Process-Level, Kinetic Models to Study the Formation, Properties, and Expt. Artifacts for SOA

Shantanu Jathar, Charles He, Kelsey Bilsback, Ali Akherati, Christopher Cappa, and Jeffrey Pierce

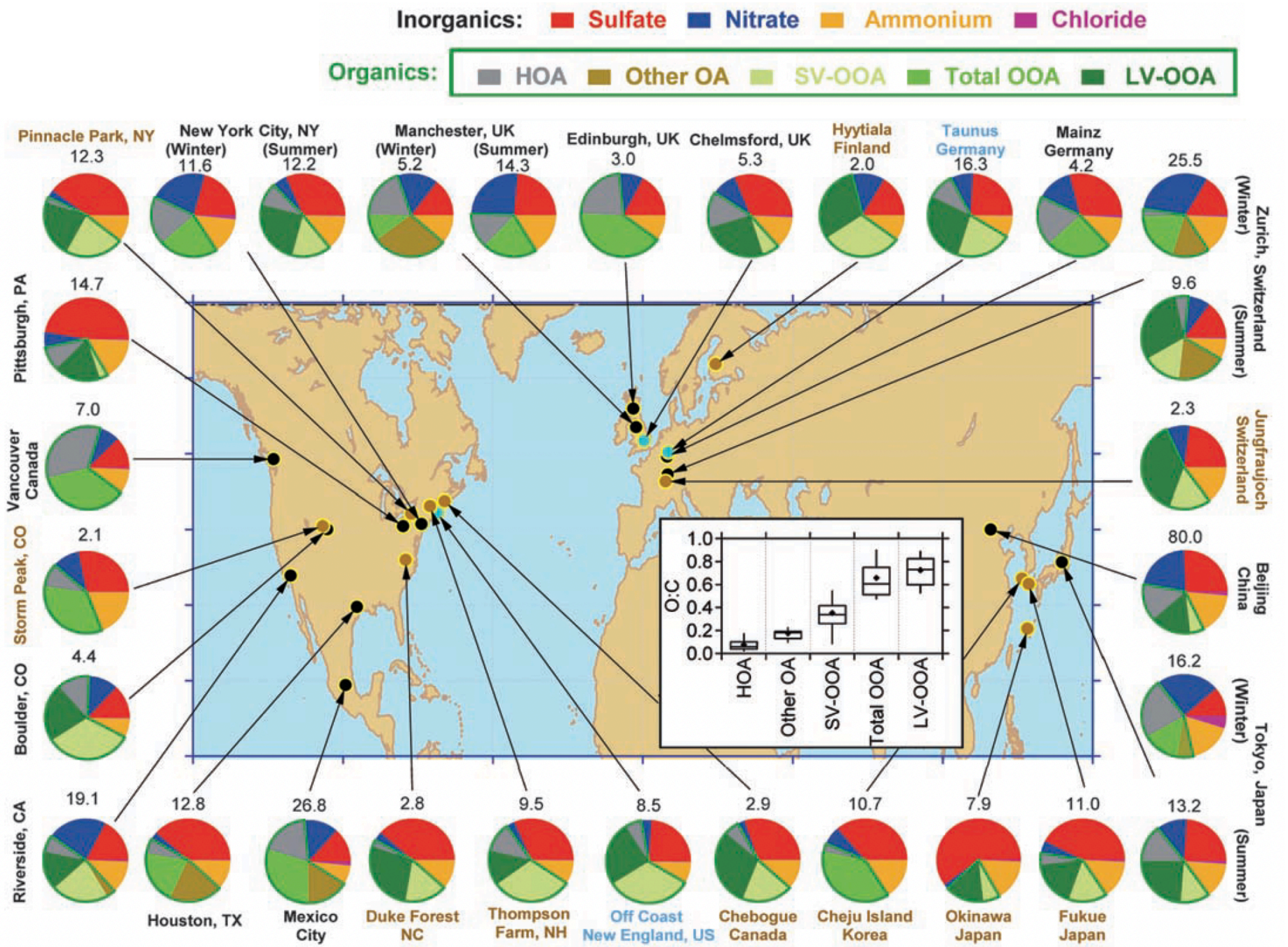
ASR Atmospheric System Research

NOAA

United States Environmental Protection Agency

International Aerosol Modeling Algorithms (IAMA) Conference, 6-8 December 2023, Davis, CA

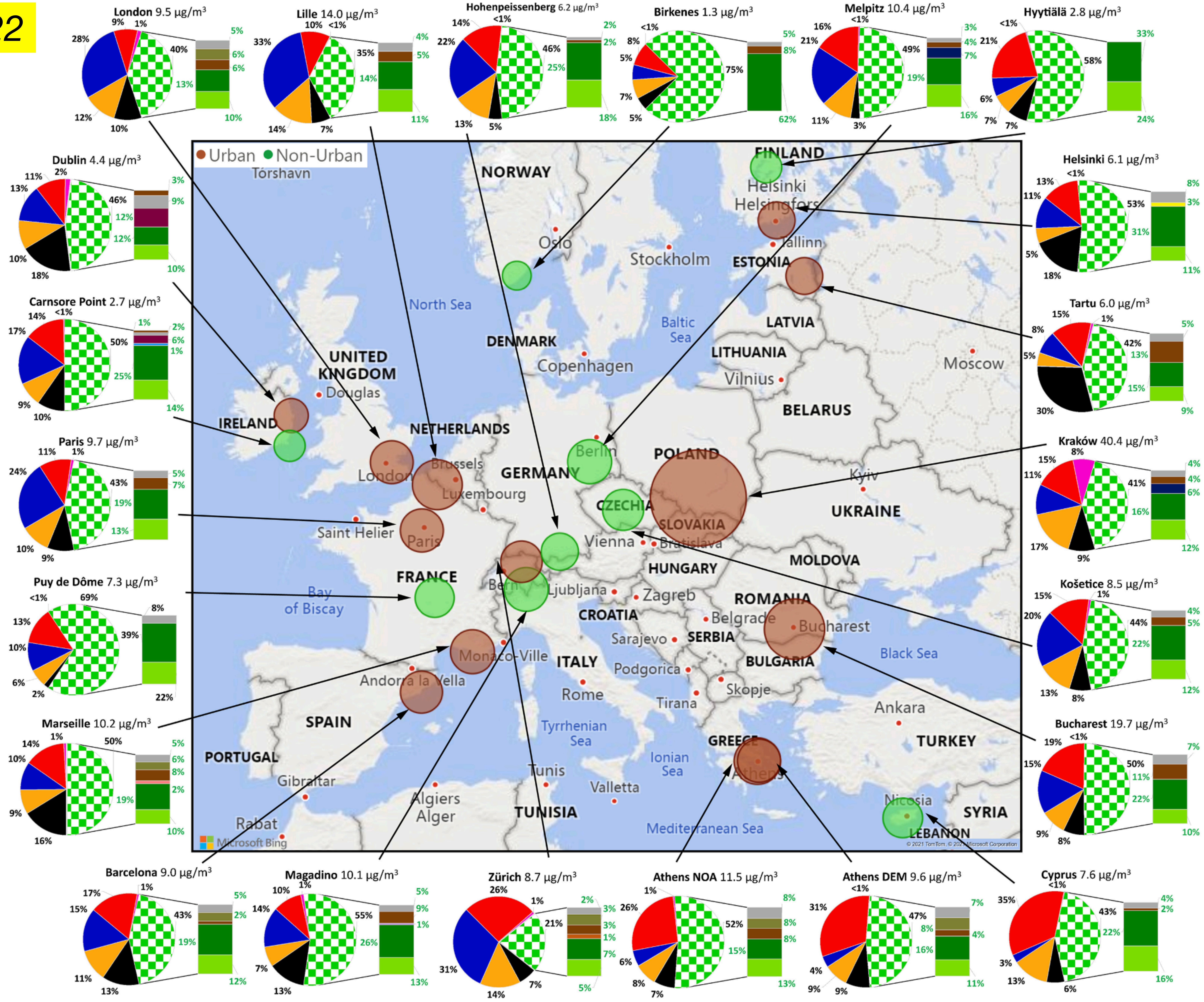
- About half of the <1 μm atmospheric aerosol mass is composed of organic compounds or organic aerosol (OA)



Jimenez et al., Science, 2009

Chen et al., AE, 2022

- … and the majority is secondary OA (SOA)



Chen et al., AE, 2022

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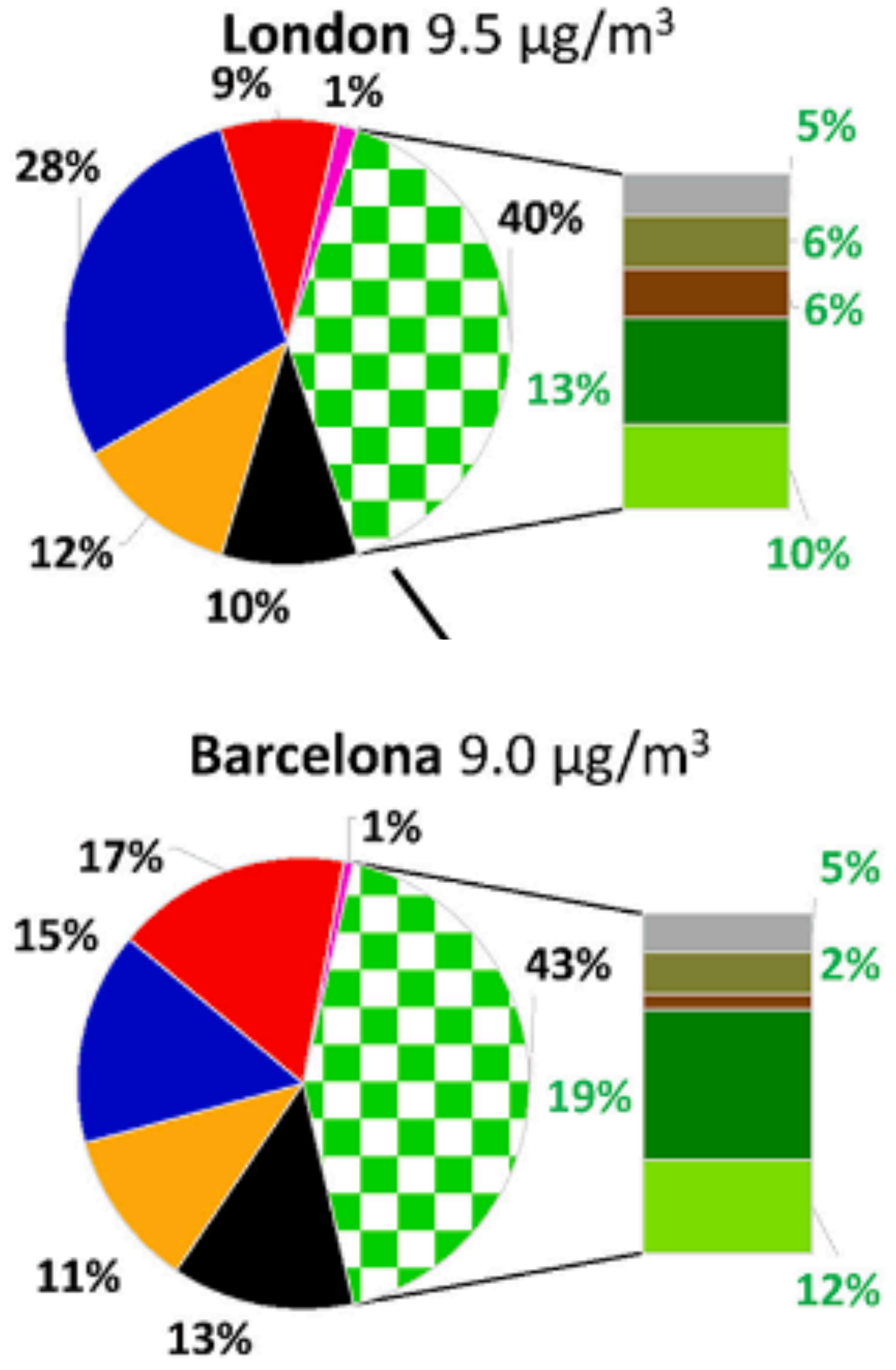

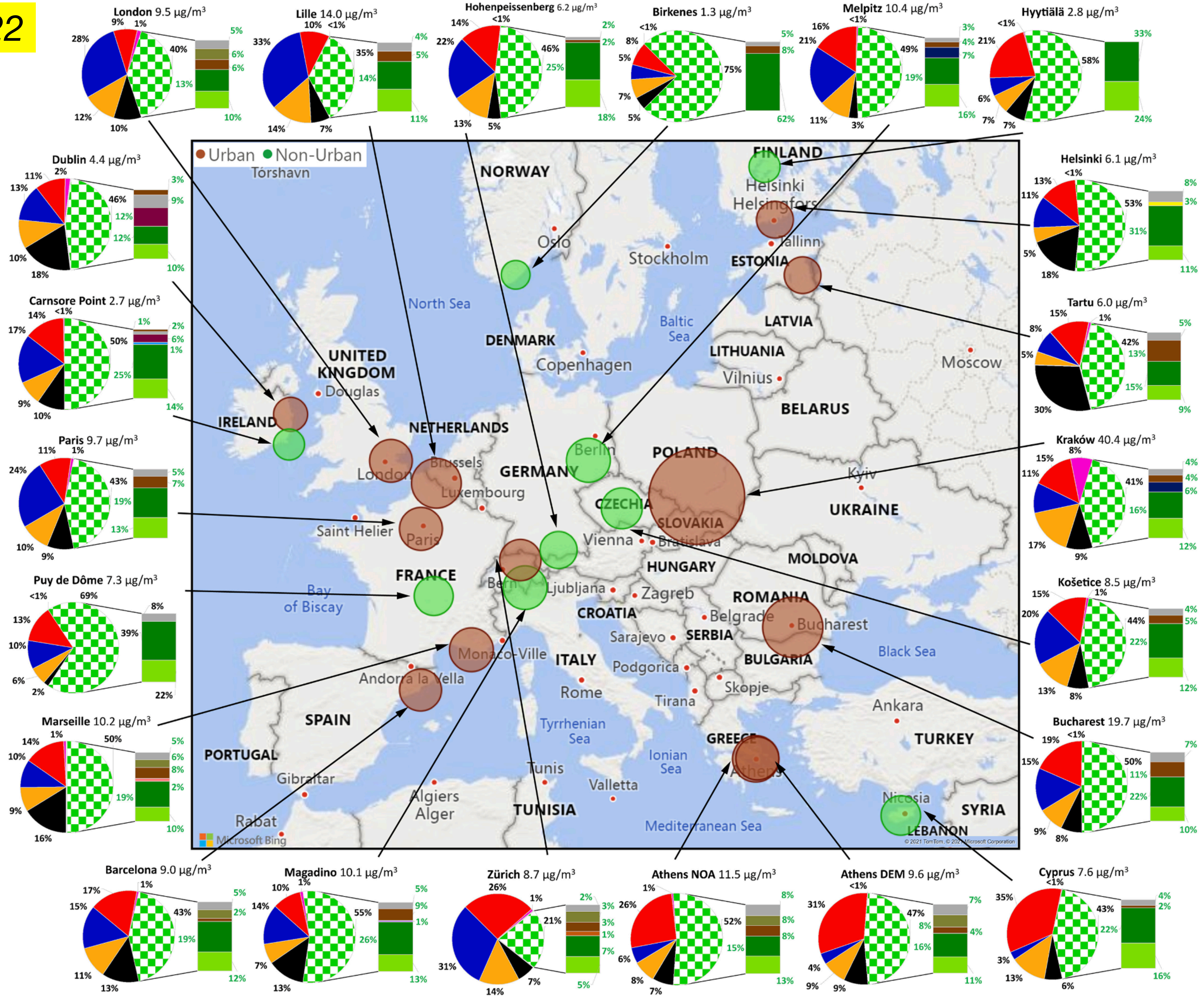

- SOA formation/evolution is complex and demands process-level models

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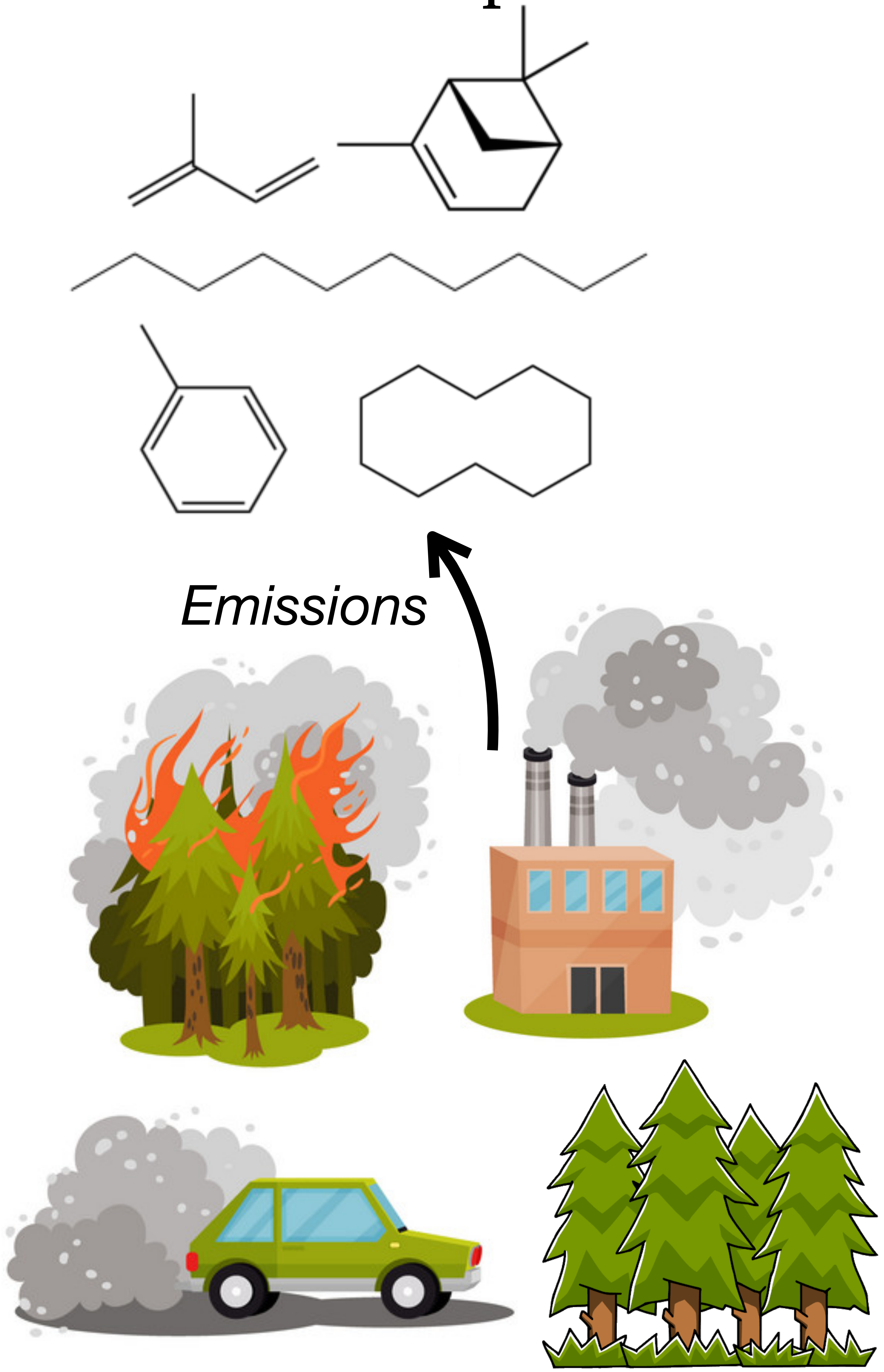

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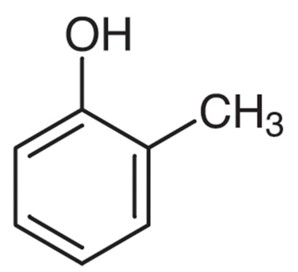

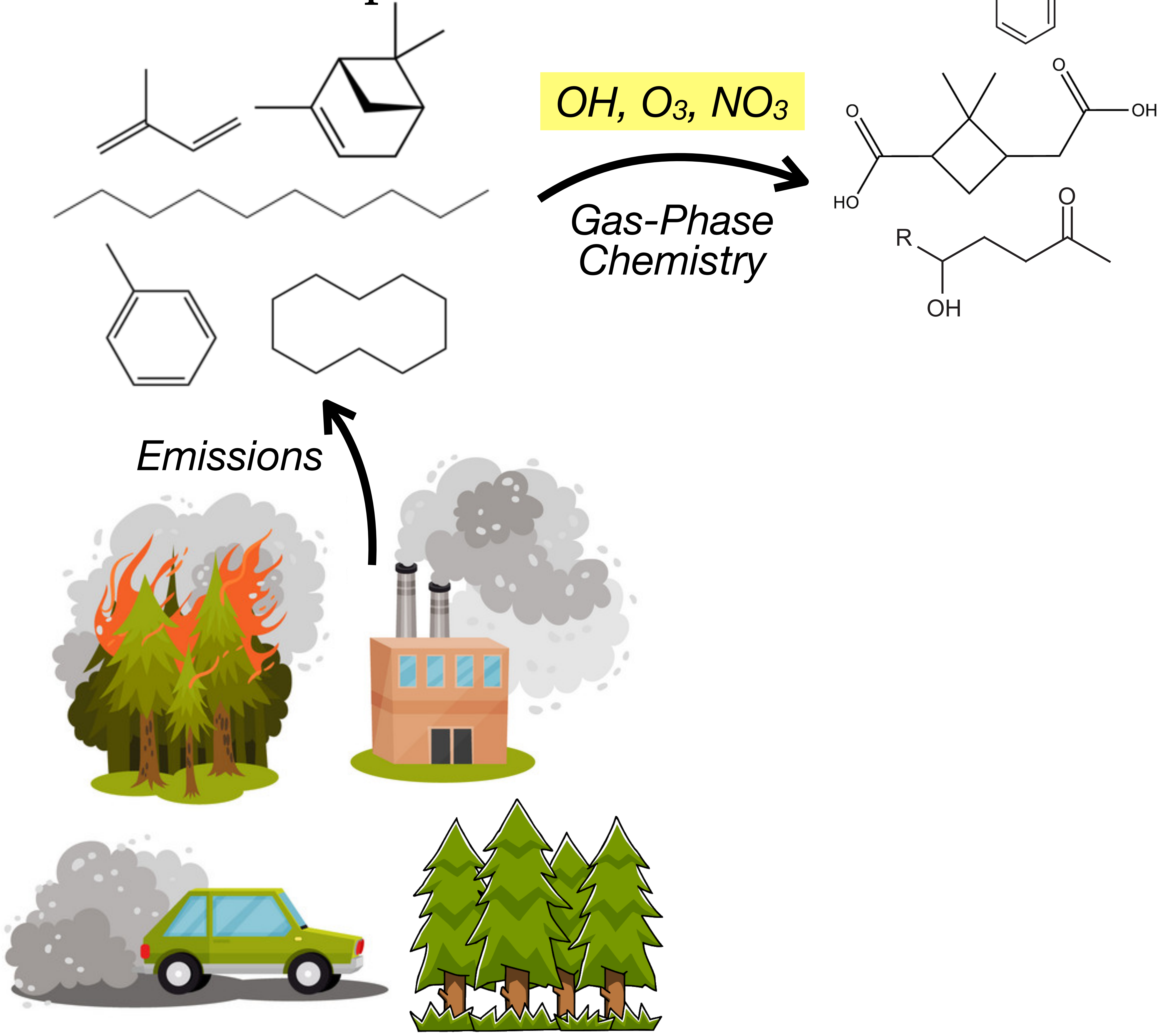

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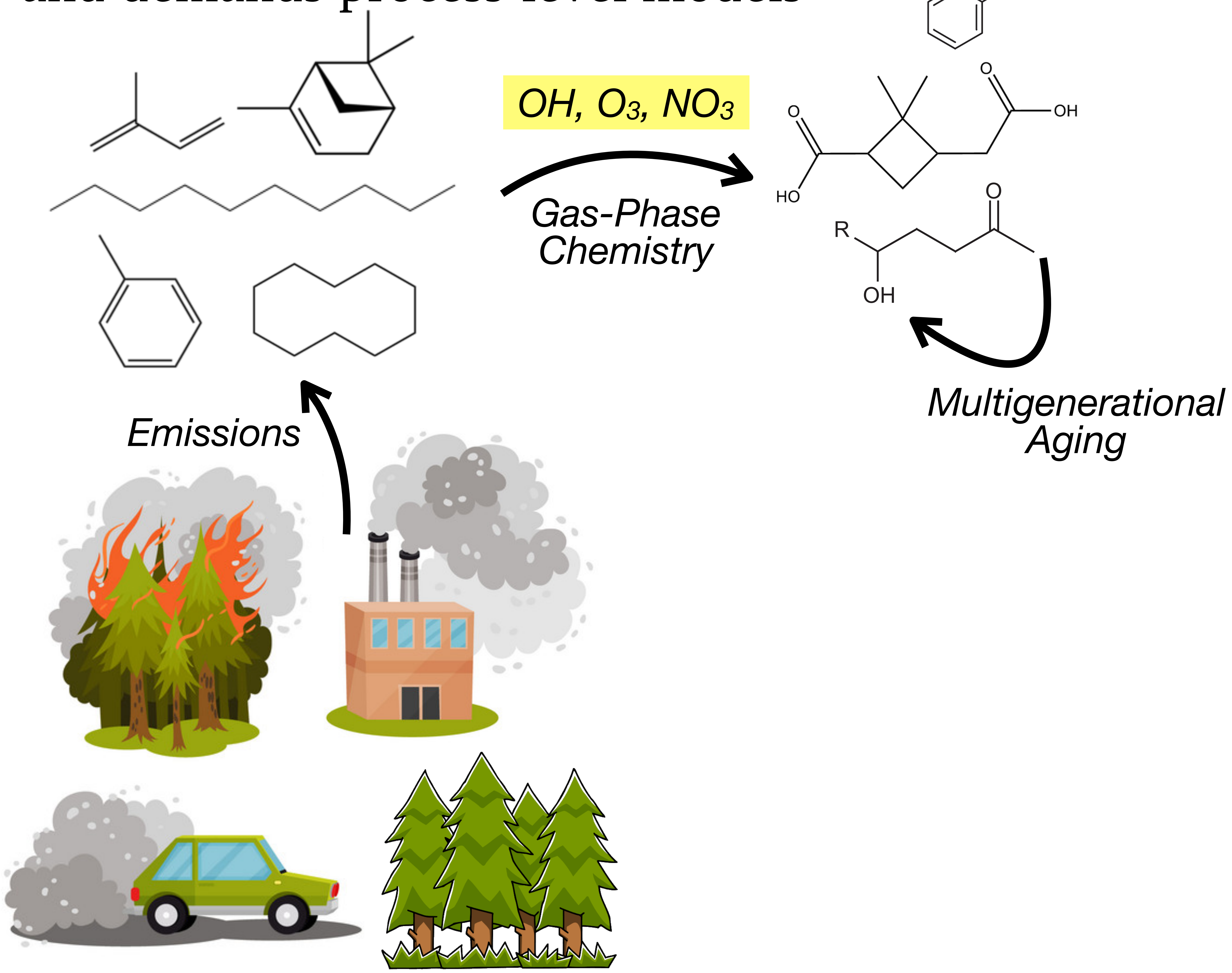

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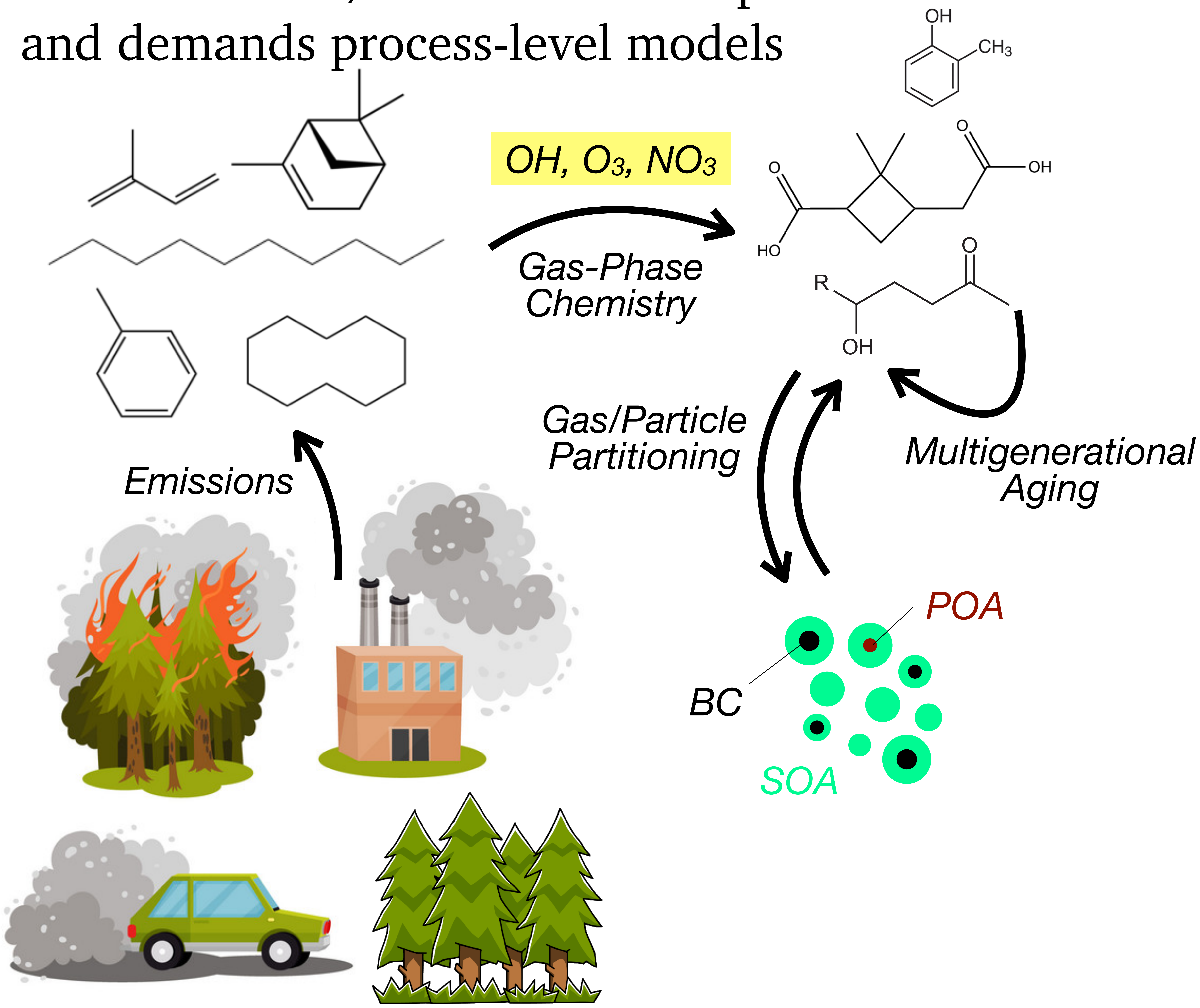

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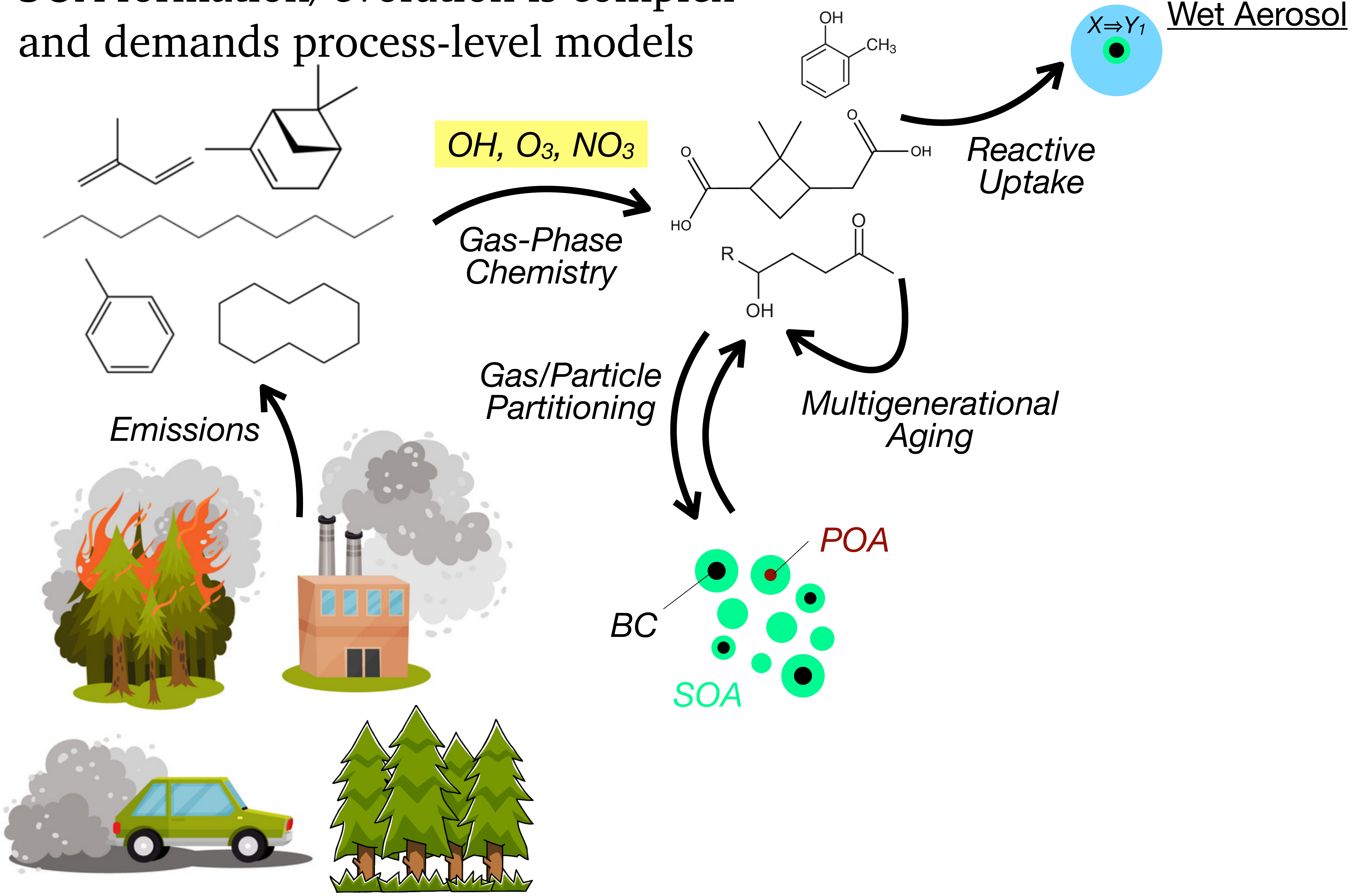

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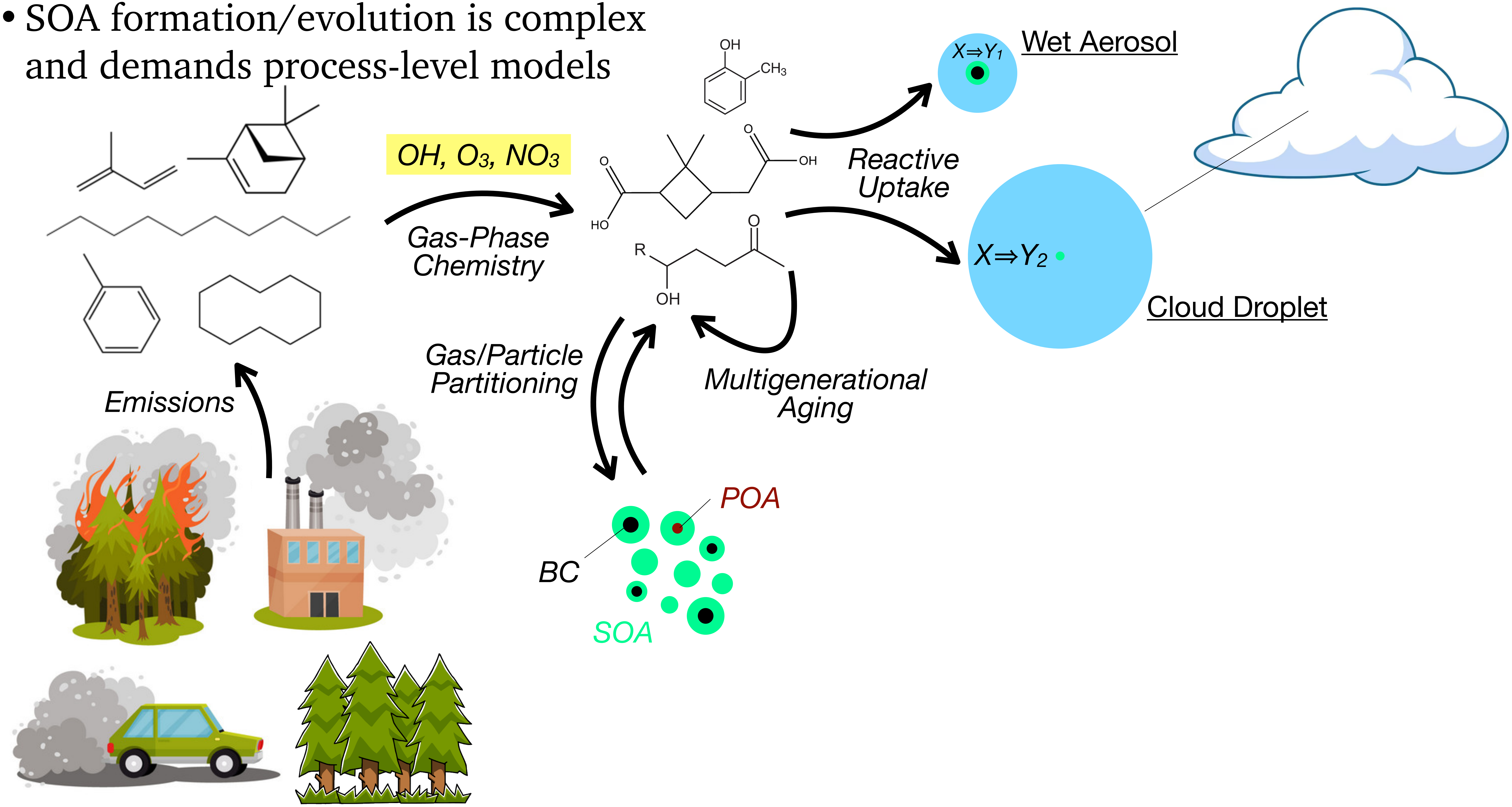

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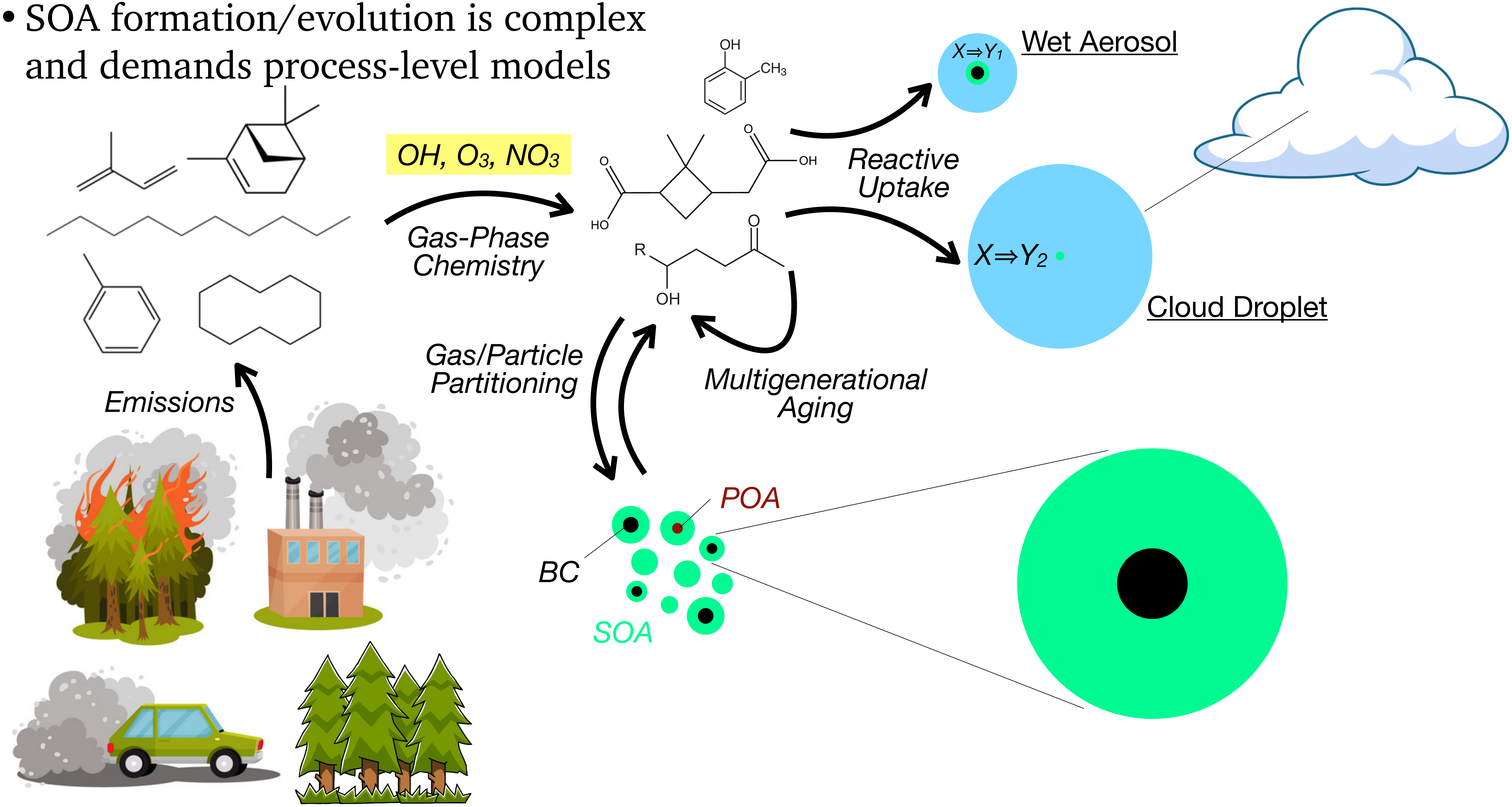

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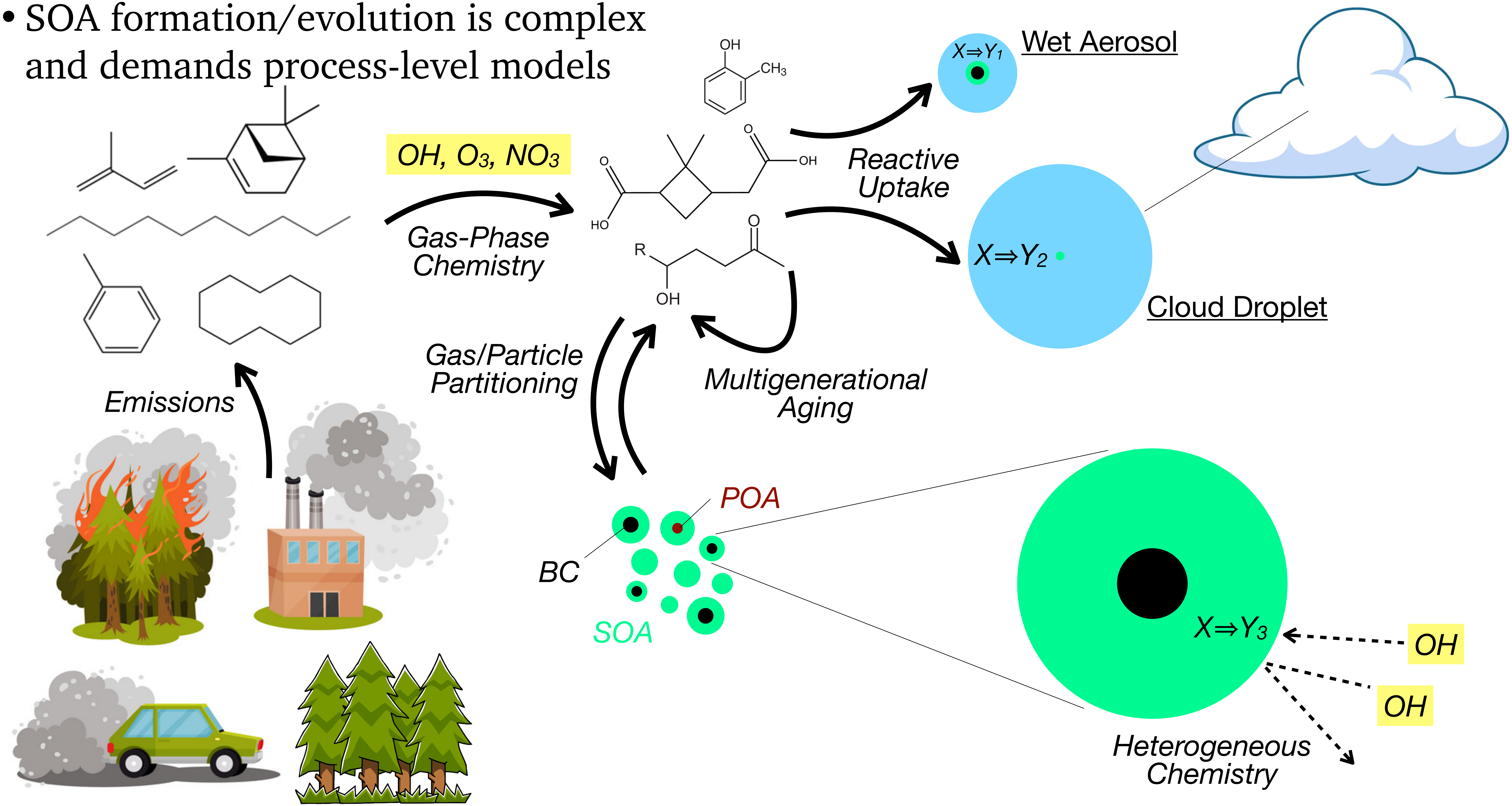

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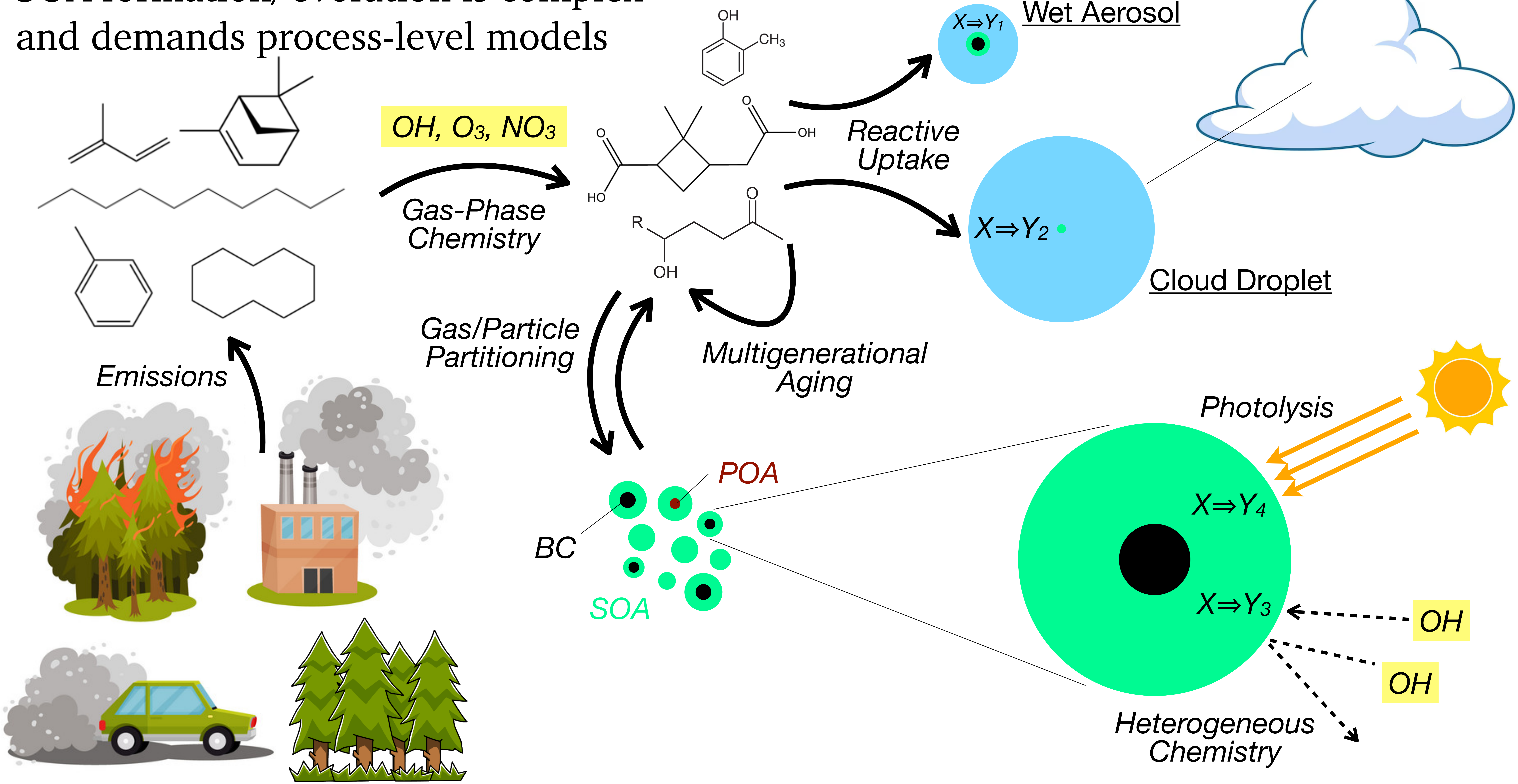

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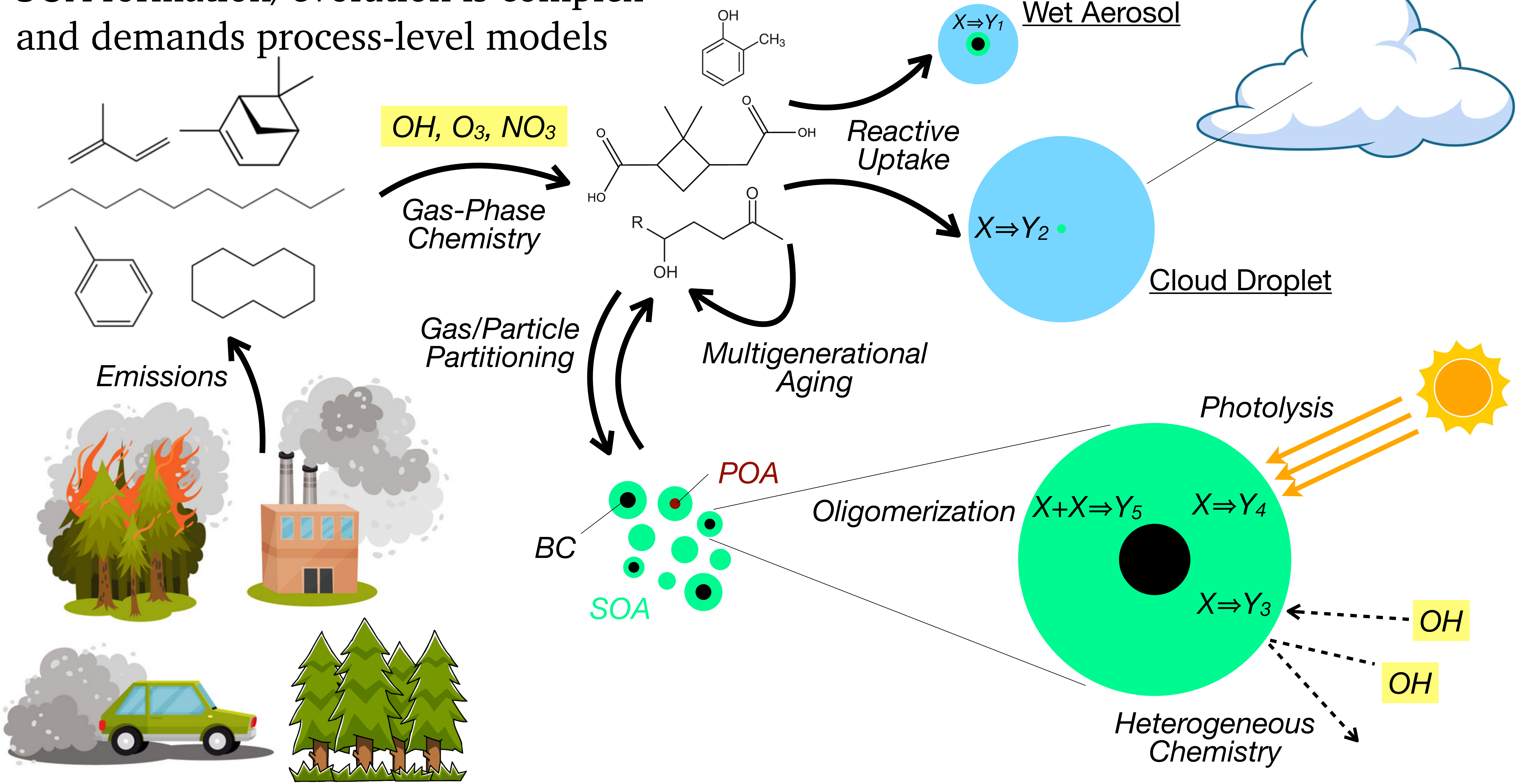

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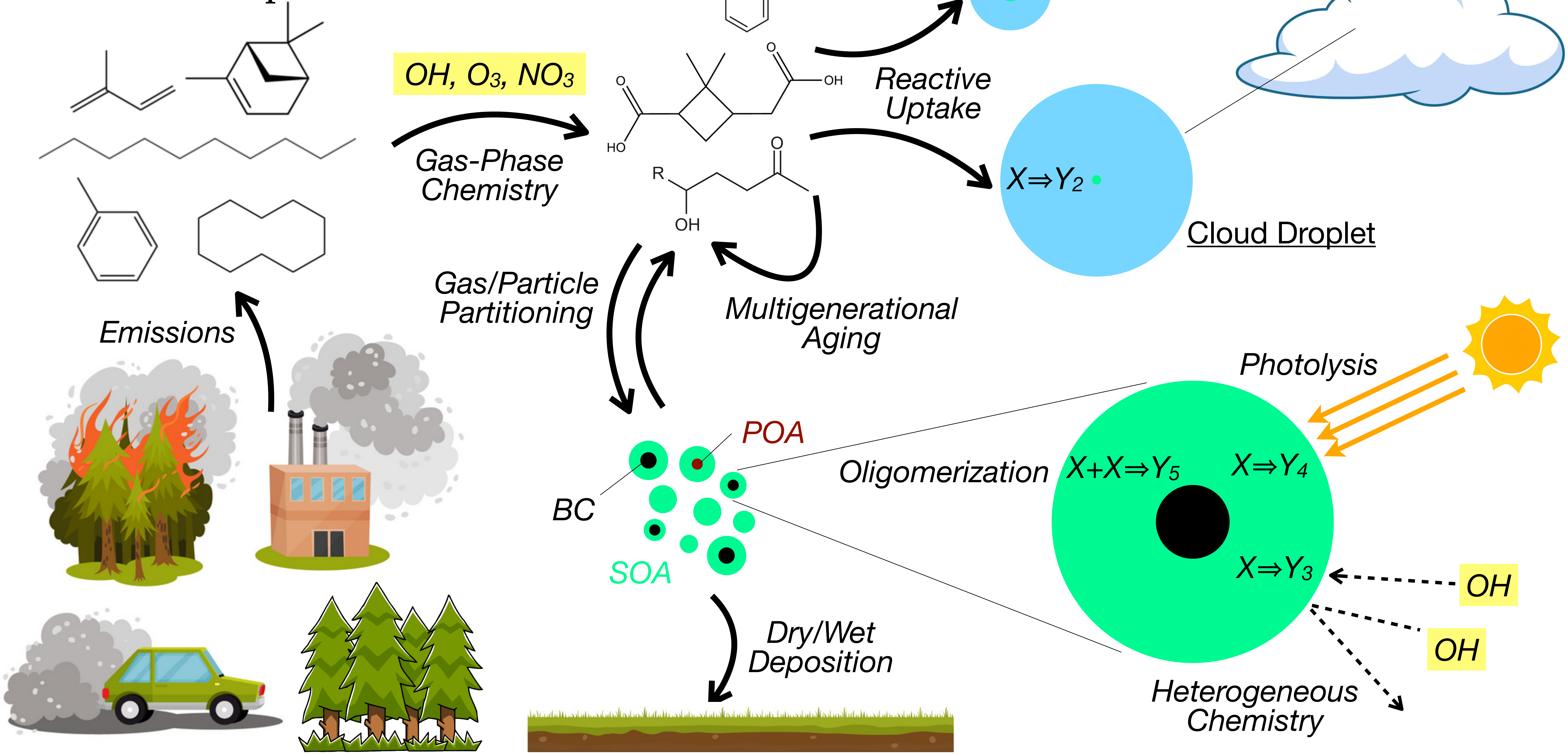
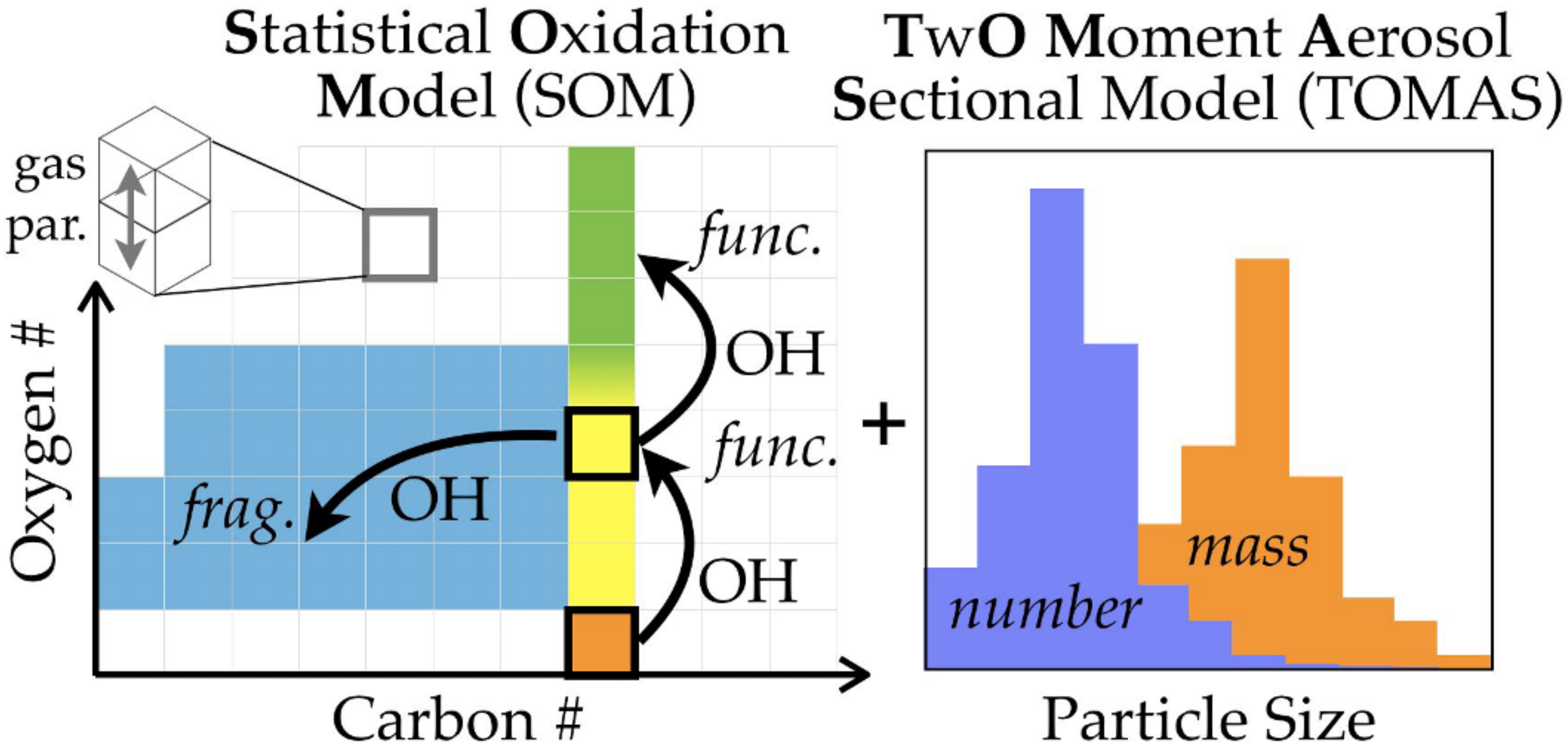
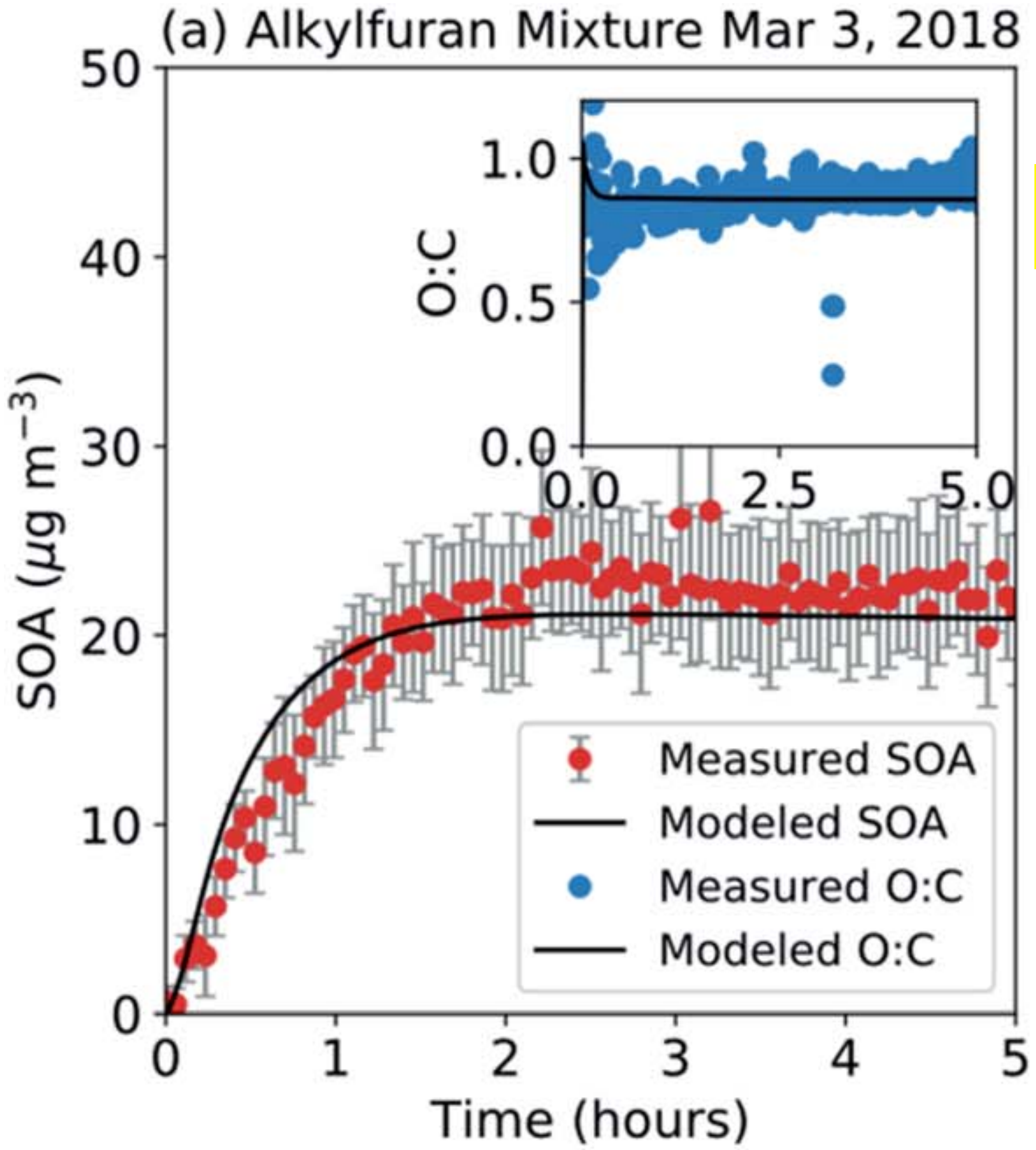


- **SOM-TOMAS**
  - Kinetic, process-level model that simulates the formation, evolution, and properties of SOA
  - Statistical approach to modeling the oxidation chemistry and thermodynamic properties



Akherati et al., ES&T, 2020



He et al., ESPI, 2020

- up to 11 tunable parameters used to run SOM-TOMAS
- gas-phase chemistry, autoxidation reactions, phase-state-influenced kinetic gas/particle partitioning, heterogeneous chemistry, oligomerization reactions

Demonstrate the value of a process-level, kinetic model through 3 case studies:

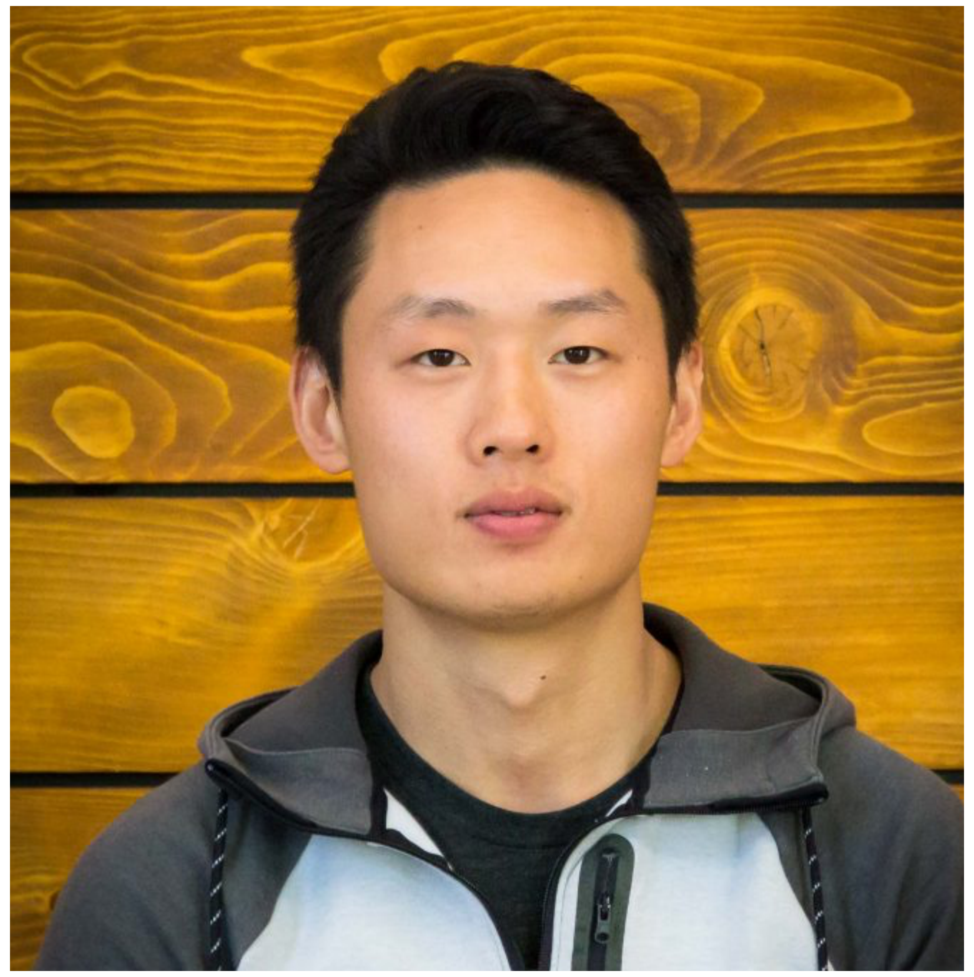
1. Determination of SOA phase state
2. Bridge chamber and OFR studies
3. Understand wall artifacts in environmental chambers

Environmental Science & Technology

pubs.acs.org/est Article

Particle Size Distribution Dynamics Can Help Constrain the Phase State of Secondary Organic Aerosol

Yicong He, Ali Akherati, Theodora Nah, Nga L. Ng, Lauren A. Garofalo, Delphine K. Farmer, Manabu Shiraiwa, Rahul A. Zaveri, Christopher D. Cappa, Jeffrey R. Pierce, and Shantanu H. Jathar*



Yicong [Charles]

U.S. DEPARTMENT OF ENERGY | Office of Science

NOAA — National Oceanic and Atmospheric Administration, U.S. Department of Commerce

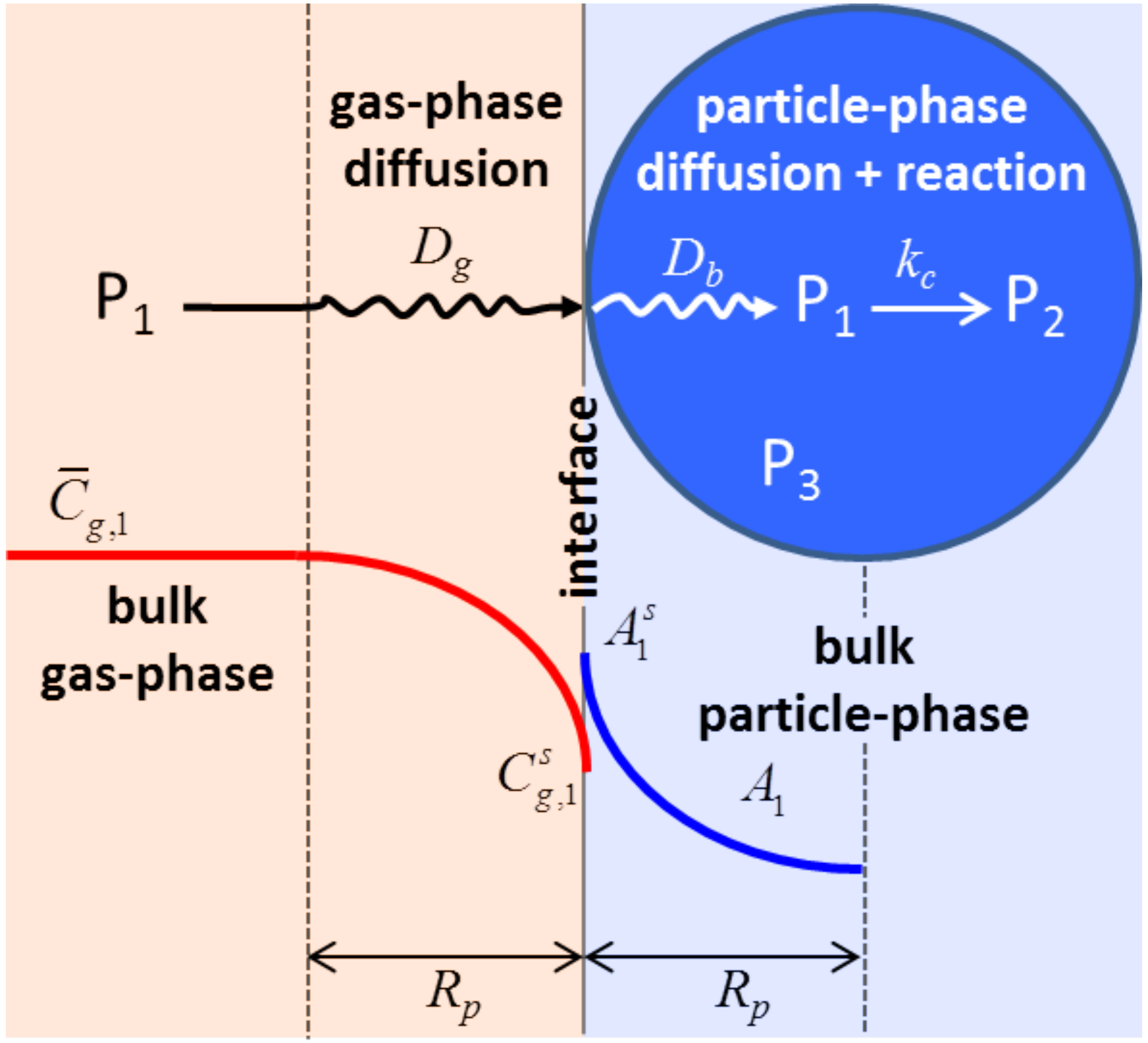
International Aerosol Modeling Algorithms (IAMA) Conference, 6-8 December 2023, Davis, CA

- Previous literature points to α-pinene SOA being semi-solid/viscous under low RH (0-30%) conditions

Tar Pitch
$D_b=10^{-16}$ cm^2 s^{-1}

reference	oxidant	SOA formed in	RH (%)	max. SOA mass conc. (μg m^{-3})	D_b (cm^2 s^{-1})	D_b estimated using
Zaveri et al.[18]	OH	10.6 m^3 chamber at 32% RH	32	110	2.5×10^{-15}	growth of SOA on different sized particles
Abramson et al.[19]	O_3	0.1 m^3 chamber at ~0% RH	~0	NM[b]	2.5×10^{-17}	evaporation of pyrene trapped inside SOA
Zhou et al.[20]	O_3	flow tube at <5% RH	~0	NM[b]	2×10^{-14}	oxidation of benzo[a]pyrene trapped inside SOA
Renbaum-Wolff et al.[11]	O_3	flow tube at <5% RH	0−30	50	$<10^{-17}$	flow properties of large SOA particles
Pajunoja et al.[13]	O_3 OH	6 m^3 chamber at 35% RH	<20	3−15	$>3 \times 10^{-21}$ $<3 \times 10^{-21}$	coalescence time of individual particles
Zhang et al.[14]	O_3	flow tube at <5% RH	<5	70	6×10^{-18}	change in particle shape factor
Grayson et al.[16]	O_3	flow tube at <5% RH	0.5	14 000	2×10^{-15}−7×10^{-14}	flow properties of large SOA particles
		chamber at <5% RH	0.5	121	6×10^{-17}−5×10^{-15}	

- SOM-TOMAS was updated to simulate (i) gas/particle partitioning influenced by the particle phase state and (ii) formation/dissociation of dimers



Zaveri et al., ACP, 2014

$$\frac{1}{K_{i,j}} = \frac{1}{k^{\mathrm{g}}_{i,j}} + \frac{1}{k^{\mathrm{p}}_{i,j}}\left(\frac{C^*_i}{\rho_{\mathrm{p}}}\right)$$

$$k^{\mathrm{g}}_{i,j} = \frac{D^{\mathrm{g}}_i \cdot FS_{i,j}}{R^{\mathrm{p}}_j}$$

$$k^{\mathrm{p}}_{i,j} = \frac{D_{\mathrm{b}}}{R^{\mathrm{p}}_j}\left(\frac{q_{i,j}\coth q_{i,j} - 1}{1 - Q_{i,j}}\right)$$

$$q_{i,j} = R^{\mathrm{p}}_j\sqrt{\frac{k^{\mathrm{c}}_{i,j}}{D_{\mathrm{b}}}}$$

$$Q_{i,j} = 3\left(\frac{q_{i,j}\coth\left(q_{i,j}\right) - 1}{q^2_{i,j}}\right)$$

Mass transfer affected by D_b

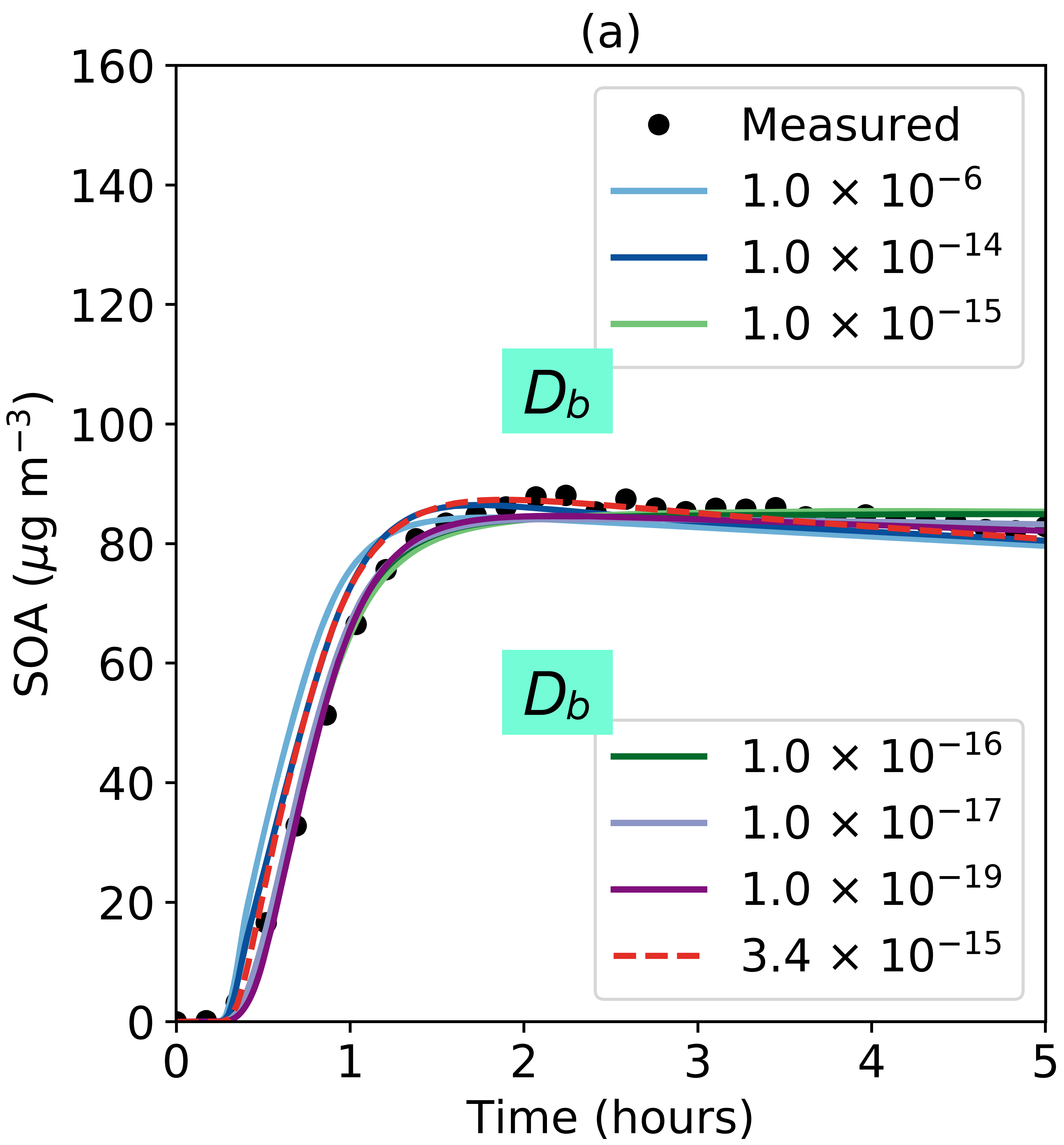
Dimer formation

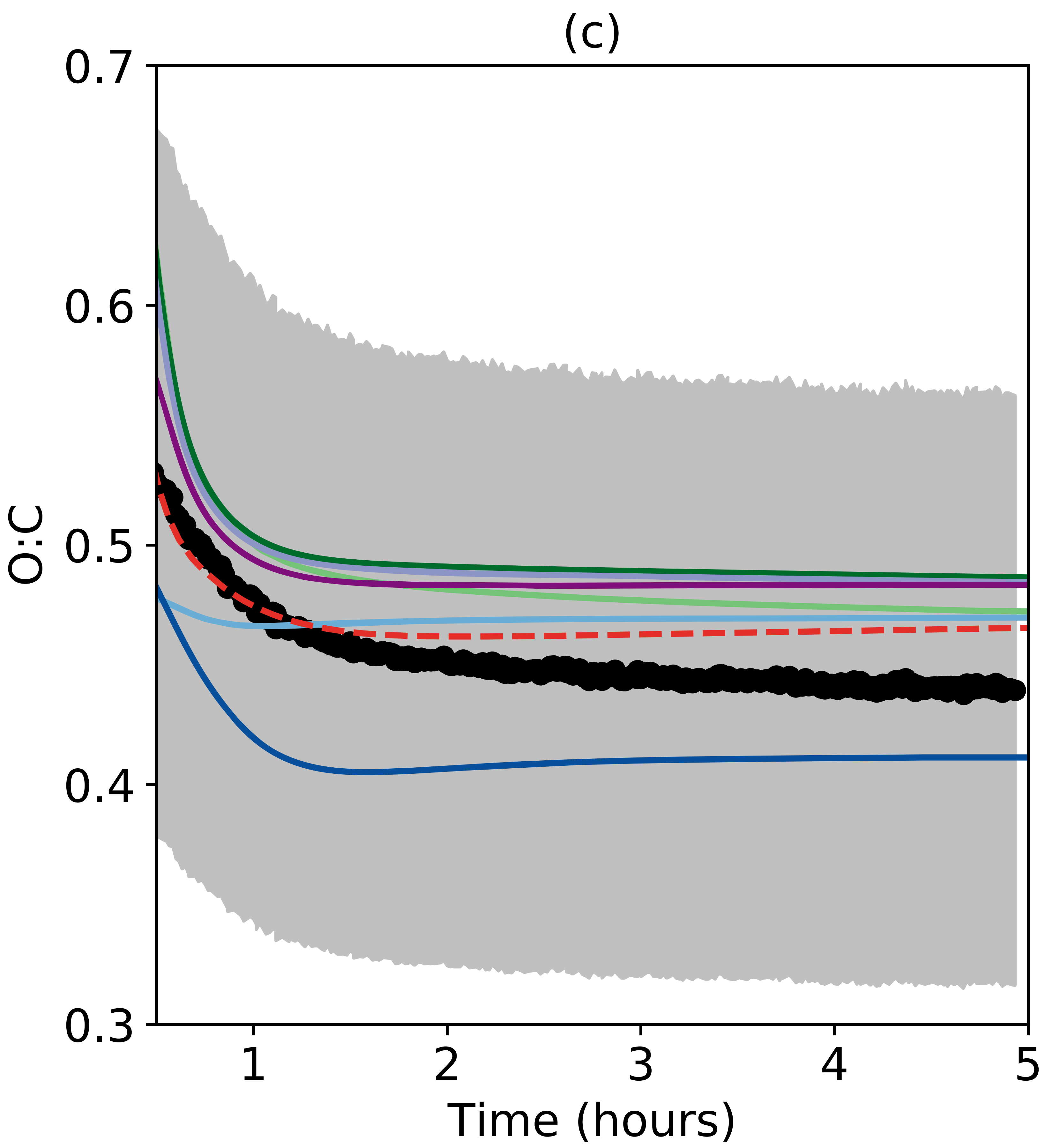
$$\frac{\mathrm{d}O_{i,j}}{\mathrm{d}t} = \sum_{k}^{i_{\max}} k_{\mathrm{f}} \cdot M_{k,j} \cdot M_{i,j} - k_{\mathrm{r}} \cdot O_{i,j}$$

$$\frac{\mathrm{d}M_{i,j}}{\mathrm{d}t} = k_{\mathrm{r}} \cdot O_{i,j} - \sum_{k}^{i_{\max}} k_{\mathrm{f}} \cdot M_{i,j} \cdot M_{k,j}$$

$$k^{\mathrm{c}}_{i,j} = \sum_{k}^{i_{\max}} k_{\mathrm{f}} \cdot M_{k,j} - k_{\mathrm{r}} \cdot \frac{O_{i,j}}{M_{i,j}}$$

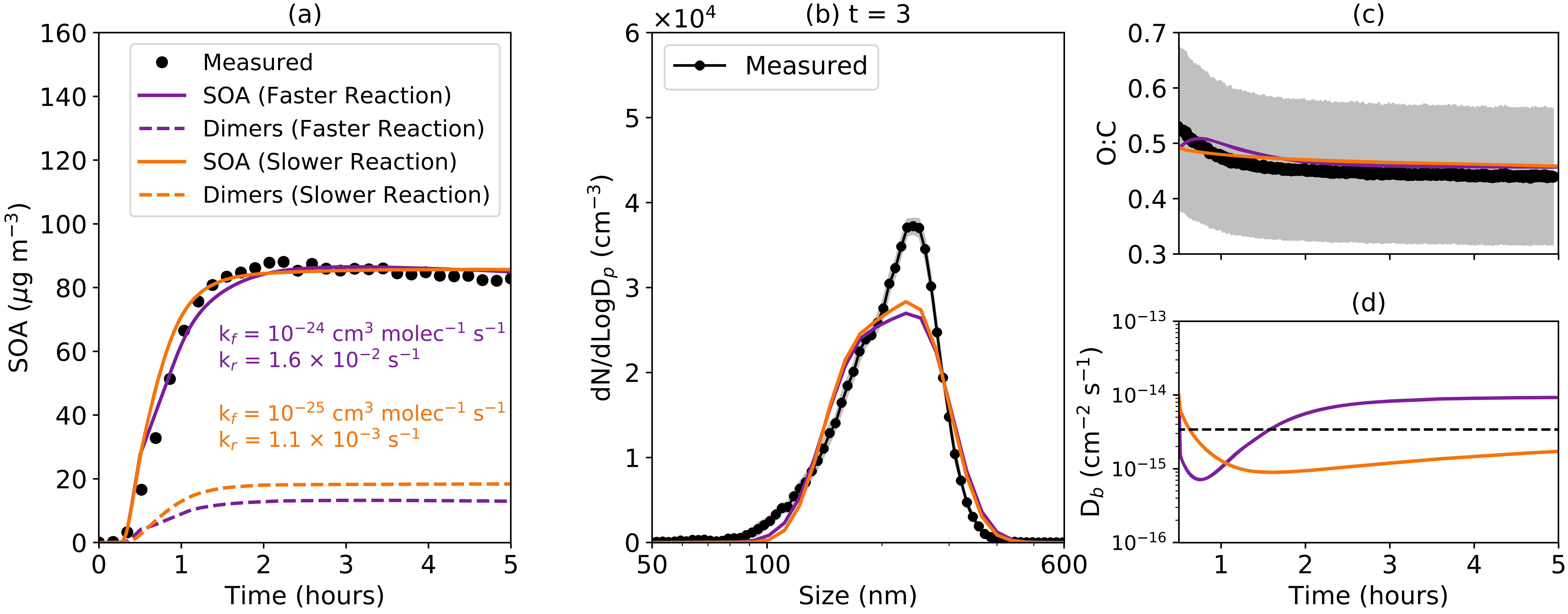
- Prescribing the diffusion coefficient (D_b) has little influence on SOA formation or composition but produces differences in the evolution of the size distribution





- Prescribing the diffusion coefficient (D_b) has little influence on SOA formation or composition but produces differences in the evolution of the size distribution

- Steady oligomer formation increases the T_g (glass transition temperature) and, hence, lowers the D_b of the particle phase



Environmental Science & Technology
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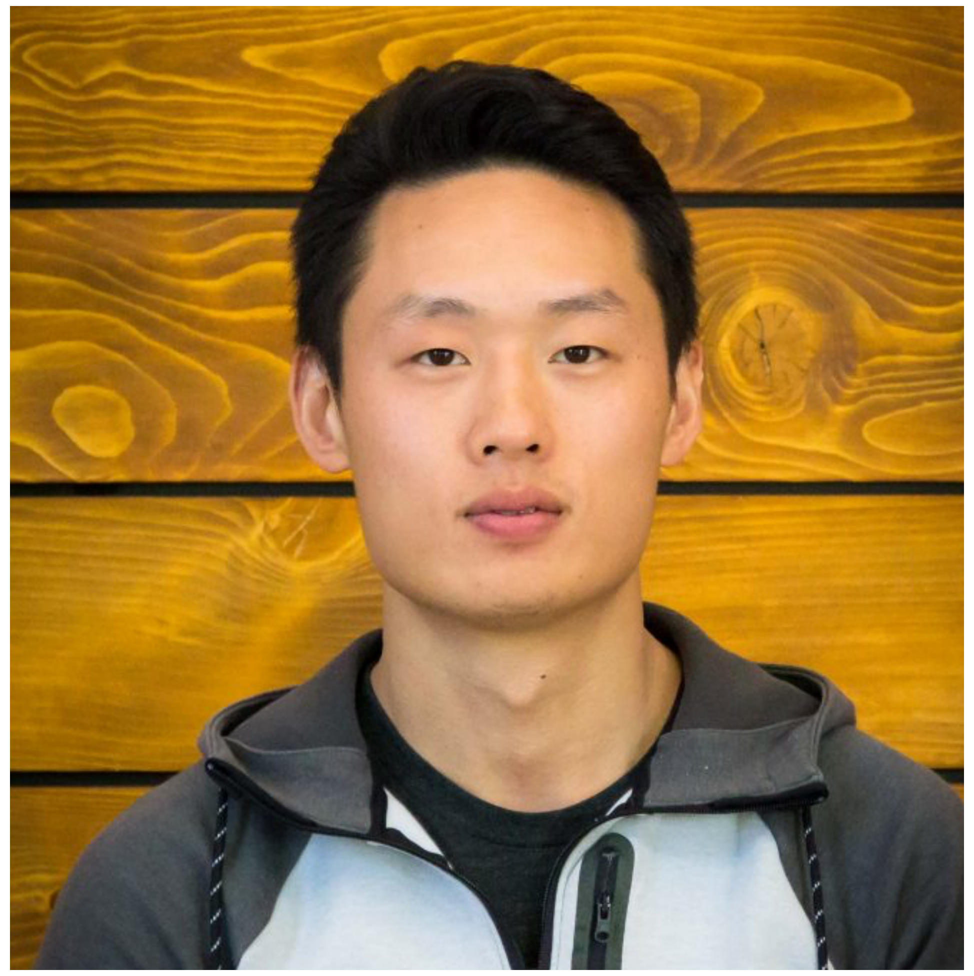
Article

Process-Level Modeling Can Simultaneously Explain Secondary Organic Aerosol Evolution in Chambers and Flow Reactors

Yicong He, Andrew T. Lambe, John H. Seinfeld, Christopher D. Cappa, Jeffrey R. Pierce, and Shantanu H. Jathar*



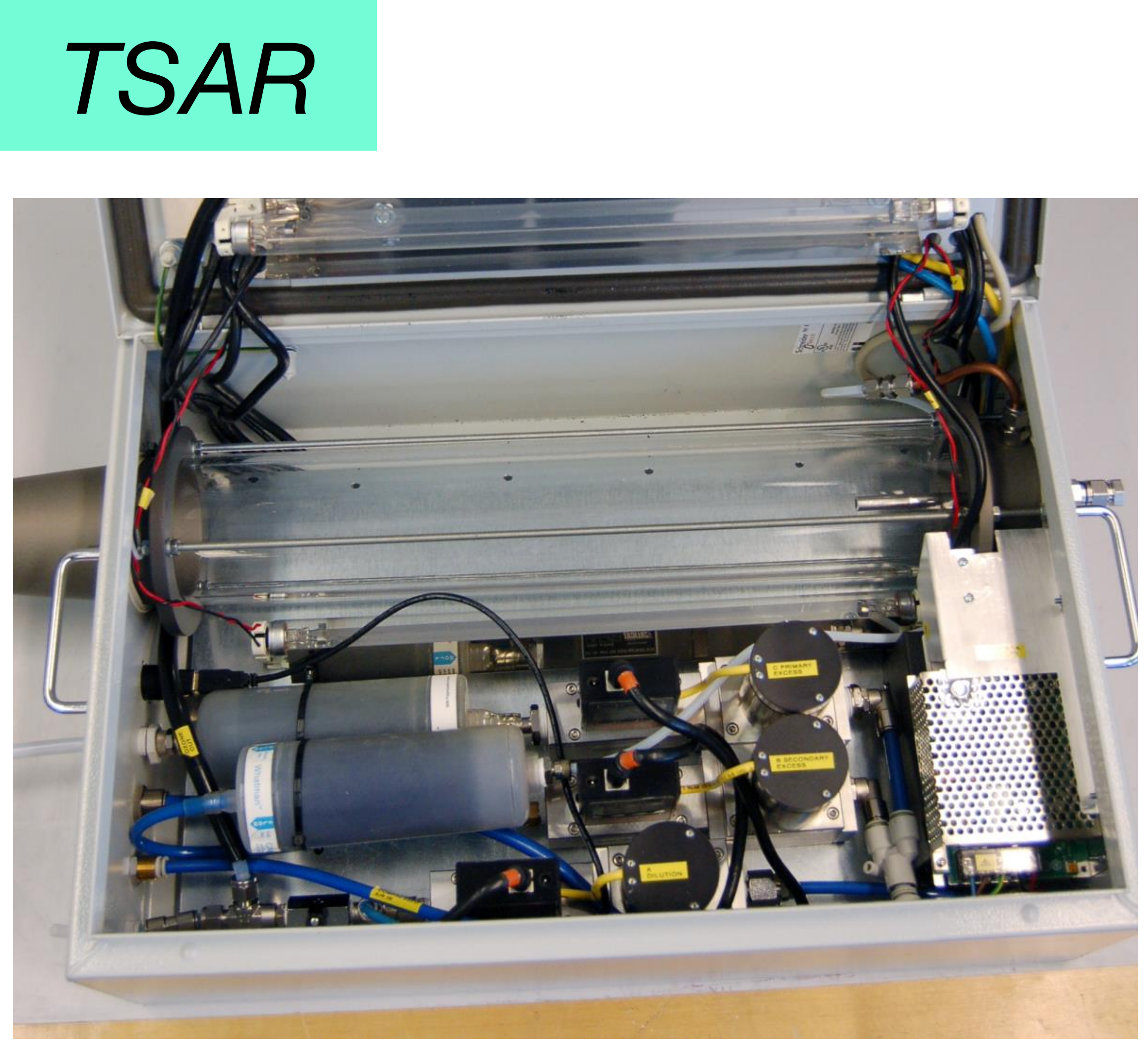
Yicong [Charles]

U.S. DEPARTMENT OF ENERGY | Office of Science

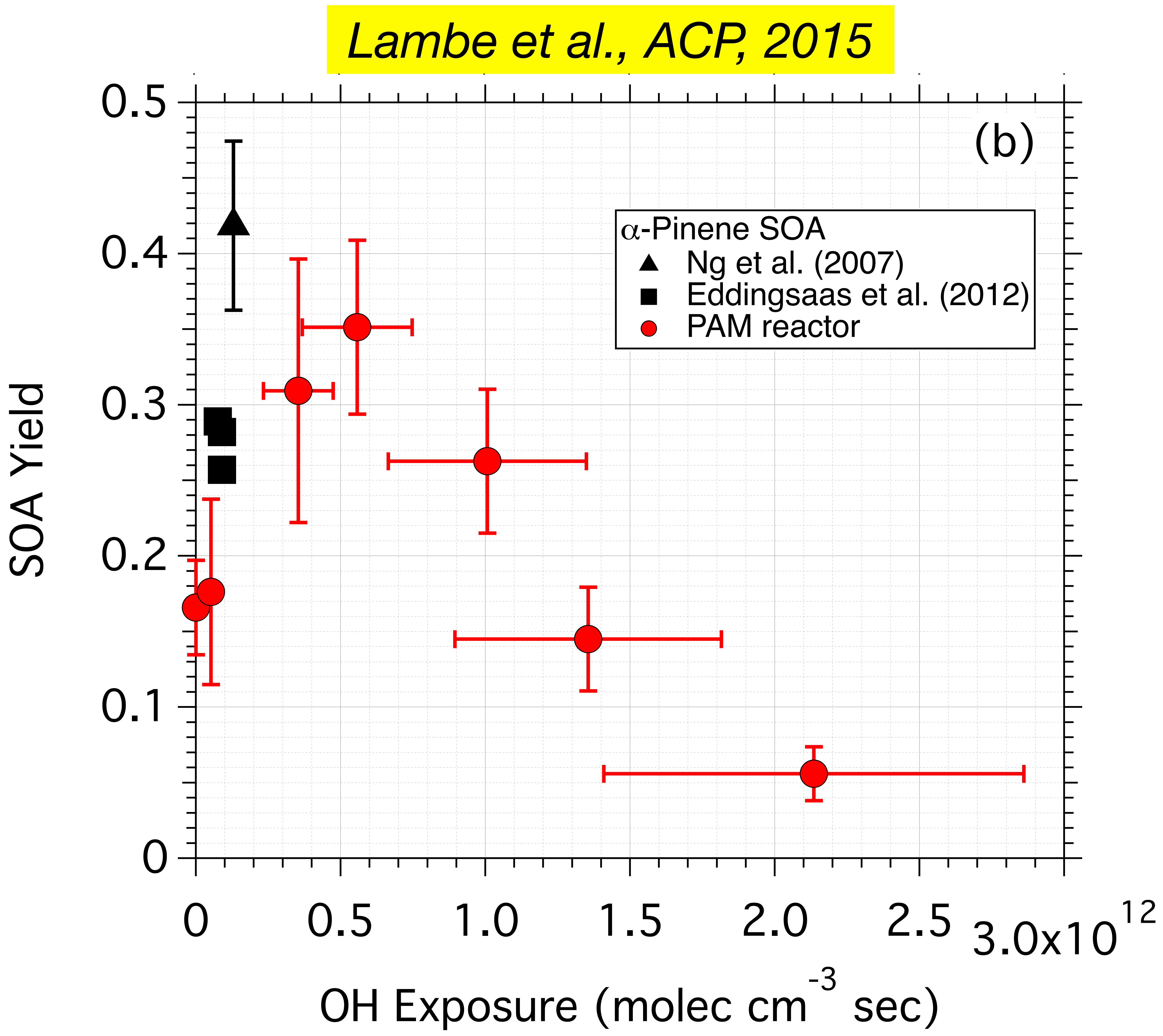
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
NOAA
U.S. DEPARTMENT OF COMMERCE

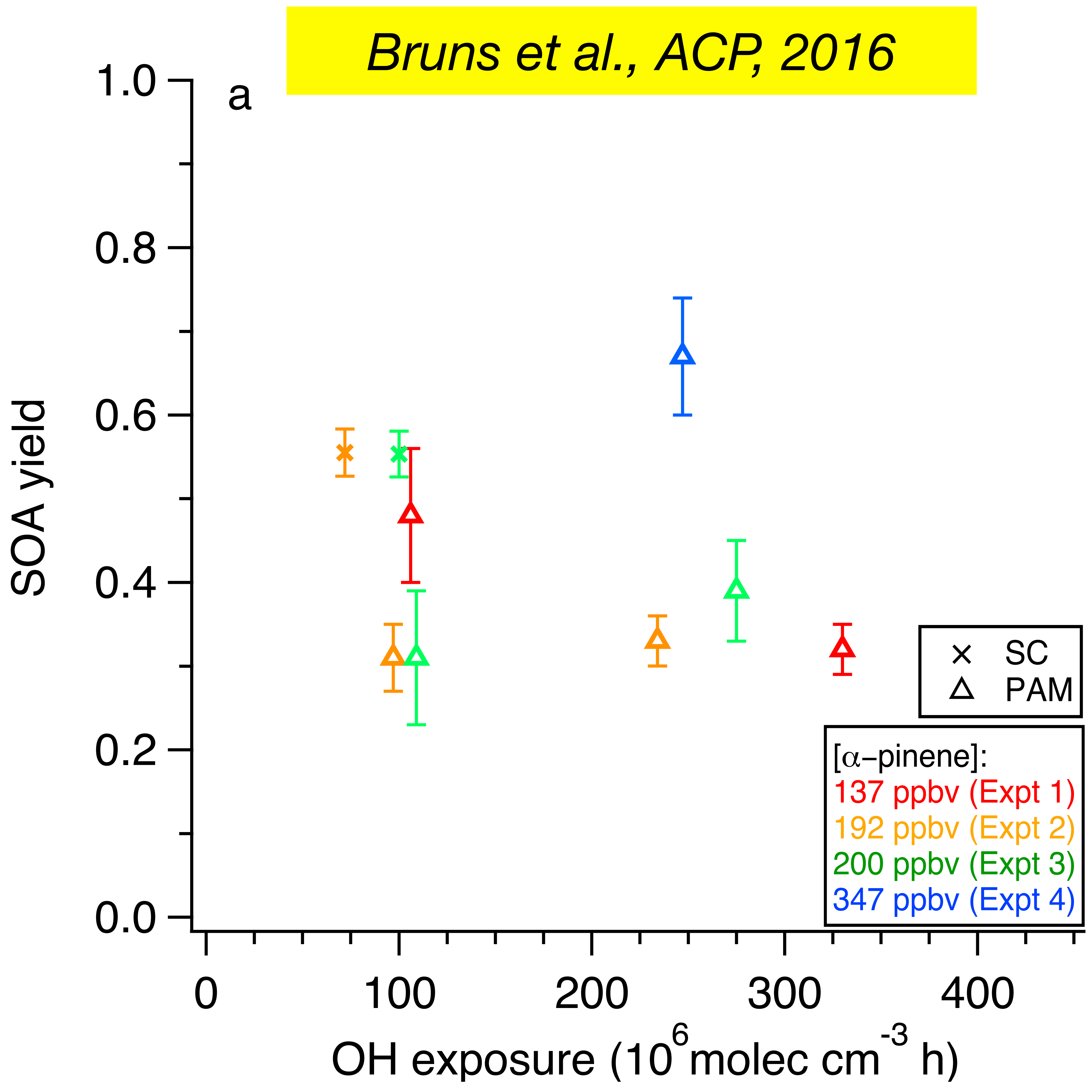
International Aerosol Modeling Algorithms (IAMA) Conference, 6-8 December 2023, Davis, CA

- Chambers and flow tubes are key tools used to understand SOA systems in controlled, laboratory settings



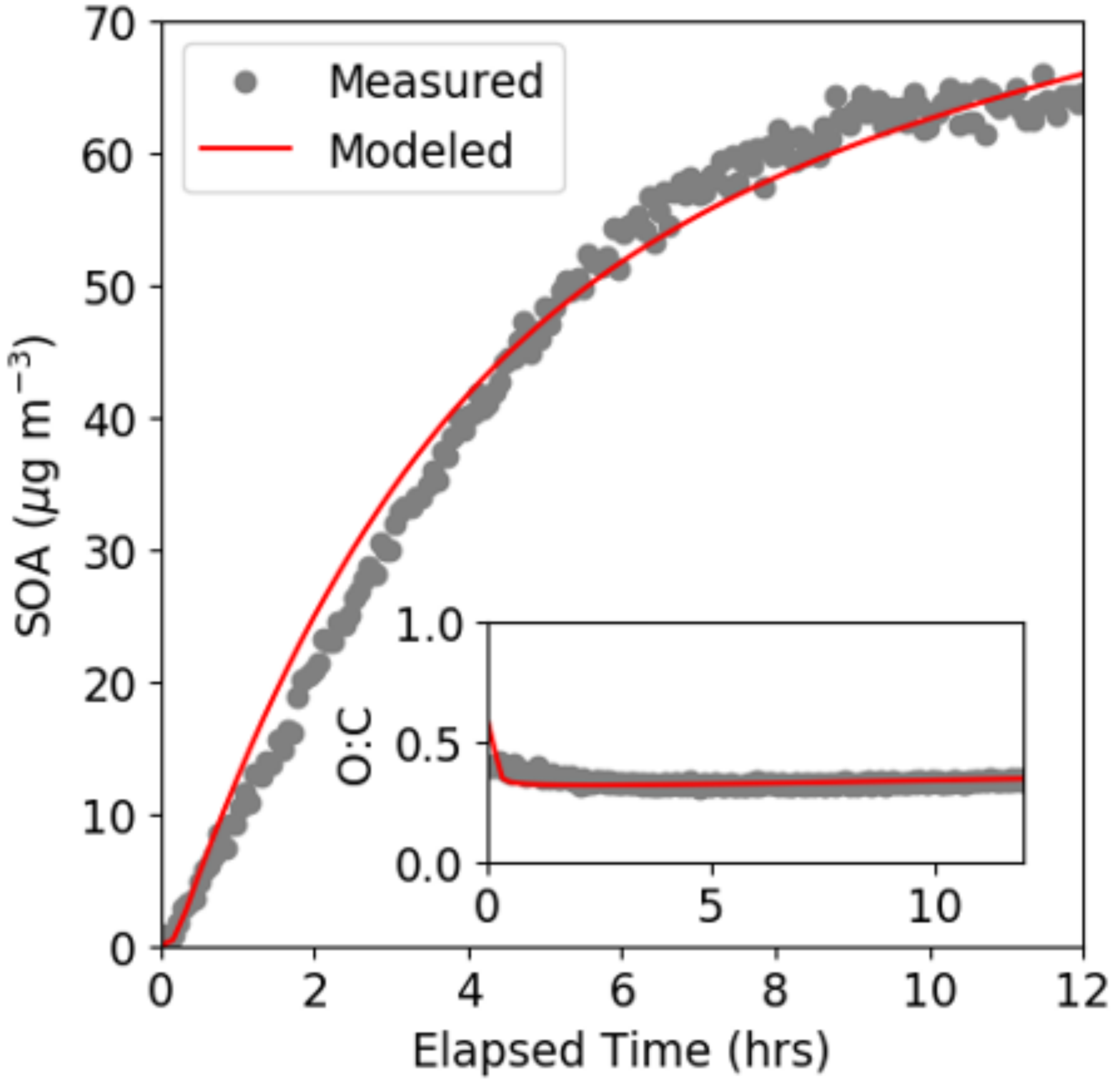
• SOA data from chamber and OFR experiments do not necessarily agree with each other ➠ large differences in oxidant concentrations, time available for partitioning, and interactions with walls





• Accounting for wall losses, assuming a semi-solid aerosol, and modeling particle-phase reactions results in chamber-OFR equivalency for α-pinene SOA

Chamber



Chhabra et al., ACP, 2011

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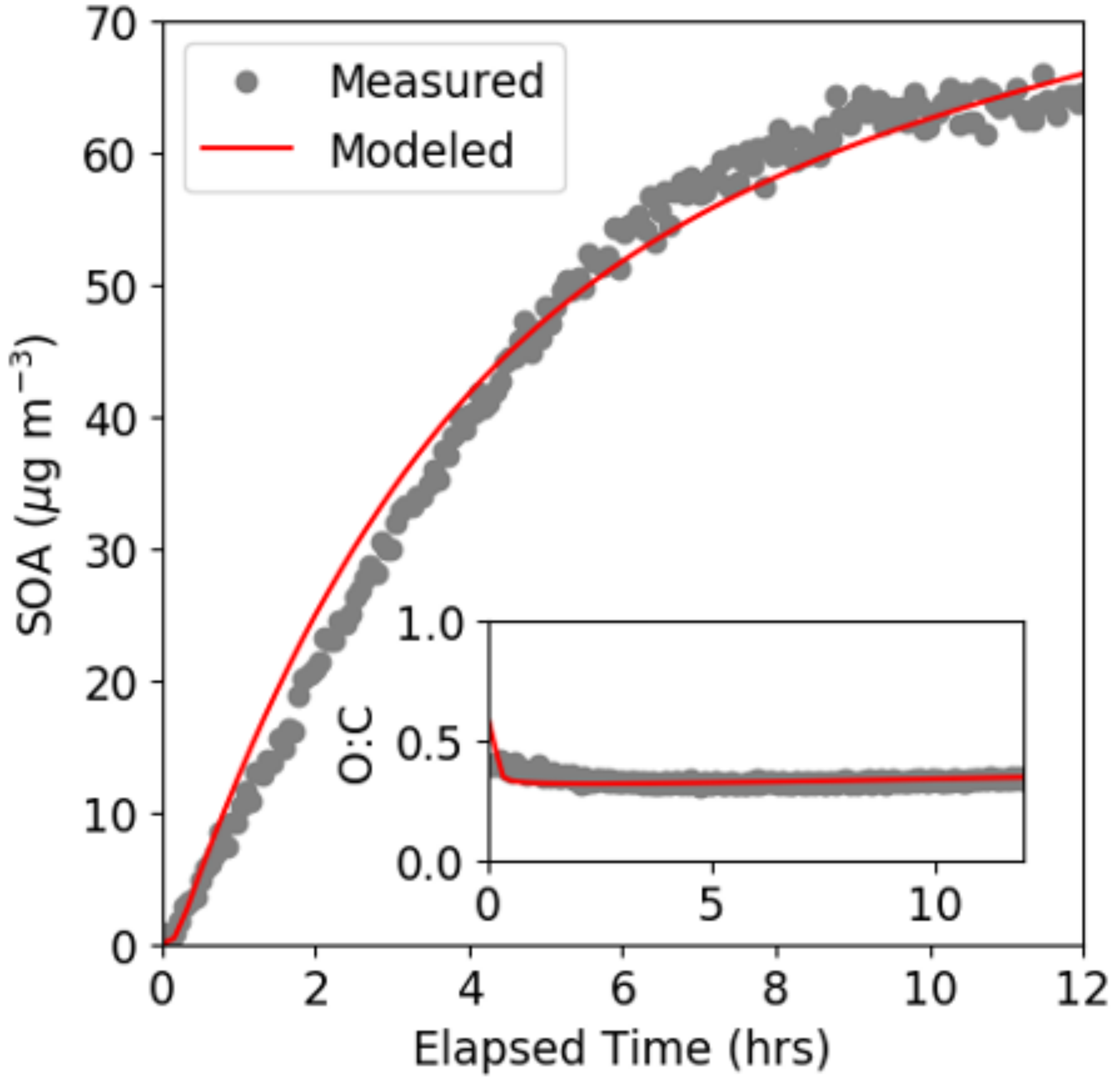

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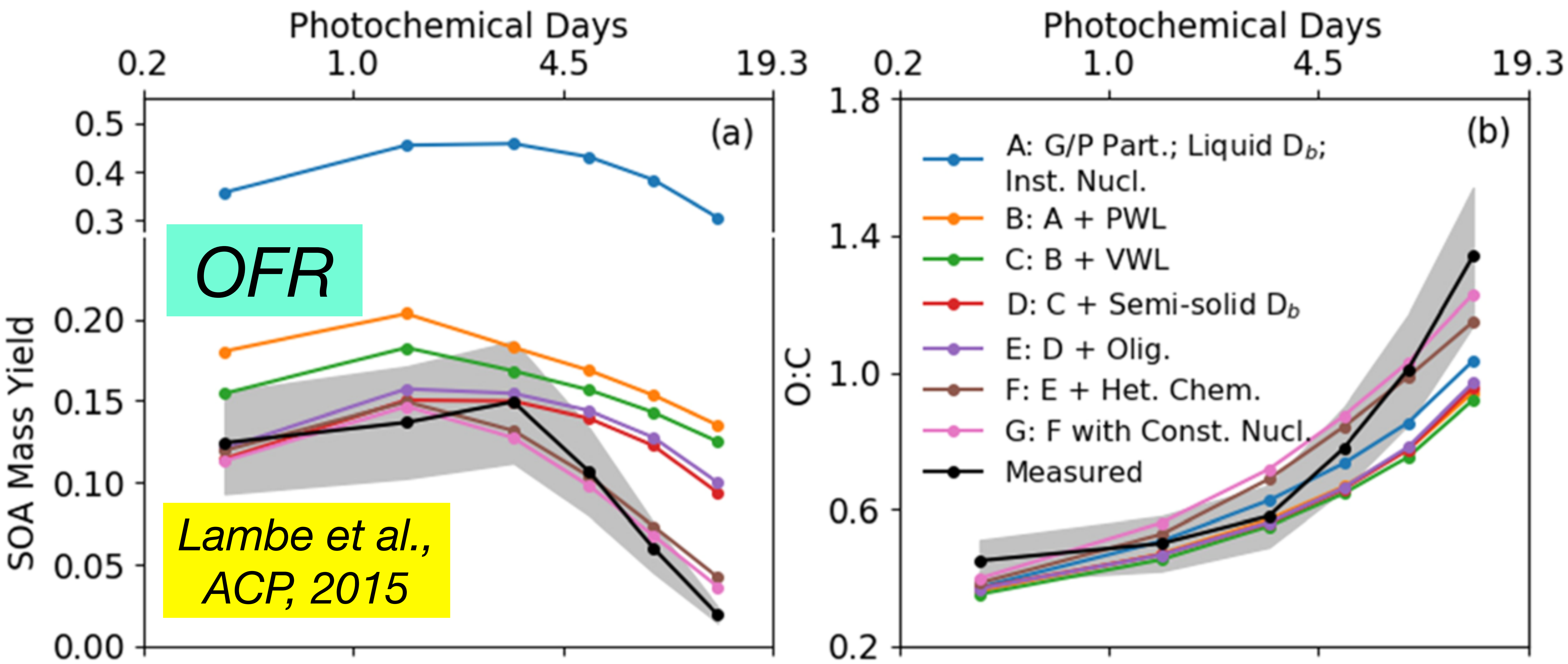

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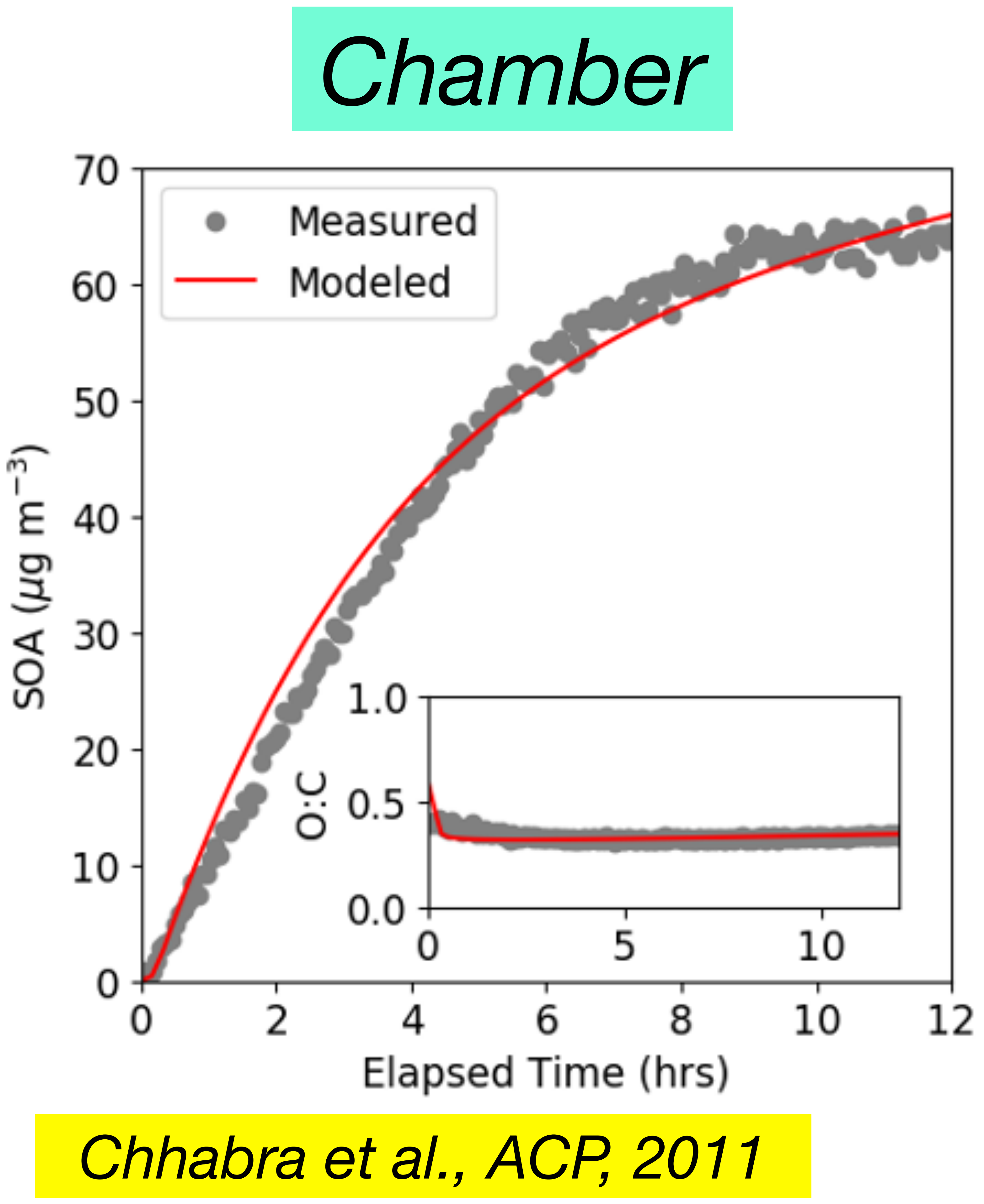
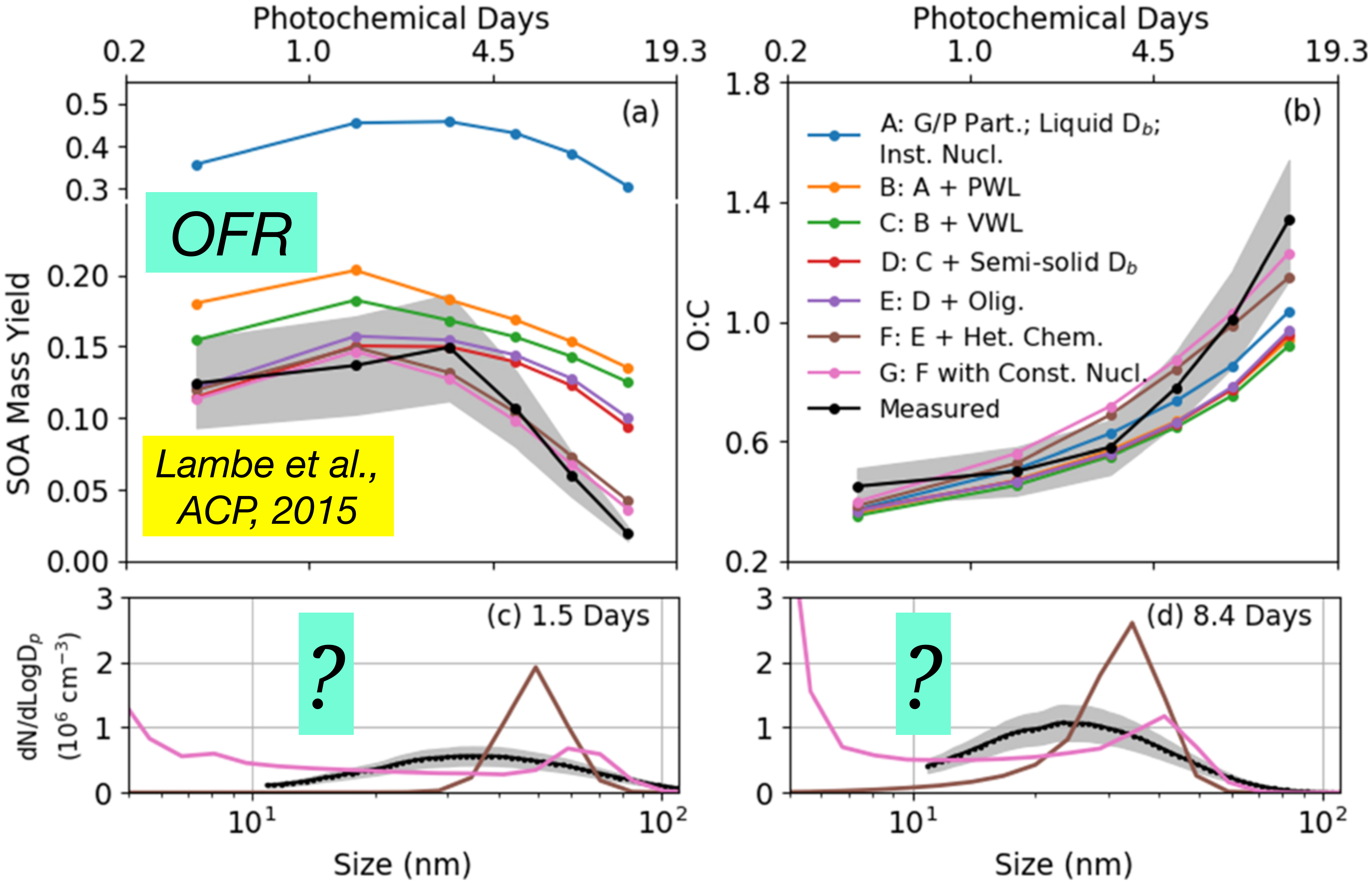




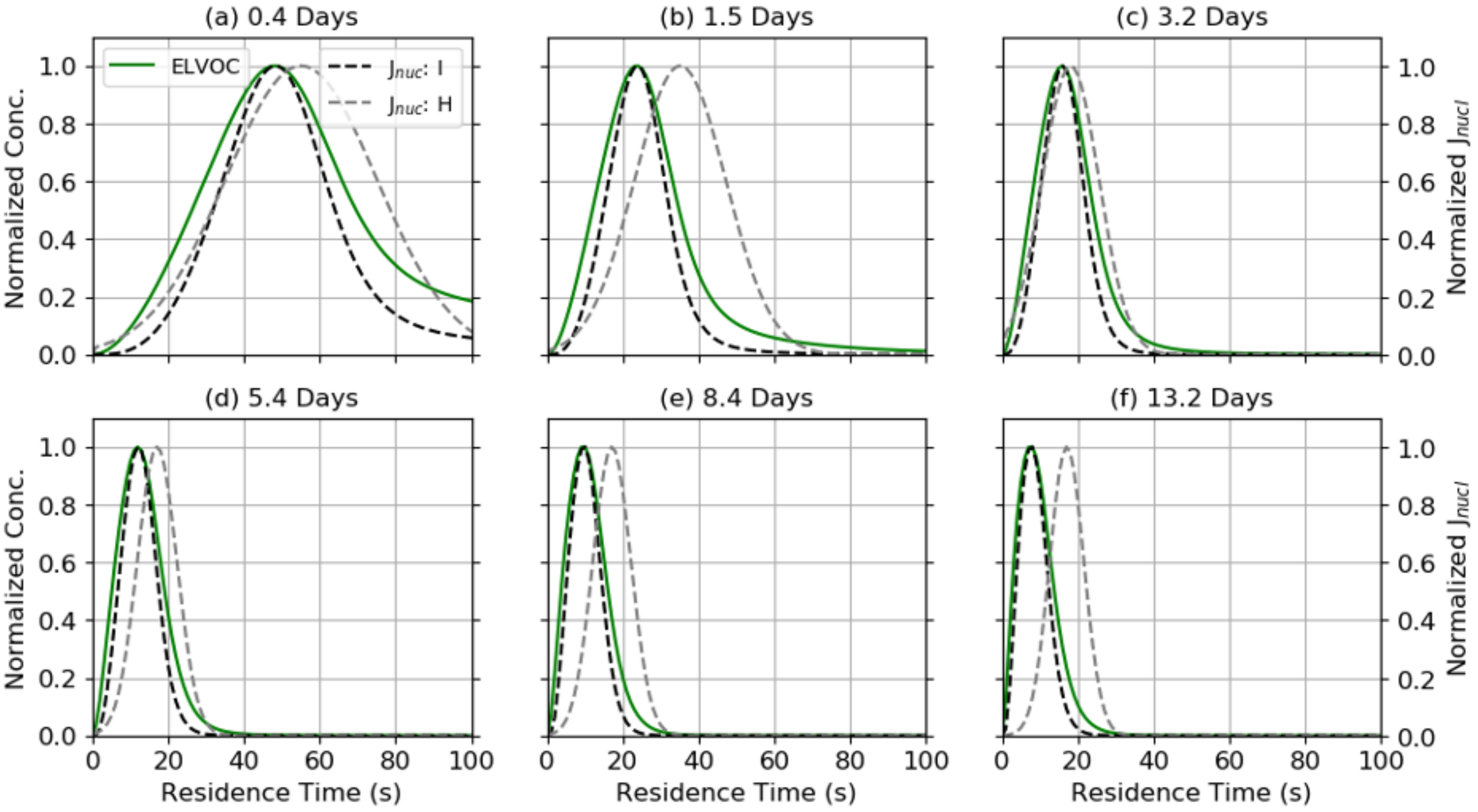
- Two different schemes were used to model the nucleation in the OFR to improve the model performance against particle size distribution data

Eqn 1

$$J_{\mathrm{nuc}} = \frac{\mathrm{TNuc}}{\sigma_{\mathrm{nuc}}\sqrt{2\pi}} \mathrm{e}^{-1/2\left(\frac{t-\mu_{\mathrm{nuc}}}{\sigma_{\mathrm{nuc}}}\right)^2}$$

Eqn 2

$$J_{\mathrm{nuc}} = a_1[\mathrm{ELVOC}]^{a_2}$$



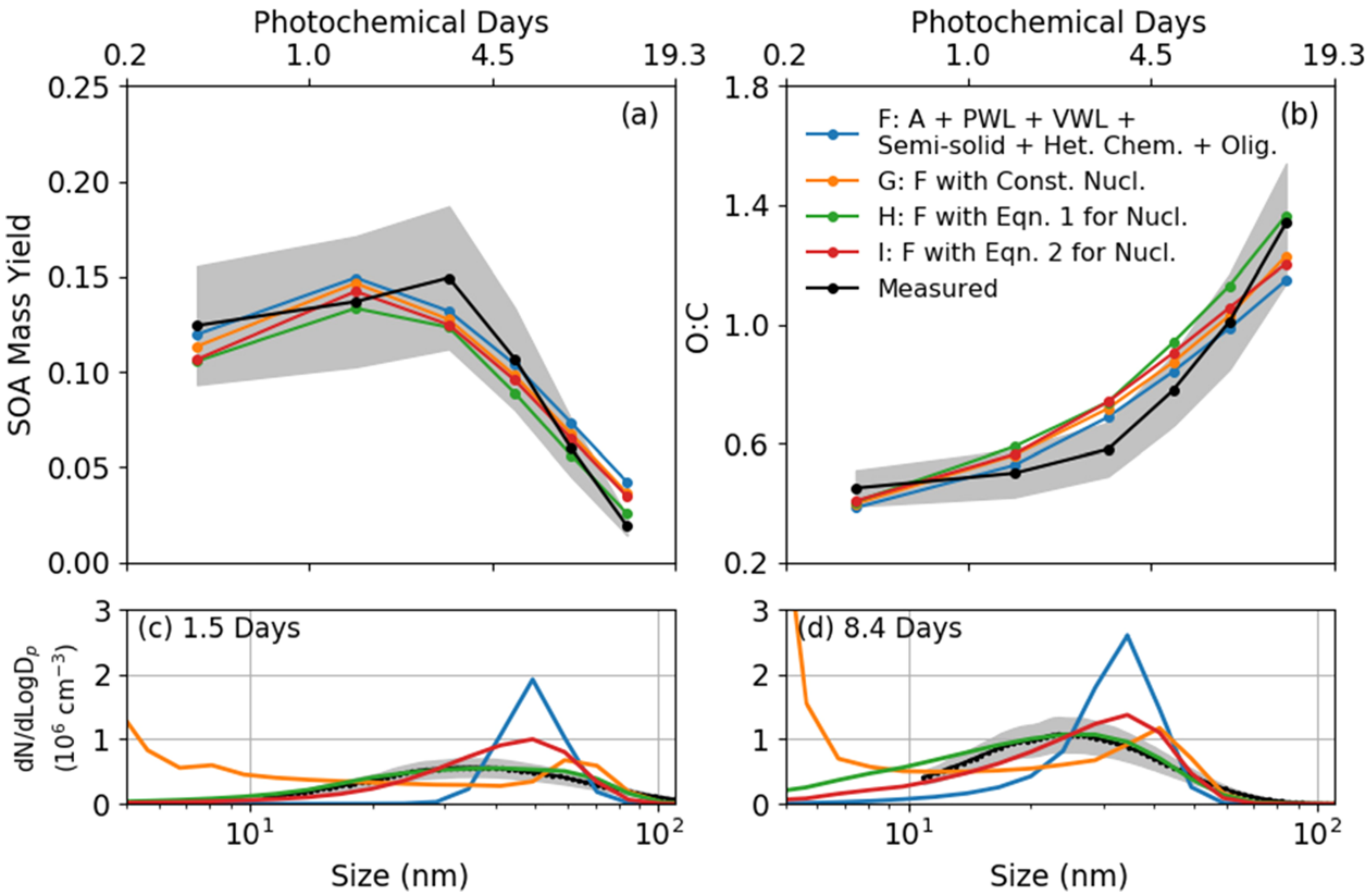
- Nucleation linked to gas-phase dimers (ELVOCs), formed from carbon-number retaining oxidation products, can explain particle size distribution data

Eqn 1 (Model H)

$$J_{nuc} = \frac{\mathrm{TNuc}}{\sigma_{nuc}\sqrt{2\pi}} e^{-1/2\left(\frac{t-\mu_{nuc}}{\sigma_{nuc}}\right)^2}$$

Eqn 2 (Model I)

$$J_{nuc} = a_1[\mathrm{ELVOC}]^{a_2}$$



Environmental Science & Technology

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Vapors Are Lost to Walls, Not to Particles on the Wall: Artifact-Corrected Parameters from Chamber Experiments and Implications for Global Secondary Organic Aerosol

Kelsey R. Bilsback,*,◊ Yicong He,◊ Christopher D. Cappa, Rachel Ying-Wen Chang, Betty Croft, Randall V. Martin, Nga Lee Ng, John H. Seinfeld, Jeffrey R. Pierce, and Shantanu H. Jathar

Kelsey

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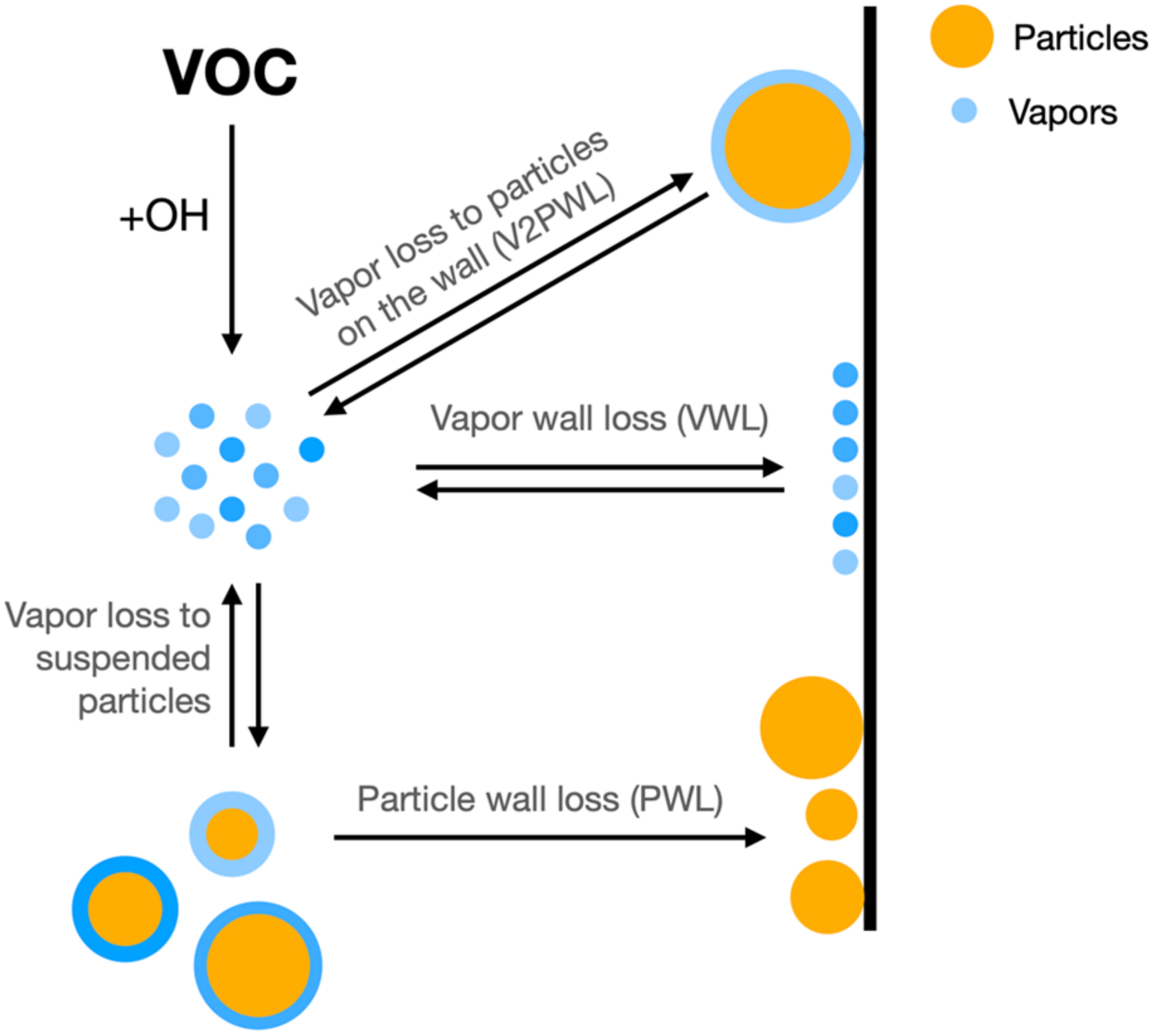
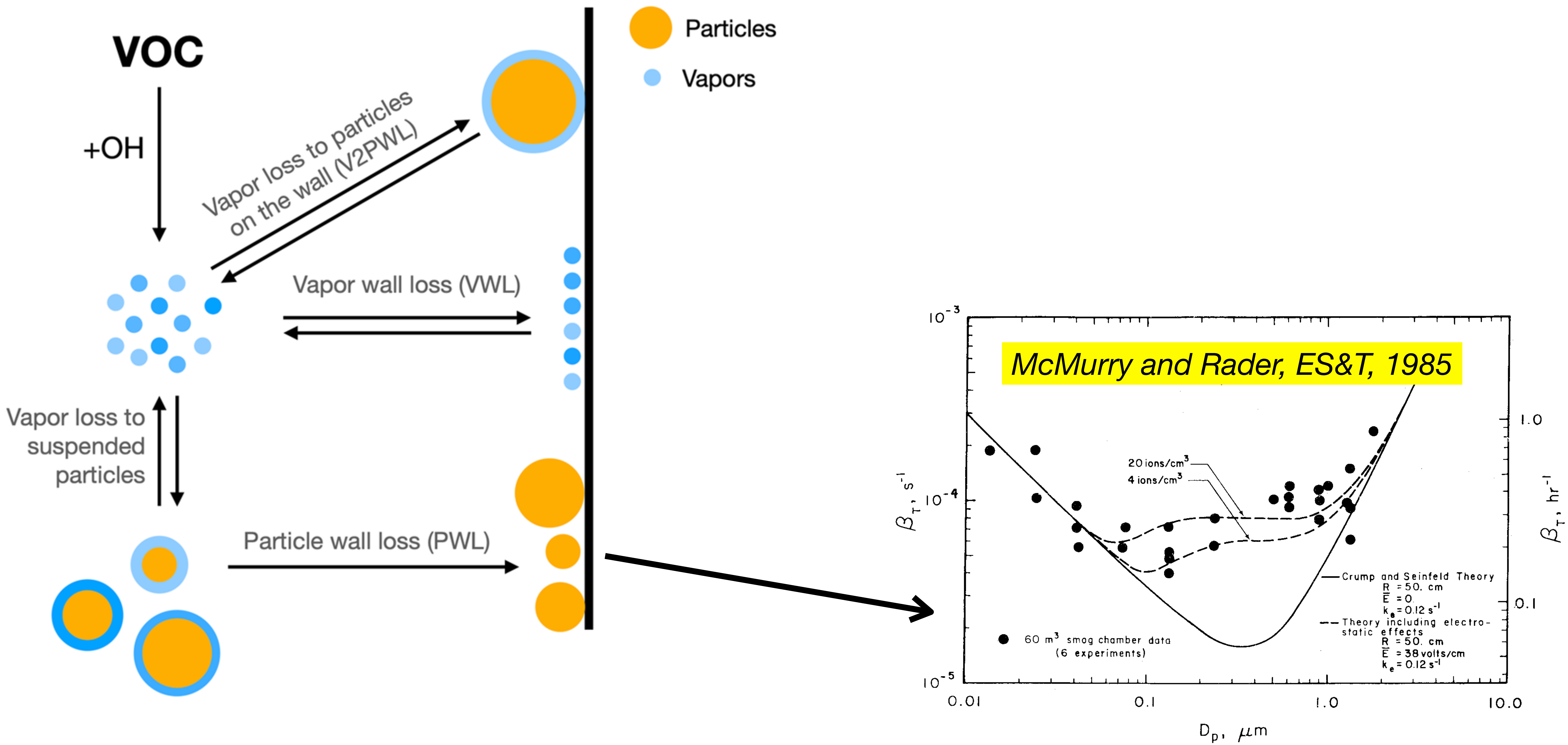

VOC
+OH
Vapor loss to particles
on the wall (V2PWL)
Vapor wall loss (VWL)
Vapor loss to
suspended
particles
Particle wall loss (PWL)
Particles
Vapors



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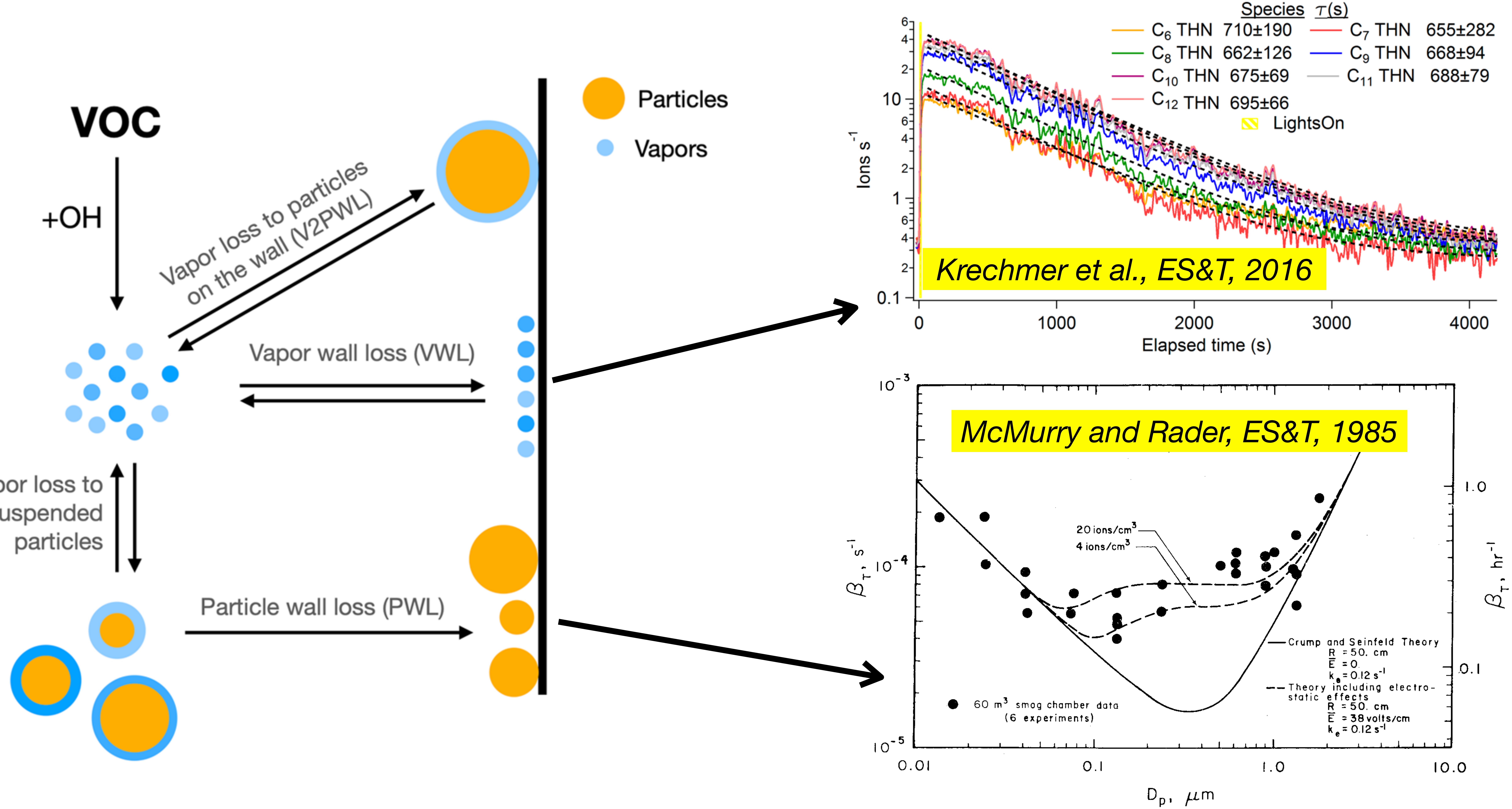
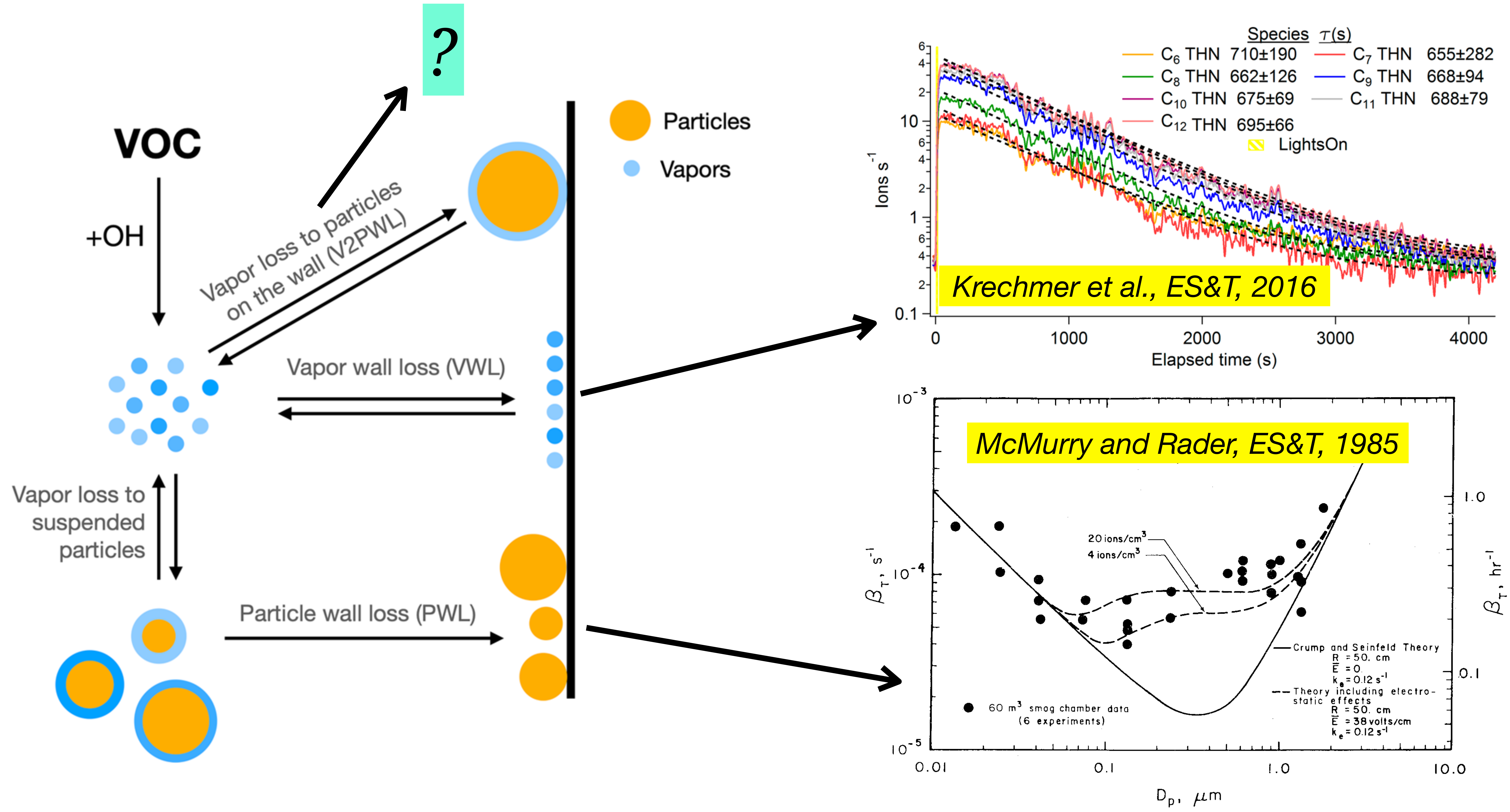


VOC
+OH
Vapor loss to particles on the wall (V2PWL)
Vapor wall loss (VWL)
Vapor loss to suspended particles
Particle wall loss (PWL)
Particles
Vapors
Species τ(s)
C6 THN 710±190
C7 THN 655±282
C8 THN 662±126
C9 THN 668±94
C10 THN 675±69
C11 THN 688±79
C12 THN 695±66
LightsOn
Ions s-1
Elapsed time (s)
Krechmer et al., ES&T, 2016
McMurry and Rader, ES&T, 1985
20 ions/cm3
4 ions/cm3
Crump and Seinfeld Theory
Theory including electrostatic effects
60 m3 smog chamber data (6 experiments)
βT, s-1
βT, hr-1
Dp, μm


?
VOC
+OH
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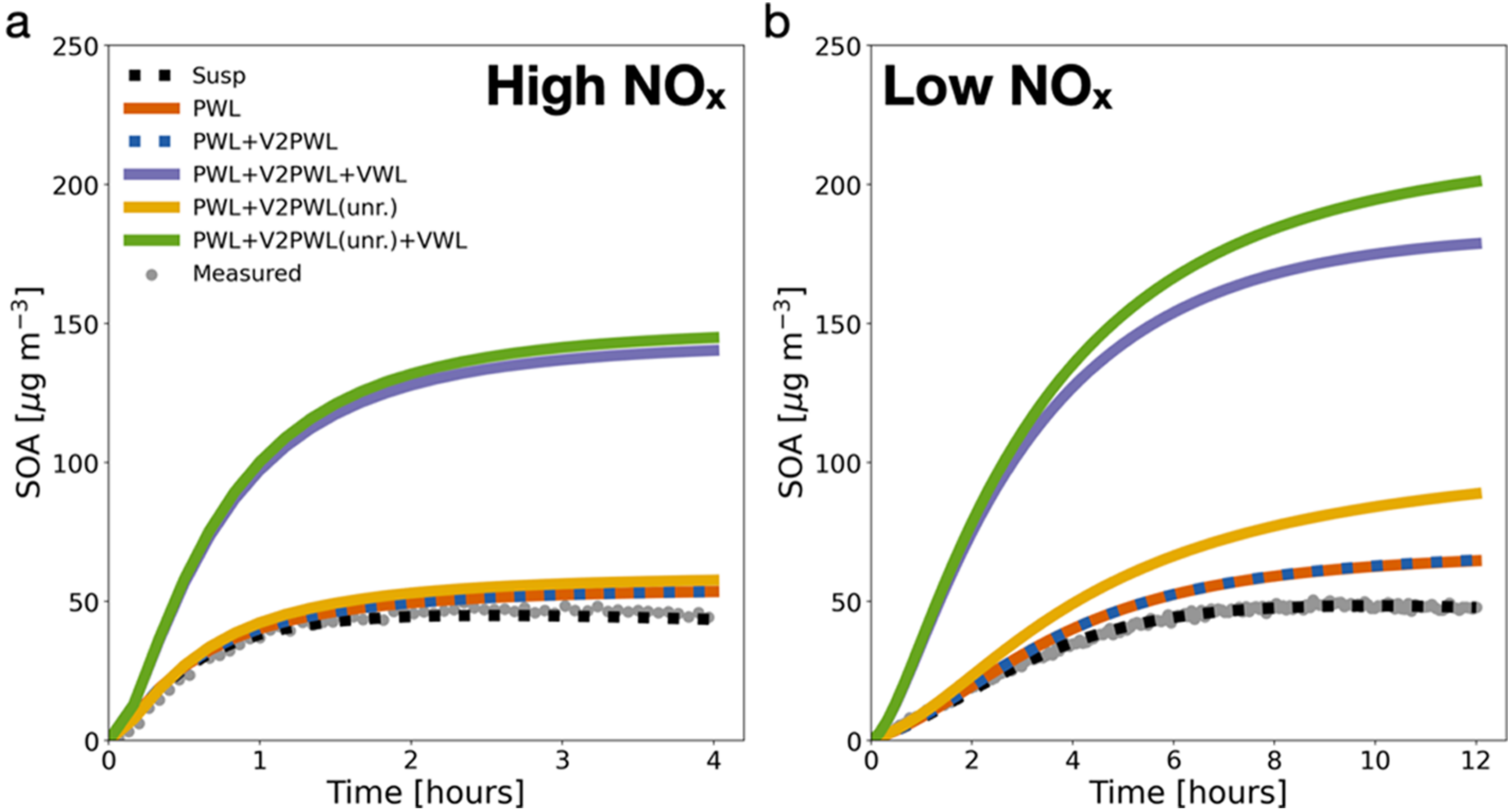
20 ions/cm3
4 ions/cm3
Crump and Seinfeld Theory
R = 50. cm
E = 0
ke = 0.12 s-1
Theory including electro-static effects
R = 50. cm
E = 38 volts/cm
ke = 0.12 s-1
60 m3 smog chamber data
(6 experiments)
βT, s-1
βT, hr-1
Dp, μm

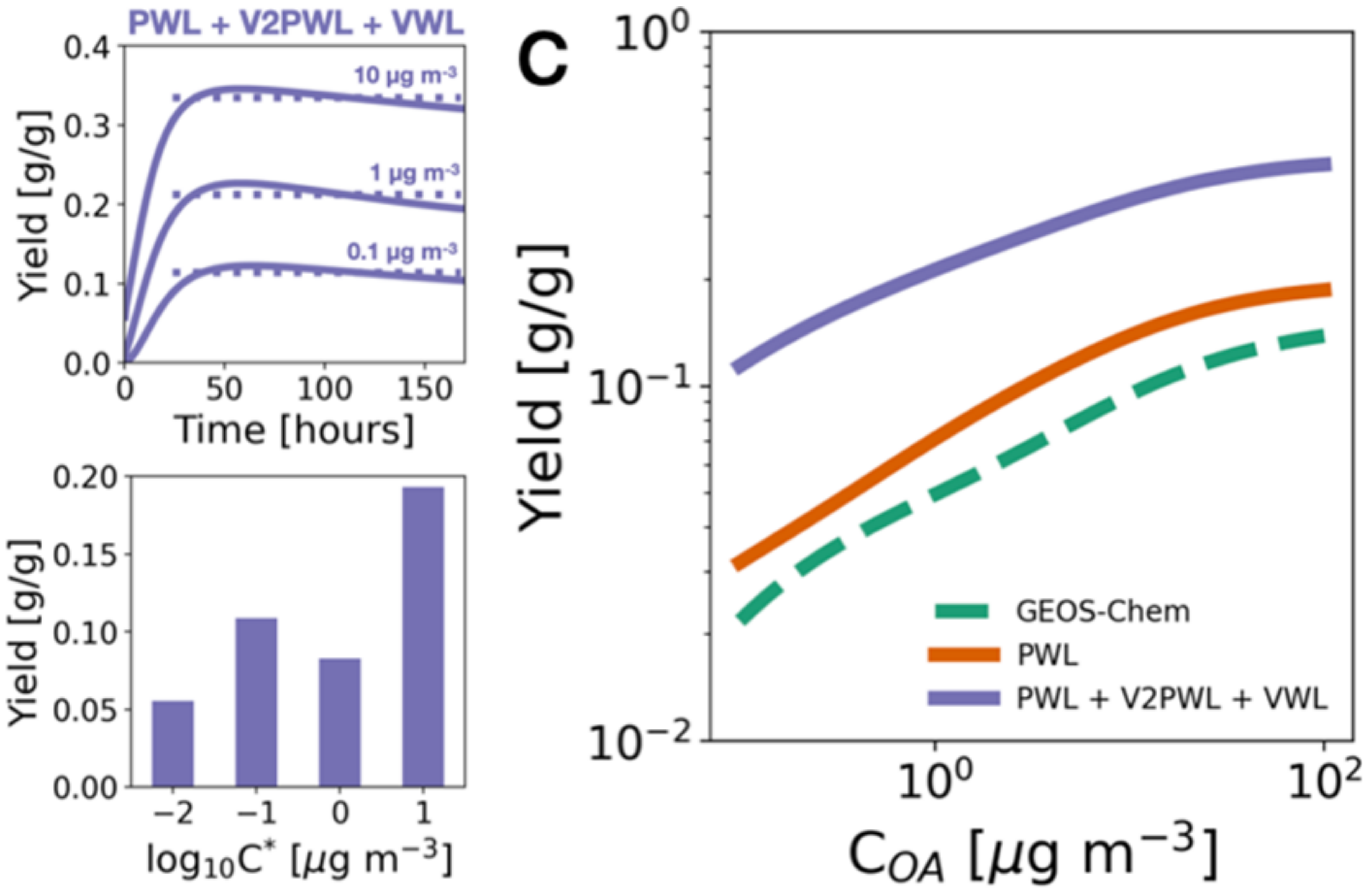
- Condensable vapors are lost to suspended particles and to the walls but NOT the particles on the wall; finding consistent for 6 other SOA precursors

α-pinene



- Pseudo-atmospheric simulations were performed with SOM-TOMAS to generate VBS parameters for GEOS-Chem
- Accounting for vapor wall losses resulted in a large increase in SOA mass yields

α-pinene High NO_X



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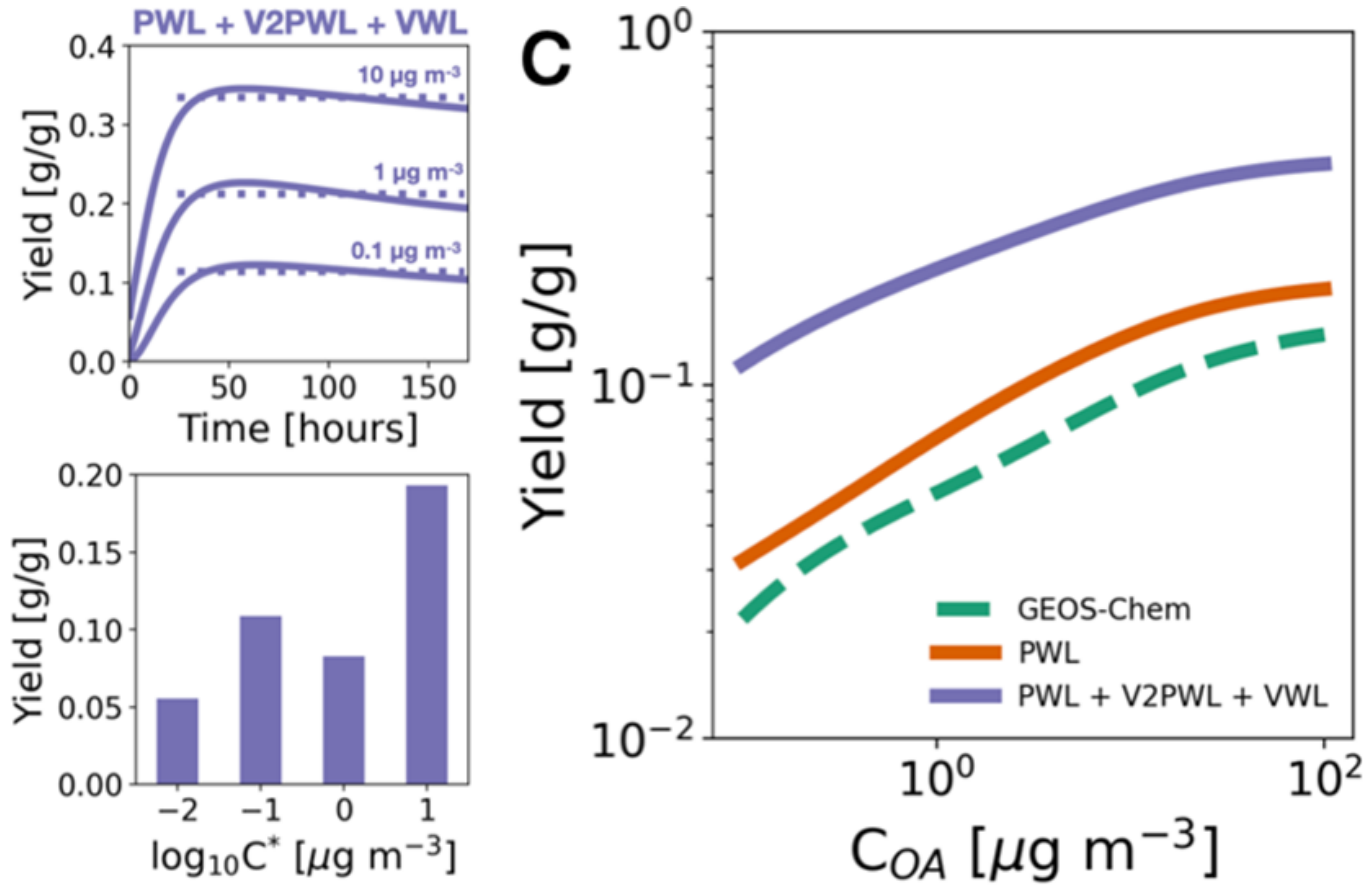
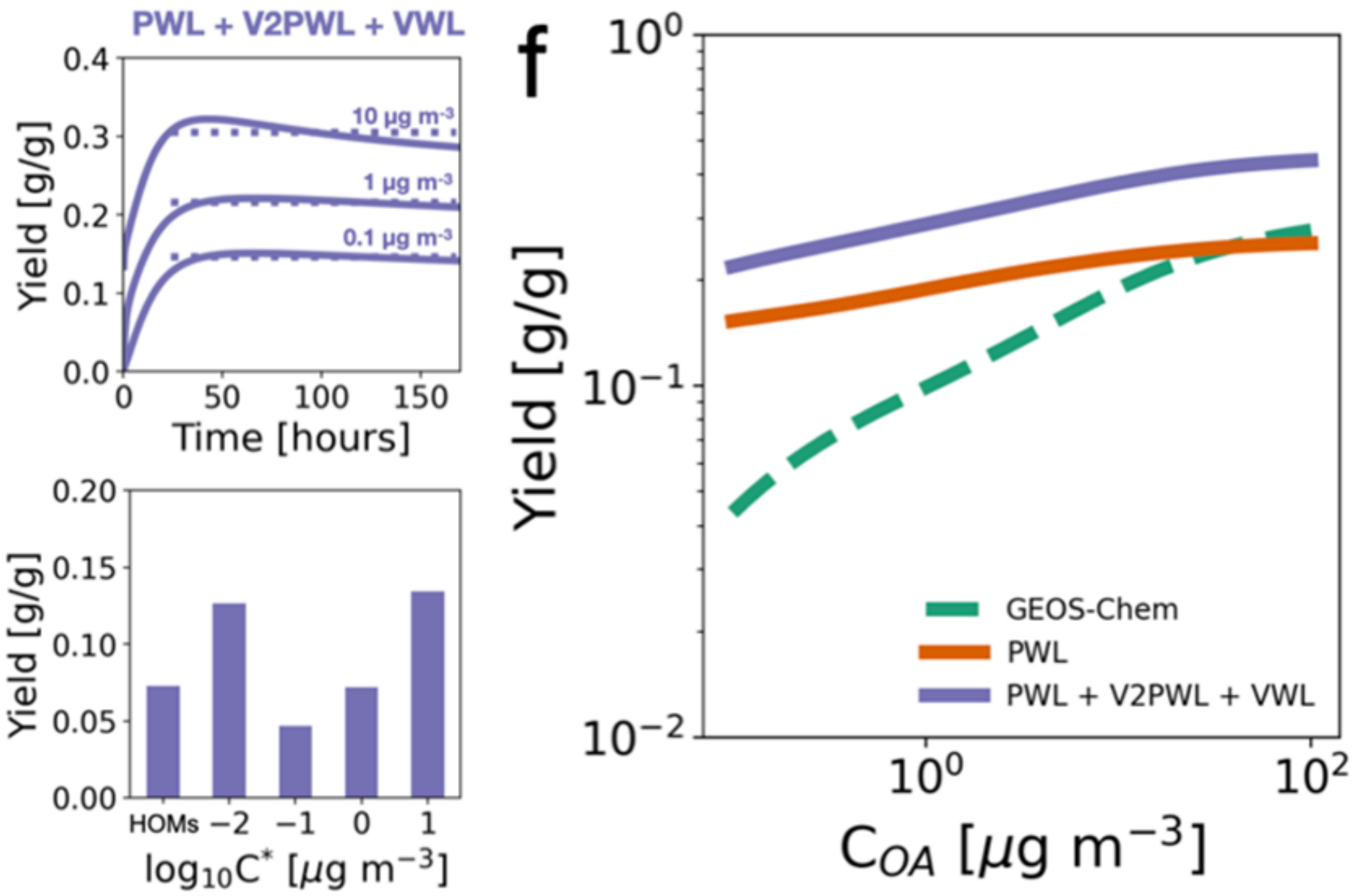
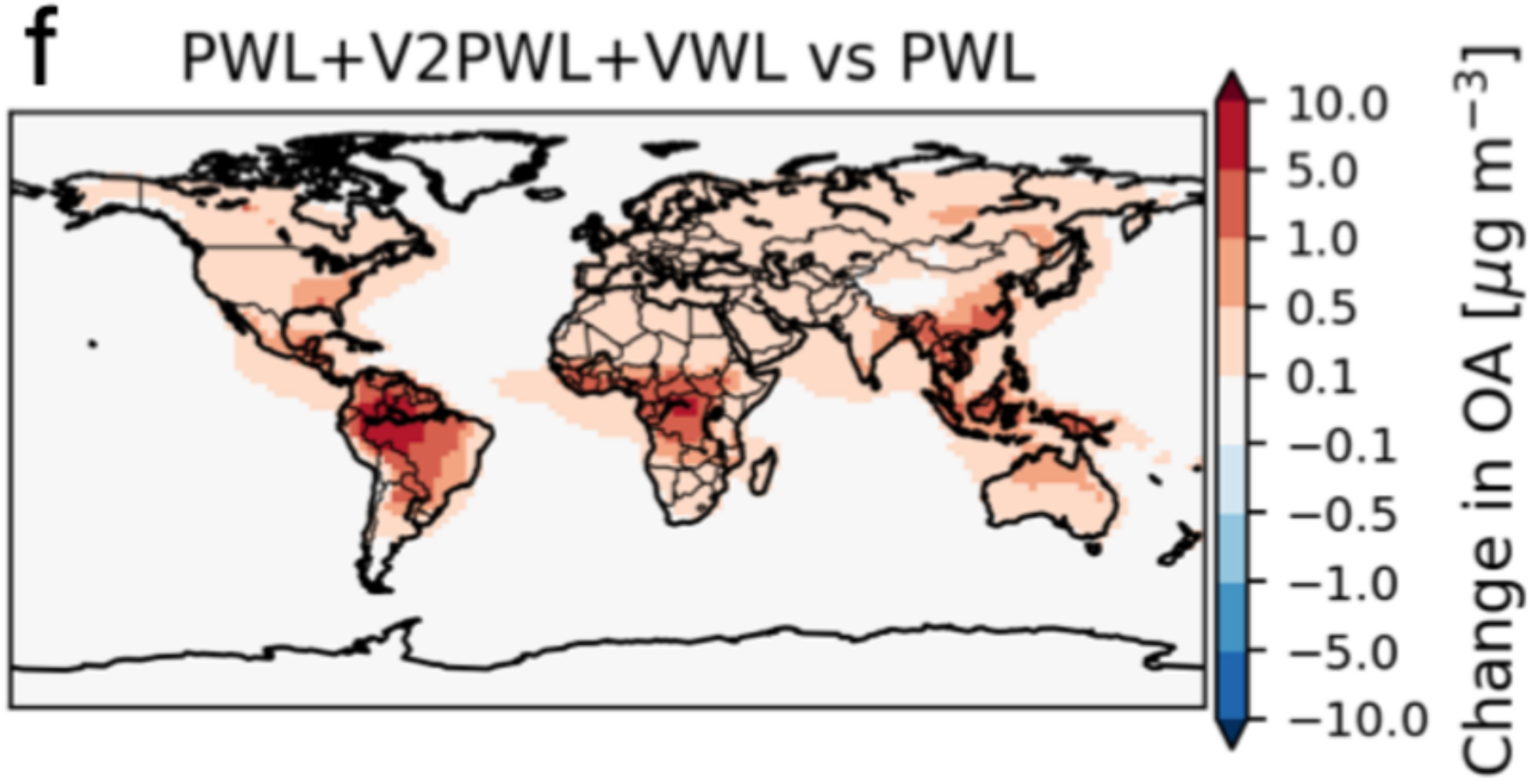


α-pinene Low NOx



- Accounting for VWL leads to an increase in SOA and OA in precursor-heavy regions



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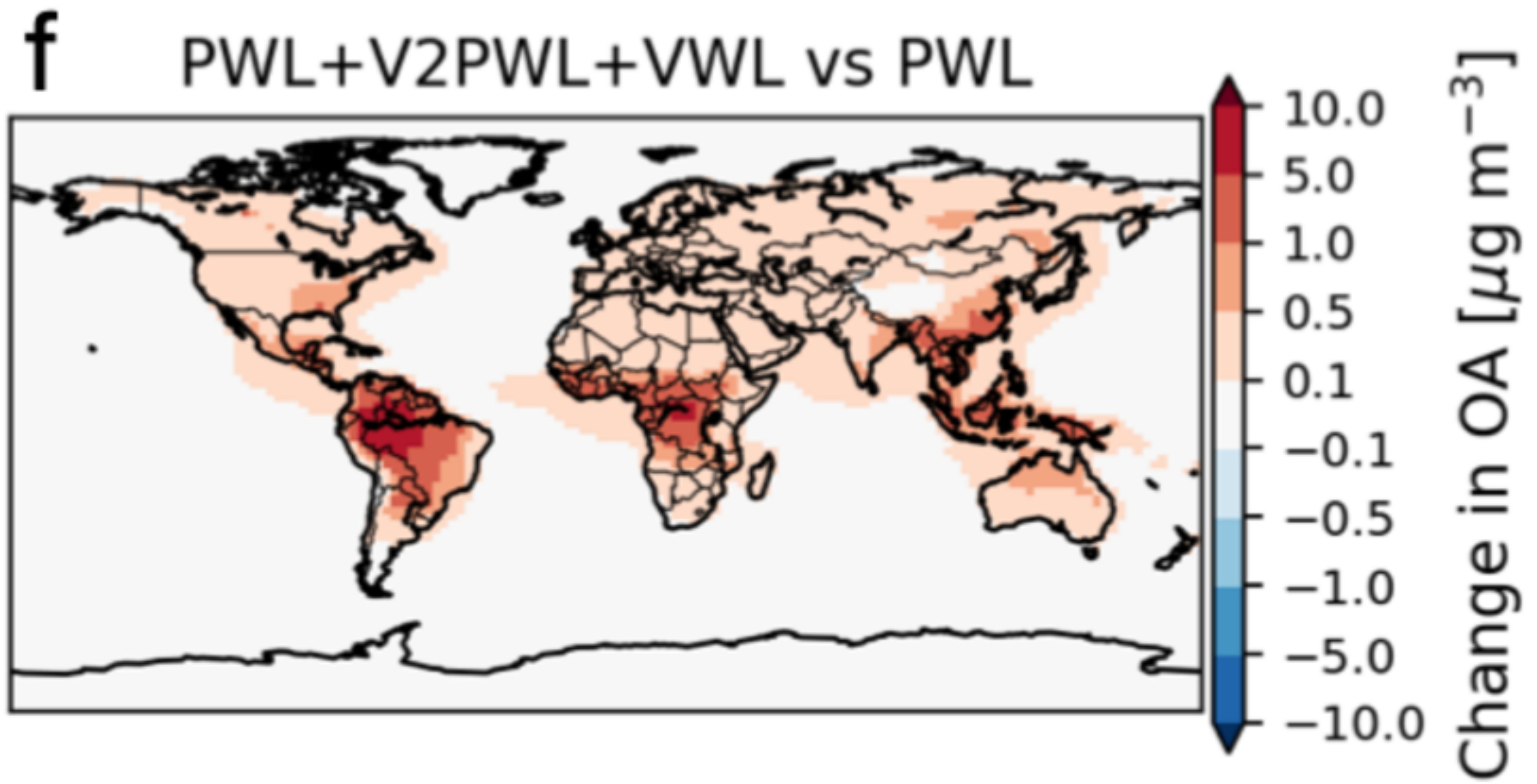

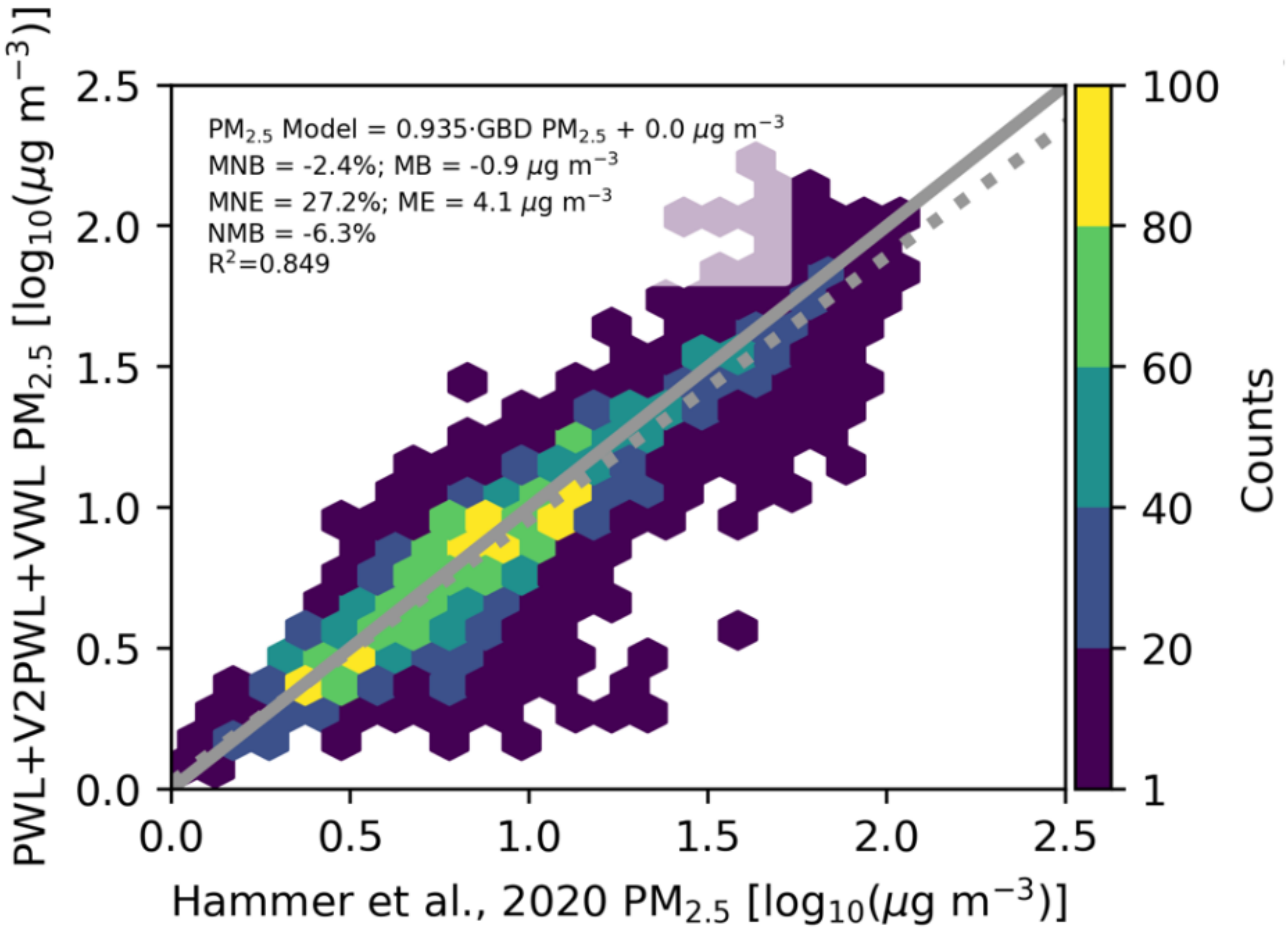

- Some indication that GEOS-Chem performance improves against $PM_{2.5}$

Key Findings:

Study 1: Observations of the particle size distribution can be used to constrain the particle phase state and oligomer formation

Study 2: Process-level modeling can explain SOA formation and composition in environmental chambers and OFRs, enabling better parameters for 3D models

Study 3: Vapors are lost to suspended particles and to the walls but NOT to wall particles

Thank You | Questions?