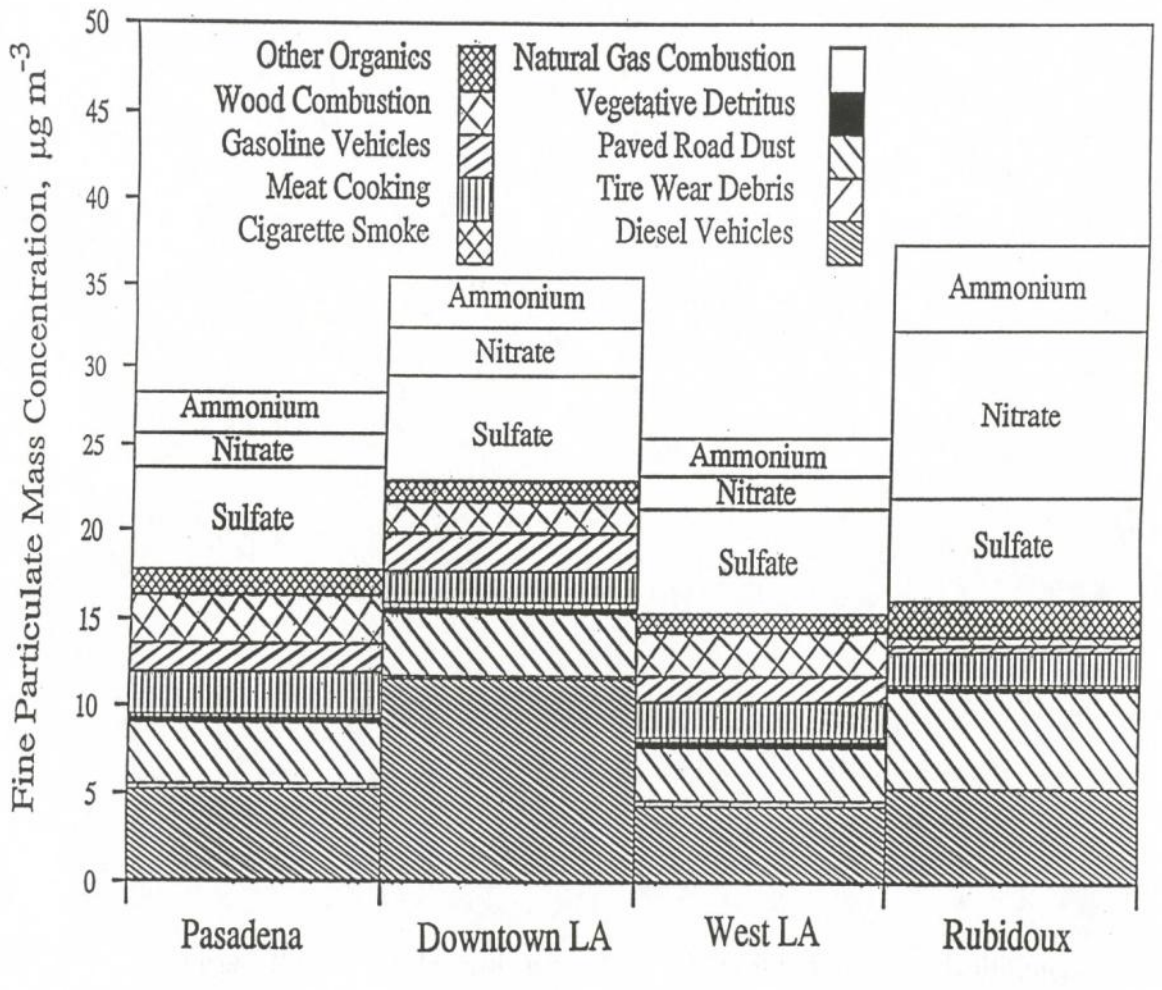
Mathematical Models Accounting for Individual Emission Contributions from Discrete Urban Sources

Urban sources of fine PM2.5 >>

Chemical Mass Balance Molecular Marker (CMB-MM) source estimation approach

- Emissions inventories for major sources PM2.5
- Ambient fine particle sampling network for a complete annual cycle
- Source emission tests to produce chemical mass balance profiles

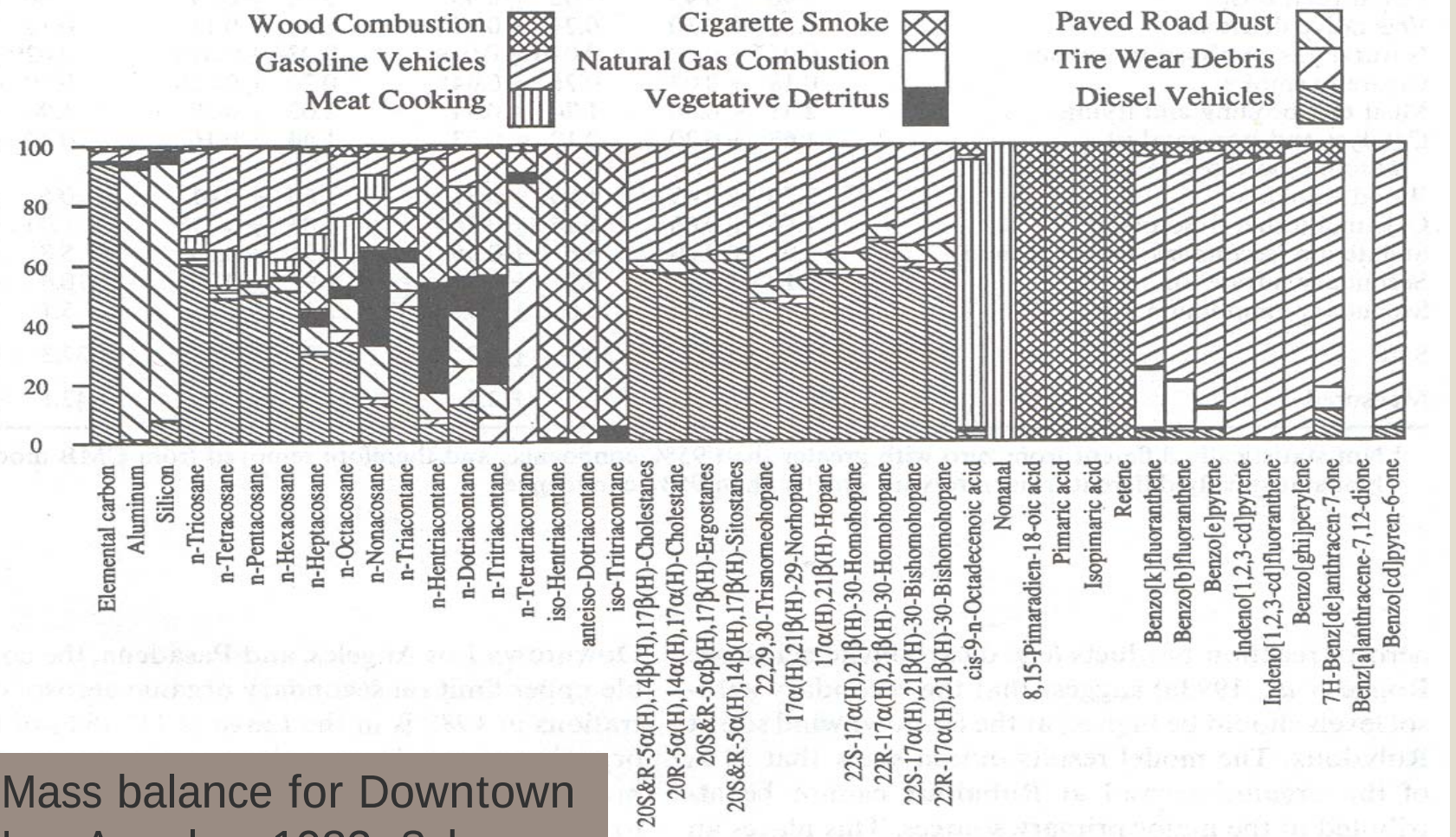
1982 Annual Mass Averages Metropolitan Los Angeles, CA



Credit: Schauer et al., *Atmos. Environ.,* 1996

Modeled source contribution >>

Chemical Mass Balance-Molecular Marker Model (CMB-MM)



Mass balance for Downtown Los Angeles, 1982, Schauer et al., 1996

Urban plume markers >>

- Motor vehicle exhaust (hopanes & steranes)
- Cooking emissions (cholesterol)
- Biomass/cellulose combustion (levoglucosan)
- Elemental carbon

SOAP 2002-2007 Field Program >>

What is the organic composition of PM 2.5?

What are its sources?

What components are directly emitted vs. secondary?

NY, NJ CT Fine Particulate Matter Study (NYSERDA) >>
NYDEC, NJDEP, CTDEP, SUNY-Albany

Toll Plaza 13, NJ Turnpike Elizabeth, NJ >> 220,000 motor vehicles per day

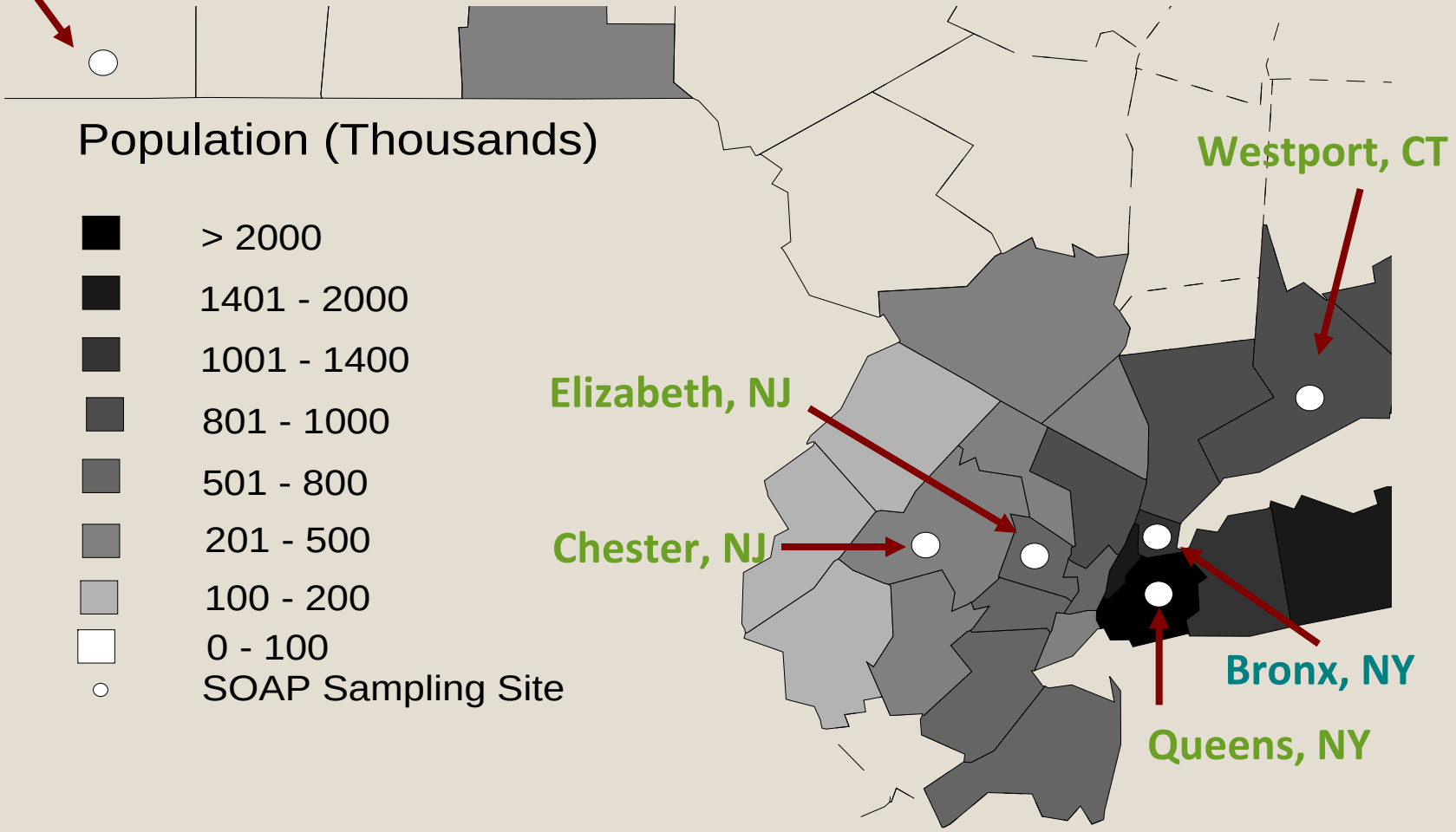
SOAP 2002-2007 Field Program >>

Pinnacle State Park, NY

PM2.5 >>

SOAP '02-'03 10 composites per site

SOAP '05-'07 16 composites per site



SOAP 2002-2007 Markers >>

Alkanes

n-pentacosane
n-hexacosane
n-heptacosane
n-octacosane
n-nonacosane
n-triacontane
n-hentriacontane
n-dotriacontane
anteiso-triacontane
iso-hentriacontane
anteiso-hentriacontane
iso-dotriacontane
anteiso-dotriacontane
iso-tritriacontane
phytane
pristane

PAHs (22 total)

benzo[b]fluoranthene
benzo[k]fluoranthene
benzo[e]pyrene
indeno[1,2,3-cd]pyrene
indeno[1,2,3-cd]fluoranthene
retene
coronene

Acids

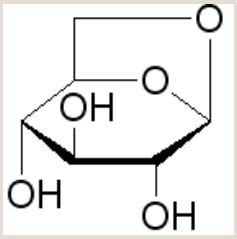
21 *n*-alkanoic acids (with C_{10} to C_{30})
10 aliphatic dicarboxylic acids (C_3 to C_{10})
1 aromatic polycarboxylic acid
cis-9-n-octadecenoic acid

Other

hopanes
steranes **Combined**
nonanal
diterpenoids
sterols
cholesterol
7H-benz[de]anthracen-7-one
benz[a]anthracene-7,12-dione

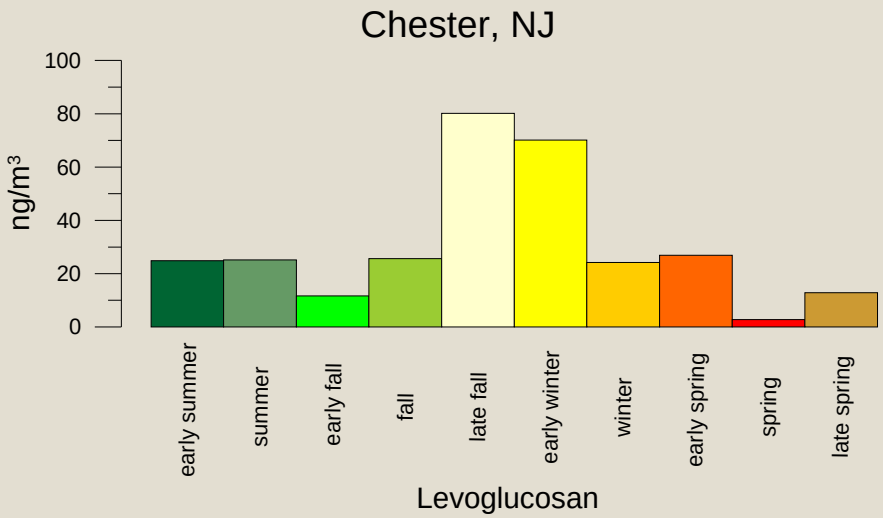
Over 100 individual organic markers quantified in SOAP 2002-2007 PM2.5 ambient samples

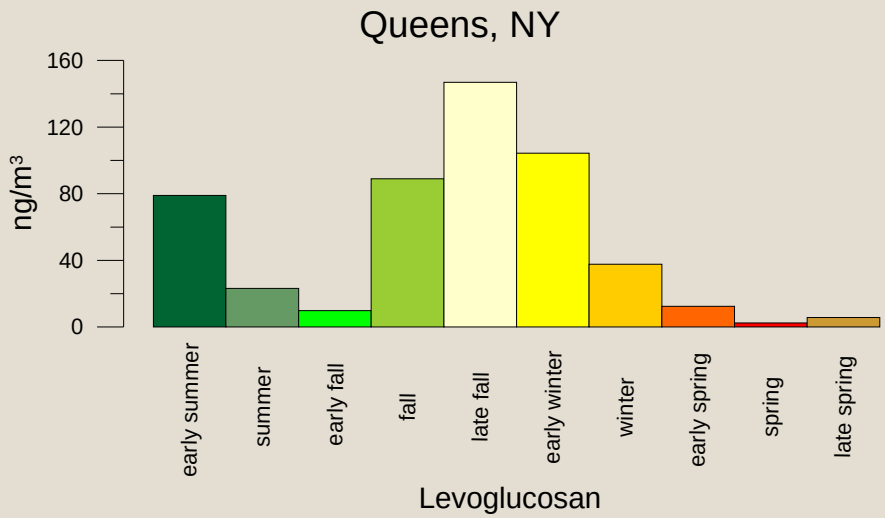
Levoglucosan >>

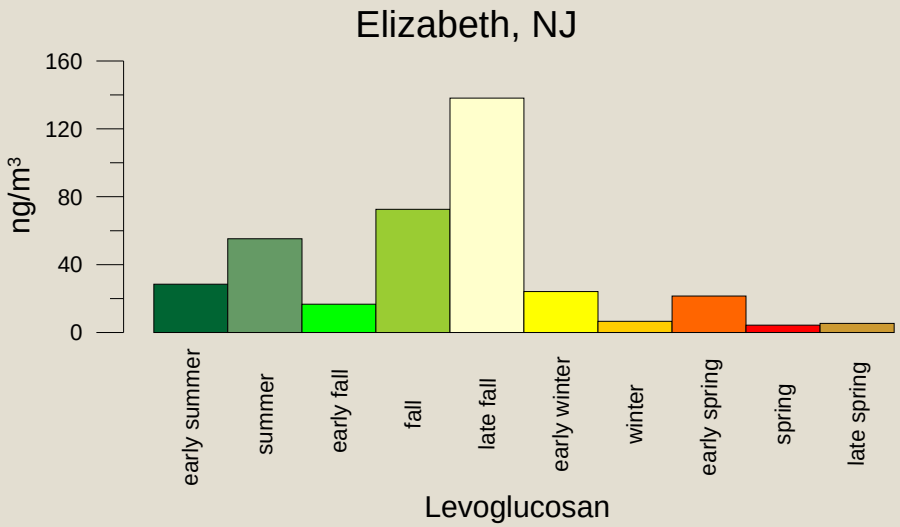


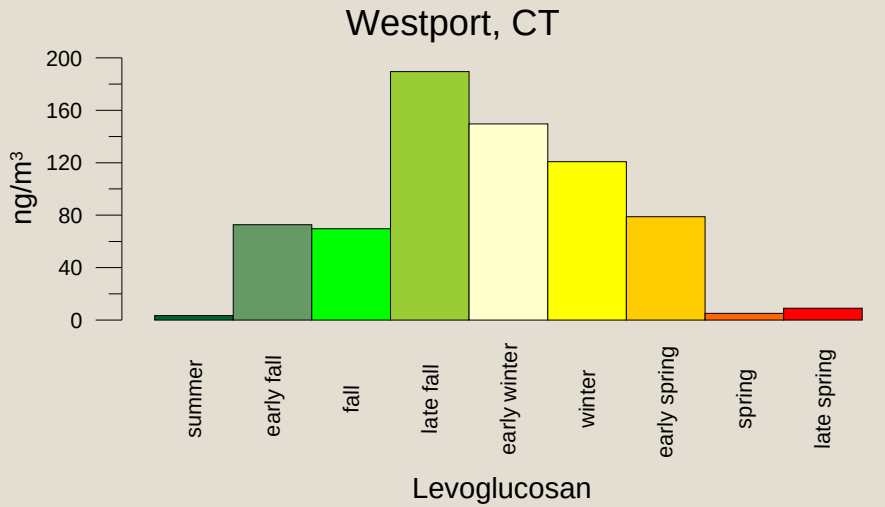
- A biomarker for the pyrolysis of cellulose ($C_6H_{10}O_5$)
- Is produced from man-made and natural combustion activities
- Is unique as a smoke marker, stability in aqueous phase << solid phase
- Is associated with particulate phase because of MW (162 amu)
- Is a polar compound that is soluble in water, alcohols, acetone
- Emission rates measured from different cellulose combustion sources

SOAP 2002-2003 Sites >>

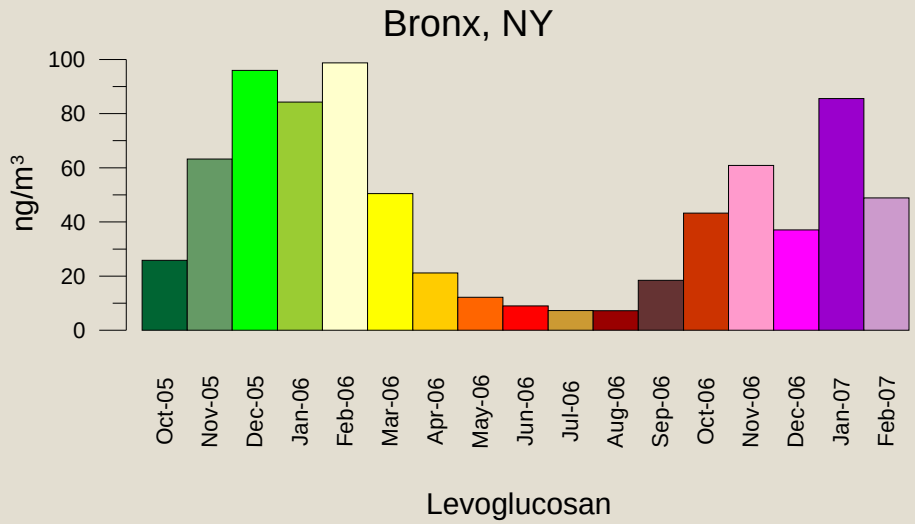


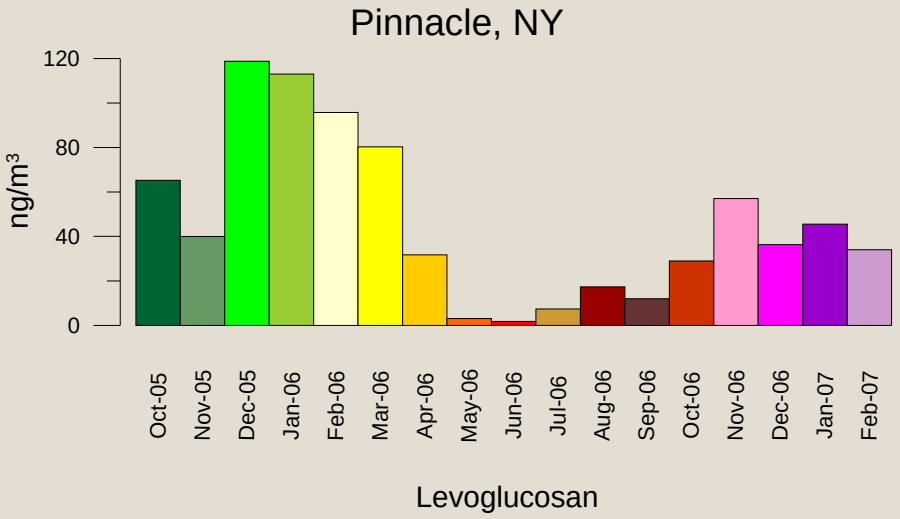






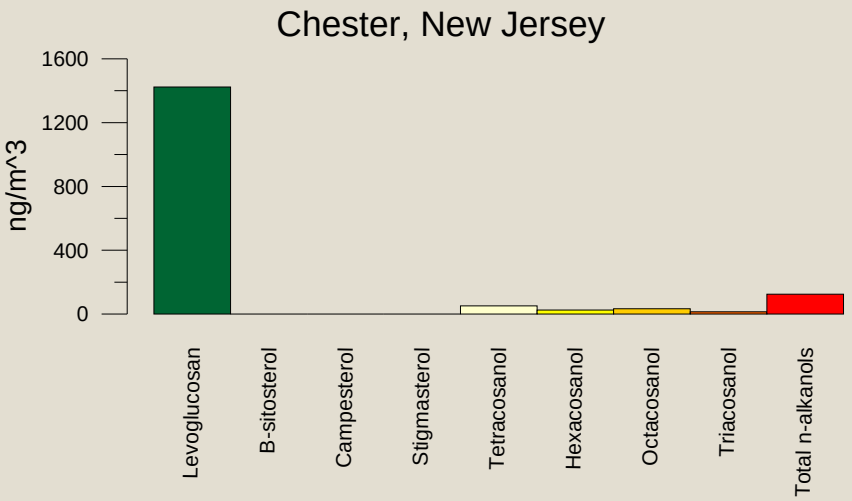
SOAP 2005-2007 Sites >>

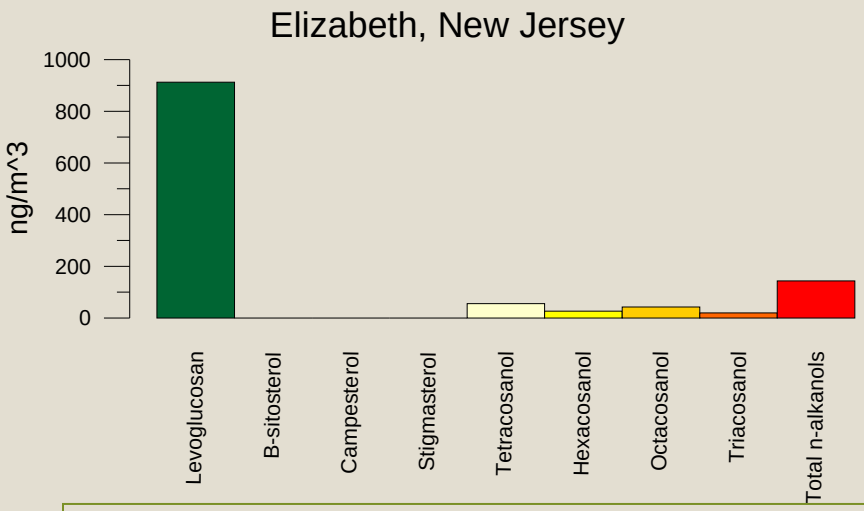


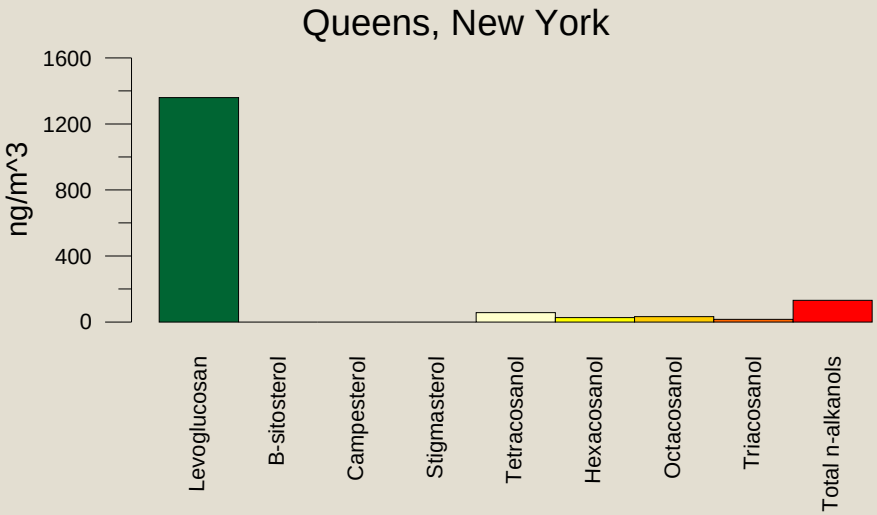


- Interannual concentration differences could be due to meteorological conditions and/or emission source strength

Quebec Wildfires July 2, 2002 >>







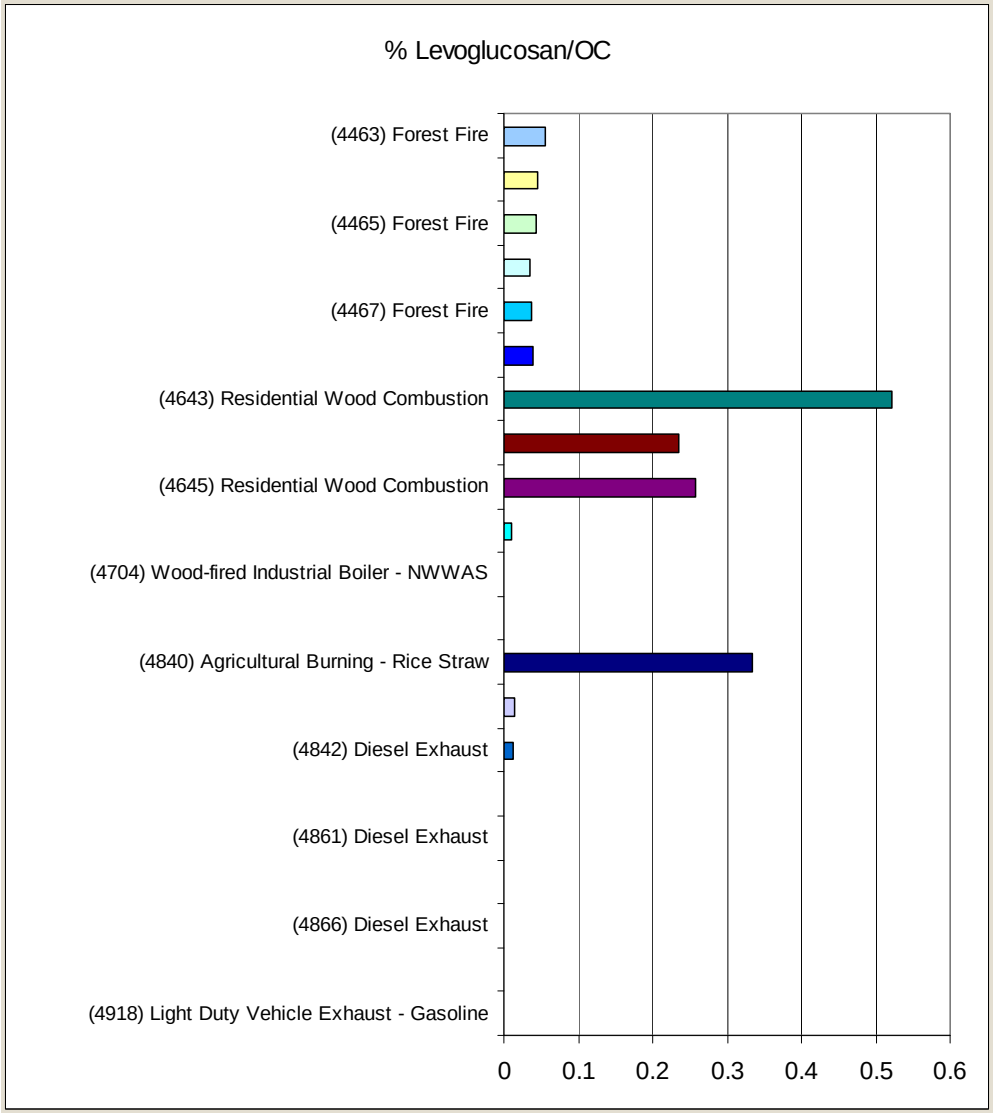
- Higher regional smoke concentrations found for SOAP 2002-2003 due to persistent wildfires in the western US and Canada.
- Levoglucosan was 10 times higher than any sample for SOAP 2002-2003

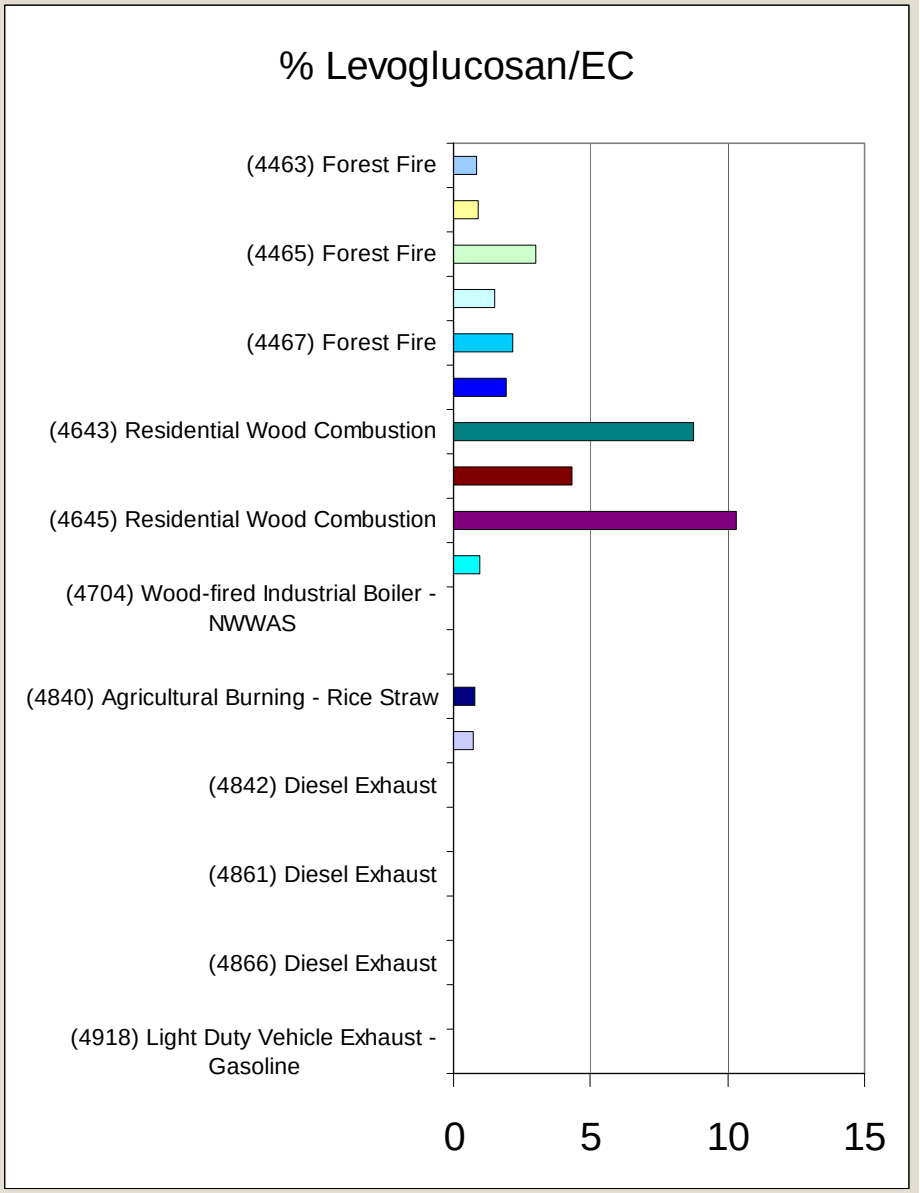
Levoglucosan SOAP 2002-2007 >>

U.S. Winter Concentrations Comparison

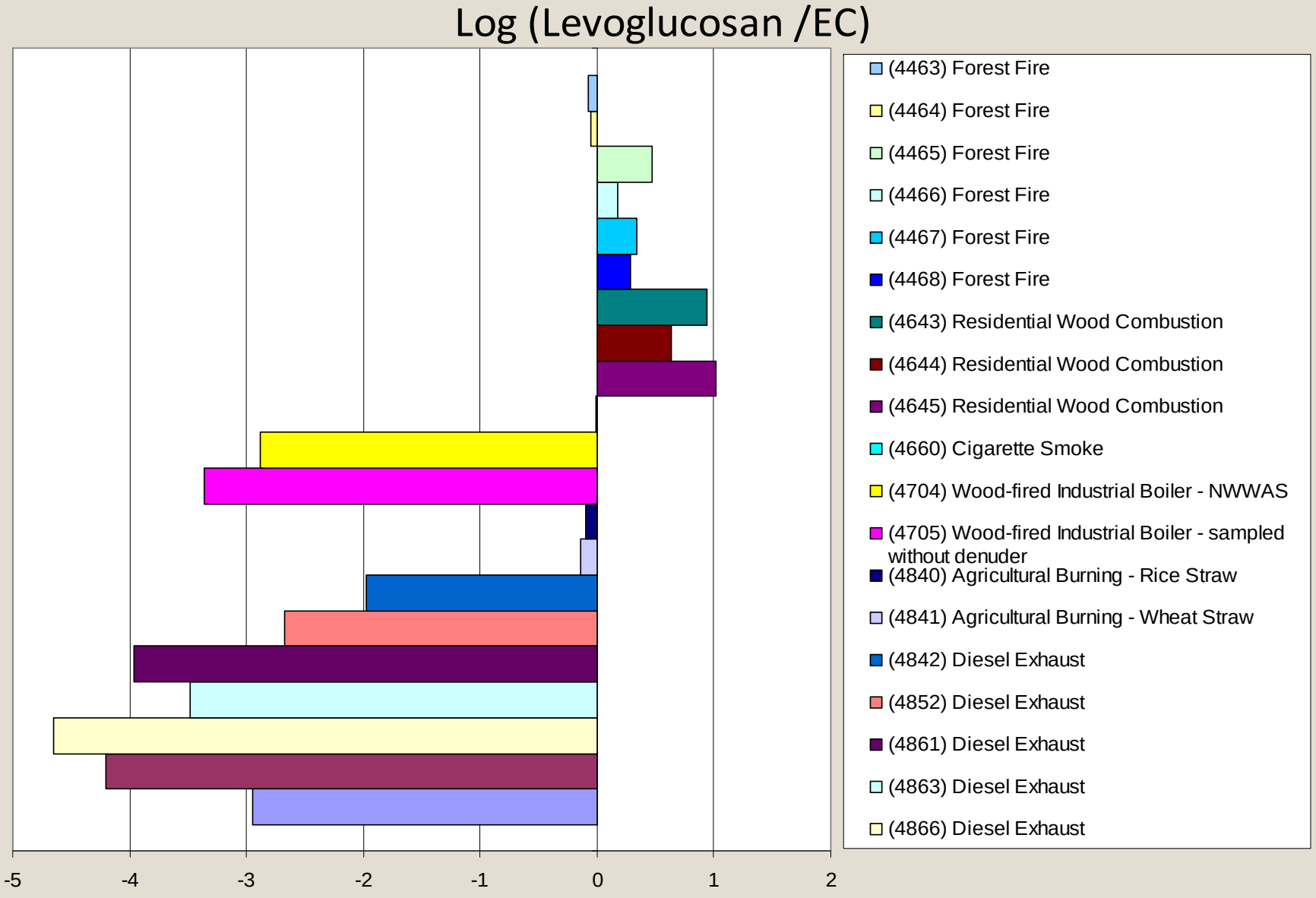
Reference	Location (Study Period)	Levoglucosan, ng/m^3
Fine et al. (2004)	Los Angeles, CA (1/13-1/17/2003)	44
Robinson et al. (2006)	Pittsburgh, PA (12/2001-1/2002)	26
Sheesley et al. (2007)	Charlotte, NC (Mid-October – December, 2003)	196
Sheesley et al. (2007)	Charlotte, NC (Mid-October – December, 2004)	519
Sheesley et al. (2007)	Hickory, NC (Mid-October – December, 2003)	329
Sheesley et al. (2007)	Hickory, NC (Mid-October – December, 2004)	198
Sheesley et al. (2007)	Winston-Salem, NC (Mid-October – December, 2003)	240
Sheesley et al. (2007)	Lexington, NC (Mid-October – December, 2004)	504
Nolte et al. 2001	San Joaquin Valley, CA (12/5/1995-1/6/1996)	106
Nolte et al. 2001	Bakersfield, CA (12/5/1995-1/6/1996)	2390
Nolte et al. 2001	Fresno, CA (12/5/1995-1/6/1996)	2980
Gorin et al. 2006	Fresno, CA (12/25/03-1/15/04)	600
Zheng et al. (2007)	Atlanta, GA (1/2/2002-1/31/2001)	433
This Study	Queens, NY (winter)	37.7
This Study	Elizabeth, NJ (winter)	6.7
This Study	Chester, NJ (winter)	24.2
This Study	Westport, CT (winter)	120.9
This Study	Bronx, NY (January, 2006)	84.3
This Study	Pinnacle State Park, NY (January, 2006)	113.0
This Study	Bronx, NY (January, 2007)	85.6
This Study	Pinnacle State Park, NY (January, 2007)	45.5

U.S. EPA Speciate Emission Rates >>





Levoglucosan Emission Rates >>



Levoglucosan SOAP 2002-2007 >>

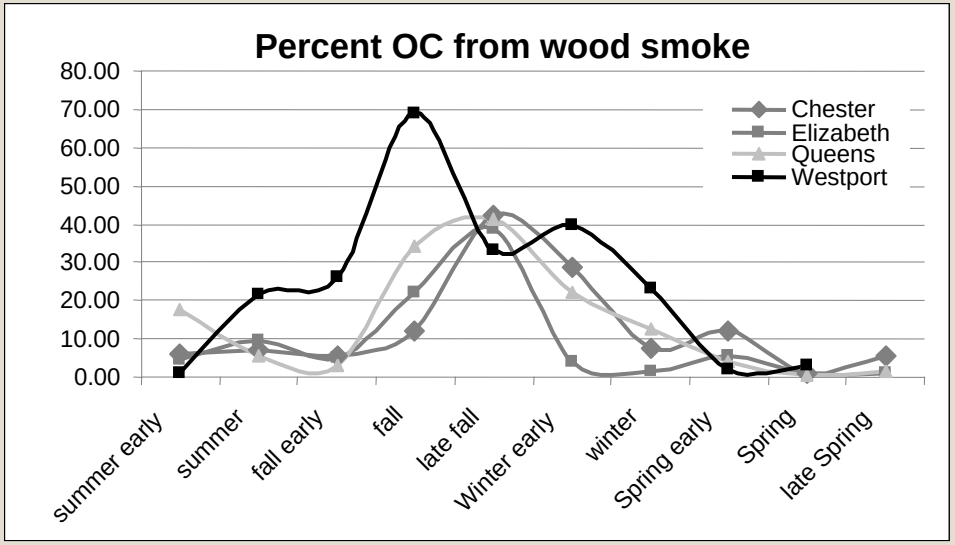
Conversion to % Ambient $PM_{2.5}$ OC Mass

$$\%\ OC = \frac{ng\ \ levoglucosan}{m^3} * \frac{m^3}{\mu g\ \ OC} * \frac{\mu g\ \ OC}{100\ \ ng\ \ levoglucosan} * 100\%$$

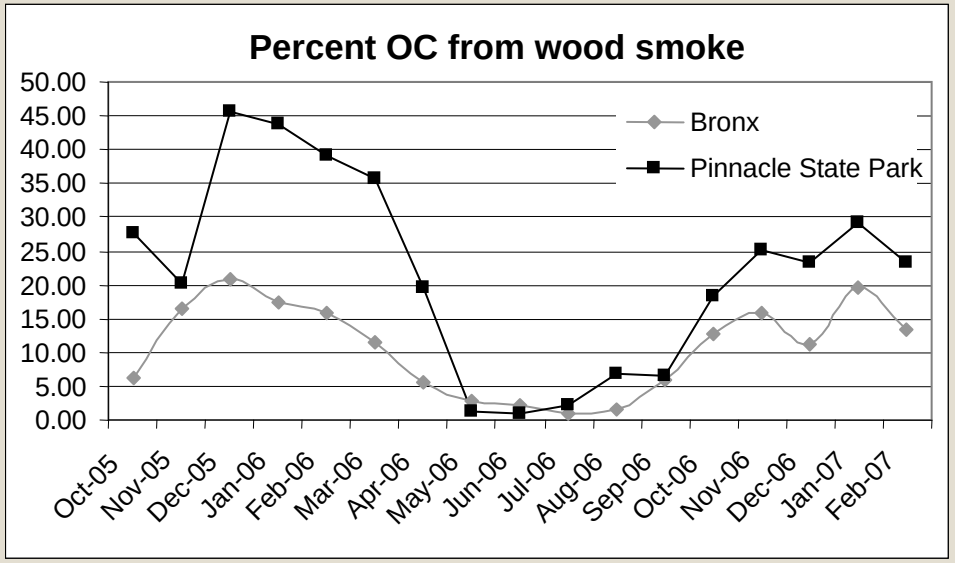
Emission factor averaged from Fine et al. 2001

Wood Smoke Estimate >>

SOAP 2002-2003
% OC mass from wood smoke



SOAP 2005-2007
% OC mass from wood smoke



Moving Forward >>

- More wood smoke emissions studies needed to improve chemical speciation and mass emission factors from biomass fuels from home heating, commercial cooking, fugitive sources (solid waste, structural fires, agricultural, food carts), and biofueled power plants
- Collaboration with U.S. EPA Biomass Emissions R&D Program (Gullett and Hays) provides fine PM emissions from wood and pellet stoves used in the NE US
- Search for additional biomarkers that can be used in combination with levoglucosan to identify emission sources

End of Presentation >>

Thank you

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