

# ENVE 576

# Indoor Air Pollution

Spring 2013

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## Lecture 4: February 5, 2013

Gaseous pollutants: Sources, emission models, and sorption

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

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# HW 1 due

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- HW1
  - If you haven't turned it in, do so now
  - Solutions
    - Emailed back to some of you
    - Some returned now in class
    - Will go over in class
      - If you turn your HW after **right now** you will receive a **maximum** of 35/50 (70%)

# Review from last time

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- Last time (Thursday) we covered:
  - Overview of types of indoor pollutants
    - Inorganic gases, organic gases
    - SVOCs, particles, biological, radioactive
  - Overview of large exposure studies
    - Indoor and personal exposures typically closely related
  - What did we learn?
  
- Today:
  - Teasing out indoor vs. outdoor contributions
    - Finish up from last lecture using RIOPA study
  - Focus on gas-phase pollutants (next 2 lectures)
    - Sources, emission models, and adsorption/desorption today
    - Reactions next week

# **LEARNING FROM EXPOSURE STUDIES**

How do we get at more fundamental parameters than just I/O concentration measurements?

# RIOPA

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- Relationship of Indoor, Outdoor and Personal Air (RIOPA)
- I, O, and P sampling over 48-hours in approximately 100 non-smoking homes in each of Elizabeth, NJ, Houston, TX, and Los Angeles, CA
  - 18 VOCs
  - 17 carbonyls
  - Fine particulate matter (PM<sub>2.5</sub>)
  - AER also measured in each home with PFT
  - Questionnaires were administered to characterize homes, neighborhoods, and personal activities
- I'm just going to show PM<sub>2.5</sub> data

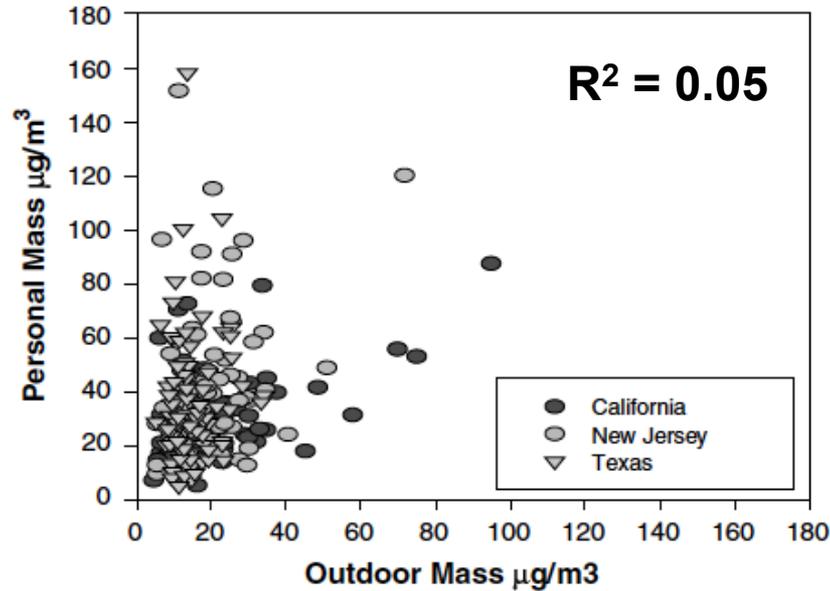
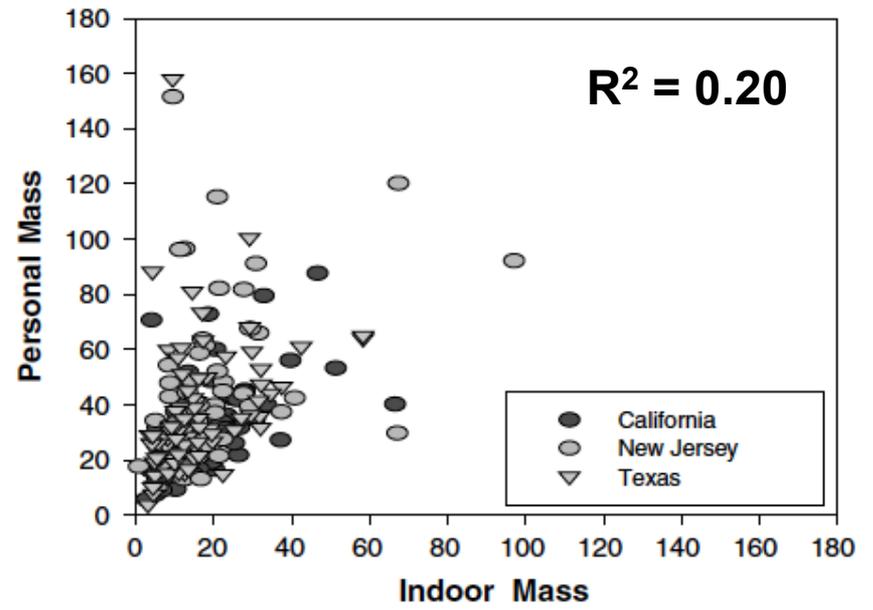
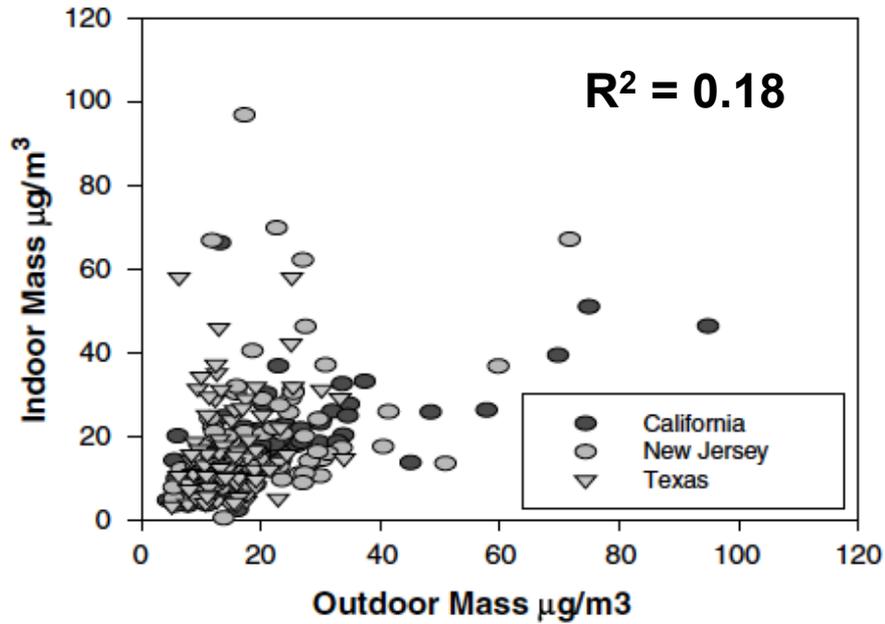
# RIOPA I/O PM<sub>2.5</sub>

- ~300 homes in NJ, TX, and CA

**Table 1.** Indoor, outdoor and personal PM<sub>2.5</sub> mass concentrations ( $\mu\text{g}/\text{m}^3$ ) and air exchange rates (AER;  $\text{h}^{-1}$ ).

Group	Category	Sample size	Mean	Median	STD
Overall study	Indoor	326	17.6	14.4	12.6
	Outdoor	334	18.1	15.5	10.7
	Personal	307	37.6	31.4	24.6
	AER	349	1.06	0.78	0.89
California	Indoor	124	16.2	14.5	9.4
	Outdoor	121	19.2	16.1	13.3
	Personal	106	29.3	26.6	14.8
	AER	131	1.22	0.93	0.87
New Jersey	Indoor	96	20.1	15.7	15.5
	Outdoor	103	20.4	18.2	10.7
	Personal	100	46.9	38.6	30.5
	AER	111	1.22	0.88	0.97
Texas	Indoor	106	17.1	13.4	12.7
	Outdoor	110	14.7	13.2	5.7
	Personal	101	37.2	31.8	23.4
	AER	107	0.71	0.46	0.73

# RIOPA I/O PM<sub>2.5</sub>

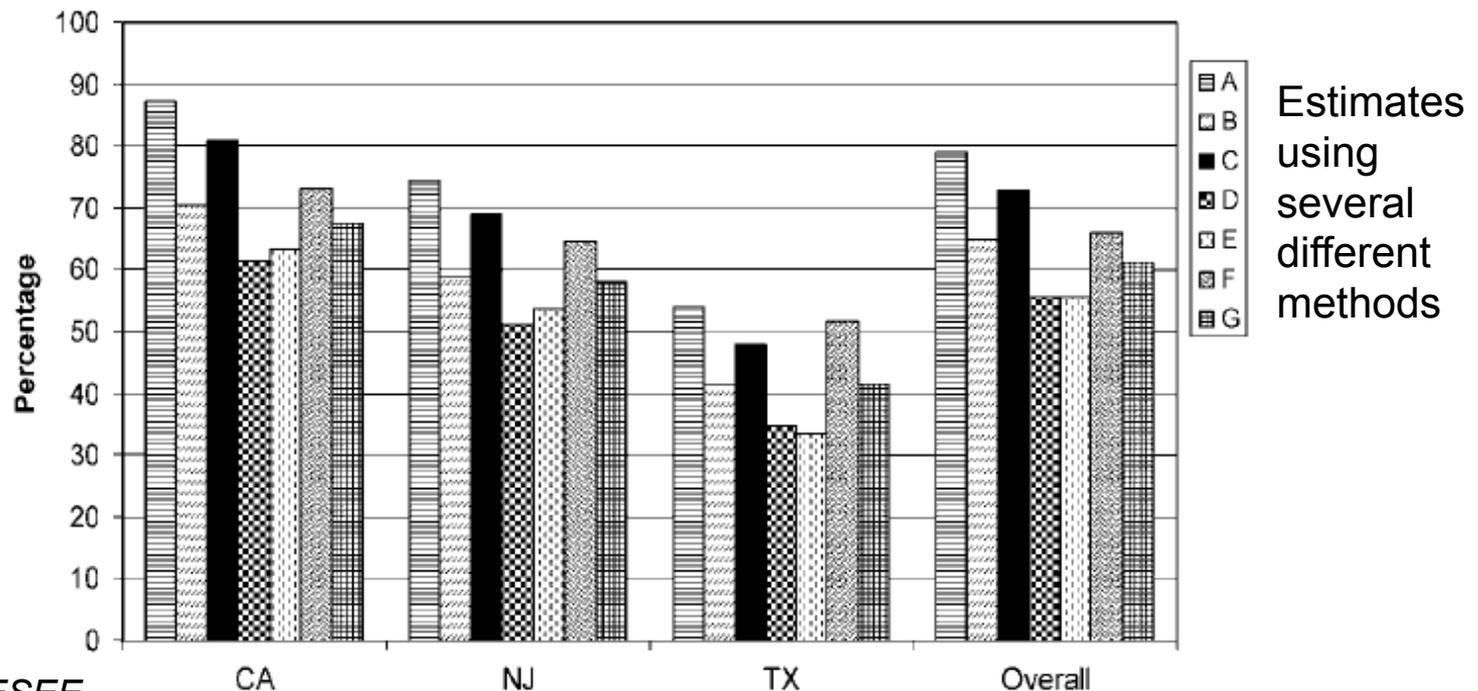


# RIOPA I/O PM<sub>2.5</sub>

- What can we learn about indoor vs. outdoor contributions to indoor PM<sub>2.5</sub> in RIOPA?
  - They fit a model that used measure  $C_i$ ,  $C_a$ , AER ( $a$ ), and estimated  $P$  and  $k$

$$C_i = \frac{PaC_a}{a+k} + \frac{Q_i/V}{a+k} = F_{INF}C_a + C_{pig} = C_{ai} + C_{pig}$$

Median percentage ambient contribution to indoor PM<sub>2.5</sub>



# Indoor and outdoor contributions

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- If we go back to our mass balance, what is a fundamental parameter we need to determine concentrations of pollutants that are primarily emitted indoors?
    - Emission rates,  $E$
- $$C_{ss} = PC_{out} + \frac{E}{\lambda V}$$
- How do we get  $E$ ?
    - Chamber testing
    - Back-calculated from I/O measurements
  - We will discuss back-calculation of I/O measurements first

# Back-calculating E/V

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$$C_{ss} = PC_{out} + \frac{E}{\lambda V}$$

- Rearrange:

$$\frac{E}{\lambda V} = C_{in} - PC_{out}$$

- Solve for E:

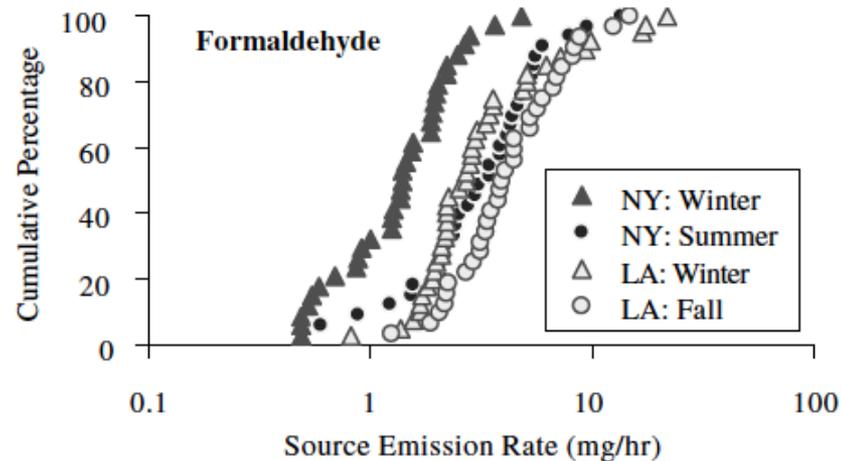
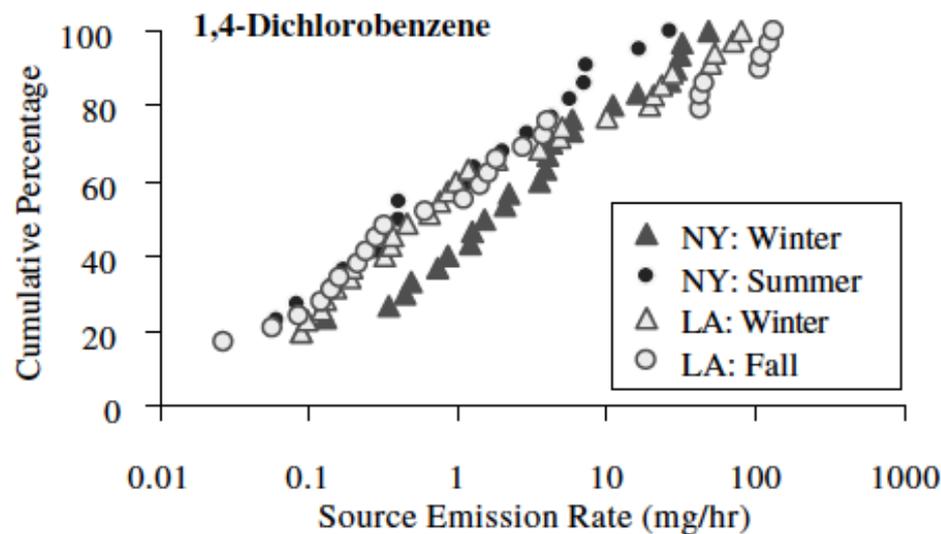
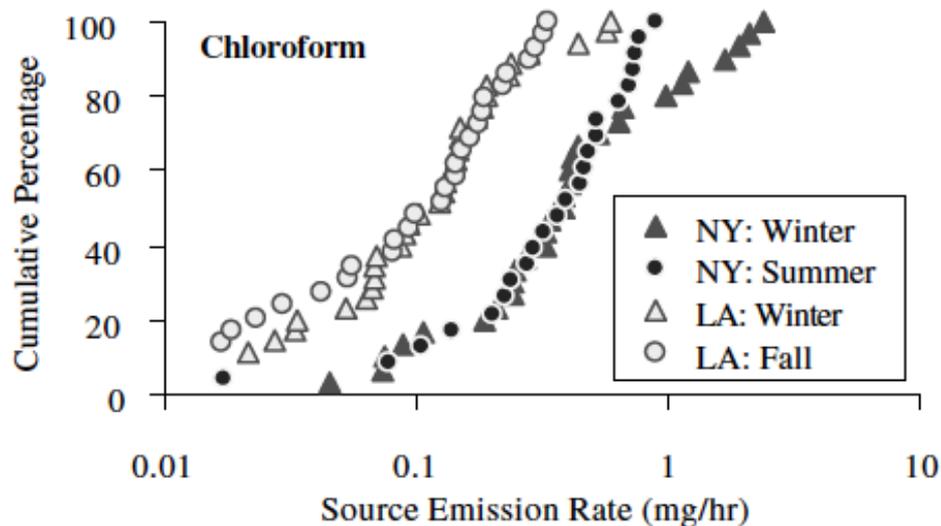
$$E = \lambda V(C_{in} - PC_{out})$$

$$\frac{E}{V} = \lambda(C_{in} - PC_{out})$$

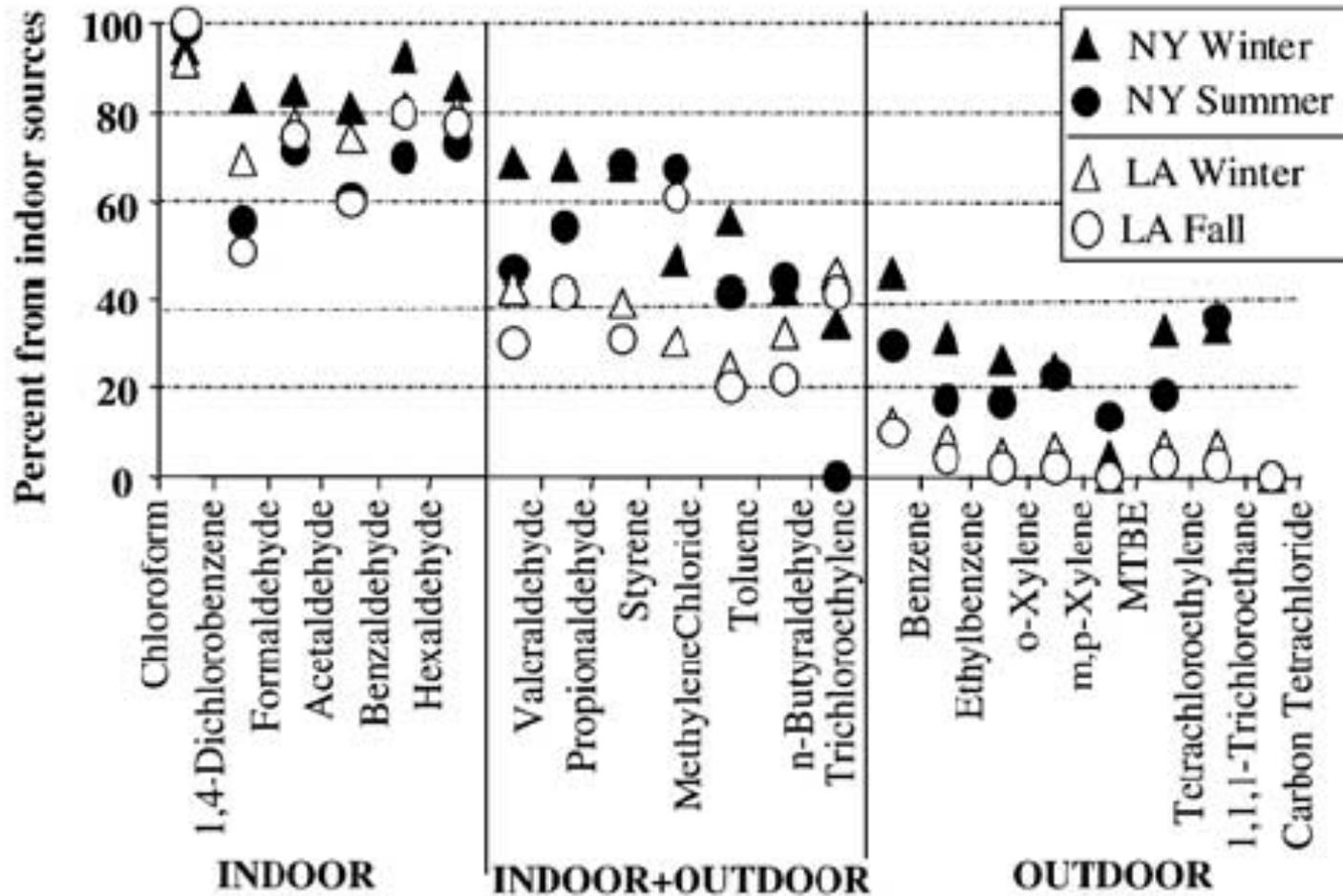
– Or E/V to normalize for volume

- These yield whole-building or **whole-house emission rates**

# Back-calculating E/V from “TEACH” VOC data



# Using E/V and AER to estimate I/O contributions



# A note on indoor emission rates

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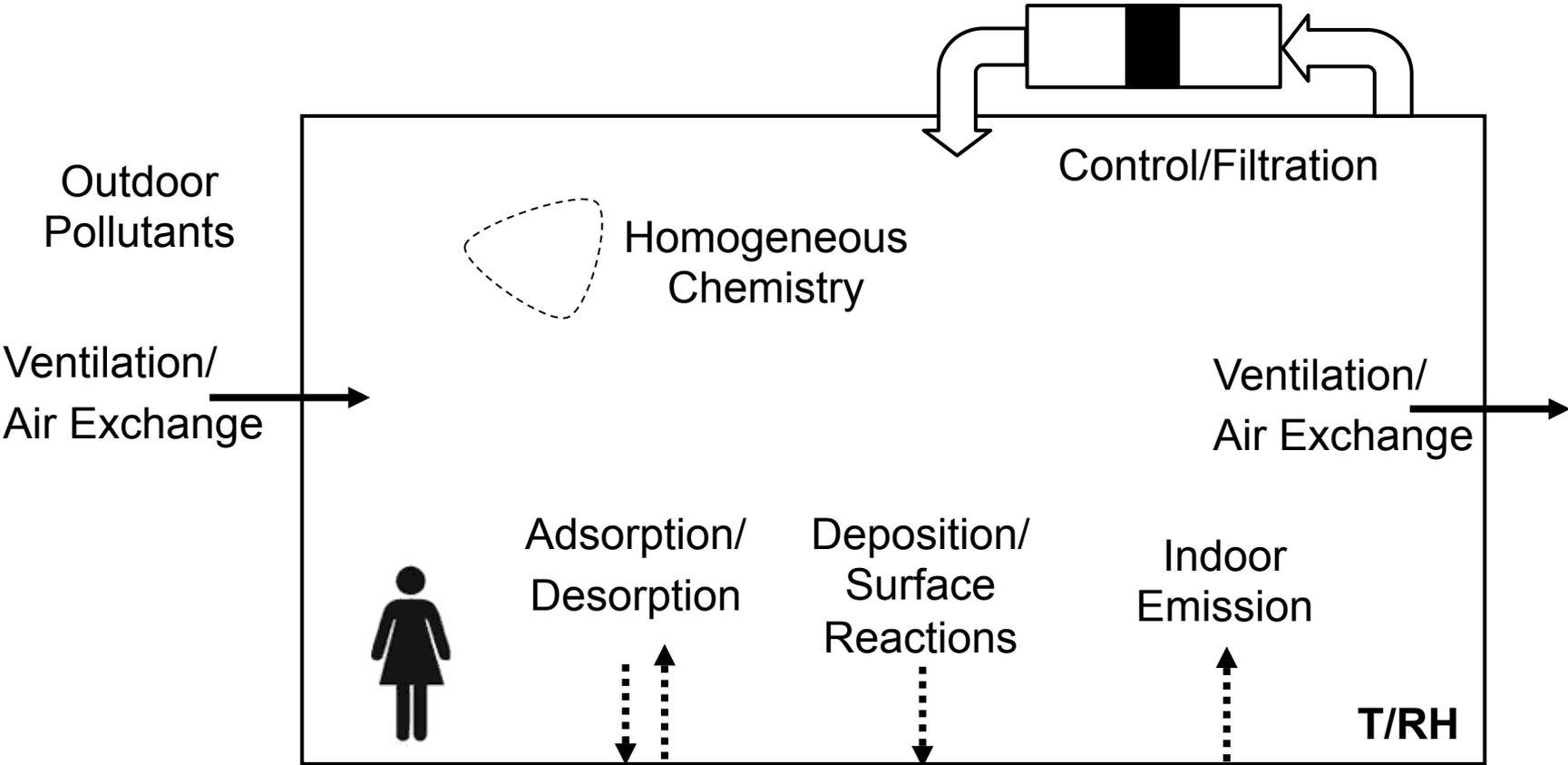
- Previous estimates of whole-house indoor emission rates
- Whole-building emission rate is just the sum of all emission rates from all materials in a building

$$E_{total} = \sum E_i$$

- These can be measured and/or simulated using basic mass transfer experiments and/or models

# **VOC EMISSION FACTORS**

# Indoor environment: Mass balance



# Emissions outline

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- Summarize some emission rate studies
  - IAQ handbook
  - Chamber testing
- Emissions modeling
  - Various sources
- Then:
- Sorption/desorption

# Gas-phase compound emission rates

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- We now know that many indoor materials emit VOCs
  - How would we get emission rates for particular materials?
    - Chamber studies
    - Modeling
- Let's review some previous studies on emission rates from real building materials
  - Then explore how they are measured
  - Then explore how to model them (and what affects them)

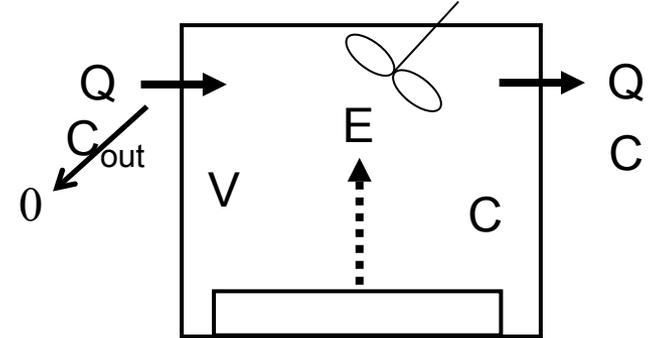
# Emission rate testing → Actual IAQ

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- We perform source testing to help link IAQ, exposure, and risk
- Source testing is typically performed in controlled environmental chambers
- Output results in time-varying concentration data
- Then we do “source modeling” to interpret the concentration data and convert them to emission rates
  - Emission rates can then be used in IAQ models
  - IAQ models can then be used in exposure and risk models

# Emission rate testing

- Begin with a chamber test
  - Well-mixed
  - Controlled inflow ( $C_{out} = 0$ )
  - Controlled T/RH and Q
  - Inert chamber walls
    - Or account for sorption if it occurs
  - Mass balance on chamber:

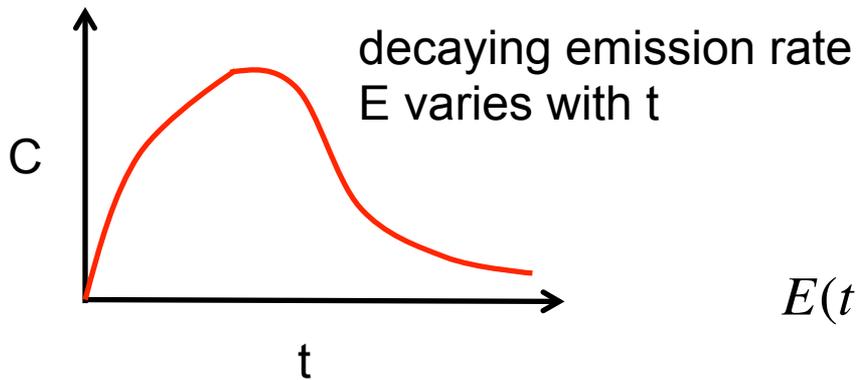
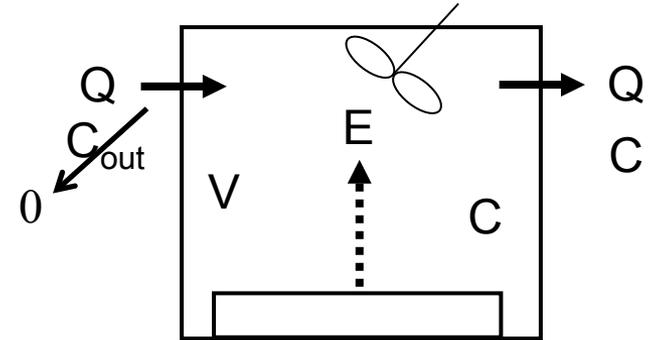
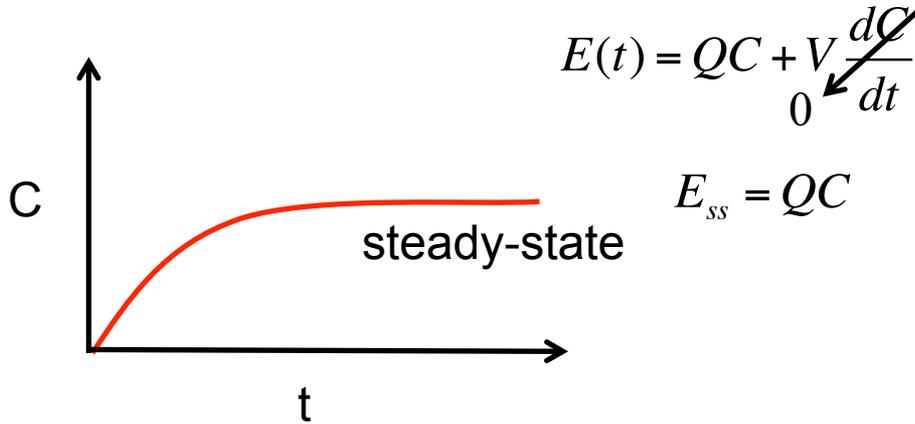


$$V \frac{dC}{dt} = \cancel{QC_{out}} - QC + E$$

$$E(t) = QC + V \frac{dC}{dt}$$

# Emission rate testing

- Two hypothetical concentration profiles



$$E(t) = QC + V \frac{dC}{dt}$$

$$E(t) = QC(t) + V \frac{dC(t)}{dt} \approx QC(t) + V \frac{\Delta C}{\Delta t}$$

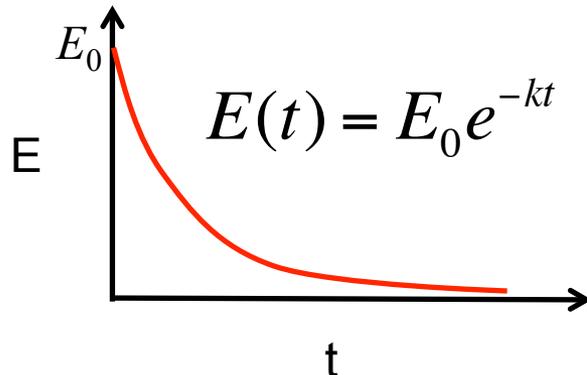
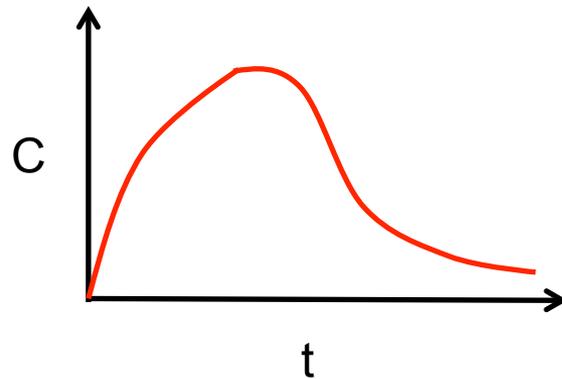
# Emissions testing

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- What do we do with data after we obtain it?
- Emission factors for constant emission rates
  - Looking for mass per time, but can also normalize by an activity
- Examples:
  - Combustion:           mg CO per kJ fuel burned    (need burn rate)  
                                  µg CO<sub>2</sub> per g candle burned (need burn rate)
  - Electronic:           µg O<sub>3</sub> per printed page        (need page/min)
  - Vinyl flooring:       ng phenol per m<sup>2</sup> per hour
- Emission factors are very source specific
  - Can also vary with time

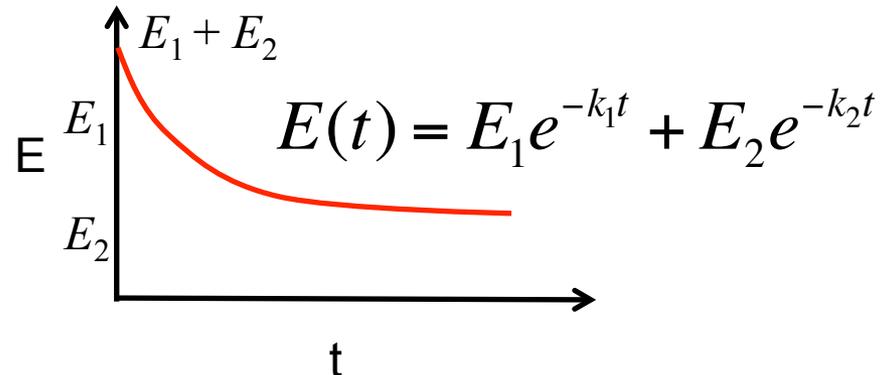
# Emissions: Exponential decay model

- Varying concentration profiles  $\rightarrow$  varying emission rates with  $t$ 
  - We can fit a model for  $E$  vs. time



**1<sup>st</sup> order exponential decay**

rapid decay



**double-exponential decay**

rapid decay w/ lower  
level persistence

*Note that there are ~50 more models used depending on nature of source (Guo, 2002)*

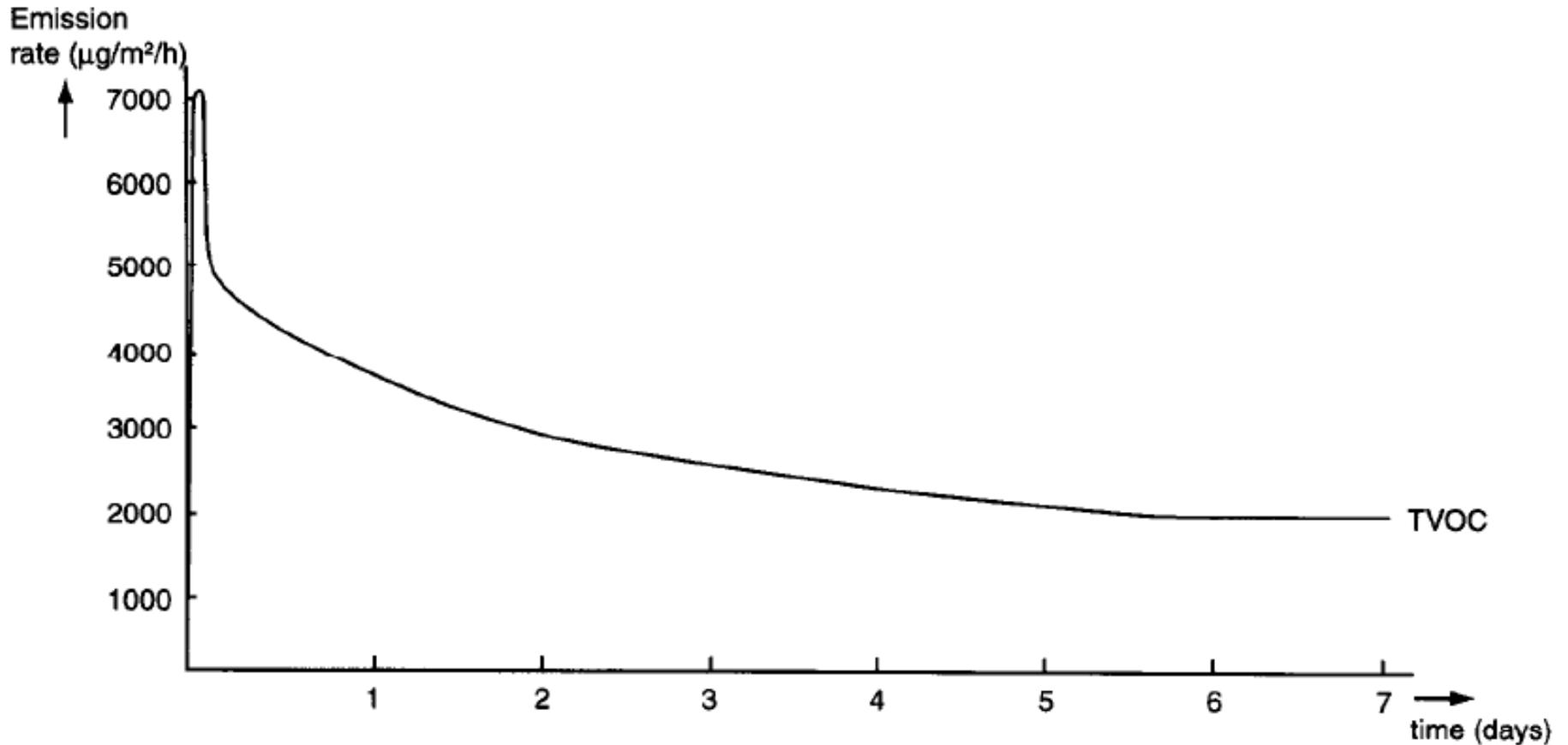
# Emissions models

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- How can there be 50+ different models for emissions?
- Nature of sources can vary widely
  - Combustion vs. ETS vs. personal care products vs. paints vs. building materials vs. animals
- The 50+ identified models can be grouped for use in 7 basic categories of emissions:
  1. Multipurpose
  2. Indoor coatings
  3. Building materials
  4. Evaporating solvent pools
  5. Contaminated household tap water
  6. Pesticide applications
  7. Combustion appliances

# Actual emissions testing: vinyl flooring

- TVOC emission rate from a sample of vinyl flooring (7 days)



# Actual emissions testing: vinyl flooring

- Different emission rate profiles for each constituent!

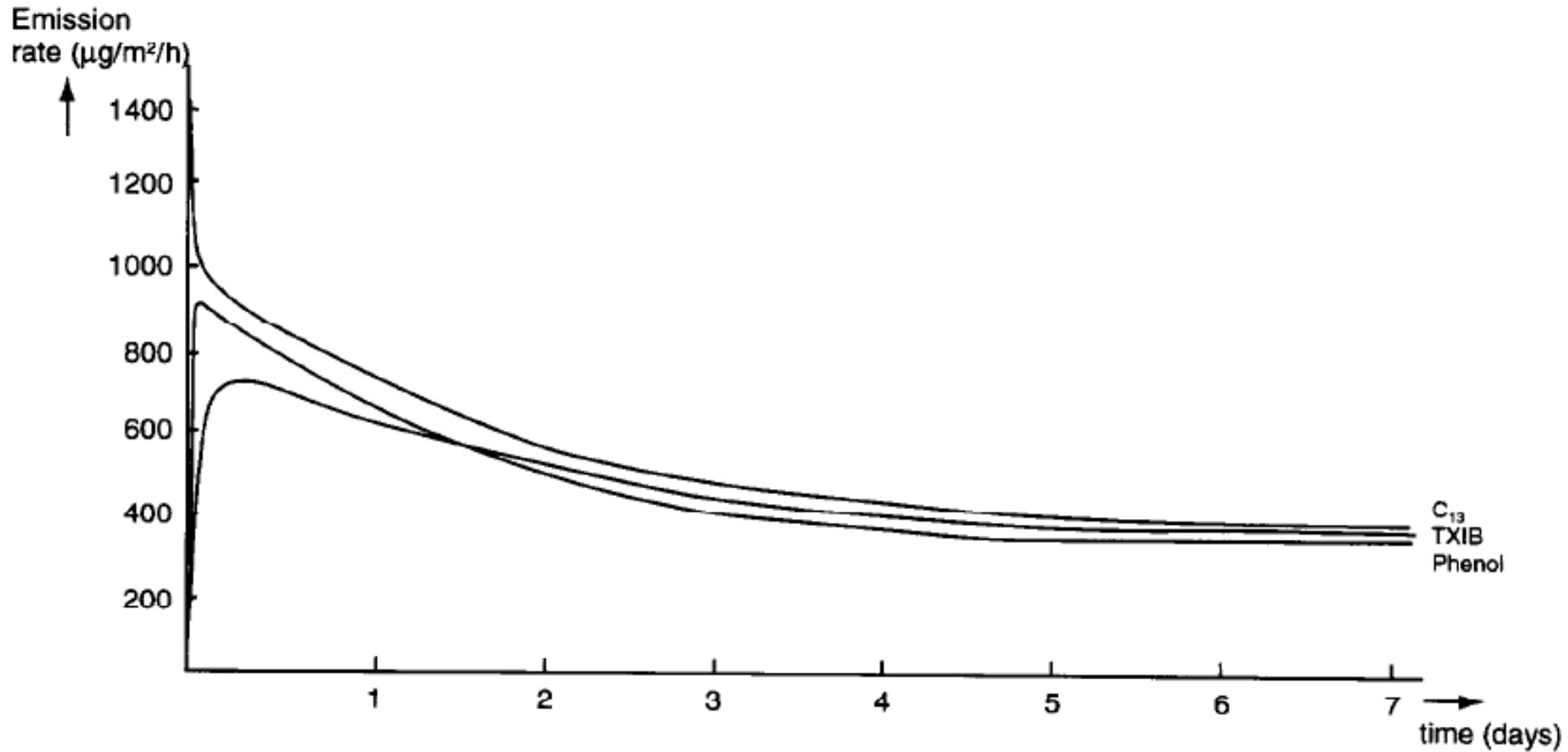


Fig. 2. VOC emission profile of a vinyl flooring sample.

# TVOC emission rates from actual materials

Table 1. A summary of TVOC emission rates from solid polymeric materials

Materials	Range of emission rates ( $\mu\text{g}/\text{m}^2/\text{h}$ )	Comment
Carpet with urethane foam backing	411–6	Emission rate varies with different batches and types of materials tested by different laboratories. The highest emission rates were obtained from materials with no seams. The emission rate declined from 411 $\mu\text{g}/\text{m}^2/\text{h}$ at the first hour of test to 111 $\mu\text{g}/\text{m}^2/\text{h}$ after 6 days. The new materials declined from 62 to 35 and 26 $\mu\text{g}/\text{m}^2/\text{h}$ after 1 day and 20 and 6 $\mu\text{g}/\text{m}^2/\text{h}$ after 6 days.
Textile carpet	83–36	83 $\mu\text{g}/\text{m}^2/\text{h}$ when tested new and 36 $\mu\text{g}/\text{m}^2/\text{h}$ after 3 months.
Carpet with synthetic/pvc fibres	120–11	Tested new as obtained from the manufacturer.
Latex-backed carpet	86–45	Emission rates at 14 days and 6 days of test of new materials obtained directly from the manufacturers.
Carpet assembly	153,000–783	Carpet assembly with adhesive on concrete tested at 24 h of exposure in chamber.
Carpet underlay	8110–12	High variations of emission rates from different types of materials tested. The emission rates were taken at day 6 of the chamber test of new material.
Vinyl/pvc flooring	22,280–91	The age range of these materials tested was from new to 0.5 years to 2 years. The emission rates were high and there was high variation from various types of materials tested.
Vinyl tiles	91–45	Age approx. <98 days.
Rubber floorings	1400	Tested new as obtained from the manufacturers.
Soft plastic flooring	590	Tested new as obtained from the manufacturers.
Linoleum flooring	220–22	New materials produced various emission rates. Aged materials (30 years) could produce high emission rate e.g. 64 $\mu\text{g}/\text{m}^2/\text{h}$ .

# TVOC emission rates from actual materials

Materials	Range of emission rates ( $\mu\text{g}/\text{m}^2/\text{h}$ )	Comment	
Mineral wool insulation batt	15-12	Obtained new from construction sites. Mineral wool and glass wool contain polymeric binding adhesives.	
Glass wool fibrous insulation	4-0.8		
Extruded polystyrene thermal insulants	1400-22	Emission rates from new materials varies, retailed material (< 76 days old) has lower emission rate.	
Extruded polyethylene duct and pipe insulants	0.8-0.28	Materials tested were usually retailed materials.	
Plastic laminated board	0.4	Tested new from manufacturers.	
Vinyl and fibre glass wallpaper	300	All tested new from manufacturers.	
PVC foam wallpaper	230		
PVC wall covering	100		
Vinyl coated wallpaper	95-20		
Vinyl wallpaper	40		
Wallpaper	100-31		
Vapour barriers (bituminous tar)	6.3		124 days old.
Black rubber trim for jointing	103		
Vinyl covering	46-30		<98 days old.
Textile wall and floor coverings	1600		Tested new from manufacturers.
Acoustic partitions	158-6	Emission rates at 1 to 581 h (~ 3.5 weeks).	
Office chair	1060-100	Emission rates at 1 h to 40 days.	
Particleboard	200-28	Emission rates varied with various types of materials tested. New materials produced emission rates from 120-140 $\mu\text{g}/\text{m}^2/\text{h}$ . Aged materials (2 year old) could produce higher emission rate (200 $\mu\text{g}/\text{m}^2/\text{h}$ ).	
Plywood panelling	1450-44	High variations of emission rates from different material. All were tested new from manufacturers.	
Cork floor tiles	805-7	Some are 0.3 years old and some are tested new and some are 2 years old used materials. Cork tiles consist of a thin laminated layer of vinyl plastic and the cork is usually bonded with plastic resins. Phenol is usually detected.	

# TVOC emission rates from actual materials

Table 2. A summary of TVOC emission rates from some liquid and paste products

Materials	Range of emission rates ( $\mu\text{g}/\text{m}^2/\text{h}$ )	Comments
Wall and floor adhesives	271,000–220,000	Emission rates of various types of products tested, at 24 h of chamber exposure.
Carpet adhesives	99,000–76,600	Various types of adhesives tested, at 24 h of exposure.
Low VOC carpet adhesives	698–76	Emission rates at 24 h and 144 h.
Carpet adhesives	17,200–3950	Emission rates obtained at day 6 of test.
Vinyl cove adhesives	5000	Emission rates obtained at day 7 of test.
Wall primer/adhesive	6.1	Emission rates obtained at day 7 of test.
PVA, water-based textured glue	2100	Emission rates obtained at 24 h of test.
Silicone caulk	13,000–< 2000	Highest emission rates were obtained within 10 h and the emission rates declined to less than 2000, between 10–100 h of test.
PVA caulk filler	10,200	Emission rates obtained at 24 h of exposure in chamber.
Sand/cement caulk hardener (water-based)	730	
Latex caulk	637	Emission rate obtained at day 7 of test.
Neoprene/polyethylene caulk	340–16	Emission rates obtained at day 1 of test.
Plasticized pvc/polyethylene caulk	56	Emission rate taken at the 24 h of test.
Caulk putty	340	Emission taken at 24 h of test.
Acrylic latex paint	430–3.2	7 day emission rates in chamber.
Wood stain	10,000 < 100	Emission rate measured at less than 10 h of test and within 100 h.
Polyurethane wood finishes	9000 4700 < 100	Emission rate measured at less than 10 h of test, emission rate at 24 h and after 3 days.
Clear epoxy floor varnish	13,000	Emission rate measured at 24 h of air exposure in chamber.
Acid hardener floor varnish	830	
Plastic sealing agent	72,000	Emission rates measured at 24 h of test.
silicone sealing agent	26,000	
urethane sealant	0.13	
Carpets seam sealants	2960 249 10	Emission rate measured at 1 h of test at 24 h of test at 144 h of test.
Furniture polish	27,100	Initial emission rate,
Floor waxes	80,000 < 5000	at less than 10 h and within 10–100 h of test.

# TVOC emission rates from actual materials

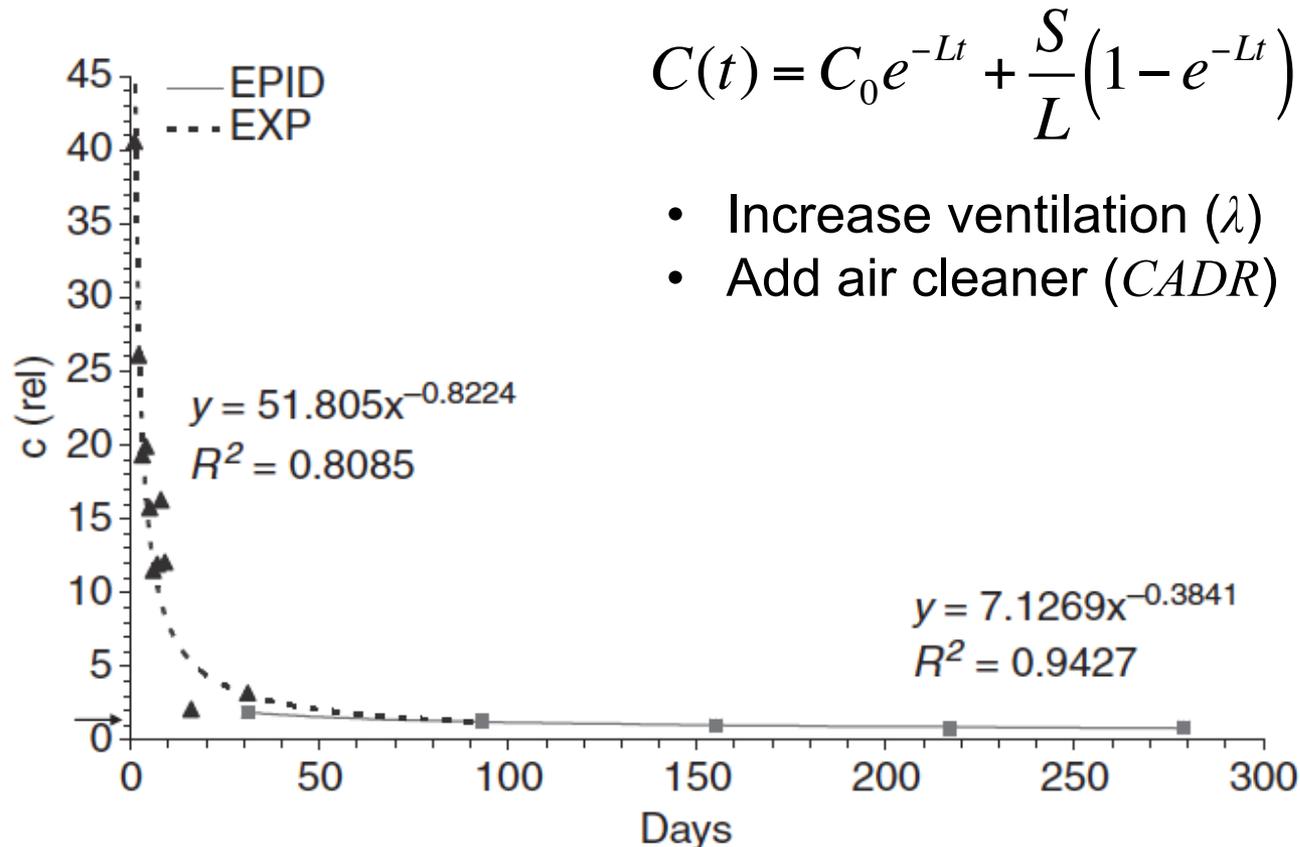
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- *IAQ Handbook* emission factors
  - Page 31.7
  - Handout on BB

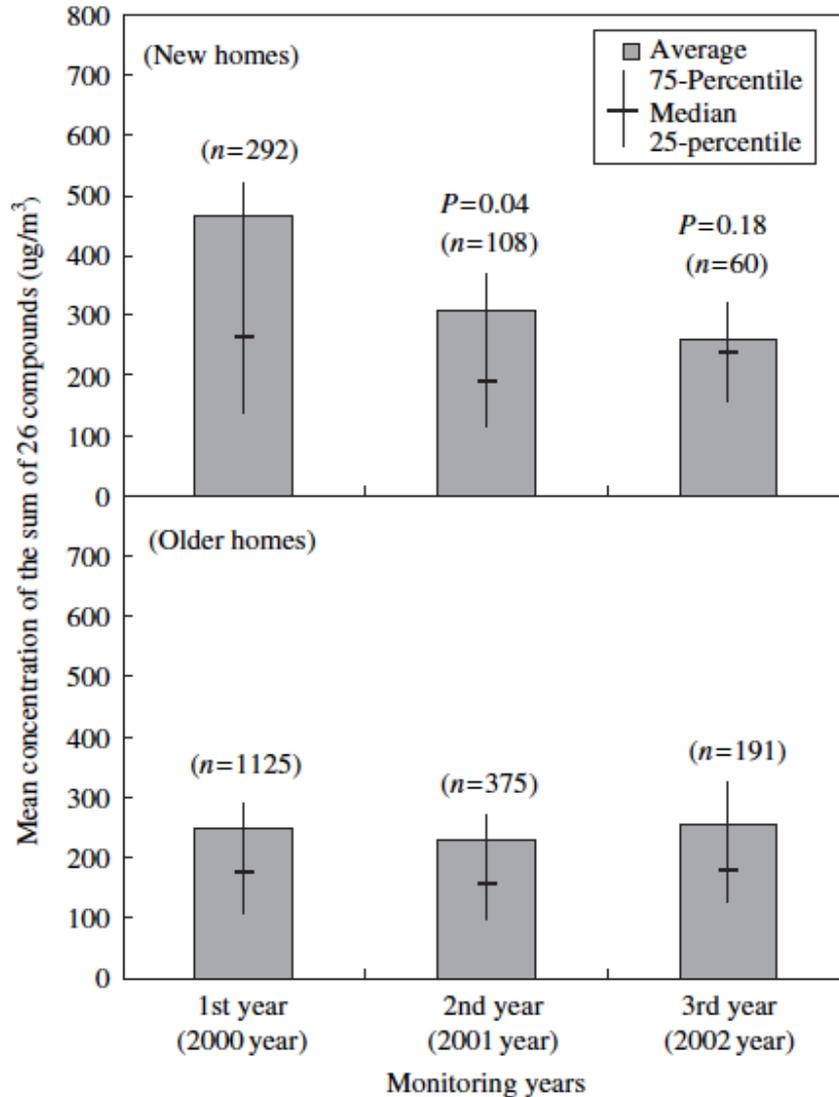
# Time-varying emissions in **real buildings**

Decreasing concentrations of volatile organic compounds (VOC) emitted following home renovations

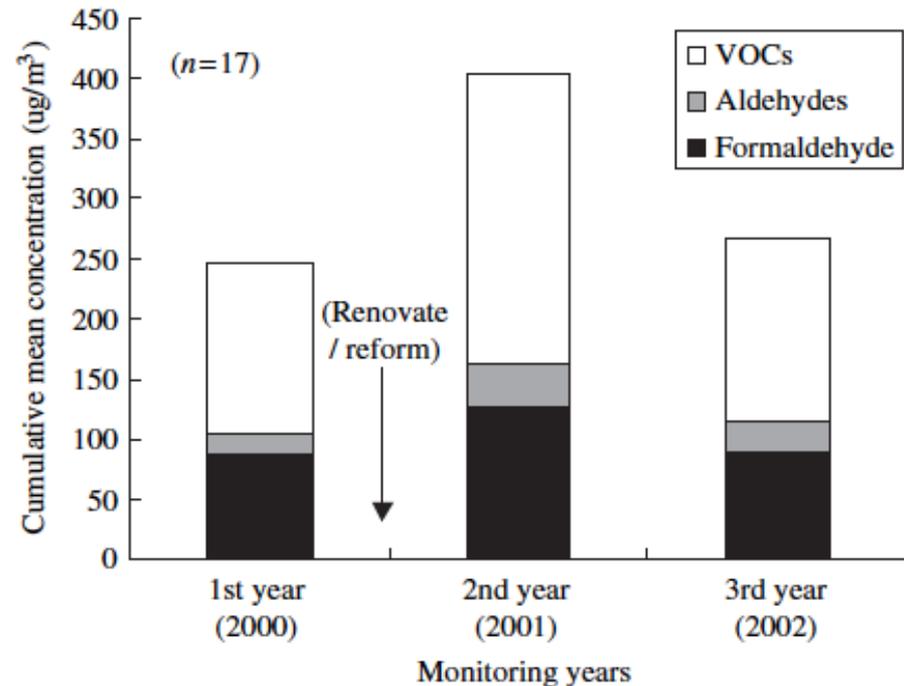
- Suggests 2 weeks to 2 months of vacancy to flush indoor air!
  - What is an alternative?



# Time-varying emissions in **real buildings**



- VOC measurements in Japanese homes over 3 years
  - New and old
  - Pre and post retrofit



# Time-varying emissions: what is happening?

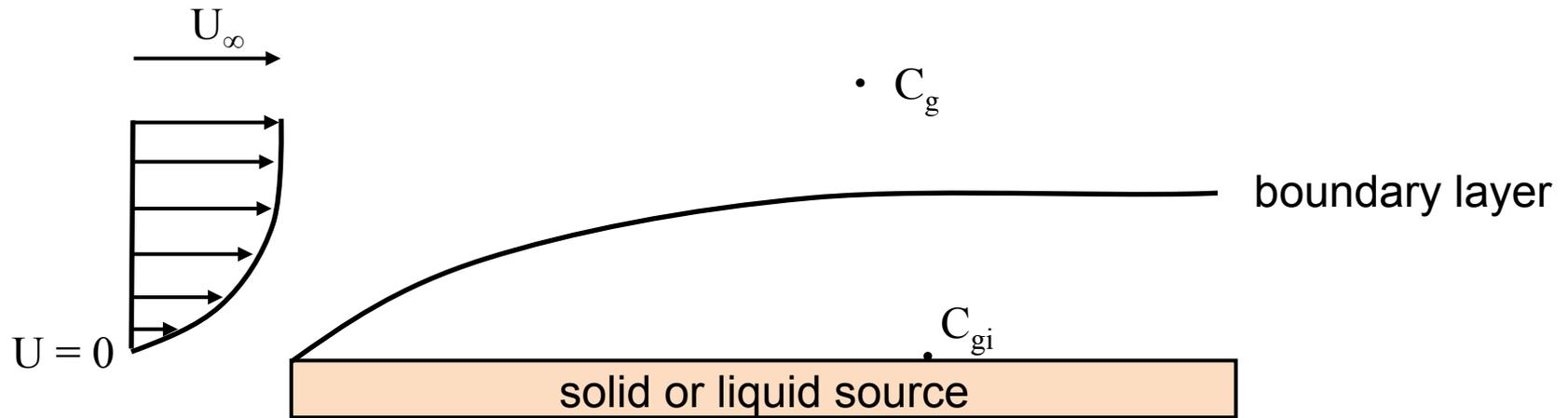
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7 basic categories of emissions from Guo (2002):

1. Multipurpose
  2. Indoor coatings
  3. Building materials
  4. Evaporating solvent pools
  5. Contaminated household tap water
  6. Pesticide applications
  7. Combustion appliances
- What is it about these sources that lead to very different time-varying emissions profiles?
    - Let's cover some basic mass transfer to better understand driving forces of a few of these categories of emissions
      - Won't go into full detail

# Basic mass transfer: smooth flat plate

- Mass transfer: single-film, no diffusion within the source



$$E = k_g (C_{gi} - C_g) A$$

$$\left[ \frac{\mu g}{hr} \right] = \left[ \frac{m}{hr} \right] \left[ \frac{\mu g}{m^3} \right] [m^2]$$

$$C_{gi} - C_g = \text{concentration "driving force"}$$

How do we get  $C_{gi}$ ?

# Concentration at gas-solid interface

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- How do we obtain  $C_{gi}$ ?
- If it is a pure chemical, we can obtain  $C_{gi}$  from vapor pressure

$$PV = nRT \rightarrow P_{vp}V = nRT$$

$$\frac{n}{V} = \frac{P_{vp}}{RT} (MW) \rightarrow C_{sat} = C_{gi} = \frac{P_{vp} (MW)}{RT}$$

- Example: 1,4-dichlorobenzene ( $C_6H_4Cl_2$ )
  - Vapor pressure = 1.76 mm Hg at 25 °C = 0.0023 atm
  - MW = 147 g/mol

$$C_{gi} = \frac{P_{vp} (MW)}{RT} = \frac{(0.0023 \text{ atm})(147 \text{ g/mol})}{(8.205 \times 10^{-5} \frac{\text{m}^3 \cdot \text{atm}}{\text{K} \cdot \text{mol}})(298 \text{ K})} = 13.8 \frac{\text{g}}{\text{m}^3}$$

# Concentration at gas-solid interface

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- If it is a dilute aqueous solution → use Henry's law
  - Think: liquid cleaner

$$H_c = \frac{C_{gas}}{C_{liq, eq}} \rightarrow C_{gi} = C_{liq, eq} H_c$$

- So if you know typical liquid concentration and know  $H_c$  for the compound of interest, you can estimate  $C_{gi}$ 
  - Example: let's say alpha-terpeniol in some liquid cleaner @ 10%
    - Say that's ~100 g/L or 100 kg/m<sup>3</sup>
  - Back to TOXNET (or other places):
    - $H_c$  for alpha-terpeniol =  $2.3 \times 10^{-6}$  atm·m<sup>3</sup>/mol

$$C_{gi} = C_{liq, eq} H_c = \left(100 \frac{\text{kg}}{\text{m}^3}\right) \left(2.3 \times 10^{-6} \frac{\text{atm} \cdot \text{m}^3}{\text{mol}}\right) \left(\frac{\text{mol}}{154\text{g}}\right) = 1.5 \times 10^{-6} = 1.5 \text{ ppm}$$

\*Note that units on  $H_c$  can vary

# Concentration driving force

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- In both example cases,  $C_{gi}$  is quite large relative to typical indoor air concentrations
  - *p*-DCB example:  $\text{g/m}^3$  vs.  $\mu\text{g/m}^3$
  - alpha-terpeniol example: ppm vs. ppb

- Driving force is very much in the direction of source-to-air

$$E = k_g (C_{gi} - C_g) A$$

- But as air concentrations increase, driving force is reduced
- And as material source off-gases or evaporates,  $C_{gi}$  decreases
  - Again reduces driving force
- Also temperature effects on both vapor pressure estimation and  $H_c$

$$k_{H,pc}(T) = k_{H,pc}(T^\ominus) \exp \left[ -C \left( \frac{1}{T} - \frac{1}{T^\ominus} \right) \right]$$

$$k_{H,pc} = \frac{p}{c_{aq}} \quad T \uparrow H_c \text{ (gas)} \uparrow C_{gi} \uparrow$$

# Mass transfer coefficient

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- Now we understand concentration gradients can change

$$E = k_g (C_{gi} - C_g) A$$

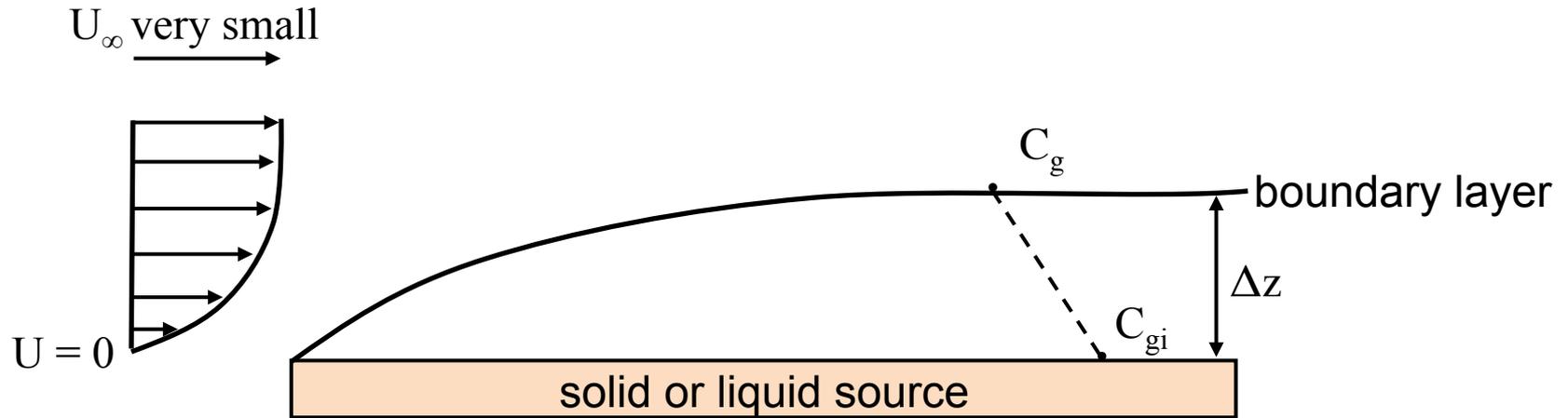
- What is this term  $k_g$ ?

$$\left[ \frac{\mu\text{g}}{\text{s}} \right] = [?] \left[ \frac{\mu\text{g}}{\text{m}^3} \right] [\text{m}^2] \rightarrow k_g = \left[ \frac{\text{m}}{\text{s}} \right]$$

- A mass transfer coefficient simply relates the overall mass transfer rate to the area and concentration driving force
  - Can be estimated theoretically, correlated with experimental data
  - Can be a function of both material properties and airflow regimes

# $k_g$ : Laminar boundary layer case

- All transport by molecular diffusion (basically still air)



- Fick's 1<sup>st</sup> law (1-D diffusion)

$$E = -D \frac{dC}{dz} A \approx -D \frac{\Delta C}{\Delta z} A = -D \frac{C_g - C_{gi}}{\Delta z} A = \frac{D}{\Delta z} (C_{gi} - C_g) A$$

$D = \left[ \frac{\text{m}^2}{\text{s}} \right]$

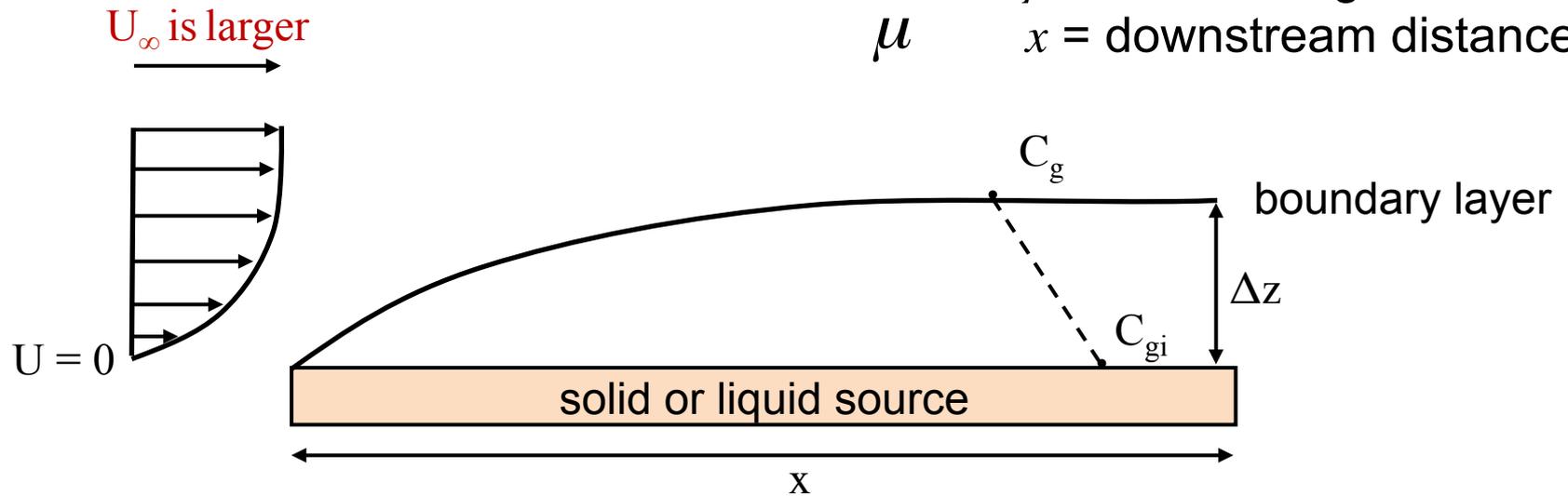
$$k_g = \frac{D}{\Delta z} \rightarrow \text{need } \Delta z, \text{ but difficult to obtain}$$

# $k_g$ : Transition from laminar to turbulent

- Depends on Reynolds # (Re)

$$Re = \frac{\rho U_{\infty} x}{\mu}$$

$\rho = 1.2 \text{ kg/m}^3$   
 $\mu = 1.8 \times 10^{-5} \text{ kg/m-s}$   
 $x = \text{downstream distance}$



- At a given  $x$ , the higher the Re, the thinner the boundary layer
- Transition begins:  $Re = 1 \times 10^5$
- Fully turbulent:  $Re = 3 \times 10^6$  (for a smooth flat plate)

# Transition from laminar to turbulent

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- Typical indoor conditions:  
 $\rho = 1.2 \text{ kg/m}^3$   
 $\mu = 1.8 \times 10^{-5} \text{ kg/m}\cdot\text{s}$   
 $x = 3 \text{ m}$   
 $U_\infty = 20 \text{ cm/s}$

$$\text{Re} = \frac{\rho U_\infty x}{\mu} = \frac{(1.2 \text{ kg/m}^3)(0.2 \text{ m/s})(3 \text{ m})}{1.8 \times 10^{-5} \text{ kg/m}\cdot\text{s}} = 3.9 \times 10^4 \text{ (laminar)}$$

- Typically laminar (unless beneath forced flow jet)
- We can estimate  $k_g$  using basic mass transfer equations
  - Refer to equations on the board / doc cam

# Diffusivities and Schmidt numbers for some VOCs

**Table 1** Diffusivities and Schmidt numbers for VOC indoor pollutants

Pollutant	Diffusivity (m <sup>2</sup> /h)	Schmidt No. Sc	Sc <sup>0.33</sup>
p-dichlorobenzene	0.026	2.12	1.28
Formaldehyde	0.06	0.92	0.97
Decane	0.021	2.63	1.38
Benzene	0.028	1.98	1.25
Perchloroethylene	0.03	1.84	1.22
Ether	0.032	1.72	1.20
m-chlorotoluene	0.023	2.35	1.33
Isopropyl iodide	0.032	1.74	1.20
Octane	0.024	2.31	1.32
Dodecene	0.018	3.06	1.45
Toluene	0.029	1.91	1.24
n-butyl acetate	0.021	2.63	1.38

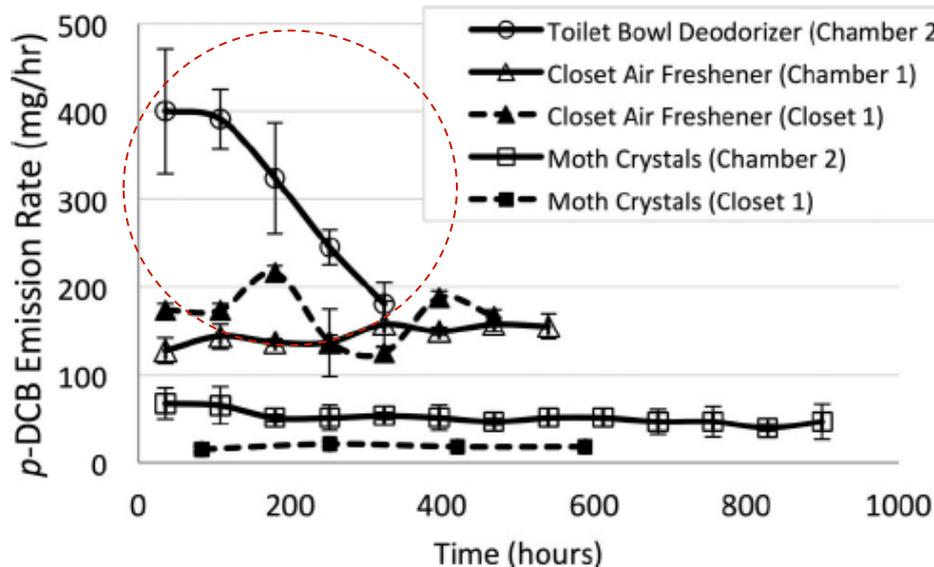
Relating diffusion coefficients with  
 ~reasonable accuracy: 
$$D_2 \approx D_1 \left( \frac{MW_1}{MW_2} \right)^{1/2}$$

# Did our emissions analysis make sense?

- Compare our estimate of ~300 mg/hr from a pure p-DCB toilet bowl deodorizer to measured values

Table 1. Conditions for p-dichlorobenzene experiments

Product	Environment	Volume (m <sup>3</sup> )	AER (hr <sup>-1</sup> )	Duration (Days)	Temperature (°C)	RH (%)	Air Speed (cm/sec)	Initial Surface Area (cm <sup>2</sup> )
Closet air freshener	Chamber 1 <sup>a</sup>	10.8	40	21	22.2 ± 1.0	59.3 ± 5.1	3.1 ± 1.1	23.4 (slots) 211 (cake) <sup>b</sup>
	Closet 1	6.9	4.3	21	23.4 ± 1.7	46.8 ± 4.2	0.8 ± 0.9	23.4 (slots) 210 (cake) <sup>b</sup>
Container of moth crystals	Chamber 2 <sup>a</sup>	12.1	36	38.5	23.3 ± 0.4	39.8 ± 11.1	4.4 ± 2.1	42
	Closet 1	6.9	4.3	28	19.7 ± 3.4	49.8 ± 6.0	0.8 ± 0.9	42
Toilet bowl deodorizer	Chamber 2 <sup>a</sup>	12.1	36	15	22.1 ± 1.0	59.6 ± 5.1	3.1 ± 1.1	121



They also measured larger surface area ( $A$ ), lower air speeds ( $U$ ), smaller  $k_g$ , and reasonably high (non-negligible)  $C_g$

# Source-dependent time-varying emissions models

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## Emission category

## Common emission model

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1. Multipurpose

$$E = E_0 e^{-kt}$$

2. Indoor coatings

$$E = k_g \left( C_T \frac{M_T}{M_{T0}} - C \right)$$

3. Building materials

$$E = k_p (C_E - C)$$

4. Evaporating solvent pools

$$E = \frac{10^3 k_g m (P - P_{\text{act}})}{R_g T_L}$$

5. Contaminated household tap water

$$R = Q_g H C_{LE}$$

6. Pesticide applications

$$N_{ij} = D_{ij} (f_i - f_j)$$

7. Combustion appliances

$$R = a + bt + ct^2 + dt^3$$

---

# Time-varying emissions and mass balances

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- Be careful when trying to incorporate time-varying emissions models into your basic unsteady mass balance
- If  $E$  is a function of  $t$ , then one of our basic assumptions is not valid
  - Not a constant  $E$
- Either need to incorporate an  $E(t)$  function and develop analytical solution that utilizes  $E(t)$
- Or (and this is generally easier) solve mass balance numerically

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

$$\frac{C_t - C_{t-1}}{t_2 - t_1} = P\lambda C_{out,t-1} - \lambda C_{t-1} + \frac{E_{t-1}}{V}$$

$$C_t = C_{t-1} + \left( P\lambda C_{out,t-1} - \lambda C_{t-1} + \frac{E_{t-1}}{V} \right) \Delta t$$

Manually build in  $E(t)$



# Why all this focus on *E* ?

- Why is all this important?
  - One reason is LEED

Table 25: Standards for Environmentally Preferable Paints and Coatings

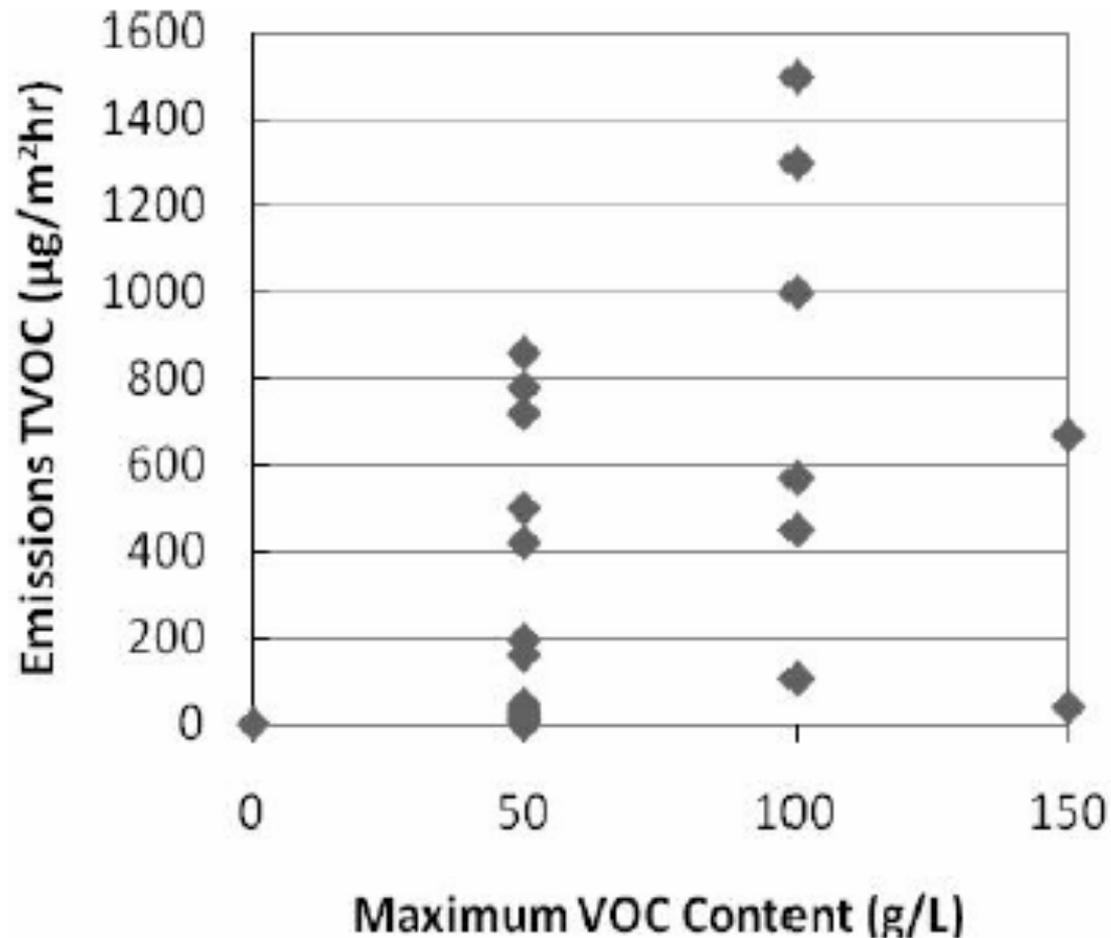
Component	Applicable standard (VOC content)	Reference
Architectural paints, coatings and primers applied to interior walls and ceilings	Flats: 50 g/L Nonflats: 150 g/L	Green Seal Standard GS-11, Paints, 1st Edition, May 20, 1993
Anticorrosive and antirust paints applied to interior ferrous metal substrates	250 g/L	Green Seal Standard GC-03, Anti-Corrosive Paints, 2nd Edition, January 7, 1997
Clear wood finishes	Varnish: 350 g/L Lacquer: 550 g/L	South Coast Air Quality Management District Rule 1113, Architectural Coatings
Floor coatings	100 g/L	
Sealers	Waterproofing: 250 g/L Sanding: 275 g/L All others: 200 g/L	
Shellacs	Clear: 730 g/L Pigmented: 550 g/L	
Stains	250 g/L	

LEED® for Homes  
Rating System



# Does VOC content correlate to emissions?

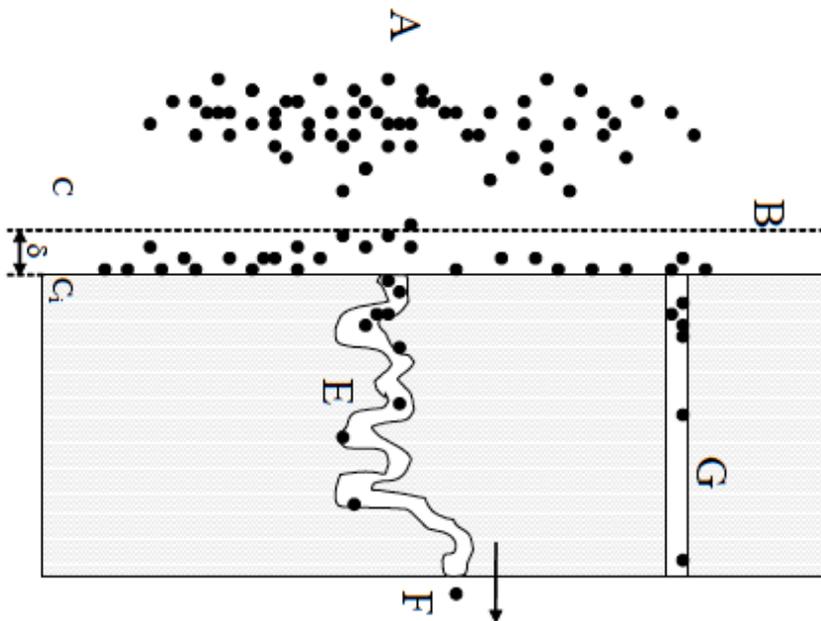
- Chamber emissions vs. VOC content for paint products applied to drywall



- Not exactly

# Does VOC content correlate to emissions?

- Why not?
- One reason may be diffusion within a material
  - We haven't accounted for this yet, and won't go into much detail
  - Diffusion through porous material will change  $C_{gi}$



$$\varepsilon V \frac{dC}{dt} = -A_x \varepsilon D \left. \frac{dC}{dx} \right|_{i-1/2} + A_x \varepsilon D \left. \frac{dC}{dx} \right|_{i+1/2}$$

$$\frac{dC}{dt} = -D \left\{ \left. \frac{dC}{dx} \right|_{i-1/2} - \left. \frac{dC}{dx} \right|_{i+1/2} \right\} \frac{A_x}{V}$$

$$\frac{dC}{dt} = -\frac{D}{\Delta x} \left\{ \left. \frac{dC}{dx} \right|_{i-1/2} - \left. \frac{dC}{dx} \right|_{i+1/2} \right\}$$

$$\frac{dC}{dt} = D \frac{d^2 C}{dx^2}$$

$$\frac{dC}{dt} = D_{eff} \frac{d^2 C}{dx^2}$$

# Effective diffusion coefficients, $D_{eff}$

- Effective diffusion coefficients account for a material's porosity, tortuous path lengths, and affinity for particular compounds

material	$D_{eff}$ [ $10^{-6}$ m <sup>2</sup> /h]
<b>Octane</b>	
PVC floor covering	23
wallpaper with paste	1261
carpet with SBR backing	32
acrylic paint on woodchip paper	2736
aerated concrete	374
solid concrete	1170
brick wall	3021
gypsum board	
<b>Ethyl Acetate</b>	
PVC floor covering	30
wallpaper with paste	1626
carpet with SBR backing	41
acrylic paint on woodchip paper	> 2038
aerated concrete	> 182
solid concrete	1705
brick wall	4051
gypsum board	

Relating  $D_{eff}$  values:

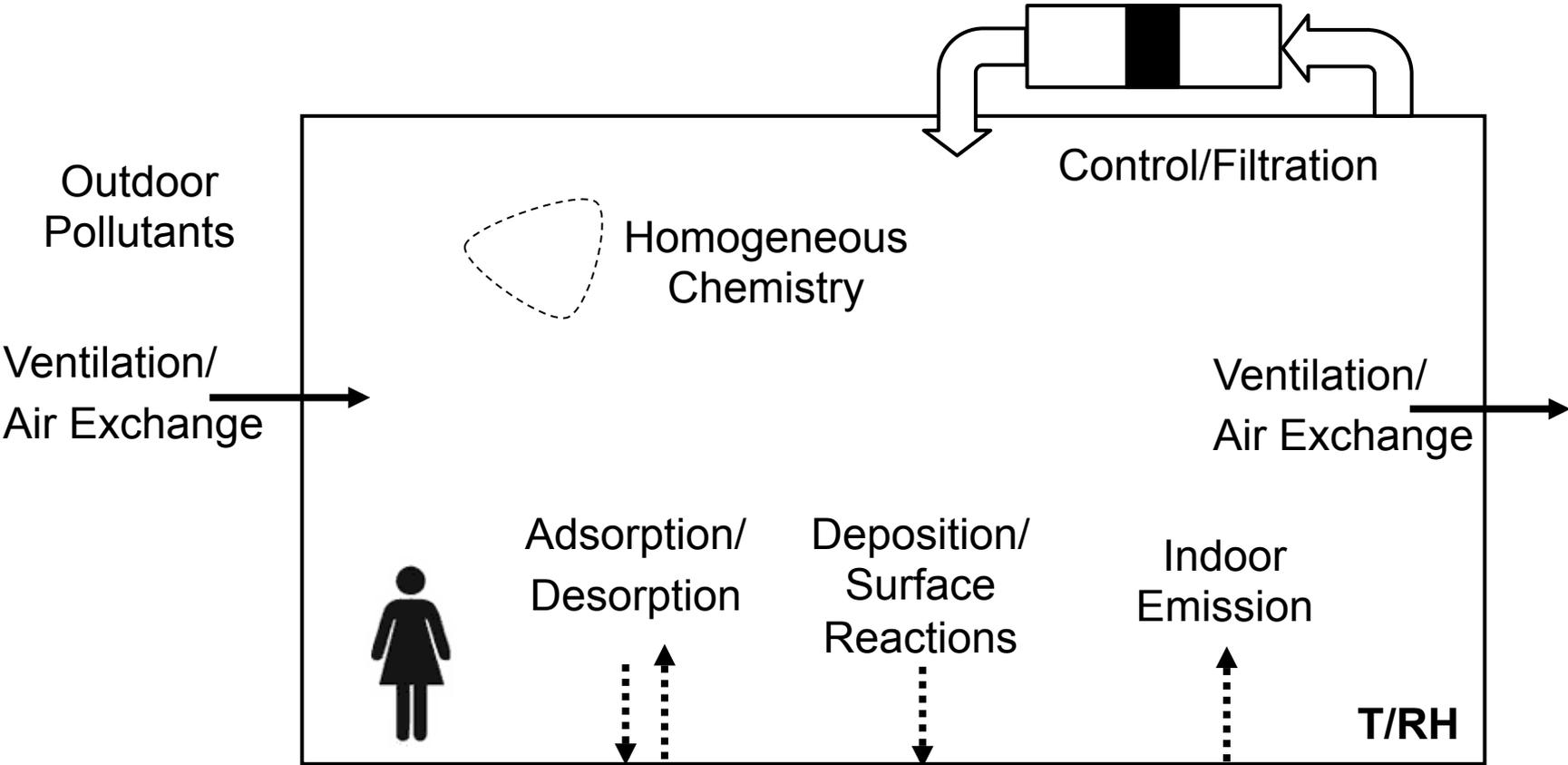
$$D_{eff,2} \approx D_{eff,1} \left( \frac{MW_2}{MW_1} \right)^{1/2} \left( \frac{k_{eq,2}}{k_{eq,1}} \right)$$

What is this??

# **SORPTION**

Adsorption and desorption

# Indoor environment: Mass balance



# 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)
  - Reduced human exposure, delays release into indoor environment, and lowers peak concentration
  - Can also be irreversibly adsorbed to a material
- Most building materials are porous
  - Gypsum board
  - Plywood
- VOCs can also adsorb onto exterior surfaces of non-porous materials
  - Glass and stainless steel

# Sorption

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

# Sorption

---

- Refer to notes on board / doc cam

# Sorption in mass balances

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- Linear isotherm

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

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

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

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

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

$Q_g$  = air flow rate through space ( $\text{m}^3/\text{hr}$ )

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

$k_a$  = adsorption rate coefficient ( $\text{m}/\text{hr}$ )

$k_d$  = desorption rate coefficient ( $1/\text{hr}$ )

$M$  = mass collected on the sink per unit area ( $\text{mg}/\text{m}^2$ )

(you would solve this numerically)

# Sorption in mass balances

---

- Linear isotherm
  - At equilibrium

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

$K_{eq}$  = linear isotherm coefficient (mg/kg sorbent / mg/m<sup>3</sup> air = m<sup>3</sup>/kg)

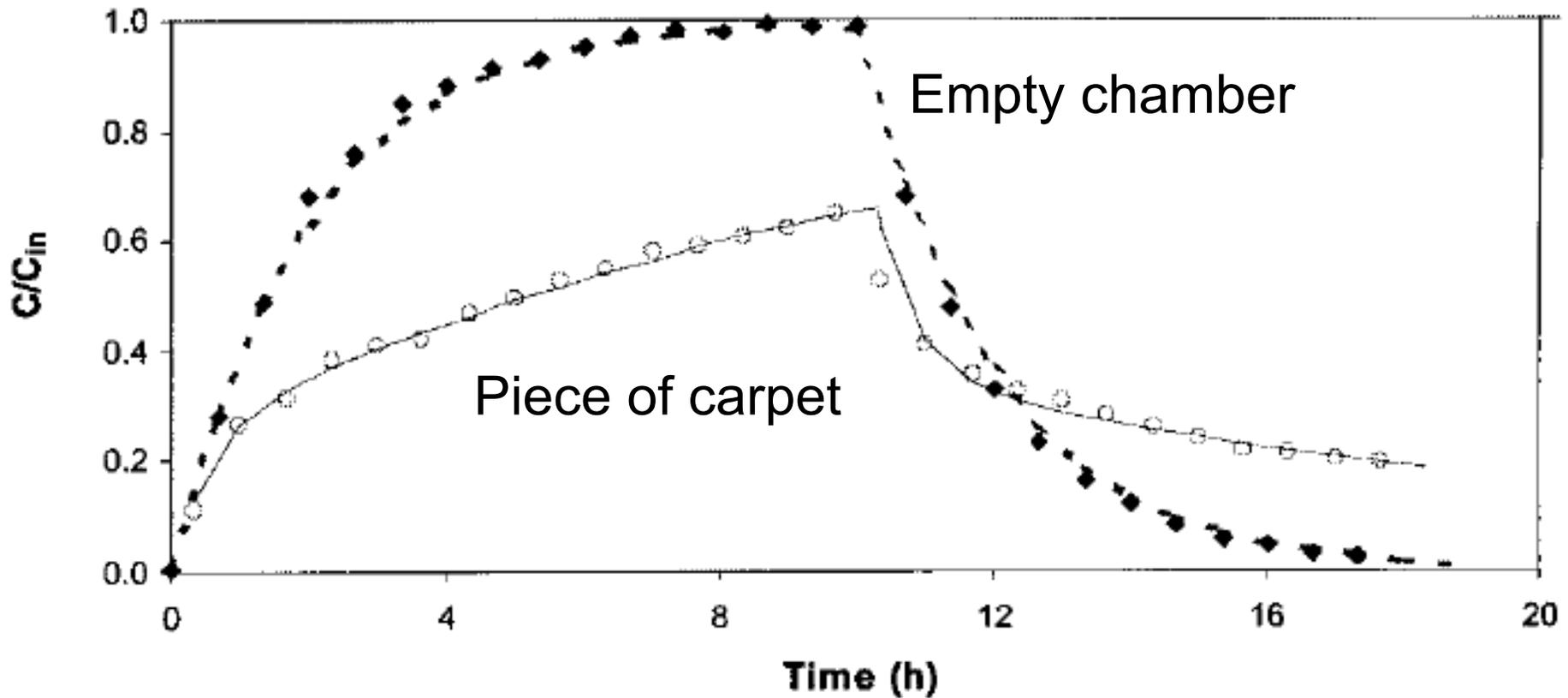
$$V \frac{dC_g}{dt} = Q_g C_{g,out} - Q_g C_g - \frac{dC_g}{dt} \sum k_{eq} A$$

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

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

# Measured impacts of sorption

- Chamber studies w/ and w/out carpet



# Measured impacts of sorption

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

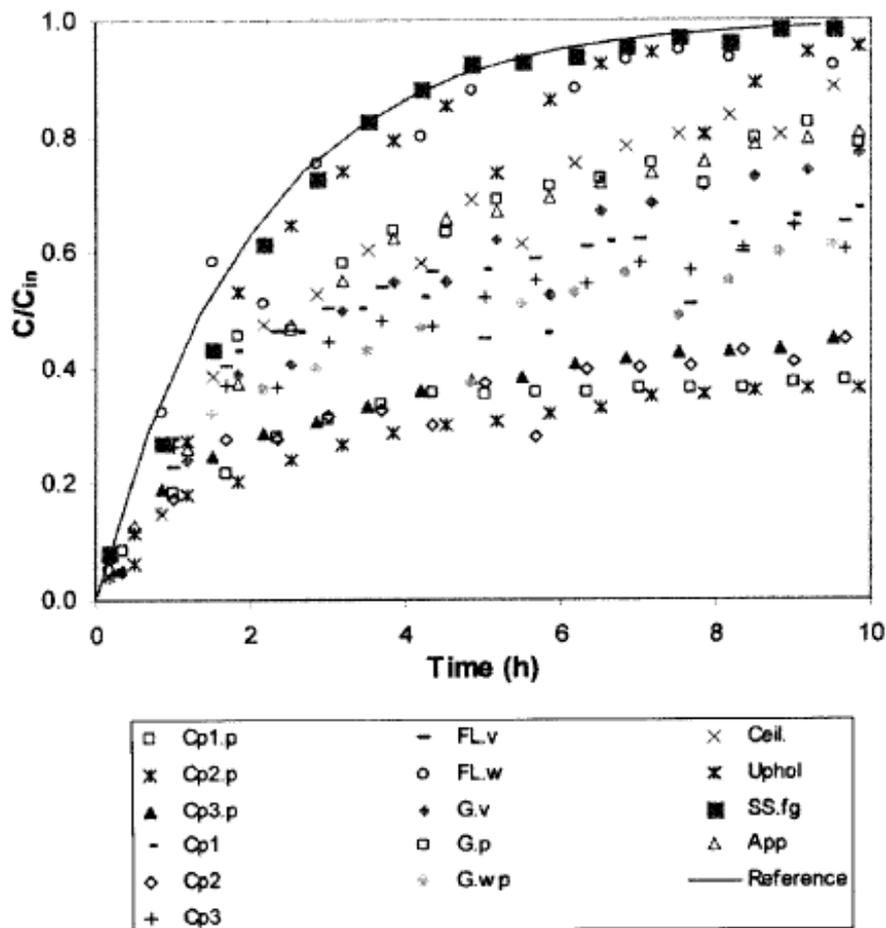


Fig. 3 Effects of Materials on Sorption (1,2-dichlorobenzene)

# 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.

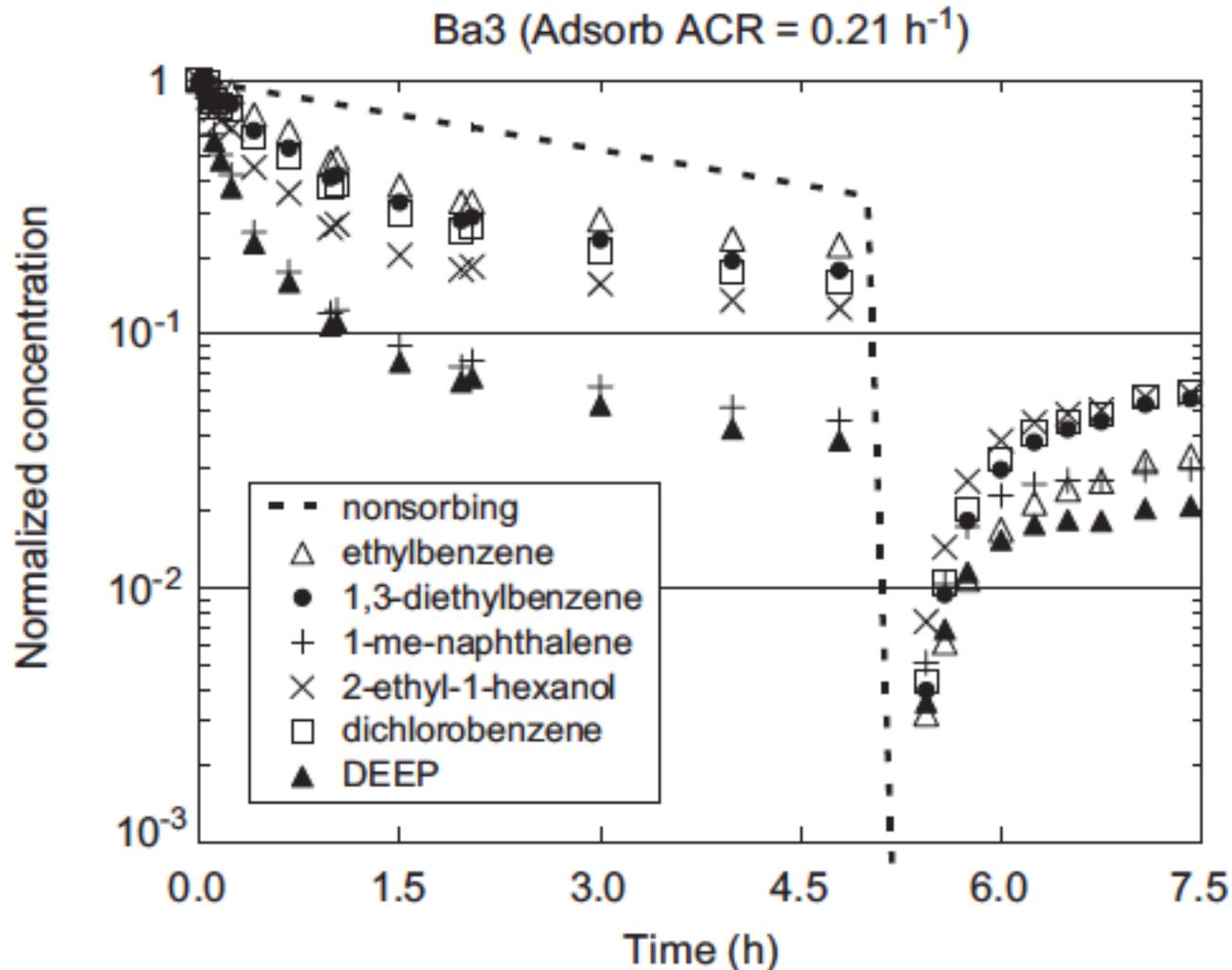
**Table 3** Summary of Equilibrium Partition Coefficients ( $K_{eq}$ ) (Average  $\pm$  Standard Deviation)

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

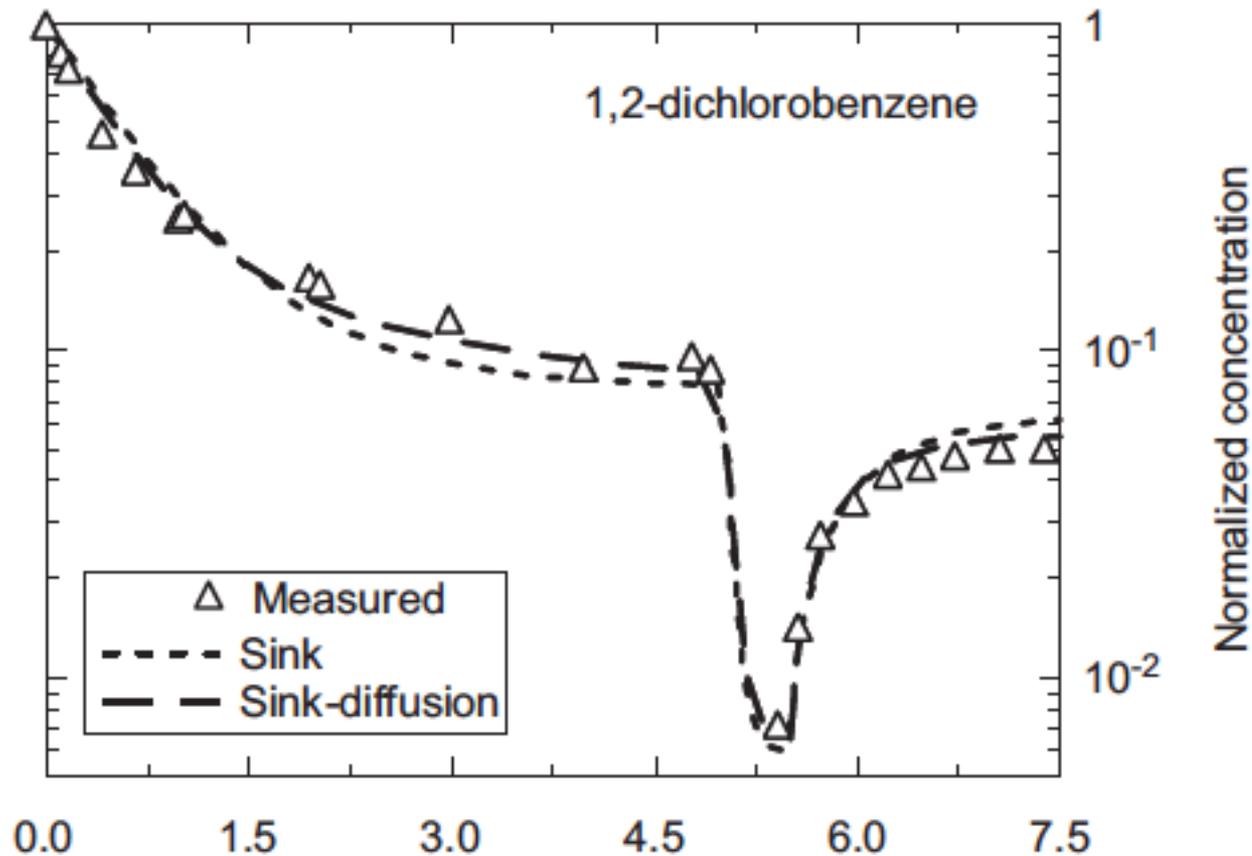
# Measured impacts of sorption in real rooms

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



# Measured impacts of sorption in real rooms

- Measured and modeled adsorption, flush out, and desorption



# Finishing up today

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- HW 2 assigned
  - Due 1 week from today
- Next time:
  - More gas-phase pollutant fundamentals:
    - Reactive deposition
    - Homogeneous chemistry