ENVE 576
Indoor Air Pollution
Fall 2016

Week 4: September 13, 2016
Gaseous pollutants: Sources, emission models, and sorption

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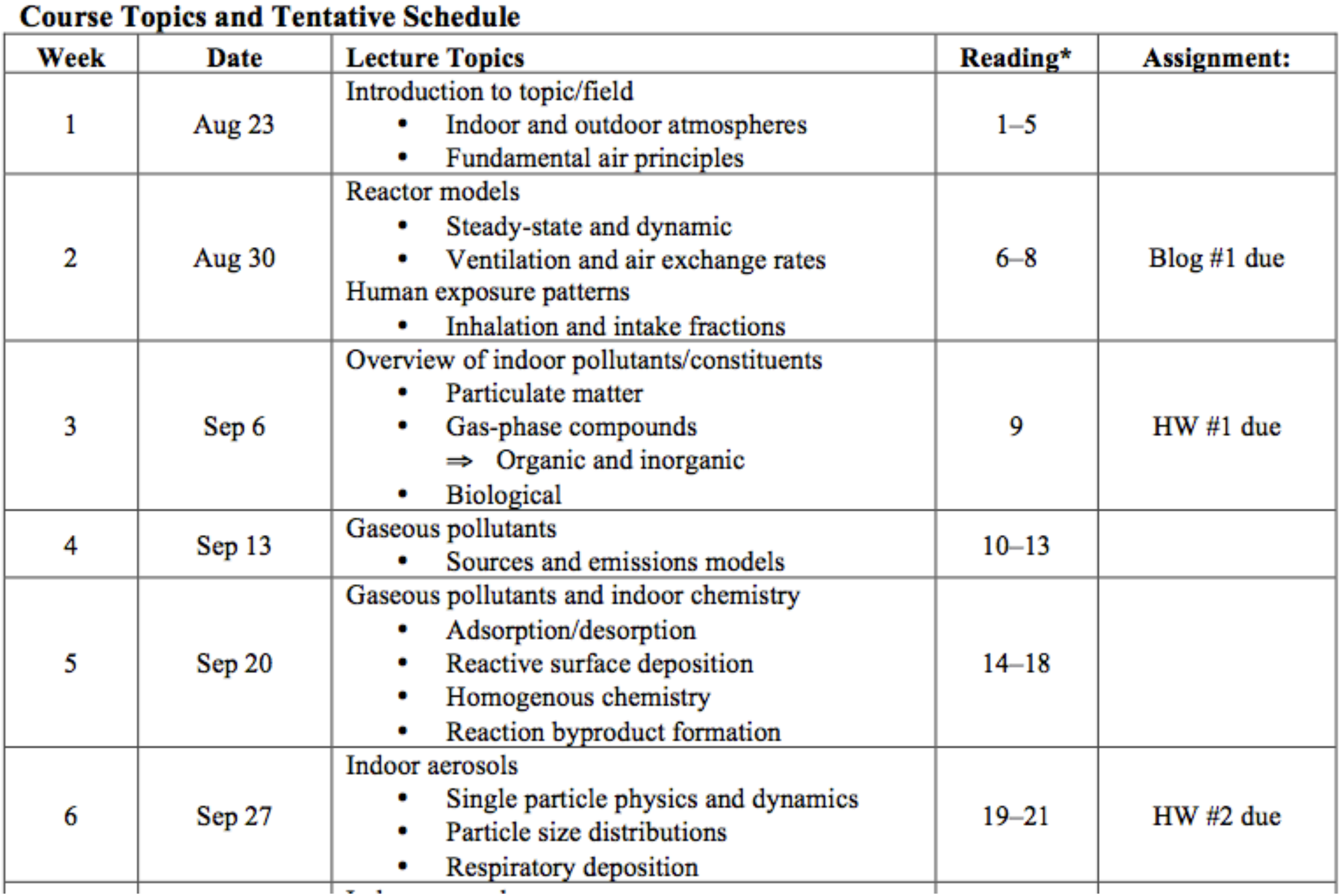
Scheduling update



Course Topics and Tentative Schedule

Week	Date	Lecture Topics	Reading*	Assignment:
1	Aug 23	Introduction to topic/field • Indoor and outdoor atmospheres • Fundamental air principles	1–5	
2	Aug 30	Reactor models • Steady-state and dynamic • Ventilation and air exchange rates Human exposure patterns • Inhalation and intake fractions	6–8	Blog #1 due
3	Sep 6	Overview of indoor pollutants/constituents • Particulate matter • Gas-phase compounds ⇒ Organic and inorganic • Biological	9	HW #1 due
4	Sep 13	Gaseous pollutants • Sources and emissions models	10–13	
5	Sep 20	Gaseous pollutants and indoor chemistry • Adsorption/desorption • Reactive surface deposition • Homogenous chemistry • Reaction byproduct formation	14–18	
6	Sep 27	Indoor aerosols • Single particle physics and dynamics • Particle size distributions • Respiratory deposition	19–21	HW #2 due

Final project expectations

- I have uploaded a project expectations document to BB
- Outlines the assignment, due dates, and expectations of your final project
- Key points:
  - You can work in teams of up to 2
  - You will write a paper and present your work
  - Read the expectations document in detail
  - Follow the specified format
  - Cite high quality references

Final project topic ideas

- Outdoor pollutant infiltration through building enclosures
- HVAC duct leakage and particle transport
- Soil vapor intrusion
- Cookstoves and IAQ
- Emissions from indoor swimming pools
- Indoor exposures to pollutants from outdoor incineration
- Natural ventilation and IAQ
- SVOC dynamics
- Formaldehyde dynamics
- Impact of plants
- Allergen exposures and dynamics
- E-cigarette emissions
- Radon control
- Size-resolved particle filtration measurements (measurements)
- Particle emissions from desktop 3D printers (measurements)

Final project topics

Name	**Project topic**
Boyer, Jeffrey L.	
Faramarzi, Afshin	
Liang, Dejun	
Liu, Xiaoqi	
Ma, Peiling	
Meng, Zhenyu	
Rice, Lindsey E.	
Shao, Zhihui (Kevin)	
Wang, Yintong	
Zeng, Yicheng	
Zhang, Peng (indoorenvir)	
Zhang, Xu	
Zhu, Guozhu	
Angulo Duato, Ana Claudia	

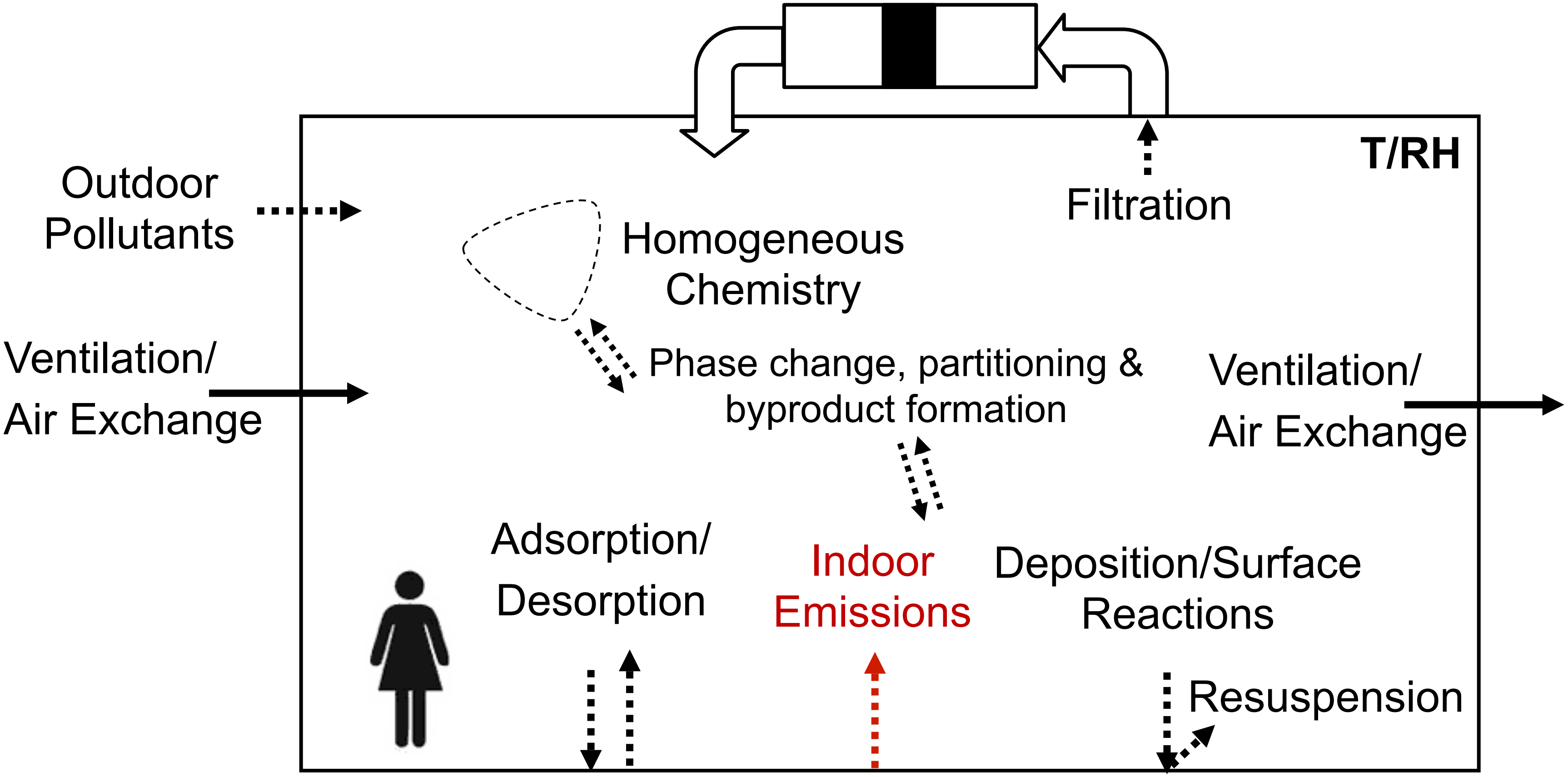
Review from last time

- Last time 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:
  - Focus on gas-phase pollutants (next 2 lectures)
    - Sources, emission models, and adsorption/desorption today
    - Reactions next week

VOC EMISSION RATES

Indoor environment: Mass balance



Outdoor Pollutants

Ventilation/ Air Exchange

Homogeneous Chemistry

Filtration

T/RH

Phase change, partitioning & byproduct formation

Ventilation/ Air Exchange

Adsorption/ Desorption

Indoor Emissions

Deposition/Surface Reactions

Resuspension

Understand gas-phase emissions

Goals:

- Summarize some emission rate studies
  - IAQ handbook
  - Chamber testing

- Emissions modeling
  - Various sources

- Then: Adsorption/desorption

Gas-phase compound emission rates

- 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)

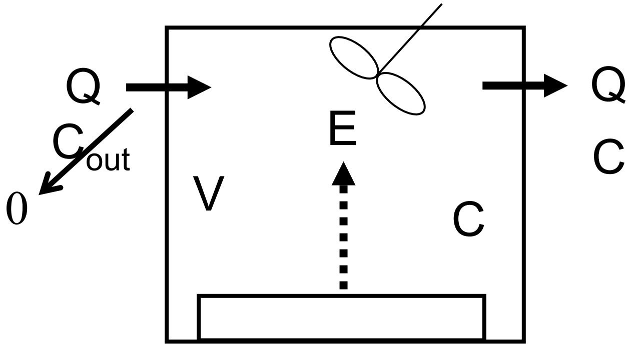
Emission rate testing → Actual IAQ

- 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

Guo 2002 *Environmental Pollution*

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 adsorption if it occurs
  - Mass balance on chamber:



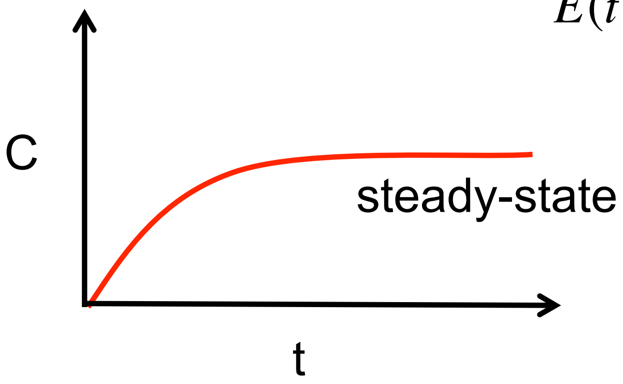
$$V\frac{dC}{dt} = \cancelto{0}{QC_{out}} - QC + E$$

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

ASTM D5116 – Small chambers / organic emissions
ASTM D6670 – Full-scale chambers / VOCs

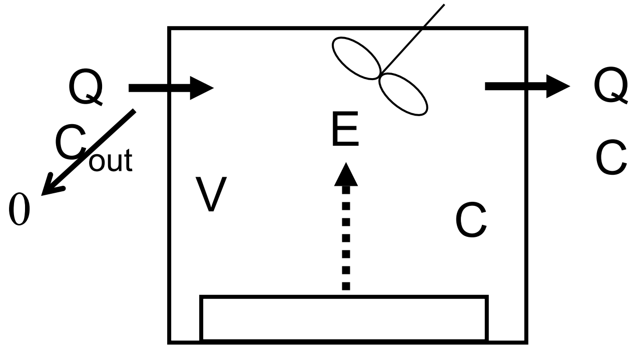
Emission rate testing

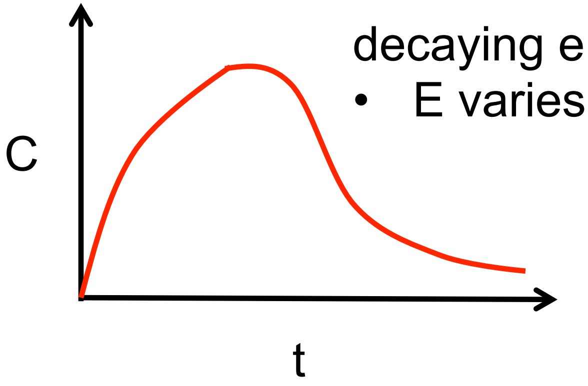
- Two hypothetical concentration profiles



$$E(t) = QC + V\underset{0}{\cancel{\frac{dC}{dt}}}$$

$$E_{ss} = QC$$





decaying emission rate

- E varies with t

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

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

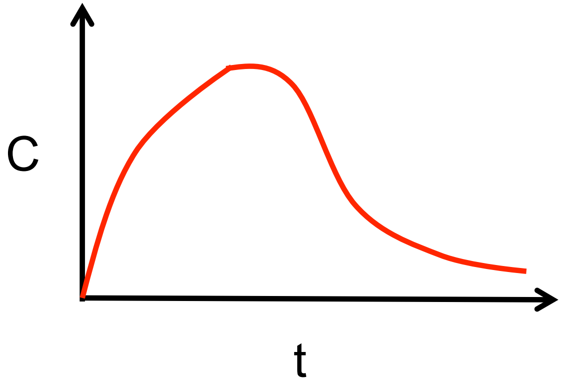
Emissions testing

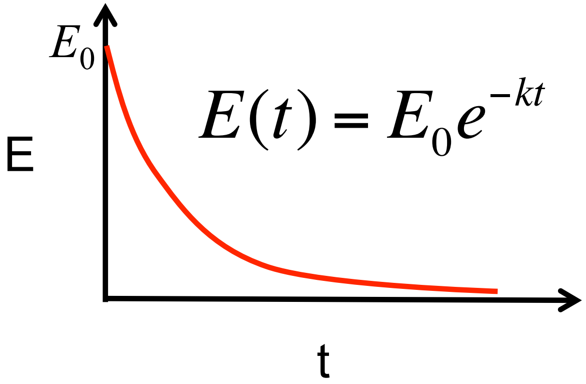
- What do we do with data after we obtain it?
- <u>Emission factors</u> for constant emission rates
  - Looking for mass per time, but can also normalize by an activity
- Examples:
  - Combustion: mg CO per kJ fuel burned (need burn rate)
    μg CO_2 per g candle burned (need burn rate)
  - O_3 from printers: μg O_3 per printed page (need page/min)
  - Vinyl flooring: ng phenol per m^2 per hour

- Emission factors are highly source-specific
  - Can also vary with time

Emissions: Exponential decay model

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

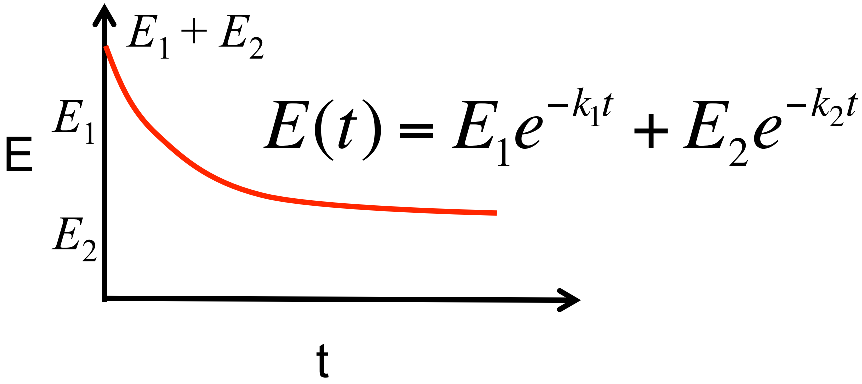




$$E(t) = E_0 e^{-kt}$$

1st order exponential decay

rapid decay



$$E(t) = E_1 e^{-k_1 t} + E_2 e^{-k_2 t}$$

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

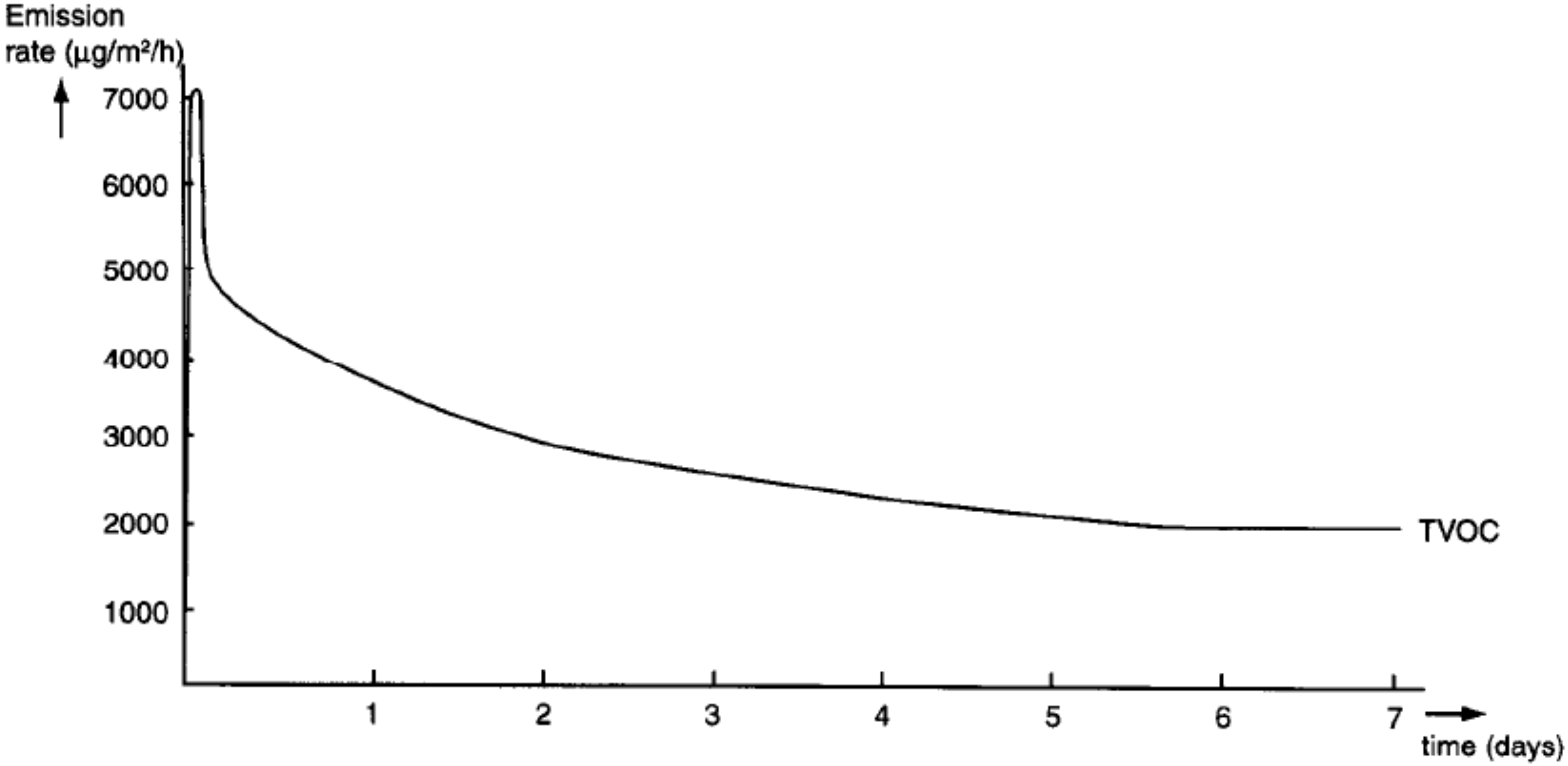
- How can there be 50+ different models for emissions?
- Nature of sources can vary widely
  - Combustion vs. ETS vs. personal care products vs. paints vs. building materials vs. animals

- 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

Guo 2002 *Environmental Pollution*

Actual emissions testing: vinyl flooring

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



Yu and Crump 1998 *Building and Environment*

Actual emissions testing: vinyl flooring

- Different emission rate profiles for each constituent!

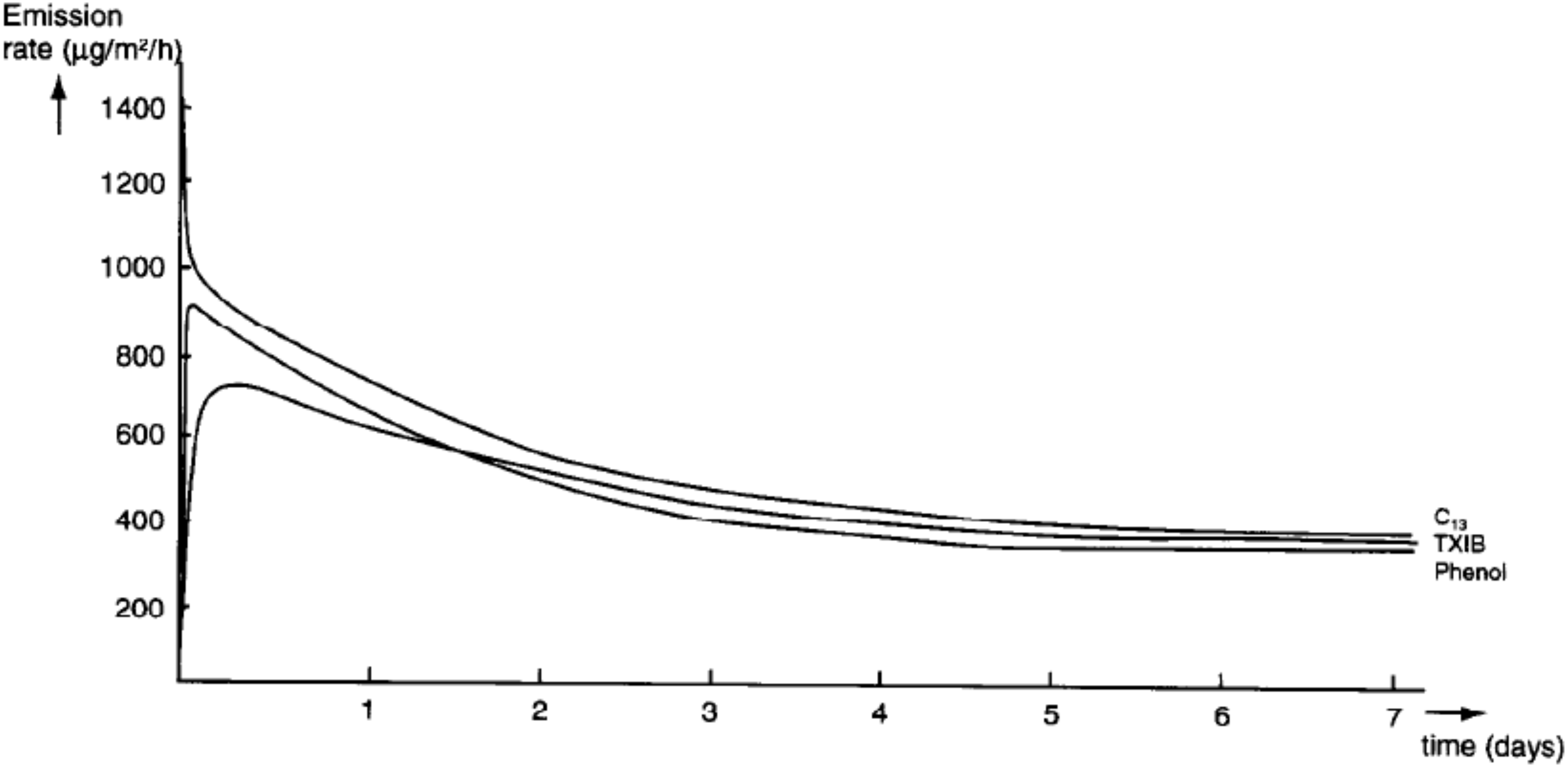


Fig. 2. VOC emission profile of a vinyl flooring sample.

Yu and Crump 1998 *Building and Environment*

TVOC emission rates from actual materials

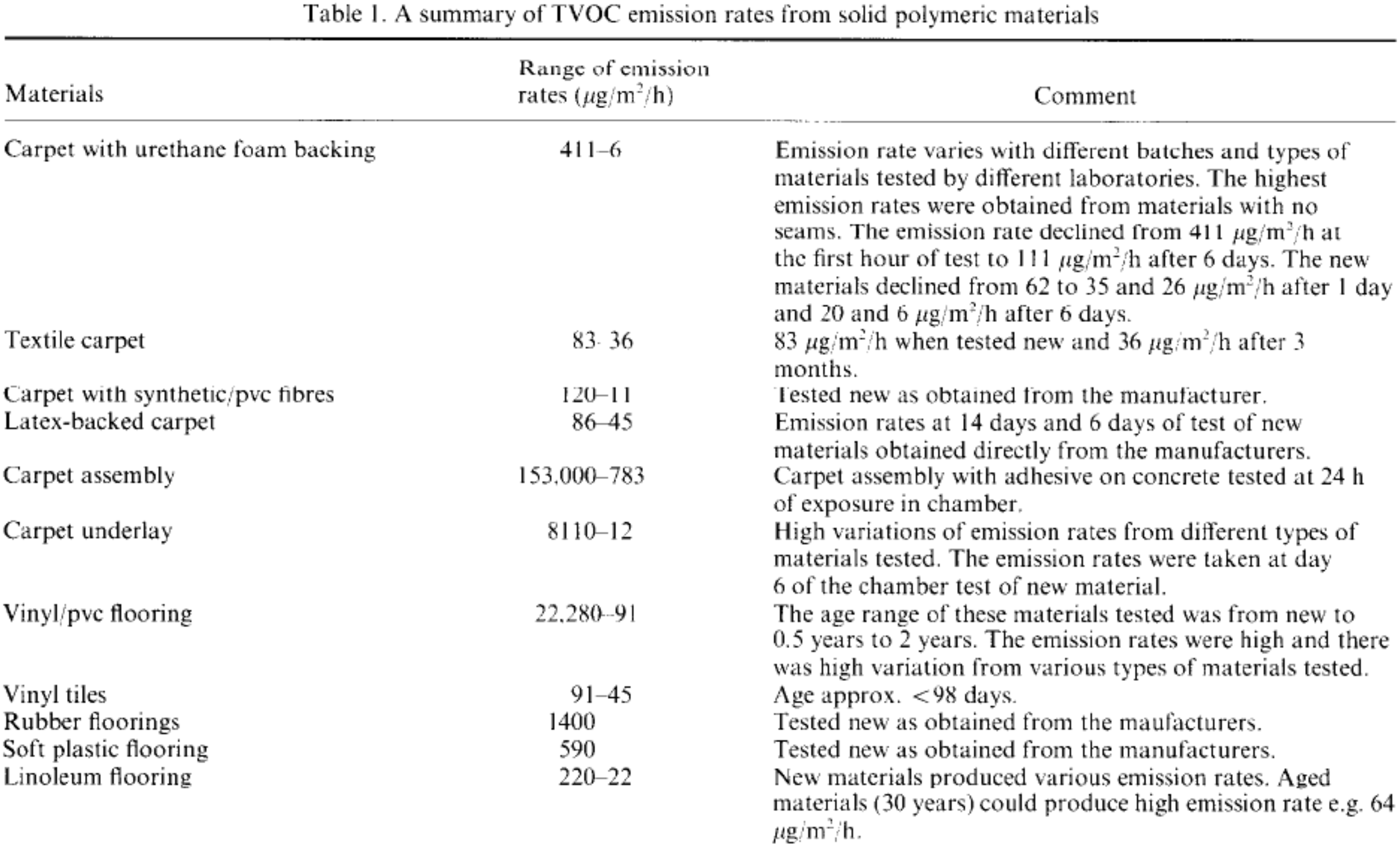
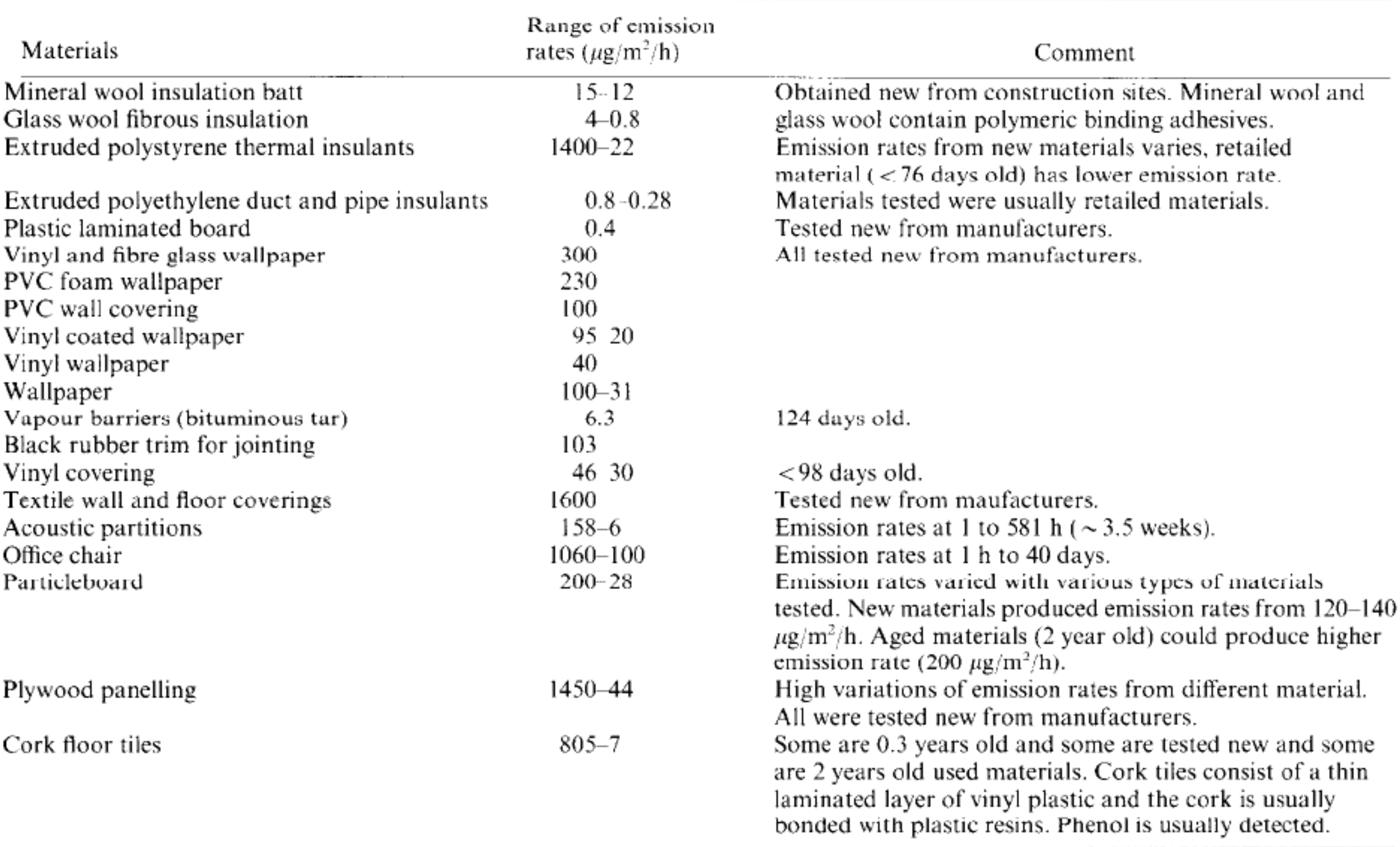


Table 1. A summary of TVOC emission rates from solid polymeric materials

Materials	Range of emission rates (μg/m^2/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 μg/m^2/h at the first hour of test to 111 μg/m^2/h after 6 days. The new materials declined from 62 to 35 and 26 μg/m^2/h after 1 day and 20 and 6 μg/m^2/h after 6 days.
Textile carpet	83–36	83 μg/m^2/h when tested new and 36 μg/m^2/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 maufacturers.
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 μg/m^2/h.

Yu and Crump 1998 *Building and Environment*

TVOC emission rates from actual materials



Materials	Range of emission rates ($\mu g/m^2/h$)	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 maufacturers.
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 $\mu g/m^2/h$. Aged materials (2 year old) could produce higher emission rate (200 $\mu g/m^2/h$).
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.

Yu and Crump 1998 *Building and Environment*

TVOC emission rates from actual materials

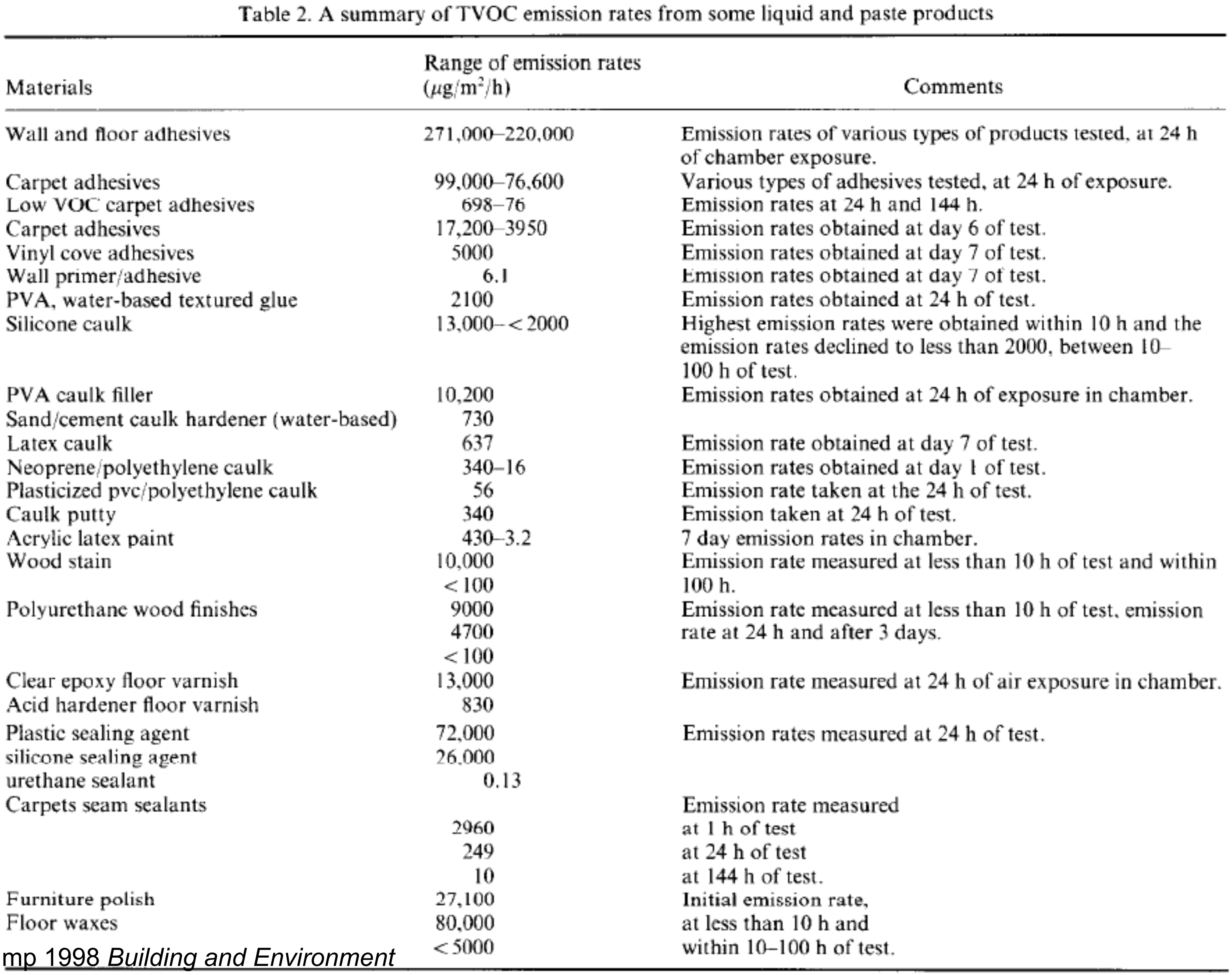


Table 2. A summary of TVOC emission rates from some liquid and paste products

Materials	Range of emission rates (μg/m^2/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		Emission rate measured
	2960	at 1 h of test
	249	at 24 h of test
	10	at 144 h of test.
Furniture polish	27,100	Initial emission rate,
Floor waxes	80,000	at less than 10 h and
	< 5000	within 10–100 h of test.

Yu and Crump 1998 *Building and Environment*

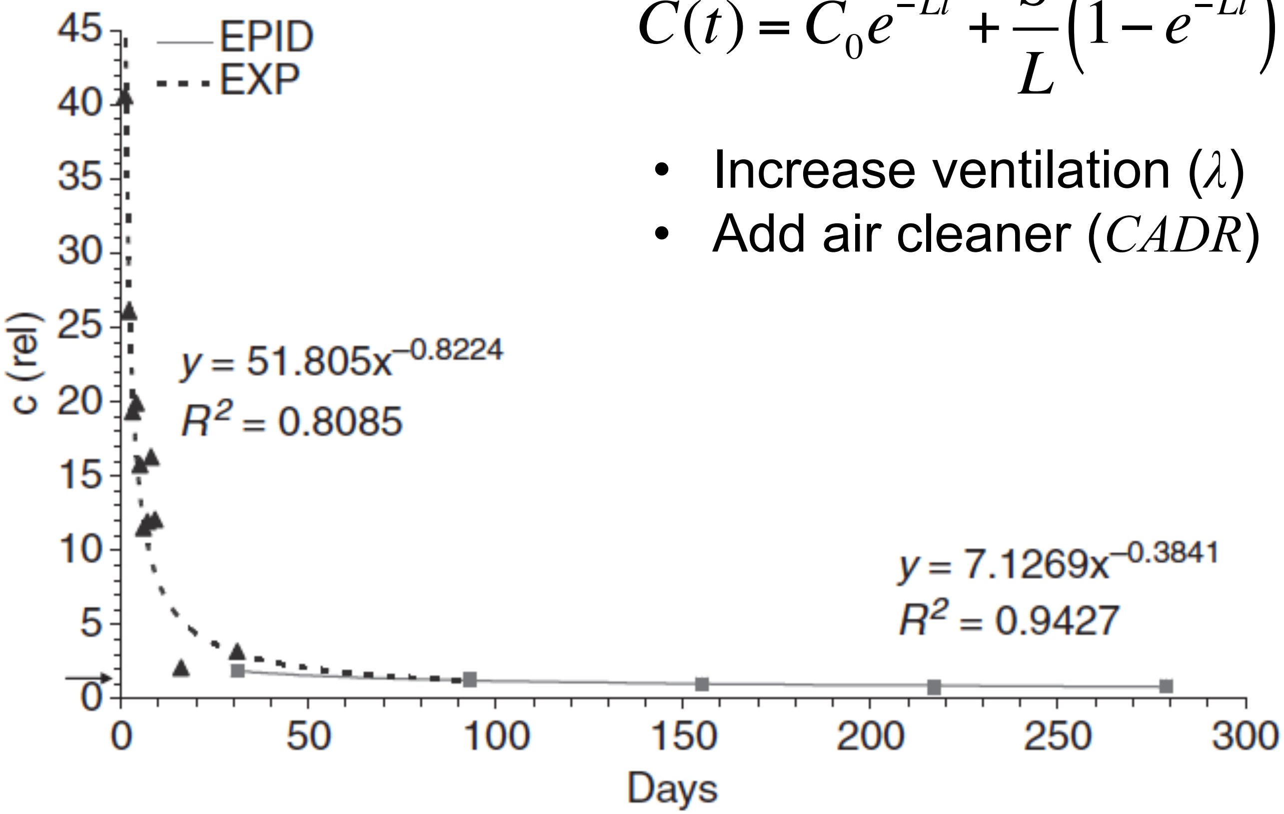
TVOC emission rates from actual materials

- *IAQ Handbook* emission factors
  - Page 31.7 on doc cam

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?

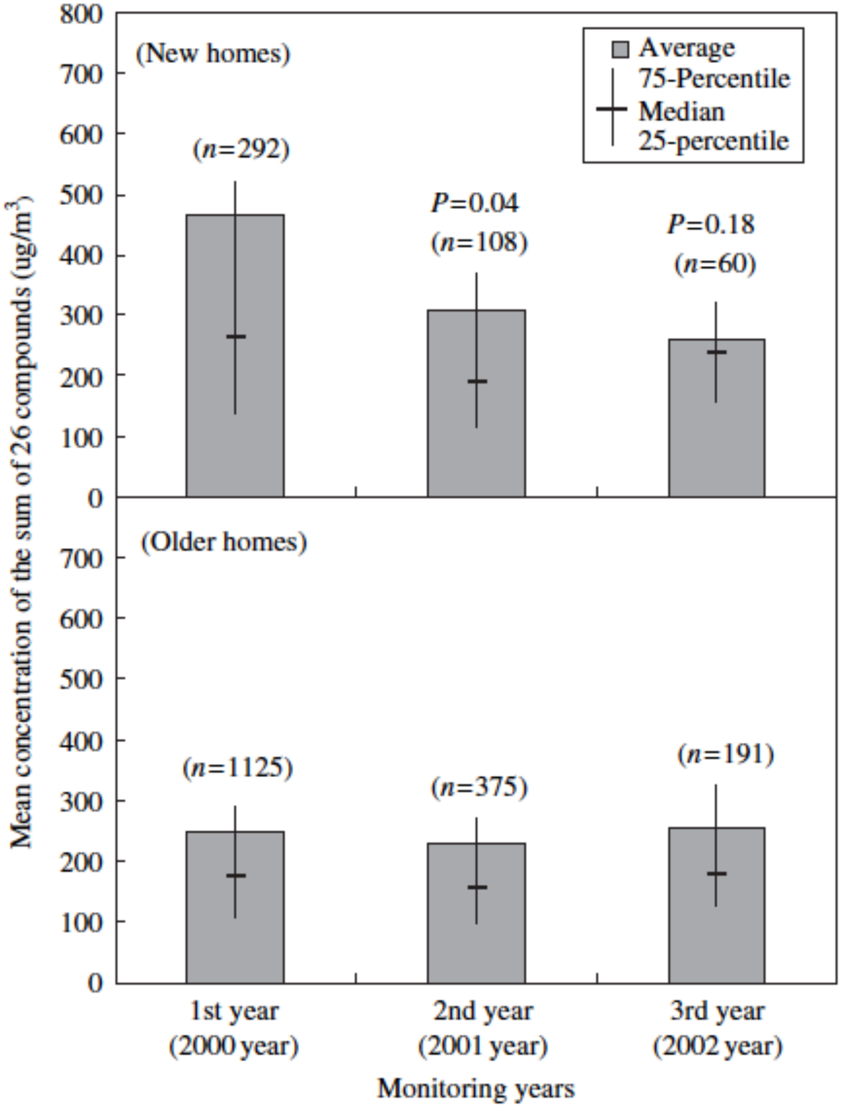


$$C(t) = C_0 e^{-Lt} + \frac{S}{L}\left(1 - e^{-Lt}\right)$$

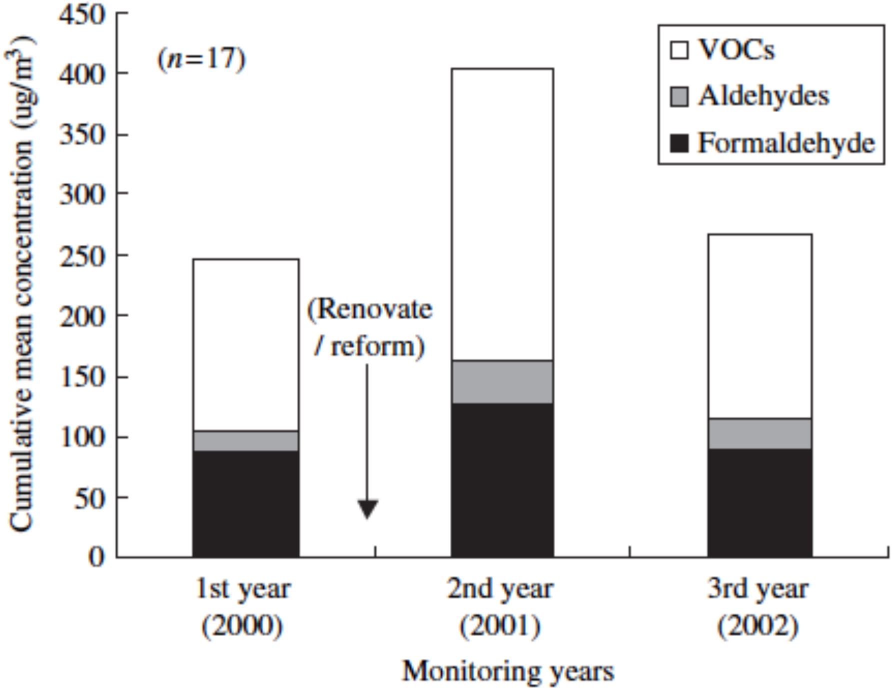
- Increase ventilation (λ)
- Add air cleaner ($CADR$)

Herbarth and Matysik 2010 *Indoor Air*

Time-varying emissions in real buildings



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



Park and Ikeda 2006 *Indoor Air*

Time-varying emissions: what is happening?

7 basic categories of emissions from Guo (2002):

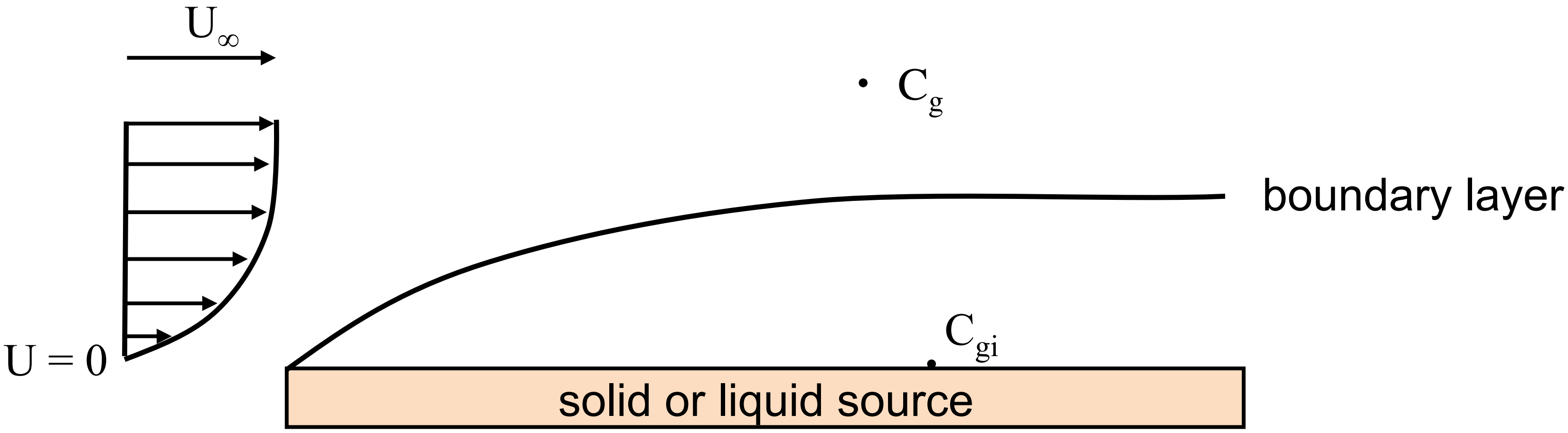
1. Multipurpose
2. Indoor coatings
3. Building materials
4. Evaporating solvent pools
5. Contaminated household tap water
6. Pesticide applications
7. Combustion appliances

- What is it about these sources that leads 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

Guo 2002 *Environmental Pollution*

Basic mass transfer: smooth flat plate

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



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

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

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

How do we get C_{gi}?

Concentration at gas-solid interface

- How do we obtain C_{gi}?
- If it is a <u>pure chemical</u>, 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

$$C_{gi} = \frac{P_{vp}(MW)}{RT} = \frac{(0.0023\ \text{atm})(147\ \text{g/mol})}{(8.205\times10^{-5}\ \frac{\text{m}^3\cdot\text{atm}}{\text{K}\cdot\text{mol}})(298\ \text{K})} = 13.8\ \frac{\text{g}}{\text{m}^3}$$

Concentration at gas-solid interface

- If it is a dilute aqueous solution → use Henry's law
  - Example: 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-terpineol ($C_{10}H_{18}O$) in a liquid cleaner @10%
    - Say that's ~100 g/L or 100 kg/m^3 (~10% of 1000 g/L or 1000 kg/m^3)
  - Back to TOXNET: H_c for alpha-terpeniol = 2.3×10^{-6} atm-m^3/mol

$$C_{gi} = C_{liq,\,eq} H_c = (649\,\frac{\text{mol}}{\text{m}^3})(2.3\times10^{-6}\,\frac{\text{atm}\cdot\text{m}^3}{\text{mol}}) = 1.5\times10^{-3}\,\text{atm} = 1500\ \text{ppm}$$

$$C_{liq,\,eq} = (100\,\frac{\text{kg}}{\text{m}^3})(\frac{\text{mol}}{154\text{g}})(\frac{1000\text{g}}{1\text{kg}}) = 649\,\frac{\text{mol}}{\text{m}^3}$$

*Note that units on H_c can vary

Concentration driving force

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

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

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

  - 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

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

Van 't Hoff equation

$$k_{\mathrm{H,pc}} = \frac{p}{c_{\mathrm{aq}}}$$

$T \uparrow H_c$ (gas) $\uparrow C_{gi} \uparrow$

Mass transfer coefficient

- Now we understand concentration gradients can change

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

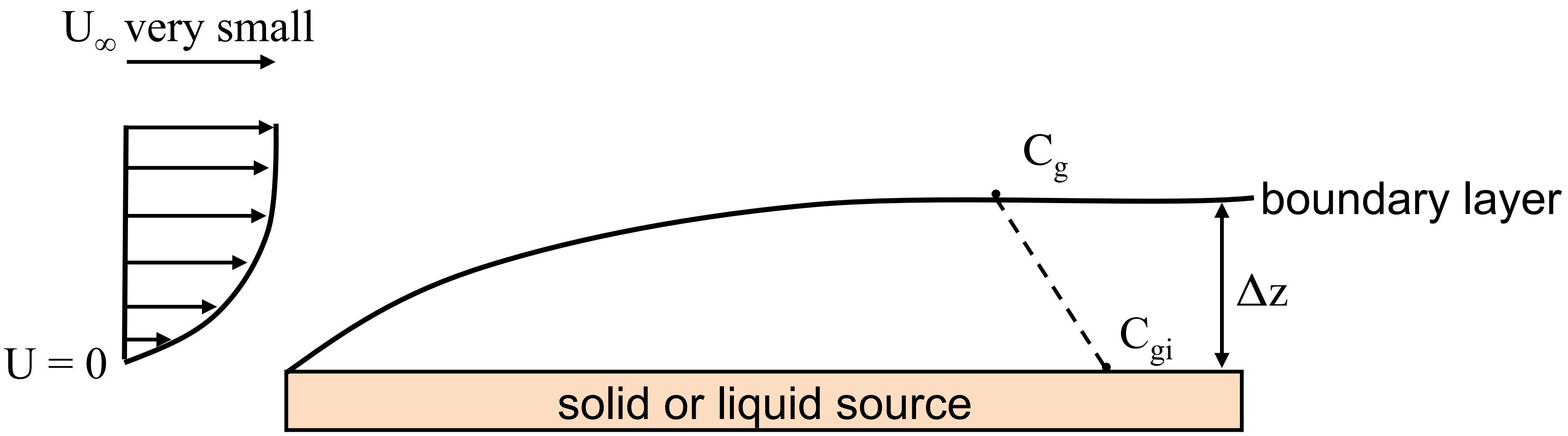
- What is this term k_g?

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

- A <u>mass transfer coefficient</u> simply relates the overall mass transfer rate to the area and concentration driving force
  - Can be estimated theoretically or 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 1st law (1-D diffusion)

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

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

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

k_g: Transition from laminar to turbulent

- Depends on Reynolds # (Re)

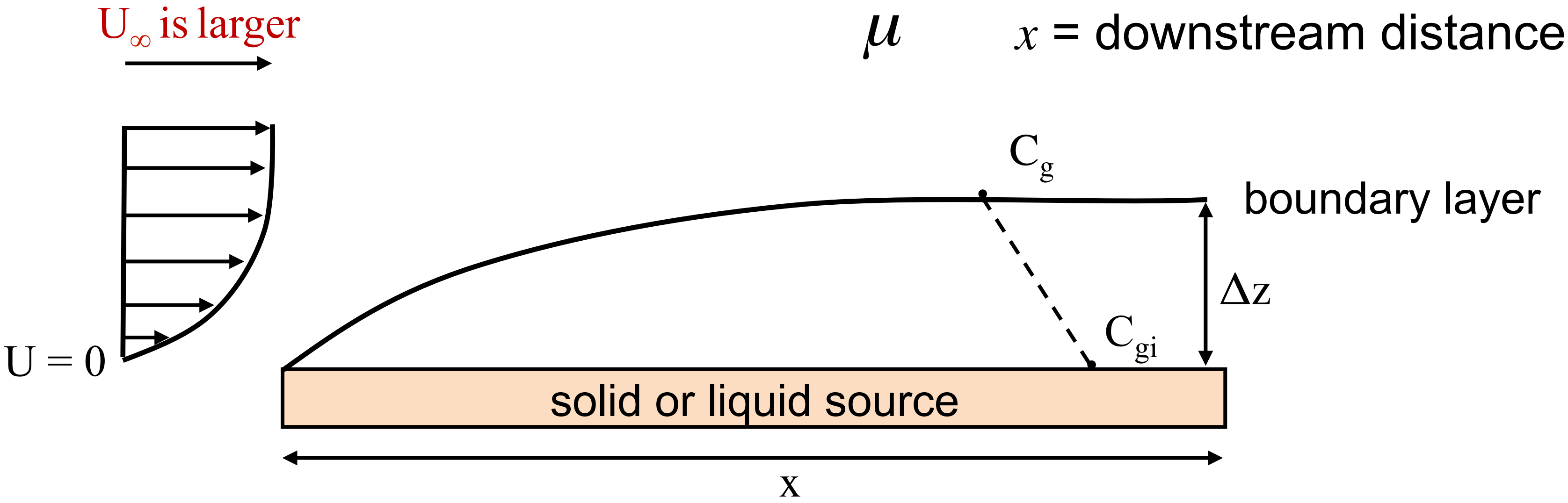
$$\mathrm{Re} = \frac{\rho U_\infty x}{\mu}$$

In typical indoor air:

ρ = 1.2 kg/m^3

μ = 1.8×10^{-5} kg/m-s

x = downstream distance



- At a given x, the higher the Re, the thinner the boundary layer

- Transition begins: $\mathrm{Re} = {\sim}10^5$
- Fully turbulent: $\mathrm{Re} > 5 \times 10^5$

(for a smooth flat plate)

Transition from laminar to turbulent

- Typical indoor conditions:

ρ = 1.2 kg/m^3
μ = 1.8×10^{-5} kg/m-s
x = 3 m
U$_\infty$ = 20 cm/s

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

- 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

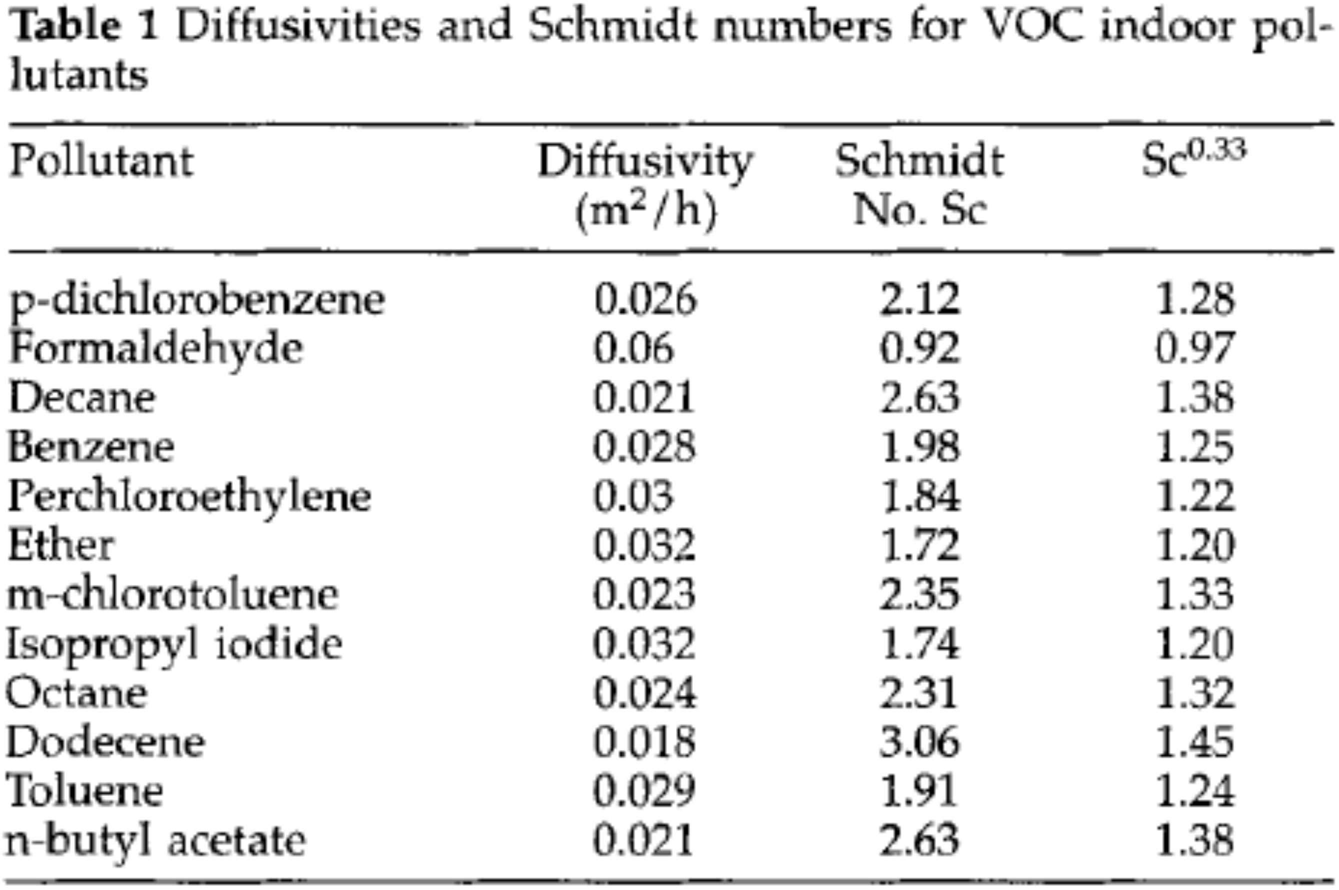


Table 1 Diffusivities and Schmidt numbers for VOC indoor pollutants

Pollutant	Diffusivity (m^2/h)	Schmidt No. Sc	$Sc^{0.33}$
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:

$$D_2 \approx D_1 \left(\frac{\mathrm{MW}_1}{\mathrm{MW}_2} \right)^{1/2}$$

Sparks et al., 1996 *Indoor Air*

Estimate emission rate of p-DCB from urinal cake

Did our emissions analysis make sense?

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

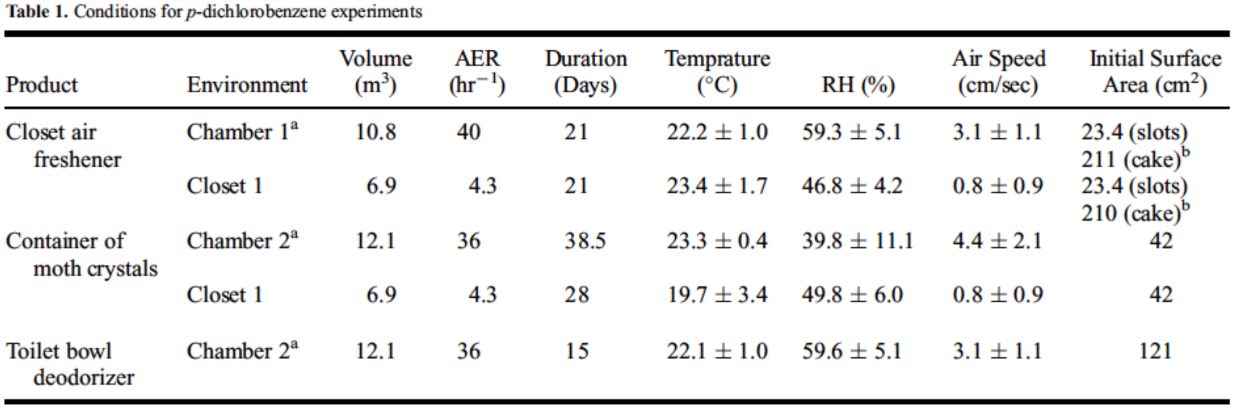
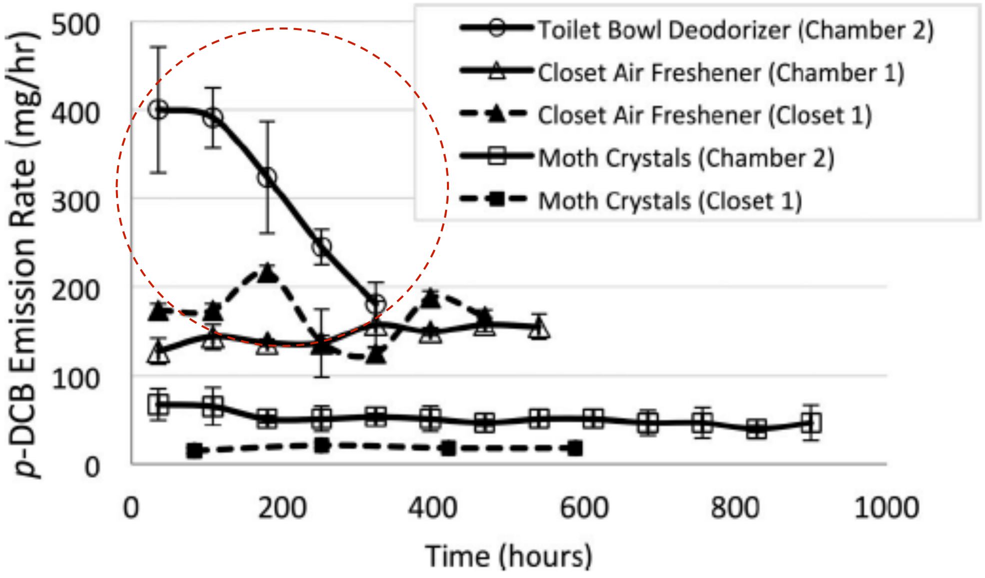


Table 1. Conditions for *p*-dichlorobenzene experiments

Product	Environment	Volume (m^3)	AER (hr^{-1})	Duration (Days)	Temprature (°C)	RH (%)	Air Speed (cm/sec)	Initial Surface Area (cm^2)
Closet air freshener	Chamber 1[a]	10.8	40	21	22.2 ± 1.0	59.3 ± 5.1	3.1 ± 1.1	23.4 (slots) 211 (cake)[b]
	Closet 1	6.9	4.3	21	23.4 ± 1.7	46.8 ± 4.2	0.8 ± 0.9	23.4 (slots) 210 (cake)[b]
Container of moth crystals	Chamber 2[a]	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[a]	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

Guerrero and Corsi, 2012 *J Air Waste Manage Assoc*

Source-dependent time-varying emissions models

Emission category	Common emission model
1. Multipurpose	$E = E_0 \mathrm{e}^{-kt}$
2. Indoor coatings	$E = k_{\mathrm{g}}\left(C_{\mathrm{T}}\dfrac{M_{\mathrm{T}}}{M_{\mathrm{T0}}} - C\right)$
3. Building materials	$E = k_{\mathrm{p}}(C_{\mathrm{E}} - C)$
4. Evaporating solvent pools	$E = \dfrac{10^3 k_{\mathrm{g}} m (P - P_{\mathrm{act}})}{R_{\mathrm{g}} T_{\mathrm{L}}}$
5. Contaminated household tap water	$R = Q_{\mathrm{g}} H C_{\mathrm{LE}}$
6. Pesticide applications	$N_{ij} = D_{ij}(f_i - f_j)$
7. Combustion appliances	$R = a + bt + ct^2 + dt^3$

Guo 2002 *Environmental Pollution*

Time-varying emissions and mass balances

- 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 in a well-mixed mass balance 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

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

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

Manually build in $E(t)$

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

Why all this focus on E ?

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

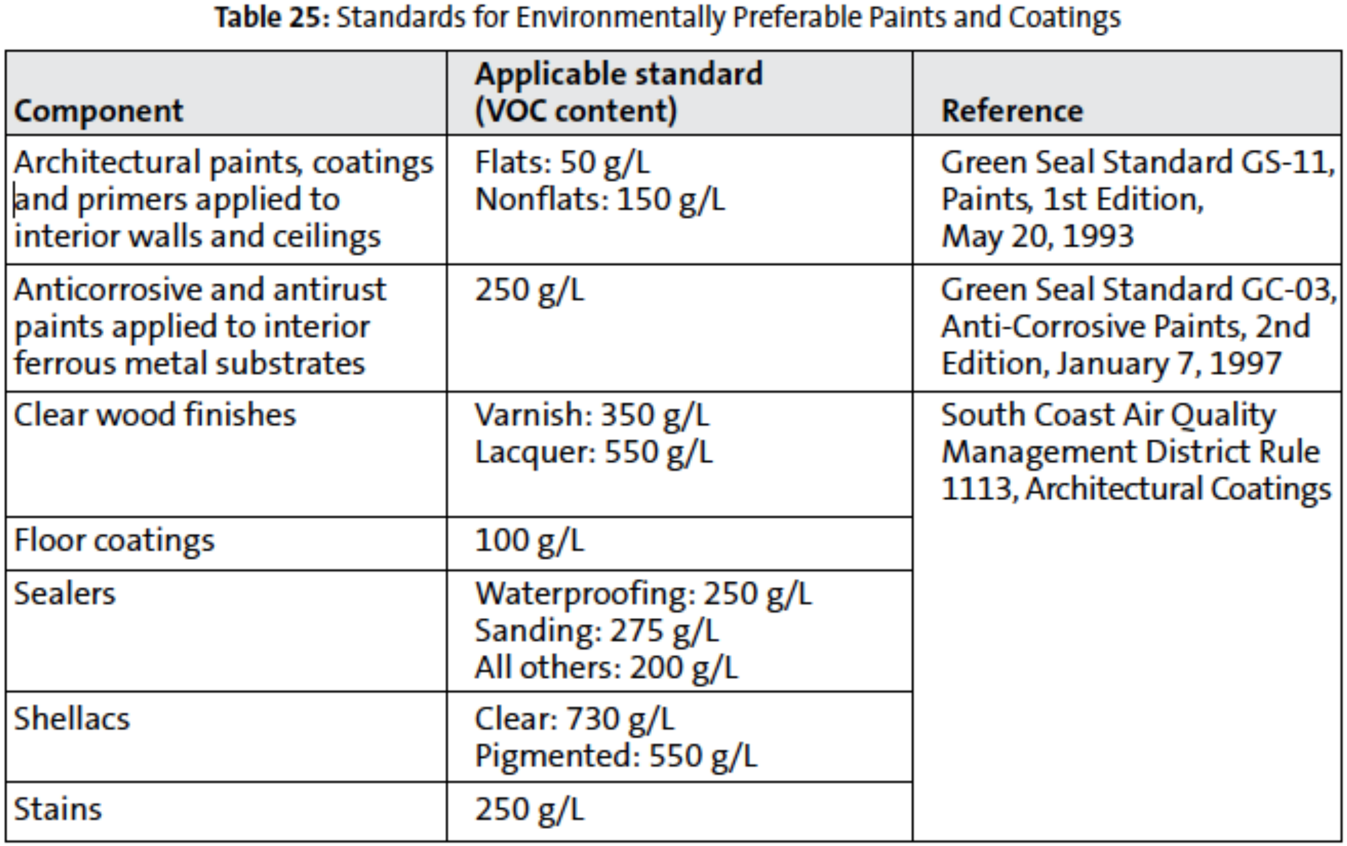


Table 25: Standards for Environmentally Preferable Paints and Coatings

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	

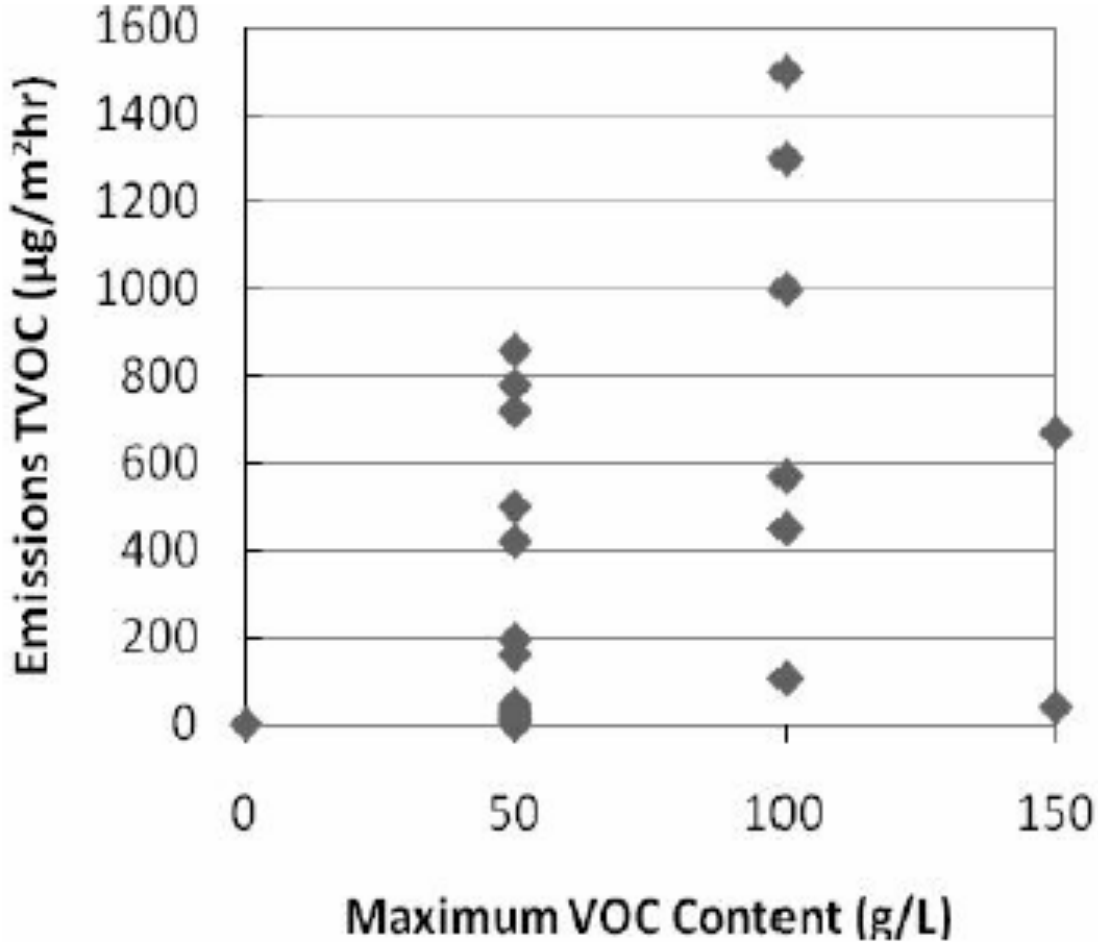
LEED® for Homes
Rating System

January 2008

LEED (and others) limit the "VOC content" that materials can have

Does VOC content correlate to emissions?

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

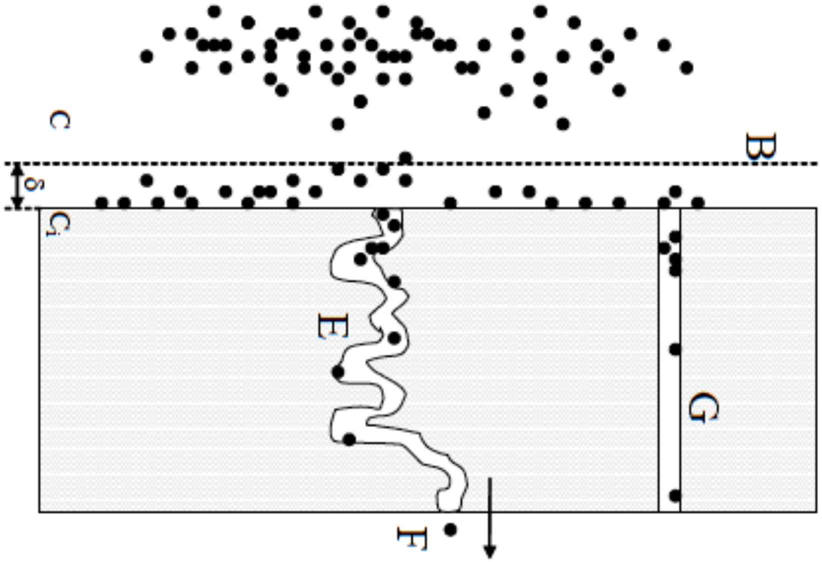


- Not exactly

Mason and Ceragioli 2011 *Proceedings of Indoor Air 2011*

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}



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

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

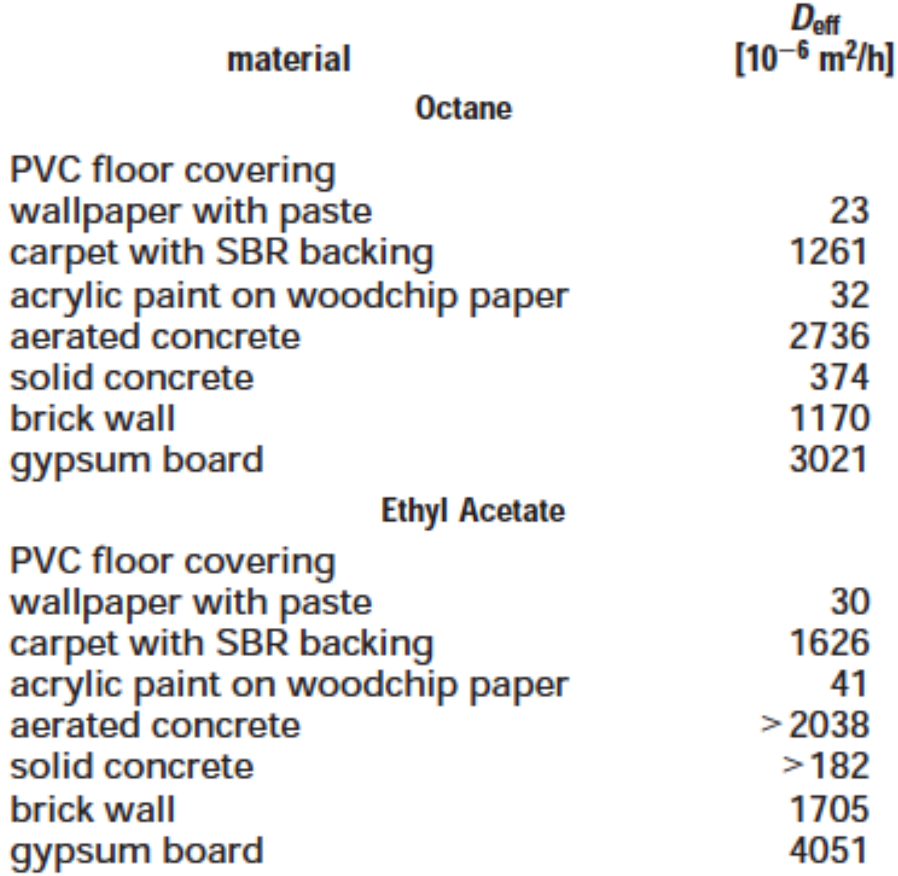
$$\frac{dC}{dt} = -\frac{D}{\Delta x}\left\{\left.\frac{dC}{dx}\right|_{i-1/2} - \left.\frac{dC}{dx}\right|_{i+1/2}\right\}$$

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

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

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^2/h]
Octane	
PVC floor covering	
wallpaper with paste	23
carpet with SBR backing	1261
acrylic paint on woodchip paper	32
aerated concrete	2736
solid concrete	374
brick wall	1170
gypsum board	3021
Ethyl Acetate	
PVC floor covering	
wallpaper with paste	30
carpet with SBR backing	1626
acrylic paint on woodchip paper	41
aerated concrete	>2038
solid concrete	>182
brick wall	1705
gypsum board	4051

Relating D_{eff} values:

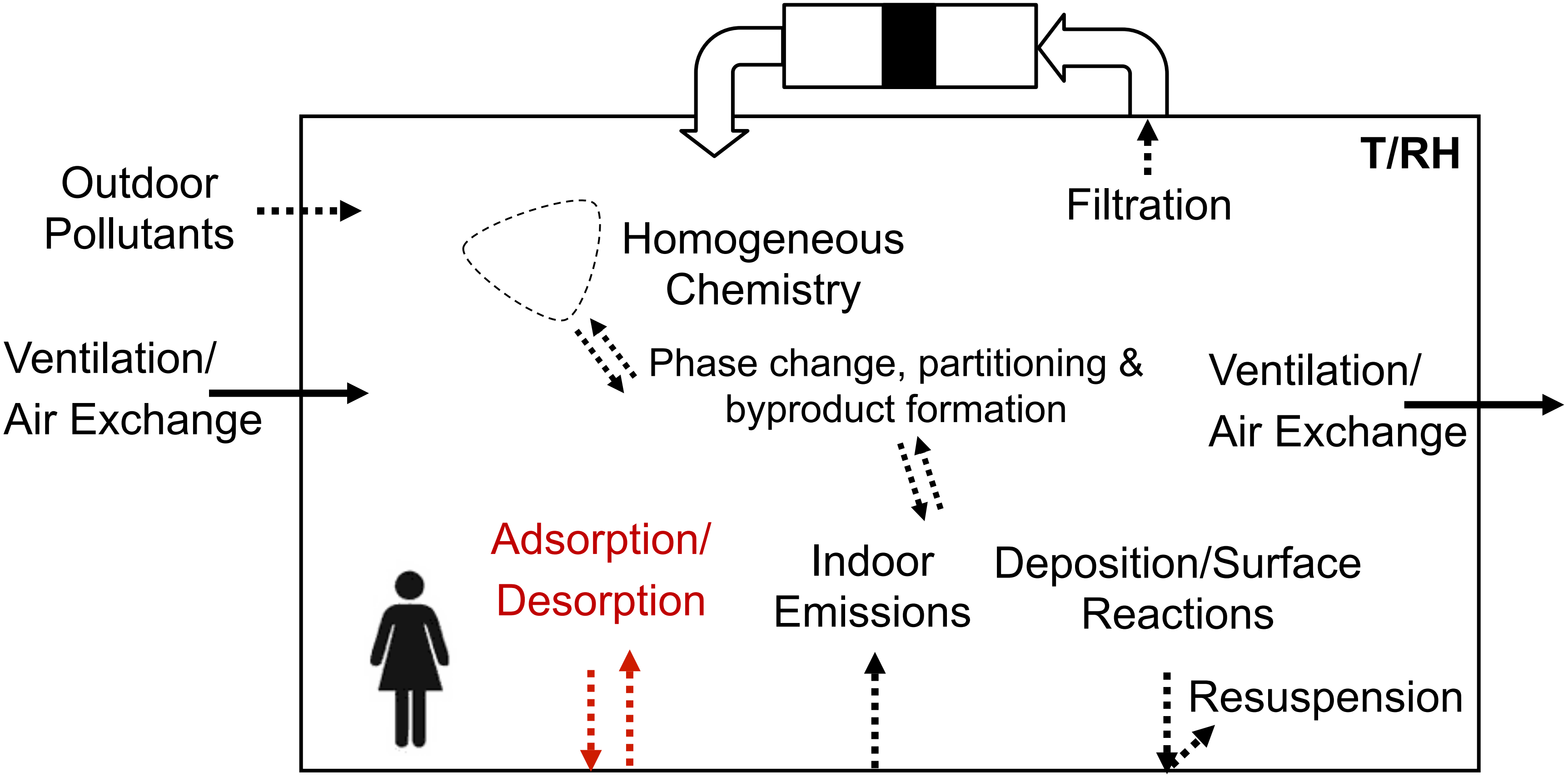
$$D_{eff,2} \approx D_{eff,1}\left(\frac{\mathrm{MW}_2}{\mathrm{MW}_1}\right)^{1/2}\left(\frac{k_{eq,2}}{k_{eq,1}}\right)$$

What is this??

SORPTION

Adsorption and desorption

Indoor environment: Mass balance



T/RH

Outdoor Pollutants

Ventilation/ Air Exchange

Homogeneous Chemistry

Filtration

Phase change, partitioning & byproduct formation

Ventilation/ Air Exchange

Adsorption/ Desorption

Indoor Emissions

Deposition/Surface Reactions

Resuspension

Sorption

- 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
  - e.g., gypsum board, plywood
- VOCs can also adsorb onto exterior surfaces of non-porous materials
  - Glass and stainless steel

Sorption

- 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 sorption on the board / doc cam

Sorption in mass balances

- Linear isotherm (non-equilibrium)

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

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

C_g = VOC concentration in air inside space of interest (mg/m^3)
$C_{g,out}$ = VOC concentration outside of space (mg/m^3)
V = chamber volume (m^3)
Q_g = air flow rate through space (m^3/hr)
A = sink area (m^2)
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^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^3 air = m^3/kg)

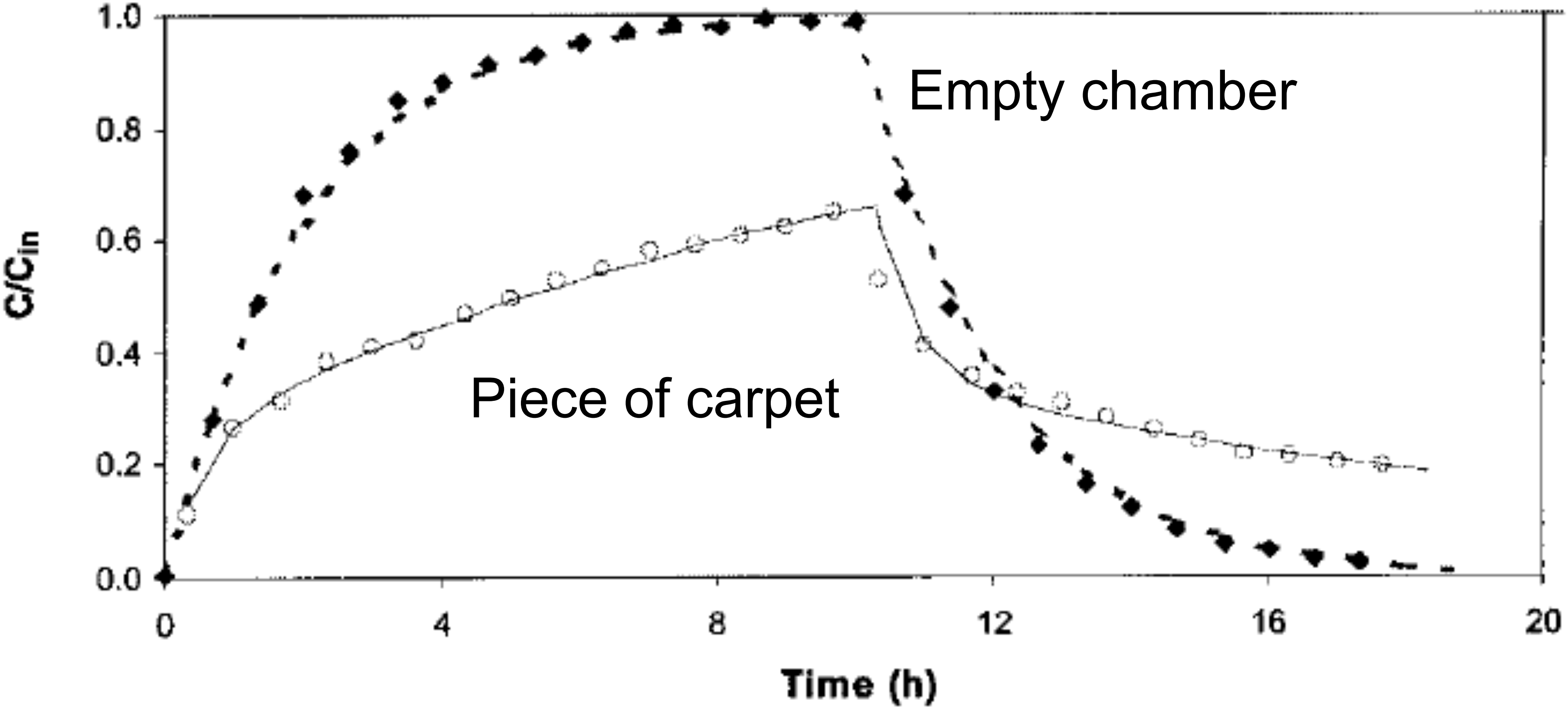
$$V\frac{dC_g}{dt} = Q_g C_{g,out} - Q_g C_g - \frac{dC_g}{dt}\sum k_{eq} A$$

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

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

Measured impacts of sorption

- Chamber studies w/ and w/out carpet



Won et al., 2001 *Indoor Air*

Measured impacts of sorption

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

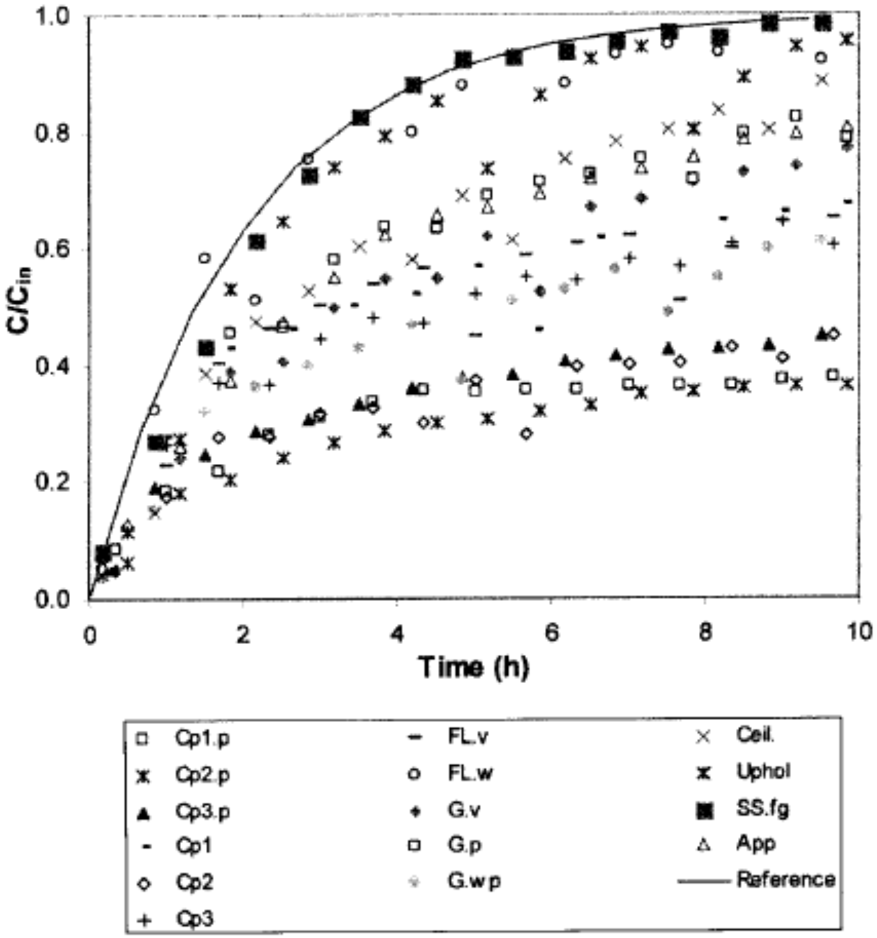


Fig. 3 Effects of Materials on Sorption (1,2-dichlorobenzene)

Won et al., 2001 *Indoor Air*

Measured impacts of sorption

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

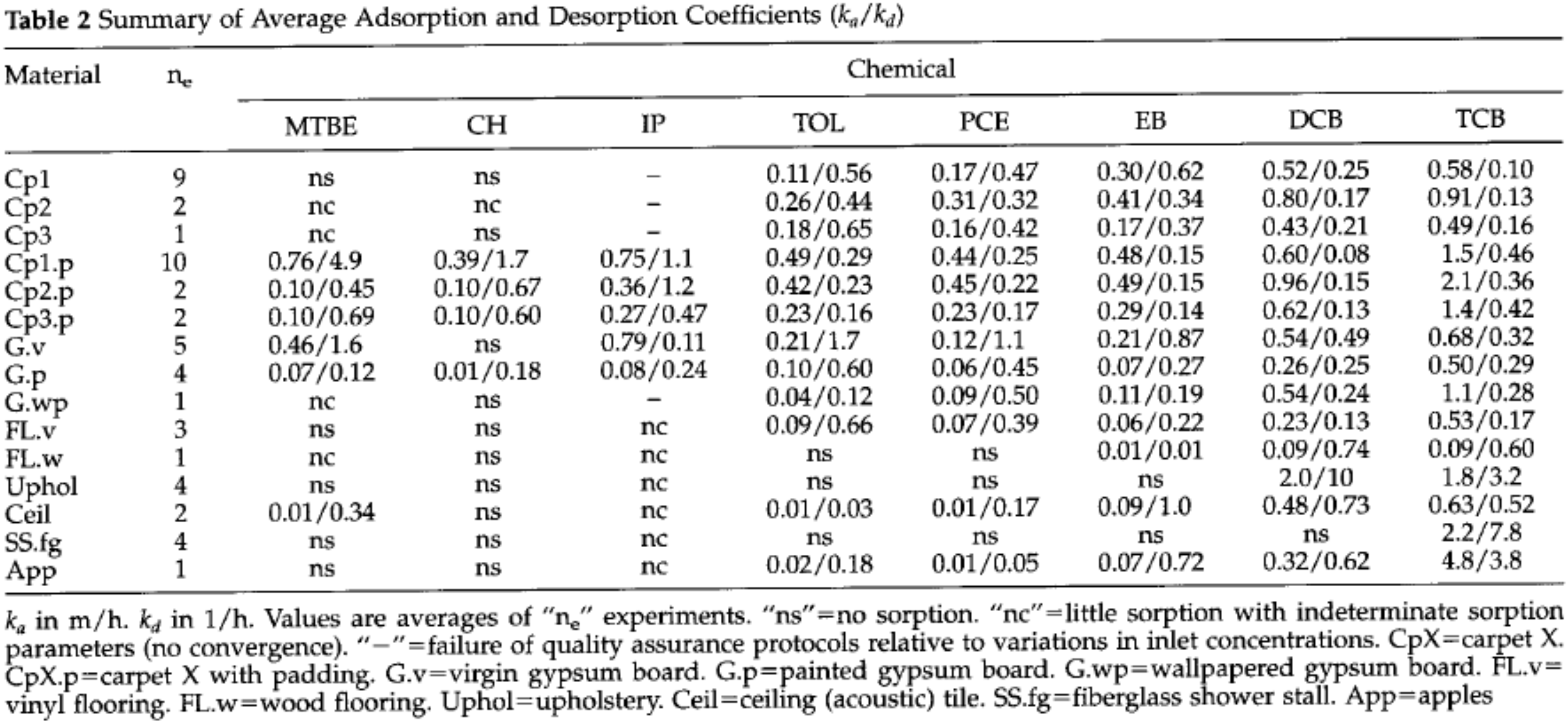


Table 2 Summary of Average Adsorption and Desorption Coefficients (k_a/k_d)

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

Won et al., 2001 *Indoor Air*

Measured impacts of sorption

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

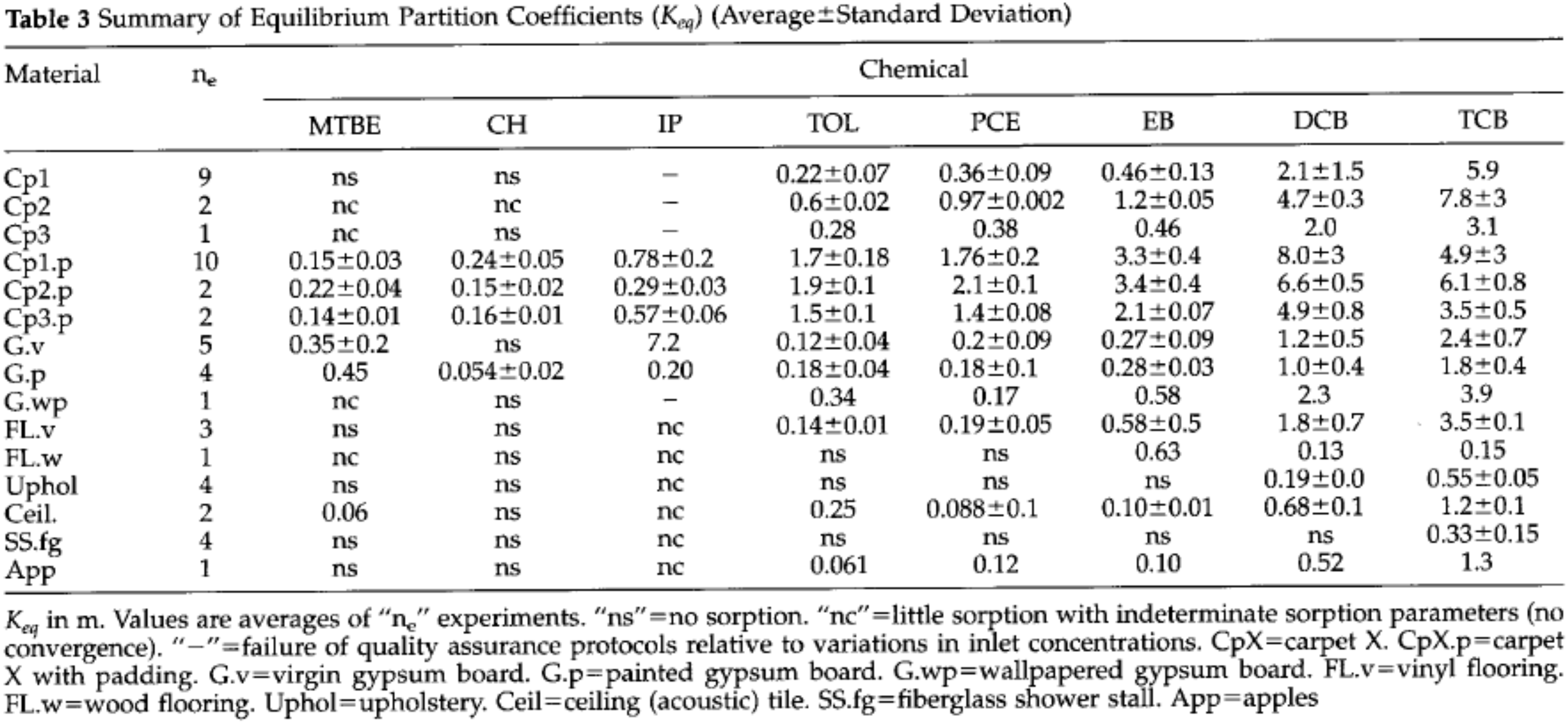


Table 3 Summary of Equilibrium Partition Coefficients (K_{eq}) (Average±Standard Deviation)

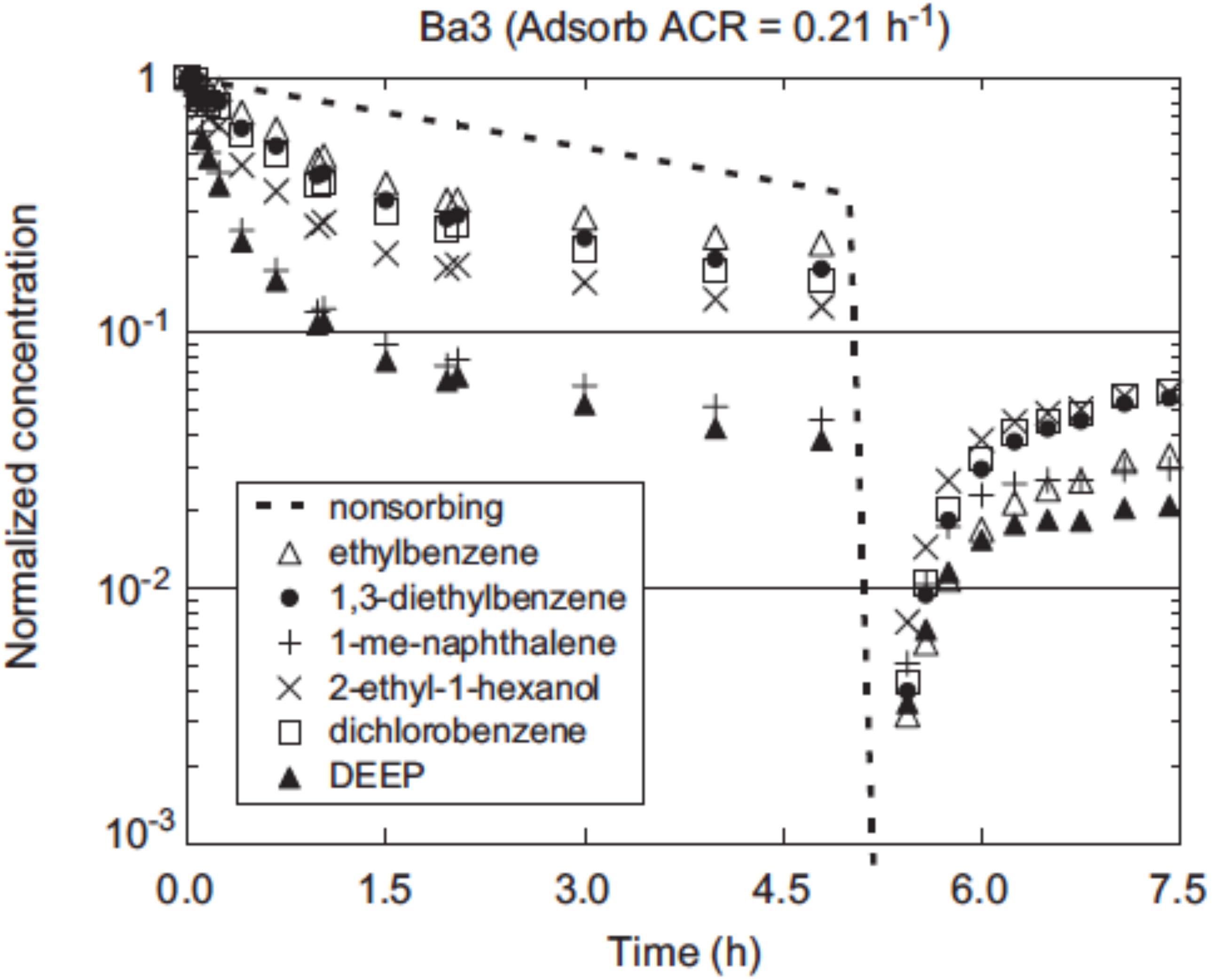
Material	n_e	Chemical							
		MTBE	CH	IP	TOL	PCE	EB	DCB	TCB
Cp1	9	ns	ns	–	0.22±0.07	0.36±0.09	0.46±0.13	2.1±1.5	5.9
Cp2	2	nc	nc	–	0.6±0.02	0.97±0.002	1.2±0.05	4.7±0.3	7.8±3
Cp3	1	nc	ns	–	0.28	0.38	0.46	2.0	3.1
Cp1.p	10	0.15±0.03	0.24±0.05	0.78±0.2	1.7±0.18	1.76±0.2	3.3±0.4	8.0±3	4.9±3
Cp2.p	2	0.22±0.04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

Won et al., 2001 *Indoor Air*

Measured impacts of sorption in real rooms

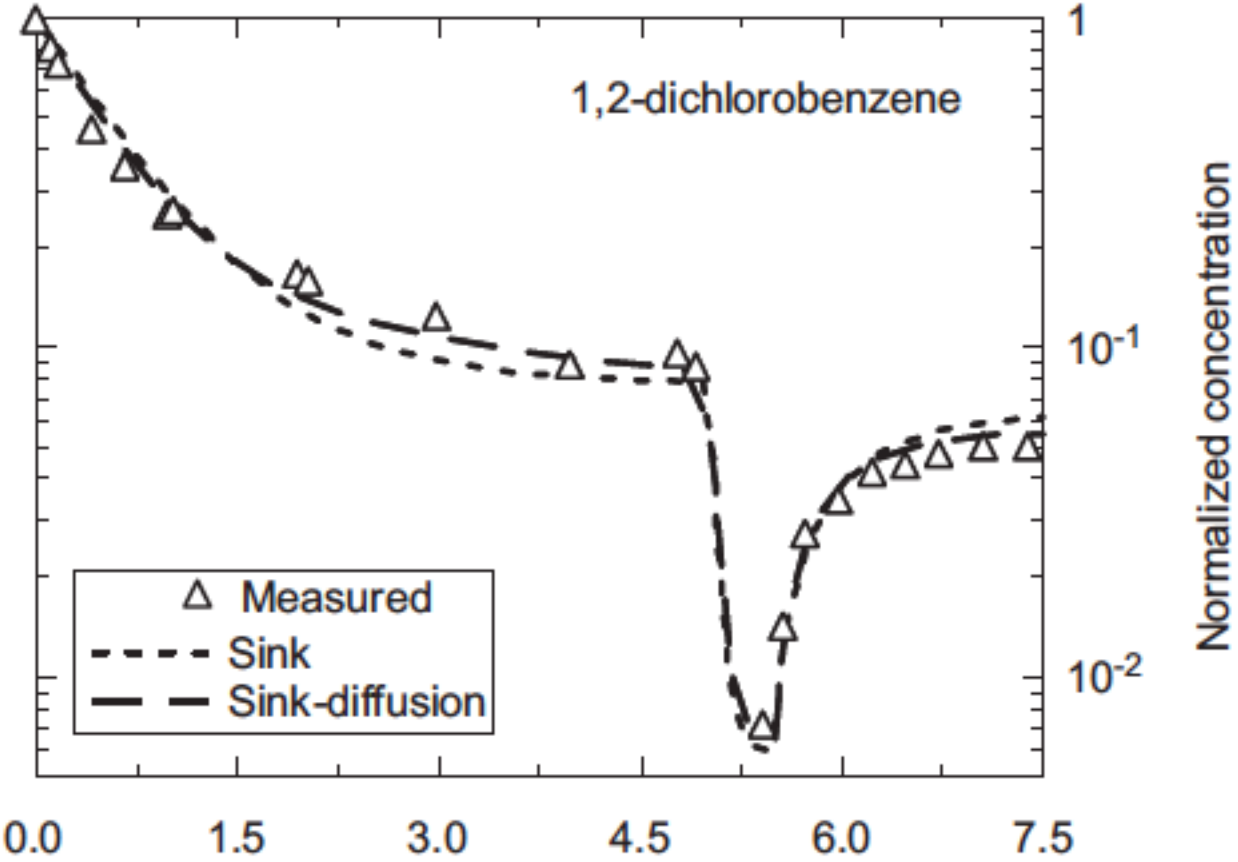
- Injection + adsorption + flush out period + desorption in a bathroom



Singer et al., 2007 *Atmos Environ*

Measured impacts of sorption in real rooms

- Measured and modeled adsorption, flush out, and desorption



Singer et al., 2007 *Atmos Environ*

Finishing up today

- Next time:
    - More gas-phase pollutant fundamentals:
        - Reactive deposition
        - Homogeneous chemistry

    - Will assign HW #2