Organic Carbon Mass Balance and Source Apportionment of Primary Organic Carbon in the Pittsburgh Region using Molecular Markers

Pittsburgh Air Quality Study (PAQS)

R SUBRAMANIAN[†], Allen Robinson[*]

Carnegie Mellon University, Pittsburgh, PA

Anna Bernardo-Bricker, Wolfgang Rogge

Florida International University, Miami, FL

† now at the University of Illinois, Urbana-Champaign, IL

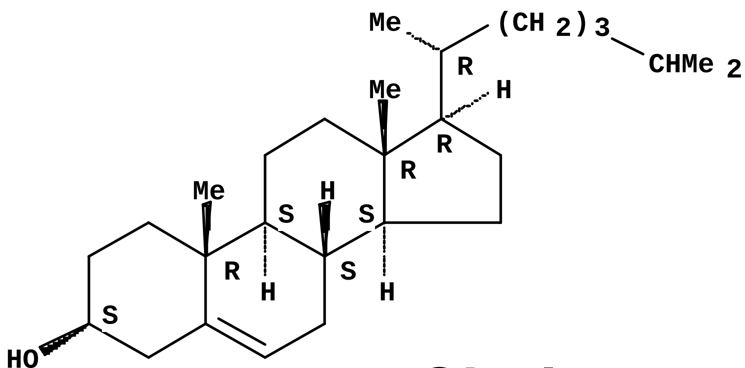
* alr@andrew.cmu.edu/ 412-268-3657

February 10, 2005: AAAR Specialty Conference, Platform #16B-3

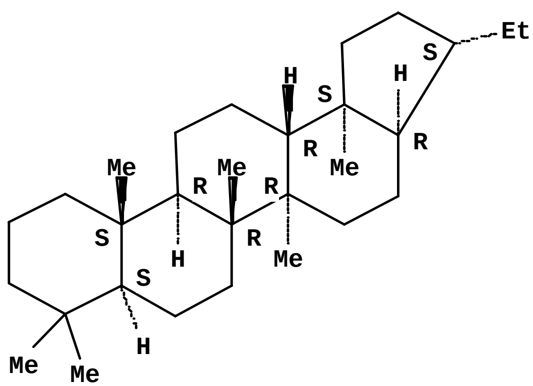
Outline of this talk

- Overview of PAQS molecular marker database
- Source profile selection: a visualization technique
  - Polycyclic aromatic hydrocarbons (PAH)
  - Hopanes and EC
  - Wood smoke tracers
- PAQS source apportionment results
- Variability in apportioned OC
  - Effect of the OC/tracer ratio
- PAQS organic carbon mass balance

Organic molecular markers



Cholesterol
(0.03 – 1% of cooking OC)



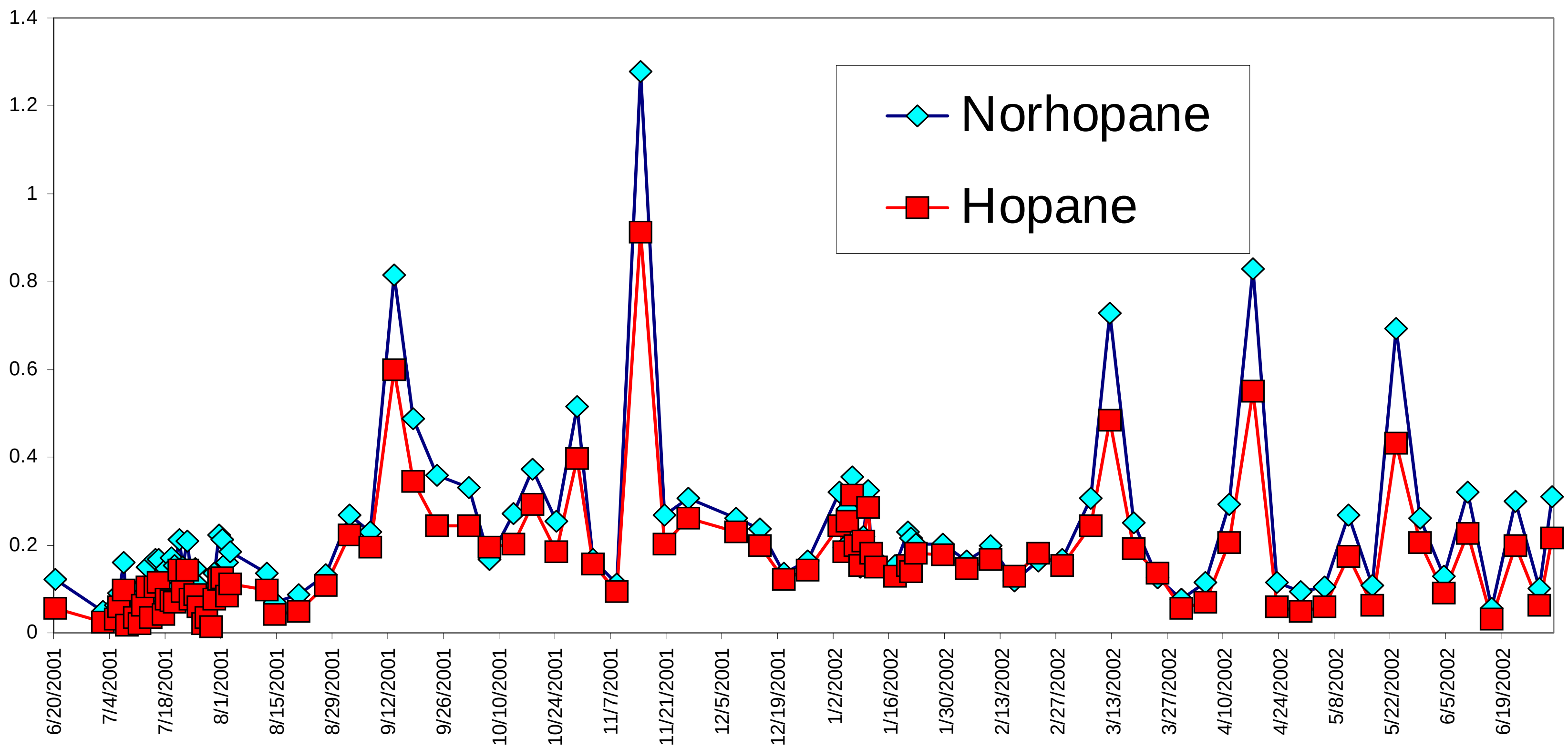
Norhopane
(0.0006% - 0.11% of vehicle OC)

- Combustion sources: similar bulk composition
- Organic compounds:
  - Highly source specific
  - Small fraction of emissions
- Examples
  - Cholesterol: meat-cooking
  - hopanes: petroleum biomarkers
    - Engine exhaust, other fossil fuel combustion

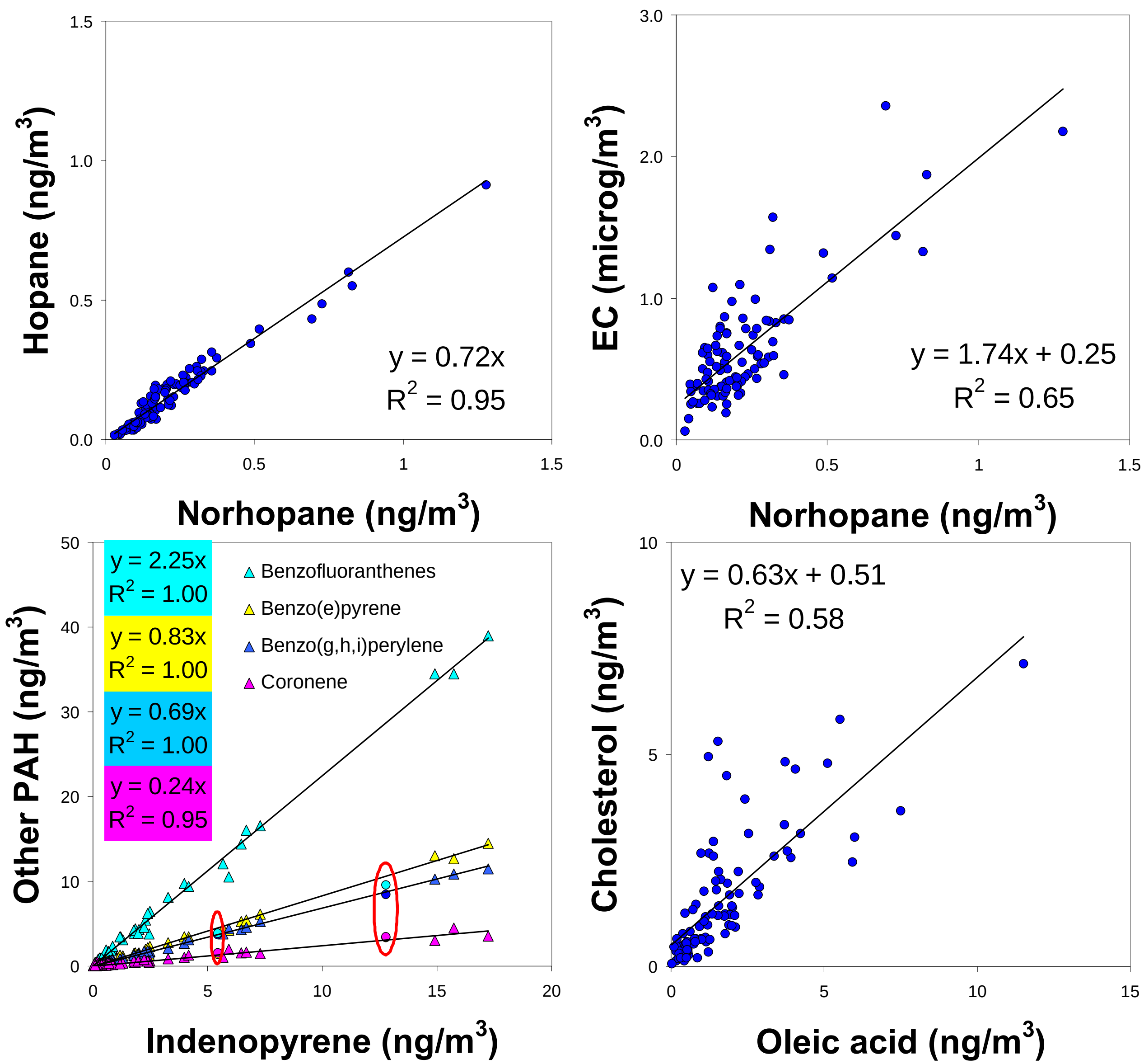
Organic molecular markers at PAQS

July 2001-June 2002

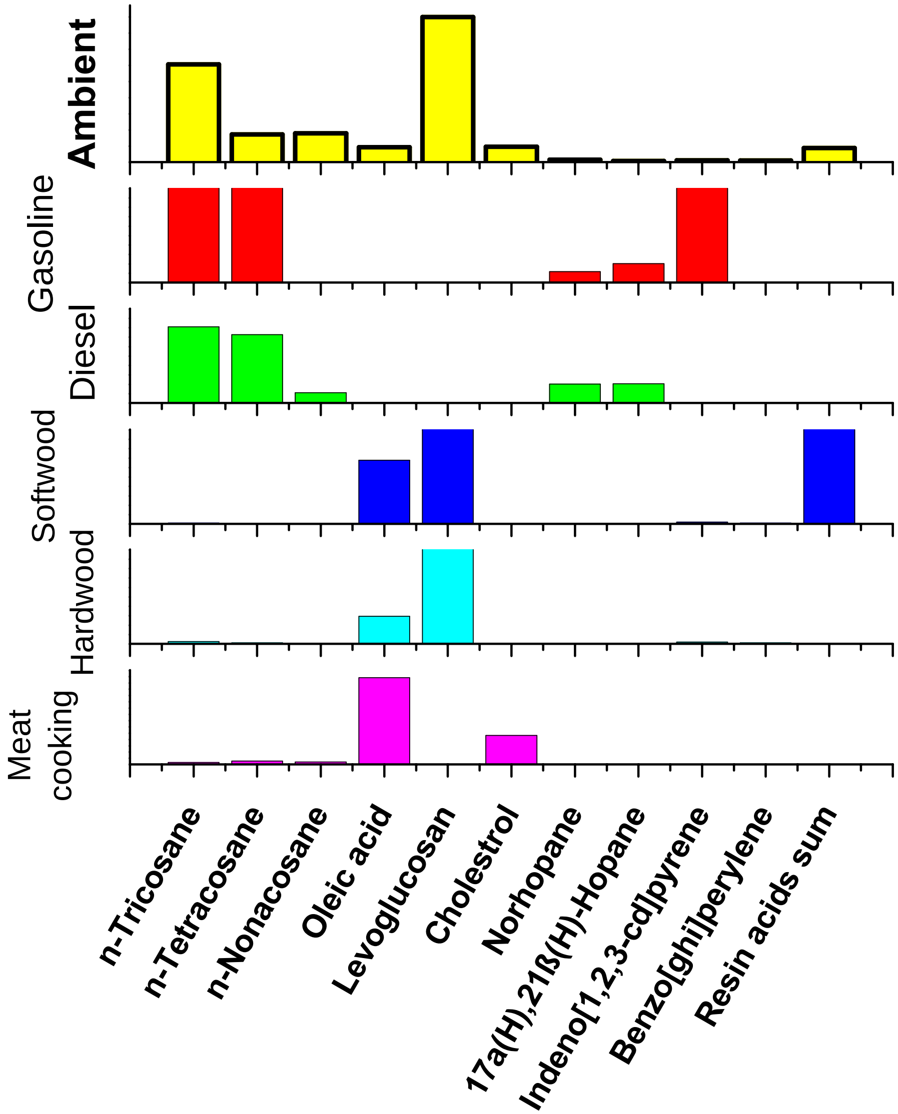
- **~ 125 24-hr quartz/PUF samples**
- **100+ compounds by GC-MS (Wolfgang Rogge, FIU)**



PAQS ambient tracer data: well-correlated



Source apportionment using CMB



$$c_i = \sum_k \alpha_{i,k} S_k + e_i$$

Critical issues

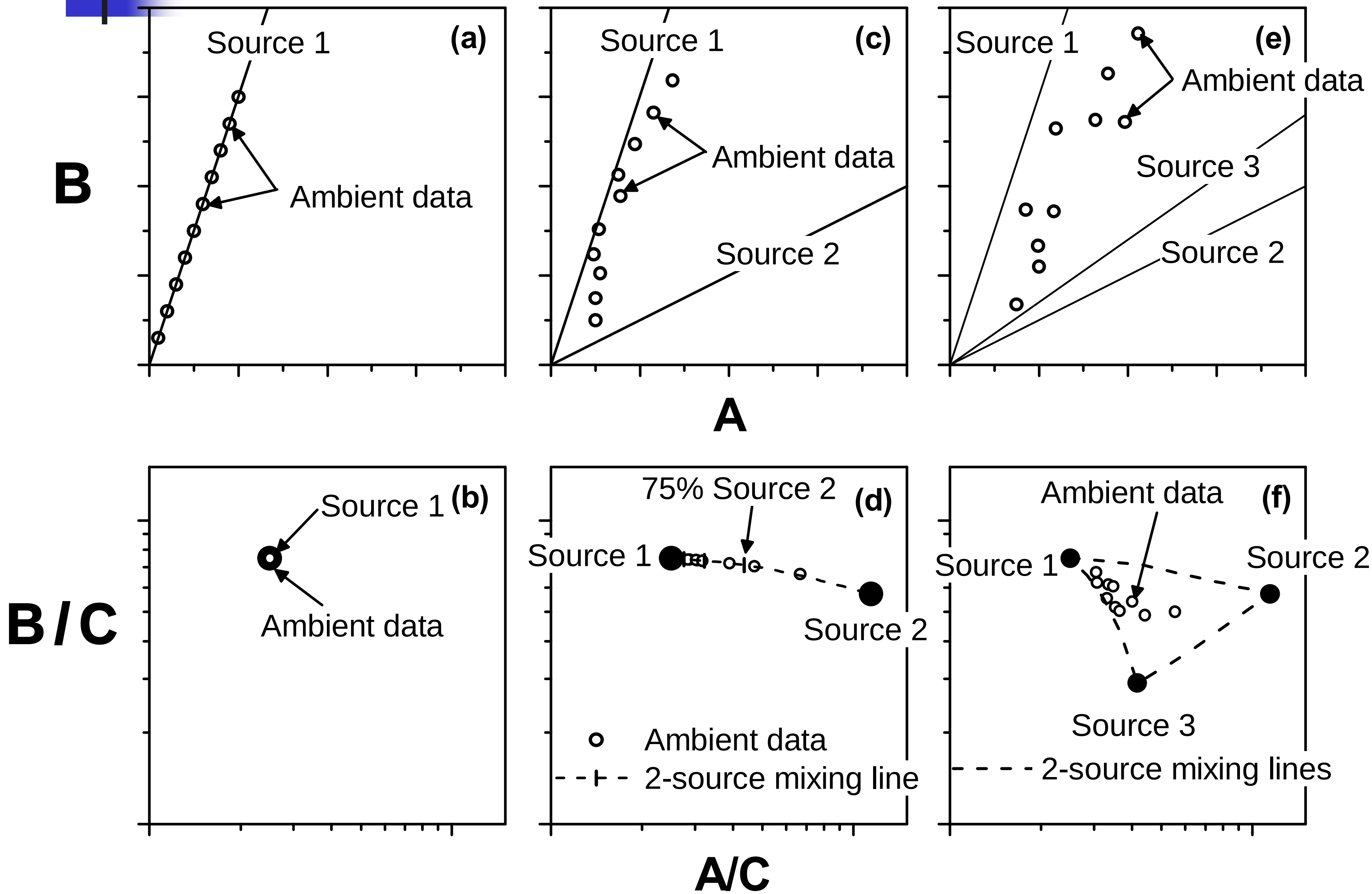
- Atmospheric stability
- Source completeness
- Representative source profiles
- Analytical accuracy and precision

Source profile selection and OC apportionment

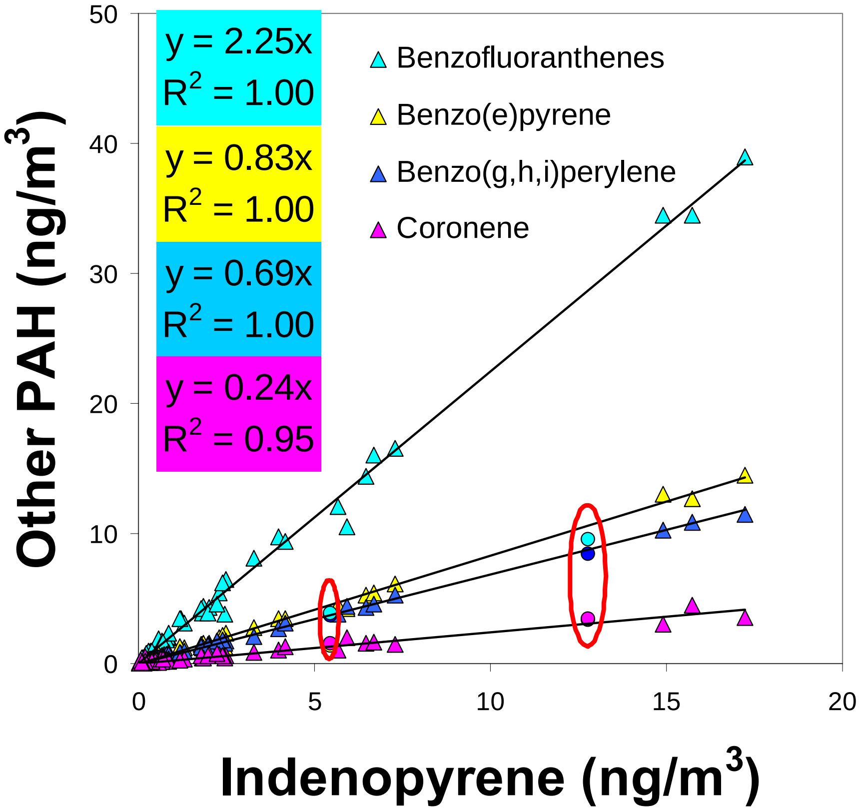
- Source profiles should explain the ambient distribution of multiple tracers

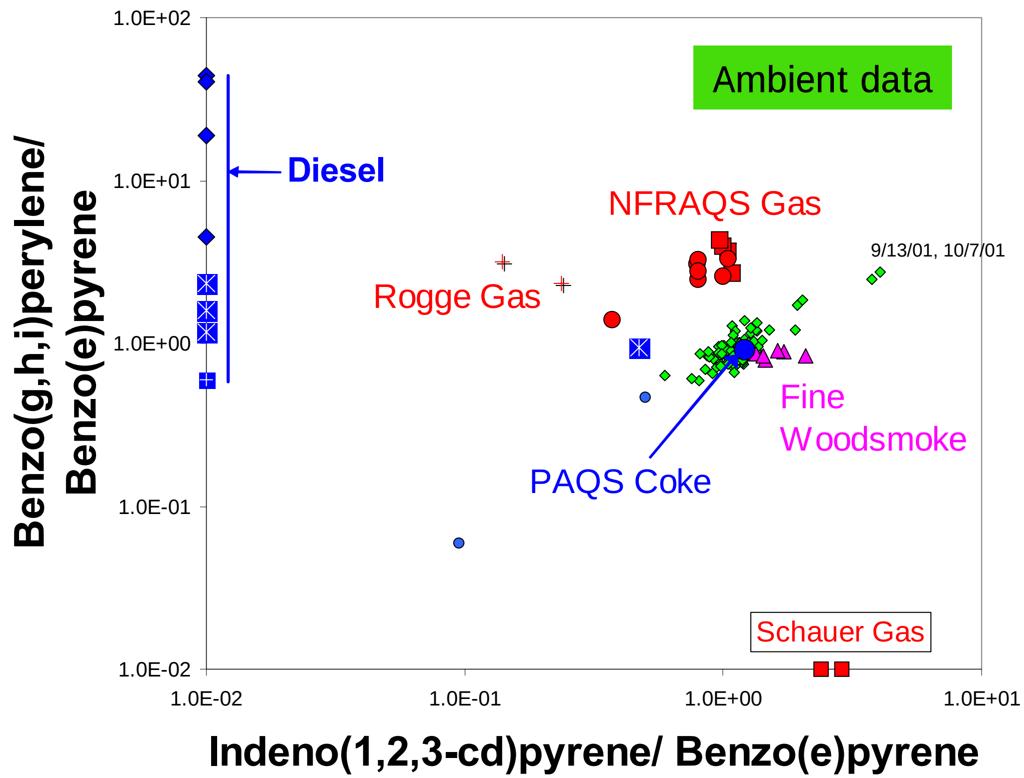
- Cannot fit OC: no “SOA profile”
- Use OC/tracer ratio

Visualization ambient tracers with scatter plots and ratio-ratio plots



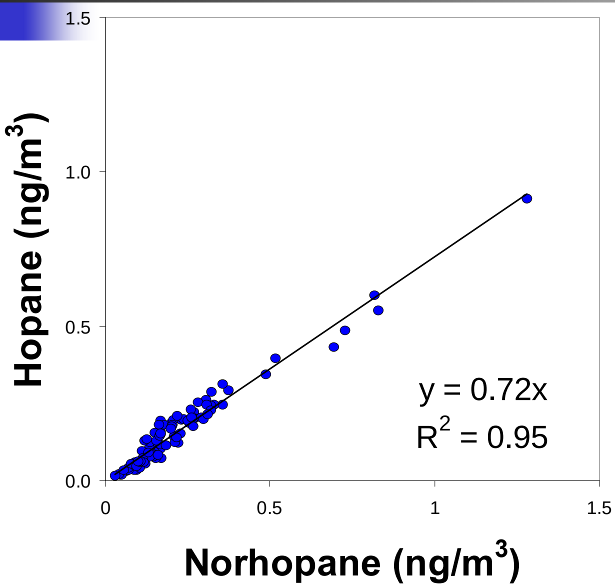
Tracers dominated by a single source: PAH and coke oven emissions

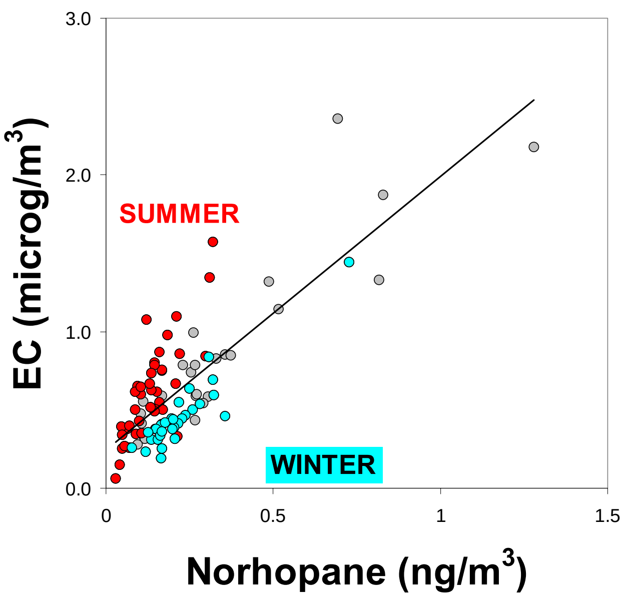


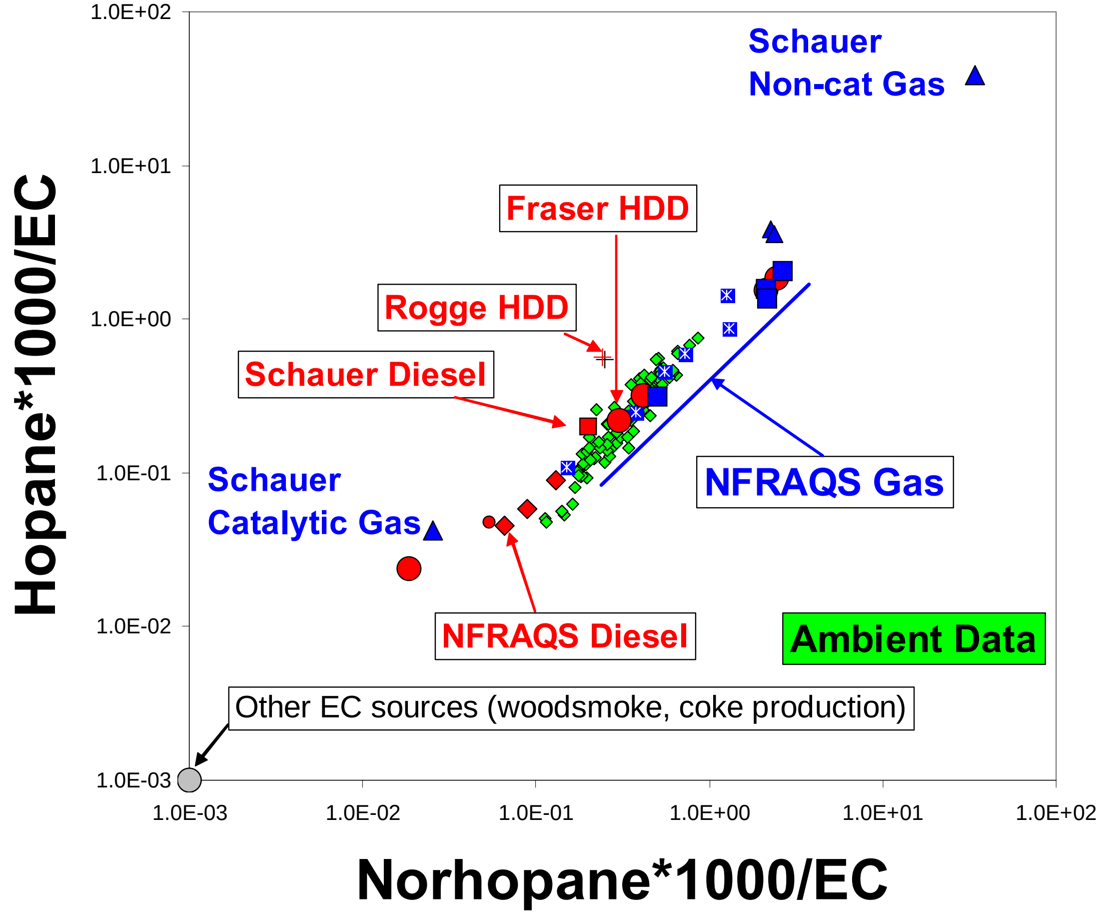


Related….
Poster 17PB-2

Tracers from two major sources: hopanes and EC; vehicular emissions

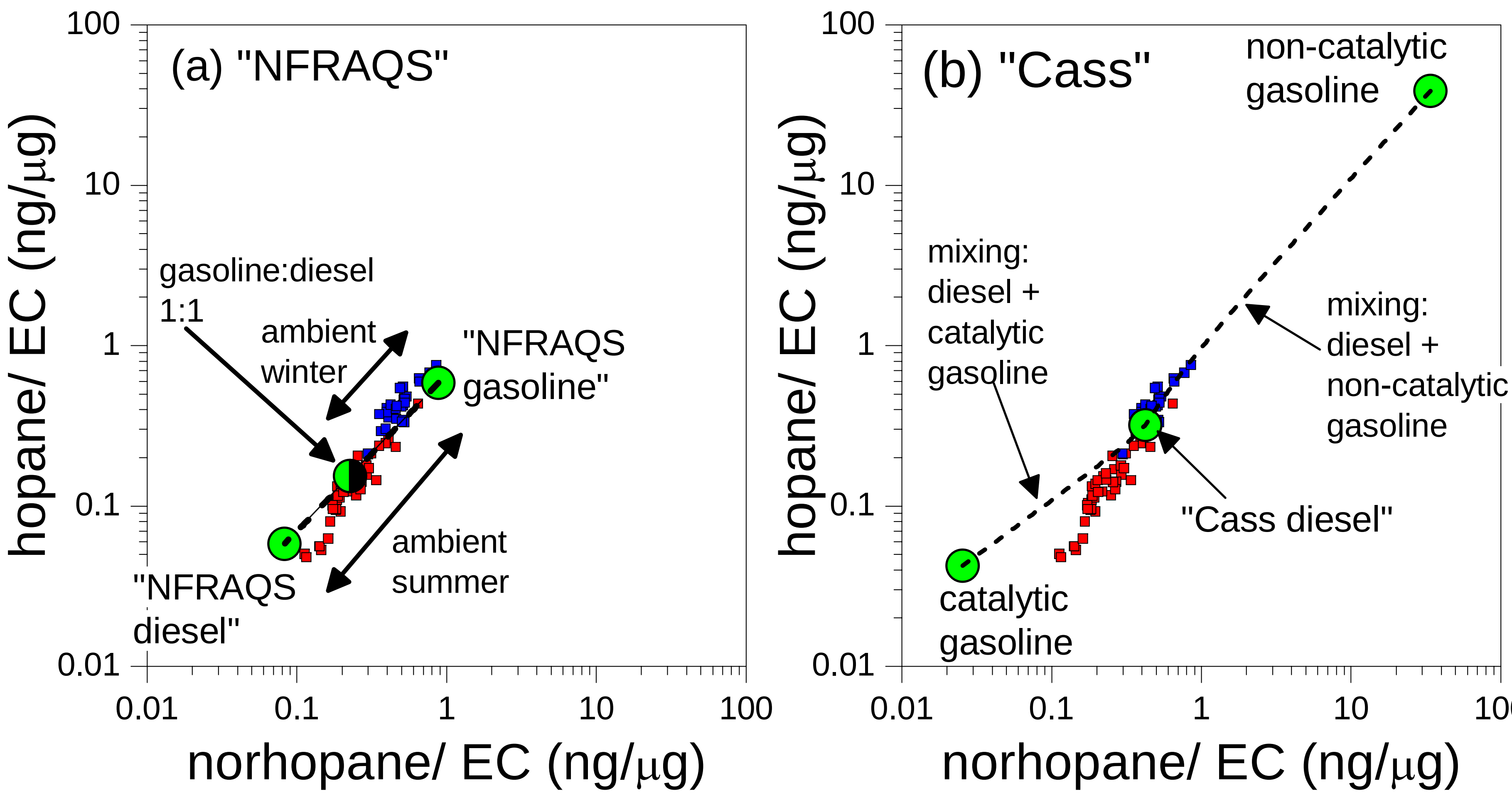




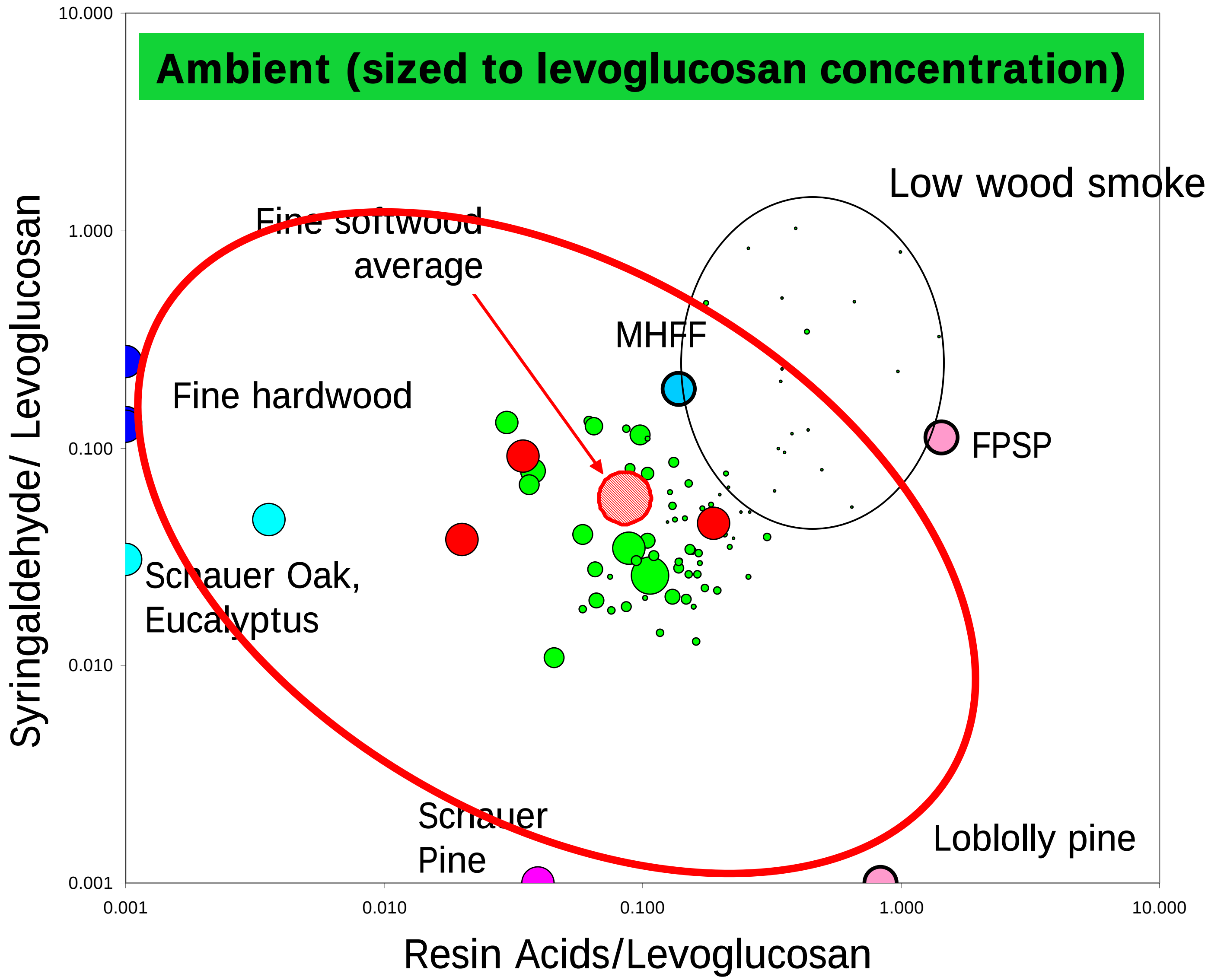


Related.... Posters 17PB-3, 12PD-27

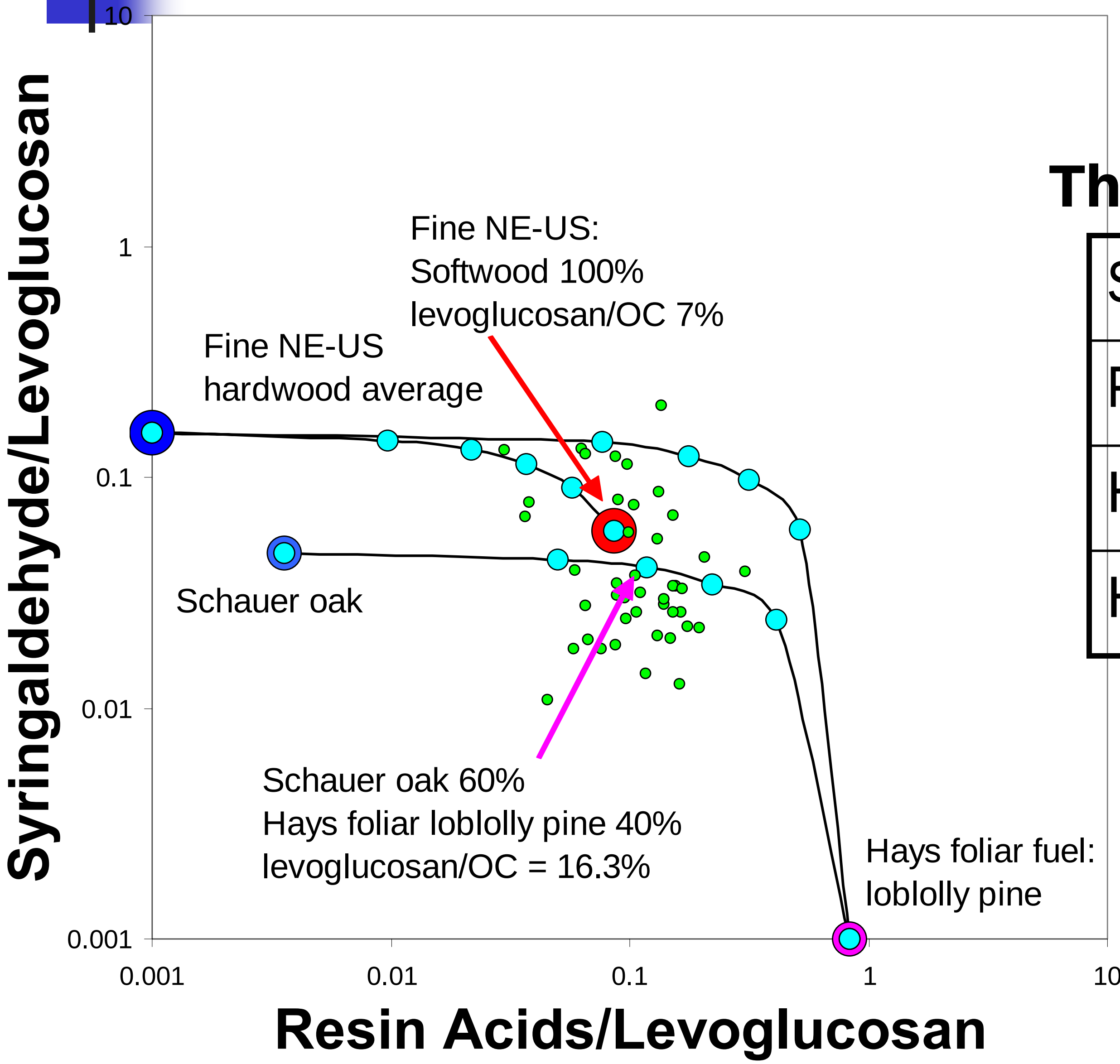
Two vehicular source profile scenarios



Wood smoke: no unique source profile?



Mixing lines for wood smoke source profiles



Three possible pairs:

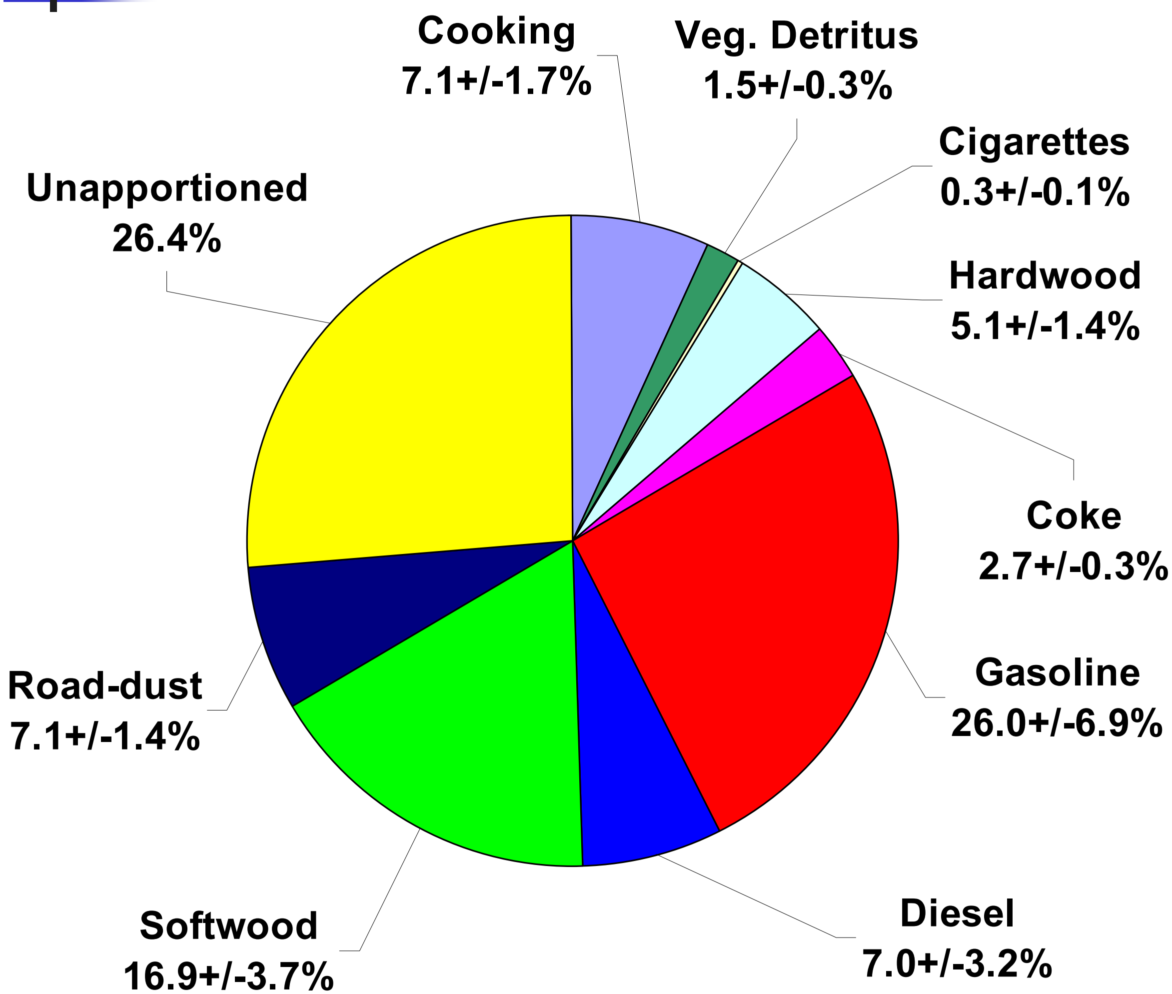
Softwood	Hardwood
Fine	Fine
Hays	Fine
Hays	Schauer

Source profiles and molecular markers used for PAQS CMB Analysis

Related....
Posters
17PB-1, 2
12PD-26

- Base Profiles
  - Softwood & Hardwood: Fine et al. 2001 average profiles
    - Levoglucosan, sum of 4 resin acids, syringaldehyde
  - Coke production: PAQS
    - 4 PAH
  - Meat cooking: Rogge et al. 1991 meat frying
    - Cholesterol
  - Road dust, cigarettes, vegetative detritus: Rogge et al. 1993 & 1994
    - Iron, iso-Hentriacontane, anteiso-Dotriacontane, and C-29, C-31 and C-33 n-alkanes
- Motor Vehicle Scenarios
  - Case 1: NFRAQS: Watson/Zielinska 1998
    - fleet average gasoline: combination of summer low, medium, and high emitter profiles
    - fleet average diesel: combination of diesel profiles
  - Case 2: Cass
    - Schauer et al. 2002 non-catalytic gasoline
    - Schauer et al. 2002 catalytic gasoline
    - Average diesel: Schauer et al. 1999, Fraser et al. 2002
  - Vehicle fitting species
    - NFRAQS – 4 hopanes + EC
    - Cass – 4 hopanes, EC, and C-24 & C-26 n-alkanes

CMB results for March 12, 2002 (NFRAQS)

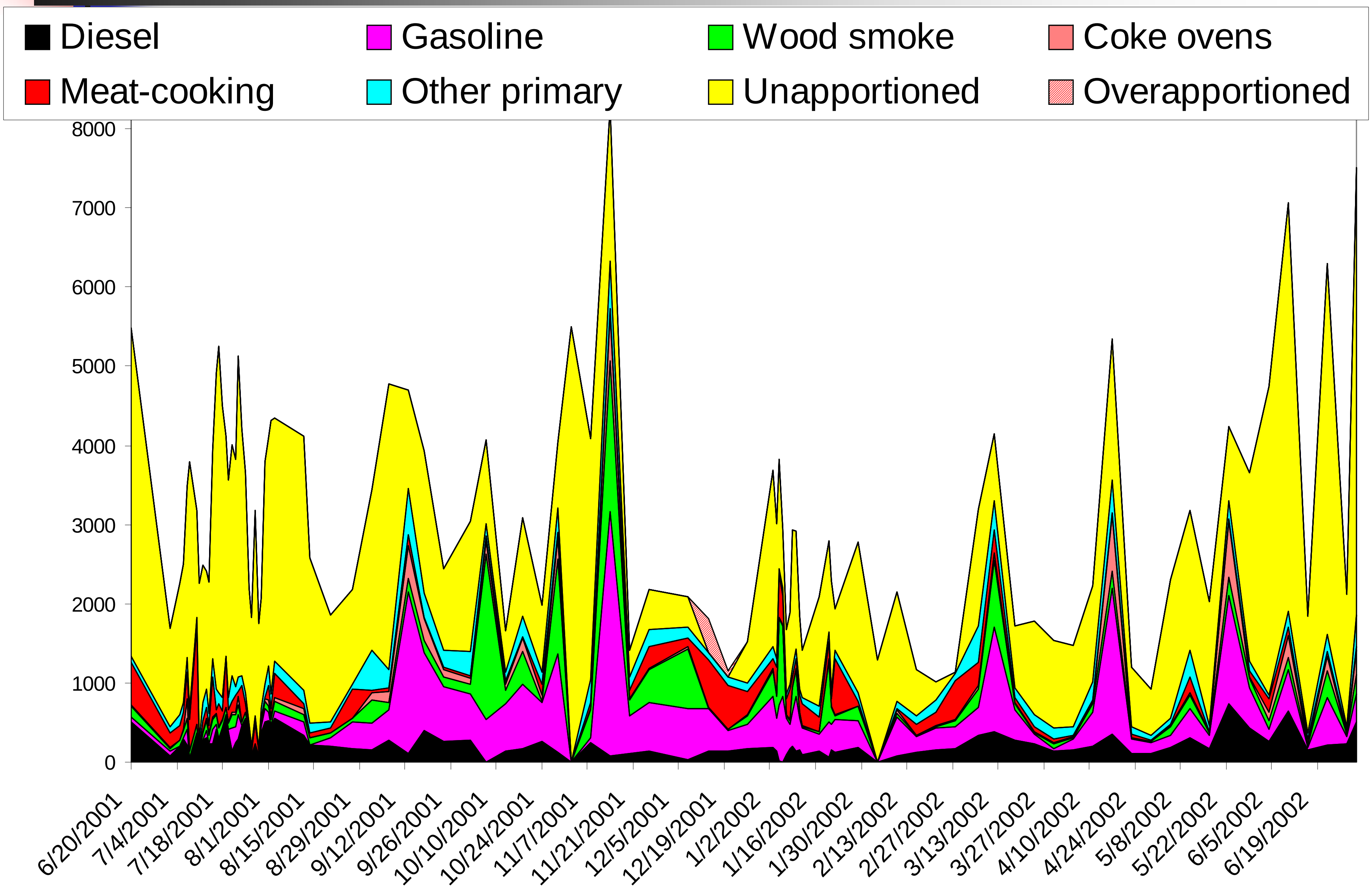


R^2 0.99
X^2 0.53
DF 9
OC 4.1 µg-C/m^3

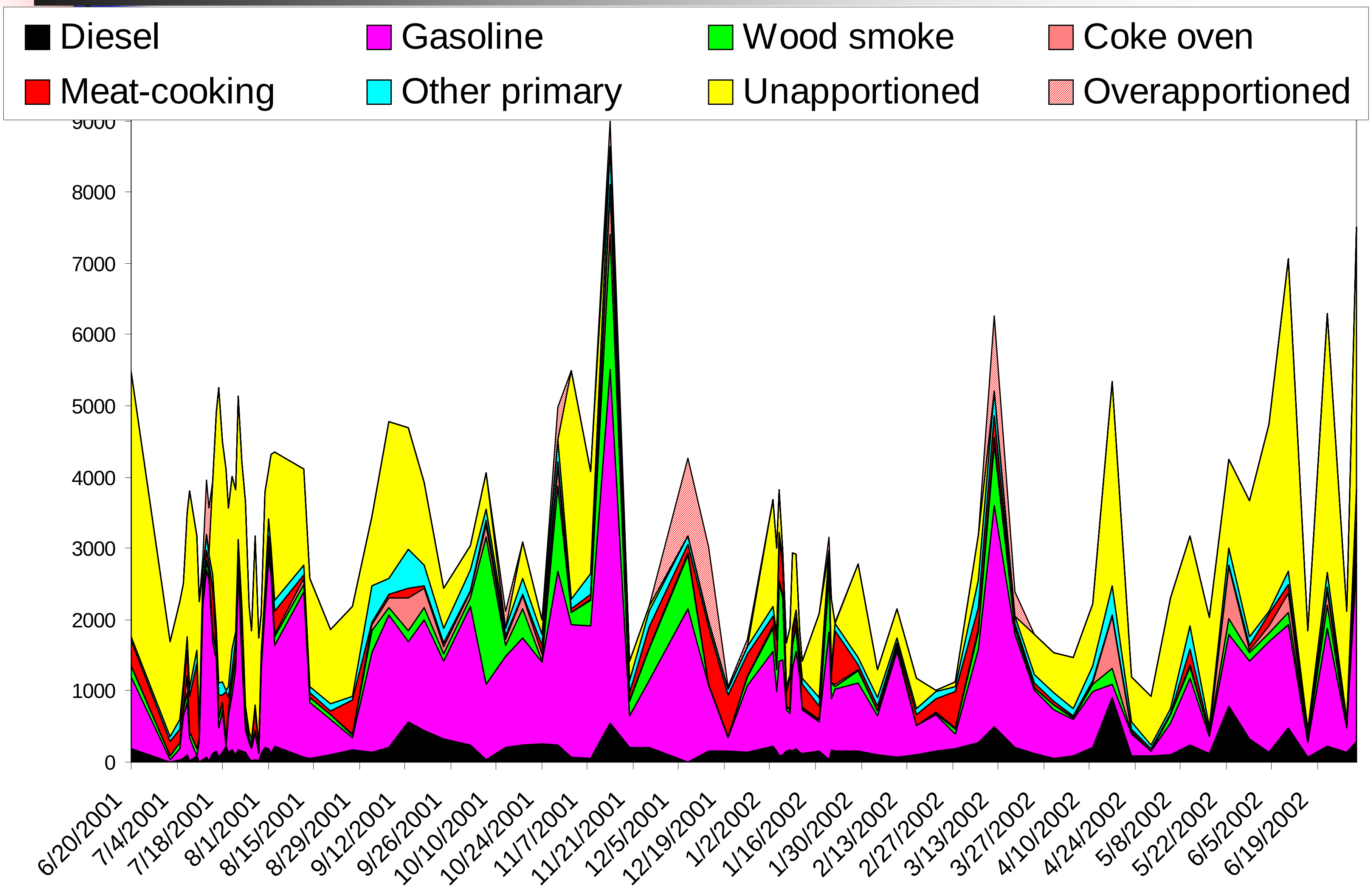
CMB Statistics

- 96 daily measurements between July 2001 and June 2002
- Average R^2 of 0.90
- $\chi^2 <= 6.3$
- Confidence:
  - Cass: 10 to 17 degrees of freedom
  - NFRAQS: 10 to 14 degrees of freedom
  - 90% or better confidence based on the χ^2
    - Just one day with 88% confidence (Cass)
  - Two days not confidently resolved with NFRAQS

CMB results with the NFRAQS vehicular profiles

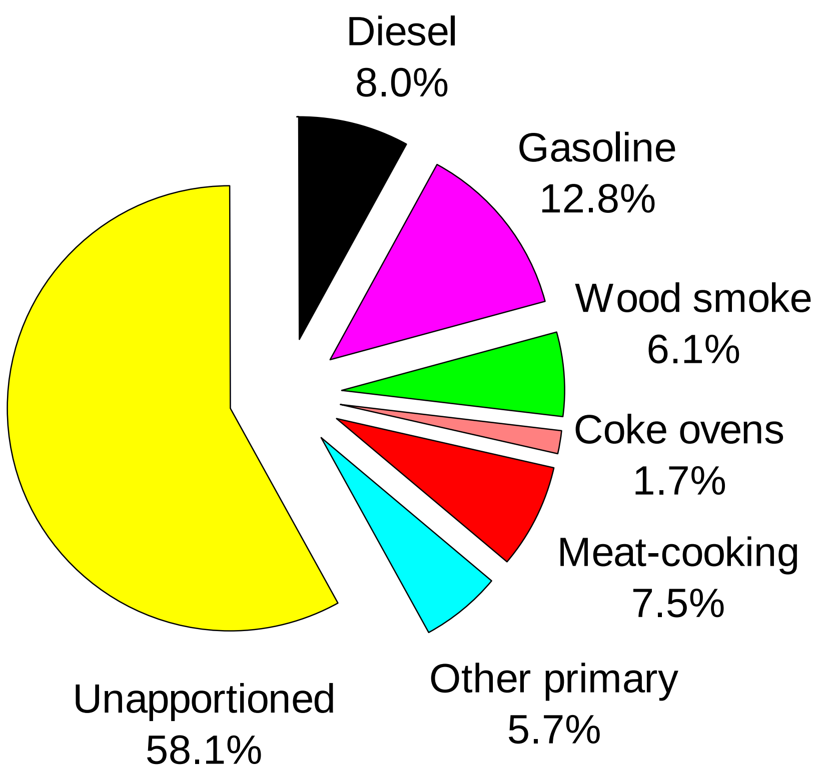


CMB results with the Cass vehicular profiles

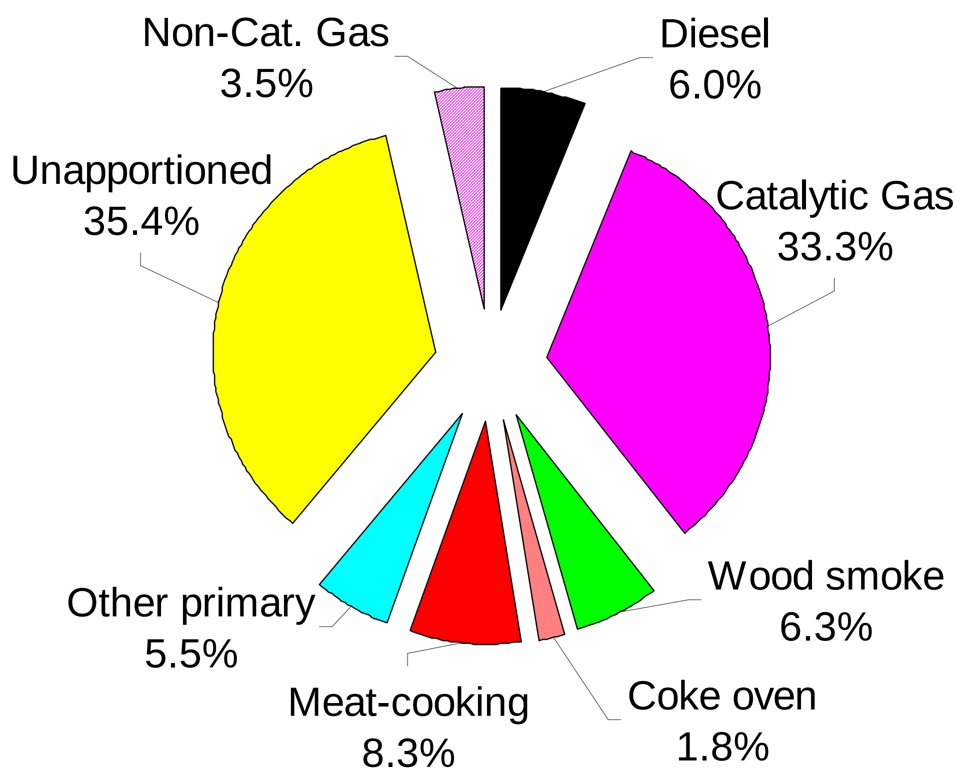


Annual Average Apportionment

NFRAQS
42% OC apportioned

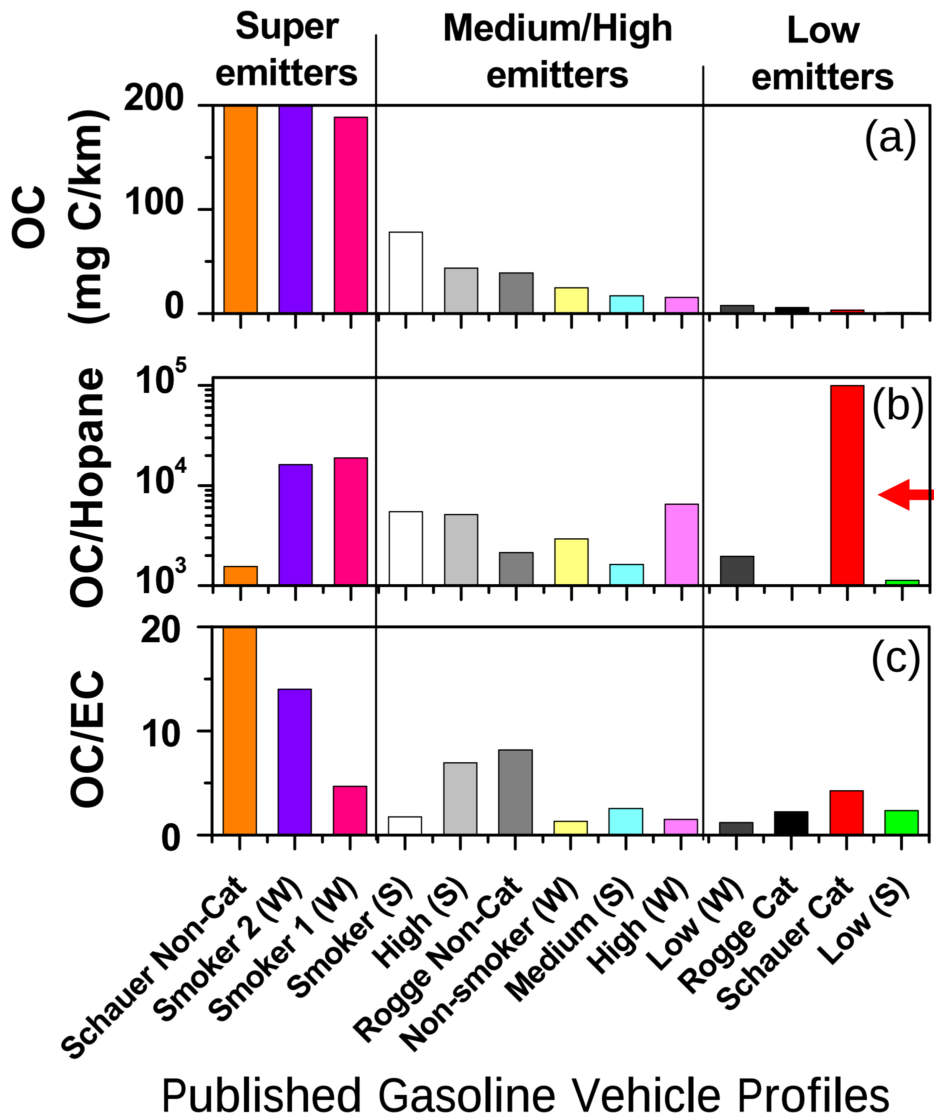


CASS
65% OC apportioned



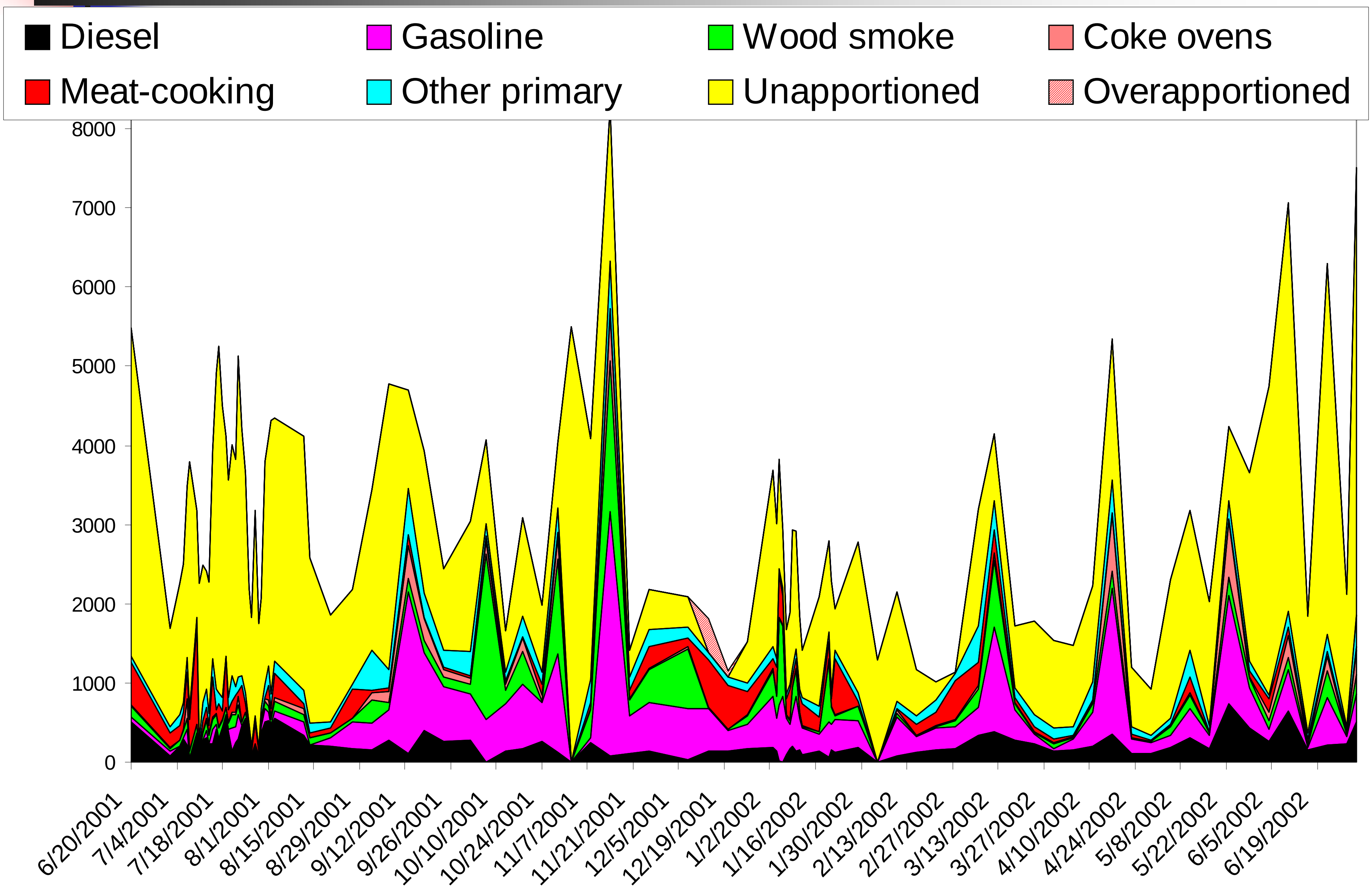
OC = 3.0 ug C/m³

Why is there so much more gasoline OC in the Cass solution?

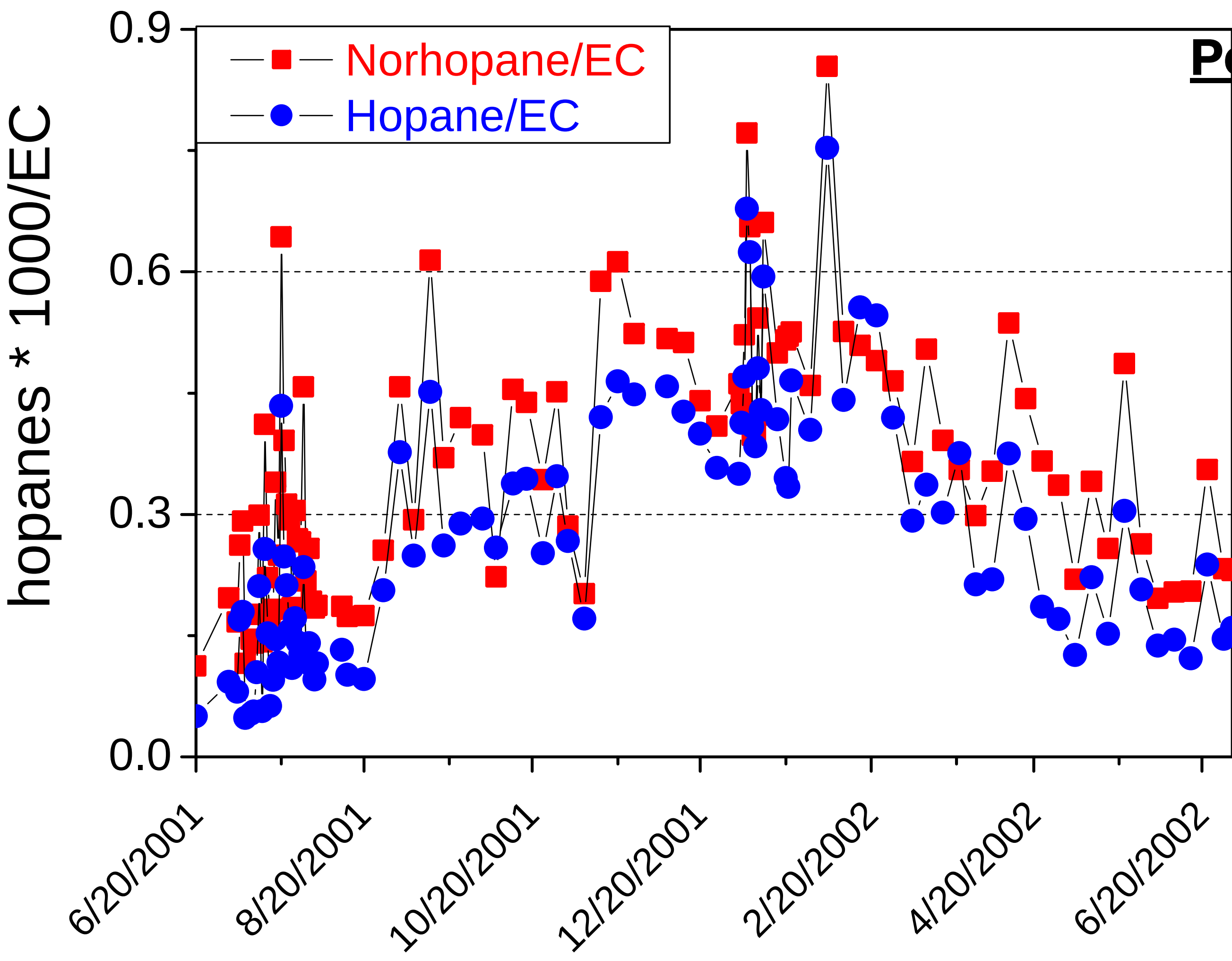


OC / Hopane ratio of Schauer Catalytic profile: a factor of 10-100 larger than other profiles

CMB results with the NFRAQS vehicular profiles: Gasoline OC highly seasonal



Seasonal variations in vehicle marker concentrations

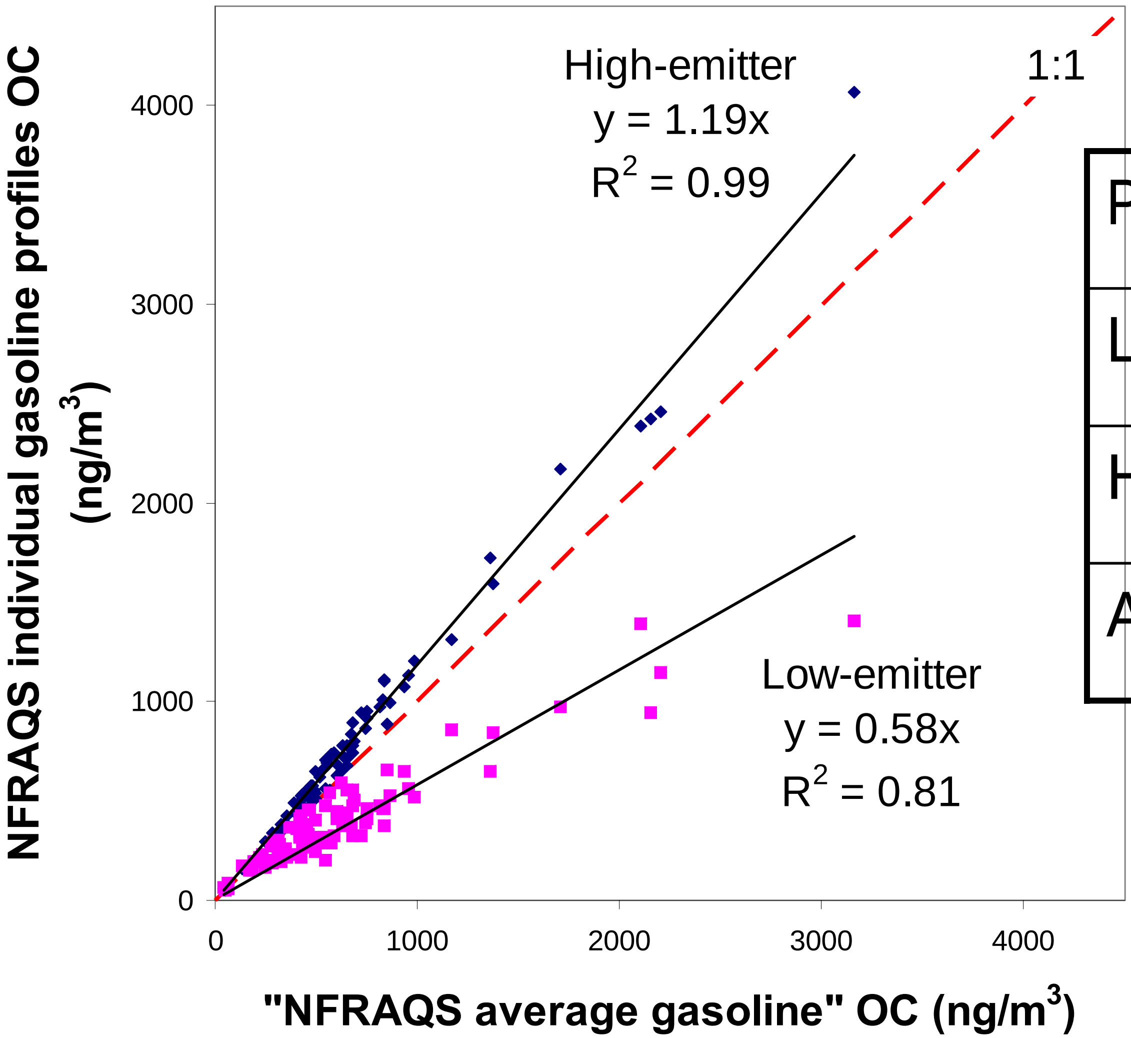


Potential Explanations

- **Seasonal non-vehicular source of EC**
- **Seasonal change in source profiles**
- **Chemistry**

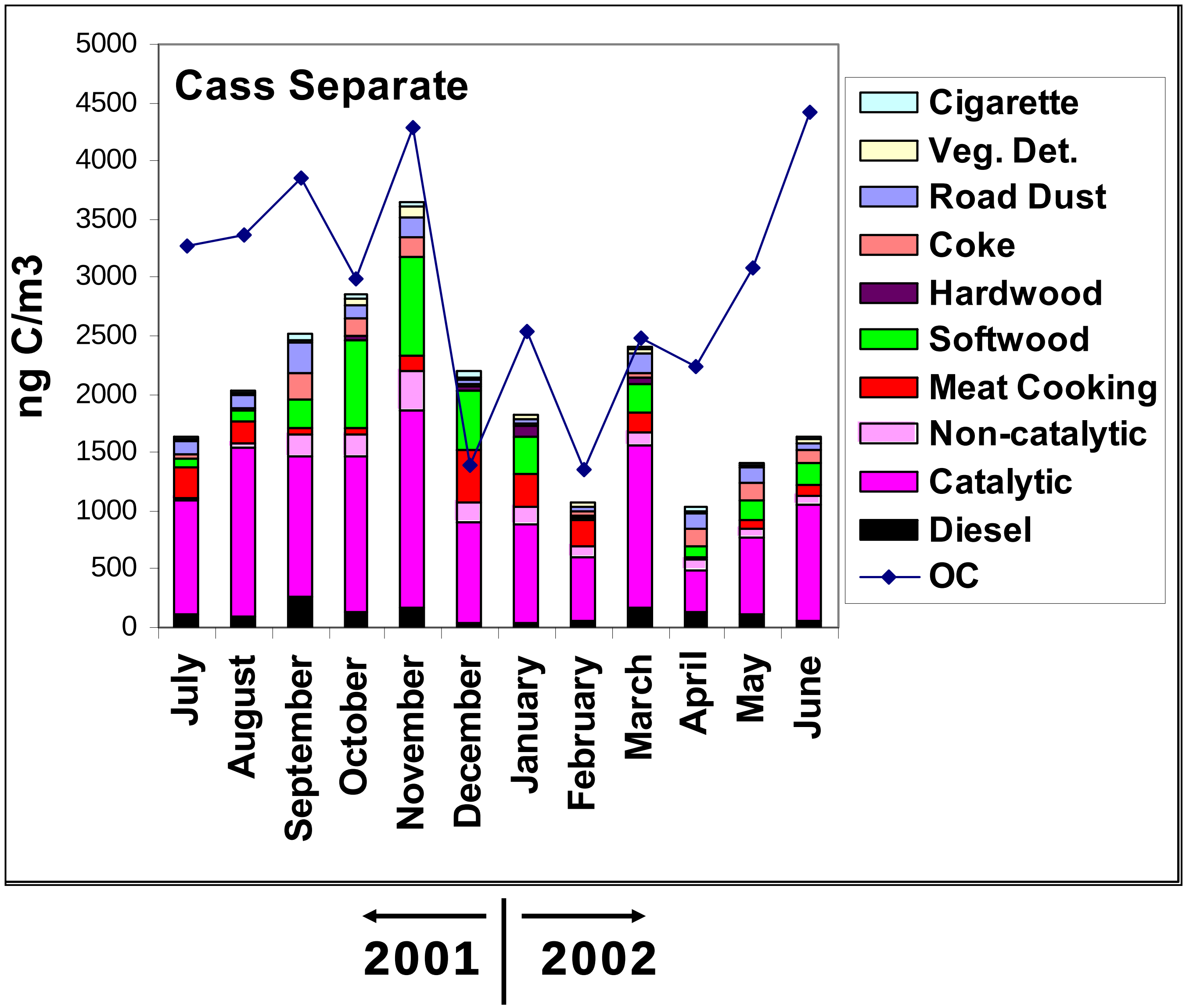
Related....
Talk 18C-5

Effect of vehicular fleet composition: NFRAQS

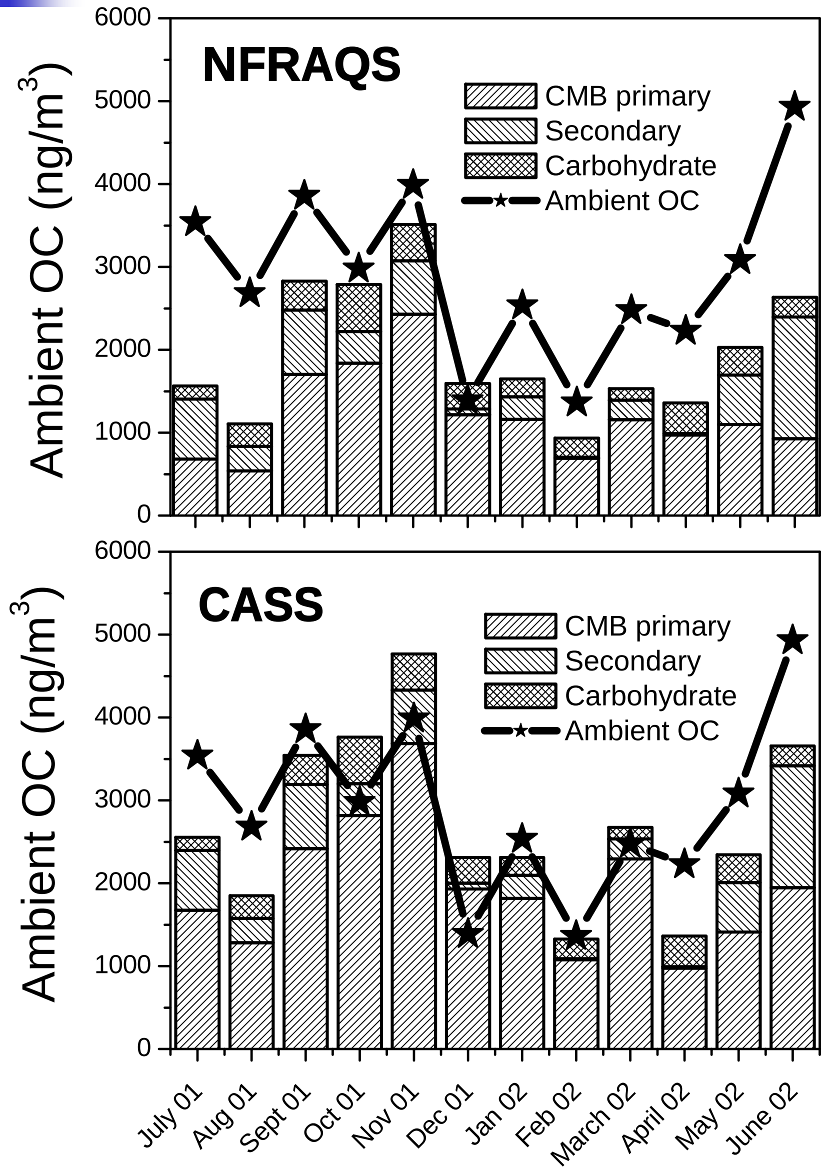


Profile	OC/norhopane
Low	880
High	3236
Average	2715

Seasonal variation in gasoline contribution



OC Mass Balance



Majority of OC is primary but many issues remain

Still gaps in summer:

- Seasonally varying emission profiles
- Oxidation of tracer
- Underestimating SOA with EC ratio technique
- Organic artifacts
- .....

Conclusions

- Molecular markers in Pittsburgh consistent with source profiles for vehicular exhaust and coke oven emissions
  - No unique source profile set for wood smoke?
- NFRAQS v/s “Cass” vehicular apportionment: factor of three difference for gasoline OC
- Uncertainties in tracer/OC ratios
  - Especially for gasoline source profiles
- Seasonal variations in vehicular tracers
  - Changes in emission profiles
  - Atmospheric processing

Conclusions

- A large fraction of the fine organic PM is primary
  - “Traditional” primary sources + primary biological
- Secondary organic aerosol
  - Summer: ~ 30% of OC
  - Winter: < 10% of OC
- Mass balance closure issues

Acknowledgements

Related....
Talk 18C-5
Posters
17PB-1, 2, 3
12PD-26, 27

- The US EPA Supersites program
- The US DOE/NETL
- AAAR travel grant for R.

- Spyros Pandis, Neil Donahue, Cliff Davidson
- Mark Hernandez
- Eric Lipsky, Sarah Rees, Juan Cabada, Charles Stanier, Tim Raymond, Wei Tang, Ann E. Wittig, Lisa Clarke, Natalie Pekney, Emily Weitkamp, Satoshi Takahama
- Leonard Lucas, Dave Wynne
- Gary Norris, Matt Fraser, Phil Fine, John Watson, Barbara Zielinska
- Paul Solomon, Tami Bond