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

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EXECUTIVE SUMMARY

The Issue

Although ozone concentrations are generally lower indoors than outdoors, the fact that Americans spend nearly 18 hours indoor 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, causing 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 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 μg/min) for a single-family detached residential home, 1.3 mg/hr (22 μg/min) for a typical office in an office building, and 9.9 mg/hr (166 μg/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 μg/min) for a single-family detached residential home, 0.041 mg/hr (0.68 μg/min) for a typical office in an office building, and 0.13 mg/hr (2.2 μg/min) for a school classroom.

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)**

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 (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 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:

$$O_3 + C{=}C \rightarrow \text{ozonide} \rightarrow \text{carbonyl} + \text{Criegee by-radical} \rightarrow OH^* + \text{other products} \qquad (1\text{-}1)$$

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, soaps and detergents. 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:

$$O_3 + NO_2 \rightarrow NO_3^* \qquad (1\text{-}2)$$

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 Sheilds, 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.

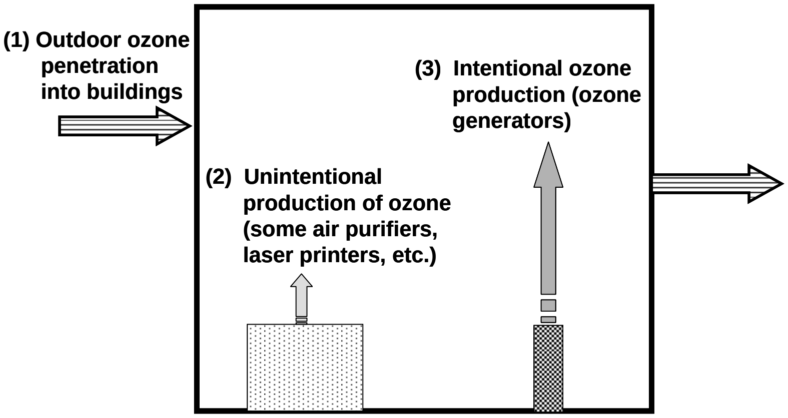

Figure 1-1. Sources of indoor ozone divided into three primary source categories.

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:

$$C_{O3} = \frac{p\lambda C_{O3,out} + E^*_{O3}}{\lambda + v^*_d + \sum k_j C_j} \qquad (2\text{-}1)$$

Where:

C_{O3} = indoor ozone concentration or incremental concentration increase (ppb)

$C_{O3,out}$ = 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^*_{O3} = 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:

$$C_{O3} = \frac{E^*_{O3}}{\lambda + v^*_d + \sum k_j C_j} \qquad (2\text{-}2)$$

Inversion of Equation 2-2 to solve for a maximum acceptable ozone emission rate ($E^*_{max,O3}$) based on a prescribed maximum acceptable indoor ozone increment ($C_{O3,max}$) leads to:

$$E^{*}_{\max,O3} \quad = \quad \left(\lambda + v_d^{*} + \sum k_j C_j\right) C_{O3,\max} \tag{2-3}$$

A conservative approach to estimating $E^{*}_{\max,O3}$, 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 $C_{O3,\max}$. 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 $E^{*}_{\max,O3}$ by use of the ideal gas law applied at typical room temperature (20 to 25 ^{o}C). For this condition:

$$E_{\max,O3} \quad = \quad \left(0.002 \times V\right) E^{*}_{\max,O3} \tag{2-4}$$

Where,

$E_{\max,O3}$ = maximum acceptable mass emission rate of ozone ($mg \cdot hr^{-1}$).

2.2 Emission Rate based on Maximum Gaseous By-Product Concentration

When ozone 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:

$$C_p \quad = \quad \frac{\left(\sum y_j \times k_j \times C_j\right) C_{O3}}{\lambda} \tag{2-5}$$

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:

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

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:

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

Where:

C_{SOA} = indoor SOA concentration (μg/m^3)

$C_{SOA,out}$ = outdoor SOA concentration (μg/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 (μg/m^3 of SOA formed per μg/m^3 terpene reacted)

$U_{c,j}$ = molar to mass conversion factor for reactant j (μg/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:

$$C_{SOA} = \frac{\sum \gamma_j k_j C_j C_{O3} U_{c,j}}{\lambda + v_d \frac{A}{V}} \tag{2-8}$$

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:

$$E_{\max,O3,SOA} = \frac{\left(\lambda + v_d^* + \sum k_j C_j\right)\left(\lambda + v_{d,p}\frac{A}{V}\right)}{\sum \gamma_j k_j C_j U_{c,j}} C_{SOA,\max} \tag{2-9}$$

Where:

$E_{max,O3,SOA}$ = 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 (µg/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" of "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 Building*s 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 to 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 if 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 2.80/hr and 1.30/hr, respectively. A value of 2.80/hr was adopted for base-case conditions for homes in this study. A value of 1.5/hr (mean – 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 an excellent review of the published literature on size-dependent particle deposition velocities and deposition parameters (v_dA/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_dA/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 ft^2 office (11.1 m^2) 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 ft^2 (10 m^2)] for base-case conditions in this study. A floor area of 75 ft^2 (7 m^2) 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 ft^2 (89 m^2) 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 ft^2 (80 m^2). A classroom floor area of 430 ft^2 (40 m^2) 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, the addition 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 = $ppb^{-1}hr^{-1}$; temperature = 20 ^oC): 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_i)

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 $\mu g/m^3$ of SOA formed per $\mu g/m^3$ 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 ^oC, 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 were derived in the presence of even higher temperatures (41 – 48 °C) and at elevated NO_2 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. Futhermore, 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 $\mu g/m^3$ without specifying air temperatures during sample collection. For this study, concentrations in $\mu g/m^3$ 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 a plug-in deodorizer 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:

$$C = \left. \left\{ \frac{E \times 1{,}000\,\mu g/mg}{\lambda V \times 24\,hr/day} \right\} \middle/ 6.4\left(\mu g/m3\right)/ppb \right. \qquad (3\text{-}1)$$

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 ($C_{O3,max}$)

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 Roanoke, Virginia, 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 manufacturer 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 death, 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 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 $\mu g/m^3$ in air) for HCHO is 1.3×10^{-5}, i.e., each increase in lifetime exposure of 1 $\mu g/m^3$ 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 $\mu g/m^3$ (2 ppb at 20 ^oC); 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 $\mu g/m^3$, the indoor REL for HCHO is adjusted upward to 33 $\mu g/m^3$ (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 ($C_{SOA,max}$)

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 $PM_{2.5}$ (mass concentration of particles with aerodynamic diameters less than 2.5 μm) (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 $PM_{2.5}$. The annual average NAAQS of 15 $\mu g/m^3$ was selected to err on the conservative side. For this study, a maximum acceptable SOA concentration increase of 5 $\mu g/m^3$ 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 $\mu g/m^3$ 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) for a school classroom, 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:

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

Where,

$E_{max,change}$ = maximum acceptable ozone emission rate after change (mg/hr)

$E_{max,\ bc}$ = 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.

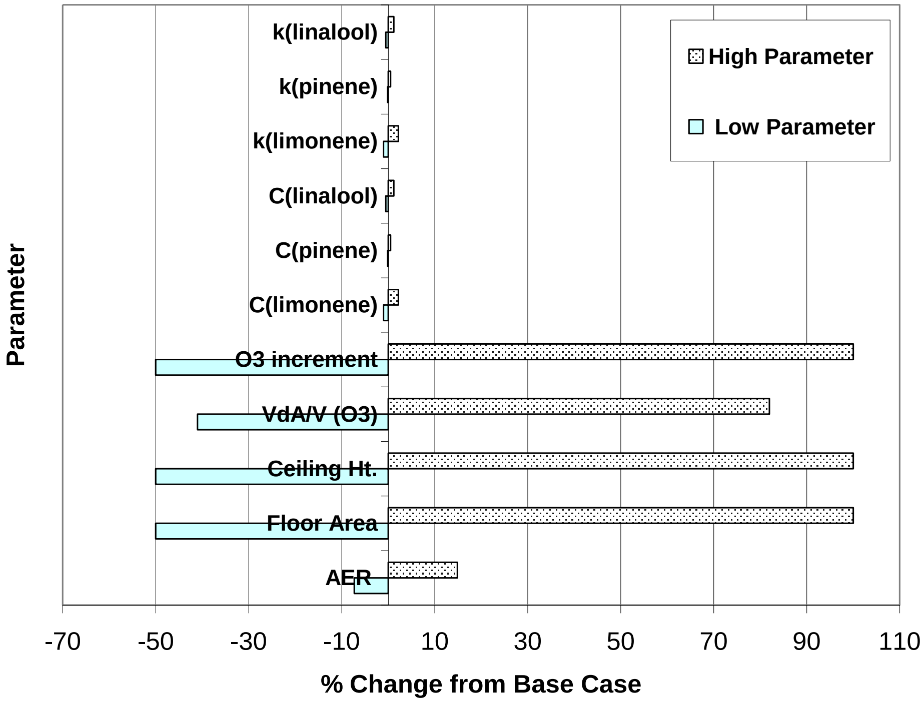

Figure 4-1. Sensitivity of acceptable ozone emission rates in **homes** for factor of two increases (high parameter) and decreases (low parameter) in model parameters, and criterion **based on maximum acceptable ozone concentration**. Here (and in all subsequent figures), k is the bi-molecular reaction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

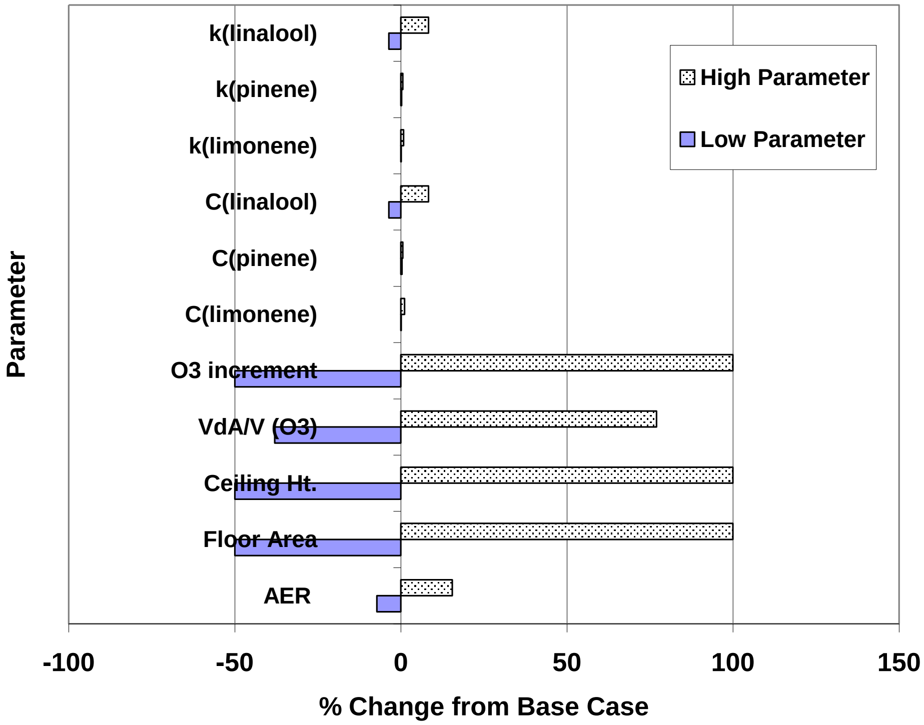

Figure 4-2. Sensitivity of acceptable ozone emission rates in **offices** for factor of two increases (high parameter) and decreases (low parameter) in model parameters, and criterion **based on maximum acceptable ozone concentration**.

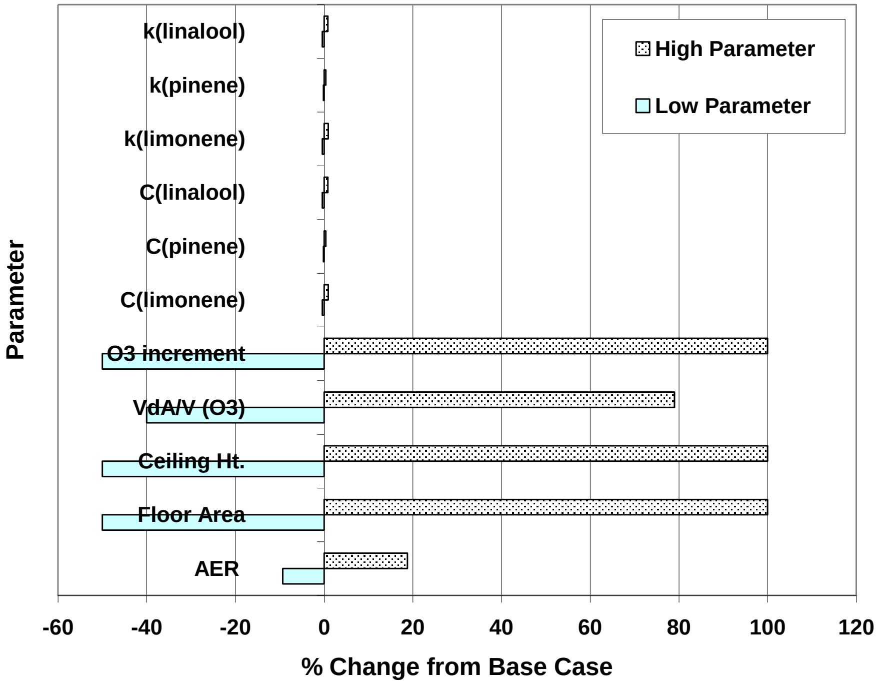

Figure 4-3. Sensitivity of predicted maximum acceptable ozone emission rates in **school classrooms** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable ozone concentration**.

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_dA/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.

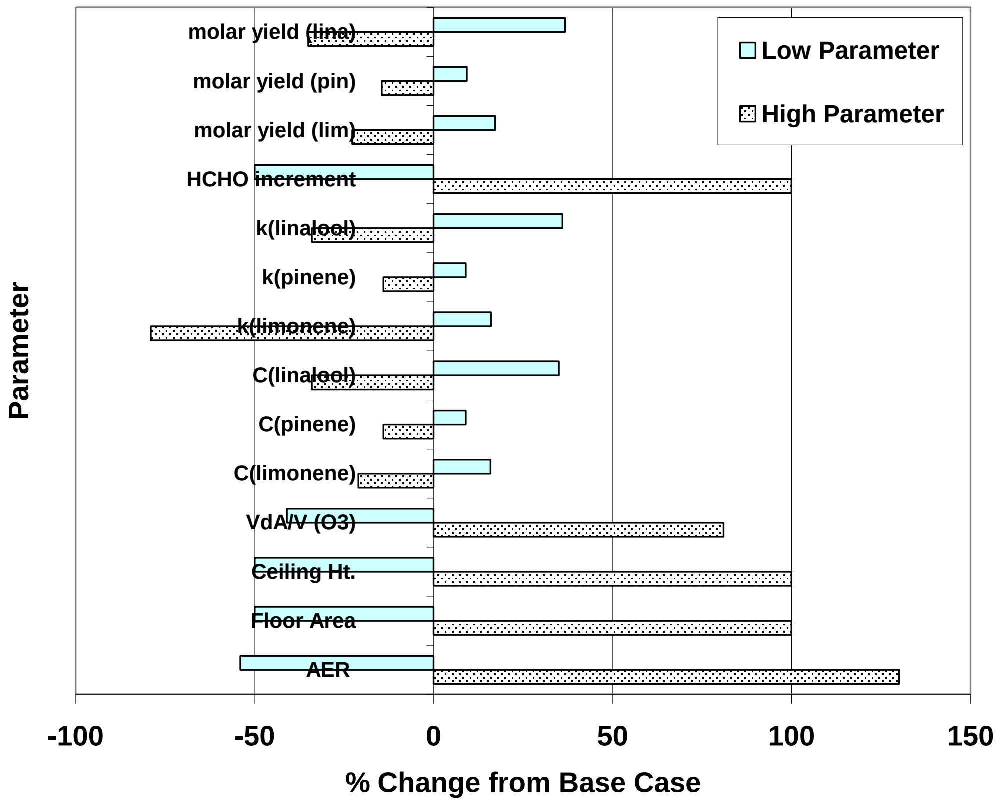

Figure 4-4. Sensitivity of predicted maximum acceptable ozone emission rates in **homes** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable formaldehyde concentration**.

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.

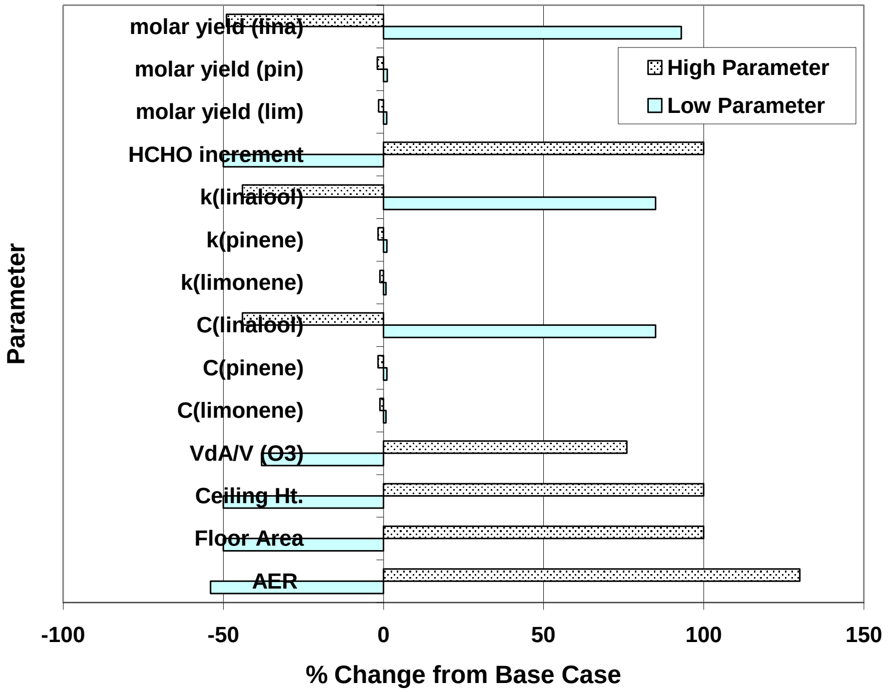

Figure 4-5. Sensitivity of predicted maximum acceptable ozone emission rates in **offices** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable formaldehyde concentration**.

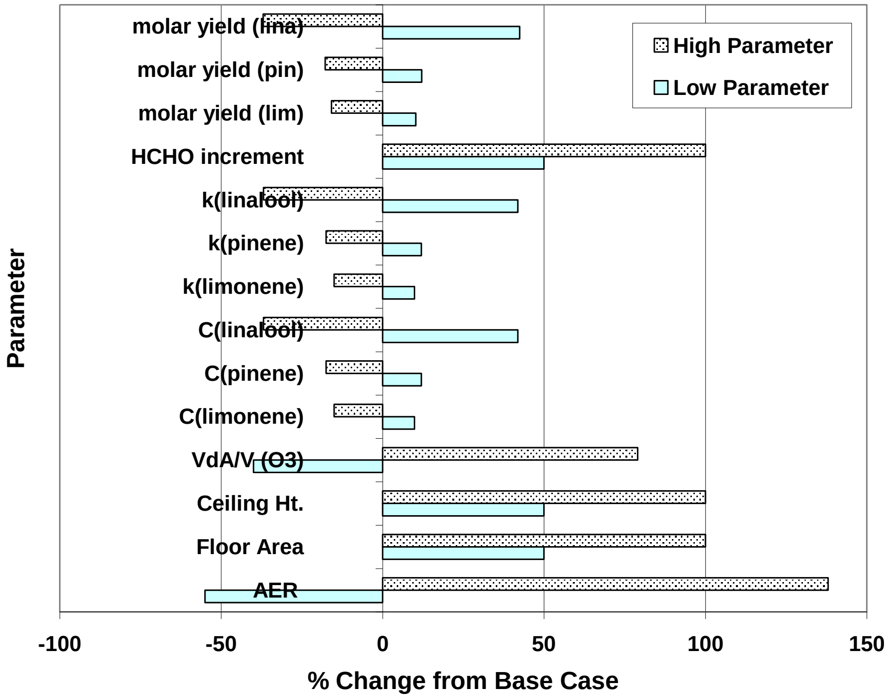

Figure 4-6. Sensitivity of predicted maximum acceptable ozone emission rates in **school classrooms** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable formaldehyde concentration**.

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.

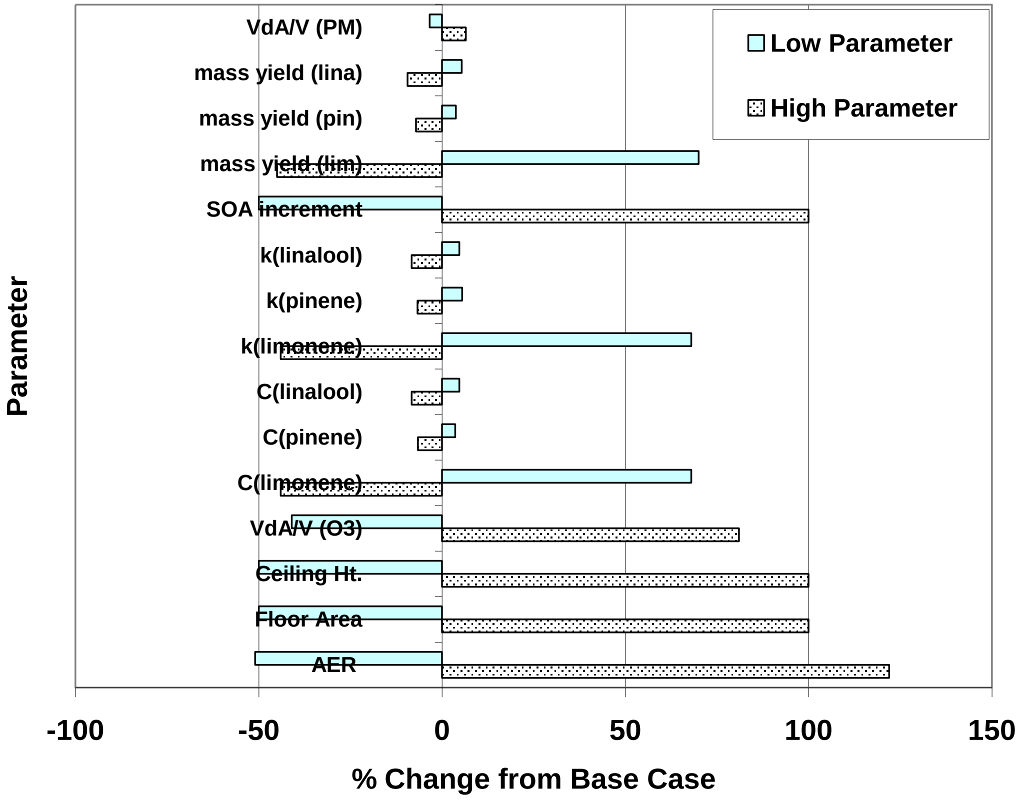

Figure 4-7. Sensitivity of predicted maximum acceptable ozone emission rates in **homes** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable SOA concentration**.

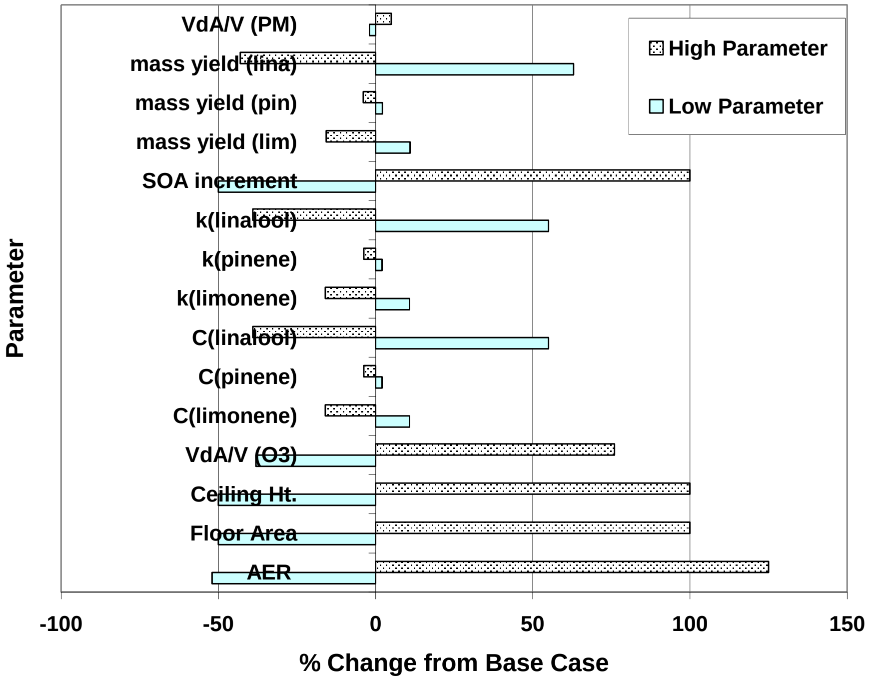

Figure 4-8. Sensitivity of predicted maximum acceptable ozone emission rates in **offices** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable SOA concentration**.

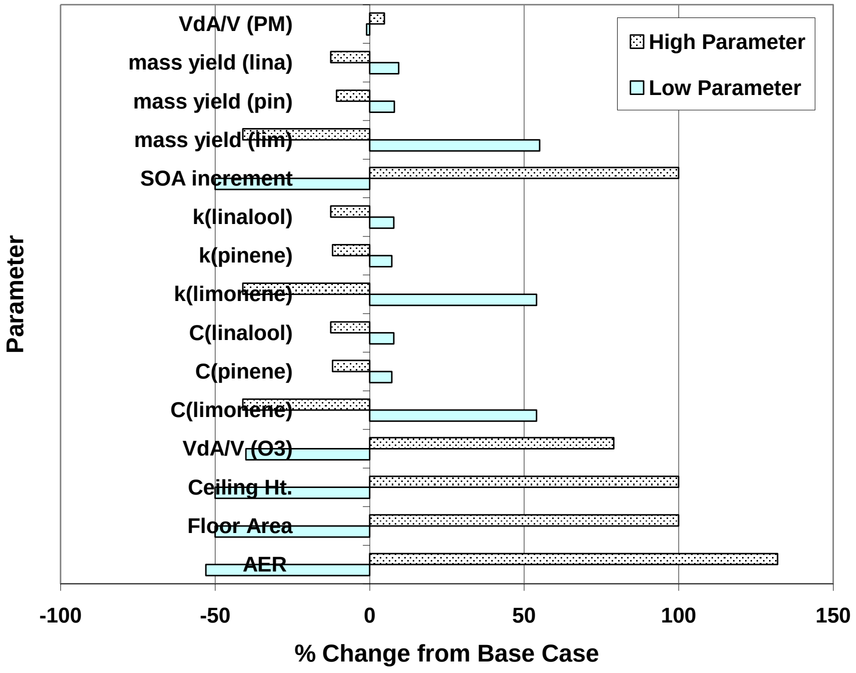

Figure 4-9. Sensitivity of predicted maximum acceptable ozone emission rates in **school classrooms** for factor of two increases (high parameter) and decreases (low parameter) in relevant model parameters, and criterion **based on maximum acceptable SOA concentration**.

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: CH3COH; 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 –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 C=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 (C=O)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 nth root of the product of n numbers. $[a(1) \times a(2) \times a(3) \times \ldots a(n)]^{1/n}$

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 bubbles in a liquid, or 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 highly 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 thousands of configurations.

Unsaturated organic compound: An organic compound that contains one or more carbon-carbon double bonds (C=C).

APPENDIX B. MODEL DERIVATION

Derivation of Equations 2-1 and 2-2

$$C_{O3} \quad = \quad \frac{p\lambda C_{O3,out} + E^{*}_{O3}}{\lambda + v^{*}_{d} + \sum k_j C_j} \qquad (2\text{-}1)$$

$$C_{O3} \quad = \quad \frac{E^{*}_{O3}}{\lambda + v^{*}_{d} + \sum k_j C_j} \qquad (2\text{-}2)$$

Where:

C_{O3} = indoor ozone concentration or incremental concentration increase (ppb)

$C_{O3,out}$ = 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^*_{O3} = 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:

$$V\frac{dC_{O3}}{dt} \quad = \quad pQC_{O3,out} - QC_{O3} - v_d C_{O3} A - \sum k_j C_j C_{O3} V + E_{O3} \qquad (A\text{-}1)$$

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_{O3} = 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:

$$\frac{dC_{O3}}{dt} \quad = \quad p\frac{Q}{V}C_{O3,out} - \frac{Q}{V}C_{O3} - v_d\frac{A}{V}C_{O3} - \sum k_j C_j C_{O3} + \frac{E_{O3}}{V} \qquad (A\text{-}2)$$

But, Q/V = λ (air exchange rate), $v_dA/V = v_d^*$ (ozone decay rate), and $E_{O3}/V = E^*_{O3}$ (volume normalized ozone emission rate of ozone), all as described above. Therefore, Equation A-2 becomes:

$$\frac{dC_{O3}}{dt} \quad = \quad p\lambda C_{O3,out} - \lambda C_{O3} - v_d^* C_{O3} - \sum k_j C_j C_{O3} + E^*_{O3} \qquad \text{(A-3)}$$

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 CO3 can be factored and moved from the right-hand-side of the equation to the left-hand-side (note that CO3 inside the summation sign is a constant and can be moved outside of the summation):

$$\left(\lambda + v_d^* + \sum k_j C_j\right) C_{O3} \quad = \quad p\lambda C_{O3,out} + E^*_{O3} \qquad \text{(A-4)}$$

Solving Equation A-4 for C_{O3} leads to Equation 2-1:

$$C_{O3} \quad = \quad \frac{p\lambda C_{O3,out} + E^*_{O3}}{\left(\lambda + v_d^* + \sum k_j C_j\right)} \qquad \text{(2-1)}$$

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

$$E^*_{\max,O3} \quad = \quad \left(\lambda + v_d^* + \sum k_j C_j\right) C_{O3,\max} \qquad \text{(2-3)}$$

Equation 2-3 is derived by simple inversion of Equation 2-2 to solve for a maximum acceptable ozone emission rate ($E^*_{\max,O3}$) based on a prescribed maximum acceptable indoor ozone increment ($C_{O3,\max}$), i.e., simply solving (algebraically) Equation 2-2 for E^*_{O3}, and establishing this as the maximum emission rate ($E^*_{\max,O3}$) based on a maximum acceptable C_{O3} ($C_{O3,\max}$).

Derivation of Equation 2-4

$$E_{\max,O3} \quad = \quad (0.002 \times V) E^*_{\max,O3} \qquad \text{(2-4)}$$

Where:

$E_{\max,O3}$ = maximum acceptable mass emission rate of ozone (mg·hr^{-1}).

The derivation of Equation 2-4 begins with $E^*_{max,O3}$ followed by an application of the ideal gas law and a series of unit conversions as follows:

$$E_{\max,O3} \quad = \quad E^*_{\max,O3} \times 10^{-9}\,\frac{moles\,O_3}{moles\,air} \times \frac{mole\,air}{24\ L} \times \frac{10^3\ L}{m^3} \times \frac{48\,g\,O_3}{mole\,O_3} \times \frac{10^3\ mg}{g} \times V \qquad \text{(A-5)}$$

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:

$$E_{\max,O3} \quad = \quad E^*_{\max,O3} \times \frac{48}{24} \times V \times 10^{-3} \quad = \quad (0.002 \times V)E^*_{\max,O3} \qquad \text{(A-6 and 2-4)}$$

Derivation of Equation 2-5

$$C_p \quad = \quad \frac{\left(\sum y_j \times k_j \times C_j\right)C_{O3}}{\lambda} \qquad \text{(2-5)}$$

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:

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

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:

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

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

$$C_p \quad = \quad \frac{\left(\sum y_j \times k_j \times C_j\right)C_{O3}}{\lambda} \qquad \text{(2-5)}$$

Derivation of Equation 2-6

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

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

$$C_p = \frac{\left(\sum y_j \times k_j \times C_j\right)}{\lambda} \times \frac{E^*_{O3}}{\lambda + v_d^* + \sum k_j C_j}$$

Now, solving algebraically for E^*_{O3} and setting it to the maximum acceptable emission rate of ozone ($E^*_{\max,O3}$) at a prescribed maximum acceptable concentration of reaction product ($C_{p,\max}$) yields Equation 2-6.

Derivation of Equations 2-7 and 2-8

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

$$C_{SOA} = \frac{\sum \gamma_j k_j C_j C_{O3} U_{c,j}}{\lambda + v_d \frac{A}{V}} \qquad (2\text{-}8)$$

Where:
C_{SOA} = indoor SOA concentration ($\mu g/m^3$)
$C_{SOA,out}$ = outdoor SOA concentration ($\mu g/m^3$)
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 ($\mu g/m^3$ of SOA formed per $\mu g/m^3$ terpene reacted)
$U_{c,j}$ = molar to mass conversion factor for reactant j ($\mu g/m^3$ 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:

$$V\frac{dC_{SOA}}{dt} = pQC_{SOA,out} - QC_{SOA} - v_d C_{SOA} A + \sum \gamma_j k_j C_j C_{O3} U_{c,j} V \qquad \text{(A-9)}$$

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:

$$0 = p\lambda C_{SOA,out} - \lambda C_{SOA} - v_d \frac{A}{V} C_{SOA} + \sum \gamma_j k_j C_j C_{O3} U_{c,j} \qquad \text{(A-10)}$$

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

$$\left(\lambda + v_d \frac{A}{V}\right) C_{SOA} = p\lambda C_{SOA,out} + \sum \gamma_j k_j C_j C_{O3} U_{c,j} \qquad \text{(A-11)}$$

Now, solving for CSOA leads to Equation 2-7:

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

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

$$E_{\max,O3,SOA} = \frac{\left(\lambda + v_d^* + \sum k_j C_j\right)\left(\lambda + v_{d,p} \frac{A}{V}\right)}{\sum \gamma_j k_j C_j U_{c,j}} C_{SOA,\max} \qquad \text{(2-9)}$$

Where:
$E_{\max,O3,SOA}$ = 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):

$$C_{SOA} = \frac{\sum \gamma_j k_j C_j U_{c,j}}{\lambda + v_d \frac{A}{V}} \times \frac{E^*_{O3}}{\lambda + v^*_d + \sum k_j C_j} \qquad \text{(A-12)}$$

Now, solving algebraically for E^*_{O3} and setting it to the maximum acceptable emission rate of ozone ($E^*_{max,O3,SOA}$) at a prescribed maximum acceptable concentration of SOA ($C_{SOA,max}$) yields Equation 2-9.

APPENDIX C. 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*.