Novel Measurements of Volatility- and Polarity-Separated Organic Aerosol Composition and Associated Hygroscopicity to Investigate the Influence of Mixed Anthropogenic-Biogenic Emissions on Atmospheric Aging Processes

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U. Minnesota (Millet)
Georgia Tech (Ng, Weber)
Penn State University (Brune)
WashU (Turner)

Washington University in St. Louis

center for aerosol science and engineering

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PhD

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Chris Oxford
Michael Walker
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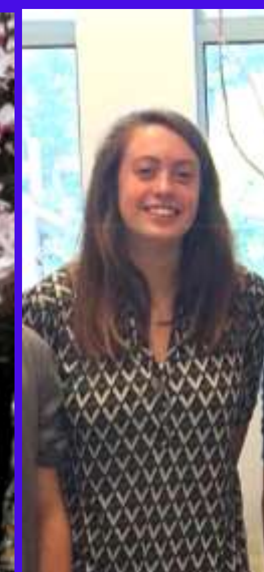

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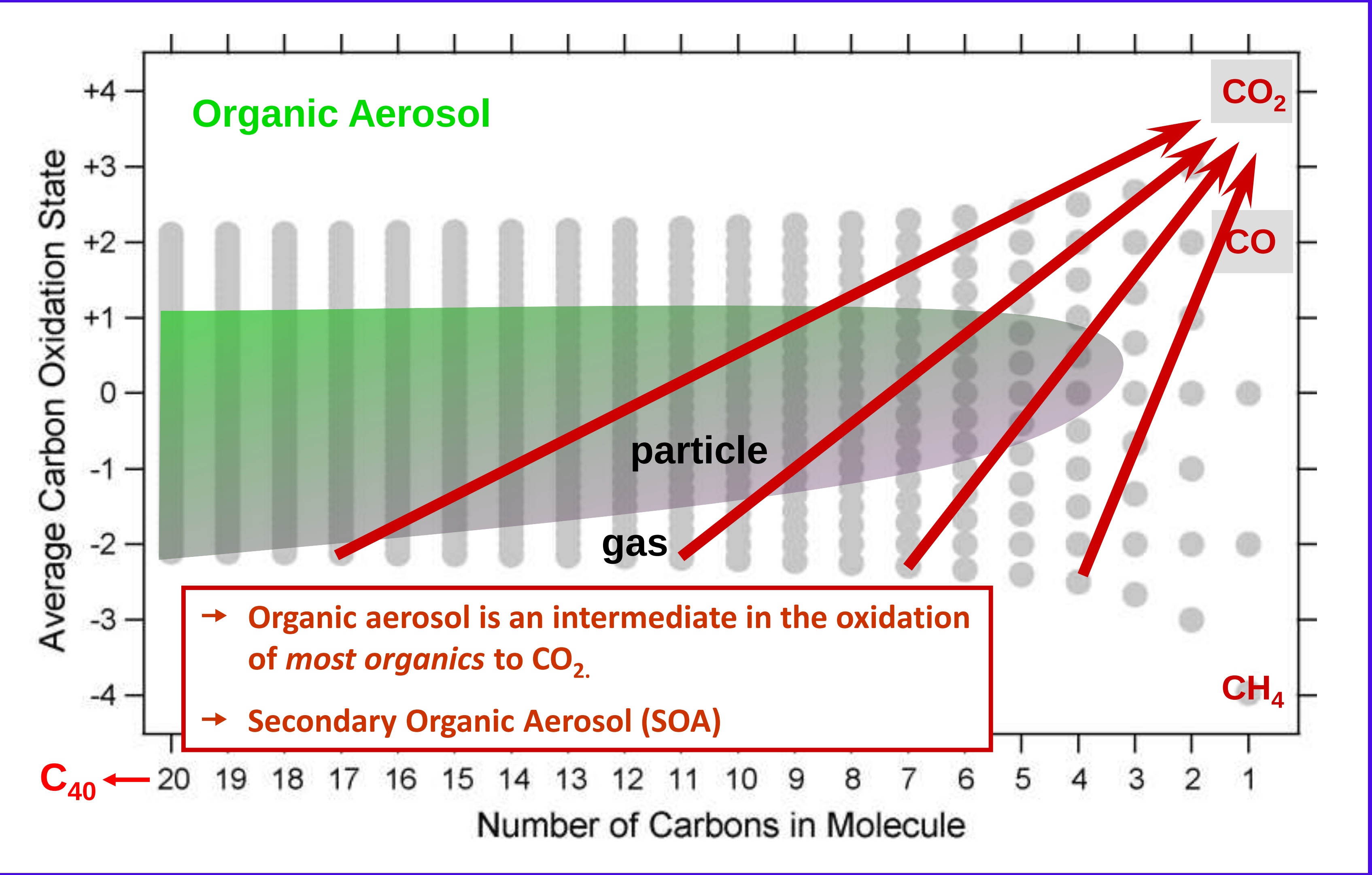
Masters: Xiaochen Zuo, Mayura Patankar
Undergrads: Hagan, Dhawan, Geyer, Streff, Sussman, Wilcosky

Motivation

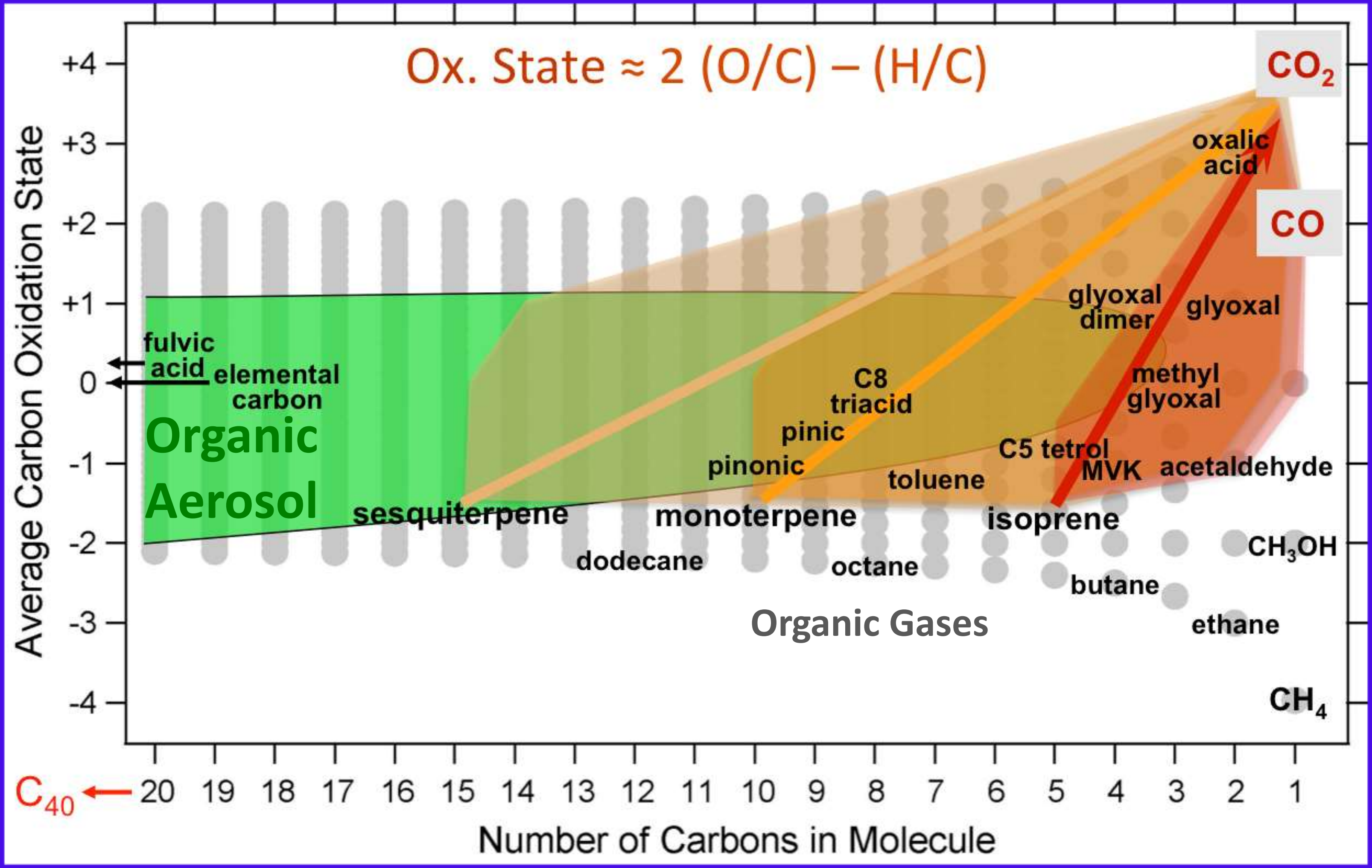
- Atmospheric **primary** and **secondary** organic gases and particles originate from **biogenic** and **anthropogenic** emissions, and **bio/anthro interactions** have been observed to alter production of secondary organic aerosol (SOA).
- Impacts health and climate
- *Uncertainty remains in determining **sources** and **evolution** of organic aerosol (OA)
- *There is a need for improved **chemical characterization** of complex OA composition
- *We want **manageable parameterizations** of this chemistry to enable modeling of complex atmospheric OA (mixture can contain tens of thousands of compounds). Approach through **novel data analysis methods** and new **measurement techniques**.

Oxidative Evolution of Organic Material in Atmosphere



Adapted from Kroll et al., Nature Chemistry, 2011

Oxidative Evolution of Organic Material in Atmosphere



- A small molecule like isoprene (C5) only crosses edge of the condensed phase
- More likely for larger molecules (e.g., C10, C15) to cross through condensed phase
- Aerosol Yield from smaller molecules may be very sensitive to altered reaction paths

Adapted from Kroll et al., Nature Chemistry, 2011

Our goal is to contribute to a better understanding of the anthropogenic enhancement of biogenic SOA production

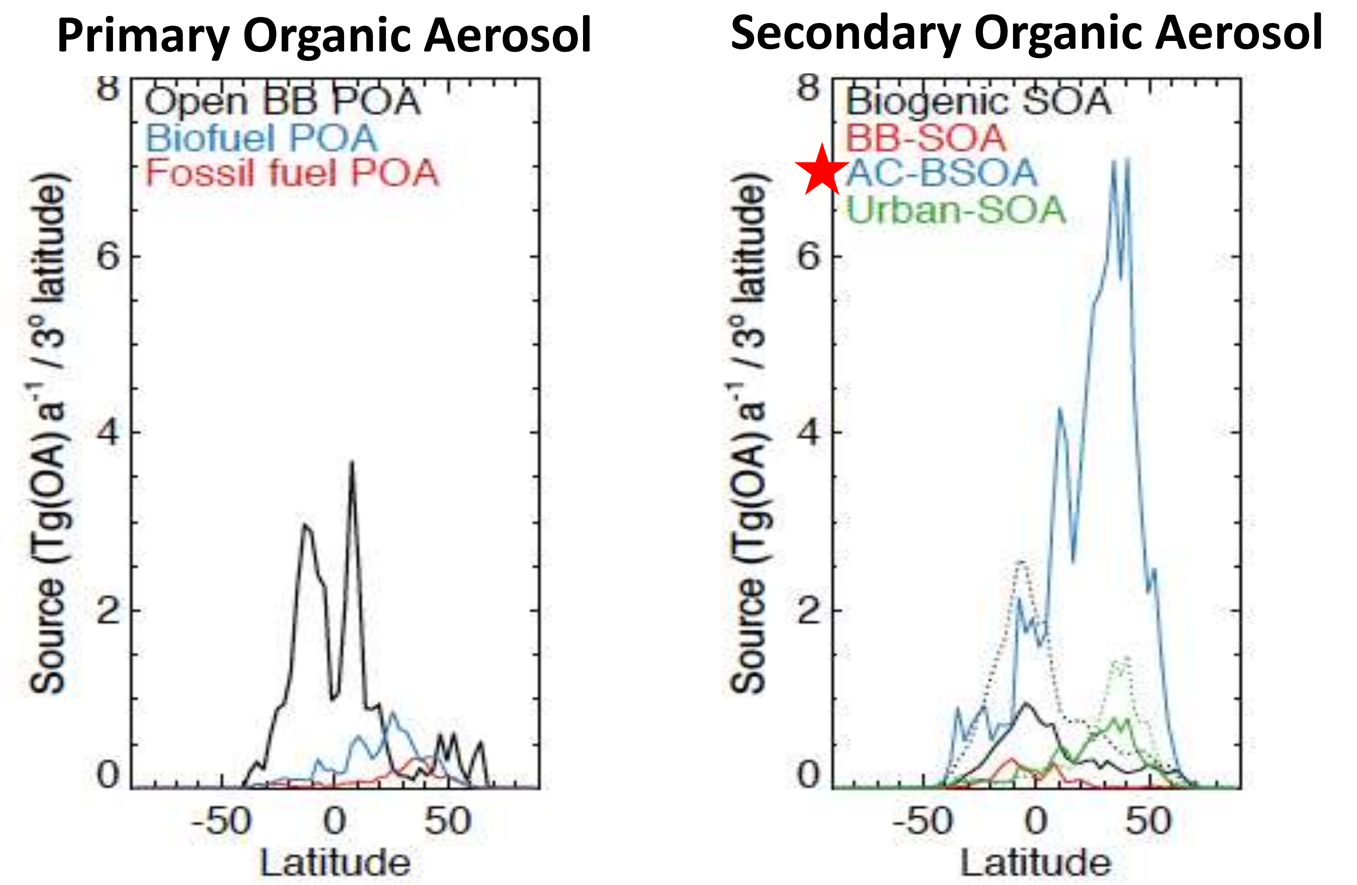
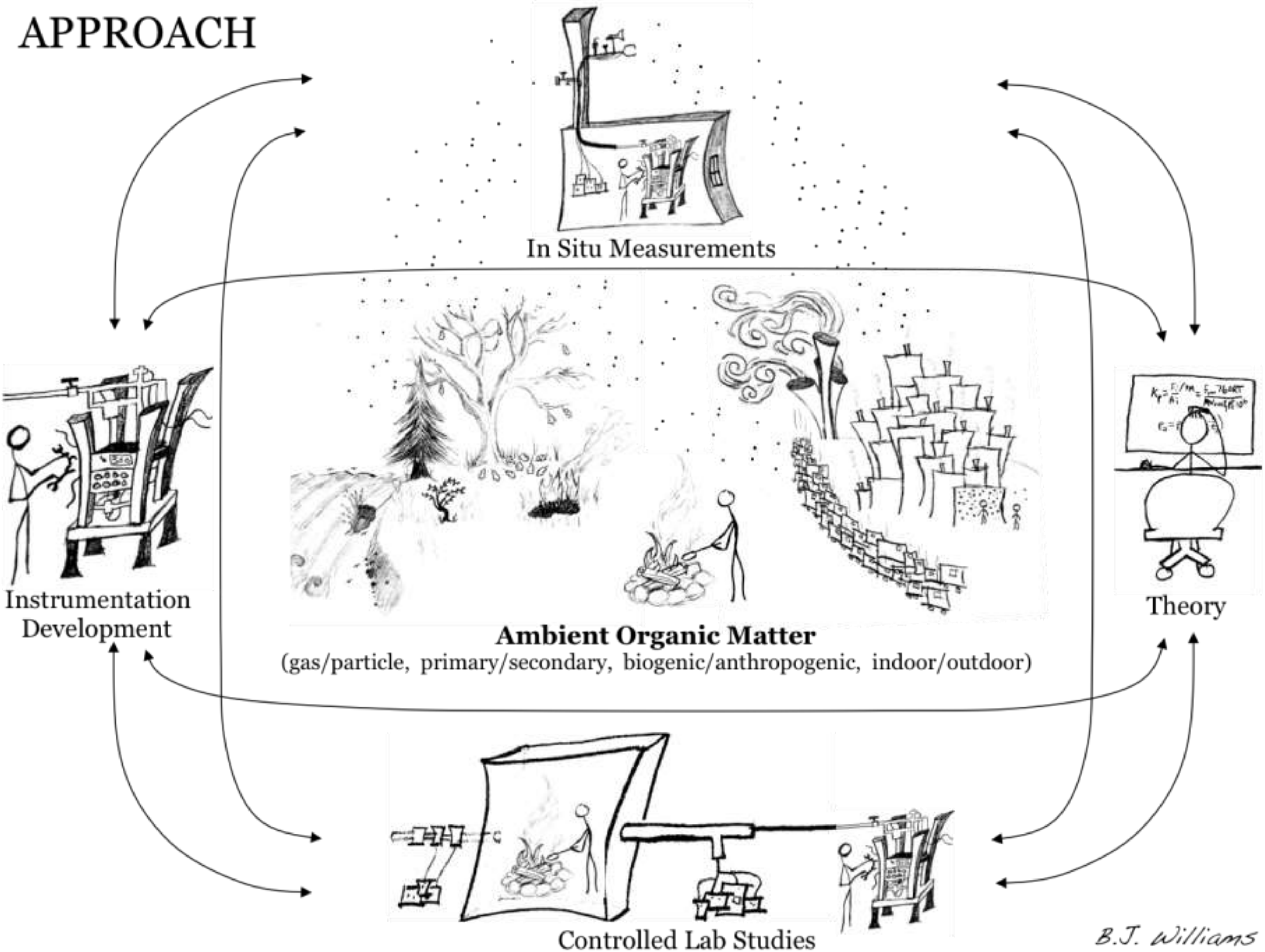


Fig. 11. Estimated zonal mean distribution of **(a)** POA and **(b)** SOA sources: biomass burning (BB-SOA); anthropogenically controlled biogenic SOA (AC-BSOA). Sources of SOA estimated in this work (solid lines) are plotted for comparison against sources estimated by de Gouw and Jimenez (2009) (dotted lines). POA emissions in the two studies are identical.

Spracklen et al., ACPD, 2011

APPROACH

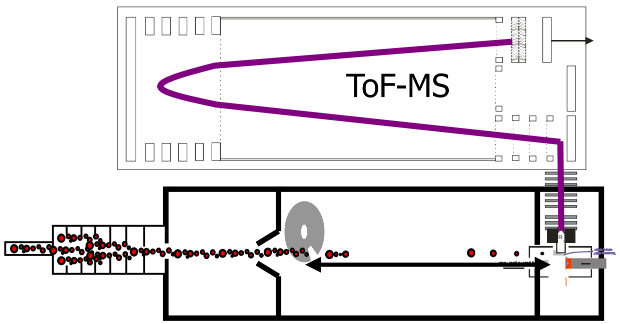

In Situ Measurements
Instrumentation Development
Theory
Ambient Organic Matter
(gas/particle, primary/secondary, biogenic/anthropogenic, indoor/outdoor)
Controlled Lab Studies
B.J. Williams

OUTLINE

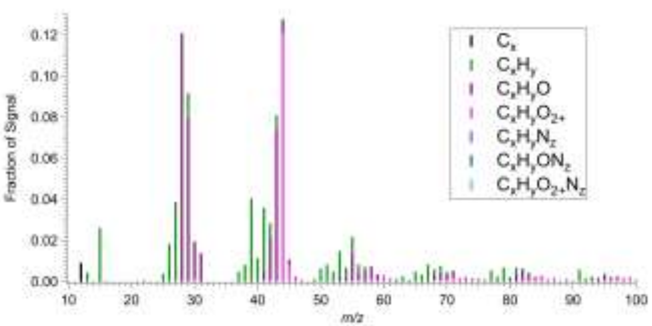
- **Instrument Development**
- **Novel Data Analysis Methods**
- **Field observations: SOAS – Centreville, AL**
- **Field observations: SLAQRS – East St. Louis, IL**
- **Laboratory-based oxidation studies**
- **Conclusions**

Our methods for *In-Situ* Organic Aerosol Chemical Characterization

Aerosol Mass Spectrometer (AMS)



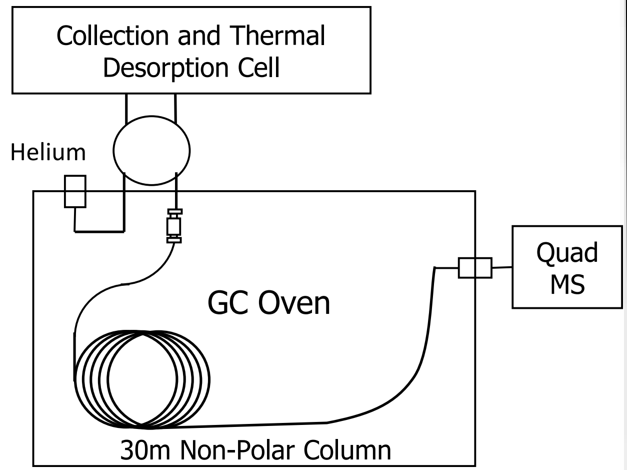
High Resolution MS



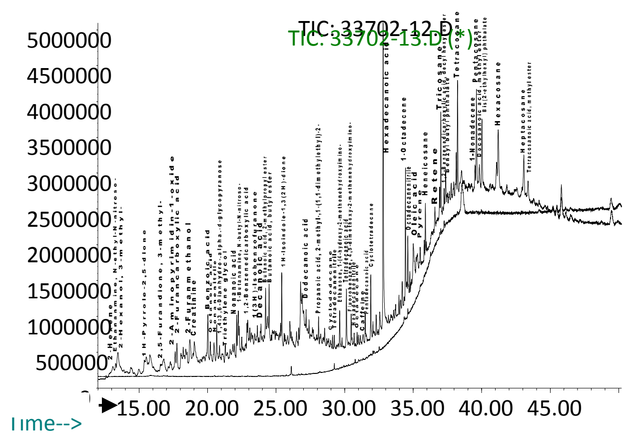
Displaying Organic Ions Only

Canagaratna et al, MS Reviews 2007

Thermal desorption Aerosol Gas chromatograph (TAG)

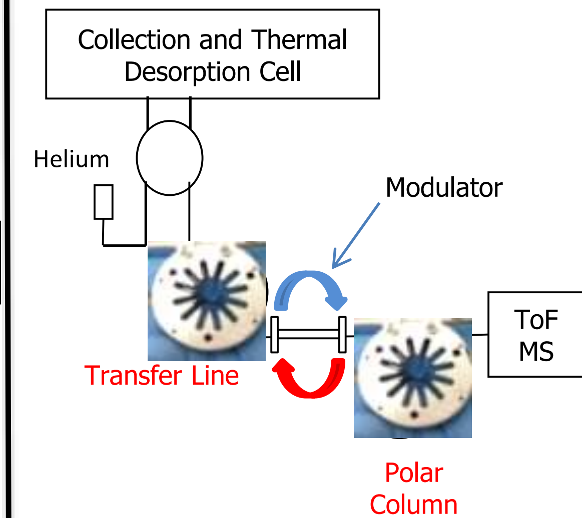


Chromatography-Separated MS

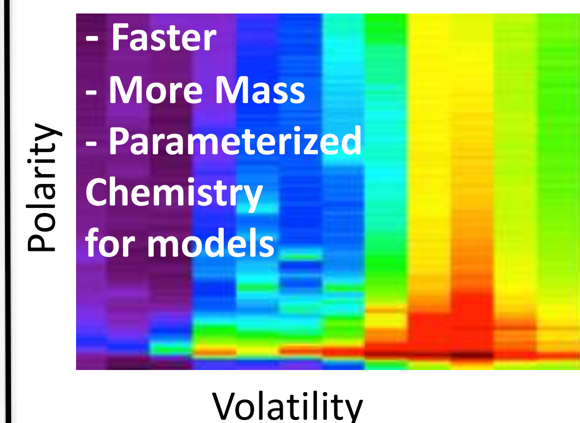


Williams et al, AS&T 2006
Goldstein et al, J.ChromA 2008

Volatility and Polarity Separator (VAPS)

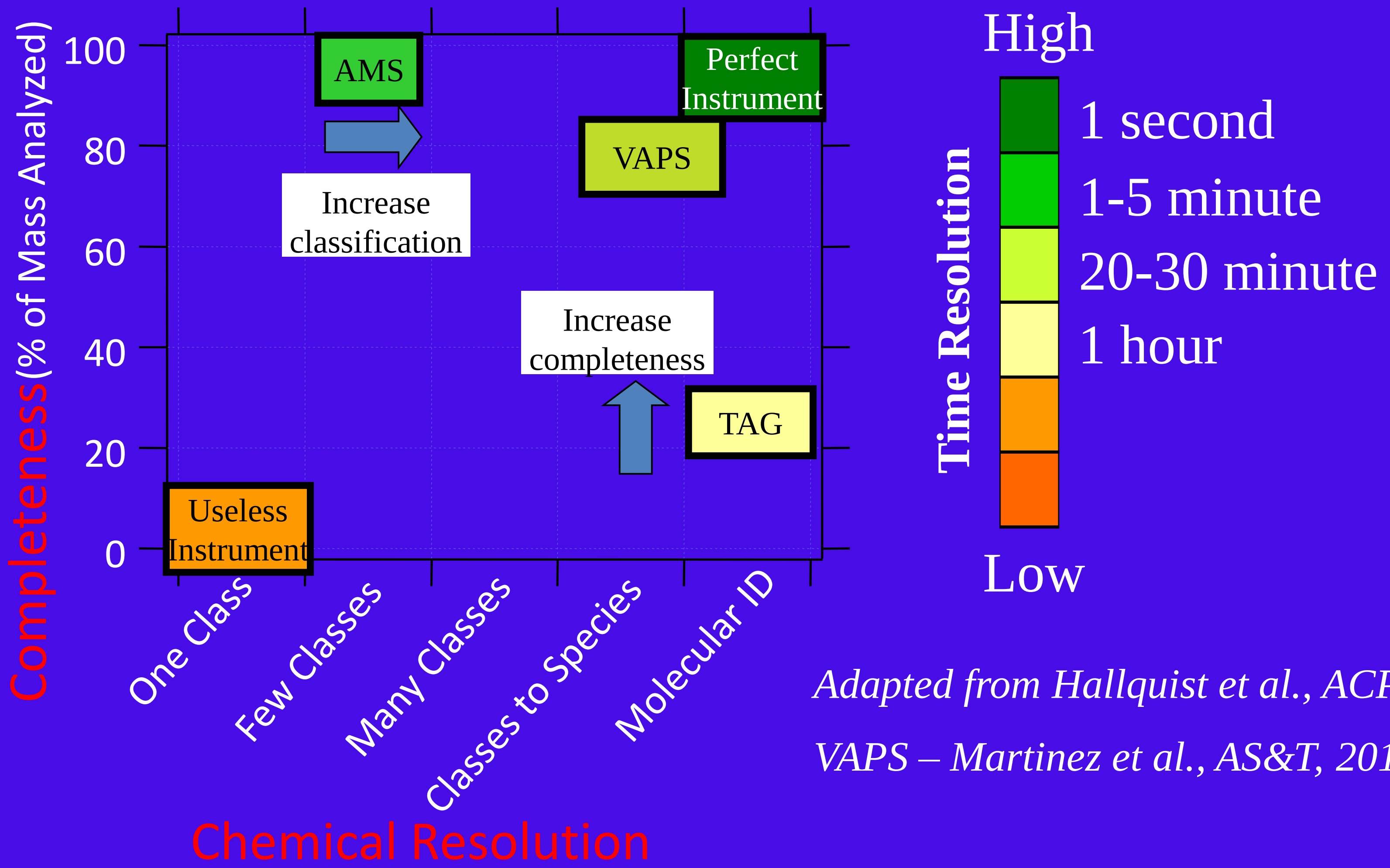


Vol. & Pol.- Separated MS



Martinez et al, AS&T 2016

Organic Aerosol Analysis in Perspective

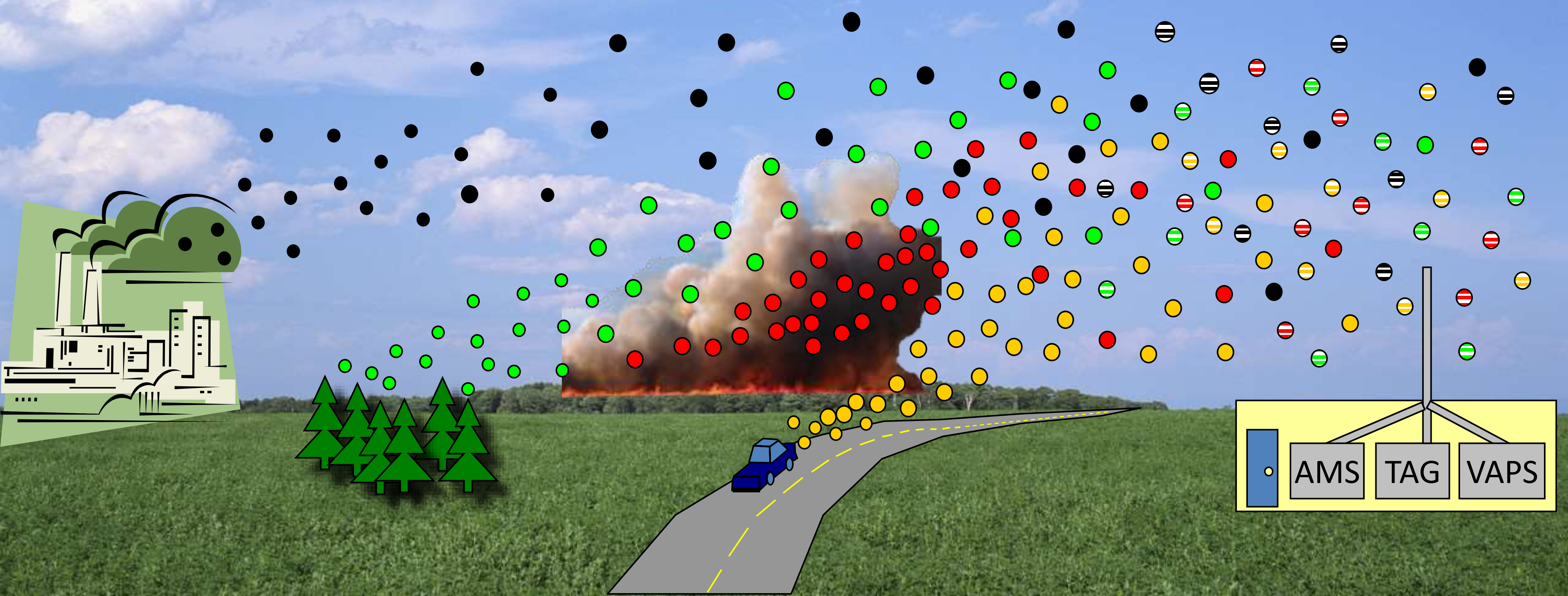


Adapted from Hallquist et al., ACP, 2009

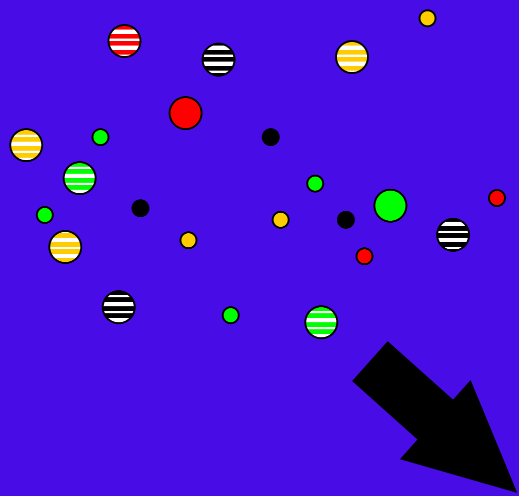
VAPS – Martinez et al., AS&T, 2016

<u>Aerodyne Research Inc. (US-DOE – SBIR, Phases I, II)</u>: *Volatility and polarity separated total organic aerosol using thermal desorption modulated chromatography*

In-Situ Measurements



In-Situ Measurements

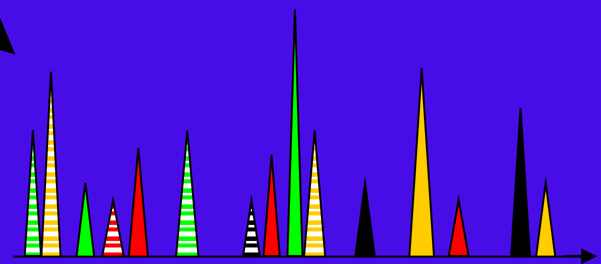


Sample and separate using complementary techniques:

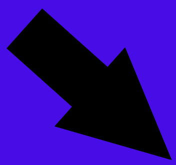
AMS (Mass Spec. of organic and inorganic components)

VAPS (organic components with additional chemical separation)

TAG (individual organic “marker” compounds)



x Time Series

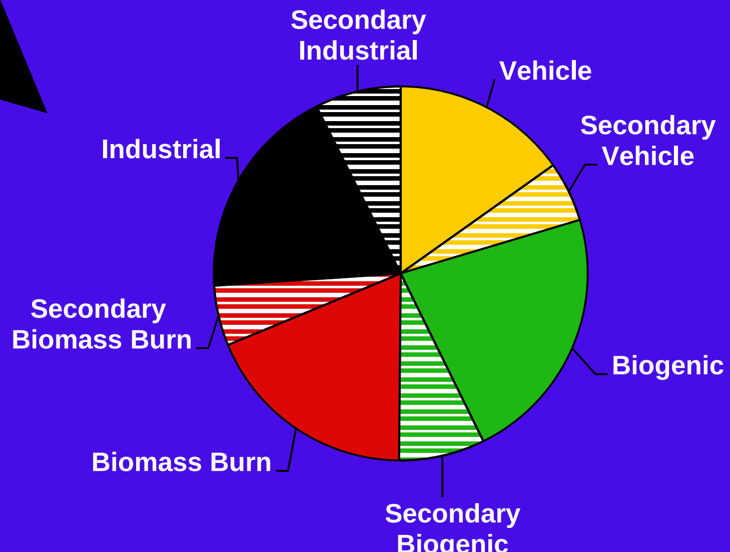


Group covarying chemical signals:

Positive Matrix Factorization (PMF)

Match to known source profiles

Factors can also represent atmospheric transformation processes



OUTLINE

- Instrument Development
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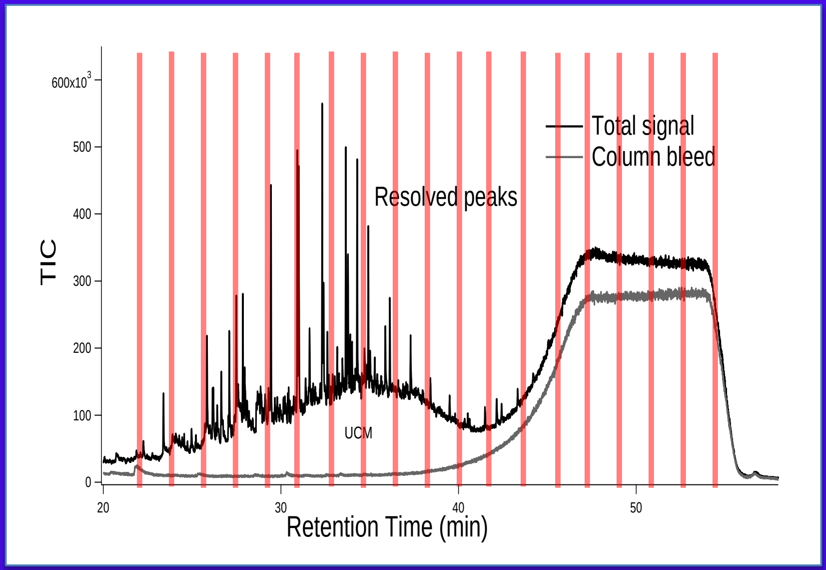
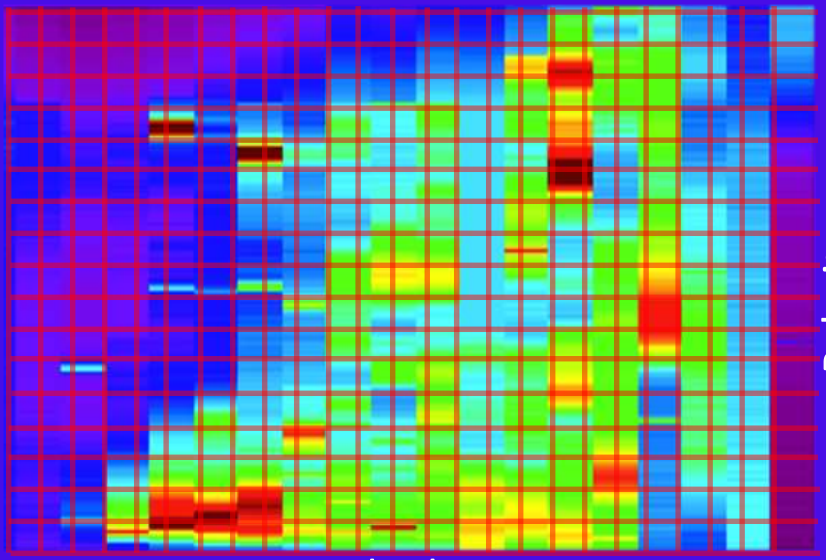
New binning method developed to directly insert a collection of TAG chromatograms or VAPS "vapograms" into PMF.

- Saves from having to integrate individual compounds
- Incorporates the unresolved complex mixture (UCM)

Chromatogram



"Vapogram"



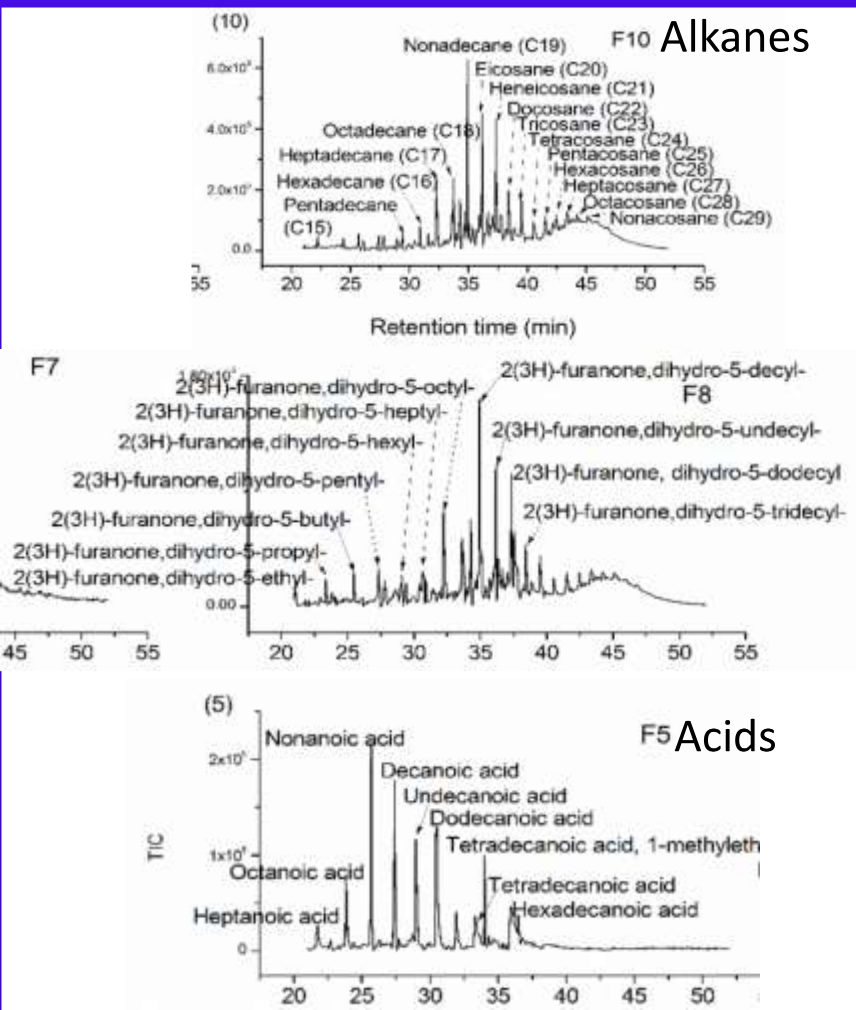
Bin size determines degree of chemical resolution

Zhang et al, AS&T 2014

Binned PMF data matrix can be arranged to separate for:

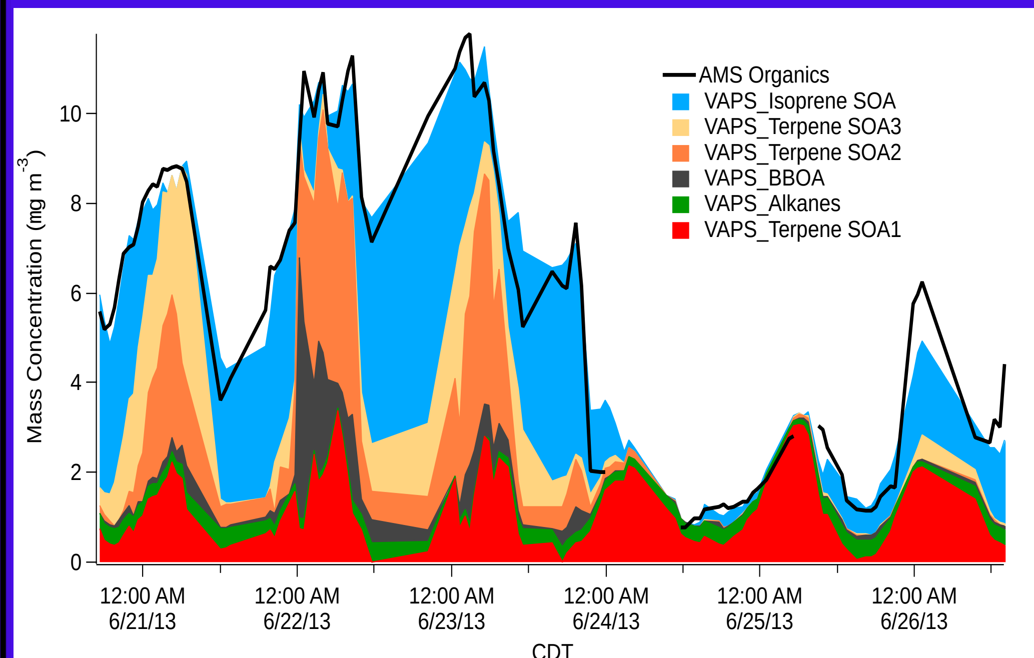
1) Major <u>chromatogram components</u> (e.g., compounds with similar mass spectral features or functionality)

Chromatogram Deconvolution PMF



2) Major study-time components (e.g., <u>Sources</u> or Transformations)

Source Apportionment PMF



Zhang et al, AS&T 2014 + In-Prep.

OUTLINE

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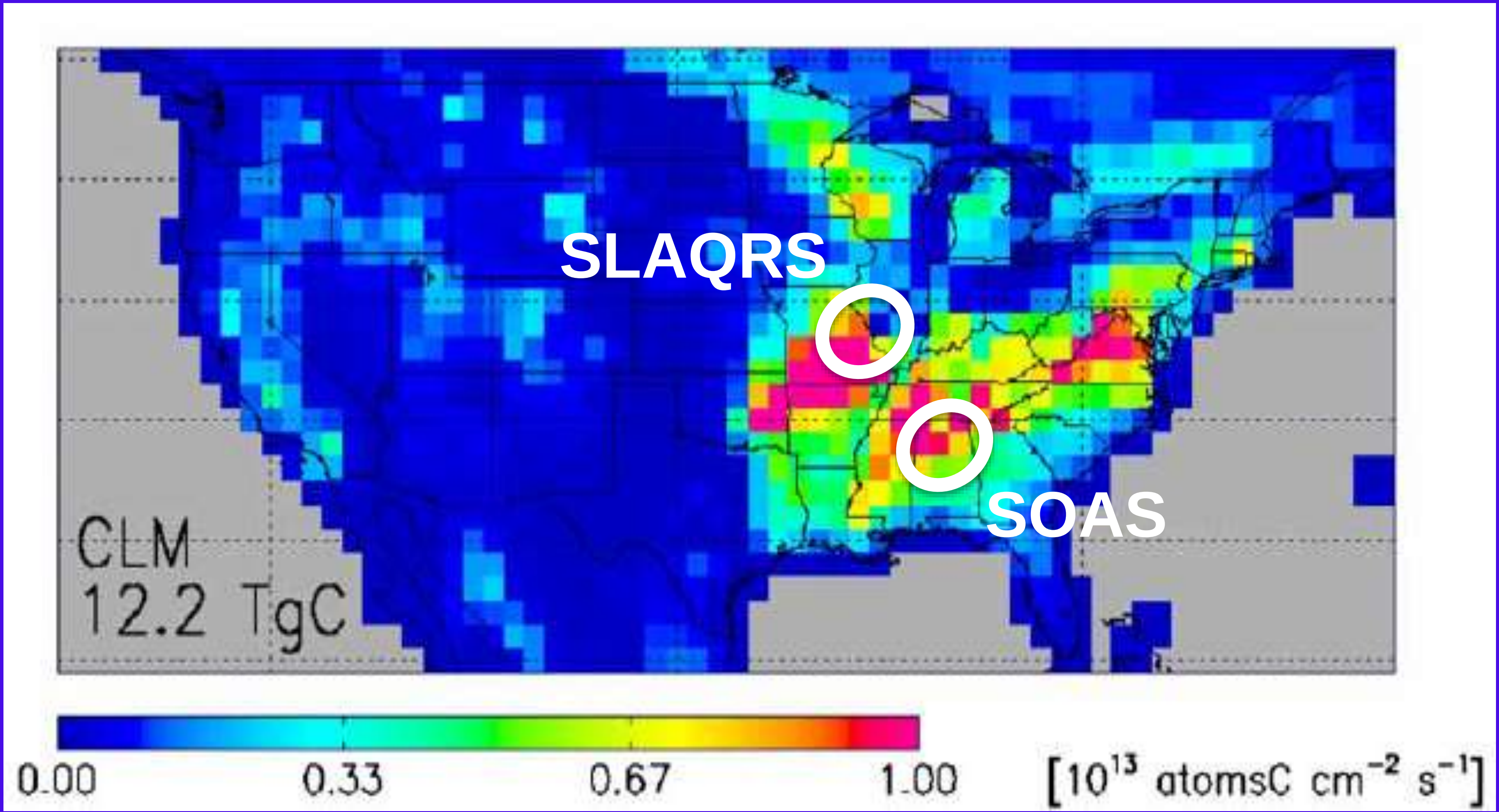
Observations from two recent field studies

Modeled Isoprene Emissions



Millet et al. (2008)

Now known that isoprene can produce SOA….

Formation of Isoprene SOA

(anthropogenic influences)

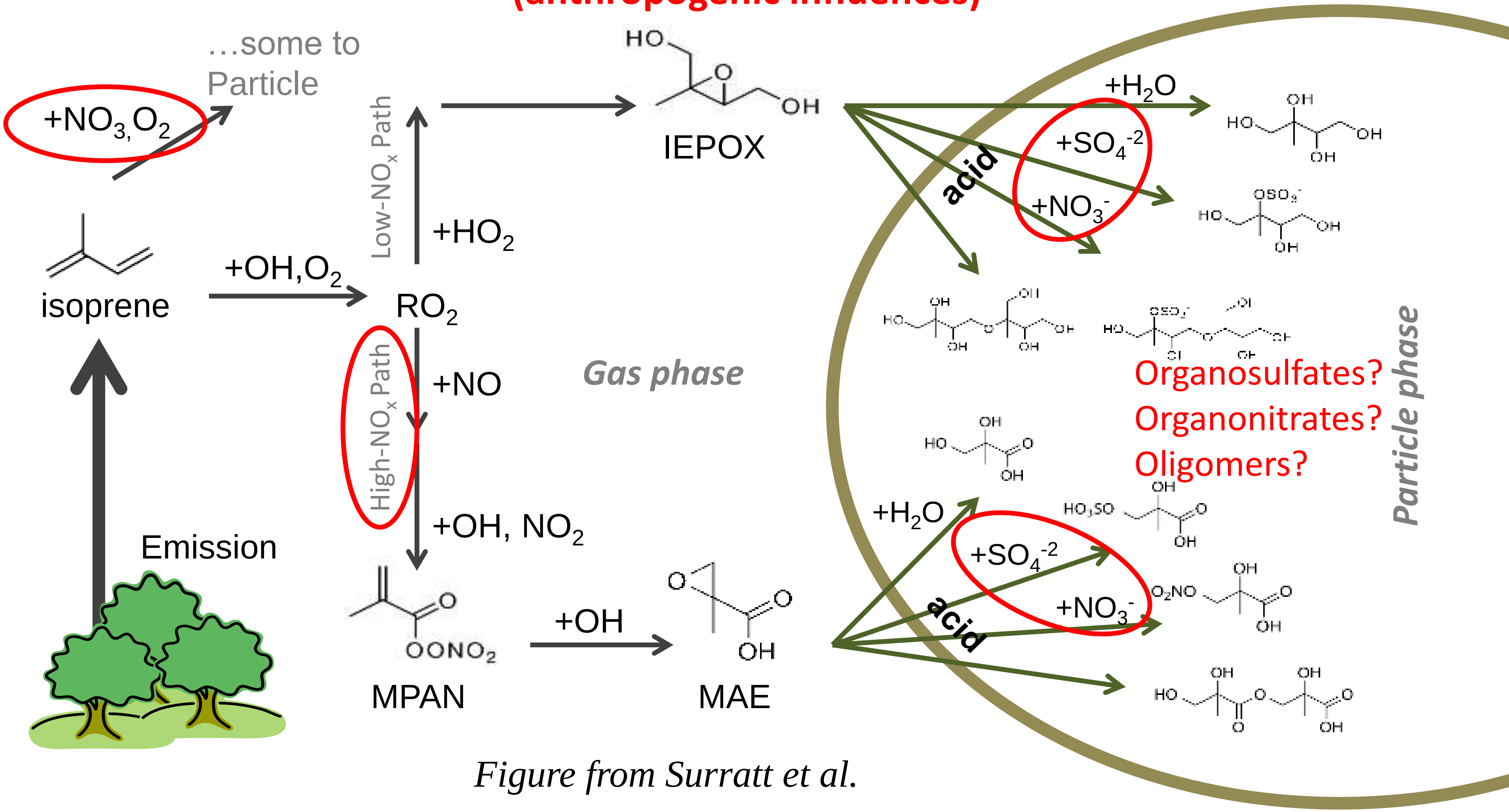


Figure from Surratt et al.

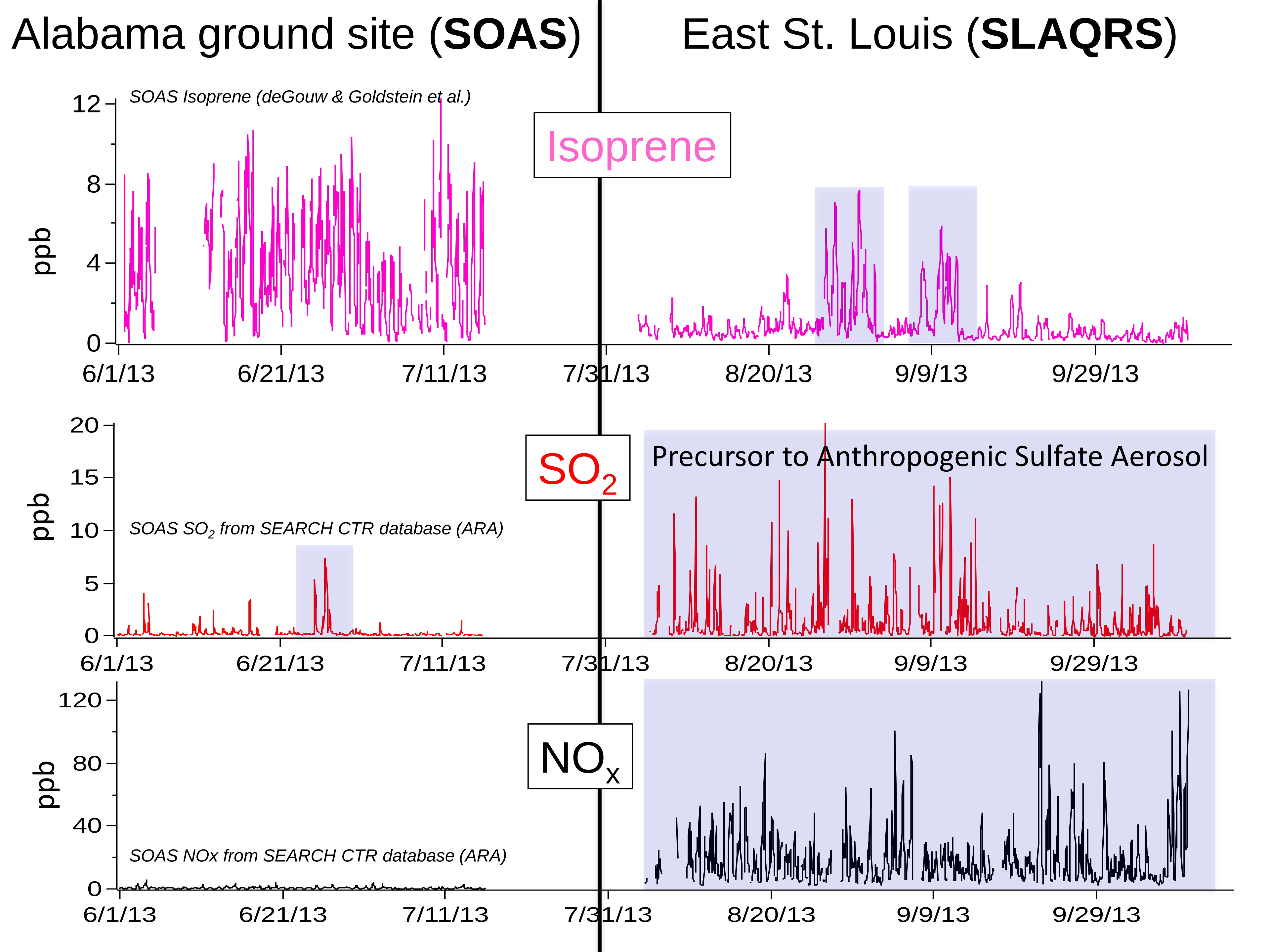
Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States

Allen H. Goldstein[1], Charles D. Koven[2], Colette L. Heald[3], and Inez Y. Fung[1]

Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA 94720

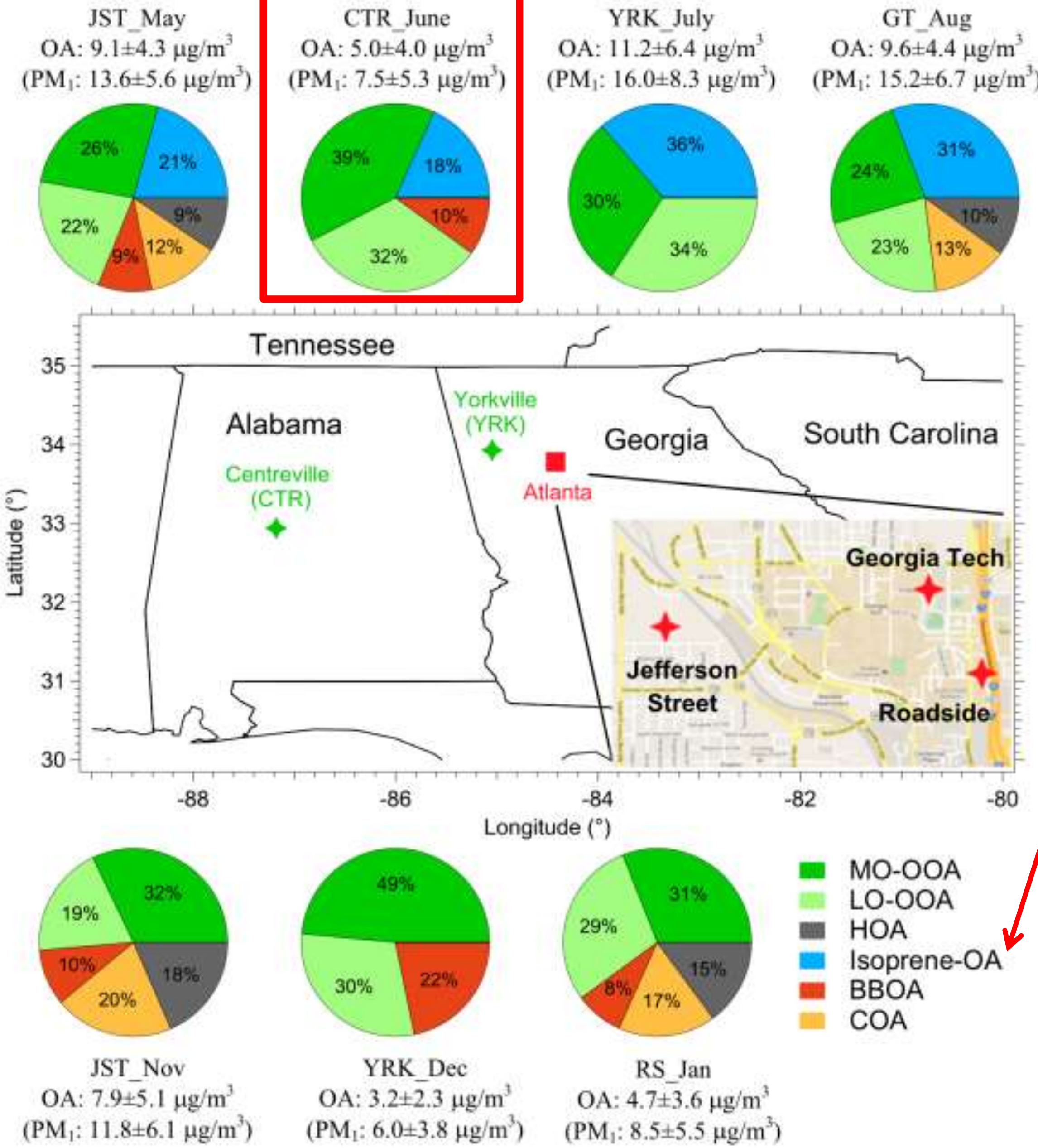
Contributed by Inez Y. Fung, April 15, 2009 (sent for review July 28, 2008)

Goldstein, Fung, et al, 2009
(satellite observations)


Alabama ground site (SOAS)
East St. Louis (SLAQRS)
SOAS Isoprene (deGouw & Goldstein et al.)
Isoprene
ppb
12
8
4
0
6/1/13
6/21/13
7/11/13
7/31/13
8/20/13
9/9/13
9/29/13
20
15
10
5
0
SO2
Precursor to Anthropogenic Sulfate Aerosol
SOAS SO2 from SEARCH CTR database (ARA)
120
80
40
0
NOx
SOAS NOx from SEARCH CTR database (ARA)

AMS Factors from SOAS

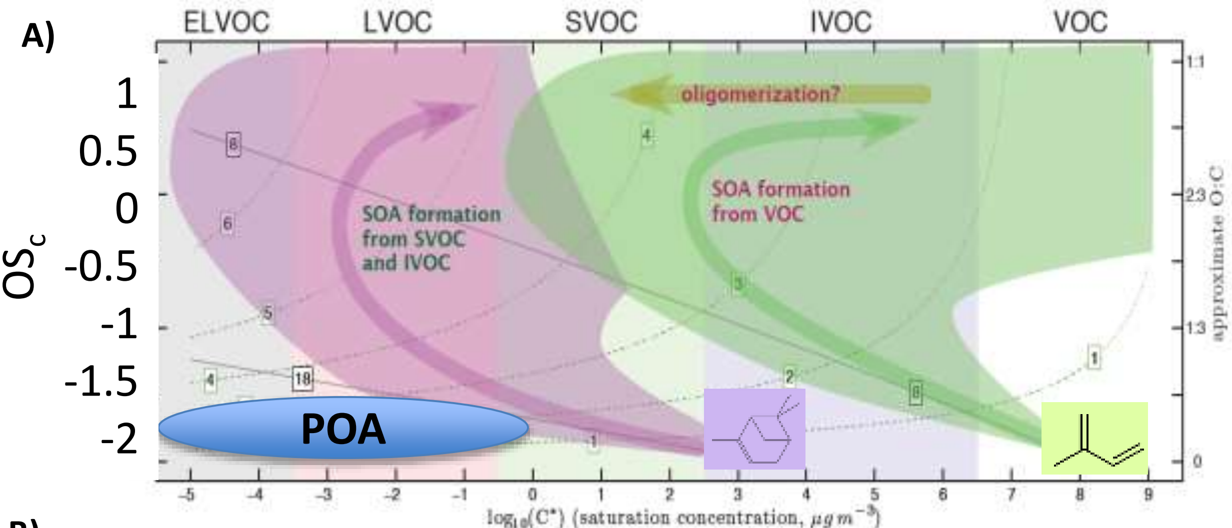
Xu et al., PNAS, 2015



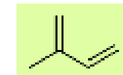
AMS only finds 1 type of isoprene SOA, although there are various formation pathways. AMS may not easil differentiate.

Some lab evidence showing LO-OOA may be terpene SOA.

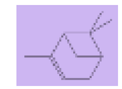
Can **VAPS** offer more information?



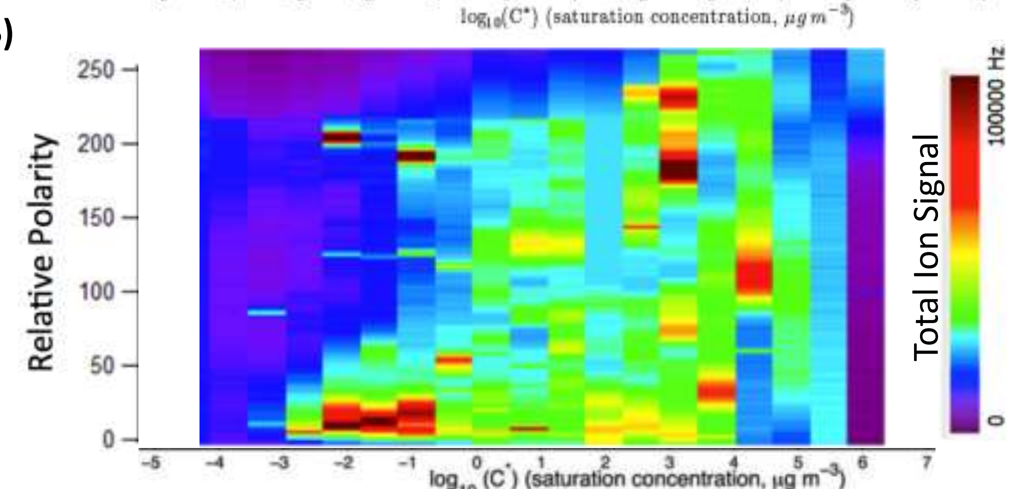
2D-VBS Oxidation pathways
(*Donahue et al., ACPD 2012*)



C_5H_8 Isoprene



$C_{10}H_{16}$ Terpenes

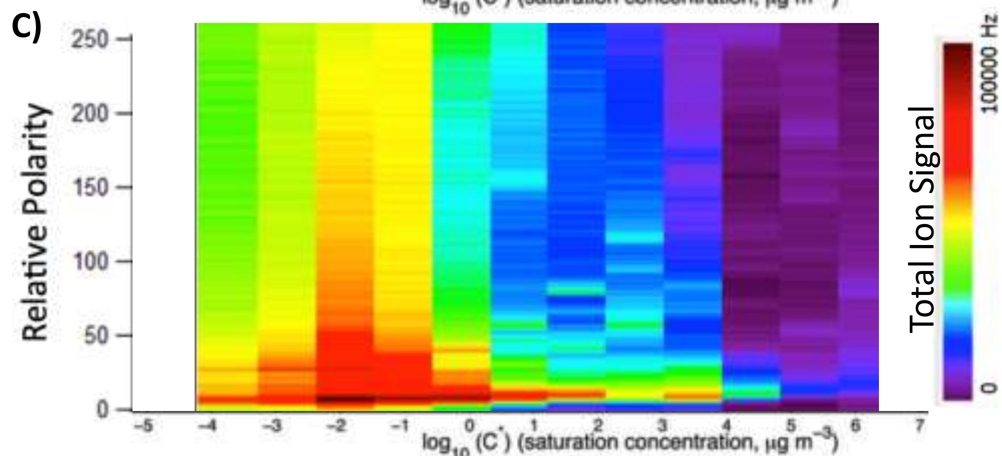


First Field deployments for VAPS

VAPS - SOAS

Rural Alabama

(lots of Isoprene and Terpene SOA)

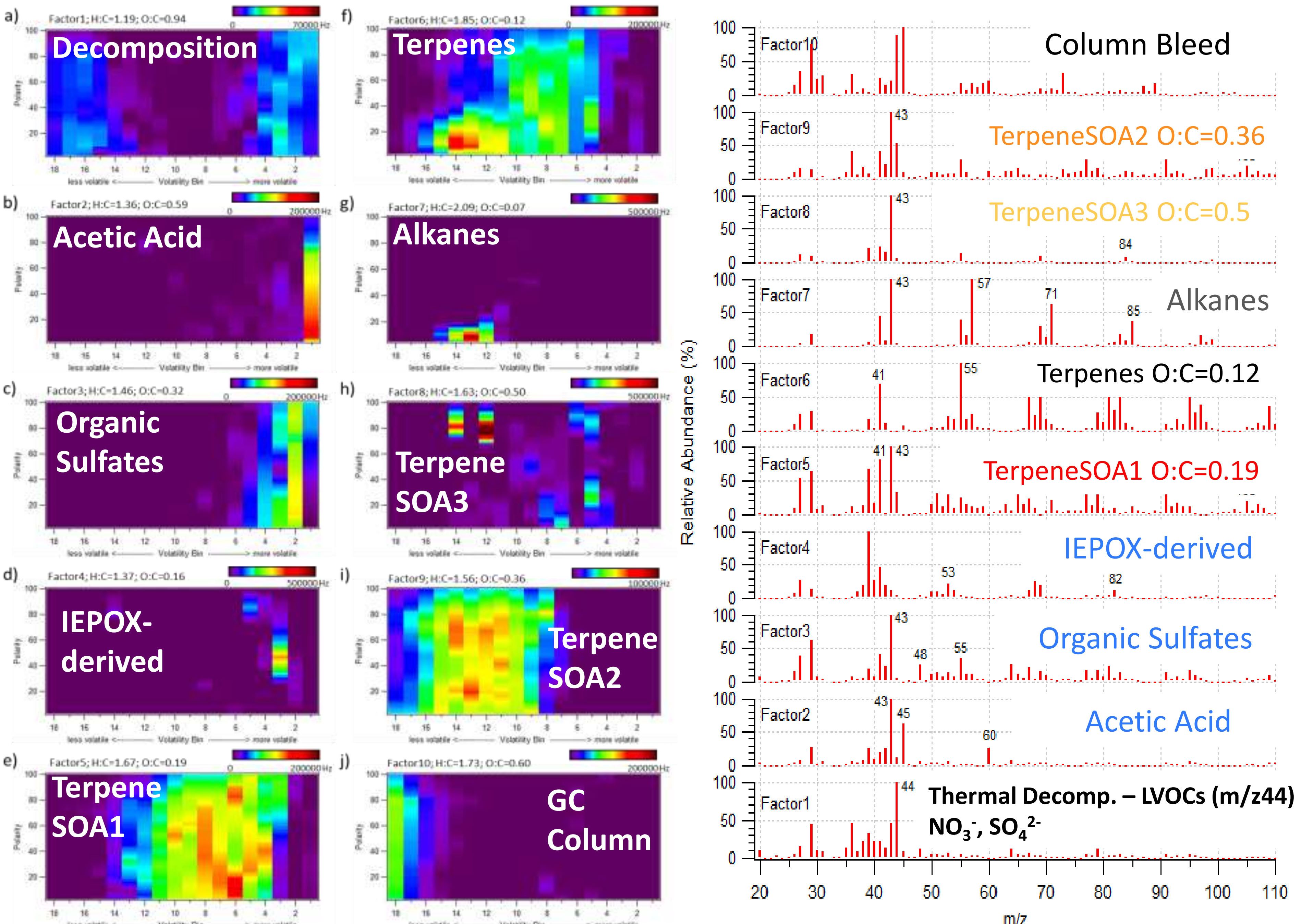


VAPS – SLAQRS

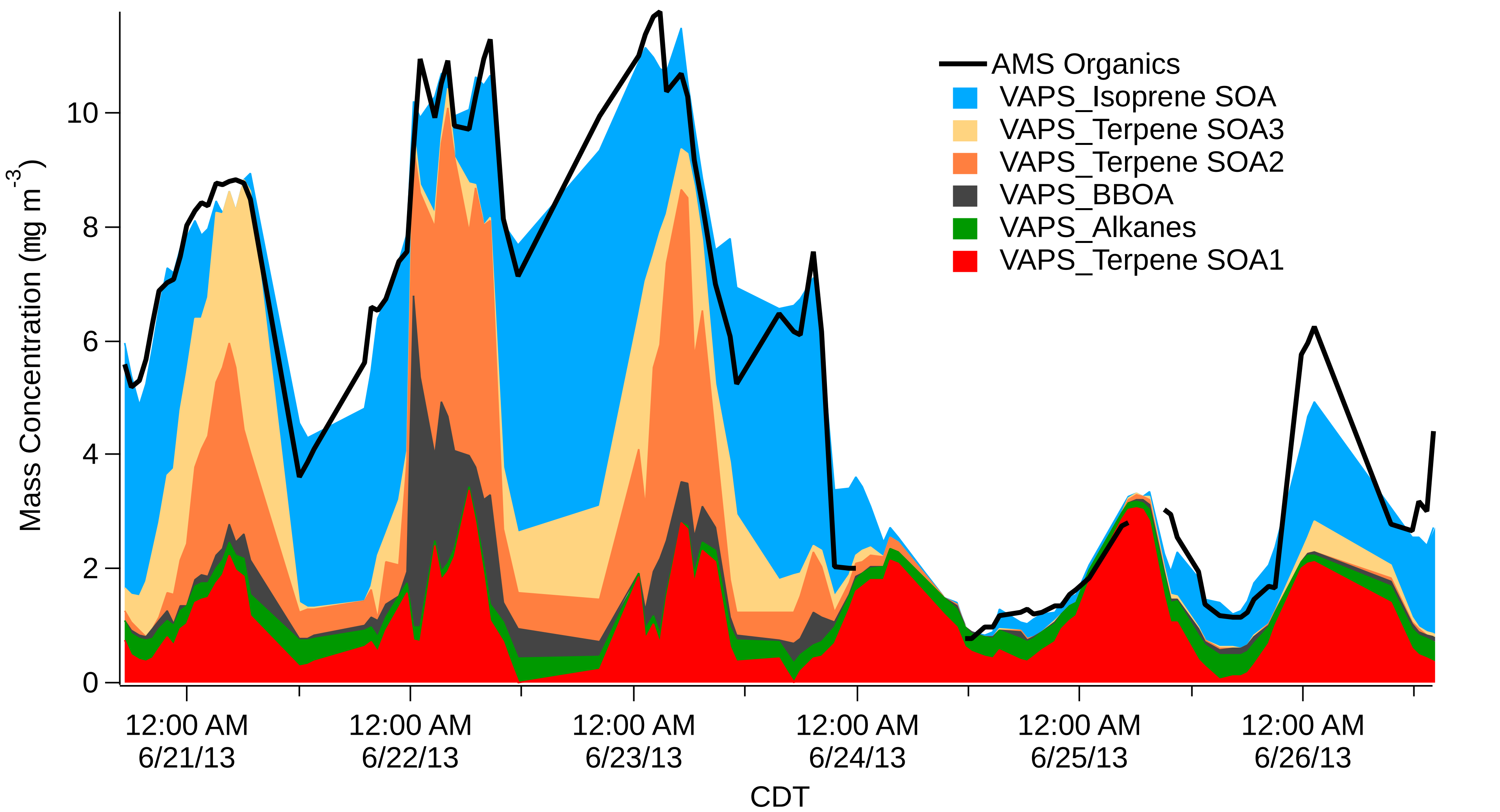
Urban St. Louis (more POA)

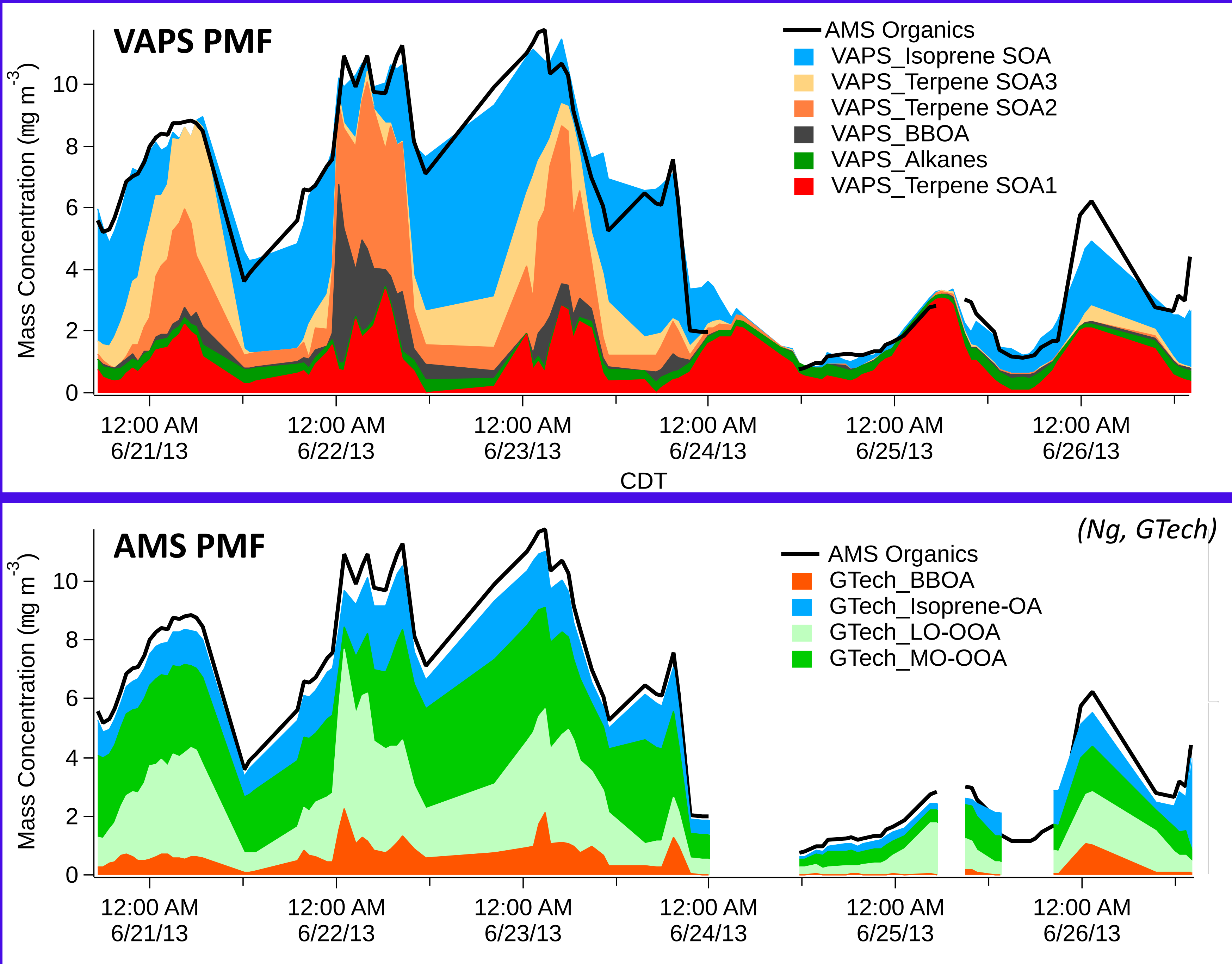
Martinez et al, AS&T 2016

Chromatogram Deconvolution PMF on Binned VAPS Data (**SOAS**)



Source Apportionment PMF on Binned VAPS Data (**SOAS**)



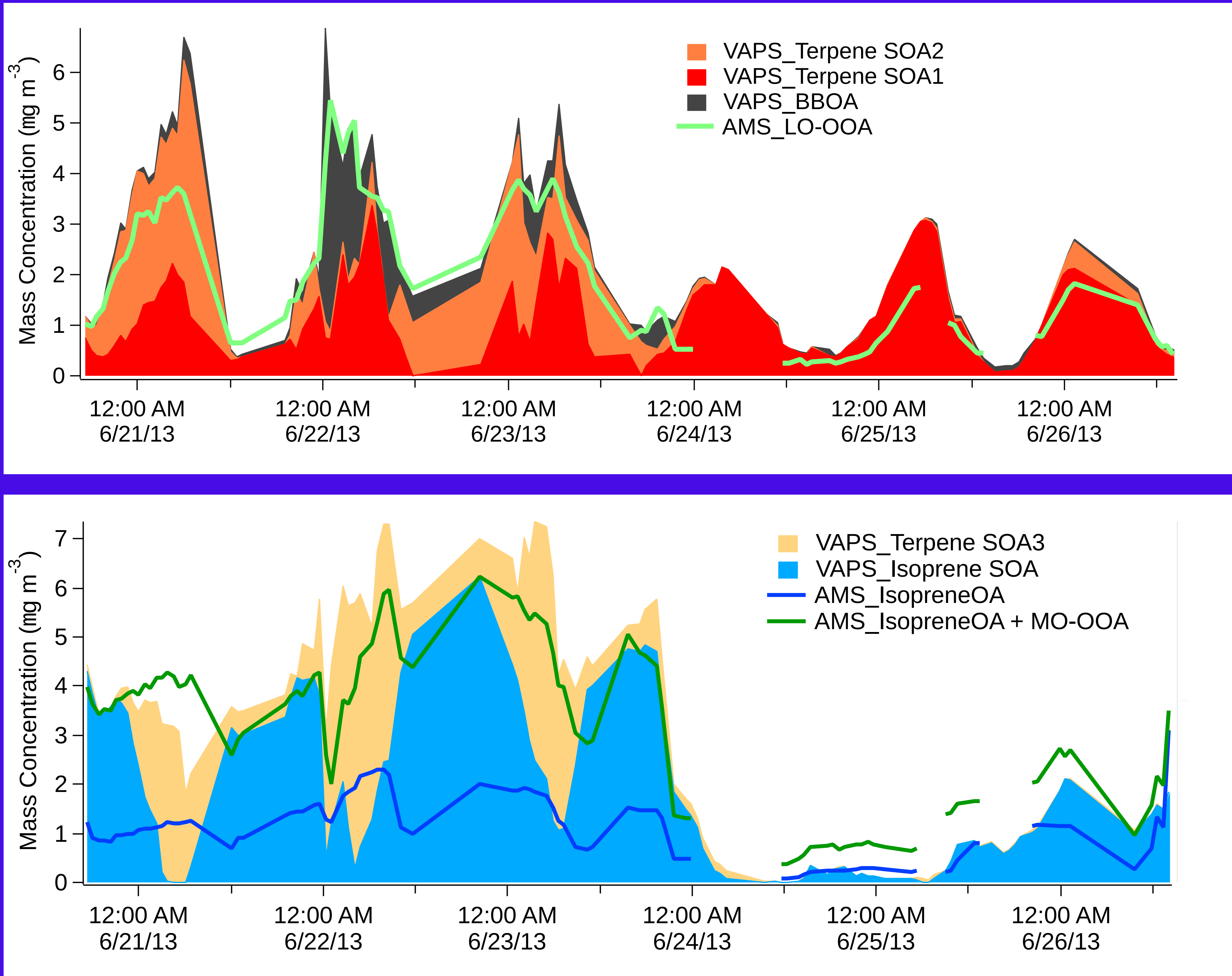

VAPS PMF
AMS Organics
VAPS_Isoprene SOA
VAPS_Terpene SOA3
VAPS_Terpene SOA2
VAPS_BBOA
VAPS_Alkanes
VAPS_Terpene SOA1
Mass Concentration (mg m-3)
0
2
4
6
8
10
12:00 AM 6/21/13
12:00 AM 6/22/13
12:00 AM 6/23/13
12:00 AM 6/24/13
12:00 AM 6/25/13
12:00 AM 6/26/13
CDT
AMS PMF
(Ng, GTech)
AMS Organics
GTech_BBOA
GTech_Isoprene-OA
GTech_LO-OOA
GTech_MO-OOA
Mass Concentration (mg m-3)
0
2
4
6
8
10
12:00 AM 6/21/13
12:00 AM 6/22/13
12:00 AM 6/23/13
12:00 AM 6/24/13
12:00 AM 6/25/13
12:00 AM 6/26/13

Correlations (Pearson r)

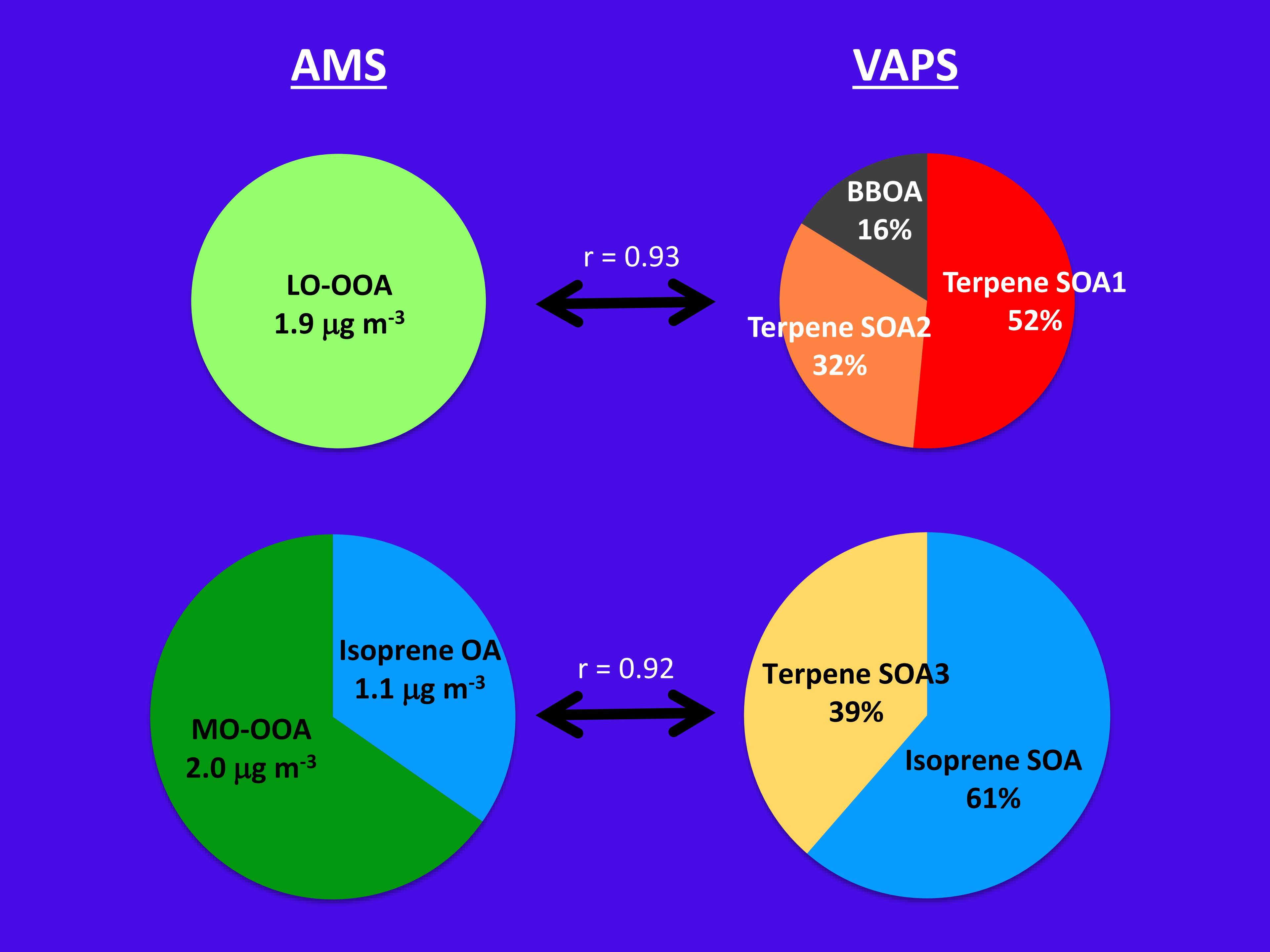
		SV-TAG (UC-Berkeley)									AMS				
		C5 alkene triol 1	C5 alkene triol 2	2-methyltetrol 1	2-methyltetrol 2	methylglyceric acid	pinic acid	pinonic acid	hydroxyglutaric acid	levoglucosan	Isoprene OA	LO-OOA	MO-OOA	BBOA	Isoprene OA + MO-OOA
VAPS	Isoprene SOA	0.67	0.67	0.53	0.55	0.45	-0.04	0.29	0.55	0.22	0.43	0.04	0.65	0.28	0.67
	Terpene SOA1	-0.18	-0.25	-0.10	-0.28	-0.46	0.56	0.27	0.17	0.19	0.24	0.56	0.14	0.28	0.06
	Terpene SOA2	0.43	0.39	0.59	0.50	0.08	0.70	0.40	0.65	0.60	0.23	0.54	0.60	0.30	0.55
	Terpene SOA3	0.44	0.32	0.51	0.31	0.17	0.73	0.79	0.55	0.35	0.66	0.86	0.55	0.70	0.65
	BBOA	0.25	0.15	0.18	0.08	0.20	0.29	0.63	0.27	0.15	0.37	0.62	0.10	0.67	0.26
	IsopreneSOA + TerpeneSOA3	0.78	0.69	0.73	0.60	0.40	0.47	0.75	0.76	0.40	0.80	0.67	0.87	0.73	**0.92**
	TerpeneSOA1+2 + BBOA	0.31	0.20	0.43	0.23	-0.11	0.87	0.70	0.64	0.55	0.45	**0.93**	0.51	0.67	0.52

		C5 alkene triol 1	C5 alkene triol 2	2-methyltetrol 1	2-methyltetrol 2	methylglyceric acid	pinic acid	pinonic acid	hydroxyglutaric acid	levoglucosan
AMS	IsopreneOA	0.78	0.67	0.69	0.61	0.68	0.40	0.62	0.52	0.25
	LO-OOA	0.52	0.38	0.53	0.38	0.23	0.83	0.85	0.68	0.51
	MO-OOA	0.77	0.74	0.79	0.73	0.43	0.54	0.54	0.85	0.46
	BBOA	0.62	0.54	0.50	0.40	0.28	0.51	0.71	0.61	0.50
	Isoprene+MO-OOA	0.79	0.70	0.81	0.68	0.40	0.55	0.69	0.80	0.51

Combinations of Components
Provides highest correlations



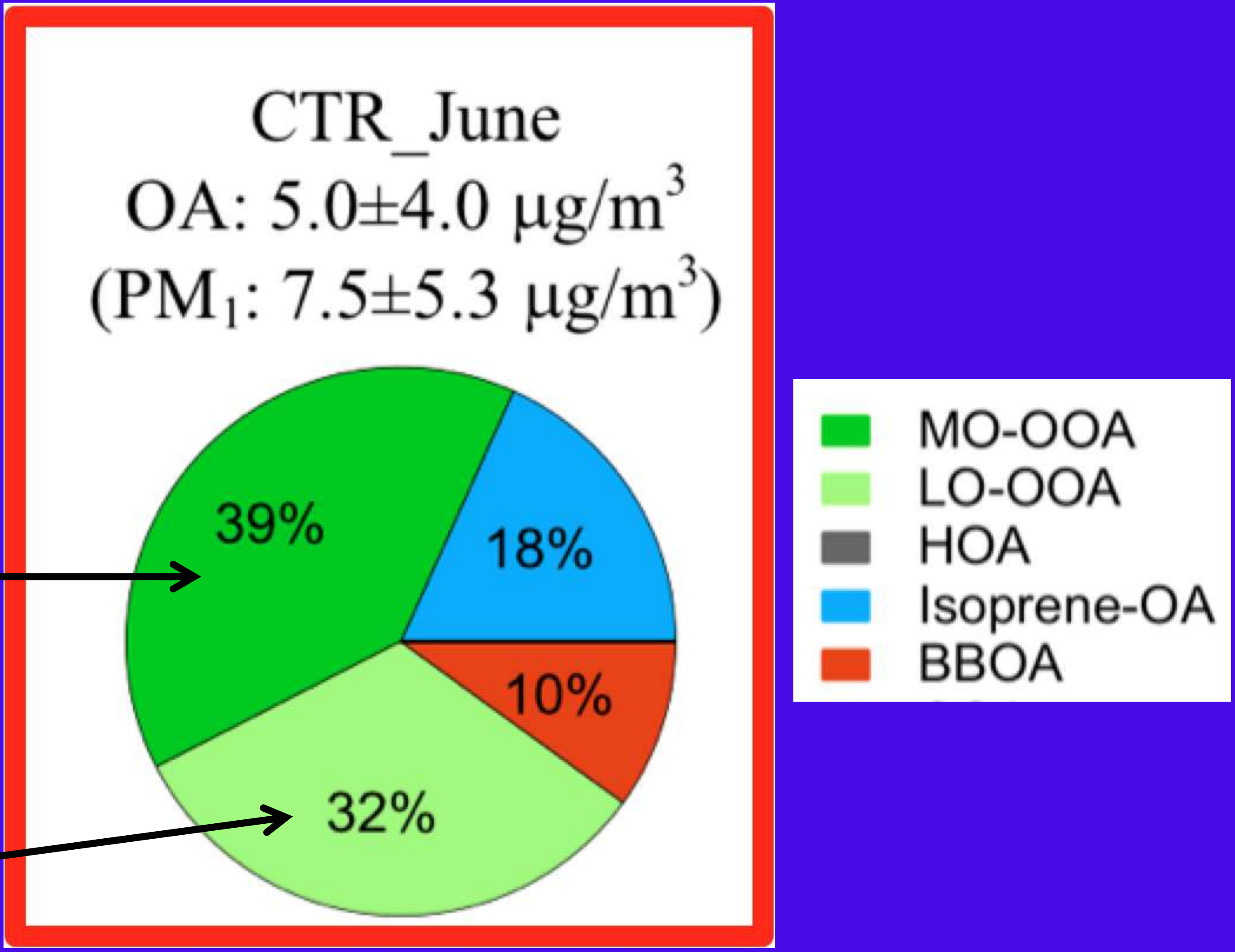
VAPS_Terpene SOA2
VAPS_Terpene SOA1
VAPS_BBOA
AMS_LO-OOA
Mass Concentration (mg m-3)
0
1
2
3
4
5
6
12:00 AM 6/21/13
12:00 AM 6/22/13
12:00 AM 6/23/13
12:00 AM 6/24/13
12:00 AM 6/25/13
12:00 AM 6/26/13
VAPS_Terpene SOA3
VAPS_Isoprene SOA
AMS_IsopreneOA
AMS_IsopreneOA + MO-OOA
Mass Concentration (mg m-3)
0
1
2
3
4
5
6
7
12:00 AM 6/21/13
12:00 AM 6/22/13
12:00 AM 6/23/13
12:00 AM 6/24/13
12:00 AM 6/25/13
12:00 AM 6/26/13



AMS
VAPS
LO-OOA
1.9 μg m-3
r = 0.93
BBOA
16%
Terpene SOA1
52%
Terpene SOA2
32%
Isoprene OA
1.1 μg m-3
MO-OOA
2.0 μg m-3
r = 0.92
Terpene SOA3
39%
Isoprene SOA
61%

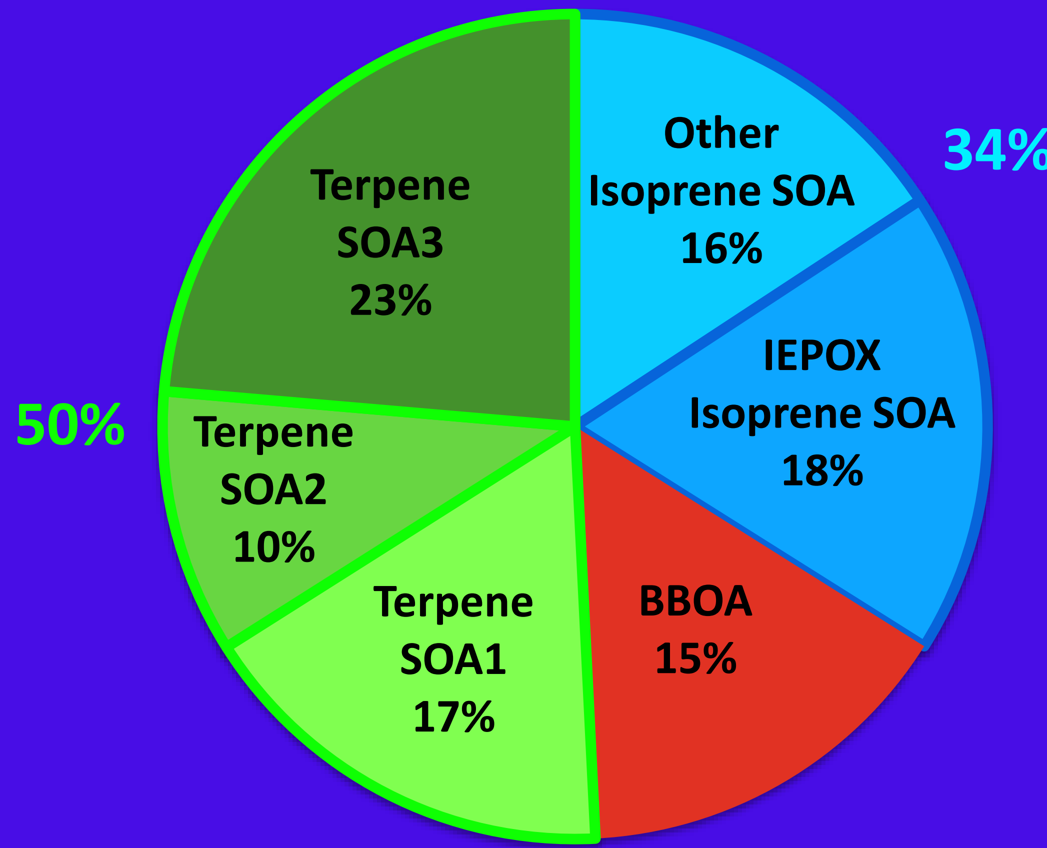
GTech AMS results (*Xu et al., PNAS, 2015*)

VAPS Indicates:

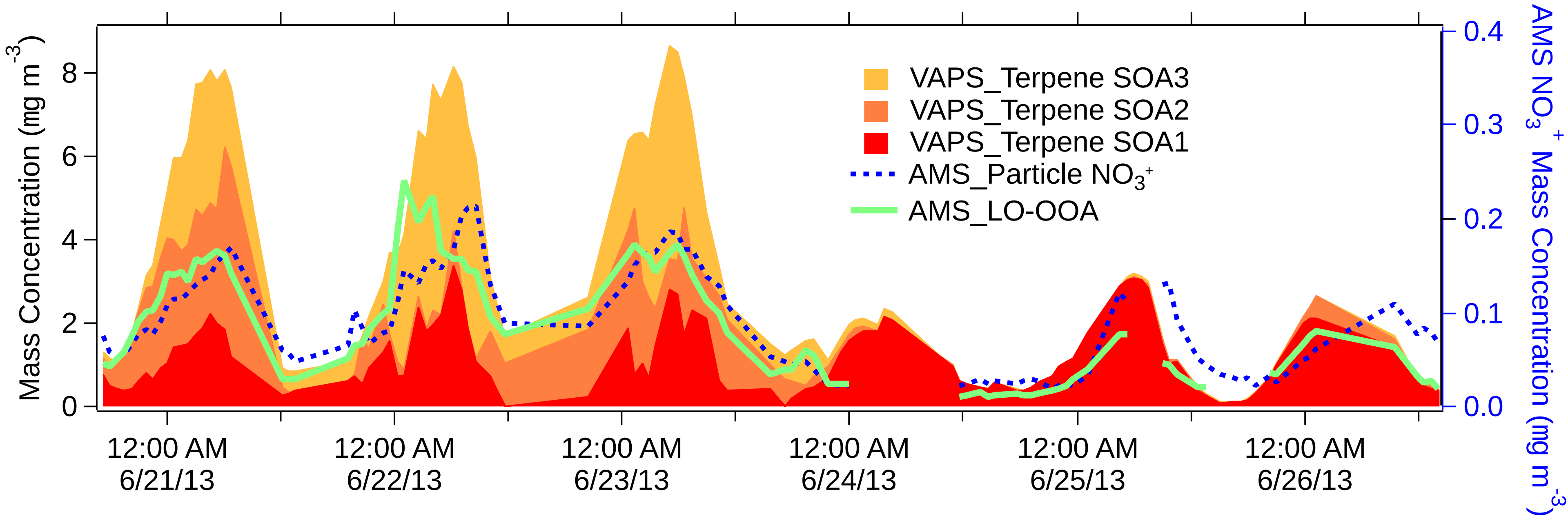


40% Isoprene SOA
60% Terpene SOA3

52% Terpene SOA1
32% Terpene SOA2
16% BBOA



*VAPS analysis based only on 1 week time period, AMS analysis was over entire month



- *Xu et al.* (2015) suggests LO-OOA is largely from terpene **BVOC+NO_3•** and **locally** produced.
- VAPS Terpene SOA3 is in excess of LO-OOA and has highest O:C ratio. It may represent a more aged – regional component.
- Or altered chemistry……need additional lab studies to test

- Currently developing **Isoprene/Terpene + NO_3•** lab studies + analysis of **standards**

- Many of the compounds observed by VAPS do not exist in current “underivatized” mass spectral libraries!

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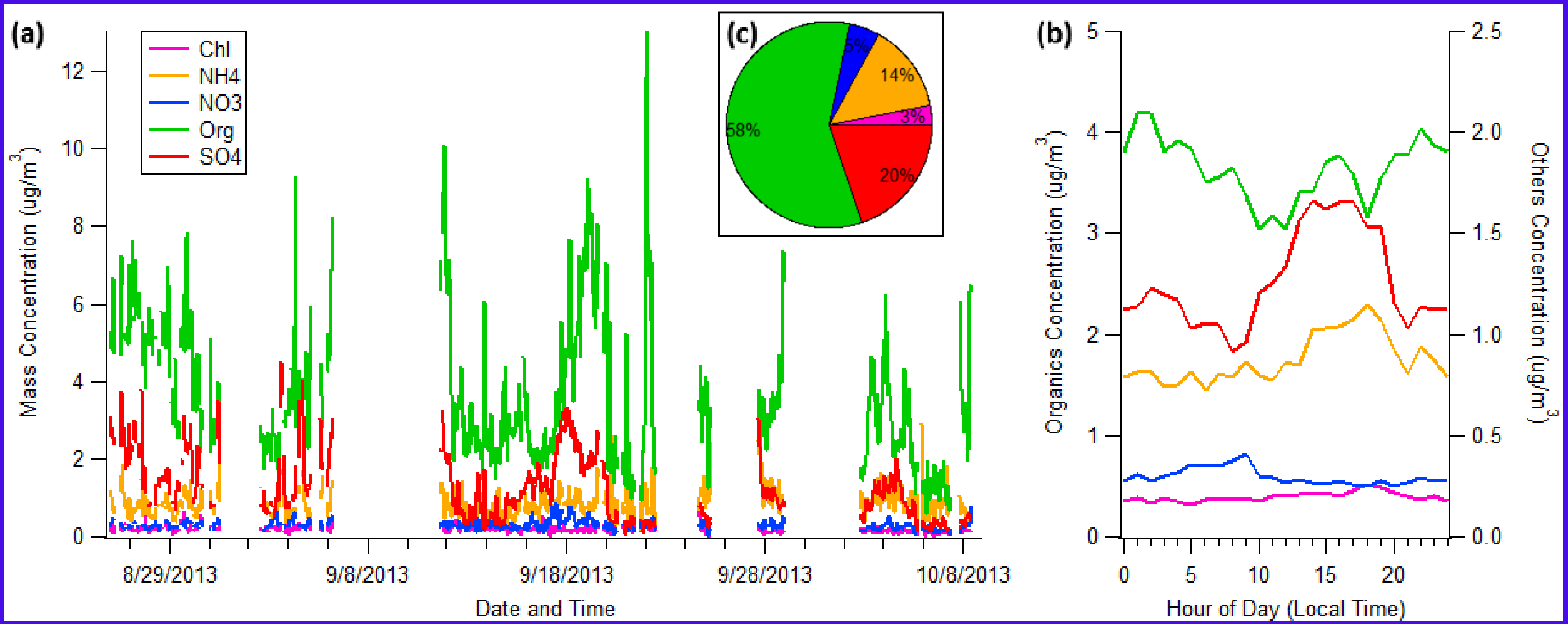
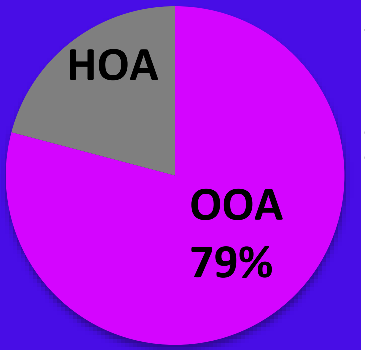
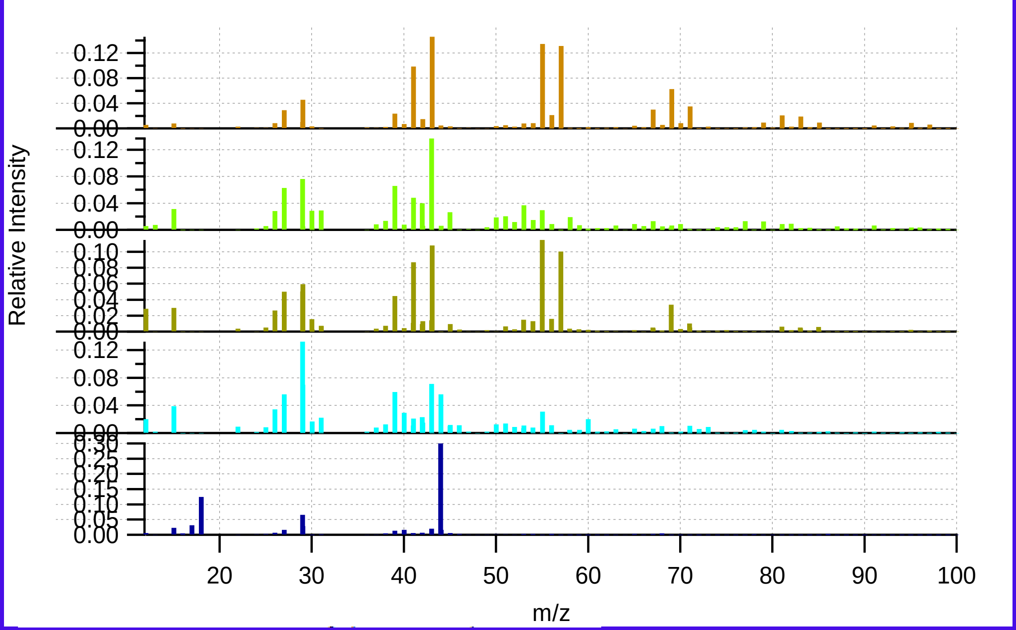
St. Louis Air Quality Regional Study (SLAQRS)

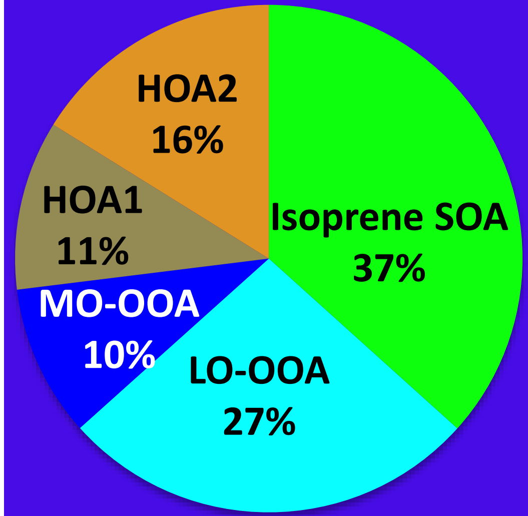
Aug.3 – Oct.15, 2013

1) PMF results from SLAQRS, East St. Louis: (AMS Data)

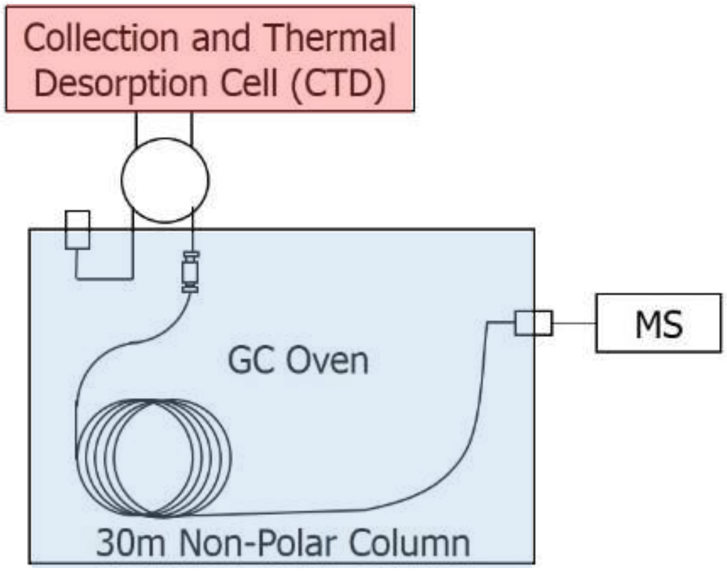


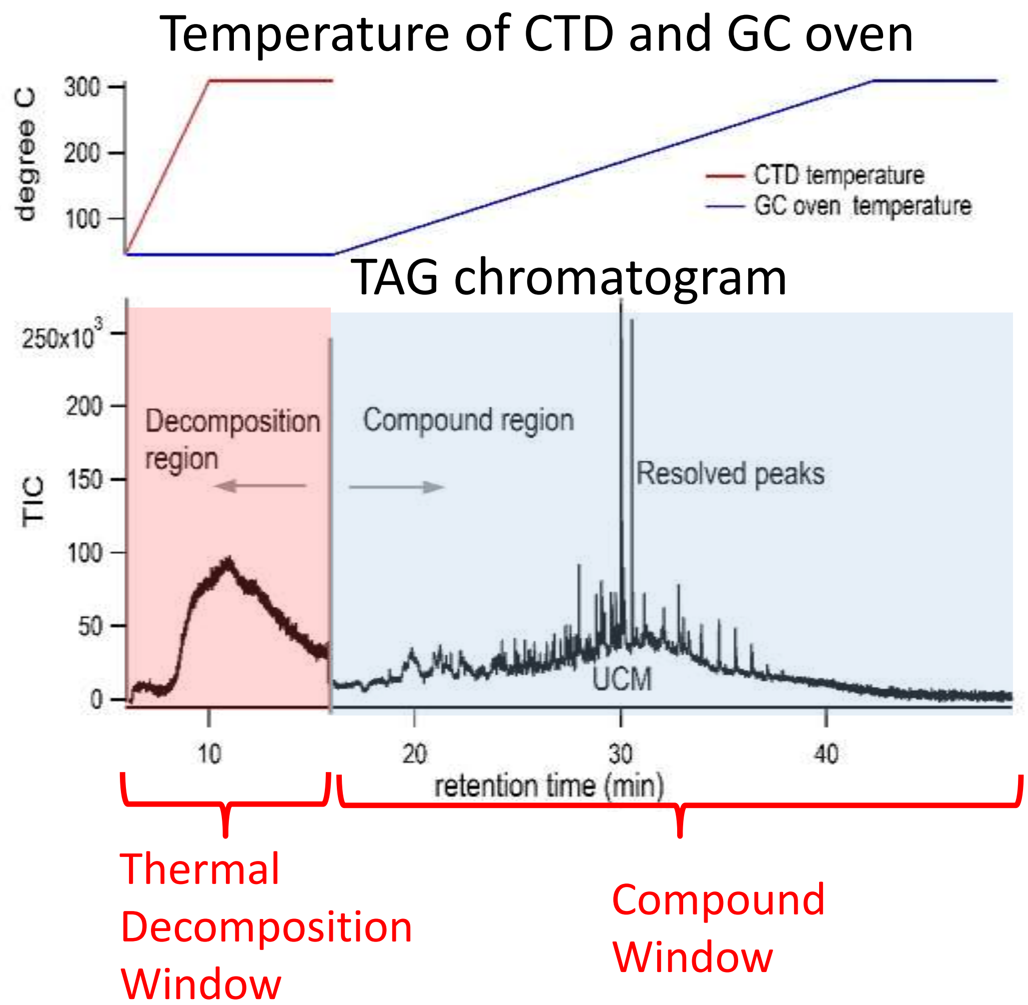






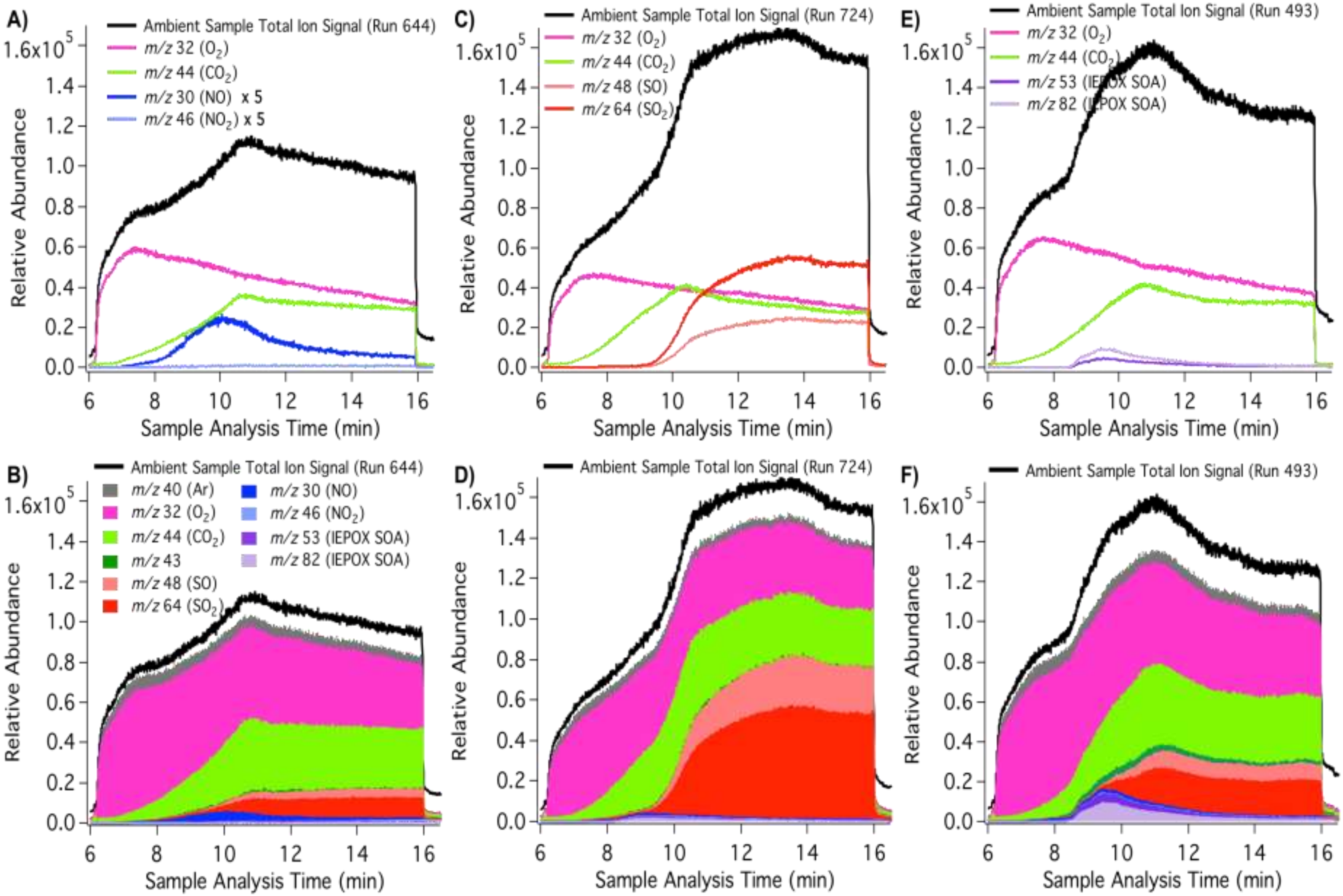
Made an interesting discovery during SLAQRS (TAG and VAPS decomposition signal)





The <u>thermal decomposition</u> signal seems to contain information on the fraction of the aerosol that traditional operation of TAG and VAPS are not capable of detecting

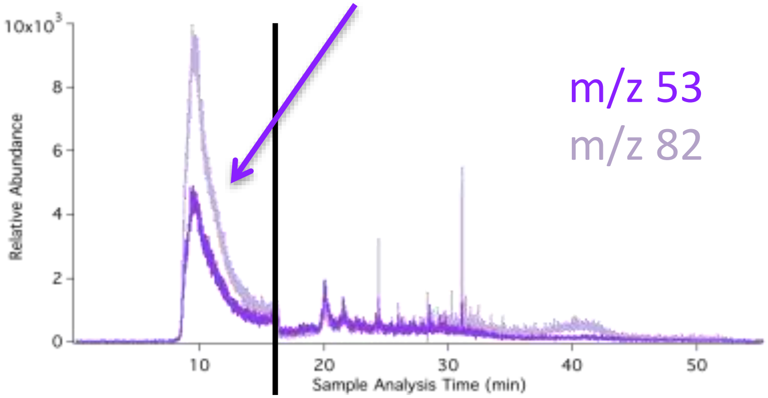
Williams et al., AMTD 2015



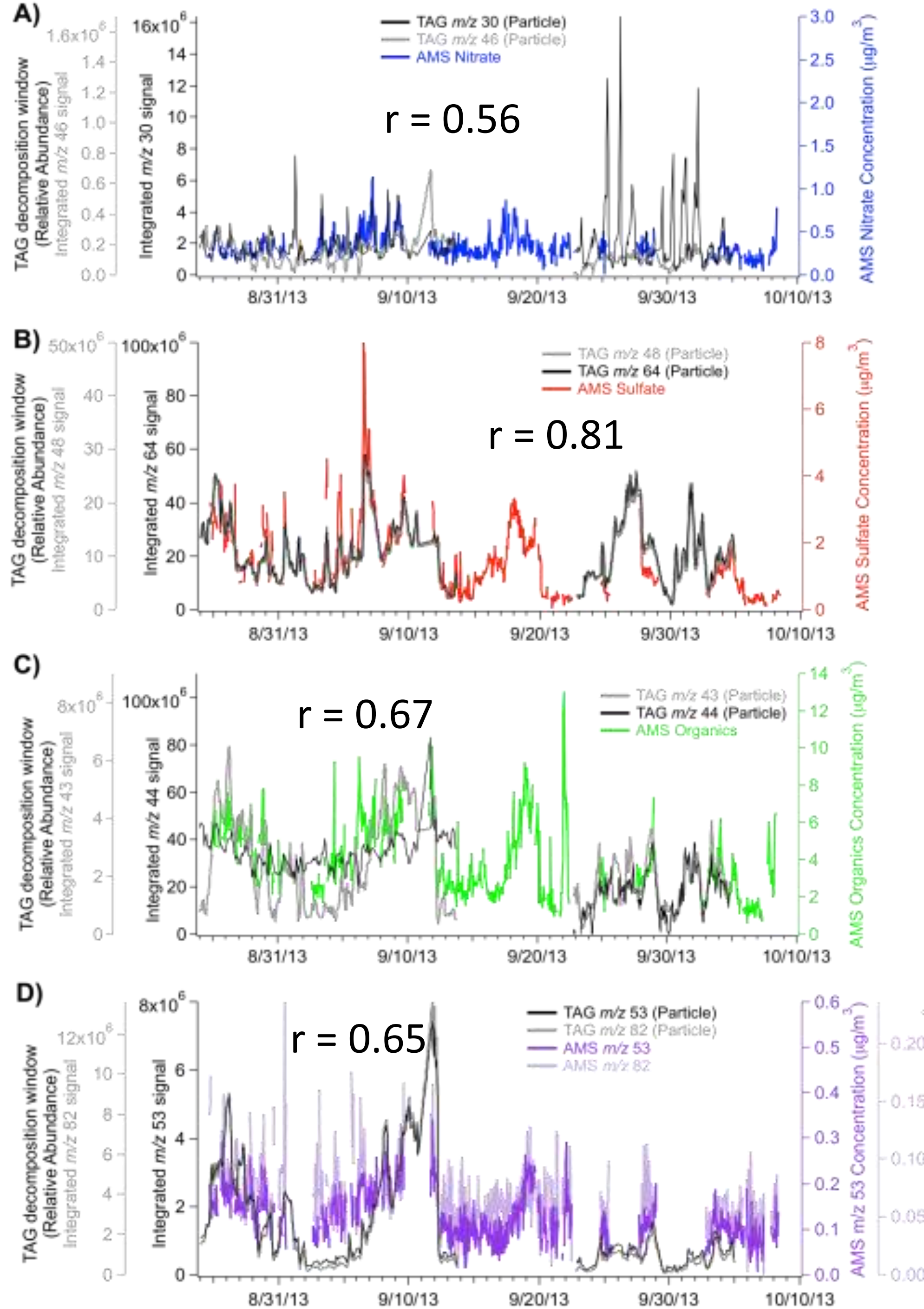
A)
Ambient Sample Total Ion Signal (Run 644)
m/z 32 (O2)
m/z 44 (CO2)
m/z 30 (NO) x 5
m/z 46 (NO2) x 5
1.6x10^5
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Relative Abundance
6
8
10
12
14
16
Sample Analysis Time (min)
C)
Ambient Sample Total Ion Signal (Run 724)
m/z 32 (O2)
m/z 44 (CO2)
m/z 48 (SO)
m/z 64 (SO2)
E)
Ambient Sample Total Ion Signal (Run 493)
m/z 32 (O2)
m/z 44 (CO2)
m/z 53 (IEPOX SOA)
m/z 82 (IEPOX SOA)
B)
Ambient Sample Total Ion Signal (Run 644)
m/z 40 (Ar)
m/z 32 (O2)
m/z 44 (CO2)
m/z 43
m/z 48 (SO)
m/z 64 (SO2)
m/z 30 (NO)
m/z 46 (NO2)
m/z 53 (IEPOX SOA)
m/z 82 (IEPOX SOA)
D)
Ambient Sample Total Ion Signal (Run 724)
F)
Ambient Sample Total Ion Signal (Run 493)

Tracking major ions in the **decomposition window** reveals some good correlations to major AMS components:

A large fraction of the IEPOX signal is in the Decomposition Window



Williams et al., AMTD 2015



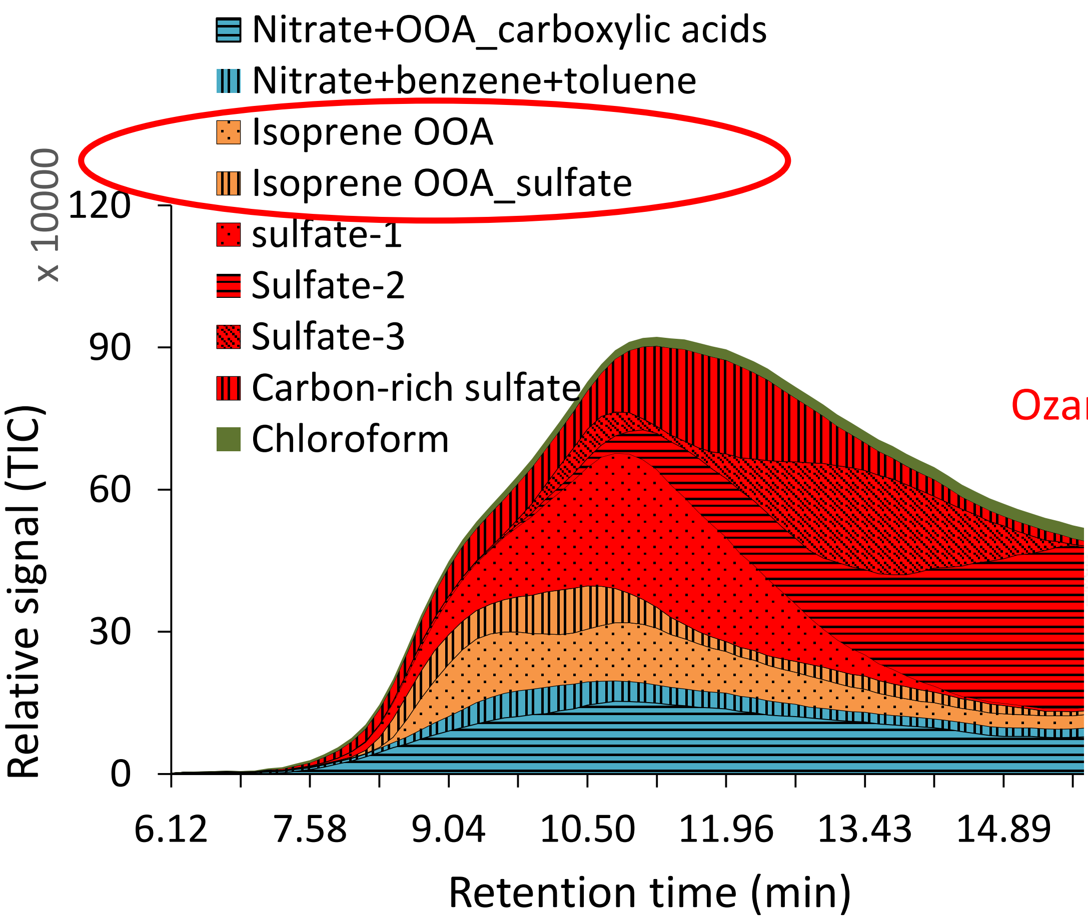
Nitrate

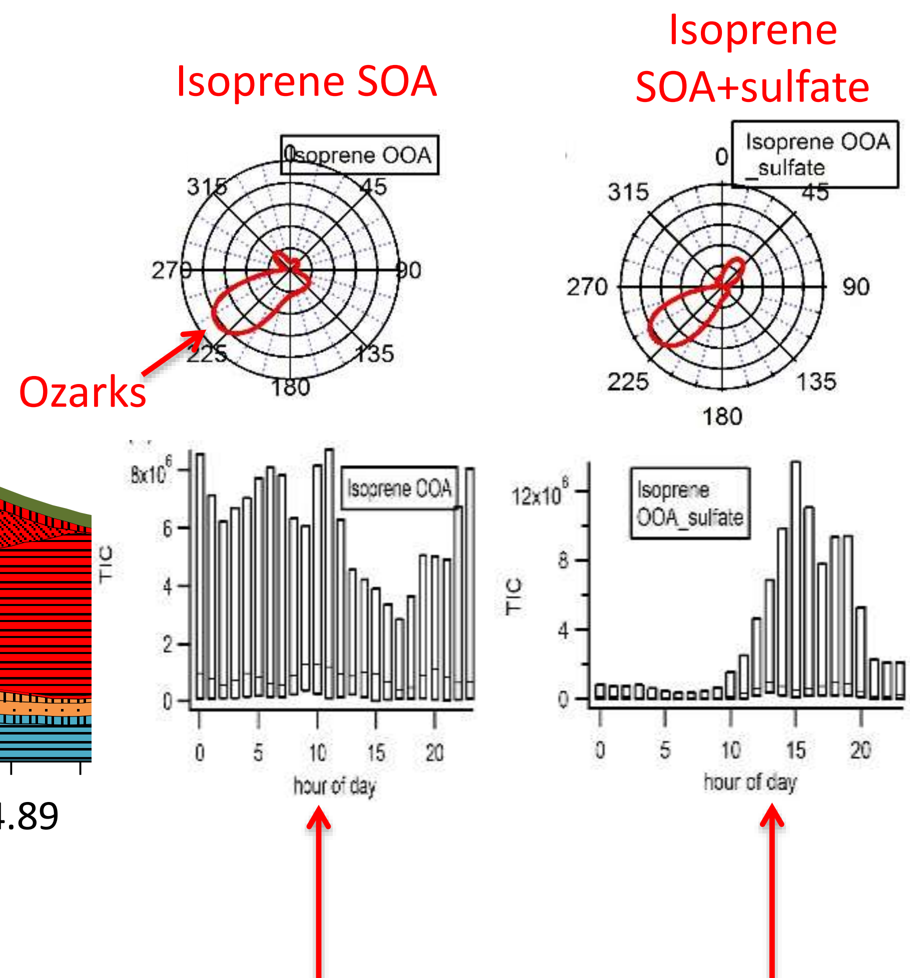
Sulfate

Organics

Isoprene IEPOX

2) PMF results from SLAQRS, East St. Louis: (TAG decomposition signal)



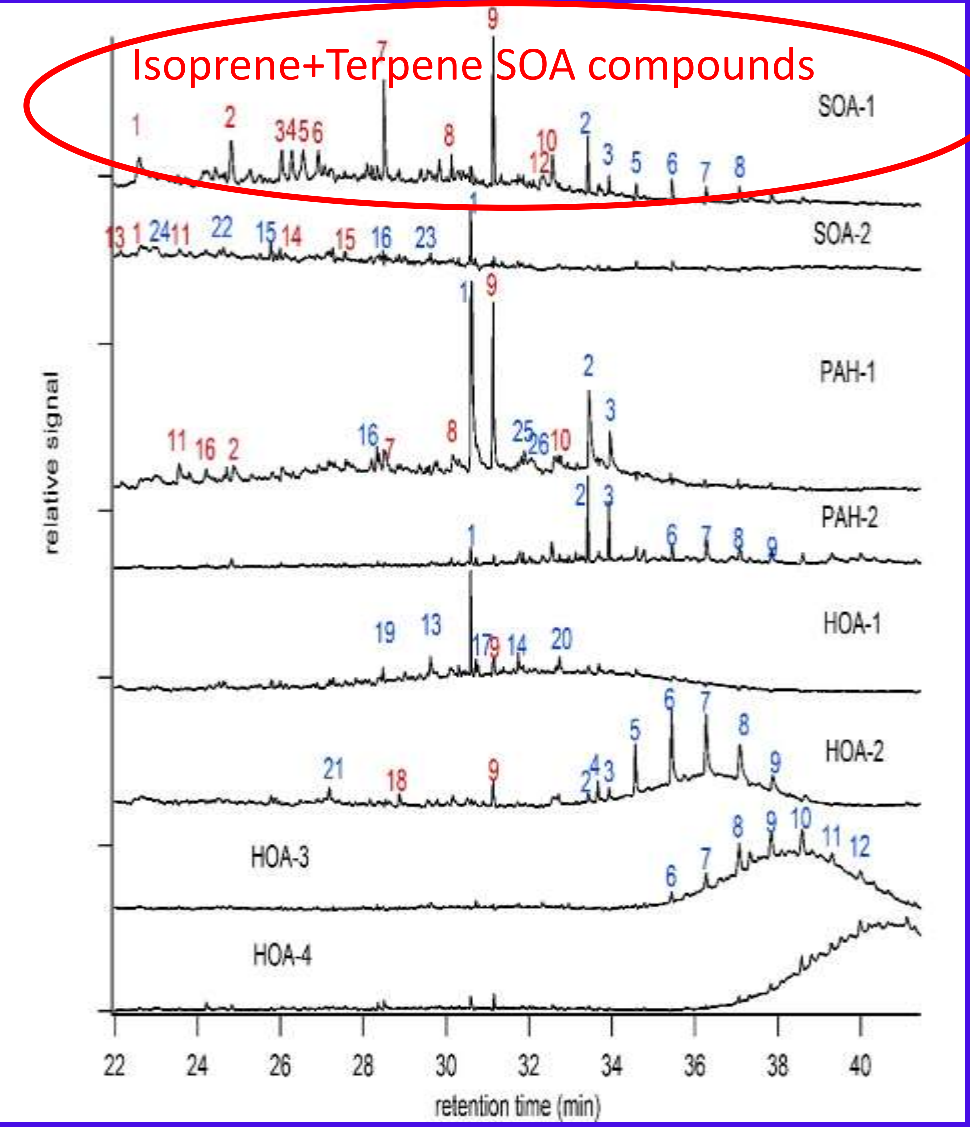


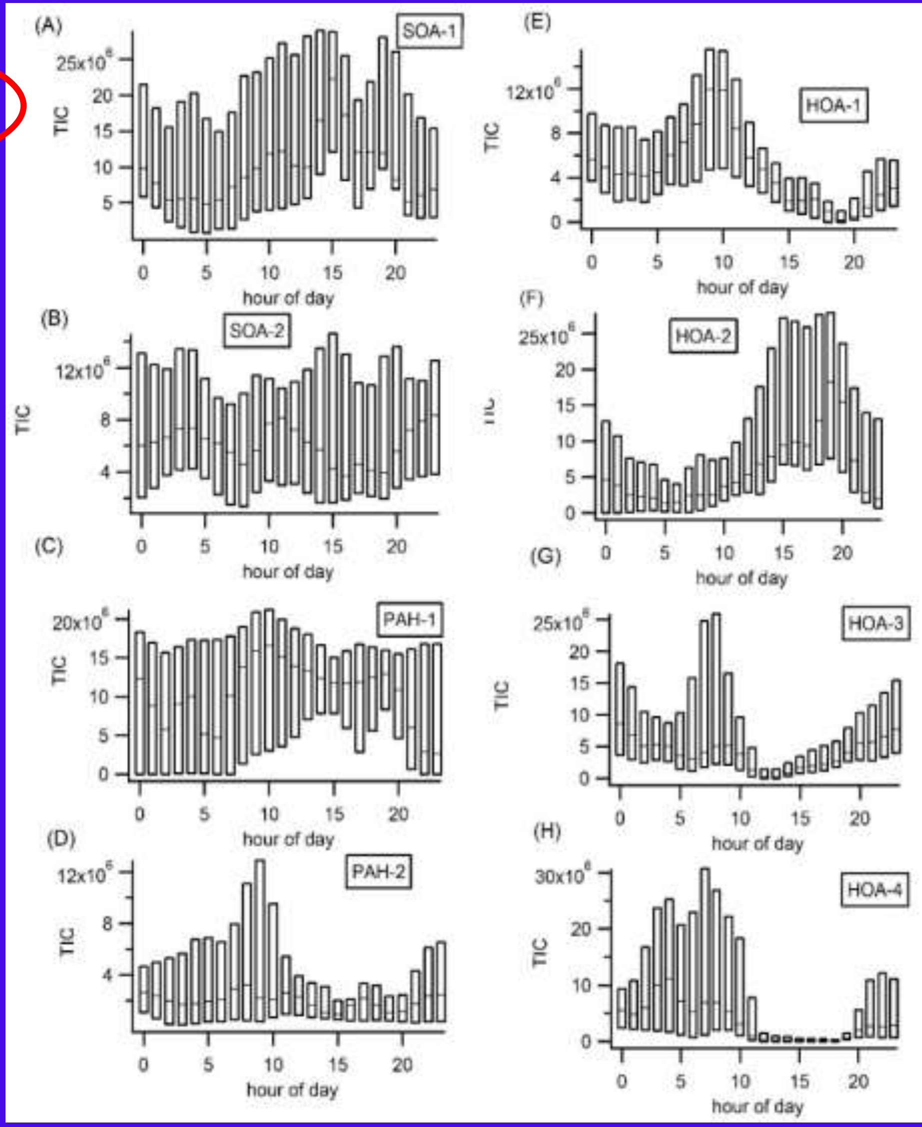
Indicators that this factor represents fresh isoprene SOA, not chemically processed

Isoprene SOA enhancement from presence of acidic seed aerosol

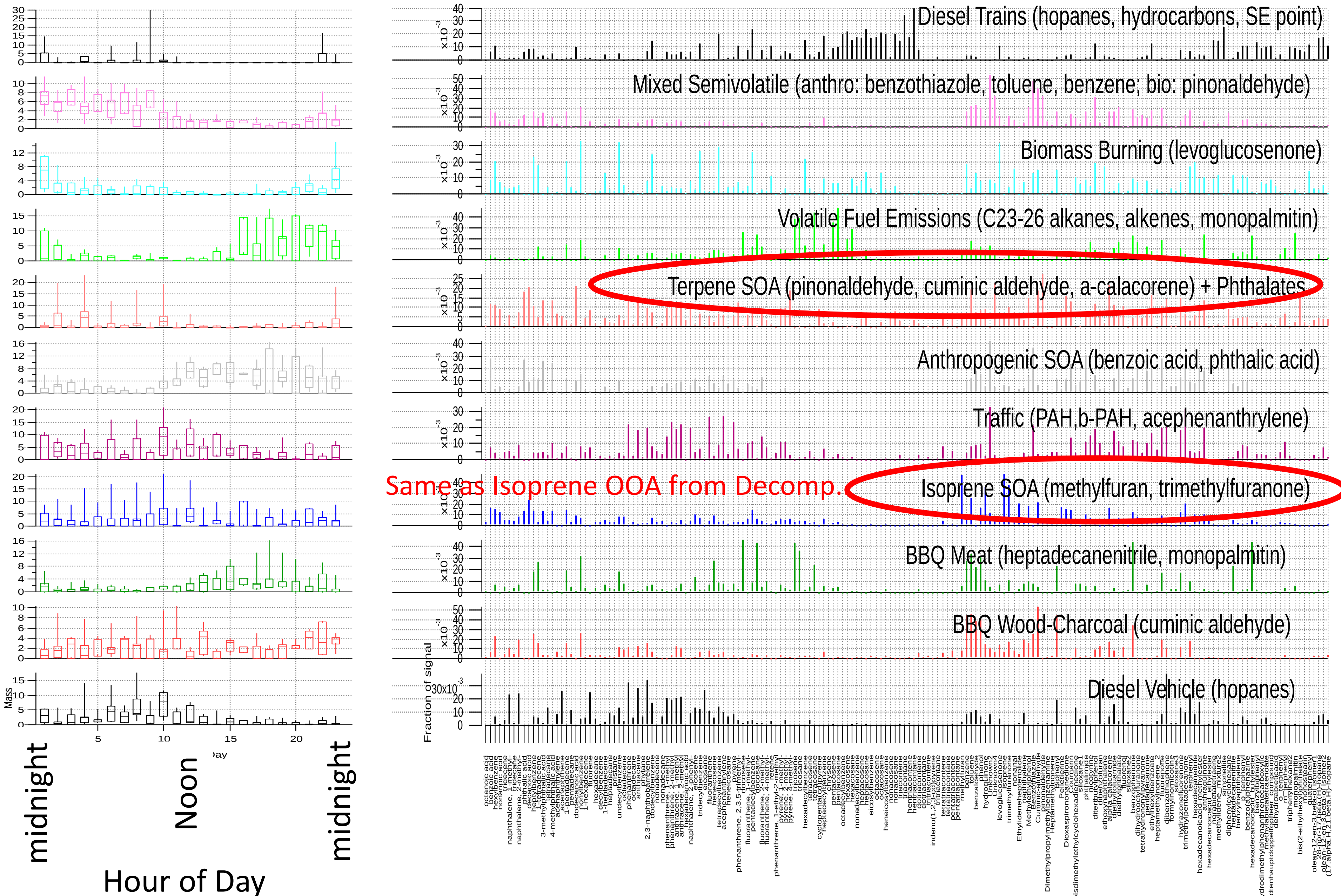
Zhang et al., In-Prep

3) PMF results from SLAQRS, East St. Louis: (TAG binned compounds)





4) PMF results from SLAQRS, East St. Louis: (TAG individual compounds)



Zuo et al., In-Prep

Currently working to combine SLAQRS PMF results from:

1) AMS
2) TAG (decomposition signal)
3) TAG (binned compounds + UCM)
4) TAG (integrated compounds)
5) VAPS

Created a bit of a data monster, but learning a lot as we now make comparisons!

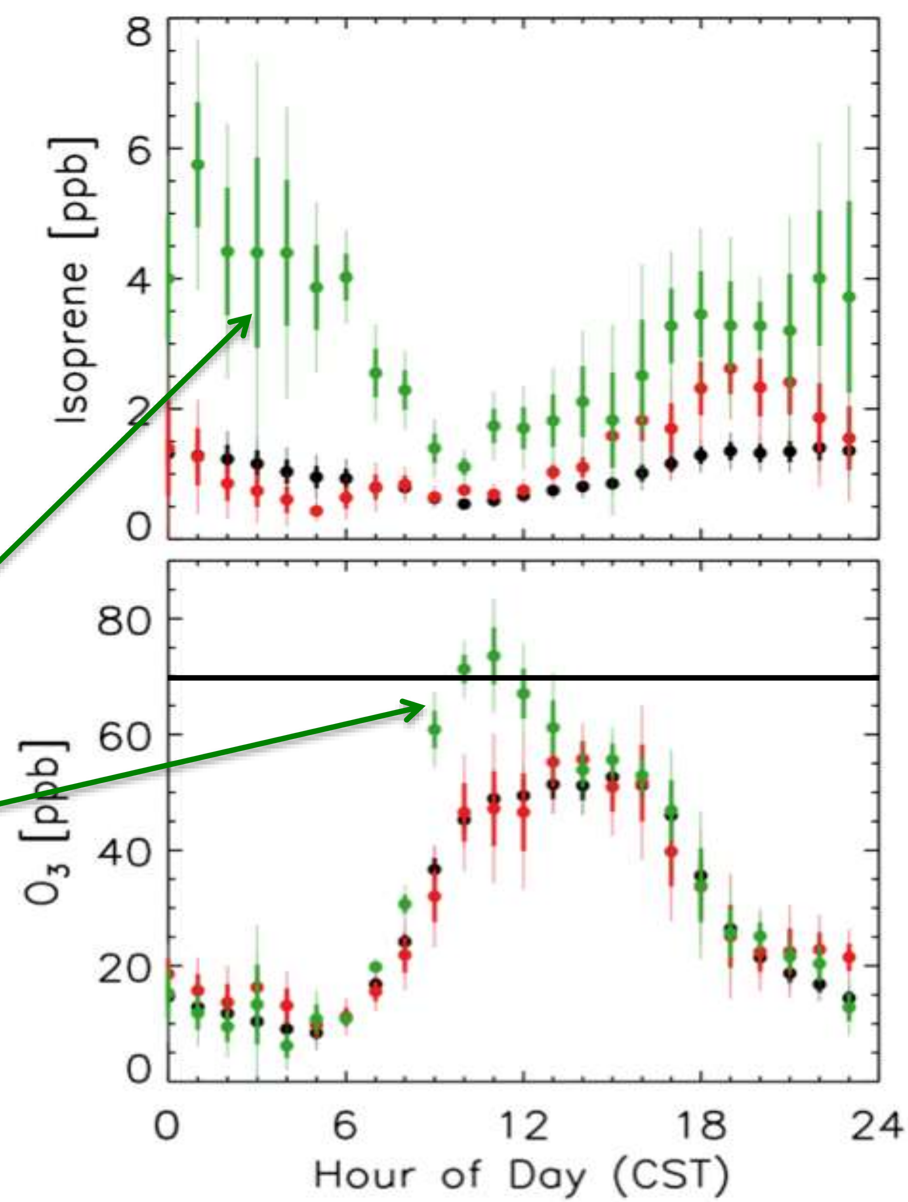
Good correlations amongst the various Isoprene SOA factors and major Anthropogenic HOA/POA factors.

Observations of Nighttime Chemistry during SLAQRS

Study Average (black dots)

<u>Winds from Ozarks</u>:
Active NO_3 chemistry to remove Isoprene

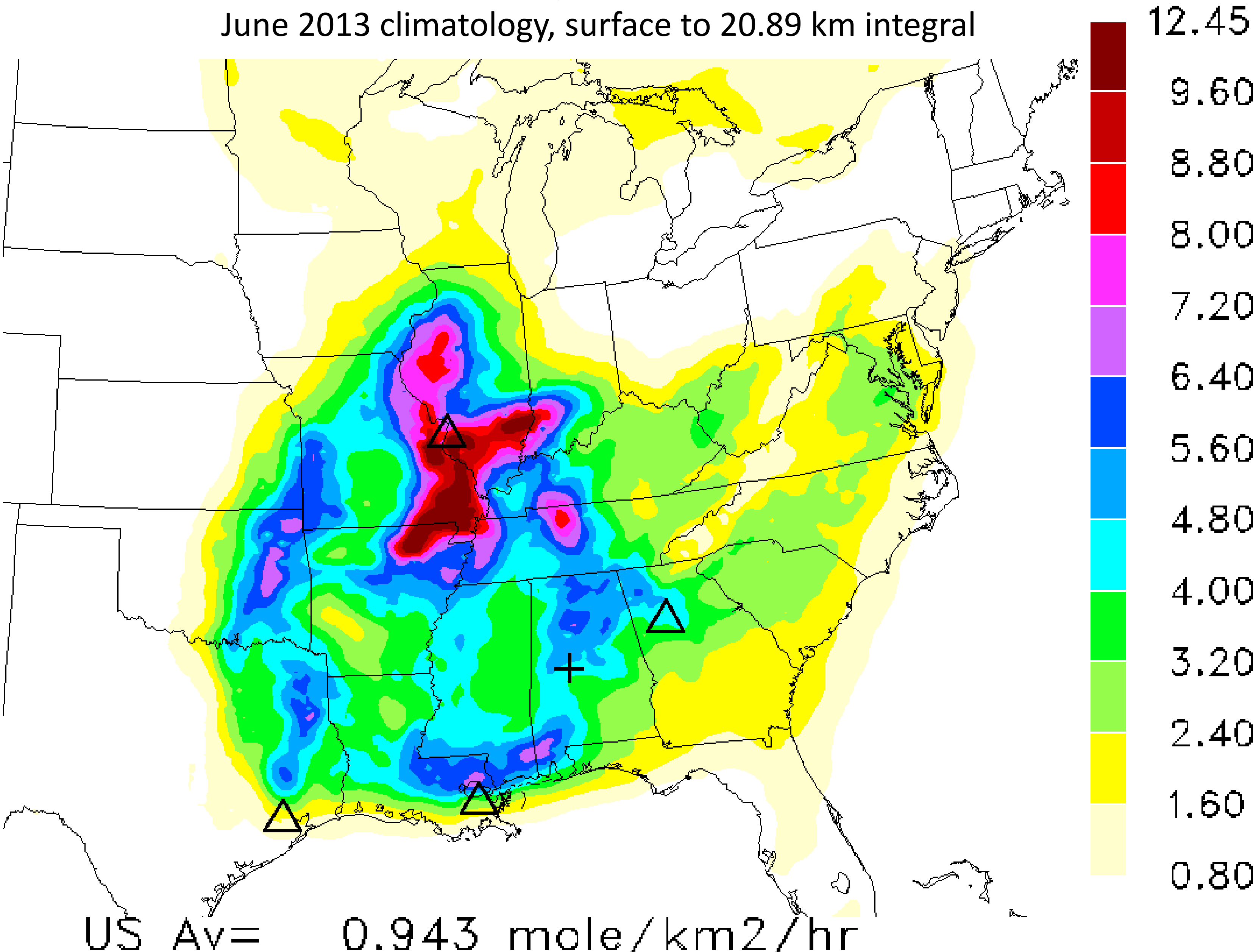
<u>Winds from Ozarks</u>:
No active NO_3 chemistry
= results in elevated morning O3



Millet et al., ES&T (In-Review)

Diurnal Average NO_3+Isoprene reaction rate

June 2013 climatology, surface to 20.89 km integral

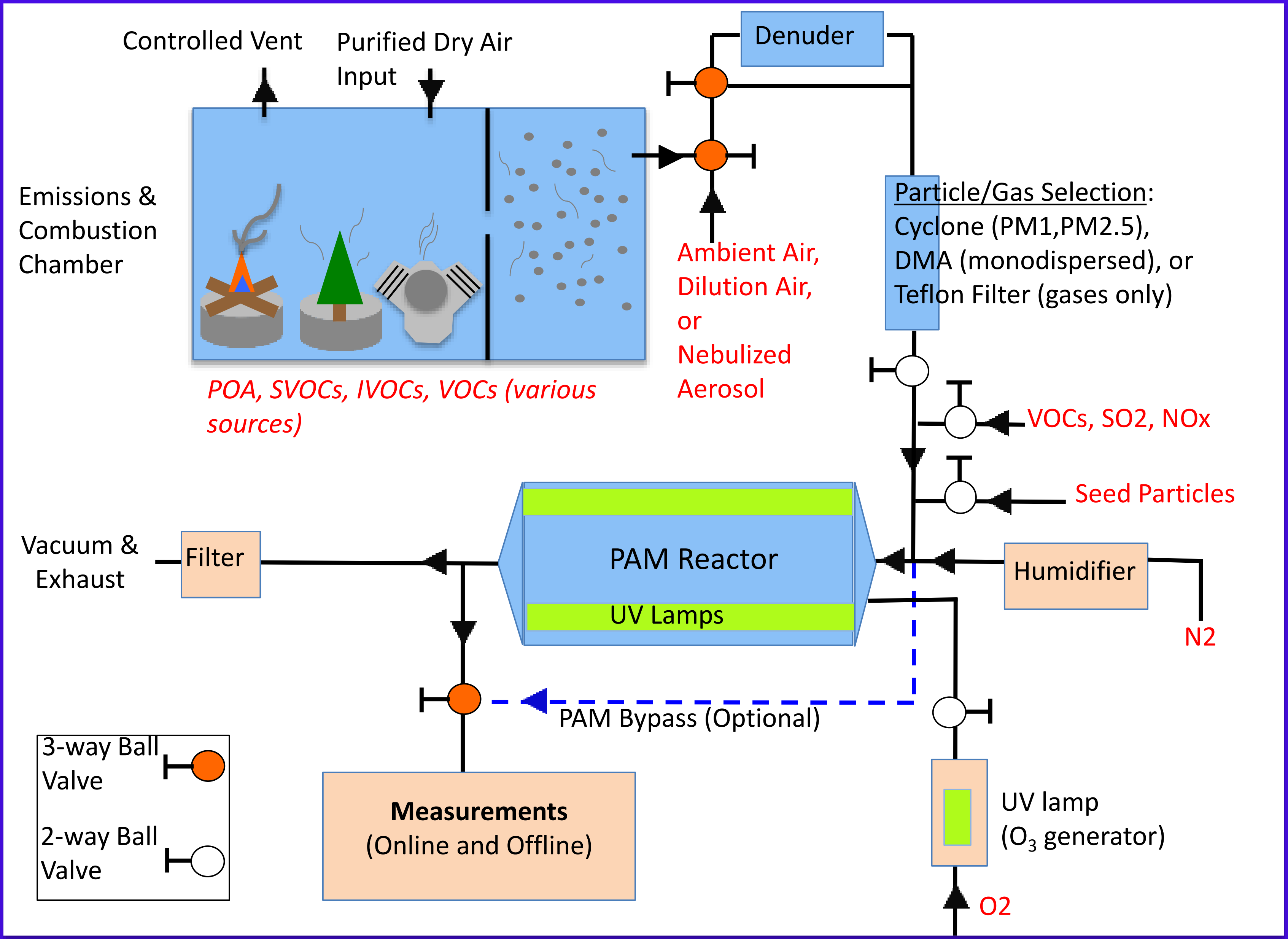


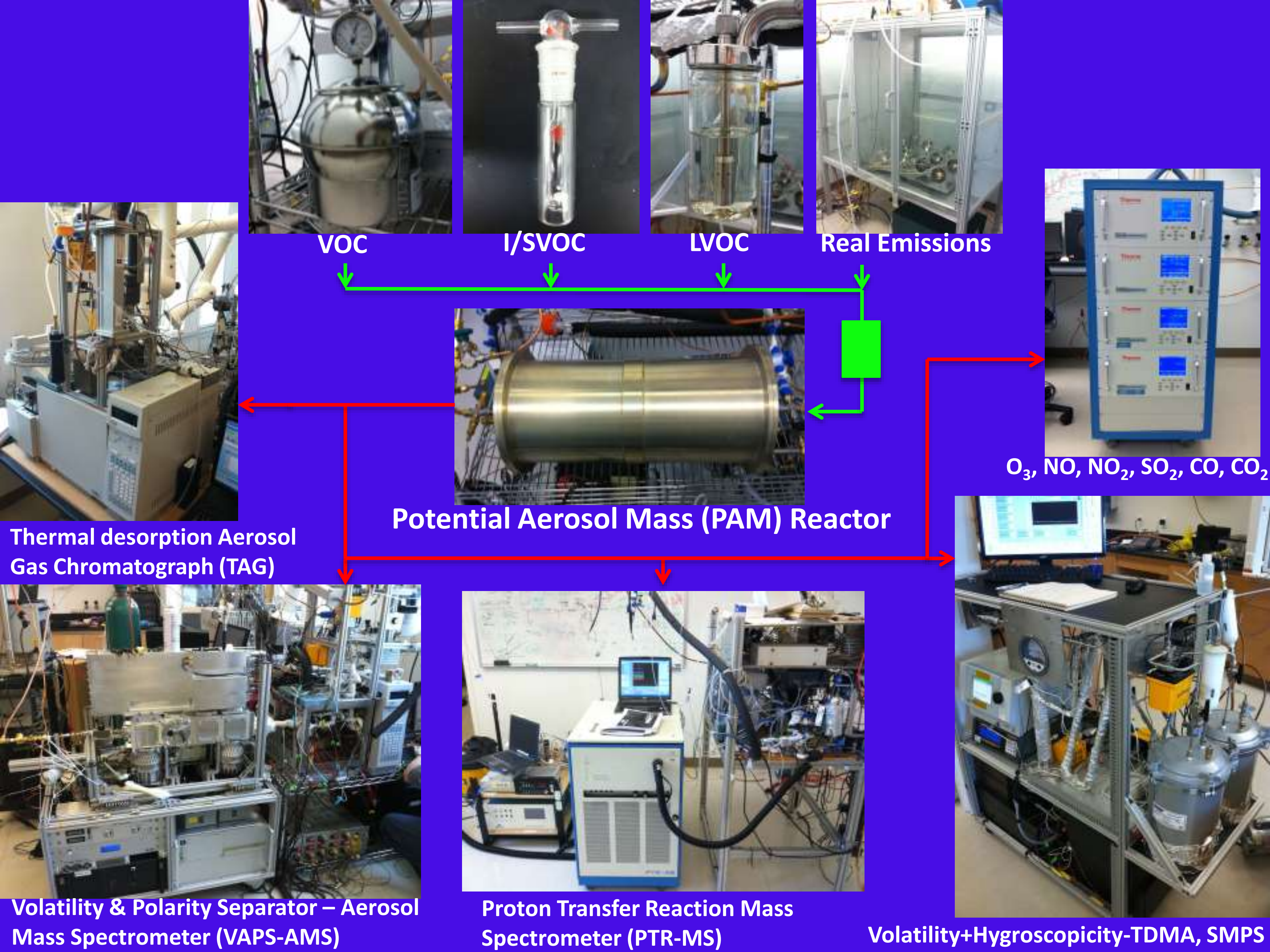
McKeen, Brown (NOAA)

OUTLINE

- Instrument Development
- Novel Data Analysis Methods
- Field observations: SOAS – Centreville, AL
- Field observations: SLAQRS – East St. Louis, IL
- **Laboratory-based oxidation studies**
- Conclusions

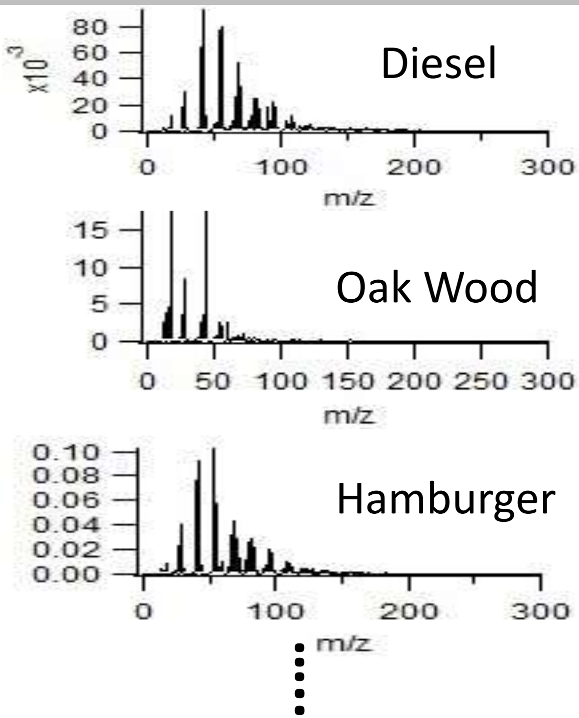
Design for Laboratory-based Oxidation Studies

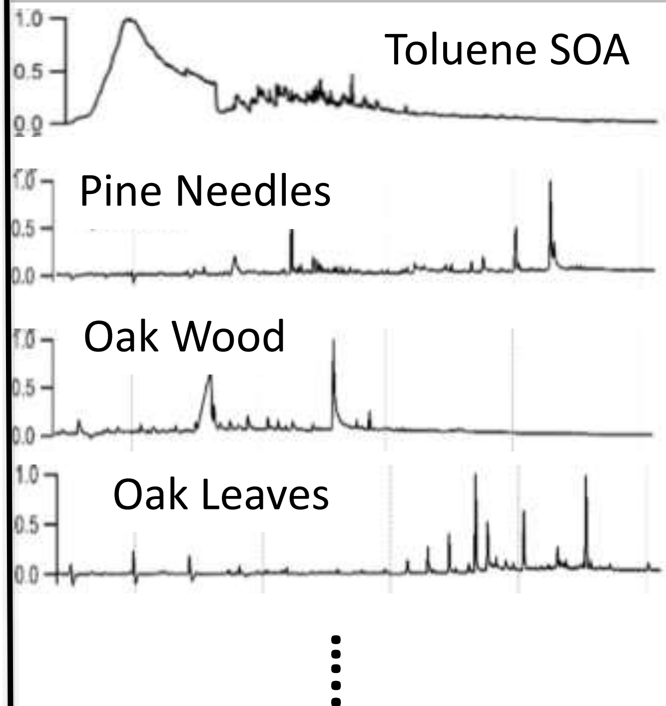


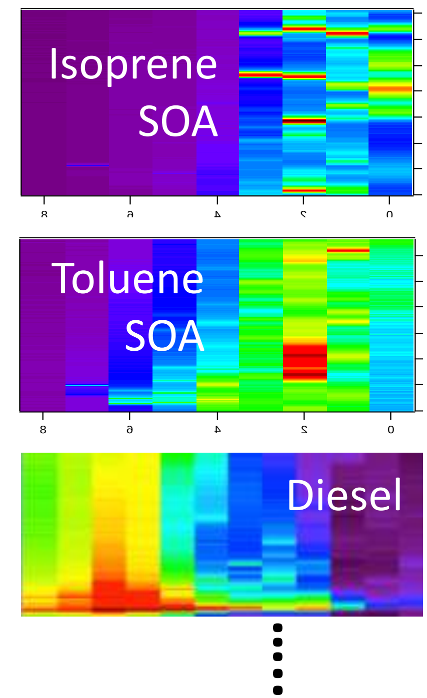

VOC
I/SVOC
LVOC
Real Emissions
Potential Aerosol Mass (PAM) Reactor
O_3, NO, NO_2, SO_2, CO, CO_2
Thermal desorption Aerosol Gas Chromatograph (TAG)
Volatility & Polarity Separator – Aerosol Mass Spectrometer (VAPS-AMS)
Proton Transfer Reaction Mass Spectrometer (PTR-MS)
Volatility+Hygroscopicity-TDMA, SMPS

Building and Adding to Chemical Databases

Aerosol Mass Spectrometer (AMS)	Thermal desorption Aerosol Gas chromatograph (TAG)	Volatility and Polarity Separator (VAPS)



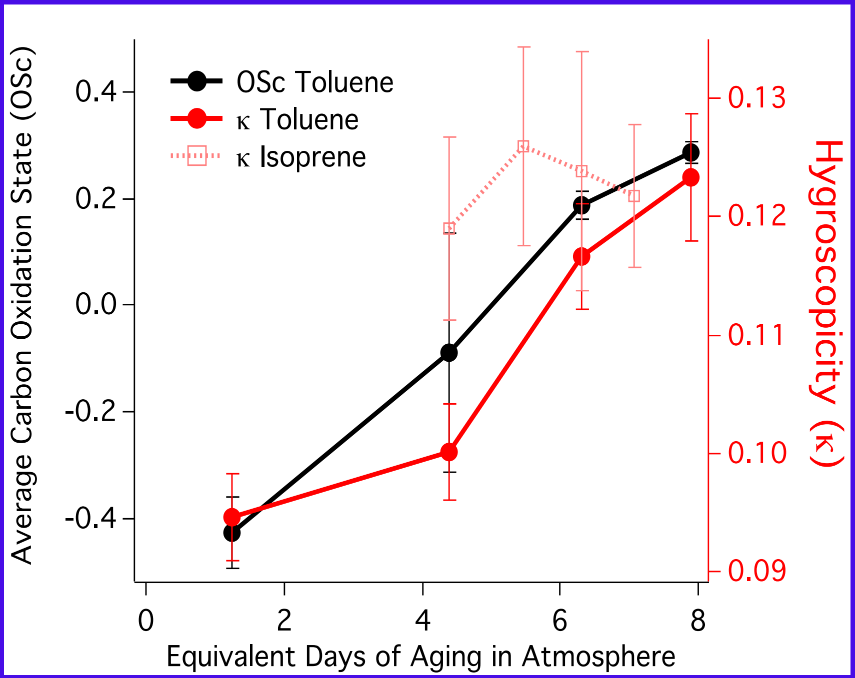


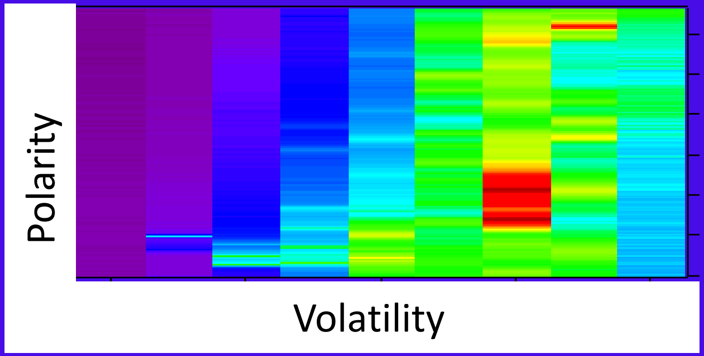


For purpose of this project we are characterizing oxidation of **Isoprene + several Terpenes** (*over a range of: oxidation states, humidity, oxidants, acidity,* NO_x)

Connecting chemistry to hygroscopicity

Multi-Channel TDMA
hygroscopicity, volatility, etc.
(developed through EPA Early Career award)





Currently attempting to <u>map hygroscopicity onto 2D VAPS maps</u> of volatility- and polarity-separated OA functional groups.

Conclusions

- Our novel research tools are offering new insights on the chemical composition of atmospheric OA
- A combination of new binning analysis techniques, incorporation of thermal decomposition data, and controlled lab studies are improving our understanding of complex ambient chemical signatures observed by TAG, VAPS, and AMS
- VAPS data from **SOAS** (Alabama) suggests major contributions to OA loadings from Terpene SOA and additional contributions from Isoprene SOA not previously reported.
- OA observed during **SLAQRS** (St. Louis Region) was composed of a mix of anthropogenic sources with biogenic events delivered from the Ozarks. Nighttime chemistry plays an important role during these periods of biogenic influence. Larger-scale studies should be performed in this region of interest.

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