Character of Baltimore PM as derived from detailed Characterization of Molecular Organic Source Markers in 3-hr Samples

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Problem:

No knowledge available about the diurnal concentration patterns and dynamics of organic compounds associated with PM2.5

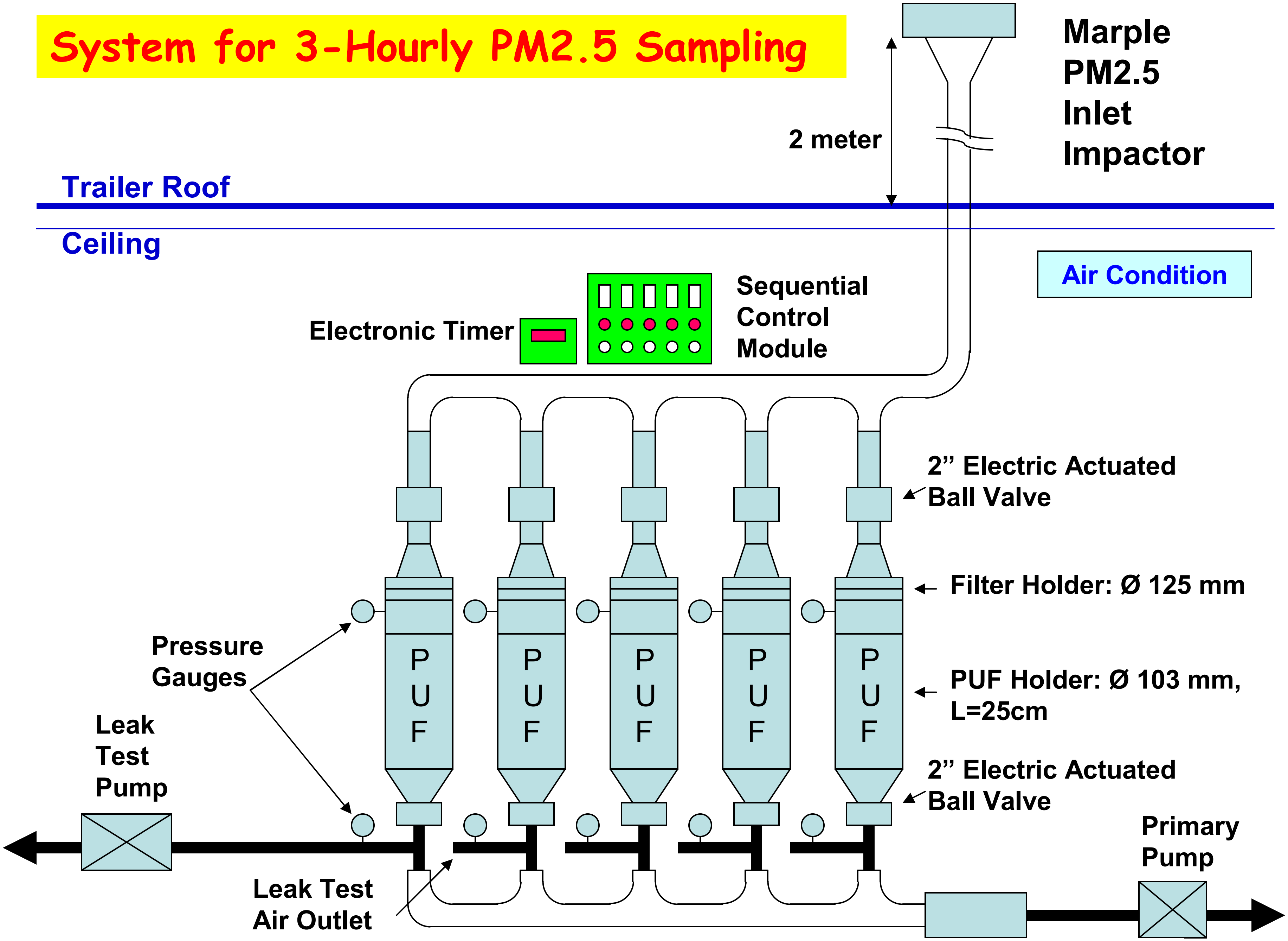
Time resolved data needed for:

- Health Effects Studies
- Atmospheric Chemistry
- Source/Receptor Reconciliation
- Regional Scale Atmospheric Transport Modeling

Approach:

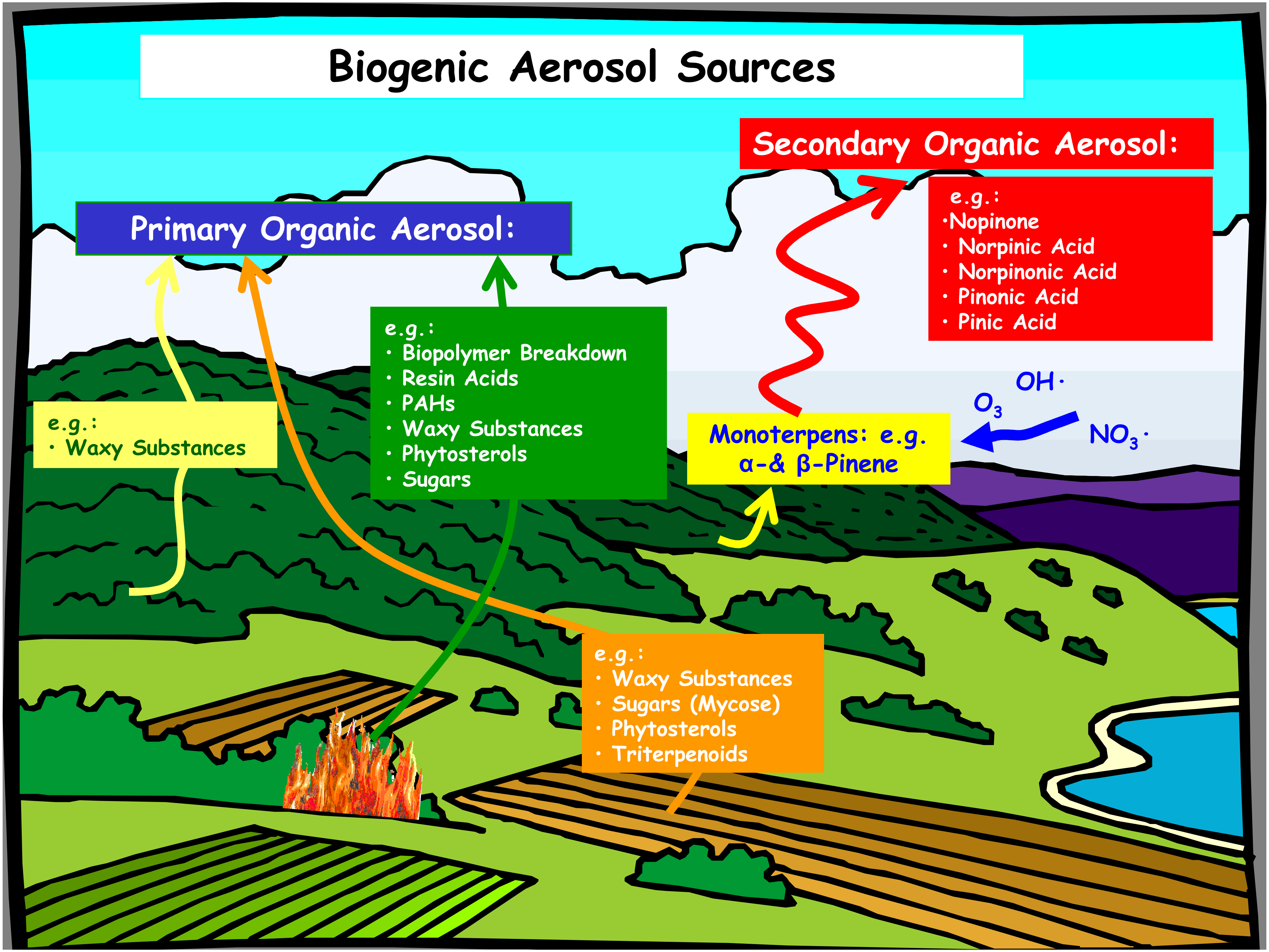
- Design and test sequential multi-channel PM2.5 sampler
- 3-Hourly sampling with Filter/PUF in Baltimore during a Summer 2002 and Winter 2002/2003
- Analyze Filter and PUF for organic constituents using GC/MS

System for 3-Hourly PM2.5 Sampling

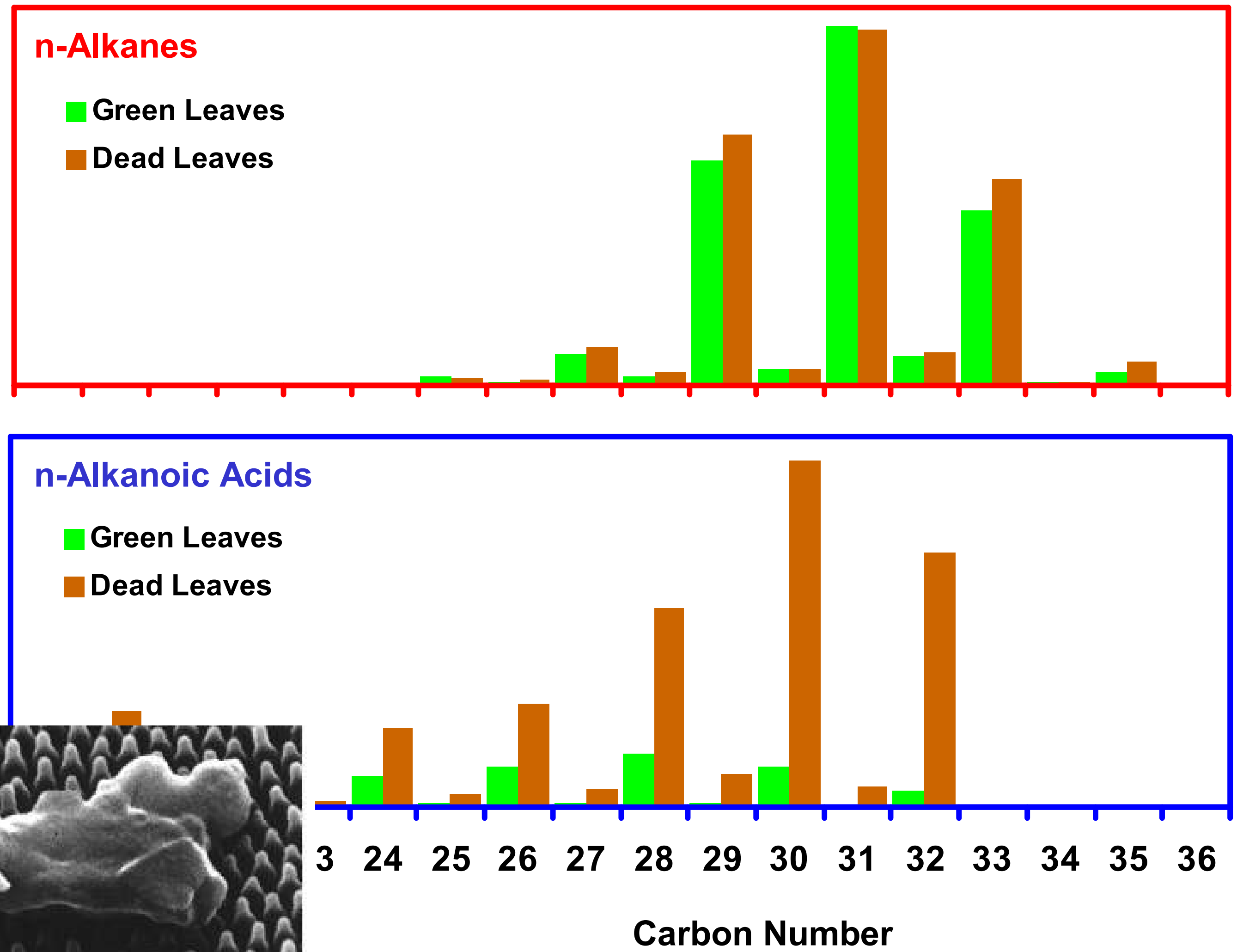


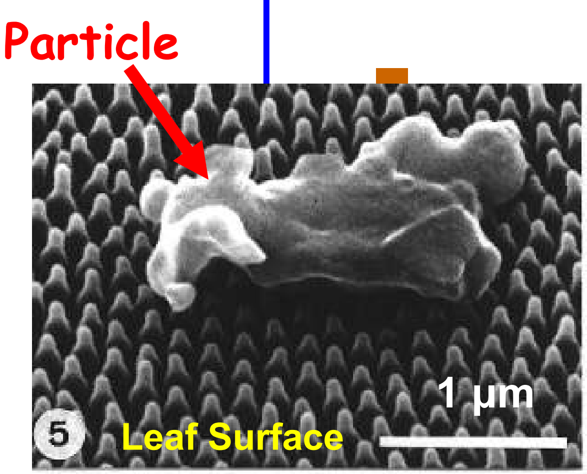
Major Organic Source Marker

<table>
<tr><th>Source Markers</th><th>Source Indicators</th><th>Major Source Type</th><th>Associated Sources</th></tr>
<tr><td>Odd-Carbon n-Alkanes $(>C_{25})$
Even-Carbon n-Alkanoic Acids $(>C_{23})$</td><td></td><td>Leaf Surface Waxes</td><td>Burning of Vegetative Detritus, Soil Dust, Vegetarian Cooking</td></tr>
<tr><td>Even-Carbon n-Alkanes</td><td></td><td>Plastic Waste Burning</td><td></td></tr>
<tr><td>Cholesterol</td><td>Palmitic & Stearic Acids
Palmitoleic & Oleic Acids</td><td>Meat Cooking</td><td></td></tr>
<tr><td>Levoglucosan</td><td rowspan="4">Phytosterol:
ß-Sitosterol, Stigmasterol, Campesterol
Saccharides</td><td>Biomass Burning (Cellulose)</td><td rowspan="4">Wildfires, Forest Fires</td></tr>
<tr><td>Resin Acids</td><td>Soft Wood Burning</td></tr>
<tr><td>Syringyl Derivatives</td><td>Hard Wood Lignin</td></tr>
<tr><td>Saccharides: Mycose, Sucrose, α-, β-Glucose</td><td>Fugitive Dust from Cultivated Land</td></tr>
<tr><td>Iso-, Anteiso-Alkanes $(>C_{26})$</td><td></td><td>Cigarette Smoke</td><td></td></tr>
<tr><td>Hopanes & Steranes</td><td>n-Alkanes $(< C_{25})$
Alkylcyclohexanes, PAHs</td><td>Vehicular Emission</td><td>Heavy Oil Burning</td></tr>
</table>


Biogenic Aerosol Sources
Primary Organic Aerosol:
Secondary Organic Aerosol:
e.g.:
•Nopinone
• Norpinic Acid
• Norpinonic Acid
• Pinonic Acid
• Pinic Acid
e.g.:
• Waxy Substances
e.g.:
• Biopolymer Breakdown
• Resin Acids
• PAHs
• Waxy Substances
• Phytosterols
• Sugars
Monoterpens: e.g.
α-& β-Pinene
OH·
O_3
NO_3·
e.g.:
• Waxy Substances
• Sugars (Mycose)
• Phytosterols
• Triterpenoids

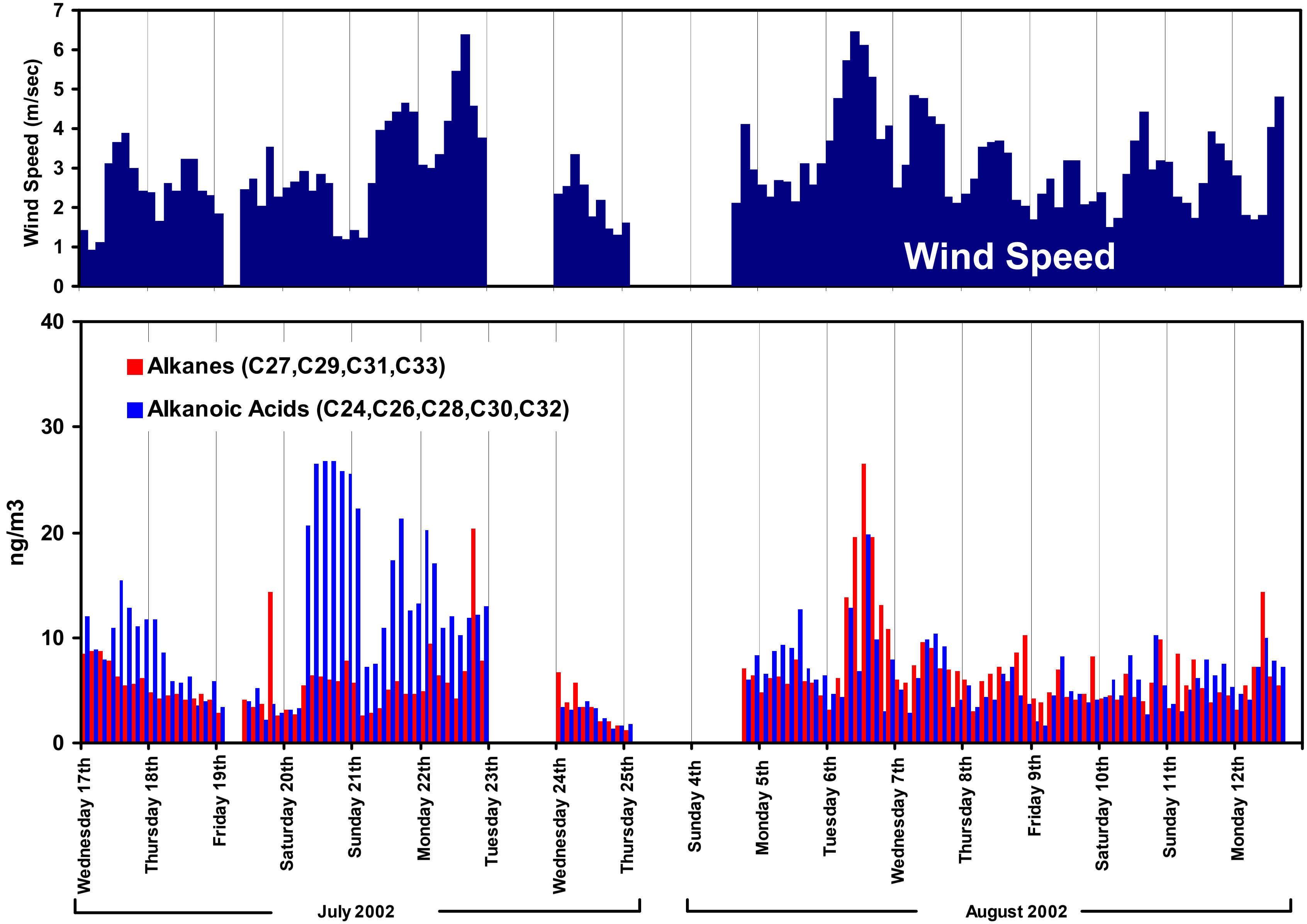
Particulate (PM2.5) Leaves Surface Abrasion Products



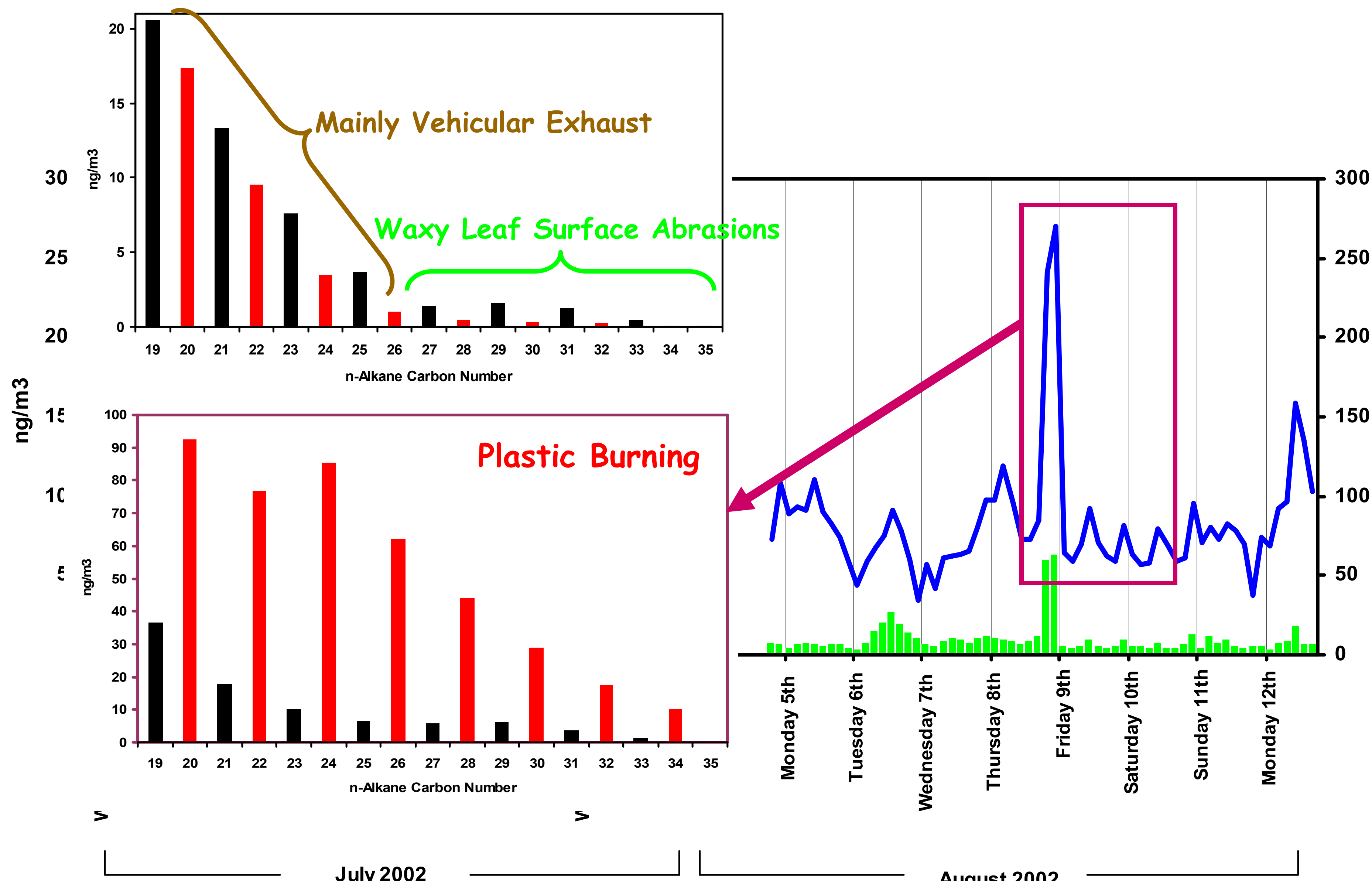


Sources: Waxes on Leaf Surfaces, Burning of Vegetative Detritus, Soil Dust, Vegetarian Cooking

Leaf Surface Waxes



Ambient Concentrations of n-Alkanes for Summer 2002 – Short Time Compositional Changes of Organic Compounds in PM2.5



Organic Markers in Wood Smoke

Wood Constituents		Conifers (gymnosperms) "Softwood"	Deciduous Trees (angiosperms) "Hard Wood"
Polymers Major	Cellulose	40 – 50%	
	Hemicelluloses	25 – 35%	
	Lignins	30 – 40%	20 – 30%
Minor	Extraneous Substances	4 – 10%	
		Resins	Gums
		Fats, waxes, starches, terpenes, tannins, phenolics, pectins, sugars, sapins, mucilages, glycosides, essential oils, sterols, others	
	Inorganics (Ash)	< 1%	

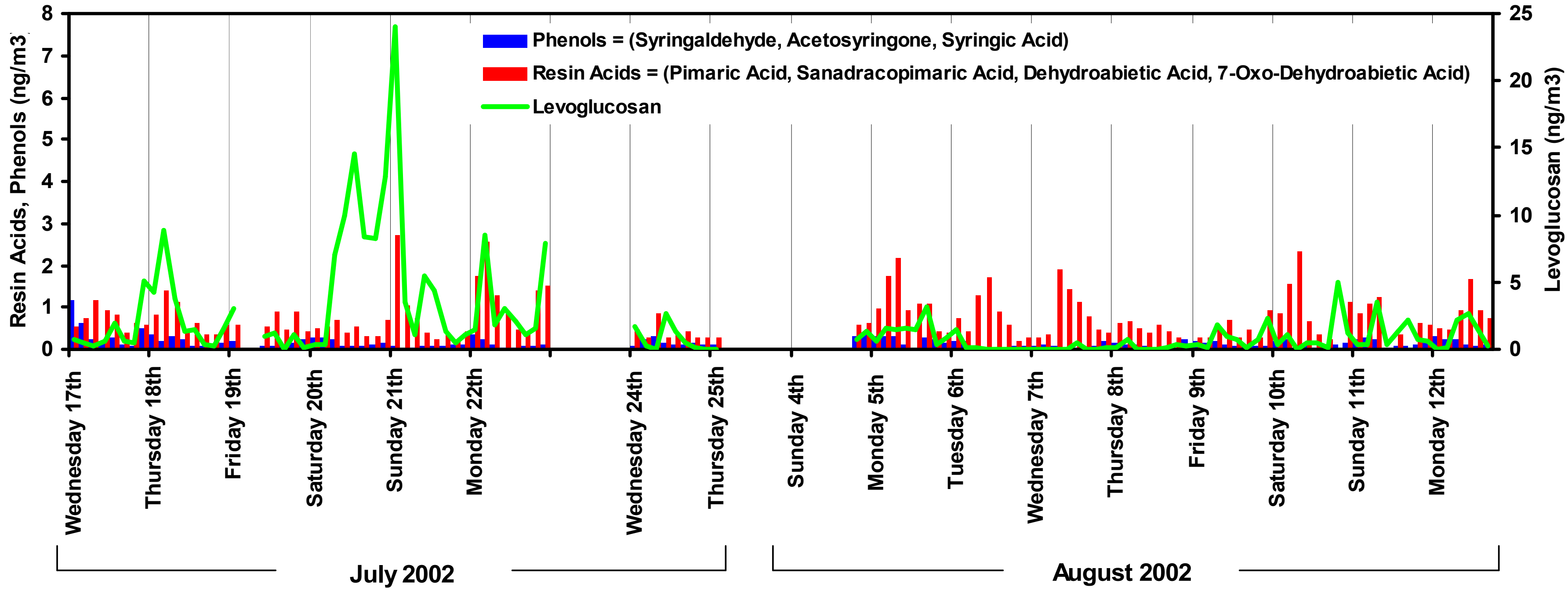
- **Marker for Cellulose Burning: Levoglucosan**

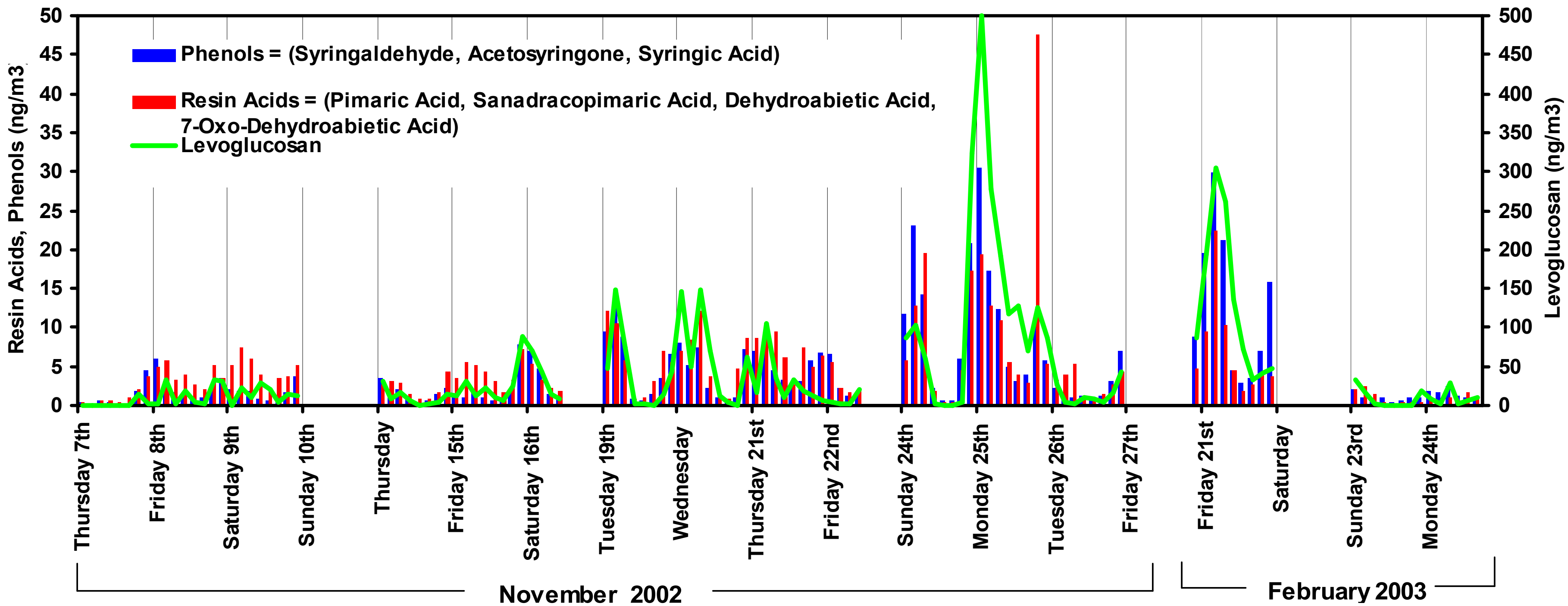
  Cellulose is the abundant organic polymer on earth, found in any wood, vegetative detritus, biomass, etc.

- **Markers for Lignins from Hardwood Burning: Syringyl Derivatives (Syringaldehyde, Acetosyringone, Syringic acid)**

  Second most abundant organic polymer on earth:
  Hardwoods have about 50% guaiacyl and 50% syringyl units
  Softwoods have 90% - 100% guaiacyl units

- **Markers for Softwood Burning: Resin Acids [dehydroabietic acid (major), 7-oxo-dehydroabietic acid, pimaric acid, abietic acid, etc.]**


Phenols = (Syringaldehyde, Acetosyringone, Syringic Acid)
Resin Acids = (Pimaric Acid, Sanadracopimaric Acid, Dehydroabietic Acid, 7-Oxo-Dehydroabietic Acid)
Levoglucosan
Resin Acids, Phenols (ng/m3)
Levoglucosan (ng/m3)
Wednesday 17th
Thursday 18th
Friday 19th
Saturday 20th
Sunday 21th
Monday 22th
Wednesday 24th
Thursday 25th
Sunday 4th
Monday 5th
Tuesday 6th
Wednesday 7th
Thursday 8th
Friday 9th
Saturday 10th
Sunday 11th
Monday 12th
July 2002
August 2002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Levoglucosan
Resin Acids, Phenols (ng/m3)
Levoglucosan (ng/m3)
Thursday 7th
Friday 8th
Saturday 9th
Sunday 10th
Thursday
Friday 15th
Saturday 16th
Tuesday 19th
Wednesday
Thursday 21st
Friday 22nd
Sunday 24th
Monday 25th
Tuesday 26th
Friday 27th
Friday 21st
Saturday
Sunday 23rd
Monday 24th
November 2002
February 2003

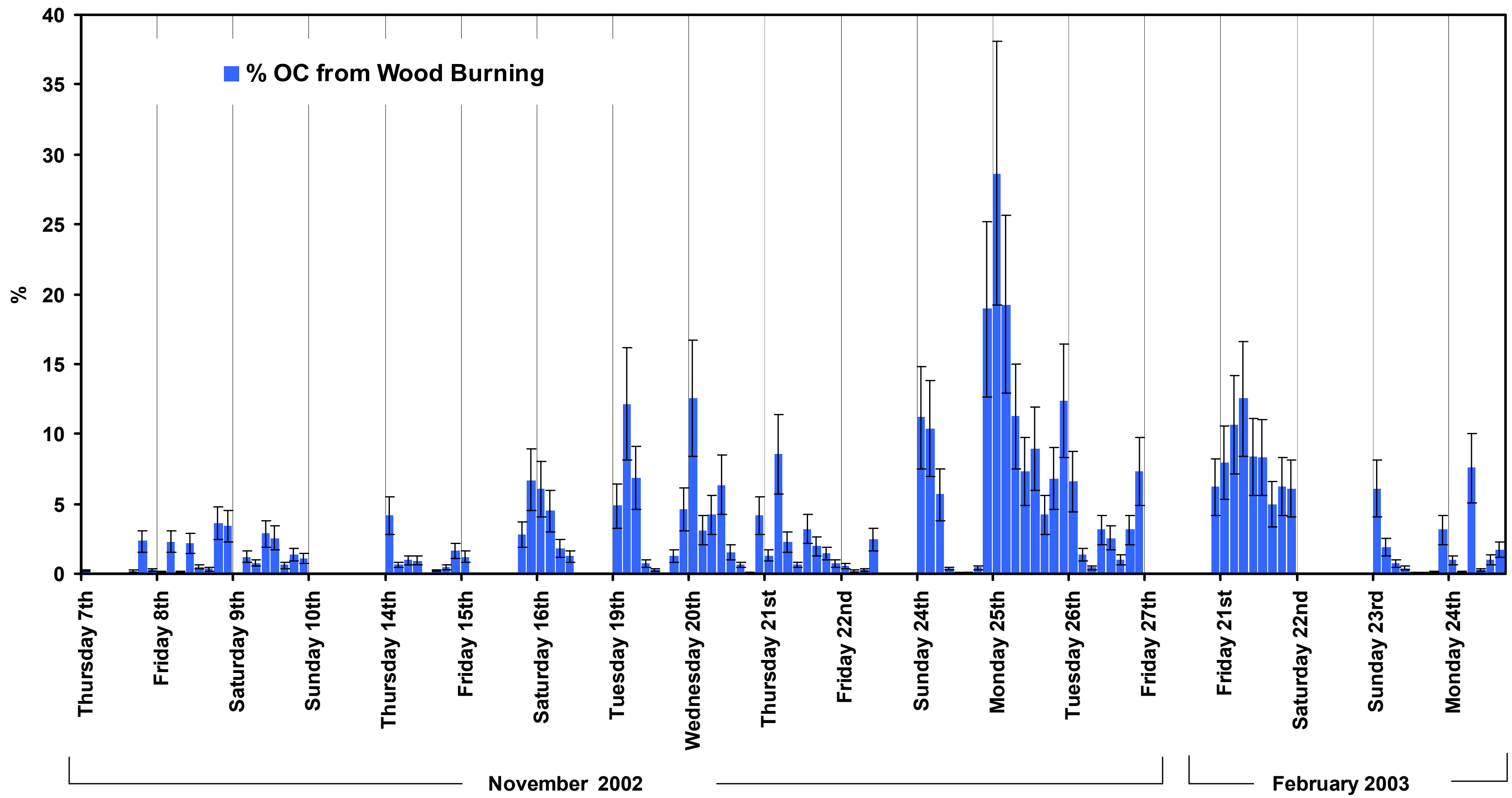
Estimating Ambient OC Contributions from Wood Burning

Fuel Type	Combustor	OC/Levoglucosan	Reference
Hardwood	Fire Place Northeast US	7.8	Fine et al., 2001
Softwood		13.1	
Hardwood	Fire Place South US	7.4	Fine et al., 2002
Softwood		23.5	
Hardwood	Fire Place West-Midwest US	5.5	Fine et al., 2004a
Softwood		8.1	
Hardwood	Wood Stove	8.1	Fine et al., 2004b
Softwood		2.8	
Hardwood	Fire Place West US	3.1	Schauer et al., 2001
Softwood		3.9	
	Average	6.6 ± 3.2	

$$\%\ \text{Ambient OC from Wood Burning} = \left(\frac{OC}{Levoglucosan}\right)_{Woodsmoke} \left(\frac{Levoglucosan}{OC}\right)_{Ambient}$$

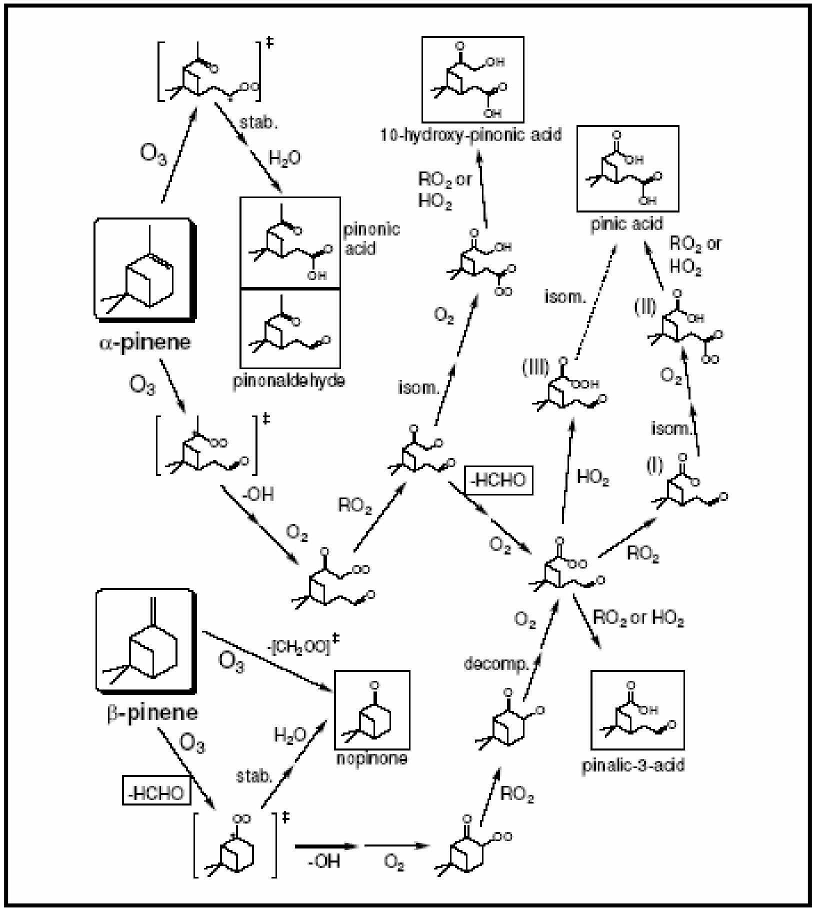
$$\%\ \text{Ambient OC from Wood Burning} = 6.6 \pm 3.2 \left(\frac{Levoglucosan}{OC}\right)_{Ambient}$$

Estimating Ambient OC Contributions from Wood Burning



Baltimore Supersite:

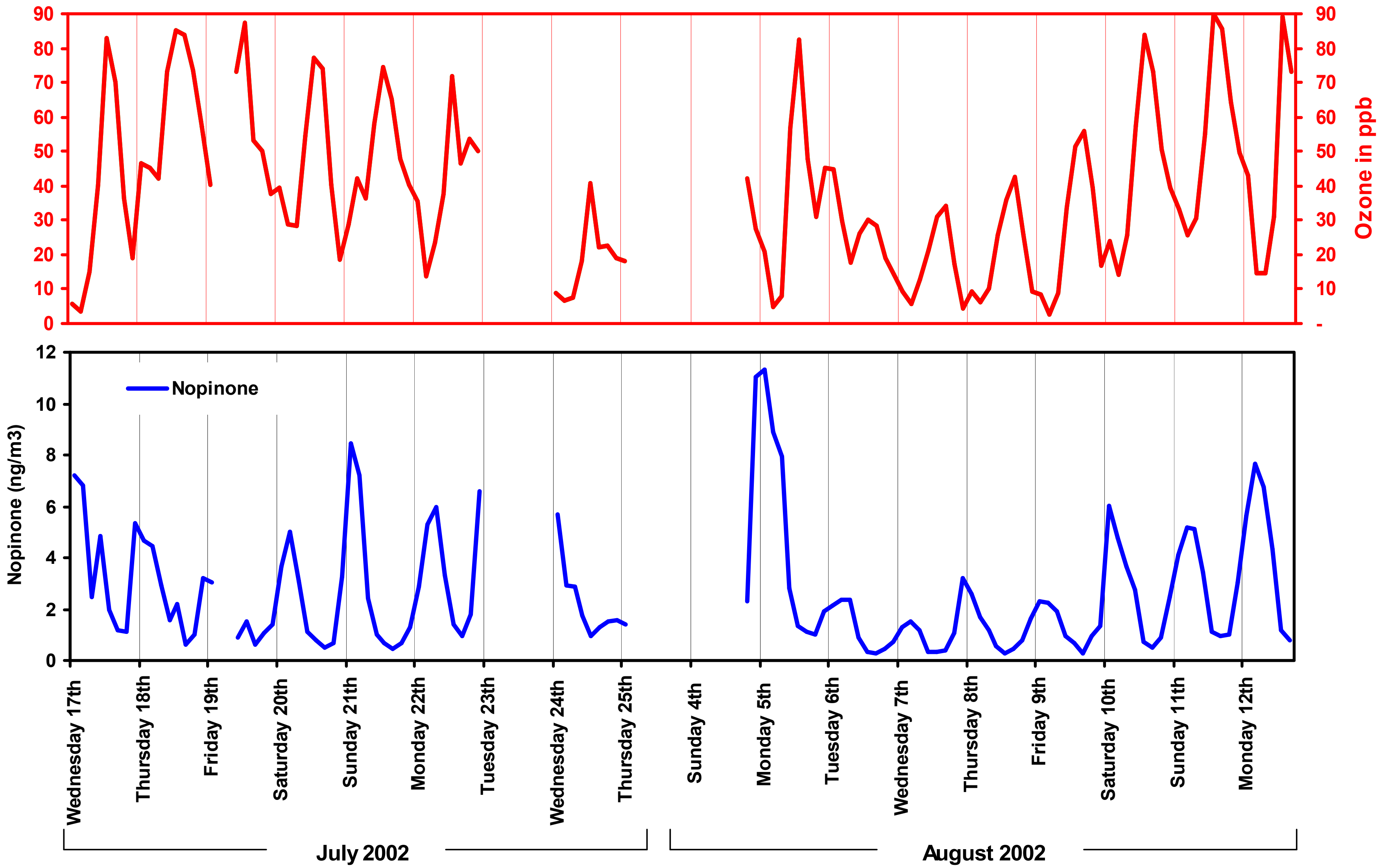
Secondary Biogenic Atmospheric Reaction Products: Nopinone, Pinonic Acid, Norpinonic Acid



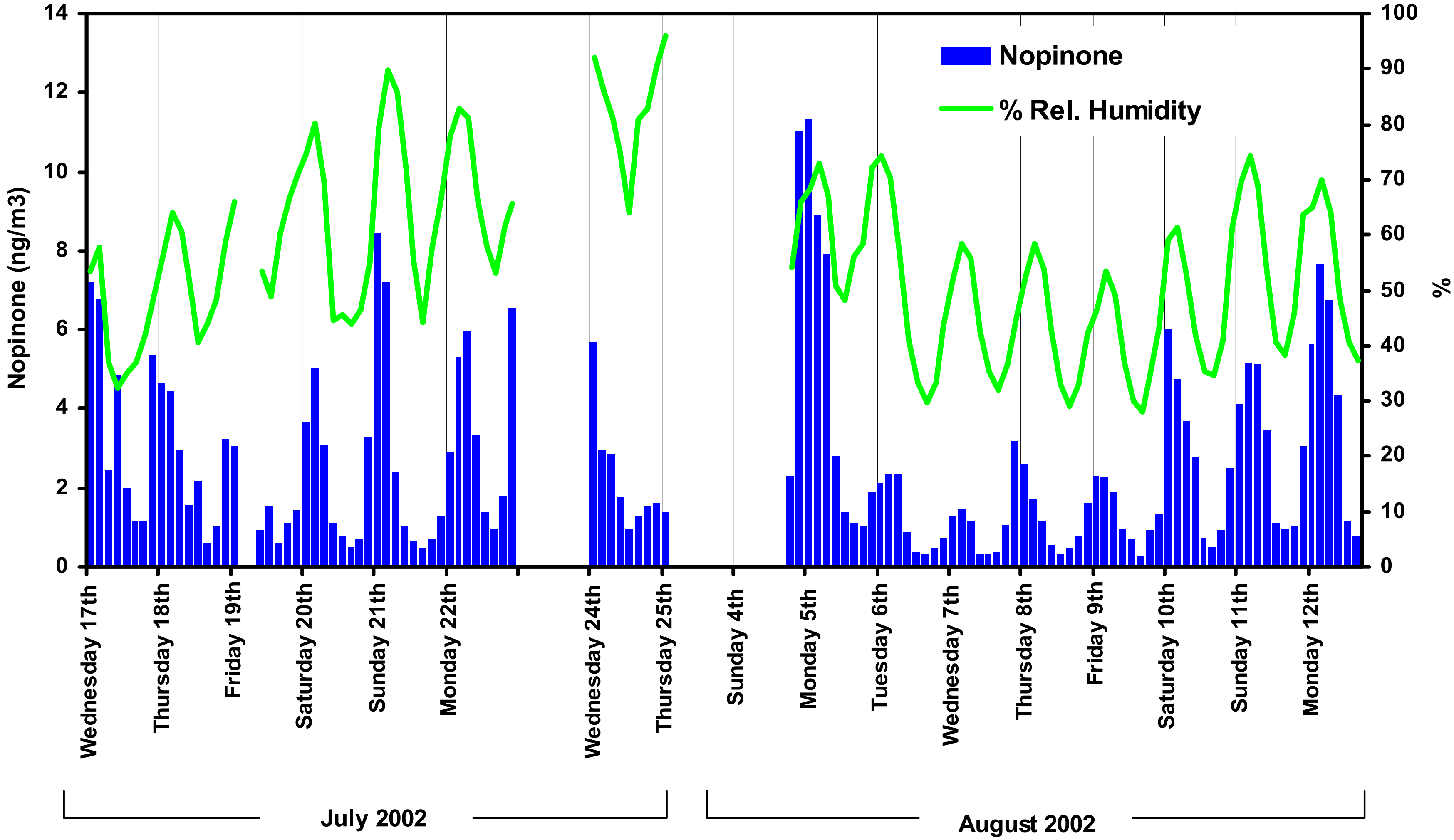
Schematics for the formation routes of secondary biogenic reaction products following the ozonolysis of α-pinene and β-pinene.

(from Kamens)

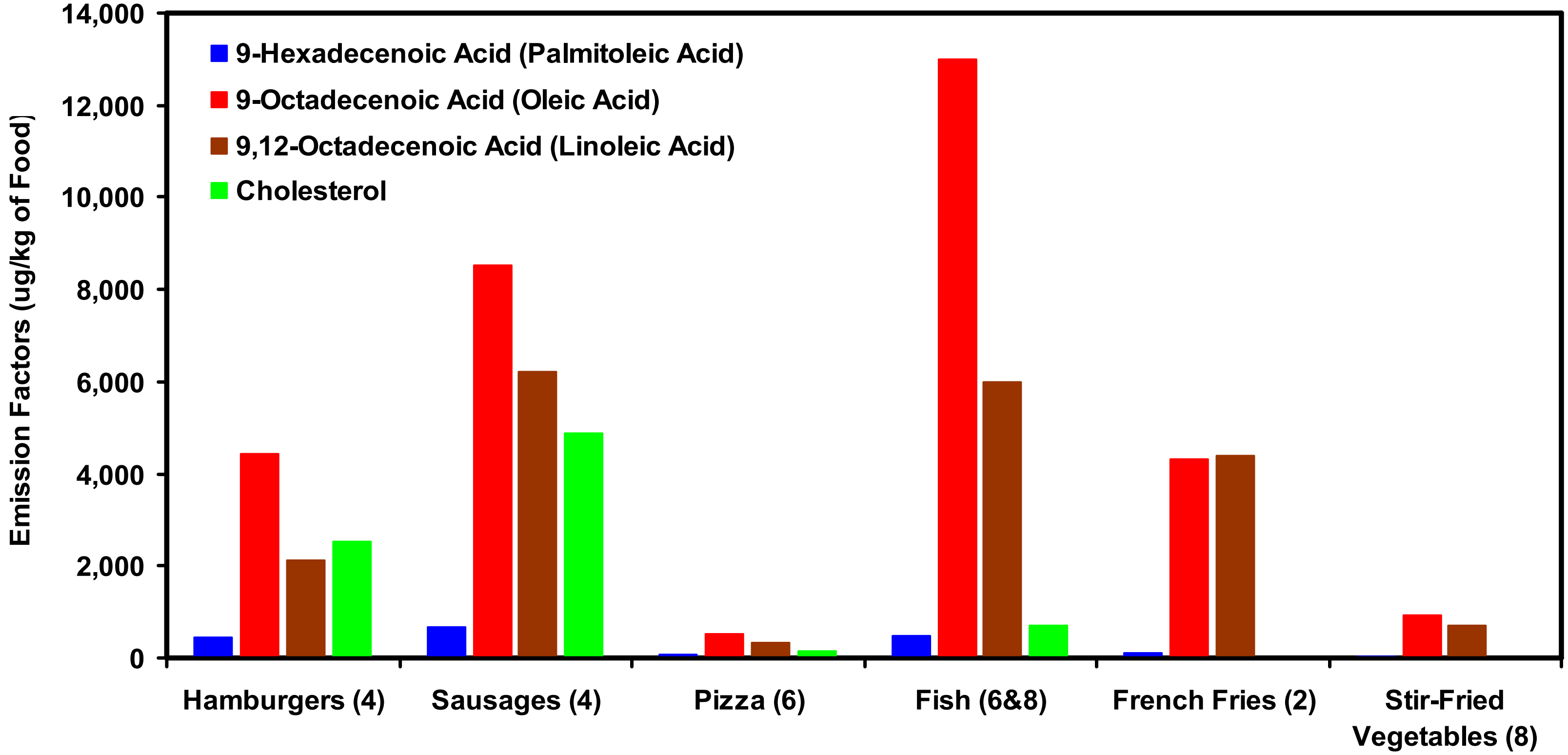
Nopinone: Secondary Biogenic Reaction Products - Summer 2002



Nopinone: Secondary Biogenic Reaction Products - Summer 2002



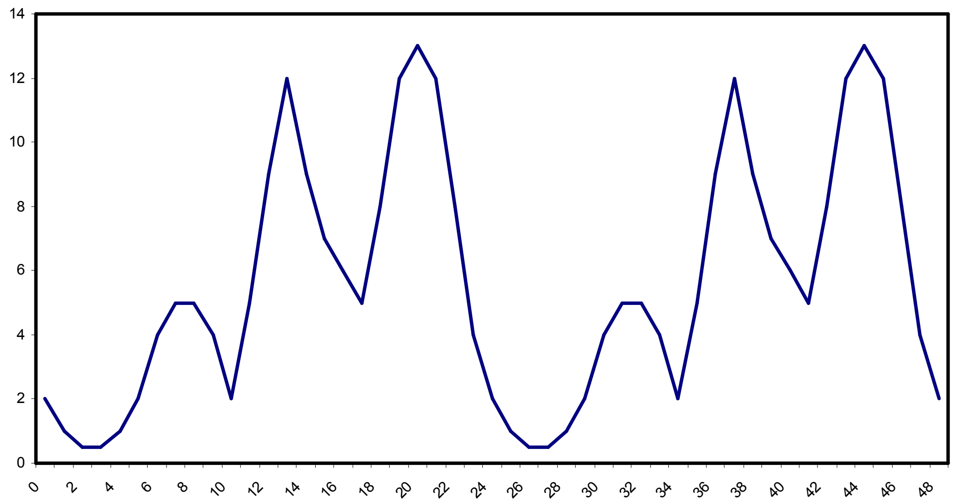
Major Organic Compounds associated with PM2.5 Cooking Emissions



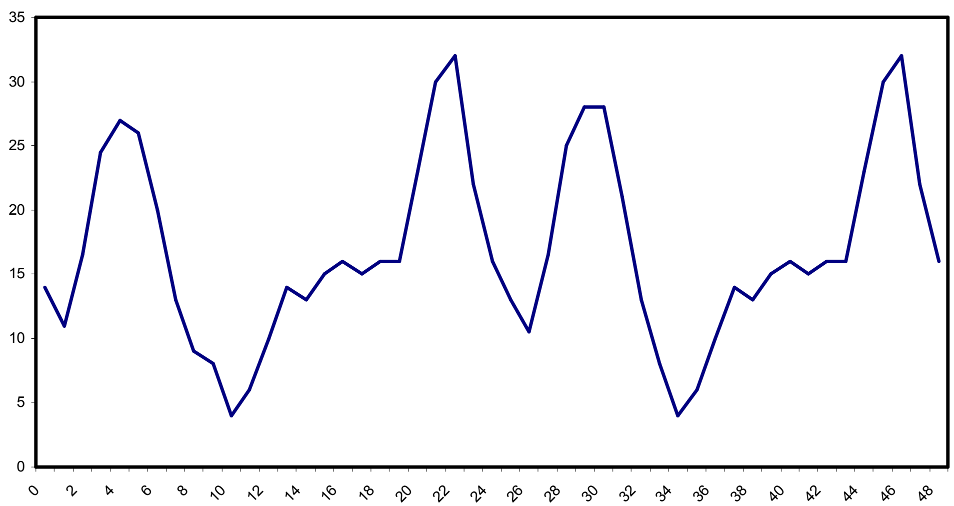
Number of Experiments in ( )

From: Rogge et al., Emission Factors for Residential Cooking

Diurnal Cooking Activities over 48 Hours

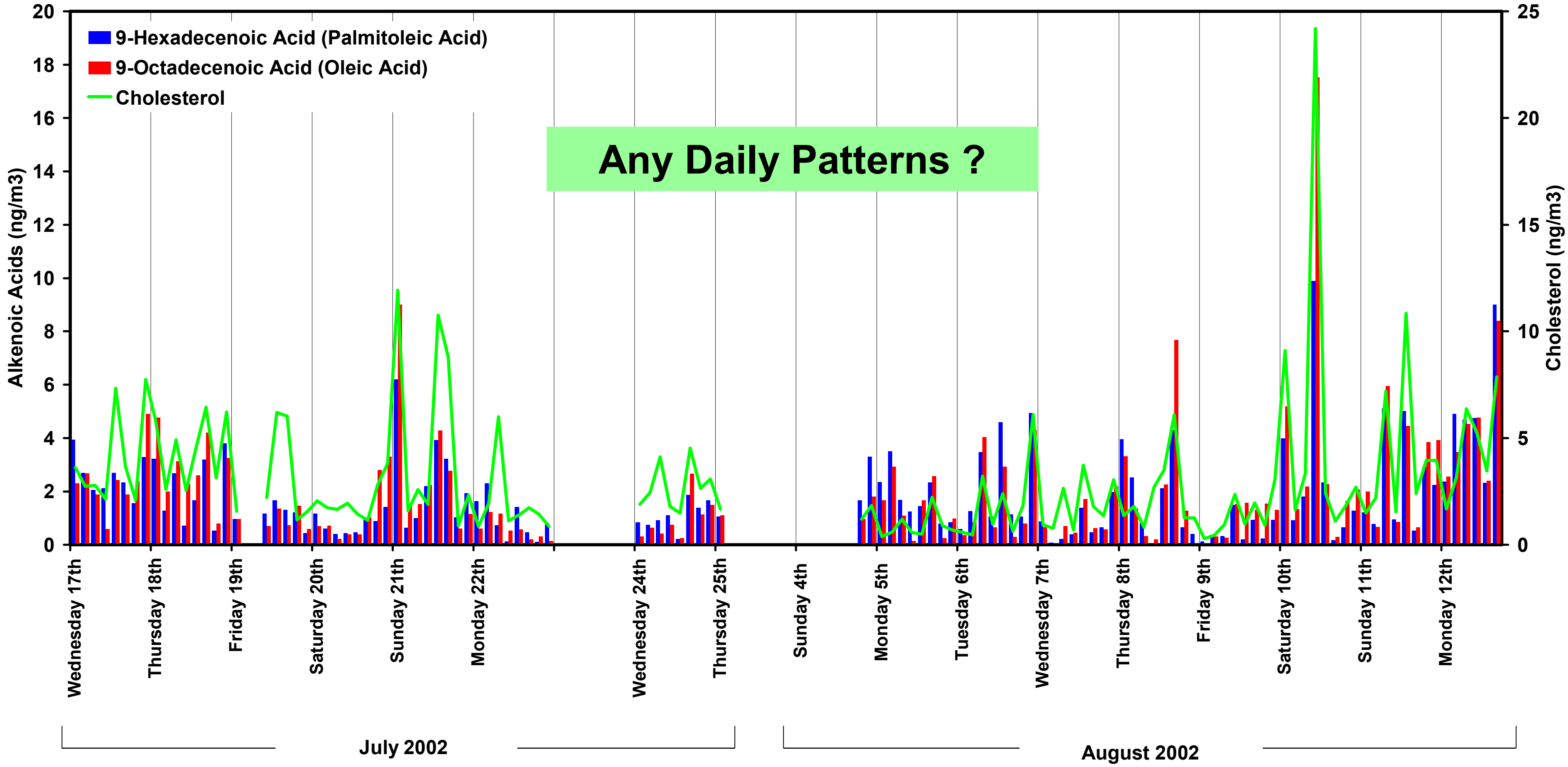


Local Cooking Source

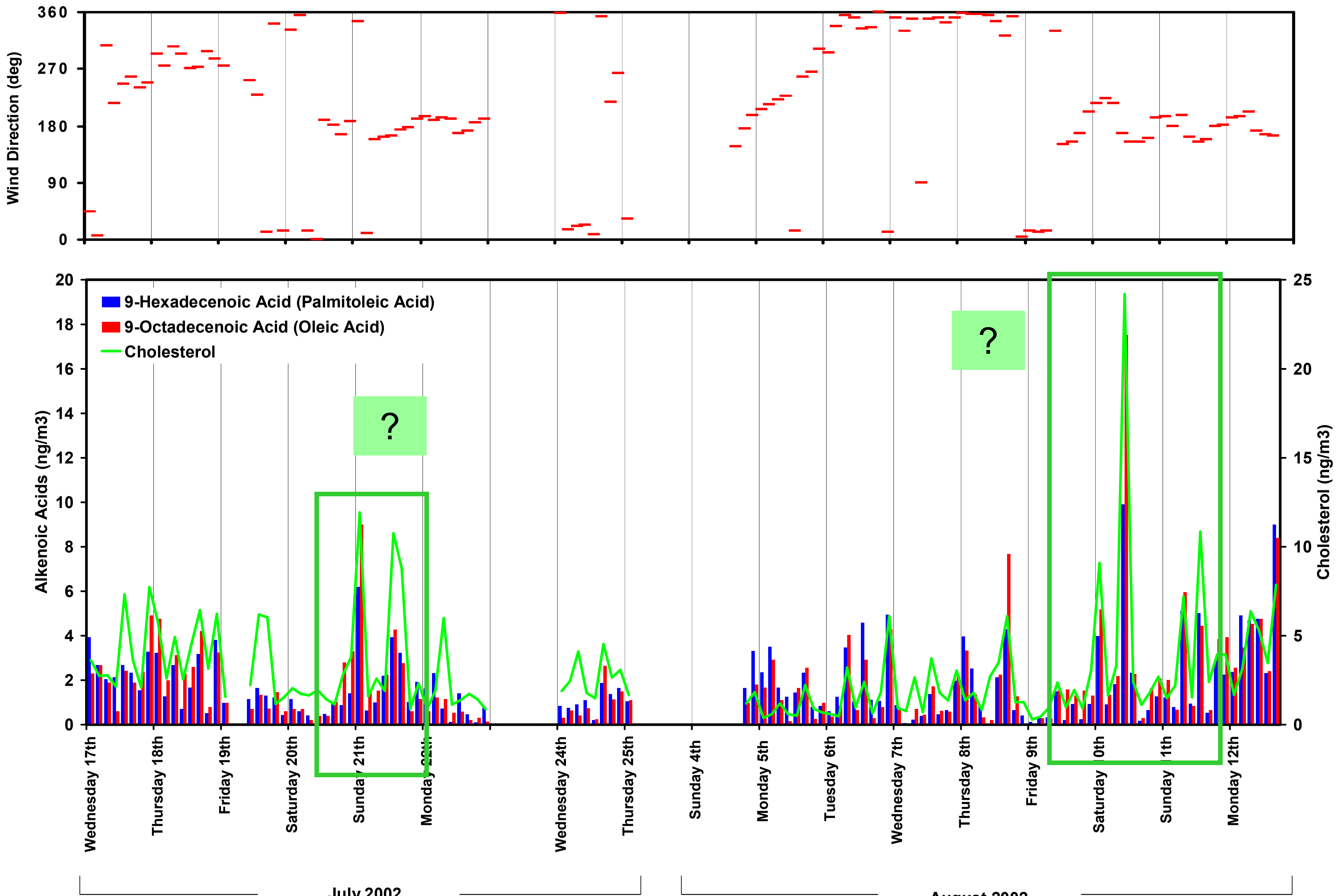


Distant Cooking Source (travel time 8 hrs) + Local Cooking Source

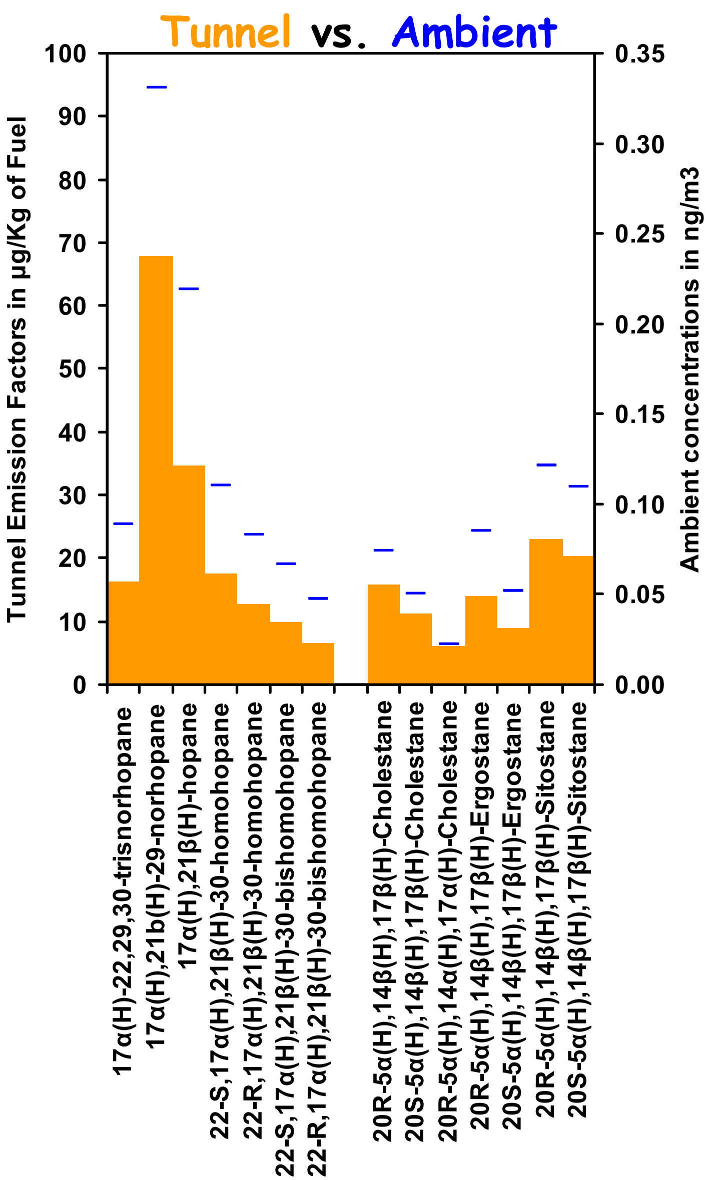
Ambient Concentrations of Palmitoleic Acid, Oleic Acid, and Cholesterol Summer 2002

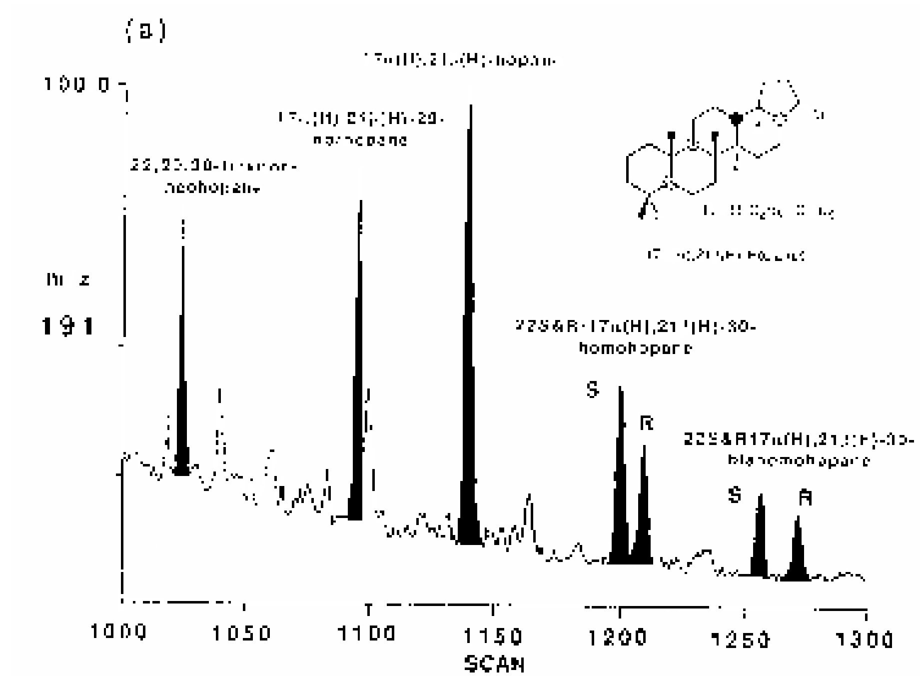


Ambient Concentrations of Palmitoleic Acid, Oleic Acid, and Cholesterol vs. Wind Direction - Summer 2002

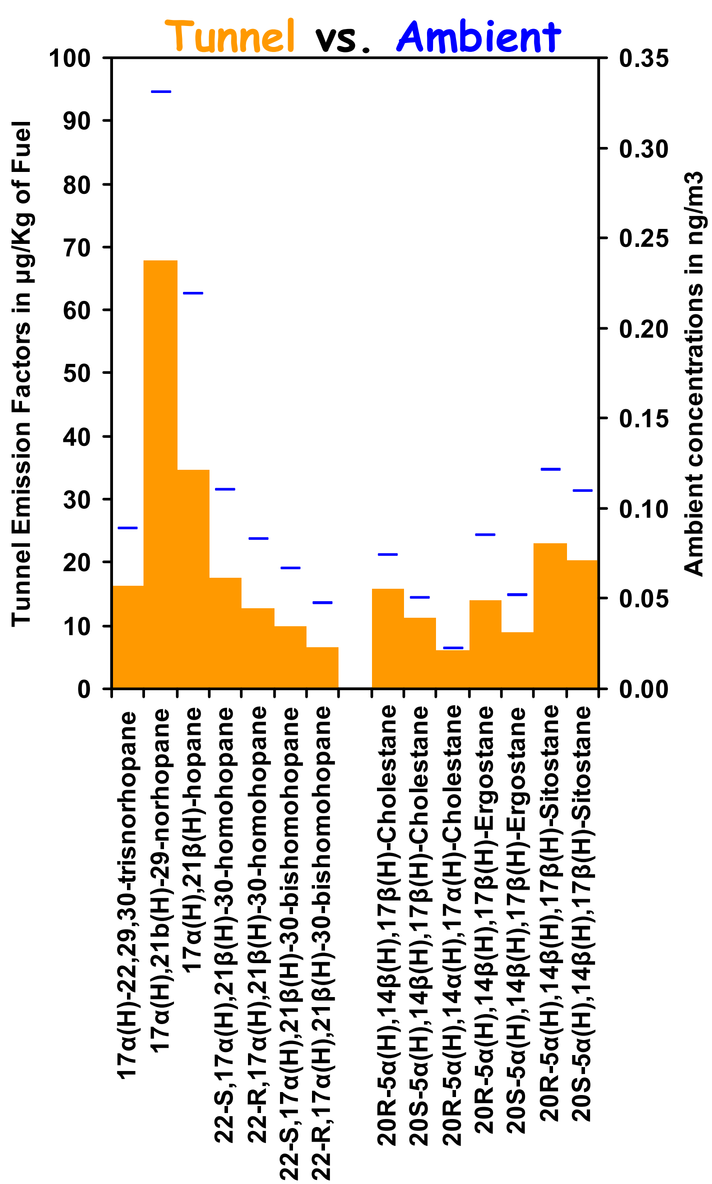


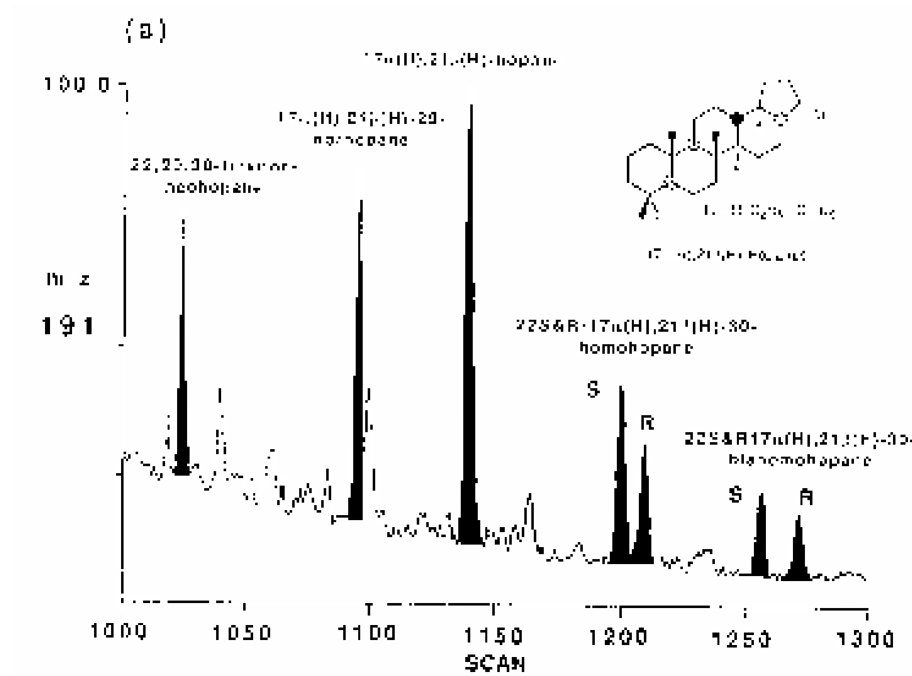
Organic Markers for Vehicle Exhaust: Hopanes & Steranes





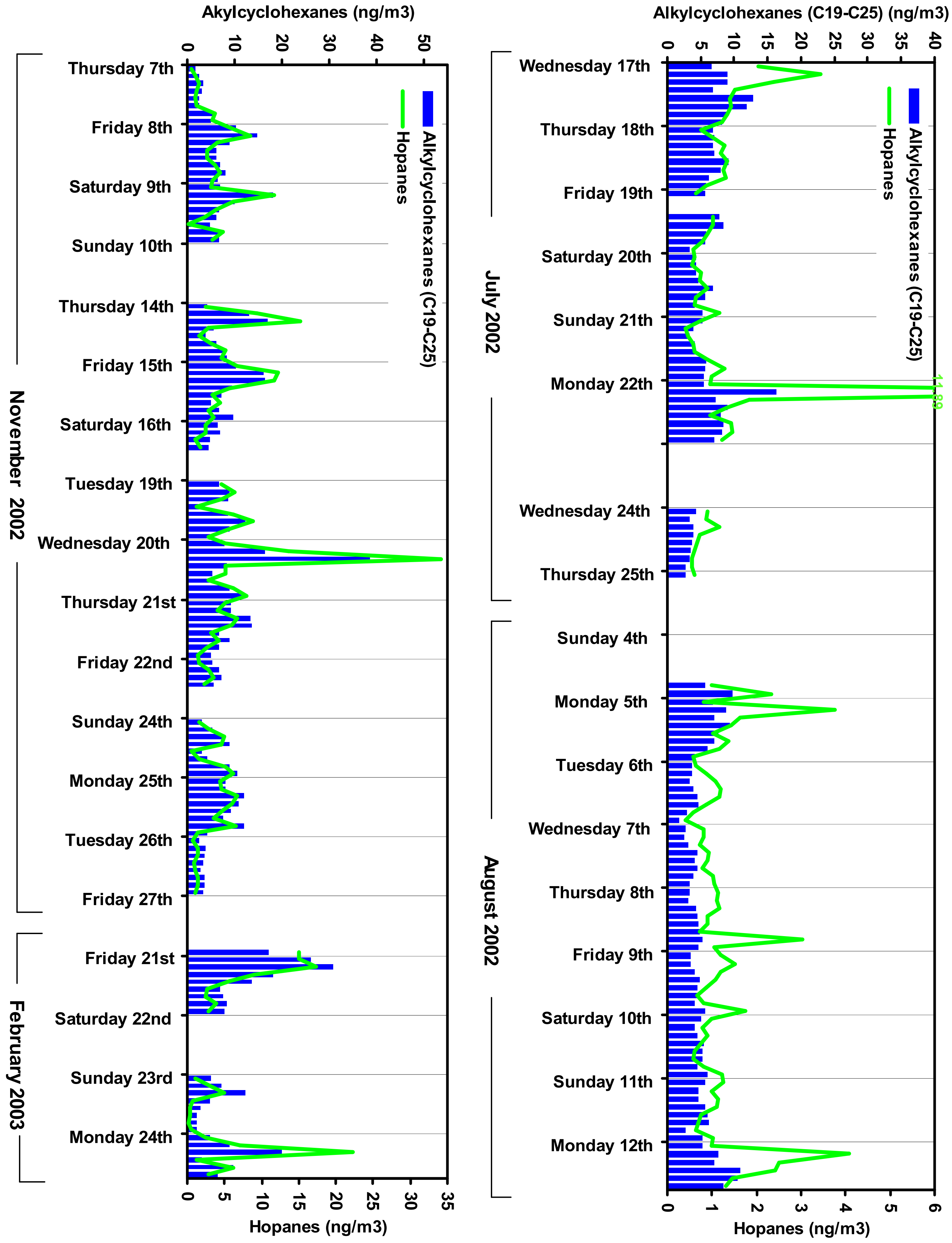
Organic Markers for Vehicle Exhaust: Hopanes & Steranes





How do ambient concentration patterns for the Hopanes compare to:

1. Alkylcyclohexanes ?
2. n-Alkanes (C19-C25) ?
3. PAHs ?



Alkylcyclohexanes (C19-C25) (ng/m3)
Hopanes (ng/m3)
Alkylcyclohexanes (C19-C25)
Hopanes
11.89
Wednesday 17th
Thursday 18th
Friday 19th
Saturday 20th
Sunday 21th
Monday 22th
Wednesday 24th
Thursday 25th
Sunday 4th
Monday 5th
Tuesday 6th
Wednesday 7th
Thursday 8th
Friday 9th
Saturday 10th
Sunday 11th
Monday 12th
July 2002
August 2002
Akylcyclohexanes (ng/m3)
Hopanes (ng/m3)
Thursday 7th
Friday 8th
Saturday 9th
Sunday 10th
Thursday 14th
Friday 15th
Saturday 16th
Tuesday 19th
Wednesday 20th
Thursday 21st
Friday 22nd
Sunday 24th
Monday 25th
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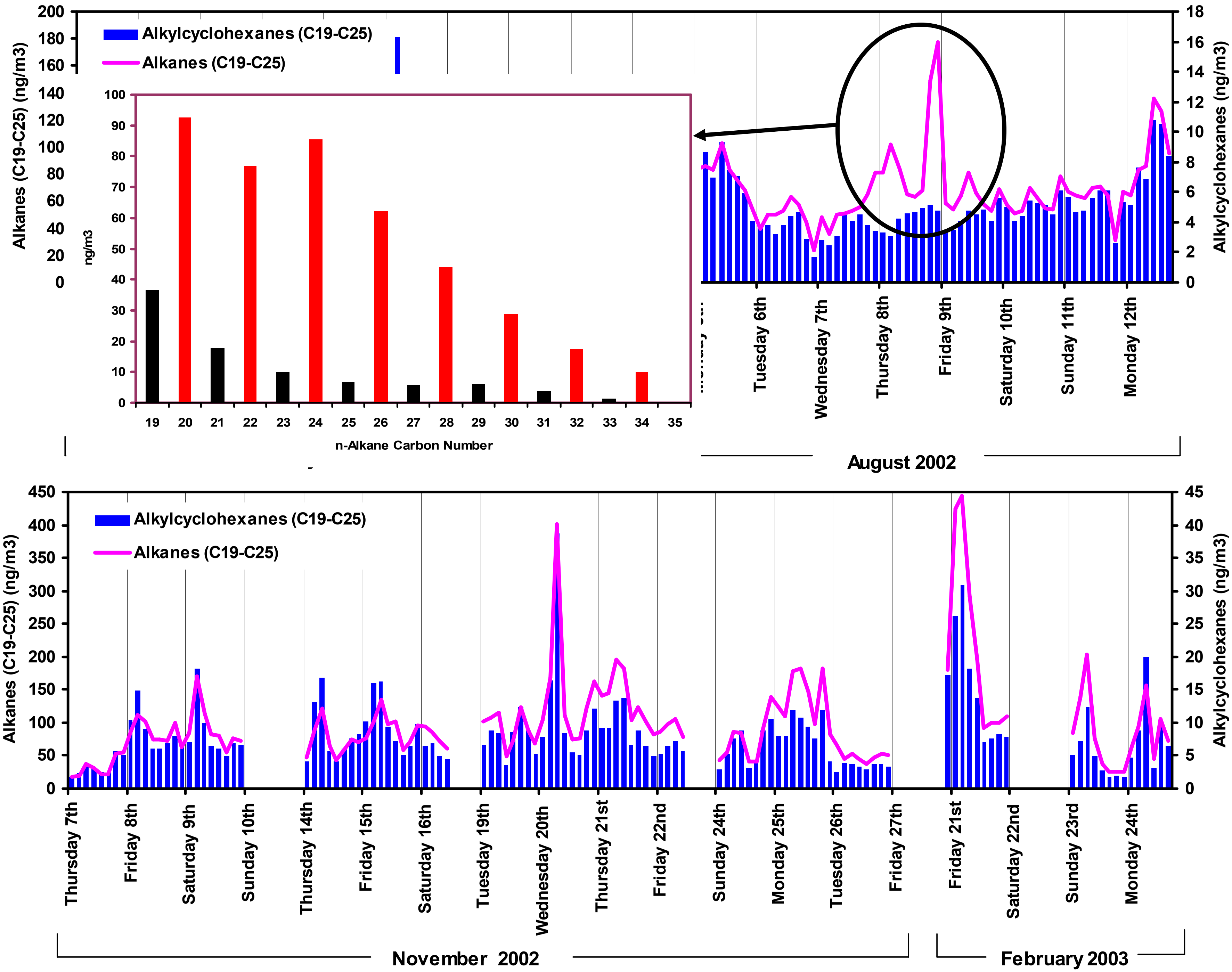
Friday 27th
Friday 21st
Saturday 22nd
Sunday 23rd
Monday 24th
November 2002
February 2003



Alkylcyclohexanes (C19-C25)
Alkanes (C19-C25)
Alkanes (C19-C25) (ng/m3)
Alkylcyclohexanes (ng/m3)
ng/m3
n-Alkane Carbon Number
Tuesday 6th
Wednesday 7th
Thursday 8th
Friday 9th
Saturday 10th
Sunday 11th
Monday 12th
August 2002
Thursday 7th
Friday 8th
Saturday 9th
Sunday 10th
Thursday 14th
Friday 15th
Saturday 16th
Tuesday 19th
Wednesday 20th
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November 2002
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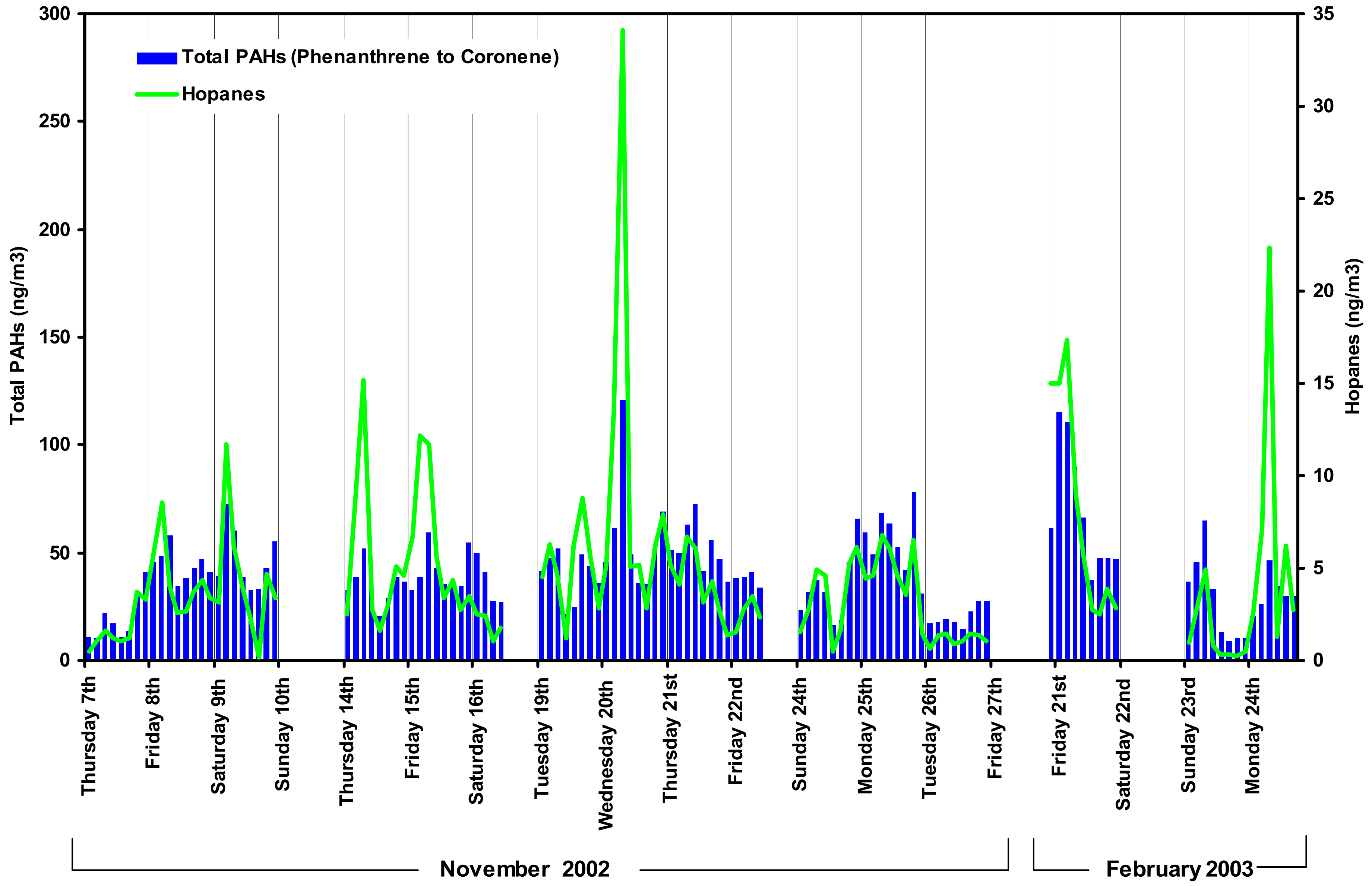

Total PAHs (Phenanthrene to Coronene)
Hopanes
Total PAHs (ng/m3)
Hopanes (ng/m3)
0
50
100
150
200
250
300
0
5
10
15
20
25
30
35
Thursday 7th
Friday 8th
Saturday 9th
Sunday 10th
Thursday 14th
Friday 15th
Saturday 16th
Tuesday 19th
Wednesday 20th
Thursday 21st
Friday 22nd
Sunday 24th
Monday 25th
Tuesday 26th
Friday 27th
Friday 21st
Saturday 22nd
Sunday 23rd
Monday 24th
November 2002
February 2003

Conclusions:

- For the very first time, insight into the daily patterns of atmospheric organic compounds associated with PM2.5 with an 3 hourly time-resolution
- For Summer 2002: 18 days of data available
- For Winter 2002-03: 17 days of data available
- For 111 individual organic compounds, about 62,000 data points have been generated
- Although, only a very short view into the data set has been presented, already several interesting aspects about the atmospheric dynamic of fine particle bound organic compounds have been demonstrated:
  - Compositional changes of organic matter associated with PM2.5 occurs with a time scale of less than 3 hours
  - With very few exceptions, no diurnal concentration patterns have been found for individual organic compounds, indicating that PM2.5 at the sampling site is impacted by sources close and far
  - Wood smoke markers are also detectable in summer time
  - Wood smoke from softwood burning and hardwood burning can be distinguished well using resin acids and phenolic derivatives from the syringyl type "building blocks" in lignins
  - Vehicular marker concentrations (hopanes) compare very well to n-alkanes (C19-C25) and alkylcyclohexanes and is responsible for most of the PAH emissions