

# ENVE 576

# Indoor Air Pollution

Spring 2013

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## Lecture 5: February 12, 2013

Gaseous pollutants: Sorption, reactive deposition, and chemistry

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

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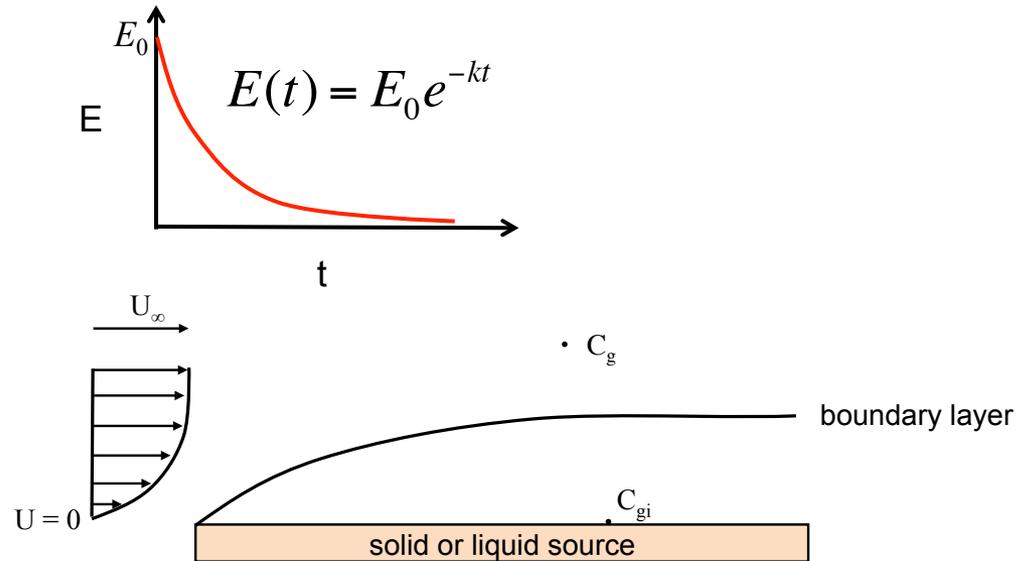
# HW 2 due today

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- Questions?

# Review from last time

- Last time we covered:
  - Indoor vs. outdoor contributions to indoor concentrations
  - Gas-phase pollutants
    - VOC sources
    - Emissions testing
    - Emissions models

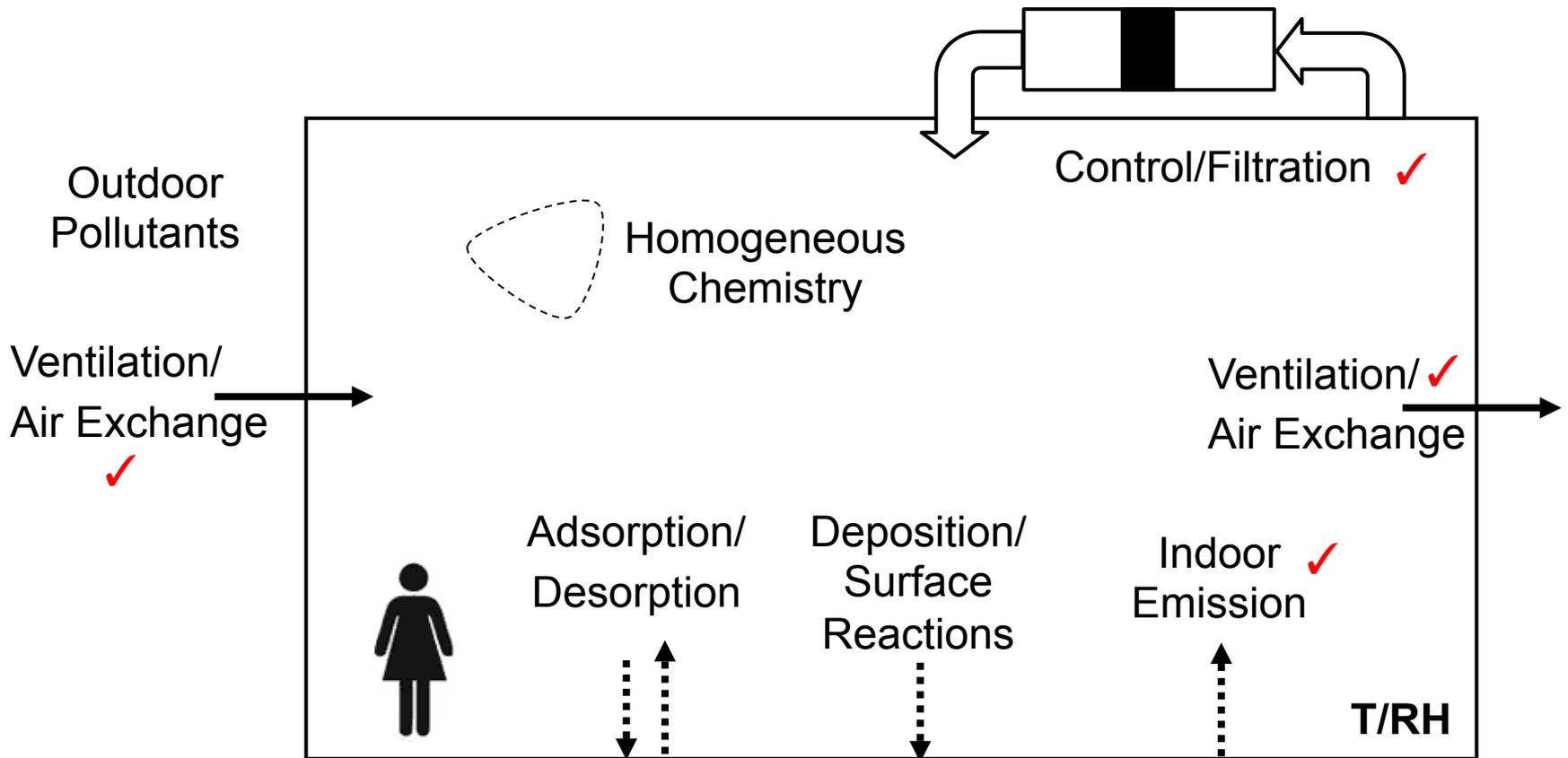


- Today we will cover:
  - Adsorption/desorption of gas-phase compounds
  - Reactions of gas-phase compounds
    - Heterogeneous (reactive deposition)
    - Homogeneous (gas-phase chemistry)

# **SORPTION**

Adsorption and desorption

# Indoor environment: Mass balance on gas-phase



# Sorption

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- Sorption between VOCs and building materials can affect the time profile of emissions and indoor concentrations
- Indoor materials can act as “sinks” or reservoirs that remove VOCs from indoor air (often temporarily)
  - Delays the release into indoor environment and lowers peak concentration
    - Reduced inhalation exposure
  - Can also be *irreversibly* adsorbed to a material
    - Meaning no re-emission back indoors
- Many building materials are porous (high surface area for sorption)
  - e.g., gypsum board, wood, carpet
- VOCs can also adsorb onto exterior surfaces of non-porous materials
  - e.g., glass and stainless steel

# Sorption

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- Different surfaces have different affinities for adsorbing chemicals
  - Adsorption = **on to** a material
  - Desorption = **away from** a material
- Physi-sorption
  - Intermolecular van der Waals forces
  - Electrostatic forces
  - Usually reversible
- Chemi-sorption
  - Chemical reaction between gas and surface molecules
  - Often irreversible

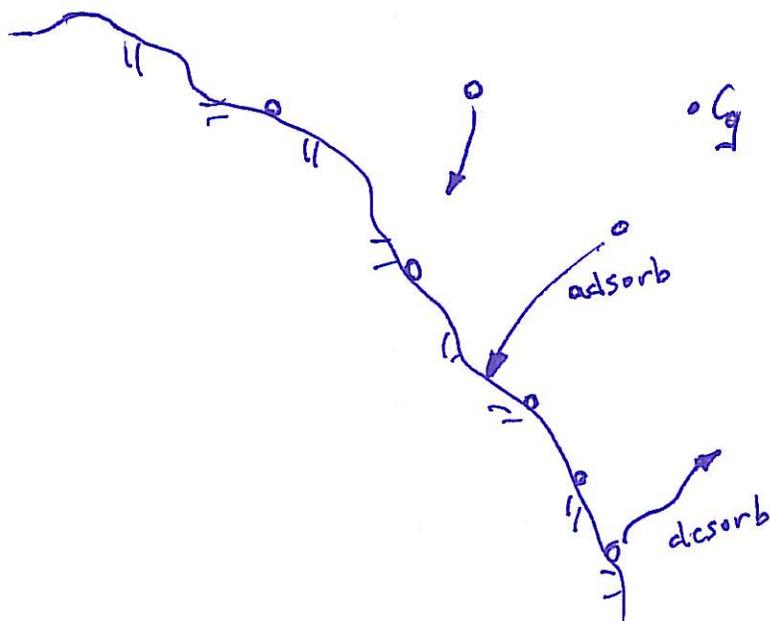
# Sorption

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- Refer to notes on doc cam and uploaded to BB

"SORPTIVE INTERACTIONS" <sup>Actually not a word  $\Rightarrow$  "sink effects"</sup>

①



@ Equilibrium:

Adsorption rate = desorption rate

i.e., # of molecules on the surface is constant

⊛ For most compounds, desorption rates are slower than adsorption rates

Key terms:

$M_{eq}$  = concentration @ equilibrium on the material  $\left[ \frac{mg}{g} \right]$  or  $\left[ \frac{mg}{m^2} \right]$

$C_{eq}$  = concentration in air  $\left[ \frac{mg}{m^3} \right]$

$M_{eq} = f * C_{eq}$  where  $f$  = mathematical operator

Finding "f": Mono-layer theory (molecules are NOT sitting on top of each other)

\* Assume: 1) Adsorbed layer is 1 molecule thick

2) Material is homogeneous in regards to affinity for sorption

3) Equilibrium conditions

Let  $F$  = fraction of surface area covered by molecules

Define:  $v_a$  (rate of adsorption)  $\Rightarrow v_a = k_1 C (1 - F)$  [mass/time]

$\uparrow$  Some constant      $\uparrow$   $C_g$       $\uparrow$   $F=0$ , no adsorbed molecules on surface  
 $\uparrow$   $F=1$ , no more adsorption sites left

$v_d$  (rate of desorption)  $\Rightarrow v_d = k_2 F$  [mass/time]

$\uparrow$  another constant      $\uparrow$  how "covered" is the surface?

Equilibrium,  $v_a = v_d$ :

$$k_1 C (1 - F) = k_2 F$$

$$k_1 C - k_1 C F = k_2 F$$

$$k_1 C = (k_1 C + k_2) F$$

$$F = \frac{k_1 C}{k_1 C + k_2} \quad [-]$$

Define: Mass concentration at surface  $\rightarrow M = k_3 F$

$\uparrow$  some other constant

$\uparrow$  substitute

$$M = k_3 \frac{k_1 C}{k_1 C + k_2}$$

$k_3 = M_0 = \text{max. } M$

Divide by  $k_2$   $\rightarrow M = \frac{\left(\frac{k_3 k_1}{k_2}\right) C}{\left(\frac{k_1}{k_2}\right) C + 1} = \frac{k_3 K C}{1 + K C}$  }  $M = \frac{M_0 K C}{1 + K C}$

$\frac{k_1}{k_2} = K$

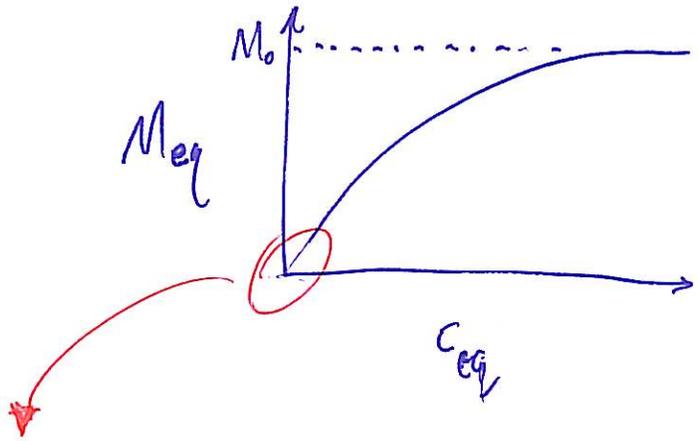
look familiar?

$$M = M_0 \left( \frac{kC}{1+kC} \right)$$

at equilibrium

$$M_{eq} = M_0 \left( \frac{k C_{eq}}{1+k C_{eq}} \right)$$

Langmuir (mono-layer) isotherm



⊛ For low  $C_{eq}$  (usually found indoors):

$$k C_{eq} \ll 1 \rightarrow M_{eq} = M_0 k C_{eq}$$

lump together as  $K_{eq}$

$$\therefore M_{eq} = K_{eq} C_{eq} \leftarrow \text{Linear isotherm}$$

usually appropriate in most indoor environments

UNITS:

$$\left[ \frac{mg}{m^2} \right] = [?] \left[ \frac{mg}{m^3} \right]$$

$$\rightarrow K_{eq} = [m]$$

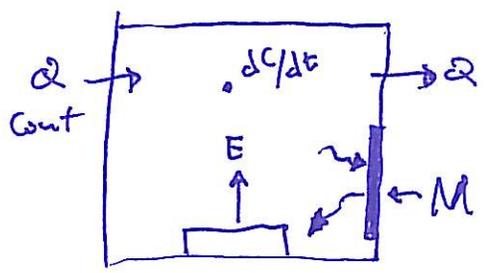
⊛ Note for isotherm purists: There is another common model (we won't use)

$$\text{Freundlich: } M_e = K_f C_e^{1/n} \leftarrow n = \text{power constant}$$

Freundlich isotherm coeff. =  $K_f$

# How do we incorporate sorption in a mass balance?

$$V \frac{dc}{dt} = Q_{Cont} - QC + E - \sum \frac{dM}{dt} A$$



so  $\frac{dM}{dC} = K_{eq}$   
 @ equilibrium  $M = K_{eq} C$   
 $\frac{dM}{dt} = \frac{dM}{dC} \frac{dC}{dt} = K_{eq} \frac{dC}{dt}$

$$\therefore V \frac{dc}{dt} = Q_{Cont} - QC + E - \sum K_{eq} A \frac{dc}{dt}$$

$$\frac{dc}{dt} = \lambda_{Cont} - \lambda C + \frac{E}{V} - \frac{dc}{dt} \left( \sum K_{eq} \frac{A}{V} \right)$$

$$\frac{dc}{dt} \left( 1 + \sum K_{eq} \frac{A}{V} \right) = \lambda_{Cont} - \lambda C + \frac{E}{V}$$

"β"

$$\beta \frac{dc}{dt} = \lambda_{Cont} - \lambda C + \frac{E}{V} \rightarrow (-1) \frac{1}{\lambda_{Cont} - \lambda C + \frac{E}{V}} dc = \frac{1}{\beta} dt (-1)$$

$$\frac{1}{\lambda C - \lambda_{Cont} - \frac{E}{V}} dc = -\frac{1}{\beta} dt$$

"x"

$$\rightarrow \frac{dx}{dc} = \frac{d \left( \lambda C - \lambda_{Cont} - \frac{E}{V} \right)}{dc} = \lambda \rightarrow dc = \left( \frac{1}{\lambda} \right) dx$$

$$\therefore \frac{1}{x} dC = -\frac{1}{\beta} dt \quad \left| \quad dC = \left(\frac{1}{\lambda}\right) dx \Rightarrow \frac{1}{x} \left(\frac{1}{\lambda}\right) dx = -\frac{1}{\beta} dt \right.$$

$$\therefore \int \frac{1}{x} dx = \int -\frac{\lambda}{\beta} dt \Rightarrow \ln x \Big|_{x=0}^x = -\frac{\lambda}{\beta} t$$

$$\therefore \ln \left\{ \frac{\lambda C - \lambda C_{out} - E/\psi}{\lambda C_{t=0} - \lambda C_{out} - E/\psi} \right\} = -\frac{\lambda}{\beta} t$$

$$\therefore C(t) = C(t=0) e^{-\frac{\lambda}{\beta} t} + \left[ C_{out} + \frac{E}{\lambda \psi} \right] \left( 1 - e^{-\frac{\lambda}{\beta} t} \right)$$

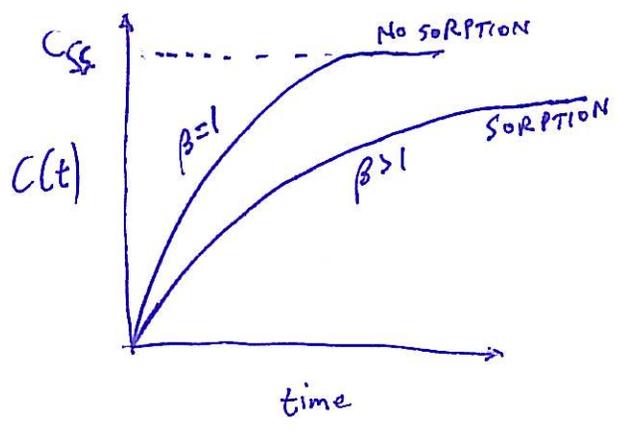
$\beta = 1 \longrightarrow$  No sorption

$$\beta = 1 + \sum k_{eq} \frac{A}{\psi} \quad (so, \beta > 1)$$

\* Sorption slows the process to steady-state

$\beta \gg 1 \longrightarrow$  slower process

\* Concentration profile:



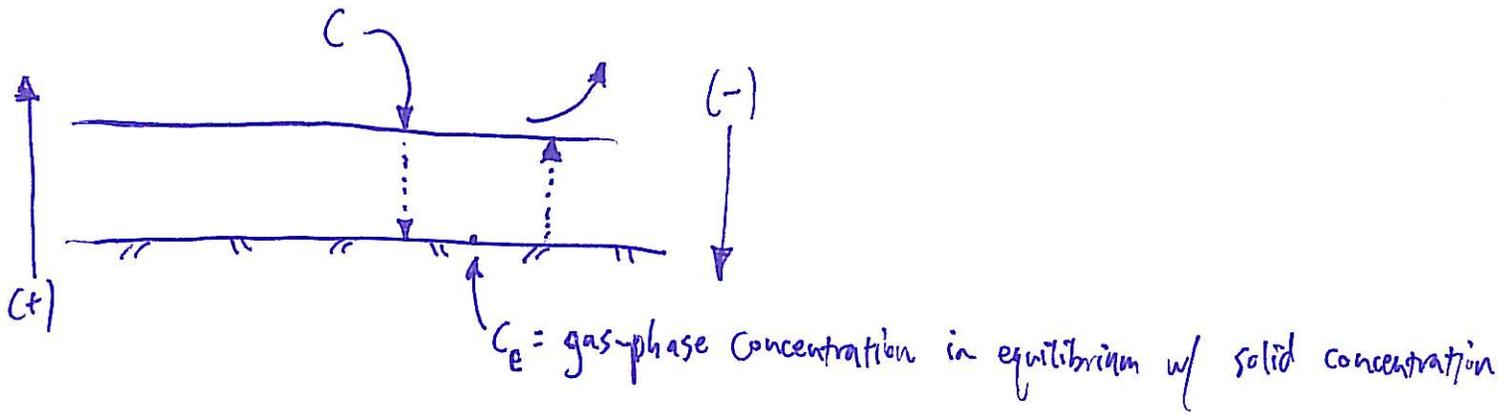
\* Important parameters:

$$k_{eq} = f(\text{chemical, material})$$

$$A = f(\text{material})$$

$$\psi = f(\text{building})$$

\* Non-equilibrium sorption :



Define:  $R_s = \text{net rate of mass transfer through boundary layer } \left(\frac{\text{mg}}{\text{s}}\right)$

$$R_s = -k_g(C - C_e)A$$

\* Assuming linear isotherm  $\Rightarrow M = K_{eq} C_e \Rightarrow C_e = \frac{M}{K_{eq}}$

$$\therefore R_s = -k_g \left( C - \frac{M}{K_{eq}} \right) A \quad \left[ \frac{\text{mass}}{\text{time}} \right]$$

$$R_s = -k_g C + \underbrace{k_g \frac{M}{K_{eq}} A}_{k_d MA} = -\underbrace{k_a CA}_{\text{adsorption coefficient } [m/s]} + \underbrace{k_d MA}_{\text{desorption coefficient } [1/s]}$$

\* Reality check:

When  $R_s = 0$ , equilibrium conditions exist

$$0 = -k_a CA + k_d MA$$

$$k_a C = k_d M$$

$$k_g = \frac{M}{C} = \frac{k_a}{k_d}$$

$$K_{eq} = \frac{k_a}{k_d} \quad \checkmark$$

## Non-equilibrium sorption in mass balances:

(7)

$$\frac{dc}{dt} = P\lambda C_{out} + \frac{E}{V} - \lambda C - \frac{k_d CA}{V} + k_d \frac{MA}{V} \quad \text{Eq'n (1)}$$

$$\frac{dM}{dt} = k_a C - k_d M \quad \text{Eq'n (2)}$$

To solve, discretize over small time step:

$$(1) \quad \frac{C_{t+1} - C_t}{\Delta t} = P\lambda C_{out,t} + \frac{E_t}{V} - \lambda C_t - k_a C_t \frac{A}{V} + k_d M_t$$

$$(2) \quad \frac{M_{t+1} - M_t}{\Delta t} = k_a C_t - k_d M_t$$

\* Initial conditions:  $C_t$  known (e.g. 0 @  $t=0$ )

$M_t$  known (e.g. 0 @  $t=0$ )

# Sorption in mass balances

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- Linear isotherm: Adsorption and desorption separately

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

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

$C_g$  = VOC concentration in air inside space of interest (mg/m<sup>3</sup>)

$C_{g,out}$  = VOC concentration outside of space (mg/m<sup>3</sup>)

$V$  = chamber volume (m<sup>3</sup>)

$Q_g$  = air flow rate through space (m<sup>3</sup>/hr)

$A$  = sink area (m<sup>2</sup>)

$k_a$  = adsorption rate coefficient (m/hr)

$k_d$  = desorption rate coefficient (1/hr)

$M$  = mass collected on the sink per unit area (mg/m<sup>2</sup>)

(you would solve this numerically)

# Sorption in mass balances

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- Linear isotherm
  - At equilibrium

$$K_{eq} = \frac{k_a}{k_d}$$

$K_{eq}$  = linear isotherm coefficient  $[\text{mg}/\text{m}^2 \text{ sorbent}] / [\text{mg}/\text{m}^3 \text{ air}] = [\text{m}]$

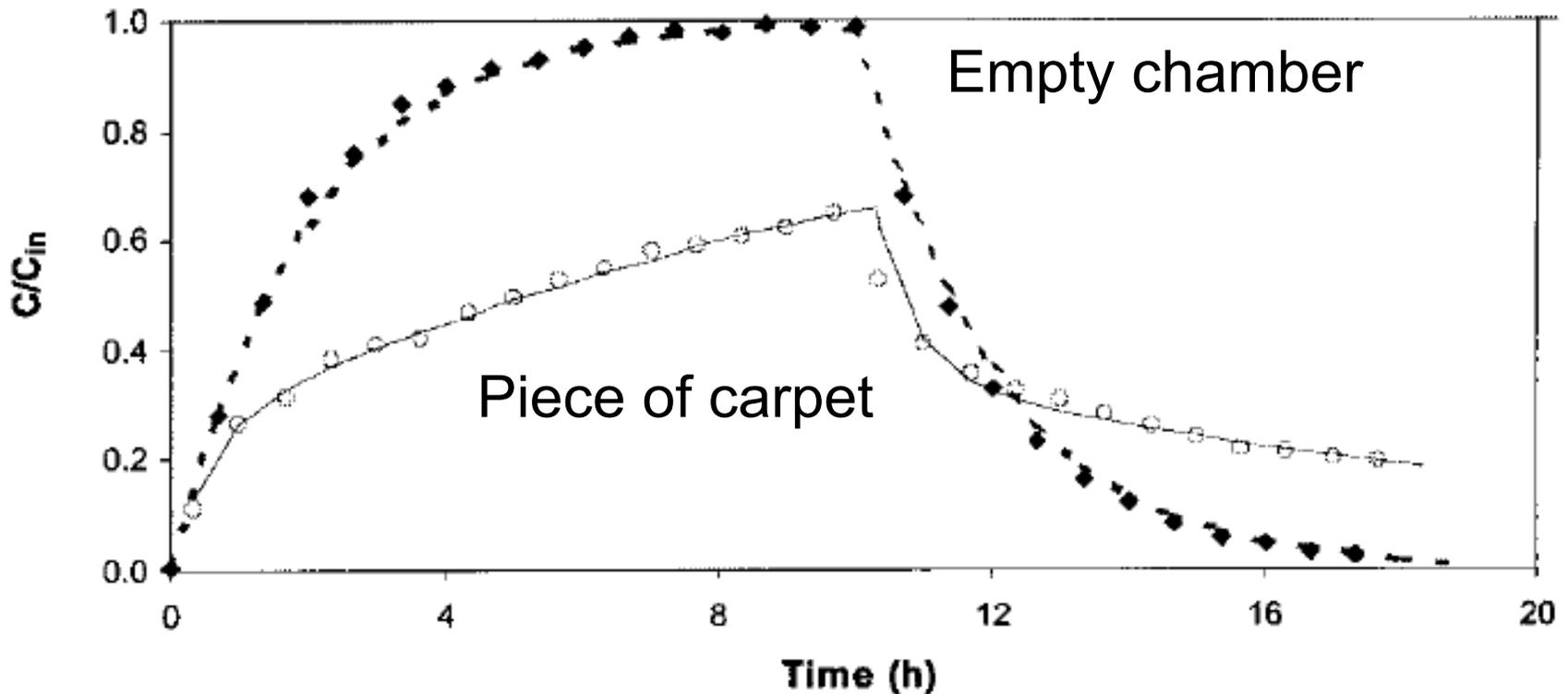
$$V \frac{dC_g}{dt} = Q_g C_{g,out} - Q_g C_g - \frac{dC_g}{dt} \sum k_{eq} A$$

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

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

# Measured impacts of sorption

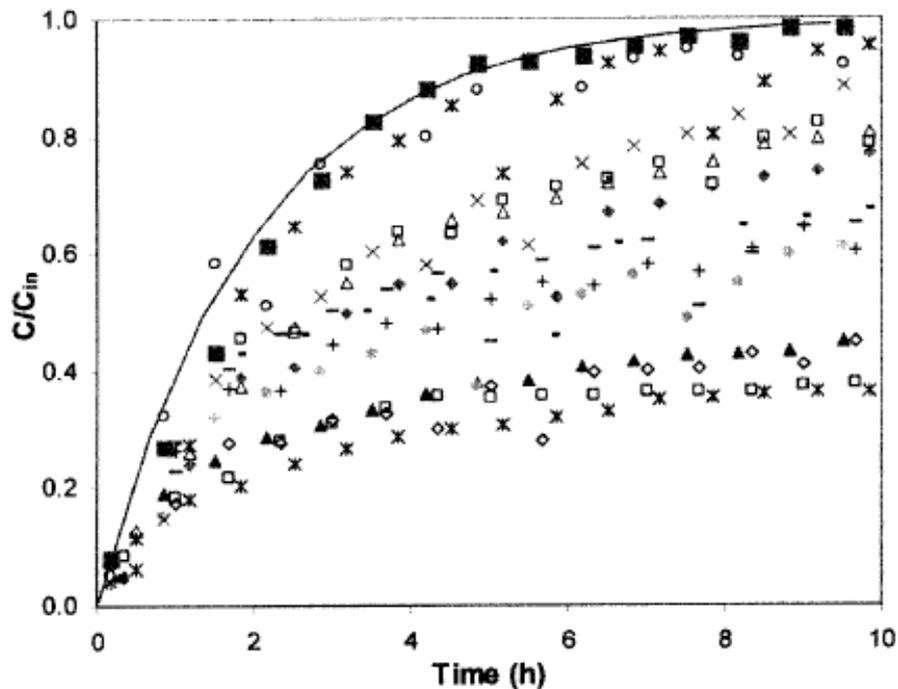
- Chamber studies w/ and w/out carpet
  - 10-hour source injection, then removal



# Measured impacts of sorption

- Chamber studies w/ many materials
  - Gypsum board, vinyl and wood floorings, carpet, carpet pads, etc.

Increasing  $k_a/k_d$



SS.fg = fiberglass shower stall  
 FL.w = wood flooring  
 Uphol = upholstery  
 Ceil = ceiling (acoustic) tile  
 G.p = painted gypsum board  
 App = apples  
 G.v = virgin gypsum board  
 Cp1 = carpet 1  
 FL.v = virgin vinyl flooring  
 G.wp = wallpapered gypsum board  
 Cp3 = carpet 3  
 Cp3.p = carpet 3 with pad  
 Cp2 = carpet 2  
 Cp1.p = carpet 1 with pad  
 Cp2.p = carpet 2 with pad

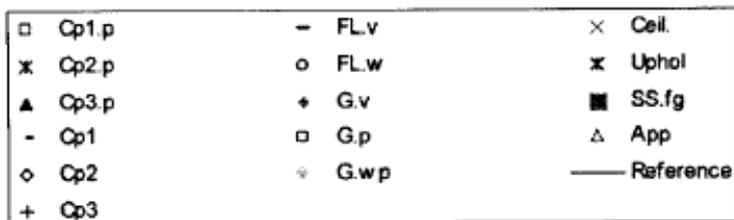


Fig. 3 Effects of Materials on Sorption (1,2-dichlorobenzene)

# Measured impacts of sorption

- Chamber studies w/ many materials
  - Gypsum board, vinyl and wood floorings, carpet, carpet pads, etc.

**Table 2** Summary of Average Adsorption and Desorption Coefficients ( $k_a/k_d$ )

Material	$n_e$	Chemical							
		MTBE	CH	IP	TOL	PCE	EB	DCB	TCB
Cp1	9	ns	ns	–	0.11/0.56	0.17/0.47	0.30/0.62	0.52/0.25	0.58/0.10
Cp2	2	nc	nc	–	0.26/0.44	0.31/0.32	0.41/0.34	0.80/0.17	0.91/0.13
Cp3	1	nc	ns	–	0.18/0.65	0.16/0.42	0.17/0.37	0.43/0.21	0.49/0.16
Cp1.p	10	0.76/4.9	0.39/1.7	0.75/1.1	0.49/0.29	0.44/0.25	0.48/0.15	0.60/0.08	1.5/0.46
Cp2.p	2	0.10/0.45	0.10/0.67	0.36/1.2	0.42/0.23	0.45/0.22	0.49/0.15	0.96/0.15	2.1/0.36
Cp3.p	2	0.10/0.69	0.10/0.60	0.27/0.47	0.23/0.16	0.23/0.17	0.29/0.14	0.62/0.13	1.4/0.42
G.v	5	0.46/1.6	ns	0.79/0.11	0.21/1.7	0.12/1.1	0.21/0.87	0.54/0.49	0.68/0.32
G.p	4	0.07/0.12	0.01/0.18	0.08/0.24	0.10/0.60	0.06/0.45	0.07/0.27	0.26/0.25	0.50/0.29
G.wp	1	nc	ns	–	0.04/0.12	0.09/0.50	0.11/0.19	0.54/0.24	1.1/0.28
FL.v	3	ns	ns	nc	0.09/0.66	0.07/0.39	0.06/0.22	0.23/0.13	0.53/0.17
FL.w	1	nc	ns	nc	ns	ns	0.01/0.01	0.09/0.74	0.09/0.60
Uphol	4	ns	ns	nc	ns	ns	ns	2.0/10	1.8/3.2
Ceil	2	0.01/0.34	ns	nc	0.01/0.03	0.01/0.17	0.09/1.0	0.48/0.73	0.63/0.52
SS.fg	4	ns	ns	nc	ns	ns	ns	ns	2.2/7.8
App	1	ns	ns	nc	0.02/0.18	0.01/0.05	0.07/0.72	0.32/0.62	4.8/3.8

$k_a$  in m/h.  $k_d$  in 1/h. Values are averages of " $n_e$ " experiments. "ns"=no sorption. "nc"=little sorption with indeterminate sorption parameters (no convergence). "–"=failure of quality assurance protocols relative to variations in inlet concentrations. CpX=carpet X. CpX.p=carpet X with padding. G.v=virgin gypsum board. G.p=painted gypsum board. G.wp=wallpapered gypsum board. FL.v=vinyl flooring. FL.w=wood flooring. Uphol=upholstery. Ceil=ceiling (acoustic) tile. SS.fg=fiberglass shower stall. App=apples

# Measured impacts of sorption

- Chamber studies w/ many materials
  - Gypsum board, vinyl and wood floorings, carpet, carpet pads, etc.

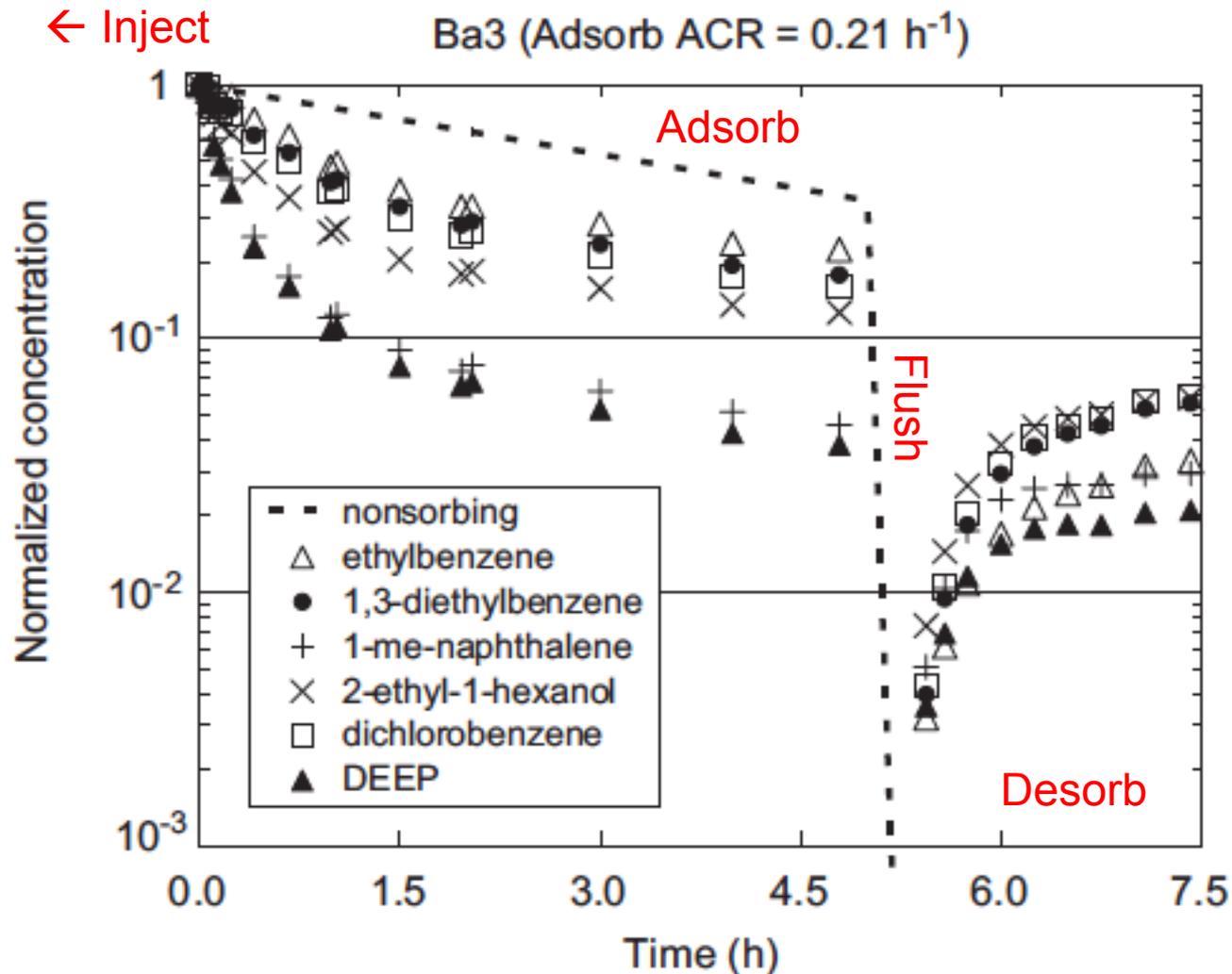
**Table 3** Summary of Equilibrium Partition Coefficients ( $K_{eq}$ ) (Average  $\pm$  Standard Deviation)

Material	$n_e$	Chemical							
		MTBE	CH	IP	TOL	PCE	EB	DCB	TCB
Cp1	9	ns	ns	–	0.22 $\pm$ 0.07	0.36 $\pm$ 0.09	0.46 $\pm$ 0.13	2.1 $\pm$ 1.5	5.9
Cp2	2	nc	nc	–	0.6 $\pm$ 0.02	0.97 $\pm$ 0.002	1.2 $\pm$ 0.05	4.7 $\pm$ 0.3	7.8 $\pm$ 3
Cp3	1	nc	ns	–	0.28	0.38	0.46	2.0	3.1
Cp1.p	10	0.15 $\pm$ 0.03	0.24 $\pm$ 0.05	0.78 $\pm$ 0.2	1.7 $\pm$ 0.18	1.76 $\pm$ 0.2	3.3 $\pm$ 0.4	8.0 $\pm$ 3	4.9 $\pm$ 3
Cp2.p	2	0.22 $\pm$ 0.04	0.15 $\pm$ 0.02	0.29 $\pm$ 0.03	1.9 $\pm$ 0.1	2.1 $\pm$ 0.1	3.4 $\pm$ 0.4	6.6 $\pm$ 0.5	6.1 $\pm$ 0.8
Cp3.p	2	0.14 $\pm$ 0.01	0.16 $\pm$ 0.01	0.57 $\pm$ 0.06	1.5 $\pm$ 0.1	1.4 $\pm$ 0.08	2.1 $\pm$ 0.07	4.9 $\pm$ 0.8	3.5 $\pm$ 0.5
G.v	5	0.35 $\pm$ 0.2	ns	7.2	0.12 $\pm$ 0.04	0.2 $\pm$ 0.09	0.27 $\pm$ 0.09	1.2 $\pm$ 0.5	2.4 $\pm$ 0.7
G.p	4	0.45	0.054 $\pm$ 0.02	0.20	0.18 $\pm$ 0.04	0.18 $\pm$ 0.1	0.28 $\pm$ 0.03	1.0 $\pm$ 0.4	1.8 $\pm$ 0.4
G.wp	1	nc	ns	–	0.34	0.17	0.58	2.3	3.9
FL.v	3	ns	ns	nc	0.14 $\pm$ 0.01	0.19 $\pm$ 0.05	0.58 $\pm$ 0.5	1.8 $\pm$ 0.7	3.5 $\pm$ 0.1
FL.w	1	nc	ns	nc	ns	ns	0.63	0.13	0.15
Uphol	4	ns	ns	nc	ns	ns	ns	0.19 $\pm$ 0.0	0.55 $\pm$ 0.05
Ceil.	2	0.06	ns	nc	0.25	0.088 $\pm$ 0.1	0.10 $\pm$ 0.01	0.68 $\pm$ 0.1	1.2 $\pm$ 0.1
SS.fg	4	ns	ns	nc	ns	ns	ns	ns	0.33 $\pm$ 0.15
App	1	ns	ns	nc	0.061	0.12	0.10	0.52	1.3

$K_{eq}$  in m. Values are averages of " $n_e$ " experiments. "ns"=no sorption. "nc"=little sorption with indeterminate sorption parameters (no convergence). "–"=failure of quality assurance protocols relative to variations in inlet concentrations. CpX=carpet X. CpX.p=carpet X with padding. G.v=virgin gypsum board. G.p=painted gypsum board. G.wp=wallpapered gypsum board. FL.v=vinyl flooring. FL.w=wood flooring. Uphol=upholstery. Ceil=ceiling (acoustic) tile. SS.fg=fiberglass shower stall. App=apples

# Measured impacts of sorption in real rooms

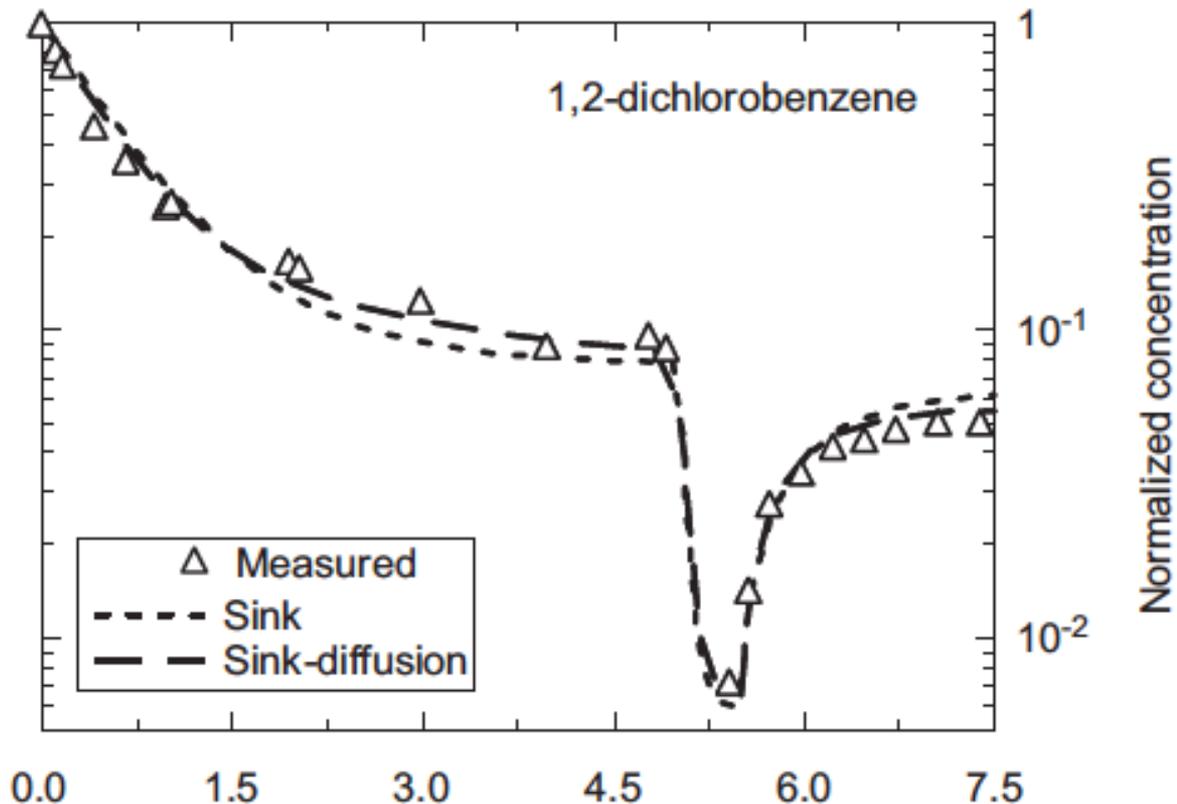
- Injection + adsorption + flush out period + desorption in a bathroom



# Measured impacts of sorption in real rooms

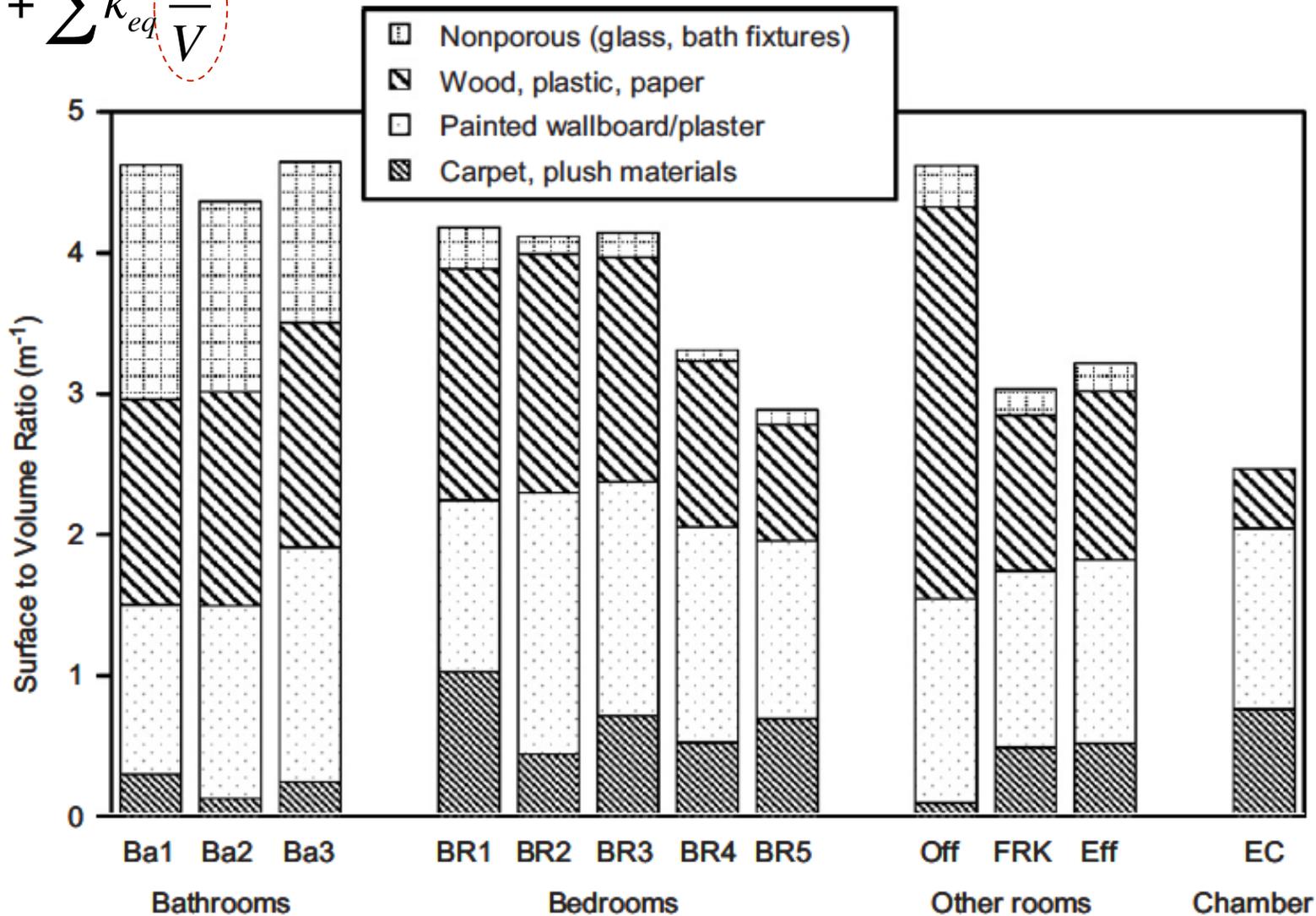
- Measured and modeled adsorption, flush out, and desorption

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



# A note on $A/V$

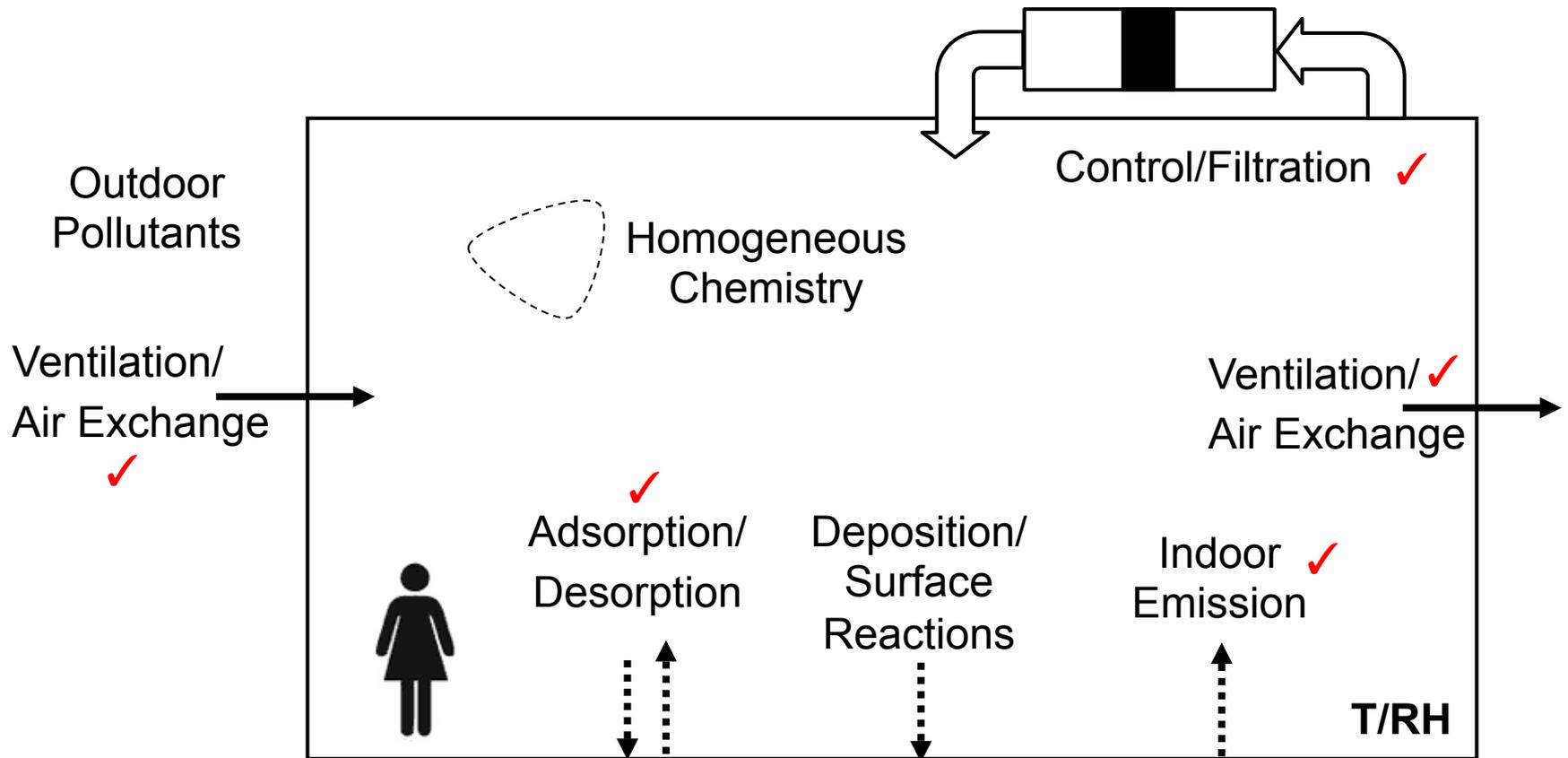
$$\beta = 1 + \sum k_{eq} \frac{A}{V}$$



# **REACTIVE DEPOSITION**

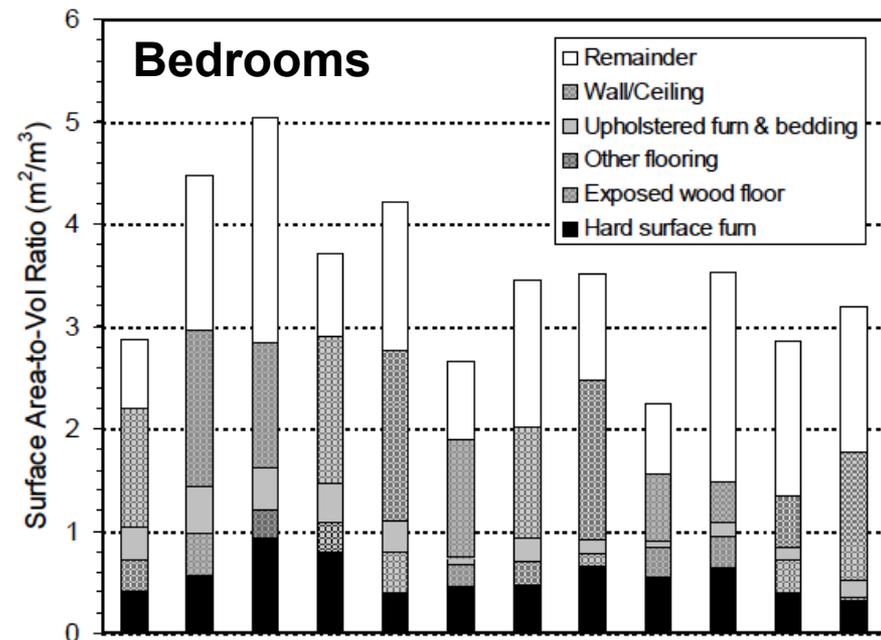
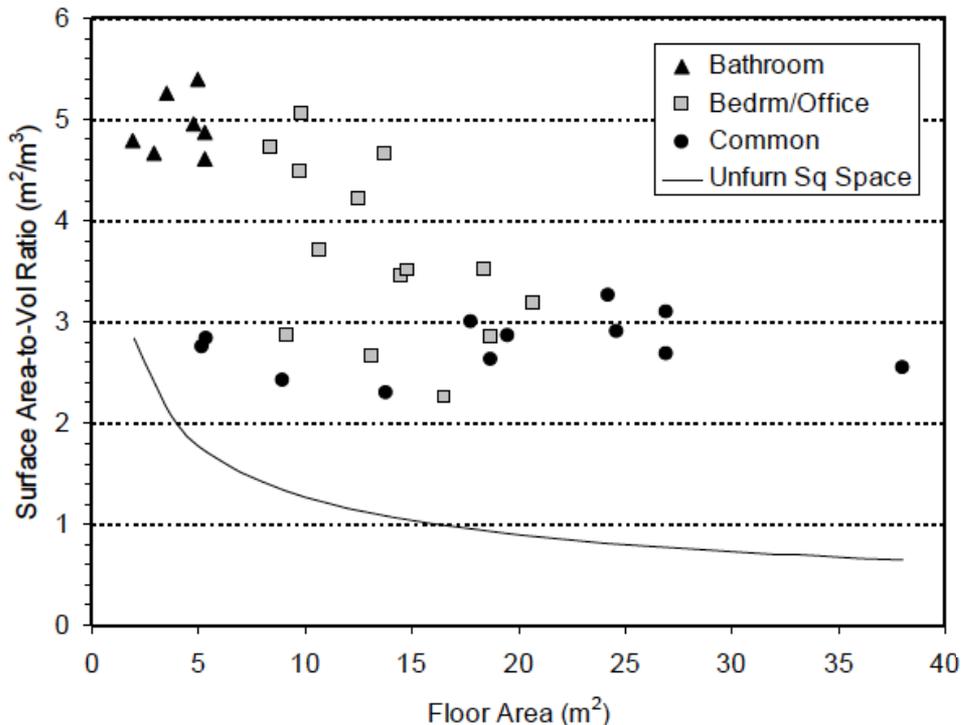
Heterogeneous chemistry

# Indoor environment: Mass balance on gas-phase



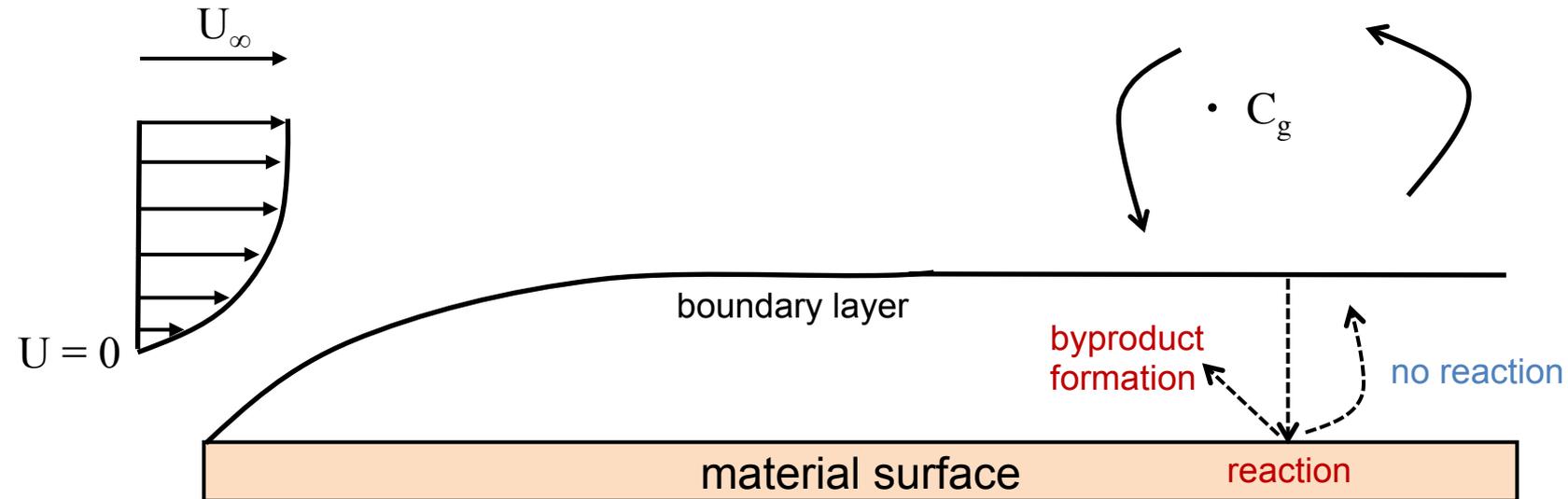
# Reactive deposition: Why is it important?

- 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)

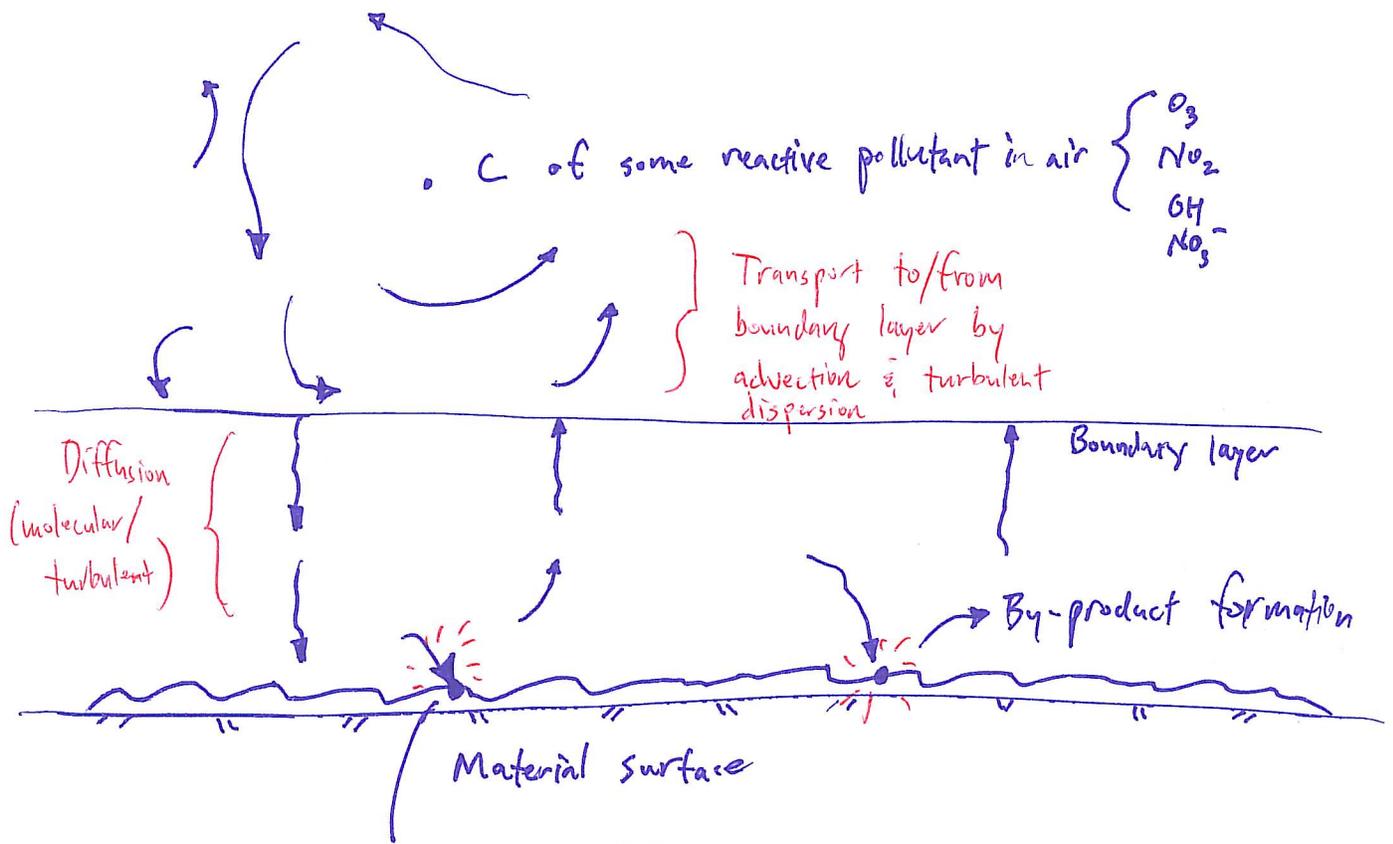
# Reactive deposition

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- Refer to notes on doc cam and uploaded to BB

# Reactive Deposition

CONCEPTUAL



Chemical reaction (!)  
 with other molecules at material surface  
 → Could be the material itself or deposited/adsorbed compound

\* Mathematical setup :

$$R_s = -k_g(C - C_e)A \quad * \text{Treat removal as positive (+)}$$

$$\therefore R_s = k_g(C - C_e)A$$

Assume  $C_e = 0$  for irreversible reaction  $\Rightarrow R_s = k_g CA$

let's call this " $v_d$ " or "deposition velocity"

$$\therefore R_s = v_d CA \quad \text{where } v_d = \text{deposition velocity (m/hr)}$$

$R_s = v_d CA$

Molar consumption at a surface

$R_{dep} = -v_d CA$

Loss rate from gas-phase

$F_{BP} = \gamma_i v_d CA \left( \frac{1}{MW_{reactant}} \right)$

By-product formation rate

moles reacted / time

UNITS:  $R_{dep} = \left[ \frac{m}{hr} \right] \left[ \frac{mg}{m^3} \right] \left[ m^2 \right] = \frac{mg}{hr} \cdot \frac{1}{MW} = \frac{moles}{hr}$

$\frac{Moles \ i}{moles \ reacted} = \text{chemical yield "molar" yield}$

$R_{dep} = -v_d CA \rightarrow v_d = \frac{R_{dep}}{CA} \left( \frac{mass/time}{area} = \frac{mass/volume}{length/time} \right)$

$\therefore v_d = \frac{\text{Species flux}}{\text{Concentration in air}} = \frac{J}{C}$  } analogy --  $v_d$  isn't really  $f(C)$

$v_d A \rightarrow \text{UNITS: } \left[ \frac{m}{hr} \right] \left[ m^2 \right] = \left[ \frac{m^3}{hr} \right]$

$v_d A$  is analogous to a volumetric flow rate  
- Equivalent to a 100% efficient air cleaner operating @  $Q_c = v_d A$

What affects  $v_d$ ?

- \* Transport to surface
- \* Interactions at surface
- \* Surface / Material characteristics
- \* Chemical characteristics } connected
- \* RH / T
- \* age of material
- \* ability to regenerate

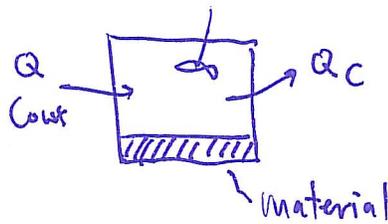
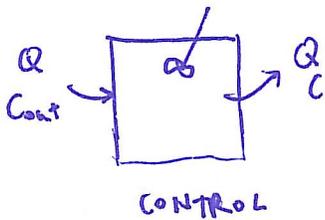
# How do we determine $V_d$ ?

③

for fluid dynamics

- Chamber experiments
- I/O species of outdoor origin
- Measure deposition flux & concentration
- Decay analysis following emissions

## Chamber experiments:

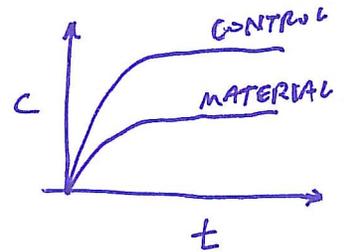


CONTROL:  $\frac{dc}{dt} = Q_{Cout} - Q_C - v_{d,walls} A_{walls} C$

$$V_{d,walls} = \frac{-Q(C - C_{out})}{A_{walls} C} = \frac{Q(C_{out} - C)}{A_{walls} C}$$

MATERIAL CHAMBER:  $\frac{dc}{dt} = Q_{Cout} - Q_C - v_{d,walls} A_{walls} C - v_d A C$

$$V_d = \frac{Q(C_{out} - C) - v_{d,walls} A_{walls} C}{CA}$$



## I/O RATIO: (actual buildings)

$\frac{dc}{dt} = Q_{Cout} - Q_C - v_d A C$

$$0 = \lambda C_{out} - \lambda C - \frac{v_d A}{V} C$$

$$0 = \lambda C_{out} - \left( \lambda + \frac{v_d A}{V} \right) C$$

$$C = \frac{\lambda C_{out}}{\lambda + \frac{v_d A}{V}}$$

$$\frac{C_{in}}{C_{out}} = \frac{\lambda}{\lambda + \frac{v_d A}{V}}$$

Assuming  $P=1$

Decay following strong emissions : (chamber or full scale)

(4)

$$\forall \frac{dc}{dt} = Q_{cont} - \lambda C - v d A C \Rightarrow \frac{dc}{dt} = \cancel{\lambda C_{cont}} - \lambda C - \frac{v d A}{f} C$$

$$\frac{dc}{dt} = -\lambda C - \frac{v d A}{f} C = -C \left( \lambda + \frac{v d A}{f} \right)$$

$$\frac{dc}{\left( \lambda + \frac{v d A}{f} \right) C} = -dt \rightarrow \int_{C_{t=0}}^{C_t} \frac{dc}{C} = - \left( \lambda + \frac{v d A}{f} \right) \int_0^t dt$$

- |   |   |   |
|---|---|---|
| $\ln \left\{ \frac{C_t}{C_{t=0}} \right\} = - \left( \lambda + \frac{v d A}{f} \right) t$ | } | • Measure $C(t=0)$<br>• Measure $C(t)$<br>• plot $-\ln \left( \frac{C_t}{C_{t=0}} \right)$ vs. time |
| $-\ln \left\{ \frac{C(t)}{C_{t=0}} \right\} = \left( \lambda + \frac{v d A}{f} \right) t$ |   |   |
- Force through zero
  - Slope =  $\left( \lambda + \frac{v d A}{f} \right)$
  - Measure  $\lambda$  simultaneously
  - Subtract  $\lambda$  from  $\lambda + \frac{v d A}{f}$   
to get  $\frac{v d A}{f}$  !

# RESISTANCES TO DEPOSITION

$$R_{TOTAL} = R_{TRANSPORT} + R_{SURFACE REACTION} = r_t + r_s \quad \left[ \frac{hr}{m} \right]$$

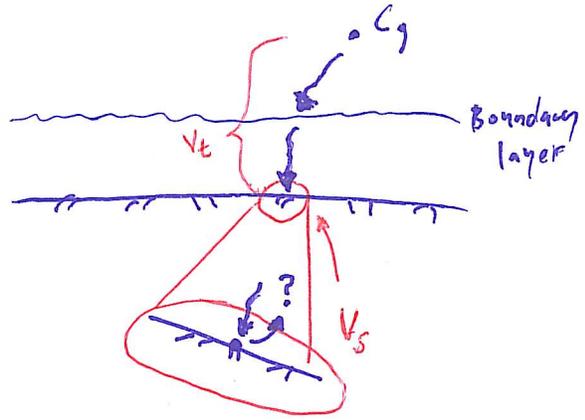
$$\frac{1}{V_d} = \frac{1}{V_t} + \frac{1}{V_s}$$

$V_d$  = deposition velocity [m/hr]     $V_s$  = Surface-limited deposition velocity [m/hr]

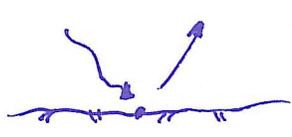
$V_t$  = transport-limited deposition velocity } effectively  $k_g$  from emissions study [m/hr]

$$V_d = \left( \frac{1}{V_t} + \frac{1}{V_s} \right)^{-1} = \frac{1}{\frac{1}{V_t} + \frac{1}{V_s}} = \frac{1}{r_t + r_s}$$

$$V_d = \frac{V_t V_s}{V_s + V_t}$$



Let's consider surface uptake  
(i.e., does a reaction occur?)



$J_s$  = flux of pollutant to surface

$$J_s = \left( \text{rate of molecular collisions w/ surface} \right) \times \left( \text{reaction probability} \right)$$

$y_p = \frac{\text{Pollutant removal rate}}{\text{Pollutant collision rate}} = 0-1 = \text{fraction of all pollutant molecules that collide with a surface that are irreversibly removed.}$     "y"

\* Rate of molecular collisions:

Based on molecular theory of gases, rate =  $\frac{\langle v \rangle}{4} C_s$

$\langle v \rangle$  = the pollutant's Boltzmann velocity = mean velocity of pollutant molecules [m/s]

$C_s$  = pollutant concentration in air adjacent to surface (actually within  $2/3$  of mean free path of air molecules, or within  $2/3$  of  $6.5 \times 10^{-8}$  m (65 nm) @ 25°C 1 atm)

$$\langle v \rangle = \left\{ \frac{8kT}{\pi m} \right\}^{1/2}$$

$k$  = Boltzmann constant =  $1.38 \times 10^{-23}$  J/K

$T$  = absolute air temperature (K)

$m$  = mass of individual pollutant molecule (kg)

$$m = \frac{\text{MW (g/mole)}}{\text{molecules/mole}} \times \frac{\text{kg}}{1000 \text{ g}}$$

Avogadro's # =  $6.023 \times 10^{23}$

Example:  $\text{O}_3$  @ S.T.P  $\Rightarrow \langle v \rangle = \left\{ \frac{8(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(293 \text{ K})}{\pi \left( \frac{48 \text{ g/mol}}{6.023 \times 10^{23}} \right) \left( \frac{1 \text{ kg}}{1000 \text{ g}} \right)} \right\}^{1/2}$

$\approx 360 \frac{\text{m}}{\text{s}}$

$= 3.6 \times 10^4 \frac{\text{cm}}{\text{s}}$

$= \langle v \rangle_{\text{O}_3}$

\* Combining rate of collisions + reaction probability:

$$\frac{J_s}{C_s} = \gamma \frac{\langle v \rangle}{4} C_s / C_s$$

$$\frac{J_s}{C_s} = v_s = \frac{\gamma \langle v \rangle}{4} \rightarrow r_s = \frac{1}{v_s} = \frac{4}{\gamma \langle v \rangle}$$

$$\frac{1}{V_d} = \frac{1}{V_t} + \frac{1}{V_s} \leftarrow \frac{4}{\gamma \langle v \rangle}$$

$$V_d = \frac{V_t V_s}{V_s + V_t}$$

$$\frac{1}{V_d} = \frac{1}{V_t} + \frac{4}{\gamma \langle v \rangle}$$

$$V_d = \frac{V_t \frac{\gamma \langle v \rangle}{4}}{\frac{\gamma \langle v \rangle}{4} + V_t}$$



$$\left( \frac{1}{V_d} - \frac{1}{V_t} \right) = \frac{4}{\gamma \langle v \rangle}$$

$$\therefore \gamma = \frac{4}{\langle v \rangle} \left( \frac{1}{V_d} - \frac{1}{V_t} \right)^{-1}$$

relatively easy to measure

more difficult to measure (function of fluid dynamics)

\* If material is not very reactive ( $\gamma$  is very small):

$$\frac{1}{V_d} = \frac{1}{V_t} + \frac{4}{\gamma \langle v \rangle}$$

then  $\frac{1}{V_d} \approx \frac{4}{\gamma \langle v \rangle}$   
or  
 $V_d \approx \frac{\gamma \langle v \rangle}{4}$

Reactive deposition governed by reactivity of material surface

\* If material is VERY REACTIVE ( $\gamma$  approaches 1):

$V_d \approx V_t$  ← Reactive deposition is governed by  $V_t$ , or the ability to break the boundary layer and come in contact with the material surface

# Reactive deposition

---

- 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 to all materials (1/hr)

# Reactive deposition: Surface vs. Transport

---

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

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

$v_s$  = 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 $\gamma$

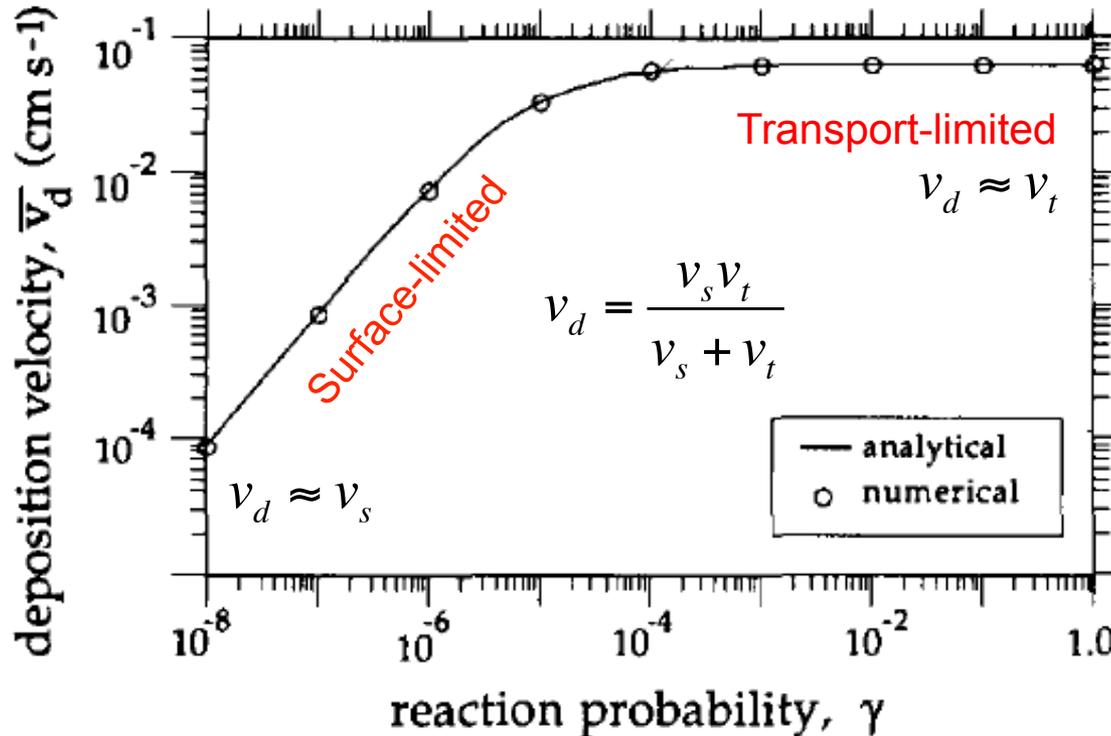


Fig. 1. Average ozone deposition velocity as a function of reaction probability from laminar forced convection flow parallel to a flat plate, with free stream velocity  $U_\infty = 0.1 \text{ m s}^{-1}$ , plate length  $L = 2 \text{ m}$ , ozone diffusivity  $\mathcal{D} = 1.82 \times 10^{-5} \text{ m}^2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

# 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	$2.3 \times 10^{-7}$

# 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	$1.1 \times 10^{-6}$	

# Notes on reaction probability

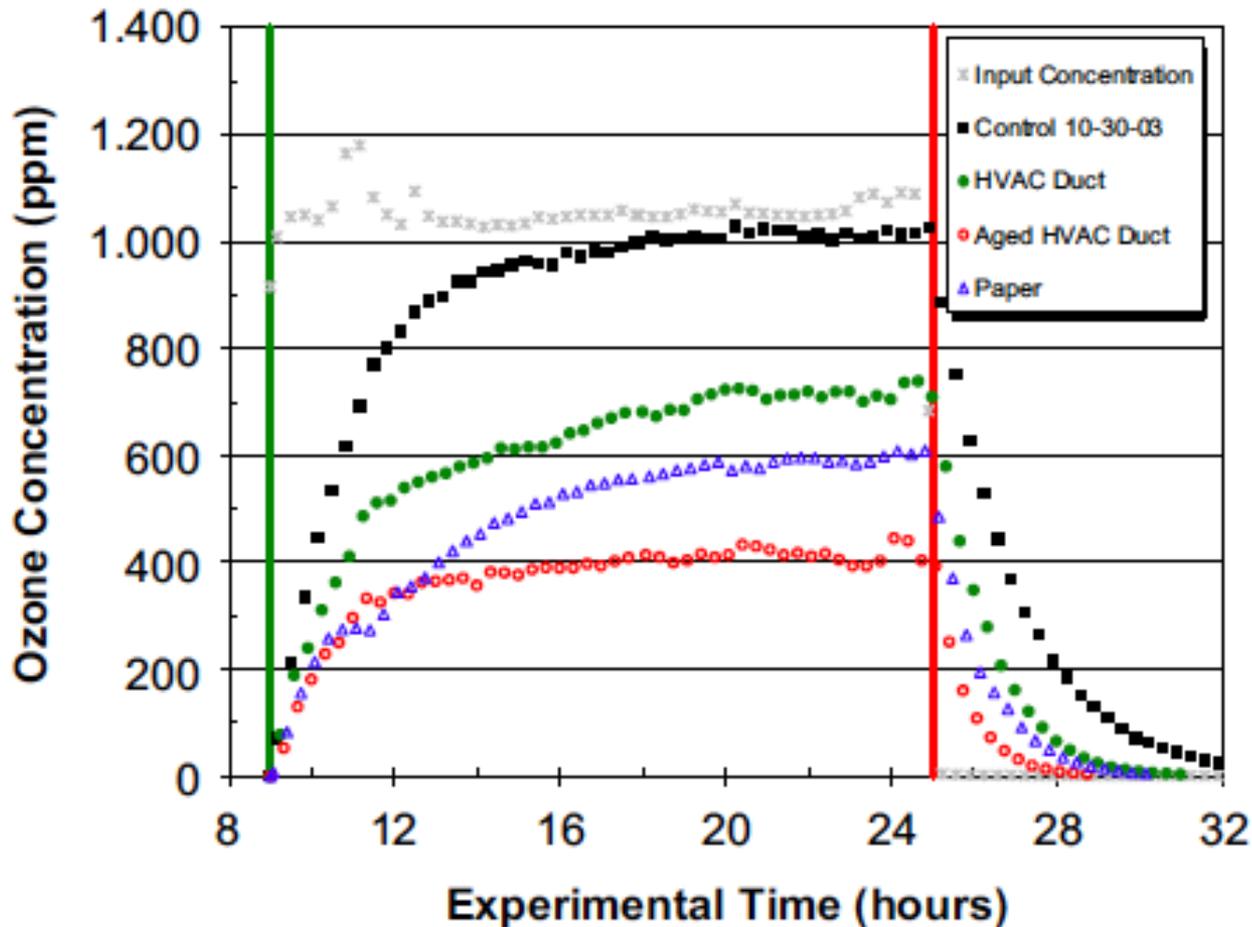
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- Can  $\gamma$  change over time?
  - Yes
- Why?
  - Wipe out reaction sites over time (decreases  $\gamma$ )
  - Humidity effects (water chemistry)
    - RH can increase  $\gamma$
  - Regeneration of reaction sites
    - Diffusion within material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

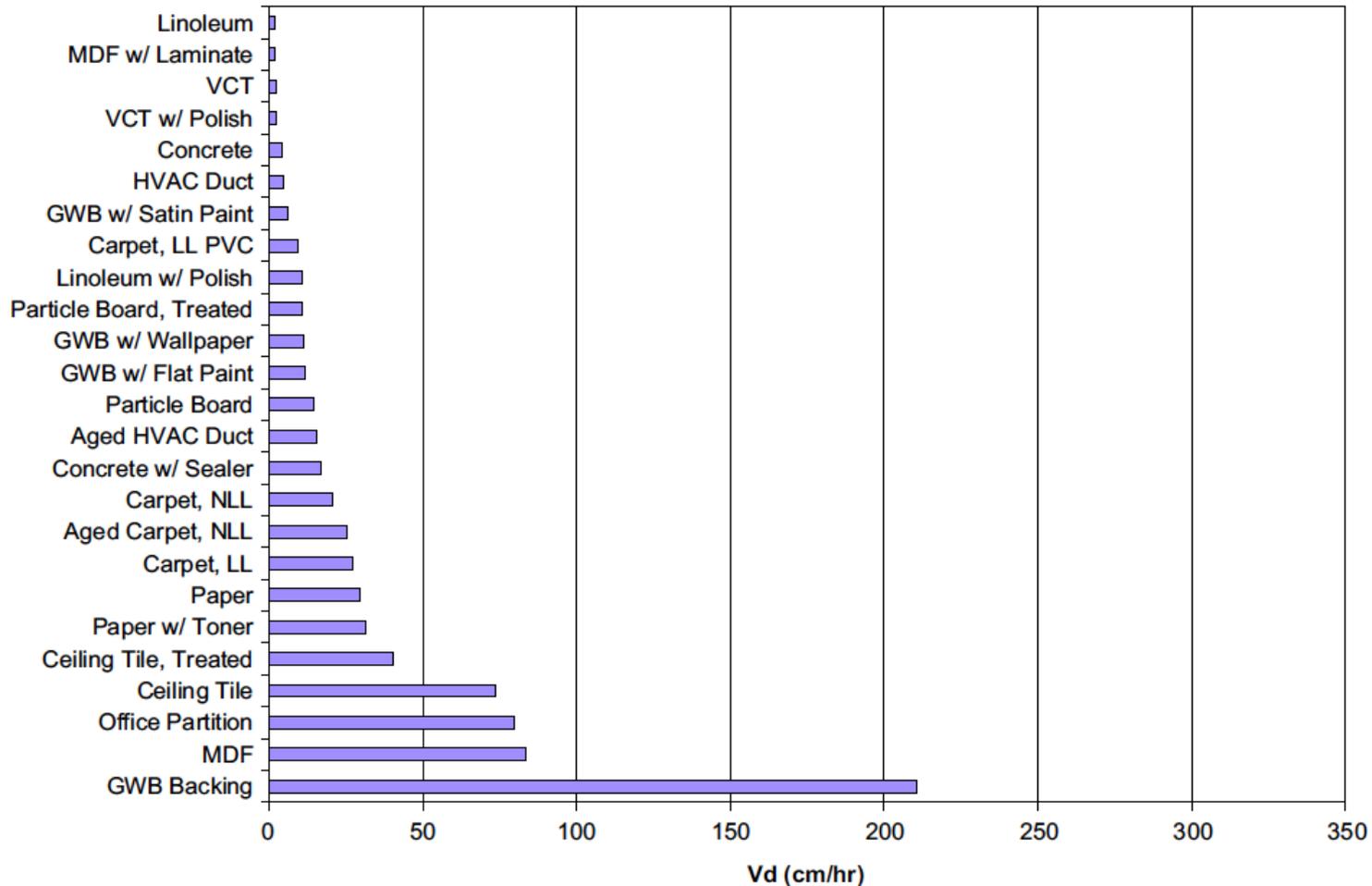


Fig. 5. Geometric mean ozone deposition velocities for last 5 h of disinfection stage.

# Measured $v_d$

- For ozone ( $O_3$ ) on different materials

Material	RH (%)	Temp. (K)	$v_d$ (cm s <sup>-1</sup> )	$v_d$ , aged (cm s <sup>-1</sup> )	$v_t$ (cm s <sup>-1</sup> )	$v_s$ (cm s <sup>-1</sup> )	$v_s$ , aged (cm s <sup>-1</sup> )	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

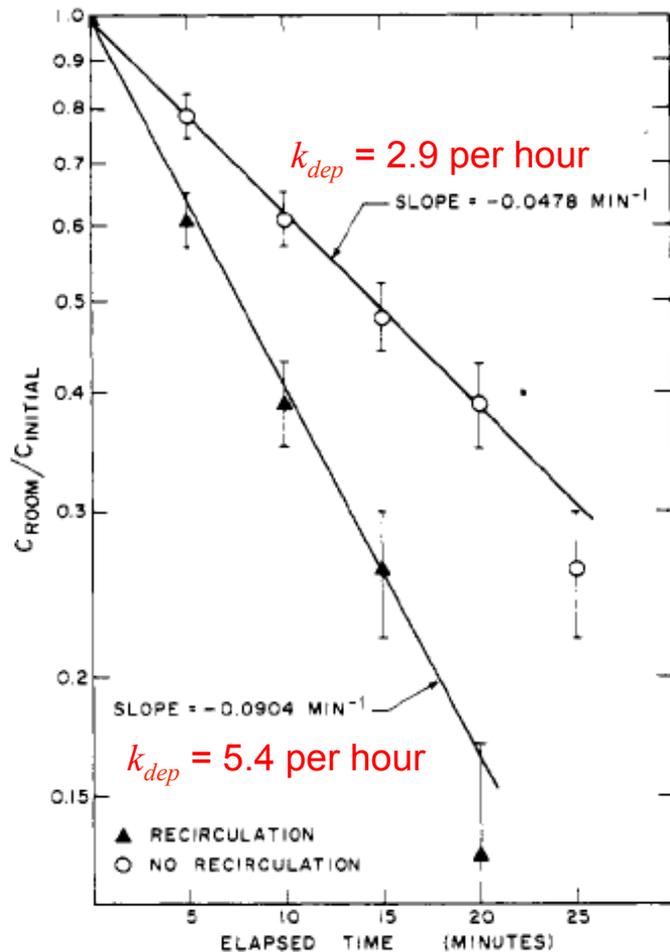
Table 3 Rate Constants ( $h^{-1}$ ) for the Removal of Ozone by Surfaces in Different Indoor Environments

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

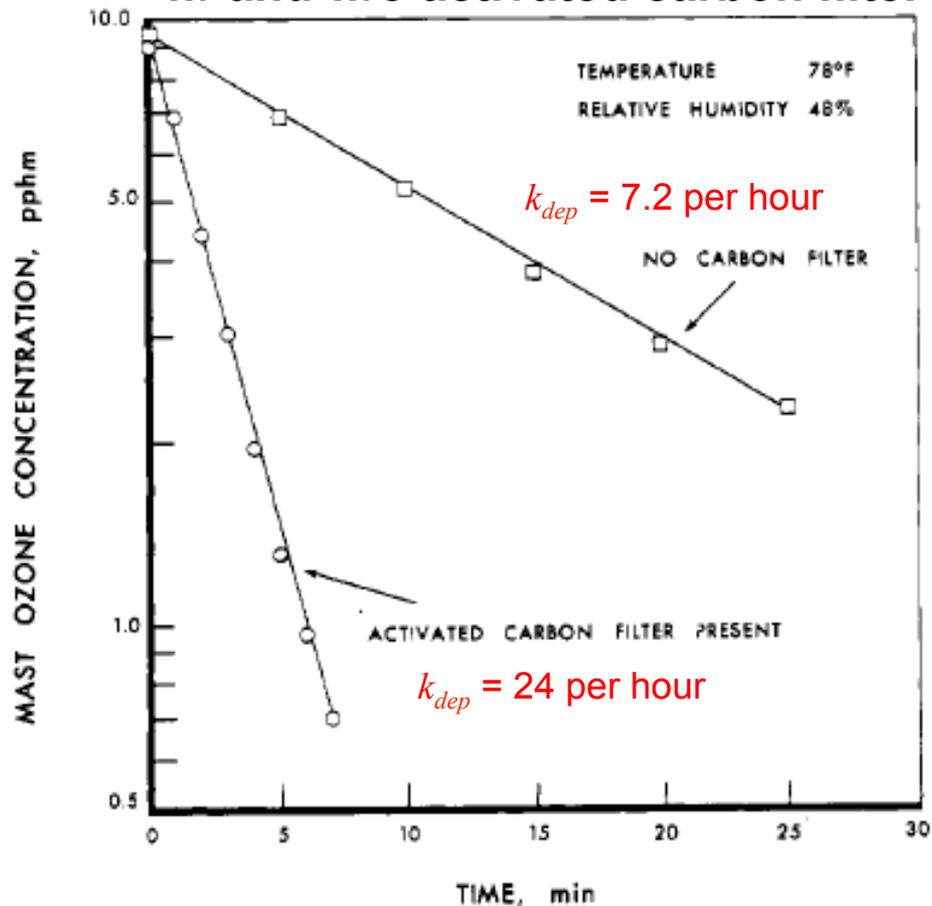
- $k_{dep}$  for ozone ( $O_3$ ) in one room with different HVAC operation

w/ and w/o HVAC on



Sabersky et al., 1973 *Environ Sci Technol*

w/ and w/o activated carbon filter



Mueller et al., 1973 *Environ Sci Technol*

# Measured $v_d A/V$ in real environments

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

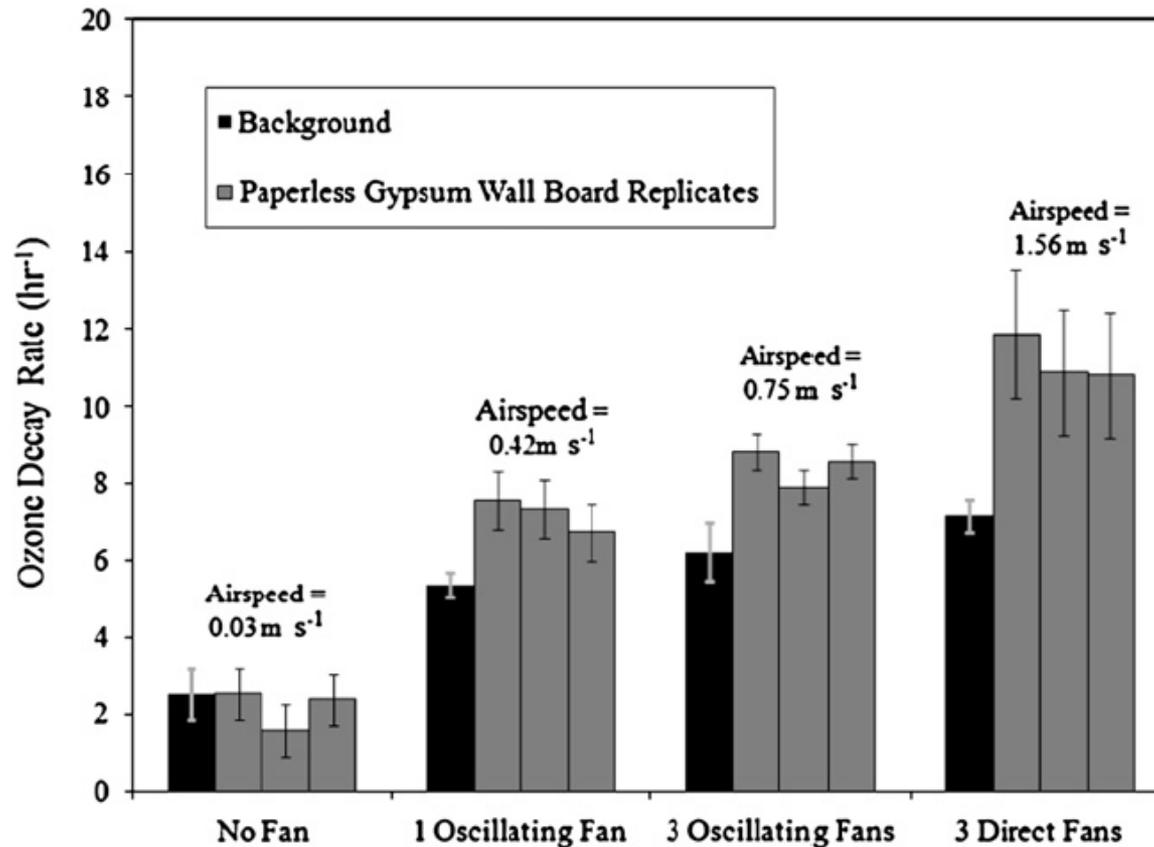


Fig. 5. Ozone decay rates for bedroom with 4.4 m<sup>2</sup> of paperless gypsum wallboard (PLGWB) PRM placed on a vertical wall.

# 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

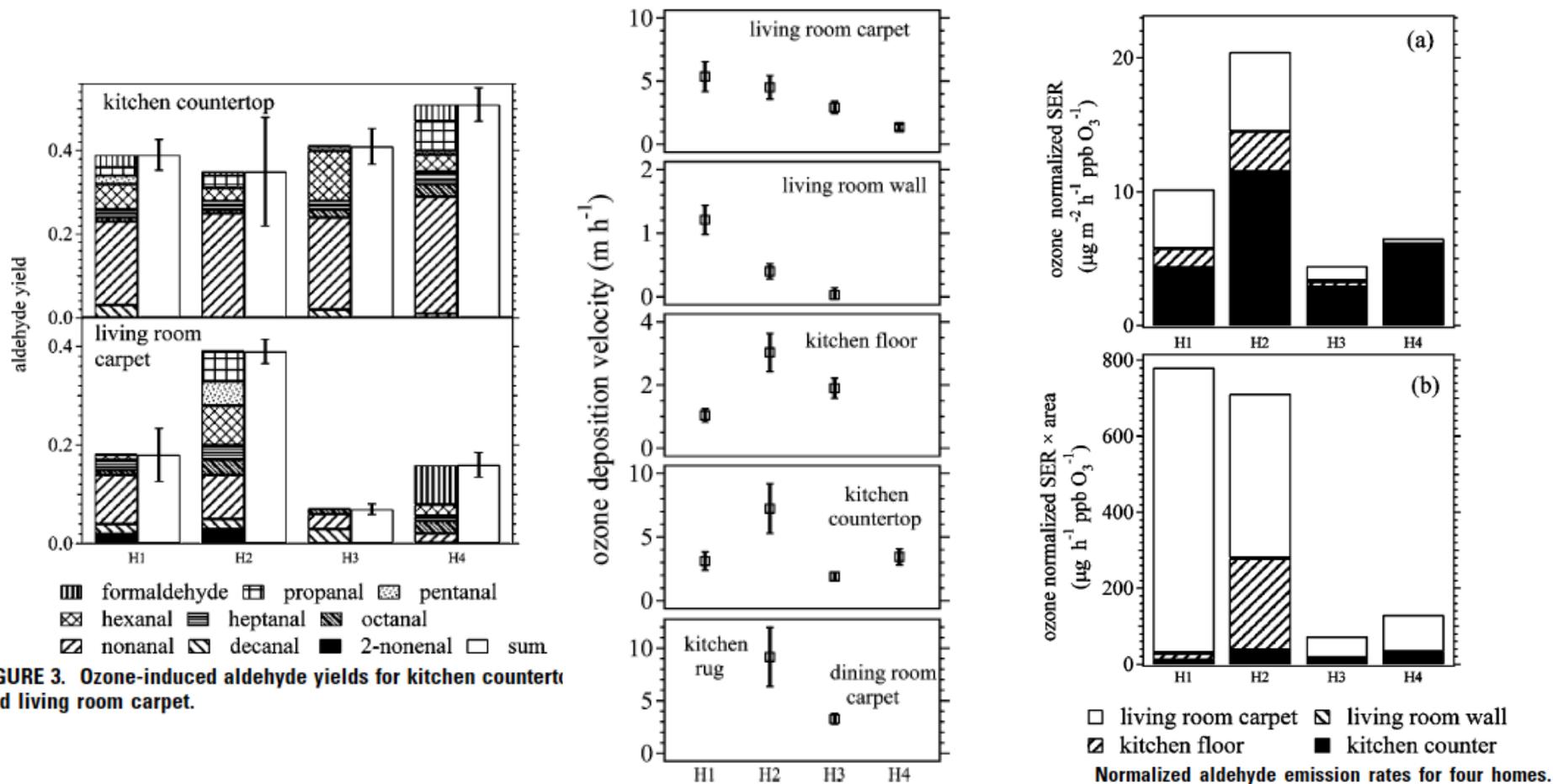


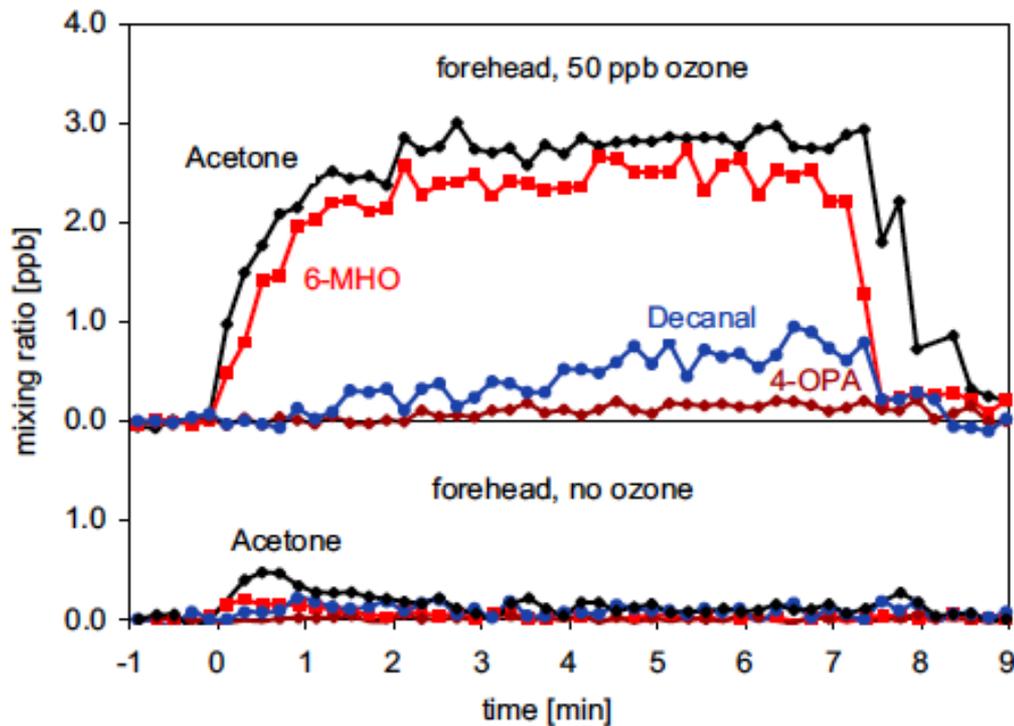
FIGURE 3. Ozone-induced aldehyde yields for kitchen countertop and living room carpet.

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)

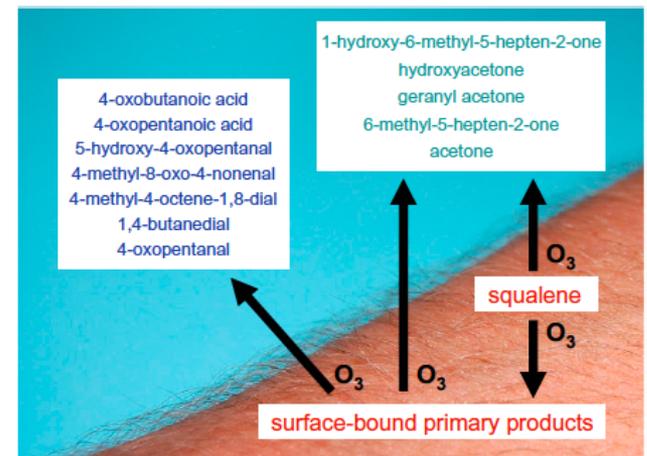


Fig. 4. Schematic of ozone reacting with squalene on exposed skin. The initial reaction produces both gas phase and surface-bound primary products. Ozone further reacts with surface bound primary products (see Table 3) to produce additional gas-phase products.

# **HOMOGENEOUS CHEMISTRY**

# Homogeneous chemistry

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

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

$R_{\text{homogeneous}}$  = 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)

- 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

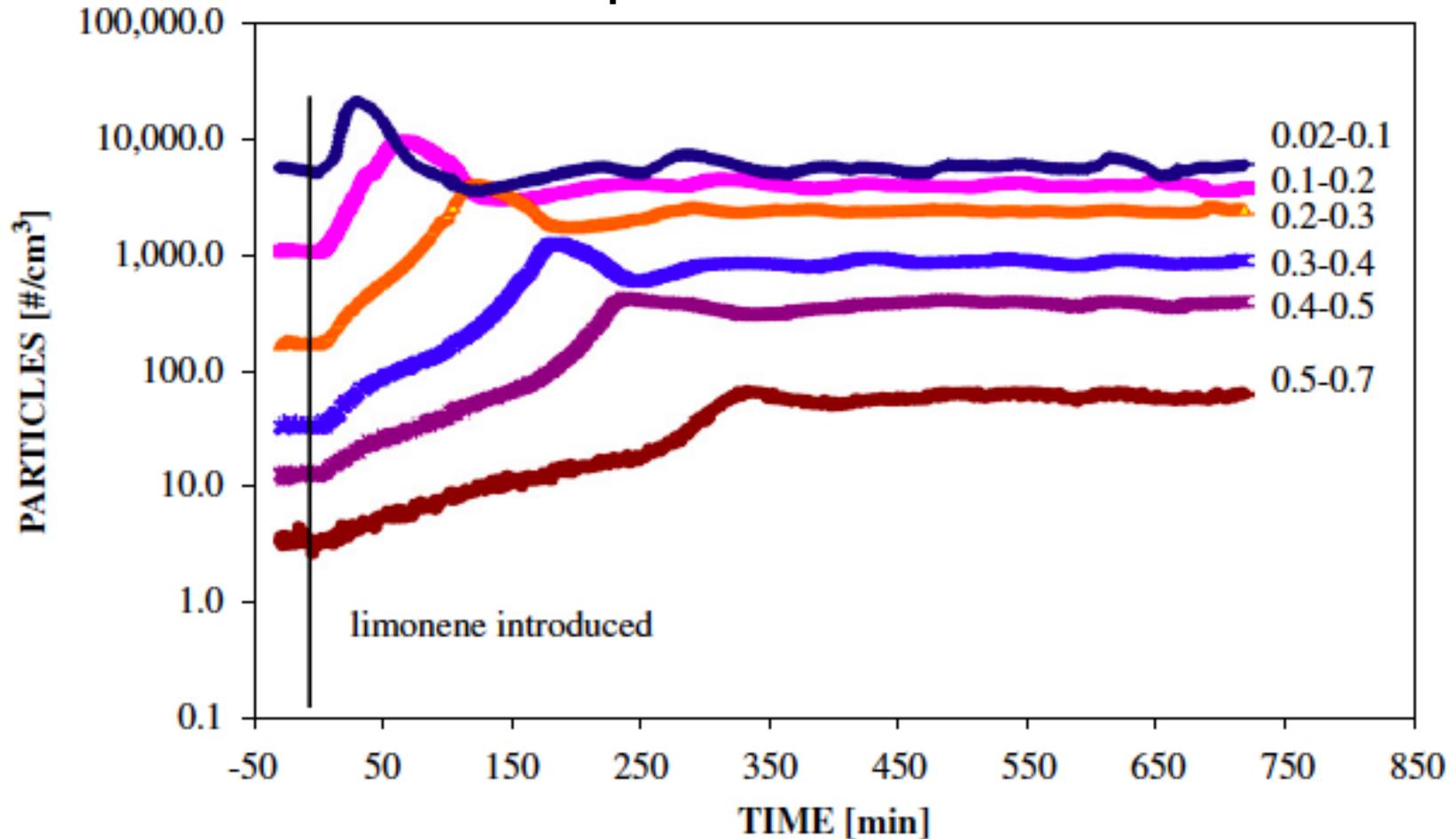
# Homogeneous chemistry

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- Ozone: important driver of homogeneous chemistry indoors
  - 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
  - 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)

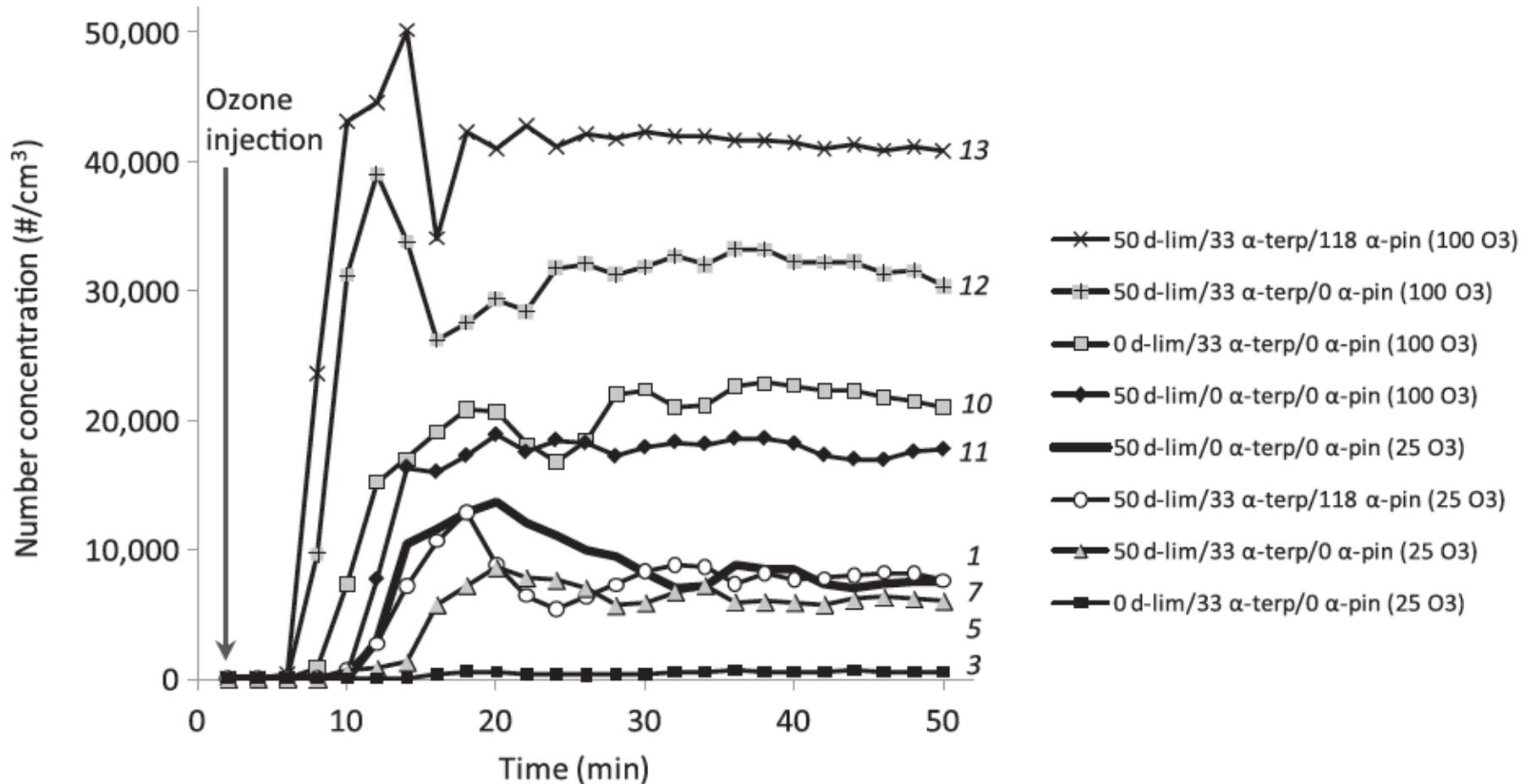
# SOA formation from homogeneous chemistry

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)



# 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
  - Concentrations typically ppt
- 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
- Byproducts from indoor chemistry can be respiratory or skin irritants

# Next time

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- HW 3 assigned today
  - Due next week
- Next week:
  - Discuss project expectations
  - Begin ~3 weeks on particulate matter