Estimating Total Particle Formation Using Environmental Chambers

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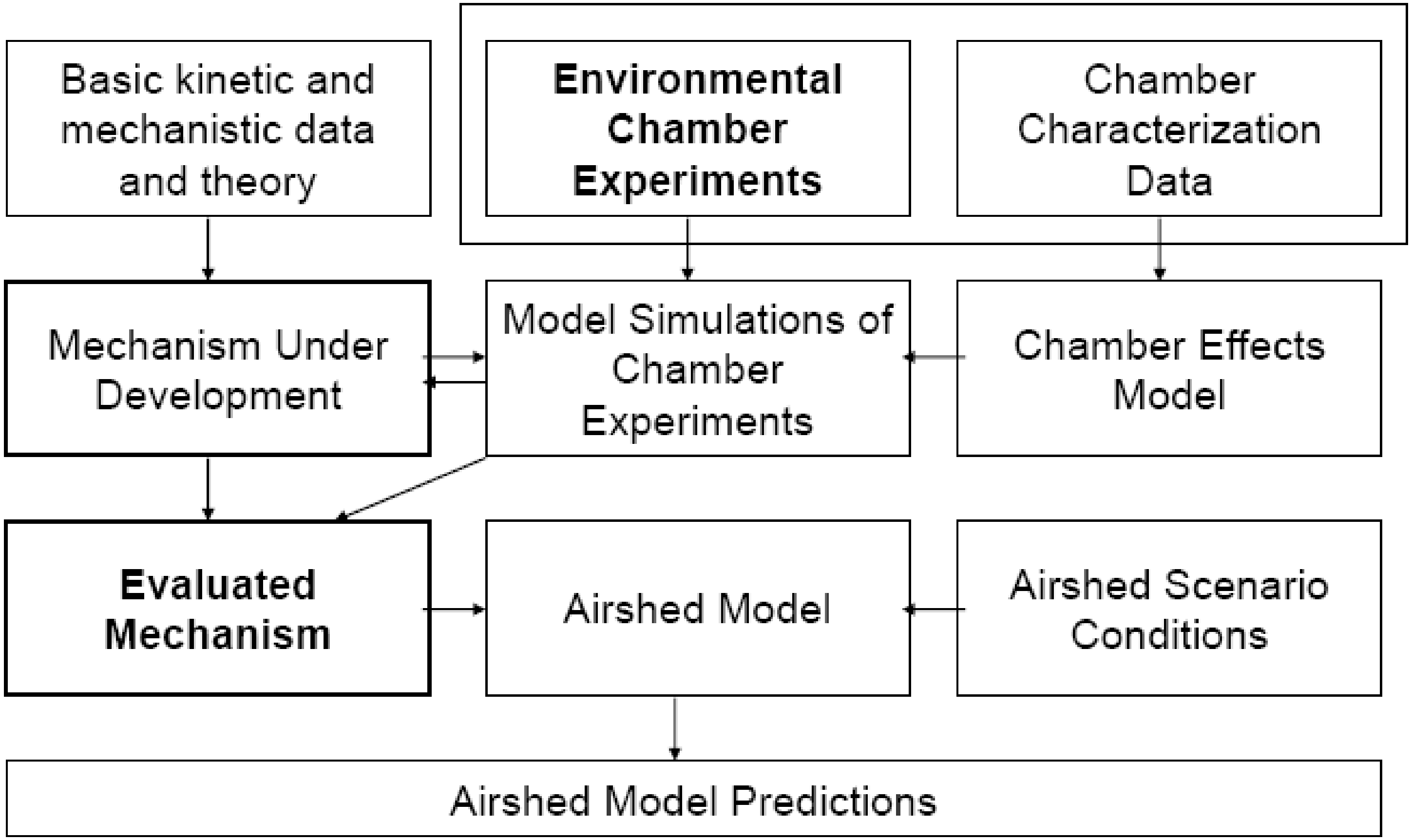
Traditional Environmental Chambers

- Laboratory chambers are indispensable in the study of gas-phase atmospheric chemistry and atmospheric aerosol formation and growth. Because of the difficulty of isolating chemical and microphysical processes in the atmosphere from flow and mixing effects, chamber studies provide the means to develop mechanistic understanding of such processes. In this context, a laboratory chamber constitutes a well-mixed batch reactor in which the chemical processes of interest can be isolated directly.

Relationship Between Mechanisms, Chamber Data and Airshed Models



Basic kinetic and mechanistic data and theory

Environmental Chamber Experiments

Chamber Characterization Data

Mechanism Under Development

Model Simulations of Chamber Experiments

Chamber Effects Model

Evaluated Mechanism

Airshed Model

Airshed Scenario Conditions

Airshed Model Predictions

Carter et al., 2006, Mechanism Conference, http://www.cert.ucr.edu/~carter/Mechanism_Conference/17%20C%20carter.pdf
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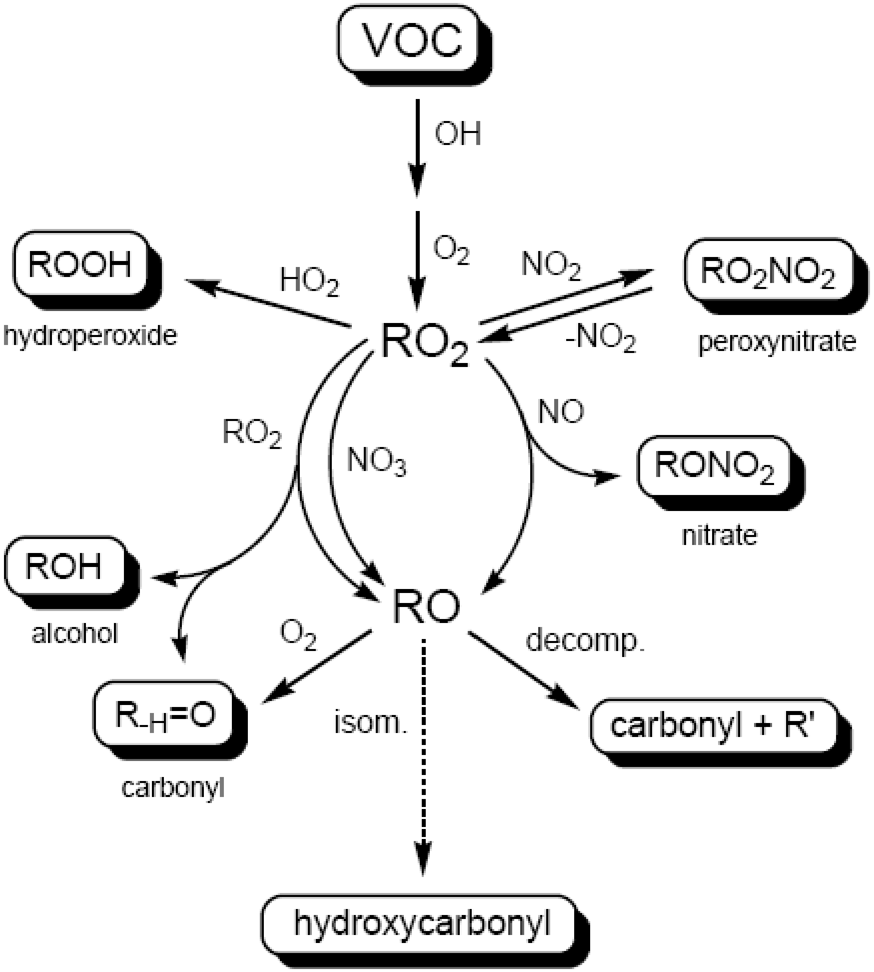


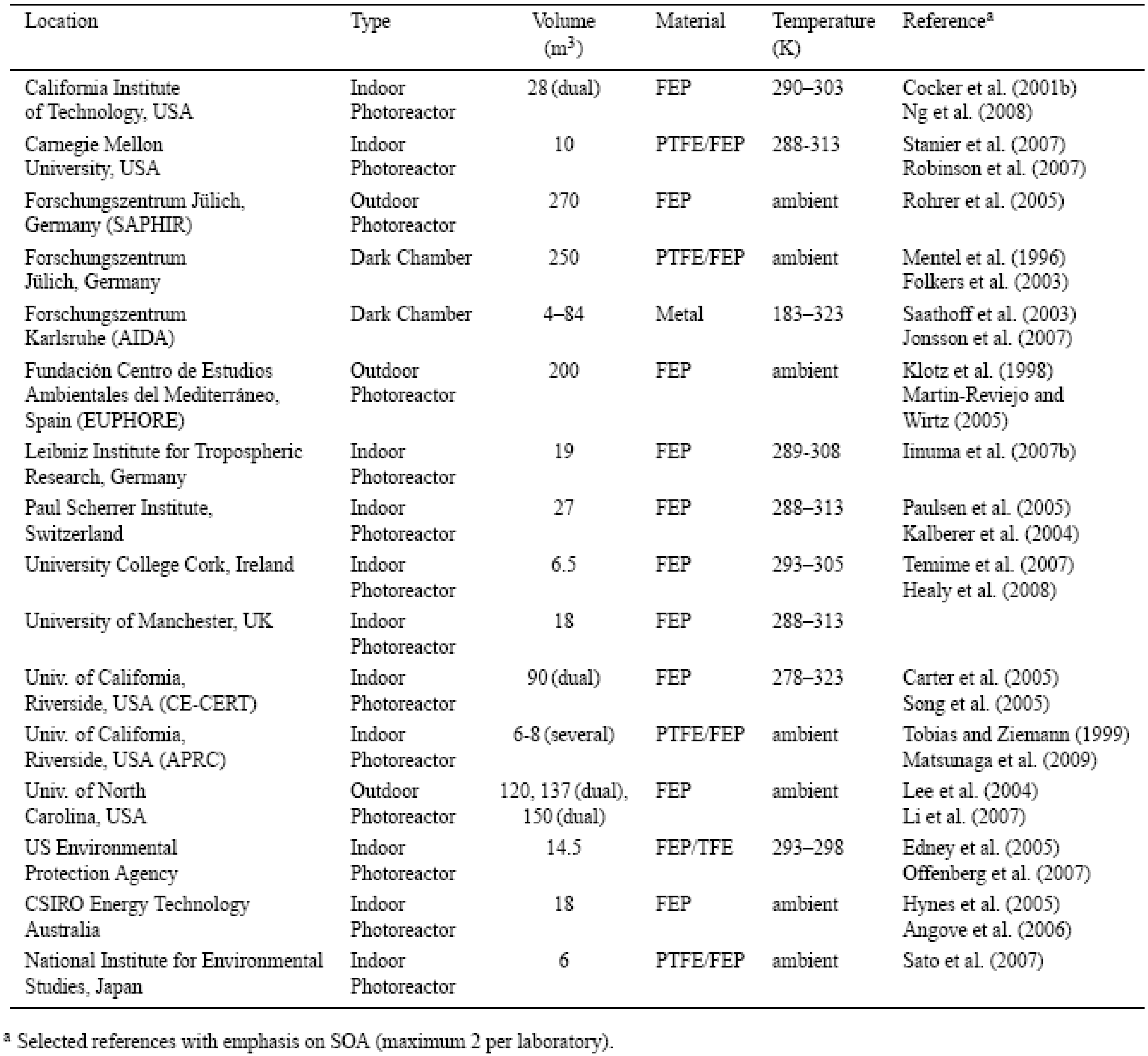
Fig. 2. Simplified schematic of the OH-initiated degradation of generic VOCs to form first-generation products.

Hallquist et al., 2009, ACP:9, 5155-5236

Indoor vs. Outdoor

- Pros (Outdoor) – Natural sunlight provides full spectrum of wavelengths; allows for photolysis of more products
- Con (Outoor) – Difficult to control photolysis due to changes in weather, clouds, etc. makes replication of experiment difficult; temperature and relative humidity are dictated by environment and will fluctuate during course of experiment

Select Chambers



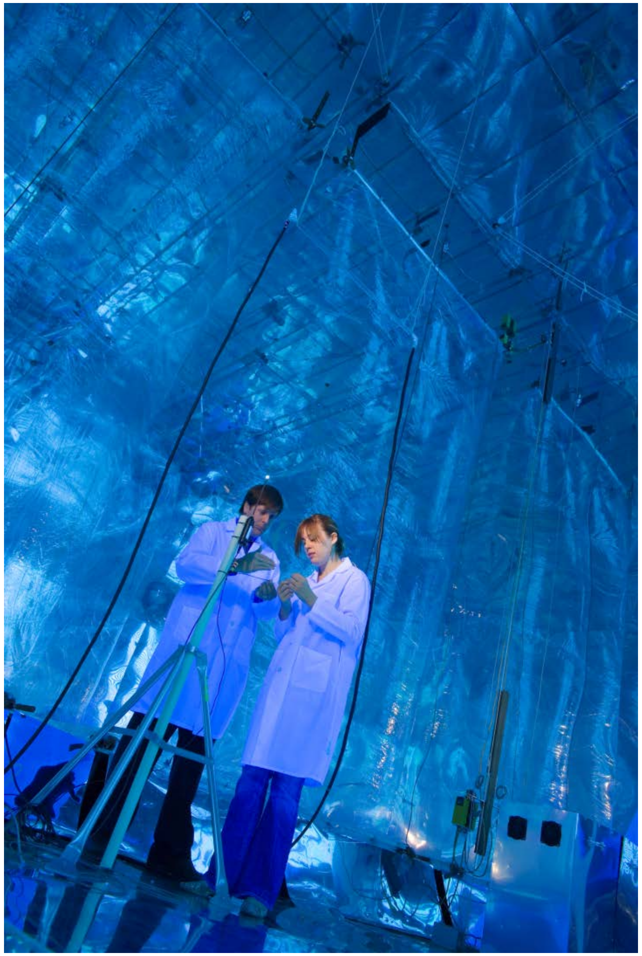
Location	Type	Volume (m^3)	Material	Temperature (K)	Reference[a]
California Institute of Technology, USA	Indoor Photoreactor	28 (dual)	FEP	290–303	Cocker et al. (2001b) Ng et al. (2008)
Carnegie Mellon University, USA	Indoor Photoreactor	10	PTFE/FEP	288-313	Stanier et al. (2007) Robinson et al. (2007)
Forschungszentrum Jülich, Germany (SAPHIR)	Outdoor Photoreactor	270	FEP	ambient	Rohrer et al. (2005)
Forschungszentrum Jülich, Germany	Dark Chamber	250	PTFE/FEP	ambient	Mentel et al. (1996) Folkers et al. (2003)
Forschungszentrum Karlsruhe (AIDA)	Dark Chamber	4–84	Metal	183–323	Saathoff et al. (2003) Jonsson et al. (2007)
Fundación Centro de Estudios Ambientales del Mediterráneo, Spain (EUPHORE)	Outdoor Photoreactor	200	FEP	ambient	Klotz et al. (1998) Martin-Reviejo and Wirtz (2005)
Leibniz Institute for Tropospheric Research, Germany	Indoor Photoreactor	19	FEP	289-308	Iinuma et al. (2007b)
Paul Scherrer Institute, Switzerland	Indoor Photoreactor	27	FEP	288–313	Paulsen et al. (2005) Kalberer et al. (2004)
University College Cork, Ireland	Indoor Photoreactor	6.5	FEP	293–305	Temime et al. (2007) Healy et al. (2008)
University of Manchester, UK	Indoor Photoreactor	18	FEP	288–313	
Univ. of California, Riverside, USA (CE-CERT)	Indoor Photoreactor	90 (dual)	FEP	278–323	Carter et al. (2005) Song et al. (2005)
Univ. of California, Riverside, USA (APRC)	Indoor Photoreactor	6-8 (several)	PTFE/FEP	ambient	Tobias and Ziemann (1999) Matsunaga et al. (2009)
Univ. of North Carolina, USA	Outdoor Photoreactor	120, 137 (dual), 150 (dual)	FEP	ambient	Lee et al. (2004) Li et al. (2007)
US Environmental Protection Agency	Indoor Photoreactor	14.5	FEP/TFE	293–298	Edney et al. (2005) Offenberg et al. (2007)
CSIRO Energy Technology Australia	Indoor Photoreactor	18	FEP	ambient	Hynes et al. (2005) Angove et al. (2006)
National Institute for Environmental Studies, Japan	Indoor Photoreactor	6	PTFE/FEP	ambient	Sato et al. (2007)

[a] Selected references with emphasis on SOA (maximum 2 per laboratory).

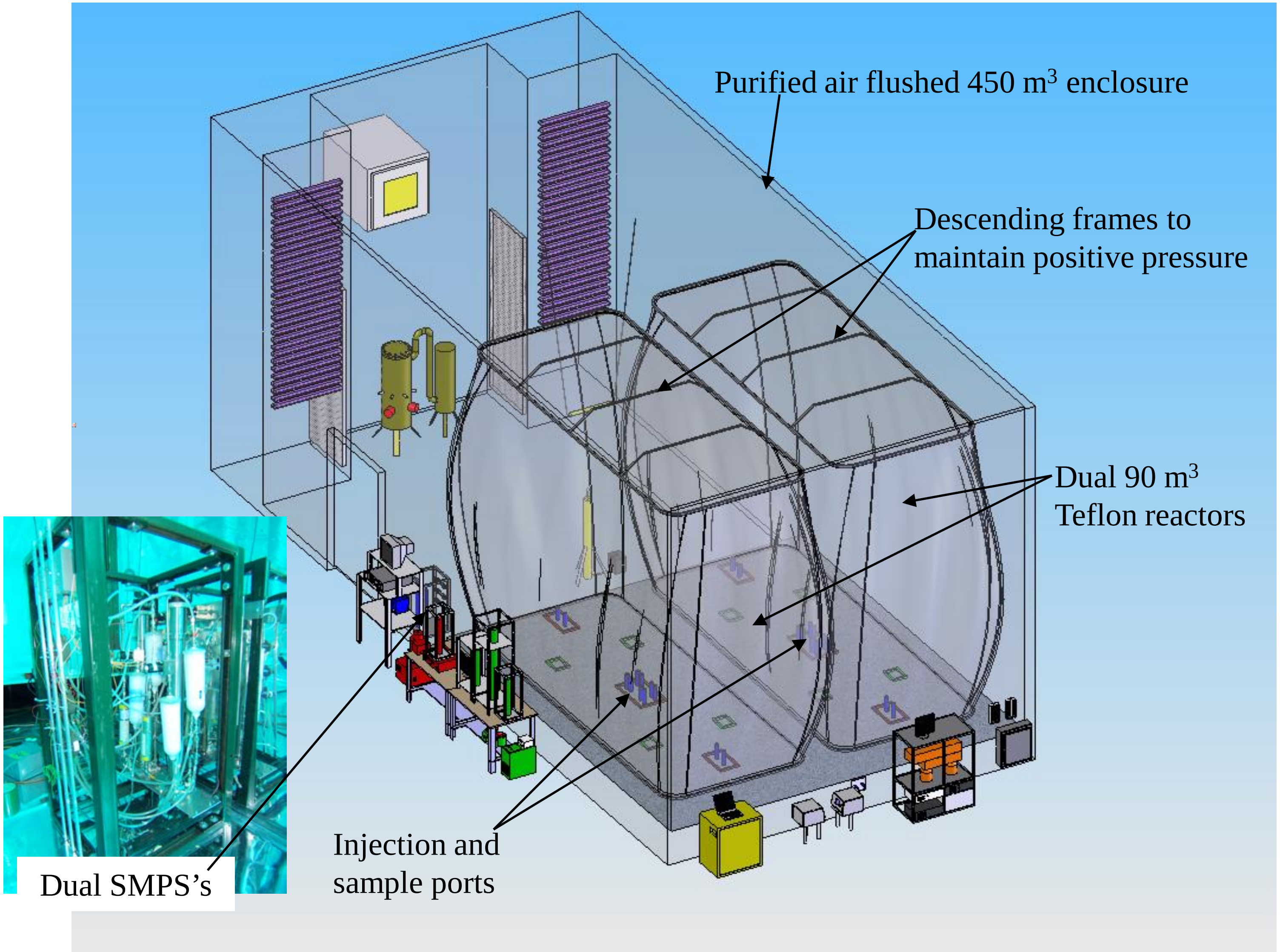
SAPHIR

Simulation of Atmospheric PHotochemistry In a large Reaction (SAPHIR) chamber in Jülich, Germany (http://www.eurochamp.org/chambers/saphir/): 270 m3

UCR Chamber Facility



UC Riverside/CE-CERT Environmental Chamber



Purified air flushed 450 m^3 enclosure

Descending frames to maintain positive pressure

Dual 90 m^3 Teflon reactors

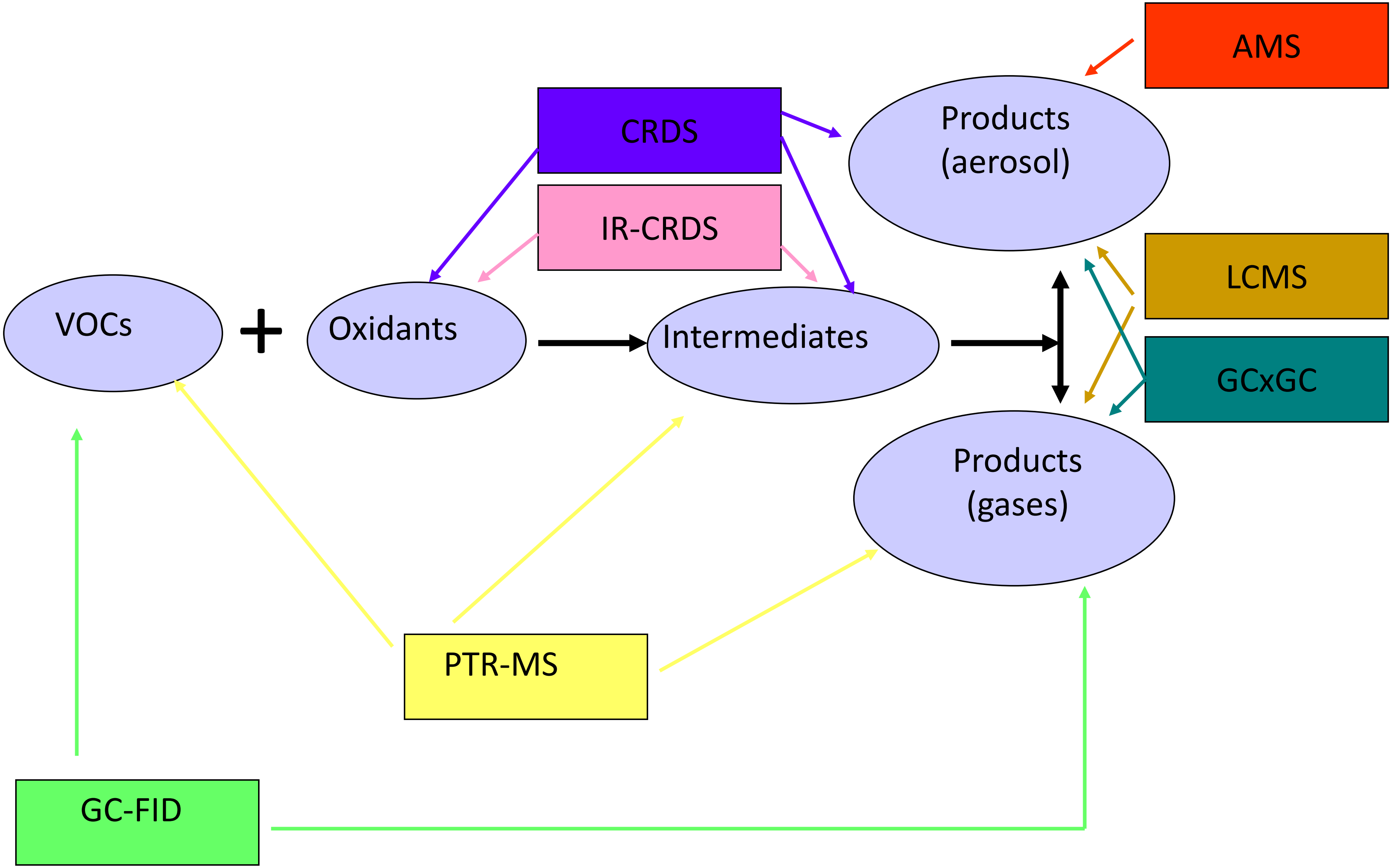
Injection and sample ports

Dual SMPS’s

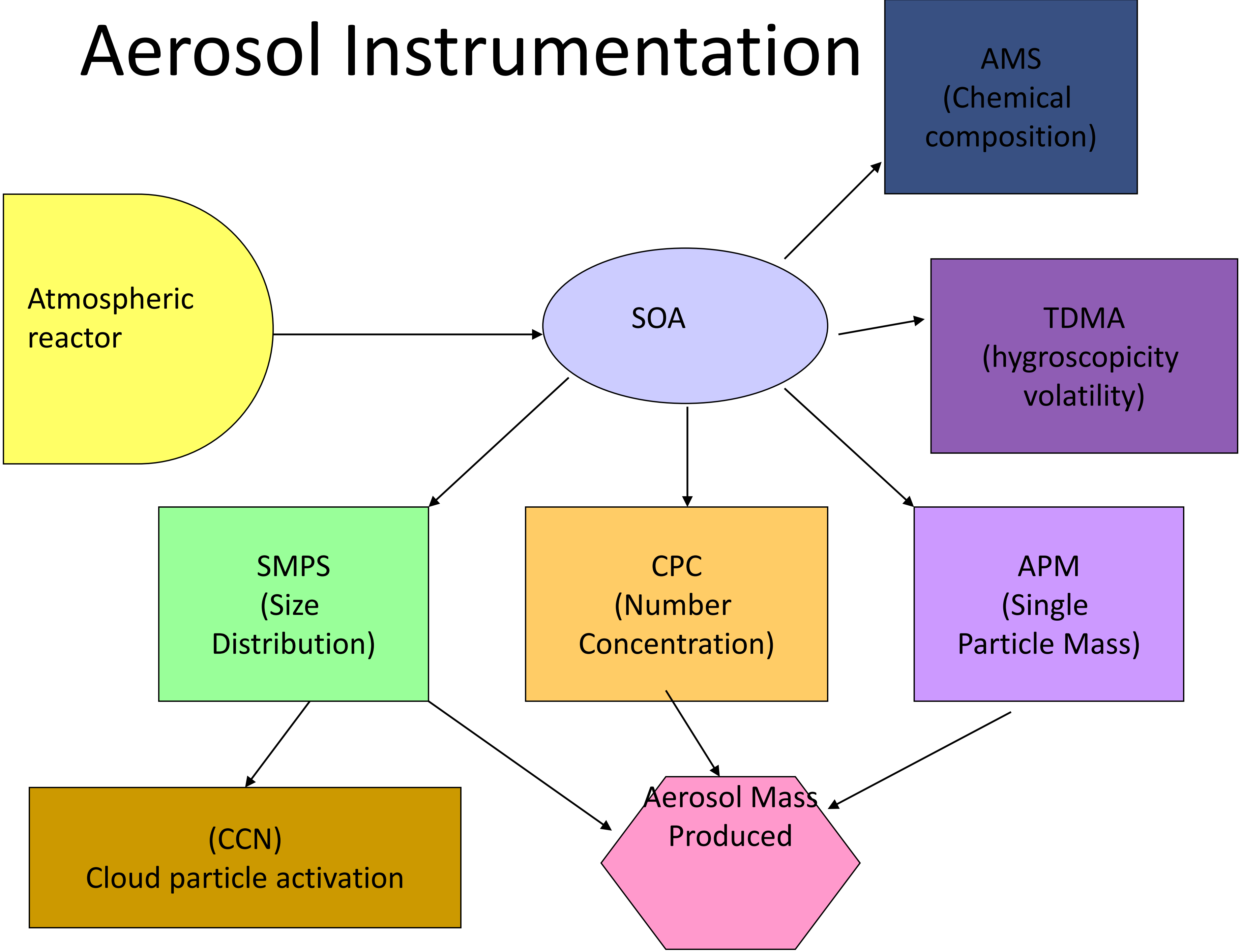
EUPHORE

EUPHORE (European PHOtoREactor) chamber in Valencia, Spain (http://www.eurochamp.org/chambers/euphore): volume = 200m3 each.

Chemical Instrumentation



Aerosol Instrumentation



Atmospheric reactor

SOA

AMS
(Chemical composition)

TDMA
(hygroscopicity volatility)

SMPS
(Size Distribution)

CPC
(Number Concentration)

APM
(Single Particle Mass)

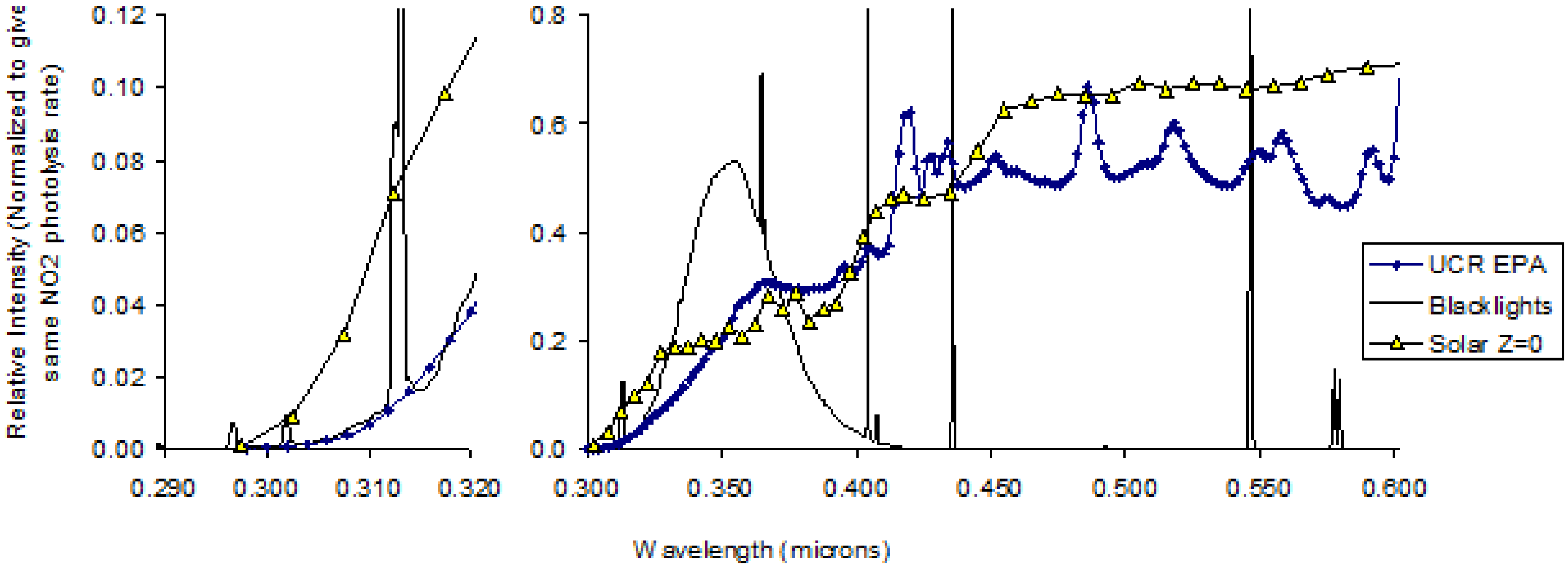
(CCN)
Cloud particle activation

Aerosol Mass Produced

Indoor vs. Outdoor

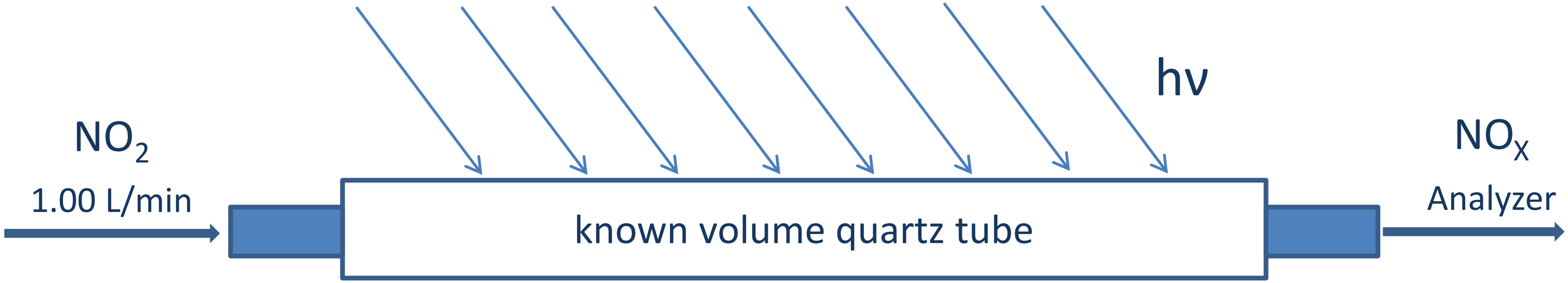
- Pros (Indoor) – Can de designed for excellent temperature and RH control, repeatable photolysis conditions
- Cons (Indoor) – Difficult to simulate natural sunlight across the solar spectrum – relative rates of photolysis may be affected

Comparison of Light Spectra



Carter et al., 2004, ARB report
http://www.cert.ucr.edu/~carter/pubs/lnoxrpt.pdf

k_1 measurement



NO_2

1.00 L/min

hν

known volume quartz tube

NO_X

Analyzer

- $NO_2 + hv \rightarrow NO + O$
- NO_2 photolysis rate k_1

$$k_1 = \frac{\Delta NO}{NO_2} \times \frac{F}{V} \times \frac{1}{\varphi} \times \frac{1}{T}$$

$(NO_2) = (NO_2)_{final} + ½ \Delta(NO)$

F: total flow rate in reactor

V: volume of quartz reactor

ϕ: quantum yield for the production of nitric oxide

T: overall transmission factor of the quartz tube for UV light

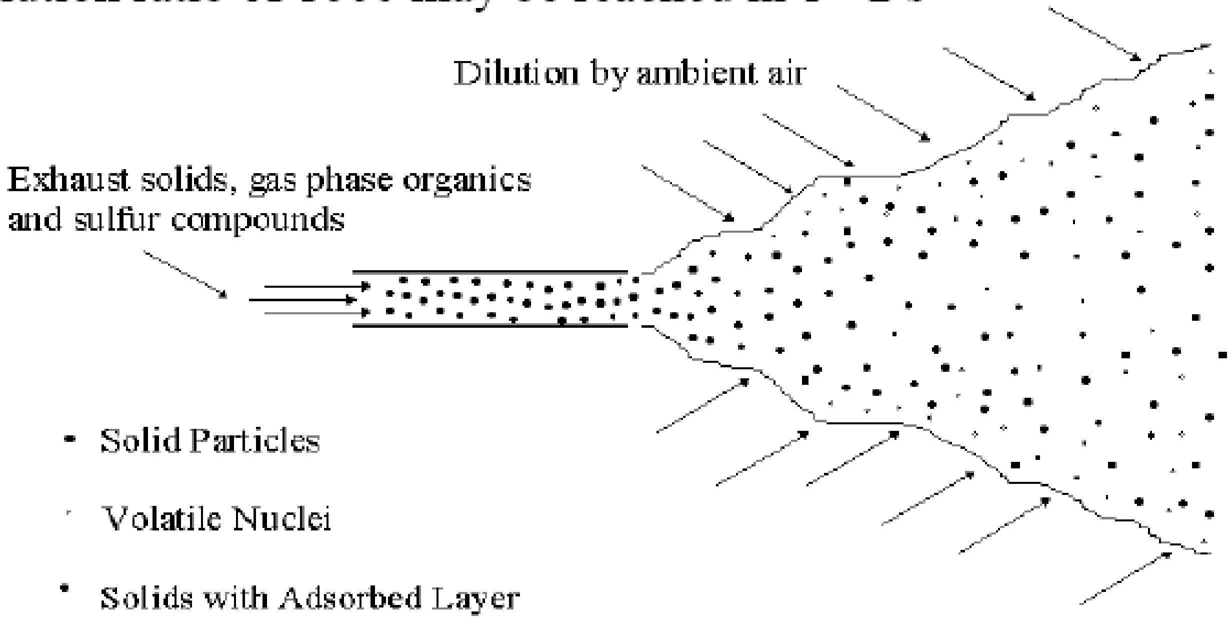
Primary vs. Secondary Particulate

Primary (direct) particulate emissions – defined by source and measurement method

(Focus of PEMS conference)

Atmospheric dilution leads to nucleation, absorption, and adsorption - in excess of 90 % of the particle number may form as the exhaust dilutes

A dilution ratio of 1000 may be reached in 1 - 2 s



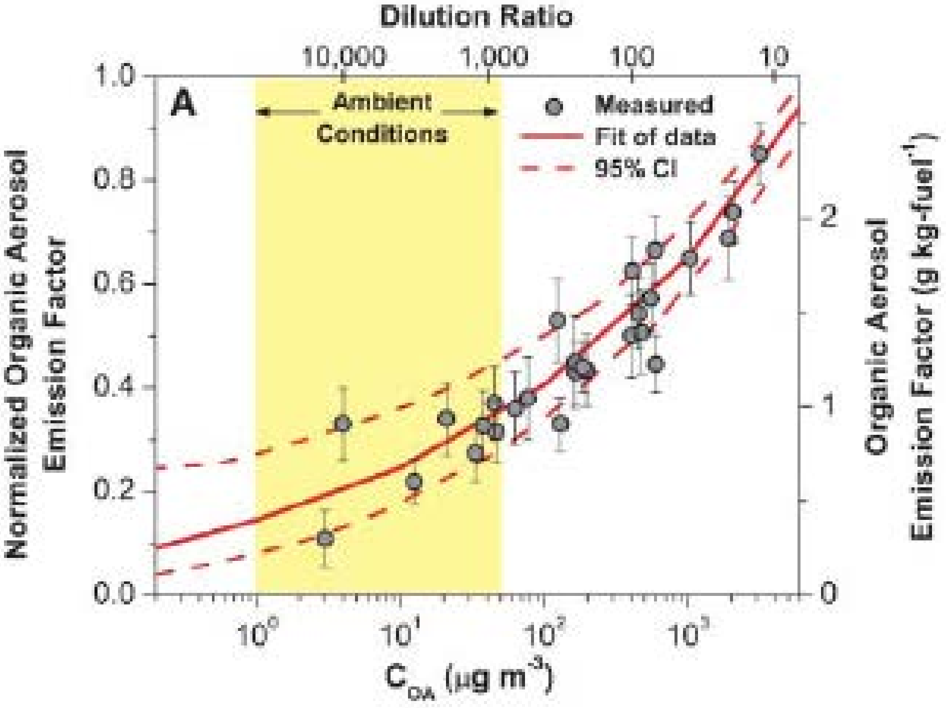
Exhaust solids are mainly solid carbon (EC) and ash from lube oil
Volatiles include organic carbon (OC) and sulfuric acid

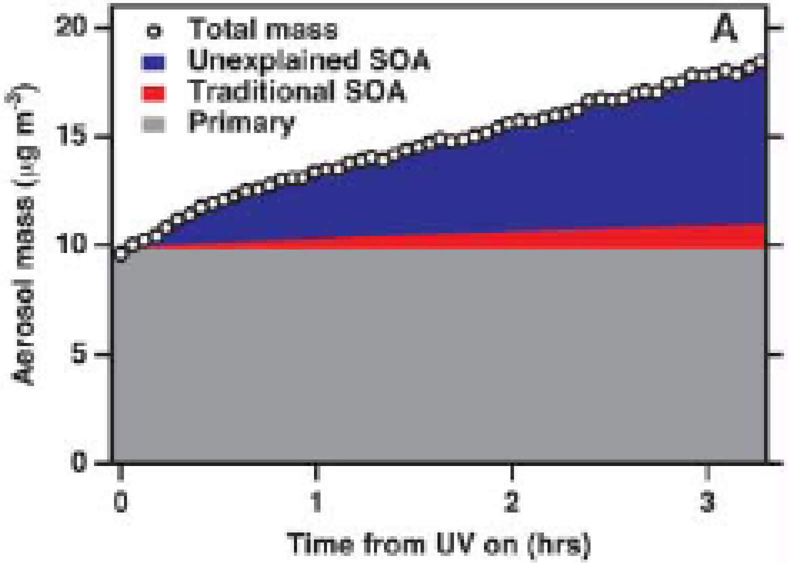
Kittelson, 2008, AQMD Ultrafine Conference

SOA from POA?

- Significant fraction of POA volatilize at higher dilution ratio (~ambient condition)
- Traditional SOA precursors cannot explain SOA from diesel exhaust

SOA from “Intermediate/Semi”-volatility Organic Compounds (IVOCs, SVOCs)





Robinson et al., 2007, *Science*

Primary vs. Secondary Particulate

Primary (direct) particulate emissions – defined by source and measurement method

+ NO_x

(Also focus of PEMS conference)

Primary vs. Secondary Particulate

Primary (direct) particulate emissions – defined by source and measurement method

+ NO_x

+ organic vapors

Primary vs. Secondary Particulate

Primary (direct) particulate emissions – defined by source and measurement method

+ ammonia

+ NO_x

+ organic vapors

Primary vs. Secondary Particulate

Primary (direct) particulate emissions – defined by source and measurement method

+ ammonia

+ NO_x

+ organic vapors

Gases undergo subsequent reaction in the atmosphere leading to the formation of additional particulate referred to as secondary particulate

Atmospheric Chemistry Takes Over

Organic vapors + NO_x + sunlight → ozone

Atmospheric Chemistry Takes Over

Organic vapors + NO_x + sunlight → ozone

AND Organic vapors with decreasing vapor pressure (condensable vapors)

Atmospheric Chemistry Takes Over

Organic vapors + NO_x + sunlight → ozone

AND Organic vapors with decreasing vapor pressure (condensable vapors)

AND Nitric acid

Atmospheric Chemistry Takes Over

Organic vapors + NO_x + sunlight → ozone

AND Organic vapors with decreasing vapor pressure (condensable vapors)
AND Nitric acid
AND Ammonium nitrate (if ammonia present)

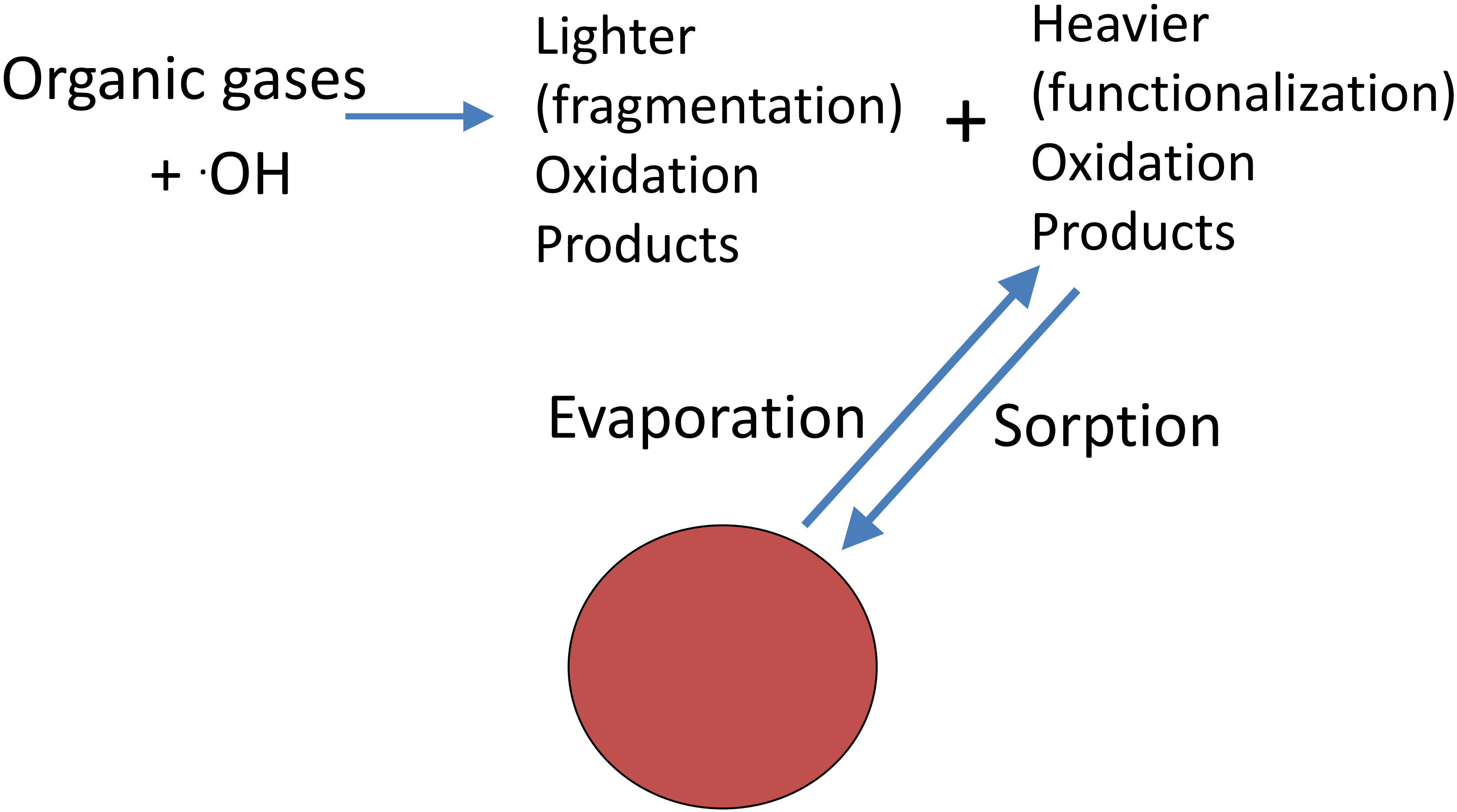
Inorganic Secondary Particulate

$$\text{NO + ozone} \longrightarrow NO_2 \xrightarrow{\cdot OH} HNO_3 \xrightarrow{NH_3} NH_4NO_3$$

Similarly,

$$SO_2 \text{ + oxidant} \longrightarrow SO_3 \xrightarrow{H_2O} H_2SO_4 \xrightarrow{NH_3} (NH_4)_2SO_4$$

Secondary Organic Aerosol



Organic gases

+ ·OH

Lighter
(fragmentation)
Oxidation
Products

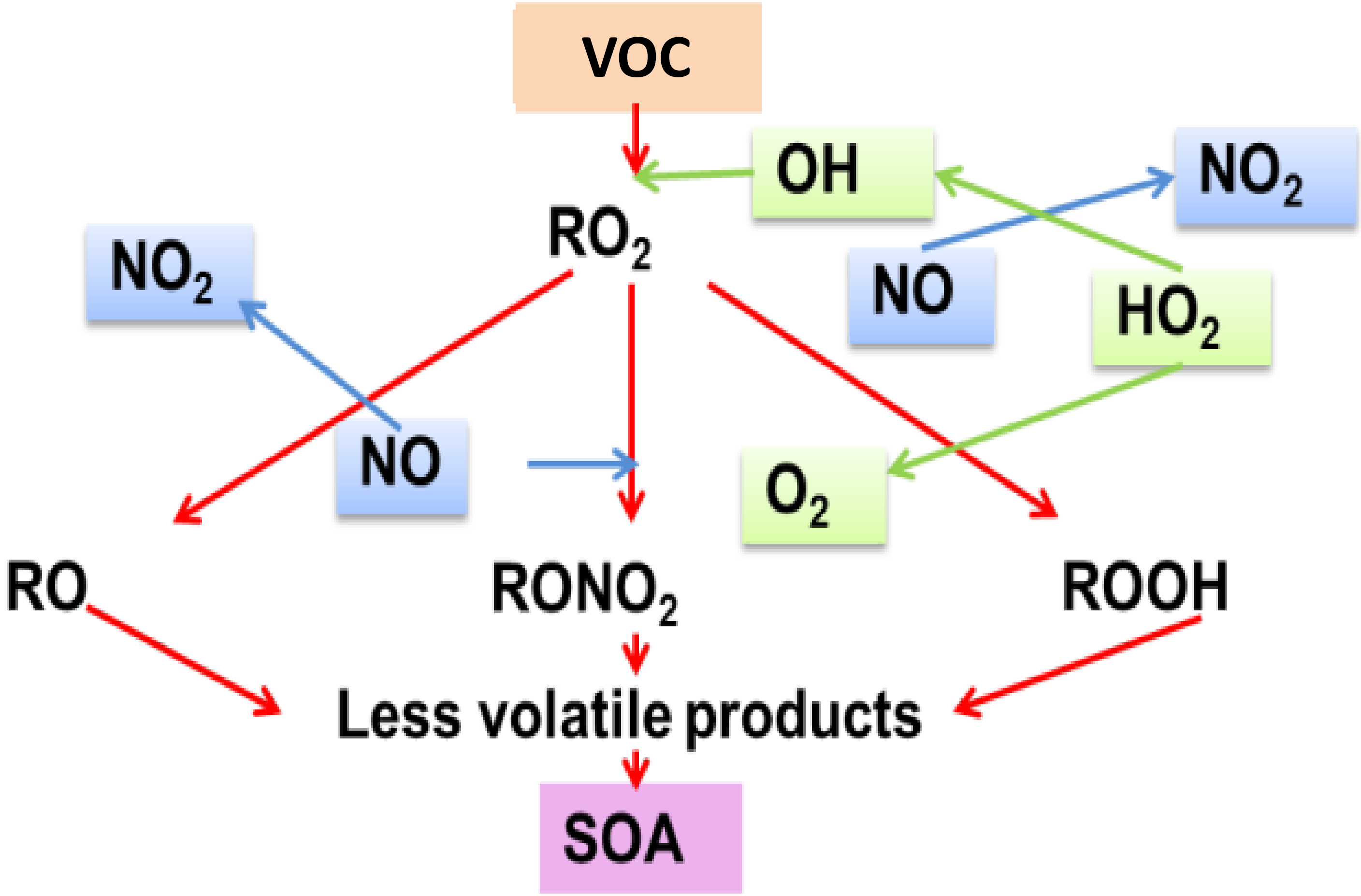
+

Heavier
(functionalization)
Oxidation
Products

Evaporation

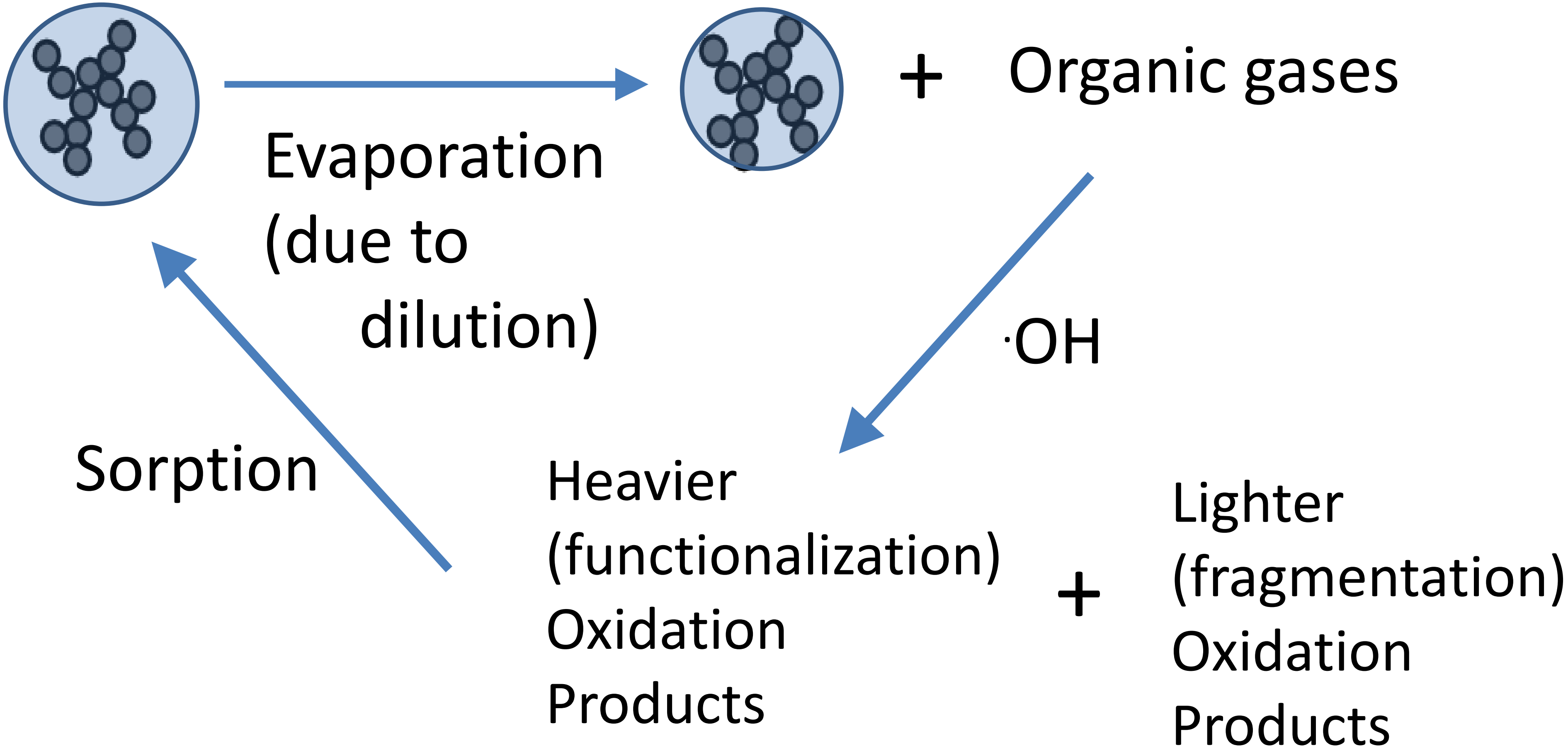
Sorption

Chemistry of SOA Formation is Complicated!



Plus additional SOA formation through oligomerization …

Primary/Secondary Organic Aerosol



Evaporation (due to dilution)

+ Organic gases

·OH

Sorption

Heavier (functionalization) Oxidation Products

+ Lighter (fragmentation) Oxidation Products

How do we look at SOA Formation?

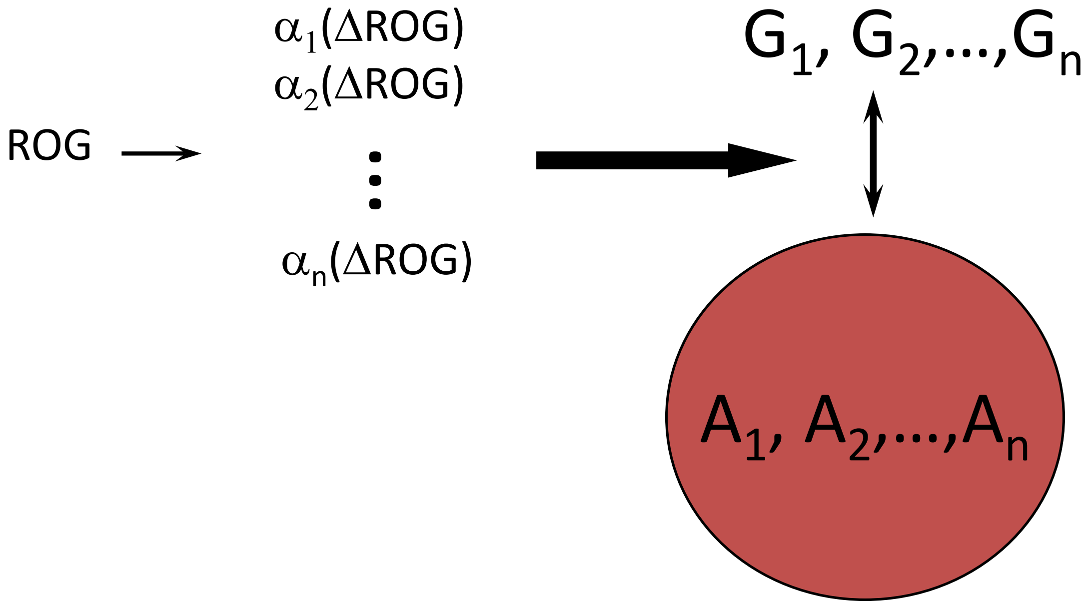
SOA formation is driven by gas-to-particle partitioning, with the gas-to-particle partitioning coefficient defined as:

$$\boxed{K_{om,i} = \frac{RT}{MW_{om,i}\gamma_i p_{L,i}^{o}}}$$

activity coefficient

saturation liquid
vapor pressure

Equilibrium Partitioning of Semi-Volatile Compounds



ROG →

$\alpha_1(\Delta ROG)$

$\alpha_2(\Delta ROG)$

⋮

$\alpha_n(\Delta ROG)$

$G_1, G_2,\dots,G_n$

$A_1, A_2,\dots,A_n$

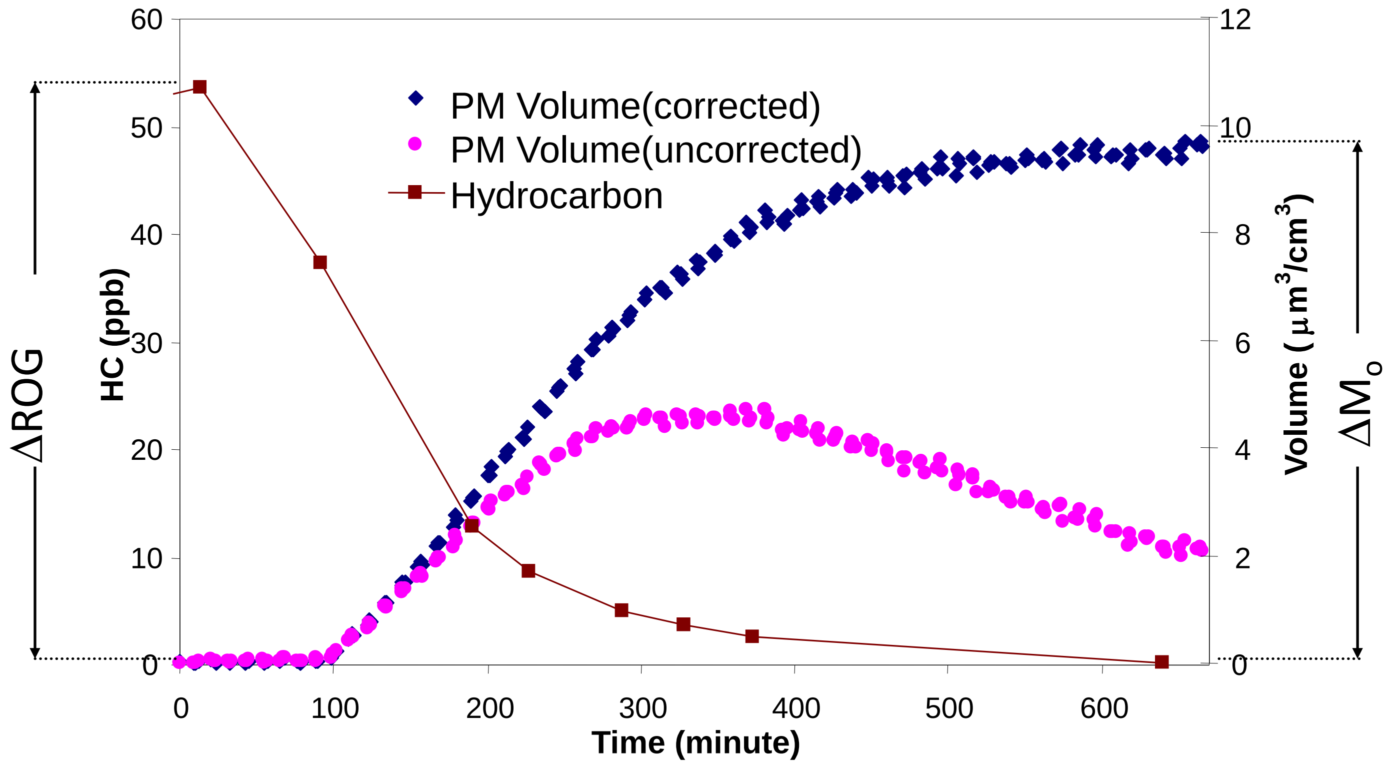
$$Y_{\text{experiment}} = \frac{\Delta M_o}{\Delta ROG}$$

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

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

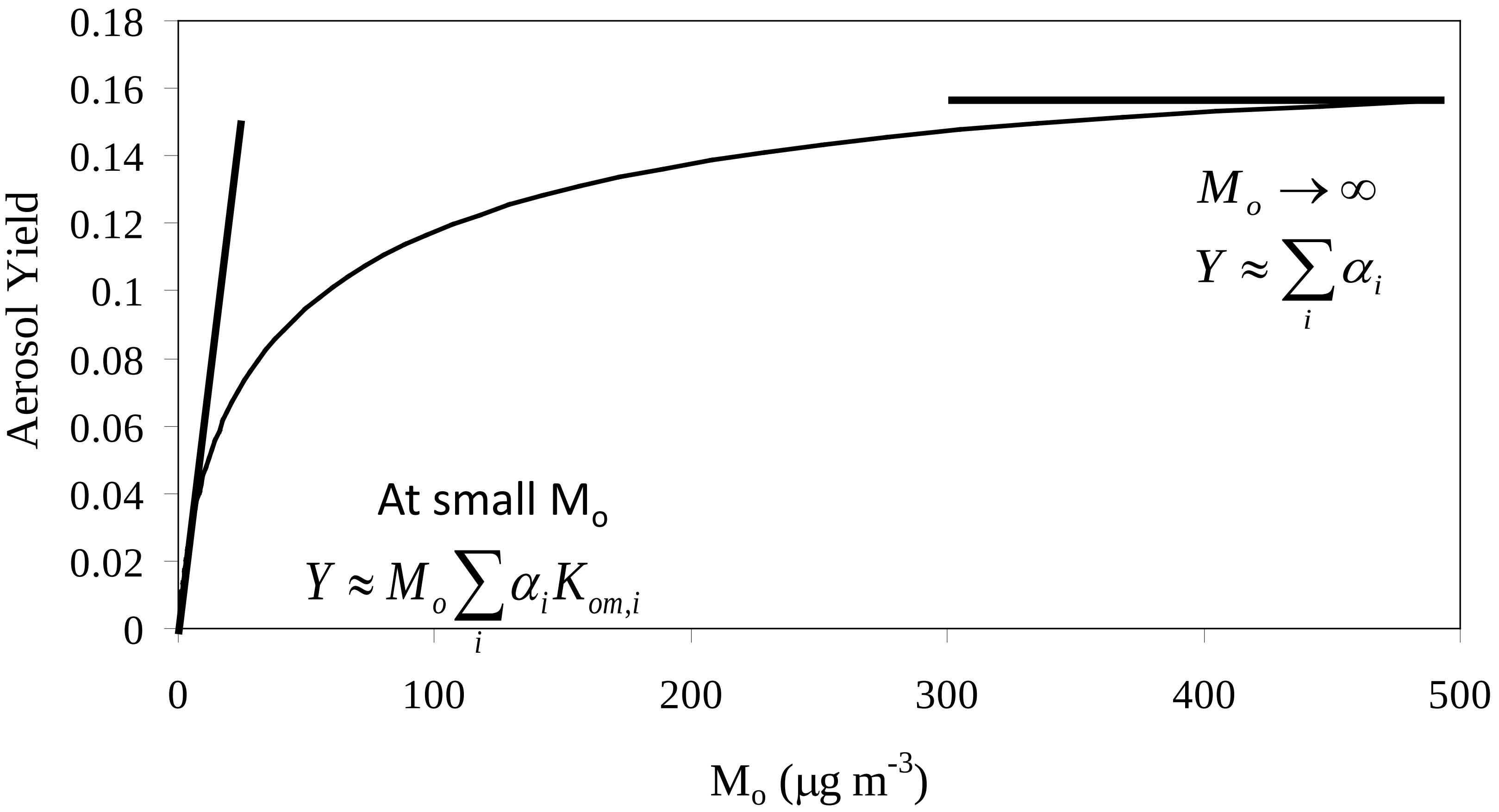
$$p^o_{L,i} = p^o_{L,i}\,(T)$$

SOA formation potential



$$Y = \frac{\Delta M_o}{\Delta ROG} = \sum_i Y_i = M_o \sum_i \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o}$$

SOA formation as a function of organic aerosol mass



$$M_o \rightarrow \infty$$

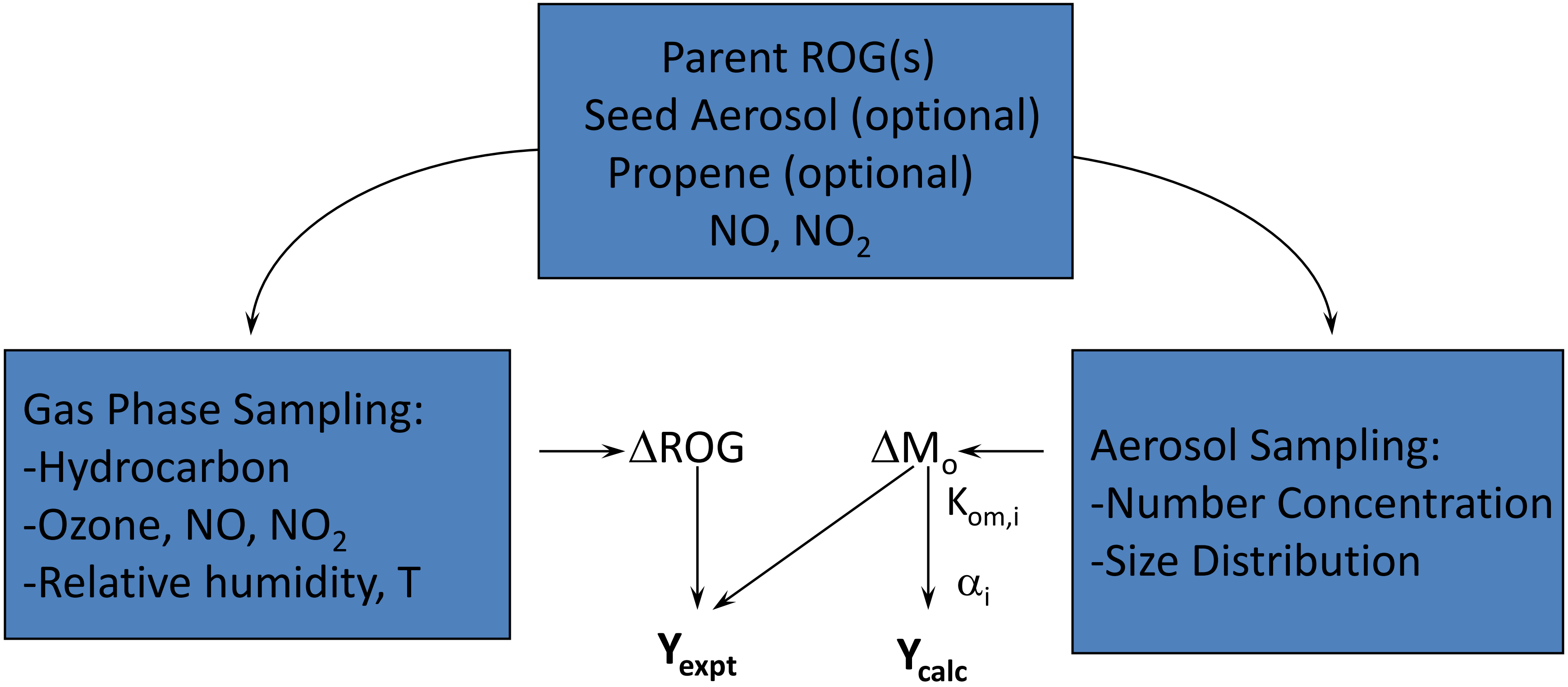
$$Y \approx \sum_i \alpha_i$$

At small M$_o$

$$Y \approx M_o \sum_i \alpha_i K_{om,i}$$

$$\boxed{Y = \sum_i Y_i = M_o \sum_i \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o}}$$

General SOA Experimental Protocol



Parent ROG(s)
Seed Aerosol (optional)
Propene (optional)
NO, NO_2

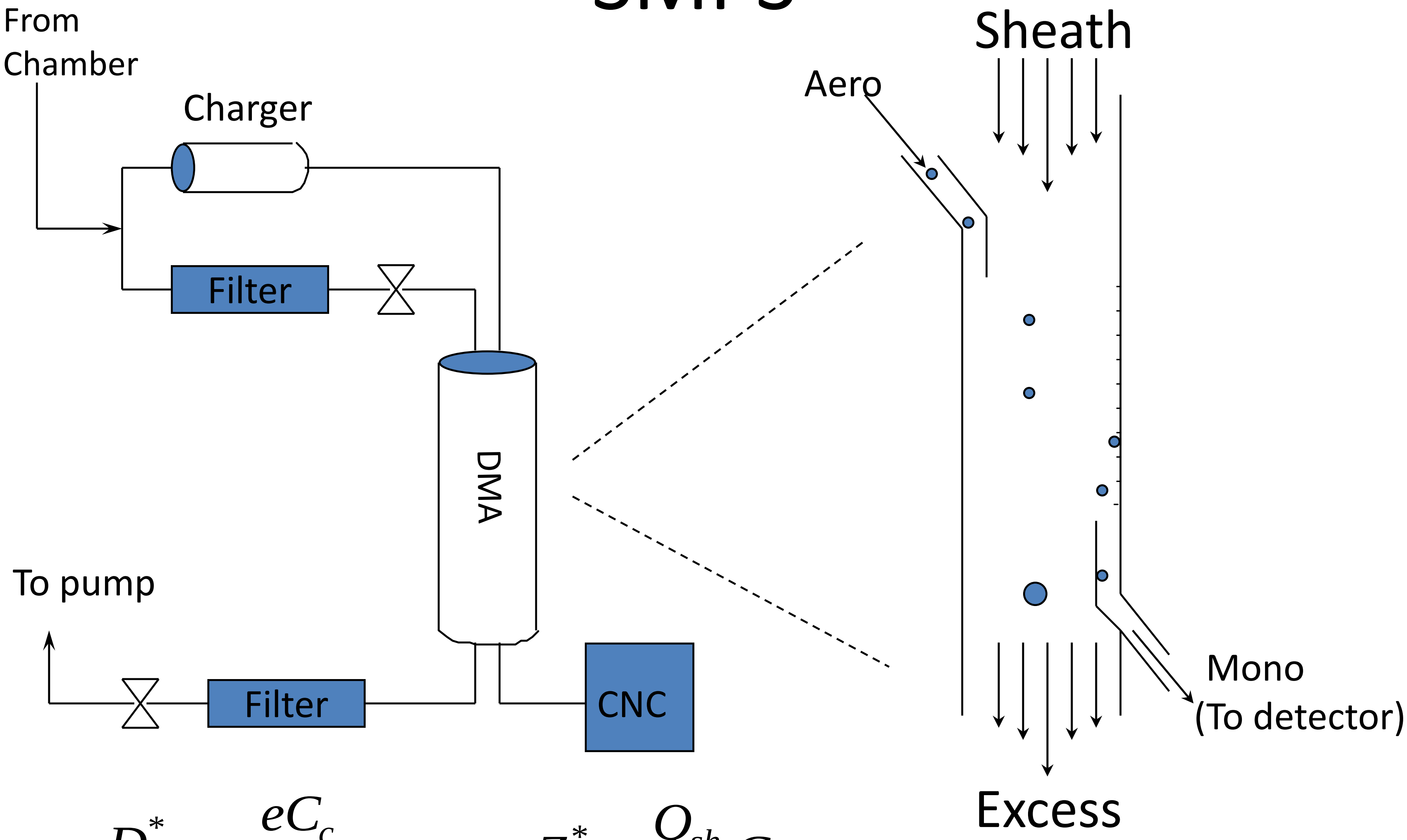
Gas Phase Sampling:
- Hydrocarbon
- Ozone, NO, NO_2
- Relative humidity, T

Aerosol Sampling:
- Number Concentration
- Size Distribution

--Assume two product classes

--Coefficients $K_{om.i}$ 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.

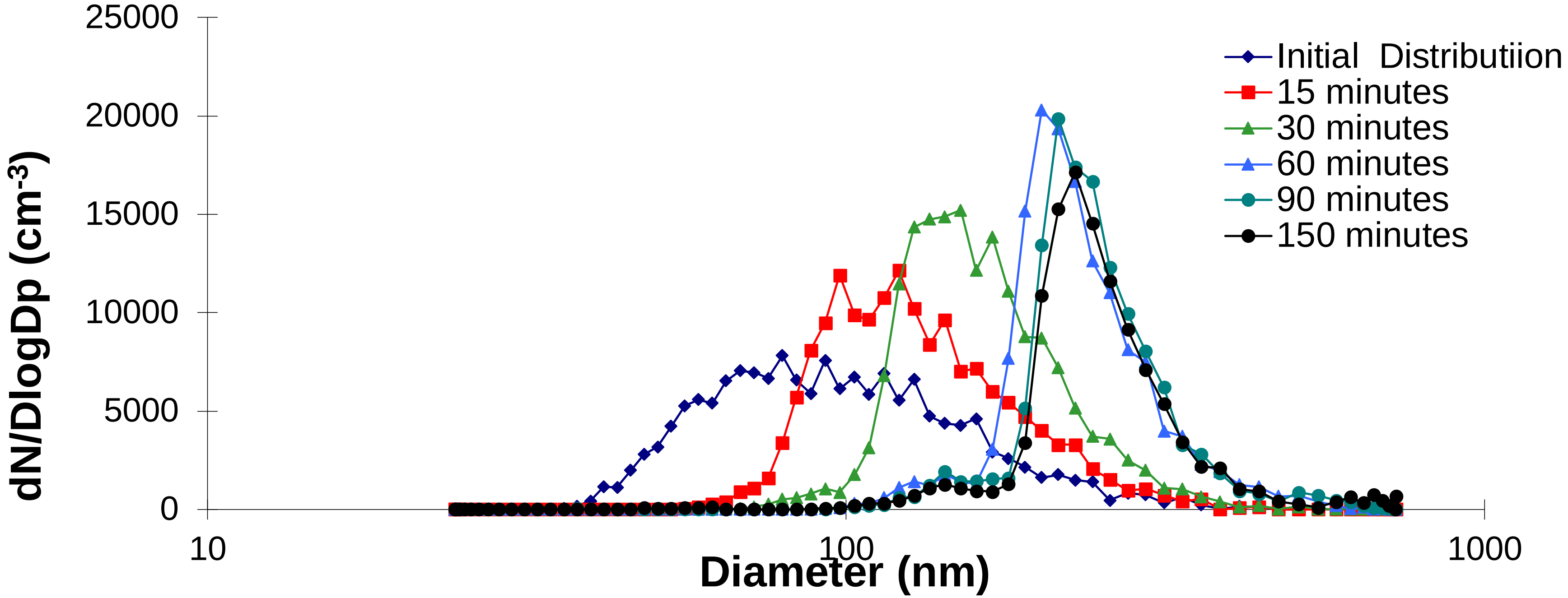
SMPS



$$D_p^* = \frac{eC_c}{3\pi\mu Z_p^*}$$

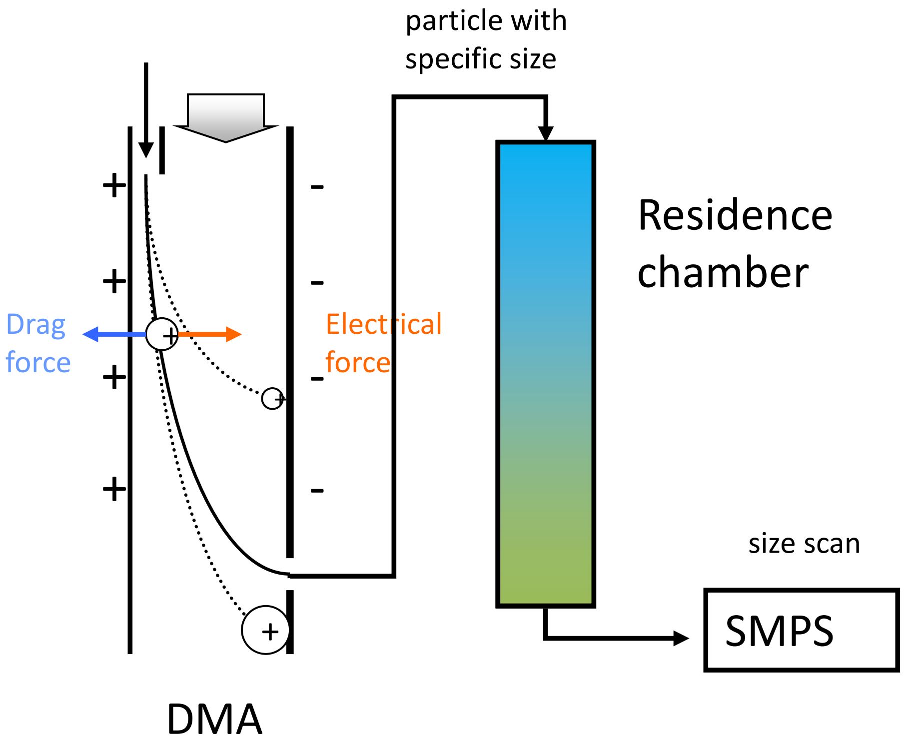
$$Z_p^* = \frac{Q_{sh}}{V} G_f$$

Size Distribution as a Function of Time

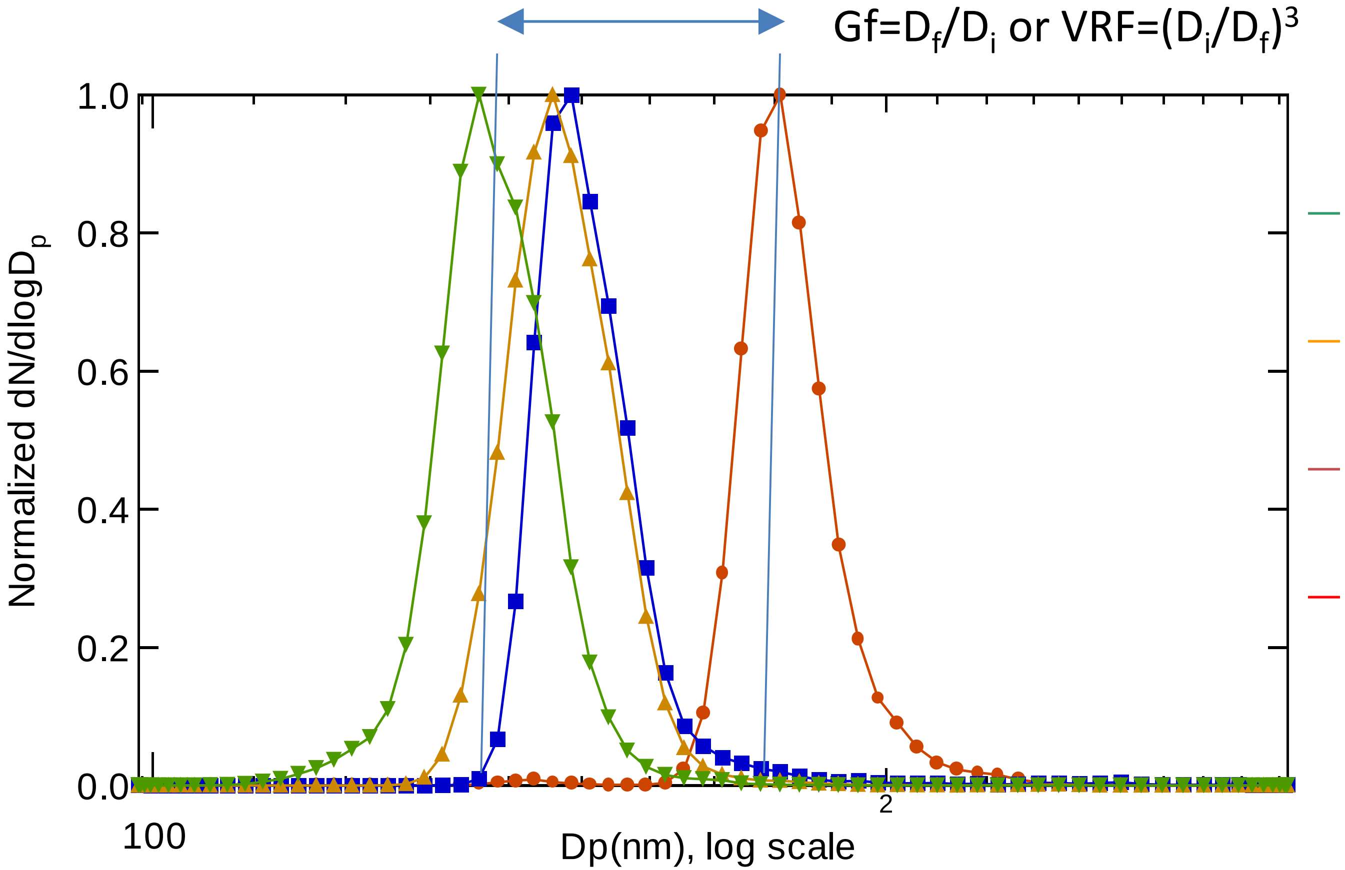


HTDMA

Hygroscopicity Tandem Differential Mobility Analyzer

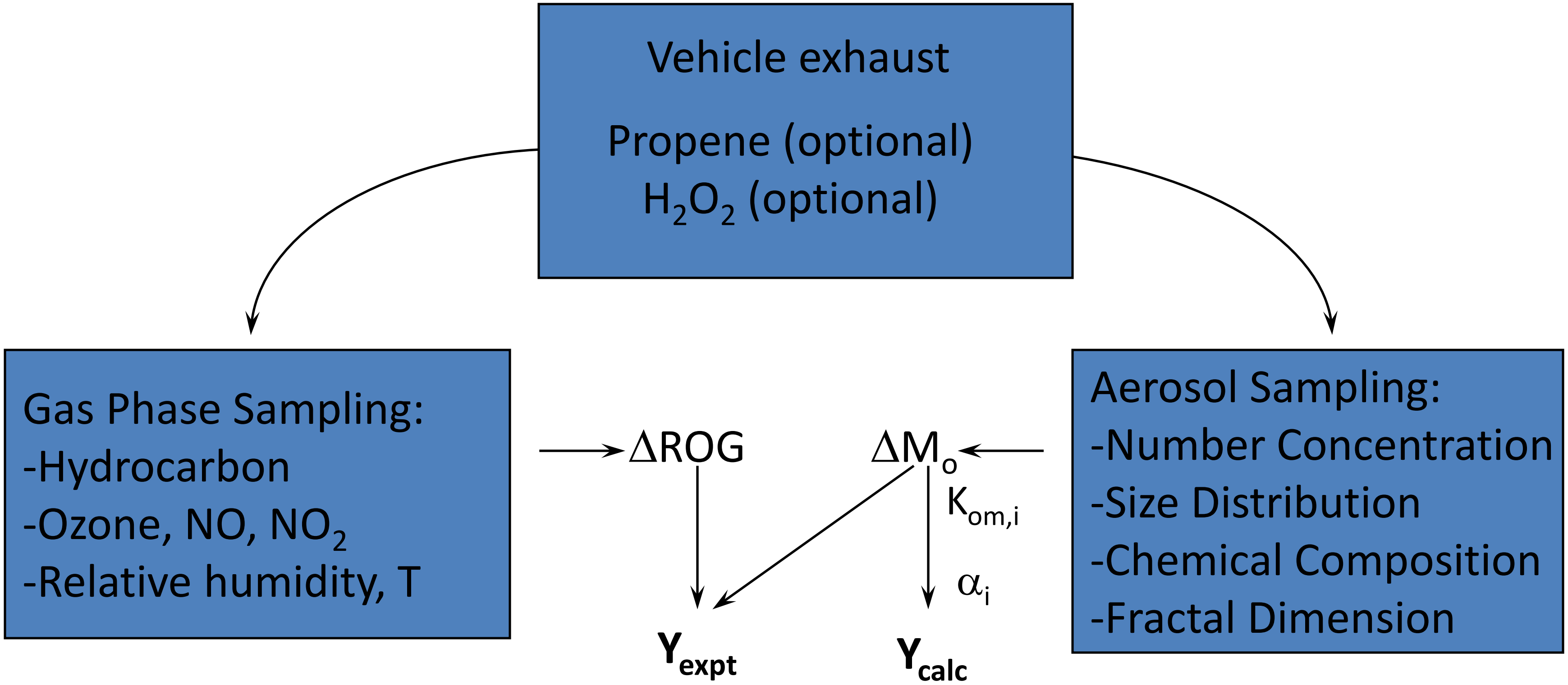


TDMA analysis (volatility or hygroscopicity)



$Gf = D_f/D_i$ or $VRF = (D_i/D_f)^3$

General Emission Protocol



Vehicle exhaust

Propene (optional)
H_2O_2 (optional)

Gas Phase Sampling:
-Hydrocarbon
-Ozone, NO, NO_2
-Relative humidity, T

ΔROG

ΔM_o

$K_{om,i}$

α_i

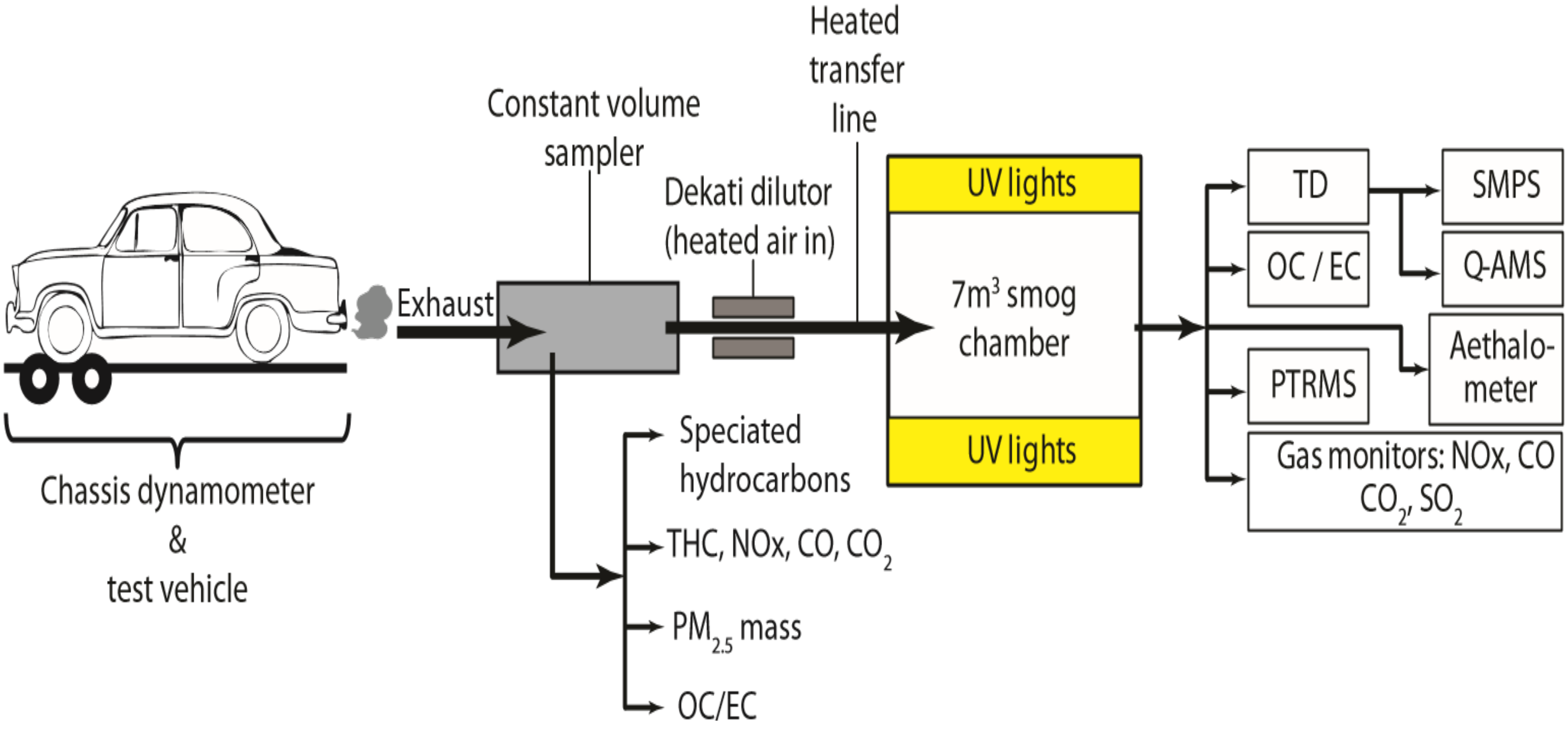
$\mathbf{Y_{expt}}$

$\mathbf{Y_{calc}}$

Aerosol Sampling:
-Number Concentration
-Size Distribution
-Chemical Composition
-Fractal Dimension

--Assume two product classes

--Coefficients $K_{om.i}$ 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.



Chassis dynamometer
&
test vehicle

Exhaust

Constant volume sampler

Dekati dilutor (heated air in)

Heated transfer line

Speciated hydrocarbons

THC, NOx, CO, CO_2

$PM_{2.5}$ mass

OC/EC

UV lights

$7m^3$ smog chamber

UV lights

TD

OC / EC

PTRMS

Gas monitors: NOx, CO CO_2, SO_2

SMPS

Q-AMS

Aethalo-meter

Gordon et al., www.atmos-chem-phys.net/14/4661/2014/

Why fractal dimension matters

Condensing organic material will fill voids while potentially not changing mobility diameter

Must be careful to not use SMPS only and assume constant density

Shape of primary aerosol influenced by dilution….

Particle measurement methods

1. SMPS

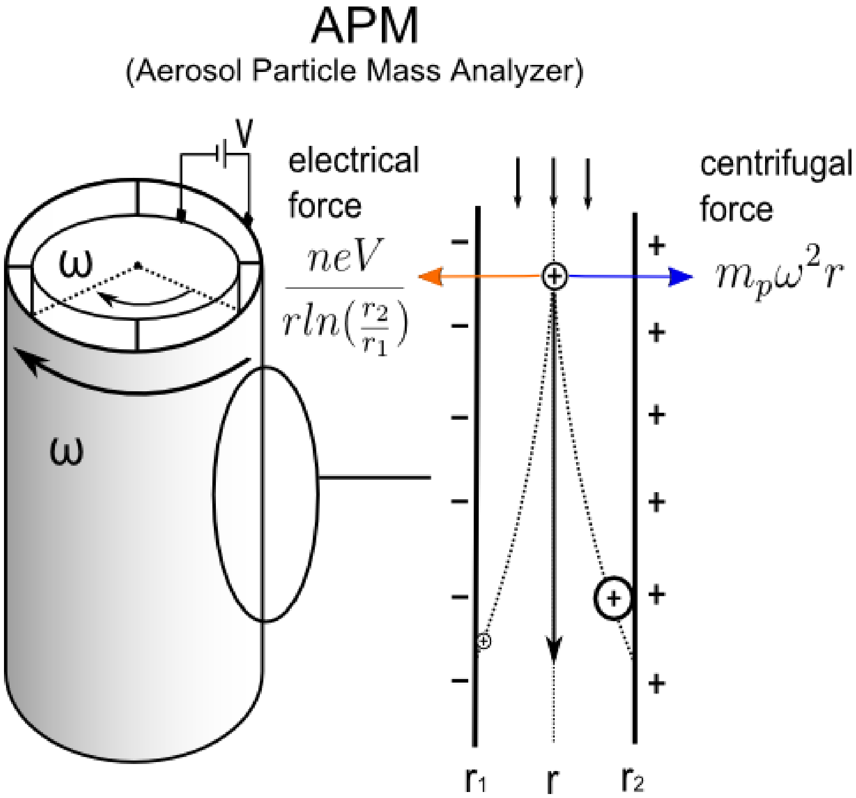
- volume (based on d_m)

2. APM – SMPS

- **m_p**, d_m → ρ_{eff}

3. HR-ToF-AMS

- Non refractory organics

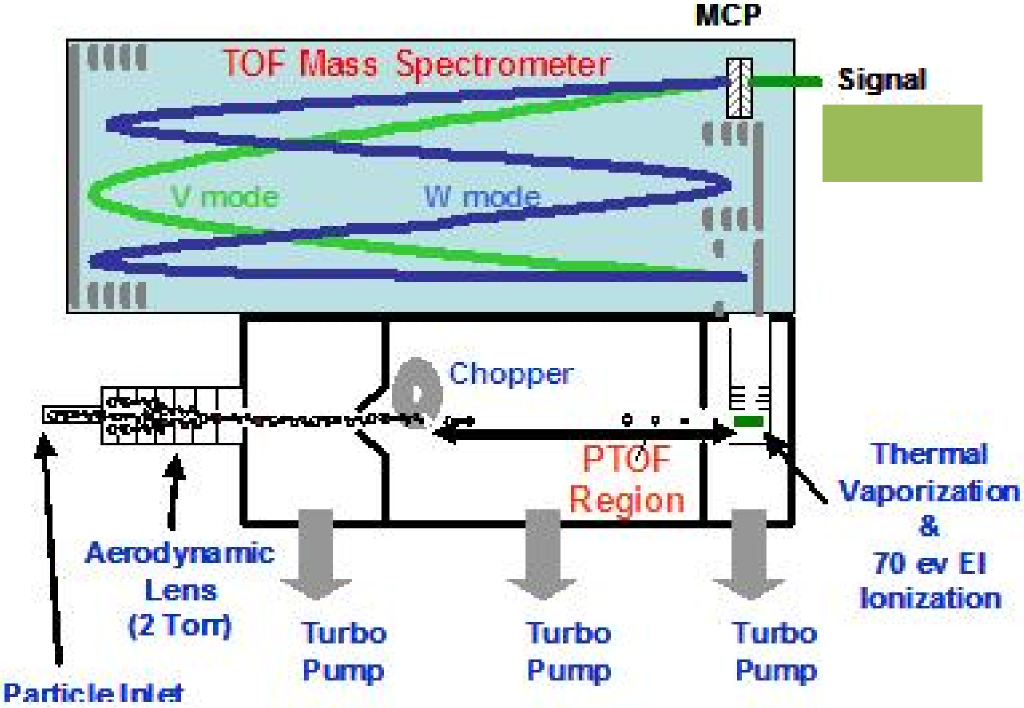


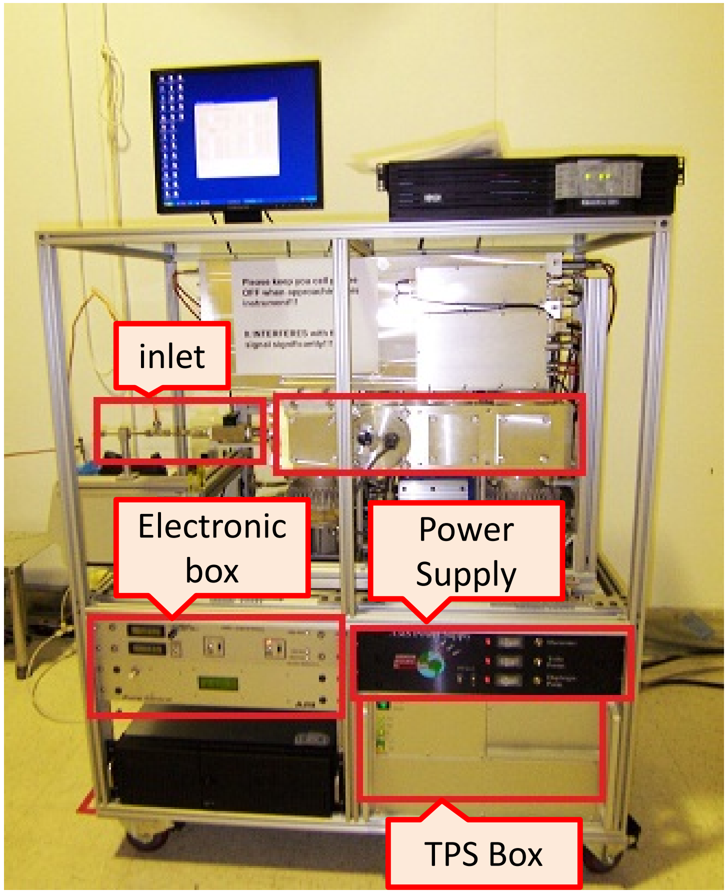
SMPS: Scanning Mobility Particle Sizer
APM: Aerosol Particle Mass Analyzer
HR-ToF-AMS: High Resolution-Time-of-Flight Aerosol Mass Spectrometer

d_m: mobility diameter
m_p: mass of particle
ρ_{eff}: effective density

HR-ToF-AMS

Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer

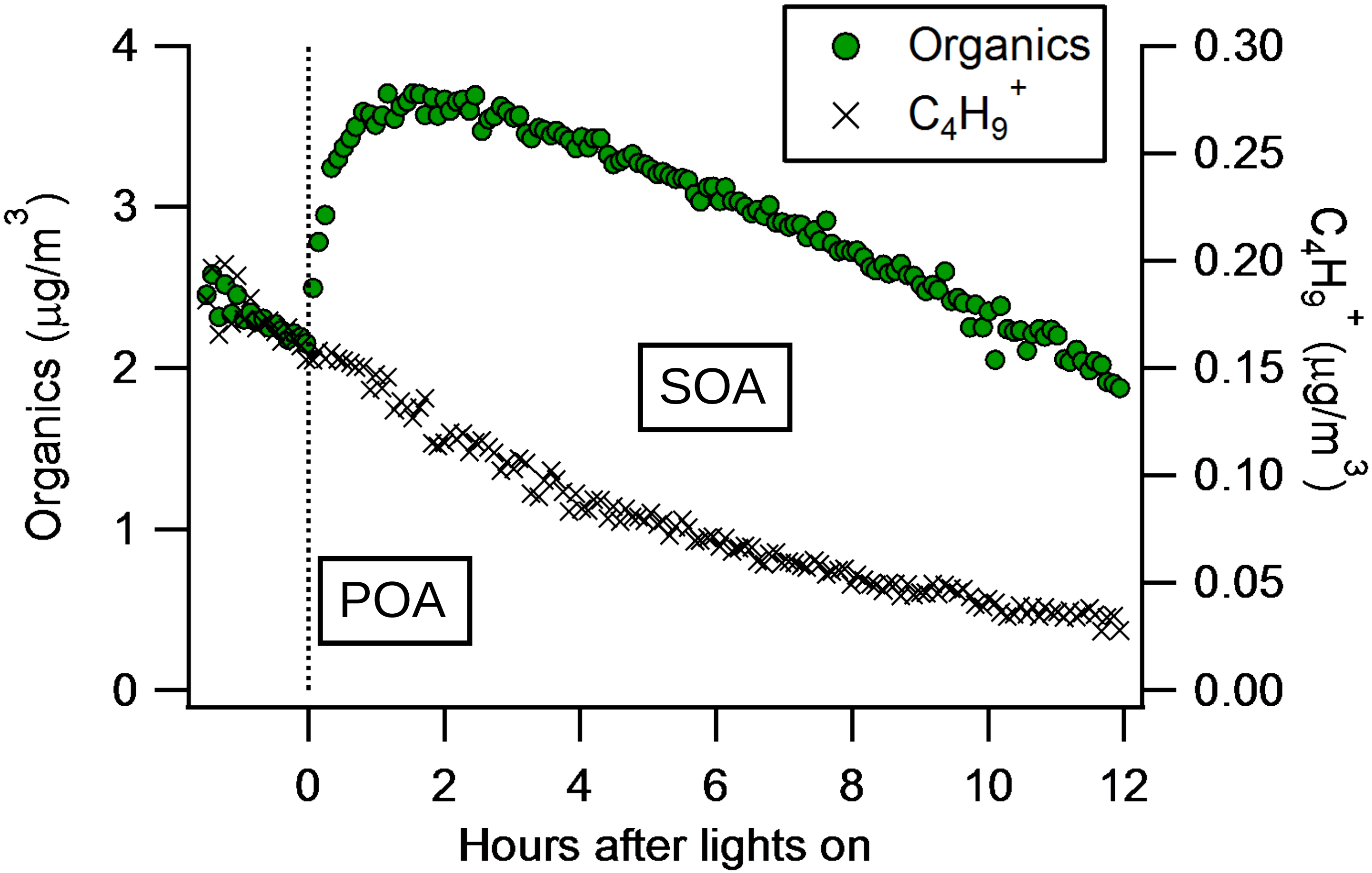




- **Higher resolution for W mode**
- **Higher sensitivity for V mode**

Source: DeCarlo et al., 2006

Measurement of SOA by AMS

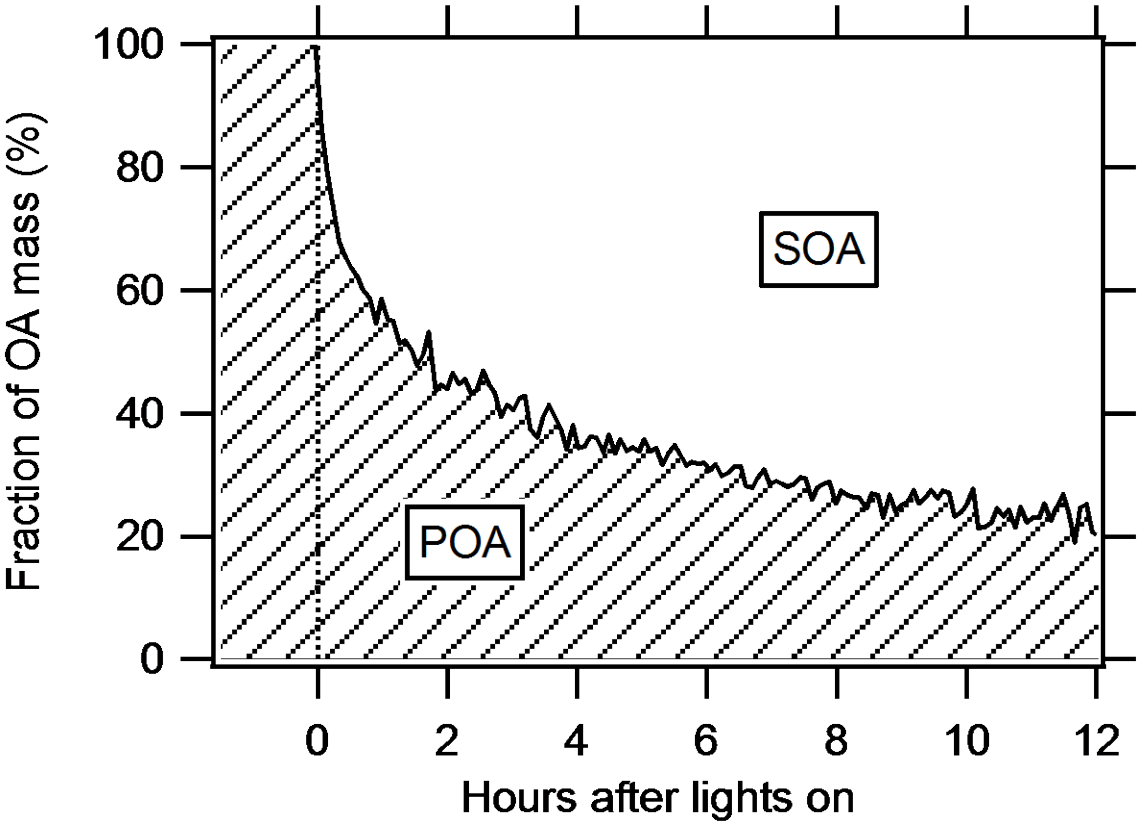


$C_4H_9^+$: tracer of primary organic aerosol*

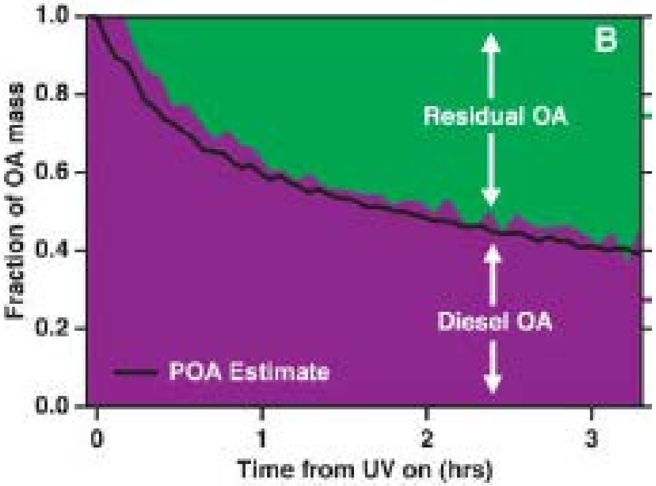
*Chirico et al. 2010, APCD

Run 1 (engine idle,short transfer line, DR: 114)

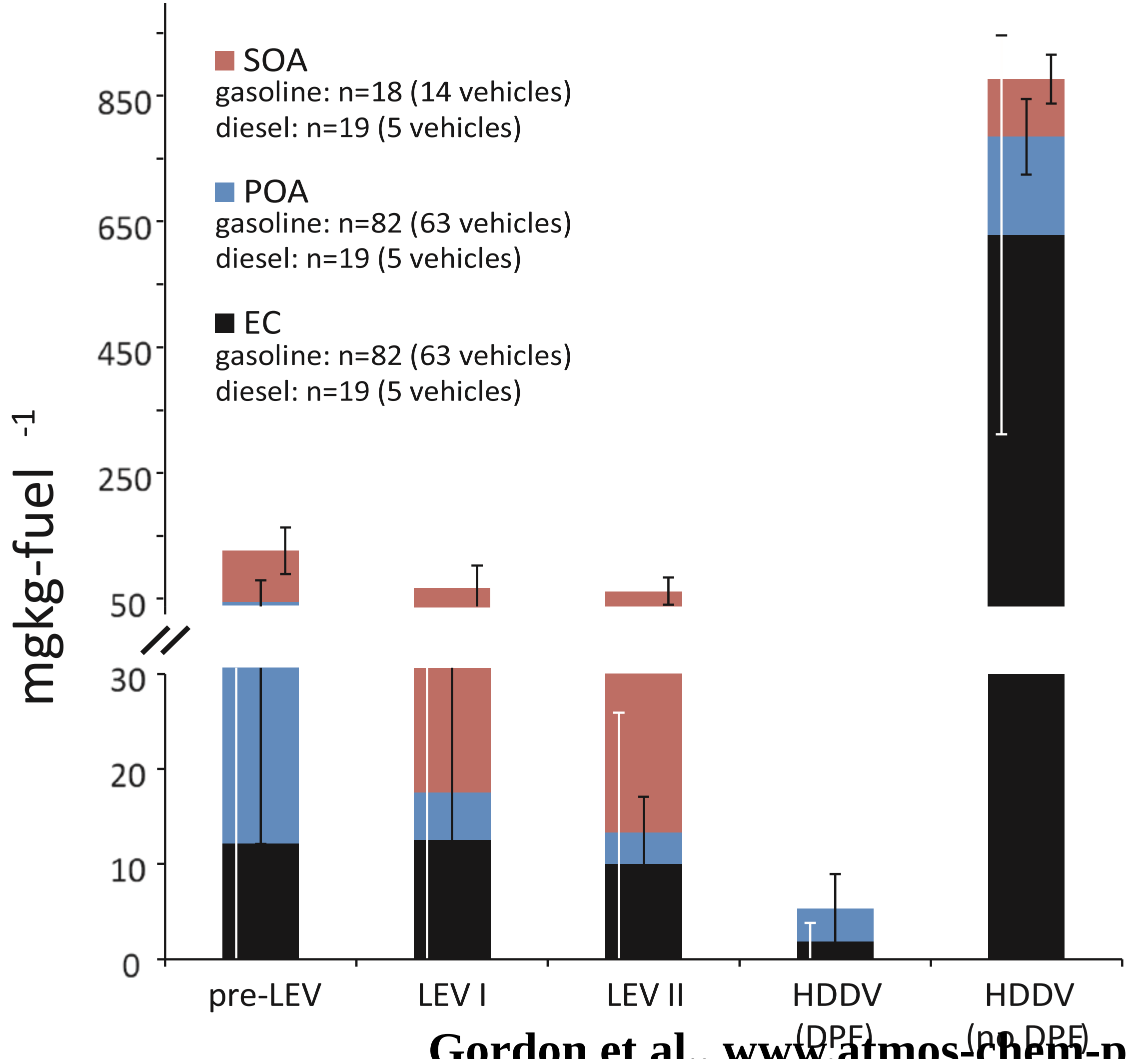
Measurement of SOA by AMS



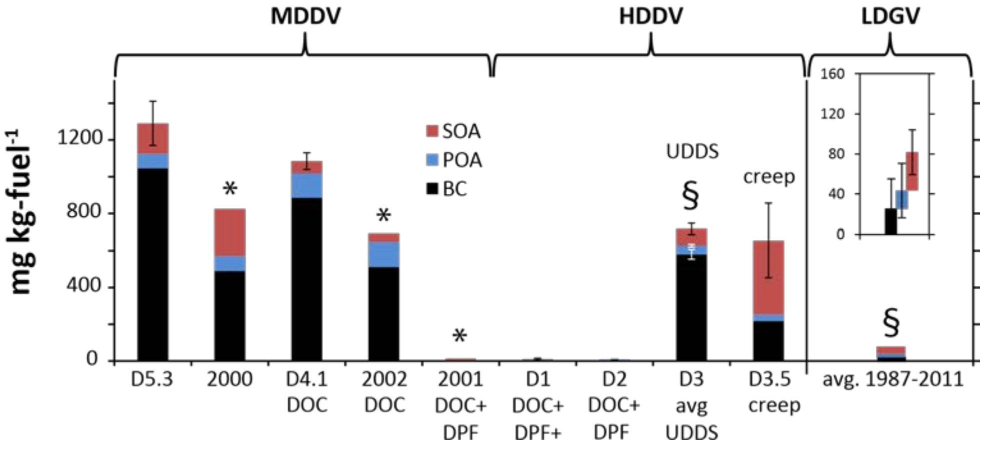
Robinson et al. (2007) *Science*



Nakao et al. (2011) AS&T



Gordon et al., www.atmos-chem-phys.net/14/4661/2014/

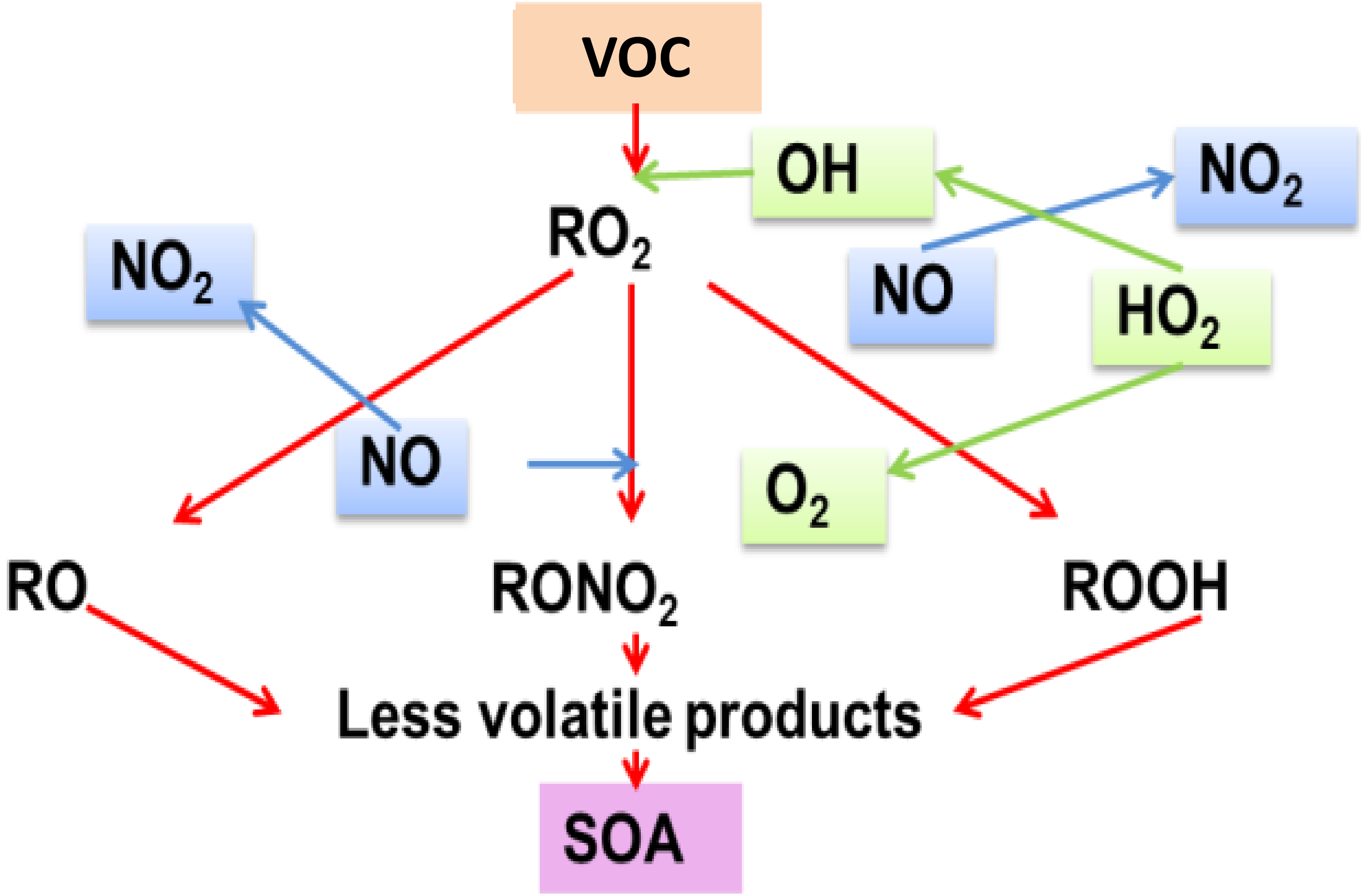


Gordon et al., www.atmos-chem-phys.net/14/4643/2014/

Challenges

- Oxidizing environment controlled by exhaust gases (organics and NO_x)
- Limited oxidation time
- Wall effects can be important (loss of SOA precursor gases to walls, interaction of sorbing gases to particles on the surface)

Chemistry of SOA Formation is Complicated!



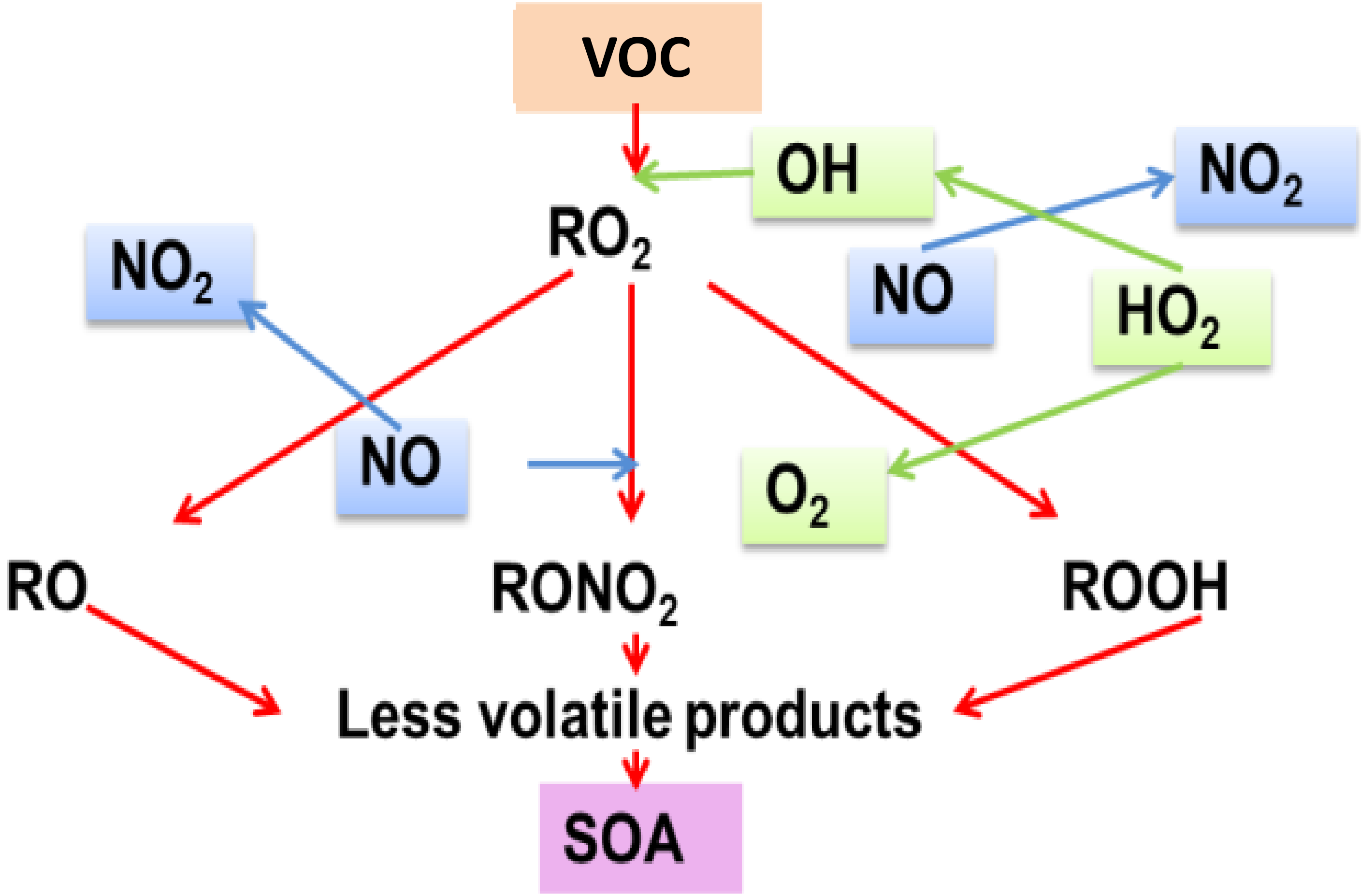
Plus additional SOA formation through oligomerization …

Kinetics very important

- $d[C]/dt = k[A][B]$

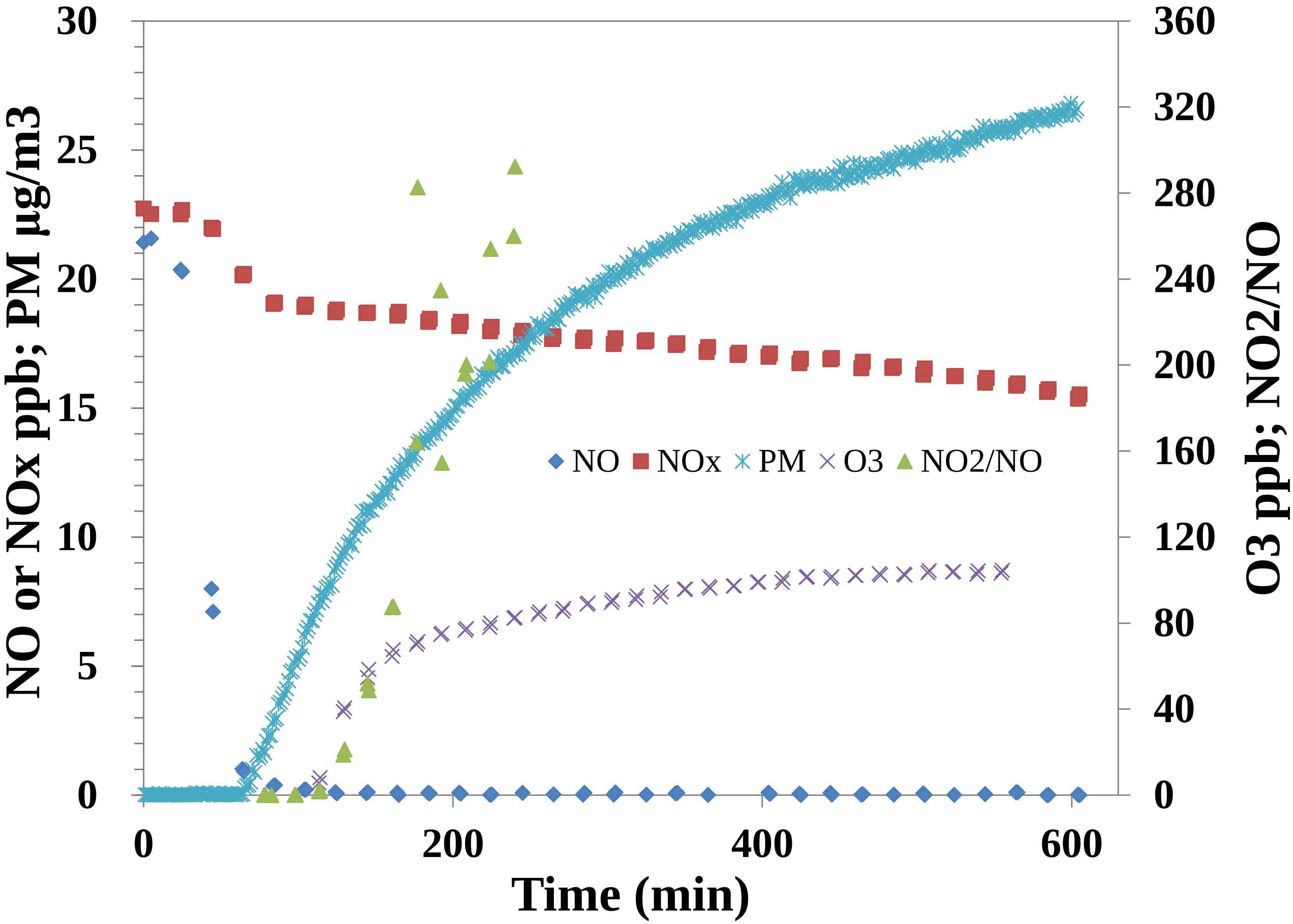
$RO_2 + HO_2 \rightarrow$ heavier oxidation product (e.g., hydroperoxide)

- $d[\text{oxidation product}]/dt = k[\cdot RO_2][\cdot HO_2]$
- NO competes for $\cdot RO_2$ and $\cdot HO_2$
  - $[\cdot RO_2]$ and $[\cdot HO_2]$ very dependent on [NO] as NO quickly reacts with $\cdot RO_2$ and $\cdot HO_2$ to form $\cdot RO$ and $\cdot HO$.

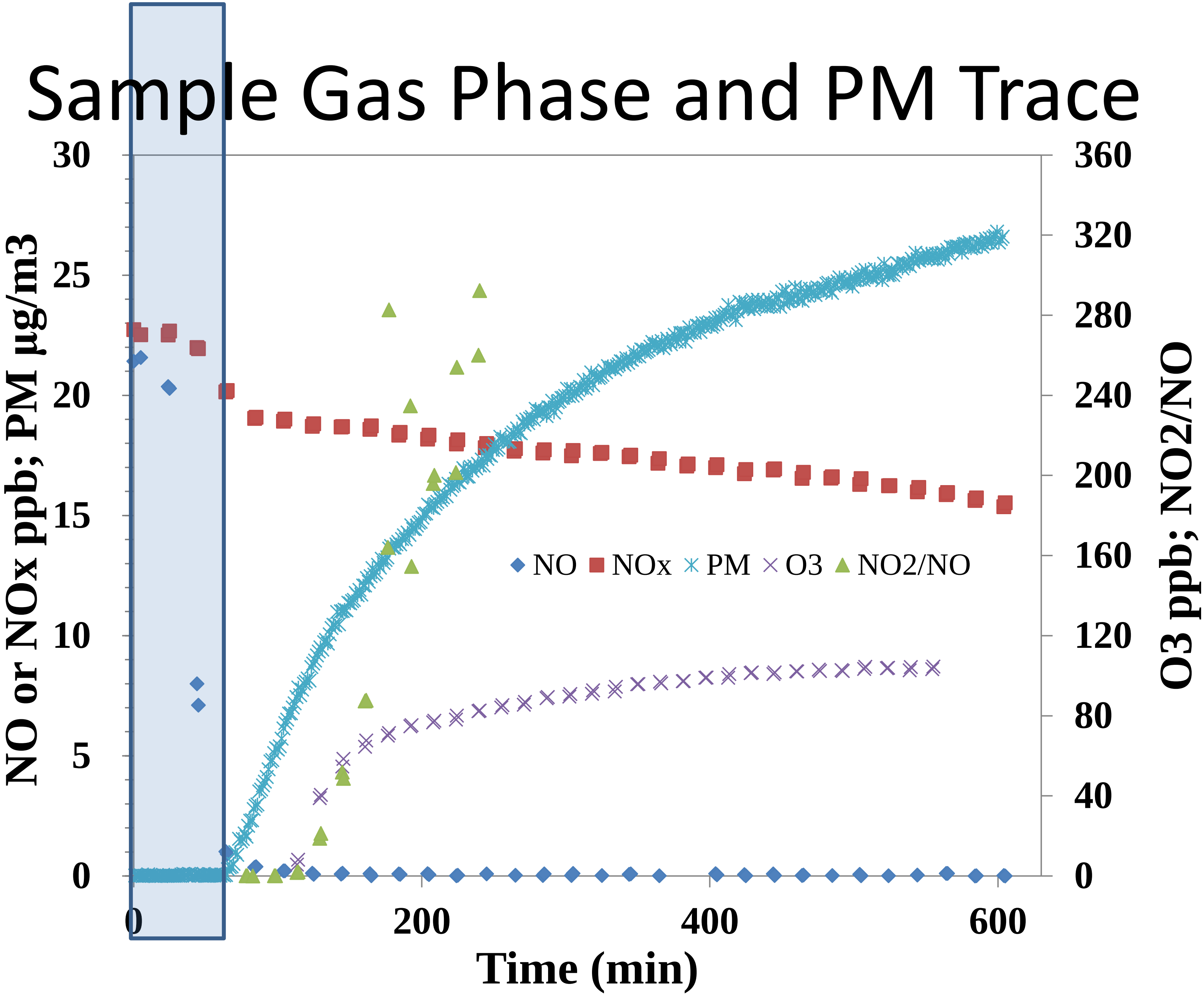


Plus additional SOA formation through oligomerization …

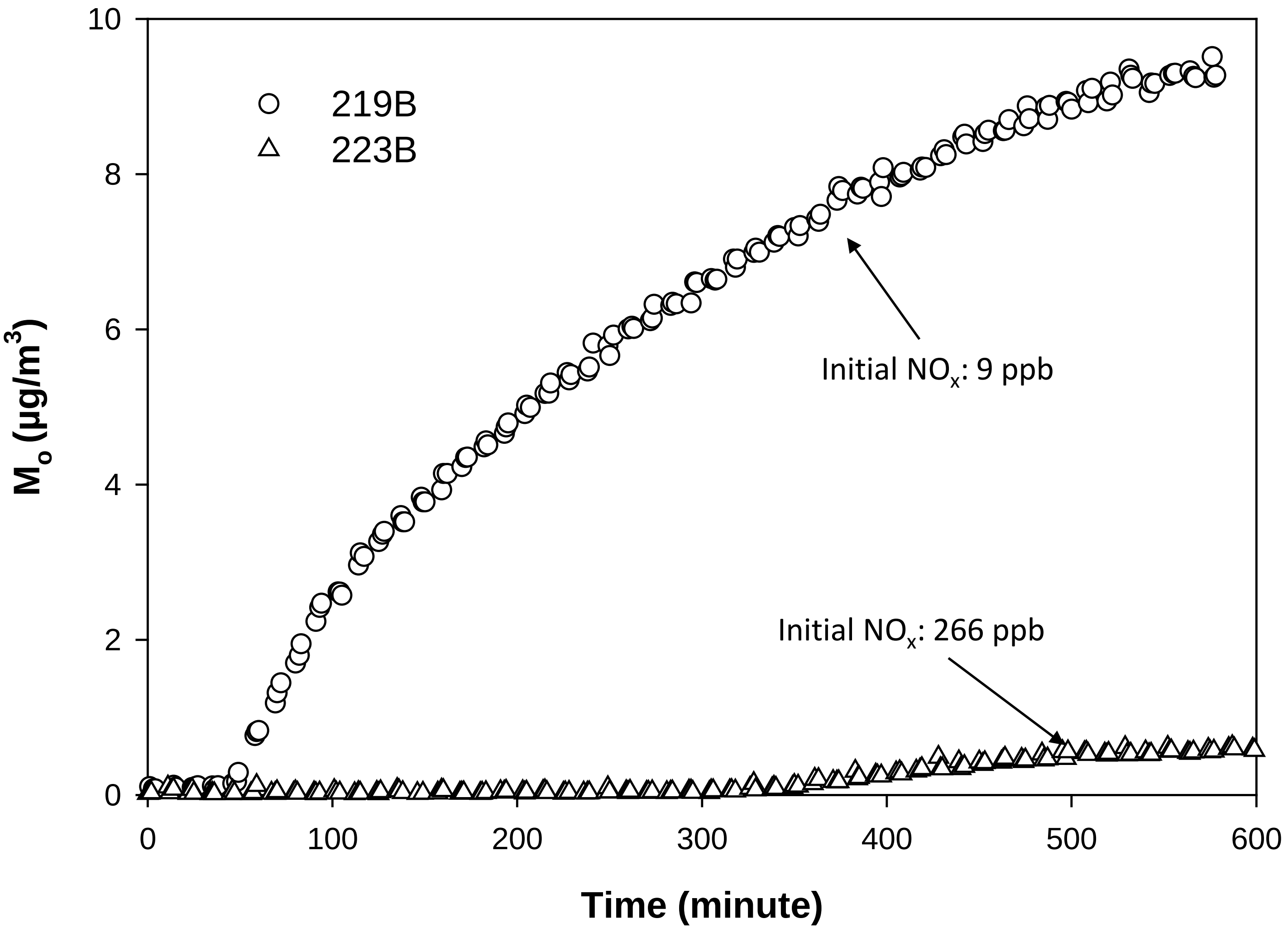
Sample Gas Phase and PM Trace



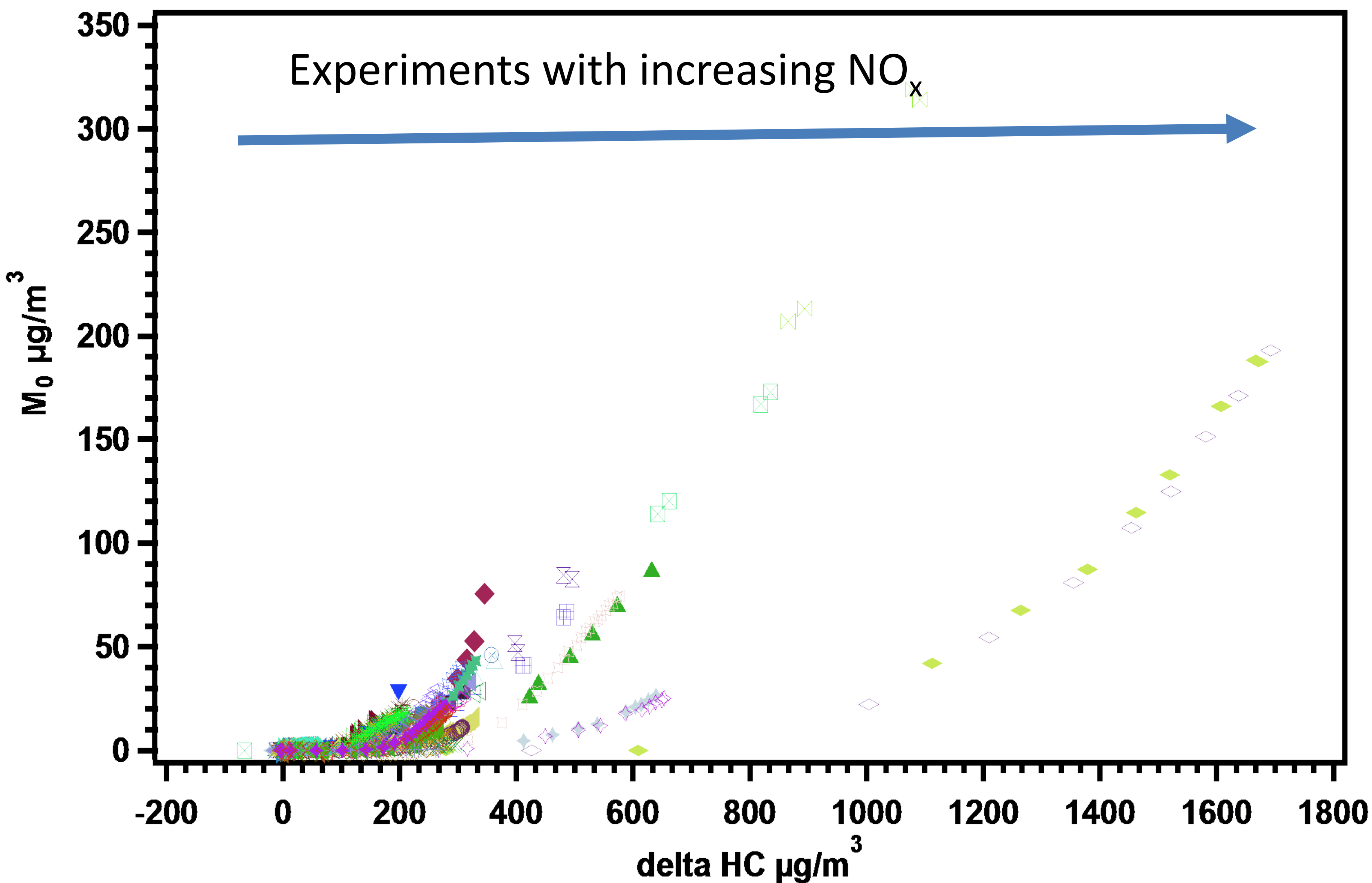
Sample Gas Phase and PM Trace

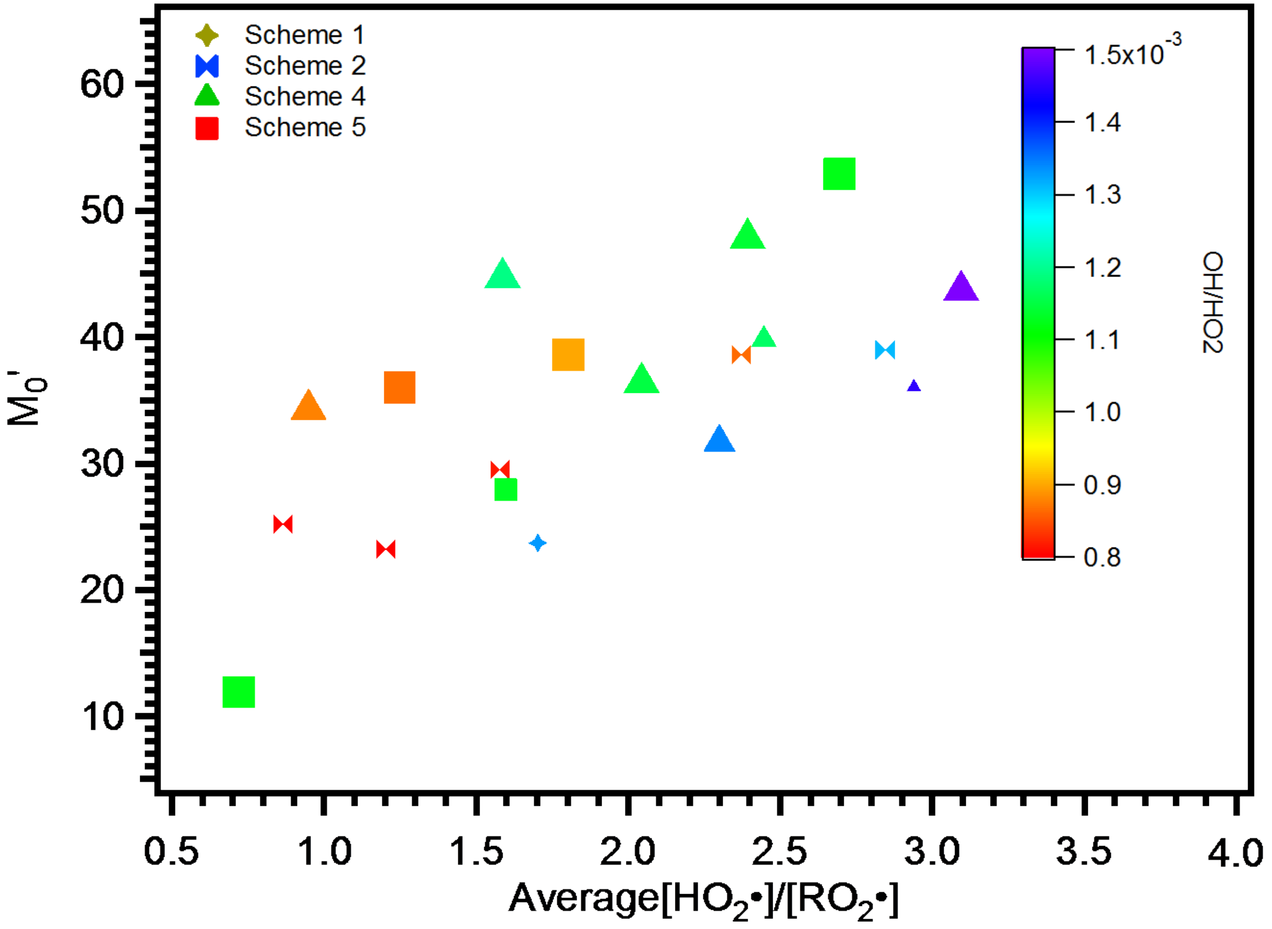


Comparison of Two Experiments with the Same Initial and Reacted *m*-Xylene Concentrations



Example of how NO_x influences SOA yield



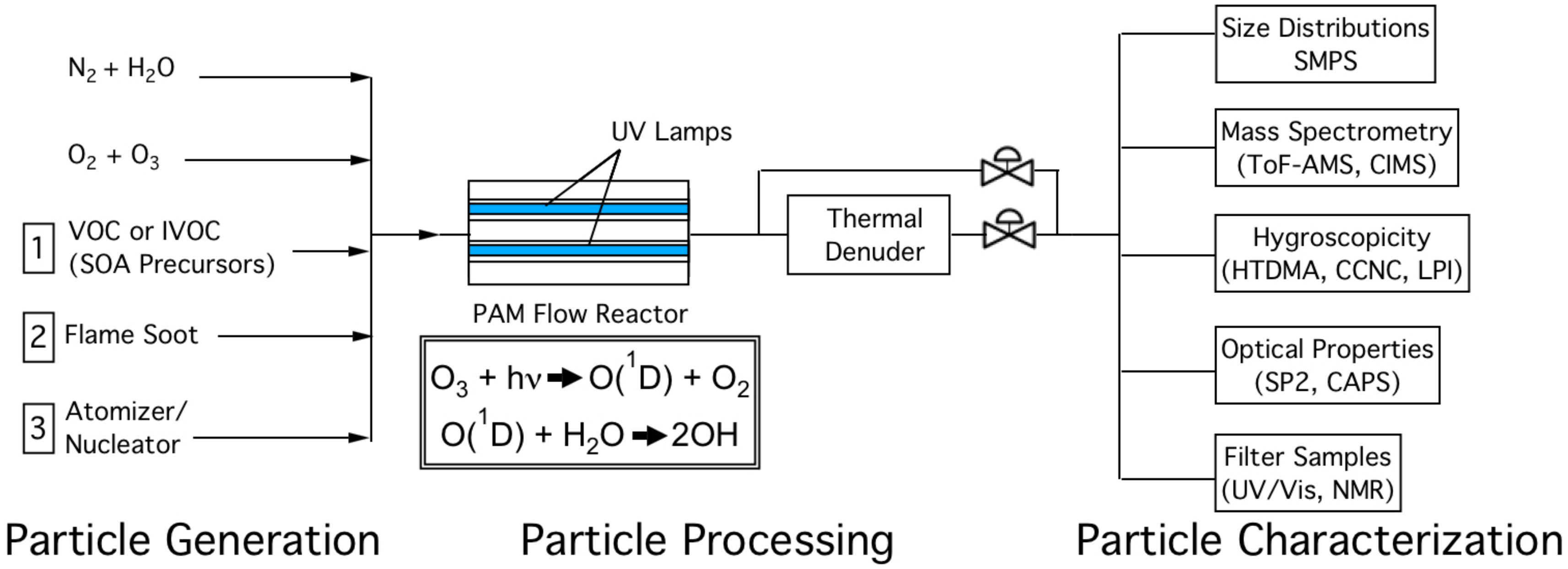

Scheme 1
Scheme 2
Scheme 4
Scheme 5
M_0'
Average$[HO_2•]/[RO_2•]$
10
20
30
40
50
60
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
$1.5x10^{-3}$
1.4
1.3
1.2
1.1
1.0
0.9
0.8
OH/HO2

So how do we best mimic atmosphere

- Clearly SOA formation is driven by the gas-phase chemistry leading to oxidation of organic vapors, which in turn, can condense/sorb into existing organic matter.
- Option 1a: Inject gases and particles directly from tailpipe (after dilution and cooling) and turn on lights. Gas-phase chemistry will be dominated by organic gases and NO_x from vehicle
- Option 1b: inject organic gases and particles into system with surrogate atmosphere (e.g., VOC dominated by anthropogenic or biogenic sources) already present
- Option 1c: reduce NO_x during injection into chamber
- Option 1d: Alter reactivity of system by injecting propene, H_2O_2, HONO or other species.
- Option 2: Mimic total oxidation of atmosphere on days scale in short time by elevating oxidants. (PAMS)

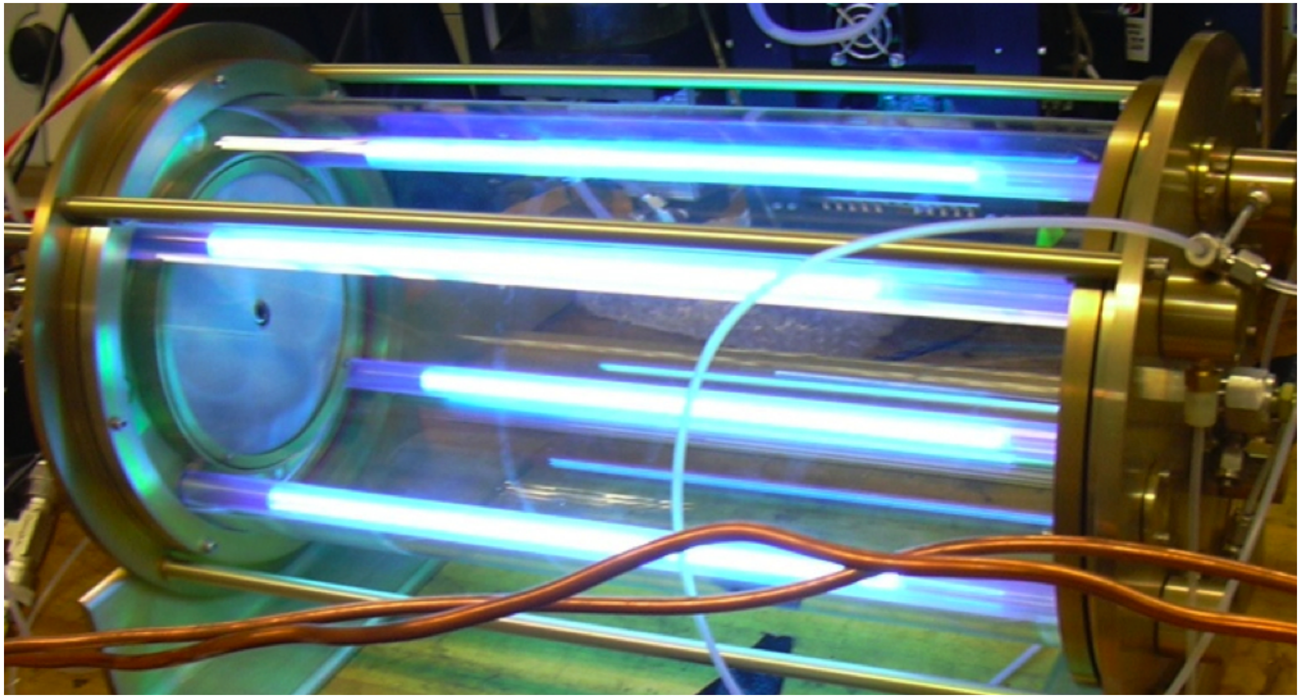
Option 2: PAMS

Photochemical Measurement



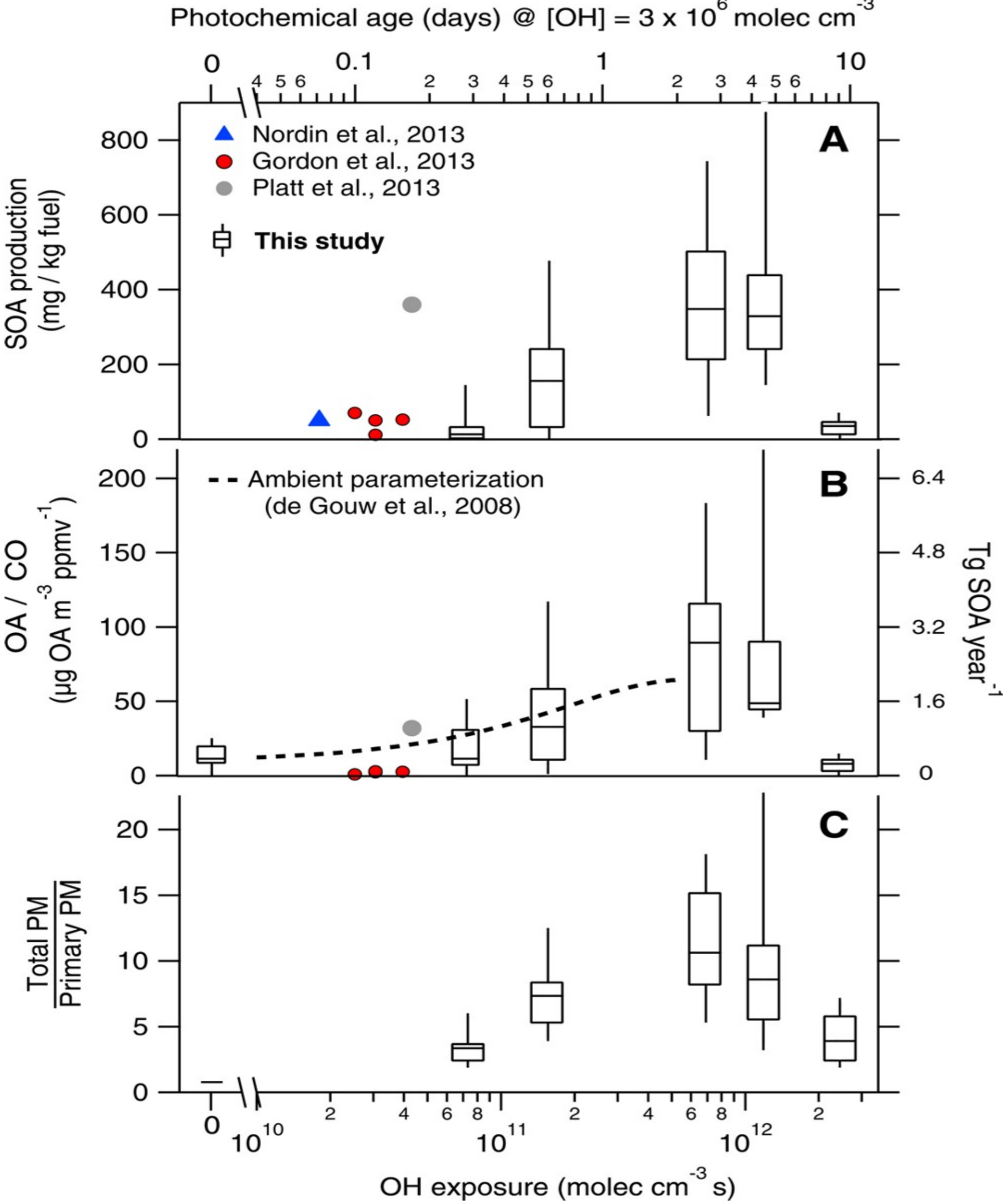
Example PAM reactor setup/applications (from T.B. Onasch et al., DoE ASR Meeting, Spr 2012).

PAMS system



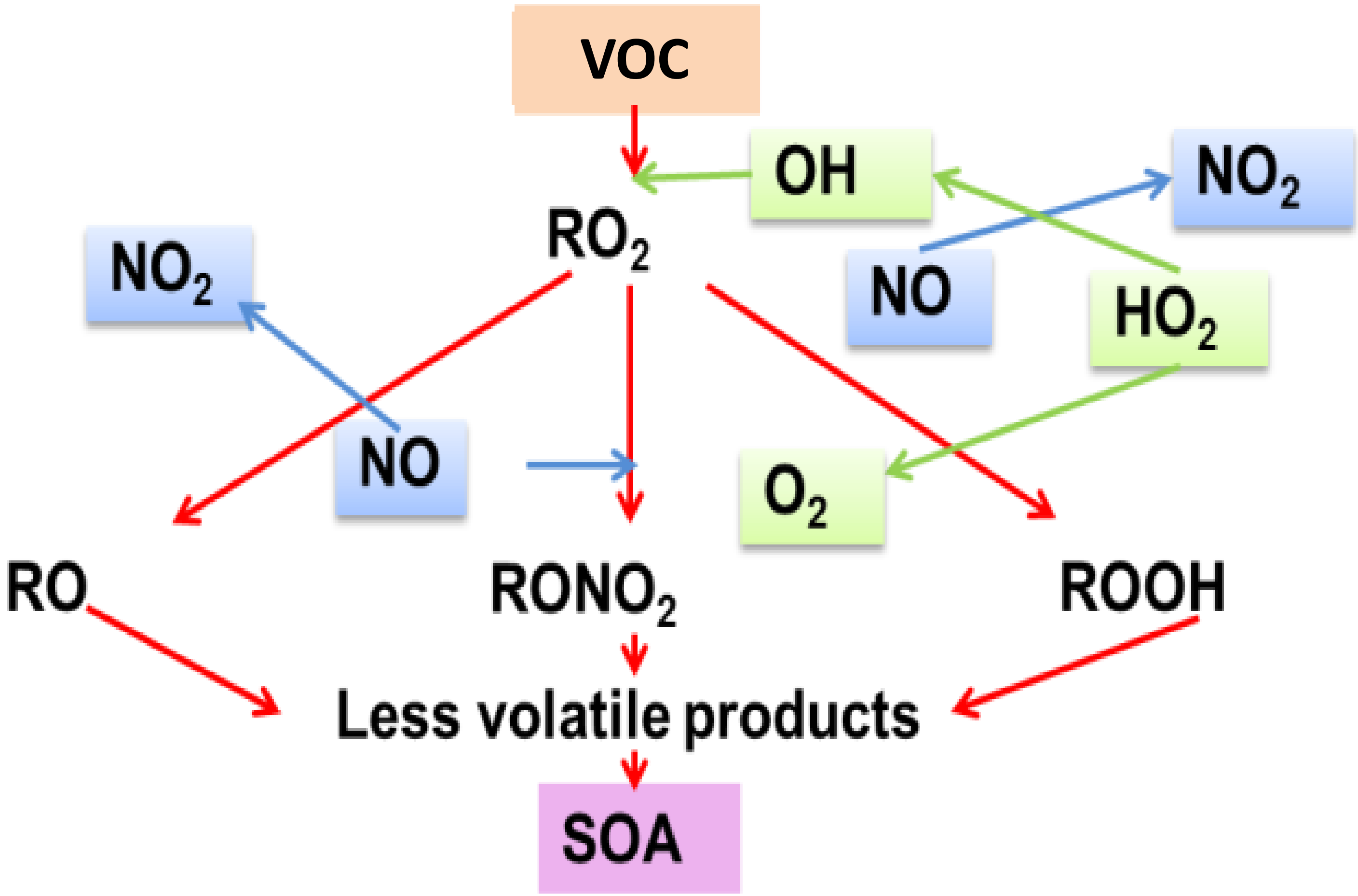
- Advantages:
  - Wider range of oxidant exposure time (1–30 days vs. 1 day)
  - Shorter experiment duration (minutes vs. hours or days)

  Disadvantages:
  - High OH concentrations required to simulate atmospherical aging timescales (10^{10} - 10^{12} vs. 10^{6} - 10^{7} molec cm^{-3})
  - High (parts-per-million) levels of O_3 required for OH production
  - UV emission spectrum different than troposphere (peak $\lambda = 254$ nm vs $\lambda > 300$ nm)



OH exposures ranged from 7.4 × 10^{10} to 2.4 × 10^{12} molecules cm^{-3} s or approximately 0.3−9.3 days of equivalent photochemical aging at a typical urban OH concentration of 3 × 10^{6} molecules cm^{-3}

Tkacik et al., Environ. Sci. Technol. 2014, 48, 11235−11242



VOC

OH

NO_2

RO_2

NO_2

NO

HO_2

NO

O_2

RO

$RONO_2$

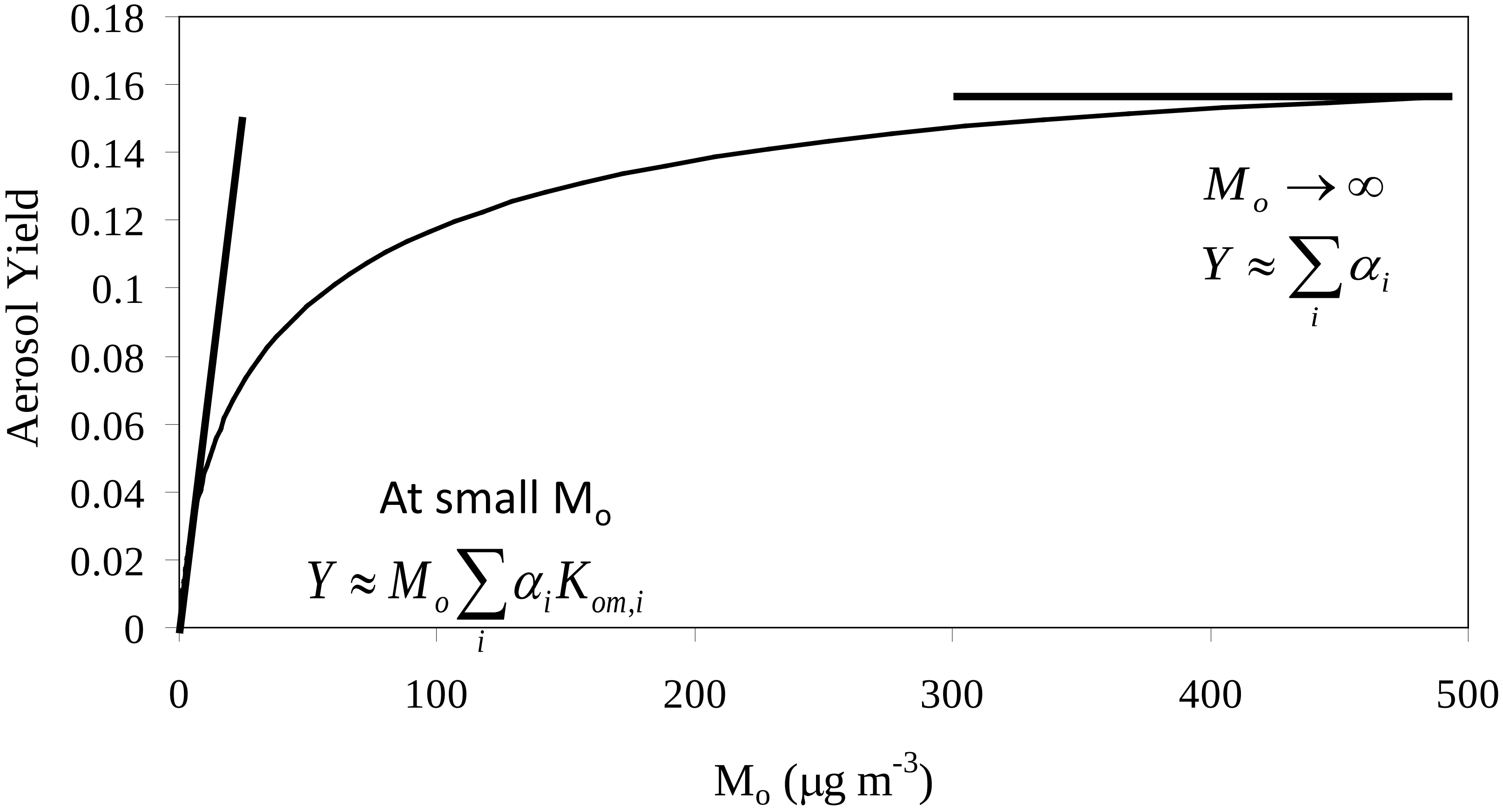
ROOH

Less volatile products

SOA

Plus additional SOA formation through oligomerization …

SOA formation as a function of organic aerosol mass



$$M_o \rightarrow \infty$$

$$Y \approx \sum_i \alpha_i$$

At small M_o

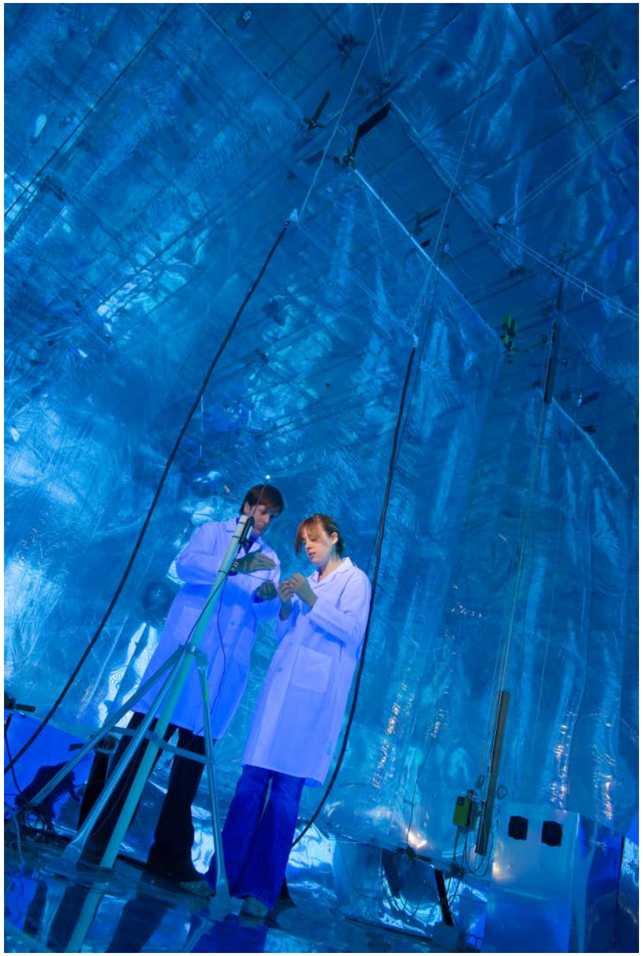
$$Y \approx M_o \sum_i \alpha_i K_{om,i}$$

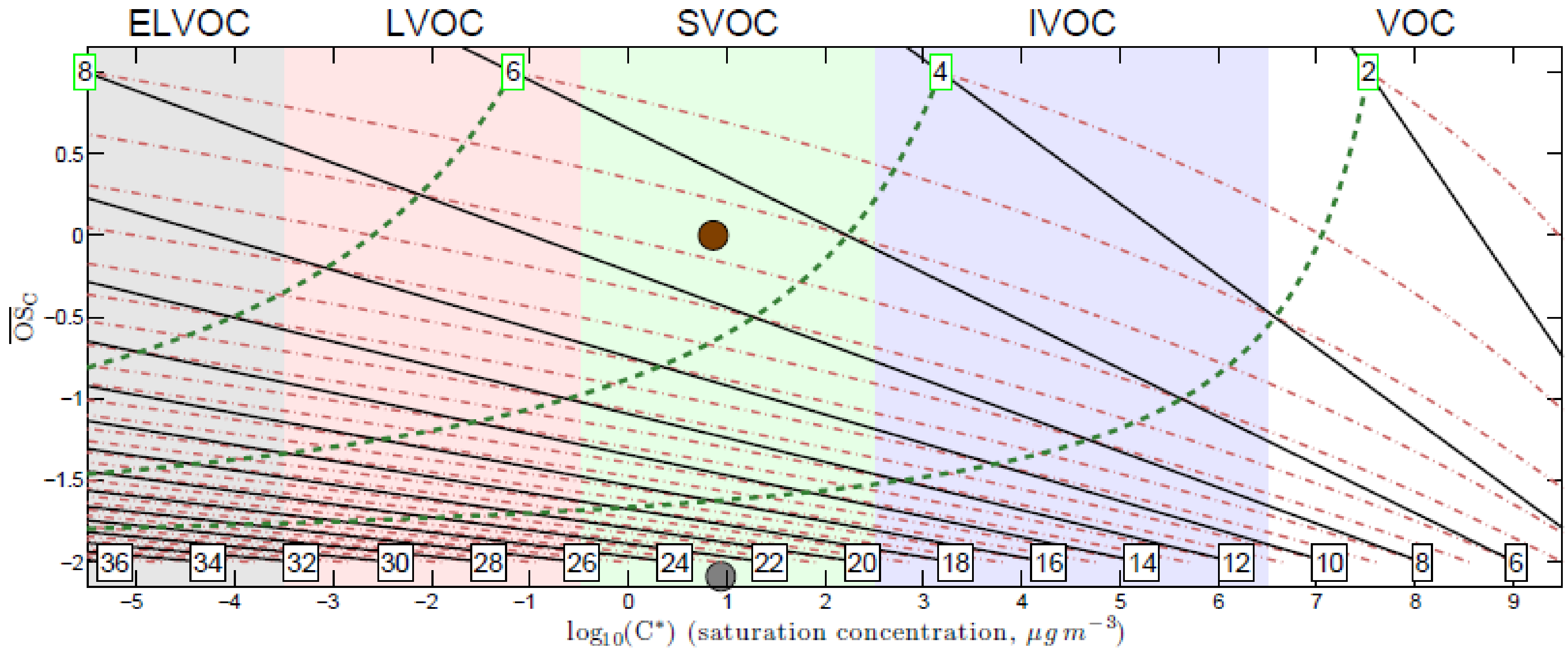
$$\boxed{Y = \sum_i Y_i = M_o \sum_i \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o}}$$

So what did we learn?

- How environmental chambers and PAMS used to study secondary aerosol formation
- Difficulties in simulating atmosphere and interpreting results
  - Regardless of measurement challenges, secondary PM formation clearly important and may dominate PM from engines in many situations with respect to atmospheric particle mass loadings
- Need to better mimic atmospheric processes

Come by for tour!





Donahue et al., AAAR, 2010