Formation and Oxidative Aging of Secondary Organic Aerosols Using the Potential Aerosol Mass Oxidation Flow Reactor

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Tesscorn Webinar – 31 May 2021

Outline

1. Background
2. Intro to Oxidation Flow Reactors (OFRs)
3. Laboratory and Field Applications of OFRs

Aerodyne Research

Providing research and development services and advanced instrument and software products to industrial, academic and government customers addressing national and international environmental, energy and defense challenges.
– Dr. Charles E. Kolb, Former President

Charles Kolb (dec. 2020)

Dave Nelson

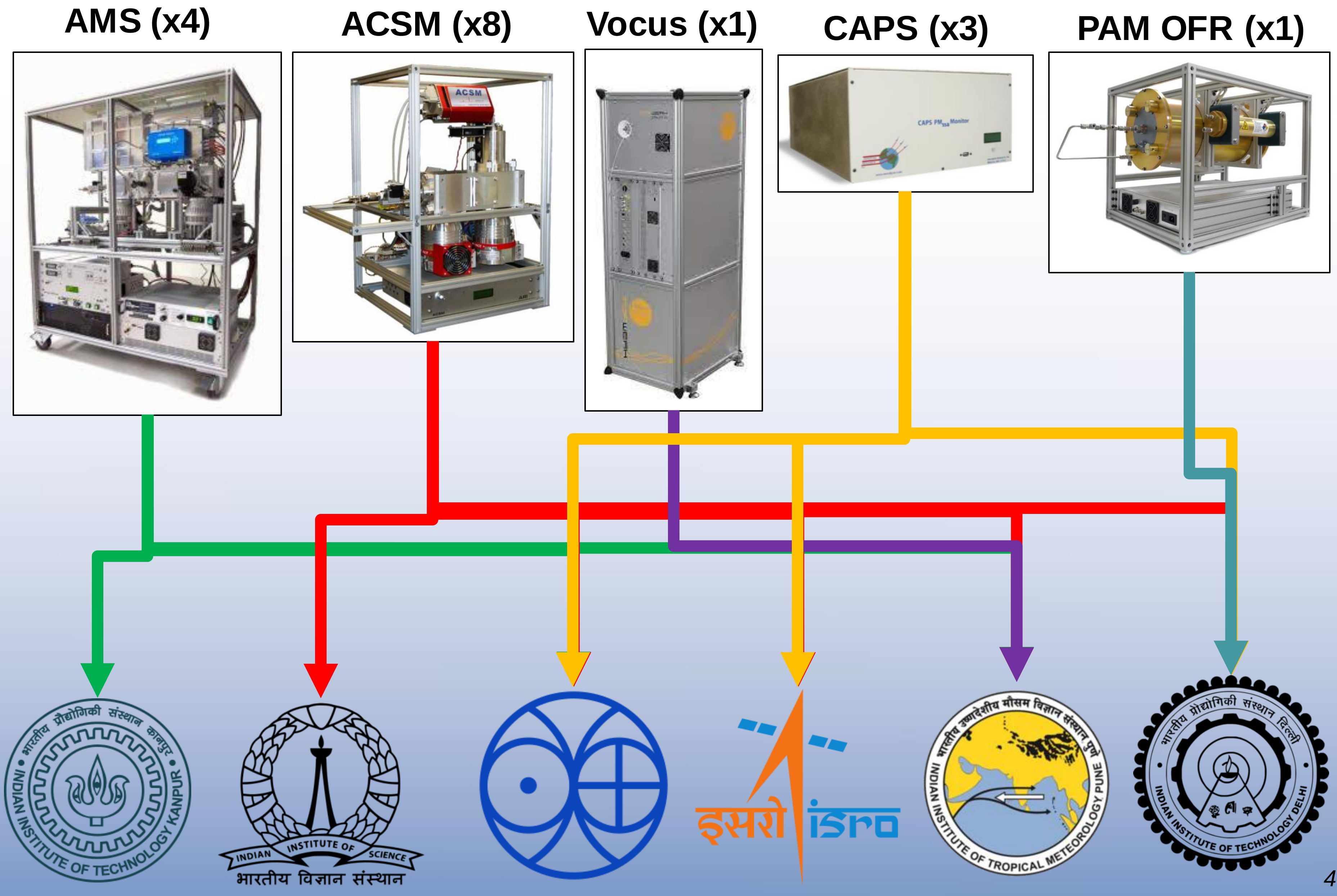
Aerodyne Research, Inc.

- **Founded in 1970**
- **Located in Billerica, MA, USA**
- **About 70 scientists and support staff**

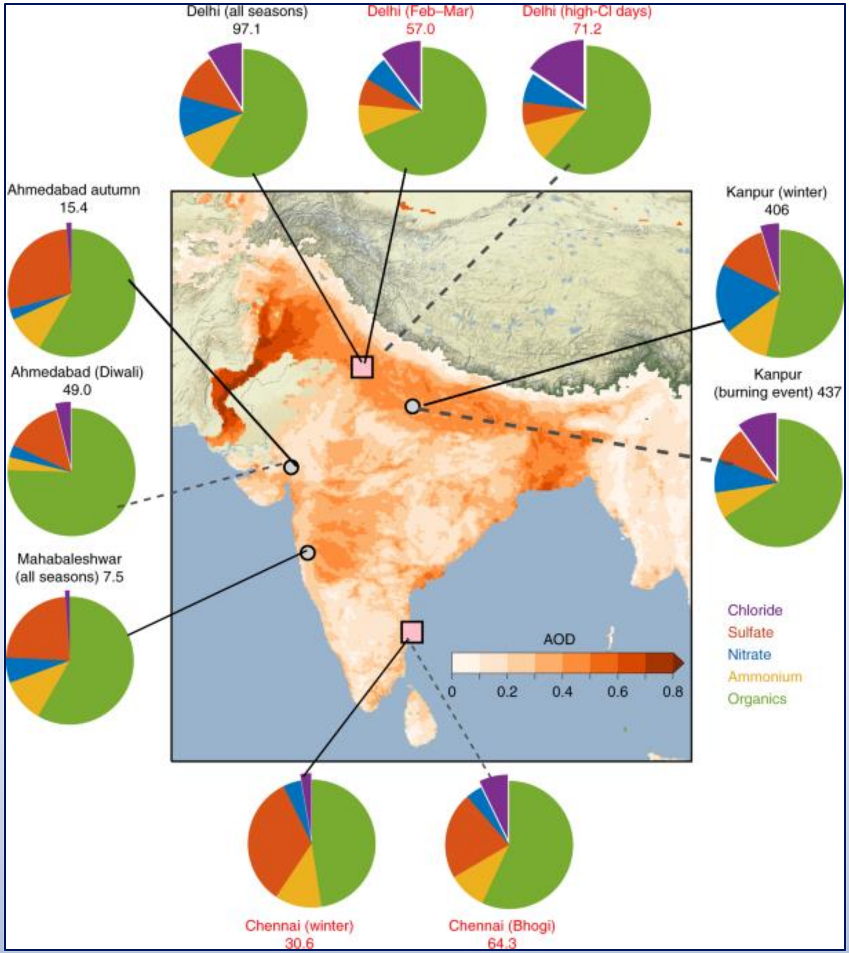
- ***Research Centers:***
  - ***Aerosol and Cloud Chemistry***
  - ***Atmospheric and Environmental Chemistry***
  - ***Aero-Thermodynamics***
  - ***Optical Signature Recognition***
  - ***Sensor Systems and Technology***

(17+) Aerodyne Instruments in India

Aerodyne
Research, Inc.



AMS measurements of aerosols in India

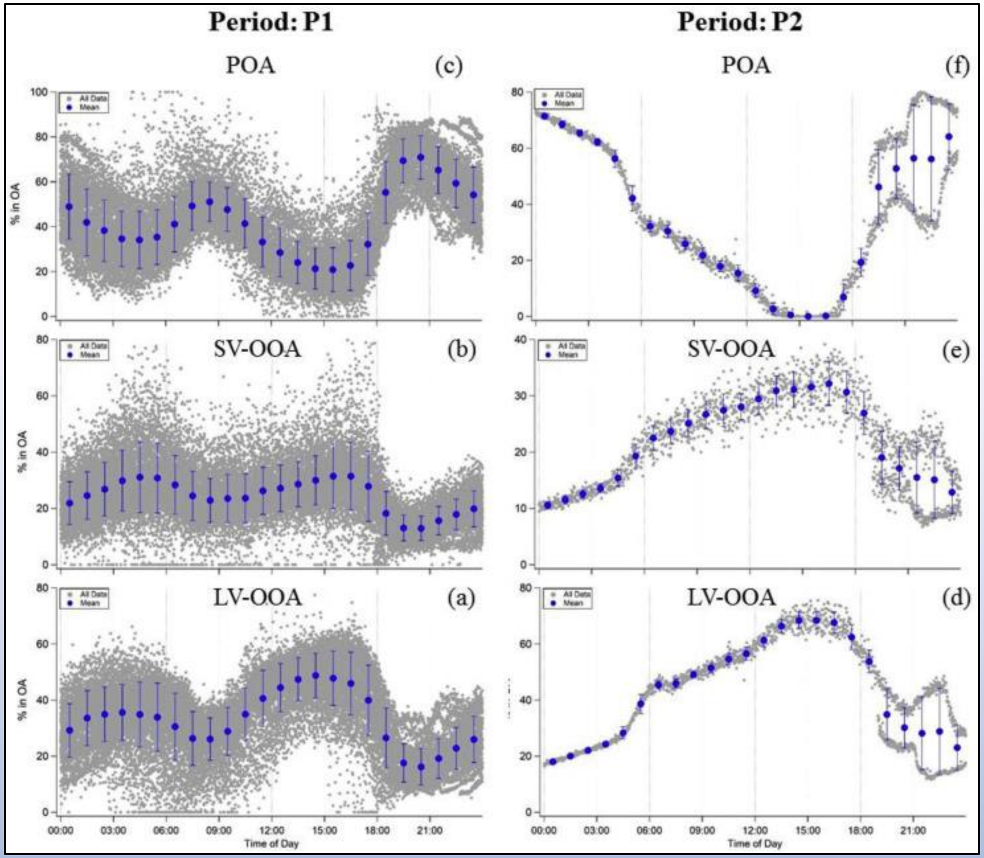


Guenthe et al.,
Nat. Geosci., **2021**

- *Nonrefractory submicron aerosols dominated by organics*

Primary/secondary OA split

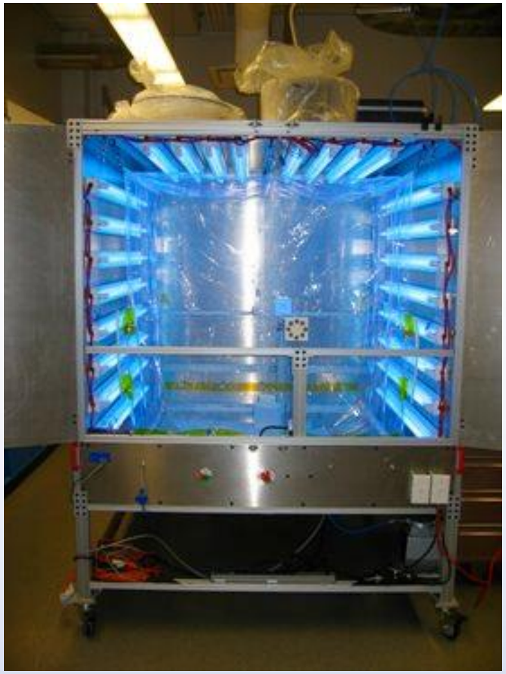
Ahmedabad, Gujarat, India



Singh et al., *Atmos. Environ.*, **2019**

- *What are the precursors to OOA (SOA)?*

Environmental chambers: traditional laboratory SOA generation



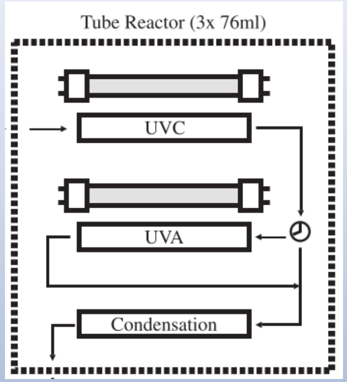
Hours/days of real time ≈(?) 1-2 days' equivalent aging time

- Large batch reactors (1-100 m^3)
- Resource-intensive, slow, contamination/wall losses

OFRs: laboratory and *in situ* SOA generation

l time ≈(?)
alent aging time

MSC

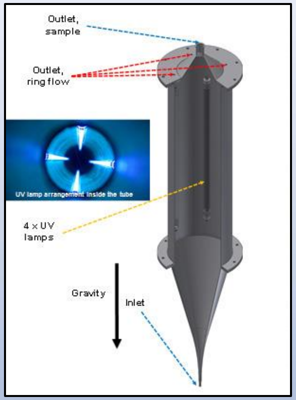


TSAR

Go:PAM

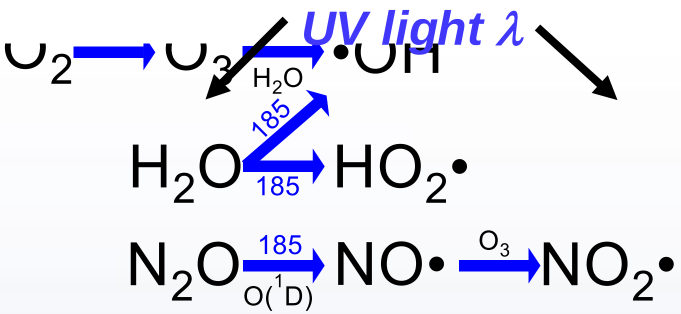
PAM

PEAR



<0.1 L ⟷ **>100 L**

Radical production in OFRs


UV light λ

$O_2 \rightarrow O_3 \xrightarrow[H_2O]{} \bullet OH$

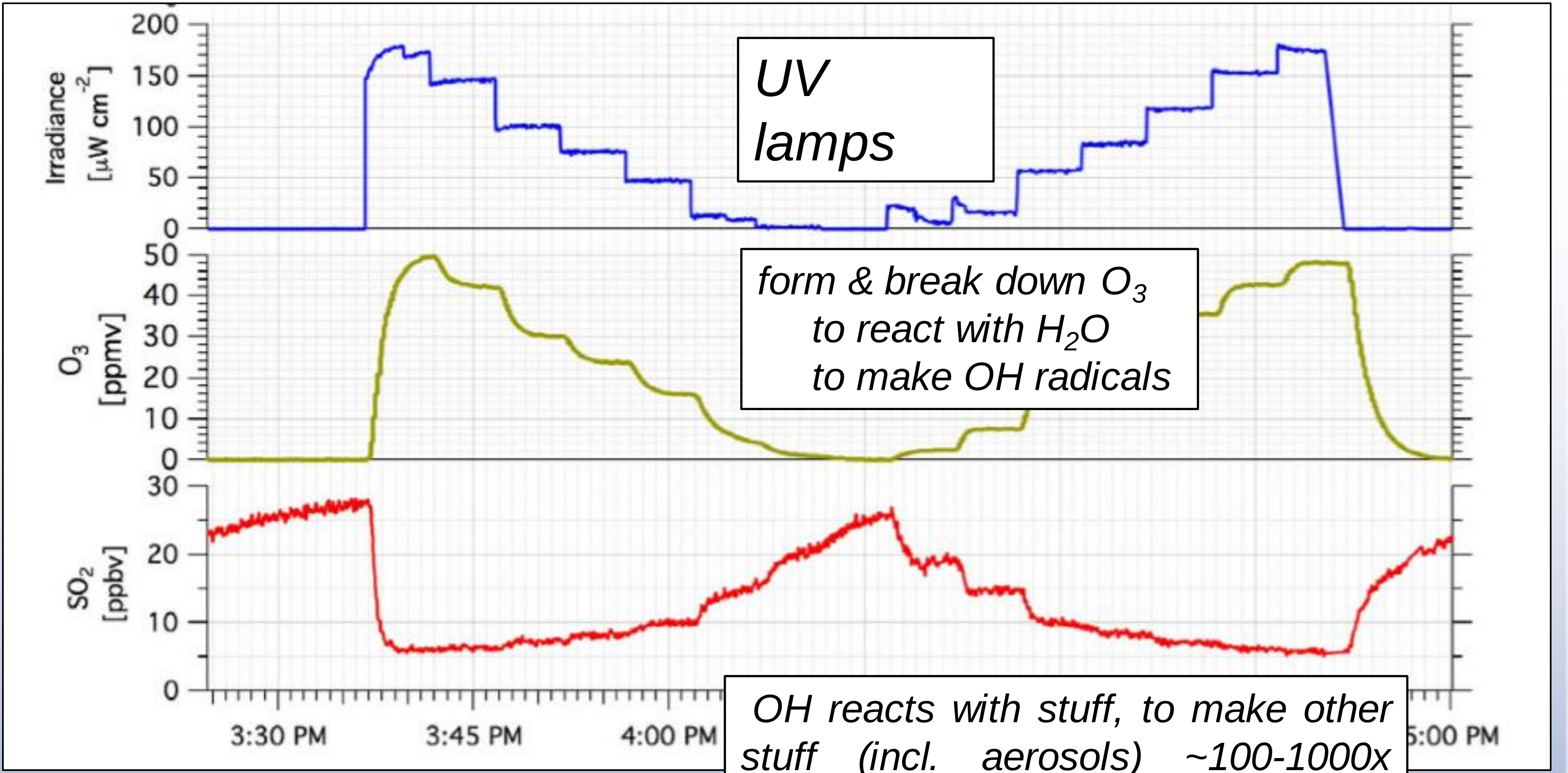
$H_2O \xrightarrow{185} \bullet OH$

$H_2O \xrightarrow{185} HO_2\bullet$

$N_2O \xrightarrow[O(^1D)]{185} NO\bullet \xrightarrow{O_3} NO_2\bullet$

- Oxidative aging timescales of days to weeks
- Low- to high-NO_x with N_2O addition (Lambe et al., *AMT*, **2017**)
- Other oxidants: O_3, NO_3, Cl, Br

Stepping through OFR conditions

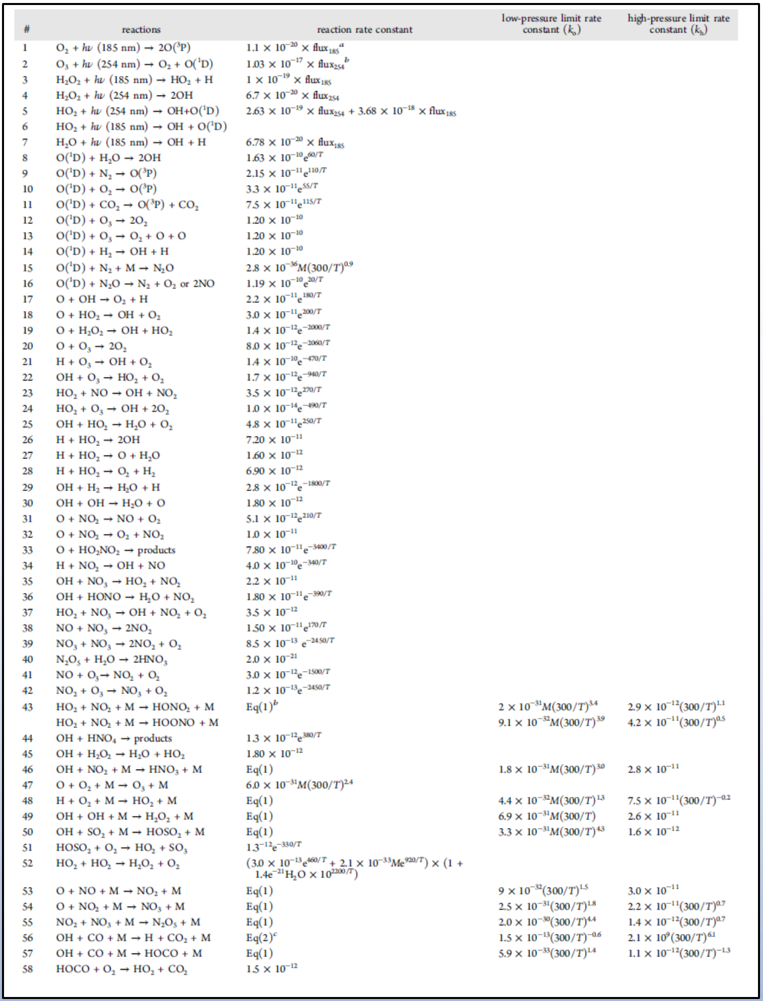


UV lamps

form & break down O_3
to react with H_2O
to make OH radicals

OH reacts with stuff, to make other stuff (incl. aerosols) ~100-1000x faster than in atmosphere

OFR photochemical box model



#	reactions	reaction rate constant	low-pressure limit rate constant (k_o)	high-pressure limit rate constant (k_h)
1	$O_2 + h\nu$ (185 nm) $\rightarrow 2O(^3P)$	$1.1 \times 10^{-20} \times \text{flux}_{185}{}^{a}$		
2	$O_3 + h\nu$ (254 nm) $\rightarrow O_2 + O(^1D)$	$1.03 \times 10^{-17} \times \text{flux}_{254}{}^{b}$		
3	$H_2O_2 + h\nu$ (185 nm) $\rightarrow HO_2 + H$	$1 \times 10^{-19} \times \text{flux}_{185}$		
4	$H_2O_2 + h\nu$ (254 nm) $\rightarrow 2OH$	$6.7 \times 10^{-20} \times \text{flux}_{254}$		
5	$HO_2 + h\nu$ (254 nm) $\rightarrow OH + O(^1D)$	$2.63 \times 10^{-19} \times \text{flux}_{254} + 3.68 \times 10^{-18} \times \text{flux}_{185}$		
6	$HO_2 + h\nu$ (185 nm) $\rightarrow OH + O(^1D)$			
7	$H_2O + h\nu$ (185 nm) $\rightarrow OH + H$	$6.78 \times 10^{-20} \times \text{flux}_{185}$		
8	$O(^1D) + H_2O \rightarrow 2OH$	$1.63 \times 10^{-10} e^{60/T}$		
9	$O(^1D) + N_2 \rightarrow O(^3P)$	$2.15 \times 10^{-11} e^{110/T}$		
10	$O(^1D) + O_2 \rightarrow O(^3P)$	$3.3 \times 10^{-11} e^{55/T}$		
11	$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$	$7.5 \times 10^{-11} e^{115/T}$		
12	$O(^1D) + O_3 \rightarrow 2O_2$	1.20×10^{-10}		
13	$O(^1D) + O_3 \rightarrow O_2 + O + O$	1.20×10^{-10}		
14	$O(^1D) + H_2 \rightarrow OH + H$	1.20×10^{-10}		
15	$O(^1D) + N_2 + M \rightarrow N_2O$	$2.8 \times 10^{-36} M(300/T)^{0.9}$		
16	$O(^1D) + N_2O \rightarrow N_2 + O_2$ or $2NO$	$1.19 \times 10^{-10} e^{20/T}$		
17	$O + OH \rightarrow O_2 + H$	$2.2 \times 10^{-11} e^{180/T}$		
18	$O + HO_2 \rightarrow OH + O_2$	$3.0 \times 10^{-11} e^{200/T}$		
19	$O + H_2O_2 \rightarrow OH + HO_2$	$1.4 \times 10^{-12} e^{-2000/T}$		
20	$O + O_3 \rightarrow 2O_2$	$8.0 \times 10^{-12} e^{-2060/T}$		
21	$H + O_3 \rightarrow OH + O_2$	$1.4 \times 10^{-10} e^{-470/T}$		
22	$OH + O_3 \rightarrow HO_2 + O_2$	$1.7 \times 10^{-12} e^{-940/T}$		
23	$HO_2 + NO \rightarrow OH + NO_2$	$3.5 \times 10^{-12} e^{270/T}$		
24	$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.0 \times 10^{-14} e^{-490/T}$		
25	$OH + HO_2 \rightarrow H_2O + O_2$	$4.8 \times 10^{-11} e^{250/T}$		
26	$H + HO_2 \rightarrow 2OH$	7.20×10^{-11}		
27	$H + HO_2 \rightarrow O + H_2O$	1.60×10^{-12}		
28	$H + HO_2 \rightarrow O_2 + H_2$	6.90×10^{-12}		
29	$OH + H_2 \rightarrow H_2O + H$	$2.8 \times 10^{-12} e^{-1800/T}$		
30	$OH + OH \rightarrow H_2O + O$	1.80×10^{-12}		
31	$O + NO_2 \rightarrow NO + O_2$	$5.1 \times 10^{-12} e^{210/T}$		
32	$O + NO_2 \rightarrow O_2 + NO_2$	1.0×10^{-11}		
33	$O + HO_2NO_2 \rightarrow$ products	$7.80 \times 10^{-11} e^{-3400/T}$		
34	$H + NO_2 \rightarrow OH + NO$	$4.0 \times 10^{-10} e^{-340/T}$		
35	$OH + NO_3 \rightarrow HO_2 + NO_2$	2.2×10^{-11}		
36	$OH + HONO \rightarrow H_2O + NO_2$	$1.80 \times 10^{-11} e^{-390/T}$		
37	$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2$	3.5×10^{-12}		
38	$NO + NO_3 \rightarrow 2NO_2$	$1.50 \times 10^{-11} e^{170/T}$		
39	$NO_3 + NO_3 \rightarrow 2NO_2 + O_2$	$8.5 \times 10^{-13}\ e^{-2450/T}$		
40	$N_2O_5 + H_2O \rightarrow 2HNO_3$	2.0×10^{-21}		
41	$NO + O_3 \rightarrow NO_2 + O_2$	$3.0 \times 10^{-12} e^{-1500/T}$		
42	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2 \times 10^{-13} e^{-2450/T}$		
43	$HO_2 + NO_2 + M \rightarrow HONO_2 + M$	Eq(1)[b]	$2 \times 10^{-31} M(300/T)^{3.4}$	$2.9 \times 10^{-12}(300/T)^{1.1}$
	$HO_2 + NO_2 + M \rightarrow HOONO + M$		$9.1 \times 10^{-32} M(300/T)^{3.9}$	$4.2 \times 10^{-11}(300/T)^{0.5}$
44	$OH + HNO_4 \rightarrow$ products	$1.3 \times 10^{-12} e^{380/T}$		
45	$OH + H_2O_2 \rightarrow H_2O + HO_2$	1.80×10^{-12}		
46	$OH + NO_2 + M \rightarrow HNO_3 + M$	Eq(1)	$1.8 \times 10^{-31} M(300/T)^{3.0}$	2.8×10^{-11}
47	$O + O_2 + M \rightarrow O_3 + M$	$6.0 \times 10^{-31} M(300/T)^{2.4}$		
48	$H + O_2 + M \rightarrow HO_2 + M$	Eq(1)	$4.4 \times 10^{-32} M(300/T)^{1.3}$	$7.5 \times 10^{-11}(300/T)^{-0.2}$
49	$OH + OH + M \rightarrow H_2O_2 + M$	Eq(1)	$6.9 \times 10^{-31} M(300/T)$	2.6×10^{-11}
50	$OH + SO_2 + M \rightarrow HOSO_2 + M$	Eq(1)	$3.3 \times 10^{-31} M(300/T)^{4.3}$	1.6×10^{-12}
51	$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	$1.3^{-12} e^{-330/T}$		
52	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$(3.0 \times 10^{-13} e^{460/T} + 2.1 \times 10^{-33} M e^{920/T}) \times (1 + 1.4e^{-21} H_2O \times 10^{2200/T})$		
53	$O + NO + M \rightarrow NO_2 + M$	Eq(1)	$9 \times 10^{-32}(300/T)^{1.5}$	3.0×10^{-11}
54	$O + NO_2 + M \rightarrow NO_3 + M$	Eq(1)	$2.5 \times 10^{-31}(300/T)^{1.8}$	$2.2 \times 10^{-11}(300/T)^{0.7}$
55	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	Eq(1)	$2.0 \times 10^{-30}(300/T)^{4.4}$	$1.4 \times 10^{-12}(300/T)^{0.7}$
56	$OH + CO + M \rightarrow H + CO_2 + M$	Eq(2)[c]	$1.5 \times 10^{-13}(300/T)^{-0.6}$	$2.1 \times 10^{9}(300/T)^{6.1}$
57	$OH + CO + M \rightarrow HOCO + M$	Eq(1)	$5.9 \times 10^{-33}(300/T)^{1.4}$	$1.1 \times 10^{-12}(300/T)^{-1.3}$
58	$HOCO + O_2 \rightarrow HO_2 + CO_2$	1.5×10^{-12}		

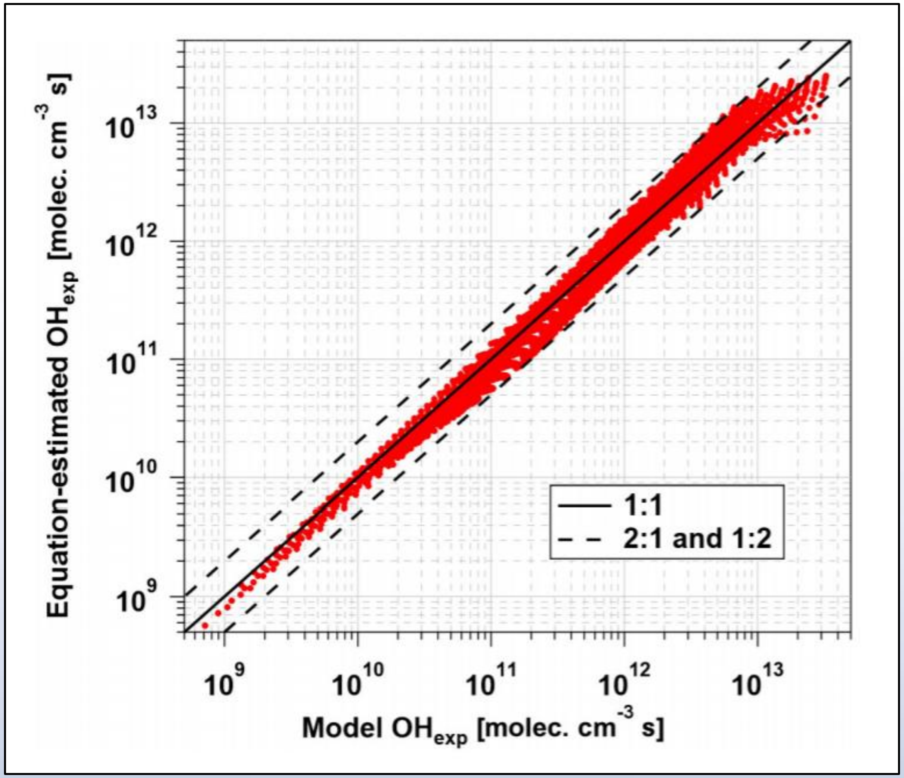
Li et al., *J. Phys. Chem. A*, **2015**

- *Reactions describing formation and destruction of radicals (incl. OH)*

Simplified OFR model representation

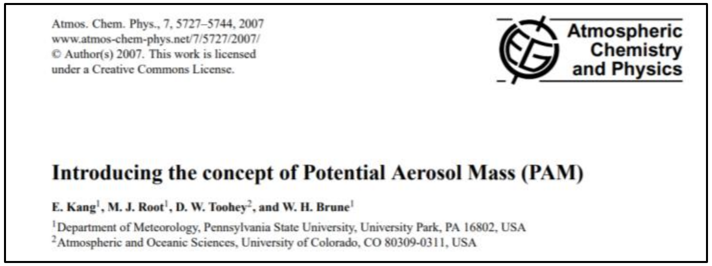
$$\log[\mathrm{OH}_{\mathrm{exp}}] = \Big(a + \big(b + c \times \mathrm{OHR}_{\mathrm{ext}}^{d} + e \times \log[\mathrm{O_3}] \times \mathrm{OHR}_{\mathrm{ext}}^{f}\big) \times \log[\mathrm{O_3}] + \log[\mathrm{H_2O}]\Big) + \log\left(\frac{\tau}{124}\right).$$

“Estimation Equation”



Rowe et al., *ACP*, **2020**

- *Photochemical age (days) ≈ OH exposure *10^{-11}*
- See also: Li et al., J. Phys. Chem. A, **2015**; Peng et al., ACP, **2016**



Atmos. Chem. Phys., 7, 5727–5744, 2007
www.atmos-chem-phys.net/7/5727/2007/
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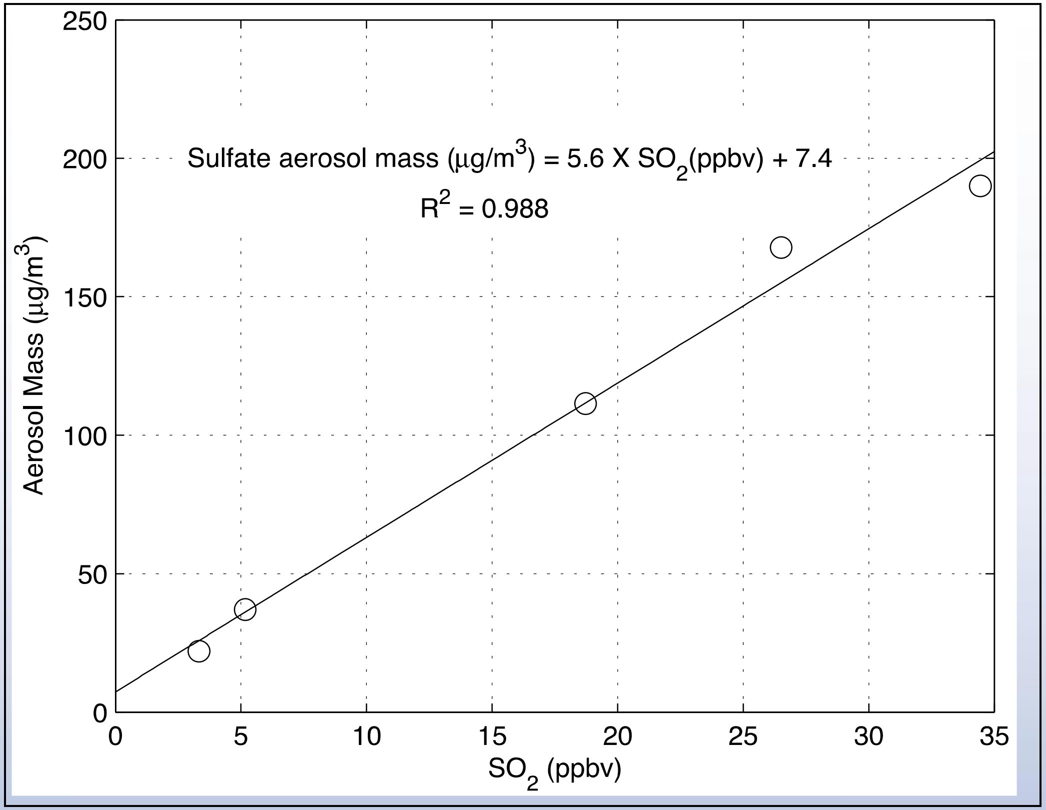
Atmospheric
Chemistry
and Physics

Introducing the concept of Potential Aerosol Mass (PAM)

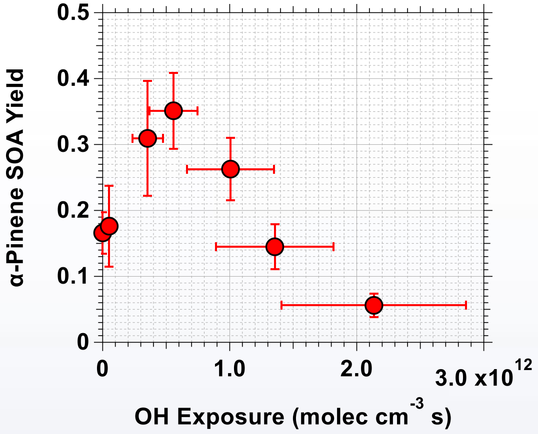
E. Kang[1], M. J. Root[1], D. W. Toohey[2], and W. H. Brune[1]

[1]Department of Meteorology, Pennsylvania State University, University Park, PA 16802, USA
[2]Atmospheric and Oceanic Sciences, University of Colorado, CO 80309-0311, USA



- Early definition of “PAM” = maximum aerosol mass that oxidation of precursor gas(es) produces

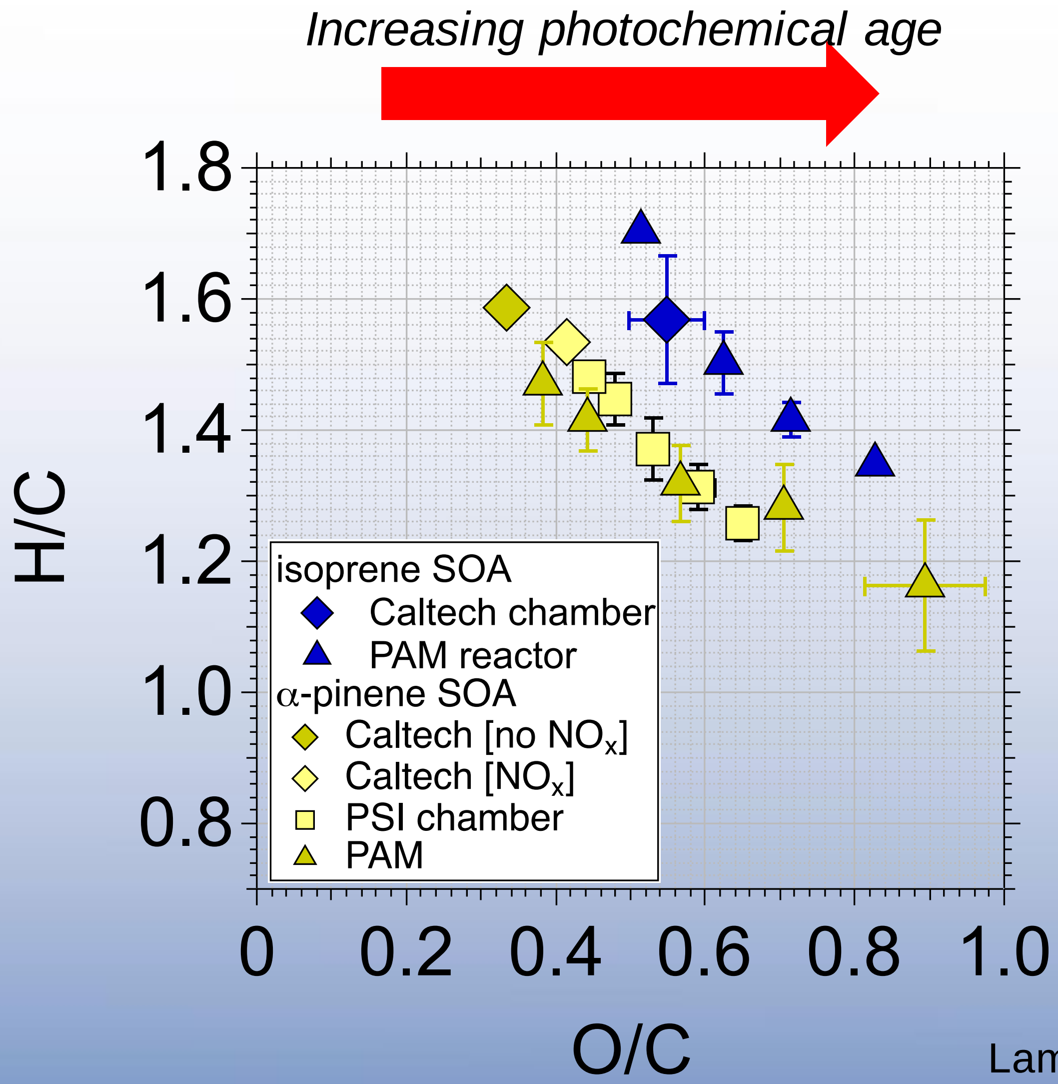
Potential Aerosol Mass of …VOCs?



Lambe et al.,
ACP, **2015**

- SOA composition is dynamic as a function of photochemical age

Elemental composition of SOA generated in chambers versus OFRs



Lambe et al., *ACP*, **2015**

PAM OFR community (65+ groups)

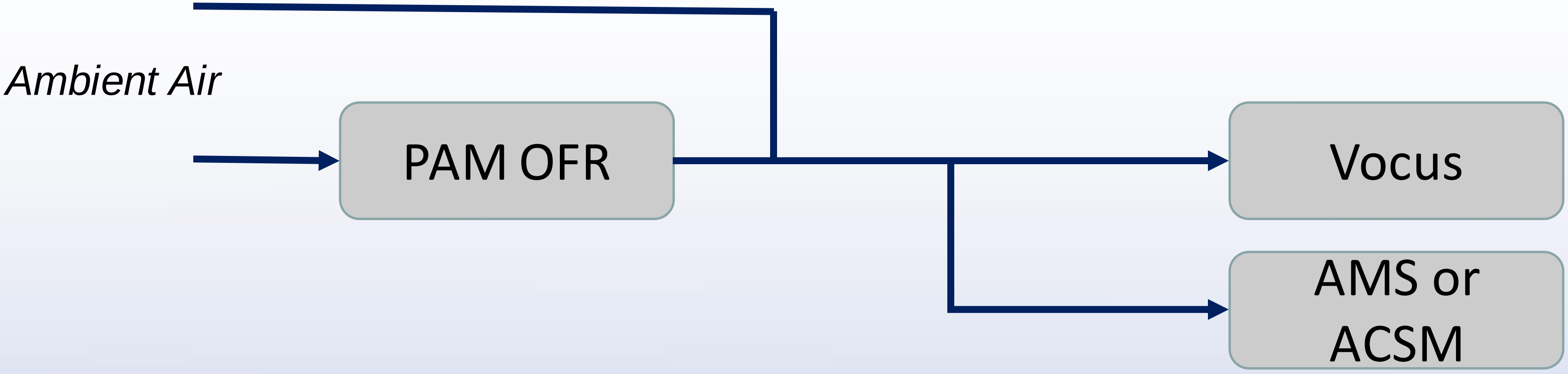
Bill Brune
Penn State

Andy Lambe et al.
Aerodyne

Rajan Chakrabarty
WashU – St Louis
PAM-001

Mayank Kumar,
IIT Delhi
PAM-042

What can be Learned from SOA Chemistry Studies in India?



Ambient Air

PAM OFR

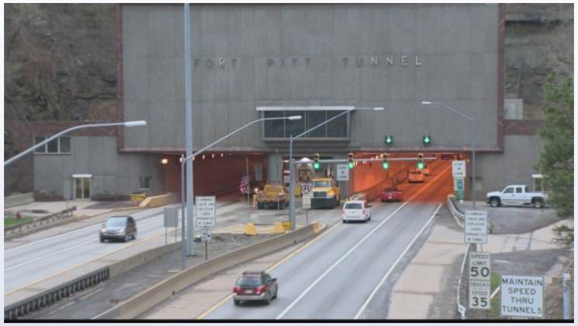
Vocus

AMS or ACSM

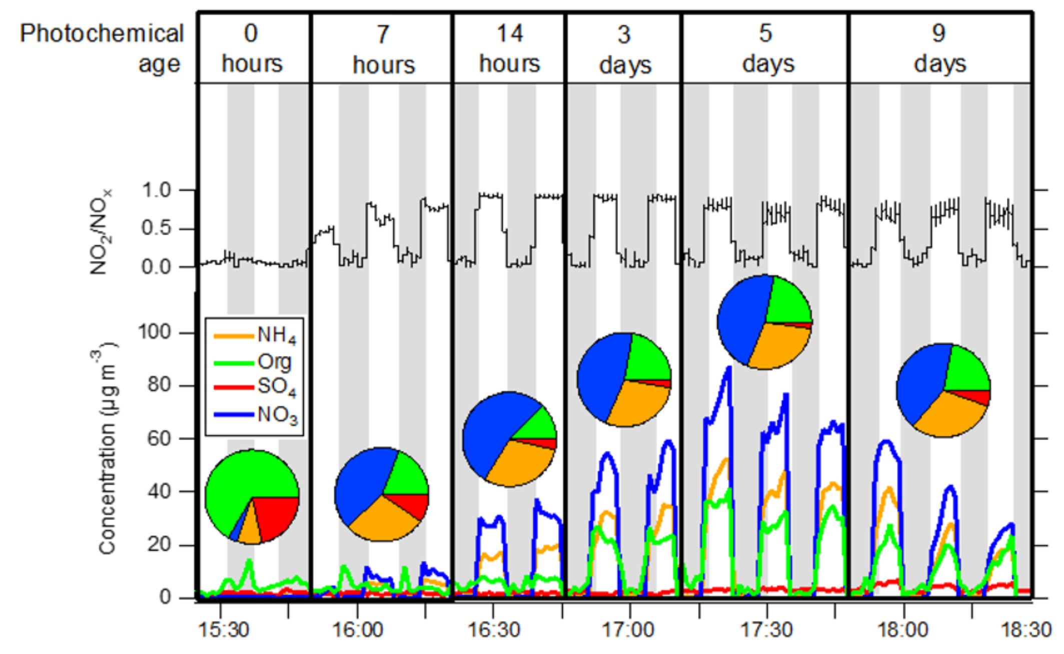
adapted from Joost de Gouw, CU Boulder

1. What fraction of SOA formation is explained by oxidation of measured VOCs?
2. What are the gas- and particle-phase products from the OFR and are they also observed in aged air masses?

Aging motor vehicle emissions in a traffic tunnel

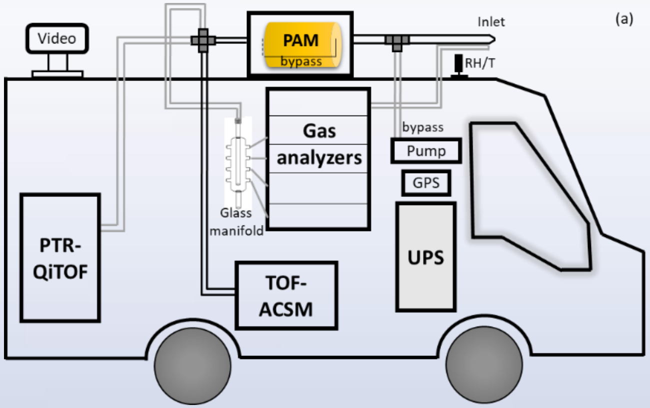


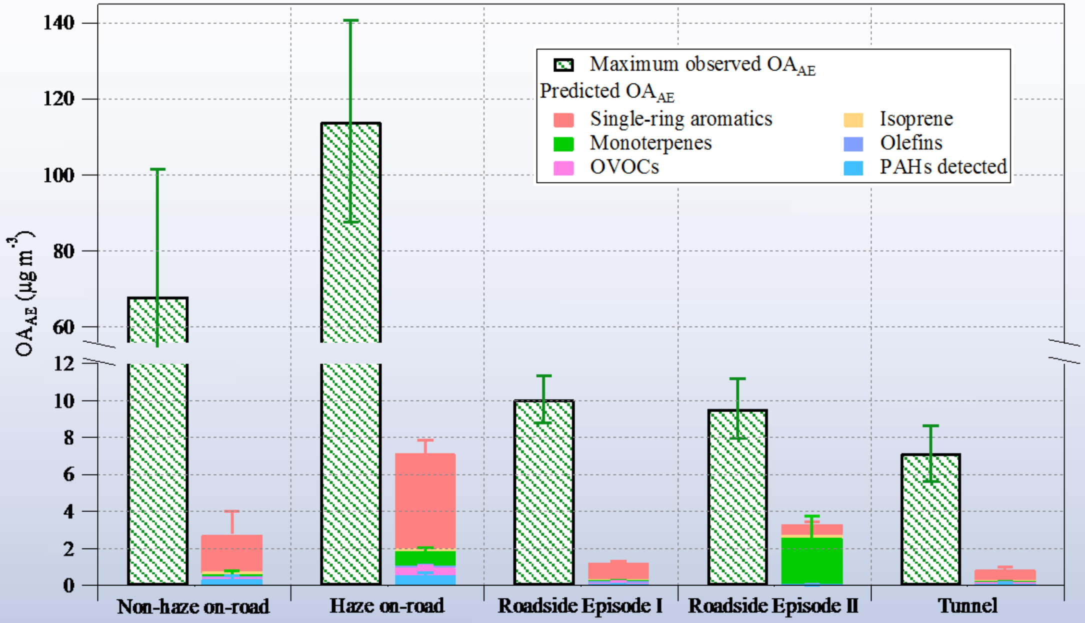
Fort Pitt Tunnel
Pittsburgh, PA, USA



Tkacik et al., ES&T, 2014

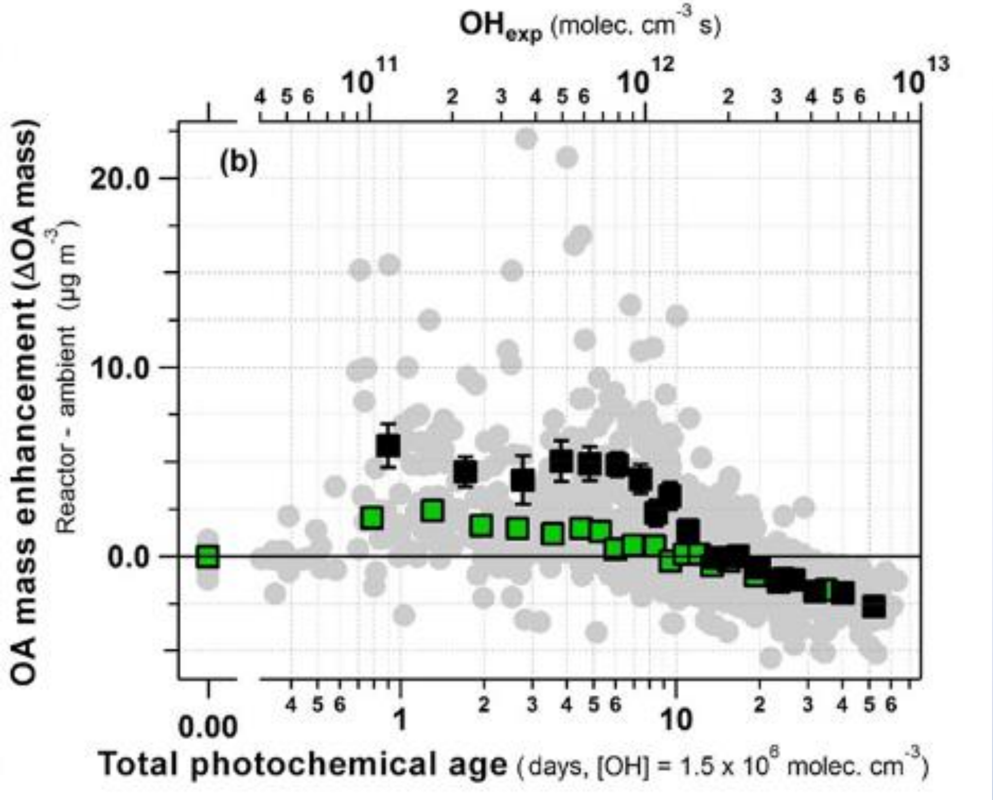
Aging on-road motor vehicle emissions





4th Ring Road, Beijing, China
Liao et al., *ES&T*, 2021

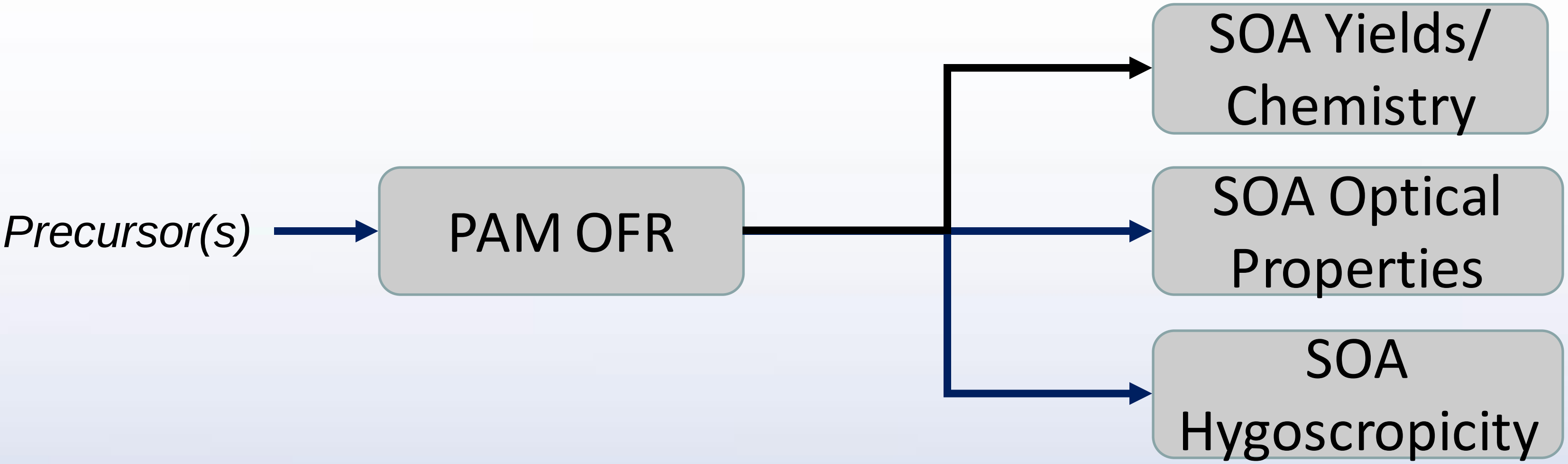
Aging urban background air



CalNex, Pasadena, CA, USA
Ortega et al., ACP, ***2016***

<u>Other studies:</u> Palm et al., ACP, 2016, 2017, 2018; Hu et al., ACP, 2016; Hu et al., ES&T, under review; Kang et al., ACP, 2018; Nault et al., ACP, 2018; Ahlberg et al., Atmosphere, 2020

What Can Be Learned about SOA Physicochemical Properties using OFRs?



Precursor(s)

PAM OFR

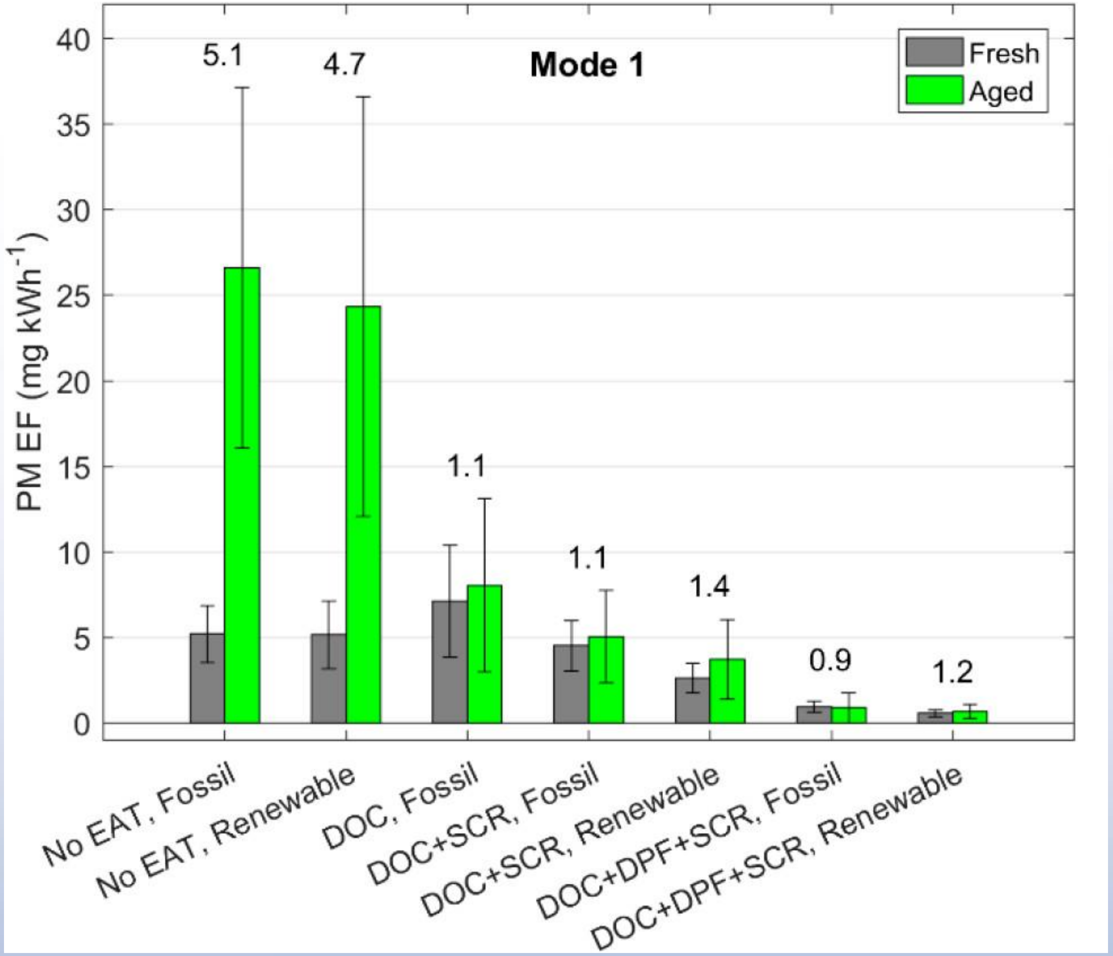
SOA Yields/ Chemistry

SOA Optical Properties

SOA Hygoscropicity

1. What are SOA yields and composition over multiple generations of aging?
2. What precursor(s) are necessary to explain ambient SOA formation?
3. How do SOA properties such as light absorption and water uptake change with aging?

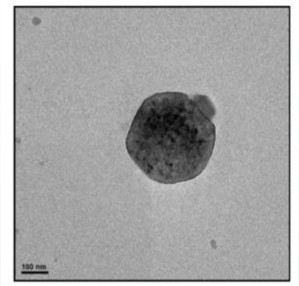
Aging laboratory diesel emissions



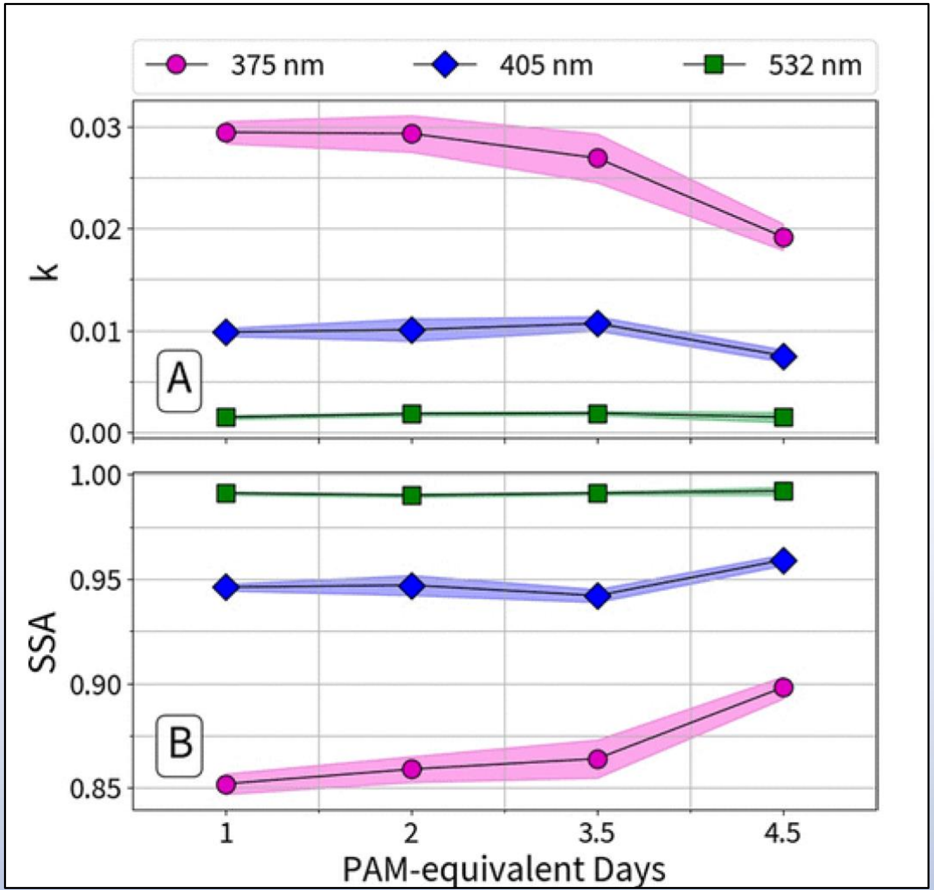
*Karjalainen et al., ES&T, **2019***

<u>Other studies:</u> Karjalainen et al., *ACP*, **2016;** Link et al., *Atmos. Environ*, **2017;** Zhao et al., *ES&T*, **2018;** Pieber et al., *ACP*, **2018**

Aging biomass burning emissions



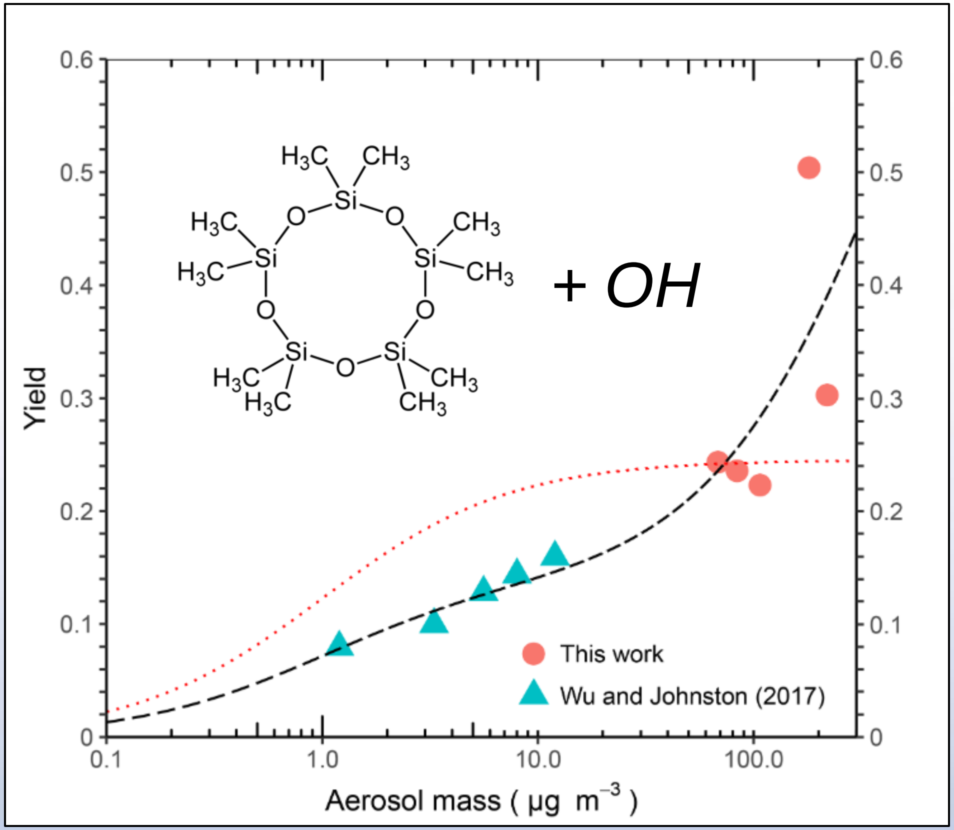
“Tar balls”



Sumlin et al., ES&T Letters, 2017
[Chakrabarty Group]

Other studies: Cubison et al., *ACP*, 2011; Ortega et al., *ACP*, 2013; Martinsson et al., *ES&T*, 2015; Fortenberry et al., *ACP*, 2018; Pieber et al., *ES&T*, 2019; Sangupta et al., ACP, 2019

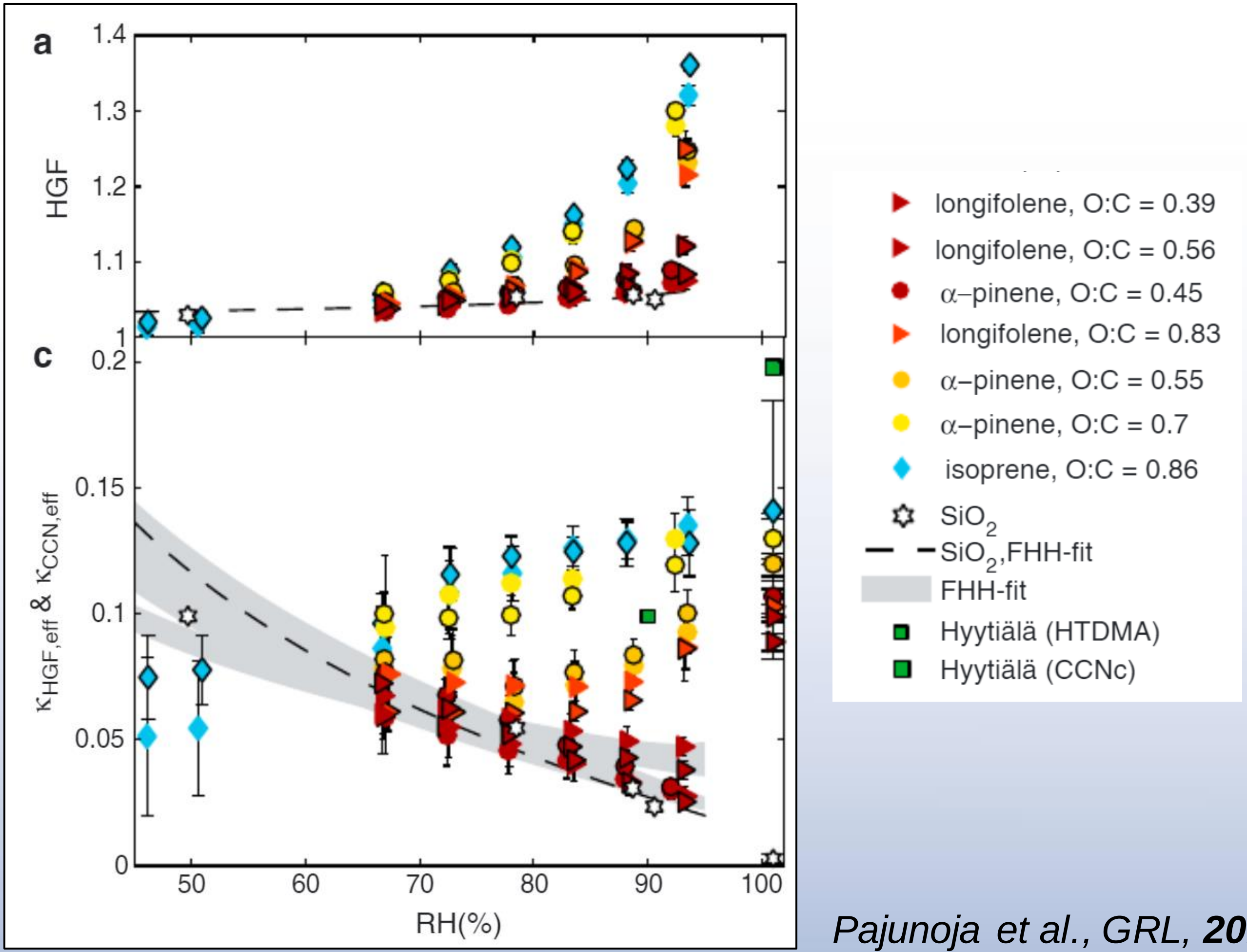
Laboratory SOA Yield Studies



Janecheck et al., ACP, ***2019***

Other Studies: Lambe et al., ES&T, **2012;** Li et al., ES&T, **2013;** Chen et al., ACP, **2013;** Bruns et al., AMT, **2015** Jathar et al., ES&T, **2017;** Ahlberg et al., Atmos. Environ., **2017;** Friedman et al., ES&T, **2017;** Eluri et al, ACP, **2018**; Ahlberg et al., ACP, **2019;** Khalej et al., **2021**

SOA hygroscopicity studies

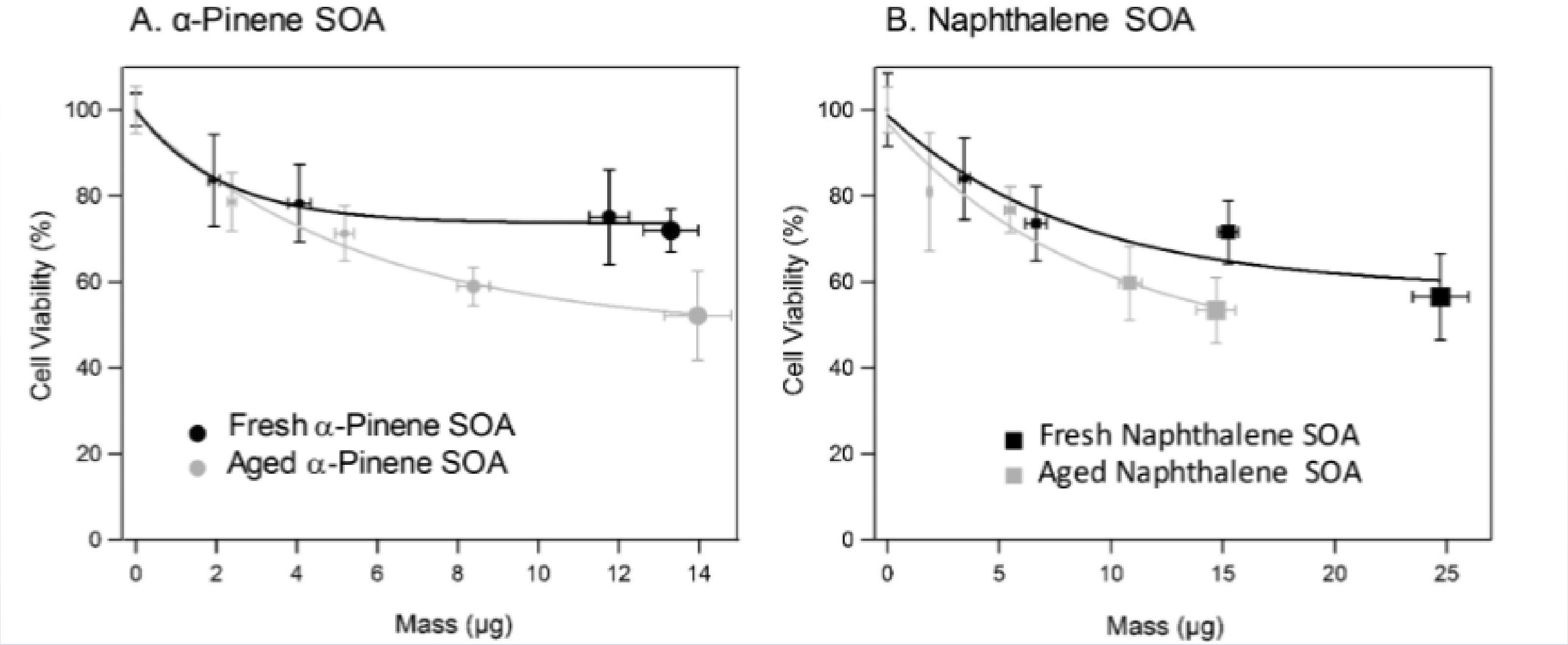


Pajunoja et al., GRL, ***2015***

Other studies

Massoli et al., *GRL*, **2010;** Saukko et al., *ACP*, **2012;** Wang et al., *JGR-A*,**2012;** Lambe et al., *ES&T*, **2013;** Lienhard et al., *ACP*, **2015;** Liu et al., *ACP*, **2015;** Schill et al., *GRL*, **2016;** Watne et al., *ES&T*, **2017;** Charnawskas et al., *Faraday Discuss*., **2017;** He et al., *ES&T*, **2018;** Zhang et al., *ES&T Letters*, **2018;** Buchholz et al., *ACP*, **2019**

SOA toxicity studies



Chowdhury et al., *ES&T Letters*, **2018**

__**Other studies:**__ Chowdhury et al., *ES&T*, **2019;** King et al., *Chemosphere*, **2021;** Li et al., *J. Haz. Mat.*, **2021;** Khan et al., *Chem. Res. Toxicol.*, **2021**

Summary

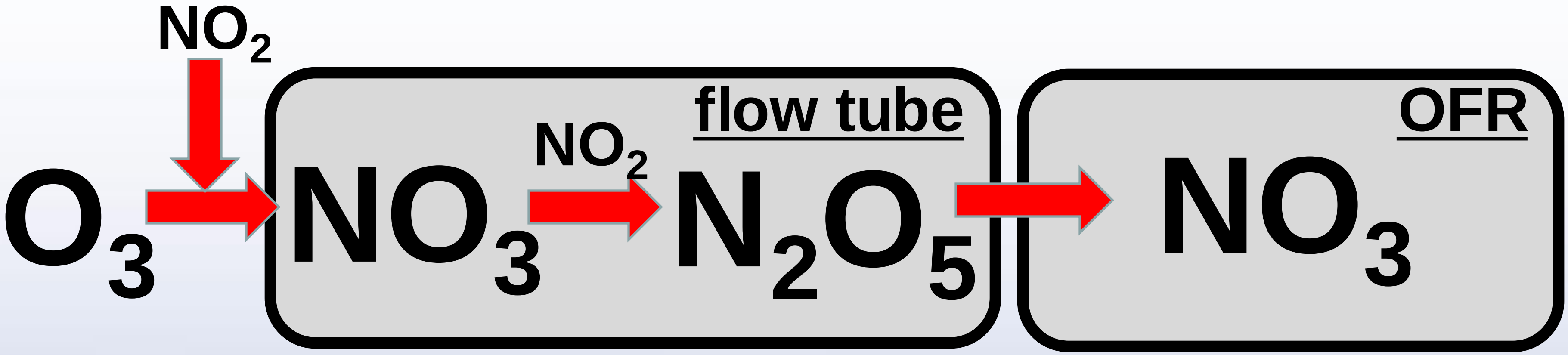
- OFRs can be used for understanding OVOC/SOA formation and aging
- OFR perturbations of ambient air aid interpretation of OVOC/SOA precursors and source factors (PMF)
- OFRs complement and extend the capabilities of environmental chambers, usually at much lower cost

Resources

- Wiki: https://sites.google.com/site/pamwiki/
- Manual (moving to ARI knowledge base): https://pamusersmanual.jimdo.com/
- aerodyne-pam-users@aerodyne.com

Thank you!

“On demand” N_2O_5 & NO_3 generation via OFR_{dark}-iN_2O_5



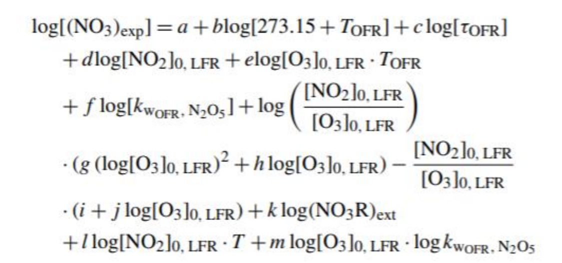
NO_2

$O_3 \rightarrow NO_3 \xrightarrow{NO_2} N_2O_5 \rightarrow NO_3$

flow tube

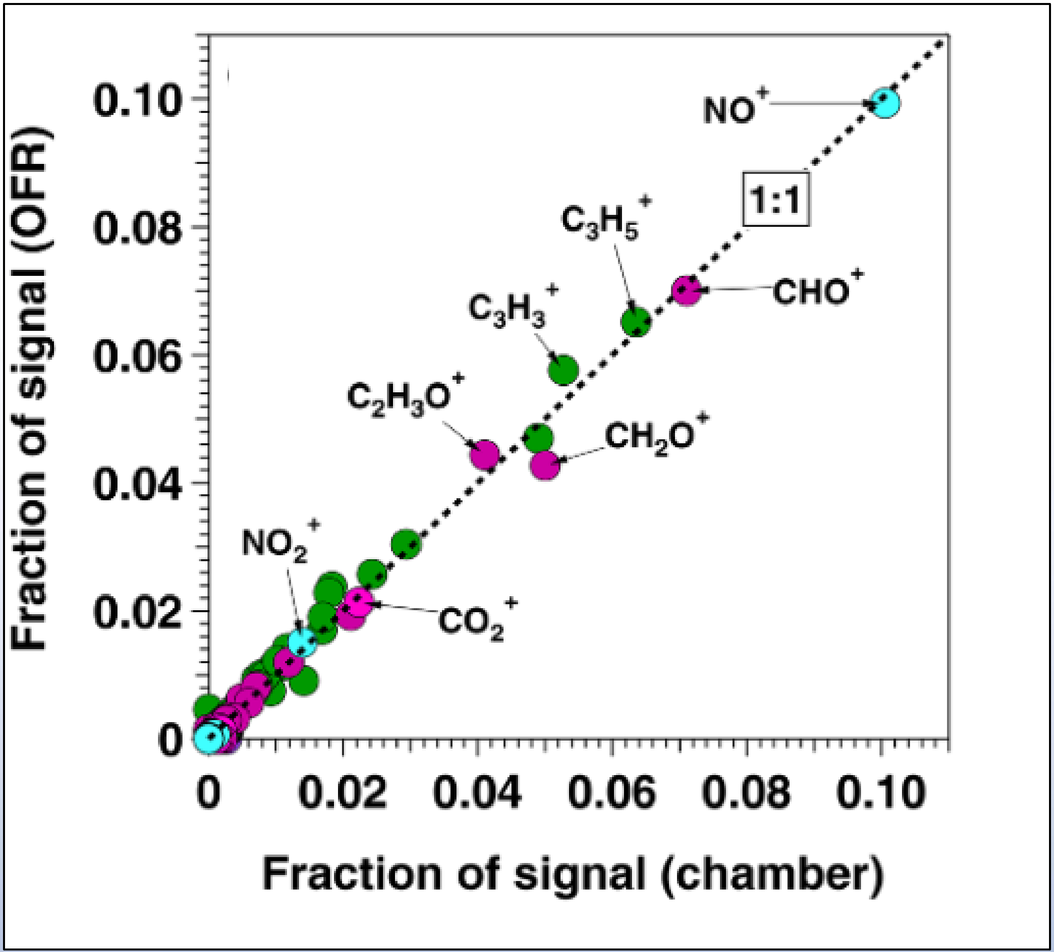
OFR

Lambe et al., AMT, ***2020***



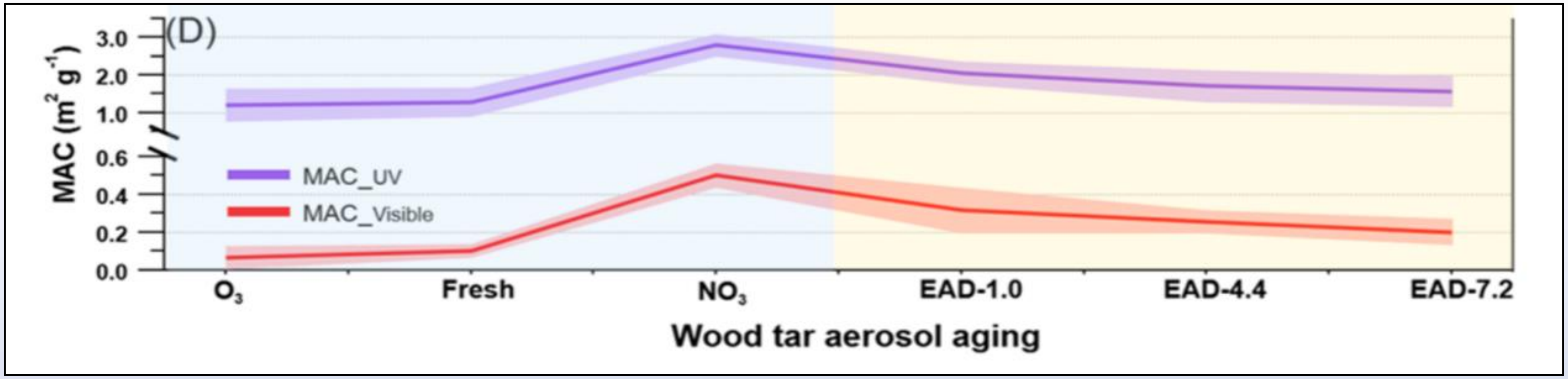
$$\begin{aligned}
\log[(\mathrm{NO_3})_{\mathrm{exp}}] &= a + b\log[273.15 + T_{\mathrm{OFR}}] + c\log[\tau_{\mathrm{OFR}}] \\
&+ d\log[\mathrm{NO_2}]_{0,\,\mathrm{LFR}} + e\log[\mathrm{O_3}]_{0,\,\mathrm{LFR}} \cdot T_{\mathrm{OFR}} \\
&+ f\log[k_{\mathrm{w_{OFR}},\,\mathrm{N_2O_5}}] + \log\left(\frac{[\mathrm{NO_2}]_{0,\,\mathrm{LFR}}}{[\mathrm{O_3}]_{0,\,\mathrm{LFR}}}\right) \\
&\cdot (g\,(\log[\mathrm{O_3}]_{0,\,\mathrm{LFR}})^2 + h\log[\mathrm{O_3}]_{0,\,\mathrm{LFR}}) - \frac{[\mathrm{NO_2}]_{0,\,\mathrm{LFR}}}{[\mathrm{O_3}]_{0,\,\mathrm{LFR}}} \\
&\cdot (i + j\log[\mathrm{O_3}]_{0,\,\mathrm{LFR}}) + k\log(\mathrm{NO_3R})_{\mathrm{ext}} \\
&+ l\log[\mathrm{NO_2}]_{0,\,\mathrm{LFR}} \cdot T + m\log[\mathrm{O_3}]_{0,\,\mathrm{LFR}} \cdot \log k_{\mathrm{w_{OFR}},\,\mathrm{N_2O_5}}
\end{aligned}$$

Particulate organic nitrate generation via OFR-iN_2O_5



β-pinene + NO_3 SOA
Lambe et al., AMT, **2020**

Diel oxidative aging of aerosols



Li et al., ES&T, **2020a**

Other studies: Cheng et al., Aerosol Sci. Technol, **2020**; Li et al., ES&T, **2020b**; He et al., ES&T, **2021**; Li et al., Science of the Total Environment, **2021**; Sumlin et al., ACP, **under review**