Sources of Organic $PM_{2.5}$ in the Pittsburgh Region

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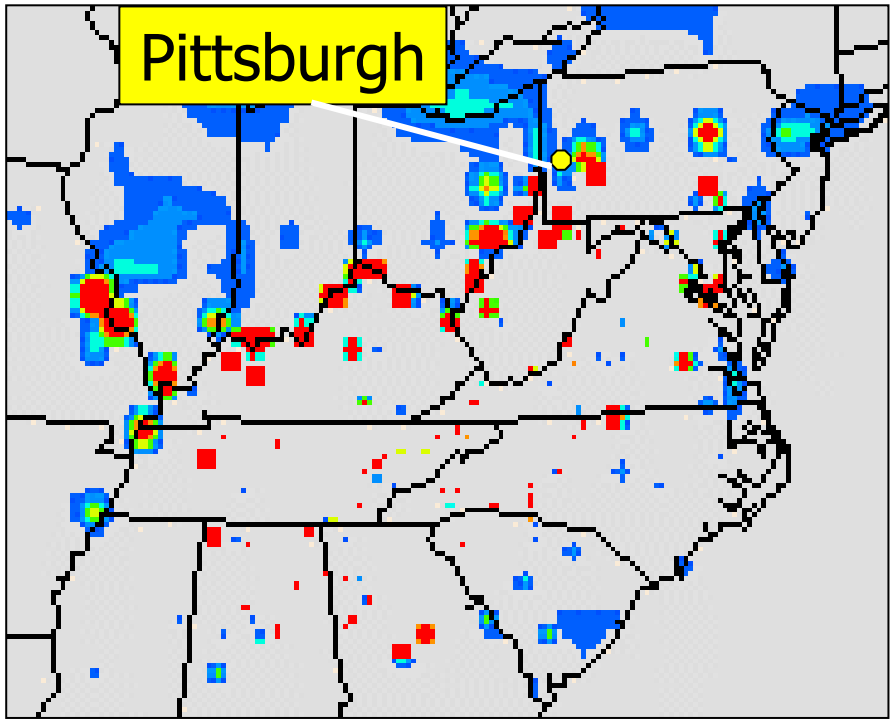
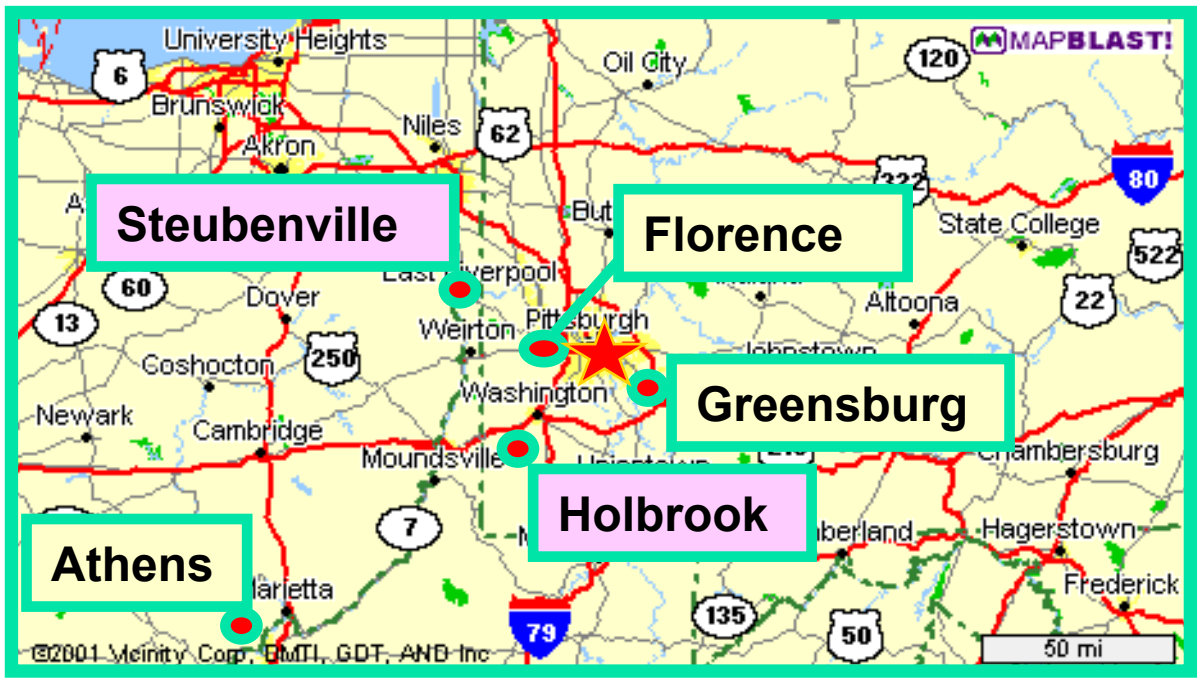
Pittsburgh Air Quality Study



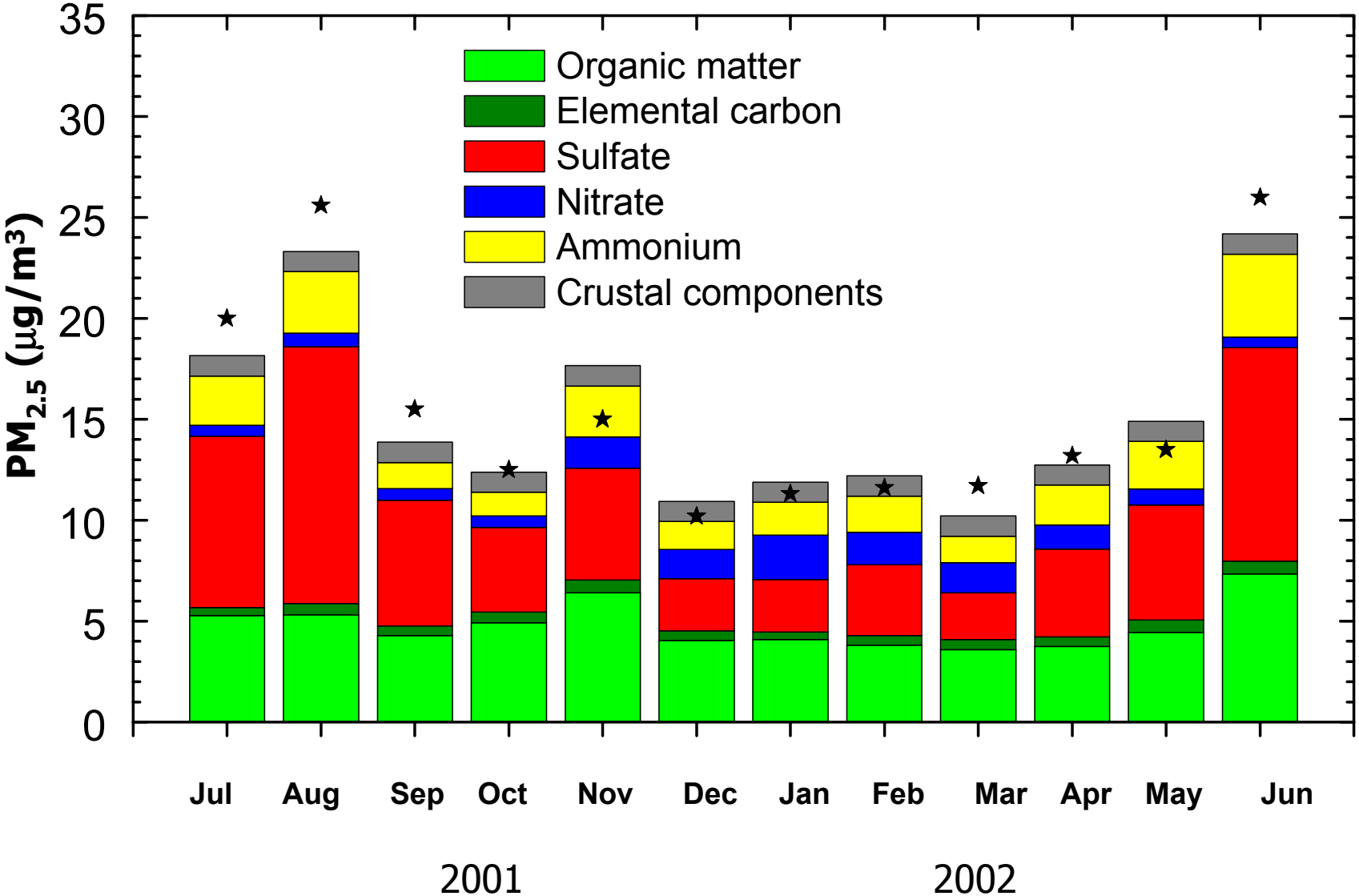
- Develop and evaluate the next generation of atmospheric PM monitoring techniques
- Improve our understanding of the physical and chemical properties of fine PM
- Characterize the major pollution sources in the area taking advantage of the new measurement techniques
- Quantify the impact of the various sources to the fine PM concentrations in the area
- Quantify the responses of PM to changes in emissions

PAQS Central Monitoring Station

Remote Satellite Sites



Pittsburgh $PM_{2.5}$ Composition



Source Apportionment of Organic Aerosol

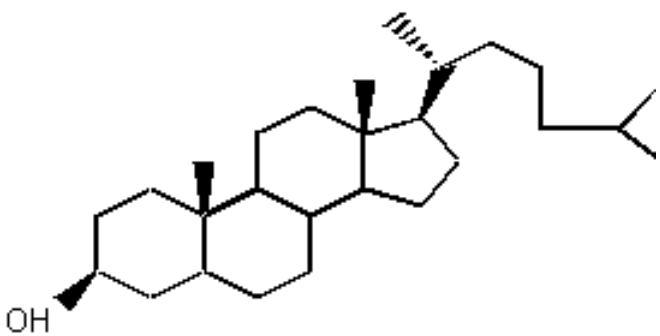
Organic Aerosol

- **Primary**
  - **Anthropogenic**
    - Gasoline
    - Diesel
    - Wood Smoke
    - Meat Cooking
    - …
  - **Biogenic**
- **Secondary**

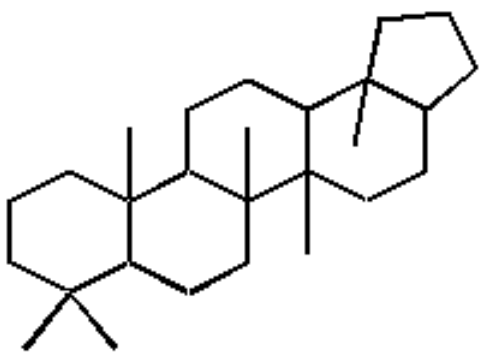
<u>Tools:</u>

- **<u>CMB w/ tracers</u>**
- 3-D Model
- EC-tracer
- Direct Measurements

Tracers for Primary Organic Aerosol Sources



Cholesterol

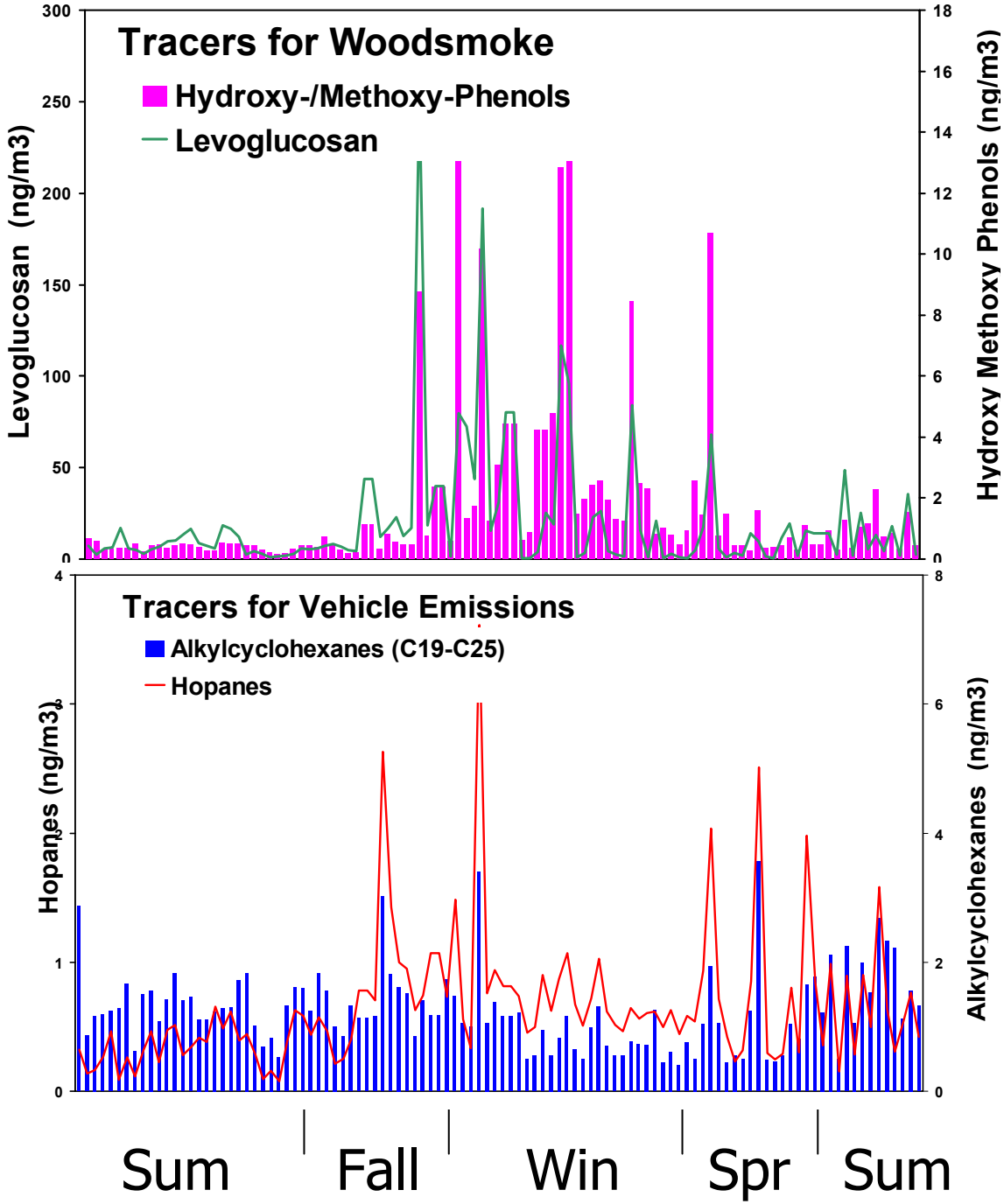


Trisnorneohopane

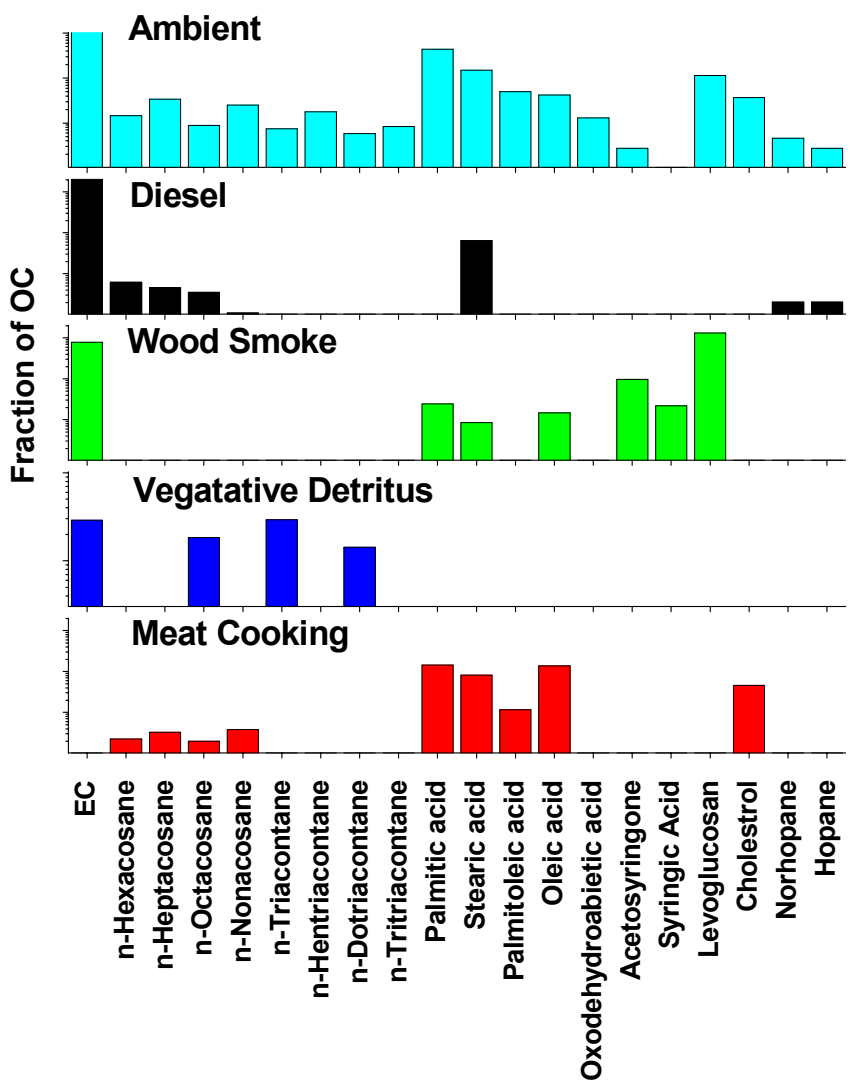
- Receptor modeling requires unique source profiles
- Challenges for organic source apportionment
  - Few organic sources have unique elemental composition
  - Many sources emit primarily organic and elemental carbon
- Molecular Markers:
  - Compounds present in the emissions from an air pollution source that are relatively unique to that source
  - Rich literature

Ambient Sampling and Analysis

- Sampling:
  - Medium Volume Q+PUF
  - ~ 125 24-hr samples
    - Intensives – daily
    - Baseline – 1 in 6
- Analysis
  - 100+ compounds via GC-MS
  - Solvent extraction
    - Derivitization
  - Standards
    - Compound identification
    - Deuterated


Tracers for Woodsmoke
Hydroxy-/Methoxy-Phenols
Levoglucosan
Levoglucosan (ng/m3)
Hydroxy Methoxy Phenols (ng/m3)
Tracers for Vehicle Emissions
Alkylcyclohexanes (C19-C25)
Hopanes
Hopanes (ng/m3)
Alkylcyclohexanes (ng/m3)
Sum
Fall
Win
Spr
Sum

Chemical Mass Balance Modeling



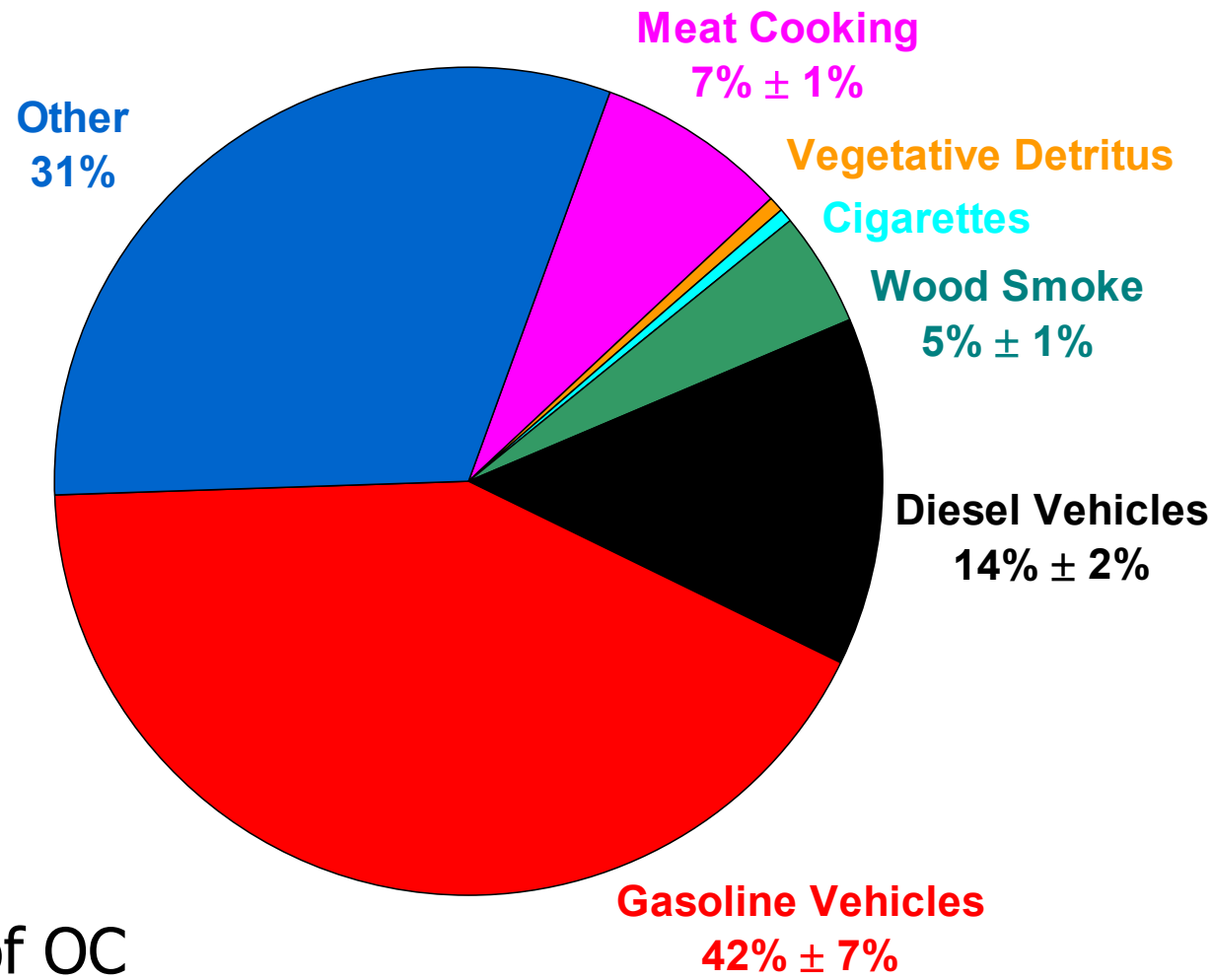
$$c_i = \sum_k \alpha_k S_{i,k} + e_i$$

- Critical issues
  - Atmospheric stability
  - Source completeness
  - Representative source profiles
  - Analytical accuracy and precision
- Literature Emission Profiles

Table of Sources and Tracers

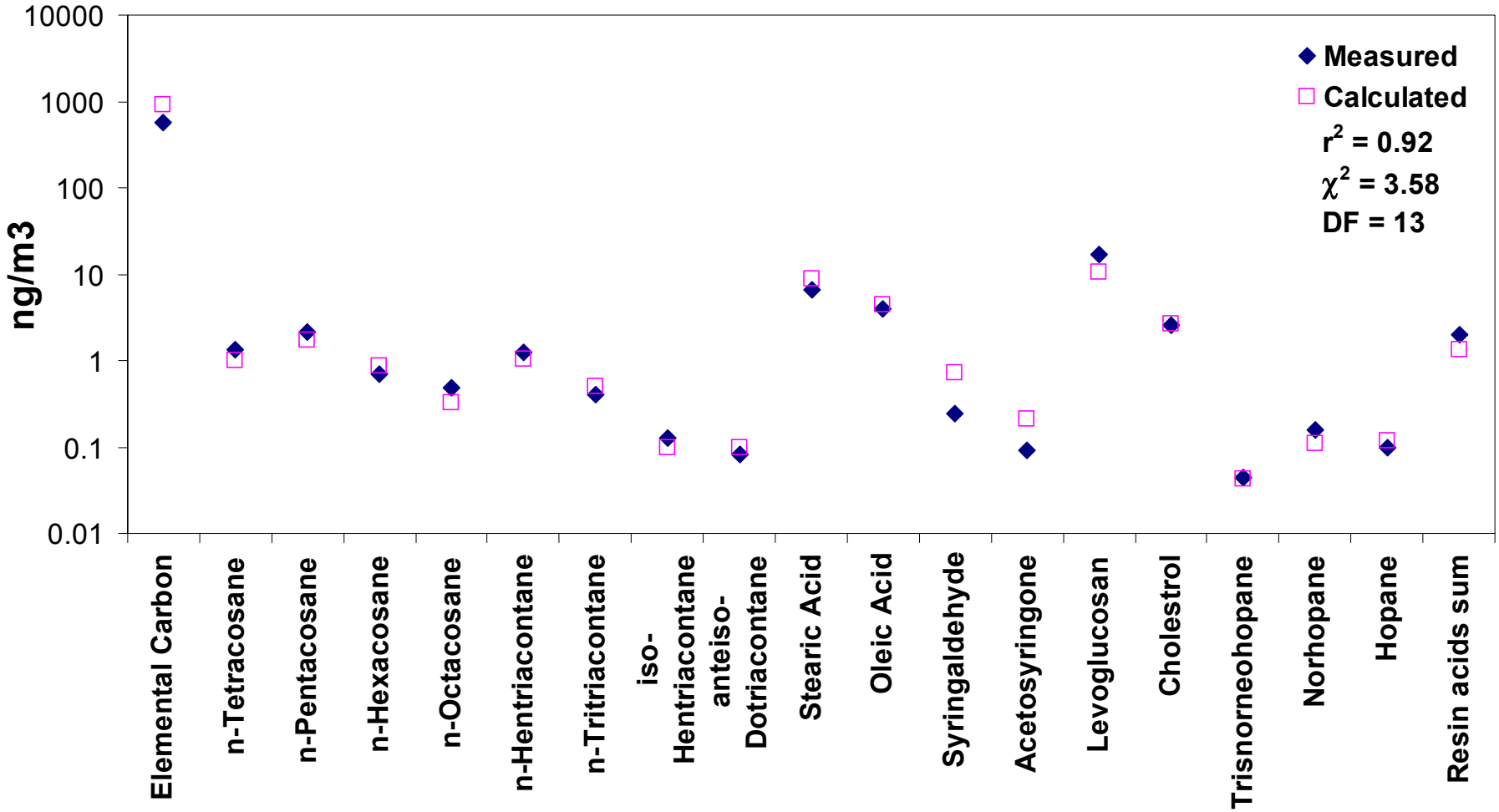
Compound	Source
1. Elemental Carbon	Vehicles
2. n-Tetracosane	All
3. n-Pentacosane	All
4. n-Hexacosane	All
5. n-Octacosane	All
6. n-Hentriacontane	Vegetative Detritus
7. n-Tritriacontane	Vegetative Detritus
8. iso-Hentriacontane	Cigarettes
9. anteiso-Dotriacontane	Cigarettes
10.octadecanoic acid	All
11. cis-9-n-Octadecenoic acid	Meat Cooking
12. Syringaldehyde	Wood Smoke
13. Acetosyringone	Wood Smoke
14. Levoglucosan	Wood Smoke
15. Cholestrol	Meat Cooking
16. 22,29,30-Trisnorneohopane	Vehicles
17. 17α(H),21β(H)-29-Norhopane	Vehicles
18. 17α(H),21β(H)-Hopane	Vehicles
19. Resin acids sum	Wood Smoke

Source Apportionment for July 7, 2001

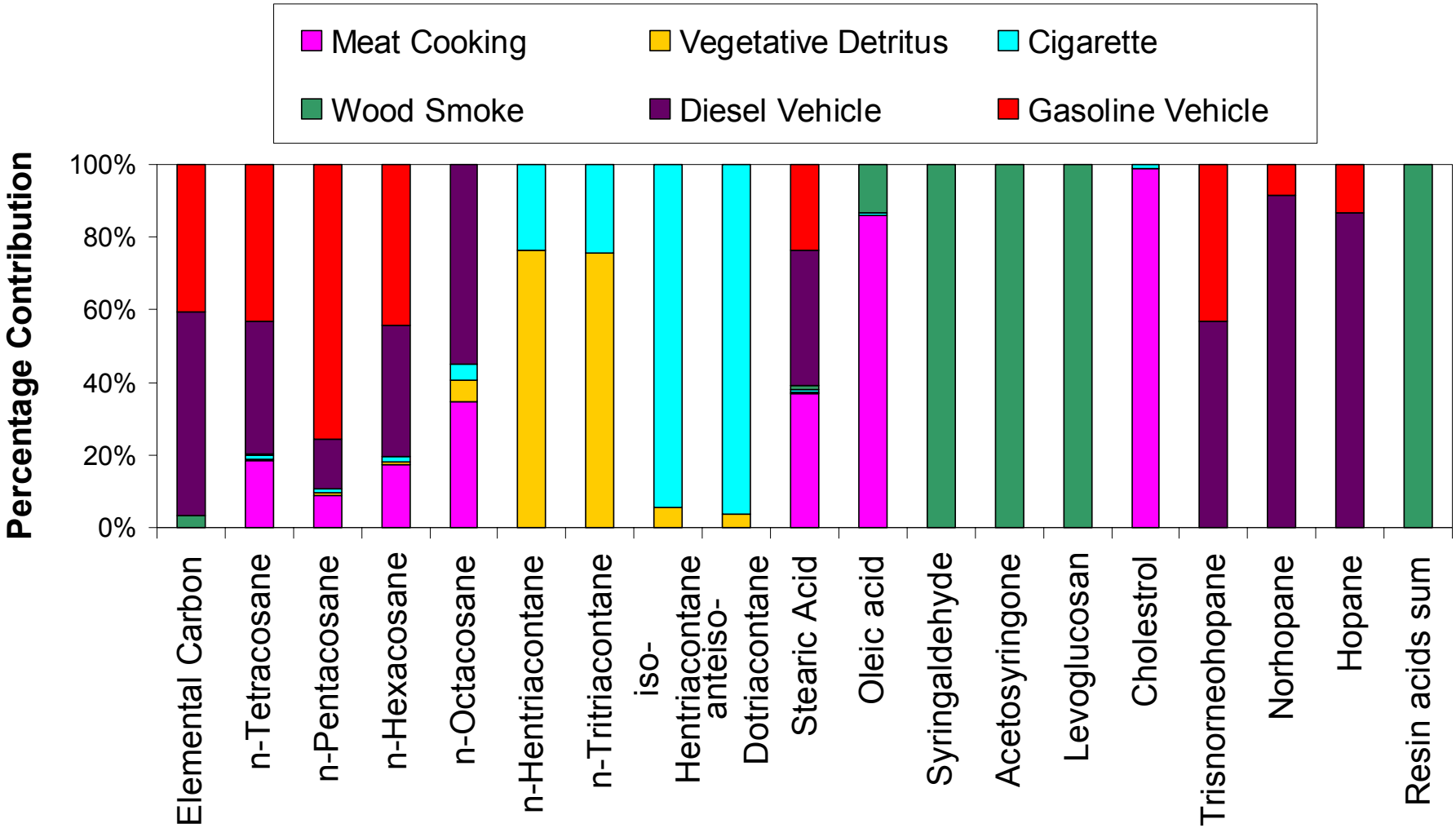


3.7 $\mu g/m^3$ of OC

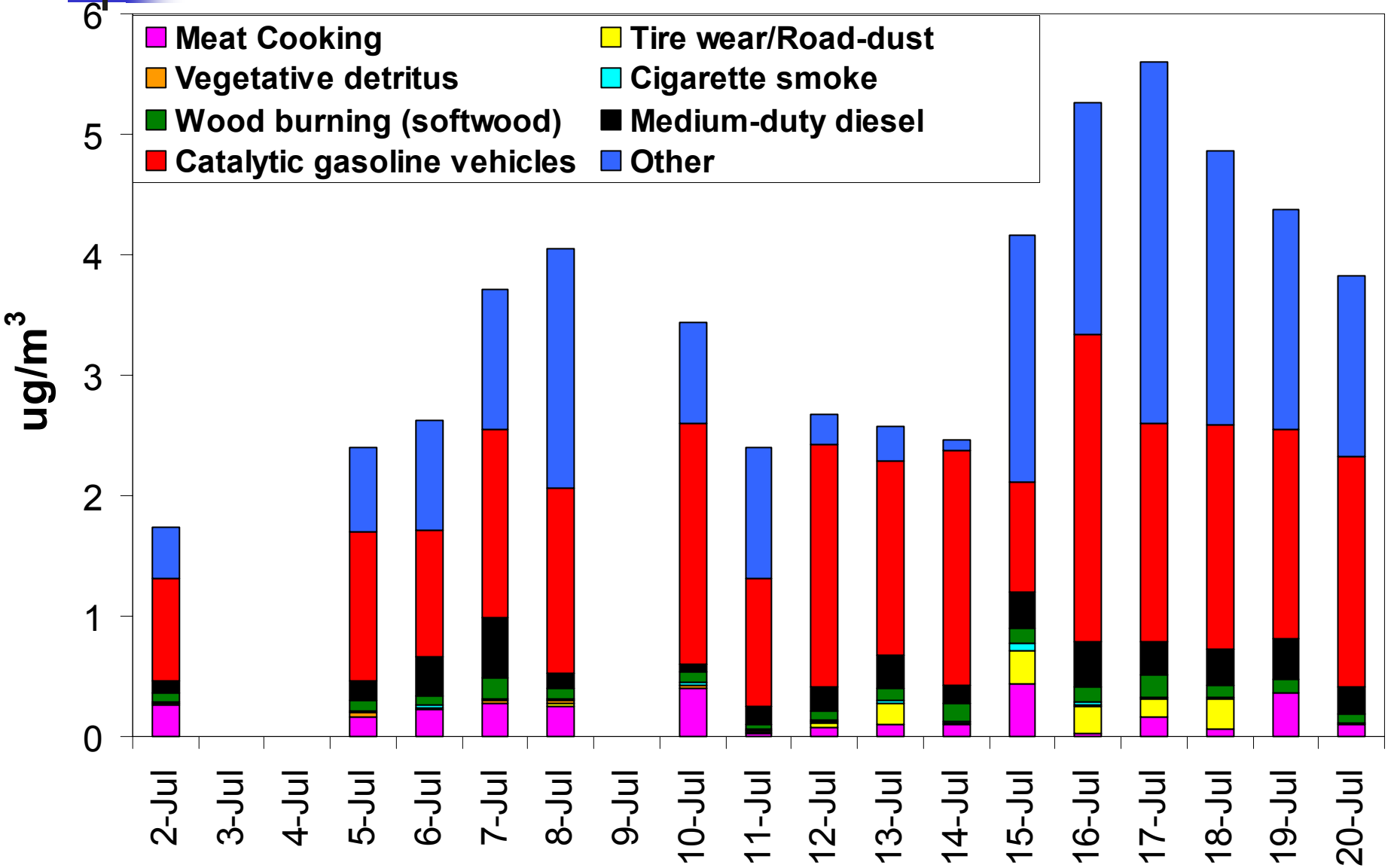
Comparison of Measured and Predicted Concentrations for July 7, 2001



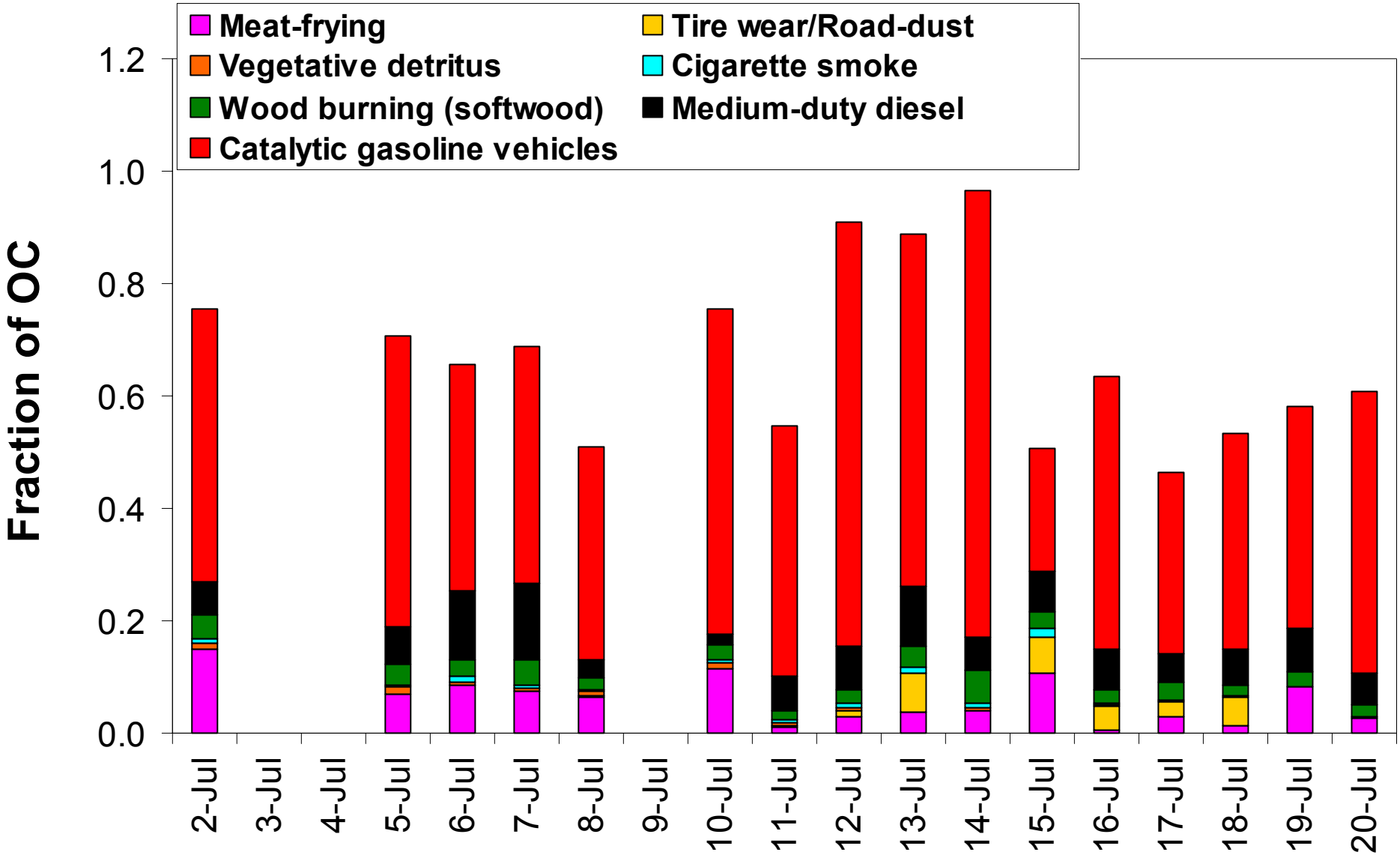
Source Contribution to Tracers for July 7, 2001



Source Apportionment for July 2001



Source Apportionment for July 2001



“Other” or Unexplained Mass

- Missing Sources
  - Secondary Organic Aerosol
  - Primary Biogenic
  - …
- Model Problems
  - Tracer Stability

Is unexplained mass SOA?

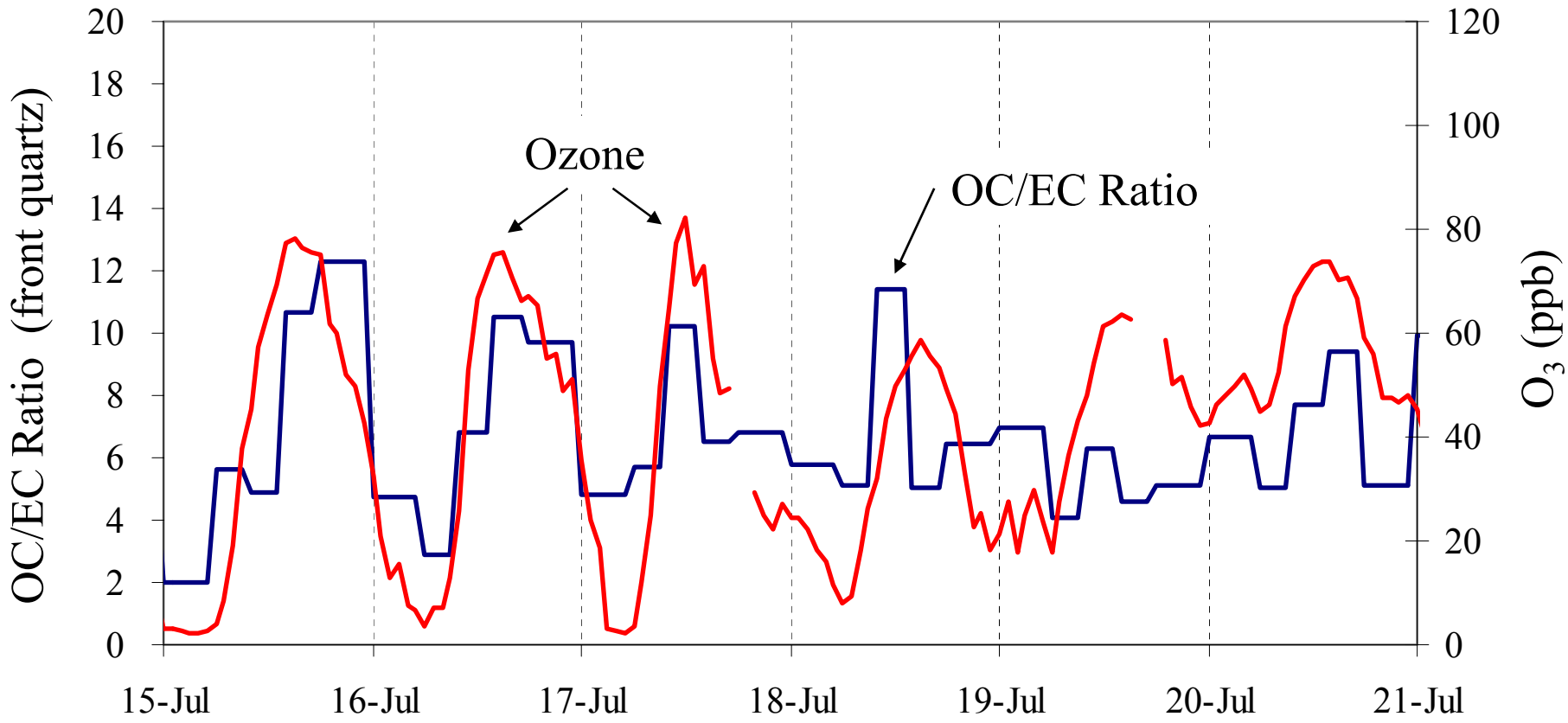
- OC/EC ratio method to estimate SOA
  - EC can be used as tracer for primary OC.

$$OC|_{secondary} = OC|_{total} - (EC|_{total} * OC/EC|_{emitted} + b)$$

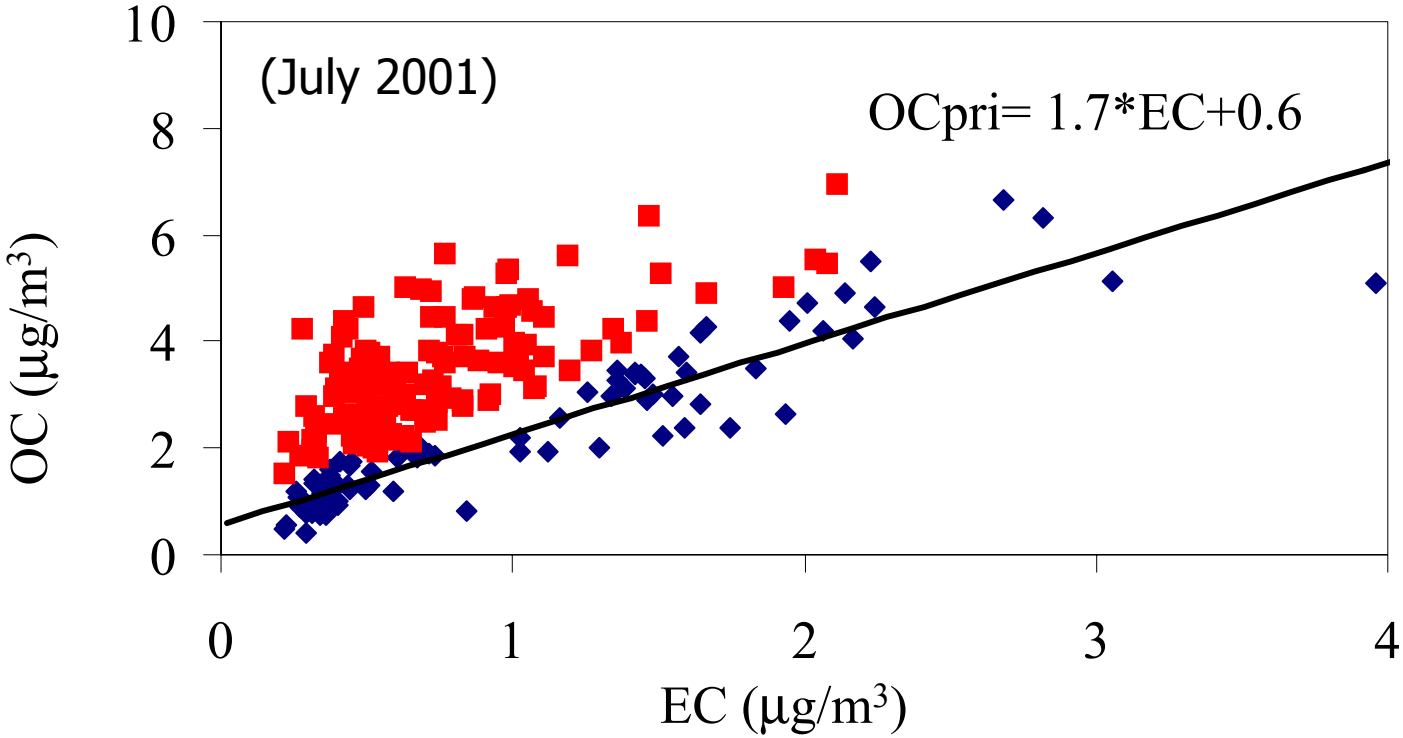
- Ambient Samples ($OC|_{total}$ and $EC|_{total}$)
- Determine ratio of OC/EC & b of primary emissions. ($OC/EC|_{emitted}$)

(Cabada et al. AS&T in press)

Ozone as indicator of SOA Production

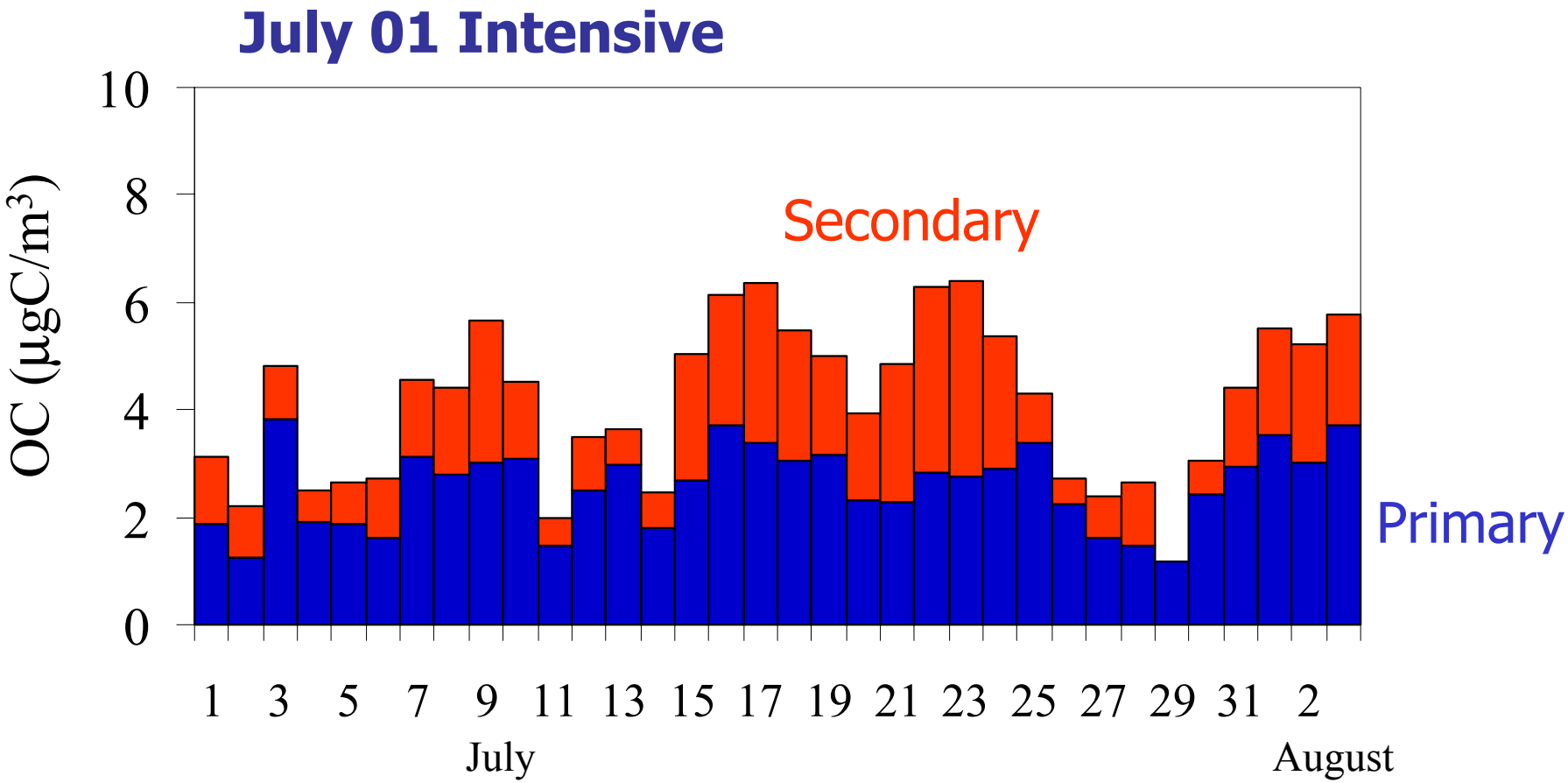


OC/EC Ratio from measurements

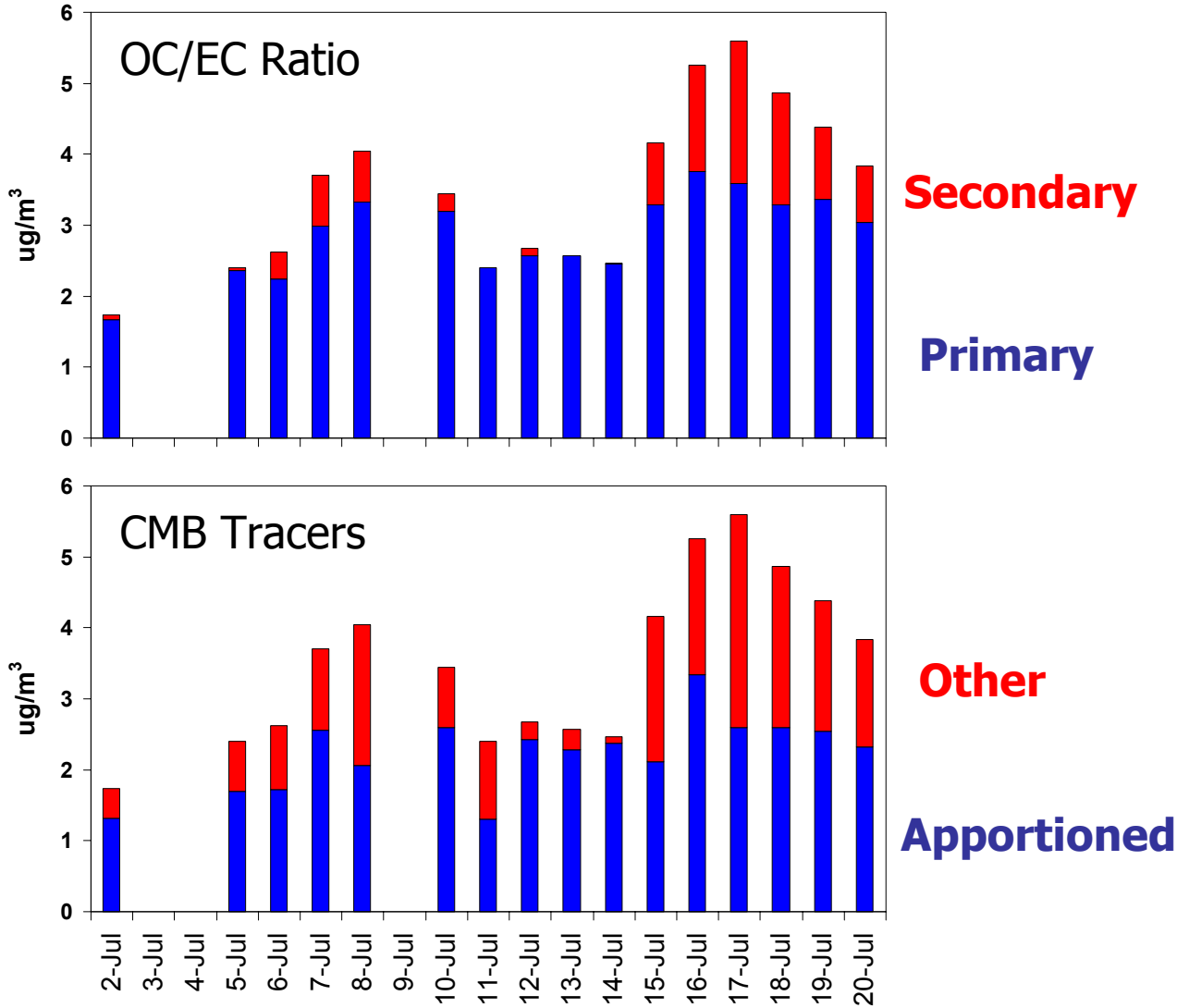


Denuded
In-situ Analyzer
(2-4 hrs samples)

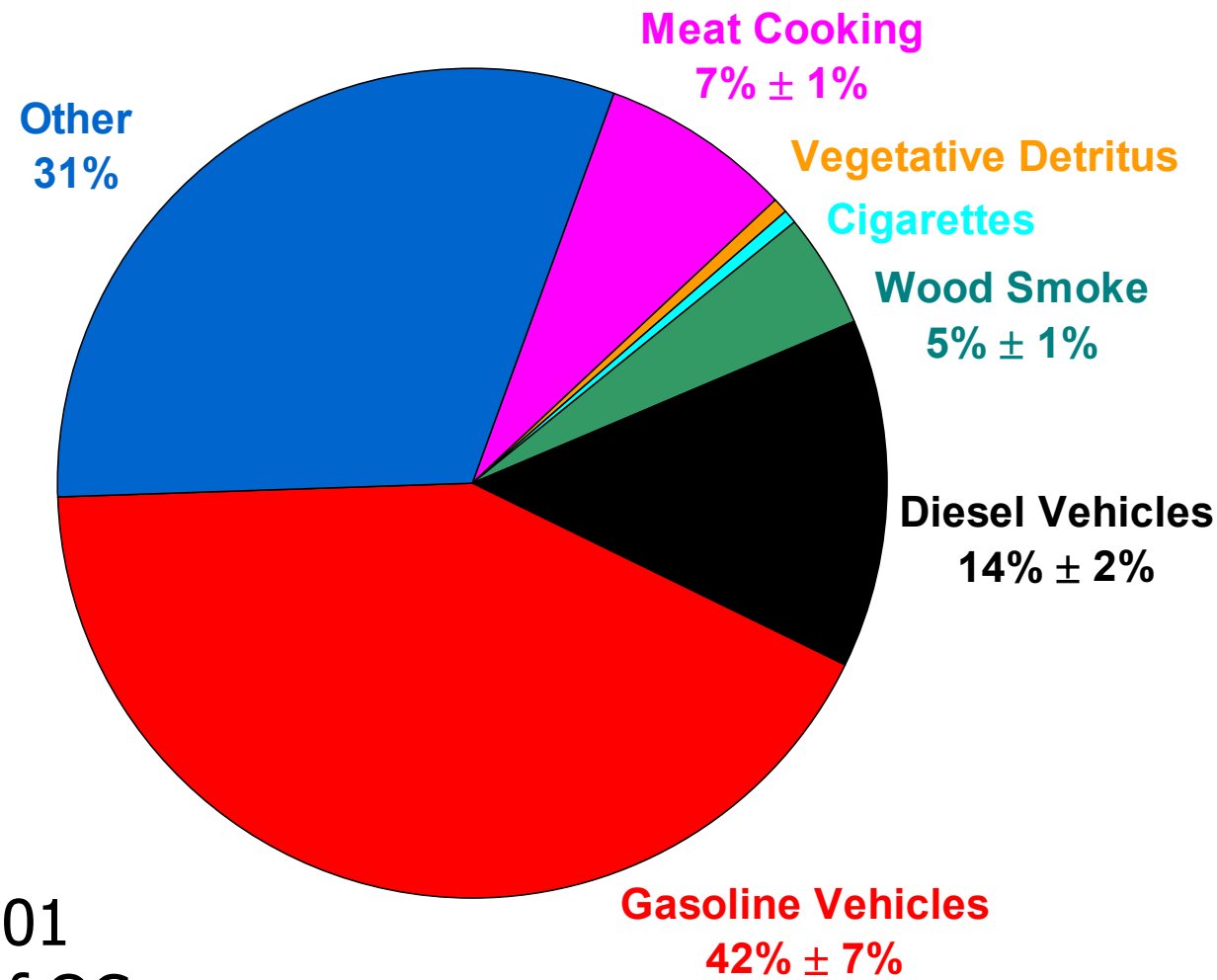
Daily Averaged SOA Contribution



Comparison of "Other" to SOA Estimates

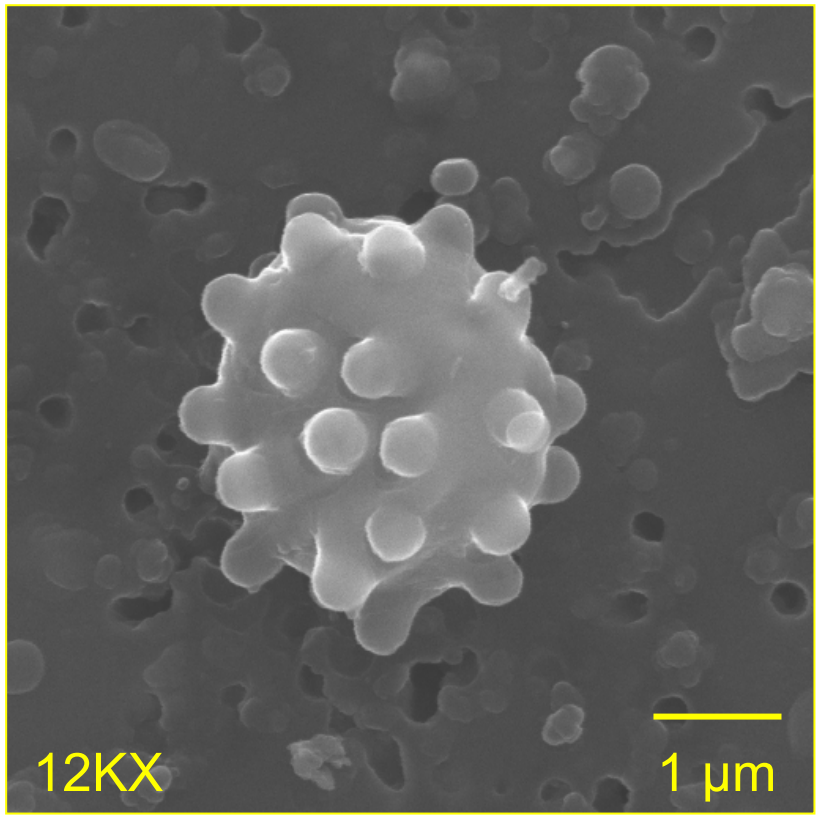


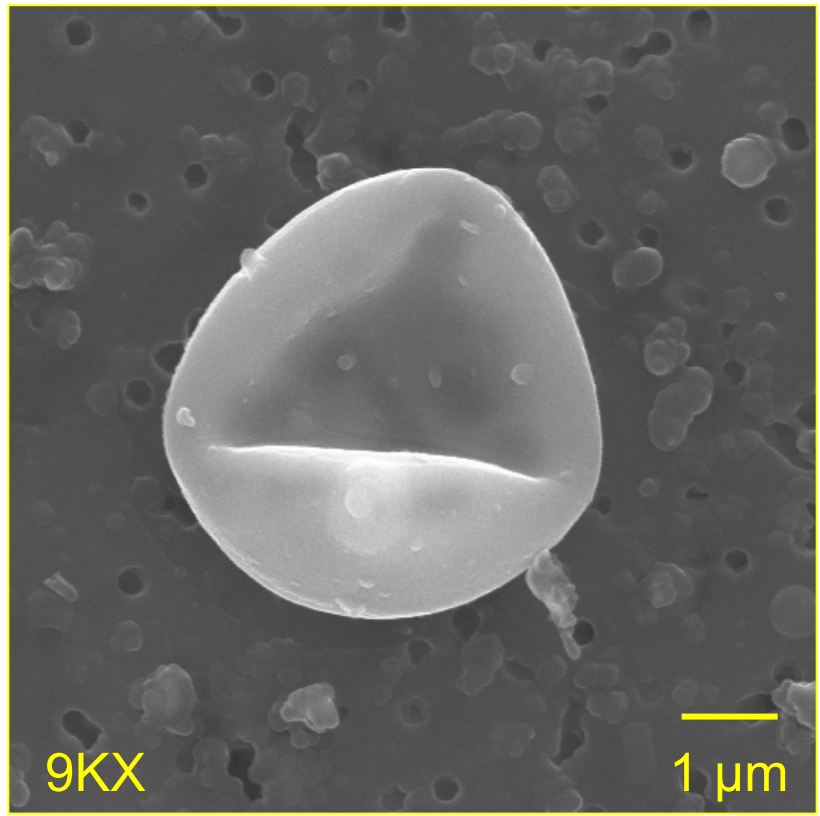
Primary Biological?



July 7, 2001
3.7 $\mu g/m^3$ of OC

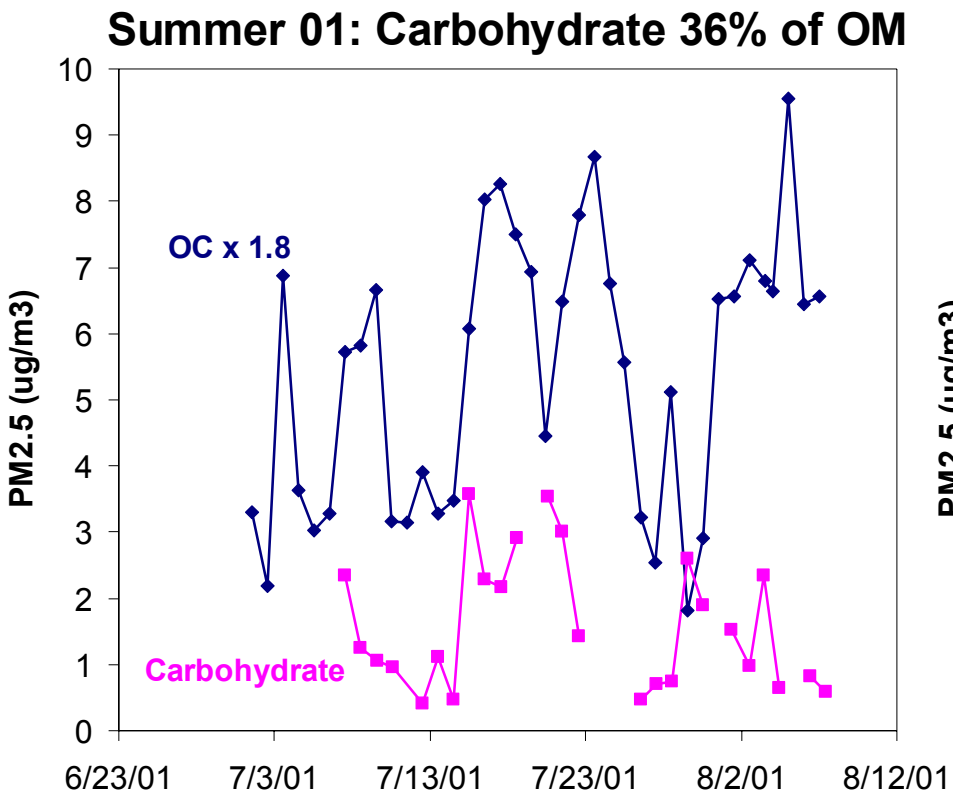
Evidence of Fine Primary Biological Material

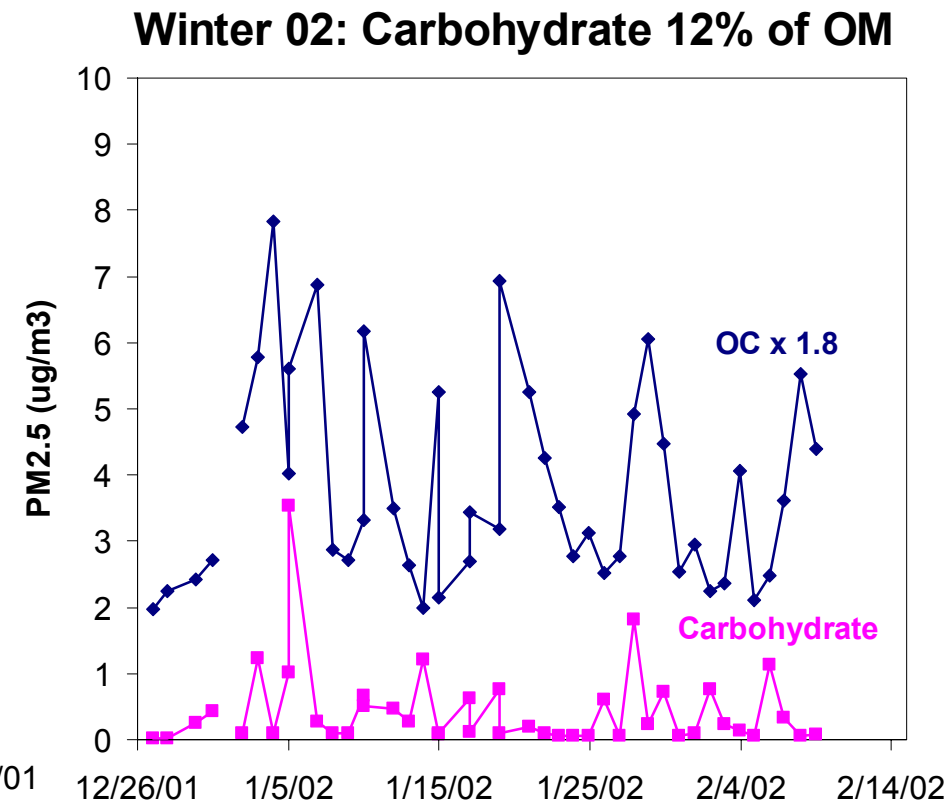




From G. Cassucio @ R.J. Lee

Primary Biogenic Contribution





From M. Hernandez @ UC Boulder

Conclusions

- Apportioned Primary Organic Aerosol for July 2001
  - Identified 46% - 97% of OC
  - Vehicle Emissions
- Potential Explanations for “Other” Mass
  - SOA
  - Primary Biogenic

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