Effects of Environmental and Test Conditions on VOC Emissions from "Wet" Coating Materials

X. Yang[1*], Q. Chen[1], J. Zeng[2], J.S. Zhang[3], and C.Y. Shaw[2]

1 Building Technology Program, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
2 National Research Council of Canada, Institute for Research in Construction, Indoor Environment Program, M-24, Montreal Road, Ottawa, Ontario K1A 0R6, Canada.
3 Department of Mechanical, Aerospace & Manufacturing Engineering, Syracuse University, 147 Link Hall, Syracuse, NY 13244, USA
* Corresponding author present address: Department of Civil, Architectural, and Environmental Engineering, University of Miami, Coral Gables, FL 33124-0630, USA, Tel: +1 305 284 3456, Fax: +1 305 284 3492, e-mail: xudongy@miami.edu

Abstract In this paper, numerical simulations have been conducted to study the effects of key environmental and test conditions (air velocity, temperature, film thickness, and sample application time) on VOC emissions from a "wet" coating material (wood stain). Simulation results indicate that air velocity and sample application time only significantly affect the emission profiles in the early stage. Film thickness, on the other hand, affects long-term emissions. Temperature can affect both the short-term and long-term emissions.

Key words VOC; Emissions; "Wet" coating material; Modeling; Numerical simulation.

Practical Implications
The volatile organic compound (VOC) emissions from "wet" coating materials are more likely to be affected by environmental and test conditions such as air velocity, temperature, film thickness, and sample application time. There is a question whether the measured emission data using a small-scale environmental chamber can be applied to buildings, considering the different environmental conditions between a chamber and a building. Results obtained from numerical simulations show that when transforming emission data of a "wet" source with a realistic substrate, temperature and film thickness should be paid special attention as they affect the long-term emissions. Air velocity and sample application time affect only the short-term emission behavior and are thus secondary factors to the long-tem indoor air quality (IAQ) evaluation.

Nomenclature

A	constant of compounds (see Table 2)
A_s	surface area of the test sample [m^2]
B	constant of compounds (see Table 2)
C_a	air phase VOC concentration [mg m^{-3}]
C_{a0}	equilibrium vapor phase concentration for the wood stain [mg m^{-3}]
C_l	initial VOC concentration in the wood stain [mg m^{-3}]
C_m	VOC concentration in the material film [mg m^{-3}]
$C_{m,0}$	initial VOC concentration in the material film [mg m^{-3}]
C_s	VOC concentration in the substrate [mg m^{-3}]
D_0 (or D_{m0})	initial diffusion coefficient in the material film [m^2 s^{-1}]
D_a	VOC diffusion coefficient in the air [m^2 s^{-1}]
D_m	effective diffusion coefficient in the material film [m^2 s^{-1}]
D_s	VOC diffusion coefficient in the substrate [m^2 s^{-1}]
E	emission rate per unit area of the source [mg m^{-2} h^{-1})]
E_d	activation energy [kJ mol^{-1}]
g_j	component j of the gravitation vector [m s^{-2}]
h_c	convective mass transfer coefficient [m h^{-1}]
K_{ma}	material-air partition coefficient [-]
K_{ma0}	material-air partition coefficient at the reference temperature [-]
L	loading ratio of the test material [m^2 m^{-3}]
M	molecular weight of the compound
m	total mass of wood stain applied [g]
N	air exchange rate [h^{-1}]
P	vapor pressure [mmHg]
p	air pressure [Pa]
Pr	Prandtl number
R	universal gas constant (=8.3145 J mol^{-1} K^{-1})
S_ϕ	source term for ϕ (see Table 1)
Sc	Schmidt number of VOC
S_T	source term for temperature
T	absolute temperature [K]
T_0	reference temperature [K]
u_j (j=1,2,3)	three components of air velocity vector [m s^{-1}]
V	air velocity above the tested material [m s^{-1}]
x_j (j=1,2,3)	coordinates
y	the normal direction of the film or substrate surface

Greek Symbols

α	liquid expansion factor
β	thermal expansion factor [K^{-1}]
δ	nominal thickness of the "wet" film [m]
τ	time [sec]

μ	molecular viscosity of air [Pa.s]
ρ_a	air density [kg m^{-3}]
ρ_l	density of the wood stain [mg m^{-3}]
Γ_ϕ	effective diffusion coefficient for ϕ (see Table 1)

Subscripts

a	air phase
j	spatial coordinate indices
m	material film
ma	material film - air interface
s	substrate

Introduction

Most architectural coatings ("wet" materials) that contain petroleum-based solvents emit a wide variety of volatile organic compounds (VOCs). Traditionally, a small-scale environmental chamber (ASTM, 1990) is used to measure the emission characteristics of these materials. One goal of emission testing is transforming the measured emission data in small chambers to actual buildings for the purpose of health and comfort evaluation (Wolkoff, 1998). Such transformation requires a complete understanding of how environmental and other factors (e.g., air velocity, temperature, humidity, substrate) can influence emissions (Guo et al., 1996; Wolkoff, 1995). The knowledge is also essential for reliable assessment of the impact of building materials on indoor air quality.

In the past, the effects of air velocity on "wet" material emissions have been studied by several researchers. Sparks et al. (1996) measured several sources with gas-phase-limited emissions for the purpose of generalizing a gas-phase mass transfer model. Different velocities above the test sample were generated by a small fan inside the small-scale chamber. Although they found an increase of the gas-phase mass transfer coefficient with the increase of air velocity, they did not give the emission profiles for the entire process (from "wet" to dry) under different airflow conditions. Wolkoff (1998) measured the emissions of two "wet" sources, a sealant and a water-borne wall paint on gypsum board, under air velocities ranging from 0.01 m/s to 0.09 m/s. He found modest impact (<20%) of air velocity on the concentration/time profiles of VOCs after less than one week. He speculated that when a paint was applied to a realistic substrate (e.g., gypsum board), the mechanism of emission may be evaporation and/or diffusion controlled and their relative proportions change over time. Zhang et al. (1996) and Zhang and Haghighat (1997) designed small-scale chambers that can provide controlled mean air velocity and turbulence level over the surface of the tested material. They both found that for "wet" sources, the emission rates were higher during the initial period of testing at the higher surface velocity, and became lower or undistinguishable near the end. Zhang and Haghighat also found that the turbulent fluctuation had an insignificant effect on emissions. Very recently, Yang et al. (2001a) compared the VOC emission characteristics of a pure decane and a wood stain applied to an oak substrate using both a small-scale (0.4 m^3) and a full-scale (55 m^3) environmental chamber under different airflow conditions. Their experimental data indicated that only during the initial period of time (< 1 h) could the effects of airflow be clearly shown. After that, no clear trend could be observed. By using a comprehensive mass transfer model, Yang et al. (2001b) confirmed that when a "wet" source (wood stain) was applied to a realistic substrate, the dominant emission mechanism could be transferred from surface evaporation to internal diffusion quickly (within hours). As such, the effect of air velocity itself on emissions may become insignificant after certain period of time.

The impact of other factors such as temperature, humidity, and substrate on "wet" material emissions has also been investigated experimentally. Haghighat and De Bellis (1998) reviewed previous research and further presented the results of VOC emissions from a paint and a varnish under different temperatures and relative humidity levels. They noted that as the temperature increased, the total VOC (TVOC) emission rates increased for both the paint and varnish. However, due to the limitation of the experimental facility, it remained unclear how long this would last. Also, they found the individual compounds did not necessarily follow the same trend established to the TVOC. With regard to the effect of relative humidity on the emissions,

significant fluctuations were found for different humidity levels and no clear trend could be established. Wolkoff (1998), based on the measured emission data of a sealant and a paint under different temperatures and humidity levels, also concluded that both temperature and relative humidity affected the emission rates, but depended strongly on the type of material and the type of VOC. Van der Wal et al. (1997), however, found a clear trend of increased initial emission rate and an increased decay rate with increasing temperature for a paint. The total emitted mass from the paint was independent of temperature, which means that bake-out was expected to be successful.

With regard to the influence of substrate on the emissions from "wet" sources, Jorgensen et al. (1995) and Chang et al. (1997) found significant differences in emission rates and patterns between the VOCs released from the same paint applied to non-absorptive substrates (such as stainless steel or aluminum plate) or absorptive substrates (such as gypsum board). They suggested that realistic substrates such as wood or gypsum board should be used for the evaluation of emissions in indoor environment.

The above review indicates that although there is general agreement that emissions from "wet" sources could be affected by environmental and test conditions, the relative importance of each individual factor to the entire emission process deserves further investigation. In fact, some of the experimental data may reflect the effects of multiple factors, instead of one single factor, on emissions. The problem arises because in the experiments we usually could not control many factors to their "idealized" conditions. An example is that when we intend to measure the effect of temperature on emissions, ideally all the factors except for temperature should be unchanged between different experiments. This however is very difficult to achieve because it's hard to maintain consistency with some factors, such as sample application time and film thickness between different experiments. If the emissions are also sensitive to these factors, the actual temperature effect may be masked and the results could be misleading.

Recently, Yang et al. (2001b) developed a mass transfer-based model to simulate VOC emissions from "wet" coating materials applied to a realistic substrate such as oak boards. Using experimental data obtained from a small-scale and a full-scale environmental chamber, they showed that the model can simulate "wet" material emissions under different temperatures and airflow conditions with reasonable accuracy (Yang et al., 2001a, 2001b). This paper intends to use the model to study the effects of several key environmental and experimental factors, including air velocity, temperature, film thickness, and sample application time on the VOC emissions from a "wet" coating material – wood stain.

In the following, the mathematical model that describes the VOC emissions from the "wet" source is briefly reviewed. Methods for determining material properties and simulation results are then presented.

The Mathematical Model

The physical system considered is a "wet" coating material applied to a porous, absorptive substrate. We assume that the amount of coating applied is small so that the liquid is quickly absorbed by the porous substrate after the application, and a wet layer with a uniform initial VOC concentration is formed inside the substrate. The upper boundary of the wet layer is

exposed to ambient airflow and the lower boundary is the substrate initially unaffected by the wet film.

Figure 1 shows that VOC emissions from the "wet" source can be described by mass transfer in four different layers: the material film, the substrate, the material-air interface, and the air phase (Yang et al., 2001b). The governing equations for each layer, starting from the substrate, are:

- Substrate: one-dimensional transient diffusion equation

$$\frac{\partial C_s}{\partial \tau} = D_s \frac{\partial^2 C_s}{\partial y^2} \tag{1}$$

- Material film: three-dimensional transient diffusion equation for free and bound VOCs

$$\frac{\partial C_m}{\partial \tau} = \frac{\partial}{\partial x_j}(D_m \frac{\partial C_m}{\partial x_j}) \tag{2}$$

   where

$$D_m = D_0(\frac{C_m}{C_{m,0}})^3 \exp(-\frac{E_d}{RT}) \tag{3}$$

- Interface: partition coefficient to relate the VOC concentrations between the material side and the air side of the interface

$$C_m = K_{ma} C_a \tag{4}$$

- Boundary layer and above: three-dimensional conservation equations for mass, momentum, energy, and VOC species

$$\frac{\partial}{\partial \tau}(\rho_a \phi) + \frac{\partial}{\partial x_j}(\rho_a u_j \phi) = \frac{\partial}{\partial x_j}(\Gamma_\phi \frac{\partial \phi}{\partial x_j}) + S_\phi \tag{5}$$

where
ϕ = 1 for mass continuity
ϕ = u_j (j = 1, 2, and 3) for three components of velocity vector
ϕ = T for temperature
ϕ = C_a for VOC concentrations

The values of Γ_ϕ and S_ϕ for each ϕ are given in Table 1.

Boundary and Initial Conditions
The boundary conditions for VOCs are:

$$-D_m \frac{\partial C_m}{\partial y} = -D_a \frac{\partial C_a}{\partial y} \quad \text{at the material-air interface} \tag{6}$$

$$-D_m \frac{\partial C_m}{\partial y} = -D_s \frac{\partial C_s}{\partial y} \quad \text{at the film-substrate interface} \tag{7}$$

6

$$C_m = C_s \qquad \text{at the film-substrate interface} \qquad (8)$$
$$C_s = 0 \qquad \text{at the bottom of the substrate} \qquad (9)$$

The VOC initial conditions are at $\tau=0$:

$$C_a = 0 \quad \text{in the air} \qquad (10)$$
$$C_{m,0} = C_l/\alpha \quad \text{in the material film} \qquad (11)$$
$$C_s = 0 \quad \text{in the substrate} \qquad (12)$$

In Equation (11) the liquid expansion factor (α) was introduced to represent the absorptivity of the substrate. Physically, α means that once a "wet" material is applied to an absorptive substrate, the volume of the wet film absorbed by the substrate will expand by a factor of α to the initial volume. Consequently, the initial VOC concentration of the film being absorbed inside the substrate will be decreased by a factor of α compared to that of the original "wet" source.

Determination of Material Properties for Numerical Simulation

In order to simulate VOC emissions from the "wet" material using the above mathematical model, the following material properties are needed:

(a) VOC initial concentration in the "wet" source, C_l
(b) VOC partition coefficient in the material-air interface, K_{ma}
(c) Liquid expansion factor in the substrate, α
(d) VOC diffusivities

- In the air, D_a
- In the material film (initial), $D_{m0} \ (= D_0 \exp(-\dfrac{E_d}{RT}))$
- In the substrate, D_s

In this study, we assume that the TVOC mixture has lumped properties as if it were a single compound. Based on this assumption, one question must first be resolved: how do we determine the properties (e.g., the diffusivity) of TVOC? We propose to use the properties of the most dominant component in the solvent mixture to approximate the average properties of the TVOC mixture. This is clearly an approximation because the composition of the mixture usually changes over time. However, Guo et al. (1999) have shown that the assumption is adequate for petroleum-based "wet" sources such as wood stain.

Methods for determining the aforementioned material properties are now discussed.

The VOC Initial Concentration in the "Wet" Source

For a pure compound (e.g., decane), C_l is the density of the saturated liquid at the temperature tested. For a mixture such as wood stain, C_l for TVOC can be measured by monitoring the weight loss of the VOC using a glass substrate for a long period (e.g., 1 week), while C_l for a

single compound in the material can be obtained by integrating the measured compound concentrations using a small-scale test chamber.

The Partition Coefficient
The partition coefficient represents the ratio of concentrations between two different phases assuming the equilibrium at the interface is achieved instantaneously. For a compound in the material film, K_{ma} can be obtained by:

$$K_{ma} = \frac{C_l}{C_{a0}} \tag{13}$$

Notice C_{ao} is a function of temperature and so is K_{ma}. In practice, headspace analysis can be employed to obtain the C_{ao} (and hence K_{ma}) for both TVOC and single compounds at room temperature (e.g., 296 K). The C_{ao} at a different temperature may be calculated based on the ideal gas law:

$$C_{a0} = \frac{1.33 \times 10^8 P}{8314T/M} \tag{14}$$

Several equations have been proposed to calculate the vapor pressure (P) for a pure compound (e.g., Reid et al., 1977). For the application of petroleum-based "wet" coating materials, Chang and Guo (1992) suggested the use of following equation:

$$\log_{10} P = -0.2185\frac{A}{T} + B \tag{15}$$

Assuming the K_{ma} at a reference temperature, T_0, is K_{ma0}, combining Equations (13) - (15) gives K_{ma} at any temperature T:

$$K_{ma} = K_{ma0}\frac{T}{T_0}10^{0.2185A(\frac{1}{T}-\frac{1}{T_0})} \tag{16}$$

The molecular weight (M) and other properties (A, B) for the three major compounds emitted from the wood stain are given in Table 2. Note that property values for the most dominant compound (decane) are used for TVOC.

The Liquid Expansion Factor (α)
Equation (11) indicates that due to the liquid expansion factor (α), the initial VOC concentration of the "wet" film being absorbed into the substrate ($C_{m,0}$) should be smaller than that of the "wet" source (C_l). The α value can be estimated by assuming that when a "wet' source is applied to a porous substrate, emissions at the beginning must be evaporation dominated and hence the VB model (Guo and Tichenor, 1992) applies for the beginning. The following procedures provide the details.

(1) Give an initial estimation of α, and calculate $C_{m,0}$ using Equation (11).

(2) Calculate the dynamic emission rates using the following equation:

$$E = \frac{h_c C_{m,0}}{K_{ma}(r_1 - r_2)}[(r_1 + N)e^{-r_1\tau} - (r_2 + N)e^{-r_2\tau}]$$ (17)

where

$$r_{1,2} = 0.5\{-[N + Lh_c + \frac{h_c}{K_{ma}\delta}] \pm [(N + Lh_c + \frac{h_c}{K_{ma}\delta})^2 - \frac{4NLh_c}{K_{ma}\delta}]^{0.5}\}$$

$$\delta = \frac{1000m}{\rho_l A_s \alpha}$$

Equation (17) is the VB model (Guo and Tichenor, 1992) for evaporative sources only. It is based on the assumption that the concentration at the surface is proportional to the ratio between the remaining VOC mass and the initial VOC mass applied. The VOC emissions from a "wet" coating during the initial period (e.g., from 0 – 0.2 h) can be assumed to be evaporation dominated and thus the VB model applies. Then we can adjust the α until the early stage emission rates (e.g., from 0 - 0.2 h), as calculated by the VB model, agree with the measured data.

It should be noted that the key to using this approach is to provide the accurate mass transfer coefficient when using the VB model. In our study, we used a commercial computational fluid dynamics (CFD) code (CHAM, 1996) to calculate the average mass transfer coefficient.

The Diffusivities
As for the diffusivities, D_a can be easily found in the literature (e.g., Reid et al., 1977). However, no sufficient information is available regarding the D_{mo} and D_s. In this study, they are obtained by fitting the predicted VOC emission rates with the measured data, based on a reference case (details of the reference case is give below)

Table 3 lists the physical properties used for numerical simulation of TVOC emissions from the wood stain (Yang et al., 2001b).

Results and Discussion
A small-scale environmental chamber with the controlled mean air velocity (Zhang et al., 1996) has been used to measure the VOC emissions from the wood stain (Yang et al., 2001b). The purpose of the test was to obtain the reference emission data under a set of pre-defined environmental conditions, and to estimate the unknown property data of the "wet" source (D_{mo} and D_s). For this reference case, the chamber was operated at a temperature of 23±0.5°C and relative humidity of 50±2%. The air velocity above the material was controlled at approximately 0.15 m/s in the experiment, which corresponds to a common air velocity found indoors (Hart and Int-Hout, 1980; Zhang et al., 1995). The air exchange rate of the entire chamber was 1.0 air change per hour (ACH). More details about the reference case are given by Yang et al. (2001b).

To examine the effects of environmental and test conditions on the VOC emissions from the "wet" source, a series of numerical simulations have been conducted in which all the parameters are kept the same as those of the reference case except for the one to be examined. The results are presented and discussed below.

Impact of Air Velocity on Emissions
Figure 2 shows the predicted VOC emissions under different air velocities ranging from 0.15 m/s to 0.5 m/s. At the beginning, cases with higher air velocity emit faster but also decay faster. This has been confirmed by the previous experimental data (Yang et al., 2001a). Based on the mass transfer theory, greater air velocity will generate larger mass transfer coefficients. At the early stage when the material is still relatively wet, the emissions are likely dominated by evaporation at the material surface. Thus, higher air velocity can lead to an increase in initial emissions. This period however only lasts less than 1 h. After that, Figure 4 shows that the impact of air velocity becomes insignificant especially for $\tau > 8$ h. This indicates that internal diffusion begins to dominate the interfacial mass transfer rendering air velocity less influential.

Impact of Temperature on Emissions
Figure 3 gives the simulated TVOC emission rates from the wood stain at four different temperatures, 20.5 °C, 23.5 °C, 27.5 °C, and 31.5 °C. The results indicate that temperature can affect the emissions throughout the entire period. Figure 3a shows that the initial emission rates are significantly higher at a higher temperature. As the emissions during this period are likely dominated by evaporation, the emission rates depend on the equilibrium vapor pressure of emitted VOCs, which is higher for a higher temperature. Meanwhile, the decay of emission rates also increased with the chamber air temperature and because of this, the above trend is reversed from the 0.7 h point.

Notice the above results are based on the assumption that neither chemical reaction nor secondary source emissions exist inside the "wet" source and the total amount of emittable VOCs remains unchanged at different temperatures. For certain materials this assumption may not hold (see, for example, Wolkoff, 1998) and the results should be used with caution.

Impact of Film Thickness on Emissions
The effect of film thickness on the emission rates has not received much attention, but preliminary observations indicated that it could be a key factor affecting the emission rates (Guo et al., 1996). Understanding the impact of film thickness on emissions is critical for both the emission measurements and study of material emissions in buildings.

To investigate the potential effect of film thickness, we conducted additional simulations in which different film thickness were achieved by assuming various applied mass of wood stain. The nominal film thickness of the reference case is 1.2238×10^{-4} m, calculated based on the applied mass (4.5162 g), density of the wood stain (818 kg/m^3), applied area (0.06 m^2), and the liquid expansion factor (1.33). Two more cases, one with a film thickness of 1.1014×10^{-4} m (10% lower than that of the reference case), and the other case with a film thickness of 1.3462×10^{-4} m (10% higher than that of the reference case) are simulated.

10

Figure 4 gives the predicted emission rates for the above three cases. The results indicate that all these cases had approximately the same emission rates during the first hour. After that, the emission rates began to deviate. Cases with larger film thickness had higher emission rates and also slower decay rates than cases with smaller film thickness. The difference tends to be more pronounced as time goes on. A change of 10% in film thickness may also result in a change of approximately 10% in emission rate at $\tau = 24$ hours. This indicates that the film thickness does not influence the early stage emissions but will affect the long-term emission profiles. This may be explained by two factors. First, for a "wet" material, the emission rates during the initial period are mainly dominated by evaporation. Hence, the film thickness is immaterial. As time goes on, a thinner film depletes faster, resulting in smaller concentrations in both the material phase and the material-air interface. The emission rates for smaller film thickness will thus be smaller.

The above results indicate that when comparative experiments are conducted to identify the impact of a specific factor on emissions, the film thickness must be controlled within a very small range, 5 - 10%, in order to obtain repeatable and comparable results.

Impact of Sample Application Time on Emissions
When an indoor coating material is tested in a chamber, it must be applied to an appropriate substrate before the testing. This procedure usually takes several minutes, sometimes longer. If the source is highly evaporative, losses of volatile components during the application could cause errors in the estimation of the emission rates.

In order to determine the impact of the sample application time on the emission measurements, computer simulations were performed for the wood stain reference case. Since the emission process during the sample application could be very complicated, an accurate simulation of such a process is very difficult. To demonstrate the approach, the "wet" material emissions during the application time were simulated by assuming the material was in the small-scale chamber (V = 0.15 m/s above the material). A numerical simulation was conducted for that period. The concentration distributions in the material film (which was not uniform) were then used as the initial conditions for a new simulation. Results of the new simulation give the emissions by considering the VOC loss during the application period.

Figure 5 demonstrates the simulated TVOC emission rates for three different application time and an idealized zero application time (that is, uniform initial concentration in the material film). The results show that potential loss of VOCs during sample preparation significantly affects emissions during the early phase. A longer application time yields smaller early-stage emission rates. The application time, on the other hand, is expected to have less impact on long-term emissions. Nevertheless, given the importance of early-stage emissions for highly evaporative coating material such as wood stain, the application period should be kept as short as possible in order to obtain good repeatability and reproducibility (current standards use 2 - 3 minutes).

Conclusions
A numerical model has been used to simulate the effects of air velocity, temperature, film thickness, and sample application time on the VOC emissions from a wood stain applied to an oak substrate. The following conclusions can be made based on the simulation results:

(1) At the beginning (τ < 1 h), cases with higher air velocity emit faster but also decay faster. However, air velocity becomes a secondary factor when τ > 8 h.

(3) Temperature can affect the emissions throughout the entire emission period. Higher temperature results in higher emission rates and faster decay at the beginning (0 – 0.7 h), but smaller emission rates afterwards.

(2) Film thickness does not influence the early stage (0 – 1 h) emissions but affects the emission profiles afterwards. After the initial period, cases with larger film thickness have higher emission rates and also slower decay rates than cases with smaller film thickness. The difference tends to be more pronounced as time goes on.

 (4) Potential loss of VOCs during sample preparation significantly affects emissions during the early phase. A longer application time yields smaller early-stage emission rates. The application time, on the other hand, has less impact on long-term emissions.

Acknowledgements

References

ASTM (1990) *Standard Guide for Small-scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/products*, Philadelphia, PA, American Society for Testing and Materials, (ASTM, D5116).

CHAM (1996) *PHOENICS Version 2.1*, CHAM Ltd, UK.

Chang, J.C.S. and Guo, Z. (1992) "Characterization of organic emissions from a wood finishing product - wood stain", *Indoor Air*, **2**, 146-153.

Chang, J.C.S., Tichenor, B.A., Guo, Z. and Kreb, K. (1997) "Substrate effects on VOC emissions from a latex paint", *Indoor Air*, **7**, 241-247.

Guo, Z. and Tichenor, B.A. (1992) "Fundamental mass transfer models applied to evaluating the emissions of vapor-phase organics from interior architectural coatings", In: *Proceedings of EPA/AWMA Symposium*, Durham, NC.

Guo, Z., Tichenor, B.A., Krebs, K.A., and Roache, N.F. (1996) "Considerations on revision of emissions testing protocols, Characterizing sources of indoor air pollution and related sink effects", *ASTM STP 1287,* Philadelphia, PA, American Society for Testing and Materials, 225-236.

Guo, Z., Chang, J.C.S., Sparks, L.E., and Fortmann, R.C. (1999) "Estimation of the rate of VOC emissions from solvent-based indoor coating materials based on product formulation", *Atmospheric Environment*, **33**, 1205-1215.

Haghighat, F. and De Bellis, L. (1998) "Material emission rates: literature review, and the impact of indoor air temperature and relative humidity", *Building and Environment*, **33**, 261-277.

Hart, G.H. and Int-Hout, D. (1980) "The performance of a continuous linear air diffuser in the perimeter zone of an office environment", *ASHRAE Transactions*, Vol. **86**, Part 2, 107-124.

Jorgensen, R.B., Bjorseth, O. and Malvik, B. (1995) "Emission from wall paints – the influence of the wall material", In: *Proceedings of the 5th International Conference on Healthy Buildings*, Milano, pp977-982.

Reid, R.C., Prausnitz, J.M. and Sherwood, T.K. (1977) *The Properties of Gases and Liquids*, McGraw-Hill, New York.

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.

Van der Wal, J.F., Hoogeveen, A.W. and Wouda, P. (1997) "The influence of temperature on the emission of volatile organic compounds from PVC flooring, carpet, and paint", *Indoor Air*, **7**, 215-221.

Wolkoff, P. (1995) "Volatile organic compounds – sources, measurements, emissions, and the impact on indoor air quality", *Indoor Air* (Suppl. 3), 6-73.

Wolkoff, P. (1998) "Impact of air velocity, temperature, humidity, and air on long-term VOC emissions from building products", *Atmospheric Environment*, **32**, 2659-2668.

Yang, X., Chen, Q., Zeng, J., Zhang, J.S., Nong, G. and Shaw, C.Y. (2001a) "Effects of airflow on VOC emissions from 'wet' coating materials: experimental measurements and numerical simulation", *ASHRAE Transactions* in press.

Yang, X., Chen, Q., Zeng, J., Zhang, J.S. and Shaw, C.Y. (2001b) "A mass transfer model for simulating volatile organic compound emissions from 'wet' coating materials applied to absorptive substrates", *International Journal of Heat and Mass Transfer* in press.

Zhang, J.S., Shaw, C.Y., Nguyen-Thi, L.C., Macdonald, R.A. and Kerr, G. (1995) "Field measurements of boundary layer flows in ventilated rooms", *ASHRAE Transactions*, Vol. **101,** Part 2.

Zhang, J.S., Shaw, C.Y., Kanabus-Kaminska, J.M., MacDonald, R.A., Magee, R.J., Lusztyk, E. and Weichert, H.J. (1996) "Study of air velocity and turbulence effects on organic

compound emissions from building materials/furnishings using a new small test chamber",
ASTM STP 1287, Philadelphia, PA, American Society for Testing and Materials, 184-199.

Zhang Y. and Haghighat, F. (1997) "The impact of surface air movement on material emissions",
Building and Environment, **32**, 551-556.

Figure caption

Fig. 1 Physical configuration of VOC emission mechanisms for a "wet" material applied onto an absorptive substrate. 1 = boundary layer diffusion; 2 = phase change; 3 = in-film diffusion; 4 = in-substrate diffusion

Fig. 2 Predicted TVOC emission rates from wood stain under different velocities: (A) 0 – 4 hour; (B) 4 – 16 hour; (C) 16 – 24 hour

Fig. 3 Predicted TVOC emission rates from wood stain under different temperatures: (A) 0 - 2 hour; (B) 4 - 24 hour; (C) 0 – 24 hour

Fig. 4 Predicted TVOC emission rates from wood stain for different film thickness: (A) 0 - 2 hour; (B) 4 - 24 hour; (C) 0 – 24 hour

Fig. 5 Predicted TVOC emission rates from wood stain for different sample application time: (A) 0 - 2 hour; (B) 4 - 24 hour

Table 1 Values of Γ_ϕ and S_ϕ in Equation (5)

ϕ	Γ_ϕ	S_ϕ
1	0	0
u_j (j=1,2,3)	μ	$-\dfrac{\partial p}{\partial x_j} - \rho_a g_j \beta(T - T_0)$
T	μ/Pr	S_T
C_a	μ/Sc	0

Table 2 Properties of major compounds emitted from the wood stain

Compound	Formula	Molecular Weight (M)	A	B
Nonane	C_9H_{20}	128.3	10456.9	8.332532
Decane	$C_{10}H_{22}$	142.3	10912.0	8.248089
Undecane	$C_{11}H_{24}$	156.3	11481.7	8.260477

Table 3: Physical properties of the wood stain applied to an oak substrate (23 °C)

Property	Symbol (unit)	Value
Liquid density of wood stain	ρ_l (mg/m^3) [a]	8.18×10^8
Initial TVOC concentration in wood stain	C_l (mg/m^3) [b]	6.91×10^8
Equilibrium vapor phase concentration	C_{a0} (mg/m^3) [c]	1.71×10^4
Partition coefficient of TVOC	K_{ma} (-) [d]	4.03×10^4
Liquid expansion factor in substrate	α (-) [e]	1.33
Initial TVOC concentration in film	$C_{m,0}$ (mg/m^3) [f]	5.20×10^8
TVOC Schmidt number	Sc (-) [g]	2.6
Initial TVOC diffusivity in film	D_{m0} (m^2/s) [h]	1×10^{-11}
TVOC diffusivity in substrate	D_s (m^2/s) [h]	1×10^{-14}

[a] Lab measurement
[b] Lab measurement using glass substrates
[c] Headspace analysis
[d] $K_{ma} = C_l/C_{a0}$
[e] Obtained by using the VB model (Guo and Tichenor, 1992) for the initial period (0 - 0.2 h) and comparing the calculated initial emission rate with the small-scale chamber data
[f] $C_{m,0} = C_l/\alpha$
[g] Sparks et al., 1996
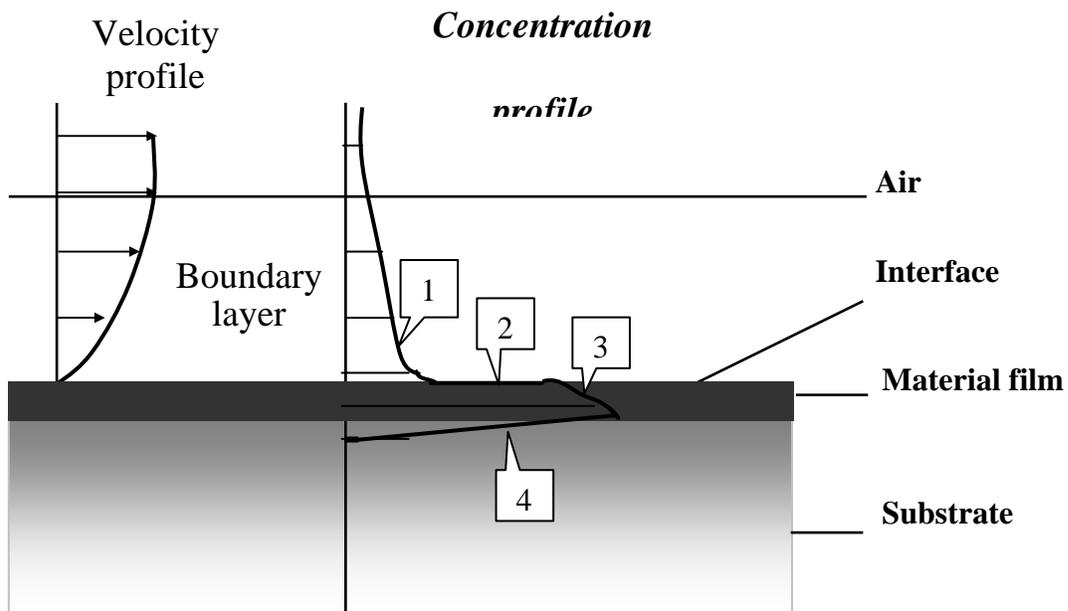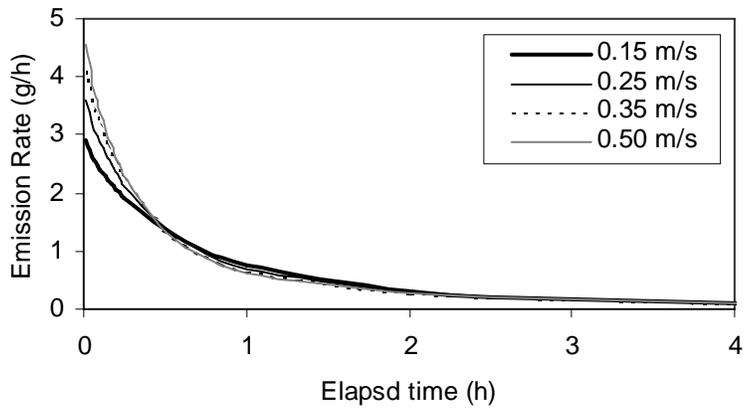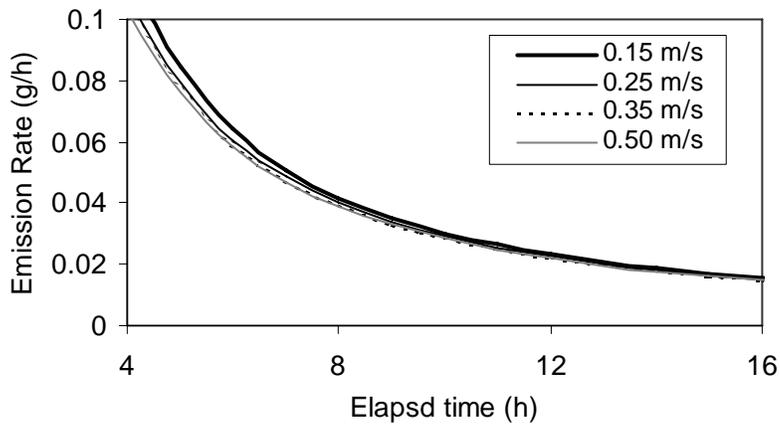[h] Obtained by matching the simulated emission rates with the small-scale chamber data
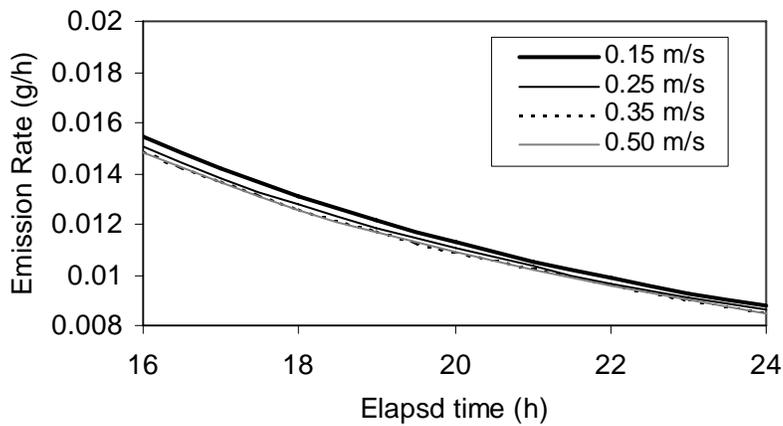
Figure 1: Physical configuration of VOC emission mechanisms for a "wet" material applied onto an absorptive substrate. 1 = boundary layer diffusion; 2 = phase change; 3 = in-film diffusion; 4 = in-substrate diffusion.
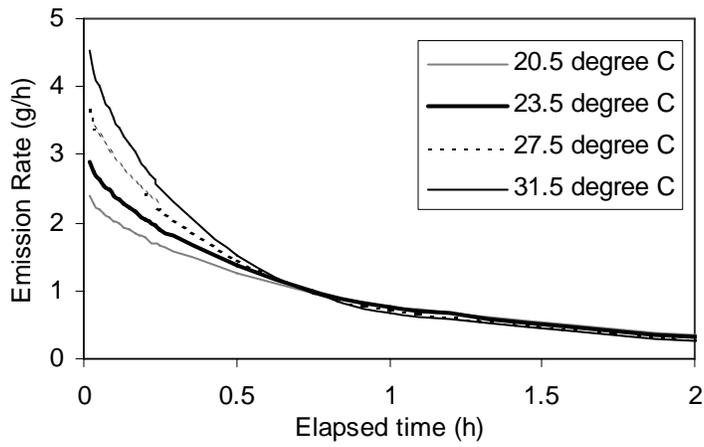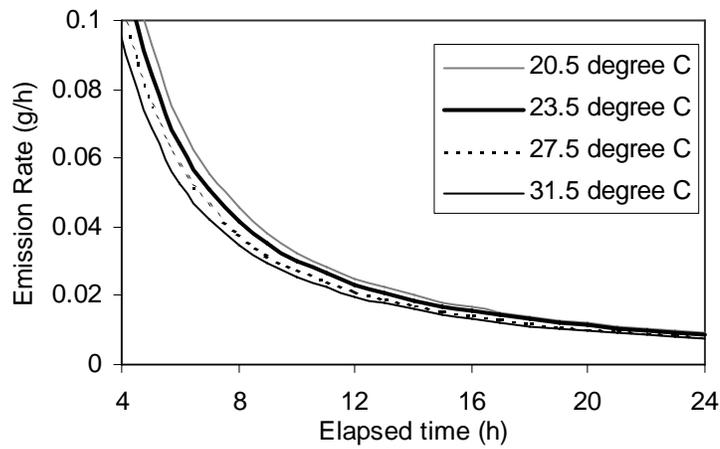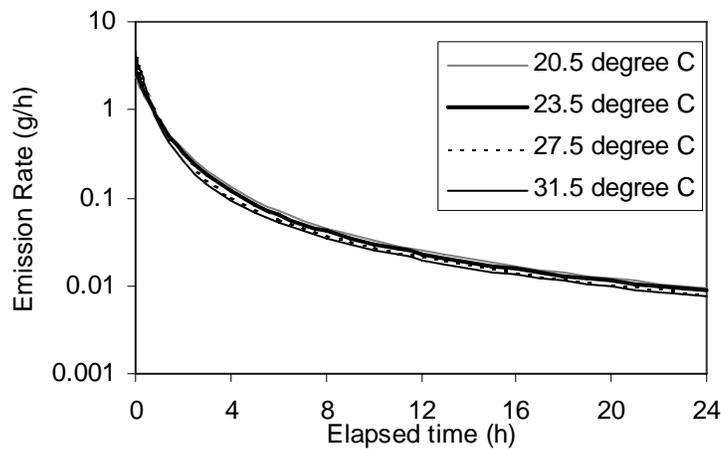
(a)

(b)

(c)

Figure 2 Simulated TVOC emission rates from wood stain under four different velocities: (a) 0 – 4 hour, (b) 4 – 16 hour, (c) 16 – 24 hour.

(a)

(b)

(c)

Figure 3 Predicted emission rates in the small-scale chamber under different temperatures: (a) 0 - 2 hour, (b) 4 - 24 hour, (c) 0 – 24 hour.
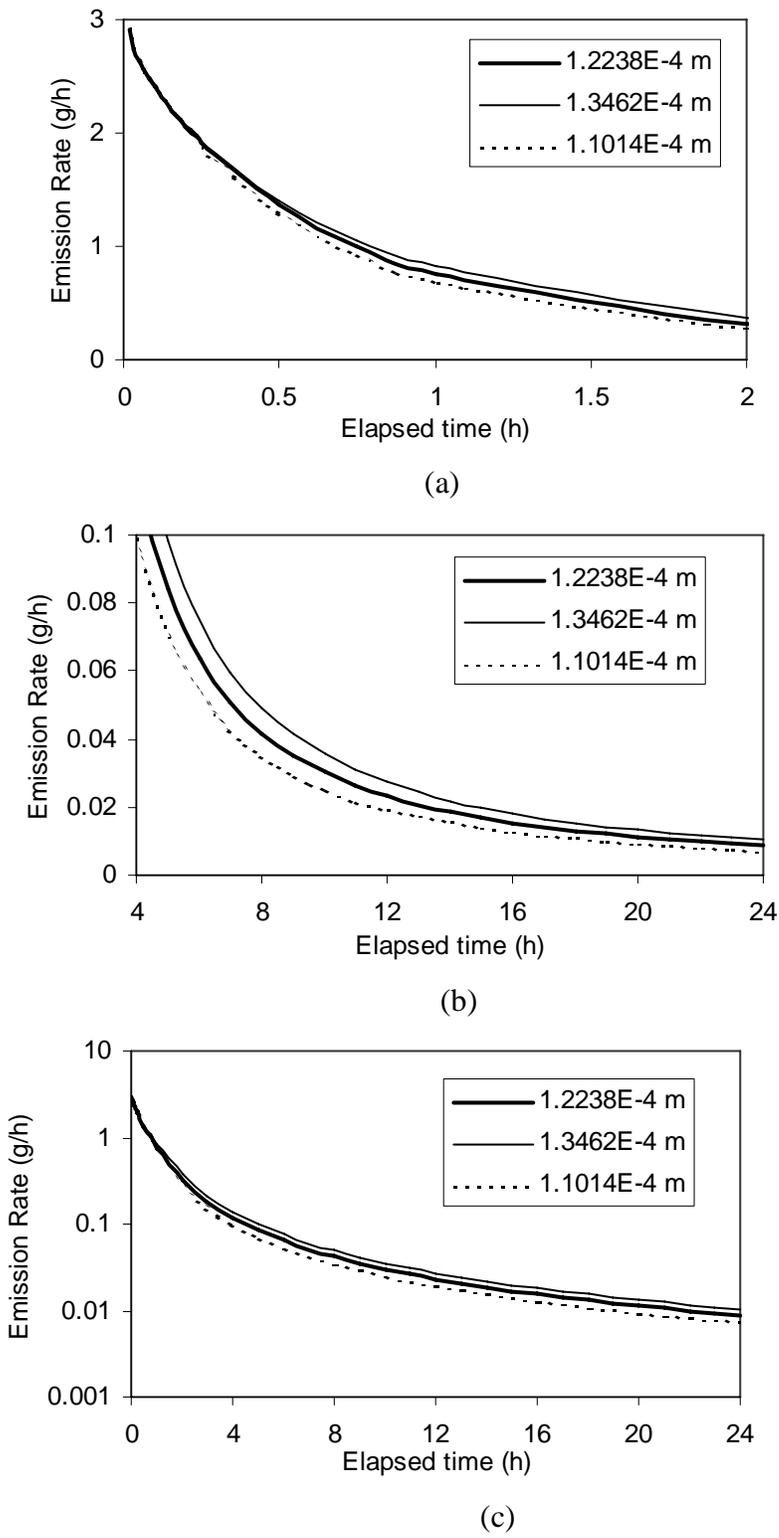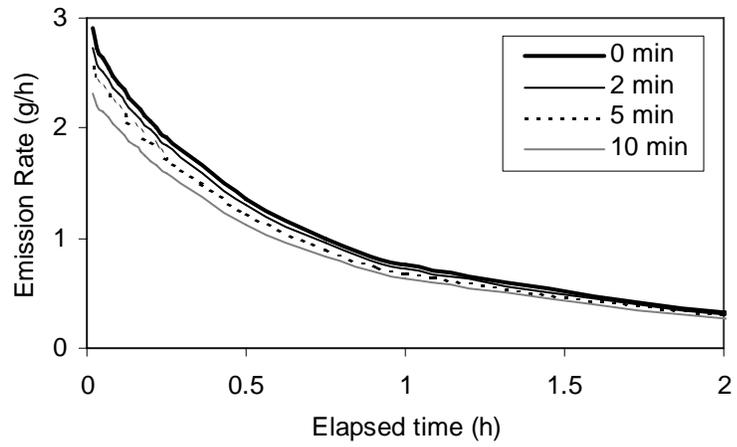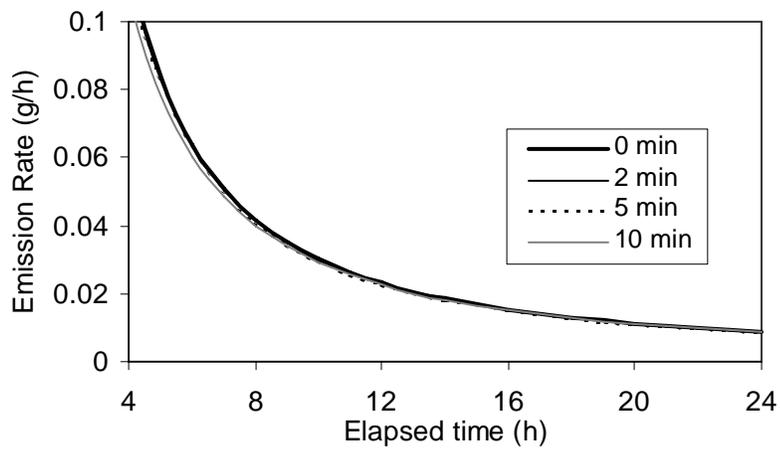
(a)

(b)

(c)

Figure 4 Predicted emission rates in the small-scale chamber under different film thickness: (a) 0 - 2 hour, (b) 4 - 24 hour, (c) 0 – 24 hour.

(a)

(b)

Figure 5 Predicted emission rates in the small-scale chamber with different sample application times: (a) 0 - 2 hour, (b) 4 - 24 hour.