A Two-Zone Model to Predict Inhalation Exposure to Toxic Chemicals in Cleaning Products

by

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Dedication and Epigraph

"Man has learned very slowly the condition of his own safe living. Of the three essentials, air, food, water, the air he breathes and is surrounded by, being invisible, is the least known of all…It is not to be wondered at that to most persons the word *air* means very little. They are so used to taking air like other cosmical phenomena, "as it comes," that they are not conscious of the effect of different qualities of air upon their brains and bodies. It is only when they themselves are smitten with the more spectacular forms of disease caused by bad air, such as tuberculosis, and when a physician in whom they have confidence assures them that their only chance for life is to live out of doors, that they begin to realize that the indoor air they have been taking must have been bad."

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Thanks to Mark Jackson for being both a great travel companion and for putting a human face on indoor air quality problems. His courage is inspiring.

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SUPERVISOR: Richard L. Corsi

The use of cleaning products can lead to indoor concentrations of toxic air contaminants above regulatory levels. Studies show that the use of cleaning products is related to adverse respiratory health effects in adults ranging from irritation to asthma. Yet exposure to these chemicals is poorly understood. This thesis summarizes the current state of knowledge of inhalation exposure to toxic chemicals in consumer cleaning products. A new two-compartment model that treats personal air space as distinct from bulk room air is presented. The model accounts for air exchange between the two compartments and fresh air, dynamic source characteristics (i.e., the time-varying liquid concentrations and emission rates of pollutants within a mixture), the characteristics of

chemical use (e.g., how frequently a cleaning chemical is applied to a new area), and reactive chemistry with ozone. The model's applicability is restricted by limited data available for parameterization. Key components that are missing include composition data for consumer cleaning products and activity patterns. Extensive effort went into calculating the air exchange rate between the two zones.

Twelve computational fluid dynamic simulations and two model scenarios were completed. The predicted concentration in the inner-zone (C_{in}) was divided by the room concentration predicted by the traditional well-mixed model (C_{wm}). Concentration ratios (C_{in}/C_{wm}) ranged from 1.1 to 700. In terms of real cleaning events, results indicate that the beginning (where the only emission source is near the person) of events taking place in large indoor environments with high air exchange rates are the situations for which well-mixed models are most likely to fail in predicting actual exposures.

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1. Introduction

1.1. Problem Statement

People frequently bring indoor pollutants in the form of cleaning products into their homes, workplaces, and schools because cleanliness is generally associated with good health. American consumers purchased roughly four-billion dollars in cleaning products annually between 2000 and 2004 (Packaged Facts, 2005). Although this does not translate directly into volume of chemicals produced and consumed, it indicates the pervasiveness of cleaning products in the American marketplace. Cleaning activity pattern surveys estimate that US adults devote an average of 20-30 min/day to house cleaning (Wiley et al., 1991).

While the use of cleaning products can improve the quality of indoor environments, research shows that some cleaning products can yield high levels of toxic air contaminants that are regulated in the outdoor environment. Furthermore, people use these products under the assumption that they will improve the quality of their indoor environment. This assumption can be flawed. Persons involved in cleaning, particularly those three million people who clean by occupation (US Department of Labor, 2001), or who clean often, are especially at risk of being exposed to excessive concentrations of toxic chemicals

1.2. Research Objectives

The specific objectives of this research were to:

1. Improve understanding of cleaning product exposure

2. Develop a two-compartment model that treats personal air space as distinct from bulk room air. This model should include:
    - air exchange between the two compartments and fresh air,
    - dynamic source characteristics (i.e., the time-varying liquid concentrations and emission rates of pollutants within a mixture),
    - the characteristics of chemical use (e.g., how frequently a cleaning chemical is applied to a new area), and
    - reactive chemistry with ozone.
3. Identify scenarios for which well-mixed models are inappropriate.
4. Identify factors that most influence exposure.
5. Identify methods for reducing exposure.

1.3. Scope Of Research

The current state of knowledge of inhalation exposure to toxic chemicals in consumer cleaning products is reviewed in this thesis. A model was developed and employed in two possible cleaning scenarios. The model's applicability is restricted by limited data available for parameterization. Key components that are missing include composition data for consumer cleaning products and activity patterns. Extensive effort went into calculating other variables. This work involves only modeling. No experiments were completed.

1.4. Organization Of Report

Chapter two of this report provides the background information of the current state of knowledge of near source effects, cleaning product chemical composition and health

effects of cleaning products. A summary of previous exposure modeling approaches is also provided. A novel model is introduced in chapter three. The model is described, and input parameter are discussed and justified. Significant emphasis is placed on the inter-zonal air exchange rate. Chapter three concludes with a discussion of how a sensitivity analysis was performed on the model. Results and discussion are presented in chapter four. Two cleaning scenarios are described and their results are discussed and compared to previous literature. Results of the sensitivity analysis are also discussed. Conclusions and a discussion of future work are summarized in chapter five.

2. Background

2.1. Near Source Effects

When a chemical is emitted from a localized source, spatial variability occurs (McBride et al., 1999).This has been well understood since early work on radioactive aerosols in the 1960s. Multiple large field studies of volatile organic compounds (VOCs) and particulate matter were completed in the 1980s and 1990s (McBride et al., 1999; Rodes et al.; 1991, Sexton et al. 2004; Wallace, 1985; Wolkoff et al., 1998). These studies showed that outdoor concentrations of VOCs are generally lower than indoor concentrations, which are generally lower than concentrations in the immediate vicinity of the body.

The USEPA's TEAM study involved measurement of 20 VOCs in the personal and outdoor air of 355 participants. Personal exposures were consistently higher than outdoor concentrations for VOCs, and were sometimes ten times higher than what would have been predicted from ambient monitoring alone. Indoor sources appeared responsible for much of the difference (Wallace, 1985).

Sexton et al. (2004) measured personal, indoor, and outdoor air concentrations for 71 adults in Minneapolis. Personal concentration measurements exceeded indoor air concentrations which exceeded outdoor air concentrations for 13 of the 15 measured VOCs, with the exceptions being carbon tetrachloride and chloroform. Also, personal sampling of VOCs and airborne dust shows higher concentrations than stationary sampling (Wolkoff et al., 1998). Rodes et al. (1991) reports that ratios from personal monitors to those made by micro-environmental exposure monitors are typically 1.2-3.3

for residential settings, and that the ratio is dependant primarily on the proximity of the occupant to the source.

The near source effect is particularly important for cleaning situations because a characteristic of the cleaning activity is that the person cleaning puts themselves within an arms length of the cleaning product. Further, depending on the occupants' orientation low pressure areas can form around the body due to the thermal plume. It has been shown that low pressure areas within 0.5-1 meter of the body can draw pollutants into the breathing zone (George et al., 1990; Rodes et al., 1991). Also, beyond simple dispersion, loss mechanisms (e.g. sorption, reactive chemistry, settling, etc.) typically increase as a pollutant is transported away from the occupant, increasing the concentration gradient.

Spatial variability can occur over very short distances. Early studies related to exposure to lead showed variations of as much as 22% for samples taken at the belt versus the lapel (Chatterjee et al., 1969). Measurements of xylene averaged 50% higher when taken on the right lapel of a right handed worker than when taken on the left lapel (Coker, 1981). The concentrations of respirable particles between the nose and lapel of foundry workers were shown to be as high as three (Martinelli et al., 1983). Although some of these results deal with particles, they certainly warrant further investigation and provide cause to move away from a well mixed model

2.2. Cleaning Chemicals

2.2.1. Composition

A significant challenge to understanding the health effects of cleaning products is that their compositions are not readily available. No producers of cleaning products

publish complete chemical compositions, while some publish concentration ranges of active ingredients on their Material Safety Data Sheets. Further, few studies exist in the literature that investigate compositions beyond what has been published by the producers. Many of these studies are dated, reporting on cleaning products whose compositions no longer correspond with those of current products. For example, the Clean Air Act (CAA) Amendments of 1990 restricted the production of chemicals associated with cancer, birth defects, respiratory disease, neurological damage, environmental damage, and other harms (Hodgson and Levin, 2003). Hodgson and Levin compared current and historical concentrations of several chemicals in indoor air, finding that such chemicals as benzene,1,1,1-trichloroethane, and tetrachloroethene have decreased. They attribute this difference to the CAA. Thus, the studies reviewed in this report represent cleaning products produced after the passage of the CAA. Further, authors do not list liquid concentrations or the particular products that the analysis was run on. This limits the usefulness of their results.

Another hurdle to understand the composition of cleaning products is the regulatory structure in the United States. No law in the United States requires the disclosure of the individual chemical constituents in consumer products. Steinemann (2009) preformed an analysis of the limits of disclosure as well as chemical composition tests for six products. Her regulatory analysis found that the Federal Food, Drug, and Cosmetic Act (FFDAC) requires that products containing fragrances must list the word “fragrance”, but listing the individual chemicals making up the fragrance is not required. But “fragrance” may not need to be listed at all, since more general rules that regulate products other than food,

drugs, cosmetics, tobacco and pesticides fall under the Consumer Product Safety Act (CPSA). This act relies on voluntary product safety standards and only requires labeling of date, and place of manufacture, identification of the manufacturer, and certification that the product meets all consumer product safety standards if they exist. One of the goals of this legislation is to make matching the product to its proper Material Safety Data Sheet (MSDS,) easier. Unfortunately the MSDS is also not always helpful. Ingredients are not required to be included in the MSDS if the manufacturer deems that the ingredient is not hazardous. Further, ingredients deemed trade secrets are exempt from disclosure under the Freedom of Information Act, the FFDCA and the CSPA. A trade secret is anything not known to the public, provides independent economic value, and is the subject of reasonable effort by its owner to maintain its secrecy. These two points has lead the government to admit that the "accuracy and completeness of MSDSs is vulnerable" (GAO, 1991). Surveys have found that most were "incomplete, inaccurate or both" (GAO, 1991).

Steinemann (2009) determined the compositions of six cleaning products (3 air fresheners and 3 laundry supplies) using GC/MS. A total of 98 VOCs (58 unique VOCs) were reported in tabular form for each of the cleaning products. They were arranged in order of strength of signal, but actual concentrations were not reported. Compounds with headspace concentrations below 300 $\mu g/m^3$ were not reported. The most commonly identified VOCs were the following: ethanol, d-limonene (in all six products); α-pinene, β-pinene (in five); carene isomer, 2,4-dimethyl-3-cyclohexene-1-carboxaldehyde (Triplal 1) (in four); and acetaldehyde, benzyl acetate, 3-hexen-1-ol, and linalool (in three). Five

of the six products emitted one or more Hazardous Air Pollutants (acetaldehyde, chloromethane, and 1,4-dioxane). For five of the six products, none of the chemicals found using GC/MS were listed on the label or the MSDS. In the final product, ethanol was the only chemical found by GC/MS that was listed on the MSDS; it was not on the label.

Kwon et al. (2008) identified the composition of VOCs in 29 cleaning products covering ten product classes. However, VOC concentrations were not reported individually within each product class. For example, rather than providing ten concentrations of ten VOCs in one product, one value was given for the product regardless of the number of constituent chemicals. Sack et al. (1992) determined chemical compositions for more than 100 cleaning products in 15 product classes. However, they reported a single chemical composition for all cleaning products, rather than report on each product or class separately. Wolkoff et al. (1998) grouped cleaners by their purposes (disinfecting agents, surfactants, acids, bases, complexing agents, ect.) and reported compositions, but did not include concentrations. Nazaroff and Weschler (2004) listed 21 chemicals found in cleaning products that are listed as toxic air contaminates under California's Proposition 65 and the type of cleaning product they are found in, but they did not report concentrations. Finally, Zhu et al. (2001) and Singer et al. (2006) reported chemical compositions for several individual cleaning products. A summary of these results is presented in Table 1. 2-Butoxyethanol, α-pinene and limonene appeared in many product classes. Because of 2-butoxyethanol's prevalence in consumer products and the amount of attention it has garnered in the literature, an in-depth report dedicated

exclusively to 2-butoxyethanol exposure is attached in appendix 1. The report was completed by the author of this thesis.

The studies described above do not encompass the entire body of literature on cleaning product chemical compositions. However, they cover a wide range of cleaning products and serve as a strong foundation for the present study.

Table 1: Chemical Constituents of Common Cleaning Products

Product Class	Chemical	Source
Bleach	Acetone, chloroform, 1,8-cineole, limonene, *cis*-limonene oxide, *trans*-limonene oxide, α-pinene, *β*-pinene	Kwon et al., 2008
	Bromodichloromethane, chlorobenzene, chloroform, carbon tetrachloride, dibromochloromethane, 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethene, 1,2-dichloroethene, trichloroethene, tetrachloroethylene	Odabasi, 2008
Dishwashing detergent	1,4-Dioxane, ethanol, ethyl acetate, 1-hexadecanol, limonene, 1-propanol. *β*-myrcene, 3-pentanol, *α*-pinene, limonene, *β*-myrcene, 1-tetradecane	Kwon et al., 2008
Disinfectants	Ammonia, *iso*-amyl acetate, camphene, chloroform, 1,8-cineole, iso-cineole, decane, ethanol, hexane, limonene, 3-methyl pentane, octane, α–pinene, *β*-pinene, toluene, undecane	Kwon et al., 2008
	2-Butoxyethanol, *d*-limonene, α–pinene, *β*–pinene, toluene	Zhu et al., 2001
Floor cleaners	2-(2-Butoxyethoxy)ethanol, *n*-butyl ether, *d*-limonene, *α*-pinene, *β*-pinene	Zhu et al., 2001
General purpose cleaners	Ammonia, chloroform, 1,8-cineole, *iso*-cienole, limonene, *β*-myrcene, octane, *α*-pinene, *β*-terpinene	Kwon et al., 2008
	2-Butoxyethanol, camphene, d-limonene, α -phellandrene α,*β*-pinene, *α,γ*-terpinene, *1*-terpineol, *4*-terpineol, *α*-terpineol, *β*-terpineol, *γ*-terpineol, terpinolene	Singer et al., 2006
	2-Butoxyethanol, camphene, *β*-myrcene, *β*-pinene, *d*-limonene	Zhu et al., 2001
Glass cleaners	2-Butoxy ethanol, 1,8-cineole, ethanol, limonene	Kwon et al., 2008
	2-Butoxyethanol, 2-hexyloxyethanol	Singer et al., 2006

	2-Butoxyethanol, camphene, 3-carene, 2-hexyloxyethanol, *d*-limonene, *β*-myrcene, *α-phellandrene,* *α*-pinene, *β*-pinene,	Zhu et al., 2001
Household cleaners and polishes	Acetone, ethylbenzene, *n*-hexane, methylcyclohexane, methylene chloride, *n*-octane, tetrachloroethylene, tetrahydrofuran, toluene, 1,1,1-trichloroethane, *m*-xylene,	Sack et al., 1992
Laundry detergents	Acetone, benzene, ethanol, limonene	Kwon et al., 2008
Laundry stain removers	Acetone, ammonia, decane, 3,7-dimethyl-3-octanol	Kwon et al., 2008
Oven cleaners	Ammonia, camphene, 1,8-cineole, *iso*-cineole, ethanol, limonene, *β*-myrcene, *α*-pinene, sabinene, *α*-terpinolene	Kwon et al., 2008

2.2.2. **Health Effects**

Recent studies show that the use of cleaning chemicals is related to adverse respiratory health effects in humans (Zock et al., 2007), and that many of the chemicals found in cleaning products are known irritants and allergens (Nazaroff et al., 2006). While many of the chemicals in cleaning agents are hazardous, VOCs have the most toxicological significant because they are more toxic and have higher exposures than non-volatile toxic substances (Wolkoff et al., 1998) For example, Kwon et al. (2008) found that more than two-thirds of 29 cleaning products contained tetrachloroethylene, which is a known respiratory tract irritant (HSDB, 2005).

Zock et al. (2007) demonstrated a direct relationship between cleaning chemicals and negative health effects. They analyzed data from 22 groups in 10 countries that participated in the European Community Respiratory Health Survey, and found a statistically significant correlation between the use of cleaning sprays in the home and new onset of wheeze, nocturnal attacks of shortness of breath, and/or asthma in adults. Their results show that the risk is associated with inhalation exposure potential, and that

those using cleaning products in their homes at least four days a week and/or use more than three different types of products at least one day per week experience the greatest risk (Zock et al., 2007).

The association between the use of cleaning products in the home and the onset of adult asthma is consistent with previous findings of adverse respiratory effects related to cleaning products. There have also been several epidemiologic studies, along with multiple individual case reports of workers who clean residential, commercial, or industrial facilities that describe increased incidents of asthma and respiratory symptoms related to the use of cleaning products. (Nazaroff et al., 2006; Rosenman, 2006; Jaakkola and Jaakkola, 2006). Wolkoff et al. (1998) reported an association between VOC exposure from cleaning agents and increased reporting of symptoms, especially eye symptoms among people that clean occupationally. Nazaroff and Weschler (2004) compiled a list of 13 documented asthma and/or allergy associations related to cleaning products.

Cleaning products also pose cancer risks. Singer et al. (2006) conducted simulated cleaning scenarios in the presence of ozone in a 50 m^3 chamber mocked up to resemble a room, and found that a single cleaning event could contribute 20-50% of the weekly average exposure allowable under California's cancer exposure guidelines. Thus, more frequent cleaning by professional or fastidious house cleaners could lead to exposure that exceeds chronic weekly standards.

Cleaning products can also lead to acute health risks. In the years leading up to 2005, cleaning agents were responsible for 70,000 to 80,000 reports per year to either the

American Association of Poison Control Centers or the Toxic Exposure Surveillance System. Accounting for roughly 10% of annual reports, cleaning products were among the top three most frequently reported poison exposures among adults (Lai et al., 2006).

In addition to adult health risks, exposure to cleaning chemicals poses a health risk to children. A number of researchers have found a link between exposure in utero and the development of respiratory disease in early childhood. For example, Sherriff et al. (2005) found a correlation between increased domestic household chemical use by women during pregnancy and an increased risk of persistent wheezing in young children. Furthermore, they identified cleaning products as the primary source of exposure to such chemicals. Henderson et al. (2008) reported similar findings; however, they also found an increased prevalence of wheezing in non-atopic children who were exposed to cleaning chemicals while in the womb (Henderson et al., 2008). This finding is troublesome, as it demonstrates a clear environmental factor in the aetiology of childhood respiratory disease. Recent research has also revealed that during pregnancy women spend more time cleaning (Uguz et al., 2007b). Since these behaviors continue postnatally, they pose further exposure risk to newborns and young children (Uguz et al., 2007a). Collectively, these findings demonstrate that a clean indoor environment does not necessarily equate to a healthy one, as exposure to cleaning chemicals has clear negative health effects.

2.3. Previous Models

Few field studies have dealt specifically with exposure to VOCs from cleaning agents (Wolkoff et al., 1998). To fill this vacuum several models have been used to predict exposure to cleaning products, of which the well-mixed box method is the most

prevalent. This model assumes an instantaneous uniform distribution of pollutants across an entire indoor space, with constant air exchange and emission rates. These assumptions are invalid for an activity like cleaning, as they ignore the dynamic behavior of indoor air. When a chemical is emitted from a localized source, spatial variability occurs (McBride et al., 1999). Girman et al. (1987) showed that at a high air exchange rate (3.2 hr^{-1}) personal exposure to methylene chloride (CH_2Cl_2) during a simulated use experiment in a chamber was 22% higher than would have been expected from calculations based on the room air sampler. The same experiment showed that the well-mixed assumption underestimates the personal peak concentration by 36%. This is the only published study that addressed peak concentrations. Most researchers fail to report the peak concentrations because passive samplers average exposure over long sampling times, up to 24 to 48 hours. Cleaning events, where the occupant is very close to a strong source for a short period of time, are "lost" if averaged over long periods of time even though they are likely to produce high peak concentrations.

The assumption of a constant air exchange rate can predict incorrect concentrations in some situations. This assumption can produce valid results over long time periods because the short-term fluctuations above and below the average will cancel out. However, most cleaning events occur in the short-term, where phenomena like wind gusts, HVAC system cycles, and the use of an exhaust fan can have a significant impact on indoor concentrations. Finally, the constant emission rate assumption is flawed because it ignores the fact that higher vapor pressure components will evaporate first,

changing the composition of the remaining liquid, and thereby changing the emission profile associated with cleaning products.

To describe concentrations and dispersion in a space that is not perfectly mixed, Nicas (1992) divided the space into two distinct zones. He treated each zone as well mixed and limited the airflow between the zones even though they are physically continuous. He described the two zones as near field and far field, where the near field is the area immediately around the source and the remainder of the space is the far field. He treated the near field zone as a sphere with a radius of the distance between the source and occupant, and defined the volumetric exchange between the two zones as the product of the room random air speed the surface area of the theoretical boundary between the two zones. Although this model does not describe the concentration at every point in the room, it provides an improvement over the well-mixed model. A variation of this model is employed later in this report.

A popular conservative estimate of an emission rate is to divide the total liquid volume of the chemical by the emission duration (Nazaroff and Weschler, 2004). This method assumes that the entire chemical is dispersed and that the space is occupied for the entire emission duration, neither of which usually occurs while cleaning. Typically, excess chemicals (e.g., on rags, in mop buckets, etc.) are not used, and such chemicals as 2-butoxyethanol emit very slowly (on the order of hours to days; Nazaroff and Wechsler, 2004). Another method of calculating emission rates is to assume the initial concentration at the interface (determined using head space analysis) is constant over the duration of an

emission event. This method also ignores the fact that the liquid composition varies with time.

Most researchers ignore sorption to indoor surfaces and homogeneous reactions between chemicals in cleaning agents and other gaseous chemicals such as ozone. Sorption can greatly decrease peak concentrations. Tichenor et al. (1991) developed a model of reversible sorption that can be added as a term in a mass balance equation. Since then, many researchers have published rate constants for sorptive uptake and desorption (Jorgensen and Bjorseth 1999; Singer et al., 2007; and Won et al., 2001). Nazaroff and Weschler (2004) utilized data reported by Sparks et al. (1999) for 2-(2-butoxyethoxy)ethanol interactions with carpet and gypsum board to model a periodic event with and without sorption. They showed that during and shortly after the pollutant release, sorption decreased exposure by a factor of four; but in the hours after, exposure was higher than would be predicted without sorption.

Gas-phase reactions among oxidants such as ozone, radicals such as $OH^{\cdot}$ and $NO_3^{\cdot}$, and cleaning chemicals can have a meaningful impact on indoor air quality when the reactions occur at a rate competitive with air exchange rates or other removal processes (Nazaroff and Weschler, 2004). Several publications dating to the mid-1980s include rate constants for these reactions, but few studies of cleaning products have included ozone reactions as part of exposure estimates.

3. Model Development

In this chapter a new model is developed to predict inhalation exposures to toxic chemicals emitted from cleaning products. The intent is to provide a model that improves

upon a single well-mixed zone model, but does not require time-intensive computational fluid dynamic analysis.

3.1. Model Formulation

The model developed for this thesis predicts concentrations of specific VOCs emitted from a cleaning product in inner and outer zones. The inner zone comprises the air space immediately surrounding the person who applies a cleaning product. The outer zone is all remaining volume in the interior zone occupied by the person. Air flows freely between the two zones and is also exchanged with outdoor air.

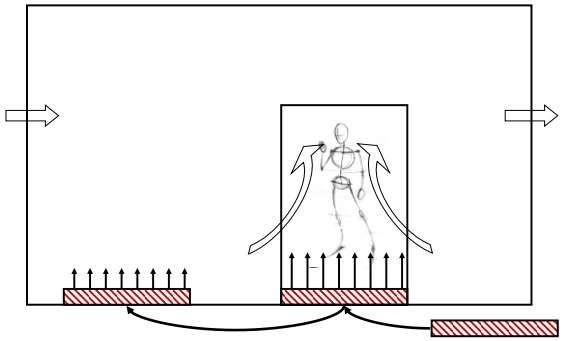

Figure 1: Schematic representing major features of the two-zone model.

As the indoor environment is divided into zones, the liquid cleaning product is divided into portions, which are referred to here as source cells. Each source cell represents the dispersal of product with each application (e.g., each time the mop is dipped in the bucket or each time a product is sprayed). Source cells are assumed to be well-mixed, and added to the space at a constant frequency (f, in cells/time). The newest source cell emits directly to the inner zone, while all other source cells emit to the outer zone. This mimics the real world, where the person cleaning is in closest proximity to the most recently applied product. Other factors that affect VOC concentrations in the inner

zone include inter-zonal air exchange and homogeneous reactions with ozone. Equation 1 was used to calculate the concentration of each VOC in the inner zone.

$$\frac{dC_{in}}{dt} = \lambda_{in}(C_{out} - C_{in}) + \frac{E}{V} - kC_{in}C_{O3} \quad (1)$$

In this equation, λ_{in} is the inter-zonal air exchange rate in inverse seconds; C_{out} and C_{in} are the concentrations of the VOC in the outer and inner zone, respectively, in milligrams per cubic centimeter; E is the emission rate for the VOC in the most recent source cell in milligrams per second; k is the reaction rate constant between the VOC and ozone in cubic centimeters per milligram per second; C_{O3} is the concentration of ozone in the zone in milligrams per cubic centimeter; and V is the volume of the inner zone in cubic centimeters.

The volume of the inner zone is an important parameter that has not been determined in previous research. A large volume would be expected to reduce the difference in concentration between the zones (i.e., the concentrations would approach convergence), while a small volume would be expected to increase the difference in concentration between the zones.

The outer zone comprises the air in the room excluding the inner zone. Factors that affect VOC concentrations in the outer zone include air exchange with the inner zone and with fresh outdoor air, volatilization from cleaning products on surfaces outside the inner zone (i.e., older source cells), and homogeneous reactions. Equation 2 was used to calculate the concentration of each VOC in the outer zone.

$$\frac{dC_{out}}{dt} = \lambda_{out}(C_o - C_{out}) + \lambda_{in}(C_{in} - C_{out}) + \frac{\sum E}{V} - kC_{out}C_{O3} \quad (2)$$

In this equation, λ_{out} is the air exchange rate for the outer zone in inverse seconds; λ_{in} is the inter-zonal air exchange rate in inverse seconds, but in this equation it is respective to the volume of the outer zone; ΣE is the sum of all but the newest source cell emissions in milligrams per second; and V is the volume of the outer zone in cubic centimeters. All other variables are as described previously.

The occupant will have a large effect on the inter-zonal air exchange rate. Unfortunately, this effect is not well-quantified. More movement by the occupant might increase airflow, and increase the inter-zonal air exchange rate in turn. However, more movement might also disrupt the occupant's thermal plume, which would affect airflow in the room. It would also be useful to know how changes in the air exchange rate in the outer zone (e.g., switching on the bathroom exhaust fan) affects the air exchange rate between zones. This modeling exercise is described in detail in a later chapter of this thesis.

In addition to calculating concentrations in the inner and outer zones, the concentration in a single-zone in a well-mixed model was calculated for model comparison. Single-zone concentration (C_{wm}) was calculated using a modified form of equation 2, excluding the $\lambda_{in}(C_{in} - C_{out})$ term but including the most recent source cell in the ΣE term. Emission rates for each VOC were calculated from each source cell using equation 3.

$$E = k_g(HC_{liq} - C_{in})A \quad (3)$$

In this equation, k_g is the mass transfer coefficient in centimeters per second; H is the Henry's Law coefficient in liquid concentration per gas concentration $[(mg/cm^3)_{liq}/(mg/cm^3)_{gas}]$; C_{liq} is the concentration of pollutant in solution in mg/cm^3; and A is the area of the solution film in cm^2. In calculating the emission rate of water, a constant relative humidity of 44% at 295.25K was assumed, and thus a constant concentration gradient between liquid and gaseous water was assumed. This emission rate is important because it affects the mass fraction of VOCs in the aqueous solution.

The concentrations of VOCs in both zones should be positively related to the amount of chemical dispersed with each application. The amount of chemical dispersed is a function of the properties of chemicals used. Kovacs et al. (1997) found that scented cleaning products are used in smaller volumes than unscented volumes. Other factors, such as the surfaces being cleaned and the amount of surface soiling, might also affect the amount of chemical dispersed. A better understanding of cleaning product use patterns would better inform the model and provide a more representative result.

The amount of cleaning chemical used also affects the surface area of the liquid film in the source cell. This area is used for determining emission rates, and is based on human activity as discussed above, as well as properties of the fluid, such as viscosity.

The final terms in the mass balance equations described above are ozone reactions. Equation 4 was used to calculate the concentration of ozone in the inner and outer zones.

$$\frac{dC}{dt} = \lambda(C_o - C) - \sum_i V_d C \frac{A_i}{V} - \sum_j kCC_j \quad (4)$$

In this equation, C is the concentration of ozone in milligrams per cubic centimeter, and V_d is the deposition velocity of ozone to *i* surface of area A_i in cm^2, summed across all surfaces. All other variables are as described previously. Furthermore, homogeneous reactions are summed across *j* VOCs. The outdoor concentration of ozone (C_o) is given in milligrams per cubic centimeter. To calculate ozone concentration in the inner zone, the same equation is used, and C_o is the concentration of ozone in the outer zone.

The model requires solving equations 1 to 4 simultaneously to obtain a solution. Equations were discretized in time and Matlab was employed to solve the equations. The corresponding code is attached in appendix 2.

3.2. Model Parameters

The model developed for this study requires thirty input variables. Those used in equations 1-4 are listed below in alphabetical order starting with the variable name, followed by factors that affect the parameter, values gleaned from literature, and reasonable ranges if applicable.

- Application area: area covered by cleaning product for each source cell (cm^2). It could also be thought of as the total surface area cleaned during a cleaning event divided by the number of source cells applied during the cleaning event. This value, along with the other activity pattern parameters, is not reported in the literature.
- Deposition velocity: deposition of chemical i to occupant surfaces (clothing, hair, skin etc.). Deposition to these surfaces is not described in the literature and so was

assumed to be zero, but it is common sense that this type of deposition does occur in the real world. Neglecting deposition will provide a conservative estimate of exposure, as deposition can only decrease exposure since it is exclusively a loss term in the mass balance. More research is needed to accurately characterize the effects of chemical deposition. Deposition rates to room surfaces (walls, floor etc.) are also used. These data is available in the literature, or can be calculated, for the most studied chemicals.

- Frequency of application: amount of time between source cell applications of how frequently during the cleaning event fresh product is dispersed (e.g. sprayed or sponge dipped in bucket) No data on this parameter exist in the literature. Values were chosen from personal experience.
- Fresh air exchange rate: air exchange rate between the outer-zone and fresh outdoor air. This parameter is assumed to remain constant throughout the model duration, even though it is known to vary based on mechanical ventilation and outdoor meteorological conditions, especially wind. Murray and Burmaster (1995) provided an extensive study of residential fresh air exchange rates and reported that they range from 0.05-6.5 hr^{-1} with a median of 0.5 hr^{-1}. More recently, Howard-Reed et al. (2002) published a study based on just two residences that compared fresh air exchange rates with windows open and closed and found that that they range from 0.10-0.82 hr^{-1} with windows closed and 0.44-1.66 hr^{-1} with windows open. Also, there is reason to believe beyond this newer publication that residential air

exchange rates are decreasing due to an increased public consciousness of the energy implications of leaky houses.

- Henry's constant: dimensionless Henry's constant for chemical i (C_{gas}/ C_{aq}). Henry's constants are readily available for many, but not all, chemicals found in cleaning products.
- Inter-zonal air exchange rate: air exchange rate between the inner- and outer-zone (s^{-1}). Nicas (1992) used the product of the random air speed and the free surface area of the near- and far-field interface divided by two. Some information is available about random air speeds indoors, but the speeds vary widely depending on fluid dynamic conditions in the room. To address this irregularity, Futaw (1996) varied the inter-zonal air exchange rate by a statistical distribution. Since the model was found to be most sensitive to this parameter, further study was conducted using computational fluid dynamics (CFD) and is reported in the next section.
- Mass transfer coefficient: overall mass transfer coefficient in the gas phase (cm/s). The mass transfer coefficient is specific for each chemical and flow condition and is governed by a theoretical relationship involving the Reynolds number, Schmidt number, molecular diffusion coefficient of a chemical and area of application. Once the mass transfer coefficient is determined for one chemical (e.g., water) the mass transfer coefficient can be derived for the other chemicals of interest. A reasonable range from a synthesis of many sources is about 0.5-10 m/hr (e.g. CanoRuiz et al., 1993 and Sparks et al., 1996)

- Ozone concentrations: C_o is the ozone concentration in fresh air in milligrams per cubic centimeter and is assumed to remain constant through the model duration. Outdoor ozone concentrations vary depending on season, time of day, meteorological/atmospheric conditions, population, and geographical location. C_{o3} is the initial concentrations of ozone in the inner- or outer-zones. Indoor ozone tends to be 30-70% of outdoor levels (Weschler, 2000).
- Ozone deposition velocity: deposition velocity of ozone to room and occupant surfaces in centimeters per second. A few deposition rates, mostly to surfaces found in offices, are reported by Weschler (2000). Wolkoff et al. (1999) and Kleno et al. (2001) provided deposition velocities for a wider variety of surfaces. Deposition to occupant surfaces is not well characterized in the literature.
- Ozone deposition surface area: surface area of materials that ozone deposits to in square centimeters. These surfaces are treated differently than surfaces that chemicals found in the cleaning product deposit to, even though there is usually some overlap.
- Ozone reaction rate: homogenous reaction rate between ozone and chemical i ($(mg/cm^3)^{-1}\ s^{-1}$). These are taken from literature. Weschler (2000) and Atkinson et al. (1995) present a fairly large range of values for chemicals of relevance to indoor surfaces.
- Relative humidity: relative humidity of room air. It is treated as a constant throughout the modeling period. Evaporation of liquid water is considered a negligible contributor to the humidity in the room. Relative humidity depends on

season, time of day, temperature, meteorological conditions, and geographical location.

- Surface area: surface area to which individual constituents of the cleaning product deposit (cm^3). This parameter encompasses surface area of occupant the surfaces (clothing, hair, skin ect.) and the surface area of room surfaces (walls, floor etc.)
- Temperature: air temperature in the room in Kelvin.
- Volume of inner-zone (cm^3). Previous literature has used a sphere with a radius of the distance between the source and the receptor with the center of the sphere being the source (Nicas, 1992) and the center being the receptor (Futaw, 1996). Rhodes (1991) advocated the use of a model more complex than the well-mixed model whenever the occupant is closer to the source than "an arm's length", implying that the characteristic length of the inner zone should be based on the length of an arm. These studies deal with point sources. Although a previous study in the literature could not be found to support it, a box around the occupant was used in this model. The box is as tall as the occupant with a base of area A. This makes sense because a sphere cannot capture the emission of a broad area covered by a cleaning product, and the thermal plume of the occupant draws air up in the shape of a column, not a sphere.
- Volume of outer-zone: Volume of the occupied space minus the volume of the inner-zone (cm^3).
- Volume of product: liquid volume of cleaning product dispersed (V). This parameter does not include the volume of the product that is not dispersed but still

in the occupied space, e.g., product left in a bucket or on a mop. It is also a parameter that is not well understood in the literature. Some manufacturers report how much surface area their cleaners will cover, but this is not indicative of how the product is actually used, as not all people read and follow the directions. Nazaroff et al. (2006) reports the mass dispersed of a few cleaning products but does not indicate which products they are or the product composition or average density, limiting the usefulness of the data.

This chapter highlights glaring deficiencies in knowledge available to calculate exposure to toxic chemicals found in cleaning products. Specifically, more research is needed on sorption, ozone deposition, cleaning activity patterns (frequency of application, area of application) chemical compositions, volume of the inner-zone, and the inter-zonal air exchange rate.

3.3. CFD Analysis of Inter-Zonal Air Exchange Rate

The inter-zonal air exchange rate is the least understood of all the parameters in the model.. Because the boundary between the inner- and outer-zone is purely theoretical, experimental determination of the inter-zonal air exchange rate is not practical. Thus, CFD was employed. Twelve scenarios were constructed to represent four fresh air exchange rates and three source configurations. The results of these 12 simulations showed that the minimum inter-zonal air exchange rate is $170 \pm 29\ hr^{-1}$. The remainder of this section is dedicated to how this value was obtained.

As seen in Figure 2, the model set up in FLUENT consisted of a cube room with a person, modeled as a cylindrical (radius=0.33m; height=1.5m) heat source, in the center

of the room. The cylinder was heated (energy=45w) to determine the contribution of the thermal plume to the inter-zonal air exchange rate. Forty-five watts was chosen as the convective contribution. The heat generated by the cylinder remained constant across all trial runs. A chemical source representing a thin film of cleaning product sits directly under the cylinder.

The emission of the chemical was modeled using FLUENT's flux setting, this forced the emission rate to remain constant even though the fluid conditions above the source changed. This will allow for better comparison of the final results. The average flux of 2-butoxyethanol (a toxic surfactant found in many cleaning products) from a one square meter surface covered with a typical floor cleaning product was previously determined to be 18 mg/s (see Appendix 1 for calculation).

Each source cell represents a fresh application of cleaning product that is dispersed each time that a mop is dipped in a bucket or each time a cleaning solution is sprayed out of a bottle. Thus, for each cleaning event multiple source cells were applied. Due to the nature of cleaning activities, the freshest source cell is always closest to the person cleaning, i.e., in the inner zone. After the person applies a source cell they move away from it to clean a new area. Thus, after a new cell is applied the old one continues to emit but it moves to the outer zone and emits there.

Three source configuration scenarios were analyzed in this study; one with a single source cell in the inner-zone; another where there was one source cell in the inner zone and one source cell in the outer zone; and a third where there was one source cell in the inner-zone and two cells in the outer zone. The final scenario is illustrated in Figure 2.

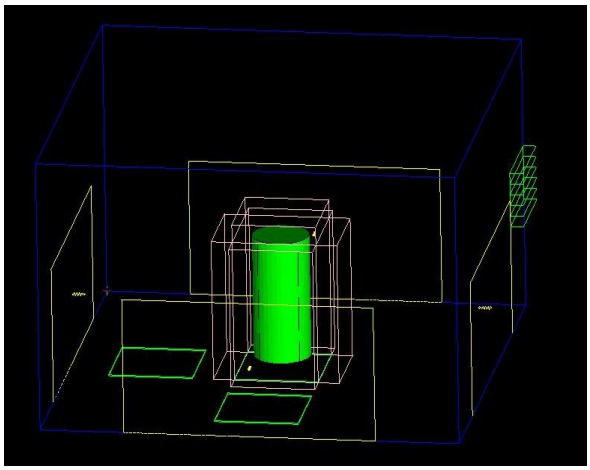

Figure 2: FLUENT model geometry

Five (one on top and four sides) fluid boxes formed an enclosure around the cylinder and chemical source. The boxes did not affect the air flow. They were used to calculate total volumetric air flow into and out of the inner-zone using FLUENT's report features. The air flow was calculated two different ways to verify the results. The first used the orthogonal velocity vector coming out of the top of the box; the second involved the sum the orthogonal velocities on all four sides. Each velocity was multiplied by the respective surface area to obtain a volumetric flow rate in cubic meters per hour. This air flow was divided by the inner-zone's volume (1.06 m^2) to obtain the inter-zonal air exchange rate.

Air flowed into the room through four symmetric openings and out through a vent in the center of one wall. Four openings were used to minimize the impact of the incoming momentum. This air speed through each opening provided negligible momentum compared to the momentum provided by the thermal plume.

Basic CFD Parameters and Settings

The velocity vectors in all three directions, pressure, temperature, continuity and concentration equations were all solved by FLUENT. For simplicity, only one chemical was used in the simulation. Sulfur hexafluoride (SF_6) was an acceptable surrogate because it has similar properties to 2-butoxyethanol, namely a similar density and diffusivity.

Turbulence can be modeled several ways in FLUENT. For this thesis the "indoor zero equations" were used to model turbulence. The mesh was generated using FLUENT's mesh generator with the most refined mesh being around the cylinder and the species source on the floor. The density of the mesh around the cylinder was at least twice that of the rest of the room.

Although the model is steady-state, the actual flow would be unsteady due to eddies around the top of the cylinder. Therefore the momentum, temperature, and SF_6 equations were under-relaxed beyond FLUENT's default settings. This made the model more (not completely) stable, but also extended the computation time.

CFD Modeling accuracy verification

The residuals never became completely level because of eddy formation above the cylinder. An acceptable level of convergence (no more than 7% variance) was reached when the model was run with two different grid sizes. When the grid size was changed, the temperature, momentum, and concentration residuals still varied by approximately 5% around the mean. A similar solution was achieved with both grid sizes, meaning that the solution was grid independent. The solution was not exactly the same

because the different sized grid caused different numerical errors. Two monitoring points (one 0.5 m above the cylinder and one on the vent) were used to track concentration and temperature throughout the model runtime. The model was assumed to converge when both variables at both monitoring points became relatively steady.

To further verify the accuracy of the solution, simple mass (mass in-mass out) and energy ($VC_p\rho\Delta T$) balances were performed. Also, FLUENT's solution overview report tool was used to ensure that the mass and heat entering the room equaled the mass and heat exiting the room.

A clear and well developed thermal plume can be seen in Figure 3 and Figure 4, providing visual verification of the convergence of the model. To further improve accuracy and reduce modeling error, 12 trial runs were averaged together to find the inter-zonal air exchange rate.

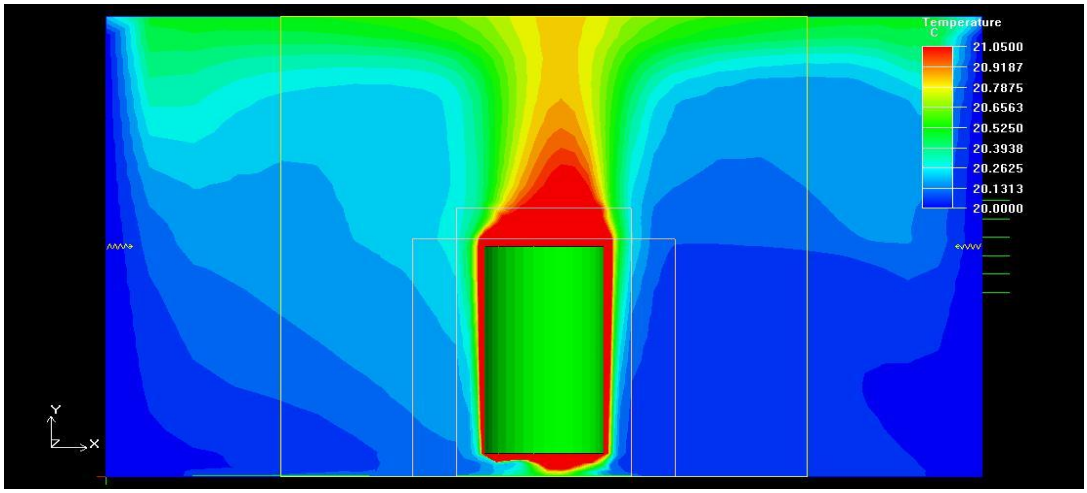

Figure 3: Temperature contours illustrating a developed thermal plume

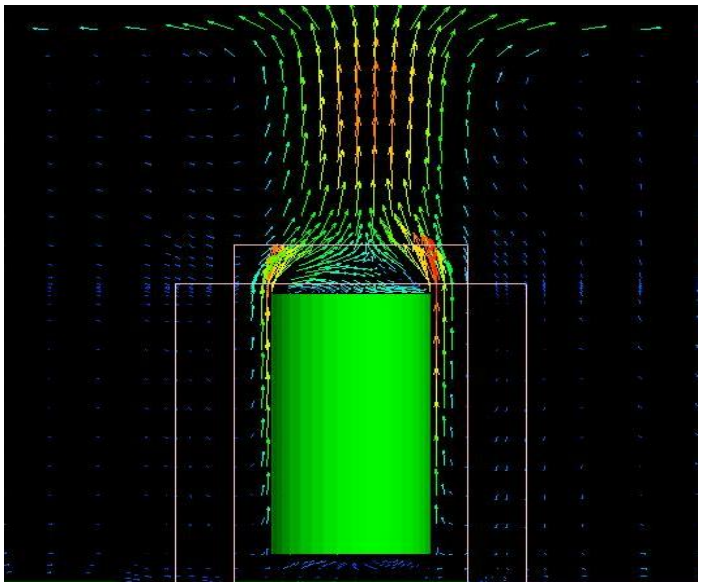

Figure 4: Air speed vector plane cut illustrating a developed thermal plume

CFD Results and Discussion

After finding the volumetric flow rates and dividing by the inner-volume, the inter-zonal air exchange rates from each type of calculation described above were averaged. Results are presented in Figure 5. The error bars represent the standard deviation of the six individual air exchanges (one for each source cell configurations, calculated using the top box and the side box method). Over all simulations the average air exchange rate was 170 ± 29 hr^{-1}. The fact that the external ventilation rate had no discernable effect on the inter-zonal air exchange rate shows that the goal of limiting the influence of ventilation was achieved.

The rate reported above is representative of the contribution of air exchange due to the thermal plume. Thus, it represents the minimum bound of the inter-zonal air

exchange rate. Higher mixing intensity due to forced ventilation or the occupant moving could increase the inter-zonal air exchange rate.

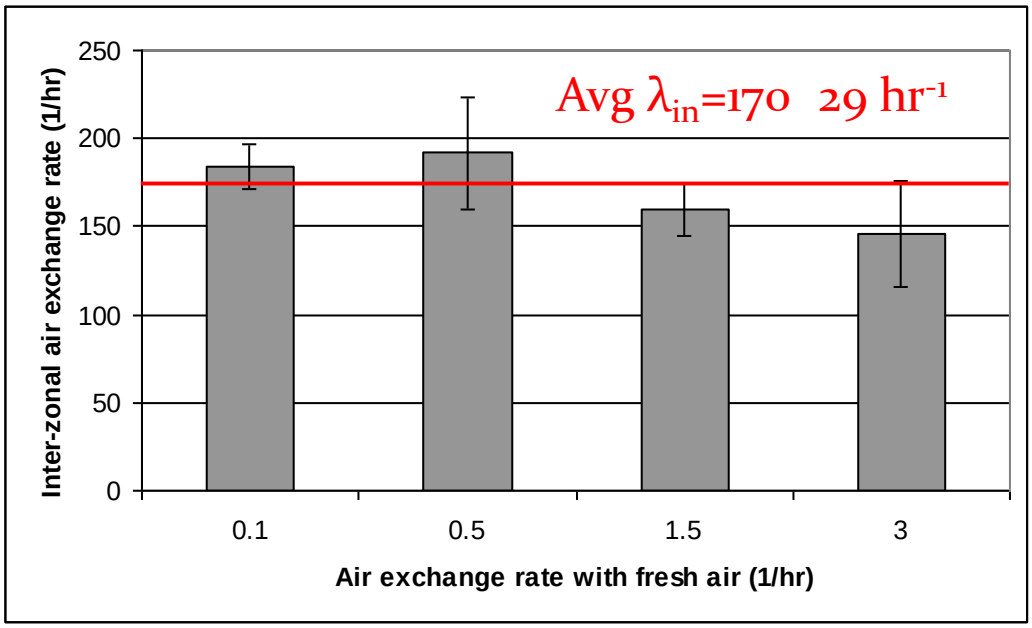

Figure 5: Inter-zonal air exchange rates for all model scenarios.

Concentration ratios

From the CFD analysis the concentration ratios (C_{in}/C_{wm}) were calculated by dividing the average concentration in the inner-zone by the concentration predicted using the steady-state single-zone well-mixed model. Concentration averages were determined using FLUENT's "full report" tool. If the C_{in}/C_{mix} ratio was 1.4 (as it is for two source cells at λ_{out} = 0.5 hr^{-1}) the actual exposure to 2-butoxyethanol would be 1.4 times higher than well-mixed model predictions.

Ratios for each individual simulation scenario are presented in Table 2. These results agree with those previously reported in published literature. For example, Rhodes

et al. (1991) found that ratios of personal concentrations to bulk air concentrations ranged from 1.2-3.3. Also Girman et al. (1987) showed that at a air exchange rate of 3.2 hr^{-1}, personal exposure to methylene chloride (CH_2Cl_2) during a simulated use experiment in a chamber was 22% higher than would have been expected from calculations based on the room air sampler, a ratio of 1.22.

Table 2: Concentration ratios (C_{in}/C_{wm}) for the 12 CFD simulations

	# of source cells		
λ_{out} (1/hr)	**1**	**2**	**3**
0.1	1.3	1.2	1.1
0.5	1.8	1.4	1.3
1.5	2.4	1.8	1.4
3	3.8	2.5	2.0

As can be seen in Table 2, the ratio decreases as more source cells are added to the outer zone. This is expected because more source cells in the outer-zone will increase the outer-zone concentration and lower the relative concentration of the inner-zones. This phenomenon is illustrated in Figure 6, where the left hand side shows a concentration isosurface for the scenario with a single source cell and an external air exchange rate of 0.5 hr^{-1}. The right hand side shows a concentration isosurface for the scenario with three source cells at the same air exchange rate. The isosurfaces represent the average concentration in the inner zone for each scenario (2.76 and 5.61 mg/m^3, respectively).

Much more of the area inside the isosurface is inside the inner-zone on the left hand side than on the right hand side.

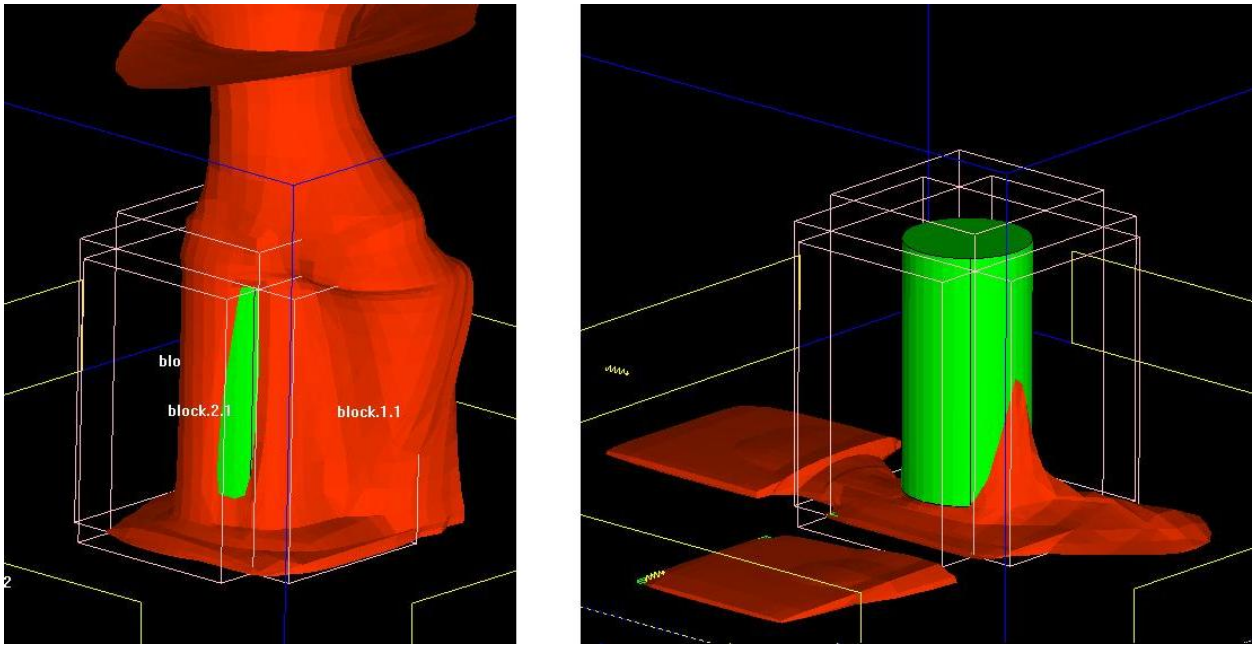

Figure 6: concentration isosurfaces based on average concentration in the inner-zone for two simulation scenarios showing why the concentration ratio decreases as more source cells are added.

3.4. Sensitivity Analysis

A sensitivity analysis was performed on the model presented in this thesis. Typical sensitivity analysis approaches such as Monte Carlo simulations could not be performed because ranges and distributions were not available for several of the most important parameters as discussed above. Instead, a model was developed for emissions from a pure chemical. All parameters were varied one by one. If their typical distributions

were known, they were used. However, in many cases a range was chosen that extends roughly equally on both sides of the value chosen for the first typical cleaning scenario (bathroom cleaning). The absolute change in C_{in}, C_{out}, number of moles remaining in the liquid phase, and emission rate after varying each parameter independently was studied. Then, the relative change in C_{in}, C_{out}, number of moles remaining in the liquid phase, and emission rate were studied for the variable that the model was most sensitive to, inter-zonal air exchange rate.

4. Results & Discussion

4.1. Typical Cleaning Scenarios

Two cleaning scenarios were studied using the model described above. First, a typical bathroom cleaning event was modeled because it represents a worst-case exposure scenario by combining a small room volume and low air exchange rate. Second, a large room (gymnasium or ballroom) cleaning event was modeled because it represents the case where a traditional well-mixed model would most underestimate exposure.

A number of VOCs fit the criterion of being found in a wide array of products, including acetone, ammonia, 2-butoxyethanol, ethanol, toluene, and several terpenes (see Table 1). Since combinations of the non-terpene compounds are limited to one or two classes of cleaning products (e.g., ammonia is found together in only two product classes), the most prevalent non-terpene VOC was combined with two terpenes.

2-Butoxyethanol (2-BE) was selected as the primary VOC, as it is present in three classes of cleaning product (disinfectants, general purpose cleaners, and glass cleaners). Readily absorbed via dermal, oral, or inhalation exposure, 2-butoxyethanol presents health hazards that include moderate acute toxicity; eye, skin, and respiratory tract irritation; and possible carcinogenicity (HSDB, 2005). A more in-depth discussion of 2-BE is provided in appendix 1.

Based on the prevalence of terpenes in cleaning products, as well as the availability of ozone reaction coefficients, *a*-pinene and *d*-limonene were included in the model cleaning product. These terpenes have been identified as skin and eye irritants (HSDB, 2005). Although the combination of 2-butoxyethanol, *a*-pinene, and *d*-limonene

is present in only one class of cleaning products noted in Table 1 (glass cleaners), *a*-pinene and *d*-limonene are used primarily as scenting agents, and this combination would not be unreasonable in other classes.

Since solving for VOC concentrations in both zones requires solving Equations 1-4 simultaneously, the problem was discretized in time and iterated with a time-step of 0.025 seconds. Frequency of application was determined by dividing eight applications by a total cleaning time of 900 seconds. Although it would take substantially longer to clean a gymnasium then a bathroom, only the first 15 minutes of each scenario were analyzed for comparison. Other parameters were selected to represent typical cleaning events. Sorption was assumed to be zero in both rooms because of the nature of the room surfaces. Physical properties of the VOCs used in this analysis are presented in Table 3. Input values for both scenarios are presented in Table 4.

Ozone Consumption

An outdoor ozone concentration that is higher than typical for U.S. cities, but not unrealistic for large cities and summer conditions, was selected in order to highlight the role of homogeneous chemistry indoors. All of the ozone was consumed nearly instantly following the application of the cleaning product to the initial source cell in both scenarios. The majority of ozone consumption was due to the emission of *d*-limonene, which volatilized much faster than the other two chemicals.

Table 3: Physical Properties of VOCs

	P_{vp} (mm Hg)	H ($Pa*m^3/mol$)	ρ (g/cm^3)	k ($ppb^{-1}s^{-1}$)	Mass Frac. (%)
2-butoxyethanol	0.88 @ 25C[a]	0.551 @ 25C[b]	0.901 @ 20C[a]	*	6.20
d-limonene	4.75 @ 25C[a]	2.73E+3 @ 25C[c]	0.859 @ 25C[a]	2.14E-6[d]	0.15
a-pinene	1.98 @ 25C[a]	0.194 @ 25C[c]	0.840 @ 20C[a]	5.14E-6[d]	11.0

[a]HSDB, 2005. [b]US EPA, 2006. [c]Mackay et al., 2006. [d]Weschler, 2000. *The reaction rate constant is assumed to be negligible, as 2-butoxyethanol is a saturated molecule.

Table 4:Model Inputs

Variable Name	Label		Value
Outdoor Ozone Conc.	$C_{o,\ O3}$		100 ppb
Initial Indoor Ozone Conc.	$C_{O3,t=0}$		70ppb
Fresh Air exchange rate (Fan Off)	λ_{out}		0.3 h^{-1}
Fresh Air exchange rate (Fan On)	λ_{out}		12h^{-1}
Inter-zonal Air Exchange Rate	λ_{in}*		160 h^{-1}
Inter-zonal Air Exchange Rate	λ_{in}**		5.7h^{-1}
Surface Area In Inner-zone	A_{in}	Linoleum	0.25 m^2
		Occupant	1.7 m^2
Volume of Room	V_{out}***		14 m^3/3,300m^3
Volume of Inner-zone	V_{in}		0.5 m^3
Relative Humidity	RH		0.44
Frequency of Application	f		8.8E-3 s^{-1}
Total Mass Distributed	M_{tot}		103 g
Surface Area In Outer-zone	A_{out}	Clean Glass	1.0 m^2
		Linoleum	5.6 m^2
		Painted Gypsum	14.5 m^2
Ozone Deposition Velocity	$V_{d,o3}$	Clean Glass	7.5E-3 m/s[a]
		Linoleum	5.5E-3 m/s[b]
		Painted Gypsum	4.2E-2 m/s[b]
		Occupant	0.215[c]

[a]Wolkoff et al., 1999. [b]Kleno et al., 2001. [c]Tamas et al., 2006. * λ with respect to V_{in}. ** λ with respect to V_{out}. ***V_{out} for bathroom/large room.

VOC Concentration Between Zones

For all three VOCs studied in both scenarios, concentrations in the inner-zone were higher than in the outer zone (Figure 7-12). For the bathroom scenario, it is notable that the difference in concentration between the two zones for 2-butoxyethanol and *a*-

pinene diverged during emissions from the initial source cell, and then approached convergence during subsequent applications, while *d*-limonene concentration diverged and approached convergence at much faster rates. This can be attributed to two phenomena. First, during emissions from the initial source cell, there are no emissions in the outer zone. Later, the concentration in the outer zone was determined by emissions from the current source cell via air exchange with the inner-zone, as well as by earlier source cells that continue to emit directly to the outer zone. Second, the relatively low Henry's Law constants of 2-butoxyethanol and *a*-pinene result in low emission rates, and inter-zonal air exchange becomes the dominant factor. With a λ_{in} of 160 h^{-1}, concentrations in both zones equilibrate shortly after application of the final source cell, which is not depicted in Figure 7, 8 and 9.

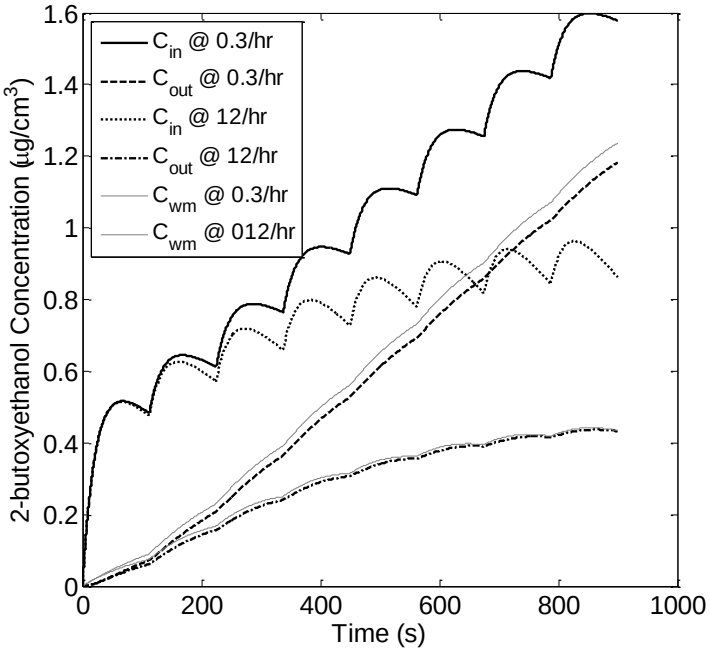

Figure 7: Time varying 2-butoxyethanol concentration for bathroom scenario.

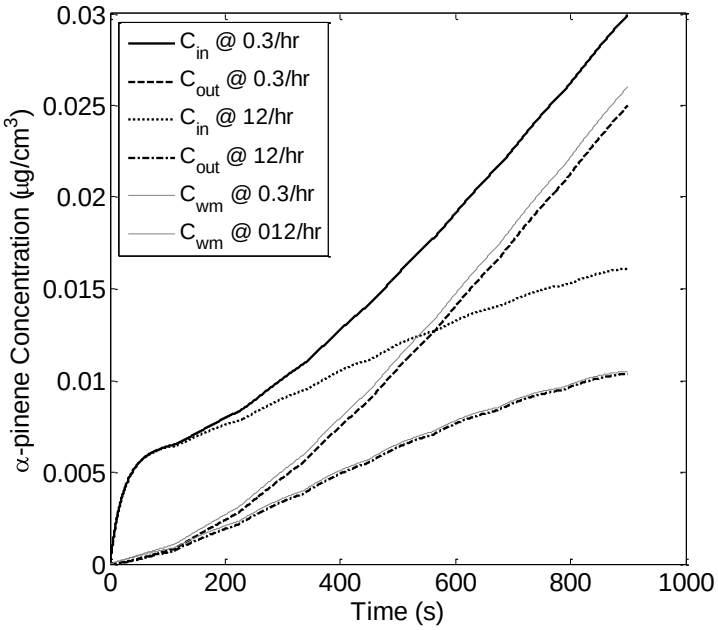

Figure 8: Time varying concentrations of α-pinene for bathroom scenario.

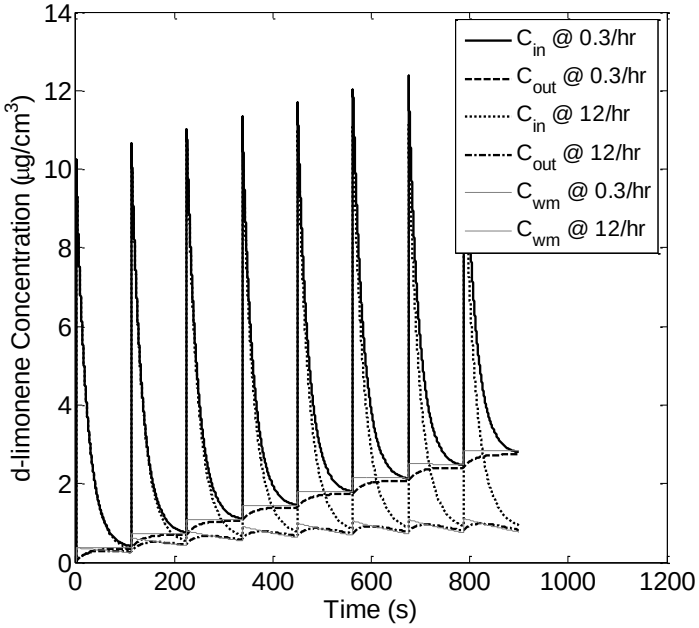

Figure 9: Time varying d-limonene concentrations for bathroom scenario.

A different phenomenon occurs in the large room scenario. As seen in Figures 10, 11 and 12 the concentration in the inner zone quickly rises to a steady-state concentration that is significantly lower than concentrations in the bathroom scenario. This is because the outer volume effectively acts as an infinite sink compared to the outer volume of the bathroom scenario. Said another way, in the large room scenario, any pollutant that is emitted into the inner-zone is rapidly swept into the outer zone by the large inter-zonal air exchange rate where it is instantly diluted into the outer-zone's volume of 3,300 m^3. This dilution prevents the feedback effect that causes the inner-zone concentration to continue to increase.

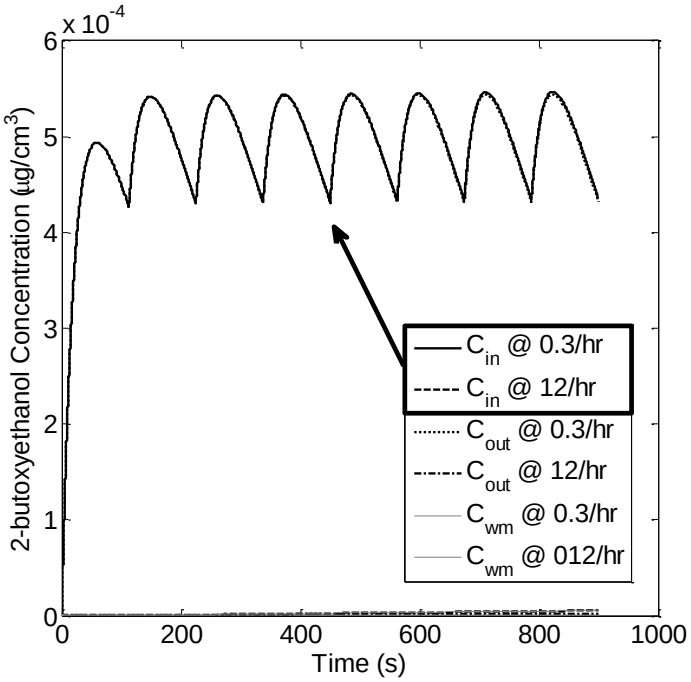

Figure 10: Time varying 2-butoxyethanol concentration for large room scenario.

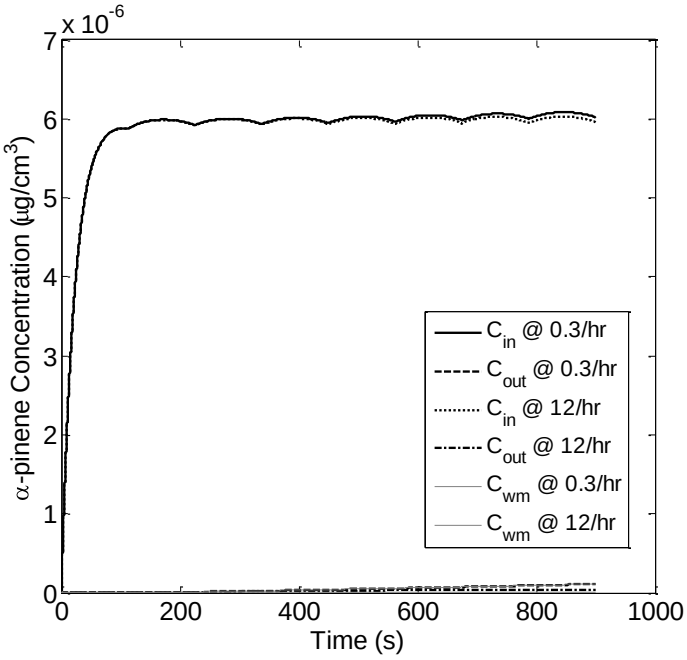

Figure 11: Time varying a-pinene concentrations for large room scenario.

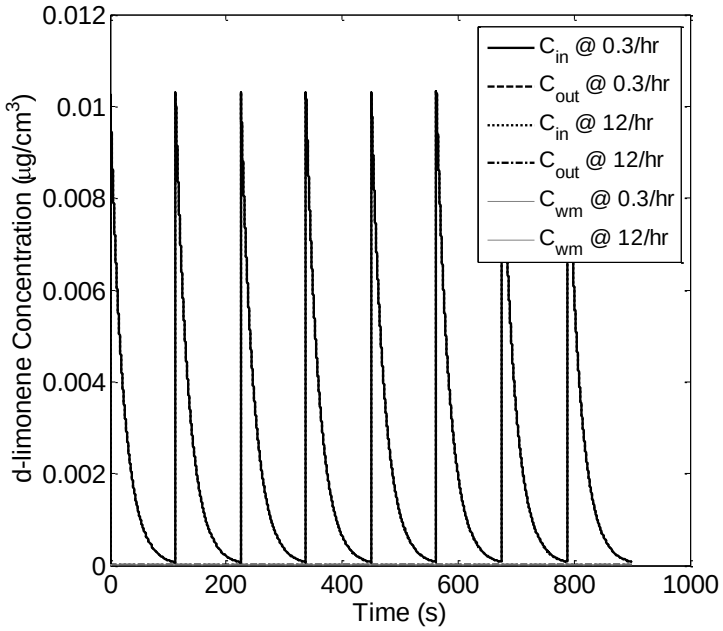

Figure 12: Time varying d-limonene concentrations for large room scenario.

Another effect of Henry's law coefficients was the perturbations of the inner-zone concentration curves for 2-butoxyethanol and *d*-limonene, which were not as apparent in the inner-zone concentration curves for *a*-pinene. Rapid emission of *d*-limonene from the source cell caused a concentration spike, followed by exponential decay until the next source cell was applied. A similar process occurred with 2-butoxyethanol; however, since the emission rate of 2-butoxyethanol was considerably slower, air exchange tempered the perturbations, and the concentration spike was less pronounced. Similarly, air exchange between the inner and outer zones was responsible for the mild perturbations in the outer-zone concentration curves of 2-butoxyethanol and *d*-limonene. These perturbations were not apparent in the inner-zone concentration curves for *a*-pinene due to its low emission rate.

Effects of Ventilation on VOC Concentration

Simulating the effect of a bathroom exhaust fan resulted in significant changes of concentration in both the inner and outer zone (Figure 7, 8 and 9). The effect is most dramatic in the outer zone, where λ_{out} increased more than 30-fold for a bathroom relative to a large room. Nonetheless, the large drop of inner-zone concentrations for all three VOCs demonstrates the importance of increasing ventilation in the outer zone in confined spaces. As the duration of cleaning increases, the effect of outer-zone ventilation on inner-zone concentration increases to the point that inner-zone concentration is less than outer-zone concentration with the exhaust fan off. While the two-zone model predicts higher occupant exposure levels, the inner zone is largely affected by conditions in the outer zone and vice-versa. As such, methods of reducing chemical concentrations in the

outer zone can result in meaningful reductions of chemical concentrations in the inner zone.

When the outer zone is significantly larger than the inner zone, as is the case in the large room scenario, the interplay between the two zones is less important because the concentration in the outer zone is negligible compared to the concentration in the inner-zone, as can be seen in Figures 10, 11 and 12.

Comparison with Well-Mixed Model

For all three VOCs, single-zone concentrations in the well-mixed model were slightly higher than the outer-zone concentrations in the two-zone model at both external air exchange rates. This suggests that calculations based on the well-mixed model will underestimate exposure for an occupant engaged in a cleaning activity. It also shows that the well-mixed assumption is appropriate for calculating exposure of an occupant not engaged in a cleaning activity (not in close proximity to the source).

Concentration ratios

The ratio of the integrated concentration in the inner-zone of the model presented here relative to integrated concentration using the well-mixed model is presented in Table 5. These ratios are the same metric as the ratios presented in Table 2. The smallest ratio is for a-pinene at an air exchange rate of 0.3 h^{-1}. At these conditions exposure predicted by the model described here is 1.5 time higher than exposure predicted by the well-mixed model. As can be seen, all of the ratios are greater than one. This is a significant finding because it shows that well-mixed models underestimate exposure to cleaning products in all of the scenarios analyzed in this study.

Table 5: integrated concentration ratios C_{in}/C_{wm} from two-zone model

	Bathroom		**Large Room**	
λ_{out}	**0.3**	**12**	**0.3**	**12**
2-butoxyethanol	1.8	2.7	200	420
a-pinene	1.5	2	130	250
d-limonene	2.3	3.9	320	700

As expected the C_{in}/C_{wm} ratios get larger as λ_{out} increases . This is because the higher fresh air exchange rate removes the pollutant from the outer box, but the occupant is very near to the source so the concentration in the inner-zone remains relatively constant. The inter-zonal air exchange rate remains constant over all the scenarios meaning that the concentration in the inner-zone remains effectively the same since it is dominated by the emission of the most recent source cell. Table 5 also shows that the well-mixed model substantially under predicts exposure in large rooms more. This is evident by the ratios of C_{in}/C_{wm}, which range from 130-700. This result is expected considering the proximity to the source involved in cleaning. It is logical that a model that assumes instant uniform distribution will under predict exposure more as the volume of the room gets larger.

4.2. Sensitivity Analysis

As discussed above, a parametric analysis was performed by varying each parameter independently even though several of the input parameters are coupled with other input parameters. For example, as mixing in the room increases the inter-zonal air exchange rate will increase, but increased mixing will also increase the mass transfer coefficient

and chemical emission rate. These interdependencies were not analyzed specifically in this sensitivity analysis, but some are discussed qualitatively.

The model's predicted sensitivity to changes in the Henry's law constant are presented in Figure 13. The Henry's constant was varied from 0.1 to 0.5 $((mg/m^3)_{gas}/(mg/m^3)_{liq})$. As can be seen in (a), the concentration in the inner-zone of a pollutant will be higher for chemicals with higher Henry's constants. This result is expected as the Henry's constant is the concentration in the gas phase divided by the concentration in the liquid phase at equilibrium. It could also be thought of as an indicator of the chemicals affinity for the gas phase. As can be seen in (b), the higher Henry's constants also lead to higher concentrations in outer-zone air but, the differences are far less dramatic than the results for the inner-zone. This is also expected because the volume of the outer zone is much larger than the volume of the inner-zone. Following this logic, the amount of the chemical remaining in the liquid phase (c) is inversely related to the Henry's constant. Note that the scale on the x-axis of (c and d) is shortened to show more detail of what happens with the application of each new source cell. The pattern of the first source cell is not discernibly different from any other. The relationship between Henry's constant and emission rate as seen in (d) is not as straight forward. Essentially a higher Henry's constant translates to a higher initial emission rate, but this higher initial emission rate drives down the concentration in the liquid product. If the liquid were considered an infinite source the emission rate would remain constant and the higher Henry's constants would produce higher emission rates at all time steps.

Figure 14 depicts the model's sensitivity to changes in the mass transfer coefficient. The mass transfer coefficient was varied from 10 to 800 cm/hr (0.1 to 8 m/hr). As illustrated in (a), the concentration in the inner-zone of a pollutant will be higher for a higher mass transfer coefficient. This was expected. In fact, once the mass transfer coefficient gets above 100 cm/hr there is nearly instantaneous volatilization of the chemical, explaining the dramatic spikes that are seen when the mass transfer coefficient was set at 8m/h. This is supported by Figure 14 (c), where it can be seen that the moles of a chemical with a mass transfer coefficient of 8 m/hr would leave the liquid phase in mere seconds. Figure 14 (b) shows a similar trend but, as with Figure 13, there are no perturbations and the difference between the curves is smaller. This is due to the fact that the outer-zone's volume is much larger.

The most sensitive parameter to changes in mass transfer coefficient is the emission rate. This is expected since the mass transfer coefficient is a key variable in the equation governing the emission rate and is only tied to the other output variables indirectly. The window plot inside (d) shows a magnified view for more clarity, and to draw further similarity to the effects of varying the Henry's constant. It is expected that the two responses would be similar, since one governs how a chemical transports from the liquid phase to the interface and the other governs how quickly the chemical transports from the interface to the bulk room air.

The four plots in Figure 14 show that the model is especially sensitive to changes made at the lower end of the range of mass transfer coefficient. As the mass transfer coefficient gets larger, changes of 0.05m/hr represent a much smaller relative change in

the parameter and this translate into a much smaller change in the output variables of the model

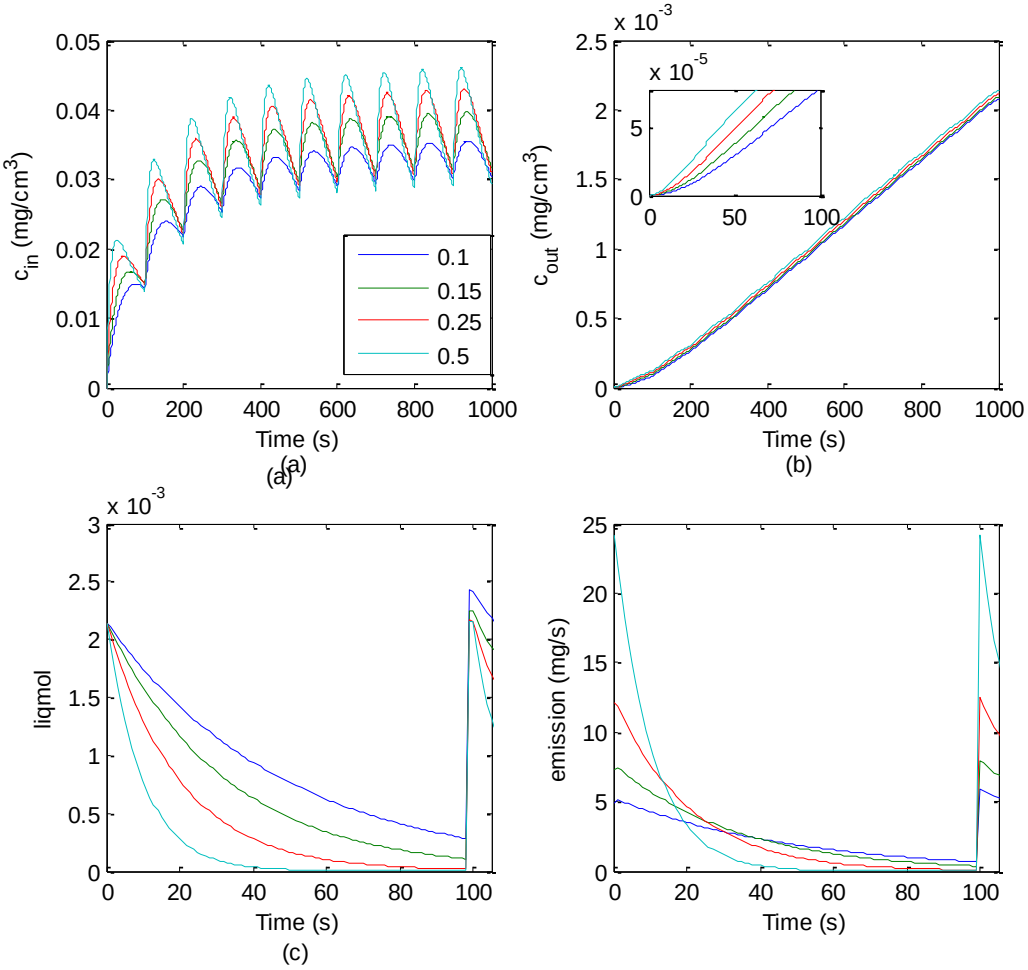

Figure 13: Sensitivity to Henry's Constant where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of mols in the liquid phase and (d) shows the time varying emission rate.

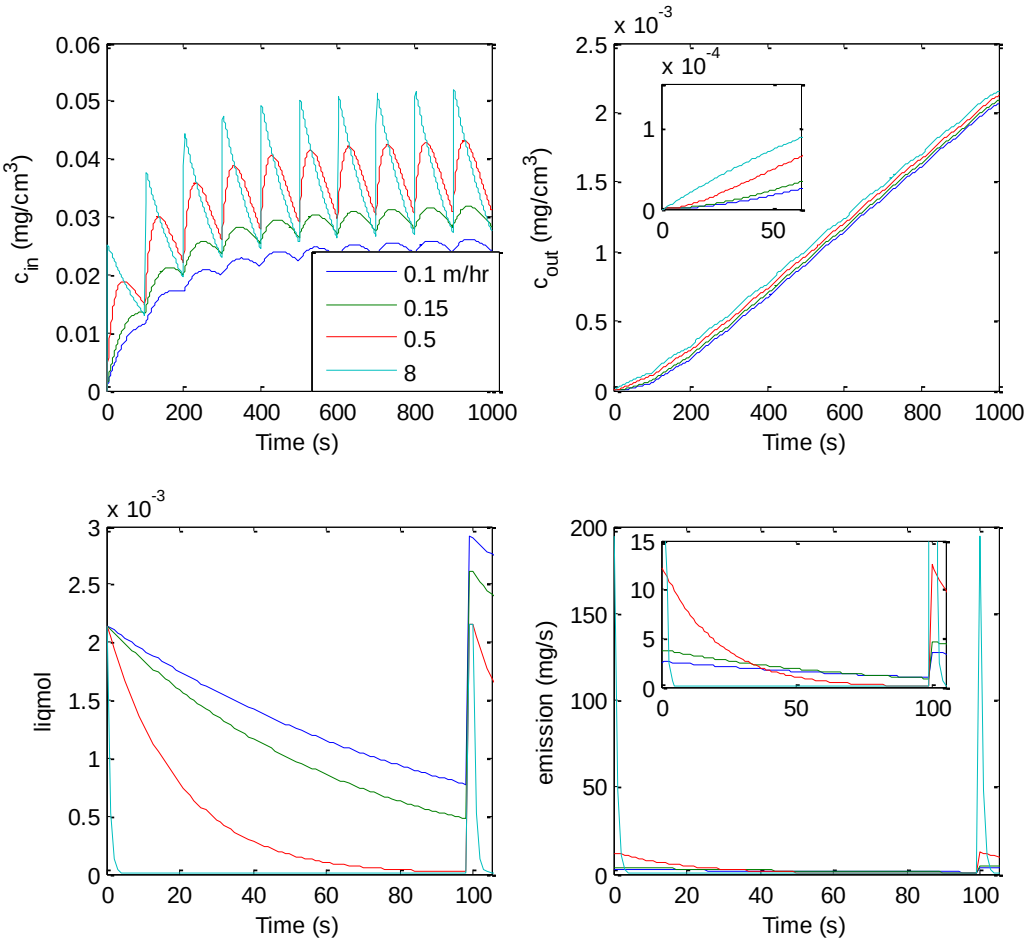

Figure 14: Sensitivity to mass transfer coefficient where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

Figure 15 depicts the model's sensitivity to changes in the molecular weight of a component. The molecular weight was varied from 80 to 140 g/mol. As illustrated in (a), the concentration in the inner-zone of a pollutant will be higher for a higher molecular weight, everything else being equal. Of course vapor pressure typically decreases with

increases in molecular weight and would offset the trends shown here.

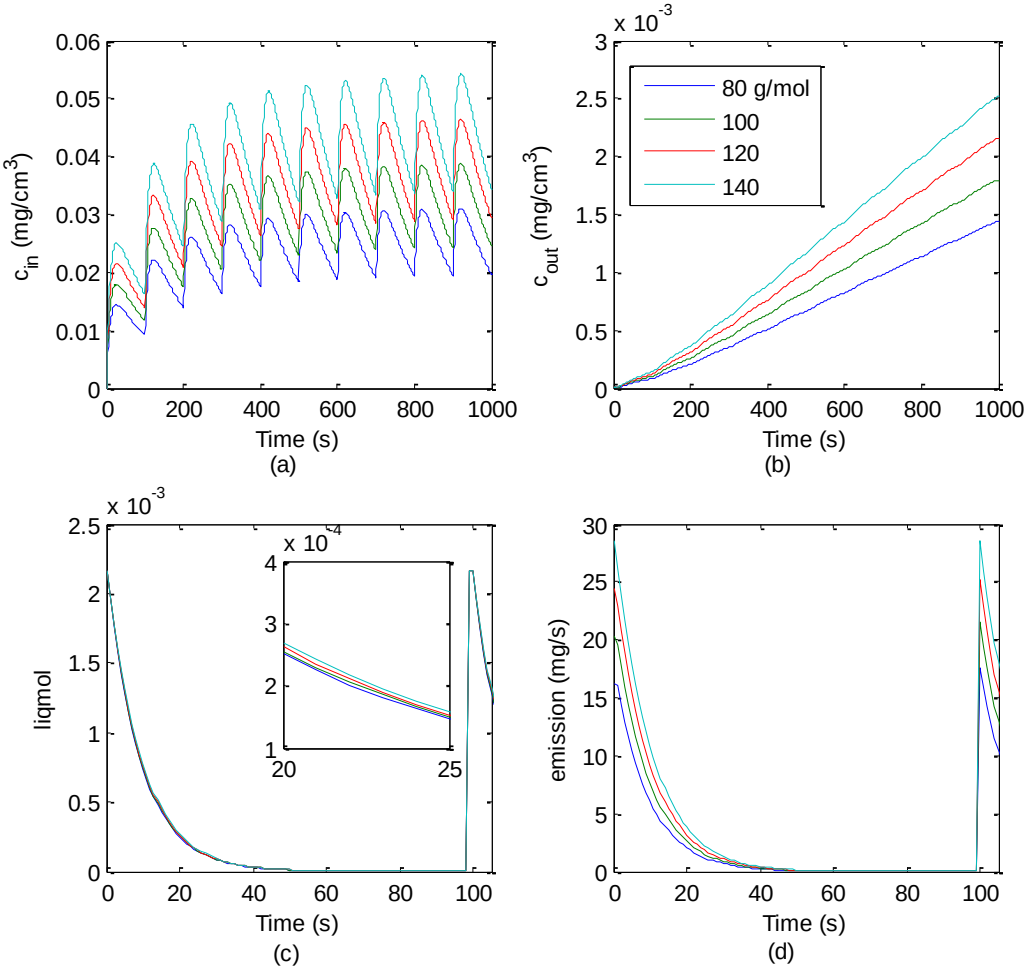

Figure 15: Sensitivity to Molecular Weight where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in theouter-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

The model was run with four different values for total mass dispersed ranging from 50-200 g. Figure 16 (a and b) show that higher concentrations result in both the inner- and outer-zones when more chemical is dispersed. They further illustrate that as

time proceeds the concentrations diverge. This is explained by the way the source cells are applied. The total mass dispersed is divided by the number of source cells, and then the source cells are applied one by one with a frequency of f. For the first source cell the differences in liquid mass are not as great and therefore gas concentrations are more similar. At longer times the difference in mass dispersed increases and thus the concentration curves diverge. Figure 16 (c and d) show that higher masses dispersed result in higher emissions and more moles in the liquid phase, as would be expected. The number of moles in the liquid phase drops off faster than the emission rate. There are two explanations for this. First, liquid phase curves do not all start at the same value. It is natural that those starting off lower would drop faster, since Figure 16 shows only absolute changes. The second reason is that the emission rate is based on the molar concentration, and thus the emission rate falls slower than the molar concentration.

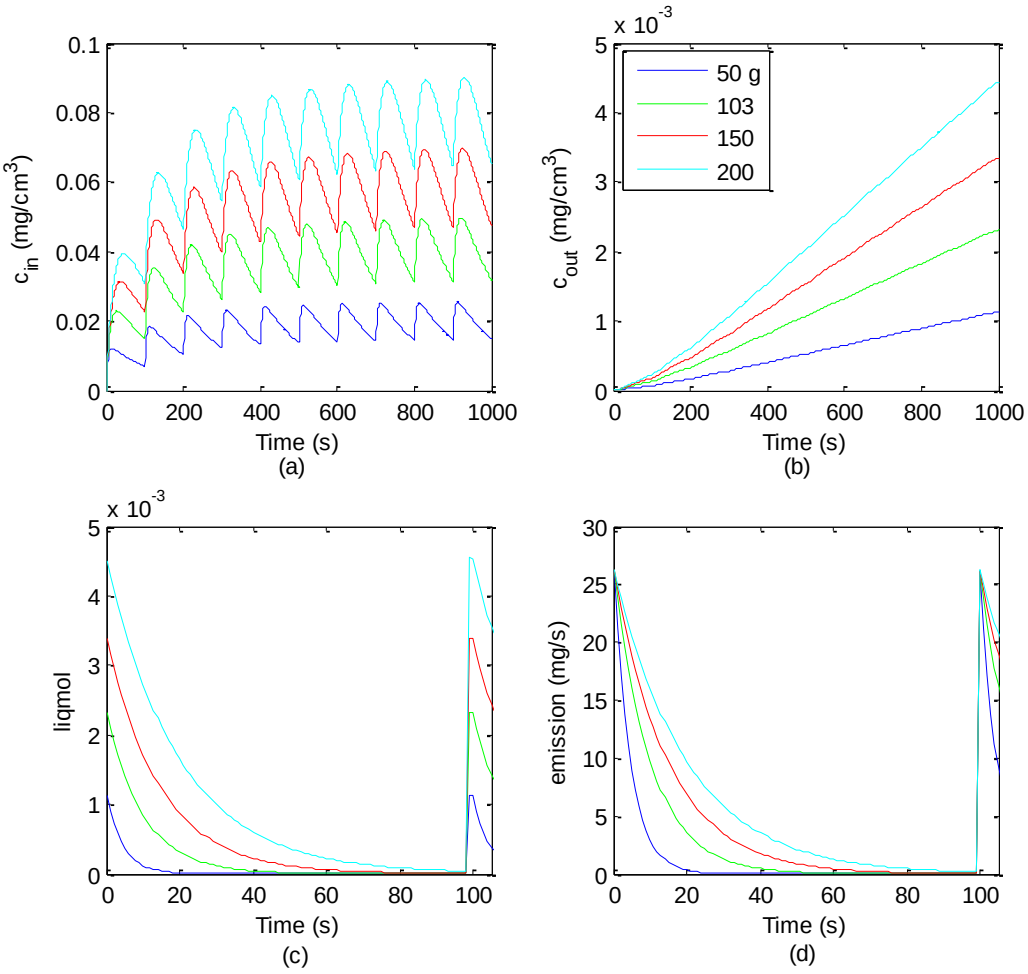

Figure 16: Sensitivity to total mass dispersed where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

The model's sensitivity to changes in the area of applications are shown in Figure 17. The model was run with four different values of the area of application parameter ranging from 400-850 cm^2 per source cell. As can be seen in Figure 17 (a and b), the concentrations in the inner- and outer-zone are not particularly sensitive to variations in

the area of application. But they do show that larger areas result in higher concentrations. This is because the area is an important term in the emission equation. The differences between the curves remain constant, they neither converge nor diverge. The reason that the differences are not as dramatic as with other parameters is because the area variable is the only variable being changed. The correlation between area of application and the total mass dispersed is poorly understood. The mass dispersed per area will vary depending on how soiled the surface is, the type of cleaner being used, the dispersion method and the methods of the person cleaning. In Figure 17, the mass of chemical dispersed remains constant for all four curves. This is an important finding that has real world applications. If people spread cleaning products out over a larger area they could clean more area without increasing their exposure to toxic chemcials found in their cleaning products.

Figure 17 (c and d) show more variation. Variations here are similar to those of the Henry's Constant and mass transfer coefficient because all three play similar roles in the calculation of the emission rate. Changes in the mass transfer coefficient and the area will lead to identical results because they are equally weighted in the emission equation (equation 3). The only reason that the plots for the two parameters appear different is because the range over which the mass transfer coefficient was varied is substantially larger than the range over which the area was varied.

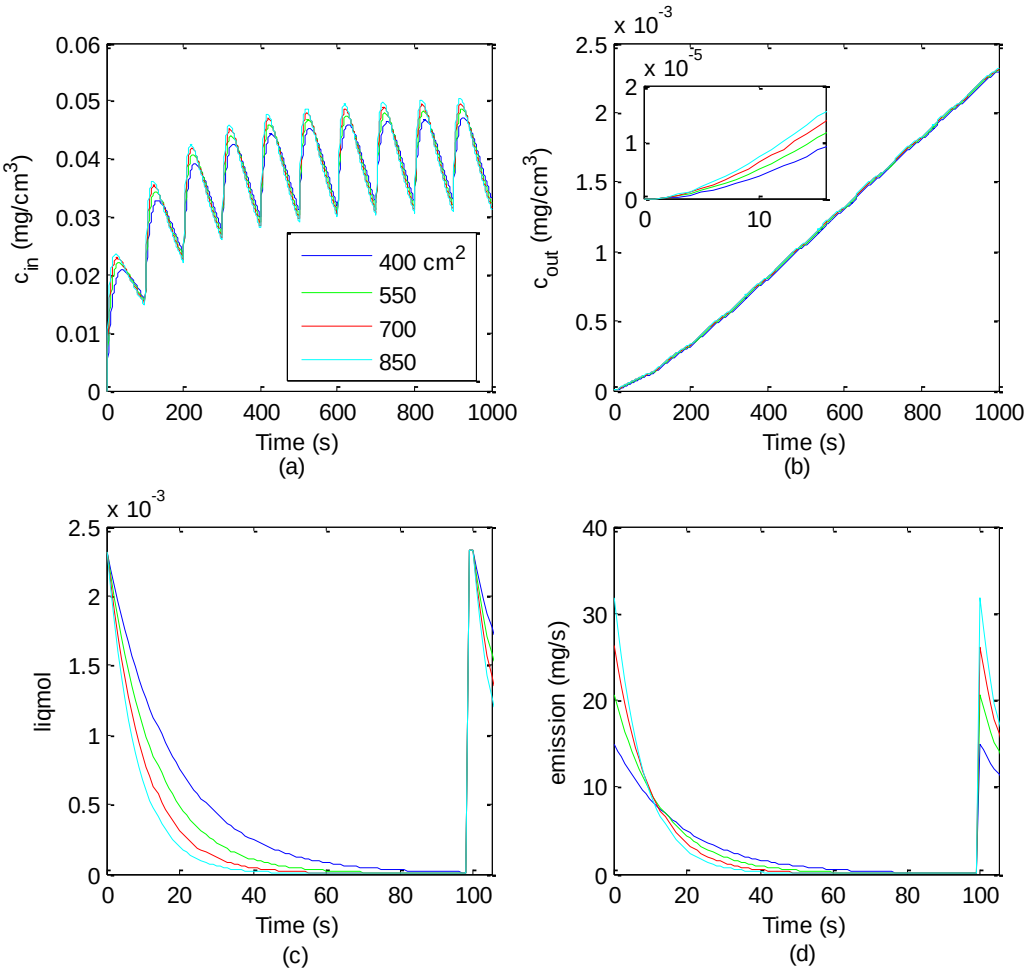

Figure 17: Sensitivity to area where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

Figure 18 shows the model's sensitivity to changes in the frequency of application. The frequency of application was varied from 25-200s. As can be seen in Figure 18 (a), longer frequencies of application don't result in higher average concentration, but result in greater variation around the average concentration. Essentially, longer frequencies of application cause more dramatic perturbations in the

concentrations in the inner-zone. This is also true, but to a lesser extent, for the outer-zone as is illustrated in Figure 18 (b). The take home point of Figure 18 is that frequency does not greatly impact integrated concentrations. On the other hand, it does impact the peak concentration. Unfortunately, little is known about health effects of the peak concentrations that occur on short time scales. Also, little is known about the distribution of the frequency parameter.

Figure 19 shows the model's sensitivity to changes in the outer-zone volume. The outer-zone's volume was varied between 10,000,000 – 5,000,000,000 cm^3 (10-5,000m^3). Figure 19 (a) shows no difference in the inner-zone concentration over a wide variety of room sizes. Figure 19 (b) shows concentration curves diverge as time proceeds indicating that the size of the room is an important parameter for occupants that are not near the source for longer cleaning scenarios. Figure 19 (c and d) show that the volume of the outer-zone has no effect on either the emission rate or the amount of the chemical remaining in the liquid phase. While results presented in Figure 19 were unexpected. Cleaning smaller rooms does not lead to greater near-body concentrations during the cleaning event. This is because even in small rooms, the outer-zone accounts for the majority of the volume. Thus, the concentration will be much lower in the outer-zone than the inner-zone, even in small rooms as is illustrated in

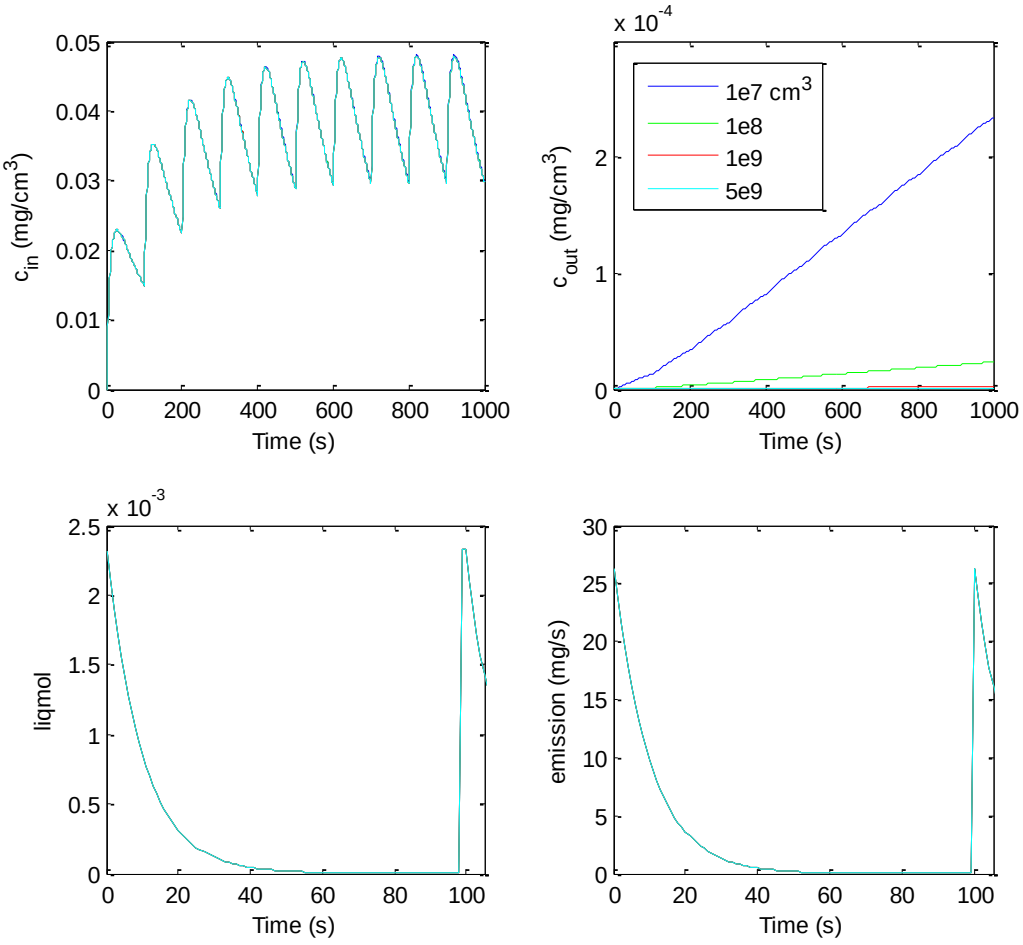

Figure 19 (a and b). The contribution of the mass in the outer-zone from inter-zonal air exchange will be negligible compared to the emission from the newest source cell no matter what size the room is.

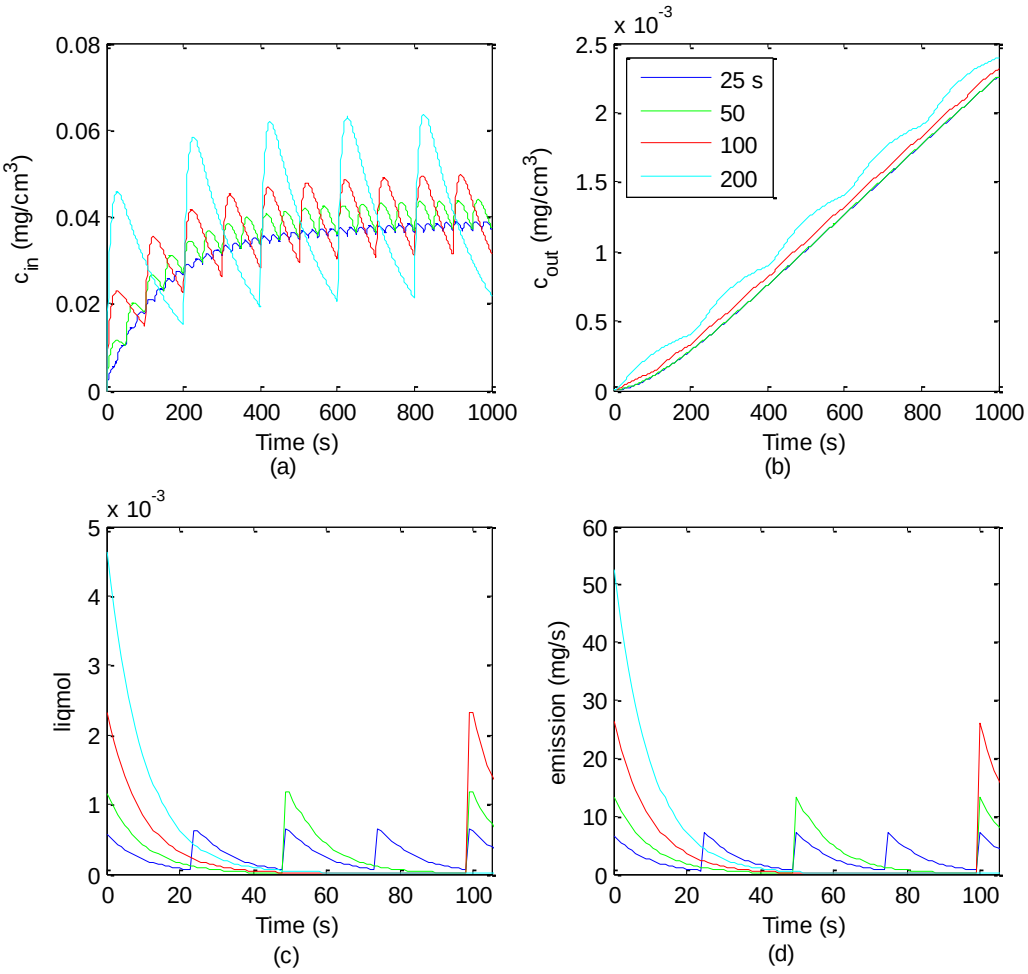

Figure 18: Sensitivity to application frequency where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

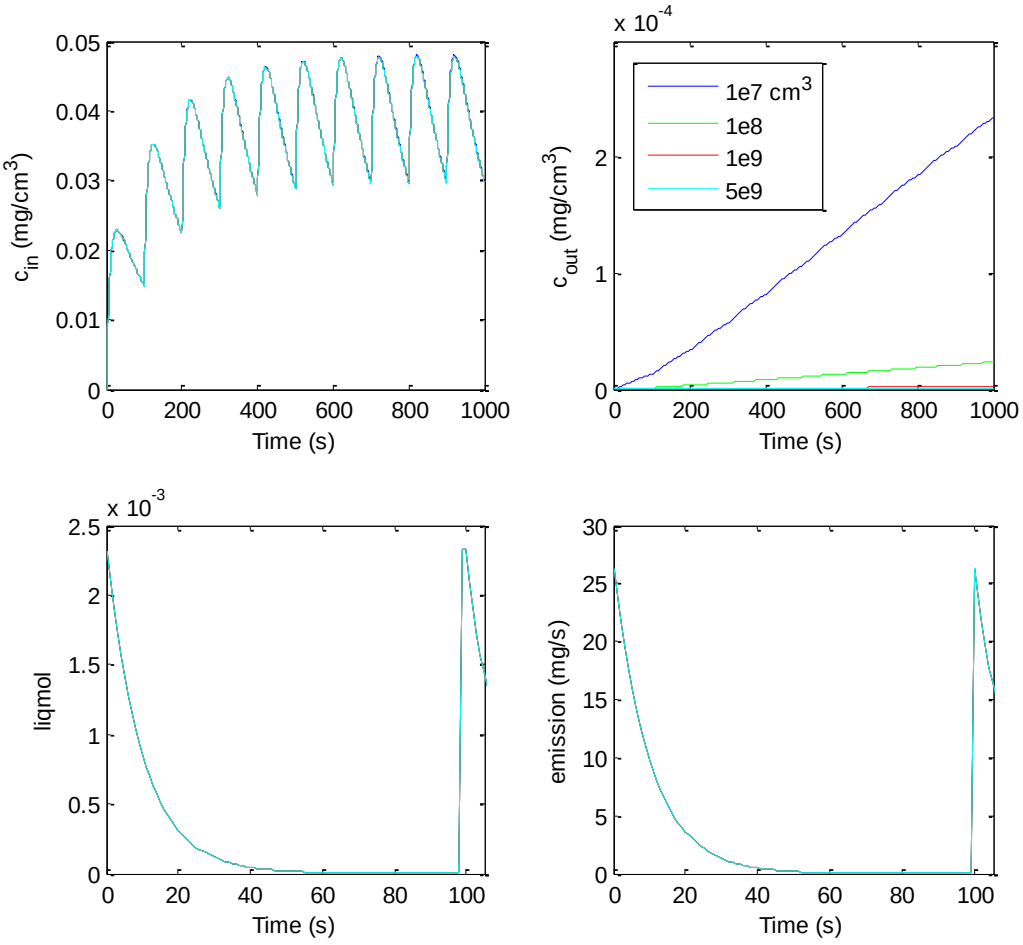

Figure 19: Sensitivity to volume of outer zone where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

The model's sensitivity to changes in the inner-zone volume is displayed in Figure 20. The inner-zone volume was varied from 50,000-1,000,000cm^3 (0.5-10% of the outer-zone volume). As expected, the largest effect was on concentrations in the inner-zone, as can be seen in (a). The other model outputs were not sensitive to changes in the

inner-volume. Unlike the volume of the outer-zone, the volume of the inner-zone is an adjustable parameter not fixed by the geometry of the room. But it is coupled mathematically to the inter-zonal air exchange rate. If the inner-zone volume changes then the boundary between the two zones changes and the inter-zonal air exchange rate changes. This change is very complex and cannot be described by a normal function because the airflow across the boundary between the two zones is irregular. So, either the volume of the inner-zone or the inter-zonal air exchange rate must be fixed. The inter-zonal air exchange rate has a greater chance of varying due to environmental conditions (occupant orientations, fluid dynamic conditions etc.) So, the inner-volume, as opposed to the inter-zonal air exchange rate, was fixed and its affect on the model was not analyzed further.

Figure 21 shows the models sensitivity to changes in the inter-zonal air exchange rate. The inter-zonal air exchange rate was varied between 7.5-50 hr^{-1}. This parameter was determined to be a key variable as discussed in section 3.3. While this range does not encompass the entire possible range of the inter-zonal air exchange rate, it does provide a qualitative comparison. Further analysis is presented below.

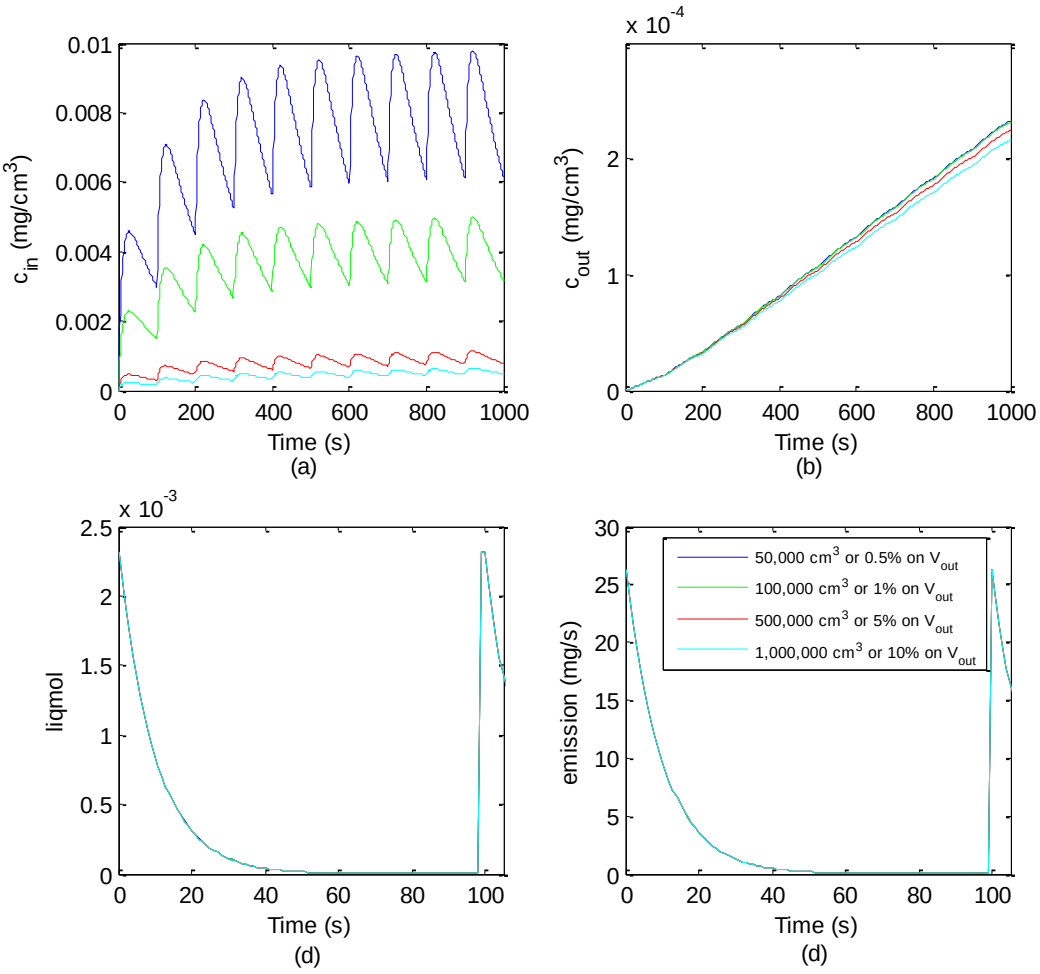

Figure 20: Sensitivity to volume of inner zone where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

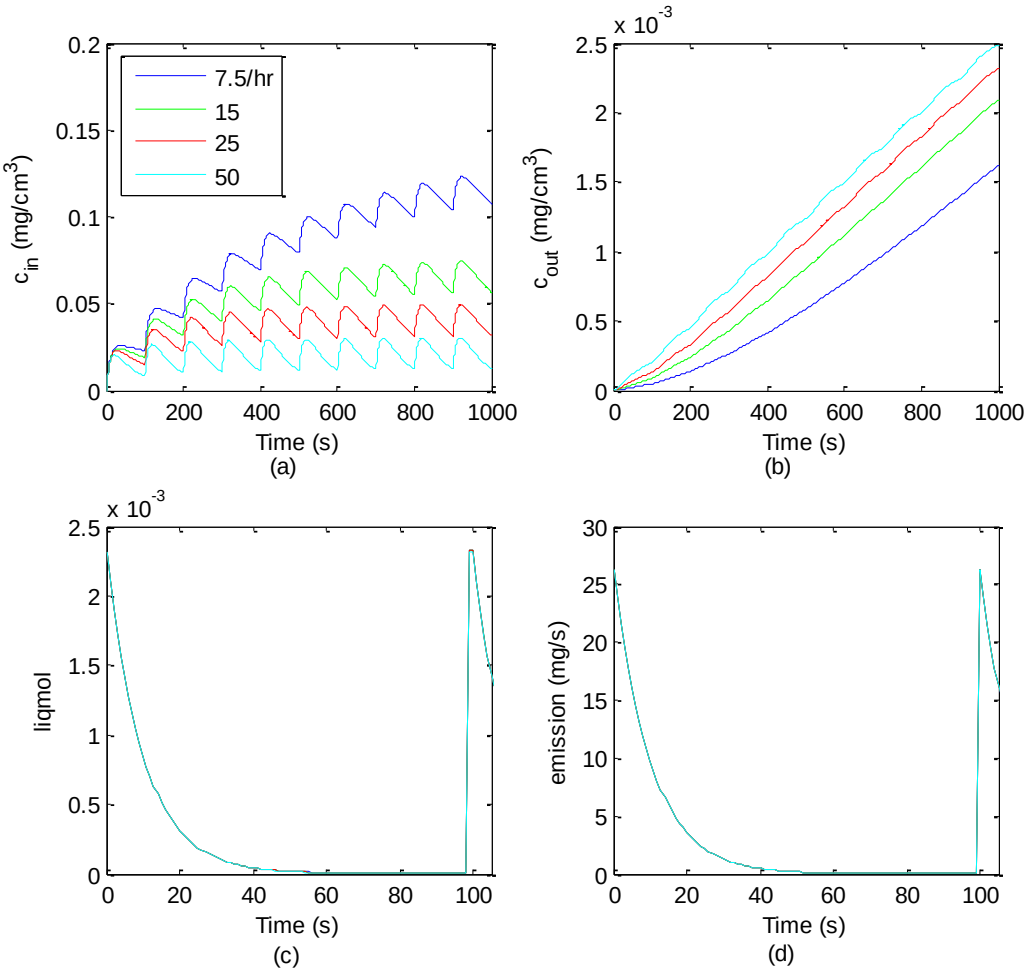

Figure 21: Sensitivity to inter-zonal air exchange rate where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

Because of the importance of the inter-zonal air exchange rate, further sensitivity analysis was performed. The results of this analysis are presented in Figure 22. The relative effect of changing the inter-zonal air exchange rate was determined by doubling, quadrupling, halving and quartering the base case of 170 hr^{-1}, and analyzing the change in

each of the four output parameters relative to the base case. The curves were found by dividing the output values at each time step by the input value from the base case at that time step. This calculation yields the change in the output variable relative to the base case and is why the curve for the base case is a horizontal line at one.

As can be seen in Figure 22(a - c), the relative difference is greater at early time periods than at late ones, indicating that the contributions to exposure at early times needs more in-depth analysis as it could be underrepresented by the current well-mixed model. Since the CFD analysis indicates that the base case is probably the lower bound of the inter-zonal air exchange rate, predictions in Figure 22 (a and b) were rearranged to highlight the effects of doubling and quadrupling the inter-zonal air exchange rate in Figure 23.

Figure 23 and Figure 22 show the same predicted values rearranged to highlight different things.

Figure 23 illustrates the effect of increasing the inter-zonal air exchange rate. As would be expected, increasing the inter-zonal air exchange rate can have a profound effect on exposure. The top plot shows that increasing the inter-zonal air exchange rate by a factor of 4 can decrease the concentration in the inner-zone almost tenfold at the start of the cleaning event. Increasing the inter-zonal air exchange rate increases concentrations in the outer-zone, but due to the difference in volume the relative increase is not as dramatic.

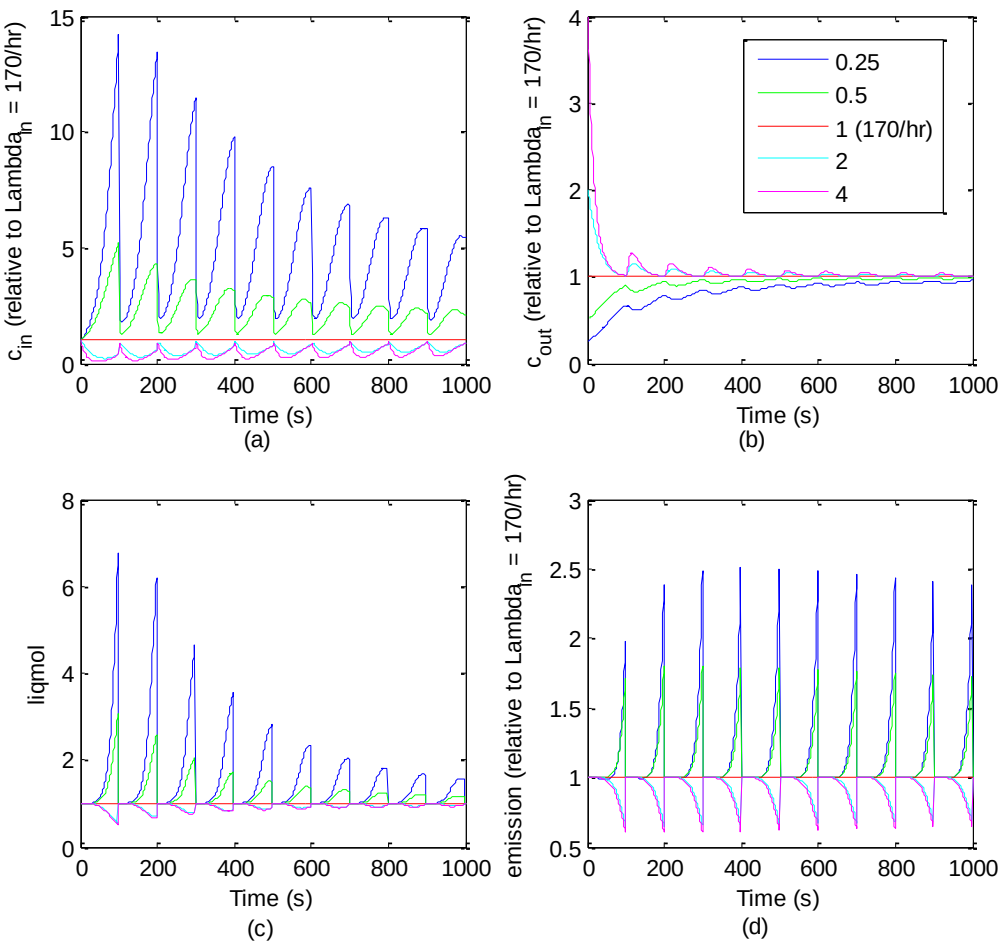

Figure 22: Relative sensitivity to inter-zonal air exchange rate where (a) shows the time varying concentration in the inner-zone, (b) shows the time varying concentration in the outer-zone, (c) shows the number of moles in the liquid phase and (d) shows the time varying emission rate.

Figure 23 illustrates the importance of the inter-zonal air exchange rate, which can greatly influence the concentration in the inner zone. The inter-zonal air exchange rate will be affected by occupant movements, the thermal plume, and mixing intensity in the room. The latter is affected by whether a forced air ventilation system is cycling on or off, the design of the systems vents, the placement of the vents in relation to the source or occupant, and the presence of fans or open windows.

The mixing intensity in the room will also affect the mass transfer coefficient in the room. A higher mixing intensity will cause a higher mass transfer coefficient. As can be seen in Figure 16, when the mass transfer coefficient increases emissions increase as well. So, there is a balancing between increased emission and increased inter-zonal air exchange rate, both of which are caused by increased mixing intensity, which is not addressed in either Figure 16 or

Figure 23. This type of interdependency was not addressed in this sensitivity analysis.

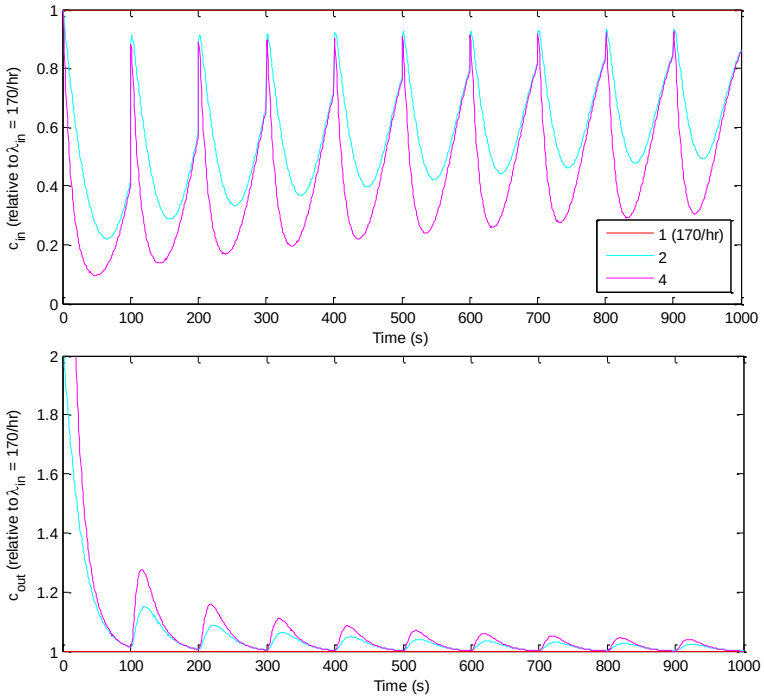

Figure 23: Relative sensitivity to inter-zonal air exchange rate

5. Conclusions

5.1 Summary

A two-compartment model for exposure to toxic chemicals during cleaning events was presented in this thesis. The model accounts for air exchange between an inner- (near person) and outer-zones, dynamic source characteristics, characteristics of chemical use, and reactive chemistry with ozone. However, due to the novelty of this study, the initial conditions (e.g., mass of chemical used, area of chemical film, and source cell application frequency) and some of the parameters (e.g., volume of inner zone and air exchange rate between zones) are unknown. Until these variables have been determined, the model's representation of real cleaning situations is limited. The unknown initial conditions and parameters make verification and comparison with other models and experimental results difficult. Other variables that warrant consideration include the effects of sorption to occupant and building surfaces, radical chemistry, and byproduct formation. Although it is expected that these variables have a meaningful impact on indoor environmental quality as predicted by our model, they were excluded from the model because the necessary parameters for all three VOCs are currently unavailable in the literature. Even lacking these parameters, this study shows that models that neglect source proximity and source dynamics will underestimate exposure to toxic cleaning chemicals.

5.2 Conclusions

1. A two-zone model can allow more realistic predictions of personal exposure to toxic chemicals in cleaning products than the more often used single zone well-mixed model.

2. High air exchange rates, large volumes and short cleaning events produced the highest C_{in}/C_{wm} ratios of the inner-zone (personal) concentration to the concentrations predicted with a single well-mixed zone model.
3. Changing cleaning practices can reduce inner-zone (personal) concentrations and therefore inhalation exposure. These changes include dispersing less cleaning product, turning on exhaust fans or otherwise increasing ventilation with fresh air, and spreading the cleaning product over a larger area,
4. Effective means of reducing exposure to toxic chemicals in cleaning products are increasing the external air exchange rate, reducing the mass of chemical dispersed, and spreading the chemical out over a larger area.

5.3Future Work

Future work will include:

- Determination of key activity parameters (frequency of application, total mass of cleaning product dispersed, area of application, etc.) by observing janitorial staff and recording pertinent data. If possible, room air and personal air samples will be collected while they clean to compare model results to field data.
- Completion of chamber experiments with pure chemicals, measuring room and personal air concentrations to validate the two-zone model with experimental data.
- Characterization of the effect of mixing in a room, occupant orientation (sitting, crouching, bending over, etc.) and occupant movement on the inter-zonal air exchange rate.

- Determination of sorption and desorption rates to occupant surfaces, particularly clothing.
- Analysis of liquid compositions and headspace concentration of several cleaning products, with subsequent analysis of the validity of Henry's law.

6. Appendices

Appendix 1

2-Butoxyethanol (2-BE)

This appendix specifically addresses personal exposure to 2-butoxyethanol ($C_6H_{14}O_2$ CAS number 111-76-2) (2-BE), a common glycol ether. The properties and health effects of 2-BE are considered. Regulatory analysis, exposure and pharmacokinetic considerations are also discussed.

Chemical Background and Properties

2-BE is colorless with a mild ester-like smell. Due to its exceptional solvency, chemical stability, and miscibility in water and organic media, glycol ethers are good solvents for a wide array of applications. In 1983 (the most recent data available) 2-BE was the most produced glycol ether, with total production topping 1.23E9 kg (Toxnet, 2007). 2-BE became the most popular glycol ether when it was discovered that shorter chain glycol ethers such as methoxy- and ethoxyethanol (ME, EE) exhibited developmental and bone marrow toxicity. The discovery of this toxicity prompted chemical manufacturers and industry to simply add another carbon to the chain and phase out the shorter chains' production and use. This happened to both ME and EE. Currently, some manufacturers have abandoned 2-BE while some still consider it safe enough, and profitable enough, to continue its production and use. Current manufactureis in the U.S. include Dow Chemical USA, Eastman Chemical Co., Equistar Chemicals LP and Shell Chemical Co. (Toxnet, 2007)

Industrial applications include use as a solvent in both water and organic based mixtures. Explicit uses include, in no particular order: hydraulic fluid; solvents for protective coatings such as lacquers, varnishes, nitrocellulose resins, and enamels; synthesis ingredients of acetate esters, of di(2-butoxyethyl) phthalate, and other stearate plasticizers; coupling agents to stabilize immiscible ingredients in metal cleaners, textile lubricants, cutting oils, and household products (Toxnet, 2007).

2-BE is used extensively in consumer products ranging from: hard surface cleaners for use of glass, plastic, tile, porcelain, chrome, painted surfaces, aluminum, countertops, stove tops, ovens, bathroom fixtures and kitchen appliances; other cleaners for use on carpets, fabrics and upholstery; ingredients in caulking, sealant, linoleum, permanent hair color, nail polish remover and cosmetics. It can also be found in disinfection agents that require leaving the product on the surface for up to 15 minutes before wiping it away, giving 2-BE ample time to volatilize. Some of the products can be used pure or diluted. Dispersion methods include trigger spray bottles, aerosol cans and capped bottles. The actual concentration of 2-BE in these products is unlisted but Singer et al. (2006) found concentrations ranging from 6 to 62 mg/ml in six common products.

Environmental fate

2-BE's industrial production and use result in its release to the environment through various liquid and vapor waste streams. at standard conditions, a vapor pressure of 0.88 mm Hg indicates 2-BE will exist solely as a vapor if exposed to air (Toxnet, 2007). 2-BE in the vapor-phase will readily degrade in the outdoor environment via reaction with photochemically-produced hydroxyl radicals. The half-life for this reaction

is approximately 16 hours. Based upon an estimated K_{oc} of 67, 2-BE is expected to have high mobility if released to soil. Volatilization from moist soil interfaces and water surfaces is expected to be an important environmental fate process based upon a Henry's Law constant of 1.60E-6 atm m^3/mol. This K_{oc} also indicates that 2-BE will not adsorb to suspended solids or sediments in aqueous environments. More chemical properties can be found in Table 1.

Table 1: physical and chemical properties of 2-BE (Vapor pressure, Henry's Constant and Diffusivity Coefficient are measured at 25 ˚C)

Molecular weight	118.2	Toxnet, 2007
Boiling point	444.2 K	Toxnet, 2007
Vapor pressure	0.88 mm Hg	Toxnet, 2007
Heat capacity	274.1 J/mol K	NIST Webook 2007
Henry's constant	1.6E-6 atm m^3/mol	Toxnet, 2007
Vapor density	4.1 (air=1)	Toxnet, 2007
log K_{ow}	0.83	NIST Webook 2007
Odor threshold	9.3 mg/L	Toxnet, 2007
Flashpoint	353.15 K	Toxnet, 2007
K_{oc}	67	Toxnet, 2007
Diffusivity Coefficient	0.0249 m^2/h	NIST Webook 2007

Health Risks

2-BE itself is not toxic but its metabolites are. There are two main oxidative pathways of metabolism following either alcohol dehydrogenease or cytochrome P450. Alcohol dehydrogenease is the most important pathway. It leads to the formation of 2-BE's main metabolite, butoxyacetic acid (BAA). Cytochrome P450 produces ethylene glycol and finally carbon dioxide. Unfortunately, genetic polymorphism affects both of these pathways, making 2-BE metabolism difficult to predict and model.(Haufroid et al 1997)

Non-human animal evidence

2-BE has expressed toxicity in non-human animals via hemolysis (rupturing the of red blood cell membrane causing the release of hemoglobin and other cellular components, illustrated in Figure 1) through a direct action on erythrocytes (red blood cells) rather than on the bone marrow. The National Toxicity Program reports equivocal evidence of carcinogenic activity in female F344/N rats and little evidence of carcinogenic activity in males of the same species (Toxnet, 2007). Decreased body weight gains, liver and kidney toxicity are considered secondary to hemolysis (Corley et al., 1991). However, Haufroid et al. (1997) reports no evidence of kidney toxicity in rats. Regardless, these expressions seem to be limited to non-human animals. Both in vitro and in vivo studies on human erythrocytes exposed to 2-BE or BAA did not show any response (Haufroid et al 1997). This is because human erythrocytes are less susceptible to the hemolytic action of BAA than the animals that are historically used for toxicity evaluation such as rats, mice and rabbits (Corley et al., 1994).

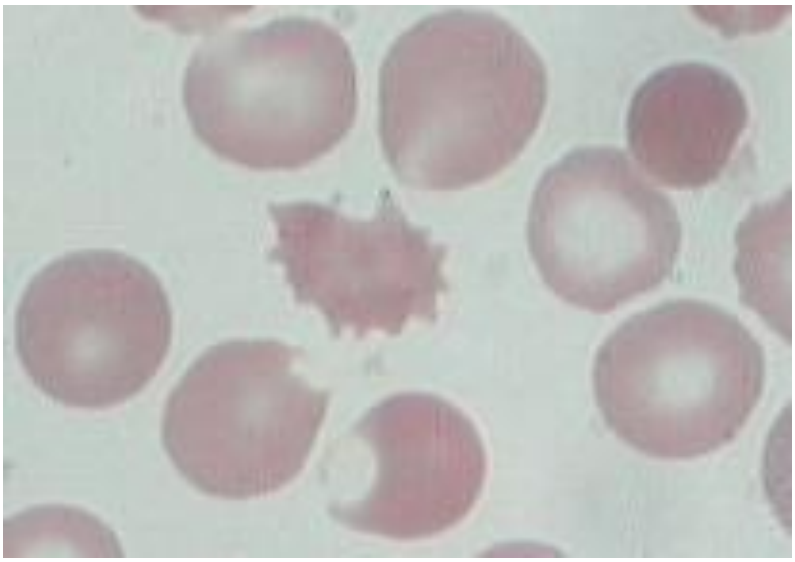

Figure 1: Illustration of hemolysis. (Cells with hemolysis appear asymmetrical and misshapen) (http://www.med-ed.virginia.edu, 2007)

Human evidence

There is no evidence that 2-BE is mutagenic, nor is it a reproductive or developmental toxicant. It is fetotoxic only at maternally toxic dose levels. There is considerably less risk of hemolysis in humans than would have been predicted solely from toxicity studies on non-human animals, highlighting the need for human toxicity testing (Corley et al., 1994). Occupationally exposed individuals do attest that 2-BE is a skin irritant (Jones and Cocker, 2003), and 2-BE has been listed as a class A3 carcinogen (confirmed animal carcinogen with unknown relevance to humans) (Toxnet, 2007).

Regulatory analysis

United States' regulatory environment and history

The United States Environmental Protection Agency (USEPA, 2006) classified glycol ethers as hazardous air pollutants (HAP) under the 1990 Clean Air Act. In November 2004 the USEPA delisted 2-BE after it determined "emissions, ambient concentrations, bioaccumulation or deposition of [2-BE] may not reasonably be anticipated to cause adverse human health or environmental effects" (USEPA, 2004). To support this finding the USEPA offered an exposure assessment. Unfortunately, the exposure assessment only considered inhalation exposure due to emissions to ambient outdoor air and does not consider the higher concentrations, and therefore exposure, associated with emissions indoors (Singer et al., 2006). Although 2-BE is no longer a HAP, it still has a federal reference concentration for chronic inhalation exposure (RfC). Several other agencies, including The National Institute for Occupational Safety and Health (NIOSH) and The American Conference of Governmental Industrial Hygienist (ACGIH) have published limits that can be found in Table 2. Both the NIOSH and ACGIH values were published with a 'skin' notation indicating that they were based on dermal absorption. Dermal absorption is the main exposure route (Toxnet, 2007). More discussion of this can be found in the Exposure Analysis section of this paper.

The California Air Resources Board (CARB) lists glycol ethers as toxic air contaminates (TAC). Within the TAC list, CARB establishes reference exposure limits (REL) for several specific glycol ethers. 2-BE's RfC and REL are comparable and are reported in Table 2.

Table 2: Regulatory and recommended levels for 2-BE

Federal reference concentration for chronic inhalation exposure (RfC)	13 mg/m^3
Reference exposure limits (REL) for acute (1-hr.) exposure	14 mg/m^3
ACGIH 8-hr Time Weighted Avg (TWA)	9.8 mg/m^3
Permissible Exposure Limit (PEL) 8-hr TWA	24.5 mg/m^3
NIOSH Recommended Exposure Limit: 10-hr TWA	2.45 mg/m^3
NIOSH Immediately Dangerous to Life or Health (IDLH)	343 mg/m^3

Canada's regulatory environment and history

The Canadian government has been reviewing 2-BE under the Priority Substances List assessment program in accordance with the Canadian Environmental Protection Act since 1995. It is currently under the risk management phase of the review. Indoor air exposure research is being included in their risk management process (Zhu et al., 2005).

United Kingdom's regulatory environment and history

Europe has been leading the charge against 2-BE. The UK, in particular, is taking decisive action in the area of pharmacokinetic modeling and in vitro human testing. The UK occupational exposure standards are 25 ppm (8-hr TWA) and 50 ppm (15-min Short Term Exposure Limit). Their government has also set maximum recommended urinary monitoring values for occupationally exposed people (Franks et al., 2006).

Exposure analysis

2-BE readily absorbs into the body following inhalation, dermal contact, or ingestion. Occupational exposure occurs through inhalation and dermal contact. In 1983

NIOSH estimated that approximately 2,100,000 workers were potentially exposed to 2-BE in the United States. According to the National Ambient VOC Database (1988), the median workplace atmospheric concentration of 2-BE was 0.075 ppb (Toxnet, 2007).

Inhalation exposure

Inhalation is the easiest exposure pathway to model. It received the most attention in the early years but recent findings have shifted the research focus away from inhalation to dermal exposure.

Zhu et al. (2001) used small chamber experiments to characterize emissions of 2-BE from selected consumer products, including some cleaning agents. They also measured headspace concentrations of 2-BE in several cleaning products ranging from 7.9 to 90.7%. They also studied the effect of dilution on emission and found that the emission rate of 2-BE from diluted solutions can be estimated with good accuracy by applying a dilution factor to the emission rate of the initial product. That is, emission rates of 2-BE are proportional to the product's mole fraction in water. Emission rates ranged from 145 to 938 mg m^{-2} h^{-1} with the highest rates coming from concentrated floor cleaning agents and the lowest coming from trigger spray glass cleaners. Using their experimentally derived emission rates, they calculated possible human inhalation exposures ranging from 0.048 to 0.001 mg (kg b.w.)$^{-1}$ day^{-1} under normal indoor conditions and multiple cleaning scenarios. For their exposure values they assumed 2-BE followed first order decay and no surface deposition.

I developed a simple emissions model that takes emission and ventilation into account. Details can be seen in the appendix. I timed myself cleaning my bathroom to

determine the time each task took and measured the surface areas and volume of the room. I used emission factors from Zhu et al. (2001). Time dependant concentrations in my small apartment bathroom of 2-BE from three cleaning tasks (glass, hard surface and floor) are presented in Figure 2. The model predicts concentrations an order of magnitude above REL for acute 1-hr exposure. The dose for this hour long cleaning event 115.5 mg which yields an intake fraction of 0.0127.

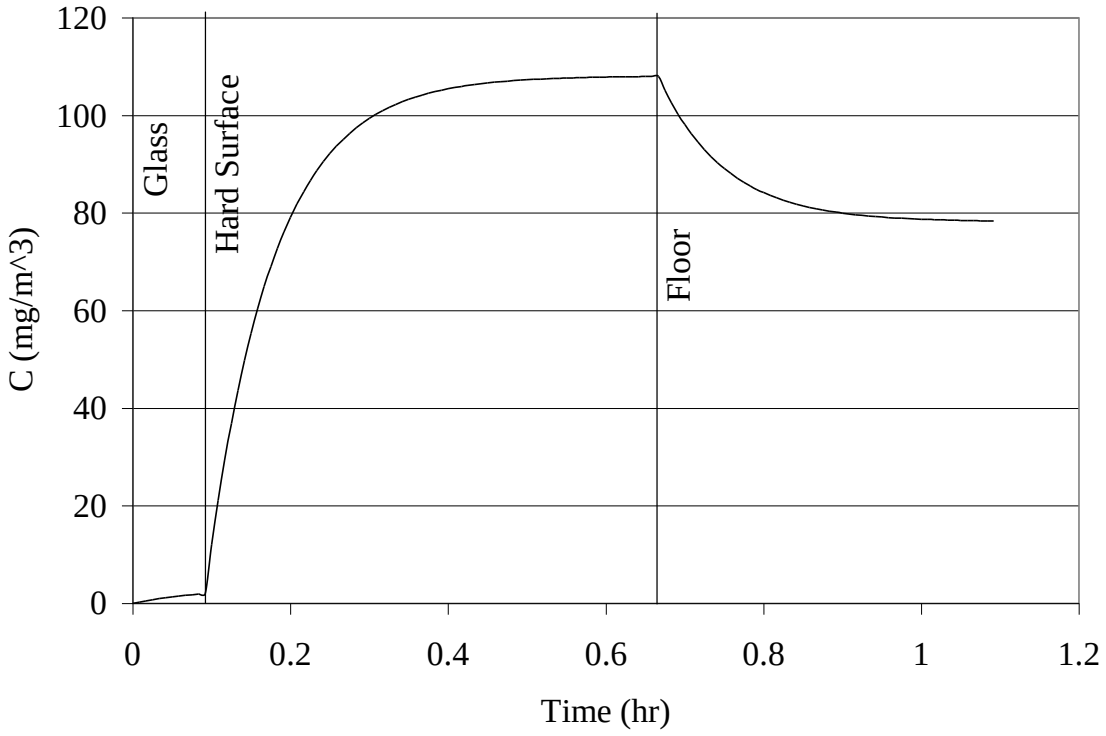

Figure 2: Time dependant concentrations in my small apartment bathroom of 2-BE from three cleaning tasks.

Singer et al. (2006) conducted emissions experiments in a large chamber designed to simulate a typical residential environment using six consumer products. Via simulated

use experiments, including rinsing with a sponge and wiping with a towel, emissions of full strength and diluted mixtures were characterized. Fractional emissions (mass volatilized/mass dispersed) were also calculated. When the towel or sponge was left in the chamber after the cleaning event, fractional emissions were 50 to 130%. Fractions over 100% are due to volatilization of 2-BE from chemicals that were not dispersed, either from rags or unsealed dilution mop buckets left in the chamber. Fractional emissions of 25 to 50% were recorded when the towel or sponge was removed. Even lower fractions (2 to 11%) resulted from diluted use. With an air exchange rate of 0.5/h and a chamber volume of 50 m^3, full strength application yielded 1-hr concentrations of 300 to 5000 ug/m^3 for normal use.

Using emissions calculated in their study, Singer et al. (2006) modeled cleaning scenarios. They proposed a possible cleaning scenario with typical air exchange rates, surface area to volume ratios, use patterns and product concentration in which concentrations of 2-BE could reach CARB's REL of 14 mg/m^3. A similar scenario is posed at the end of this paper.

Singer et al. (2006) also showed time dependence of peak concentrations. For most experiments, concentrations reached their peak within 30 minutes of application. However, the peak concentrations for the experiments where the towel or sponge was left in the chamber were not reached until 4 hours after application. This further illustrates the potential to decrease exposure by removing cleaning supplies after cleaning events. Further study should be done to determine the impact of rinsing the towel or sponge after use.

Inhalation models

A double-exponent model often characterizes emissions from wet materials and products. These models usually have a high, or fast, decay emission in the first phase which represents the chemical's rapid initial volatilization from the liquid phase (Zhu et al., 2005). The second phase has a relatively low, or slow, decay rate. The initial emission rate, signifying the emission rate at the instant the emission process begins, is one of two parameters (the other being the decay constant) used to describe the first phase of emission. Zhu et al. (2005) extended the vapor pressure boundary layer model from petroleum based surface coatings to aqueous based surface coatings such as 2-BE to describe emissions in the first phase. These water based coatings are more complicated to model because, unlike nonpolar chemicals in petroleum based products, the hydroxy group in polar or semi-polar compounds has strong hydrogen bonding interactions with water. Using equilibrium headspace concentrations, Zhu et al. (2005) predicted several products' initial emission rates for application in the model discussed above. Typically the ratio of headspace concentration to liquid concentration is the saturated vapor pressure of the pure component. This is Raoult's law. However, Zhu et al. (2005) showed that headspace concentrations were closely dependent on water content in the liquid phase. Such dependence indicates that 2-BE does not follow ideal behavior and that Raoult's law does not apply. Consequently, Zhu et al. (2006) performed dynamic chamber experiments to determine initial emission rates. Through these experiments, they found a correlation between the initial emission rate and headspace concentration. Thus, they proved headspace concentrations can predict initial emission rates. These rates were

then inserted, along with previously determined mass transfer coefficients, into the model to predict exposure. Their results are significant because headspace analysis is simpler and more cost effective than dynamic chamber test. Thus, emissions from building materials and consumer products' emissions could be easily calculated from simple, inexpensive headspace tests.

Dermal exposure

Dermal uptake is an often overlooked exposure route, but in many cases it plays an important role. In 2-BE's case it can be the predominate means of exposure in some situations. Traynor et al. (2007) reports that a 1-hr exposure of the human forearm to a 50% 2-BE/50% water mixture can exceed the body burden which would be caused by an 8-hr inhalation exposure to the threshold limit set by the ACGIH. During full body occupational exposure, dermal uptake can account for 75% of the total exposure (Haufroid et al. 1997). Traynor et al. (2007) hypothesizes this level of dermal uptake can be achieved because of 2-BE's rapid transport through the skin. They explain that although the epidermis has been shown to contain alcohol and aldehyde dehydrogenases, no local metabolism is observed, indicating transport across skin is fast. The barrier to chemicals like 2-BE in skin lies in the stratum corneum, the outermost layer of the epidermis, shown in Figure 2. The organized structure of lipid layers and corneocytes within the stratum cormeum are responsible for the skin's normally low permeability. However, perturbation of this highly ordered structure can result in increased permeability. 2-BE is a good solvent for lipophilic and hydrophilic compounds, so it may have a solubalising effect on the stratum corneum lipids. Pure 2-BE is dehydrating which

leads to less flux. However, when dehydrating solvents are mixed with water, increased flux of both the solvent and water is observed. Also, at certain concentrations 2-BE molecules can cluster together to form pseudomicelles. If these come in contact with skin, they might preferably partition out of the mixture and into the lipid rich skin. Further, the solvent does not need to be mixed with water at the time of dermal contact for flux to be increased. The lipid rich layers of the skin can be disturbed by contact with water alone. Later exposure to 2-BE (within a few hours) can still result in fluxes up to three times the flux of pure 2-BE (Traynor et al., 2007).

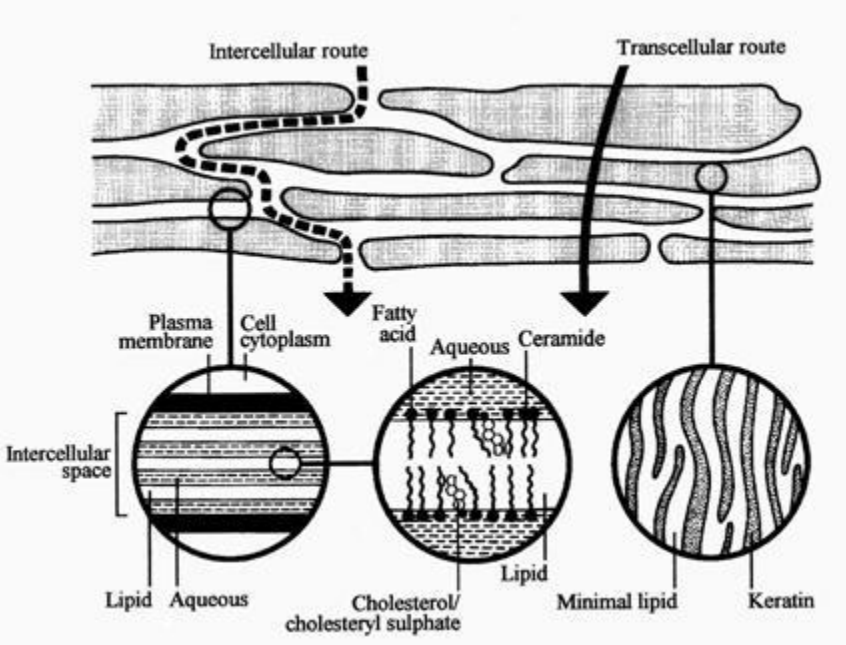

Figure 2: Diagram of stratum corneum. Each globule at top is a corneocyte and 2-BE follows the intercellular route. (http://www.ijpr-online.com/Docs/20041/IJPR226_files/image002.jpg, 2007)

The Traynor et al. (2007) study applied 2-BE in different concentrations to the human forearm in infinite and finite doses. They found that the maximum flux of pure 2-BE through human skin was 0.64±0.9 mg/cm^2 /hr. The greatest flux occurred with a 50% 2-BE/50% water mixture. The flux of 2-BE in this case was six times higher than pure 2-BE. Additionally, the flux of water from the mixture was higher than the flux from pure water. This non-linear relationship between flux and concentration is not accounted for in current predictive models based on quantitative structure activity relationships. These models predict permeability coefficients (k_p) for substances for which experimental data is not available. Exposures predicted by these coefficients will be wrong for water-miscible, lipophillic solvents like 2-BE, which further emphasizes the need for in vitro human studies. More discussion about the need for human studies can be found in the section on pharmacokinetic modeling.

Ingestion exposure

To reach toxic levels large oral doses would be required because conditions in the stomach readily destroy 2-BE and there is not enough uptake between the mouth and the stomach to reach toxic levels (Corley et al., 2007). Small amounts of 2-BE have been found in food because of its used as a solvent in food grade adhesives, however few studies about exposure to 2-BE via ingestion exist (Toxnet, 2007). These quantities, which are negligible compared to the inhalation or dermal exposure, combined with the need for large oral doses to reach toxic levels, are likely to be the reason for lack of studies.

Exposure monitoring

Given the prevalence, wide range of dermal contact, absorptive behavior and complex metabolism of 2-BE, biological monitoring is favored for a complete exposure assessment. A number of biological markers have been tested to determine the body burden caused by exposure to 2-BE, including 2-BE in the blood, BAA (2-BE's major metabolite) in the blood, 2-BE on the breath, and free and total (free + conjugate) BAA in the urine (Jones and Cocker, 2003; Haufroid et al., 1997; Corley et al., 1994). Due to sampling difficulties, invasiveness, and different rates of metabolism, 2-BE and BAA in the blood are unsuitable biomarkers for the determination of the extent of exposure. Also, due to minute levels on exhaled breath, 2-BE's polar nature and lack of instrument sensitivity at low levels, 2-BE on the breath is a poor marker (Jones and Cocker, 2003). Urine testing is preferred because it is less invasive and cost effective. Free and total BAA in urine are currently used for determination of exposure. The UK has established a biological monitoring guidance value for BAA of 240 mmol/ mol creatinine in urine. Creatinine is a breakdown product of phosphate in muscles and is produced at relatively constant rate. Germany has set a biological tolerance value of 100 mg/l for BAA in urine. Both countries based their guidance on free BAA and both recommend sampling post shift towards the end of the work week (Haufroid et al., 1997). This period was picked because peak excretion does not occur until 6 to 12 hours after exposure. With repeated exposure throughout the work week, accumulation becomes possible and only end of week testing will indicate overall exposure. Germany stated that measuring the conjugate BAA levels, in addition to the free BAA, is advised but not required (Jones and Cocker, 2003).

As discussed previously, 2-BE is metabolized into BAA in the body. BAA excreted in urine appears in free and conjugated forms which are measured independently. Of the many conjugation pathways, BAA may only be conjugated to glutamine. The extent of conjugation varies markedly from person to person and exposure scenario to exposure scenario. Only when saturation occurs in the kidney is BAA exceeded. Compounding the problem is the fact that saturation points are difficult to predict because the saturation point differs based on genetic polymorphism and environmental factors such as injury, stress or disease. The scientific consensus in 1994, the time when monitoring values were established, was that free BAA was the best marker. They chose free BAA because it would best predict risk, as free BAA is the active metabolite that causes hemolysis. However, occupational exposure levels are likely to be much lower than those needed to actually cause a risk of hemolysis. Currently, both Jones and Cocker (2003) and Haufroid et al. (1997) agree that total BAA is a better marker because it indicates exposure to 2-BE. Also, Jones and Cocker (2003) showed that monitoring free BAA alone may underestimate the absorbed doses of workers because of the wide and unpredictable variability in conjugation of BAA.

Methods for reducing exposure

Although 2-BE is not proven to be toxic in humans, it is an irritant and exposure should be minimized. Adequate ventilation with air flow patterns that direct vapors away from people could significantly reduce dermal and inhalation exposure in many occupational settings. Simply wearing gloves while cleaning, especially with diluted aqueous solutions, could reduce dermal exposure to zero which would reduce the overall

body burden by up to 75%. Prompt removal of cleaning supplies such a sponges, rags, and mop buckets is another means to reducing inhalation exposure. These precautions are easy, inexpensive, and could provide health and quality of life increases.

Pharmacokinetic analysis

A physiologically based pharmacokinetic model (PBPK) that describes uptake through dermal and inhalation exposure, metabolism and the disposition of 2-BE and BAA is useful for simulating concentrations of BAA in the blood for most exposure scenarios**.**

The seminal study addressing PBPK modeling of 2-BE was published by Corley et al. in 1994. They developed a PBPK that included all routes of exposure, competing metabolic pathways, and previously measured partition coefficients of both 2-BE and BAA in both rats and humans. This was the first pharmacokinetic study of 2-BE to address the difference between rat and human physiology. Corely et al. also included equations in their model for protein binding of BAA in the blood and saturable elimination of BAA by the kidneys. Although their model predicted that rats eliminate BAA from their bodies quicker than humans, the rats had higher predicted peak BAA concentrations in the blood than humans. Also the area under the BAA blood concentration time curve was higher for rats than humans. This can be explained by physiological differences between the species. These species differences coupled with the fact that human blood is less susceptible to hemolysis showed, for the first time, that humans were at less of a risk than rats from exposure to 2-BE. It also showed the need for human study before adequate determinations of toxicity can be made.

Franks et al. (2005) extended Corley's findings to predict concentrations of BAA in urine. They developed equations that described the saturable elimination of BAA in the kidneys that took into account glomerular filtration (the process by which blood is filtered in the kidney) and acid transport (an important biological function of the kidney is to maintain the blood's pH by transporting acid from blood to urine). They added a bladder compartment to the model to imitate urination at discrete intervals. This allows the model to simulate fluctuations in BAA concentration cause by urination. A schematic of their PBPK model can be found in Figure 3 below. These additions to Corley's model allowed accurate prediction of post-shift urinary concentration of BAA. Using their model they derived a biological monitoring guidance value of 250 mmol/mol creatinine of total BAA in urine. This corresponds to 8-hr exposure of 25 ppm 2-BE at resting working conditions.

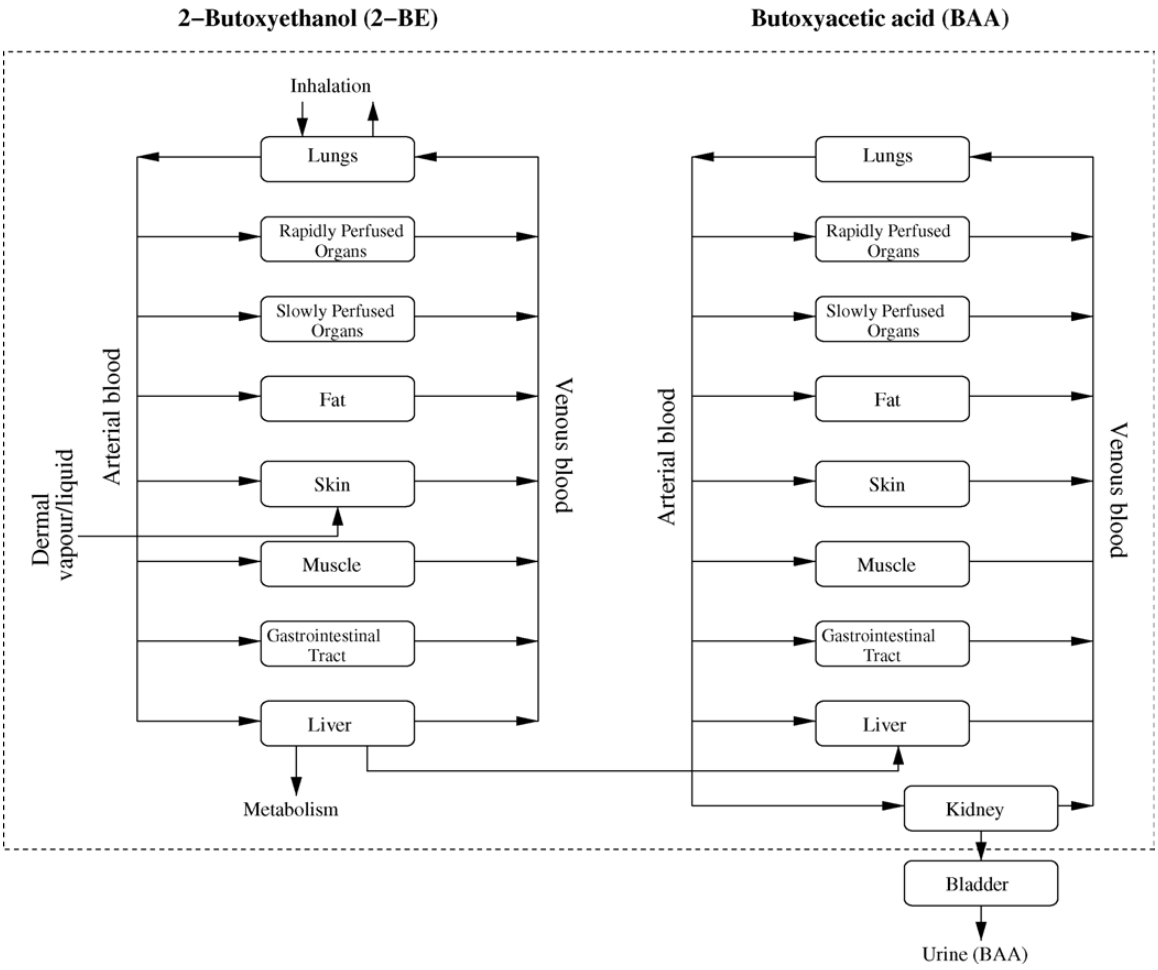

Figure 3. PBPK model describing the kinetics of 2-BE and BAA for human exposure developed by Franks et al. (2006). Corley et al. (1994) developed the schematic inside the dotted line.

Summary

2-BE is the most abundant glycol ether and can be found in a plethora of consumer products. It has been proven to be toxic in non-human animals but no evidence of human toxicity exists. While it is not regulated in the United States other nations have established regulatory guidelines, including biological monitoring levels. Dermal

exposure is far more important than inhalation. Recent pharmacokinetic models have been developed that accurately predict both blood and urinary levels of 2-BE major metabolite Butoxyacetic acid. Using simple controls, such as ventilation and personal protection like long gloves can significantly reduce exposure.

Appendix 2:

```
%%%VARIABLE DEFINITIONS

%INDEXS
%i=chemical index (each chemical gets a row)
%           Water is alawys the first row (i=1)
%j=time index (each column is the same time)
%    the actual time is Delta_t *j
%k=source index (each source is a two demensional matrix in the 3D
%     e-matrix)

%VECTORS AND MATRIX
%liqmol= mols in liquid liquid phase of chemical i
%e=emmisions matrix (mg/s)
%cmol_inter=conc. at interface (mol/cm^3)
%c_inter=interface concentration (mg/cm^3)
%c_in=conc. in the inner box (mg/cm^3)
%c_out=conc. in the outer box (mg/cm^3)
% c_o3_in=o3 conc. in inner zone (mg/cm^3)
% c_o3_out=o3 conc. in outer zone (mg/cm^3)
%kg=mass transfer coeif. vector (cm/s)
%MW=molecular weight (g/mol)
%roh=density (g/cm^3)
% %heterogreous rxns
% Vd_in=deposition velocity to surfaces in inner box(cm/s)
% SA_in=surface area for deposition in inner box(cm^2)
% Vd_out=deposition velocity to surfaces in outer box(cm/s)
% SA_out=surface area for deposition in outer box(cm^2)
% %homogreous rxns
% k_o3=reaction rate with o3 ((mg/cm^3)^-1 (s)^-1)
% Vd_o3_in=o3 deposition velocity to surfaces in inner box(cm/s)
% SA_o3_in=surface area for o3 deposition in inner box(cm^2)
% Vd_o3_out=o3 deposition velocity to surfaces in outer box(cm/s)
% SA_o3_out=surface area for o3 deposition in outer box(cm^2)

%SCALORS
%A=area of each application (cm^2)
%delta_t=time step (s)
%end_time= model duration (s)
%H=deminisonless henery's constant (c_aq/c_gas)
%V=volume of cleaning chamical dispersed (cm^3)
%V_in=volume of inner box (cm^3)
%V_out=volume of outer box (cm^3)
%Lambda_in=air exchange rate between inner and outer box (1/s)
%Lambda_out=air exchange rate outer box and fresh air (1/s)
%f=frequency of aplication (s)
%T=temperature (k)
%RH=relitive humidity (fraction)(less than one)
%R=ideal gas constant (cm^3 mmHg/(K*mol))
% c_o3_outside=conc. of o3 in incoming air (mg/cm^2)
```

```
function
[t,c_in,c_out,e,liqmolconc,liqmol,liqmoltotal,etotal,c_inter,kmax,c_o3_
in,c_o3_out]=corsi_class
%%%%MODEL INPUTS [water;2-BE;a-Pine;d-lime]
massfrac_int=[.8263;.0622;.0015;.11]; %2-BE from C.5 GPC-3; a-Pine from
B.2 GPC-1,6&7
total_mass_dispersed=103;       %g  %Table3.26 Exp 1O % but towel was
retained
V=3785;                          %should be 1 gallon %Table3.26 Exp 1O
T=295.25; %(k)                  %Table3.26 Exp 1O
H=[0;.551/(8.3144*T);.194/(8.3144*T);2725/(8.3144*T)];
kg=[0.0277;0.0277;0.0277;0.0277];
%kg=[0.0277;0.0367;0.0316];    %1;1.32;1.14 m/hr
MW=[18;118.1742;136.234;136.234];   %from NIST
rho=[1;0.9012;0.8592;.8402];
A=55741; %sum of all source cells, 60sft
delta_t=0.025;
end_time=15*60;
f=15*60/8;
V_in=100^3*.5; %cm^3
V_out=3300*100^3;
Lambda_in= 160/60^2;%(1/s)
Lambda_out= 0.3/60^2; %(1/s)
RH=0.44;
R=62363.67; %(cm^3 mmHg/(K*mol))
%heterogreous rxns
Vd_in=[0;0;0;0];
SA_in=[0];        %go back to add new index of surfaces
Vd_out=[0 0 0;0 0 0; 0 0 0;0 0 0];
SA_out=[145000,56000,10000];  %SA=[painted gypsum,linoleum,glass]
%homogreous rxns
c_o3_outside=[100*48/24.4/10^9];
c_o3_in=0.7*c_o3_outside;
c_o3_out=0.7*c_o3_outside;
k_o3=[0, 0,2.16e-6*10^9*24.4/136.234, 5.14e-
6*10^9*24.4/136.234];%converts ((ppb)^-1 (s)^-1) to ((mg/cm^3)^-1 (s)^-
1) WATCH OUT FOR MW in denom
Vd_o3_in=[.215];
SA_o3_in=[1.7*100^2];
Vd_o3_out=[.042 .0055 .00075];
SA_o3_out=[145000 56000 10000];%SA=[painted gypsum,linoleum,glass]

[t,c_in,c_out,e,liqmolconc,liqmol,c_inter,kmax,c_o3_in,c_o3_out]=s_mode
l_corsi_class(massfrac_int,total_mass_dispersed,V,H,kg,MW,rho,A,delta_t
,end_time,f,V_in,V_out,Lambda_in,Lambda_out,T,RH,Vd_in,SA_in,k_o3,c_o3_
in,Vd_out,SA_out,c_o3_out,Vd_o3_in,SA_o3_in,Vd_o3_out,SA_o3_out,c_o3_ou
tside);
[m n z]=size(liqmol);
    for x=1:m;
        for y=1:n;
```

```
        liqmoltotal(x,y)=sum(liqmol(x,y,:));
        etotal(x,y)=sum(e(x,y,:));
    end
end
```

```
function
[t,c_in,c_out,e,liqmolconc,liqmol,c_inter,kmax,c_o3_in,c_o3_out]=s_mode
l_corsi_class(massfrac_int,total_mass_dispersed,V,H,kg,MW,rho,A,delta_t
,end_time,f,V_in,V_out,Lambda_in,Lambda_out,T,RH,Vd_in,SA_in,k_o3,c_o3_
in,Vd_out,SA_out,c_o3_out,Vd_o3_in,SA_o3_in,Vd_o3_out,SA_o3_out,c_o3_ou
tside)

jmax=ceil(end_time/delta_t)+1;
avgMW=sum(massfrac_int.*MW);
liqmol=total_mass_dispersed/avgMW/ceil(end_time/f)*massfrac_int;
A=A/ceil(end_time/f);
t=[0];
k=1;
kmax=1;
j=1;
frequency=f;
vp=10^(8.10765-1750.286/(T-273.15+235)); %antoine equation give mm Hg

for i=1:length(MW); % conversions needed to calculate 1st time step
   V(i,j)=liqmol(i)*MW(i)/rho(i); %converts mols to volume for each chem
   liqmolfrac(i)=liqmol(i)/sum(liqmol); %calculates mol frac in liquid for each chem
end
for i=1:length(MW); %this loop calculate 1st time step(j=1 AKA t=0)values
   liqmolconc(i,1)=liqmol(i,1)/sum(V);
   if i==1 %(water)
      vp_inter=liqmolfrac(i)*vp;
      cmol_inter(i,1)=vp_inter/(R*T);
      c_in(i,1)=(RH*vp/(R*T))*MW(i)*1000;
      c_out(i,1)=(RH*vp/(R*T))*MW(i)*1000;
   else %(everything else)
      cmol_inter(i,1)=liqmolconc(i,1)*H(i);
      c_in(i,1)=0;
      c_out(i,1)=0;
   end
   c_inter(i,1)=cmol_inter(i,1)*MW(i)*1000;
   e(i,1,1)=kg(i)*(c_inter(i,1)-c_in(i,1))*A;
end
for j=2:jmax; %steps through time starting at j=2 (AKA t=delta_t)
   for i=1:length(MW);%at each time step values for each chemical are calculated
      t(j)=delta_t*j-delta_t; %creates a time vector used for the x-axis in ploting values vs time
      if t(j)>=f; %determines if a new source cell should be added
         f=f+frequency;%tells when the next souce cells should be added
         kmax=k+1;
         e(:,1,kmax)=0;
         liqmol(:,j-1,kmax)=liqmol(:,1,1);
      end
      for k=1:kmax;%everything in this loop is done to each source cell individually
         liqmol(i,j,k)=liqmol(i,j-1,k)-e(i,j-1,k)/1000/MW(i)*delta_t;
         V(i,j,k)=liqmol(i,j,k)*MW(i)/rho(i);
         liqmolconc(i,j,k)=liqmol(i,j,k)/sum(V(:,j,k));
         liqmolfrac(i,j,k)=liqmol(i,j,k)/sum(liqmol(:,j,k));
         if i==1
```

```
            vp_inter(i,j,k)=liqmolfrac(i,j,k)*vp;
            cmol_inter(i,j,k)=vp_inter(i)/(R*T);
          else
            cmol_inter(i,j,k)=liqmolconc(i,j,k)*H(i);
          end
          c_inter(i,j,k)=cmol_inter(i,j,k)*MW(i)*1000;
        end
        if i==1
          c_in(i,j)=(RH*vp/(R*T))*MW(i)*1000;
          c_out(i,j)=(RH*vp/(R*T))*MW(i)*1000;
        else
          % for use when calculating just one box (be sure to change V_in and lambda_in on input file)
c_in(i,j)=c_in(i,j-1)+delta_t*(sum(e(i,j-1,:))/V_in+Lambda_in*(c_out(i,j-1)-c_in(i,j-1))-
Vd_in(i,:)*SA_in.'/V_in*c_in(i,j-1)-k_o3(i)*c_in(i,j-1)*c_o3_in(j-1)-Vd_out(i,:)*SA_out.'/V_out*c_in(i,j-
1));
          c_in(i,j)=c_in(i,j-1)+delta_t*(e(i,j-1,kmax)/V_in+Lambda_in*(c_out(i,j-1)-c_in(i,j-1))-
Vd_in(i,:)*SA_in.'/V_in*c_in(i,j-1)-k_o3(i)*c_in(i,j-1)*c_o3_in(j-1));
          c_out(i,j)=c_out(i,j-1)+delta_t*(sum(e(i,j-1,1:kmax-1))/V_out-Lambda_out*c_out(i,j-
1)+Lambda_in*V_in/V_out*(c_in(i,j-1)-c_out(i,j-1))-Vd_out(i,:)*SA_out.'/V_out*c_out(i,j-1)-
k_o3(i)*c_out(i,j-1)*c_o3_out(j-1));
          % for use when calculating just one box       c_out(i,j)=0;
        end
        for k=1:kmax;
          % e(i,j,k)=kg(i)*(c_inter(i,j,k)-c_in(i,j))*A; use this when
          % doing just one box
          %
          if k==kmax
            e(i,j,k)=kg(i)*(c_inter(i,j,k)-c_in(i,j))*A;
          else
            e(i,j,k)=kg(i)*(c_inter(i,j,k)-c_out(i,j))*A;
          end
        end
    end
    % for use when calculating just one box (be sure to change V_in and lambda_in on input file)
c_o3_in(j)=c_o3_in(j-1)+delta_t*(Lambda_in*(c_o3_out(j-1)-c_o3_in(j-1))-
Vd_o3_in*(SA_o3_in.')/V_in*c_o3_in(j-1)-k_o3*c_in(:,j-1)*c_o3_in(j-1)-
Vd_o3_out*(SA_o3_out.')/V_out*c_o3_in(j-1));
    c_o3_in(j)=c_o3_in(j-1)+delta_t*(Lambda_in*(c_o3_out(j-1)-c_o3_in(j-1))-
Vd_o3_in*(SA_o3_in.')/V_in*c_o3_in(j-1)-k_o3*c_in(:,j-1)*c_o3_in(j-1));
    c_o3_out(j)=c_o3_out(j-1)+delta_t*(-Lambda_out*(c_o3_out(j-1)-
c_o3_outside)+Lambda_in*V_in/V_out*(c_o3_in(j-1)-c_o3_out(j-1))-
Vd_o3_out*(SA_o3_out.')/V_out*c_o3_out(j-1)-k_o3*c_out(:,j-1)*c_o3_out(j-1));
    %for use when calculating just one box         c_o3_out(j)=0;
end
```

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