

Living in a Material World

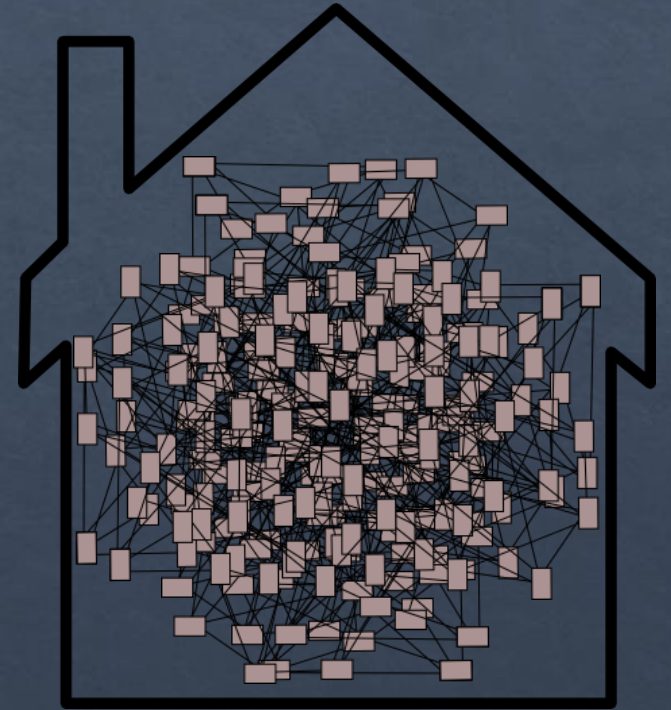
How the Surfaces that Surround You Affect what You Breathe

Richard L. Corsi, Ph.D., P.E.

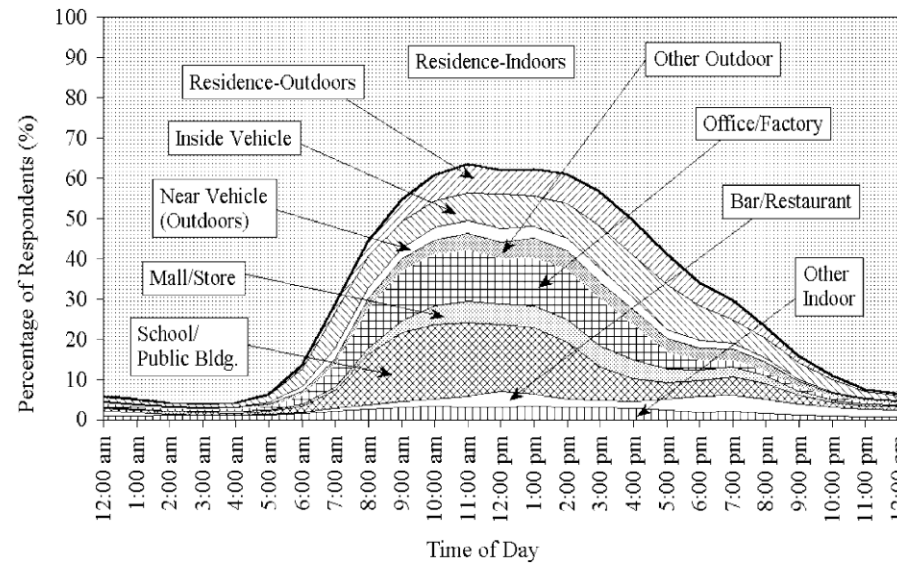
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Motivation



Klepeis et al., J. Exposure Analysis & Environ. Epidemiol., 11: 231-252 (2001)

$$\text{Inhaled (I/O)} = \frac{C_{\text{in}} t_{\text{in}} B_{\text{in}}}{C_{\text{out}} t_{\text{out}} B_{\text{out}}} = \left\{ \frac{C_{\text{in}}}{C_{\text{out}}} \right\} \left\{ \frac{t_{\text{in}}}{t_{\text{out}}} \right\} \left\{ \frac{B_{\text{in}}}{B_{\text{out}}} \right\}$$

Outdoor origin $\approx 1 - 10$

Indoor origin $\approx 25 - 100$

Indoor exposure critical. Buildings = underutilized “tool”

Major Differences: Indoor vs. Outdoor

- Sunlight (UV) ($I \ll O$)
- Washout/rainout ($I \ll O$)
- Time scales ($I < O$)
- Ozone ($I \ll O$)
- Terpenes ($I \gg O$)
- WSOG ($I \gg O$)
- Density of people ($I \gg O$)
- Control strategies ($I \gg O$)

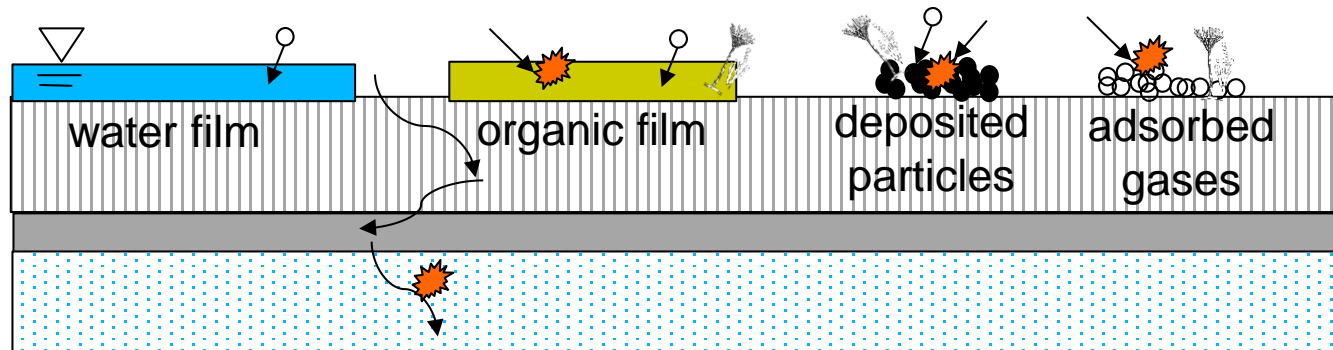


A/V: Indoor \approx 300 – 1,000 x Outdoor

Underscores importance of pollutant/material interactions

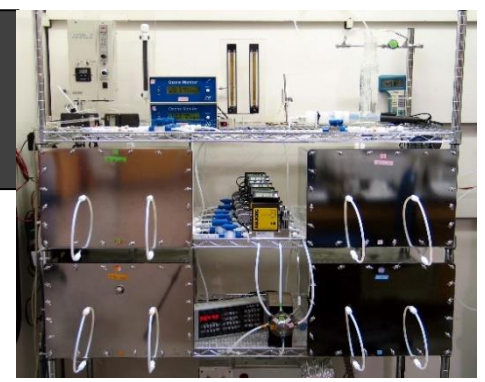
Material Complexities

- Surface films
 - Contaminant accumulation
 - Process interactions
- } = $f_n(t)$

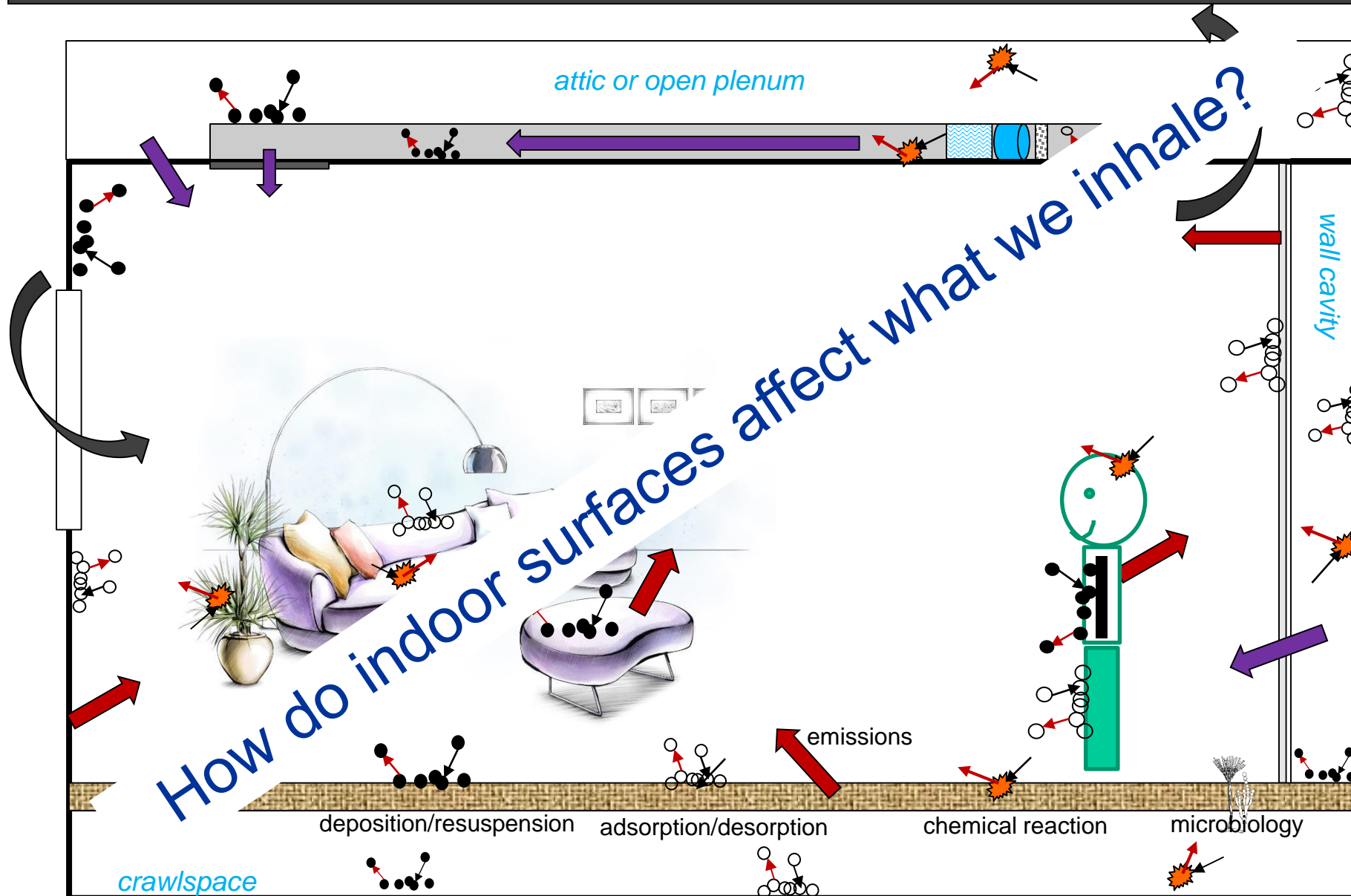


- Complex materials & material systems
- Materials generally poorly characterized

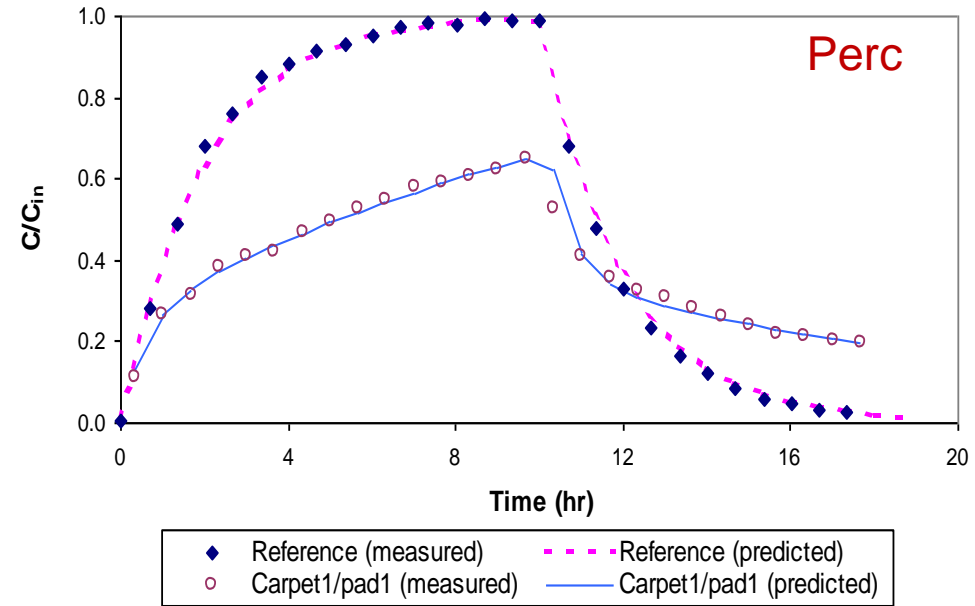
Study of indoor materials has great intellectual merit



Occupied & Unoccupied Spaces



1. Sorptive Interactions



Won, D., et al., "Sorptive interactions between VOCs and indoor materials," *Indoor Air*, **11**(4): 246-256 (2001).

- Indoor materials reduce exposure if you are present with source
- Indoor materials increase exposure if you are present during desorption

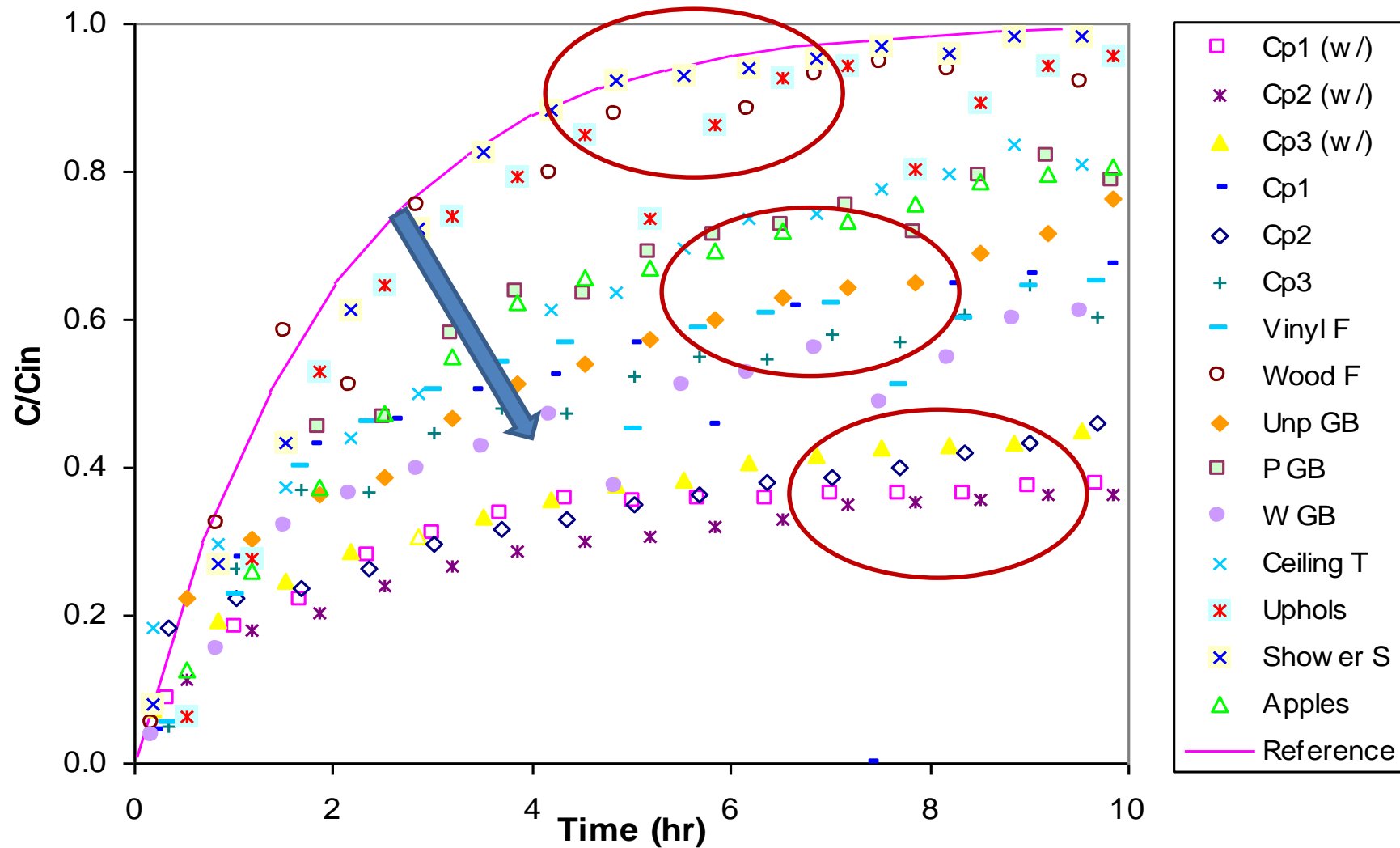
Adsorbates & Adsorbents

	P_{vp} (atm)	
MTBE	0.32	Vinyl flooring
Cyclohexane	0.13	Wood flooring
Isopropanol	0.042	Gypsum board (3 types)
Toluene	0.038	<ul style="list-style-type: none">• virgin• painted• wallpapered
Tetrachloroethene	0.025	Acoustic ceiling tile
Ethylbenzene	0.013	Cotton upholstery
1,2-Dichlorobenzene	0.002	Plastic shower stall
1,2,4-Trichlorobenzene	0.00045	Carpet
		<ul style="list-style-type: none">• without PUF cushion• with PUF cushion• components
		Apples



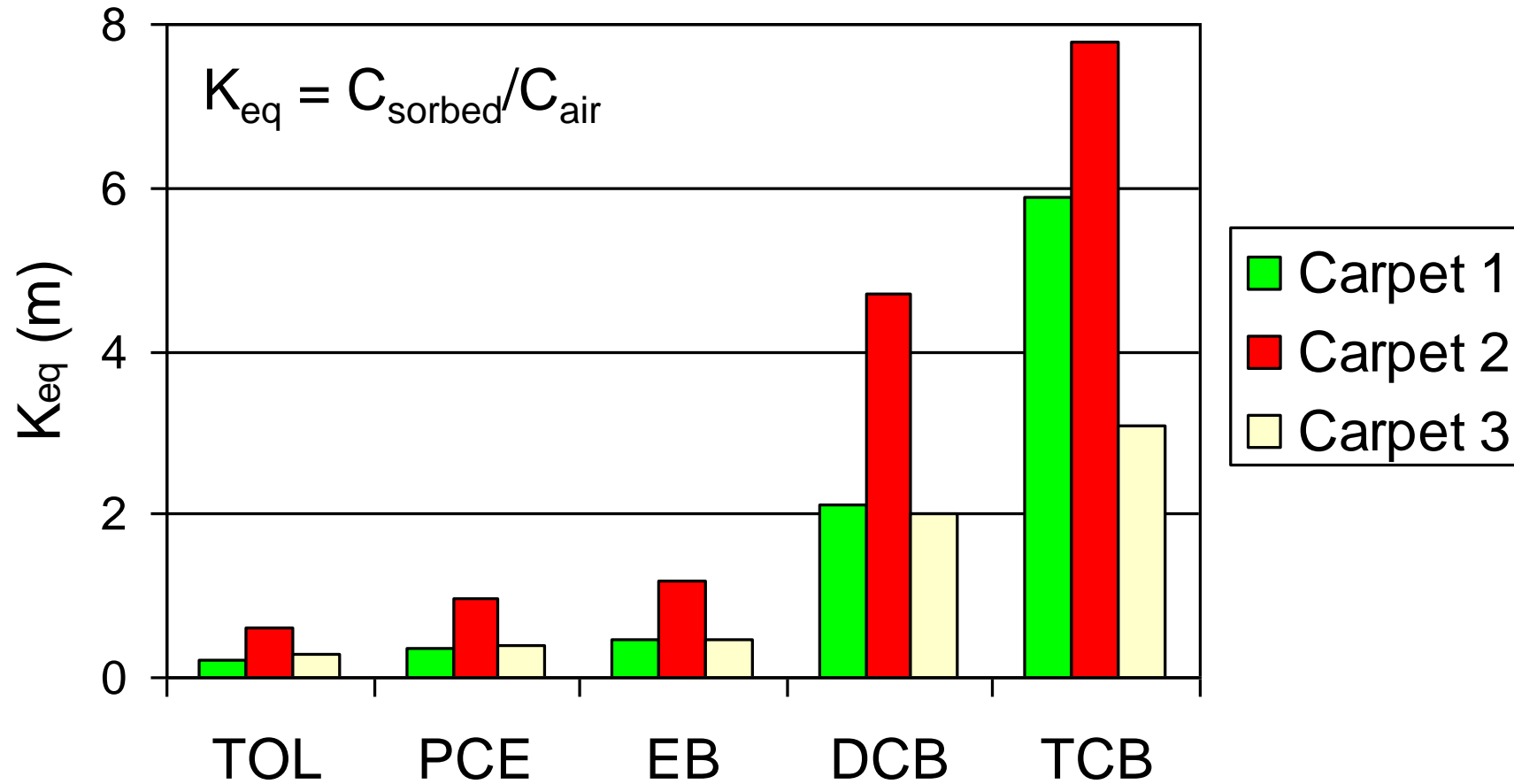
Varied: concentrations, RH, multi-adsorbates, AER; $T = 24-25\text{ }^{\circ}\text{C}$

Adsorption of 1,2-Dichlorobenzene



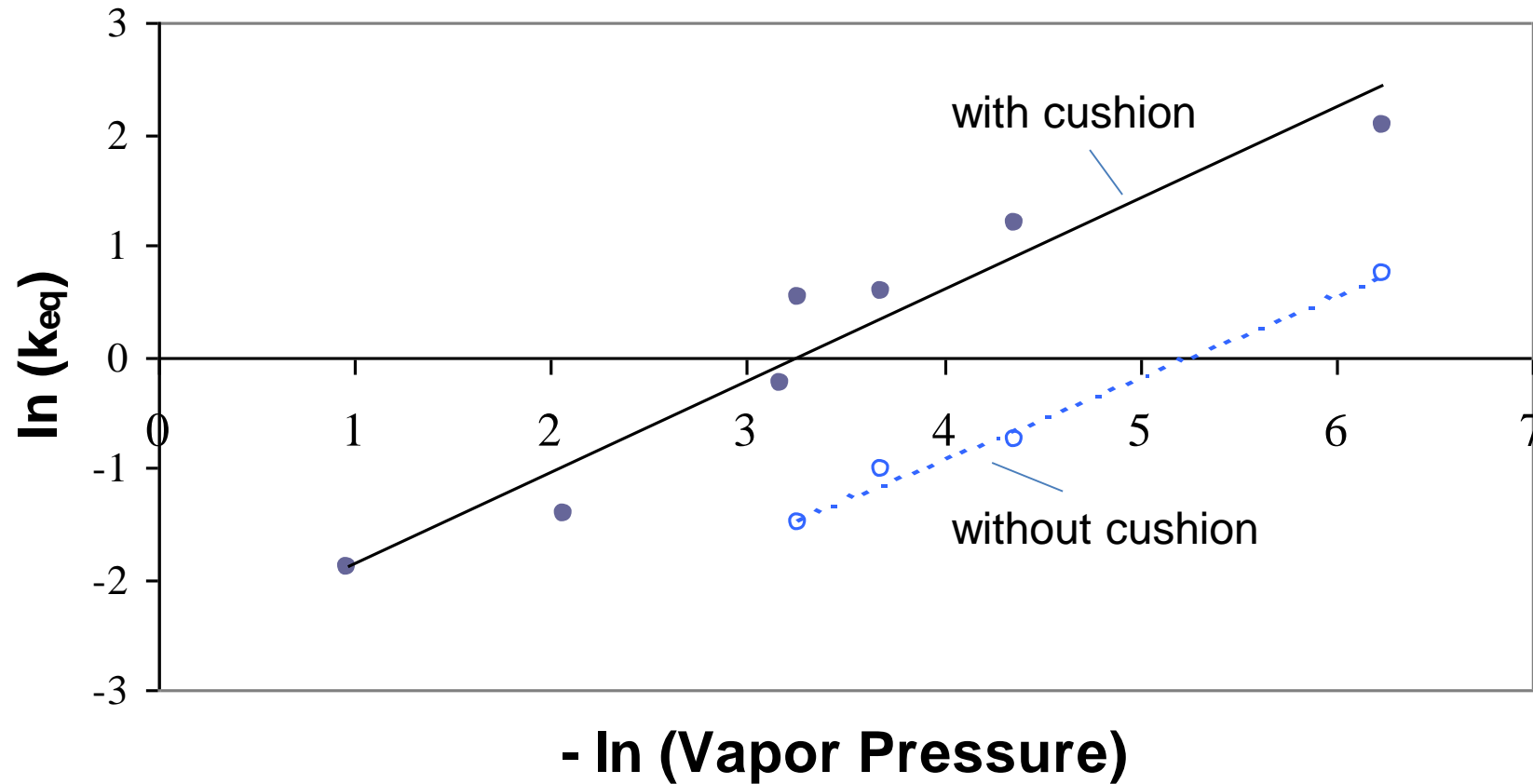
Equilibrium Partition Coefficients

Carpet *without* Cushion



Carpet 2: 90% olefin (polypropylene)
(material composition matters)

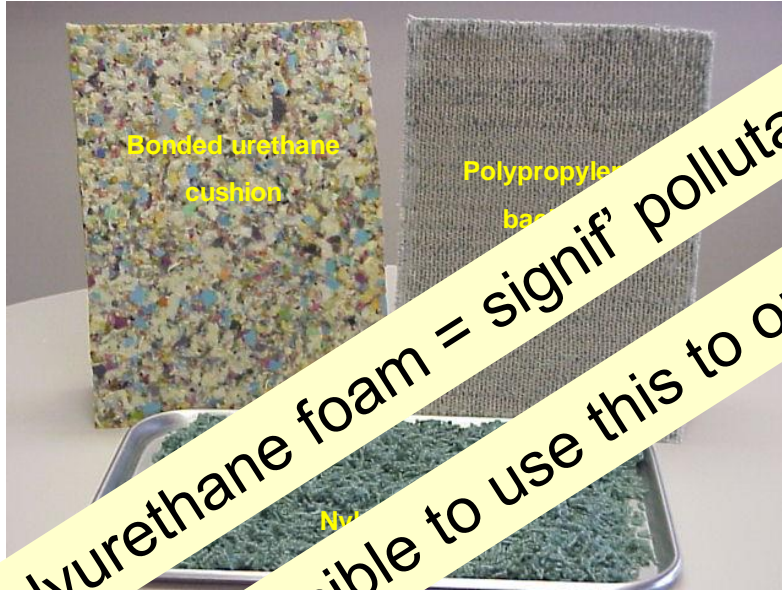
K_{eq} – Chemical & Material Properties



K_{eq} (m)

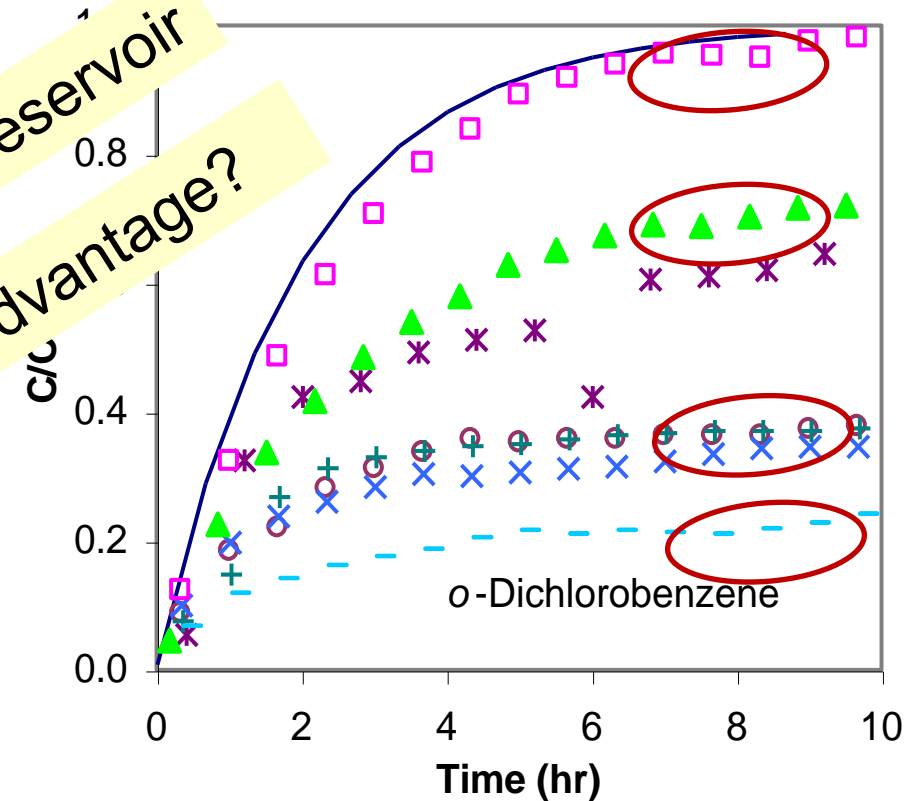
P_{vp} (Pa)

Adsorption to Carpet Components



Polyurethane foam = signif' pollutant reservoir

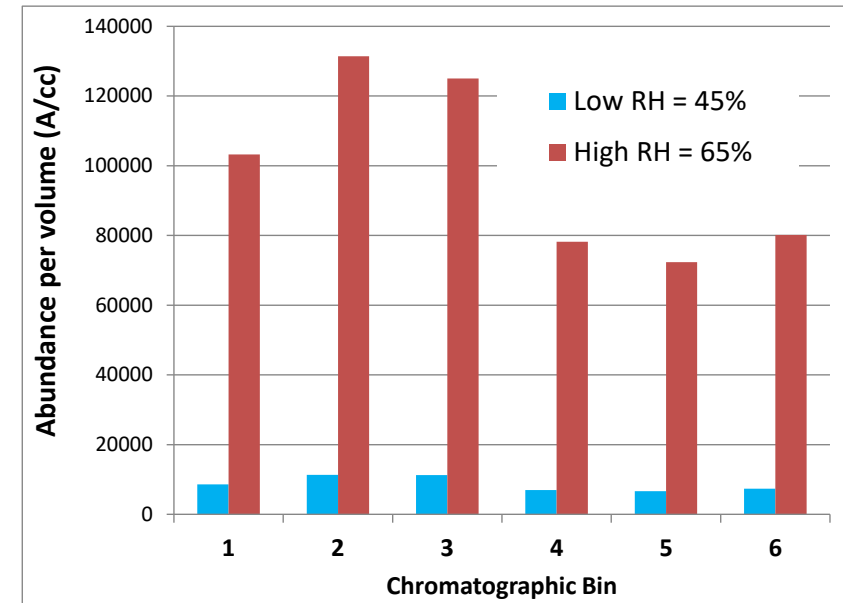
Is it possible to use this to our advantage?



- Fiber (E45)
- △ Backing (E46)
- Pad 1 (E47)
- × Fiber + backing (E1)
- Fiber, back, & pad 1 (E15)
- + Fiber, back, & pad 2 (E21)
- × Fiber, back, & 2 pad 1 (E43)
- Reference

Humidity Effects – 6 (x 2) Home Study

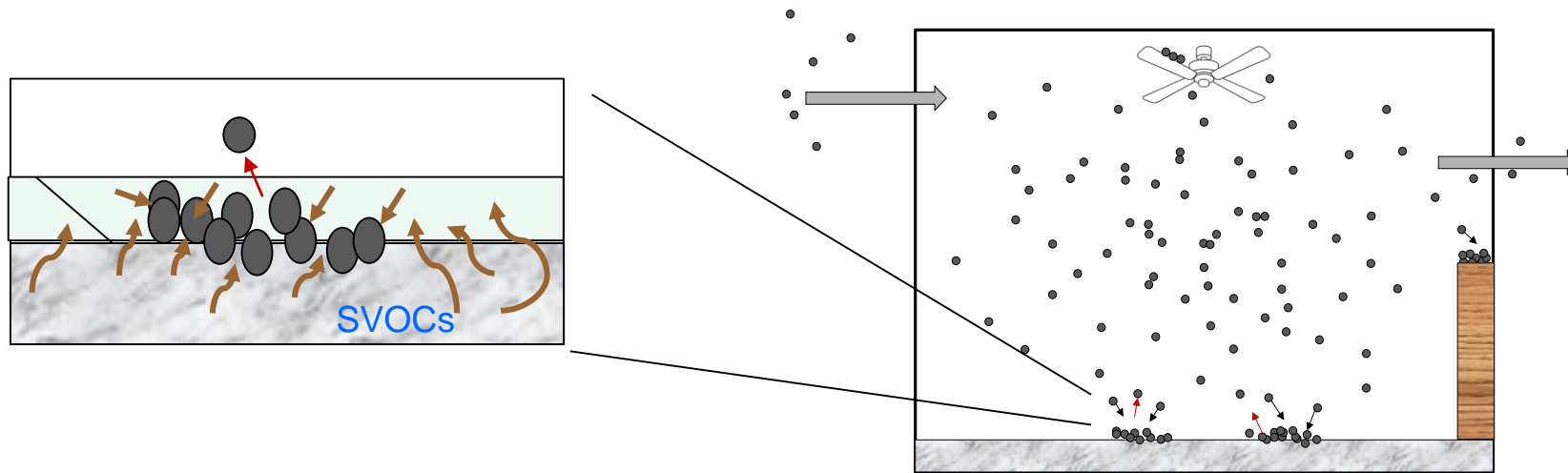
- Mean multiplier = 2.6
- Signif' variation between homes
- Magnified VOCs
 - Texanol™ in all homes
 - Terpenes/terpene alcohols
 - Stable carbonyls
 - *p*-Dichlorobenzene (1 home x 2)
 - A lot more



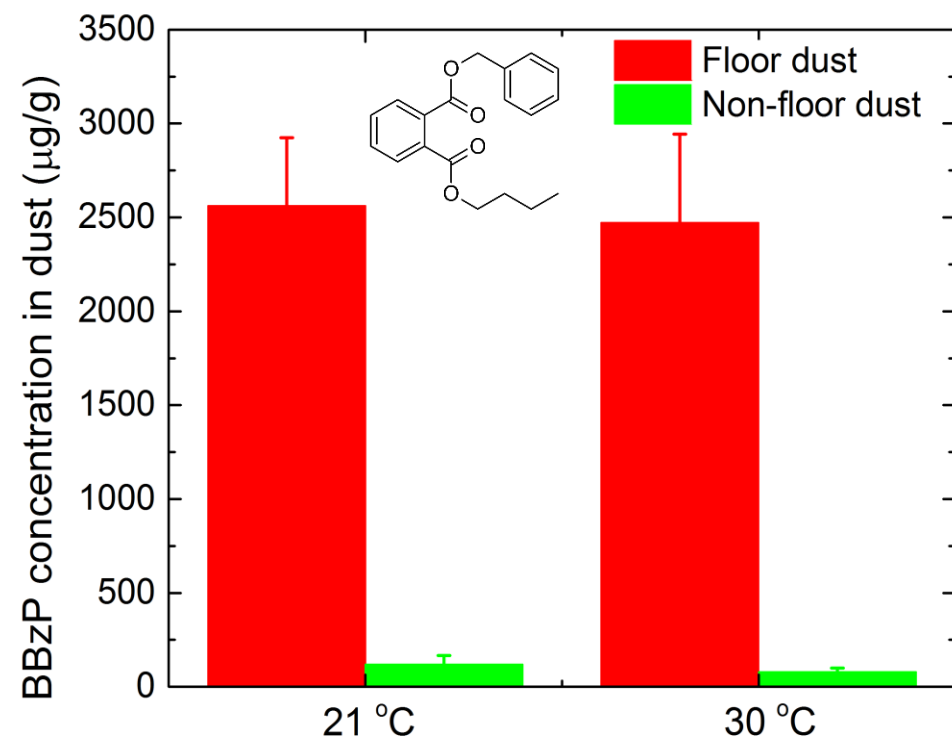
- A lot appears stored on/in materials.
- Realistic changes in RH can significantly increase VOCs in air.
- Impacts on exposure? Possibilities for harnessing?

2. Particle Deposition / Transformation

- PM vehicle for chem transport into respiratory system.
- Particles deposit on & re-suspend from surfaces.
- **Do materials alter composition of particles?**



Particles & Surface Uptake

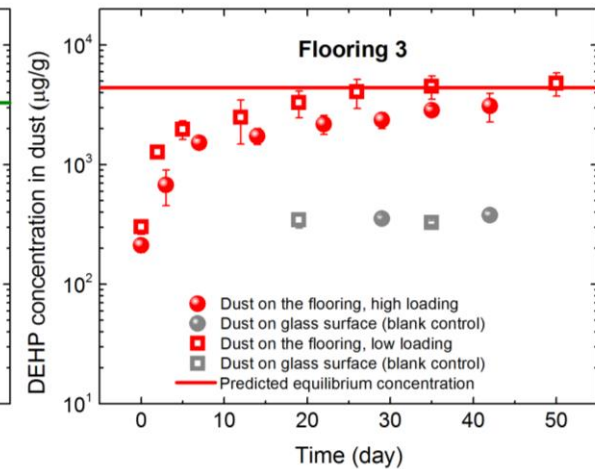
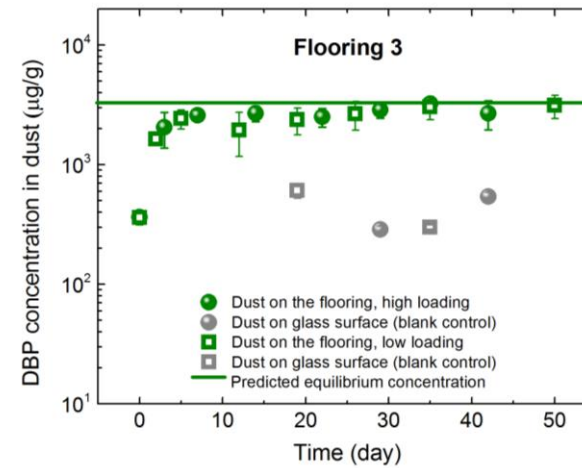
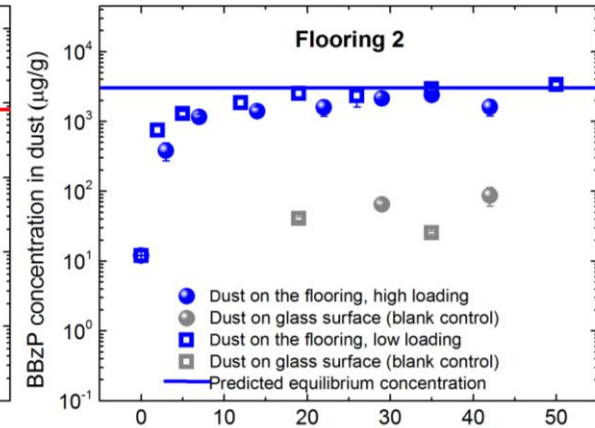
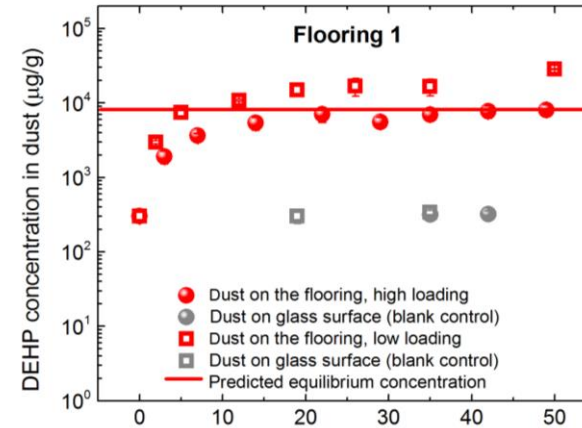
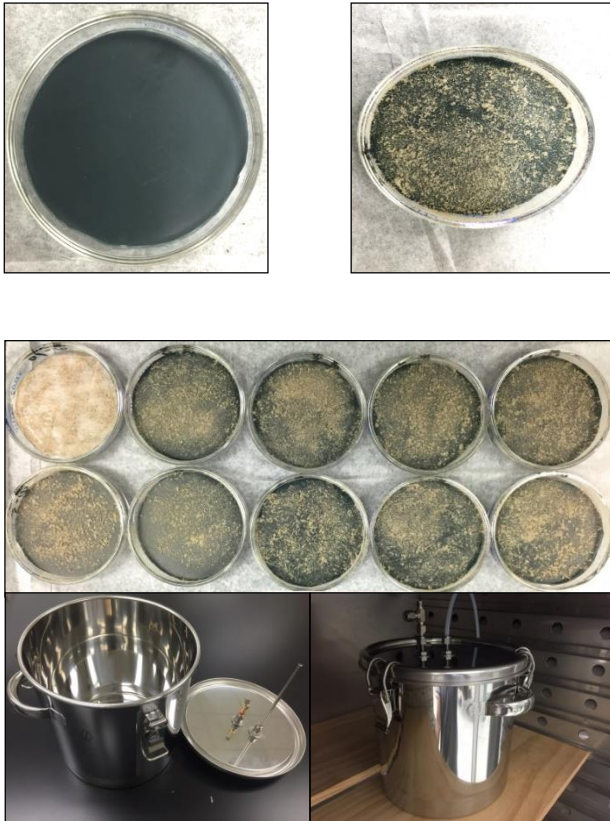


C. Bi et al., *Environ. Sci. Technol.*, 2015, 49, 9674-9681

Courtesy Dr. Ying Xu & Chenyang Bi

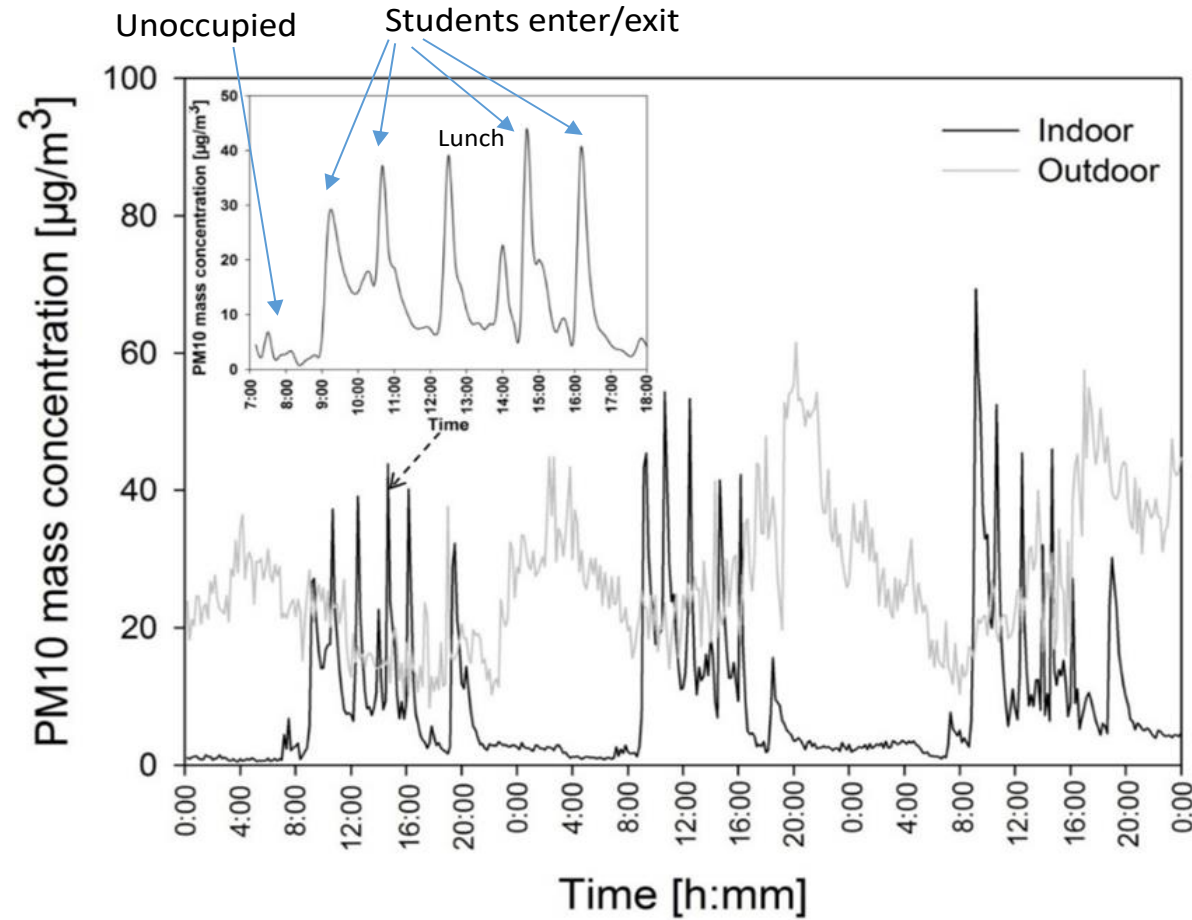
BBzP in floor dust \approx 20-30 x non-floor dust

Transfer from Flooring to Dust

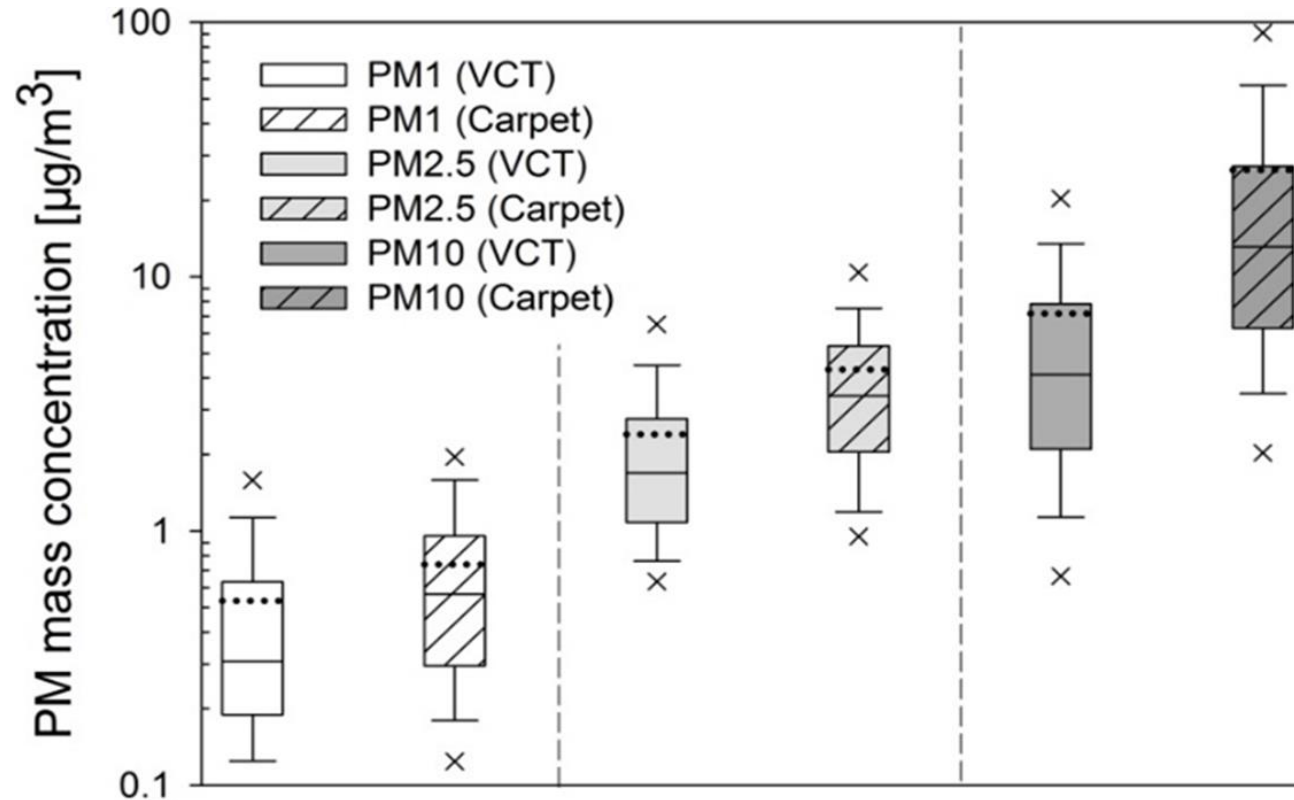


(unpublished) Courtesy Dr. Ying Xu & Chenyang Bi

Particle Resuspension



Influence of Flooring



Ren, J. *et al. Building & Environment* (accepted)

Should carpet in schools/offices be replaced to avoid resuspension of particles, e.g., containing SARS-CoV-2?

Carpet Crawlers

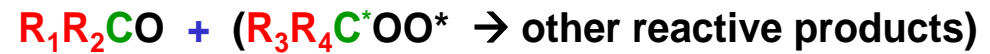
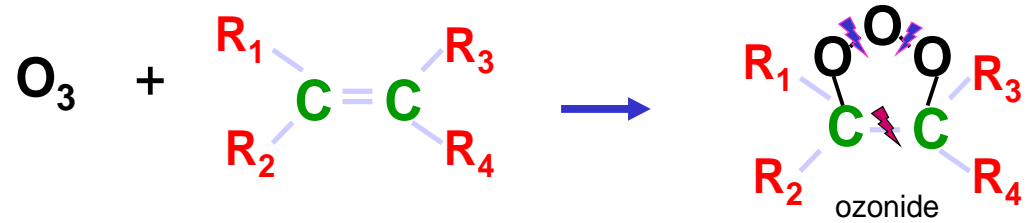
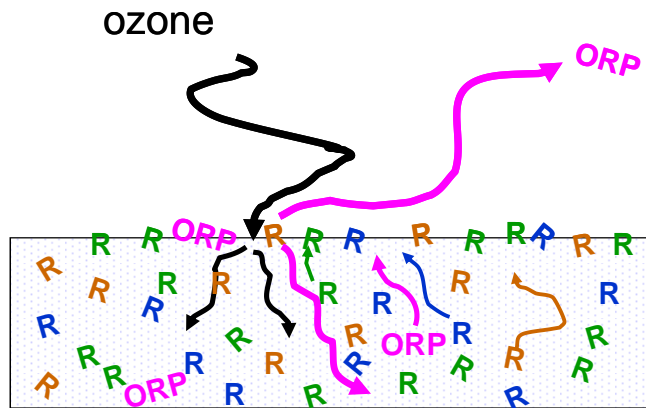


- 360 mid-western homes (1992 – 1993)
- Pesticides and PAH
- DDT in 25% of homes (banned in 1972!) – persistence!
- PAH levels in > 50% of homes exceed haz site triggers

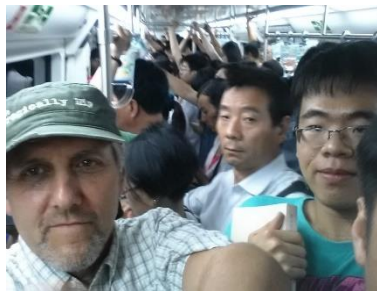
“If truckloads of dust with the same concentration of toxic chemicals as is found in most carpets were deposited outside, these locations would be considered hazardous waste dumps”

Ott & Roberts, “Everyday Exposure to Toxic Pollutants,” Scientific American, 1998

3. Ozone Reactions

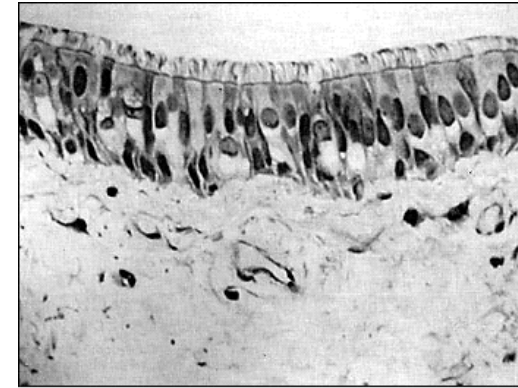
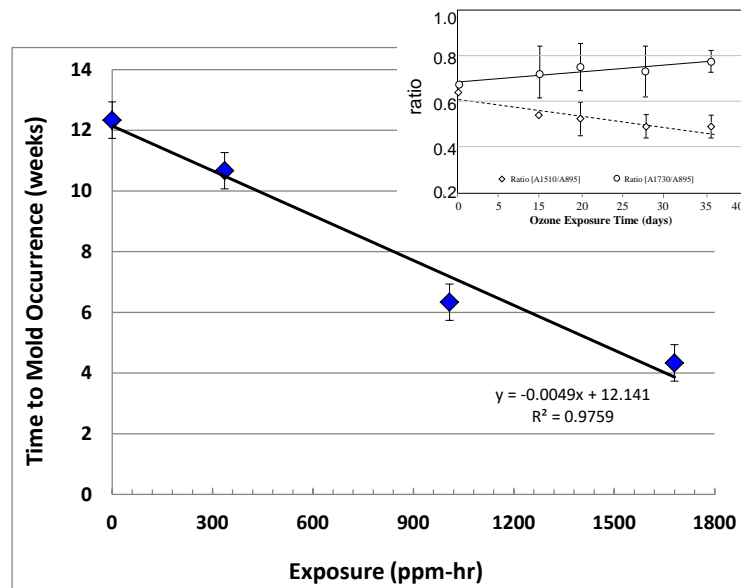


$$R_{O_3} = -v_d CA \quad \frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle}$$

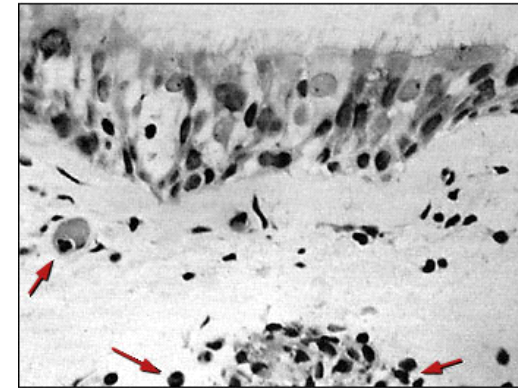


Impacts of Ozone

- Unhealthy to breathe
- Degradation of works of art & rubber
- Leaching of lead from lead-based paints
- Reaction product release to indoor air
- Changes in susceptibility to fungal growth



Healthy Lung Tissue

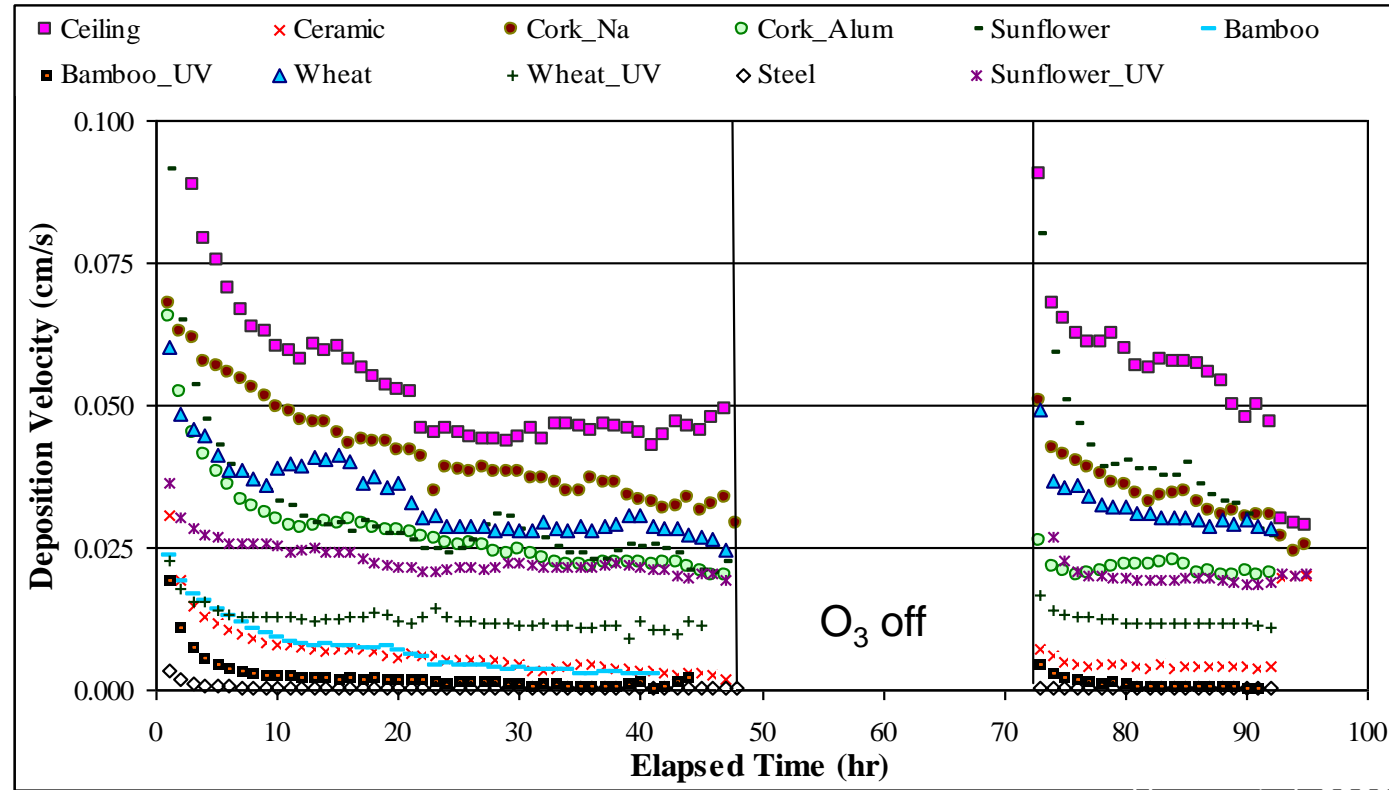


Ozone-damaged Lung Tissue

(Micrographs from American Thoracic Society, from *American Review of Respiratory Diseases*, Vol. 148, 1993, Robert Aris et al., pp. 1368 -1369.)

Dynamics of Surface Reactivity

Hoang C., et al., *Building and Environment*, 44: 1627-1633 (2009)

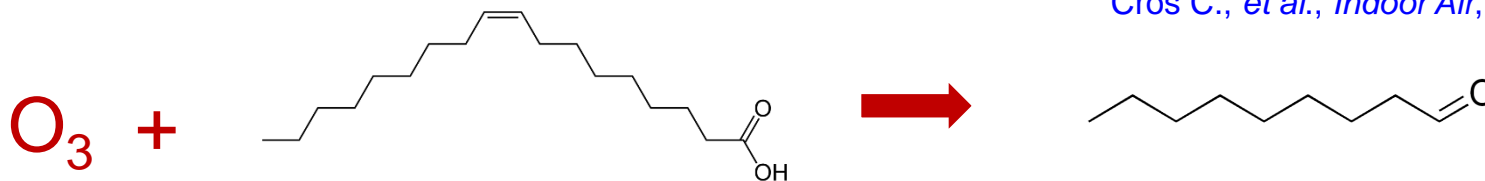
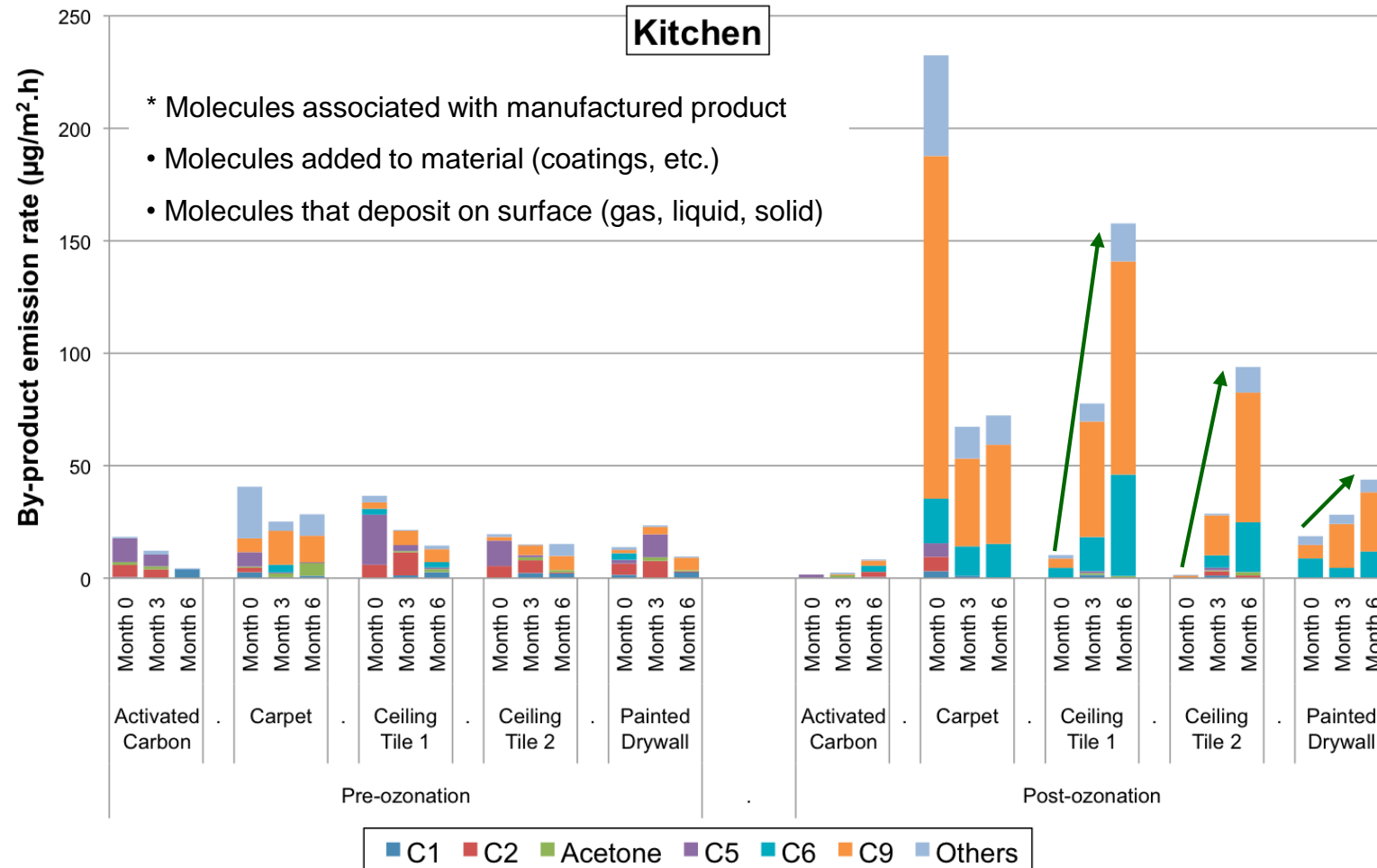


$$R_{O_3} = -v_d CA$$

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

- Transport-limited deposition velocity similar in each case
- Significant differences in reactivity
- Declining reactivity
- Regeneration

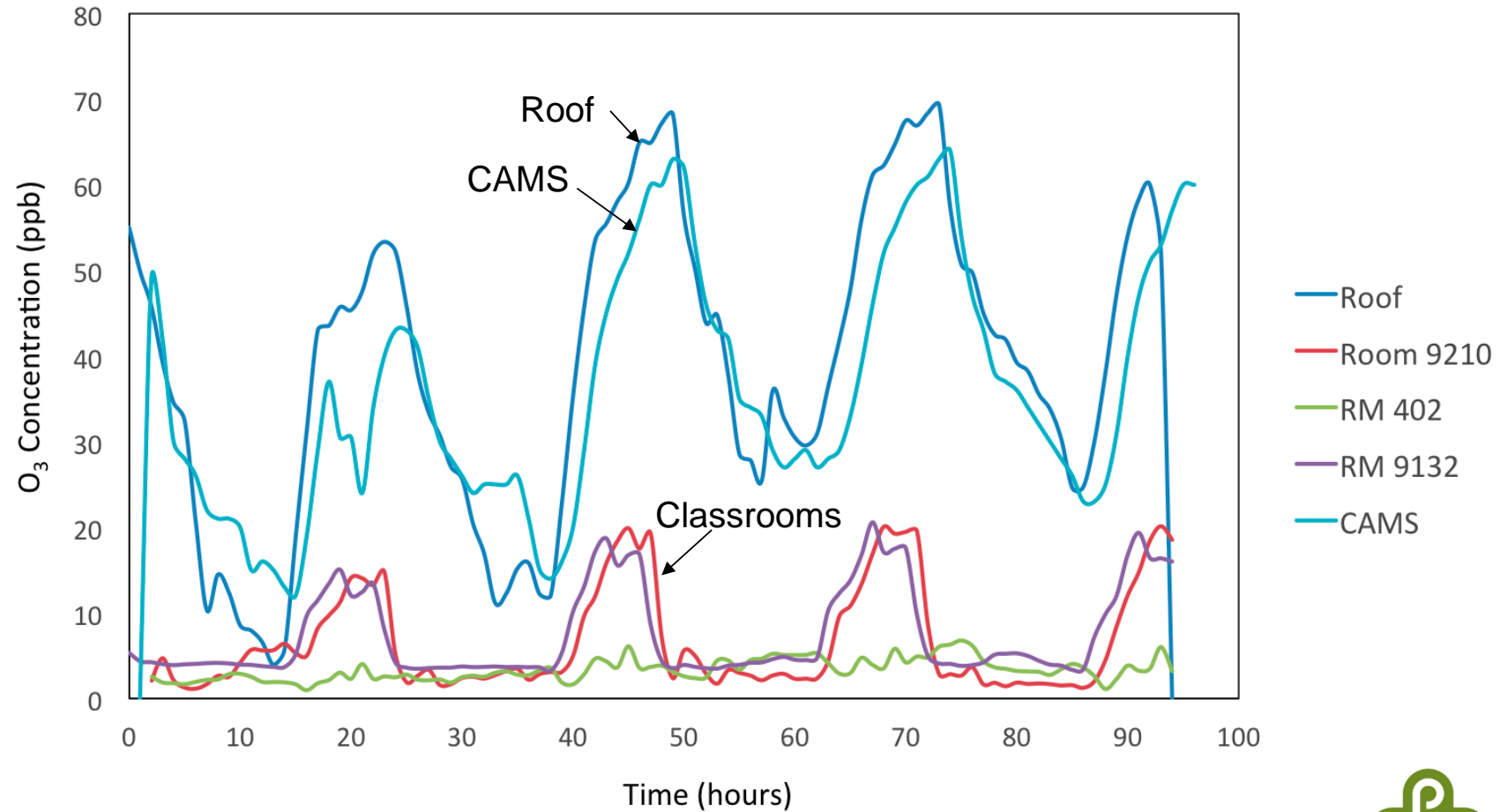
Materials in Field: Secondary Emissions



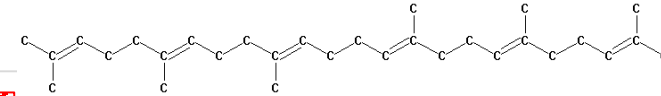
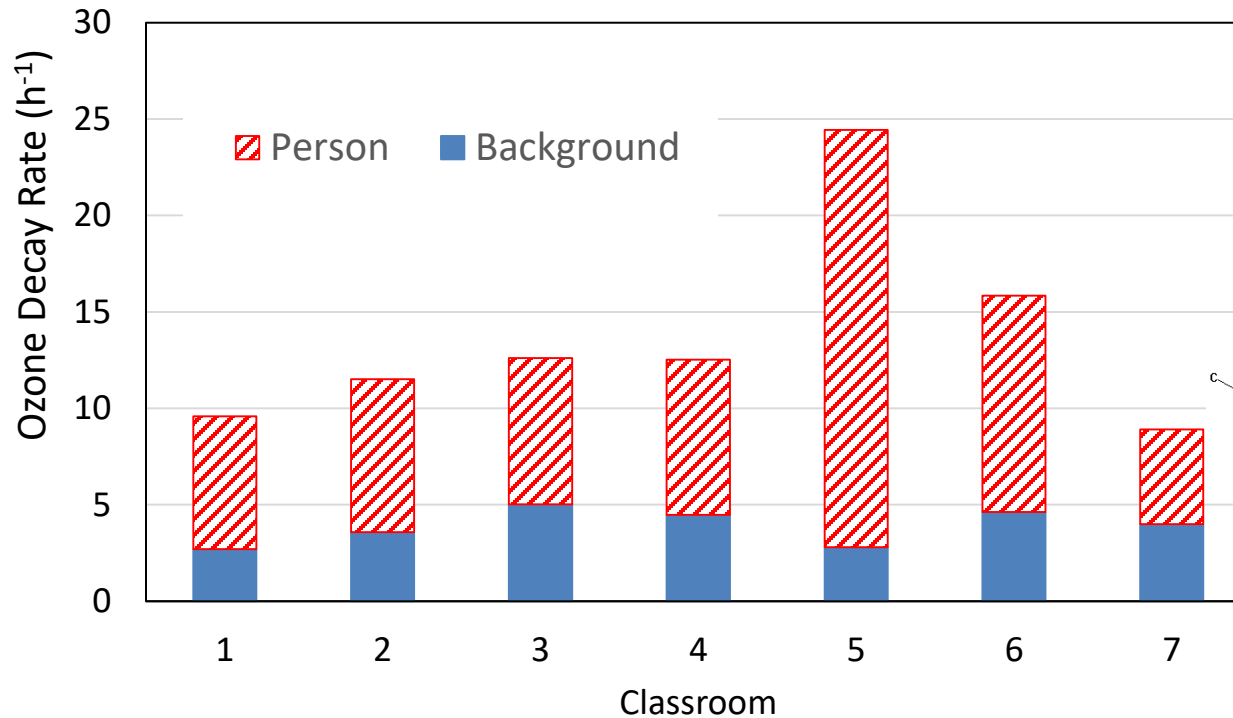
Cros C., et al., *Indoor Air*, 22: 43-53 (2012)

Ozone in Classrooms

University of Texas Healthy High School PRIDE field sampling campaign



Reactivity of Occupants

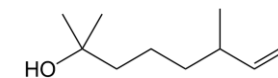


v_d /person average (cm/s): **1.1**

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

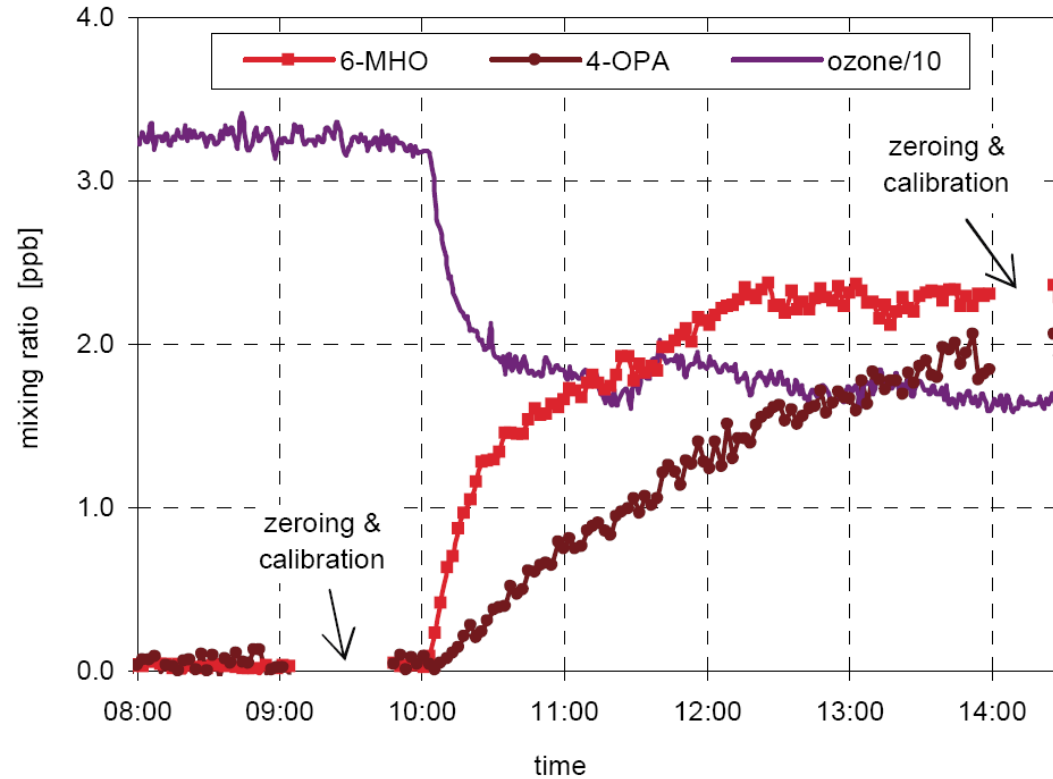
0.45 cm/s: A. Wisthaler & CJ Weschler, *PNAS*, 2010, 7(15), 6568-6575

0.5 cm/s: A. Fischer et al., *Atmospheric Environment*, 2013, 81, 11-17



Ozone Reactions with Human Surfaces

- 30 m³ room
- Sparsely furnished
- $\lambda \approx 1 \text{ hr}^{-1}$
- O₃ at 33 ppb
- 2 people enter
- Rapid O₃ decay
- Rapid increase in 6-methyl-5-hepten-2-one
- Rapid increase in 4-oxopentanal



Wisthaler, A and Weschler CJ, *PNAS*, 107(15): 6569-6575 (2010)

4. Putting Materials to Work for Us

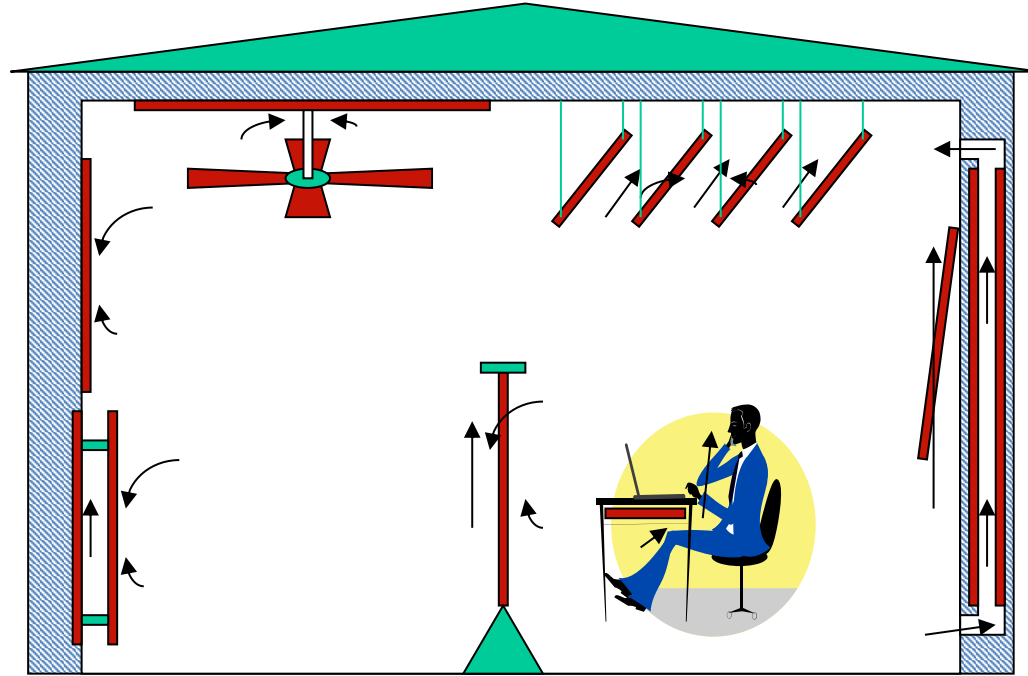


Image courtesy of Glenn Morrison

- Conceptual shift to materials/furnishings as beneficial
- Harnessing of existing/novel manufactured materials
- Take advantage of material properties & fluid mechanics

Passive Removal Materials (PRMs)

- Particles and gases deposit on surfaces
- **Potential removal**
Mass-transfer (v_t) rates 4 to 8 m h⁻¹
Area to volume ratio (A/V) 2 to 4 m² m⁻³
 $v_t A/V = 8$ to 32 h⁻¹
- Contrast: Residential AER ~ 0.5 h⁻¹
- Huge potential for **PASSIVE** removal of



Adsorption/desorption (equalization; occupancy driven)

Particle deposition & removal

Reactions w/o harmful products

Passive Removal of Ozone

- High & sustained reactivity
- Good fluid mechanics
- Minimal reaction product yield
- Large surface area
- Low to no energy use
- Aesthetically appealing
- Economical

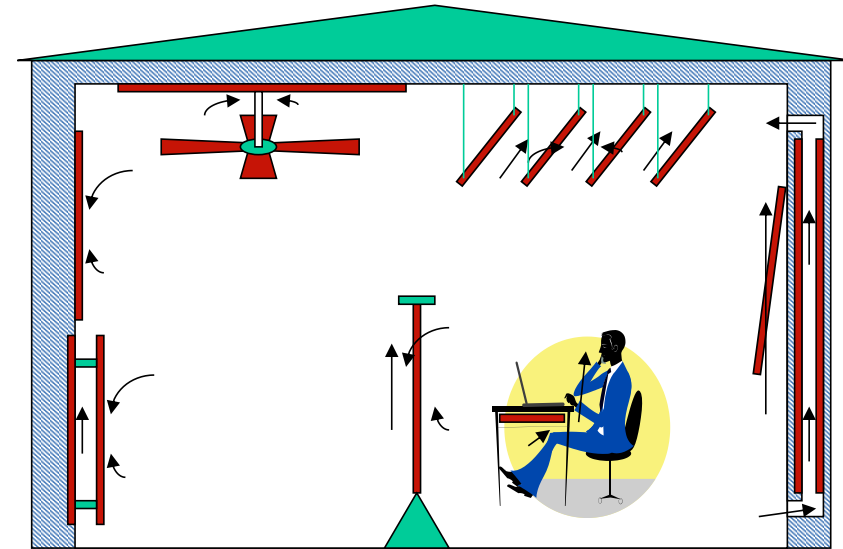
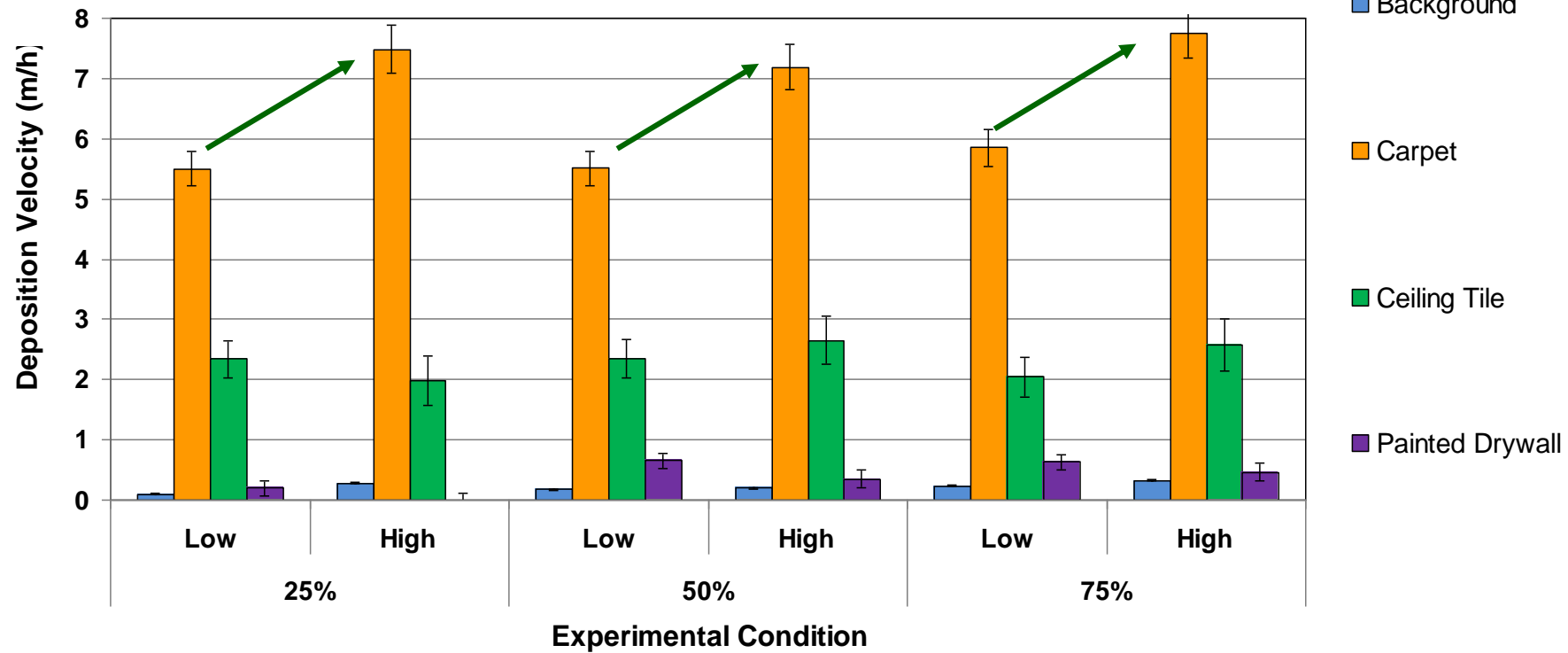


Image courtesy of Glenn Morrison

Tested 32 materials to date - examples:

Activated carbon, Unfired clay brick, Limestone, Perlite,
Clay paint & plaster

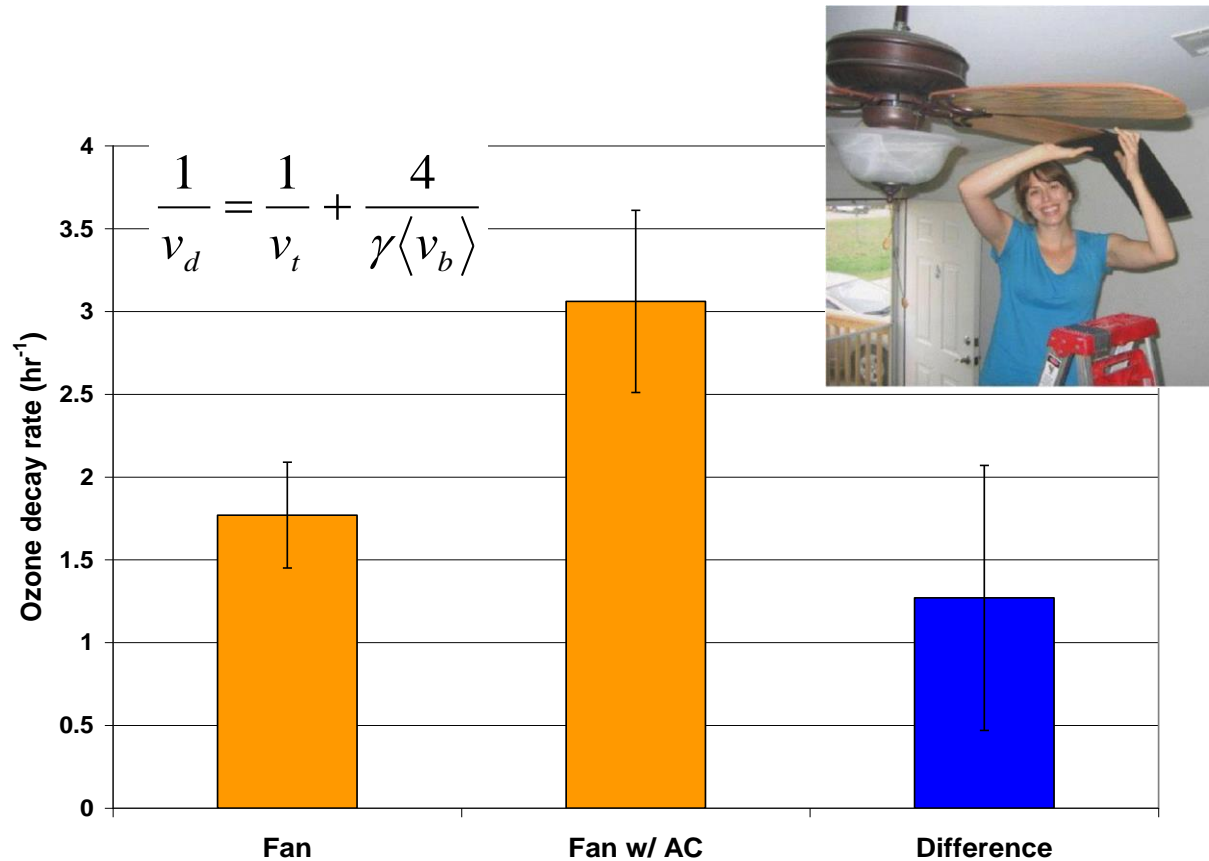
Reactivity & Fluid Mechanics



Gall E, et al., *Atmos Environ*, 77: 910-918 (2013)

$$R_{O_3} = -v_d CA \qquad \frac{1}{v_d} = \frac{1}{v_t} + \frac{4}{\gamma \langle v_b \rangle}$$

Activated Carbon Sleeves on Fan Blades



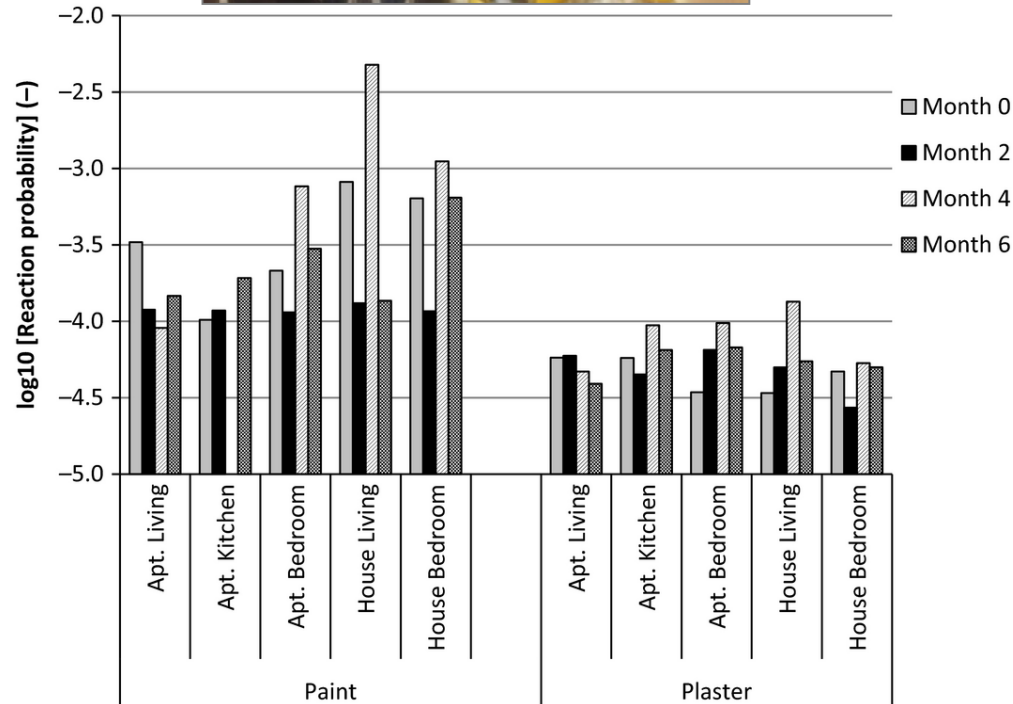
- AC on fan blades: O_3 decay up 1.25 hr^{-1}
- Average 33% decrease in indoor ozone

Clay Paint & Plaster

- Small chamber; Large chamber
- UTest House; Human panels
- Signif' ozone reaction
- Insignificant reaction products
- Scavenges organic acids
- Buffers increased water vapor
- Improved human perceptions
 - Blind tests; significant gender effects
 - Darling et al., Building & Environment (2012)



Clay Paint & Plaster: “Matured In Field”



Ozone **reaction probabilities** of **clay plaster** were on the order of those associated with its major component, **kaolinite**.

Reaction probability of kaolinite, a hydrous aluminosilicate mineral that comprises 50% of the clay plaster, was reported by Michel et al. to be 3×10^{-5} ($\pm 1 \times 10^{-5}$). Reactions of mineral oxides with ozone are catalytic, resulting in net **destruction of ozone without depletion of the reactivity** of the metal oxide surface.

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

Some References on Clay as PRMs

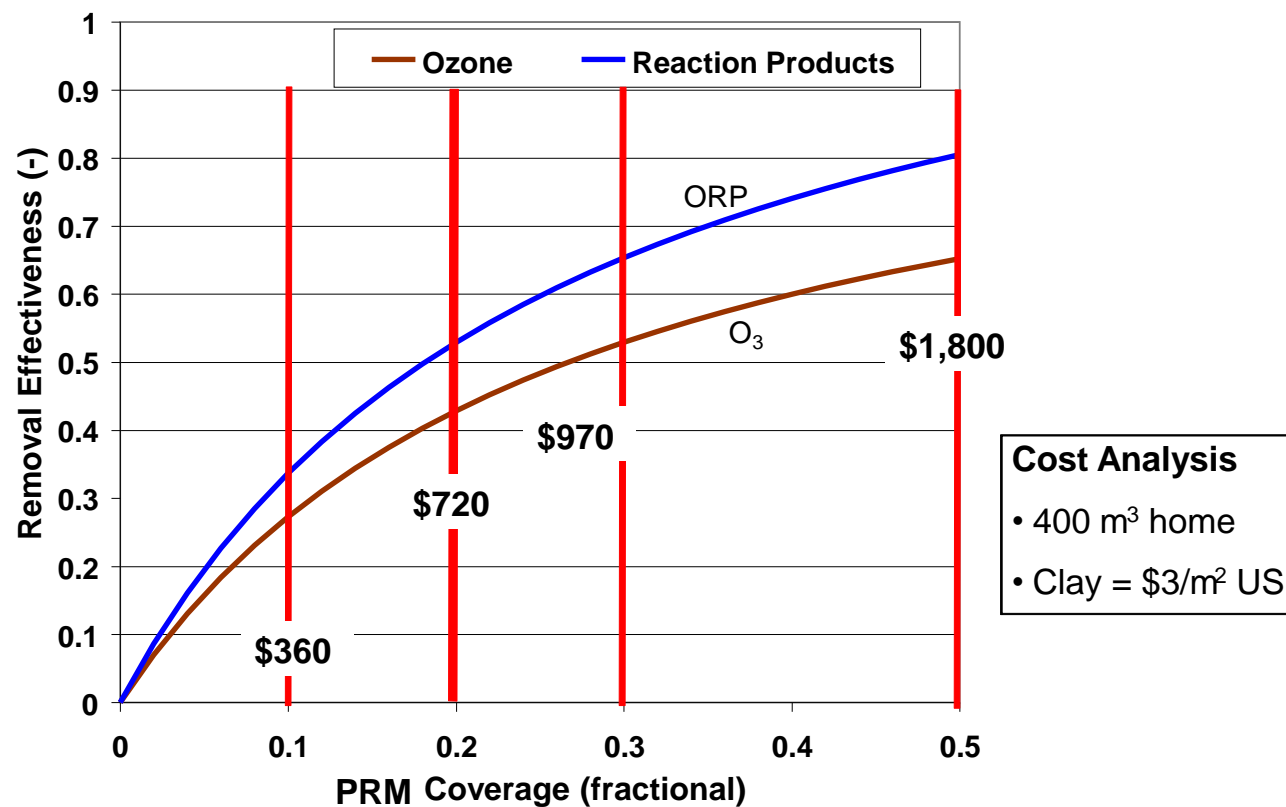
Lamble, SP, *et al.*, *Atmos Environ*, 45: 6965-6972 (2011)

Darling, E, *et al.*, *Building and Environment*, 57: 370-376 (2012)

Darling E. and Corsi RL, *Indoor Air*, DOI:10.1111/ina.12345 (2016)

Practical Implications

$$\text{Removal Effectiveness} = 1 - C_{\text{PRM}}/C_{\text{no_PRM}}$$



$$C_{\text{out}} = 80 \text{ ppb} \quad \lambda = 1/\text{hr} \quad v_d(\text{background}) = 1 \text{ m/hr} \quad v_d(\text{PRM}) = 5 \text{ m/hr}$$

$$y(\text{background}) = 0.5 \text{ mol/mol} \quad y(\text{PRM}) = 0.01 \text{ mol/mol}$$

Take Home Points

- Buildings have deep & broad impacts
 - Health, productivity, learning
- Materials significantly impact exposure to air pollution
- Phenomena that occur on indoor materials are complex
- Opportunities to rethink indoor materials as beneficial
- Tremendous intellectual merit in addressing this issue
- A lot of important research still to be done (open field)

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- All participants are encouraged to read and follow applicable standards, codes and regulations related to this topic.
- The views and opinions following are the presenter's opinions and not necessarily the official position of the Maine IAQ Council, IAQnet LLC, or Healthy Indoors.