Hourly In-Situ Quantification of Organic Aerosol Marker Compounds

Allen Goldstein
University of California at Berkeley

ARB Chair's Seminar Series
July 1, 2008

Brent Williams, Angie Miller, UC Berkeley
Nathan Kreisberg, Susanne Hering, Aerosol Dynamics Inc.

Photo by Mike Cubison (U.Colorado-Boulder)

ACKNOWLEDGEMENTS

Funding

California Air Resources Board (ARB award 03-324)

ARB Staff Support

Nehzat Motallebi, William Vance, Eileen McCauley, Chris Jakober

SOAR Host

Paul Ziemann (UC Riverside)

SOAR Coordinator

Ken Docherty (University of Colorado Boulder)

Operation of Goldstein mobile lab

Angela Miller, Megan McKay (UC Berkeley)

SOAR Participants

Ziemann et al., Prather et al., Jimenez et al., Worsnop et al., Schauer et al., Hannigan et al., Eatough et al., Weber et al., Arey et al., Fitz et al., Paulson et al., etc.

Overview

Quantification of organic marker compounds

- **Motivation- importance of organic aerosols**
- **Organic aerosol measurement approaches**
- **New in situ instrument**
  - *Thermal desorption Aerosol GC/MS* – **TAG**
- **Study of Organic Aerosol in Riverside (SOAR)**
- **TAG in action: hourly measurements of marker compounds and resolution of source contributions**

Further TAG developments (if time allows)

- **Semi-volatile phase partitioning (SV-TAG)**
- **Introduction of multidimensional GC (2D-TAG)**

Motivation

Regulatory efforts to attain fine particulate matter (PM2.5) standards require improvements in our knowledge of the factors controlling PM concentration, size, and chemical composition. Organics are typically the largest and least understood fraction of PM.

Objective

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), and what are its composition and transformation pathways?

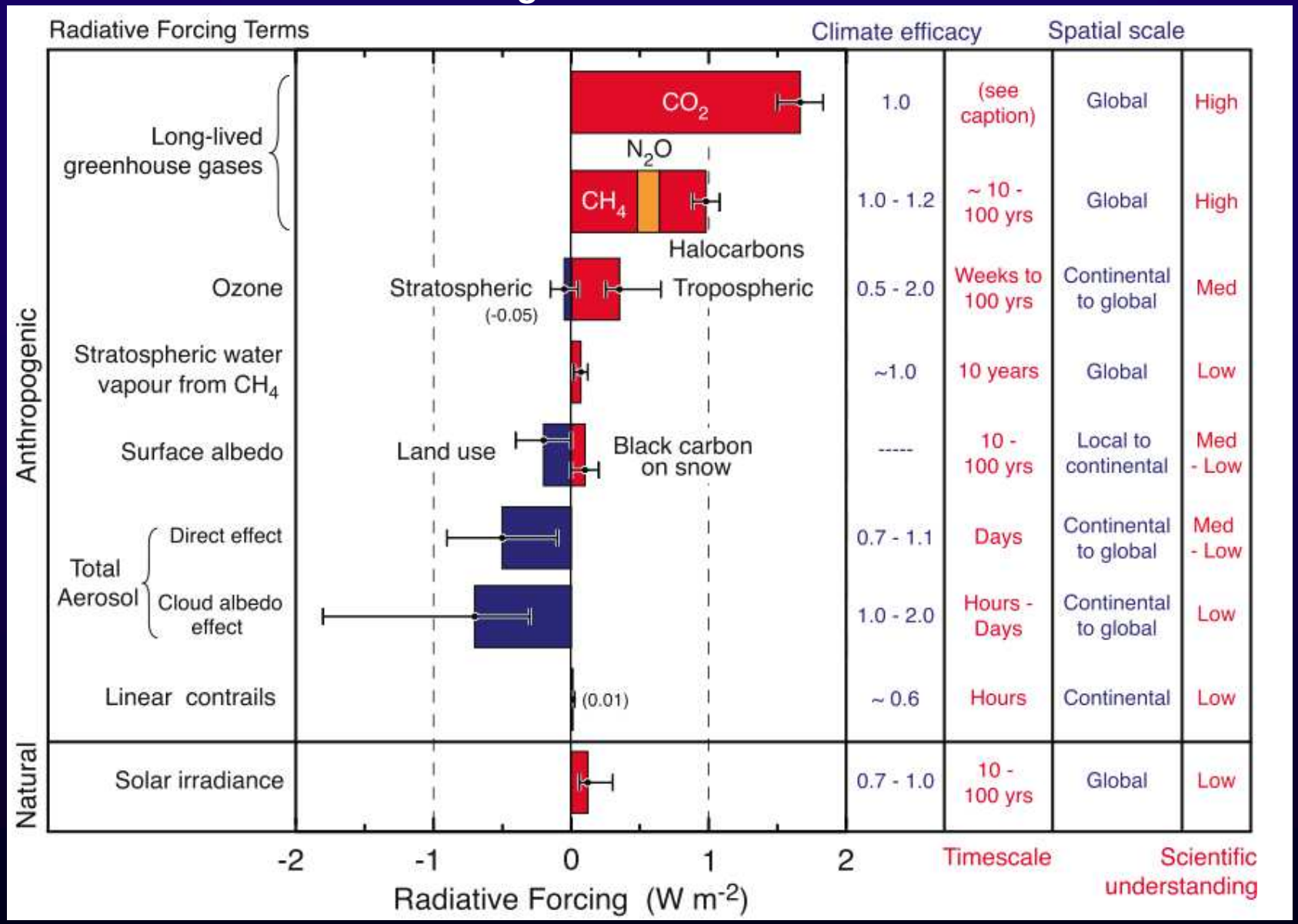
Aerosols impact climate and health

J. Allen/NASA

L. T. Molina, MIT

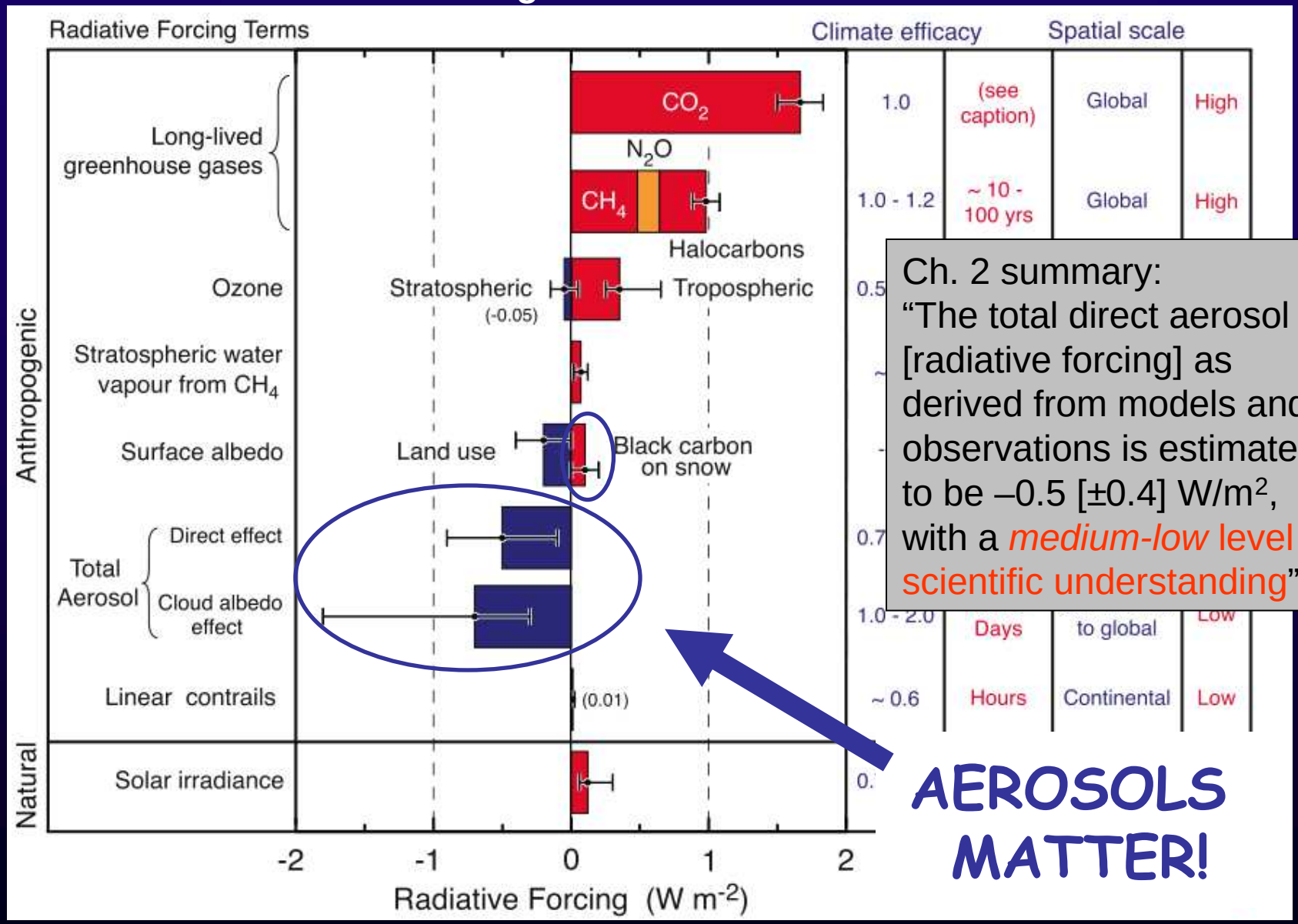
N. Marley, Univ. of Arkansas

Radiative forcing of climate between 1750 and 2005



Intergovernmental Panel on Climate Change (2007)
Working Group I: The Physical Science Basis of Climate Change

Radiative forcing of climate between 1750 and 2005



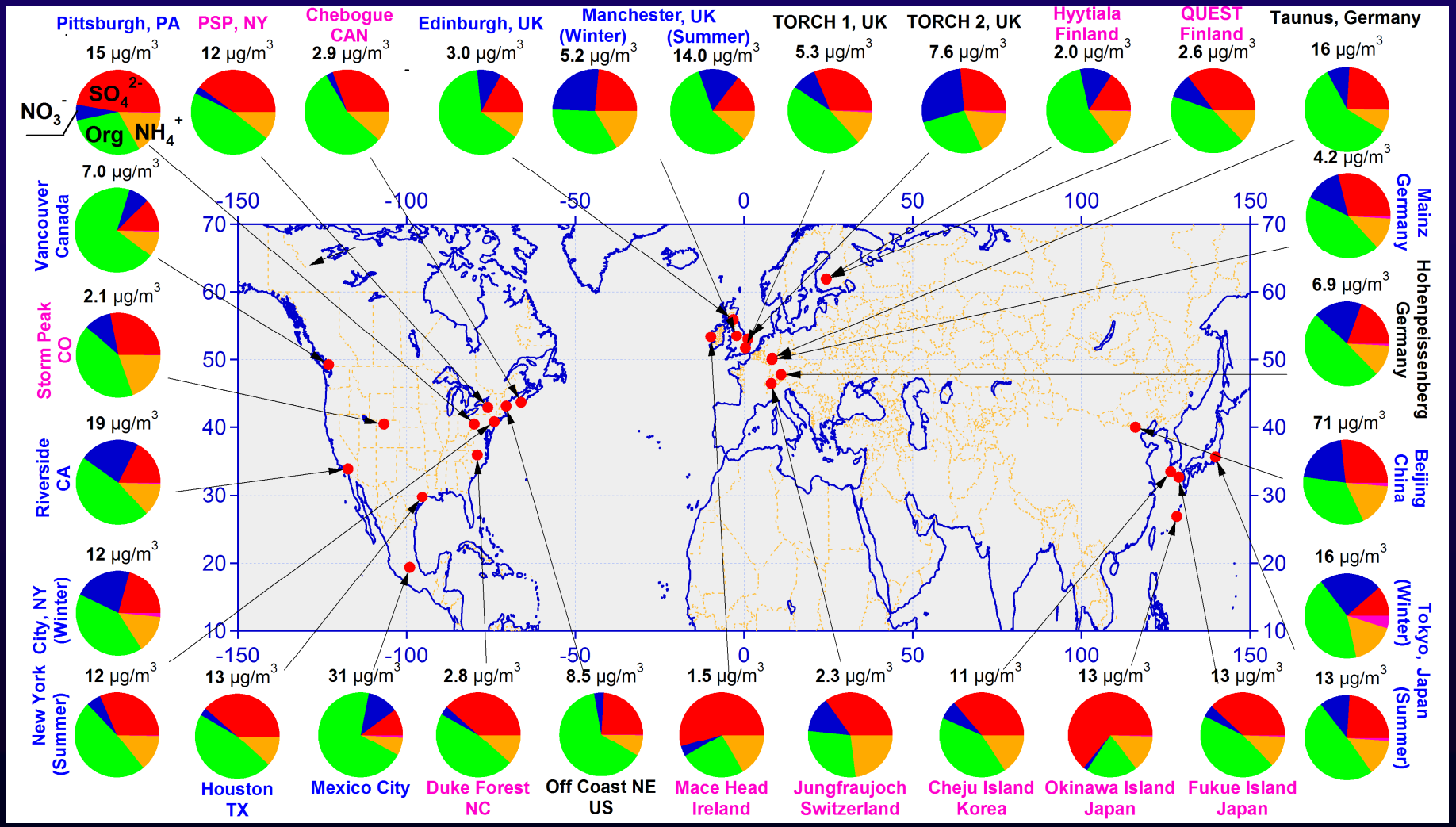
Ch. 2 summary:
"The total direct aerosol [radiative forcing] as derived from models and observations is estimated to be –0.5 [±0.4] W/m^2, with a *medium-low* level of scientific understanding"

AEROSOLS MATTER!

Intergovernmental Panel on Climate Change (2007)
Working Group I: The Physical Science Basis of Climate Change

Organic aerosol is typically largest fraction

(Tropospheric non-refractory PM_1 via Aerosol Mass Spectrometer)



"Ubiquity and Dominance of Oxygenated Species in Organic Aerosols in Anthropogenically-Influenced Northern Hemisphere Midlatitudes", Zhang et al. Geophysical Research Letter, 34 (2007)

Org	SO_4^{2-}	NO_3^-	NH_4^+

Organic aerosol Characterization methods

Sampling method continuum

bulk ⇨ size classified ⇨ single particle

Organic aerosol Characterization methods

Sampling method continuum

bulk ⇨ size classified ⇨ single particle

filter

impactor

In-situ mass spectrometry

Organic aerosol Characterization methods

Sampling method continuum

bulk ⇨ size classified ⇨ single particle

filter

impactor

In-situ mass spectrometry

Characterization methods

- group properties – OC/EC, FTIR (bonds), water soluble OC
- molecular level – GC/MS, LC/MS, some single particle MS

Organic aerosol Characterization methods

Sampling method continuum

bulk ⇨ size classified ⇨ single particle

filter

impactor

In-situ mass spectrometry

Solvent extraction/
thermal desorption

Characterization methods

- group properties – OC/EC, FTIR (bonds), water soluble fraction
- molecular level – GC/MS, LC/MS, some single particle MS (e.g. UVI)

Organic aerosol Characterization methods

Sampling method continuum

bulk ⇨ **size classified** ⇨ **single particle**

filter

impactor

In-situ mass spectrometry

Manual collection
time – integrated sampling
often on selected days only

Detailed speciation possible

Automated
Time-resolved, continuous

No molecular level characterization

Genesis of TAG: in-situ field instrument

Past $PM_{2.5}$ organic measurements:

In-Situ particle (no individual compound separation)
Filter collection (12 to 24-hour time resolution)

Need an instrument capable of:

Separating / Identifying / Quantifying individual organic marker compounds from ambient $PM_{2.5}$ with hourly time resolution (to track diurnal changes)

Genesis of TAG: in-situ field instrument

Goldstein et al. methods for VOCs:

"In situ measurements of C_2-C_{10} volatile organic compounds above a Sierra Nevada ponderosa pine plantation"

M.S. Lamanna and A.H. Goldstein, *J.Geophys. Res.* 104 (1999)

"VOC measurements at Trinidad Head, CA …Analysis of sources, atmospheric composition and aerosol residence times"

D.B. Millet, A.H. Goldstein et al., *J.Geophys. Res.* 109 (2004)

Hering et al. methods for inorganic aerosols:

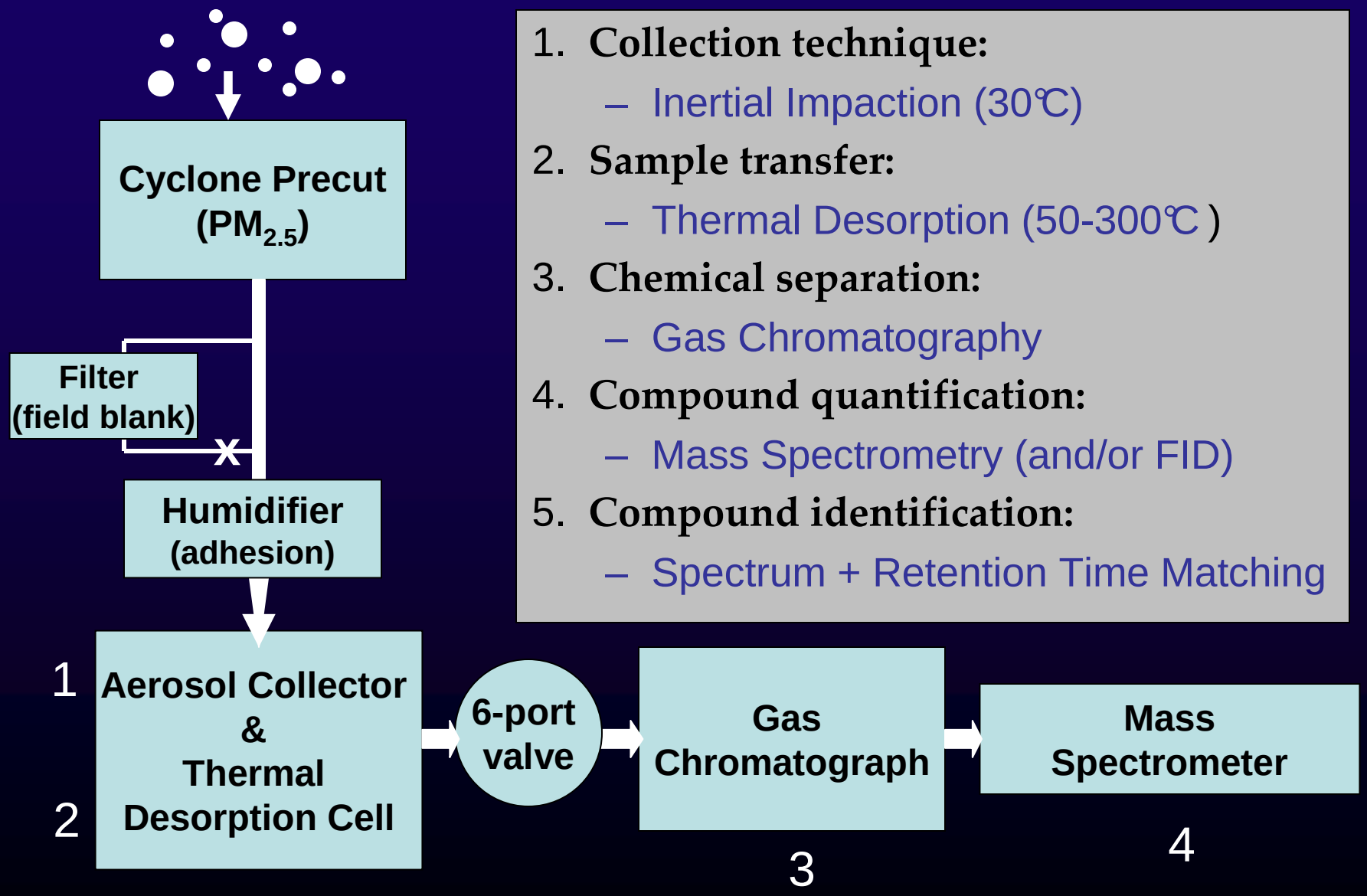
"A new method for the automated measurement of atmospheric fine particle nitrate"

M.R. Stolzenburg and S.V. Hering, *Environ. Sci. and Technol.* 34 (2000)

"Hourly concentrations and light scattering cross sections for fine particle sulfate at Big Bend National Park"

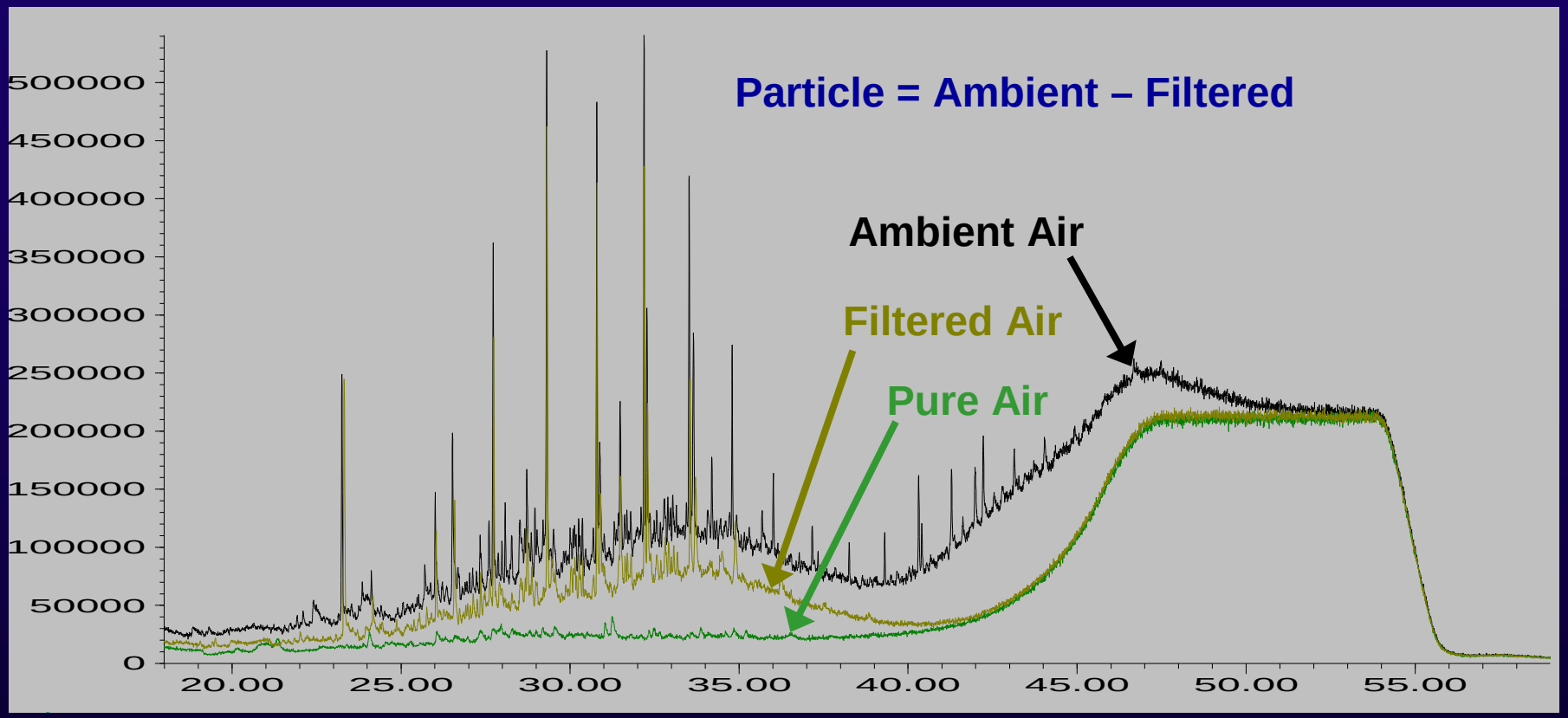
S.V. Hering et al. *Atmospheric Environment* 37 (2003)

TAG= Thermal desorption Aerosol Gas chromatograph (MS/FID)



1. **Collection technique:**
   - Inertial Impaction (30℃)
2. **Sample transfer:**
   - Thermal Desorption (50-300℃)
3. **Chemical separation:**
   - Gas Chromatography
4. **Compound quantification:**
   - Mass Spectrometry (and/or FID)
5. **Compound identification:**
   - Spectrum + Retention Time Matching

TAG urban ambient data



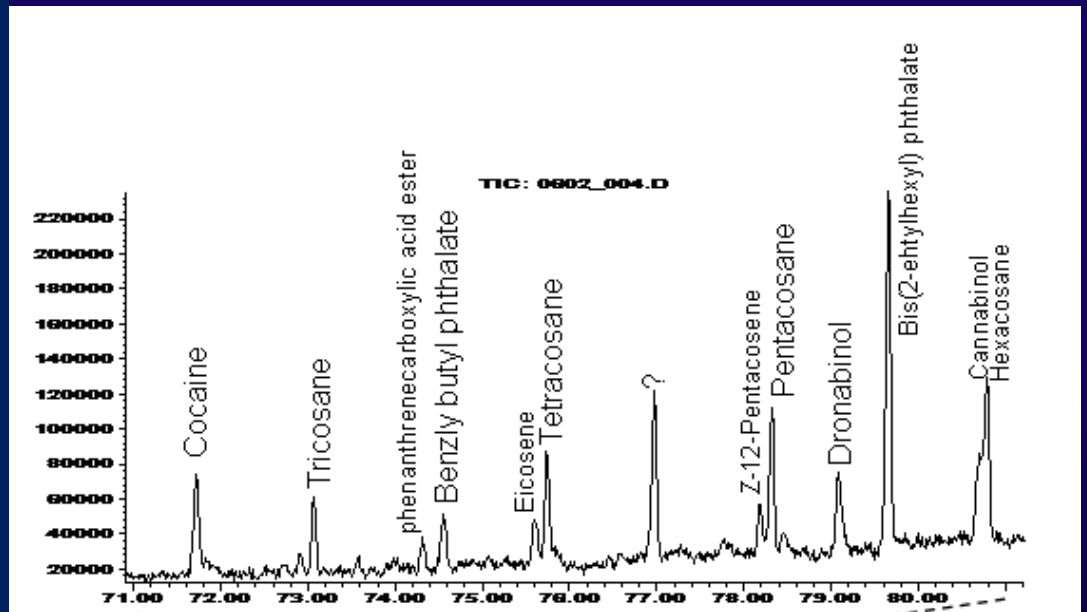
Time Resolution: 1 hour
Collection: 0.5 hour
Sample Volume: 0.25 m^3
Thermal Desorption: 50-300^{0}C
GC oven temp. range shown here: ~ 45^{0}C to 300^{0}C

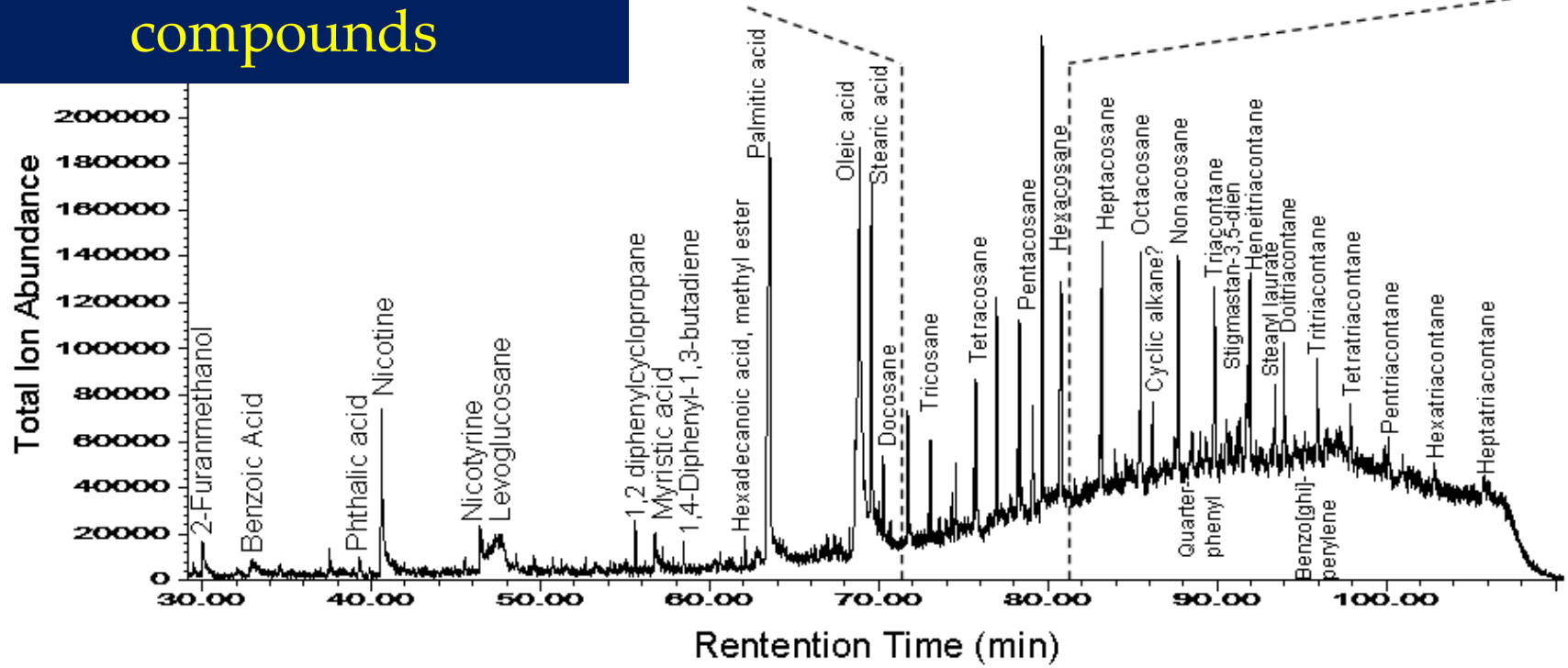
Resolved compounds will determine the aerosol source (i.e. markers)

TAG

Example Chromatogram
Berkeley Ambient Air
February 7, 2006
22:30-24:00

100's of identifiable compounds





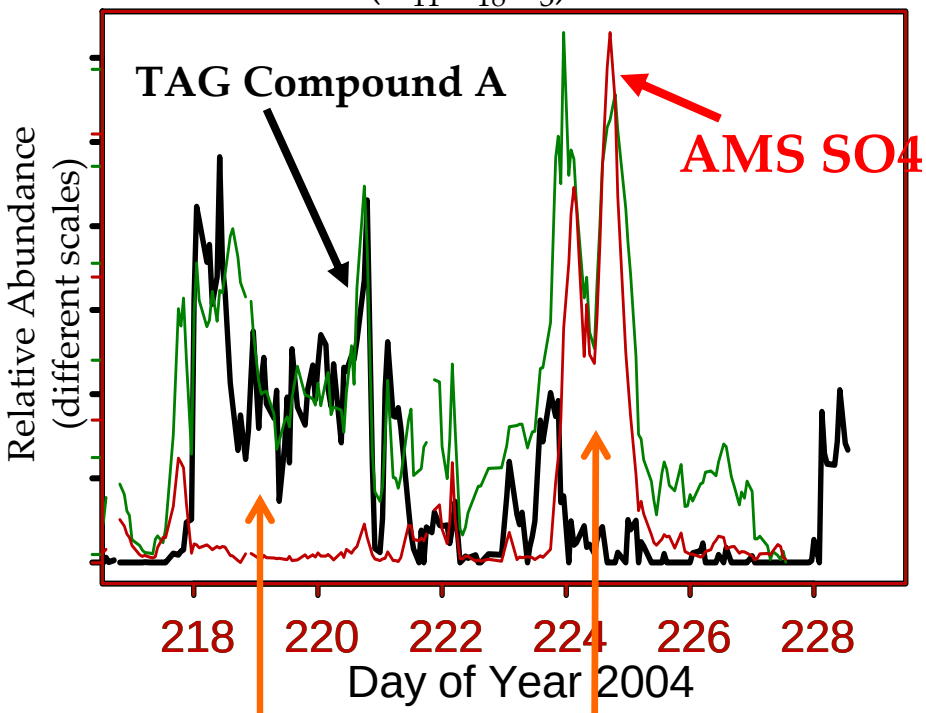
TAG Applications To Date

- Field Sampling
  - ICARTT 2004, Chebogue Point, Nova Scotia
    - Ambient sampling downwind of United States and Canada
  - SOAR 2005, Riverside, California
    - Ambient sampling downwind of Los Angeles
  - BEARPEX 2007, Blodgett Forest, California
    - Ambient sampling within a forest canopy
  - Pittsburgh Toxics Study 2008, Pittsburgh, Pennsylvania
    - Ambient sampling within urban center
  - Carnegie Mellon University
    - Reaction chamber studies

Individual TAG Compounds vs. Aerosol Mass Spectrometer (AMS) Total Organics and Total SO_4^{2-} Chebogue Point Nova Scotia 2004

Compound: A

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

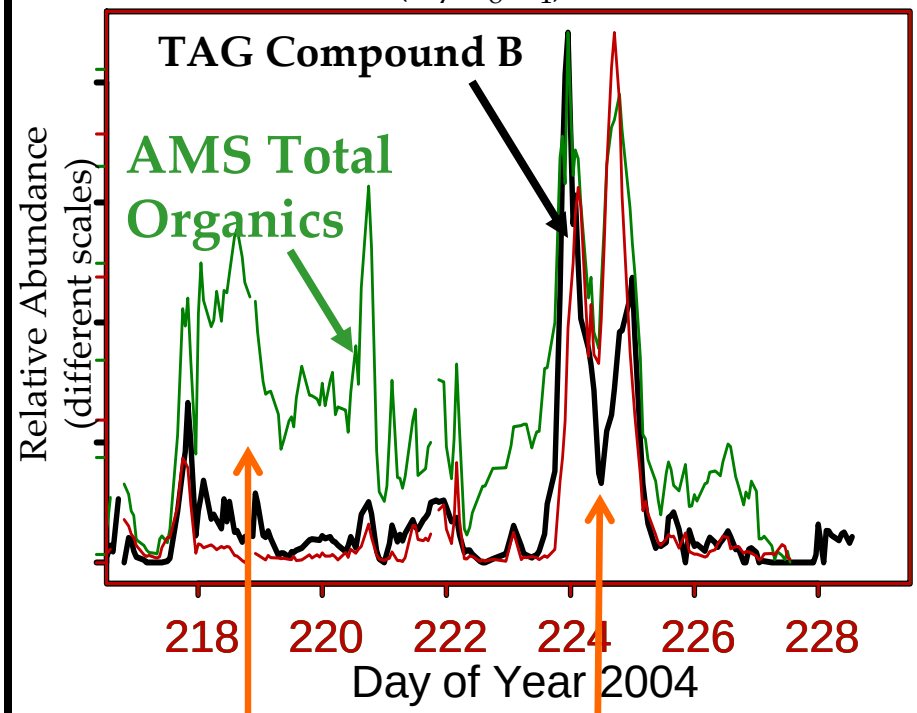


Event Type 1 No SO4

Event Type 2 SO4

Compound: B

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



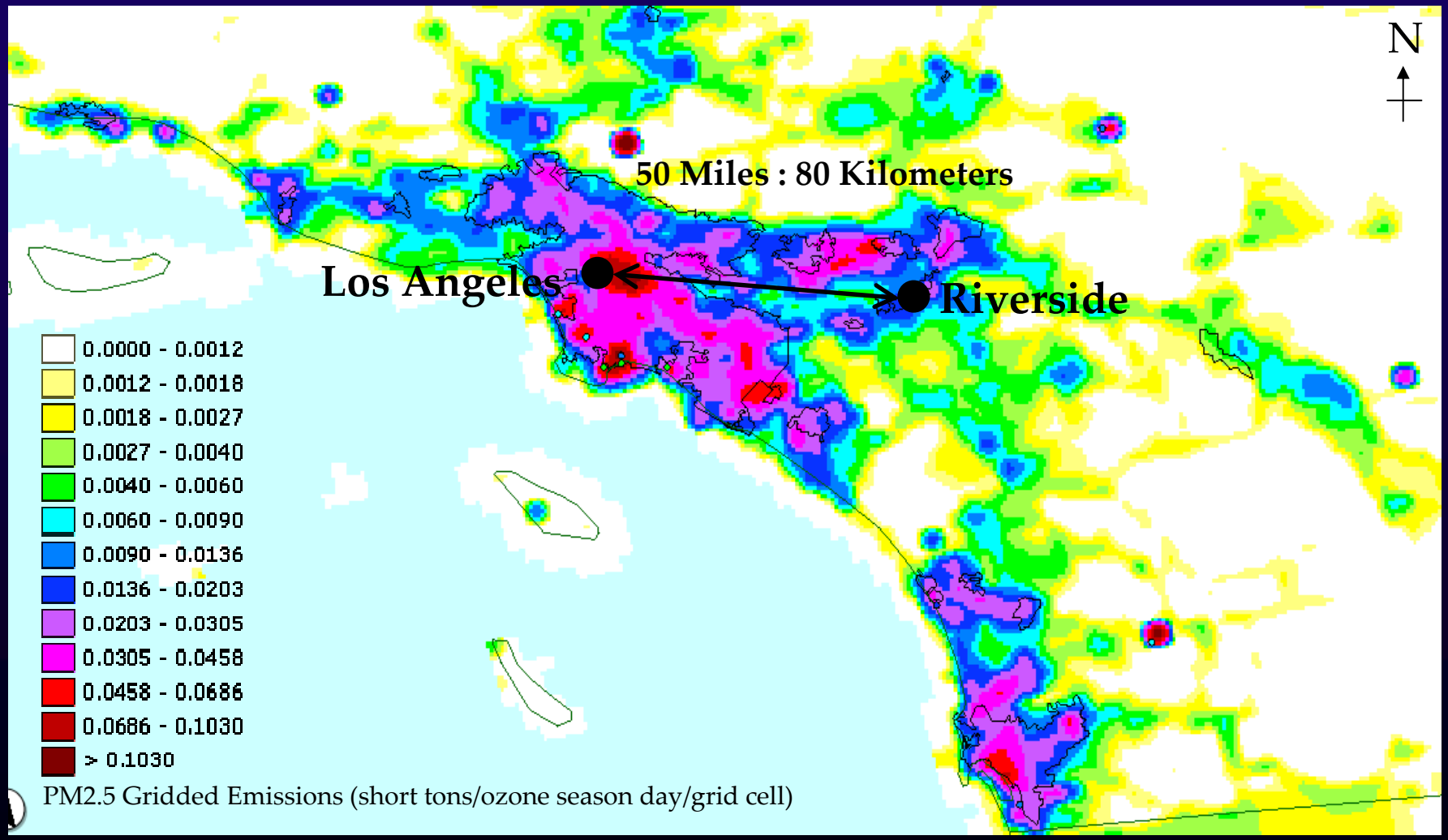
Event Type 1 No SO4

Event Type 2 SO4

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 2005

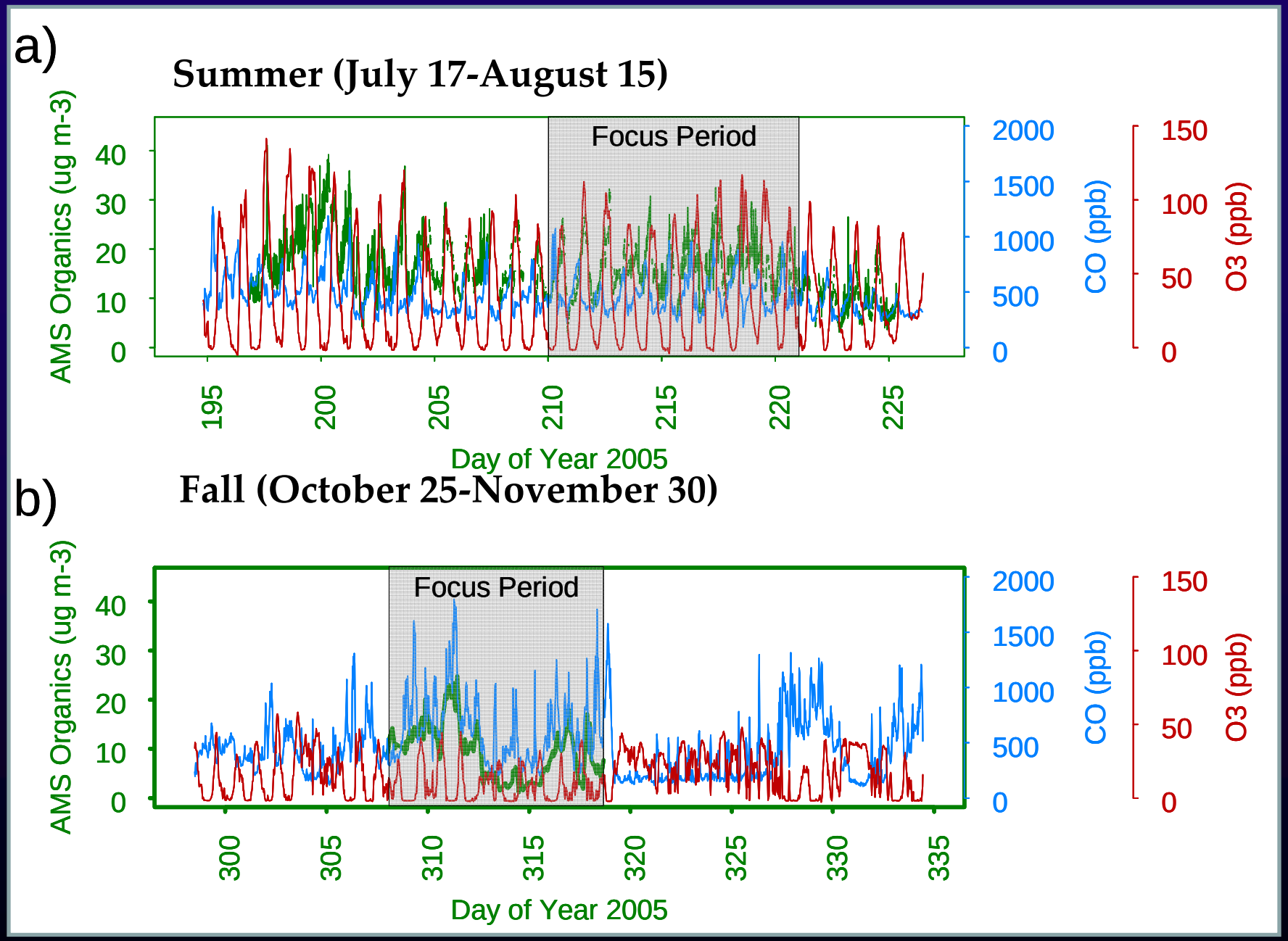
2 Measurement Periods

- Summer (July 18 – August 15, 2005)
- Fall (October 28 – November 30, 2005)

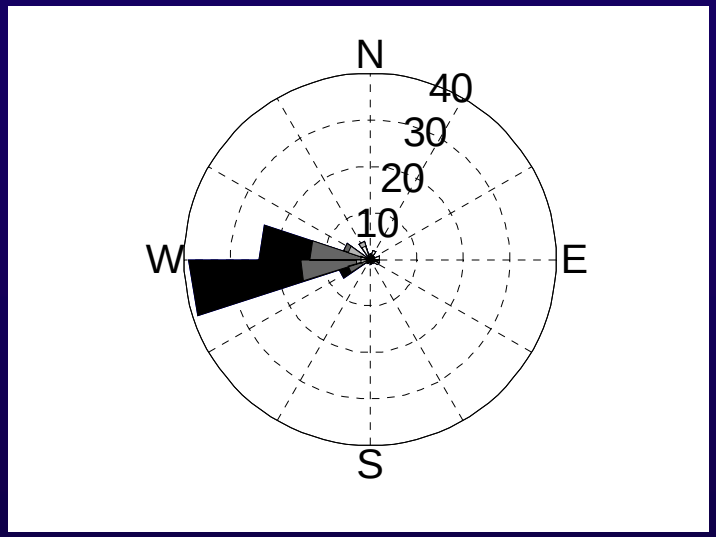
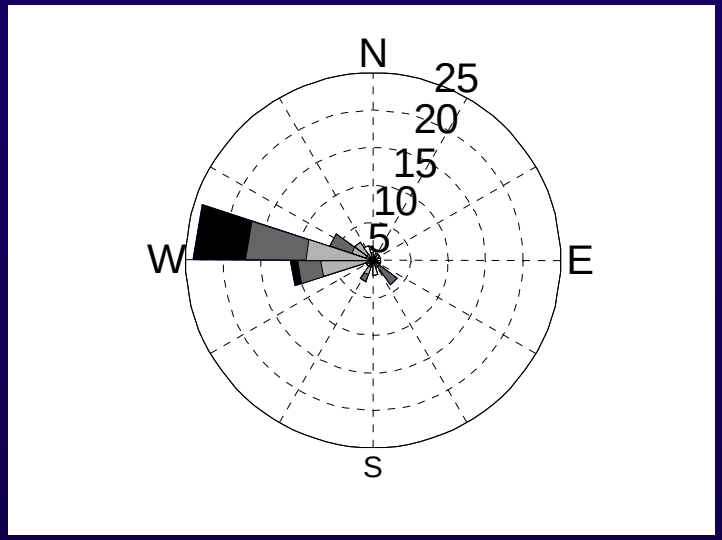
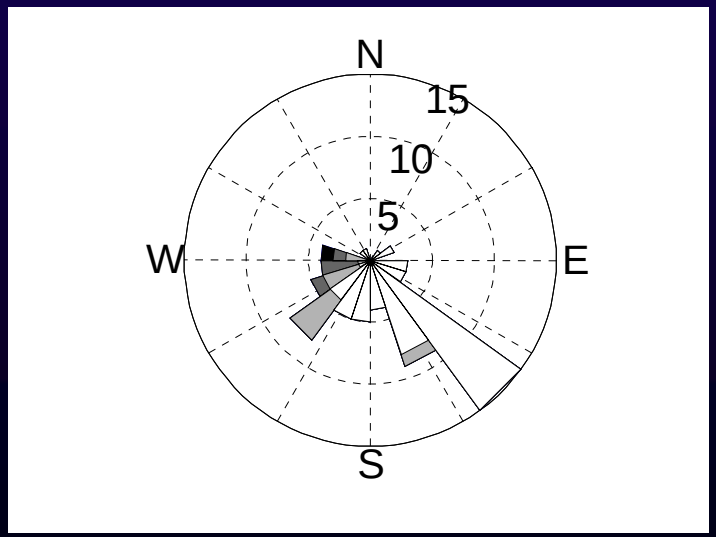
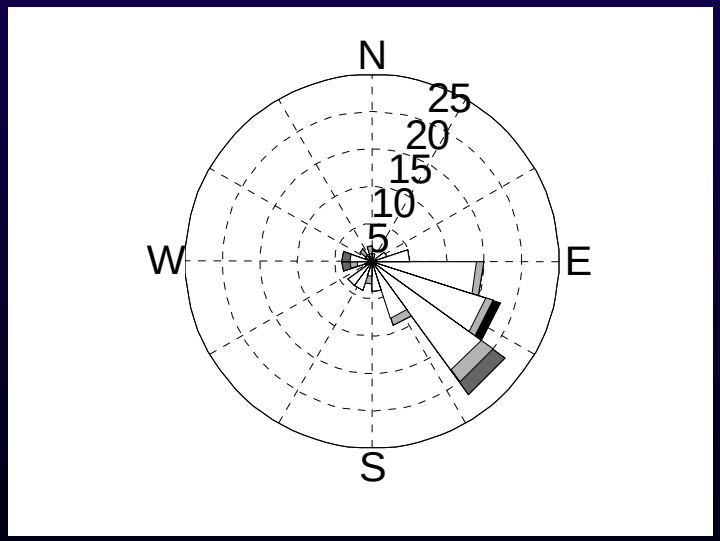
Instrumentation

- Meteorological, radiation, trace gas, and aerosol measurements
- TAG, VOC-GC/MS, O_3 (x2), CO (x2), NOx (x2), Aerodyne AMS (x5), Thermal desorption particle beam MS, ATOFMS (x3), CPC (x8), EC/OC (x2), PILS-WSOC, High Volume filter samplers (multiple), aethelometer (multiple), nephelometer (multiple), OPC, DMA, MAAP, SMPS (multiple), APS, TEOM (multiple),Hg speciation, DMT CCN, meteorological and radiation equipment
- See study website for more details: (http://cires.colorado.edu/jimenez-group/Field/Riverside05/)

SOAR Measurement Periods



Very different Photochemistry (and Meteorology)

	Summer Winds (11 days)	Fall Winds (11 days)
Day		
Night		

Wind Speed = 0.0 - 0.4 m/s 0.4 - 0.8 m/s 0.8 - 1.2 m/s >1.2 m/s

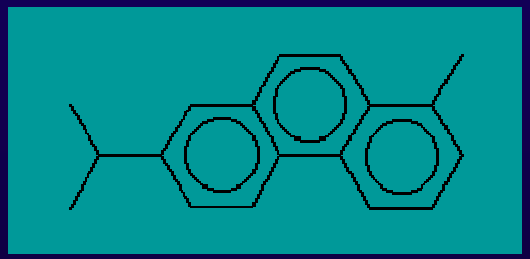
Frequency = Length of Wedge

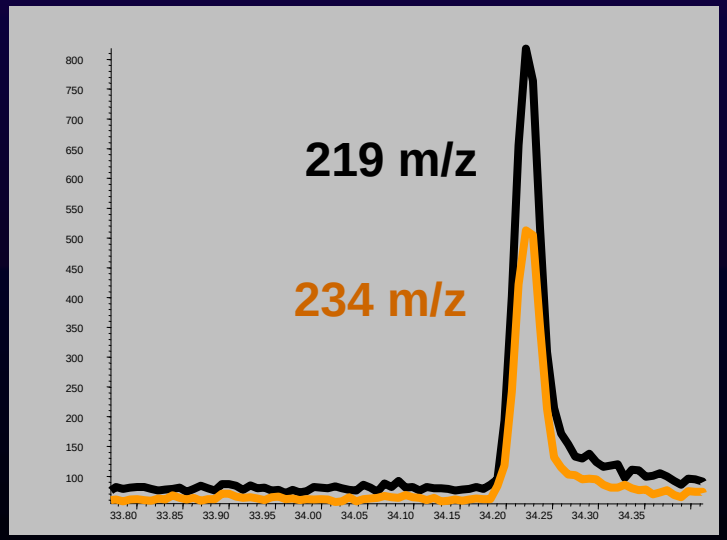
SOAR TAG Measurements and Source Apportionment

- Resolved >300 organic marker compounds hourly
- Positive Matrix Factorization (PMF)
  - 128 of 300 resolved TAG organic compounds in Summer
  - 144 of 300 resolved TAG organic compounds in Fall
- Identified organic aerosol sources based on PMF groupings
  - 8 in Summer
  - 7 in Fall

Marker compounds for source identification

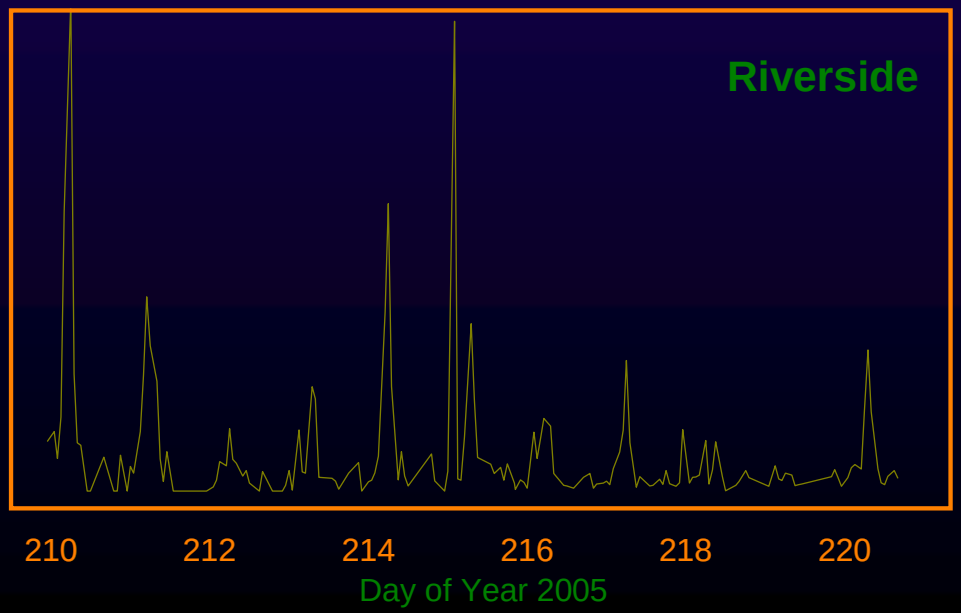
Wood combustion ~ retene

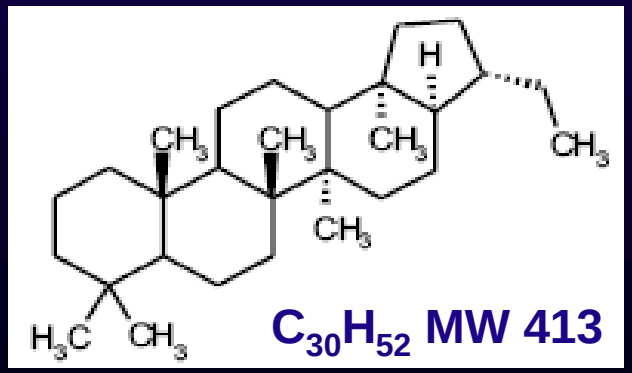




Examples of marker compounds for source identification

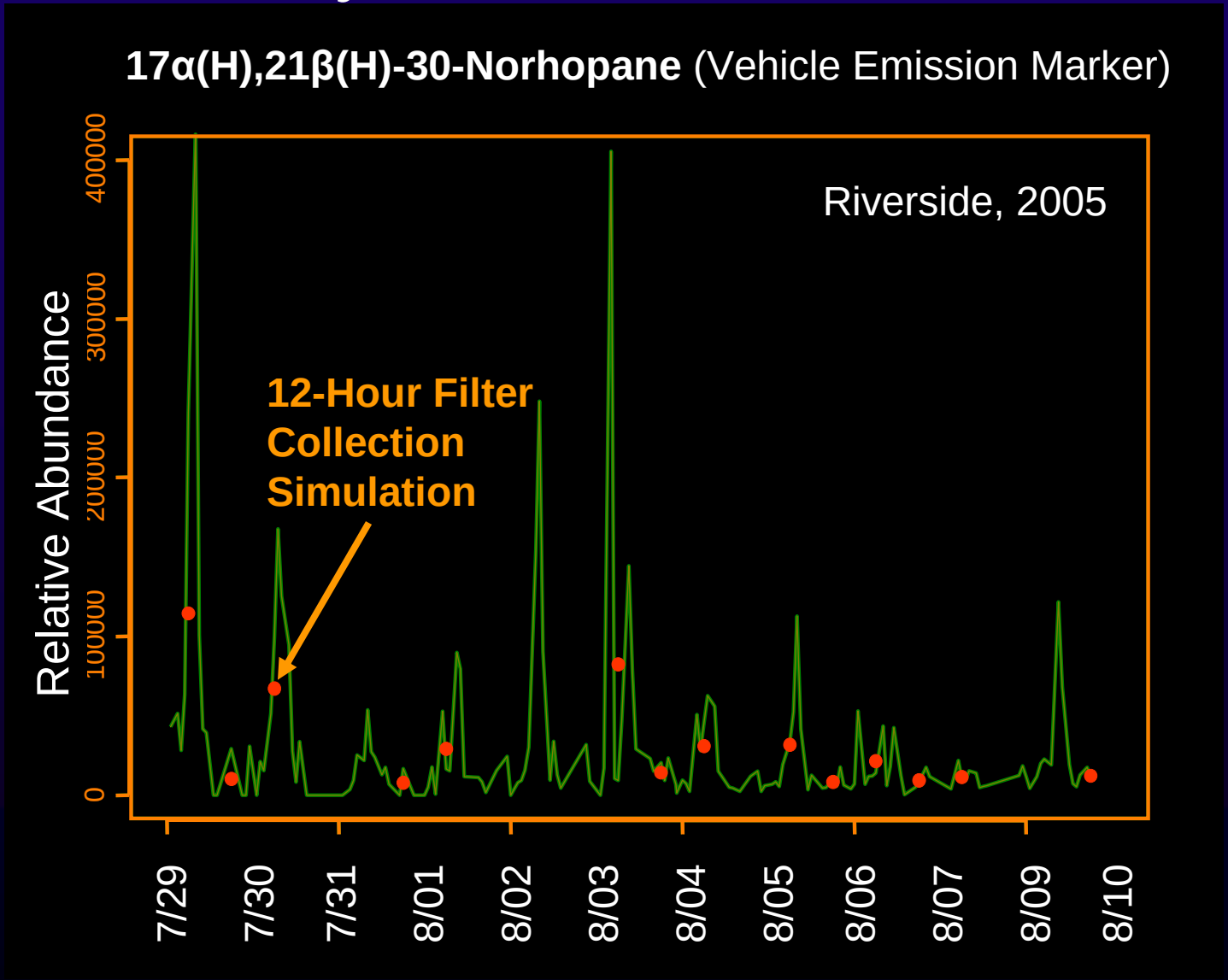
Motor vehicles ~ hopanes, steranes



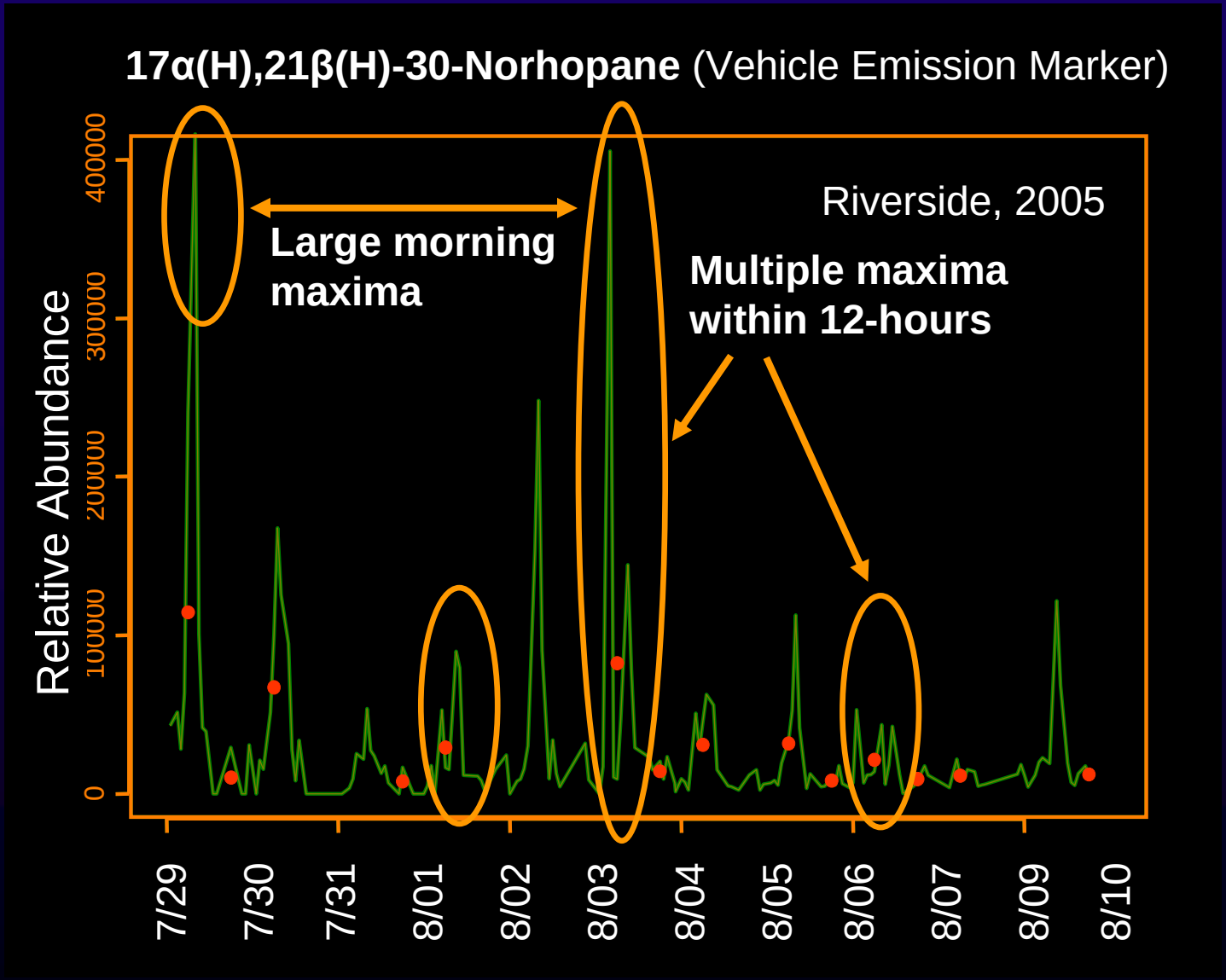


17α(H),21β(H)-30-Norhopane

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

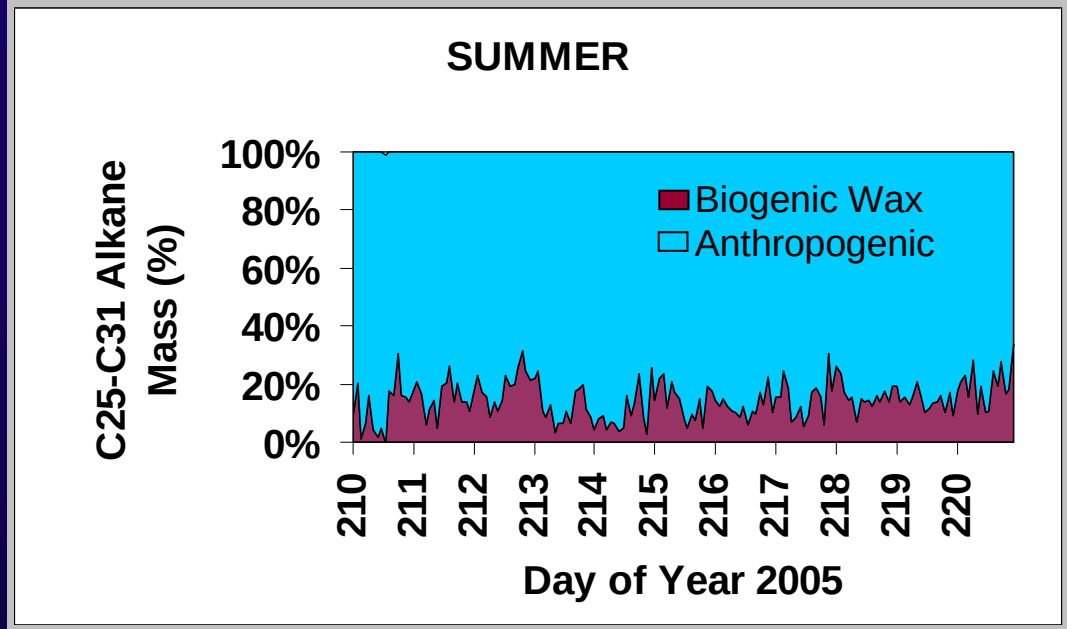


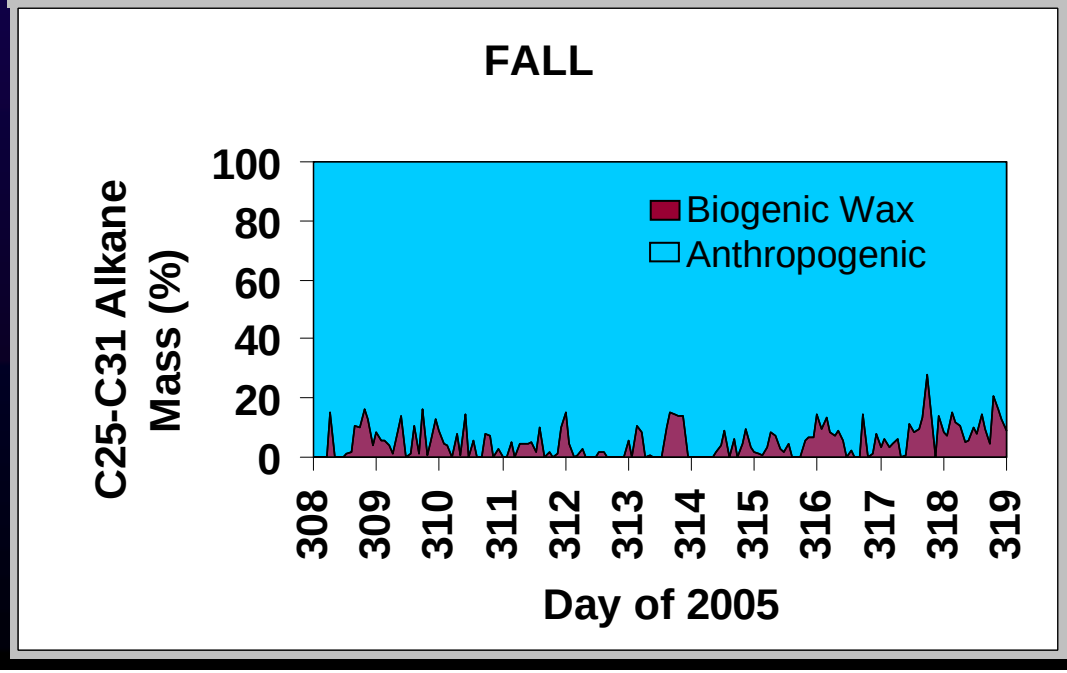
Time resolved data captures dynamics



Riverside, CA

Biogenic vs. Anthropogenic Alkanes

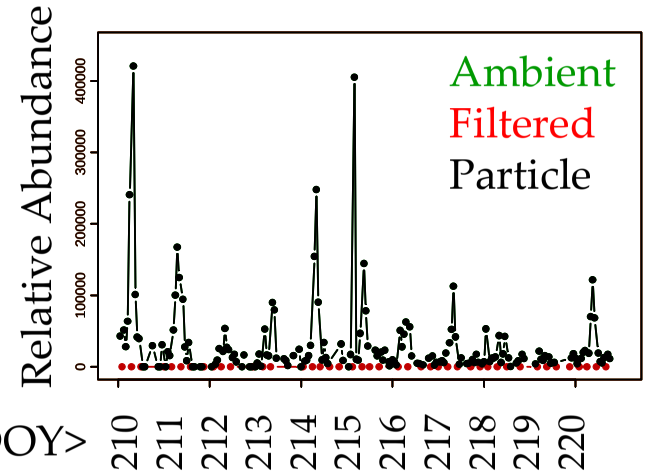


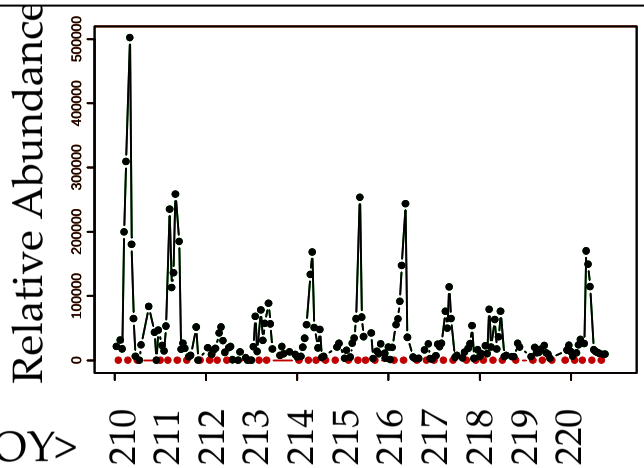


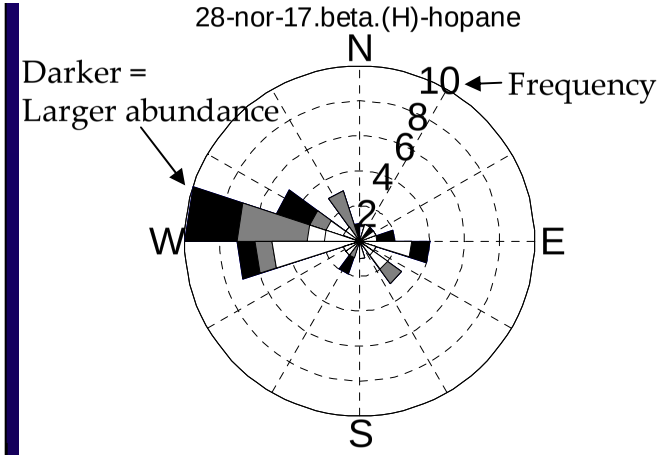
$$C_{wax} = \sum_{n=25}^{31} [C_n - \frac{(C_{n-1} + C_{n+1})}{2}]$$

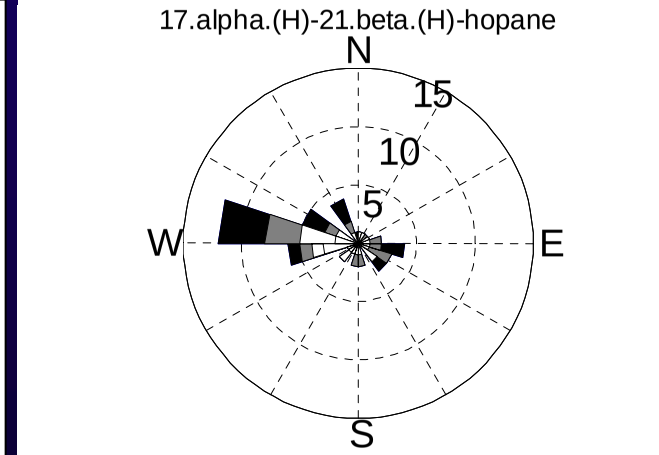
Adapted from *Simoneit 1989 J.Atmos.Chem.*

Primary Anthropogenic (vehicle)

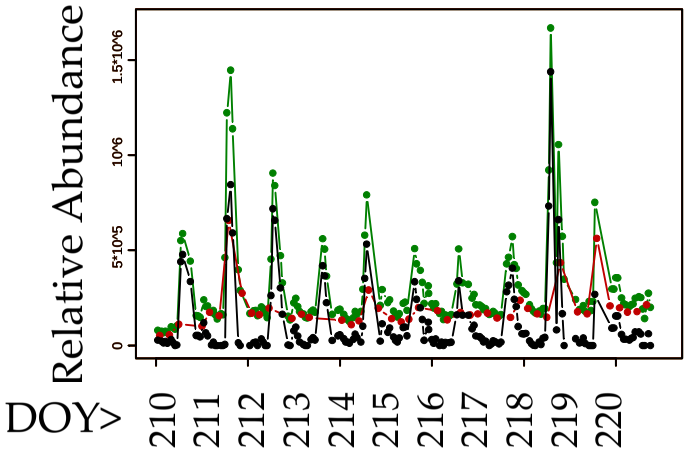


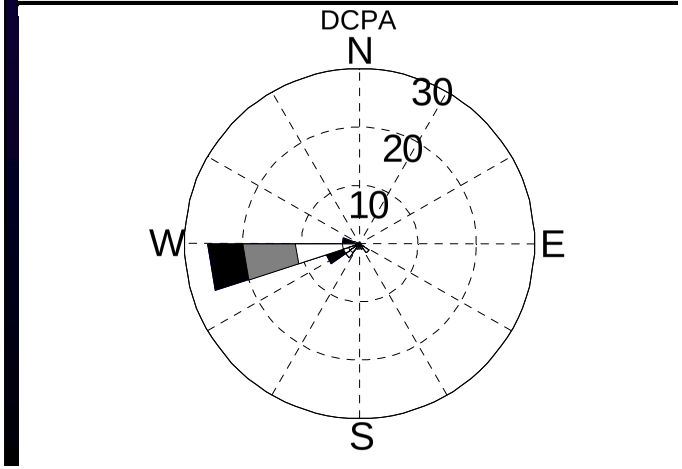




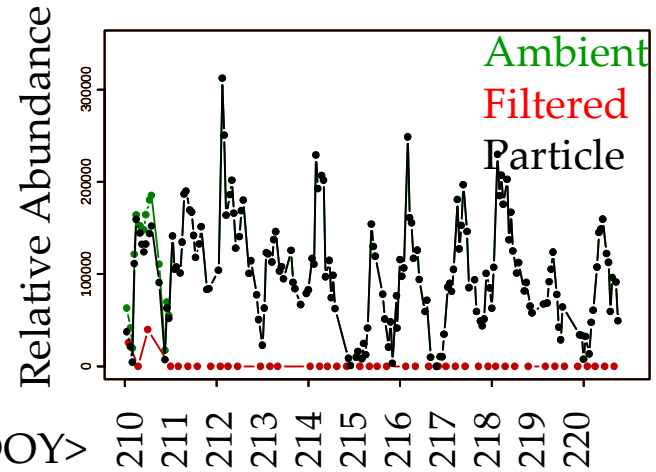


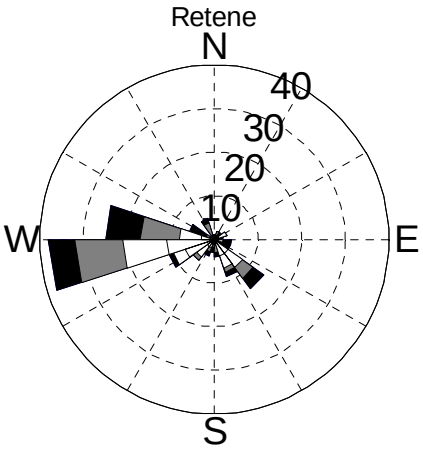
Herbicide



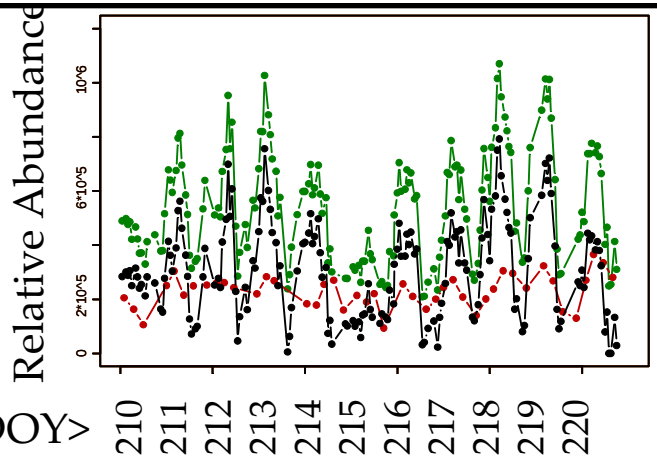


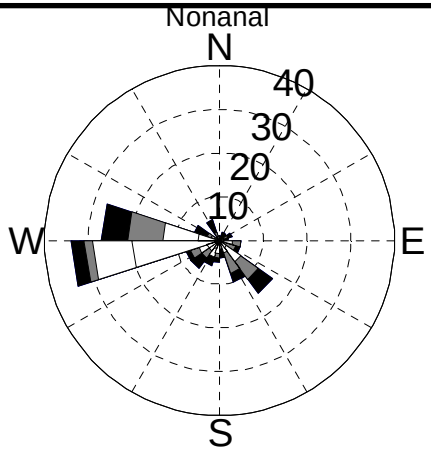
Biomass Burning



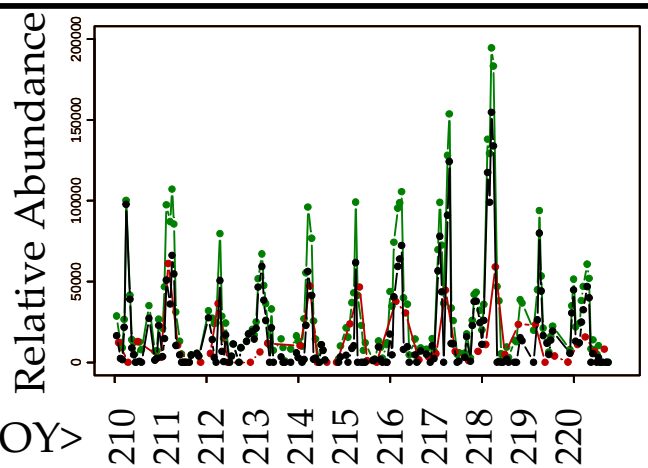


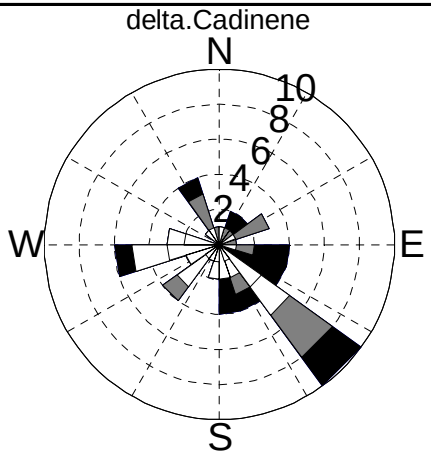
Meat Cooking



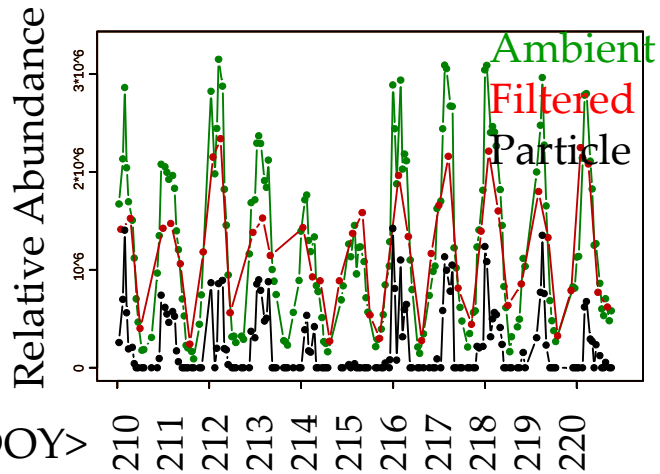


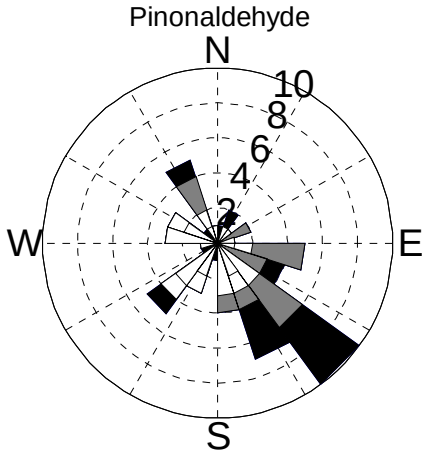
Primary Biogenic



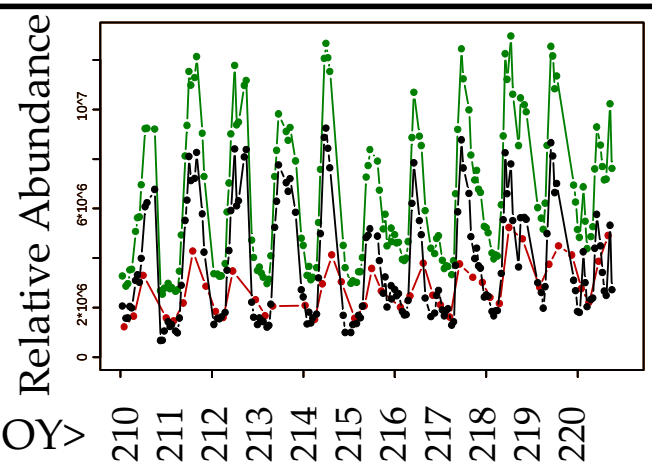


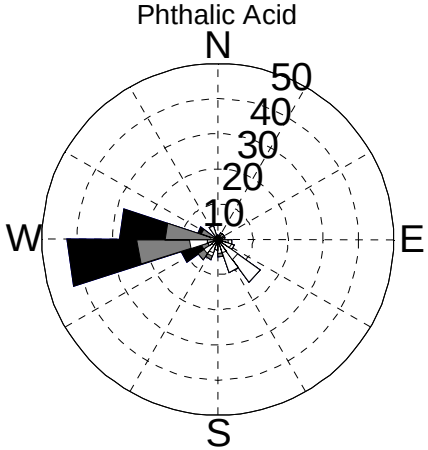
Secondary Biogenic

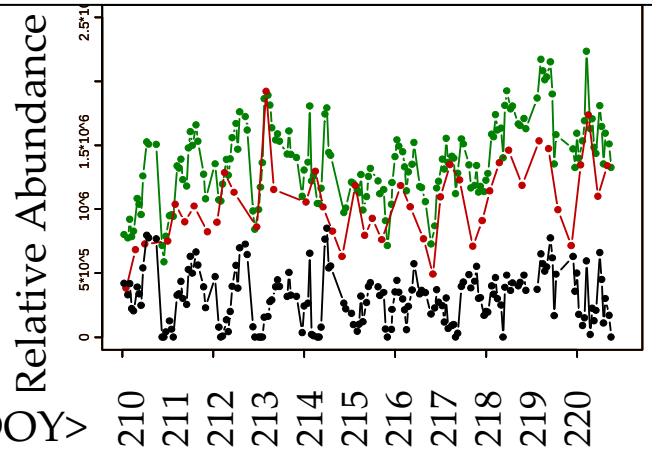


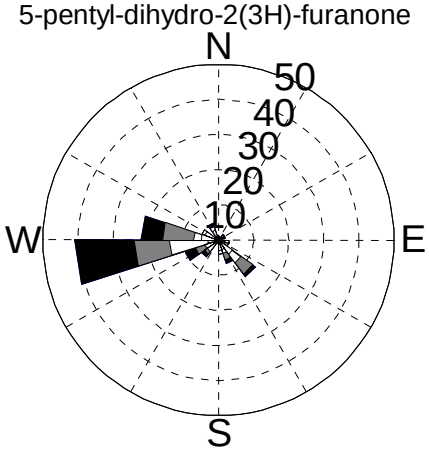


Secondary Anthropogenic

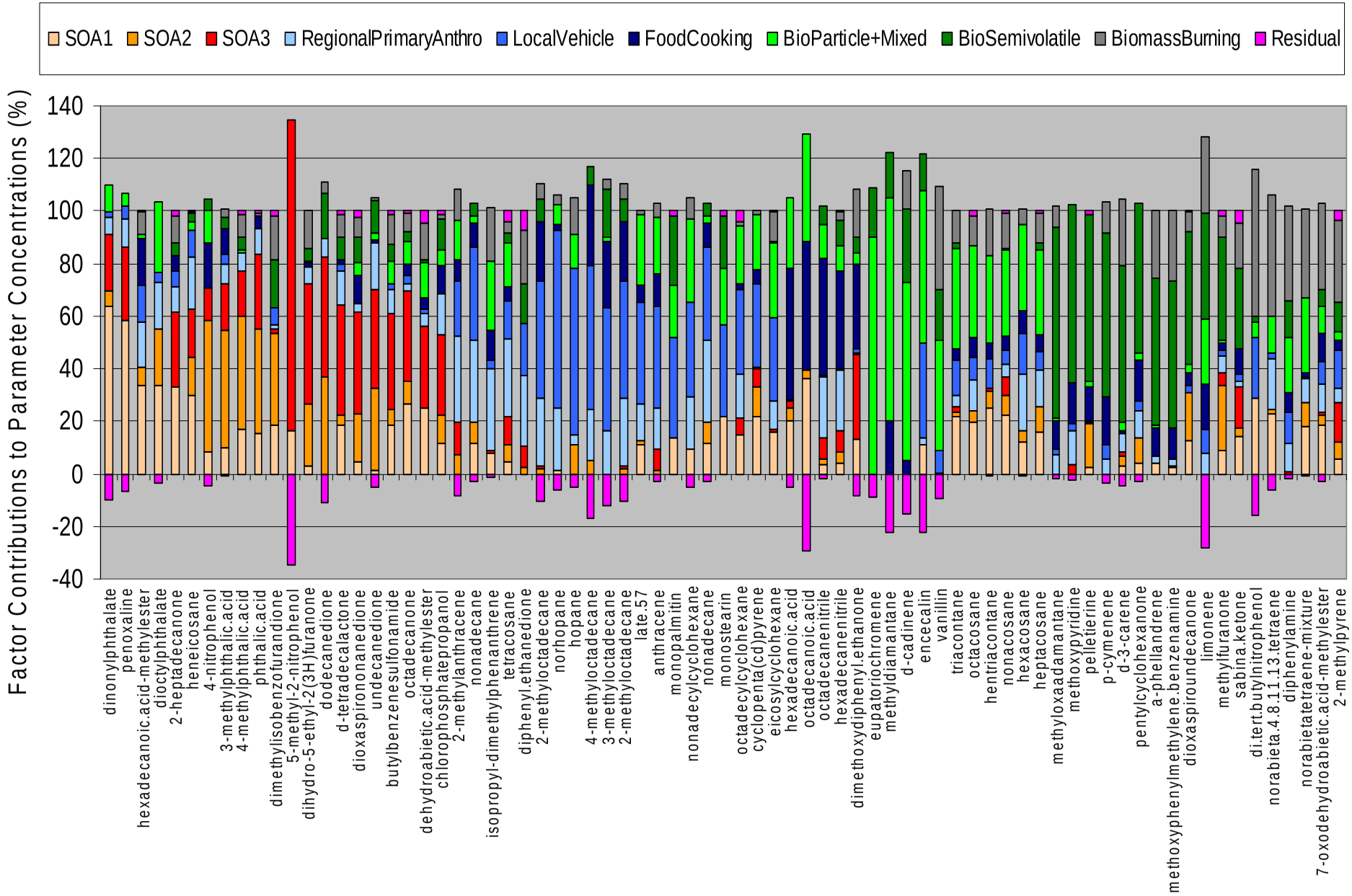




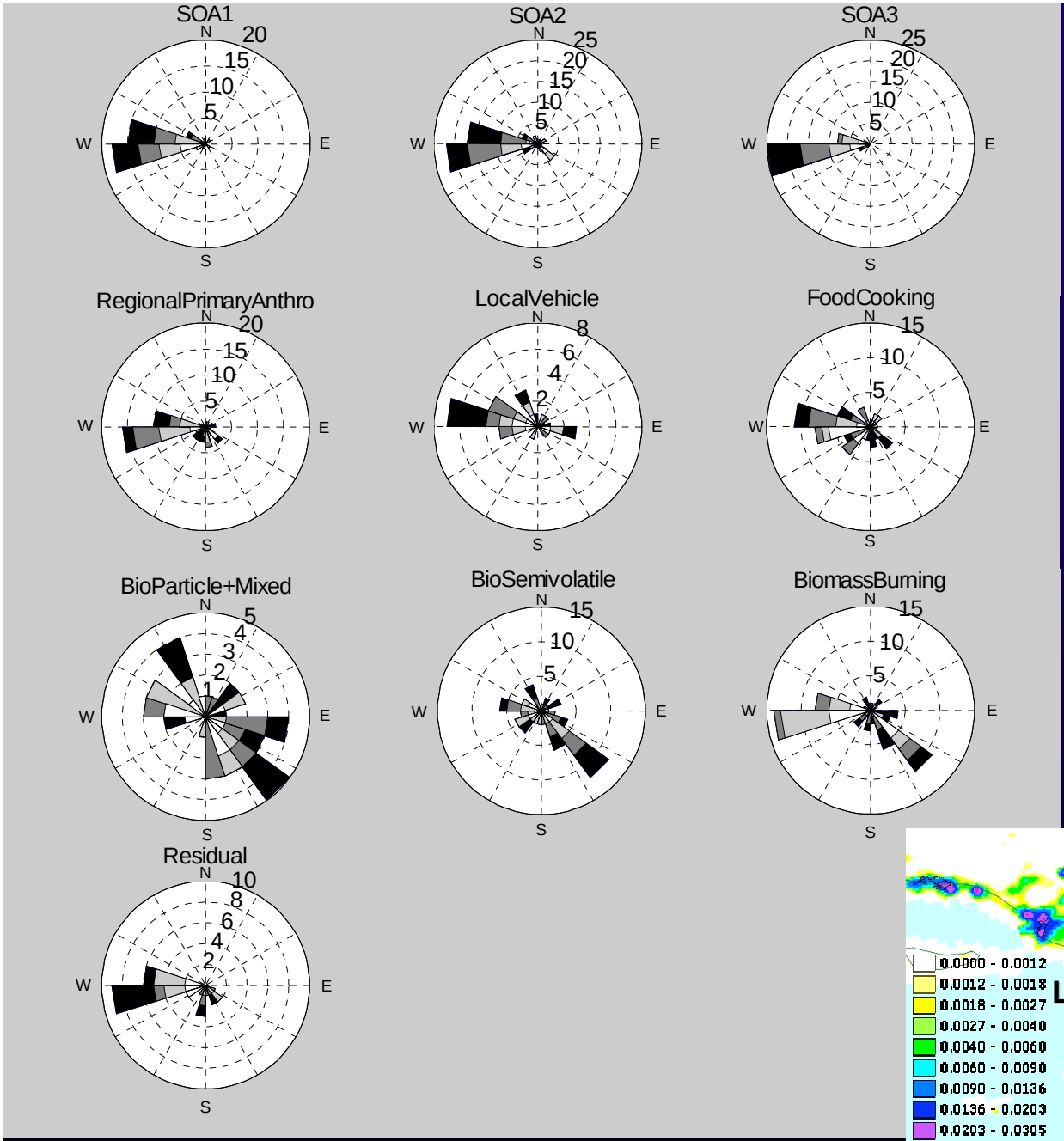


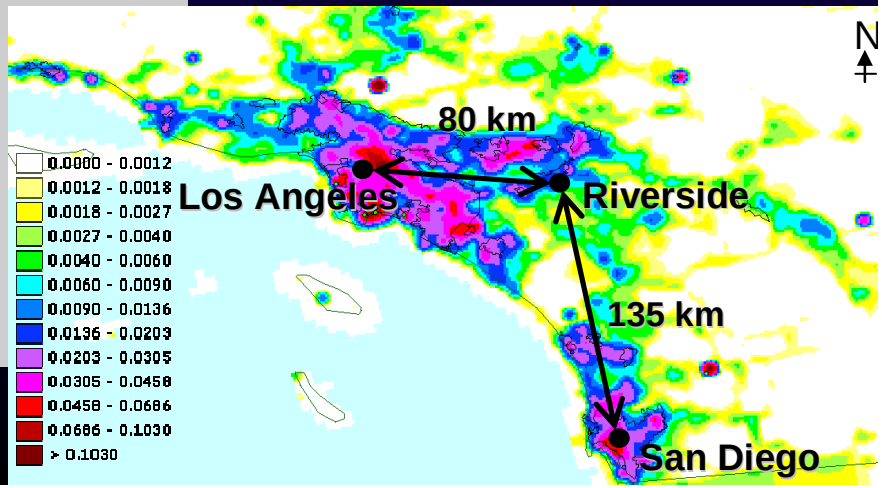


SOAR Summer Organic Aerosol Factor Profiles

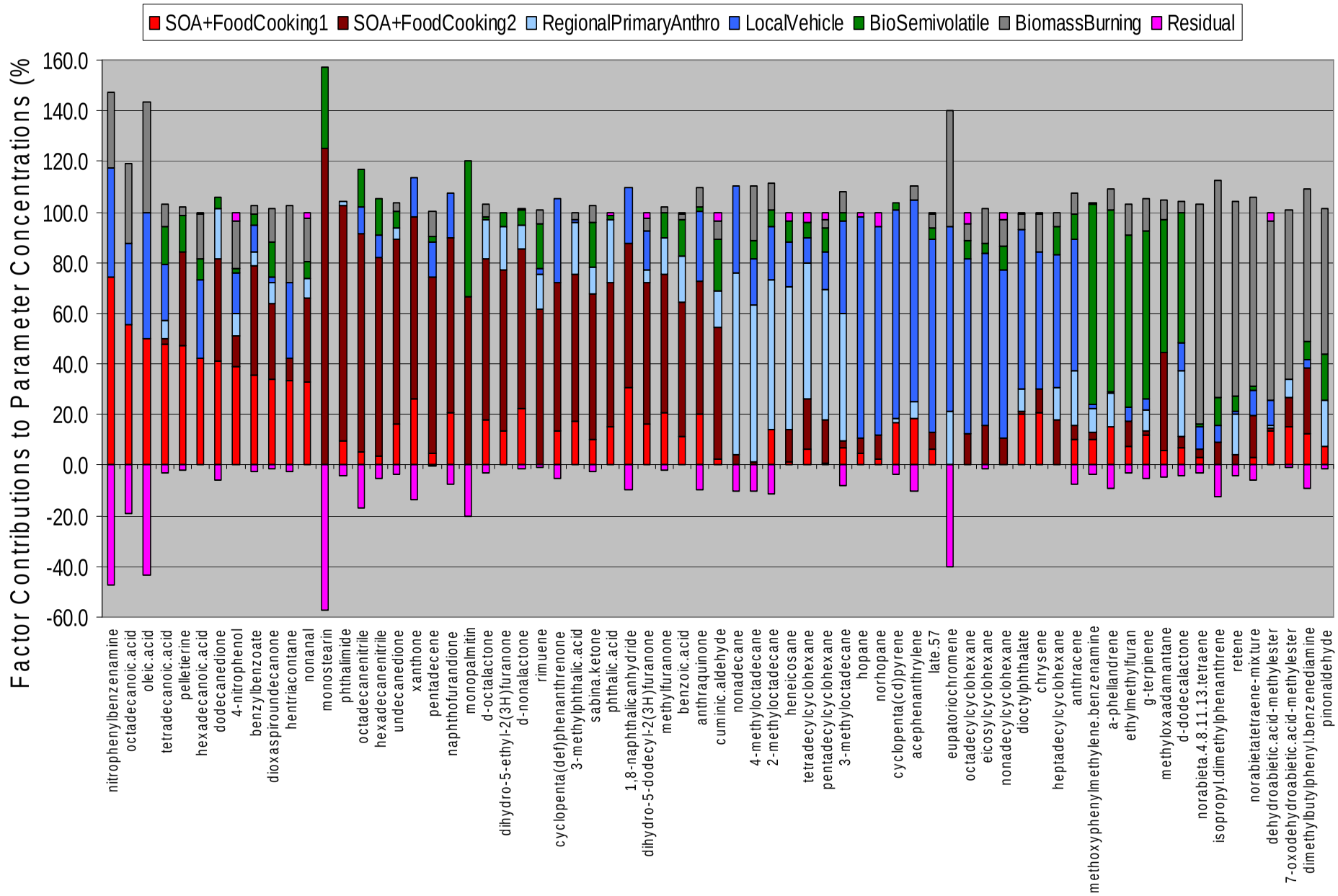


SOAR Summer Organic Aerosol Sources

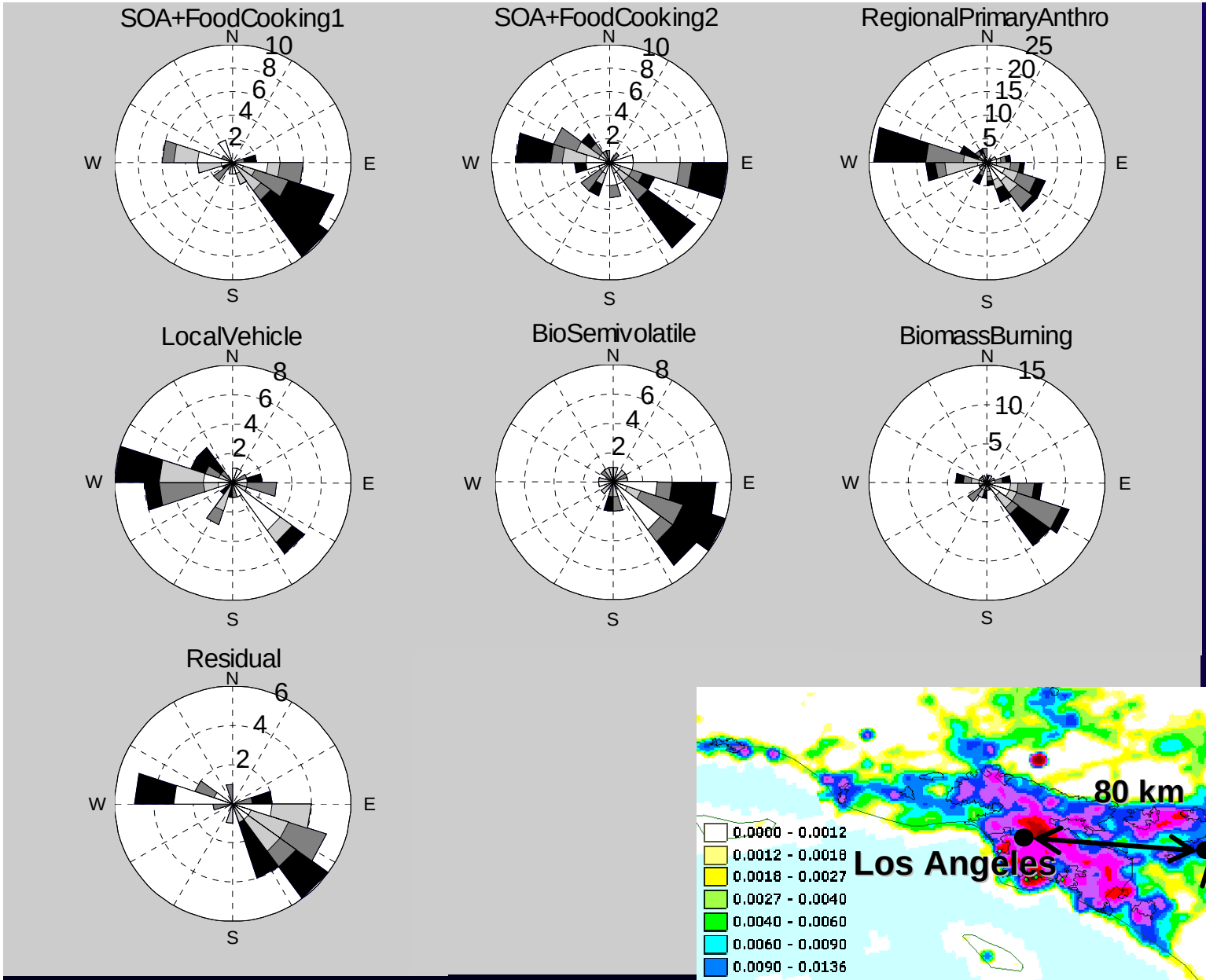


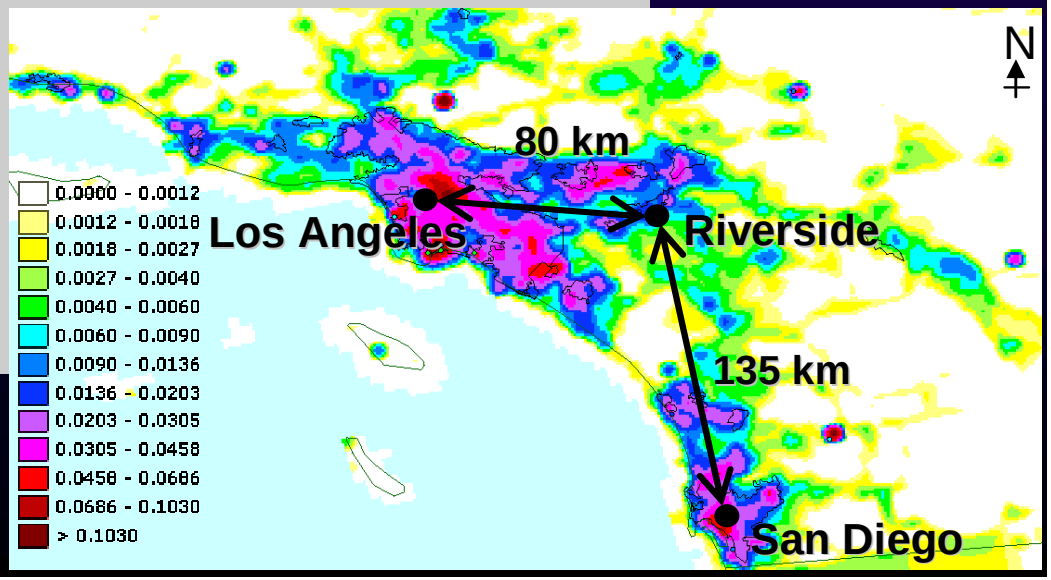


SOAR Fall Organic Aerosol Factor Profiles

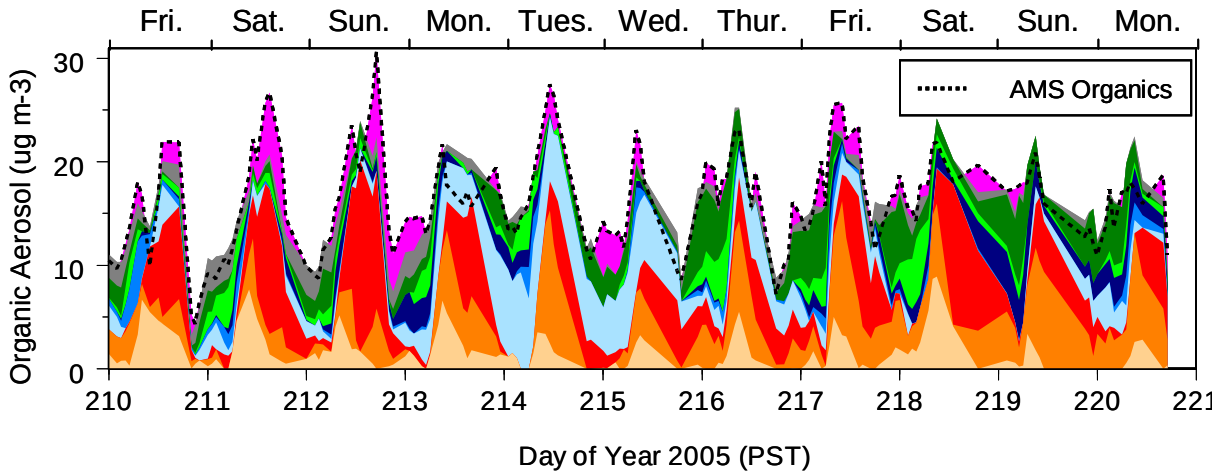


SOAR Fall Organic Aerosol Sources



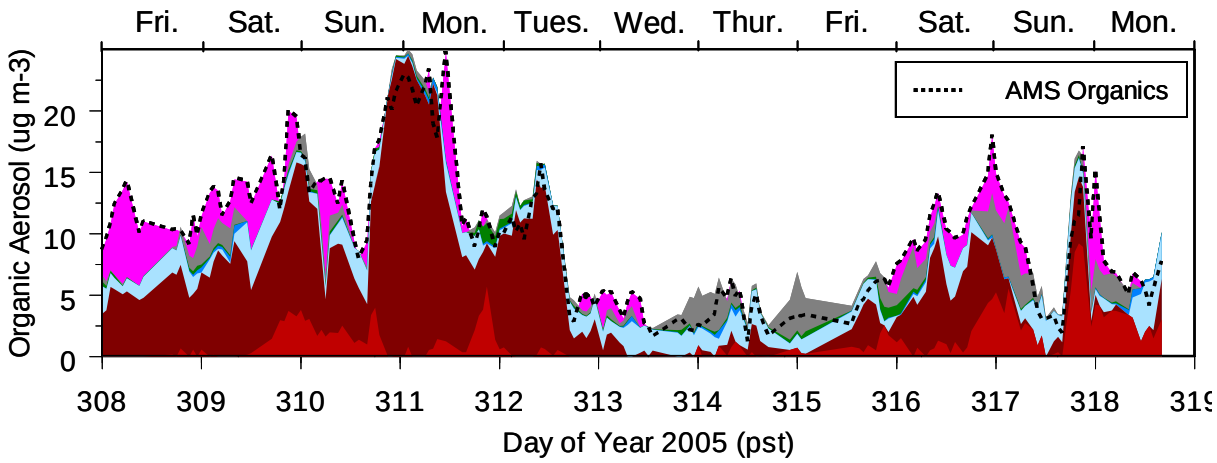


SOAR Summer

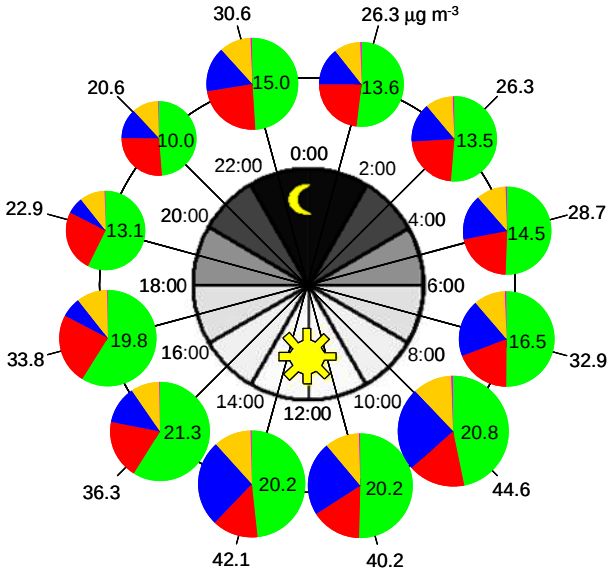


SOA1
SOA2
SOA3
RegionalPrimaryAnthro
LocalVehicle
FoodCooking
BioParticle+Mixed
BioSemivolatile
BiomassBurning
Residual

SOAR Fall



SOA+FoodCooking1
SOA+FoodCooking2
RegionalPrimaryAnthro
LocalVehicle
BioSemivolatile
BiomassBurning
Residual

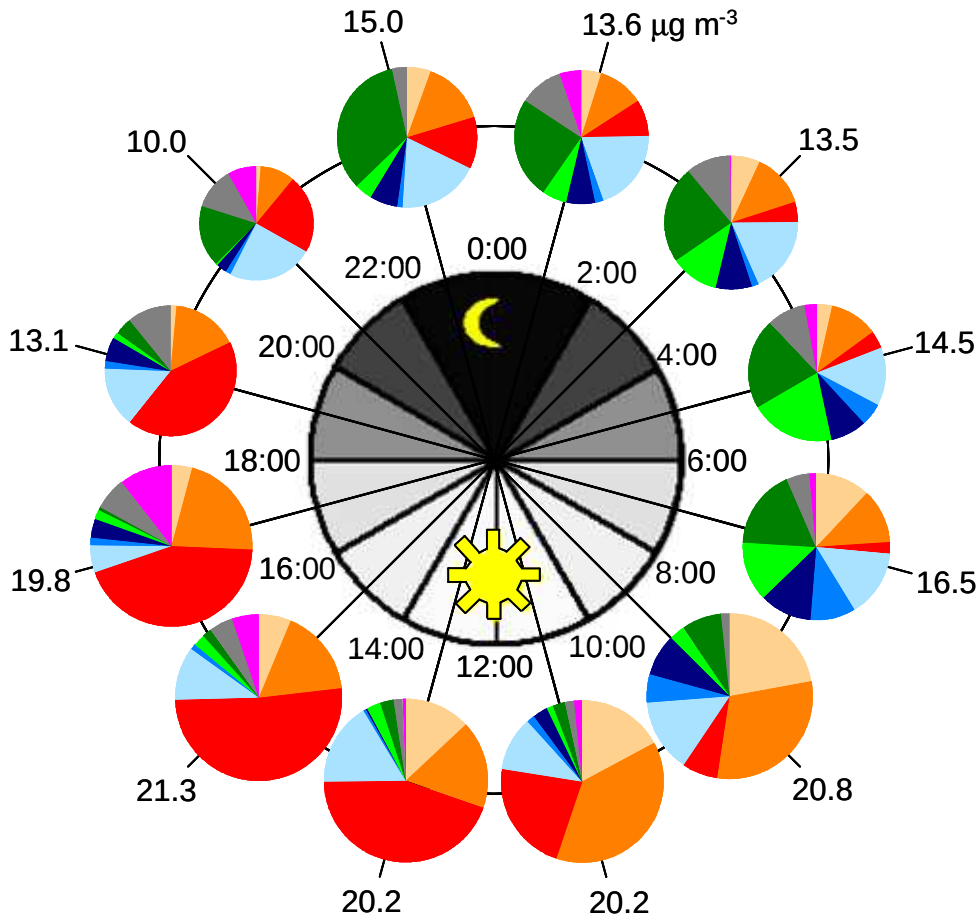


Organics (µg m-3) | NO_3^- | Chloride | SO_4^{2-} | NH_4^+

AMS Total Organic Aerosol = 10.0 - 20.8 µg m-3

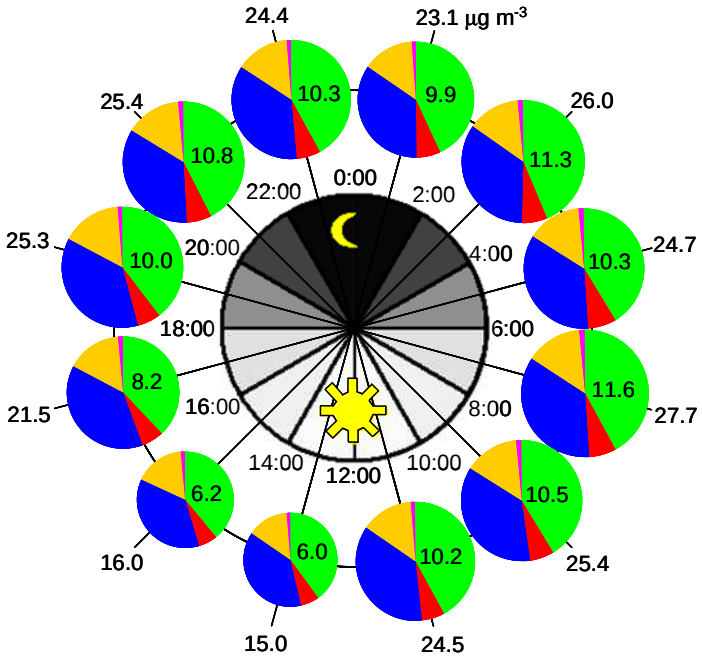
SOAR Summer

TAG-defined Organic Aerosol Sources



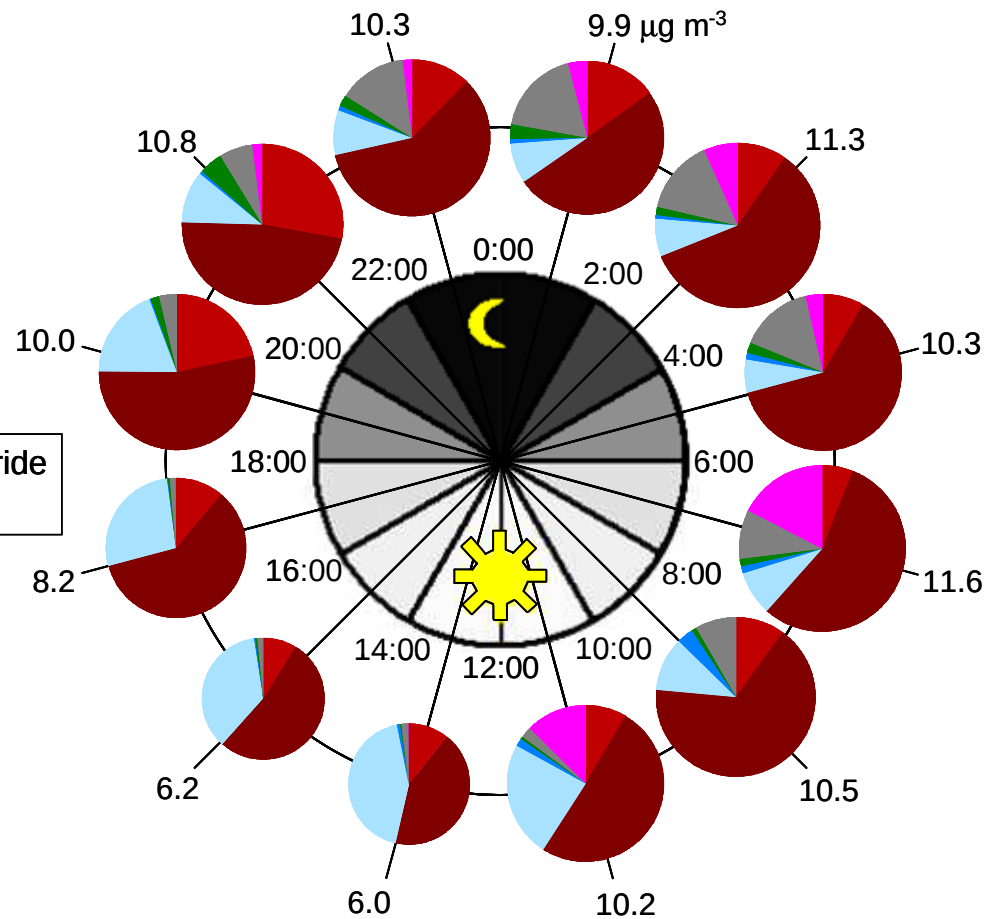
SOA1 | RegionalPrimaryAnthro | BioParticle+Mixed
SOA2 | LocalVehicle | BioSemivolatile
SOA3 | FoodCooking | BiomassBurning
Residual

AMS Total Organic Aerosol = 10.0 - 20.8 µg m-3



AMS Total Organic Aerosol = 6.0 – 11.6 µg m^{-3}

TAG-defined Organic Aerosol Sources



AMS Total Organic Aerosol = 6.0 – 11.6 µg m^{-3}

SOAR Fall

Average Source Concentrations and Contributions to Total OA during SOAR 2005.

SUMMER			FALL		
	Average Concentration (ug m-3)	Contribution to Total Organics (%)		Average Concentration (ug m-3)	Contribution to Total Organics (%)
SOA1	1.61	9.9	**SOA+FoodCooking1**	1.26	13.0
SOA2	3.06	18.9	**SOA+FoodCooking2**	5.47	56.3
SOA3	2.92	18.0	**RegPrimAnthro**	1.46	15.0
RegPrimAnthro	2.43	15.0	**LocalVehicle**	0.11	1.1
LocalVehicle	0.57	3.5	**BioSemivolatile**	0.18	1.9
FoodCooking	1.01	6.2	**BiomassBurning**	0.91	9.4
BioParticle+Mixed	1.10	6.8	**Residual**	0.33	3.4
BioSemivolatile	2.18	13.5			

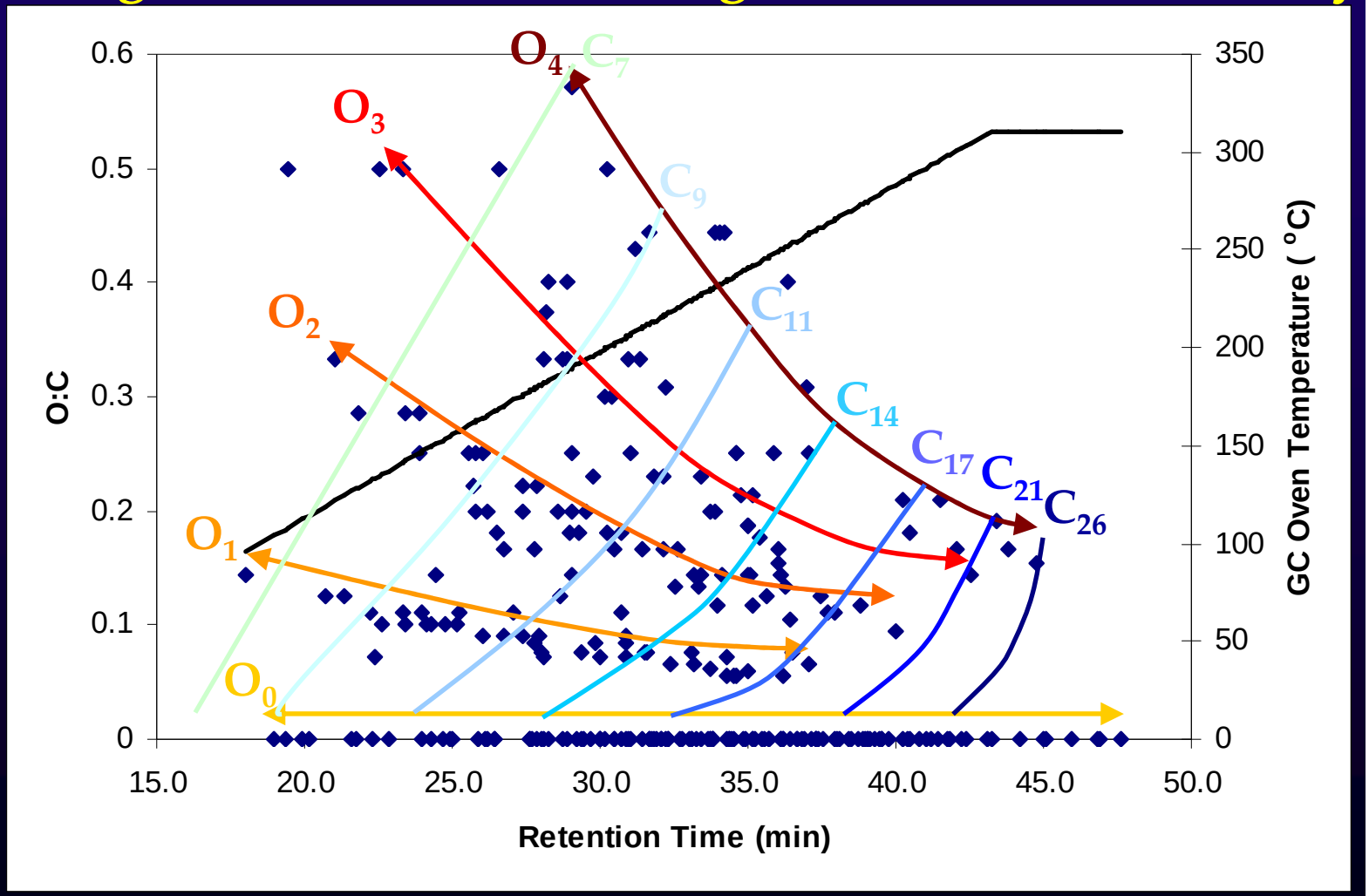
AMS O:C ~
OOA1 (0.9)

TAG Compounds Measured during SOAR 2005
300 Identified Hourly (~10-20% of organic mass)
Increasing oxidation → increasing measurement difficulty

OOA2 (0.55)

BBOA (0.35)

HOA (0.08)

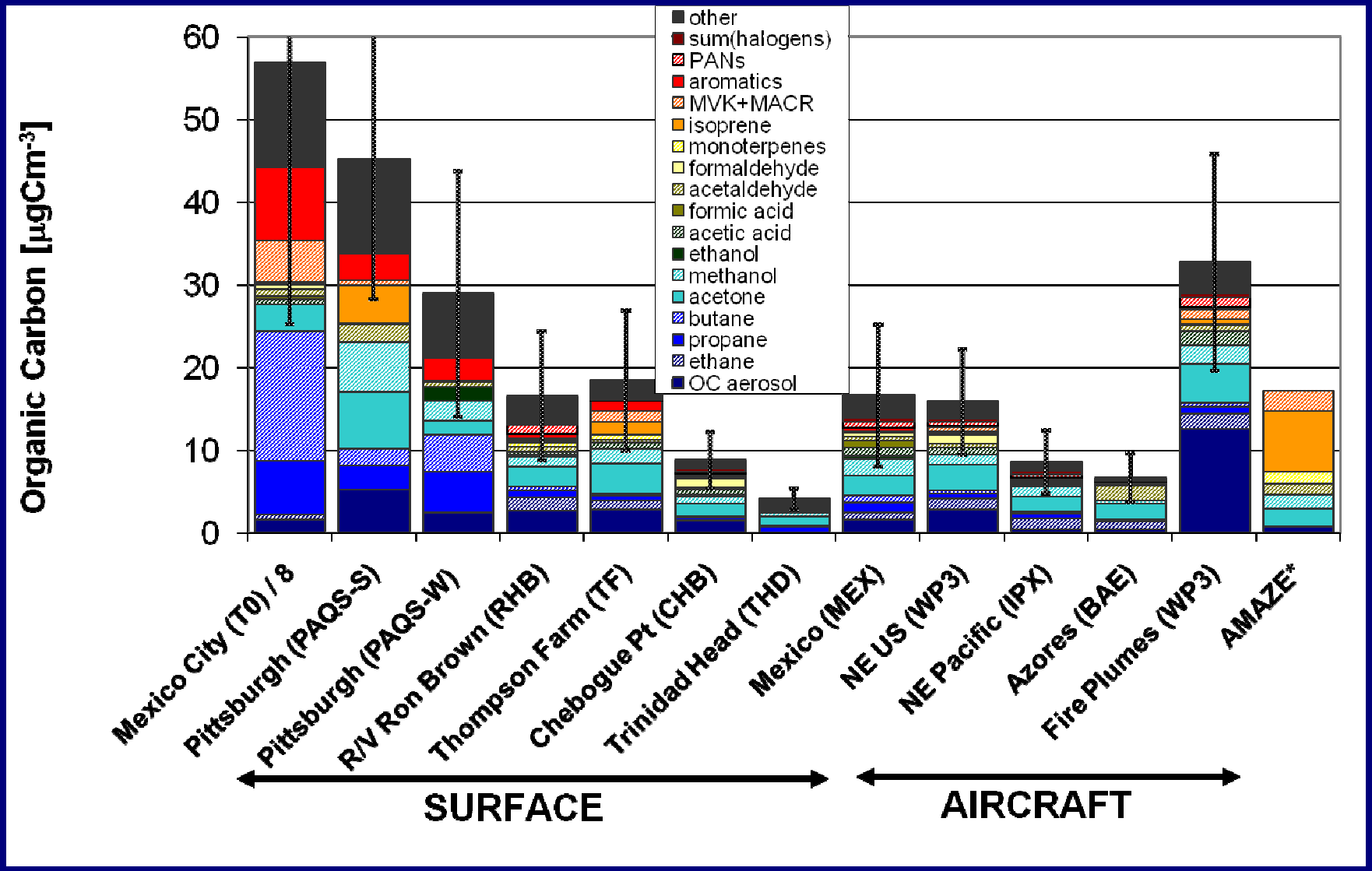


Aiken et al., submitted ES&T

Williams et al., in prep

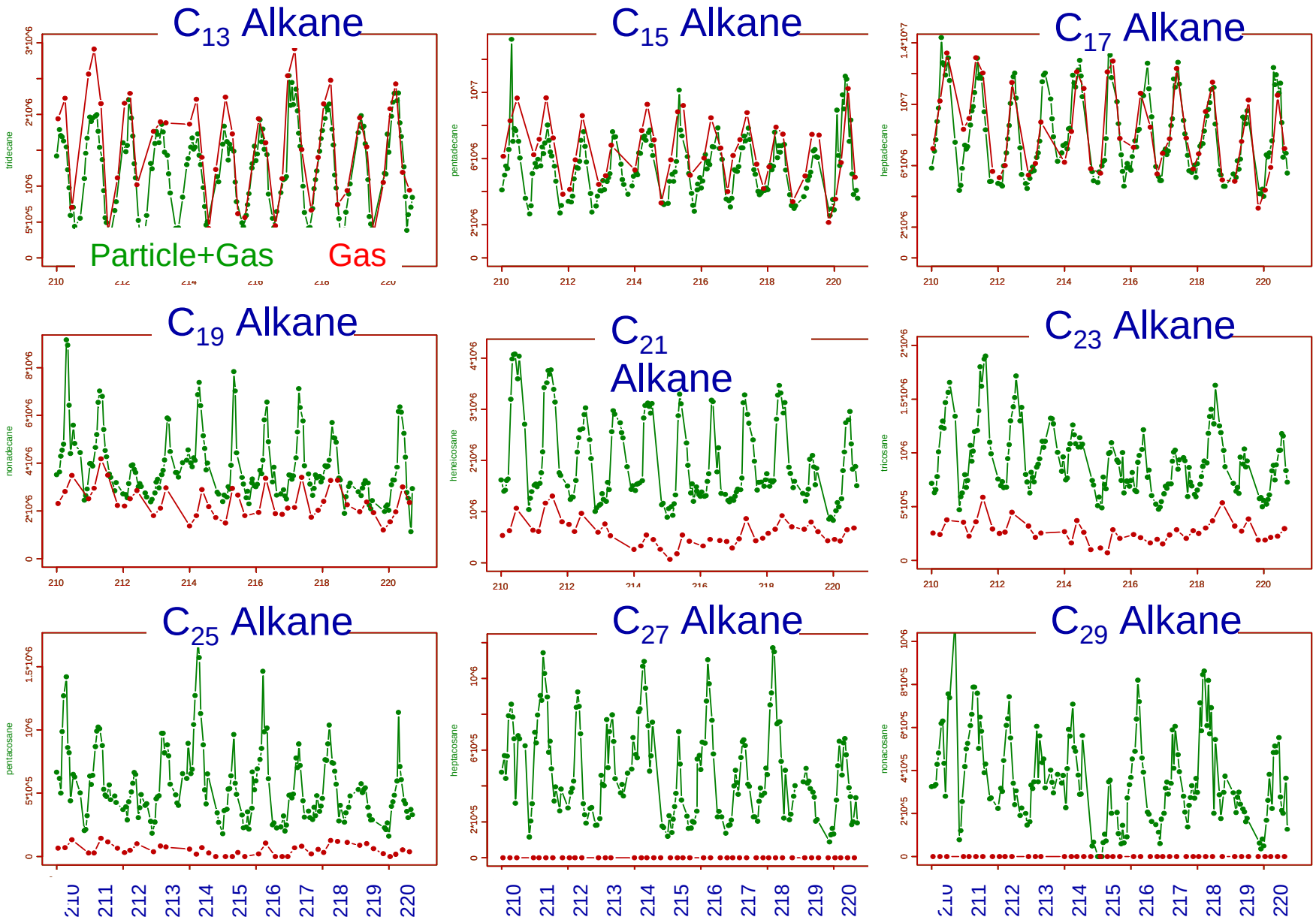
Total Observed Organic Carbon (TOOC)

Organic aerosol = 3-17%



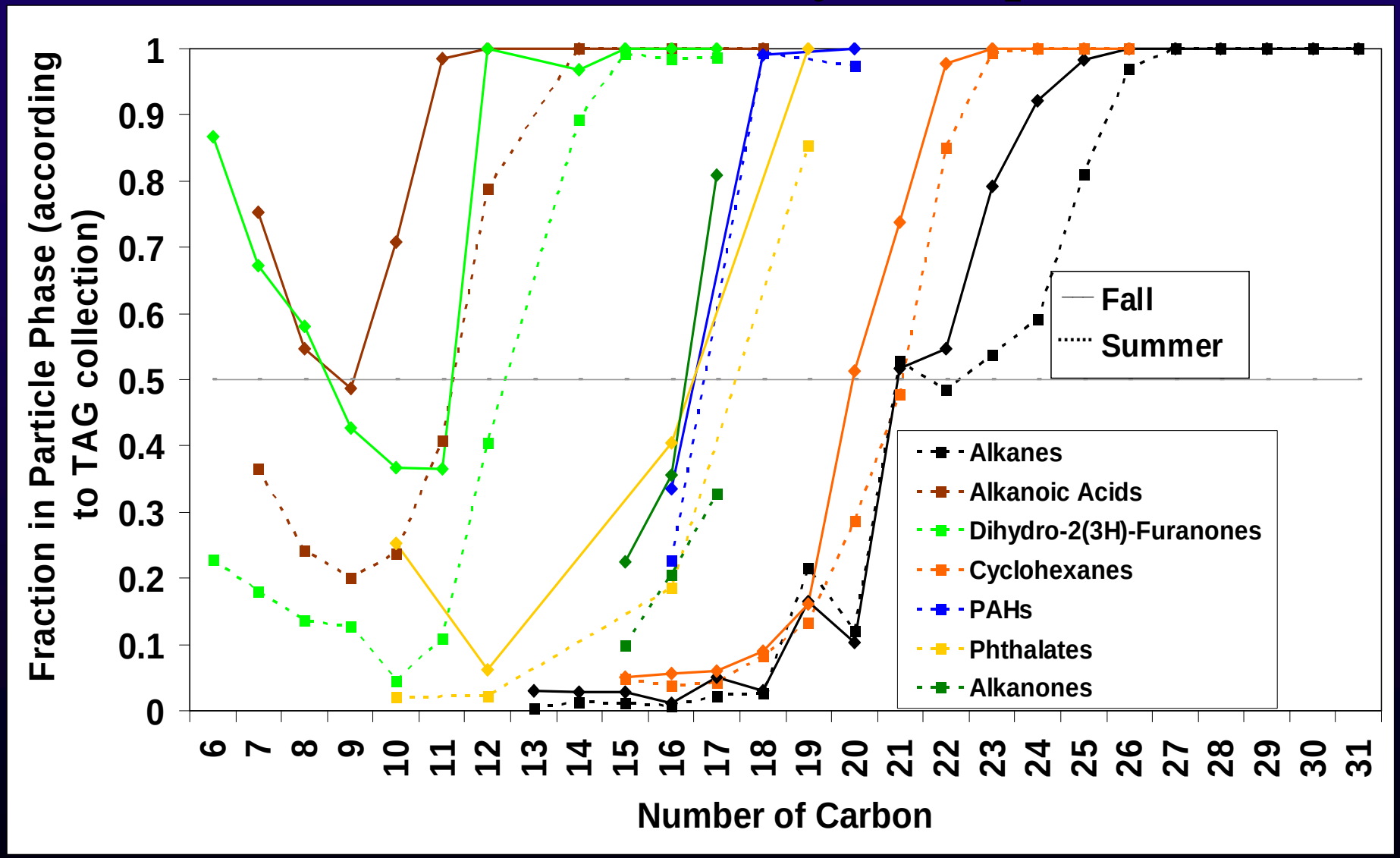
[*Heald et al.*, ACP 2008]

TAG Particle+Gas Ambient Measurements



Williams et al in prep

Gas-Particle Partitioning from TAG Ambient Measurements by Compound Class



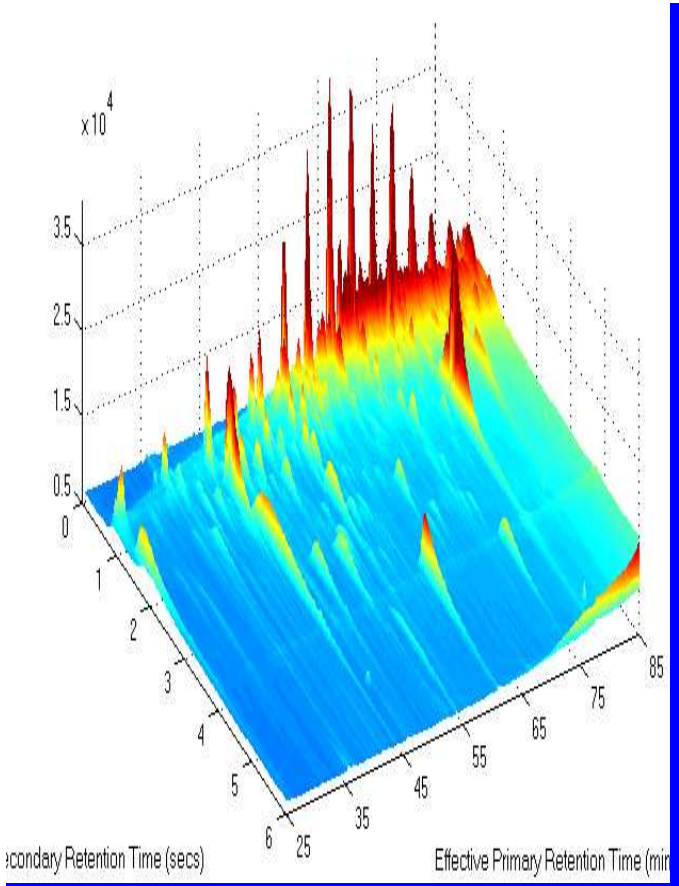
Williams et al in prep

Summary

- Achieved hourly speciated organic aerosol measurements during SOAR campaign for >300 compounds
- Differentiated biogenic and anthropogenic contributions of primary and secondary organic aerosol in Riverside, and quantified large diurnal cycles in source contributions
- Secondary compounds, many of which are semi-volatile, dominate the organic aerosol in Riverside in afternoon
- TAG measurements observe ambient gas-particle partitioning and hence offer insight to the formation of SOA

Future

- Analyzing 2007 BEARPEX data from Blodgett Forest
- Developing multi-dimensional TAG (2D-TAG) for improved compound separation
- Developing Semi-Volatile TAG (SV-TAG) for simultaneous quantitative measurements of gas and particle composition
- Planning additional urban and rural field measurements



2D-TAG

TWO-DIMENSIONAL CHROMATOGRAPHY OF ATMOSPHERIC AEROSOLS: A NEW IN-SITU INSTRUMENT

Allen H. Goldstein, Brent J. Williams
University of California, Berkeley

Susanne V. Hering, Nathan M. Kreisberg
Aerosol Dynamics Inc.

Tadeusz Górecki, Ognjen Panic
University of Waterloo

Funding
DOE STTR
DOE SBIR

TAG (1D)
Thermal desorption Aerosol GC

-Hourly, in-situ characterization of organic marker compounds in ambient aerosols ***(Williams et al AS&T 2006)***

2D-TAG
2-Dimensional
Thermal desorption Aerosol GC

-Vastly increase number of separated compounds

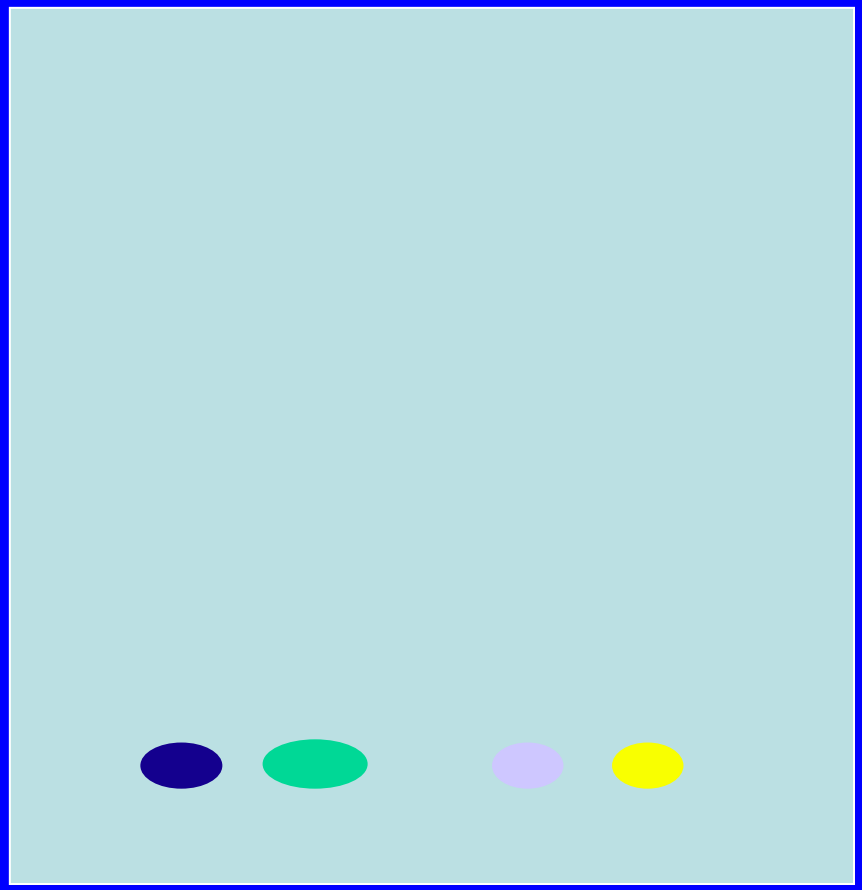
-Classify compounds by chemical family and size

(Goldstein et al J Chrom A 2008)

1-D Chromatography

Separation limited by column capacity

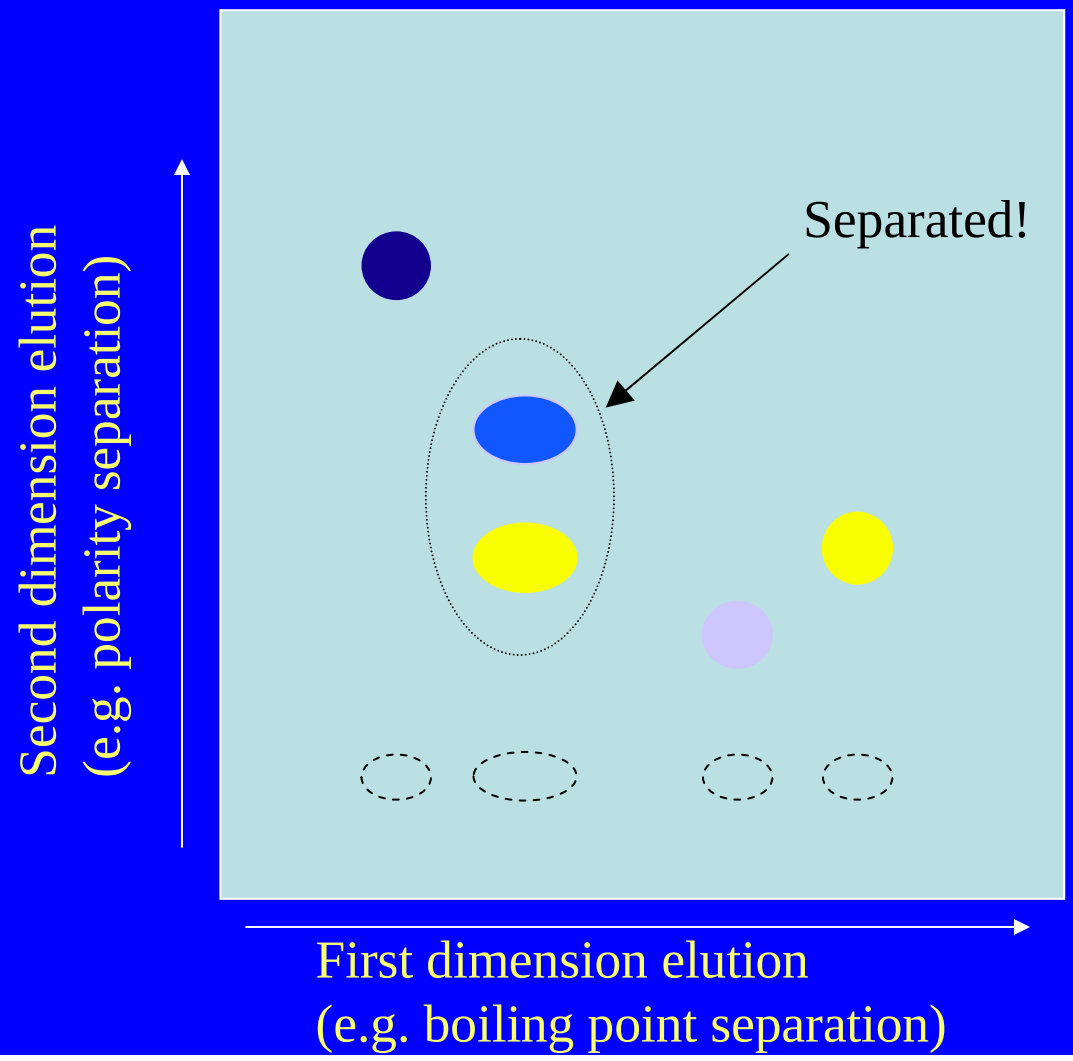
Difficult separating highly complex samples



First dimension elution

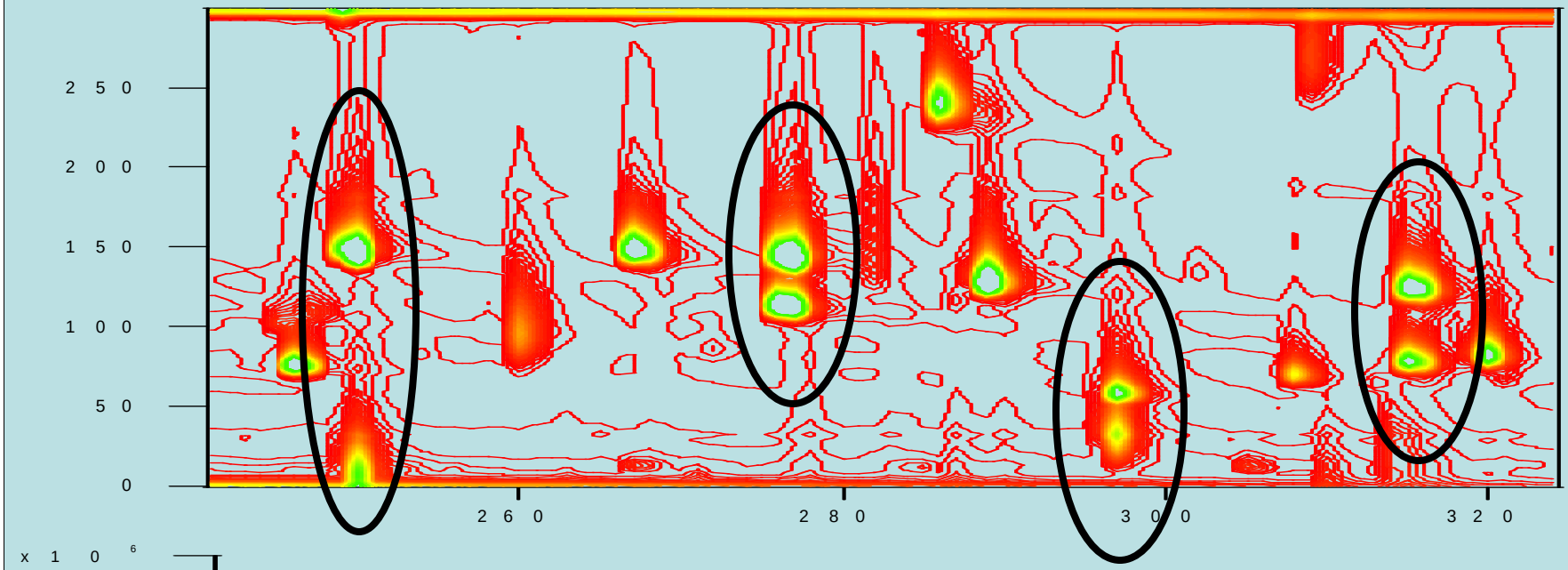
2-D Chromatography

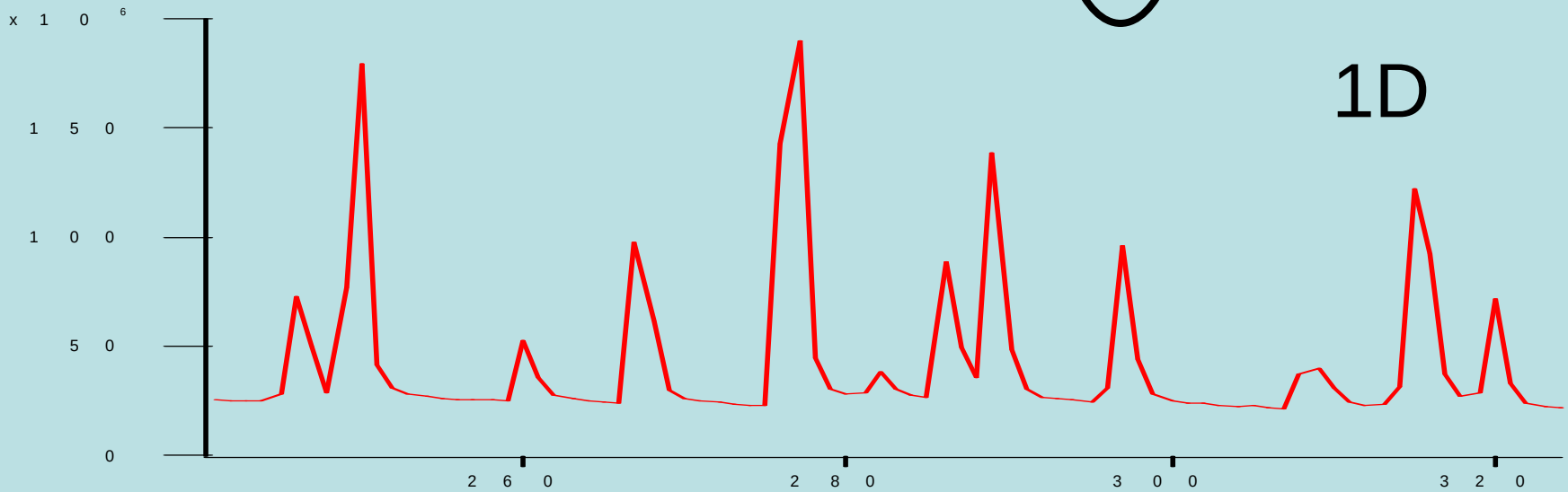
Increased separation using orthogonal column phases



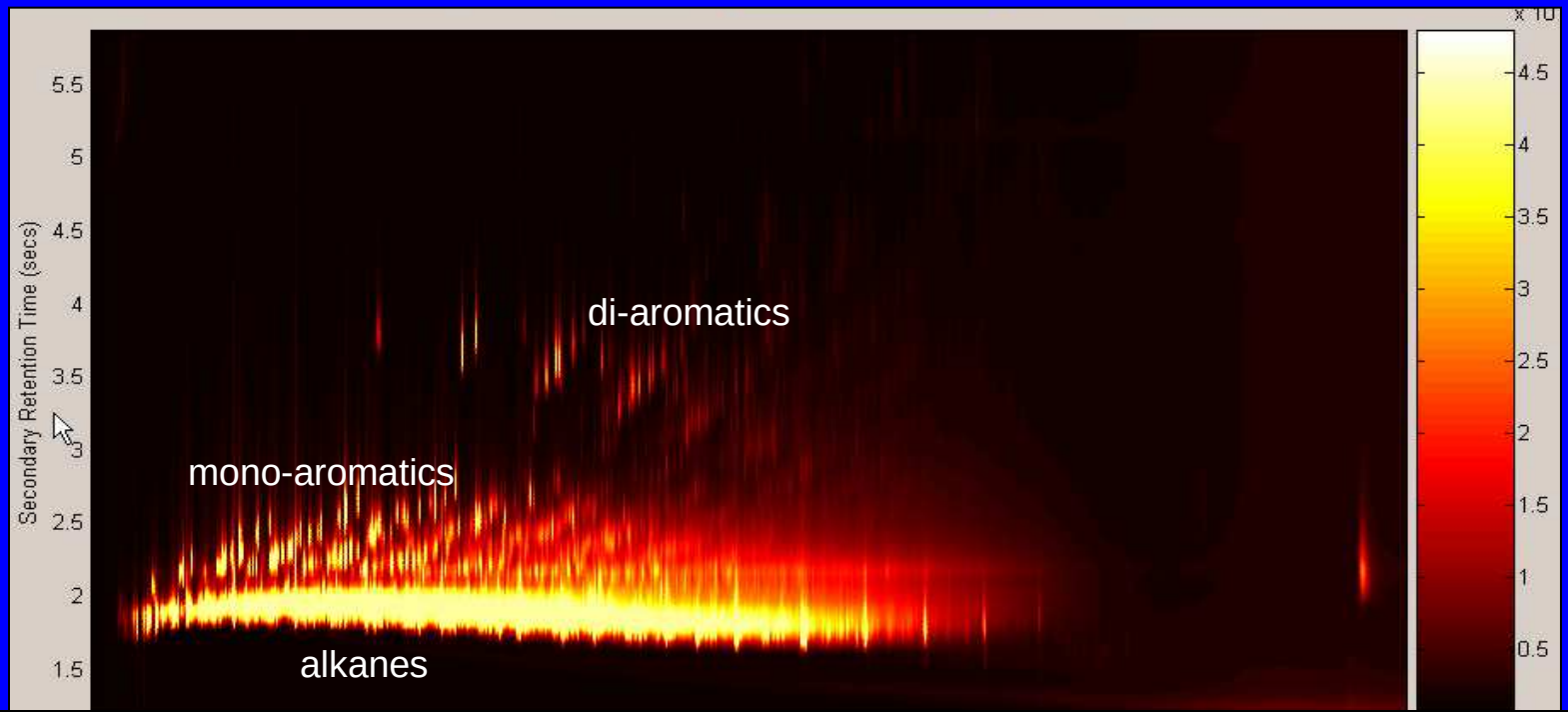
1D vs 2D Separations with TAG

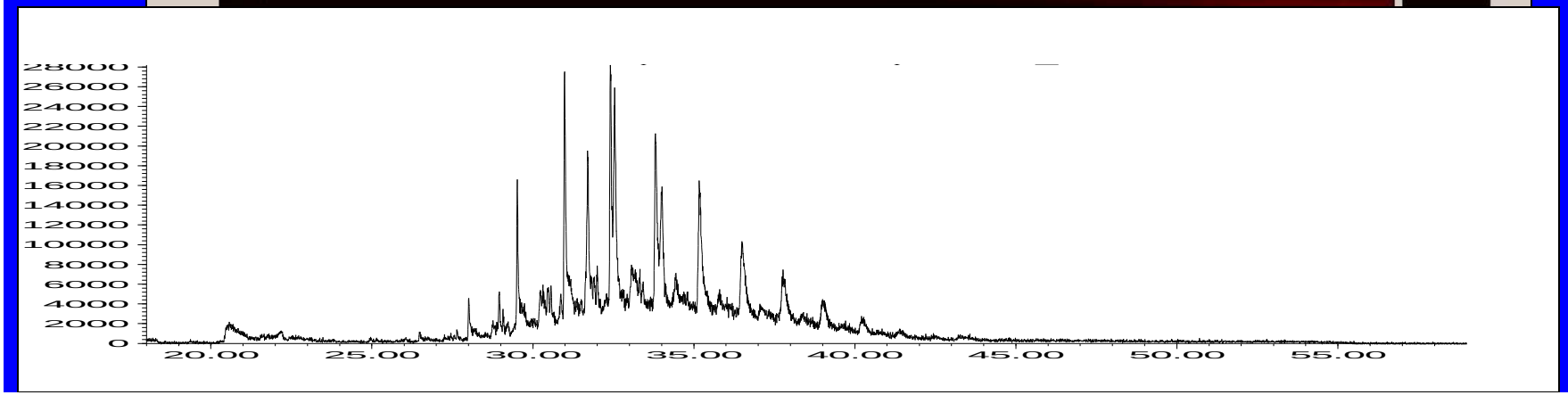
EPA Standard Method 8270



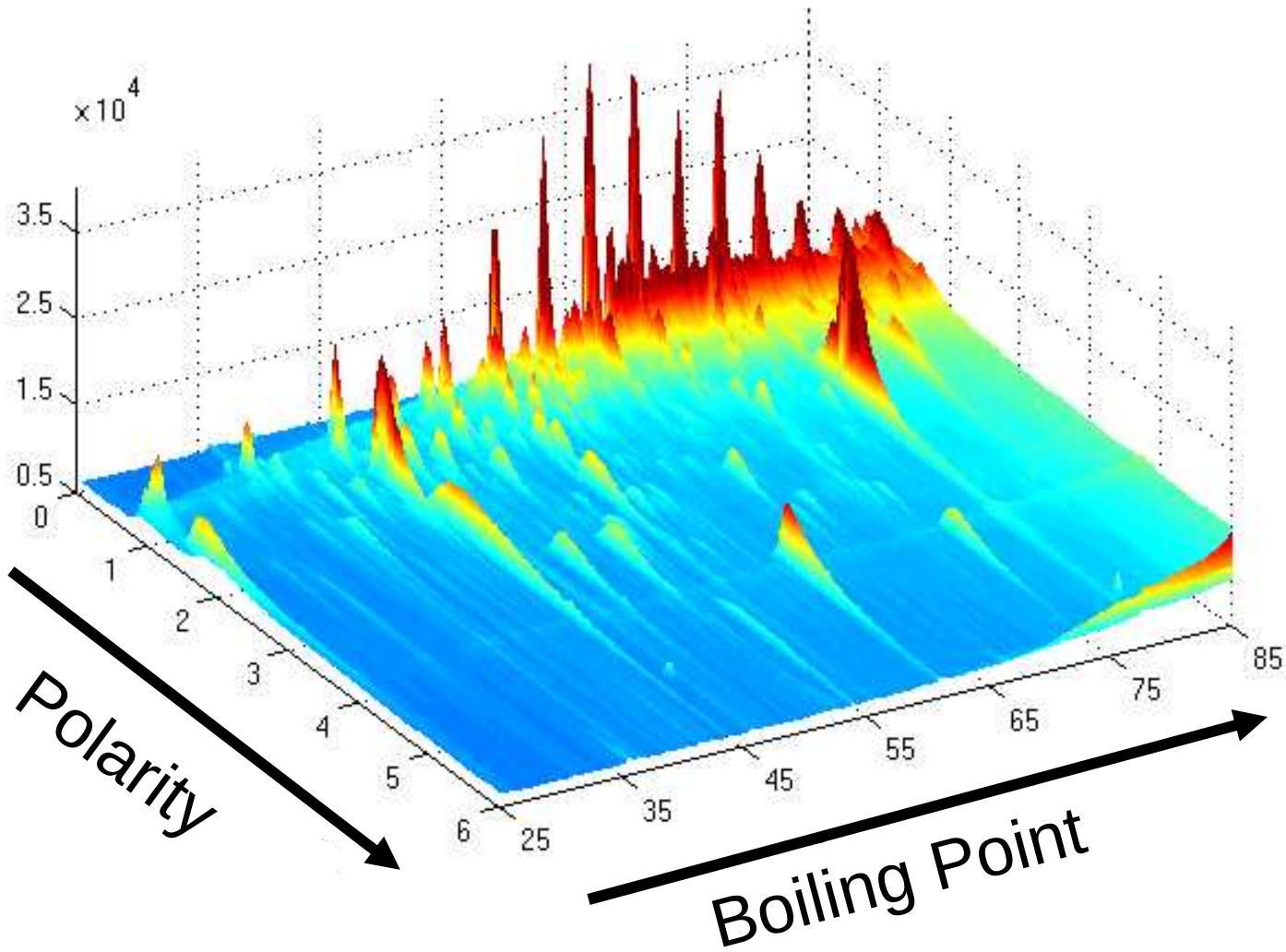


Separation of Diesel Fuel Using 2D-TAG VS 1D-TAG (note compound class structures)



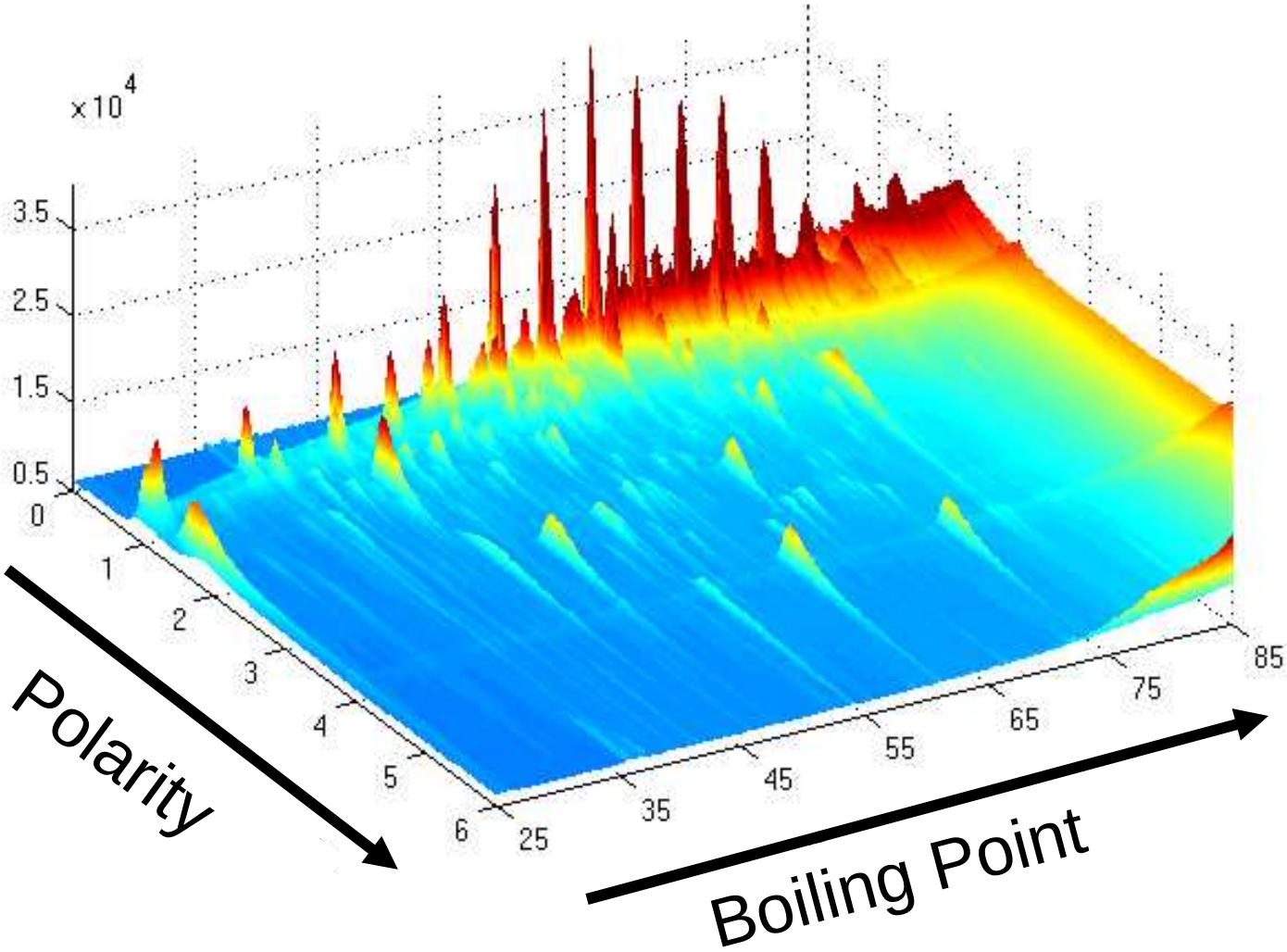


2D-TAG-FID Berkeley Air



90 minute sample

12:00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2.5
1.5
0.5
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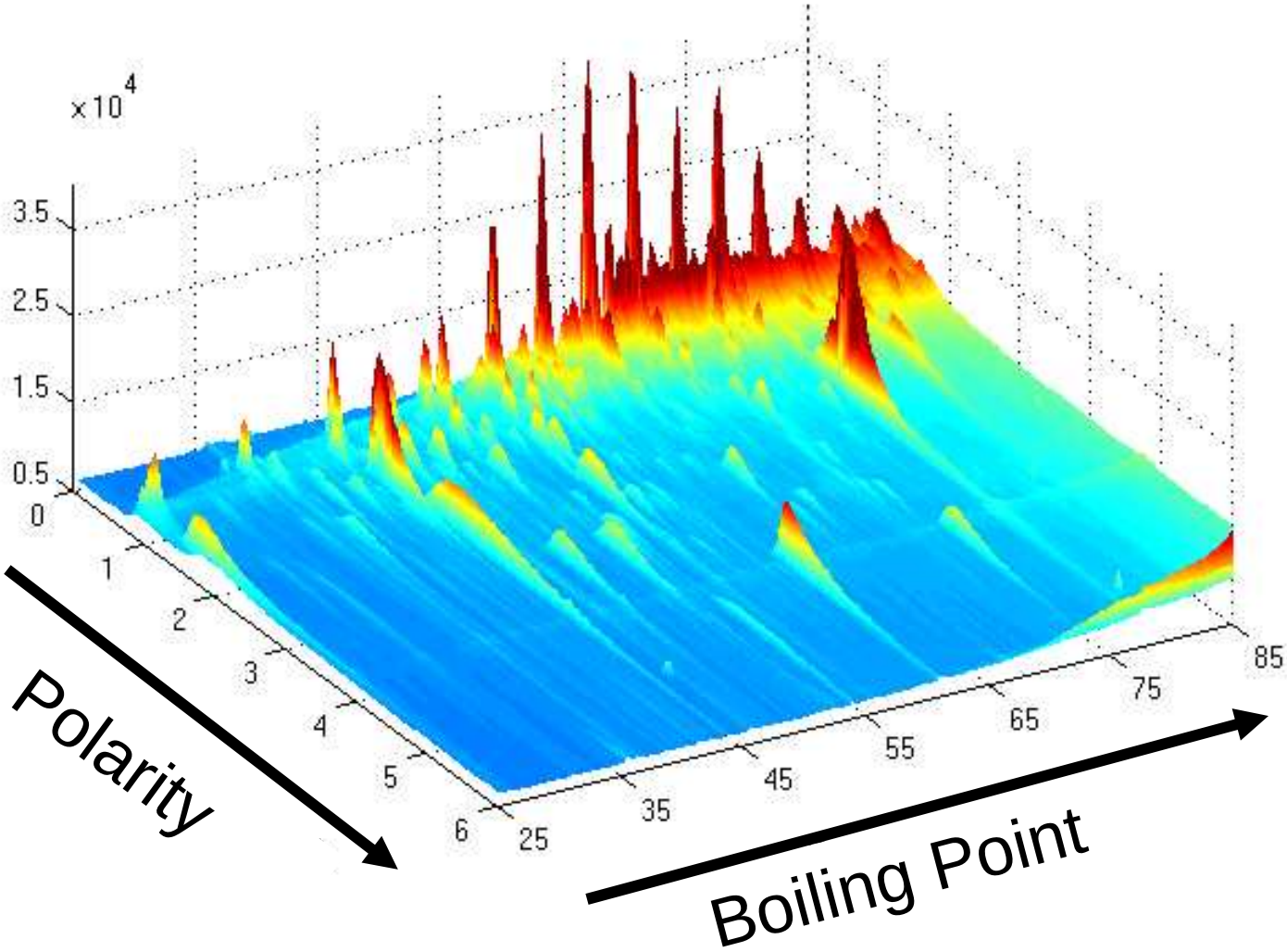
3
4
5
6
25
35
45
55
65
75
85
Polarity
Boiling Point

14:00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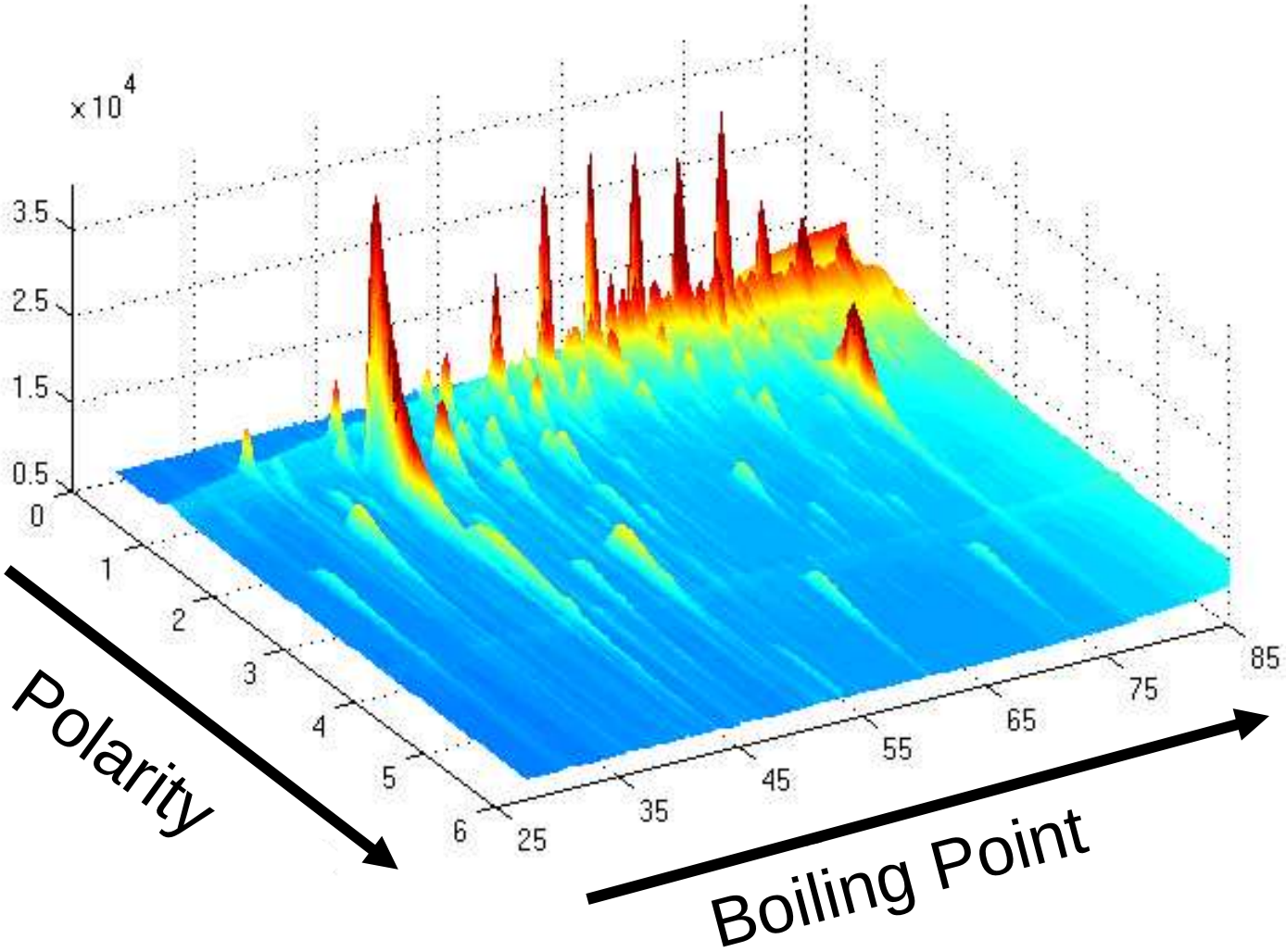
Polarity
Boiling Point

16:00


x 10^4
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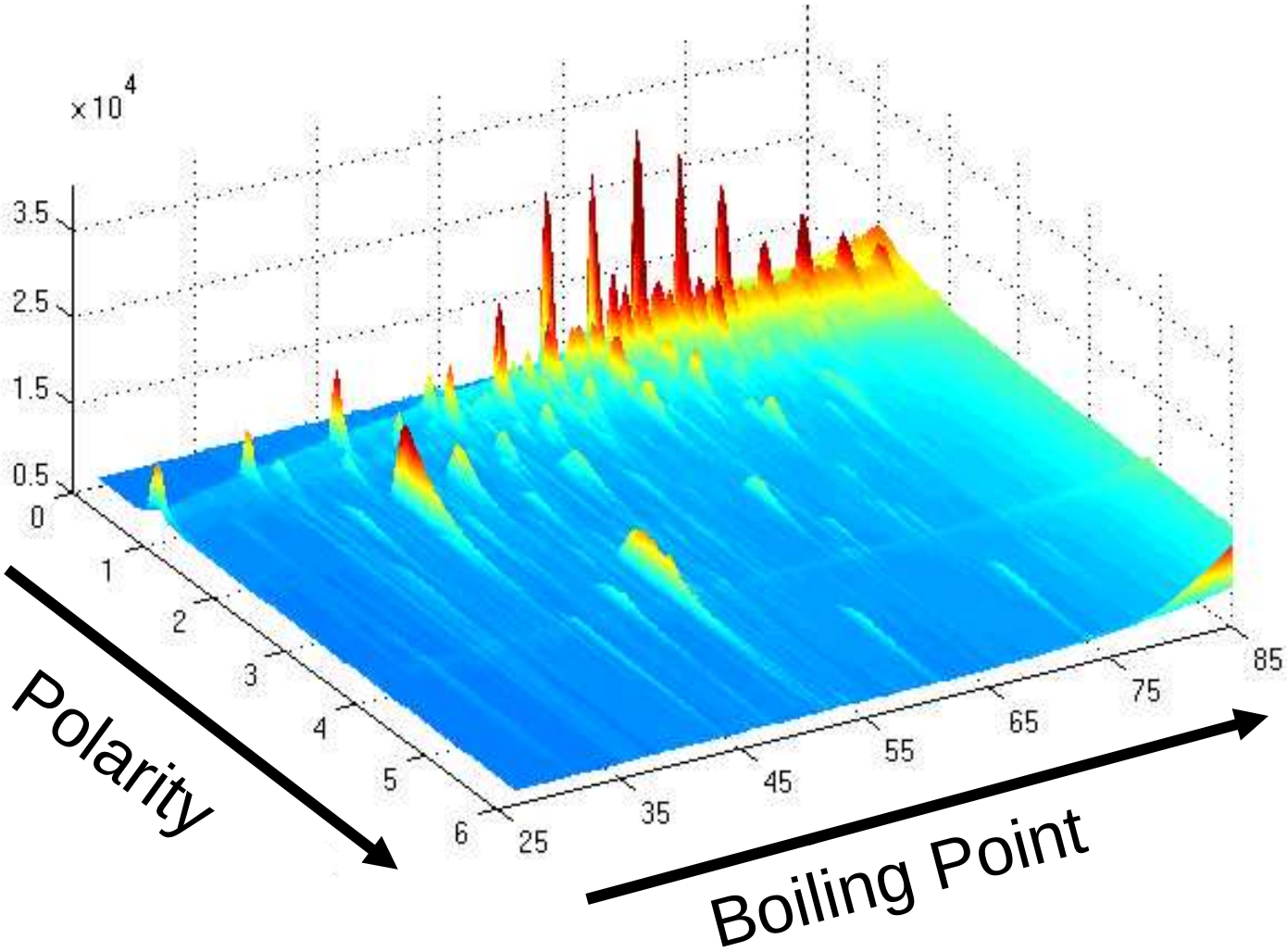
75
85
Polarity
Boiling Point

18:00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Polarity
Boiling Point

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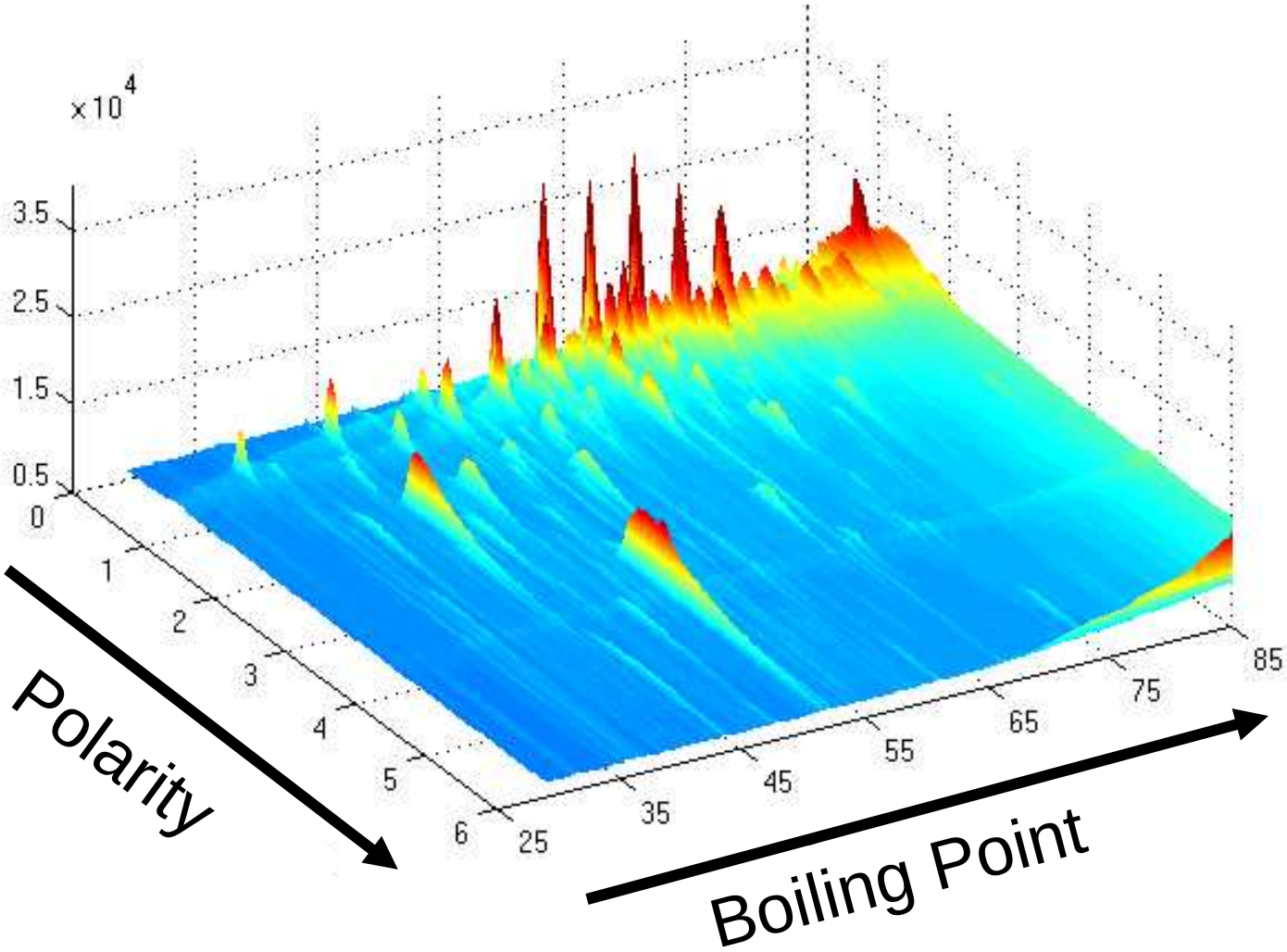
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Polarity
Boiling Point

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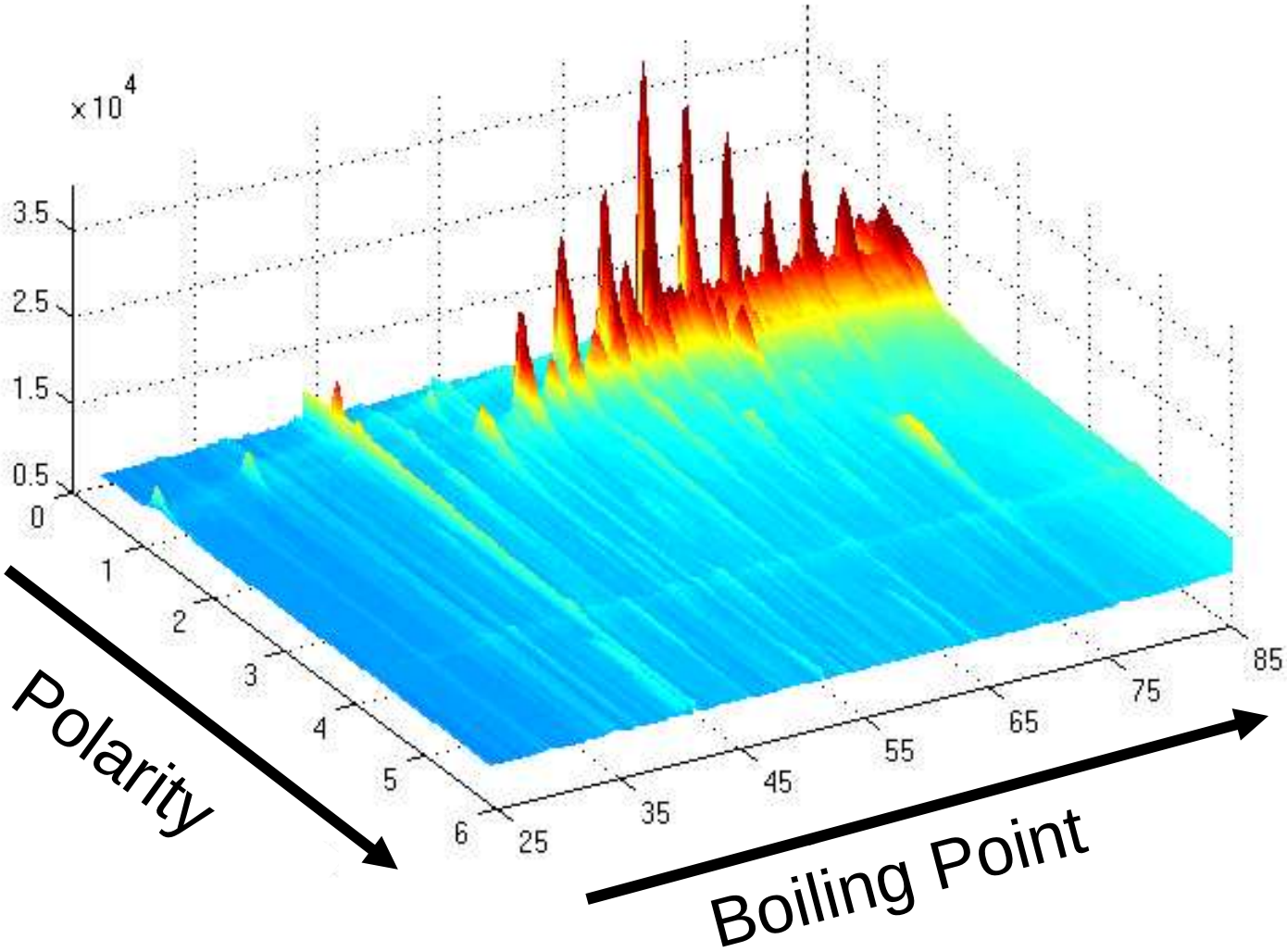
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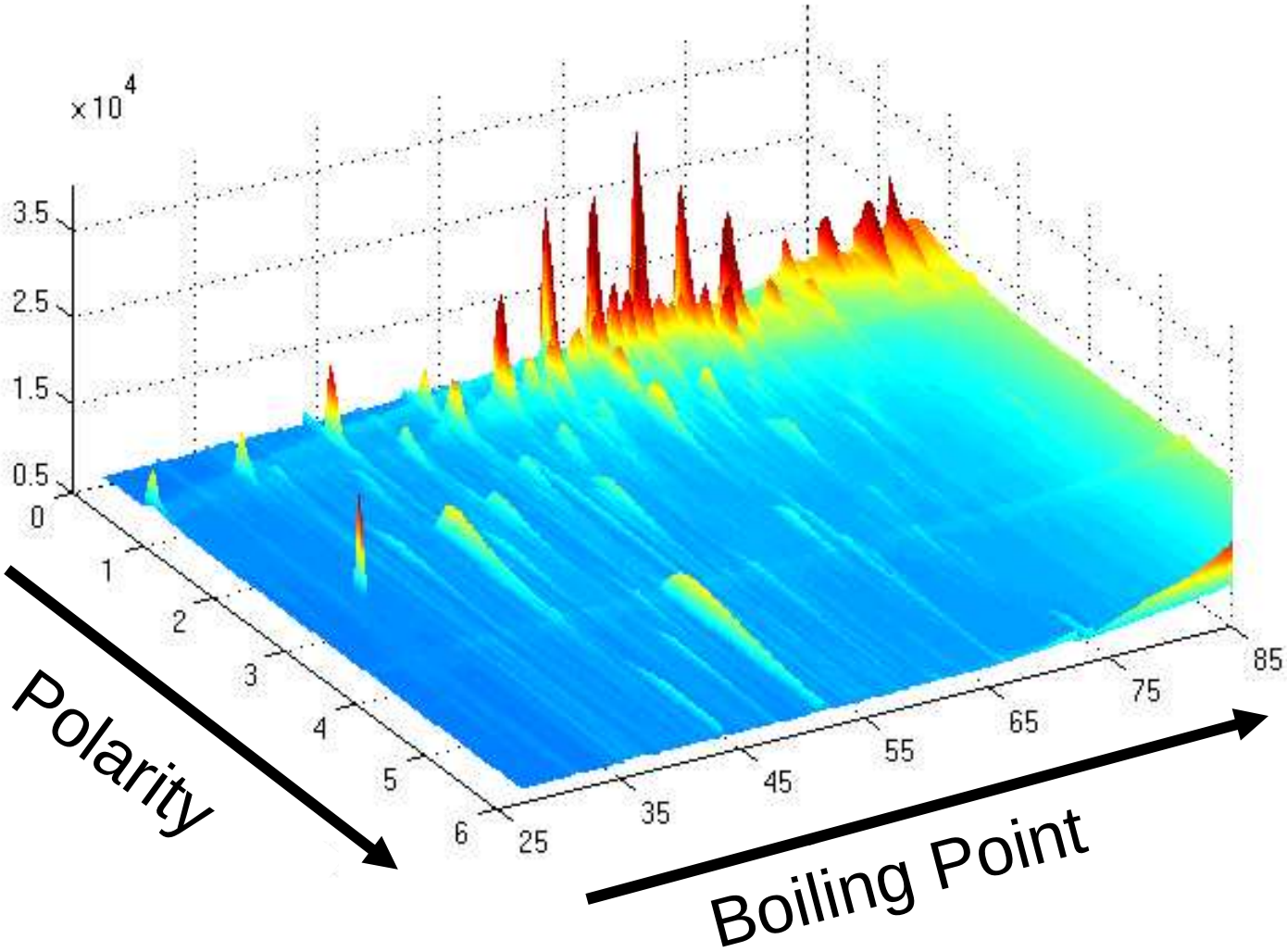
Polarity
Boiling Point

00:00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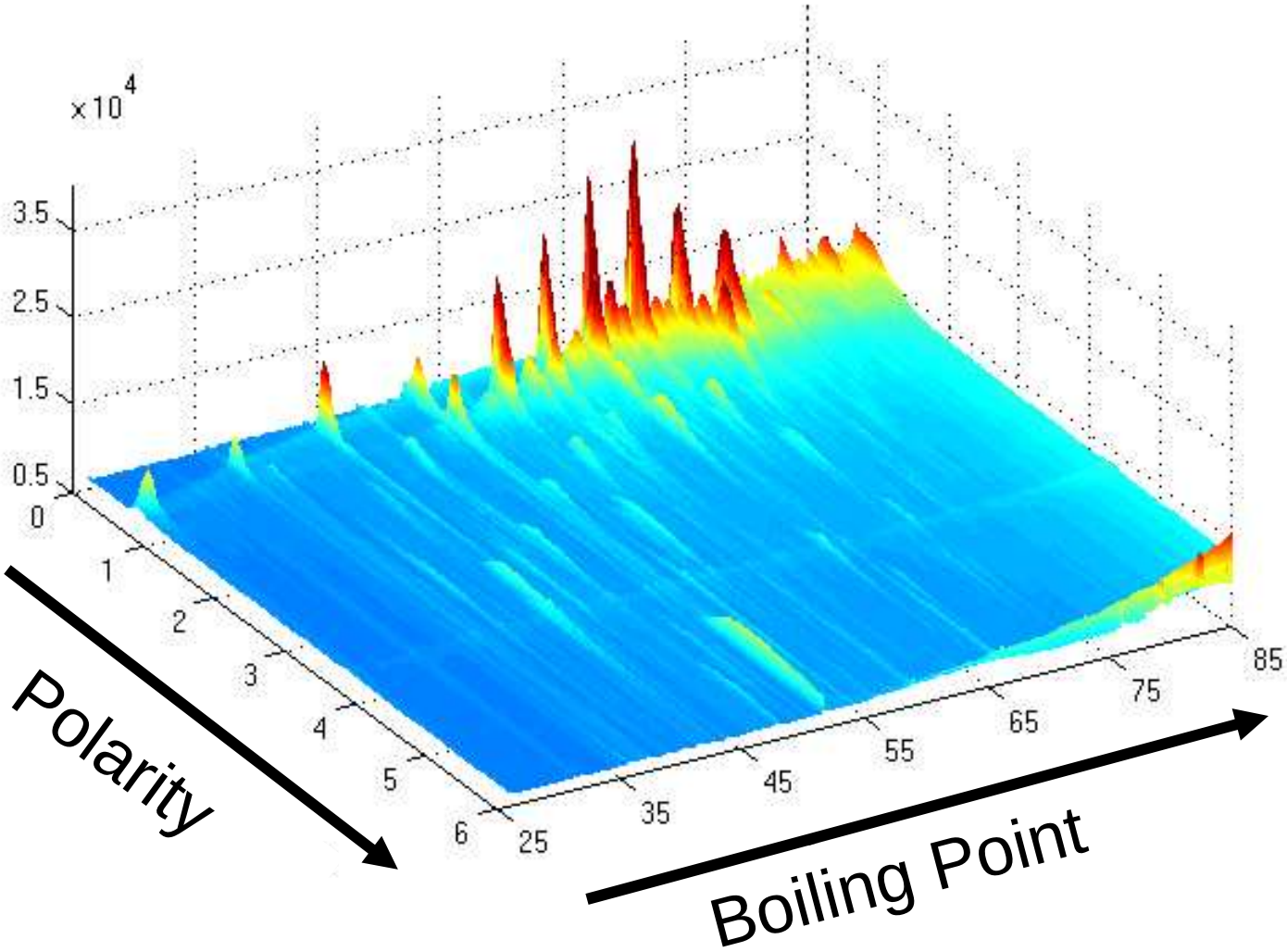
Polarity
Boiling Point

02:00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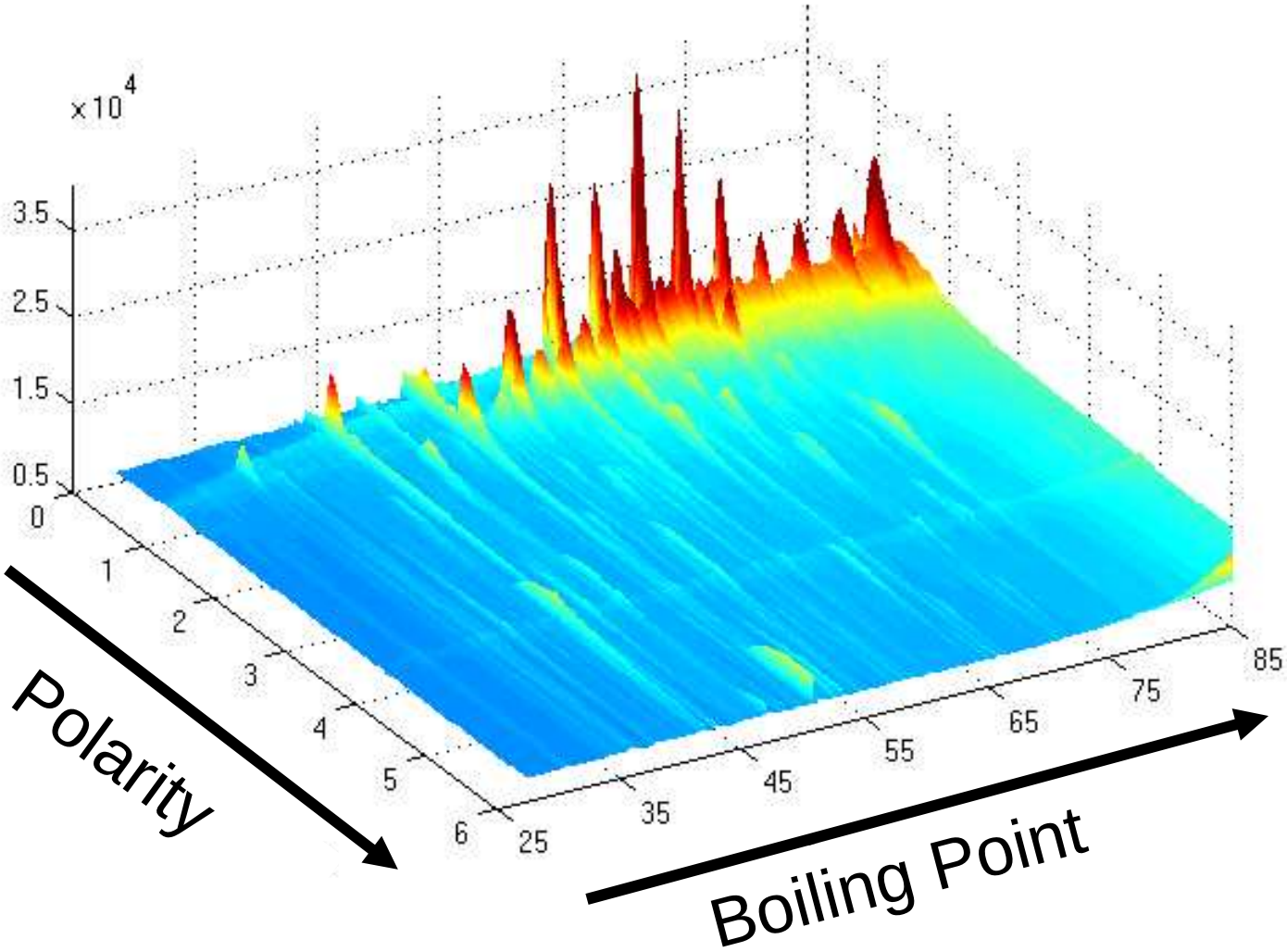
Polarity
Boiling Point

04:00


x 10^4
3.5
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35
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65
75
85
Polarity
Boiling Point

Summary

- **2D TAG-FID is now operational**
- **Optimizing chromatography**
- **Building 2D-TAG with TOF-MS (DOE STTR)**
- **2nd dimension aids identification and quantification**
- **Goal – hourly quantitative timelines for extensive range of marker compounds in ambient aerosols**
- **Data analysis presents many challenges and also opportunities to consider classes of compounds**