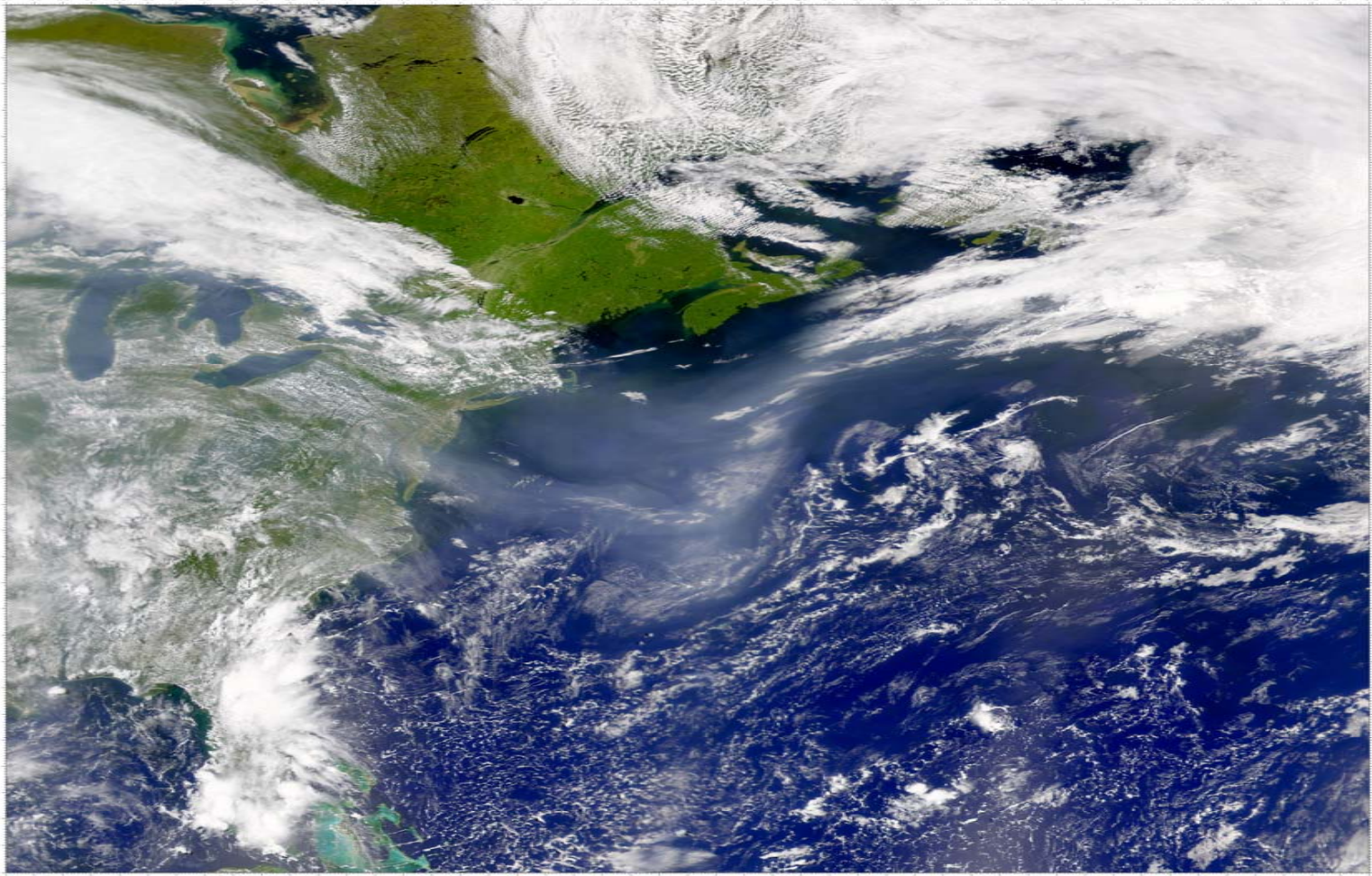


US EPA ARCHIVE DOCUMENT

Formation of Secondary Organic Aerosol

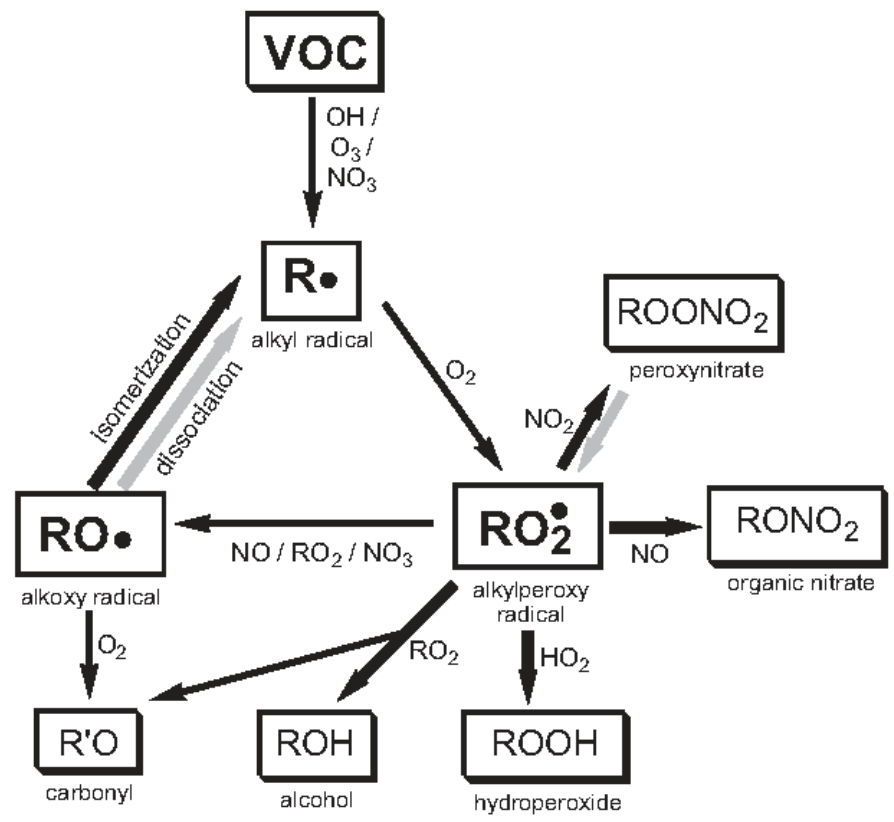


John H. Seinfeld
California Institute of Technology
EPA STAR September 21, 2010

Ambient Organic Aerosol

- About 5 years ago: Higher SOA Levels in the atmosphere than models predicted. Finding “missing SOA” is no longer the issue. We need to understand the complete life cycle of the VOC/SOA system.
- We have learned in the last 5 years:
 - Gas-phase oxidation chemistry is critical in establishing path to SOA formation; role of NO_x key
 - Laboratory chamber experiments do not account fully for ambient aging; functionalization vs. fragmentation, gas-phase aging vs. OH surface reactions uncertain
 - Role of aerosol acidity, aqueous-phase uptake and reaction of small molecules like glyoxal, and heterogeneous chemistry in overall SOA formation not yet fully understood
 - Models now have the machinery to represent SOA formation and aging but at present the parameterization of aging awaits experimental input

Fate of Peroxy (RO₂) Radicals Determines Product Volatility



Changes to vapor pressure of a VOC upon addition of common functional groups

Functional group	Structure	Change in vapor pressure (298 K) ^a
Ketone	-C(O)-	0.10
Aldehyde	-C(O)H	0.085
Hydroxyl	-OH	5.7×10^{-3}
Hydroperoxyl	-OOH	2.5×10^{-3}
Nitrate	-ONO ₂	6.8×10^{-3}
Carboxylic acid	-C(O)OH	3.1×10^{-4}
Peroxyacid	-C(O)OOH	3.2×10^{-3}
Acyl peroxyxynitrate	-C(O)OONO ₂	2.7×10^{-3}
Extra carbon ^b	-CH ₂ -, etc.	0.35^b

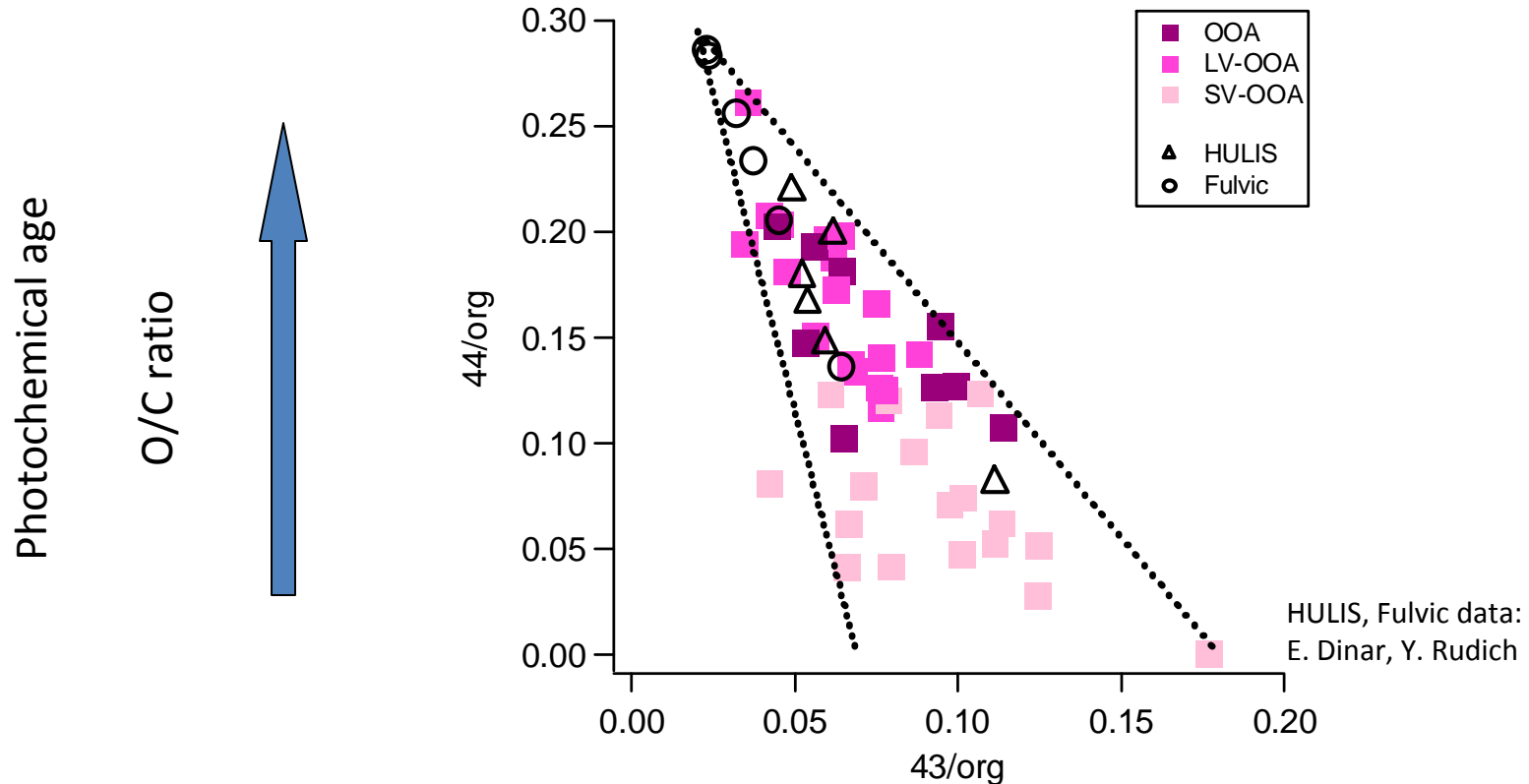
Pankow and Asher (2007)

Level of NO_x (= NO + NO₂) Determines Fate of RO₂ Radicals:

Small VOCs - \uparrow NO_x yields high-volatility fragmentation products (e.g., alkyl radical + small carbonyls)
 \leq C10 NO_x \downarrow yields lower-volatility products (e.g., hydroperoxides) **Higher SOA Yields**

Large VOCs - \uparrow NO_x yields low-volatility products (large organic nitrates + isom. products) **Higher SOA Yields**
 C15 \downarrow NO_x yields higher-volatility products

Comparison of Atmospheric AMS Components



- SV-OOA has larger variability in 43/org; Increasing photochemical age collapses variability, OOA components become increasingly similar to each other
- 44/org ratios of the LV-OOA components similar to those from HULIS collected in filter samples
- Increasing photochemical age: increasing O/C, 44/43 ratio

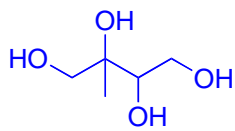
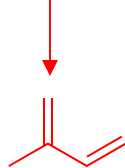
SOA Formation from Isoprene

- Previously Assumed Not to be Significant Source of SOA Despite High Emissions:

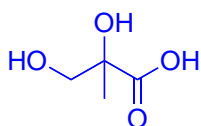
Estimated Global VOC and Methane Emissions (TgC yr⁻¹)

Biogenic VOCs			Anthropogenic VOCs	Methane
Isoprene (C ₅ H ₈)	Monoterpenes (C ₁₀ H ₁₆)	Other		
~500	~130	~562	~93	~510

Guenther et al. [1999]



diastereoisomeric
2-methyltetrols
MW 136



2-methylglyceric (2-MG) acid
MW 120

Detection in Ambient Aerosol
Indicated Isoprene as Likely Source
[Claeys et al., 2004; Edney et al., 2005]

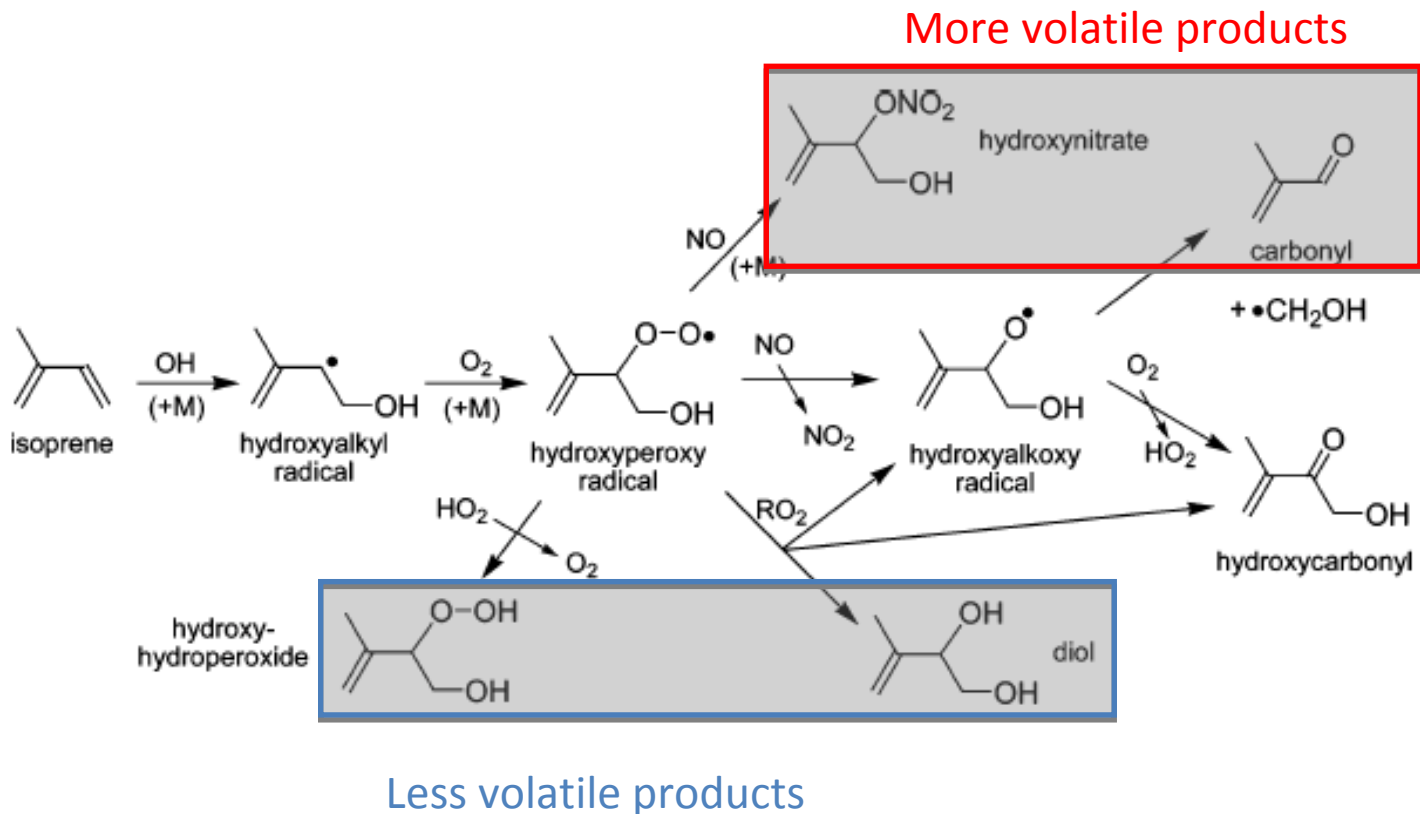
- Laboratory Experiments Confirm Isoprene as SOA Source

[Kroll et al., 2006; Surratt et al., 2006]

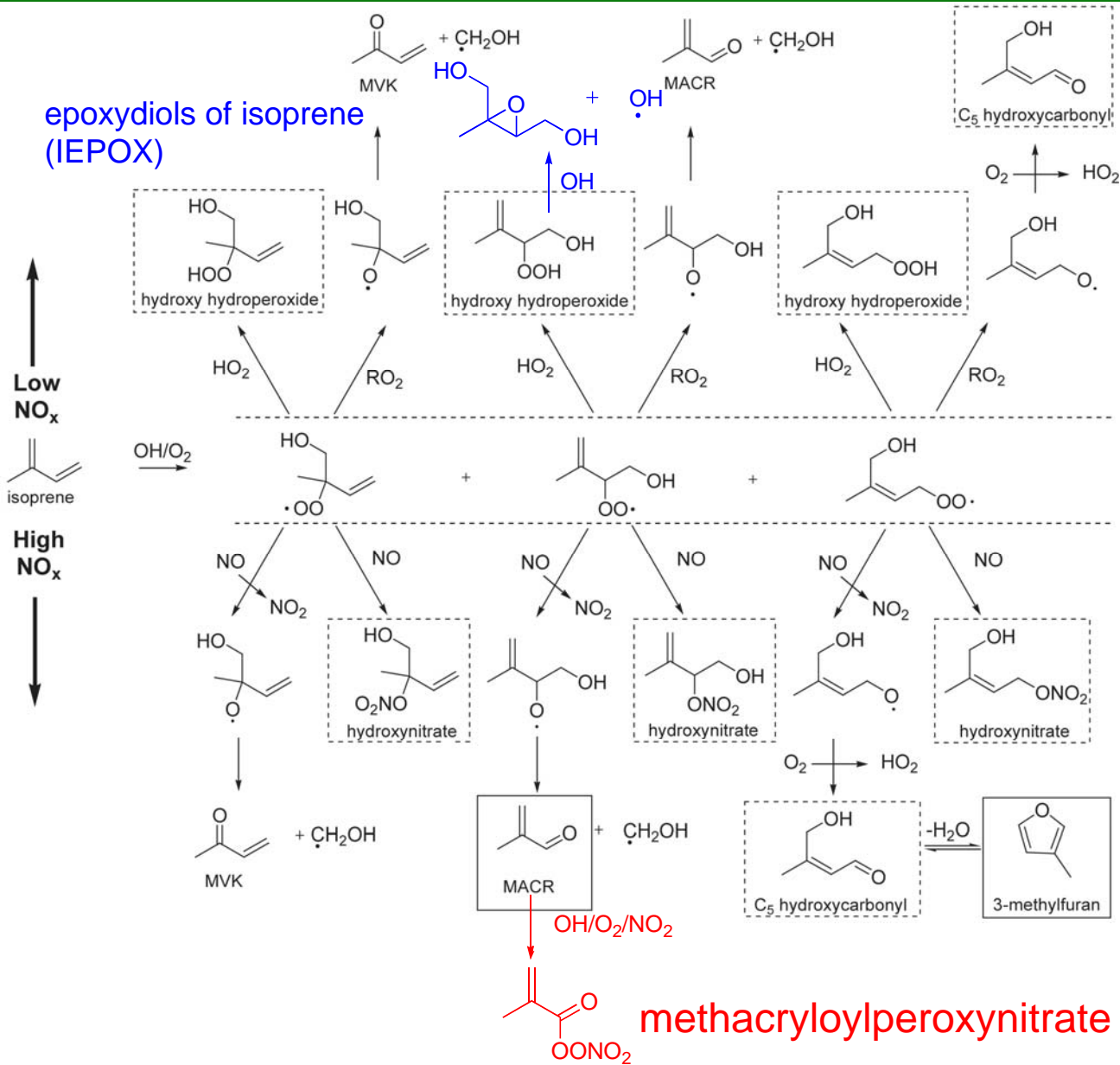
- Isoprene Estimated to Contribute Significantly to Global SOA Burden

Role of NO_x in Isoprene Oxidation

- Peroxy radical chemistry: RO₂+HO₂ vs RO₂+NO



OH-initiated Oxidation of Isoprene: First-Generation Products



epoxydiols of isoprene (IEPOX)

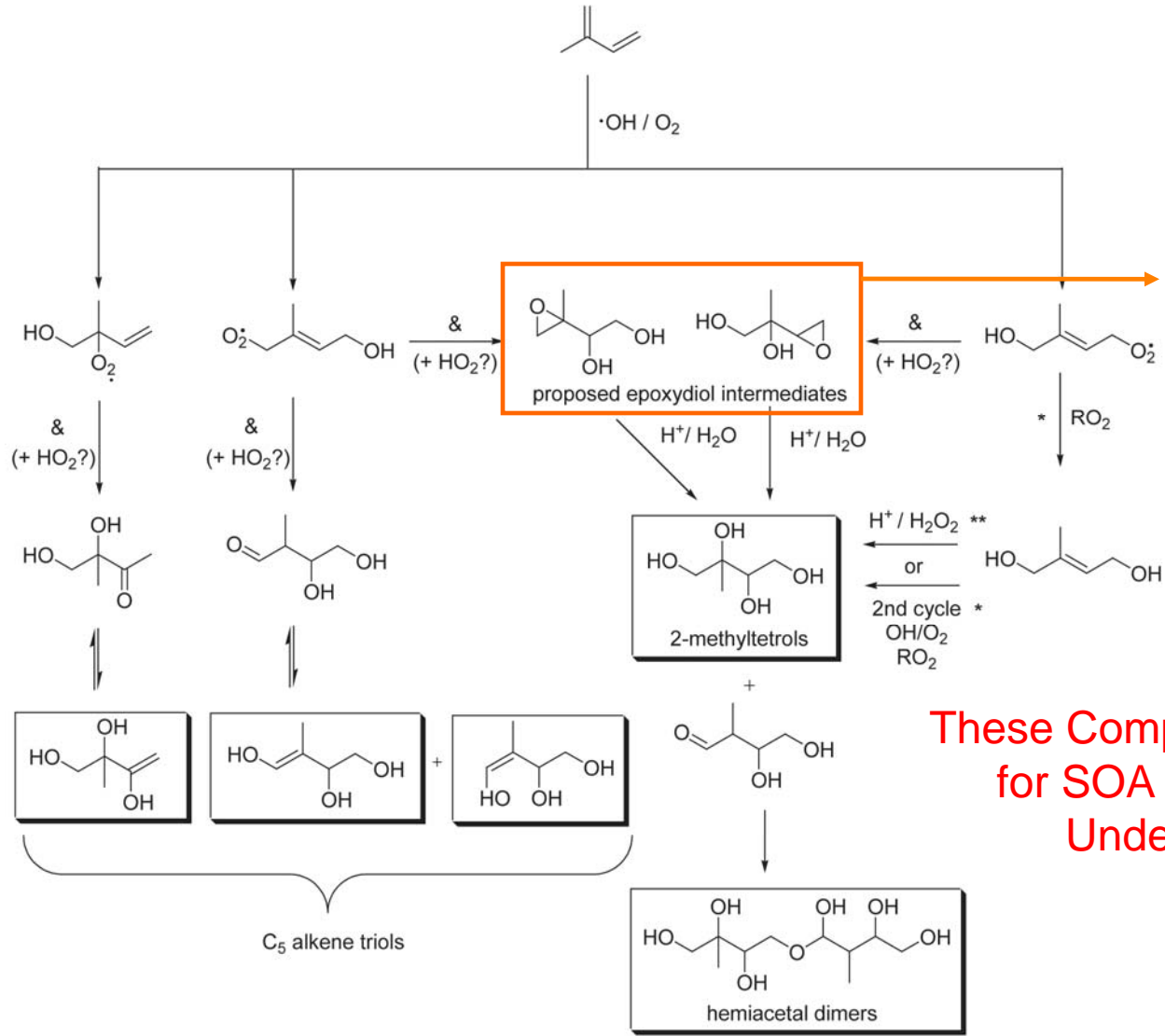
IEPOX only recently discovered
Paulot et al., *Science* (2009)

Measured Yields under High- NO_x
 MVK 32-44%
 MACR 22-28%
 3-methylfuran <2-5%
 Hydroxynitrate (and isomers) 4-14%
 C_5 -hydroxycarbonyl 15-19%

methacryloylperoxynitrate (MPAN)

Formation of Isoprene Low-NO_x SOA Constituents and Oligomers

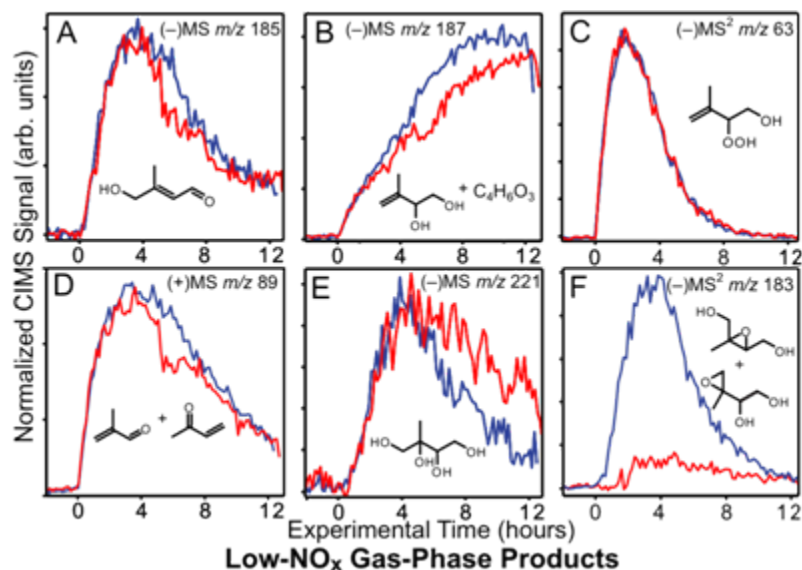
Products Characterized by GC/ITMS with prior derivatization:



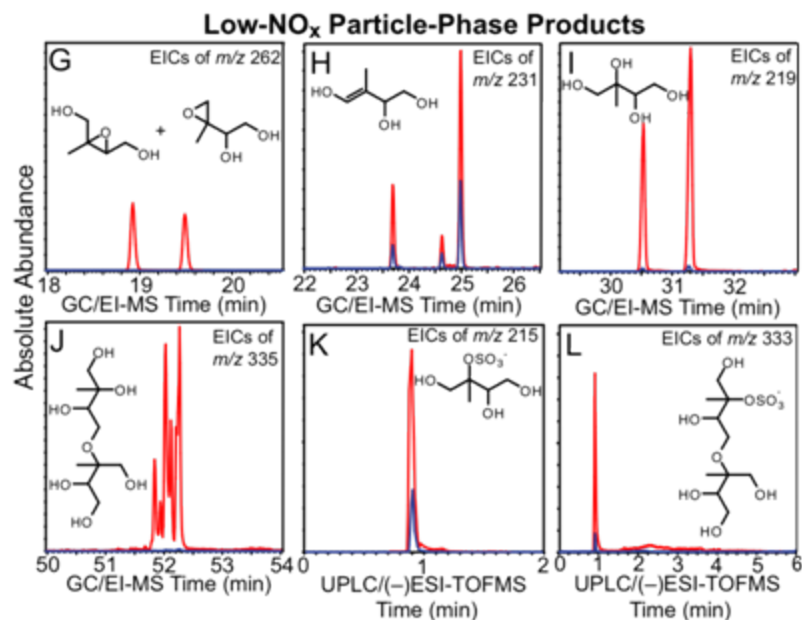
Key to the Low-NO_x Mechanism

These Compounds are Ambient Tracers for SOA Formation from Isoprene Under Low-NO_x Conditions

Increased Aerosol Acidity Reveals Role of IEPOX in Low-NO_x SOA Formation



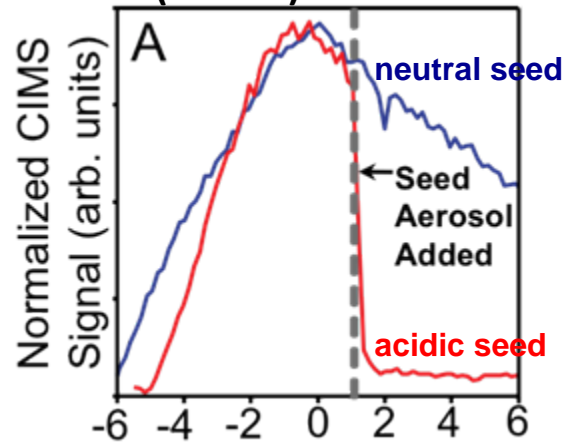
- Photooxidation of 49 and 40 ppb of isoprene in presence of **acidified** or **neutral** sulfate seed aerosol, respectively.
- RO₂ + HO₂ reactions dominate.
- 9 ppb to 0.6 ppb of IEPOX was measured in the **neutral** and **acidic** cases, respectively; no other differences observed for other isoprene oxidation products
- Mixing ratios of other gas-phase products: ROOH ~ 12 ppb, and diols, hydroxycarbonyls, and tetrols all < 0.8 ppb



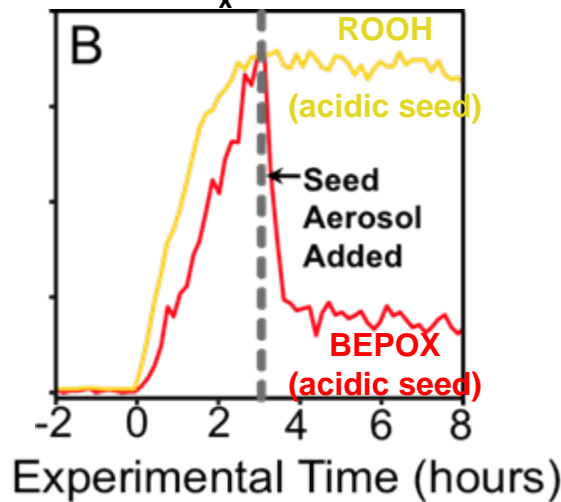
- SOA mass yield increased from 1.3% for the **neutral** case to 28.6% for the **acidic** case.
- All particle-phase products substantially increase in presence of **acidic** seed; for example, 2-methyltetrols increased from 0.1 μg m⁻³ for the **neutral** case to 5.1 μg m⁻³ for the **acidic** case.
- Particle-phase IEPOX could be due to un-reacted IEPOX that partitioned favorably into wet aerosol.

(📄) CIMS Time Traces Further Demonstrate Role of IEPOX

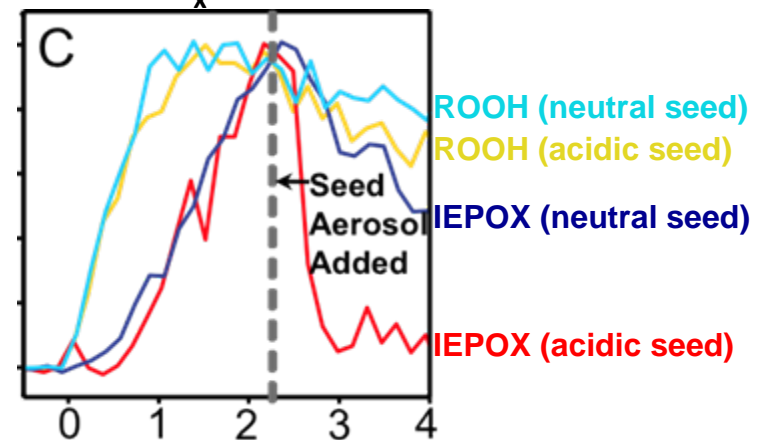
Dark Reactive Uptake of
2,3-epoxy-1,4-butanediol
(BEPOX) Standard



Butadiene
Photooxidation under
Low-NO_x Conditions



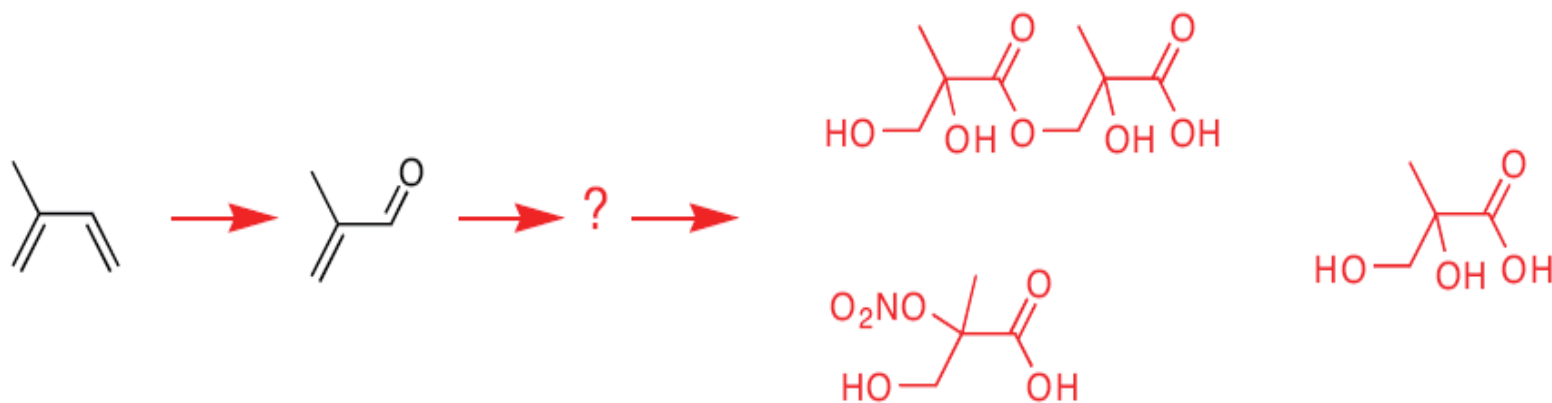
Isoprene
Photooxidation under
Low-NO_x Conditions



- Synthesized BEPOX standard, which is butadiene derivative of IEPOX, shows exact same reactive uptake behavior as that found for BEPOX produced from butadiene photooxidation and IEPOX produced from isoprene photooxidation in presence of acid seed
- **Conclusion:** Significant loss of epoxydiols (i.e., BEPOX and IEPOX) to highly acidic seed aerosol results from acid-catalyzed particle-phase reactions
- All of the detected particle-phase constituents in BEPOX or butadiene SOA are exact analogues of isoprene low-NO_x SOA (i.e., differ by a mass of 14 amu, which corresponds to CH₂ group)

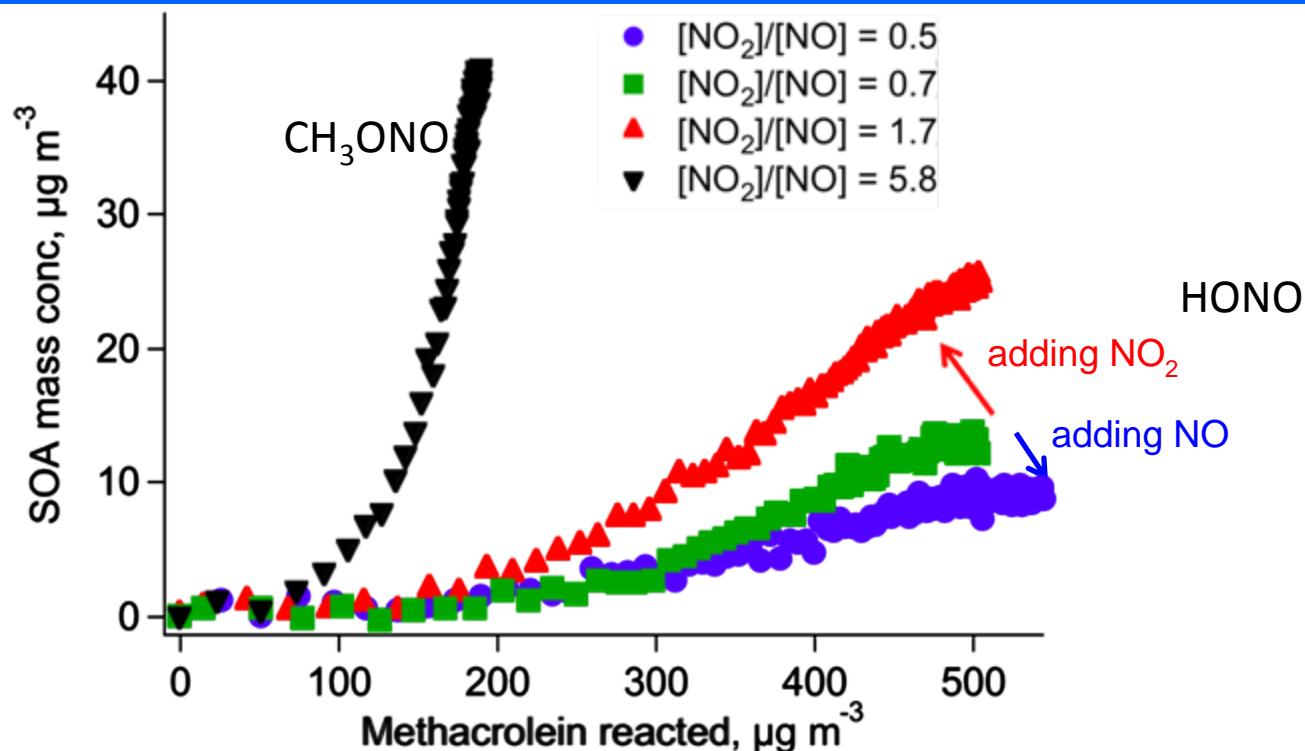
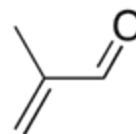
ISOPRENE PHOTOOXIDATION: HIGH NO_x

- ▶ Aerosol yields of 0.9–3% [Kroll et al., 2005]
- ▶ High-NO_x: SOA formation proceeds via methacrolein (C₄-aldehyde)



- ▶ Objective: to understand the mechanism by which methacrolein forms SOA

Methacrolein photooxidation

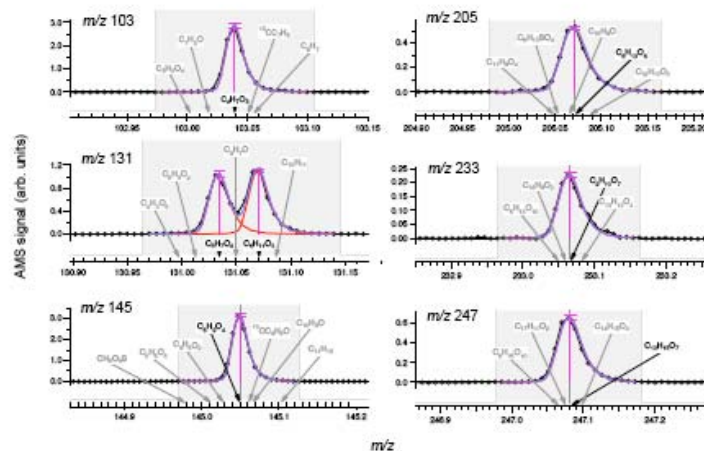
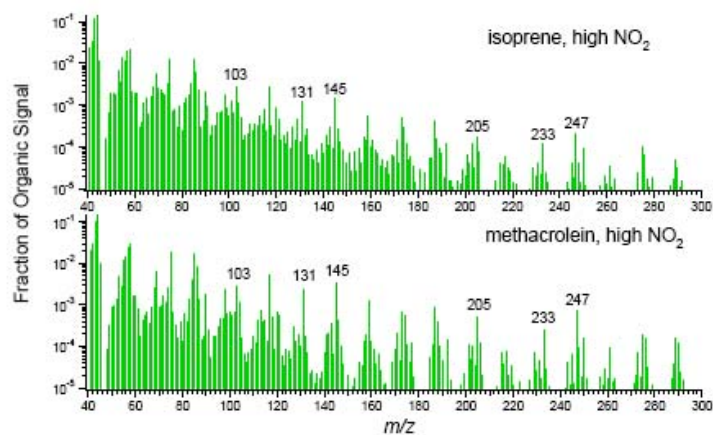


- $\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$
- CH_3ONO (no net NO production):
 - $\text{CH}_3\text{ONO} \rightarrow \text{CH}_3\text{O} + \text{NO}$
 - $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO}$
 - $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$
- Not an effect of enhanced HNO_3

→ Total amount of SOA trends with NO_2/NO ratio

SOA COMPOSITION FROM METHACROLEIN PHOTOOXIDATION

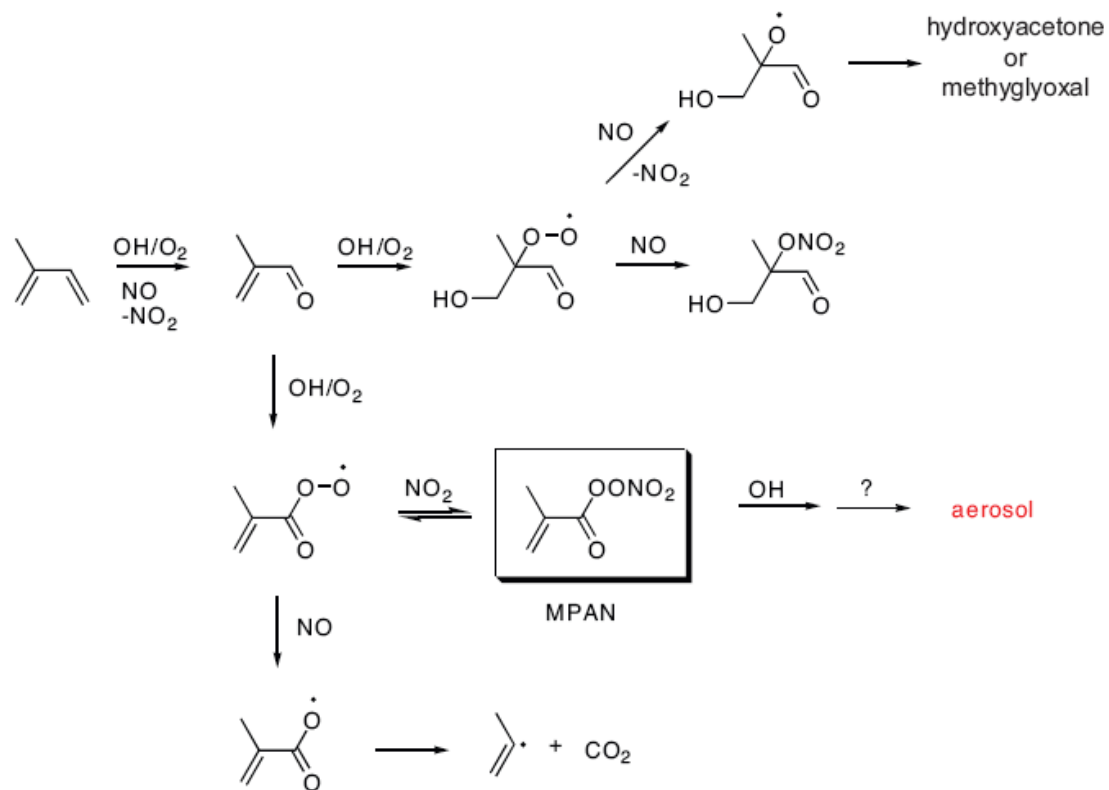
- ▶ Online chemical composition analysis (HR-ToF-AMS):



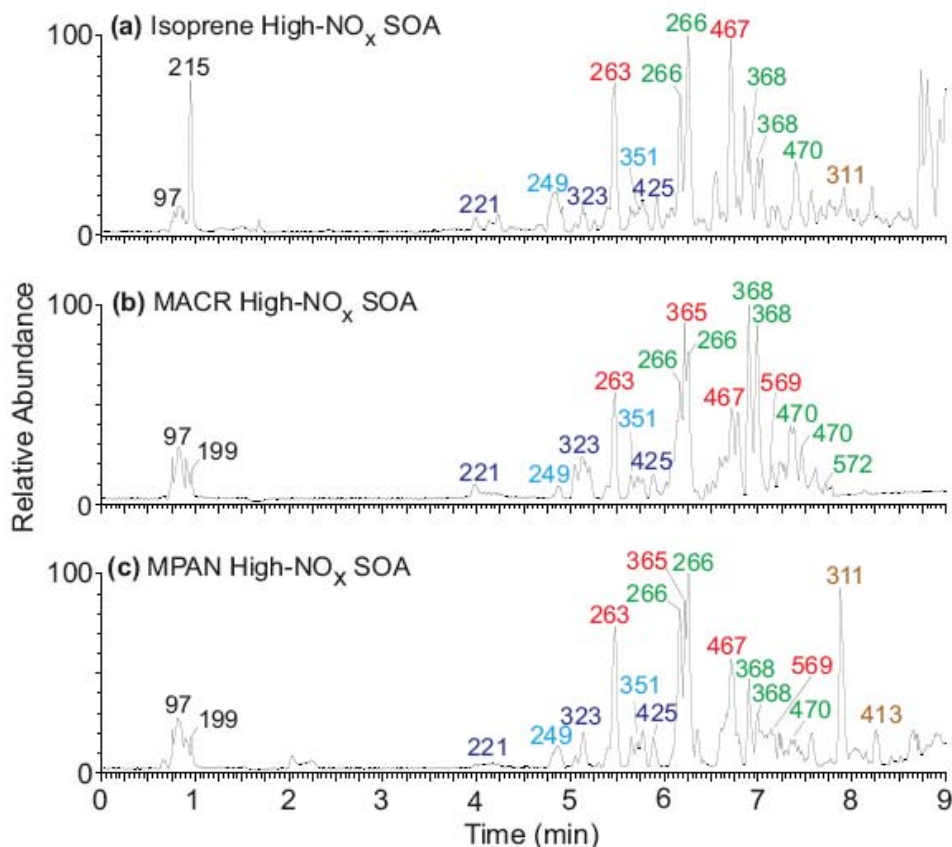
- ▶ Identification by online and offline high-resolution mass spectrometry are consistent

MPAN AS SOA INTERMEDIATE

- ▶ Why does SOA formation from methacrolein depend on NO_2/NO ? Aldehyde chemistry

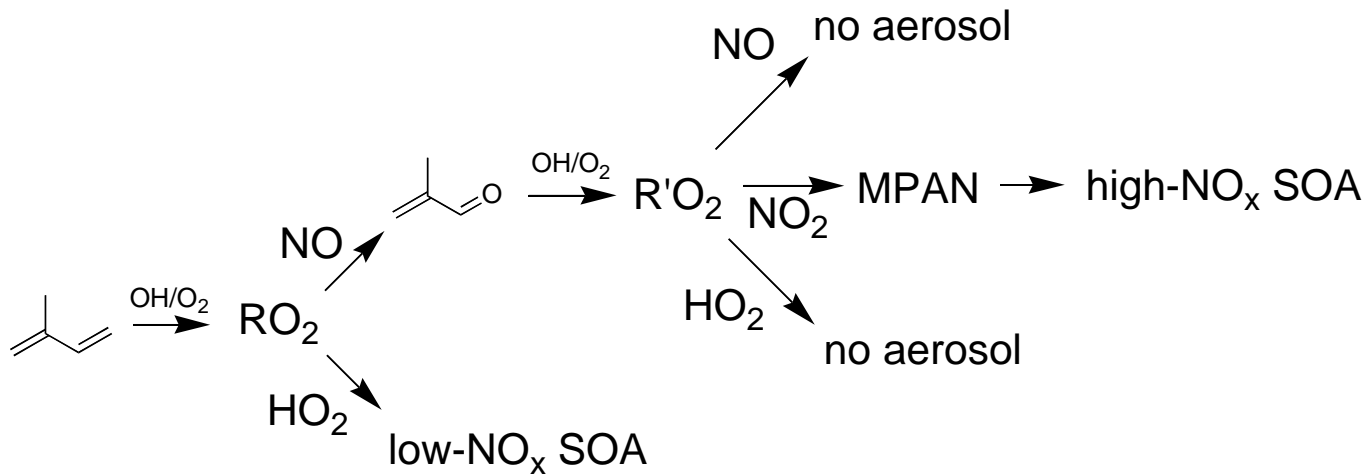
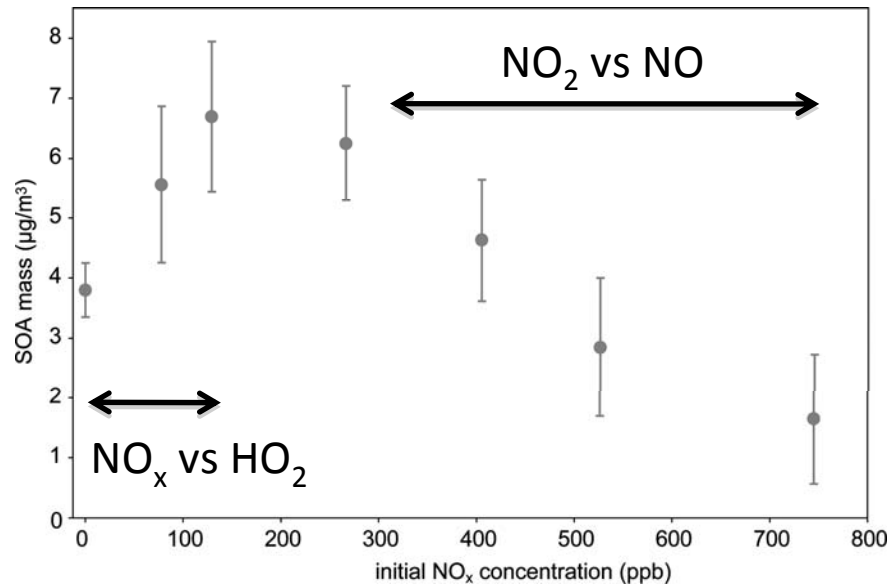


MPAN AS SOA INTERMEDIATE



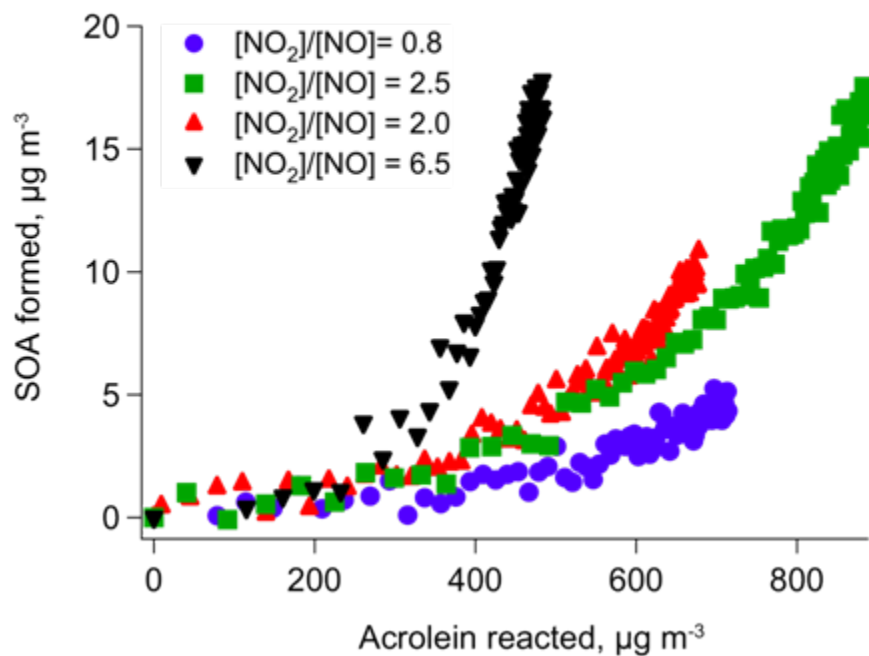
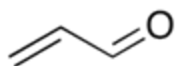
- ▶ SOA formed from MPAN+OH
- ▶ Similar compositions
- ▶ AMS shows similar oligomers at high m/z's
- ▶ **MPAN is the precursor to isoprene and methacrolein SOA**

Summary of NO_x on Isoprene SOA

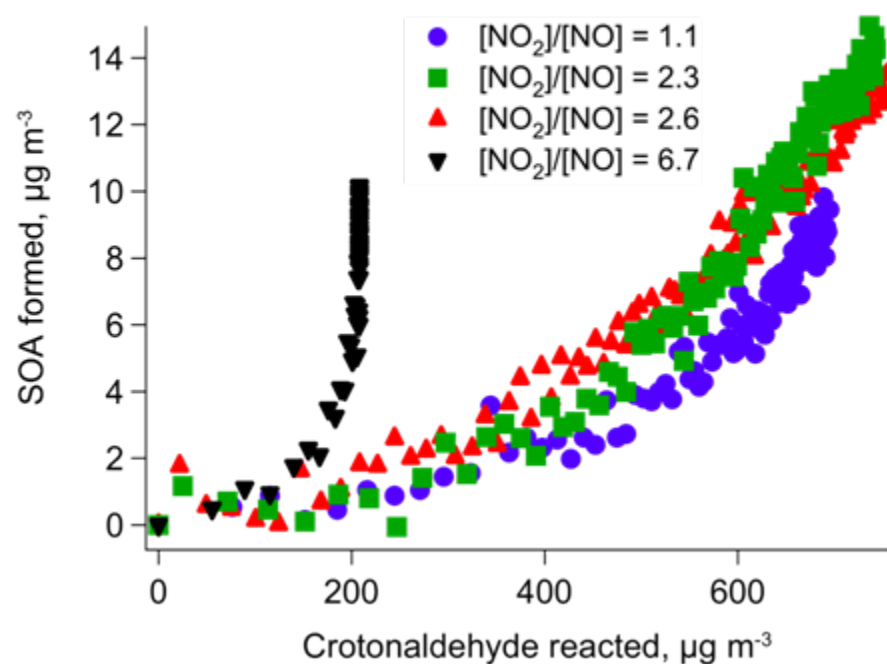
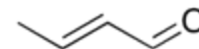


Other unsaturated aldehydes

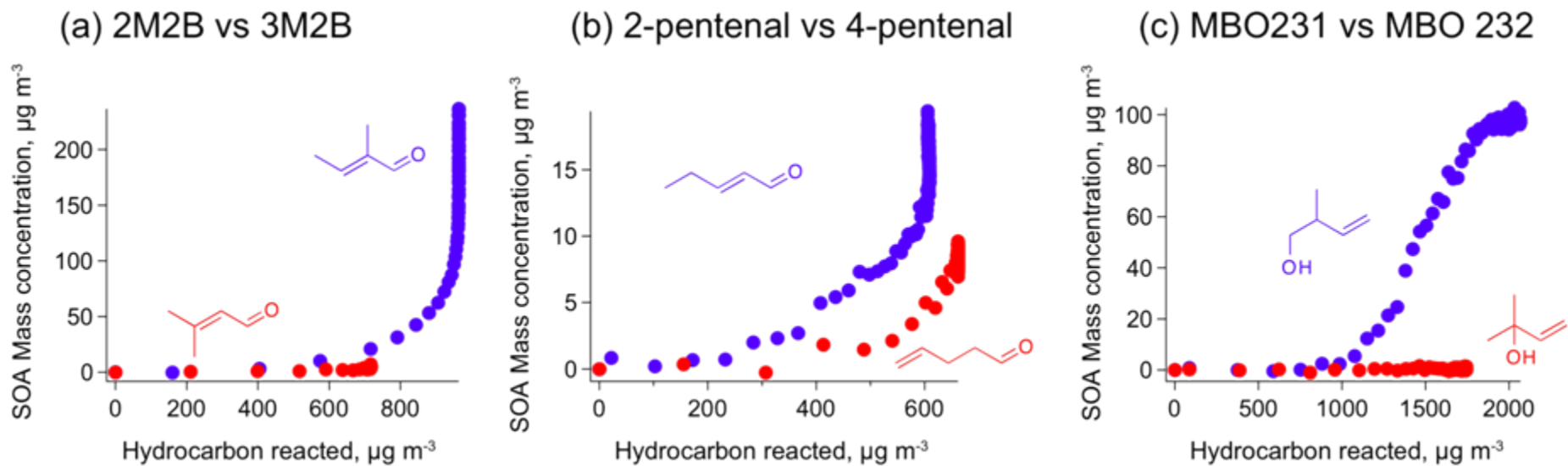
acrolein



crotonaldehyde

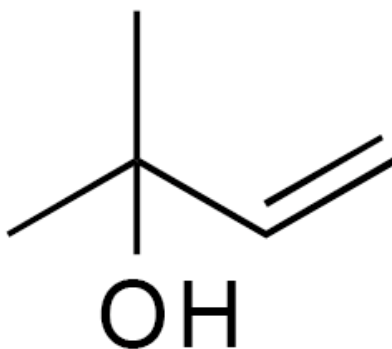


SOA formation from aldehydes/alcohols



2-METHYL-3-BUTEN-2-OL (MBO-232)

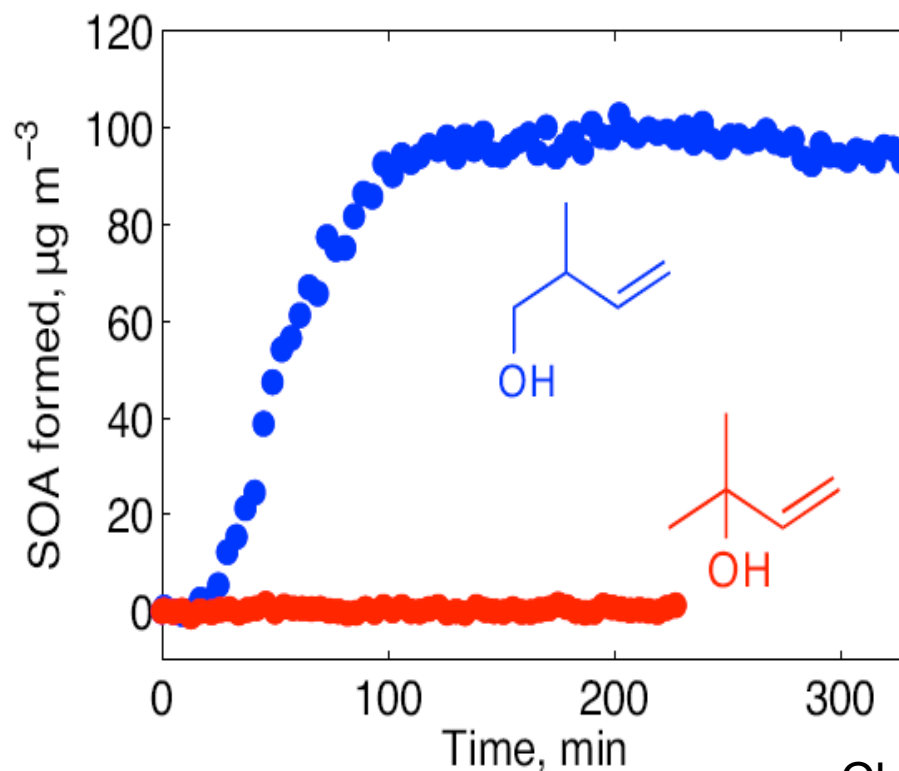
- ▶ Emitted from pine trees [Goldan et al., 1993, Harley et al., 1998, Baker et al., 1999]
- ▶ Effects on local photochemistry
 - ▶ Can be more important than isoprene locally
 - ▶ Increases production of HO_x and O₃ [Steiner et al., 2007]
- ▶ Important biogenic compound in the Western United States



MBO PHOTOOXIDATION: PAN INTERMEDIATE

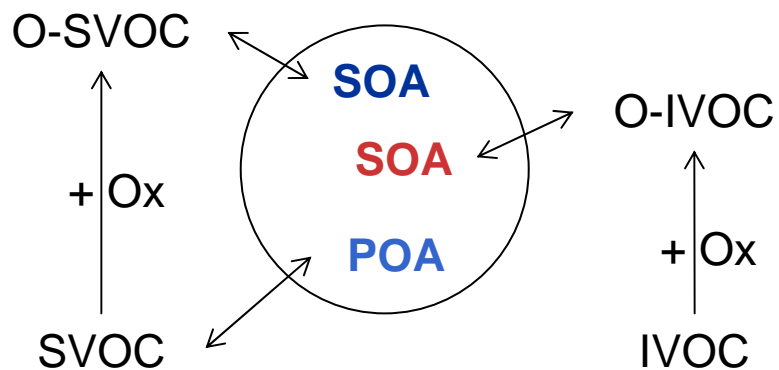
- ▶ SOA formation not observed, even under high NO_2 conditions:

MBO-231/ CH_3ONO vs MBO-232/ CH_3ONO

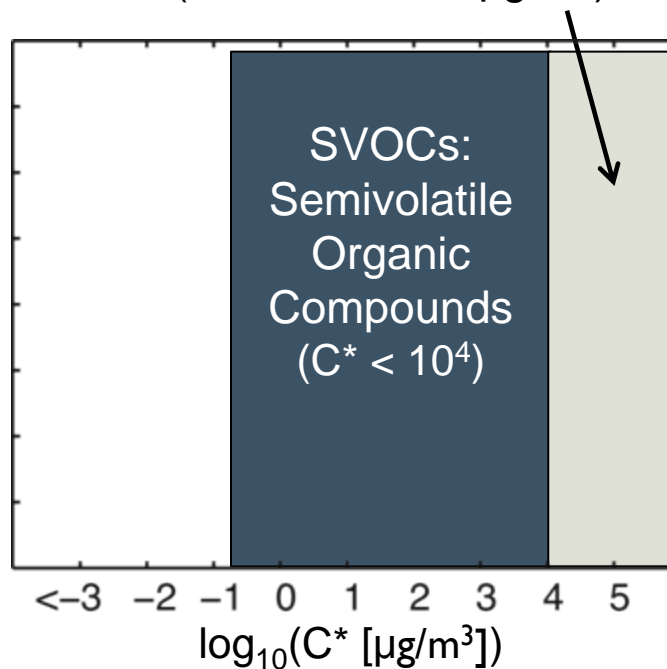


Low-Volatility Organics

Recent work (CMU) indicates there is a large potential for low-volatility organic compounds ($C^* < 10^6 \mu\text{g}/\text{m}^3$) to form organic aerosol

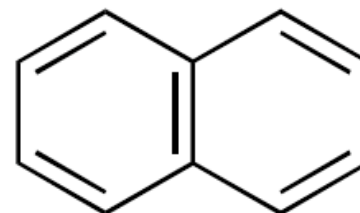


IVOCs: Intermediate Volatility Organic Compounds ($10^4 < C^* < 10^6 \mu\text{g}/\text{m}^3$)

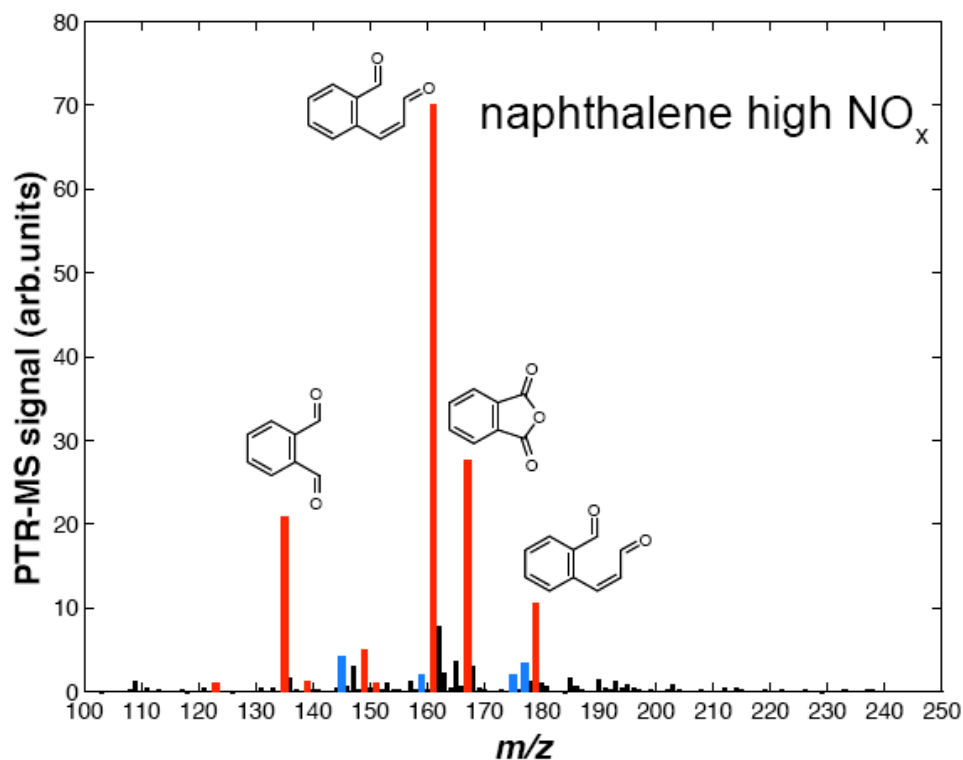
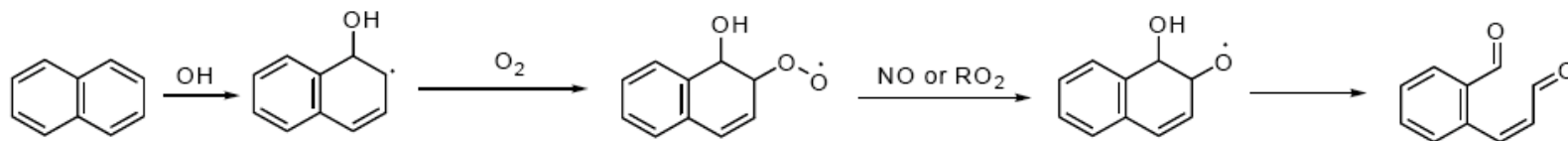


NAPHTHALENE

- ▶ Most abundant polycyclic aromatic hydrocarbon (PAH)
- ▶ Sources:
 - ▶ Wood burning
 - ▶ Diesel exhaust
 - ▶ Gasoline exhaust
- ▶ Sinks:
 - ▶ Reaction with OH (lifetime of 5.5 hours)
- ▶ Objective: to study SOA formation from PAHs and calculate the contribution of PAH oxidation to SOA formed from semivolatile emissions

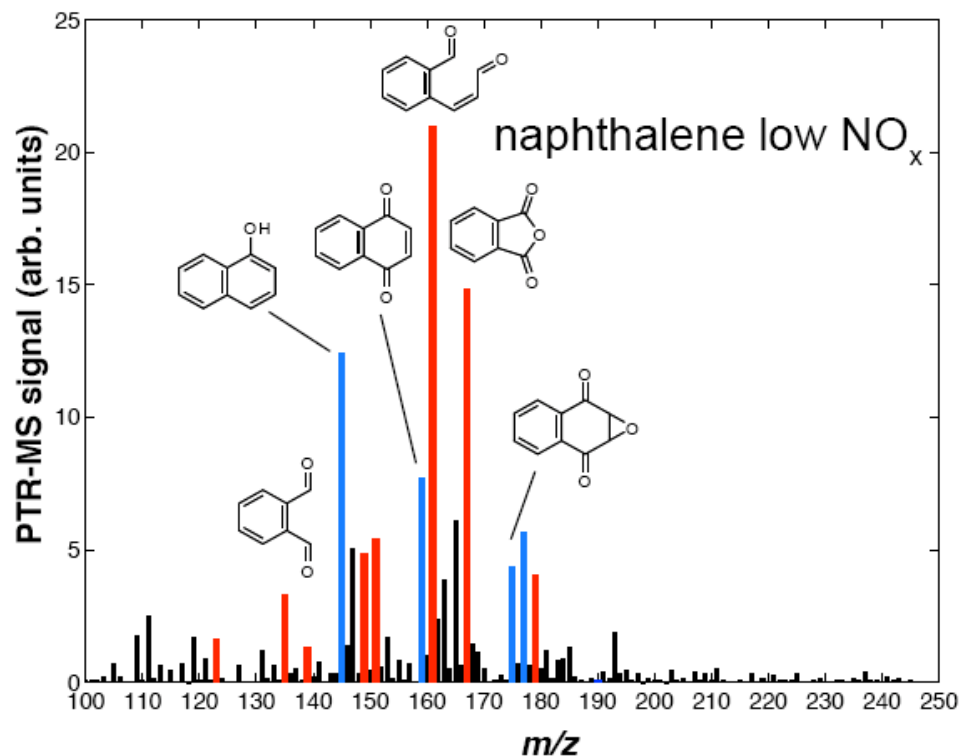


GAS-PHASE MECHANISM: NAPHTHALENE HIGH NO_x



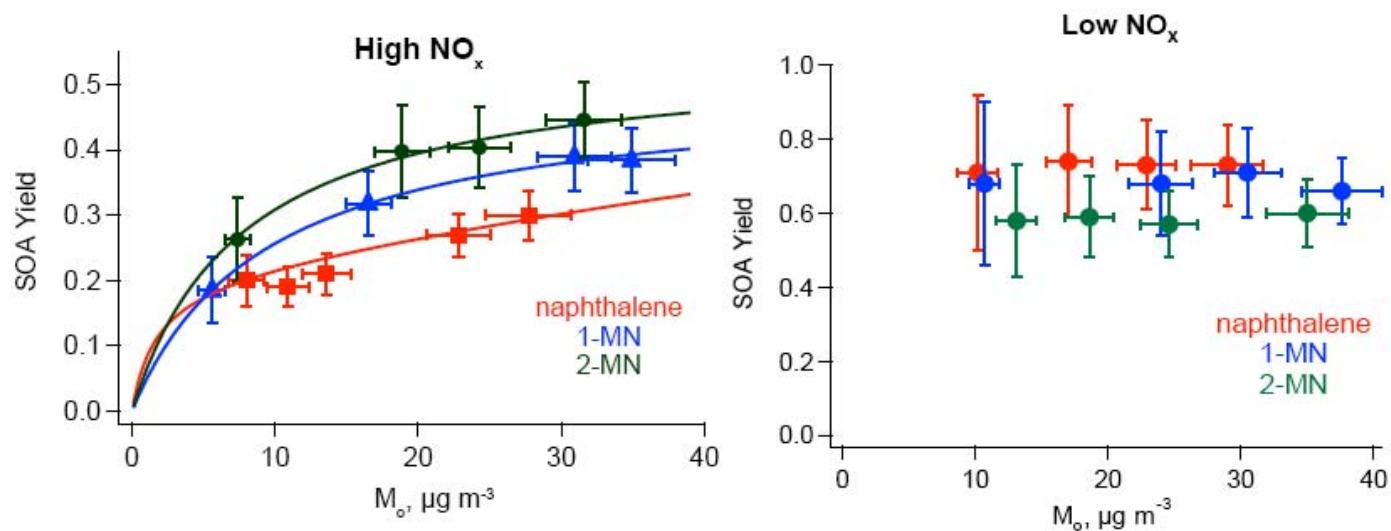
- ▶ Fraction of naphthalene reacted = 0.66
- ▶ PTR-MS:
 $A + H_3O^+ \rightarrow A \cdot H^+ + H_2O$
- ▶ Fragmentation products dominate under high NO_x

GAS-PHASE MECHANISM: NAPHTHALENE LOW NO_x



- ▶ Fraction of naphthalene reacted = 0.67
- ▶ Fragmentation products still dominate, but relative amounts of ring-retaining products are larger

SOA YIELDS



	α_1	$K_1, \text{m}^3 \mu\text{g}^{-1}$	α_2	$K_2, \text{m}^3 \mu\text{g}^{-1}$	SOA Yield at $15 \mu\text{g m}^{-3}$
high-NO_x					
naphthalene	0.21	0.59	1.07	0.0037	0.26
1-MN	0.50	0.11	—	—	0.33
2-MN	0.55	0.13	—	—	0.38
1,2-DMN	0.31	^a	—	—	0.31
low-NO_x					
naphthalene	0.73	^a	—	—	0.73
1-MN	0.68	^a	—	—	0.68
2-MN	0.58	^a	—	—	0.58

An aerial photograph of a large-scale forest fire. The fire is a bright orange and yellow line cutting through a dense green forest. A massive, billowing plume of white and grey smoke rises from the fire, filling the upper right portion of the frame. The background shows rolling hills and mountains under a clear sky.

**SOA from biomass burning:
A case for studying methoxyphenols**

Schauer et al. (2001)

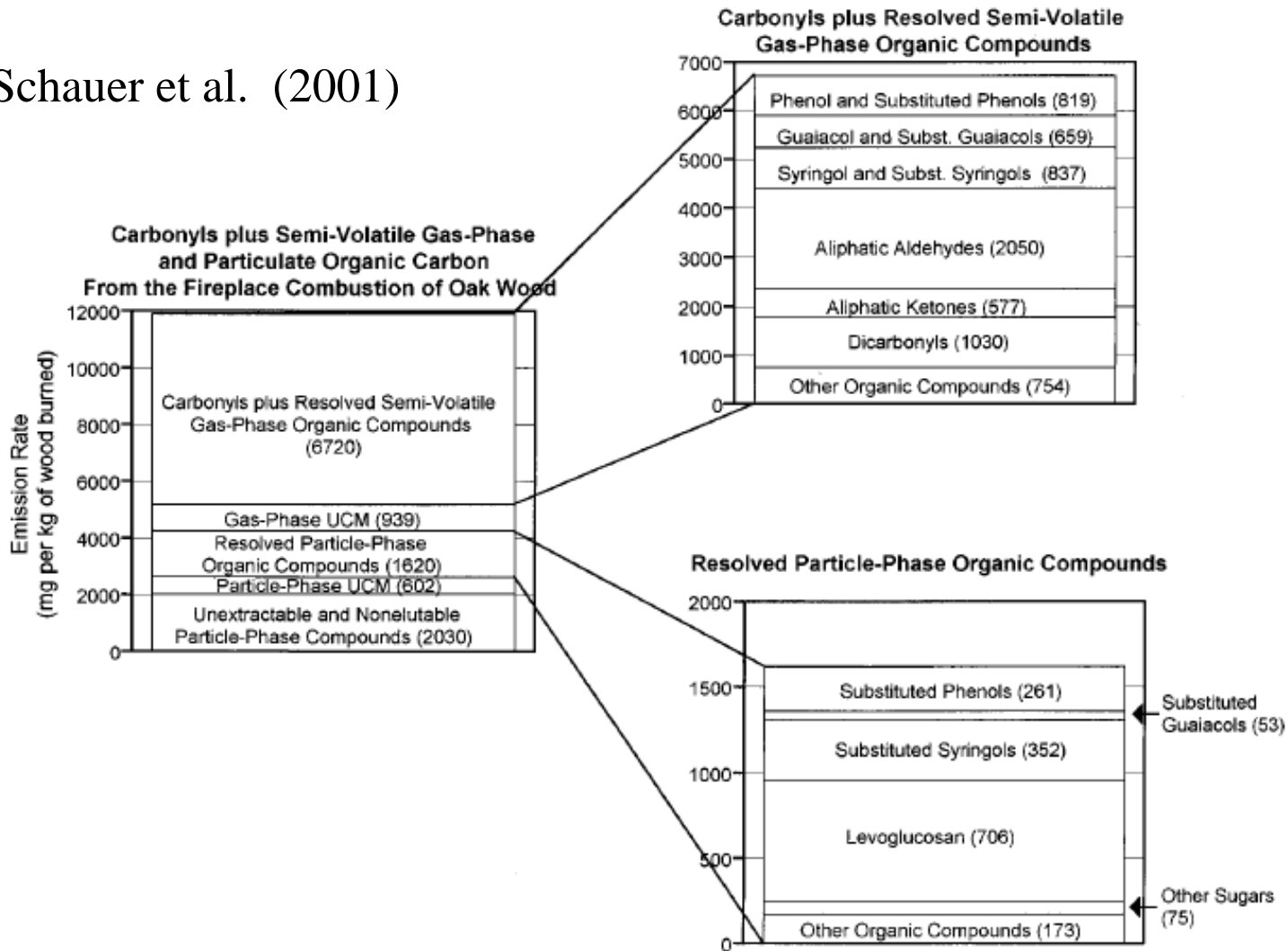
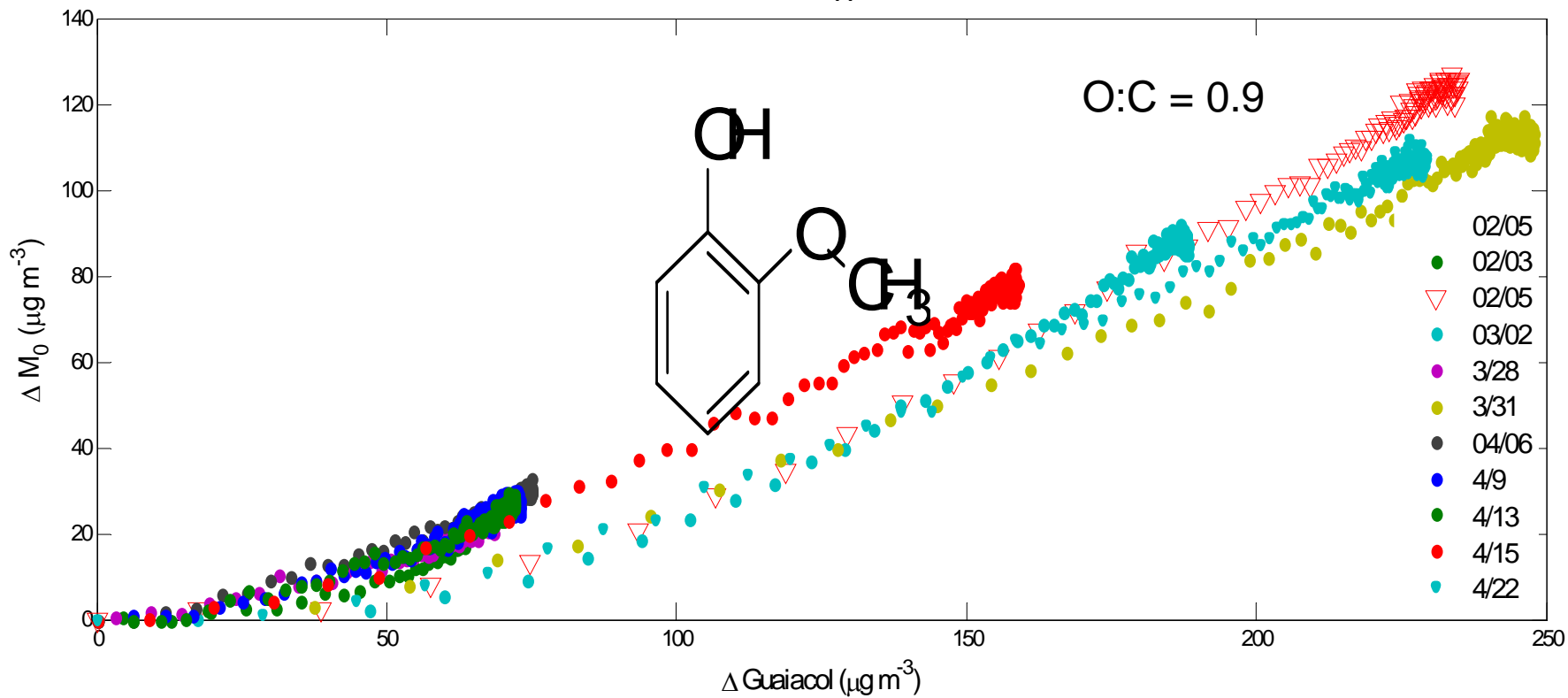
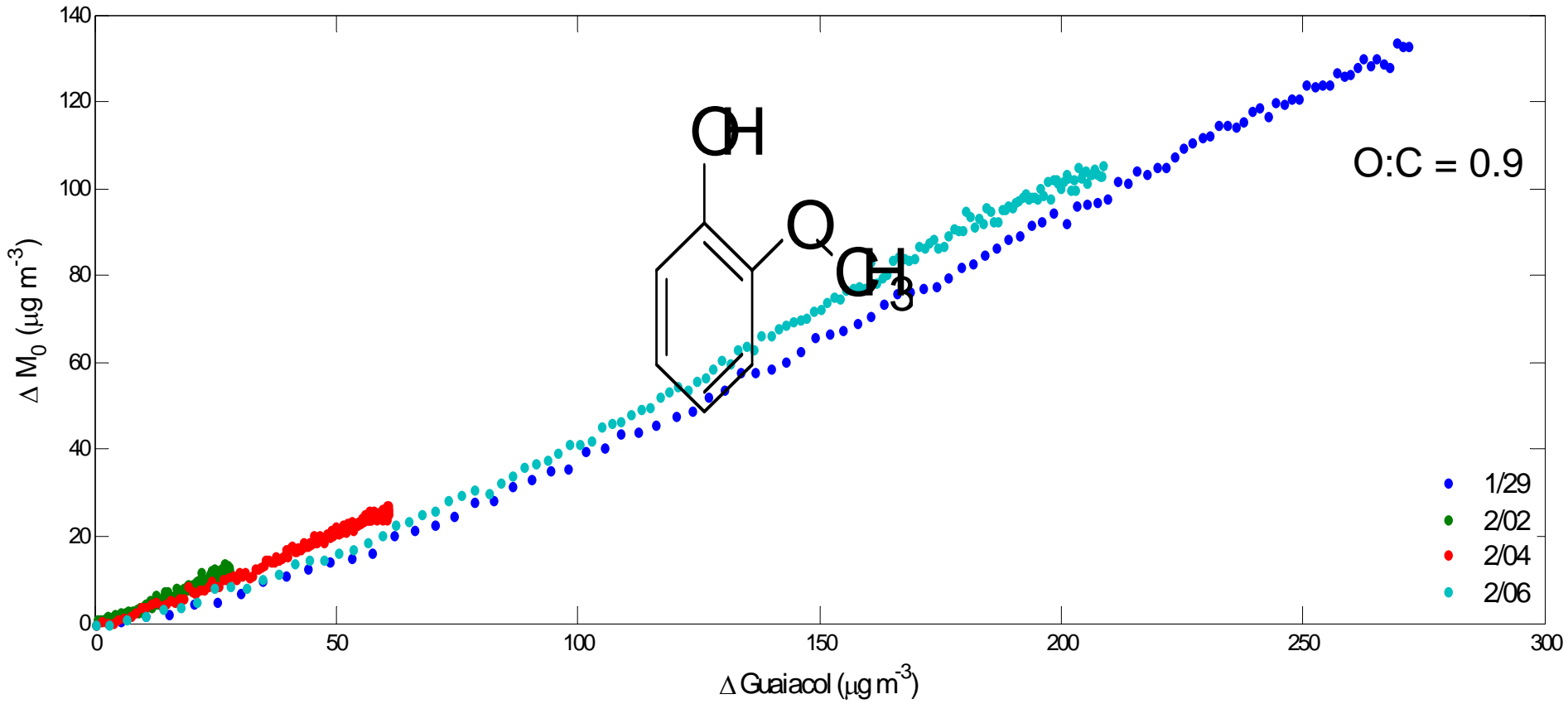


FIGURE 2. Mass balance on the carbonyl, semivolatile, and particulate organic compounds emitted from the fireplace combustion of oak wood.

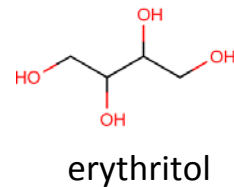
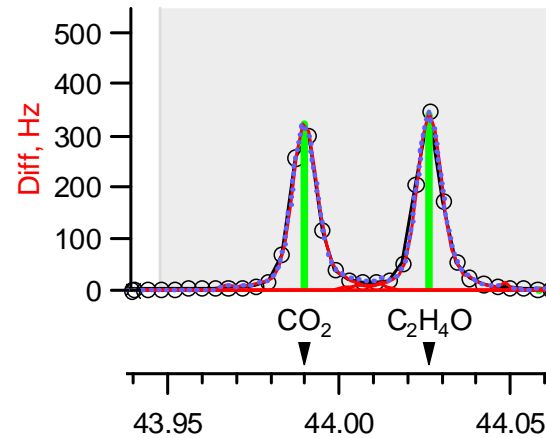
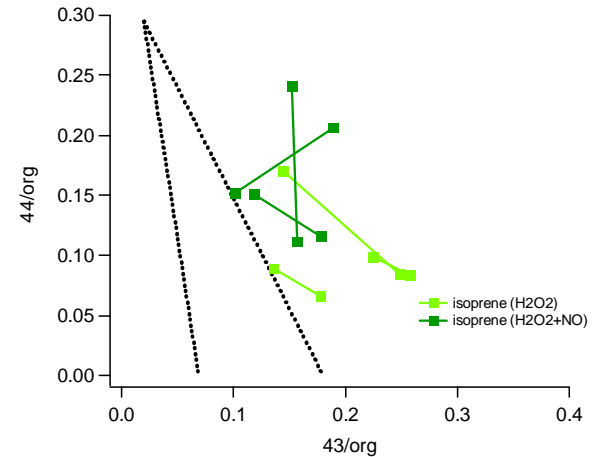
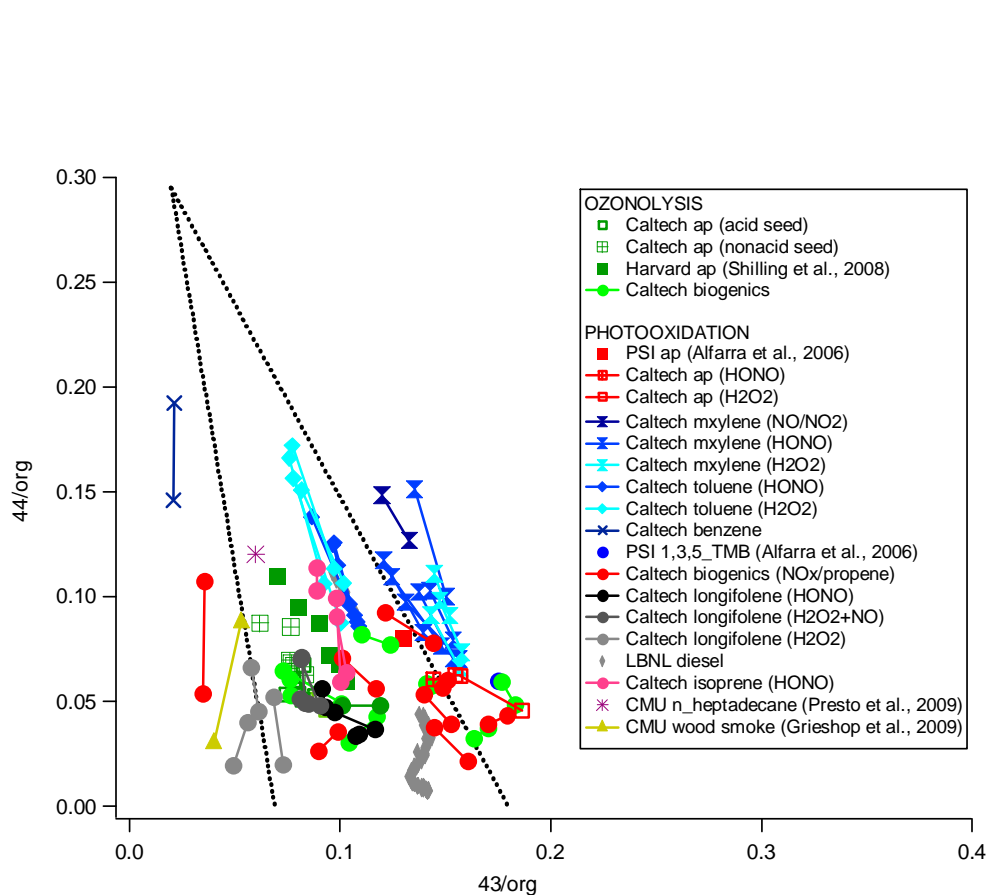
Guaiacol High NO_x Growth Curve



Guaiacol Low-NO_x Growth Curve



Laboratory SOA



Data from Sean Kessler,
Jesse Kroll

- Data from chamber experiments fall into the same space as ambient data; 44/org of most of the chamber data are < 0.1, indicating that chamber SOA is not as oxidized as ambient aerosol (2010)]

Ng et al., *ACP*

The Future

- Seek to bridge the gap between detailed molecular mechanisms of VOC oxidation leading to SOA and the ultimate ambient state that is characterized by O:C, H:C, volatility, polarity.
- Laboratory chamber experiments are the essential source of information on SOA formation; need to devise ways to extend the chemical lifetime of such experiments (within the confines of inevitable wall loss) to simulate ambient aging.
- Atmospheric models need to be able to track the sources of SOA; the challenge is to retain this identification in view of the evolution of SOA towards its highly oxidized state.