

# ENVE 576

## Indoor Air Pollution

Fall 2014

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### Week 5: September 23, 2014

Gaseous pollutants: Reactive deposition and heterogeneous/homogeneous chemistry

Built  
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*Advancing energy, environmental, and  
sustainability research within the built environment*

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# HW 2 due today

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- Questions?

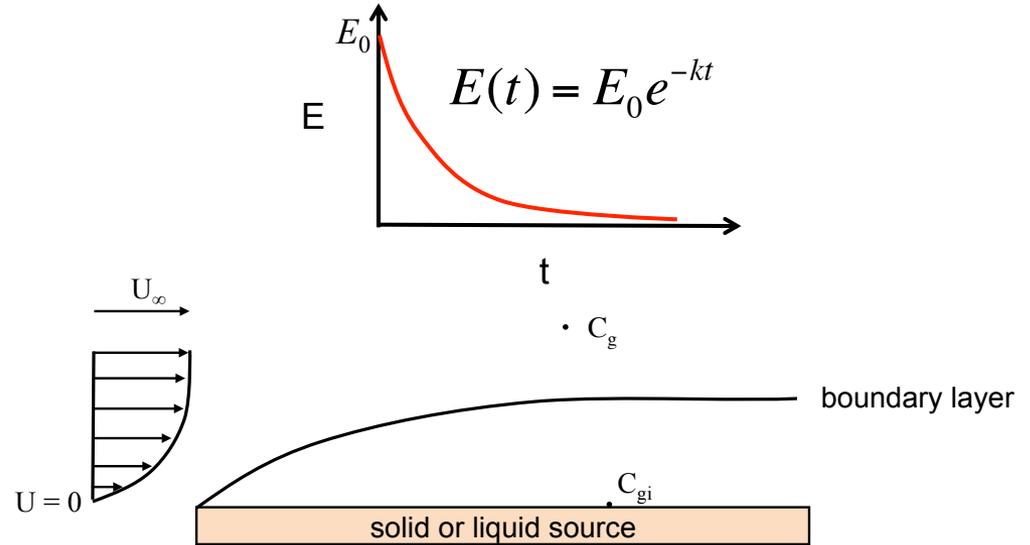
# Project topics

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# Review from last time

- Last time we covered:
  - Gas-phase pollutants
    - VOC sources
    - Emissions testing
    - Emissions models
  - Adsorption/desorption
    - Equilibrium
    - Non-equilibrium



## Non-equilibrium

$$V \frac{dC_g}{dt} = Q_g C_{g,out} - Q_g C_g - k_a C_g A + k_d M A$$

$$\frac{dM}{dt} = k_a C_g - k_d M$$

## Equilibrium

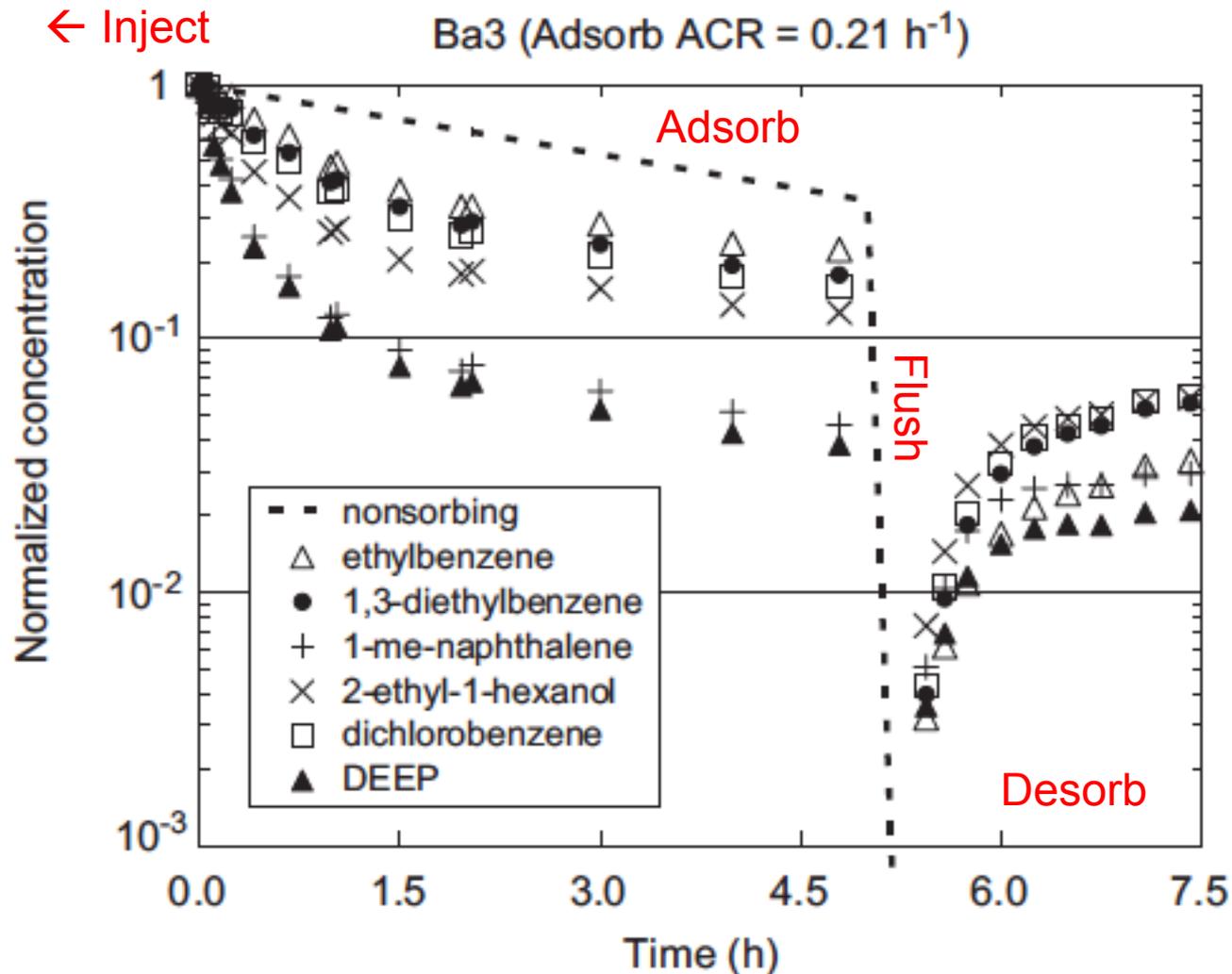
$$V \frac{dC_g}{dt} = Q_g C_{g,out} - Q_g C_g - \frac{dC_g}{dt} \sum k_{eq} A$$

$$C(t) = C_0 e^{-\frac{\lambda}{\beta} t} + \left( C_{out} + \frac{E}{\lambda V} \right) \left( 1 - e^{-\frac{\lambda}{\beta} t} \right)$$

$$\beta = 1 + \sum k_{eq} \frac{A}{V} \quad K_{eq} = \frac{k_a}{k_d}$$

# Measured impacts of sorption in real rooms

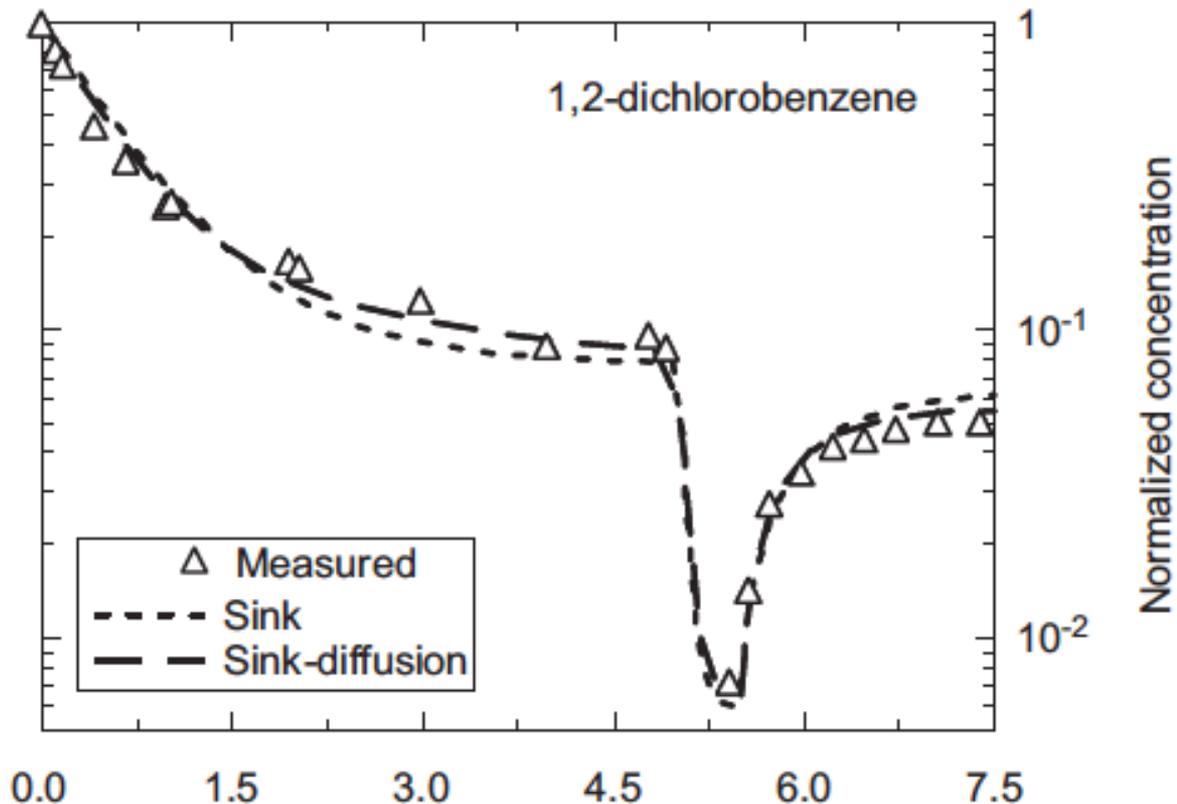
- Injection + adsorption + flush out period + desorption in a bathroom



# Measured impacts of sorption in real rooms

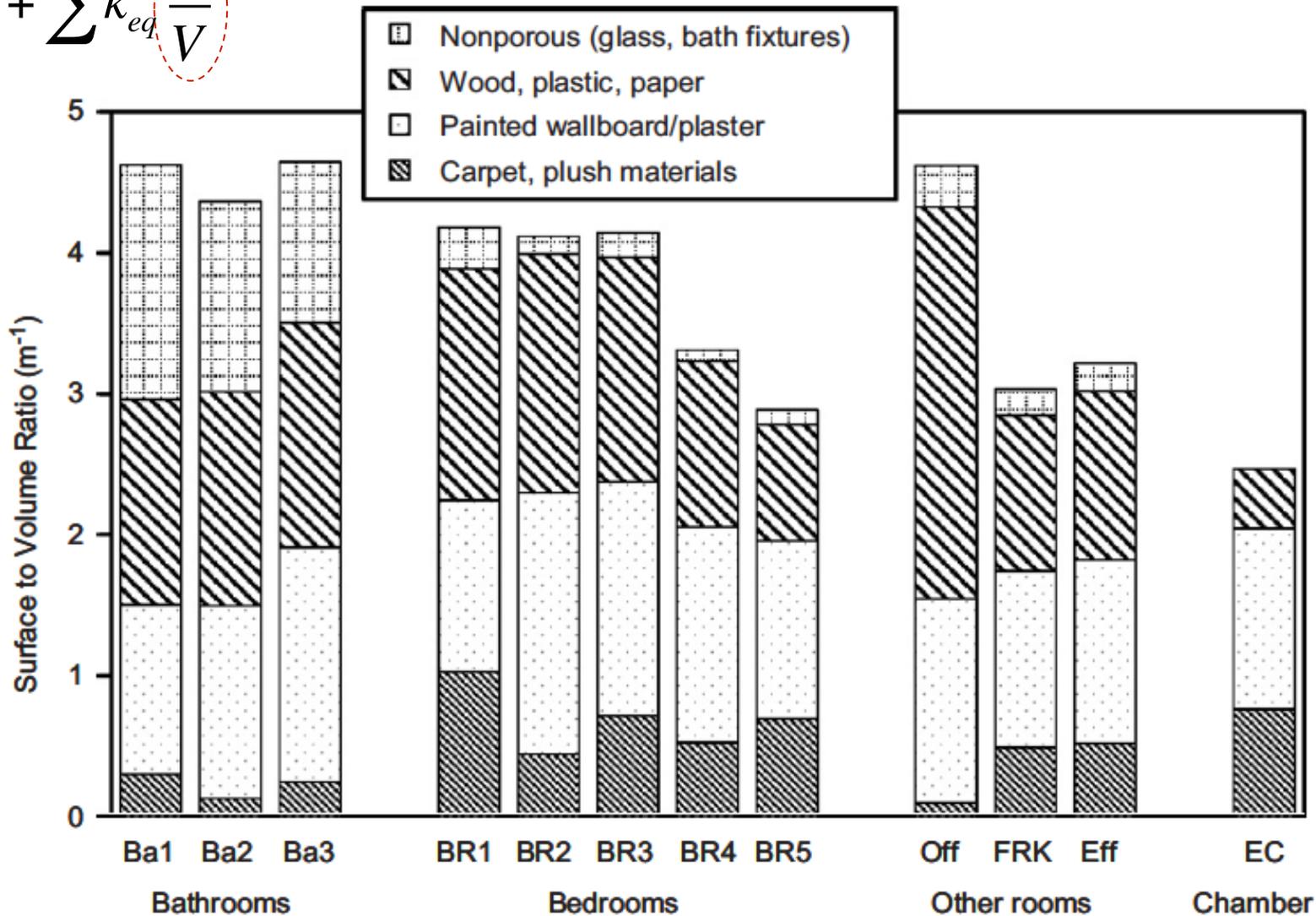
- Measured and modeled adsorption, flush out, and desorption

$$\frac{dC}{dt} = -\left(\lambda + k_a \frac{A}{V}\right)C + k_d \frac{A}{V}M \quad \frac{dM}{dt} = k_a C - k_d M$$



# A note on $A/V$

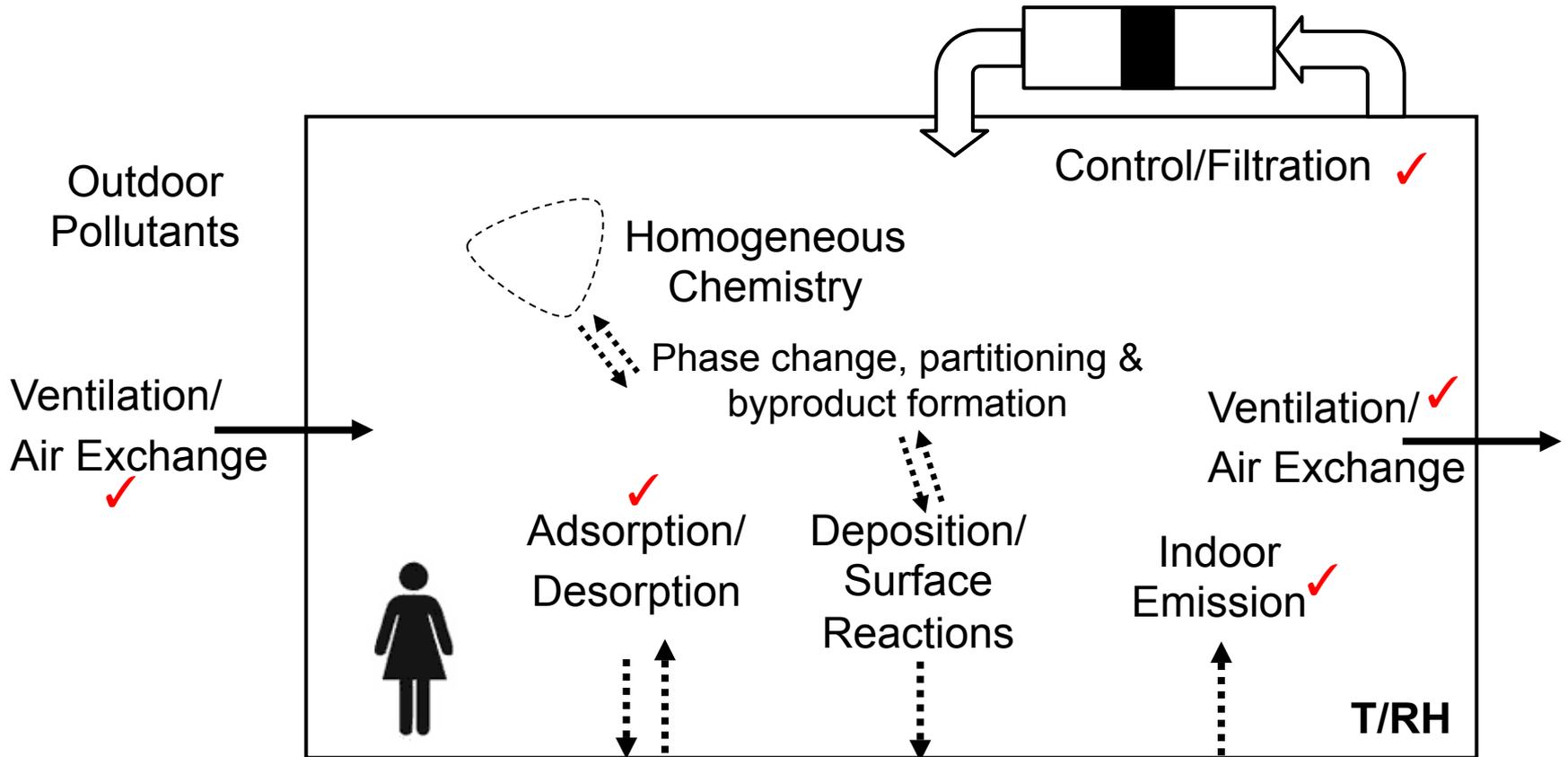
$$\beta = 1 + \sum k_{eq} \frac{A}{V}$$



# **REACTIVE DEPOSITION**

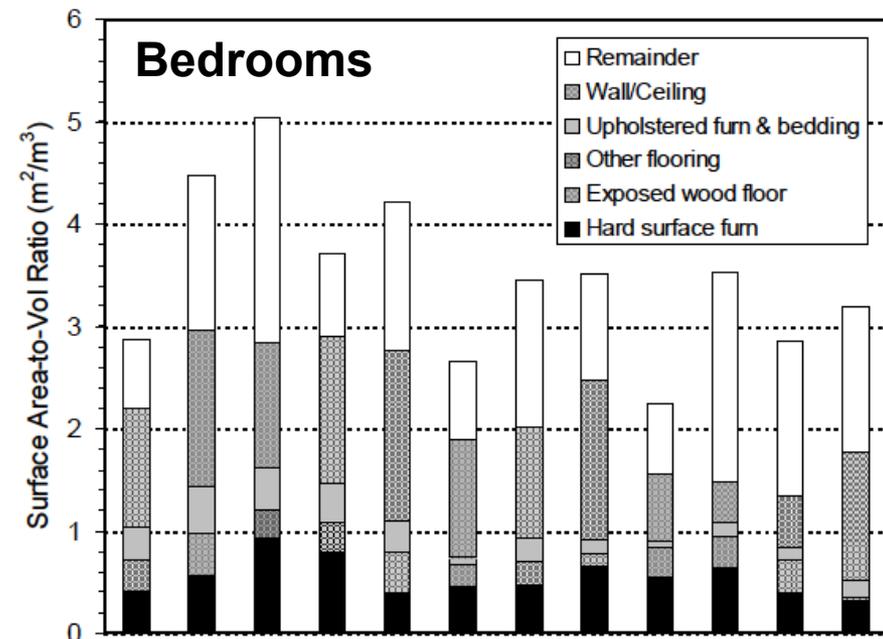
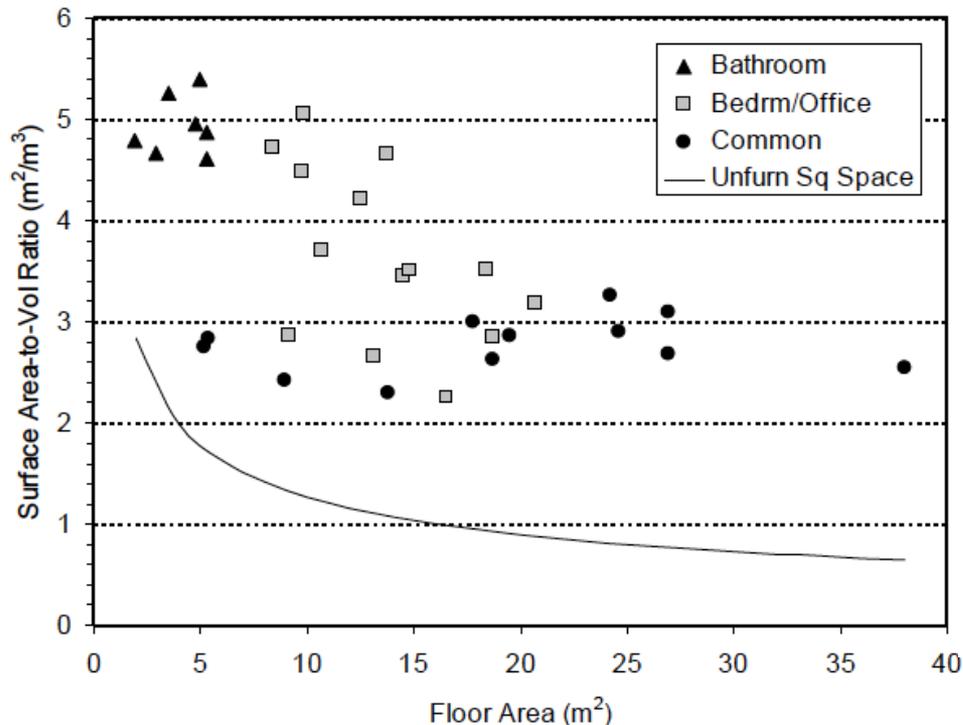
Heterogeneous chemistry

# Indoor environment: Mass balance on gas-phase



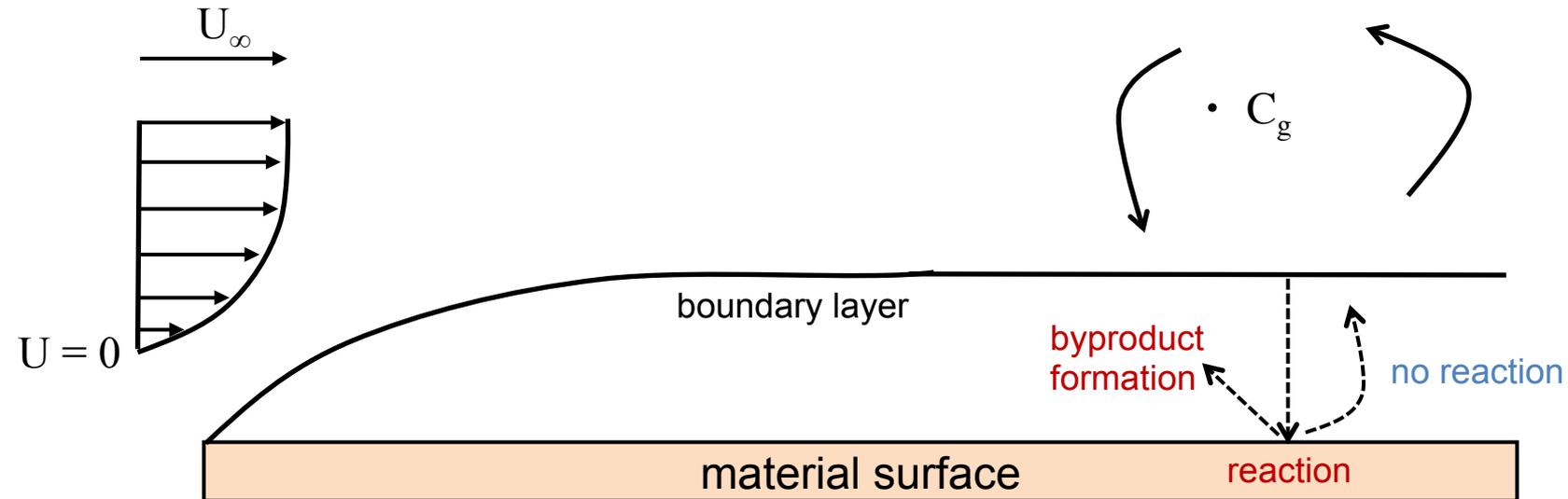
# Reactive deposition: Why is it important?

- In lecture 1, we mentioned surface area to volume ratios
  - Average A/V outdoors  $\sim 0.01 \text{ m}^2/\text{m}^3$  (Nazaroff et al., 2003)
  - Average A/V indoors  $\sim 3 \text{ m}^2/\text{m}^3$
  - Varies  $\sim 2\text{-}5 \text{ m}^2/\text{m}^3$  in residences and varies by material



# Reactive deposition

- Because of large surface area to volume ratios indoors
  - Surface chemistry is potentially very important



- Why bother with surface chemistry?
  - Lowers indoor concentration (potentially beneficial)
  - Some by-product formation (potentially harmful)
  - Possible degradation of materials (seldom anything but bad)

# Reactive deposition

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- Refer to notes on doc cam and uploaded to BB

# Reactive deposition

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- Summary of mass balance terms (ignoring indoor sources)

$$\frac{dC}{dt} = P\lambda C_{out} - \lambda C - \frac{v_d A}{V} C$$

$C$  = concentration in air inside space of interest ( $\text{mg}/\text{m}^3$ )

$C_{out}$  = concentration outside of space ( $\text{mg}/\text{m}^3$ )

$V$  = chamber volume ( $\text{m}^3$ )

$\lambda$  = air exchange rate through space (1/hr)

$P$  = penetration factor (-)

$A$  = material area ( $\text{m}^2$ )

$v_d$  = deposition velocity to material (m/hr)

$$C_{ss} = \frac{P\lambda C_{out}}{\lambda + \frac{v_d A}{V}} = \frac{P\lambda C_{out}}{\lambda + k_{dep}}$$

$k_{dep}$  = deposition loss rate coefficient to all materials (1/hr)

# Reactive deposition: Surface vs. Transport

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- Deposition velocity ( $v_d$ ) is often surface-uptake-limited indoors
  - Not always
  - Depends on reactivity of material and fluid dynamics in indoor environment

– Think in a series of resistances:

$$\frac{1}{v_d} = \frac{1}{v_t} + \frac{1}{v_s} = \frac{1}{v_t} + \frac{4}{\gamma \langle v \rangle}$$

$$k_{dep} = \frac{v_d A}{V}$$

$$v_d = \frac{v_s v_t}{v_s + v_t}$$

$v_s$  = surface-limited deposition velocity (m/hr)

$v_t$  = transport-limited deposition velocity (m/hr)

$\gamma$  = reaction probability (-)

$\langle v \rangle$  = Boltzmann velocity (m/hr)

# $v_d$ and $\gamma$

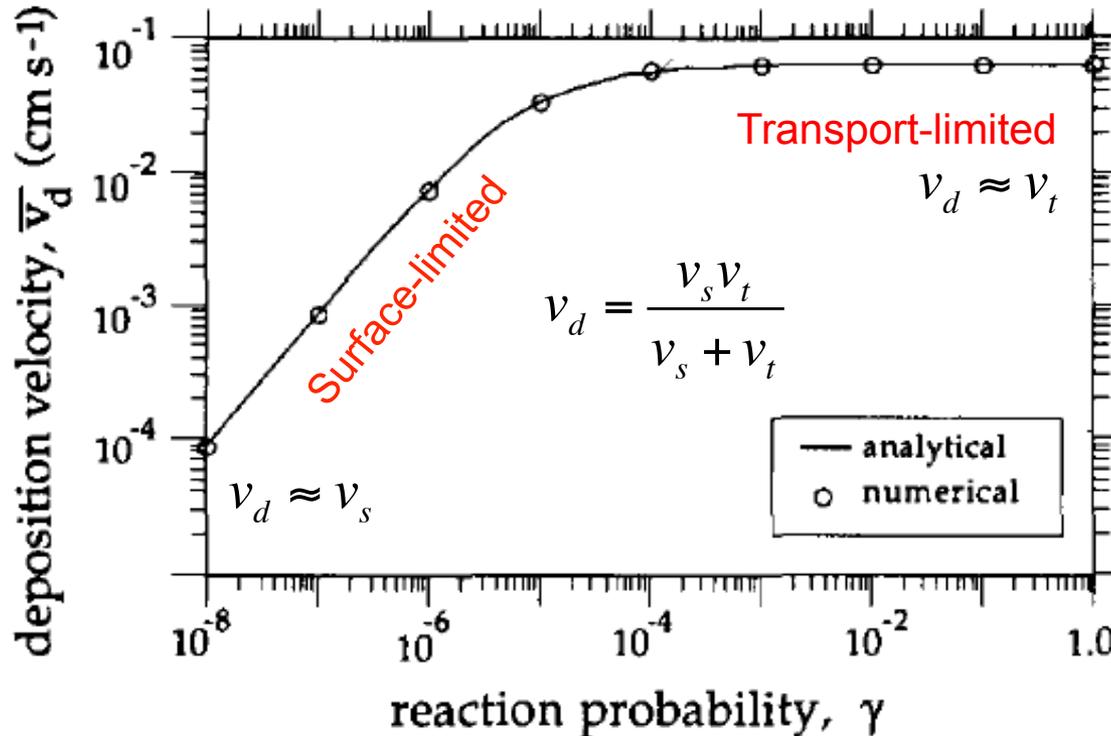


Fig. 1. Average ozone deposition velocity as a function of reaction probability from laminar forced convection flow parallel to a flat plate, with free stream velocity  $U_\infty = 0.1 \text{ m s}^{-1}$ , plate length  $L = 2 \text{ m}$ , ozone diffusivity  $\mathcal{D} = 1.82 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ . The analytical predictions are obtained from equation (31).

# Reaction probability: Measured $\gamma$

- For ozone ( $O_3$ ) on different materials

Table 1. Ozone reaction probabilities from chamber decay experiments

Reference	Material	$v_d(\text{cm s}^{-1})^*$	$v_t(\text{cm s}^{-1})^\dagger$	$\gamma^*$
Simmons and Colbeck, 1990‡	FEP Teflon	0.005	1.5	$5.5 \times 10^{-7}$
	Dirty glass	0.026	1.37	$2.9 \times 10^{-6}$
	Clean glass	0.048	1.37	$5.5 \times 10^{-6}$
	Gray tiles (new)	0.31	3.45	$3.8 \times 10^{-5}$
	Red tiles (new)	0.32	1.49	$4.5 \times 10^{-5}$
	Gravel	0.39	3.45	$4.8 \times 10^{-5}$
	Concrete slab	0.58	3.13	$7.9 \times 10^{-5}$
	Outdoor concrete	0.32	1.59	$4.4 \times 10^{-5}$
	Bricks (new)	1.03	2.13	$2.2 \times 10^{-4}$
	Old bricks	1.22	3.13	$2.2 \times 10^{-4}$
Sutton <i>et al.</i> , 1976§	Polyethylene sheet			
	8% rel. humidity	0.006	0.4	$7 \times 10^{-7}$
	70% rel. humidity	0.012	0.4	$1.4 \times 10^{-6}$
Sabersky <i>et al.</i> , 1973	Cotton muslin	0.109–0.015	0.1	$> 2 \times 10^{-4}$ – $1.9 \times 10^{-6}$
	Lamb's wool	0.106–0.004	0.1	$> 2 \times 10^{-4}$ – $4.6 \times 10^{-7}$
	Neoprene	0.097–0.015	0.1	$> 2 \times 10^{-4}$ – $1.9 \times 10^{-6}$
	Plywood	0.030–0.005	0.1	$4.7 \times 10^{-6}$ – $5.8 \times 10^{-7}$
	Nylon	0.032–0.0005	0.1	$5.1 \times 10^{-6}$ – $5.5 \times 10^{-8}$
	Polyethylene sheet	0.024–0.010	0.1	$3.5 \times 10^{-6}$ – $1.2 \times 10^{-6}$
	Linen	0.009–0.005	0.1	$1.1 \times 10^{-6}$ – $6.3 \times 10^{-7}$
	Lucite	0.006–0.0005	0.1	$7.0 \times 10^{-7}$ – $5.5 \times 10^{-8}$
	Aluminium	0.001–0.0005	0.1	$1.1 \times 10^{-7}$ – $5.5 \times 10^{-8}$
	Plate glass	0.001–0.0005	0.1	$1.1 \times 10^{-7}$ – $5.5 \times 10^{-8}$
	Mueller <i>et al.</i> , 1973	Aluminium¶		
5% rel. humidity		0.00044	0.1	$4.9 \times 10^{-8}$
40–50% r.h.		0.006–0.0012	0.1	$7.0 \times 10^{-7}$ – $1.3 \times 10^{-7}$
87% rel. humidity		0.0176	0.1	$2.4 \times 10^{-6}$
	Stainless steel**	0.015–0.008	0.4	$1.7 \times 10^{-6}$ – $9 \times 10^{-7}$
Cox and Penkett, 1972††	Aluminium			
	32% rel. humidity	0.00698	0.19	$7.7 \times 10^{-8}$
	83% rel. humidity	0.00206	0.19	$2.3 \times 10^{-7}$

# Reaction probability: Measured $\gamma$

- For ozone (O<sub>3</sub>), sarin, and SO<sub>2</sub> on different materials

Reaction probability ( $\gamma$ ) for sarin, SO<sub>2</sub>, and ozone on selected building materials

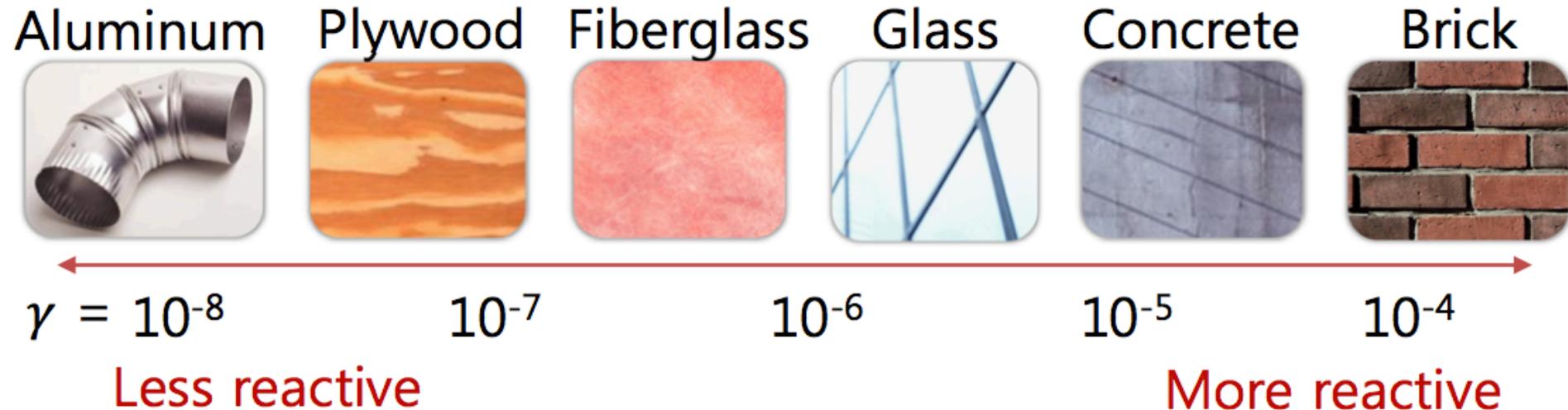
Species	Material	$\gamma^a$
Sarin	Silanized glass, 0–60% RH	$1.6 \times 10^{-8}$
	Plastic coated wallpaper	$2.1 \times 10^{-8}$
	Rough spruce, 50–60% RH	$1.9 \times 10^{-8}$
	Chalking paint on concrete	$5.1 \times 10^{-7}$
SO <sub>2</sub>	Gloss paint, 32% RH	$1.5 \times 10^{-7}$
	Gloss paint, 84% RH	$5.0 \times 10^{-6}$
	Aluminum, 78% RH	$5.7 \times 10^{-6}$
	Softwood	$3.1 \times 10^{-4}$
	Hardwood, 65% RH	$6.2 \times 10^{-4}$
Ozone	PVC wall covering, 60% RH	$3.9 \times 10^{-5}$
	Dirty glass	$2.9 \times 10^{-6}$
	Clean glass	$5.5 \times 10^{-6}$
	Bricks (new and old)	$2.2 \times 10^{-4}$
	Outdoor concrete	$4.4 \times 10^{-5}$
	Concrete slab	$7.9 \times 10^{-5}$
	Plywood <sup>f</sup>	$4.7 \times 10^{-6}$ – $5.8 \times 10^{-7}$
	Plate glass <sup>f</sup>	$1.1 \times 10^{-7}$ – $5.5 \times 10^{-8}$
	Aluminum <sup>f</sup>	$1.1 \times 10^{-6}$ – $5.5 \times 10^{-8}$
	Aluminum, 5% RH	$4.9 \times 10^{-8}$
	Aluminum, 40–50% RH	$7.0 \times 10^{-7}$ – $1.3 \times 10^{-7}$
	Aluminum, 32% RH	$7.7 \times 10^{-8}$
	Aluminum, 83% RH	$2.3 \times 10^{-7}$
	Latex paint, <10% RH <sup>f</sup>	$2 \times 10^{-6}$ – $7 \times 10^{-7}$
	Latex paint, ~80% RH <sup>f</sup>	$2 \times 10^{-5}$ – $1 \times 10^{-6}$
	Glass	$<1 \times 10^{-6}$
Vinyl wallpaper	$5 \times 10^{-6}$	
Paper wallpaper	$1 \times 10^{-6}$	
Galvanized sheet steel	$1.1 \times 10^{-6}$	

# Reaction probability: Measured $\gamma$

- For ozone ( $O_3$ ) on different materials

## $O_3$ Reaction Probability, $\gamma$

From Liu and Nazaroff (2001)



# Notes on reaction probability

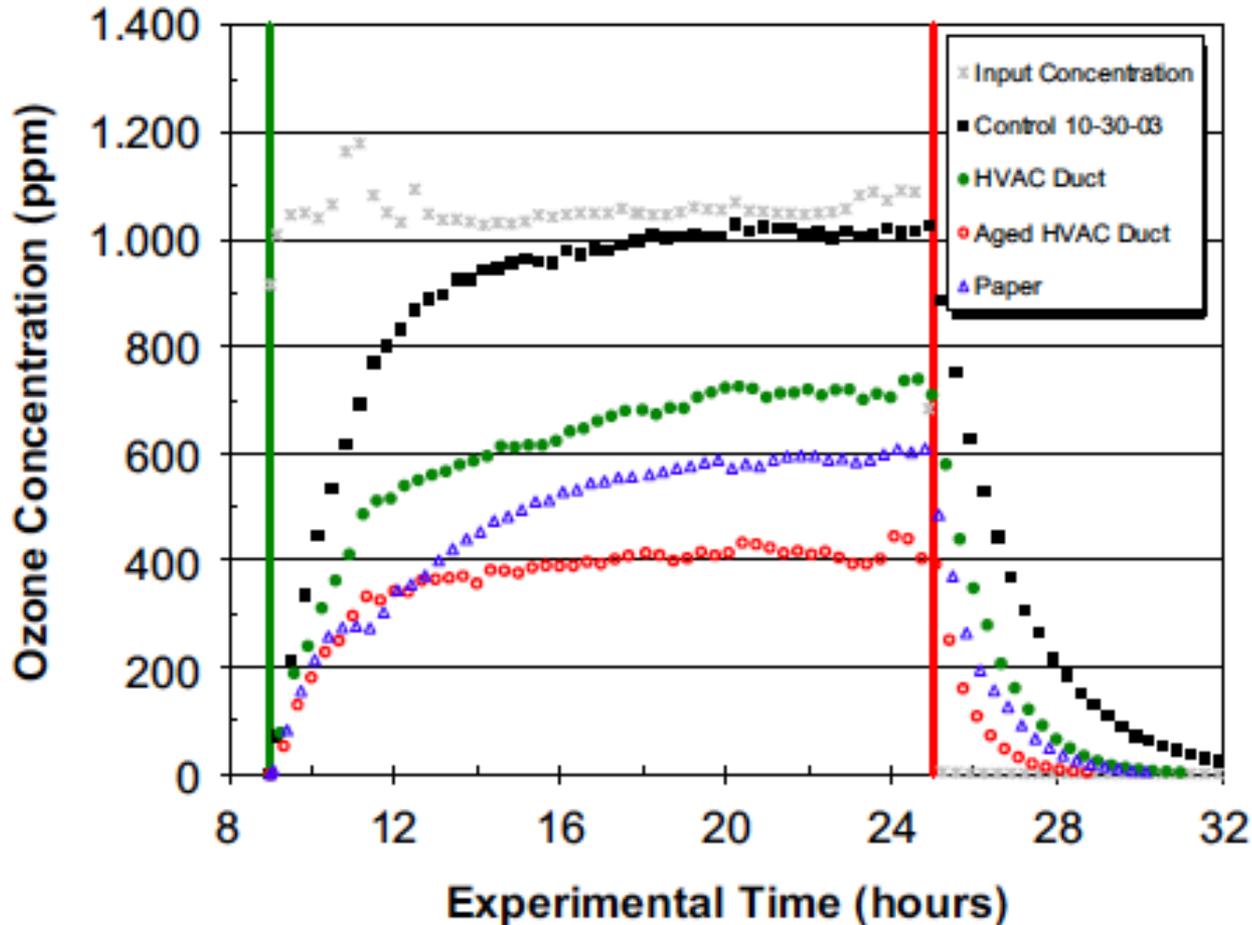
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- Can  $\gamma$  change over time?
  - Yes
- Why?
  - Wipe out reaction sites over time (decreases  $\gamma$ )
  - Humidity effects (water chemistry)
    - RH can increase  $\gamma$
  - Regeneration of reaction sites
    - Diffusion within material matrix changes concentration gradient
      - Increases  $\gamma$

# Measuring $v_d$

- Chamber testing for ozone ( $O_3$ ) on different materials

$$\frac{dC}{dt} = \lambda C_o - \lambda C - v_d C \frac{A}{V} - v_{d,ss} C \frac{A_{ss}}{V}$$



# Measured $v_d$

- Chamber testing for ozone ( $O_3$ ) on different materials

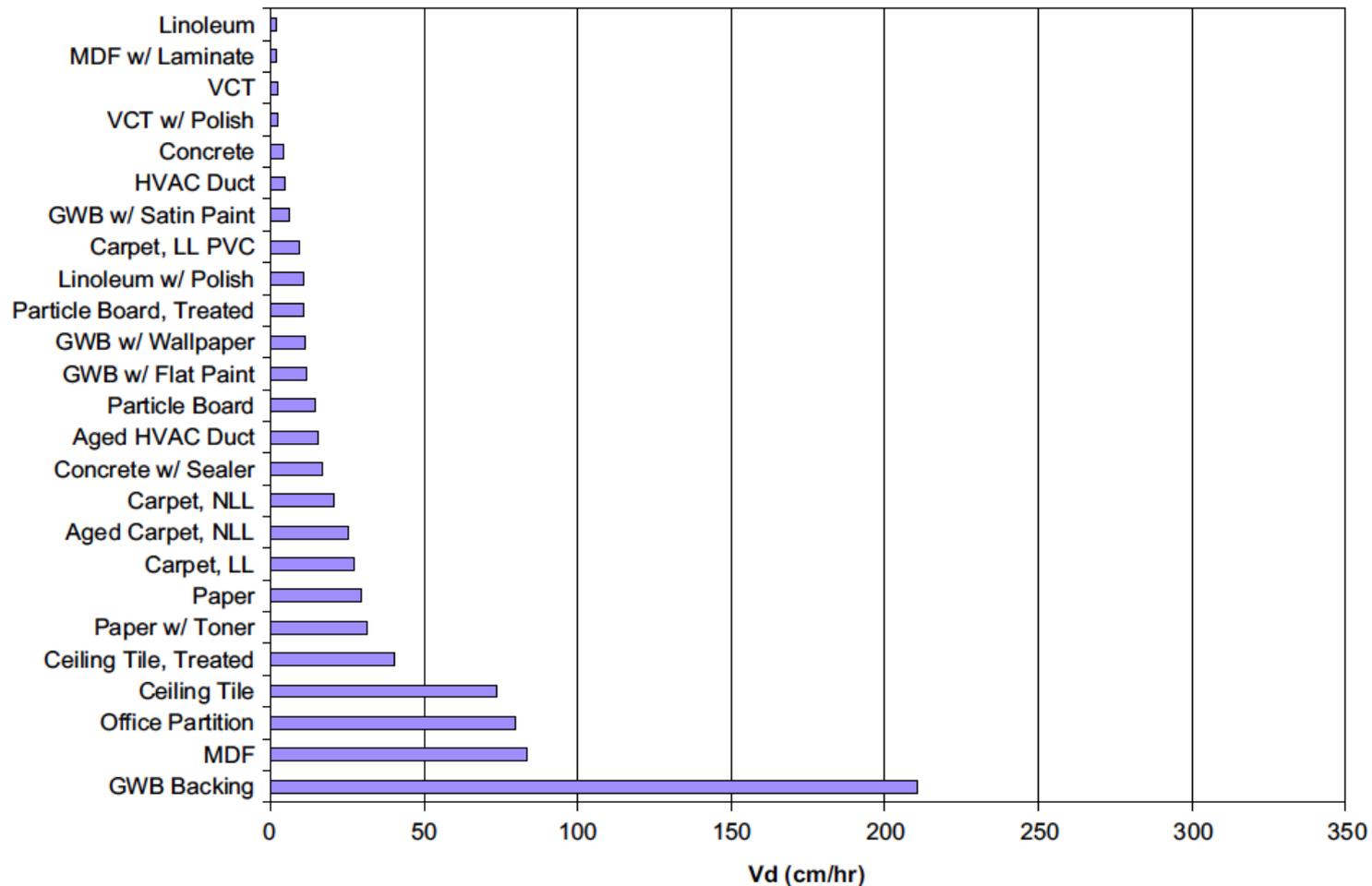


Fig. 5. Geometric mean ozone deposition velocities for last 5 h of disinfection stage.

# Measured $v_d$

- For ozone ( $O_3$ ) on different materials

Material	RH (%)	Temp. (K)	$v_d$ ( $cm\ s^{-1}$ )	$v_d$ , aged ( $cm\ s^{-1}$ )	$v_t$ ( $cm\ s^{-1}$ )	$v_s$ ( $cm\ s^{-1}$ )	$v_s$ , aged ( $cm\ s^{-1}$ )	Author
<i>(a) Values of <math>v_s</math> for <math>O_3</math> calculated from the literature, inferring <math>v_t</math> where necessary</i>								
Lacquered ash	50	294 ± 2	0.0007 ± 0.0008		0.7	0.0007		Klenø et al. (2001)
Oiled ash	50	294 ± 2	0.003 ± 0.0007		0.7	0.003		Klenø et al. (2001)
Oiled beech parquet	50	294 ± 2	0.0078 ± 0.0027		0.7	0.0079		Klenø et al. (2001)
Plywood	50	295	0.030	0.005 <sup>a</sup>	0.75	0.031	0.005 <sup>a</sup>	Sabersky et al. (1973)
Aluminium	87	299	0.0294		0.1	0.042		Mueller et al. (1973)
Aluminium	32	—	0.000698		0.19 <sup>b</sup>	0.00070		Cox and Penkett (1972)
Aluminium	83	—	0.00206		0.19	0.0021		Cox and Penkett (1972)
Carpet nylon fibre latex backing	50	294 ± 2	0.032 ± 0.0043		0.7	0.034		Klenø et al. (2001)
Cotton muslin	50	295	0.109	0.015 <sup>a</sup>	0.75	0.128	0.015 <sup>a</sup>	Sabersky et al. (1973)
Linen	50	295	0.0095	0.0055 <sup>a</sup>	0.75	0.0096	0.0055 <sup>a</sup>	Sabersky et al. (1973)
Nylon	50	295	0.032	0.0005 <sup>a</sup>	0.75	0.033	0.0005 <sup>a</sup>	Sabersky et al. (1973)
Wool (lamb)	50	295	0.107	0.004 <sup>a</sup>	0.75	0.12	0.004 <sup>a</sup>	Sabersky et al. (1973)
Linoleum	50	294 ± 2	0.007 ± 0.004 <sup>e</sup>	0.004 ± 0.005 <sup>f</sup>	0.7	0.0071 <sup>e</sup>	0.004 <sup>f</sup>	Klenø et al. (2001)
Paper wall paper	50	—	4% <sup>d</sup>		<sup>c</sup>	0.042		Reiss et al. (1994)
Painted gypsum board (urethan modified alkyd binding agent)	50	294 ± 2	0.03 ± 0.0052		0.7	0.031		Klenø et al. (2001)
Painted gypsum board (acrylic binding agent)	50	294 ± 2	0.042 ± 0.0023		0.7	0.044		Klenø et al. (2001)

# Measured $v_d$

- For nitrogen dioxide (NO<sub>2</sub>) on different materials

Material	RH (%)	Temp. (K)	$v_d$ (cm s <sup>-1</sup> )	$v_t$ (cm s <sup>-1</sup> )	$v_s$ (cm s <sup>-1</sup> )	Author
<i>(a) Values of <math>v_s</math> for NO<sub>2</sub> calculated from the literature, inferring <math>v_t</math> where necessary</i>						
Lacquered plywood	50	292	0.00639	3.7	0.0064	Miyazaki (1984)
Painted wood	58	295.5	0.003	3.7	0.003	Miyazaki (1984)
Aluminium	30	304	0.0006	0.13	0.00060	Leaderer et al. (1986)
Aluminium	60	304	0.002	0.13	0.0020	Leaderer et al. (1986)
Painted stainless steel	65	293	0.00083	3.7	0.00083	Miyazaki (1984)
Particle board	50		0.0124	1	0.013	Spicer et al. (1989)
Wool carpet	50		0.0856	1	0.094	Spicer et al. (1989)
Wool carpet	50	294.5	0.0919	3.7	0.094	Miyazaki (1984)
Vinylchloride treated floor-sheet	45	291	0.0022	3.7	0.0022	Miyazaki (1984)
Vinylchloride treated floorsheet	70	292.5	0.00278	3.7	0.00278	Miyazaki (1984)
Plastic tile	52	294	0.00333	3.7	0.00333	Miyazaki (1984)
Cotton bathmat	41	291	0.0211	0.13	0.025	Miyazaki (1984)
Cotton bathmat	55	293.5	0.0542	3.7	0.057	Miyazaki (1984)
Cotton bathmat	67	294	0.055	3.7	0.058	Miyazaki (1984)
Curtain (material not stated)	30	296.5	0.00083	3.7	0.00083	Miyazaki (1984)
Cotton terry cloth	50		0.0047	1	0.0047	Spicer et al. (1989)
Cotton/polyester bedspread	50		0.0386	1	0.040	Spicer et al. (1989)
Wool/polyester fabric	50		0.0047	1	0.0047	Spicer et al. (1989)
Plasterboard	44	295.5	0.0169	3.7	0.017	Miyazaki (1984)
Plasterboard	59	293.5	0.02	3.7	0.020	Miyazaki (1984)
Plasterboard	67	293.5	0.0272	3.7	0.027	Miyazaki (1984)
Sandstone	80	295	0.02	1	0.020	Behlen et al. (1996)
Used brick	50		0.059	1	0.063	Spicer et al. (1989)

# Measured $v_d A/V$ in real environments

- $k_{dep}$  for ozone ( $O_3$ ) in different environments

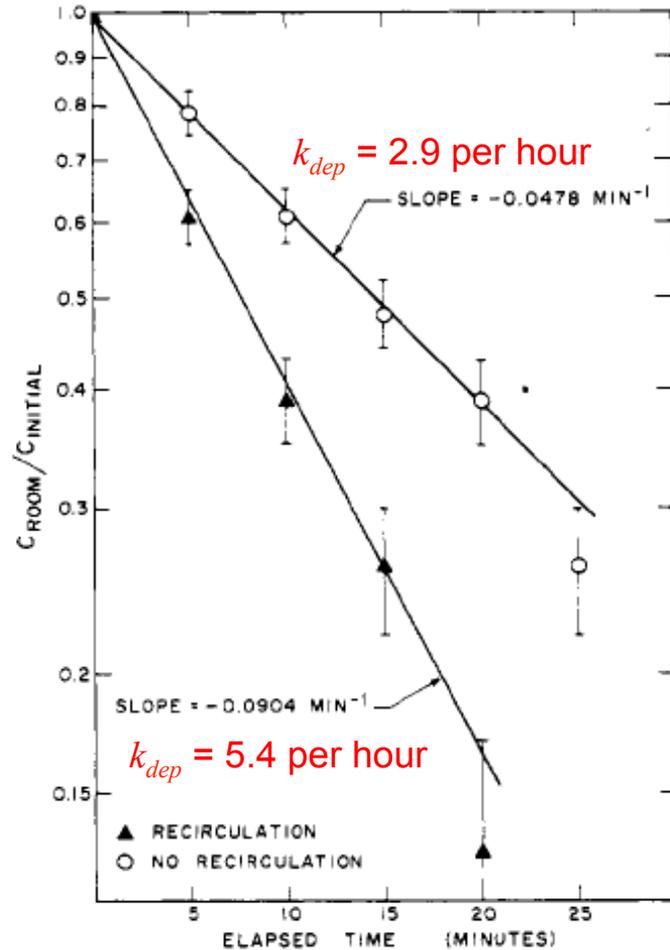
Table 3 Rate Constants ( $h^{-1}$ ) for the Removal of Ozone by Surfaces in Different Indoor Environments

Indoor environment	Surface removal rate, $k_d(A/V), h^{-1}$	Reference
Aluminum Room (11.9 m <sup>3</sup> )	3.2	Mueller et al., 1973
Stainless Steel Room (14.9 m <sup>3</sup> )	1.4	Ibid.
Bedroom (40.8 m <sup>3</sup> )	7.2	Ibid.
Office (55.2 m <sup>3</sup> )	4.0	Ibid.
Home (no forced air)	2.9	Sabersky et al., 1973
Home (forced air)	5.4	Ibid.
Department Store	4.3	Thompson et al., 1973
Office (24.1 m <sup>3</sup> )	4.0	Allen et al., 1978
Office (20.7 m <sup>3</sup> )	4.3	Ibid.
Office/Lab	4.3	Shair and Heitner, 1974
Office/Lab	3.2	Ibid.
Office/Lab	3.6	Ibid.
13 Buildings, 24 Ventilation Systems	3.6	Shair, 1981; assumes $A/V = 2.8 m^{-1}$
Museum	4.3	Nazaroff and Cass, 1986
Museum	4.3	Ibid.
Office/Lab	4.0	Weschler et al., 1989
Office/Lab	3.2	Ibid.
Office	2.5	Ibid.
Lab	2.5	Ibid.
Cleanroom	7.6	Ibid.
Telephone Office	0.8–1.0	Weschler et al., 1994; large office, small $A/V$
43 Homes	2.8±1.3	Lee et al., 1999

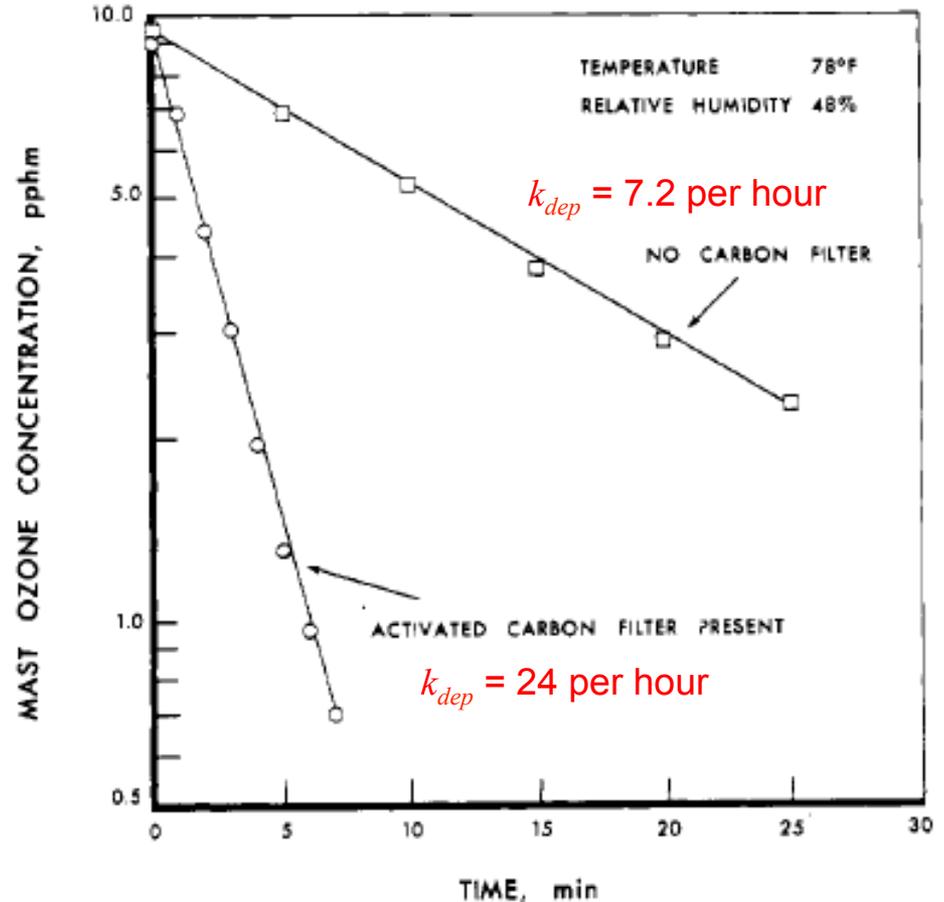
# Measured $v_d A/V$ in real environments

- $k_{dep}$  for ozone ( $O_3$ ) in one room with different HVAC operation

w/ and w/o HVAC on



w/ and w/o activated carbon filter



# Measured $v_d A/V$ in real environments

- $k_{dep}$  for ozone ( $O_3$ ) in the same environment w/ different fan speeds and materials

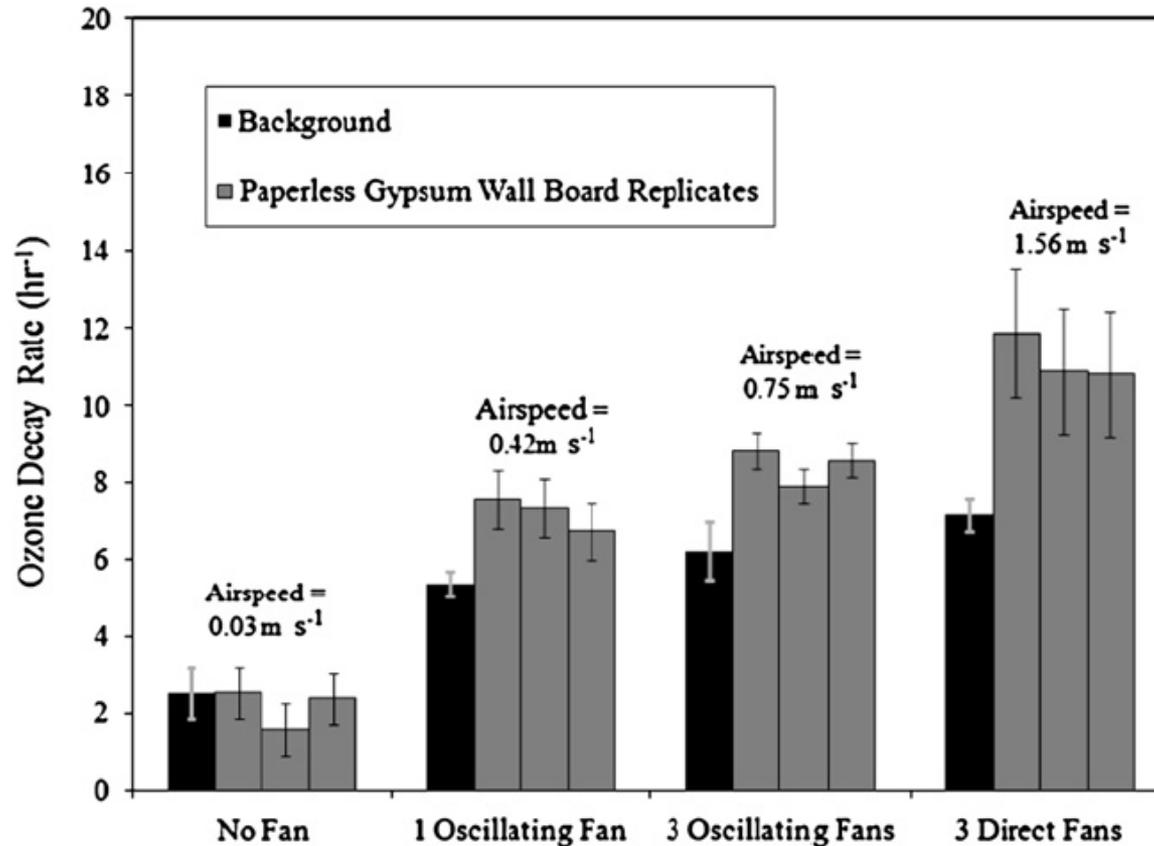


Fig. 5. Ozone decay rates for bedroom with 4.4 m<sup>2</sup> of paperless gypsum wallboard (PLGWB) PRM placed on a vertical wall.

# Reactive deposition: **Byproduct formation**

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- Reactive deposition to surfaces removes indoor pollutants
  - Can also generate others in the form of reaction by-products

$$R_{byproduct} = Y_i v_d A C f_{conversion}$$

$R_{byproduct,i}$  = by-product  $i$  production rate (moles/hr)

$Y_i$  = molar yield of  $i$  (moles  $i$  per moles of gas consumed)

$f_{conversion}$  = conversion factor (e.g.,  $\frac{10^{-6}}{MW}$  to convert from  $\frac{\mu\text{g}}{\text{m}^3}$  to  $\frac{\text{moles}}{\text{hour}}$ )

# Byproduct formation: mass balance

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- Mass balance on reactive pollutant (e.g., ozone)

$$\frac{dC}{dt} = P\lambda C_{O_3,out} - \lambda C_{O_3} - \frac{v_d A}{V} C_{O_3}$$

- Mass balance on **byproduct  $i$**

$$\frac{dC_i}{dt} = P\lambda C_{i,out} - \lambda C_i + Y_i \frac{v_{d,O_3} A}{V} f_{conversion} C_{O_3}$$

# Example heterogeneous byproduct formation

- Ozone deposition velocity, yields, and secondary emission rates of aldehydes after ozone exposure in 4 homes

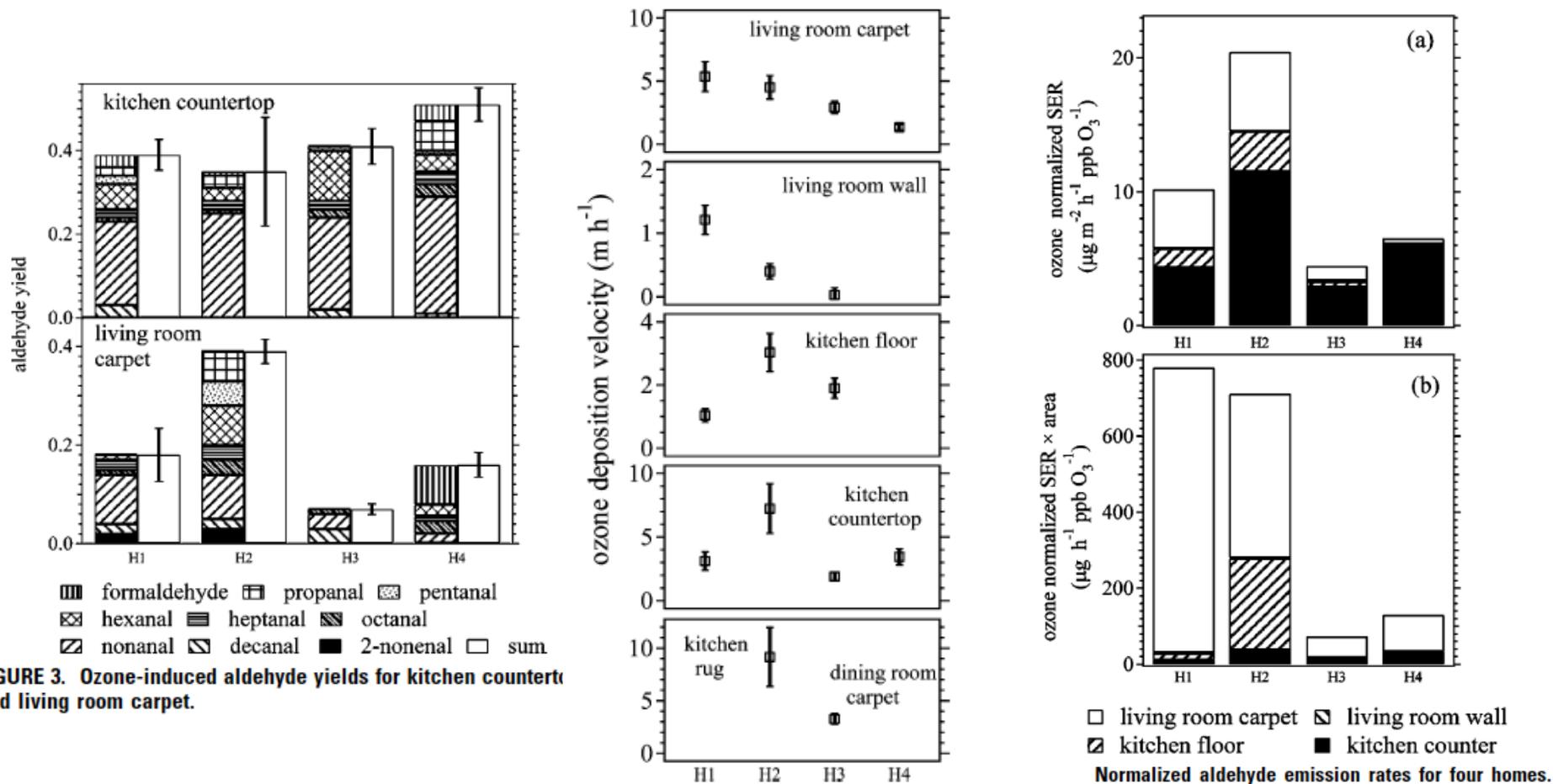


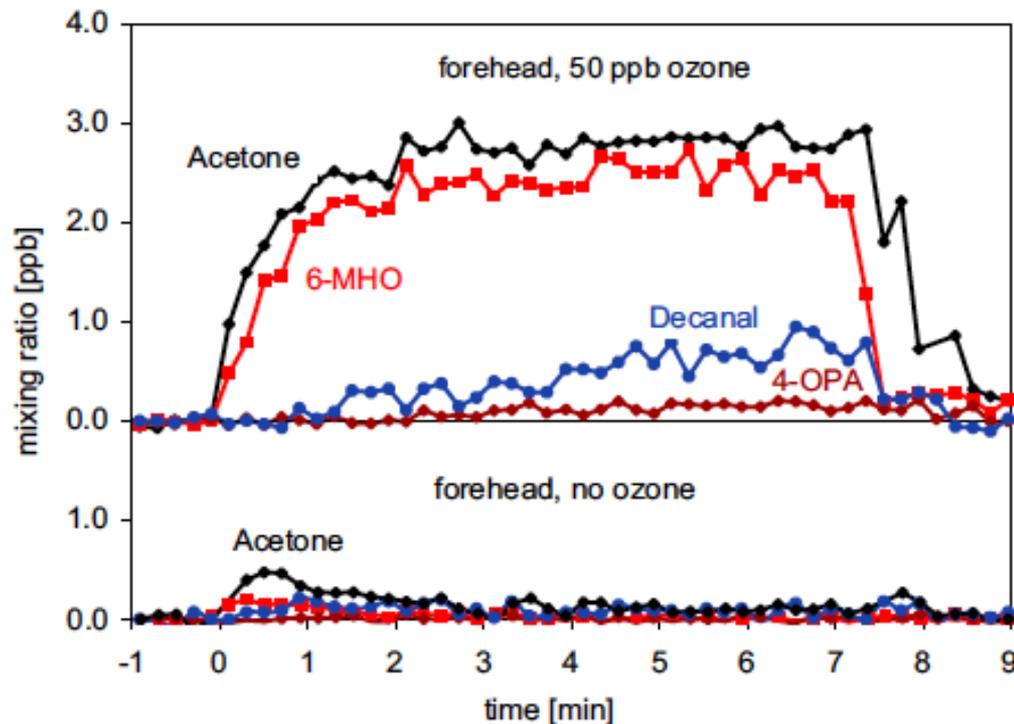
FIGURE 3. Ozone-induced aldehyde yields for kitchen countertop and living room carpet.

Ozone deposition velocity for each surface.

Normalized aldehyde emission rates for four homes.

# Example heterogeneous byproduct formation

- Skin oils have recently been identified as being potentially important for ozone chemistry



Acetone ( $C_3H_6O$ )  
 6-MHO (6-methyl-5-hepten-2-one)  
 Decanal ( $C_{10}H_{20}O$ )  
 4-OPA (4-oxo-pentanal)

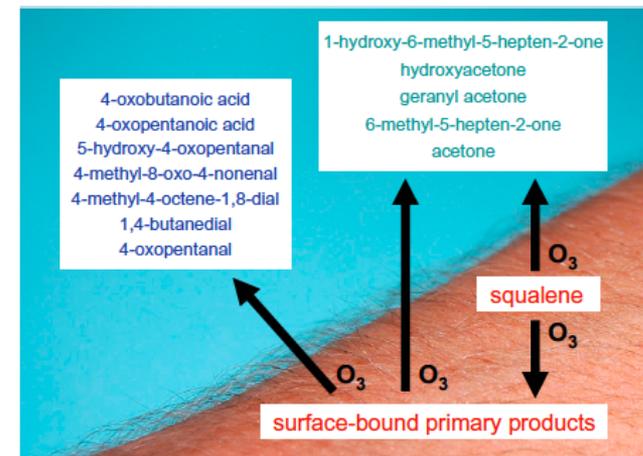
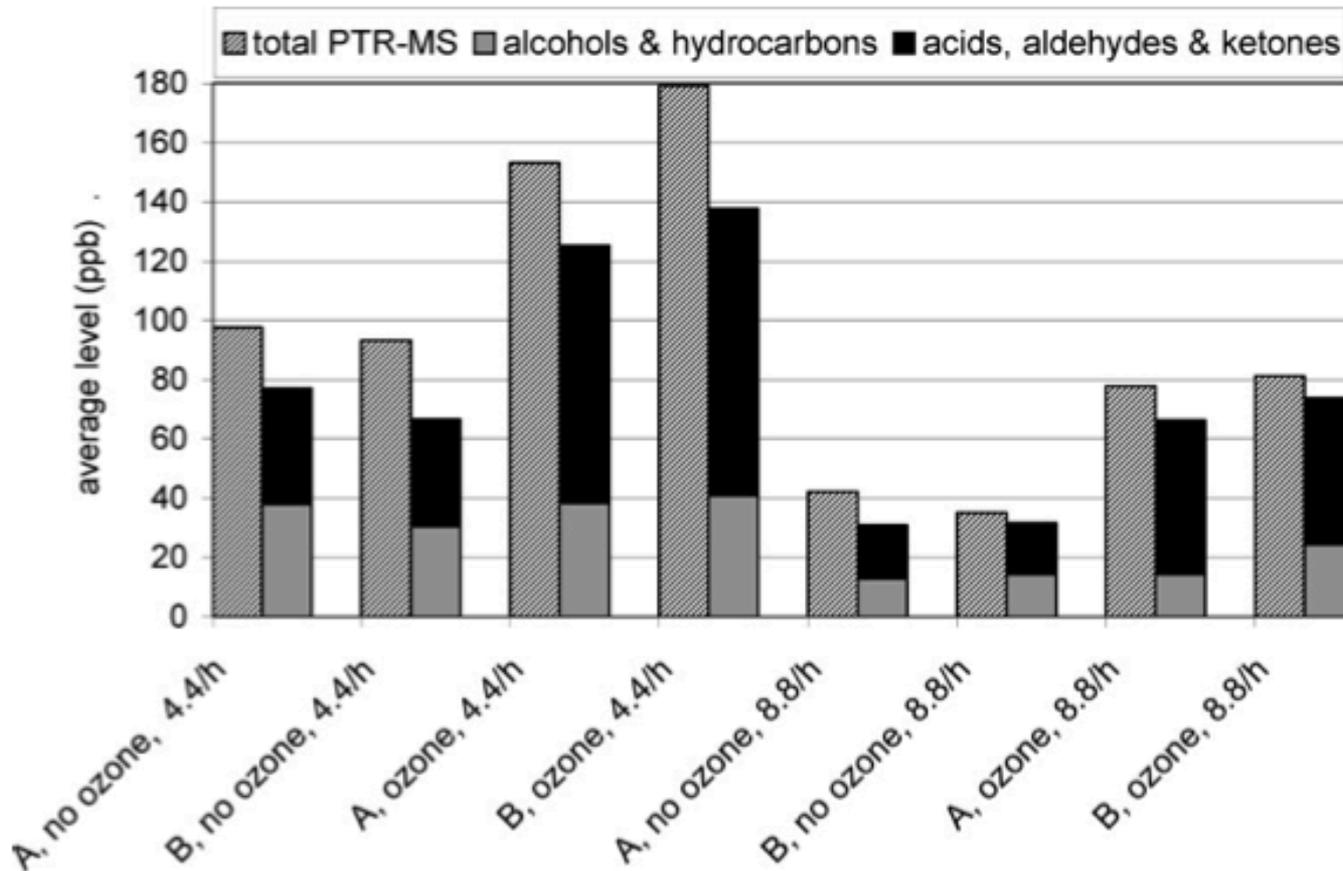


Fig. 4. Schematic of ozone reacting with squalene on exposed skin. The initial reaction produces both gas phase and surface-bound primary products. Ozone further reacts with surface bound primary products (see Table 3) to produce additional gas-phase products.

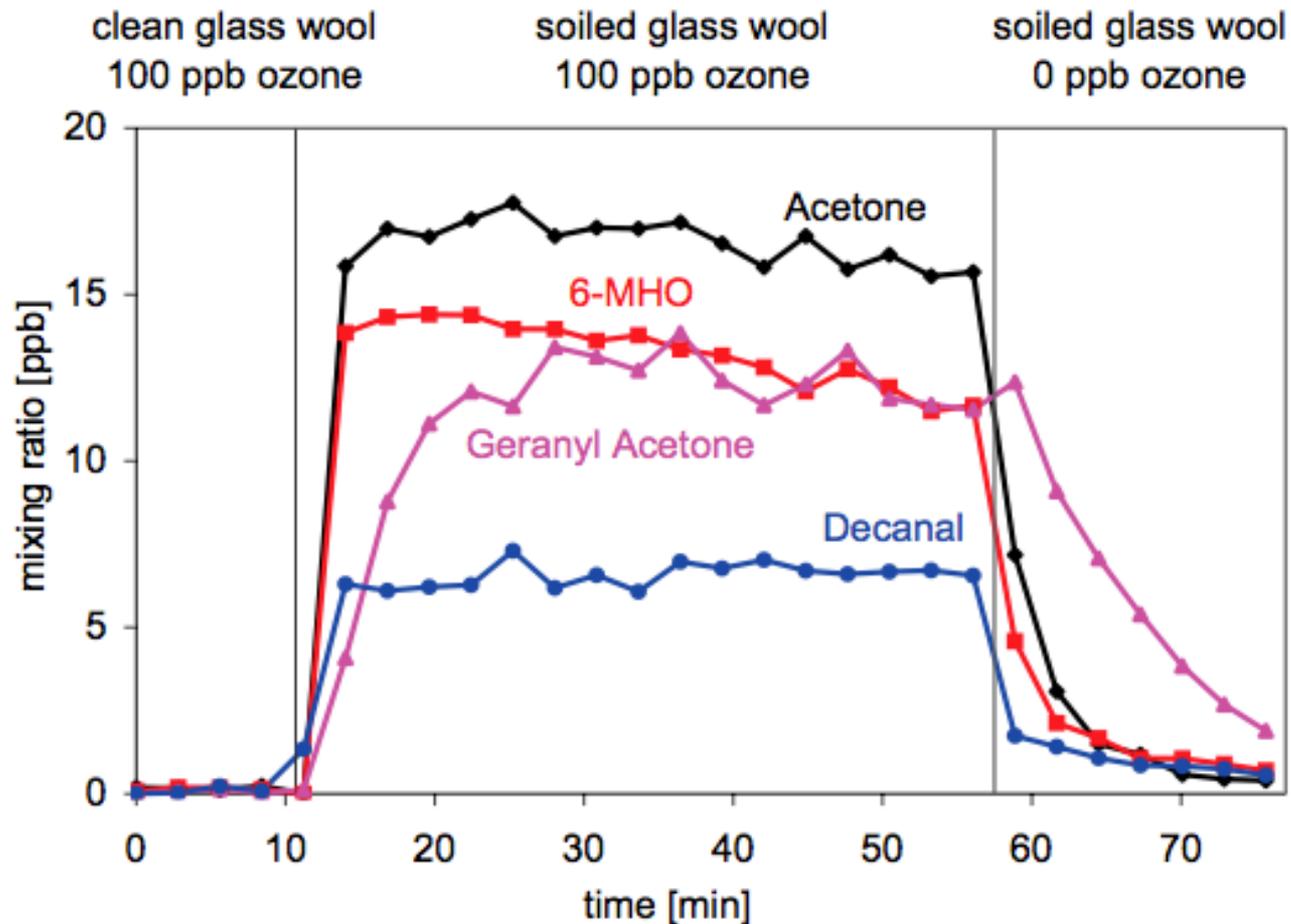
# O<sub>3</sub> + skin oil in a simulated aircraft cabin

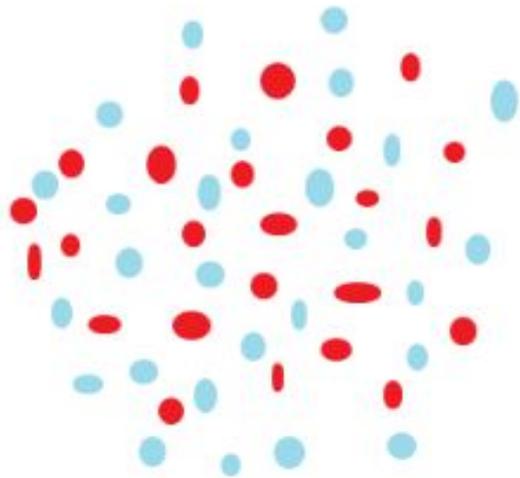


**FIGURE 1.** Total levels, determined by PTR-MS, of the gaseous organic compounds in the cabin air during 14:00–16:00 for each of the 8 experiments with human subjects present. Also displayed, as stacked bars, are the sums of the positively identified “aldehydes, ketones & organic acids” and “alcohols & hydrocarbons”.

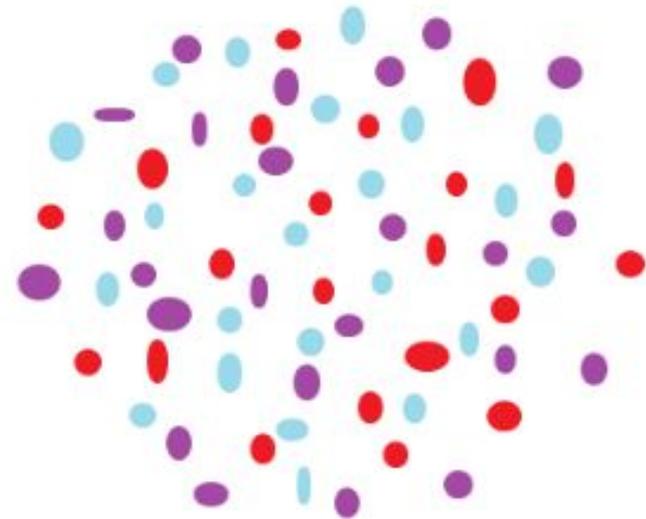
# Example heterogeneous byproduct formation

- Skin oils have recently been identified as being potentially important for ozone chemistry





Initial: Reactants A  
and B



Equilibrium: Reactants  
A and B. Product AB

# HOMOGENEOUS CHEMISTRY

Gas-phase to gas-phase reactions

# Homogeneous chemistry

---

- Homogeneous reactions also occur in indoor environments
  - Gas  $i$  + Gas  $j$   $\rightarrow$  Byproduct  $k$

$$R_{\text{homogeneous}} = -k_{ij}C_iC_jV$$

$R_{\text{homogeneous}}$  = loss rate due to homogeneous reactions between  $i$  and  $j$   
(moles/hr or  $\mu\text{g/hr}$ )

$k_{ij}$  = reaction rate constant ( $\text{ppb}^{-1} \text{hr}^{-1}$ )

$k_{ij}C_j$  = reaction rate (1/hr)

- Need at least 3 mass balances:

– Two reactants + product(s)  $R_{\text{byproduct},k} = (k_{ij}C_iC_j)Y_k f_{\text{conversion}}$

- For a reaction to be relevant indoors, it must occur on a relevant time scale

–  $k_jC_j$  (1/hr) needs to be on the same order as  $\lambda$  (1/hr)

- Reaction must be reasonably fast

# Homogenous chemistry: Mass balance

---

- Summary of mass balance terms:

$$\frac{dC}{dt} = P\lambda C_{out} + \frac{E}{V} - \lambda C - \sum k_j C C_j$$

$C$  = concentration in air inside space of interest ( $\text{mg}/\text{m}^3$ )

$C_{out}$  = concentration outside of space ( $\text{mg}/\text{m}^3$ )

$V$  = chamber volume ( $\text{m}^3$ )

$\lambda$  = air exchange rate through space (1/hr)

$C_j$  = concentration of species  $j$  in indoor air ( $\text{mg}/\text{m}^3$ )

$k_j$  = reaction rate constant ( $\frac{\text{m}^3}{\text{mg hr}}$  or  $\frac{1}{\text{ppb hr}}$ )

$k_j = f(\text{temperature, reactants})$

# Homogenous chemistry: Mass balance

---

- Summary of mass balance terms (steady-state):

$$C_{ss} = \frac{P\lambda C_{out} + E/V}{\lambda + \sum k_j C_j} \quad k_j = f(\text{temperature, reactants})$$

$$\text{If: } \sum k_j C_j \ll \lambda$$

$$\text{If: } \sum k_j C_j \approx \lambda$$

Then: reactions aren't important

Then: reactions **are** important

(reaction must occur reasonably fast)

- Mass balance for estimating by-production formation:

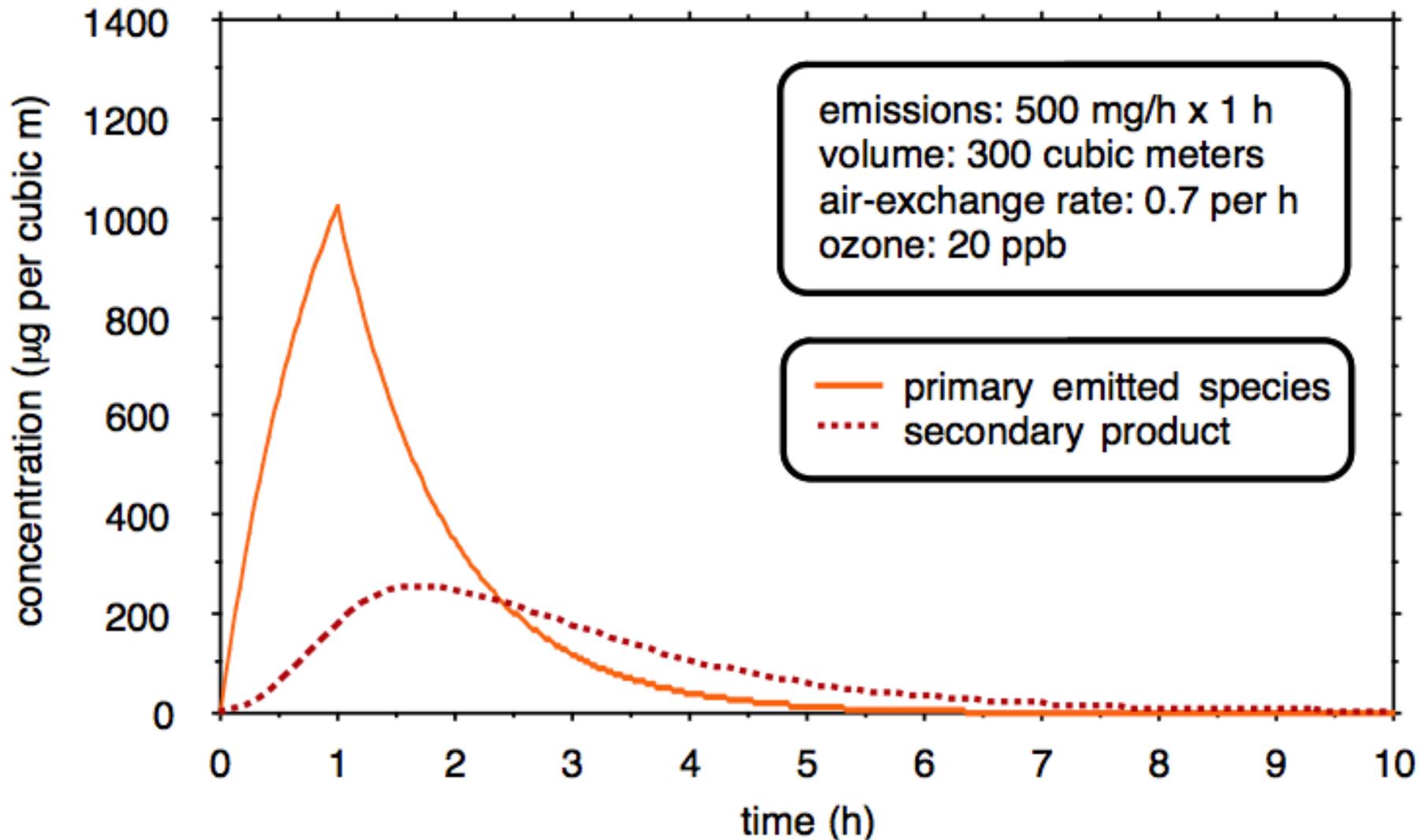
$$C_{byproduct,ss} = \frac{\sum y_p k_j C_j C}{\lambda} \quad y_p = \text{byproduct yield}$$

# Homogeneous chemistry

---

- **Ozone (O<sub>3</sub>)** is an important driver of homogeneous chemistry
  - Oxidation chemistry with unsaturated (C=C double bond) VOCs
  - Weschler (2000) *Indoor Air* provides great review of ozone chemistry
    - Including what reactants are important
  - Important reactants include:
    - Terpenes (limonene, pinene, and others)
      - Household cleaners, scented products
    - Fatty acids (oleic acid, linoleic acid)
    - Squalene
  - Important byproducts include:
    - Gas phase: aldehydes (including HCHO), carbonyls
    - Particle phase: **secondary organic aerosols** (low-vapor pressure species that self-nucleate to form small particles or condense on and increase the mass of existing particles)
  - Byproducts from indoor chemistry can be respiratory or skin irritants

# Reaction byproducts: O<sub>3</sub> + VOCs from cleaning products



# Gas phase reaction byproducts (O<sub>3</sub> + VOCs)

Products (reported or inferred for indoor settings) derived from reactions between unsaturated organic compounds and ozone, hydroxyl radicals or nitrate radicals

Product	Product of reaction with			Refs <sup>a</sup>
	O <sub>3</sub>	OH	NO <sub>3</sub>	
Primary ozonides	✓			a, d
Stabilized Crige biradicals	✓			d, p, q
Hydroxyl radical	✓			l, o, t, u
Alkyl radicals		✓	✓	a, d
Hydroxyalkyl radicals		✓		a
Nitrooxyalkyl radicals			✓	a
Hydroperoxy radical	✓	✓	✓	l, n, v
Alkoxy radicals	✓	✓	✓	a, d, n
Unidentified radical	✓			b
α-Hydroxyhydroperoxides	✓	✓		a, c
Hydrogen Peroxide	✓			h, i
Hydroperoxides	✓			a, h, i, p, q
Peroxy-hemiacetals	✓			p, q
Secondary ozonides	✓			k, p, q
Epoxides	✓			a
Hydroxy carbonyls		✓		a
Dihydroxy carbonyls		✓		a
Hydroxy nitrates			✓	a
Carbonyl nitrates			✓	a
Formaldehyde	✓	✓		a, d
Other aldehydes	✓	✓	✓	a, d
Acetone	✓	✓		a, d
Other ketones	✓	✓	✓	a, d
Formic acid	✓	✓		a
Other carboxylic acids	✓	✓		a
Organic nitrates		✓	✓	a
Multifunctional oxidation products with carbonyl, carboxylate and/or hydroxyl groups	✓	✓	✓	d, e, f, r, x
Secondary organic aerosols via gas/particle partitioning of low volatility products	✓	✓	✓	i, l, s, v, w

# O<sub>3</sub> chemistry: Typical VOC concentrations + rate constants indoors

**Table 4** Volatile organic compounds commonly found indoors: typical indoor concentrations and rate constants for their reaction with ozone. N. B.: units of concentration are “ $\mu\text{g}/\text{m}^3$ ” rather than “ppb”, reflecting units used by Brown et al. (1994) in their review of the literature

Common indoor organic	Brown et al., 1994; weighted average <sup>a</sup>	Daisey et al., 1994; geo. mean <sup>b</sup>	Shields et al., 1996; median <sup>c</sup>	Girman et al., 1999; range, median <sup>d</sup>	Rate constant <sup>e</sup>
	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$	
Ethanol	50–100	36	–	–	$2.46 \times 10^{-10}$
Acetone	20–50	10.2	–	7.1–220, 29	$2.46 \times 10^{-10}$
2-Propanol	–	5.6	–	–	$2.46 \times 10^{-10}$
Toluene	20–50	9.8	6	1.6–360, 9	$3.69 \times 10^{-12}$
1,1,1-Trichloroethane	20–50	24.3	–	0.6–450, 3.6	$2.46 \times 10^{-11}$
m- & p-Xylene	10–20	9.1	5	0.8–96, 5.2	$1.48 \times 10^{-11}$
Dichloromethane	10–20	1.4	–	0.5–360	$2.46 \times 10^{-11}$
Decamethylcyclopentasiloxane	–	–	40	–	$2.46 \times 10^{-13}$
p-Dichlorobenzene	5–10	–	0.2	0.3–85	$1.72 \times 10^{-12}$
Ethyl acetate	5–10	1.1	–	0.2–65	$2.46 \times 10^{-10}$
n-Decane	5–10	2.9	6	0.3–50	$2.46 \times 10^{-13}$
Branched C10	–	–	5	–	$2.46 \times 10^{-13}$
n-Undecane	1–5	7	9	0.6–58, 3.7	$2.46 \times 10^{-13}$
n-Dodecane	1–5	10.4	7	0.5–72, 3.5	$2.46 \times 10^{-13}$
n-Pentadecane	1–5	–	13	–	$2.46 \times 10^{-13}$
n-Hexadecane	<1	–	11	–	$2.46 \times 10^{-13}$
n-Tetradecane	1–5	–	11	–	$2.46 \times 10^{-13}$
1,2,4-Trimethylbenzene	5–10	3.9	5	0.3–25	$3.20 \times 10^{-11}$
Octamethylcyclotetrasiloxane	–	–	10	–	$2.46 \times 10^{-13}$
Ethylbenzene	5–10	2.2	2	0.3–30	$3.69 \times 10^{-12}$
Nonanal	5–10	–	–	1.2–7.9, 3.1	$2.46 \times 10^{-10}$
2-Butanone	1–5	–	–	0.7–18	$2.46 \times 10^{-10}$
Benzene	5–10	3.2	–	0.6–17, 3.7	$1.72 \times 10^{-12}$
Tetrachloroethylene	5–10	2.7	4	0.3–50	$2.46 \times 10^{-11}$
o-Xylene	5–10	3	2	0.3–38	$2.46 \times 10^{-10}$
n-Hexane	1–5	1.8	–	0.6–21, 2.9	$2.46 \times 10^{-13}$
Camphene	10–20	–	–	–	$2.21 \times 10^{-8}$
1,2-Dichloroethylene	10–20	–	–	–	$6.05 \times 10^{-9}$
Isoprene	–	–	–	–	$2.95 \times 10^{-7}$
d-Limonene	20–50	6.7	6	0.3–140, 7.1	$5.14 \times 10^{-6}$
a-Pinene	1–5	–	0.2	0.3–8.4	$2.14 \times 10^{-6}$
Styrene	1–5	1.7	1.5	0.2–6.7	$5.31 \times 10^{-7}$

# O<sub>3</sub> chemistry: Typical VOC concentrations + half-lives indoors

**Table 5** Half-lives for the reaction of ozone with volatile organic compounds commonly found in indoor air

Common indoor organics	50 ppb O <sub>3</sub> half-life	50 ppb O <sub>3</sub> half-life	100 ppb O <sub>3</sub> half-life	100 ppb O <sub>3</sub> half-life
	hours	days	hours	days
Ethanol	15700	650	7850	325
Acetone	15700	650	7850	325
2-Propanol	15700	650	7850	325
Toluene	1040000	43500	522000	21700
1,1,1-Trichloroethane	157000	6500	78300	3250
m-p-Xylene	260840	10868	130420	5434
Dichloromethane	156504	6521	78252	3261
Decamethylcyclopentasiloxane	15700000	652000	7820000	326000
p-Dichlorobenzene	2240000	93000	1120000	46500
Ethyl acetate	15700	650	7850	325
n-Decane	15700000	652000	7820000	326000
Branched C10	15700000	652000	7820000	326000
n-Undecane	15700000	652000	7820000	326000
n-Dodecane	15700000	652000	7820000	326000
n-Pentadecane	15700000	652000	7820000	326000
n-Hexadecane	15700000	652000	7820000	326000
n-Tetradecane	15700000	652000	7820000	326000
1,2,4-Trimethylbenzene	120000	5020	60200	2510
Octamethylcyclotetrasiloxane	15700000	652000	7820000	326000
Ethylbenzene	1040000	44000	520000	22000
Nonanal	15700	650	7850	325
2-Butanone	15700	650	7850	325
Benzene	2230000	93000	1120000	46500
Tetrachloroethylene	157000	6500	78300	3250
o-Xylene	15700	650	7850	325
n-Hexane	15700000	652000	7820000	326000
1,2-Dichloroethylene	636	27	318	13
Camphene	174	7.2	87	3.6
Isoprene	13	0.54	6.5	0.27
d-Limonene	0.75	0.03	0.37	0.02
a-Pinene	1.80	0.08	0.90	0.04
Styrene	7.25	0.30	3.62	0.15

# Other homogeneous chemistry

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- Hydroxyl radical ( $\cdot\text{OH}$ )
  - Formed during ozone-terpene chemistry
  - Strong oxidant and reacts with almost any hydrocarbon (very fast)
  - Concentrations typically ppt
  - Byproducts from oxidation are expected to be more irritating and corrosive than their precursors

Weschler and Shields 1996 *Environ Sci Technol*

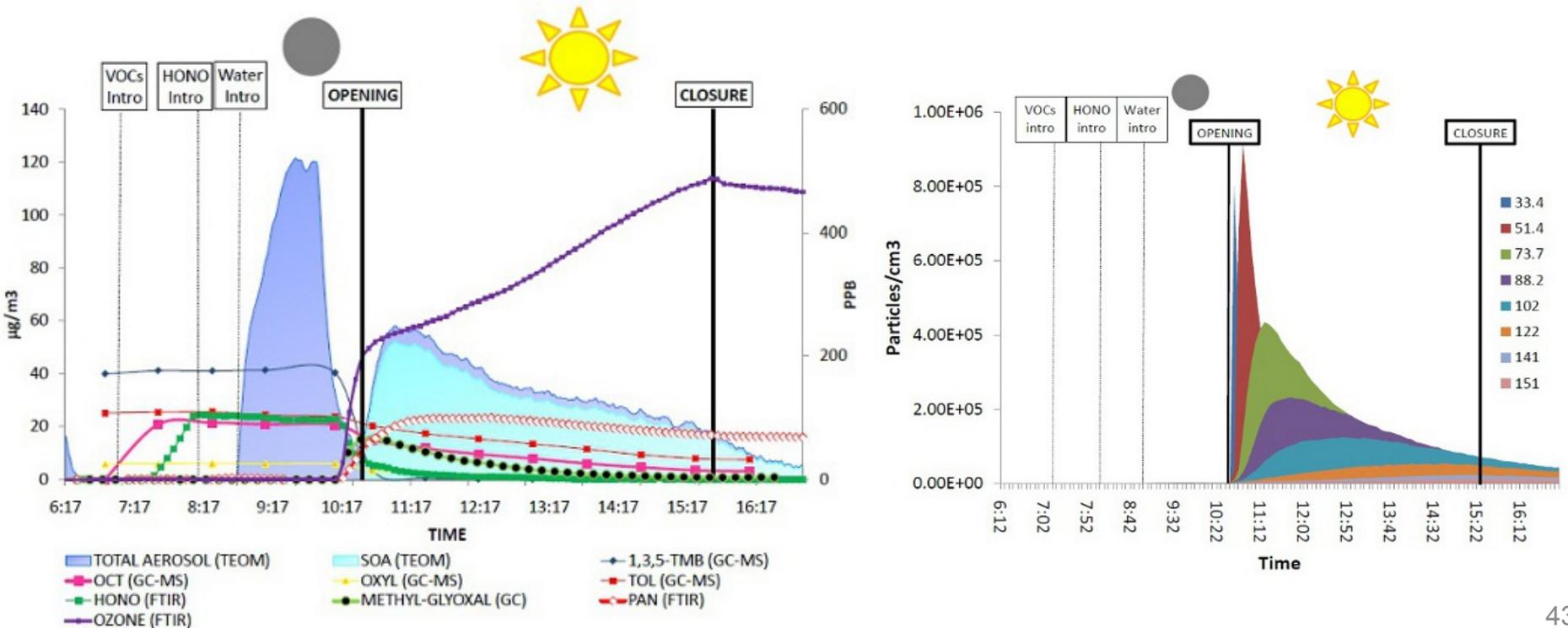
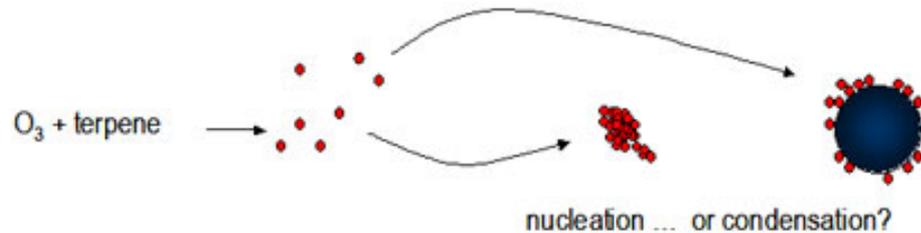
- Nitrate radical ( $\text{NO}_3\cdot$ )
  - Forms as product of reaction between  $\text{O}_3$  and  $\text{NO}_2$
  - Targets reactions with terpenes
  - Concentrations typically ppt

Weschler et al. 1992 *Environ Sci Technol*

# SOA: Secondary organic aerosols

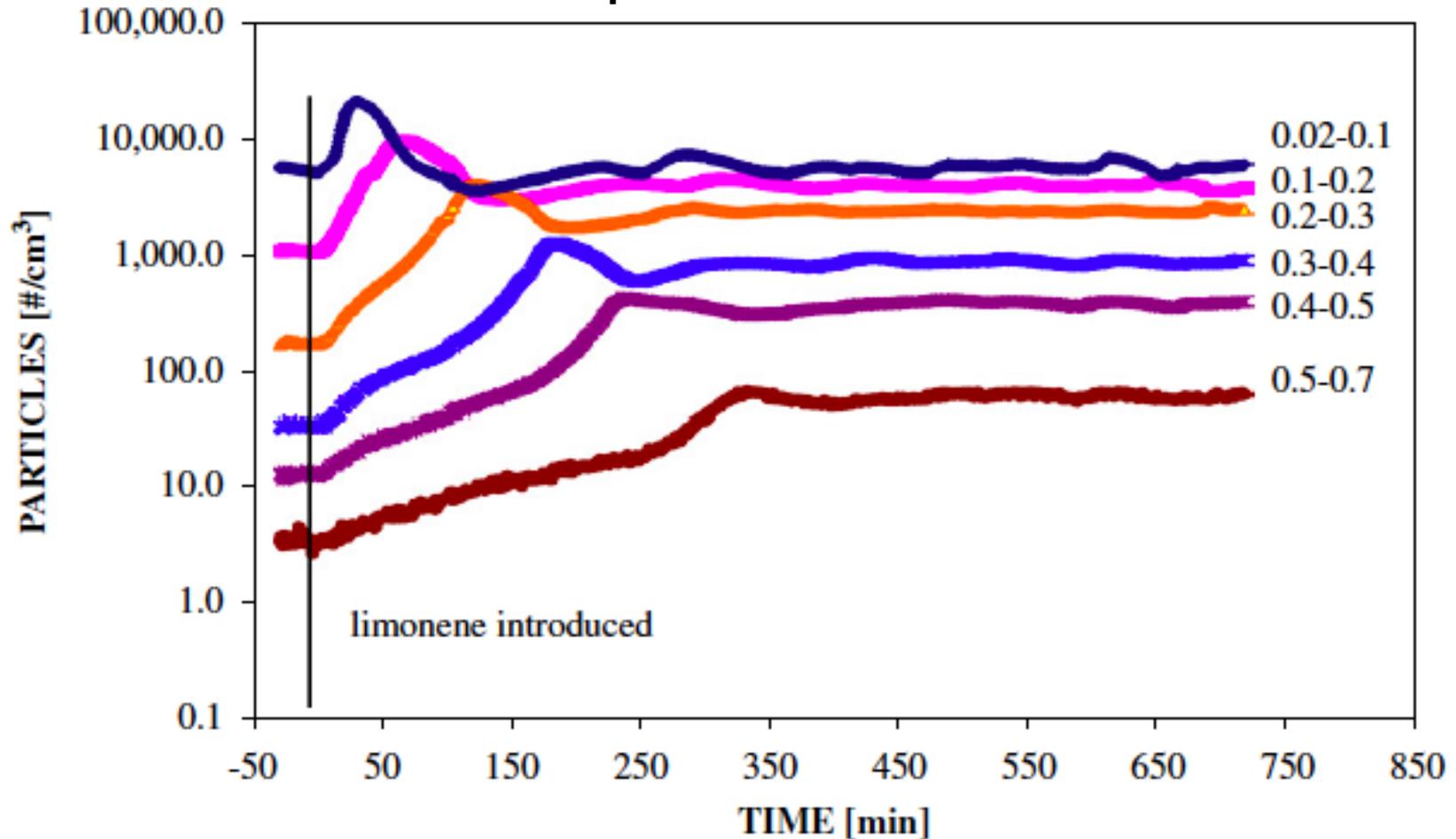
## Secondary organic aerosol (SOA) formation

<http://hdestailats.lbl.gov/research.htm>



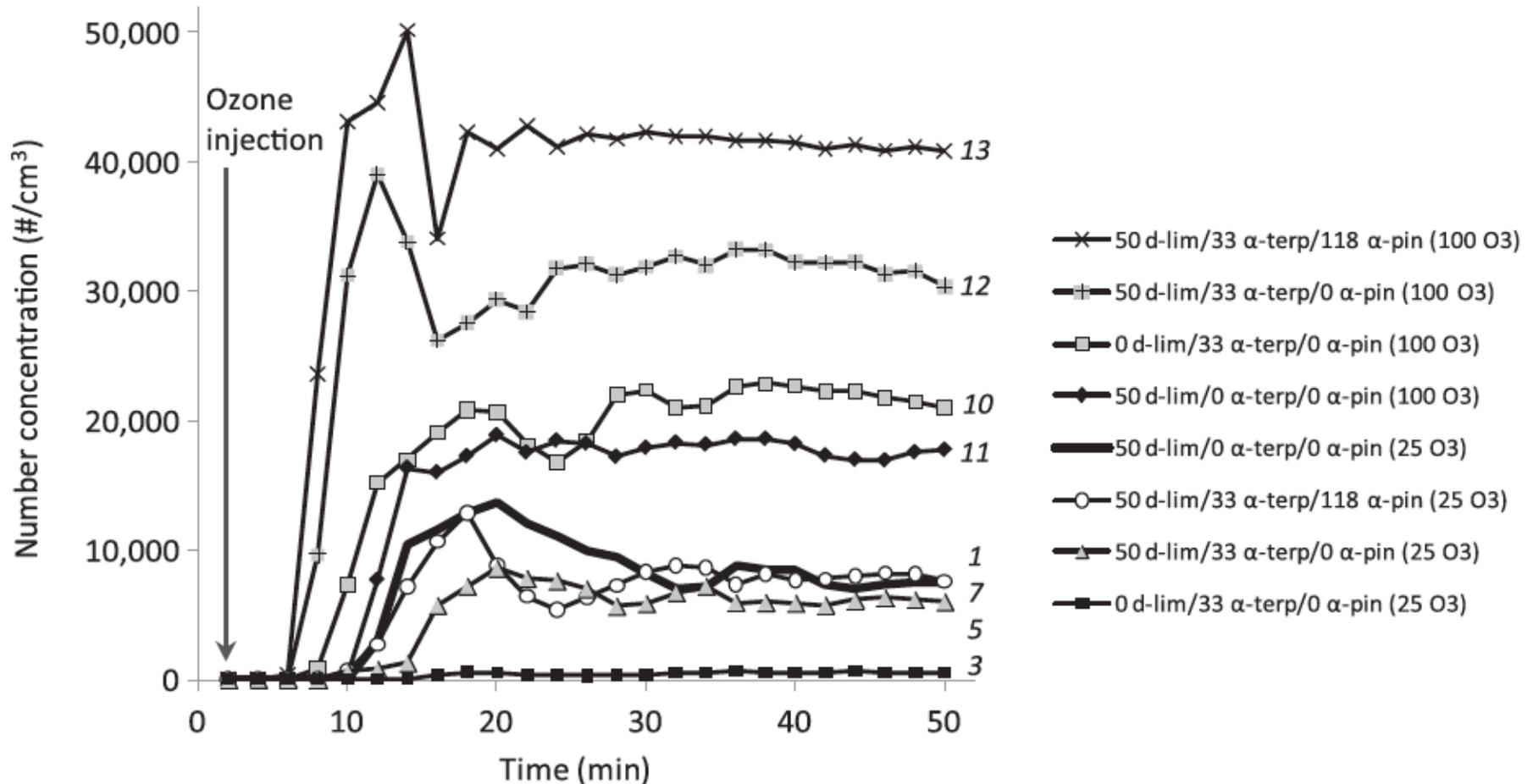
# SOA formation from homogeneous chemistry

Limone injection (air fresheners and perfumes) in the presence of ozone indoors



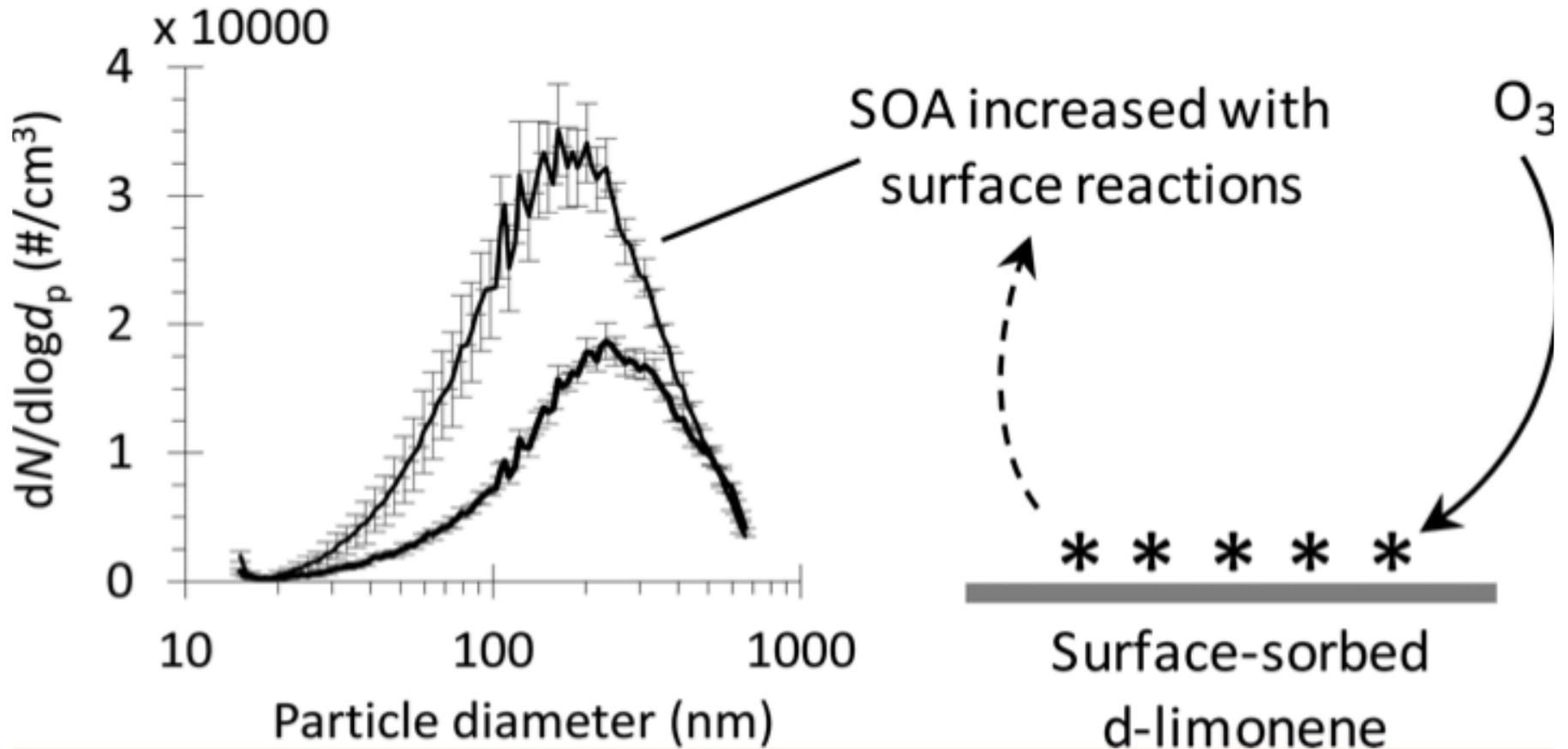
# SOA formation from homogeneous chemistry

Chamber experiments with mixtures of terpenes and more realistic O<sub>3</sub>  
(10-500 nm particles)



# Heterogeneous SOA formation

**O<sub>3</sub> + Surface-sorbed Terpenes → Secondary Organic Aerosol**



Before moving on to particulate matter in the next lecture ...

## **CONTROL OF GAS PHASE COMPOUNDS**

# Control of VOCs and inorganic gases

---

- There are a few important ways to control (i.e., remove) VOCs and inorganic gases:
  1. Source control
  2. Adsorption-based air-cleaning (e.g., activated carbon)
  3. Photocatalytic air-cleaning (e.g., UV/PCO)
- We won't spend much time on these but we need to know they exist
  - You may incorporate into your final project too

# Source control/substitution

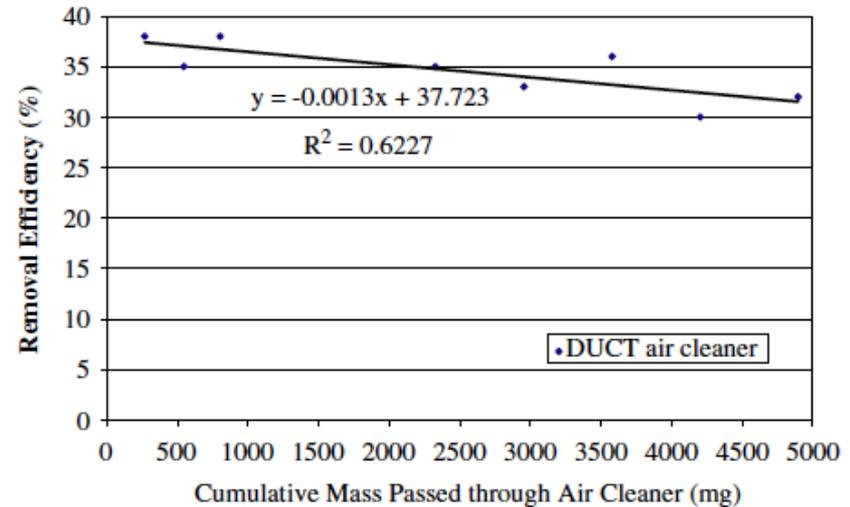
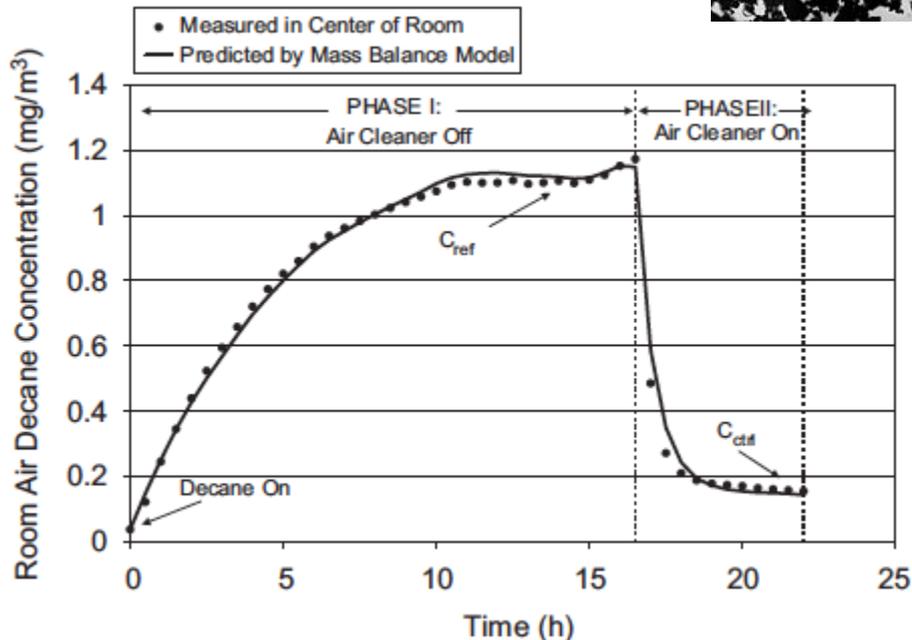
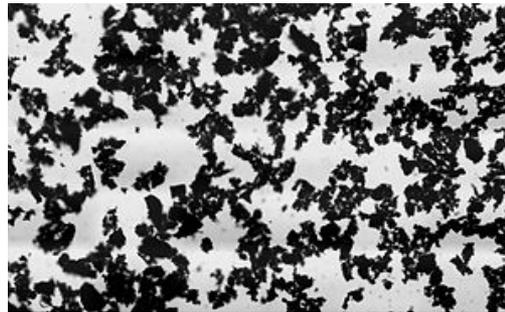
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- Simple enough: this involves switching to low-emitting materials
  - We've discussed this already in some form



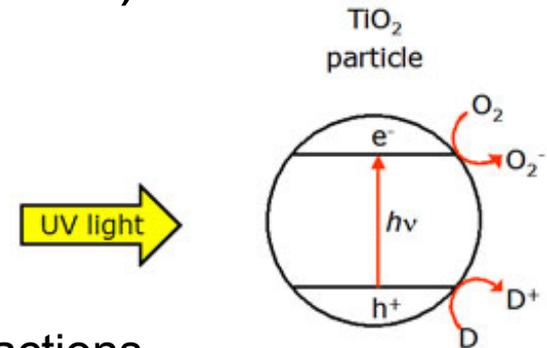
# Adsorption: activated carbon

- Microporous activated carbon adsorbents
  - Very high surface areas
    - e.g., 800-2000 m<sup>2</sup>/g

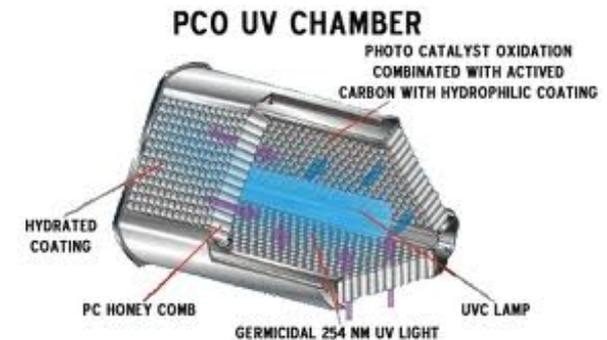
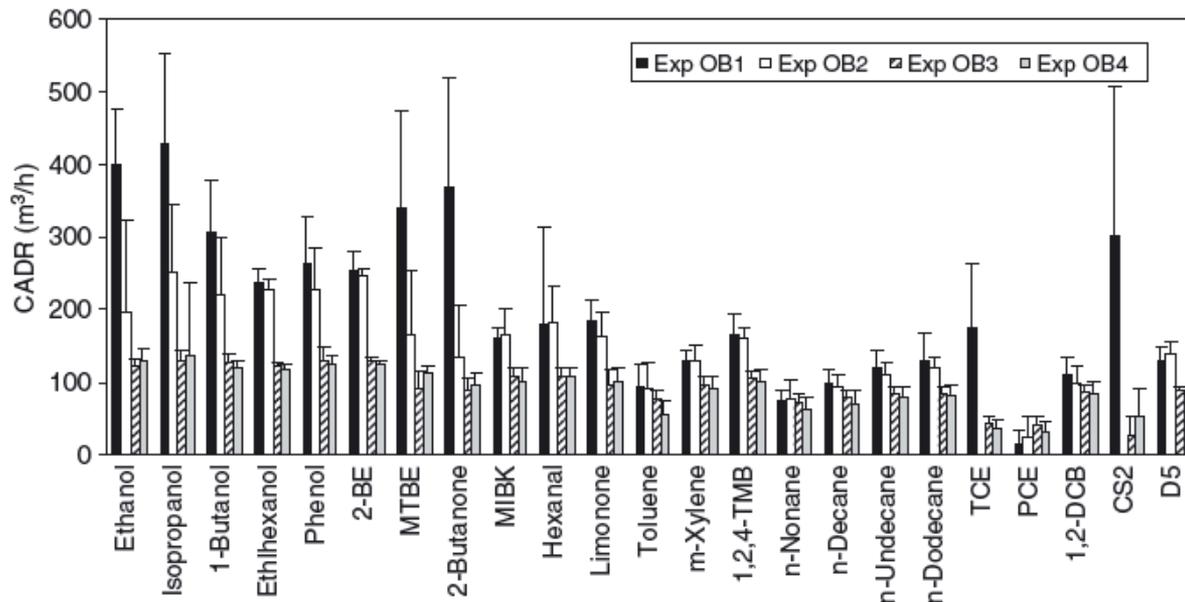


# UV+PCO

- Ultraviolet (UV) photocatalytic oxidation (PCO)
  - Honeycomb reactor coated with  $\text{TiO}_2$
  - Structure is irradiated with UV light
  - VOCs adsorb reversibly on the catalyst
  - React to form  $\text{CO}_2$  and water
    - $\text{TiO}_2$  semi-conductor sensitizes light-induced reactions



<http://hdestailats.lbl.gov/research.htm>



# Blog post #2

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- Due next Tuesday