Atmospheric Organic Aerosols

Atmospheric System Research (ASR)
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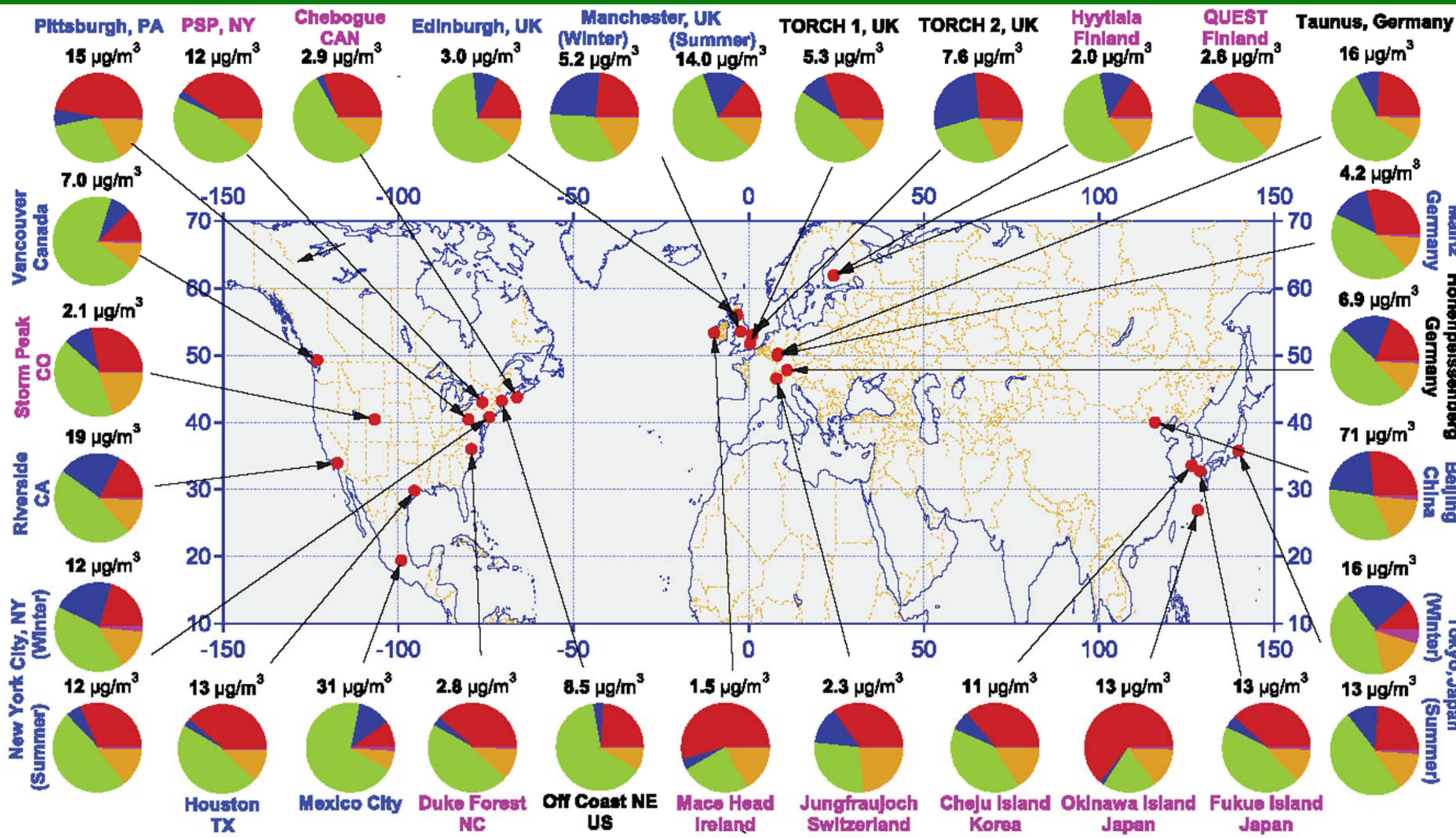
John H. Seinfeld
California Institute of Technology

ASR Science and Program Plan

Measurements downwind of urban sources of aerosol particles and precursor gases have shown that the mass concentration of *secondary organic aerosol* (SOA) can be several-fold greater than can be explained on the basis of current model calculations using observed precursor concentrations. ASR will continue conducting laboratory experiments on both gas-phase and aqueous-phase SOA formation to characterize the particle formation and the organic gases that react to form new organic aerosol material on aerosol seeds. ASR will use these experiments to guide the development of comprehensive chemical mechanisms… to guide the development of parameterizations that are simple enough to be applied to aerosol life cycle models.

Global Aerosol Chemical Composition



- Organic Mass
- Sulfate Mass
- Ammonium Mass
- Nitrate Mass
- Chloride Mass

Zhang et al., GRL [2007]

Organics Contribute Significantly to Mass of Fine Aerosol

Organic Sources = Primary + <u>SECONDARY</u>

~ 70–90%

Global Organic Aerosol Mass

Total Flux of Non-Methane Hydrocarbons to the atmosphere ~ 1350 Tg/y

Percent that condenses into particles directly ~ 1%

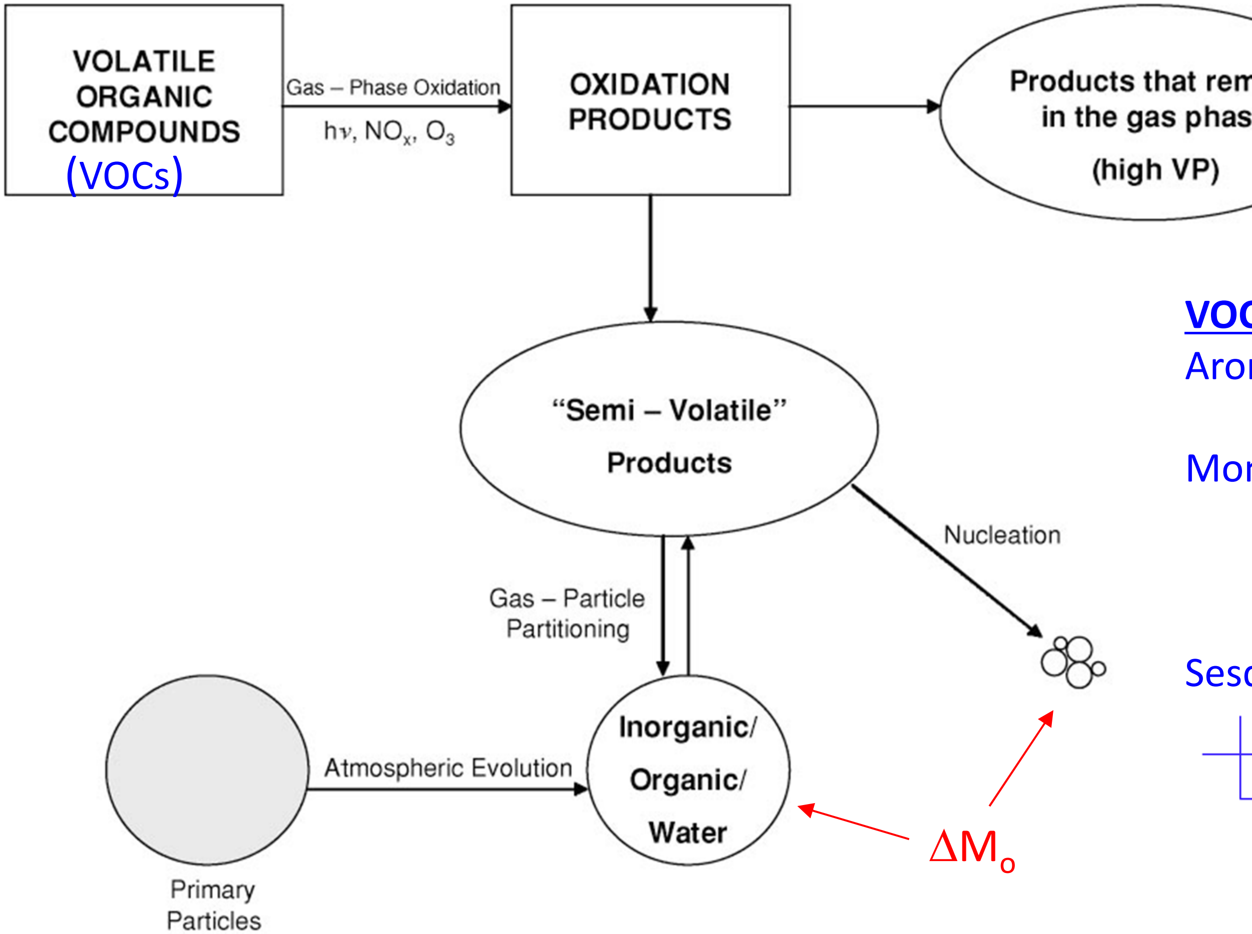
Percent of the global NMHC flux to organic aerosol ~ 10%

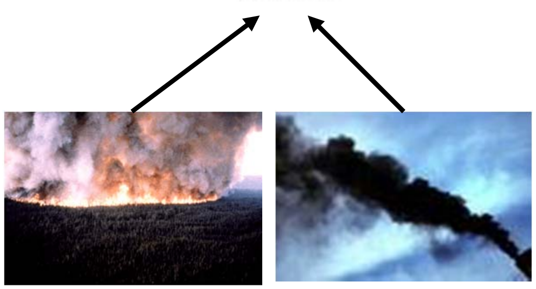
Conclusion: ~ 90% of organic aerosol comes from oxidation of NMHC
(Secondary Organic Aerosol)

Of total global aerosol mass ~ 50% is organic

Goldstein and Galbally, ES&T (2007); Donahue et al., AE (2009)

Secondary Organic Aerosol (SOA) Formation

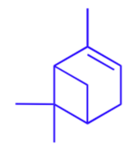




VOC Examples:

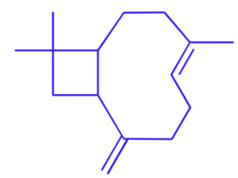
Aromatics (e.g., Toluene)

Monterpenes ($C_{10}H_{16}$)



α-pinene

Sesquiterpenes ($C_{15}H_{24}$)



β-caryophyllene

This Process is Studied in Laboratory Chambers

$$\text{SOA Yield} = \Delta M_o / \Delta VOC$$

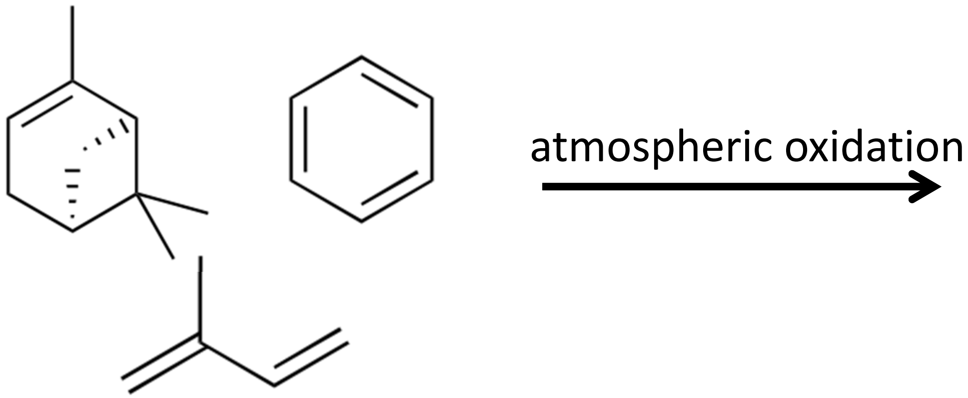
ΔM_o = organic mass produced (μg/m^3)

ΔVOC = mass of reacted VOC (μg/m^3)

Primary vs. Secondary Organic Aerosol

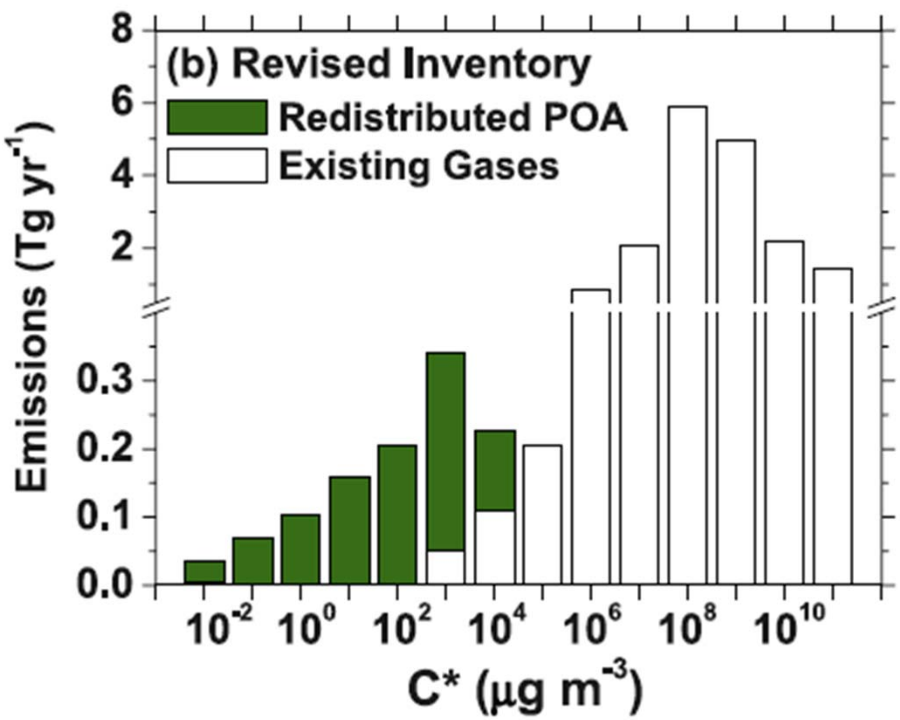
- Primary (POA):
  - Directly emitted
  - Traditionally
    considered non-volatile and
  - Non-reactive

- Secondary (SOA)

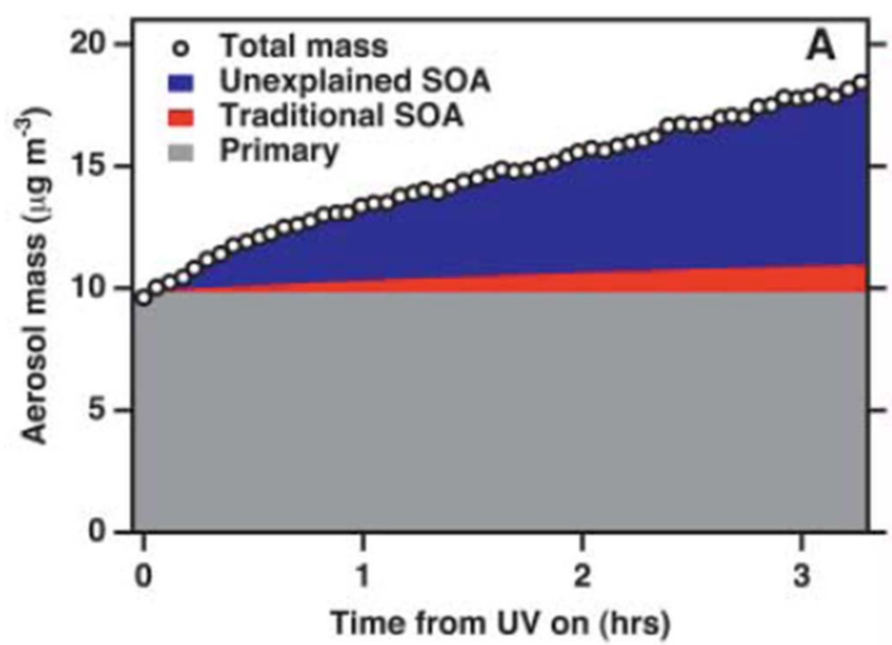


condensable products

Semivolatile Emissions



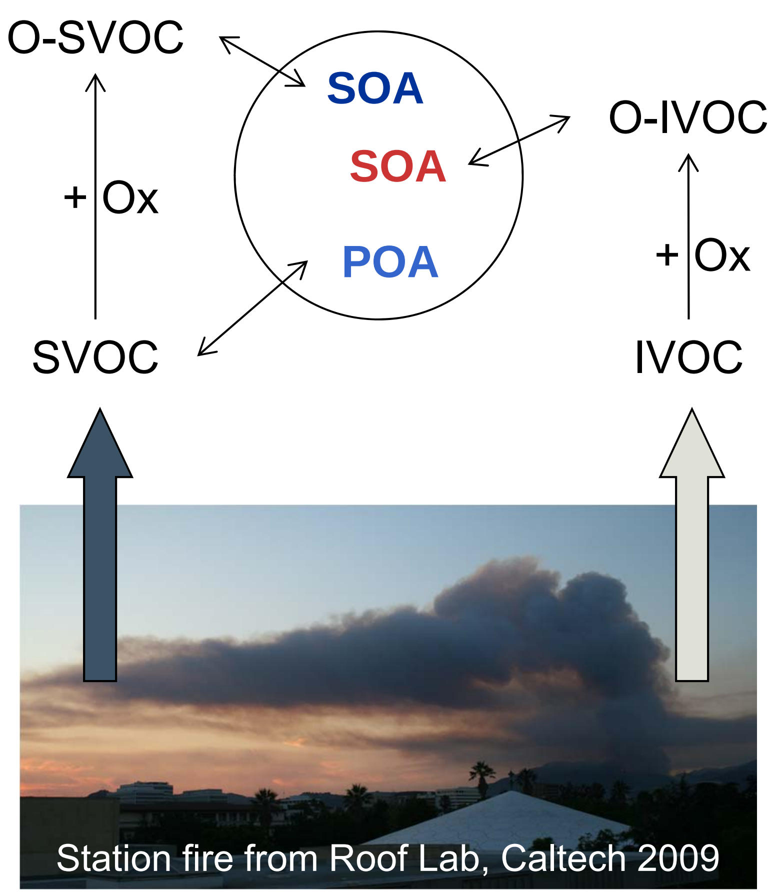
Shrivastava et al., *JGR* [2008]

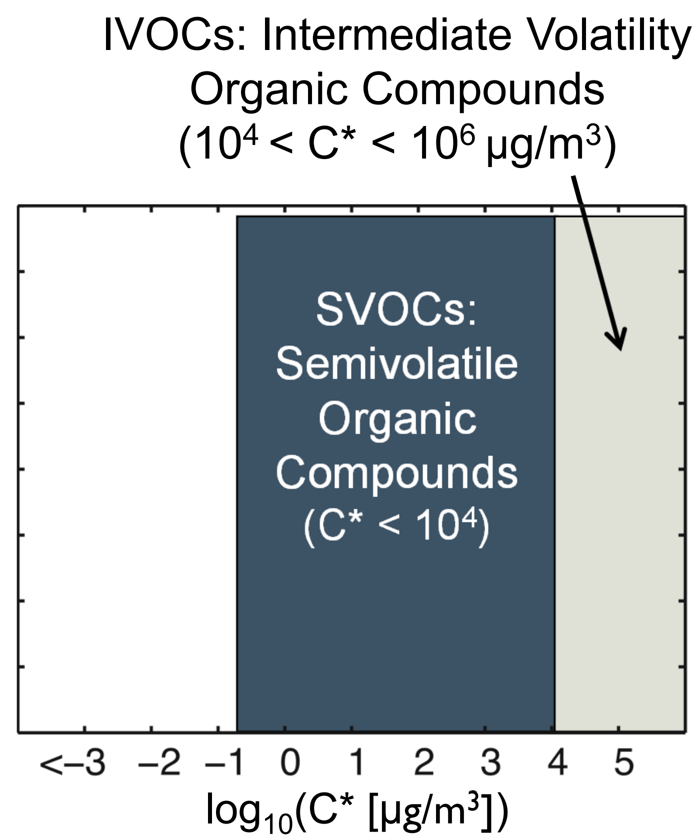


Robinson et al., *Science* [2007]

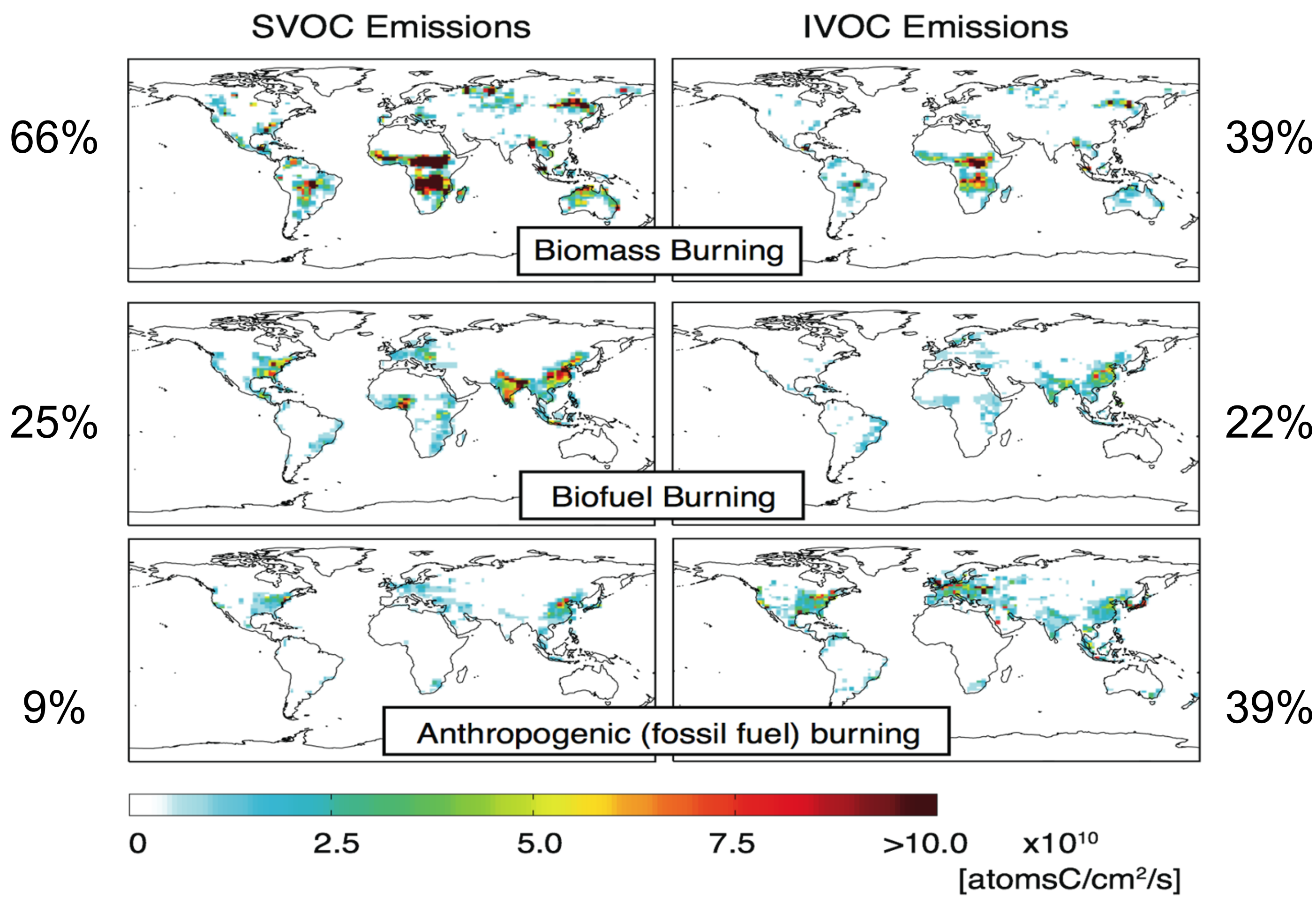
Low-Volatility Organics

There is a large potential for low-volatility organics ($C^* < 10^6$ µg/m^3) to form organic aerosol





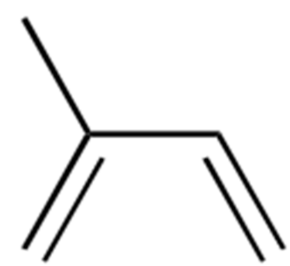
SVOC and IVOC Emissions



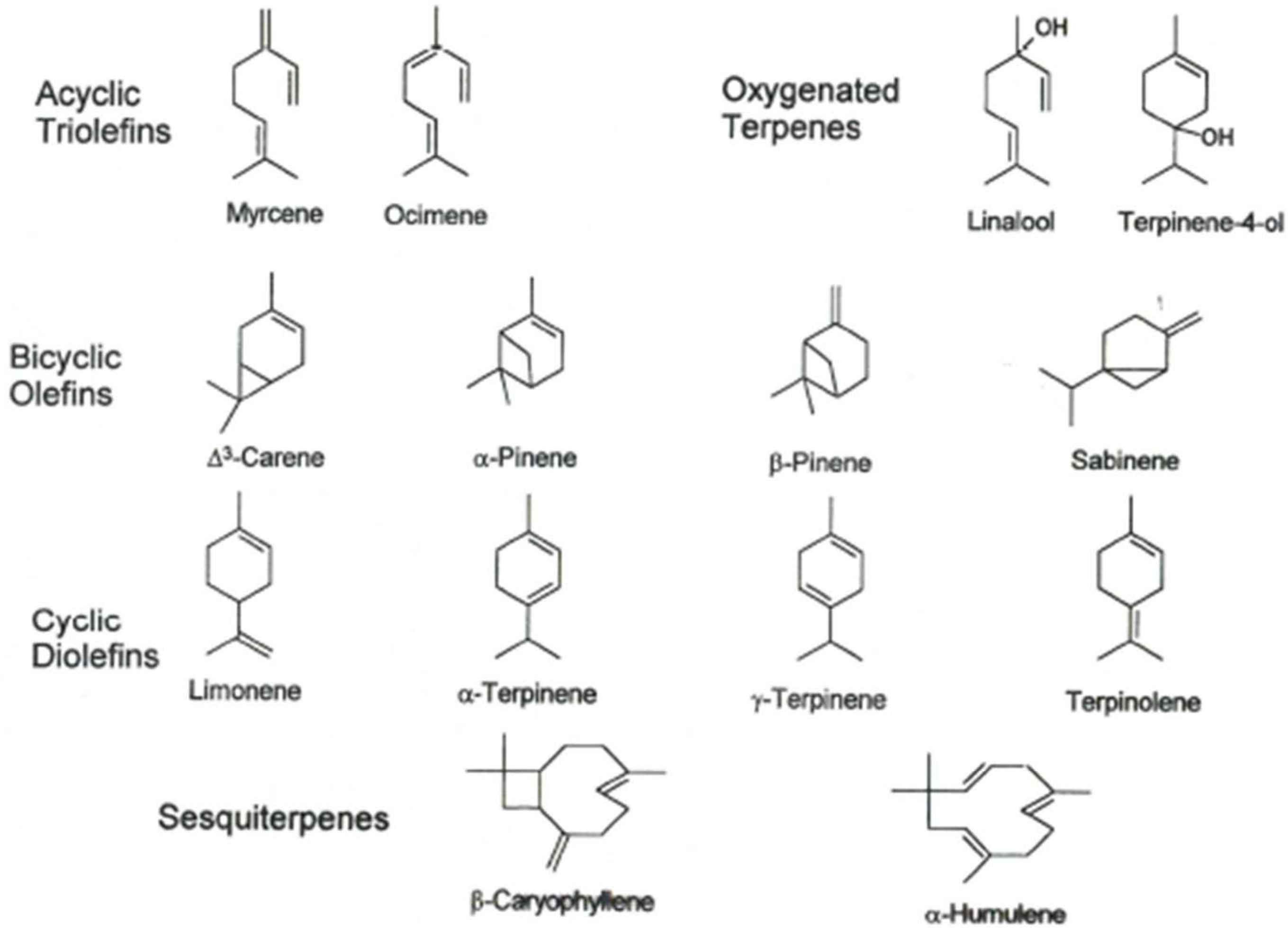
Isoprene (C_5H_8)

- Highest emissions among all non-methane hydrocarbons (~600 Tg/year) [Guenther et al., 2006]

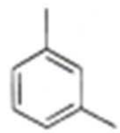
- Photooxidation of isoprene leads to SOA formation, with complex behavior depending on the NO_x level and NO_2/NO ratio

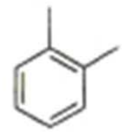


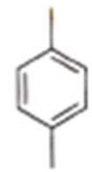
Biogenic Hydrocarbons

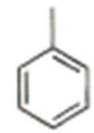


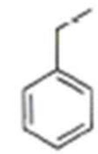
Aromatic Hydrocarbons

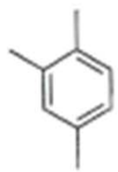

m-xylene

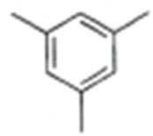

o-xylene

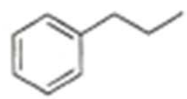

p-xylene

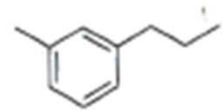

toluene

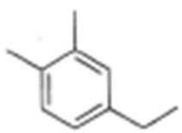

ethylbenzene

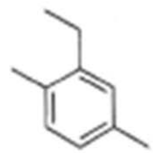

1,2,4-trimethylbenzene

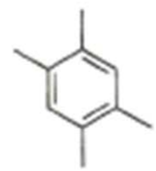

1,3,5-trimethylbenzene

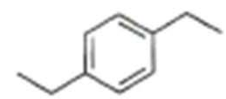

n-propylbenzene

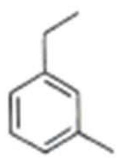

1-methyl-3-n-propylbenzene

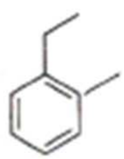

1,2-dimethyl-4-ethylbenzene


1,4-dimethyl-2-ethylbenzene

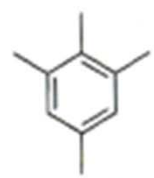

1,2,4,5-tetramethylbenzene

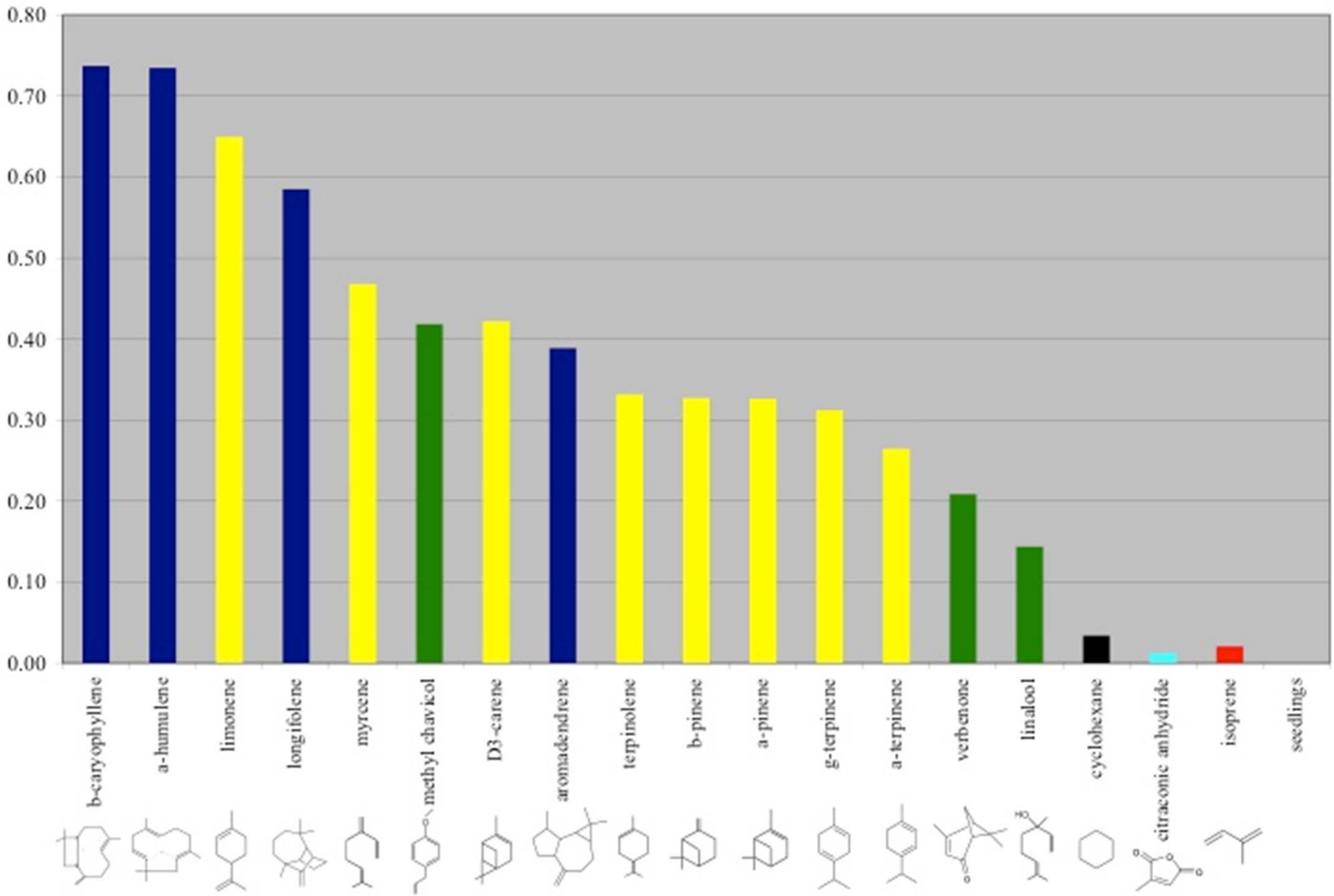

p-diethylbenzene


m-ethyltoluene

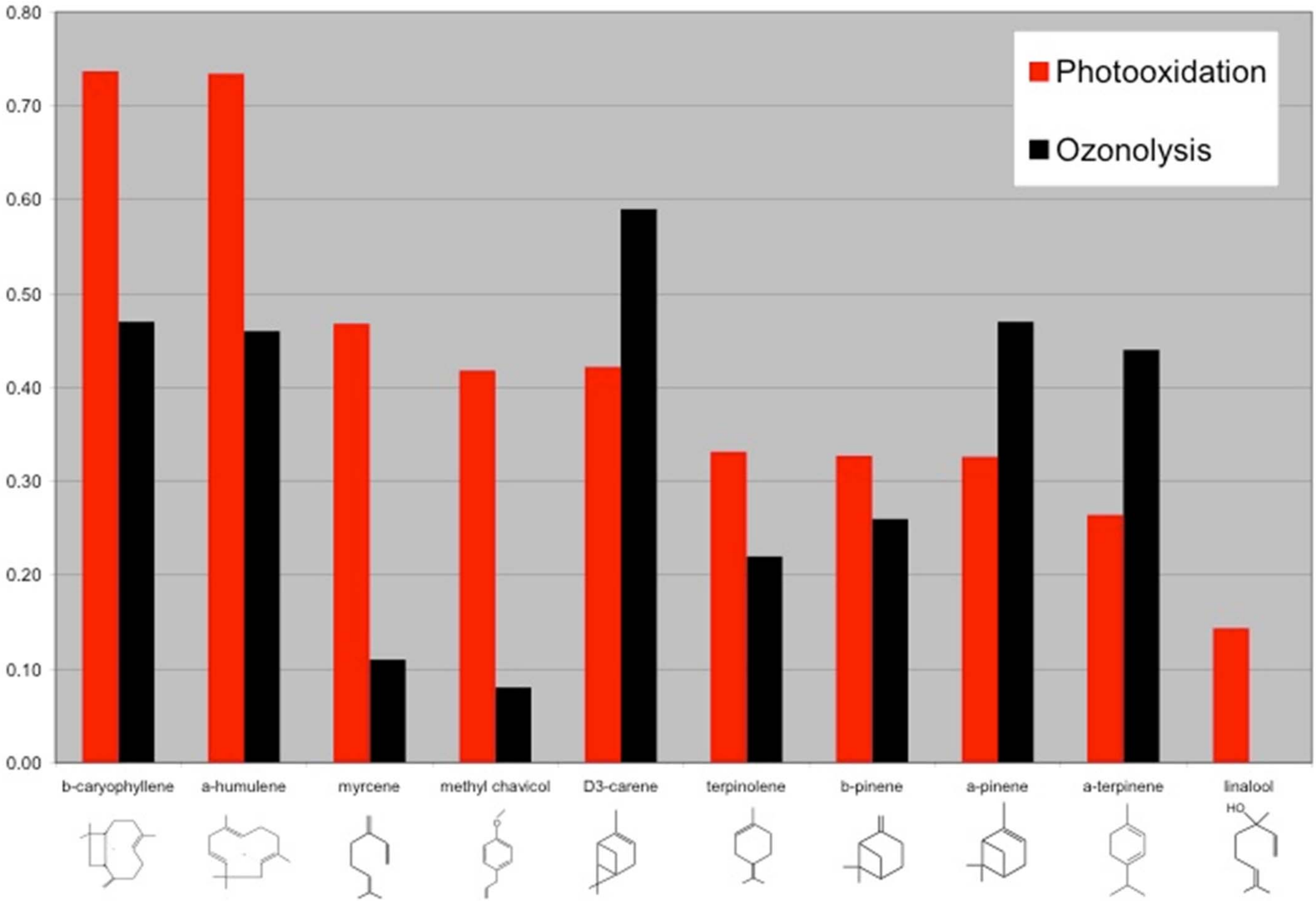

o-ethyltoluene


p-ethyltoluene


1,2,3,5-tetramethylbenzene

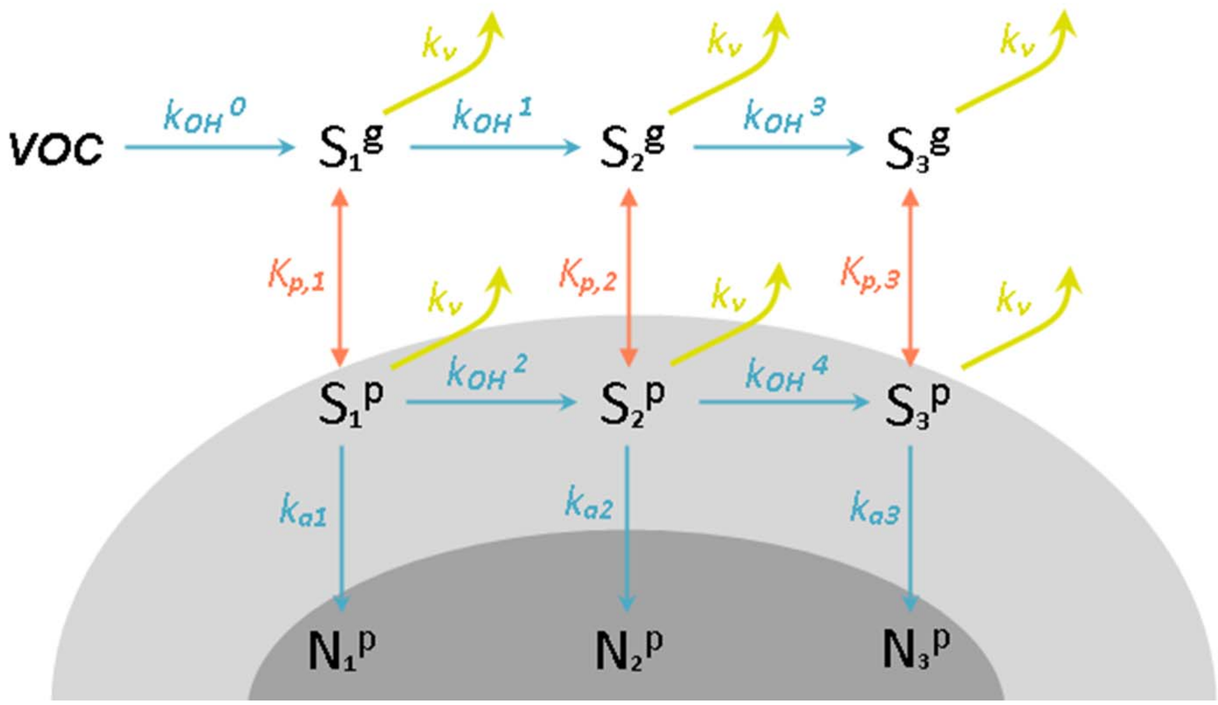


0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
b-caryophyllene
a-humulene
limonene
longifolene
myrcene
methyl chavicol
D3-carene
aromadendrene
terpinolene
b-pinene
a-pinene
g-terpinene
a-terpinene
verbenone
linalool
cyclohexane
citraconic anhydride
isoprene
seedlings



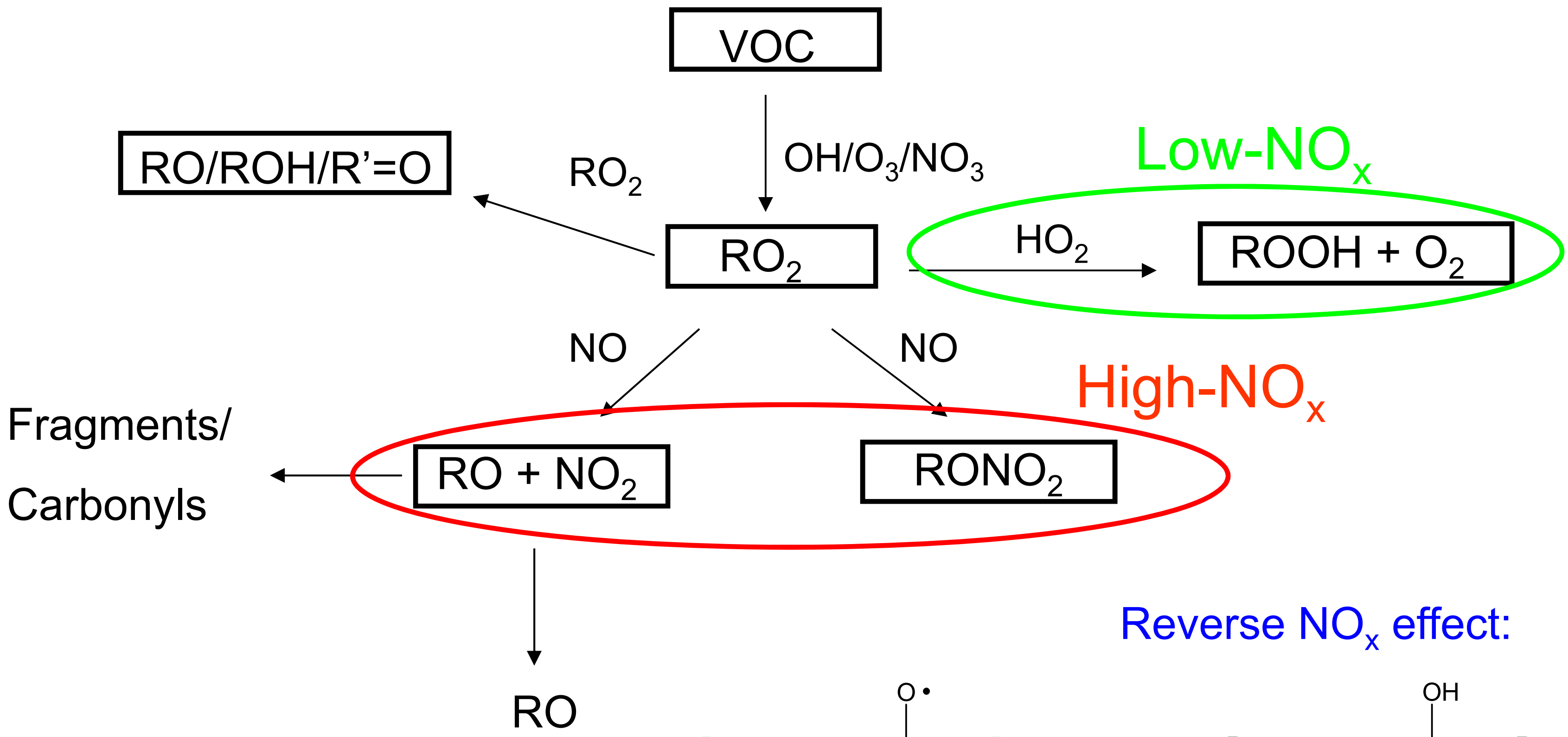
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Photooxidation
Ozonolysis
b-caryophyllene
a-humulene
myrcene
methyl chavicol
D3-carene
terpinolene
b-pinene
a-pinene
a-terpinene
linalool
HO

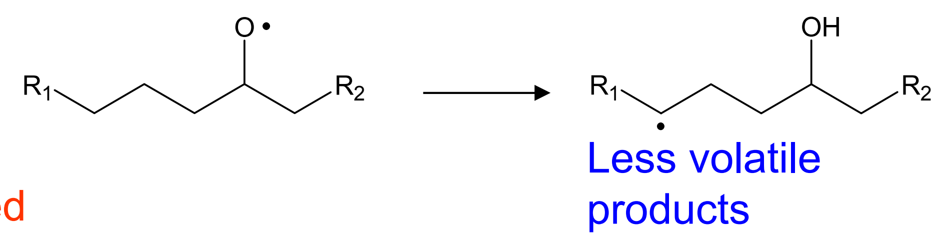
General Mechanism of SOA Formation and Evolution



S_i^g : i^{th}-generation semi-volatile products in the gas phase
S_i^p : i^{th}-generation semi-volatile products in the particle phase
N_i^p : i^{th}-generation non-volatile products in the particle phase (e.g. semi-solid)

Peroxy radical chemistry

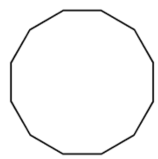




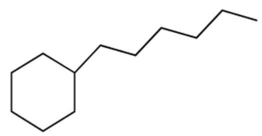
- Small alkoxy radical easily fragmented
- Organic nitrates relatively volatile
- Peroxides: important SOA components

Photooxidation of C_{12} Alkanes

- Compounds studied:



cyclododecane
$C_{12}H_{24}$



hexylclohexane
$C_{12}H_{24}$

dodecane
$C_{12}H_{26}$

2-methylundecane
$C_{12}H_{26}$

- Experimental conditions:

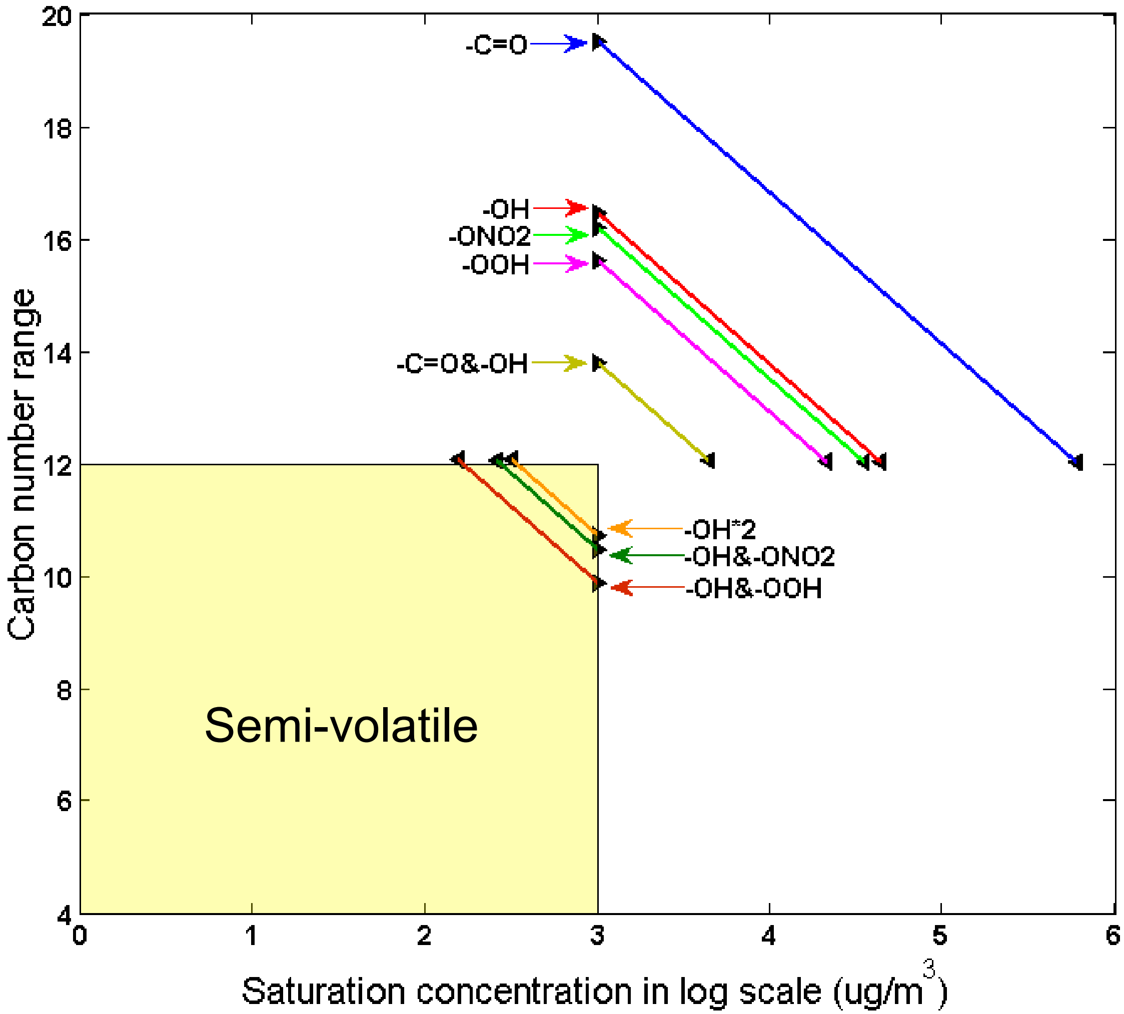
  Ammonium sulfate seed; T~25^{o}C, RH<5%

  Low-NO_x experiments: $H_2O_2 + h\nu \rightarrow 2OH$

  High-NO_x experiments: $HONO + h\nu \rightarrow OH + NO$

SOA Formation from C_{12} Alkanes as an Illustration of the Nature of Multi-generation Oxidation

1st-generation products [Functional groups from Master Chemical Mechanism (MCM) University of Leeds]



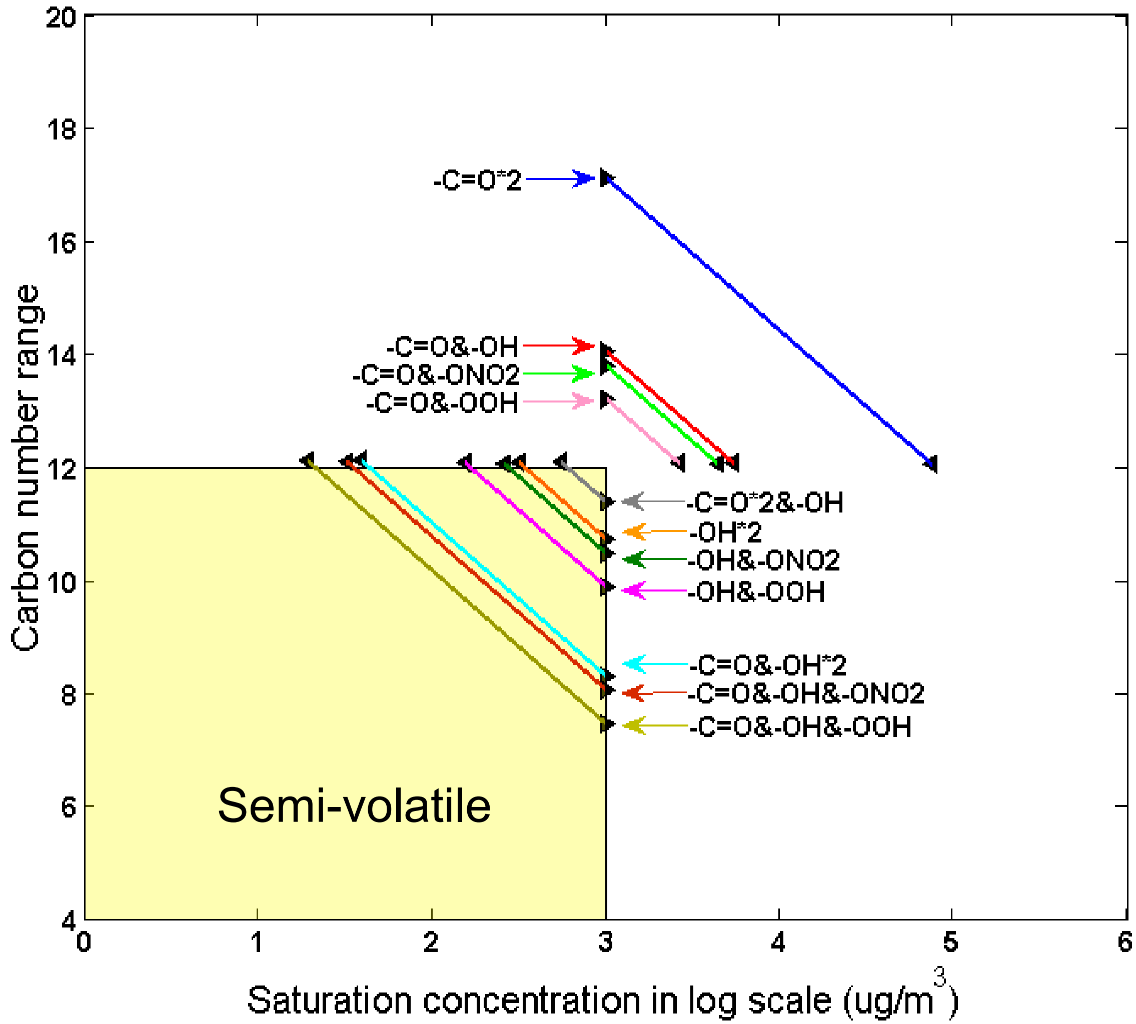
The upper limit of n_c should be the same as parent VOC.

The lower limit of n_c lies in the domain of semi-volatile compounds.

The possible carbon number after multi-generation oxidation lies in the range between upper and lower limits.

3 products in 1st generation ($10 \leq n_c \leq 12$)

C_{12} Alkanes – 2^{nd} Generation



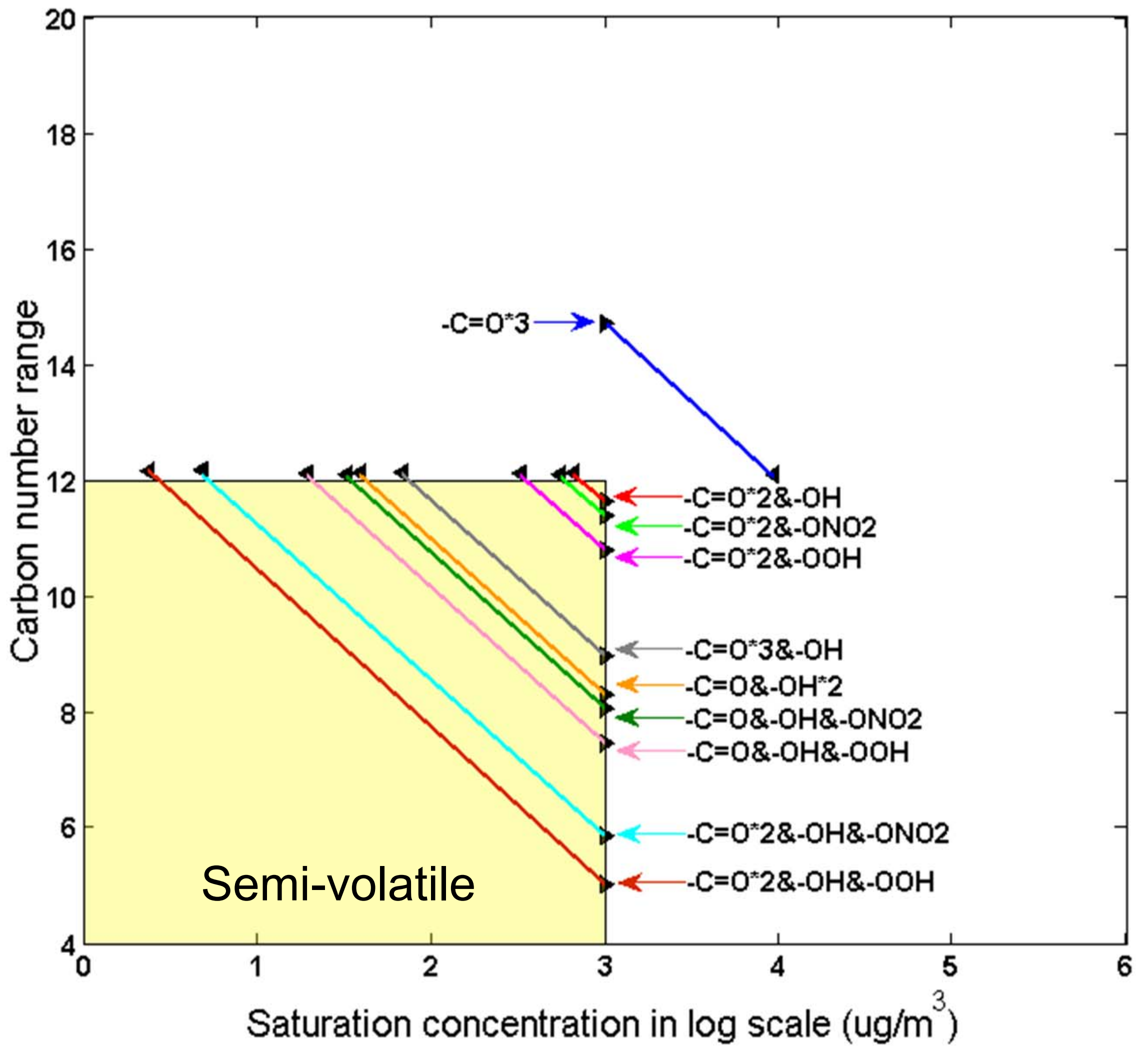
The upper limit of n_C should be the same as parent VOC.

The lower limit of n_C lies in the domain of semi-volatile compounds.

The possible carbon number after multi-generation oxidation lies in the range between upper and lower limits.

7 products in 2nd generation
($8 \leq n_C \leq 12$)

C_{12} Alkanes – 3rd Generation



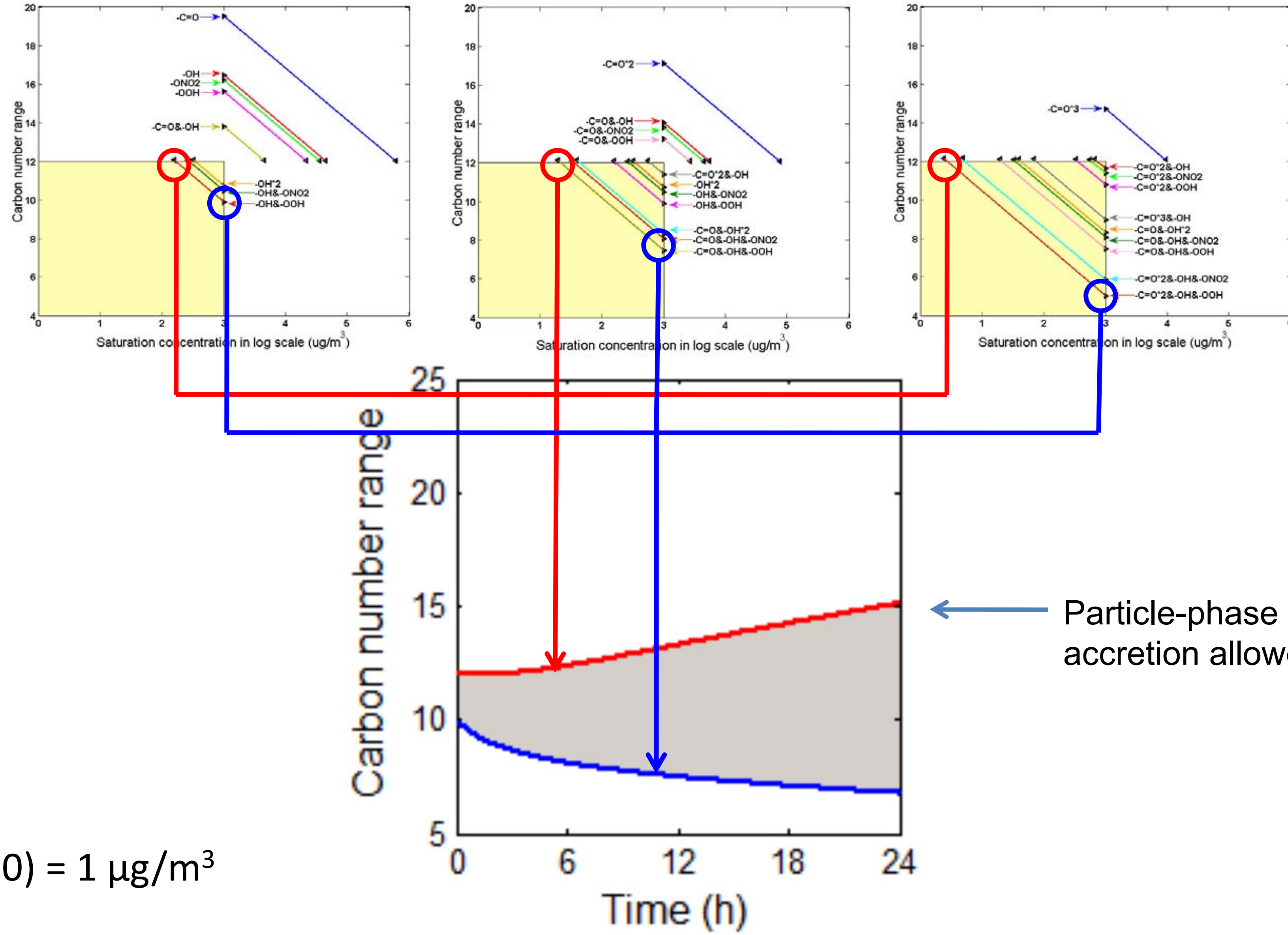
The upper limit of n_C should be the same as parent VOC.

The lower limit of n_C lies in the domain of semi-volatile compounds.

The possible carbon number after multi-generation oxidation lies in the range between upper and lower limits.

9 products in 3rd generation
($6 \leq n_C \leq 12$)

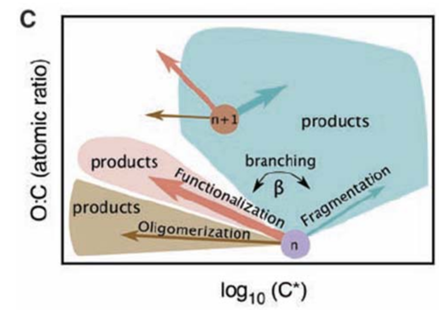
Carbon Number Range



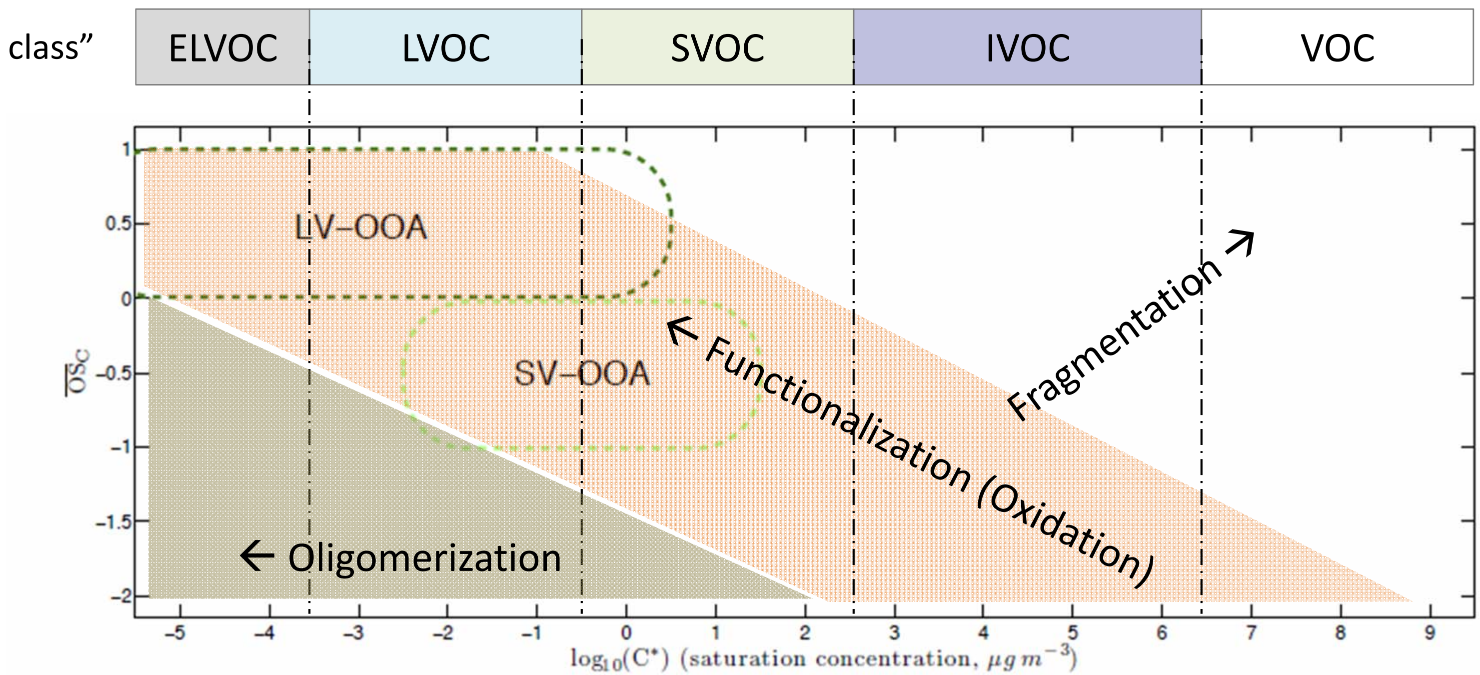
Particle-phase accretion allowed

$M_0(0) = 1\ \mu g/m^3$

2-D mapping of SOA: Oxidation state vs. volatility



"volatility class"



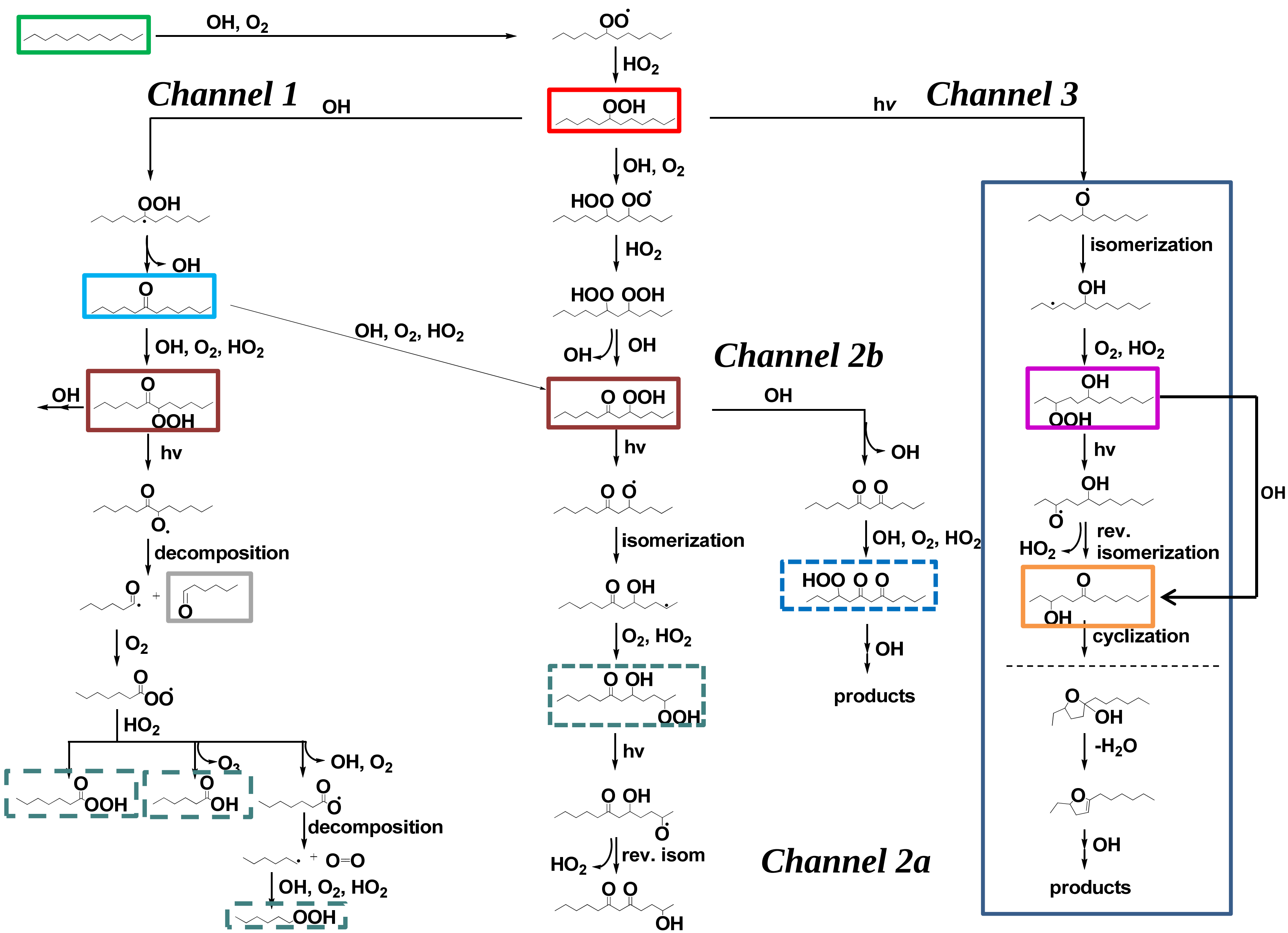
Donahue et al., ACP, 2011

Caltech Laboratory Chambers

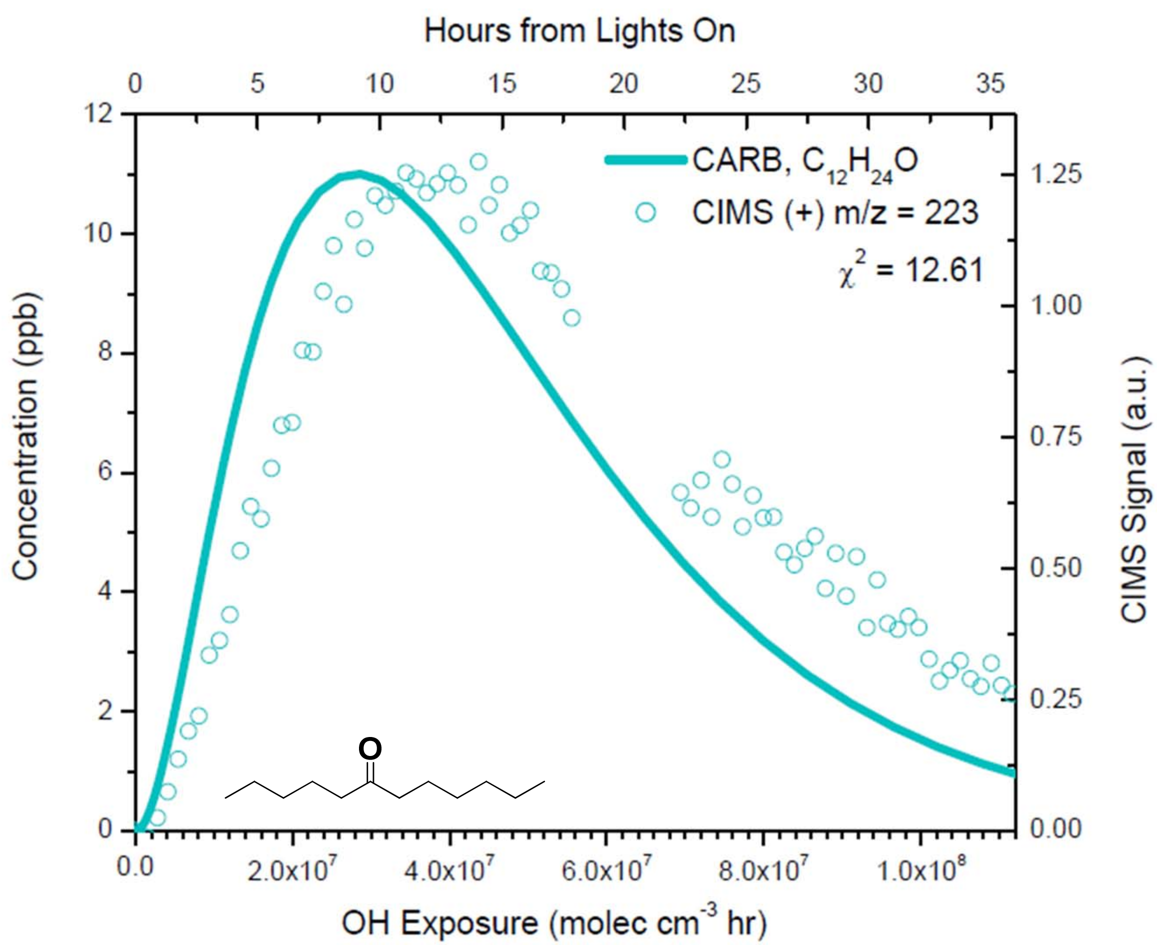
- 2 Teflon chambers, 28 m^3 each
- Scanning differential mobility analyzer (DMA): particle size distribution, volume
- GC-FID: hydrocarbon and NO_x, O_3, RH, T
- CIMS and GC-TOFMS: gas-phase organics
- Aerodyne Aerosol Mass Spectrometer (AMS): on-line particle mass, composition
- Particle into Liquid Sampler coupled to IC (PILS/IC): organic and inorganic ions
- Teflon filters: off-line chemical analysis

- UPLC/ESI-high resolution-TOFMS:
  - ❖ mass resolution ~ 12 000
  - ❖ accurate mass measurements (elemental compositions)
- HPLC/ESI-Linear Ion Trap MS:
  - ❖ tandem MS measurements
  - ❖ structural elucidation & confirmation
- GC/Ion Trap MS with prior derivatization

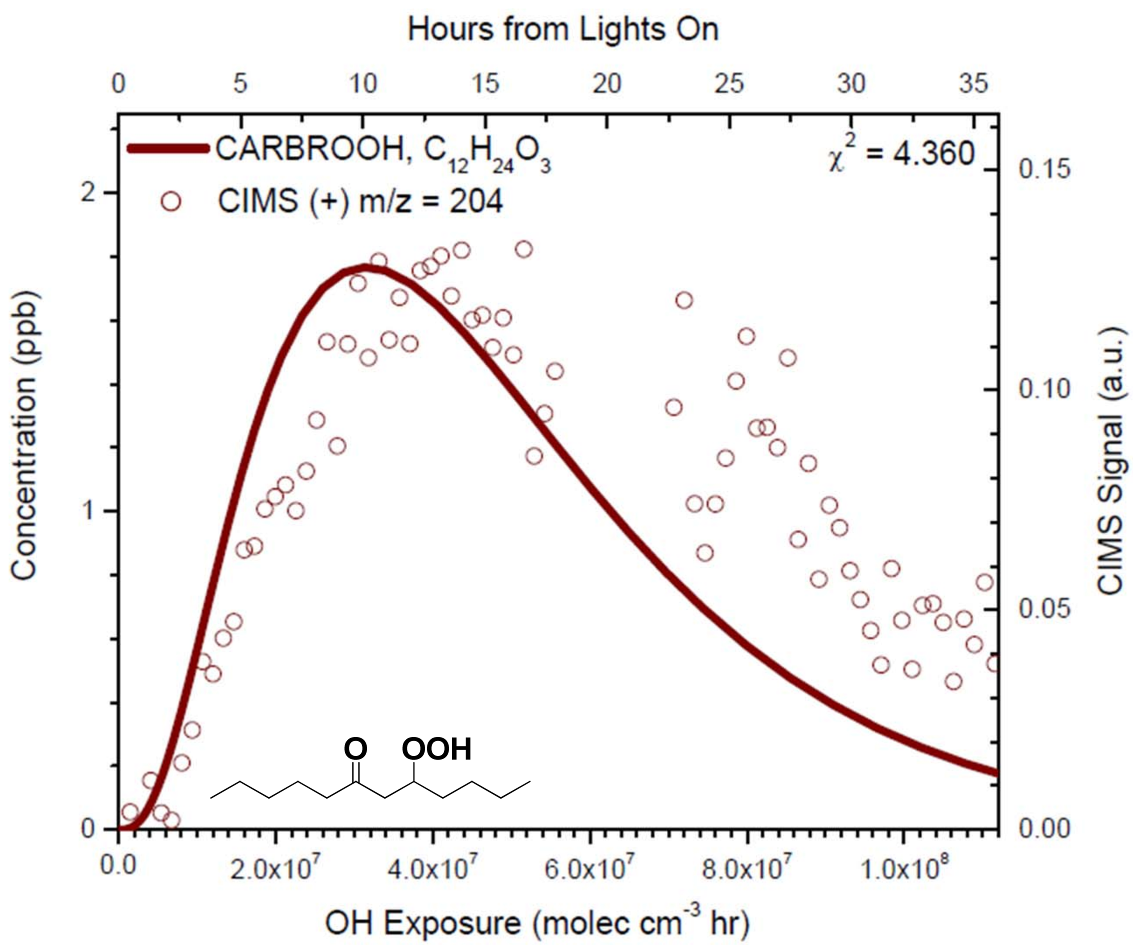
Dodecane Low-NO_x Oxidation



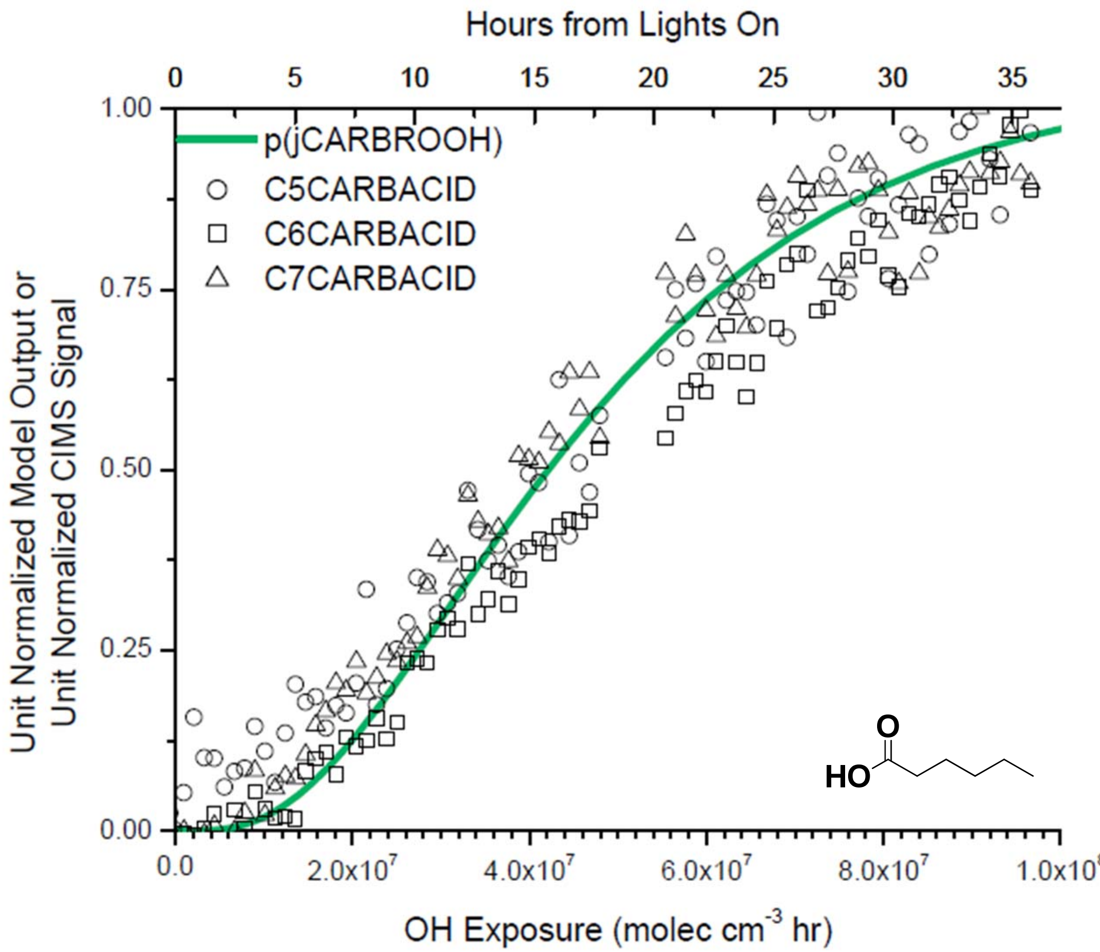
Mechanism and CIMS measurement: Carbonyl formation



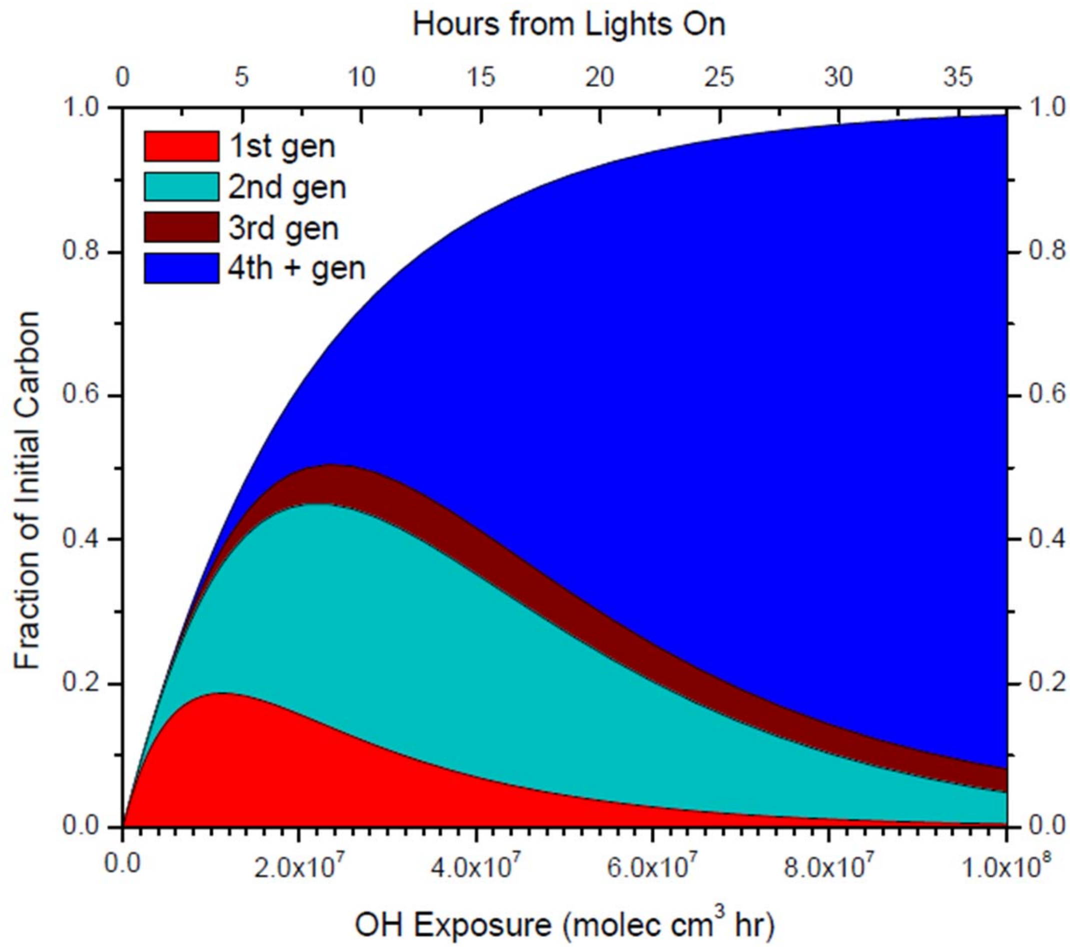
Mechanism and CIMS measurement: Carbonyl hydroperoxide



Mechanism and CIMS measurement: Acid formation

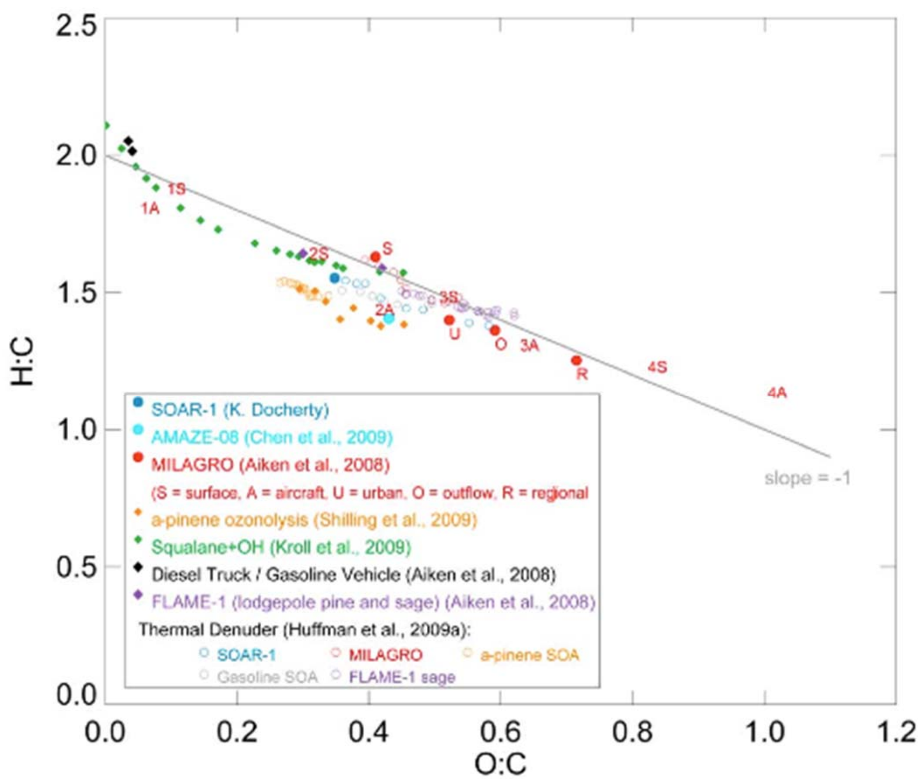


Carbon Balance



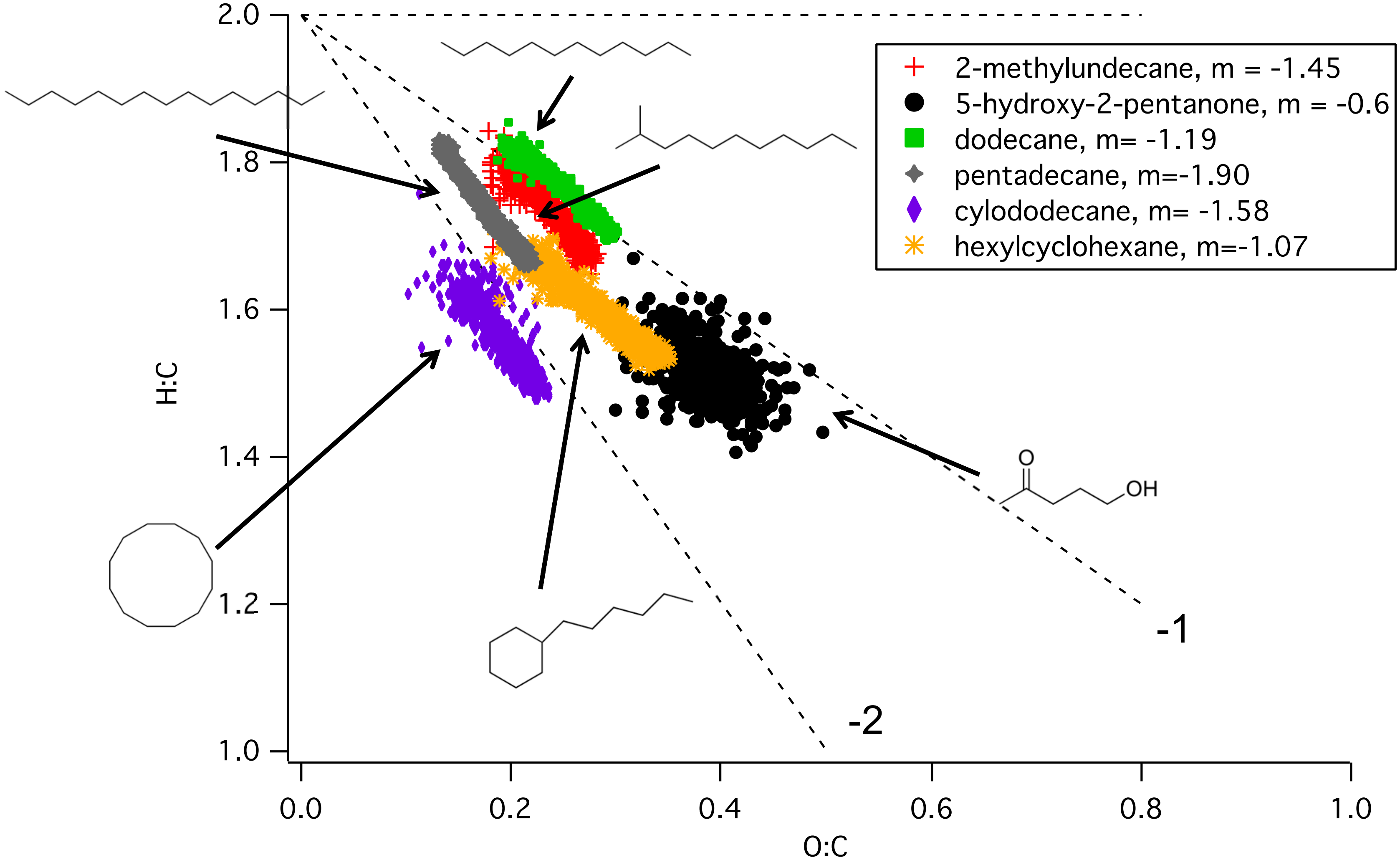
Majority of initial carbon ends up as ≥ 4th generation compounds.

Van Krevelen Diagram - H:C vs. O:C for Organic Aerosol



- **Heald et al., GRL, 2010** showed a slope of -1 for ambient and laboratory data
- **Ng et al., ACP 2011** showed a slope of -0.5 for ambient aerosol
- **Chhabra et al., ACP 2011** showed how atmospherically relevant SOA chamber studies, when averaged, show similar slope on VK diagram as ambient aerosol
- **Lambe et al., ACP 2011** present how PAM flow tube data has slope that is consistent with chamber and ambient data, and then extends the range for very high H:C/lowO:C to lower H:C/highO:C.

Low-NO_x Alkane SOA

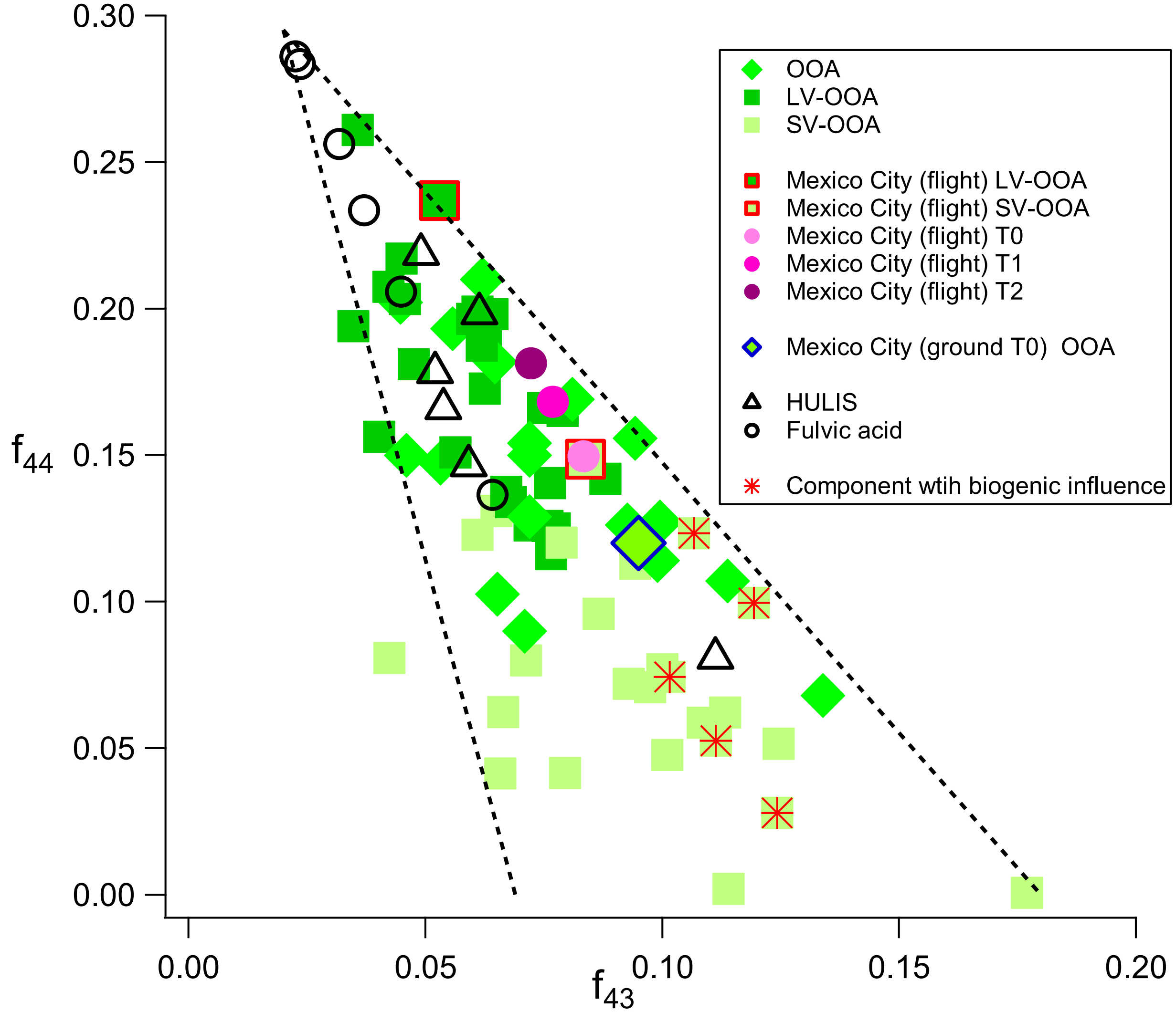


- Cumulative OH exposure for Low NO_X: 70-100 $\times 10^6$ molec. cm^{-3} min

Triangle plot

Photochemical age

O/C ratio

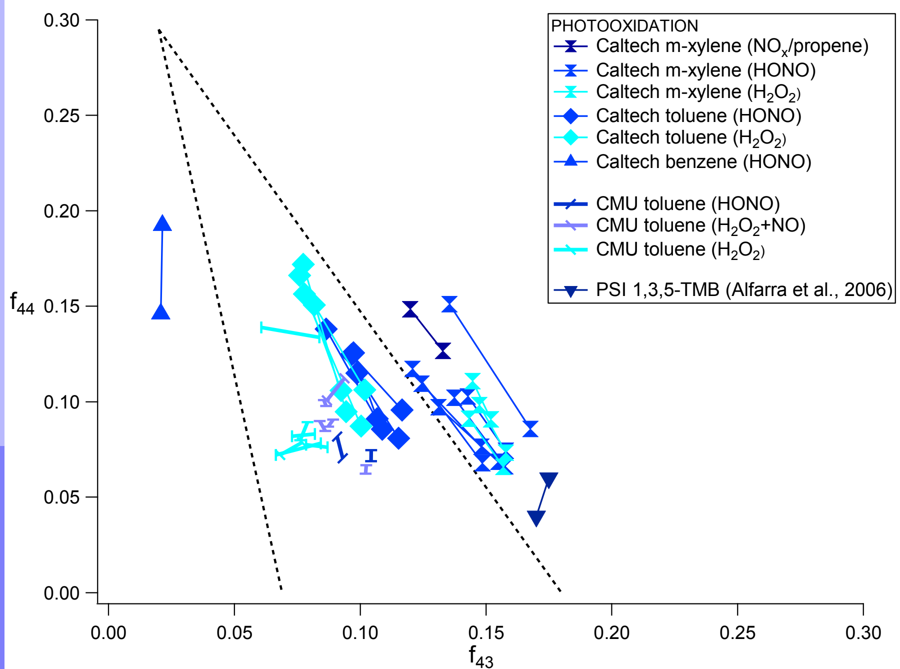


- SV-OOA has larger variability in f_{43}; Increasing photochemical age collapses variability, OOA components become increasing similar to each other
- f_{44} of the LV-OOA components similar to those from HULIS collected in filter samples
- Increasing photochemical age: increasing O/C, 44/43 ratio

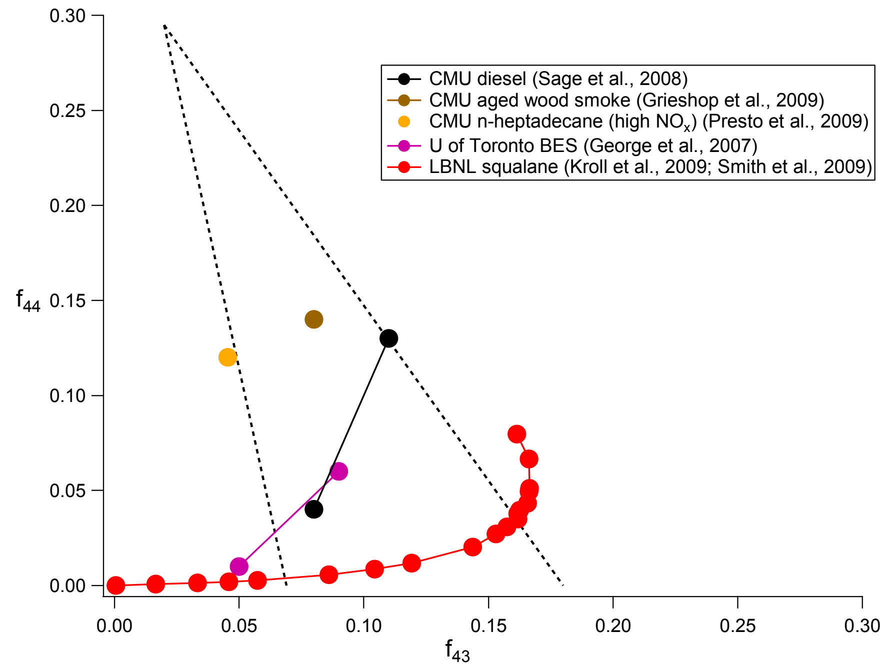
Ng et al., ACP (2010)

Degree of oxidation obtained in chamber studies

Aromatic hydrocarbons

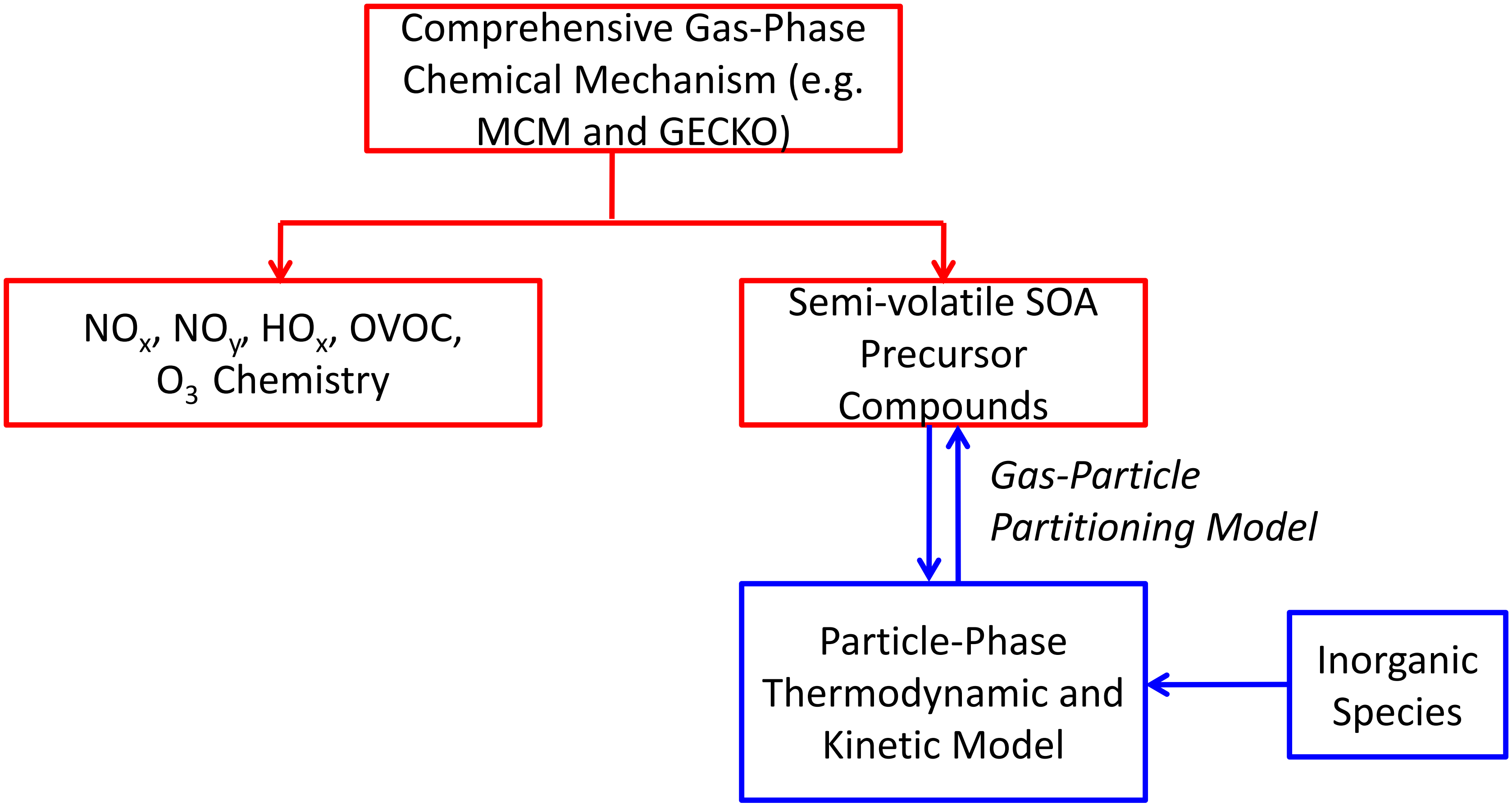


Photooxidation/heterogeneous oxidation of POA



Ng et al., ACP (2010)

SOA: Explicit Chemical Modeling



This degree of chemical specificity is not possible in atmospheric models (even if all the reactions were known)

Cappa and Wilson Statistical Oxidation Model

- Oxidation kinetics in a multi-dimensional space defined by n_C and n_O
- Tunable parameters:

  (1) Avg # of O atoms added/reaction

  (2) Decrease in volatility/O added

  (3) Probability that a given product fragments

P_{frag} (per reaction) = $c_{frag} N_O$

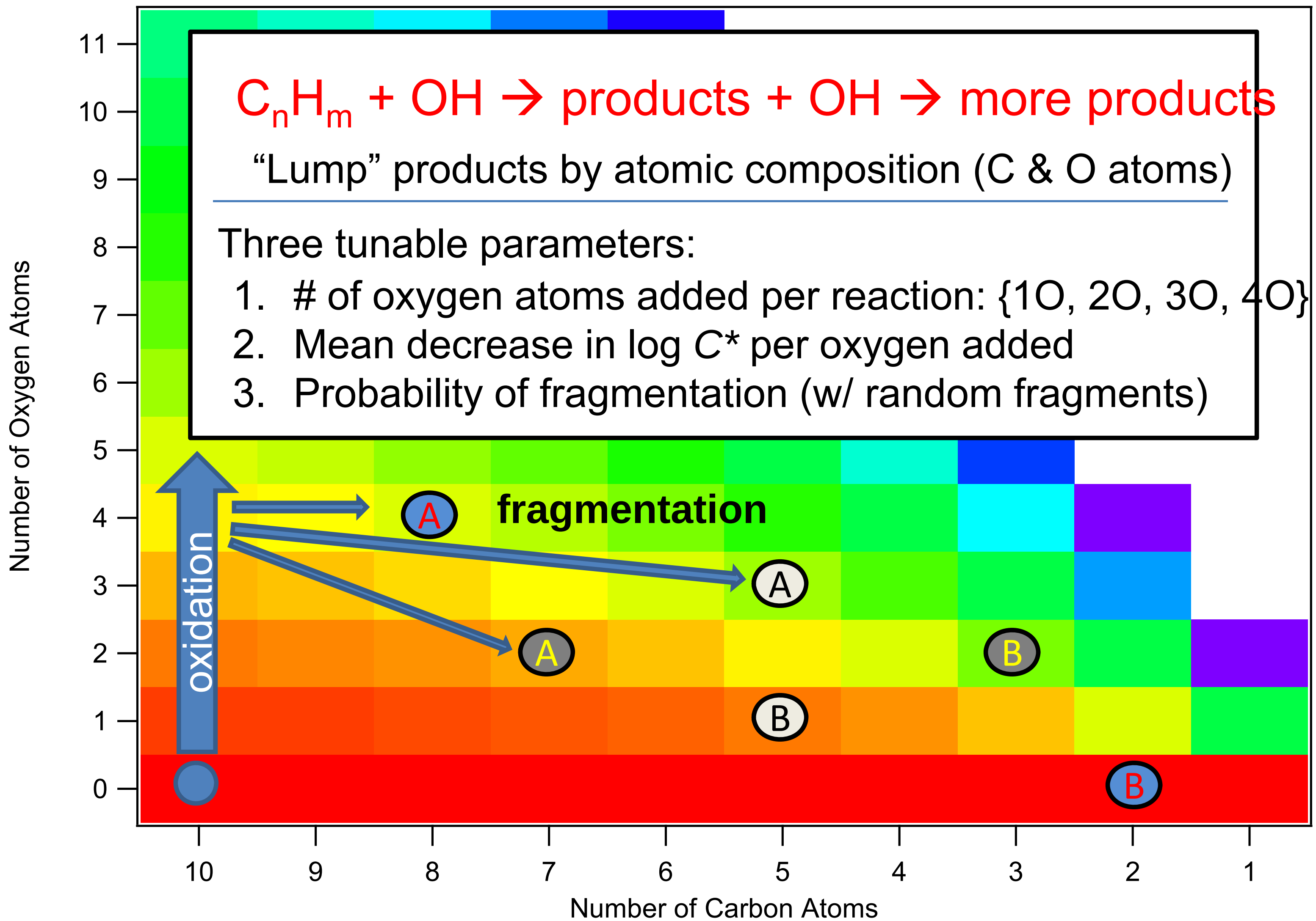
or

P_{frag} (per reaction) = $(N_O/N_C)^m$

Random probability for location of C-C bond scission or only C1 species

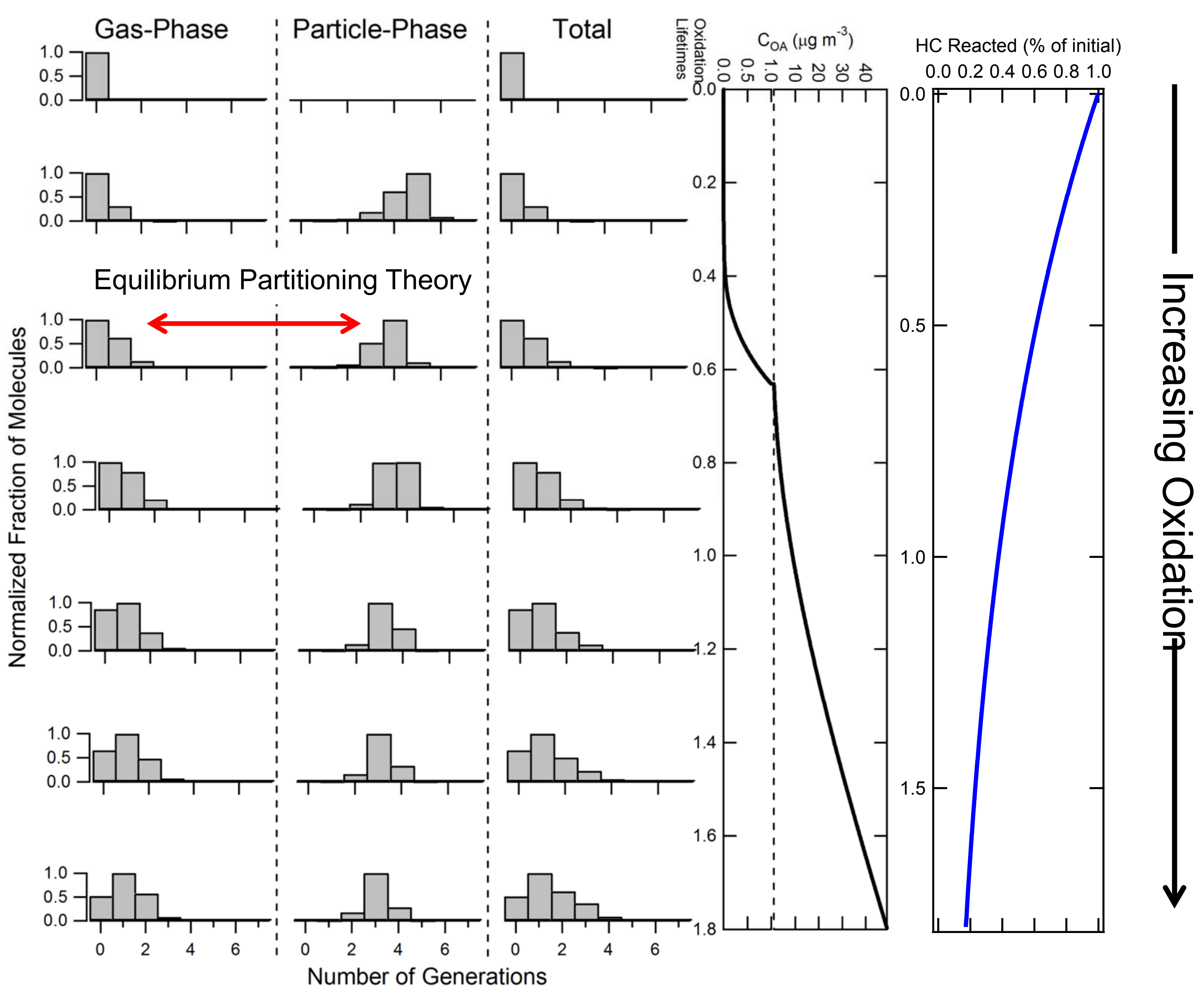
Cappa and Wilson, ACPD (2012)

Statistical Oxidation Model



Cappa and Wilson, ACPD (2012)

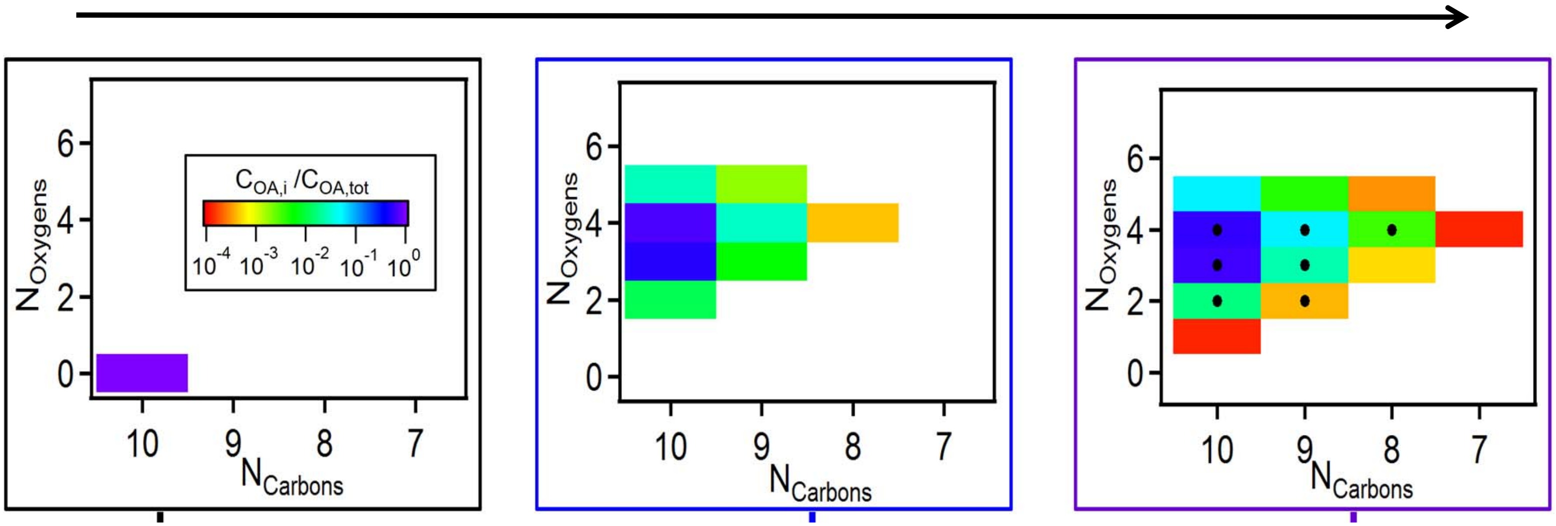
Statistical Oxidation Model: No Fragmentation (1-D)



Cappa and Wilson, *Submitted to ACP*

Statistical Oxidation Model: With Fragmentation

Increasing Oxidation

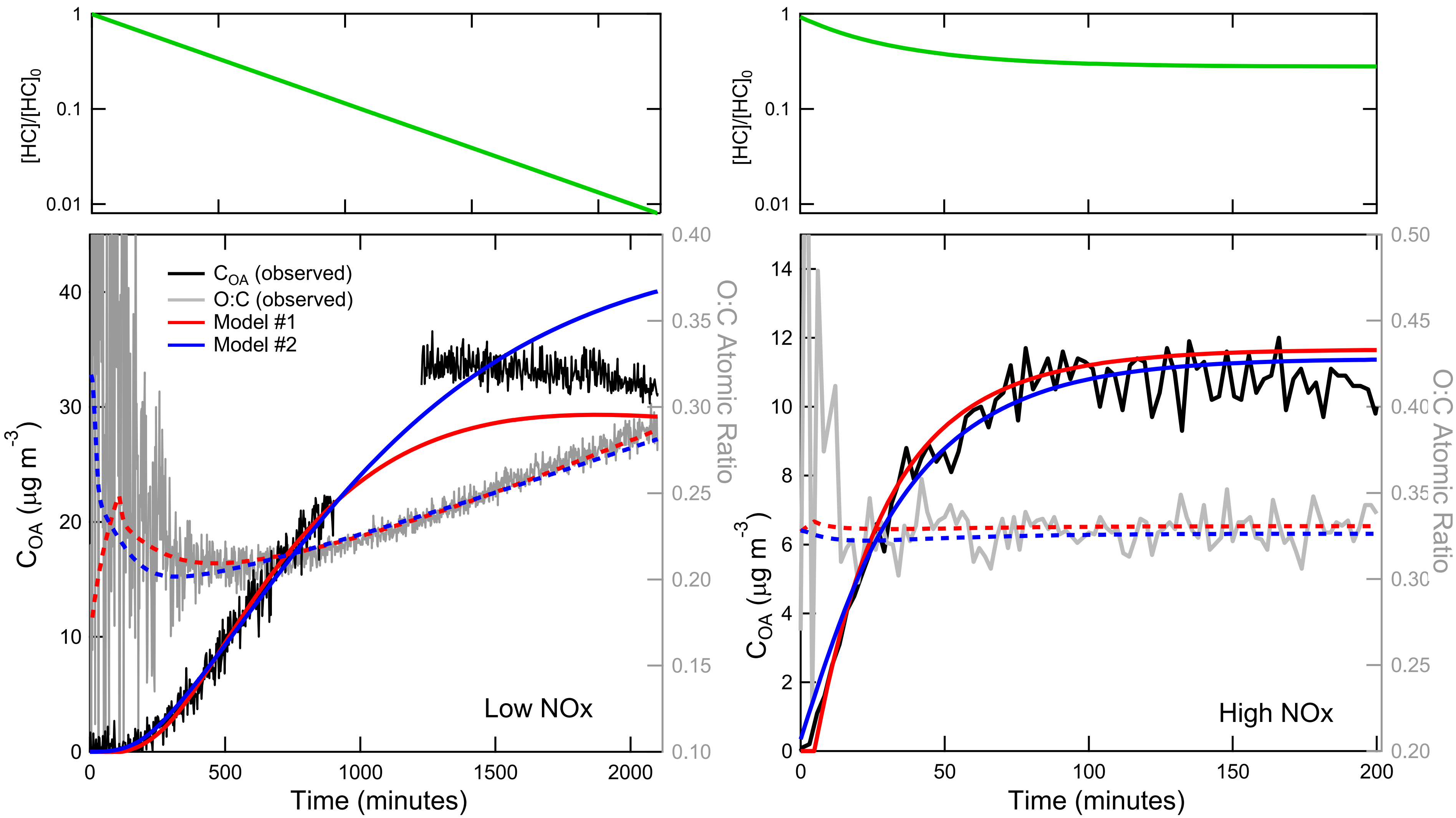


2-D distributions of “molecules” in particle phase

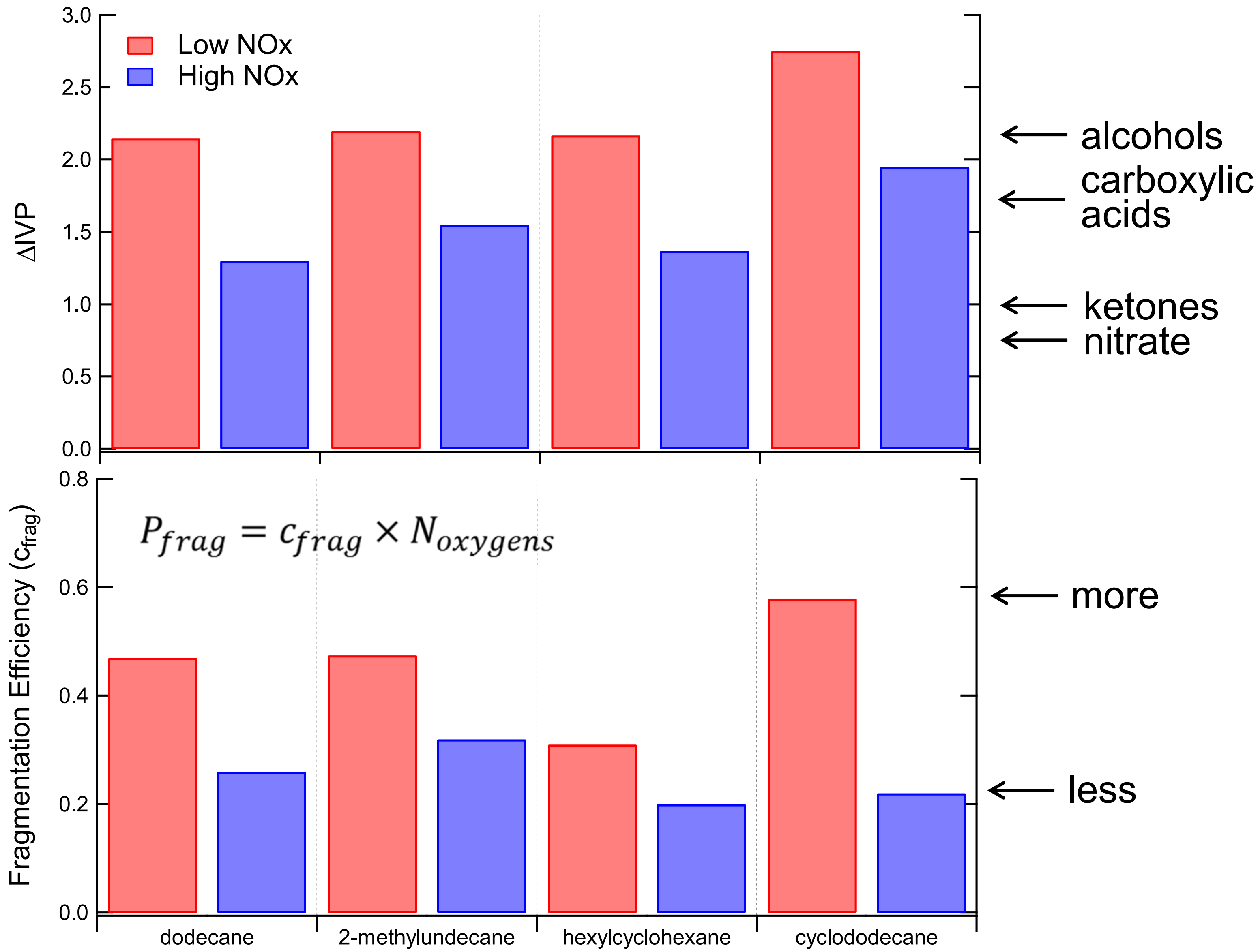
Actual distribution depends on tunable parameters

Model vs. Measurement: C_{OA} and O:C

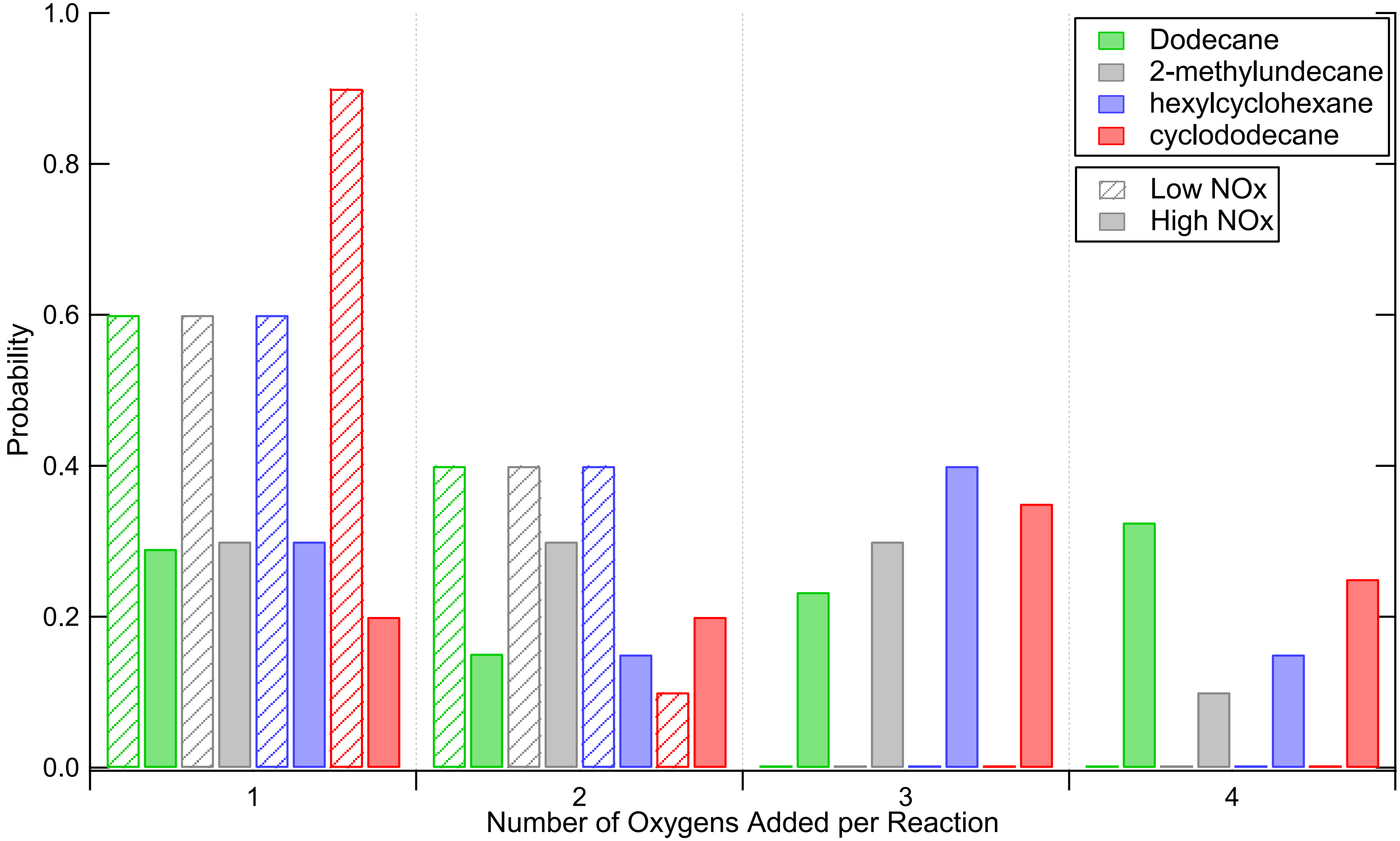
Dodecane + OH



Model Results: Volatility and Fragmentation



Model Results: Oxygen Addition



High NO_x adds more oxygens per reaction than low NO_x

Secondary Organic Aerosol (SOA) Formation: Phase State of Particles

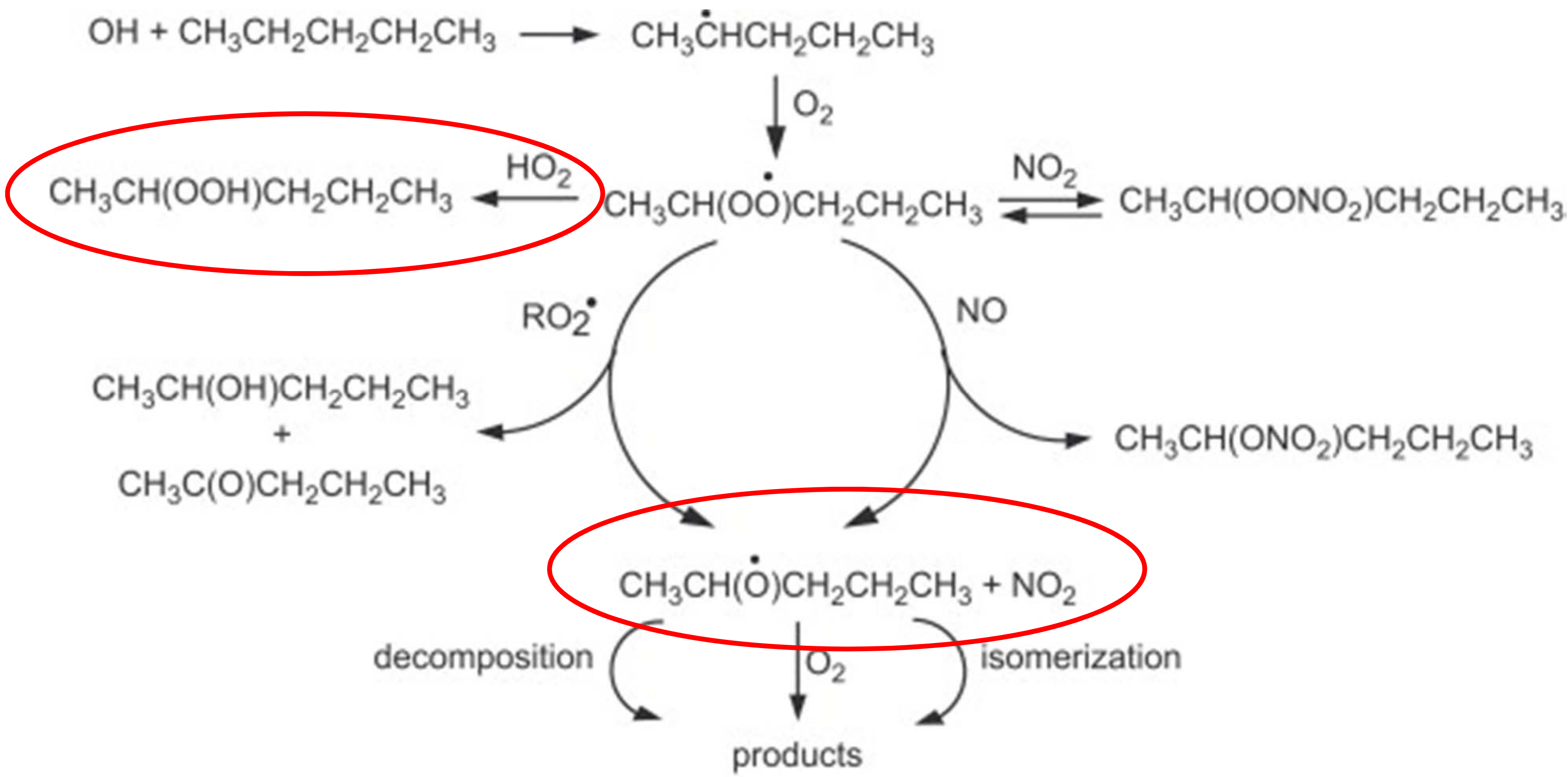
Recent evidence for semi-solid behavior of SOA

Virtanen et al., *Nature* (2010)	Terpene SOA	Particle bounce in an impactor ➡ glassy solid
Vaden et al., *PNAS* (2010, 2011)	α-pinene SOA ambient SOA	Delayed evaporation upon dilution ➡ coated SOA, non-liquid like behavior
Shiraiwa et al., *PNAS* (2011)	O_3 uptake by amorphous protein and oxidative aging in flow tube	Kinetically limited by bulk diffusion

Secondary Organic Aerosol Formation and Aging

- SOA formation is characterized by multi-generational chemistry that involves both functionalization and fragmentation reactions, leading to higher oxidation state and lower volatility. NO_x level is key.
- The relative importance of gas-phase oxidation vs. particle-phase reactions is not well established for most SOA-forming organic compounds.
- Laboratory chamber experiments remain the "gold standard" for studying SOA formation; both gas and particle phase mass spectrometry is crucial. Chamber SOA tends not to be as oxidized as ambient (loading effect, OH exposure?).
- A new frontier in SOA research involves understanding the importance of the particle phase state, e.g. multiple liquid phases in equilibrium, liquid-solid equilibrium, and the formation of semi-solid phases.
- Apply the new generation of SOA models to chamber data and implement into atmospheric models.

Alkane Photooxidation Chemistry



Semi-Explicit Chemical Modeling