Secondary Aerosol Formation of Fine Particulate Matter in the Indoor Environment

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Outline of talk

- SOA basic information and historical investigation
- SOA modeling as tool to improve our understanding
- SOA emission strengths and future research needs

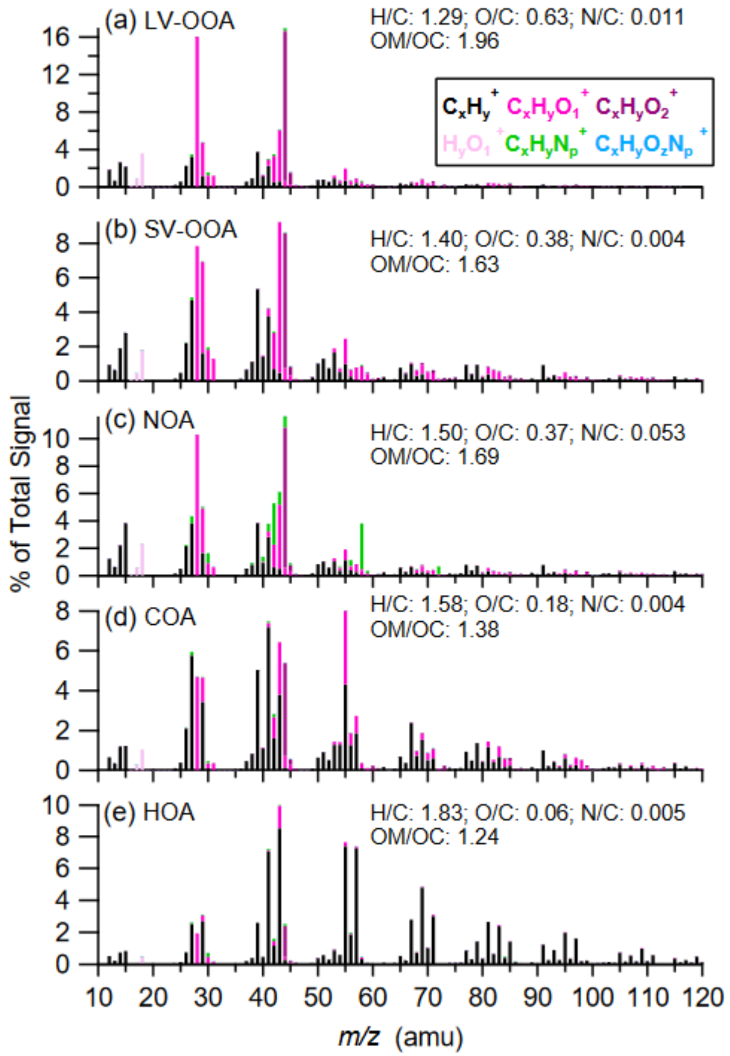
Organic Aerosol (OA) types

OA "factors"

- Hydrocarbon-like (HOA)
- Biomass-burning (BBOA)
- Cooking (COA)
- Oxygenated (OOA), SV-OOA and LV-OOA

Source processes

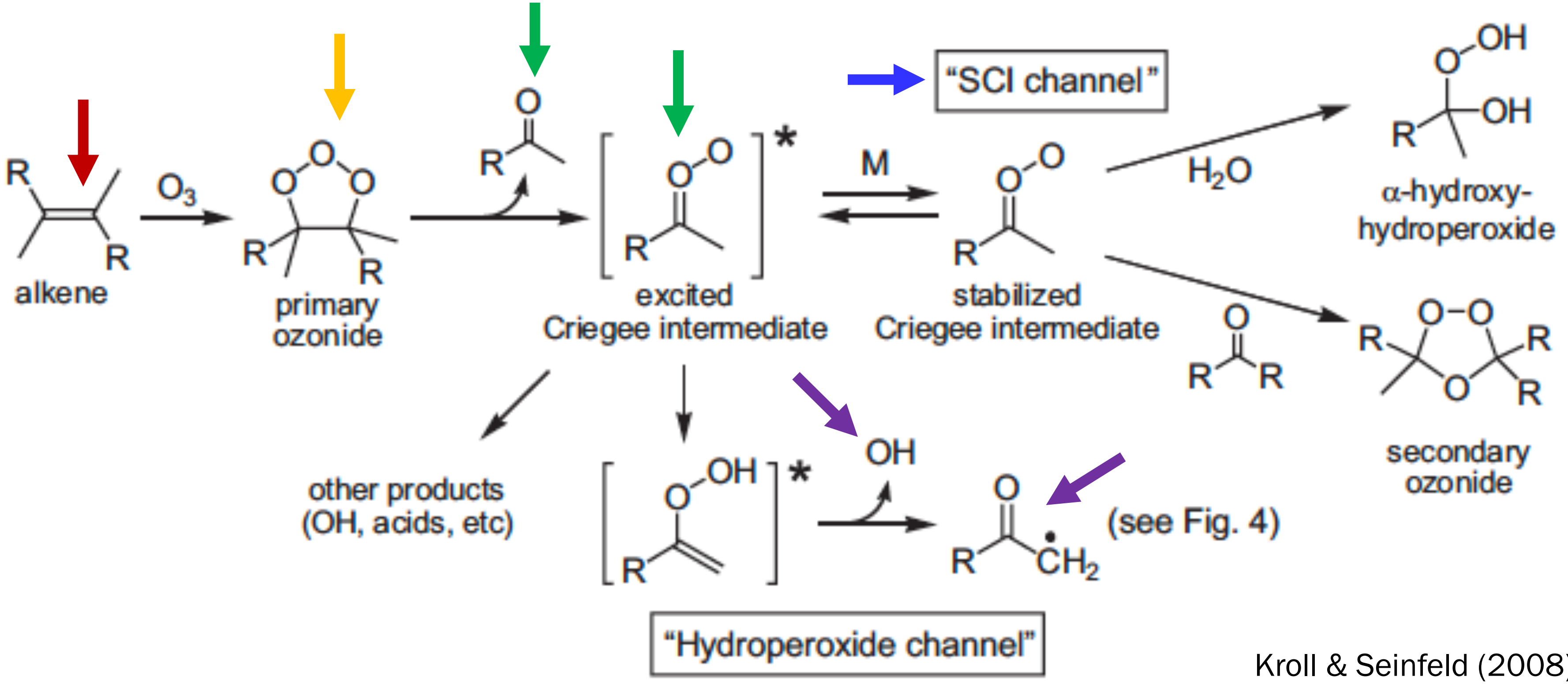
- Primary (POA)
  - Combustion, cooking
  - Corresponds with HOA, BBOA, COA
- **Secondary (SOA)**
  - Products of gas-phase reactions
  - Corresponds with SVOOA and LVOOA



Sun et al. (2011)

Alkene ozonolysis initial steps

- Follows the so-called Criegee mechanism, generates OH, R˙, SCI, and other products

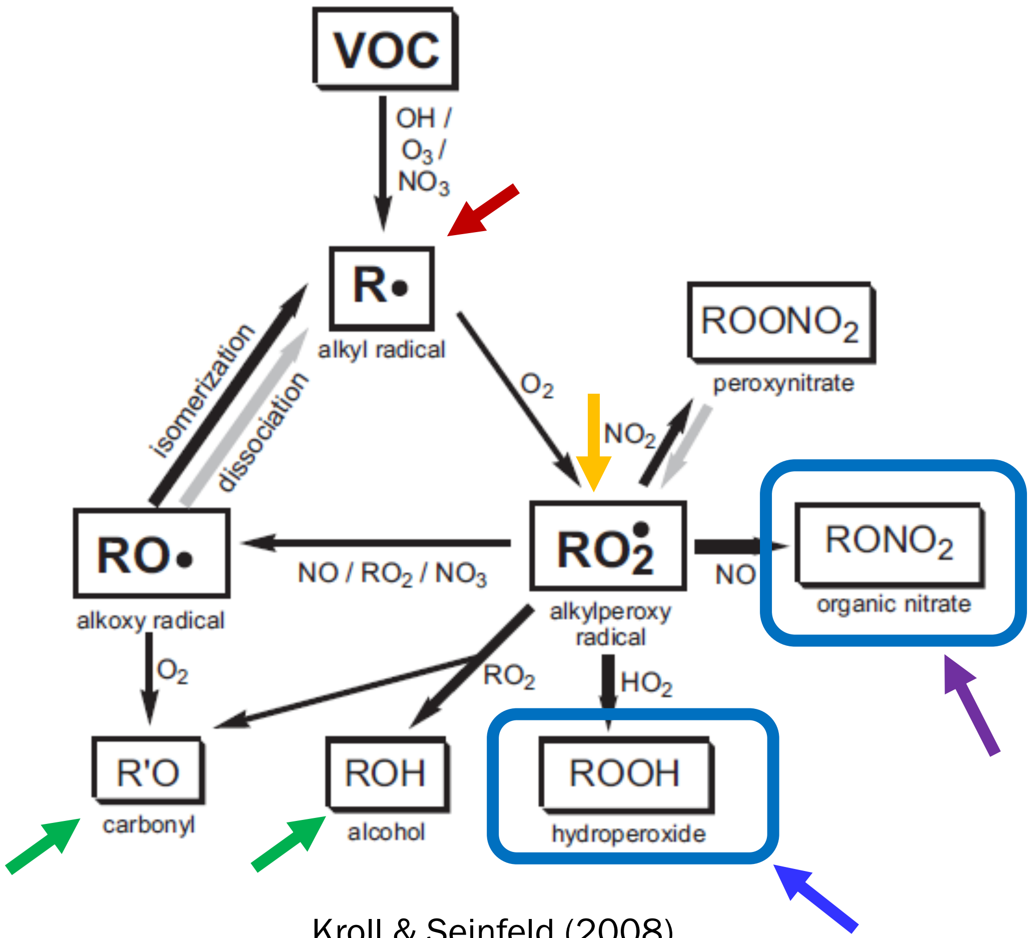


Kroll & Seinfeld (2008)

VOC oxidation starts complex mechanism

- **Reactions with oxidants** lead to multistep processes, which form **many products**, such as:
  - Carbonyls (=O)
  - Alcohols (—OH)
  - Carboxylic acids ((=O)OH)
  - Peroxides (—OOH)
  - Organic nitrates (—ONO_2)

Lower volatility products with large functionality partition to form secondary organic aerosol (SOA)



Kroll & Seinfeld (2008)

Indoor SOA formation

- Most studies on indoor SOA in chambers or test rooms
  - **Ozone + common terpene** (Weschler and Shields, 1999; Youssefi and Waring, 2014, 2015; many others)
  - **Ozone + consumer product** (Sarwar et al., 2003; Destaillats et al., 2006; Singer et al., 2006; many others)

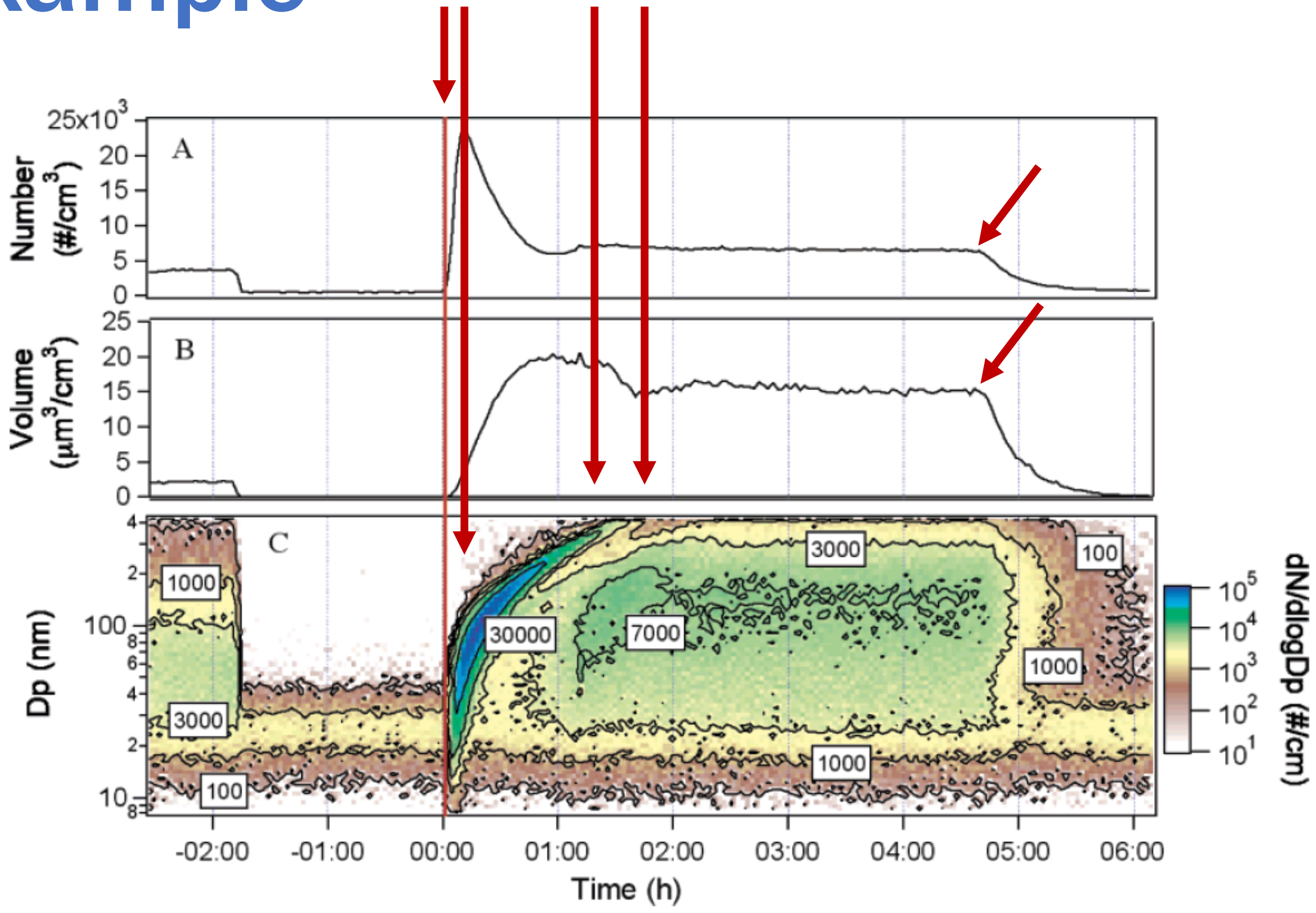
- Scanning mobility particle sizers (SMPS) had difficulty separating background PM from SOA
- Aerosol mass spectrometers (AMS) produce spectra for interpretation (but can be messy in field studies)

- **SOA formation models** used to estimate indoor SOA concentrations and explore uncertainties

SOA formation example

SOA experiment run to steady state
(Destaillats et al., 2006)

- Air freshener operated continuously in a chamber at 3 ACH
- Ozone supply = 63 ppb started at red line on plot (time zero)
- Nucleation occurred at onset of experiment after ozone started
- Size distribution then stabilized
- Gas-to-particle partitioning of products afterward
- Steady number and volume until ozone supply turned off



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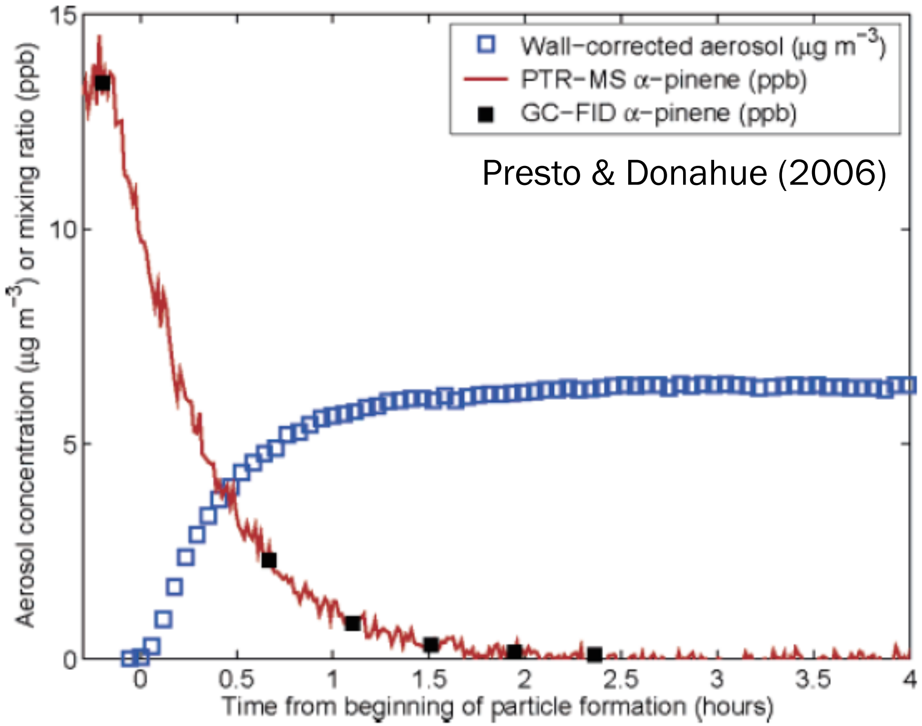
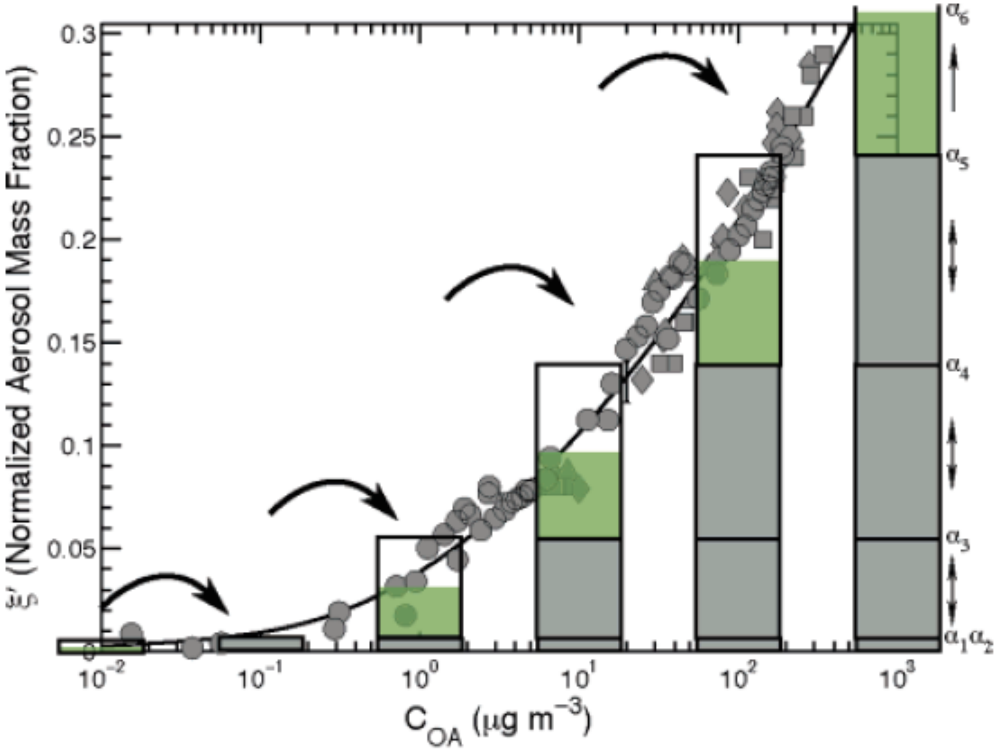
Indoor SOA modeling types

- **Explicit product model** (Carlsaw, 2007; Carslaw et al., 2012; Kruza et al., 2020)
- **Lumped product model** (Youssefi and Waring, 2012; Waring 2014; Cummings and Waring, 2019; Cummings et al., 2020)
  - Simplified mechanism for oxidation reactions and products, first generation reactions only
  - VOC oxidation reaction product yields of organic matter (OM) lumped into volatility bins
  - Partitioning of all OM determined by solving gas-to-particle partitioning equations
  - All types of organic aerosol can be accommodated (e.g. outdoor OA, BBOA, OOA, HOA, indoor SOA)
  - Bulk aerosol properties can be determined easily (density, phase state, hygroscopicity)

    (**IMAGES = Indoor Model of Gases, Aerosols, Emissions, and Surfaces**)

Indoor SOA modeling w/ yields





$$Y \text{ or AMF} = \frac{\Delta C_{\mathrm{SOA}}}{\Delta \mathrm{ROG}} = \sum_{i=1}^{n} \alpha_i \left(1 + \frac{c_i^*}{C_{\mathrm{SOA}}}\right)^{-1}$$

$$\alpha_i = \{0.004, 0, 0.051, 0.09, 0.12, 0.18\}$$

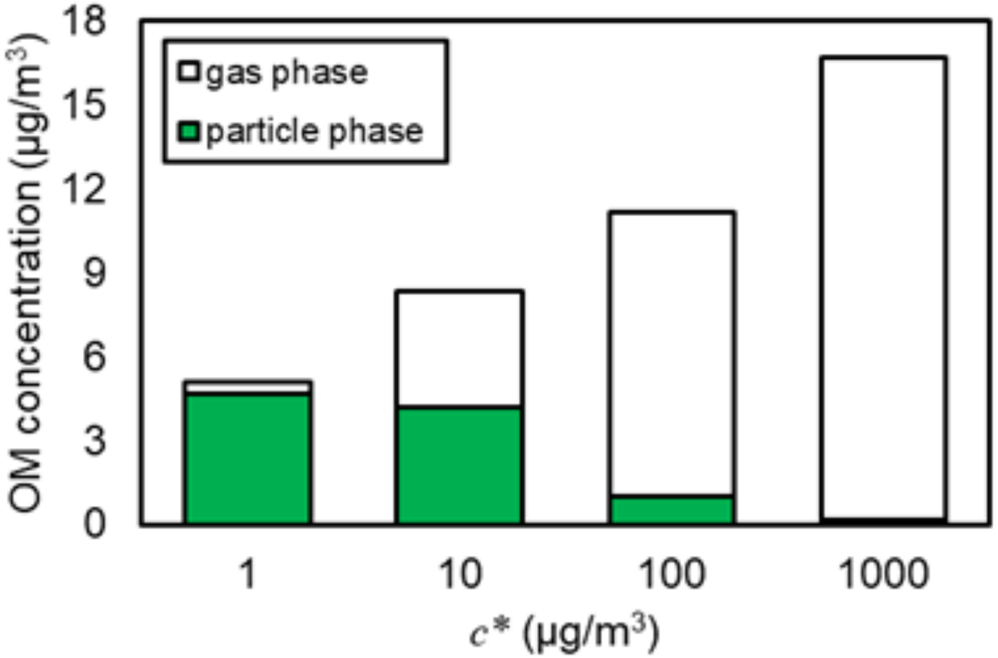
$$\text{at } c_i^* = \{0.01, 0.1, 1, 10, 100, 1000\ \mu\text{g/m}^3\}$$

Indoor SOA modeling w/ 1D-VBS

- **1D-VBS** **organizes organic matter (OM) components** (gas or particle) based on
  - **Volatility** using saturation conc. (c^*, µg/m^3)
- Example:
  - Organic mass ($C_{\mathrm{OM},i}$, µg/m^3) lumped in c_i^* bins
  - Aerosol mass fraction (AMF) predicted by partitioning of $C_{\mathrm{OM},i}$ in c_i^* for total C_{OA} (µg/m^3)

$$\mathrm{AMF}_i = \left(1 + \frac{c_i^*}{C_{\mathrm{OA}}}\right)^{-1} \Longleftrightarrow C_{\mathrm{OA}} = \sum_i C_{\mathrm{OM},i}\mathrm{AMF}_i$$

1D-VBS
10 µg/m^3 SOA from α-pinene ozonolysis



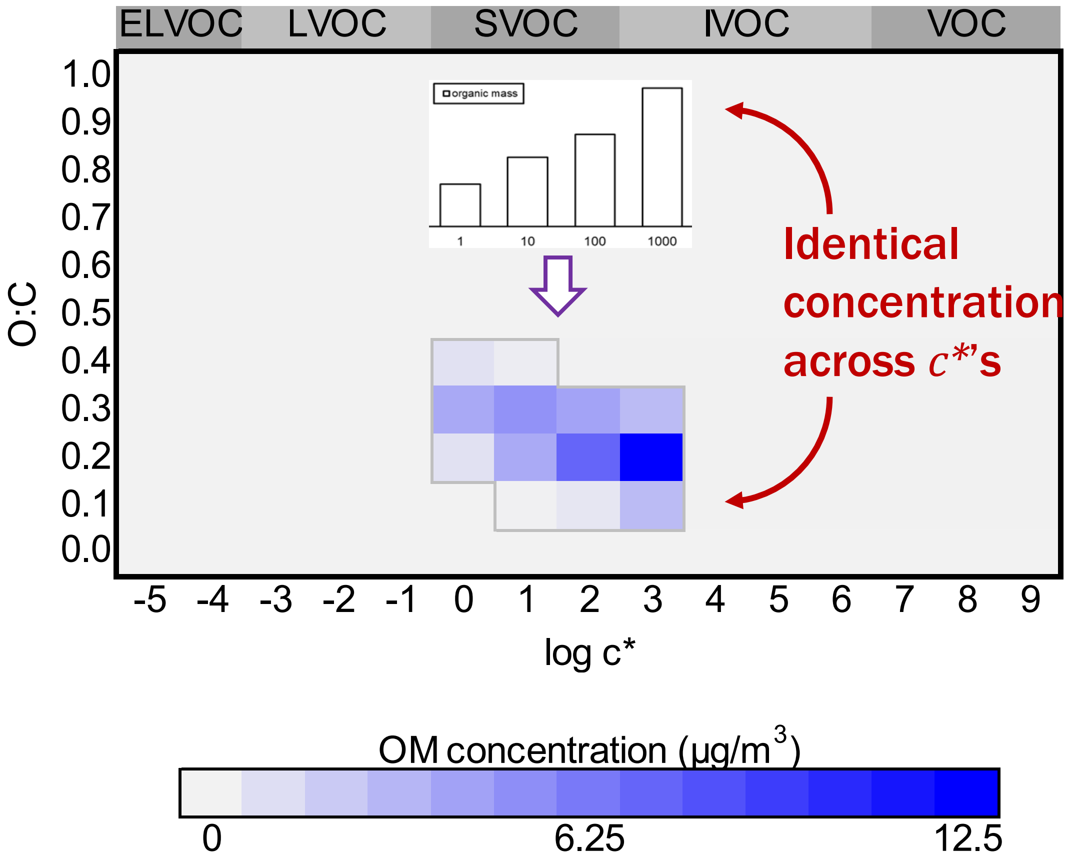
From 1D to 2D-VBS

- **2D-VBS organizes organic matter (OM) components** (gas or particle) based on
  - **Volatility** using saturation conc. (c^*, μg/m^3)
  - **Oxidation** degree using O:C ratio or OS_C
- Example:
  - 1D-VBS distribution spread into O:C "dimension"
  - Partitioning calculation proceeds unchanged

$$\mathrm{AMF}_i = \left(1 + \frac{c_i^*}{C_{\mathrm{OA}}}\right)^{-1} \Longleftrightarrow C_{\mathrm{OA}} = \sum_i C_{\mathrm{OM},i}\mathrm{AMF}_i$$

2D-VBS

10 μg/m^3 SOA from α-pinene ozonolysis

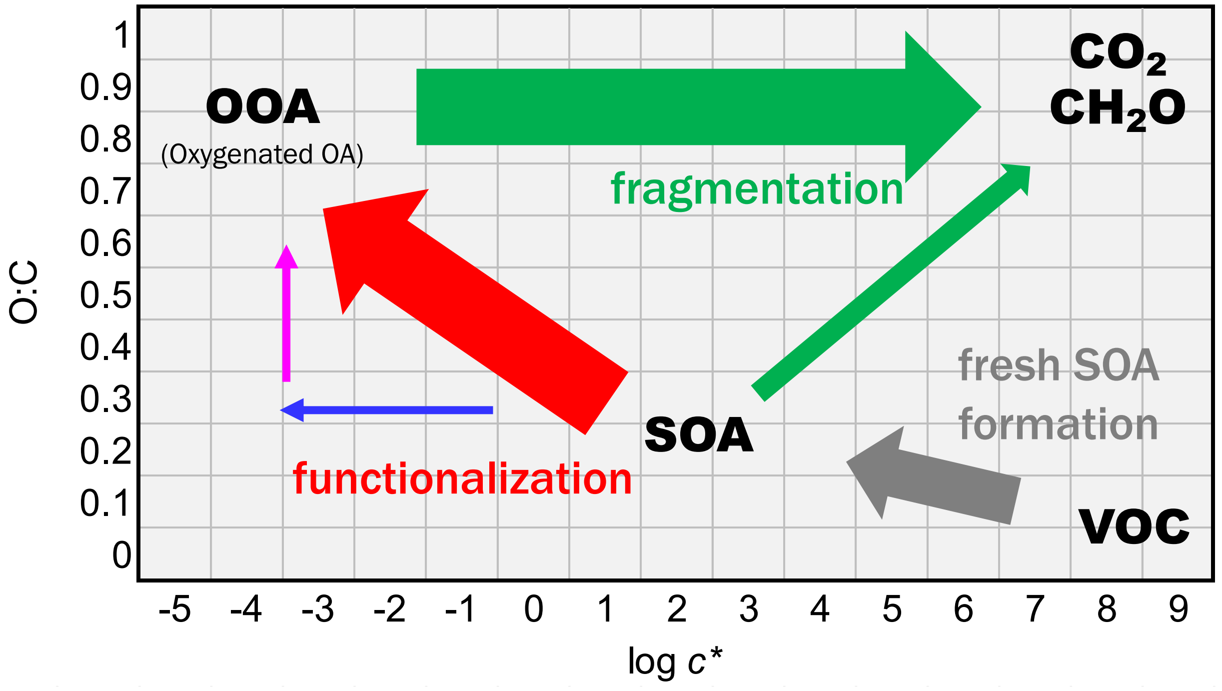


OA evolution through 2D-VBS

OM forms, then ages via 2 processes:

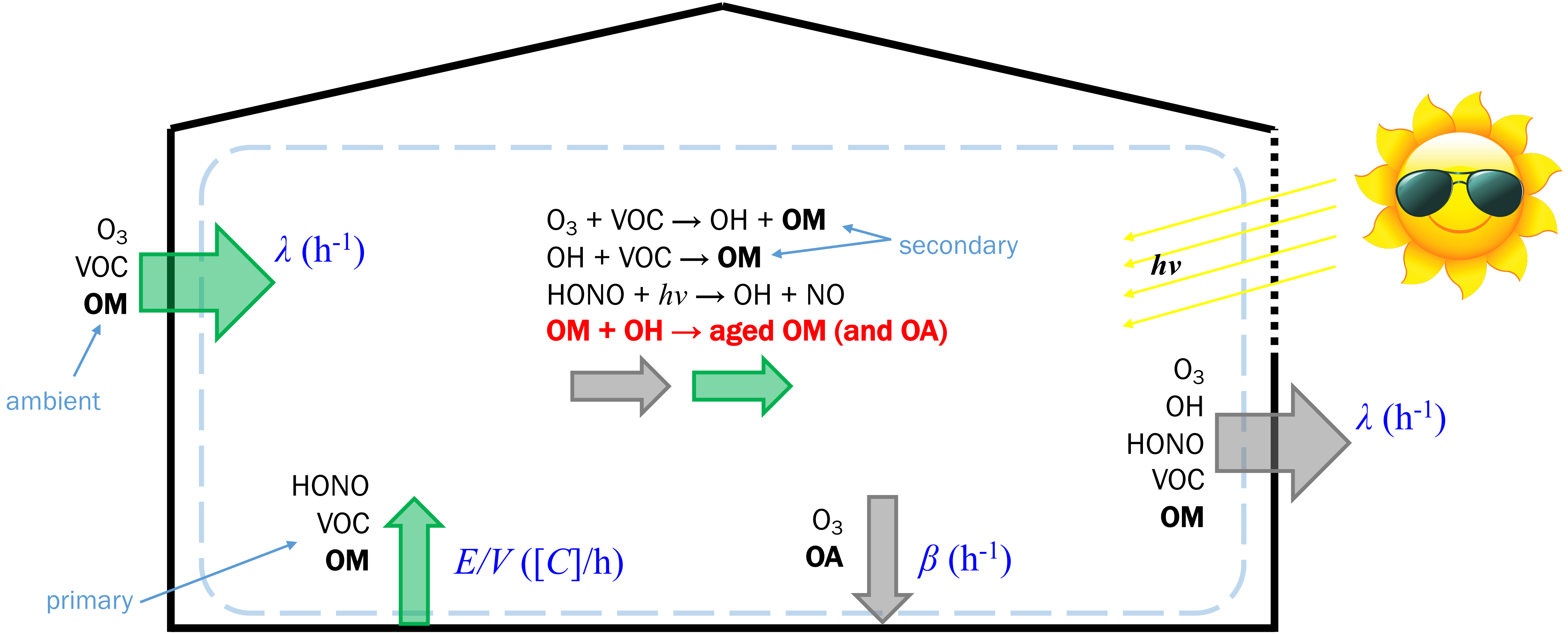
- **Functionalization**
  - Molecule **gains** **oxygen-containing** functional group(s)
  - **Enhances** particle-phase concentration
- **Fragmentation**
  - Molecule breaks into lighter fragments
  - Particle-phase molecules may evaporate into the gas phase
  - **Reduces** particle-phase concentration

OM mass resides and moves in the 2D-VBS space



SOA modeling as tool to improve our understanding

IMAGES framework overview



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Indoor SOA concentration ranges

- Monte Carlo simulations of **day-averaged SOA** in **typical U.S. residences** (Waring, 2014)
- SOA from ozone/OH + VOCs

Lognormal distributions

- Air exchange rates
- Deposition of ozone and PM
- Outdoor conc. of ozone, OA, IA
- Indoor emissions POA, PIA
- Outdoor conc. of 66 VOCs
- Indoor emissions of 66 VOCs

Simulated 10,000 cases

Result distributions generated

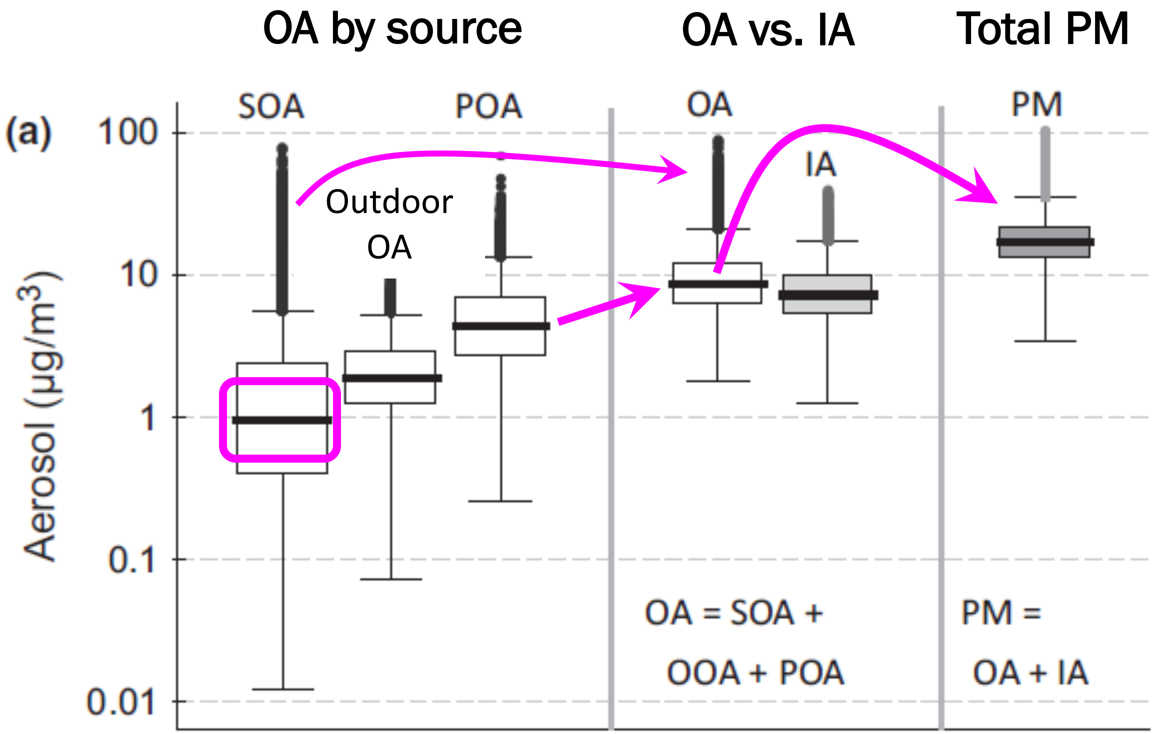
Parameter	GM	GSD	1st Percentile	99th Percentile	Source
λ (h^{-1})	0.75	2.1	0.135	4.14	1
β_{O3} (h^{-1})	2.5	1.5	1.08	6.36	2, 3, 4
β_{PM} (h^{-1})	0.79	1.35	0.395	1.57	1
$C_{O3,o}$ (ppb)	25.5	2.04	4.91	108	5
$C_{OA,o}$ ($\mu g/m^3$)	4.02	1.65	1.53	12.6	1, 6
$C_{IA,o}$ ($\mu g/m^3$)	11.5	1.65	4.36	36.6	1, 6
E_{POA}/V ($\mu g/m^3$ h)	7.0	1.75	1.88	26.1	1, 6
E_{PIA}/V ($\mu g/m^3$ h)	2.2	1.75	0.611	8.06	1, 6
$C_{j,o}$ (ppb)	Table 2 for 66 ROG j				1, 7, 8
E_j/V (ppb/h)	Table 2 for 66 ROG j				1, 7, 8
	AM	SD			
T (K)	296.9	3.0	290	302	1

Indoor SOA concentration ranges

- Monte Carlo simulations of **day-averaged SOA** in **typical U.S. residences** (Waring, 2014)

Box plots of result distributions

- Much of indoor PM is OA
- Primary OA dominates OA (cooking)
- SOA typically lowest OA (med 1 μg/m³)
- SOA can dominate indoor OA & PM
  - High ozone, terpene, low AER combos



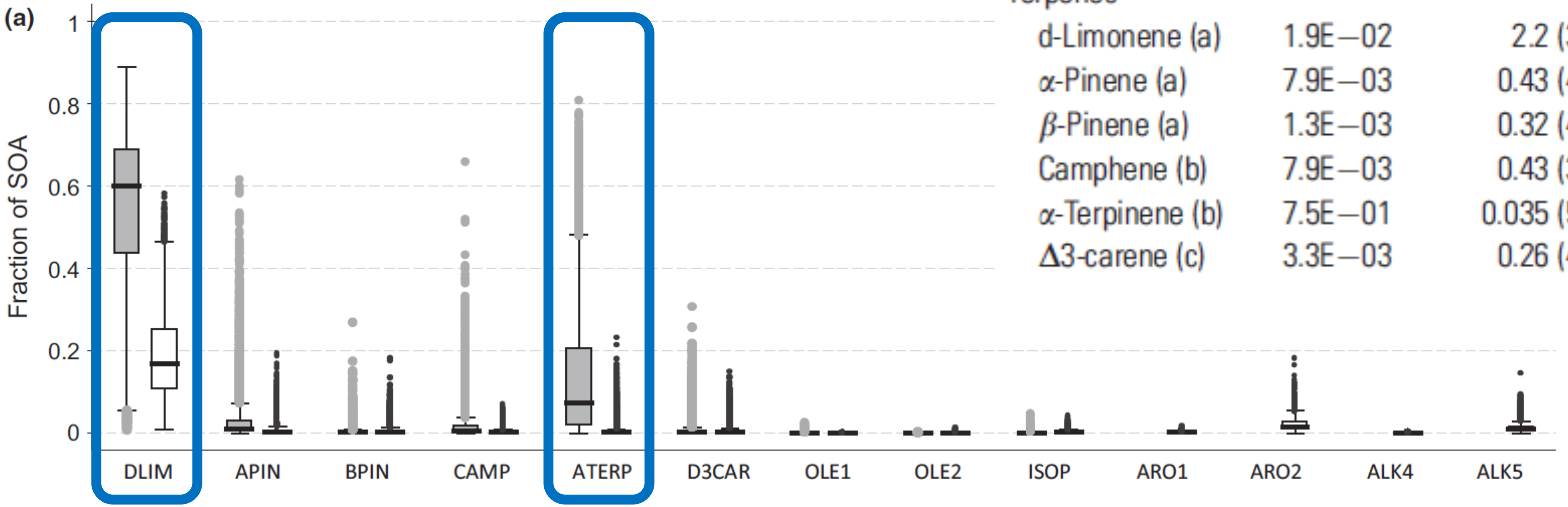
(+R) VOCs driving SOA fromation?

- Monte Carlo simulations of **day-averaged SOA** in **typical U.S. residences** (Waring, 2014)

Box plots of SOA-driving VOCs

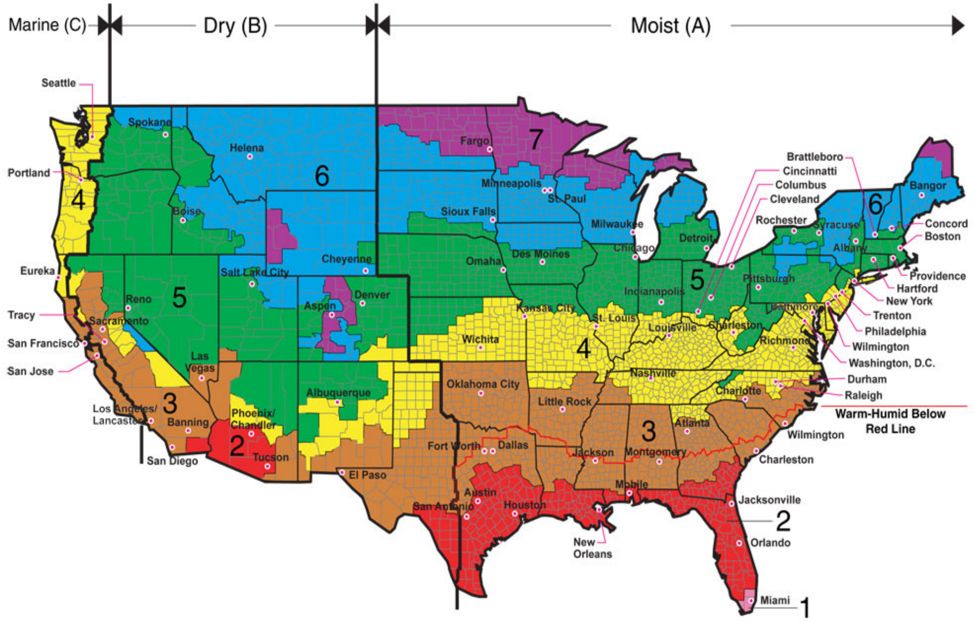
- SOA driven by d-limonene
- SOA driven by α-terpinene

Compound[1]	$k_{j(O3)}$[2] ($ppb^{-1}\ h^{-1}$)	C_j[7] (ppb) GM (GSD)
Terpenes		
d-Limonene (a)	1.9E−02	2.2 (3.8)
α-Pinene (a)	7.9E−03	0.43 (4.3)
β-Pinene (a)	1.3E−03	0.32 (4.1)
Camphene (b)	7.9E−03	0.43 (3.5)
α-Terpinene (b)	7.5E−01	0.035 (5.2)
Δ3-carene (c)	3.3E−03	0.26 (4.3)



(+R) OA phase state inhibit SOA?

- Does OA phase state change enough to influence equilibrium SOA formation?
- Further residential simulations conducted using housing/VOC inputs as above, but with:
- Outdoor inputs from historical data (trends exhibited seasonally & regionally)
  - 16 representative U.S. cities
    - Outdoor T, RH (NOAA)
    - Outdoor ozone (EPA Criteria)
    - Outdoor chemically resolved PM (EPA CSN)
      - Organics: HOA, SV-OOA, LV-OOA
      - Inorganics: AN, AS, SS, BC, geological



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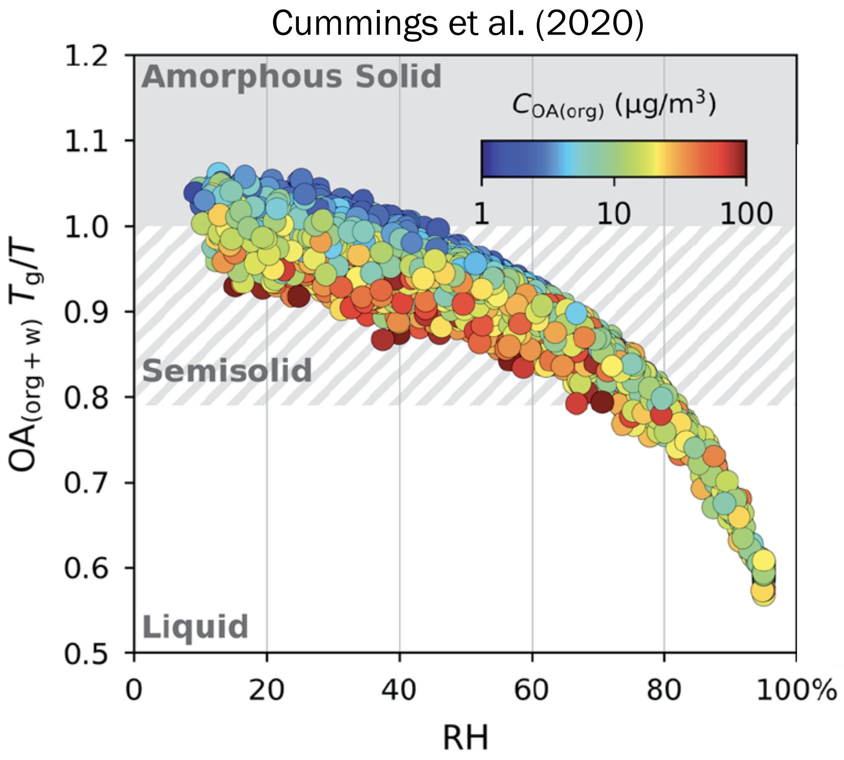
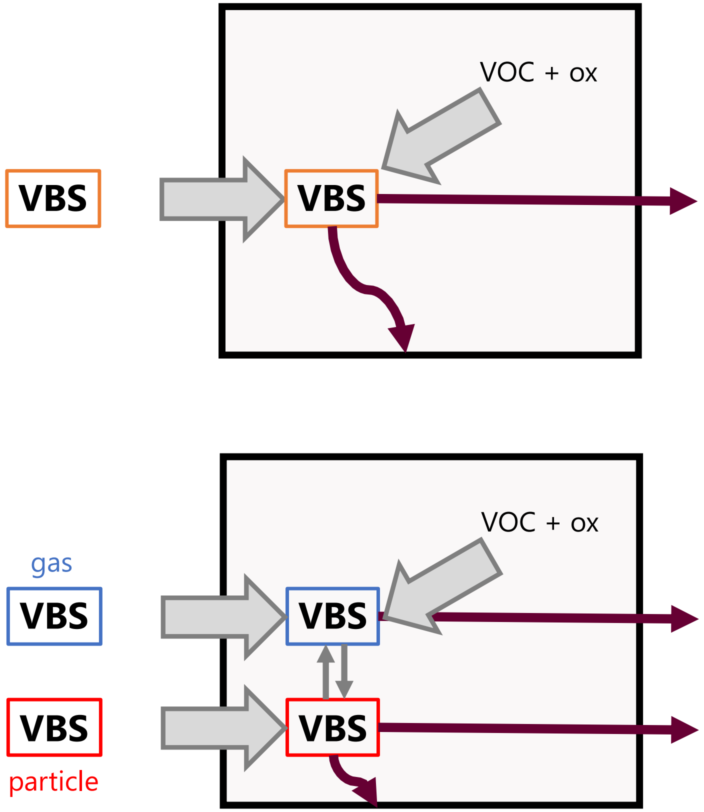


OA phase state results
- Monte Carlo simulations

Implications
- VBS assumes equilibrium partitioning gas/particle
- Should VBS use kinetic partitioning instead?



(+R) Nucleation vs. partitioning formation?

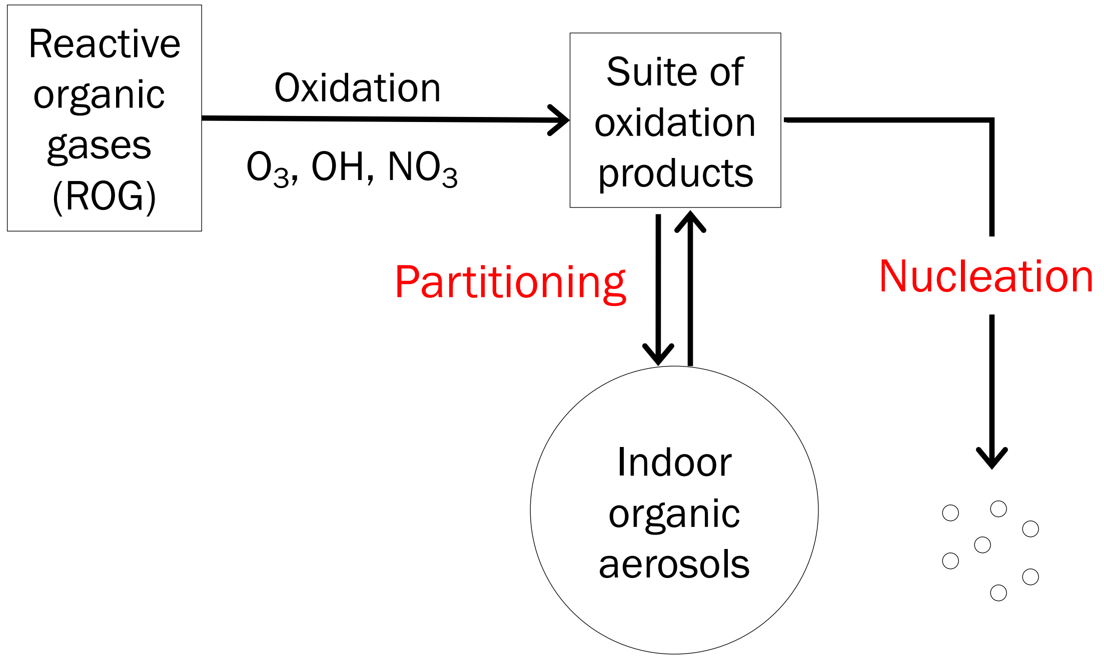
- **What conditions promote nucleation and/or gas-to-particle partitioning?**

Experiments show:

- Nucleation common at start
- Partitioning common later

Framework for delineating?

- Ozone/VOC ratios
- Existing particle availability

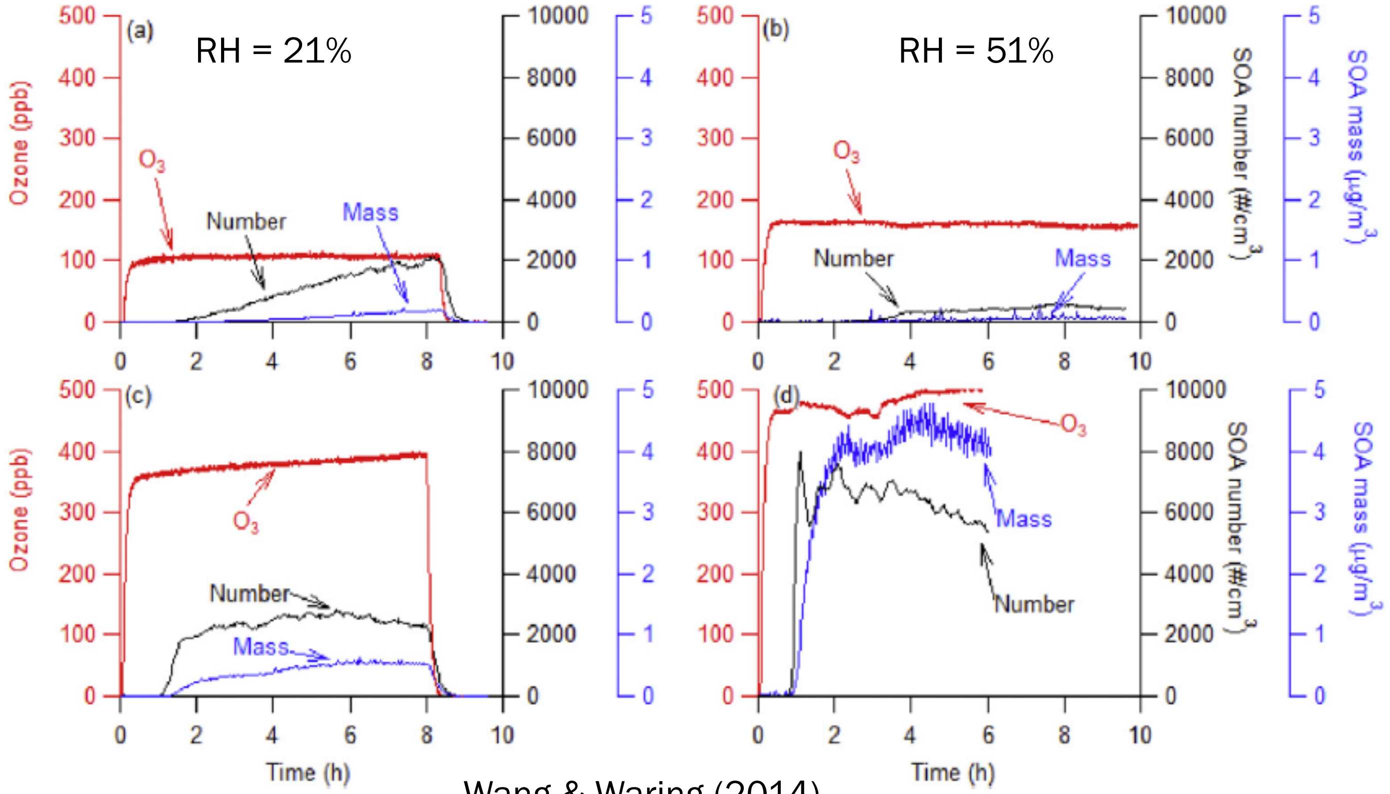


(+R) Surface processes as SOA source?

- How important is ozone + humans (squalene) to generate SOA formation?

Experiment w/O_3 + squalene:

- 36 L stainless steel chamber
- Steady state, well-mixed without background particles
- Air exchange rate = 5.4 h^{-1};
- Steady O_3 of 57–500 ppb
- Initial squalene coverage 3.9×10^{16} molec/cm^2 for 250cm^2



Wang & Waring (2014)

(+R) Mitigation for SOA?

- **What are best mitigation measures for indoor SOA formation?**
  - Which terpenes are most important to remove from indoor formulations?
  - How effective are standard particle filters that remove SOA?
  - What is the influence of OH producing tech (e.g. BPI or UV) on indoor SOA?

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- **SOA emission strengths and future research needs**
  - What are typical indoor SOA concentration ranges?
  - What VOCs are driving indoor SOA formation?
  - Does OA phase state inhibit SOA formation?
  - When does nucleation vs. gas-to-particle growth matter?
  - Do surface processes act as SOA sources?
  - What is the best way to mitigate indoor SOA formation?

Thank you! Questions?

Collaborators

- Bryan Cummings (PhD student, future post-doc)
- Somayeh Youssefi, Chunyi Wang, Yanan Yang, Anita Avery (PhD grads)
- Peter DeCarlo, Manabu Shiraiwa