Development of a general dynamic Multimedia Indoor Model for SVOCs: Applications to PBDEs

by

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
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Abstract

An unsteady-state, fugacity-based, indoor chemical fate model was developed to explore kinetic resistance of multilayer of polyurethane foam (PUF) commonly found in upholstered furniture. The Dynamic Layered PUF Simplified Multimedia Indoor Model (DLP-sMIM) was based on the Multimedia Indoor Model created by Zhang et al. (Zhang, Diamond et al. 2009). DLP-sMIM was applied to real and hypothetical scenarios indoor environments consisting of air, carpet, PUF furniture and the surface film on walls. The model showed good agreement with reported concentrations from a study of indoor polybrominated diphenyl ethers (PBDE) air concentrations over nine months. The PUF compartment was predicted to experience long PBDE residence time. It is suggested that steady-state models and using the well-mixed assumption for a single PUF compartment causes an orders-of-magnitude overestimation of the mass of chemicals in PUF. Rather, two vertical layers of PUF need to be considered in a time-dependent model of indoor chemical fate.
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Chapter 1

Introduction

1 Introduction

One group of chemical of concern in the indoor environment are semi-volatile organic compounds (SVOCs) (Bidleman, Billings et al. 1986). SVOCs are ingredients commonly found within household consumer products and building materials (La Guardia, Hale et al. 2006). SVOCs have the ability to undergo multi-media partitioning according to their thermodynamic properties (Bidleman, Billings et al. 1986), and as a result, have the ability to migrate from materials to which they have been added, and partition into other materials. As a result of the slow rate of release from sources, SVOCs have been detected in the multiple compartments in the environment, and have the ability to persist indoors for a long time (Zhang, Diamond et al. 2009).

Polybrominated diphenyl ethers (PBDEs) are a group of SVOCs widely used and continuously present in the indoor environment. PBDEs have been of increasing concern due to the high concentrations detected indoors (Butt, Diamond et al. 2004; Shoeib, Harner et al. 2004; Wilford, Harner et al. 2004; Björklund, Thuresson et al. 2012), along with the associated adverse health effects (Zhou, Taylor et al. 2002; Birnbaum and Staskal 2004; Madia, Giordano et al. 2004; Kodavanti and Ward 2005; Costa and Giordano 2007; Coburn, Curras-Collazo et al. 2008; Meeker, Johnson et al. 2009; Alm, Scholz et al. 2010; Costa and Giordano 2011; Buttke, Wolkin et al. 2013; Eskenazi, Chevrier et al. 2013; Slotkin, Card et al. 2013; Costa, de Laat et al. 2014). Despite the knowledge of the elevated concentrations of PBDEs in indoor environments, little information is available regarding the transport, emissions, and fate in the indoor environment.

The combination of spending most of our time indoors (Leech, Nelson et al. 2002), along with higher concentrations indoors than outdoor of particular SVOCs provides the motivation and overall goal of this thesis to better understand indoor SVOC emissions and fate. This chapter provides the background for the study, characteristics of PBDEs, multimedia modeling, and its application in the indoor environment.
1.1 Chemicals of Interest: PBDEs

Globally, Polybrominated Diphenyl Ethers (PBDEs) have been the most widely used brominated flame retardant (Ali, Harrad et al. 2011), and thus they have received significant attention from academics, media, and policy makers. There are a total of 209 congeners, with one to ten bromine atoms, varying in both number and position of bromines (Birnbaum and Staskal 2004). PBDEs have been used as additive flame retardants, which are released over the lifetime of the products to which they were added (Main, Kiviranta et al. 2007; Stapleton, Sjödin et al. 2008).

PBDEs were commercially manufactured in three mixtures, pentabromodiphenyl ether (Penta-BDE), octabromodiphenyl ether (Octa-BDE) and decabromodiphenyl ether (Deca-BDE). Penta-BDE has been found in commercial products including polyurethane foam (PUF), carpet underlay, furniture, bedding and vehicle interiors (de Wit 2002; Birnbaum and Staskal 2004), with a reported global production of as high as 105,000 tonnes since 1970 (United Nations Environment Programme 2010). Penta-BDE has been found to account for up to 30% of the weight of PUF (Hale, La Guardia et al. 2002). Octa-BDE have been used in thermoplastics including high-impact polystyrene for equipment casting (Birnbaum and Staskal 2004), with a global production of ~118,500 tonnes (United Nations Environment Programme 2010). Deca-BDE has been used in the housing for electrical products and textiles (Birnbaum and Staskal 2004; Stapleton, Sjödin et al. 2008), with a global production estimated as high as 1.25 million tonnes between 1970 and 2005 (United Nations Environment Programme 2010), and recent estimated global production of ~60,000 tonnes per year (Environmental Protection Agency 2006).

Due to the high usage of products containing these chemicals being found within the indoor environment, many studies have found higher concentrations of PBDEs indoors versus the outdoors (Butt, Diamond et al. 2004; Shoeib, Harner et al. 2004; Wilford, Harner et al. 2004; Björklund, Thuresson et al. 2012; Goosey and Harrad 2012). Björklund et al. (2012) found PBDEs indoor air concentrations ~30 times higher that of the outdoor concentrations (Björklund, Thuresson et al. 2012), while Wilford et al found indoor air concentrations ~50 times higher than outdoor (Wilford, Harner et al. 2004). Schecter et al found the indoor air concentration was on average ~5 times higher than the outdoors (Schecter, Colacino et al. 2010). From this it has been
speculated that a large percentage of these chemicals originate from indoor residential environments (Björklund, Thuresson et al. 2012).

Human exposure to PBDE is directly related to the uses, transport, and fate in the environment. The dominant human exposure pathway of PBDEs is founded to be through dust and proximity to chemical source (Jones-Otazo, Clarke et al. 2005; Johnson-Restrepo and Kannan 2009; Johnson, Stapleton et al. 2010; Stapleton, Misenheimer et al. 2014). A secondary exposure route for PBDE exposure is through diet, as PBDEs move from indoor to outdoor environments entering the food chain (Harrad and Diamond 2006; Fraser, Webster et al. 2009; Domingo 2012).

With these PBDEs, found in high usage and concentrations indoors, studies have shown that they have associated health impacts. In vitro and in vivo studies have found that PBDE causes endocrine disruption (Zhou, Taylor et al. 2002; Costa and Giordano 2007; Costa and Giordano 2011; Costa, de Laat et al. 2014), causing neurological impairments (Madia, Giordano et al. 2004; Costa and Giordano 2007; Costa and Giordano 2011; Slotkin, Card et al. 2013; Costa, de Laat et al. 2014). Epidemiological studies have shown that PBDEs have the potential to disrupt the endocrine system (Meeker, Johnson et al. 2009), decreased fertility (Meeker, Johnson et al. 2009), developmental and neurological impairments (Eskenazi, Chevrier et al. 2013), and lower IQ in children exposure to ambient levels (Eskenazi, Chevrier et al. 2013).

In response to the evidence of human exposure and toxicity, many countries and organizations have banned the production and uses of PBDEs. The Stockholm Convention has declared Penta-BDE and Octa-BDE as persistent organic pollutants (POPs) as of due to their persistent, bioaccumulative, toxic, and long-range transport characteristics (United Nations Environment Programme 2007). Penta-BDE and Octa-BDE have been banned in the European Union, Japan, and China (Kierkegaard, Sellstrom et al. 2009). In late 2004, the U.S. Environmental Protection Agency brokered a voluntary agreement with the two main chemical producers to cease production of their Penta- and Octa-BDEs. Under the Significant New Use rule, new uses of these mixtures by US manufacturers are prohibited. The use of Deca- BDE has been banned in the European Union as of 2008 (Ravnum, Zimmer et al. 2012). Canada declared congeners of Penta-BDE and Octa-BDE toxic under the Canadian Environmental Protection Act as of 2006, after which their production and use in new products were banned in 2009 (Environment Canada 2012).
1.2 Fugacity Modeling

The models developed for this thesis were based on the original principles of fugacity, developed by Don Mackay (Mackay and Paterson 1986; Mackay and Janicak 2001). Fugacity is defined as the “partial pressure” or “escaping potential exerted by a chemical in one physical phase on another” (Mackay and Janicak 2001). As a result, these fugacity models are best applied to chemicals with a non-negligible vapour pressure, such as SVOCs (Mackay and Janicak 2001). Fugacity \( f, \text{Pa} \) is linearly related to the mass \( M, \text{mol} \) of a chemical in the defined compartment by the fugacity capacity \( Z, \text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1} \), defined as the holding capacity of a material for a chemical based on both the physical chemical properties of the chemical and the properties of the material and \( V \) is the defined volume of the compartment (Mackay and Janicak 2001) (Equation 1).

\[
M = fZV
\]  

(1)

The fugacity capacity for each compartment is derived from the chemical partitioning coefficient between the two compartments. For example, the \( Z \) value for water is determined from the Henry’s law constant. Mass transport between media is defined by the partitioning coefficients and the mass transfer velocities, diffusivity or rate constant, as expressed by \( D \) values. The two modes of chemical transport are through diffusive and advective transport. The system may also undergo chemical losses through advection, removal, and chemical degradation/biotransformation. For each compartment studied, a mass balance equation can be written specifying the input, output, and any fugacity changes over time. The system is governed by a set of mass balance equations which are solved simultaneously. In a system of \( n \) compartments, it will be governed by \( n \) mass balance equations.

In the event where two or more chemicals have the same fugacity, these compartments are considered to be at equilibrium. Equilibrium conditions are often assumed for multiple phases within a particular media. An example of this would be dust, where it has been assumed that chemical in the gas phase of air is in equilibrium with chemical in the particle phase of air. Fugacity models can be solved under both steady-state or unsteady state conditions, where the mass of the chemical in each compartment remains either constant or varies in time.
Fugacity modeling has become a widely used form to study the fate and transport of chemicals found in multiple environments, including but not limited to urban, global, aquatic, indoor and various others (Diamond, Priemer et al. 2001; Zhang, Diamond et al. 2009; Csiszar, Diamond et al. 2012) (MacLeod et al. 2001, Wania and Mackay 1995). The use of fugacity multimedia modeling to quantify the indoor environment has been published by both Bennett et al. and Zhang et al. (2009) (Bennett and Furtaw 2004; Zhang, Diamond et al. 2009).

### 1.3 Characteristics of the Indoor Environment

For the purpose of computational modeling, the indoor environment treated as a “box model” where each component of the environment, “compartment”, was broken up into specified volumes. Each compartment was assumed to have a constant volume, and to be completely homogeneous. By breaking the indoor environment down to the principle elements, the model can be applicable to every environment by simple adjustments to the properties of each compartment.

The indoor environment is comprised of a mixture of materials, depending on the function of the room. A few examples of common materials include vinyl flooring, carpet, foam furniture, non-foam furniture (wood, plastic, or a combination of materials), fabrics, electronic devices, building materials, and many more. Each material has its defining characteristics, which can account for different partitioning factors. One important factor is the fraction of organic carbons, which determines the likelihood of a non-polar chemical to partition into the material.

In comparison to the outdoor environment, we see that the indoor environment has the ability to be a more constant environment, with little variability in terms of parameters within the home. The indoor environment typically maintains a constant temperature, with any variability accounted for by ventilation systems, or human activities as well as seasonal fluctuations (Wallace, Emmerich et al. 2002). Human activity will affect the influence of particles within the indoor environment, through creation, movement, and removal (Thatcher and Layton 1995).

Sorptive compartments within the indoor environment consist of, but are not limited to: airborne particles, settled dust, fixed surfaces, surfaces of human occupants (Weschler and Nazaroff 2008), and upholstered furniture. Upholstered furniture consisting of PUF is a large sorptive
compartment, as such will typically become the largest sink for chemicals (Zhang, Diamond et al. 2009).

As previously mentioned, chemicals of interest are typically found in high concentrations within the indoor environment (Butt, Diamond et al. 2004; Shoeib, Harner et al. 2004; Wilford, Harner et al. 2004; Björklund, Thuresson et al. 2012; Goosey and Harrad 2012), based on the high volume of consumer products which can be found indoors. The indoor environment is important with regards to the chemical exposure, as previously mentioned, a typical North American will spend over 90% of the time in an indoor environment, whether it be residential, or place of work (Leech, Nelson et al. 2002).

1.4 Study Purpose

This thesis presents a study examining the fate, emissions, and transport of SVOCs in the indoor environment. An indoor fugacity based model was developed based on that of Zhang and Diamond (Zhang, Diamond et al. 2009; Zhang, Diamond et al. 2011), known as the Simplified Multimedia Model (sMIM) and then further developed to examine the role of multi-layer PUF and the effects of time dependence. The principal goal of the thesis was to quantitatively understand the concentrations, emissions, and fate of chemicals in the indoor environment with a focus on PUF realism.

This thesis has been structured into three chapters. Chapter 1 presents a general introduction to the thesis. Chapter 2 describes the development and application of the simplified multimedia indoor model (sMIM), the layered PUF simplified multimedia model (LP-sMIM), and dynamic layered PUF simplified multimedia model (DLP-sMIM). Through the development of these models, the estimation of chemical fate and transport in the indoor environment under various conditions was possible. In Chapter 3, the thesis presents overall conclusions and several suggestions for future studies.
1.5 References


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Chapter 2
Dynamic Layered PUF Multimedia Indoor Model

2 Introduction

Despite North Americans spending over 90% of the time indoors (Leech, Nelson et al. 2002), surprisingly little is known about emissions, fate and exposure to chemicals of concern in the indoor environment. One group of chemical which are of concern in the indoor environment are known as semi-volatile organic compounds (SVOCs) (Bidleman, Billings et al. 1986). SVOCs undergo multi-media partitioning according to their thermodynamic properties (Bidleman, Billings et al. 1986). As a result, SVOCs have the ability to migrate from materials to which they have been added but not bonded, and partition into other materials, including particles. As a result of the slow rate of release from sources, SVOCs have been detected in the multiple compartments in the environment, and have the ability to persist indoors for a long time. Increasing concern regarding indoor exposures has come from reports of elevated concentrations of some SVOCs in indoor air (Wilford, Harner et al. 2004; Zhang, Diamond et al. 2011), film (Butt, Diamond et al. 2004), and dust (Harrad, Ibarra et al. 2009; Muenhor and Harrad 2012). Studies have also shown that the indoor environment experiences higher concentrations of some SVOCs in comparison to the outdoor environment (Butt, Diamond et al. 2004; Shoeib, Harner et al. 2004; Wilford, Harner et al. 2004; Rudel and Perovich 2009; Björklund, Thuresson et al. 2012; Goosey and Harrad 2012). Flame retardants, such as polybrominated diphenyl ethers (PBDEs), are one group of SVOCs with high indoor concentrations (Butt, Diamond et al. 2004; Wilford, Harner et al. 2004; Allen et al. 2008; Björklund, Thuresson et al. 2012) and have been added in many household items from PUF furniture to electronic equipment (La Guardia, Hale et al. 2006).

Polyurethane foam (PUF) is a material found in the cushions of upholstered furniture and mattress (Singh and Jain 2009), that has a high sorption capacity for non-polar organic compounds (Braun 1989). Using the fugacity-based Multimedia Indoor Model or MIM, Zhang et al (2009) found that PUF in furniture is significant as it will act as either a sink or a source of SVOCs such as flame retardants (Zhang, Diamond et al. 2009). It can also buffer or prolong the chemical’s residence time in the indoor environment. In the event where flame retardants are intentionally added to the PUF materials such as flame retardants, the PUF initially acts as a
source to the indoor environment (Zhang, Diamond et al. 2009). PUF can have porosity as high as 97.6% (Zhao, Little et al. 2004). With its use in furniture, chemical exchange can occur between air and the PUF material via three processes: gas-phase diffusion, particle deposition, and particle resuspension. Air-PUF chemical exchange may be accelerated by compression and decompression, such might occur with humans or animals bouncing or sitting and rising on or from PUF seating, respectively (Zhang, Diamond et al. 2009).

Because of its enormous sorptive capacity, PUF has been widely used as passive air samplers (Shoeib and Harner 2002; Harrad, Ibarra et al. 2009; Melymuk, Robson et al. 2012). While examining its use as passive samplers, Shoeib and Harner (2002) posited that the chemical resistance to uptake by the PUF was limited by the boundary layer immediately at the air-PUF interface. Gas-phase diffusion between air and PUF has been modeled based on molecular diffusion and mathematically described using the two-film model theory developed by Lewis and Whitman (Lewis and Whitman 1924). The two-film theory was originally used to describe the mass transfer of chemicals between air and water interfaces (Lewis and Whitman 1924), and was later used to describe chemical exchange at the interface between the air outside and inside the PUF (Shoeib and Harner 2002). This formulation was used in the MIM by Zhang et al. (2009). MIM also assumed that PUF in furniture constituted a single, bulk, well mixed homogenous compartment, in which chemicals emitted indoors could partition into PUF in accordance to the chemical’s K_{OA}, such that it would be uniformly distributed throughout the PUF (Zhang, Diamond et al. 2009). Zhang et al. (2009) estimated SVOCs could have an enormous residence time in the indoor environment due to the relatively large volume of PUF material, in combination with its large sorptive capacity.

However, in experiments conducted to characterize PUF as a passive air sampler, Zhang et al. (2011) found that chemicals were not uniformly distributed within concentrically segmented PUF discs that were deployed indoors (Zhang, Tsurukawa et al. 2011). After a 90 day deployment, the surface layer of less than 0.4 cm thickness typically contained more than 90% of the amount of chemical accumulated in the PUF (Zhang, Tsurukawa et al. 2011). Two conclusions can be formulated based on these experiments. First, the resistance to uptake occurs through the PUF pore spaces, not the in the stagnant air boundary layer above the PUF. Secondly, the assumption of a uniform distribution through the depth of a foam cushion in the case of indoor SVOC dynamics is unreasonable on an environmentally relevant time scale.
As an alternative to the two-film model, Zhang and Wania (2012) hypothesized that the PUF compartment experiences PUF-side kinetic resistances to air-PUF chemical exchange and proposed a three-stage model of chemical mass transfer: in the stagnant air layer above the PUF, in macropores within the PUF and in the PUF material (Zhang and Wania 2012). In first stage, chemical mass transfer occurs through the stagnant air layer above the PUF interface. In the second stage, the chemical diffuses through the PUF macropores, and finally, in the third stage the chemical sorbs into the solid PUF material from the macropores. Diffusion-reaction equations based on Fick’s law, the principles of mass conservation, and the law of mass action were applied to the experimental data to determine the effective diffusivity in PUF (Zhang and Wania 2012).

Multimedia Indoor Model (MIM) (Zhang, Diamond et al. 2009) is, to our knowledge, the only indoor model that includes PUF as a compartment. The model assumed that the mass of chemical was evenly distributed throughout the PUF furniture. In the present study, as a result of evidence showing that the chemicals are dominantly founded within the outer portion of PUF (Zhang, Tsurukawa et al. 2011), a more detailed treatment of the PUF compartment was developed. The MIM was modified to create the Dynamic Layered PUF Simplified Multimedia Model (DLP-sMIM); a dynamic fugacity model which includes the kinetic resistance through multiple layers PUF compartment. Previous attempts to quantify the residences time, estimated large residence time (Zhang, Diamond et al. 2009), which would imply that the PUF would never fully reach steady state. The goal of this study was to improve the realism of the MIM model by improving the consideration of PUF furniture compartment in the indoor environment and the dynamic nature of indoor chemical fate. This study asked three research questions: (1) How does the unsteady-state, layered PUF model perform in comparison to real world environments? (2) What is the time-dependent fate of PBDEs indoors? (3) How does PUF affect the fate and transport of PBDEs indoors (a) when PUF is a sink for chemicals and (b) when PUF is a source of chemicals? This chapter first explains the modifications undertaken to adapt MIM to DLP-sMIM and then addresses each research question.
2.1 Model Development

Three versions of the multimedia indoor model were created for this study, simplified multimedia indoor model (sMIM), layered PUF sMIM (LP-sMIM), and dynamic layered PUF sMIM (DLP-sMIM).

The Simplified Multimedia Model (sMIM) reduced the complexity of MIM by examining only two particle size fractions (0-1 and 2.5-10 μm) in the indoor environment in comparison to MIM’s six particle size fractions. Similar to MIM, the defined indoor environment considered in this model includes five compartments of air (gas and particle phases), PUF furniture, film on vinyl floors (referred to as “vinyl” throughout the paper), carpet, and the surface films on walls. While chemical diffusion through drywall material has been observed (Van Loy, Riley et al. 2001), for simplicity the model does not include this process. The model assumes that the environment is in steady state and that each compartment is well mixed. The model also assumes the same transport mechanisms as MIM, with ultimate chemical loss from the modelled room being advection, chemical reactions, and dust removal through cleaning. The model assumes that the inter-compartmental chemical movement occurs through bidirectional diffusion of gas-phase chemicals, and particle deposition and resuspension of particle-sorbed chemicals. The chemical sorption to particles is derived from the theory presented by Harner and Bidleman (Harner and Bidleman 1998). Chemical resistance within the PUF was not included, and therefore the chemical distribution within the bulk PUF material was assumed to be spatially uniform.

The Layered PUF Simplified Multimedia Model (LP-sMIM) is a modification of sMIM, through the addition of a second layer of PUF furniture underlying a thin surface layer. Kinetic resistance was assumed between the top active layer and the lower subsequent layer, analogously to chemical exchange between vertical layers of lake sediments and soil (Diamond, Mackay et al. 1990; Harner, Bidleman et al. 2001; Ghirardello, Morselli et al. 2010). Kinetic resistance is inversely proportional to the chemical uptake, and depends on the thickness and diffusion length of the material (Danckwerts 1965).

In greater detail, PUF Layer 1 interacts with both the air compartment and PUF Layer 2. These two layers were assigned thicknesses of 1 and 4 cm, respectively, based on diffusion distances for Layer 1 defined in Zhang et al. (2011) (Zhang, Tsurukawa et al. 2011). As such, PUF Layer
1 experiences gas diffusion, particle movement, and chemical reaction. PUF Layer 2 only interacts with PUF Layer 1 and thus the transport process between the two layers is limited to gas diffusion. It is assumed that the particle movement between the layers is negligible and that chemical reaction occur in PUF layer 1, and not in PUF layer 2. The D-value (mol h\(^{-1}\) Pa\(^{-1}\)) for gas diffusion between PUF Layers 1 and 2 is given by:

\[
D_{\text{Diffusion,P1-P2}} = ((k_{P1-P2} \cdot A_P \cdot Z_{P1})^{-1} + (k_{P1-P2} \cdot A_P \cdot Z_{P2})^{-1})^{-1}
\]  

(1)

where \(k_{P1,P2}\) is the mass transfer coefficient (m s\(^{-1}\)) between PUF Layer 1 and PUF Layer 2, \(A_P\) (m\(^2\)) is the surface area between PUF Layer 1 and 2, and \(Z_{P1}\) and \(Z_{P2}\) are the Z-values for PUF Layers 1 and 2, respectively.

The mass transfer coefficient, \(k_{P1,P2}\), is given by,

\[
k_{P1-P2} = (f \cdot D)/(r_{SA} \cdot K_{\text{PUF/AIR}} \cdot \delta)
\]  

(2)

where \(f\) (dimensionless) is the correction factor for intra-aggregate porosity and tortuosity, \(r_{SA}\) (m\(^3\)(PUF) m\(^{-3}\)(air)) is the volume ratio between solid PUF material and porous air space in PUF, \(D\) (m\(^2\) s\(^{-1}\)) is the molecular diffusivity of the chemical in bulk air, \(K_{\text{PUF/AIR}}\) (m\(^3\)(air) m\(^{-3}\)(PUF)) is the chemical partitioning coefficient between PUF and air, and \(\delta\) (m) is the diffusion path length of the chemical in PUF (Zhang, Tsurukawa et al. 2011). The estimated value of the coefficient \(f/r_{SA}\) was between 0.18 and 0.45, based on experimentally fitted \(D\) results for polychlorinated biphenyl (PCB) (Zhang, Tsurukawa et al. 2011). The estimated values were based on the properties of the porous medium which decreases with increasing density and tortuosity of the PUF (Zhang, Tsurukawa et al. 2011).

The generalized mass balance matrix can be defined by Equation 3, where \(D\) (mol h\(^{-1}\) Pa\(^{-1}\)) is a matrix consisting of \(-D_{ij}\) values on the diagonal, defined as total losses for compartment i, and the \(D_{ij}\) values on the off diagonal, defined as the chemical transport from compartment j to i, \(E\) (mol h\(^{-1}\)) is the vector of sources and sinks, and \(\bar{M}\) (Pa) is the chemical mass vector (Csiszar, Diamond et al. 2012).

\[
\frac{d\bar{M}}{dt} = D\bar{M} + \bar{E}
\]  

(3)
The steady-state mass balance equations were discretized using the implicit Euler approach to produce a dynamic model (DLP-sMIM), as was done previously with the Multimedia Urban Model, MUM (Csiszar, Diamond et al. 2012). By using the implicit Euler approach the model is unconditionally stable and will work for any time step (Mang, Toma et al. 2012). A brief overview of the theory and equations are included below.

Applying the implicit Euler approximation results in the following equation (Equation 4),

\[
\frac{\bar{M}_i^{i+1} - \bar{M}_i^i}{\Delta t} = D_i^{i+1} \bar{M}_i^{i+1} + E_i^{i+1} + S_i^i
\]

where S is a vector representing the sink/sources at the beginning of time step i. The time component was treated using the current time, \( t_i = i\Delta t \), where i represents the time step number, while \( \Delta t \) represents the length of the time step. Using the implicit Euler method, it necessary for all other sink/sources be evaluated at the future time step i+1.

### 2.2 Model Parameterization

The chemicals used to examine the model were a suite of PBDEs (BDE-3, -28, -47, -66, -99, -100, -138, -153, -154, -190, and -209). The physical-chemical properties used in this model were obtained from the U.S. Environmental Protection Agency’s program EPISuite Version 4.11 (EPA 2014), and are listed in Table S1. The reaction rate constants for films (on walls and vinyl) were assumed to be 10 times less than the gas-phase reaction rate constant (Csiszar, Diamond et al. 2012), while the reaction rate constants for PUF was assumed to be 1,000 times less than the gas-phase reaction rate constant. The molar volume of each chemical was calculated using the LeBas method (EPA 2014).

To address research questions 2 and 3 (Section 2.4, 2.5 and 2.6) the model was parameterized to portray a basic bedroom of five metres by five metres by three metres height, consisting of either vinyl flooring, and PUF containing mattress. Physical property values are listed in Table S2. An indoor temperature of 25°C was assumed. The air exchange rate for the bedroom was assumed to be 0.7 h\(^{-1}\) (Du, Batterman et al. 2012) which is typical of the North American environment. Parameter properties and rates of movement for dust were obtained from Bennett et al. (Bennett and Furtaw 2004; Shin, McKone et al. 2012) and are listed in Table S3.
2.3 Model Evaluation

2.3.1 Methods

In order to evaluate the model, DLP-sMIM was used to consider the scenario described by Hazrati and Harrad (2006), in which a university office in the United Kingdom was monitored for PBDEs and PCBs over a nine month period (Hazrati and Harrad 2006). The office environment consisted of air, film on walls, carpet, and PUF furniture. The dimensions of the office had an area of 4.8 metres squared by 2.7 metres height. The PUF furniture had the dimensions of 1.7 metres squared by 0.05 metres height. The carpet had a thickness of 0.005 metres. During this time an older computer was used for approximately two months, after which the computer was replaced by a newer computer. This situation was modelled by Zhang et al. (2009), using the steady-state version of MIM. The air exchange rate was assumed to be 1.5\(^{-1}\) (Dimitroulopoulou, Ashmore et al. 2001). The initial gas-phase air concentrations values were taken from Hazrati and Harrad (2006) (Hazrati and Harrad 2006), from which bulk air concentrations (gas and particle phase) were calculated based on the method described by Zhang et al. (2009) (Zhang, Diamond et al. 2009). PBDE concentrations were measured in PUF from the office chair and in the carpet (Zhang, Diamond et al. 2009). These were specified in the model. PBDE emission rates that appeared to be due to the computer were back calculated from the bulk air concentrations using the method described by Zhang et al. (2009) (Zhang, Diamond et al. 2009), before and after the removal of the computer. In this model run, the initial film concentration was calculated using sMIM. Using the initial air, film, carpet, and PUF concentrations the model was then run using DLP-sMIM for the nine months during which the computer usage changed and air concentrations were measured. The measured air concentrations for select PBDEs were compared to the modeled air concentrations.

2.3.2 Results

The revised aggregate emission rates for \(\Sigma\text{BDE}\) of seven congeners for the old and new computer scenarios were 49 and 9 ng/h, respectively, in comparison to the previously calculated 35 ng/h and 5 ng/h, respectively. The calculated emission rate was higher than previously calculated due to the higher air exchange rate.
Based on the initial concentrations, the model was able to reproduce the measured air concentrations with respect to the changing computer usage (and concomitant change in emission rate) within a factors of 0.8 and 1.6 (old and new computer, respectively) of the measured air concentrations, with the average modeled air concentrations higher by a factor of 1.1 (Figure 2.1). The modelled results predicted the overall time trend in concentration changes. The modeled environment responded quickly to the reduced emission rate. The largest loss mechanism of PBDE was advection (room ventilation), which quickly reduced the air concentrations in the room.

When looking at individual congeners (Fig S2.1), the best correlation between measured and modelled results was evident for BDE-47 and -99. The worst correlation was for the higher brominated compounds for which, it should be noted, the air measurements are more uncertain.

Based on the comparison of modelled and measured results for this environment, it can be concluded that DLP-sMIM can serve as a tool to predict the concentrations in the indoor environment, even in the event where the concentrations change over a time scale of months.

### 2.4 Effect of Time Dependency and Layered PUF

#### 2.4.1 Methods

The chemical mass distribution of PBDEs estimated by the DLP-sMIM was compared to results from sMIM and LP-sMIM to understand the implications of both the time dependant behaviour and the effect of PUF layering on PBDE fate. All models were run for PBDEs using the external constant emission of 1 mmol h$^{-1}$ into the bedroom air with no prior emissions or concentrations. DLP-sMIM was run for a time period of 365 days.

#### 2.4.2 Results

The mass distribution can be compared for the system with two PUF layers at steady state versus after one year (Fig. 2.2, 2.3 and S2.2). For Log $K_{OA} \sim 7 – 9.5$ (e.g., BDE-3, -28), total mass in the system was $\sim 10^{10}$ ng, but 74% of that was in vinyl after one year versus 45% at steady state. Air-vinyl diffusion was dominant inter-compartmental transport process.

For Log $K_{OA} 10-11.5$ (BDE-47, -66, -99), the greatest mass was in PUF Layer 1 after one year in comparison to PUF Layer 2 for steady-state conditions, and the total mass in the system was
\( \sim 10^{11} \) (unsteady state) versus \( \sim 10^{13} \) ng (steady state). The dominant net transport process was air-PUF Layer 1 diffusion and dust removal accounted for \( \sim 75\% \) of chemical loss from the system at one year.

For Log \( K_{OA} \sim 11.5 - 13 \) (BDE-100), the greatest mass was about equally in film and PUF Layer 1 after one year, which attributed to the air-film and air-PUF Layer 1 diffusion. The importance of film in this situation is it having a large surface area but thin, allowing for efficient air-film diffusion. In comparison, under steady-state conditions PUF Layer 2 had the greatest mass in this range of Log \( K_{OA} \).

At Log \( K_{OA} \sim 14 - 19 \) (BDE-138, -153, -154, -190, -209), the difference between the unsteady-state and steady-state simulations was most dramatic, with the total mass in the system of \( 10^{11} \) versus \( 10^{15} \), respectively, attributable to mass accumulate in PUF Layer 2 at steady state. In this range of Log \( K_{OA} \) chemical movement via the particle phase dominates, i.e., particle deposition to PUF Layer 1 and vinyl.

The effect of the steady-state assumption and PUF layering was further analyzed using BDE-47. After one year, air, film, and vinyl approximately reached the mass estimated at steady state (Fig. 2.2). Further, BDE-47 mass in PUF Layer 1 was within a factor of 10 of the mass at steady state, while the mass in PUF Layer 2 was four orders of magnitude lower than the mass at steady state.

To understand the effect of PUF layering, the chemical distribution of BDE-47 between sMIM, LP-sMIM and DLP-sMIM, after one year, were compared (Fig. S2.3). The mass of BDE-47 was also nearly identical between the 1 and 2 PUF layer models at steady state (sMIM and LP-sMIM), with the mass was distributed according to the ratio of the volumes of the two PUF layers in LP-sMIM (Fig 2.4a). Overall, \( \sim 98\% \) of total mass in the room was in PUF. However, after one year under unsteady-state conditions (DLP-sMIM), about 70\% of total mass in the system was in PUF and of that, almost exclusively in PUF Layer 1 (Fig S2.4a), consistent with the results of Zhang et al. (2011). The remainder of BDE-47 mass partitioned into film and vinyl after one year, with those two compartments having reached steady state with respect to air. Minimal BDE-47 entered PUF Layer 2 because of the kinetic resistance involved with diffusive transport between the two PUF layers.
2.5 Chemical Transport Rates

2.5.1 Methods

Although steady state will not be reached in the context of a typical indoor environment, we examined the dominant processes responsible for chemical fate over the range of K\textsubscript{OA} values at steady state to eliminate the effect of differences in time to steady state amongst these chemicals. The layered PUF model (LP-sMIM) with a constant emission source of 1 mmol h\textsuperscript{-1} into air was used to so that the effect of the two PUF layering could be better understood. The model investigated the condition of no prior emissions to the room and thus the initial concentration in each compartment was zero. Chemical residence time was calculated in each compartment, as well as the chemical residence time in the overall system. The rate constants for air-PUF, air-vinyl, and air-film chemical transport were calculated following Diamond et al. (1990).

2.5.2 Results

Chemicals in air with Log K\textsubscript{OA} 7-11 were on average 83% in the gas phase versus 17% in the particle phase, and above Log K\textsubscript{OA} 11, were predominantly in the particle phase (Figure S2.5). At Log K\textsubscript{OA} ~7-8.5 (BDE-3), 83% of the chemical mass was in vinyl while 16% was in PUF Layer 2 (Fig. 2.3).

For Log K\textsubscript{OA} 10-18.5 (BDE-28, -47, -66, -99, -100, -138, -153, -154, -190, -209), 93-94% of the mass was in PUF Layer 2, while only 5-6% was found in PUF Layer 1, recalling that this is at steady state and that the difference in chemical mass distribution was due to the difference in PUF layer volume.

Similar to the analysis of Diamond et al. (1990), the dominant transport rate of a chemical as a function of a partitioning coefficient (here log K\textsubscript{OA}) was examined by comparing the magnitude of the overall rate constant, k (h\textsuperscript{-1}) which is determined as k\textsubscript{i}=D\textsubscript{i}/V\textsubscript{i}Z\textsubscript{i}, where D\textsubscript{i} is the specific rate of transfer (mol h\textsuperscript{-1} Pa\textsuperscript{-1}), and Z\textsubscript{i} is the fugacity capacity (mol m\textsuperscript{3} h\textsuperscript{-1}). The four main inter-compartmental transport mechanisms examined in DLP-sMIM were gas diffusion and particle exchange (deposition and resuspension) between air and PUF, vinyl, and film.

The fastest rate constant for chemicals Log K\textsubscript{OA} 4 - 7 was PUF Layer 1-to-air diffusion which decreased logarithmically with increasing Log K\textsubscript{OA} due to increasing kinetic resistance to diffusive transport as a function of increasing molecular weight (Fig S2.6a). The complimentary...
process of air-PUF Layer 1 diffusion had a consistent rate constant between Log $K_{OA}$ 4 – 11 controlled by PUF-side diffusion, after which the rate constant decreases with increasing Log $K_{OA}$ due to decreasing chemical in the gas phase. After Log $K_{OA}$ ~7, the rate constant for air-PUF Layer 1 is faster than the converse due to increases within-PUF diffusive resistance. In contrast to air-PUF Layer 1, the rate constant for particle-sorbed chemical deposition increases until Log $K_{OA}$ 11, above which it reaches an asymptote because most chemical in air is particle sorbed. The rate constant for resuspension is independent of Log $K_{OA}$.

Next, we examined inter-compartmental transport rates which are calculated as the product of the rate constant and mass in a compartment (Fig. S2.7). Diffusive processes dominate transport of chemicals with Log $K_{OA}$ 4 – 11. Beyond Log $K_{OA}$ 12, particle deposition to PUF Layer 1 and vinyl dominates because, as noted above, the kinetic resistance of diffusive transport limits chemical movement. However, because the film layer (on walls) is thinner than the vinyl layer, and because particle deposition and resuspension rates to film are less than that for vinyl, air-film diffusion dominates over particle-related processes up to Log $K_{OA}$ 14.5. Also because of the thin layer of film, air-to-film and film-to-air exchange rates are equal until Log $K_{OA}$ 12, i.e., air and film are in equilibrium, similarly to that found by Csiszar et al. 2012 who examine air-film exchange in the outdoor urban environment.

For BDE-47 (Log $K_{OA}$ 10.7, Fig. 2.4), the dominant net transport process was air to vinyl transport, due to diffusion followed by particle deposition. As the two PUF layers have equifugacity at steady state, there is no net transport between the layers. Loss from the system was attributable to dust removal from vinyl (70%) and air advection (30%). We note that this behaviour as similar under unsteady-state conditions after one year except that there was a net transport of chemical from PUF Layer 1 to 2 (Fig S2.4).

Large differences in chemical transport rates and mass distribution in each compartment resulted in a wide range of chemical residence times, with the shortest being minutes in air controlled by ventilation rate (Fig. 2.5). Chemical in vinyl had a consistent residence time of 86 hours for the range of Log $K_{OA}$, controlled by the dust removal rate. Chemical residence time in film varied from four minutes (BDE-3) to 12 years (BDE-209). For PUF Layer 1, residence time varied from 12 hours to 600 years for BDE-3 and 209, whereas these chemicals had residence times of 1.4 years to 115 billion years in PUF Layer 2. The model results indicate that the potential for
the chemicals to reside in PUF furniture is longer than their usable life span. The overall residence time of the system ranges from three days to 175 years.

2.6 PUF as a Chemical Source

2.6.1 Methods
Flame retardants have been commonly added to PUF furniture to meet flammability requirements. Here we used DLP-sMIM to examine the effect on chemical fate under unsteady-state conditions, with chemical added to PUF. Using the same hypothetical bedroom environment, PUF Layers 1 and 2 were assumed to have concentrations of 1 mol m\(^{-3}\) of each PBDE congener. The model was run for one year with no additional emission source.

2.6.2 Application Results
The introduction of PUF loaded with chemical into a clean indoor environment caused the PUF compartments to act as a source to air and the other compartments, rather than a sink as with the previous scenarios. Considering unsteady-state conditions after one year, the greatest mass in the system is by far in PUF Layer 2 over the range of Log \(K_{OA}\) values. Diffusive release decreased the mass of chemicals with from PUF Layer 2 and between Log \(K_{OA}\) 7.5-11 for PUF Layer 2 (Fig. 2.6). The main recipients of the chemical from PUF are vinyl and film (Fig S2.8).

In more detail, after one year BDE-3 experienced a loss of 95% or 94.8 mmol out of a total of 100 mmol of total PUF (Layer 1 and 2). In comparison, BDE-28, -47, -66 and -99 lost on average 11% or 11.16 mmol out of a total of 100 mmol. However, BDE-100, -138, -153, -154, -190 and 209 experienced <1% depletion of chemical or ~0.3 mmol out of a total of 100 mmol.

Over a 20 year period, 100% of BDE-3 left the two PUF layers. Meanwhile the mass of BDE-28, -47, -66, -99 decreased by ~33% in the two PUF layers. However, for BDE-209 with Log \(K_{OA}\) of 18.5, <1% or 0.6 g was lost from only PUF Layers 1. These results suggest it would be difficult to detect a significant change in in PUF concentrations of higher molecular weight flame retardants (i.e., Log \(K_{OA}\) > 13) when sampled over several years, which is the point of impregnating PUF with flame retardants. Conversely, flame retardants with Log \(K_{OA}\) < 8 would be entirely depleted from PUF after 20 years, having been released to other compartments in the indoor environment and beyond.
2.7 Conclusions

The Multimedia Indoor Model, MIM, was modified by dissecting the compartment signifying PUF furniture into two vertical layers to account for the influence of this compartment as a sink/source of chemicals to the indoor environment. The model was also modified to simulate time dependent or unsteady-state conditions.

The model was evaluated using a case study of PBDEs of a UK office over nine months during which the total PBDE air concentrations decreased by ~80%. The unsteady-state model was able to capture a decrease in air concentrations in response to a change in emission rate. The greatest loss mechanism for this environment was advection (room ventilation), which quickly reduced air concentrations.

The results of this modelling effort show that the PUF compartment is critical to consider when modelling chemical dynamics indoors as it can be a significant sink or source of chemical mass within a room and thus influences overall chemical fate. Moreover, a model of the indoor environment should consider unsteady-state conditions, especially for chemicals with Log $K_{OA} > 10$. The modelling results indicated that chemical in the lower PUF layer will never realistically reach steady-state conditions as the residence time of chemical in the PUF is far longer than the lifespan of furniture. A steady-state assumption is reasonable when examining chemicals with Log $K_{OA} < 10$ in air, surface films on walls, and surface films on vinyl as chemical residence times in these compartments is relatively short.

When considering a room receiving an emission of PBDEs to air, the model showed that most mass accumulated in the top PUF layer (85% for BDE-28), which was consist with the results of Zhang et al (2012). From the analysis of rate constants, it was evident that diffusive transport dominated, with the exception of particle deposition to vinyl and PUF Layer 1 at Log $K_{OA} >12$, and film at Log $K_{OA} >15$. Diffusive movement between PUF layers was limited.

In the circumstance of chemical intentionally added to PUF, as with flame retardants, after one year nearly 100% mass of chemical with Log $K_{OA} < 8$ diffused from PUF Layer 1 into the room in comparison to <1% loss of chemicals with Log $K_{OA} > 13$ after 20 years.
2.8 References


Figure 2.1. Comparison of the DLP-sMIM modeled and Hazarti & Harrad (2006) measured $\Sigma_7$BDEs air concentrations (ng m$^{-3}$) for United Kingdom office over a nine month period.
Figure 2.2 Comparing mass distribution of PBDES at steady state using LP-sMIM versus mass distribution over 365 days using the LP-sMIM model. Assumed a 1 mmol hr\(^{-1}\) emission rate into a zero prior emission and concentration environment.
Figure 2.3 Mass distribution of PBDES at steady state using the LP-sMIM model. Assumed a 1 mmol hr⁻¹ emission rate into a zero prior emission and concentration environment.
Figure 2.4 Fate [mol] and transport [mol h\(^{-1}\)] of (a) BDE-47 and (b) BDE-153 using the LP-sMIM model. Assumed a 1 mmol hr\(^{-1}\) emission rate into a zero prior emission and concentration environment.
Figure 2.5 Relationship between the log $K_{OA}$ and the half-life (system and compartmental) for a range of PBDEs under PUF as a sink conditions using the LP-sMIM.
Figure 2.6 Mass distribution of PBDES at one year using the DLP-sMIM model. Assumed PUF layers have an initial concentration of 1 mmol m\(^{-3}\).
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Dynamic Layered PUF Multimedia Indoor Model
Figures

(a) BDE-28

(b) BDE-47

(c) BDE-66

(d) BDE-99

(e) BDE-100

(f) BDE-153
Figure S2.1 Comparison of the DLP-sMIM modeled and Hazarti & Harrad (2006) measured PBDEs air concentration (ng m\(^{-3}\)) for the United Kingdom office over a nine month period. (a) BDE-28, (b) BDE-47, (c) BDE-66, (d) BDE-99, (e) BDE-100, (f) BDE-153, and (g) BDE-154.

Figure S2.2 Mass distribution of PBDES at one year using the DLP-sMIM model. Assumed a 1 mmol hr\(^{-1}\) emission rate into a zero prior emission and concentration environment.
Figure S2.3 Model comparison of percent mass distribution of BDE-47 between sMIM, LP-sMIM and DLP-sMIM in each compartment.
Figure S2.4 Fate and transport of (a) BDE-47 and (b) BDE-153 at one year using the DLP-sMIM model. Assumed a mmol hr⁻¹ emission rate into a zero prior emission and concentration environment.
Figure S2.5 Gas-phase and particle-phase mass distribution in air for the system using LP-sMIM.
Figure S2.6 Components of the rate constants [h⁻¹] as a function of log $K_{OA}$ for PBDEs for the interactions between (a) air to PUF Layer 1, (b) air to vinyl and (c) air to film.
(a) Transport Process [mol/h] vs. Log $K_{OA}$

- Air to PUF Layer 1 Diffusion
- PUF Layer 1 to Air Diffusion
- Particle Deposition
- Particle Resuspension

(b) Transport Process [mol/h] vs. Log $K_{OA}$

- Air to Vinyl Diffusion [1/h]
- Vinyl to Air Diffusion [1/h]
- Particle Deposition [1/h]
- Particle Resuspension [1/h]
Figure S2.7 Components of the transport mechanism [mol h⁻¹] as a function of log $K_{OA}$ for PBDEs for the interactions between (a) air to PUF Layer 1, (b) air to vinyl and (c) air to film
Figure S2.8  Fate and transport of (a) BDE-47 and (b) BDE-153 at one year using the DLP-sMIM model. Assumed PUF layers have an initial concentration of 1 mmol m$^{-3}$. 
# Tables

## Table S2.1 Physical Chemical Properties of the Studied PBDE Congeners

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<th>Chemical Name</th>
<th>CAS #</th>
<th>Molar Mass (g/mol)</th>
<th>Molar Volume (cm³/mol)</th>
<th>Log₁₀ KₐOA</th>
<th>Reaction HL Air (h)</th>
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### Table S2.3 Dust parameter Properties

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*Reference used for carpet
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Chapter 3
Conclusions

The overarching goal of this research was to estimate the fate and transport of semi-volatile organic compounds, (SVOCs) in the indoor environment, with a focus on improving the polyurethane foam (PUF) compartment. This was accomplished by first simplifying the original Multimedia Indoor Model (MIM), secondly, adding the effect of kinetic resistance between each layer of PUF (LP-sMIM), and finally, and extending the model to treat dynamic conditions (DLP-sMIM). DLP-sMIM was evaluated using measured indoor air concentrations from an office environment. The model also investigated the effect of the inclusion of time dependence and kinetic resistance, in comparison to steady-state results. In addition, the model was investigated for the two applications where PUF is treated as a sink and as a source to the indoor environment.

3 Conclusions

3.1 Research Summary

DLP-sMIM was able to replicate the measured air concentrations from the nine month study over the time course with changing emissions based on the case study of Hazarti and Harrad (Hazrati and Harrad 2006). The modelled air concentrations were on average a factor of 1.1 higher than the measured air concentrations. The quick response regarding the air concentrations adjusting to the new emission rates was attributed to the air exchange rate within the modelled environment.

A model comparison between steady-state and unsteady-state conditions demonstrated that unsteady-state conditions are needed to consider SVOC fate as the system could take an unreasonably long time to reach steady state, longer than the average lifespan of typical household products containing PUF. This is problematic since the steady-state model overestimated the amount of chemical found in the PUF compartments after a short duration of time. Based on this, it can be assumed that for the purposes of modeling, the PUF compartments will never fully reach steady-state condition, and thus the inclusion of a layered PUF compartment assuming unsteady-state conditions is important.
The DLP-sMIM model demonstrated the importance of the PUF compartments, as it was seen as the largest sorptive compartment, as well as the second largest volume in the indoor environment (second to the air compartment, which has a lower fugacity capacity).

Results from the “PUF as a sink” scenario demonstrated that the PUF surface layer was most significant, as it contained the largest amount of chemical in the system. The results were consistent with the study by Zhang et al. (2011), with ~99% of PBDEs were in the first layer (85% for BDE-28) after one year (Zhang, Tsurukawa et al. 2011).

Results from the “PUF as a source scenario” demonstrated that although the PUF will be a source to the indoor environment, the mass of the heavier chemicals will remain unchanged within the PUF layers. The model demonstrated that chemicals in the surface layer were the largest emission source to the indoor environment, while chemicals within the deeper layer remained and could be considered “buried”.

In summary, this thesis presented an updated method to examine the fate and transport of chemicals in the indoor environment. This updated model was able to provide a further understanding of chemical dynamics in the indoor environment, as the indoor environment will tend to vary in terms of environmental parameters and chemical emissions. This model can now be applied to examine the effects of human activities and other activities which can alter the concentration of chemical in the indoor environment, by examining the change in concentration over time, and determining how the system will respond. The model can also be applied to different groups of SVOCs to assess the effect of fate and transport of chemicals with different physical-chemical properties.

3.2 Recommendations for Further Study

To improve the overall quality of the results generated from the model, it is important to obtain the most reasonable estimates for both chemical properties and room (environmental) parameters. As a result of experimental challenges and analytical difficulties, physical-chemical properties may not be available for all chemicals, especially “novel” flame retardants (Covaci, Harrad et al. 2011). Physical-chemical properties such as Log $K_{OA}$ and chemical degradation in various media should be further investigated to properly quantify the chemical fate and transport. Environmental parameters regarding the room (air exchange rates, particle dynamics, and the
partitioning characteristics to materials) are difficult to obtain per room and contribute to uncertainty in the model. To achieve a more complete understanding of the fate and transport of these chemicals, it is suggested that efforts be devoted into obtaining comprehensive realistic properties.

Similarly, the rate of which SVOCs migrate from consumer products and building materials to the indoor environment remain very poorly known. Emission rates are expected to vary according to the properties of the product (density, age of product, operating temperature, etc.), as well as how the external environment can impact the emission rates of certain products. Currently, chemical emissions from selected materials have been derived from individual chamber studies (Rauert, Lazarov et al. 2014). Although these chamber studies provide insight to emission rates, studies have shown that they may not be representative of the emission rate indoors (Xu, Hubal et al. 2009). Increased efforts must be devoted to obtaining a method to determine the emission rates of SVOCs from products.

Multiple studies have shown variability in different room types (bathroom, kitchen, and bedrooms) based on the differentiating room parameters (Xu, Hubal et al. 2010). Each room type will differ in terms of temperature, humidity, dust creation rate and the various sorptive compartments found within each environment. Based on this understanding, it is recommended that the model examine the various room types, to evaluate how the fate and transport of chemical will be altered.

It is well known that any activities within the indoor environment will alter the chemical fate and transport (cleaning, cooking, running, bouncing on furniture, etc.). A major removal pathway for this model was the chemical dust removal through vinyl cleaning. This removal rate will vary and as such could either underestimate or overestimate the removal pathway. While this is a basic understanding, surprisingly little knowledge exists to parameterize a model. As such, it is recommended that further work be done to develop a quantitative understanding to include in a mathematical model.
3.3 References


