Defining Atmospheric Aerosol Sources using Thermal Desorption Aerosol GC/MS-FID (TAG)

Brent J. Williams
Dept. of Environmental Science, Policy, & Management
Ecosystem Sciences Division
University of California, Berkeley

Guiding Professor: Allen H. Goldstein (UC-Berkeley)

DOE Mentor: Tica Novakov (Lawrence Berkeley National Laboratory)

In Collaboration with: Nathan M. Kreisberg, Susanne V. Hering (Aerosol Dynamics Inc.)

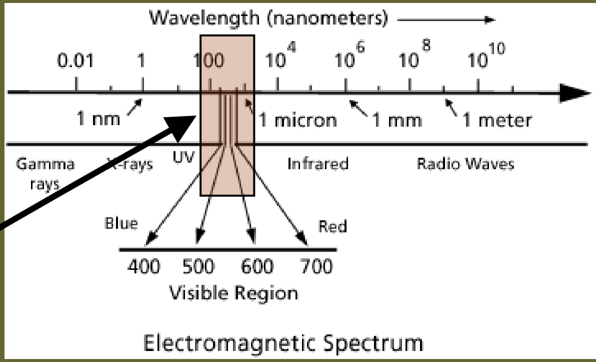
Funding:
Department of Energy: Global Change Education Program
Department of Energy: SBIR Phase I and II; STTR Phase I and II
National Oceanic and Atmospheric Administration: ICARTT 2004
California Air Resources Board: SOAR 2005

August 22, 2006: GCEP End of Summer Workshop, Washington D.C.

ISSUE
(why study aerosols?)

- Atmospheric Aerosols ($PM_{2.5}$):
  - Decreases Atmospheric Visibility
  - Affects H_2O Budget
  - Affects Global Energy Balance
  - Detrimental to Human Health
- Organic portion (avg. 20-50% of total mass) is helpful in determining and understanding:
  - Particle sources
  - Particle formation processes
- Past $PM_{2.5}$ measurements:
  - In-Situ particle (no individual compound separation)
  - Filter collection (12 to 24-hour time resolution)

- Atmospheric Aerosols ($PM_{2.5}$):
  - Decreases Atmospheric Visibility
  - Affects H_2O Budget
  - Affects Global Energy Balance
  - Longest Lifetime of all aerosol sizes



Particle collection range ($PM_{2.5}$)

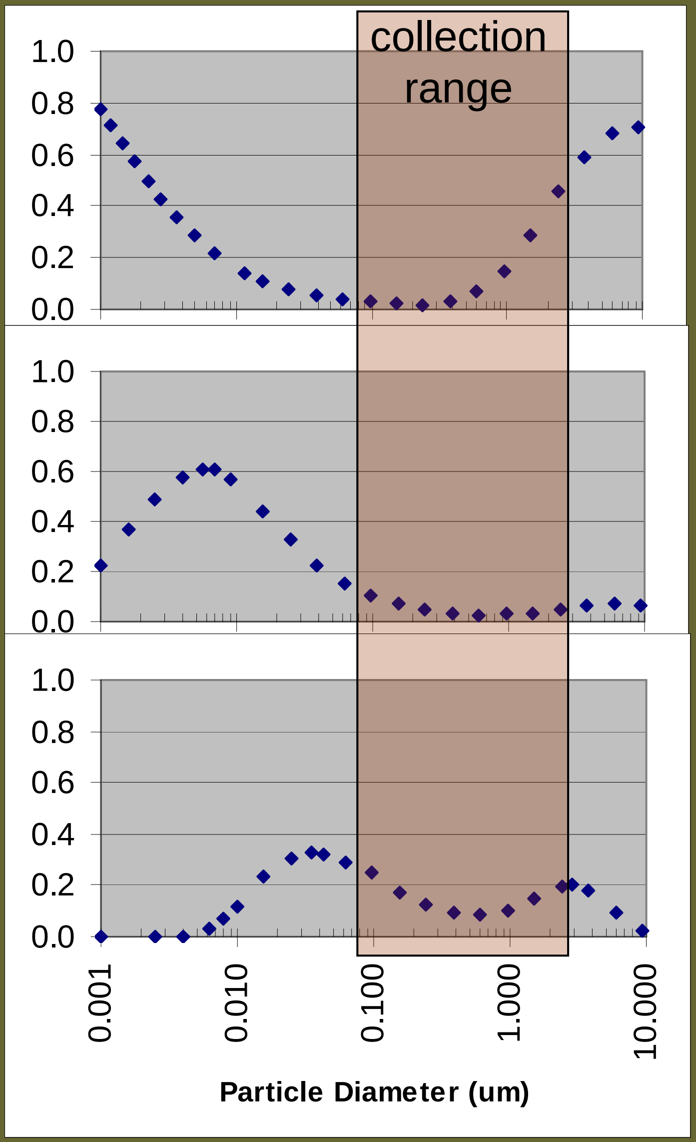
Aerial photograph with adequately clear atmosphere

Aerial photograph with a smoke filled atmosphere

Olympus Aerial Surveys, Inc.

- Atmospheric Aerosols ($PM_{2.5}$):
  - Detrimental to Human Health

Deposition efficiency of inhaled particles in the respiratory tract.



Naso-Oro-Pharyngeal-Laryngeal (NOPL)

Tracheobronchial (TB)

Pulmonary (no cleaning mechanism)

-Bulk of ETS mass in this size range
-Wood and meat smoke
-Secondary Organic Aerosols

HC Yeh et al., Aerosol Science & Technology, 25, 134-140, 1996.

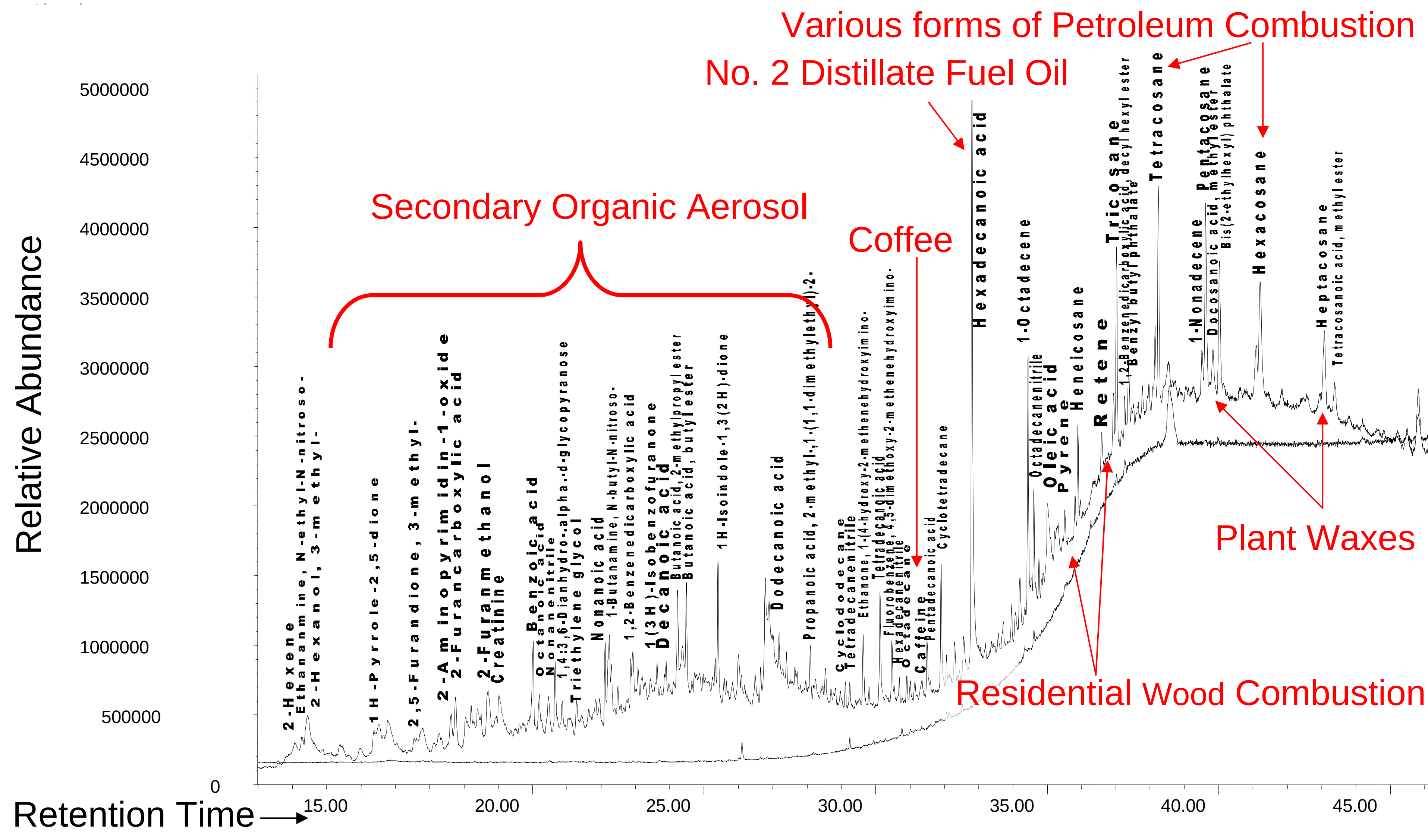
ISSUE
(why study the organic fraction?)

- Atmospheric Aerosols ($PM_{2.5}$):
  - Decreases Atmospheric Visibility
  - Affects Regional H_2O Budget
  - Affects Global Energy Balance
  - Detrimental to Human Health

- Organic portion (avg. 20-50% of total mass) is helpful in determining and understanding:
  - Particle sources
  - Particle formation processes

- Past $PM_{2.5}$ measurements:
  - In-Situ particle (no individual compound separation)
  - Filter collection (12 to 24-hour time resolution)

- Organic portion (20-50% of total mass) is helpful in determining and understanding:
  - Particle sources
  - Particle formation processes



ISSUE
(what needs improvement?)

- Atmospheric Aerosols ($PM_{2.5}$):
  - Decreases Atmospheric Visibility
  - Affects Regional H_2O Budget
  - Affects Global Energy Balance
  - Detrimental to Human Health

- Organic portion (avg. 20-50% of total mass) is helpful in determining and understanding:
  - Particle sources
  - Particle formation processes

- Past $PM_{2.5}$ measurements:
  - In-Situ particle (no individual compound separation)
  - Filter collection (12 to 24-hour time resolution)

- Creates a need for an instrument capable of:
  - Separating / Identifying / Quantifying individual organic marker compounds from ambient $PM_{2.5}$
  - In-Situ, Automated measurements
  - 1-hour time resolution (to track diurnal changes)

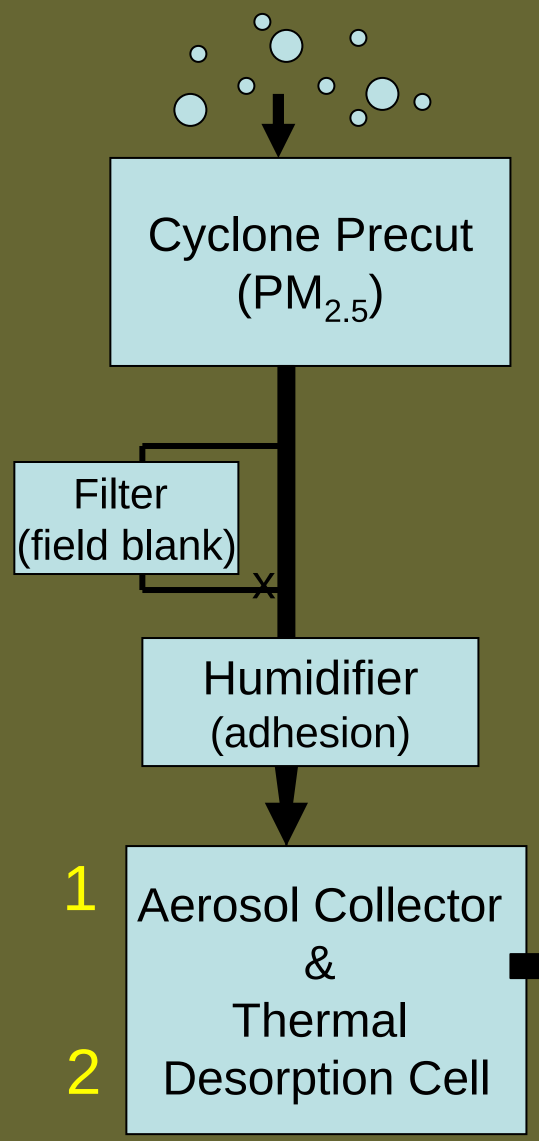
- Creates a need for an instrument capable of:
  - Separating / Identifying / Quantifying individual organic marker compounds from ambient $PM_{2.5}$
  - In-Situ, Automated measurements
  - 1-hour time resolution (to track diurnal changes)

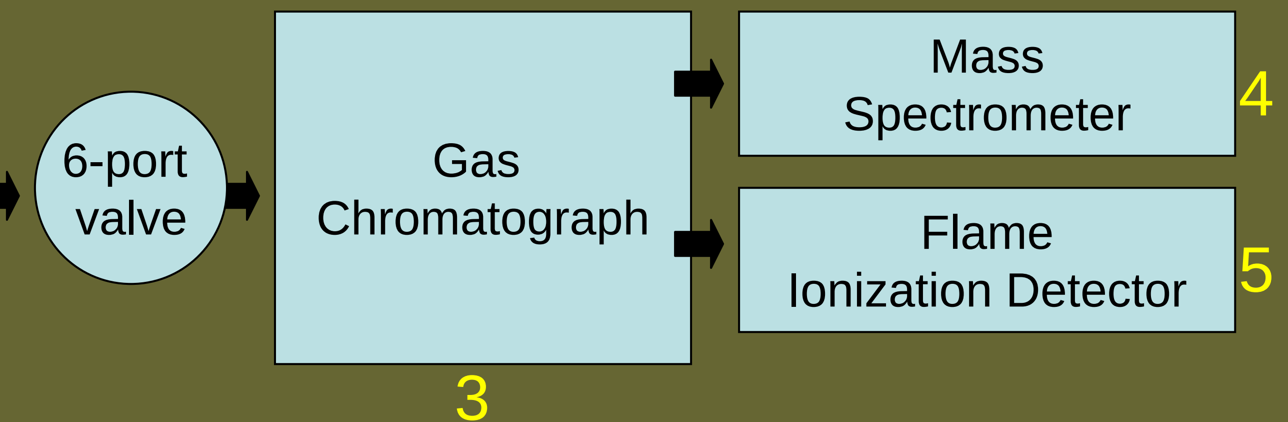
→ Thermal Desorption Aerosol GC/MS-FID (TAG)

APPROACH

TAG: Thermal Desorption Aerosol GC/MS-FID

1. Collection technique:
   – Inertial Impaction (30^0C)
2. Sample transfer:
   – Thermal Desorption ($50\text{-}300^0$C)
3. Chemical separation:
   – Gas Chromatography
4. Compound identification:
   – Mass Spectrometry (Quadrupole)
5. Compound quantification:
   – Flame Ionization Detection



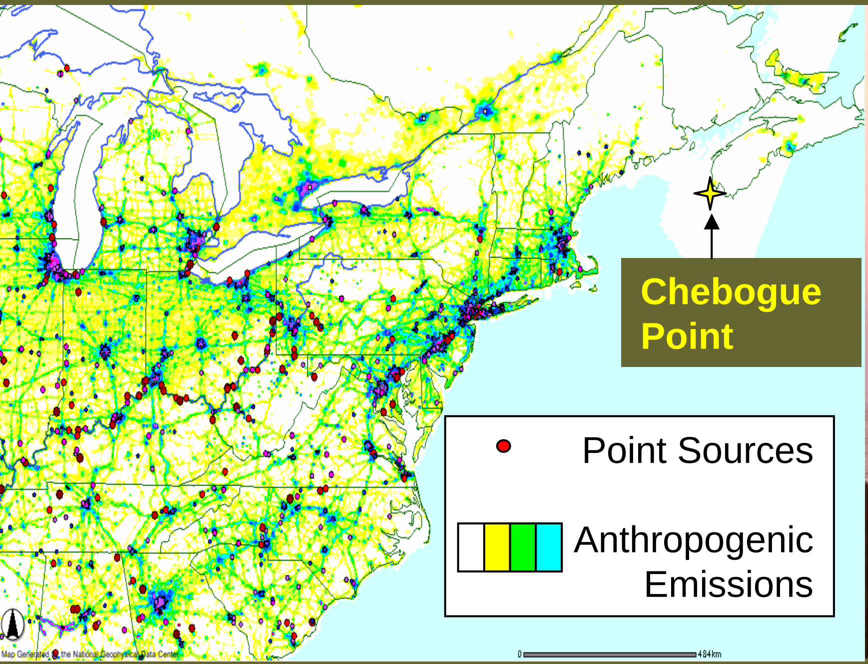


TAG Applications To Date

- In-Laboratory Trial Runs
  - UC Berkeley
    - ambient sampling on campus
  - ADI in Berkeley
    - ambient sampling in business district

- 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

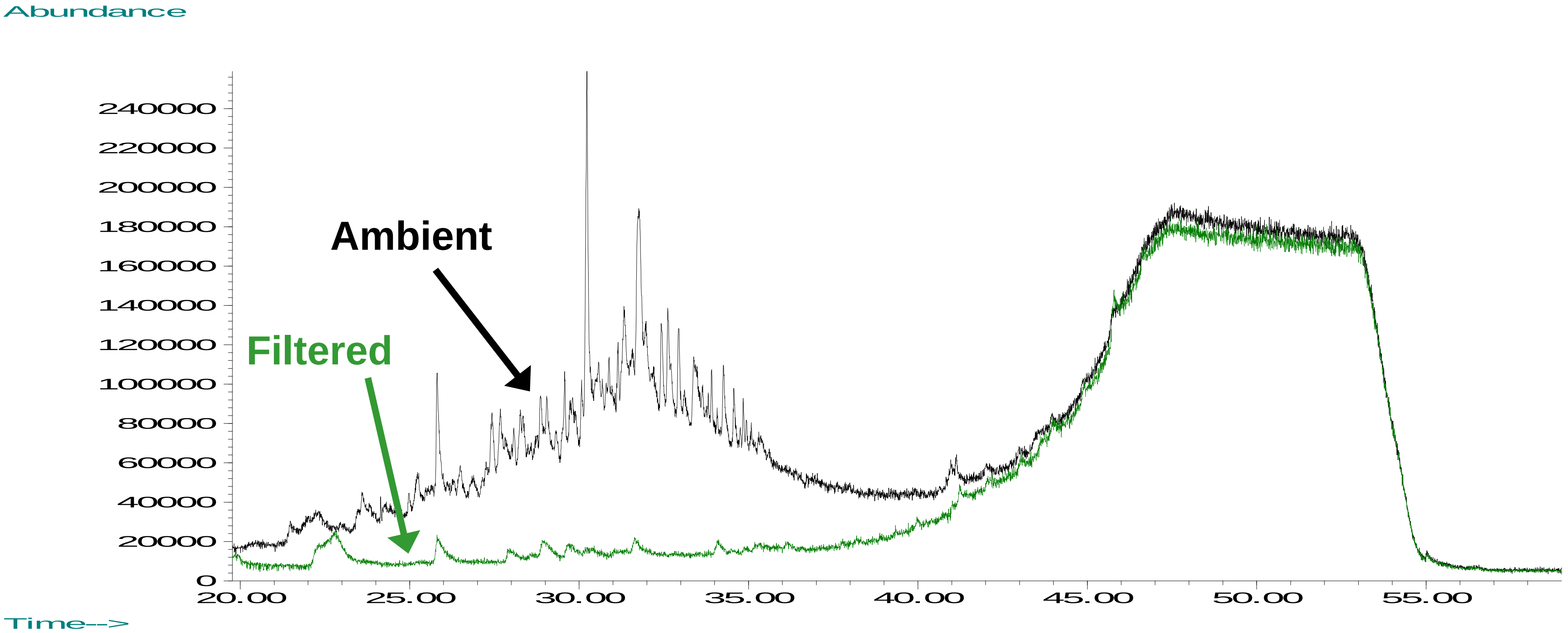
ICARTT Measurements at Chebogue Point



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

- ICARTT campaign at Chebogue Point during summer of 2004.
- Full range of meteorological, radiation, trace gas, and aerosol measurements
- TAG analysis focused on period of July 26 – Aug.15, 2004 (~3 weeks)
- Hourly data (750 chromatograms x 2 detectors)
- Manual calibration with directly applied standards
- Automated filtered and zero air blanks

TAG
Chebogue Point, Nova Scotia
ICARTT 2004



Location: Chebogue Point, Nova Scotia. August 7, 2004
Sample time: 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

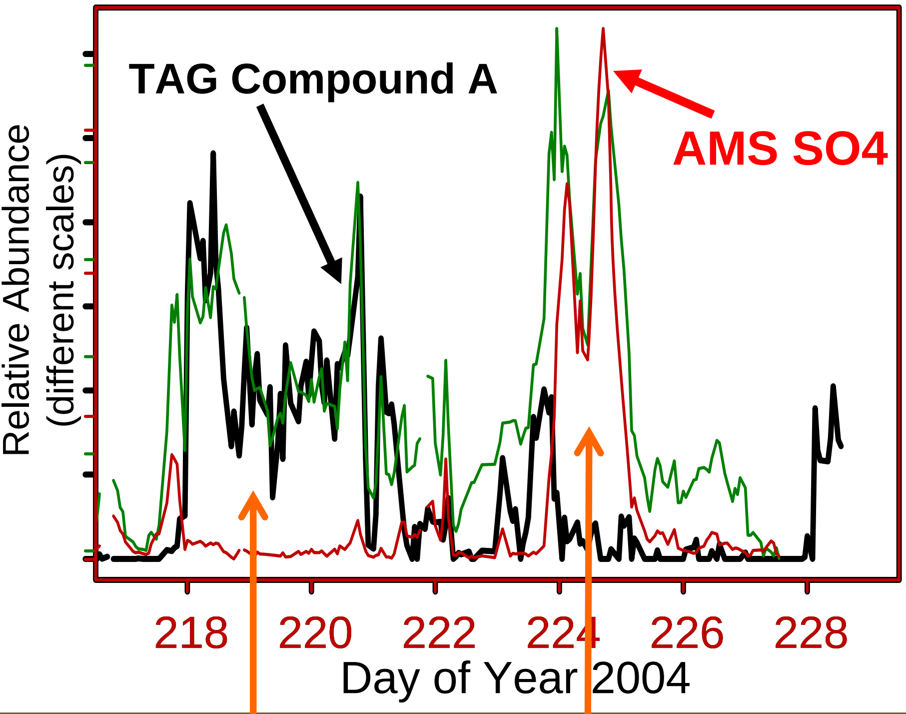
Total Organic Aerosol = (Resolved Compounds + Unresolved Compounds + Non-Eluting Compounds)

Resolved compounds will determine the aerosol source

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

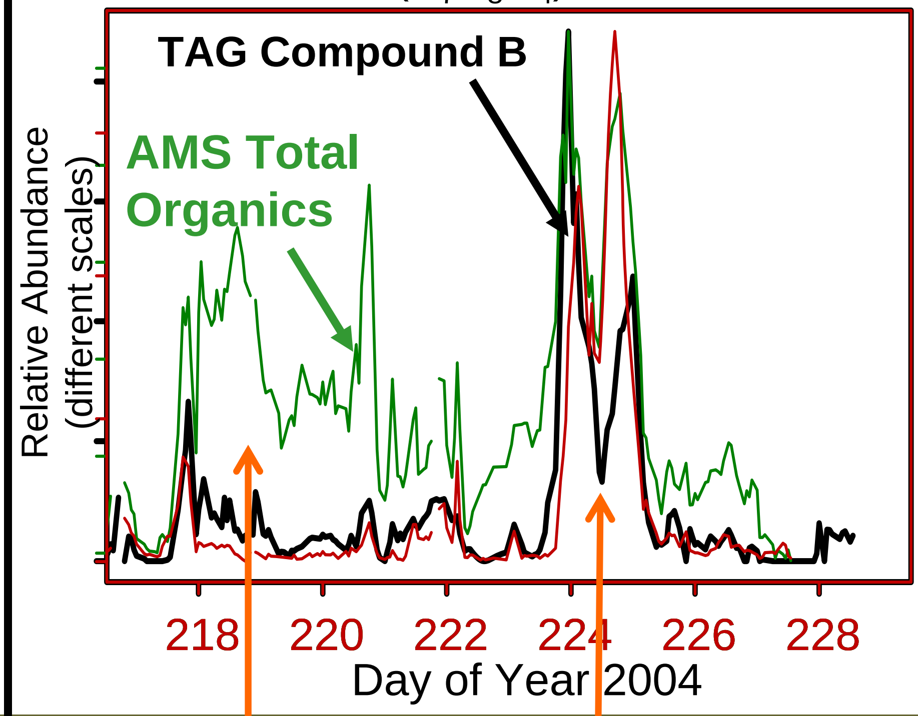
Compound: A

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 ($C_7H_8O_4$)



Event Type 1
No SO4

Event Type 2
SO4

Event Type 1
No SO4

Event Type 2
SO4

AMS data supports the fact that these two compounds represent two different events.

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

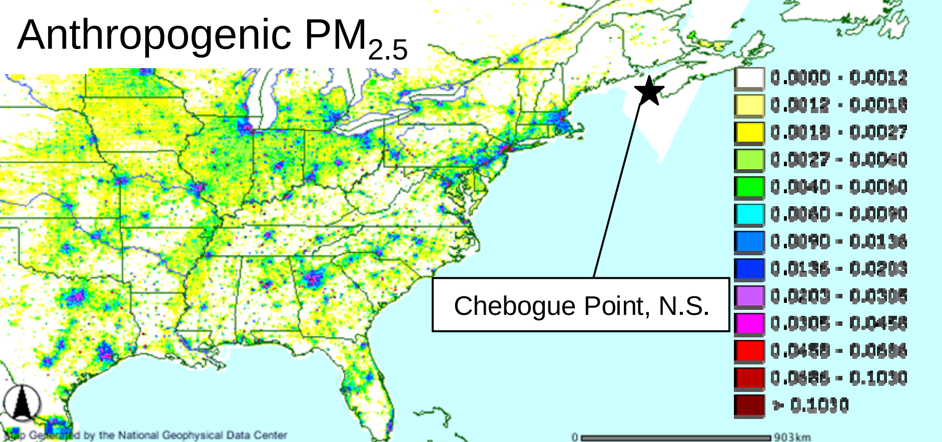
FACTOR ANALYSIS

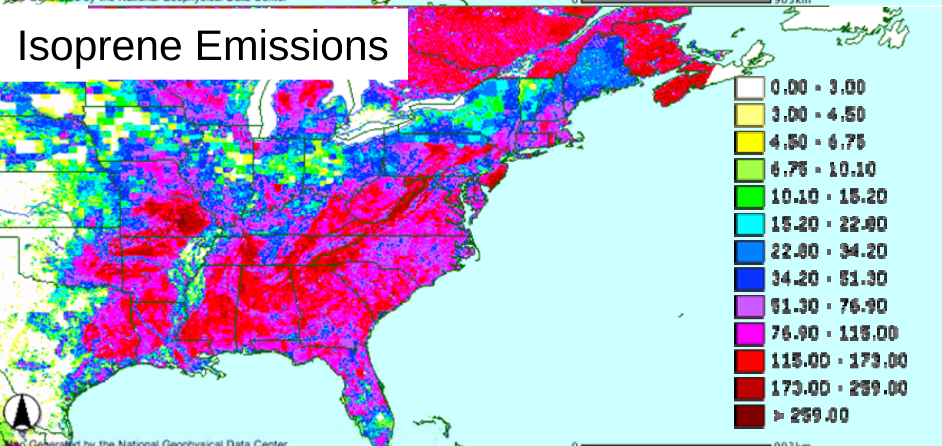
- Data in Principal Component Factor Analysis
  - 37 resolved TAG organic compounds
  - O3, CO, Radon
  - AMS (Organic carbon, SO_4^{2-},NO_3^-,NH_4^+)

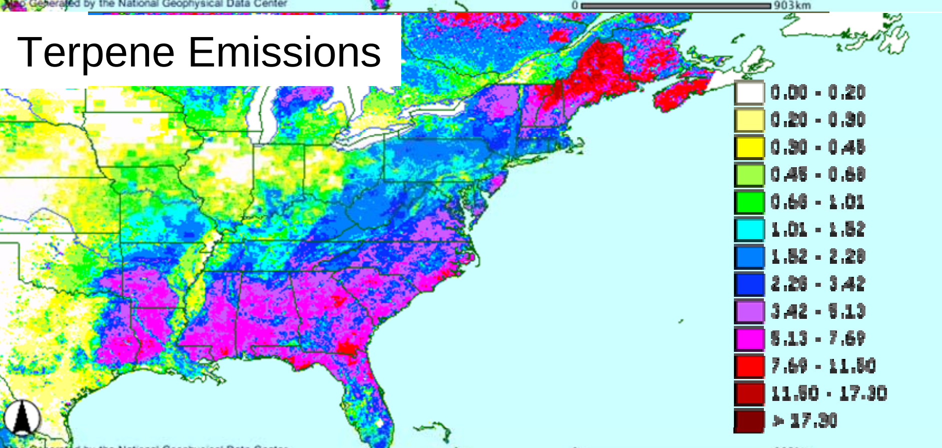
- See how these 44 components vary with each other
  - Factor analysis finds some underlying process or source type

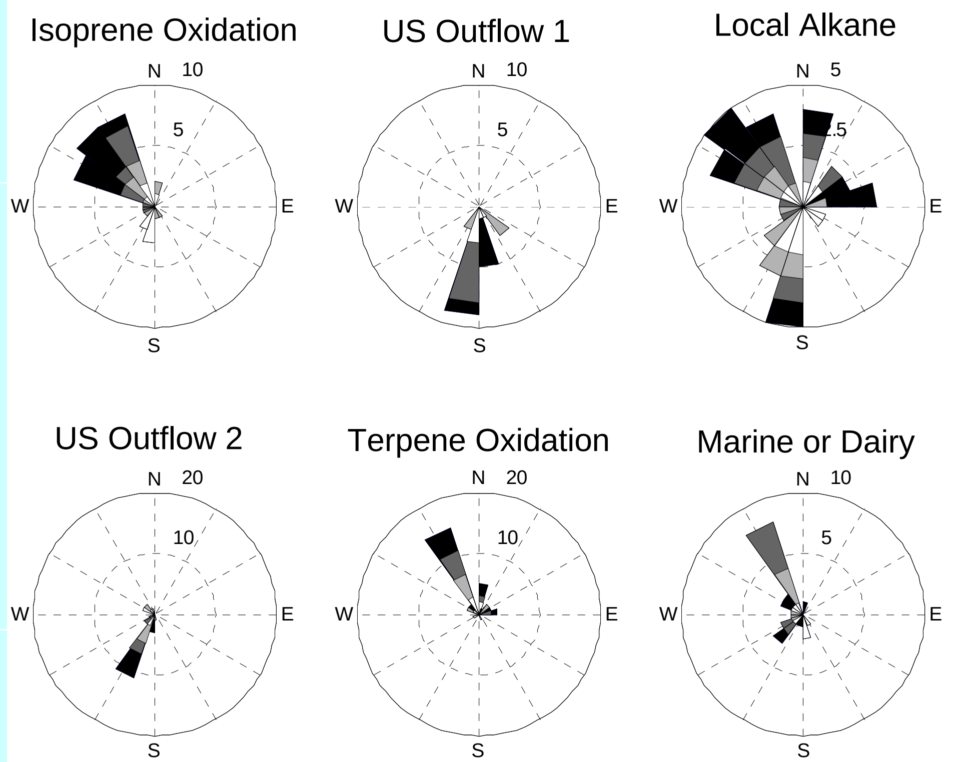
- Have identified 6 major organic aerosol sources
  - Factor 1: Isoprene Oxidation
  - Factor 2: US Outflow type 1
  - Factor 3: Local Alkane Emission
  - Factor 4: US Outflow type 2
  - Factor 5: Terpene Oxidation
  - Factor 6: Marine or Dairy

6 Particle Sources







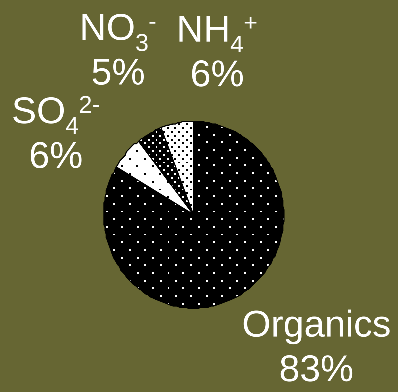


- Shade of wedge = Intensity of events
- Length of wedge = Frequency of events

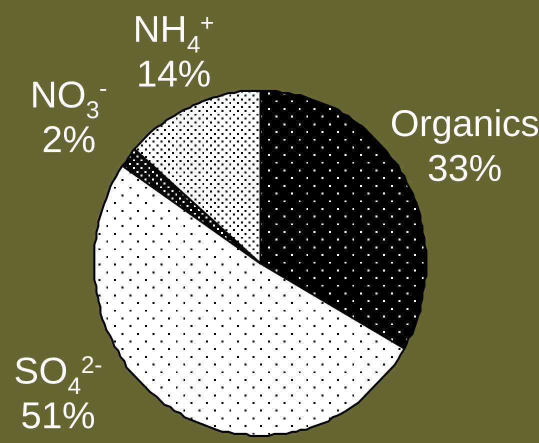
NOAA-NESDIS/OAR Emission Inventory Mapviewer: (http://map.ngdc.noaa.gov/website/al/emissions/viewer.htm)

AMS speciation during TAG-defined events

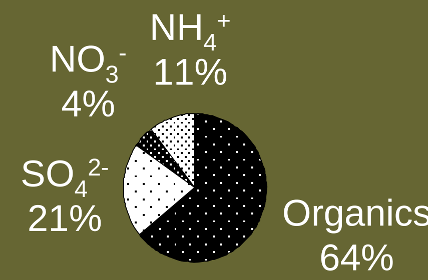
Isoprene Oxidation



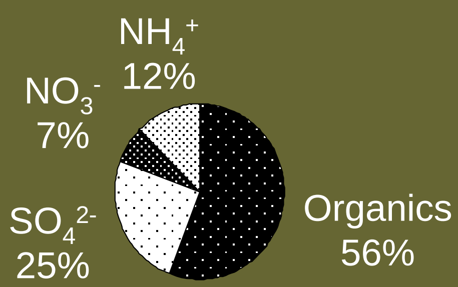
US Outflow 1



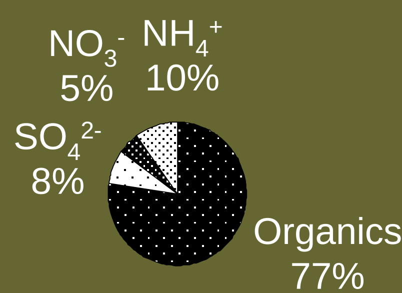
Local Alkane



US Outflow 2



Terpene Oxidation



Marine or Dairy

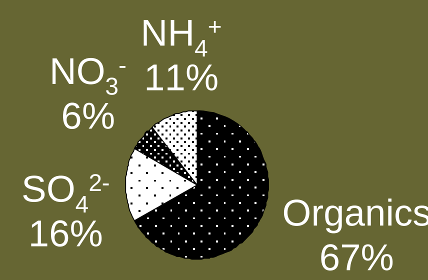


Chart size scaled to average aerosol concentration for each factor

ICARTT CONCLUSIONS

- TAG instrument successfully deployed
- First in-situ hourly measurements of speciated ambient organic aerosol composition
- Analysis of 37 TAG compounds
  - See 6 distinct source types, each w/ different organic marker compounds
- Organic aerosol in Nova Scotia is consistently composed of mostly oxygenated compounds that are both biogenic and anthropogenic in origin

SOAR 2005 Status

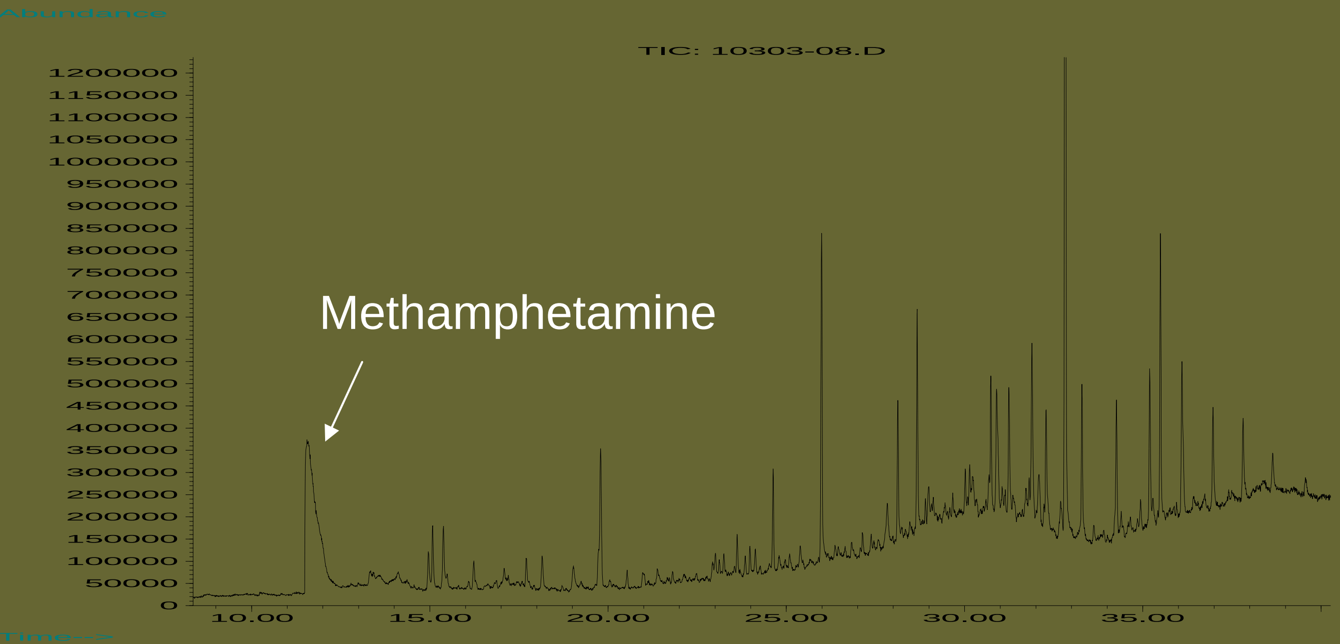
Riverside, CA

- Overview
  - 5 weeks in summer, 5 weeks in fall
  - Large suite of aerosol instrumentation

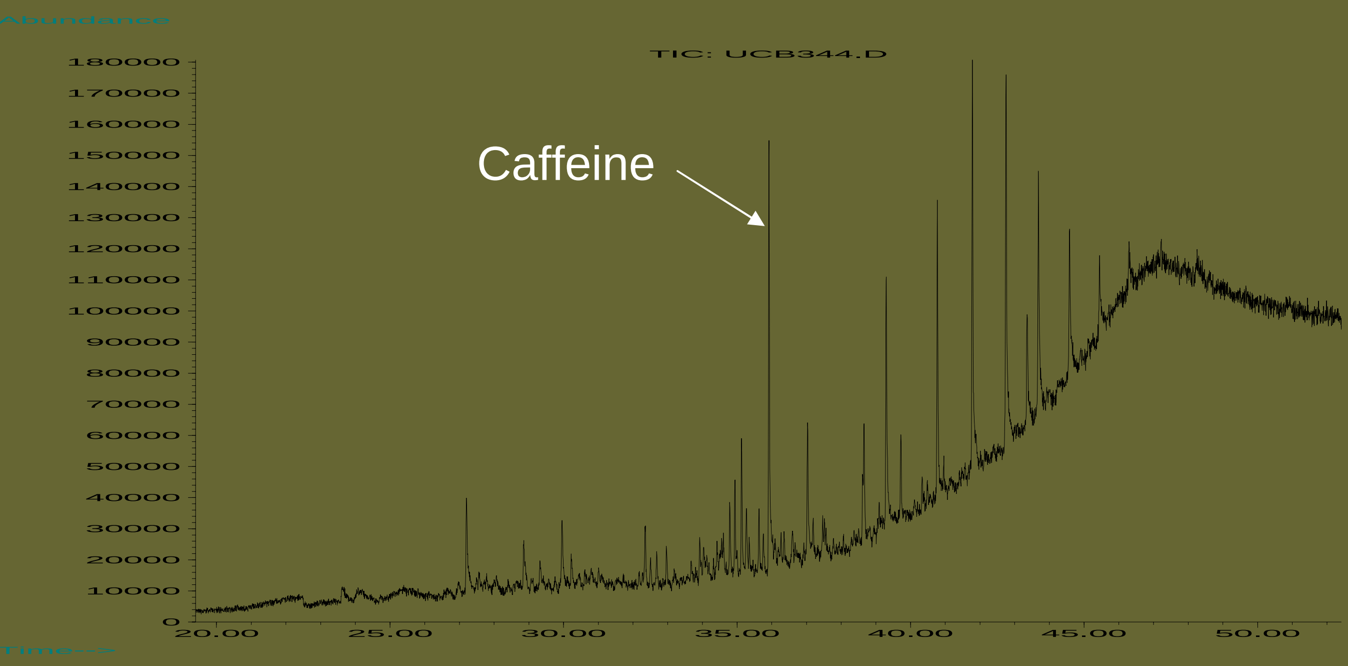
- TAG identified over 300 ambient compounds w/ various sources
  - Gasoline
  - Diesel
  - Plastics
  - Biogenics
  - Pesticides
  - Wood combustion
  - Plus many secondary organic sources

- Still integrating chromatograms
  - 1,530 hours from summer and fall
  - 2 detectors
  - 300 compounds
  - 918,000 peaks to integrate

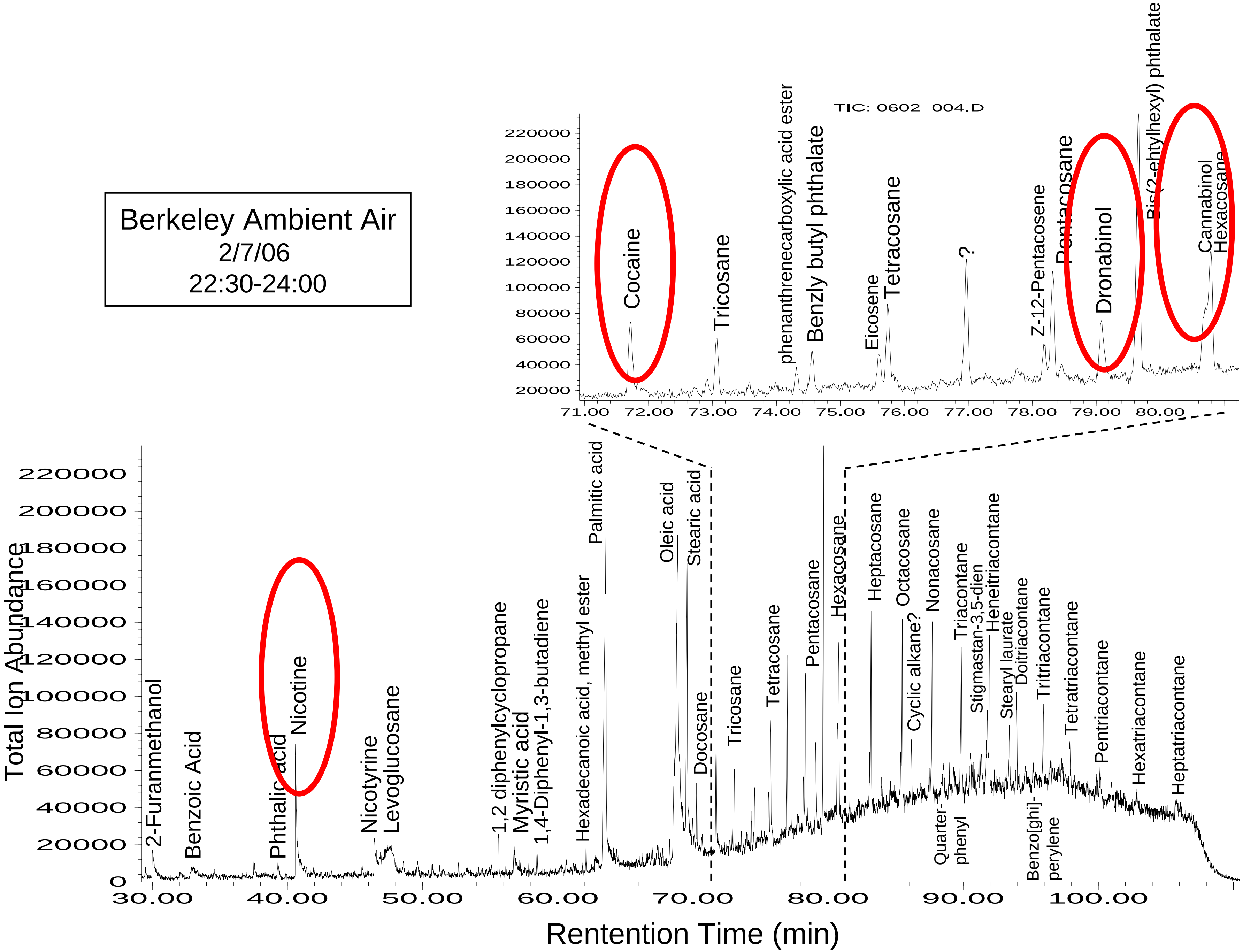
Interesting Discoveries in Berkeley



Nighttime in the warehouse district



Morning on Campus


Berkeley Ambient Air
2/7/06
22:30-24:00
TIC: 0602_004.D
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
71.00
72.00
73.00
74.00
75.00
76.00
77.00
78.00
79.00
80.00
Cocaine
Tricosane
phenanthrenecarboxylic acid ester
Benzly butyl phthalate
Eicosene
Tetracosane
?
Z-12-Pentacosene
Pentacosane
Dronabinol
Bis(2-ehtylhexyl) phthalate
Cannabinol
Hexacosane
Total Ion Abundance
0
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
Rentention Time (min)
2-Furanmethanol
Benzoic Acid
Phthalic acid
Nicotine
Nicotyrine
Levoglucosane
1,2 diphenylcyclopropane
Myristic acid
1,4-Diphenyl-1,3-butadiene
Hexadecanoic acid, methyl ester
Palmitic acid
Oleic acid
Stearic acid
Docosane
Tricosane
Tetracosane
Pentacosane
Hexacosane
Heptacosane
Octacosane
Cyclic alkane?
Nonacosane
Quarter-
phenyl
Triacontane
Stigmastan-3,5-dien
Heneitriacontane
Stearyl laurate
Doitriacontane
Benzo[ghi]-
perylene
Tritriacontane
Tetratriacontane
Pentriacontane
Hexatriacontane
Heptatriacontane

Future Plans for TAG

- Development
  - 2 Dimensional TAG w/ TOF mass spectrometer (STTR grant)
    - Increase number of compounds from several hundred to several thousand
  - Online Chemical Derivatization Technique
    - Analyze more polar compounds
  - Commercialize 1 dimensional TAG (phase 3 of SBIR grant)
    - TSI
    - Marketing as a tool in atmospheric science, drug enforcement, and chemical warfare detection

- Planned Atmospheric Science Studies
  - Pittsburgh, PA (urban aerosol)
  - Blodgett Forest, CA (biogenic aerosol)
  - San Joaquin Valley, CA (agriculture influenced aerosol)

ACKNOWLEDGMENTS

VOC and Meteorological Data
UC-Berkeley
Dylan Millet, Megan McKay

AMS Data
Aerodyne Research, Inc. / University of Manchester, UK / University of Colorado, Boulder
Allan, Cross, DeCarlo, Northway, Canagaratna, Huffman, Jimenez, Coe, Worsnop

Radon Data
U. Washington, Bothell
Dan Jaffe, Isaac Bertschi

Backtrajectories
NOAA
Allen White

Funding:

Department of Energy: Global Change Education Program

Department of Energy: SBIR Phase I and II; STTR Phase I and II

National Oceanic and Atmospheric Administration: ICARTT 2004

California Air Resources Board: SOAR 2005

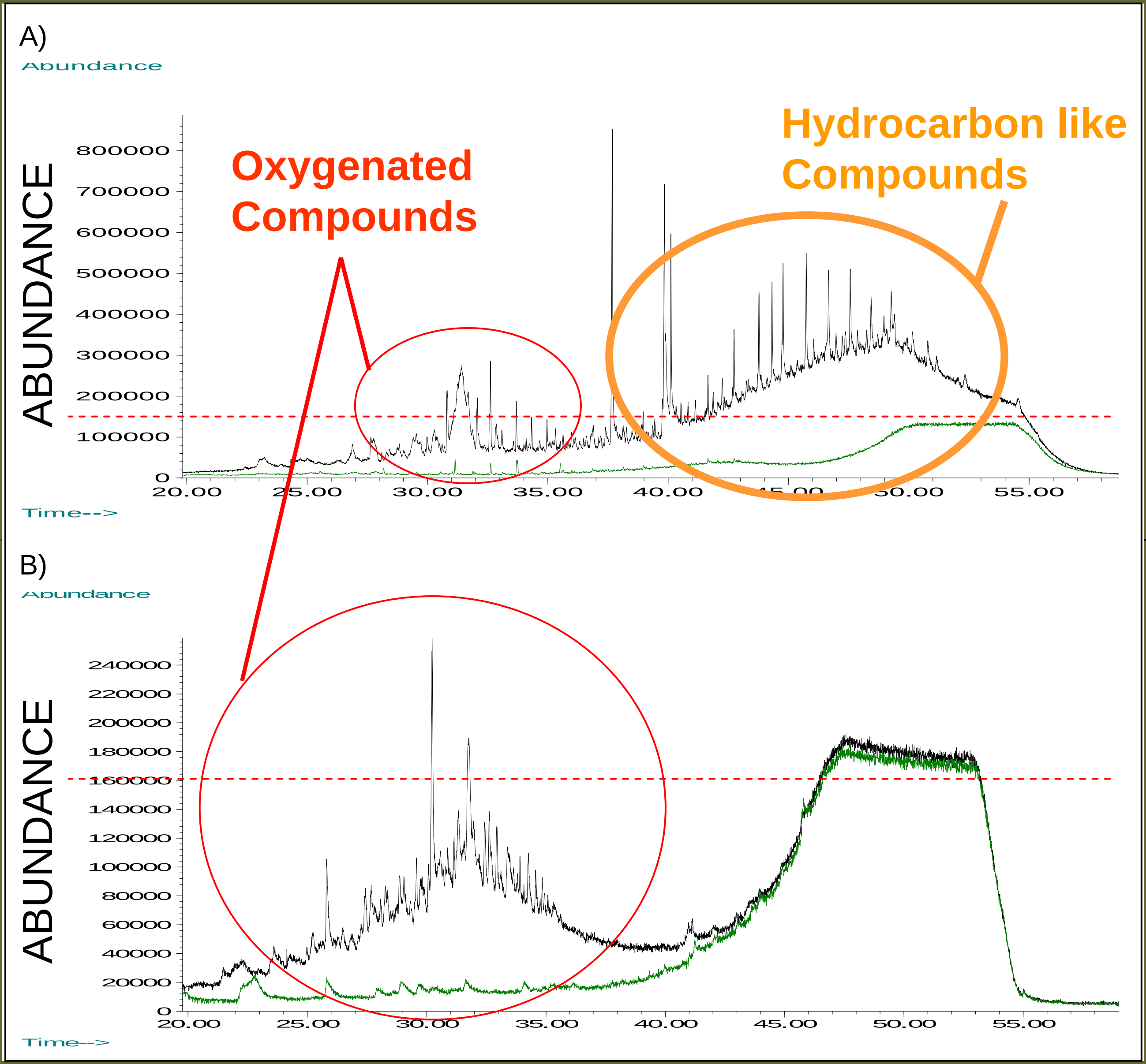
For Detailed TAG description:

Williams, B.J., A.H. Goldstein, N.M. Kreisberg, S.V. Hering (2006) An In-Situ Instrument for Speciated Organic Composition of Atmospheric Aerosols: Thermal Desorption Aerosol GC/MS-FID (TAG), *Aerosol Sci. and Technol.*, 40, 627-638.

EXTRA SLIDES

ASIDE:

-Compounds collected in Nova Scotia are extremely oxygenated
-Difficult to identify using only mass spectra database



Berkeley, CA
Winter Evening 2004

Resolved Compounds Matched by Palisade library: **85%**

Nova Scotia, Canada
Summer Evening 2004

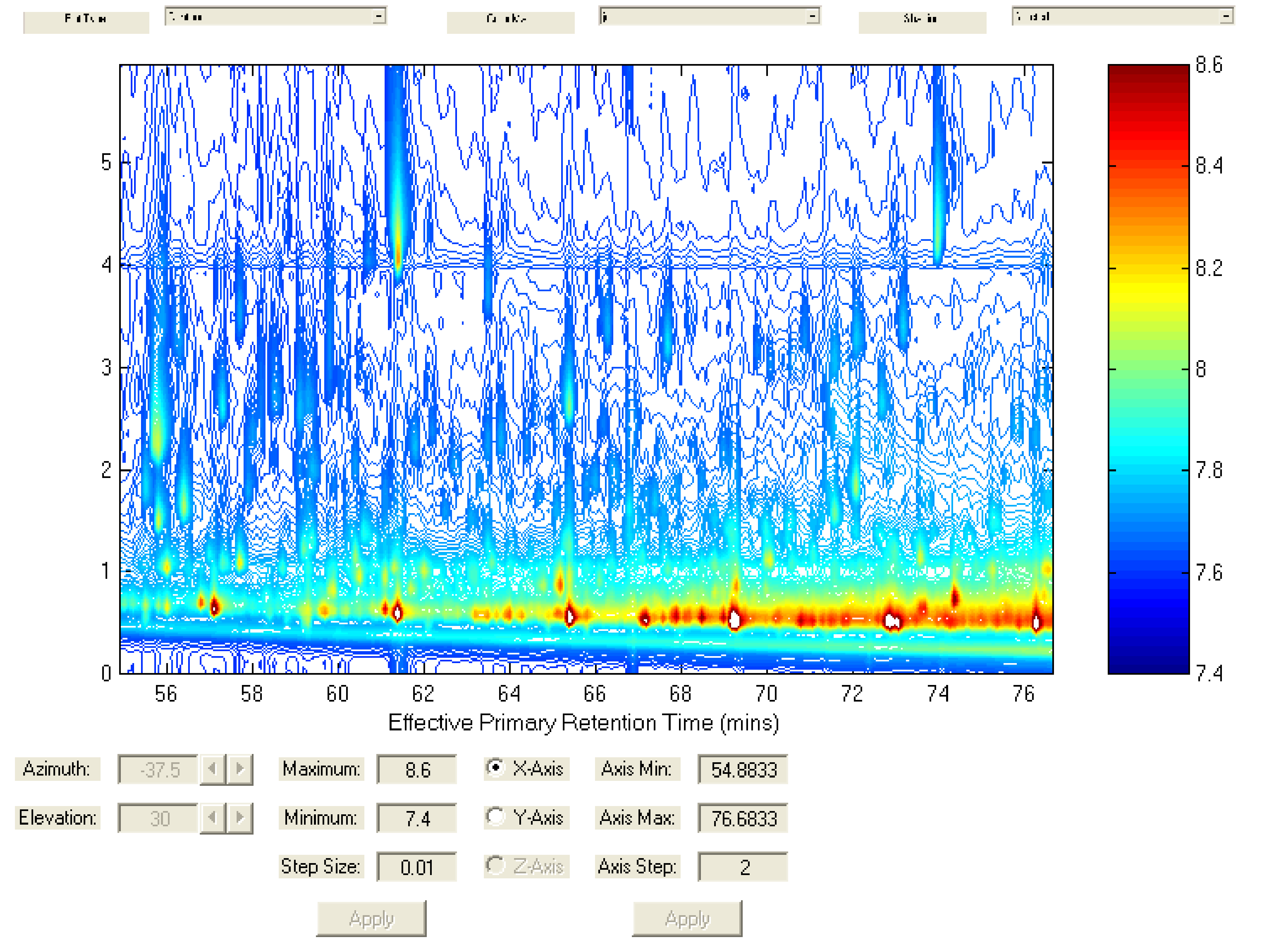
Resolved Compounds Matched by Palisade library**:** **50%**

The dotted red line represents equivalent abundance between graphs A and B.

Table 3. Impact periods of TAG factors during July 26 – August 15, 2004.

Factor	Source Description	Impact Periods: Avg. Windspeed ($m\ s^{-1}$)	Avg. Duration (h)	Percentage of Total Time (%)	Avg. Aerosol Concentration ($\mu g\ m^{-3}$)	Avg. Organics Concentration ($\mu g\ m^{-3}$)	Relative Importance for Organics
F1	Isoprene Oxidation	3.3	6.7	10.5	6.8	5.7	1.00
F2	U.S. Outflow 1	4.7	31.0	6.9	21.9	7.3	0.84
F3	Local Alkane	1.7	6.5	11.6	4.3	2.8	0.54
F4	U.S. Outflow 2	4.0	4.3	7.6	6.0	3.3	0.43
F5	Terpene Oxidation	2.4	3.6	8.9	4.0	3.1	0.46
F6	Marine or Dairy	1.5	3.1	6.9	4.3	2.9	0.33

All values calculated using dominant factor > 1σ criteria, except average duration and percentage of total time which were calculated using f > 1σ criteria. Aerosol concentrations calculated using sum of all AMS aerosol species reported (i.e. organic carbon, sulfate, nitrate, and ammonium). Relative Importance for Organics is calculated as the product of Avg. Organics Concentration times the Percentage of Total Time, normalized to Factor 1. This value provides a relative scale to compare each factor's contribution to total organic aerosol loading at Chebogue Point.



5
4
3
2
1
0
56
58
60
62
64
66
68
70
72
74
76
Effective Primary Retention Time (mins)
8.6
8.4
8.2
8
7.8
7.6
7.4
Azimuth:
-37.5
Elevation:
30
Maximum:
8.6
Minimum:
7.4
Step Size:
0.01
X-Axis
Y-Axis
Z-Axis
Axis Min:
54.8833
Axis Max:
76.6833
Axis Step:
2
Apply
Apply