Indoor Chemistry: Pollutant Production and Removal

Symposium on Indoor Environmental Quality

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Indoor Environment Department

Credits

Intellectual and Experimental Contributions:

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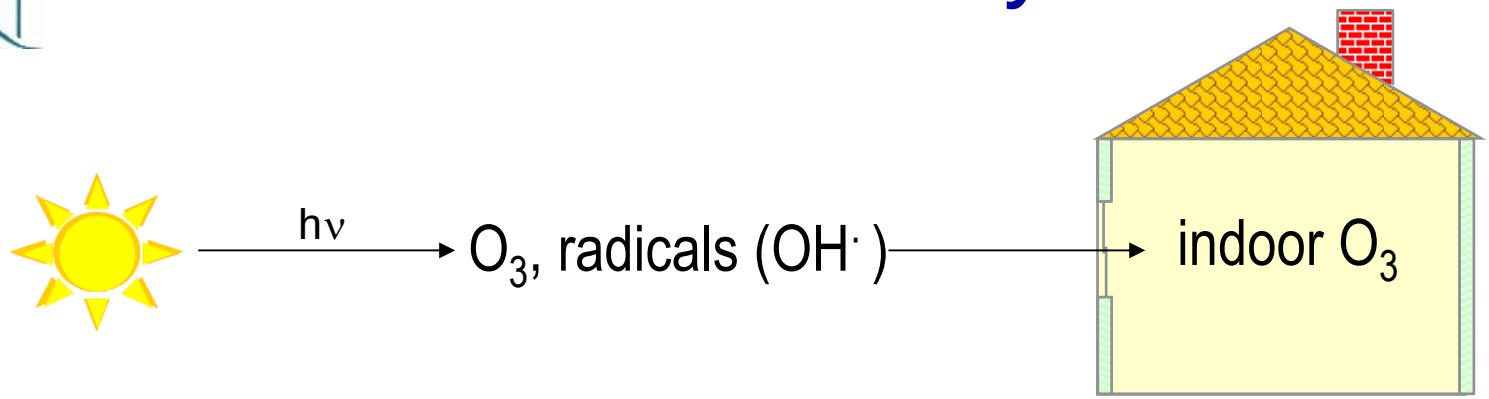
Alfred T. Hodgson, Toshifumi Hotchi, De-Ling Liu,
Melissa M. Lunden, William W. Nazaroff, Charles J. Weschler

Research Funding*

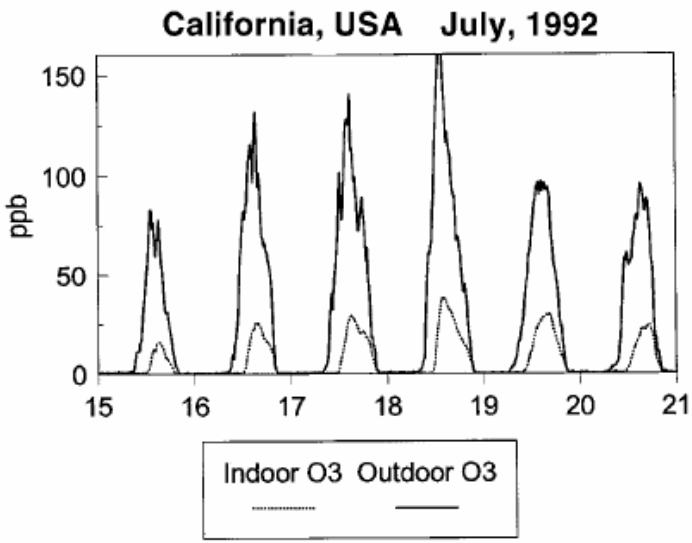
California Air Resources Board
Tobacco-Related Disease Research Program
U.S. Department of Energy

*Disclaimer: Don't blame our sponsors if you have a problem with this presentation!

Indoor chemistry



- O_3 + surfaces → less O_3
  - Sabersky, Sinema & Shair, ES&T, 1973
- O_3 + carpet → aldehydes, less O_3
  - Weschler, Hodgson & Wooley, ES&T, 1992
  - Morrison & Nazaroff, ES&T, 2000, 2002
- O_3 + terpenes → $OH^{\cdot}$, particles, formaldehyde
  - Weschler & Shields, ES&T, 1996, 1997
  - Weschler & Shields, Atmos. Environ., 1997, 1999



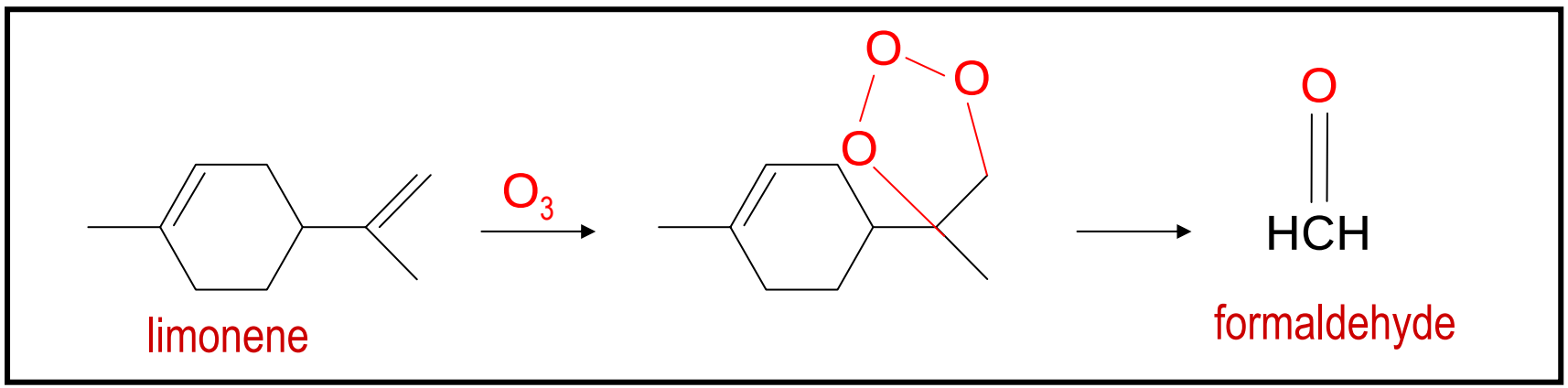
Weschler et al.
Indoor Air, 2000

Outline

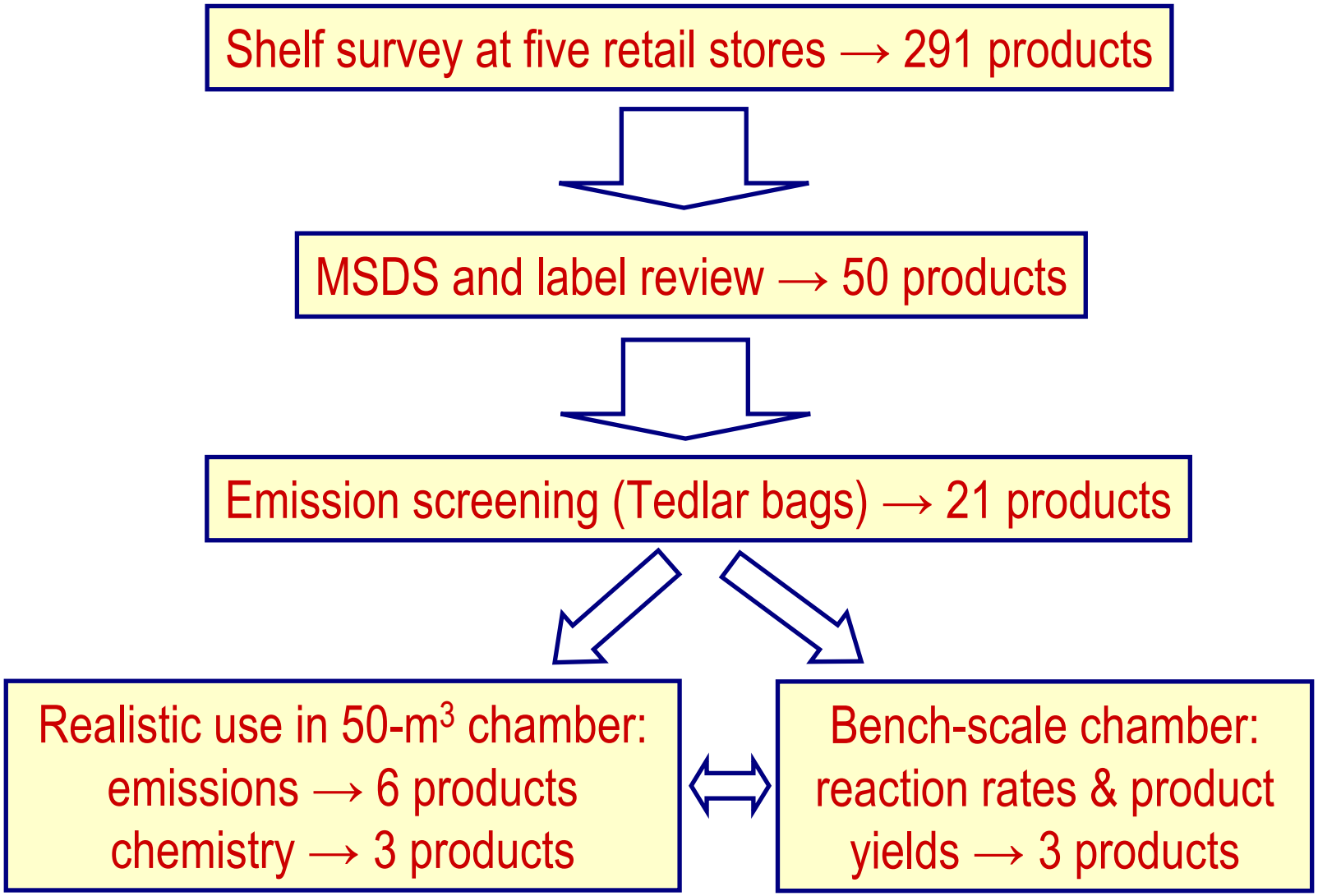
- O_3 + terpenes in cleaners and air fresheners (15 min)
- O_3 oxidation of sorbed nicotine (5 min)
- UV photocatalytic air cleaners (1 min)

Cleaners & air fresheners

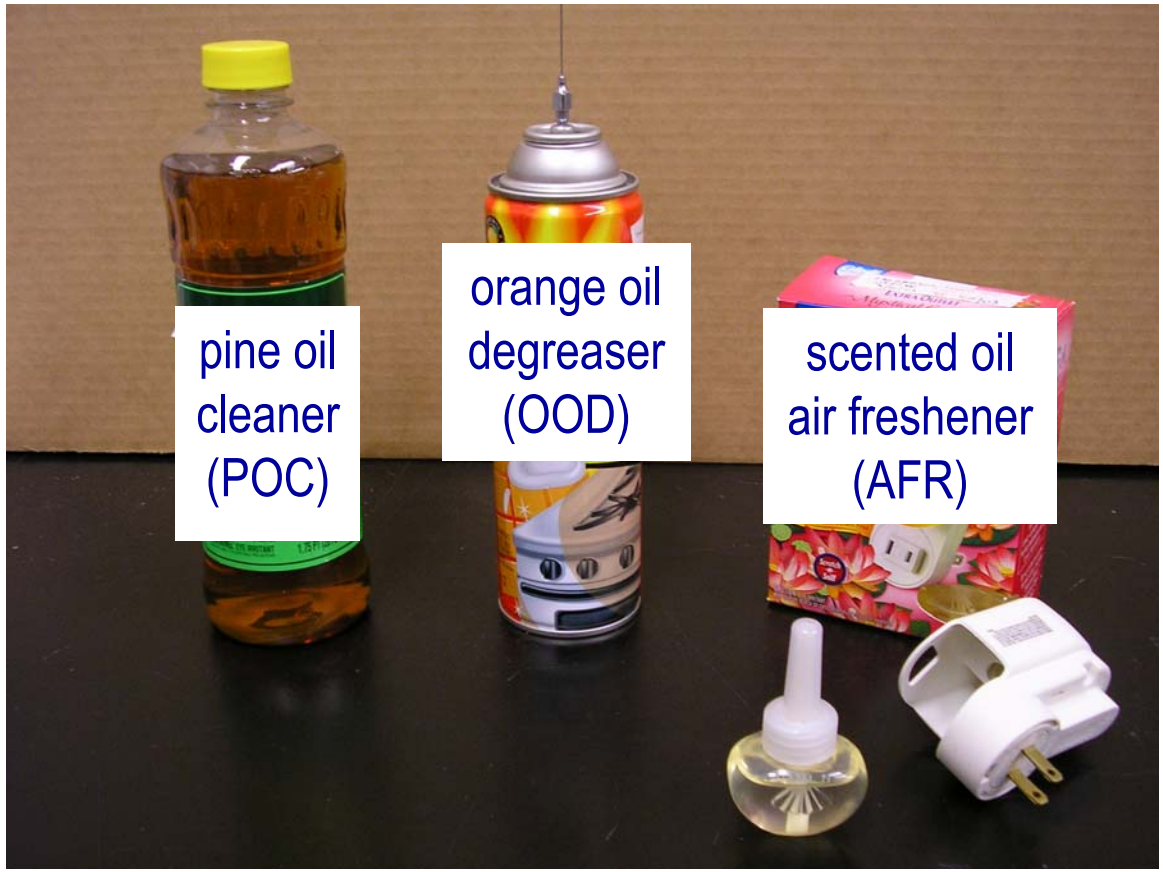
- Terpenes and terpene alcohols used as solvents and fragrances
- Indoor use ⟶ high concentrations
- Epidemiological studies link cleaning to occupational asthma
- Human experiments show sensitivity to products of O_3-terpene reactions



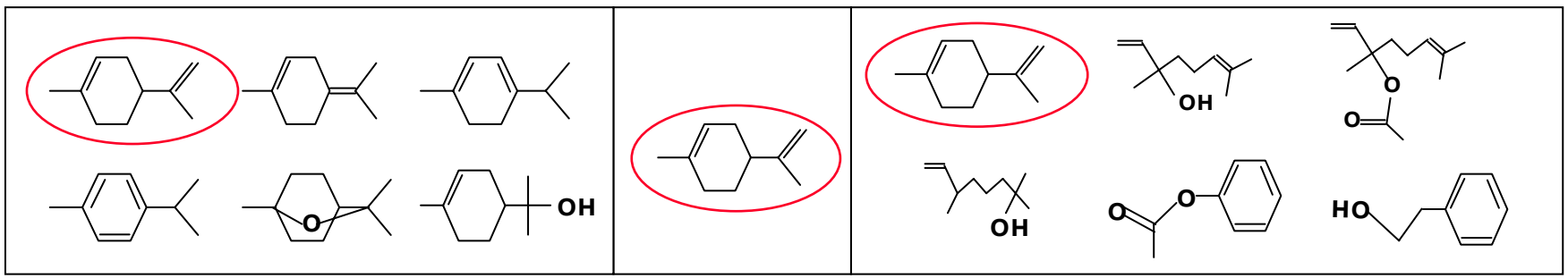
Product selection



Chemistry experiments

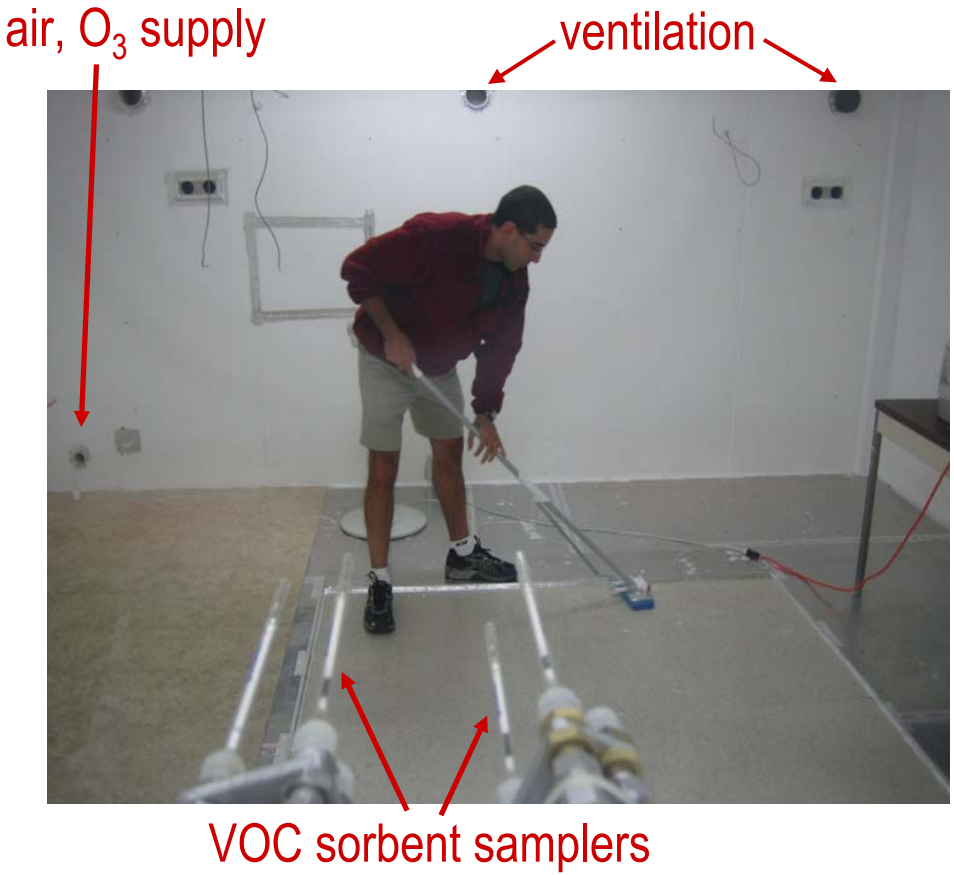


Primary emissions:



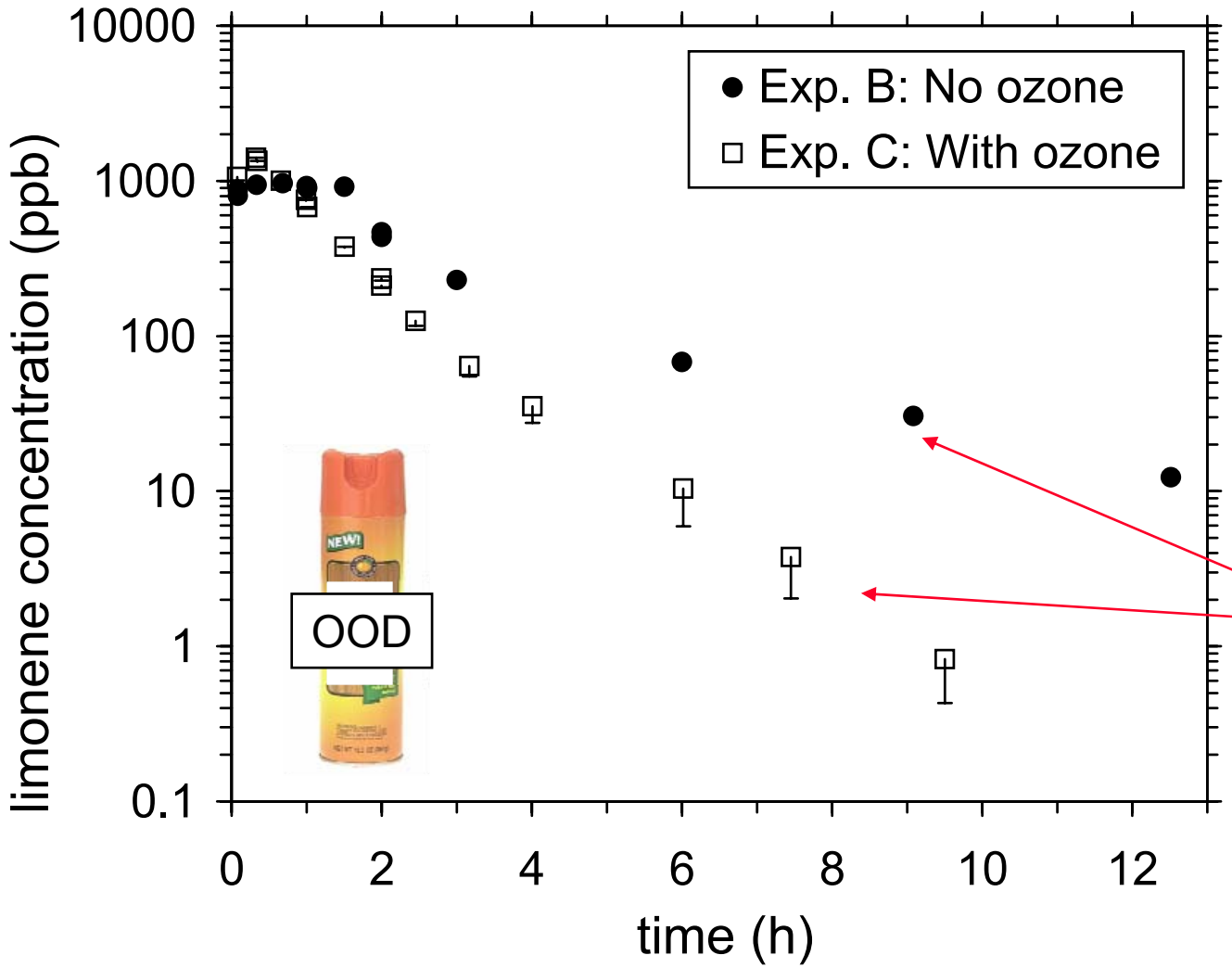
Realistic use experiments

- Ventilate at 0.53 h^{-1}
- Scale product use to simulate realistic home concentrations
- Degreaser: spray & wipe
  - 0.11-m^2 polished aluminum
- Pine oil cleaner: mop floor
  - 4.2 m^2 vinyl tile floor
  - 4-L solution mixed in room
- Air freshener: one plug-in unit



Measure: VOCs, O_3, T, RH, aldehydes, OH (indirect), particles

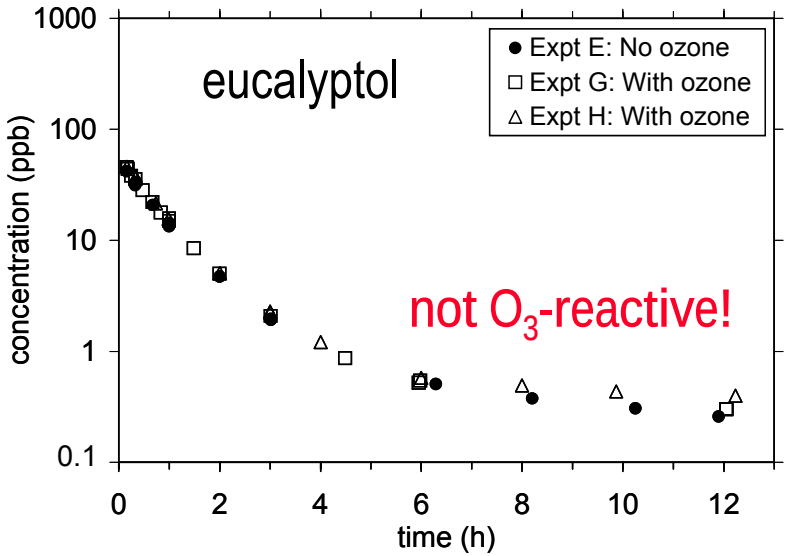
Orange oil degreaser in room

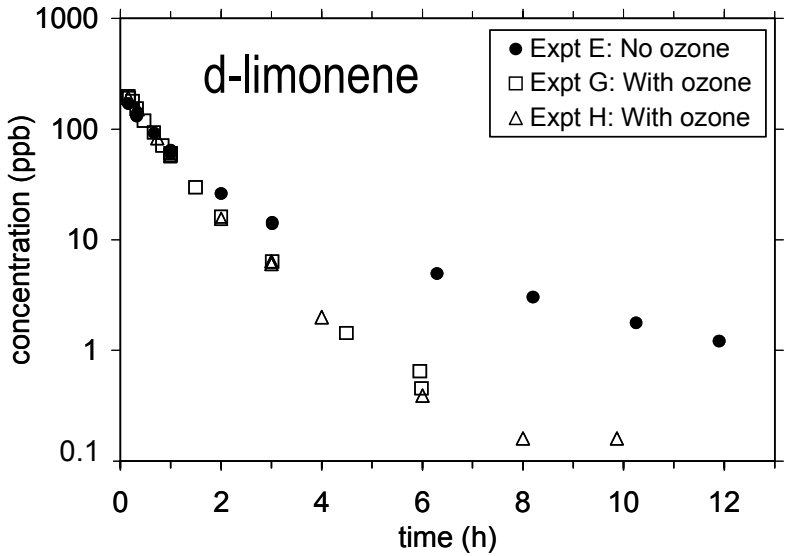


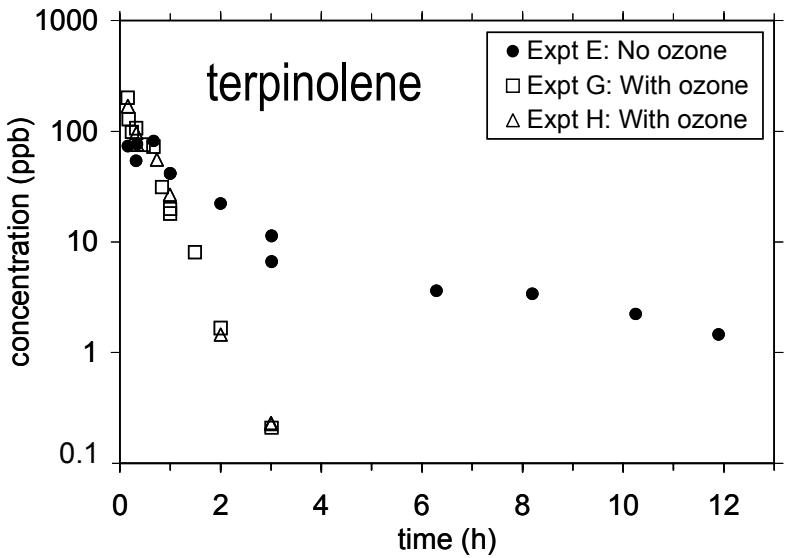
VOC levels reduced by reaction with ozone!

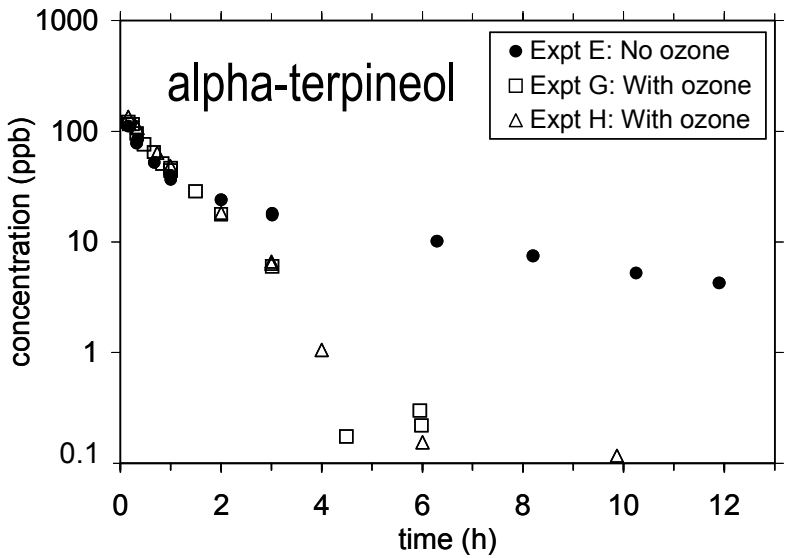
Singer et al., Atmos. Environ., 2006

Pine oil cleaner in room



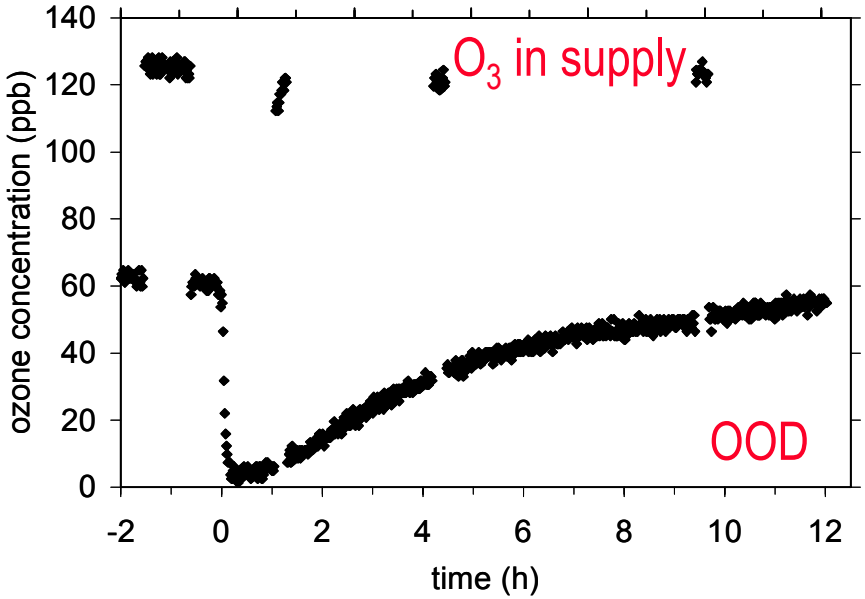


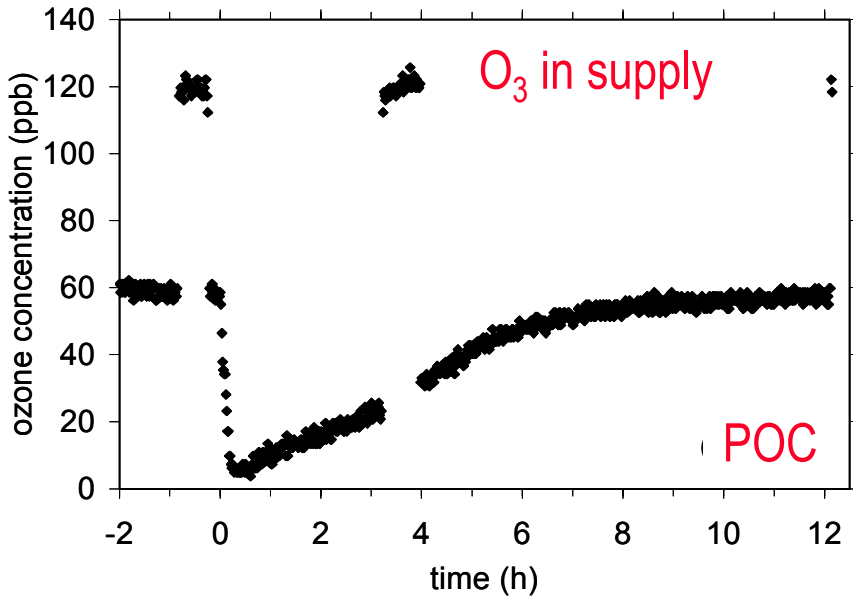


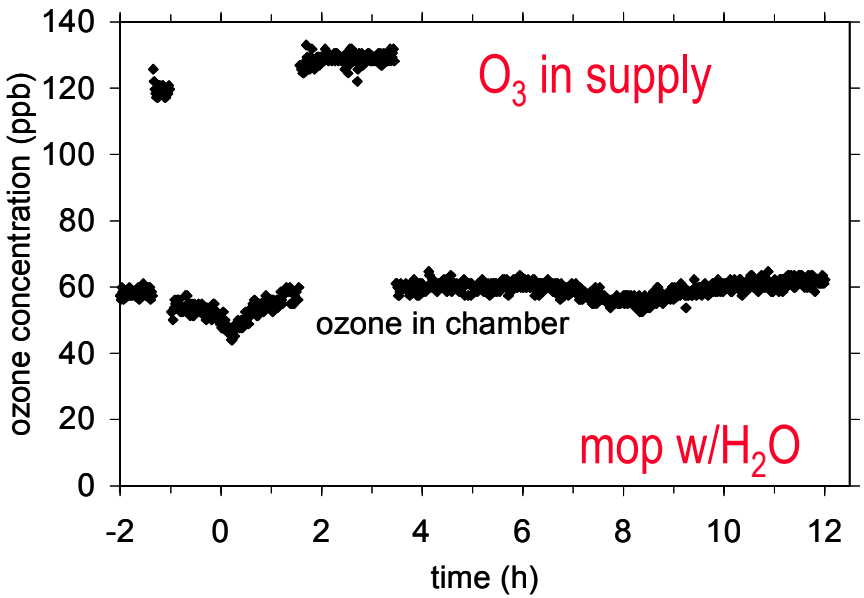


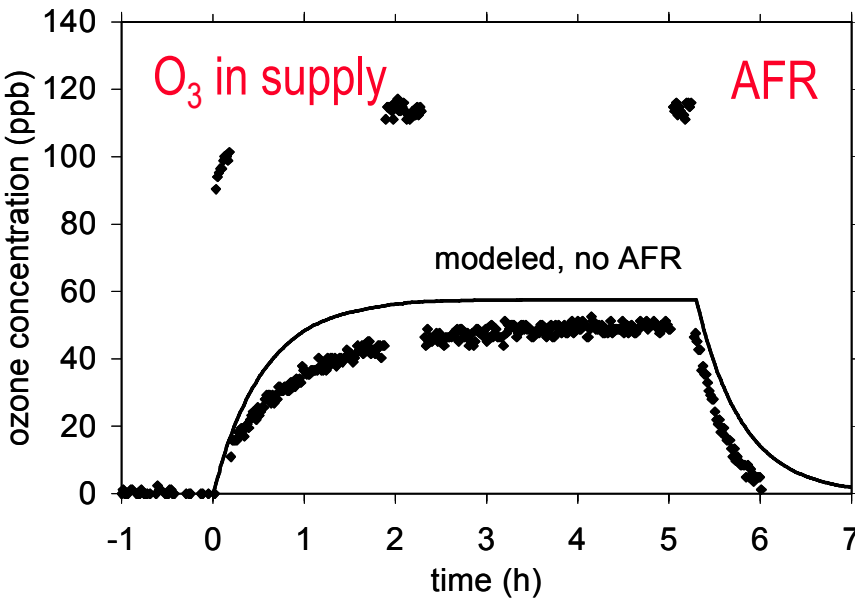
Singer et al., Atmos. Environ., 2006

Ozone in room



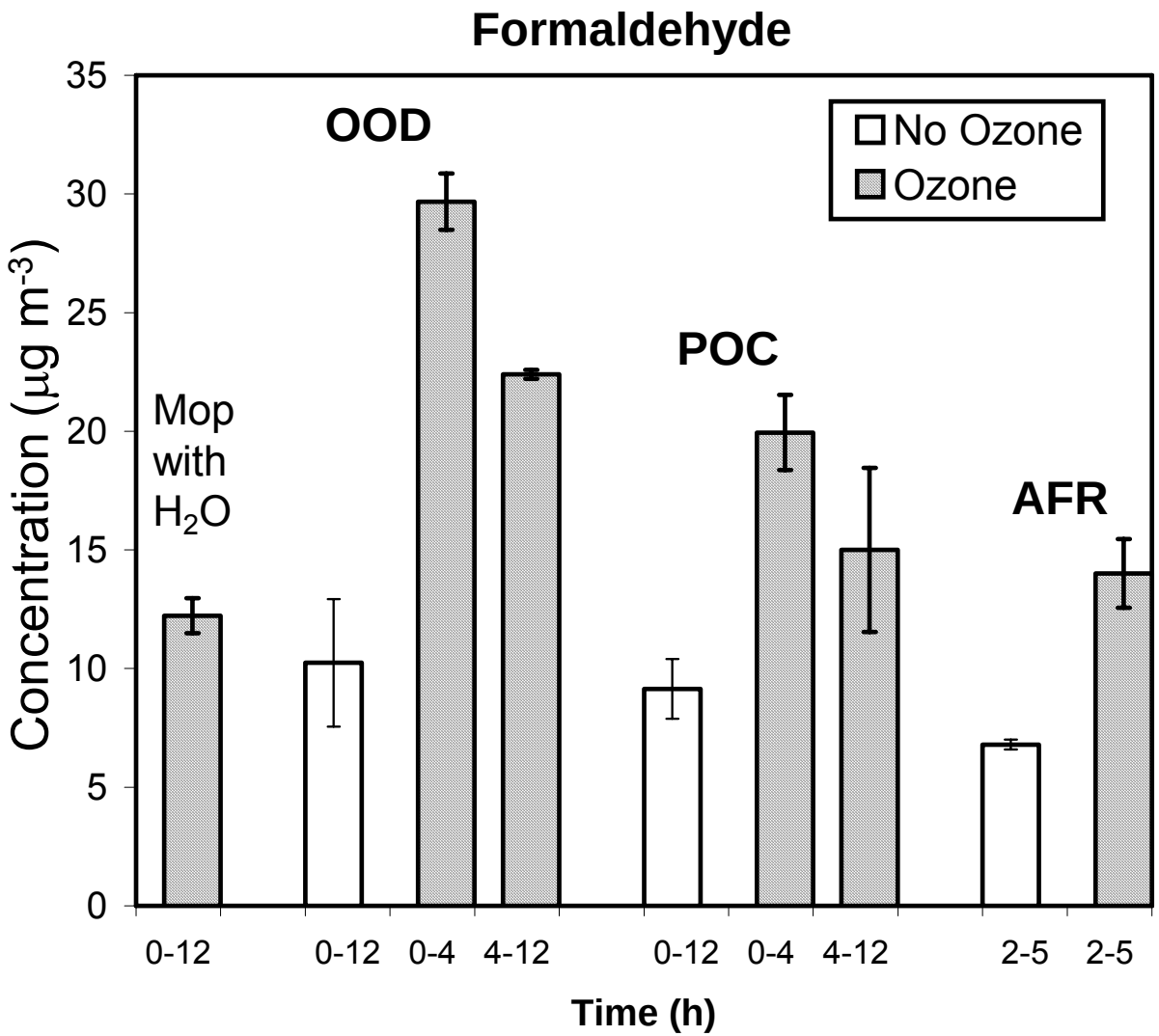






Singer et al., Atmos. Environ., 2006

Formaldehyde in room

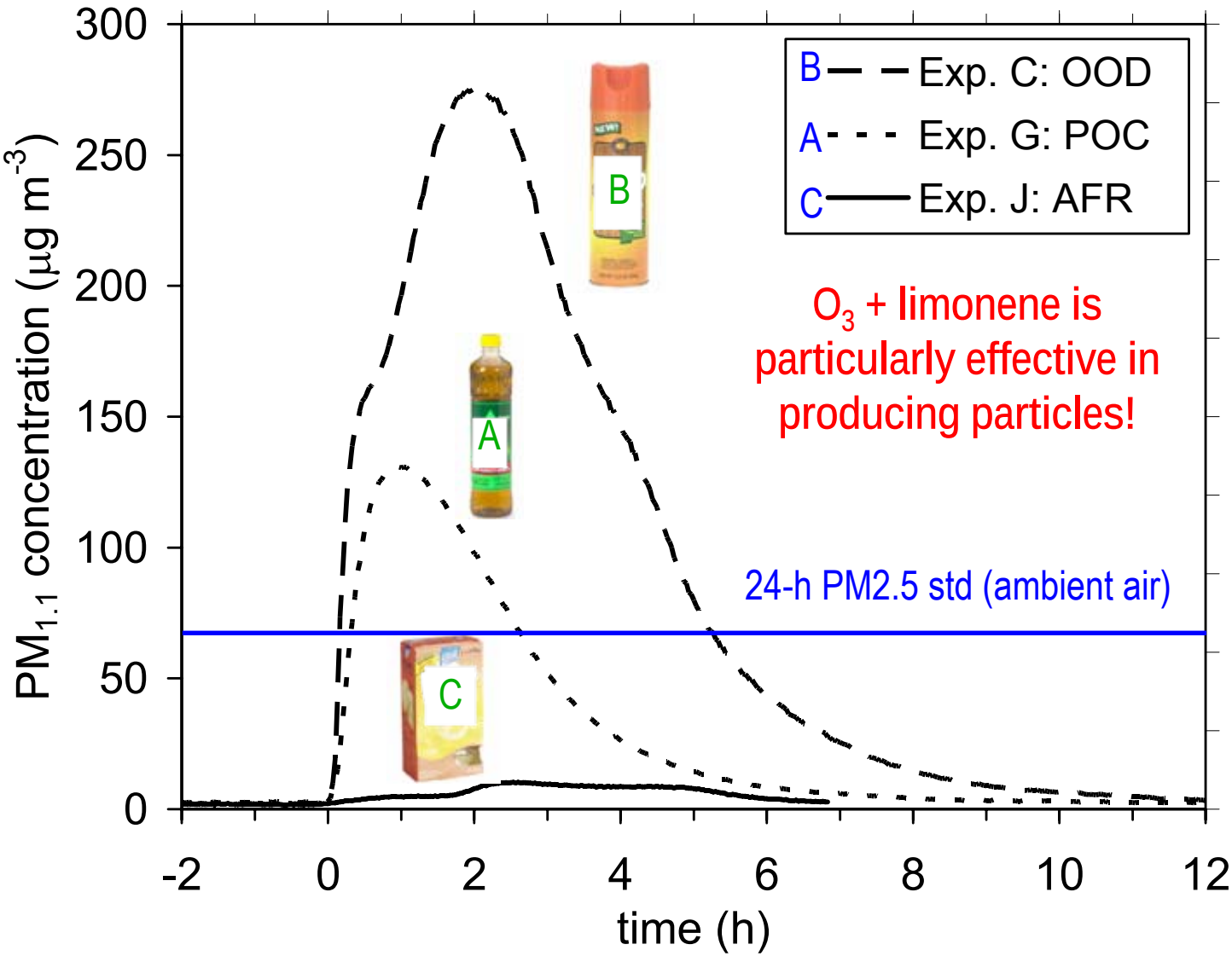


Product use in presence of O_3 produces formaldehyde!

note: multiply by 0.8 for ppb

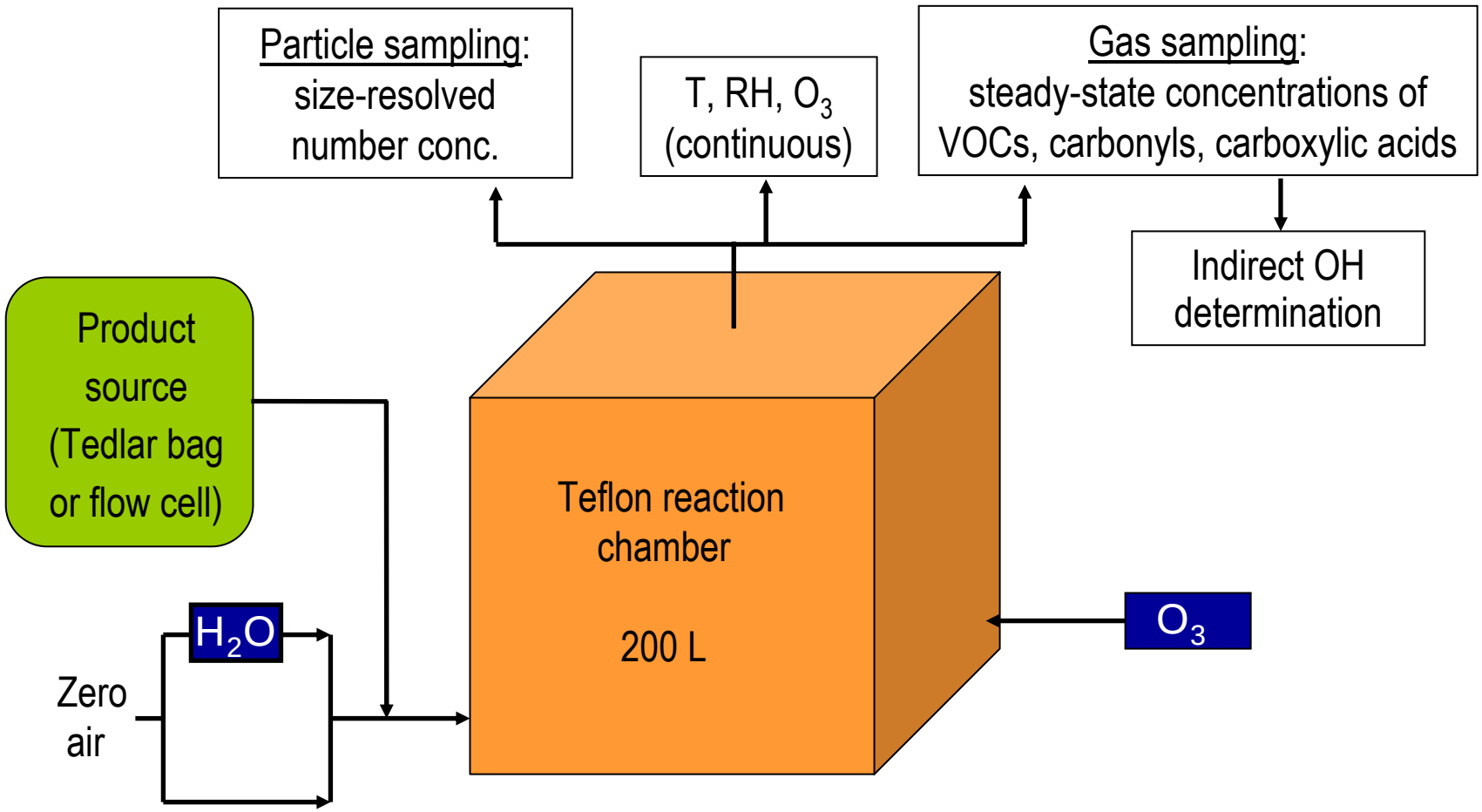
Singer et al., Atmos. Environ., 2006

Particle mass in room



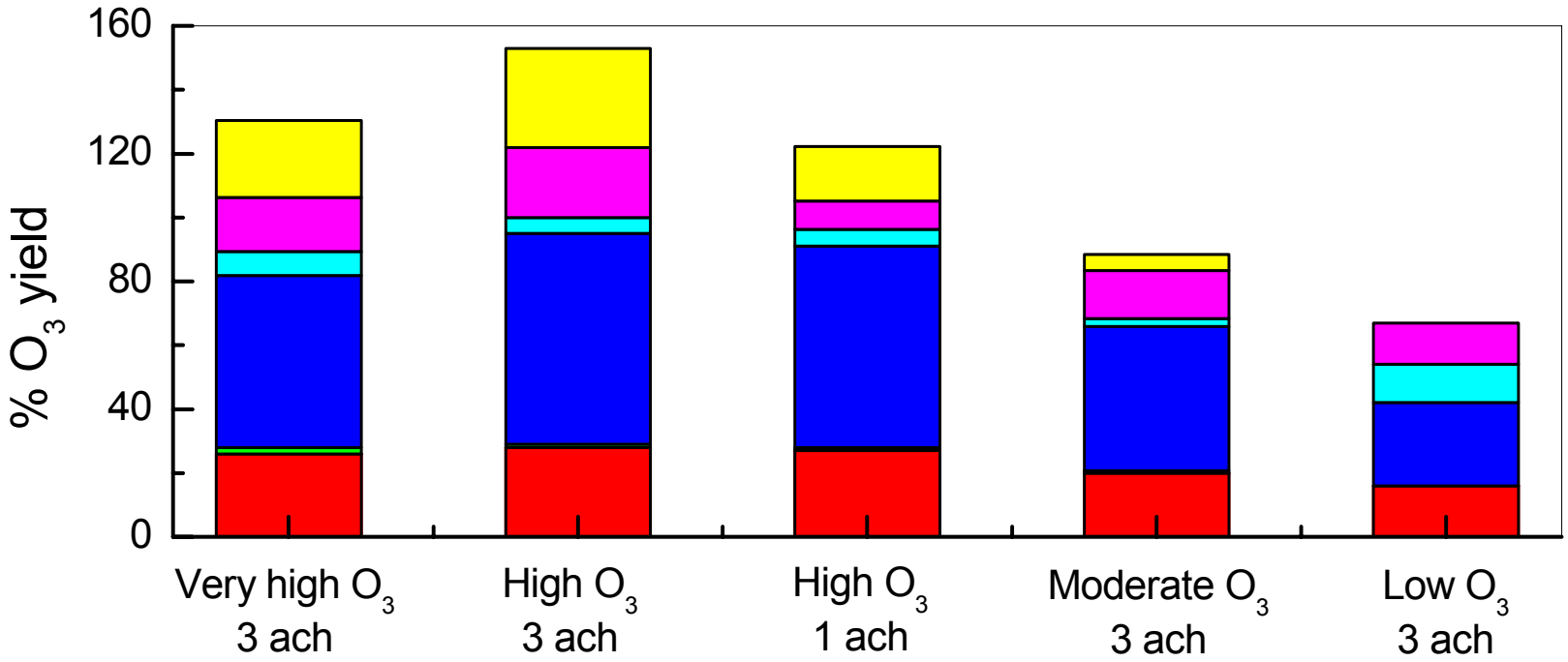
Singer et al., Atmos. Environ., 2006

Bench-scale experiments



Destaillats et al., Environ. Sci. Technol., 2006

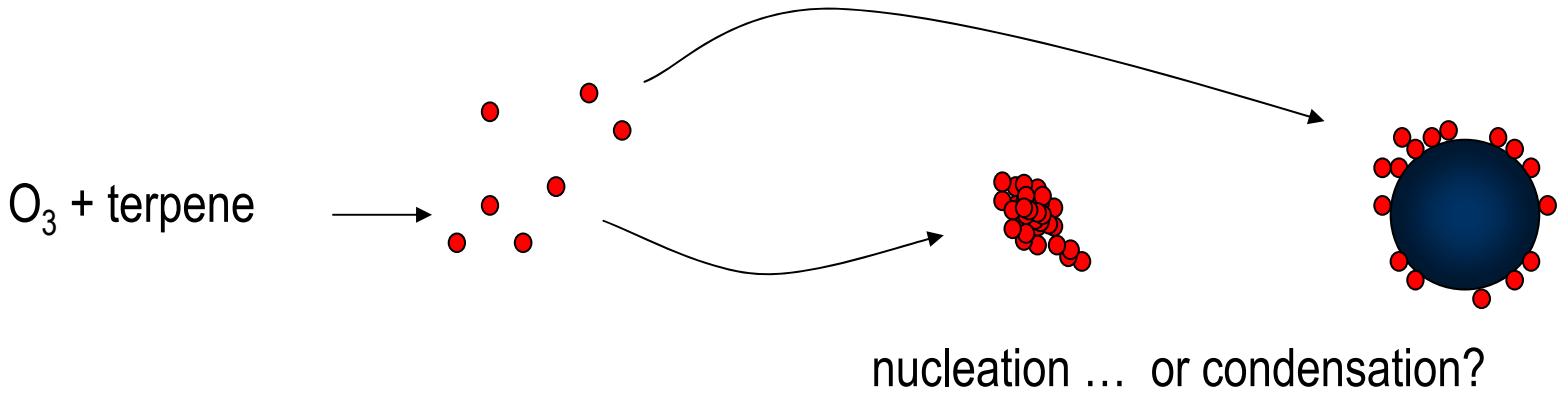
High yields of stable oxidation products

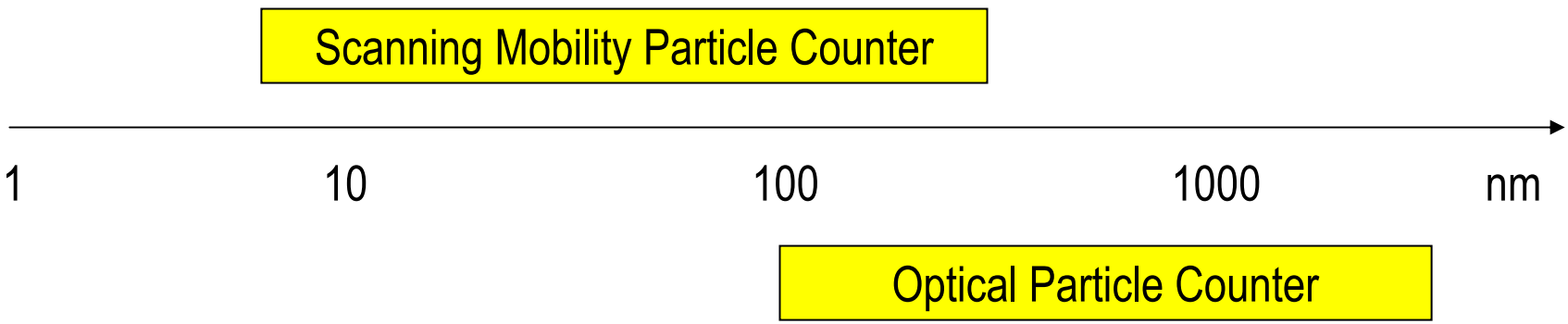


$$\% \text{ yield} = \frac{100 \times c}{\Delta (O_3)}$$

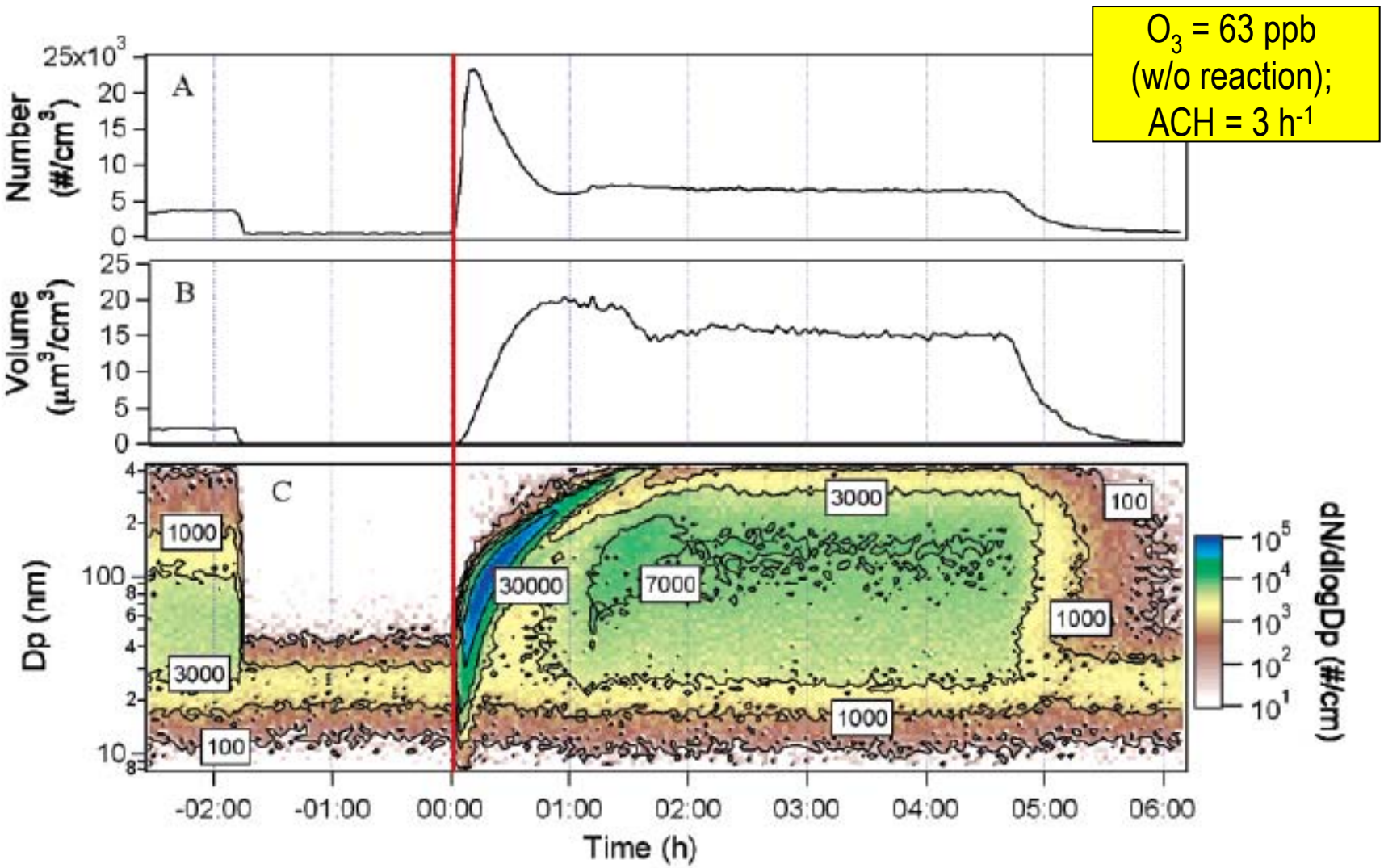
Destaillats et al., *Environ. Sci. Technol.*, 2006

Secondary organic aerosol (SOA) formation





Ultrafine particles formed in all experiments



Destaillats et al., Environ. Sci. Technol., 2006

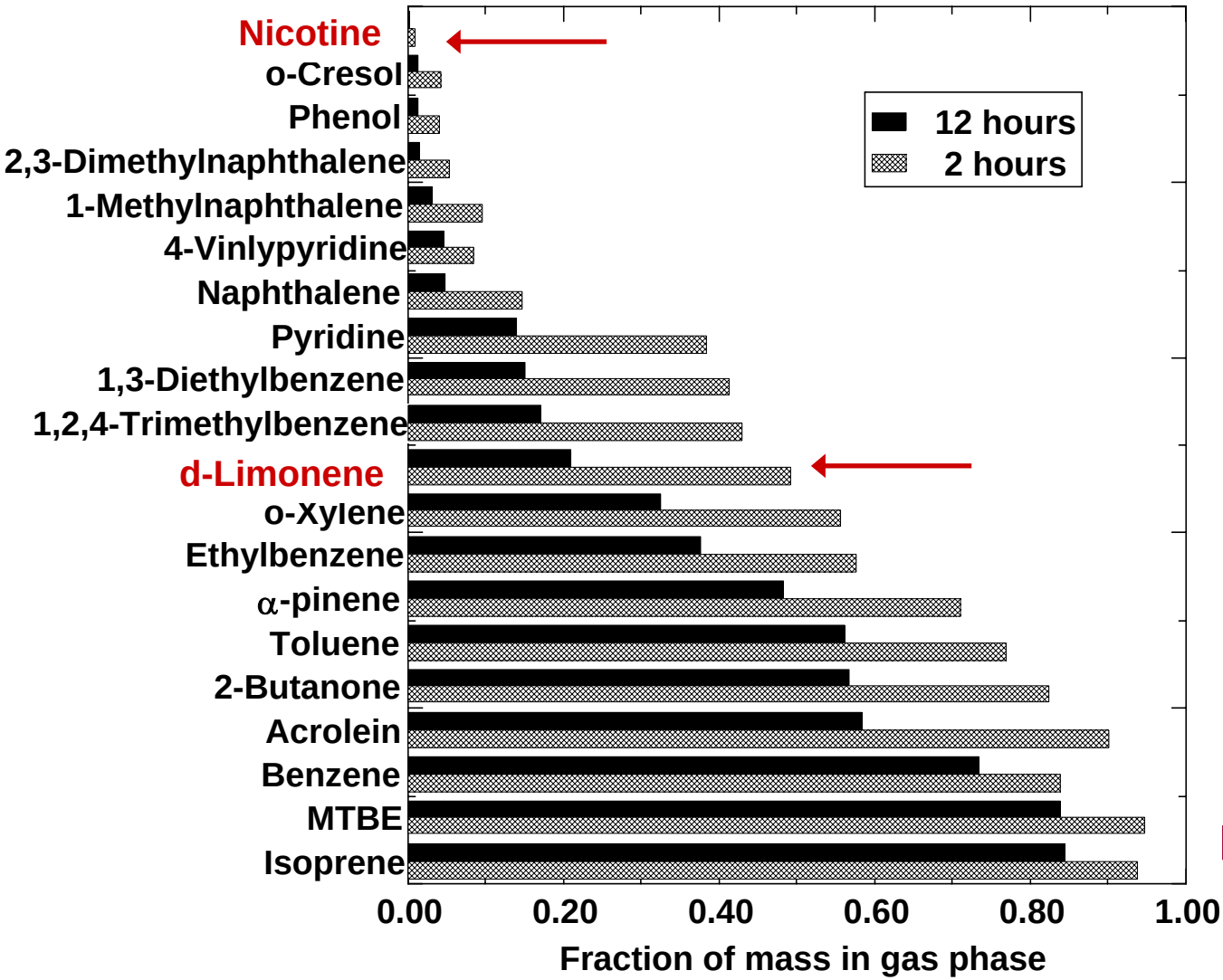
O_3-terpene reactions on surfaces

- VOCs sorb to materials → possible O_3 reactions on surfaces
- Room experiments:

  "Fresh" emissions from air freshener account for only half of observed O_3-terpene reactions
- Bench scale experiments :

  Particles and formaldehyde formed when ozone exposed to glass plate with POC residual

Sorption & surface chemistry



Plot shows fraction of mass in gas-phase at 2 h and 12 h.

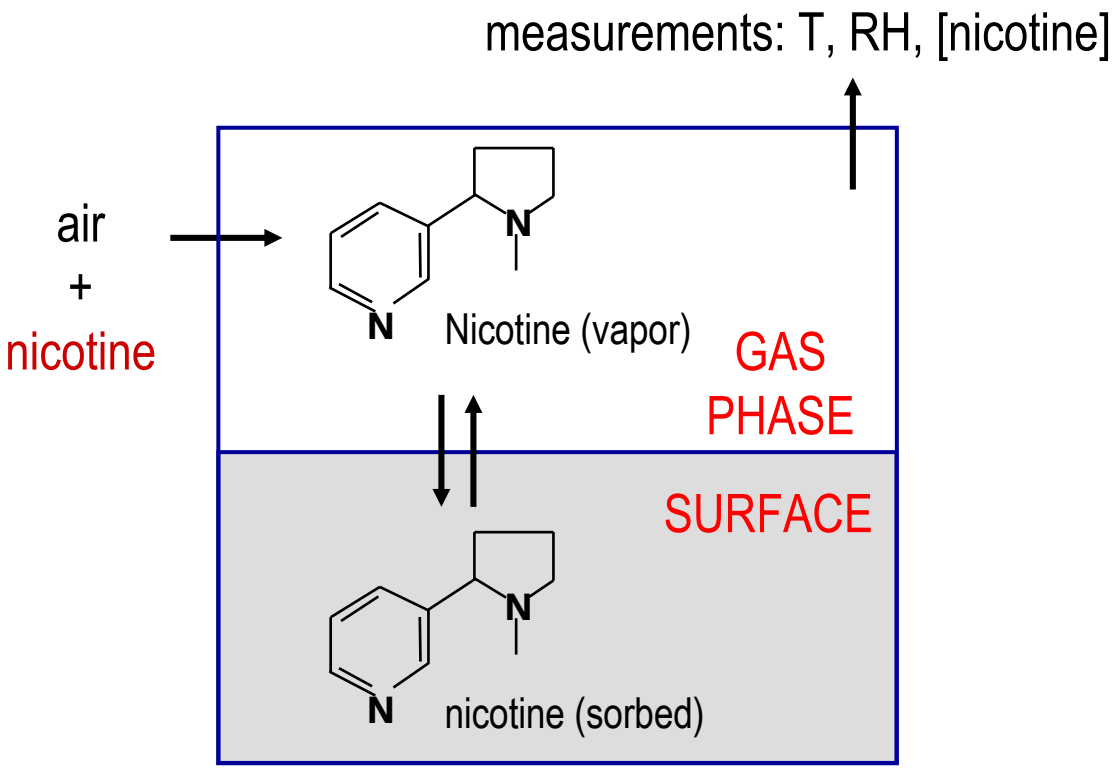
Some VOCs partition almost entirely to sorbed phase.

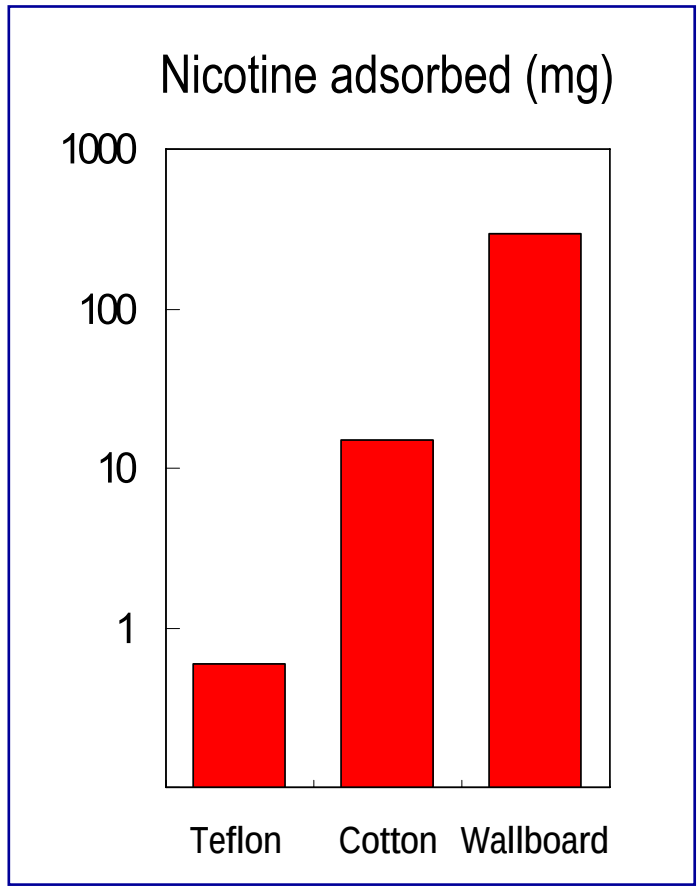
Over time, mass of VOCs sorbed to materials can far exceed amount in air!

Long residence time, high concentrations → more reactions possible!

Oxidation of sorbed nicotine

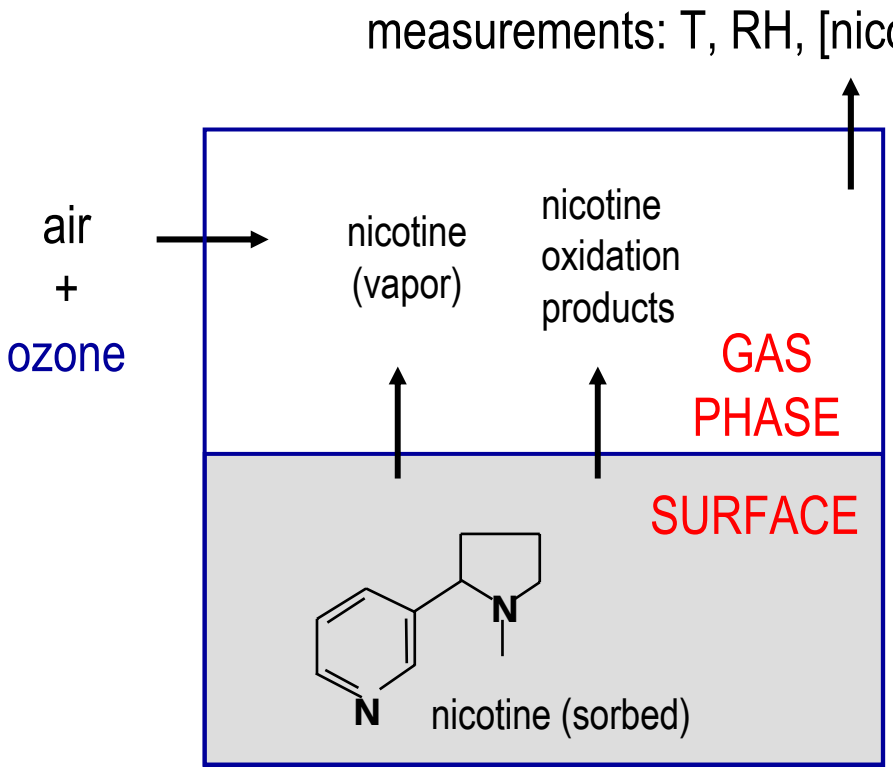
Bench chamber study – Phase I: nicotine sorption

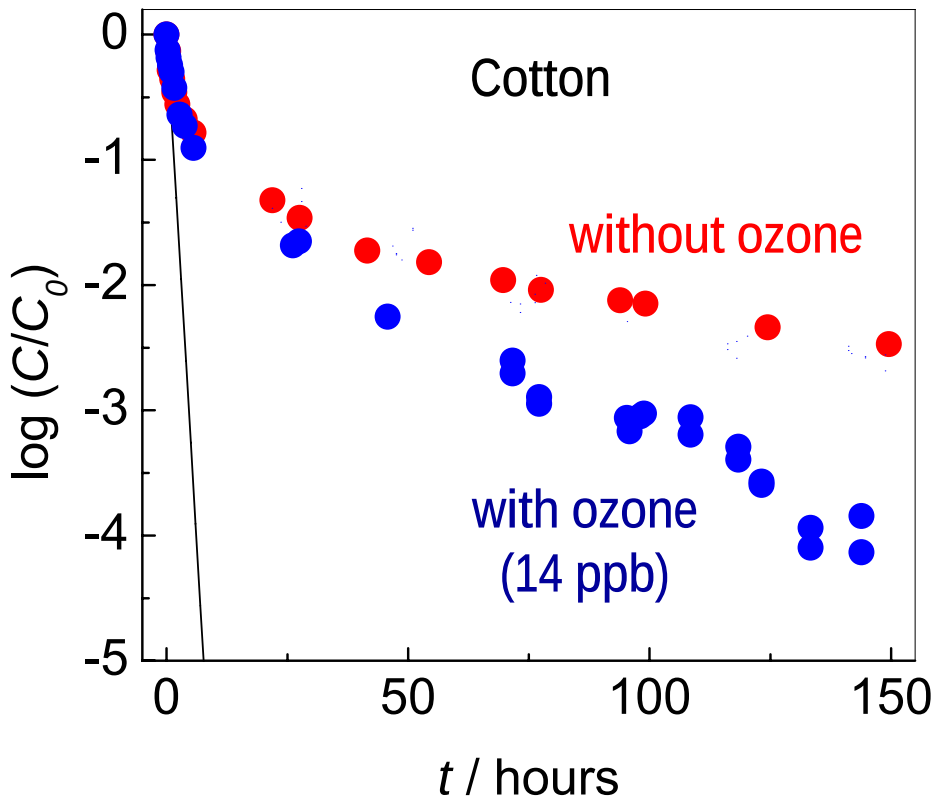




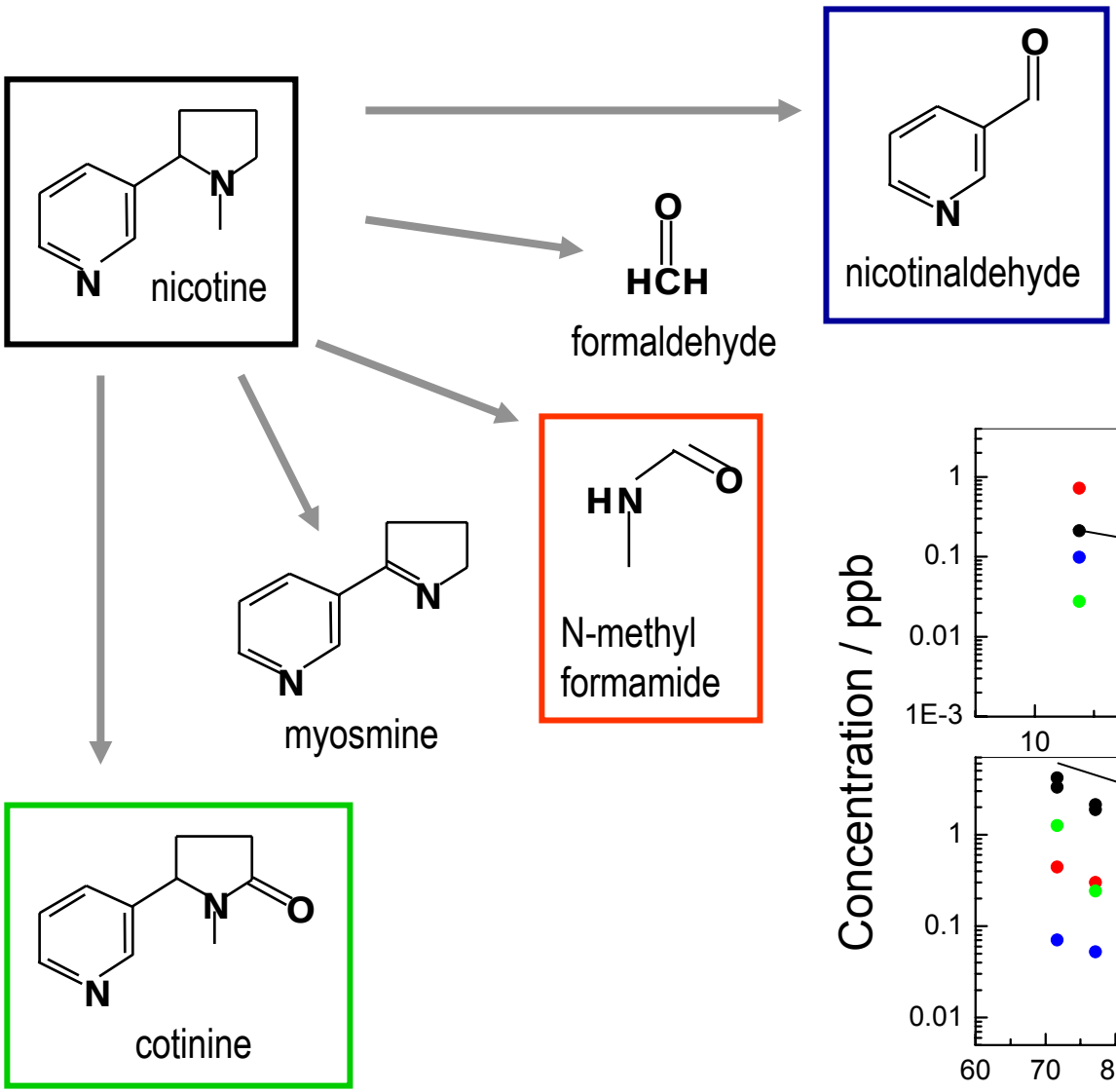
Oxidation of sorbed nicotine

Bench chamber study – Phase II: oxidation of sorbed nicotine

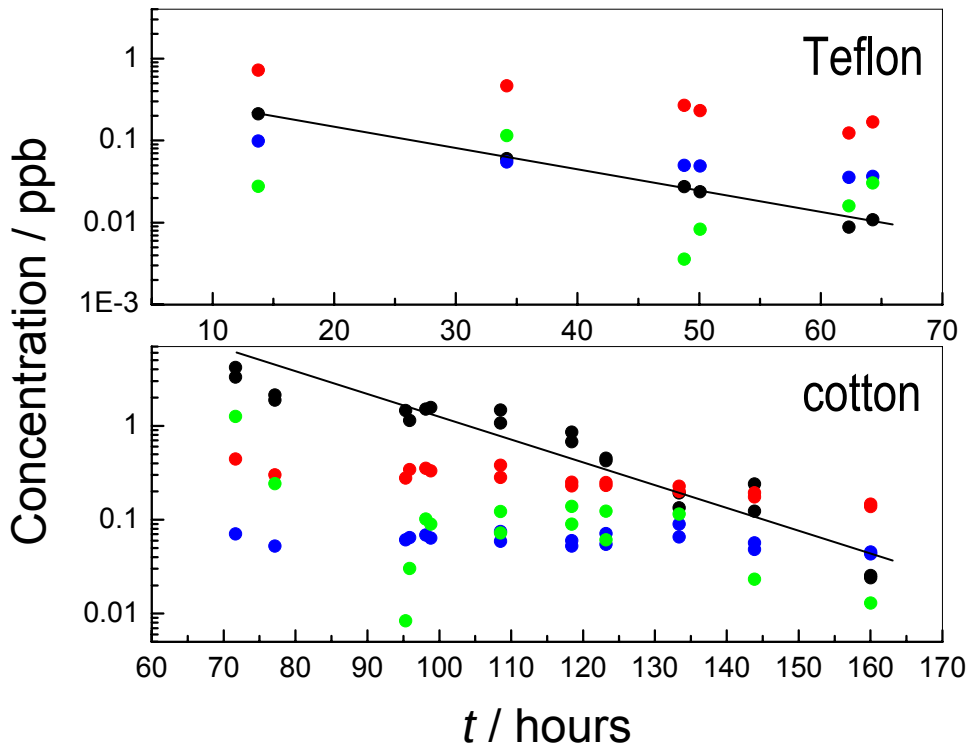




Nicotine oxidation products



Destaillats et al,
Environ. Sci. Technol.
2006, *40*, 1799-1805.



Nicotine - O_3: Summary findings

- Ozone reacts with sorbed species to create secondary pollutants
- Long residence times and high concentrations of sorbed mass → many more reaction combinations are possible (not just alkenes!)
- Nicotine oxidation rates competitive with desorption

Oxidation of sorbed nicotine
(tobacco smoke ageing)

VOCs, PM

"direct" exposure
secondhand smoke

organic gases

indirect exposure
third-hand smoke

$+ O_3$

formaldehyde &
other pollutants

INDOOR SURFACES

Air cleaning with chemistry

Can we use chemical reactions to eliminate airborne pollutants?

Are air cleaning technologies energy-efficient and safe?

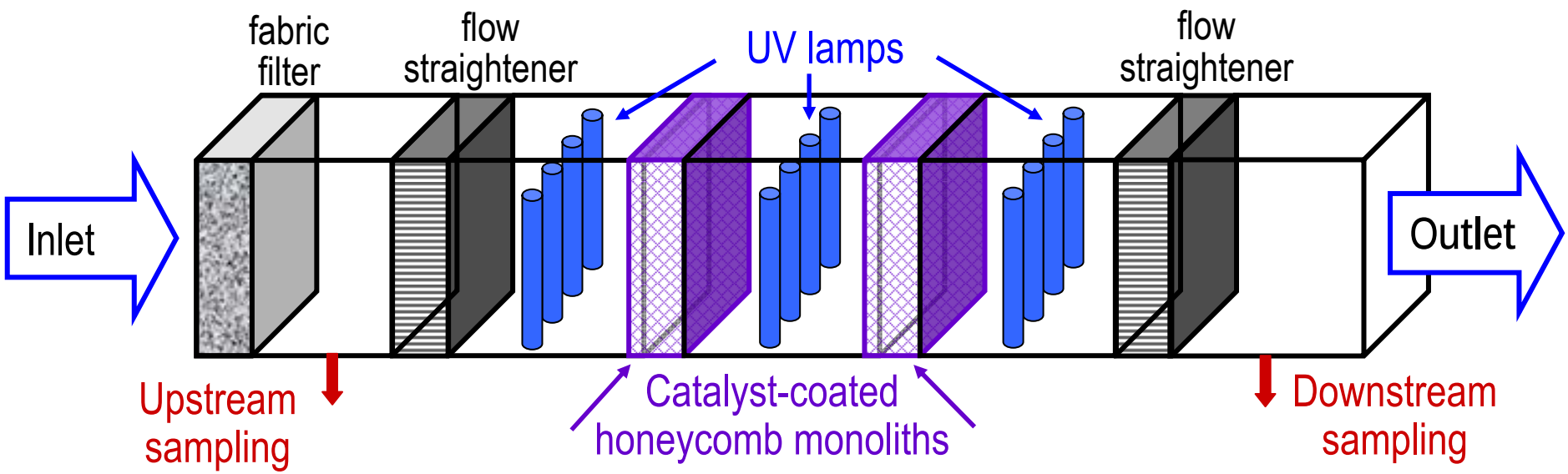
UV photocatalytic oxidation (UVPCO)

Outdoor or recirculated indoor air with VOCs → UVPCO → "Clean" air with lower VOCs

In-duct systems

Standalone home air cleaners

Evaluation of in-duct UVPCO



VOCs sorb to monolith coated with TiO_2 nanoparticles → UV light induces catalytic photooxidation of sorbed VOCs → Reaction products desorb, exit

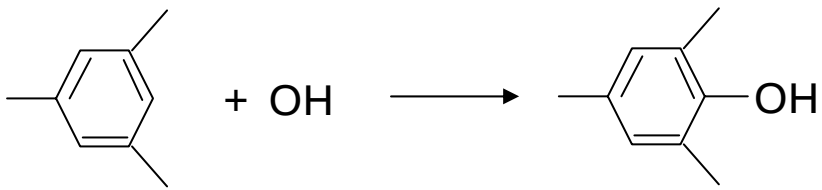
UVPCO summary

- Potential for VOC removal and ventilation energy savings
- Partially oxidized byproduct emissions should be controlled
- Long-term catalyst performance needs to be assessed

EXTRAS

- The following two slides present supporting material for comments made during the verbal presentation.

OH radical concentrations



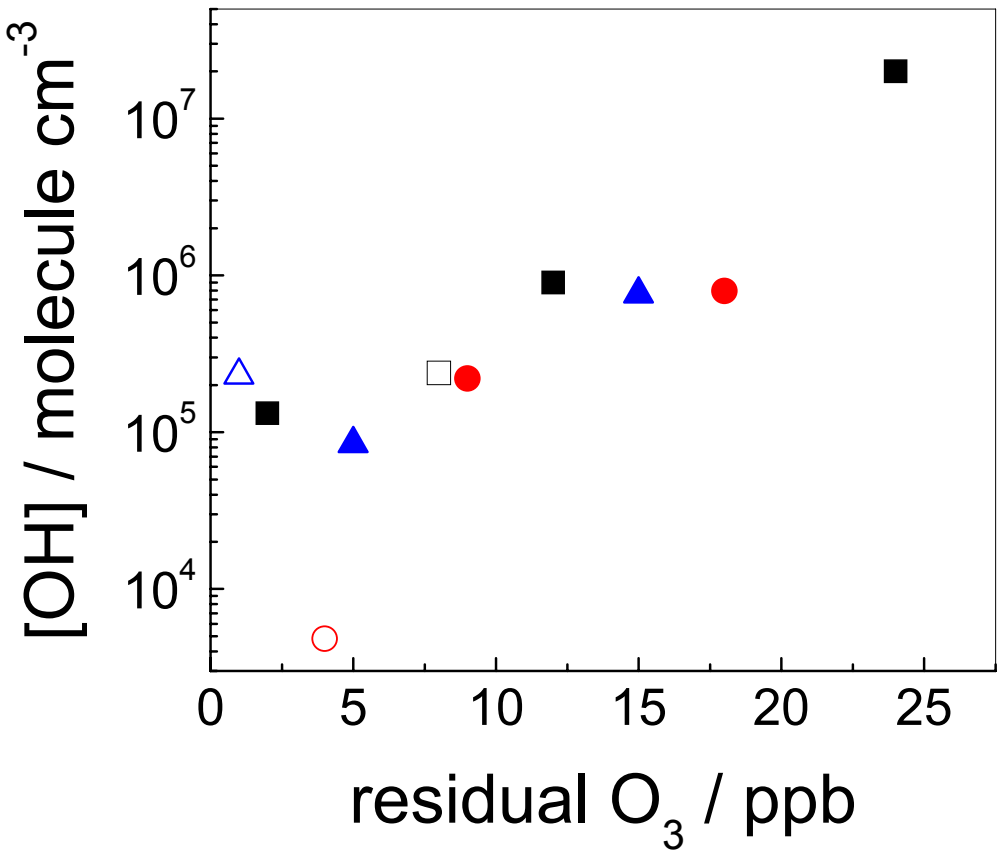
published OH levels (10^5 molec cm^{-3}):

7 indoor *

10-50 outdoor, winter daytime †

50-100 outdoor, summer daytime †

notes: * manipulated experiment in office (Weschler & Shields, 1997); † typical levels for clean troposphere (Seinfeld and Pandis, 1998)



Pine oil cleaner

■ 3 h^{-1} □ 1 h^{-1}

Orange oil degreaser

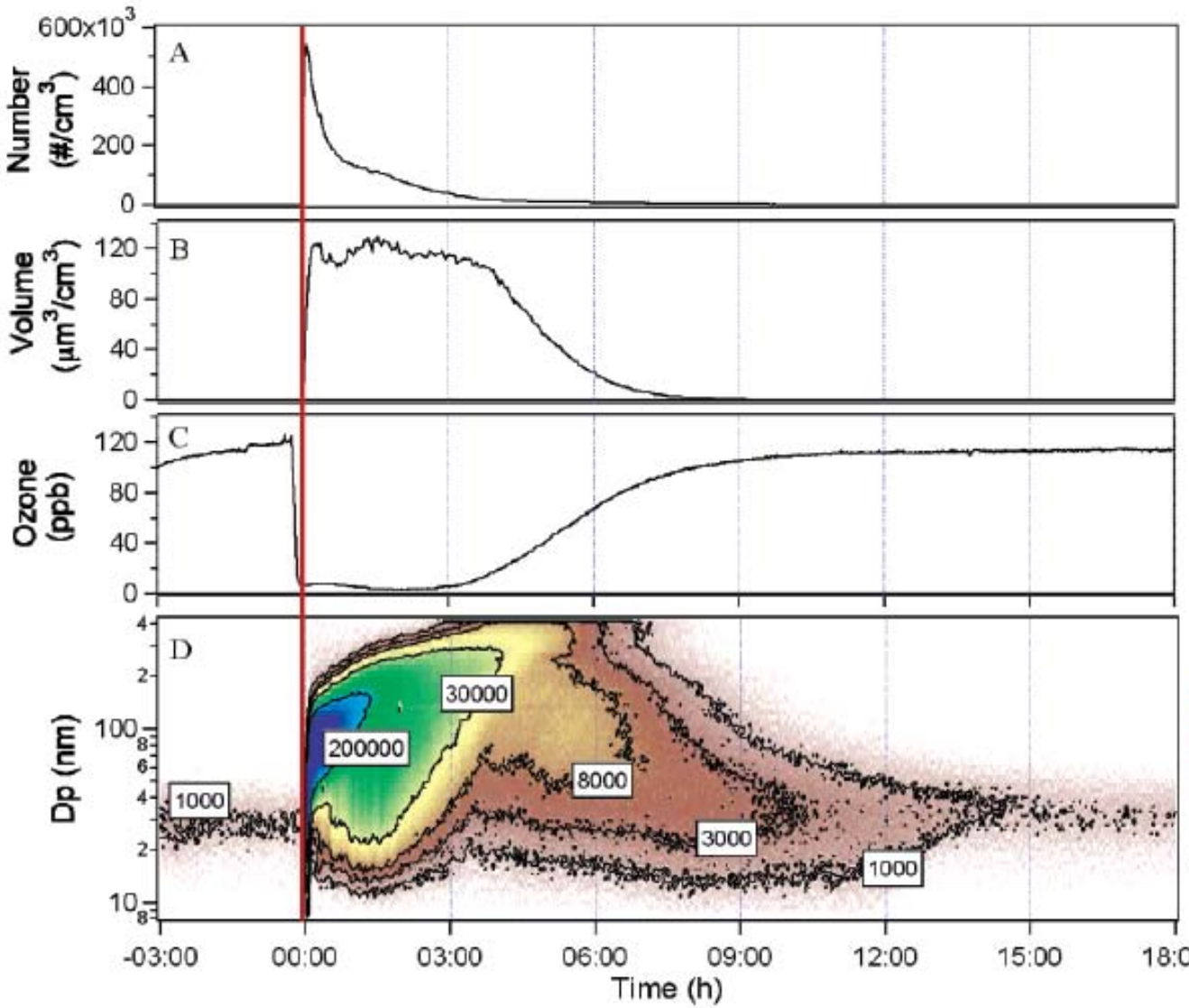
● 3 h^{-1} ○ 1 h^{-1}

Plug-in air freshener

▲ 3 h^{-1} △ 1 h^{-1}

Destaillats et al., *Environ. Sci. Technol.*, 2006

Terpene surface chemistry



applied on a glass plate & allowed to evaporate