Indoor Air Chemistry:

Cleaning Agents, Ozone, and Toxic Air Contaminants

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Credits

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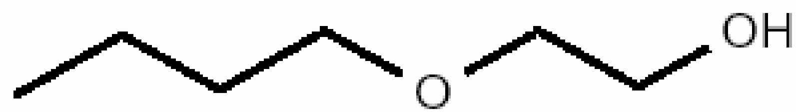
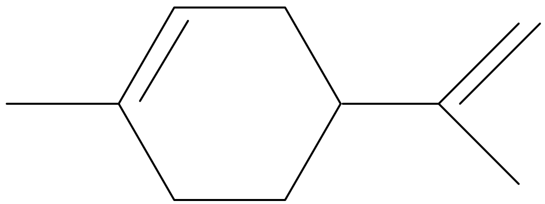
Motivation

- Epidemiological evidence links cleaning to occupational asthma
- Some cleaning solvents are toxic
  - 2-butoxyethanol
  - 2-hexyloxyethanol
- Terpenes and terpene alcohols used as solvents and fragrances
- Terpenes + ozone ⇒
  - OH radical
  - aldehydes and other oxidized organics
  - particles (secondary organic aerosol)



2-butoxyethanol

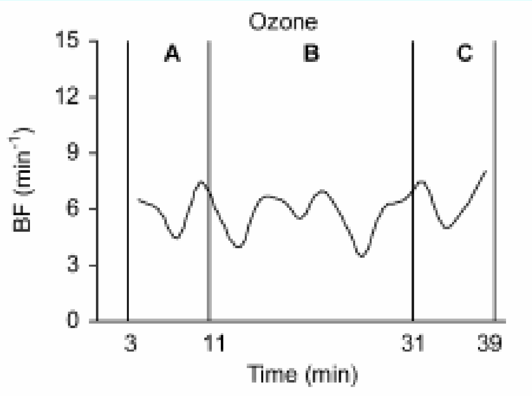


d-limonene

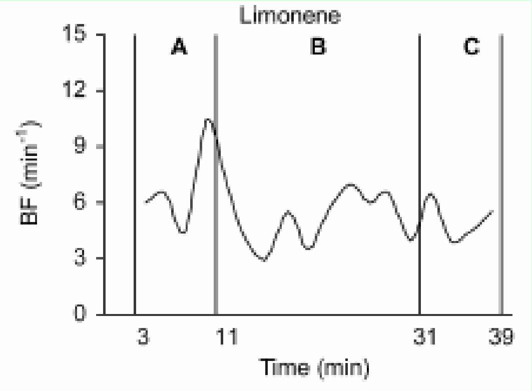
Toxicological evidence: eye irritancy

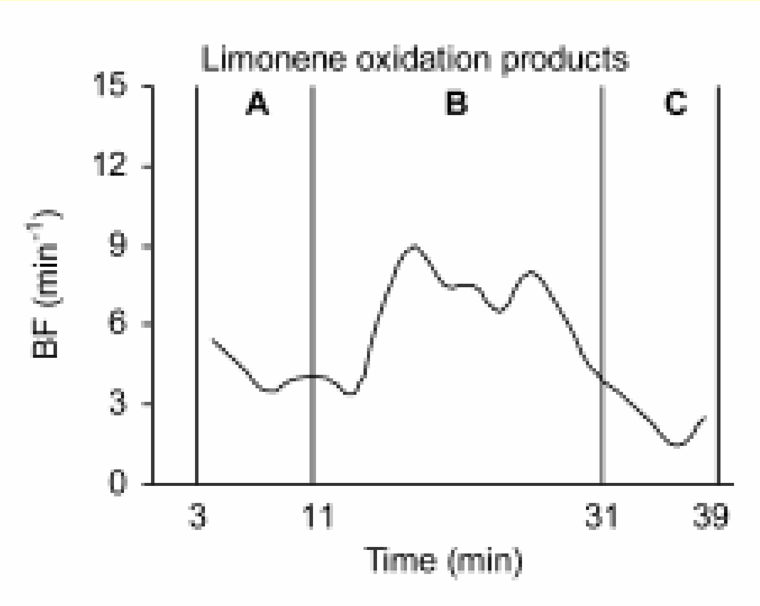
Changes in eye blink frequency (8 male subjects):
A = clean air; B = polluted air; C = clean air

130 ppb O_3



220 ppb limonene





75 ppb limonene + 40 ppb O_3

Ref: J Kleno and P Wolkoff, *Int Arch Occup Environ Health*, **77**, 235-243, 2004

Project overview

1. Literature Review

Nazaroff and Weschler
Atmospheric Environment
38, 2841-2865, 2004

2. Product Composition and Emissions

Shelf survey; MSDS review; composition screening; primary emissions during use.

BC Singer et al., *Indoor Air* **16**, 179-191, 2006

3. Bench-Scale Chemistry Experiments

Constituent consumption rates, secondary pollutant formation and yields, detailed study of ultrafine particles.

H Destaillats et al., *Environ. Sci. Technol.* **40**, 4421-4428, 2006

5. Exposure Analysis

Chapter 5,
Final Report

4. Room-Scale Chemistry Experiments

Secondary pollutants from product use with ozone.

BC Singer et al., *Atmospheric Environment* **40**, 6696-6710, 2006

Full technical report available
Indoor Air Chemistry: Cleaning Agents, Ozone and Toxic Air Contaminants
California Air Resources Board (http://www.arb.ca.gov/research/abstracts/01-336.htm)

Composition and emissions

- Shelf survey of five chain retailers (291 products)
- MSDS and label reviews (50 products)
- Screen for emissions in Tedlar bags (21 products)
- Primary emissions during use (6 products)

Shelf survey of five California retail outlets

Category	On shelves	Number reviewed	Ozone-reactive[1]	Glycol ethers[2]
Degreaser	**28**	**6**	**3**	**2**
General Cleaner	**52**	**13**	**3**	**4**
Glass Cleaner	**20**	**4**	**-**	**3**
Antibacterial, Deodorizer	**39**	**6**	**1**	**-**
Floor Cleaner	**48**	**7**	**-**	**3**
Furniture Polish	**30**	**5**	**1**	**-**
Air Freshener	**71**	**9**	**8**	**-**

[1] Contains limonene, orange oil, pine oil, perfume oil, or alkenes

[2] Contains ethylene-based glycol ethers, including 2-butoxyethanol

Emissions screening method

- Add 3 L nitrogen + 2-5 mL product to 5 L Tedlar bag
- Or spray aerosol into 80 L Tedlar bag with 50 L N_2
- Heat 1 h at 45 or 65 °C
- Stabilize at room T for 1 h
- Draw gas sample from bag, load onto sorbent tube
- Analyze by thermal desorption GC/MS

Emissions screening results

Product	Form	Glycol ethers (%)	Ozone-reactive (%)[1]
Citrus degreaser	Liquid	-	9.6
Orange oil degreaser	Foam	-	26
HD degreaser/disinfectant	Trigger	4.7	-
Citrus cleaner/degreaser	Trigger	1.6	4.0
Pine oil cleaner (n=3)	Liquid	-	0.4 - 7.7
"Green" cleaner	Trigger	4.1	-
All-purpose cleaner	Trigger	2.6	-
Glass cleaner	Trigger	0.8	-

[1] Includes terpenes and other alkenes

Emissions screening results (2)

Product	Form	Glycol ethers (%)	Ozone-reactive (%)[1]
Carpet stain remover	Aerosol	9.6	-
Wood cleaner/polish	Aerosol	-	5.6
Plug-in air fresher	Gel	-	9.6
Scented oil (n=2)	Liquid	-	13–14

[1] Includes terpenes and other alkenes

6 products contained <0.1% of study compounds:

- Kitchen cleaner (disinfectant-antibacterial)
- Tobacco odor neutralizer
- Wood floor cleaner, wood cleaner/preservative
- 2 Furniture polishes

Primary emissions experiments

- **Full strength use**
  - 0.56-m^2 laminate tabletop
  - Spray + wipe, or
  - Spray, Scrub, Rinse, Wipe
  - Remove or retain towels
- **Dilute use**
  - 4.2 m^2 vinyl tile floor
  - 4-L solutions mixed in room
  - Detailed mopping procedure
- **Experimental room**
  - 50-m^3; residential construction
  - Ventilated at 0.53 h^{-1}

Was that 8 or 9 mop strokes?

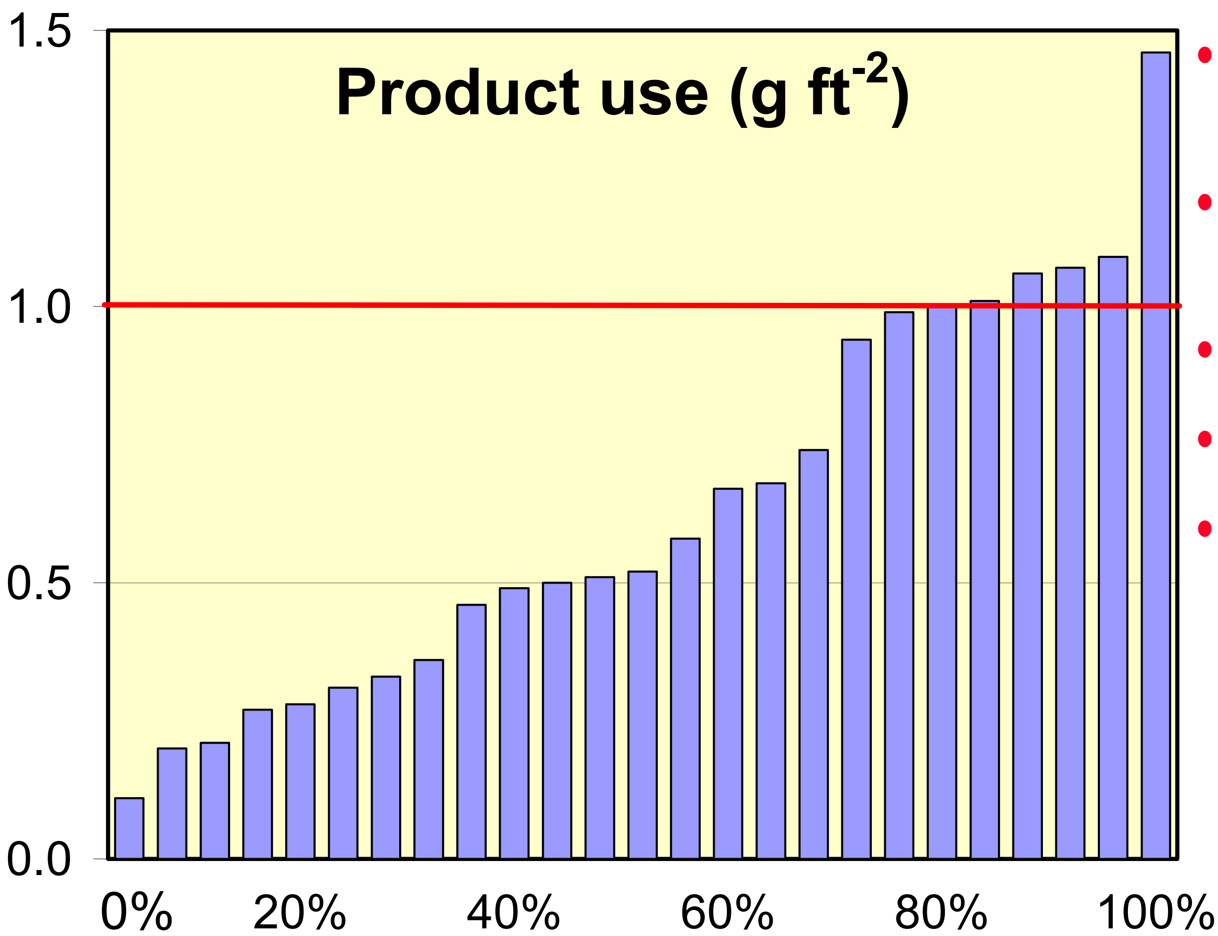
Floor mopping procedure

Emissions during product use

Product	Constituents	Package	Full strength spray, wipe	Full strength scrub, rinse	Dilute (mop)
Glass cleaner (GLC-1)	2-butoxyethanol 2-hexyloxyethanol	trigger spray			
General purpose cleaner (GPC-1)	pine oil: terpenes, terpene alcohols	capped bottle			
General purpose cleaner (GPC-2)	2-butoxyethanol	trigger spray			
General purpose cleaner (GPC-3)	2-butoxyethanol	trigger spray			
General purpose cleaner (GPC-4)	2-butoxyethanol, limonene	trigger spray			
Air freshener (AFR1)	unsaturated terpenoids	heating dispenser	Plug in for several days		

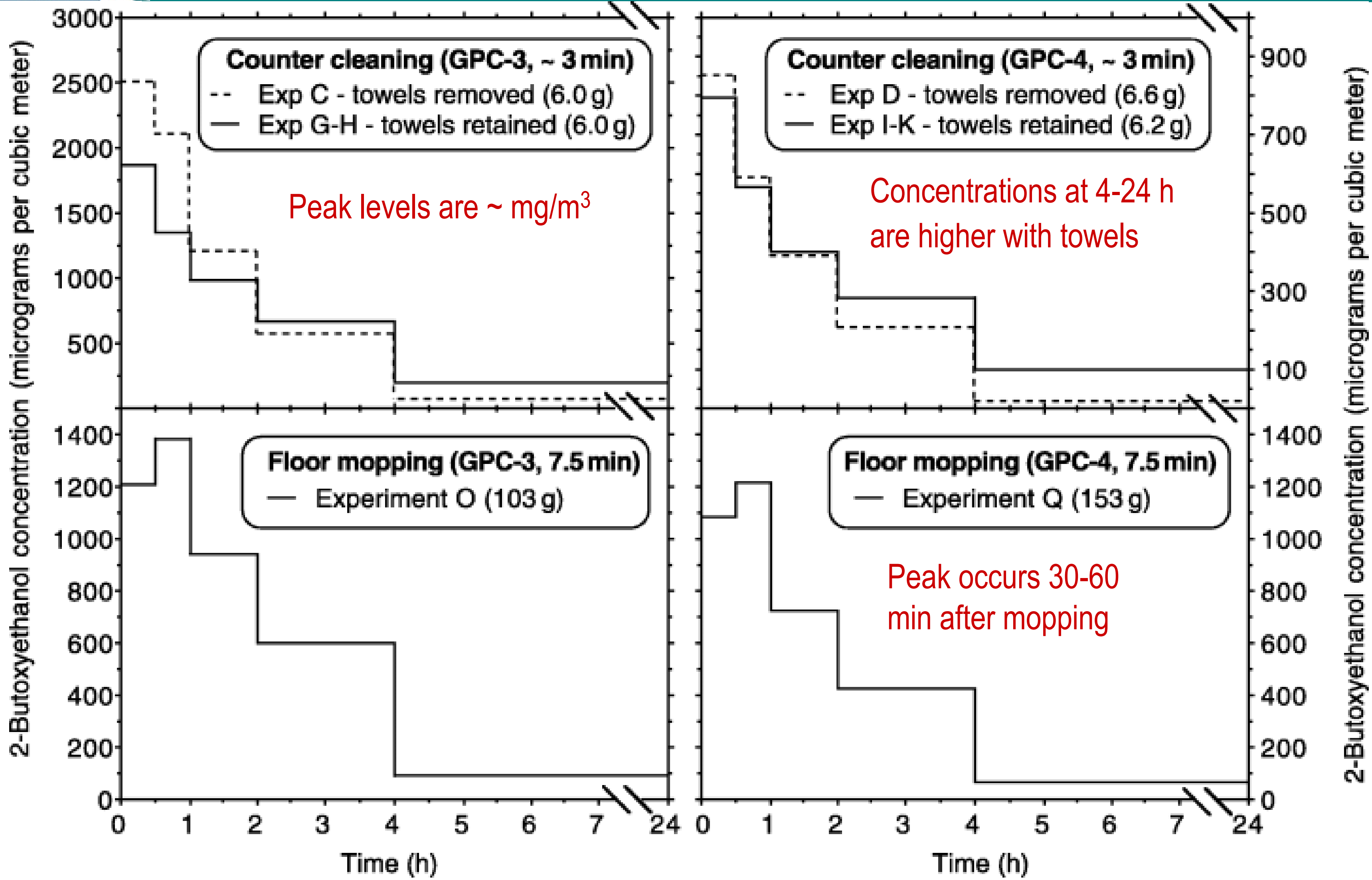
Singer et al., Indoor Air, 2006

Trigger spray product use



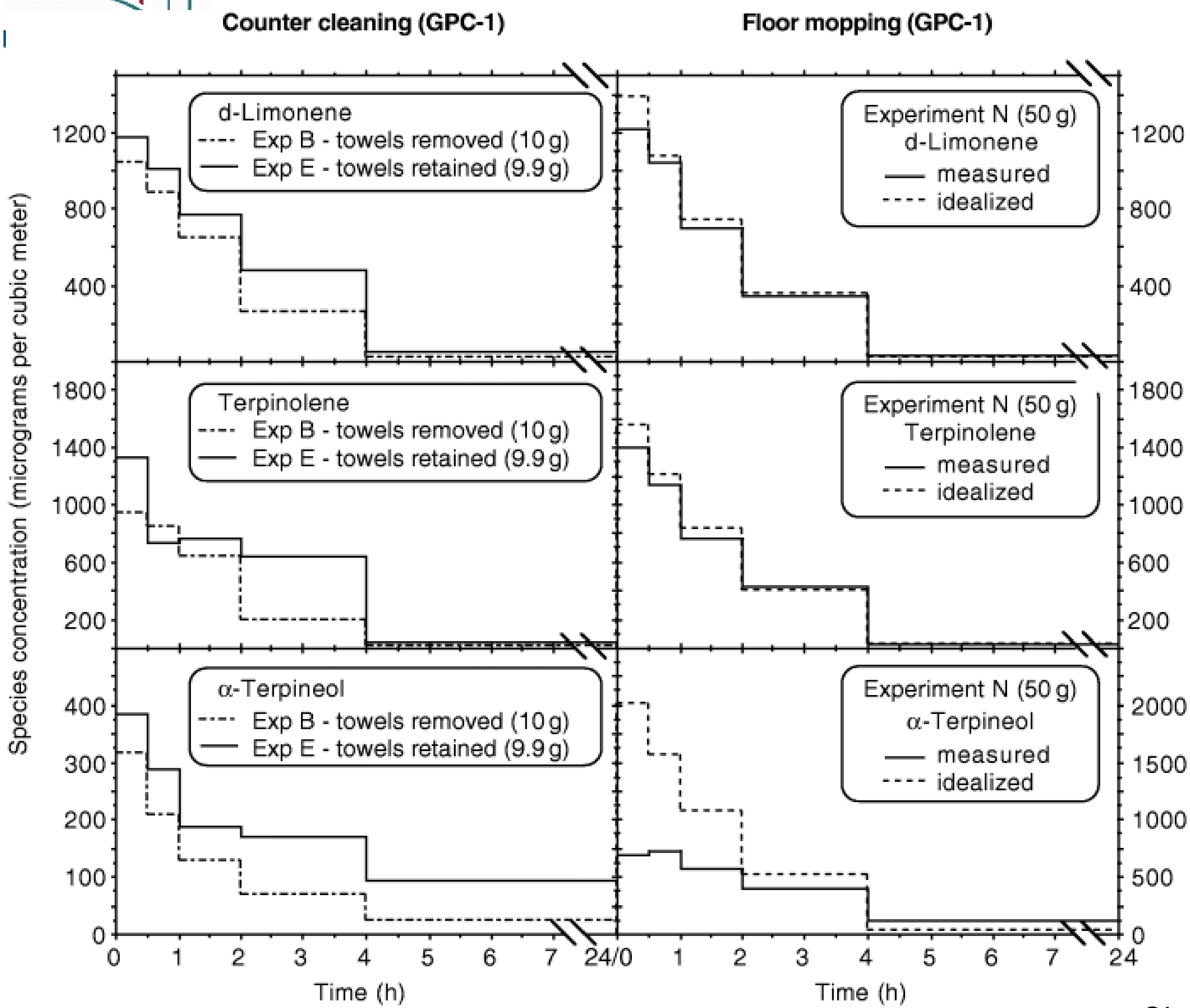
- Objective: Identify high but reasonable use rate
- Volunteers asked to simulate cleaning of 1 m^2 tabletop
- 25 LBNL employees
- Bottle weighed before, after
- Note: 1 g ft^{-2} = 10.8 g m^{-2}

Concentration patterns: 2-butoxyethanol



Singer et al., Indoor Air, 2006

Concentration patterns: terpenes



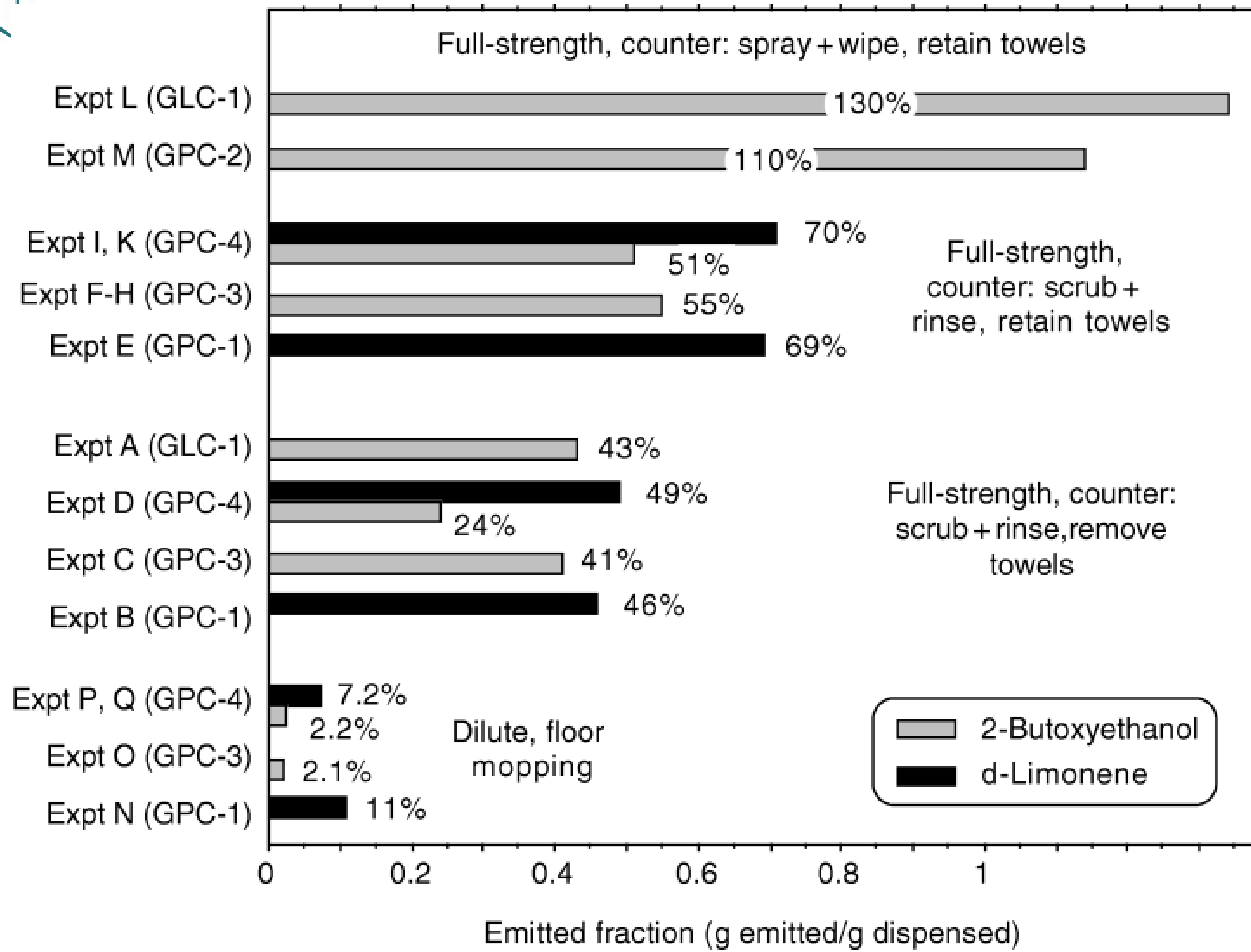
towel removal = VOC removal; concentrations and exposures reduced

towel retention: terpenes emitted over time

hydrocarbons follow non-sorbing decay; alcohols adsorb then desorb over time

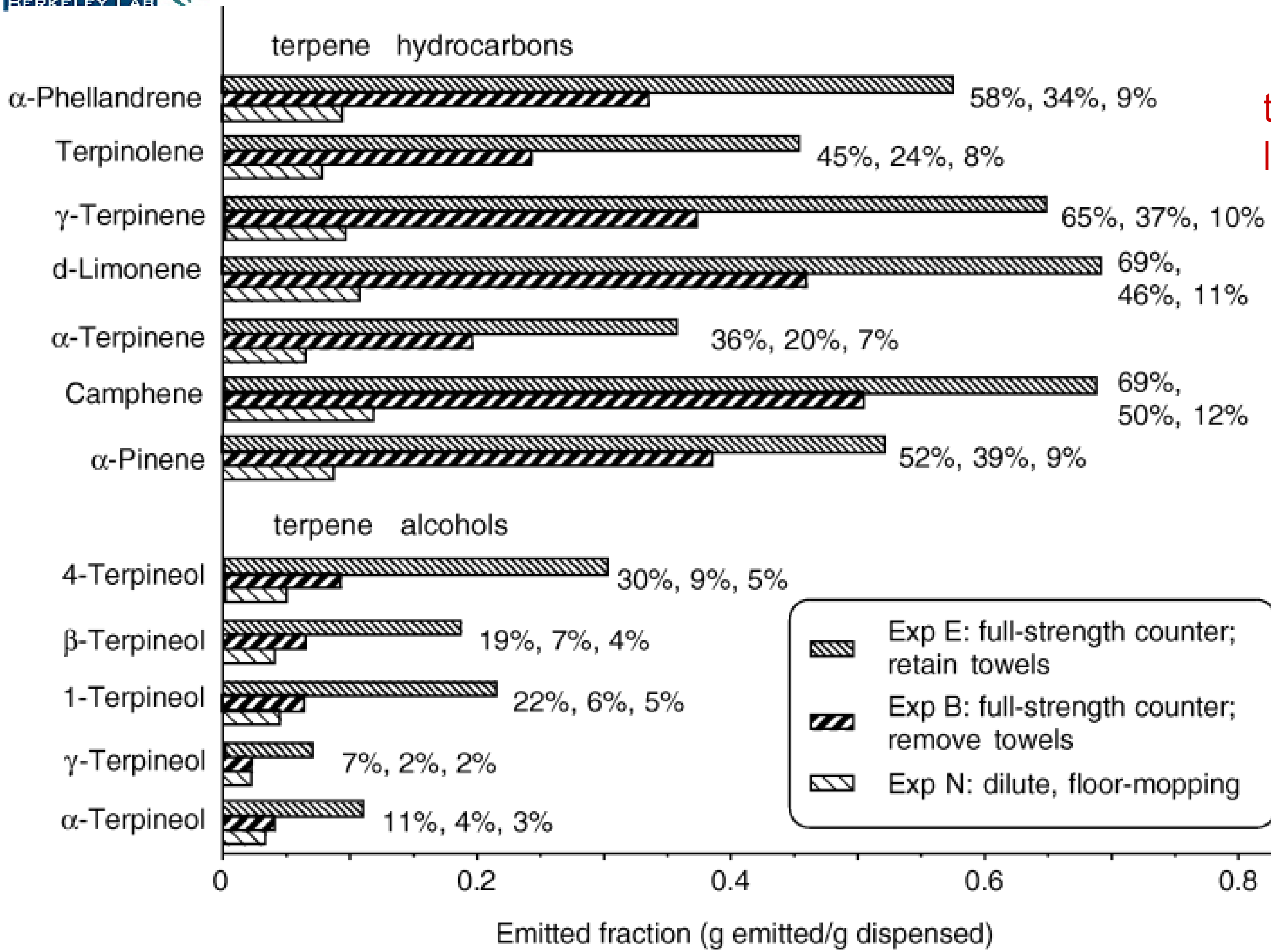
Singer et al., Indoor Air, 2006

Fractional emissions vary with usage



Singer et al., Indoor Air, 2006

Fractional emissions vary by compound



towel removal lowers emissions

emitted fractions much lower with dilute use

terpene alcohols volatilize more slowly than HCs

Singer et al., Indoor Air, 2006

Primary emissions summary

- Peak exposure concentrations are ~ mg/m^3
- Exposure patterns affected by delayed volatilization and sorption
- Constituent emission fractions vary:

  ~ 100% for spray + wipe, towels left in room (full strength)

  ~ 50% released when towels removed (full strength)

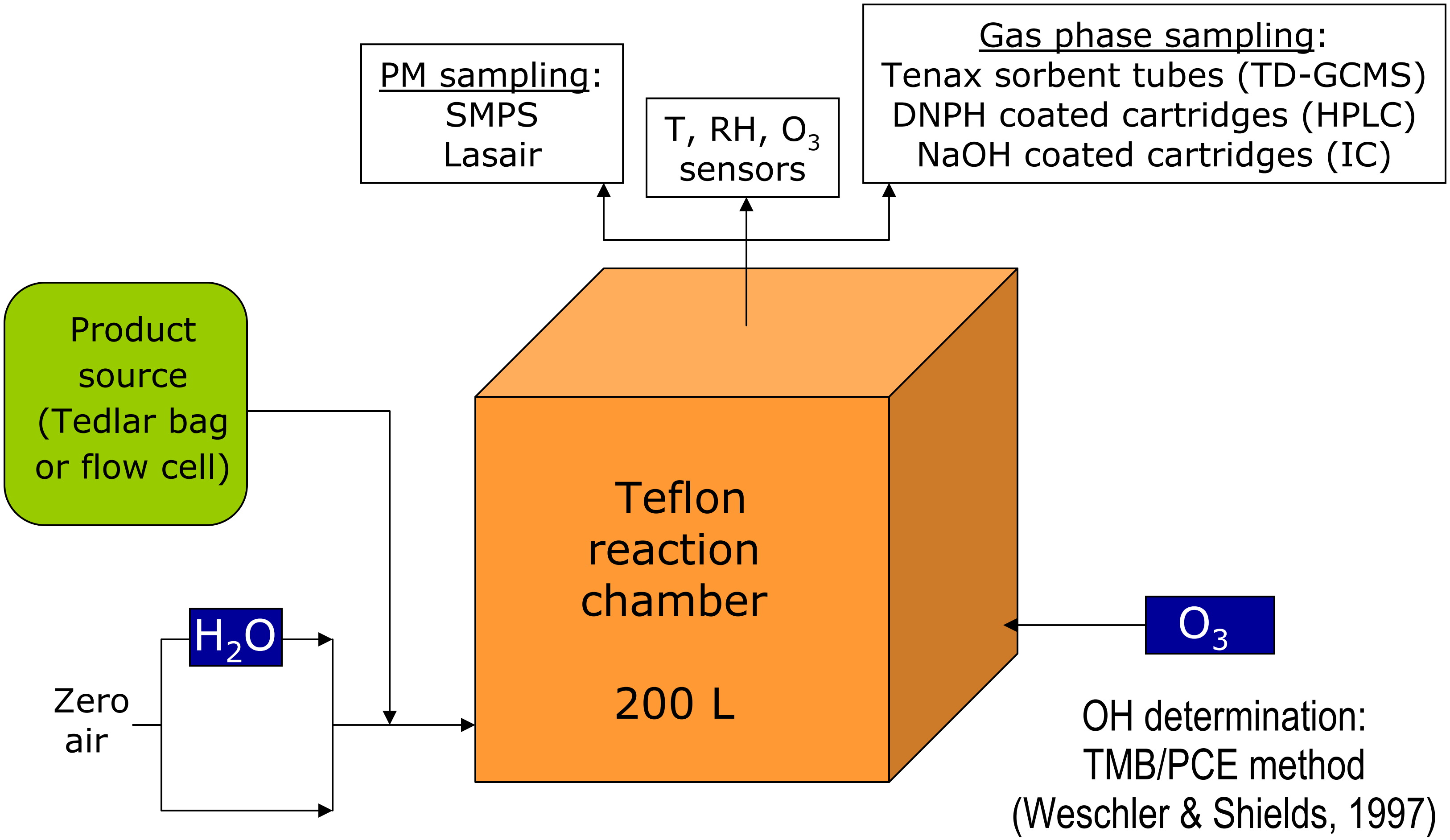
  ~ 5-15% released from dilute solution

  alcohols preferentially retained in solution
- Exposure concentrations can be modeled using
  - product bulk composition or screening emissions data
  - cleaning surface areas and product use rates
  - home volumes and air exchange rates

Bench-scale chemistry experiments

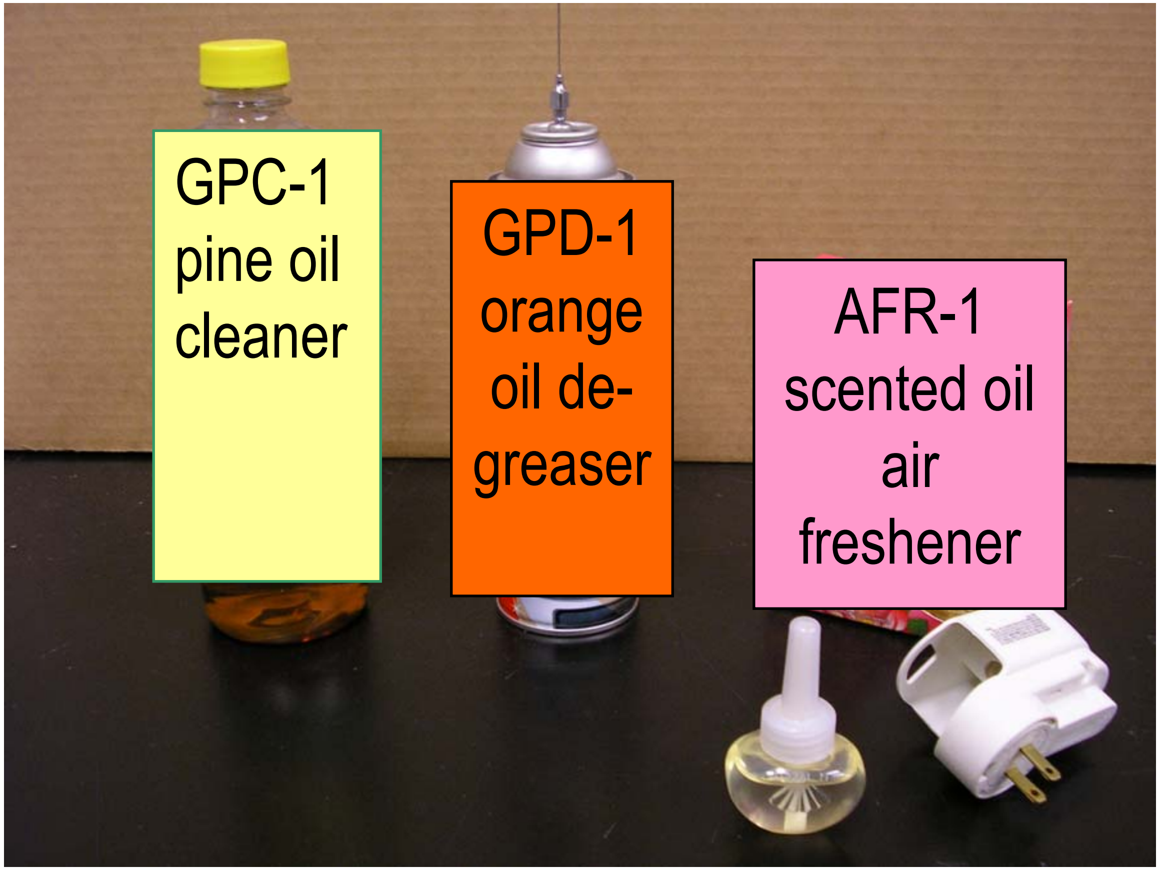
- Quantify consumption of individual VOC constituents
- Identify and quantify stable oxidation products
- Calculate product yields
- Estimate OH concentrations as indicator of chemistry
- Investigate particle formation and growth mechanisms
- Vary ozone and air exchange rate

Bench-scale experimental apparatus

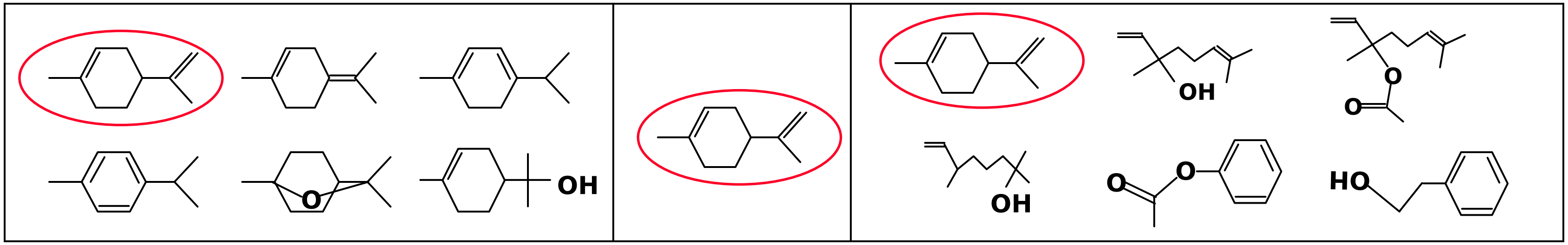


Destaillats et al., Environ. Sci. Technol., 2006

Products studied for reactive chemistry



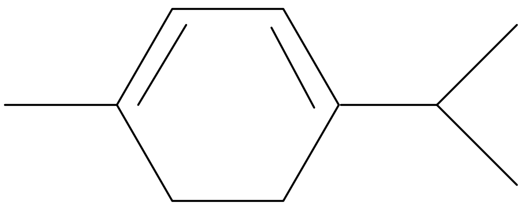
Primary emissions:



Ozone-reactive product constituents

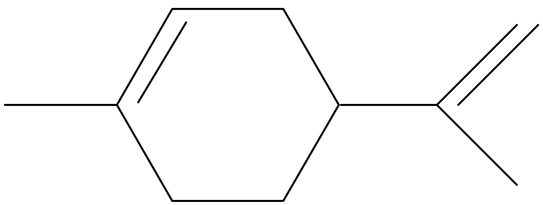
Monoterpenes ($C_{10}H_{16}$)

α-terpinene



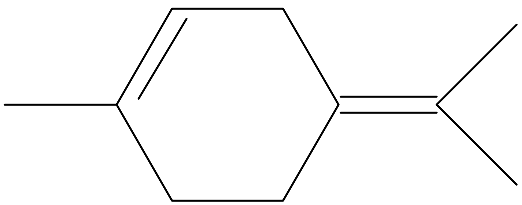
$k_{O3} = 5x10^{-4}$ ppb^{-1} s^{-1}

d-limonene



$k_{O3} = 5x10^{-6}$ ppb^{-1} s^{-1}

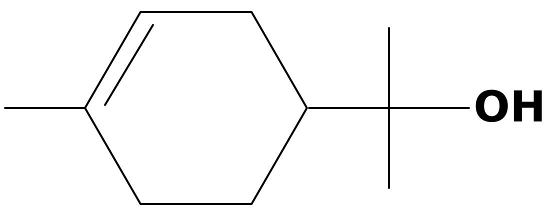
terpinolene



$k_{O3} = 5x10^{-5}$ ppb^{-1} s^{-1}

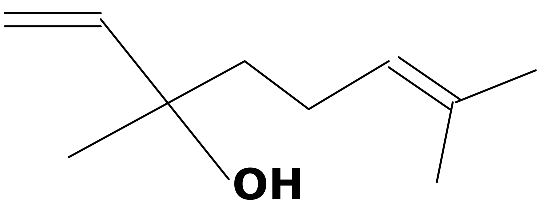
Terpenoids

α-terpineol



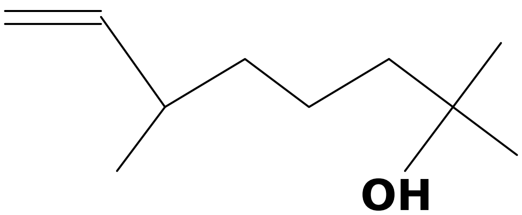
$k_{O3} = 7.5x10^{-6}$ ppb^{-1} s^{-1}

linalool



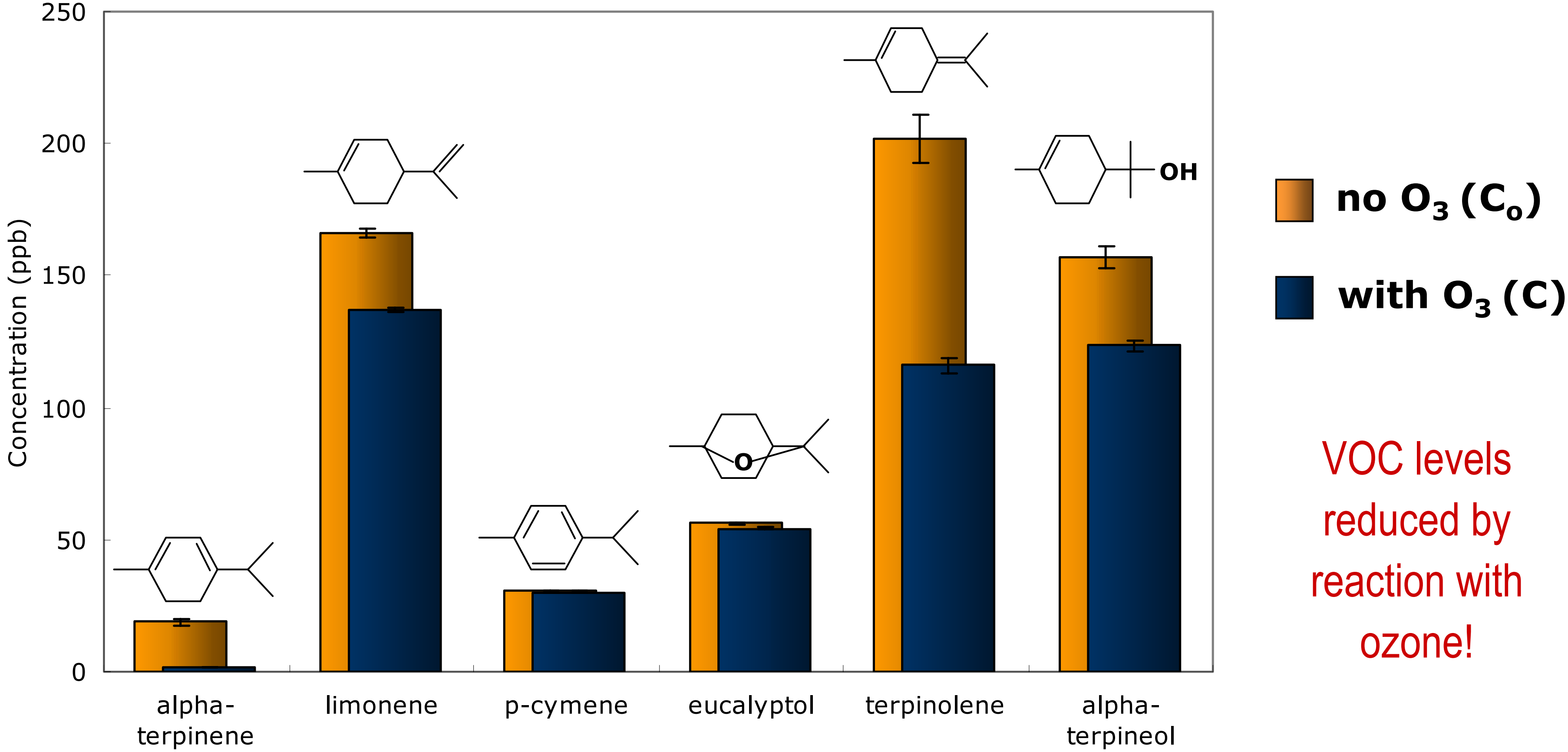
$k_{O3} = 1x10^{-5}$ ppb^{-1} s^{-1}

dihydromyrcenol



$k_{O3} \leq 5x10^{-8}$ ppb^{-1} s^{-1}

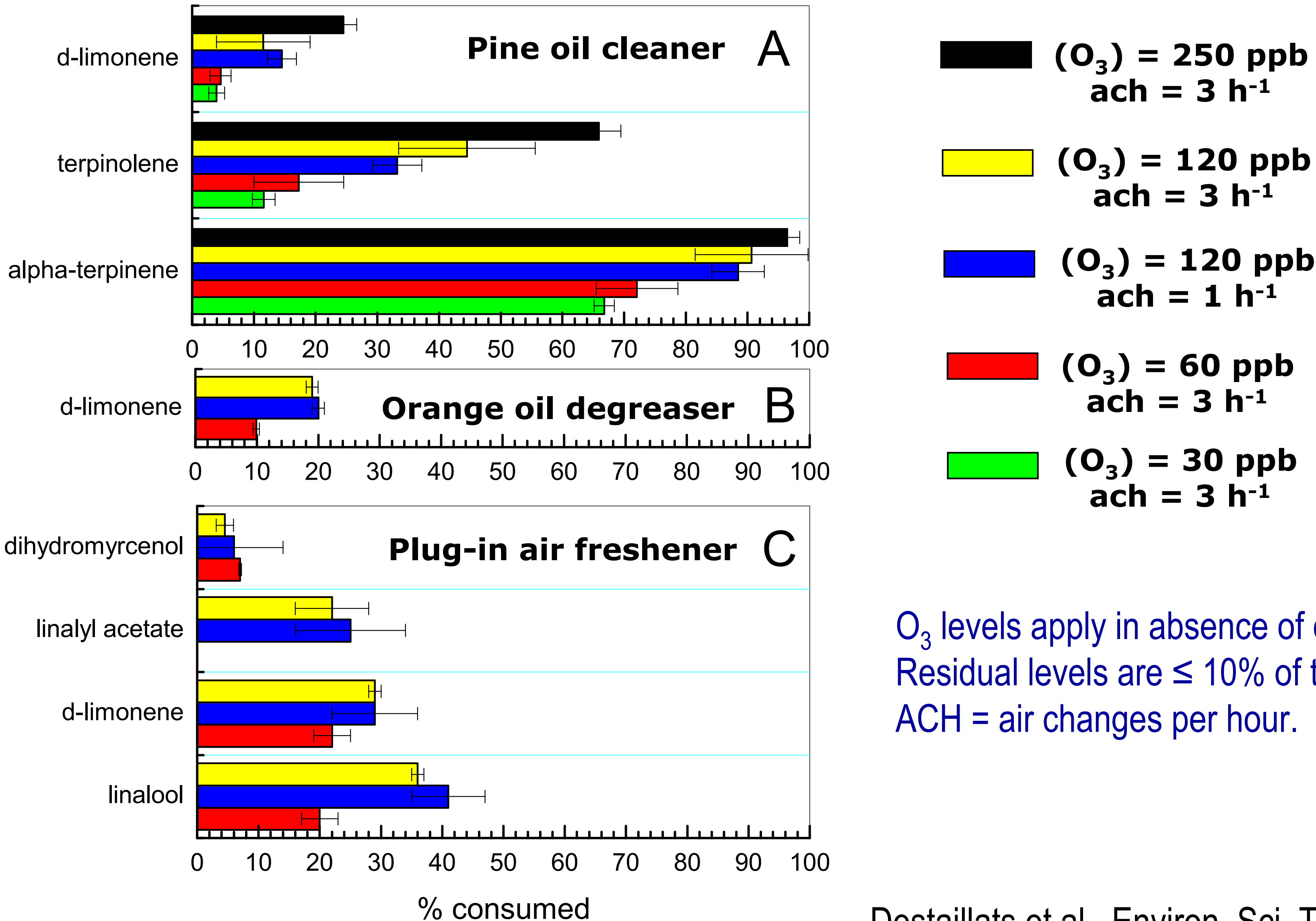
VOCs measured in chamber



VOC levels reduced by reaction with ozone!

inlet ozone concentration: 120 ppb
residual ozone: 13 ppb
air exchange rate 3 h^{-1}

Consumption of reactive VOCs

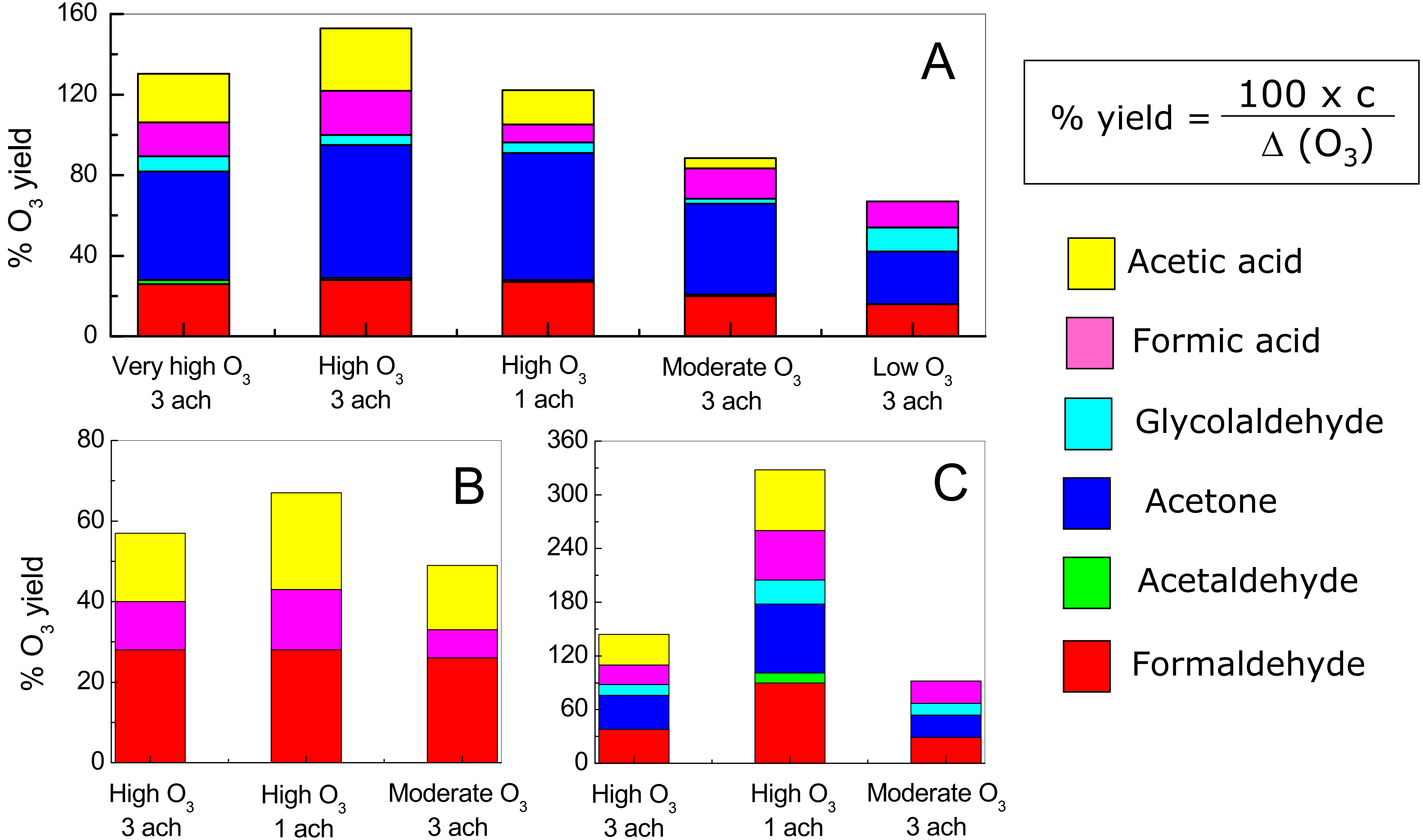


O_3 levels apply in absence of chemistry;
Residual levels are ≤ 10% of these;
ACH = air changes per hour.

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

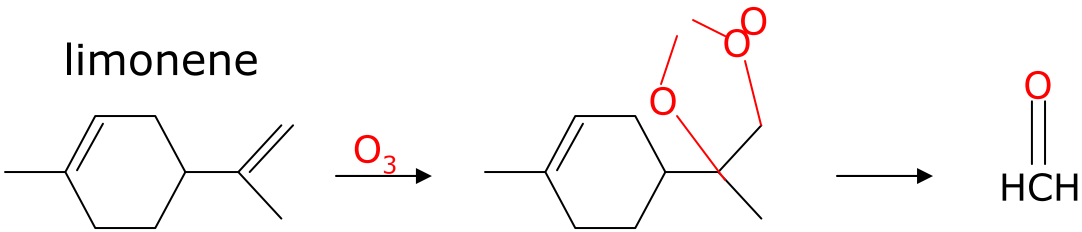
High yields of stable oxidation products

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

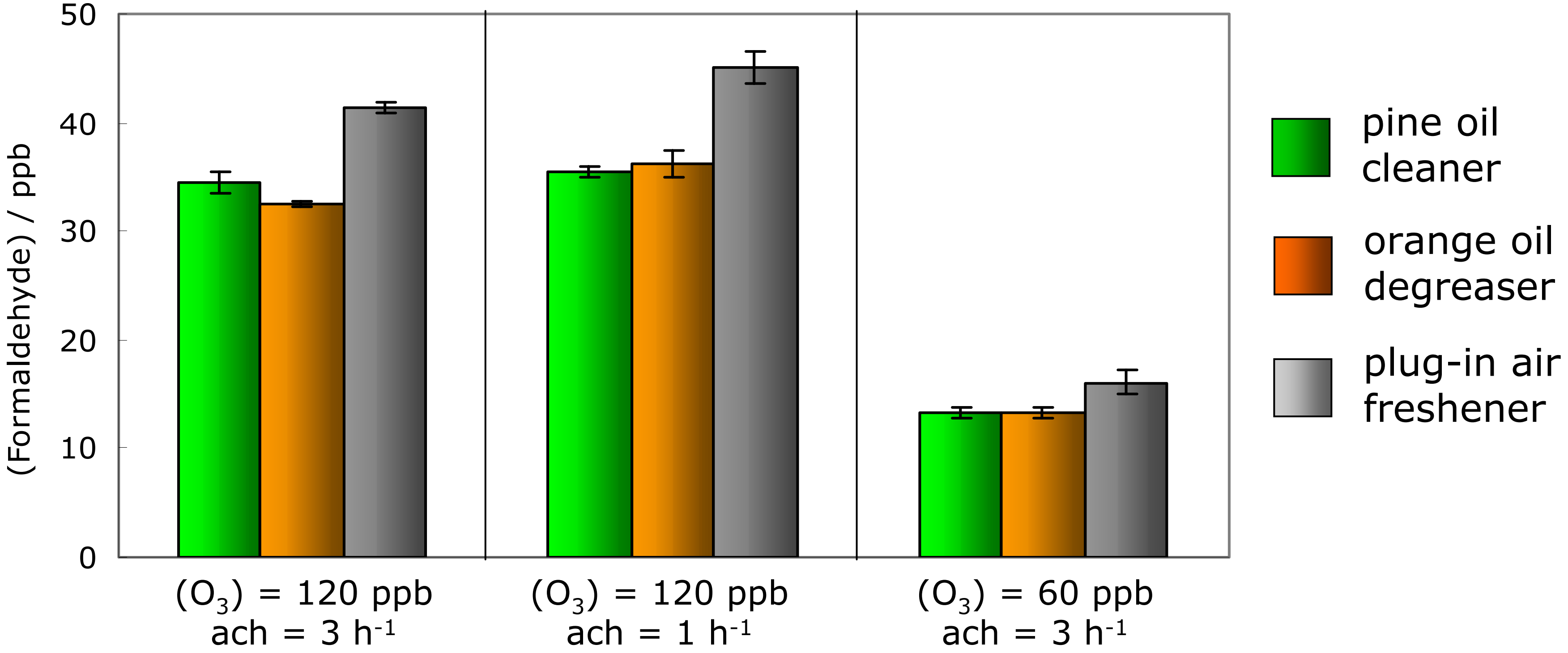


Destaillats et al., Environ. Sci. Technol., 2006

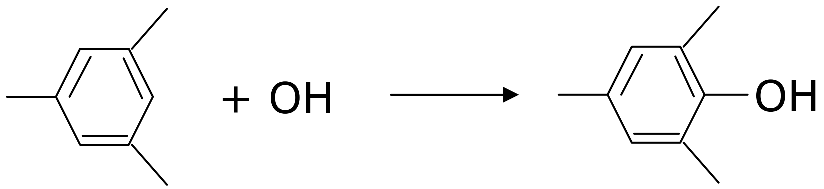
Formaldehyde formation



Yield = 0.10 – 0.19



OH radical concentrations



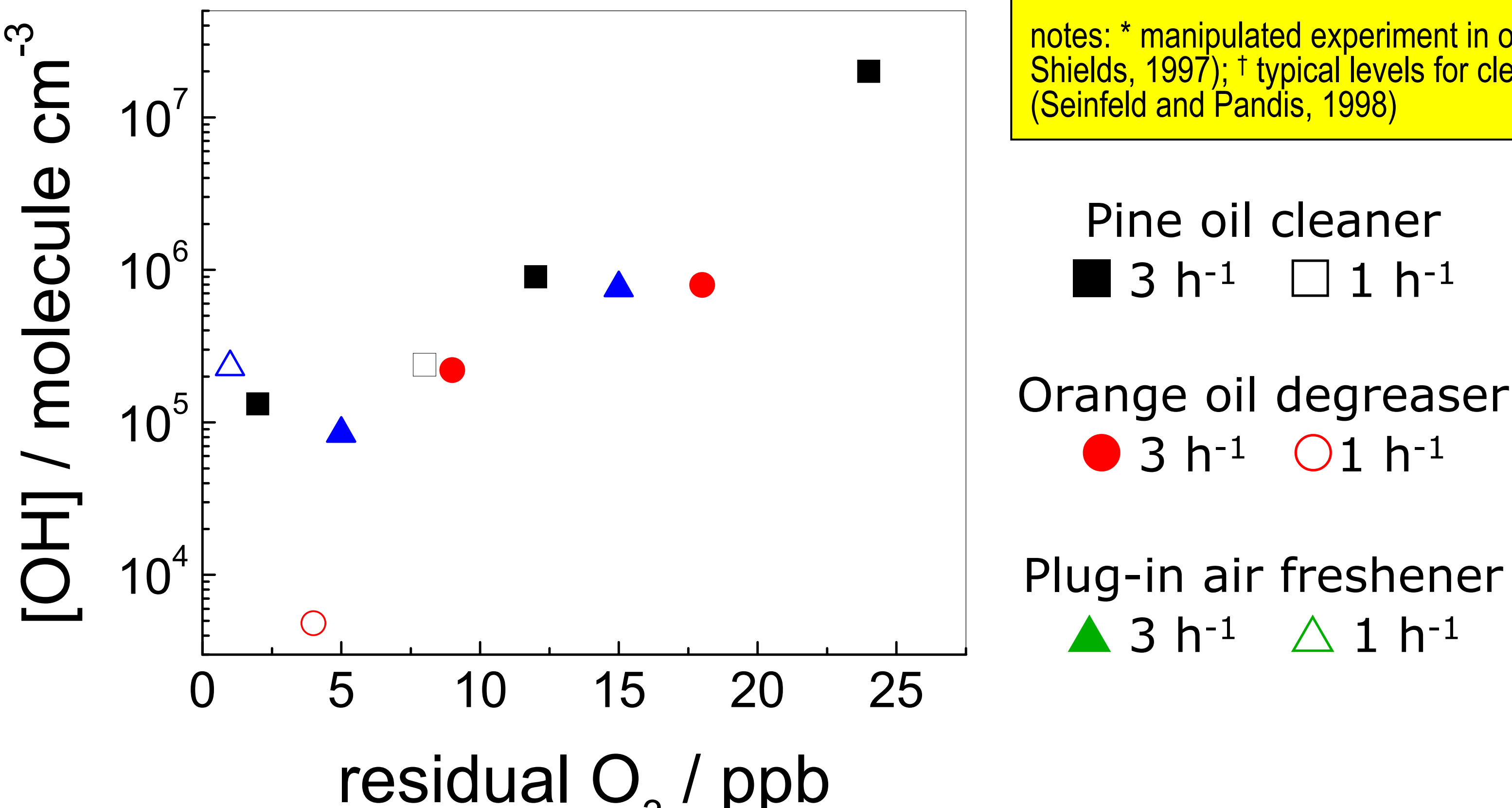
published OH levels (10^5 molec cm^{-3}):

7 indoor *

10-50 outdoor, winter daytime †

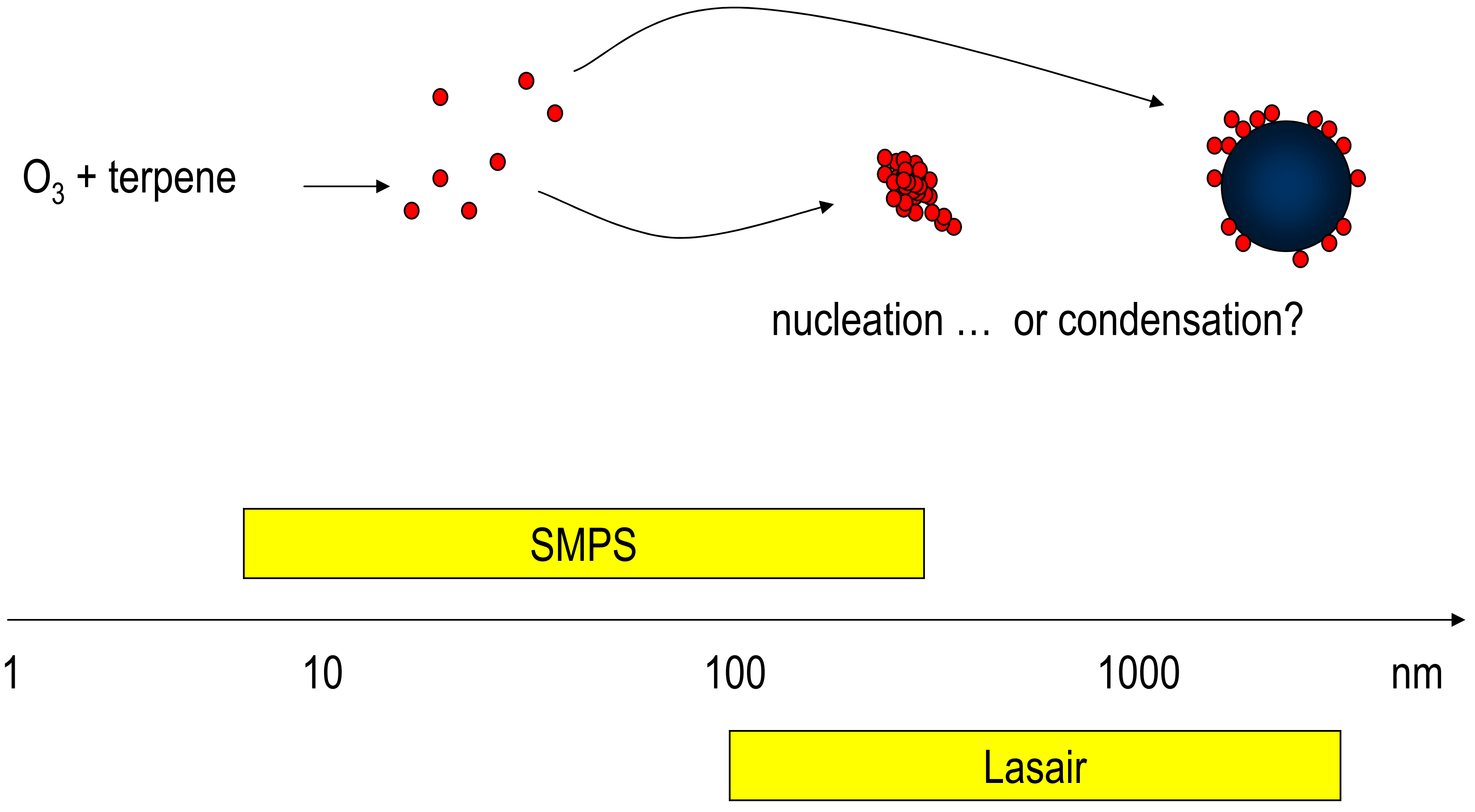
50-100 outdoor, summer daytime †

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

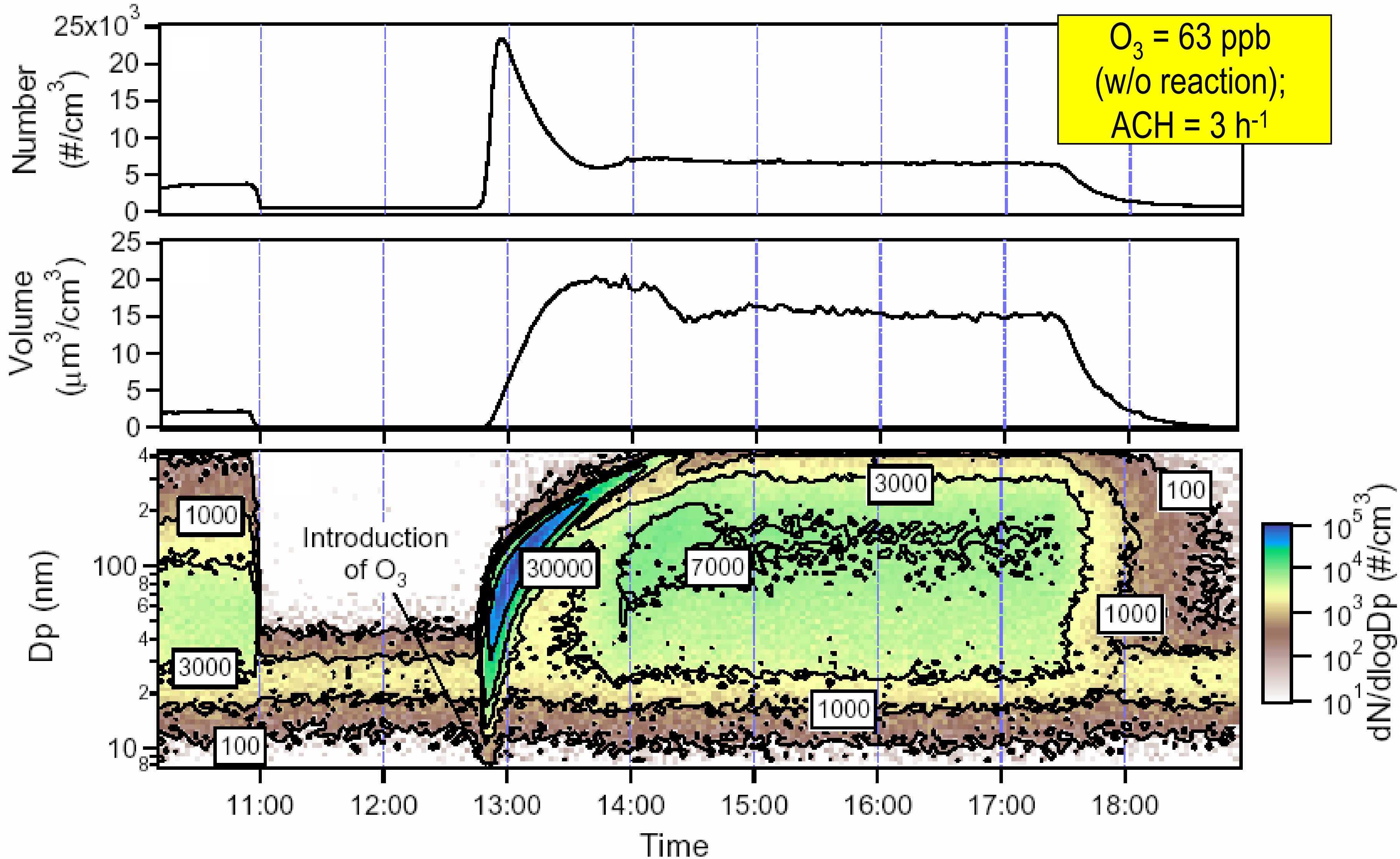


Destaillats et al., Environ. Sci. Technol., 2006

Secondary organic aerosol (SOA) formation



Ultrafine particles formed in all experiments



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

Bench-scale chemistry results

- Individual terpenes are consumed in proportion to product of O_3 reaction rate, $[O_3]$ and [terpene]
- OH formation and consumption dominated by unsaturated species
- Evidence of new particle formation upon initial mixing of O_3 and VOCs from household products
- Aerosol size distribution changes over time affected by air change rate, O_3 level, RH, existing particles and product composition

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

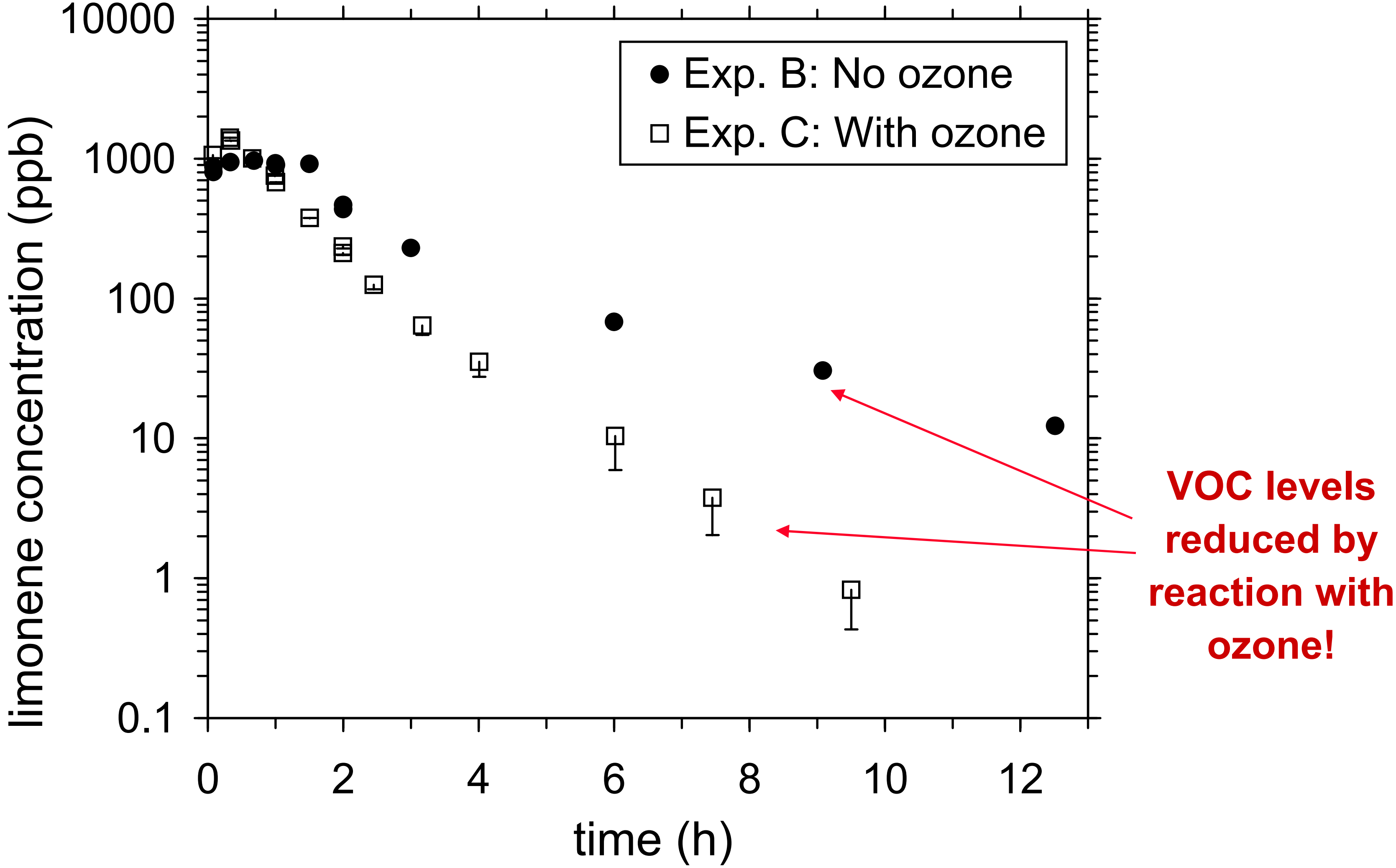
Room-scale chemistry experiments

- Quantify secondary pollutant formation under realistic ozone concentrations and product use
  - Very volatile carbonyls (focus on formaldehyde)
  - Fine particles and $PM_{2.5}$ (really $PM_{1.1}$)
  - Duration and magnitude of pollutant formation
- Estimate OH concentrations as metric of chemistry
- Provide input for scenario analysis

Procedure:

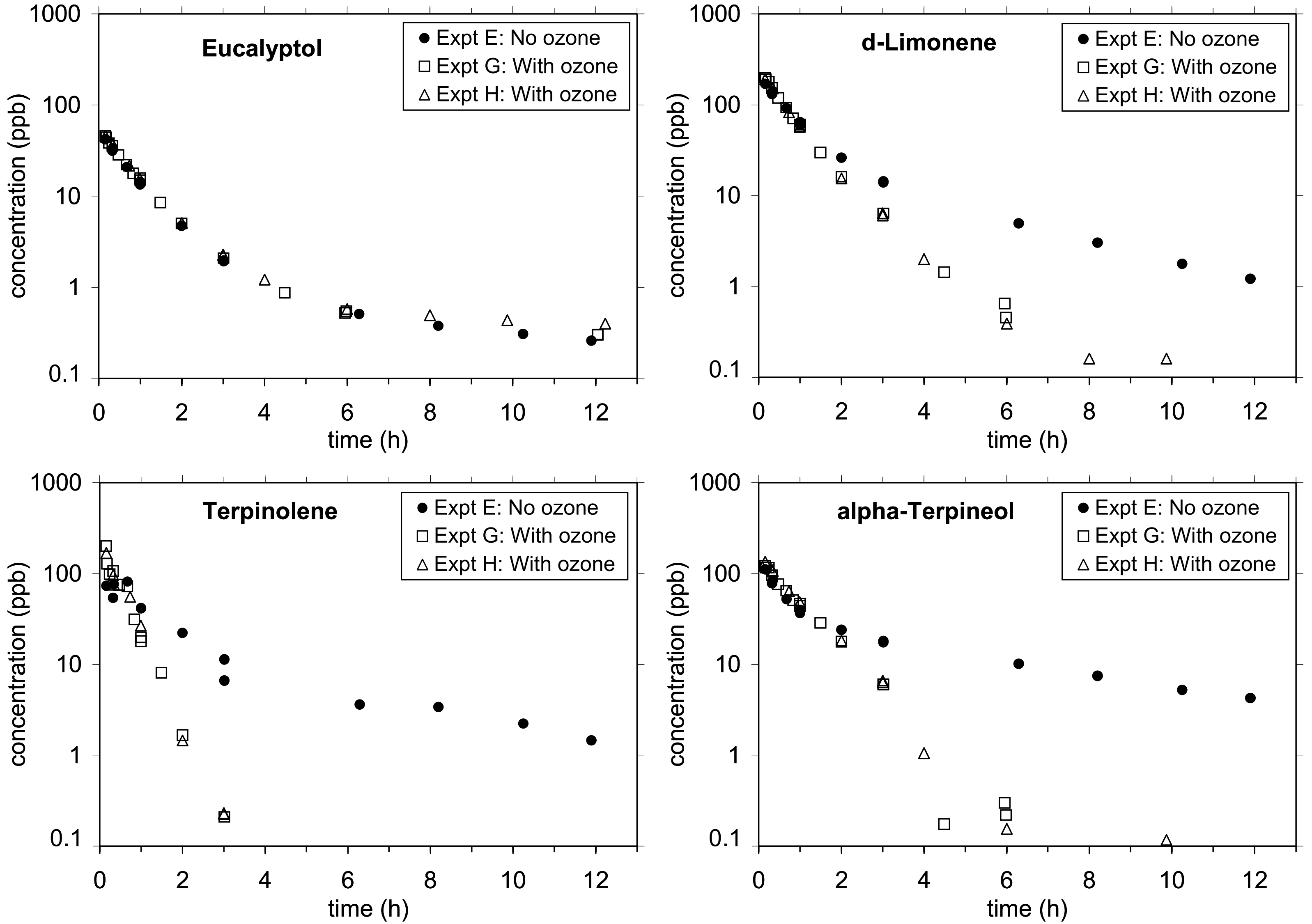
- Scripted cleaning activities with/out 120 ppb ozone in supply air

Orange oil degreaser in full-scale room



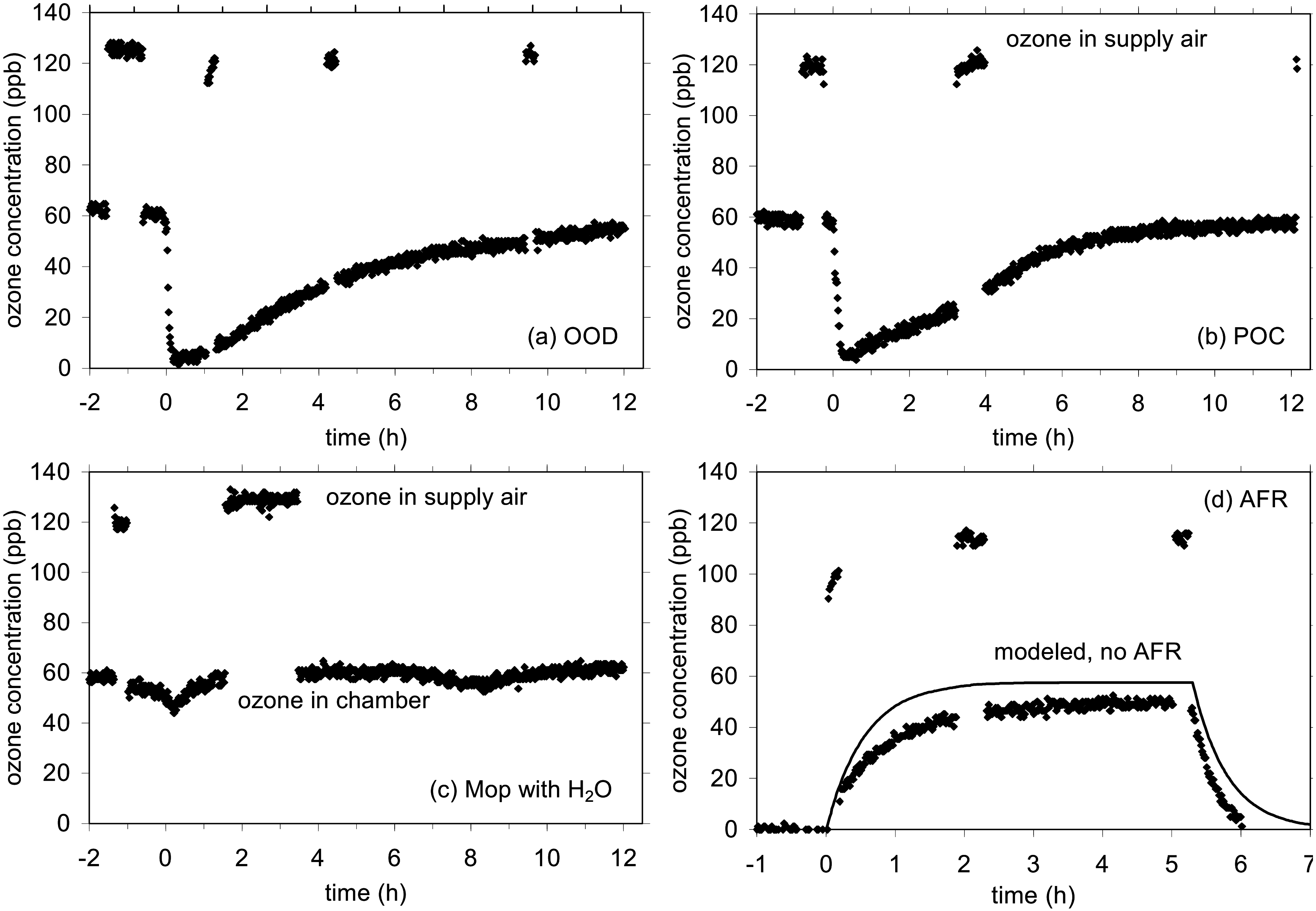
Singer et al., Atmos. Environ., 2006

Pine oil cleaner in room



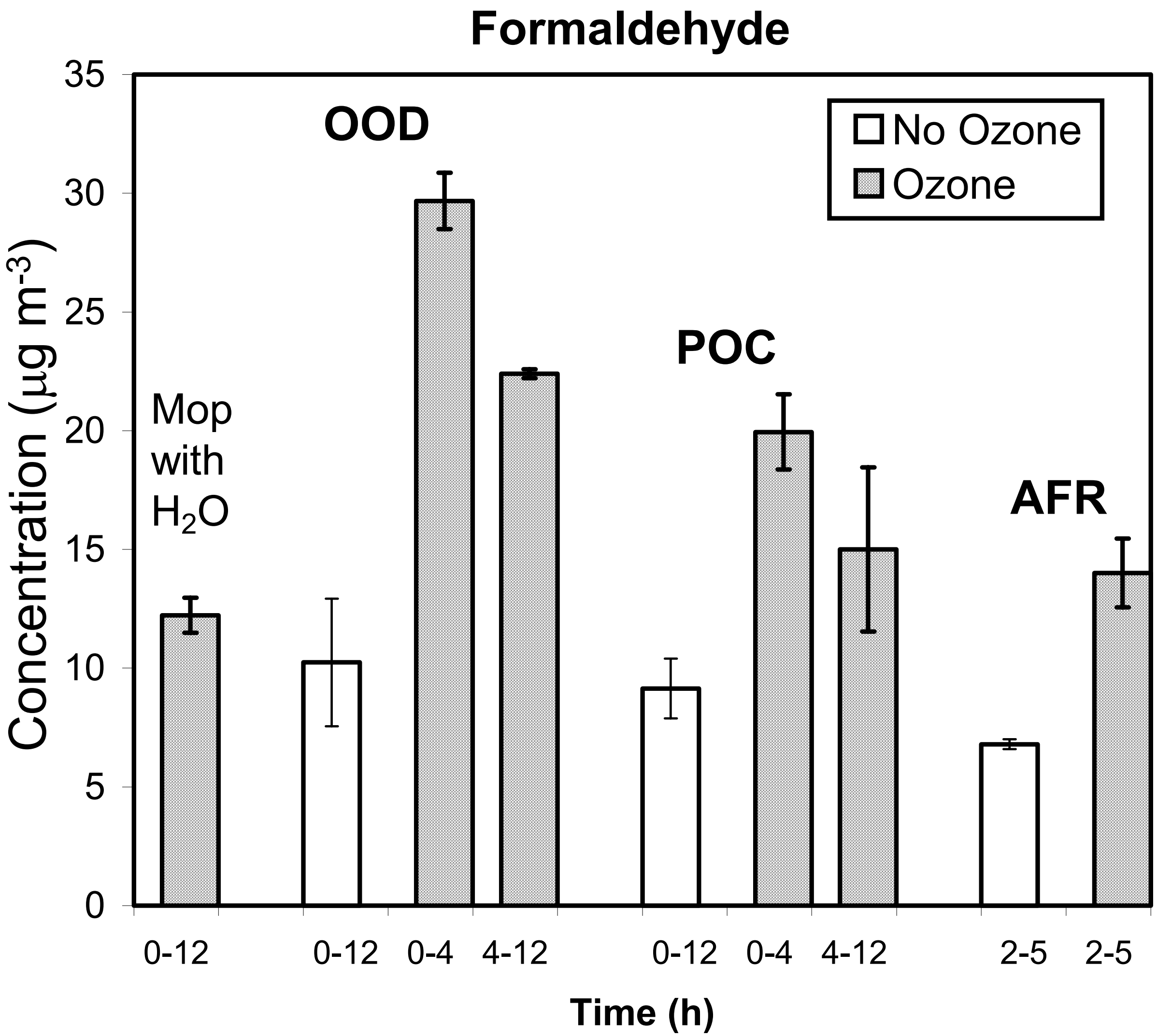
Singer et al., Atmos. Environ., 2006

Ozone in room



Singer et al., Atmos. Environ., 2006

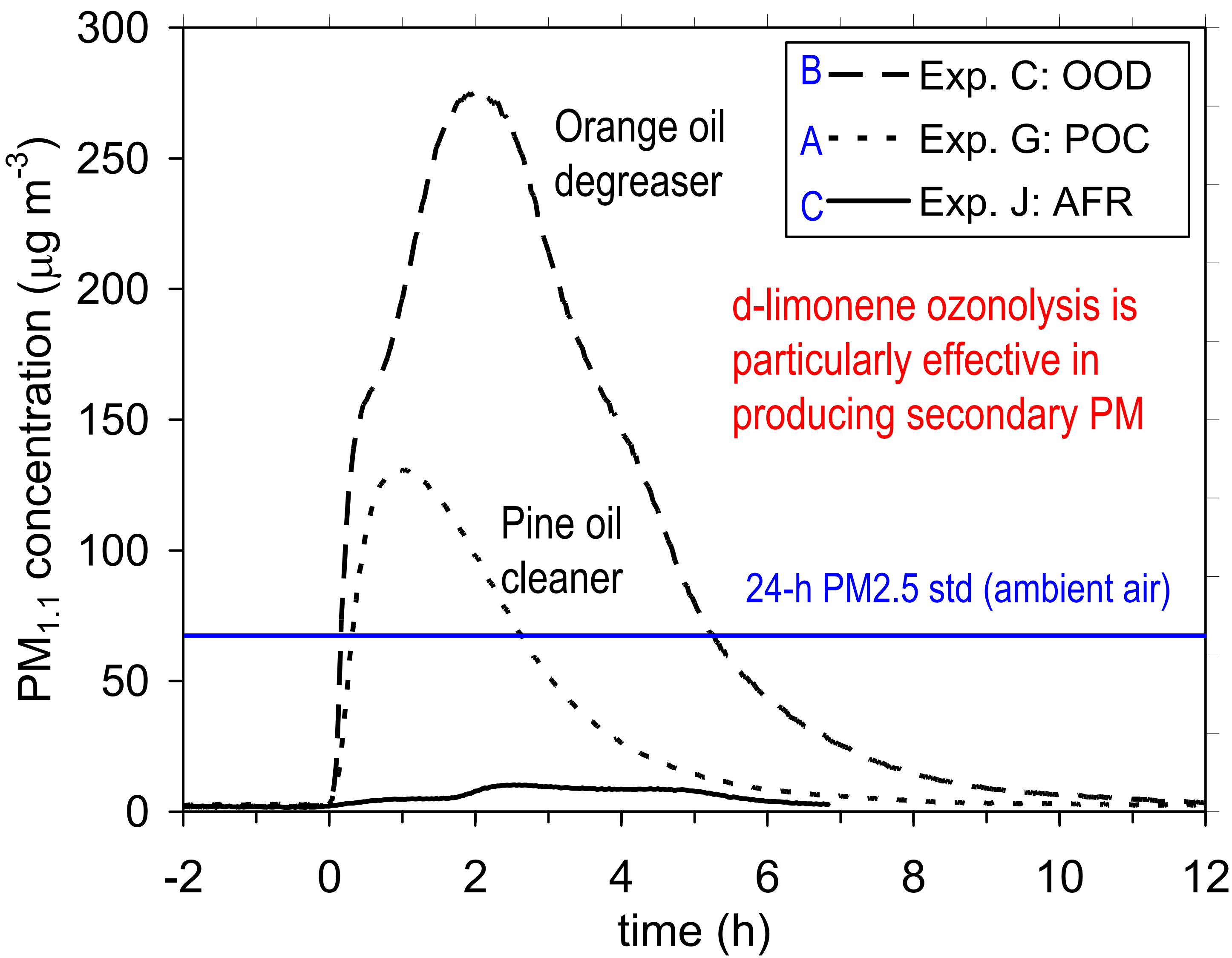
Formaldehyde in room



Product use in presence of O_3 produces formaldehyde!

Singer et al., Atmos. Environ., 2006

Particle concentrations in room



Singer et al., Atmos. Environ., 2006

Room-scale chemistry summary

- Formaldehyde and particle concentrations elevated for several hours after cleaning event.
- Secondary pollutant concentrations comparable to reference exposure levels.
- OH radical concentrations elevated for 10-12 h!
- Gas-phase reactions don’t account for all air freshener reactivity; heterogeneous reactions involving sorbed compounds account for about half of ozone reactions with terpenoids from air freshener

Exposure scenario analysis

- Examine moderate and high use plus some extreme scenarios
- Scale experimental results based on assumed product use, application areas, air change rates, etc.
  - assume ozone present at moderate level
  - assume use of products tested
- Compare results to available points of reference
  - 2-butoxyethanol: California 1-h REL; federal RfC
  - formaldehyde: California chronic NSRL
  - SOA: $PM_{2.5}$ standards: 24-h national; annual CA

Scenario analysis

Scenario	Result
Routine cleaning by occupant	Exposure well below reference levels
Professional domestic cleaner	Formaldehyde exceeds NSRL, SOA exceeds annual $PM_{2.5}$ standard
Clean soap scum in small bathroom	Exceed acute REL for 2-butoxyethanol
All interior windows with low ventilation	Approach/exceed REL for 2-butoxyethanol
Air freshener + ozone in bedroom	Exceed formaldehyde NSRL
Cleaning with high outdoor ozone	Daily average is 25% of $PM_{2.5}$ limit
Cleaning with high ozone, NO_2	Not able to fully analyze

Recommendations

- Use only as much product as needed
- Use dilute solutions to the extent possible
- Open windows (promote ventilation) and avoid closed spaces to reduce exposures to primary emissions
- Avoid cleaning during high ozone periods to reduce exposure to secondary pollutants
- Rinse thoroughly and collect excess water
- Promptly remove cleaning materials from living area
- Take precautions commensurate with frequency of use