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# Validation of a Mass-Transfer Model for VOC Emissions from Wet Building Materials : Final Report 4.2 Won, D.Y.; Yang, W.; Shaw, C.Y.

**IRC-RR-322** 







Conseil national de recherches Canada

Institute for Research in Construction Institut de recherche en construction

## Validation of a Mass-transfer Model for VOC Emissions from Wet Building Materials

D. Won, W. Yang and C.Y. Shaw

Final Report 4.2 CMEIAQ-II: Consortium for Material Emissions and IAQ Modelling II

Date of issue: March 2005

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#### Consortium for Material Emissions and Indoor Air Quality Modelling II (CMEIAQ-II)

In 2000, the Institute for Research in Construction, National Research Council Canada (IRC/NRC) launched the second phase of the Material Emissions and Indoor Air Quality Modelling project (CMEIAQ-II). The second phase of this project is the direct result of the support and suggestions from the first phase's consortium members for continued work on this research topic. In the second phase, the research is directed towards two principal objectives. The first is to develop the knowledge and tools needed to estimate concentrations of volatile organic compounds (VOCs) generated by the emissions from building materials and furnishings in order to gain a better understanding of the effects of those products on indoor air quality (IAQ). The second is to provide the scientific bases needed to enhance indoor air quality guidelines for office and residential buildings. An important addition to the project in this phase was the Health and End Users Advisory Committee, which was tasked to provide much needed input from the health sector and advice to help tailor the project outputs to better meet the needs of end-users.

#### Phase II Tasks

The specific tasks of the phase II research were:

- To assemble a target VOC list on which to focus our efforts for the analysis of the emission test results. The list includes chemicals which are known to be emitted from various materials, and, especially, chemicals known to have health effects;
- To determine the ranges of variation of the emissions from selected materials, which may result from material variability or environmental influences;
- To expand the database to include a total of 69 materials, and to re-analyze the existing data to cover as many VOCs on the new target list as possible;
- To refine the Material Emission DataBase and Indoor Air Quality (MEDB-IAQ) simulation program to make it more user-friendly;
- To develop and validate empirical and mass-transfer based source models; and
- To develop a best practice guide for managing VOCs/IAQ in office buildings.

#### Significance of the Project

A recent report by a multidisciplinary group of European scientists (EUROVEN) based on existing and limited literature, recommends that outdoor air supply rates need to be increased to 30 L/s per person from the current ASHRAE recommendation of 10 L/s per person to improve indoor air quality for health, comfort, and productivity concerns. On the other hand, a previous NRC experimental study indicates that increasing the ventilation rate to speed up the removal of air-borne VOCs, even when energy use is not a concern, is not effective. The most efficient strategy to maintain indoor air quality is to remove the contaminants at the source (source control) and then to rely on ventilation (dilution) to remove the air-borne VOCs.

This research contributes to improve indoor air quality by developing knowledge and tools for effectively applying source control to reduce ventilation needs (and hence, save

energy). The work provides the relative contribution by a given product to up to 90 VOC concentrations (some of which are known to have adverse health effects), allowing intelligent, informed choices of building materials and indoor consumer products. Product manufacturers will benefit by learning how their products can be improved with respect to VOC emissions, and where their products stand relative to others in simulations of their actual use. The information collected in Phase II will also make it easier for investigators to diagnose possible IAQ problems in buildings, and explore trade-offs between increased ventilation and source control.

The consortium for Phase II (which has a Steering Committee, a Technical Advisory Committee, and a Health & End Users Advisory Committee) was established to set the research priorities and help fund the project. Members of the consortium include: Public Works & Government Services Canada, Natural Resources Canada, Canada Mortgage and Housing Corporation, Health Canada and the National Research Council. In addition, the following organizations have made significant in-kind contributions to the consortium project through close research collaboration with the IRC/NRC project team: Canadian Composite Panel Association, Carleton University, Chemical Manufactures Association (Rohm & Haas), Dalhousie University, Gypsum Board Association, Saskatchewan Research Council, Syracuse University, University of Calgary, University of Miami, U.S. Environmental Protection Agency (EPA), U.S. National Institute of Standards and Technology (NIST), and Virginia Polytechnic Institute & State University.

The CMEIAQ-II final research reports include:

Report 1.1	Target VOC list
Report 1.2	Methodology for Analysis of VOCs in Emission Testing of Building Materials
Report 2.1	Specimen Variability: A Case Study
Report 2.2	Effects of Environmental Factors on VOC Emissions from a Wet Material
Report 2.3	Effects of Material Temperature on VOC Emissions from a Dry Building Material
Report 3.1	Material Emission Data: Small Environmental Chamber Tests
Report 3.2	MEDB-IAQ Version 4.1 Beta
Report 4.1	Model Development for VOC Emissions from Wet Building Materials
Report 4.2	Validation of a Mass-transfer Model for VOC Emissions from Wet Building Materials
Report 4.3	Validation of Empirical Models with Long-term Emission Testing Data
Report 5.1	Indoor Air Quality Guidelines and Standards
Report 5.2	Managing VOCs and Indoor Air Quality in Office Buildings: An Engineering Approach

Reports 1.1 and 1.2 provide the information on the Target VOC list and the analysis method for the VOCs on the list. Reports 2.1 and 2.2 present research outcomes on both inherent and environmental factors inducing variability in material emissions. Report 2.3 discusses VOC emissions as a function of surface temperatures, which can be applied to emissions from a radiant floor heating system. Report 3.1 provides material emission testing data and the resulting coefficients for empirical emission models for the expansion of MEDB-IAQ simulation software. Report 3.2 is a user manual for the revised MEDB-IAQ. Reports 4.1 and 4.2 deal with the development of a mass-transfer based model for wet building materials and the validation of the model with experimental data. Report 4.3 compares empirical models based on short-term emission testing data with those based on long-term data. Report 5.1 contains summaries of existing guidelines and standards associated with indoor air quality. Report 5.2 is a manual for property managers and building operators for their duties in managing VOCs in office buildings.

#### Validation of a Mass-transfer Model for VOC Emissions from Wet Building Materials

#### Summary

In this report, a mass-transfer model developed for VOC emissions from wet building materials based on internal diffusion and convection mechanisms was validated with experimental data. The validation was done for 10 compounds emitted from an oil-based paint applied on a primer-coated gypsum wallboard specimen. The chamber test was conducted in accordance with ASTM Standard D6803–02.

The performance of the model for predicting emissions from paint is very encouraging The model performance for 5 compounds successfully passed all the statistical measures provided in ASTM Standard D5157-97 for assessing the general agreement and bias between the measured and predicted values. The model predictions for the other 5 compounds did not pass most of those statistical measures. Of these five compounds whose emission characteristics were not predicted very well by the model, four compounds are more volatile than the five compounds with good agreement. The measurements in initial concentration were identified as an error source. With modified initial concentration data, the model performance for the four more volatile compounds was improved to similar levels of agreement for the first 5 compounds. The discrepancy between the measured and predicted concentration for the remaining one compound could be attributed to multiple error sources including errors in measurements of model parameters and/or errors in the assumption of no mass flux at the interface between the paint coating and the substrate.

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#### Validation of a Mass-transfer based Model for VOC Emissions from Wet Building Materials

#### 1. Introduction

In recent years, there has been growing interest in developing mass-transfer models for predicting VOC emissions from building materials. Since mass-transfer models employ fundamental mass-transfer principles, the model parameters can be estimated for individual VOCs based on their chemical properties (e.g., molecular weight, vapor pressure) and the environmental conditions (e.g., air velocity, temperature) in the absence of experimental data. As a result, mass-transfer models are, at least in theory, more versatile and useful than conventional empirical models that are applicable only within the range of measurements from which they were developed (ASTM, 1997).

However, as pointed out by Guo (2002), validity does not guarantee usefulness of models, partly because the advantages of mass-transfer models are gained at the expense of simplicity. The accuracy of both mass-transfer and empirical models depends on the accuracy of model parameters. Therefore, it is still necessary to develop reliable methods to estimate model parameters. The mass-transfer models also need to be validated to assess their performance and to identify their limitations.

Several methods are available to estimate model parameters. The techniques to estimate diffusion coefficients can be grouped into three broad categories: a non-steady analysis method, a steady-state analysis method, and a porosity-based method. The two-chamber system with no flow (Bodalal et al., 2000) and the flow-through microbalance system (Cox et al., 2001) belong to the first category. The second category includes the cup method adopted by Kirchner et al. (1999) and the twin chamber methods used by Meininghaus et al. (2000 and 2002). Blondeau et al. (2003) used mercury intrusion porosimetry tests to obtain diffusion coefficients. While the aforementioned studies deal with emissions from dry materials, very little research has focussed on diffusion coefficients for wet materials.

Also, there has been very little effort to develop methods for determining mass-transfer coefficients that are used to describe mass-transfer resistances at the material-air interface and in the boundary layer above it. This is because there has been a large amount of research focused on heat transfer research in a boundary layer. Through the analogy between heat and mass transfer, the theories developed for thermal boundary layer behaviour are commonly used for the concentration boundary layer. The mass-transfer coefficient used in Huang and Haghighat (2002) and Deng and Kim (2004) was based on the relationship between dimensionless numbers of Sherwood number, Reynolds number, and Schmidt number, which were developed originally from heat-transfer research. More research is needed to confirm whether the relationships from heat transfer behavior hold for mass transfer in a boundary layer.

Several attempts have been made to validate a mass-transfer model for emissions from building materials based on theoretically or experimentally estimated model parameters. However, most validation work has been done for dry materials such as vinyl flooring and particleboard. Cox et al. (2002) validated a mass-transfer model, which is based on internal diffusion, assuming no mass-transfer resistance at the material surface (infinite mass-transfer coefficient) and instant equilibrium between the material and air phase, with air concentration data from a chamber test of vinyl flooring. The model coefficients were estimated independently of the chamber test. Reasonably good performance of the model was reported.

Huang and Haghighat (2002) and Deng and Kim (2004) used a mass-transfer model based on internal diffusion, allowing mass-transfer resistance at the material surface, and assuming instant equilibrium between the material and air phase, to predict air concentrations in a chamber test of particleboard. While good agreement was reported between the predicted and measured concentrations, their validation efforts were not as rigorous as that of Cox et al. (2002). The same data sets used for validation were also used to estimate two model parameters, which in turn, were used to predict the concentrations. The experimental data and the two model parameters reported in Yang et al. (2001) were used both in Huang and Haghighat (2002) and Deng and Kim (2004).

There has been only one report on the validation of a mass-transfer model for emissions from wet materials. Zhang and Niu (2003) validated a mass-transfer model with TVOC data from a FLEC (field and laboratory emission cell) test of a paint sample. While good agreement was reported between the measured and predicted air concentrations, the experiment lasted for less than 8 hours and therefore, the validation was applicable only for short-term emissions. The fact that no detailed information was given on the methods used to obtain model parameters makes it difficult to duplicate the validation work.

The purpose of this work is to validate the mass-transfer model and the experimental methods to determine model parameters for VOC emissions from the oil-based paint reported in Report 4.1. While models in other studies need three parameters (diffusion, mass-transfer, and partition coefficient) (Huang and Haghighat, 2002; Zhang and Niu, 2003; Deng and Kim 2004), the new model does not need the partition coefficient. The model adopts the concept of an evaporation coefficient, which is equivalent to the mass-transfer coefficient divided by the partition coefficient. While the model is validated for VOC emissions from paint, it can be applied to other wet materials.

#### 2. Model Development for Indoor Air Concentration

The air concentration of a single chemical compound in a chamber or room with a wet emission source (Figure 1) can be described by using a mass balance equation for a well-mixed flow-through system.

$$V\frac{dC_a}{dt} = QC_{a,in} - QC_a + JA \tag{1}$$

where

- $C_a$ : the air concentration of the chemical in the chamber or room (mg m<sup>-3</sup>).
- $C_{a,in}$ : the concentration of the chemical in the air stream entering into the space from other spaces (mg m<sup>-3</sup>).
- *Q*: the flow rate of the air stream  $(m^3 h^{-1})$ . *A*: the surface area of the wet source  $(m^2)$ .
- *V*: the volume of the chamber or room  $(m^3)$ .
- A: the surface area of the wet source  $(m^2)$ .
- *J*: the mass flux of the chemical coming from the wet source to the space (mg m<sup>-2</sup>  $h^{-1}$ ).



#### Figure 1. Schematic diagram of a chamber or room with a wet emission source

Assuming that only evaporation occurs at the surface and diffusion takes place within the wet source, the mass flux, *J*, can be expressed as:

$$J = -D_m \frac{\partial C_m}{\partial x} = \alpha \left( C_m - C_m^* \right) \quad \text{at} \quad x = l \tag{2}$$

where

- $C_m$ : the concentration of the chemical in the wet source (mg m<sup>-3</sup>).
- $C_m^*$ : the concentration (in the wet source layer) that would be in equilibrium with the vapour pressure in the room or chamber air remote from the surface (mg m<sup>-3</sup>).
- $D_m$ : the diffusion coefficient of the chemical in the wet source (m<sup>2</sup> s<sup>-1</sup>).
- $\alpha$ : the evaporation coefficient (m h<sup>-1</sup>).
- *l*: the thickness of the source (m).
- *x*: the distance upwards from the substrate (m).

The concentration of the chemical at the surface of the source can be expressed as Equation 3 with the additional assumption of no mass flux at the bottom of the source layer (interface with the substrate) (see Report 4.1):

$$\frac{C_m - C_o}{C_m^* - C_o} = 1 - \sum_{n=1}^{\infty} \frac{2\gamma \exp\left(-\beta_n^2 D_m t/l^2\right)}{\left(\beta_n^2 + \gamma^2 + \gamma\right)} \quad \text{at } x = l$$
(3)

where

 $C_o$ : the initial concentration of the chemical in the wet source (mg m<sup>-3</sup>).

 $\beta$ s: positive roots of  $\beta \tan \beta = \gamma$  and  $\gamma = l\alpha/D_m$ .

Incorporating Equations 2 and 3 into Equation 1 provides:

$$\frac{dC_a}{dt} = NC_{a,in} - NC_a + \alpha L \left(C_o - C_m^*\right) \sum_{n=1}^{\infty} \frac{2\gamma \exp\left(-\beta_n^2 D_m t/l^2\right)}{\left(\beta_n^2 + \gamma^2 + \gamma\right)}$$
(4)

where

- *N*: the air change rate, the ratio of Q and  $V(1 \text{ h}^{-1})$ .
- *L*: the material loading ratio as a ratio of *A* and  $V (m^{-2} m^{-3})$ .

Assuming  $C_o >> C_m^*$  and  $C_{a,in} = 0$ , Equation 4 can be simplified as:

$$\frac{dC_a}{dt} = -NC_a + \alpha LC_o \sum_{n=1}^{\infty} \frac{2\gamma \exp\left(-\beta_n^2 D_m t/l^2\right)}{\left(\beta_n^2 + \gamma^2 + \gamma\right)}$$
(5)

With the initial condition of  $C_a = 0$  at t = 0, the differential equation's solution is:

$$C_{a} = 2\alpha \gamma L C_{o} \sum_{n=1}^{\infty} \frac{\left[ \exp\left(-\beta_{n}^{2} D_{m} t/l^{2}\right) - \exp\left(-Nt\right) \right]}{\left(\beta_{n}^{2} + \gamma^{2} + \gamma\right) \left(N - \beta_{n}^{2} D_{m}/l^{2}\right)}$$
(6)

where

$$\beta$$
s: positive roots of  $\beta \tan \beta = \gamma$  and  $\gamma = l\alpha/D_m$ . (7)

#### 3. Methodology of Chamber Testing

#### 3.1 Specimen Preparation

Specimen preparation and chamber testing were conducted in accordance with ASTM standard practice D6803-02 (ASTM, 2002). Gypsum wallboard coated with latex primer was used as a substrate to reflect more realistic applications as well as to ensure negligible mass flux between the substrate and the paint coating. The oil-based paint tested was identical to that used in determining model coefficients of D and  $\alpha$ . More detailed information on the paint can be found in Report 4.1. The type of latex primer was chosen based on the recommendation by the manufacturer of the oil-based paint being tested.

#### **3.1.1 Preparation of Substrate**

A panel of gypsum wallboard with a thickness of  $\frac{1}{2}$  inch (13 mm) was purchased at a local store. The panel was cut into several 0.2 m × 0.098 m pieces. The edges of the pieces were sealed with wax. The piece for actual testing was put into a stainless steel holder, which was designed to expose only the coated surface to air. The pieces with and without a holder were conditioned in individual clean chambers under the same conditions as the actual test for approximately one week.

Latex primer was purchased at a local store and was tinted with blue to differentiate the primer coating from the white paint coating. The container of primer was shaken for 5 minutes with a reciprocating shaker before the application. Two gypsum wallboard pieces were coated with the blue latex primer with a clean paint roller to use as the substrate. A disc with a diameter of 0.01 m was cut from the center of one piece with a clean hole-saw and was used later to measure the thickness of the primer coating with a microscope.

Both substrates were conditioned separately in a chamber with the same environmental condition as the actual test for 5.8 days. At the end of the conditioning period, samples of the chamber air were collected on a multi-sorbent tube to check the background level. After it was assured that the chambers were free of target VOCs, both substrates were taken from each chamber for the application of paint.

#### 3.1.2 Preparation of Specimen

A container of paint spiked with 7 chemicals (see Report 4.1) was shaken for 5 minutes before the application. An amber vial of 2 mL was filled with the paint mixture, sealed and stored in a refrigerator for the analysis of initial concentration of VOCs in the paint mixture, leaving no head space in the vial. A portion of the remaining paint was poured

into a clean tray where a clean roller was covered with paint. The roller applied the paint on the substrate lengthwise from left to right and widthwise from top to bottom, twice for each direction. The edge of the substrate surface (2mm in thickness) was then temporally masked with a Teflon tape to prevent paint from spilling over to invisible crevices between the specimen and the specimen holder. The masking Teflon tape was removed after the application of paint. The resulting paint coverage was within  $\pm 15\%$  of the recommended value. The weight of paint applied was determined by weighing the specimen before and after the application.

Table 1 summarizes the information on both specimens. Specimen A was used to measure the thickness of the paint coating, while Specimen B was used in the actual test. There was a 6-minute lapse between the application of the paint on the substrate and the complete closure of the chamber.

	Specimen A	Specimen B
Purpose	Thickness measurement	Actual testing
Substrate	Gypsum wallboard coated with latex paint <sup>1</sup>	Gypsum wallboard coated with latex paint
Final coating	Oil-based paint <sup>2</sup>	Oil-based paint
Surface area of substrate (m <sup>2</sup> )	0.02 (0.2 m × 0.098 m)	0.02 (0.2 m × 0.098 m)
Weight of primer applied (g)	2.550	2.430
Weight of paint applied (g)	2.605	2.704
Coverage of paint $(1 \text{ m}^{-2})^3$	0.113	0.123

Table 1. Summary description of test specimen.

<sup>1</sup> Density of latex primer: 1.307 g ml<sup>-1</sup>.

<sup>2</sup> Density of oil based paint: 1.270 g ml<sup>-1</sup>.

<sup>3</sup> The paint coverage was estimated based on the weight of paint applied, density of paint, and surface area.

#### 3.2 Chamber Testing

The emissions testing protocol was in accordance with guidelines specified by D6803–02 (ASTM, 2002) and has been previously described (CMEIAQ Phase I Report 1.2). A 50-L stainless steel chamber was operated under the conditions summarized in Figure 2. The data were recorded at one-minute intervals and were averaged every 5 minutes for plotting. The average flow rate (*Q*) for the total experimental period was 49.98 L/h, or one air change per hour (N = 1). The relative humidity (*RH*) was maintained at an average of 52%, while the air temperature (*T*) was 23.14 °C on average. The starting point of relative humidity and temperature depends on the laboratory condition at the time of the initiation of the chamber. The relative humidity and air temperature were measured at the exhaust of the chamber. The pressure difference between the chamber and the laboratory ( $\Delta P = P_{chamber} - P_{laboratory}$ ) was 6.4 Pa on average. Since  $\Delta P$  was not as closely controlled as that of *RH*, *T*, and *Q*, there were more variations.

Samples of exhaust air of the chamber were collected on multi-sorbent tubes over time starting 15 minutes after the closure of the chamber. The sampled tubes were thermally desorbed using a Perkin-Elmer ATD 400 thermal desorber and were subsequently analyzed on an Agilent GC/MS system (6890N GC and 5973 mass selective detector). The ten compounds, which were calibrated individually, are 6 aliphatic hydrocarbons (heptane, octane, nonane, decane, undecane and dodecane) and 4 aromatic hydrocarbons (toluene, ethylbenzene, 1,2,4-trimethylbenzene and 1,2,4,5-tetramethylbenzene). The six aliphatic compounds and toluene are mostly originated from spiking the paint with pure chemicals. More detailed information on the GC/MS analysis procedure can be found in Report 2.1.



Figure 2. Chamber interior environment conditions during the experiment.

#### 4. Methodology for Model Parameters

While model parameters such as flow rate (here reported as air change rate) and surface area of the source can be obtained relatively easily, it is more difficult to determine the magnitude of the parameters such as paint coating thickness, initial concentration of chemicals in the coating, diffusion coefficient and evaporation coefficient of chemicals. This section explains the methods used to estimate the four parameters.

#### 4.1 Coating Thickness (1)

Figure 3 shows the cross-sectional image of the test specimen with a light microscope. The specimen for the microscopic analysis was prepared by cutting a thin slice of the specimen disc with a sharp stainless steel knife. The sample slice was then mounted onto a glass slide for examination by the microscope. The microscope scanned the prepared slide to find areas where the cut section was smooth and the various layers were identifiable. Images were captured using a digital image capture system attached to the light microscope. The microscope used was a Nikon Optiphot II fitted with a Dage Cooled Colour CCD camera. Four to five measurements were made each time and the averaged value was reported.



Figure 3. Cross-sectional image of a test specimen photographed with a light microscope.

As shown in Figure 3, a clear distinction can be seen between the primer and paint coating. It also shows that the paper cover of the gypsum wallboard appears to be composed of two layers, which was not obvious to the naked eye. Figure 4 summarizes the measurements of the coating thickness over time. The symbols correspond to the measurements. The two solid lines in Figure 4 are the results of modeling assuming that the coating thickness follows an exponential decay function with three parameters, while the dotted line is the average of two measurements. The modeling attempt was to show the possibility of using a model to predict the coating thickness as a function of time. It was recognized that measurements done in a better-designed and controlled experiment can provide very useful information.

The primer thickness appears to level out at approximately 62 um and then increased to 124 um after the application of paint. This may imply that the primer coating was expanded after absorbing some paint. The measured paint thickness of Specimen A was 155.43 um at 7.5 h and 133 um on average afterwards. The highest value among measurements of the paint thickness was chosen for modeling since *D* and  $\alpha$  were estimated based on the maximum film thickness, assuming no evaporation loss and no shrinkage of paint thickness over time. The resulting paint thickness (*l*) of Specimen B was estimated to be 169.93 um considering the difference in the paint coverage for two specimens (ratio of Specimen B and Specimen A coverage = 1.09).



Figure 4. Measurements of coating thickness of Specimen A before and after the application of paint.

#### **4.2** Initial Concentration of Chemicals (*C*<sub>o</sub>)

To measure the initial concentration of chemicals ( $C_o$ ), a volume of 2 µL of paint mixture from the 2 mL vial stored in a fridge was injected onto a piece of glass wool blocking a sorbent tube. Clean air was then drawn through the sorbent tube at a flow rate of 100 mL/min for 2 minutes. The sorbent tubes were subjected to the same GC/MS analysis as the tubes for chamber air.

To take into account the decrease of initial concentration of chemicals in the paint coating due to the absorption of chemicals by the primer coating, an expansion factor  $\lambda$  was used as suggested in Yang et al. (2001):

$$C_o = \frac{C_{o,m}}{\lambda} \tag{7}$$

where

 $C_{o,m}$ : the measurement of initial concentration of a chemical.

 $\lambda$ : a factor to account for the absorption of chemicals of paint by primer coating.

The value of  $\lambda$  was estimated based on the increased primer coating thickness after the application of paint. Assuming the increased primer coating is a part of the paint coating, the actual paint thickness ( $l_a$ ) of Specimen B can be estimated to be 237.51 um (169.93 + 62\*1.09 um).  $\lambda$  was defined as the ratio of  $l_a$  and l. The value of  $\lambda$  is ~1.40 when l is 169.93 um.

Table 2 is a summary of initial concentrations for 10 compounds, which were calibrated individually using their own authentic samples.

		Coefficient of	95% Confidence Interval <sup>2</sup>		
Compound	Average $(C_o)$	Variance <sup>1</sup>	$C_{o,min}$	$C_{o,max}$	
Heptane	174.36	20.46	117.60	231.12	
Octane	274.02	47.09	185.91	362.13	
Nonane	383.80	35.09	280.02	487.58	
Decane	797.30	37.55	629.99	964.60	
Undecane	829.53	6.35	765.86	893.20	
Dodecane	857.11	6.15	782.12	932.09	
Toluene	514.19	11.68	368.82	659.57	
Ethylbenzene	974.18	39.51	742.33	1206.03	
1,2,4-trimethylbenzene	34.87	0.63	27.43	42.31	
1.2.4.5-tetramethylbenzene	5.82	1.89	5.00	6.65	

Table 2. Initial concentration of chemicals in paint coating  $(g/m^3)$ .

<sup>1</sup> Coefficient of Variance = Standard Deviation/Average\*100

 $^{2}$  The 95% confidence interval was determined assuming no population standard is known and the degree of freedom is 3.

#### **4.3** Diffusion (D) and evaporation ( $\alpha$ ) coefficient

Tables 3 and 4 summarize information on diffusion and evaporation coefficients respectively. The coefficients were the results of the experiments conducted to investigate the effects of relative humidity, which was concluded to have no effect on either coefficient. Report 4.1 provides more detailed information on estimating D and  $\alpha$ .

		Coefficient of	95% Confidence Interval <sup>2</sup>	
Compound	Average (D)	Variance <sup>1</sup>	$D_{,min}$	$D_{max}$
Heptane	2.61E-11	44.44	1.17E-11	4.06E-11
Octane	1.26E-11	36.03	6.93E-12	1.82E-11
Nonane	1.04E-11	33.94	6.03E-12	1.48E-11
Decane	5.30E-12	48.30	2.12E-12	8.48E-12
Undecane	4.80E-12	61.88	1.12E-12	8.48E-12
Dodecane	2.22E-12	64.41	4.50E-13	4.00E-12
Toluene	1.86E-11	41.94	8.92E-12	2.83E-11
Ethylbenzene	1.44E-11	28.54	9.25E-12	1.95E-11
1,2,4-trimethylbenzene	5.05E-12	55.05	2.48E-12	7.62E-12
1,2,4,5-tetramethylbenzene	1.33E-12	71.65	4.51E-13	2.21E-12

Table 3. Diffusion coefficient of chemicals in paint coating  $(m^2/s)$ 

<sup>1</sup> Coefficient of Variance = Standard Deviation/Average\*100

 $^{2}$  The 95% confidence interval was determined assuming no population standard is known and the degree of freedom is 4.

		Coefficient of	95% Confidence Interval <sup>2</sup>		
Compound	Average ( $\alpha$ )	Variance <sup>1</sup>	$\alpha_{min}$	$\alpha_{max}$	
Heptane	2.62E-03	20.11	1.97E-03	3.28E-03	
Octane	9.02E-04	26.27	6.08E-04	1.20E-03	
Nonane	3.18E-04	19.62	2.40E-04	3.95E-04	
Decane	1.10E-04	29.82	6.95E-05	1.51E-04	
Undecane	2.80E-05	41.79	1.35E-05	4.25E-05	
Dodecane	9.51E-06	78.02	2.94E-07	1.87E-05	
Toluene	2.00E-03	24.45	1.39E-03	2.60E-03	
Ethylbenzene	7.87E-04	17.92	6.12E-04	9.62E-04	
1,2,4-trimethylbenzene	1.33E-04	36.99	8.70E-05	1.78E-04	
1,2,4,5-tetramethylbenzene	1.25E-04	42.48	7.62E-05	1.74E-04	

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<sup>1</sup> Coefficient of Variance = Standard Deviation/Average\*100

 $^{2}$  The 95% confidence interval was determined assuming no population standard is known and the degree of freedom is 4.

#### 5. Statistical Analysis Approach

The model performance was evaluated qualitatively and quantitatively by comparing the measured concentrations obtained using the methodology in Section 3 with the predicted concentrations obtained with Equation 6 along with model parameters in Section 4. A qualitative approach is based on visual inspection, while a quantitative approach uses statistical measures provided in ASTM Standard D5157-97 (ASTM, 1997).

The ASTM Standard recommends four measures to assess the general agreement between the predicted  $(C_p)$  and the measured  $(C_m)$  values: correlation coefficient (r), slope (b) and intercept (a) of the regression line between  $C_m$  and  $C_p$ , and normalized mean square error (NMSE). Two measures can be used to assess bias: normalized or fractional bias (FB) of the mean concentrations and bias (FS) based on the variance of the concentrations. The measures and criteria to judge the adequacy of model performance are summarized in Table 5.

	Measures	Equations	Criteria for Adequacy	Notes
General Agreement	Correlation Coefficient ( <i>r</i> )	$r = \frac{\sum_{i=1}^{n} \left[ \left( C_{mi} - \overline{C}_{m} \right) \left( C_{pi} - \overline{C}_{p} \right) \right]}{\sqrt{\left[ \sum_{i=1}^{n} \left( C_{mi} - \overline{C}_{m} \right)^{2} \right] \left[ \sum_{i=1}^{n} \left( C_{pi} - \overline{C}_{p} \right)^{2} \right]}}$ where $\overline{C}_{m} \& \overline{C}_{p}$ are averages of $C_{m} \& C_{p}$ .	r > 0.9	<ul> <li>1: strong &amp; direct relationship</li> <li>-1: strong but inverse relationship</li> </ul>
	Slope (b) of Regression Line between $C_p$ and $C_m$	$b = \frac{\sum_{i=1}^{n} \left[ \left( C_{mi} - \overline{C}_{m} \right) \left( C_{pi} - \overline{C}_{p} \right) \right]}{\sum_{i=1}^{n} \left[ \left( C_{mi} - \overline{C}_{m} \right)^{2} \right]}$	0.75 < <i>b</i> < 1.25	• 1: perfect agreement
	Intercept ( <i>a</i> ) of Regression Line between $C_p$ and $C_m$	$a = \overline{C}_p - b  \overline{C}_m$	$a < \pm 25\%$ of the average measured value	• 0: perfect agreement
	Normalized Mean Square Error (NMSE)	$NMSE = \frac{\sum_{i=1}^{n} (C_{pi} - C_{mi})^{2}}{n} \frac{1}{\overline{C}_{m} \overline{C}_{p}}$	NMSE < 0.25	• 0: perfect agreement
Bias	Normalized or Fractional Bias of Mean Value (FB)	$FB = \frac{2\left(\overline{C}_{p} - \overline{C}_{m}\right)}{\left(\overline{C}_{p} + \overline{C}_{m}\right)}$	FB < ±0.25	<ul> <li>0: perfect agreement</li> <li>close to 2 or -2: greater difference</li> </ul>
	Bias based on Variance (FS)	$FS = \frac{2\left(\sigma_{C_p}^2 - \sigma_{C_m}^2\right)}{\left(\sigma_{C_p}^2 + \sigma_{C_m}^2\right)}$	FS < ±0.5	

Table 5. Statistical measures to assess general agreement between  $C_p$  and  $C_m$  and bias.

Reference: ASTM (1997)

#### 6. Results and Discussion

Chamber air concentrations of each chemical were predicted using the average values of model parameters provided in Sections 4.1 to 4.3. Values of  $\beta$  satisfying Equation 7 were determined using Solver in Microsoft Excel®<sup>TM</sup>. Although the smallest  $\beta$  value dominates the infinite series of Equation 6, the series were repeated for n = 30.

#### 6.1 Qualitative Analysis with Visual Comparison

When indoor air quality is assessed from the point of view of reducing occupant exposure to contaminants, it is important to know what is the maximum level of the indoor air concentrations and when it occurs. Consequently, it is important to assess model performance for these two factors: the maximum indoor air concentration ( $C_{a,max}$ ) and the time ( $t_{max}$ ) when  $C_{a,max}$  occurs. Table 6 compares the predicted and measured values of these two parameters for 10 compounds. The cases with reasonable agreements are indicated in bold format.

	t <sub>max</sub>			C <sub>a,max</sub>		
Compound	Meas.	Pred.	Ratio	Meas.	Pred.	Ratio
Heptane	0.54	0.54	1.00	0.45	6.73	0.07
Octane	0.54	0.54	1.00	3.60	8.52	0.42
Nonane	1.02	1.02	1.00	8.89	9.10	0.98
Decane	1.55	1.55	1.00	10.76	11.40	0.94
Undecane	4.06	2.56	1.59	5.84	5.24	1.12
Dodecane	4.88	3.06	1.59	2.28	2.24	1.02
Toluene	0.25 or 0.54	0.54	<b>1</b> or 0.46	2.53	18.78	0.13
Ethylbenzene	0.54	0.54	1.00	11.62	30.38	0.38
1,2,4-trimethylbenzene	1.02	1.55	0.66	0.51	0.53	0.96
1,2,4,5-tetramethylbenzene	2.02	1.55	1.30	0.05	0.06	0.83

Table 6. The time  $(t_{max})$  corresponding to the maximum air concentration  $(C_{a,max})$ .

Meas. = Measured, Pred .= Predicted, Ratio = Measured Value /Predicted Value

#### 6.1.1 Cases with Good Agreement

Compounds with good agreement in both  $t_{max}$  and  $C_{a,max}$  include nonane, decane, 1,2,4trimethylbenzene, and 1,2,4,5-tetramethylbenzene. Similar observations can be made from the graphical comparison of the measured and predicted concentrations for those compounds (Figures 5 to 8). While the agreement for 1,2,4,5-tetramethylbenzene is slightly worse than that for the other three compounds, a similar level of agreement can be achieved for this compound with a smaller value of  $\alpha$  within the 95% confidence interval. Figure 9 shows excellent agreement for the predictions with the lower limit of the 95% confidence level as  $\alpha$  for 1,2,4,5-tetramethylbenzene.

#### 6.1.2 Cases with Errors in *C*<sub>o</sub> Measurements

Compounds with a large discrepancy in  $C_{a,max}$  are the more volatile compounds including heptane, octane, toluene, and ethylbenzene (Table 5). The discrepancy can be observed

more clearly in Figures 10 to 13. Interestingly, the magnitude of the discrepancy increases with increasing vapor pressure. Based on the observation, the initial concentration ( $C_o$ ) measurement can be suspected as a potential source of the disagreement. Since the four compounds are more volatile than others, it is reasonable to assume that the loss during the preparation of the specimen is greater and the initial concentration measured by the method outlined in Section 4.2 is greater than that in the test chamber.

To test the hypothesis, the comparison between the measured  $(C_m)$  and predicted  $(C_p)$  concentrations was repeated using the lower limit of the 95% confidence interval in Table 2 as  $C_o$ . Although the magnitude of the discrepancy was reduced, the agreement between  $C_m$  and  $C_p$  was not as good as expected. As a next trial, the comparison was repeated with a modified initial concentration, which is the average value (the 2<sup>nd</sup> column of Table 2) multiplied by the ratio of the measured and predicted  $C_{a,max}$  (the 7<sup>th</sup> column of Table 5). The results are presented in Figures 14 to 17. As intended, good agreement between  $C_m$  and  $C_p$  can be observed with modified  $C_o$ .

This exercise demonstrates that the error in the initial concentration measurements can be significant for more volatile compounds such as heptane, toluene, octane, and ethylbenzene. Therefore, the methodology of measuring  $C_o$  needs to be improved. In this study, the initial concentration was measured by drawing 2  $\mu$ L of the paint sample from the 2 mL vial and injecting it into a sorbent tube. During this process, little or no loss of VOCs from the paint sample was expected. On the other hand, it required about 6 minutes to apply the paint onto the substrate, put the specimen into the chamber, and close the chamber door. Because the specimen was almost entirely exposed to the laboratory air during this 6 min period, some loss of VOCs from the specimen was unavoidable. The loss of each specific VOC is expected to be proportional to its volatility. To ensure that the estimate of  $C_o$  is closer to that in the chamber, it is suggested that the preparation for  $C_o$  analysis follows the same procedures as that for the preparation of the specimen, i.e., pouring the paint mixture into a paint tray, leaving it exposed in the laboratory for about 6 min, and then collecting it in a vial before injecting it into a sorbent tube for analysis.

#### 6.1.3 Cases with Errors from Various Potential Sources

Compounds with large discrepancies in  $t_{max}$  in Table 5 are less volatile alkanes such as undecane and dodecane. Again, similar conclusions can be made from the graphical presentation of Figures 18 and 19. While the discrepancies in the maximum air concentration ( $C_{a,max}$ ) can be considered reasonable, the discrepancy in air concentrations after approximately the 10<sup>th</sup> hour is significant, in particular, for dodecane.

Various combinations of the 95% confidence intervals' limits for  $C_o$ , D, and  $\alpha$  in Tables 2 to 4 were used in attempts to improve the model predictions but they failed to provide better agreement. Consequently, a sensitivity analysis was conducted for  $C_o$ , D,  $\alpha$  and l using dodecane as a base case to identify the error source. Figure 20 compares the concentrations for three levels of  $C_o$  including  $C_o$ ,  $0.2 C_o$ , and  $2 C_o$ . As shown in Section 6.1.2,  $C_{a,max}$  is greatly affected by the value of initial concentration, while  $t_{max}$  is almost independent of  $C_o$ . Figure 21 shows the results of the sensitivity analysis for D. A smaller D tends to decrease  $C_{a,max}$ , while  $t_{max}$  is almost independent of D. The effect of

diffusion coefficient on  $C_{a,max}$  appears to be much smaller than that of initial concentration  $C_o$ .

Figure 22 compares the predicted concentrations for three levels of  $\alpha$ . The effects of  $\alpha$  on predicted concentrations seem to be more complex. A smaller  $\alpha$  tends to be associated with shifting  $t_{max}$  to the longer times, while lowering the level of  $C_{a,max}$ , and providing a slower decay of concentrations. The effects of  $\alpha$  on the concentration decay trend are particularly pronounced.

Figure 23 presents the effects of coating thickness (l) on air concentrations. While  $C_{a,max}$  and  $t_{max}$  are a weak function of l, the concentration decay trend is a strong function of l. Since l affects the decay rate without significantly affecting  $C_{a,max}$ , it might seem reasonable to suspect that the measurement error in l could be the source of error for dodecane. However, this hypothesis is not supported by the fact that l is a physical parameter rather a chemical parameter and the measurement of l worked for the other chemical compounds. No significant improvement in  $t_{max}$  predictions for dodecane was observed through simultaneous variations of two or more model parameters either.

Another potential error source could be associated with the assumption of no mass flux at the interface between the paint and primer coating. Dodecane might be absorbed by the primer coating more than other compounds and, therefore, may need more time to come out of the absorption sites. This might be remedied by adopting a mass-transfer model for a multi-layer system. In conclusion, the disagreements between predicted and measured concentrations of the various VOCs may be able to be explained only by combined effects of various error sources.



**Figure 5. Comparison of predicted and measured chamber air concentration** (nonane).



Figure 6. Comparison of predicted and measured chamber air concentration (decane).



**Figure 7. Comparison of predicted and measured chamber air concentration** (1,2,4-trimethylbenzene).



Figure 8. Comparison of measured and predicted chamber air concentration with modified initial concentration (1,2,4,5-tetramethylbenzene).



Figure 9. Comparison of measured and predicted chamber air concentration with modified initial concentration (1,2,4,5-tetramethylbenzene with  $\alpha$  = 7.62E-5 m/h, which is the lower limit of 95% confidence interval).



Figure 10. Comparison of predicted and measured chamber air concentration (heptane).







Figure 12. Comparison of predicted and measured chamber air concentration (toluene).



Figure 13. Comparison of predicted and measured chamber air concentration (ethylbenzene).



Figure 14. Comparison of measured and predicted chamber air concentration with modified initial concentration (heptane with modified C<sub>o</sub>).



Figure 15. Comparison of measured and predicted chamber air concentration with modified initial concentration (octane with modified C<sub>o</sub>).



Figure 16. Comparison of measured and predicted chamber air concentration with modified initial concentration (toluene with modified C<sub>o</sub>).



Figure 17. Comparison of measured and predicted chamber air concentration with modified initial concentration (ethylbenzene with modified C<sub>o</sub>).



Figure 18. Comparison of measured and predicted chamber air concentration with modified initial concentration (undecane).



Figure 19. Comparison of measured and predicted chamber air concentration with modified initial concentration (dodecane).



Figure 20. Sensitivity analysis based on  $C_o$  (Base case with  $C_o$  for dodecane)



Figure 21. Sensitivity analysis based on *D* (Base case with *D* for dodecane)



Figure 22. Sensitivity analysis based on  $\alpha$  (Base case with  $\alpha$  for dodecane)



Figure 23. Sensitivity analysis based on *l* (Base case with *l* for dodecane)

#### 6.2 Quantitative Analysis with Statistical Measures

Qualitative analyses were conducted to assess model performance using statistical tools provided in ASTM Standard D5157. The outcomes of the statistical analyses are summarized in Table 7. The cases satisfying the criteria for adequate model performance are indicated in bold typeface.

Compounds satisfying all categories include nonane, decane, undecane, 1,2,4trimethylbenzene, and 1,2,4,5-tetramethylbenzene. More volatile chemicals such as heptane, octane, toluene, and ethylbenzene and less volatile chemicals such as dodecane did not satisfy most of the criteria. The results of the statistical analysis are similar to those of the qualitative analysis reported in Section 6.1.

Compounds	r	Ь	a	NMSE	FB	FS
Heptane	0.96	16.24	-0.25	64.87	1.71	1.99
Octane	0.98	2.38	0.04	4.29	1.43	1.42
Nonane	0.98	0.97	0.02	0.07	-0.03	-0.01
Decane	0.99	1.03	-0.05	0.03	0.02	0.11
Undecane	0.96	0.90	0.23	0.07	0.06	-0.10
Dodecane	0.87	0.96	0.37	0.38	0.75	0.22
Toluene	0.99	7.43	0.03	31.24	1.93	1.93
Ethylbenzene	0.99	2.52	0.05	4.72	1.47	1.47
1,2,4-trimethylbenzene	0.98	1.00	0.00	0.06	0.02	0.06
1,2,4,5-tetramethylbenzene	0.96	1.15	0.00	0.13	0.20	0.37

Table 7. Results of statistical analysis of model performance.

#### 7. Conclusions and Recommendations

An emission model based on mass-transfer theory was validated with concentration measurements from a chamber test with of oil-based paint applied on a primer-coated substrate of gypsum wallboard. The conclusions are:

• Nonane, decane, undecane, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene: Excellent agreement between the measured and predicted concentrations was achieved for nonane, decane, 1,2,4-trimethylbenzene. The model performance for 1,2,4,5tetramethyl benzene and undecane was good.

• Heptane, octane, toluene, and ethylbenzene: The model over-predicted the maximum air concentrations for more volatile compounds such as heptane, octane, toluene, and ethylbenzene. The discrepancy increases with increasing vapor pressure. Uncertainties in the independent measurements of initial concentration ( $C_o$ ) were identified as the principal source of the discrepancy. To ensure that the estimate of  $C_o$  is closer to that in the chamber, it was suggested that the preparation for  $C_o$  analysis follow the same procedures as for the preparation of the chamber specimen.

• Dodecane: While the predictions of the maximum air concentration ( $C_{a.max}$ ) and the time corresponding to  $C_{a.max}$  were in reasonably good agreement with the measurements for dodecane, a large level of disagreement was observed between the predicted and measured concentration decay rate, i.e., the shape of the concentration decay curve for the same compound. The discrepancy is likely due to the combined effects of multiple error factors including measurement errors in  $C_o$ , D,  $\alpha$  and l, and the assumption of no mass flux at the interface between the paint coating and the substrate. A mass-transfer model for a multi-layer system was suggested for dodecane.

• In general, the performance of the mass-transfer model described in Report 4.1 along with methods to obtain model parameters is encouraging.

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