An In-situ Method for Organic Aerosol Speciation via Thermal Desoprtion Gas Chromatography – Mass Spectrometry

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Objective

Automated, hourly measurements of organic marker compounds in ambient aerosols.

Science Questions

What are the major sources for organic aerosols?

How important is secondary organic aerosol (SOA)?

What compounds comprise SOA, and how are they formed?

Organic Matter

(blue)

20% – 40%

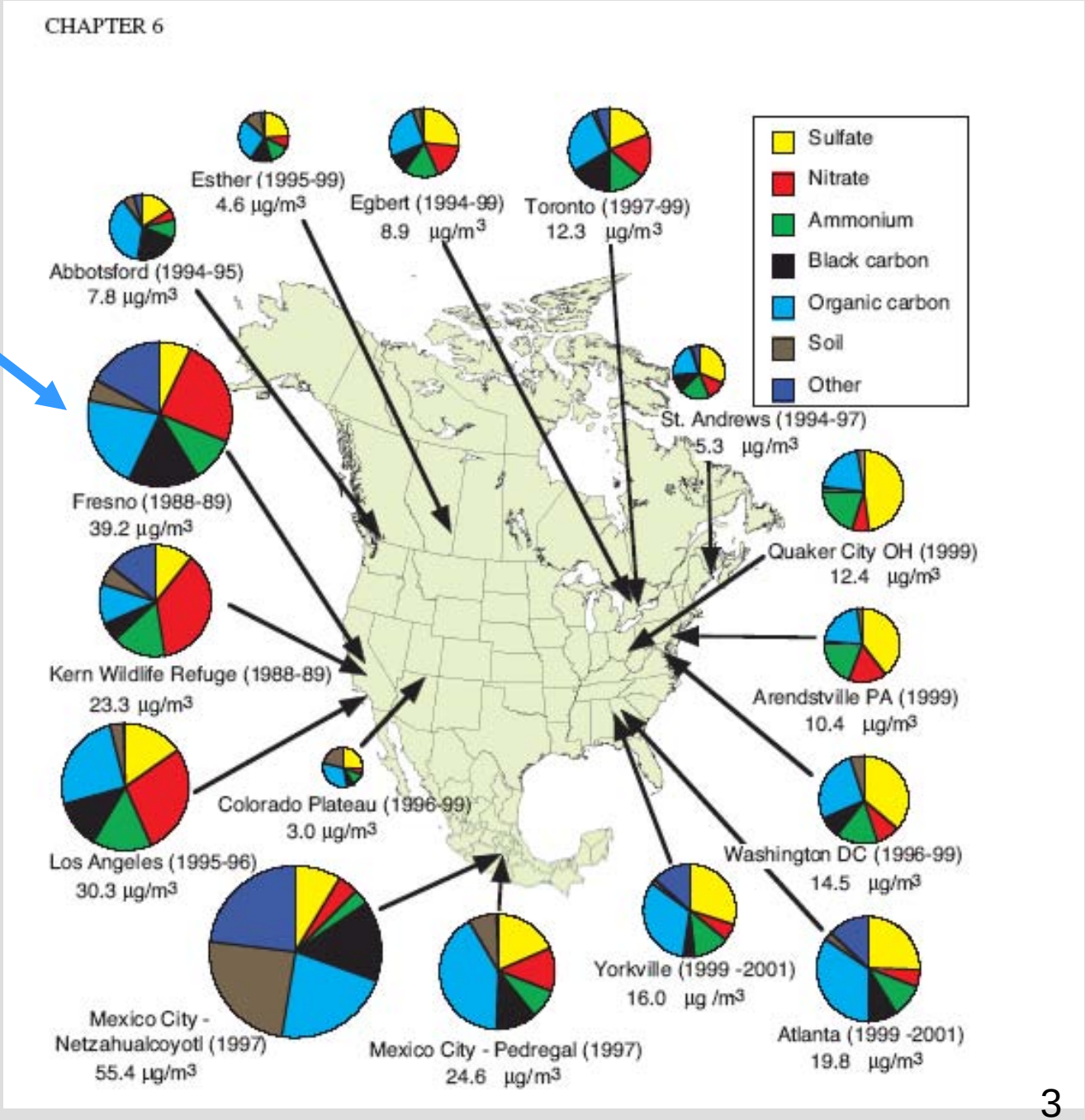
of $PM_{2.5}$

NARSTO Assessment on Particulate Matter

February 2003

Chapter 6

(C. Blanchard)



What are the Constituents of Organic PM?

Hundreds – Thousands of individual compounds:

- Alkanes
- Polycyclic aromatic hydrocarbons
- Substituted phenols
- Mono- and Di-carboxylic acids
- Sugars

Analysis of Organic Matter at the Compound Level

B. Simoneit, M. Mazurek, G. Cass

J. Schauer, W. Rogge, M. Fraser

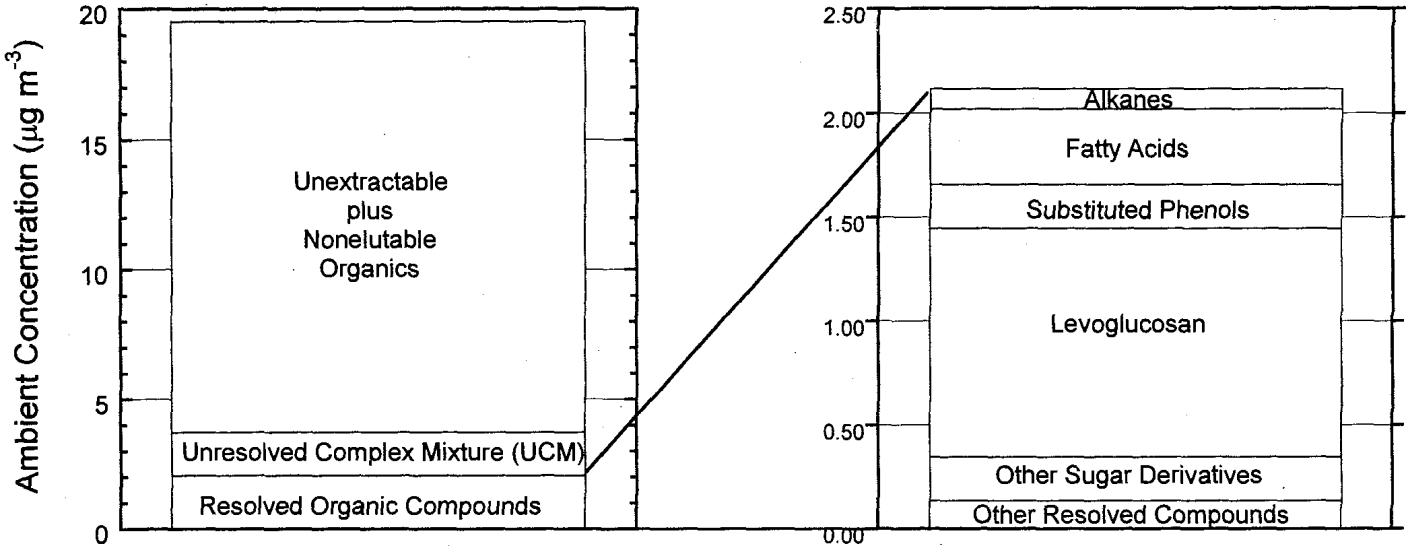
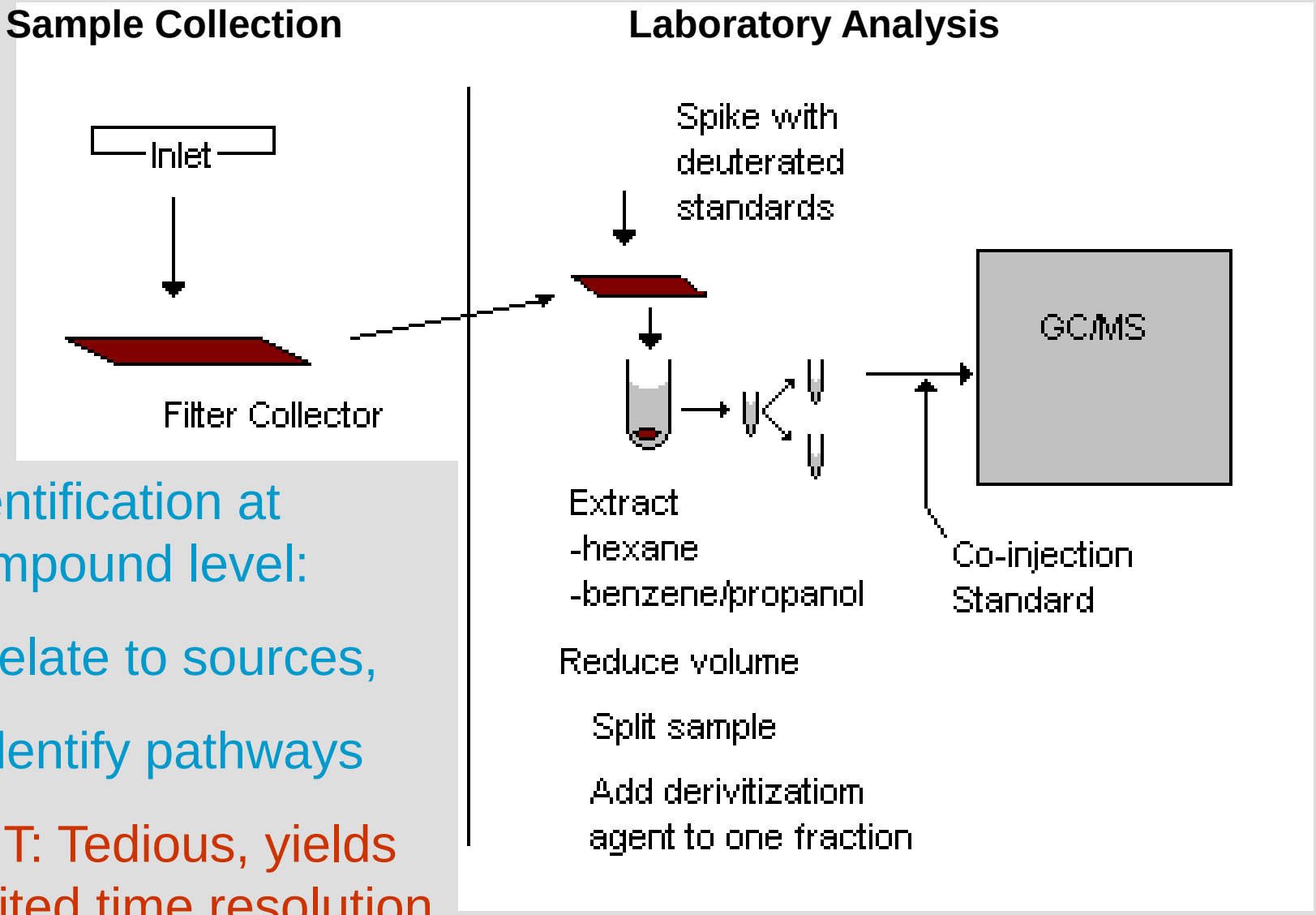


FIGURE 1. Mass balance on the fine particle organic compounds measured at Bakersfield, CA, between December 26 and 28

Schauer and Cass, Environ Sci Technol 43: 1826, 2000

Resolved compounds ~10% of total organic matter.
Analysis provides marker compounds, such as levoglucosan, useful for tracing sources.

Steps in GC/MS Analysis of Filter Samples



Identification at compound level:

-- relate to sources,

--identify pathways

BUT: Tedious, yields limited time resolution

Automated Measurements:

In-Situ Mass Spectrometry (ATOFMS, AMS, others) –

high time resolution

no individual compound identification

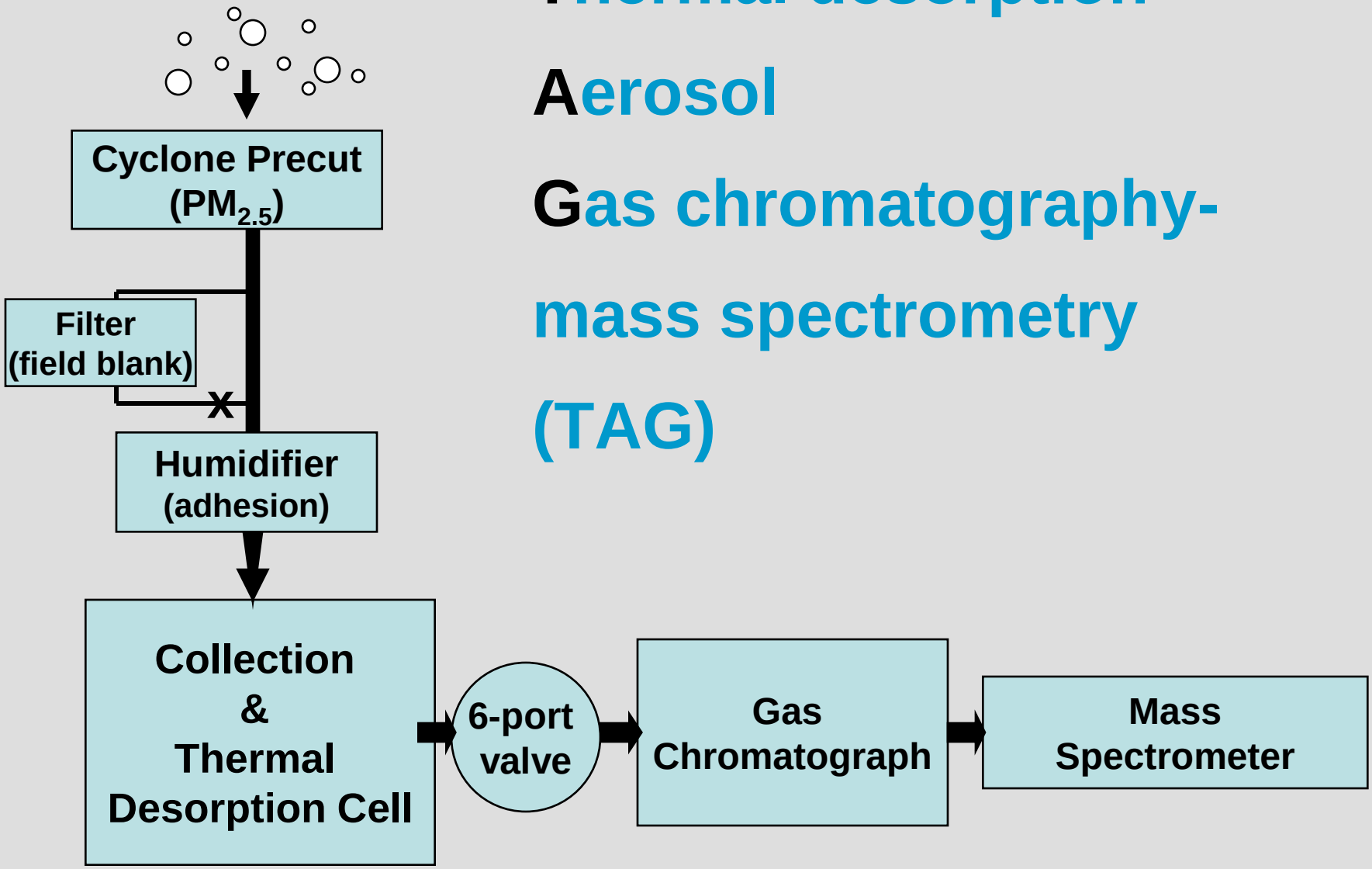
Our Aim – to combine advantages of the speciation of filter measurements with the time resolution of automated methods :

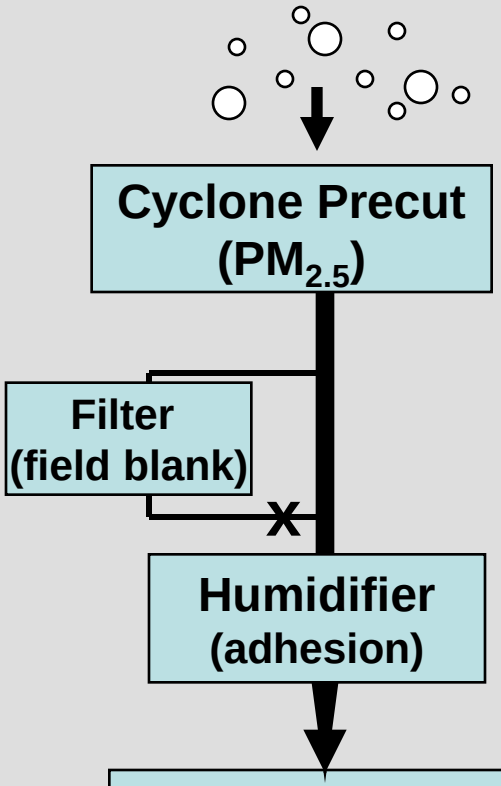
Separating / Identifying / Quantifying individual organic aerosol marker compounds with hourly time resolution

Thermal desorption

Aerosol

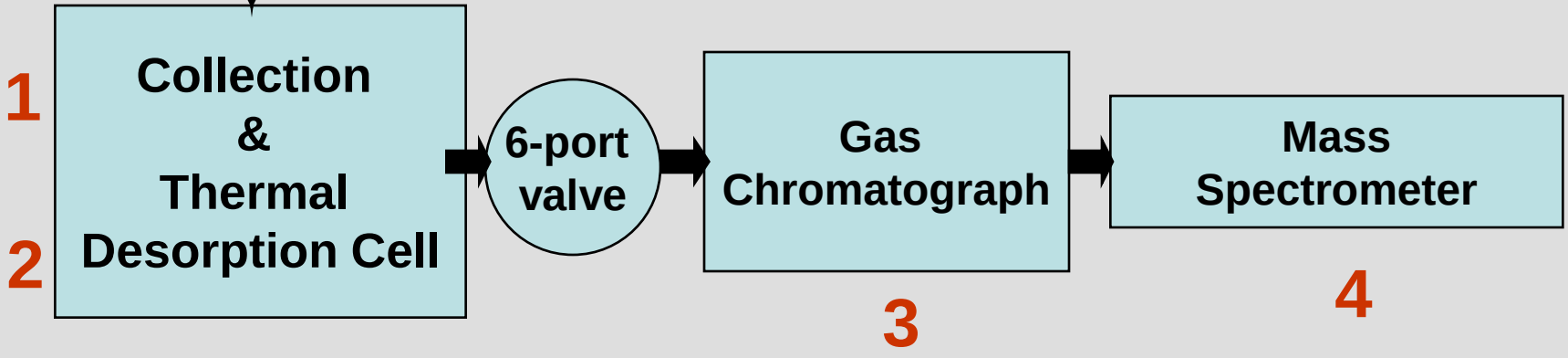
Gas chromatography-mass spectrometry (TAG)



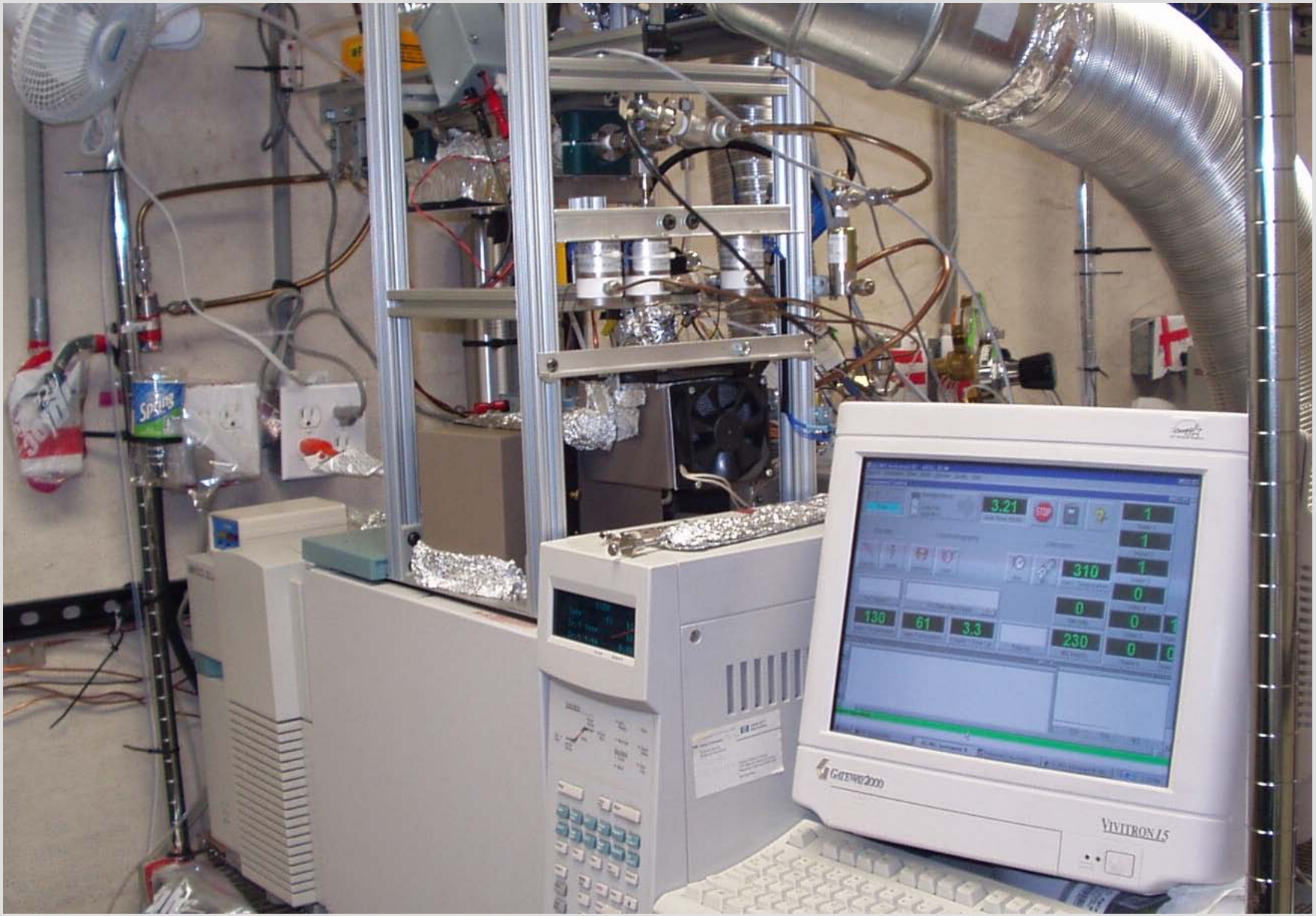


1. **Aerosol Collection:**
   - Humidification / Inertial Impaction (30 C)
2. **Sample transfer:**
   - Thermal Desorption (50-300 C)
3. **Chemical separation:**
   - Gas Chromatography
4. **Identification & quantification:**
   - Mass Spectrometry (and/or FID)
   - Spectrum + Retention Time Matching
   - Standards

Cycle time = 1 hour,
Provision for standards, automated blanks

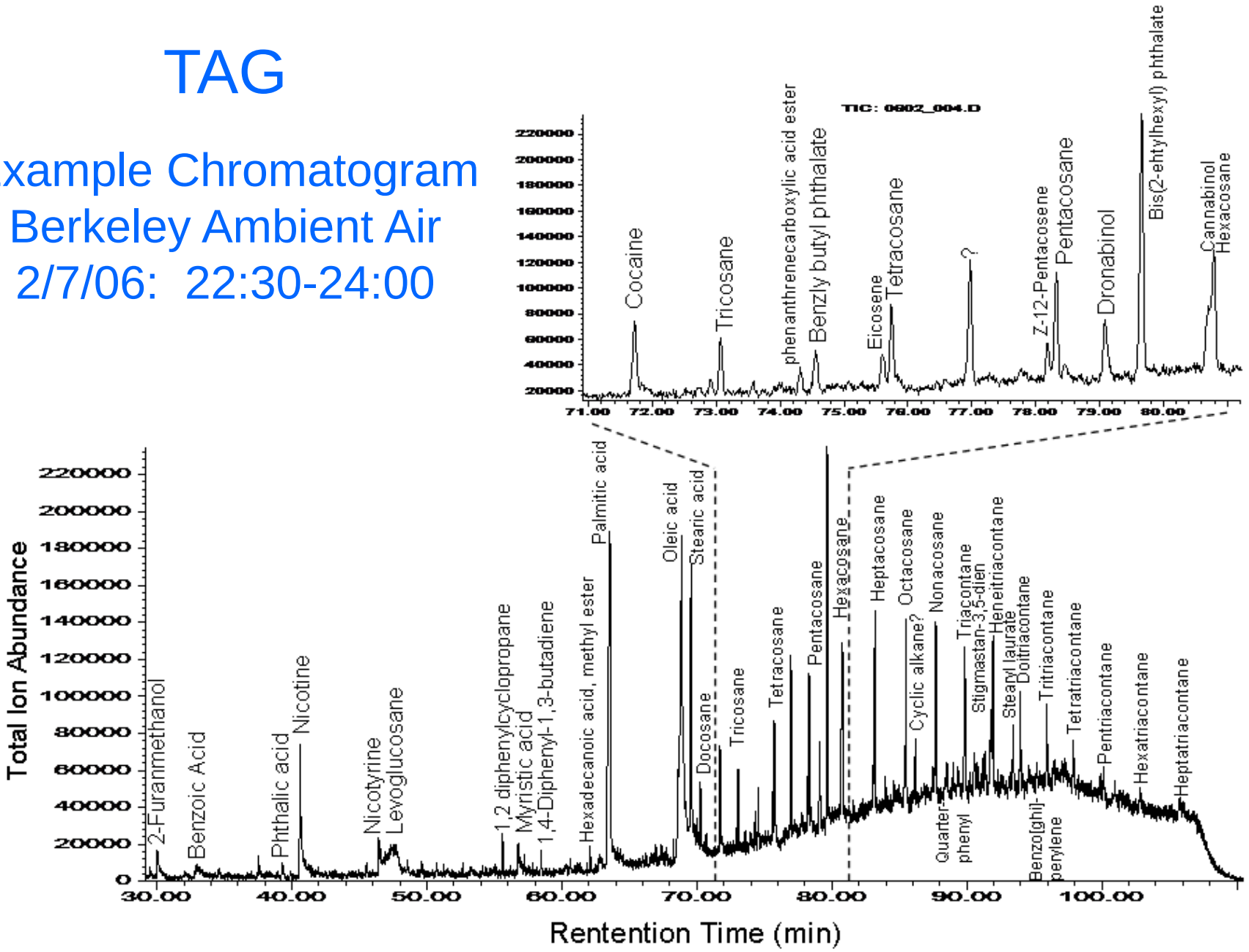


TAG in Nova Scotia

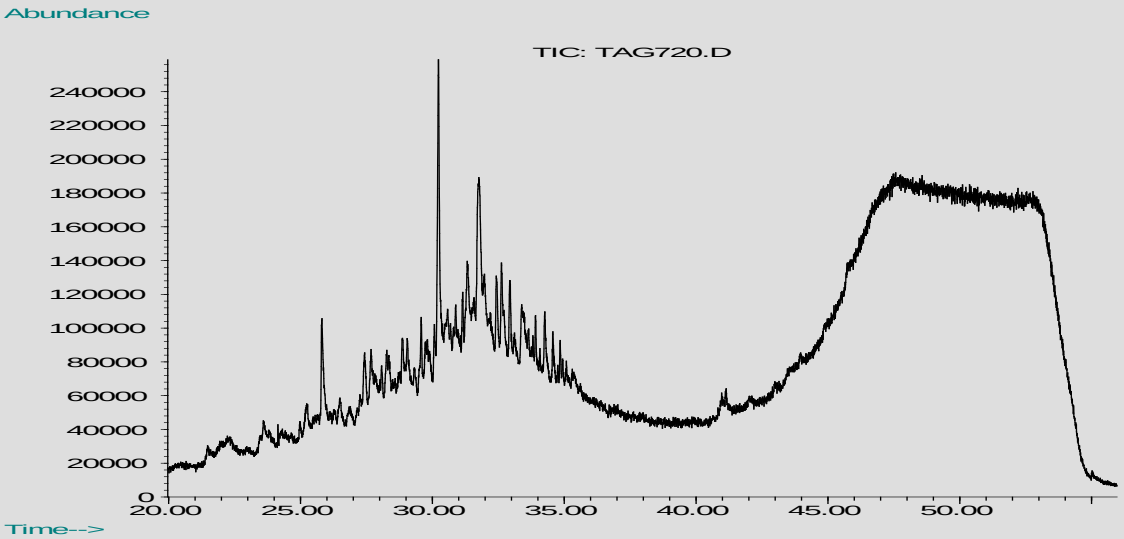


TAG

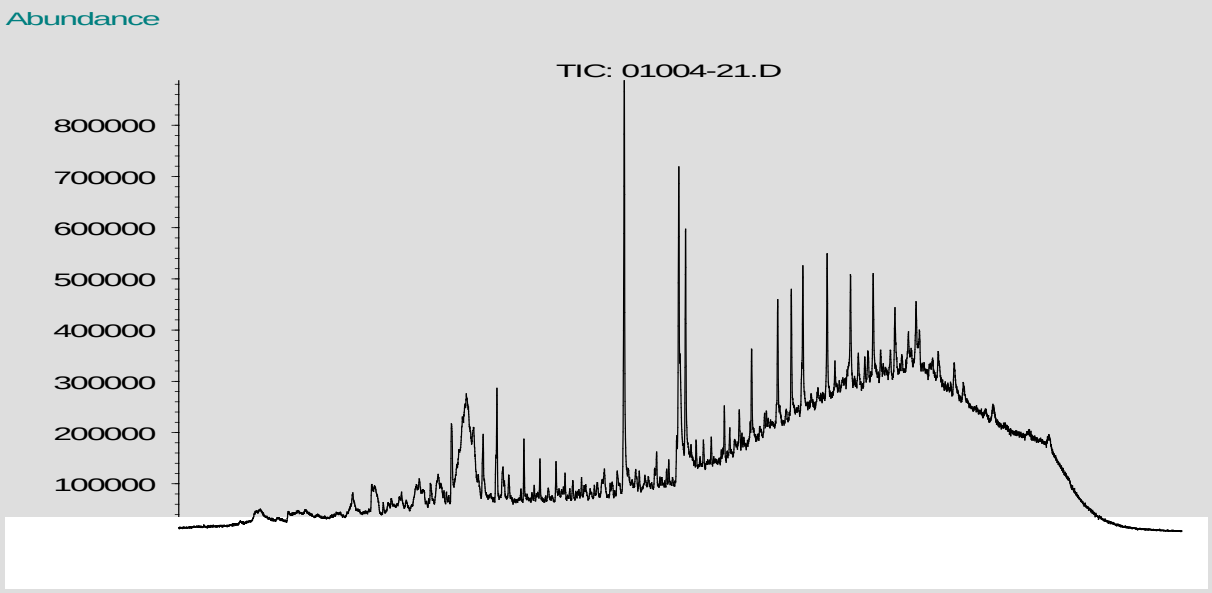
Example Chromatogram
Berkeley Ambient Air
2/7/06: 22:30-24:00



Comparison of Chromatograms from Nova Scotia (remote site) with Berkeley, CA (urban site)



Chebogue Point, Nova Scotia 8/7/04
-- more oxygenated
-- elute sooner



Berkeley, CA
1/10/04

Some Identified Compounds from Nova Scotia

5-Hexenoic acid, 5-methyl-	$C_7H_{12}O_2$
5,6-Dihydropyran-2-one, 5-acetoxy-6-(1,2-epoxypropyl)-	$C_{10}H_{12}O_5$
Pelletierine	$C_8H_{15}NO$
2,2-Dimethyl-3-heptene trans	C_9H_{18}
4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester	$C_{11}H_{18}O_3$
4s,6s-Dimethyl-7R-acetoxy-3-nonanone (acetyl serricornin)	$C_{13}H_{24}O_3$
2(3H)-Furanone, 5-methyl-	$C_5H_6O_2$
Spiro[1,3-dioxolane-2,2'-[6,7]diazabicyclo[3.2.2]non-6-ene	$C_9H_{14}N_2O_2$
2(3H)-Furanone, 3-acetyldihydro-	$C_6H_8O_3$
1,6-Dioxaspiro[4,4]nonane-2,7-dione	$C_7H_8O_4$
Cyclohexanone, 2-ethyl-	$C_8H_{14}O$
2,3-Pinanediol	$C_{10}H_{18}O_2$
Phthalic acid	$C_8H_6O_4$
3,5-di-tert-Butyl-4-hydroxybenzaldehyde	$C_{15}H_{22}O_2$
Dibenz[c,d]hydrooxepin	$C_{14}H_{12}O$

Timelines for Individual Compounds

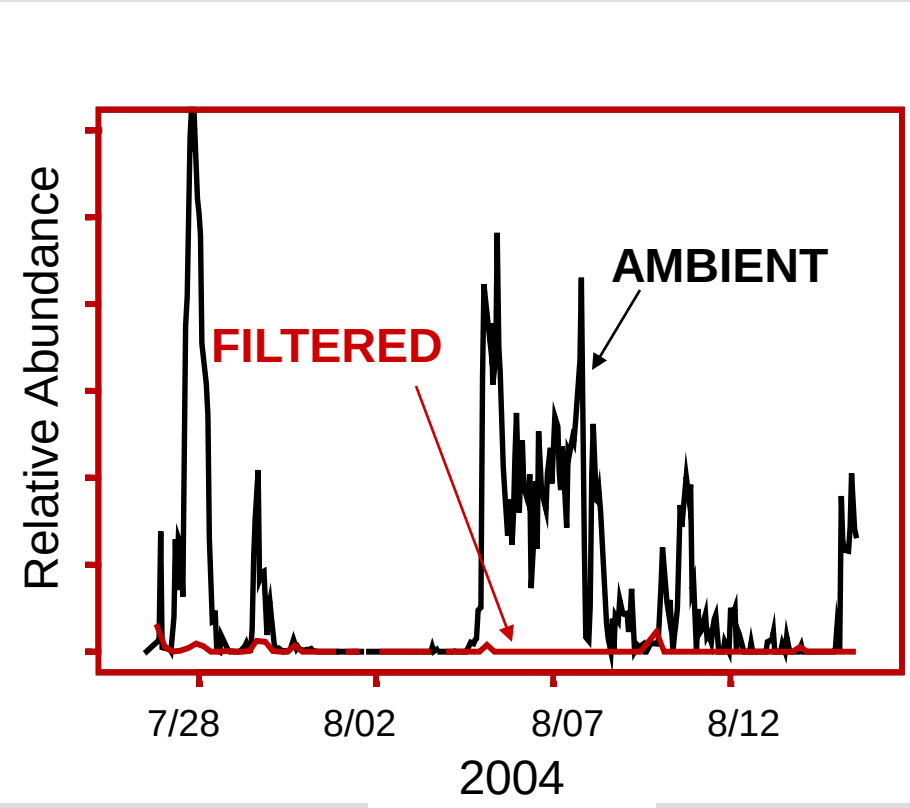
Chebogue Point Nova Scotia 2004

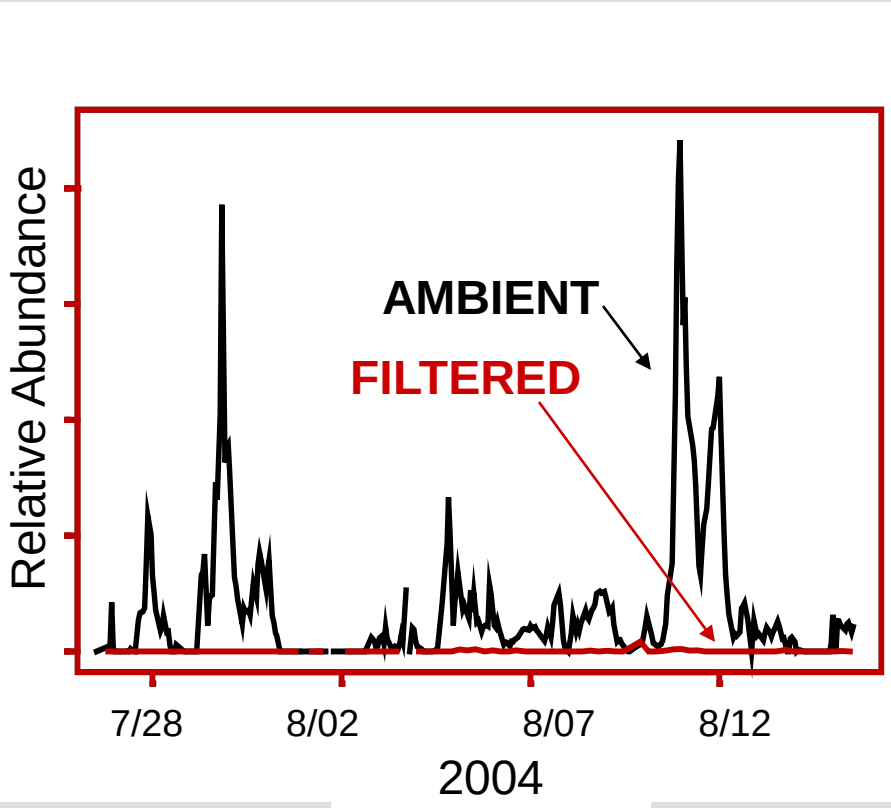
Compound A:

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester ($C_{11}H_{18}O_3$)

Compound B:

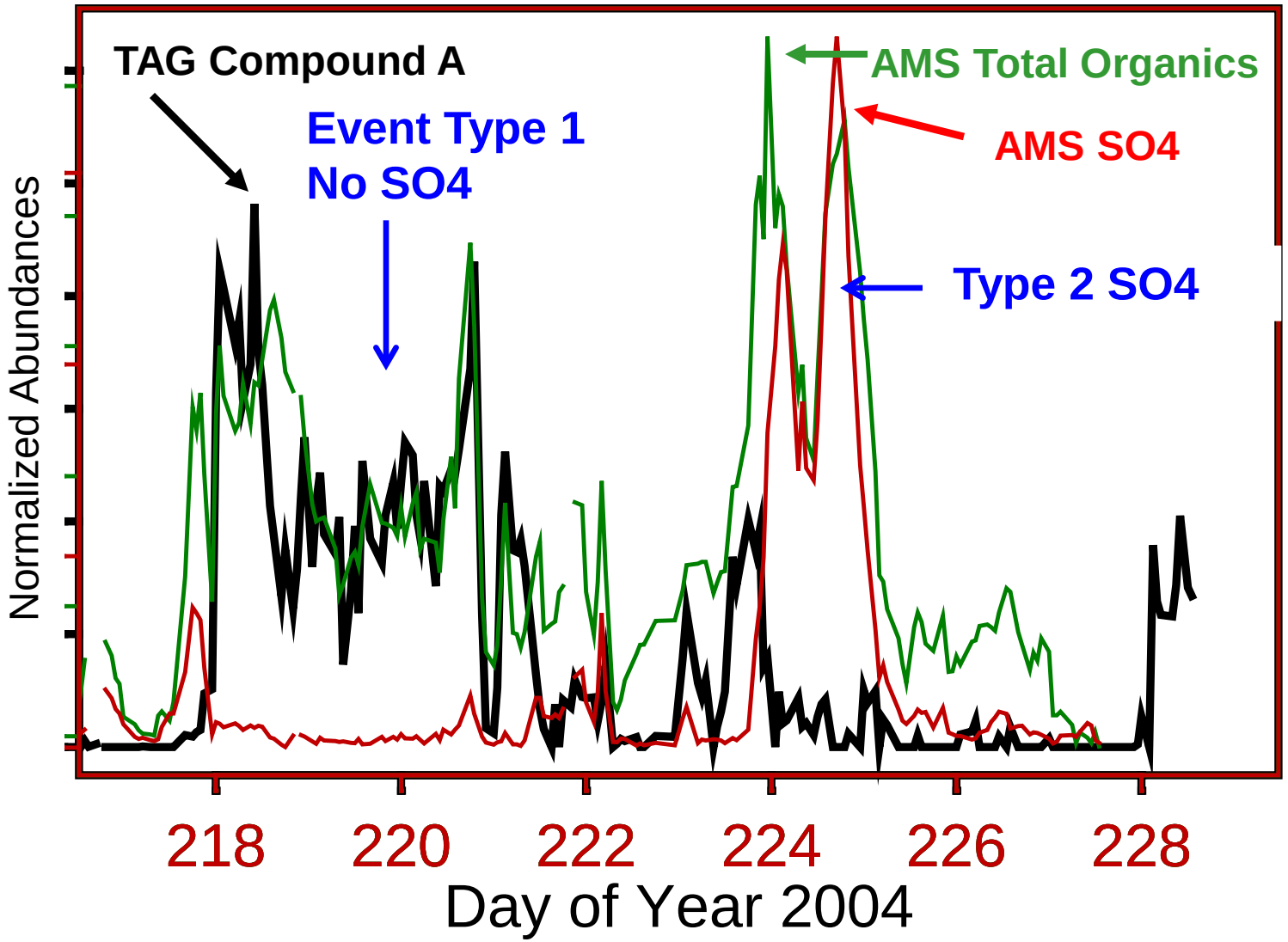
1,6-Dioxaspiro[4,4]nonane-2,7-dione ($C_7H_8O_4$)





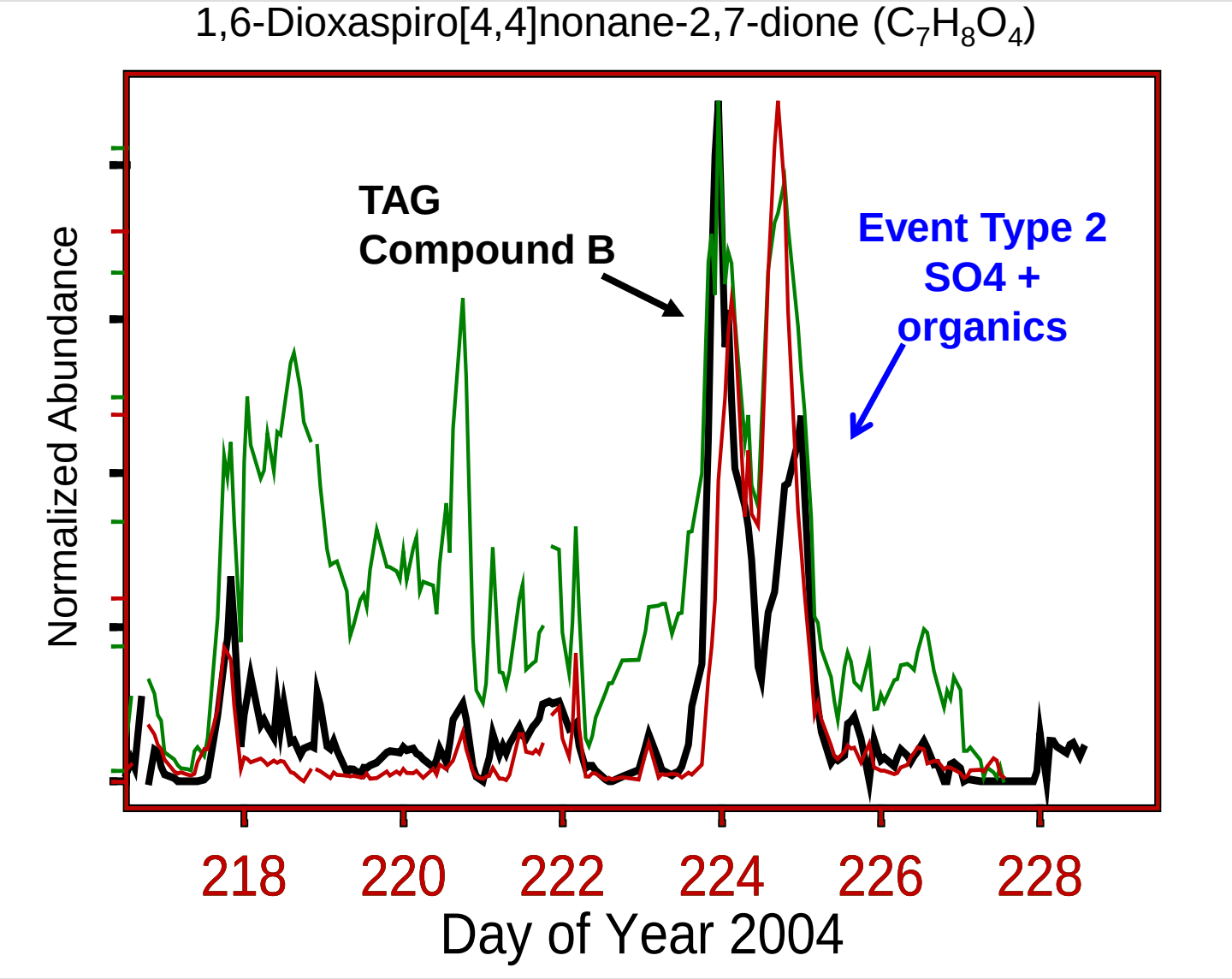
TAG Compound A vs AMS Total Organics and Total SO4

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester ($C_{11}H_{18}O_3$)



AMS Total Organic, Total SO4 data (Aerodyne Research, Inc.: Worsnop et al.)

Tag Compound B vs AMS Organics and Sulfates

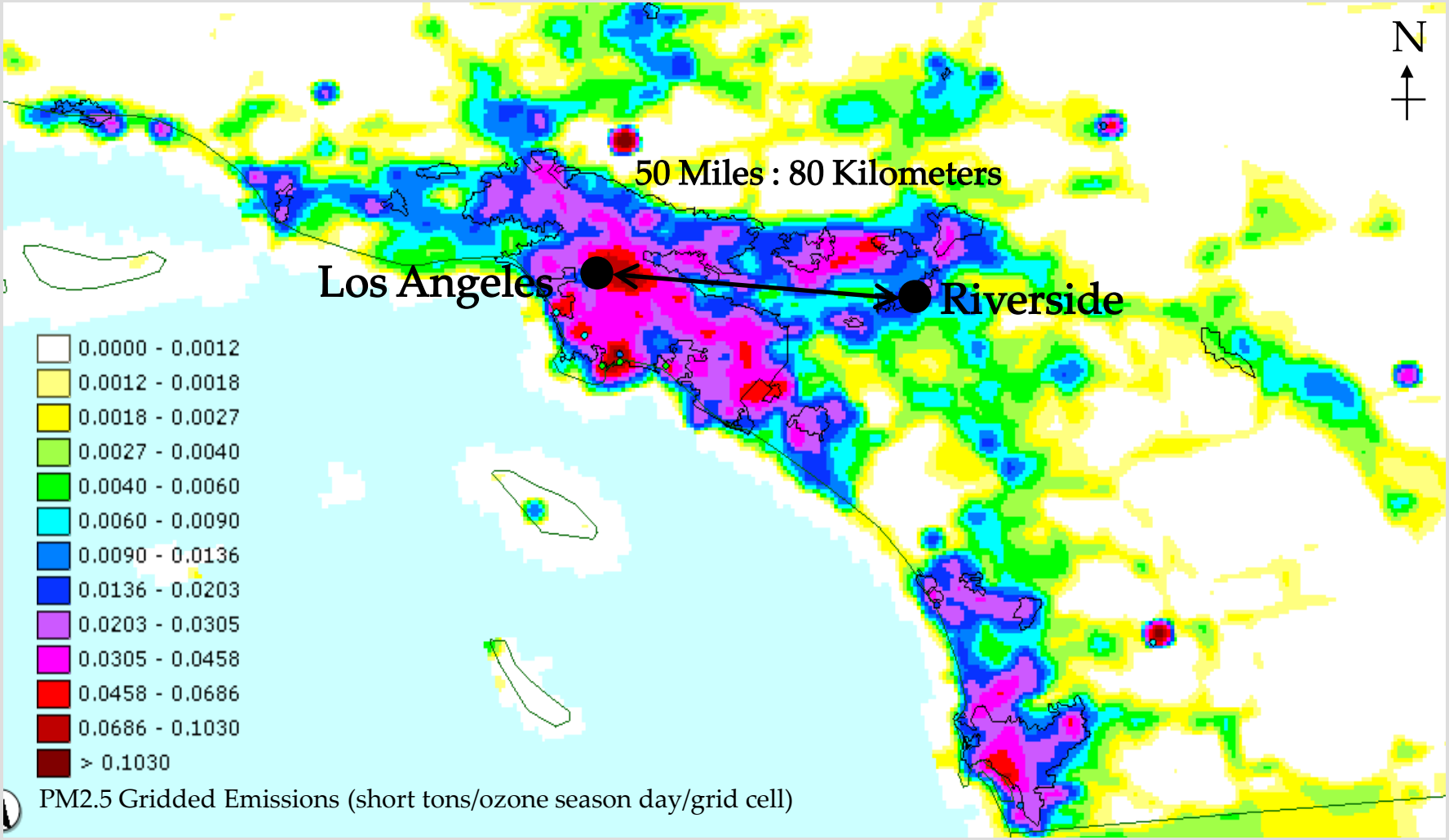


These two compounds represent two different events.

AMS data (Aerodyne Research, Inc.: Worsnop et al.)

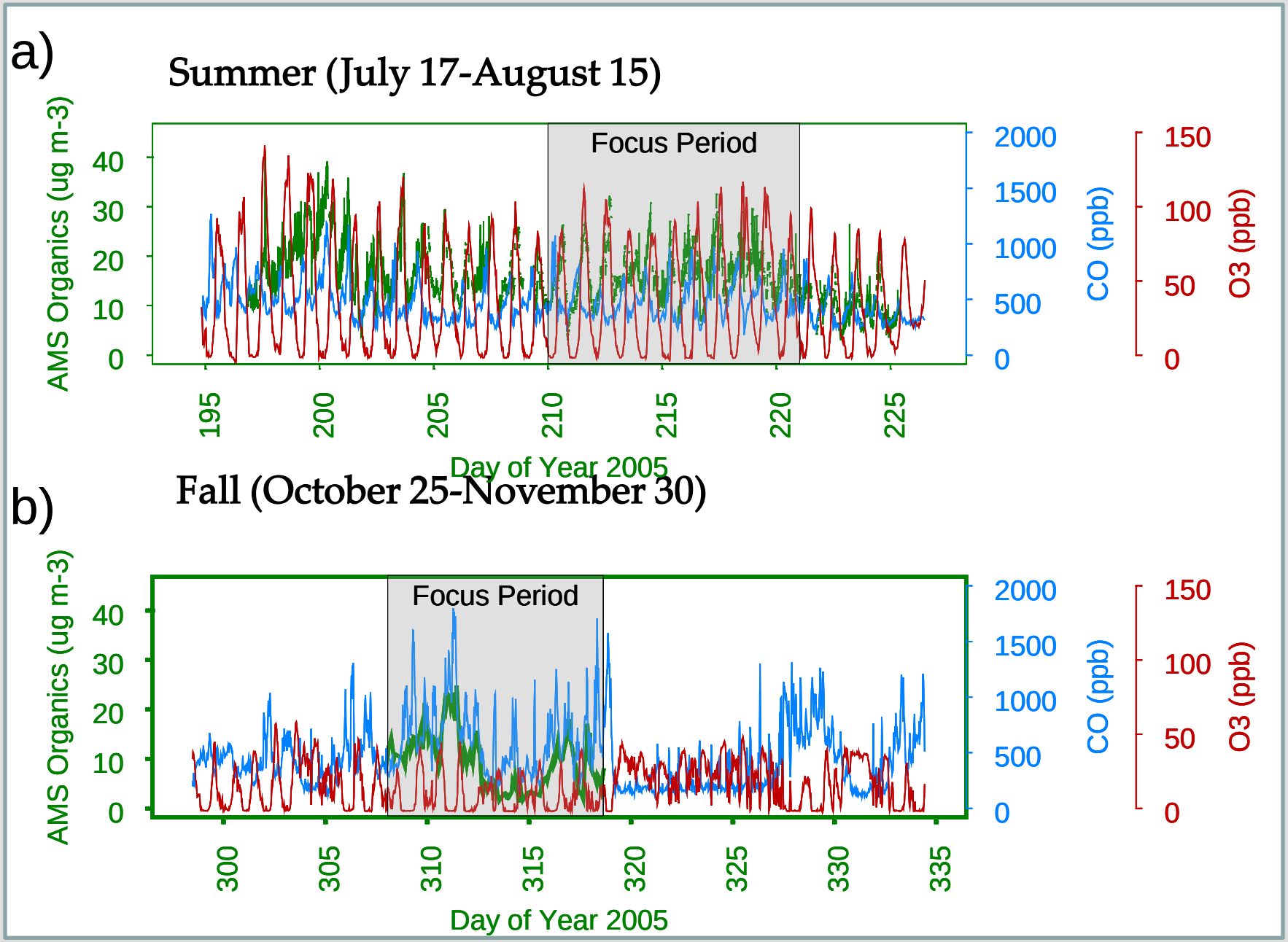
Study of Organic Aerosols at Riverside (SOAR)

Location: University of California, Riverside



NOAA http://map.ngdc.noaa.gov/website/al/emissions/Run.htm

SOAR Measurement Periods

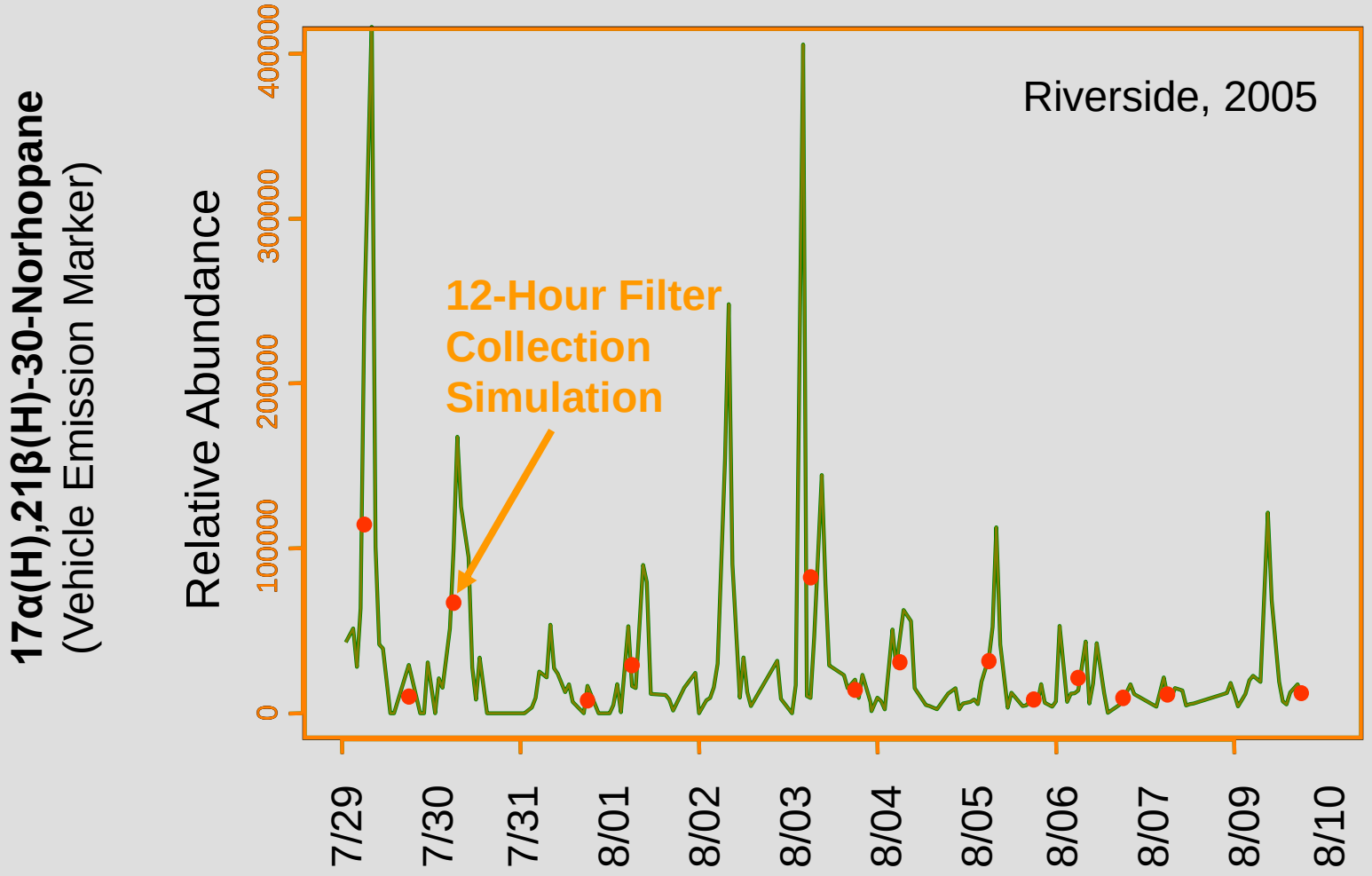


Very different Photochemistry (and Meteorology)

SOAR TAG Measurements and Source Apportionment

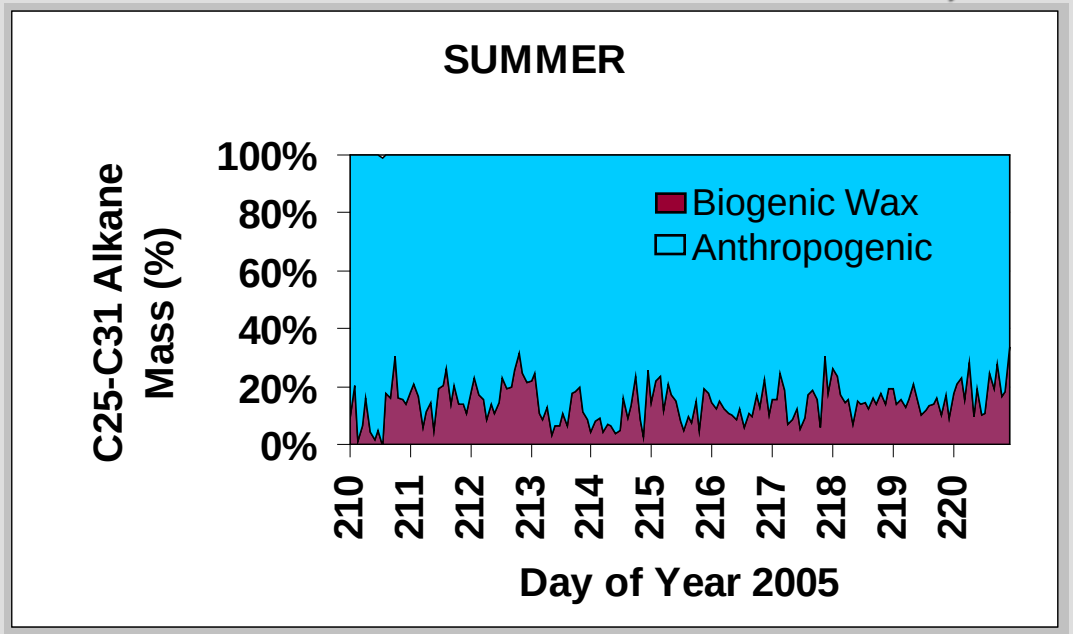
- **Resolved >300 organic marker compounds hourly**
- **Positive Matrix Factorization (PMF)**
  - 124 of 300 resolved TAG organic compounds in Summer
  - 141 of 300 resolved TAG organic compounds in Fall
- **Identified organic aerosol sources based on PMF groupings**
  - 9 in Summer
  - 6 in Fall

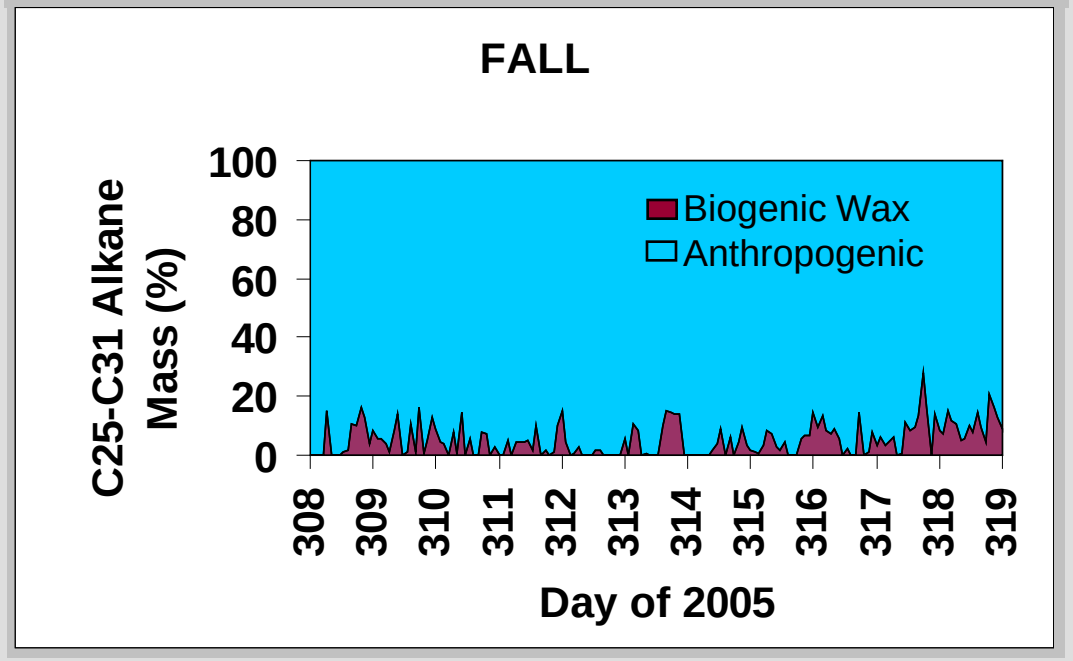
Hourly (TAG) data captures dynamics missed by 12 hour filter collections



Riverside, CA

Biogenic vs. Anthropogenic Alkanes

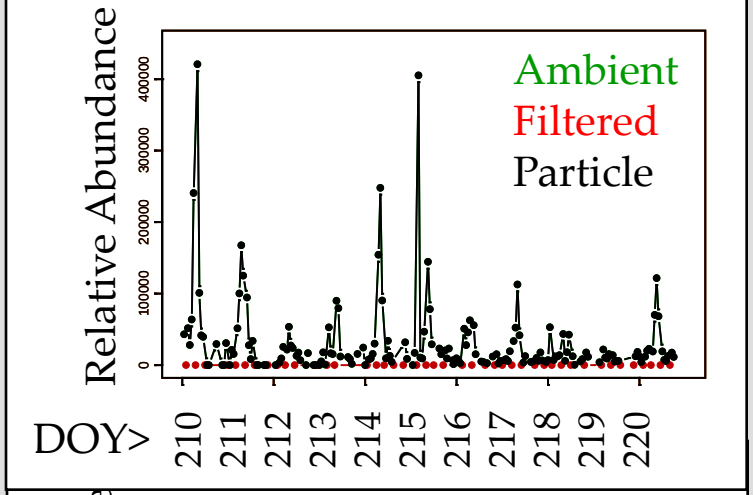


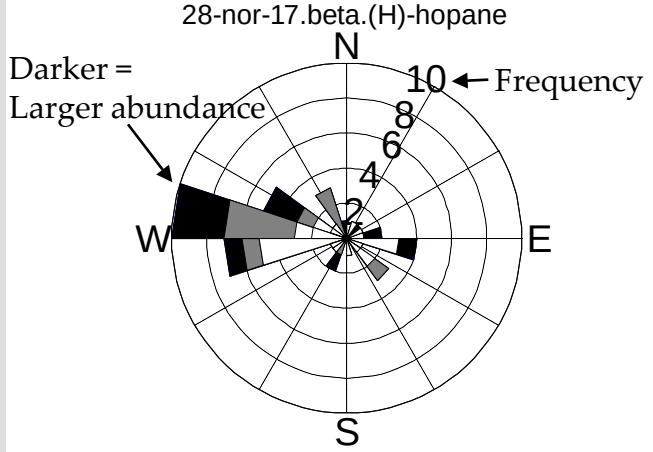


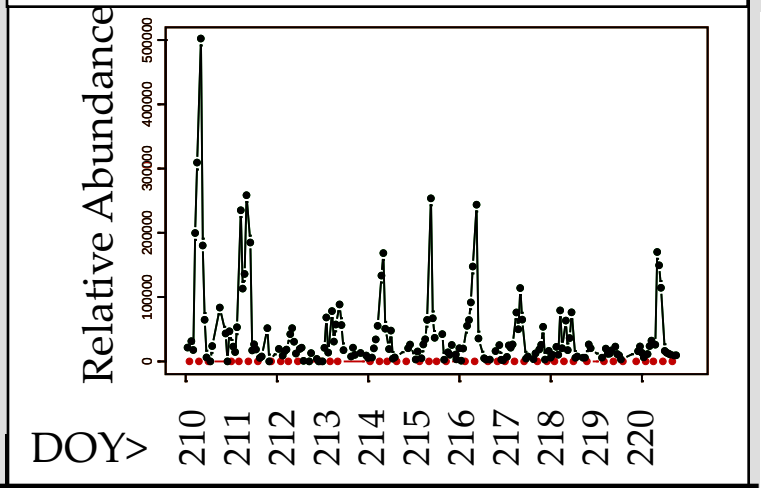
$$C_{wax} = \sum_{n=25}^{31} [C_n - \frac{(C_{n-1} + C_{n+1})}{2}]$$

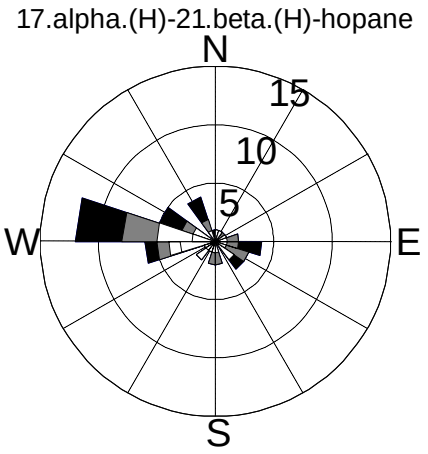
Adapted from *Simoneit 1989 J.Atmos.Chem.*

Primary Anthropogenic (vehicle)

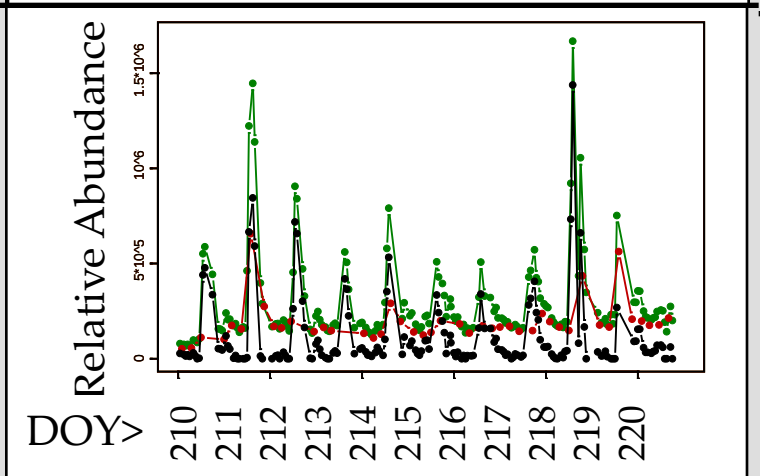


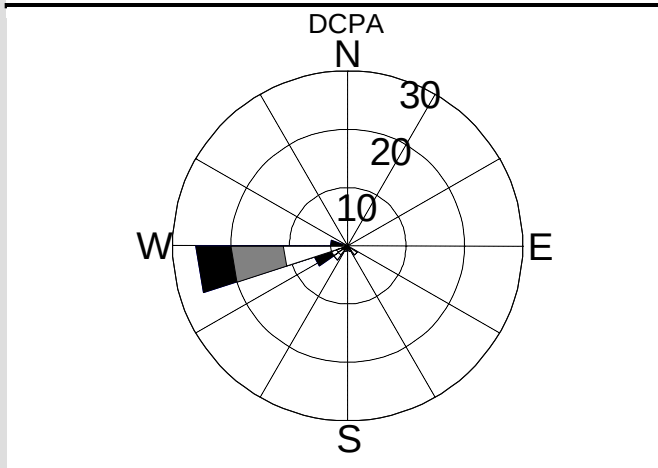




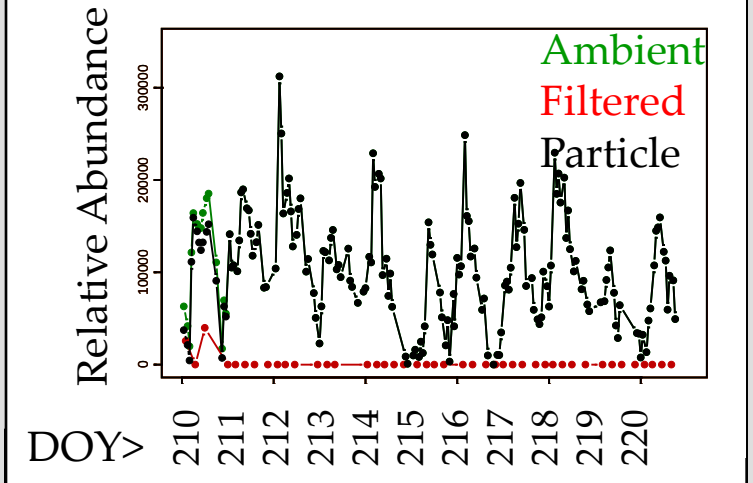


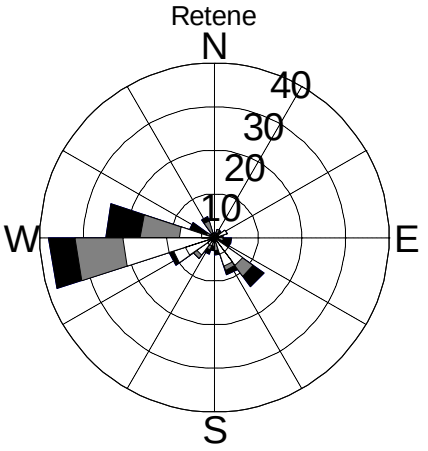
Herbicide



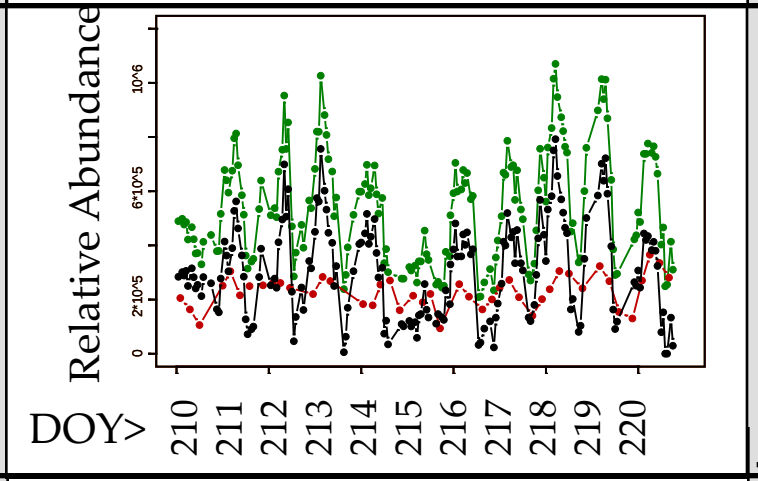


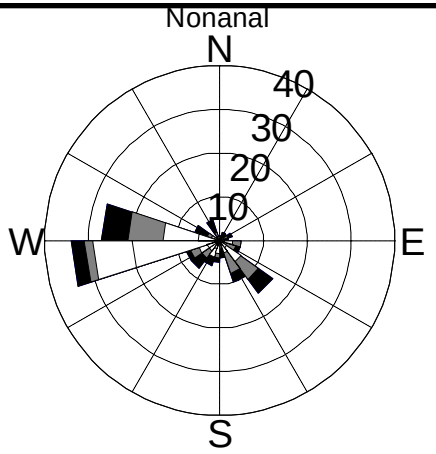
Biomass Burning



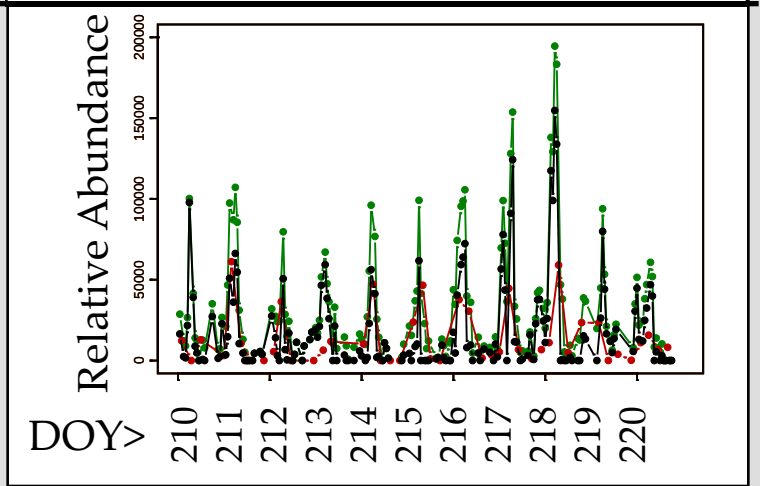


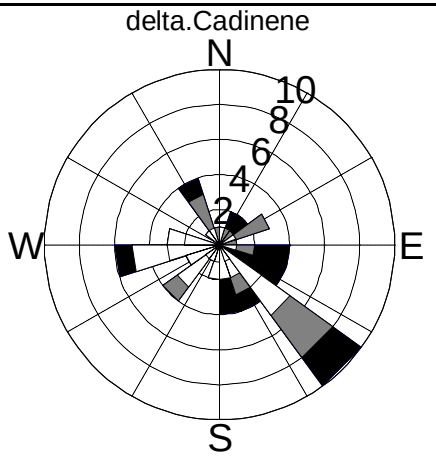
Meat Cooking



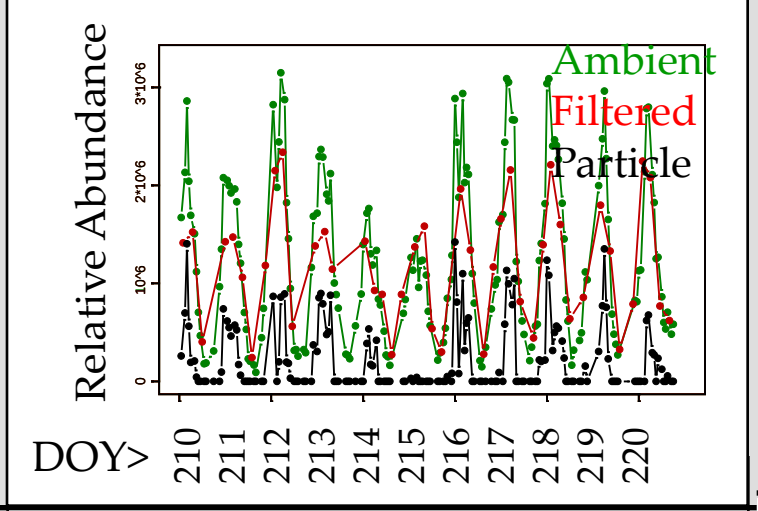


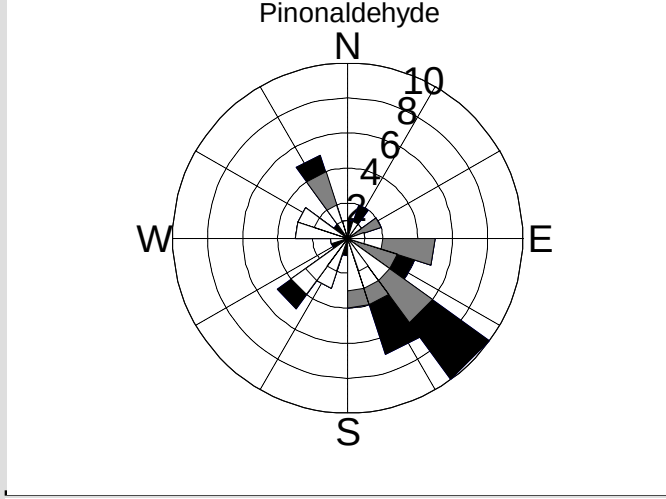
Primary Biogenic



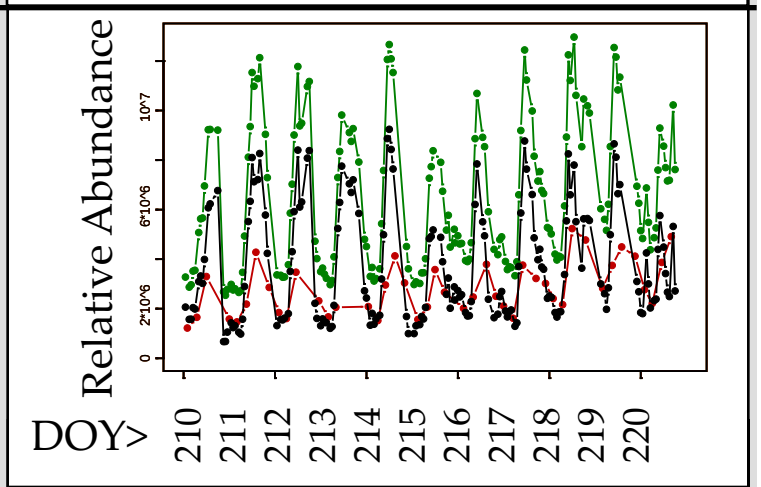


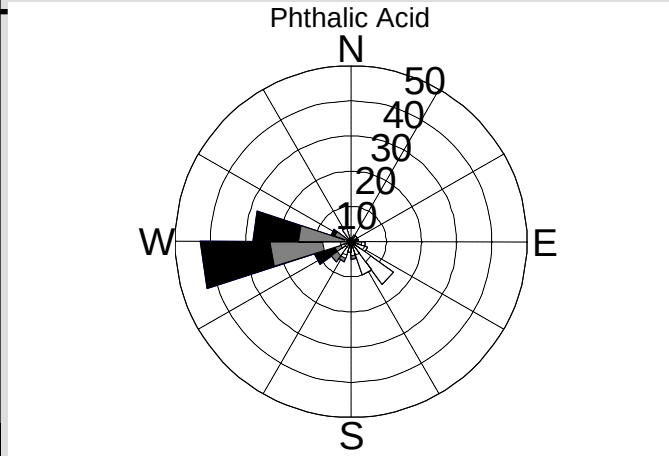
Secondary Biogenic

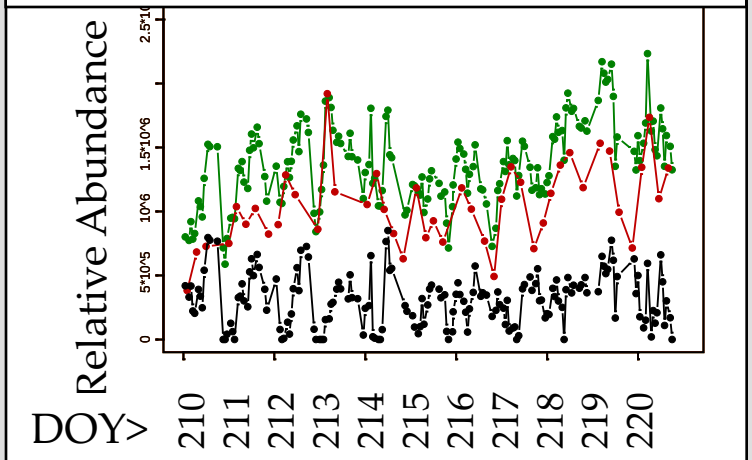


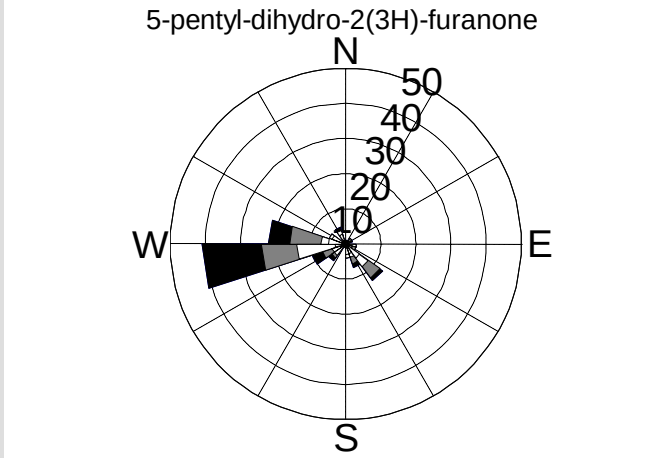


Secondary Anthropogenic

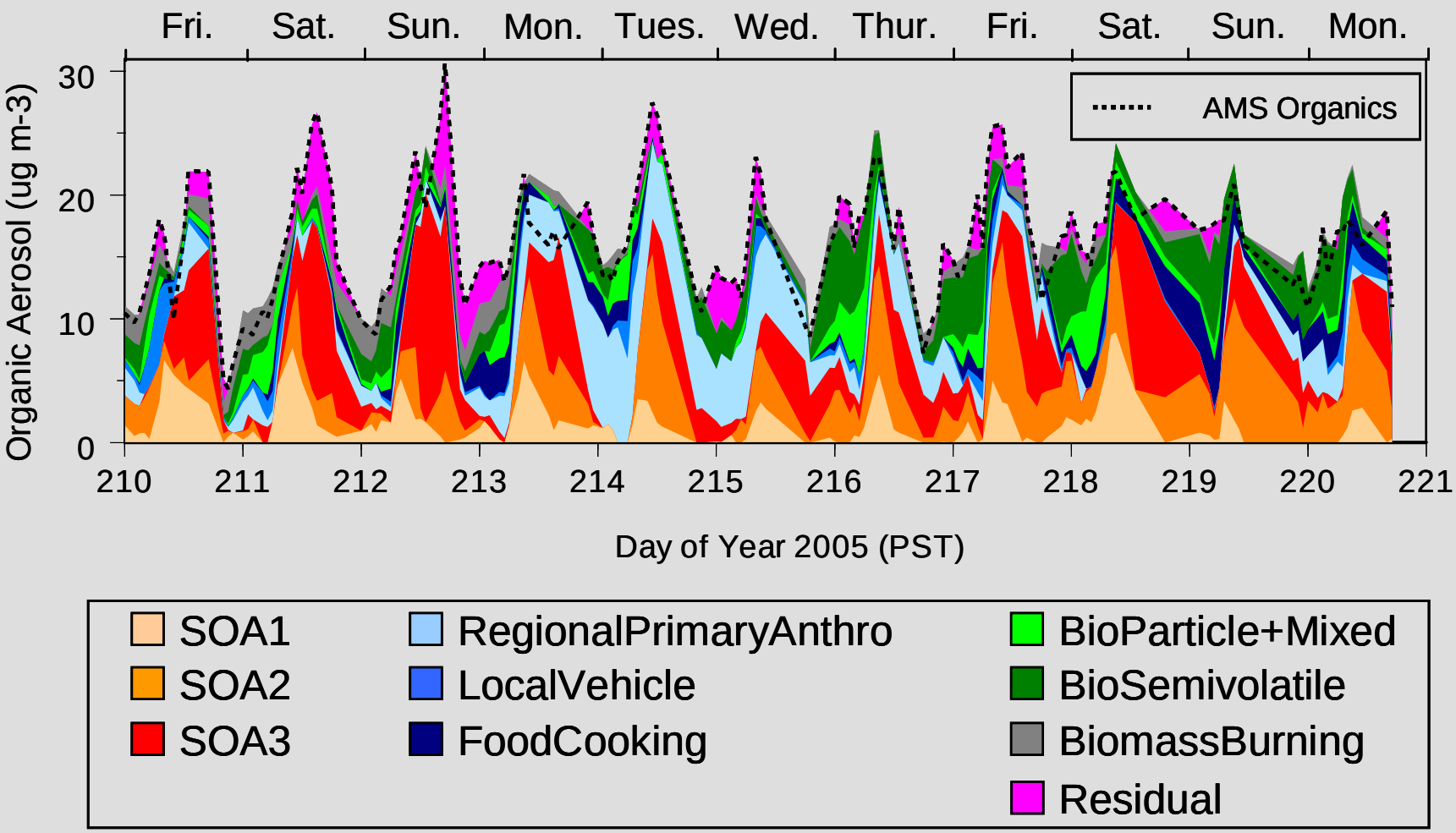




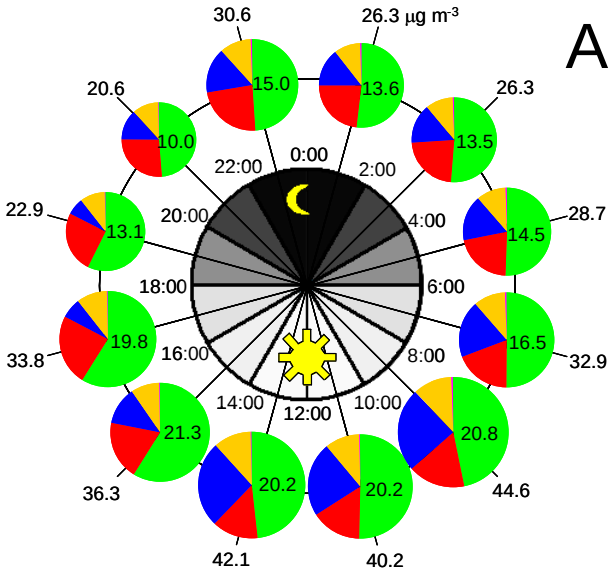




SOAR Summer: PMF Results



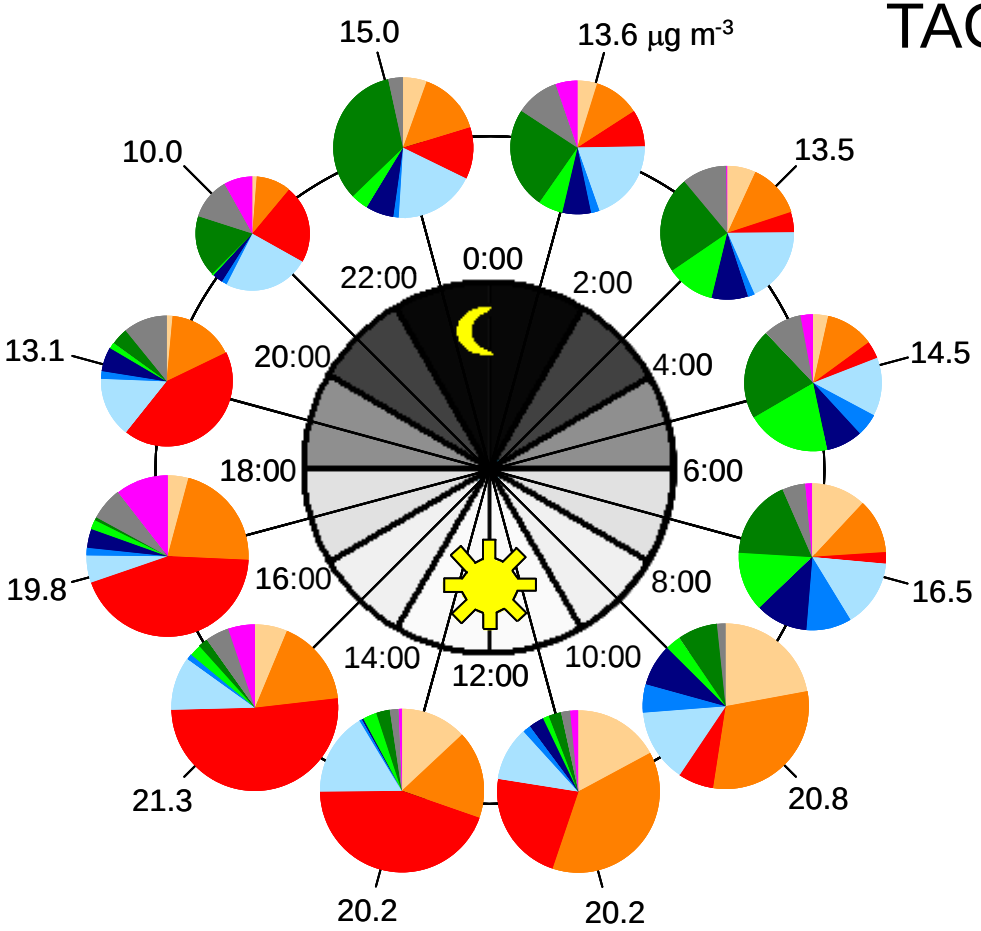
AMS



Organics (µg m^{-3}) | NO_3^- | Chloride | SO_4^{2-} | NH_4^+

AMS Total Organic Aerosol = 10.0 - 20.8 µg m^{-3}

TAG



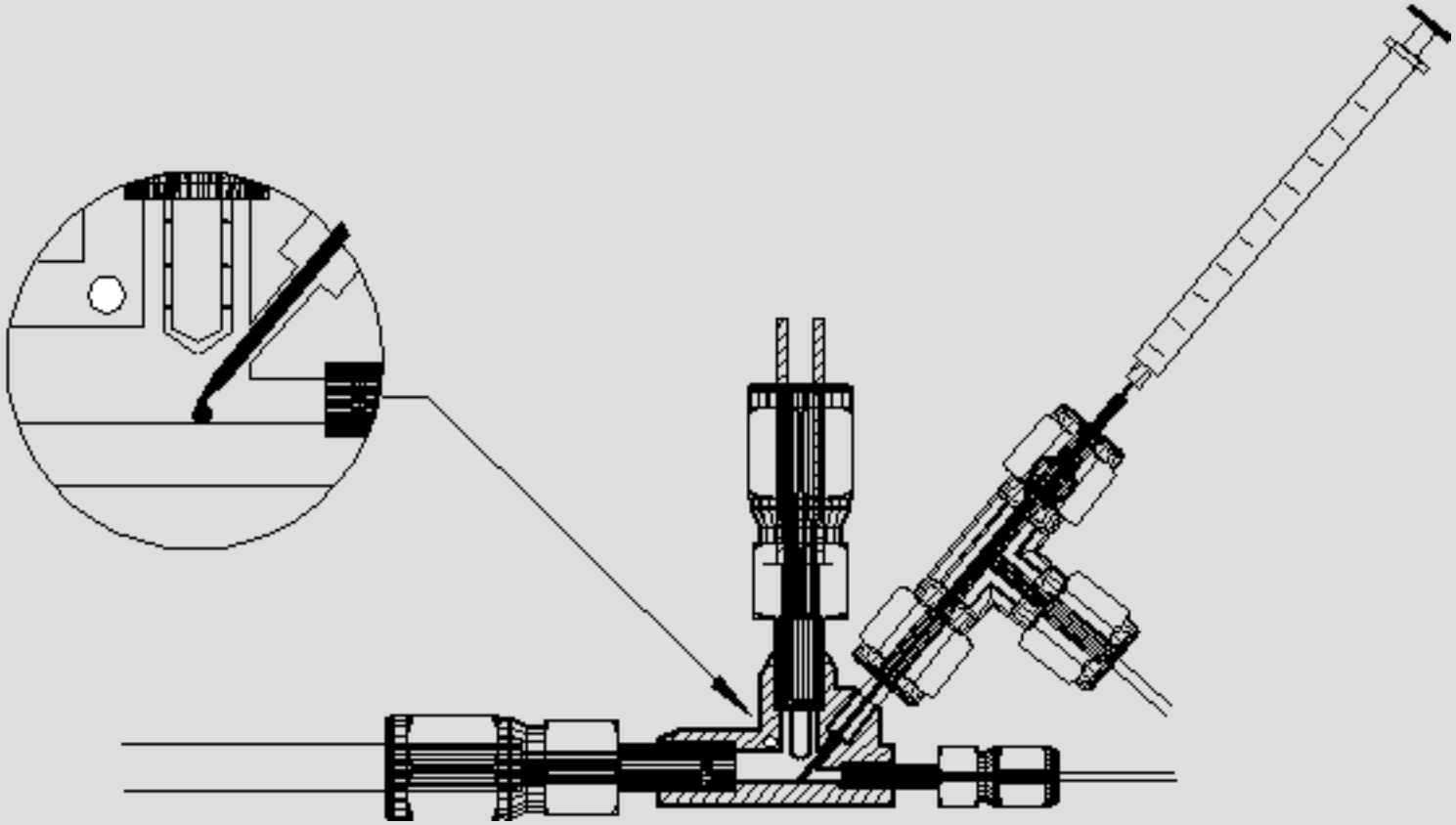
SOA1 | SOA2 | SOA3 | RegionalPrimaryAnthro | LocalVehicle | FoodCooking | BioParticle+Mixed | BioSemivolatile | BiomassBurning | Residual

AMS Total Organic Aerosol = 10.0 - 20.8 µg m^{-3}

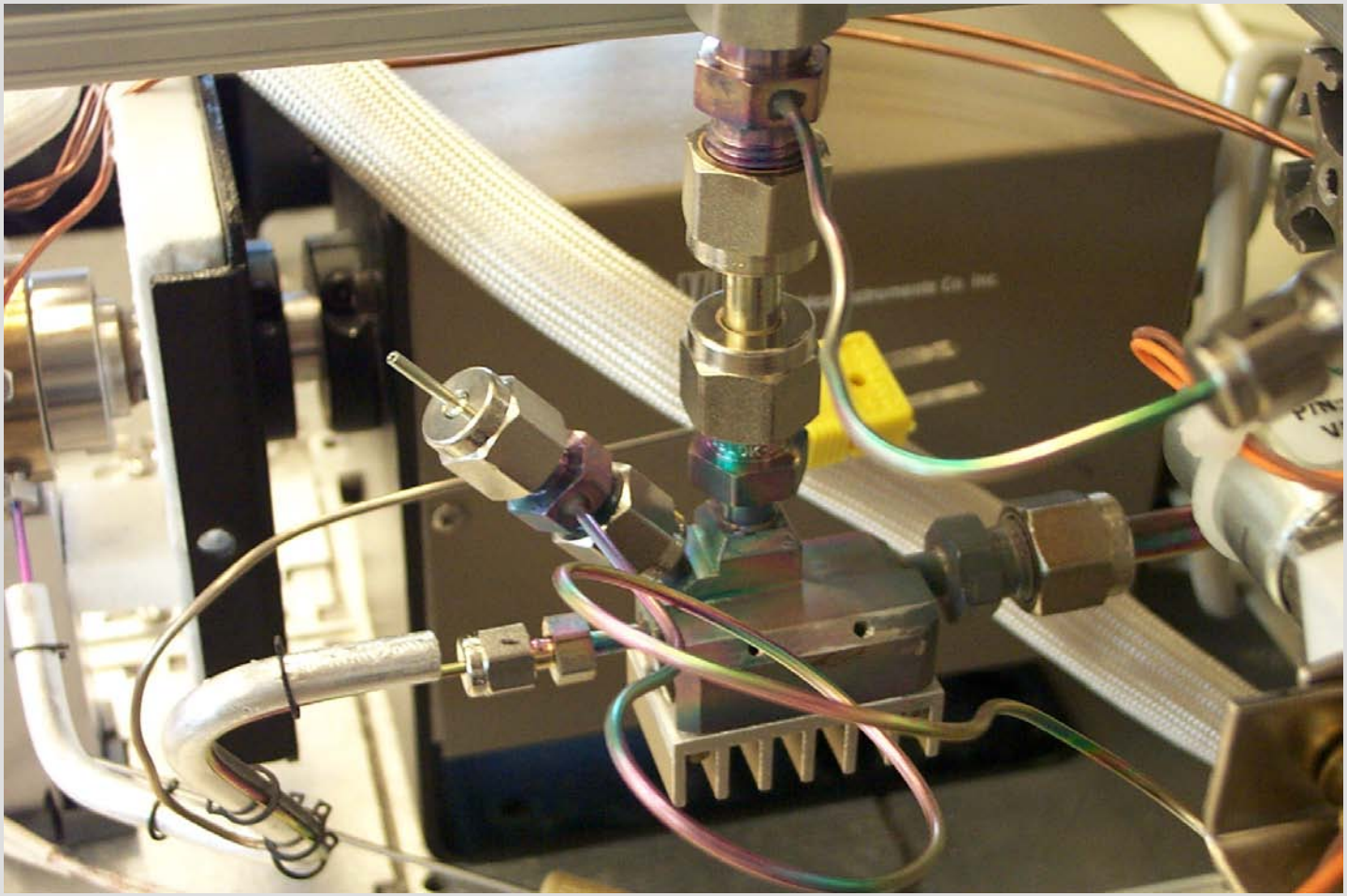
Average by Time of Day SOAR Summer

Calibrations: Liquid Standards

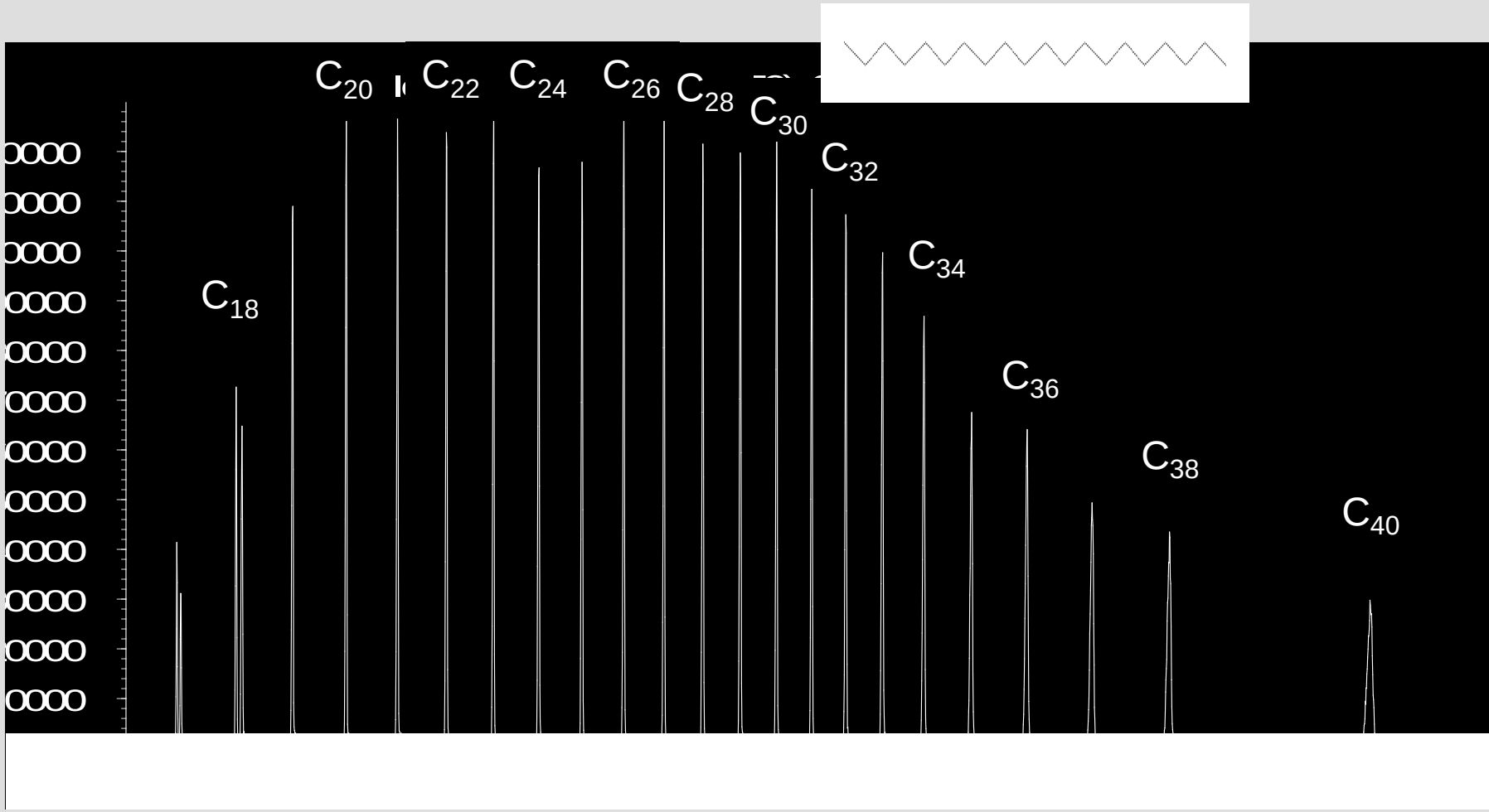
- injected directly into aerosol collection cell
- analyzed with same protocol as ambient sample



Collection Cell with Standards Injection Port



Response for n-Alkanes Standard (10ng/compound)



Balance between Standards and Time for Ambient Measurement

- **Tracking standard**

  Daily @ one level (mulitpoint cal 1-2x/study)

  – alkanes, PAHs, sterane, acids

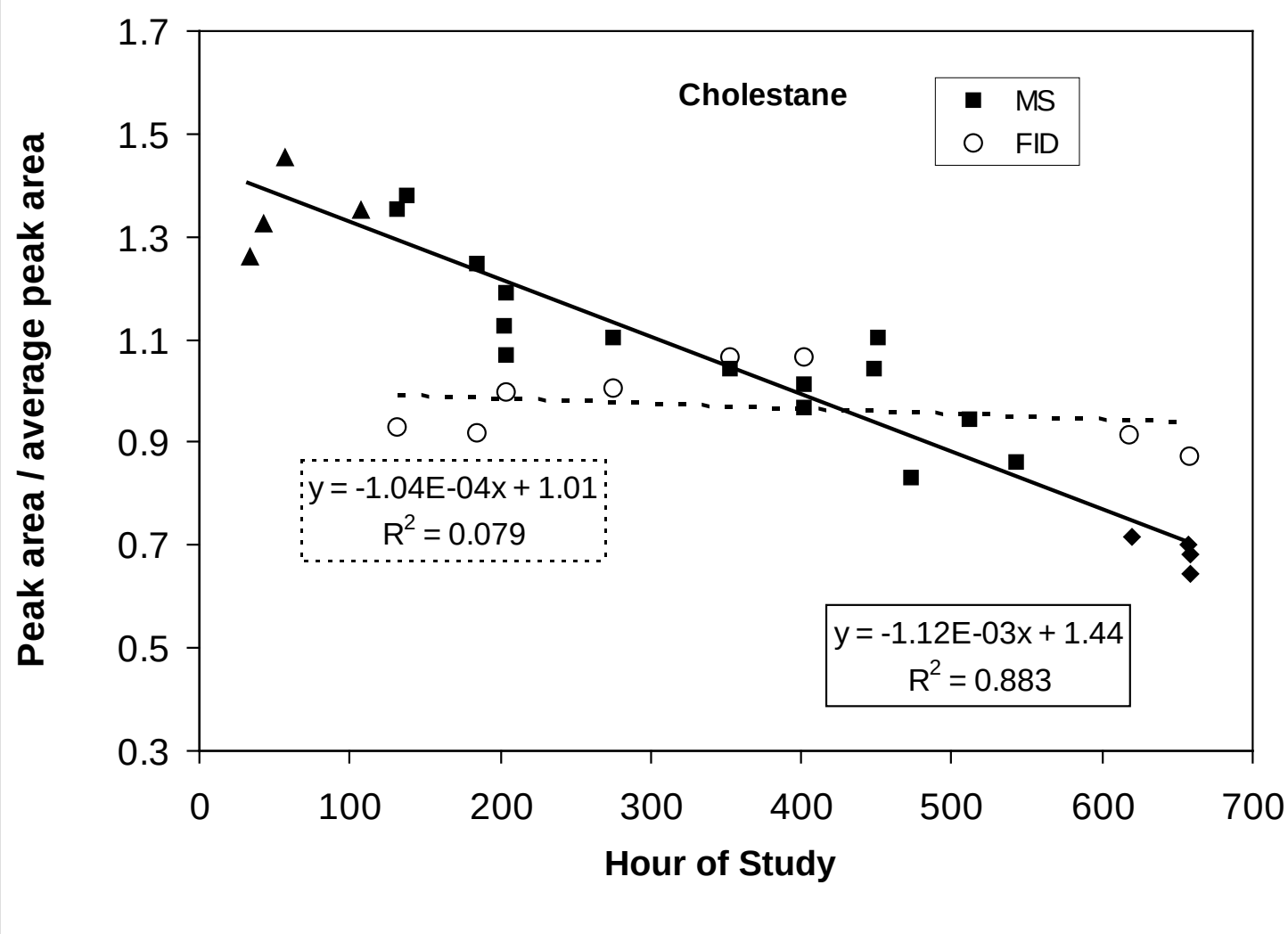
  – mix of compound classes

- **Authentic standards** (multipoint cals, 1-2x)

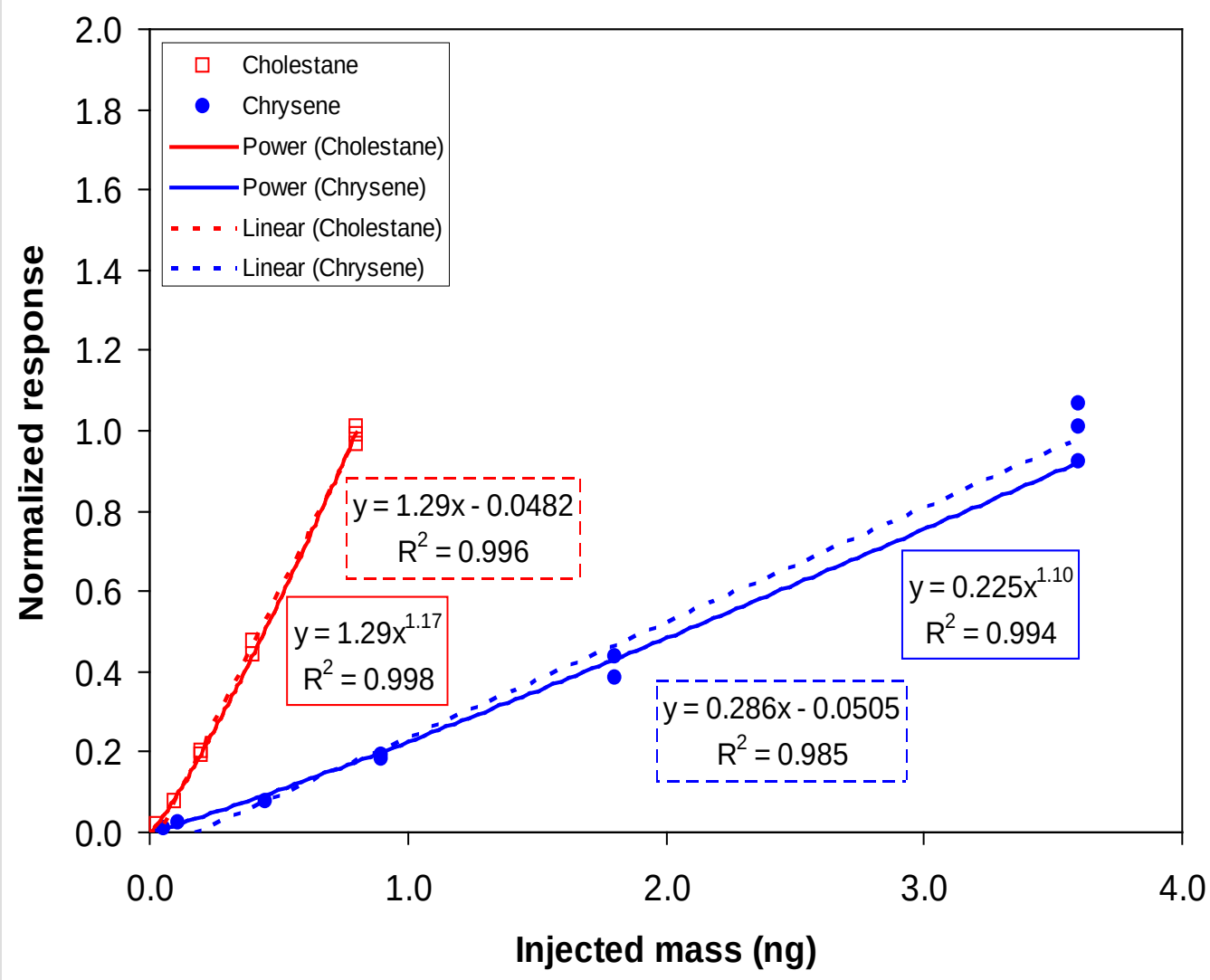
  – Series of PAHs, series of alkanes, monoacids…

  – Overlap of ~one compound with tracking standard

Tracking Standard Response over 25 days

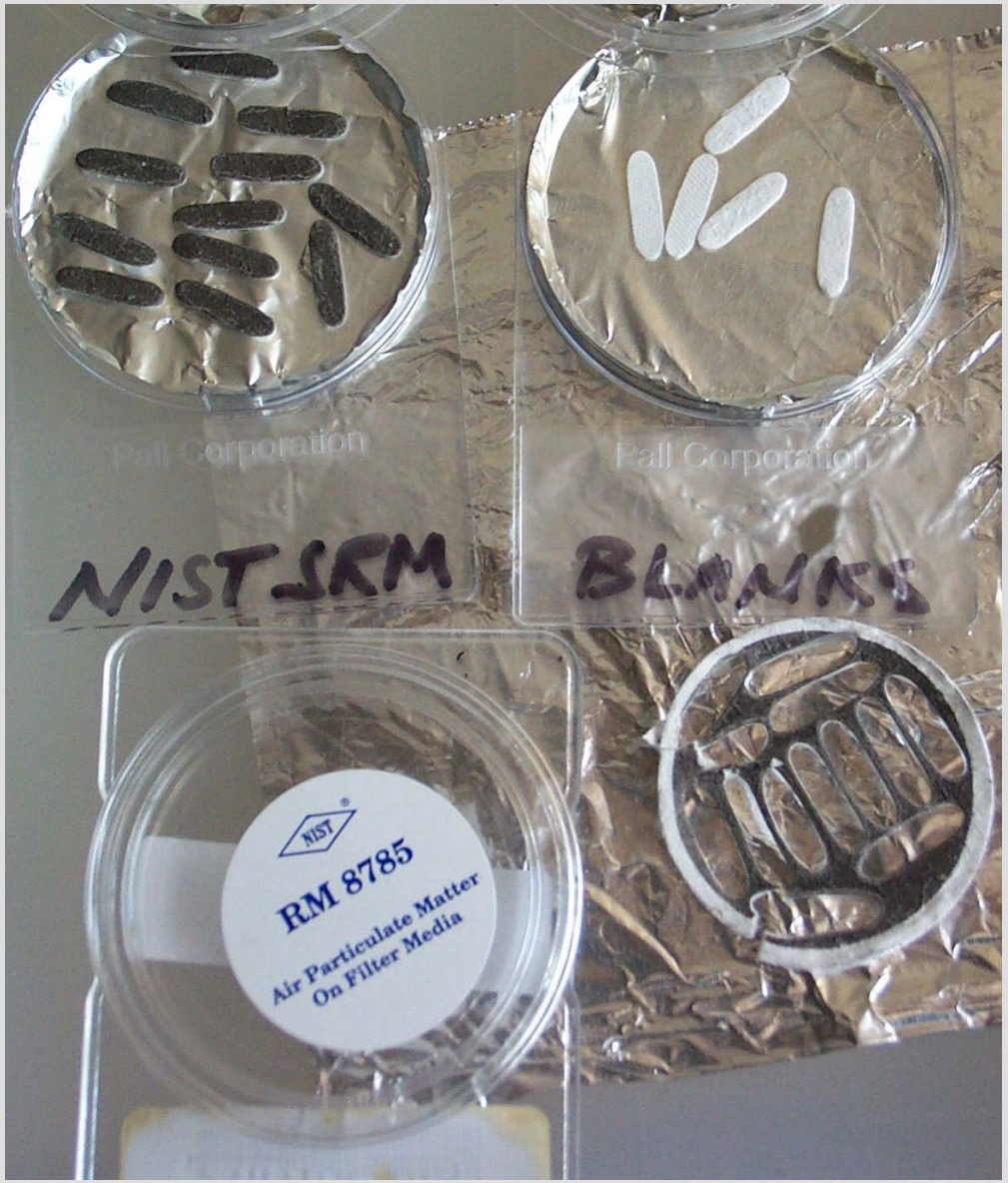


Calibration Curves for Cholestane and Chrysene

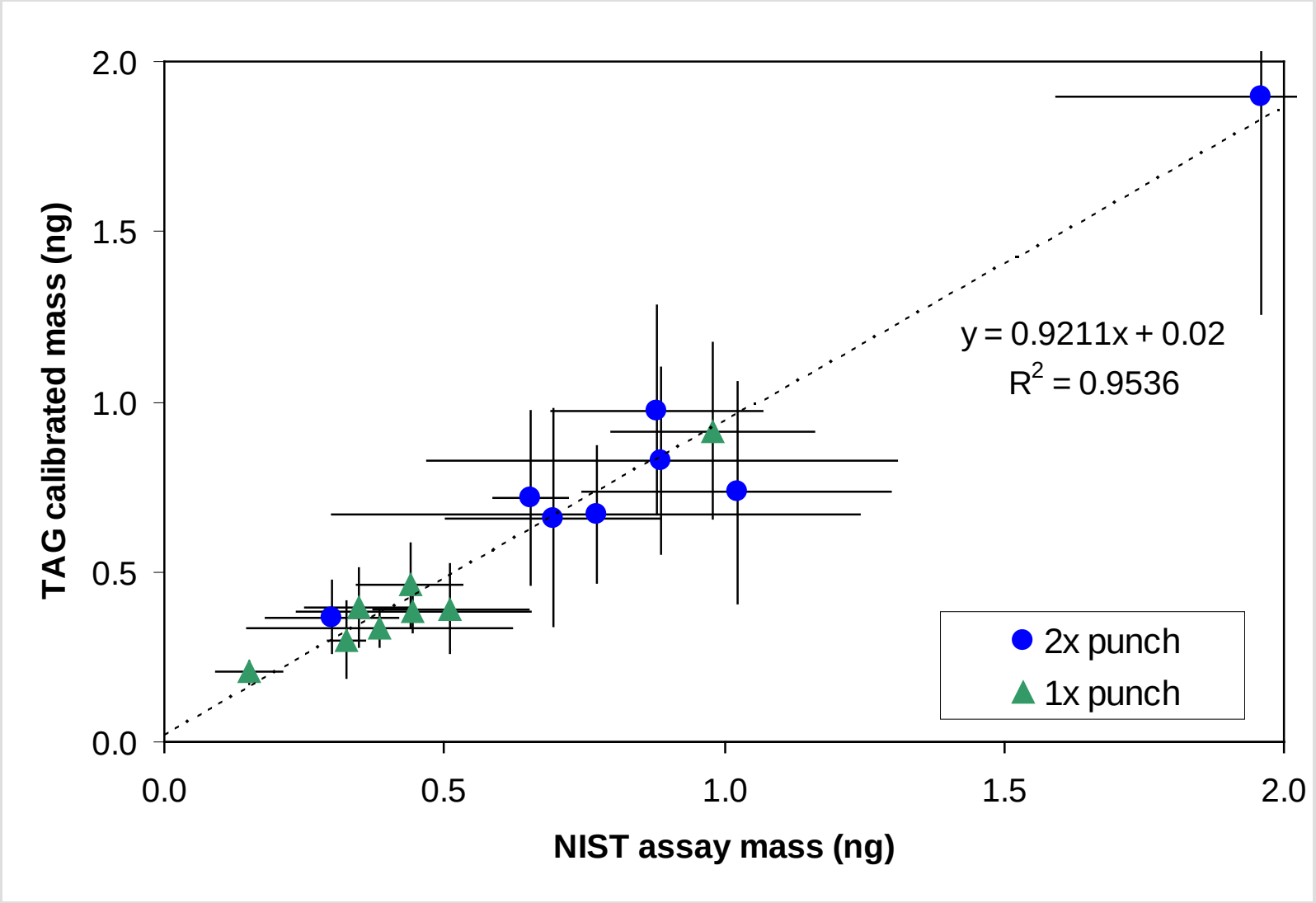


Tests with NIST Reference Filters

1 or 2 punches inserted directly in cell and analzyed



TAG response Compared to NIST Multilab Assay

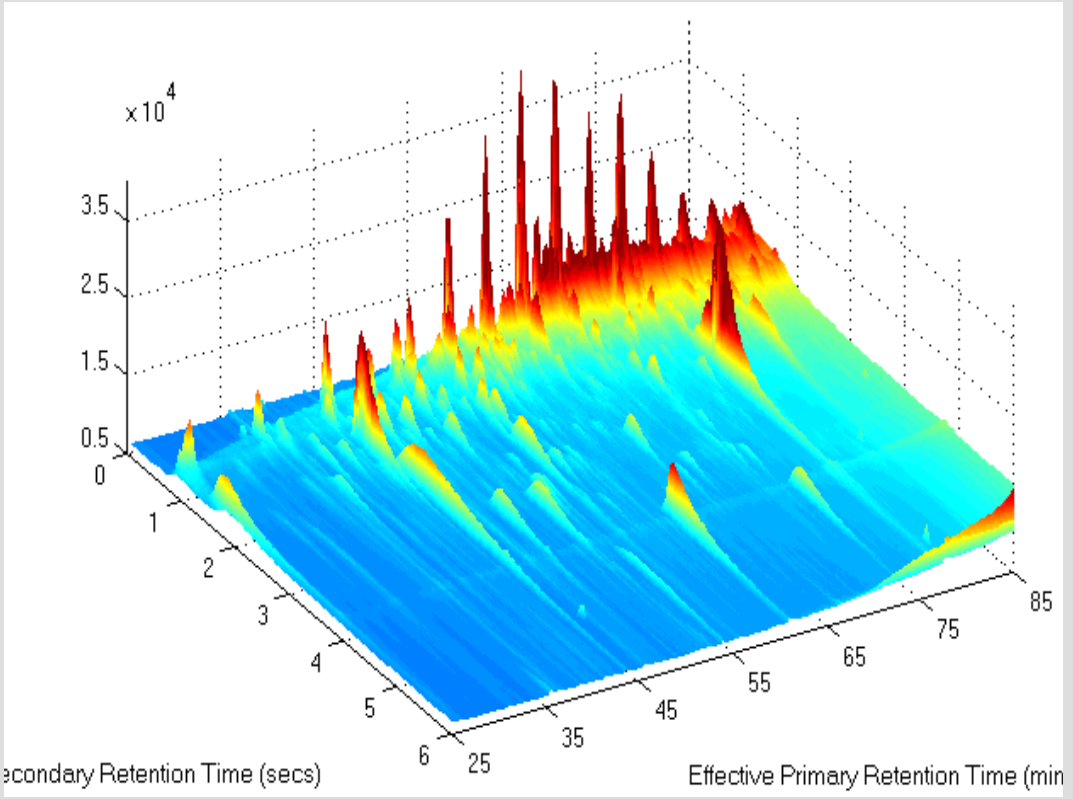


Summary: Where we have come

- Automated, In-situ instrument for identifying individual organic compounds
- Applied PMF analysis to identify sources and different types of SOA
- Calibration with liquid standards, equivalent to NIST assay for filter punches

Summary: Where we are Going

- Extending compound separation with two-dimensional chromatography
- Further improvements in Quantification



ACKNOWLEDGEMENTS

Instrument Development

DOE SBIR Phase I & II:DE-FG0203ER83825

DOE STTR Phase I & II : DE-FG0205ER86235

Field Campaigns

NOAA

California Air Resources Board