Diffusion-Controlled Reference Material for VOC Emissions Testing: Proof of Concept

Steven S.Cox[1]
Zhe Liu [1]
John C. Little [1]
Cynthia Howard- Reed[2]
Steven J.Nabinger[2]
Andrew Persily[2]

[1]Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA 24061-0246

[2]Indoor Air Quality and Ventilation Group, Energy and Environment Division Engineering Laboratory, National Institute of Standards and Technology 100 Bureau Drive Gaithersburg, MD 20899

U.S. Department of Commerce
Dr. Rebecca M. Blank, Acting Secretary

National Institute of Standards and Technology
Patrick D. Gallagher, Director

National Institute of Standards and Technology • U.S. Department of Commerce

DISCLAIMERS

Certain commercial entities, equipment, or materials may be identified in this document in order to describe an experimental procedure or concept adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the entities, materials, or equipment are necessarily the best available for the purpose.

Any link(s) to website(s) in this document have been provided because they may have information of interest to our readers. NIST does not necessarily endorse the views expressed or the facts presented on these sites. Further, NIST does not endorse any commercial products that may be advertised or available on these sites.

Diffusion-Controlled Reference Material for VOC Emissions Testing: Proof of Concept

Steven S. Cox, Zhe Liu, John C. Little, Cynthia Howard-Reed,
Steven J. Nabinger, and Andrew Persily

Abstract

Because of concerns about indoor air quality, there is growing awareness of the need to reduce the rate at which indoor materials and products emit volatile organic compounds (VOCs). To meet consumer demand for low emitting products, manufacturers are increasingly submitting materials to independent laboratories for emissions testing. However the same product tested by different laboratories can result in very different emissions profiles due to a general lack of test validation procedures. There is a need for a reference material that can be used as a known emissions source and that will have the same emission rate when tested by different laboratories under the same conditions. A reference material was created by loading toluene into a polymethyl pentene film. A fundamental emissions model was used to predict the toluene emissions profile. Measured VOC emissions profiles using small-chamber emissions tests compared reasonably well to the emissions profile predicted using the emissions model, demonstrating the feasibility of the proposed approach to create a diffusion-controlled reference material. Practical Implications to calibrate emissions test chambers and improve the reproducibility of VOC emission measurements among different laboratories, a reference material has been created using a polymer film loaded with a representative VOC. Initial results show that the film's VOC emission profile measured in a conventional test chamber compares well to predictions based on independently determined material/chemical properties and a fundamental emissions model. The use of such reference materials has the potential to build consensus and confidence in emissions testing as well as "level the playing field" for product testing laboratories and manufacturers.

Key Words: Diffusion model, emission testing, inter-laboratory study, reference material, VOC

Introduction

Exposures related to indoor sources of volatile organic compounds (VOC) such as building materials, consumer products, and office equipment have been linked to occupant discomfort, illness (Mølhave, 1991; Wolkoff and Nielsen, 2001; Rennix et al., 2005; Boeglin et al., 2006) and reduced worker productivity (Bako-Biro et al., 2004; Fanger, 2006). Indoor VOC levels associated with these sources can be reduced by increasing outdoor air ventilation rates, but this entails increased costs for building construction, operation, and energy. As a result, low VOC emitting products are being promoted and used more widely in buildings to help achieve healthier and more productive indoor environments. Building rating systems, such as the U.S. Green Building Council's Leadership in Energy and Environmental Design (USGBC 2009), encourage the use of low emitting building products by rewarding credits for buildings that incorporate these products in their construction. To demonstrate compliance, manufacturers frequently submit products to independent laboratories for VOC emissions testing. Typically, these laboratories conduct emissions measurements following standard methods on a portion of the product in small scale chambers with environmental conditions similar to a real building. The uncertainties involved in these measurements are not well established and there is concern that results for the same materials may vary significantly when tested by different laboratories. Most published inter-laboratory studies have shown coefficients of variation between measured emission rates on the order of 50 % and as large as 300 % (Howard-Reed et al., 2007), although a recent inter-laboratory study has shown improved variation between labs (Wilke et al., 2009).

In addition to inter-laboratory studies of real or simulated product sources, chamber performance can be evaluated using permeation tube sources or by injection of gas mixtures

from cylinders. While these approaches are useful for accounting for all of the mass entering a chamber, their results are not affected by all chamber parameters (e.g., temperature, humidity and air velocity), or by the procedures associated with preparing and loading the material in the chamber. As a result, it is possible for two laboratories to both demonstrate adequate mass recovery but still obtain significantly different emission rates. There is a compelling need for greater understanding of emissions from indoor materials and the associated measurement methods and uncertainties. The creation of well characterized reference materials for VOC emissions testing is a critical prerequisite for improving emissions measurement methods. Once acceptable reference materials have been developed, they can be used by laboratories to begin the process of identifying and eliminating the root causes of variability in emissions testing.

The objective of this work is to develop a reference material for VOC emissions testing of dry, diffusion-controlled materials and evaluate the feasibility of using this source to characterize chamber performance. The mechanisms that govern the rate of emissions of VOCs from several commonly encountered materials are well established (Sparks et al., 1996). This basic understanding can be used together with a fundamental emissions model to design a suitable material that has the appropriate emissions characteristics. When the material is placed in a small chamber, the expected emissions profile predicted by the model can be compared to the observed emissions profile. This will be of great benefit, because the results can be used to provide insight into the likely causes of experimental error. In this paper, we demonstrate the feasibility of our proposed approach.

Materials and Methods

Development of an appropriate reference material requires the following steps: 1) selecting a suitable material; 2) loading a sample of the material with one or more VOCs; 3) measuring key material properties, including the material-phase diffusion coefficient, D, the material/air partition coefficient, K, and the initial effective material-phase VOC concentration, C_0; 4) using a fundamental emissions model together with the independently measured parameters (C_0, K and D) to predict the emissions profile; 5) using a small-scale environmental chamber to measure the emissions profile of the reference VOC material; and, 6) comparing the measured emissions profile to the predicted emissions profile, taking into account the uncertainty of both the experimental measurements and model predictions.

Material Selection

An ideal reference material will emit VOCs at a predictable rate and in quantities sufficient for detection and quantification over the required period of time. Chamber concentrations should be similar to those generated by typical building product sources. Critical material properties include purity, thickness, and the fundamental mass transfer parameters D and K. Thickness affects the rate, duration, and total emissions of VOCs from the material. Critical characteristics of the mass transfer parameters include the magnitude of D and K as well as the concentration independence of D and K. The magnitude of D and K affect the rate at which VOCs are emitted from a material, while concentration independence of D and K provide the ability to predict emissions behavior over a range of VOC material concentrations.

A commercially available polymer film that appears to possess suitable properties is polymethyl pentene (PMP). PMP is a copolymer of 4-methyl-1-pentene and alpha-olefin. PMP

4

film is available without organic additives such as plasticizers or stabilizers, and in film thickness from 0.025 mm to 0.25 mm.

Material Purity

Although PMP film is marketed as not containing additives, a high-resolution (±0.1 µg) dynamic microbalance was used to assess purity (Cox et al., 2001). A PMP sample was cut to dimensions of 3.65 cm by 3.65 cm using a punch press, and placed on the microbalance with clean air passing over the sample. As shown in Figure 1, the sample mass stabilized after approximately 5 h, suggesting that the PMP sample did not contain significant amounts of volatile additives or contaminants that could confound the emission tests. In contrast, other polymeric materials that have been evaluated on the recording microbalance have exhibited mass loss from additives and contaminant emissions over weeks to months. The mass loss during the first 5 h of the experiment may be moisture the PMP sample had absorbed during transportation and handling. The potential interfering affect of moisture needs to be considered, especially if gravimetric procedures are used to ascertain material properties.

Evaluating D and K

PMP mass transfer parameters D and K were also measured using the microbalance procedure (Cox et al., 2001). The recording microbalance was used to monitor and record PMP sample mass during toluene sorption/desorption cycles. The effective D was determined by fitting a Fickian diffusion model to the sorption and desorption data. Under the experimental conditions, the mass change due to Fickian diffusion in a film is given by (Crank, 1975):

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

where M_t (mg) is the total toluene mass that has entered or left the film in time t, M_∞ (mg) is the toluene mass in the film when gas-phase/material-phase equilibrium is reached, and 2L (m) is the film thickness. K was estimated using the known gas-phase toluene concentration and the total mass of toluene absorbed by the known volume of PMP at gas-phase/material-phase equilibrium.

Toluene sorption/desorption cycles were conducted on 0.254 mm thick PMP film samples at 25 ^{o}C over a range of gas-phase concentrations from 650 mg/m^3 to 2600 mg/m^3 to assess concentration dependency of the mass transfer parameters and variability of PMP properties. Gas-phase toluene concentrations were controlled using a calibration gas generator with a diffusion vial. Toluene emission rates in the calibration gas generator were determined gravimetrically using a mechanical balance accurate to ±10 μg. Mass-flow controllers were used to control gas flow rates, which were determined using a primary flow calibrator.

Loading VOC into Substrate

Substrate films with dimensions of 3.65 cm by 3.65 cm were cut from a 0.0254 cm thick PMP sheet using a punch press. Films were loaded with toluene using two different methods. In one method, four PMP films were placed onto a stainless steel screen inside a 7 L stainless steel (316L) chamber fitted with inlet and outlet ports and a fluoroelastomer gasket. A gas stream containing a known toluene concentration was passed through the chamber until gas-phase/material-phase equilibrium was reached. In the other method, films were placed in a borosilicate glass chamber attached to the recording microbalance. A gas stream of known toluene concentration was passed through the glass chamber until gas-phase/material-phase equilibrium was reached. The gas-phase toluene concentration was controlled using the

calibration gas generator and mass-flow controllers. In both methods material-phase/gas-phase equilibrium was reached in approximately 80 h. Toluene-loaded films were then wrapped in aluminum foil, sealed in plastic specimen bags, placed into a small cooler with an ice pack, and sent by overnight delivery to the National Institute of Standards and Technology (NIST) for emissions profile measurement.

Determining the Initial Material-phase VOC Concentration (C_0)

C_0 of the toluene-loaded film samples was determined gravimetrically using the recording microbalance in two different procedures. In one procedure, PMP samples were loaded with toluene directly on the recording microbalance until gas-phase/material-phase equilibrium was reached. The toluene mass gained by the PMP film during the loading process was divided by the film volume to obtain C_0. In the other procedure, PMP samples were loaded with toluene in the 7 L stainless-steel vessel and then transferred to two recording microbalances and simultaneously subjected to a background flow of clean air until the toluene completely desorbed (gas-phase/material-phase partition equilibrium at a gas-phase concentration of zero). The measured toluene mass that desorbed from the PMP film was divided by the film volume to obtain C_0.

Emissions Profile Measurement Using a Small-scale Chamber

Toluene emissions from the polymer film were measured in a rectangular dynamic stainless steel chamber following the guidelines of ASTM *Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products* (ASTM D5116-06) (ASTM 2006a). Two similar chambers (Chamber 1 and Chamber 2) were housed in a temperature controlled cabinet and provided clean, humidified air at a specified flow

rate through calibrated mass flow controllers. The chamber characteristics, including emissions test set points and measured values, as well as information regarding the methods used to measure each parameter, are listed in Table 1.

Several quality assurance tests were performed to characterize the performance of the chamber. Background VOC concentrations were measured before every test and met the ASTM D5116-06 criteria for being ≤ 2 $\mu g/m^3$ for individual VOCs and ≤ 10 $\mu g/m^3$ for the sum of all VOCs. The chamber air concentration uniformity was determined with an SF_6 decay test (ASTM 2006b). SF_6 was injected at a constant rate to reach a steady-state concentration in the chamber outlet air. Once steady-state had been reached, the SF_6 injection was stopped to allow the chamber SF_6 concentration to decay. The degree of mixing was assessed based on the concentration difference between the measured value in the chamber outlet to that predicted for a perfectly mixed chamber. All mixing tests were completed with the mixing fan on and achieved mixing levels greater than 94 % (mean = 97 %, standard deviation = 2 %), well above the required 80 % threshold in ASTM D5116-06. Similar tests were conducted with a toluene injection to assess unintentional losses (e.g., adsorption to chamber walls) of each chamber. Mass recovery values for these tests were 93 % $\pm$ 6 % (with uncertainty here and henceforth expressed as mean $\pm$ standard deviation).

The test procedure to measure emissions from the reference material included the following steps. Once the samples were received from Virginia Tech, they were retained in the original packing material and stored in a freezer at -20 °C. Prior to a test, the chambers were pre-conditioned at the set points shown in Table 1 for several hours. During the preconditioning

period, the background concentration in the chamber air was measured and verified to meet the ASTM D5116-06 criteria listed above. Sample preparation included removing the sealed film from the freezer for 5 min before unwrapping and placing it flat on the chamber floor. A wire mesh screen (3 mm by 3 mm mesh) was used to ensure the film lay flat with only its top surface and edges exposed during the test. The chamber test time started when the chamber was resealed after installing the film sample.

Air samples were collected from the chamber outlet using a vacuum pump regulated by a mass flow controller (with uncertainty of ±1 %). Chamber air samples were collected automatically every 30 min at 100 mL/min for 10 min. Prior to collecting each sample, the sample line was purged for 2 min to ensure no contamination from the previous sample. The sample volume was concentrated on a Tenax® cold trap before injection to a gas chromatograph with a mass spectrometer detector (GC/MS). The GC/MS was calibrated before every test in the range of 10 ng to 400 ng with $R^2 > 0.999$. The chamber test was run until the sample mass collected fell below the calibration minimum.

Emissions Model

Mass transfer mechanisms describing emissions from a homogeneous dry material have been well documented in the literature (Little et al., 1994; Cox et al., 2002; Xu and Zhang, 2003; Deng and Kim, 2004). Two approaches are commonly used. One approach considers the porous structure of the solid material. VOC molecules are present in pores (gas phase) and on the solid (adsorbed phase) and undergo mass transfer by gas-phase diffusion in the pores and surface diffusion on the solid. Solid-phase diffusion is usually negligible compared with the much faster diffusion through pores (Lee et al., 2005; Lee et al., 2006). To apply this approach, the porosity

of the material must be known. The second approach assumes a representative homogeneous

medium and an effective material-phase VOC concentration within the material (Little et al.,

1994; Xu and Zhang, 2003; Deng and Kim, 2004). The mass transfer of VOC within the material

is represented by an effective diffusion coefficient within the homogeneous medium.

Partitioning between the material and the air at the material surface is described by an effective

partition coefficient. The two approaches are closely interrelated (Haghighat et al., 2005; Xu et

al., 2009). In the current study, the second approach, which lumps the porous and solid

components of the reference material into a representative homogeneous solid material, is used.

As suggested in a detailed discussion on the effects of porosity (Haghighat et al., 2005), using

this simpler approach is valid for our purposes.

Figure 2 shows the mechanisms governing emissions of VOCs from a film of material in

a test chamber. These mechanisms include the internal diffusion of VOCs within the material

(characterized by the diffusion coefficient, D), partition between the material and chamber air at

the surface of the material (characterized by the equilibrium partition coefficient between the

material and air, K), the external convective mass-transfer from the air at the material surface to

the bulk air in the chamber (characterized by the convective mass-transfer coefficient, h_m), and

adsorption of VOCs onto the interior chamber walls (characterized by the equilibrium partition

coefficient between air and the chamber surface, K_s). The adsorption onto the chamber walls of a

VOC such as toluene is negligible due to the high volatility (and therefore very low K_s), while

the impact of the external convective mass-transfer depends on its relative magnitude compared

to internal diffusion. When the internal mass-transfer resistance is small, which may be due to a

large D, the external convective mass-transfer has a noticeable impact, especially during the

10

early stage of the emissions process. In contrast, the effect of external convective mass-transfer is negligible when the internal mass-transfer resistance is large. Many indoor materials, including our reference material, belong to the latter category, and therefore, emissions of VOCs from these materials are largely controlled by internal diffusion. If the chamber wall sink-effect is neglected and a uniform initial VOC concentration in the material is assumed, the material-phase concentration as a function of the distance from the base of the material and time is given by (Little et al., 1994):

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

$$\text{where} \quad h = \frac{Q}{ADK} \qquad (3)$$

$$k = \frac{V}{AK} \qquad (4)$$

and the q_n are the positive roots of

$$q_n \tan\left(q_n L\right) = h - kq_n^2 \qquad (5)$$

In equation 2, C (in mg VOC/m^3 material) is the VOC concentration in the material, x (m) is distance from the base of the material, t (s) is time, A (m^2) is the exposed material surface area, L (m) is material thickness, Q (m^3/s) is the volumetric air flow rate, and V (m^3) is the well-mixed chamber volume. Since the external convective mass-transfer is ignored, the chamber air concentration can be obtained according to the instantaneous reversible equilibrium between air and the material surface, or

$$y = \frac{C\big|_{x=L}}{K} \qquad\qquad (6)$$

where y (mg VOC/m³ air) is the VOC concentration in the well-mixed chamber air. Because the material phase concentration at the surface (C(x=L, t)) is known as an explicit function of time (equation 2), y can also be calculated as a function of time (equation 6).

Emissions profile prediction

The VOC emissions model was used to predict the VOC emissions profile of the reference material in the NIST chamber tests. Using equations 2 and 6, it is possible to predict y at any time t based on the material parameters (C_0, K and D), the dimensions of the material film (L and A) and the chamber configuration (Q and V). The uncertainty due to measurement error of C_0, K and D was taken into account using the Monte Carlo method (Kim et al., 2004). C_0, K and D were all assumed to follow normal distributions, whose means and standard deviations were estimated from replicate measurements of the parameters. Repeated model predictions (10,000) were carried out for each chamber test, with C_0, K and D randomly sampled from their distributions, and with the other parameters (L, A, Q and V) fixed for each individual prediction. The results of all the model predictions were then pooled to assess the expected variation in y as a function of time.

External convective mass-transfer resistance

External convective mass-transfer resistance during chamber tests was theoretically investigated. The air speed at 1 cm above the PMP sample was measured using a hot-wire anemometer. The average convective mass transfer coefficient, h_m, was then estimated using correlation equations that express the mass transfer coefficient as a function of the Reynolds

12

number and Schmidt number (Axley, 1991). To incorporate this effect, the mass-transfer model of Deng and Kim (2004) was employed and compared to our diffusion-controlled model to evaluate the effect of external convective mass-transfer on emissions from the reference material.

Results

Measuring D and K

Microbalance data during a toluene/PMP sorption/desorption cycle at $y = 2600$ mg/m^3 are shown in Figure 3. Figure 4 and 5 show Equation 1 fitted to these data to estimate D. Values of D and K for each experiment are summarized in Table 2. The data suggest that D and K determined from sorption are essentially the same as those determined from desorption showing that mass transfer is reversible, and that both D and K are independent of concentration for the range of concentrations evaluated. Based upon the pooled results, D and K were $(3.6 \pm 0.7) \times 10^{-14}$ m^2/s and 370 ± 50, respectively.

Estimating C_0

In one loading procedure, two PMP samples were simultaneously loaded with toluene with $y = 2600$ mg/m^3 on two nearly identical microbalances and C_0 was determined by dividing toluene mass gained during the loading process by the volume of the PMP sample. Using this procedure the C_0 value obtained was 1100 ± 200 g/m^3. In the other loading procedure, four PMP samples were simultaneously loaded with toluene with $y = 1700$ mg/m^3 in the 7 L stainless steel chamber until sorption equilibrium was reached, followed by exposure to clean air on the microbalances to assess desorption. The toluene mass that desorbed from each PMP film was divided by the film volume to obtain C_0. The value of C_0 for these samples was 550 ± 7 g/m^3.

Emissions Profile Measurement Using Small-Scale Chamber

In one experiment, the emission profiles of two toluene-loaded samples with C_0 of 550 ± 7 g/m^3 were measured in small-scale chambers at NIST. These emissions measurements were conducted over a 94 h period. Emission profiles of the two samples were very similar, as shown in Figure 6. The error bars represent the uncertainty associated with each measured chamber concentration. Using the constant chamber and sample characteristics (L, A, Q and V) and variable mass-transfer properties (K, D, C_0) of the toluene-loaded PMP films, the emissions model was used to predict the emissions profile of the two samples in the small-scale chambers, using the Monte Carlo method to estimate uncertainty. Figure 6 also shows the model prediction, with the black solid line indicating the mean of the transient gas-phase concentration and the grey area indicating the range of mean ± standard deviation of transient gas-phase concentration. Although not shown here, the black solid line constructed based upon the mean of transient gas-phase concentration was almost the same as the individual prediction using the mean values of K, D and C_0. In another experiment, one PMP sample loaded with a C_0 of 1100 ± 200 g/m^3 was sent to NIST for chamber emission testing. Emissions profile measurements were limited to 38 h due to an equipment malfunction. Figure 7 shows the emissions profile predicted by the model compared to the measured emissions profile. The larger uncertainty implied by the wider grey area of prediction compared with Figure 6 is due to the larger uncertainty in C_0 for this sample. The relative difference between measured and predicted concentrations ((measured - predicted)/measured) is also shown in Figures 6 and 7.

Discussion

Comparison of emission tests and model prediction

As demonstrated in Figure 6, the chamber emission measurements were reproducible. With regard to the individual model predictions using mean values of K, D and C_0, which coincide with the black solid lines in Figure 6 and 7, the measured concentrations were higher than model predictions during the early period, but lower in the later period. The total amount of toluene emitted during the test period can be calculated from the flow rate multiplied by the numerical integration of effluent concentration over time. For the two PMP samples with C_0 equal to 550 g/m^3, which were tested for 94 h as shown in Figure 6, the total emitted toluene was calculated to be 110 μg and 117 μg, respectively. The model predicted amount during this period was 97 μg, which is close to the experiment results. Since the total amount of toluene initially contained in the two PMP samples was 186 μg, about 60 % of the toluene was emitted from the PMP sample during the chamber test. Emissions from the PMP samples would last much longer than 94 h with the emission rate and gas-phase concentration quite low, as expected for a diffusion–controlled material. Similarly, for the PMP sample with C_0 equal to 1100 g/m^3, which was tested for 38 h as shown in Figure 7, the total emitted toluene mass was 104 μg (28 % of the total amount in the sample) while the model predicted amount during 38 h was 121 μg (32 % of the total amount in the sample).

The relative difference between the measured and predicted results is high initially and decreases rapidly below 40%. Although during the later period the model prediction and experimental results are quite close, the relative difference becomes larger due to the low concentrations. The discrepancy between experimental measurement and model prediction may

result from an underestimation of D, which controls the emission rate (higher D increases emission rate), resulting in higher gas-phase concentrations at the beginning and lower concentrations later. The difference could also be due to rapid emissions of VOCs from the samples when the fully-loaded samples were placed in the chamber before the chamber test began. Another reason may be that the chamber air is not completely mixed, although this is assumed for the model. Considering the uncertainties of both experiment measurement and model prediction, the results agree fairly well.

Effect of external convective mass-transfer and its implication

As described above, the emissions model (referred to here as Little's model) ignores external mass transfer. The convective mass transfer coefficient, h_m, shown in Figure 2, is not included in Little's model. Deng and Kim (2004) (referred to here as Deng's model) extended Little's model by considering the effect of external mass transfer. When h_m is infinitely large and the external mass-transfer resistance is eliminated, Deng's model is equivalent to Little's model. Based upon the flow velocity over the reference material measured in the chamber tests, h_m was estimated using correlation equations (Axley, 1991) to be 3×10^{-3} m/s. Employing the mean values of K, D and C_0 as well as the other parameters (L, A, Q, and V), Deng's model can be used to predict the chamber test results, as shown in Figure 8 together with the prediction of Little's model. As expected, Deng's model predicts chamber air concentrations lower than Little's model in the early stage of emission, but the difference is very small, indicating that external mass-transfer resistance is negligible compared to the internal mass-transfer resistance. In fact, due to the small D and corresponding large internal mass-transfer resistance, decreasing

h_m by one or two orders of magnitude still leads to almost no change in the model prediction, as shown in Figure 8. Although not shown, increasing h_m also causes little change.

The effect may be different, however, for some other materials or for VOCs with larger D. Figure 9 shows the effect of increasing D by two orders of magnitude (3.6×10^{-12} m^2/s) while maintaining other parameters unchanged and using a series of h_m values. In contrast to Figure 8, the emission rate is much faster. Deng's model still generates essentially the same prediction as Little's model when h_m is 0.003 m/s while decreasing h_m leads to much larger difference compared to that shown in Figure 8. Obviously, the effect of external mass-transfer is enhanced by the decreased internal mass-transfer resistance due to the higher D.

When VOCs with larger D are used, or when different emission materials are considered, the external convective mass transfer may play a significant role. For inter-laboratory comparisons, especially those using different chamber configurations, the effect of mixing and fluid flow on the external convective mass transfer may then be a cause of some variation. By using a well-characterized reference material, whose emission can be predicted using mass-transfer models, the external convective mass transfer as well as other factors controlling emissions can be systematically investigated and the chamber testing procedures can be improved.

Conclusions and Future Work

The results of this study demonstrate that it is possible to create a reference VOC source that mimics a real material. Because the emissions profile can be predicted based on a mechanistic understanding, our knowledge of mass transfer characteristics can be used to create

representative materials with a range of emissions profiles. When these materials are placed in small chambers, the expected emissions profile predicted by the model can be compared to the observed emissions profiles. This will be of benefit, because the model can be used to provide insight into the likely causes of experimental error. Our promising initial results provide a "proof of concept" for the approach used to develop the VOC emissions reference material.

Although it appears possible to produce a VOC reference material with controllable and predictable emissions, the PMP film used for these experiments possesses a relatively low diffusion coefficient and a relatively small affinity between toluene, the chemical selected for this demonstration, and the polymer material (in other words, a relatively low K). These characteristics mimic dry materials with slower rates of mass transfer (e.g., vinyl flooring) and require longer chamber times and lower concentrations for analytical measurements. In future work, polymer materials with a range of D and K values will be investigated to represent a wider range of dry materials and allow for shorter chamber durations and higher concentrations. It is also anticipated that materials can be selected in such a way that the external mass transfer resistance either plays a role in determining the emissions profile or is completely negligible. This will provide a means to determine whether chamber-induced variations in the external mass transfer coefficient are a possible source of experimental error. Indoor sources of VOCs also include many wet materials, such as paint, glue and sealant. VOC emissions from wet materials are controlled largely by surface emission so that they are characterized by initial high emission rates and fast decay (Guo, 2002). Different reference materials may need to be developed to represent the wet sources.

In addition, the stability of the reference material is critical for the inter-laboratory comparison, i.e. the mass-transfer characteristics such as D, K and C_0 must not change during loading, storage and transportation so that the variations in emission profiles from different laboratories are exclusively caused by variations in chamber performance. Although beyond the scope of our preliminary study, the stability of the reference material will be evaluated in future work.

Finally, it is believed that interaction of individual VOCs within building materials is generally independent of the presence of other VOCs (Jørgensen and Bjørseth, 1999; Cox et al., 2001; Meininghaus and Uhde, 2002; Luo and Niu, 2006; Farajollahi et al., 2009) because the concentrations in the materials are relatively low. It would be desirable to have an emission reference material that can be loaded with more than one VOC and to simultaneous measure emissions of these VOCs in a single chamber test. The emission-controlling parameters (D, K, and C_0, and h_m, if needed) can be evaluated separately for each VOC. The chamber testing procedures would be similar to those for a single VOC, but a single emissions reference material loaded with a mixture of VOCs could be used to validate chamber experiments for simultaneous emissions of multiple VOCs.

Acknowledgements

References

ASTM (2006a) *Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products*, West Conshohocken PA, ASTM International (ASTM Standard D5116-06).

ASTM (2006b) *Standard Test Method for Determining Air Change in a Single Zone by Means of a Tracer Gas Dilution*, West Conshohocken PA, ASTM International (ASTM Standard E0741-00R06).

Axley, J.W. (1991) Adsorption modeling for building contaminant dispersal analysis, *Indoor Air*, 2, 147-171.

Boeglin, M.L., Wessels, D. and Henshel, D. (2006) An investigation of the relationship between air emissions of volatile organic compounds and the incidence of cancer in Indiana counties, *Environ. Res.*, 100, 242-254.

Bako-Biro, Z., Wargocki, P., Weschler, C.K. and Fanger, P.O. (2004) Effects of pollution from personal computers on perceived air quality, SBS symptoms and productivity in offices, *Indoor Air*, 14, 178-187.

Cox, S.S., Little, J.C. and Hodgson, A.T. (2002) Predicting the emission rate of volatile organic compounds from vinyl flooring, *Environ. Sci. Technol.*, 36, 709-714.

Cox, S.S., Zhao, D. and Little, J.C. (2001) Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring, *Atmos. Environ.*, 35, 3823-3830.

Crank, J. (1975) *The Mathematics of Diffusion*, 2nd Ed., Oxford, England, Clarendon Press.

Deng, B. and Kim, C.N. (2004) An analytical model for VOCs emission from dry building materials, *Atmos. Environ.*, 38, 1173-1180.

Fanger, P.O. (2006) What is IAQ? *Indoor Air*, 16, 328-334.

Farajollahi, Y., Chen, Z. and Haghighat, F. (2009) An experimental study for examining the effects of environmental conditions on diffusion coefficient of VOCs in building materials, *Clean*, 37, 436-443.

Guo, Z. (2002) Review of indoor emission source models. Part 1. Overview, *Environ. Pollut.*, 120, 533-549.

Haghighat, F., Huang, H. and Lee, C.-S. (2005) Modeling approaches for indoor air VOC emissons from dry building materials- A review, *ASHRAE Trans.*, 111, 635-645.

Howard-Reed, C., Little, J.C, Marand, E., Cox, S.S., Nabinger, S.J., and Persily, A.K. (2007) 'Improving the reliability of VOC emissions testing of building products' In: *Proceedings of ASHRAE IAQ 2007*, Baltimore, American Society of Heating, Refrigerating and Air-Conditioning Engineers' (ASHRAE) conference, pp. 1-9.

Jørgensen, R.B. and Bjørseth, O. (1999) Sorption behavior of volatile organic compounds on material surfaces - the influence of combinations of compounds and materials compared to sorption of single compounds on single materials, *Environ. Int.*, 25, 17-27.

Kim, E., Little, J. C. and Chiu, N. (2004) Estimating Exposure to Chemical Contaminants in Drinking Water, *Environ. Sci. Technol.*, 38, 1799-1806.

Lee, C.-S., Haghighat, F. and Ghaly. W.S. (2005) A study on VOC source and sink behavior in porous building materials – analytical model development and assessment, *Indoor Air*, 15, 183-196.

Lee, C.-S., Haghighat, F. and Ghaly. W.S. (2006) Conjugate mass transfer modeling for VOC source and sink behavior of porous building materials: When to apply it? *J. Building Phys.*, 30, 91-111.

Little, J.C., Hodgson, A.T. and Gadgil, A.J. (1994) Modeling emissions of volatile organic compounds from new carpets, *Atmos. Environ.*, **28**, 227-234.

Luo, R. and Niu, J.L. (2006) Determining diffusion and partition coefficients of VOCs in cement using on FLEC, *Build. Environ.*, **41**, 1148-1160.

Meininghaus, R. and Uhde, E. (2002) Diffusion studies of VOC mixtures in a building material, *Indoor Air*, **12**, 215-222.

Mølhave, L. (1991) Volatile organic compounds, Indoor air quality and health, *Indoor Air*, **1**, 357-376.

Rennix, C.P., Quinn, M.M., Amoroso, P.J., Eisen, E.A. and Wegman, D.H. (2005) Risk of breast cancer among enlisted army women occupationally exposed to volatile organic compounds, *Am. J. Ind. Med.*, **48**, 157-167.

Sparks, L.E., Tichenor, B.A., Chang, J., and Guo, Z. (1996) Gas-phase mass transfer model for predicting volatile organic compound (VOC) emission rates from indoor pollutant sources, *Indoor Air*, **6**, 31 – 40.

US Green Building Council (2009) Leasdership in Energy and Environmental Design, v3.

Wilke, O., Horn, W., Wiegner, K, et al. (2009) Investigations for the improvement of the measurement of volatile organic compounds from floor coverings within the health-related evaluation of construction products, BAM Final Report (ZP 52-5-20.49.1-1251/07).

Wolkoff, P. and Nielsen, G.D. (2001) Organic compounds in indoor air - their relevance for perceived indoor air quality? *Atmos. Environ.*, **35**, 4407-4417.

Xu, Y. and Zhang Y. (2003) An improved mass transfer based model for analyzing VOC emissions from building materials, *Atmos. Environ.*, **37**, 2497-2505.

Xu, J., Zhang, J.S., Grunewald, J., Zhao, J., Plagge, R., Ouali, A. and Allard, F (2009) A study on the similarities between water vapor and VOC diffusion in porous media by a dual chamber method, *Clean*, **37**, 444-453.

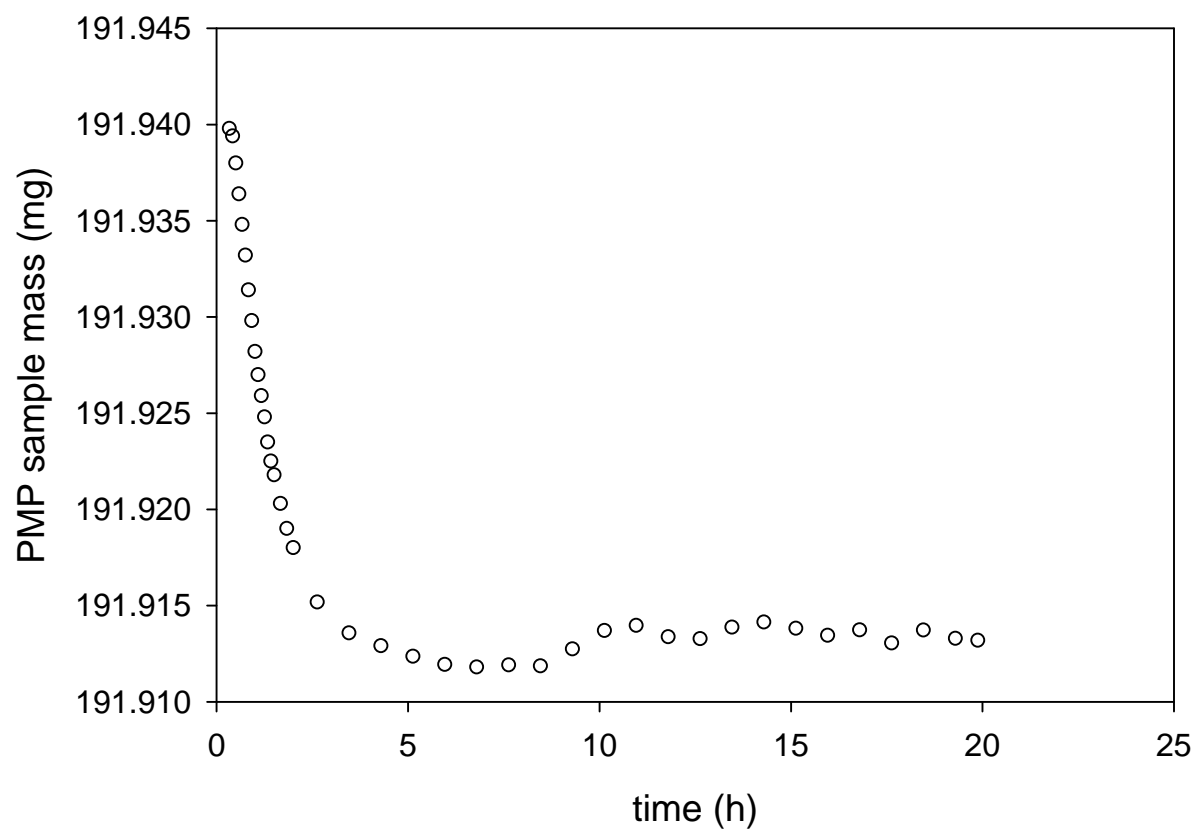Figure 1. Emissions from an untreated PMP film measured on the microbalance in the presence of clean air

Figure 2. Schematic representation of reference material for VOC emission testing in chamber showing various mechanisms governing VOC emission rate
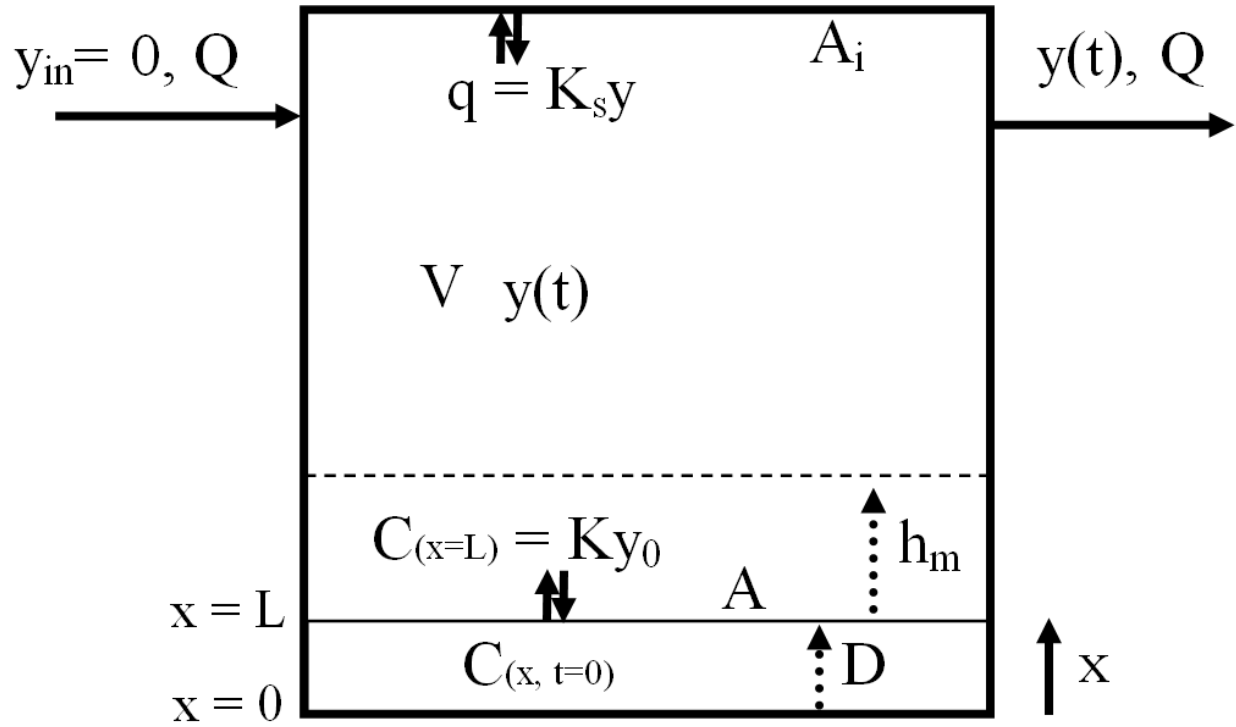
Figure 3. Representative sorption/desorption cycle of toluene in PMP film as measured on the microbalance
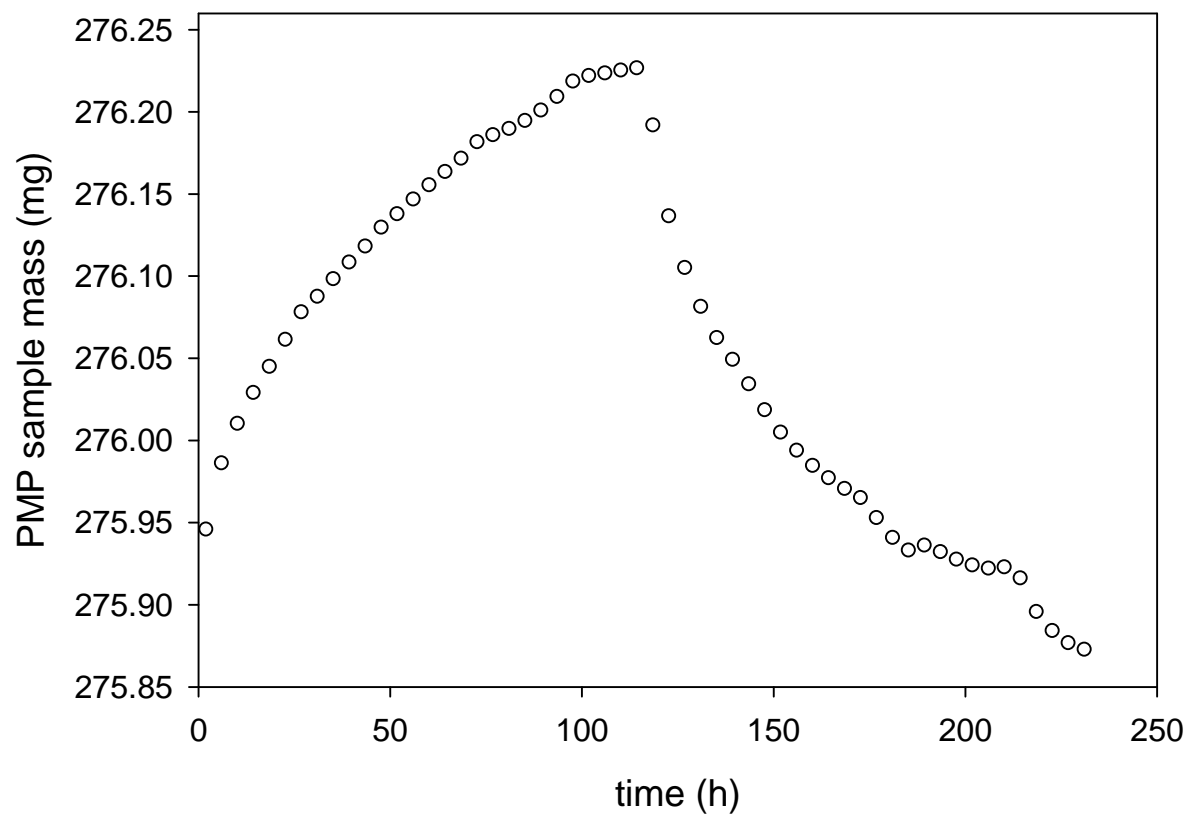
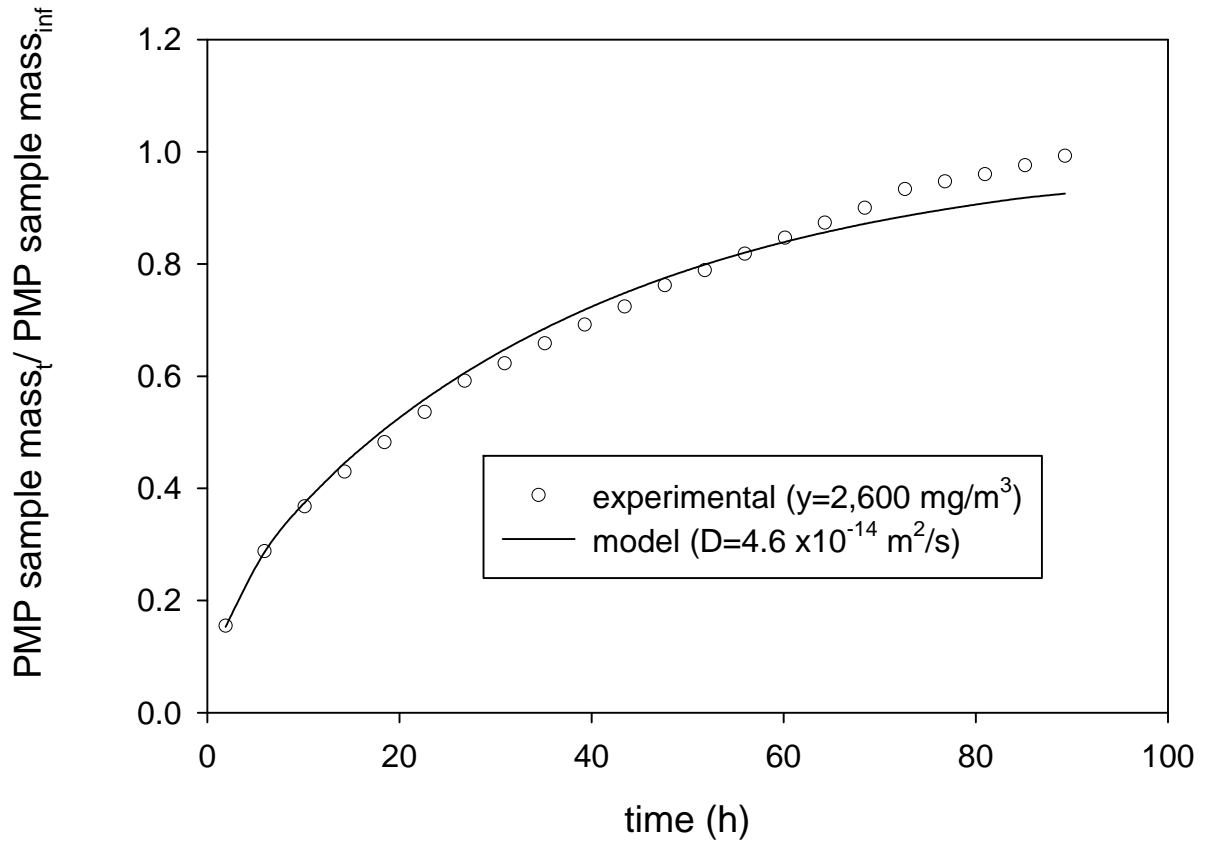Figure 4. Diffusion of toluene into PMP film showing best fit of diffusion model

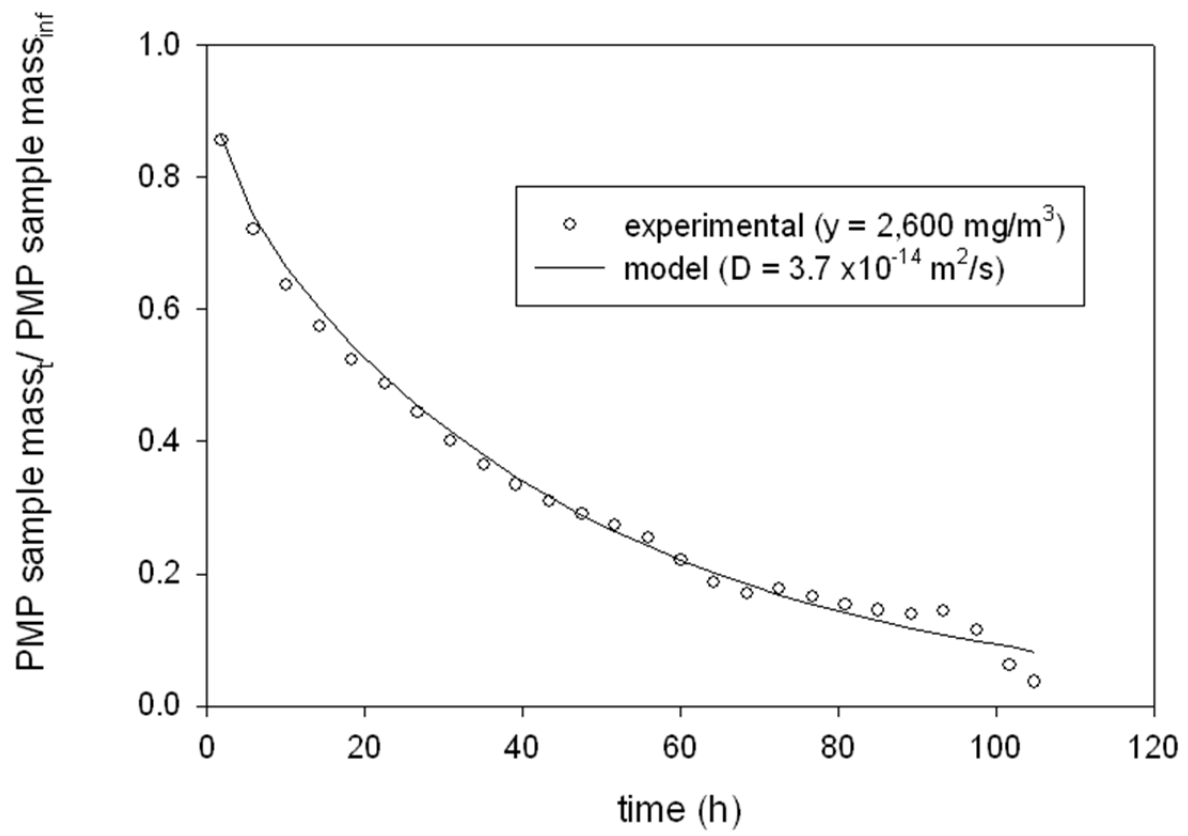Figure 5. Diffusion of toluene out of PMP film showing best fit of diffusion model

Figure 6. Comparison of duplicate observed toluene emissions profiles in test chamber and emissions model prediction
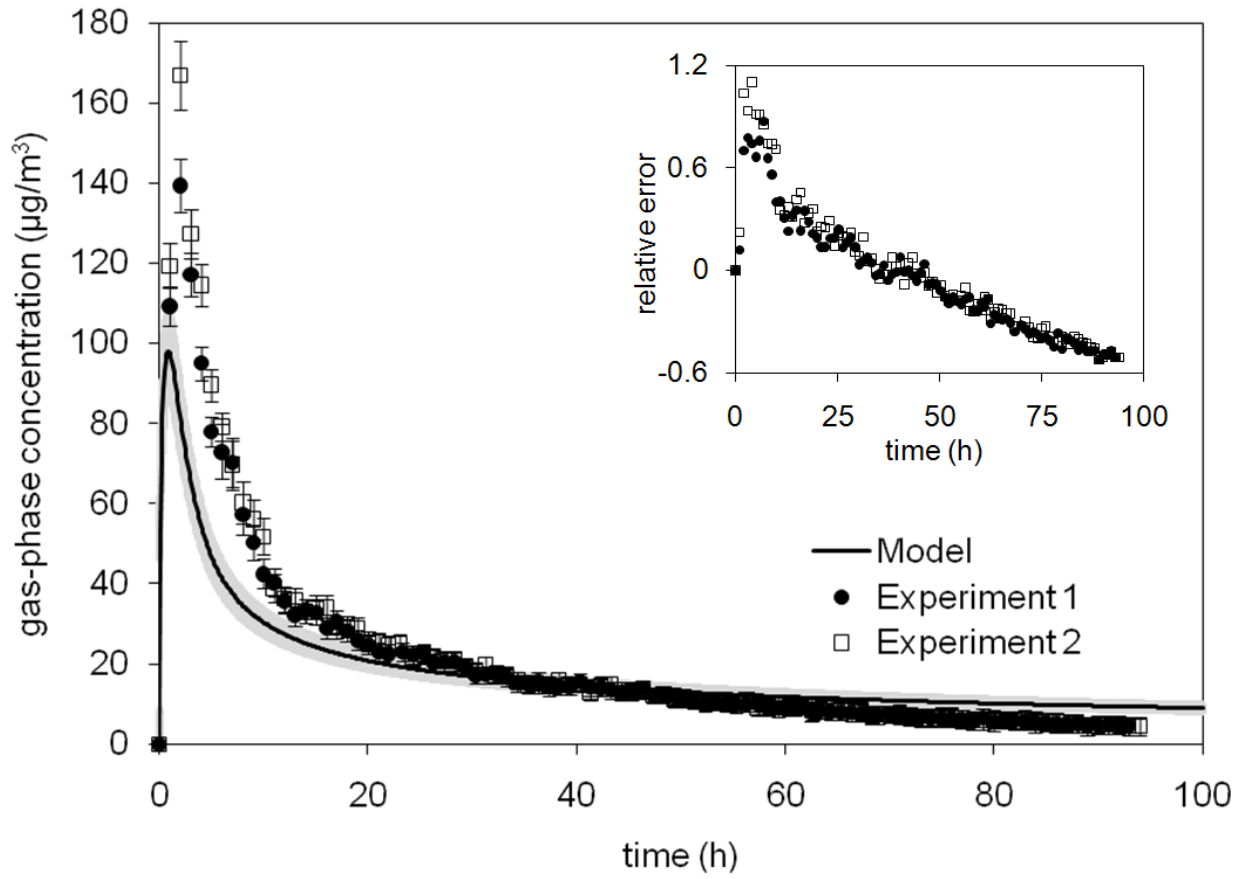
Figure 7. Comparison of observed toluene emissions profile in test chamber and emissions model prediction
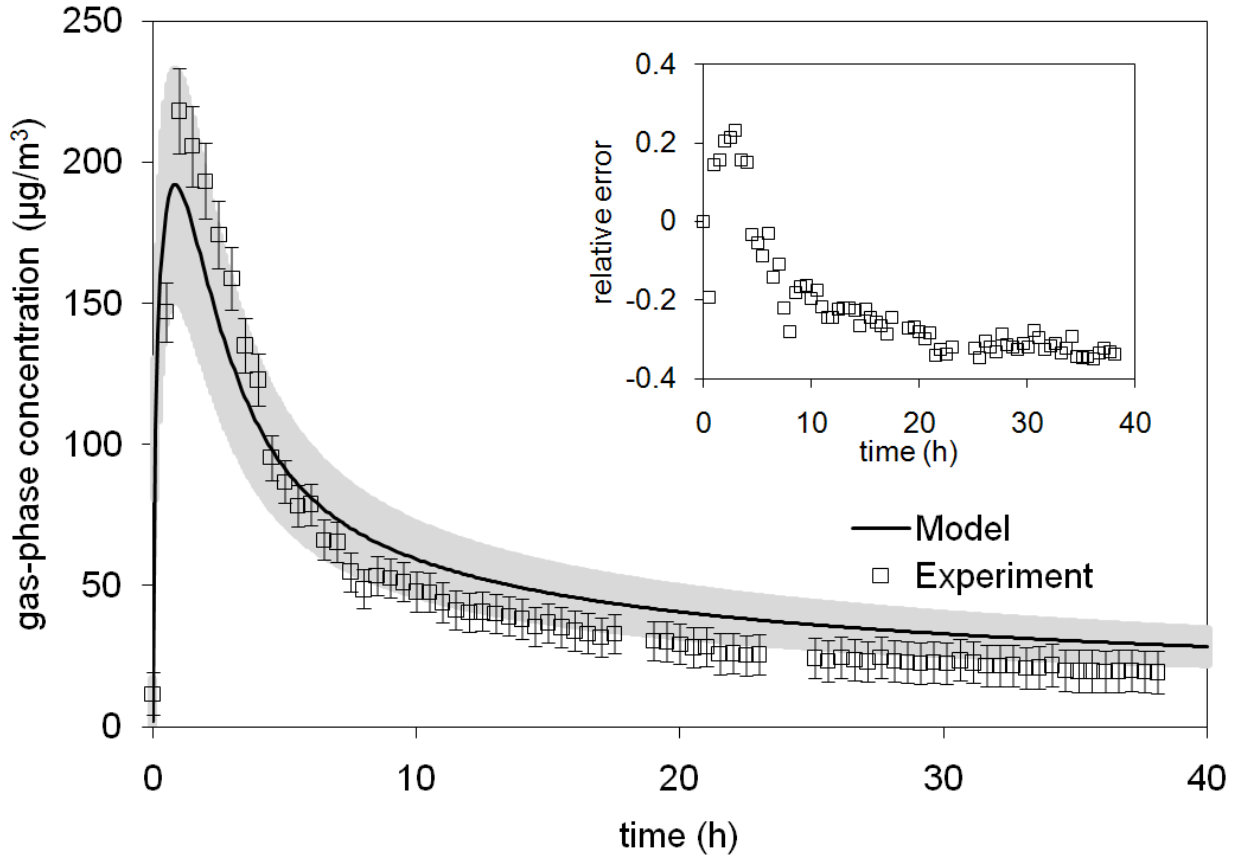
Figure 8. Comparison of Little's model and Deng's model showing influence of external mass transfer coefficient for low D (high internal mass-transfer resistance)
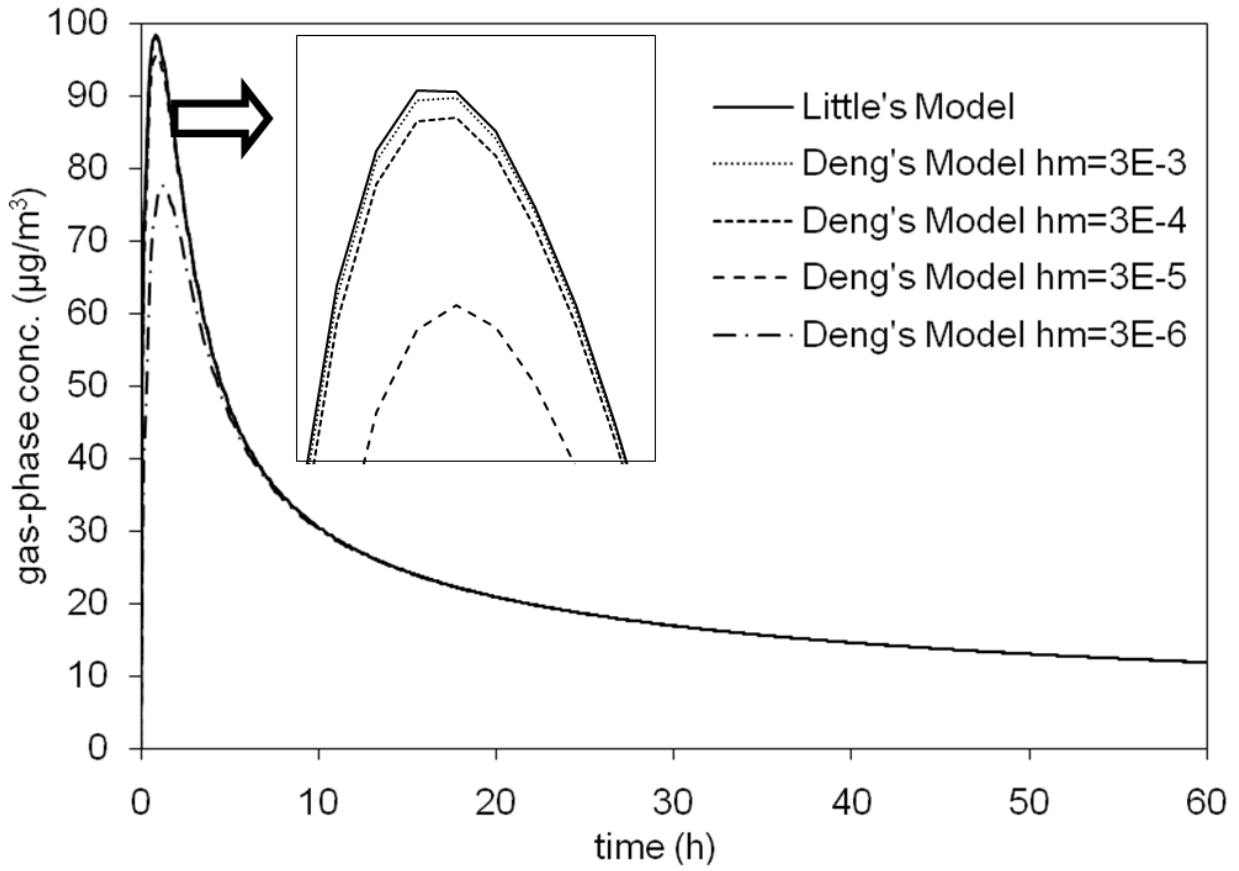
Figure 9. Comparison of Little's model and Deng's model showing influence of external mass transfer coefficient for high D (low internal mass-transfer resistance)
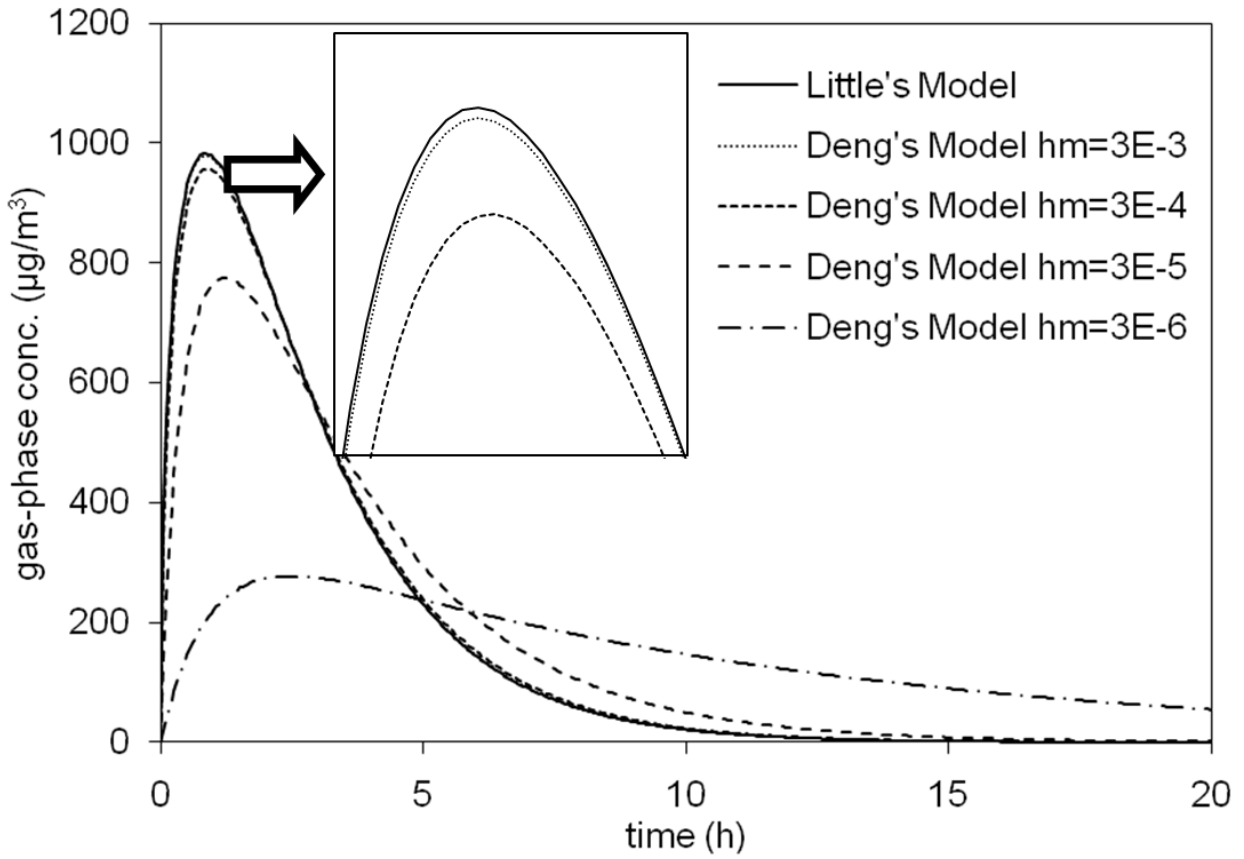
Table 1. NIST small chamber characteristics and test set points

Parameter	Chamber Setpoint/ Nominal Value	Chamber 1 Measured Value	Chamber 2 Measured Value	Measurement Verification Method
Volume (m^3)	0.053	0.051 ± 0.0001	0.051 ± 0.0001	Filled chamber multiple times w/water and graduated cylinder
Air change rate (h^{-1})	1.00	1.15 ± 0.01	1.07 ± 0.01	SF_6 decay method (ASTM 2006b)
		1.13 ± 0.01	1.08 ± 0.01	Measured inlet and outlet airflow (± 0.5 %)
Temperature (°C)	23	23.4 ± 0.06	23.3 ± 0.03	Type E thermocouple (± 1.0 °C)
Relative humidity (%)	50	50 ± 0.1	50 ± 0.04	Capacitive thin-film polymer sensor (± 1.0 %)
Mixing fan	On	9.5 V	9.5 V	Volt meter
Air velocity (cm/s)	5– 10	Not measured	12.5 ± 1.5	Hot-wire anemometer (± 3 %)
Barometric pressure (hPa)	Not given	999 ± 5.6	999 ± 5.6	Silicon-based capacitive pressure sensor (± 0.3 hPa)
Diff. pressure (chamber to incubator) (Pa)	ΔP(chamber – lab air) > 0	+ 0.93 ± 0.15	+ 1.1 ± 0.15	Ultra-low differential pressure transmitter (± 0.3 hPa)

Table 2. Toluene/PMP measurement results for D and K

Gas-Phase Toluene Concentration, y (mg/m^3)	Test Cycle	Diffusion Coefficient, D (m^2/s)	Partition Coefficient, K (-)
650	Sorption	2.9×10^{-14}	370
650	Desorption	3.6×10^{-14}	330
2600	Sorption	4.6×10^{-14}	360
2600	Desorption	3.7×10^{-14}	460
2600	Sorption	4.1×10^{-14}	430
1700	Sorption	3.3×10^{-14}	320
1700	Desorption	2.7×10^{-14}	330