EMISSION OF VOLATILE ORGANIC COMPOUNDS FROM MULTI-LAYER STRUCTURAL INSULATED PANELS

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Dissertation submitted to the Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Civil Engineering

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25 August 2005

Blacksburg, Virginia

Keywords: VOC, emission, indoor, modeling, transport, diffusion, SIPs, multi-layer

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ABSTRACT

Indoor air quality is recognized as one of the most important environmental concerns, since people spend almost 90% of their lifetime indoors. Indoor sources of volatile organic compounds (VOCs) are a determinant of air quality in houses. Many materials used to construct and finish the interiors of new houses emit VOCs. These emissions are a probable cause of acute health effects and discomfort among occupants. Ventilation is another determinant of indoor air quality in houses, because it serves as the primary mechanism for removal of gaseous contaminants generated indoors. Thus, higher contaminant concentrations are expected at lower ventilation rates given constant emission rates. The trend in new construction is to make house envelopes tighter for higher energy efficiency. The use of Structural Insulated Panels (SIPs) in new construction and major renovation to create very tight building envelopes is one popular approach to realizing this goal. The basic SIPs configuration uses oriented strand board (OSB) and polystyrene foam (PSF) in a multi-layered sandwich-like structure. Specific benefits of SIPs include lower energy consumption, stronger more durable structures and better resource efficiency. These advantages make panelized systems very attractive from both environmental impact and energy use perspectives. However, there is a potential for houses constructed with SIPs to have degraded air quality relative to conventionally constructed houses that utilize fewer engineered wood products. OSB emits pentanal and hexanal, two odorous aldehydes. These contaminants originate in the wood drying process through the breakdown of wood tissue and are, thus, inherent to most engineered wood products. The PSF in SIPs is a major source of styrene. The large surface area of installed SIPs systems (typically the entire exterior shell), combined with the resulting decrease in ventilation rate due to very low infiltration, exacerbates the

indoor air problem. Thus, the potential release of volatile contaminants must be taken into careful consideration when designing homes constructed with SIPs. The ability to predict and ultimately minimize the negative impact of panel systems on indoor concentrations of contaminants of concern would be extremely useful for advancing housing technologies. No prior investigations of VOC emissions from SIPs have been reported in the literature.

Two main methods are used to characterize emissions from building materials: chamber studies and mathematical modeling. While chamber studies are costly and time-consuming, mathematical modeling is becoming an economical and effective alternative. Physically-based models are especially useful because they provide insight into the governing mechanisms and the factors that control the emissions process. Although emissions from building materials have traditionally been empirically characterized in chambers, we have recently validated a mechanistic model that predicts VOC emissions from vinyl flooring. The approach involved independently measuring C_0 (the initial material-phase concentration), D (the material-phase diffusion coefficient), K (the material/air partition coefficient) and then predicting the emission rate *a priori* using a fundamental mass-transfer model We now wish to generalize this approach and use it to predict emissions from multi-layered SIPs. To begin with, we will apply a single-layer model to predict emissions from each of the two SIP components: OSB and PSF. Once this has been accomplished, it should be possible to develop a multi-layer model to predict emissions from the composite SIPs.

Our first research objective was to characterize transport of volatile organic compounds (VOCs) in polystyrene foam (PSF), a diffusion-controlled building material. The sorption/desorption behavior of the polystyrene foam was investigated using a single-component system. A microbalance was used to measure the sorption/desorption kinetics and to obtain equilibrium relationships. Hexanal and styrene were selected as the target compounds. While styrene transport in PSF can be described by Fickian diffusion with a symmetrical and reversible sorption/desorption process, the hexanal transport process exhibited significant hysteresis, with desorption being much slower than sorption. To address this hysteresis, a porous media diffusion model that assumes local equilibrium

governed by a non-linear Freundlich isotherm was developed. The model was found to conform closely to the experimental kinetic data for both sorption and desorption. By incorporating the Freundlich sorption mechanism into the traditional Fickian diffusion model, the hysteresis in the hexanal transport process in PSF was explained.

Contaminant emissions from building materials may tail extensively and require longer times to desorb than absorb. This slow desorption or hysteresis problem has been an obstacle to understanding VOC emissions from building materials. The overall goal of our second research objective was to (i) develop a predictive nonlinear emission model by incorporating a local Freundlich sorption equilibrium to account for the slow desorption; (ii) validate the new nonlinear emission model using independent chamber data; and (iii) compare the new nonlinear emission model with a previously published linear emission model. Styrene in polystyrene foam (PSF) and hexanal in oriented strand board (OSB) were selected as the target compounds and materials, respectively. Sorption/desorption kinetic experimental data show that while styrene sorption/desorption in PSF is symmetrical, hexanal sorption/desorption in OSB is not symmetrical. For hexanal in OSB, slower desorption was observed. Model validation results show that while the simple linear emission model can predict styrene emissions from PSF, it underestimates hexanal emissions from OSB. With the new nonlinear emission model developed in this research, hexanal emission from OSB can be predicted. These results suggest that local sorption equilibrium needs to be considered when predicting the emission rate of polar compounds from building materials.

The final objective was to develop a new multi-layer model for a layered SIP system. Composite layered building materials are widely used in indoor environments due to their environmental and energy advantages. However, the tight structure may result in degraded indoor air quality and the potential release of volatile organic compounds (VOCs) from these layered materials must be considered. A theoretical physically-based diffusion model for predicting VOCs emissions from such multi-layer materials is described in this research. It is assumed that the individual layers are flat homogeneous slabs, that internal mass transfer is governed by diffusion, and that the indoor air is well mixed. For each layer, the material-phase diffusion coefficient (D), the material-phase

partition coefficient (K), and the initial material-phase concentration (C_0) are the key model parameters. In this model, fugacity is used to numerically solve the model because this eliminates the discontinuities in concentration at the interface between layers. This overcomes an insurmountable obstacle associated with numerically simulating mass transfer in composite layers. The fugacity-based numerical model is checked by comparing predicted concentrations to those obtained with a previously published analytical model for double-layered materials. In addition, transport of hexanal and styrene within, and emissions of hexanal and styrene from, multi-layer Structural Insulated Panels (SIPs) are simulated to demonstrate the usefulness of the model. These preliminary results establish the viability of the fugacity approach. Finally, the multi-layer layer model is used to demonstrate the impact that barrier materials can have. Results show that contaminant gas phase concentration can be reduced greatly with a barrier layer on the surface. This deomonstrates the potential of thin barrier layers to minimize the environmental impact of panelized systems. Future work will focus on a more complete experimental validation of the multi-layer model.

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REVIEW: PHYSICALLY-BASED MODELING OF VOC EMISSIONS FROM DIFFUSION-CONTROLLED BUILDING MATERIALS

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ABSTRACT

When predicting VOC emissions from building materials, physically-based models are of greater value than empirical models. The value of these models is that they decouple the emission behavior from the experimental test conditions and provide an insight into the controlling mechanisms of the emissions process. They do this by taking the controlling mechanism into account, especially in complex situations. Another desirable feature of physically-based models is that each parameter essentially represents a property of either the building material or of the environment, but not both. Current levels of understanding, development and extensions of a basic single-layer, physically-based, diffusion model are discussed in this paper. Emphasis is first placed on the model concept and assumptions, on the model parameters, and on the model limitations. In a subsequent step, various extensions of the basic single layer diffusion model are reviewed. Finally, attention is given to future research that is needed or currently underway.

KEYWORDS

Modeling, emissions, physically-based, diffusion, dry building materials, indoor air quality

INTRODUCTION

Over the past decades, volatile organic compound (VOC) emissions from building materials such as vinyl flooring, polymeric materials, engineered wood, carpet, and paint have continuously been reported, and have been a major concern of indoor air quality

(IAQ) problems (Baumann, 1988, Colombo, 1990, Haghighat and Donnini, 1993, Yu, 1998). To date, there are two primary methods applied to the study of VOC emissions from building materials: an experimental chamber test and mathematical modeling. A chamber test can be costly and time-consuming and cannot necessarily be scaled up to represent real indoor conditions. Providing mathematical models can be adequately validated, they may provide a more cost effective and powerful way to characterize VOC emissions from a wide range of building materials.

Typically, three steps are considered in the VOC emissions process: internal diffusion in the material phase; partitioning into the air at the material-air interface, and convective mass transfer through a boundary layer into the bulk air phase. These same three steps are reversed during sorption, or what is sometime referred to as the sink effect. The very simplest emission models consider only sorption/desorption at the material-air interface. Together with mass balance equations, such simple surface models have been developed and widely used to predict VOC release from building materials (Dunn, 1987, Tichenor, 1991, Bouhamra, 1999, Won, 2000). However, the limitations that exist in this simple surface emission model cannot be neglected. First, the model parameters, such as the sorption/desorption coefficients, are almost always obtained by curve fitting the experimental chamber data (Corsi, 1999, Tichenor, 1990, Van der Wal, 1998). Due to this semi-empirical feature, the model prediction depends on both the properties of the materials and the environmental parameters, such as ventilation, temperature, humidity and chamber pollutant concentration (Jorgensen, 1999). This means that one model developed for a specific chamber environment cannot be used under other conditions and that the model validated in a small test chamber cannot be scaled up and applied to real indoor environments. In addition, these models are unable to characterize the long "tail" of the desorption curve from more complex materials like carpets (Jorgensen, 2000).

For most dry building materials such as carpet, vinyl floor, gypsum board and wood-based panels, it is not enough to consider only the surface sorption/desorption process. Several researchers have found that VOC emissions from these building materials are controlled by internal diffusion (Clausen, 1993, Hehl, 1999, Meininghaus, 2000). Thus,

physically-based emission models considering internal diffusion in the source had to be developed. Compared with the simple surface model, such models take the physical controlling phenomena into more complete consideration. The value of these models is that they decouple the emissions behavior from the experimental test conditions and provide an insight into the controlling mechanisms of the emission process. Another desirable feature of this physically-based modeling approach is that each parameter essentially represents a property of either the building material or the environment, but not both. The earliest diffusion models were developed for an infinitely deep source (Dunn, 1987), but cannot be used for a finite source (Little et al., 1994). In a further step, a finite source was considered by some researchers (Clausen, 1993, Dunn and Chen, 1992), but this model invoked concentration-dependent diffusion, which is not usually necessary at the relatively low VOC concentrations found indoors. In addition, these early diffusion models ignored the equilibrium partitioning between the bulk air and the source surface, because the VOCs had relatively high vapor pressures. Starting from the basic single-layer emissions model (Little et al., 1994), which addressed the shortcomings of these earlier emission models, we will review the limitations and extensions of the physically-based modeling approach. In addition, possible directions for future research will be discussed.

BASIC SINGLE-LAYER DIFFUSION-CONTROLLED EMISSION MODEL

The basic physically-based diffusion model was first proposed to account for observed emissions of VOCs from new carpets (Little et al., 1994). The model is based on Fick's Law of diffusion. Several assumptions were made in the development of the initial model:

1. The source material is homogenous, and the initial concentration is uniform in the materials.
2. The material can be regarded as a finite source.
3. The material-phase diffusion coefficient, D, and the material/air partition coefficient, K, are both independent of concentration.

4. The chamber air is well mixed.

5. The internal chamber surface sink effect is neglected.

6. The convective mass-transfer between the material surface and the bulk air in the chamber is rapid in comparison to the rate of diffusion within the material and can be neglected.

7. The material-phase diffusion is one-dimensional.

8. There is no flux out of the base of the material.

9. Equilibrium exists between the VOC concentrations in the material surface layer and the chamber air.

The model provided a good fit to the experimental data for most compounds emitted from the polymer backing of new carpets (Little et al., 1994). However, the model parameters (the initial material-phase concentration of a VOC, the material-phase diffusion coefficient and the equilibrium material/air partition coefficient) were obtained to some extent by fitting the model to the observed gas-phase chamber concentration data. In a subsequent study, the model was further explored and validated for three contaminants (n-pentadecane, n-tetradecane, and phenol) found in vinyl flooring (VF) (Cox et al., 2002). In this validation process, the assumption that the chamber sink is negligible was also examined. The model was validated by comparing the predicted gas-phase concentration against the experimental data obtained during small-scale chamber tests, and by comparing predicted material-phase concentrations to those measured at the conclusion of the chamber tests. The results indicated that there is, in general, very good agreement between the model predictions and the experimental results, and that the chamber sink effect is not significant. These results are very promising since the model parameters (C_0, K, and D) were measured using procedures completely independent of the chamber test.

An equivalent sink model describing VOC uptake by a homogenous, diffusion-controlled, building material has also been developed (Little and Hodgson, 1996). For the sink model, the initial condition assumes that the concentration of VOCs in both the air and the material phase is zero and that there is an influent pollutant gas flow into the chamber.

Except for this, the governing equations and assumptions remain the same as for the basic source model. The model enables transient VOC concentrations to be predicted based on the known K and D of the specific material/VOC combination. In a subsequent step, this sink model was successfully validated with n-dodecane and phenol as the influent VOCs and vinyl flooring (VF) as the sink material in a small stainless steel chamber (Kumar and Little, 2003). Finally, the basic source/sink model was applied to predict indoor VOC concentrations using three realistic source scenarios, a sinusoidal input, a double exponential decaying input, and an episodic chemical spill (Zhao et al., 2001), in which a styrene butadiene rubber (SBR) backed carpet, vinyl flooring (VF) and a polyurethane foam (PUF) were considered as typical indoor sinks and styrene, phenol, and naphthalene were used as representative VOCs.

MODEL PARAMETERS

In the development of the diffusion-controlled models, the key parameters are the initial concentration in the material phase (C_0), the material/air partition coefficient (K), the material-phase diffusion coefficient (D) and the external convective mass transfer coefficient (h_m). These are shown schematically in Figure 1. The impact of these parameters on VOC emissions from building materials and model prediction have recently been studied (Huang et al., 2003, Yang et al., 2001a). The parameters can be measured independently, or if this is not possible, inferred from chamber test data.
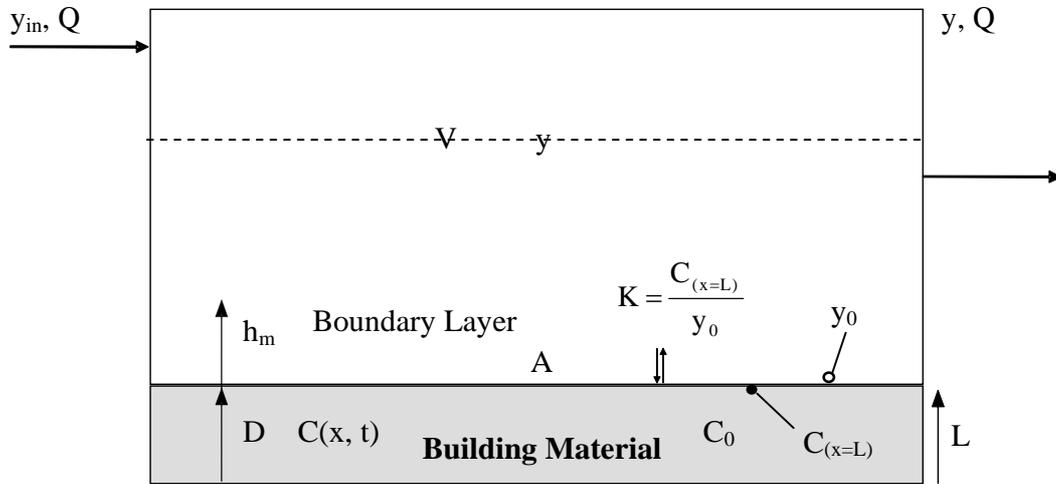
Figure 1.   Schematic representation of the basic single layer model

C_0

Special attention should be paid to C_0 because the gas-phase VOC concentration in the chamber air depends linearly on C_0, and C_0 determines both the short-term and long-term emission characteristics (Yang et al., 2001b).   An error in the initial concentration estimate will cause a proportional error in prediction results. The effect of a non-uniform distribution of the initial concentration in the material phase on VOC emissions is especially important during the early emission period (Xu and Zhang, 2003).

For a single compound, C_0 is defined as the readily emitted mass of compound per unit mass of the material subject to certain environmental conditions. Several methods have been used to obtain C_0 experimentally: solvent extraction; high temperature thermal desorption; direct headspace analysis; and cryogenic milling/fluidized bed desorption. The first three of these methods either use high temperatures or chemical solvents, which can modify the physical structure of polymeric materials and, consequently, affect mass transfer characteristics. The fourth and last method developed avoids these limitations. The benefits of the cryogenic milling/fluidized bed desorption method include reduced

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potential for VOC loss during sample preparation, reduced VOC extraction time, and improved representative sampling of the material phase (Cox et al., 2001a).

D and K

The diffusion coefficient (D) determines the rate of diffusion of a VOC through the material and is usually a function of several factors such as material type, compound properties, temperature, as well, in some circumstances, as the material-phase VOC concentration. The material/air partition coefficient (K) describes the equilibrium relationship between the concentration in the gas phase and the concentration in the material phase. The dependence of K and D on concentration is usually ignored since the VOC concentration in the material is usually relatively low.

Several procedures have been used to measure the D and K values of volatile compounds in building materials. These are (1) Cup method: the diffusion coefficient of the test material is assessed by measuring the weight loss caused by VOC diffusion through a material sample covering a cup containing a liquid VOC at saturation under controlled temperature and humidity conditions. It is the simplest method, but the main drawback is that the liquid VOC placed in the cup creates a saturation concentration, which is unrealistically high for indoor air applications. To overcome this, the dry cup method can be used, but it takes a longer time (Haghighat et al., 2002). (2) The two chamber method. In this method, a sample of building material is installed between two compartments and a particular concentration of compound is introduced into the gas-phase of one compartment while the gas-phase concentration in the other compartment is monitored over time. D and K are then indirectly estimated from the gas-phase concentration data (Haghighat et al., 2002). A complicating feature of this method is that VOC transport between the two chambers may occur by rapid gas-phase diffusion if the material being studied is relatively porous. This two chamber method can be used to determine K and D under steady state or transient conditions (Bodalal et al., 2000, Meininghaus et al., 1999). (3) Porosity test method. This method is only for measuring D and can only be applied to homogeneous and single layer materials. (4) Microbalance method. In this method, the

parameters are obtained by weighing a test sample on a microbalance and sweeping the sample chamber with an inert gas containing a known VOC concentration. This simple and rapid experimental method can be used for directly measuring the K and D values, and can be applied to diffusion-controlled materials such as VF (Cox et al., 2001). A recent study extended this method to porous materials such as polyurethane foam (Zhao et al., 2004).

When direct experimental measurements are not available, there are two methods that can be used to obtain K and D. The first is to fit the chamber emission data with the emission models (Yang et al., 1998, Xu and Zhang, 2003). Second, since D and K are related to compound properties such as vapor pressure and molecular weight, it is possible to develop correlations between them for specific materials. Such correlations for three classes of VOCs: aliphatic hydrocarbons, aromatic hydrocarbons and aromatic hydrocarbons diffusing through the building materials (plywood, particleboard, vinyl floor tile, gypsum board, subfloor tile and oriented strand board) were developed recently (Bodalal et al., 2001). Similarly, relationships between K and vapor pressure and D and the molecular free surface area were used to develop correlation equations for a series of aromatic compounds interacting with polyurethane foam (Zhao et al., 2004).

Gas Phase Convective Mass Transfer Coefficient

The external convective mass-transfer coefficient is denoted h_m. It is affected by both environmental factors and compound properties and is usually determined by the fluid dynamic conditions of the environment. This is a result of the fact that the coefficient in test chambers can differ from those in indoor environments. Such differences may cause scaling-up problems in the use of chamber-derived emission rates in IAQ models. The gas phase mass-transfer coefficient is difficult to determine experimentally. Correlations with the Reynolds and Nusselt numbers can be used to scale this coefficient. Such correlations have been reported in the literature (Haghighat and Zhang, 1999 and Sparks et al., 1996).

EXTENSIONS TO THE BASIC SINGLE LAYER MODEL

Starting with the basic single layer model (both source and sink), research has recently been done to consider more general conditions. One type of extension concerns the initial concentration conditions. In the single-layer emission model, it is assumed that the initial material-phase concentration is uniform, and that the inlet air stream contains no VOCs. However, a recent study of VF has revealed a non-uniform initial concentration profile for some compounds (Cox et al., 2002). In addition, in a real situation, some outdoor pollutants can also enter the indoor environment by infiltration or ventilation. Thus, the simple single-layer model needs to be extended to include more generalized initial and boundary conditions in order to be more widely applicable. Such a generalized model has recently been developed and validated (Kumar and Little, 2003). A non-uniform initial material-phase concentration and a transient influent gas-phase concentration were simultaneously considered. Similarly, a model in which a non-uniform initial VOC concentration distribution was considered, has been developed (Xu and Zhang, 2003), but it was only validated for the specific case where the initial concentration was uniform.

Another important and popular extension of the basic single layer emission model is the assumption that the resistance between the bulk air and the air layer near the material surface is negligible. Researchers think that this assumption may be true for some dry materials, but it has not been well justified in general. When the near-surface concentration gradient is relatively high, such simplified assumptions might cause an underestimation of VOC emissions at an early stage (Xu and Zhang, 2003). In recently developed models, both the boundary layer resistance and the internal resistance were considered. A complete numerical model and an analytical model considering both resistances have been developed to simulate dry material emissions for short and long periods, respectively (Yang et al., 1998, Huang et al., 2002, Xu and Zhang, 2003). Although the parameters in these models were obtained by curve fitting or numerical methods, the theoretical development is a good addition to the basic single layer model.

Such a numerical model was used to describe emissions from vinyl wallpaper and gypsum board (Park et al., 1999).

The third extension has to do with the source material dimensions. Based on the fact that the thickness of the material is negligible compared to the overall emissions surface area, and that emissions from the edges of the test sample and concentration gradients parallel to the surface can be ignored, most diffusion-controlled models are developed in one dimension (1-D). However, in practice, emissions can be 2-D or 3-D with complicated boundary conditions, so a multi-dimensional model may be a useful extension to the research. A 2-D numerical model has been developed to simulate VOC emissions from a styrene-butadiene rubber (SBR) backed carpet, but the partition coefficient at the material-air interface was ignored, and use of the model is limited to materials with extremely small diffusivity or very long-term emissions (Yang et al., 1998). A comprehensive mass transfer model including the mechanisms that affect dry material emissions was developed, and has been validated for two different particle board samples (Yang et al., 2001). However, the four model parameters were determined by fitting the model to the gas-phase chamber data, and a more rigorous validation process is needed.

Other extensions are concerned with particular dry building materials, such as porous materials. These dry materials were viewed as single phase and homogeneous in the basic model, which can also be called a continuum model from this point of view. Comparatively, considering dry materials to be porous materials, some researchers developed another kind of diffusion-controlled model, called a multi-phase model (Meininghaus and Uhde, 2002, Murakami et al., 2003). The feature of this type of model is that porosity is taken into account and that diffusion within the nonporous part is neglected.

FUTURE RESEARCH

Although there have been many advances in the development of mathematical models for building materials, a model which can overcome all the existing shortcomings is not yet available and more aspects need to be considered in future research.

Multi-layer Model

The basic model can only be used for a single-layer system. In reality, many products used in buildings are comprised of one or more layers of material. For example, wallboard is a layered system of paper and gypsum, and VF is usually installed using an adhesive that is also a source of VOCs. A logical and promising extension of the single-layer approach is to apply the model to predict the behavior of double-layer or multi-layer systems. However, almost no research has been done on multi-layer systems. A theoretical basis for extending the single-layer model to a double-layer system was recently described and an analytical solution was provided (Kumar and Little, 2003), but it has not been strictly validated. In future, a numerical or analytical solution for a multi-layer model needs to be obtained and generalized to allow for the incorporation of any number of layers. The model also needs to be validated using small- or medium-scale environmental chamber data.

Multi-sources and Multi-sinks

The foregoing models that have been described in this paper address the very simple case of source/sink effects from building materials: a single VOC with a single source/sink in a single room. In reality, an observed organic concentration cannot easily be assigned to any one particular source. Similarly, more than one sink exists in a real room. When multiple materials exist in a room, one material might serve as a sink while another serves as a source. The difficulty is how to include all the sources and sinks in the model. In addition, the variations in individual sources and their strengths with time make the task difficult. In the future, more work needs to be done to consider multiple sources and sinks.

Chemical Reactions

One of the implicit assumptions in the previous models is that there are no chemical reactions at the surface and in the material that either generate or consume VOCs. However, it is recognized that some chemical reactions might occur between chemical compounds and the material surface (Salthammer et al., 1999, Salthammer et al., 2002, Szekely et al., 1963). It will be of interest to examine the effect of chemical reaction at the interface on the mass-transfer rate.

Incomplete Mixing

Care should be taken in assuring instantaneous and complete mixing. Under incomplete mixing conditions, the single layer model would tend to over-predict the early chamber data and under-predict the later data. It is suggested that some discrepancies between predicted and measured results might be due to instability and partial mixing in the chamber at the beginning of the tests (Yang et al., 2001, Huang et al., 2001). Future research should take into account this effect.

SVOCs

With some similarities to VOCs, applying the developed emission model to SVOCs will be of great interest. The strategy to directly measure the model parameters and then predict the emission rate appears to be very promising. However, some difficulties also exist. The primary difficulty is the need to establish the concentration dependence of the permeation parameters, and to take into account the significant sink effect. Due to the much higher concentration of SVOCs in the source material, D is almost certain to be dependent on concentration, and this dependence will need to be established. K is also expected to be concentration dependent. In addition, the low vapor pressure of the SVOCs means that there will be a significant "sink" effect with the SVOCs adsorbing strongly to the interior chamber walls.

Integrating with Other Models

Five principal factors control the generation and ultimate fate of emissions in a room with restricted flow: sources, sorption/desorption, mixing volume, air exchange, and removal. Thus future research needs to be considered that combines emission source and sink models with other room air models. For example, a multi-layer emission model, a single layer material sink model and a room air VOC concentration model have been integrated to study the material's substrate and sink effects (Haghighat et al., 2001). It was applied to a room with a floor assembly as source material and with plywood walls as sink materials. In addition, a trade-off exists between good indoor air quality, which requires sufficient ventilation, and energy saving, which in turn requires that ventilation be kept to a minimum. Some computational fluid dynamics (CFD) models, which are capable of dealing with pollutant transport across the boundary layer, as well as internal diffusion, without having prior knowledge of which is the limiting process, can also be combined with emission models. Future mathematical emission models may be used with other room air models for better adjustment of room ventilation to the actual needs of occupants.

ACKNOWLEDGEMENT

REFERENCES

An, Y., Zhang, J. S. and Shaw, C. Y., 1999, Measurements of Voc Adsorption/Desorption Characteristics of Typical Interior Building Material Surfaces, *International Journal of HVAC&R Research*, Vol.5, No.4, 297-316.

Baumann, M., 1996, Volatile Organic Chemical Emissions from Composite Wood Products: A Review. USDA Forest Service, Forest Products Laboratory, *Technology Summaries*, 5-12.

Bjorn, L., Beng, J. and Birgitta E., 1999, Materials Emission of Chemicals-PVC Flooring Materials, *Indoor Air*, Vol.9, 202-208.

Bodalal, A., et al., 2001, Correaltions between Internal Diffusion and Equilibrium Partition Coefficients of Volatile Organic Compounds in Building Materials and the VOC Properties, *ASHRAE Transactions*, Vol.107, No.1, 789-800.

Bodaldal, A., Zhang J. S. and Plett E. G., 2000, A Method for Measuring Internal Diffusion and Equilibrium Partition Coefficients of Volatile Organic Compounds for Building Materials, *Building and Environment*, Vol.35, 101-110.

Bortoli, D. et al., 1996, Attempting to Characterize the Sink Effect in a Small Stainless Steel Test Chamber, Characterizing Sources of Indoor Air Pollution and Related Sink Effects, *ASTM STP 1287*, 307-320.

Bouhamra, W. and Elkilani, A., 1999, Development of a Model for Estimation of Indoor Volatile Organic Compounds Concentration Based on Experimental Sorption Parameters, *Environmental Science and Technology*, Vol.33, 2100-2105.

Clausen, P.A. et al., 1993, Emission of Volatile Organic Compounds from a Vinyl Floor Covering, In Modeling of Indoor Air Quality and Exposure, N L Nagda, ed. Philadelphia: *ASTM STP 1205*.

Colombo, A. et al., 1990, Chamber Testing of Organic Emissions from Building and Furnishing Materials, *Science of Total Environment*, Vol.91, 237-249.

Colombo, A. et al., 1993, Adsorption of Selected Volatile Organic Compounds on a Carpet, a Wall Coating, and a Gypsum Board in a Test Chamber, *Indoor Air*, Vol.3, 276-282.

Corsi, R. L., Won, D. and Rynes, M., 1999, The Interaction of VOCs and Indoor Materials: an Experimental Evaluation of Adsorptive Sinks and Influencing Factors, *Proceedings of the 8th international conference on Indoor Air Quality and climate*, Edinburgh, Vol.1, 390-395.

Cox, S. S. et al., 2002, Predicting the Emission Rate of Volatile Organic Compounds from Vinyl Flooring, *Environmental Science and Technology*, Vol.36, 709-714.

Cox, S. S., Little C. J. and Hodgson T. A., 2001a, Measuring Concentrations of Volatile Organic Compounds in Vinyl Flooring, *Journal of Air & Waste Management Association*, Vol.51, 1195-1201.

Cox, S. S., Zhao D. and Little C. J., 2001b, Measuring Partition and Diffusion Coefficients for Volatile Organic Compounds in Vinyl Flooring, *Atmospheric Environment*, Vol.35, 3283-3830.

Dunn, J. E., 1987, Models and Statistical Methods for Gaseous Emission Testing of Finite Sources in Well-mixed Chambers, *Atmospheric Environment*, Vol.21, No.2, 425-430.

Dunn, J. E. and Tichenor, B. A., 1988, Compensation of Sink Effects in Emission Test Chambers by Mathematical Modeling, *Atmospheric Environment*, Vol.22, No.5, 885-894.

Dunn, J. E. and Chen, T., 1992, Critical Evaluation of the Diffusion Hypothesis in the Theory of VOC Sources and Sinks, *Symposium on Modeling Indoor Air Quality and Exposure*, Pittsburgh, PA, ASTM, Philadelphia, PA, 27-28.

Haghighat, F., Lee, C. S. and Ghaly, W. S., 2002, Measurement of Diffusion Coefficients of VOCs from Building Materials: Review and Development of Calculation Procedures, *Indoor Air*, Vol.12, 81-91.

Haghighat, F and Zhang, Y., 1999, Modeling of Emissions of Volatile Organic Compounds from Building Materials-Estimation of Gas-Phase Mass Transfer Coefficient, *Building and Environment*, Vol.34, 377-389.

Haghighat, F. and Donnini, G., 1993, Emission of Indoor Pollutants from Building Materials- State of the Art Review, *Architectural Science Review*, Vol.36, 13-22.

Hansson, P. and Stymne, H., 2000, VOCs Diffusion and Absorption Properties of Indoor Materials- Consequences for Indoor Air Quality, In: seppanene, O. and Sateri, J. (eds) *Healthy Buildings 2000*, Vol.4, 151-156.

Hehl, O., Horn, W. and Seifert, B., 1999, Numerical Simulation of VOC Emission Rates from Building Products Based on the Physical Processes, *Proceeding of Indoor Air'99*, No.5, 217-222.

Huang, H. and Haghighat, F., 2003, Building Materials VOC Emissions- A Systematic Parametric Study*, Building and Environment*, Vol.38, No.11, 995-1005.

Huang, H and Haghighat, F., 2002, Modeling of Volatile Organic Compounds Emission from Dry Building Materials, *Building and Environment*, Vol.37, No.11, 1127-1138.

Jorgensen, R .B., Bjorseth, O. and Malvik, B., 1999, Chamber Testing of Adsorption of VOC on Material Surfaces, *Indoor Air*, Vol.9, 2-9.

Jorgensen, R .B., Dokka, T. H. and Bjorseth, O., 2000, Introduction of a Sink-Diffusion Model to Describe the Interaction between Volatile Organic Compounds (VOCs) and Material Surfaces, *Indoor Air*, Vol.10, 27-38.

Kumar, D. and Little, C. J., 2003, A Single-Layer Model to Predict the Source/Sink Behavior of Diffusion-Controlled Building Materials, *Environmental Science and Technology*, Vol.37, 3821-3827.

Kumar, D. and Little, C. J., 2003, Characterizing the Source/Sink Behavior of Double-layer Building Materials, *Atmospheric Environment,* Vol.37, No.39, 5529-5537.

Lee, C. S, Ghaly, W. and Haghighat, F., 2000, VOC Emission from Diffusion Controlled Building Material: Analogy with Conjugate Heat Transfer, *Proceeding of Healthy Building 2000*, Vol.4, 163-168.

Little, C. J. and Hodgson, A. T., 1996, A Strategy for Characterizing Homogenous, Diffusion-Controlled, Indoor Sources and Sinks, *Standard Technical Publication 1287, ASTM*, 294-304.

Little,.C. J., Hodgson, A. T. and Gadgil, A. J., 1994, Modeling Emissions of Volatile Organic Compounds from New Carpets, *Atmospheric Environment*, Vol. 28, No.2, 227-234.

Mattews, T. G., Hawthorne, A. R. and Thompson, C. V., 1987, Formaldehyde Sorption and Desorption Characteristics of Gypsum Wallboard, *Environmental Science and Technology*, Vol.21, 629-634.

Meininghaus, R., Gunnarsen, L. and Knudsen, H. N., 2000, Diffusion and Sorption Of Volatile Organic Compounds in Building Materials Impact on Indoor Air Quality, *Environment Science and Technology*, Vol.34, 3101-3108.

Meininghaus, R., Salthammer, T. and Knoppel, H., 1999, Interaction of Volatile Organic Compounds with Indoor Materials- A Small-Scale Screening Method, *Atmospheric Environment*, Vol.33, 2395-2401.
Molhave, L., 1982, Indoor Air Pollution Due to Organic Gases and Vapours of Solvents in Building Materials, *Environmental International*, Vol.8, 117-127.

Murakami, S. et al., 2003, Modeling and CFD Predictions for Diffusion and Adsorption within Room with Various Adsorption Isotherms, *Indoor Air*, Vol.13, No.6, 20-27.

Park, J. S. and Fuji, S., 1999, Evaluation Of VOCs Emissions from Solid Building Materials by Diffusion Model, *Proceeding of Indoor Air'99,* No.5,161-166

Meininghaus, R. and Uhde, E, 2002, Diffusion Studies of VOCs Mixtures in Building Material, *Indoor Air*, Vol.12, 215-222.

Salthammer, T. et al., 2002, Formation of Organic Indoor Pollutants by Uv-Curing Chemistry, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol.152, 1-9.

Salthammer, T., Schwarz, A. and Fuhrmann, F., 1999, Emission of Reactive Compounds and Secondary Products from Wood-Based Furniture Coatings, *Atmospheric Environment*, Vol.33, 75-84.

Sparks, L. E. et al., 1996, Gas-Phase Mass Transfer Model for Predicting Volatile Organic Compound Emission Rates from Indoor Pollutant Sources, *Indoor Air*, Vol.6, 31-40.

Sparks, L. E. et al., 1991, Comparison of Data from the IAQ Test House with Predictions of an IAQ Computer Model, *Indoor Air*, Vol.1, 577-592.

Szekely, J., 1963, The Effect of Instantaneous Chemical Reactions at the Interface on Diffusion in a Composite Medium, *Int. J. Heat Mass Transfer*, Vol.6, 1077-1082.

Tichenor, B. A. et al., 1991, The Interaction of Vapor Phase Organic Compounds with Indoor Sinks, *Journal of Indoor Air*, Vol.1, 23-25.

Van der Wal, J. F., Hoogeveen, A. W. and Van L., 1998, A Quick Screening Method for Sorption Effects of Volatile Organic Compounds on Indoor Materials, *Indoor air*, Vol.8, 103-112.

Won, D., Corsi, R. L. and Rynes, M., 2000, Sorptive Interactions between VOCs and Indoor Materials, *Environmental Science and Technology*, Vol.34, 4193-4198.

Xu, Y. and Zhang, Y., 2003, An Improved Mass Transfer Based Model for Analyzing VOC Emissions from Building Materials, *Atmospheric Environment*, Vol.37, 2497-2505.

Yang, X et al., 2001a, A Mass Transfer Model for Simulating VOC Sorption on Building Materials, *Atmospheric Environment*, Vol.35, 1291-1299.

Yang, X. and Chen, Q., 2001b, Numerical Simulation of VOC Emissions from Dry Materials, *Building and Environment*, Vol.36, 1099-1107.

Yang, X., Chen, Q. and Bluyssen, P. M., 1998, Prediction of Short-Term and Long-Term Volatile Organic Compound Emissions from SBR Bitumen-Backed Carpet at Different Temperature, *ASHRAE Transactions*, Vol.104, No.2, 1297-1308.

Yu, C. and Crump, D., 1998, A Review of the Emission of VOCs from Polymeric Materials Used in Buildings, *Building and Environment*, Vol.33, 357-374.

Zhao, D., Little, C. J. and Cox, S. S., 2003, Characterizing Polyurethane Foam as a Sink for or Sources of VOCs in Indoor Air, *Journal of Environmental Engineering*, Vol.130, No.9, 983-989.

Zhao, D., Little, C. J. and Hodgson, T. A., 2002, Modeling the Reversible, Diffusive Sink Effect in Response to Transient Contaminant Sources, *Indoor Air*, Vol.12, 184-190.

CHAPTER 1: SORPTION/DESORPTION OF VOCS IN POLYSTYRENE FOAM

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ABSTRACT

Transport of volatile organic compounds (VOCs) in polystyrene foam (PSF), a diffusion-controlled building material, was characterized. The sorption/desorption behavior of the polystyrene foam was investigated using a single-component system. A microbalance was used to measure the sorption/desorption kinetics and to obtain equilibrium data. Hexanal and styrene were selected as the target compounds. While styrene transport in PSF can be described by Fickian diffusion with a symmetrical and reversible sorption/desorption process, hexanal transport exhibited significant hysteresis, with desorption being much slower than sorption. To address this hysteresis, a porous media diffusion model that assumes local equilibrium governed by a non-linear Freundlich isotherm was developed. The model was found to conform closely to the experimental data for both sorption and desorption. By incorporating the rapidly reversible Freundlich sorption mechanism with the traditional Fickian diffusion process, the hysteresis in the hexanal transport process was explained.

KEYWORDS

Modeling, transport, sorption, desorption, diffusion, hysteresis, VOCs, polystyrene foam, styrene, hexanal, sorption isotherm

INTRODUCTION

In recent years, significant attention has been given to investigating indoor air contamination caused by the emissions of volatile organic compounds (VOCs) from

different building materials. Polystyrene foam (PSF) is a porous material widely used for thermal insulation of walls, roofs and ceilings (Wong and Liang, 2004). A typical example of PSF application is structural insulated panels (SIPs), which use oriented strand board (OSB) and PSF in a multi-layered, sandwich-like structure. OSB is a source of pentanal and hexanal, two odorous aldehydes (Barry and Corneau, 1999). Polystyrene foam emits styrene and ethylbenzene as the monomer impurities, and low amounts of other monoaromatic hydrocarbons (Hodgson, 2004). In addition, a significant amount of the total polystyrene market is used to produce foam articles that are used in many food-contact applications (Lickly et al., 1995). Many of these applications are food service products, such as foam plates, cups, bowls and hinged containers. Past studies identified that vapor-phase migration of styrene and hexanal from a packaging material to food does occur and is significant (Linssen et al., 1991; Lehr et al., 1993, Nobile et al., 2002). However, very little published data exists on the mass transport and migration of VOCs from PSF either in the food industry or in the building environment field.

In this paper, we characterize interactions between VOCs and polystyrene foam, a diffusion controlled building material. The sorption/desorption behavior of polystyrene foam is investigated using a single-component system. Rapid determination of the material/air partition coefficient and the material-phase diffusion coefficient for each VOC was achieved by placing thin foam slabs in a dynamic microbalance and subjecting them to controlled sorption/desorption cycles. Styrene and hexanal were selected as two typical compounds to investigate. Styrene is a slightly polar aromatic compound while hexanal is a polar aldehyde compound. We found that while the sorption/desorption cycle for styrene in PSF is symmetrical and the Fickian diffusion model fits the sorption/desorption data well, the sorption/desorption process for hexanal in PSF is not symmetrical with hexanal sorbing quickly and taking much longer to desorb. A similar response was found with VOC sorption and desorption on soil organic matter (Lu and Pignatello, 2002) and activated carbon (Lin et al., 1996). In the indoor air quality field, a "steady state" continuous emission level or "tail" is often found when testing VOC emissions from building materials, and many empirical models were built in an attempt to curve fit the slow desorption stages (Yu, 1998, Axley and Lorenzetti, 1993, Van Der Wal

et al., 1997). However, there remains a void in the understanding of the factors that control the slow desorption process. In order to address the observed hysteresis, a porous diffusion model, coupled with the Freundlich isotherm, is developed to describe hexanal transport in PSF. The model and the experimental results contribute to a more complete understanding of the mechanisms that control the slow desorption of polar organic chemicals from consumer products and building materials.

EXPERIMENTS AND METHODS

Kinetic Experiments

A high-resolution (0.1-0.5 μg) dynamic microbalance (Cahn Model D200-02) equipped with a PC-based data acquisition system (DAQ) is used to measure and record changes in the sample weight during sorption/desorption tests. A schematic diagram of the system is shown in Figure 2. To minimize mechanical vibration, the microbalance is placed on a marble balance stand isolated from the floor by vibration dampening pads. The temperature in the microbalance enclosure is maintained at 25 ± 0.3 ^{o}C using a constant temperature circulator (Isotemp, 1028 D, Fisher Scientific) connected to a heat exchanger in the enclosure. The sample chamber temperature is monitored with a temperature transducer (RTD, Model 2Pt100G3050, Omega). Clean air is supplied from gas cylinders (Medical Air USP, UN1002, Air Products). The flow path is constructed of 3.2-mm O.D. 304 stainless steel and Teflon tubing with stainless steel fittings. The sample chamber is constructed of borosilicate glass. A glass frit is installed at the inlet end of the sample chamber to improve gas flow distribution.

For sorption tests, a gas concentration of a specific VOC is generated using a constant temperature diffusion cell (VICI Metronics Dynacalibrator Model 190), modified by substituting a stainless steel/glass flow path. Mass flow controllers (MFC, Model FC-280S, Tylan-General) are used to control the air flow rate. The gas-phase VOC concentration is determined by dividing the diffusion cell VOC emission rate by the air flow rate. The VOC emission rate is determined gravimetrically by dividing the weight difference by the time period. To minimize errors induced by drag force on the PSF/OSB

sample, gas-phase VOC concentrations are controlled by adjusting the diffusion cell temperature, while the air flow rate is held constant. The MFCs are calibrated using a soap bubble meter. An air stream containing a constant and known VOC concentration is passed through the microbalance sample chamber. The sample mass gain over time is monitored until equilibrium is reached. Influent air is then switched to clean air and the desorption process is monitored until equilibrium with the VOC-free air is re-established.
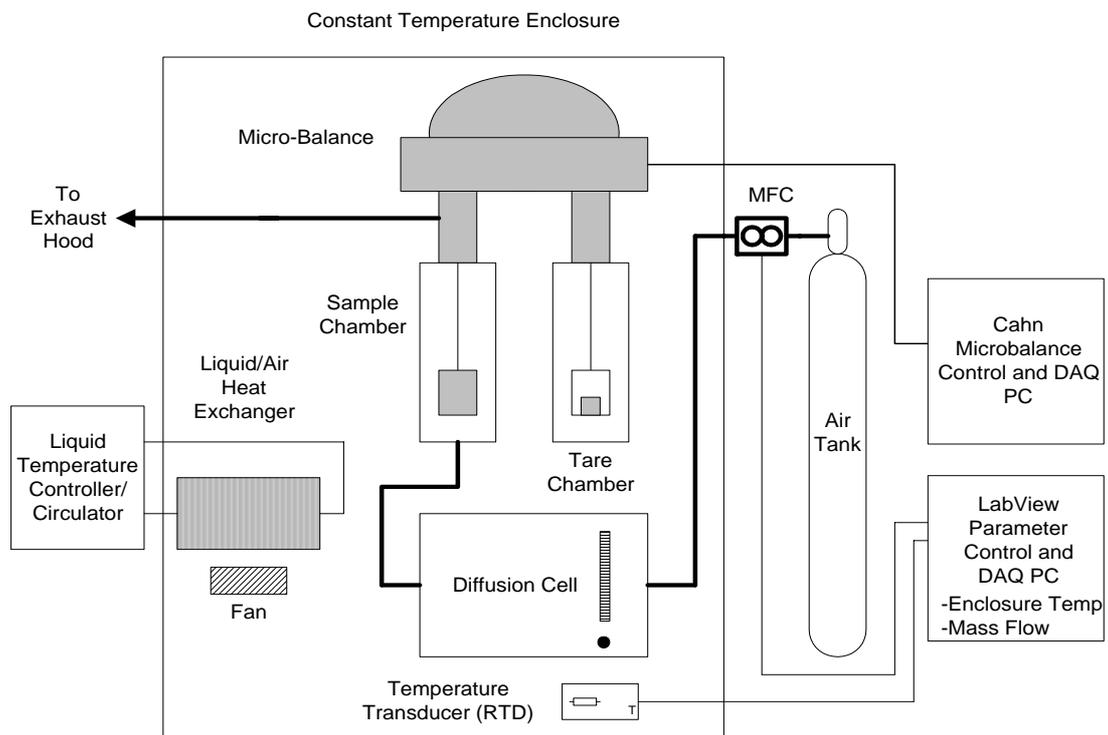
Figure 2. Diagram of the microbalance test system

Sorption Isotherm

A known gas phase concentration of a specific VOC is generated using the diffusion cell, and then passed through the sample chamber. To create the sorption isotherm, the gas-phase concentration was increased sequentially in several steps. The gas-phase VOC concentrations are controlled by adjusting the diffusion cell temperature, while the airflow rate is held constant. A four-step concentration profile was created by controlling

the diffusion cell temperature at 55 $^{\circ}$C, 65 $^{\circ}$C, 75 $^{\circ}$C and 85 $^{\circ}$C in sequence. For each step, the sample mass gain over time is monitored until equilibrium is reached. Once equilibrium is established at a particular concentration, a step-up in the VOC gas-phase concentration is created by increasing the diffusion cell temperature and the sorption process is monitored until equilibrium at this higher concentration is again established.

MODEL DEVELOPMENT

Fickian Diffusion

This section presents the theoretical model considering only Fickian diffusion. Under the experimental conditions, the rate of change in mass due to Fickian diffusion is given (Crank, 1976) by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left\{\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right\} \tag{1}$$

where M_t is the total mass of a VOC that has entered or left the material in time t, M_∞ is the corresponding quantity after equilibrium has been reached, and 2L is the thickness of the sample.

Diffusion with Local Equilibrium Defined by the Freundlich Equation

This section presents the new sorption and transport model used in this study. Considering transient diffusion and sorption, a differential mass balance on a small element of material volume is combined with Fick's law to yield (Lin et al., 1996):

$$\varepsilon_p \frac{\partial C}{\partial t} + (1 - \varepsilon_p)\rho_p \frac{\partial q}{\partial t} = \varepsilon_p \frac{\partial}{\partial x}\left(D_p \frac{\partial C}{\partial x}\right) \tag{2}$$

where q is the sorbed mass; C is the gas-phase concentration; ε_p is the porosity; ρ_p is the density of the material; t is time; and D_p is the gas diffusivity of the sorbate molecules through the pore space in the material. The first and second terms in Equation 2 represent the accumulation of sorbate molecules in the gas and solid phases within the

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material respectively, while the term on the right represents diffusion of sorbate molecules in the gas-phase. We assume gaseous diffusion is the only means of VOC transport. As will be shown, the close agreement between the model's predictions and the measurements substantiates this assumption for the system considered here. In sorption of VOCs by PSF, the sorbed phase is strongly favored and so the first term in Equation 2 can be neglected without loss of accuracy. Within the pores, an instantaneously established local equilibrium, following the Freudlich equation, is assumed to describe the partitioning between gas and the sorbed phase, or

$$q = kC^n \tag{3}$$

where k and n are constants.

Combing (1) and (2) and assuming D_p is independent of x, we find

$$\frac{\partial C}{\partial t} = De \left(\frac{C}{C_0} \right)^{1-n} \frac{\partial^2 C}{\partial x^2} \tag{4}$$

$$\text{where } De = \frac{D_p \varepsilon_p}{(1-\varepsilon_p)\rho_p nk} C_0^{1-n} \tag{5}$$

is an effective diffusivity and C_0 is the imposed external gas-phase concentration for sorption or the initial uniform internal gas-phase concentration for desorption. Converting (4) into dimensionless terms yields

$$\frac{\partial Q}{\partial \theta} = Q^{1-n} \frac{\partial^2 Q}{\partial X^2} \tag{6}$$

where Q=C/C_0, X=x/L, θ=tDe/L^2, and L is half of the thickness of the slab.

The kinetic experiments begin with the material in equilibrium with constant gaseous VOC concentration. The mass sorbed is monitored as a function of time until equilibrium is achieved. Desorption data are generated by suddenly reducing the external gas-phase VOC concentration to zero while continuing to monitor the total amount sorbed. The appropriate initial and boundary conditions for the sorption phase of the experiments are as follows:

$$Q \ (0<X<1, \theta=0) = 0 \tag{7a}$$

$$Q\ (X=1,\theta) = 1 \tag{7b}$$

$$\left.\frac{\partial Q}{\partial X}\right|_{(X=0,\theta)} = 0 \tag{7c}$$

For the desorption period, the corresponding initial and boundary conditions are

$$Q\ (0<X<1,\theta=0) = 1 \tag{8a}$$

$$Q\ (X=1,\theta) = 0 \tag{8b}$$

$$\left.\frac{\partial Q}{\partial X}\right|_{(X=0,\theta)} = 0 \tag{8c}$$

These initial and boundary conditions state (1) that the initial VOC concentration in the material is zero; (2) that the resistance effect over the material surface is negligible; and (3) that the center of the material must represent an extreme with respect to the local amount sorbed. The schematic description of the transport model under sorption and desorption conditions are shown in Figures 3 and 4.

Figure 3. Schematic of the new transport model under sorption condition

Figure 4. Schematic of the new transport model under desorption condition

The relative mass uptake during sorption (M_θ / M_∞), or loss during desorption (1 - M_θ / M_∞), at a specific time can be found by integrating the mass sorbed over the entire material slab, or

$$\frac{M_\theta}{M_\infty} = \int_0^1 Q^n(x,\theta)dx \qquad (9)$$

where M_θ is the total mass sorbed at time θ, and M_∞ is the equilibrium mass sorbed at an external gas-phase concentration of C_0.

RESULTS AND DISCUSSION

Sorption/Desorption Kinetics

Figure 5 shows sorption and subsequent desorption mass change for styrene with PSF. Equilibrium was reached in about 30 hours for both sorption and desorption. The sorption and desorption profiles are highly symmetrical. It is also evident that the sorption of styrene is completely reversible. The experimental data in Figure 5 were normalized by dividing M_t by M_∞, as shown in Figure 6. Figure 6 also shows the excellent fit of the simple diffusion model (Equation 1) to the styrene sorption and desorption data, indicating that migration of styrene in PSF is Fickian in nature. The average D value of 6.20×10^{-12} m^2 s^{-1} is essentially the same for both sorption and desorption.
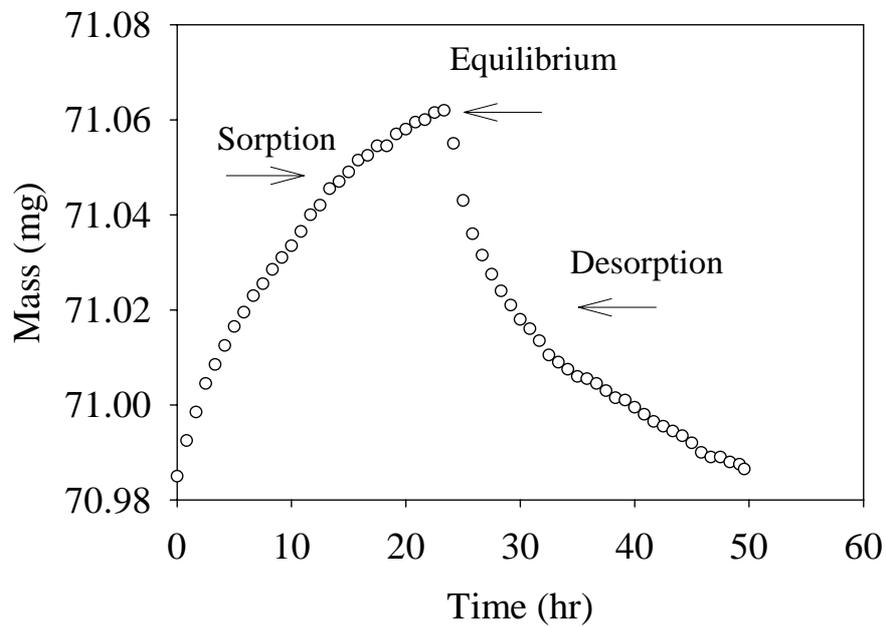
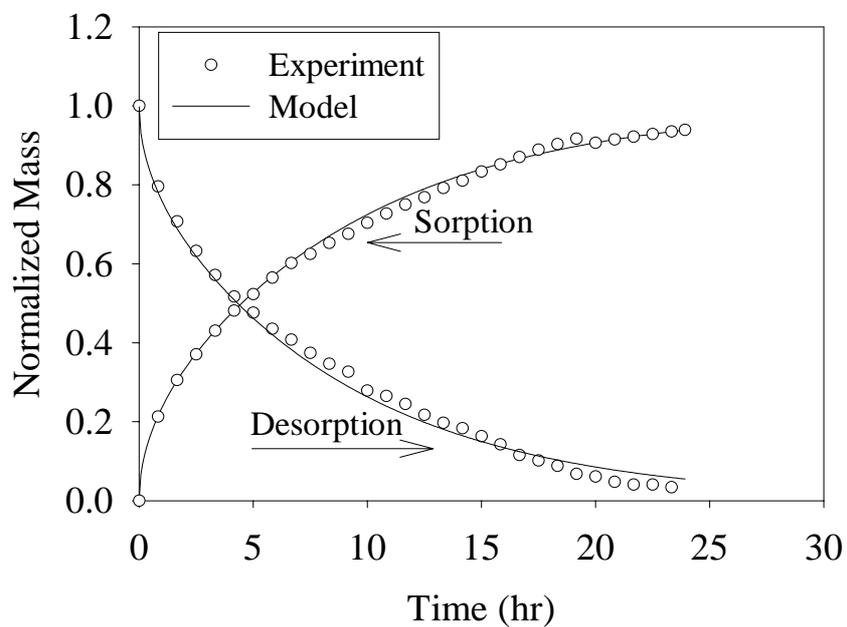Figure 5. Mass change for styrene sorption/desorption in PSF

Figure 6. Styrene sorption/desorption kinetics fitted with Fickian diffusion model

Typical sorption/desorption kinetic data for hexanal and PSF are shown in Figures 7 and 8. As shown in Figure 7, the sorption/desorption experimental curves were found to be asymmetrical, with desorption occurring far more slowly than sorption. Figure 8 shows the results obtained when fitting the Fickian diffusion model with the normalized mass for hexanal in PSF. Although the sorption data fits the model reasonably well, the desorption data do not fit as well. Indeed, the D of 5.2×10^{-12} m^2 s^{-1} obtained from the sorption data is around 10 times greater than the D of 6.6×10^{-13} m^2 s^{-1} obtained from the desorption data. This asymmetry, with faster sorption than desorption, implies that simple Fickian diffusion is not the only mechanism controlling hexanal transport in PSF.
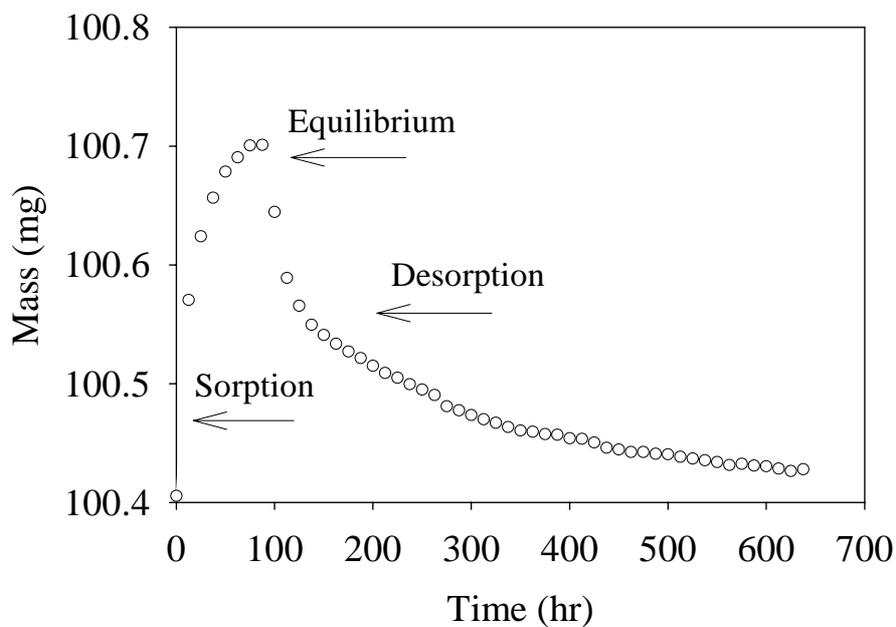

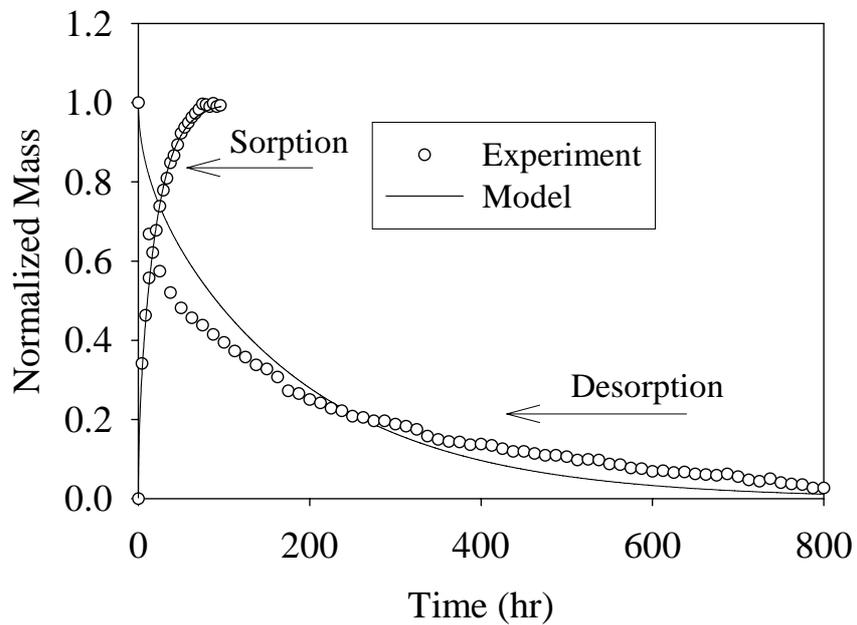Figure 7. Mass change for hexanal sorption/desorption in PSF

Figure 8. Hexanal sorption/desorption kinetics fitted with Fickian diffusion model

A possible mechanism is that diffusion depends on the mobility of the solute, which can depend on its size and its interaction with the material matrix (Frisch, 1980, Weber, 1991). Hence, chemical structure has an effect on diffusion. Non (or very slightly) polar styrene does not "stick" to the polar PSF due to weaker cohesive forces and Fickian diffusion dominates the transport. However, for hexanal, the electrons in the C=O double bond are not equally shared, with the electronegative oxygen taking proportionally more charge. This gives the carbonyl group polarity. Although aldehydes do not hydrogen bond among themselves, they do have some dipole/dipole attraction between the molecules and they "stick" to other polar materials, such as PSF (Del Nobile et al., 2002). This stronger interaction with the material matrix provides a reasonable explanation for the sorption/desorption hysteresis observed with hexanal in PSF.

Sorption Isotherm

The sorption isotherm for hexanal in PSF was constructed from the sorption equilibrium data obtained in the sequential concentration microbalance experiments. Figure 9 shows the actual step-up sorption equilibrium profile. Figure 10 shows the conformity of the equilibrium data to the nonlinear Freundlich equation:

$$\log q = \log k + n \log C \tag{10}$$

The fitting results (n= 0.68; k=0.020; r^2= 0.9663) show that the equilibrium data are well described by the Freundlich equation.
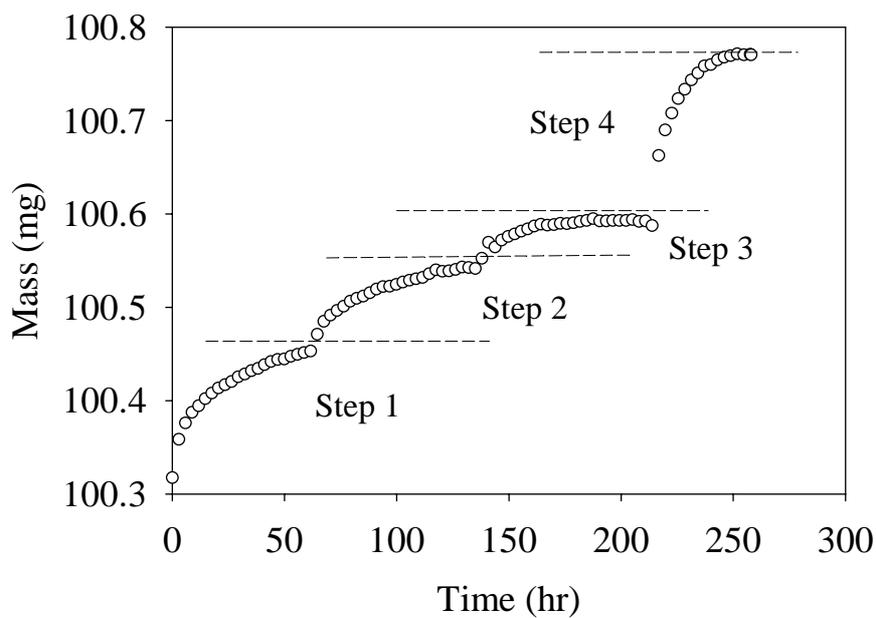

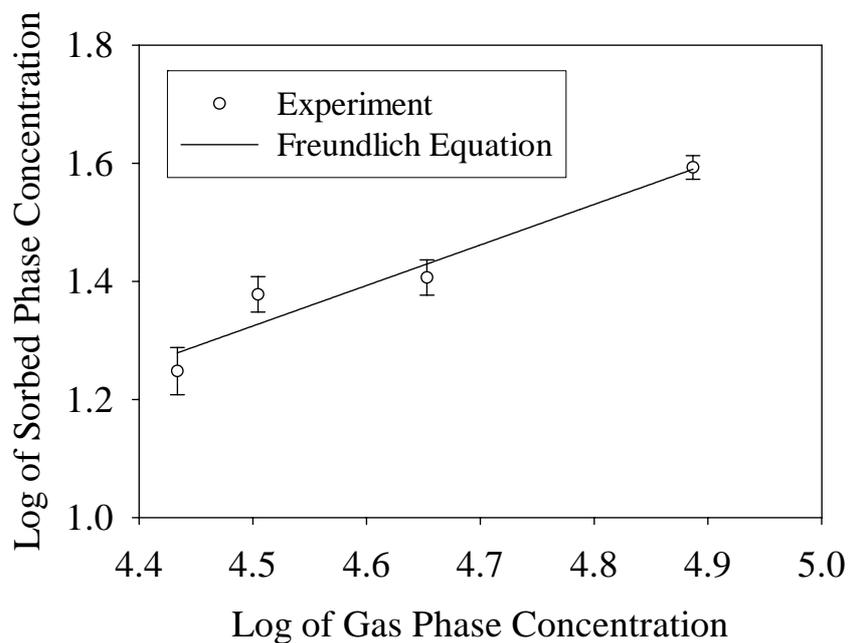Figure 9. Step-up sorption equilibrium profile

Figure 10. Fitting hexanal sorption isotherm with the Freundlich equation

Some researchers found that the apparent diffusivity of a solute that produces nonlinear equilibrium sorption might be expected to be concentration dependent (Thiminlioglu and Danner, 2000, Kamiya et al., 1995). However, in our case, the individual contaminant concentration range (from 27,000 µg/m^3 to 77,000 µg/m^3) is low compared to the vapor pressure (4.6 × 10^7 µg/m^3), and sorption to a material of this nature under the low VOC concentration is expected to be concentration-independent. Figure 11 shows the results fitting the Fickian diffusion model with normalized sorption data for hexanal in PSF for the first three gas-phase concentration steps. The coincidence of the normalized mass change data supports the assumption that D is independent of concentration. The only exception is the fourth concentration step, which does not fit as well as the data from the previous three steps. One possible reason is that, as the concentration of dissolved hexanal is increased to the highest level in the experiment, the extent of the interaction between hexanal and PSF increases, leading to a change in the physical or chemical structure of the PSF, and consequently to a change in the affinity between hexanal and PSF. For example, chemical solvents may result in the structural relaxation of polymers,

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which increases the ability of polymers to absorb VOCs (Dhoot et al., 2001, Chen and Edin, 1980).
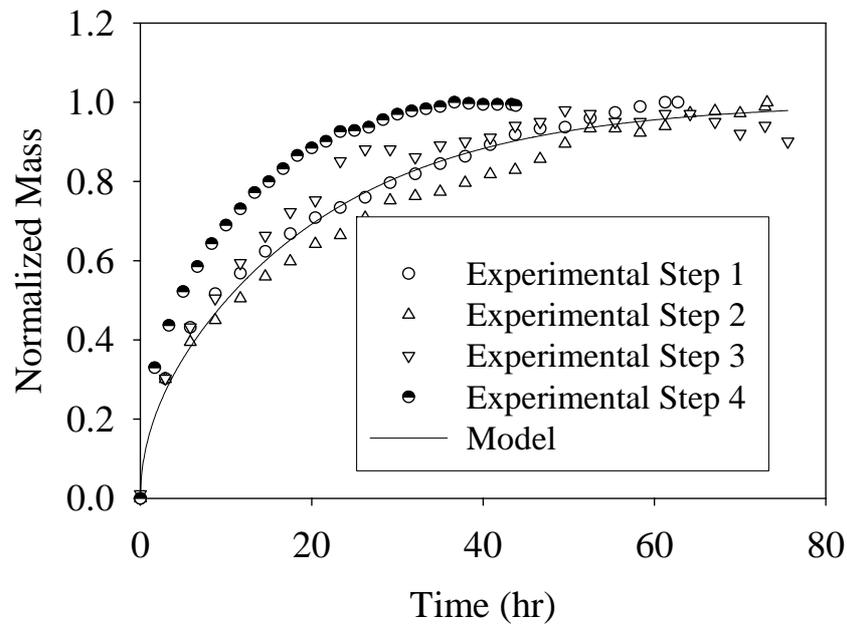

Figure 11. Fickian diffusion model fitting at different concentrations

Transport of Hexanal in PSF Considering Local Freundlich Sorption Equlibrium

Figure 12 and 13 show the experimental kinetic data and the best fit model results for two separate experimental data sets. In these two experiments, two different PSF samples were used with two different gas-phase concentrations. The gas phase concentration is 31,900 µg/m^3 for the first PSF sample and 27,100 µg/m^3 for the second PSF sample. A least-squares method was used to determine the best fit of the experimental data to the model. In this scheme, De was varied and the difference in M_t/M_∞ between experimental data points and the corresponding model predictions were squared and summed. The value of De that yielded the minimum summation value was considered to be the best fit. Note that in fitting the model, the long "stretched-out" desorption data of the VOCs are ascribed less weight compared with the sorption data in order to even out the weight

between the sorption and desorption process. In this process, the effective diffusivity, De, is the only adjustable parameter and a single value for De is used for both sorption and desorption curves for each hexanal/PSF sample combination. The best fit De values are 4.2×10^{-10} m^2 s^{-1} for the first sample and 3.0×10^{-10} m^2 s^{-1} for the second sample run.
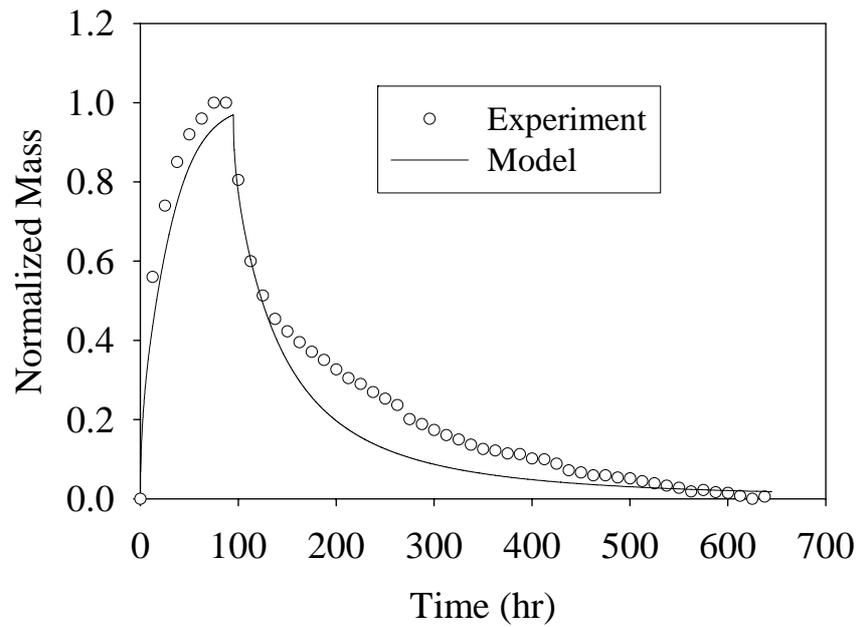

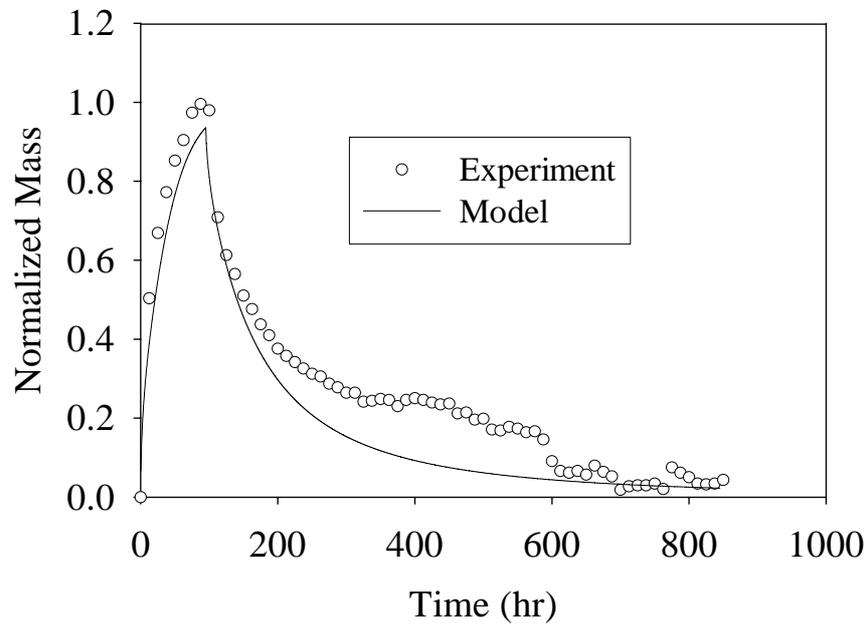Figure 12. Model prediction considering Freundlich equilibrium for PSF sample 1

Figure 13. Model prediction considering the Freundlich equilibrium in PSF sample 2

The pore diffusivity, Dp, can be calculated from the estimated values for the effective diffusivity, De, using Equation 5. The required parameters (ρ_p, ε_p, n and k) were either properties of the PSF material or were obtained from the experimental sorption isotherm data as shown in Table 1. If the proposed model closely approximates the actual sorption/desorption process, the calculated Dp should be close to the diffusion coefficient of the same compound in air, D_{air}. Actually, the corresponding Dp values for the two experimental runs are 4.0×10^{-4} m^2 s^{-1} and 2.5×10^{-4} m^2 s^{-1} respectively, which somewhat higher than D_{air}, which is around 1×10^{-5} m^2 s^{-1}.

Table 1. Properties of PSF Sample

Parameters	Porosity	Density	n	k
Value	0.54	2.5×10^3 g/m^3	0.68	0.020

In the desorption process for both data sets, hexanal exhibits an initial rapid desorption followed by a slower desorption stage. Such a two stage process was also found in other

VOCs and materials by other researchers, such as the desorption of toluene from poly aryl ether ketone (Wolf and Grayson, 1993). A possible reason is that the kinetics for the slow stage might involves the protracted polymer structural relaxation process at longer time (Dhoot et al., 2001). The model fits better in the rapid stage than in the slow stage, although the reason for this difference remains unclear. Overall, the model conforms reasonably well to the experimental data and the asymmetry in sorption and desorption rate is well resolved. By incorporating the independently measured Freundlish isotherm, the ten-fold discrepancy in the simple diffusion coefficients is collapsed, with a single effective diffusion coefficient applying to both sorption and desorption data.

CONCLUSIONS

Transport of VOCs in polystyrene foam, a diffusion-controlled building material, was explored in this paper. Styrene and hexanal were selected as the two target compounds. While simple Fickian diffusion dominates and can describe the transport of styrene in PSF, it cannot explain the hysteresis in the hexanal migration process. A porous model is developed, considering local equilibrium between the PSF material pore wall and the adjacent pore air and assuming that the equilibrium is established instantaneously during the diffusion transport process. The model conforms fairly closely to the experimental data for sorption/desorption of hexanal in PSF, and resolves the hysteresis. It should be possible to use this approach to describe the transport of other polar compounds in PSF.

REFERENCES

Axley, J. W. and Lorenzetti, D., 1993, Sorption and Transport Models for Indoor Air Quality Analysis, Modeling of Indoor Air Quality and Exposure, *ASTM STP 1205*, 105-127.

Barry, A. and Corneau, D., 1999, The Impact of Wood Composite Panel Products Such as OSB, Particleboard, MDF and Plywood on Indoor Air Quality, *Indoor Air 99, Proceedings of the 8th International Conference on Indoor Air Quality and Climate*, Edinburgh, Scotland, Aug. 8-13, Vol.5, 129-134.

Chen, P. S. and Edin, J. A. D., 1980, Fickian Diffusion of Alkanes through Glassy Polymers: Effects of Temperature, Diffusant Size, and Polymer Structure, *Polymer Engineering and Science, Mid-January*, Vol.20, No.1, 40-49.

Crank, J., 1976, *The Mathematics of Diffusion,* 2nd Edition, Oxford University Press, New York, 44-49.

Del Nobile, M. A. et al., 2002, Modeling of Hexanal Sorption Kinetics in an Aldehydes Scavenger Film Intended for Food Packaging Applications, *Journal of Food Science*, Vol. 6, No.7, 2687-2692.

Dhoot, N. S. et al., 2001, Sorption and Transport of Linear Alkane Hydrocarbons in Biaxially Oriented Polyethylene Terephthalate, *Journal of Polymer Science: Part B: Polymer Physics*, Vol.39, 1160-1172.

Frisch, H. L., 1980, Sorption and Transport in Glassy Polymers-A Review, *Polymer Engineering and Science*, Vol.20, No.1, 2-13.

Hodgson A. T. 2003, Volatile Organic Chemical Emissions from Structural Insulated Panel (SIP) Materials and Implications for Indoor Air Quality, Berkeley, CA, Lawrence Berkeley National Laboratory (LBNL-53768).

Lehr, K. M. et al., 1993, The Vapor-phase Migration of Styrene from General Purpose and High-impact Polystyrene into Cooking Oil, *Food and Chemical Toxicology*, Vol.31, 793-798.

Lickly, T. D., Lehr, K. M. and Welsh, G. C., 1995, Migration of Styrene from Polystyrene Foam Food-contact Articles, *Food Chemical Toxicology,* Vol.33, No.6, 475-481.

Lin, T., Little, C. J. and Nazaroff, W. W., 1996, Transport and Sorption of Organic Gases in Activated Carbon, *Journal of Environmental Engineering*, Vol.22, No.3, 169-175.

Linssen, J. P. H., Reitsma, J. C. E. and Roozen, J. P., 1991, Effect of Sampling Method on the Level of Styrene Monomer Migrated from Polystyrene Packaging Material, *Packaging Technology and Science*, Vol.4, 171-175.

Lu, Y. and Pignatello, J. J., 2002, Demonstration of the "Conditioning Effect" in Soil Organic Matter in Support of a Pore Deformation Mechanism for Sorption Hysteresis, *Environmental Science and Technology*, Vol.36, 4553-4561.

Tihminlioglu, F. and Danner, P. R., 2000, Solvent Diffusion in Amorphous Polymers: Polystyrene-Solvent Systems, *Journal of Polymer Science: Part B: Polymer Physics*, Vol.38, 1965-1974.

Van Der Wal, J. F., Hoogeveen, W. and Wouda P., 1997, The Influence of Temperature on the Emission of Volatile Organic Compounds from PVC Flooring, Carpet and Paint, *Indoor Air*, No.7, 215-221.

Walter, J. et al., 1991, Sorption Phenomena in Subsurface Systems: Concepts, Models and Effects on Contaminant Fate and Transport, *Water Research*, Vol.25, No.5, 499-528.

Wolf, J. C. and Grayson, A. M., 1993, Transport Behavior of Toluene into Poly Aryl Ether Ether Ketone, Polymer, Vol.34, 746-751.

Wong, C. and Liang, W., 2004, Porous Polystyrene Foam Produced at Supercritical Conditions, *Journal of Cellular Plastics*, Vol.40, 421-430.

Yoshinori, K. et al., 1995, Sorption, Diffusion, and Partial Molar Volumes of C4 Hydrocarbons in Rubbery Polymers, *Journal of Polymer Science: Part B: Polymer Physics*, Vol.33, 1663-1671.

Yu, C. and Crump, D., 1998, A Review of the Emission of VOCs from Polymeric Materials Used in Buildings, *Building and Environment*, Vol.33, No.6, 357-374.

CHAPTER 2: MODELING VOC EMISSIONS FROM ORIENTED STRAND BOARD AND POLYSTYRENE FOAM

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ABSTRACT

Contaminant emissions from building materials may tail extensively and require longer times to desorb than absorb. This slow desorption or hysteresis problem has been an obstacle to understanding VOC emissions from building materials. The research proposed here seeks to (i) develop a predictive emission model by incorporating a local Freundlich sorption equilibrium to account for the slow desorption; and (ii) validate the new nonlinear emission model using independent chamber data. Styrene in polystyrene foam (PSF) and hexanal in oriented strand board (OSB) were selected as the target compounds and materials, respectively. Sorption/desorption kinetic experimental data show that while styrene sorption/desorption in PSF is symmetrical, hexanal sorption/desorption in OSB is not symmetrical. For hexanal in OSB, slower desorption was observed. Model validation results show that while a simple linear emissions model can predict styrene emissions from PSF, it underestimates hexanal emissions from OSB. With the nonlinear emission model developed in this research, hexanal emission from OSB can be predicted. These results suggest that local sorption equilibrium needs to be considered when predicting the emission rate of polar compounds from building materials.

KEYWORDS

Emission, modeling, diffusion, sorption, slow desorption, VOCs, building materials, hysteresis

INTRODUCTION

Indoor sources of volatile organic compounds (VOCs) are a determinant of air quality in houses. Many materials used to construct and finish the interiors of new houses emit VOCs. These emissions are a probable cause of acute health effects and discomfort among occupants (Andersson et al., 1997). Understanding the source characteristics of these materials is crucial if indoor air quality problems are to be solved (Tichenor, 1990). Mathematical modeling is increasingly used to characterize emissions from building materials. Among all types of mathematical models, physically-based models are of particular significance for describing emission characteristics. One desirable feature of such models is that each parameter of the model represents a property of the building material and that they provide insight into the controlling mechanisms (Haghighat and Donnini, 1993, Yang et al., 2001, Little et al., 1994). One example is a physically-based model that predicts emissions from a single-layer, diffusion-controlled source (Little et al., 1994; Little and Hodgson, 1996). This model has only been validated for vinyl flooring (Cox et al., 2002), where simple Fickian diffusion was shown to govern the sorption and desorption behavior.

However, in a recent paper (Yuan and Little, 2005), a local sorption/desorption mechanism was found to be necessary in addition to diffusion to accurately represent transport of hexanal in polystyrene foam. By including this additional non-linear mechanism, the hysteresis in the rate of sorption and desorption was resolved. When testing VOC emissions from building materials, a long-term continuous emission level or "tail" was often found, and many empirical models were developed in an attempt to fit the slow desorption data. None of them however, can characterize the slow desorption stages in complex materials such as carpet (Jorgensen, 2000, Yu, 1998, Axley and Lorenzetti, 1993, Van Der Wal et al., 1997). Similar observations were made for VOC sorption and desorption on soil organic matter and activated carbon (Lu and Pignatello, 2002, Lin et al., 1996).

Oriented strand board (OSB) and polystyrene foam (PSF) were selected as the target building materials. They are popular building materials and the main components of Structural Insulated Panels (SIPs), which are attractive from both environmental impact and energy use perspectives. SIPs are a significant source of volatile organic compounds (VOCs) (Hodgson, 2003). OSB emits pentanal and hexanal, two odorous aldehydes (Barry and Corneau, 1999) and acetic acid. PSF emits styrene. The large surface area of installed SIP systems and the resulting decrease in ventilation rate due to the very tight energy efficient structure usually exacerbates the potential indoor air quality problem. Styrene and hexanal were selected as the two compounds to be investigated. Styrene is a relatively nonpolar aromatic while hexanal is a polar aldehyde compound. Yuan and Little (2005) showed that while the sorption/desorption cycle for styrene in PSF is symmetrical, for hexanal in PSF, desorption takes much longer than sorption (Yuan and Little, 2005). By incorporating the Freundlich sorption mechanism into the traditional Fickian diffusion model, the hysteresis that exists in the hexanal transport process in PSF was explained (Yuan and Little, 2005).

As a further step, a physically-based emission model that includes the nonlinear sorption isotherm is developed in this paper. The model is validated with hexanal emission from OSB and compared to a simple linear diffusion model (Little et al., 1994). A small-scale chamber was used to directly measure gas-phase VOC concentrations produced by exposure to OSB and PSF. The measured gas phase concentration was fitted to the predicted concentration obtained from the proposed non linear emission model and the simple linear diffusion model. The only adjustable parameter in the fitting process is C_0. The fitted C_0 was then compared to the measured C_0. Results show that while the simple linear model can predict styrene emissions from PSF, in which the sorption/desorption process is symmetrical; the proposed non linear model considering local equilibrium is more appropriate for the hexanal/OSB system, in which asymmetrical sorption/desorption kinetics were found.

NEW EMISSION MODEL DEVELOPMENT

A model describing emissions from a homogeneous porous source is developed. A schematic of this new single-layer emission model is shown in Figure 14. Considering both transient diffusion and a local instantaneously-reversible Freundlich sorption equilibrium, a mass balance on a small element of volume within the material yields:

$$\varepsilon_p \frac{\partial C}{\partial t} + (1-\varepsilon_p)\rho_p \frac{\partial q}{\partial t} = \varepsilon_p \frac{\partial}{\partial x}\left(D_p \frac{\partial C}{\partial x}\right) \tag{1}$$

where q is the sorbed mass, C is the gas-phase concentration, ε_p is porosity, ρ_p is the density of the material, t is time, and D_p is the gas diffusivity in the pore space. The first and second terms in Equation 1 represent the accumulation of VOC molecules in gaseous and solid phases within the material, respectively, while the term on the right-hand side represents diffusion of the VOC in the gas-phase within the material. We assume gaseous diffusion is the only means of VOC transport in the material. Between the pores space and the solid material phases, an instantaneously established local equilibrium, following the Freundlich equation, is assumed to describe the partitioning between gas and sorbed phases:

$$q = kC^n \tag{2}$$

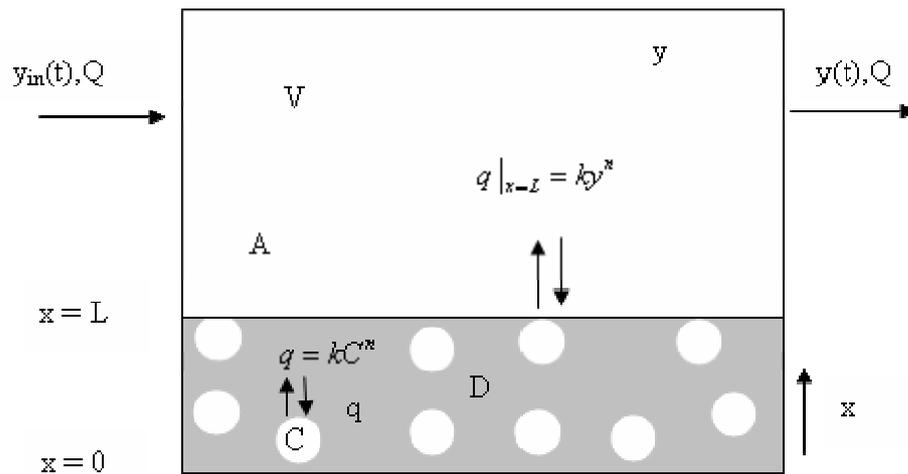where k and n are parameter constants.

Figure 14. Schematic of new nonlinear single-layer emission model

In sorption of VOCs by building material, the sorbed phase is strongly favored and so the first term in Equation 1 can be neglected without any loss of accuracy. Combining Equations 1 and 2 and assuming D_p is independent of x, we find

$$\frac{\partial C}{\partial t} = De \left(\frac{C}{C_m} \right)^{1-n} \frac{\partial^2 C}{\partial x^2} \tag{3}$$

where $De = \dfrac{D_p \varepsilon_p}{(1 - \varepsilon_p) \rho_p nk} C_m^{1-n}$ $\qquad$ (4)

is an effective diffusivity, and C_m is the initial gas-phase concentration. Converting Equation 4 into dimensionless terms yields the governing equation:

$$\frac{\partial G}{\partial \theta} = G^{1-n} \frac{\partial^2 G}{\partial X^2} \tag{5}$$

where $G = C/C_m$, $X = x/L$, $\theta = tDe/L^2$, and L is the thickness of the slab.

The initial condition assumes a uniform solid material-phase concentration of the VOC, C_0. The dimensionless form is

$$G = 1 \quad \theta = 0 \tag{6}$$

The first boundary condition assumes there is no flux from the base of the slab. The dimensionless form is

$$\frac{\partial G}{\partial X} = 0 \quad X = 0 \tag{7}$$

The second boundary condition is imposed via a mass balance on the VOC in the chamber air, or

$$\frac{\partial y}{\partial t} V = Q \cdot y_{in} - De \cdot A \cdot \rho_p \frac{\partial q}{\partial x} \bigg|_{x=L} - Q \cdot y \tag{8}$$

where y_{in} and y are the concentrations of the VOC in the influent and effluent chamber air, respectively, Q is the volumetric air flow rate, V is the well-mixed chamber volume, A is the exposed surface area of the slab, and L is the thickness of the slab. A nonlinear

and instantaneously reversible Freundlich equilibrium relationship is assumed to exist between the slab surface and the chamber air, or

$$q\big|_{x=L} = k \cdot y^n \tag{9}$$

The instantaneously reversible assumption implies that resistance to mass transfer between the material surface and the bulk chamber air is negligible. Combining Equations 8 and 9 and assuming y_{in} is zero, yields

$$\frac{V}{n} \cdot q^{\frac{1-n}{n}} \cdot \frac{\partial q}{\partial t}\bigg|_{x=L} + De \cdot \rho_p \cdot A \cdot k^{(1/n)} \frac{\partial q}{\partial x}\bigg|_{x=L} + Q \cdot q^{(1/n)}\big|_{x=L} = 0 \tag{10}$$

Combing Equations 2 and 10 and converting to the dimensionless form yields

$$\frac{VD_e}{AkL^2} \cdot \frac{\partial G}{\partial \theta}\bigg|_{X=1} + \frac{nD_e}{L} \cdot \rho_p \cdot C_m^{n-1} \cdot G^{n-1} \cdot \frac{\partial G}{\partial X}\bigg|_{X=1} + \frac{Q}{Ak} \cdot G\big|_{X=1} = 0 \tag{11}$$

EXPERIMENTAL METHODS

Sorption/desorption Kinetics

A high-resolution (0.1 – 0.5 µg) dynamic microbalance (Cahn Model D200-02) equipped with a PC-based data acquisition system (DAQ) is used to measure and record changes in the sample weight during sorption/desorption tests. To minimize mechanical vibration, the microbalance is placed on a marble balance stand isolated from the floor by vibration dampening pads. The temperature in the microbalance enclosure is maintained at 25 ± 0.3 °C using a constant temperature circulator (Isotemp, 1028 D, Fisher Scientific) connected to a heat exchanger in the enclosure. The sample chamber temperature is monitored with a temperature transducer (RTD, Model 2Pt100G3050, Omega). Clean air is supplied from gas cylinders (Medical Air USP, UN1002, Air Products). The flow path is constructed of 3.2-mm O.D. 304 stainless steel and Teflon tubing with stainless steel fittings. The sample chamber is constructed of borosilicate glass. A glass frit is installed at the inlet end of the sample chamber to improve gas flow distribution.

For sorption tests, a gas concentration of a specific VOC is generated using a constant temperature diffusion cell (VICI Metronics Dynacalibrator Model 190), modified by substituting a stainless steel/glass flow path. Mass flow controllers (MFC, Model FC-280S, Tylan-General) are used to control the airflow rate. The gas-phase VOC concentration is determined by dividing the diffusion cell VOC emission rate by the airflow rate. The VOC emission rate is determined gravimetrically by dividing the weight difference by the time period. To minimize errors induced by drag force on the PSF/OSB sample, gas-phase VOC concentrations are controlled by adjusting the diffusion cell temperature, while the airflow rate is held constant. The MFCs are calibrated using a soap bubble meter. An air stream containing a constant and known VOC concentration is then passed through the microbalance sample chamber. VOC sample mass gain over time is monitored until equilibrium is reached. Influent air is then switched to clean air and the desorption process is monitored until equilibrium with the VOC-free air is re-established.

C_0 Measurement

Independent measurements of C_0 in OSB are obtained using the method of cryogenic milling (CM) followed by VOC extraction during thermal desorption. An OSB sample is obtained from an OSB sheet by punching several small disks from a large area of the material. The samples are then pulverized into small pieces in a ball mill under a liquid nitrogen bath at temperatures of -140^0C. The CM homogenizes the sample, decreases the diffusion path length, and increases the surface area of the OSB materials. For measurements of C_0 in PSF, randomly selected pieces of foam are submerged in liquid nitrogen for around 5 minutes, and then small foam slivers are cut. The OSB powder and PSF sliver are transferred to a glass tube, which is then inserted into the sleeve heater of a direct thermal desorption apparatus. In all experiments, gas samples for VOCs are collected on Tenax®-TA sorbent tubes. The tubes are analyzed for individual VOCs by thermal desorption gas chromatography/mass spectrometry using a modification of U.S. EPA Method TO-1 (U.S. EPA). The target compounds were hexanal and styrene. A schematic diagram for C_0 measurement is shown in Figure 15.
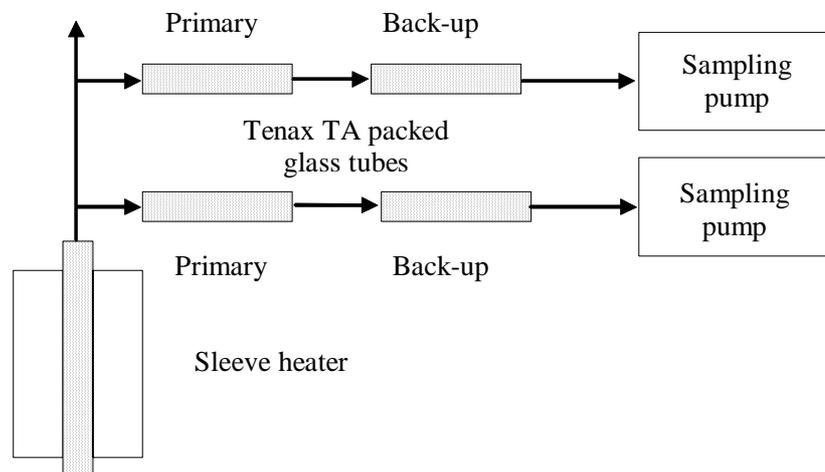
Figure 15. Diagram of direct thermal desorption apparatus for C0 measurement

RESULTS AND DISCUSSION

Measured Partition and Diffusion Coefficients

Model parameters are the initial VOC concentration in the material-phase (C_0), the material/air partition coefficient (K), and the material-phase diffusion coefficient (D). Using the sorption and desorption data recorded by the microbalance, the equilibrium and kinetic parameters, K and D, were determined. The target compounds selected here are hexanal and styrene, which are the main compounds emitted from OSB and polystyrene foam, respectively. For a particular VOC, the sorption equilibrium is described using a partition coefficient, or

$$K = \frac{M}{y} \tag{12}$$

where K is a material/air partition coefficient with units of mass per volume/mass per volume, M is the equilibrium concentration in the material-phase (g-VOC m^{-3}), and y is the corresponding concentration of the species in the gas-phase (g-VOC m^{-3}). M is

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obtained from the difference between the initial and equilibrium weight of the specimen divided by specimen volume, whereas y is calculated from

$$y = \frac{E}{Q} \qquad (13)$$

where E is the constant emission rate of VOC generated by the diffusion cell, and Q is the airflow rate through the system.

The Fickian diffusion coefficient, D, is determined by fitting a diffusion model to the experimental sorption and desorption data. For the specific experimental conditions, the rate of change in mass due to Fickian diffusion is given (Crank, 1976) by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left\{ \frac{-D(2n+1)^2 \pi^2 t}{L^2} \right\} \qquad (14)$$

where M_t is the total mass of a VOC that has entered or left the material in time t, M_∞ is the corresponding quantity after equilibrium has been reached, and L is the thickness of the sample.

Figure 16 shows the results of fitting transient sorption/desorption data to a Fickian diffusion model for estimation of D for styrene in PSF. The experimental data were normalized by dividing M_t by M_∞. The figure shows a good fit of the Fickian diffusion model (Equation 14) to styrene sorption and desorption data. For the styrene/PSF system, the sorption/desorption process of styrene is symmetric and reversible.
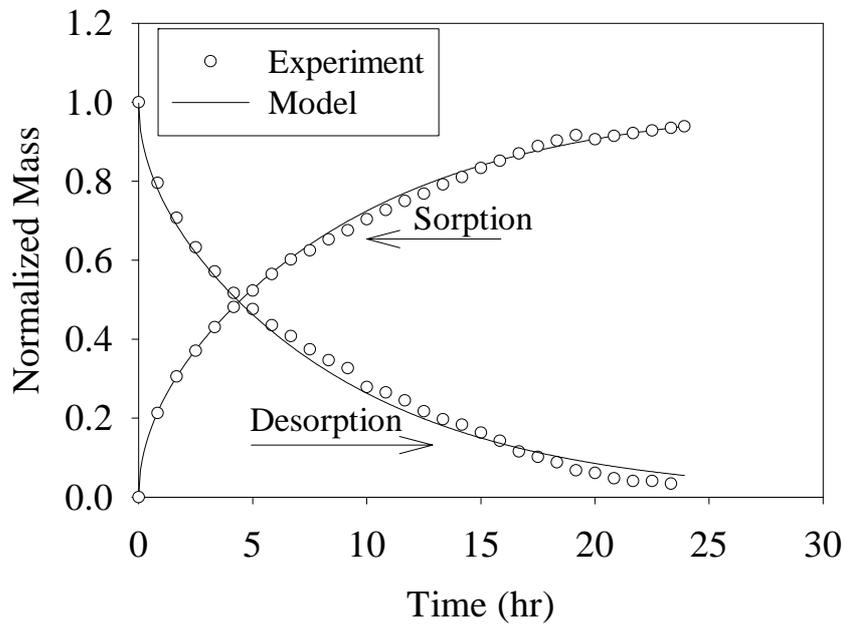
Figure 16. Styrene/PSF diffusion model

The results of fitting transient sorption/desorption data to the diffusion model for hexanal in OSB are shown in Figure 17. Although the data fit the Fickian diffusion model well, it takes longer to reach equilibrium in the desorption phase than in the sorption phase. Typically, a sorption time of 40 hr was required for the OSB sample to reach equilibrium, while more than 120 hr was needed for complete desorption. Compared to the styrene in PSF, the sorption/desorption process of hexanal in OSB is not symmetrical. Also, while the Fickian diffusion coefficient for sorption and desorption is the same for the styrene/PSF system, the fitted diffusion coefficient for the desorption process is around three times smaller than for the sorption process in the hexanal/ OSB system. Such sorption/desorption asymmetry is referred to as "hysteresis" (Lin et al., 1996, Yuan and Little, 2005). Table 2 summarizes the K and D values measured for the above compounds. Data were obtained by subjecting the OSB and PSF samples to multiple sorption/desorption cycles at various gas-phase concentrations. Gas-phase concentrations ranged from 91,000 to 121,000 µg/m^3 for styrene and from 27,000 to 63,000 µg/m^3 for hexanal.
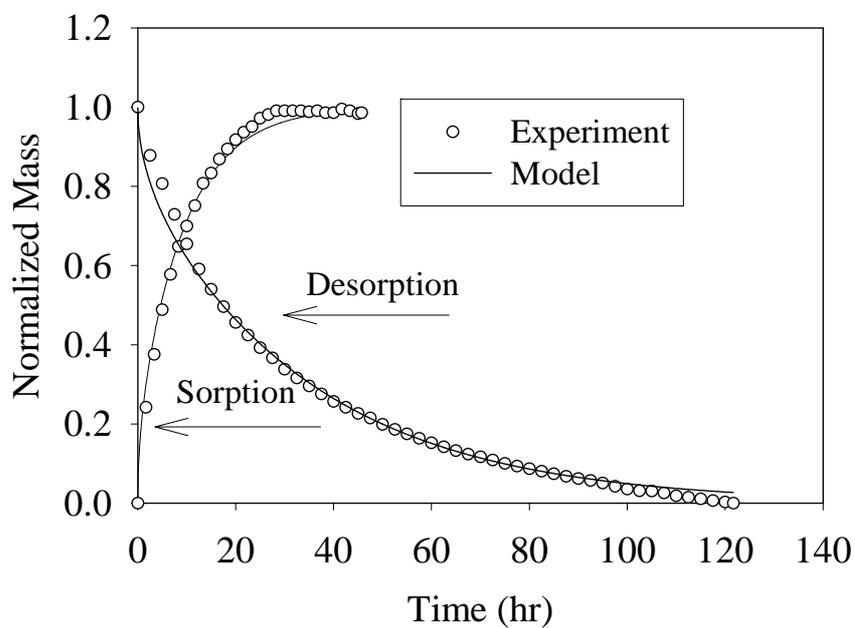
Figure 17. Hexanal/OSB diffusion model

Table 2. Summarized values of D and K obtained from sorption/desorption experiments.

Compound	Material	K^a (-)	$D^{a, b}$ (m^2/s)	$D^{a, c}$ (m^2/s)	Cycles^d
Hexanal	OSB	6600 ± 400	$4.2 \pm 1.0 \times 10^{-12}$	$1.8 \pm 0.2 \times 10^{-12}$	4
Styrene	PSF	260 ± 17	$6.2 \pm 0.4 \times 10^{-12}$	$6.2 \pm 0.4 \times 10^{-12}$	4

[a] Mean ± standard deviation

[b] Obtained from sorption rate measurements

[c] Obtained from desorption rate measurements

[d] Number of experimental sorption/desorption cycles

Diffusion Model Considering Local Freundlich Equilibrium

In order to get a better understanding of the sorption kinetics for hexanal in OSB, the sorption isotherms were constructed from sorption equilibrium data obtained from microbalance experiments. Figure 18 shows the conformity of the equilibrium data to the following nonlinear Freundlich equation:

$$\log q = \log k + n \log C \tag{15}$$

The fitting results (n= 0.84 ± 0.04; k=$7.0 \pm 0.5 \times 10^{-8}$; r^2= 0.9914) show that the isotherm can be described by the Freundlich equation.
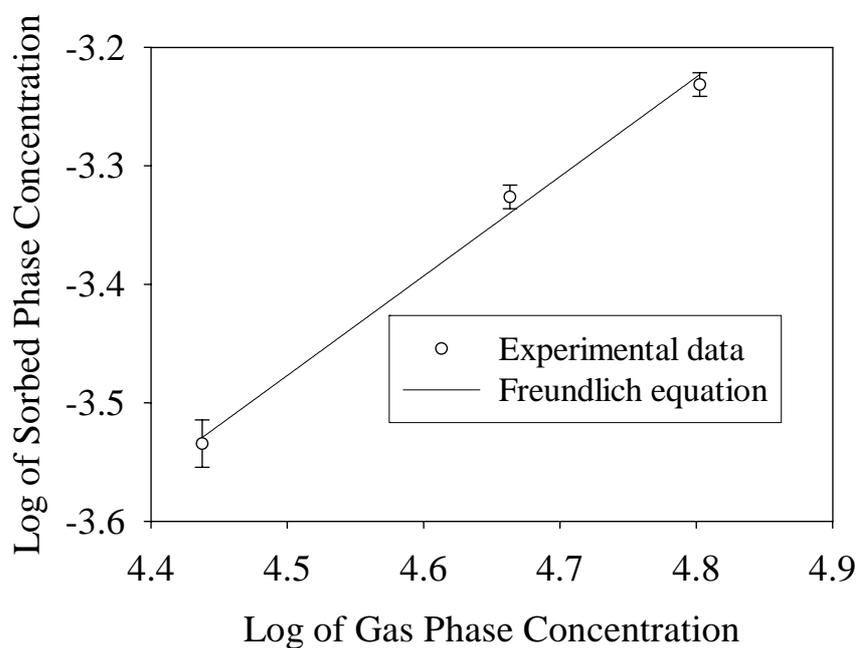

Figure 18. Freundlich sorption isotherm for hexanal/OSB

The sorption/desorption model considering diffusion and a local Freundlich equilibrium is described by Yuan and Little (2005). Figure 19 shows the experimental kinetic data and the best-fit model results. A single value for De of $3.3 \times 10^{-12}\,\text{m}^2/\text{s}$ is used for both sorption and desorption. Overall, the model conforms well to the experimental data and the asymmetry in the sorption and desorption rates is adequately resolved. The good fit of the model to the experimental data suggests that equilibrium sorption cannot be neglected in studying the transport of hexanal in OSB. A pore diffusivity, Dp, can be calculated from the estimated values for the effective diffusivity, De, using Equation 4.

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The required parameters density of OSB ρ_p is 6.5×10^5 g/m^3. The porosity ε_p is 0.002. The calculated D_p is 6.6×10^{-8} m^2/s. This value is not close to the diffusion coefficient of the same compound in air, D_{air} (1×10^{-5} m^2/s), but it is consistent with the value found previously in closely related research (Lin et al., 1994, Lin et al., 1996). Those authors mentioned that the reason for such a difference might be that pore size in the material is not sufficiently large to avoid surface hindered (Knudsen) diffusion. Thus both Kundsen diffusion and molecular diffusion occurred simultaneously.
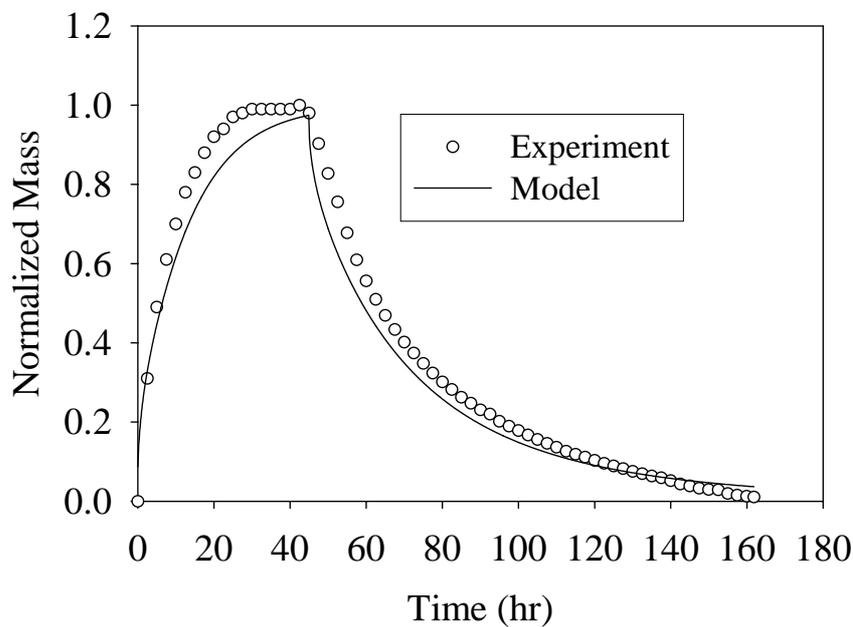

Figure 19. Hexanal/OSB diffusion model considering local Freundlich equilibrium

Validation of Single-layer Emissions Model for OSB and PSF

Using small-scale chambers, emissions of VOCs from OSB and PSF were measured over a period of four months (Hodgson, 2004). The predominant VOCs emitted by the materials included acetic acid, pentanal, hexanal and styrene. Acetic acid and the aldehydes derived from the OSB, while styrene derived from the PSF. The chamber parameters used in the experiment are listed in Table 3.

Table 3. Parameters for conditioning and testing material specimens for emissions of VOCs using small-volume chambers (Hodgson, 2004).

Parameter		Units	Value
Conditioning Period	Temperature	^{o}C	21 ± 2
	Relative humidity	% RH	Ambient
	Volume	m^3	0.019
	Flow rate	m^3 h^{-1}	0.066 ± 0.010
Test Period	Temperature	^{o}C	23 ± 1
	Relative Humidity	% RH	50 ± 5
	Volume	m^3	0.0105
	Flow rate	m^3 h^{-1}	0.059 ± 0.003
	Ventilation rate	h^{-1}	5.66
Specimen area		m^2	~0.02
Loading ratio		m^2 m^{-3}	~2
Specimen area/Flow rate ratio		m^2/m^3 h^{-1}	~0.35

Figure 20 shows the gas-phase chamber concentrations fitted to the simple linear emissions model (Cox et al., 2002) for styrene release from PSF. While the model parameters (K and D) were obtained in independent experiments, the parameter C_0 was estimated by fitting the model to the data. The fitted value for the initial concentration of styrene in PSF was 2.3×10^7 µg/m^3. This value compares well to the measured value of 1.9×10^7 µg/m^3. The PSF density value used for this measurement is 33 kg/m^3.
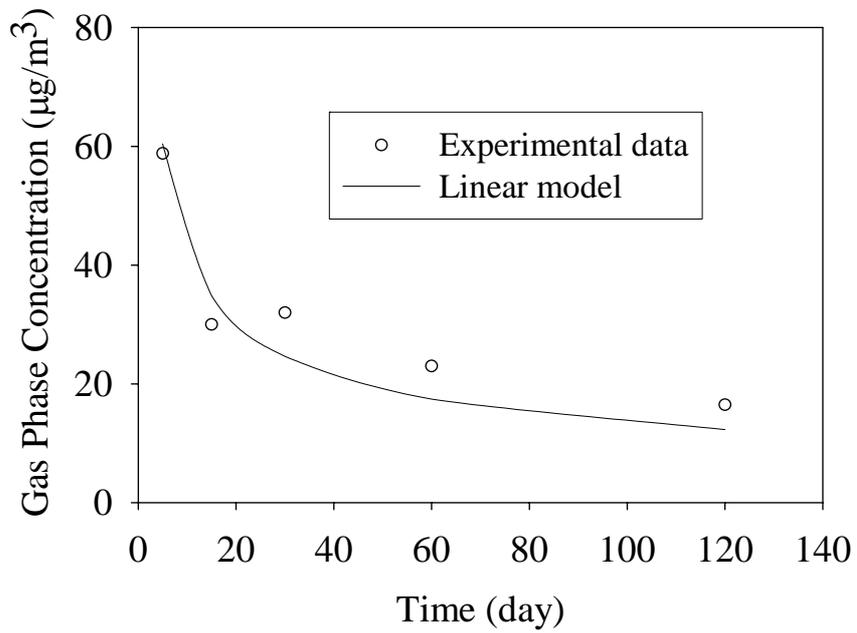
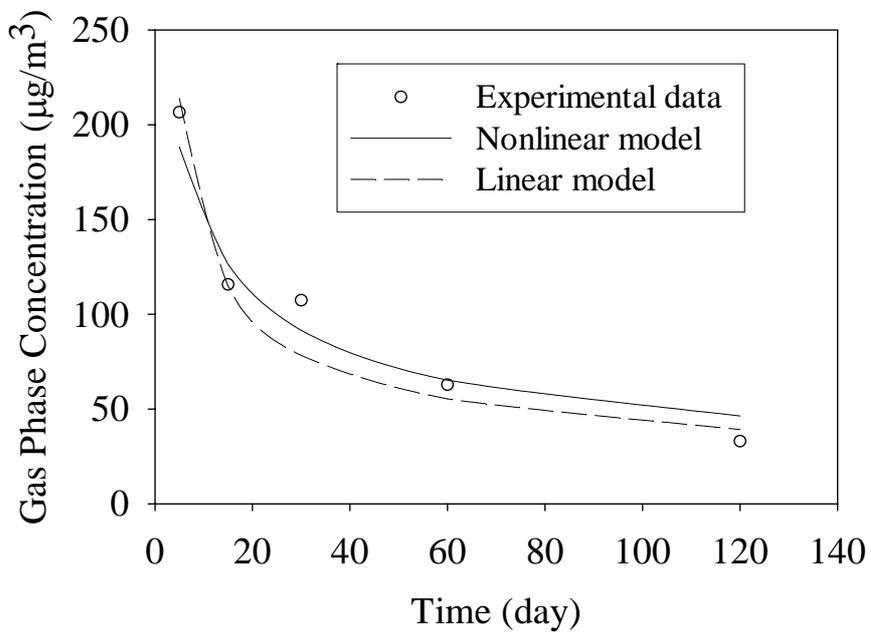Figure 20. Validation for styrene/PSF with linear emissions model

Figure 21. Validation for hexanal/OSB with linear and non linear emissions models

Figure 21 shows the measured concentrations of hexanal emitted from OSB in the small chamber experiments, and the fitted gas-phase concentrations with the simple linear model and proposed non-linear emission model respectively. The Fickian D (1.8×10^{-12} m^2/s) was used in the simple linear diffusion model while the effective De (3.3×10^{-12} m^2/s) was used in the new non-linear model as the diffusion coefficient. The experimentally determined material/air partition coefficient K was also used in the simple linear model validation. The measured C_0 value ranges from 6.3×10^6 µg/m^3 to 5.5×10^7 µg/m^3 in our duplicated experimental measurements. This initial concentration variation might be due to the OSB density variation, since the OSB density is normally not uniform across the thickness of board (ranging from 0.25-0.8 g/cm^3) (Rao, J., 1999). An average measured C_0 is 3.1×10^7 µg/m^3 is used to compare to the estimated C_0 obtained from the new non-linear emission model, which is 2.2×10^7 µg/m^3. The estimated and measured C_0 are quite close and the new non linear emission model provides a good prediction of the hexanal emissions from OSB. At the same time, as a comparison, the estimated C_0 value obtained from the simple linear diffusion model is 1.32×10^8 µg/m^3, which is far greater than the measured value. These results show that if sorption/desorption kinetics is asymmetrical, the linear model can not be used to predict VOC emissions. The non linear emission model proposed in this paper should prove to be of value for predicting emissions of polar compounds from building materials.

CONCLUSIONS

Kinetic sorption/desorption data should be obtained and analyzed before using any emission models on building materials. For symetrical sorption/desorption kinetic data with a linear sorption isotherm, a simple linear diffusion model can be used to predict VOC emissions from building materials. For the asymmetrical sorption/desorption case, where desorption usually takes longer than sorption, the sorption isotherm should be carefully examined. In this case, the local equilibrium in the materials should not be neglected. The new non-linear model developed in this paper can provide a convenient prediction for such an application.

ACKNOWLEDGEMENT

REFERENCES

Andersson, K. et al., 1997, "TVOC and Health in Non-industrial Indoor Environments, Report from a Nordic Scientific Consensus Meeting at Langholmen in Stockholm, 1996". *Indoor Air,* Vol.7, 78-91.

Axley, W. J. and Lorenzetti, D., 1993, Sorption Transport Models for Indoor Air Quality Analysis, Modeling of Indoor Air Quality and Exposure, *ASTM STP 1205,* 105-127.

Barry, A. and Corneau, D., 1999, "The Impact of Wood Composite Panel Products Such as OSB, Particleboard, MDF and Plywood on Indoor Air Quality", *Indoor Air 99, Proceedings of the 8th International Conference on Indoor Air Quality and Climate*, Edinburgh, Scotland, Aug. 8-13, Vol.5, 129-134.

Cox, S. S., Little, J. C. and Hodgson, A. T., 2002, Predicting the Emission Rate of Volatile Organic Compounds from Vinyl Flooring, *Environmental Science and Technology*, Vol.36, 7-9.

Crank, J., 1976, *The Mathematics of Diffusion*, 2nd Edition, Oxford University Press, New York, 44-49.

Haghighat, F. and Donnini, G., 1993, Emission of Indoor Pollutants from Building Materials- State of the Art Review, *Architectural Science Review*, Vol.36, 13-22.

Hodgson, A. T., 2003, Volatile Organic Chemical Emissions from Structural Insulated Panel (SIP) Materials and Implications for Indoor Air Quality. Berkeley, CA, Lawrence Berkeley National Laboratory (LBNL-53768).

Jorgensen, R. B., Dokka, T. H. and Bjorseth, O., 2000, Introduction of a Sink-diffusion Model to Describe the Interaction between Volatile Organic Compounds (VOCs) and Material Surfaces, *Indoor Air*, No.10, 27-38.

Lin, T., Little, C. J. and Nazaroff, W. W., 1994, Transport and Sorption of Volatile Organic Compounds and Water Vapor within Dry Soil Grains, *Environmental Science and Technology*, Vol.28, 322-330.

Lin, T., Little, C. J. and Nazaroff, W. W., 1996, Transport and Sorption of Organic Gases in Activated Carbon, *Journal of Environmental Engineering*, Vol.22, No.3, 169-175.

Little, C. J. and Hodgson, T. A., 1996, A Strategy for Characterizing Homogeneous, Diffusion-controlled, Indoor Sources and Sinks, *Standard Technical Publication 1287*, American Society for Testing and Materials, 294-304.

Little, C. J., Hodgson, T. A. and Gadgil, J. A., 1994, Modeling Emissions of Volatile Organic Compounds from New Carpets, Atmospheric Environment, Vol.28, 227-234.

Lu, Y. and Pignatello, J. J., 2002, Demonstration of the "Conditioning Effect" in Soil Organic Matter in Support of a Pore Deformation Mechanism for Sorption Hysteresis, *Environmental Science and Technology*, Vol.36, 4553-4561.

Rao J., 1999, OSB-hygrothermal Properties as Compared to Other Sheathing Panels, *Conceptual Reference Database for Building Envelop Research,* http://alcor.concordia.ca/~raojw/crd/essay/essay000129.html.

Van Der Wal, F. J., Hoogeveen, W. A. and Wouda P., 1997, The Influence of Temperature on the Emission of Volatile Organic Compounds from PVC Flooring, Carpet and Paint, *Indoor Air*, No.7, 215-221.

Yang, X. et al., 2001, A Mass Transfer Model for Simulating VOC Sorption on Building Materials, *Atmospheric Environment*, Vol.35, 1291-1299.

Yu, C. and Crump, D., 1998, A Review of the Emission of VOCs from Polymeric Materials Used in Buildings, *Building and Environment*, Vol.33, No.6, 357-374.

CHAPTER 3: USING FUGACITY TO MODEL VOC EMISSIONS FROM MULTI-LAYER BUILDING MATERIALS

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ABSTRACT

Composite layered building materials are widely used in indoor environments due to their environmental and energy advantages. However, the tight structure may result in degraded indoor air quality and the potential release of volatile organic compounds (VOCs) from these layered materials must be considered. A theoretical physically-based diffusion model for predicting VOCs emissions from multi-layer materials is described in this paper. It is assumed that the individual layers are flat homogeneous slabs, that internal mass transfer is governed by diffusion, and that the indoor air is well mixed. For each layer, the diffusion coefficient (D), the partition coefficient (K), and the initial concentration (C_0) are the key model parameters. In this model, a fugacity approach is presented to numerically solve the model and is used to eliminate the concentration discontinuities at the interface between layers. This overcomes an insurmountable obstacle associated with numerically simulating mass transfer in composite layers. The numerical model is partially validated with a double-layer system by comparing predicted concentrations to those obtained by a previously published analytical solution. In addition, hexanal and styrene emissions from multi-layer Structural Insulated Panels (SIPs) are simulated to demonstrate the usefulness of the model. These preliminary results establish the viability of the fugacity approach. Finally, the multi-layer layer model is used to demonstrate the impact that barrier materials can have. Results show that contaminant gas phase concentration can be greatly reduced with a barrier layer on the surface. This reveals the potential of thin barrier layers to minimize the environmental impact of panelized systems. Future work will focus on a more complete experimental validation of the multi-layer model.

KEYWORDS

Diffusion, Emission, Mass transfer, Fugacity, Multi-layer, Modeling, Volatile Organic Compounds, Building materials, Indoor air.

NOTATION

A   surface area of building material (m^2)

C_i concentration of compound in the ith material phase (mg m^{-3})

$f_i(x)$ initial concentration of compound in the ith material phase (mg m^{-3})

F_i fugacity in the ith material phase

Z_i fugacity capacity in the ith material phase

Z_{air} air fugacity capacity

D_i diffusion coefficient for compound in the ith material phase (m^2 s^{-1})

$K_{i/air}$ partition coefficient between material phase i and gas phase (dimensionless)

L_i thickness of the ith layer in building material (m)

L   total thickness of layers in building material (m)

Q   volumetric air flow rate (m^3 s^{-1})

t   time (s)

V   volume of air in chamber or room (m^3)

x   distance (m)

y   concentration of compound in gas phase (µg m^{-3})

y_{in} influent concentration of compound in gas phase (µg m^{-3})

λ_i mesh ratio for the ith layer

r, r+1   denote the start and end of any space interval

s, s+1   denote the start and end of any time interval

$u_i^{r,s}$ fugacity at discrete nodes

N_i number of nodes in the ith layer

INTRODUCTION

Volatile organic compounds emitted from building materials are important contributors to indoor air pollution in buildings. For dry building materials, the diffusion within the material cannot be ignored and the internal diffusion is more likely to be the dominating resistance. In previous work, a physically-based model that predicts emissions from a single-layer, diffusion-controlled VOC source has been validated (Cox et al., 2002). Recently, the single-layer model was extended to a double-layer assembly on a theoretical basis, and an analytical solution to the double-layer model was obtained (Kumar, 2003). However, compared to the single-layer model, finding the roots for the double-layer analytical solution is fairly involved. In addition, the composition of building materials ranges from single homogeneous materials to layered systems with different diffusion characteristics. When addressing composites with more than two layers, the usual analytical techniques become formidably complicated. Many approximations must be made in the analytical model and it is unclear, after these approximations have been made, just how well an analytical model will describe the real performance (Cunningham, 1990). It is therefore tempting to consider a numerical solution for the multi-layer composites. However, in general, arbitrary composite systems present serious obstacles to numerical computation. One of the obstacles arises from the difficulty for solving sharply discontinuous concentration profiles due to partitioning and sorption phenomena (Trefry, 1999). These discontinuities at the interior interfaces are likely to cause aliasing problems (Demeio, 1998). Thus it is very complicated and almost impossible to find the numerical solution of the model in multi-layer systems.

In this paper, the particular numerical difficulty of mass transfer through composite media is solved. We introduce an equilibrium criterion, in which an intermediate quantity can be separately related to the concentrations at different phases. Chemical potential, fugacity and activity are suitable criteria, with fugacity being preferred for most organic compounds assuming it is linearly related to concentration (Mackay, 2001). The advantage of the fugacity approach is that the quantities are equal at the interface between adjacent layers. Thus the discontinuities generated when using concentrations are removed. Such fugacity continuity makes the numerical solution of the multilayer

diffusion problem possible. The existence of such a model should allow predictions to be made and allow a check on the predictive power of simpler analytical models. In order to test calculation methods, comparisons between numerical solution using fugacity method and analytical solution are made. A multi-layer model simulation for predicting hexanal and styrene emission in Structural Insulated Panels (SIPs) is also presented. The results establish the viability of the fugacity approach in the numerical multi-layer model. As a further step, the multi-layer layer model is used to demonstrate the impact that barrier materials can have. Results show that contaminant gas phase concentration can be reduced greatly with a barrier layer on the surface. This reveals the potential of thin barrier layers to minimize the environmental impact of panelized systems.

MODEL DEVELOPMENT USING FUGACITY

This section summarizes the physical multi-layer model expressed in fugacity. The material configuration is shown in Figure 22.
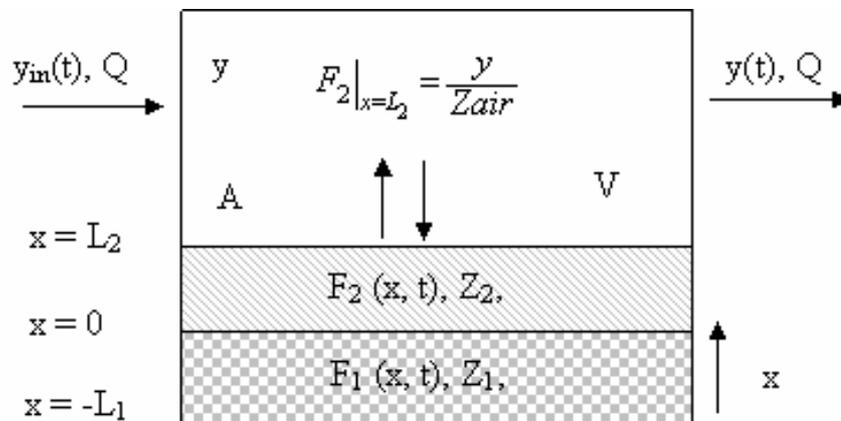

Figure 22. Schematic representation of double-layer model

It is assumed that only upper layer surface is exposed to the room air. At low concentrations, fugacity is proportional to concentration. To express concentration in terms of fugacity, we use

$$C = ZF \tag{1}$$

where C is concentration (mol m^{-3}), Z is fugacity capacity (mol/m^3.Pa), and F is fugacity (Pa). The fugacity capacity Z is different for different environments. The fugacity of the pollutant F(x, t) in each layer is governed by the one-dimensional diffusion equation:

$$\frac{\partial F_i}{\partial t} = D_i \frac{\partial^2 F_i}{\partial x^2} \tag{2}$$

where F_i is the material-phase fugacity in the ith layer, i=1,2,3…n, D_i is the diffusion coefficient in the ith layer, t is the time and x is the distance from the bottom layer. The initial condition is given by a general non-uniform fugacity profile in each material slab layer:

$$F_i = \frac{f_i(x)}{Z_i} \text{ at } t = 0 \tag{3}$$

The first boundary condition assumes no flux through the bottom of the lowest layer:

$$\frac{\partial F_1}{\partial x}\bigg|_{x=0} = 0 \tag{4}$$

The second boundary condition is based on a mass balance about the chamber air:

$$V\frac{\partial y_n}{\partial t} = Qy_{in} + D_n A Z_n \frac{\partial F_n}{\partial x} - Qy_n \text{ at } \quad x = L_1 + L_2 + ...L_n \tag{5}$$

The top layer surface is assumed to be in equilibrium with the chamber air at all time:

$$y_n = Z_{air} F_n \bigg|_{x=L1+L2+...Ln} \tag{6}$$

where Z_{air} is the air fugacity capacity, its value is about 4×10^{-4} mol/m^{3}Pa and it is the same for all non-interacting substances. The second boundary condition becomes:

$$V Z_{air} \frac{\partial F_n}{\partial t} = Q Z_{air} F_{in} + D_n A Z_n \frac{\partial F_n}{\partial x} - Q Z_{air} F_n \tag{7}$$

After transformations

$$D_n \frac{\partial F_n}{\partial x} - k_n \frac{\partial F_n}{\partial t} - h_n D_n F_n + h_n D_n F_{in} = 0 \tag{8}$$

where $F_{in} = \dfrac{y_{in}}{Z_{air}}$, $h_n = \dfrac{Q}{AK_{n/air}D_n}$, $k_n = \dfrac{V}{AK_{n/air}}$, $K_{n/air} = \dfrac{Z_n}{Z_{air}}$ (9)

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The contacts between the adjacent layers are considered to be perfect, thus the two fugacity and flux continuity equations at different interfaces take the following form:

$$F_i = F_{i+1} \tag{10}$$

$$D_i Z_i \frac{\partial F_i}{\partial x} = D_{i+1} Z_{i+1} \frac{\partial F_{i+1}}{\partial x} \qquad \text{i=1,2…n} \tag{11}$$

NUMERICAL MODEL FORMULATIONS AND NODE DISTRIBUTION

A Forward Time and Centered Space (FTCS) scheme is used to discretize time and space, as the central difference formulae give the greatest accuracy compared to the other difference methods and the forward time formula has the advantage that it allows for the quantities at time step t+1 being calculated only from those known at time step t (Alejandro, 1994, Griffiths and Smith, 1997). In order to approximate the differential equation by a finite difference expression we divide the spatial domain into N_i sections, each of length a_i for different layers, and consider as many time steps as required, each of duration b. Correspondingly, let $u_i^{r,s}$ be the values of fugacity at the discrete mesh points in the ith layer at the node $x=ra_i$ and time sb.

Numerical Model Formulations

The mass balance equation for boundary nodes between layer i and layer i+1 is:

$$
\begin{aligned}
(\lambda_{i+1} + \alpha_{i+1,i} K_{i+1,i} \lambda_i) u_i^{r,s+1} &= 2\alpha_{i+1,i} K_{i+1,i} \lambda_i \lambda_{i+1} u_{i+1}^{r+1,s} + 2\lambda_i \lambda_{i+1} u_i^{r-1,s} \\
&+ (-2\alpha_{i+1,i} K_{i+1,i} \lambda_i \lambda_{i+1} + \alpha_{i+1,i} K_{i+1,i} \lambda_i - 2\lambda_i \lambda_{i+1} + \lambda_{i+1}) u_i^{r,s}
\end{aligned}
$$

$$\tag{12}$$

The mass balance equation for the node on the exterior boundary surface which is in contact with chamber air is:

$$
\begin{aligned}
(D_{i+1} b + 2a_{i+1} k_{i+1} \lambda_{i+1}) u_{i+1}^{r,s+1} &= 2D_{i+1} b \lambda_{i+1} u_{i+1}^{r-1,s} + (2a_{i+1} k_{i+1} \lambda_{i+1} - 2D_{i+1} b \lambda_{i+1} + D_{i+1} b \\
&- 2a_{i+1} b h_{i+1} D_{i+1} \lambda_{i+1}) u_{i+1}^{r,s} + 2a_{i+1} b h_{i+1} D_{i+1} \lambda_{i+1} u_{in}
\end{aligned}
$$

$$\tag{13}$$

The equation for the node on the bottom boundary surface with no flux is:

$$u_1{}^{r,s+1} = (1-2\lambda_1)u_1{}^{r-1,s} + 2\lambda_1 u_1{}^{r,s} \tag{14}$$

The equation for the nodes in the layers:

$$u_i{}^{r,s+1} = (1-2\lambda_i)u_i{}^{r,s} + \lambda_i u_i{}^{r-1,s} + \lambda_i u_i{}^{r+1,s} \tag{15}$$

The coefficients of the above equations are:

$$\lambda_i = \frac{D_i b}{a_i{}^2} \tag{16}$$

$$\alpha_{i+1,i} = \frac{a_{i+1}}{a_i} \tag{17}$$

$$K_{i+1,i} = \frac{K_{i+1/air}}{K_{i/air}} \tag{18}$$

Node Distribution Criteria

An important aspect of the numerical solution is correctly distributing the nodes and choosing the mesh ratio. When using the finite-difference method, the overall accuracy can always be improved by increasing the total number of nodes if they are distributed correctly, thus establishing the node distribution is the first step. It has been found that placing a node on each internal boundary provides satisfactory results when addressing finite-difference modeling of multi-layered walls (Waters, 1985). In addition, the use of boundary nodes will result in a more efficient formulation of the problem, since material properties will be constant between any two nodes on the boundary (Budaiwi, 1999). In this paper, we choose the points of the mesh so that all interface boundary points fall on the grid. In addition, in order to ensure the error in all parts of the model is approximately the same, we make the mesh ratio the same in different layers. Based on these conditions, the node distribution criterion can be formulated. For the two adjacent layers, the following criterion needs to be satisfied: $\dfrac{N_i}{N_{i+1}} = \dfrac{L_i}{L_{i+1}}\sqrt{\dfrac{D_{i+1}}{D_i}}$, where N_i and N_{i+1} are the number of nodes in the lower layer and upper layer, respectively. The only remaining concern about the FTCS method is its accuracy and stability. It can be proved

that for choice of time and space step that yield the mesh ratio less or equal than 0.5, the method is guaranteed stable and accurate (Borse, 1997; Lindfield and Penny, 1995). The significance of this result is that the time should not exceed the characteristic diffusion time across a cell of space step.

RESULTS AND DISCUSSIONS

Simulation of Double-layer Model for Pentadecane Emission in OSB+VF

A real environmental chamber situation in which pentadecane diffuses through a double layer system composed of oriented strand board (OSB) and VF is simulated in this part. The schematic is shown in Figure 22. It is assumed that each material layer has zero initial concentration and acts as a sink for the compound. A constant influent gas phase concentration is used. Instead of using hypothetical parameters, we take the parameters K and D from the experimental results of Cox et al. (2001). The parameters used in this case are listed in Table 4. For this double-layer model, a relatively complicated analytical solution is available (Kumar, 2003). This provides an opportunity to check the accuracy of the fugacity-based numerical model. A careful comparison (for both gas phase and material phase concentrations) between numerical and analytical results is therefore made, as shown in Figures 23 and 24, respectively. The numerical and analytical results agree well, and suggest that the fugacity-based numerical model is reliable.

Table 4. Basic parameter values for double-layer simulation

Parameters	Value	Units
Partition coefficient in the bottom layer, $K_{1/air}$	3000	
Partition coefficient in the top layer, $K_{2/air}$	12027	
Diffusion coefficient in the bottom layer, D_1	4.50×10^{-13}	m^2/s
Diffusion Coefficient in the top layer, D_2	1.07×10^{-11}	m^2/s
Volume of room, V	0.0069	m^3

Flow rate through room, Q	0.0000107	m^3/s
Surface area of VF exposed to air, A	0.0064	m^2
Thickness of bottom layer, L_1	0.0015	m
Thickness of top layer, L_2	0.0012	m
Initial concentration of source, C_{10}	0	$\mu g/m^3$
Initial concentration of source, C_{10}	0	$\mu g/m^3$
Influent gas phase concentration, y_{in}	2500	$\mu g/m^3$
Molecular weight of pentadecane	212.42	g/mole
Fugacity capacity of air, Z_{air}	4.00×10^{-4}	$mol/m^3 pa$
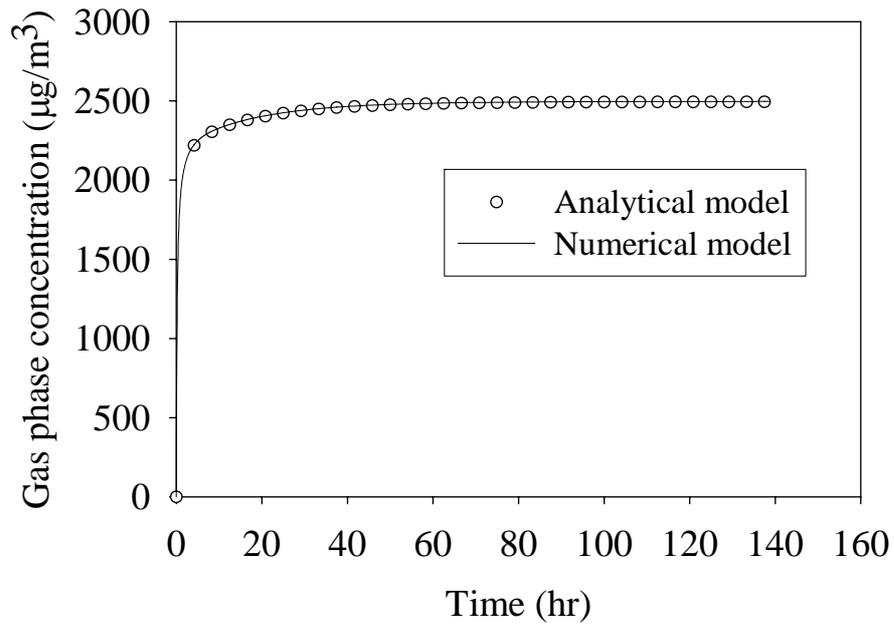
Figure 23. Gas phase concentration comparison
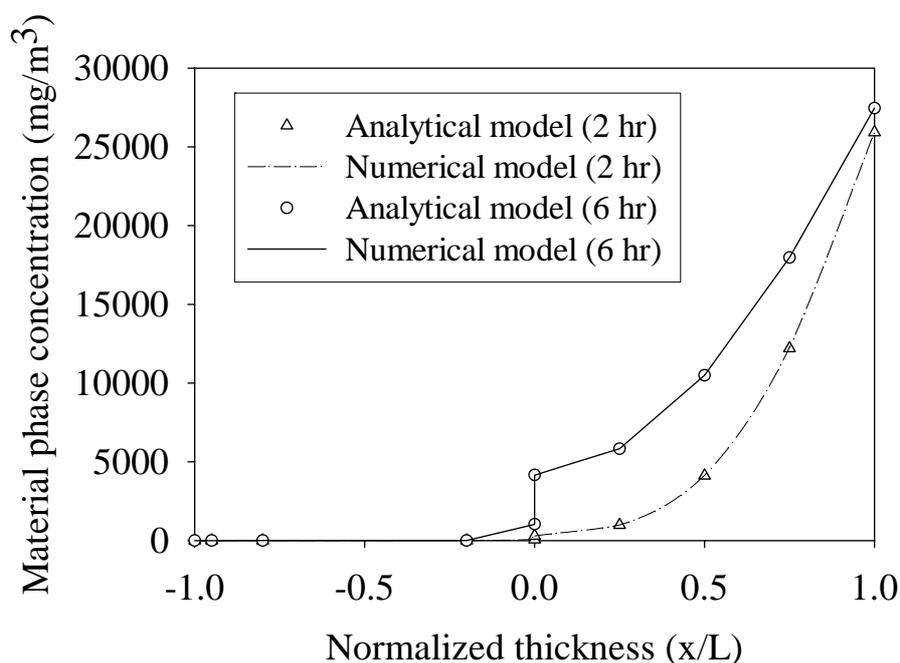
Figure 24. Material phase concentration comparison

Multi-layer Model Simulation for Hexanal and Styrene Emission in SIPs

The basic SIPs configuration uses oriented strand board (OSB) and polystyrene foam (PSF) in a multi-layered sandwich-like structure. A schematic representation of the SIPs system in a real room is given in Figure 25. In this simulation, mass transfer from both external surfaces of the SIPs is considered. In contrast to the chamber model, an outdoor side is also considered in the simulation. The model parameters K and D were measured experimentally, as described by Yuan et al. (2005). The C_0 values were obtained by model fitting. The room dimension and the model parameters are listed in Table 5. The predicted material-phase hexanal fugacity and concentration profiles (shown at 5 days, 30 days and 120 days after the SIP installation) are presented in Figures 26 and 27, respectively. Although the multi-layer model has not yet been validated, a reasonable concentration change is observed. With the diffusion of hexanal from OSB into the foam, which is initially devoid of hexanal, the concentration in both the OSB layers decreases, while the concentration in the interior PSF layer increases. Likewise, the predicted

material-phase styrene fugacity and concentration profiles (shown at 5 days, 30 days and 120 days after the SIP installation) are listed in Figure 28 and 29, respectively. The styrene concentration in both the OSB layers increases while the concentration in the interior PSF layer decreases with time, which is different from hexanal diffusion, since PSF is the only styrene source in SIPs.
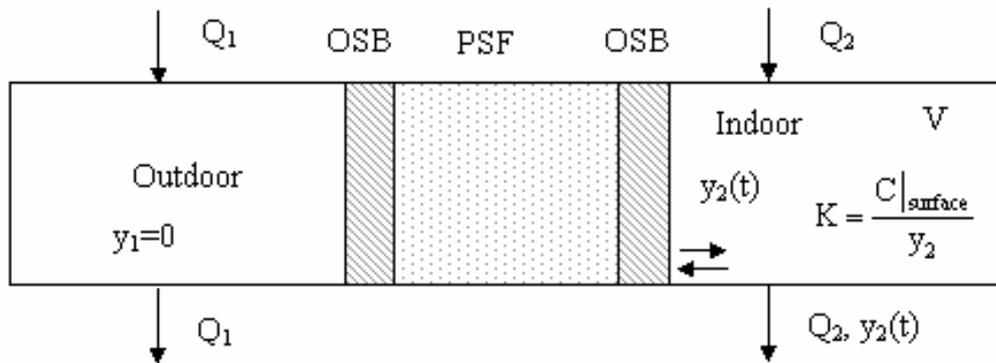

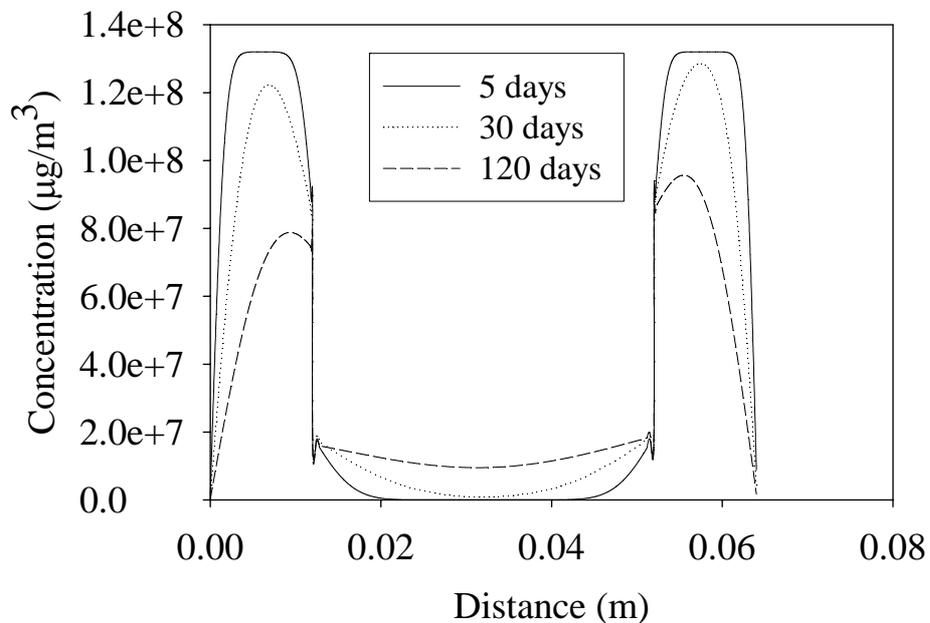Figure 25. Schematic of a SIP system installed on the outside wall of an exterior room

Figure 26. Material-phase hexanal fugacity

Table 5. Basic parameter values for multi-layer simulation

| Compounds	Parameters	Value	Units
Hexanal	Partition coefficient in OSB	6900	
	Partition coefficient in PSF	1500	
	Diffusion coefficient in OSB	2.0×10^{-12}	m^2/s
	Diffusion Coefficient in PSF	1.5×10^{-11}	m^2/s
	Initial concentration of OSB	1.3×10^8	$\mu g/m^3$
	Initial concentration of PSF	0	$\mu g/m^3$
Styrene	Partition coefficient in OSB	560	
	Partition coefficient in PSF	260	
	Diffusion coefficient in OSB	6.7×10^{-12}	m^2/s
	Diffusion Coefficient in PSF	6.2×10^{-12}	m^2/s
	Initial concentration of OSB	0	$\mu g/m^3$
	Initial concentration of PSF	4×10^7	$\mu g/m^3$
	Thickness of OSB	0.0012	m
	Thickness of PSF	0.04	m
	Surface area exposed to air, A	45	m^2
	Influent gas phase concentration, yin	0	$\mu g/m^3$
	Volume of room, V	60	m^3
	Air exchange rate, Q	0.5	h^{-1}
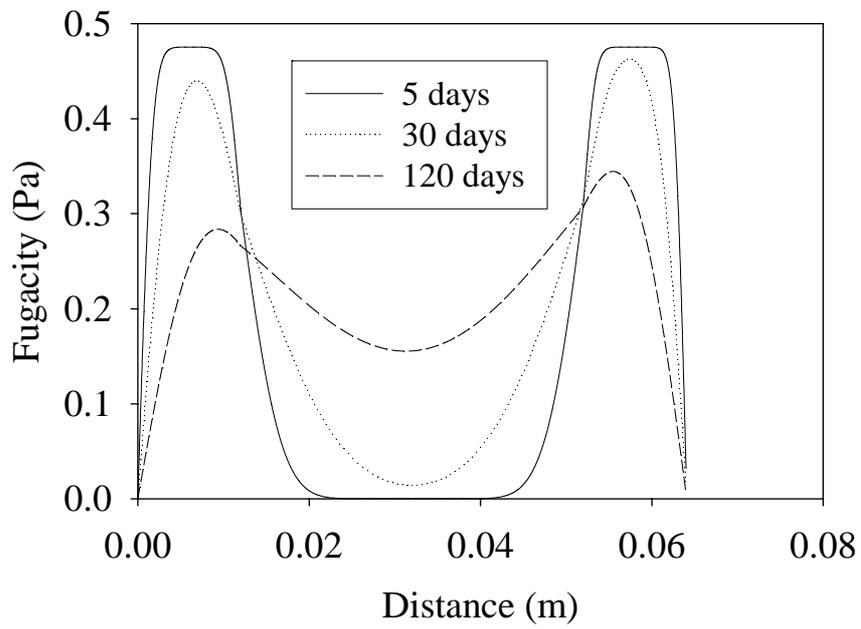
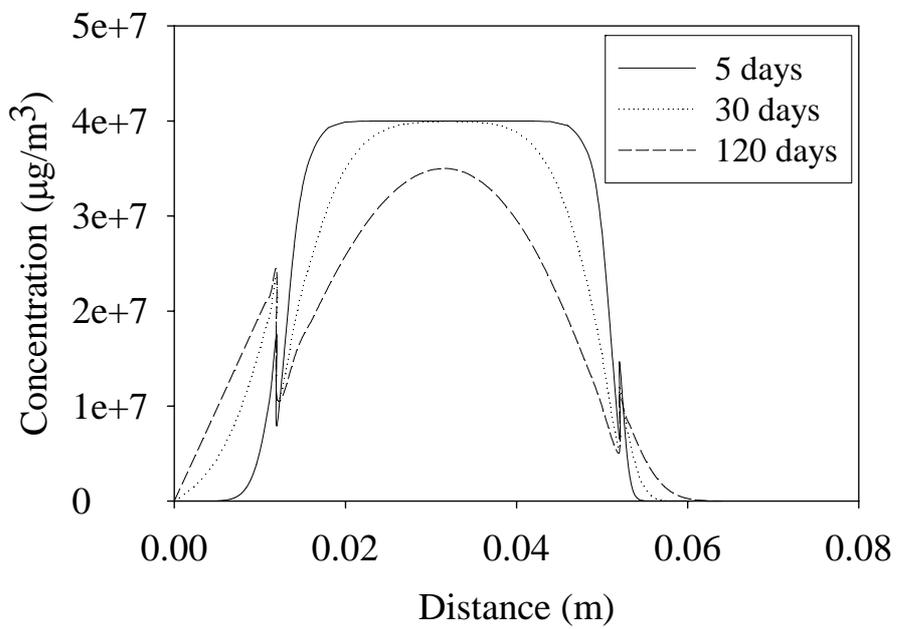Figure 27. Material-phase hexanal concentration

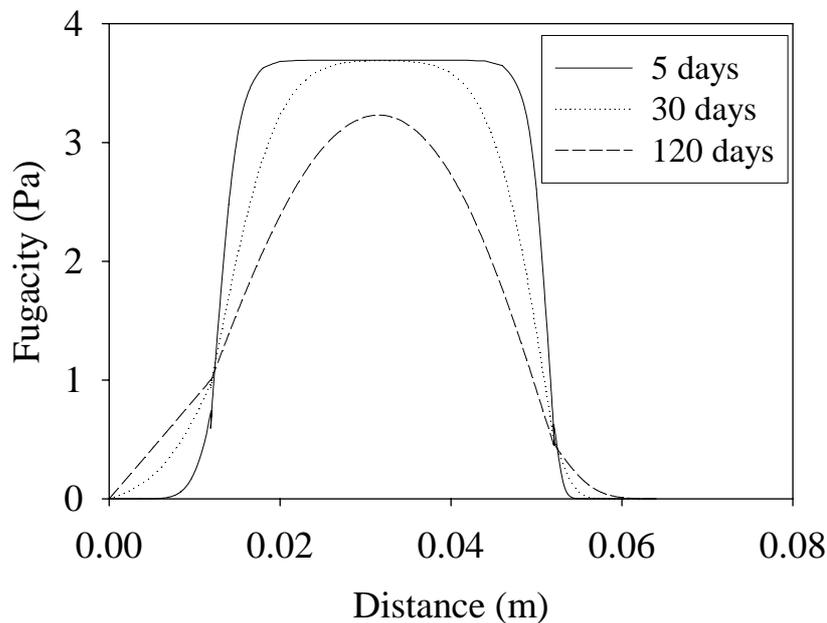Figure 28. Material-phase styrene fugacity

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Figure 29. Material-phase styrene concentration

Simulation of Hexanal Emission with a Barrier Layer in SIPs

The presence of hexanal can be minimized by incorporating an absorbent into the polymer during the processing of the material. Dupont Polymers (USA) has patented an absorbent (a molecular sieve) that is a crystalline zeolite with pores that attract and trap odor within its structure (Brody, 2002). A number of patents describe the incorporation of activated carbon as odor adsorbent. However, activated carbon picks up moisture and, when heated or saturated with odor, can surrender some or all the adsorbed compounds (Brody et al., 2001).

It also might be useful to coat the SIPs with an additional polymer layer, which may serve as a barrier layer to retard the diffusion of hexanal. The barrier layer may be selected from those polymer membranes that are effective to retard diffusion. Figure 30 illustrates the SIPs system with a barrier layer on the surface. In this section, a hexanal emission simulation for this SIP system is conducted. The much higher K value and

lower D value for hexanal in the barrier layer than that in the OSB layer were selected. Figure 31 shows the material phase concentration within the barrier layer. The barrier layer with the high K value works like a strong sink and takes up some of the hexanal. With the lower D, it also works to retard the diffusion process from the material into the indoor air. Figure 32 shows that a much lower gas phase hexanal concentration will be achieved with a barrier layer than without a barrier layer.
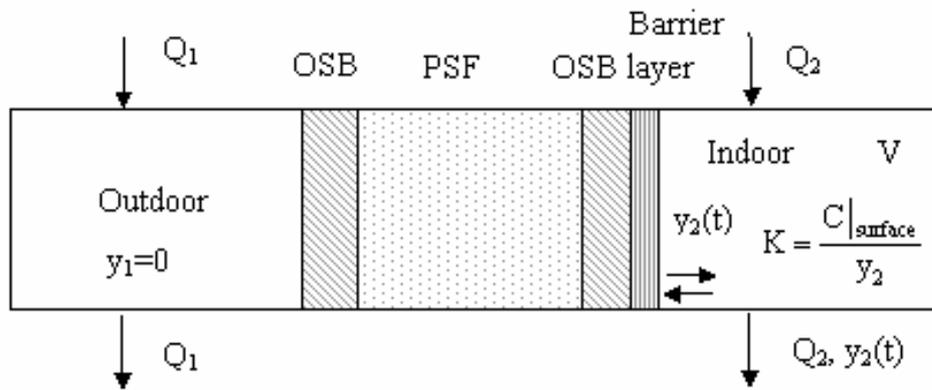

Figure 30. Schematic of a SIP system with a barrier layer installed on the OSB surface
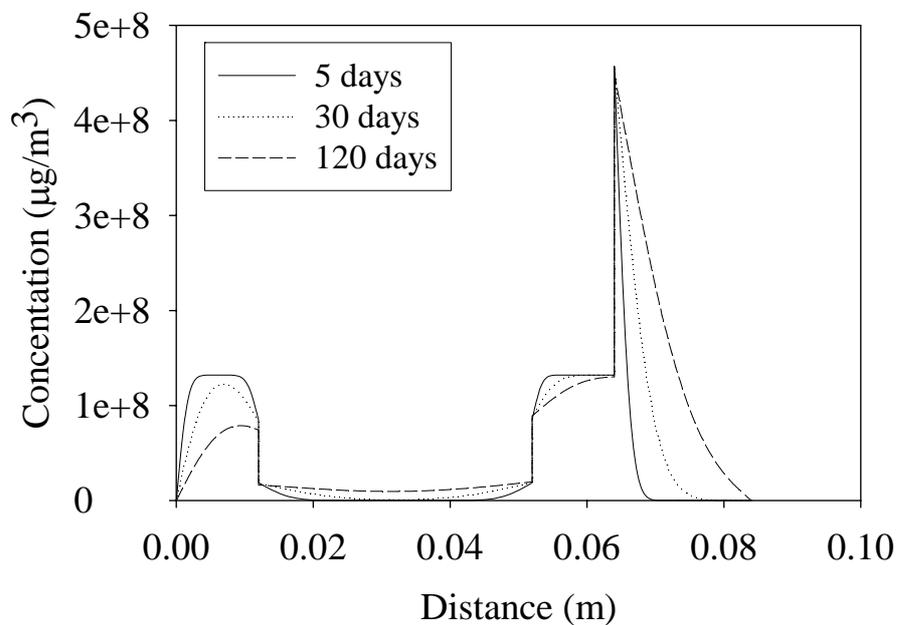

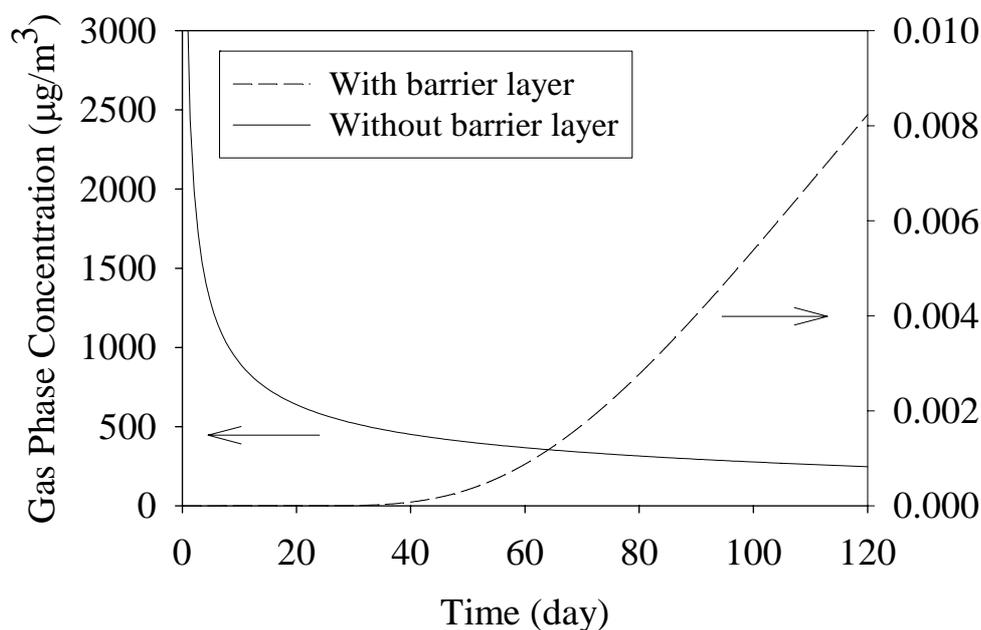Figure 31. Material-phase hexanal concentration in SIPs with barrier layer

Figure 32. Gas-phase hexanal concentration with and without barrier layer

CONCLUSIONS

The paper presents a fugacity approach for numerical simulating volatile organic compound emissions from multi-layer system. The solution of the diffusion equations was obtained by implementing forward time and centered space (FTCS) scheme. For this numerical approach, the node distribution criterion is used. At each node, the mass balance was performed. Emissions from a double layer system were illustrated in order to compare the predictions of the numerical fugacity-based model with the analytical concentration-based model. The results show good agreement between the analytical and numerical solution. In addition, hexanal and styrene emission from a multi-layer system SIPs were simulated, and fugacity and concentration profiles were compared. The results show that the fugacity approach can successfully smooth the concentration "jumps" between adjacent layers, and provides a viable solution to the numerical difficulties when modeling mass transfer through the multi-layer systems. Finally, the multi-layer layer model is used to demonstrate the impact that barrier materials can have. Results show

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that contaminant gas phase concentration can be reduced greatly with a barrier layer on the surface. This reveals the potential of thin barrier layers to minimize the environmental impact of panelized systems.

ACKNOWLEDGEMENT

REFERENCES

Alejandro, L. G., 1994, *Numerical Methods for Physics*, Prentice Hall, Englewood Cliffs, New Jersey 07632, 166-172.

Borse, G. J., 1997, *Numerical Methods with MATLAB, A Resource for Scientists and Engineers,* PWS Publishing Company, 484-486.

Budaiwi, I., El-Diasty, R. and Abdou, A., 1999, Modeling of Moisture and Thermal Transient Behavior of Multi-layer Non-cavity Walls, *Building and Environment*, Vol.34, 537-551.

Cox, S. S., Zhao, D.Y. and Little, J. C., 2001, Measuring Partition and Diffusion Coefficients of Volatile Organic Compounds in Vinyl Flooring, *Atmospheric Environment*, Vol.35, 3823-3830.

Cunningham, M. J., 1990, Modeling of Moisture Transfer in Structures-I. A Description of a Finite-difference Nodal Model, *Building and Environment*, Vol.25, No.1, 55-61.

Demeio, L., Manassero, M. and Sani, D., 1998, A Numerical Method for the Solution of the Diffusion Equation in Multilayered Systems, *Internal Report*, No.5.

Griffithis, D.V. and Smith, L. M., 1997, *Numerical Methods for Engineers, A Programming Approach*, Blackwell Scientific Publications, 283-288.

Kumar, D. and Little, J. C., 2003, Characterizing the Source/sink Behavior of Double-Layer Building Materials, *Atmospheric Environment*, Vol.37, 5529-5537.

Lindfield, G. and Penny, J., 1995, *Numerical methods using Matlab*, Ellis Horwood Limited, 215-217.

Little, C. J., Hodgson, T. A. and Gadgi, J. A., 1994, Modeling Emissions of Volatile Organic Compounds from New Carpets, *Atmospheric Environment*, Vol.28, 227-234.

Little, C. J. and Hodgson, T. A., 1996, A Strategy for Characterizing Homogeneous, Diffusion-controlled Indoor Sources and Sinks, In: Tichenor, B.A. (Ed.), *ASTM STP 1287,* American Society for Testing and Materials, Philadephia, 294-304.

Mackay, D., 2001, *Multimedia Environmental Models, the Fugacity Approach*, Lewis Publishers, 69-83.

Trefry, M. G. and Whyte, D. S., 1999, Analytical Solution for Partitioned Diffusion in Laminates: I: Initial Value Problem with Steady Cauchy Conditions, *Transport in Porous Media*, Vol.37, 93-128.

Waters, J. R. and Wright, A. J., 1985, Criteria for the Distribution of Nodes in Multilayer Walls in Finite-difference Thermal Modeling, *Building and Environment*, Vol.20, No.3, 151-162.