Aerosol Formation from Atmospheric Organics

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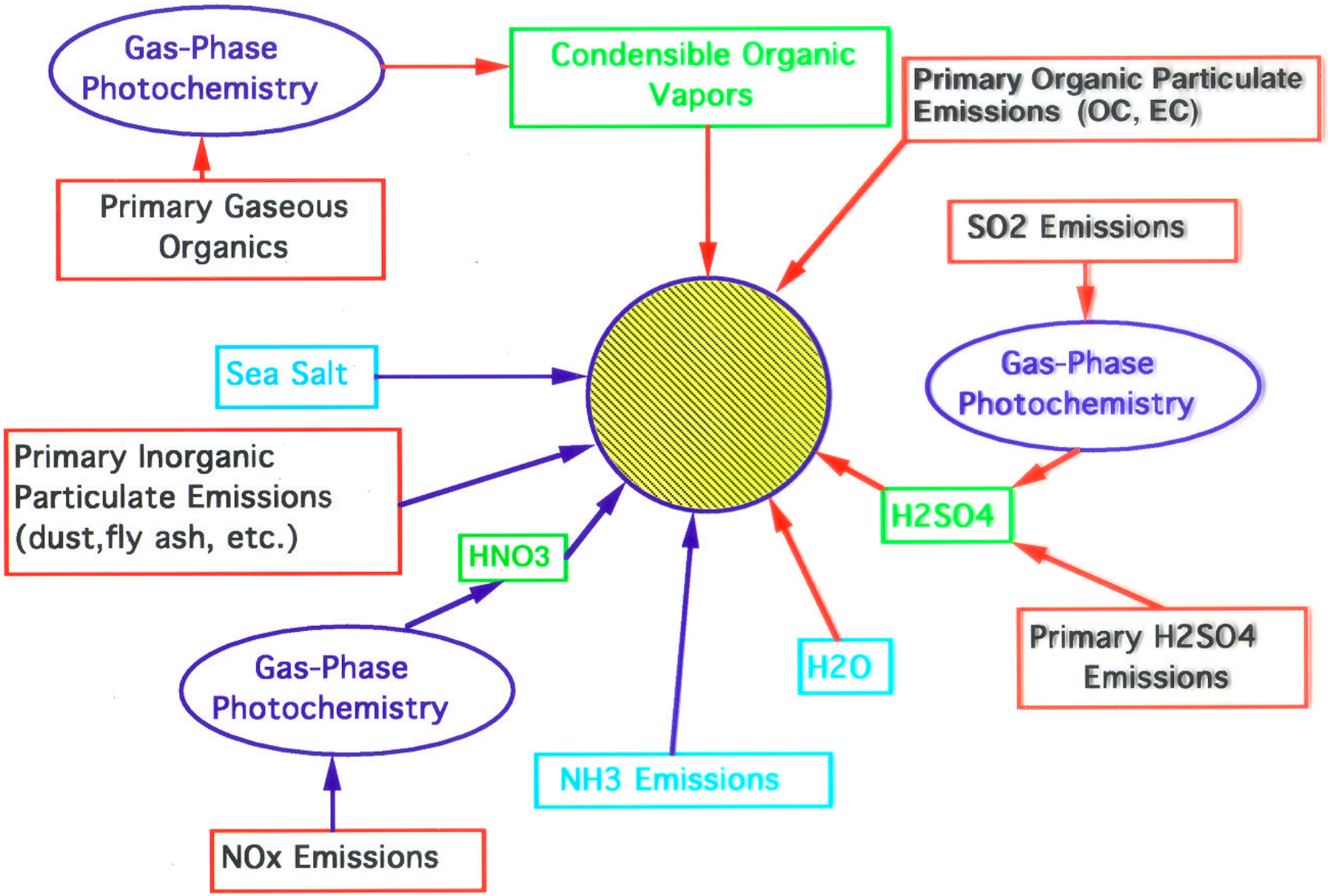
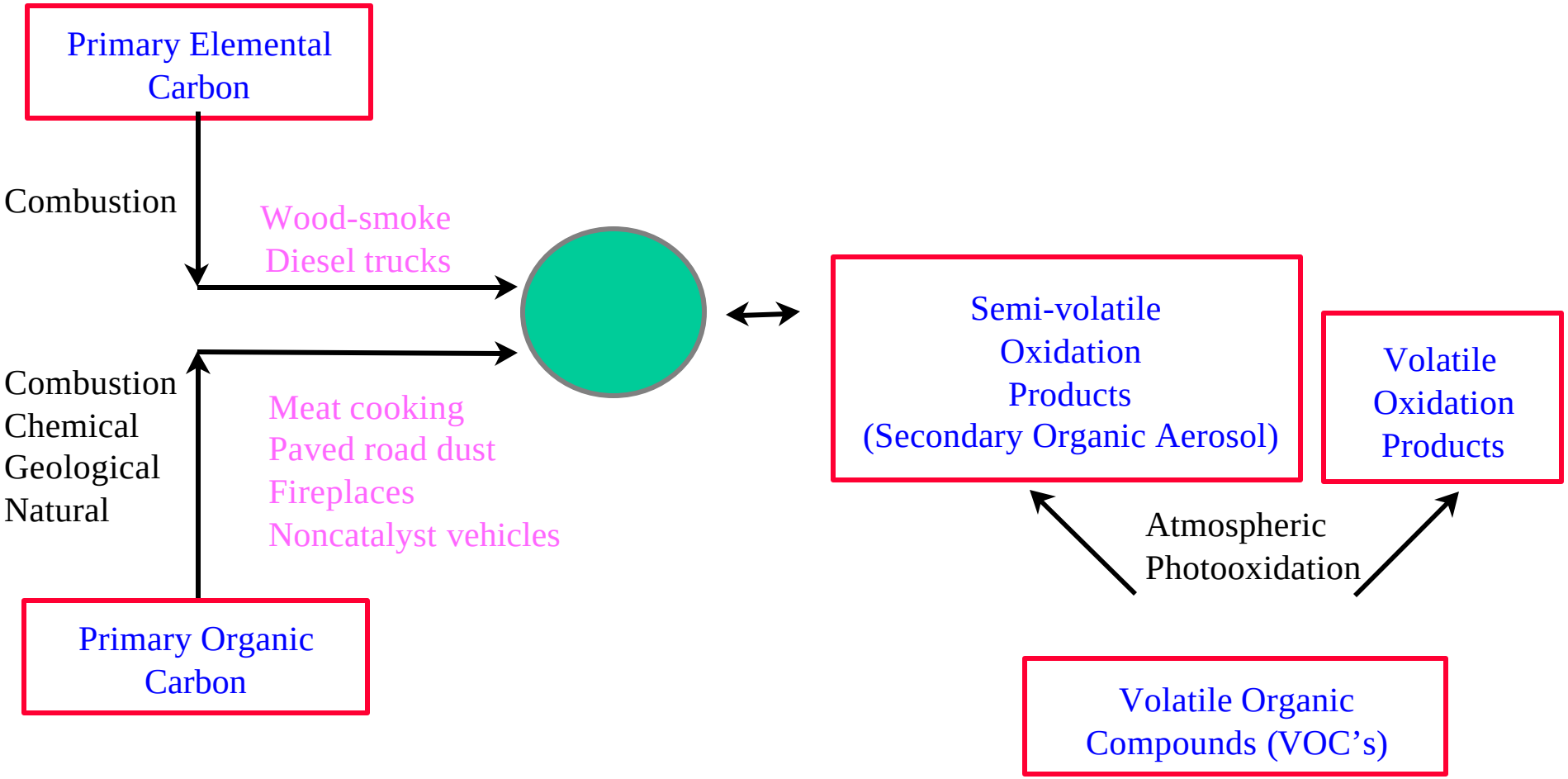
California Institute of Technology

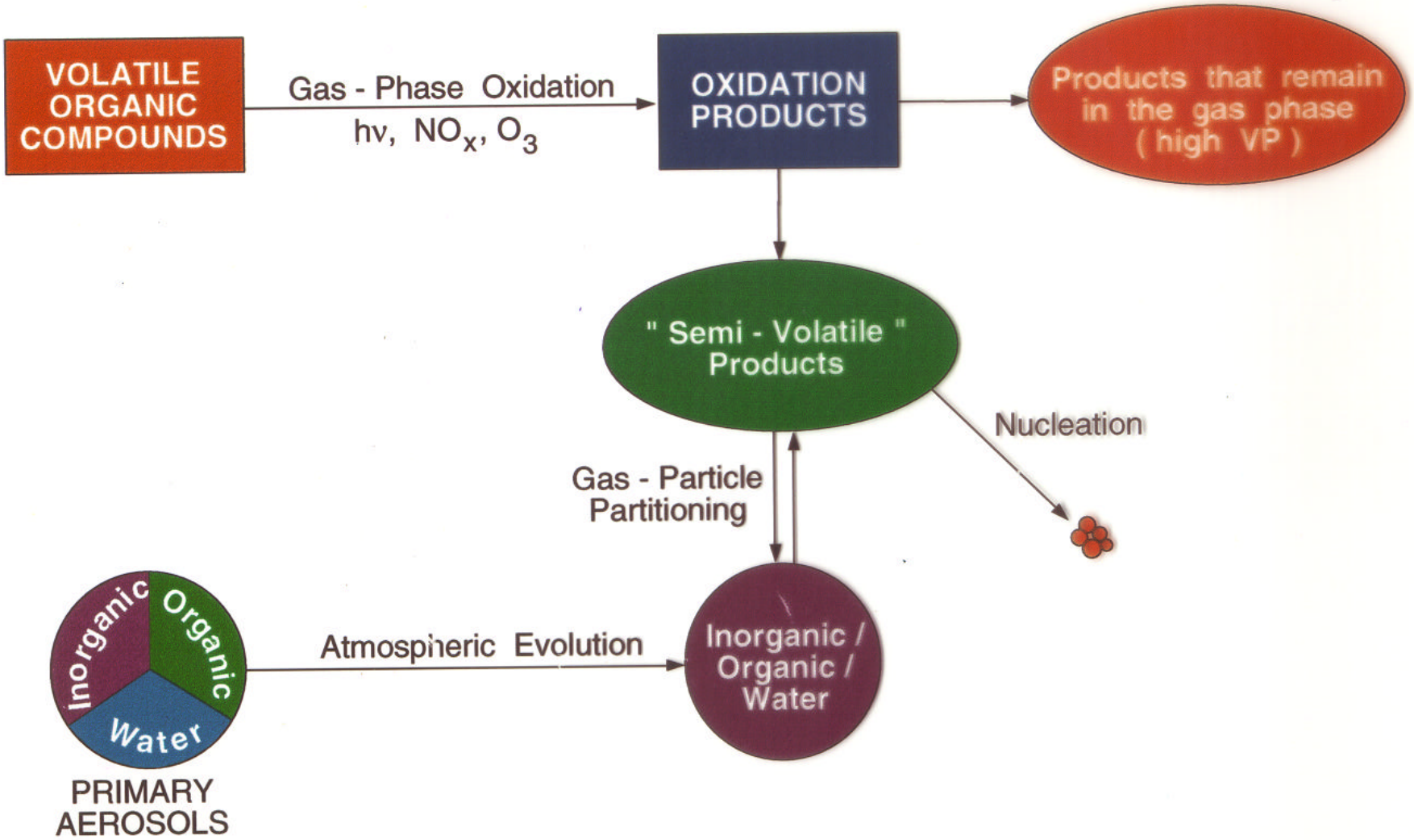
ATMOSPHERIC AEROSOL



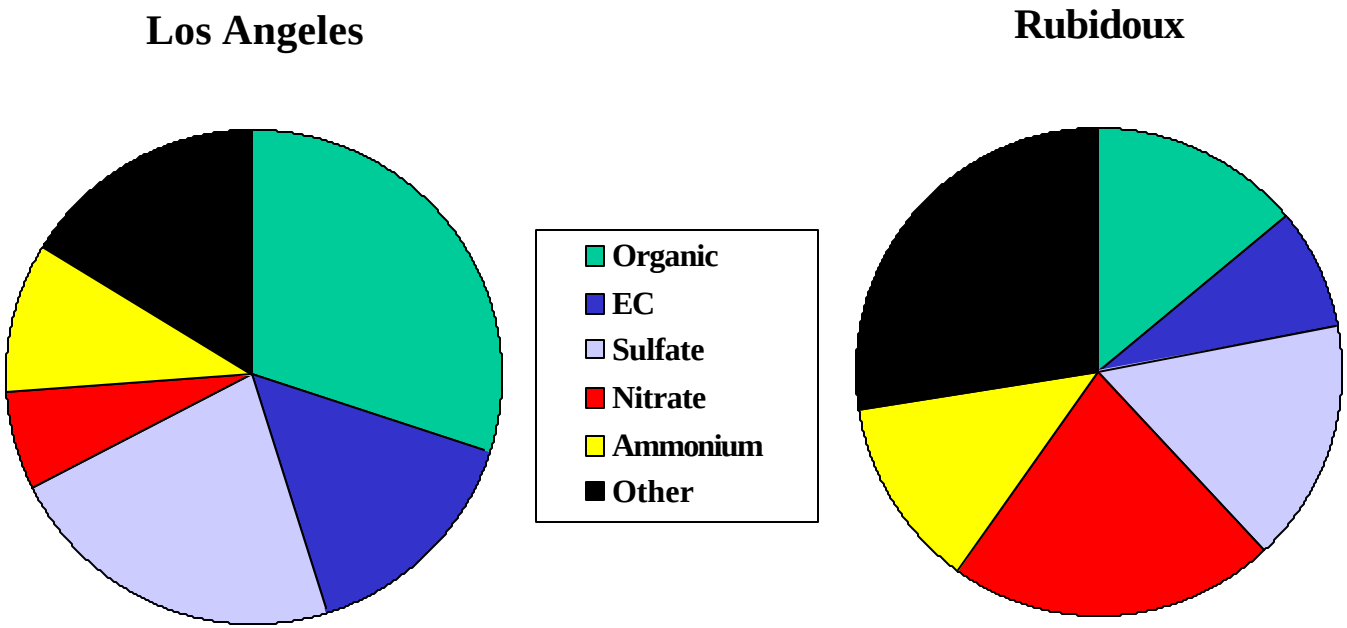
Sources of Carbonaceous Aerosol



FORMATION OF SECONDARY ORGANIC AEROSOLS



Importance of Secondary Organic Aerosol

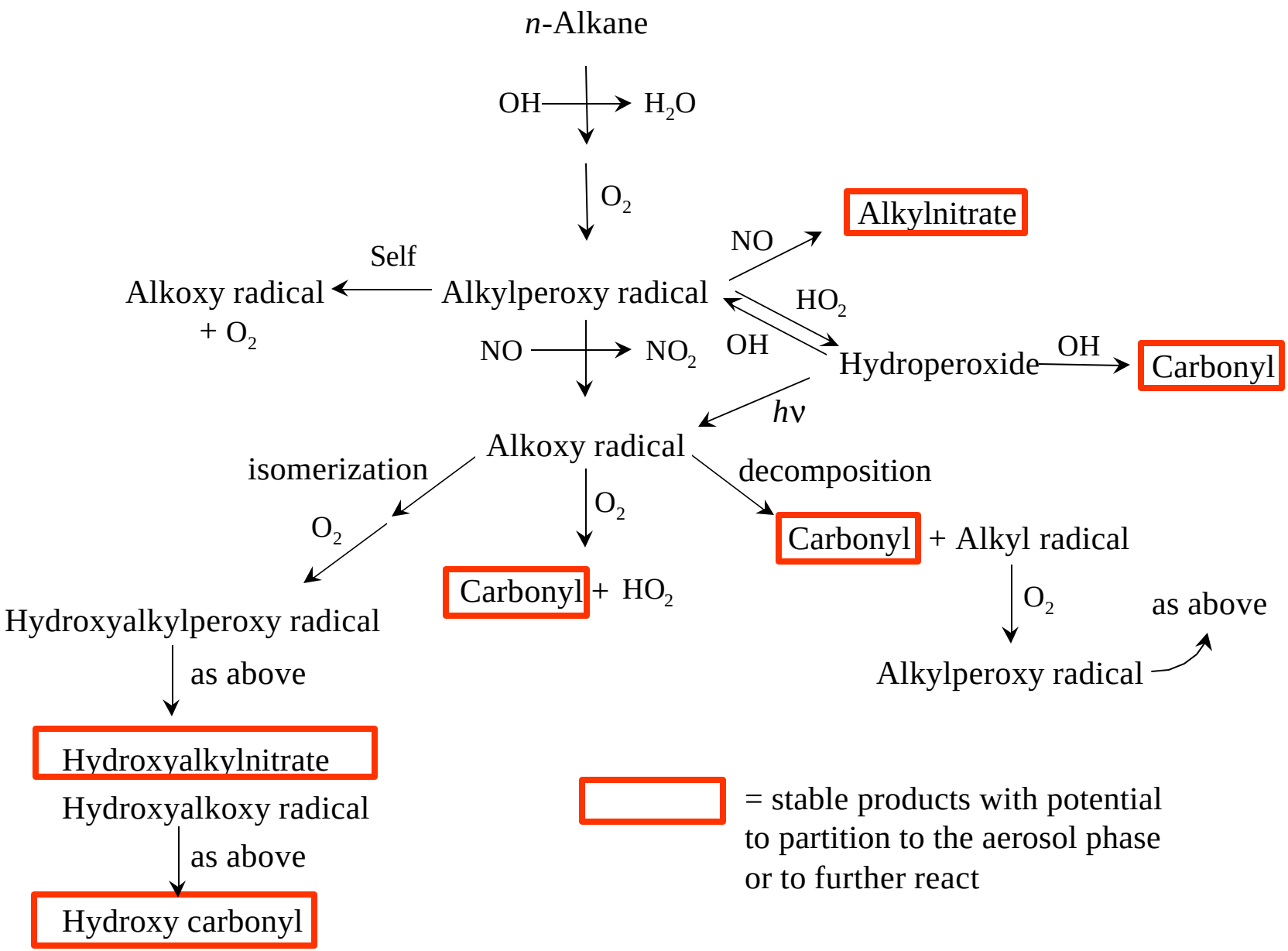


In the SoCAB, SOA *generally* contributes 20-80% of the observed total organic aerosol

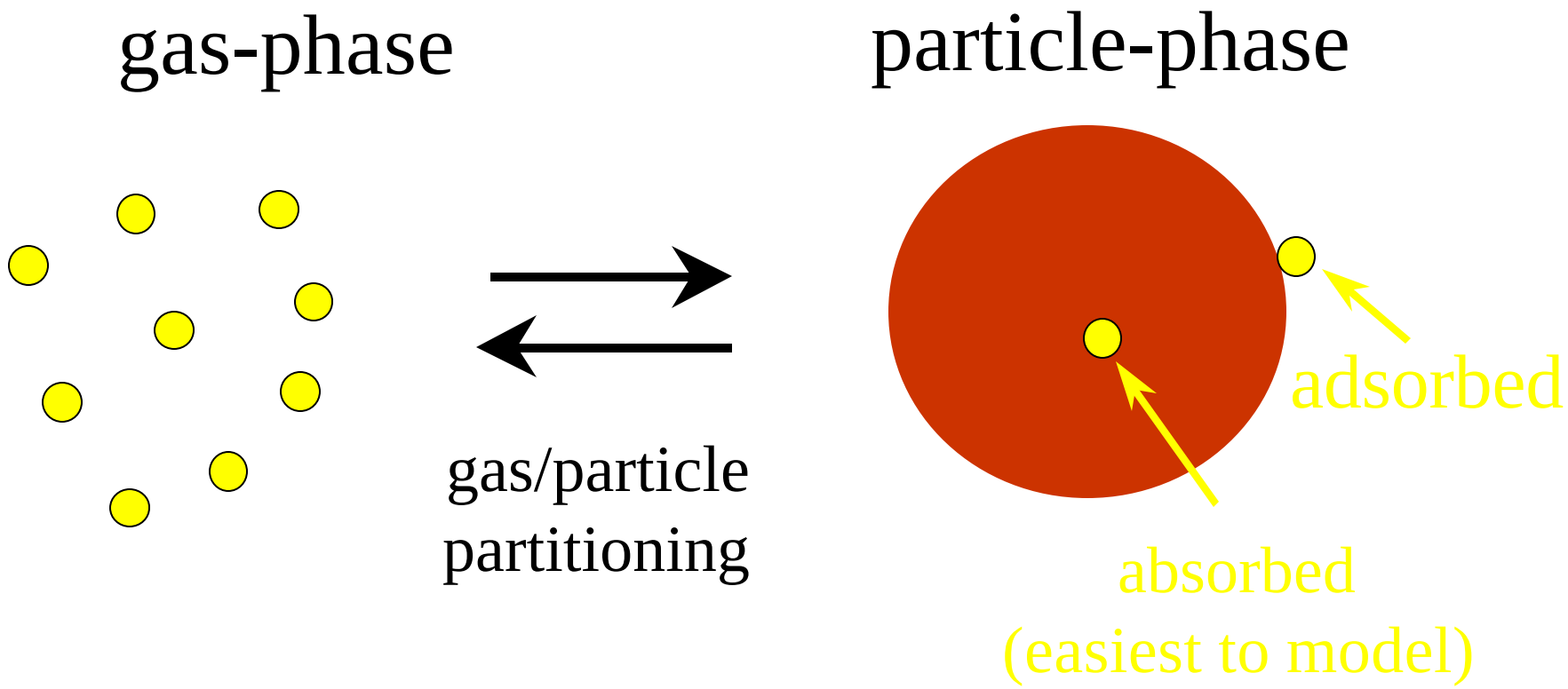
Major Questions of SOA Formation

- What are the gas-phase mechanisms leading to semi-volatile species? What are the molecular identities of these species? Are these first- or higher-generation products of the oxidation of the parent molecule?
- Can we predict from first principles the gas-particle partitioning of semi-volatile organic products to particles that consist of organics, water, and dissolved electrolytes?

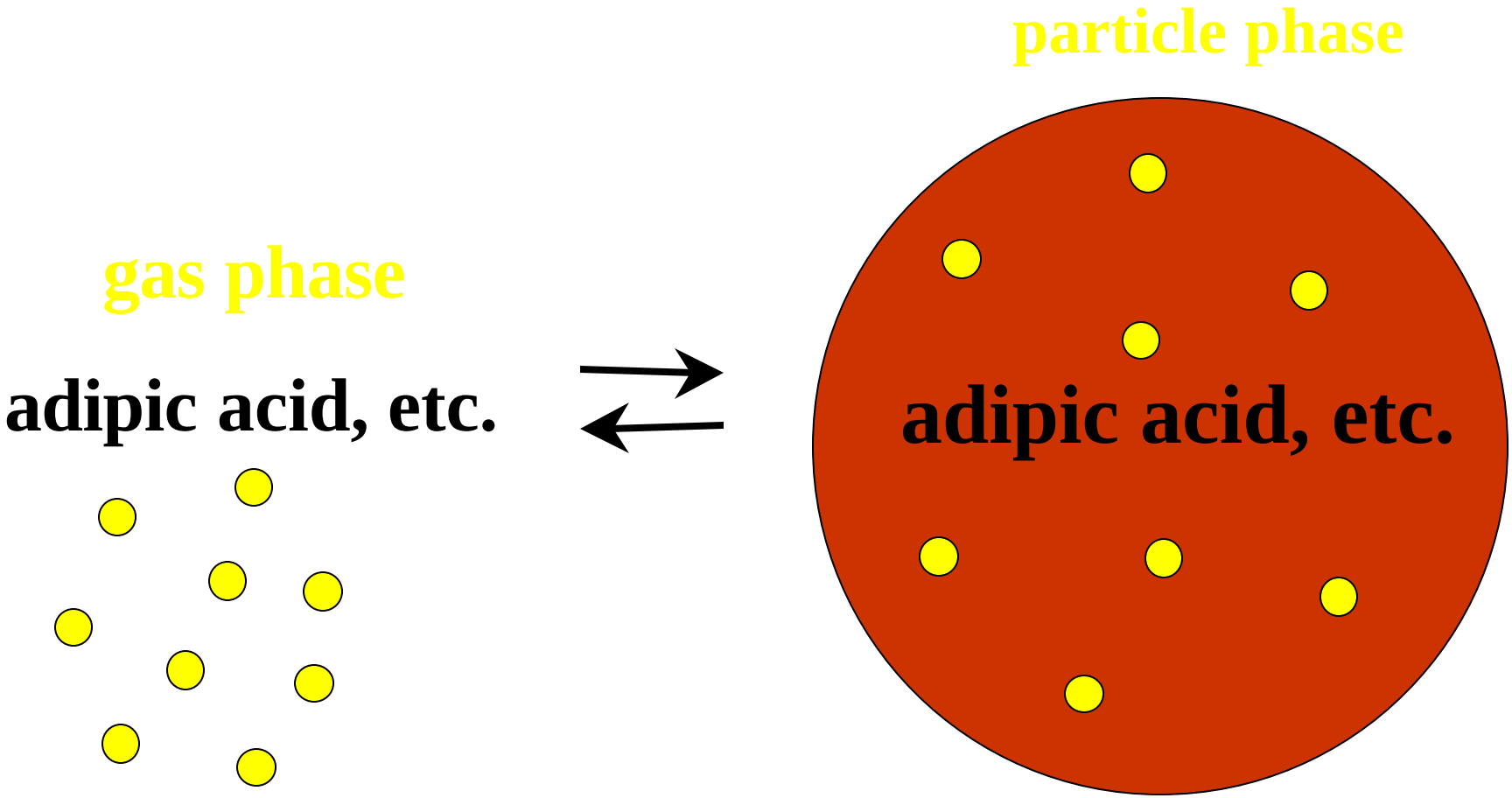
Example Mechanism



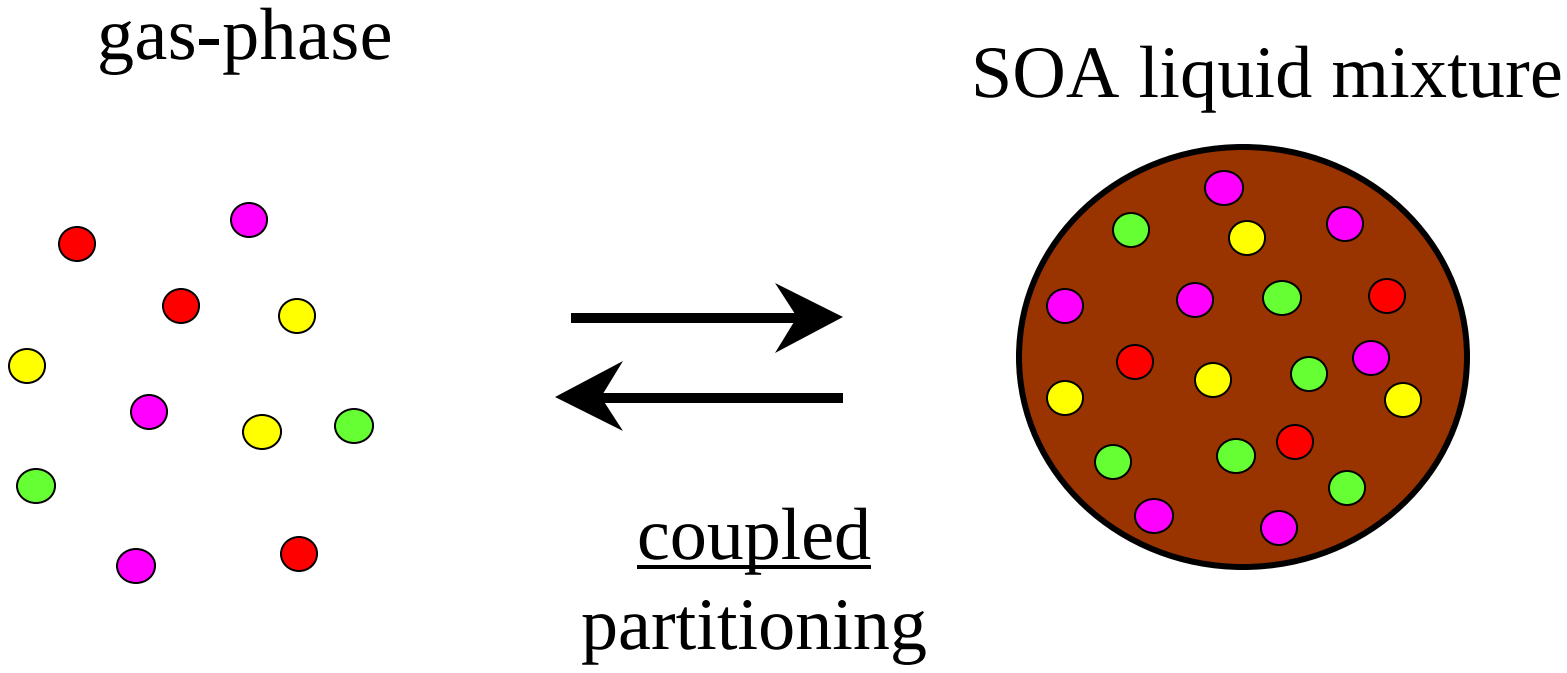
Gas/Particle Partitioning (condensation)



e.g., adipic acid… <u>just one</u> oxidation product of cyclohexene



The Skittles Model of Gas/Particle Partitioning†

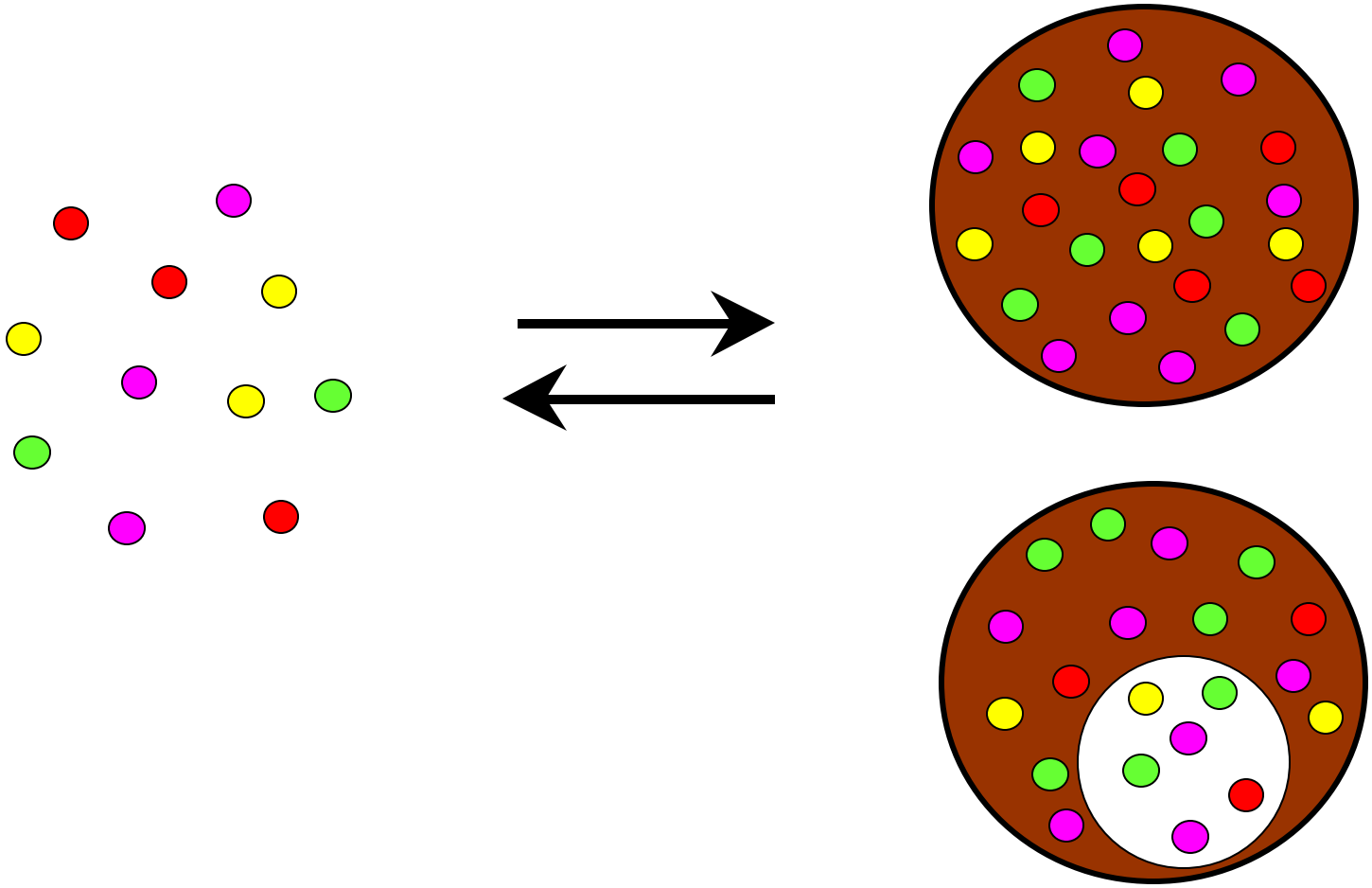


†water will also partition

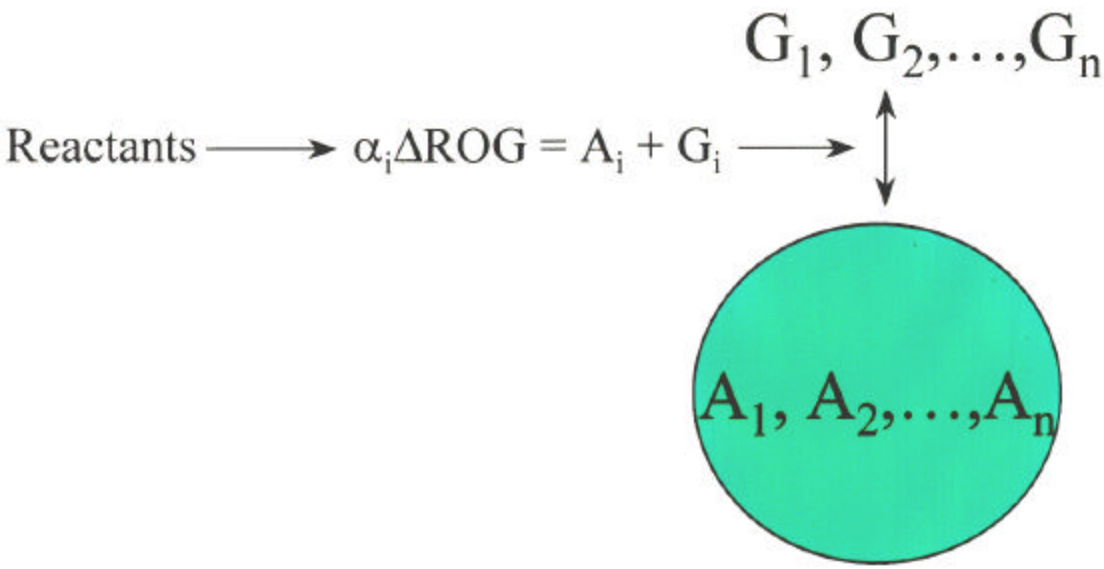
Possible Paradigms…

gas-phase

particle phase



Equilibrium Partitioning of Semi-Volatile Compounds

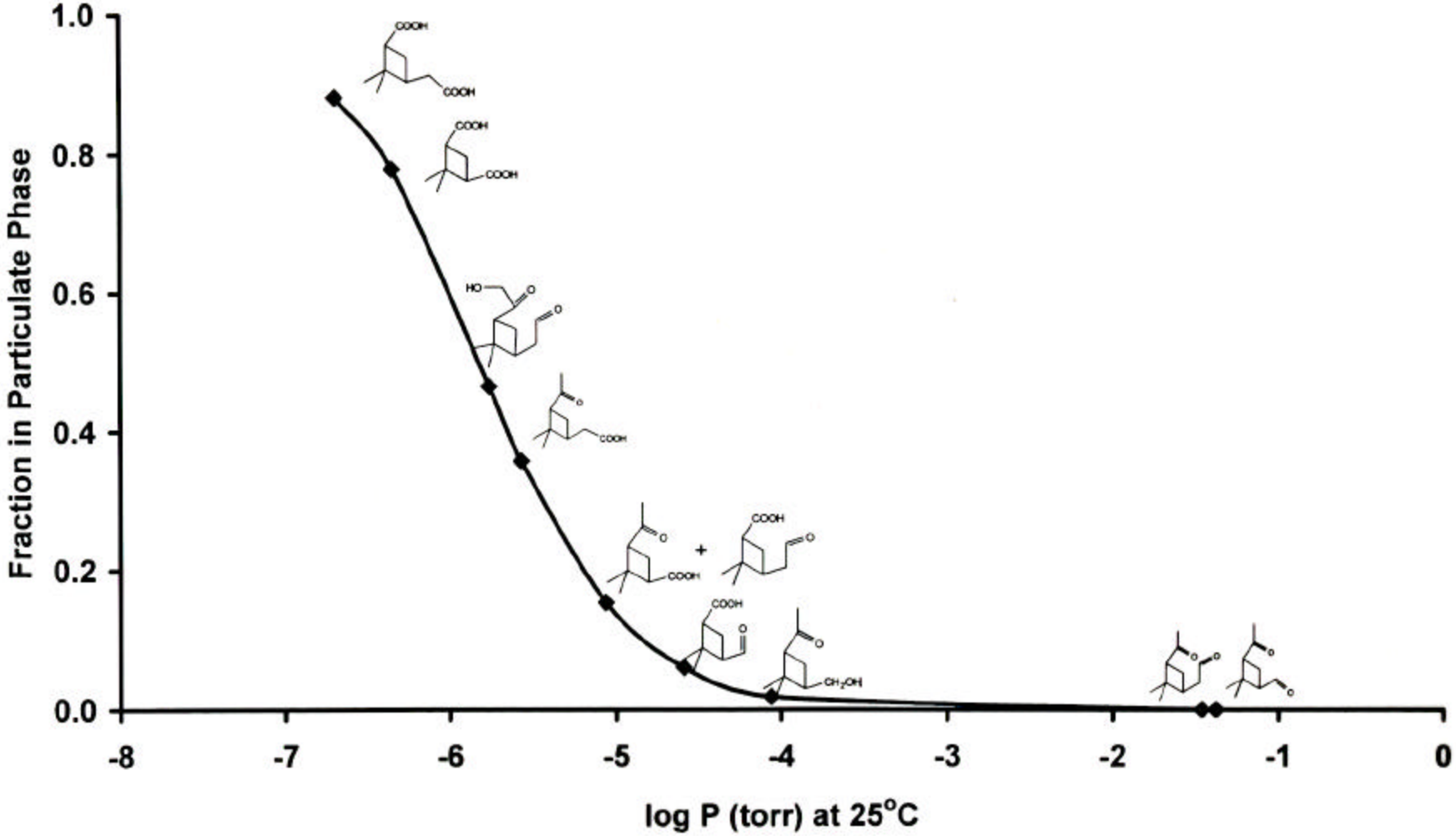


$$K_{om,i} = \frac{A_i/\Delta M_o}{G_i} = \frac{RT}{MW_{om}\gamma_i p^o_{L,i}}$$

$$\gamma_i = \gamma_i(x_1, x_2, \ldots, x_n)$$

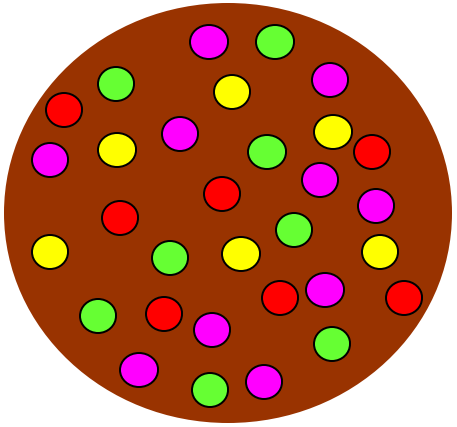
$$p^o_{L,i} = p^o_{L,i}(T)$$

Partitioning of Products from the O3 Oxidation of a-Pinene between the Particulate and Gas Phase (Assuming a Total Organic Aerosol Mass of 50 μg/m^3)



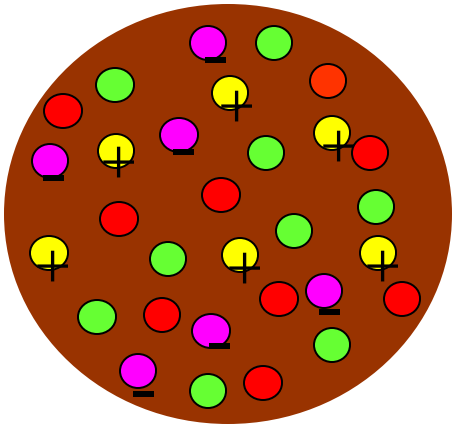
…predicting activity coefficients…

organic/water
liquid mixtures



can use *UNIFAC*

organic/water
salt
liquid mixtures



will use
ionic-*UNIFAC*

June 15, 2001

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A State-of-the-Art Chamber for Investigating Aerosol Chemistry

Endocrine Disrupters in Pulp Mill Effluent

Coastal Marsh Impacts on Water Quality

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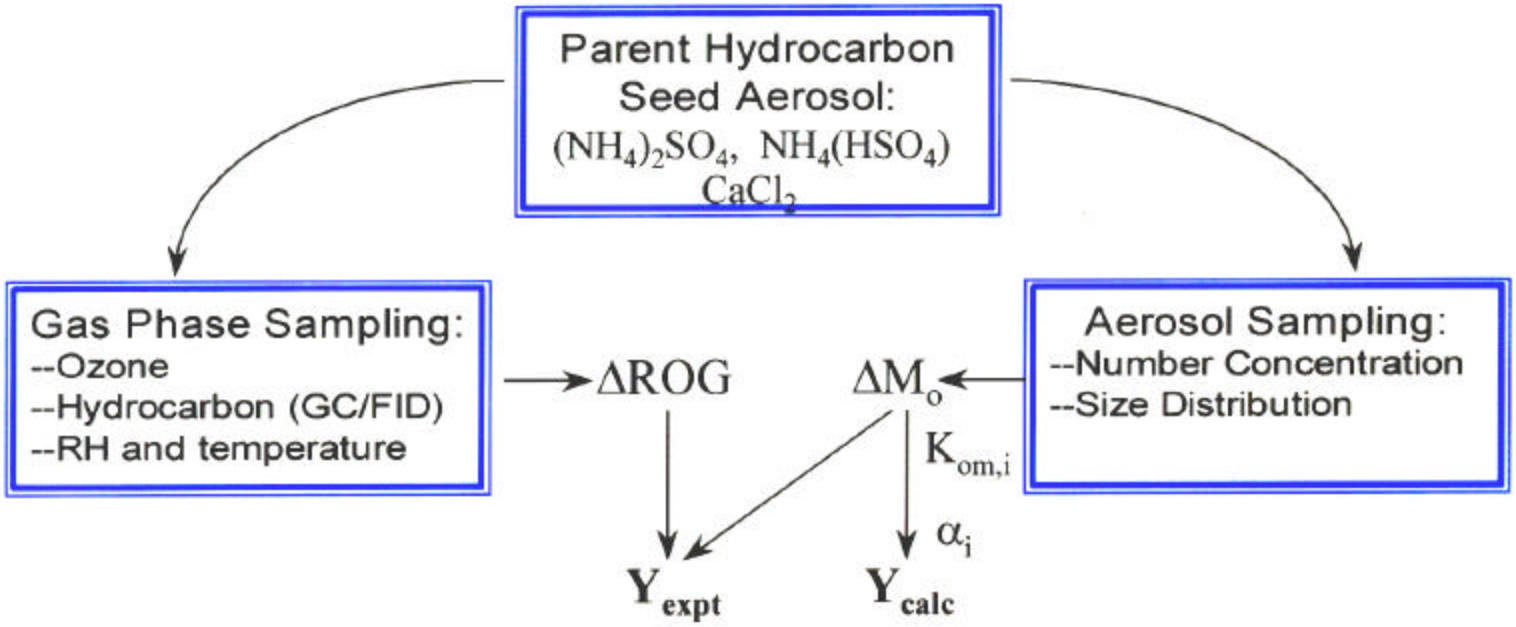
Experimental Protocol

Indoor Teflon Reactor



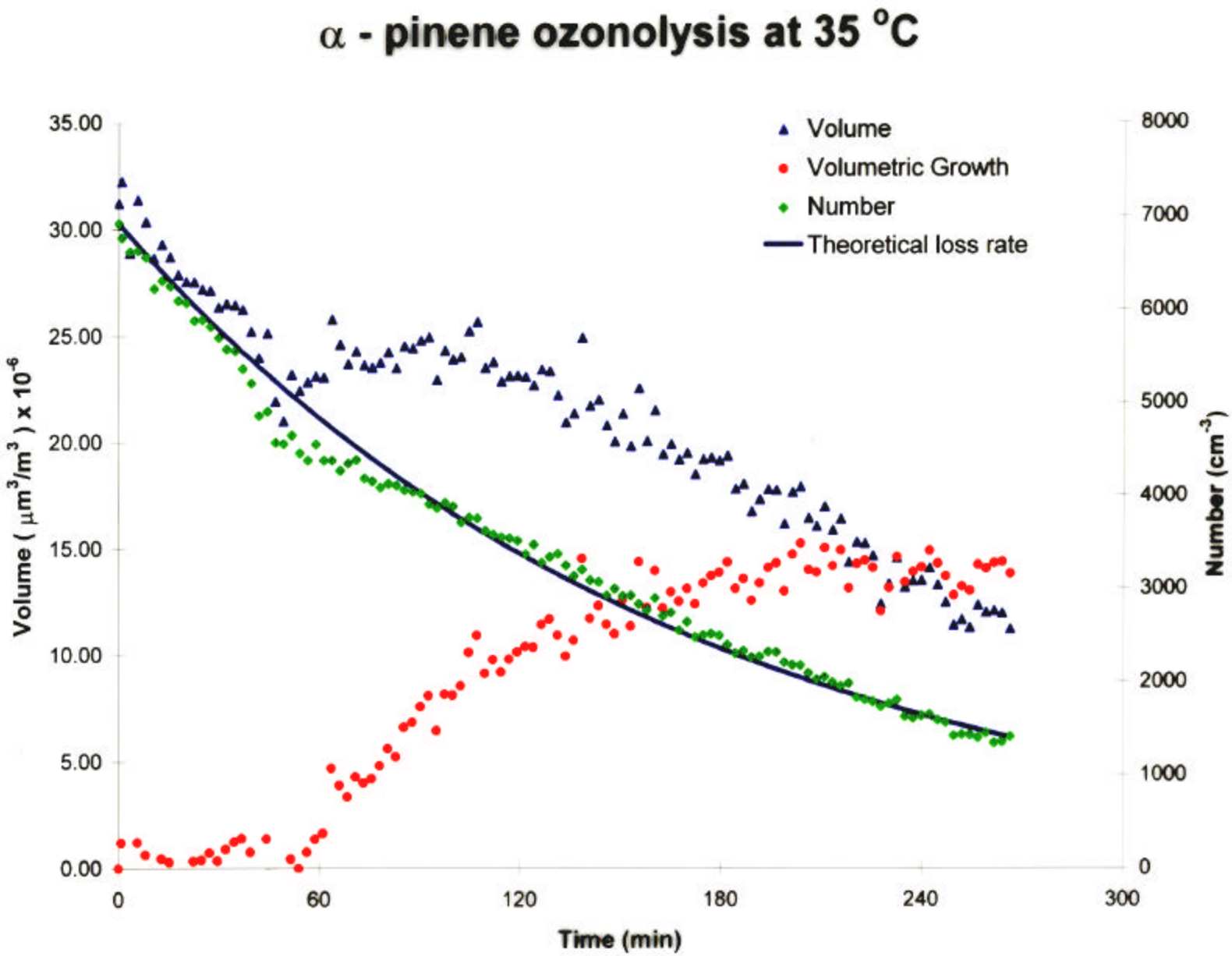
Two $K_{om,i}$ and α_i values are then varied so that the sum of the residuals between experimental and calculated yields for a single parent is minimized.

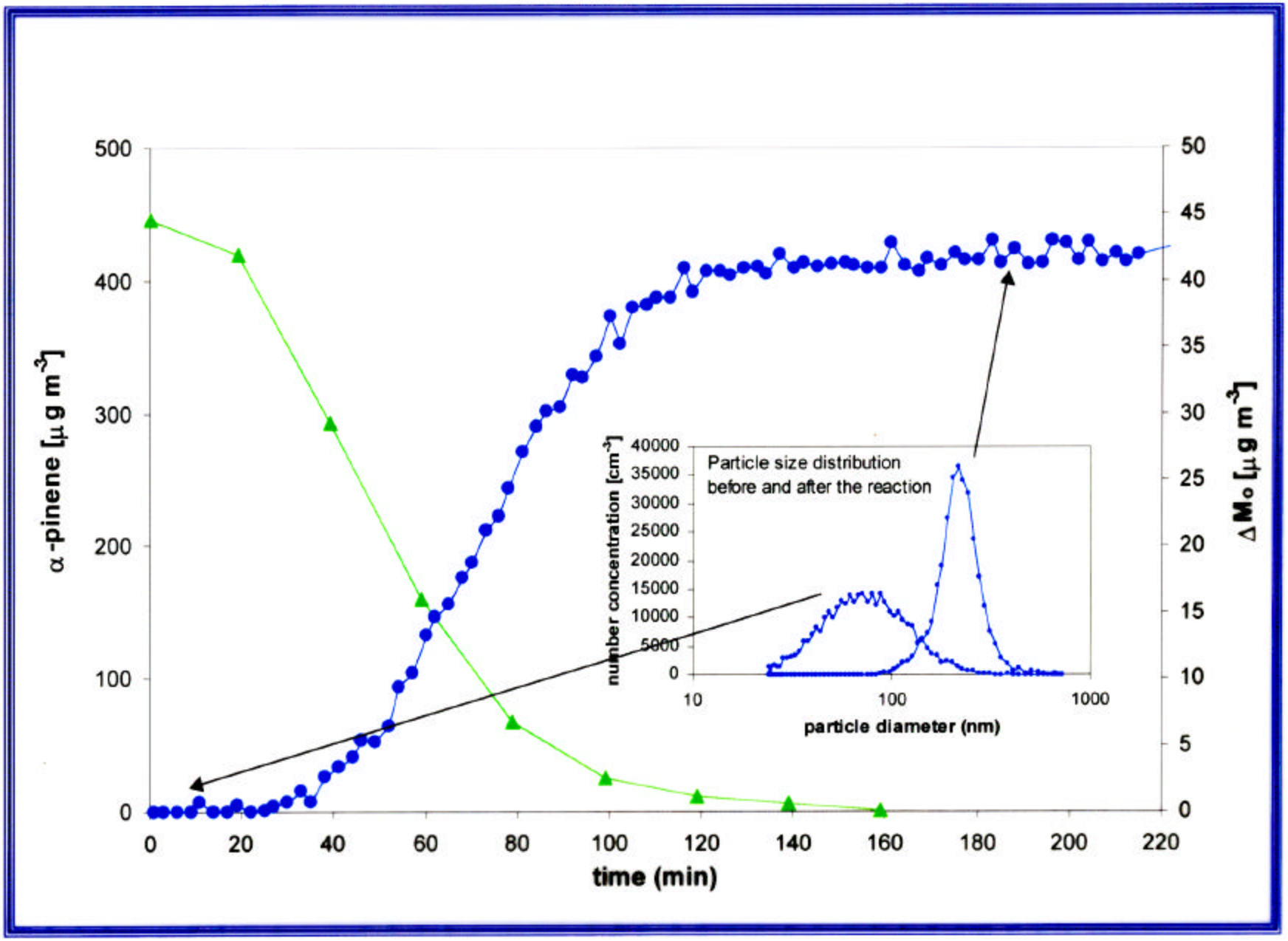
$$Yield_{expt} = \Delta M_o / \Delta ROG$$

Analytical Instruments Used

Samples from two 28-m^3 indoor Teflon chambers are drawn to be analyzed by:

Instrument	Analytical Information	On/off-line	Sampled Chamber
DMA (Differential Mobility Analyzer)	- Size distribution - Number, mass, and volume concentrations	On-line	Both (dedicated)
H-TDMA (Humidity Tandem DMA)	Hygroscopicity of the aerosol	On-line	Both (switching)
CNC (Condensation Nucleus Counter)	Number concentration (>3 nm and >10 nm)	On-line	Both (dedicated)
GC-FID (Gas Chromatograph)	Reactant hydrocarbon concentration	On-line	Both (switching)
AMS (Aerosol Mass Spectrometer)	Aerosol phase composition and mass distribution	On-line	High-conc. run only
CIMS (Chemical Ionization Mass Spec.)	Gas phase composition	On-line	High-conc. run only
Ozone/NO_x analyzers	Ozone, NO_x concentrations	On-line	Both (dedicated)
Filter Samples - GC/MS and LC/MS - OC analysis	- Aerosol phase composition - OM/OC ratio for organics	Off-line	High-conc. run only


α - pinene ozonolysis at 35 °C
Volume
Volumetric Growth
Number
Theoretical loss rate
Volume (μm³/m³) x 10⁻⁶
Number (cm⁻³)
Time (min)
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
8000
7000
6000
5000
4000
3000
2000
1000
0
0
60
120
180
240
300


α -pinene [μ g m-3]
ΔM° [μ g m-3]
time (min)
Particle size distribution
before and after the reaction
number concentration [cm-3]
particle diameter (nm)

Calculation of Yield

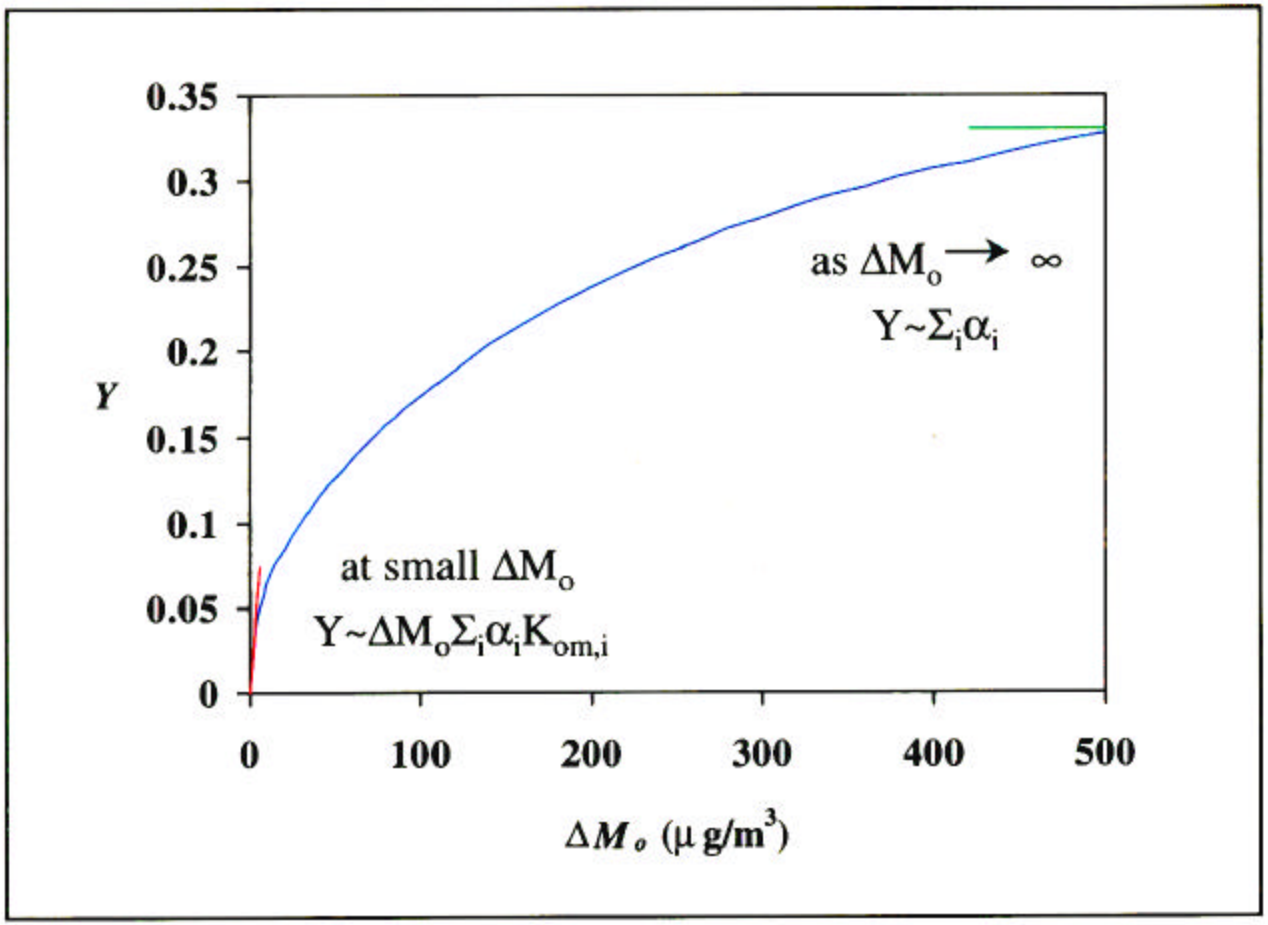
- At low RH, and only semi-volatile products of the parent hydrocarbon partition to the aerosol phase.

$$Yield = \frac{\Delta Mass_{organic}(\mu g / m^3)}{\Delta HC(\mu g / m^3)}$$

- At higher RH, aerosol growth is governed by partitioning of both organic and water to the aerosol phase.

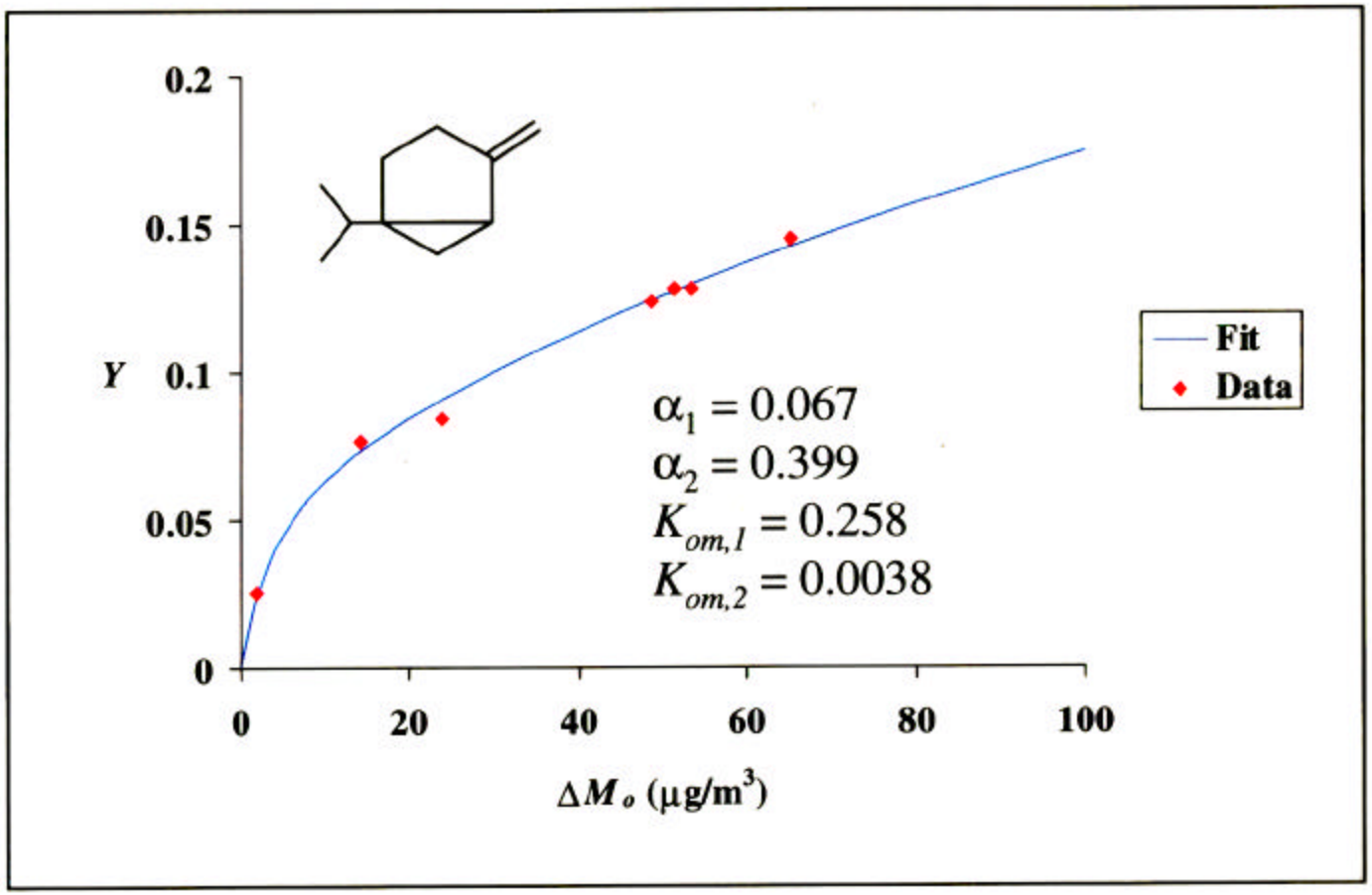
$$Yield^* = \frac{\Delta Mass_{aerosol}(\mu g / m^3)}{\Delta HC(\mu g / m^3)} = \frac{\Delta Mass_{organic}(\mu g / m^3) + \Delta Mass_{water}(\mu g / m^3)}{\Delta HC(\mu g / m^3)}$$

Characteristics of the Aerosol Yield



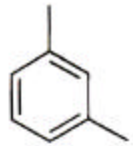
$$Y = \sum_i Y_i = \Delta M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} \Delta M_o} \right)$$

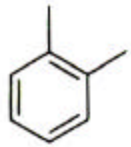
Fitted Curve for Sabinene in Photooxidation Experiments

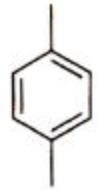


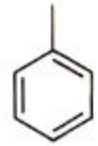
$$Y = \sum_i Y_i = \Delta M_o \sum_i \left(\frac{\alpha_i K_{om,i}}{1 + K_{om,i} \Delta M_o} \right)$$

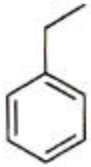
Aromatic Hydrocarbons Previously Studied

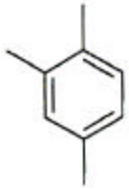

m-xylene

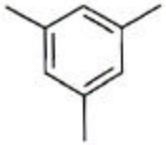

o-xylene

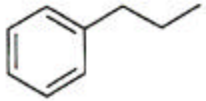

p-xylene

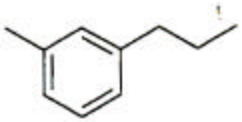

toluene

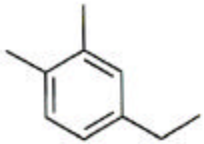

ethylbenzene

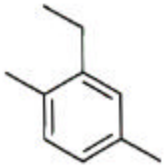

1,2,4-trimethylbenzene

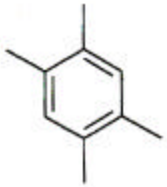

1,3,5-trimethylbenzene

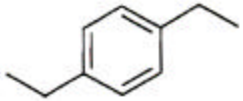

n-propylbenzene

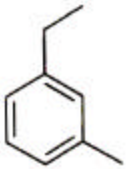

1-methyl-3-n-propylbenzene

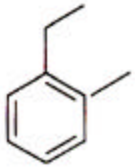

1,2-dimethyl-4-ethylbenzene

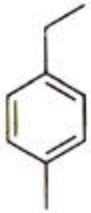

1,4-dimethyl-2-ethylbenzene

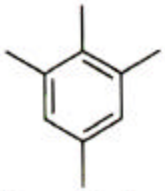

1,2,4,5-tetramethylbenzene


p-diethylbenzene


m-ethyltoluene

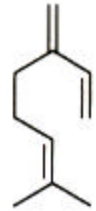

o-ethyltoluene


p-ethyltoluene

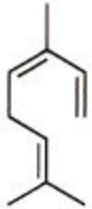

1,2,3,5-tetramethylbenzene

Biogenic Hydrocarbons Previously Studied

Acyclic Triolefins

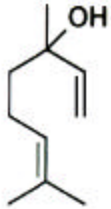


Myrcene

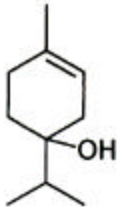


Ocimene

Oxygenated Terpenes

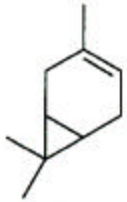


Linalool

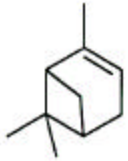


Terpinene-4-ol

Bicyclic Olefins

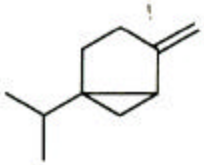


Δ^3-Carene



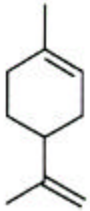
α-Pinene

β-Pinene

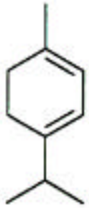


Sabinene

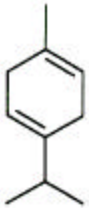
Cyclic Diolefins



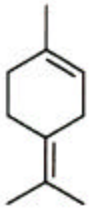
Limonene



α-Terpinene

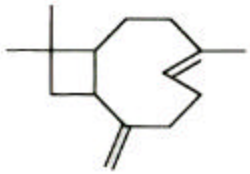


γ-Terpinene

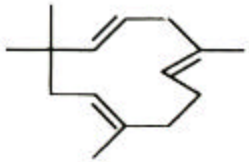


Terpinolene

Sesquiterpenes

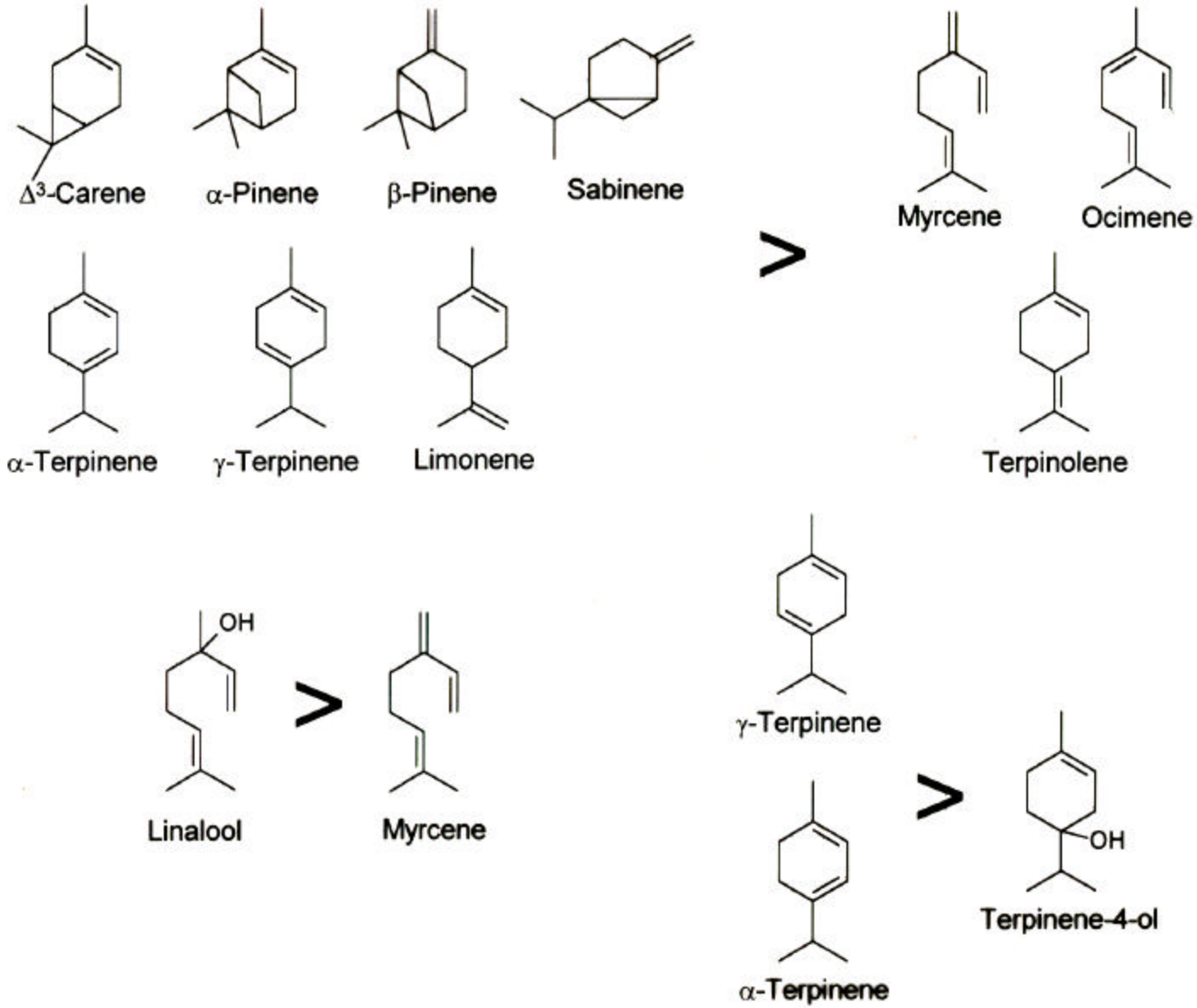


β-Caryophyllene

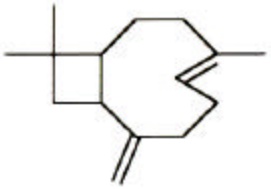


α-Humulene

Cyclic structures have higher yields than open chain compounds

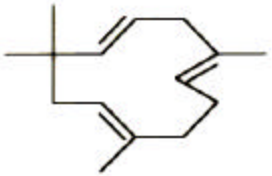


Sesquiterpenes have highest yield due to carbon number



β-Caryophyllene

$C_{15}C_{24}$



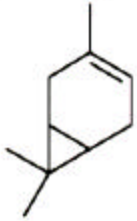
α-Humulene

vs. $C_{10}C_{24}$ monoterpenes

Location of double bonds and number of carbon in secondary ring important: photooxidation

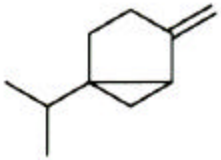
β-Pinene

>



Δ^3-Carene

>

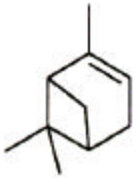


Sabinene

>

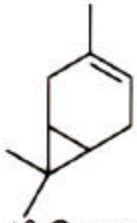
α-Pinene

As well as type of oxidant: ozone reaction



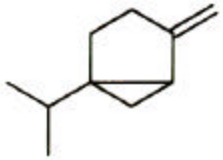
α-Pinene

>



Δ^3-Carene

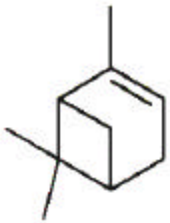
>



Sabinene

>

β-Pinene

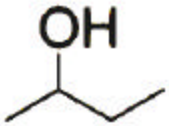


O_3 → Products: $A_1 + A_2 + \ldots$

$\bullet OH$ → Products: $B_1 + B_2 + \ldots$

$\bullet NO_3$ → Products: $C_1 + C_2 + \ldots$

Dark reaction



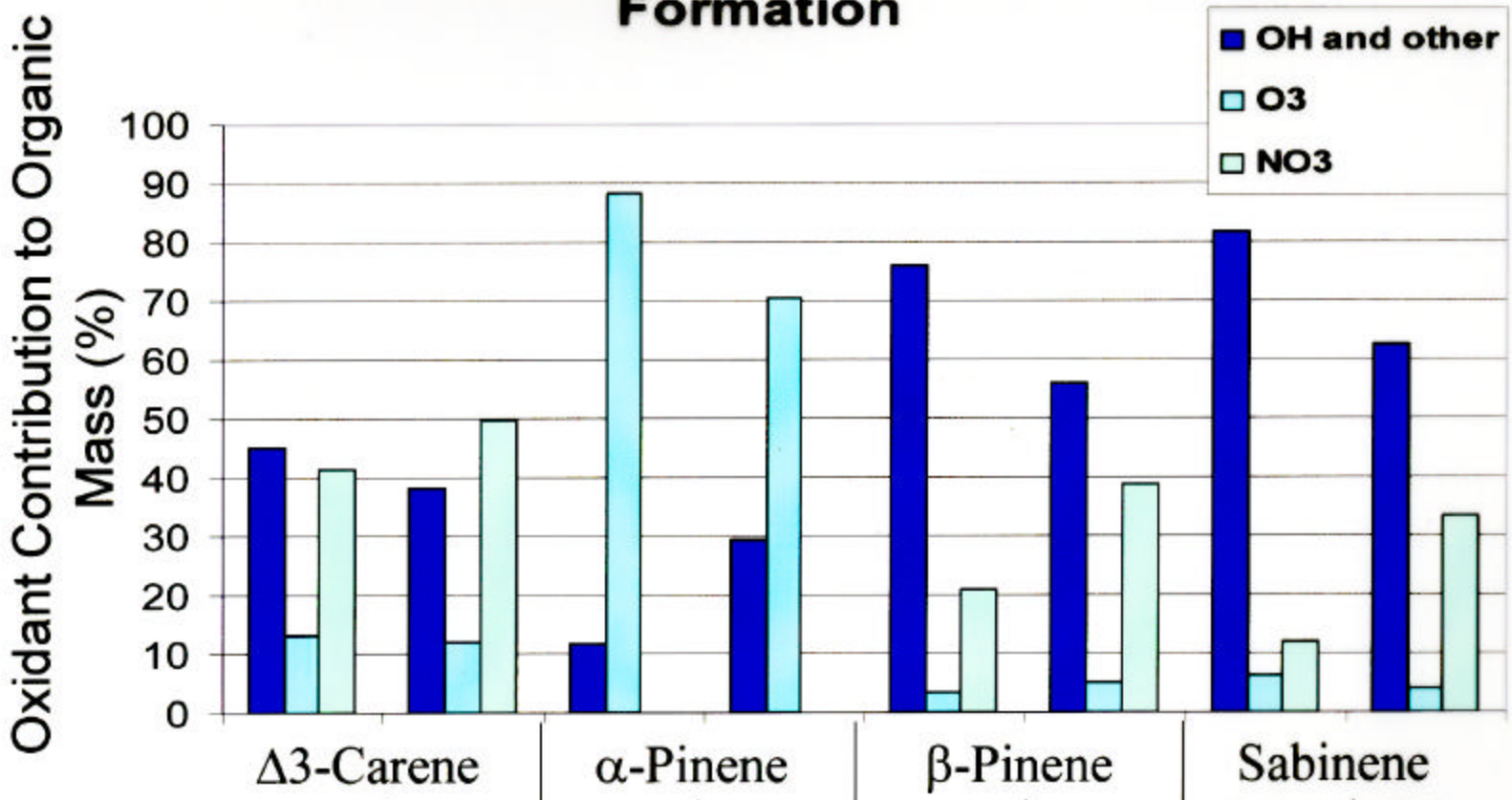
2 - BuOH as •OH scavenger

Photooxidation: subtract out O_3 and $\bullet NO_3$ contributions

$N_2O_5 \longrightarrow NO_2 + \bullet NO_3$

Dark reaction

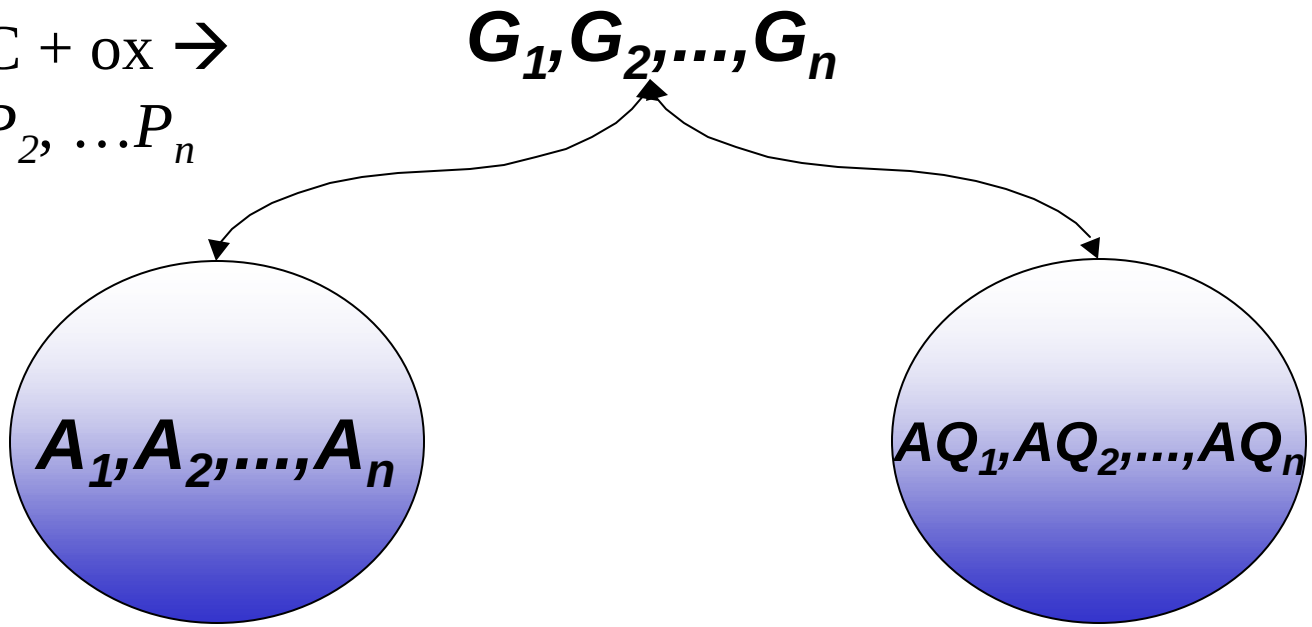
Individual Oxidant Contribution to Aerosol Formation



	Δ3-Carene		α-Pinene		β-Pinene		Sabinene	
C_o (ppb)	72.5	104.6	72.4	94.8	32.3	79.0	34.9	83.3
NO_x level (ppb)	128	162	203	124	135	153	102	199
M_o (μg/ml)	54.6	99.7	22.7	39.3	20.4	109.4	14.8	65.2
Yield	14.2%	17.9%	5.9%	7.7%	11.8%	26.0%	6.4%	14.5%

Formation of Secondary Organic Aerosol: The Combined Module

VOC + ox →
$P_1, P_2, \ldots P_n$



Partitioning Theory

$$K_{om,i} = \frac{A_i / M_o}{G_i} \sim \frac{RT}{p^o_{L,i}\,\mathrm{MW}_{om}\gamma_i}$$

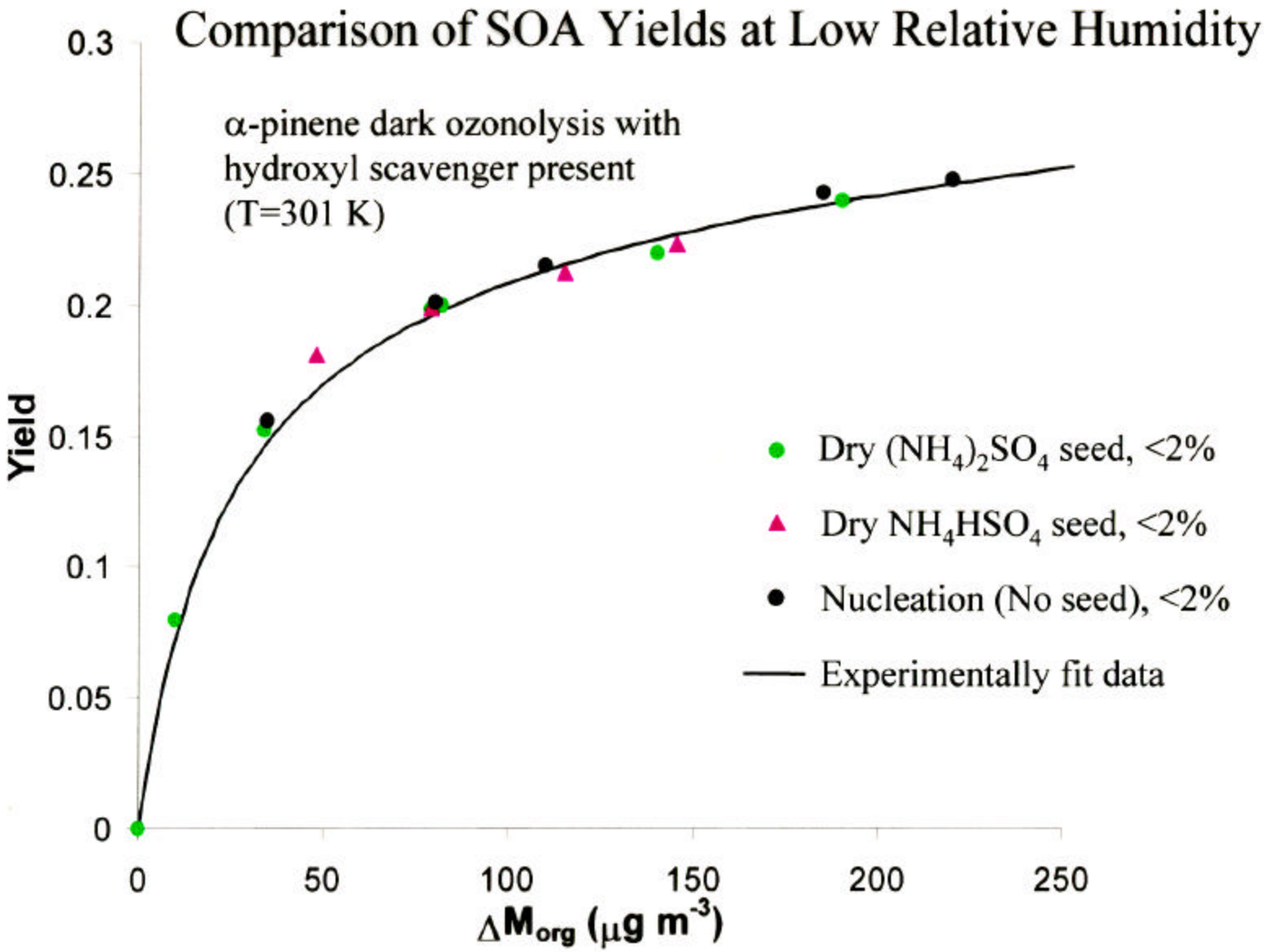
Henry's Law and Dissociation

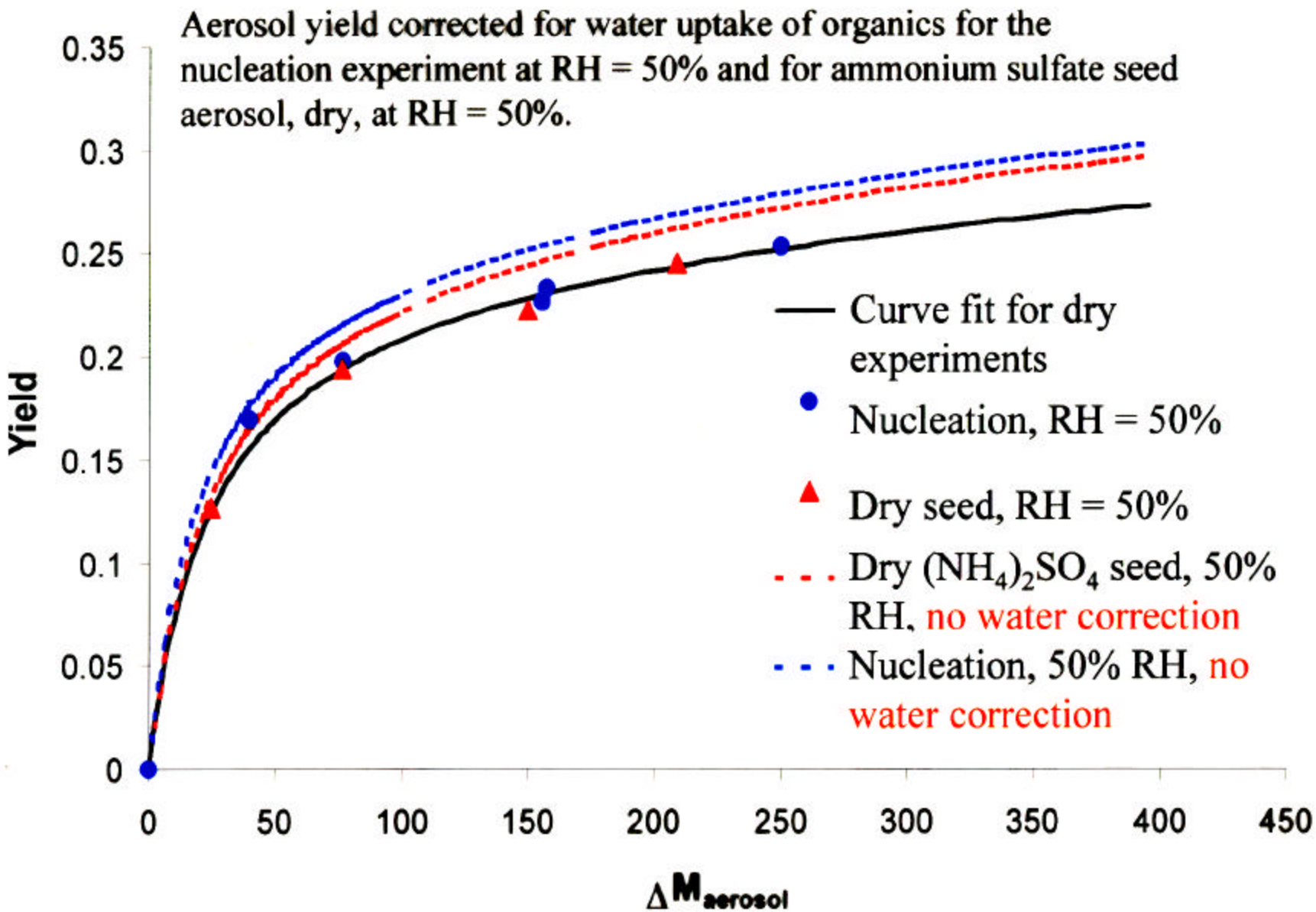
$$H_i = AQ_i \gamma_{i,aq} / G_i$$

$$AQ_i \longleftrightarrow AQ_i^- \longleftrightarrow AQ_i^{2-}$$

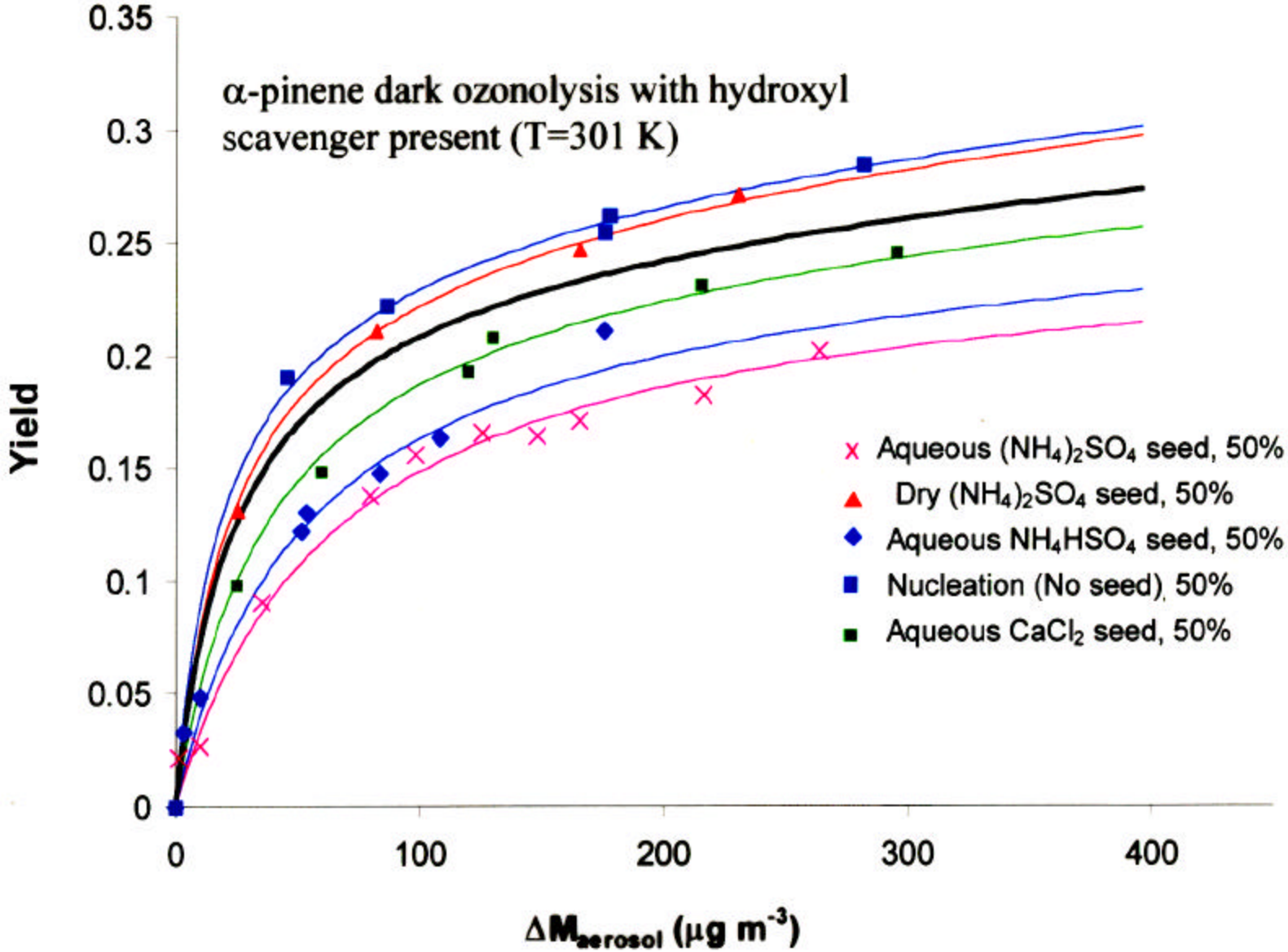
Types of Experiments

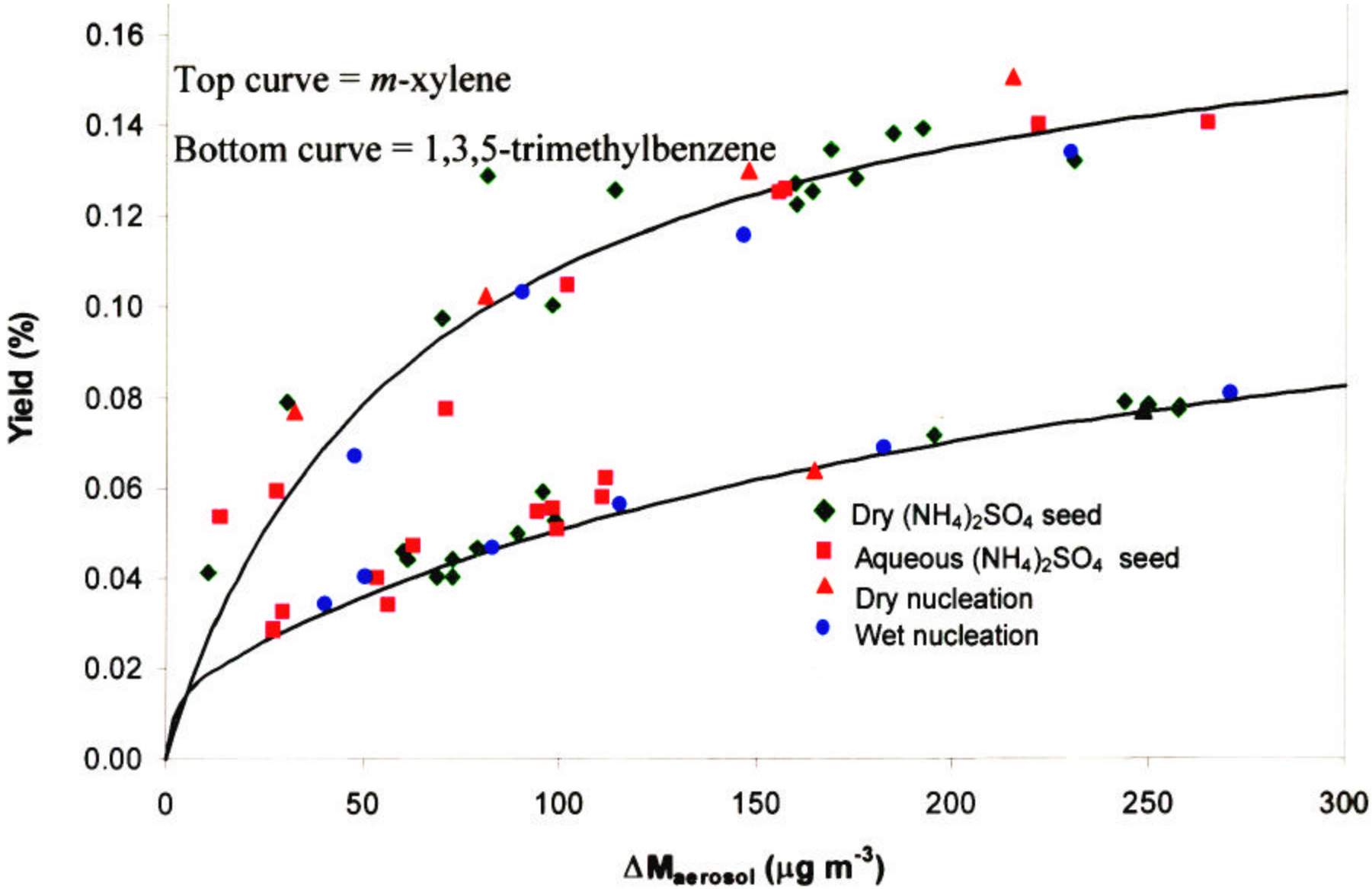
- Nucleation-no seed
  - RH<2%
  - RH=50%
- Dry seed
  - RH<2% $(NH_4)_2(SO_4)$, $(NH_4)HSO_4$
  - RH=50% $(NH_4)_2(SO_4)$
- Aqueous seed
  - RH=50% $(NH_4)_2(SO_4)$, $(NH_4)HSO_4$, $CaCl_2$

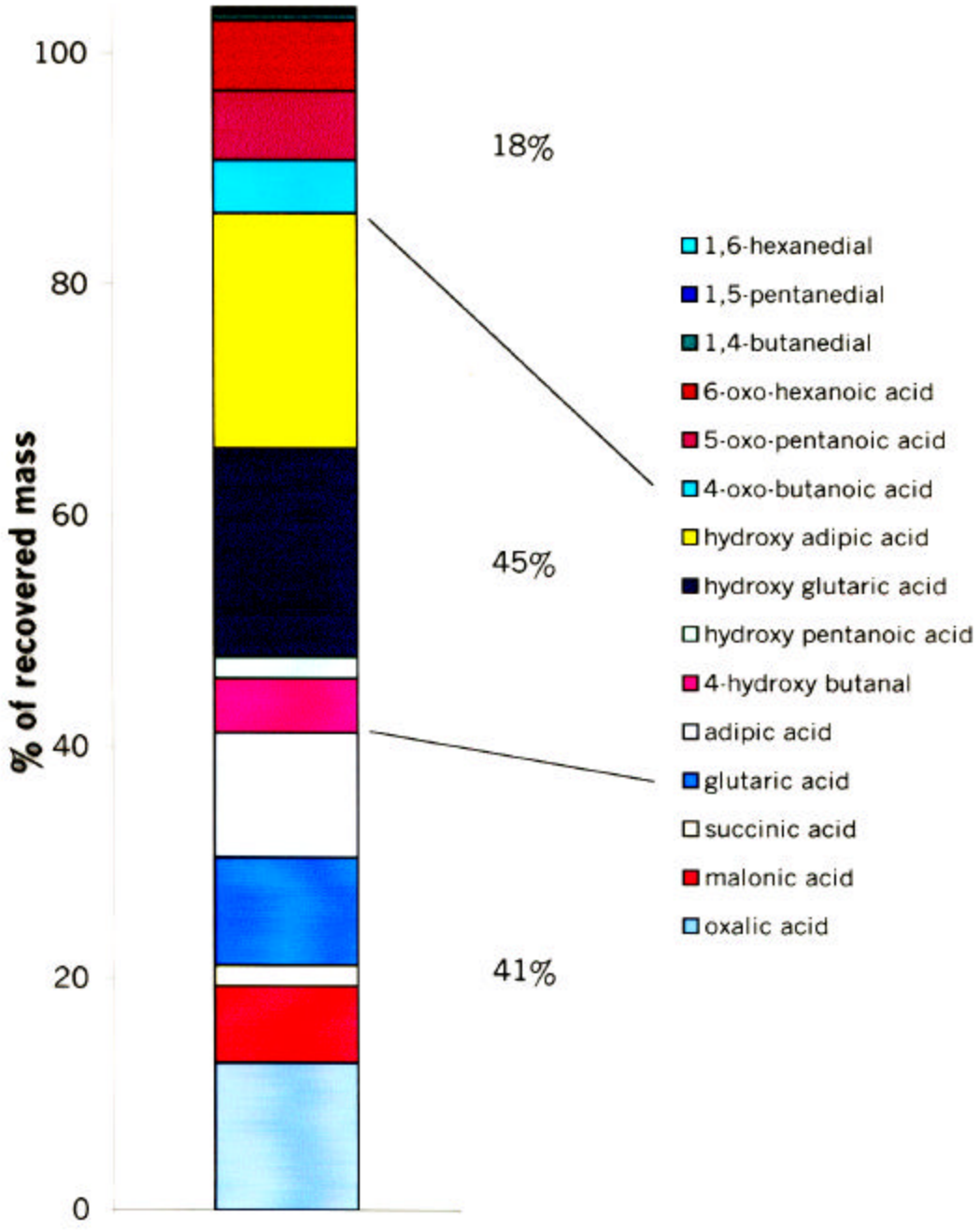

Comparison of SOA Yields at Low Relative Humidity
α-pinene dark ozonolysis with
hydroxyl scavenger present
(T=301 K)
Yield
0.3
0.25
0.2
0.15
0.1
0.05
0
0
50
100
150
200
250
ΔM_org (μg m^-3)
Dry (NH4)2SO4 seed, <2%
Dry NH4HSO4 seed, <2%
Nucleation (No seed), <2%
Experimentally fit data


Aerosol yield corrected for water uptake of organics for the nucleation experiment at RH = 50% and for ammonium sulfate seed aerosol, dry, at RH = 50%.
Yield
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
50
100
150
200
250
300
350
400
450
ΔM aerosol
Curve fit for dry experiments
Nucleation, RH = 50%
Dry seed, RH = 50%
Dry $(NH_4)_2SO_4$ seed, 50% RH, no water correction
Nucleation, 50% RH, no water correction

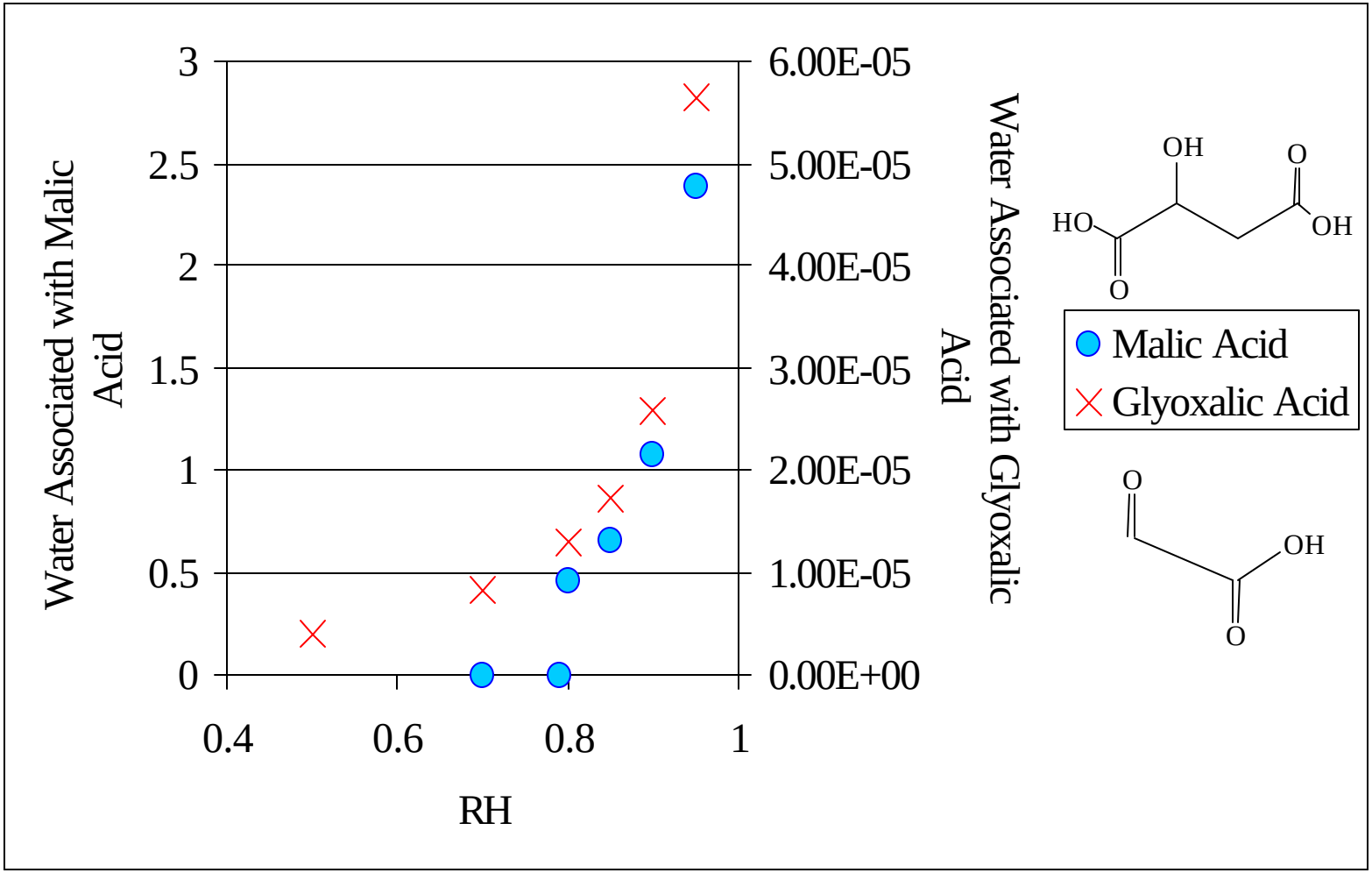
Aerosol Yield not Corrected for Water Uptake




Top curve = *m*-xylene
Bottom curve = 1,3,5-trimethylbenzene
Yield (%)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
250
300
$\Delta M_{aerosol}$ ($\mu g\ m^{-3}$)
Dry $(NH_4)_2SO_4$ seed
Aqueous $(NH_4)_2SO_4$ seed
Dry nucleation
Wet nucleation

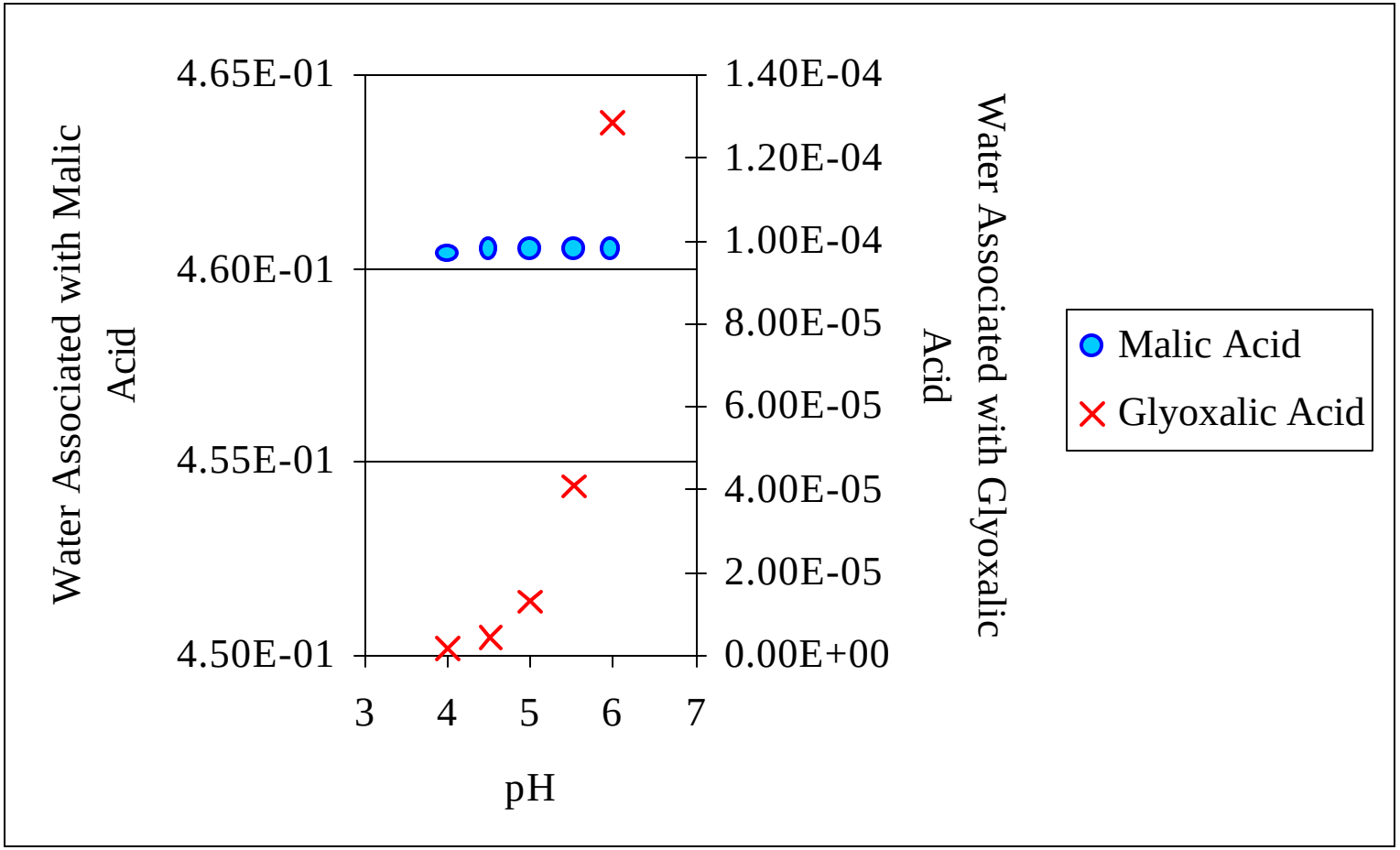

% of recovered mass
100
80
60
40
20
0
18%
45%
41%
1,6-hexanedial
1,5-pentanedial
1,4-butanedial
6-oxo-hexanoic acid
5-oxo-pentanoic acid
4-oxo-butanoic acid
hydroxy adipic acid
hydroxy glutaric acid
hydroxy pentanoic acid
4-hydroxy butanal
adipic acid
glutaric acid
succinic acid
malonic acid
oxalic acid

Hydrophilic Module Evaluation



Units: ng m^{-3} LWC = 1 μg m^{-3}, pH = 5, solute 1 ng m^{-3}

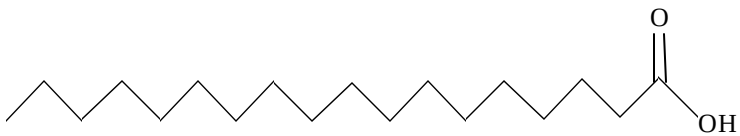
Hydrophilic Module Evaluation



Units: ng m^{-3}

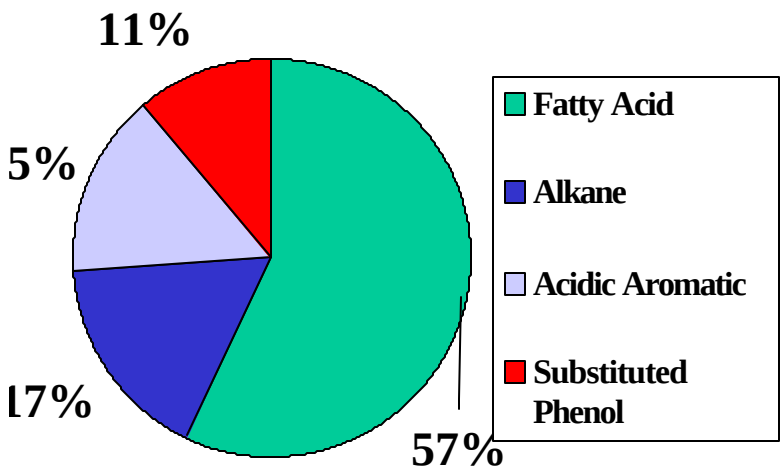
LWC = 1 μg m^{-3}, RH = 0.8, solute 1 ng m^{-3}

Hydrophobic Module Evaluation



Octadecanoic Acid

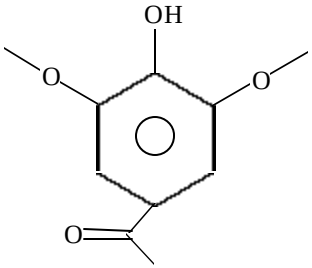
Partitioning medium (f_{om} = 0.1):



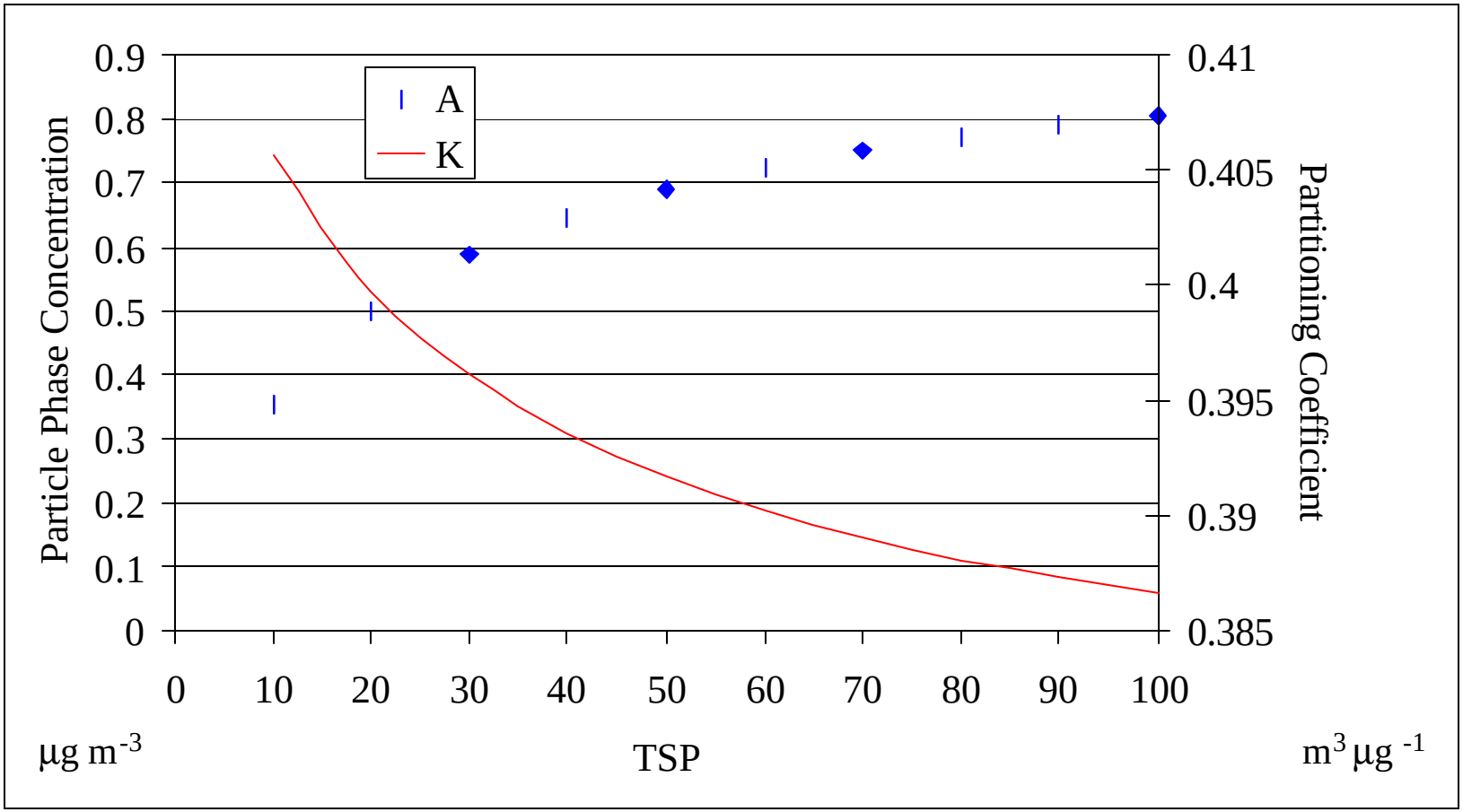
C_{24}

C_{29}

Phthalic

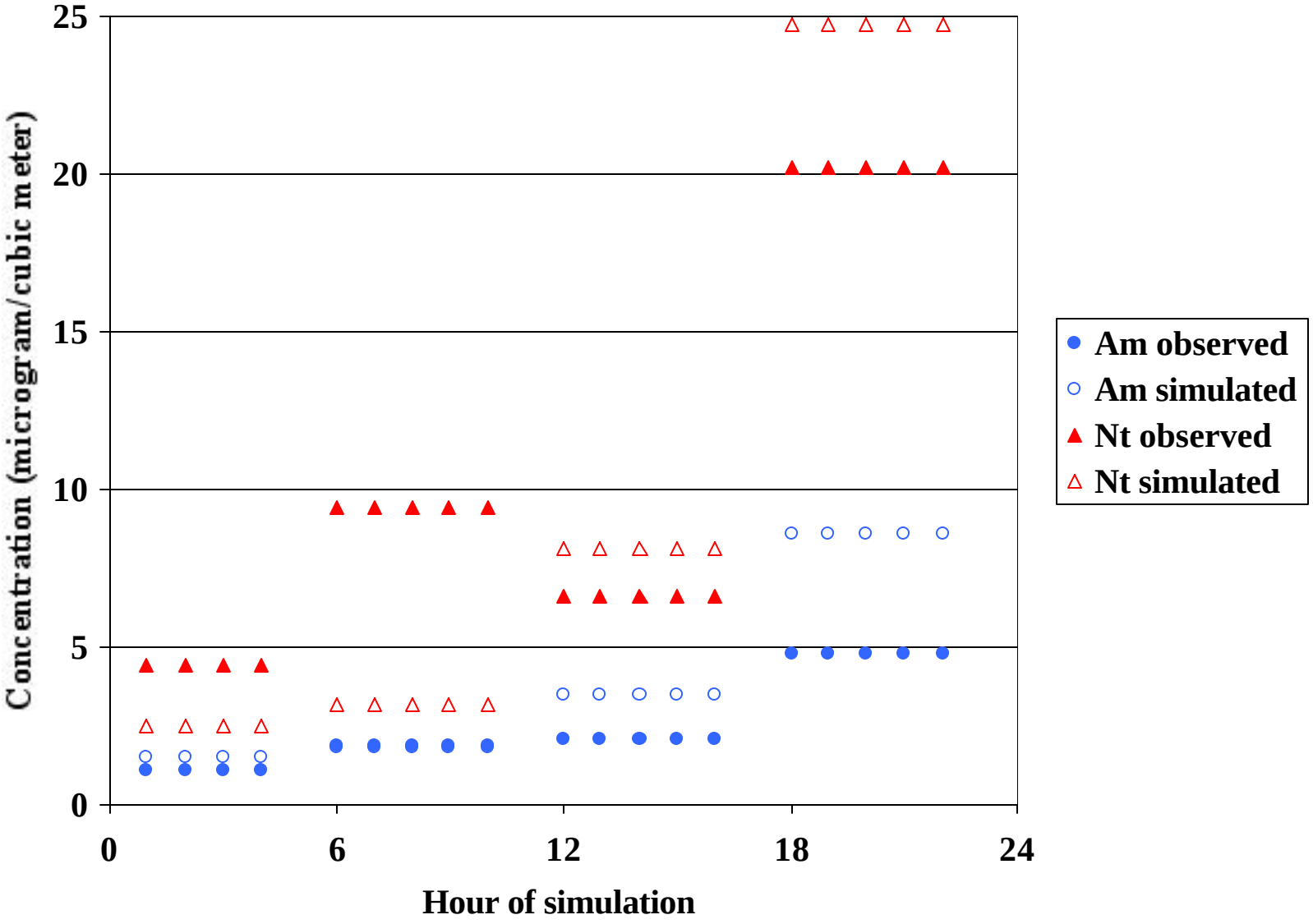


Hydrophobic Module Evaluation

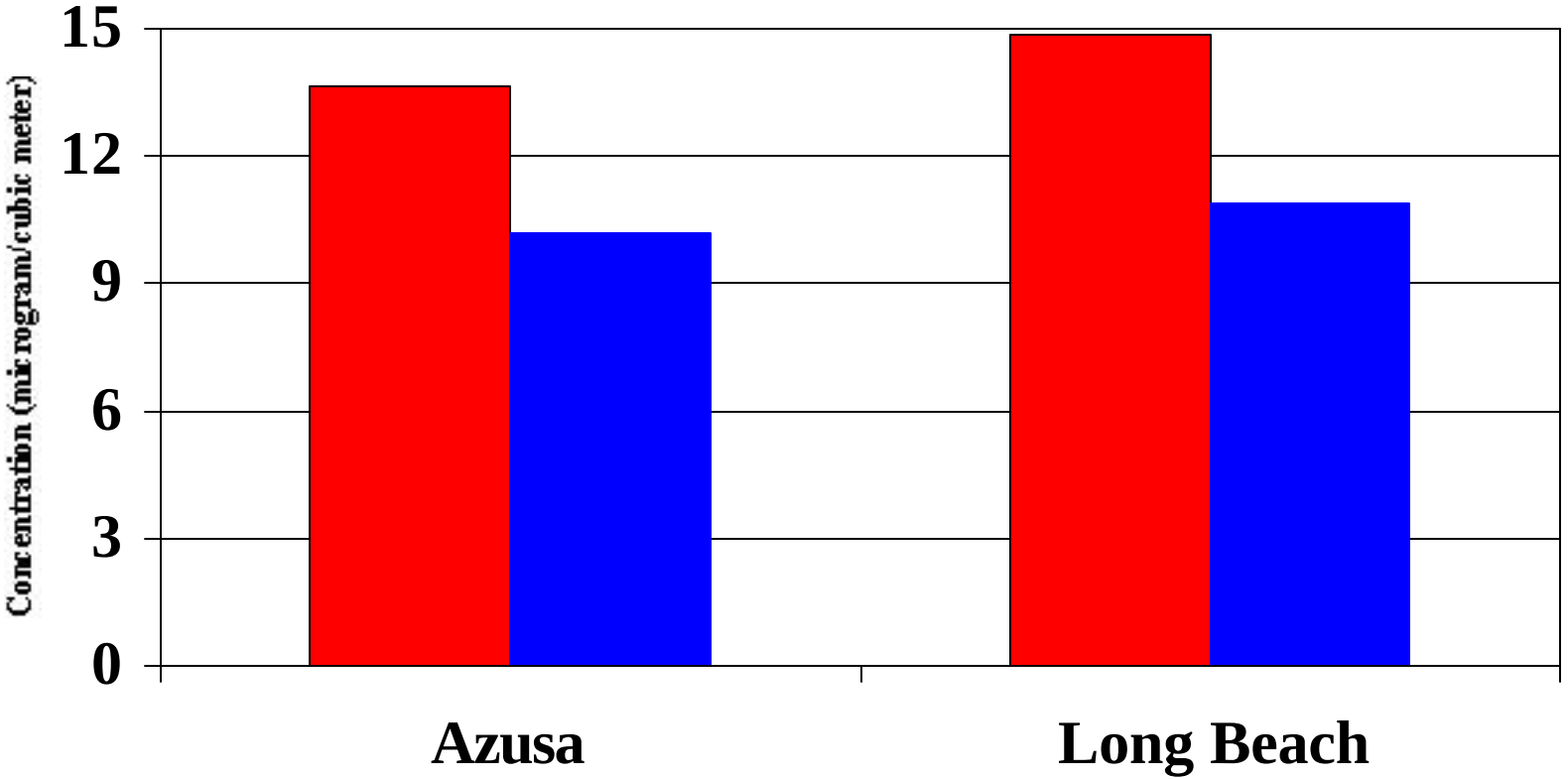


Total condensable = 1 µg m^{-3}

Inorganic Aerosol Predictions, Azusa, September 8, 1993



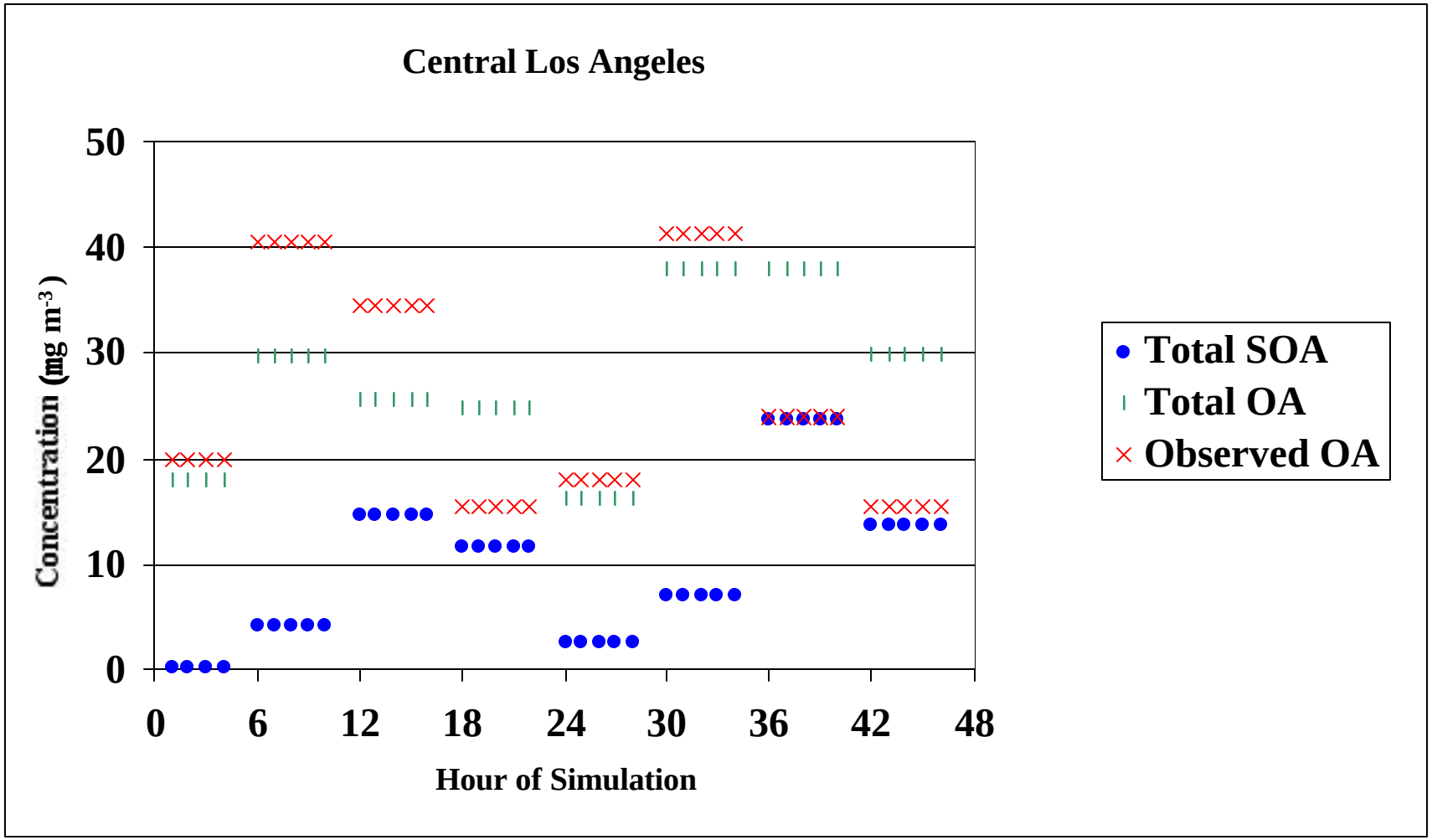
Nitrate PM_{10}: September 8, 1993



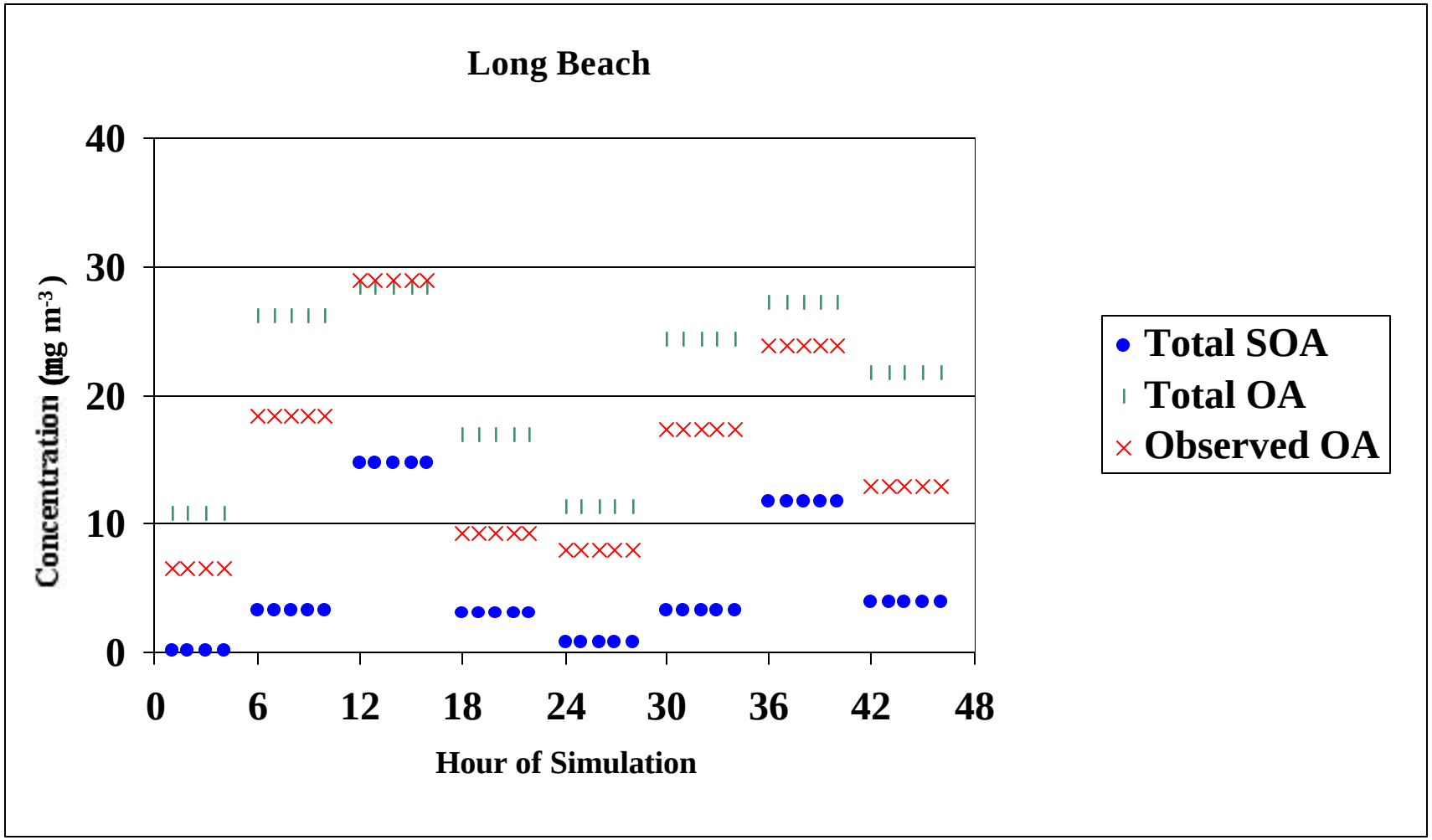
Red, Simulation

Blue, Observed

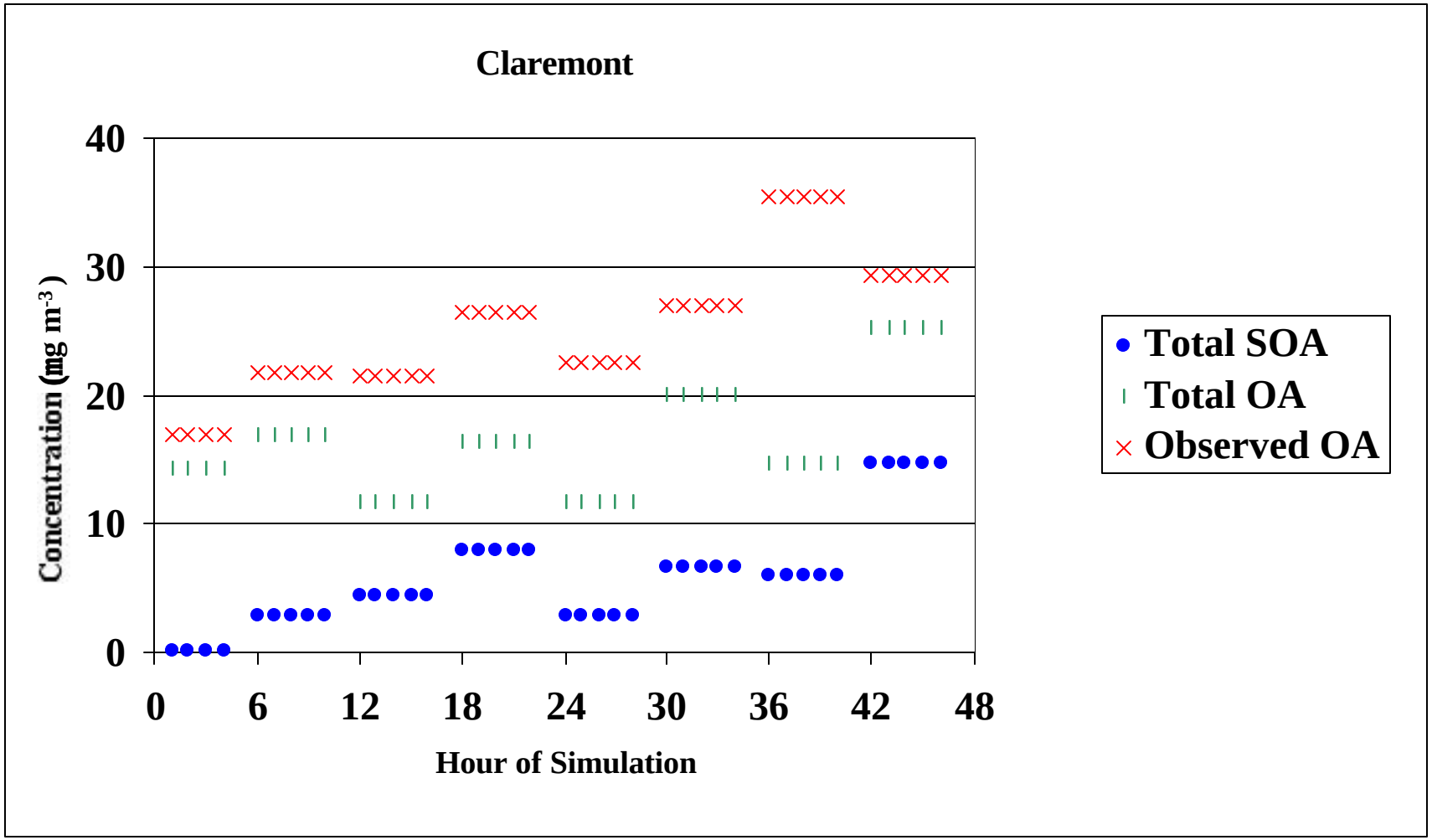
Organic Aerosol PM_{10}: September 8-9, 1993



Organic Aerosol PM_{10}: September 8-9, 1993

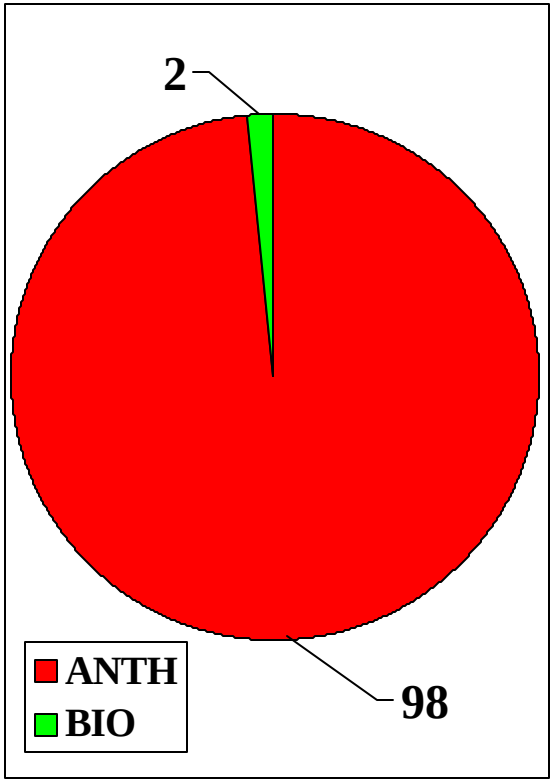


Organic Aerosol PM_{10}: September 8-9, 1993

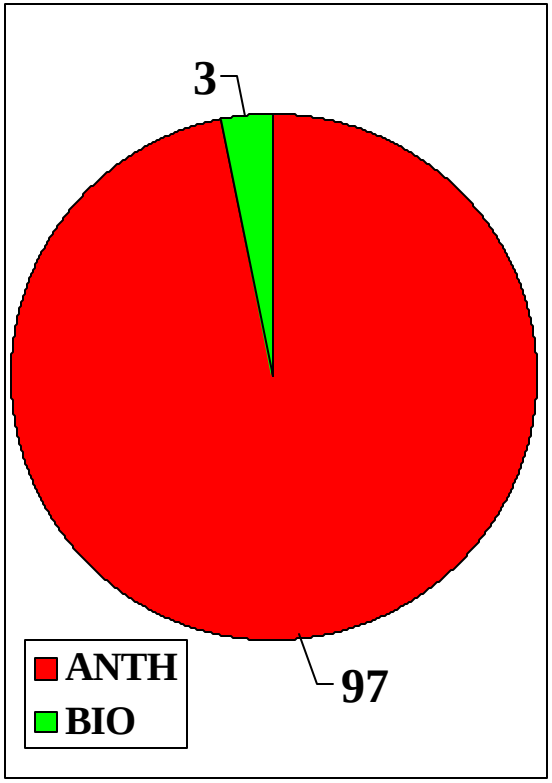


Anthropogenic versus Biogenic: 2PM September 8

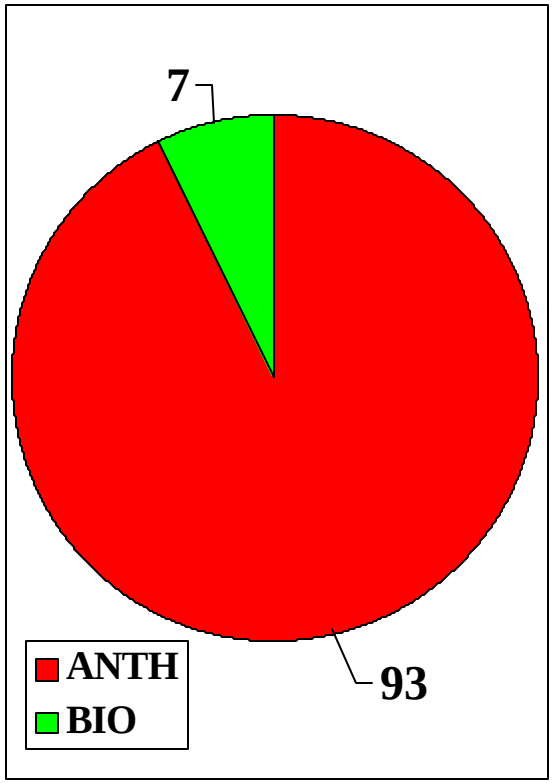
Central LA



Azusa

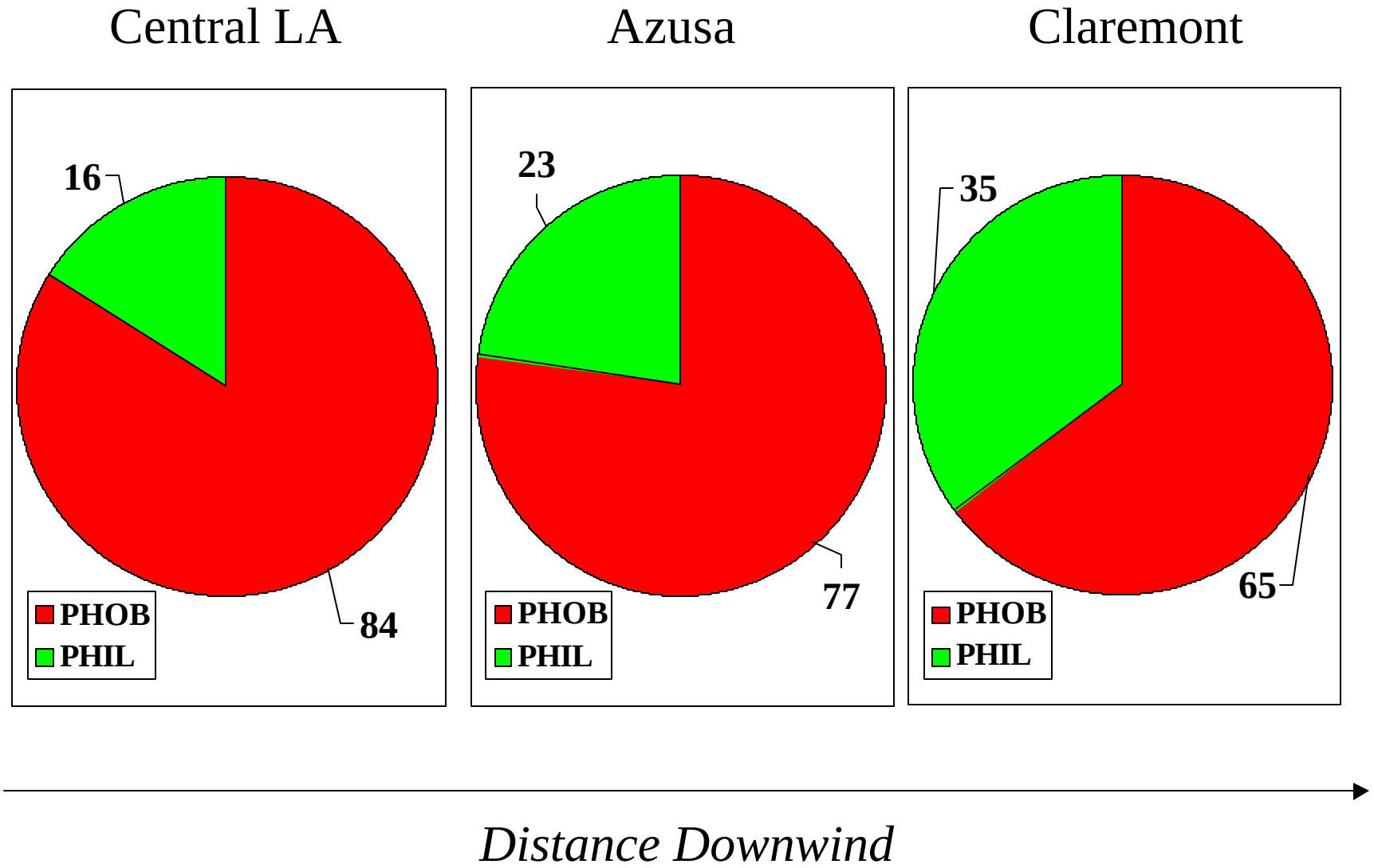


Claremont

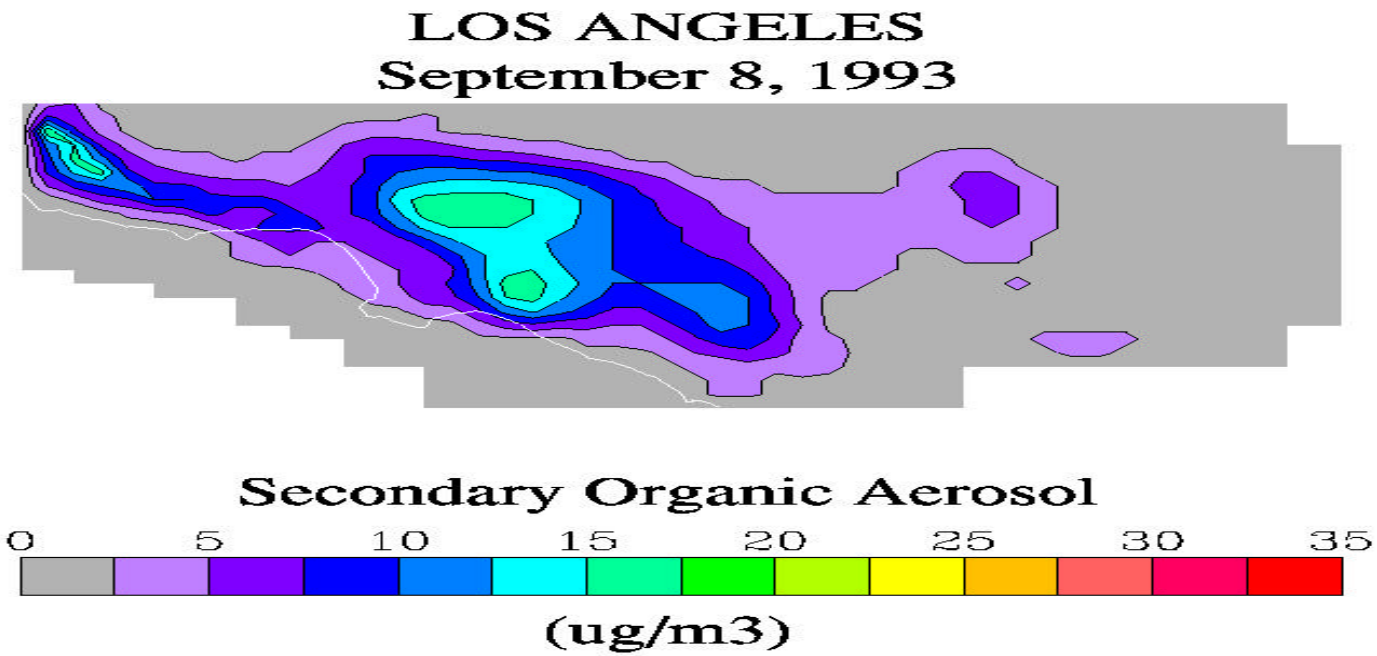
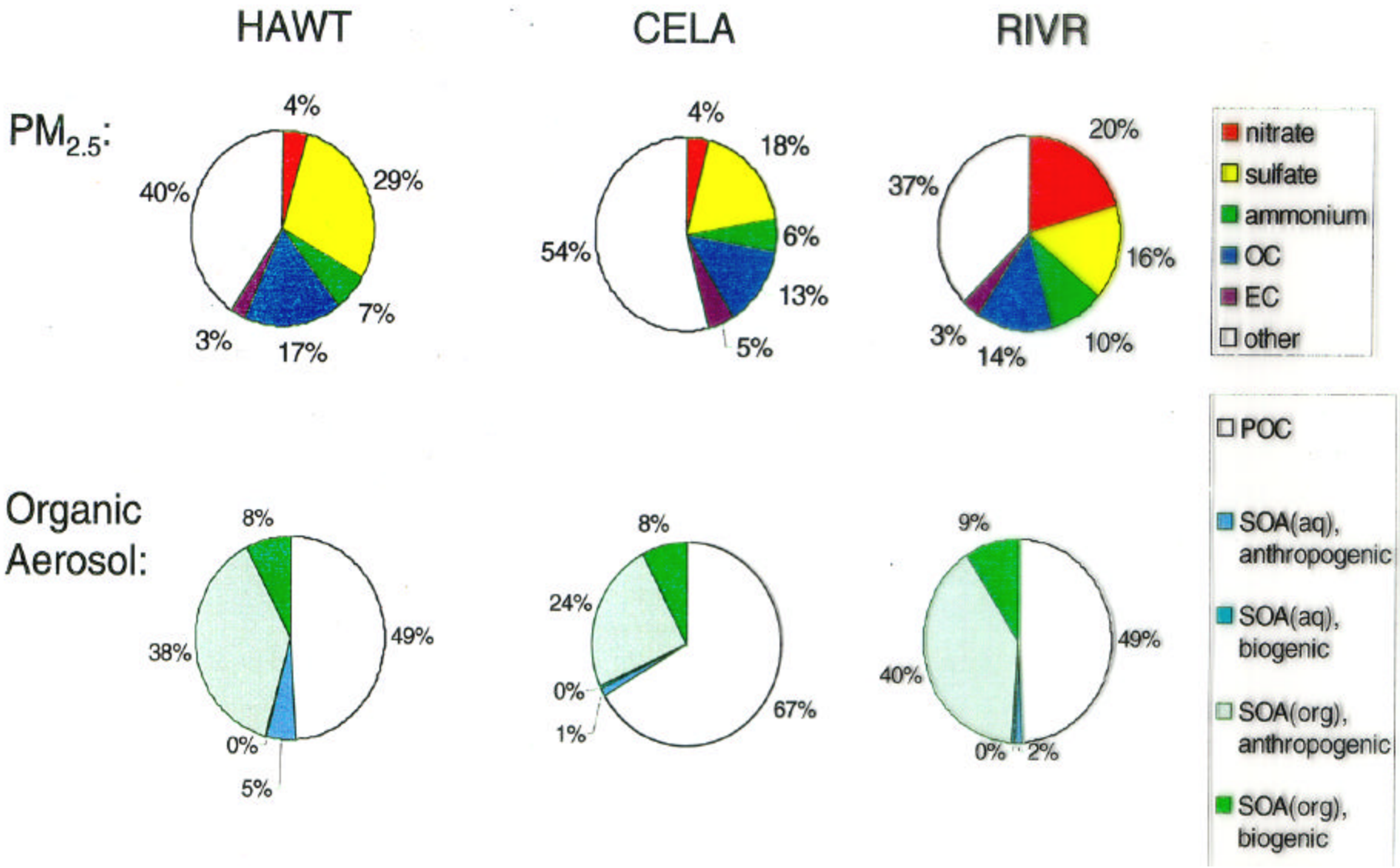


Distance Downwind

Hydrophobic versus Hydrophilic: 2PM September 8



SOA in the SOCAB: Decoupled Module, 2PM



SOA Contribution