

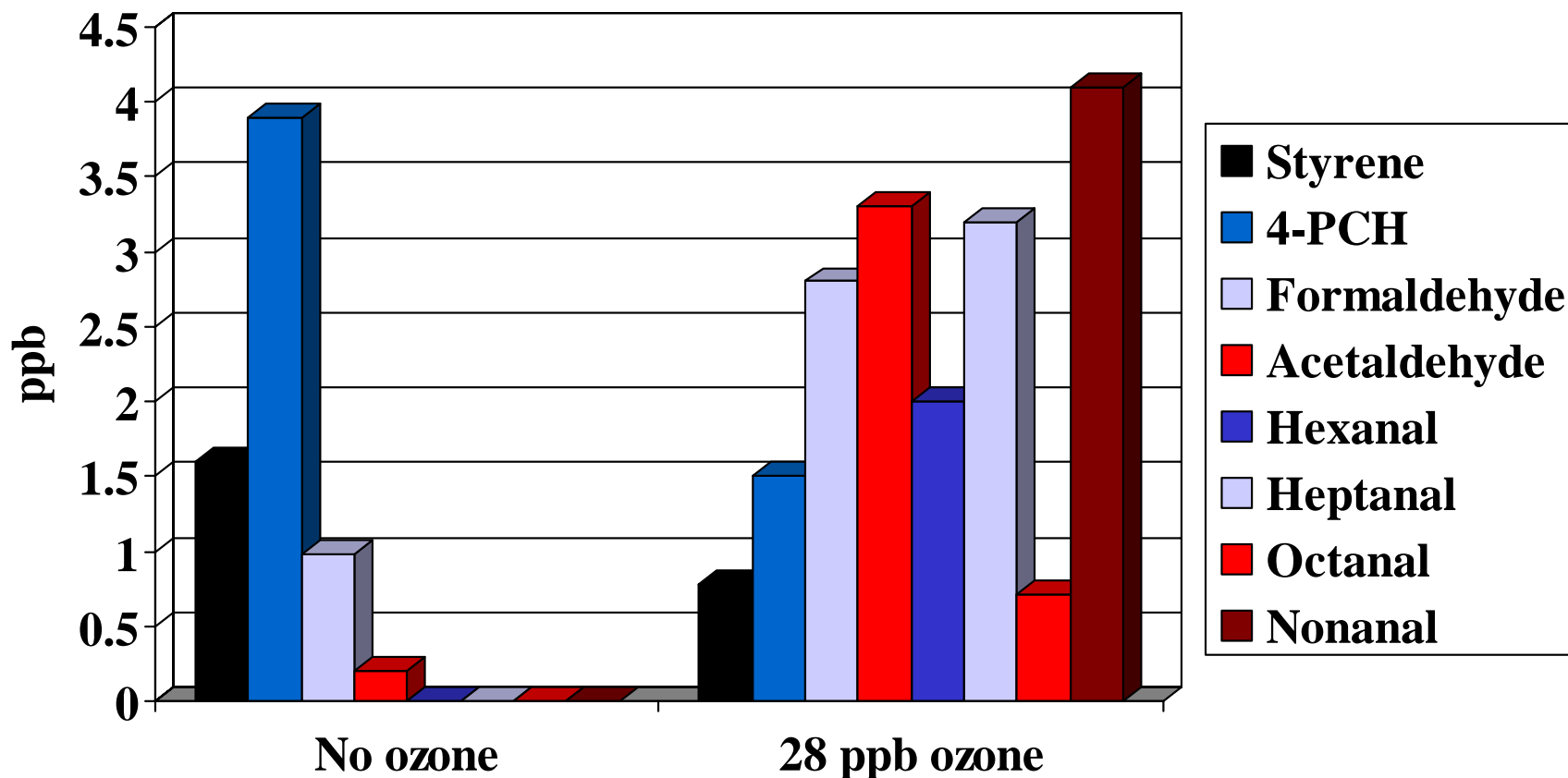
KEMISKA REAKTIONER I INDEKLIMAET

Charles J. Weschler

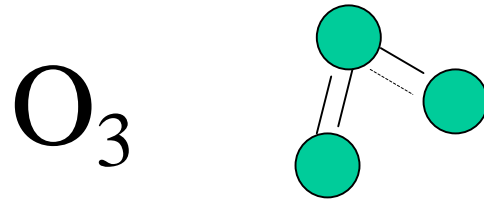
Environmental and Occupational Health Sciences Institute
UMDNJ and Rutgers University
International Centre for Indoor Environment and Energy
Technical University of Denmark



Chemistry can influence the **kind** and **concentration** of chemicals in indoor air



Weschler, Hodgson, Wooley, Environmental Science & Technology 26, 2371, 1991.



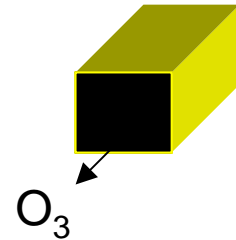
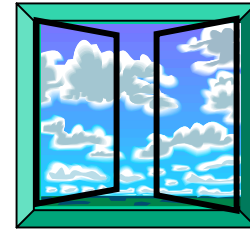
Ozone Initiated Reactions

An important class of indoor
reactions

Ozone

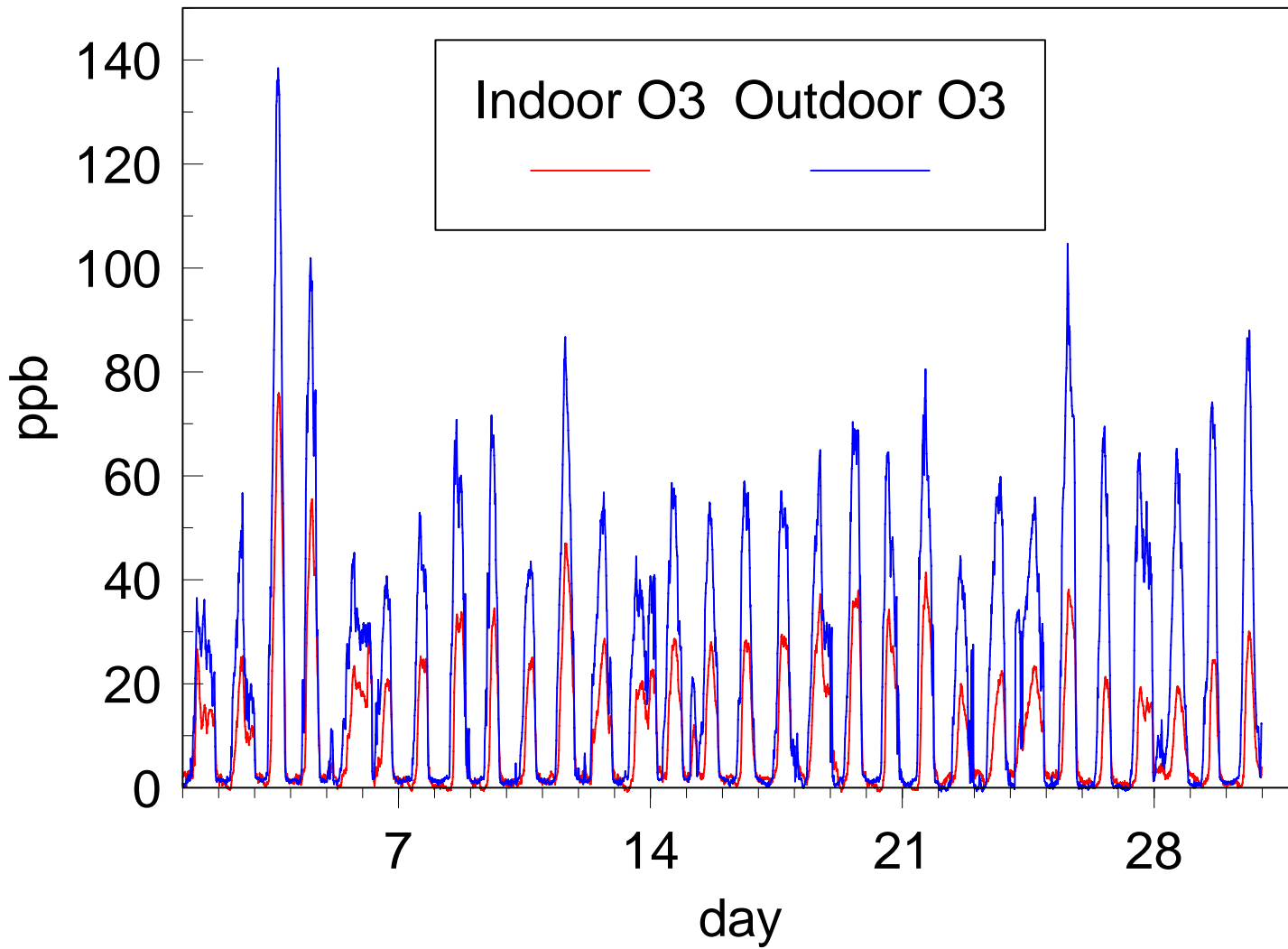
- Sources

- outdoor to indoor transport
- photocopiers
- laser printers
- ozone generators



- Indoor levels normally smaller than outdoor
- Large variations with time of day, day of week and season

Burbank April, 1993



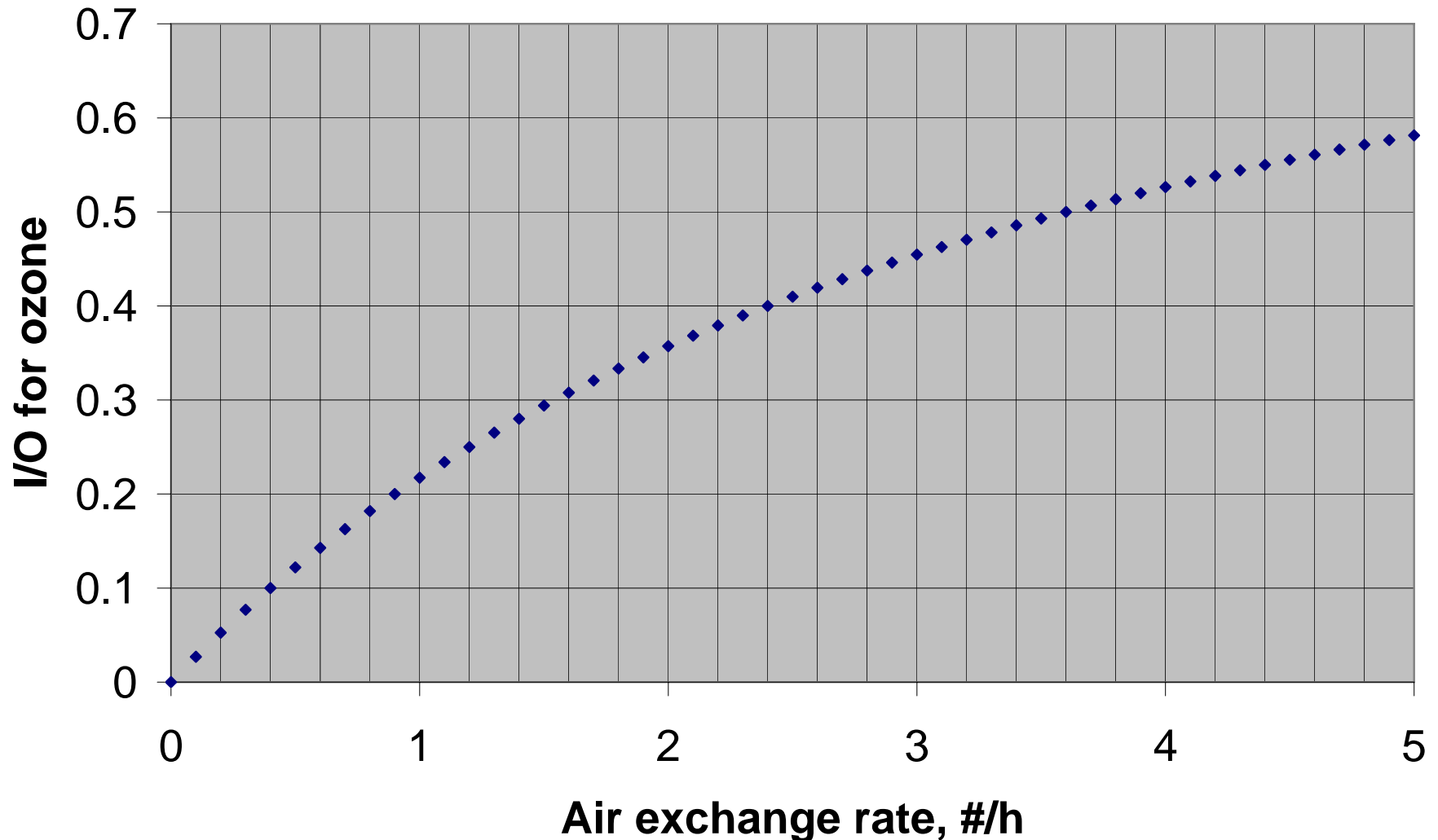
Indoor ozone concentrations

- Low in air conditioned homes & offices
- 15-30% of outdoors (moderate air exchange)
- 50-70% of outdoors (high air exchange)

- $[\text{O}_3]_{\text{indoor}}$ greater than 15 ppb common in cities during the summer

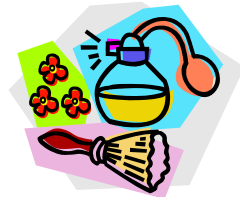
Indoor/outdoor O_3 vs air exchange rates

(surface removal = 3.6 h^{-1})



Examples of common indoor pollutants that react with ozone in the air

- Nitric oxide, nitrogen dioxide
- Terpenoids (e.g., d-limonene, α -pinene, linalool)



- Unsaturated fatty acids (e.g., oleic, linoleic)



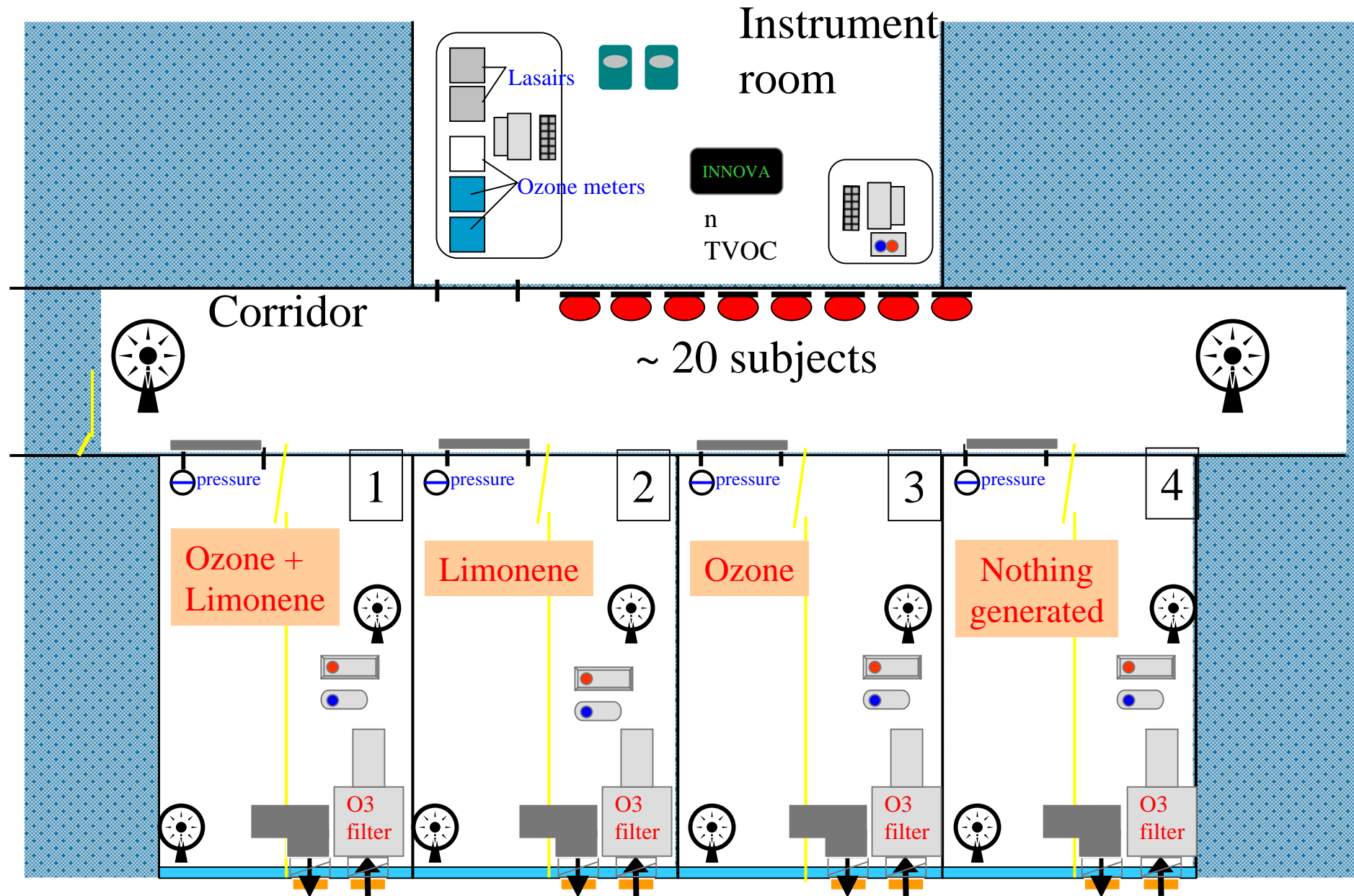
Products of indoor ozone chemistry

- Free radicals (e.g., hydroxyl and nitrate)
- Peroxides (e.g., hydroperoxides)
- Unstable organics (e.g., secondary ozonides)
- Stable organics, including secondary organic aerosols (SOA)

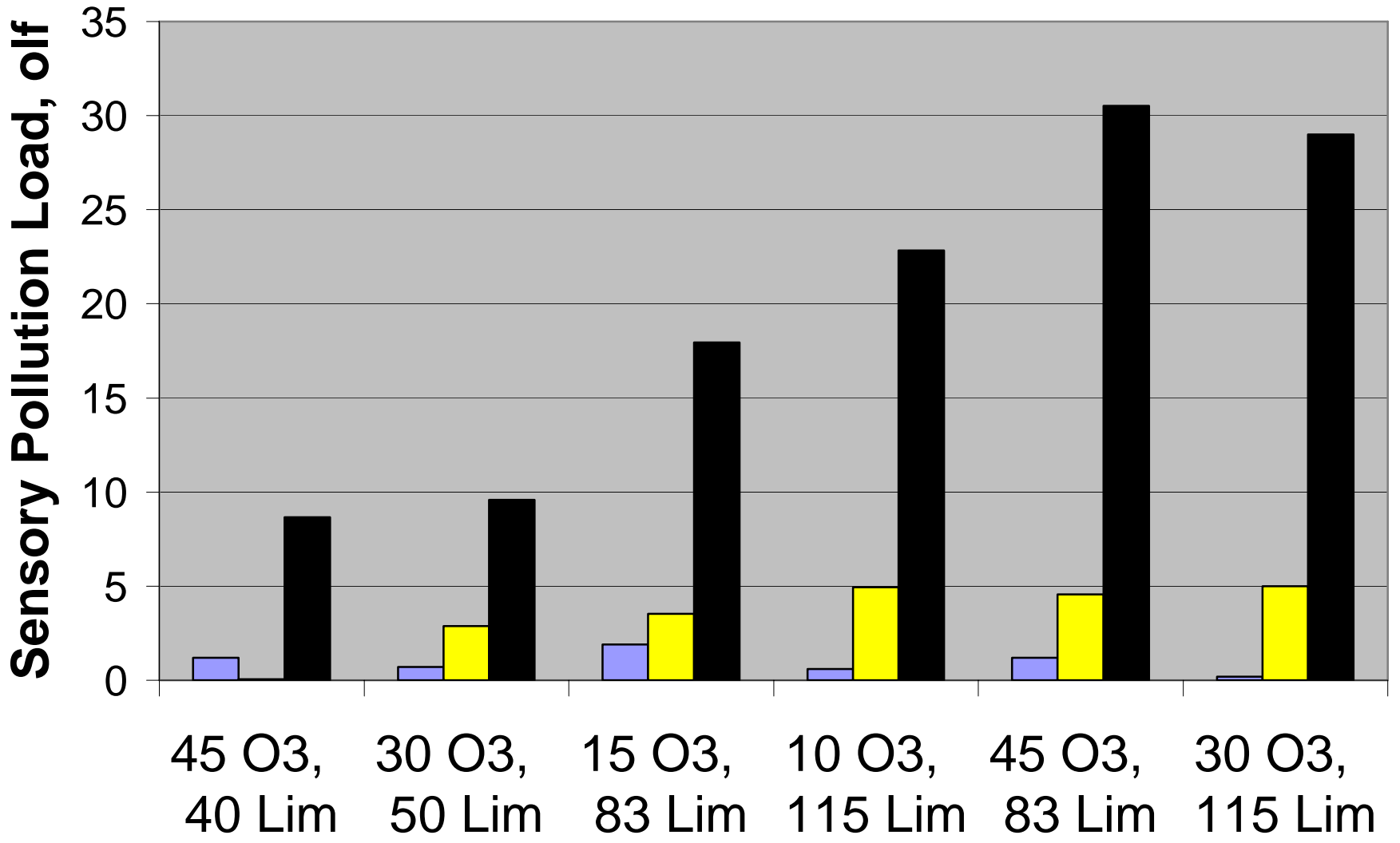
Products: potential health and comfort effects

- Acute health effects
 - Mucous membrane irritants (e.g., acrolein; methacrolein, secondary ozonides, organic peroxides)
 - Contact allergens (e.g., hydroperoxides)
 - Eye irritants (e.g., PAN, terpene oxidation products)
- Chronic health effects
 - Cancer, cardiopulmonary disease, asthma (e.g., acrolein, formaldehyde, (SOA)/ultrafines)
- Discomfort
 - Certain products have very low odor thresholds (e.g., 2 ppt for *cis*- 2-nonenal)

Sensory effects from ozone + limonene

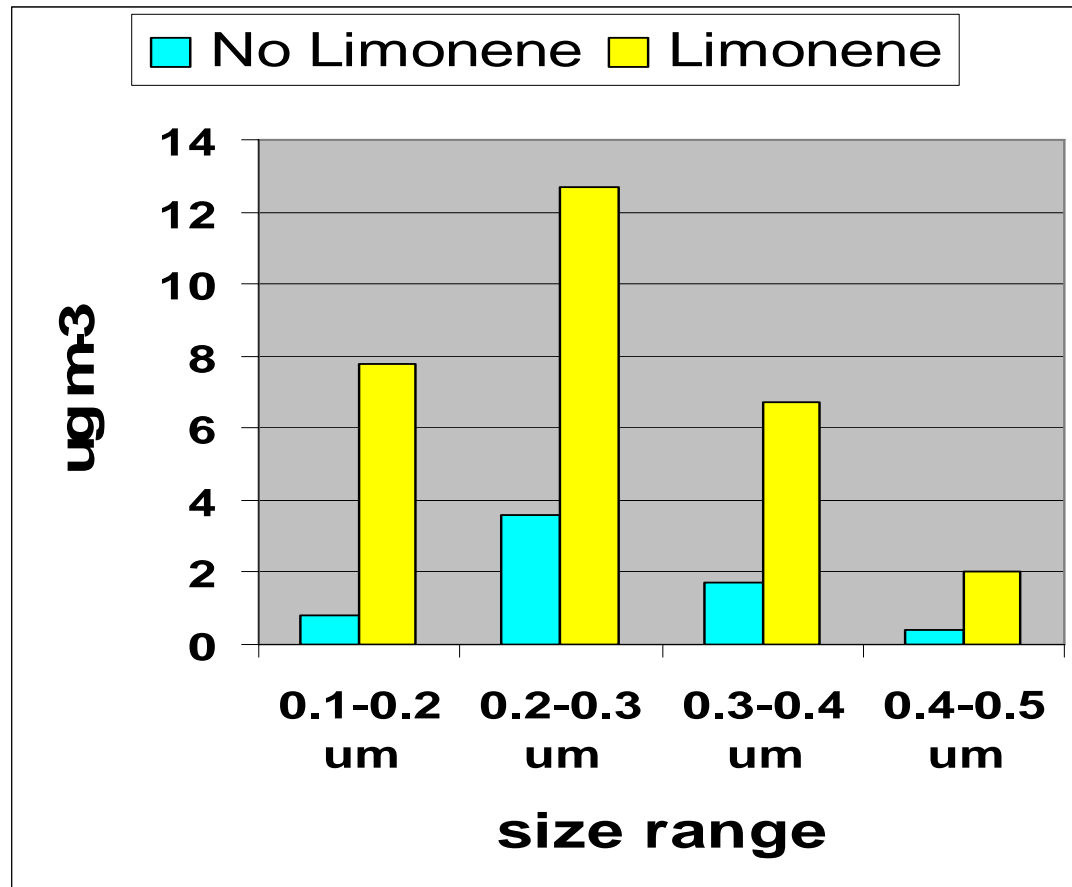


■ Only Ozone..
 ■ Only Limonene..
 ■ Ozone + Limonene

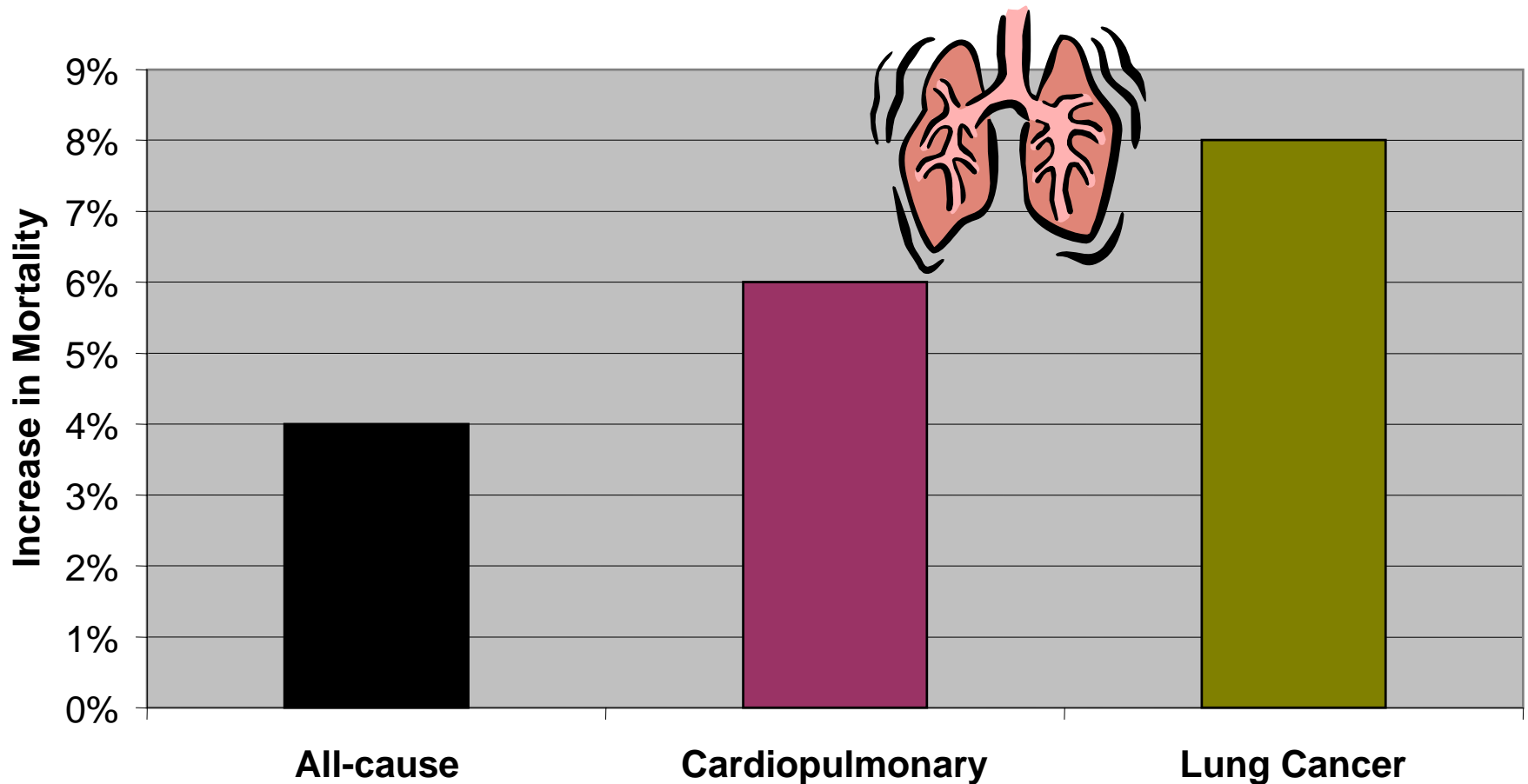


Tamás, Weschler, Toftum, Fanger, Indoor Air 16, 168, 2006.

Particle concentrations in rooms without and with a limonene source (28 ppb O₃)



Increase in mortality for each 10 $\mu\text{g}/\text{m}^3$ increase in fine particles



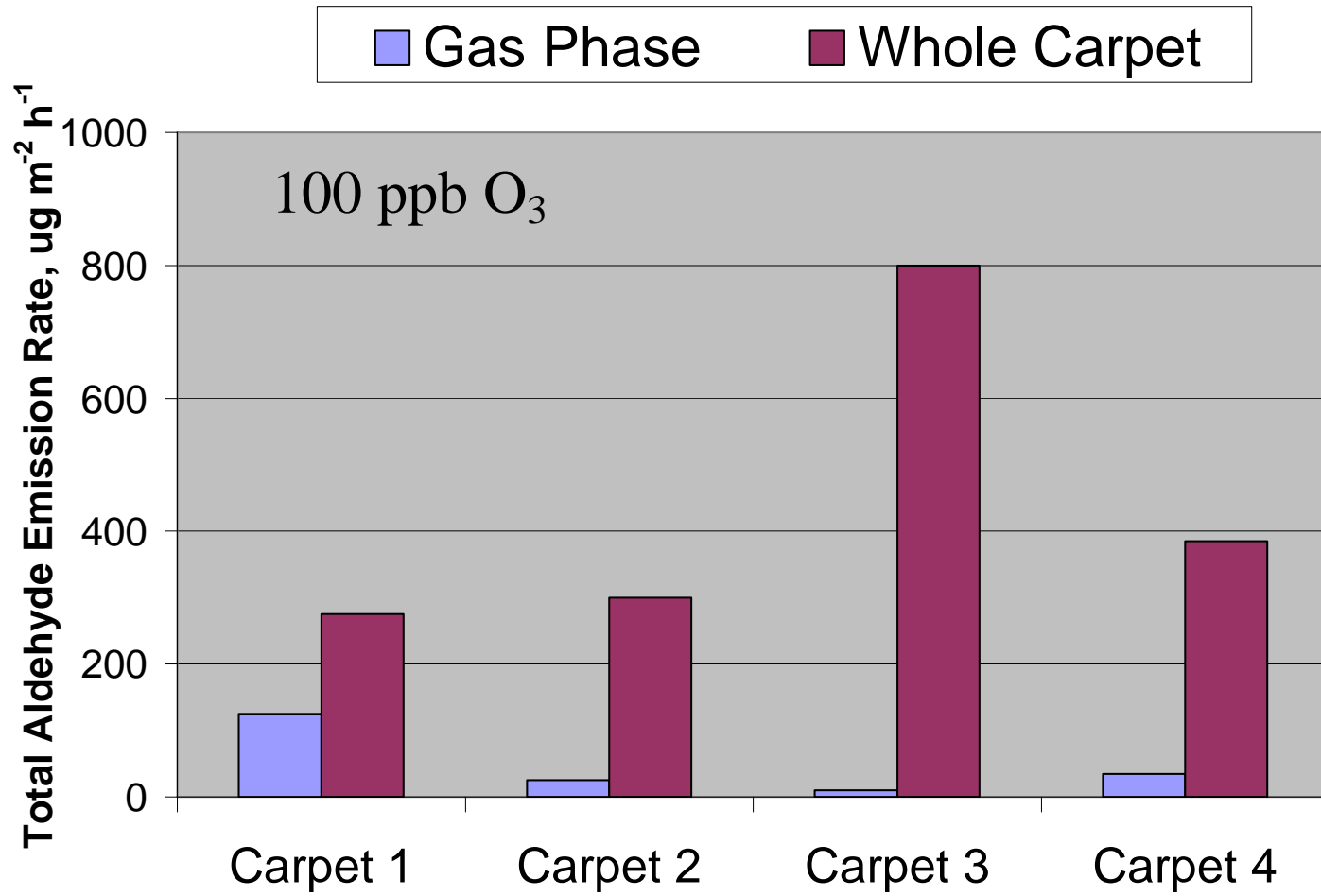
Pope et al., J. Amer. Medical Assn., 287, 1132, 2002

CHEMICAL REACTIONS ON SURFACES

Indoor surface chemistry

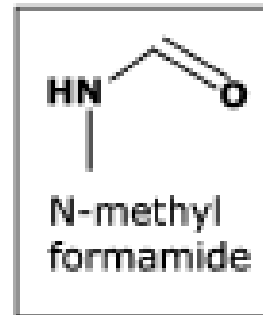
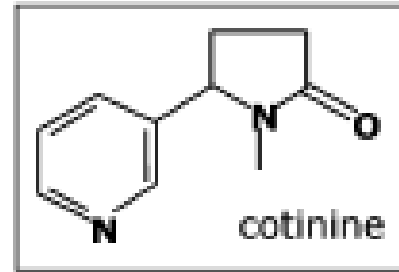
- Surface Area/Volume
 - Outdoors: $\sim 0.01 \text{ m}^2/\text{m}^3$
 - Indoors: $\sim 3 \text{ m}^2/\text{m}^3$
- High indoor surface-to-volume ratios
 \Rightarrow surface reactions can strongly influence indoor environments

Surface versus gas phase

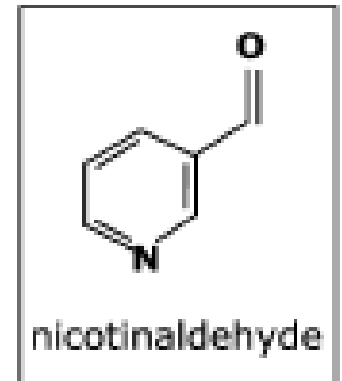


Sorption promotes chemistry

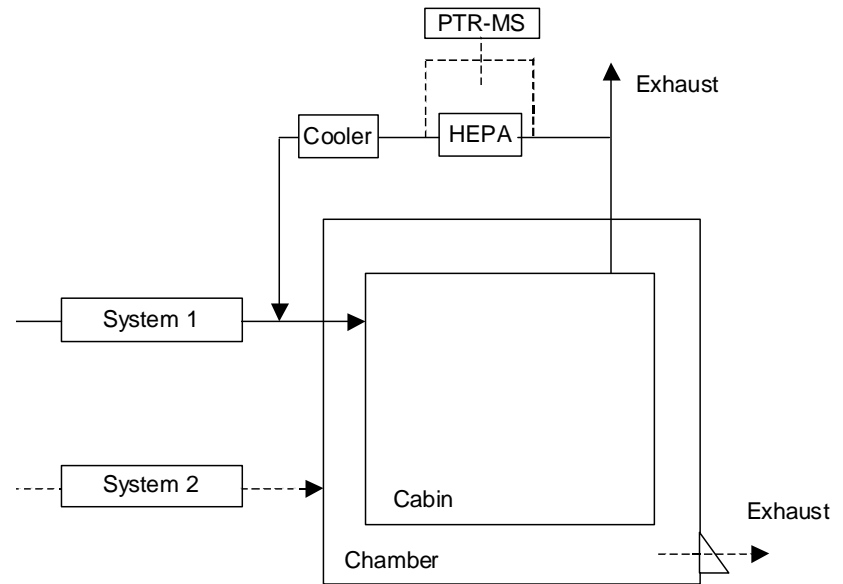
- $O_3 + \text{gas phase nicotine} \rightarrow \text{nothing}$
- $O_3 + \text{sorbed nicotine} \rightarrow$
 - cotinine
 - n-methylformamide
 - nicotinaldehyde
 - formaldehyde



+

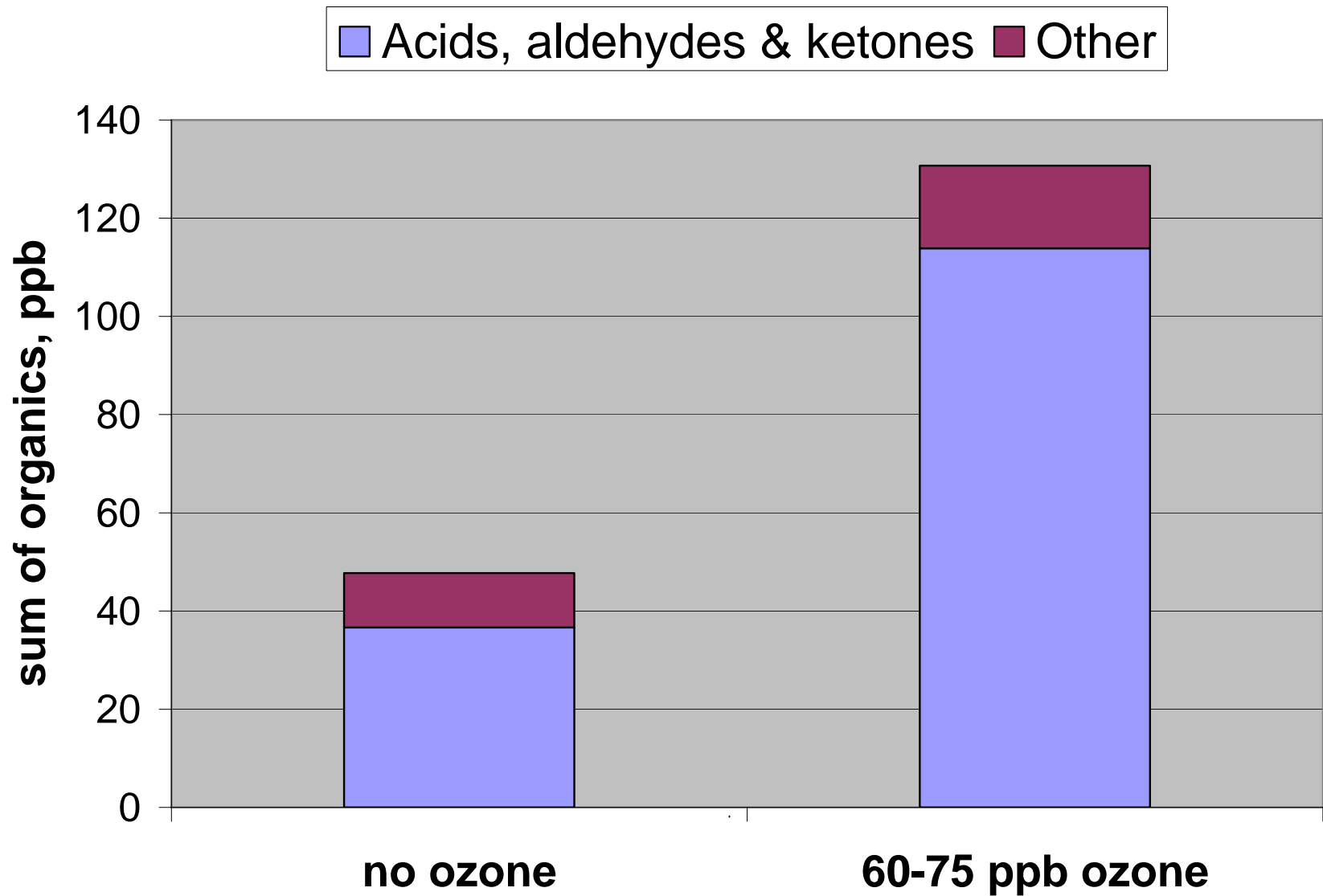


O₃ chemistry in a simulated B-767 aircraft

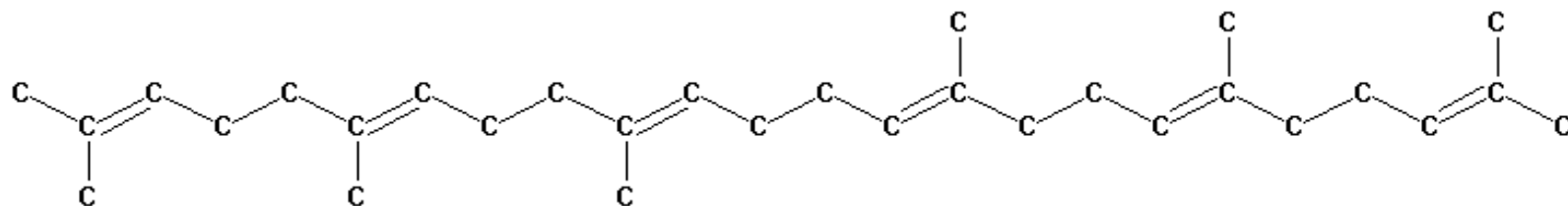


- 28.5 m³; used seats, carpet, wall sections and HEPA filter
- 16 passengers
- Outdoor airflow: 4.4 h⁻¹ (2.4 L/s/p) and 8.8 h⁻¹ (4.8 L/s/p)
- O₃ levels: 60 to 80 ppb

Detected compounds (Outdoor airflow: 4.4 h⁻¹)

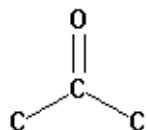


Squalene

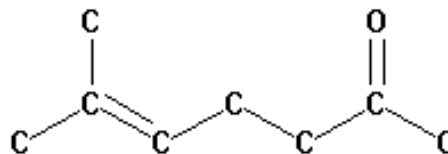


- Present in skin oil
- Oxidized by ozone
- Oxidation products include:

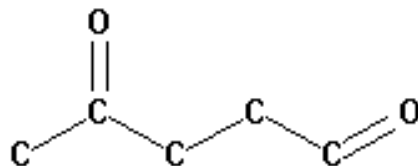
– Acetone



– 6-methyl-5-hepten-2-one

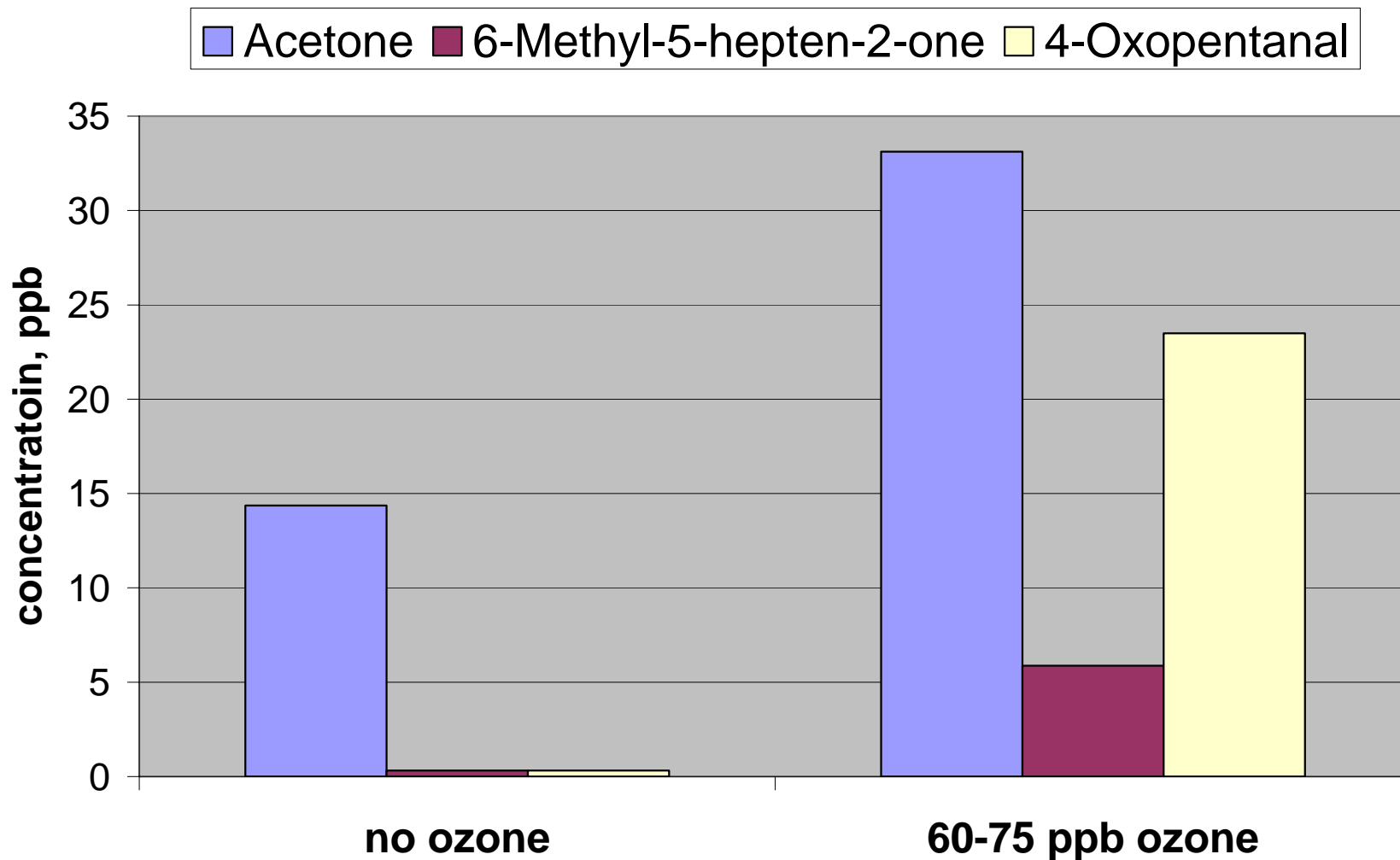


– 4-oxopentanal



Squalene oxidation products

(Outdoor airflow: 4.4 h⁻¹)

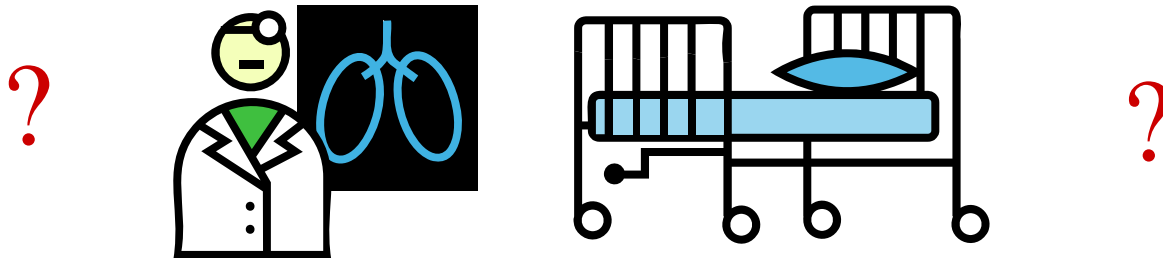


When is indoor chemistry most likely to occur?

- High O₃ levels
- High terpene levels
- High occupant densities
- Low ventilation rates
- High temperatures
- High humidities
- High surface area/volume

Summary – indoor chemistry

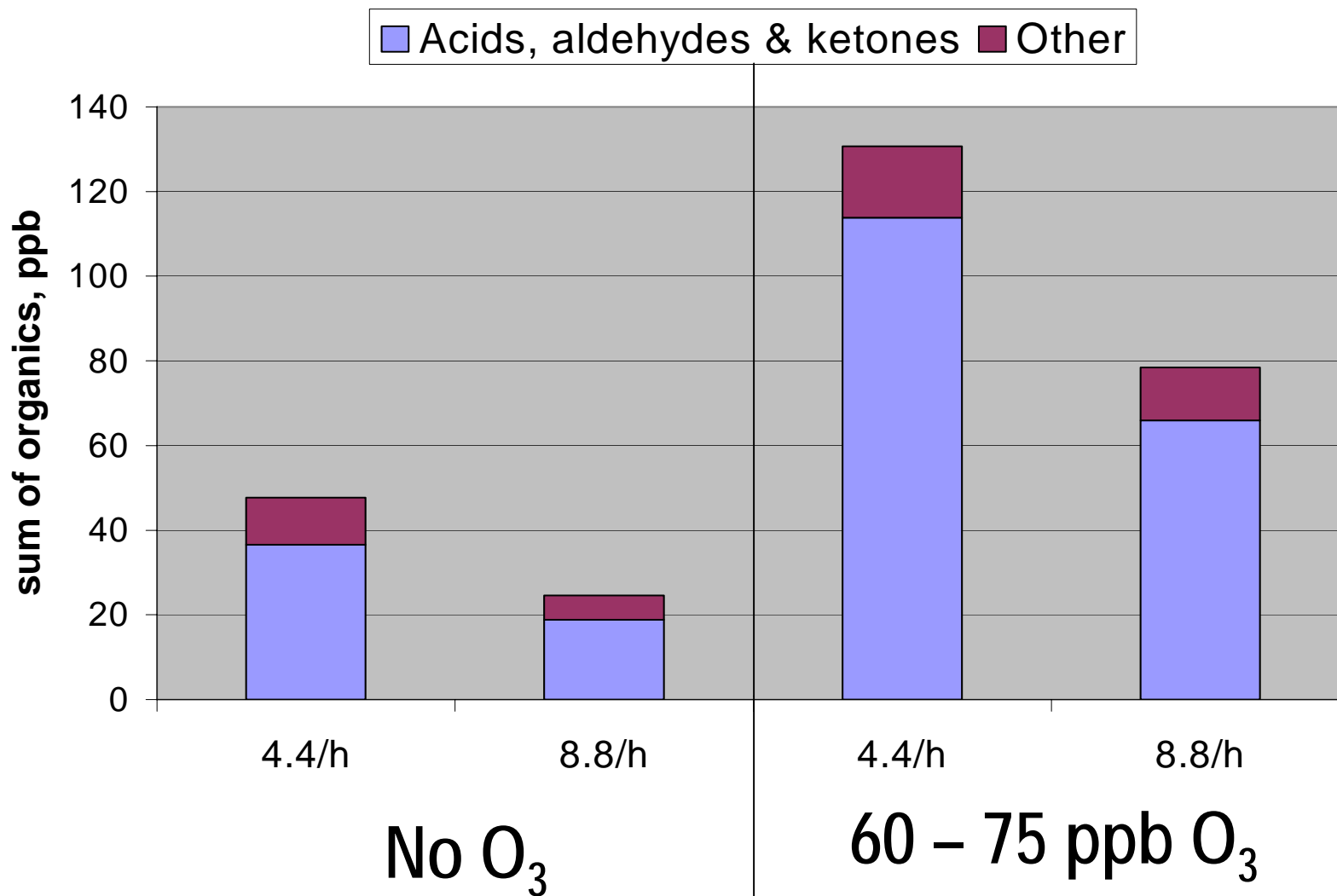
- Influences human exposure to pollutants
- Often the dominant source of highly reactive compounds indoors
- Occurs on **surfaces** as well as in the air
- Effects on occupant health an active research area



Chemical transformations

- Sinks for the reacting pollutants and sources for reaction products
- Occur in the **gas phase** (homogeneous reactions) and on **surfaces** (heterogeneous reactions)

Total concentration of detected compounds



Intake of ozone-initiated-chemistry products

- In a typical room, 1 to 6 molecules of O_3 have been removed for every molecule of O_3 in the air
- For every molecule of ozone removed by surfaces, roughly 0.2 to 0.7 product molecules enter the air
- O_3 oxidation products anticipated to be present indoors at 1/3 to 2 times the concentration of O_3

Surfaces of Interest

- Room surfaces
- Wall cavities & other hidden-space surfaces
- Occupants: skin, clothing, lungs
- Air-handling systems: ducts, filters
- Airborne particles
- Settled dust

O₃ oxidation products often more irritating than precursors

- Ozone/Isoprene ⇒
 - formaldehyde, methacrolein, methyl vinyl ketone
- Ozone/Limonene ⇒
 - formaldehyde, hydrogen peroxide, carboxylic acids, submicron particles

Properties that influence indoor surface chemistry

- Surface area: projected and actual
- Chemical nature of surface (e.g., pH, polarity, water content)
- Environmental conditions: temperature, RH
- History of surface: oxidative aging, sorbed organic films, soiling by particles, residual cleaning products