Formation of Secondary Organic Aerosol

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Conundrums

- Radiocarbon (^{14}C) data consistently indicate that well over half of ambient SOA is of modern (biogenic) origin.

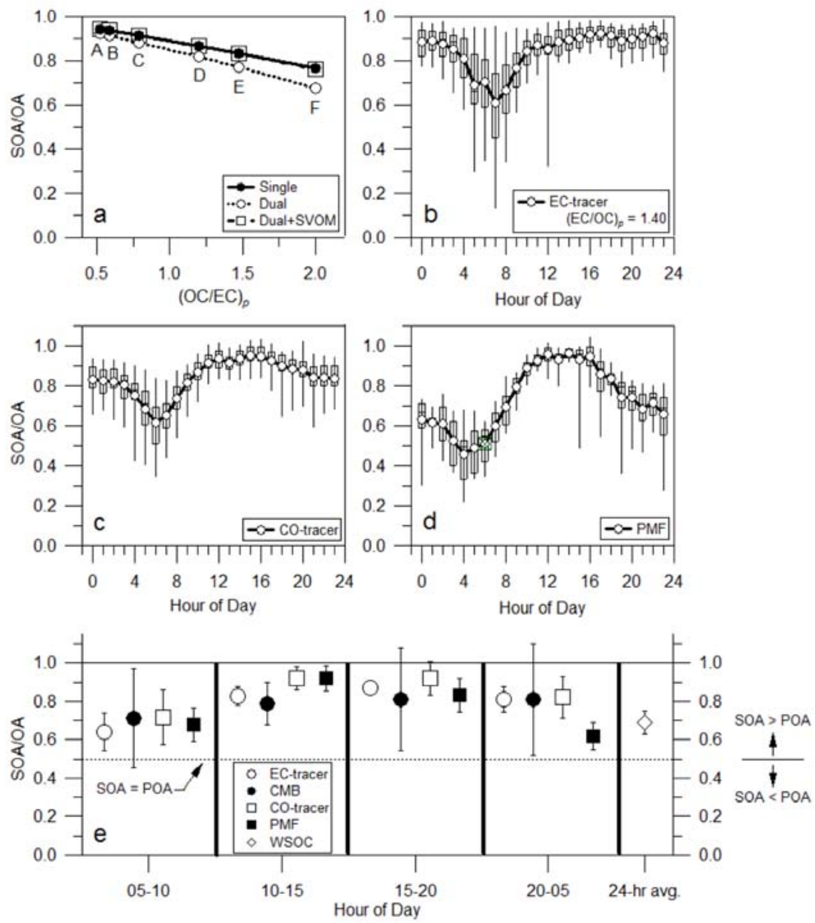
- Field measurements show correlation between WSOC (or AMS OOA spectra) and anthropogenic tracers, such as CO, suggesting that much of ambient SOA is of anthropogenic origin.

- Comparisons between ambient measured SOA and that predicted based on known precursors suggest that there is a substantial amount of "missing carbon" not in current models [*De Gouw et al.,* 2005; *Volkamer et al.,* 2006].

Table 5. Global SOA budgets.

Hydrocarbon	Emission (Tg/yr)	SOA Production (Tg/yr)	Burden (Tg)
terpenes	121	8.2	0.21
alcohols	38.3	1.5	0.03
sesquiterpenes	14.8	2.0	0.03
isoprene	461	13.2	0.43
aromatics	18.8	3.5	0.08
total	654	28.4	0.78

Henze, D.K. et al., Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high vs. low yield pathways, *Atmos. Chem. Phys.,* in press.



SOA/OA
(OC/EC)$_p$
Hour of Day
A
B
C
D
E
F
Single
Dual
Dual+SVOM
a
EC-tracer
(EC/OC)$_p$ = 1.40
b
CO-tracer
c
PMF
d
SOA = POA
EC-tracer
CMB
CO-tracer
PMF
WSOC
e
SOA > POA
SOA < POA
05-10
10-15
15-20
20-05
24-hr avg.

Secondary Organic Aerosol:

Predictions versus Observations

Possible reasons for discrepancy between predictions and observations:

1. Ambient SOA yields for those parent hydrocarbons known to produce SOA exceed those measured in laboratory chambers.

2. Classes of SOA-forming organics exist that have yet to be studied in the laboratory or included in atmospheric models.

3. Uncertainties in current treatments of SOA formation in global models lead to biases that result in underpredictions.

1. Ambient SOA yields for those parent hydrocarbons known to produce SOA exceed those measured in laboratory chambers.

- SOA yields determined in laboratory chambers until recently were not fully controlled for NO_x level.
- For isoprene, monoterpenes, and aromatics, SOA yields increase strongly as NO_x decreases toward non-urban levels.
- For sesquiterpenes, SOA yields increase as NO_x increases, owing to formation of nitrate-containing products and/or efficient isomerization of alkoxy radicals to form relatively nonvolatile products (Ng et al., 2007).*

* Ng, N. L. et al., Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, *ACP*, 2007.

2. Classes of SOA - forming organics exist that have yet to be studied in the laboratory or included in atmospheric models.

- At present, biogenic VOCs, isoprene and the terpenes, are considered as the dominant global sources of SOA.
- Aromatic SOA production has been re-evaluated (Ng et al., 2007)* and contribution can be appreciable at the urban/regional scale.
- Robinson et al. (*Science,* 2007): The gas-phase component of primary semivolatile OA emissions can be photooxidized to lead to SOA. This source of SOA is potentially significant.
- Potential of both larger, e.g. diesel hydrocarbons, and smaller molecules, e.g. acetylene, to serve as parent VOCs?

*Ng, N. L. et al., Secondary organic aerosol formation from *m*-xylene, toluene, and benzene, *ACP*, **7**, 3909-3922 (2007)

3. Uncertainties in current treatments of SOA formation in global models lead to biases that result in underpredictions.

- Updating of SOA yields to account for NO_x dependence, aerosol acidity, RH (Henze et al., 2007)*
- Addition of VOCs not currently considered as SOA sources, e.g. primary semivolatile VOCs
- Effect of SOA volatility (V.P., ΔH_v) uncertain: ΔH_v estimates in current models range from 156 kJ/mol to 42 kJ/mol

*Henze, D. K. et al., Global modeling of secondary organic aerosol from aromatic hydrocarbons: High- vs. low-yield pathways, *ACP*, in press.

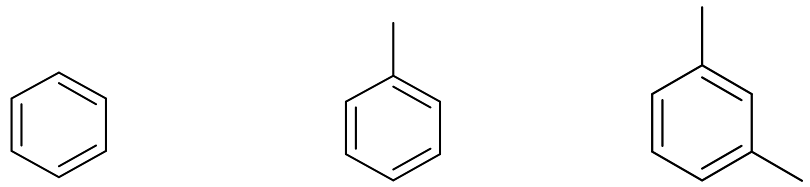
Goals of Caltech Project

- To continue to elucidate the mechanisms of formation and SOA yields of all important classes of atmospheric hydrocarbons (to attempt to understand discrepancy between observed and modeled ambient SOA levels).

- To develop a “next-generation” SOA model, constrained by laboratory data, for inclusion in chemical transport and general circulation models. Model should account for:
  - Effects of NO_x level on mechanisms
  - Evolution of volatility of oxidation products
  - Particle-phase chemistry

Aromatic SOA

- Study systematically the effect of NO_x on SOA formation from selected aromatic hydrocarbons

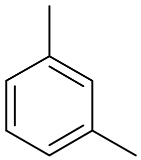


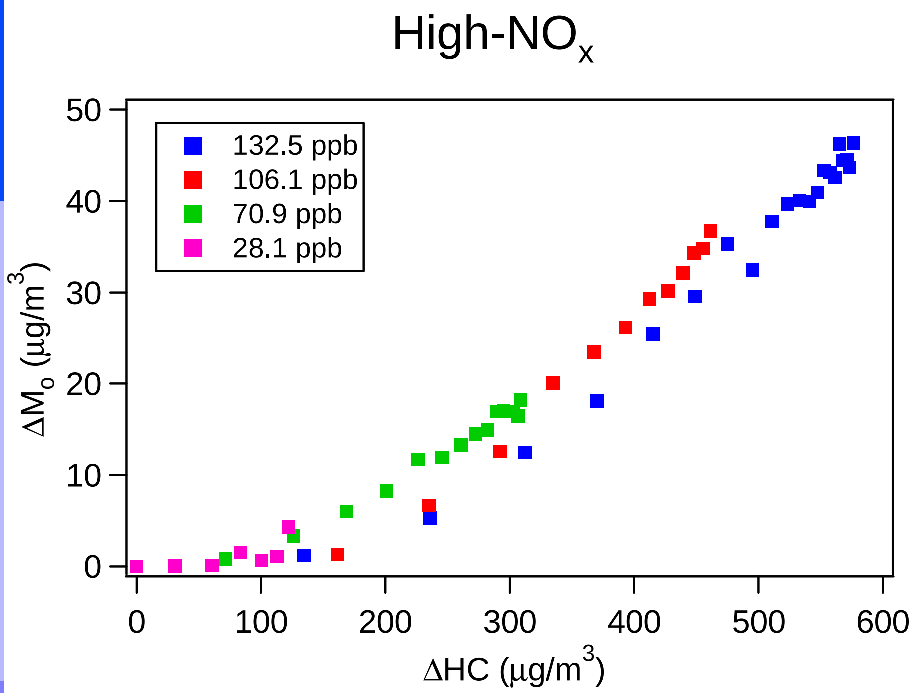
Benzene Toluene *m*-xylene

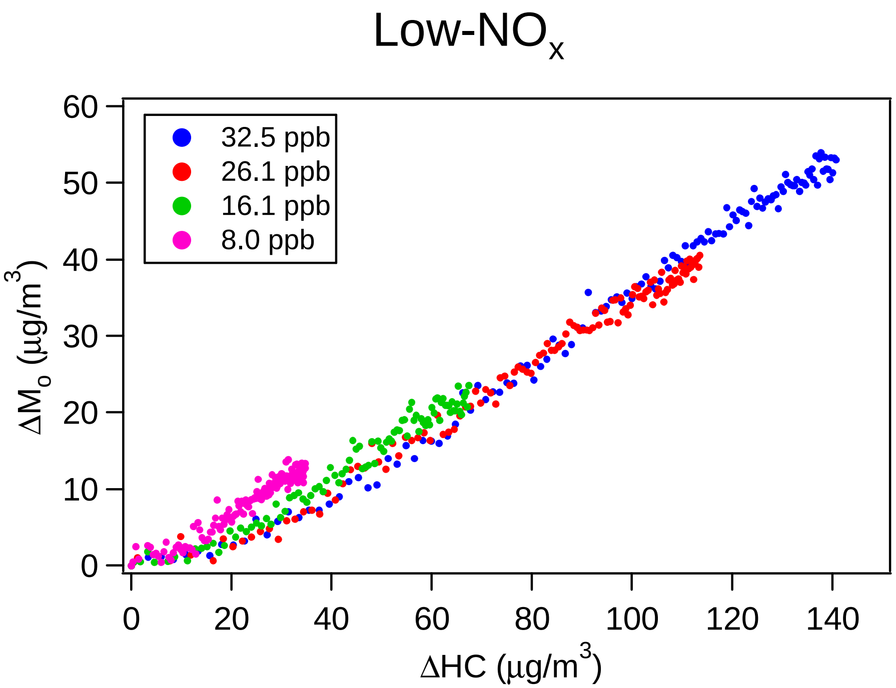
- Obtain SOA yields at high- and low-NO_x conditions (the limiting cases), parameterize the NO_x dependence for modeling purposes

- Investigate the effect of particle phase acidity on aerosol growth

Growth curves: *m*-xylene



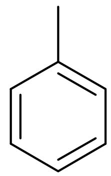


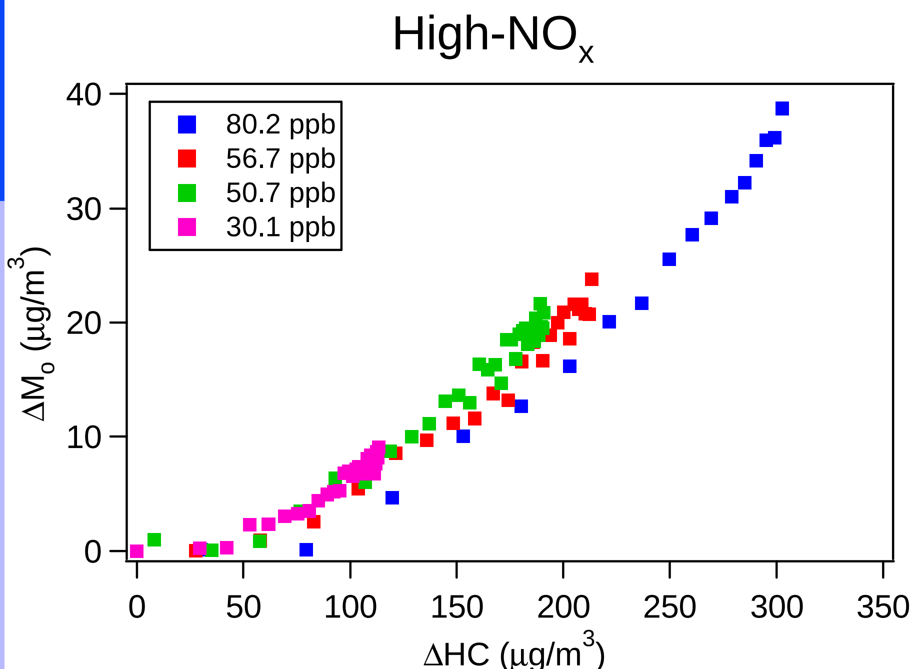


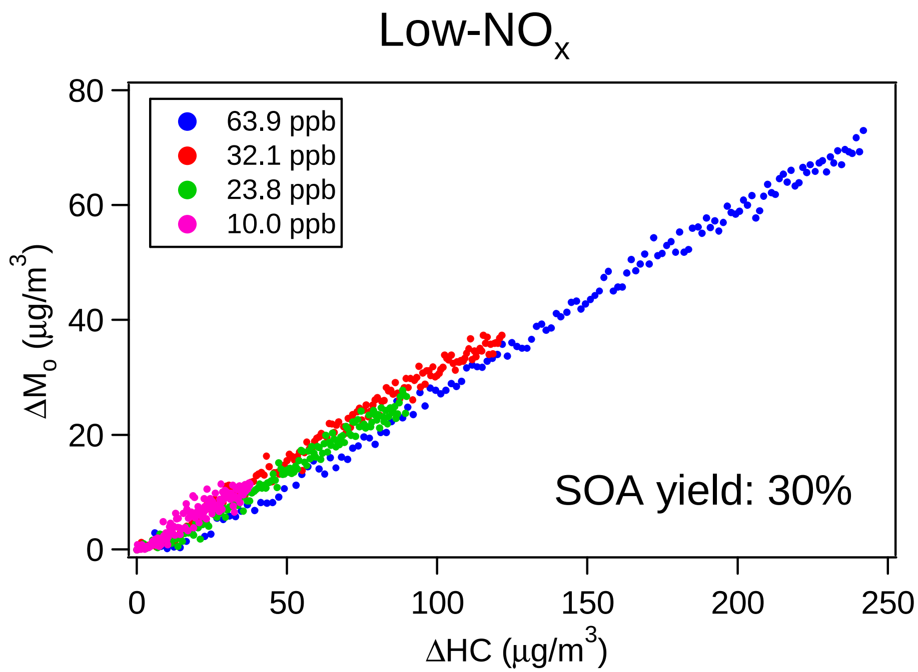
- High-NO_x: Growth curves do not overlap, multiple rate-limiting steps in SOA formation (first step is the slowest)
- Further-generation oxidation products

- SOA yields much higher than high-NO_x experiments
- Constant SOA yield implies essentially nonvolatile oxidation products (36% yield)

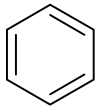
Growth curves: toluene

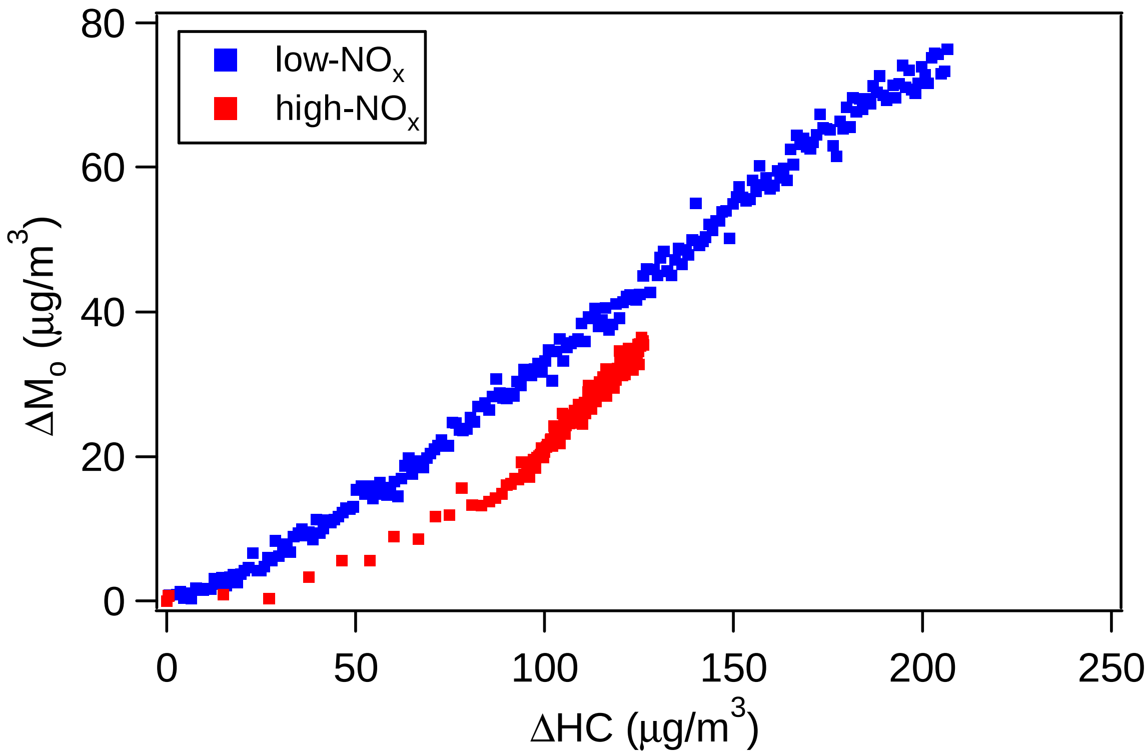






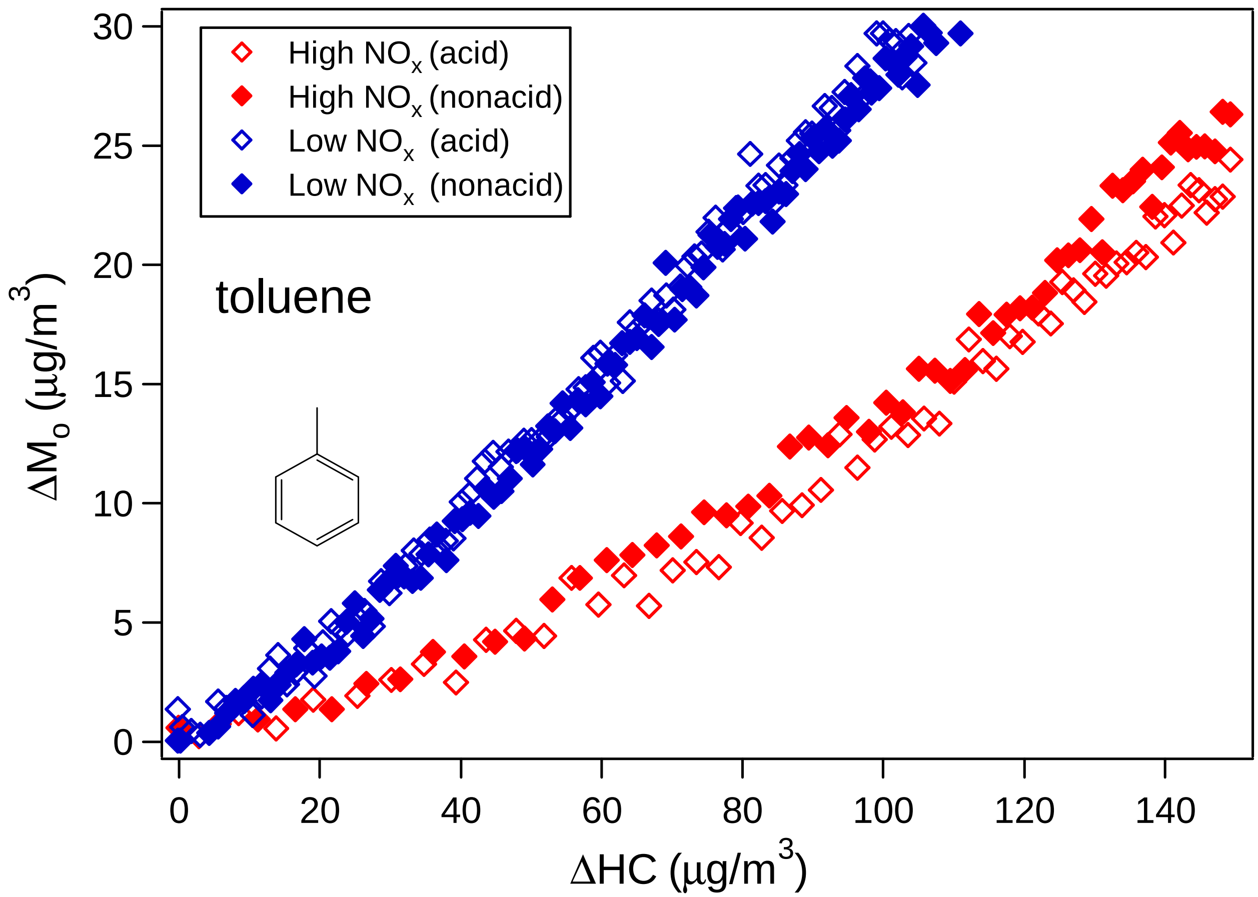
Growth curves: benzene





- ~400 ppb benzene (slow reaction rate, <20% reacted)
- Same NO_x dependence as *m*-xylene and toluene: high NO_x, lower yields
- Low NO_x: constant yield of 37%

Seed acidity: acid seed vs. non-acid seed



- No acid effect observed
- Same observations in *m*-xylene oxidation

Effect of Acidity on Hydrocarbons Studied at Caltech

Parent Hydrocarbon	T (K)	RH (%)	Oxidant	NO_x Condition	Seed Type	ΔHC (ppb)	ΔM_o (μg/m^3)	SOA Yield (%)
α-pinene	293	55	O_3	n/a	neutral	12	20.4	30.1
α-pinene	293	55	O_3	n/a	highly acidic	12	28.0	41.3
isoprene	297	~9	OH radical	Low-NO_x	neutral	500	73	5.2
isoprene	297	~9	OH radical	Low-NO_x	acidic	500	259	18.5
m-xylene	297	5.0	OH radical	High-NO_x	neutral	68.9	78.9	26.3
m-xylene	298	4.2	OH radical	High-NO_x	acidic	68.5	78.3	26.3
m-xylene	297	4.3	OH radical	Low-NO_x	neutral	60.2	101.3	38.6
m-xylene	297	4.5	OH radical	Low-NO_x	acidic	58.8	103.5	40.4
toluene	296	4.9	OH radical	High-NO_x	neutral	60.0	43.8	19.3
toluene	298	4.9	OH radical	High-NO_x	acidic	58.2	38.4	17.4
toluene	298	5.9	OH radical	Low-NO_x	neutral	37.9	41.0	38.7
toluene	299	4.6	OH radical	Low-NO_x	acidic	38.9	43.2	29.5

no enhancements in aromatic SOA mass observed with increasing aerosol acidity

neutral = 15 mM $(NH_4)_2SO_4$

acidic = 15 mM $(NH_4)_2SO_4$ + 15 mM H_2SO_4

highly acidic = 30 mM $(NH_4)_2SO_4$ + 50 mM H_2SO_4

- Currently, only enhancements in biogenic SOA have been observed with increasing aerosol acidity - consistent with composition data (i.e. organosulfates)

Mechanism for SOA from Aromatics (SOAa)

Aromatic oxidized by OH to form peroxy radical (assumed only product)

$$\mathrm{AROM} + \mathrm{OH} \rightarrow \mathrm{ARO_2}$$

HO_2 and NO compete for ARO_2

$$\mathrm{ARO_2} + \mathrm{HO_2} \rightarrow \alpha_H \mathrm{SOG}_H$$

$$\mathrm{ARO_2} + \mathrm{NO} \rightarrow \alpha_{N,1} \mathrm{SOG}_{N,1} + \alpha_{N,2} \mathrm{SOG}_{N,2}$$

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$$\mathrm{ARO_2} + \mathrm{HO_2} \rightarrow \alpha_H \mathrm{SOG}_H$$

$$\downarrow$$

SOA Partitioning: SOAa

$$\rightleftharpoons K_{N,1} \qquad \rightleftharpoons K_{N,2}$$

$$\mathrm{ARO_2} + \mathrm{NO} \rightarrow \alpha_{N,1}\mathrm{SOG}_{N,1} + \alpha_{N,2}\mathrm{SOG}_{N,2}$$

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$$\mathrm{ARO_2} + \mathrm{HO_2} \rightarrow \alpha_H \mathrm{SOG}_H$$

High yield

SOA Partitioning:

$$\mathrm{SOAa}$$

Low yield

$$\rightleftharpoons K_{N,1} \qquad \rightleftharpoons K_{N,2}$$

$$\mathrm{ARO_2} + \mathrm{NO} \rightarrow \alpha_{N,1}\mathrm{SOG}_{N,1} + \alpha_{N,2}\mathrm{SOG}_{N,2}$$

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$$\mathrm{ARO_2} + \mathrm{HO_2} \rightarrow \alpha_H \mathrm{SOG}_H$$

High yield

? Which route ?

$$\mathrm{SOAa}$$

Low yield

$\rightleftharpoons K_{N,1}$ $\rightleftharpoons K_{N,2}$

$$\mathrm{ARO_2} + \mathrm{NO} \rightarrow \alpha_{N,1}\mathrm{SOG}_{N,1} + \alpha_{N,2}\mathrm{SOG}_{N,2}$$

Anthropogenic SOA Formation Pathways

Dominant pathway depends upon aromatic

Benzene, Toluene, Xylene

$$\mathrm{ARO_2 + HO_2} \rightarrow \alpha_H \mathrm{SOG}_H$$

74%, 64%, 45%

High yield

SOAa

Low yield

$\rightleftharpoons K_{N,1}$ $\rightleftharpoons K_{N,2}$

$$\mathrm{ARO_2 + NO} \rightarrow \alpha_{N,1}\mathrm{SOG}_{N,1} + \alpha_{N,2}\mathrm{SOG}_{N,2}$$

26%, 36%, 55%

Less reactive aromatics --> more SOA

Anthropogenic SOA Formation Pathways

Total from all sources

63% $$\mathrm{ARO_2} + \mathrm{HO_2} \rightarrow \alpha_H \mathrm{SOG}_H$$

High yield 20%

SOAa

3% Low yield

$\rightleftharpoons K_{N,1}$ $\rightleftharpoons K_{N,2}$

37% $$\mathrm{ARO_2} + \mathrm{NO} \rightarrow \alpha_{N,1}\mathrm{SOG}_{N,1} + \alpha_{N,2}\mathrm{SOG}_{N,2}$$

90% of SOAa comes from low NO_x pathway

Observations on NO_X Dependence

- In summary, isoprene shown to have lower SOA yields under high-NO_x conditions and seems to be consistent with our understanding of RO_2 chemistry
- Monoterpenes ($C_{10}H_{16}$) and aromatic VOCs found to have same NO_x dependence on SOA formation as isoprene (i.e. higher SOA yields under low- NO_x conditions) [Ng et al., *ACP*, 2007ab]
- Larger VOCs, such as sesquiterpenes ($C_{15}H_{24}$) and large alkanes (> C_{10}), have been shown to produce higher SOA yields under high-NOx conditions [Ng et al., *ACP*, 2007a; Lim et al., *ES&T*, 2005]
- Chemical compositions of monoterpenes and aromatic VOCs need to be fully characterized, as this may provide further insights as to why SOA yields are higher at low-NO_x conditions
- Fully and accurately characterizing NOx dependences of all SOA precursors will likely help to close gap between modeled and observed SOA

SOA from Isoprene + NO_3

Ng, N.L. et al., *Atmos. Chem. Phys. Disc*., **8**, 3163-3226 (2008)

Experimental conditions

- Ammonium sulfate seed; T~21^{o}C, RH<10%, dark

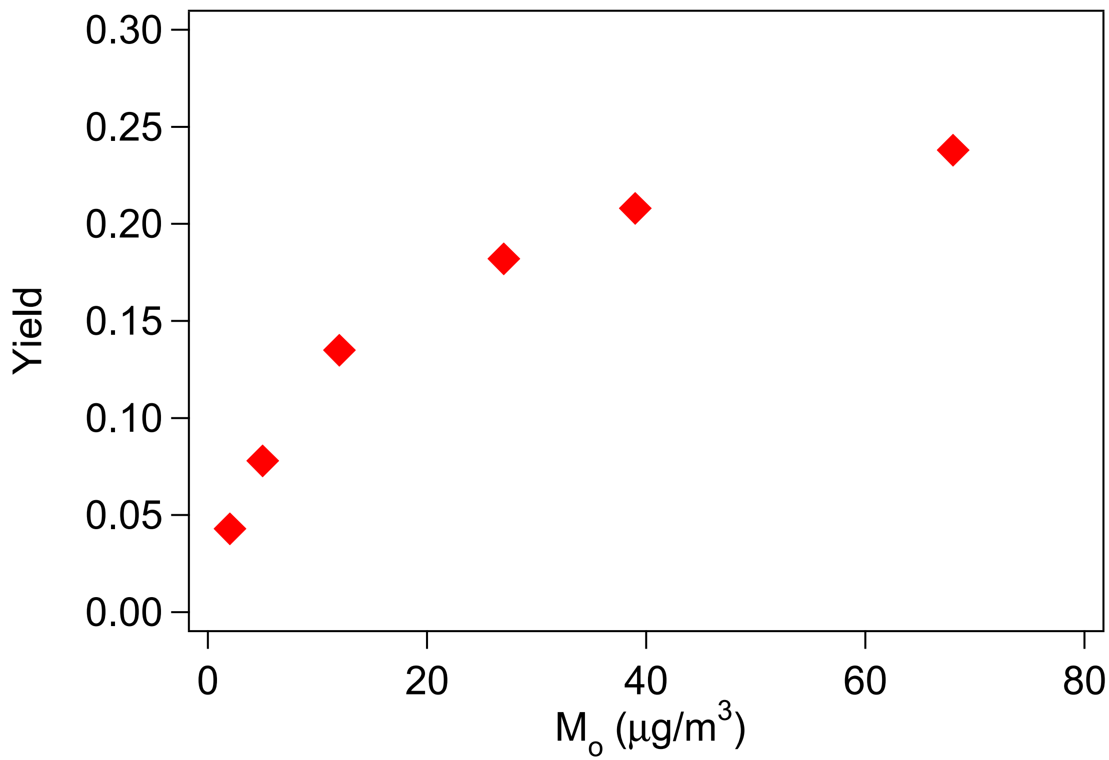
- N_2O_5 preparation:
  - Mix 2% ozone in oxygen with pure NO
  - N_2O_5 trapped with a bubbler under dry ice temperature (-70℃)
  - FTIR analysis shows ~95% N_2O_5

- SOA Yield experiments:
  - Isoprene injected first and allowed to mix
  - Experiment initiated by injecting ~1 ppm N_2O_5 into chamber; N_2O_5 quickly decomposes to form NO_2 and NO_3

- CIMS experiments:
  - Vary the amount of N_2O_5 and isoprene injected to study mechanisms of SOA formation

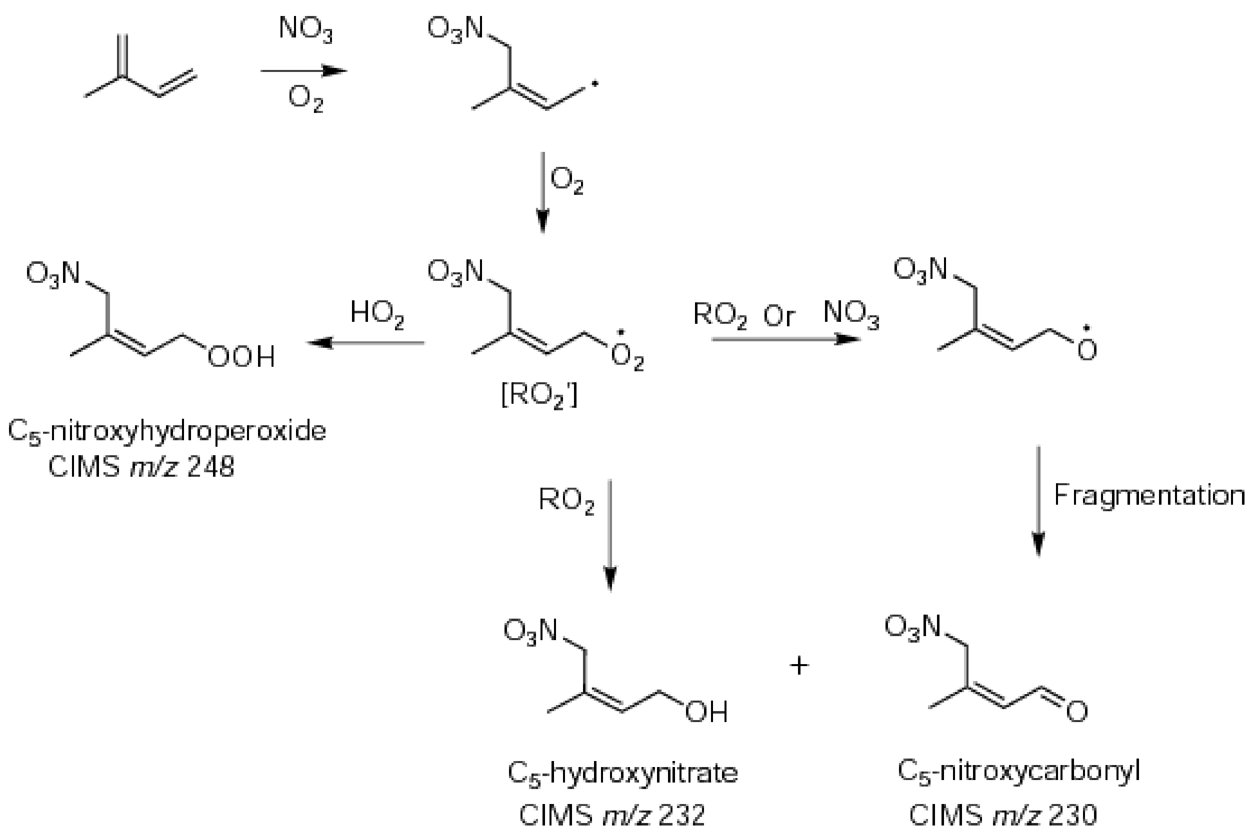
- "Slow Injection" experiments:
  - Isoprene injected first, then inject N_2O_5 slowly through a 65 L Teflon bag
  - N_2O_5 injected first, then inject isoprene slowly through 65 L bag

Secondary organic aerosol (SOA) yield

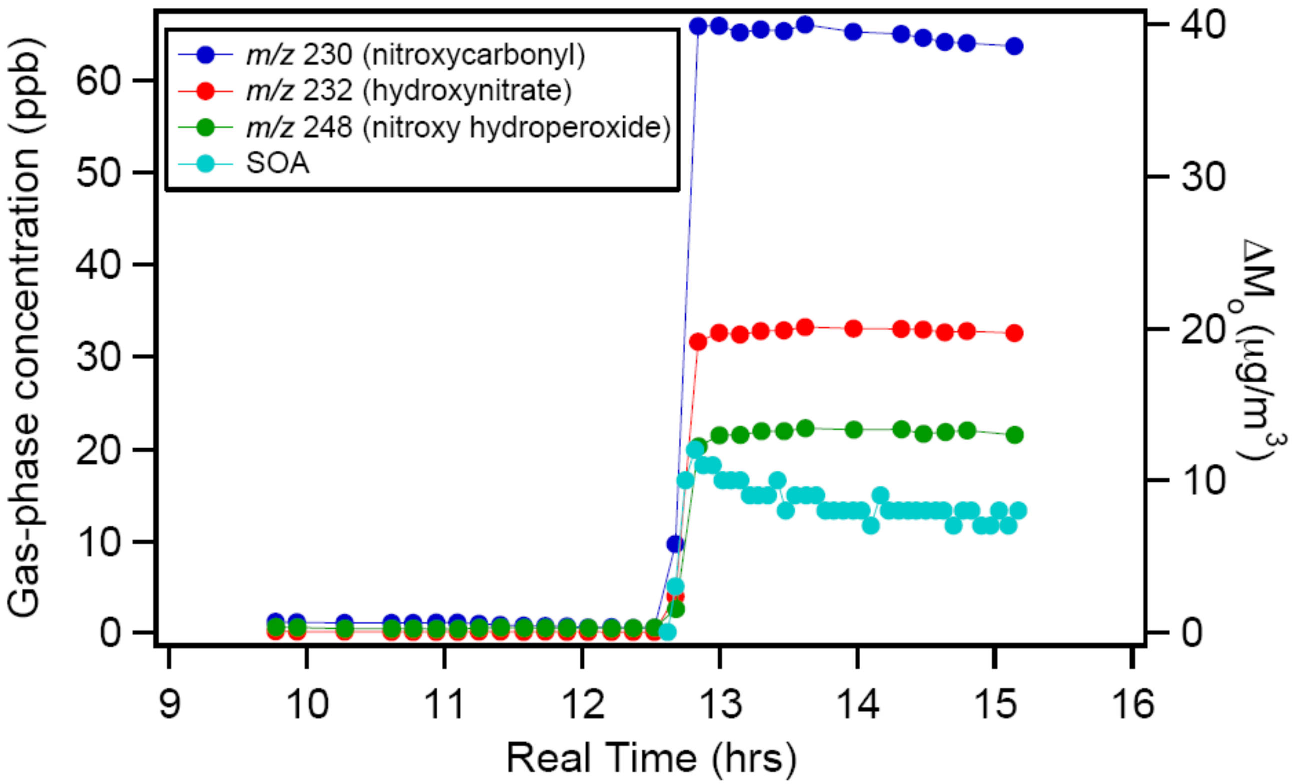


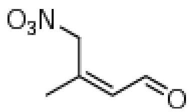
- Isoprene reacted: 18 - 102 ppb
- SOA density: 1.42 g/cm^3
- Inorganic nitrate measured by PILS: 1.6 to 2.6 μg/m^3

Peroxy Radical Chemistry

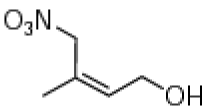


Major First-Generation Products

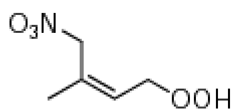




C_5-nitroxycarbonyl
CIMS *m/z* 230



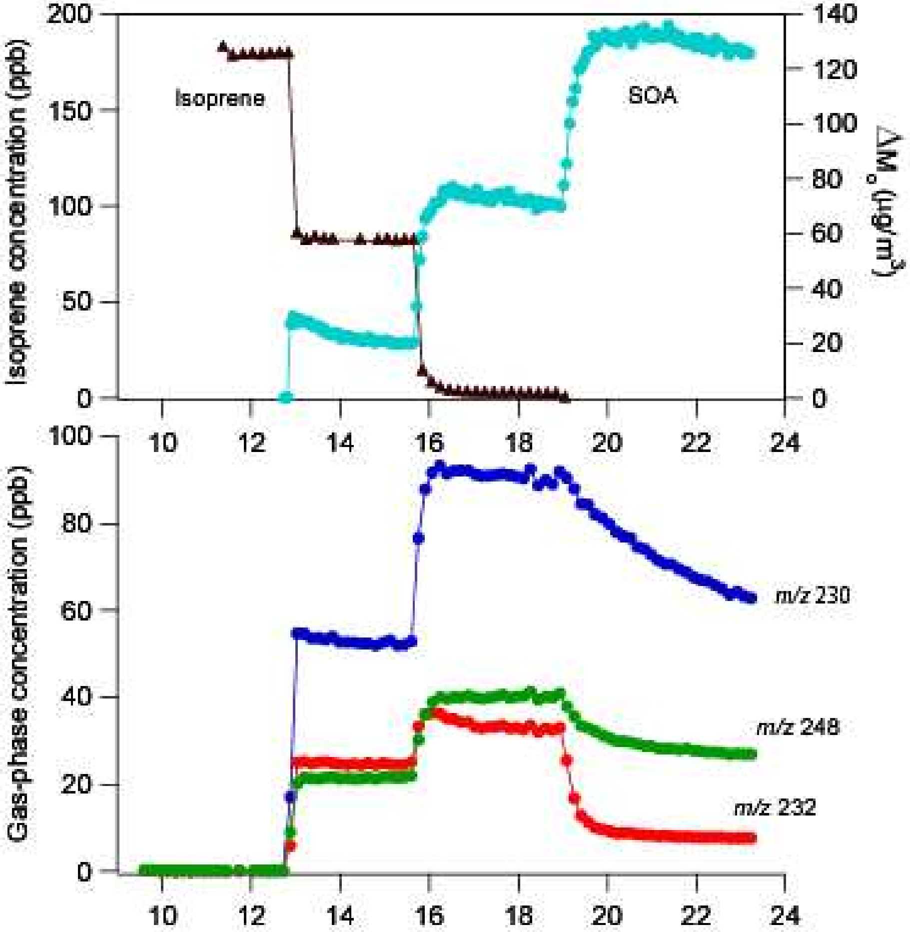
C_5-hydroxynitrate
CIMS *m/z* 232

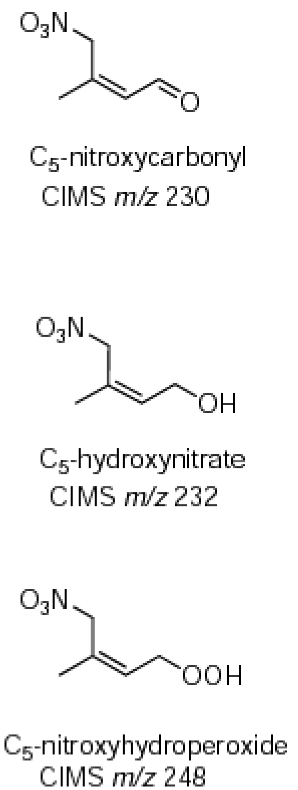


C_5-nitroxyhydroperoxide
CIMS *m/z* 248

800 ppb isoprene injected into 130 ppb N_2O_5

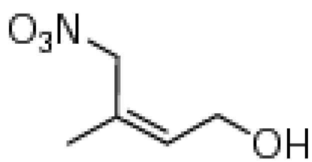
Major First-Generation Products



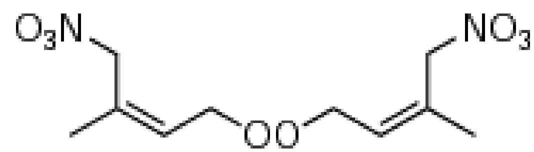


200 ppb isoprene, add 3 pulses of N_2O_5

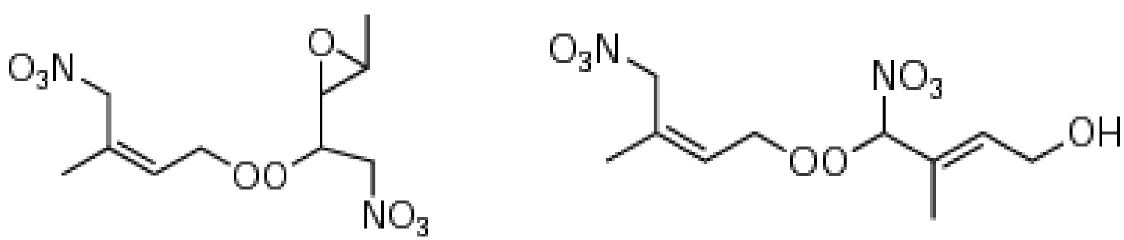
Conclusion: Important masses for SOA formation



C_5-hydroxynitrate
CIMS *m/z* 232



CIMS *m/z* 377



CIMS *m/z* 393

Global predictions of SOA from isoprene + NO_3

- Two global isoprene emissions are available in GEOS-Chem:
  - GEIA (Global Emission Inventory Activity) [*Guenther et al.*, 1995]
  - MEGAN (Model of Emissions and Gases from Nature) [*Guenther et al.*, 2006]

	GEIA	MEGAN
Isoprene emission (Tg/y)	507	389
Isoprene reacted (Tg/y) by		
Isoprene + OH	407	304
Isoprene + O_3	69	62
Isoprene + NO_3	29	21

Assume 10% SOA yield

2 -3 Tg/y SOA formed

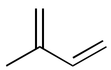
Organosulfates in Ambient Aerosol

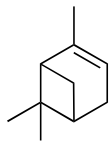
Surratt et al., *ES&T*, **41**, 517-527 (2007)

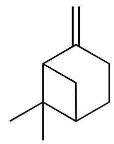
Surratt et al., *J. Phys. Chem.*, in press (2008)

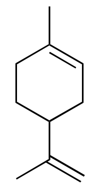
Organosulfates in Ambient Aerosol

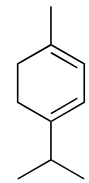
- Comprehensive laboratory investigation of organosulfate formation from the oxidation of 10 terpenes:

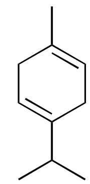

isoprene

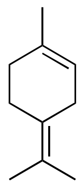

α-pinene

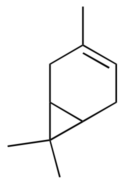

β-pinene

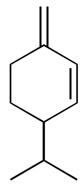

d- and *l*-limonene


α-terpinene


γ-terpinene


terpinolene


Δ^3-carene


β-phellandrene

- Reanalyze ambient aerosol collected from the southeastern U.S. [Gao et al., *JGR*, 2006] using more advanced MS techniques

- Compare the laboratory and field MS data to evaluate atmospheric significance

Atmospheric Significance of Organosulfates

- An upper limit estimate indicates that ~ 30% of the total ambient organic aerosol mass could be in the form of organosulfates

- Organosulfate formation from BVOCs appears to be ubiquitous in ambient aerosol collected from the S.E. USA and Europe

- These compounds are ambient tracers for biogenic SOA formation under acidic conditions

- Both the OH-initiated (in presence/absence NO_x) and NO_3-initiated oxidation of BVOCs in the presence of acidified ammonium sulfate seed aerosol leads to organosulfates

- Organosulfates can be regarded as humic-like substances (i.e. multifunctional compounds containing hydroxyl, carboxyl, sulfate, and nitrooxy groups)

Estimation Method for Organosulfate Contribution

- No authentic and/or suitable surrogate standards are currently available for quantification of characterized organosulfates by UPLC/ESI-TOFMS or HPLC/ESI-linear ITMS

- Contribution of organosulfates to ambient organic aerosol can be derived from the analysis of aerosol samples for total sulfur (measured by x-ray emission techniques - e.g. PIXE or XRF) and water-soluble sulfate (measured by IC)

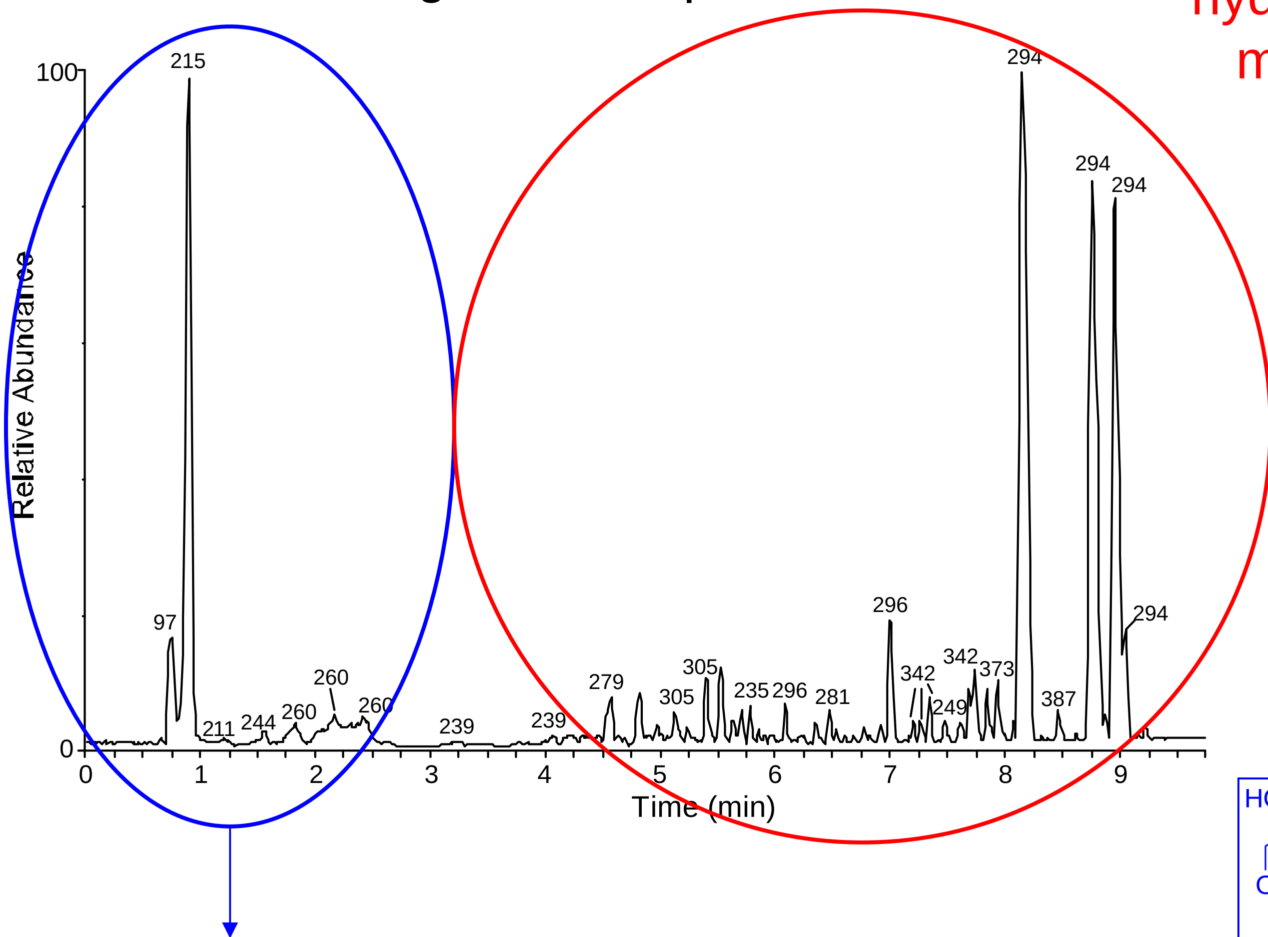
- Upper limit for sulfur that is associated with organosulfates provided by the subtraction of IC sulfate-sulfur from the PIXE sulfur

- IC sulfate-sulfur and PIXE sulfur data sets were available for 63 PM_{10} samples collected from K-puszta in Hungary (organosulfate composition very similar to that of S.E. USA) and were used for our estimate

- Mass percentages of sulfur in some common BSOA organosulfates characterized in this study (e.g. nitrooxy organosulfate of α-pinene with MW 295) were also used in our estimate in order to convert non-sulfate-sulfur into OM

UPLC/(–)ESI-TOFMS Data: S.E. USA Summer Aerosol

BPC for 24 hr integrated sample:



hydrophobic organosulfates: monoterpenes are likely precursors

m/z 235: $C_9H_{15}O_5S^-$

m/z 249: $C_{10}H_{17}O_5S^-$

m/z 279: $C_{10}H_{15}O_7S^-$

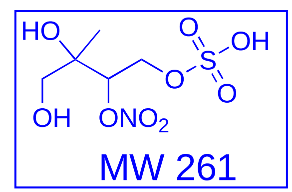
m/z 294: $C_{10}H_{16}NO_7S^-$

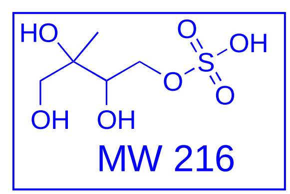
m/z 296: $C_9H_{14}NO_8S^-$

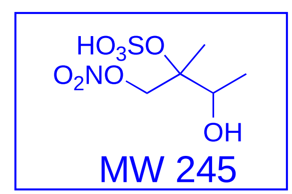
m/z 342: $C_{10}H_{16}NO_{10}S^-$

m/z 373: $C_{10}H_{17}N_2O_{11}S^-$

m/z 387: $C_{10}H_{15}N_2O_{12}S^-$







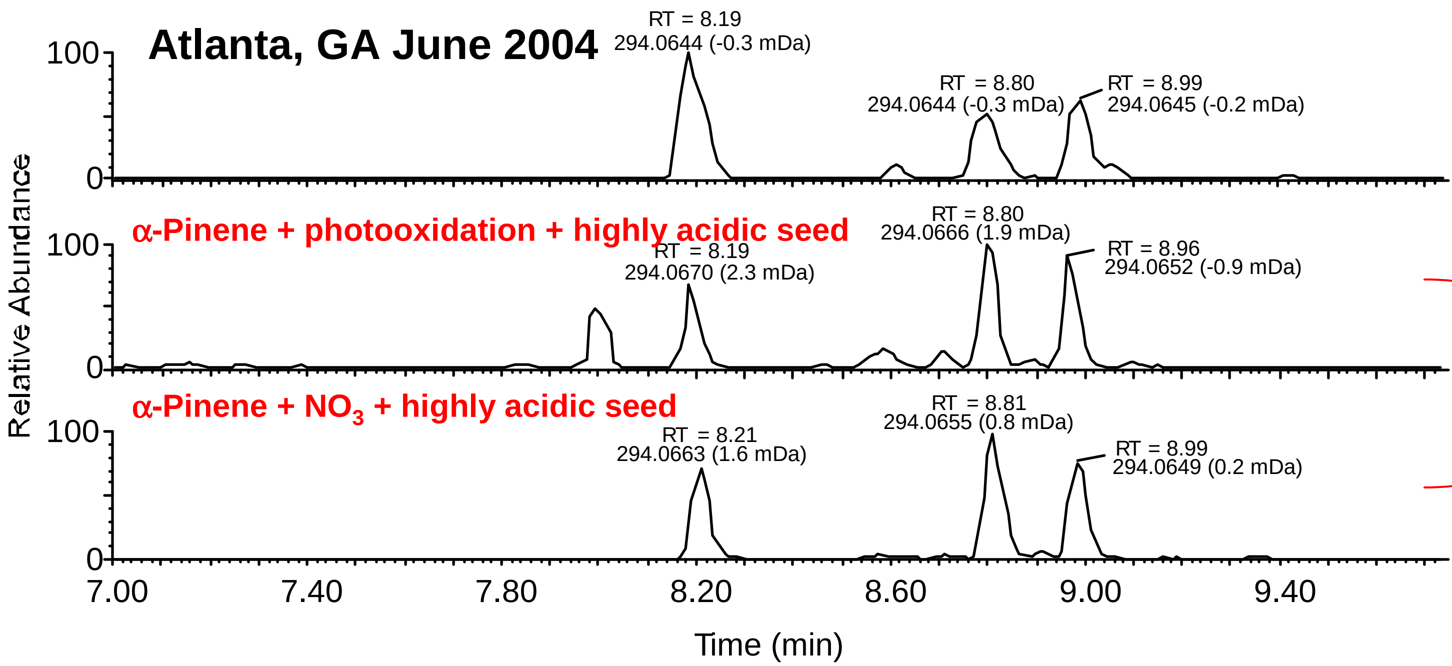
polar organosulfates: isoprene is main precursor

[*Surratt et al*., ES&T, 2007a,b; *Gomez-Gonzalez et al*., *J. Mass. Spectrom*., 2008]

Source of *m/z* 294 Nitroxy-Organosulfates ($C_{10}H_{16}NO_7S^-$)

- Previously observed in ambient aerosol [*Gao et al*., 2006; *Surratt et al*. 2007; *Iinuma et al*., 2007] - α-pinene appears to be only precursor

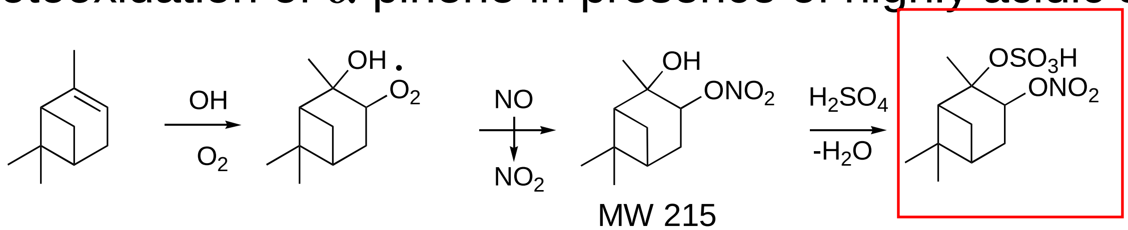
- UPLC/(–)ESI-TOFMS EICs of *m/z* 294:



α-pinene appears to be only source as MS^2/MS^3 spectra agreed well with ambient samples

Proposed Formation of α-Pinene *m/z* 294 Nitroxy-Organosulfates ($C_{10}H_{16}NO_7S^-$)

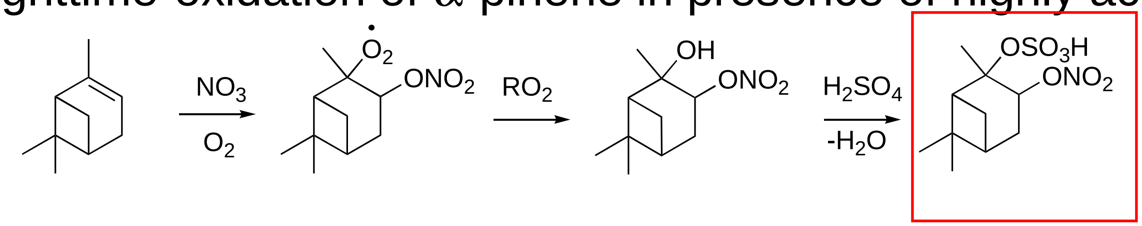
Photooxidation of α-pinene in presence of highly acidic seed



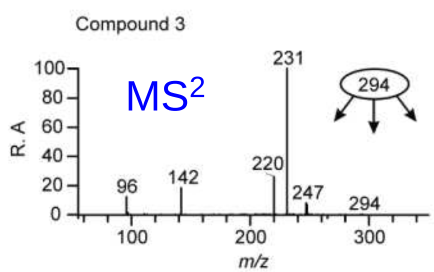
[*Aschmann et al*., JGR, 1998]

Proposed structure for 3rd isomer observed in UPLC chromatogram

Nighttime-oxidation of α-pinene in presence of highly acidic seed



Proposed structure for 3rd isomer observed in UPLC chromatogram



m/z 247: loss of HONO (47 Da)

m/z 231: loss of HNO_3 (63 Da)

m/z 142: $O_2NOSO_3^-$ (neighboring nitroxy and sulfate groups)

m/z 96: SO_4^-· (tertiary sulfate group)