The Thesis Committee for Jonathan David Gingrich
Certifies that this is the approved version of the following Thesis:

Ozone Reactions in Unoccupied Spaces of Residences

APPROVED BY
SUPERVISING COMMITTEE:

Richard L. Corsi, Supervisor

Atila Novoselac

Ozone Reactions in Unoccupied Spaces of Residences

by

Jonathan David Gingrich

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Abstract

Ozone Reactions in Unoccupied Spaces of Residences

Jonathan David Gingrich, MSE
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Supervisor: Richard L. Corsi

Ozone has the potential to cause many health problems. Most of the human population exposure to ozone occurs indoors. It has been previously reported that the average ozone penetration factor into the occupied space is 0.79. However, this value does not account for the pathway by which ozone enters the occupied space. A model to determine the amount that unoccupied spaces contribute to the ozone concentration in the occupied space is presented in this thesis. A literature review was then performed to identify parameters for the model as well as gaps that exist in the literature pertaining to the model developed. One of the biggest gaps was the lack of ozone decay rates in unoccupied spaces, such as garages, attics and crawl spaces. Because of this, a field study was designed and completed to determine the ozone decay rate in garages.

It was determined that the average ozone decay rate in garages is 2.7 (± 1.1) hr^{-1}. This value is comparable to previous data for occupied space ozone decay rates. Using these data as well as other published data, it was determined that, under normal conditions, ozone penetration through unoccupied spaces to the occupied space is not a significant pathway. However, there are some conditions for which unoccupied spaces may be a major

pathway for ozone entry into homes. One example of this is when both the garage door and the door connecting to garage to the occupied space is opened for a long time. Under these conditions, the occupied space can reach an indoor/outdoor (IO) concentration of 0.46. As can be seen, under this condition, unoccupied spaces do provide substantial contribution of ozone to the occupied space.

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Chapter 1: Overview

1.1 THE ISSUE

Ozone (O_3) has been an air pollutant a chemical of concern for many decades [1,2]. In tropospheric regions, O_3 is created mostly due to photochemical reactions with automobile emissions, which means that in locations with a higher concentration of motor vehicles, such as cities, there is normally a higher concentration of ozone[3]. Over time, the concentration of O_3, especially in these cities, has increased in both urban and rural areas near urban centers [4]. This increase has shown to increase mortality. Epidemiological studies indicate that every 10 ppb increase in O_3 results in a 0.41% increase in mortality [5].

Ozone has been shown to irritate the epithelial lining of the esophagus and cause an increase in the prevalence of asthma and allergies [6,7]. Ozone also reacts with many different surfaces and chemicals indoors, producing reaction byproducts that also cause damage to humans [8]. These reactions occur readily in most indoor environments, so not only is outdoor ozone of concern; indoor ozone also can have negative health impacts on humans [9,10].

The primary source of ozone indoors is the penetration into indoor spaces from outdoors. Ozone levels inside a building are normally about 10-20 percent of the outdoor concentration, depending on the method of ventilation used. But humans also spend a large majority of their time indoors, especially in homes [11]. Because of this, up to 60% of an individual's ozone exposure occurs indoors [8]. Therefore, it is important to try to reduce the concentration of ozone entering the residence.

Stephens et al. estimated that the fractional penetration of ozone into the residential occupied space averages 0.79 [12]. It is thought that ozone enters the occupied space via cracks in walls and through openings around windows and doors. However, other pathways are possible. One of these is the transport of ozone into the occupied space via unoccupied spaces. Examples of these spaces are attached garages, attics, and crawl spaces.

1.2 OBJECTIVES

The overall objective of this research was to provide to the scientific community data pertaining to the contribution of ozone from unoccupied spaces to occupied spaces of residences. This was accomplished in two different ways:

1. The development of a four-zone model (one occupied space and three unoccupied spaces) to model the transport of ozone from the outside through the unoccupied spaces and into the occupied space
2. Field tests to determine the ozone decay rate of ozone in garages

1.3 GENERAL METHODOLOGY

1.3.1 Model Development

A model was developed to estimate the contribution of unoccupied spaces to the penetration of ozone from outdoors to indoors. A series of mass balance equations was developed to predict the ozone concentration in the occupied and each unoccupied space. It was assumed that the outdoor concentration was 75 ppb, which was the highest ozone concentration recorded in June 2017 in Austin, Texas [13]. The volumes of each of the spaces were estimated from the median size of homes in the United States. After the model was developed and parameters established, the model was run to determine the effects of different scenarios. The scenarios tested were:

1. Decreasing the reaction rate of ozone in each zone
2. Base case scenario

3. Removing the Crawl Space
4. Removing the Attached Garage
5. Removing the Attic
6. Opening, then closing the garage door

For all six of the simulations, ozone levels were simulated either under steady-state conditions or until a steady-state condition was reached. The ratio between the zonal and the outdoor concentration of ozone was used to determine how much of an impact these spaces had on the occupied space.

1.3.2 Literature Review

A literature review was conducted in order to determine values for the model parameters. The Web of Science was used with a Boolean search structure to identify papers related to reaction rates of ozone with surfaces and materials commonly found in unoccupied spaces, such as wood, plastic coverings, concreted and insulation. Further literature searches identified papers concerning flow rates from the unoccupied spaces to the occupied space. A search of the literature revealed that there was very little literature concerning reaction of ozone in residential unoccupied spaces. The data that was found for both flow rates between zones in the residence as well as reaction rates in the occupied space were used in the model described in the previous section. Gaps that remain in the literature include ozone decay rates in garages, crawl spaces and attics, as well as flow rates between garages and attics, and between crawl spaces and occupied spaces. There is also little air exchange rate data for both crawl spaces and attics.

1.3.3 Field testing

Because of the lack of ozone decay rates in unoccupied spaces, it was decided to determine the ozone decay rate for garages. To do this, a volunteer sample of 12 garages in Central Texas were used to determine the ozone decay rate of a garage. These garages ranged in size (1 car vs. 2 car garages) and level of attachment to the occupied space. Of the 12 garages tested, seven were attached and five were detached. Seven were two-car and five were single car garages.

In each garage, the same protocol was followed. Carbon dioxide (CO_2) decay rates were used to determine air exchange rates of each garage. The CO_2 was released by a pressurized cylinder to artificially increase the concentration of CO_2 before terminating the source for the decay phase. Simultaneously, the ozone concentration was increased in each garage until it reached a maximum concentration using a commercial ozone generator. The ozone generator was then turned off and the concentration was measured in order to determine the rate of decay of ozone. The air exchange rate was subtracted from this rate to determine the ozone decay rate due to ozone reactions with surfaces in each garage. This process was repeated at least three times for each garage tested. The empty garage volume and surface area was also measured in order to determine the deposition velocity of ozone in each of the garages tested. A minimum of three runs were performed in each garage.

Chapter 2: Results and Conclusions

2 RESULTS

2.1 Model Applications

The model and application results can be found in Appendix 1. Through the specific applications modeled for this study, unoccupied spaces, under normal conditions, appear to have little effect on the concentration of ozone in the occupied space. Very few changes in model parameters had any effect on the concentration of ozone in the occupied space. Further modelling was performed considering only two zones, a garage and an occupied space, as presented in Appendix 2. Using the data found from the field studies, it was again seen that under regular conditions with a closed door between the attached garage and the occupied space, the change in ozone concentration when the garage was "seeded" with ozone after a large air exchange with the outside air had little impact on the indoor occupied space. However, when the air flow between the garage and the occupied space increases, e.g. when a connecting door between the garage and occupied space is also left open, the concentration in the occupied space can increase to almost half of the outdoor concentration. This shows that under certain circumstances, unoccupied spaces and their connections to the occupied space may have an effect on the concentration of ozone in the occupied space.

2.2 Literature Review

A total of 189 papers were identified and reviewed for this study. From the literature review, found in Appendix 1, it was seen that there exists a large gap in the knowledge of ozone reactions in unoccupied spaces. To date, no known publication reports ozone decay rates of ozone in any unoccupied space. In order to estimate ozone decay rates in each of the spaces, literature ozone decay rates on common materials found in each space were used to determine a relative reactivity of each space. Interzonal flow rates between different unoccupied and occupied spaces were found in the literature and were used in the model above.

2.3 Field Study

The average garage air exchange rate determined in this study was 0.47 (± 0.18) h^{-1}. This garage air exchange rate was comparable with previous studies of garage air exchange rates [9, and articles within]. The decay rate of ozone (k_{dep}) in the garages tested had an average value of 2.7 (± 1.1) hr^{-1}. For attached garages, the ozone decay rate was determined assuming 100% of airflow into the garage originates or conversely, 100% orginates from the occupied space. This resulted in a k_{dep} range of 2.4-2.6 h^{-1}, for 100% indoors and 100% outdoors, respectively. Comparing between one car and two car garages showed that one car garages had a larger average ozone decay rate (3.5 ± 0.4 hr^{-1}), than did two car garages (2.5 ± 1.1 hr^{-1}). Comparing between attached and detached garages, the average decay rates were nearly identical (2.6 ± 1.4 hr^{-1}) and (2.9 ± 0.5 hr^{-1}), respectively. This suggests that it is very likely that most of the air entering the attached garages comes from outdoors rather than indoors.

To compare between one car and two car garages further, the deposition velocity, which is a measure of the decay rate taking into account the surface area to volume (S/V) ratio, was calculated. When this is calculated, then the deposition velocities become much closer, showing that the most probable effect for the large ozone decay rates in one car garages are the higher S/V ratios.

The average ozone decay rate measured in garages is very close to the average decay rate of occupied spaces reported in the literature. For example, Lee et al. (1999)

reported an average ozone decay rate across homes of 2.8 ± 1.3 hr^{-1} [15]. Several researchers claim that the consistency of ozone decay rates between different occupied spaces is due to the interactions of humans with those environments, as humans and our skin oils are a reactive sink for ozone [16–18]. But the ozone decay rate in garages show that there could be another underlying factor that defines ozone decay in residences. More research is needed to determine what these factors may be, but a major area in most garages is gypsum wallboard, which is also a large area in the occupied space.

2.4 Overall Conclusions and Future Research

More research needs to be performed in order to fully determine the contributions of unoccupied spaces to the concentration of ozone in the occupied space. While models showed that little ozone is transferred from the unoccupied spaces under normal conditions, there were conditions in which the ozone concentration indoors increased dramatically based on scenarios that provided large flows of air from one area of the house to the occupied space. For such cases, it is possible that unoccupied spaces could affect the concentration of ozone in the occupied space.

To fully explore these possibilities, ozone decay rate studies should be performed on both crawl spaces and attic spaces. These spaces have large connections to the occupied space and no research teams have studied ozone decay rates for these spaces. Secondly, interzonal air flows between the unoccupied spaces and the occupied space should be measured to improve multi-zone models for ozone migration in homes. Finally, because ozone is such a strong reactant, it often forms reaction byproducts that could be dangerous to people's health. These byproducts could also be transported into occupied spaces, so research should be done to determine the presence of ozone reaction products in both unoccupied and occupied spaces of homes.

Appendices

APPENDIX 1

Ozone Reactions in the Unoccupied Spaces of Single-Family Homes: A Screening Analysis

Introduction

Ozone has been a subject of extensive study due to the detrimental effects it has on human health. It reacts with polyunsaturated fatty acids in fluids lining the lung with subsequent adverse effects in the airway epithelium [19]. Numerous studies have linked ozone exposure to decreased lung function, as well as asthma and premature mortality [2–8 and references provided therein].

The effects of exposure to ozone in buildings have not been extensively studied. Weschler [8] reported that indoor exposure accounts for 43% to 76% of total daily exposure to O_3, with a mean of 60% across seven cities. Chen et al. [9,26] showed that differences in ozone mortality coefficients (increases in short-term mortality for a given increase in ozone concentration) between cities can be partially explained by differences in total ozone exposure resulting from differences in the amount of ozone transported from outdoors to residential indoor environments. This finding is consistent with observations that the prevalence of centralized air conditioning systems, which are associated with lower air exchange rates and lower indoor ozone concentrations, is inversely associated with ozone-related mortality [24].

Ozone is a moderate oxidant and reacts with many chemicals found in indoor air or associated with indoor surfaces, leading to a spectrum of secondary products. These include C_1-C_{10} carbonyls, dicarbonyls, hydroxycarbonyls, secondary organic aerosols, and additional oxidized products that may be irritating or harmful to building occupants [16,27–42]. Weschler [8] provided a summary of stable oxidation products that result from indoor ozone chemistry.

Numerous researchers have studied ozone concentrations in residences [43–49]. The ratio of indoor to outdoor ozone concentrations (I/O) generally ranges from less than 0.1 to 0.7, depending on different housing characteristics. In cases involving natural ventilation, e.g., via open windows, the I/O tends to be greater due to higher air exchange rates and less time for reactions to occur in indoor air or on indoor surfaces [49,50]. Homes with lower air exchange rates have lower I/O due to the extra time available for ozone to react indoors.

Although there are some indoor sources of ozone in residential buildings [50,51] the primary source of indoor ozone is outdoor ozone that penetrates through the building envelope. Stephens et al. [12] and Zhao and Stephens [52] measured a penetration factor (fraction of outdoor ozone that penetrates through the building envelope) for residences. However, these studies assumed that the house was a single zone, and penetration pathways were not identified. In effect, the penetration factor reflects integration of ozone penetration over all flow pathways from outdoors to indoors.

There are multiple locations in houses with connections to the outdoor atmosphere and to other zones within the house [53,54]. Many of these locations can generally be categorized as unoccupied spaces, e.g., attics, garages and crawl spaces. These spaces are directly connected to the outdoor atmosphere via vents, doors, and unintentional cracks. They are also connected to the interior occupied space of homes through various flow pathways, including doors/access hatches, leaks in HVAC ducts, leaks around pipes and other protrusions between spaces, or cracks between walls, ceilings, and floors. However, the connections between these unoccupied spaces and the occupied space have been only sparsely studied, particularly with respect to pollutant transport.

Little research has been completed on ozone reactions in the unoccupied spaces of homes and flow pathways that transport ozone and its reaction products between the occupied and unoccupied spaces. In this paper, we provide a screening assessment of potential ozone reactions and flow pathways in single-family homes. Four major zones are considered, including garages, attics, crawlspaces, and the occupied space. A four-compartment model is presented with example simulations based on parameters available in the published literature. This screening assessment is intended to guide future research on the importance of chemistry in unoccupied spaces and related impacts on the occupied spaces of homes.

Ozone Chemistry

There are two types of reactions involving ozone in indoor environments, heterogenous (surface) reactions and homogeneous (in air) reactions. Heterogeneous reactions are generally assumed to be first order. The reaction rate for a single surface is modeled by the following equation:

$$R_s = -v_d C_{O_3} A \qquad \text{(Equation 1)}$$

Where R_s is the surface reaction rate (µg/hr), v_d is the deposition velocity (m/hr), C_{O3} is the concentration of ozone (µg/m^3), and A is the area over which reactions occur (m^2).

The inverse of the deposition velocity is taken as an overall resistance to ozone removal to a surface; which is typically modeled as the sum of a transport resistance and reaction resistance for that surface:

$$\frac{1}{v_{d_i}} = \frac{1}{v_{t_i}} + \frac{4}{\gamma_i \langle v \rangle} \qquad \text{(Equation 2)}$$

where v_{ti} is the transport-limited deposition velocity for surface i, γ_i is the reaction probability for surface i, and $\langle v \rangle$ is the Boltzmann velocity for ozone (362 m/s at 25 degrees Celsius).

Many researchers present only the deposition velocity based on exposure of materials to ozone in laboratory chambers. However, in these cases the deposition velocity for many reactive materials depends on the specific fluid mechanic conditions of the experimental chamber, and the effects of those conditions on the transport-limited deposition velocity. This makes it difficult to compare the potential for ozone removal to materials based solely on deposition velocity. For this reason, it is better to present the reaction data in the form of a reaction probability rather than the deposition velocity. Reported reaction probabilities for indoor materials generally range from 10^{-8} – 10^{-4}, depending on the specific material [32,55–58].

The volume-normalized sum of ozone reactions across n materials in an indoor zone is:

$$R_{s/v} = \sum_{i=1}^{n} v_{d_i} \frac{A_i}{V} C_{O_3} \qquad \text{(Equation 3)}$$

The term $\sum_{i=1}^{n} v_{d_i} \frac{A_i}{V}$ is often referred to as an ozone decay rate (k_{dep}; 1/hr), such that Equation 3 can be rewritten as:

$$R_{s/v} = k_{dep} C_{O_3} \qquad \text{(Equation 4)}$$

Homogeneous reactions in indoor air are generally bimolecular. As such, the reaction rate is modeled by

$$R_{air} = -k_{b_j} C_j C_{O_3} V \qquad \text{(Equation 5)}$$

where R_{air} is the reaction rate in air (μg/hr), k_b is the bimolecular reaction rate constant between ozone and reactant j (m^3/μg hr), and C_j is the concentration of reactant j (μg/m^3). Homogeneous reactions are normally less significant than surface reactions in terms of ozone removal, but may still lead to important reaction products [59]. As such, homogeneous reactions are omitted from the screening model described in this paper, which focuses on ozone balances in residences.

Screening Model

The same form of mass balance model is applied to each of the four zones (occupied space, garage, attic, crawl space) considered in this screening assessment. Due to the connections between each zone, the model equations are interdependent. Each zone is treated as a well-mixed reactor. For the four zones considered in this screening analysis, the following four equations (equations 4-7) were used with variables as denoted in Figure 1.

$$V_1 \frac{dC_1}{dt} = Q_{10}C_{out} + Q_4C_3 + Q_2C_2 - Q_9C_1 - Q_3C_1 - Q_1C_1 - k_{dep_1}C_1 \qquad \text{(Equation 6)}$$

$$V_2 \frac{dC_2}{dt} = Q_{14}C_{out} + Q_7C_4 + Q_1C_1 + Q_5C_3 - Q_{13}C_2 - Q_8C_2 - Q_2C_2 - Q_6C_2 - k_{dep_2}C_2 \qquad \text{(Equation 7)}$$

$$V_3 \frac{dC_3}{dt} = Q_{11}C_{out} + Q_3C_1 + Q_6C_2 - Q_4C_3 - Q_5C_3 - Q_{12}C_3 - k_{dep_3}C_3 \qquad \text{(Equation 8)}$$

$$V_4 \frac{dC_4}{dt} = Q_{15}C_{out} + Q_8C_2 - Q_{16}C_4 - Q_7C_4 - k_{dep_4}C_4 \qquad \text{(Equation 9)}$$

Solving these four differential equations simultaneously results in the change in concentration of the species of interest for each zone over time.

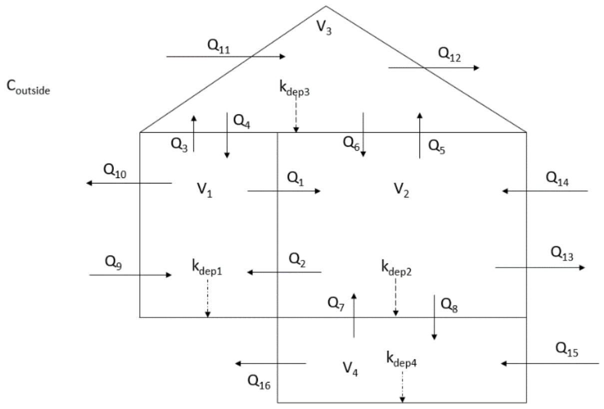

Figure 1. Four-zone model with three unoccupied spaces and one occupied space

For the above equations, the volume of each zone can be easily determined, and the outdoor concentration is assumed to be known and constant over the period of interest. However, the flow rates into and out of the zones as well as ozone decay rates are also required to solve the model. Flow rates change greatly based on pressure differences, which can vary due to external factors such as wind direction and strength, or internal factors such as turning on a vent or opening a window [60,61]. For this screening analysis, we assume steady flow rate conditions.

Ozone chemistry in garages

Materials with large surfaces in garages generally include concrete flooring, painted and/or unpainted gypsum board walls and ceiling, metal or wooden garage doors, and glass windows (some garages). Other materials include car exteriors, including rubber tires, and other items stored in garages. Chemicals in garage air include those entering from outdoors or other zones, emitted from building materials and stored consumer products, and gasoline vapors.

For concrete, Simmons and Colbeck found a surface deposition velocity for a concrete slab of 25.6 m/hr whereas Grøntoft and Raychaudhuri reported a range of 0.6-3.6 m/hr [62,63]. Poppendieck et al. [32] found that the initial reaction probability for sealed concrete when exposed to high doses of ozone to have a reaction probability of 2.6 x 10^{-6}.

No data could be found for rubber tires, however rubber crumb had a decay rate of 18.1 (1/hr g of rubber crumb) and rubber floor tiles had a reaction probability of 7.5 x10^{-6} [64,65]. Simmons and Colbeck found a reaction probability of 5.5 x 10^{-6} for clean glass, and 2.9 x 10^{-6} for dirty glass [62]. This is not the tempered glass that are on cars but reaction probability is fairly unimportant in comparison to other materials. There were no data found for painted metal.

The ozone deposition velocity for treated gypsum board was found to be between 0.6- 5.0 m/hr according to Grøntoft and Raychaudhuri [63] and 28.8 ±14.4 (m/hr) according Klenø et al. [66]. For gypsum board that is painted, the ozone deposition velocity ranges from 1.1 to 24.1 m/h depending on the binding agent that is used [66]. Lin and Hsu [29] reported an ozone reaction probability for gypsum board of 2.6 x 10^{-6}.

The ozone reaction probability for latex paint ranges from 7 x 10^{-7} at low humidity to 2 x 10^{-5} at high humidity [67].

There are no reported values of ozone decay rates (k_{dep}) for garages. Based on the relatively large area of painted and unpainted gypsum board in most garages, these materials likely have a significant impact on ozone removal. But other materials that vary significantly between garages will impact ozone removal as well. For this screening analysis the ozone decay rate for garages is assumed to be somewhat less than that for the occupied space as described below.

Garage air exchange rates have been studied multiple times. Batterman et al. measured outdoor air exchange rates (AERs) and flows between the garage and the occupied space in 15 houses. The average AER for garages was 0.77 ± 0.51 h^{-1} [68]. Batterman et al. also measured the 4-day average AER for a single garage to be 0.80 h^{-1} [69]. These occurred when the garage door was closed. Emmerich et al. (2003) reported results by Furtaw et al. who observed garage AERs of 17-104 h^{-1} with an open garage door [14,70].

Treating the garage as a single zone with airflow in from outdoors, the steady state equation becomes

$$\frac{C}{C_{out}} = \frac{1}{1 + \frac{kdep}{\lambda}} \qquad \text{(Equation 10)}$$

Using an assumed k_{dep} of 1-4 (1/hr) and an air exchange rate of 0.5-1 (1/hr) to simulate a garage with a closed door, the C/C_{out} has a range of 0.2-0.5 However, if the garage door is open, and the AER becomes 35 h^{-1}, the ratio becomes 0.9-0.97. This means that periods during which the garage door is open can provide a significant reservoir of potential O_3 entry to the occupied space.

There may be several connections between a garage and other zones. Garages, especially attached garages, are attached to the occupied space, either by means of the basement, in the case of a tuck-under garage, or directly to the occupied space, usually by means of a mud room, laundry room, or kitchen [14,71]. There are also connections through the wall separating the garage and the occupied space, via cracks and pores in the wall.

Dodson et al.[53] determined the flow rate from the garage to the occupied space to change between the summer and winter months for a home in Boston, Massachusetts. In the summer, the flow rate was 67 m^3/h, and in the winter the flow rate was 174 m^3/h. Batterman et al. [72]measured air exchange rates and flows between the garage and the occupied space in 15 houses and found that the average air exchange rates of the houses and garages were 0.43 h^{-1} and 0.77 h^{-1}, respectively, and the flow contribution from the house to the garage and the garage to house was 4.9 and 6.5% respectively.

There are also connections between the garage and the attic in some homes. However, we were unable to find any reported flow rates for this connection.

Ozone chemistry in attics

Materials with large surface areas in attics usually include bare wood and insulation. There may be other materials that vary from house to house, such as cardboard boxes, paints, and HVAC ducts, but these vary considerably between houses. Only wood and insulation are considered here.

Reported ozone deposition velocities to wood range from 0.08-3.2 (m/hr) depending on the type of wood [63]. To the author's knowledge, there are no reaction probabilities available in the literature for wood. The reported ozone reaction probability with fiberglass insulation ranges from 1 x 10^{-7} – 6 x 10^{-6} [58].

There are no reported values of ozone decay rates (k_{dep}) for attics. Based on the relatively large area of wood and insulation in most garages, these materials likely dominate ozone removal in many attics. But other materials that vary significantly between garages will impact ozone removal in attics as well.

Very few studies have been performed on the connections between attics and the occupied space. Walker et al. [73] modeled attic ventilation rates, including a flow into the occupied space, calculating an exchange rate from the attic to the occupied space to be 0.03-0.23 air changes/ hour for a 63 m^3 attic.

We were unable to find any publications related to contaminant transport from attics to occupied spaces. This may be because temperature differences between the attic and the occupied space often creates a “stack effect” which results in air rising from the cooler, higher pressure, occupied space, to the warmer, lower pressure attic space [74–77]. However, these effects are shown to be greater in the winter than in the summer, when ozone levels are normally lower[22,78]. There are conditions for which it is likely that attic air may flow to the occupied space. For example, if one or more exhaust fans are turned on in the bathroom or the kitchen, the underpressurized occupied space may draw in attic air. In addition, for HVAC systems that are ducted into the attic, there is potential for attic air to flow into leaky return-side duct work. The leakage rate for HVAC ducts generally rages from 10-30% [79,80]. This is the most likely transfer pathway for contaminants from attics to the occupied space, although, there are chances that air can flow through cracks in the ceiling, as well as through spaces in recessed lighting [81]. Iffa and Tariku [75] determined overall attic AERs ranging from 10 to 20 h^{-1}. This is much higher than air exchange rates found in the closed door garage and the occupied space. Using a value of 10-20 1/hr and assumed reaction rate constants of 1-4 1/hr leads to a C/C_{out} of 0.71 to 0.95 based on equation 10. So, because the AER is so large, even with a relatively large reaction rate, the concentration of ozone in the attic might be substantial on days with high outdoor ozone concentrations, which means that there is potential for transport of ozone to the occupied space under favorable conditions.

Ozone chemistry in crawl spaces

Crawl spaces are mostly composed of wood and dirt, and sometimes insulation. The dirt is often covered by a plastic sheet to prevent moisture and odors soil microbial activities from getting into the air in the crawlspace.

No data could be found for reactions between ozone and soil. The ozone reaction probability with plastic was found by Sutton et al. [82] to have a reaction probability of $7 \times 10^{-7} – 1.4 \times 10^{-6}$.

Mechanically ventilated crawl space air exchange rates have been determined by Kurnitski [83] to be between 2.3 and 4.4 1/hr depending on the number of supply and exhaust fans. Nazaroff and Doyle [84] determined that between 30 and 65% of the air entered from the crawl space to the living space. There were no data reported for the opposite flow from the occupied space to the crawl space.

For the single zone, steady state concentration in the crawl space, the k_{dep} is assumed to be 1-3 1/hr and the air exchange rate is 1-4 1/hr. Using this information, the steady state C/C_o is 0.25-0.8. Because the connections will mostly be to the occupied space, if there is a large amount of air entering the occupied space, then the crawl space could have a large influence on the occupied space.

Ozone chemistry in Occupied Spaces

Surfaces in the occupied space include building materials, furnishings, and occupants (skin oils on the body, on clothing, or shed skin flakes to interior surfaces). Heterogeneous reactions between ozone and indoor surfaces have been studied for a large number of materials, including carpet, painted gypsum wallboard, cabinetry, concrete, paper, linoleum, ceiling tile, and more [12,14,74–78] . Ozone reactions with surface modifiers such as cooking oils have also been studied [27,88–91].

Materials in residences differ from house to house, but there has been a fair amount of research investigating the decay rates of ozone in residences. Lee et al. [15] found the mean decay rate to be 2.8 ± 1.3 1/hr. Sabersky et al. [92] reported a reaction rate of 2.9 and 5.4 1/hr with non recirculated and recirculated air, respectively. For the purposes of the screening model described below, we will assume that the decay rate in the occupied space will be 3 1/hr.

Ozone chemistry in wall spaces

Researchers have also studied how ozone transfers from outdoors to the occupied space through wall cavities. Liu and Nazaroff modeled ozone penetration across the building envelope and found that, based on how reactive the fiberglass insulation was to ozone, ozone penetration through wall cavities can range anywhere from >90% to 10-40% [58]. Because there is such discrepancy, our model does not include ozone reactions for air transport from outdoors through wall cavities.

Flow rates

Data related to flow rates between zones in residential buildings is sparse. There are two methods for doing this. First, blower door tests have been used to measure the leakage areas of a single zone as well as the interface between two zones (e.g., the garage and the residence) [14]. These areas, coupled with differential pressure measurements can be used to estimate air flows. This is useful for approximations of the overall leakage area between zones, but it is challenging to perform for multiple zones. For multi-zone airflows, it is more common to utilize tracer gases. Ideal tracer gases are inert. Common tracer gases utilized in field experiments include carbon dioxide (CO_2), sulfur hexafluoride (SF_6), and perfluorocarbon tracers (PFTs), [53,93].

There has been little study on flow rates between zones in buildings, especially when considering more than two zones. It is difficult to gain anything but a rough estimate of the actual flow rates because weather patterns and human activity changes these flow rates, the flow rates employed in this screening analysis are meant solely as “reasonable” values.

Model Simulations

Because of the high uncertainties in several model parameters, we provide several simulation results here for illustrative purposes. We present three different scenarios resulting in six different simulations. For scenario 1, the concentration in each zone with respect to the outdoor ozone concentration will be modeled against a changing ozone decay rate. Each zonal decay rate will change at the same rate, going from a decay rate of zero to the maximum decay rate for each room (shown in table 1). A value of 75 ppb for outdoor ozone will be used, the highest 8-hour value of ozone in the Austin, Texas, area recorded through June of 2017[94]. Also in scenario 1, a simulation will be run keeping the ozone decay rate at 3 hr^{-1} for the occupied space. All other spaces will follow the same decrease as in simulation 1. For scenario 2, an exploration into the contribution of ozone from each of the three unoccupied spaces by removing each zone in succession is completed. Finally, scenario 3 explores increasing the flow rates into the respective zones. One simulation will look at increasing the AER of the garage, as if the garage door opens. For scenario 1, a steady-state concentration will be calculated, whereas for scenarios 2 and 3 the ozone concentration in each zone will start with a value of zero.

Table 1. k_{dep} values for simulation 1

% of $k_{dep\ maximum}$	k_{dep} (h^{-1}) value for each zone			
	Garage	Occupied Space	Attic	Crawl Space
k_{max}	2.25	3.5	3.25	2
90%	2.025	3.15	2.925	1.8
80%	1.8	2.8	2.6	1.6
70%	1.575	2.45	2.275	1.4
60%	1.35	2.1	1.95	1.2
50%	1.125	1.75	1.625	1
40%	0.9	1.4	1.3	0.8
30%	0.675	1.05	0.975	0.6
20%	0.45	0.7	0.65	0.4
10%	0.225	0.35	0.325	0.2
0%	0	0	0	0

The values for all of the variables for the base case are shown in Table 2**.** Simulations were performed using a differential equation solver, Polymath 6.10.

Table 2. Base case values for simulation

V1 (m^3)	160	Q10 (m^3/h)	106.6
V2 (m^3)	500	Q11 (m^3/h)	910
V3 (m^3)	63	Q12 (m^3/h)	912.4
V4 (m^3)	50	Q13 (m^3/h)	174.25
Q1 (m^3/h)	6.4	Q14 (m^3/h)	151
Q2 (m^3/h)	10.75	Q15 (m^3/h)	140
Q3 (m^3/h)	15	Q16 (m^3/h)	105
Q4 (m^3/h)	20	kdep1 (1/h)	1.575
Q5 (m^3/h)	20	kdep2 (1/h)	2.45
Q6 (m^3/h)	12.6	kdep3 (1/h)	2.275
Q7 (m^3/h)	45	kdep4 (1/h)	1.4
Q8 (m^3/h)	10	Cout (ppb)	75
Q9 (m^3/h)	97.25		

Results

Figure 2 shows the results of scenario 1. In simulation 1, as k_{dep} increases in each zone, the ratio between the respective zone and the outside ozone concentration decreases. This is to be expected, as k_{dep} measures how quickly ozone reacts with surfaces in the zone. When k_{dep} increases, the rate that ozone decays also increases. Therefore, the ozone concentration will be lower when k_{dep} is larger. What is interesting is that the rate of decrease in each zone is not constant, but rather it goes in order of AER, where the zone with the smallest AER is the zone where k_{dep} had the most effect on the ozone concentration.

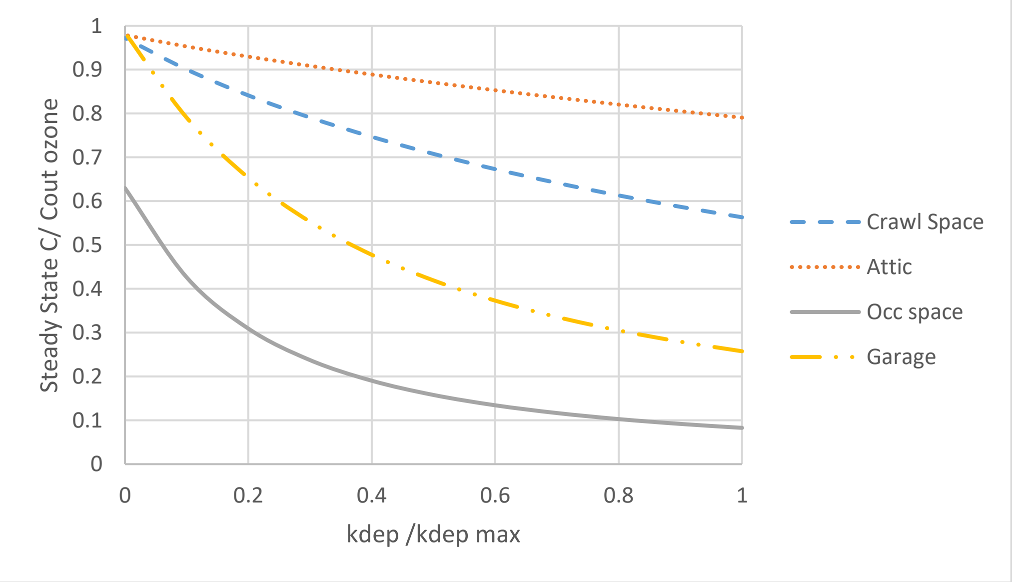

Figure 2. Steady state ratio of concentrations as k_{dep} changes

For simulation 2, as decay rate changes in the three unoccupied spaces, it can be seen that the ozone concentration in the occupied space does not change at all. This could indicate that the unoccupied spaces do not greatly affect the occupied space.

In scenario two, each of the unoccupied spaces were removed from the simulation in succession. The results of these simulations are presented in Figures 2 a-c. These simulations can be compared to the base case presented in Figure 2d. As can be seen in these figures, the unoccupied spaces have little effect on the ozone concentration of the occupied space. Taking away each unoccupied space in succession does little to change the occupied space concentration. The space with the largest effect is the crawl space. Removing this space does not change the concentration of the occupied space but it increases the concentration in the garage and decreases in the attic. The full steady state results from all four runs is found in Table 3. These results show that at the present flow rates, none of the unoccupied spaces had much of an impact on the ozone concentration of the occupied space.

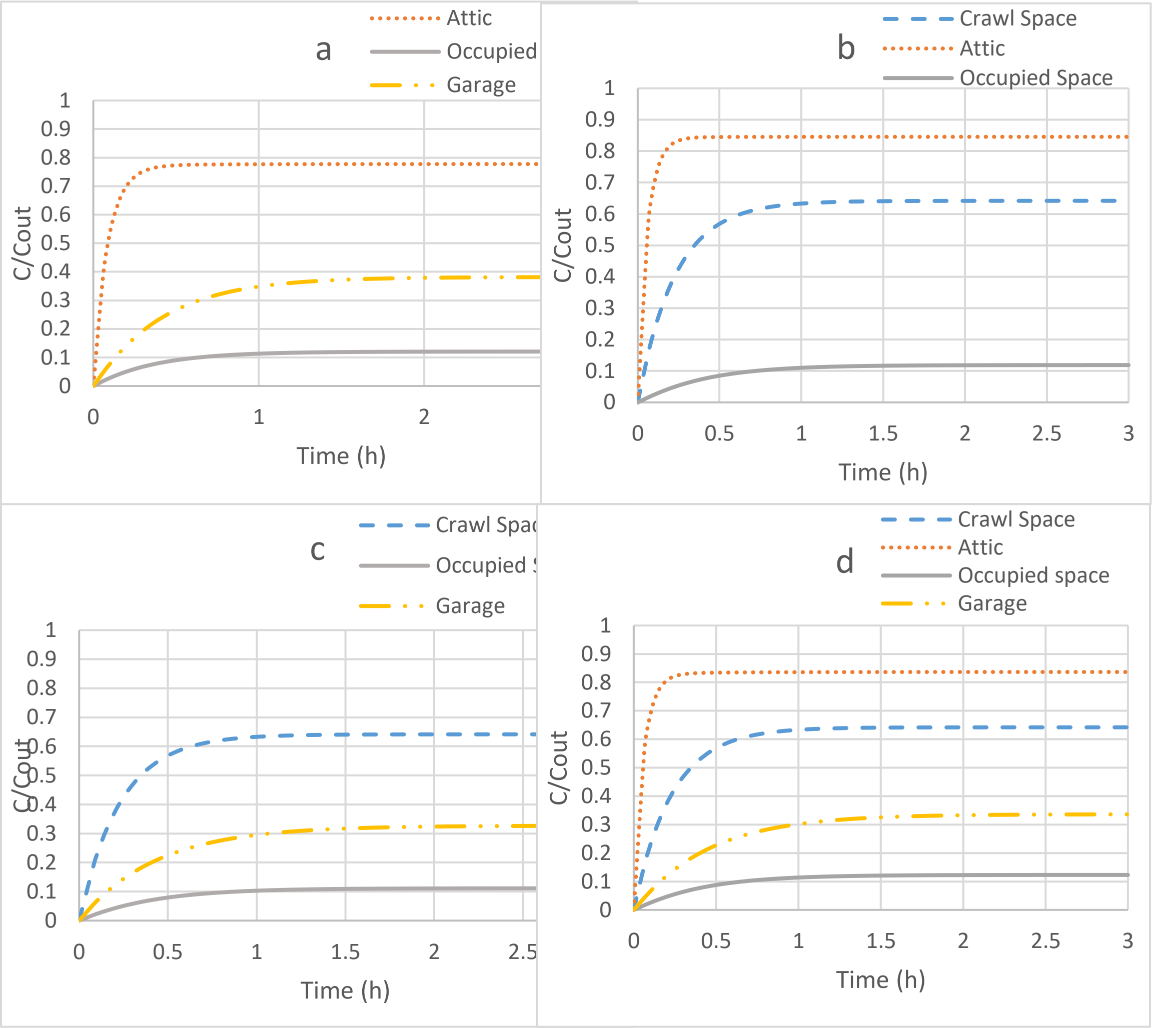

Figure 3. a. Simulation results with no crawl space; b. Simulation results with no attached garage; c. Simulation results with no attic; d. Simulation results base case

Table 3. indoor to outdoor ozone concentration ratios in each zone

Scenario	Steady State ratio zone: outside			
	Occupied Space	Crawl Space	Attic	Garage
Base Case	0.123	0.642	0.837	0.336
No Crawl Space	0.120	--	0.777	0.381
No Attic	0.111	0.641	--	0.327
No Garage	0.120	0.642	0.846	--

Finally, a scenario involving the change in the air exchange rate in the garage was tested. The AER increased for one hour to 15 h^{-1} (simulating a garage door opening), and then decreased to the original value (0.8 h^{-1}). The resulting simulation is shown in Figure 3. As can be seen, the garage ozone concentration increases to a high level from 0-1 hours. Once the AER changes at 1 hour, the concentration drops to a level similar to the base case Figure 2d**.** The attic concentration rises to a value that is just below the base case value. However, once the AER changes, the value actually increases slightly, resulting in an ozone concentration that is slightly elevated in comparison to the base case. These are the most significant changes due to the change in air exchange rate for the garage. There is, however, one other result. Both the occupied space and the crawl space exhibited no discernable change in ozone concentration when the AER changed. This is an interesting result. Even though the flow rates into the living space changed, once the ozone concentration reached steady state, a change in the flow rate did not affect its steady state concentration. This is most likely due to the occupied space having such a large volume, so only a large change in flow rates would affect the concentration of ozone in the zone. Because flows from the unoccupied spaces to the occupied space are so low, the occupied space has a lot of “buffering” ability and can withstand increases in airflow to its space. This results in relatively constant concentrations of ozone within the space.

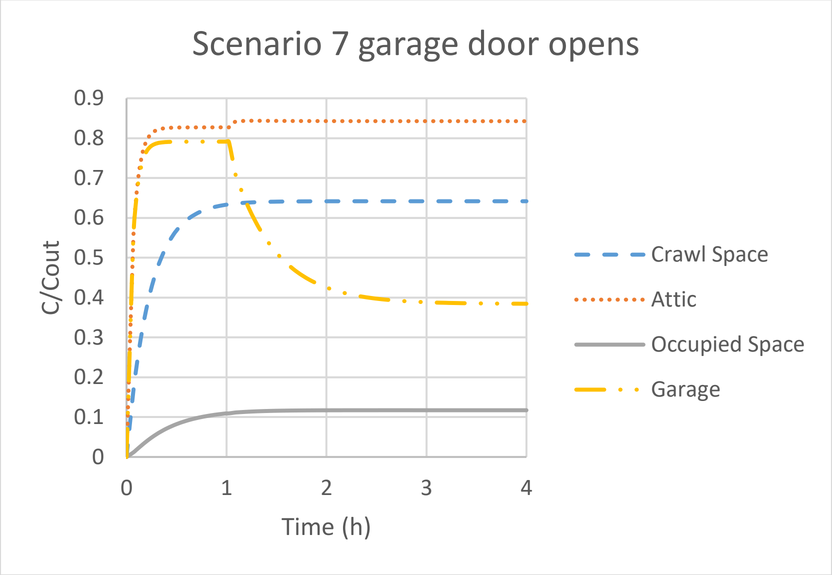

Figure 4. Simulation results with opening and closing of garage door

Limitations

Because this model only takes into account the data pieced together from many different studies, the numbers in no way are comprehensive for a single home let alone all homes. Every building is different and the flows within a building change constantly depending on pressure forces and activity within the building. Even activities such as opening and closing a door can have an effect on the pressure differences in a building [95]. Wind was also not taken into account, though it is questionable as to how great of an impact wind has in changing the air flows and air exchange rates [74,96]. Finally, temperature was also not considered, and it was assumed that all zones were at the same temperature. Some of the zones used, especially attics and crawl spaces, when poorly insulated, can be at drastically different temperatures than the occupied space. This would change the density of the air which would affect the flow rates from one zone to another. While we did not address this issue, we felt it was more beneficial to present the contributions of these unoccupied spaces to the ozone concentration of the occupied space, and the needed information directly pertaining to this problem, and temperature effects would fall under the needed information. Therefore, for the purpose of the model, the temperature was assumed to be constant. Finally, as stated before, this model does not assume any homogenous reactions are involved separately in the reaction, and that the reaction rate of each zone is only dependent on the concentration of the ozone in that space. While it is known that ozone will react with other compounds in the gaseous state, we did not consider it for the purposes of this screening assessment.

Conclusion

In this paper, a model for a four-zone residence, with three unoccupied spaces and one occupied space, was presented for the purpose of determining the contribution of each zone to the occupied space ozone concentration. We presented the equations needed to model this problem, and all of the knowns and unknowns so far associated with solving the problem. In order to find the solution for such a residence, deposition velocities and reaction probabilities were found for materials commonly associated with the zones used in the model. These were then used to estimate approximate reaction rates for ozone in those zones. Also, data on interzonal transport of air was used to determine the airflow from the unoccupied spaces to the occupied space. All of these values were then used in the created model to estimate the contribution of the unoccupied spaces to the concentration of ozone for the occupied space. From this model, it was found that the contribution from all four zones was minimal. However, because the data came from many different studies, and there was no single study on a complete house, it is still beneficial to find a reaction rate of ozone in each of the three unoccupied space, as well as to determine the actual flow rate from each of these zones to the occupied space, and in the case of connections between the garage and the attic, to contribute an unknown value to the literature. If this is accomplished, then we will truly be able to learn if the contribution of the unoccupied spaces to the occupied space is really as minimal as the model makes it out to be.

APPENDIX 2

OZONE DECAY RATES WITH GARAGES

Jonathan Gingrich and Richard L. Corsi

Introduction

Increased concentrations of outdoor ozone have shown to have a variety of negative health effects on humans [24,97–99]. Ozone causes inflammation in the epithelial lining of the lungs which can exacerbate symptoms in asthma patients [25]. Many studies have shown that there is a link between ozone exposure and premature mortality [8, 21, 22, 98–100]. About one third of Americans live in areas that exceed National Ambient Air Quality standards for ozone [101].

Ozone does not only exist outdoors. Ozone concentrations in buildings, including residences, have been reported by many researchers [20, 44, 45, 47, 49, 102]. These concentrations are lower than outdoor ozone concentrations, but Americans and those in many other developed countries spend almost 90% of their time indoors [11]. As such, the exposure to indoor ozone constitutes up to 60% of a person's total exposure [8]. Ozone exposure indoors also results in exposure to ozone reaction byproducts. Ozone reacts with many different surfaces in the indoor environment [46, 102]. It also reacts homogeneously with many chemicals in indoor air, including terpenes and terpene alcohols used in many consumer products [34,103,104]. These reactions often produce byproducts that can be irritating or worse to building occupants [27, 105].

Ozone may originate indoors from sources like photocopiers and ionic air purifiers [50,106–108]. However, the majority of ozone entering the occupied space comes from outdoors [58, 109]. This ozone enters the building through cracks in walls and through openings like windows and doors. Stephens et al.[12] calculated a mean penetration factor of ozone into the occupied space of 0.79 ± 0.13, i.e., on average 21% of the outdoor ozone is removed before the ozone enters the occupied space[12].

Ozone enters the occupied space through cracks in walls and through openings in spaces between doors and windows. However, there are other openings in homes that may allow ozone into the occupied space. For example, a relatively unexplored pathway for ozone entry into homes are unoccupied spaces, such as crawl spaces, attics, and garages. These spaces normally have a high air exchange rate and direct connection to both the outdoors and the occupied space. Batterman et al. [72] reported that benzene is transported from the garage to the occupied space. Zielinska et al. [110] reported that turning a car on in the garage could result in a spike of many different compounds in the connected kitchen. Because of these studies it can be assumed that ozone may also enter the occupied space through this pathway.

In order to determine the extent to which ozone enters the occupied space through garages, the interactions of ozone with surfaces in garages must also be characterized, along with air exchange rates when the garage door is closed. Ozone reactions with materials in garages are missing in the published literature. Because of this, we measured the air exchange rate and ozone decay rate in 12 different garages in Austin, Texas. This study reports the results of those experiments and the resulting implications.

Methods and Analysis

A convenience sample of garages were chosen based on garage volume and connections to the occupied space. No cars were present in the garages during experiments. The dimensions of the garages were measured to determine the empty volume. Surface areas of gypsum wallboard and concrete floors were also determined for each garage. A list of the 12 garages are shown in Table 4, as well as qualitative measures of the degree of connectedness to the occupied space and level of clutter in each garage. A score from one to five was given for the level of clutter, with 1 being clean and 5 having a large amount of clutter. Comments about general contents of each garage and their connectedness are also provided in Table 4.

Air exchange rates were measured by increasing the carbon dioxide concentration using a pressurized tank of CO_2. The CO_2 was released in the garage to increase the concentration to over 2000 ppm. The decay was measured over time using a Telaire 7001 CO_2 sensor and a HOBO data logger. Simultaneously, the outdoor CO_2 concentration was measured.

The ozone concentration both within the garage and outside of the house was measured using Horiba-APOA 370 ambient ozone monitors. If there was a connection between the garage and the occupied space, simultaneous ozone measurements were made in the occupied space using a model 202 ozone monitor (2B technologies). Ozone monitors were calibrated with a calibration source (2B technologies model 306) before each field study was performed. For each run, ozone levels were increased in the garage using an ozone generator and mixed using a fan. This generally led to peak ozone concentrations of 40-250 ppb, depending on the garage tested.

Table 4. List of garages used in study as well as respective empty volumes, surface areas and qualitative scoring of clutter and connectedness.

#	Age of House	Connected vs Unconnected (C vs U)	Empty garage volume (m^3)	Empty garage surface area (m^2)	Clutter rating	Comments
1	1968	C	128	163	2	Connection to attic and mod room, also window connection
2	1984	C	100	144	2	Connection to attic and laundry room also window connection
3	1994	C	107	157	2	Connection to attic and occupied space
4	2010	C	143	184	1	Connected to kitchen
5	1990	U	93	135	3	Cardboard boxes and workbench attic above detached garage
6	2003	U	139	197	3	Two doors exiting to outside apartment above garage, but no connections, bikes washer and dryer, large plastic and cardboard boxes
7	2003	C	100	139	2	Connected to attic and laundry room
8	2005	C	55	101	4	Connected to kitchen couch with plastic covering, washer and dryer, 2 mini fridges, lots of wooden bookcases and shelving
9	1929	U	48	84	2	Small attic connection, adjacent apartment but no direct connections to apartment, garage door only exit and entrance to garage
10	1942	U	57	92	4	10 bikes, bundles of vinyl flooring, tools, work bench, jmetal shelves, paint, lawn mower, adjacent apartment, but no direct connection
11	1971	C	56	98	5	Window, bookcases, lots of plastic and cardboard boxes, washer and dryer, bikes. wooden shelves, chalkboard and a tire, connected to occupied space and attic
12	2010	U	41	76	4	Shelving, bikes, table, rack with tools, connected to occupied space only via attic, and shard back wall with occupied space

After forty minutes, both the ozone generator and the fan were turned off and recording of the decay of both CO_2 and O_3 began. The decay of both the ozone and the CO_2 was measured until the CO_2 was less than half the value of the peak concentration. The CO_2 and ozone tests were restarted. This protocol was completed at least three times for each garage.

Air exchange rate

Air exchange rates were calculated using a dynamic mass balance on an assumed well-mixed garage atmosphere. The resulting equation assuming CO_2 entry dominated by outdoor air is:

$$-\ln\left(\frac{C_t - C_{out}}{C_{t=0} - C_{out}}\right) = \lambda t \qquad \text{(Equation 11)}$$

where λ is the air exchange rate (1/hr), t is the time (hr), C_t is the concentration of CO_2 at time t (ppm), C_{out} is the concentration of CO_2 outside (ppm), and $C_{t=0}$ is the peak concentration of CO_2 in the garage at the time the analysis began (ppm). The right side of the above equation was plotted against time and a best-fit line was forced through the zero intercept to determine the air exchange rate from the resulting slope. An example decay curve is shown in Figure 5 and all other air exchange rate curves are provided in the supplementary information. For the example shown here, the air exchange rate was 0.29 hr^{-1}.

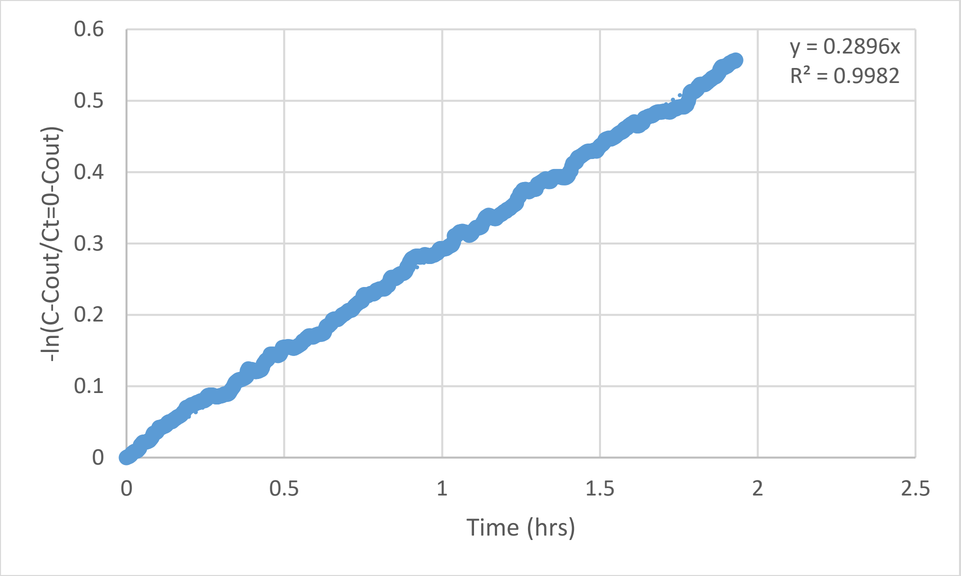

Figure 5. Air exchange rate analysis with AER = 0.29 1/hr

Ozone decay rate

The following mass balance equation was used to determine the decay rate for ozone:

$$V\frac{dC}{dt} = QC_{out} - QC - Vk_{dep}C \qquad \text{(Equation 12)}$$

where V is the volume (m^3), dC/dt is the change in concentration of ozone (ppb/hr), Q is the flow rate of air into and out of the garage (it is assumed that the flow into and out of the garage is equal) (m^3/hr), C_{out} is the outside ozone concentration (ppb), C is the garage ozone concentration (ppb), and k_{dep} is the decay rate of ozone due to reactions, primarily with indoor surfaces (1/h). This equation was solved for C to obtain the following equation:

$$C = C_{t=0}e^{-\beta t} + \frac{\lambda}{\beta}C_o\left(1 - e^{-\beta t}\right) \quad \text{(Equation 13)}$$

where $C_{t=0}$ is the peak ozone concentration in the garage (ppb), λ is the air exchange rate calculated by equation 1 and β is found by:

$$\beta = \lambda + k_{dep} \quad \text{(Equation 14)}$$

Equation 13 was used assuming the outdoor ozone concentration remained relatively steady. If this was not the case, a discretized form of the mass balance equation was used:

$$C^{n+1} = \frac{C^n\left(\frac{1 - \beta\Delta t}{2}\right) + \lambda\Delta t\left(\frac{C_0^{n+1} - C_0^n}{2}\right)}{\left(1 + \frac{\beta\Delta t}{2}\right)} \quad \text{(Equation 15)}$$

where C^{n+1} is the next concentration in the time step (ppb), C^n is the current concentration in the time step (ppb), Δt is the time step (h), C_0^{n+1}, is the next outdoor concentration in the time step (ppb) and C_0^n is the current outdoor concentration in the time step (ppb). β is the rate of removal for ozone in the garage as described in Equation 14.

The ozone data were recorded in 3-minute intervals throughout the experiment. The peak concentration during each ozone release experiment was used as $C_{t=0}$ in the decay analysis. The decay analysis continued until the ozone concentration reached a minimum or dropped below 5 ppb. These data and the time they occurred were then plotted against results for equations 13 or 15**.** The sum of the residual difference was minimized by iterating the value of k_{dep}. The value of k_{dep} that resulted in the lowest summed residual was taken as the k_{dep} of that experimental run. This was done for each experimental run. An example of this is shown in Figure 6.

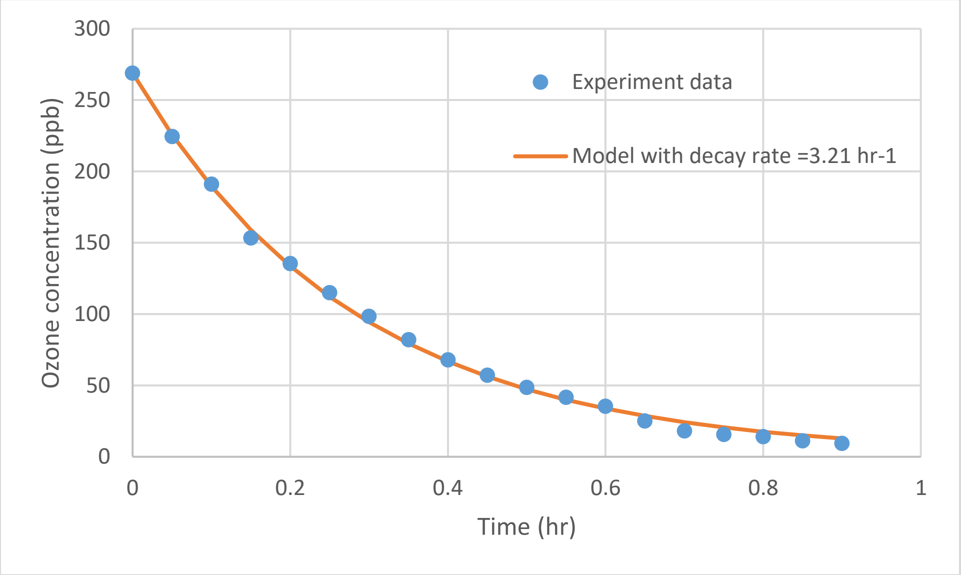

Figure 6. Ozone decay rate with model kdep = 3.2 /hr

For garages that were connected directly to the occupied space by a door, the ozone concentration measured in the interior space adjacent to the door over the day of testing was averaged throughout the day to obtain a single ozone concentration indoors. Indoor concentrations were generally low and relatively constant. Then, using equation 13**,** the decay rate of ozone in the garage was calculated, assuming 100% of the air entering the garage came from the occupied space. This then provided a range of decay rates for attached garages, with one bound assuming all of the air entering from the occupied space, and the other assuming all of the air entering from outdoors. In general, these two approaches led to only small differences in back-calculated k_{dep}, i.e, less than 7 percent.

Results and Discussion

Air Exchange rates

A total of 30 air exchange rate measurements were completed over all 12 garages. The arithmetic mean (± standard deviation) air exchange rate of a garage with the garage door closed was 0.47 (±0.18) hr^{-1}. A cumulative frequency plot of these air exchange rates is shown in Figure 7.

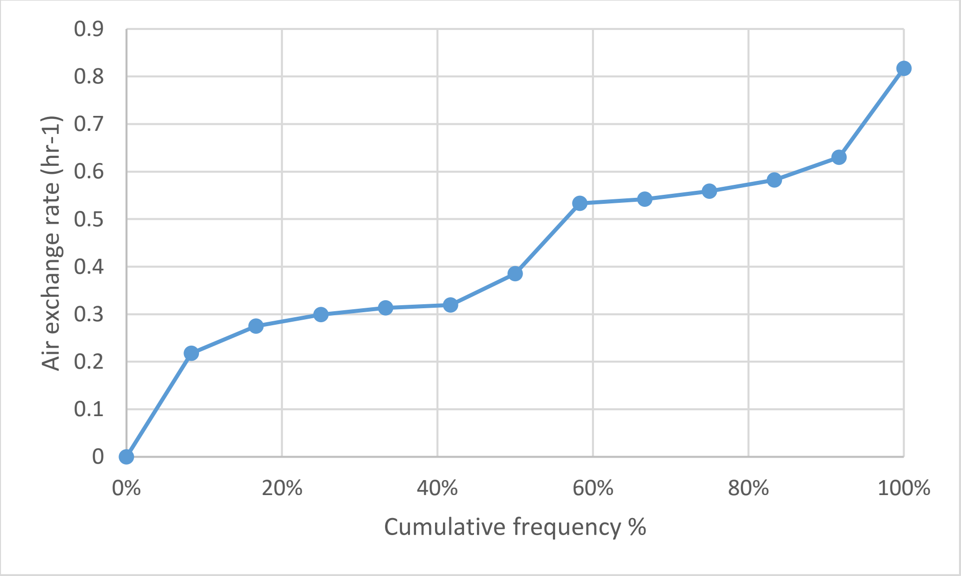

Figure 7. Cumulative frequency of air exchange rates in garages

This air exchange rate was slightly lower than the mean air exchange rates for garages reported previously in the literature. For example, Furtaw et al. (1993) reported a garage air exchange rate between 0.3 and 1.5 hr^{-1}. Graham et al. (1999) estimated garage air exchanges between 1.8 h^{-1} and 2.7 h^{-1}. Batterman et al. (2006) measured an air exchange rate of 0.77 (±0.51) in 15 garages [68]. Our data are within one standard deviation of these studies, with the exception of Graham et al. (1999).

Ozone decay rates

The mean ozone decay rate for garages, over all ozone decay tests was 2.7 (± 1.1) hr^{-1}. For two of the garages (garages 2 and 4) five and four ozone decay tests were run over two days, respectively, instead of the normal three tests in one day. In order to ensure that these extra tests did not skew the results of the mean decay rate, a mean of the means was calculated for each garage and averaged. This mean decay rate was 2.7 (± 1.1) hr^{-1}, which shows that the extra data taken on the two garages does little to skew the results. Because of this, the individual runs are all used for the remaining analysis.
The cumulative frequency plot for ozone decay rates is shown in Figure 8. This figure contains all of the garage tests and all types of garages. The median decay rate was equal to the mean, i.e., 2.7 hr^{-1}, with a first and third quartile of 2.0 and 3.4 hr^{-1}, respectively. This shows that there is very little skewness and that the data appear to be normally distributed.

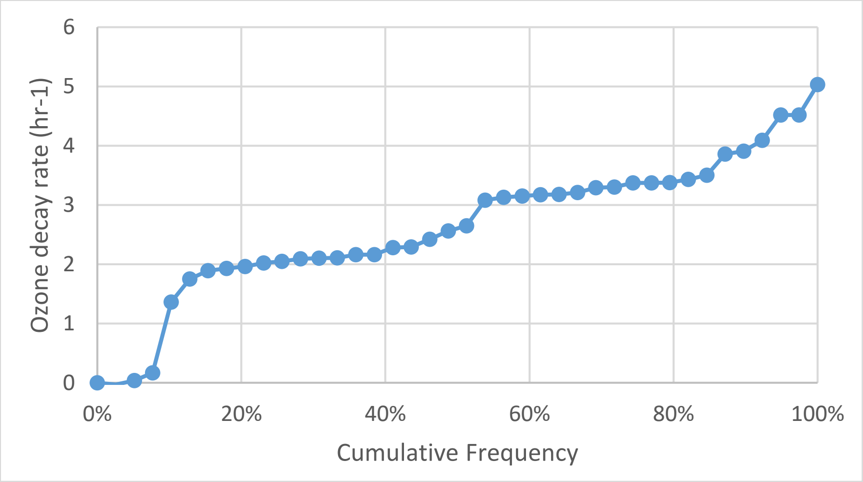

Figure 8. Cumulative Frequency ozone decay rate with individual tests

Multiple types of garages were tested in this study, both one car and two car garages, as well as attached and detached garages of each type. The differences in garage type resulted in slightly different ozone decay rates. One car garages had a higher average decay rate (3.5 ± 0.4 hr^{-1}) than did two car garages (2.5 ± 1.1 hr^{-1}). However, there was little change between average decay rates of attached (2.6 ± 1.4 hr^{-1}) and detached garages (2.9 ± 0.5 hr^{-1}). This gives good evidence that most of the air entering from the garage comes from outdoors rather than indoors. In fact, after further separating into two car attached, two car detached, one car attached and one car detached, it is evident that very little change exists between the level of attachment and the average decay rate of ozone (Figure 9).

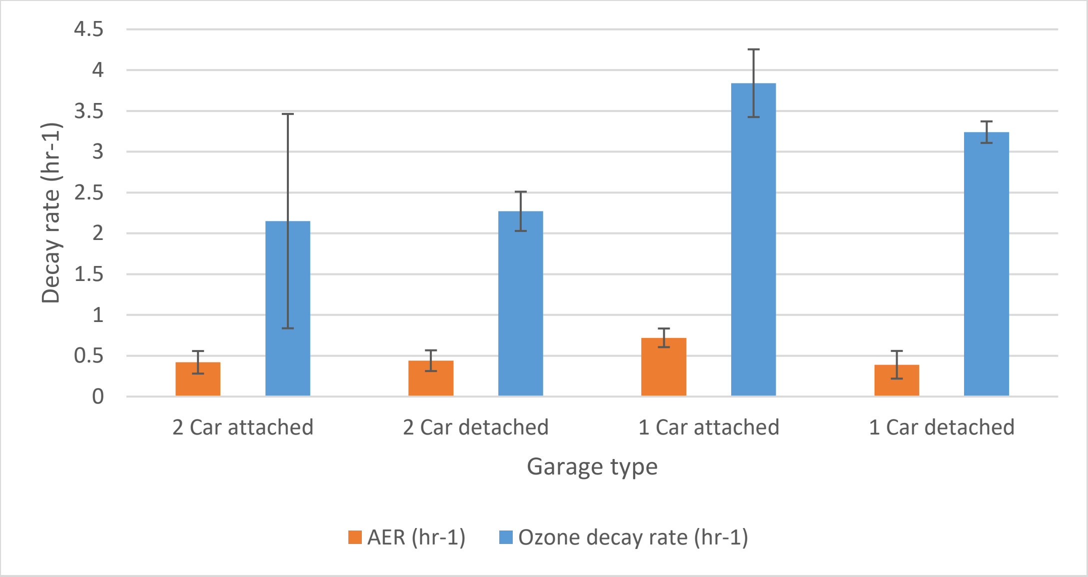

Figure 9. Decay rate for each garage type for both CO_2 and O_3

In order to confirm that the assumption that a large fraction of air is coming from outdoors as opposed to the occupied space indoors, we did the reverse analysis on the attached garages. These changes do not significantly affect the overall results that ozone decay rates don't differ greatly from the occupied space decay rates.

The ozone decay rates observed in this study are similar to decay rates found in residences [15]. Several researchers have observed that skin lipids associated with occupants in a building or aircraft are an important reactive sink for ozone [16, 37, 111]. Garages are not normally occupied for long periods of time. Therefore, the human influenced sink observed inside residences should not be as pronounced in garages. One garage of interest was garage 7. This garage had a much lower ozone decay rate than any of the other garages tested. There was no apparent reason for the low values, as much of the materials in the garage were found in the other garages. One reason that this garage could have a lower decay rate could be due to the location of the air entering the garage. Contrary to results for the other 11 garages, an assumption of all air entering the garage from the occupied spaces had a significant effect for this garage. In that case, the average decay rate was 1.7 /hr, which is much closer to the average decay rate of the other garages. If this garage was removed from the overall data set, the new decay rate would be 2.9 (±0.9). The average decay rate of two-car attached garages would be 2.6 (±1.0). So, while the individual garage has a low ozone decay rate, the result does not greatly affect the average decay rate of the overall data set.

As can be seen in Figure 9, one car garages on average had larger decay rates than two car garages. However, when deposition velocities are calculated (Figure 10), the deposition velocities are much closer. This makes sense as the deposition velocity is the ozone decay rate multiplied by the volume/area ratio. One car garages have a larger empty volume surface area/volume ratio so their ozone decay rates are much higher. By normalizing the ozone decay rates by the surface area/volume ratio, it shows that the decay rate of the garage is proportional to its empty room surface area to volume ratio. There are other variables that could be at play though. One car garages were largely used for storage. Much of the space was filled with other items and had a higher amount of clutter. Owners of two car garages were much more likely to park cars in the garage. Though they were not parked in the garage during the tests, there was still a much larger space, in two car garages that was empty. Therefore, more testing needs to be done in order to ensure that the major contribution to ozone decay rate in garages is ozone deposition onto the walls, ceilings and floors.

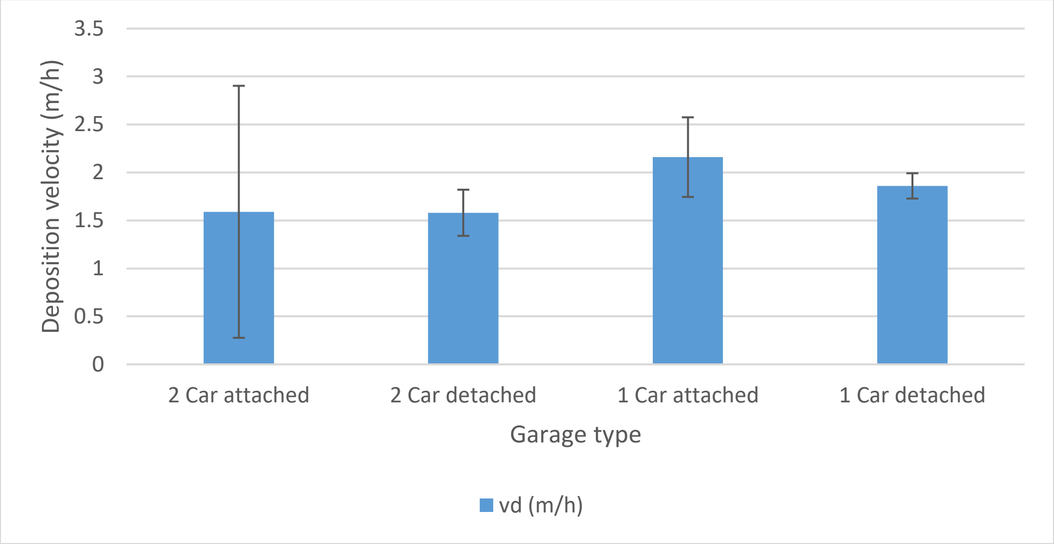

Figure 10. Deposition velocity for each garage type

Implications

The time for ozone to decay following a garage door being open affects the period of potentially elevated ozone penetration to the occupied space. Using Equation 3 with mean values of air exchange rate and ozone decay rate suggests a time of 40 minutes for ozone to decay from 90% of its outdoor concentration to 10% of its outdoor concentration.

A simple two-zone steady-state mass balance model was developed to explore the extent of ozone penetration from a garage to the occupied space. A diagram showing volumetric flow rates (Q_x), ozone decay rates (k_x), concentrations (C_x), and volumes (V_x) is provided in Figure 11. Resulting well-mixed mass balance equations are provided below as Equations 17 and 18. The flow from the outside to the occupied space was multiplied by the penetration factor reported by Stephens et al. (2012) [12].

$$0 = \frac{Q_1}{V_1} C_{out} + \frac{Q_5}{V_1} C_2 - \frac{Q_6}{V_1} C_1 - \frac{Q_2}{V_1} C_1 - k_1 C_1 \qquad \text{(Equation 17)}$$

$$0 = 0.79 * \frac{Q_3}{V_2} C_{out} + \frac{Q_2}{V_2} C_1 - \frac{Q_4}{V_2} C_2 - \frac{Q_5}{V_2} C_2 - k_2 C_2 \qquad \text{(Equation 18)}$$

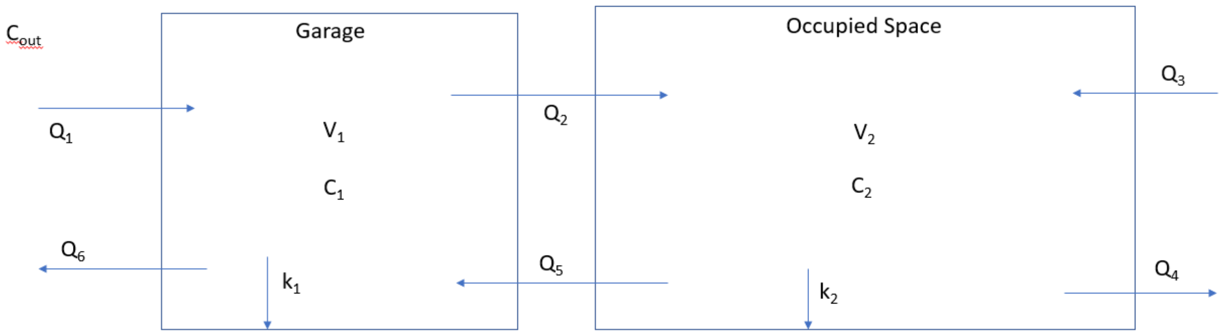

Figure 11. Two-zone model for ozone removal in a garage and occupied space

The volume of the garage (V_1) was assumed to be 100 m^3 and the occupied space (V_2) was assumed to be 600 m^3. Two scenarios where considered, one with the garage door closed (AER in the garage is the reported value) and one with the garage door open. For the open garage door case, the AER was determined using a single zone steady state model. We observed in our tests that with the garage door open, $\frac{C_{in}}{C_{out}}$ was about 0.9, which results in an air exchange rate of about 27 h^{-1}. Assuming infiltration conditions, it was assumed that air flow into the garage from the occupied space was negligible. Batterman et al. (2007) found that 6.5% of the total occupied space air exchange rate (assumed to be 0.5 h^{-1}) was due to air flow from the garage, so our value for Q_2 was taken to be 13.5 m^3h^{-1} [72]. The other flow rates were determined by using air exchange rates calculated in our field tests as well as the calculated open garage door air exchange rate of 27 h^{-1}.

A case 0 was also created as a single zone occupied space with an ozone decay rate of 2.80 hr^{-1} and a penetration factor of 0.79. The outdoor concentration was set at 80 ppb which is above the National Ambient Air Quality Standard (NAAQS) of 70 ppb (set by the EPA) [101]. This case 0 had an occupied space ozone concentration of 9.6 ppb and an indoor/ outdoor (I/O) ratio of 0.12. For case 1, with the garage door closed, the occupied space concentration was 9.1 ppb with an I/O ratio of 0.11. For case 2, with the garage door open, the occupied space concentration was 9.7 ppb with an I/O ratio of 0.12.

As can be seen, while the occupied space ozone concentration changes slightly by having the garage door open on a bad ozone day, the change is not substantial. First, the volume of the garage is much smaller than the volume of the occupied space. At a ratio of 1 to 6 in our simulation, a value which matches the average of the attached garages in our study to the average home size, assuming 10 foot ceiling heights, A large concentration of ozone in the garage results in only a small difference in the much larger occupied space. Therefore, even with the garage door open and the I/O ratio in the garage being 0.9, as it was in both the study and our simulation, the indoor ozone concentration did not change much. Secondly, our research showed that the reaction rate of the garage is very similar to the reaction rate in the occupied space as recorded by Lee et al. (1999). Because of this, much of the ozone that entered the garage reacted with surfaces, lowering the concentration that enters the occupied space. But because ozone reacts readily with surfaces and chemicals in the air, reaction byproducts of ozone could very well transfer into the occupied space. Further study of reaction byproducts of ozone with surfaces in garages, as well as chemicals stored in garages, is needed to determine if this occurs to an appreciable extent.

If, however, the garage door is open and the door connecting the garage and occupied space is open, the change in I/O ratio is much greater. For this scenario the same flow directions apply, but the flow from the garage to the occupied space is much greater (assumed to be .1 m/s multiplied by the area of a door, about 1.85 m^2 which results in a flow rate of 670 m^3/hr). This results in an indoor concentration of 37.1 ppb and an I/O of 0.46. So, by increasing the connection between the garage and the house, a scenario does exist in which the ozone concentration could increase dramatically.

Conclusion

Garage air exchange rates and the ozone decay rates were determined using 12 garages in the Austin, Texas area. The average air exchange rate for the garages with the garage door closed was 0.47 (± 0.18) h^{-1}. The average ozone decay rate in garages was determined to be 2.7 (±1.1) hr^{-1}. This is similar to the occupied space ozone decay rate calculated by Lee et al. (1999). Ozone decay rates did not change substantially from attached garages to detached garages, suggesting that most of the air entering the garage comes from outdoors. Our results also indicate that the increased surface area to volume ratio for one- car garages leads to higher ozone decay rates relative to two-car garages. Finally, simulations were run with the air exchange rate and ozone decay rate data found in this study to determine if garages could be a potentially important pathway for ozone penetration into the occupied space. When both the garage door and the door connecting that occupied space and the attached garage are closed, it is likely that ozone infiltration into the occupied space via garages will have little impact on the overall occupied space ozone concentration. However, if both the garage door and the door connecting the occupied space are both open for a long period of time, then the concentration of ozone in the occupied space will rise dramatically. More research is needed to identify and quantify reaction byproducts of ozone in garages and whether such products are cause for concern in the occupied space.

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