8-30-2015

Modeling volatile organic compound emission from materials used in passenger vehicle interiors

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Modeling Volatile Organic Compound Emission from Materials Used in Passenger Vehicle Interiors

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Thesis

Submitted to the Department of Chemistry

Eastern Michigan University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

in

Chemistry

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August 30, 2015

Ypsilanti, Michigan

DEDICATION

I would like to dedicate this thesis to my parents, Doug and Joy Canaday. Their hard work has not only given me the opportunity to pursue a graduate degree, but it has also been an inspiration for me over the years. I hope this thesis makes them as proud of me as I am proud to call myself their son. I would also like to dedicate this thesis to my grandfather, David McCarthy, who instilled his curiosity for learning science and technology to me as a young boy. I am forever grateful Pops. I would also like to dedicate this thesis to my brothers, Corey and Ryan Canaday. They have always been there for me during difficult and stressful times. More than any brother could ask for. I would also like to dedicate this thesis to my girlfriend, Alexandra Phelps. She did everything in her power to make these last two years as easy and stress-free as possible for me. Her support was unending, even when it was at the expense of her free time. Finally, I would like to dedicate this thesis to the rest of my family and friends. Your love and support does not go unnoticed. Without you, this wouldn't have been possible.

ACKNOWLEDGMENTS

I would like to thank my committee chair, Dr. Gavin Edwards, for giving me the opportunity to work with him these past two years. The support and guidance he has given me since my first day at Eastern Michigan University will forever be appreciated. I would also like to thank my thesis committee members, Dr. Heather Holmes and Dr. Andrew Ross. Their positive feedback and support during this project has been more than I could ask for. I would also like to thank the Eastern Michigan University Chemistry Department. The people of this department are nothing but outstanding individuals. Their eagerness to teach is passed on to their students as eagerness to learn. I learned so much during my two short years here at Eastern Michigan University, and I am forever grateful for this school and department. I would like to thank USCAR for passing on their vast knowledge of vehicle interior air quality during our meetings. I learned so much from that great group of people. I would also like to thank the folks at Virginia Tech who have generously shared their VOC emission data with us. It was greatly appreciated. Lastly, I would like to thank the Atmospheric Chemistry group, past and present. The people of this group were nothing but helpful during my times of need, and I am very thankful.

ABSTRACT

Travel is an everyday necessity for many people, making the environment of a passenger vehicle a place where they spend a significant amount of time. Previous studies have indicated that more than 100 volatile organic compounds (VOCs) are present in ambient air within the cabins of new cars, some of which have been found to have adverse health effects. While previous VOC models have been produced, there is still uncertainty in these models with respect to changing variables such as temperature, sunlight, and the presence of multiple VOCs. An accurate and reliable model, capable of determining the concentration of different VOCs in a car cabin as a function of time, is the focus of this research. Using data from VOC determinations in environmental test chambers emitted from polymethylpentene (PMP) films, and previous chamber modeling studies, models for VOC air concentration were produced. These models were programmed using Python, an open-source programming language that can easily be used for scientific studies. Current models give accurate estimations for chambers with and without airflow. An equation to predict the surface temperature, based on incident solar irradiance, of materials was used to adjust the VOC emission models to account for sunlight. This theoretical adjustment, while still needing to be tested, provides a good foundation for accounting for sunlight in the interior of vehicles. Overall, this work builds a better understanding of vehicle indoor air quality (VIAQ) and exposes the difficulties of modeling the complicated interior environments of passenger vehicles.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

1.1 The role of volatile organic compounds in vehicle interior air quality

The air quality of the indoor environment of an automobile should be considered important as millions of people rely on an automobile for their everyday travel. The average American will spend 1.5 hours a day in their car.[1] The interior of a vehicle is a relatively small, confined space that has the potential to host a variety of different contaminants from numerous sources. One of these sources is the vehicle interior itself. The off-gassing of volatile organic compounds (VOCs) from materials such as paints, plastics, adhesives, carpets, and rubbers, give the vehicle the "new car smell."[2] VOCs play a major role in Vehicle Interior Air Quality (VIAQ).

VOCs are classified into three different groups. Very volatile organic compounds (VVOCs) have boiling points less than 50 ºC.[2] Volatile organic compounds have boiling points between 50 ºC and 260 ºC.[2] Lastly, semi volatile organic compounds (SVOCs) have boiling points between 260 ºC and 400 ºC.[2] VOCs have been shown to cause "sick building syndrome" in newly constructed buildings.[2] Symptoms for sick building syndrome include: nausea, dizziness, coughing, eye/respiratory irritations, and headache.[3] A few VOCs are classified as carcinogens such as benzene and formaldehyde.[4] Regulations for these VOCs for the interior air of vehicles are shown in Table 1. The Japanese Auto Manufacturers Associations (JAMA) has set limits for Japan.[5] The International Organization for Standardization has the test method ISO 12219 for the interior air of road vehicles.[5] This test method contains no limits for interior vehicle air.[5] This forces companies that use the method to create their own set of standards.

There is a proposed total volatile organic compound (TVOC) concentration limit by Seifert of 3000 μg/m^3.[6]

Table 1.1 - VOC limits in μg/m3 for the interior air of road vehicles

Compound	Japan	Korea	China	ISO 12219
Formaldehyde	100	210	100	--
Acetaldehyde	48	--	50	--
Acrolein	--	40	50	--
Benzene	--	30	110	--
Toluene	260	1000	1100	--
Ethylbenzene	3800	1000	1500	--
Xylenes	870	870	1500	--
Styrene	220	220	260	--
Tetradecane	330	--	--	--
p-Dichlorobenzene	240	--	--	--
di-n-Butylphthalate	220	--	--	--
di-n-Hexlyphthalate	330	--	--	--

Owing to the potential human health impacts caused by the emission of VOCs from the materials used to make up the interior of cars, knowing their concentrations is important. Modeling these emissions would provide valuable information to automakers and consumers by giving them confidence that the air quality of their vehicles is acceptable. Experimentation using instrumentation is expensive and can be difficult to reproduce, providing good reasoning for modeling.[8] Previous work has been done in both identifying which VOCs are being emitted into the interior air of cars, and modeling VOC emission from building materials.

1.2 Review of the literature

In order to know what specific compounds to model, it is important to look at previous studies characterizing contaminants in the interior air of vehicles. By knowing what compounds are generally in the largest concentrations, one can focus on modeling those compounds with higher priority. This review intends to give one an idea of the concentrations of VOCs present in vehicle interior air, how current emission models are estimating concentrations of VOCs in the air after being off-gassed by building materials, and how some of modeling parameters are being estimated in the absence of experimental work. Studies have been done to both identify and quantify the VOCs present in vehicle interior air for multiple cars of different makes and models.[1,2] The effects of temperature and sunlight on these VOC concentrations have also been looked at.[6,7,16,18] A reference material for the emission of toluene has also been produced and certified by the National Institute of Standards and Technology (NIST).[8,15,16] Models predicting the emission of VOCs from materials have been created.[9-14] There have been models created to predict VOC emission under airflow.[9-12] There are also models that predict emissions under the absence of airflow.[11,17] Changes to the initial VOC concentration in the materials, in order to increase the accuracy of a model, have been done.[13,14] Also, some parameters, needed for modeling, can be calculated in a variety of different ways, without the need for experimental determinations.[19.20]

Yoshida *et al.*[2] looked at the VOCs in the interior air of 101 different vehicles. The vehicles were numerous makes and models between new and three years old.[2] They identified 70 different aliphatic hydrocarbons, 49 different aromatic hydrocarbons, 32 different esters, 10 different aldehydes/ketones, and 60 other compounds.[2] Eighteen of the 60 other compounds were alcohols/glycols.[2] They also reported TVOC concentrations for the interior air of the 101

vehicles they tested between 136 μg/m^3 and 3968 μg/m^3.[2] Some of their VOC findings include 7.5-61 μg/m^3 for formaldehyde, 0.61-266 μg/m^3 for methylethylketone, 12-356 μg/m^3 for toluene, 2.2-538 μg/m^3 1-butanol, 0-1025 μg/m^3 for 2,2'-azobis(isobutyronitrile), and 11-459 μg/m^3 for n-hexane.[2] Data reported by Yoshida also showed levels of 2,2'-azobis(isobutyronitrile), an important precursor to tetramethylsuccinonitrile, a strong convulsant.[2]

Chien[1] tested five different brands of vehicles. Three of the brands were labeled as domestic vehicles (imported brands, but assembled in Taiwan), and two were labeled as imported brands assembled in different parts of Europe and imported in to Taiwan.[1] Due to this, the time since assembly was different for the domestic and imported vehicles.[1] The domestic vehicles were assembled no later than three months before the study, while the imported vehicles were assembled over four months before the study took place.[1] The number of compounds that were measured was restricted to twelve.[1] The authors also attempted to identify some of the VOC sources within the vehicle.[1] Results showed 12 different VOCs emitted from the trim of the test vehicle, six from the grease, two from the seat, three from the door panel, four from the roof lining, five from the carpet, and 14 from the rear panel.[1] Imported vehicles all gave results for VOC concentrations that were less than those for the domestics.[1] This was most likely due to the longer time between assembly and testing. Average VOC concentrations for individual VOCs ranged from below the detection limit to almost 8000 μg/m^3.[1]

The effects of temperature can be seen in the results of Fedoruk and Kerger.[6] TVOC concentrations were found to be 400-800 μg/m^3 in a static vehicle with an internal temperature at 80 ºF.[6] Under even warmer temperatures (up to 145 ºF), the internal TVOC air concentrations rose to be 1900-1500 μg/m^3.[6] These same TVOC concentrations were much lower during

operation of the car at 50-160 μg/m^3, when air conditioning was running or the windows were down.[6] The most predominant VOCs that were identified were styrene, toluene, and 8- and 12-carbon compounds.[6]

VOC concentrations for a new vehicle and a used vehicle, three years in age, were also quantified when vehicles were exposed to 14 kilowatt light bulbs.[7] The bulbs were used to simulate solar influences on vehicle interiors.[7] The main compounds found in samples from the new car were *ortho*-, *meta*-, and *para*-xylene, dodecane, and tridecane.[7] All of these compounds had concentrations above 500 μg/m^3.[7] VOCs found in the air of the new vehicle were about nine times higher than those found in the used vehicle.[6] The new vehicle had a total VOC concentration of 10900 μg/m^3 while the older vehicle had a TVOC of 1200 μg/m^3.[7] This can be compared to other studies where no radiation exposure took place to give an idea of how sunlight intensifies VOC emission into vehicle interior air.

Cox *et al*.[8] developed a reference material for the emission of toluene for the direct application to assess interior air quality in various enclosed spaces. The reference material, a polymethyl pentene (PMP) film, was made to help minimize the interlaboratory variation that is associated with VOC emission testing of building materials.[8] Such an interlaboratory experiment showed that the toluene emission profile from the material was within the quoted precision across all laboratories.[15] Variations in humidity were found to not play a significant factor in toluene emission from this reference material, but toluene emission was found to increase as temperature increased.[16] By knowing the standard emission rate and how this changes as a function of parameters such as time, humidity, temperature, and light, any unexpected results or statistical outliers sometimes identified between both experimental runs and laboratories can be eliminated. The authors suggested data from a reference material could prove to be very useful

when developing a VOC emission model. Since the PMP film always produces the same emission profile, it provides repeatable, reliable data to fit a model to. Thus, it verifies that a model is working correctly and should work when modeling other compounds in the same testing environment.

Literature shows there have been models created to estimate the emission of VOCs from building materials. These models concentrate on the indoor building environment and provide a good foundation from which a vehicle environment model can be established. Little *et al*.[9] created a very simple model that accurately predicted VOC emission from new carpets while focusing on properties of diffusion that had been overlooked in previous models. Diffusion coefficients tend to decrease with increasing molecular weight (MW) of the VOC of interest, while the material/air partition coefficient decreases with increasing vapor pressure.[9] Using the specific parameters — diffusion coefficient, partition coefficient, initial VOC concentration, material surface area, material thickness, air volume, and air flow rate — the model made a good fit to experimental emission data obtained from an environmental test chamber with constant airflow.[9] The simplicity of the model created by Little *et al*.[9] makes it an ideal model to use as the framework for the VIAQ model discussed in this thesis. Identifying important parameters such as the diffusion coefficient, partition coefficient, and initial VOC concentration in the material, provides insight into what drives diffusion from building materials.

Some VOC emission modeling has incorporated the convective mass transfer coefficient to account for movement of VOCs over the surface of dry building materials experiencing convection currents.[10,12] It was also found that the rate of VOC emission increased with increasing air velocity over building materials, and that this increase was dependent upon the diffusion coefficient of the material.[10] This method could be applicable to VIAQ in situations

where air-conditioning or open windows are allowing air to flow over interior materials. While adding the mass transfer coefficient parameter to an emission model helps to account for convection over the surface of a material, it takes away some of the simplicity that can be seen in models such as the one by Little *et al*. and also adds another parameter that must be determined before running the model.

Another model capable of predicting four different scenarios with respect to VOCs and building materials was described by Xiong *et al*.[11] There, authors were able to create a model that could be easily adjusted to adapt to VOC emission with and without airflow and account for sorption of the VOC from the air into the materials. Therefore, this model provides much more versatility than other models. Sorption data was then used to estimate the diffusion coefficient and partition coefficient that could be used for modeling in both environmental test chambers with and without airflow.[11] This study provides support for the idea that these materials can act as "sinks" for VOCs in the air and emit the VOCs at a later time.[11]

One model adjusts the initial VOC concentration in the material based on the age it was manufactured.[13] Those materials that are new (*i.e*. age = 0) were considered to have a uniform distribution of VOC concentration throughout them, while those with age > 0 were given a distribution that was not uniform.[13] The age of the material was determined by observing the time it took a material with uniform VOC distribution to reach the initial VOC distribution of the material being studied.[13] The results showed that the age of the material greatly affected the VOC air concentrations during the materials initial emission period, but this large difference minimized as these materials continued to emit VOCs over longer time periods.[13] Knowing how age influences emission, a vehicle model could adjust for the time between manufacturing and when the vehicle is first driven.

The initial concentration of VOC in the material was also adjusted in a different way in another model. Crawford and Lungu[14] determined the initial concentration of emittable VOCs within the material. This was done to adjust for the amount of VOCs that get trapped in the solid material.[14] Complete diffusion of a VOC out of a material is dependent upon aspects of the material such as density and porosity.[14] By replacing the material's initial VOC concentration with the initial emittable VOC concentration in their model, results for the VOC concentration in the air correlated much better for times greater than 48 hours.[14] Using the amount of VOC that can be emitted by a material within a vehicle, may help to give better predictions when modeling.

In order to model VOC emission, certain parameters are needed by the model and therefore must be known. Three parameters — the initial VOC concentration in the material (C_0), the diffusion coefficient (D), and the material-air partition coefficient (K) — can be experimentally determined, but this is labor intensive and time consuming.[19] Ye *et al.*[19] were able to estimate initial VOC material concentrations and diffusion coefficients based on previous ventilated chamber tests. These were calculated using piecewise cubic "Hermite interpolating polynomial" (PCHIP).[19] Their results showed good correlations between modeled VOC air concentrations using calculated initial VOC material concentrations and diffusion coefficients, and experimental data.[19] Not having to experimentally determine these parameters will save time when having to model emissions from multiple sources from within a vehicle. Similarly, Li[20] was also able to calculate the diffusion coefficient and initial VOC material concentration using previous chamber data. Their method only needs two VOC air concentrations to calculate both parameters.[20] The VOC air concentrations modeled using these predicted parameters produced values similar to those from the experiment, especially at later times.[20]

1.3 Conclusions

While previous models provide viable ways to model VOC emission from building materials, they have not been used to model emissions from materials within the cabin of a passenger vehicle. These models need fine-tuning in order to be more accurate for the complicated environment of the automobile interior. Complications such as the effect of solar radiation on VOC emissions need to be addressed. Modeling the diffusion of VOCs from the vehicle interior air to the external ambient air while the windows are down should also be considered. Knowing the rate of loss of VOCs out of an open window would allow for one to determine when the air is safe.

1.4 Goal of project

The purpose of this project is to further develop an accurate and reliable model capable of predicting the VOC concentrations in the air inside of a vehicle after the VOCs have been emitted from the materials that make up the interior of the car. Using toluene emission data from PMP films, provided by Steven Cox and co-workers from Virginia Tech University, and previous emission data from other studies, models have been created using Python, an open source programming language. Adjustments to temperature-dependent parameters for these models have produced theories for ways to account for the effects of solar radiation on VOC emission.

1.5 Objectives

1. To produce a working model for the emission of VOCs from materials used in passenger vehicle interiors.
2. To gain a better understanding of the influences of parameter changes on emission profiles generated by the model.
3. To adjust the model to account for vehicle-specific conditions such as solar radiation and diffusion through an open window.
4. To compare the model to *in-situ* data taken from the interior air of the cars and make further corrections to the model to improve accuracy.

CHAPTER 2: BACKGROUND

2.1 What is Python?

Python is a programming language created in the late 1980s by Guido van Rossum.[21] This language is based off of other languages such as C++ and C.[21] Python is open-source and has the support of numerous downloadable module and packages, including NumPy and Matplotlib. NumPy is a package that adds features for multi-dimensional arrays and simplifies complicated mathematics on these arrays.[22] Another package, Matplotlib, allows both 2D and 3D plotting of large data sets with as few lines of code as possible.[22] Python is easy to read as it uses indentations to create blocks of code instead of text or keywords.[21] This creates a lot less clutter in the code. The most important feature of Python, for our purposes, is that it is free. While Python has many advantages, it also comes with some disadvantages. One disadvantage is that Python code runs slower than code written in Visual Basic or C++.[23] Other disadvantages include a fewer number of scientific packages compared to Fortran, and the absence of literature about using Python compared to than other languages.[23]

2.2 Measuring volatile organic compound emission from materials

In order to model VOC emissions from materials within a car, air VOC concentration data must be obtained experimentally. If emission from a specific material is desired, the material is placed in an Environmental Test Chamber (ETC) to simulate an enclosed space.[8,15,16,24,] This type of experiment is used frequently in model development as it simplifies variables for predictions.[9-14,25] Due to the environment of a car being much more complicated, *in-situ* vehicle testing requires sampling using a suction pump.[1,2,4,6,26] This section will explain the

multiple ways in which these data are collected and provide reasoning why modeling VOC emissions within vehicles is the better option for the automotive industry when trying to improve VIAQ.

ETCs provide a simple environment to model VOC emissions. These chambers are constructed of stainless steel and have two openings for incoming and outgoing air, allowing for air exchange within chamber.[8,24] The volume of air in the chamber and the air flow rate are therefore known parameters, and other parameters such as temperature and humidity can be held constant. A material with known dimensions is placed in the chamber. Outgoing air from the chamber is collected in thermal desorption tubes such as Tenax® TA[24,28], Carbotrap®[,27], or charcoal sorbent tubes.[14] Tenax® TA tubes are considered the best for sampling air VOCs and are therefore used the most frequently.[29] The trapped VOCs are desorbed and analyzed using a thermal desorption-gas chromatograph/mass spectrometer or flame ionization detector (TD-GC/MS or FID).[1,28] Volatile aldehydes, such as formaldehyde, are derivatized when collected in a DNPH (2,4-dinitrophenylhydrazone) cartridge, and the derivatized aldehydes are extracted with acetonitrile and analyzed using high-performance liquid chromatography (HPLC).[28,30] Standard chamber test methods such as one from the American Society for Testing and Materials (ASTM D5116)[8,16,24,27], and California Department of Public Health (CDPH)[15] are frequently followed when determining VOCs in test chamber air. Taking *in-situ* vehicle air samples requires using portable pumps to pull interior air through thermal desorption tubes such as those mentioned above.[1] Varying methods for determining VOC emission from individual vehicle interior components can be seen across the automotive industry. The Society of Automotive Engineering for Japan (JASO) has implemented a method using a sampling bag (JASO M902) as an industry standard in Japan.[28] This method uses a plastic bag instead of an ETC to define an air

volume. Harmonization of these methods would benefit the automotive industry immensely by eliminating competing methodologies.

2.3 Modeling parameters

There are a select number of parameters that show up frequently when modeling VOC emission from materials. A list of these parameters and their units are in Table 2.1.

Table 2.1 - Common modeling parameters

Parameter	Units
Material Thickness	Meter
Material Surface Area	$Meter^2$
Air Volume	$Meter^3$
Air Flow Rate	$Meter^3$ / Second
Diffusion Coefficient	$Meter^2$ / Second
Material/Air Partition Coefficient	Unitless
Initial Material VOC Concentration	Microgram / $Meter^3$
Convective Mass Transfer Coefficient	Meter / Second

Parameters such as material thickness, material surface area, air volume, and air flow rate, can be directly measured from either the environmental test chamber being used, or the material being placed in the chamber.[31] The diffusion coefficient, partition coefficient, initial material VOC concentration, and convective mass transfer coefficient are estimated or measured using methods that require more effort.[31] The accuracy of these parameters greatly affects the accuracy of the predictions made by the model.[31] Where some of these parameters come from can be visualized in Figure 2.1.

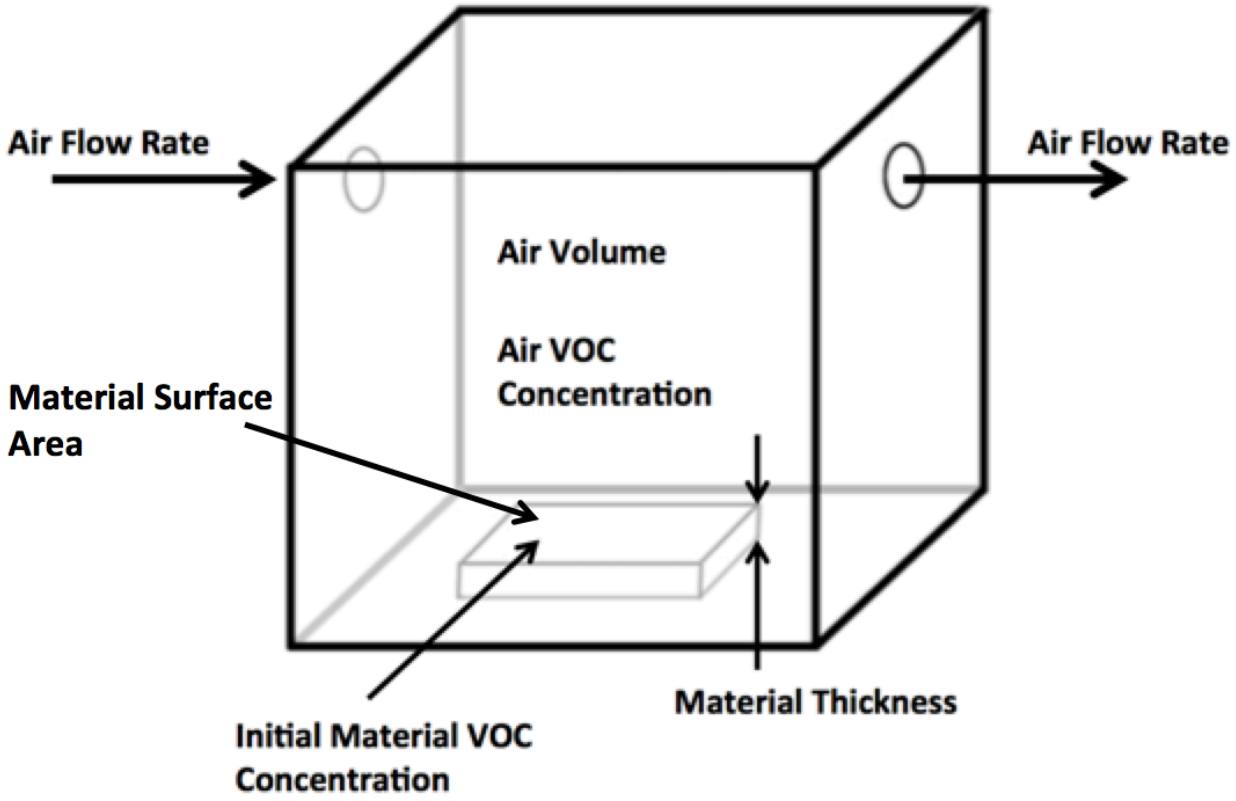


Figure 2.1 - Schematic of test chamber showing some common modeling parameters

Due to diffusion through the material playing a large role in how these VOCs are emitted, having an accurate diffusion coefficient is important. Fick's laws describe the diffusion coefficient where Fick's second law states

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is the concentration of the VOC in the material, t is time, x is distance from the base of the material, and D is the diffusion coefficient.[24,32] The diffusion coefficient is dependent on temperature, pressure, and the size of the VOC diffusion through the material; it is also dependent on the type of material, and VOC concentration.[32,10] The partition coefficient (K), for

our purposes, corresponds to the ratio of the concentration of VOC found in the air and the concentration found in the material at equilibrium.[31] Both the diffusion coefficient and partition coefficient can be determined using a microbalance.[31] The material is placed in a chamber, and a sorption curve is generated using a carrier gas with a known concentration of VOC and a microbalance to weigh the VOC being absorbed into the material or to the material's surface.[31] Clean carrier gas is then sent through the chamber, and a desorption curve is generated. The data generated by these curves can be used to calculate both *D* and *K*.[31] Another experiment to determine both *D* and *K* includes using two chambers.[31] For this experiment, the material has no VOCs within and is used to separate a chamber with a high concentration of VOCs from a VOC-free chamber.[31] The VOCs then diffuse through the material into the VOC-free chamber and the data obtained from this experiment can be used to determine the diffusion and partition coefficients.[31] There are numerous other ways to experimentally determine and estimate *D* and *K* in the literature.[19,20,31]

When moving air passes over a surface, a small layer of air becomes laminar, creating a boundary layer.[10,33] Convective mass transfer involves the movement of materials from a boundary surface and a moving fluid, in our case moving air.[33] Previous studies have shown that the convective mass transfer coefficient only has a significant effect on initial periods of emission.[31] Estimations of the convective mass transfer coefficient are done using the Sherwood (*Sh*), Reynolds (*Re*), and Schmidt (*Sc*) numbers.[10] This type of estimation requires knowing more parameters such as the kinematic viscosity of air and the mean air velocity.[10] Accounting for convective mass transfer in a model requires more work as described later.

CHAPTER 3: EXPERIMENTAL

3.1 Building a model in Python using previous literature

The first step in the project was to build a working model in Python. Python version 2.7.6 was used through the Enthought Canopy environment (version 1.4.0).[35] Many models from previous studies described in the introduction section were evaluated to assess their stability in this work. Due to the simplicity of the model created by Little *et al.*[9], this model was to be the backbone of our research, with gradual improvements and refinements discussed later. The Little *et al.*[9] model has the following governing equations:

$$C(x,t) = 2C_0 \sum_{n=1}^{\infty} \left\{ \frac{\exp(-Dq_n^2 t)\,(h - kq_n^2)\cos(q_n x)}{[L(h - kq_n^2)^2 + q_n^2(L + k) + h]\cos(q_n L)} \right\} \quad (2)$$

$$h = \frac{(Q/A)}{(D \cdot K_v)} \quad (3)$$

$$k = \frac{(V/A)}{K_v} \quad (4)$$

where C is the VOC concentration in the material, C_0 is the initial VOC concentration in the material, D is the diffusion coefficient, x is the linear distance, L is the material thickness, Q air flow rate, A surface area of material, V is the air volume, and K_v is the partition coefficient. The q_n terms are the positive roots of

$$q\tan(qL) = h - kq^2. \quad (5)$$

The VOC concentration in the material (C) from equation 2 can then be converted to the VOC air concentration (y) using the following:

$$y = \frac{C|_{x=L}}{K_v}. \quad (6)$$

The previous equations were programmed into Python. The positive roots were found using the bisection method.[24] The bisection method narrows in on a root by successively cutting the interval that contains the root in half.[34] The model was designed to produce a plot of VOC air concentration vs. time using *matplotlib*, a Python add-on that allows for experimental data points to be added for convenient model/experimental comparisons. A comma-separated values (CSV) file was also produced upon running the model. These files stored the parameters used and each data point produced by the model. Parameters used for this model can be seen in Table 3.1.

Table 3.1 - Parameters used in Python model

Parameter	Units
Material Length	Meter
Material Width	Meter
Material Thickness	Meter
Material Surface Area	$Meter^2$
Air Volume	$Meter^3$
Air Flow Rate	$Meter^3$ / Second
Diffusion Coefficient	$Meter^2$ / Second
Material/Air Partition Coefficient	Unitless
Initial Material VOC Concentration	Microgram / $Meter^3$
Number of Time Points	Unitless
Time Between Each Data Point	Seconds

3.2 Verifying the model

The model was verified to be working correctly and producing accurate results. Many different sets of parameters were used from the literature, and initial visual comparisons were made between the model results and the results from previous work. Most of the data used for this verification were obtained from our collaborators at Virginia Tech.[16,24,36] Experimental parameters from *Little et al.* were used to model the emission of formaldehyde from

polycarbonate films.[36] Samples VT14-B2FA1 and VT15-B3FA2 were used, and their experimental parameters can be seen in Table 3.2.

Table 3.2 - Experimental parameters for samples VT14-B2FA1 and VT15-B3FA2[36]

Parameter	VT14-B2FA1[a]	VT15-B3FA2[a]
Material Length (m)	0.10	0.10
Material Width (m)	0.10	0.10
Material Thickness (m)	$2.5x10^{-4}$	$2.5x10^{-4}$
Air Volume (m^3)	0.053	0.053
Air Flow Rate (m^3/s)	$1.472x10^{-5}$	$1.472x10^{-5}$
Diffusion Coefficient (m^2/s)	$1.9x10^{-13}$	$1.9x10^{-13}$
Material/Air Partition Coefficient	230	230
Initial Material VOC Concentration ($\mu g/m^3$)	$1.6x10^{8}$	$1.7x10^{8}$
Experiment Duration (h)	144	144

[a]obtained from Little *et al.*[36]

Experimental results from Little *et al.*[36] were plotted against model results for comparison.

Raw data used in Liu *et al.*[16], provided by Virginia Tech, that contained toluene air concentrations after being emitted from PMP films, were also used to verify the model was working correctly. Toluene emission had been obtained at 10 ºC, 23 ºC, and 30 ºC, and the experimental parameters were used to model these different emissions.[16] These parameters can be found in Table 3.3.

Table 3.3 - Experimental parameters for toluene emission from PMP films at different temperatures[16]

Parameter	10 ºC [b]	23 ºC [b]	30 ºC [b]
Material Length (m)	0.06	0.06	0.06
Material Width (m)	0.06	0.06	0.06
Material Thickness (m)	$2.54x10^{-4}$	$2.54x10^{-4}$	$2.54x10^{-4}$
Air Volume (m^3)	0.051	0.051	0.051
Air Flow Rate (m^3/s)	$1.42x10^{-5}$	$1.42x10^{-5}$	$1.42x10^{-5}$
Diffusion Coefficient (m^2/s)	$1.00x10^{-14}$	$3.30x10^{-14}$	$6.40x10^{-14}$
Material/Air Partition Coefficient	1150	500	369
Initial Material VOC Concentration ($\mu g/m^3$)	$7.80x10^{8}$	$7.80x10^{8}$	$7.80x10^{8}$
Experiment Duration (h)	72.5	72.5	72.5

[b]obtained from Liu *et al.*[16]

Modeled results were then compared to experimental results.

3.3 The effects of parameter changes on the model

To obtain a better understanding of how each parameter changes the emission profile created by the model, a single parameter was changed by some factor while holding the other parameters constant. This was repeated for each one of the parameters. The values used when held constant can be seen in Table 3.4 along with the values each parameter was changed to in parentheses.

Table 3.4 - Values for parameter variations

Parameter	Constant Values (Changed Values)
Material Length (m)	0.02
Material Width (m)	0.02
Material Thickness (m)	2.54×10^{-4} (1.0×10^{-5}, 1.0×10^{-4}, 5.0×10^{-4}, 1.0×10^{-3}, 5.0×10^{-3}, 0.01, 0.05, 0.1)
Air Volume (m^3)	4.45×10^{-5} (1.0×10^{-4}, 1.0×10^{-3}, 0.01, 0.1, 1)
Air Flow Rate (m^3/s)	1.67×10^{-6} (1.0×10^{-10}, 10^{-9}, 10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4})
Diffusion Coefficient (m^2/s)	9.178×10^{-13} (1.0×10^{-16}, 10^{-15}, 10^{-14}, 10^{-13}, 10^{-12}, 10^{-11})
Material/Air Partition Coefficient	61.4397 (1.0×10^{-4}, 1.0×10^{-3}, 0.01, 0.1)
Initial Material VOC Concentration ($\mu g/m^3$)	1.446×10^{8}

Model results for each individual parameter were plotted on the same chart in order to compare changes.

3.4 Sunlight and emission

Sunlight has a significant effect on the interior temperature of a vehicle.[37] The enclosed space making up the inside of a car can behave like a greenhouse.[37] Previous work has showed that temperature plays a role on VOC emission.[38] Being able to predict the temperature of the surface of materials in vehicles will enable the adjustment of diffusion and partition coefficients, since they are temperature dependent. This would allow changes in the VOC emission model to

adjust for temperature changes caused by solar radiation. A simple solar heating equation developed by Sparrow[39] and later used by Thibadeau[40] allows for one to predict the temperature of a surface of an object. This equation can be seen below:

$$TSR \times (1 - SR) - \left(\frac{(ST - AT)}{\frac{1}{TCG \times SA}} \right) - EM \times \sigma \times SA \times (ST^4 - 255.56^4) = 0 \quad (7)$$

where *SA* is surface area (m^2) of the material, *SR* is surface reflectance of the material, *ST* is surface temperature (K) of the material, *TCG* is the thermal conductive give (3.975 W/m^2K for still air, 11.357 W/m^2K for wind), *EM* is the emissivity of the material, σ is the Stefan-Boltzmann constant ($5.67x10^{-8}$ W/m^2K^4), and *TSR* is total solar radiation (W/m^2), which is calculated using the following equation:

$$TSR = (DS \times 0.7 \times SA) + (94.64 \times SA). \quad (8)$$

Average monthly direct solar irradiances (*DS*) were obtained from Kandilli and Ulgen[41] and put into equation 8. The calculated *TSR* was put into equation 7, and a surface temperature was calculated using Microsoft Excel Solver, similarly to what had been done by Thibadeau[40].

Due to both the diffusion coefficient and partition coefficient being temperature dependent, these two parameters need to be calculated whenever there is a change in temperature. Using the data from Liu *et al.*[16] in Table 3.3, both partition and diffusion coefficients were obtained for each calculated surface temperature. Diffusion coefficients were calculated using the following equation:

$$lnD = lnD_0 - \frac{Q_d}{R}\left(\frac{1}{T}\right) \quad (9)$$

where *D* is the diffusion coefficient (m^2/s), D_0 is the temperature-independent pre-exponential (m^2/s), Q_d is the activation energy for diffusion (J/mol), *R* is the gas constant (8.314 J/molK), and

T is temperature (K).[42] An Arrhenius plot was used to calculate diffusion coefficients at higher temperatures after plotting the temperatures and diffusion coefficients from Table 3.3.[42] A power-fit line was extrapolated to obtain partition coefficients at higher temperatures. These two parameters, calculated for each month of the year, were then used while filling in the remaining parameters for the model from Table 3.3. The model results for each month were plotted on the same chart for comparisons.

3.5 *In-situ* dashboard surface temperature predictions

To see if adjustments would need to be made to the surface temperature equation, surface temperatures of the dashboard of a 2000 Honda Civic were taken using a non-contact digital laser infrared thermometer (Etekcity Lasergrip 774) that was previously calibrated with an ice water bath. The car was facing the south on a clear day in Ann Arbor Michigan on March 12, 2015 to prevent any shadows. The internal temperature of the vehicle was taken using a temperature sensor attached to a battery-powered Arduino board that was placed on the passenger seat. Solar radiation was recorded from a nearby weather station (KMIBELLE6) using data available from the website weatherunderground.com.[43] The passenger door was opened and the temperature of the dashboard portion (outlined in red in Figure 3.1) was taken every 30 minutes, starting at 11:30 AM. A total of six readings were taken. The resulting values were run in Microsoft Excel Solver to obtain a predicted surface temperature. This predicted surface temperature was then compared to the measured surface temperature. The percent transmittance of solar radiation through the window was then changed from 100 %T to 50 %T and 75 %T, and the surface temperature was re-calculated.

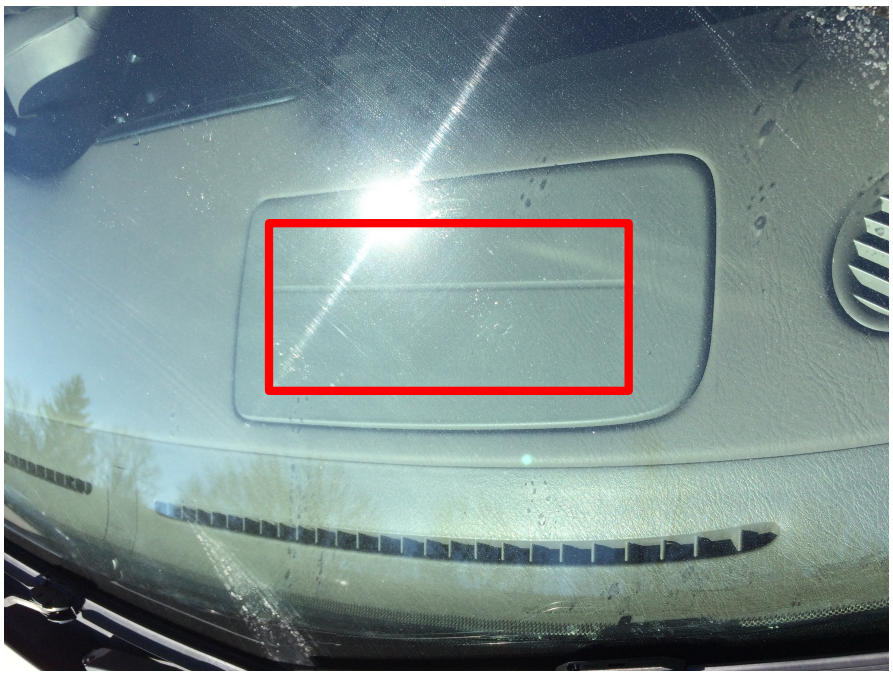


Figure 3.1 - Portion of dashboard used for surface temperature predictions

CHAPTER 4: RESULTS AND DISCUSSION

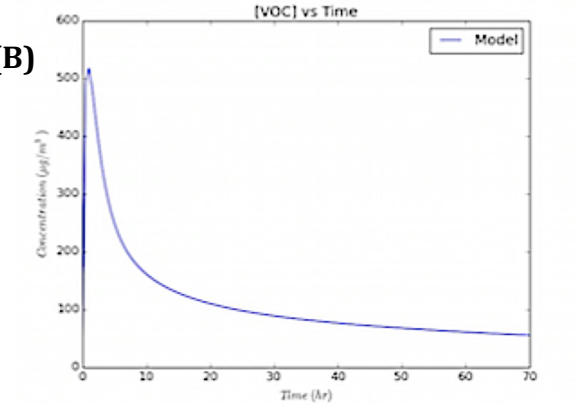
4.1 The model

As described above, a model of the vehicle interior has been built using Python. This model was designed to be as user friendly as possible, and what follows is a brief description of how the model runs. Parameters are typed next to corresponding labels, and the model is run. Upon running, the model produces a plot with air concentration ($\mu g/m^3$) on the y-axis and time (hours, minutes, or seconds) on the x-axis. Experimental data points can be plotted concurrently for better comparison to the model. A comma-separated values (CSV) file is also created with the data and parameters used, and the file is named with the date. One can see an example in Figure 4.1.

(A)

```
27 ML =0.06
28 MW =0.06
29 L =2.54e-4/2
30 MSA = (2 * ML * MW) + (2 * MW * L) + (2 * ML * L)
31
32 AV = 0.051
33 AFR = 1.42e-5
34
35 D = 1.66e-14
36 K = 748
37 C0 = 7.80e8
38
```

(B)



(C)

	A	B	C	D	E	F
1	Time (s)	Time (hr)	[VOC] (ug/m3)		Parameters:	
2	[0.]	[0.]	[20.36336517]		Material Length (m) =	0.06
3	[1800.]	[0.5]	[493.80163574]		Material Width (m) =	0.06
4	[3600.]	[1.]	[518.09301758]		Material Thickness (m) =	0.000127
5	[5400.]	[1.5]	[482.87576294]		Exposed Material Surface Area (m2) =	0.00723048
6	[7200.]	[2.]	[435.37814331]		Air Volume (m3) =	0.051
7	[9000.]	[2.5]	[389.78857422]		Air Flow Rate (m3/s) =	1.42E-05
8	[10800.]	[3.]	[350.18441772]		Initial Concentration (ug/m3) =	780000000
9	[12600.]	[3.5]	[317.08868408]		Partition Coefficient =	748
10	[14400.]	[4.]	[289.81954956]		Diffusion Coefficient (m2/s) =	1.66E-14
11	[16200.]	[4.5]	[267.39221191]			
12	[18000.]	[5.]	[248.8547821]			
13	[19800.]	[5.5]	[233.39753723]			

Figure 4.1 – Parameters (A), plot (B), and file (C) created by model

The run time for the model is about four seconds. The more data points that are desired, the longer the run time for the model. Due to the Python software being freeware, having a model in Python makes for easier distribution and dissemination giving it an advantage over other commercially available programs such as Matlab. Time is saved because there is no need to convert the raw code into another language.

4.2 Verified model results

Inserting the sample parameters from Little *et al.*[36] for VT14-B2FA1 and VT15-B3FA2 into the model resulted in two figures (Figure 4.2 and Figure 4.4) showing formaldehyde emission from polycarbonate films.

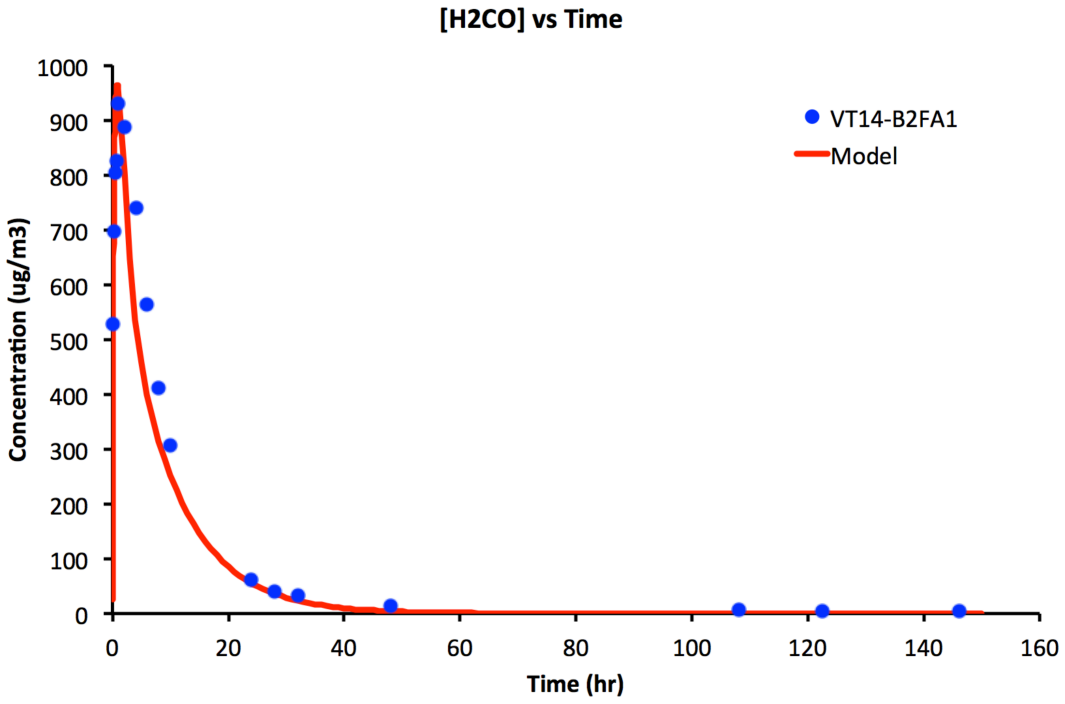


Figure 4.2 - Experimental and model data for formaldehyde emission from polycarbonate film sample VT14-B2FA1

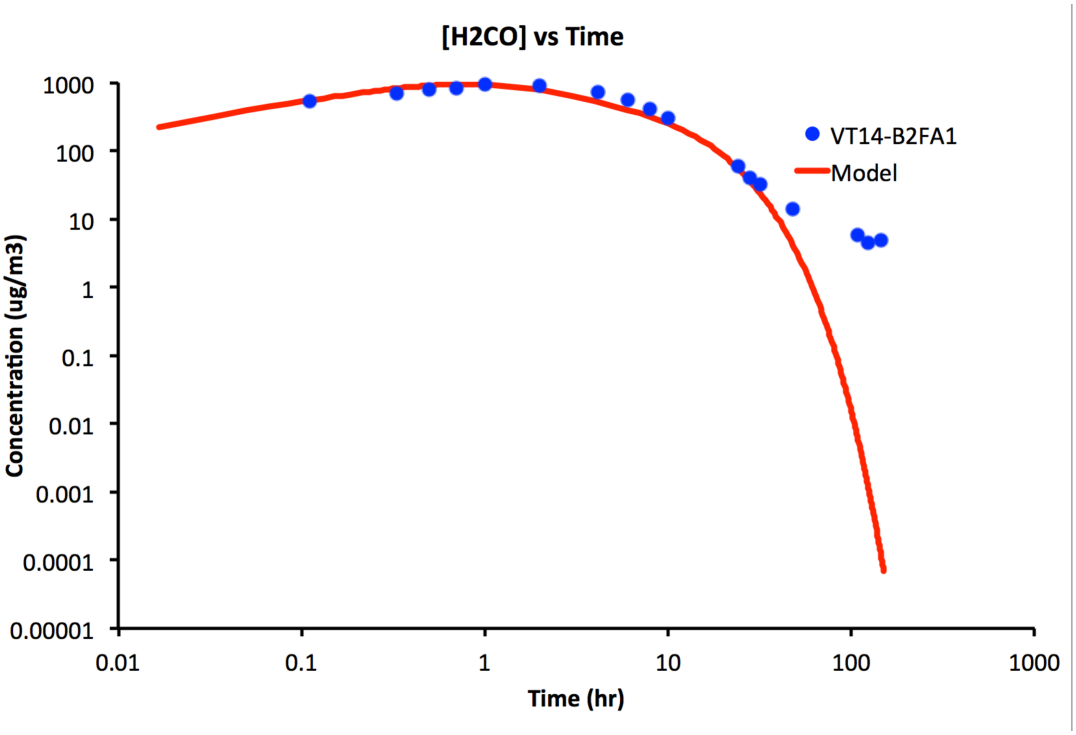


Figure 4.3 - Experimental and model data on log axes for formaldehyde emission from polycarbonate film sample VT14-B2FA1

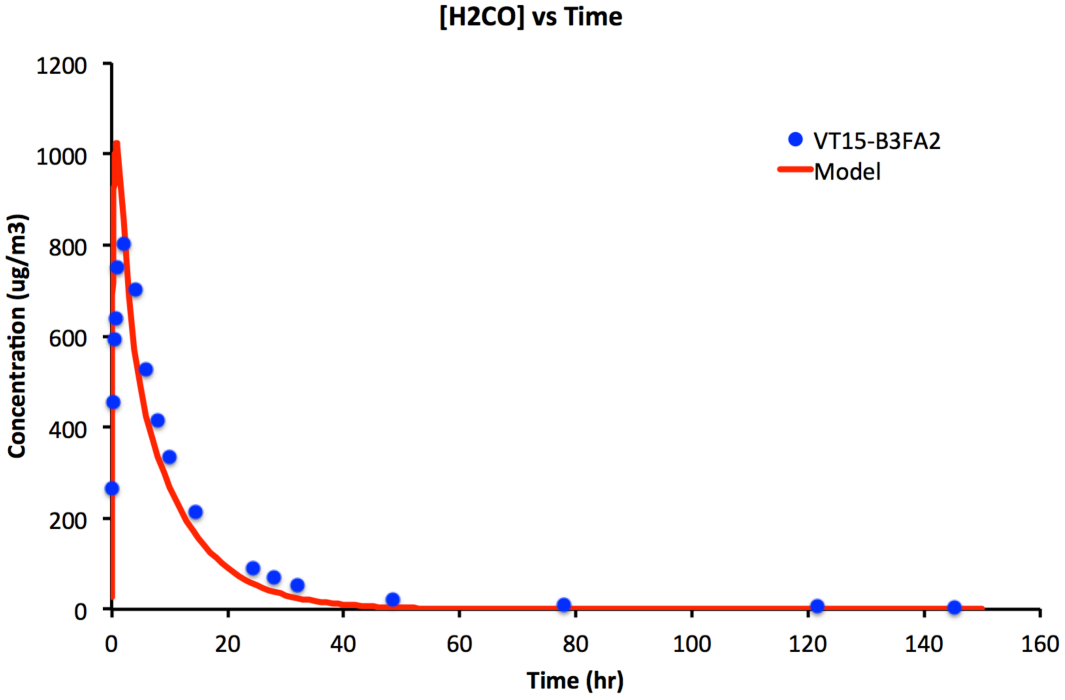


Figure 4.4 - Experimental and model data for formaldehyde emission from polycarbonate film sample VT15-B3FA2

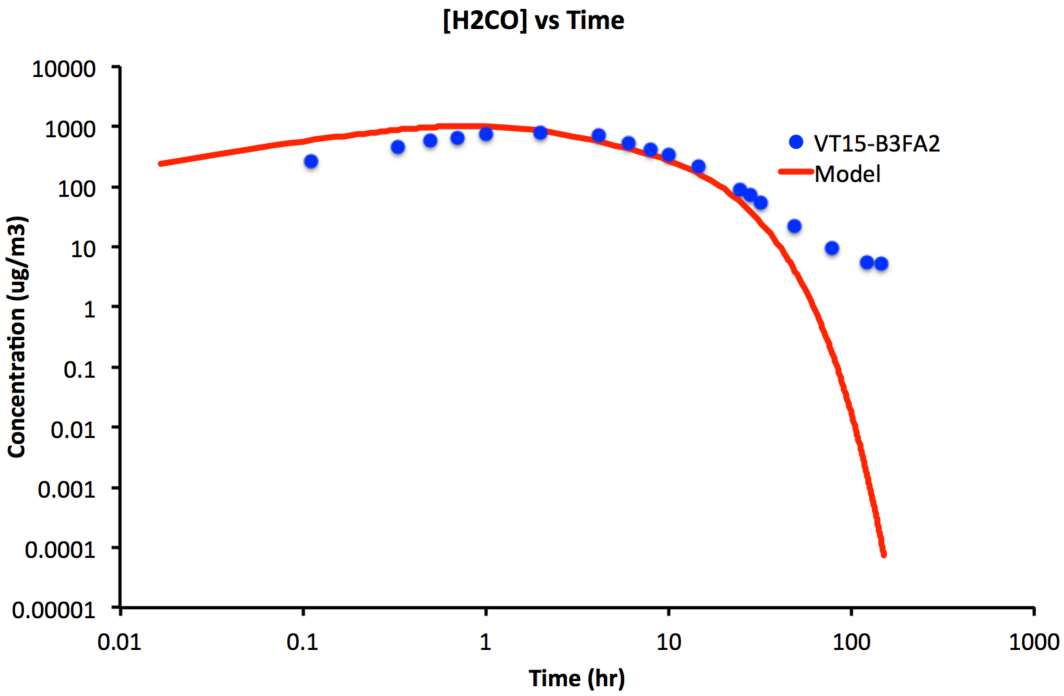


Figure 4.5 - Experimental and model data on log axes for formaldehyde emission from polycarbonate film sampleVT15-B3FA2

The resulting curve created by the model for VT14-B2FA1 shows good agreement with the experimental data. The model slightly under predicts data points between 10 and 20 hours, and at later time points the model greatly under predicts the experimental data. Results for VT15-B3FA2 modeling of formaldehyde emission shows good agreement between about 1 and 20 hours, but they greatly over estimate the initial emission peak. Convection might have played a greater role on this particular sample. Previous work has stated that not accounting for mass transfer resistance at the material/air boundary layer can cause over predictions.[10] Later time points are also greatly underestimated.

Parameters used to determine raw chamber emission data of toluene from PMP films from Lui *et al.*[16] was put into the model. Experimental data was plotted with model results to determine whether model was working correctly. Results can be seen in Figure 4.6 for 10 ºC, 23 ºC and 30 ºC.

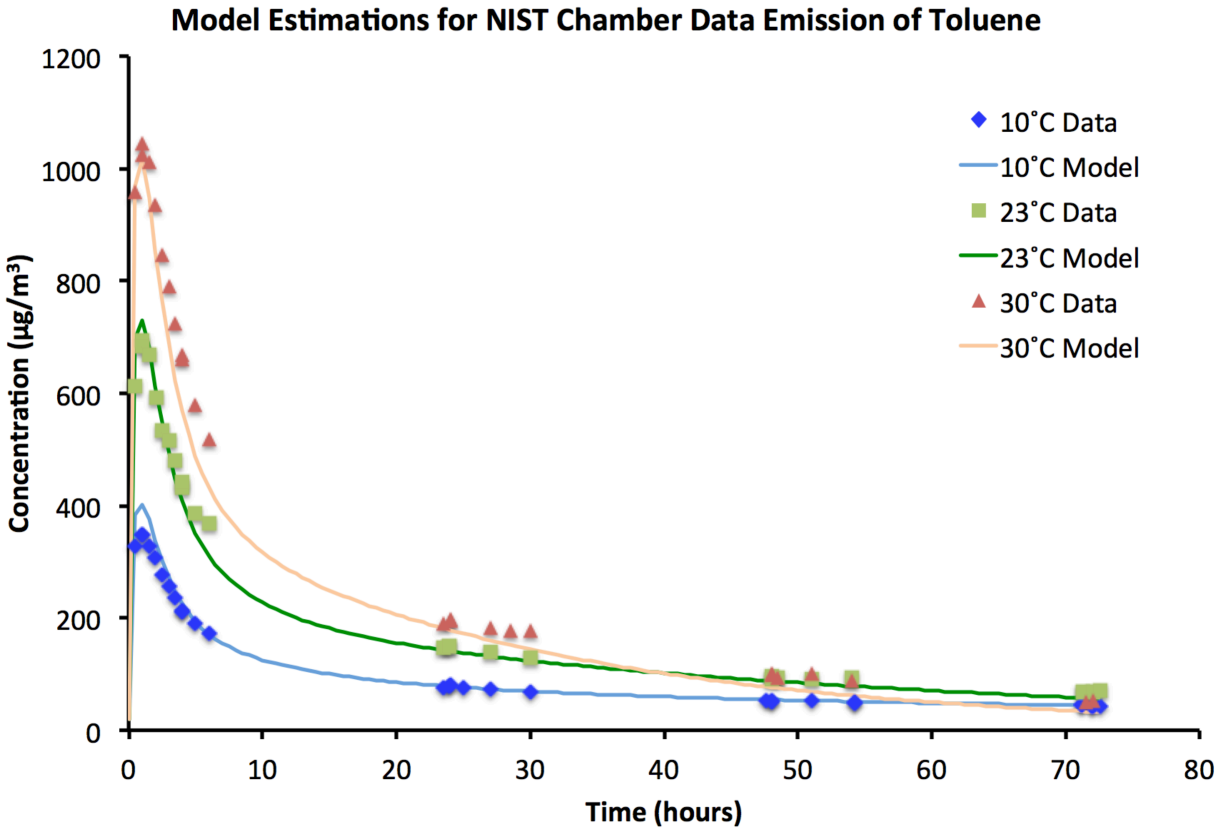


Figure 4.6 - Experimental and model data for toluene emission from PMP films at different temperatures

Overall, 23 ºC model data greatly resembled the experimental data. The 30 ºC model results were close to experimental results at the beginning of the experiment but under-predicted the results after about five hours. The antithesis occurred with the 10 ºC model data, as the data slightly over-predicted the experimental data at time greater than five hours. Convective mass transfer may dominate the colder temperatures as diffusion through the solid decreases with temperature. This could be the reason for the over-estimation of the model for the beginning of the 10 ºC emission data. Plotting the experimental data against the model data (Figure 4.7–4.9) results in best-fit lines with R^2 values above 0.98, indicating good linearity. The model data also closely resembles the experimental data because the slopes of the best-fit lines are close to one.

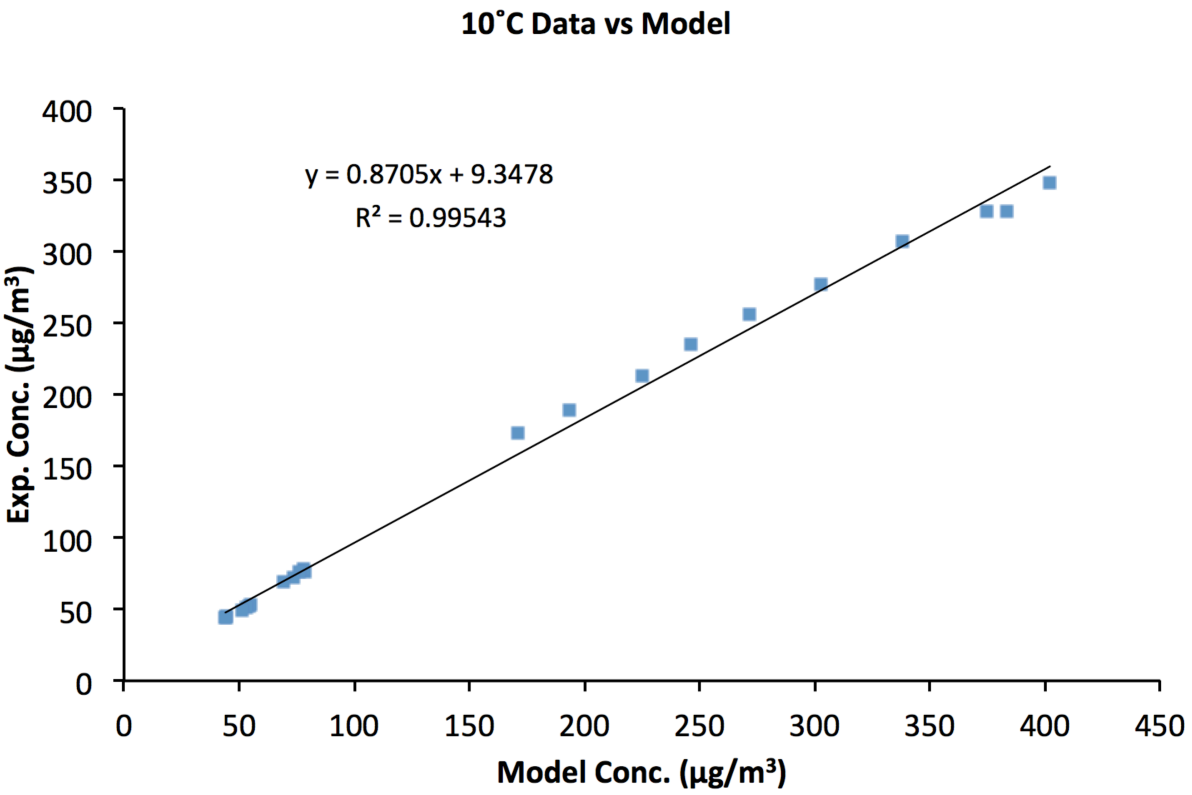


Figure 4.7 - Experimental data plotted against model data for 10 ºC.

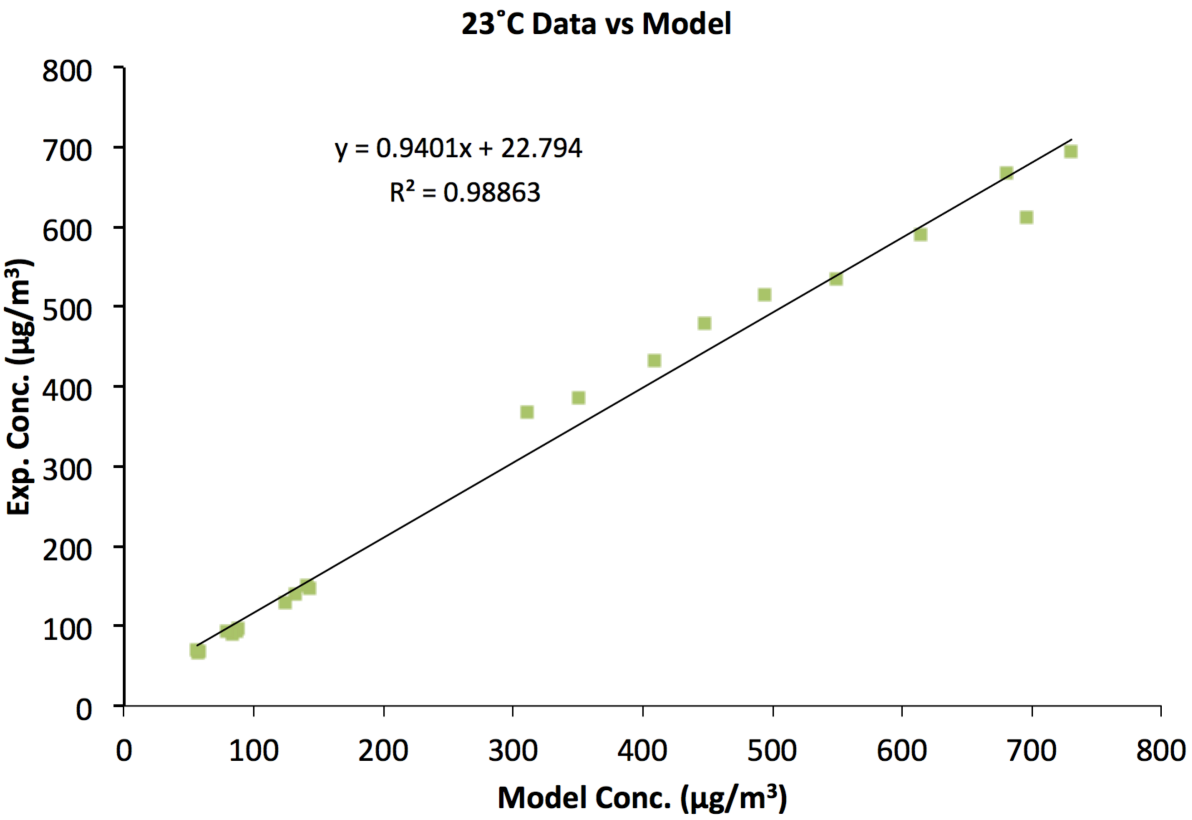


Figure 4.8 - Experimental data plotted against model data for 23 ˚C.

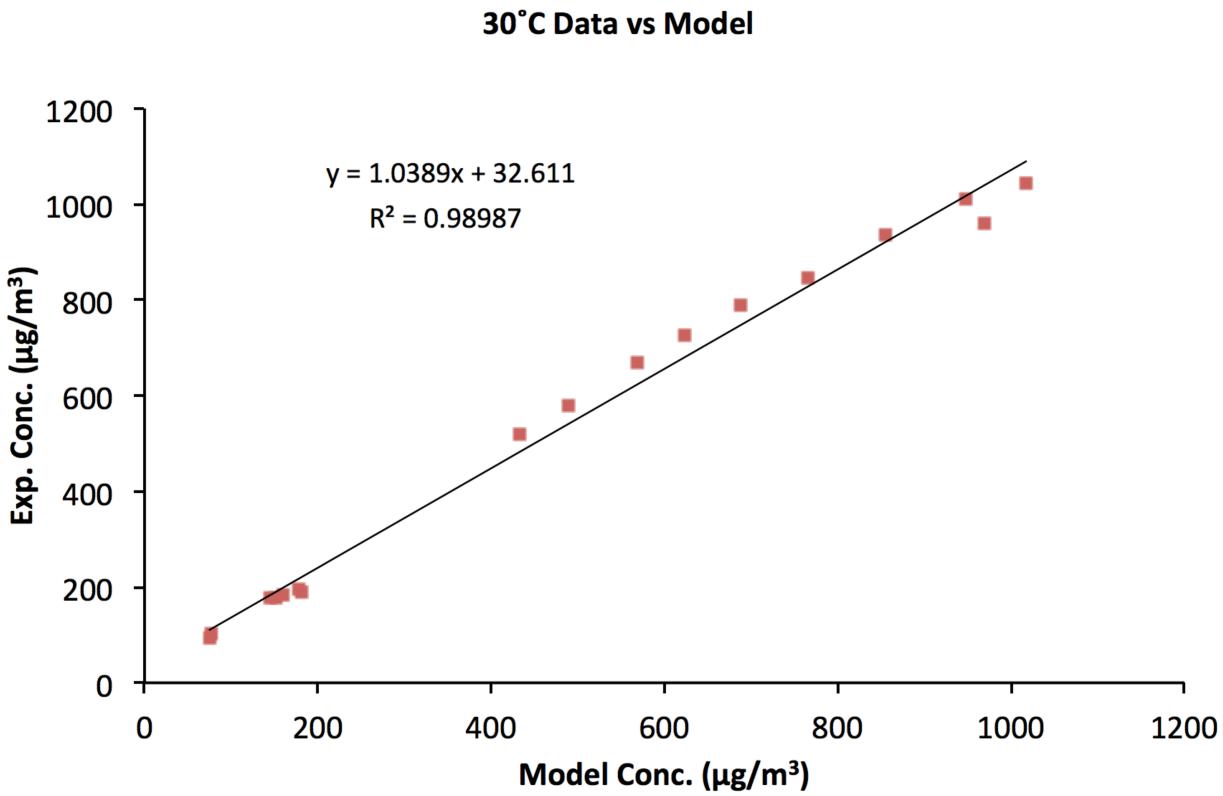


Figure 4.9 - Experimental data plotted against model data for 30 °C.

4.3 Parameter effects on model

Each parameter was changed while the other parameters were held constant as outlined in Table 3.4. Changes to material thickness while holding the others constant can be seen in Figure 4.10. Emission occurs slower for the thicker materials causing an absence of the initial "spike" in VOC air concentration. This "spike" in VOC air concentration gradually gets larger as the material thickness decreases. Due to thickness playing a role in material volume, thicker materials can hold more VOCs within them and therefore will cause higher VOC air concentrations. The thinnest materials have little VOCs within them, and they emit them in the shortest amount of time due to minimizing diffusion distance within the material that they don't affect the air quality at later times.

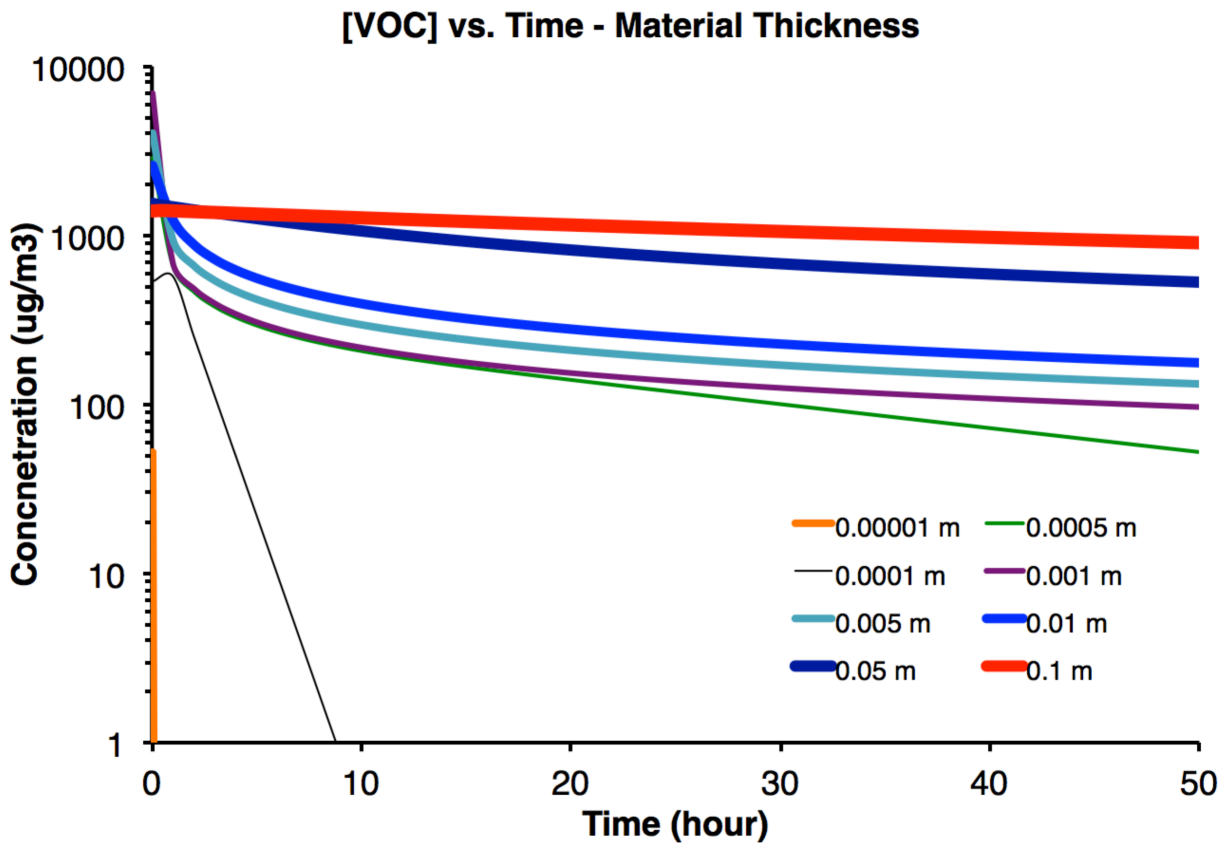


Figure 4.10 - Emission profiles for varying material thickness while holding other parameters constant

The results from changes to air volume while holding the other parameters constant can be seen in Figure 4.11. Greater volumes of air prevent higher VOC air concentrations. The smaller air volumes should have the higher VOC air concentrations, but this is not the case for 0.001 m^3 and 0.0001 m^3. The thinnest material (0.0001 m^3) causes a smaller VOC air concentration than 0.001 m^3. This may be due to the amount of time between each data point produced by the model. Having larger times between these data points may have caused the model to miss the actual peak VOC air concentration. This could have been the reason for the smaller max VOC air concentration for 0.0001 m^3.

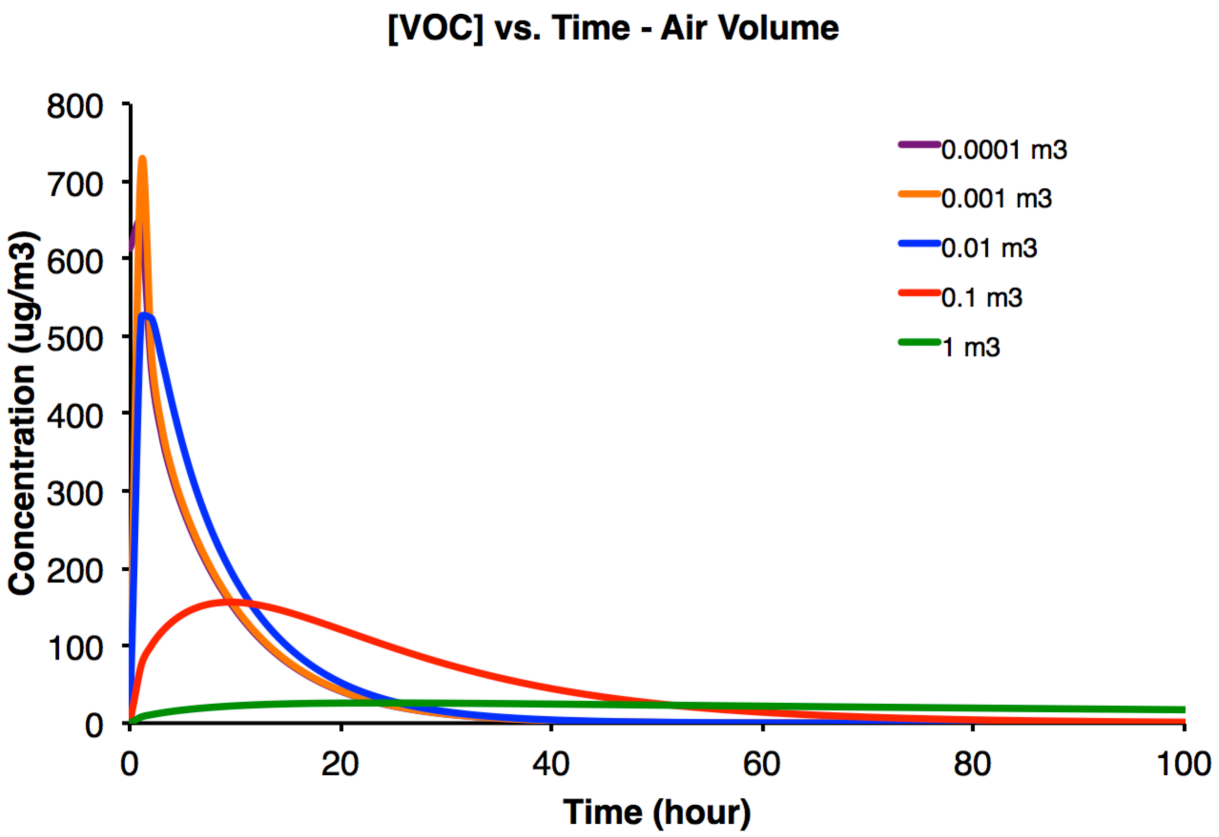


Figure 4.11 - Emission profiles for varying air volumes while holding other parameters constant

Both air volume and airflow rate are related in that they both affect the amount of air exchanges in a given amount of time. While increasing the air volume, and keeping the airflow rate the same, the decreased number of air exchanges decreases the air VOC concentration loss, and therefore, the emission profiles remain flatter. The same scenario occurs when the airflow rate decreases. In Table 4.12, the emission profiles become much flatter as the airflow rate decreases, and the absence of the initial VOC air concentration "spike" is seen.

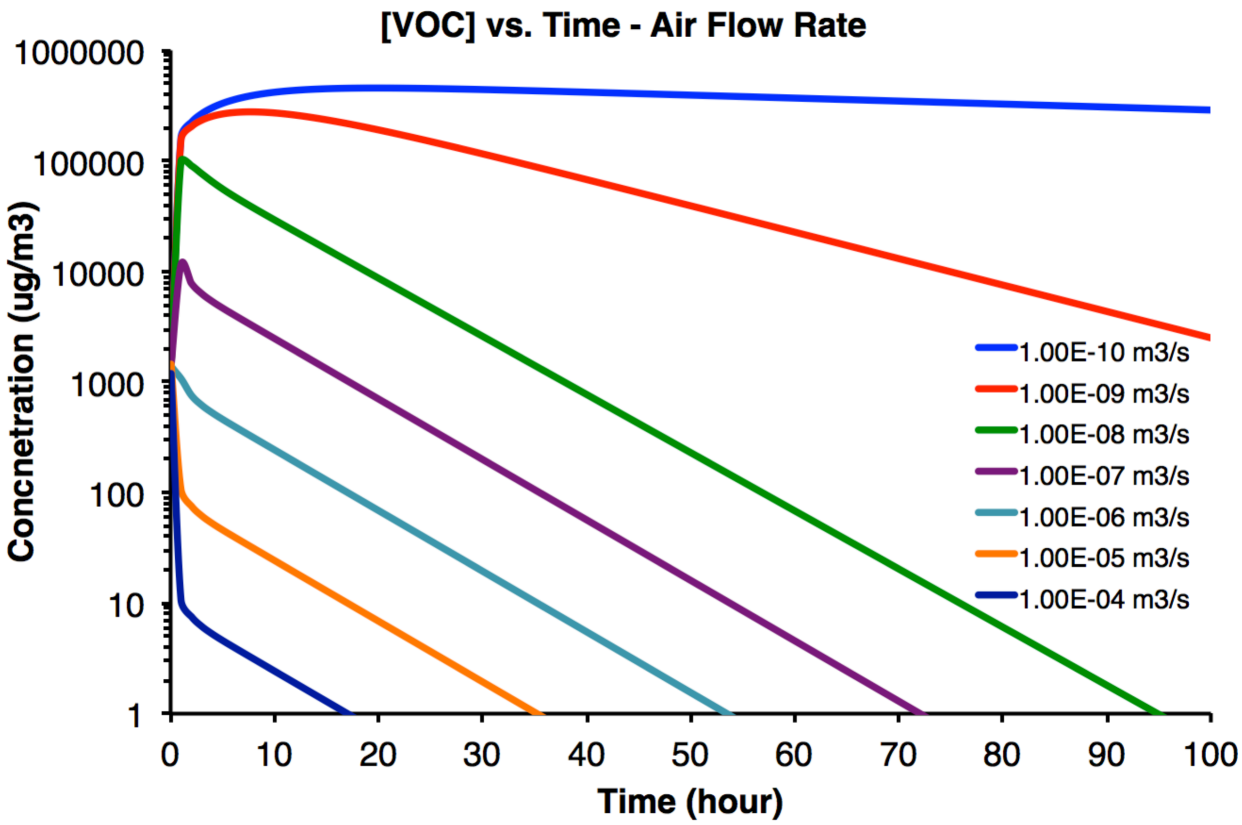


Figure 4.12 - Emission profiles for varying air flow rates while holding other parameters constant

Smaller diffusion coefficients cause less VOCs to make it into the air. This was expected due to the diffusion coefficient being a multiplier in Fick's Law (see Equation 1). The effects of the diffusion coefficient can be seen in Figure 4.13. Larger diffusion coefficients, such as $1x10^{-12}$ and $1x10^{-11}$, cause VOC emission at a fast rate, which causes increases to the rate of loss of these VOCs. This is the reason for the steeper emission profiles that don't appear to last the entire 100 hours.

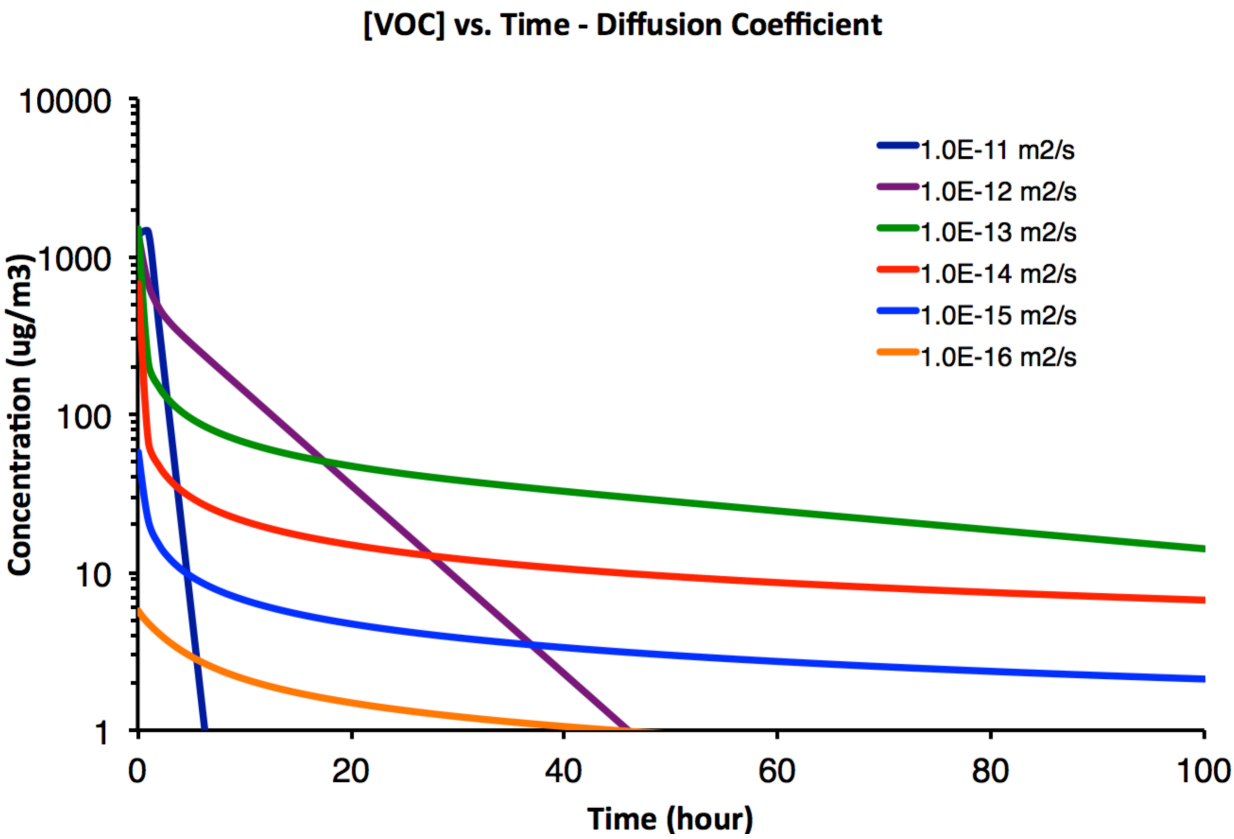


Figure 4.13 - Emission profiles for varying diffusion coefficients while holding other parameters constant

As material/air partition coefficients decrease, the air VOC concentration increases. This was expected as the partition coefficient is a ratio of the concentrations of the VOCs in the material to the VOCs in the air (material:air) at equilibrium.[33] Therefore, as the ratio becomes smaller, the VOCs are more likely to be found in the air. If this was the material/air partition coefficient, a small number would favor the material and therefore, smaller air VOC concentrations would be seen.

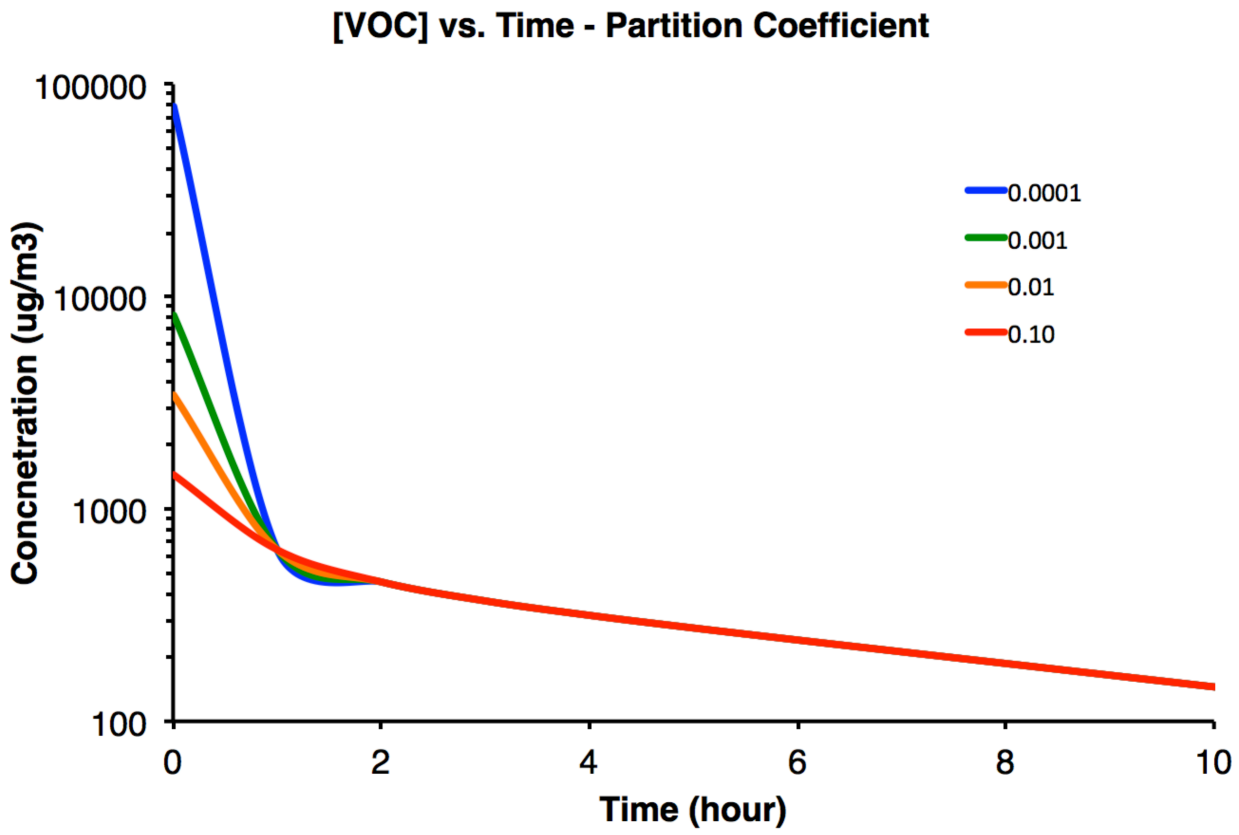


Figure 4.14 - Emission profiles for varying partition coefficients while holding other parameters constant

4.4 Sunlight to VOC diffusion theory

Predicted surface temperatures of PMP films based on average monthly solar irradiances from Kandilli[41] can be seen in Figure 4.15. Surface temperature extremes tend to jump from around 15 ºC (59 ºF) in the winter months, when there is less solar radiation, to 55 ºC (131 ºF) in the summer months when solar radiation is at it's greatest. This solar radiation data was taken from Izmir, Turkey, at latitudes significantly closer to the equator; one would expect greater extremes in southeast Michigan. Having wind blowing over the surface also decreased the surface temperature of the material by about 10 ºC in the summer months, but it didn't have as large of an effect in the cooler winter months. This is most likely due to Newton's Law of

cooling that states that the rate of heat loss of a body is proportional to the temperature difference between the body and the surrounding environment.[44]

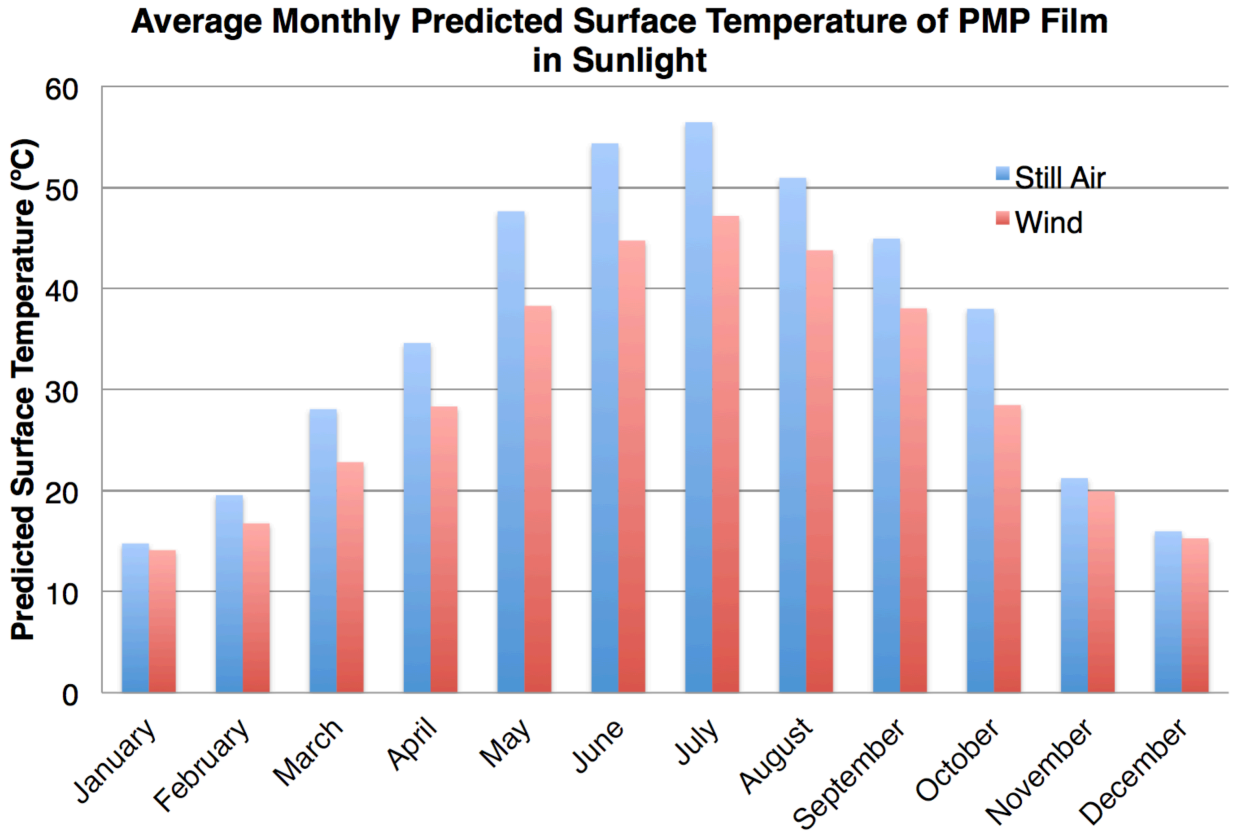


Figure 4.15 - Average monthly-predicted surface temperatures of PMP films in sunlight

Calculated diffusion and partition coefficients for toluene emission from PMP films can be seen in Table 4.1. Calculated diffusion coefficients were smaller in the winter months as expected. One would therefore expect VOC emission during these months to be less than those in the summer months. Material/air partition coefficients were much larger in the winter months, favoring the material. The partition coefficients decreased during the warmer summer months favoring the air. Both results were consistent with what has been seen in previous literature.[16] The Arrhenius plot used to estimate the diffusion coefficients can be seen in Figure 4.16, while Figure 4.17 shows the plot used to estimate the partition coefficients.

Table 4.1 - Calculated diffusion and partition coefficients based on average monthly PMP surface temperatures

Month	Diffusion Coefficient (m^2/s)	Partition Coefficient
January	1.48E-14	811
February	1.91E-14	680
March	3.34E-14	495
April	5.45E-14	397
May	1.26E-13	291
June	2.12E-13	248
July	2.57E-13	235
August	1.97E-13	254
September	1.24E-13	293
October	5.52E-14	395
November	2.57E-14	569
December	1.66E-14	748

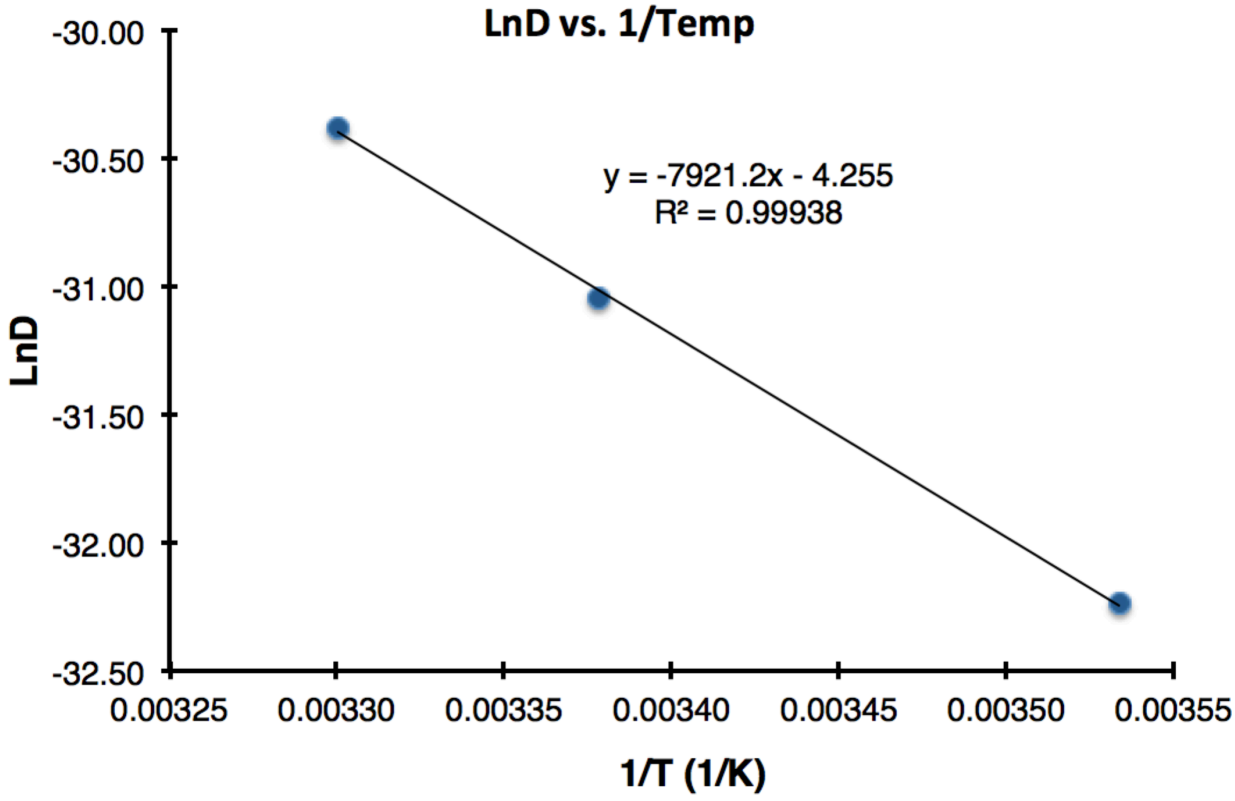


Figure 4.16 - Arrhenius plot for predicting diffusion coefficients at different surface temperatures

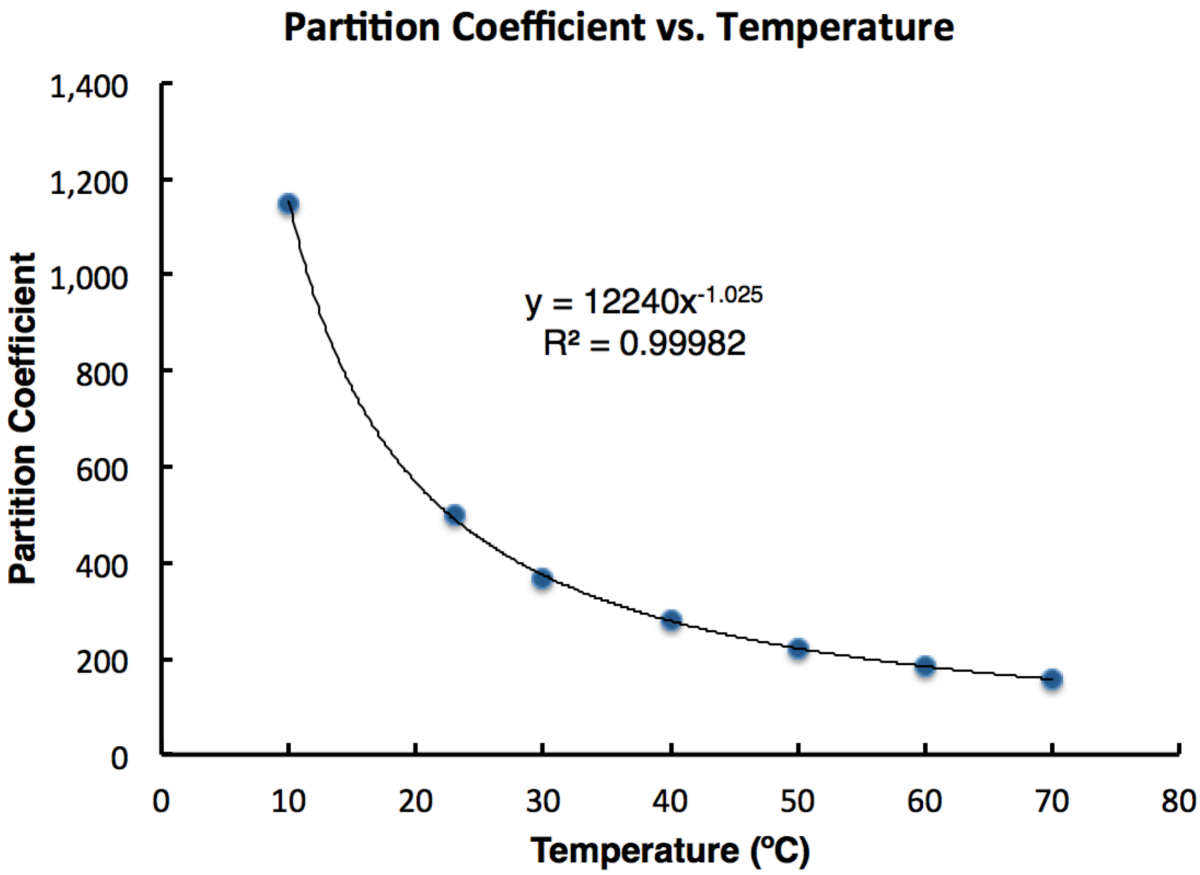


Figure 4.17 - Plot used to predict partition coefficients based on predicted surface temperatures

Model results for the emission of toluene from PMP films, using predicted temperature-dependent diffusion and partition coefficients in Table 4.1, can be seen in Figure 4.18. As expected, the summer months showed the greatest VOC air concentrations. For peak air concentrations for each generated VOC emission curve, a maximum difference of about 1500 $\mu g/m^3$ was found between the curve generated for January and for July. This shows the possible increasing dangers from VOC emission during the hot summer months compared to the cool winter months. A larger difference would be expected in southeast Michigan as temperatures have greater extremes. Colder months tend to allow VOCs to linger in the air longer due to

slower diffusion. This can be seen in Figure 4.19, as the curves generated for January and December never reach a concentration of 0 $\mu g/m^3$.

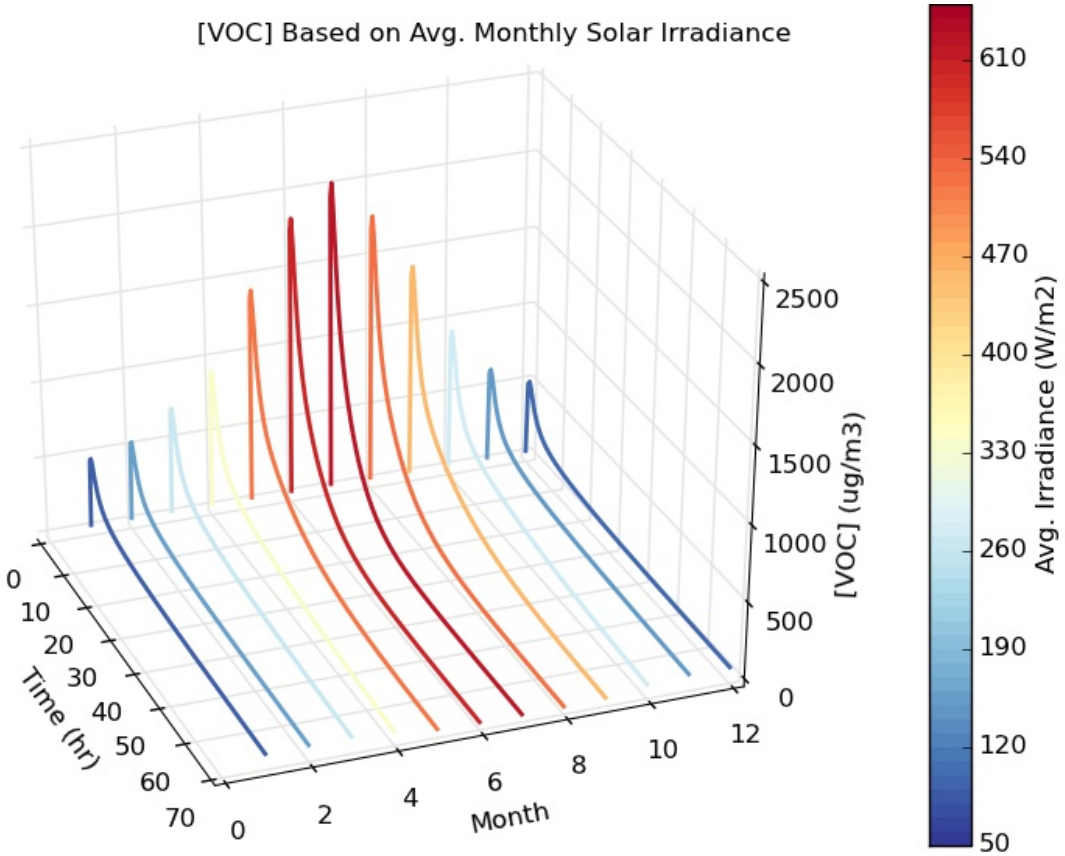


Figure 4.18 - 3D plot of toluene emission from PMP films based on average monthly solar irradiances

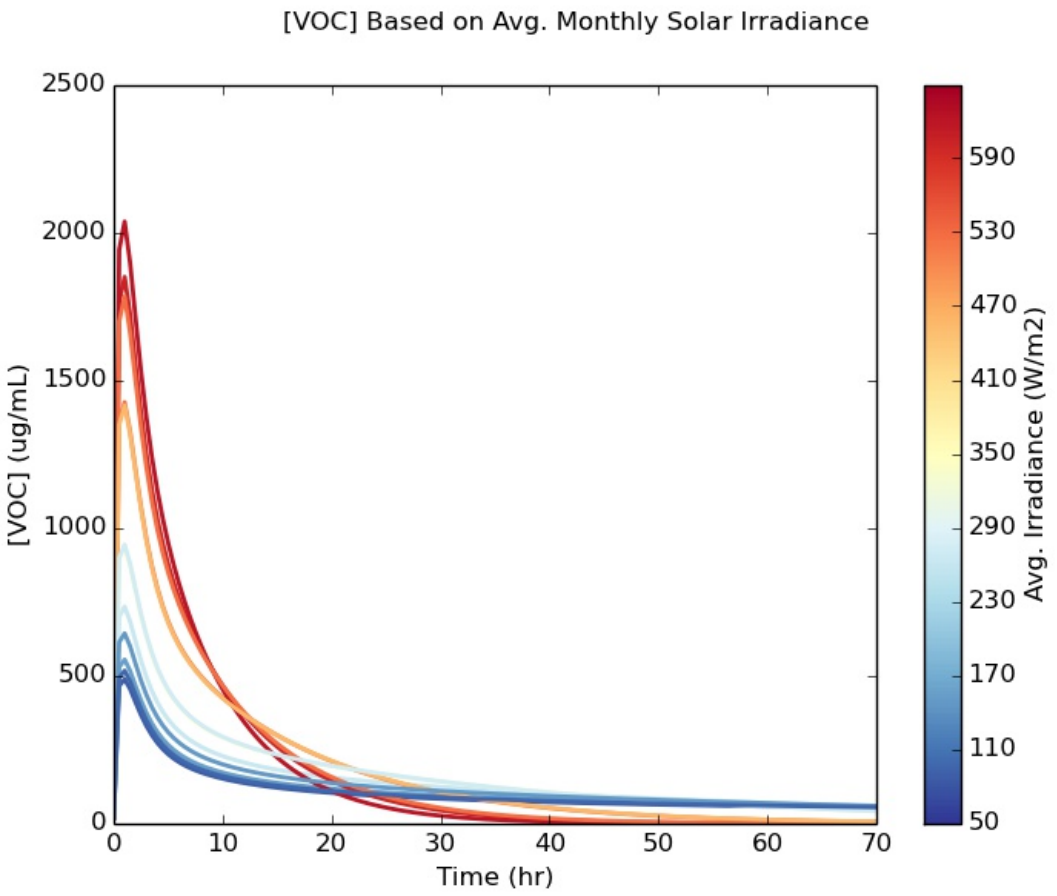


Figure 4.19 - Plot of toluene emission from PMP films based on average monthly solar irradiances

4.5 Dashboard surface temperatures

Predicted surface temperatures for the dashboard of the vehicle that underwent testing can be seen in Table 4.2. All predicted temperatures were greater than measured temperatures. This indicates that not 100% of solar radiation is being transmitted through the windshield. Measured surface temperatures were 11–19 ºC greater than temperatures predicted using 50% transmitted solar radiation. Predicted surface temperatures were closest to measured temperatures when calculated using 75% transmittance. This suggests that the glass used for windshields has a percent solar transmittance close to 75%. Other factors such as cleanliness of the window,

window tinting effects, and differences in solar radiation subjected on the vehicle to the solar radiation measured by the weather station could have also contributed to poor predictions.

Table 4.2 - Measured surface temperatures and predicted surface temperatures calculated with varying solar radiation transmittance

Time	**11:30**	**12:00**	**12:30**	**13:00**	**13:30**	**14:00**
Measured Temp (ºC)	41.2	49.0	53.3	57.2	59.6	61.4
Predicted Temp (ºC) 100%T (75%T) (50%T)	50.93 (40.6) (29.7)	53.08 (43.1) (32.6)	63.67 (52.0) (39.5)	66.18 (54.2) (41.3)	67.39 (55.2) (42.0)	67.81 (55.6) (42.5)
Measured Temp. – Predicted Temp. (ºC) 100%T (75%T) (50%T)	-9.73 (0.57) (11.5)	-4.08 (5.86) (16.4)	-10.37 (1.31) (13.8)	-8.98 (2.99) (15.9)	-7.79 (4.41) (17.6)	-6.41 (5.79) (18.9)

CHAPTER 5: CONCLUSIONS

This project has shown to have produced an accurate and reliable model in Python code that is capable of predicting VOC emissions from materials using material parameters such as diffusion and partition coefficients, surface area and thickness, and environment parameters such as airflow rate and air volume. Thicker materials provide higher VOC air concentrations for longer periods of time due to a longer diffusion distance and a larger material volume. This larger volume provides greater quantities of VOCs. Air volume and airflow rate are related in that they both affect the amount of air exchanges in a given amount of time. Larger air volumes and airflow rates decrease VOC air concentrations. Smaller diffusion coefficients cause less VOCs to diffuse into the air, consistent with Fick's Law. Decreases in material/air concentrations also cause decreases to VOC air concentrations.

Temperature was found to play an important role in VOC emission as warmer temperatures cause increases in VOC air concentrations. Temperatures of materials within the vehicle were greatly affected by solar radiation. Differences in surface temperatures between summer and winter months were estimated to be about 50 °C in the case observed. This will vary by type of material and latitude. Changes to VOC air concentrations were seen to be as different as 1500 $\mu g/m^3$ as the solar irradiance on the material changed from around 50 W/m^2 in the winter months to over 600 W/m^2 in the summer months. This large change would greatly increase the potential for adverse health effects experienced by passengers and proves that vehicle interior air quality is much worse in the summer. Using a solar pyranometer both inside and outside the window would resolve the issue with inaccurate surface temperature predictions of the dashboard. This would allow one to determine the amount of radiation absorbed by the

windshield. A solar pyranometer would greatly increase the accuracy of the experiment by removing error caused by using a weather station for solar radiation data. Based on the air volume and airflow rate parameter variation data, increasing the number of air exchanges within the cabin of the vehicle would greatly reduce air VOC concentrations. Using materials with smaller diffusion coefficients would also reduce VOC air concentrations. Overall, much more work needs to be done to ensure good vehicle interior air quality. We hope this model can be applied to real vehicle testing and simulations in the future to better the air quality of the vehicles we drive.

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