Indoor Air Chemistry: Cleaning Agents, Ozone, and Toxic Air Contaminants

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Credits

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• Presentation graphics: Nazaroff, Destaillats, Coleman, Lunden
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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 \( \Rightarrow \)
  – OH radical
  – aldehydes and other oxidized organics
  – particles (secondary organic aerosol)
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 $O_3$

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.*

4. Room-Scale Chemistry Experiments
*Secondary pollutants from product use with ozone.*
BC Singer et al., *Atmospheric Environment* 40, 6696-6710, 2006

5. Exposure Analysis
Chapter 5, Final Report

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

<table>
<thead>
<tr>
<th>Category</th>
<th>On shelves</th>
<th>Number reviewed</th>
<th>Ozone-reactive(^1)</th>
<th>Glycol ethers(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degreaser</td>
<td>28</td>
<td>6</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>General Cleaner</td>
<td>52</td>
<td>13</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Glass Cleaner</td>
<td>20</td>
<td>4</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Antibacterial, Deodorizer</td>
<td>39</td>
<td>6</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Floor Cleaner</td>
<td>48</td>
<td>7</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Furniture Polish</td>
<td>30</td>
<td>5</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Air Freshener</td>
<td>71</td>
<td>9</td>
<td>8</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^{1}\) 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 N₂
- 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

<table>
<thead>
<tr>
<th>Product</th>
<th>Form</th>
<th>Glycol ethers (%)</th>
<th>Ozone-reactive (%)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrus degreaser</td>
<td>Liquid</td>
<td>-</td>
<td>9.6</td>
</tr>
<tr>
<td>Orange oil degreaser</td>
<td>Foam</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>HD degreaser/disinfectant</td>
<td>Trigger</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>Citrus cleaner/degreaser</td>
<td>Trigger</td>
<td>1.6</td>
<td>4.0</td>
</tr>
<tr>
<td>Pine oil cleaner (n=3)</td>
<td>Liquid</td>
<td>-</td>
<td>0.4 - 7.7</td>
</tr>
<tr>
<td>“Green” cleaner</td>
<td>Trigger</td>
<td>4.1</td>
<td>-</td>
</tr>
<tr>
<td>All-purpose cleaner</td>
<td>Trigger</td>
<td>2.6</td>
<td>-</td>
</tr>
<tr>
<td>Glass cleaner</td>
<td>Trigger</td>
<td>0.8</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ Includes terpenes and other alkenes
### Emissions screening results (2)

<table>
<thead>
<tr>
<th>Product</th>
<th>Form</th>
<th>Glycol ethers (%)</th>
<th>Ozone-reactive (%)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpet stain remover</td>
<td>Aerosol</td>
<td>9.6</td>
<td>-</td>
</tr>
<tr>
<td>Wood cleaner/polish</td>
<td>Aerosol</td>
<td>-</td>
<td>5.6</td>
</tr>
<tr>
<td>Plug-in air fresher</td>
<td>Gel</td>
<td>-</td>
<td>9.6</td>
</tr>
<tr>
<td>Scented oil (n=2)</td>
<td>Liquid</td>
<td>-</td>
<td>13–14</td>
</tr>
</tbody>
</table>

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-m² laminate tabletop
  - Spray + wipe, or
  - Spray, Scrub, Rinse, Wipe
  - Remove or retain towels

- **Dilute use**
  - 4.2 m² vinyl tile floor
  - 4-L solutions mixed in room
  - Detailed mopping procedure

- **Experimental room**
  - 50-m³; residential construction
  - Ventilated at 0.53 h⁻¹

Was that 8 or 9 mop strokes?
## Emissions during product use

<table>
<thead>
<tr>
<th>Product</th>
<th>Constituents</th>
<th>Package</th>
<th>Full strength spray, wipe</th>
<th>Full strength scrub, rinse</th>
<th>Dilute (mop)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass cleaner (GLC-1)</td>
<td>2-butoxyethanol, 2-hexyloxyethanol</td>
<td>trigger spray</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General purpose cleaner (GPC-1)</td>
<td>pine oil: terpenes, terpene alcohols</td>
<td>capped bottle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General purpose cleaner (GPC-2)</td>
<td>2-butoxyethanol</td>
<td>trigger spray</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General purpose cleaner (GPC-3)</td>
<td>2-butoxyethanol</td>
<td>trigger spray</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General purpose cleaner (GPC-4)</td>
<td>2-butoxyethanol, limonene</td>
<td>trigger spray</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air freshener (AFR1)</td>
<td>unsaturated terpenoids</td>
<td>heating dispenser</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Plug in for several days

Singer et al., Indoor Air, 2006
Objective: Identify high but reasonable use rate

Volunteers asked to simulate cleaning of 1 m² tabletop

25 LBNL employees

Bottle weighed before, after

Note: 1 g ft⁻² = 10.8 g m⁻²
Concentration patterns: 2-butoxyethanol

Peak levels are $\sim \text{mg/m}^3$.

Concentrations at 4-24 h are higher with towels.

Peak occurs 30-60 min after mopping.

Singer et al., Indoor Air, 2006
Concentration patterns: terpenes

**Towel removal:**
VOC removal; concentrations and exposures reduced

**Towel retention:**
derpenes 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emitted fraction (g emitted/g dispensed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>terpene hydrocarbons</td>
<td></td>
</tr>
<tr>
<td>α-Phellandrene</td>
<td>58%, 34%, 9%</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>45%, 24%, 8%</td>
</tr>
<tr>
<td>γ-Terpinene</td>
<td>65%, 37%, 10%</td>
</tr>
<tr>
<td>d-Limonene</td>
<td>69%, 46%, 11%</td>
</tr>
<tr>
<td>α-Terpinene</td>
<td>36%, 20%, 7%</td>
</tr>
<tr>
<td>Camphene</td>
<td>69%, 50%, 12%</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>52%, 39%, 9%</td>
</tr>
<tr>
<td>terpene alcohols</td>
<td></td>
</tr>
<tr>
<td>4-Terpineol</td>
<td>30%, 9%, 5%</td>
</tr>
<tr>
<td>β-Terpineol</td>
<td>19%, 7%, 4%</td>
</tr>
<tr>
<td>1-Terpineol</td>
<td>22%, 6%, 5%</td>
</tr>
<tr>
<td>γ-Terpineol</td>
<td>7%, 2%, 2%</td>
</tr>
<tr>
<td>α-Terpineol</td>
<td>11%, 4%, 3%</td>
</tr>
</tbody>
</table>

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/m³
• 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**

**Product source**
- (Tedlar bag or flow cell)

**PM sampling:**
- SMPS
- Lasair

**Gas phase sampling:**
- Tenax sorbent tubes (TD-GCMS)
- DNPH coated cartridges (HPLC)
- NaOH coated cartridges (IC)

**PM sampling:**
- SMPS
- Lasair

**T, RH, O₃ sensors**

**Teflon reaction chamber**
- 200 L

**OH determination:**
- TMB/PCE method
- (Weschler & Shields, 1997)

**Destaillets et al., Environ. Sci. Technol., 2006**
Primary emissions:

- GPC-1 pine oil cleaner
- GPD-1 orange oil degreaser
- AFR-1 scented oil air freshener
Ozone-reactive product constituents

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

- \(\alpha\)-terpinene
  - \(k_{O3} = 5 \times 10^{-4} \text{ ppb}^{-1} s^{-1}\)

- d-limonene
  - \(k_{O3} = 5 \times 10^{-6} \text{ ppb}^{-1} s^{-1}\)

- terpinolene
  - \(k_{O3} = 5 \times 10^{-5} \text{ ppb}^{-1} s^{-1}\)

**Terpenoids**

- \(\alpha\)-terpineol
  - \(k_{O3} = 7.5 \times 10^{-6} \text{ ppb}^{-1} s^{-1}\)

- linalool
  - \(k_{O3} = 1 \times 10^{-5} \text{ ppb}^{-1} s^{-1}\)

- dihydromyrcenol
  - \(k_{O3} \leq 5 \times 10^{-8} \text{ ppb}^{-1} s^{-1}\)
VOCs measured in chamber

\[ \text{Concentration (ppb)} \]

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

\[ \text{VOC levels reduced by reaction with ozone!} \]

- **alpha-terpinene**
- **limonene**
- **p-cymene**
- **eucalyptol**
- **terpinolene**
- **alpha-terpineol**
Consumption of reactive VOCs

(O₃) = 250 ppb
ach = 3 h⁻¹

(O₃) = 120 ppb
ach = 3 h⁻¹

(O₃) = 120 ppb
ach = 1 h⁻¹

(O₃) = 60 ppb
ach = 3 h⁻¹

(O₃) = 30 ppb
ach = 3 h⁻¹

Pine oil cleaner A

Orange oil degreaser B

Plug-in air freshener C

% consumed

O₃ levels apply in absence of chemistry;
Residual levels are ≤ 10% of these;
ACH = air changes per hour.

High yields of stable oxidation products

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

Formaldehyde formation

Yield = 0.10 – 0.19

\[
\text{O}_3 + \text{limonene} \rightarrow \text{HCH}
\]

<table>
<thead>
<tr>
<th>(O₃)</th>
<th>(ach)</th>
<th>(Formaldehyde) / ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 ppb</td>
<td>3 h⁻¹</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>120 ppb</td>
<td>1 h⁻¹</td>
<td>40 ± 6</td>
</tr>
<tr>
<td>60 ppb</td>
<td>3 h⁻¹</td>
<td>10 ± 2</td>
</tr>
</tbody>
</table>

- pine oil cleaner
- orange oil degreaser
- plug-in air freshener
OH radical concentrations

\[
\text{[OH]} / \text{molecule cm}^3
\]

\[
\text{residual O}_3 / \text{ppb}
\]

Published OH levels \((10^5 \text{ molec cm}^3)\):
- 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\(^{-1}\)
Secondary organic aerosol (SOA) formation

$O_3 + \text{terpene}$

nucleation … or condensation?

SMPS

Lasair
Ultrafine particles formed in all experiments

$O_3 = 63$ ppb (w/o reaction); $ACH = 3$ h$^{-1}$

Bench-scale chemistry results

- Individual terpenes are consumed in proportion to product of $O_3$ reaction rate, $[O_3]$ and $[\text{terpene}]$
- 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

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

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!

Singer et al., Atmos. Environ., 2006
d-limonene ozonolysis is particularly effective in producing secondary PM

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

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Routine cleaning by occupant</td>
<td>Exposure well below reference levels</td>
</tr>
<tr>
<td>Professional domestic cleaner</td>
<td>Formaldehyde exceeds NSRL, SOA exceeds annual PM$_{2.5}$ standard</td>
</tr>
<tr>
<td>Clean soap scum in small bathroom</td>
<td>Exceed acute REL for 2-butoxyethanol</td>
</tr>
<tr>
<td>All interior windows with low ventilation</td>
<td>Approach/exceed REL for 2-butoxyethanol</td>
</tr>
<tr>
<td>Air freshener + ozone in bedroom</td>
<td>Exceed formaldehyde NSRL</td>
</tr>
<tr>
<td>Cleaning with high outdoor ozone</td>
<td>Daily average is 25% of PM$_{2.5}$ limit</td>
</tr>
<tr>
<td>Cleaning with high ozone, NO$_2$</td>
<td>Not able to fully analyze</td>
</tr>
</tbody>
</table>
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