

Indoor Air Chemistry and Health Implications

September 28, 2006



Air Resources Board
California Environmental Protection Agency

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Thank you Ms. Witherspoon. Good morning Dr. Sawyer and members of the Board. Thank you for this opportunity to share results from a recent ARB-funded study on indoor air chemistry and the possible health implications of this research.

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

- Objectives:
 - 1) Identify and measure emissions of TACs from cleaning products & air fresheners
 - 2) Identify and measure reaction products when cleaning agents with reactive compounds are exposed to ozone
- UC Berkeley, William W. Nazaroff, PhD.

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This study had two objectives: To identify and measure emissions of toxic air contaminants from cleaning products and air fresheners, and to identify and measure reaction products when cleaning agents with reactive compounds are exposed to ozone. The study was conducted at UC Berkeley and Lawrence Berkeley National Laboratory, with Dr. William Nazaroff as the principal investigator.

Published Work Resulting from This Study

- WW Nazaroff and CJ Weschler, Cleaning products and air fresheners: exposure to primary and secondary air pollutants. *Atmos. Environ.* 2004, 38, 2841-2865.
- ■ BC Singer *et al.*, Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air* 2006, 16, 179-191
- ■ H Destailats *et al.*, Indoor secondary pollutants from household product emissions in the presence of ozone: a bench-scale chamber study. *Environ. Sci. Technol.* 2006, 40, 4421-4428.
- ■ BC Singer *et al.*, Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. *Atmos. Environ.* in press.

Results of this project have been published in four journal articles and a final research report to ARB. The last article listed is in press. My presentation today will focus on the results from the last three papers listed.

Methods

- Task 1 – screened 21 products for chemical components
- Task 2 – measured emissions of 6 products in room-sized chamber
- Task 3 – studied 3 products with ozone in small and large chambers for secondary emissions
 - Large chamber tests: 120 ppb ozone introduced; 60 ppb available for reaction

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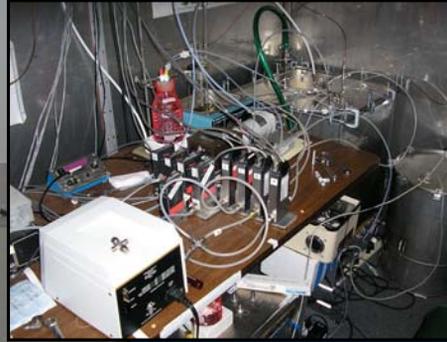
The investigators conducted the study in 3 sequential tasks. First, they conducted a shelf survey of hundreds of products, then selected 21 widely available products which they screened for compounds listed as toxic air contaminants and compounds that are reactive with ozone. They included at least one disinfectant, general-purpose degreaser, general-purpose cleaner, wood cleaner, furniture maintenance product, spot remover, multi-purpose solvent, and air freshener.

For the second task, six of the 21 products were selected for measurement of their emissions in a room-sized chamber during realistic cleaning procedures. Both full strength and dilute forms of the product were tested.

Finally, three products were selected for more detailed study in the presence and absence of ozone, to examine the resultant indoor chemistry and measure secondary emissions. A general purpose cleaner, a degreaser, and an air freshener were tested at common usage rates, and the chamber conditions simulated a residential room. In the large chamber, ozone was introduced into the room using a stream of 120 ppb, equal to the 1-hour federal standard level. About half of this ozone reacted with the surfaces inside the chamber leaving about 60 ppb available for reaction during the experiment.

How many scientists does it take to mop a floor?

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For the second and third tasks of the study, the scientists developed precise protocols to mop a floor, clean a cooktop, and use plug-in air fresheners. To answer the question posed by this slide, it took one scientist to do the cleaning and 4 or 5 to gather the air quality measurements.

Results – Primary Emissions

- 3 TACs were released during cleaning
 - 2-butoxyethanol
 - 2-hexyloxyethanol
 - *m*- and *p*-xylene
- 2-Butoxyethanol levels were below OEHHA acute reference exposure level of 14 mg/m³
- Direct emissions of TACs do not appear to pose a risk
- 12 products contained ozone-reactive compounds (terpenes) up to 26%

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The primary emission results were good news. Only 3 Toxic Air Contaminants were identified in the products tested. Six of the products tested contained glycol ethers, with levels ranging from 0.8 to 9.6% by weight.

2-Butoxyethanol was the most prevalent, and its airborne concentrations when used in the cleaning protocols were below the OEHHA acute reference level of 14 mg/m³.

Direct emissions of TACs from cleaning products and air fresheners did not appear to pose a risk to building occupants during cleaning activities. However, modeled scenarios indicate that a worst case situation, such as cleaning all interior windows with low ventilation may lead to exposure of 2-butoxyethanol above health guideline values.

Some products are now likely lower in VOC content, because while the study was underway, ARB regulations decreased the VOC limit by weight for non-aerosol general purpose cleaners, general purpose degreasers, and furniture maintenance products. Hence, some currently available products will have lower VOC content than the products studied.

Twelve of the products contained ozone-reactive compounds at levels ranging from 0.23% to 26% by weight. These were primarily terpenes.

What are Terpenes?

- A class of VOCs from plant oils
 - Pine – α -pinene
 - Citrus – d -limonene
- Pleasant odors
- Favorable solvent properties
- Generally recognized as safe (GRAS)
- Oxidants (e.g. ozone) react with terpenes to produce more irritating and toxic compounds

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What are terpenes? Terpenes are a complex class of compounds found in plant oils. Common terpenes in cleaning products and air fresheners are alpha-pinene and d-limonene, which are common to pine and citrus oil, respectively. These compounds are used in cleaning products because of their pleasant odors and favorable solvent properties. Specifically, they can remove grease and oil. Terpenes are reactive VOCs and thus, are subject to the VOC limits for consumer products that I just mentioned.

The Food and Drug Administration has classified them as generally recognized as safe, meaning they are not associated with adverse health effects, although some may cause irritation at very high levels.

In ambient air, oxidants such as ozone react with terpenes to produce more irritating and toxic compounds such as formaldehyde, acetaldehyde, acetone, formic acid, and acetic acid. Some of these products are toxic air contaminants with documented irritant and carcinogenic properties.

Results – Secondary Emissions

- **Formaldehyde**
 - Increased 9 – 16 ppb for 4 hours post cleaning
 - Exceeded OEHHA's chronic reference exposure level of 2.4 ppb
 - Exceeded Prop 65 no significant risk level for cancer of 1.6 ppb
- **Particles**
 - Emitted as ultrafines
 - Increased the estimated mean PM_{2.5} mass by 30 – 90 µg/m³ for 12-hour period
 - National 24-hour standard of 35 µg/m³ (new)
- **Modeled exposure scenarios showed user exposure may exceed health benchmarks**

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In the chamber experiments with ozone, reactive chemistry did indeed occur. Formaldehyde levels were elevated by 9 to 16 ppb for the first 4 hours after cleaning. These levels, from a single cleaning event, exceeded OEHHA's chronic REL of 2.4 ppb, and the Proposition 65 no significant risk level for cancer of 1.6 ppb.

Particles were emitted as ultrafines, then aerosol-aging processes led to particle growth from the ultrafine to the accumulation mode. Investigators estimated particle mass from particle size and number for comparison to Ambient Air Quality Standards. Results indicate that enough particles were generated to increase the average PM_{2.5} mass by 30 to 90 µg/m³ over a 12-hour averaging period. This concentration of ultrafine particles from a single cleaning event is greater than the **new** national 24-hour standard for PM_{2.5} of **35** µg/m³.

In an attempt to understand the implication of these results, the investigator modeled some high-end use scenarios to estimate exposures for a person using these products. Calculations indicate formaldehyde intake could be exceed the Prop 65 no significant risk level for a professional house cleaner, and for a child who has an air freshener and an ozone generator in his room.

Implications

- Primary emissions of TACs generally below health benchmarks
- Secondary emissions may pose a previously unrecognized exposure and health risk
- Continue to recommend further research on secondary indoor emissions
- Support further reductions of outdoor ozone levels and indoor ozone emissions

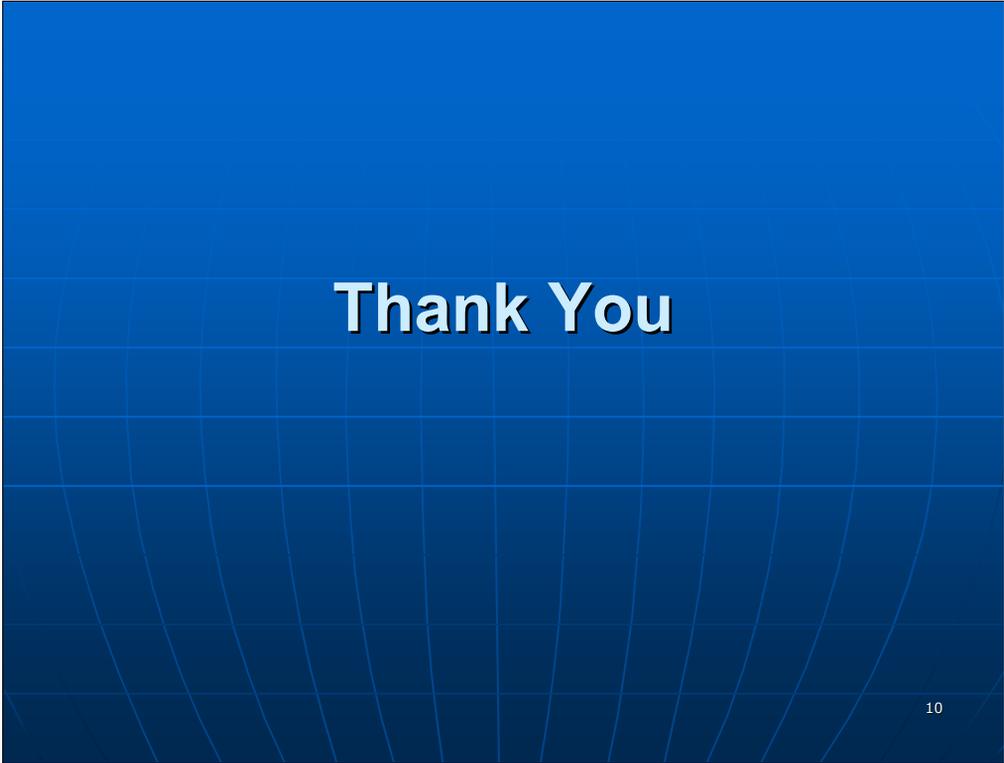
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The results of this study lead us to several conclusions and related implications. The good news, as stated earlier, is that very few TACs are directly emitted from cleaning products and exposures are generally below guideline values.

However, results of this study do have potential health implications. The secondary emissions – that is, the formaldehyde and particles that formed as a result of the reaction of terpenes with ozone – may pose a previously unrecognized exposure and health risk. Personal exposure can be elevated due to the close proximity of the person cleaning due to the generation of secondary pollutants.

As indicated in the AB1173 report to the legislature on *Indoor Air Pollution in California*, continued research is needed on secondary indoor emissions to better understand exposures; it is not adequate to examine and assess only the directly emitted pollutants.

Lastly, these results support further reduction of outdoor ozone levels and prevention of indoor ozone emissions.



Thank You

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This concludes my presentation, and I would be happy to answer any questions.