Seasonal Variations of Highly Time-resolved Organic Compounds Concentrations of Primary and Secondary Nature during the Baltimore PM2.5 – Supersite Study

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Problem:

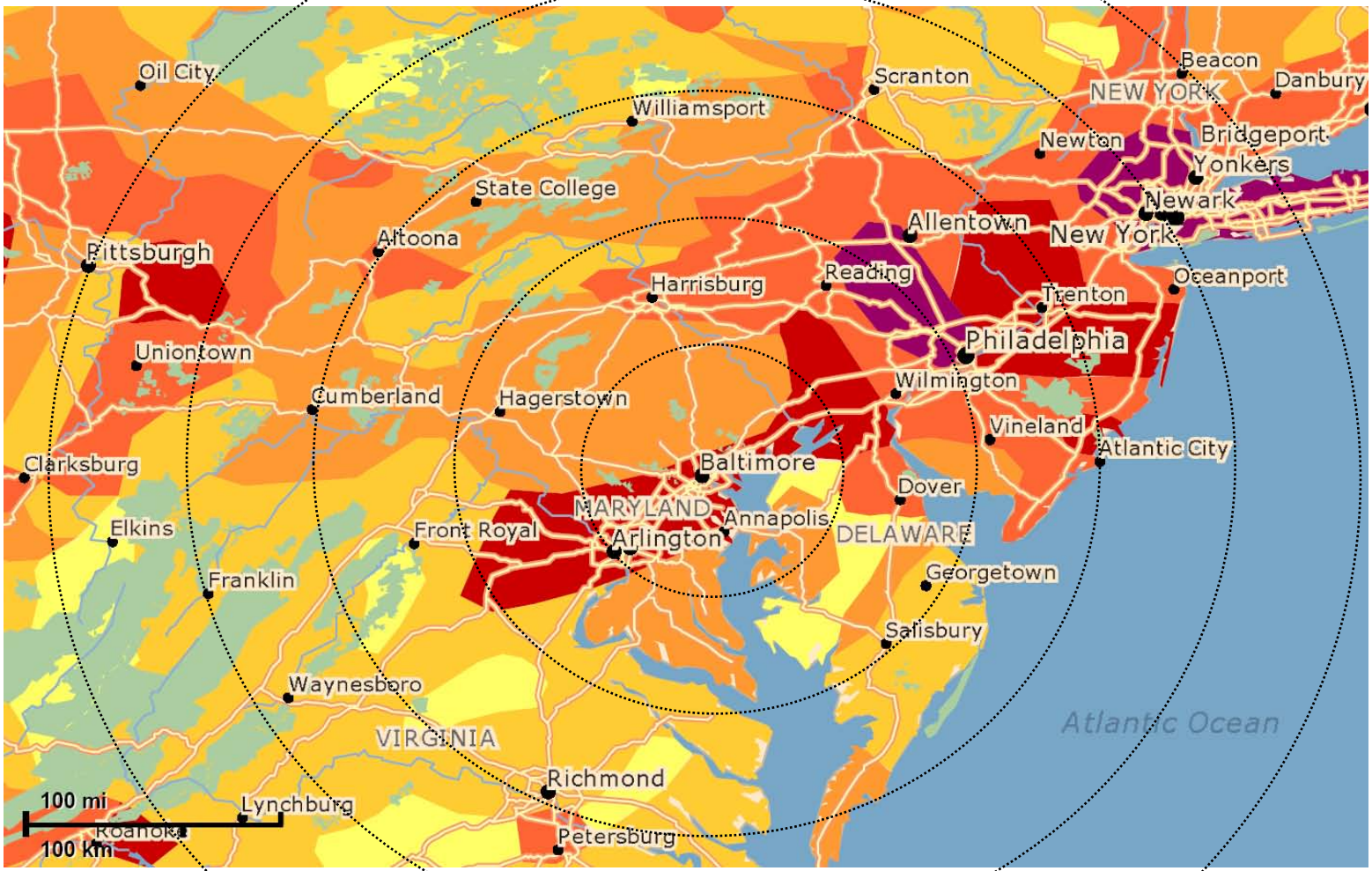
Little knowledge available for PM2.5 organics about short-term diurnal variations of ambient concentrations due to local sources, transport, and atmospheric chemistry

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

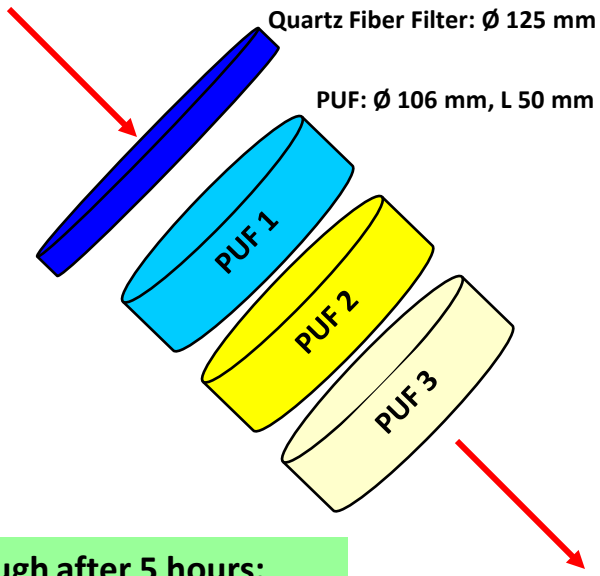

Oil City
Williamsport
Scranton
Beacon
Danbury
NEW YORK
Newton
Bridgeport
Yonkers
Newark
State College
Allentown
New York
Altoona
Pittsburgh
Reading
Harrisburg
Oceanport
Trenton
Philadelphia
Uniontown
Wilmington
Cumberland
Hagerstown
Vineland
Atlantic City
Clarksburg
Baltimore
Dover
MARYLAND
Annapolis
Elkins
Front Royal
Arlington
DELAWARE
Georgetown
Franklin
Salisbury
Waynesboro
Atlantic Ocean
VIRGINIA
Richmond
100 mi
Lynchburg
Roanoke
Petersburg
100 km
Population Density
Less than 1
1 to 10
10 to 25
25 to 50
50 to 100
100 to 200
200 to 400
400 to 800
Greater than 800
Countries and Regions

Sampling System for 3-Hourly PM2.5

Breakthrough Experiments for Semi-Volatile Organic Compounds

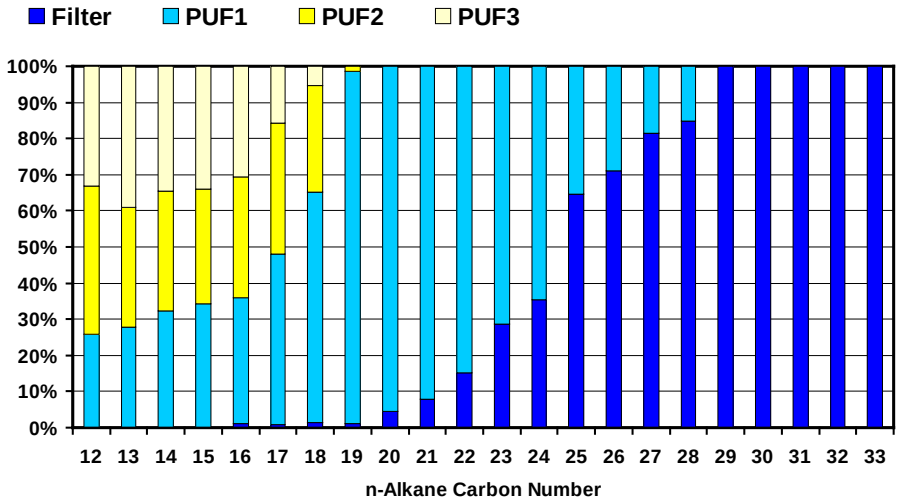
1. Experiment: 3 Hours
2. Experiment: 4 Hours
3. Experiment: 5 Hours

Flowrate: 580 L/min

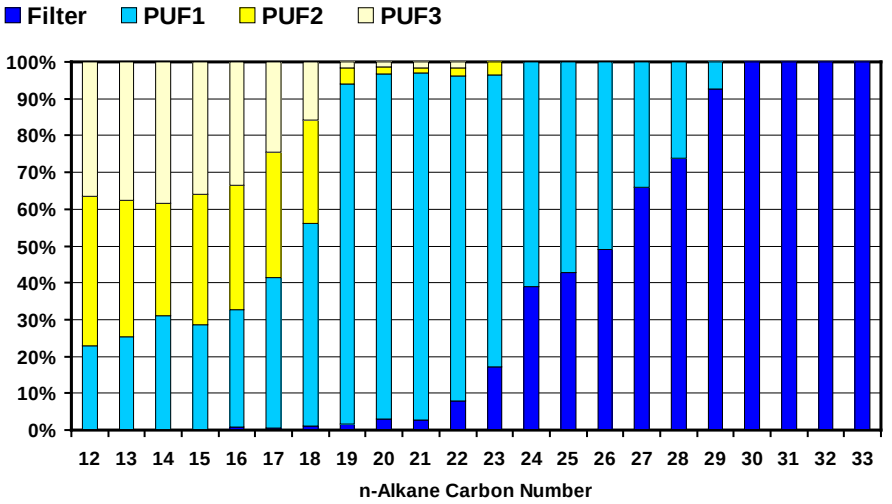


- All Filters and PUFs were individually analyzed
- Breakthrough curves for semi-volatile organic compounds determined
- Partitioning for semi-volatile on Filter/PUF depends on: Comp. Vapor pressure, temp., adsorption capacity, pressure drop via Filter/PUF

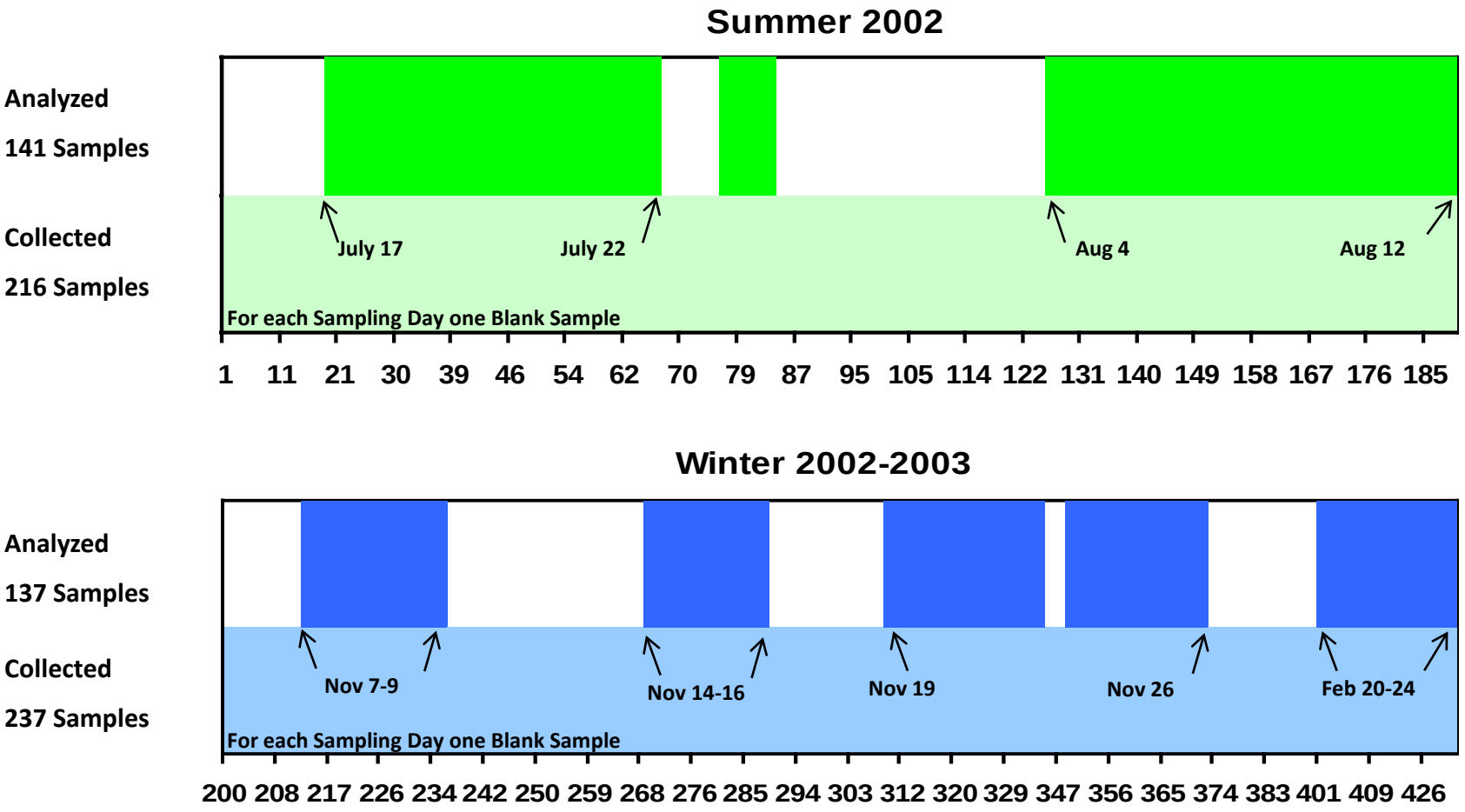
Breakthrough after 3 hours:



Breakthrough after 5 hours:

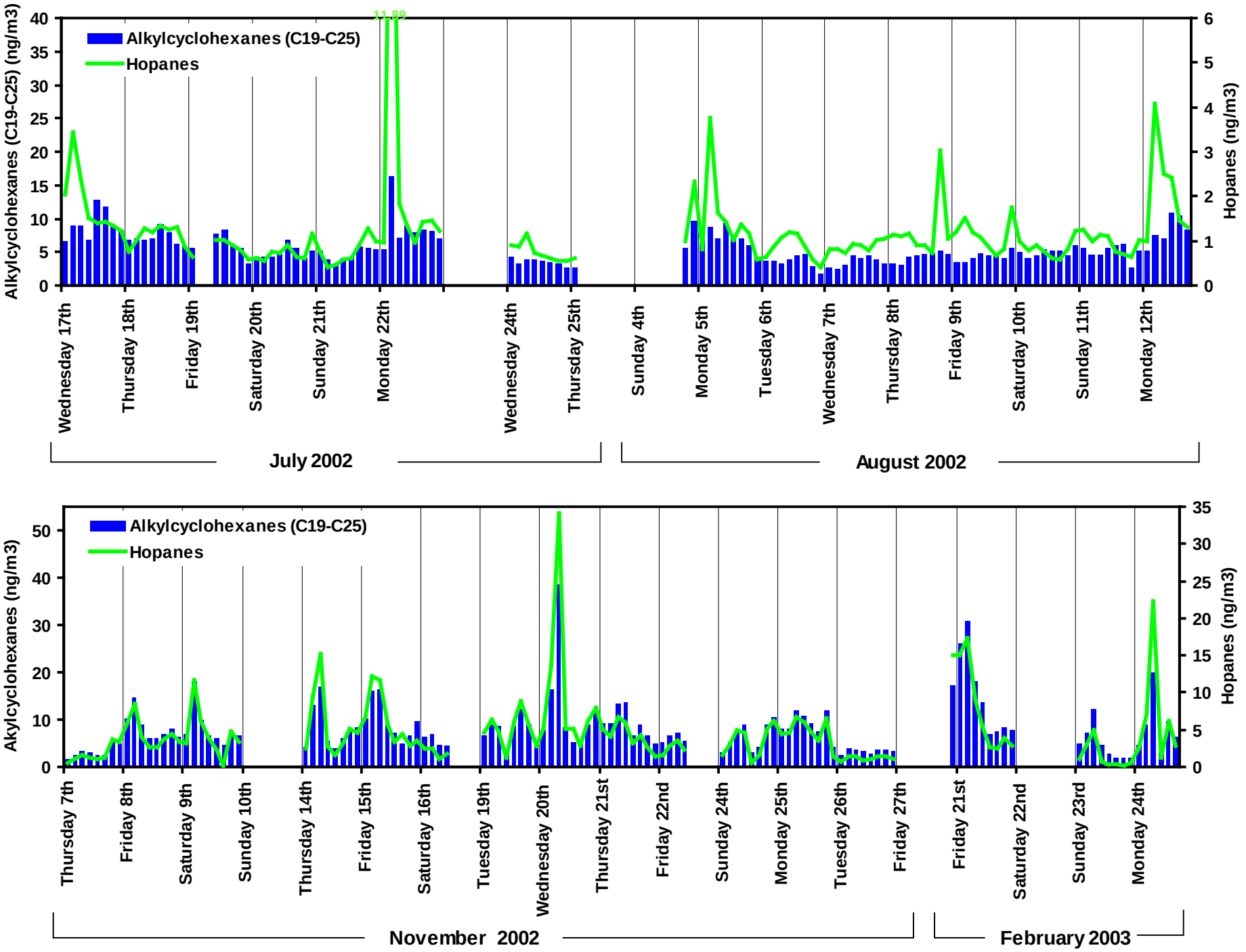


Baltimore Supersite: 3-Hourly PM2.5 Sampling Campaigns: 2002-2003

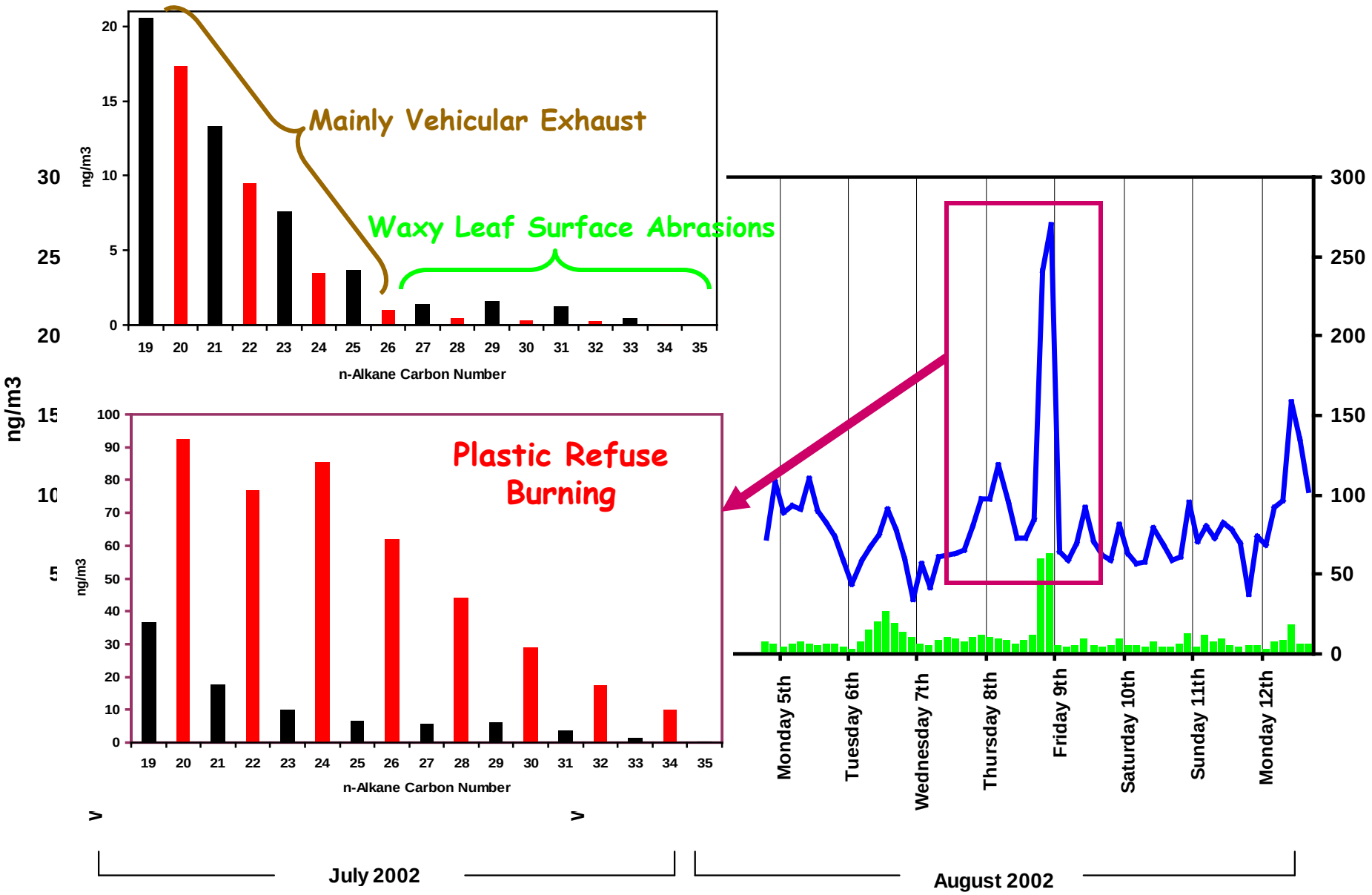


My Focus Today

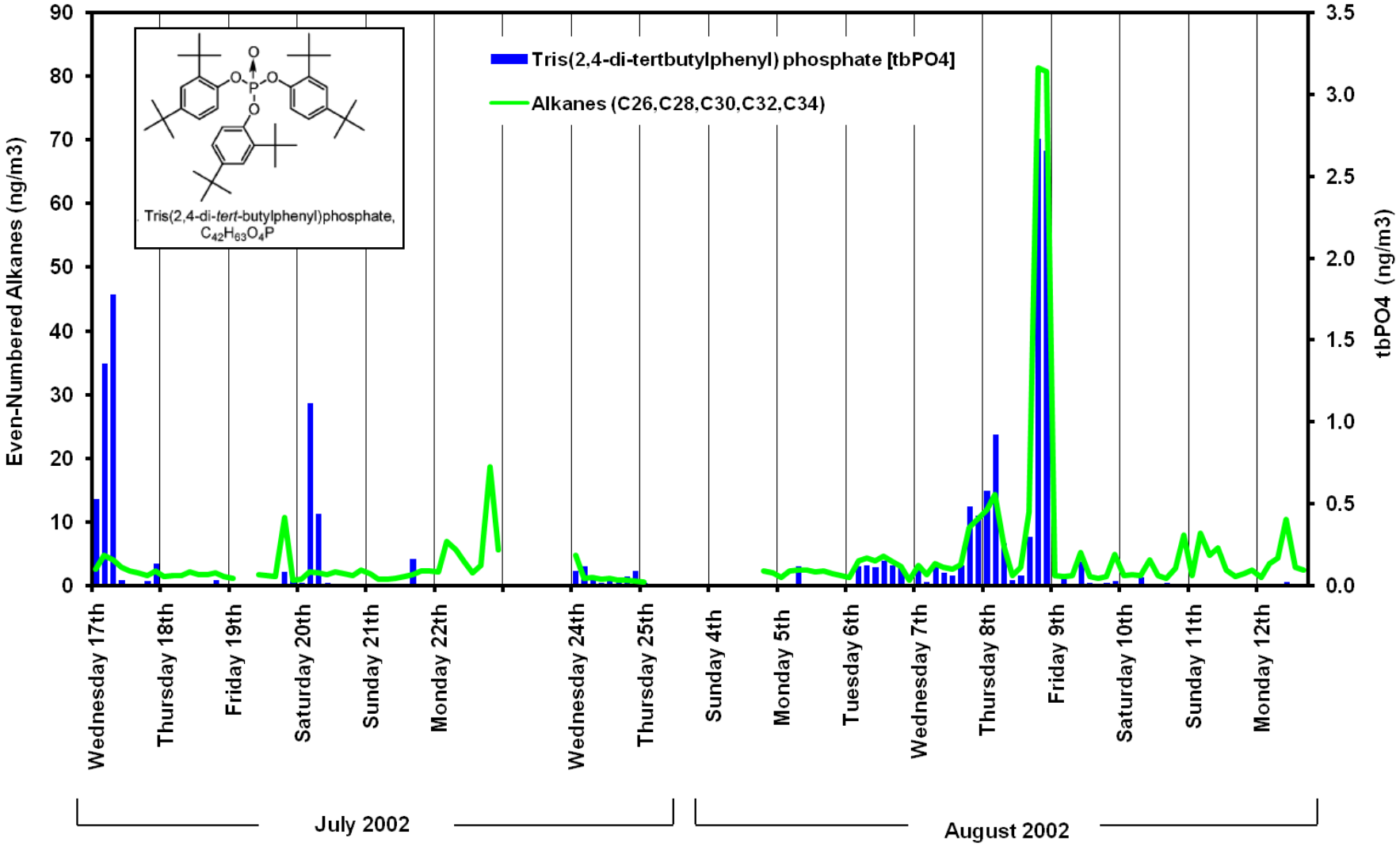
- Short-term Concentration Changes
- Markers for Plastic Refuse Burning
- Biomass Burning
- Secondary Biogenic Reaction Products - Nopinone
- Atmospheric depletion of unsaturated Fatty Acids?
- Atmospheric depletion of Cholesterol?


Alkylcyclohexanes (C19-C25) (ng/m3)
Hopanes (ng/m3)
Alkylcyclohexanes (C19-C25)
Hopanes
11.89
Wednesday 17th
Thursday 18th
Friday 19th
Saturday 20th
Sunday 21st
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)
Alkylcyclohexanes (C19-C25)
Hopanes
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

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



Ambient Concentrations of even carbon numbered n-Alkanes and Oxidation Product of antioxidant "Irganox": Organophosphate (tbPO4) for Summer 2002



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%	

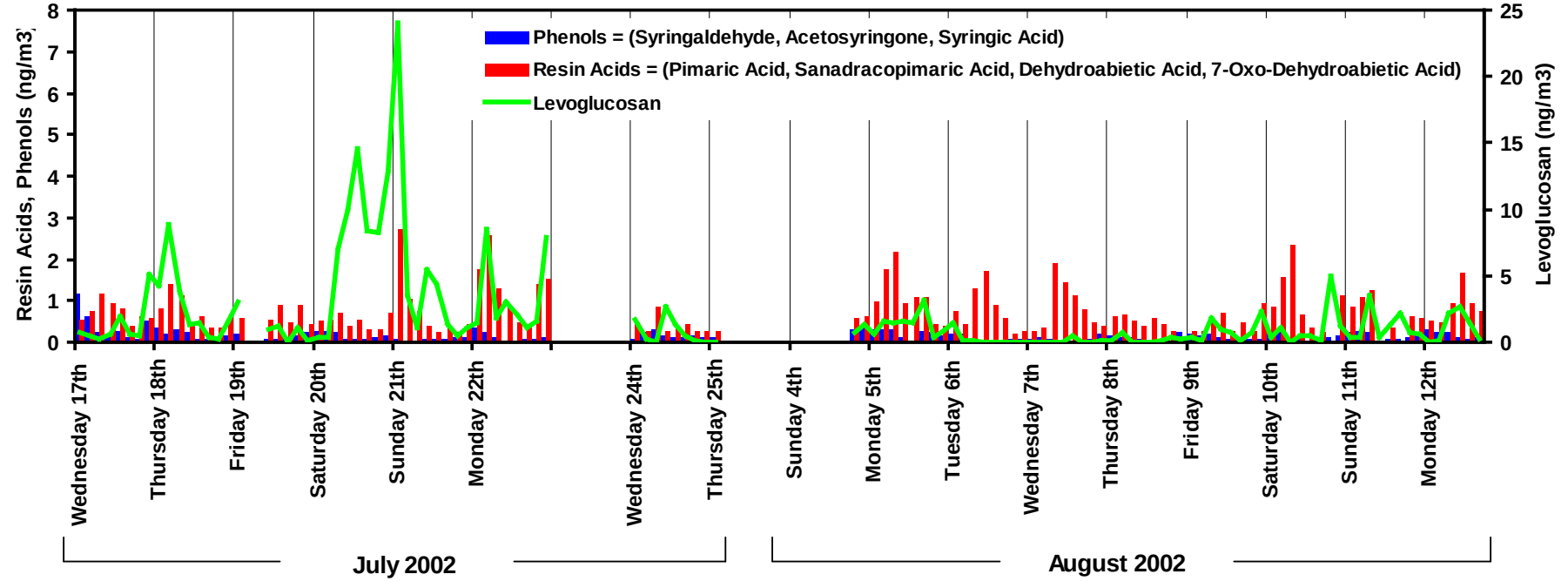
- **Marker for Cellulose Burning: Levoglucosan**

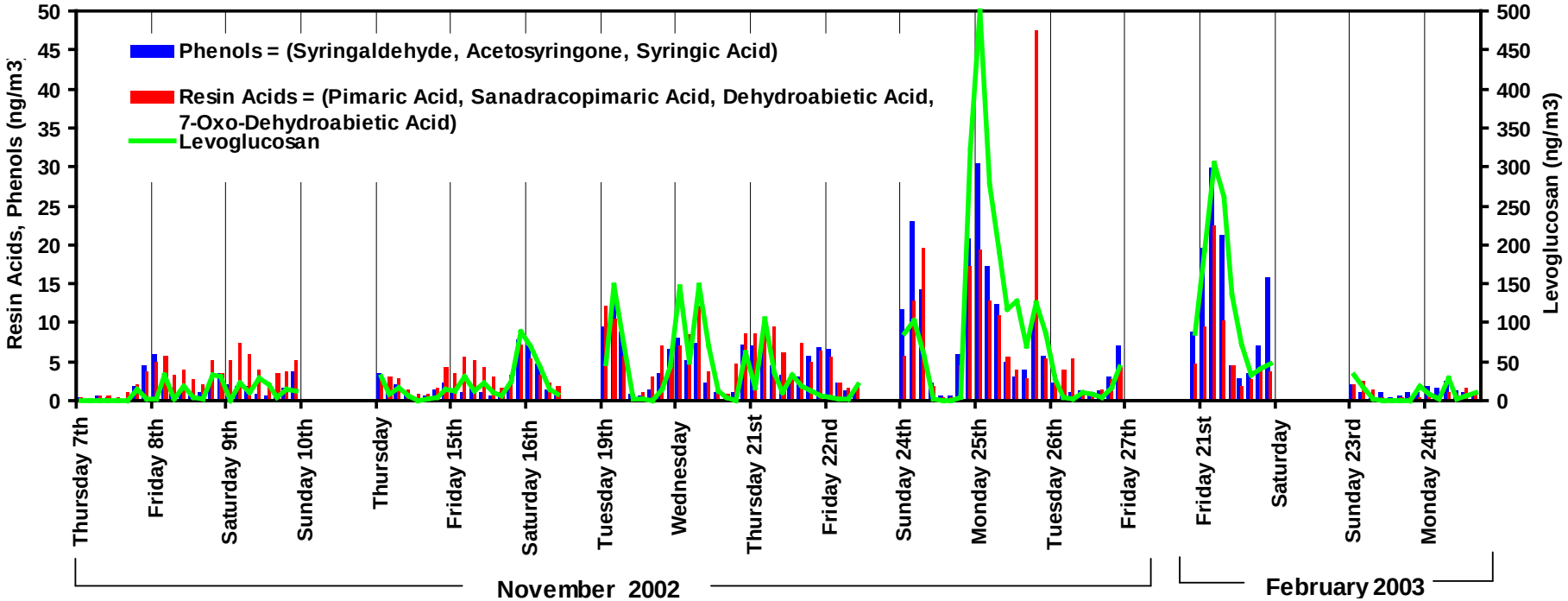
  Cellulose is the abundant organic polymer on earth, found in any wood, vegetative detritus, biomass, etc.

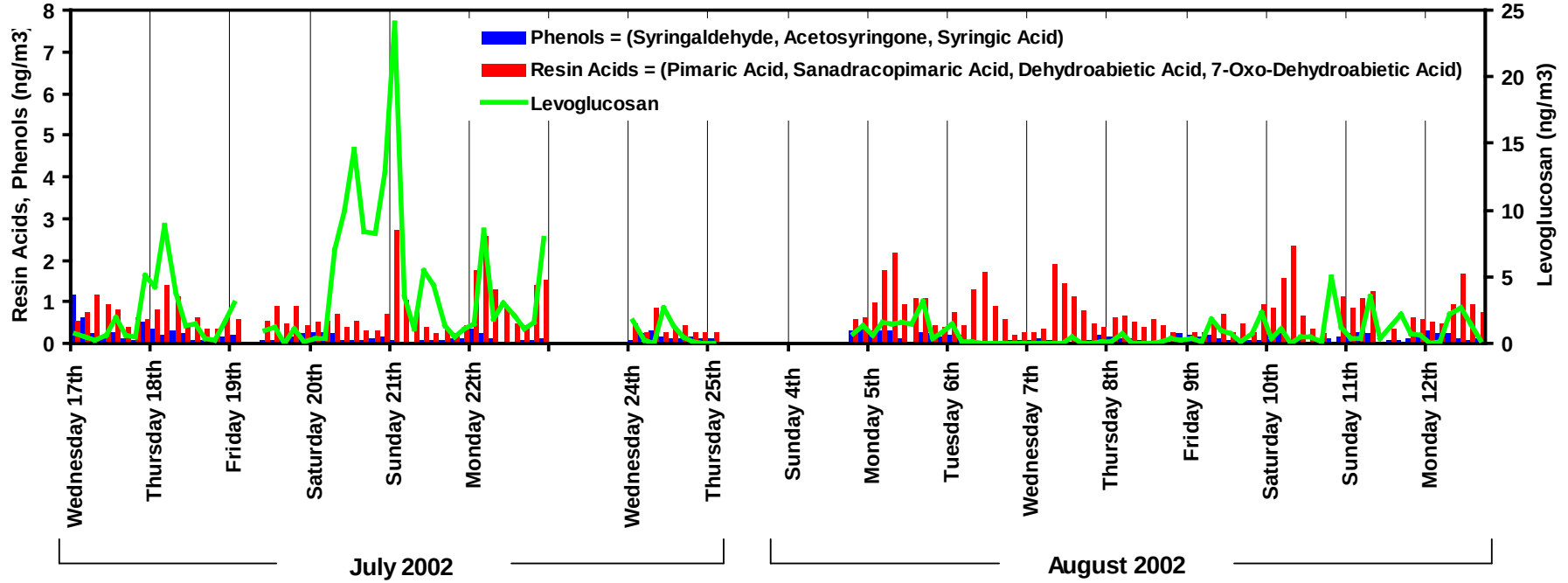
- **Markers for Lignins from Hardwood Burning: Syringyl Derivatives (Syringaldehyde, Acetosyringone, Syringic acid)**

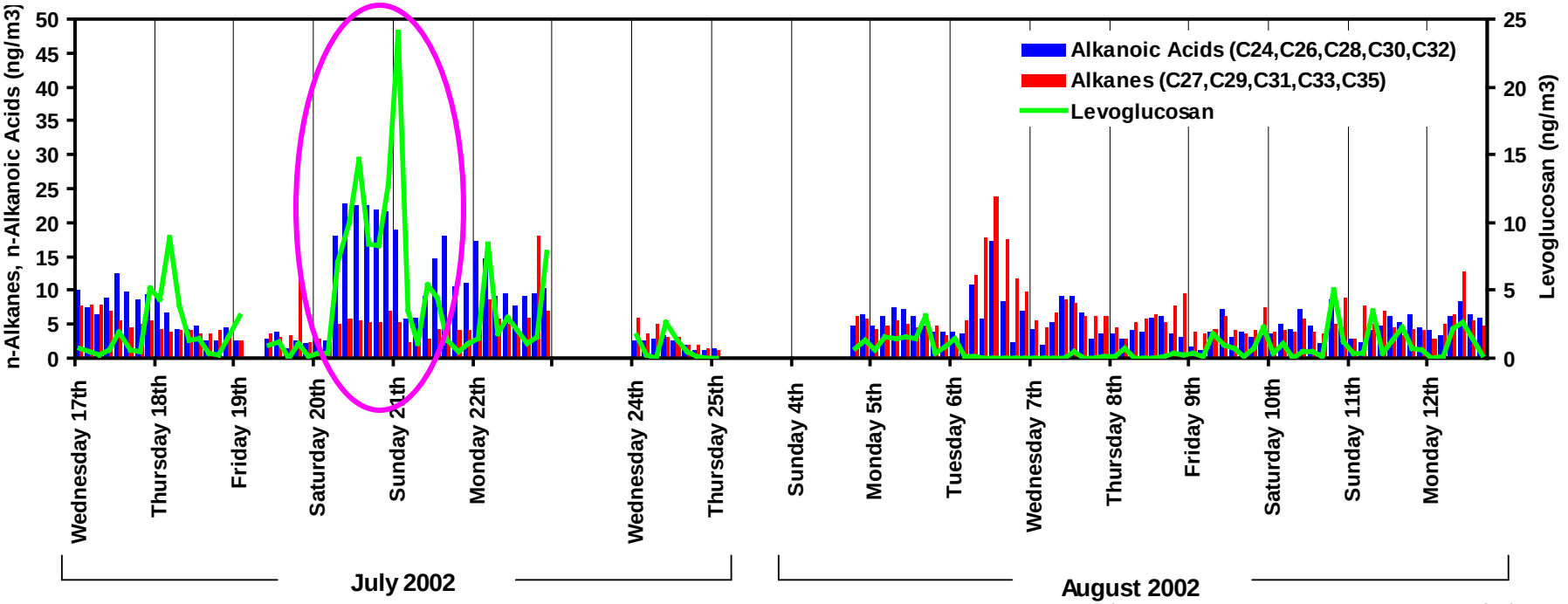
  Second most abundant organic polymer on earth:
  Hardwoods have about 50% guaiacyl and 50% syringyl units
  Softwoods have 90% - 100% guaiacyl units

- **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)
0
1
2
3
4
5
6
7
8
0
5
10
15
20
25
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

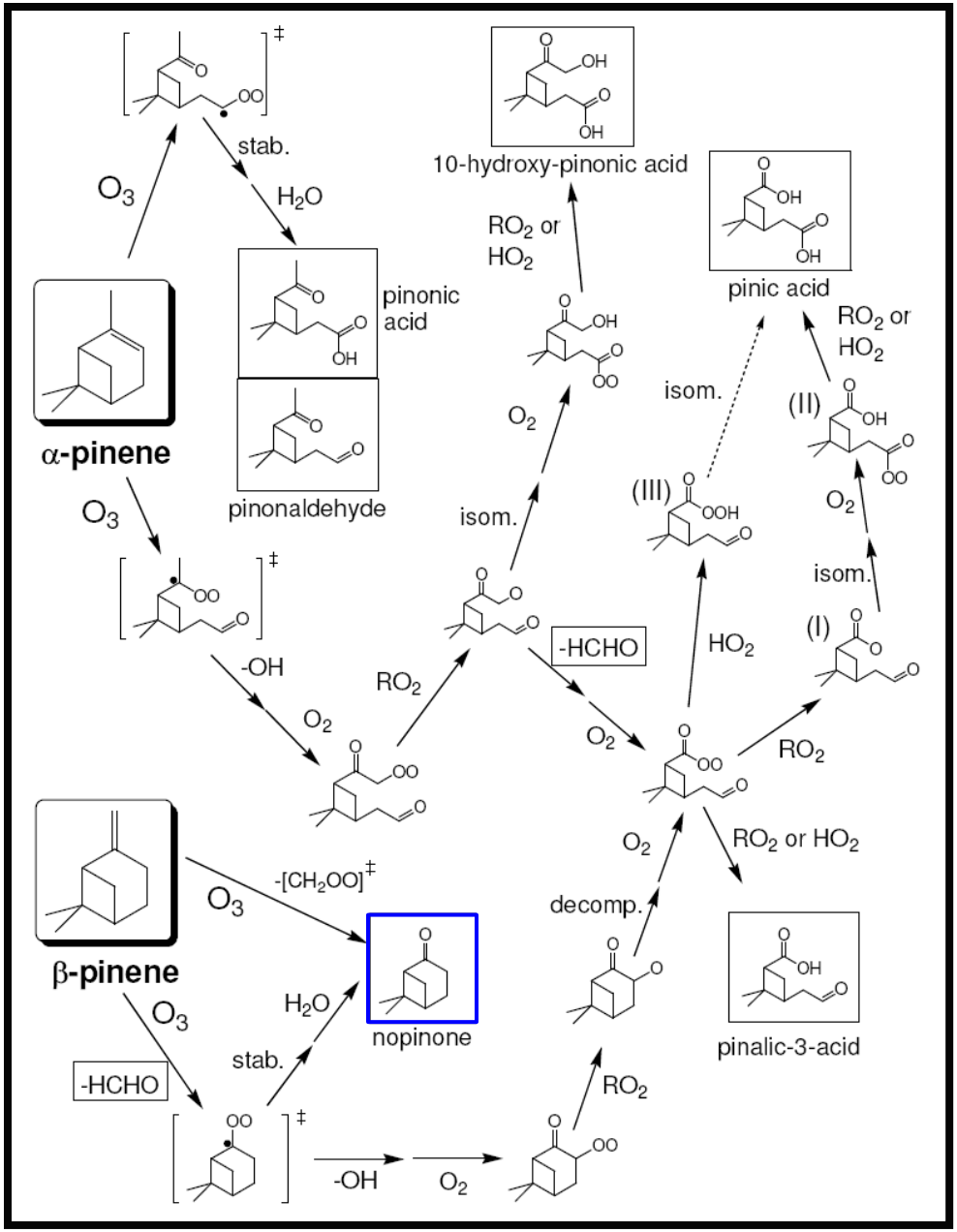

Phenols = (Syringaldehyde, Acetosyringone, Syringic Acid)
Resin Acids = (Pimaric Acid, Sanadracopimaric Acid, Dehydroabietic Acid,
7-Oxo-Dehydroabietic Acid)
Levoglucosan
Resin Acids, Phenols (ng/m3)
Levoglucosan (ng/m3)
0
5
10
15
20
25
30
35
40
45
50
0
50
100
150
200
250
300
350
400
450
500
Thursday 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


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

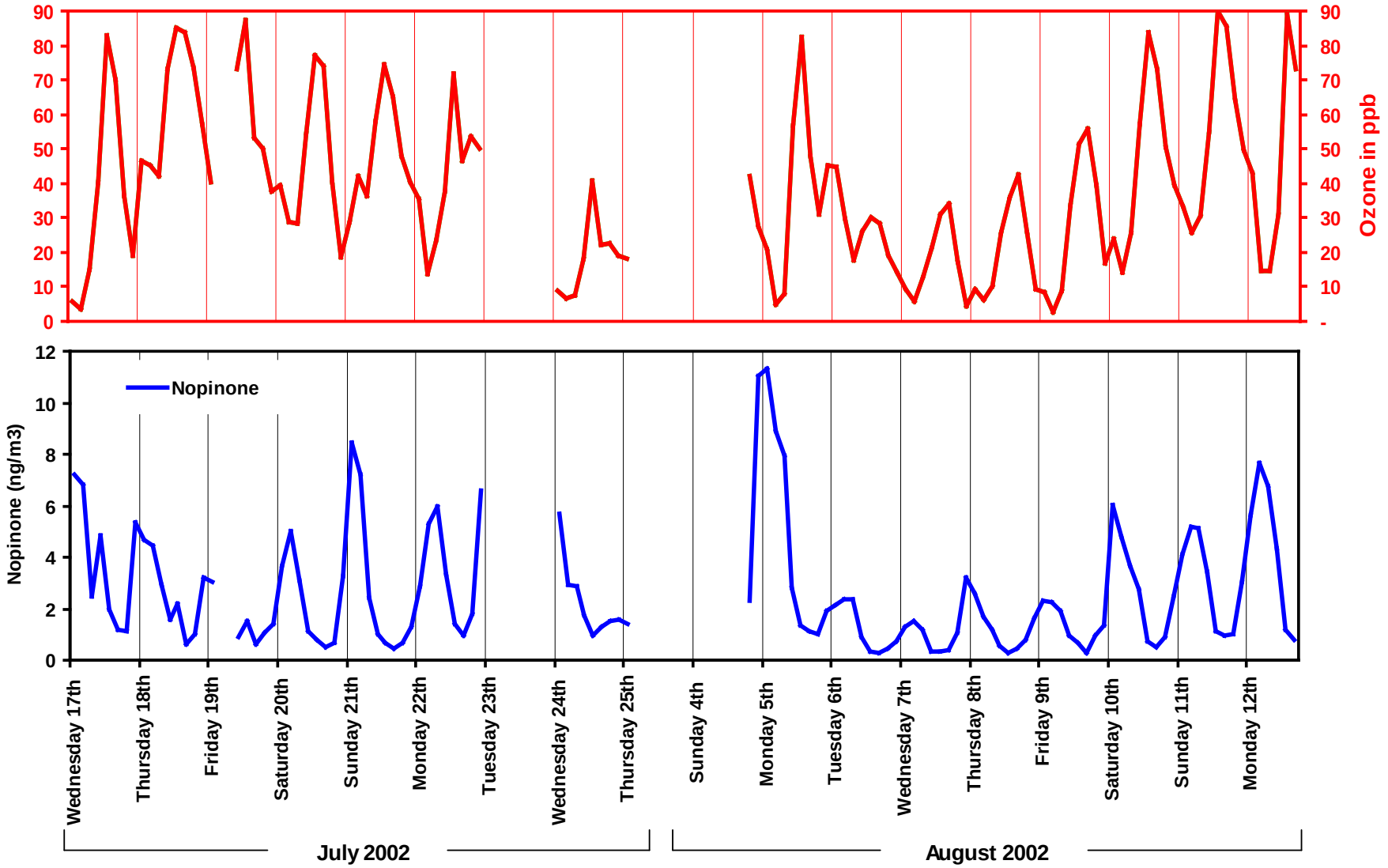

Alkanoic Acids (C24,C26,C28,C30,C32)
Alkanes (C27,C29,C31,C33,C35)
Levoglucosan
n-Alkanes, n-Alkanoic Acids (ng/m3)
Levoglucosan (ng/m3)
Wednesday 17th
Thursday 18th
Friday 19th
Saturday 20th
Sunday 21th
Monday 22th
Wednesday 24th
Thursday 25th
Sunday 4th
Monday 5th
Tuesday 6th
Wednesday 7th
Thursday 8th
Friday 9th
Saturday 10th
Sunday 11th
Monday 12th
July 2002
August 2002

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

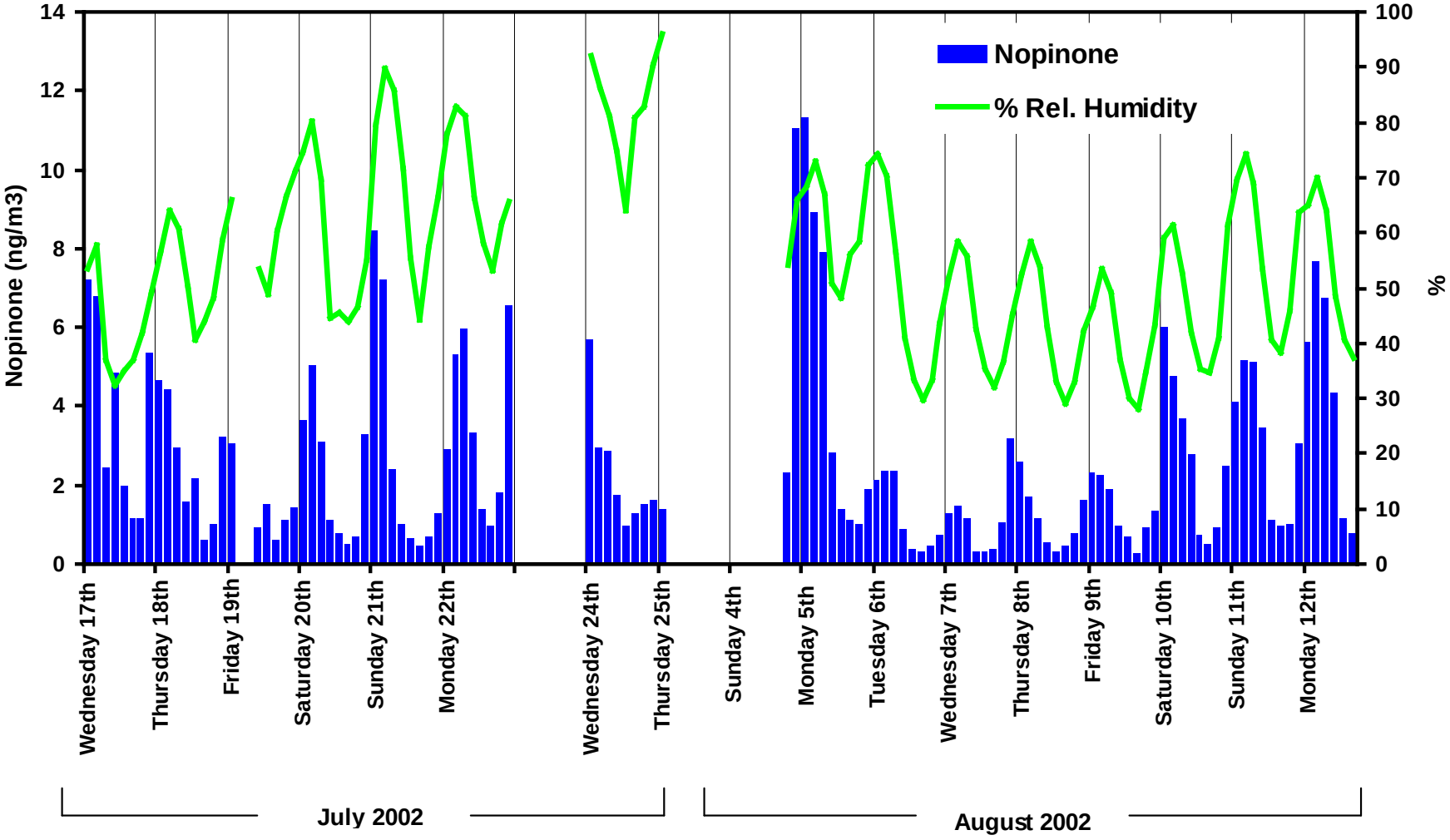
from: M.E. Jenkin, Atmos.Chem. Phys., 4, 1741-1757, 2004



Nopinone - Summer 2002

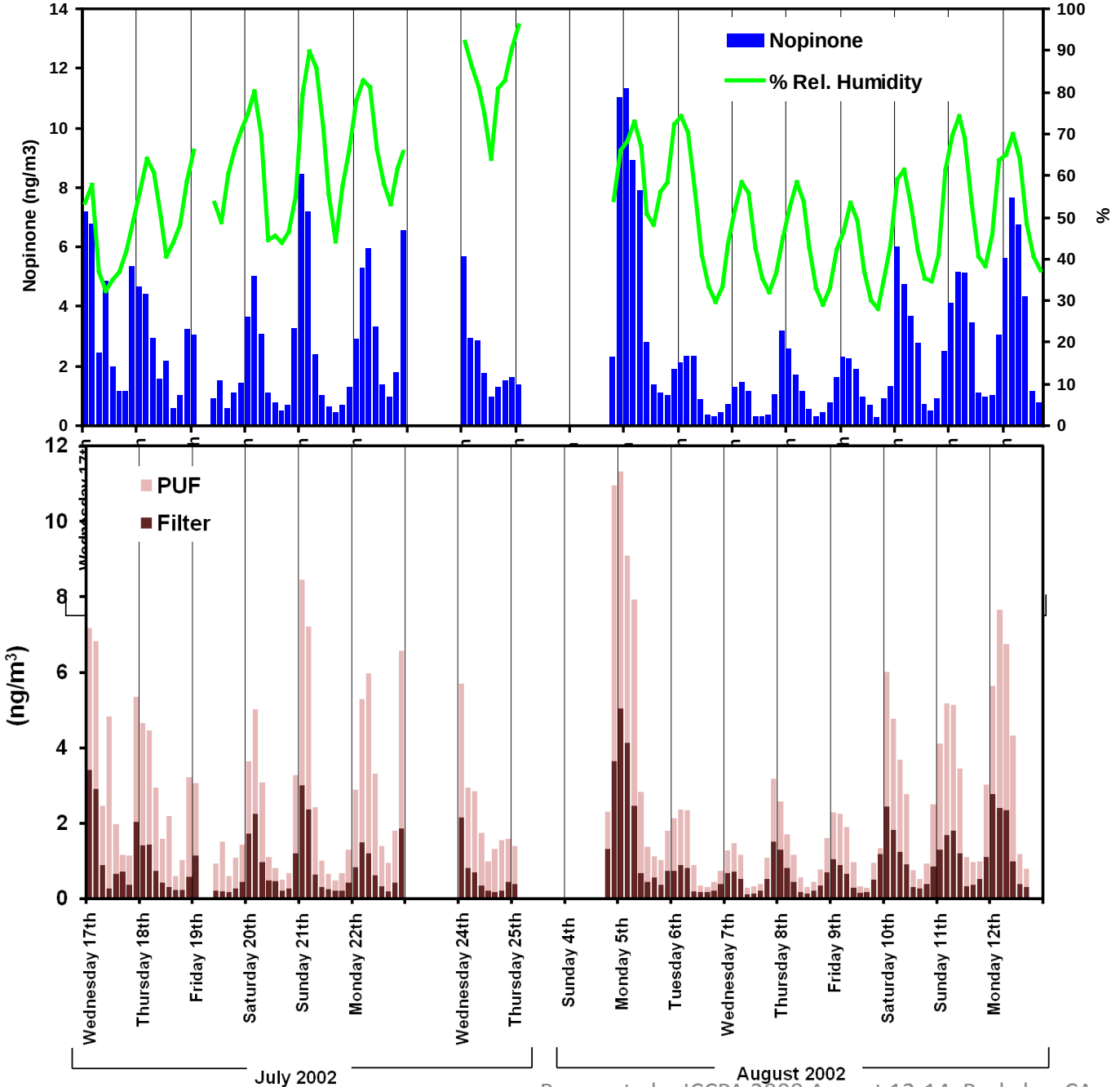


Nopinone: Secondary Biogenic Reaction Products - Summer 2002



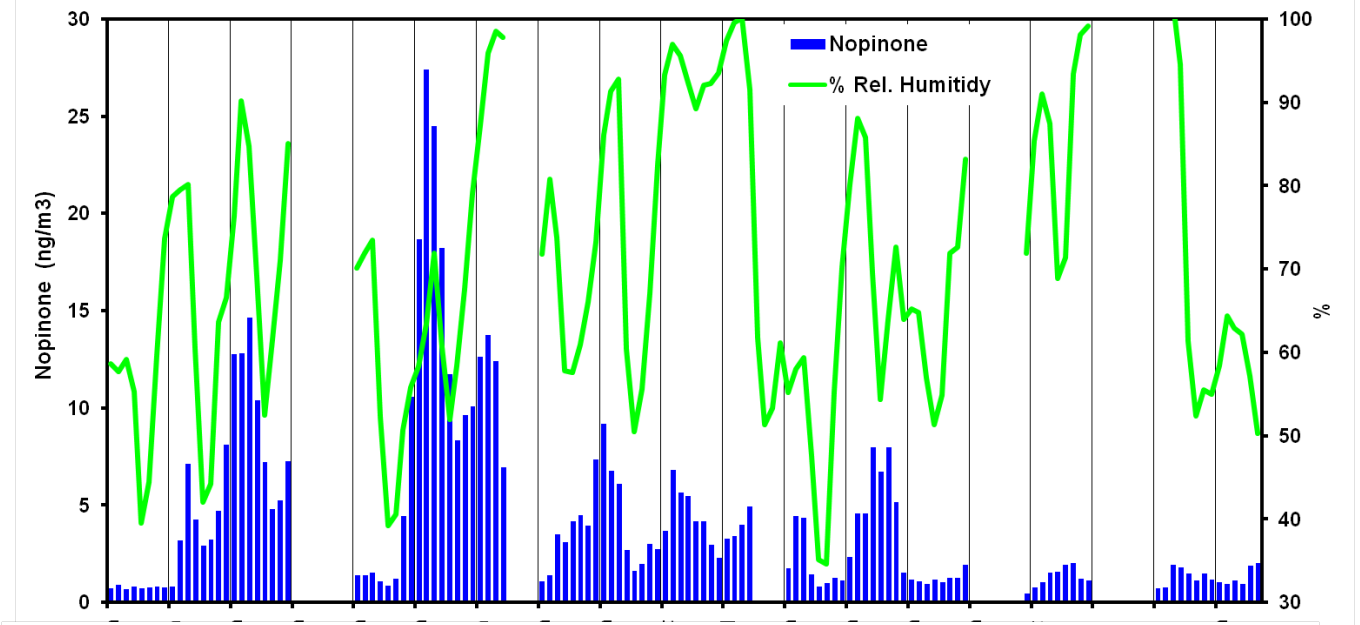
Nopinone, Rel. Humidity, & volatility:

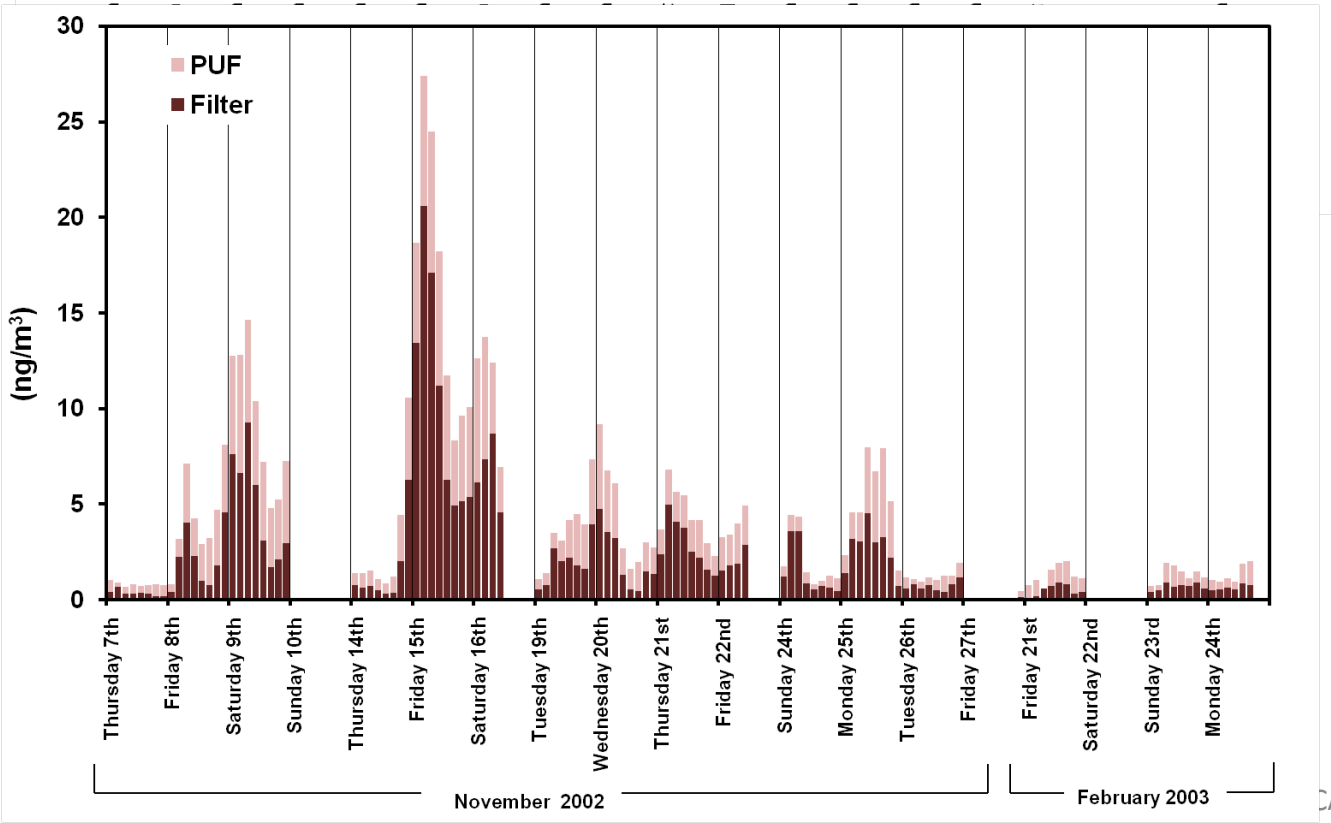
Summer 2002



Nopinone, Rel. Humidity, & volatility:

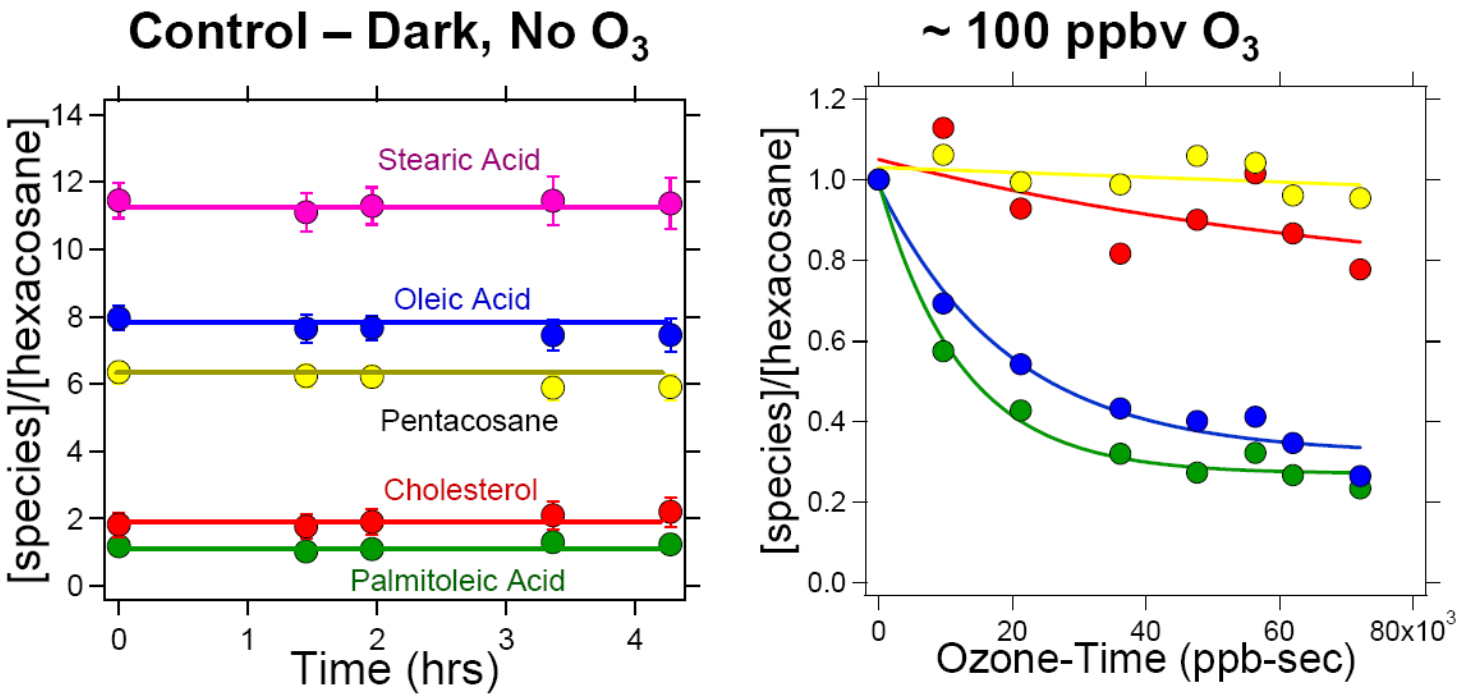
Winter 2002/03



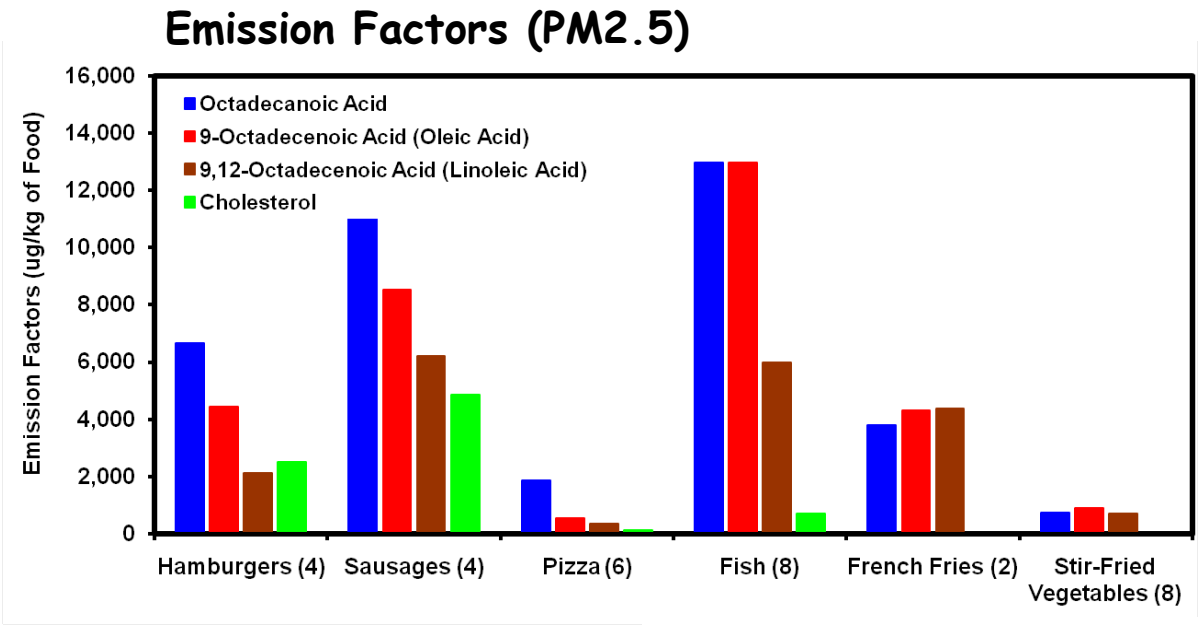


Allen Robinson:

Rapid Oxidation of Molecular Markers in Hamburger Grease Aerosol



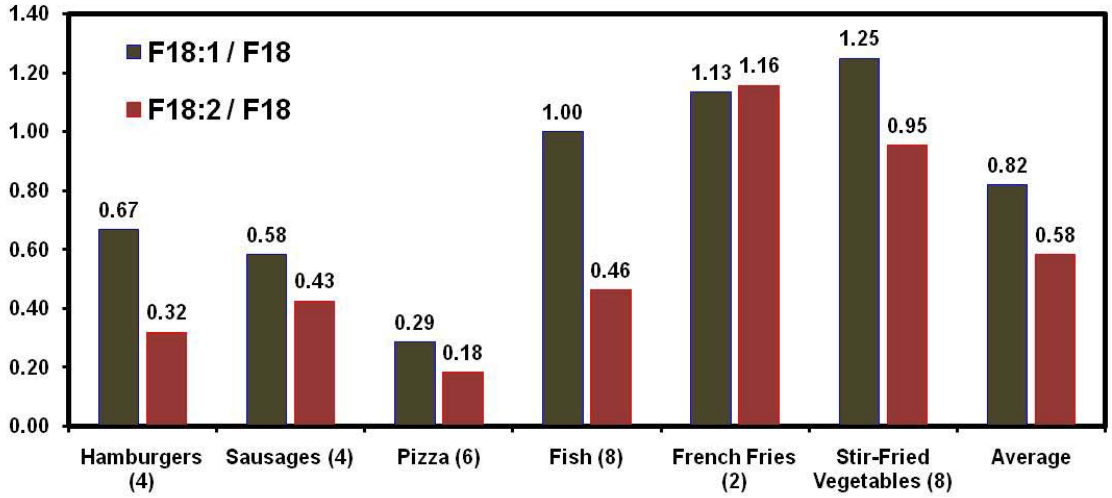
C18 Fatty Acids: What happens to Unsaturated Fatty Acids in the Baltimore Atmosphere – Summer vs. Winter



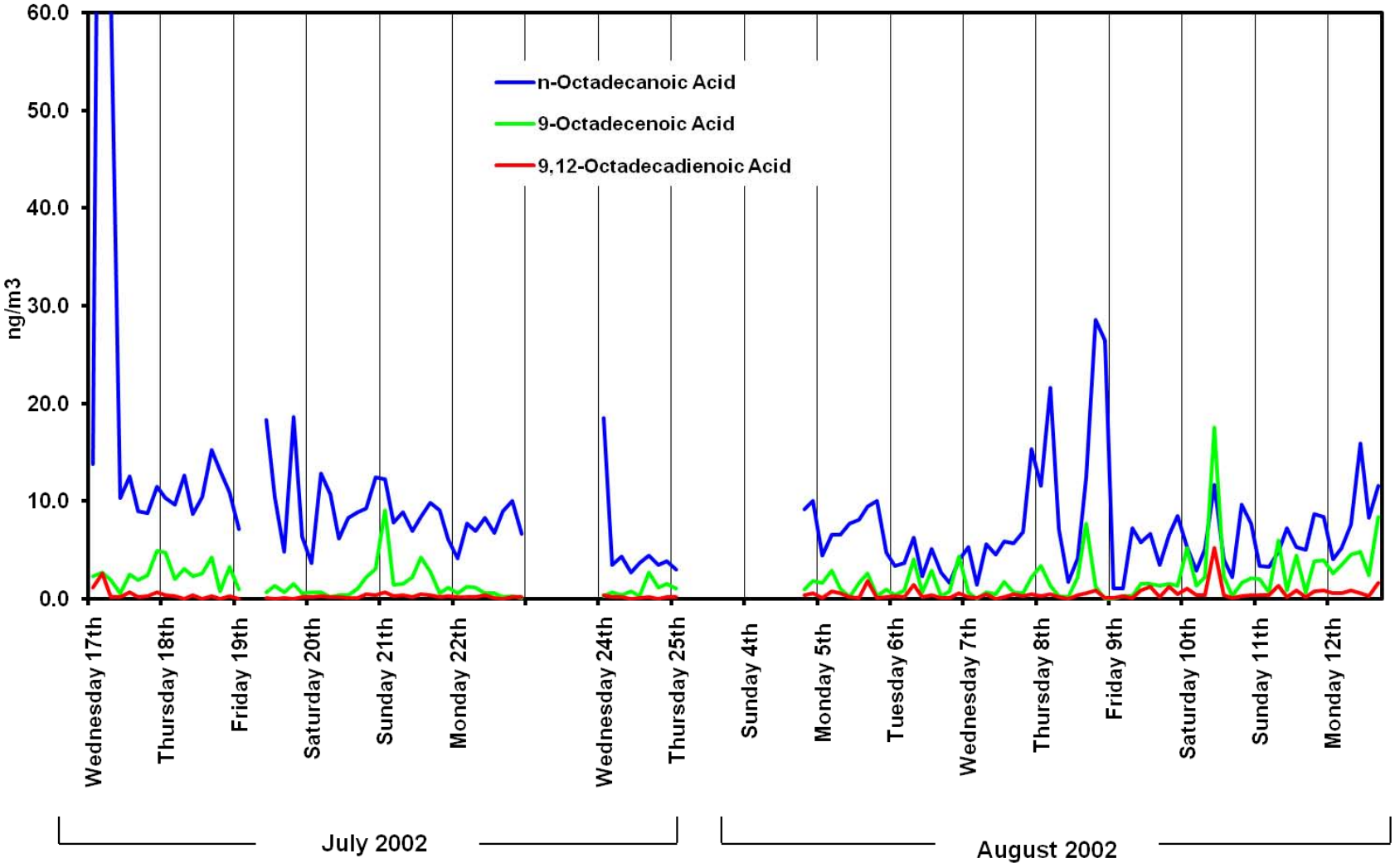
Number of Experiments in ( )

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

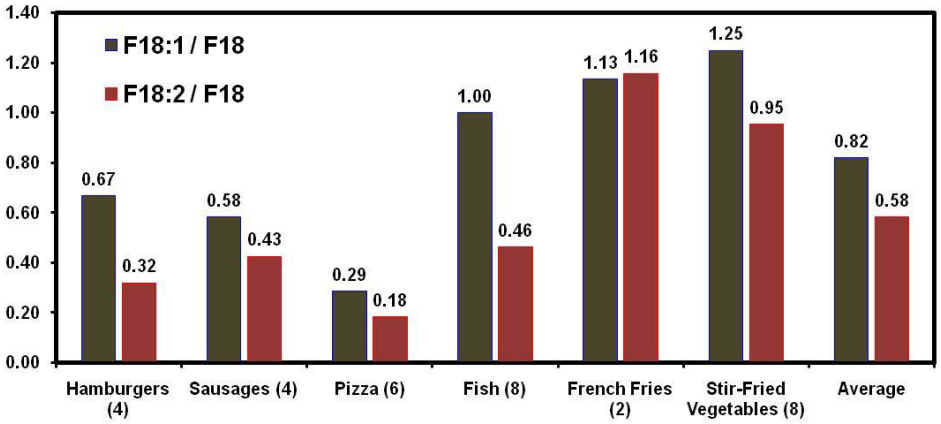
$$\text{Ratio} = \frac{\text{unsaturated fatty acid}}{\text{saturated fatty acid}}$$



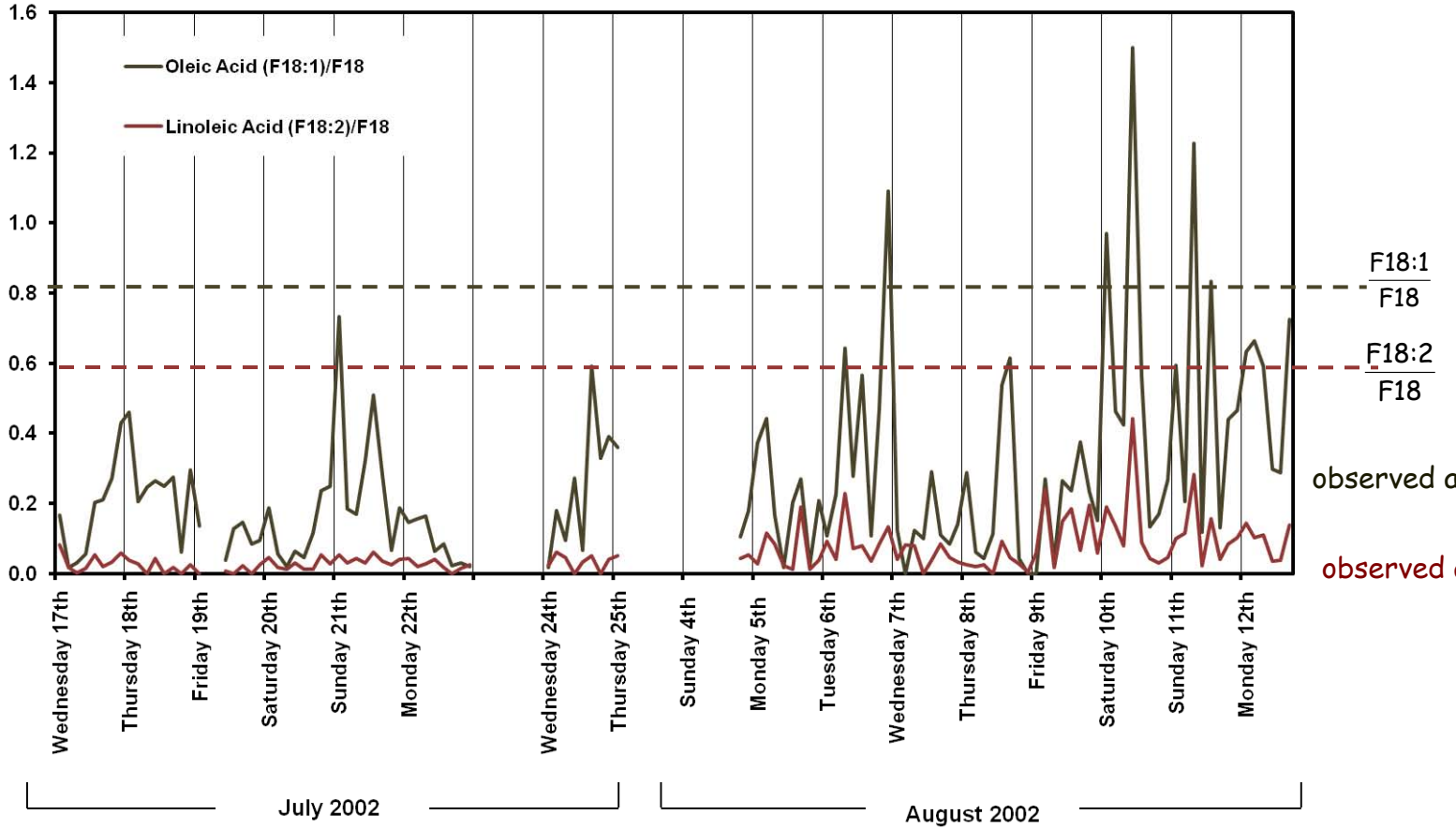
Summer 2002: Ambient Concentrations of F18 Saturated and Unsaturated Fatty Acids



$$\text{Ratio} = \frac{\text{unsaturated fatty acid}}{\text{saturated fatty acid}}$$



Summer



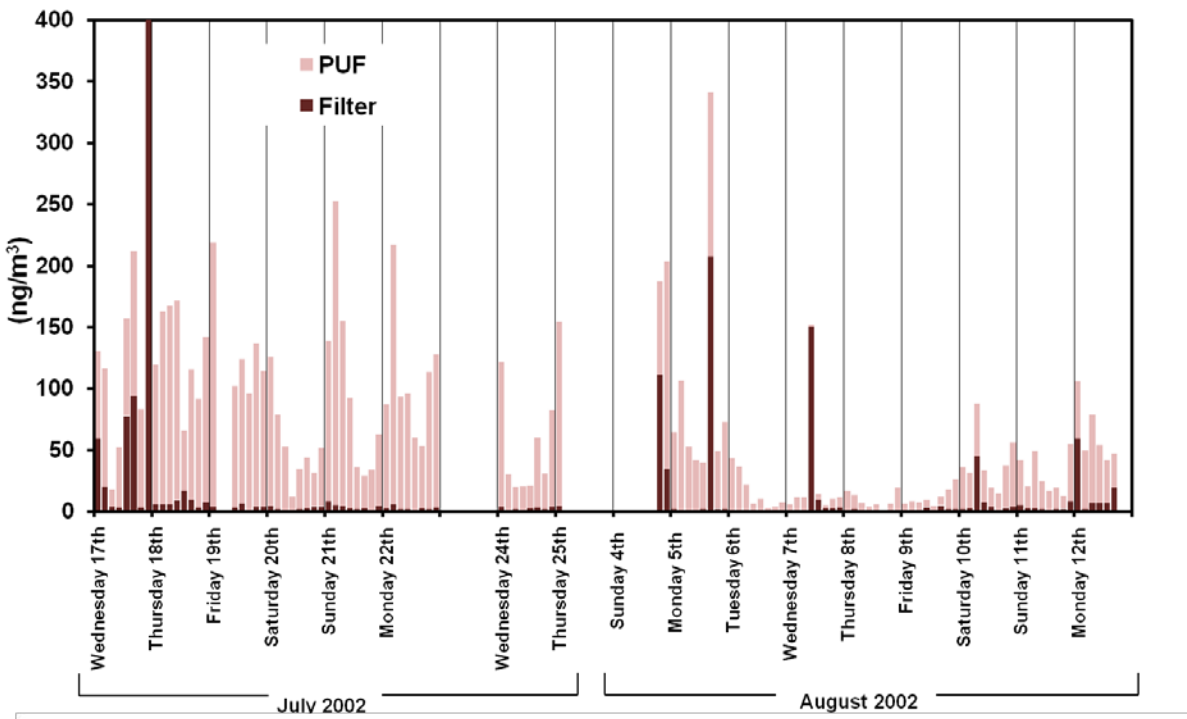
$\frac{F18:1}{F18}$

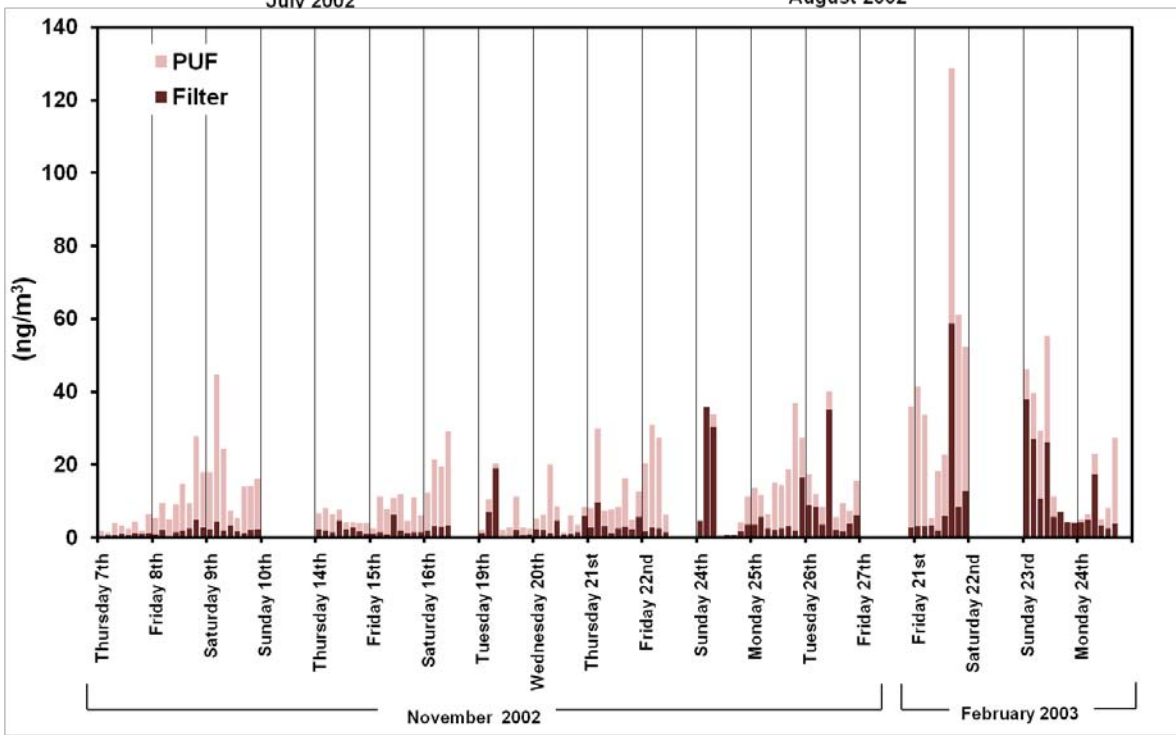
$\frac{F18:2}{F18}$

observed average $\frac{F18:1}{F18} = 0.27$

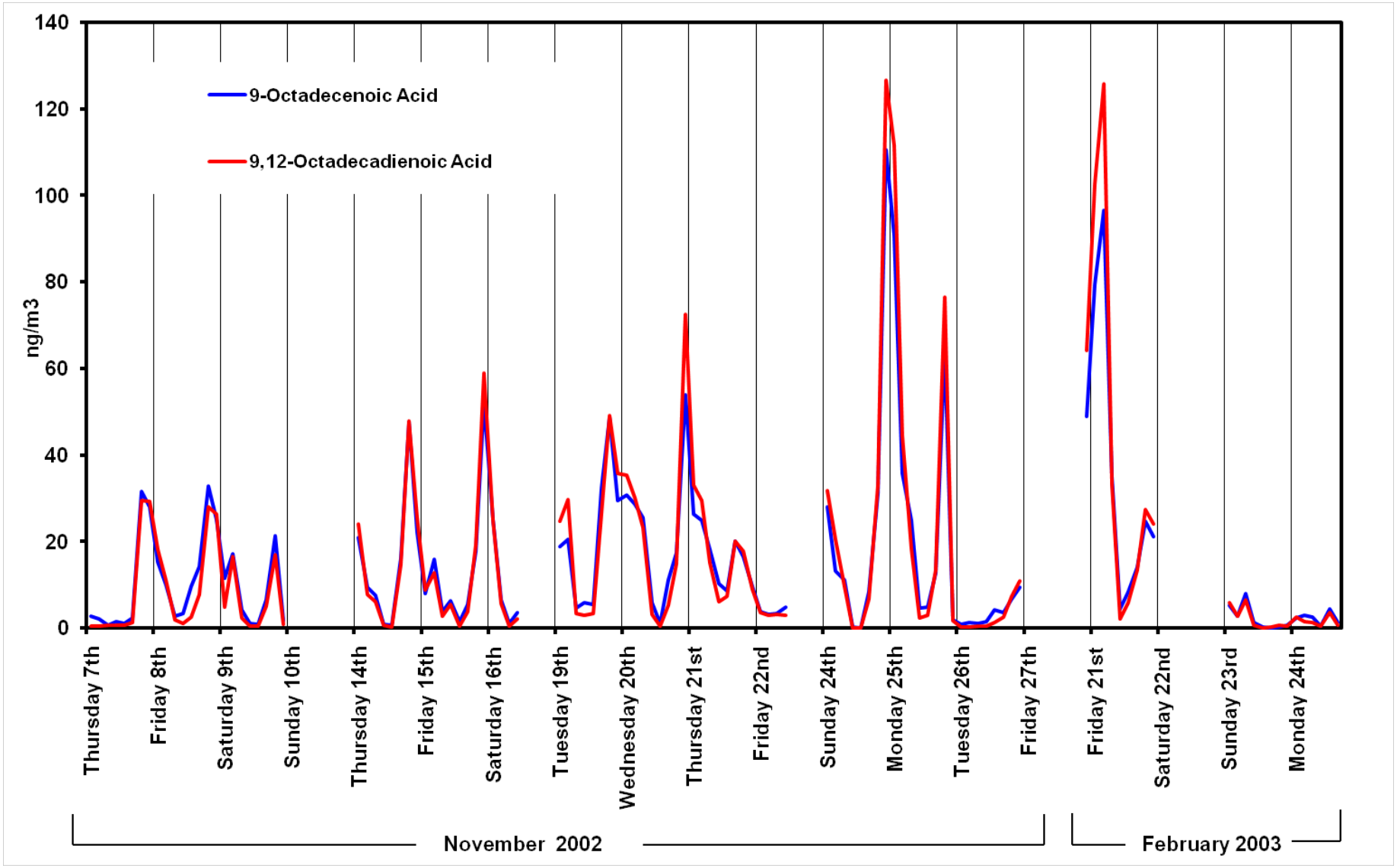
observed average $\frac{F18:2}{F18} = 0.06$

Nonanoic Acid

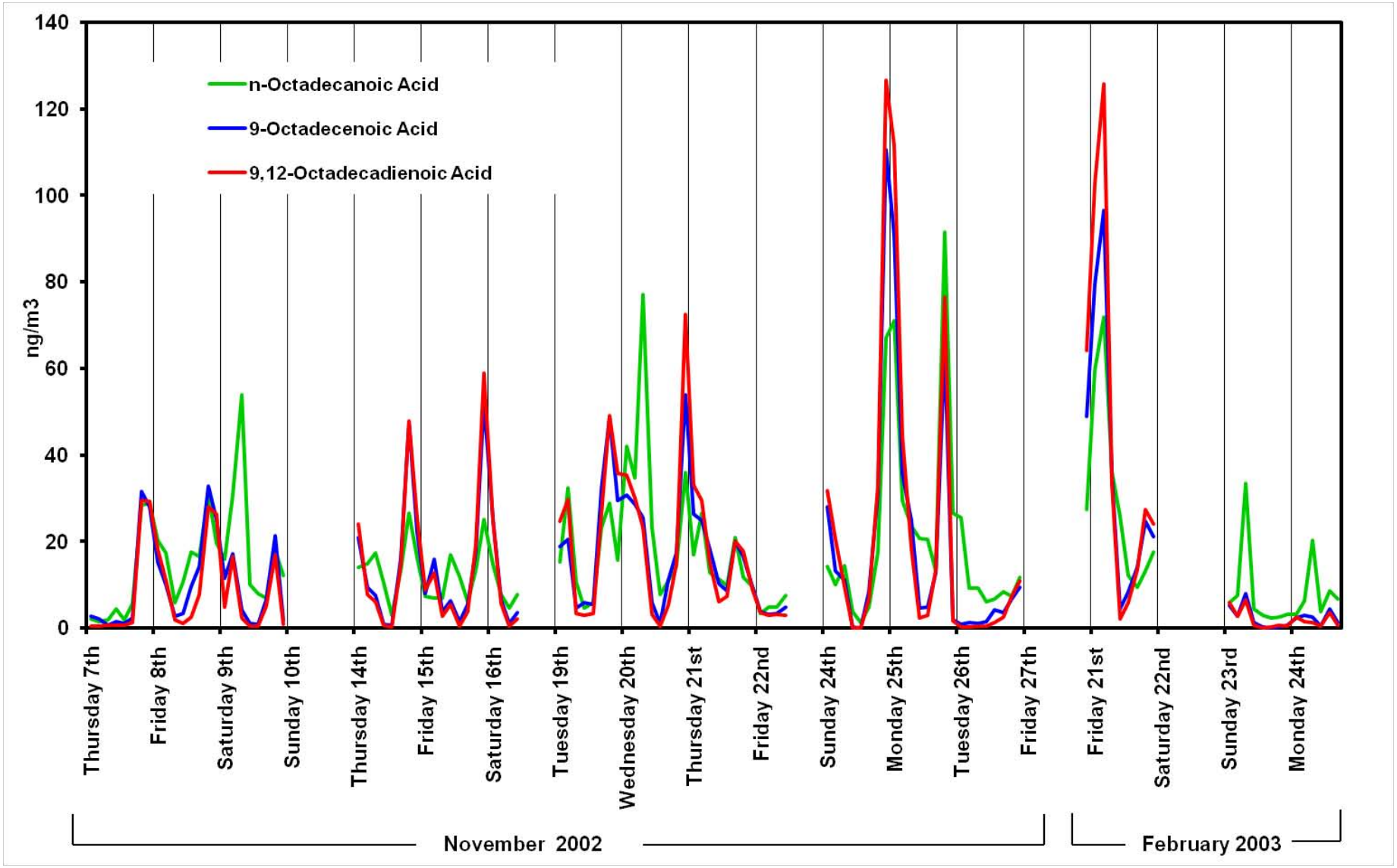




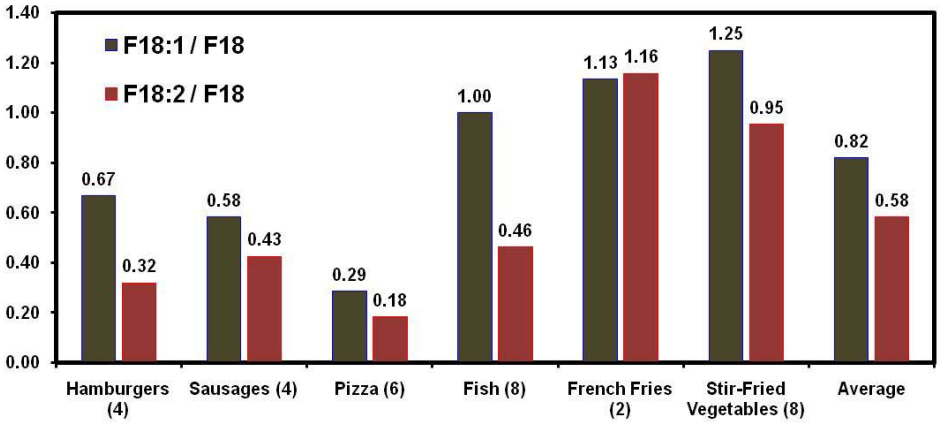
Winter 2002/03: Ambient Concentrations of F18 Unsaturated Fatty Acids



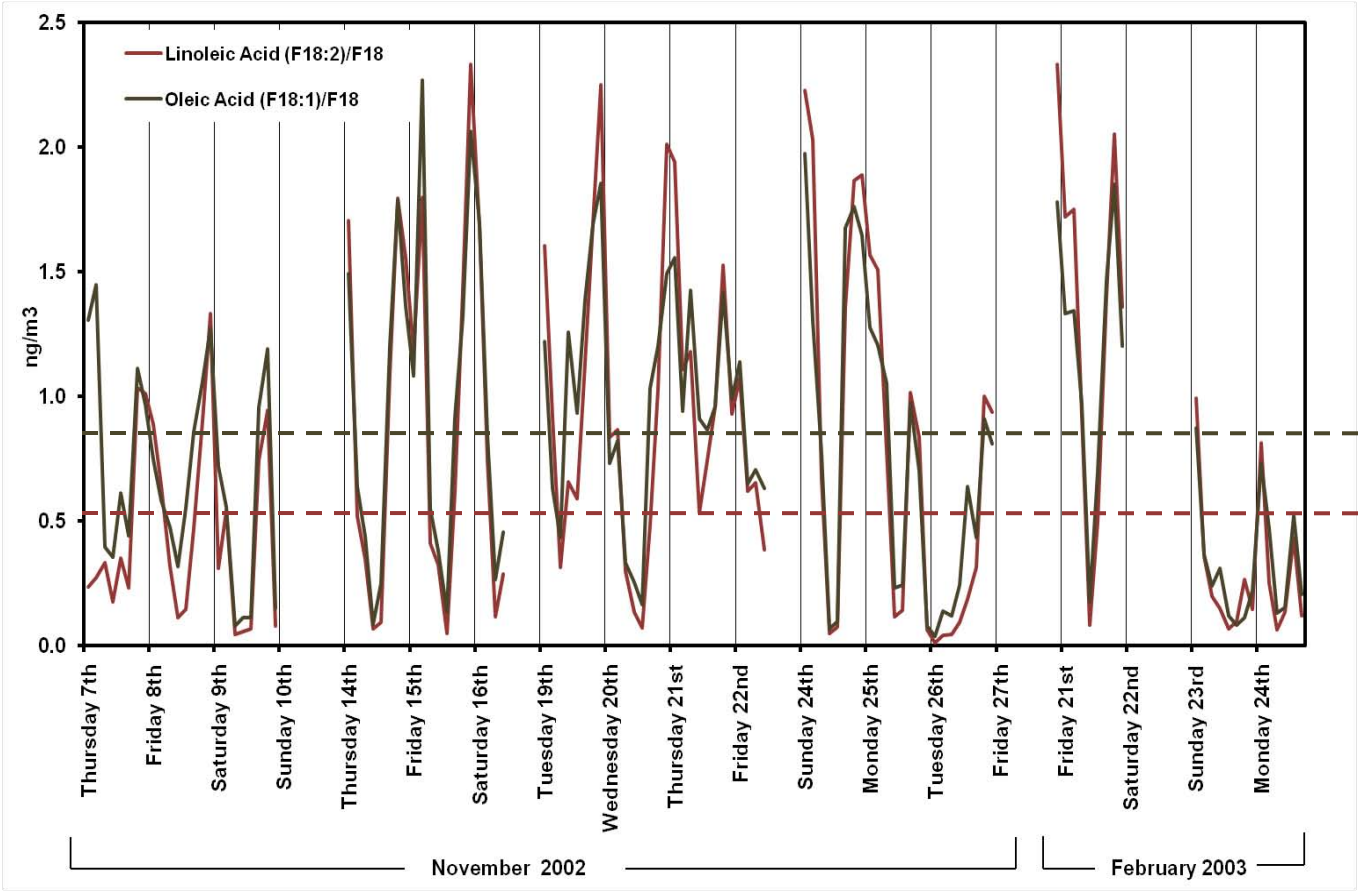
Winter 2002/03: Ambient Concentrations of F18 Saturated and Unsaturated Fatty Acids



$$\text{Ratio} = \frac{\text{unsaturated fatty acid}}{\text{saturated fatty acid}}$$



Winter



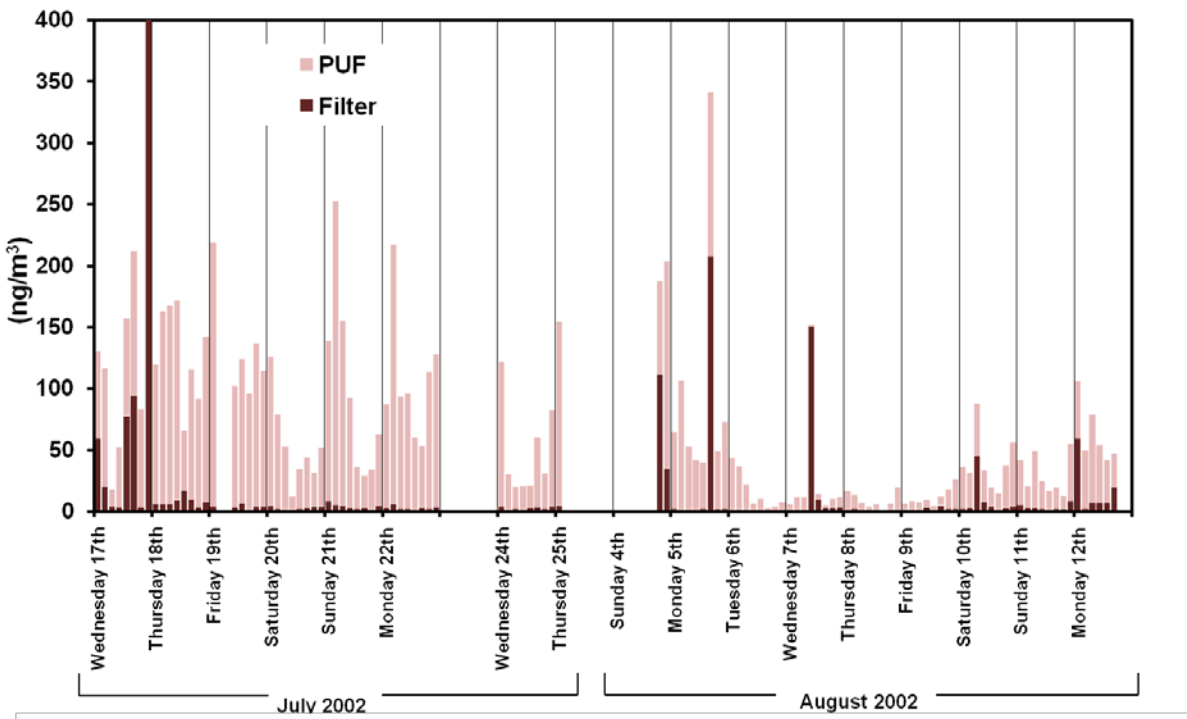
$\frac{F18:1}{F18}$

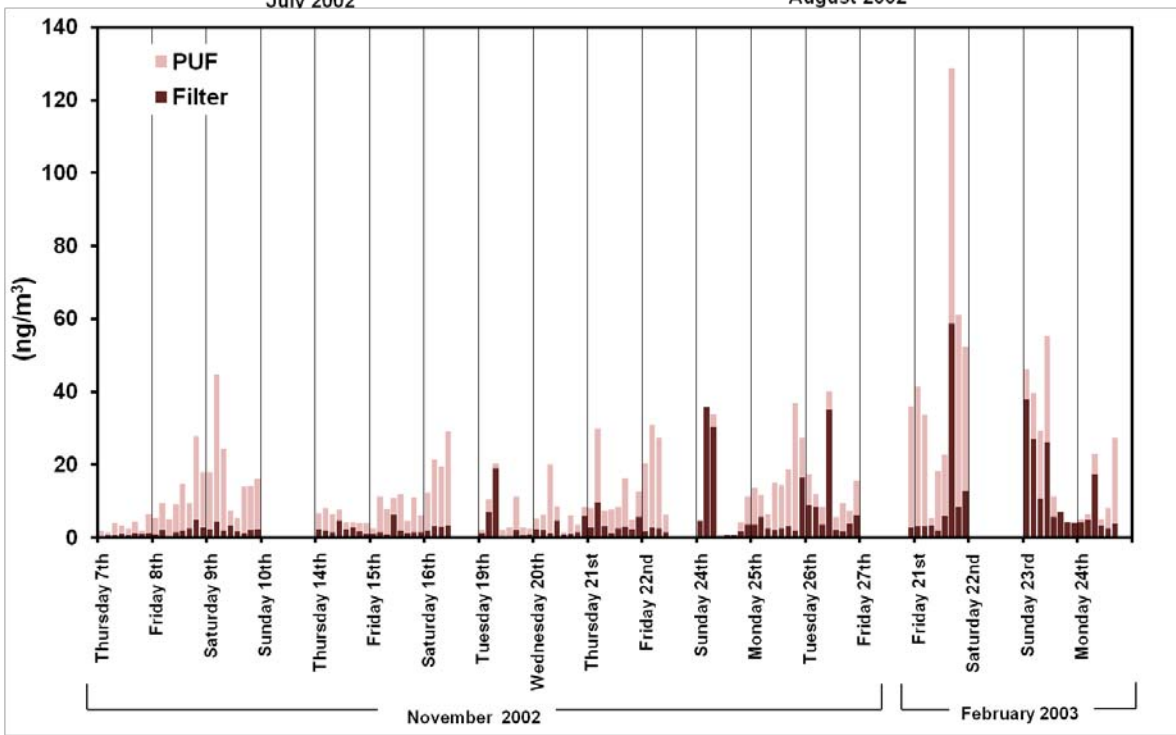
$\frac{F18:2}{F18}$

observed average $\frac{F18:1}{F18} = 0.82$

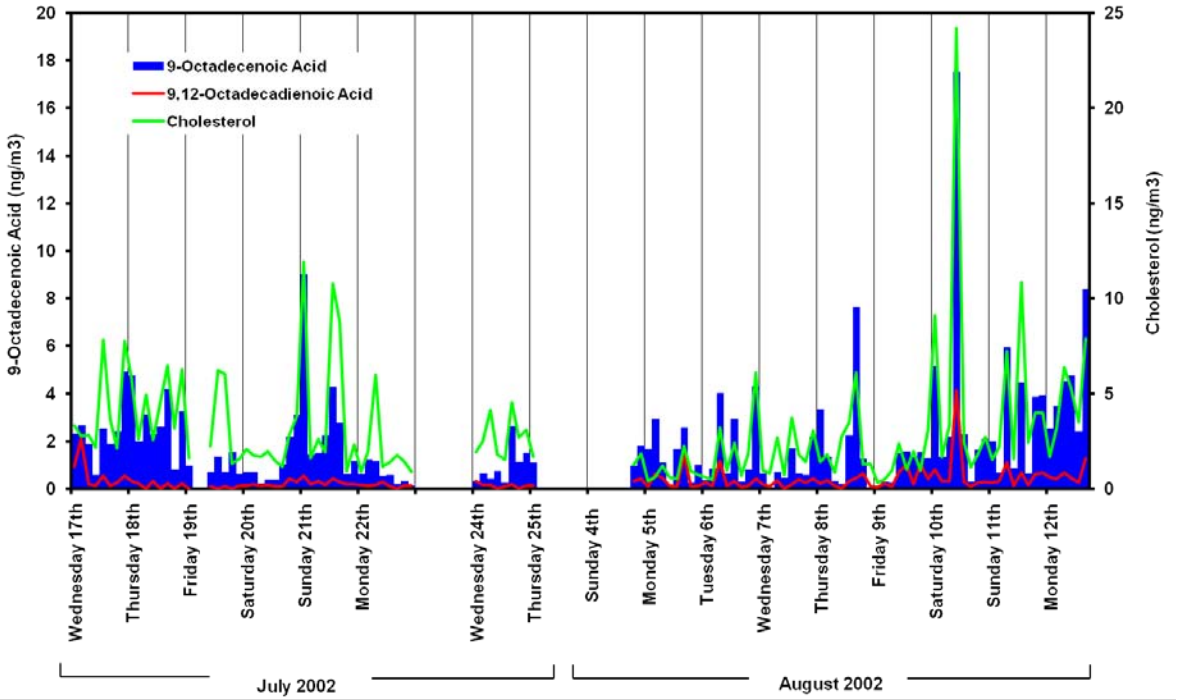
observed average $\frac{F18:2}{F18} = 0.76$

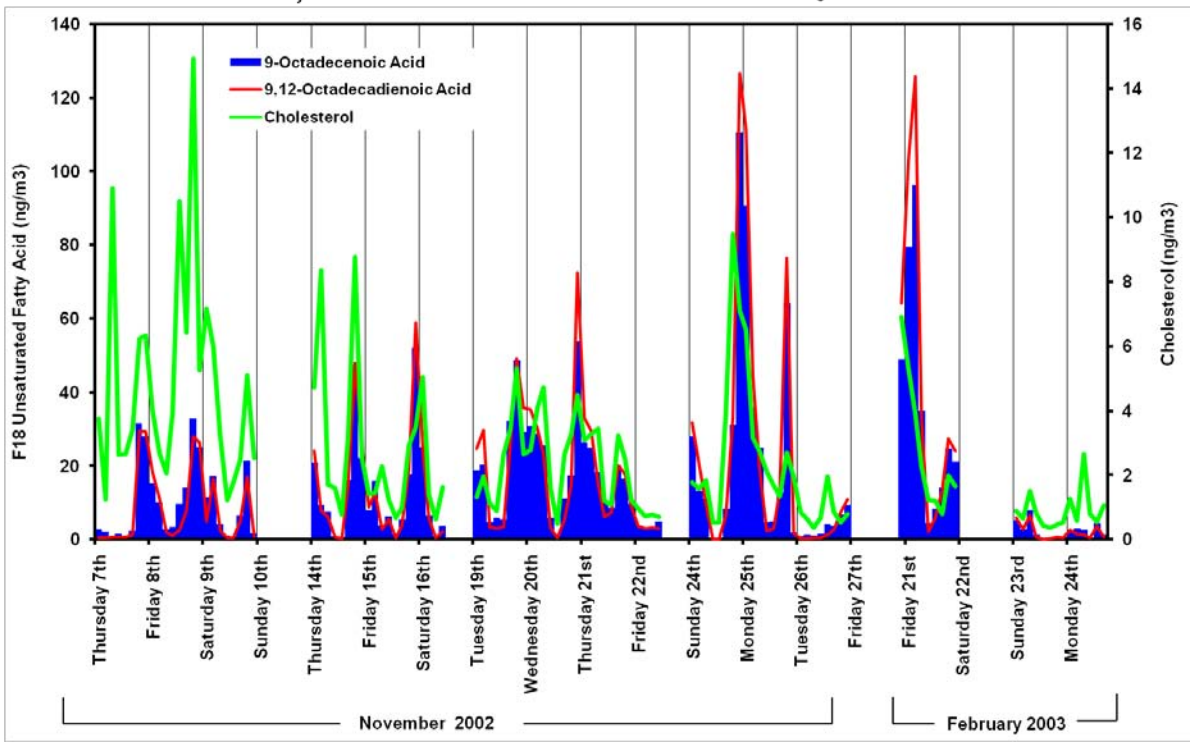
Nonanoic Acid





Ambient Concentrations of Oleic Acid, Linoleic Acid, and Cholesterol

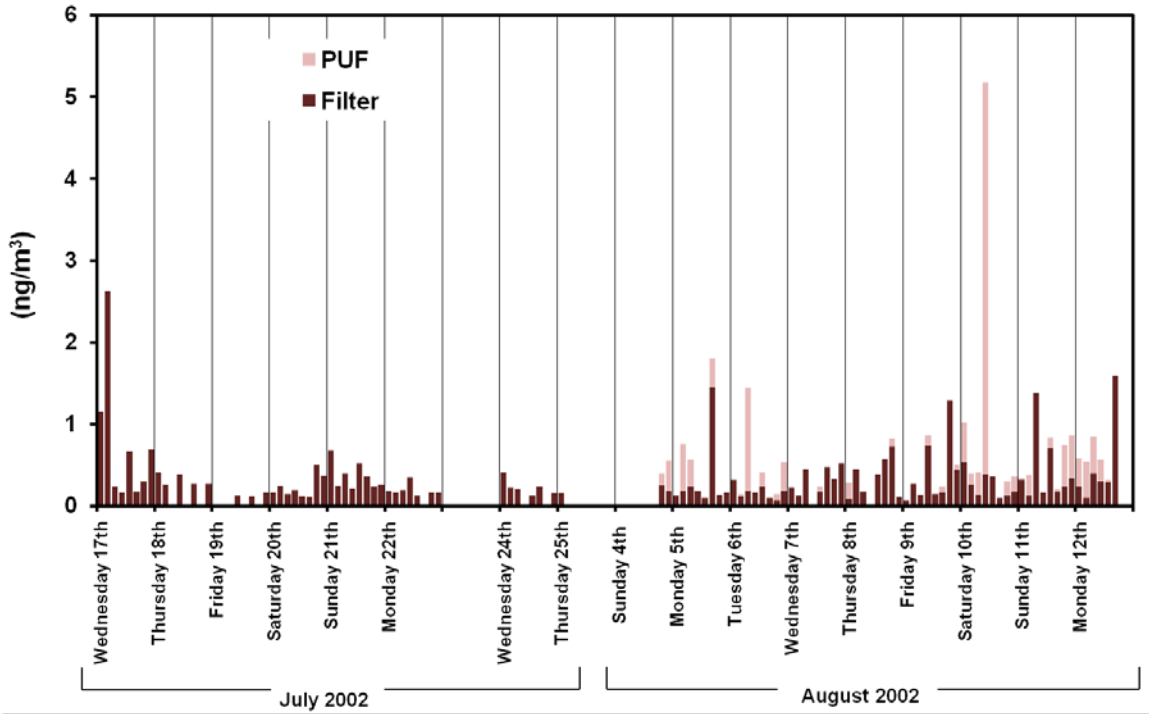


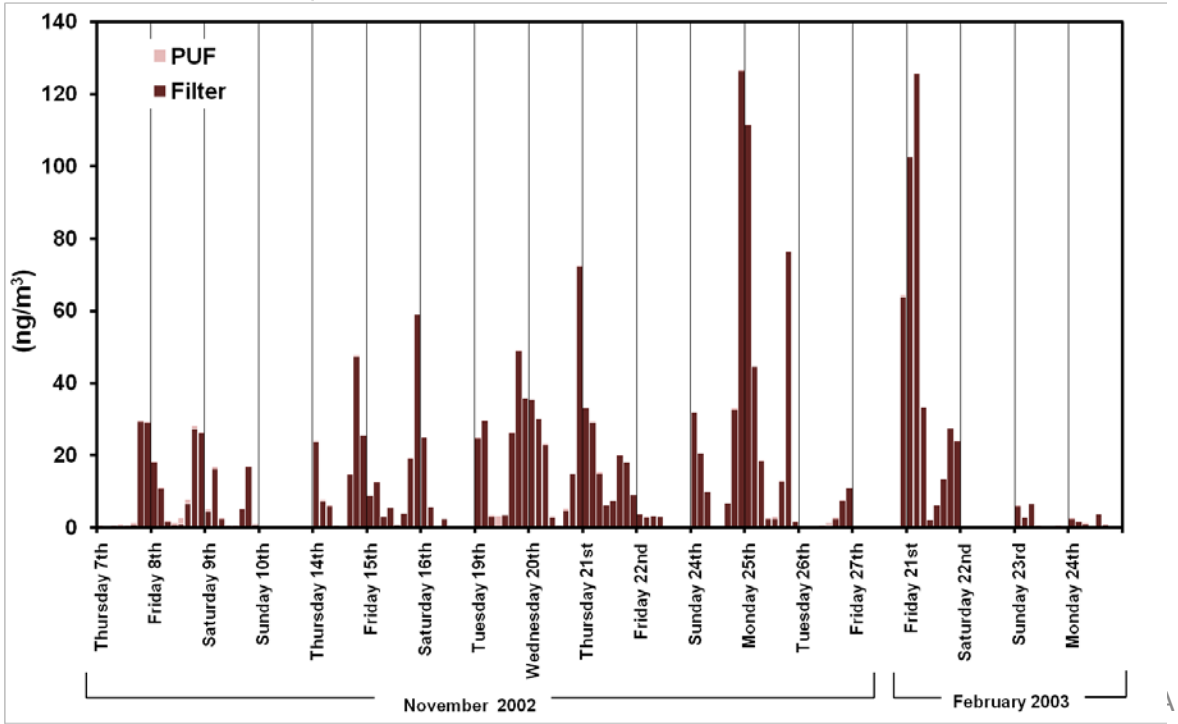


Conclusions:

- Major 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
- More than 110 individual organic compounds, about 64,000 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:
  - Substantial Compositional changes of organic matter associated with PM2.5 occurs with a time scale of less than 3 hours
  - 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
  - With few exceptions, not many diurnal concentration patterns have been found for individual organic compounds, indicating that PM2.5 at the sampling site is impacted by many sources of the same type that are located close and far
  - Nopinone, secondary biogenic reaction product, reveals highest concentrations when during night, when rel. humidity is highest
  - During summer, unsaturated fatty acids react in the atmosphere and possibly even during the daytime in winter
  - During summer, cholesterol could be depleted at a similar rate as unsaturated fatty acids

F18:2


PUF
Filter
(ng/m3)
0
1
2
3
4
5
6
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


PUF
Filter
(ng/m3)
0
20
40
60
80
100
120
140
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