



United States
CONSUMER PRODUCT SAFETY COMMISSION
4330 East-West Highway
Bethesda, Maryland, 20814

MEMORANDUM

DATE: December 5, 2006

TO : HS

Through: Todd A. Stevenson, Secretary, OS

FROM : Martha A. Kosh, OS

SUBJECT: CPSC Health Sciences Staff Report on the Work Product Resulting from CPSC Contract No. CPSC-S-04-1369, Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners - Draft - September 26, 2006

ATTACHED ARE COMMENTS ON THE 07-1

<u>COMMENT</u>	<u>DATE</u>	<u>SIGNED BY</u>	<u>AFFILIATION</u>
RR-07-1-1	11/30/06	Jim Rosenthal	<u>Jimrosenthal5757@aol.com</u>
RR-07-1-1a	11/30/06	same as above	
RR-07-1-1b	12/04/06	" " "	same as above
RR-07-1-2	12/04/06	Richard Bode Chief	California Resources Board Indoor Exposure Assessment Research Division 1001 I St P.O. Box 2815 Sacramento, CA 95812
RR-07-1-3	12/04/06	Ramona Saar Director Standards and Certification Programs	Association of Home Appliance Manufacturers 1111 19 th St, NW Suite 402 Washington, DC 20036
RR-07-1-4	12/04/06	Ricahrd Corsi Ph.D	The University of Texas at Austin, Center for Energy And Environmental Resources Bldg. 133, J.J. Pickle Research Campus (R7100) 10100 Burnet Rd. Austin, TX 78758

*Ozone
Cleaner
report***Stevenson, Todd A.****From:** Jimrosenthal5757@aol.com**Sent:** Thursday, November 30, 2006 11:29 AM**To:** Stevenson, Todd A.**Subject:** Comments on Exposure Limits for Ozone-Generating Air Cleaners Report

I have read the report prepared by Dr. Richard Shaughnessy and the comments of the CPSC staff. I have some real concerns about the conclusions - especially with respect to the recommendations for "sensitive populations."

I am the President of the Texas Chapter of the Asthma and Allergy Foundation of America. As such, my main concern is with the use or mis-use of ozone generating "air cleaners" or air purifiers by people with asthma and other respiratory diseases.

As I read the report and comments, it is the conclusion that no separate recommendation need be made for sensitive subpopulations. The reasoning is that no studies have been done to show the damaging effects or dangers of ozone generating devices at less than 50 ppb of ozone for asthmatics and others with respiratory diseases. On the other hand, we do know that ozone is a trigger for asthma. Ozone causes inflammation in asthmatics. Ozone has been shown to reduce lung capacity and lung function. And in the words of Dr. Jonathan Samet of Johns Hopkins in a recent Consumer Reports (May 2005) article: "We cannot guarantee safety at any level of ozone, so it makes sense not to contaminate your living space." I would argue that it is not the responsibility of the CPSC to show what is not safe, it is the responsibility of those who manufacture and sell these devices to show that they are safe for those with respiratory diseases. Clearly, they have not done this.

Keep in mind - these devices are sold as air cleaners. Most people would assume they clean the air. They are not aware of the potential dangers. Considering the fact that many of the devices are sold to asthmatics or relatives of asthmatics, it is imperative that consumers be made aware of the potential dangers of devices that generate ozone for sensitive populations.

Given the lack of data showing the safety of ozone generating air cleaners for sensitive populations, in my opinion the CPSC should take a position requiring the labeling of these devices clearly stating the potential dangers. Without this labeling you are perpetuating a situation where products are being purchased for the benefit of someone who has a compromised respiratory system when, in fact, it has the potential to do them harm.

11/30/2006

Ozone Air Cleaners Report

Stevenson, Todd A.

From: Jimrosenthal5757@aol.com
Sent: Saturday, December 02, 2006 11:14 AM
To: Stevenson, Todd A.
Cc: jimrosenthal@allergyclean.com
Subject: Comments on Report on Exposure Limits for Ozone Generating Air Cleaners

My name is Jim Rosenthal and I am the President of the Asthma and Allergy Foundation of America - Texas Chapter. I am also the CEO and Chairman of Allergy Clean Environments, Tex-Air Filters and Allergy, Air and More. I have been involved in the indoor air world for the past 10 years.

I do not sell ozone generating devices in my businesses. However, I certainly could. In fact, I have been approached over 50 times by companies and individuals wanting me to sell ozone generating air cleaners. I do not sell these devices because I believe that they are not safe for individuals with asthma and other respiratory diseases.

Here are some real life examples:

1. About 6 years ago I was visiting with the mother of a 2 1/2 year-old child with asthma. She told me that she had tried several things but her son's asthma kept getting worse. One of the things she tried was to buy an ozone generating "air cleaner" for her son's room. Because she wanted him to get the "best air" she placed it next to her child's crib. She had no idea that the ozone generated by her "air cleaner" could cause problems for her child. After, turning off the "air cleaner", the child's asthma miraculously improved.
2. Three years ago my best friend from college, Bob Simmons, was at home recuperating from chemo that he had received to treat cancer. A well-meaning friend purchased an ozone generating ionizer for his bedroom so that he could be more comfortable during his recovery. His family had set up a hospital-like room for him with tile floors, smooth walls, blinds and an adjustable bed. When I went to visit him, the ozone odor was overpowering. He was complaining that his "lungs hurt" and he had headaches. We turned off the "air cleaner," and his lungs stopped hurting and the headaches went away. Unfortunately, Bob passed away about a year later from the cancer.
3. About 5 years ago we received a call from the actor Noble Willingham who played in "Walker, Texas Ranger." The call came on a Saturday and he was complaining that his "asthma was killing him." We told him he did not need us, he needed a doctor. He said his doctor was not available until Monday. After much discussion, he persuaded us to deliver some products to his room at the Aerobics Center in Dallas. He was not in, but the staff let us into his room. Upon entering the odor of ozone was overpowering. He had purchased and was using three ozone generating ionizers. His theory was that "if one was good, three had to be better." He had no idea of the potential dangers. After he turned off the "air cleaners," his asthma returned to normal.

I am very concerned about the CPSC conclusions regarding exposure limits for ozone generating air cleaners. Here's why:

1. These devices are sold as "air cleaners." The public purchases them with the anticipation that they will perform as "air cleaners" and clean the air. They use them accordingly. Therefore, any comparisons with the ozone produced by photo copiers, hair driers, etc. is irrelevant. People do not run a photo copier 24/7 and stand next to it with the anticipation that they are breathing clean air.
2. There is a substantial body of evidence that shows ozone exposure can be detrimental to those with asthma and other respiratory diseases. It is a known trigger for asthma. It causes inflammation. It can damage lung tissue.
3. No where in the report or the staff summary is there proof that ozone at 50ppb is safe for asthmatics. Yet, it looks to me like that is going to be the conclusion of the CPSC. This will open the door to marketers of ozone generating air cleaning devices to make claims about the safety of their products at the peril of those with

respiratory diseases.

At the very least, sellers of ozone generating air cleaning devices should be required in their marketing literature and on their products to indicate that their product produces ozone and that ozone can be detrimental to those with asthma. As we have seen by the above examples, the public has a right to know of the dangers of using a product.

My vehement opposition to these ozone generating "air cleaners" is driven by the thought of that little boy in his crib with asthma and the loving mother doing everything in her power to "help him" by putting one of these devices in his breathing space and by the thought of my friend, Bob, going through days of unnecessary discomfort during the last days of his life because of using one of these devices in his recovery room.

*Ozone report***Stevenson, Todd A.**

From: Jimrosenthal5757@aol.com
Sent: Monday, December 04, 2006 9:33 AM
To: Rjstulsau@aol.com
Cc: Thomas, Treye A.; richard-shaughnessy@utulsa.edu; dkrauseiaq@email.msn.com; lballiaq@mindspring.com
Subject: Re: Report to the CPSC on ozone generating air cleaners

Richard

Thank you for your quick reply. I have sent this e-mail to the CPSC. (as well as several others) I will definitely keep on this issue because I believe that the conclusions of the current report are potentially harmful for asthmatics. I have discussed this with several physicians who specialize in asthma and they concur. Hopefully, they have written to the CPSC as well.

My most immediate concern is that the comment period on the report is scheduled to end today. Unfortunately, I did not learn of the report until Wednesday of last week. Consequently, I have requested an extension so that I can make sure other interested parties have an opportunity to comment as well.

Another aspect of the report that concerns me is that it looks like the CPSC is trying to establish a safe level of ozone production from an ozone generating air cleaner. The major drawback of this approach is that unknowing consumers will use these devices as "air cleaners" and thus create situations with very high and dangerous ozone levels. The following is another comment I sent to the CPSC on this subject:

"In reading the report and the staff comments again the conclusions become even more troubling to me. With the Shaughnessy model and based on staff comments it looks like the conclusion is that "ozone releases from an air cleaner should not exceed approximately 14 to 26 milligrams of ozone per hour of operation." This is a very dangerous conclusion.

Ozone accumulation levels depend upon a number of factors including outdoor ozone, the chemicals that are in the room where the ozone generating device is used, the surfaces in the room and the ozone produced by the device. In poorly ventilated, small rooms - such as a nursery - ozone levels can far exceed government standards with just 2.2 milligrams of ozone per hour of operation coming from an "air cleaner."

Researchers at the University of California Irvine found that when an Ionic Breeze (that generates about 2.2 milligrams of ozone per hour) was used in a bathroom of 5.9 cubic meters in volume that the ozone level exceeded 200 ppb. This is far above OSHA, NIOSH, EPA and all other government regulations. It is certainly not safe.

I sincerely hope that the CPSC recommendation does conclude that producing 14 to 26 milligrams of ozone is safe. Again, this is a dangerous conclusion."

My position has always been that one has to look at the "worst case scenario" for ozone exposure rather than a "normal" exposure. An example is the mother of the 2 year old with asthma using an ozone generating ionizer in a small nursery because she wanted to give her baby "the best air possible." Perhaps this example is a bit dramatic - but it is true. It happened.

Thank you again for your response and your encouragement.

Jim

Stevenson, Todd A.

From: Saltzman, Lori E.
Sent: Monday, December 04, 2006 12:53 PM
To: Stevenson, Todd A.; Danello, Mary Ann; Hatlelid, Kristina M.; Thomas, Treye A.
Subject: FW: Report to the CPSC on ozone generating air cleaners
Attachments: Re: Report to the CPSC on ozone generating air cleaners

Todd, this guy keeps sending comments directly to the contract author (Richard Shaughnessy) and Treye. Lori

From: Rjstulsau@aol.com [mailto:Rjstulsau@aol.com]
Sent: Monday, December 04, 2006 12:48 PM
To: Saltzman, Lori E.
Subject: Fwd: Report to the CPSC on ozone generating air cleaners

Lori,

More comments.

You probably already have these, but just in case....

The person here has good comments but perhaps has not read the modeling portion as well as he should. Our report simply suggests some values based on a set volume size. For smaller spaces the equation of course is modified as a function of floor area and Figure 1 in my report.

The issue of protecting the "sensitive" population is worth discussion due to the fact that normally many of the devices are targeting just that group of people.

I am open for more discussion and suggestions when all comments are fielded.

Thnx again,

Richard



Linda S. Adams
Secretary for
Environmental Protection

Air Resources Board

Robert F. Sawyer, Ph.D., Chair
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Arnold Schwarzenegger
Governor

December 4, 2006

Office of the Secretary
U.S. Consumer Product Safety Commission
Washington, D.C. 20207-0001

Subject: Comments on CPSC Health Sciences Staff Report on the Work Product Resulting from CPSC Contract No. CPSCS041369, Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners

Thank you for the opportunity to comment on the Consumer Product Safety Commission's (CPSC) recent staff report and consultant report regarding ozone's potential health effects and ozone exposure limits for ozone-generating air cleaners. This effort provides a useful assessment of an important public health issue, and we hope that your agency will use it to develop product standards to protect consumers from the adverse effects of ozone. Our primary comments are summarized below, and detailed comments are attached.

1. We largely concur with the conclusion that a 50 ppb maximum ozone accumulation limit is adequate to reduce the occurrence of adverse health effects, at least for short term exposures for most of the population. However, the 50 ppb limit may not provide adequate protection for long-term exposures, for individuals who are most susceptible, and for locations where background levels of ozone are elevated. Furthermore, newer epidemiological studies suggest that measurable health effects occur at daily levels of outdoor ozone as low as 20-30 ppb. We suggest that the scientific rationale for choosing the 50 ppb exposure limit be clarified in light of information on the threshold level of ozone health effects, and the National Research Council's recommended limit of 20 ppb for continuous exposure of healthy, active workers. Additionally, a margin of safety should be incorporated into any standard that is established. This can be accomplished in a variety of ways, such as by varying the limit for specific circumstances, modifying the test protocol, and so on.
2. We agree with the CPSC staff conclusion that an emission rate limit would meet the objective of protecting consumers. We also agree that ozone measurements at a specified distance from the device could be used to develop test standards.

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our website: <http://www.arb.ca.gov>.

California Environmental Protection Agency

However, the adequacy of this measurement approach would depend on the specific distance at which the measurement is taken. For example, a 50 ppb limit may be adequately protective if the measurement is made two inches from the discharge point of the device, but inadequate if measured several feet from the device. This is because the concentration decreases rapidly with distance from the device. This is particularly important because air cleaners are commonly used overnight at the bedside.

3. We recommend a more protective approach in modeling the accumulation of indoor ozone. The consultant's model inputs do not represent "reasonable high exposure" conditions expected to occur for a substantial portion of the product users, including sensitive and "at risk" populations. We recommend additional modeling to include lower air exchange rates, lower deposition rates, increased emission rates due to soiling and degradation, higher background levels of indoor ozone, and multiple ozone-generating air cleaners, as discussed in our detailed comments.
4. The background section of the staff report omits a critical point: there is no scientifically valid reason to allow marketing of devices that intentionally generate ozone for the purpose of cleaning indoor air or surfaces in occupied spaces. This is a key point because such devices are still being marketed as air cleaners to control indoor air pollutants and allergens.

As you may be aware, our agency was recently directed by our State Legislature to develop a regulation to limit ozone emissions for air cleaners in order to protect public health. The legislation, Assembly Bill 2276 (Pavley), and other information about our related activities, are available on our website at <http://www.arb.ca.gov/research/indoor/ozone.htm>. On December 13, 2006 we will hold our first public workshop on the regulation, and invite CPSC staff to participate. The workshop will be webcast, and a phone line will be available for participants who cannot travel to Sacramento. Details are available at the website above.

U.S. Consumer Product Safety Commission
December 4, 2006
Page 3

We look forward to working with you on this important public health problem, and hope that the CPSC will take strong action at the federal level to address ozone generators. If you more in the future have any questions, please contact Peggy Jenkins of my staff at (916) 323-1504, or by email at mjenkins@arb.ca.gov.

Sincerely,

/s/

Richard Bode, Chief
Health and Exposure Assessment Branch
Research Division

Attachment

cc: Peggy Jenkins, Manager
Indoor Exposure Assessment Section

Attachment

Detailed Comments
California Air Resources Board, Research Division
December 4, 2006

Comments on CPSC Health Sciences Staff Report, Draft, September 26, 2006 on Work Product from CPSC Contract No. CPSCS041369

1. p. 3, par. 1, lines 3-4, purported air cleaning by ozone. We suggest adding clarification to emphasize that ozone has no significant effect on removing indoor pollutants other than alkenes, which react with ozone to form toxic, irritant compounds such as formaldehyde. There is no scientifically valid reason to allow marketing of devices that intentionally generate ozone for the purpose of cleaning indoor air or surfaces. This is a key point concerning consumer protection.
2. p. 3, par. 2, line 2, FDA standard. Note that the FDA ozone concentration limit also applies to air circulating through the device.
3. p. 3, par. 2, lines 5-7, implied health benefits. Note that legal actions by the FTC and the State of Minnesota, and health warnings by USEPA and state agencies have not stemmed the growing market for so-called air cleaners that intentionally generate ozone. The report should make it clear that current regulatory and public education programs have not been effective in meeting the goal of the FDA regulations.
4. p. 3, par. 2, line 7. Incorrect as stated. To clarify, FDA does not consider air cleaners to be medical devices unless they are labeled or marketed with health- or medical-related claims (see FDA and CPSC position statements on this issue [FDA, 1979]).
5. p. 7, par. 5, line, modeling ozone accumulation. We recommend limited additional modeling to address realistic worst-case scenarios, including:
 - A. Air exchange rates of 0.1 ACH or less, vs. the 0.35 ACH used in the model. New homes in California have been built very air-tight since 1990 (Sherman, 2006), as documented by blower door test data. In a study of 37 newer single-family homes in Southern California, Wilson *et al.* (2003) reported that post-1995 homes were tighter than older homes in the region, and that the newer homes had lower air exchange rates (0.17 ACH and 0.29 ACH, respectively). In addition, California data on residential window use indicate that a substantial portion of households do not open their windows at all, especially during the winter and summer (Phillips *et al.*, 2000; Price *et al.*, 2006). Price *et al.* (2006) also found that a substantial portion of new single family homes in California had effective

ventilation from window use that was estimated to be below the 0.35 ACH recommended by ASHRAE, especially in the winter. Similarly, air exchange rates in newer manufactured housing and multi-family housing are expected to be much lower than 0.35 ACH because whole-house mechanical ventilation is rare in California and most other states.

- B. Include lower deposition rates to represent a room without substantial fleecy surfaces such as carpeting and upholstered furniture. Households with asthma or allergy patients often remove such fleecy surfaces to reduce the buildup of surface dust and other indoor triggers of asthma and allergies.
 - C. Increased emission rates (for example 100% of initial emission rates) to reflect potential degradation of device performance due to dust build up. Dust and other residue can build up on air cleaner surfaces and affect ozone output, especially in homes with significant particle sources such as cooking, smoking, and pets. Phillips *et al.* (1999) observed that ozone concentrations roughly doubled for a short-period when house dust was dropped on a personal ozone generator. Davidson and Dorsey (1994) reported that ozone emission rates from an electrostatic air cleaner increased five-fold when it was operated for several days under high PM10 conditions, and 10-fold when the discharge wires were oxidized.
 - D. Include higher background concentrations for indoor ozone, to reflect outdoor ozone episodes and to protect most of the population. For example, the median indoor concentration in Southern California single-family homes from February to December was 6 ppb ozone, and the 95th percentile value was 42 ppb ozone (Avol *et al.*, 1998). The median and 95th percentile values for outdoor ozone were 34 and 69 ppb, respectively. Outdoor ozone levels during an ozone episode can last for several days. Using these data, or even the higher ozone levels from the summer season, is appropriate for estimating a reasonable high-end exposure to indoor ozone.
 - E. Two or three ozone-generating devices in a home. Manufacturers often recommend using a unit in each bedroom and living area. We are aware of households that use multiple units continuously.
6. p. 7, par. 6, line 1, and p. 8, par. 4, line 4, testing ozone at a specified distance. We recommend considering this approach, along with room or chamber testing, in order to address the potential health risks of near-source exposure such as devices operated overnight near a bed.
7. p. 8, par. 2, line 10, protecting sensitive subpopulations, and safety factors. We recommend that the CPSC seriously consider measures, including a margin of safety and conservative assumptions, to protect sensitive subpopulations from unnecessary exposure to ozone and its reaction byproducts. Sellers of air cleaners

specifically target persons with asthma, allergies, and COPD, and families with children.

8. p. 8, par. 4. We agree that an ozone emission rate limit is appropriate for protecting consumers, because it allows estimation of human exposure under various conditions and it allows direct comparison among devices. We also agree that ozone measurements at a specific distance from the device could be considered in developing test standards, but note the adequacy of this approach depends on the distance at which the measurement is made. For example, a 50 ppb limit may not be adequately protective if measured several feet from the device, but it would be much more protective if it is measured at two inches from the discharge point of the device.
9. p. 10, *et seq.*, Appendix A, Cal/EPA report. Please correct the citation to be cited as CARB 2006; the authors are staff of the California Air Resources Board. CARB is part of Cal/EPA, which was not involved in this effort. This comment also applies to all other Cal/EPA references and web-based information cited in both the CPSC report and the contractor's report.
10. p. 11, par. 3, Appendix A, comparison of Shaughnessy modeling results to CARB (Cal/EPA) test results. A caveat should be noted regarding the differences between the two sets of results. The CARB room tests did not always reach steady state, whereas the Shaughnessy model assumed steady state. Therefore, some of the CARB results underestimate the ozone exposures from long-term or continuous ozone use of the devices, and the true difference between the two studies would be even greater.

Comments on Shaughnessy *et al.*, May 19, 2006. "Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners". CPSC Contract No. CPSCS041369.

11. p. 8, par. 1, last sentence, Continuous Exposure Limit of 20 ppb. The continuous exposure scenario is similar to that for users of air cleaners with light physical activity levels. Continuous operation of portable air cleaners, 24 hours a day and every day, was reported by most California households, according to preliminary results from a statewide survey. As pointed out in the consultant report, continuous ozone inhalation actually results in increased delivery of ozone to the deep lung, which suggests that limits for continuous exposures should be less than those based on scaling by exposure averaging times alone.
12. p. 9, par. 1, line 5, 18-35 year olds. This is incorrect as stated: the NAAQS does not apply to a particular age range, but the recent literature may do so.
13. p. 18, par. 2, clinical studies. The authors should specify and consider the health status, age, gender, race, and number of the subjects in the studies cited.

14. p. 24, par. 3, line 3, reaction products. Note that an important ARB-funded study of ozone reaction products from cleaning solutions and air fresheners was recently completed that provides additional information on this topic. Singer *et al.* (2006) and the literature review in Nazaroff *et al.* (2006) indicate that the potential impacts of such reactions on indoor formaldehyde and particulate matter on exposures can be significant. Nazaroff *et al.* (2006) found that the highly-reactive terpenoid compounds are widely used as solvents and scenting agents in cleaning products.
15. p. 25, par.1, last sentence. Note that little ozone is needed to produce significant levels of reaction products, based on work by Wechsler, Sawars *et al.*, and the studies listed above.
16. p. 25, par. 2, last sentence. Note that Weschler (2006) estimates that indoor ozone exposure, in the absence of a major indoor source of ozone, can be 43-76% of personal ozone exposure. He also presents data to suggest that indoor ozone reaction products in homes make a substantial contribution to personal PM2.5 exposures.
17. p. 25, par. 4, line 2, sensitive populations. This sentence seems to be out of place in the section on sensitive populations. The *in vivo* human study (Adams 2002 at p. 17, par. 2) used healthy adult subjects.
18. p. 26, par. 4, line 12, children's sensitivity. Change to read "... potentially more at risk than adults...". Sensitivity is not the appropriate term here because it refers to an increased biological response at the same dose rate, and there is no clinical evidence to date that children have larger responses to ozone at a given dose. Children are considered to be more susceptible or vulnerable to the adverse health effects of ozone.
19. p. 29, par. 2, line 3, significant effect of 10 ppb increment. Note that a few key studies of low-level effects have been published since the publication cut-off date:
 - A. A meta-analysis of 39 epidemiological studies found that a 10 ppb increment in daily ozone exposure was associated with a significant increase in short-term mortality (Bell *et al.*, 2005). The effect persisted at exposure levels similar to outdoor background levels of 10-25 ppb. The study also summarizes results of published single-site epidemiology studies that found adverse health effects at daily ozone levels as low as 20-30 ppb; these results were found to be consistent with the authors' results.
 - B. An epidemiological study of 639 infants with asthmatic mothers found that at 24-hour exposures to ozone near or below the current USEPA standard, infants are at increased risk of respiratory symptoms (Triche *et al.*, 2006). Significant associations were found at the interquartile range increment of 12 ppb ozone in the 24 hour average.
20. p. 29, par. 2, line 8 *et seq.*, FDA's 50 ppb limit. The author's support of this limit seems to be based on the fact that it is somewhere between the CARB 8-hour

standard of 70 ppb and the NRC's Continuous Exposure Limit of 20 ppb. To provide a more quantitative basis, we suggest that the available literature be used to adjust the 8 hour standard for continuous exposure duration that is typically seen in indoor use of air cleaners. We also suggest that a margin of safety be included to assure protection of vulnerable population groups.

21. p. 30, par. 3, lines 2-4, and p. 31, par. 2, line 1, re: limited information from human exposure studies of low-level ozone effects and sensitive populations. This sentence is not correct as worded. None of the groups listed have been shown to have increased response to ozone exposures of 80 ppb or more for the end points measured, and lower exposure levels have not been tested for these groups (see the CARB 2005 staff report cited in the consultant report).
22. p. 31, par. 2, last sentence, protecting sensitive populations. We recommend both approaches: include a margin of safety because vulnerable populations cannot always identify themselves as such or they may not read the users manual; and advise vulnerable populations and the general public to avoid the use of intentional ozone generators, as ARB and many other government agencies have advised for years.

References

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<http://www.arb.ca.gov/research/abstracts/01-336.htm>. Links to journal articles and slides at: <http://www.arb.ca.gov/research/health/healthup/citations.htm#sept28-06>.

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Stevenson, Todd A.

From: Tom Phillips [tphillips@arb.ca.gov]
Sent: Monday, December 04, 2006 8:20 PM
To: Stevenson, Todd A.
Cc: Richard Bode; JENKINS; PEGGY; Chris Jakober
Subject: CARB comments on CPSC reports on ozone-generating air cleaners
Attachments: CARB commentsonCPSCreport12-4-06w- atch.pdf

Please see our attached comments regarding:

Health Sciences Staff Report on the Work Product Resulting from CPSC Contract No. CPSCS041369,
Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-
Generating Air Cleaners.

Tom Phillips

--
Thomas J. Phillips
Indoor Exposure Assessment Section, Research Division
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CARB/RD, 1001 - I St., POB 2815, Sacramento, CA 95812
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IAQ info & guidelines: <http://www.arb.ca.gov/research/indoor/indoor.htm>
Research reports: <http://www.arb.ca.gov/research/apr/past/indoor.htm>
Customer feedback survey: <http://www.calepa.ca.gov/Customer/CSForm.asp>

December 4, 2006

Office of the Secretary
U.S. Consumer Product Safety Commission
Washington, DC 20207-0001

References:

- (1) CPSC Health Science Staff Report on the Work Product Resulting from CPSC Contract No. CPSC041369, "Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners" (Draft 9/26/2006)
- (2) "Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners." (By R. Shaughnessy, PhD.; issued May 19, 2006.)

The Association of Home Appliance Manufacturers ("AHAM") is the United States trade association representing manufacturers of portable room air cleaners. AHAM would like to thank the CPSC for the opportunity to comment on the above referenced reports.

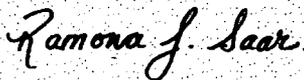
Specifically:

- (1) We have found that Dr. Shaughnessy's report is a fair and comprehensive evaluation of available literature on ozone emissions from air cleaners. We do take great exception to a comment in the Staff Report which we believe inaccurately depicts consumer complaints to CPSC about air cleaners (Refer to item 6 for further details).
- (2) AHAM supports the recommendation that - based on the comprehensive health effects review that was conducted - there is no compelling evidence to adjust the current FDA requirement of a maximum 50 ppb accumulation level of ozone for portable room air cleaners.
- (3) AHAM acknowledges the need for further research and study for those areas not covered by the available literature (including, for example, long term exposure to low levels of ozone).
- (4) AHAM acknowledges that there may be merit in the mathematical modeling derivation provided to calculate the maximum ozone release rates (emissions rates) that would correspond to the 50 ppb accumulation level in various room sizes. However, further consideration should be given to the air exchange rate that is used in the model (0.35 h^{-1} whole house air exchange rate on page 53). The exchange rate used in the model should be more reflective of real-world use of portable room air cleaners in a single room within a house. Testing will be required to validate that the mathematical model properly simulates real-world use.

- (5) AHAM requests that the CPSC identify in the Staff Report the name and affiliation of both Reviewers (#1 and #2).
- (6) The following statement at the bottom of page 3 of the Staff Report should be removed or further clarified: "CPSC has received numerous complaints from consumers who believe that their health problems, including coughing, shortness of breath, chest pain, wheezing, burning eyes, and dizziness, were caused by their use of air cleaner devices." This statement is too broad and unsubstantiated as a general product disparagement. What is the time period of the complaints? How many complaints were received? And, perhaps most importantly--what type of air cleaner devices did the consumers have? We would like to review the alleged complaints on a de-identified basis to see if they are related to intentional ozone generating units or other types of units.

If you have any questions about these comments, please feel free to contact me.

Sincerely,



Ramona J. Saar
Director of Standards & Certification Programs
AHAM

Stevenson, Todd A.

From: Saar, Ramona [RSaar@AHAM.org]
Sent: Monday, December 04, 2006 4:47 PM
To: Stevenson, Todd A.
Cc: Wethje, Larry; Morris, Wayne
Subject: AHAM Comments on CPSC Ozone Reports
Attachments: 061204_AHAM Comments_CPSC Ozone Report.doc

TO: Office of the Secretary
U.S. Consumer Product Safety Commission

RE: CPSC Health Science Staff Report on the Work Product Resulting from CPSC Contract No. CPSC041369, "Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners" (Draft 9/26/2006) and "Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners." (By R. Shaughnessy, PhD.; issued May 19, 2006.)

Attached please find AHAM's comments on the above referenced reports. Please confirm receipt at your earliest opportunity.

Thank you.

Sincerely,

Ramona J. Saar
AHAM
Director, Standards & Certification Programs
202 872 5955 x314
e-mail: rsaar@aham.org

12/5/2006

Stevenson, Todd A.

From: Dr. Richard Corsi [corsi@mail.utexas.edu]
Sent: Monday, December 04, 2006 4:32 PM
To: Stevenson, Todd A.
Subject: Comments: CPSC Health Sciences Staff Report on the Work Product Resulting from CPSC Contract No. CPSCS041369, Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners - DRAFT

Attachments: Maximum Acceptable Ozone Emissions_REPORT_Nov30_2006.doc

To Whom It May Concern:

This email is in response to your important efforts to review and establish acceptable ozone exposure limits as related to ozone-generating air purifiers, and as described in CPSC Health Sciences Staff Report on the Work Product Resulting from CPSC Contract No. CPSCS041369, Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners - DRAFT.

I am not a health scientist, but have done significant review of the recent literature on human health responses to incremental changes in ozone. Further, I have done considerable research on the subject of ozone chemistry in the interior of buildings, both in core air and surfaces.

Recently, I completed a white paper (attached) in which I have argued for a more stringent standard with respect to indoor ozone concentrations and ozone release rates into several types of indoor environments. The premise for this analysis is that most population responses to ozone reported in the published literature occur due to exposure (to outdoor ozone) inside of buildings, and the exposure concentrations in these events are actually far less than those recorded at outdoor monitoring sites. As such, our thinking on ozone concentrations that induce increases in mortality (mostly amongst the elderly) or adverse respiratory effects in infants should involve adjustments to the centralized monitoring data.

It is my opinion that standards for protection of the general public should be focused on an incremental increase in ozone concentration of 5 ppb (at most) and less than 5 ppb to protect those most sensitive to ozone and its reaction products. Further, as I outline in my paper, it would be worthwhile to remember that ozone itself is not the only chemical that can influence the indoor environment when it is present, as ozone clearly leads to increases in various other pollutants through a multitude of ozone-initiated reactions, including formaldehyde and ultrafine to fine secondary organic aerosols.

I hope that the attached white paper is considered in your deliberations and future revisions to your report.

Thanks for allowing me to comment.

With Sincerity -

Richard L. Corsi, Ph.D.
E.C.H. Bantel Professor for Professional Practice
Director - Program on Indoor Environmental Science and Engineering
Department of Civil, Architectural & Environmental Engineering
The University of Texas at Austin, Center for Energy & Environmental Resources (Bldg 133)
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512-475-8617 corsi@mail.utexas.edu

12/5/2006

Assessment of Maximum Ozone Emissions in Residential, Office and School Buildings

Prepared by

Richard L. Corsi, Ph.D.

November 30, 2006

EXECUTIVE SUMMARY

The Issue

Although ozone concentrations are generally lower indoors than outdoors, the fact that Americans spend nearly 18 hours indoors for every hour spent outdoors leads to the majority of public exposure to ozone occurring inside of buildings. The adverse effects of ozone on human health are well understood and, as such, ozone is a heavily regulated outdoor air pollutant. Ozone can cause inflammation of respiratory tissue, leading to irritation, coughing, and pain upon deep breathing (California Air Resources Board, 2005). Ozone concentrations well below the National Ambient Air Quality Standard have been associated with wheezing and difficulty breathing amongst some infants, particularly those whose mothers have physician-diagnosed asthma (Trische *et al.* 2006). Short-term exposure to increased ozone concentrations has also been linked to premature mortality (Bell *et al.*, 2006).

In addition to its direct and adverse impacts on human health, ozone is a major driver of indoor chemistry. It reacts with certain organic compounds, particularly those which are increasingly used in scented indoor consumer products. Several irritating and potentially toxic by-products have been shown to result from such reactions, although the magnitude of the adverse effects of such products has yet to be resolved.

The one ubiquitous source of indoor ozone is outdoor ozone that is transported into buildings either through intentional (mechanical) ventilation, or unintentional infiltration of air through cracks in the building envelope, e.g., around windows and doors. However, two other source categories exist. These include electronic devices that generate ozone unintentionally, e.g., laser printers, dry-toner photocopiers, and some air purification systems that are intended for the removal of particulate matter from air, as well as devices explicitly designed to generate and release ozone into indoor environments (ozone “air purifiers”). Air purification devices that emit ozone can either be of the “portable” design, i.e., devices that can be moved from location to location within a building, or devices that are used within a building’s HVAC system, thus distributing ozone (intentionally or unintentionally) throughout a building zone.

Given the direct health effects of ozone, and indirect impacts of its reaction products, it is worthwhile to consider maximum acceptable ozone emission rates. This is particularly true given that some of the devices described above provide some benefit in terms of particle removal from air. As described later in this report, a reasonable argument can be made to limit increases in indoor ozone from appliances and outdoor air ventilation to 5 ppb or less to protect sensitive or at risk individuals.

Approach

This report focuses on indoor ozone, particularly as related to determination of maximum acceptable ozone emission rates from indoor devices that generate ozone as an unintentional by-product. A spreadsheet model was developed to predict maximum acceptable mass emission rates of ozone for three types of environments: single-family detached homes, single offices,

classrooms. For each type of environment the maximum acceptable ozone emission rate was calculated based on maximum acceptable ozone concentration increase, maximum acceptable formaldehyde concentration increase, and maximum increase in secondary organic aerosol concentration. The latter two are by-products of ozone reactions with various volatile organic compounds found indoors. For this study three such compounds were used for determining by-product formation: d-limonene, α -pinene, and linalool alcohol. For each environment, the lowest of the predicted maximum acceptable emission rates (based on ozone, formaldehyde, and secondary organic aerosol concentrations) was taken as the limiting value.

Three types of model calculations were completed. Maximum acceptable mass emission rates of ozone were determined for a base-case condition and for a worst-case condition (to protect the most sensitive occupants of buildings). Additional model simulations were completed to determine the sensitivity of model predictions to factor of two changes in input parameters. Details of the model and parameters used for calculations are provided in Sections 2 and 3 of this report.

Major Findings

The results of this study indicate that the limiting maximum acceptable ozone mass emission rates for base-case conditions (see Section 3 for a definition of these conditions) are: 17.5 mg/hr (292 μ g/min) for a single-family detached residential home, 1.3 mg/hr (22 μ g/min) for a typical office in an office building, and 9.9 mg/hr (166 μ g/min) for a school classroom. Each of these limiting values was based on maximum acceptable ozone concentration increases. The limiting maximum acceptable ozone mass emission rates for worst-case conditions (see Section 3 for a definition of these conditions) are: 0.45 mg/hr (7.5 μ g/min) for a single-family detached residential home, 0.041 mg/hr (0.68 μ g/min) for a typical office in an office building, and 0.13 mg/hr (2.2 μ g/min) for a school classroom.

Table 4-1. Maximum acceptable ozone emission rates [mg/hr (μ g/min)] for **base-case** conditions.

Criteria (across) → Environment (below)	Ozone	Formaldehyde	SOA	Limiting (mg/hr)
Residential	17.5 (292)	930 (15,433)	48 (803)	17.5 (292)
Office	1.3 (22)	19 (312)	4 (66)	1.3 (22)
School	9.9 (166)	1,000 (17,168)	71 (1,176)	9.9 (166)

In contrast to the base-case condition, for the conservative (“worst-case”) analysis the maximum ozone emission rate was always limited by incremental increases in secondary organic aerosol (SOA) concentration. For each environment, even entire residential dwellings, the acceptable ozone emission rate was generally less than unintentional ozone emissions from a single portable ion generator, or from single laser printers or photocopy machines.

Table 4-2. Maximum acceptable ozone emission rates [mg/hr ($\mu\text{g}/\text{min}$)] for **worst-case** conditions.

Criteria (across) → Environment (below)	Ozone	Formaldehyde	SOA	Limiting*
Residential	1.9 (32)	2.4 (40)	0.45 (7.5)	0.45 (7.5)
Office	0.21 (3.5)	0.1 (1.7)	0.041 (0.68)	0.041 (0.68)
School	1.1 (18)	0.32 (5.3)	0.13 (2.2)	0.13 (2.2)

* The values in the right-hand column should be considered as maximum acceptable ozone mass emission rates for situations that involve particularly sensitive individuals, e.g., the elderly, infants, and those with respiratory illnesses.

Results of sensitivity analyses indicate the importance of ozone decay rates by reactions with indoor materials on the predicted maximum acceptable ozone emission rate. In the case of formaldehyde formation, parameters associated with indoor linalool alcohol (linalool alcohol concentration, reaction rate constant, formaldehyde molar yield) have a significant influence on acceptable ozone emission rates. Linalool alcohol is used in many fragrance products. In the case of secondary organic aerosol formation, parameters associated with d-limonene (limonene concentration, reaction rate constant, aerosol mass yield) have a significant influence on acceptable ozone emission rates.

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1. INTRODUCTION

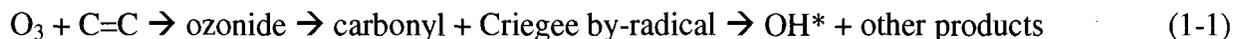
This report focuses on indoor ozone, particularly as related to determination of maximum acceptable ozone emission rates from indoor devices that generate ozone as an unintentional by-product. This section involves a discussion of concerns related to human exposure to ozone and its reaction products, sources of indoor ozone, and the objectives and scope of this study. Section 2 includes a description of the model equations used in this study. Derivations of model equations are presented in Appendix A. Parameters used in the model assessment are presented in Section 3. Results associated with model applications for this study are presented in Section 4, with comparisons to other sources of indoor ozone.

1.1 Concerns Related to Indoor Ozone

Ozone contains three oxygen atoms, is a strong oxidizing agent and a major component of urban photochemical smog. It is known to adversely affect human health at urban ambient concentrations and is heavily regulated in outdoor air. However, indoor exposures represent a major fraction of total human exposure to ozone (Weschler *et al.*, 1989).

The adverse effects of ozone on human health are well understood and, as such, ozone is a heavily regulated outdoor air pollutant. Ozone can cause inflammation of respiratory tissue, causing irritation, coughing, and pain upon deep breathing (California Air Resources Board, 2005). Outdoor ozone concentrations well below the National Ambient Air Quality Standard of 85 parts per billion by volume (ppb) averaged over eight hours have been associated with wheezing and difficulty breathing amongst some infants, particularly those whose mothers have physician-diagnosed asthma (Trische *et al.* 2006). Short-term exposure to increased ozone concentrations have also been linked to premature mortality (Bell *et al.*, 2006).

In addition to its direct and adverse impacts on human health, ozone is a major driver of indoor chemistry (Weschler, 2000). Ozone reacts with unsaturated organic compounds, i.e., organic compounds that contain carbon-carbon double bonds (C=C) as described by the following chemical reactions:



The unsaturated organic compound, depicted by C=C in Equation 1-1, can range from very small molecules, e.g., very volatile organic compounds, to large molecules associated with unsaturated fats in oils and soaps. Several recent studies have focused on the importance of ozone reactions with terpenes and terpene alcohols, which are increasingly observed in indoor environments due to their use in cleaning products and fragrances (California Air Resources Board, 2006a); Nazaroff and Weschler, 2004; Sarwar *et al.*, 2003 and 2004; Singer *et al.*, 2006; Tamas *et al.*, 2006; Weschler and Shields, 1999). The ozonide listed in Equation 1-1 is a short-lived intermediate compound that decomposes to a carbonyl (aldehyde or ketone) and a Criegee bi-radical. For unsaturated compounds with a terminal carbon-carbon double bond (C=C on last carbon in chain) formaldehyde will form as a by-product of ozonide decomposition. The Criegee bi-radical is also a short-lived intermediate compound that leads to the formation of

hydroxyl radicals (OH*) and “other products”. The hydroxyl radical is even more reactive than ozone and can attack both unsaturated and saturated organic compounds as well as a wide range of inorganic chemicals observed in indoor air. The collective “other products” associated with ozone-initiated indoor air chemistry includes a wide range of chemicals involving one or more oxygen-containing functional groups (e.g., carboxylic acids, and alcohols), and secondary organic aerosols (Nazaroff and Weschler, 2004; Weschler and Shields, 1997). These products have been implicated in reduced satisfaction of indoor environmental quality (Knudsen *et al.*, 2002; Tamas *et al.*, 2004), irritation of the respiratory system of mice (Clausen *et al.*, 2001; Wilkins *et al.*, 2003; Wolkoff *et al.*, 1999), and increased eye irritation (Kleno and Wolkoff, 2004).

Ozone also reacts with nitrogen dioxide in indoor environments, e.g., as emitted from gas stoves and burners, and other gas appliances, leading to the formation of nitrate radicals in accordance with the following chemical reaction:



The nitrate radical engages in reactions similar to the hydroxyl radical, and can lead to the production of organic nitrates and nitric acid (Weschler and Shields, 1997; Weschler *et al.*, 1992). The latter can lead to corrosion of indoor materials, with potentially devastating effects on electronic equipment and cultural artifacts (Weschler *et al.*, 1992). However, indoor nitrate chemistry and its effects are not as well understood as that of ozone or hydroxyl radicals, and were therefore not considered in this study.

1.2 Sources of Indoor Ozone

There are three general categories of sources of indoor ozone, as depicted in Figure 1-1. The first (source category 1) involves the transport of ozone in outdoor air into a building either through intentional (mechanical) ventilation, or unintentional infiltration of air through cracks in the building envelope, e.g., around windows and doors. In either case, some fraction of the ozone is usually consumed by reactions with surfaces (in the HVAC system for mechanical ventilation or in the building envelope for infiltration) prior to ozone entering the occupied space of the house. The second (source category 2) corresponds to indoor sources of ozone, generally associated with electronic devices that generate ozone unintentionally, e.g., laser printers, dry-toner photocopiers, and some air purification systems that are intended for the removal of particulate matter from air. The last category (source category 3) involves devices that are explicitly designed to generate and release ozone into indoor environments (ozone “air purifiers”). The latter devices typically emit very large amounts of ozone, are not well proven in their intended application, and are generally discouraged from being used (California Air Resources Board, 2006b; Hubbard *et al.*, 2005). This study focuses on source category 2.

1.3 Objectives and Scope of this Study

The objectives of this study were to develop a model and apply the model to estimate maximum acceptable ozone emission rates in three different indoor environments (homes, offices, and schools). This study focused on indoor devices that are intended for application in HVAC

systems or as stand-alone devices for removal of air pollutants, but that generate some ozone unintentionally. However, the resulting model and model results are generally applicable to any source of indoor ozone.

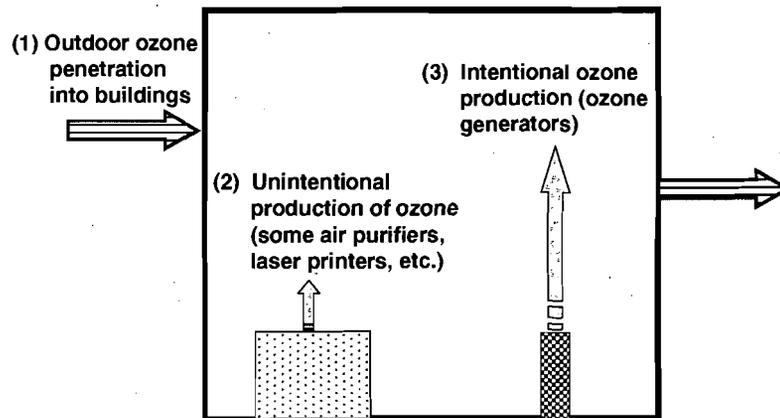


Figure 1-1. Sources of indoor ozone divided into three primary source categories.

For residential dwellings the focus was on whole house systems, i.e., for which ozone is unintentionally distributed through the entire volume of a house as opposed to a single room such as would be the case with a portable air purifier. For office buildings the focus was on a single office. Individual classrooms were used for assessing ozone emissions in school environments. Within each type of environment a maximum acceptable emission rate was estimated based on three criteria: (1) maximum acceptable indoor ozone increment, (2) maximum acceptable indoor formaldehyde increase (as a by-product of indoor ozone reactions), and (3) maximum acceptable indoor secondary organic aerosol (SOA) increase (as a by-product of indoor ozone reactions).

Experiments were not completed for this study. A model was developed based on a mass balance for ozone in each of the aforementioned types of building environments. The model was based on several simplifying assumptions, including the assumption that the space in question is well-mixed (no localized hot spots of ozone) and that steady-state conditions are achieved. Model parameters were selected based on a review of existing literature. Where parameters were not available scientific judgment was employed to estimate those parameters, e.g., based on analogies with similar systems, etc.

Ozone is known to react with indoor materials, leading to reductions in ozone concentrations in building air, but also the production of by-products that can be harmful to building occupants. Ozone removal to indoor surface was considered in this study. However, there is insufficient information in the published literature to perform an accurate estimate of by-product emissions due to ozone reactions with most indoor surfaces. As such, this source of by-products was not considered in this model and remains an area for future model improvements.

The model was used for three types of calculations, each involving determination of maximum ozone emission rates based on the three criteria described above. The first application involved a specification of "base-case" conditions and involved "typical" values of model parameters based on a review of the published literature. The second application involved a "worst-case" or conservative analysis. For these applications parameters were selected to minimize the acceptable maximum ozone emission rates for each of the three target environments. The third application involved a sensitivity analysis, for which individual model parameters were varied by a factor of two (halving and doubling) around its base-case condition, with all other parameters otherwise maintained at base-case conditions.

2. MODEL DEVELOPMENT

A model was developed to calculate maximum acceptable ozone mass emission rates for to indoor environments. The model development assumes steady-state conditions in a well-mixed room or zone. Model equations are provided below, along with descriptions and units for individual variables. A more detailed derivation of model equations is provided in Appendix A of this report. Parameter selection is described in Section 3.

2.1 Emission Rate based on Maximum Incremental Ozone Concentration

A steady-state mass balance on ozone in a well-mixed building or building zone leads to:

$$C_{O_3} = \frac{p\lambda C_{O_3,out} + E_{O_3}^*}{\lambda + v_d^* + \sum k_j C_j} \quad (2-1)$$

Where:

- C_{O_3} = indoor ozone concentration or incremental concentration increase (ppb)
- $C_{O_3,out}$ = outdoor ozone concentration (ppb)
- p = building envelope penetration factor (unitless)
- λ = air exchange rate (hr^{-1})
- v_d^* = ozone decay rate (hr^{-1})
- k_j = bi-molecular reaction rate constant for ozone reaction with reactant j ($ppb^{-1}hr^{-1}$)
- C_j = reactant j, e.g., d-limonene, concentration (ppb)
- $E_{O_3}^*$ = volume normalized molar emission rate of ozone ($ppb \cdot hr^{-1}$).

The two terms in the numerator of Equation 2-1 correspond to ozone inputs to the system (penetration from outdoors and indoor emissions). The three terms on the bottom relate to ozone losses (sinks): air exchange, surface reactions, and homogeneous reactions in air.

For this analysis the concentration of reactants are assumed to be constant and not affected by the release of ozone to the indoor environment from an indoor source. This is a reasonable assumption if the incremental concentration increase of ozone from a device is relatively small, e.g., less than 5 to 10 ppb.

If only incremental increases in ozone due to an indoor source are considered, Equation 2-1 simplifies to:

$$C_{O_3} = \frac{E_{O_3}^*}{\lambda + v_d^* + \sum k_j C_j} \quad (2-2)$$

Inversion of Equation 2-2 to solve for a maximum acceptable ozone emission rate (E_{max,O_3}^*) based on a prescribed maximum acceptable indoor ozone increment ($C_{O_3,max}$) leads to:

$$E_{\max,O_3}^* = (\lambda + v_d^* + \sum k_j C_j) C_{O_3,\max} \quad (2-3)$$

A conservative approach to estimating E_{\max,O_3}^* , i.e., one that builds in a factor of safety, would involve selection of minimum reasonable values of λ , v_d^* , and C_j (k_j are fixed values at a specific temperature), and a minimum acceptable value for $C_{O_3,\max}$. For example, the air exchange rate could be selected as typical of new energy-efficient (tight) construction for single-family residential dwellings, v_d^* could be selected as the lower-bound of published values for specific building types, and C_j could be assumed to be small (zero) in buildings with few sources of terpenes, terpenoids, or other unsaturated organic species that react with ozone.

The maximum acceptable emission rate of ozone on a mass basis can be determined through adjustment of E_{\max,O_3}^* by use of the ideal gas law applied at typical room temperature (20 to 25 °C). For this condition:

$$E_{\max,O_3} = (0.002 \times V) E_{\max,O_3}^* \quad (2-4)$$

Where,

E_{\max,O_3} = maximum acceptable mass emission rate of ozone ($\text{mg}\cdot\text{hr}^{-1}$).

2.2 Emission Rate based on Maximum Gaseous By-Product Concentration

When ozone reacts either homogeneously through bi-molecular reactions or heterogeneously (at surfaces), reaction products are formed. Some of these reaction products may be more irritating than the reactant molecule, and possibly even ozone. The literature related to reaction product yields associated with indoor heterogeneous reactions is sparse, but information related to homogeneous reactions can be gleaned from the outdoor atmospheric literature. Such reactions can be important between ozone and indoor scenting agents, particularly terpenes and terpenoids such as d-limonene, α -pinene, linalool, etc, as these reactions can lead to potentially harmful reaction products such as formaldehyde, acetaldehyde, and fine secondary organic aerosols.

A steady-state mass balance on reaction products in a well-mixed building or building zone in the absence of heterogeneous formation leads to:

$$C_p = \frac{(\sum y_j \times k_j \times C_j) C_{O_3}}{\lambda} \quad (2-5)$$

Where,

C_p = reaction product concentration (ppb)

y_j = molar yield for reaction product (moles product/moles reactant j reacted)

Substitution of Equation 2-2 into Equation 2-5 and solving for the maximum acceptable emission rate of ozone at a prescribed maximum acceptable concentration of reaction product ($C_{p,max}$) leads to:

$$E_{max,O3,p}^* = \left\{ \frac{\lambda(\lambda + v_d^* + \sum k_j C_j)}{\sum y_j \times k_j \times C_j} \right\} C_{p,max} \quad (2-6)$$

Again, the maximum acceptable emission rate for ozone on a mass basis can be calculated based on application of Equation 2-4.

Based solely on formation of reaction product, a conservative approach to estimating $E_{max,O3,p}^*$ would involve selection of minimum reasonable values of λ and v_d^* , maximum reasonable values of C_j , and a minimum acceptable value for $C_{p,max}$.

2.3 Emission Rate based on Maximum Secondary Organic Aerosol Concentration

A steady-state mass balance on secondary organic aerosol mass in a well-mixed building or building zone leads to:

$$C_{SOA} = \frac{p\lambda C_{SOA,out} + \sum \gamma_j k_j C_j C_{O3} U_{c,j}}{\lambda + v_d \frac{A}{V}} \quad (2-7)$$

Where:

- C_{SOA} = indoor SOA concentration ($\mu\text{g}/\text{m}^3$)
- $C_{SOA,out}$ = outdoor SOA concentration ($\mu\text{g}/\text{m}^3$)
- p = building envelope penetration factor for SOA (unitless)
- λ = air exchange rate (hr^{-1})
- $v_d A/V$ = SOA deposition parameter (hr^{-1})
- γ_j = SOA mass yield for reactant j ($\mu\text{g}/\text{m}^3$ of SOA formed per $\mu\text{g}/\text{m}^3$ terpene reacted)
- $U_{c,j}$ = molar to mass conversion factor for reactant j ($\mu\text{g}/\text{m}^3$ per ppb).

All other variables are as defined for equations listed above.

The two terms in the numerator of Equation 2-7 correspond to SOA inputs to the system (penetration from outdoors and formation of SOA by ozone-initiated indoor air chemistry). The two terms on the bottom relate to SOA losses (sinks): air exchange and deposition onto indoor surfaces.

If only incremental increases in SOA due to indoor reactions are considered, Equation 2-7 simplifies to:

$$C_{SOA} = \frac{\sum \gamma_j k_j C_j C_{O_3} U_{c,j}}{\lambda + v_d \frac{A}{V}} \quad (2-8)$$

Substitution of Equation 2-2 into Equation 2-8 and solving for the maximum acceptable emission rate of ozone at a prescribed maximum acceptable concentration increment of SOA ($C_{SOA,max}$) leads to:

$$E_{max,O_3,SOA} = \frac{(\lambda + v_d^* + \sum k_j C_j) \left(\lambda + v_{d,p} \frac{A}{V} \right)}{\sum \gamma_j k_j C_j U_{c,j}} C_{SOA,max} \quad (2-9)$$

Where:

- $E_{max,O_3,SOA}$ = maximum acceptable emission rate of ozone based on prescribed incremental mass concentration of SOA (ppb/hr),
- $C_{SOA,max}$ = maximum acceptable incremental increase in SOA ($\mu\text{g}/\text{m}^3$).

All other variables are as described previously. The maximum acceptable emission rate for ozone on a mass basis can be calculated based on application of Equation 2-4.

Using the model equations described above with appropriate parameter inputs, the maximum allowable ozone emission rate can be determined as the minimum of those calculated by Equations 2-3, 2-6, and 2-9.

3. PARAMETER ESTIMATION

The model described in Section 2 was used to estimate maximum acceptable ozone emissions for a set of “reasonable”, or “base-case”, conditions in residential, office, and school environments. A “worst-case” (conservative) analysis was also completed by selecting sets of parameters that minimize acceptable ozone emissions. Finally, a sensitivity analysis was completed for specific parameters. For comparing sensitivity across parameters, each parameter was analyzed by halving and doubling its value (factor of two sensitivity analysis) around otherwise base-case conditions, and comparing percent changes in acceptable ozone emissions relative to the base case condition. Where published values did not exist, scientific judgment was employed.

A brief summary related to selection of each parameter is provided below. Appropriate references are cited where applicable.

3.1 Building Air Exchange Rate (λ)

Detached Single-Family Residential Dwellings: For detached single-family residential dwellings the entire home was selected for analysis, as opposed to an individual room or zone within the home. Murray and Burmaster (1995) completed a detailed review of air exchange rates compiled by Brookhaven National Laboratory based on perfluorocarbon tracer data. For 2,844 households across the United States and over all seasons the median air exchange rate was 0.51/hr, with 10th and 90th percentile values of 0.21/hr and 1.48/hr, respectively. The median value was selected for base-case analyses and the 10th percentile value was selected for conservative analyses.

Office Buildings For office buildings a single office was selected for analysis, as opposed to an entire commercial or governmental office building or HVAC zone. In accordance with requirements of California Specification 1350 as described by the California Department of Health Services (2004), a base-case outside air exchange rate for a single windowless office was selected to be 0.75/hr. This value is slightly less than reported based on the 100 building USEPA Building Assessment Survey and Evaluation (BASE) study, for which the reported median outdoor air exchange rate was 0.98/hr, with mean and standard deviations of 2.00/hr and 2.45/hr, respectively (Persily and Gorfain, 2004). Persily and Gorfain (2004) also reported 10th percentile and 90th percentile outdoor air exchange rates from buildings in the BASE study of 0.22/hr and 4.84/hr, respectively. The lower bound (0.22/hr) was used in this study for conservative estimates.

School Classrooms: For schools, a single classroom was selected for analysis, as opposed to an entire school building or HVAC zone. In accordance with requirements of California Specification 1350 as described by the California Department of Health Services (2004), a base-case outside air exchange rate for a single classroom was selected to be 0.9/hr. This value is slightly greater than the geometric mean of 0.67/hr observed by Bartlett *et al.* (2004) in 39 elementary schools in British Columbia. Shendell *et al.* (2004) determined air exchange rates in 13 portable and seven traditional classrooms in two school districts in Southern California. Over all 20 classrooms the mean and median school day integrated air exchange rates were 0.8/hr and

0.6/hr, respectively, with a standard deviation of 0.7/hr, and a range of 0.1/hr to 2.9 /hr. The lower bound of this range (0.1/hr) was selected for conservative analyses.

3.2 Ozone Decay Rate (v_d^*)

The ozone decay rate (v_d^*) in Equation 2-1 is the product of the building averaged ozone deposition velocity and the indoor surface-to-volume ratio. The deposition velocity is a function of both the mixing conditions in a room or building and the types (reactivity) of materials in the building.

Lee *et al.* (1999) developed the most comprehensive data set of ozone decay rates in single-family detached residential dwellings. The mean and standard deviation of ozone decay rates measured in 43 homes in Southern California were 2.8/hr and 1.3/hr, respectively. A value of 2.8/hr was adopted for base-case conditions for homes in this study. A value of 1.5/hr (mean minus standard deviation) was selected as a lower-bound for conservative (worst-case) analysis.

Values of ozone decay rate for office buildings are far less numerous than for homes in the published literature. Weschler (2000) summarized 11 reported ozone decay rates for indoor environments characterized as “office” or “office/lab”. For this study, those 11 data points were averaged to determine a mean value of 3.8/hr with a standard deviation of 0.8/hr. The mean value was used for base-case calculations for offices in this study. A minimum value of 2.5/hr as reported by Weschler (2000) was adopted for conservative analysis.

Ozone decay rates for school classroom environments were not found in the published literature. For this study, the values described above for office buildings were adopted for classrooms.

3.3 Particle Deposition Parameter

Riley *et al.* (2002) presented a review of the published literature on size-dependent particle deposition velocities and deposition parameters ($v_d A/V$ in Equation 2-7). In the size range of 0.05 to 0.5 μm , a reasonable range for SOA, available data suggest values of $v_d A/V$ of approximately 10^{-5} /s (3.6×10^{-2} /hr). This value was adopted for the base-case condition. Since this loss parameter is small relative to air exchange rates, it was not varied for purposes of conservative analyses.

3.4 Zone Area and Ceiling Height

Detached Single-Family Residential Dwellings: The American Housing Survey for 2005 (U.S. Department of Housing and Urban Development and U.S. Census Bureau, 2006) was used to determine the median (50% percentile) floor area based on a survey of nearly 77,000 single detached and manufactured/mobile homes in the United States. A cited median value of 1,795 ft^2 (167 m^2) was selected as the base-case floor area for occupied homes in this study. Values of 10th and 90th percentile floor areas were approximated based on analysis of areas in discrete size bins as 1,000 ft^2 (93 m^2) and 3,500 ft^2 (325 m^2), respectively. The lower-bound was used for conservative analysis. An average ceiling height of 10 feet (3.05 m) was assumed.

Office Buildings: For office buildings a single office was selected for analysis as opposed to an entire building or HVAC zone. The following floor area and ceiling height were selected to be consistent with California Specification 1350 as described by the California Department of Health Services (2004): 10 ft x 12 ft floor space = 120 ft² office (11.1 m²) with a ceiling height of 9 ft (2.7 m). California Specification 01350 requires an assumption that only 90% of the volume is ventilated due to occupancy of the space by furnishings and other materials. To account for this, the floor area was reduced by 10% [to 108 ft² (10 m²)] for base-case conditions in this study. A floor area of 75 ft² (7 m²) was selected for conservative analysis based solely on empirical observations of small offices in a building at The University of Texas at Austin.

School Classrooms: A single classroom was selected for analysis with parameters in accordance with California Specification 1350, specifically dimensions of 24 ft x 40 ft floor space = 960 ft² (89 m²) and ceiling height of 8.5 ft (2.59 m). As per California 1350 it is assumed that only 90% of the room volume is ventilated. This reduced volume is accounted for in this study by reducing the base-case floor area by 10% to 861 ft² (80 m²). A classroom floor area of 430 ft² (40 m²) was selected for conservative analysis.

3.5 Gaseous Reactants

d-Limonene, α -pinene and linalool alcohol were selected as gaseous reactants for this study. The two mono-terpenes (d-limonene and α -pinene) were selected as they are known to exist in most indoor environments at relatively high concentrations when compared with other terpenes and are used extensively in indoor cleaning agents (Nazaroff and Weschler, 2004; and references provided therein). Furthermore, published literature exists related to reaction rate constants with ozone and subsequent molar yields of formaldehyde and secondary organic aerosols. Linalool alcohol (often simply referred to as linalool) is a terpene alcohol with a relatively high bi-molecular reaction rate with ozone and a resulting high molar yield of formaldehyde. It is used extensively in indoor fragrance products (Letizia *et al.*, 2003). Concentrations selected for all gaseous reactants are discussed in Section 3.10.

It is important to recognize that had additional reactants been included in this analysis the maximum acceptable mass emission rates of ozone based on formaldehyde and SOA formation would have been lower. However, inclusion of additional compounds is difficult at this time due to a lack of data related to by-product yields, reaction rate constants, or typical concentrations in various indoor environments. The model derived for this study can be easily adjusted in the future to simulate other compounds that react with ozone. Appropriate bi-molecular reaction rate constants and product yields for these compounds would be required.

3.6 Bi-Molecular Reaction Rate Constants (k_j)

Bi-molecular reaction rate constants, k_j , adopted for this study are (units = ppb⁻¹hr⁻¹; temperature = 20 °C): d-limonene: $k_j = 1.84 \times 10^{-2}$; α -pinene: $k_j = 7.6 \times 10^{-3}$; linalool alcohol: $k_j = 3.96 \times 10^{-2}$. In each case values were based on Nazaroff and Weschler (2004), who presented a table of values cited in the literature.

3.7 By-Products

Formaldehyde (HCHO) and secondary organic aerosols (SOA) were selected as by-products for this analysis. Formaldehyde is a gaseous product for which there exists a wealth of published information regarding health effects, including a recent study that links in-home exposure to formaldehyde to increased risk of asthma in young children (Rumchev *et al.*, 2002). A summary of the health effects of inhaled formaldehyde is available through the United States Environmental Protection Agency's IRIS database (<http://www.epa.gov/iris/subst/0419.htm>). In addition to the known adverse health effects of formaldehyde, molar yields are available to estimate its formation from reactions between ozone and several terpenes and terpene alcohols (e.g., Calogirou *et al.*, 1999; Grosjean *et al.*, 1993; Lee *et al.*, 2006).

The term secondary organic aerosol refers to the collective particulate matter formed by nucleation or condensation of gaseous by-products generated by reactions of ozone and hydroxyl radicals with volatile organic compounds. There is a growing base of evidence that ozone-initiated reactions in buildings contribute observable and potentially significant amounts of indoor SOA mass, particularly in the presence of mono-terpenes (Rohr *et al.*, 2003; Sarwar *et al.*, 2003 and 2004; Weschler and Shields, 1999). Furthermore, during the past decade there have been numerous studies indicating that increases in fine particulate matter concentration is correlated with adverse human health effects (Davidson *et al.*, 2005; and references provided therein). While in relative terms very little research has been done to correlate indoor particulate matter with health effects, Long *et al.* (2000) indicated that indoor particulate matter may be more mutagenic than outdoor particulate matter, possibly due to greater organic matter content of particles generated indoors.

3.8 Molar Yields for Formaldehyde (y_j)

The molar yields for formaldehyde (y_j in Equations 2-5 and 2-6) vary according to the specific chemical that reacts with ozone. The following molar yields were selected for each of the three gaseous reactants described in Section 3.5: y_j (d-limonene) = 0.1 (Grosjean *et al.*, 1993), y_j (α -pinene) = 0.28 (Lee *et al.*, 2006), y_j (linalool alcohol) = 0.34 (Lee *et al.*, 2006).

3.9 Mass Yields for Secondary Organic Aerosols (γ_j)

The mass yields for secondary organic aerosol formation (γ_j in Equations 2-7 to 2-9) vary according to the specific chemical that reacts with ozone. The following mass yields were selected for each of the three gaseous reactants described in Section 3.5 (in each case the units are $\mu\text{g}/\text{m}^3$ of SOA formed per $\mu\text{g}/\text{m}^3$ terpene reacted): γ_j (d-limonene) = 0.39 (Hoffmann *et al.*, 1997; average of three experiments), γ_j (α -pinene) = 0.173 (Yu *et al.*, 1999; average of three experiments), γ_j (linalool alcohol) = 0.08 (Lee *et al.*, 2006).

Note that the values for α -pinene were determined at temperatures of 33 to 35 °C, greater than expected in most air conditioned buildings. Lower temperatures would actually lead to greater SOA yields, as described by Sarwar *et al.* (2003). The value for d-limonene was derived in the

presence of even higher temperatures (41 – 48 °C) and at elevated NO₂ concentrations, each of which should lead to reductions in SOA yield.

3.10 Concentrations of Gaseous Reactants (C_j)

Existing literature related to indoor terpene and terpene alcohol concentrations is not as robust as that for other volatile organic compounds (VOCs), particularly those VOCs that are of concern because of their explicit toxicity, e.g., benzene. Furthermore, published data related to terpene concentrations in indoor air is dominated by studies completed in the early to mid-1990s. Given changes in the nature of cleaning products and increased use of fragrances over the past decade, the concentrations of indoor terpenes and terpene alcohols may well have increased significantly. For this study best available data were used from the literature for base-case and worst-case conditions. However, the reader should be aware of the potential for some of the selected reactant concentrations to be under-estimates of conditions in buildings in 2006.

Data related to linalool alcohol concentrations in indoor air were not available in the published literature. As such, an alternate approach was used to estimate base-case and worst-case concentrations as described below. Furthermore, several of the papers reviewed for this study presented indoor d-limonene and α -pinene concentrations in $\mu\text{g}/\text{m}^3$ without specifying air temperatures during sample collection. For this study, concentrations in $\mu\text{g}/\text{m}^3$ were converted to ppb using an assumed temperature of 20 °C.

Finally, since the maximum parameter increments for formaldehyde and secondary organic aerosols were not selected based on short-term exposures, the maximum concentrations for gaseous reactants were not selected to represent short-term episodic events, e.g., cleaning activities (such as those reported by CARB 2006). Rather, maximum values were selected based on what are reasonable high concentrations that may persist over many months, e.g., due to α -pinene emissions in new homes, or indefinitely, e.g., where plug-in air fresheners might continuously emit linalool alcohol.

Residential Dwellings: Brown *et al.* (1994) completed a review of data related to VOC concentrations in 584 residential dwellings. The weighted average geometric mean (WAGM) for d-limonene was reported as 3.7 ppb, with a 98th percentile value of 35 ppb. The WAGM for α -pinene was reported to be between 0.2 and 0.9 ppb. In 66 new dwellings, for which wood products can be a major source of α -pinene, the WAGM was reported as 46 ppb with a 98th percentile value of 442 ppb. Hodgson *et al.* (2000) sampled four new manufactured homes over a two to nine month period following installation and seven new site-built homes one to two months after completion. For the manufactured homes they reported concentrations of 16 ppb (geometric mean) and 5 to 35 ppb (range) for α -pinene, and 2.9 ppb (geometric mean) and 1.1 to 6.7 ppb (range) for d-limonene. For the site-built homes they reported concentrations of 28 ppb (geometric mean) and 12 to 60 ppb (range) for α -pinene, and 5.4 ppb (geometric mean) and 2.2 to 12 ppb (range) for d-limonene. Finally, Wolkoff *et al.* (2000) summarized the literature on terpene levels in different non-industrial buildings. They reported a study of 757 homes in Canada in which the mean concentrations of α -pinene and R-limonene were 3.5 ppb and 4.1 ppb, respectively.

Based on a review of the published literature, reasonable base-case concentrations for α -pinene and limonene in residential dwellings were chosen to be 2 ppb and 4 ppb, respectively. For worst-case conditions associated with ozone emissions these concentrations were set to zero (to maximize ozone concentrations and minimize acceptable emissions). For worst-case concentrations related to by-product formation the maximum concentrations of α -pinene and limonene were chosen to be 50 ppb and 35 ppb, respectively.

Office Buildings: Daisey *et al.* (as reported in Weschler, 2000) reported a geometric mean concentration of d-limonene in six office buildings in California of 1.2 ppb. Girman *et al.* (1999) reported d-limonene and α -pinene to be amongst the most ubiquitous (81-10% frequency) VOCs inside 56 U.S. office buildings. The range of d-limonene concentrations was reported to be 0.05 to 25 ppb, with a geometric mean of 1.3 ppb, i.e., consistent with that of Daisey *et al.* Girman *et al.* (1999) reported a range of α -pinene concentrations of 0.05 to 1.5 ppb. A geometric mean concentration was not reported for α -pinene. Brown *et al.* (1994) reported WAGM and 98th percentile α -pinene concentrations of 1.4 ppb and 13.5 ppb, respectively, for new office buildings. Finally, Wolkoff *et al.* (2000) summarized the literature on terpene concentrations in non-industrial indoor environments. They reported a study of 56 European office buildings in which the mean α -pinene concentration (in toluene equivalents) was 7 ppb, with a range of 0.9 to 24 ppb. For the same study the mean concentration (in toluene equivalents) of R-limonene was 8.7 ppb, with a range of 0.2 to 68 ppb.

Based on a review of the published literature, reasonable base-case concentrations for α -pinene and limonene in office buildings were chosen to be 1.4 ppb and 1.3 ppb, respectively. For worst-case conditions associated with ozone emissions these concentrations were set to zero (to maximize ozone concentrations and minimize acceptable emissions). For worst-case concentrations related to by-product formation the maximum concentrations of α -pinene and limonene were chosen to be 14 ppb and 25 ppb, respectively.

School Classrooms: There are few reported terpene concentrations in schools. Brown *et al.* (1994) summarized reported concentrations of α -pinene in seven new schools. The WAGM and 98th percentile concentrations were reported as 2.3 ppb and 21.2 ppb, respectively. These values were adopted as base-case and worst-case (for by-product formation) concentrations, respectively, for α -pinene. Due to a lack of published data for limonene, the base-case and worst-case (for by-product formation) limonene concentrations were set equal to those for α -pinene. For worst-case conditions related to incremental ozone concentration increases the concentrations for each terpene were set equal to zero.

Linalool Alcohol Concentrations: There is a paucity of reported indoor concentrations for linalool alcohol. As such, base-case and worst-case concentrations for this compound were estimated based on a single emission factor of 148 mg/day for a plug-in scented-oil air freshener (Singer *et al.*, 2006). A steady-state concentration was calculated based on a mass balance for each of the three environments as follows:

$$C = \frac{\left\{ \frac{E \times 1,000 \mu\text{g} / \text{mg}}{\lambda V \times 24 \text{ hr} / \text{day}} \right\}}{6.4 (\mu\text{g} / \text{m}^3) / \text{ppb}} \quad (3-1)$$

Where:

- C = concentration of linalool alcohol (ppb)
- E = emission rate of linalool alcohol (mg/day)
- λ = base-case or worst-case air exchange rate (hr^{-1})
- V = base-case or worst-case building/room volume (m^3).

For the worst-case condition it was assumed that two plug-in air fresheners are always operating in a residential dwelling and a single plug-in air freshener is in operation in office and school classrooms. For these conditions the worst-case air exchange rates and floor areas described in Sections 3.1 and 3.4 were employed. For the base-case condition the linalool concentration determined with Equation 3-1 was divided by five. The rationale for doing so stems from a study in Texas in which over 900 teachers were surveyed and approximately 20% claimed to use plug-in air fresheners in their classrooms (Torres *et al.*, 2002). A similar fraction was assumed for homes and for offices.

Based on this approach and rounding to the nearest 1 or 10th ppb due to the approximate nature of this approach, the base-case linalool concentrations in residential dwellings, offices, and schools were taken to be 1 ppb, 10 ppb, and 1 ppb, respectively. For worst case conditions relative to by-product formation the linalool concentrations for residential dwellings, offices, and schools were calculated to be 30 ppb, 230 ppb, and 90 ppb, respectively. For worst-case conditions relative to ozone concentration the linalool concentration was taken to be zero.

3.11 Maximum Ozone Concentration Increment ($C_{\text{O}_3, \text{max}}$)

Determination of a maximum acceptable ozone concentration increase due to an indoor source is difficult for several reasons. Past epidemiological studies have focused on human health effects correlated to central outdoor ozone monitoring stations (e.g., Triche *et al.*, 2006, amongst several others). These studies have failed to take into account that exposure to ozone is often dominated by the air that humans inhale while indoors, even when the primary source is outdoors. As such, threshold concentrations determined from such studies may be over-estimated by an explicit focus on outdoor ozone concentrations when corresponding indoor concentrations (which a large fraction of the population inhales in greater quantities than in outdoor air) are actually substantially lower. Further, variability in building design and operation can have a significant impact on the ratio of indoor-to-outdoor ozone concentrations and may lend substantial uncertainty to correlations based on central monitoring sites. For example, individuals who live in relatively “tight” homes in Houston, Texas, during the worst of the summer ozone season may actually be exposed to less ozone than individuals who live in “leaky” homes in cities where outdoor ozone concentrations are generally far lower than in Houston. Similarly, those who live in homes in Houston that are within a small radius of a centralized outdoor monitoring station may have substantially different exposures to ozone because of a wide spectrum of indoor-to-outdoor ozone concentration ratios between their homes.

An indoor ozone concentration increase of 50 ppb is often cited as a maximum acceptable value by those who manufacture or market devices that intentionally or unintentionally release ozone to indoor environments. However, the rationale for this concentration increase is tenuous at best, and does not appear to have a sound scientific basis. An increment of 50 ppb first appeared in the Federal Register in 1972 (U.S. Department of Health, Education, and Welfare, 1972). Specifically, the Department of Health, Education, and Welfare in a proposed statement of policy on ozone generators and other devices emitting ozone made the following statement: "*More recently, the American Society of Heating, Refrigerating and Air Conditioning Engineers recommended that the maximum concentration in an air conditioning and ventilation system, be 0.05 part per million in occupied areas, such as homes and hospitals, where people may be exposed continuously for up to 24 hours a day.*" The author was not able to find a published rationale upon which the American Society of Heating, Refrigerating and Air Conditioning Engineers based their recommendation. Interestingly, the original statement in the Federal Register went on to read: "*Data available to the Food and Drug Administration indicate that ozone has no useful medical application and that, in tests conducted to study the bactericidal properties of ozone, test animals have died before the bacteria were completely destroyed.*"

Trische *et al.* (2006) completed a study to assess the respiratory effects of ozone on infants. A total of 691 infants were followed for 83 days during summertime conditions in Roanoke, Virginia. The authors studied the frequency of wheeze, coughing, and difficulty breathing and correlated these observations to peak 1-hour, maximum 8-hour, and 24-hour average ozone concentrations measured at a centralized monitoring site. During the study the outdoor ozone concentrations were relatively low. The mean 8-hour maximum ozone concentration was 54.8 ppb, and exceeded the National Ambient Air Quality Standard (NAAQS) of 85 ppb only twice during the study. The mean peak 1-hour ozone concentration was 60.8 ppb. The mean 24-hour ozone concentration was 35.2 ppb +/- 8.4 ppb. Results indicated that the 24-hour average ozone concentration was more consistently and strongly associated with acute respiratory symptoms in infants than either the 1-hour or 8-hour averages. The same-day mean 24-hour average ozone concentration had a statistically significant association with both wheeze and difficulty breathing, with odds ratios (OR) of 1.32 for wheeze and 1.10 for difficulty breathing. The strongest correlation was observed in infants with mothers who had asthma, with same-day mean 24-hour ozone concentrations leading to OR = 1.65 and 2.14 for wheeze and difficulty breathing, respectively.

Bell *et al.* (2006) used four different statistical models (linear, subset, threshold, and spline) to analyze ozone and mortality data collected for 98 U.S. urban communities between 1987 and 2000. Ozone measurements at ambient monitors were used as a surrogate for community-level exposure. The actual measure of exposure was taken as the average of the same and previous days' ozone concentrations, referred to as "lag 01". The authors observed that daily increases in ambient ozone concentrations were significantly associated with daily increases in the number of deaths, on average, across the 98 U.S. communities. For example, the percentage increase in all-cause mortality associated with a 10-ppb increase in lag01 ozone concentrations was 0.30% when the data set included only days with a daily 8-hour maximum ozone concentration lower than the NAAQS for ozone. Daily changes in ambient ozone concentrations were significantly associated with daily changes in the number of deaths, on average, even when data were limited to lag01 average ozone concentrations less than 15 ppb. The authors observed that the

association between ozone concentrations and mortality declined and lost significance only when the ozone concentrations were limited to less than 10 ppb, but cautioned that the data sets are substantially reduced in size when forcing such limitations. Based on this analysis the authors concluded that, "...the subset approach suggests that a "safe" ozone level would be lower than approximately 10 ppb, for the lag01 daily ozone level, which is roughly 15-19 ppb for the maximum 8-hr average." It is important to recognize that the stated 10 ppb lag01 ozone concentration is based on outdoor measurements. If the majority of exposure occurs indoors, the indoor threshold concentration associated with 10 ppb outdoor ozone concentration would be considerably lower.

The two recent studies described above (Bell *et al.*, 2006; Triche *et al.*, 2006) deal with two different receptor groups (infants and the general population) and two different health outcomes (respiratory stress in infants and death in the general population). Each study lends new insight into the effects of ozone at concentrations less than those established as regulatory standards to protect the general public. However, each was based on correlations between health outcomes and outdoor ozone concentrations, and did not account for the fact that, on average, both the general population and infants spend much more time indoors, where the corresponding ozone concentrations are lower than outdoors.

Weschler (1998) reported typical ranges of indoor-to-outdoor ozone concentrations of 0.2 to 0.7. Taking the product of this range to the 10 ppb maximum threshold value predicted by Bell *et al.* (2006) leads to a range of indoor concentrations of 2 to 7 ppb. Taking the product of this range to the 35.2 mean 24-hour ozone concentration reported by Triche *et al.* (2006) and dividing by two for a factor of safety (Triche *et al.* did not report a threshold concentration) leads to a range of 3.5 to 12 ppb.

Based on the studies described above, a base-case maximum acceptable ozone concentration increment of 5 ppb was chosen for this study, with a worst-case (conservative) concentration increment of 2 ppb. These concentrations are much lower than the often-cited 50 ppb recommendation, but are based on peer-reviewed and robust data sets, as opposed to the original recommendation, and benefit from a nearly 35-year improvement in the scientific knowledge base relative to the original recommendation published in 1972.

3.12 Maximum Formaldehyde Concentration Increment ($C_{p,max}$)

The health effects of formaldehyde (HCHO) are well established relative to many other indoor air pollutants. Formaldehyde is a known eye irritant and listed as a California toxic air contaminant (TAC) (Nazaroff and Weschler, 2004). The international Agency for Research on Cancer (IARC) reclassified HCHO in June 2004 as Carcinogenic to Humans (IARC, 2004). The inhalation unit risk factor (probability of contracting cancer for continuous exposure to $1 \mu\text{g}/\text{m}^3$ in air) for HCHO is 1.3×10^{-5} , i.e., each increase in lifetime exposure of $1 \mu\text{g}/\text{m}^3$ in air leads to an increased probability of cancer of 13 in a million (U.S. Environmental Protection Agency, 2006).

Formaldehyde poses a long-term hazard to the human respiratory system with a chronic reference exposure level (REL) of $3 \mu\text{g}/\text{m}^3$ (2 ppb at 20°C); RELs represent exposure

concentrations that pose no significant health risks to individuals indefinitely exposed to that concentration. The California Department of Health Services (2004) makes HCHO the only exception to their maximum allowable target chemical concentrations caused by any indoor source, which is usually taken to be one-half the REL. Although the chronic REL for HCHO is $3 \mu\text{g}/\text{m}^3$, the indoor REL for HCHO is adjusted upward to $33 \mu\text{g}/\text{m}^3$ (26 ppb at 20°C) for California Specification 1350. As such, the maximum acceptable HCHO concentration increase from any source is taken to be 13 ppb (50% of 26 ppb).

For this study, the base-case maximum acceptable formaldehyde concentration was set as 13 ppb, as per California Specification 1350. The worst-case (conservative) maximum acceptable formaldehyde concentration was chosen to be 3 ppb, slightly greater than the chronic REL.

3.13 Maximum SOA Concentration Increment ($C_{\text{SOA,max}}$)

Selection of a maximum acceptable increase in indoor secondary organic aerosol (SOA) concentration is difficult for several reasons. Nearly all of the research that has been completed on the health effects of fine particulate matter has focused on outdoor particles. Associated health impacts include respiratory problems, changes in heart rhythm, heart attacks, and severe respiratory and heart malfunctions that lead to death (Davidson *et al.*, 2005). Furthermore, both the physical and chemical compositions of particles are likely to influence these health impacts, and can be considerably different between outdoor and indoor particles (particularly chemical composition), making it presumptuous to apply health associations derived from outdoor particulate matter concentrations to indoor environments. This limitation is far different than the case of ozone, which is the same molecule indoors as outdoors.

Secondary organic aerosol formation always contributes to $\text{PM}_{2.5}$ (mass concentration of particles with aerodynamic diameters less than $2.5 \mu\text{m}$) (Sarwar *et al.*, 2003 and 2004; Weschler and Shields, 1999). As such, for this study it was decided that the criterion for the maximum acceptable indoor concentration increase for SOA would be a fraction of the USEPA's National Ambient Air Quality Standard (NAAQS) for $\text{PM}_{2.5}$. The annual average NAAQS of $15 \mu\text{g}/\text{m}^3$ was selected to err on the conservative side. For this study, a maximum acceptable SOA concentration increase of $5 \mu\text{g}/\text{m}^3$ was selected. This concentration is one-third of the annual average NAAQS, a somewhat arbitrary fraction of the NAAQS but one that seems "reasonable" based on a general lack of knowledge on the health effects of indoor SOA. The worst-case (conservative) maximum acceptable increase in SOA was chosen to be $2 \mu\text{g}/\text{m}^3$ for this study.

4. MODEL APPLICATIONS

4.1 Base-Case Conditions

Maximum acceptable ozone emission rates for base-case conditions are listed in Table 4-1 for each of the three indoor environments considered in this study. Emission rates are listed for each of the three criteria used as maximum acceptable concentrations (ozone, formaldehyde and SOA). The last column in the table is simply the minimum of the maximum acceptable ozone emission rates.

Table 4-1. Maximum acceptable ozone emission rates [mg/hr (µg/min)] for **base-case** conditions.

Criteria (across) → Environment (below)	Ozone	Formaldehyde	SOA	Limiting (mg/hr)
Residential	17.5 (292)	930 (15,433)	48 (803)	17.5 (292)
Office	1.3 (22)	19 (312)	4 (66)	1.3 (22)
School	9.9 (166)	1,000 (17,168)	71 (1,176)	9.9 (166)

For base-case conditions the limiting emission rate was always defined by the base-case maximum incremental ozone concentration increase of 5 ppb. The most restrictive value is for a single office (1.3 mg/hr), and is similar to ozone emission rates from laser printers (Weschler, 2000, and references presented therein), and generally in the range of ozone emissions from portable ion generators (Mullen *et al.*, 2005, and references provided therein). The least restrictive limiting emission rate was 17.5 mg/hr for an entire house, slightly more than one-half the value of an explicit ozone generator tested by Mullen *et al.* (2005). The maximum acceptable ozone emission rate for a base-case formaldehyde increment of 13 ppb was quite large (19 mg/hr for offices to 1,000 mg/hr for school classrooms), and within the range of values reported for explicit ozone generators (Kissel, 1993). It is clear from this analysis that base-case incremental increases in formaldehyde should not be used to define a maximum acceptable ozone emission rate.

4.2 Worst-Case Conditions

Maximum acceptable ozone emission rates for worst-case (conservative) conditions are listed in Table 4-2 for each of the three indoor environments considered in this study. As expected, the maximum acceptable ozone emission rates for worst-case (conservative) conditions are much lower than those for base-case conditions, on the order of 1 to 3 orders of magnitude lower.

In contrast to the base-case condition, for the conservative (“worst-case”) analysis the maximum ozone emission rate was always limited by incremental increases in secondary organic aerosol (SOA) concentration. For each environment, even entire residential dwellings, the acceptable ozone emission rate was generally less than unintentional ozone emissions from a single portable

ion generator as reported by Mullen *et al.* (2005), or from single laser printers or photocopy machines (Weschler, 2000, and references provided therein).

Table 4-2. Maximum acceptable ozone emission rates [mg/hr (µg/min)] for **worst-case** conditions.

Criteria (across) → Environment (below)	Ozone	Formaldehyde	SOA	Limiting*
Residential	1.9 (32)	2.4 (40)	0.45 (7.5)	0.45 (7.5)
Office	0.21 (3.5)	0.1 (1.7)	0.041 (0.68)	0.041 (0.68)
School	1.1 (18)	0.32 (5.3)	0.13 (2.2)	0.13 (2.2)

The maximum acceptable ozone emission rates listed in Table 4-2 are based on model parameters that are individually realistic, but that collectively are likely a small fraction of indoor conditions. As such, the ozone emission rates listed in Table 4-2 should be considered as having a significant built-in safety factor for most indoor scenarios. The values in the right-hand column should be considered as maximum acceptable ozone mass emission rates for situations that involve particularly sensitive individuals, e.g., the elderly, infants, and those with respiratory illnesses.

4.3 Sensitivity Analysis

Results of sensitivity analyses are described in Section 4.3.1 through 4.3.3 below. Each section corresponds to a different type of pollutant increment (ozone, HCHO, SOA), and includes results for detached single-family homes, office, and school classrooms. In the resulting sensitivity figures, the bars corresponding to “High Parameter” refer to the percentage change in maximum acceptable ozone mass emission rate for a factor of two increase in the denoted parameter, with all other parameters set at the base-case condition. The bars corresponding to “Low Parameter” refer to the percentage change in maximum acceptable ozone mass emission rate for a factor of two decrease in the denoted parameter, with all other parameters set at the base-case condition.

For all analyses, percentage change from base case conditions is defined as follows:

$$\% \text{ Change} = \frac{E_{\text{max,change}} - E_{\text{max,bc}}}{E_{\text{max,bc}}} \times 100 \quad (4-1)$$

Where,

- $E_{\text{max,change}}$ = maximum acceptable ozone emission rate after change (mg/hr)
- $E_{\text{max,bc}}$ = maximum acceptable ozone emission rate (Table 4-1) for base-case (mg/hr).

For each of the scenarios described below, the 50% (factor of 2) *decrease* and 100% (factor of 2) *increase* in maximum acceptable ozone emission rates for changes in the pollutant (ozone, HCHO, SOA) increment, ceiling height, and floor area, are predictable based on the equations presented in Section 2. While predictable, these results underscore the importance of the selection of the acceptable incremental ozone, formaldehyde, and SOA concentration increases,

as well as the base-case room volume as defined by floor area and ceiling height. The discussion provided in the remainder of Section 4.3 focuses on the other key parameters that influence model predictions.

4.3.1 Results Based on Ozone Increment

The sensitivities of maximum acceptable ozone emission rates based on acceptable ozone concentration increment for factor of two variations in model parameters are shown in Figures 4-1 through 4-3 for homes, offices, and school classroom, respectively. The sensitivities to variations in model parameters are largely similar for each type of environment under the base-case conditions chosen for this study.

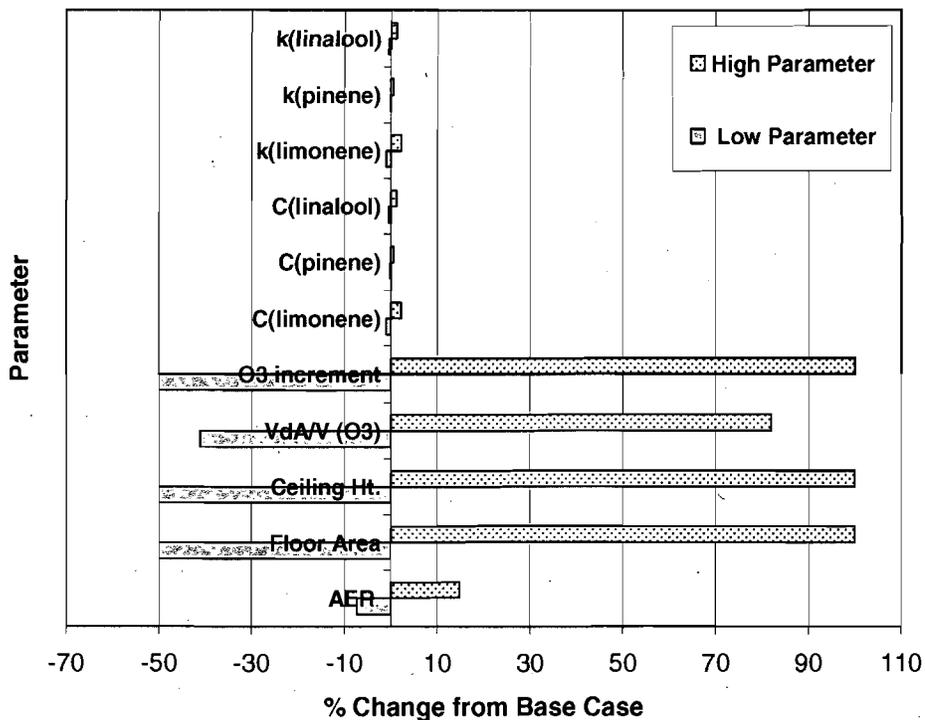


Figure 4-1. Sensitivity of acceptable ozone emission rates in **homes** for factor of two increases (high parameter) and decreases (low parameter) in model parameters, and criterion **based on maximum acceptable ozone concentration**. Here (and in all subsequent figures), k is the bi-molecular reaction rate constant between ozone and reactant in parentheses, C is the concentration of the reactant in parentheses, and AER is the air exchange rate.

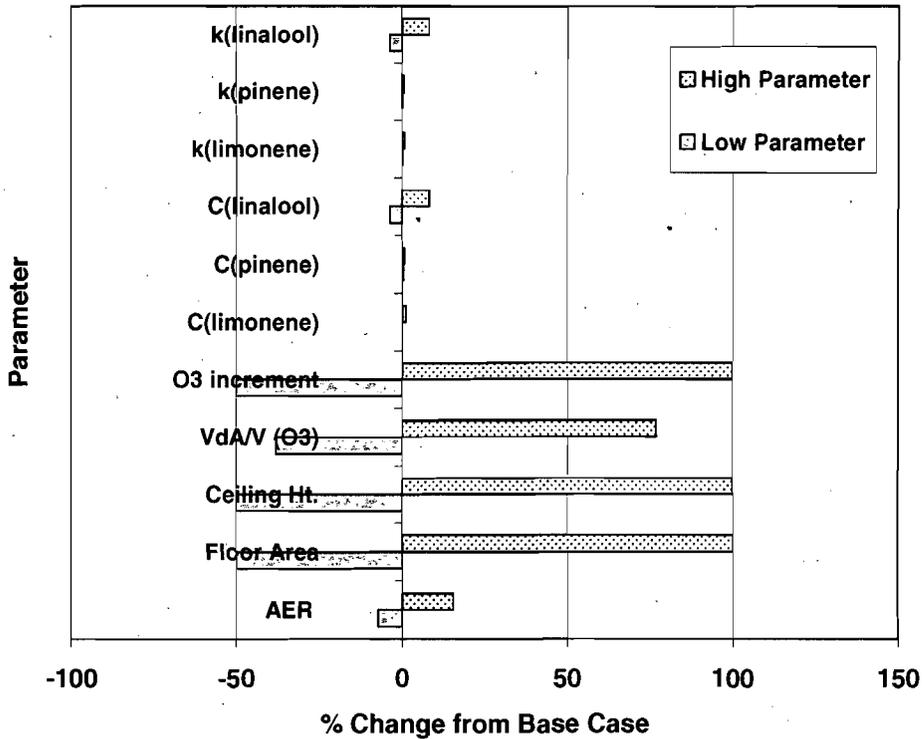


Figure 4-2. Sensitivity of acceptable ozone emission rates in **offices** for factor of two increases (high parameter) and decreases (low parameter) in model parameters, and criterion **based on maximum acceptable ozone concentration**.

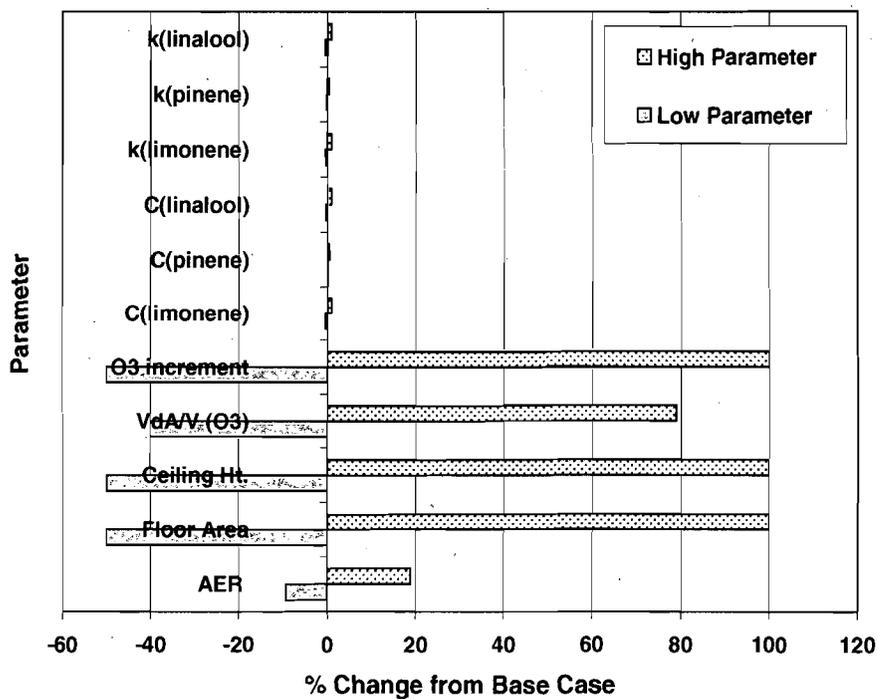


Figure 4-3. Sensitivity of predicted maximum acceptable ozone emission rates in **school classrooms** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable ozone concentration**.

For each indoor environment the ozone concentration is dominated by ozone reactions with indoor materials, as opposed to bi-molecular reactions in air or even air exchange. Thus, results are highly sensitive to variations in the ozone decay rate term ($v_d A/V$). The acceptable ozone emission rate for each indoor environment is not a strong function of bi-molecular reaction rate constant or reactant concentrations when varied around the base-case condition. It is somewhat more sensitive to air exchange rate (e.g., 10-20% increase in maximum acceptable ozone emission rate with factor of two increases in air exchange rate). However, the air exchange rate tends to be relatively small in comparison to ozone removal by reactions at surfaces.

The significance of variations in the ozone decay rate is an important result given expected differences in ozone decay rates depending on the nature of indoor materials that react with ozone. For example, homes, offices, or classrooms that contain a significant amount of “clutter” and/or fleecy materials are expected to have greater ozone decay rates, and therefore maximum acceptable ozone emission rates that exceed the base case condition. The opposite would be true for “minimalist” or “uncluttered” environments with less reactive materials. It is important to note, however, that greater ozone reactions with indoor materials would allow for greater ozone emissions based solely on acceptable ozone concentration increments, but an increase in such reactions would also lead to greater by-products such as carbonyls (aldehydes and ketones) and secondary organic aerosols. Existing literature is too sparse on this subject to allow for reasonable estimates of by-product formation.

4.3.2 Results Based on HCHO Increment

The sensitivities of maximum acceptable ozone emission rates based on acceptable formaldehyde concentration increment for factor of two variations in model parameters are shown in Figures 4-4 through 4-6 for homes, offices, and school classroom, respectively. The sensitivities to variations in model parameters are largely similar for each type of environment under the base-case conditions chosen for this study.

As with ozone, the maximum acceptable ozone emission rate based on formaldehyde formation (concentration increment) is highly sensitive to the ozone decay rate; greater ozone decay leads to less ozone, less formaldehyde formation, and therefore a greater ozone emission rate to yield the acceptable formaldehyde concentration increment.

In contrast to results based on maximum acceptable ozone concentration increment, those for formaldehyde were much more sensitive to reactant concentrations and rate constants, particularly for linalool. Linalool has a significant bi-molecular rate constant with ozone, and a higher molar yield for formaldehyde than either d-limonene or α -pinene. As such, a factor of two increase in linalool concentration leads to, for example, a 35% reduction in the maximum acceptable ozone emission rate for homes. Conversely, a factor of two decrease in linalool concentration leads to a 35% increase in maximum acceptable ozone emission rate for homes, based on the set criteria for maximum acceptable increase in formaldehyde concentration.

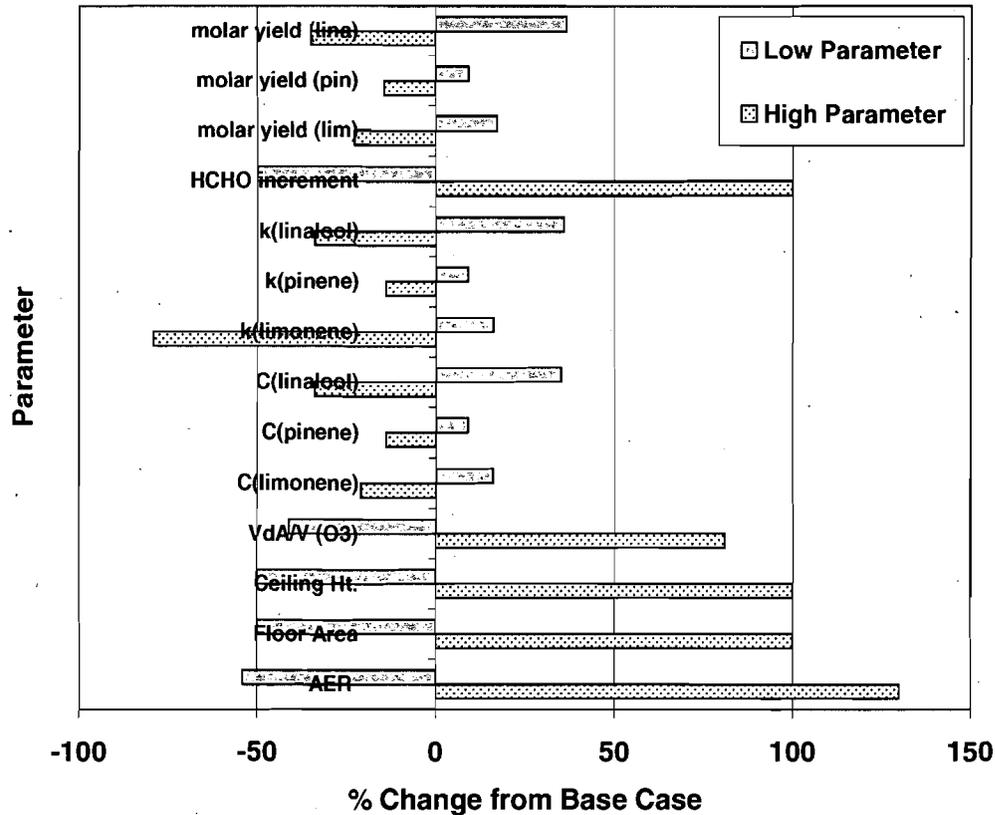


Figure 4-4. Sensitivity of predicted maximum acceptable ozone emission rates in **homes** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion based on maximum acceptable formaldehyde concentration.

As shown in Figure 4-4 to 4-6, the maximum acceptable ozone emission rate based on formaldehyde increment is highly sensitive to changes in air exchange rate. This is because the air exchange rate limits the time available for reactions that lead to the formation of formaldehyde. As such, an increase in air exchange rate reduces available reaction time, leads to less formaldehyde formation, and thus a larger maximum acceptable ozone emission rate. For example, in this analysis a factor of two increases in air exchange rate lead to a 130% increase in maximum acceptable ozone emission rate for homes, offices & classrooms. Conversely, a factor of two decrease in air exchange rate lead to a 54% decrease in maximum acceptable ozone emission rate for homes, offices & classrooms.

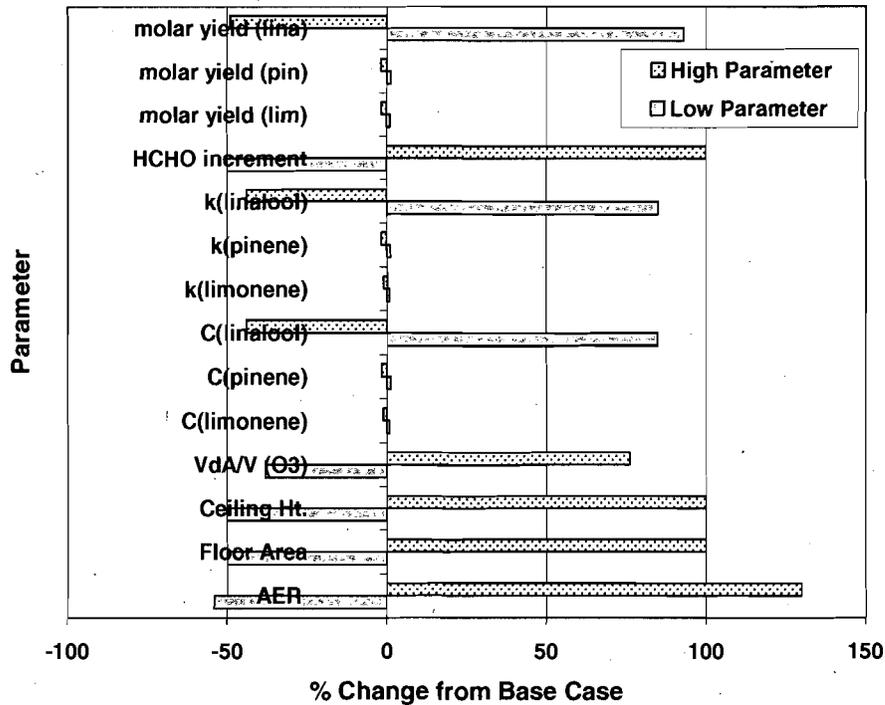


Figure 4-5. Sensitivity of predicted maximum acceptable ozone emission rates in **offices** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion based on maximum acceptable formaldehyde concentration.

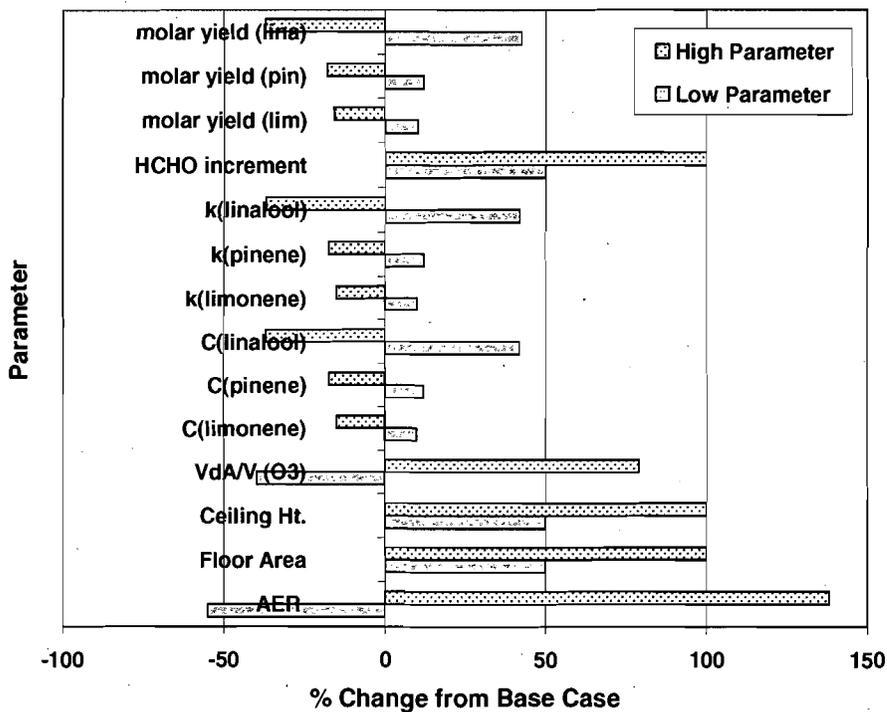


Figure 4-6. Sensitivity of predicted maximum acceptable ozone emission rates in **school classrooms** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion based on maximum acceptable formaldehyde concentration.

4.3.3 Results Based on SOA Increment

The sensitivities of maximum acceptable ozone emission rates based on acceptable secondary organic aerosol (SOA) concentration increment for factor of two variations in model parameters are shown in Figures 4-7 through 4-9 for homes, offices, and school classroom, respectively. The sensitivities to variations in model parameters are largely similar for each type of environment under the base-case conditions chosen for this study.

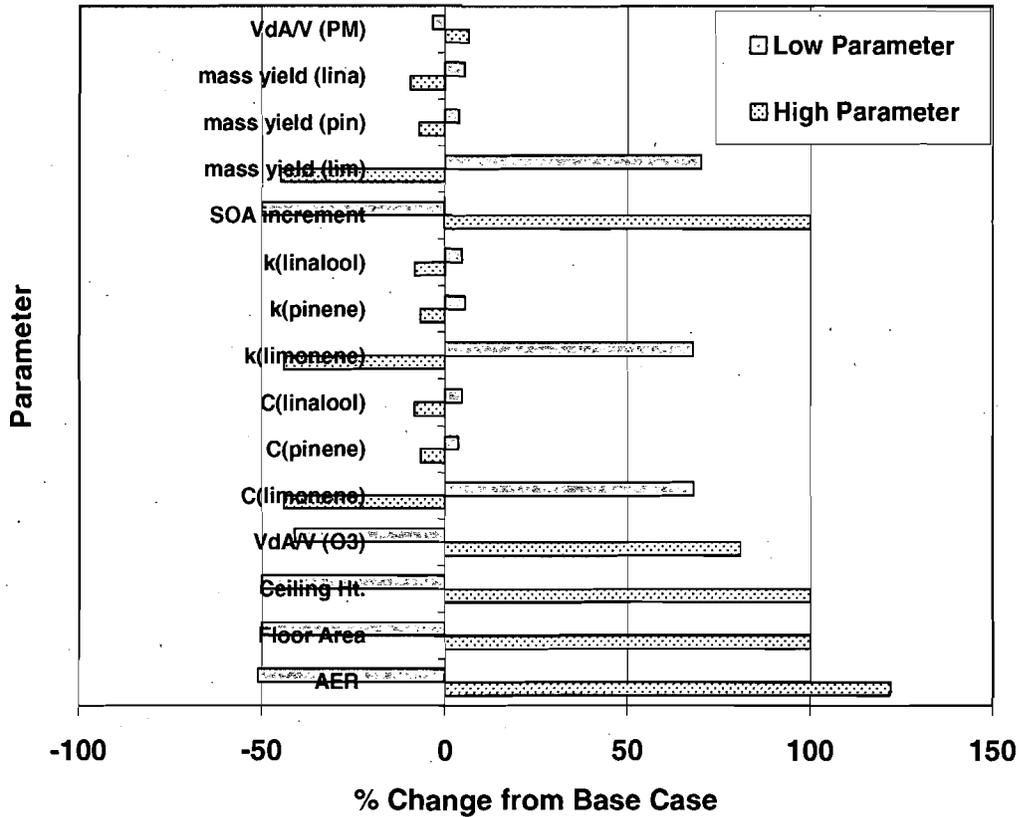


Figure 4-7. Sensitivity of predicted maximum acceptable ozone emission rates in **homes** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion based on maximum acceptable SOA concentration.

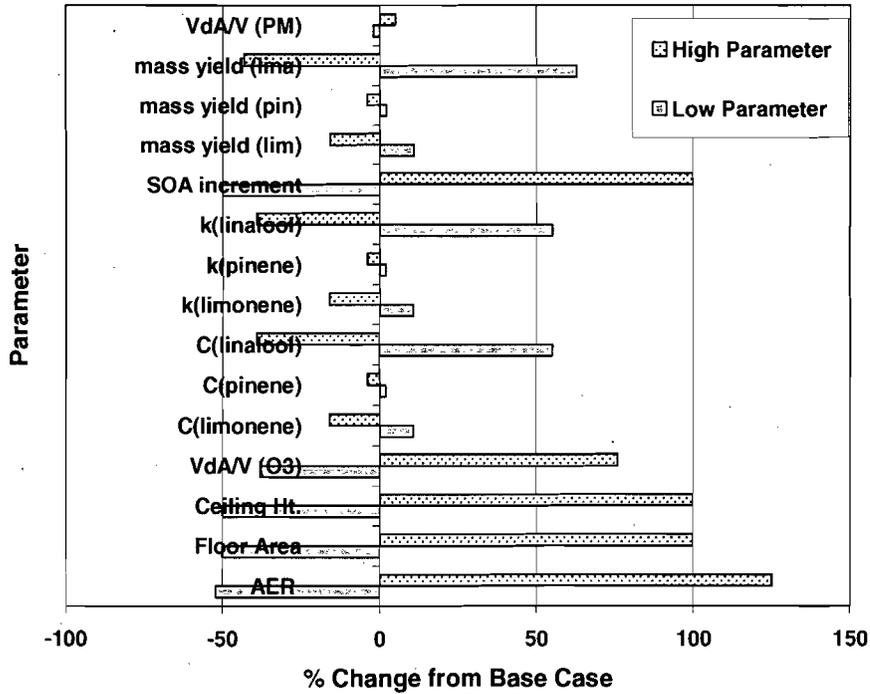


Figure 4-8. Sensitivity of predicted maximum acceptable ozone emission rates in **offices** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion based on maximum acceptable SOA concentration.

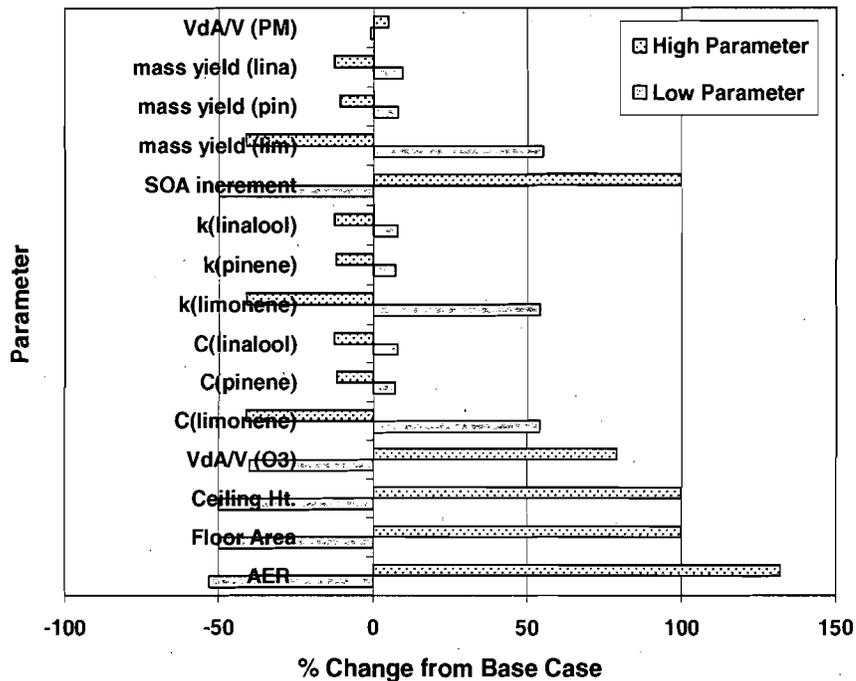


Figure 4-9. Sensitivity of predicted maximum acceptable ozone emission rates in **school classrooms** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion based on maximum acceptable SOA concentration.

Results were similar to those for the HCHO increment with respect to the sensitivity of results associated with homogeneous reactions. Again, the formation of SOA depends on the presence of ozone and reactants, and was therefore sensitive to reactant concentrations, bi-molecular reaction rate constants, mass yields for SOA, and the air exchange rate (which affects time for reactions to occur). Unlike the case of HCHO, changes in parameters (bi-molecular reaction rate constants, reactant concentration, and SOA mass yields) associated with d-limonene lead to the greatest sensitivity in the maximum acceptable emission rates for ozone. This is not surprising in so much as the SOA yield associated with the limonene/ozone reaction is over twice that of the yield for the α -pinene/ozone reaction, and nearly five times that for the linalool/ozone reaction. Increases in any of these parameters lead to decreases in the maximum acceptable ozone mass emission rate, due to the formation of greater quantities of secondary organic aerosol mass.

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APPENDIX A. GLOSSARY

Acetaldehyde: CH_3COH ; a sour tasting/smelling aldehyde. Classified by the IARC as a Group 2B carcinogen (possibly carcinogenic to humans).

AER: Air Exchange rate – see (Outside) Air exchange rate

Alcohol: A chemical containing an $-\text{OH}$ group.

Aldehyde: A carbonyl connected to a hydrogen atom and to an alkyl group.

Bi-molecular reaction: A chemical reaction that involves two molecules.

Building envelope penetration factor (p): The fraction of a pollutant in outdoor air that makes it indoors as air flows through a building envelope, e.g., cracks around windows.

By-product: A chemical that is formed as a result of a chemical reaction.

CA 1350: California specific 1350, a California standard limiting the emissions of some chemicals from some products used in California High Performance Schools.

California 1350: See CA 1350.

Carbonyl: A chemical that has a $\text{C}=\text{O}$ bond and that is connected to an alkyl group and a hydrogen atom or second alkyl group. The carbonyl family consists of aldehydes and ketones.

Carboxylic acid: A chemical that contains a carboxyl group ($\text{C}=\text{O})\text{OH}$

Concentration: The amount of a gaseous chemical or particulate matter per amount of air within which the gas or particle is suspended. Concentrations are typically reported in parts of pollutant per million (or billion) parts of air on a volume basis (for gases), or mass of pollutant per unit volume of air (for gases or particles).

Criegee bi-radical: A short-lived intermediate of ozone reactions with unsaturated organic compounds.

Formaldehyde: HCHO . A gaseous pollutant classified by the IARC as a Group 1 Carcinogen (carcinogenic to humans). It is emitted from engineered wood products and several other sources found in buildings. It is also formed as the result of bi-molecular reactions between ozone and certain unsaturated organic compounds.

Geometric mean: The n th root of the product of n numbers. $[\text{a}(1) \times \text{a}(2) \times \text{a}(3) \times \dots \times \text{a}(n)]^{1/n}$

Heterogeneous reaction: A chemical reaction that occurs at surfaces.

Homogeneous reaction: A chemical reaction that occurs in air (or other fluid medium).

HVAC: Heating, ventilating and air conditioning.

Hydroxyl radical: A molecule consisting of one oxygen and one hydrogen atom (OH*) and that has an unpaired electron. A major source of hydroxyl radical formation is reactions between ozone and unsaturated organic compounds. Hydroxyl radicals are highly reactive with a wide range of indoor pollutants, and leads to the formation of, amongst other chemicals, carbonyls and carboxylic acids.

Infiltration: The flow of air from outdoors to the interior of a building, through cracks and other such openings in the envelope of a building.

IARC: International Agency for Research on Cancer. See www.IARC.fr.

IRIS: Integrated Risk Information System, a USEPA database of human health effects that may result from exposure to various substances found in the environment. See <http://www.epa.gov/iris/>.

Ketone: A carbonyl ($R_1R_2C=O$) in which R_1 and R_2 are organic functional groups other than the hydrogen atom.

d-Limonene: A monoterpene ($C_{10}H_{16}$) that is derived from citrus and used to provide lemon scents.

Linalool (or Linalool alcohol): A terpene alcohol that is common in fragrances and floral scented personal care products such as perfume. The molecular formula for linalool is $C_{10}H_{18}O$.

Maximum acceptable ozone emission rate: The ozone mass emission rate (mass/time) that leads to a maximum acceptable concentration of ozone, or of formaldehyde or secondary organic aerosol. The latter two pollutants are by-products of ozone reactions with terpenes and terpene alcohols.

Median air exchange rate: The air exchange rate for which 50% of buildings have higher values and 50% have lower values.

Molar yield: Moles of by-product formed per mole of ozone or hydrocarbon (e.g., terpene) reacted.

Monoterpenes: A group of terpenes, each of which has the molecular formula $C_{10}H_{16}$, but differ in the structural placement of atoms in the molecular structure.

Mutagenic: Causes cell mutations, e.g., that might lead to cancer or to birth defects.

Nitrate radical: A molecule with the molecular formula NO_3^* , and that has an unpaired electron. Nitrate radicals are highly reactive with a wide range of indoor pollutants, and leads to the formation of, amongst other chemicals, nitric acid and organic nitrates.

Nitric acid: A molecule with the molecular formula HNO_3 . It is formed by nitrate radical reactions with organic molecules. A major source of nitrate radical formation is the reaction between ozone and nitrogen dioxide.

Nitrogen dioxide: A molecule with the molecular formula NO_2 . It is formed in urban ambient air, but is also emitted from indoor combustion devices such as gas stoves. It can react with ozone to form nitrate radicals (see above).

Nucleation: Forming a cluster, as in liquid out of a vapor

Organic nitrates: An organic compound that contains NOO.

(Outside) air exchange rate (AER): The rate at which outdoor air “exchanges” with indoor air. It is calculated as the volumetric flow rate of air from outdoors into an indoor space, divided by the volume of the indoor space. The units of air exchange rate are time^{-1} , where time is usually taken to be hours (hr^{-1}).

Ozone: A molecule comprised entirely of three oxygen atoms (O_3). Ozone is a major component of outdoor photochemical smog, formed in the presence of volatile organic compounds, oxides of nitrogen, and sunlight. It is also emitted indoors from laser printers, dry-toner photocopy machines, ion generators, and explicit ozone generators. Ozone is a strong oxidizing agent and engages substantially in indoor heterogeneous chemistry, and to a lesser extent in indoor homogeneous chemistry. Ozone is a lung irritant. Recent research shows that ozone has a greater impact on health, and at lower levels, than previously understood, including observable increases in mortality with relatively small increases in outdoor ozone concentrations.

Ozone decay rate: A first order decay rate constant associated with ozone reactions with indoor surfaces. The ozone decay rate is actually the product of an ozone deposition velocity and indoor surface area, divided by indoor volume. The units of ozone decay rate are the same as those for air exchange rate (time^{-1}).

Ozonide: A short-lived intermediate compound formed by the reaction of ozone with an unsaturated hydrocarbon.

Perfluorocarbon (tracer gas): A fluorine-containing chemical that is inert (non-reactive) and that is often used to determine air exchange rates of buildings.

Photochemical smog: A “soup” of gaseous chemicals and particulate matter formed from reactions between volatile organic compounds (VOCs), oxides of nitrogen (NO_x), and sunlight. Major components of photochemical smog include ozone, formaldehyde, and secondary organic aerosols, amongst many other pollutants.

α -Pinene: A monoterpene ($C_{10}H_{16}$) that is derived from pine oils and used to produce pine scents.

PM_{2.5}: Mass concentration of particles with an aerodynamic diameter less than 2.5 μm .

Secondary organic aerosol (SOA): A group of particles suspended in air and formed as a result of gaseous reactions in air. Major sources of SOA include reactions between ozone and terpenes or terpenoids.

Sensitivity analysis: A process by which parameters in a model are varied in order to ascertain the sensitivity of model output (results) to variations in the magnitudes of individual (or grouped) parameters.

Terpene: Molecules which are generally multiples of isoprene, i.e., with a general molecular formula $(C_5H_8)_n$. $n = 1$ is isoprene. If $n=2$ the terpene is a monoterpene. If $n = 3$ the compound is a sesquiterpene.

Terpene alcohol: A terpene with an $-OH$ group added, such as linalool alcohol.

Terpenoid: A large class of naturally occurring organic chemicals derived from five-carbon isoprene units assembled and modified in various configurations.

Unsaturated organic compound: An organic compound that contains one or more carbon-carbon double bonds ($C=C$). Unsaturated aliphatic compounds are particularly reactive with ozone in indoor environments.

APPENDIX B. MODEL DERIVATION

Derivation of Equations 2-1 and 2-2

$$C_{O_3} = \frac{p\lambda C_{O_3,out} + E_{O_3}^*}{\lambda + v_d^* + \sum k_j C_j} \quad (2-1)$$

$$C_{O_3} = \frac{E_{O_3}^*}{\lambda + v_d^* + \sum k_j C_j} \quad (2-2)$$

Where:

- C_{O_3} = indoor ozone concentration or incremental concentration increase (ppb)
- $C_{O_3,out}$ = outdoor ozone concentration (ppb)
- p = building envelope penetration factor for ozone (unitless)
- λ = air exchange rate (hr^{-1})
- v_d^* = ozone decay rate (hr^{-1})
- k_j = bi-molecular reaction rate constant for ozone reaction with reactant j ($ppb^{-1} \cdot hr^{-1}$)
- C_j = reactant j, e.g., d-limonene, concentration (ppb)
- $E_{O_3}^*$ = volume normalized molar emission rate of ozone ($ppb \cdot hr^{-1}$).

For this analysis the concentration of reactants are assumed to be constant and not affected by the release of ozone to the indoor environment from an indoor source.

The starting point for derivation of Equations 2-1 and 2-2 is a mass balance for ozone on a well-mixed interior space:

$$V \frac{dC_{O_3}}{dt} = pQC_{O_3,out} - QC_{O_3} - v_d C_{O_3} A - \sum k_j C_j C_{O_3} V + E_{O_3} \quad (A-1)$$

Where:

- V = volume of interior space under consideration (m^3)
- Q = ventilation rate (volumetric flow of outdoor air into the interior space) ($m^3 \cdot hr^{-1}$)
- v_d = ozone deposition velocity ($m \cdot hr^{-1}$)
- A = area of surfaces to which ozone deposits (reacts on) (m^2)
- E_{O_3} = molar emission rate of ozone ($ppb \cdot m^3 \cdot hr^{-1}$).

All other variables are as described above.

Dividing through both sides of Equation A-1 by volume leads to:

$$\frac{dC_{O_3}}{dt} = p \frac{Q}{V} C_{O_3,out} - \frac{Q}{V} C_{O_3} - v_d \frac{A}{V} C_{O_3} - \sum k_j C_j C_{O_3} + \frac{E_{O_3}}{V} \quad (A-2)$$

But, $Q/V = \lambda$ (air exchange rate), $v_d A/V = v_d^*$ (ozone decay rate), and $E_{O_3}/V = E_{O_3}^*$ (volume normalized ozone emission rate of ozone), all as described above. Therefore, Equation A-2 becomes:

$$\frac{dC_{O_3}}{dt} = p\lambda C_{O_3,out} - \lambda C_{O_3} - v_d^* C_{O_3} - \sum k_j C_j C_{O_3} + E_{O_3}^* \quad (A-3)$$

At steady-state there are no changes in ozone concentration with time, so the left-hand-side of Equation A-3 is zero. Also, the terms containing C_{O_3} can be factored and moved from the right-hand-side of the equation to the left-hand-side (note that C_{O_3} inside the summation sign is a constant and can be moved outside of the summation):

$$(\lambda + v_d^* + \sum k_j C_j) C_{O_3} = p\lambda C_{O_3,out} + E_{O_3}^* \quad (A-4)$$

Solving Equation A-4 for C_{O_3} leads to Equation 2-1:

$$C_{O_3} = \frac{p\lambda C_{O_3,out} + E_{O_3}^*}{(\lambda + v_d^* + \sum k_j C_j)} \quad (2-1)$$

If only incremental increases in ozone due to an indoor source are considered, Equation 2-1 simplifies to Equation 2-2 by dropping the first term in the numerator, i.e., the term that includes outdoor ozone penetration into the interior space.

Derivation of Equation 2-3

$$E_{max,O_3}^* = (\lambda + v_d^* + \sum k_j C_j) C_{O_3,max} \quad (2-3)$$

Equation 2-3 is derived by simple inversion of Equation 2-2 to solve for a maximum acceptable ozone emission rate (E_{max,O_3}^*) based on a prescribed maximum acceptable indoor ozone increment ($C_{O_3,max}$), i.e., simply solving (algebraically) Equation 2-2 for $E_{O_3}^*$, and establishing this as the maximum emission rate (E_{max,O_3}^*) based on a maximum acceptable C_{O_3} ($C_{O_3,max}$).

Derivation of Equation 2-4

$$E_{max,O_3} = (0.002 \times V) E_{max,O_3}^* \quad (2-4)$$

Where:

E_{max,O_3} = maximum acceptable mass emission rate of ozone ($mg \cdot hr^{-1}$).

The derivation of Equation 2-4 begins with E_{\max,O_3}^* followed by an application of the ideal gas law and a series of unit conversions as follows:

$$E_{\max,O_3} = E_{\max,O_3}^* \times 10^{-9} \frac{\text{moles } O_3}{\text{moles air}} \times \frac{\text{mole air}}{24 \text{ L}} \times \frac{10^3 \text{ L}}{\text{m}^3} \times \frac{48 \text{ g } O_3}{\text{mole } O_3} \times \frac{10^3 \text{ mg}}{\text{g}} \times V \quad (\text{A-5})$$

The factor 10^{-9} moles O_3 /mole represents the fact that a part per billion (ppb) is 1 mole of O_3 per billion moles of air. As such, multiplying by 10^{-9} leads to a direct mole O_3 /mole air basis. The 24 L/mole air term stems from application of the ideal gas law at 1 atmosphere and approximately 20 °C room temperature. The 48 g/mole is the molecular weight of ozone. The volume (V) is as defined above. Multiplying through terms in Equation A-5 leads to:

$$E_{\max,O_3} = E_{\max,O_3}^* \times \frac{48}{24} \times V \times 10^{-3} = (0.002 \times V) E_{\max,O_3}^* \quad (\text{A-6 and 2-4})$$

Derivation of Equation 2-5

$$C_p = \frac{(\sum y_j \times k_j \times C_j) C_{O_3}}{\lambda} \quad (2-5)$$

Where:

- C_p = reaction product concentration (ppb)
- y_j = molar yield for reaction product (moles product/moles reactant j reacted)

Equation 2-5 is based on a mass balance on reaction products in a well-mixed building or building zone in the absence of heterogeneous formation:

$$V \frac{dC_p}{dt} = pQC_{p,out} - QC_p + (\sum y_j \times k_j \times C_j) V \quad (\text{A-7})$$

Assuming steady-state conditions (left-hand-side = 0), no outdoor contribution of indoor reaction product (first term on right-hand-side = 0) and dividing by volume yields:

$$0 = -\lambda C_p + (\sum y_j \times k_j \times C_j) \quad (\text{A-8})$$

Moving λC_p to the left-hand-side of Equation A-8 and dividing both sides by λ yields Equation 2-5:

$$C_p = \frac{(\sum y_j \times k_j \times C_j) C_{O_3}}{\lambda} \quad (2-5)$$

Derivation of Equation 2-6

$$E_{\max, O_3, p}^* = \left\{ \frac{\lambda(\lambda + v_d^* + \sum k_j C_j)}{\sum y_j \times k_j \times C_j} \right\} C_{p, \max} \quad (2-6)$$

Equation 2-6 is based on substitution of Equation 2-2 (ozone concentration) into Equation 2-5 (by-product concentration)

$$C_p = \frac{(\sum y_j \times k_j \times C_j)}{\lambda} \times \frac{E_{O_3}^*}{\lambda + v_d^* + \sum k_j C_j}$$

Now, solving algebraically for $E_{O_3}^*$ and setting it to the maximum acceptable emission rate of ozone (E_{\max, O_3}^*) at a prescribed maximum acceptable concentration of reaction product ($C_{p, \max}$) yields Equation 2-6.

Derivation of Equations 2-7 and 2-8

$$C_{SOA} = \frac{p\lambda C_{SOA, out} + \sum \gamma_j k_j C_j C_{O_3} U_{c, j}}{\lambda + v_d \frac{A}{V}} \quad (2-7)$$

$$C_{SOA} = \frac{\sum \gamma_j k_j C_j C_{O_3} U_{c, j}}{\lambda + v_d \frac{A}{V}} \quad (2-8)$$

Where:

- C_{SOA} = indoor SOA concentration ($\mu\text{g}/\text{m}^3$)
- $C_{SOA, out}$ = outdoor SOA concentration ($\mu\text{g}/\text{m}^3$)
- p = building envelope penetration factor for SOA (unitless)
- λ = air exchange rate (hr^{-1})
- $v_d A/V$ = SOA deposition parameter (hr^{-1})
- γ_j = SOA mass yield for reactant j ($\mu\text{g}/\text{m}^3$ of SOA formed per $\mu\text{g}/\text{m}^3$ terpene reacted)
- $U_{c, j}$ = molar to mass conversion factor for reactant j ($\mu\text{g}/\text{m}^3$ per ppb).

All other variables are as defined for equations listed above.

Equations 2-7 and 2-8 result from a mass balance on secondary organic aerosol mass in a well-mixed building or building zone:

$$V \frac{dC_{SOA}}{dt} = pQC_{SOA,out} - QC_{SOA} - v_d C_{SOA} A + \sum \gamma_j k_j C_j C_{O_3} U_{c,j} V \quad (A-9)$$

Where:

v_d = particle deposition velocity ($m \cdot hr^{-1}$).

All other variables are as described above.

Dividing both sides by volume and assuming steady-state conditions (left-hand-side of equation = zero) yields:

$$0 = p\lambda C_{SOA,out} - \lambda C_{SOA} - v_d \frac{A}{V} C_{SOA} + \sum \gamma_j k_j C_j C_{O_3} U_{c,j} \quad (A-10)$$

Factoring C_{SOA} and moving the factored term to the left-hand-side of Equation A-10 yields:

$$\left(\lambda + v_d \frac{A}{V} \right) C_{SOA} = p\lambda C_{SOA,out} + \sum \gamma_j k_j C_j C_{O_3} U_{c,j} \quad (A-11)$$

Now, solving for C_{SOA} leads to Equation 2-7:

$$C_{SOA} = \frac{p\lambda C_{SOA,out} + \sum \gamma_j k_j C_j C_{O_3} U_{c,j}}{\lambda + v_d \frac{A}{V}} \quad (2-7)$$

If only incremental increases in SOA due to indoor reactions are considered, Equation 2-7 simplifies to Equation 2-8 by dropping the first term in the numerator of Equation 2-7, i.e., the term representing outdoor-to-indoor transport of particles.

Derivation of Equation 2-9

$$E_{max,O_3,SOA} = \frac{(\lambda + v_d^* + \sum k_j C_j) \left(\lambda + v_d \frac{A}{V} \right)}{\sum \gamma_j k_j C_j U_{c,j}} C_{SOA,max} \quad (2-9)$$

Where:

$E_{max,O_3,SOA}$ = maximum acceptable emission rate of ozone based on prescribed incremental mass concentration of SOA (ppb/hr),

$C_{SOA,max}$ = maximum acceptable incremental increase in SOA ($\mu g/m^3$).

All other variables are as described previously.

Equation 2-9 is derived from algebraic substitution of Equation 2-2 (ozone concentration) into Equation 2-8 (SOA concentration):

$$C_{SOA} = \frac{\sum \gamma_j k_j C_j U_{c,j}}{\lambda + v_d \frac{A}{V}} \times \frac{E_{O_3}^*}{\lambda + v_d^* + \sum k_j C_j} \quad (A-12)$$

Now, solving algebraically for $E_{O_3}^*$ and setting it to the maximum acceptable emission rate of ozone ($E_{max,O_3,SOA}^*$) at a prescribed maximum acceptable concentration of SOA ($C_{SOA,max}$) yields Equation 2-9.

APPENDIX C. Excel Spreadsheet and Equations

DETACHED SINGLE FAMILY DWELLINGS									
Input Parameters		Base Case				Worst Case			
Building Parameters		Units		Value		Default		Value	
Air exchange rate			1/hr		0.51	base -case default		0.51	
Floor area (A _f)	ft ²	1,797	m ²		167	base-case default		167	ft ² 1,001
Ceiling height (h)	ft	10	m		3.05	base-case default		3.05	ft 10
Ozone and Organic Reactant Parameters									
Ozone Decay Rate (v _d)			1/hr		2.8	base-case default		2.8	1/hr
Maximum acceptable ozone increment	μg/m ³	9.8	ppb		5	base-case default		5	μg/m ³ 3.92
Concentration of reactive species I	μg/m ³	22.6	ppb		4	default: d-limonene		4	μg/m ³ 0
Concentration of reactive species II	μg/m ³	11.3	ppb		2	default: a-pinene		2	μg/m ³ 0
Concentration of reactive species III	μg/m ³	6.4	ppb		1	default: linalool alcohol		1	μg/m ³ 0
Bimolecular rate constant (k) - Reactant I			1/ppb-hr		1.84E-02	default: d-limonene		1.84E-02	1/ppb-hr
Bimolecular rate constant (k) - Reactant II			1/ppb-hr		7.60E-03	default: a-pinene		7.60E-03	1/ppb-hr
Bimolecular rate constant (k) - Reactant III			1/ppb-hr		3.96E-02	default: linalool alcohol		3.96E-02	1/ppb-hr
By-product Parameters									
Maximum acceptable formaldehyde (HCHO) increment	μg/m ³	16.0	ppb		13	base-case default		13	μg/m ³ 3.7
Maximum acceptable secondary organic aerosol (SOA) increment			μg/m ³		5	base-case default		5	μg/m ³
Concentration of reactive species I	μg/m ³	22.6	ppb		4	default: d-limonene		4	μg/m ³ 197.8
Concentration of reactive species II	μg/m ³	11.3	ppb		2	default: a-pinene		2	μg/m ³ 262.5
Concentration of reactive species III	μg/m ³	6.4	ppb		1	default: linalool alcohol		1	μg/m ³ 192
Molar yield (y) of HCHO - Reactant I			(fraction)		0.1	default: d-limonene		0.1	(fraction)
Molar yield (y) of HCHO - Reactant II			(fraction)		0.28	default: a-pinene		0.28	(fraction)
Molar yield (y) of HCHO - Reactant III			(fraction)		0.34	default: linalool alcohol		0.34	(fraction)
Yield of SOA - Reactant I (ug/m ³ SOA / ug/m ³ hydrocarbon reacted)			(fraction)		0.39	default: d-limonene		0.39	(fraction)
Yield of SOA - Reactant II (ug/m ³ SOA / ug/m ³ hydrocarbon reacted)			(fraction)		0.173	default: a-pinene		0.173	(fraction)
Yield of SOA - Reactant III (ug/m ³ SOA / ug/m ³ hydrocarbon reacted)			(fraction)		0.08	default: linalool alcohol		0.08	(fraction)
Conversion factor at 20 oC (ug/m ³ / ppb)			(μg/m ³) / ppb		5.65	default: d-limonene		5.65	(μg/m ³) / ppb
Conversion factor at 20 oC (ug/m ³ / ppb)			(μg/m ³) / ppb		5.65	default: a-pinene		5.65	(μg/m ³) / ppb
Conversion factor at 20 oC (ug/m ³ / ppb)			(μg/m ³) / ppb		6.4	default: linalool alcohol		6.4	(μg/m ³) / ppb
Particle deposition parameter (VdAV)			1/hr		0.036	base-case default		0.036	1/hr
Maximum ozone emission rates									
			E (mg/hr)		E (μg/min)			E (mg/hr)	E (μg/min)
* Based on maximum ozone concentration increment			1.8E+01		292			1.9E+00	32
* Based on maximum HCHO concentration increment			9.3E+02		15,433			2.4E+00	41
* Based on maximum SOA concentration increment			4.8E+01		808			4.6E-01	8
* Maximum acceptable ozone emission rate			1745		292			0.46	8
	Input data								
	Calculated result								
	Final Result								

OFFICE BUILDINGS											
Input Parameters		Base Case				Worst Case					
Building Parameters		Units		Value		Default		Value			
Air exchange rate			1/hr		0.75	base - case default	0.75		1/hr	0.22	
Floor area (A)	ft ²	108	m ²		10	base-case default	10	ft ²	75	m ²	7
Ceiling height (h)	ft	9	m		2.7	base-case default	2.7	ft	9	m	2.7
Ozone and Organic Reactant Parameters											
Ozone Decay Rate (k_d)+A15			1/hr		3.8	base-case default	3.8			1/hr	2.5
Maximum acceptable ozone increment	$\mu\text{g}/\text{m}^3$	9.8	ppb		5	base-case default	5	$\mu\text{g}/\text{m}^3$	3.92	ppb	2
Concentration of reactive species I	$\mu\text{g}/\text{m}^3$	7.345	ppb		1.3	default: d-limonene	1.3	$\mu\text{g}/\text{m}^3$	0	ppb	0
Concentration of reactive species II	$\mu\text{g}/\text{m}^3$	7.91	ppb		1.4	default: a-pinene	1.4	$\mu\text{g}/\text{m}^3$	0	ppb	0
Concentration of reactive species III	$\mu\text{g}/\text{m}^3$	64	ppb		10	default: linalool alcohol	10	$\mu\text{g}/\text{m}^3$	0	ppb	0
Bimolecular rate constant (k) - Reactant I			1/ppb-hr		1.84E-02	default: d-limonene	1.84E-02			1/ppb-hr	1.84E-02
Bimolecular rate constant (k) - Reactant II			1/ppb-hr		7.60E-03	default: a-pinene	7.60E-03			1/ppb-hr	7.60E-03
Bimolecular rate constant (k) - Reactant III			1/ppb-hr		3.96E-02	default: linalool alcohol	3.96E-02			1/ppb-hr	3.96E-02
By-product Parameters											
Maximum acceptable formaldehyde (HCHO) increment	$\mu\text{g}/\text{m}^3$	16.0	ppb		13	base-case default	13	$\mu\text{g}/\text{m}^3$	3.7	ppb	3
Maximum acceptable secondary organic aerosol (SOA) increment			$\mu\text{g}/\text{m}^3$		5	base-case default	5			$\mu\text{g}/\text{m}^3$	2
Concentration of reactive species I	$\mu\text{g}/\text{m}^3$	7.345	ppb		1.3	default: d-limonene	1.3	$\mu\text{g}/\text{m}^3$	141.3	ppb	25
Concentration of reactive species II	$\mu\text{g}/\text{m}^3$	7.91	ppb		1.4	default: a-pinene	1.4	$\mu\text{g}/\text{m}^3$	79.1	ppb	14
Concentration of reactive species III	$\mu\text{g}/\text{m}^3$	64	ppb		10	default: linalool alcohol	10	$\mu\text{g}/\text{m}^3$	1472	ppb	230
Molar yield (y) of HCHO - Reactant I			(fraction)		0.1	default: d-limonene	0.1			(fraction)	0.1
Molar yield (y) of HCHO - Reactant II			(fraction)		0.28	default: a-pinene	0.28			(fraction)	0.28
Molar yield (y) of HCHO - Reactant III			(fraction)		0.34	default: linalool alcohol	0.34			(fraction)	0.34
Yield of SOA - Reactant I ($\mu\text{g}/\text{m}^3$ SOA / $\mu\text{g}/\text{m}^3$ hydrocarbon reacted)			(fraction)		0.39	default: d-limonene	0.39			(fraction)	0.39
Yield of SOA - Reactant II ($\mu\text{g}/\text{m}^3$ SOA / $\mu\text{g}/\text{m}^3$ hydrocarbon reacted)			(fraction)		0.173	default: a-pinene	0.173			(fraction)	0.186
Yield of SOA - Reactant III ($\mu\text{g}/\text{m}^3$ SOA / $\mu\text{g}/\text{m}^3$ hydrocarbon reacted)			(fraction)		0.08	default: linalool alcohol	0.08			(fraction)	0.08
Conversion factor at 20 °C ($\mu\text{g}/\text{m}^3$ / ppb)			($\mu\text{g}/\text{m}^3$) / ppb		5.65	default: d-limonene	5.65			($\mu\text{g}/\text{m}^3$) / ppb	5.65
Conversion factor at 20 °C ($\mu\text{g}/\text{m}^3$ / ppb)			($\mu\text{g}/\text{m}^3$) / ppb		5.65	default: a-pinene	5.65			($\mu\text{g}/\text{m}^3$) / ppb	5.65
Conversion factor at 20 °C ($\mu\text{g}/\text{m}^3$ / ppb)			($\mu\text{g}/\text{m}^3$) / ppb		6.4	default: linalool alcohol	6.4			($\mu\text{g}/\text{m}^3$) / ppb	6.4
Particle deposition parameter ($V_d A/V$)			1/hr		0.036	base-case default	0.036			1/hr	0.036
Maximum ozone emission rates			E (mg/hr)	E ($\mu\text{g}/\text{min}$)			E (mg/hr)	E ($\mu\text{g}/\text{min}$)			
* Based on maximum ozone concentration increment			1.3E+00	22			2.1E-01	3			
* Based on maximum HCHO concentration increment			1.9E+01	312			9.7E-02	2			
* Based on maximum SOA concentration increment			4.0E+00	66			4.1E-02	1			
* Maximum acceptable ozone emission rate			1.3	22			0.036	1			
Input data											
Calculated result											
Final Result											

APPENDIX D. ABOUT THE AUTHOR

Richard L. Corsi, Ph.D.



Dr. Richard L. Corsi is the ECH Bantel Professor for Professional Practice in the Department of Civil, Architectural and Environmental Engineering at The University of Texas at Austin. He received his B.S. degree in Environmental Resources Engineering at Humboldt State University in 1983, and his M.S. and Ph.D. degrees in Civil Engineering at UC Davis in 1985 and 1989, respectively. Dr. Corsi's research focuses on sources of indoor air pollution, the physics and chemistry of indoor air, human exposure to indoor air pollutants, and control of indoor pollutants. Dr. Corsi has served as principal investigator on approximately 60 research projects totaling approximately \$10 million and ranging from the sorptive interactions between polar/non-polar VOCs and indoor materials, homogeneous indoor air chemistry and secondary aerosol formation, and heterogeneous chemistry at and within indoor materials. Dr. Corsi has also studied a wide range of indoor sources of air pollution, from dishwashers to paint and computers. His team recently completed experiments involving building disinfection chemistry in the wake of anthrax attacks in the Fall of 2001. He and his research team (students) have published over 220 journal/conference papers and reports, and have been featured on the Canadian television series *The Nature of Things*, *National Geographic*, *The Economist*, *Business Week*, *National Wildlife*, *Prevention*, *Men's Health*, the *Dallas Morning News*, *Houston Chronicle*, *San Francisco Chronicle*, and more. In April 2006 Dr. Corsi received both of the major teaching awards in the Department of Civil, Architectural and Environmental Engineering at The University of Texas at Austin, and was also named a 2006 Distinguished Alumnus of Humboldt State University. In July 2006 Dr. Corsi became Director and PI of a new \$2.9 million NSF-funded interdisciplinary graduate program at The University of Texas. The program is entitled *Indoor Environmental Science and Engineering – An Emerging Frontier*.

*Ozone***Stevenson, Todd A.**

From: Information Center
Sent: Tuesday, December 05, 2006 9:19 AM
To: Stevenson, Todd A.
Subject: FW: Changes in the Recommended Safe Levels of Ozone

Todd,

I wasn't aware that the CPSC was looking into this matter. In light of what I found in the link below, please not the consumer's concerns as comments.

<http://www.cpsc.gov/volstd/research/ozone.pdf>

If you deem that a response is necessary, please respond as you see fit.

Thank you,

Michael June

From: John E. Finklea [mailto:j.finklea@comcast.net]
Sent: Tuesday, December 05, 2006 12:01 AM
To: Information Center
Subject: Changes in the Recommended Safe Levels of Ozone

Dear Sir:

I have been told that the CPSC plans to change their standard to recommending a minimum level of ozone be considered "safe" from the use from ionizers. This greatly concerns me. As a mother of a severe asthmatic, we have had first hand experience with the damaging effect of an ionizer.

My son had a very severe asthma attack brought on by the ozone generated by an ionizer. He described his asthma attack as feeling like an anaphylactic reaction—a sudden and complete shutdown of his airways. He quickly went outside and used his rescue inhaler which stopped the reaction. If he had not thought quickly, an ambulance and a hospital would have been his only help. We looked at that home setting to see if any other trigger could have been the cause. The only other trigger that will invoke this sudden of a reaction are cats and there were none living there. Our only conclusion—the ionizer.

It is absurd to allow a standard of air quality that is equivalent to the minimum acceptable urban polluted air levels be considered "safe" ozone levels for ionizers that are supposed to "clean" our air. There is documented research by the EPA and recommendation from the American Lung Association as to the detriment of ozone on those with asthma, chronic lung problems, the young and elderly. Our experience is that even one exposure is too much.

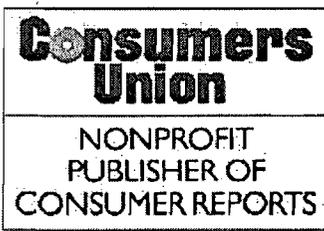
The CPSC has always been a leader to protect the people from products that can harm. Please do not recommend a minimum amount of ozone is acceptable because when you can't breathe it's too late.

Sincerely,

Jan Finklea
722 Maple Glen
Garland, TX 75043
972-240-6422
j.finklea@comcast.net

12/5/2006

Ozone report



Office of the Secretary
U.S. Consumer Product Safety Commission
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**Comments of Consumers Union of the U.S. Inc.
to the Consumer Product Safety Commission on the
"CPSC Health Sciences Staff Report on the Work Product Resulting form CPSC
Contract No. CPSC041369, Assessing Potential Health Effects and Establishing
Ozone Exposure Limits for Ozone-Generating Air Cleaners"**

Introduction

In the Fall of 2004, the U.S. Consumer Product Safety Commission ("CPSC" or "Commission"), interested in examining the "potential health effects from exposure to ozone produced by certain ozone generating air cleaners," awarded a contract to Richard Shaughnessy, Ph.D. to examine the issue.¹ Mr. Shaughnessy prepared a Technical Report, entitled "Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners." ("Shaughnessy Report").

CPSC staff prepared a draft report (dated September 26, 2006) on the Shaughnessy Report, entitled "CPSC Health Sciences Staff Report on the Work Product Resulting form CPSC Contract No. CPSC041369, Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners," ("Staff Report"). It is in response to the Staff Report that Consumers Union, publisher of *Consumer Reports Magazine*, submits these comments. The Staff Report has three parts: (1) the CPSC interpretation and summary of the Shaughnessy Report; (2) health effects in humans of indoor ozone levels at, or above, 50 ppb; and (3) the engineering modeling report on rates of ozone generation that would be limited to a 50 ppb accumulation of ozone in a room. We have considered these three parts serially, and our comments below therefore correspond to parts 1 through 3, respectively, of the Staff Report.

¹ See "CPSC Health Sciences Staff Report on the Work Product Resulting form CPSC Contract No. CPSC041369, Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners," (Draft, dated 9/26/2006), p. 1.

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I. The CPSC Health Sciences Staff Report

The Shaughnessy Report was contracted to “assess the adequacy for protection of human health of an ozone concentration in indoor air of 50 parts per billion (ppb)....”² Furthermore “If the 50 ppb level was found to be adequate, then corresponding maximum release rates for various room sizes were to be calculated.”³ The Shaughnessy report is divided into two parts. Part I, “Health Components of Ozone Review” (“Health Component”)⁴ is primarily authored by David Krause, MSPH, PhD and Lauren Ball, DO, MPH, with contributions from Shaughnessy. Part II of the Shaughnessy Report, “Ozone Devices Modeling Considerations,” (“Modeling Component”)⁵ is authored primarily by Mr. Shaughnessy, and Reviewed/Coauthored by Krause and Ball.

The Shaughnessy Report was “intended for use by CPSC staff when considering any related recommendations to the Commission or appropriate voluntary standards organizations to establish limits for the emission of ozone from ozone-generating devices.” Staff report, p2. In other words, the Staff had broad discretion as to how to weigh information generated by the Shaughnessy Report when making recommendations to the Commission. We are concerned with the apparent lack of methodology used for the Staff to generate a policy recommendation from the Shaughnessy Report. There is no language about how the reports would be used, i.e. no discussion of how the technical results of the Shaughnessy Report would be turned into policy recommendations. Because any science-based policy requires methodology, we consider this flaw to be a glaring gap in the CPSC process. How the Commission transitions from the interpretation of the technical information to the recommendations made needs explanation because differing interpretations and perceived constraints could result in widely differing recommendations, based on the same technical information. One basis for the Staff’s recommendations is a very simple equilibrium-based mathematical model. Such a model may not be appropriate for making public policy. Indeed, many public policies which were based on such models became dismal failures: the sustainable harvesting model for fisheries, the Rand Corporation model of the Indochinese War, and the Rand Corporation model for closing fire companies, to name a few. All of these are examples of the failure of models due to unrealistic assumptions, oversimplifications, and large gaps in needed data.

The Background section of the Staff Report reveals the important fact that “approximately 80 percent of air cleaner buyers cite concerns about asthma or allergies (Consumers Union, 2005).”⁶ Thus, a high proportion of these devices may be used in homes housing at least one person who is a member of a sensitive class. Yet, nothing in the Staff Report or the Shaughnessy Report analyzes the potential health impact of

² Staff Report at 1.

³ Staff Report at 1.

⁴ Shaughnessy Report at 2.

⁵ Shaughnessy Report at 47.

⁶ Staff Report at 2.

this basic fact. Because asthmatics and people with allergies have heightened sensitivities to ozone accompanied by particles, any evaluation of whether 50 ppb protects human health must include interactions of ozone with particles and chemical reactions of ozone and VOCs that produce ultrafine particles. Despite the fact that these interactions likely affect the great majority of households that buy air cleaners, the Staff Report (and the Shaughnessy Report it relies upon) fails to address these two types of potential health-affecting interactions. We conclude that the stated mission of the Staff Report, to “assess the adequacy for protection of human health of an ozone concentration in indoor air of 50 parts per billion (ppb)....”⁷ remains unfulfilled when the sensitivity of the population exposed to air cleaners, and potential adverse interactions are ignored.

In its review of Parts I and II of the Shaughnessy Report, (the literature review on health effects of low levels of ozone and the mathematical modeling), the Staff acknowledges that -- as the health effects report states -- indoor ozone levels are an product of outdoor ozone levels combined with indoor ozone generation. However, the implications of this fact are never analyzed vis-à-vis air cleaners. Instead, the Staff extrapolates from the Health Component of the Shaughnessy Report that very little data exists on the health effects of ozone at low levels and that there is no reason to reject the 50 ppb level as unsafe. The Staff then rejects the Health Component recommendation to examine reaction byproducts between ozone and volatile organic compounds (“VOCs”) simply because health effects from them have not been quantified. So the conclusion that 50 ppb may be adequate to “reduce the occurrence of adverse health effects from exposure to ozone in an indoor environment” (Staff report, p5.) is what the Staff adopted from the Health Component. The Staff also takes the Modeling Component results without apparent critical analysis: an air cleaner may generate 14 to 26 mg of ozone per hour of operation (depending on the size of the room) and keep the accumulation to 50 ppb.

The Staff allows that the 50 ppb may be subject to change if data on low level exposures merit the change. The Staff also allows that a safety margin is needed to protect sensitive groups. The Staff allows that there are numerous research needs in the health effects area of ozone, in the health effects area of reaction byproducts, and in the area of ozone infiltration from the outdoors. However, the relationship between these gaps and the public policy generated now by the staff is not explained. The Staff apparently ignores these gaps, relies upon the 50 ppb accumulation limit and the modeled generation rates, and – regardless of the fact that the product under consideration may be purchased by households largely with at least one sensitive member – fails to use any precautionary principal at all.

The CPSC had two unnamed peer-reviewers whose comments they generally discounted. The reviewers were concerned that the 50 ppb would not offer enough safety margins for asthmatic children in view of numerous publications about the effect of ozone on asthmatic children. The unnamed peer-reviewers were also concerned about reaction byproducts and thought that these reaction byproducts should be part of

⁷ Staff Report at 1.

the Health Component review. The reviewers also found the Modeling Component lacking because input values appeared to be arbitrary, ignoring the contribution of outdoor ozone.⁸ Finally, the very simplicity of the model was suspect because not all air is well-mixed.

The staff simply disagreed with the peer-reviewers about all these concerns. The staff acknowledged that "sensitive populations are typically considered by regulatory agencies by the use of an uncertainty factor or margin of safety approach (CPSC, 1992)" (Staff report, p.8). However, they refused to comment on the suggestion of the health effects contractors and the peer-reviewers to consider a margin of safety. This seems to mean that they will simply promulgate the 50 ppb unaltered.

II. The Report on Potential Health Effects and Ozone Exposure Limits for Air Cleaners

Although voluminous, with an impressive list of references attached thereto, the Health Component was completely qualitative. Regardless of this fact, the conclusion it drew was quantitative (that the 50 ppb is adequate to protect health). In our view, a solely qualitative review cannot support such a quantitative conclusion.

The appropriate methods for addressing a quantitative question in the health effects area include generating a dose/response curve and conducting a formal meta-analysis of the epidemiological and physiological data. Even if there are very few data on exposures to ozone at 50 ppb or below, the dose/response curve derived from exposures at a large range of levels is informative about the possible relationships at low levels. Once the shape of the curve at higher levels is known, then the few data points available at low levels can guide filling in the curve at the low levels. It would be a different problem if no data were available at 50 ppb or below. Then one would have to examine a range of different shapes at the low levels, given the shape at the higher levels. There is even methodology for doing that properly and deriving a range of answers.

Very few epidemiological studies are flawless. Dismissing them because of this or that flaw may throw away the good data along with the bad. What environmental health scientists often do to overcome this problem is to set criteria for inclusion in meta-analysis. These criteria whittle down the number of studies to those on which analysis can be performed with an understanding of reliability and despite potential flaws. In our view, contributors to the Shaughnessy Report should have worked with a small set of

⁸ We were surprised that CPSC did not consider outdoor ozone. If you consider that typical high outdoor ozone levels can easily cause a 10 to 20 ppb ozone level indoors, then the 50 ppb level no longer gives a factor of safety with the well supported 80 ppb outdoor limit (which was the basis for the CPSC Staff's conclusion that a 50 ppb standard is reasonably safe). The CPSC should consider existing data for summertime background indoor ozone levels, which should then be added to the ozone threshold being under consideration, to ensure the level does not exceed known acute levels. Worse yet, the EPA 80 ppb outdoor limit is based on an 8-hour exposure ---- but when indoors, the exposure hazard is continuously present. The Staff Report simply dismisses the time-weighted exposure effects ignoring the two critical factors when considering safe thresholds ---- concentration and exposure time.

studies. Instead, we believe they paid undue attention to the number of papers read, and length of the resulting list of references. We believe the researchers could have arrived at a more appropriate quantitative answer through a meta-analysis about levels of ozone and health effects that could be interpreted to suit the need of CPSC.

For the reasons stated above, we believe that the Health Effects Component of the Shaughnessy Report cannot support either retention or rejection of any particular level of indoor ozone exposure below 70 ppb.

III. The Modeling Component

In our view, the Modeling Component cannot be used for public policy decisions. It ignores the reality of the contribution of ozone from the outdoors while allowing the room to have a ventilation rate presumably, at least partly, from the outdoors. Thus, the Modeling Component is structured to disallow, omit the level of ozone reached in the room from any particular rate of ozone generation. If a ventilation rate is allowed, then outdoor ozone contribution must be considered.

The Modeling Component fixes on one ventilation rate, and does not explore the potential effects of a range of rates. This method cannot produce a realistic worst case scenario, and is limited to producing only a rather average case situation. The Modeling Component reflected a great deal of knowledge of the extent and intensity of under-ventilation in various parts of the country in various seasons. We believe that this knowledge should have been applied by running the model with a range of air changes per hour.

The Modeling Component also settled on a single rate of deposition/surface reaction, despite the fact, cited by the author, that a range of rates has been reported in the literature. We therefore believe that the model should have been run with a range.

The author did not justify use of a steady-state model. Although it may be the most tractable way of arriving at the generation rate in a particular room size that would limit ozone level to 50 ppb—is it realistic? There are surely cases where ozone never reaches a steady state but accumulates until the air cleaner is turned off. These are the most dangerous cases. Yet, these cases are nonexistent in the Modeling Component. Because we know that accumulation of CO does occur and kills and injures people, we should consider the possibility that ozone also accumulates. The model is an artificial construct designed to calculate ozone generation rates that would lead to a steady state concentration below 50 ppb. The input data are then selected to result in that condition. Considering that this manner of modeling closely resembles the modeling effort that led to the crash of the fisheries worldwide, including mistaking an equilibrium state for reality, we recommend against use of oversimplified steady-state models.

The Modeling Component should have included using the range of emission rates found by the steady state model with parameters that would produce a range of worst cases, based on the extremes of room size, under-ventilation rates, and deposition/reaction

rates found in the literature cited in the modeling report. Although still modeled on an equilibrium assumption, the exercise would shed light on what air cleaners that emit ozone at an "acceptable" rate could do under conditions that are less salubrious than the averages used in the model in the Modeling Component.

Finally, a truly complete study would have explored the conditions that lead to non-equilibrium accumulation. Do the low rates of ventilation cause accumulation of ozone, rather than the reaching of some steady level?

CU's Recommendations

We recommend that any standard for air cleaners should have a factor of safety incorporated into the allowable limit with respect to the level at which health effects are well documented. This level currently seems to be the EPA threshold of 80 ppb. Thus, using a factor of safety of 2 (not much of a safety factor compared to other design criteria), the maximum generated by an air cleaner should not be greater than 40 ppb. Further, this number should be reduced by the average daily indoor ozone levels due to the average daily outdoor ozone obtainable in a cross-section of the major metro areas during the peak ozone periods of the year. If the data is not available directly, it can be calculated. For example, if the average daily ozone in the summer for the major metro areas is 60 ppb and normal air exchange and indoor ozone sinks drops the ozone level indoors to about 20% of this, then the background indoor ozone level is 12 ppb.⁹ This value should be subtracted from the 40 ppb threshold for purposes of a standard.

Two other issues worth noting - CPSC does acknowledge that measuring ozone near the device should be considered for purposes of a standard.

They summarily dismissed the epidemiology studies like the one we referenced in our May 2005 story. They acknowledged that the study we referred to did control for particulate matter (PM10) but did not account for the risk associated with the other hazardous pollutants produced by atmospheric photochemistry. CPSC goes on to say (page 20) that exposure characterization in epidemiology studies suffer from 3 measurement errors:

1. The use of average population rather than individual exposure data
2. The difference between the average personal ambient exposure and the ambient concentrations
3. The difference between the true and measured ambient concentrations

Thus use of ambient exposure measurements will tend to overestimate true personal ozone exposure - CPSC assumes subjects spend 100% of time outdoors when it is actually only 10%.

⁹ See Shaunessy Report at 4. On page 4, Section 1.0 of the Shaunessy Report suggests that indoor ozone levels are 20 to 70% of outdoor levels or specifically that 2 to 40 ppb of ozone are added to indoor air due to air exchange with outdoors.

Conclusion

In our view, neither technical report can be used to support a quantitative public policy, especially one that affects a population that is disproportionately vulnerable to ozone and the reaction byproducts of ozone. The CPSC further diluted the small potential protection offered by these reports when it dismissed concerns raised by the authors. The CPSC also ignored the concerns of the peer-reviewers. Thus, the public policy generated by the CPSC in this matter cannot be viewed as either science-based or protective of the special population that purchases these particular products.

We appreciate the opportunity to share our views on this important proposed rule to increase the safe use of air cleaners. We strongly urge the Commission to develop a dose/response curve based on existing experimental and epidemiological data, perform a meta-analysis of epidemiological and physiological studies that meet strong methodological criteria, use all the data on housing and ventilation characteristics cited in the modeling module to judge the potential for ozone accumulation (rather than assuming a single scenario), and use all reports and publications such as the California experiment cited in the modeling module. Inclusion of interactions between ozone and other pollutants should also be considered in any health impact assessment. Finally, the path from the science to the policy recommendations should be clearly described.

December 8, 2006

Respectfully submitted,

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Subject: Comments- on "CPSC Health Sciences Staff Report...
Attachments: 1208_CU_CPSC_AirCleaner_Comments2.pdf

Attached please find Consumers Union Comments in PDF format on "CPSC Health Sciences Staff Report on the Work Product Resulting from CPSC Contract No. CPSC041369. Assessing Potential Health Effects and Establishing Ozone Exposure Limits for Ozone-Generating Air Cleaners."

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