

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

ICARTT 2004

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UC-Berkeley: Dylan Millet, Megan McKay

Major Supporting Data (ICARTT 2004):

Aerodyne Research, Inc.: Doug Worsnop et al.

University of Colorado, Boulder: Jose-Luis Jimenez et al.

University of Manchester, UK: James Allan et al.

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National Oceanic and Atmospheric Administration

NOAA: March 11, 2005; Boulder, CO

ISSUE

- Organic portion of Atmospheric PM_{2.5} Aerosols (20-60%) is helpful in determining and understanding:
 - Particle sources
 - Particle formation processes
- Past field measurements:
 - In-Situ techniques (no extensive individual organic compound separation)
 - Filter collection (12 to 24-hour time resolution)
- New measurement technique: Thermal-desorption Aerosol GC/MS-FID (TAG)
 - Faster time resolution
 - Automated: No sample handling
 - In-Situ data acquisition

OBJECTIVES

1) Test TAG's ability to achieve:

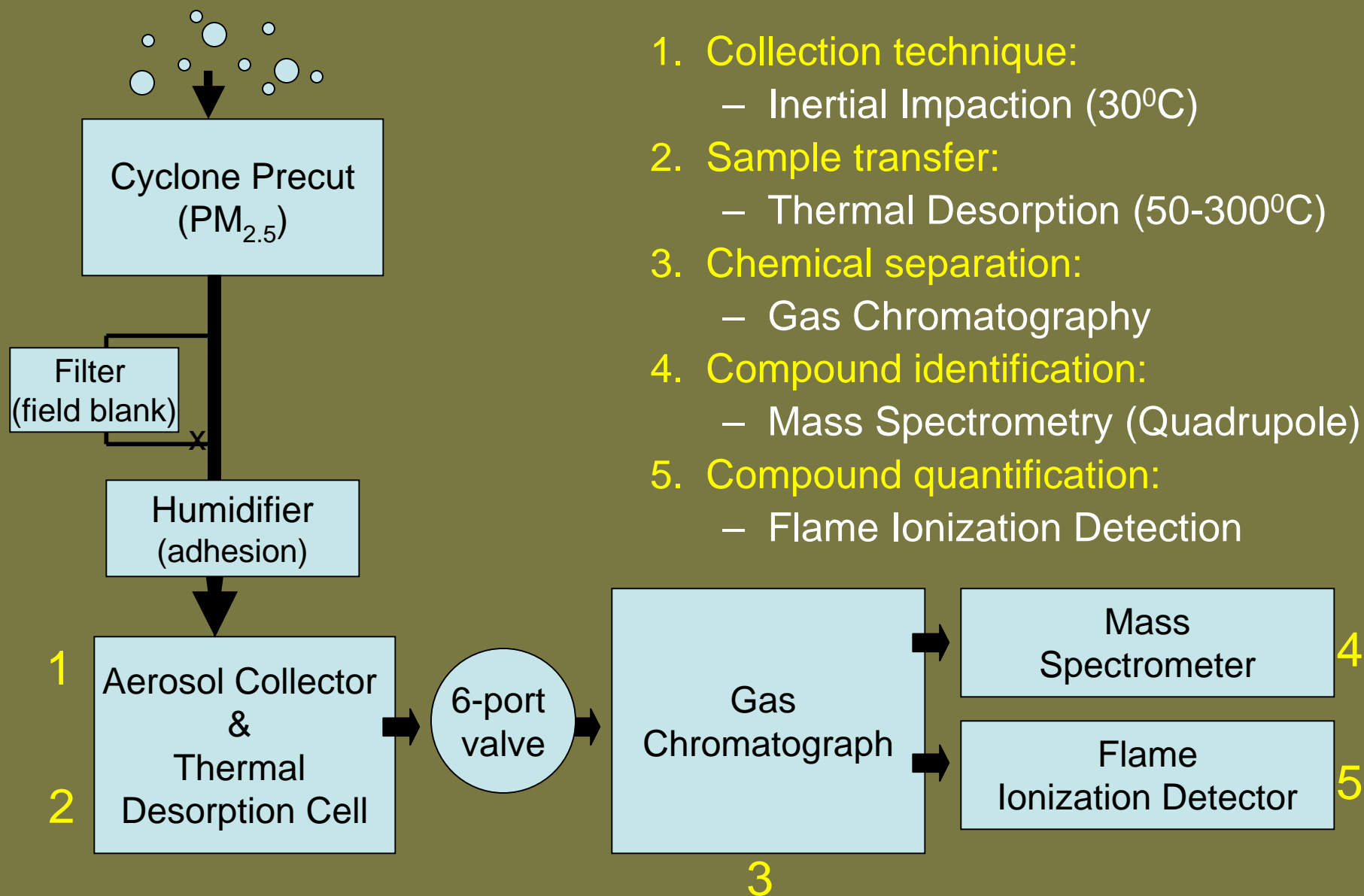
- In-Situ - Automated, semi-continuous measurements
- 1-hour time resolution in a “remote” location
- Separation / Identification / Quantification of individual organic marker compounds from particle phase

2) Preliminary Data Analysis (Today's Focus):

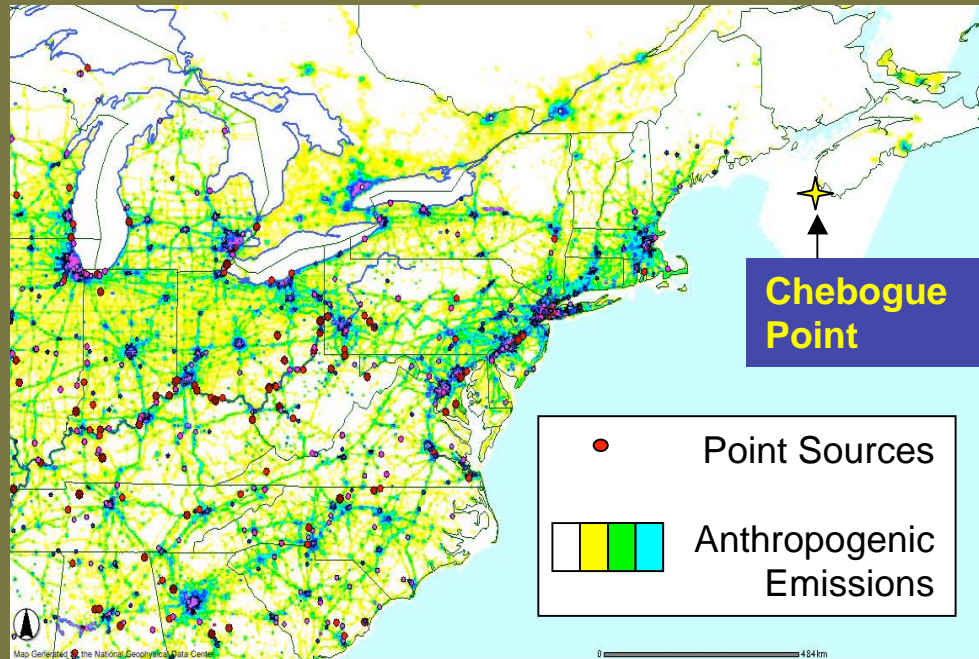
- Initial focus on resolved marker compounds to determine organic aerosol source regions

APPROACH

TAG: Thermal Desorption Aerosol GC/MS-FID



TAG's First Trip to the Field



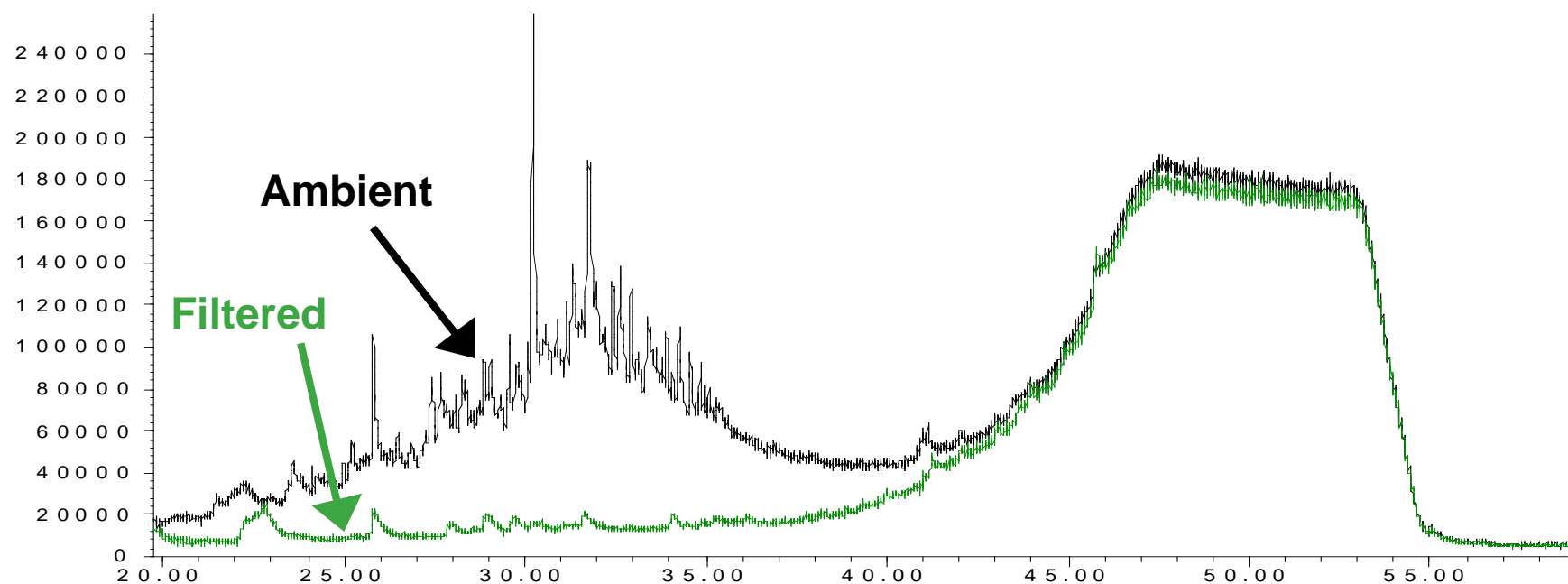
NOAA <http://map.ngdc.noaa.gov/website/al/emissions/Run.htm>

- Chebogue Point, Nova Scotia - Canada (ICARTT 2004)
- Hourly data (750 chromatograms x 2 detectors = 1500)
- First look TAG data July 26 – August 15 (~3 weeks)
- Manual calibration with directly applied standards
- Automated filtered and zero air blanks



TAG
Chebogue Point, Nova Scotia
ICARTT 2004

Abundance



Time -->

Chebogue Point, Nova Scotia. August 7, 2004

Sample time: 0.5 hour

Sample Volume: 0.25 m³

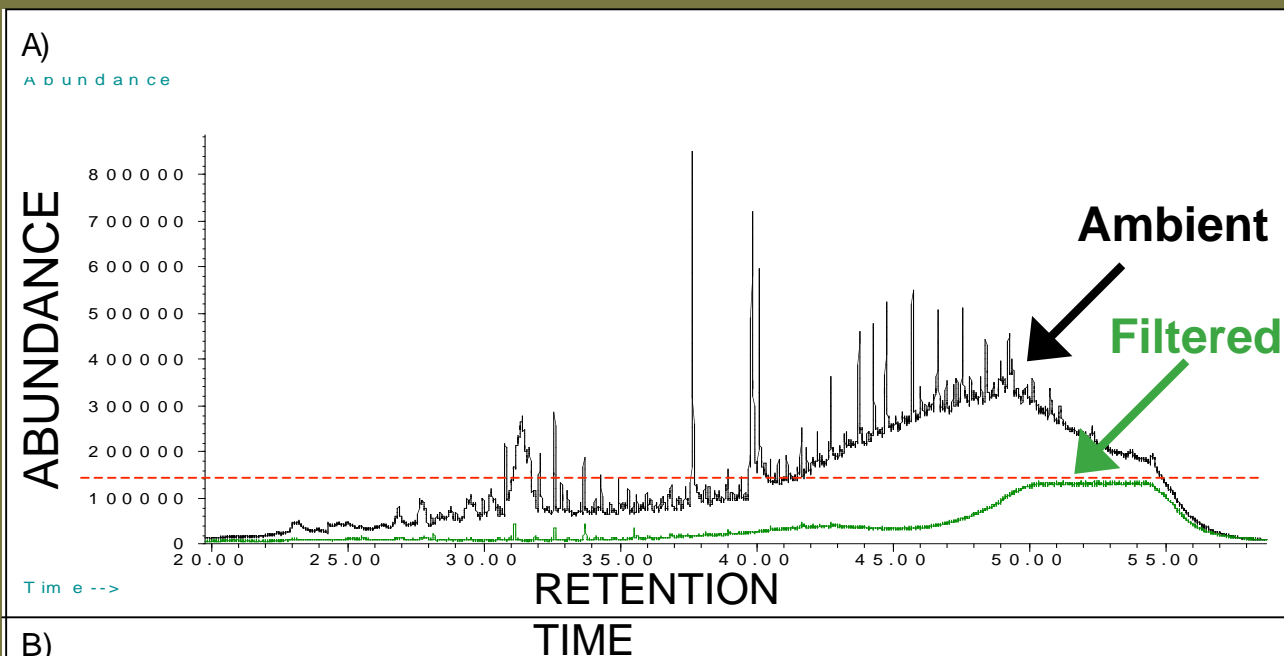
Thermal Desorption: 50-300°C

GC oven temp. range shown here: ~ 45°C to 300°C

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

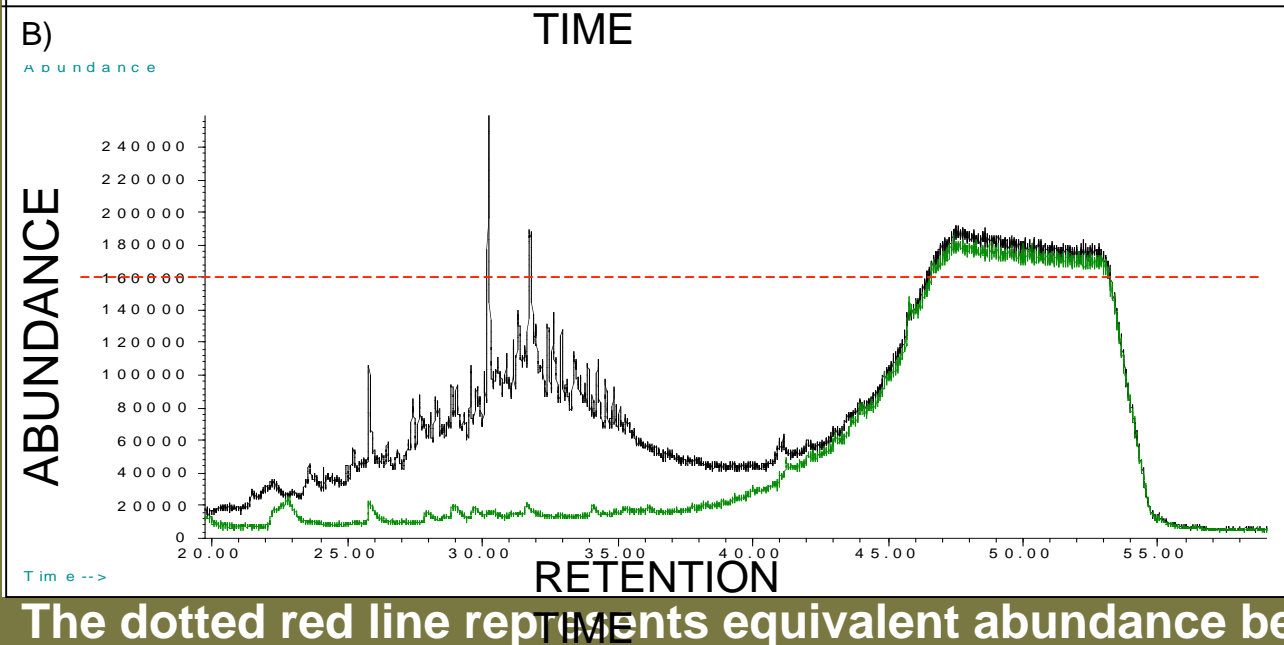
ASIDE:

- Compounds collected in Nova Scotia are extremely oxygenated
- Difficult to identify using only **NIST** database, may not be in database



Berkeley, CA
Winter Evening 2004

Resolved Compounds
Matched by NIST
library: **80%**



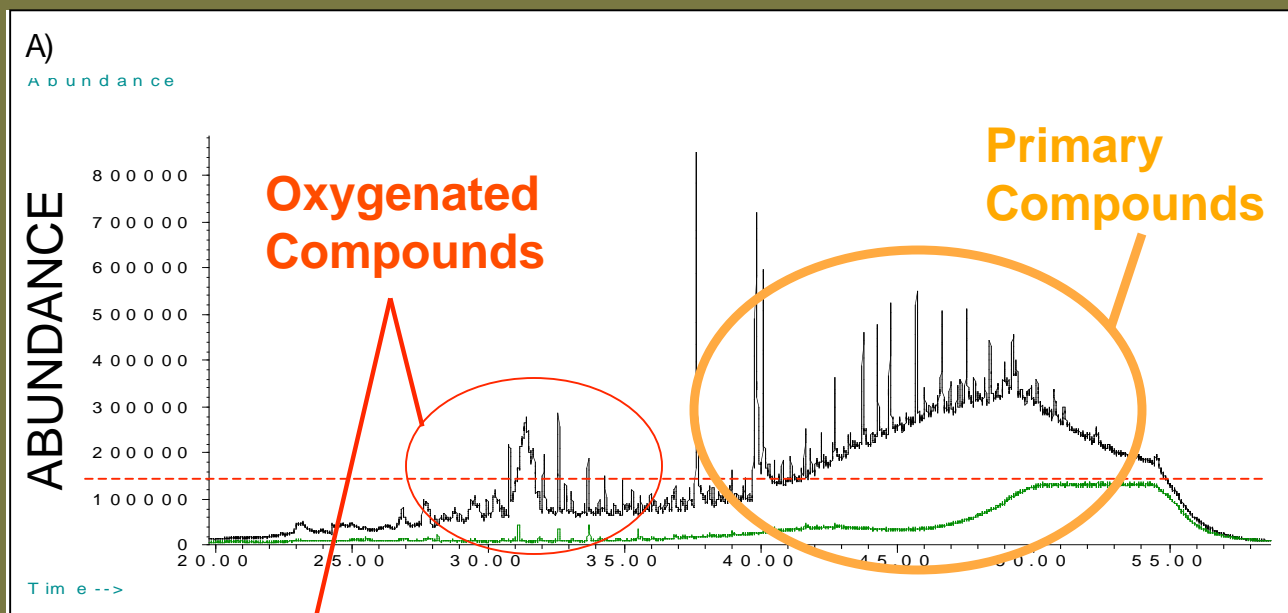
Nova Scotia, Canada
Summer Evening 2004

Resolved Compounds
Matched by NIST
library: **35%**

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

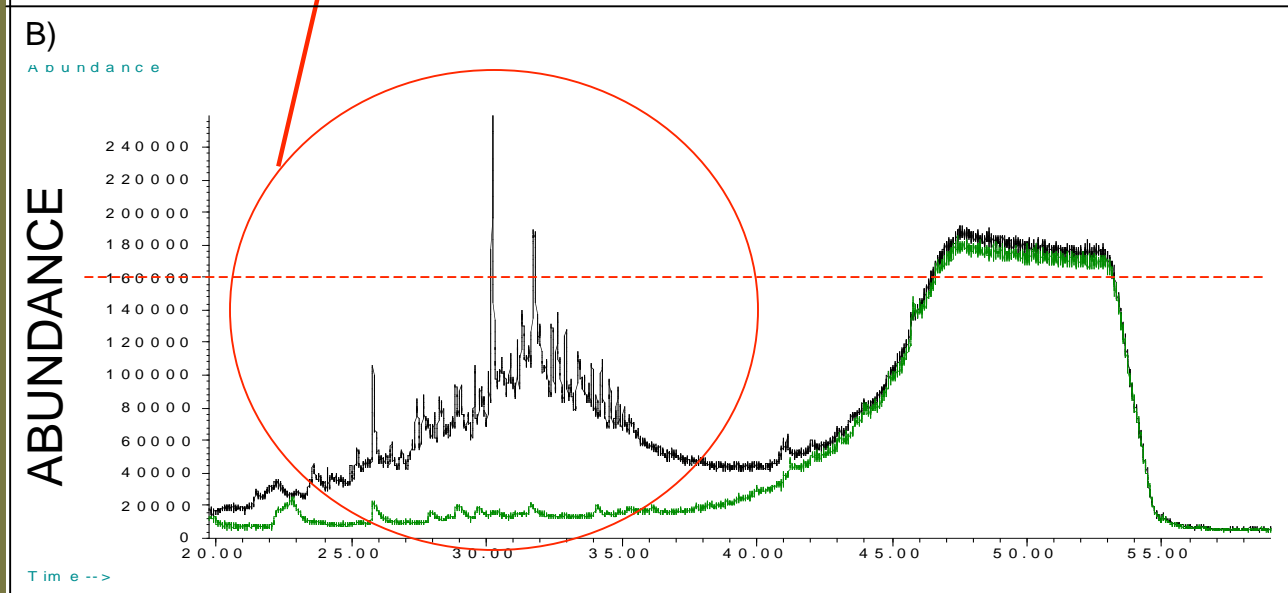
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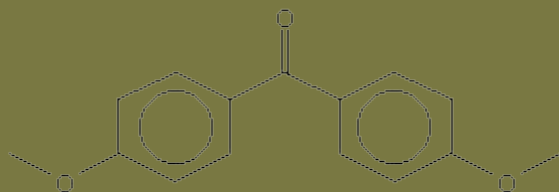
Some Identified Compounds from Nova Scotia

a1.69	5-Hexenoic acid, 5-methyl-	C7H12O2
d1.43	5,6-Dihydropyran-2-one, 5-acetoxy-6-(1,2-epoxypropyl)-	C10H12O5
h1.104	Phthalic acid	C8H6O4
j1.71	2,3-Pinenediol	C10H18O2
m1.84	Pelletierine	C8H15NO
n1.112	1,6-Dioxaspiro[4,4]nonane-2,7-dione	C7H8O4
o1.126	2,2-Dimethyl-3-heptene trans	C9H18
p1.43	4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester	C11H18O3
r1.139	4s,6s-Dimethyl-7R-acetoxy-3-nonanone (acetyl serricornin)	C13H24O3
t1.98	Cyclohexanone, 2-ethyl-	C8H14O
u1.98	2(3H)-Furanone, 5-methyl-	C5H6O2
aa1.99	Spiro[1,3-dioxolane-2,2'-[6,7]diazabicyclo[3.2.2]non-6-ene	C9H14N2O2
ee1.86	2(3H)-Furanone, 3-acetyldihydro-	C6H8O3
ff1.219	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	C15H22O2
gg1.178	Dibenz[c,d]hydrooxepin	C14H12O

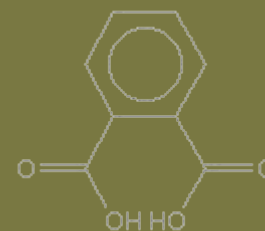
Reproducible Standards from Nova Scotia (manual injections)

Phthalic 3,4,5,6 acid	C8H6 <u>O</u> 4
Acenaphthene	C12H10
Hexadecane	C16H34
Eicosane	C20H42
4,4'-Dimethoxybenzophenone	C15H14 <u>O</u> 3
Chrysene	C18H12
Octacosane	C28H58
aaa-20R-Cholestane	C27H48

Oxygenated Standards from Nova Scotia

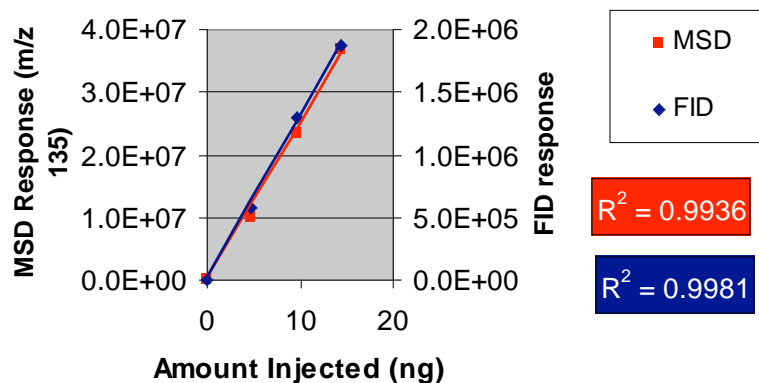


(CH₃OC₆H₄)₂CO



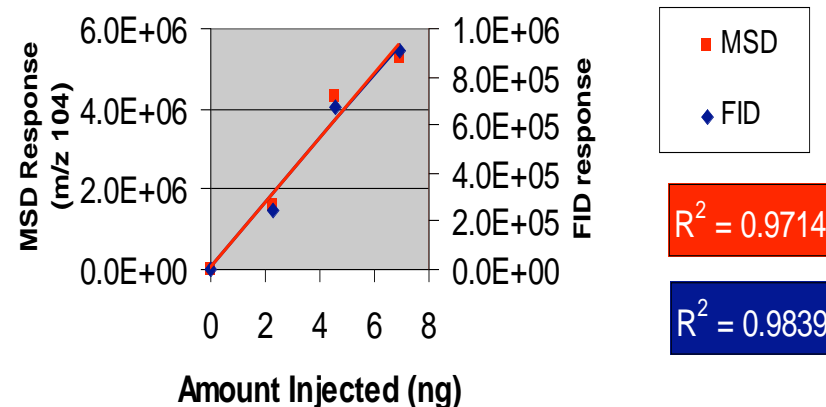
C₆H₄(COOH)₂

4,4'-dimethoxybenzophenone



FID: 1ng = 130,197

phthalic acid



FID: 1ng = 133,819

Both oxygenated standards have nearly identical response on the FID detector.
Future Analysis: may be able to “approximately” quantify oxygenated Nova Scotia compounds.

Thus far, I have only used relative abundances.

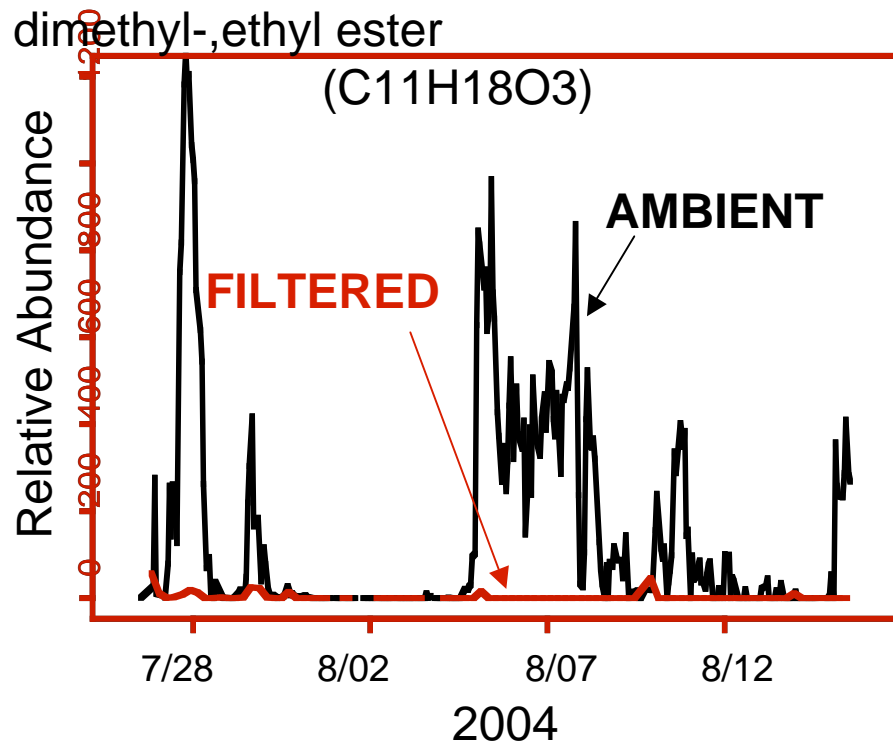
Timeline of Individual Ion Areas

Temporarily refer to Chebogue Point, NS compounds by letter

Compound: A

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-, ethyl ester

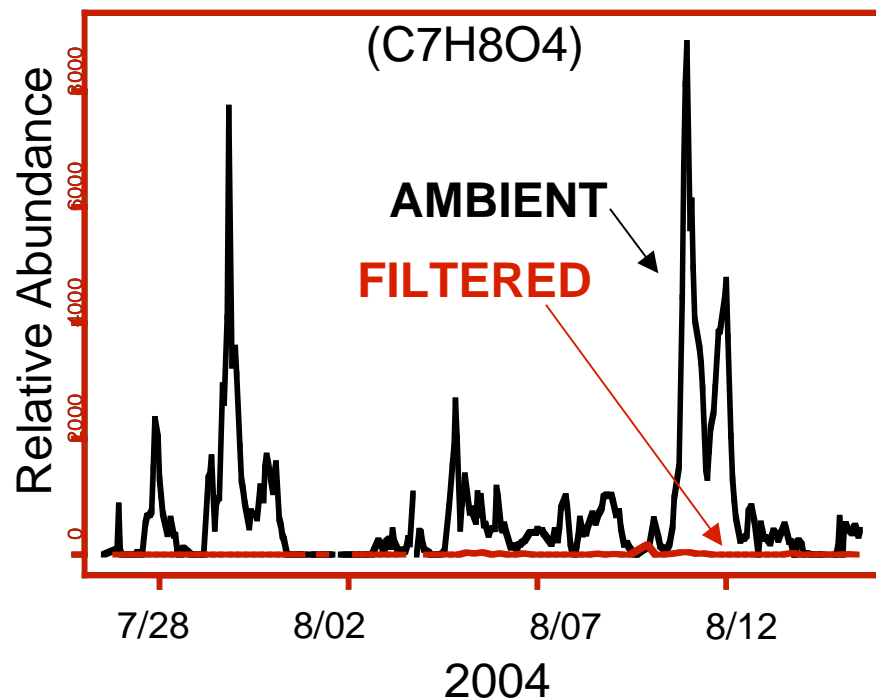
(C₁₁H₁₈O₃)



Compound: B

1,6-Dioxaspiro[4,4]nonane-2,7-dione

(C₇H₈O₄)



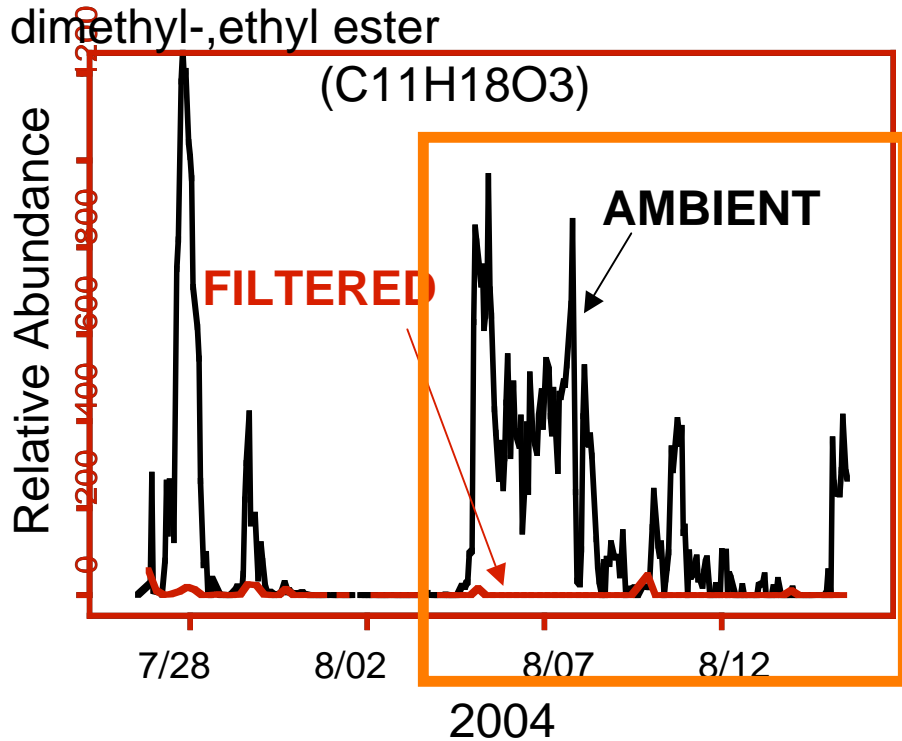
Chebogue Point, Nova Scotia

Closer Look at Compound A

Compound: A

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-, ethyl ester

(C₁₁H₁₈O₃)

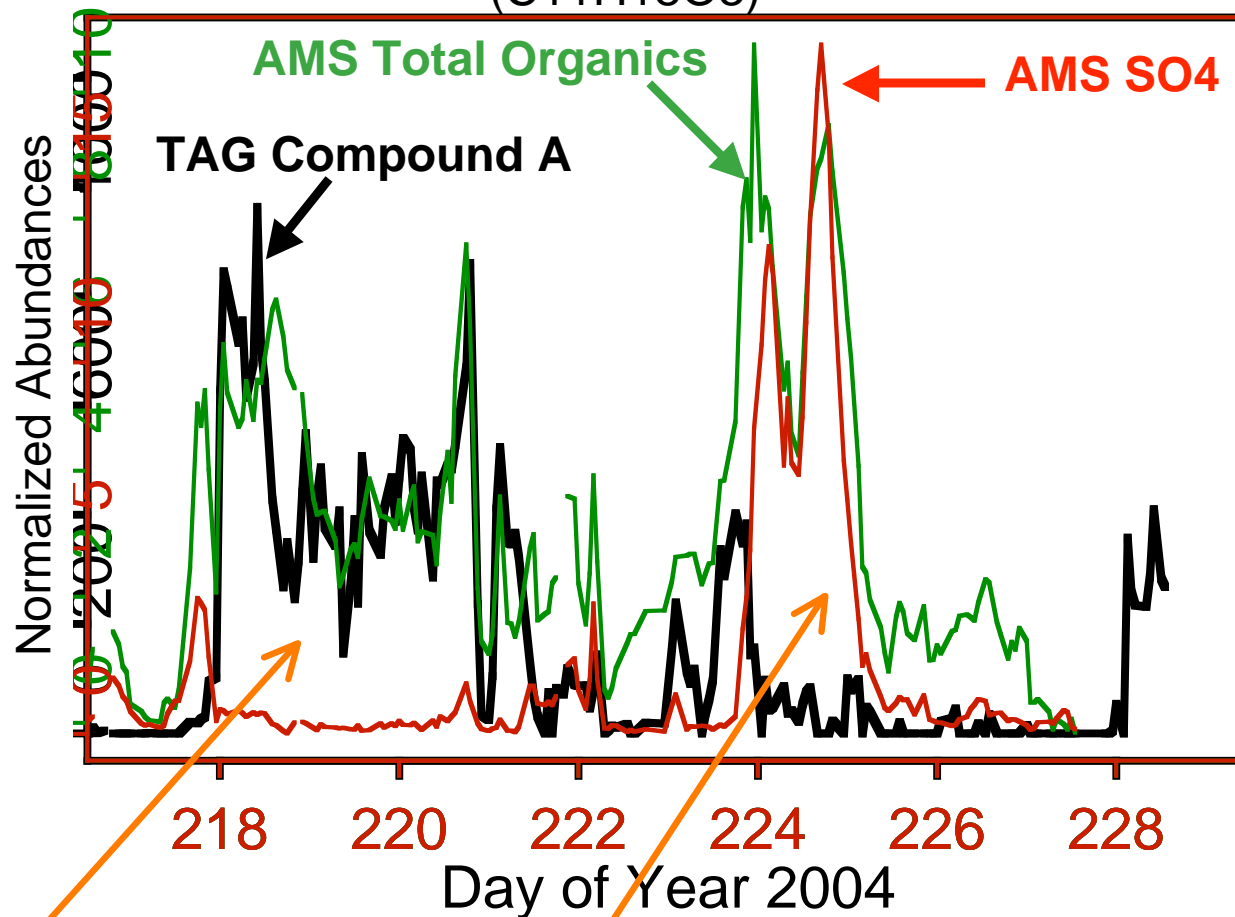


Compound: B

Compound: A

TAG Individual Compound vs. AMS Total Organics and Total SO₄

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester
(C₁₁H₁₈O₃)



Different
Scales

Event Type 1
No SO₄

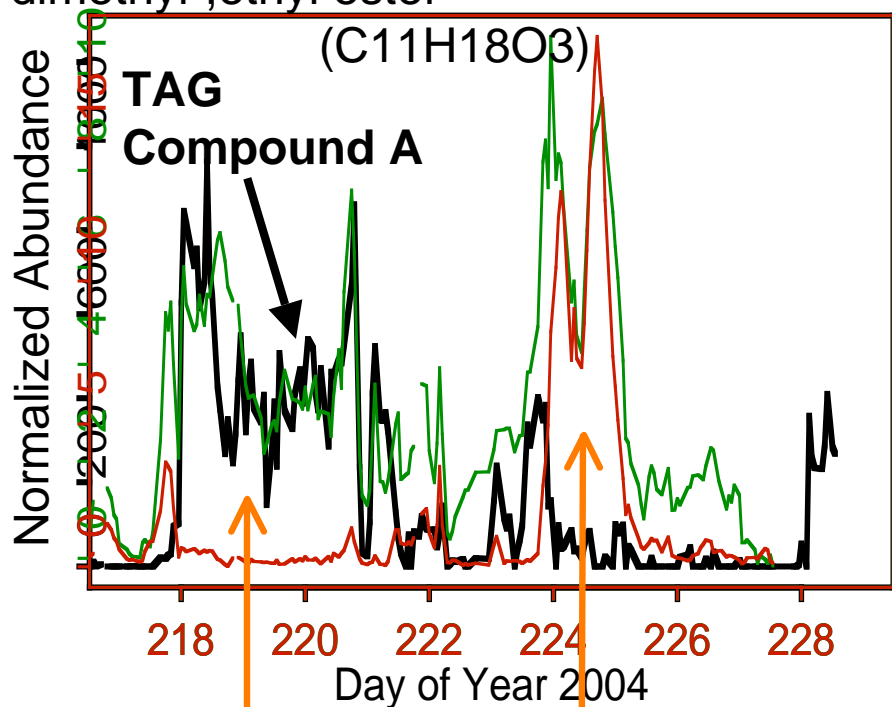
Event Type 2
SO₄

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

Individual Compounds vs. Total Organics and Total SO₄

Compound: A

4-Pentenoic acid, 2-acetyl-2,3-dimethyl-,ethyl ester

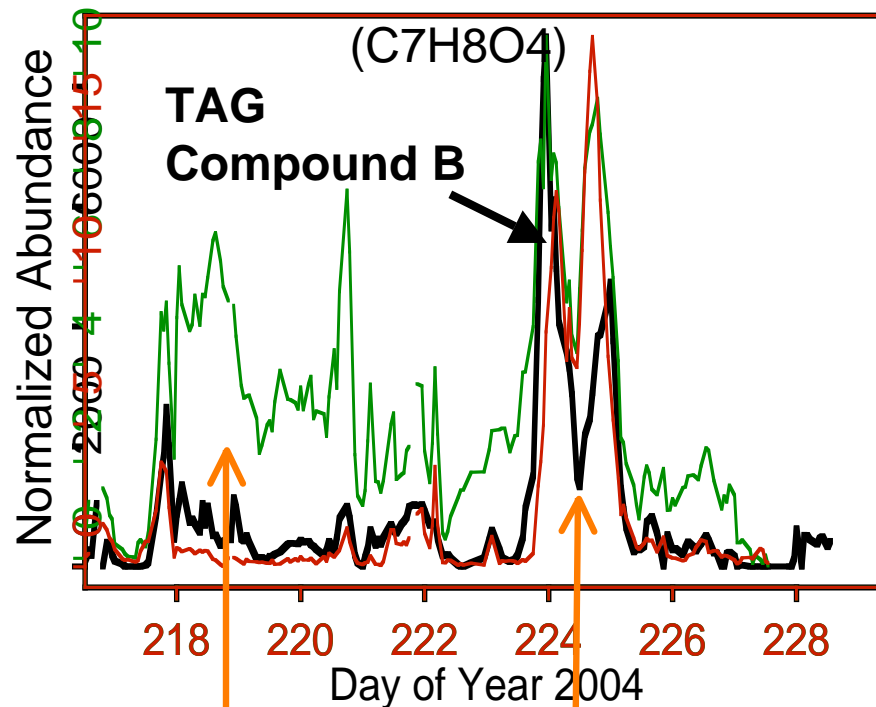


Event Type 1
No SO₄

Event Type 2
SO₄

Compound: B

1,6-Dioxaspiro[4,4]nonane-2,7-dione



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.)

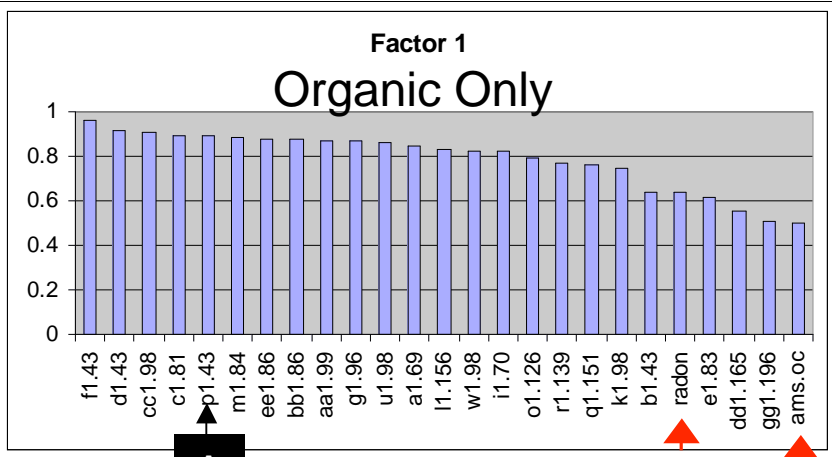
FACTOR ANALYSIS

- **Preliminary Data**

- 28 resolved compounds (using MS single ion peak area)
- O₃, CO, Radon
- AMS (Organic carbon, SO₄,NO₃,NH₄)
- Black carbon, CPC data

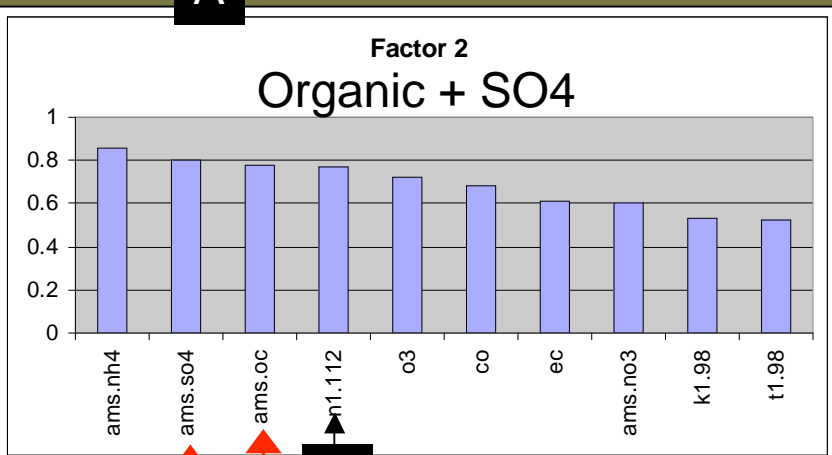
- **See how these 37 elements vary with each other**

- Factor analysis finds some underlying process or source type



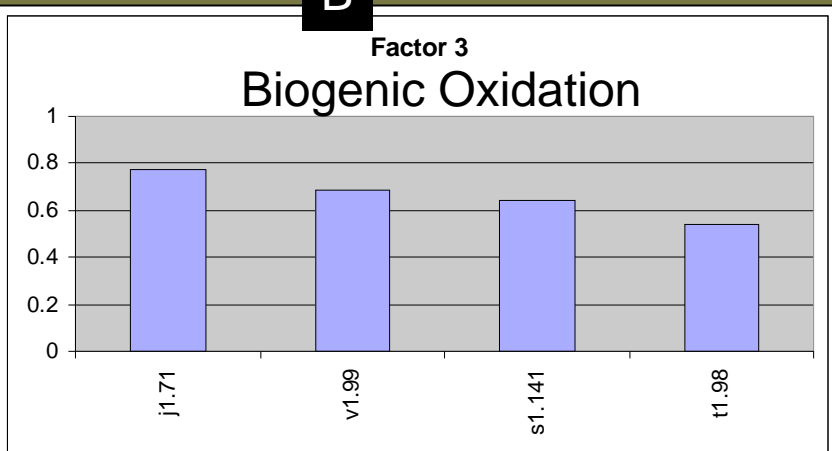
Factor 1 = Organic Only Factor

- Majority of TAG compounds (including Compound A)
- AMS Organic aerosol
- Radon



Factor 2 = Organic + SO4 Factor

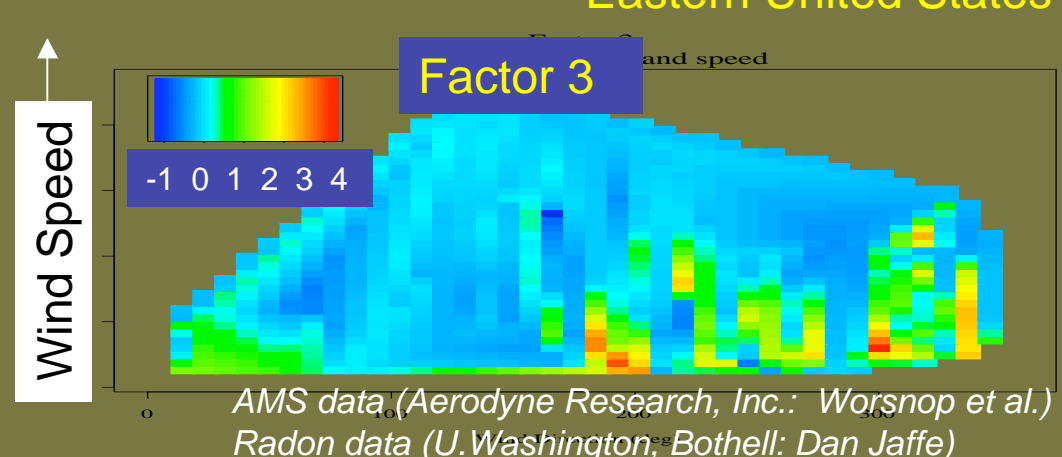
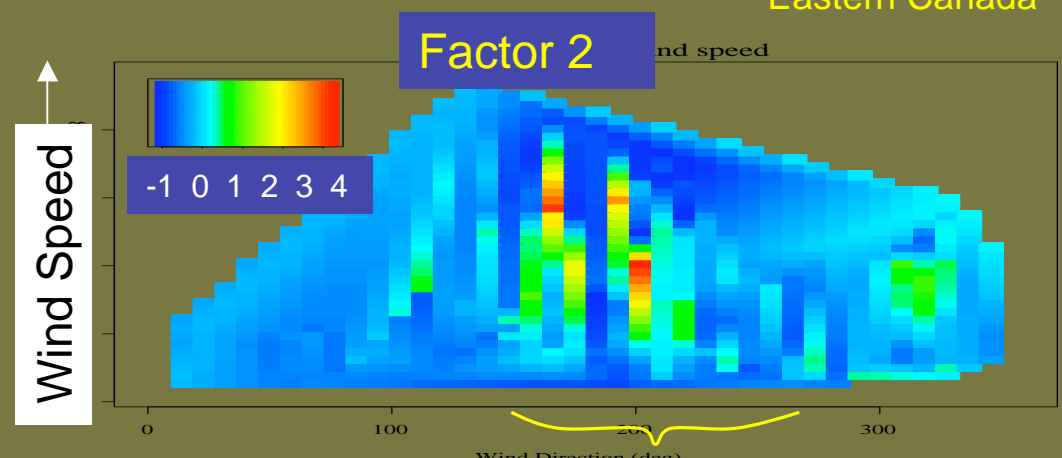
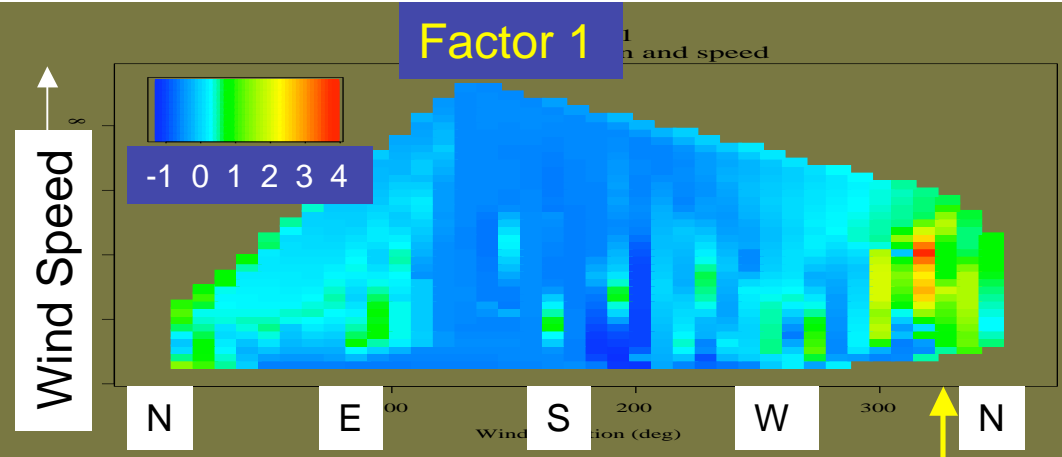
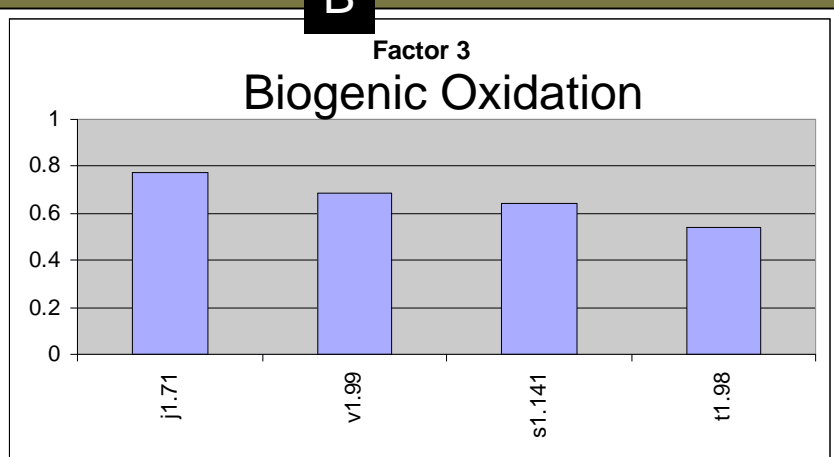
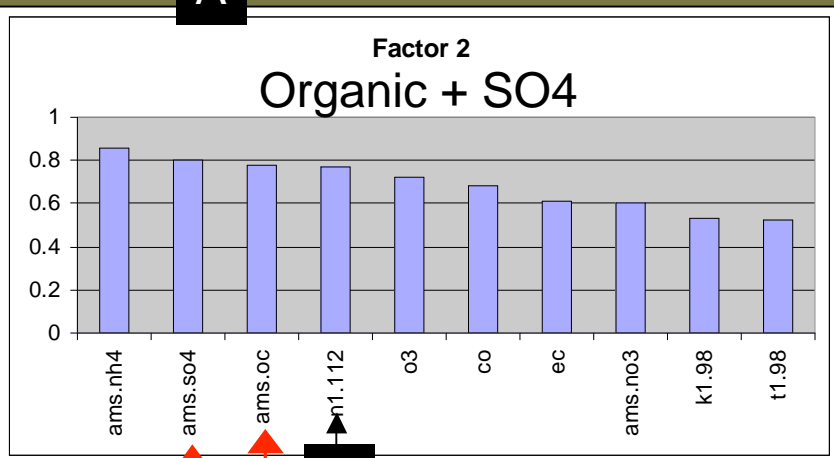
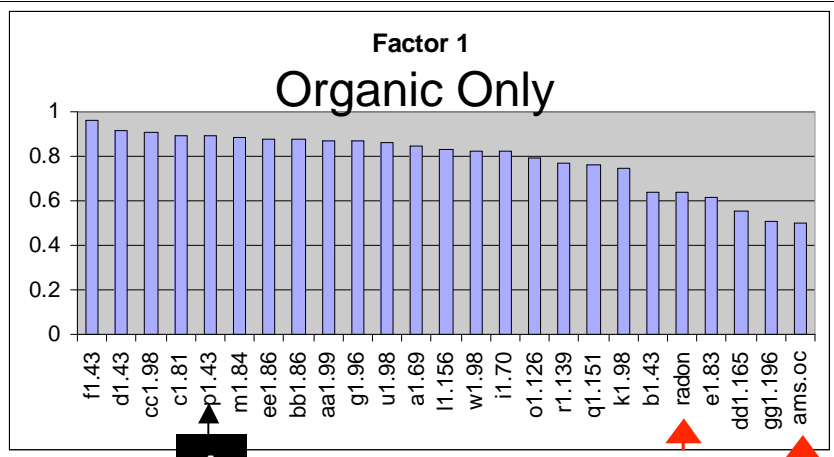
- A few TAG compounds (including Compound B)
- AMS SO4, NH4, NO3, Organic aerosol
- O3, CO, Elemental Carbon



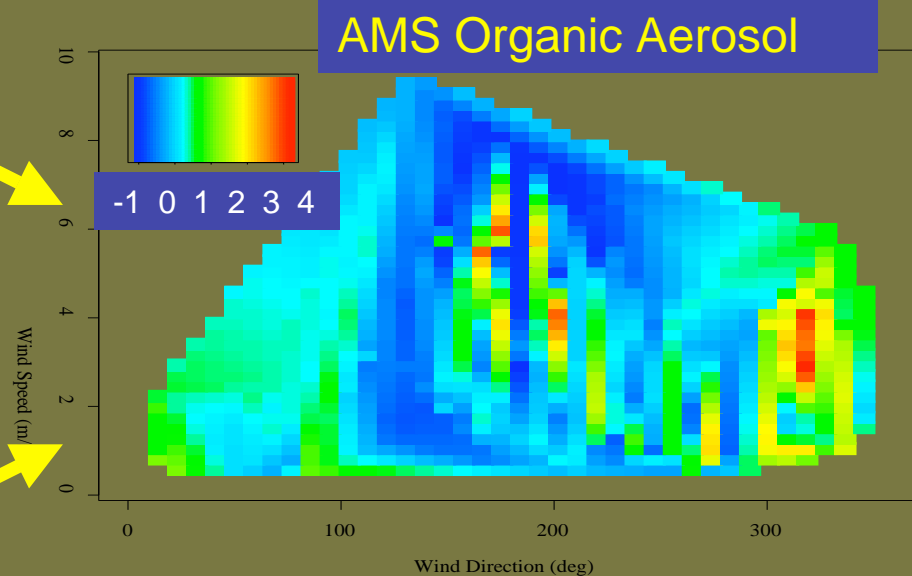
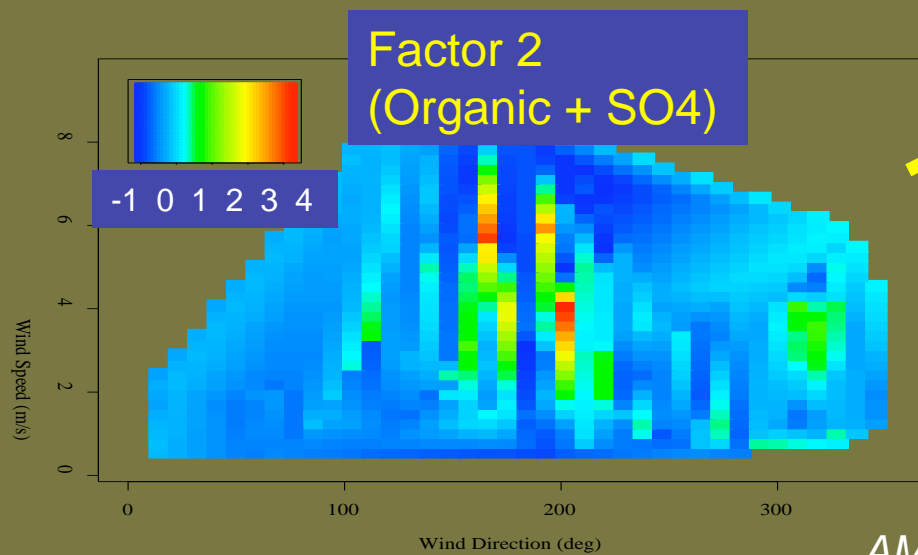
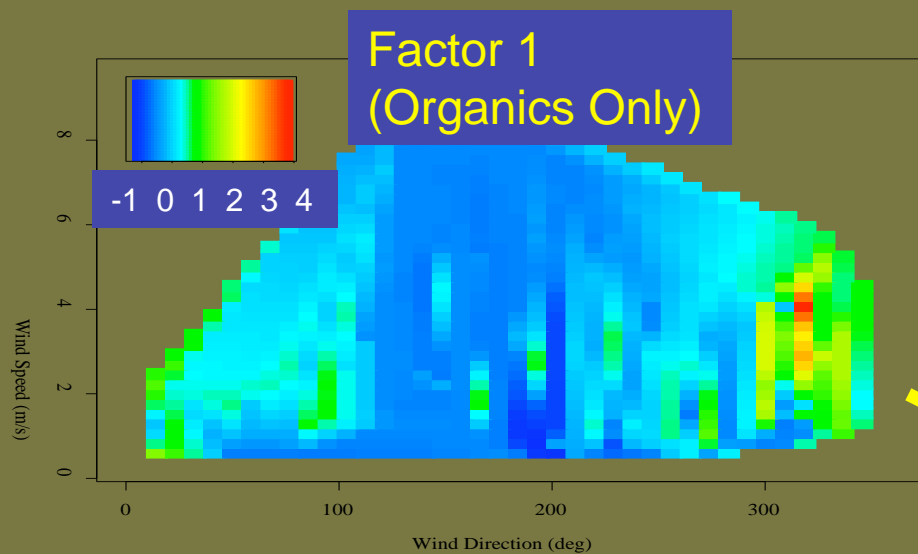
Factor 3 = Biogenic Oxidation Factor

- Four TAG compounds

AMS data (Aerodyne Research, Inc.: Worsnop et al.)
 Radon data (U.Washington, Bothell: Dan Jaffe)



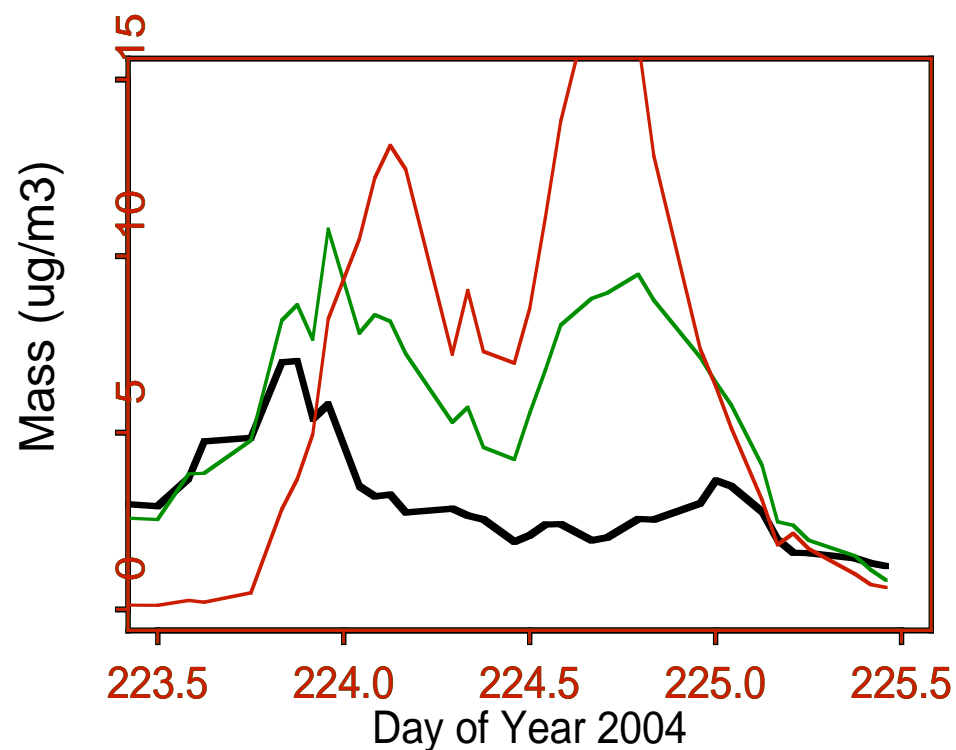
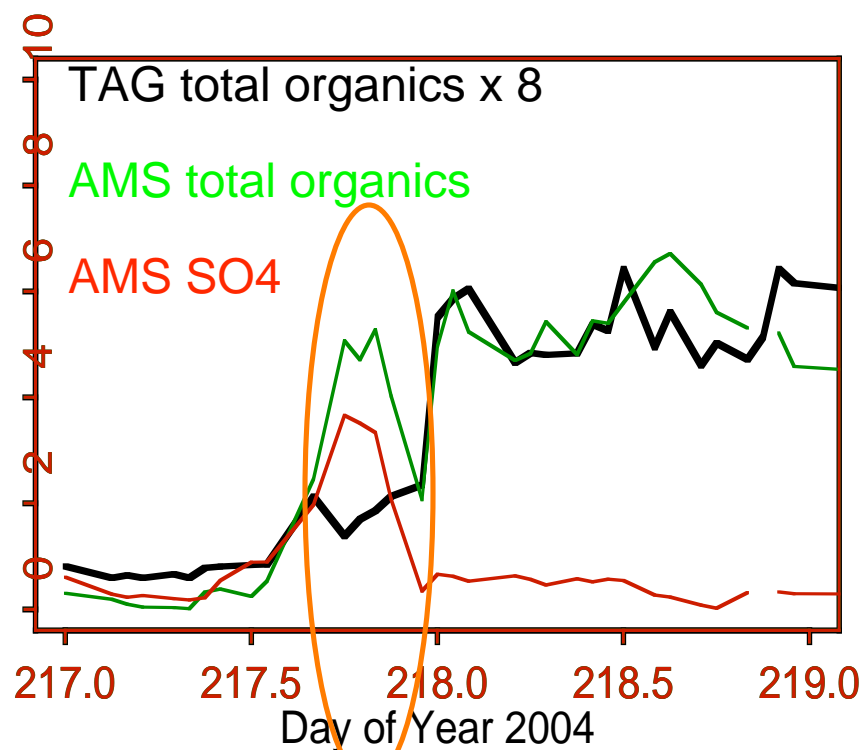
Total Organics are mostly split between Factors 1 and 2



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

Potential Reason for Fewer Factor 2 Compounds

Integrated total FID signal and used oxygenated standards to find approximate mass



- Organics present during SO₄ events may not elute through our GC column?
- On average, only getting ~ 1/8 of all organics through column, I would expect more to make it through in an urban environment.

CONCLUSIONS

- TAG instrument successfully deployed
- First in-situ hourly measurements of speciated ambient organic aerosol composition
- Preliminary analysis of 28 compounds
 - See 3 distinct source types w/ different organic marker compounds
- There are many “non-eluting” compounds in a remote environment

In the near future:

- Quantify resolved compounds
- Add more parameters to factor analysis
- Analyze Unresolved Complex Mixture to bring out information on aerosol oxidation level
- Take TAG to an urban environment

ACKNOWLEDGEMENTS

AMS Data (ICARTT 2004):

Aerodyne Research, Inc.

University of Manchester, UK

University of Colorado, Boulder

Allan, Cross, DeCarlo, Northway, Canagaratna, Huffman,
Jimenez, Coe, Worsnop

Radon Data (ICARTT 2004):

U. Washington, Bothell

Dan Jaffe

Funding:

Department of Energy – Global Change Education Program

Department of Energy – Small Business Innovative Research grant

National Oceanic and Atmospheric Administration

Factor Analysis

F1: U.S.

F2: Local
combustion

F3: Alkanes

F4: OVOC

F5: Terpenes

F6: Biogenic OX



Organic Aerosol Chemical Composition

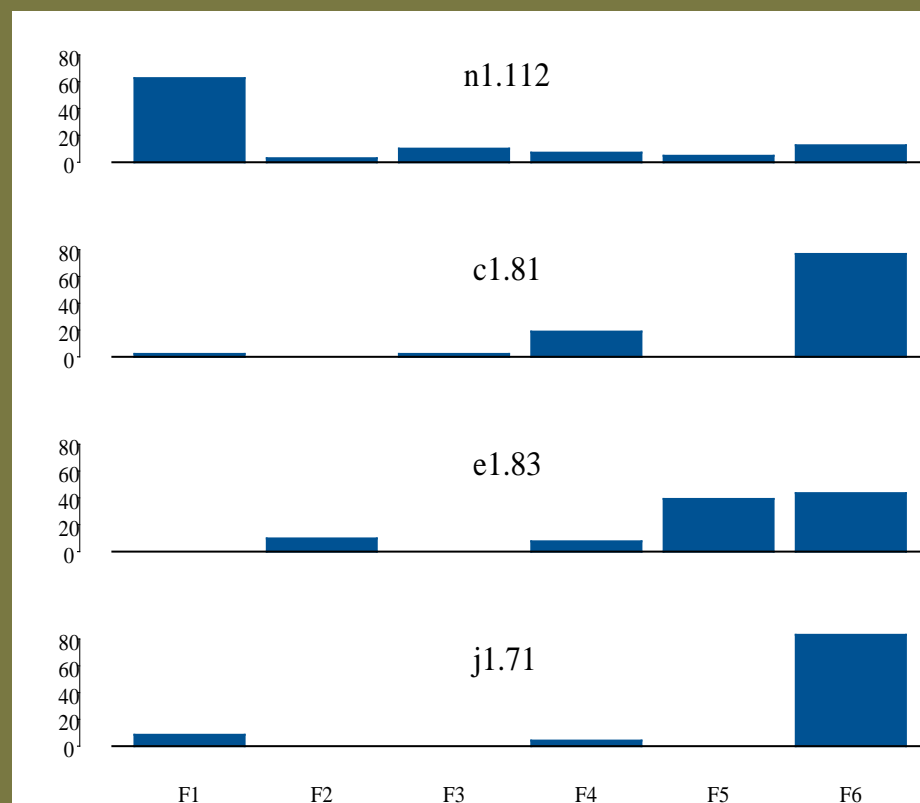
Multiple regression of OC species with 6 factors:

Tentative Compound ID:

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

7-anti-methyl-2-oxo-bicyclo[2.2.1]heptane-
7-carboxylic acid ($C_9H_{12}O_3$) ?

2,3-pinenediol ($C_{10}H_{18}O_2$) ?



U.S. Alkanes Terpenes
Local comb OVOC

