Development of a Procedure for Estimating the Parameters of Mechanistic Emission Source Models from Chamber Testing Data

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ABSTRACT

In order to evaluate the impacts of volatile organic compounds (VOCs) emissions from building materials on the indoor pollution load and indoor air quality beyond the standard chamber test conditions and test period, mechanistic emission source models have been developed in the past. However, very limited data are available for the required model parameters including the initial concentration (C_{m0}), in-material diffusion coefficient (D_m), partition coefficient (K_{ma}), and convective mass transfer coefficient (k_m). In this study, a procedure is developed for estimating the model parameters by using VOC emission data from standard small chamber tests. Multivariate regression analysis on the experimental data are used to determine the parameters. The Least Square and Global search algorithm with multi-starting points are used to achieve a good agreement in the normalized VOC concentrations between the model prediction and experimental data. To verify the procedure and estimate its uncertainty, simulated chamber test data are first generated by superposition of different levels of "experimental uncertainties" on the theoretical curve of the analytical solution to a mechanistic model, and then the procedure is used to estimate the model parameters from these data and determine how well the estimates converged to the original parameter values used for the data generation. Results indicated that the mean value of the estimated model parameters C_{m0} was within -0.04%+/-2.47% of the true values if the "experimental uncertainty" were within +/-10% (a typical uncertainty present in small-scale chamber testing). The procedure was further demonstrated by applying it to estimate the model parameters from real chamber test data. Wide applications of the procedure will result in a database of mechanistic source model parameters for assessing the impact of VOC emissions on indoor pollution load, and for evaluating the effectiveness of various IAQ design and control strategies.

KEYWORDS
Building materials, Volatile organic compounds (VOCs), Emission source model, Indoor air quality.

INTRODUCTION

Indoor air quality (IAQ) plays an important role in human health because people typically spend 80-90% of their time indoors. To evaluate the effects of volatile organic compounds (VOCs) emissions from building materials, a physical mechanistic model was developed by Little and Hodgson (1994) and improved by Yang (2001), Huang and Haghighat (2002), Zhang and Xu (2003) with their specific assumptions and solutions. Deng and Kim (2004) successfully derived the analytical solution to the model that considering the convective mass transfer resistance across the boundary layer. The model in theory can be used to evaluate and predict the emissions of VOCs from dry building materials beyond the standard chamber test condition and test period. However, very limited data are available for the required model parameters including the initial concentration (C_{m0}), in-material diffusion coefficient (D_m), partition coefficient (K_{ma}), and convective mass transfer coefficient (k_m).

Little and Hodgson (1994) also performed a series of emission test for four kinds of carpets. Bodalal et al. (1999) tested three types of VOCs through typical dry materials. The correlation for predicting D_m and K_{ma} based on molecular weight and vapor pressure were developed for each product and type of VOCs. These correlations were later verified and improved by Zhang et al. (2003) in the sorption and desorption experiments. Xu et al. (2011) implemented a Dual-chamber test that can measure D_m and K_{ma} directly. Xu's data were used for developing and verifying the method that can predict D_m and K_{ma} based on the similarity between water vapor and VOC transport in porous media. Cox (2001) measured the D_m and K_{ma} in vinyl flooring. Zhou et al. (2018) developed an alternately airtight/ventilated emission method for efficient determination of the key parameters from building materials. The measured D_m ranged across six orders of magnitudes from 1E-14 to 1E-8 m^2/s and K_{ma} ranged from 1 to 450,000 (as shown in Figure 1), depending on the Media (materials)-Environment (T and RH)-Species (VOCs) combinations.

The objective of the present study is to develop a procedure for estimating the model parameters by using gas-phase VOC concentration data from standard small chamber emission tests and explore the feasibility of using the estimated parameters in the mechanistic diffusion model to analyse and predict the long-term emissions from building materials and their impact on indoor air quality.

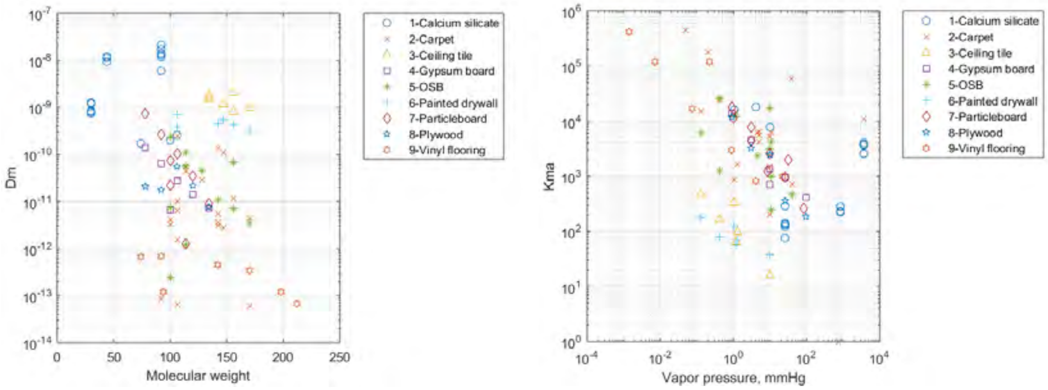
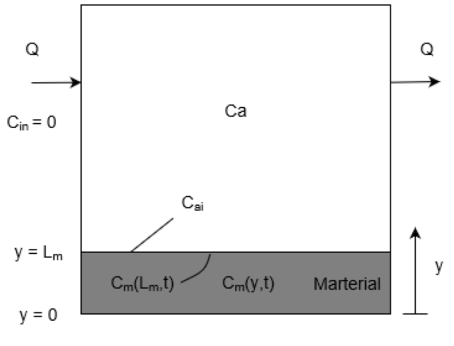


Figure 1 Summary of D_m (left) and K_{ma} (right) values from the literature

METHODS

Mathematical model



$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial y^2} \tag{1}$$

The initial condition: $C_m(y,0) = C_{m0}, 0 \leq y \leq L_m$ (2)

The boundary conditions are:

$$\frac{\partial C_m}{\partial y} = 0 \;\; at \; y = 0 \tag{3}$$

$$-D_m \frac{\partial C_m}{\partial y} = k_m \left(\frac{C_m}{K_{ma}} - C_a \right) \;\; at \; y = L_m \tag{4}$$

Figure 2 Schematic of VOC emission in a test chamber and the governing equations

A schematic of emission testing and the equations governing the material diffusion process of a dry material in a ventilated chamber is shown in Figure 2, assuming that (1) the material is homogenous with a uniform initial concentration; (2) The diffusion process is one dimensional in the material; (3) The pollutant in the chamber air is perfect mixed; and (4) the interactions between different VOCs are negligible.

For the concentration in the chamber air, the governing equation can be represented as:

$$V\frac{dC_a}{dt} = -QC_a - AD_m\frac{\partial C_m}{\partial x}\Big|_{y=L_m}$$ (5)

Initial condition: $C_a = 0\ at\ t = 0$ (6)

Where, V is the volume of the chamber, m^3. A is the top surface area of the material, m^2. Q is the air flow rate, m^3/s.

Analytical solution

Deng and Kim (2004) derived an analytical solution derived the following analytical solutions to Eqs. 1-6:

Concentration in the material:

$$C_{m(y,t)} = 2C_{m0}\sum_{n=1}^{\infty}\frac{(\alpha - {q_n}^2)}{A_n}cos\left(\frac{y}{\delta}q_n\right)e^{-D_m{L_m}^{-2}{q_n}^2t}$$ (7)

Concentration in the gas-phase:

$$C_a(t) = 2C_{m0}\beta\sum_{n=1}^{\infty}\frac{q_n\,sin\,q_n}{A_n}e^{-D_m{L_m}^{-2}{q_n}^2t}$$ ( )

$$A_n = [K_{ma}\beta + (\alpha - q_n)K_{ma}Bi_m^{-1} + 2]q_n^2\,cos\,q_n + q_n\,sin\,q_n[K_{ma}\beta + (\alpha - 3q_n^2)K_{ma}Bi_m^{-1} + \alpha - q_n^2]$$ (9)

$$Bi_m = k_mL_m/D_m$$ (0)

$$\alpha = N{L_m}^2/D_m$$ (00)

$$\beta = L \cdot L_m$$ (02)

Where, Bi_m is termed as the Biot number for mass transfer, which represents the ratio of in-material to on-surface mass transfer resistance. α is the dimensionless air exchange rate, which show the ratio of dilution rate in the chamber air to the in-material diffusion rate. L is loading ratio, area of material / volume of chamber. β is the ratio of the chamber air to the volume of the material.

The q_n are the positive roots of: $q_n\,tan\,q_n = \frac{\alpha - q_n^2}{K_{ma}\beta + (\alpha - q_n^2)K_{ma}Bi_m^{-1}}$ (03)

Approach to the determination of the model parameters

The present model has four key parameters: k_m, K_{ma}, D_m, and C_{m0}. Due to the consistent flow patterns in the standard chamber test condition, the k_m can be pre-determined as part of the chamber characterization measurements. For example, the k_m of the small scale environmental chambers used to establish the material emission database (MEDB-IAQ) at the National Research Council Canada (NRC) were measured to be 1.0 and 1.5 m/h, respectively (Zhang et al., 1999). Some empirical relations were also adopted for the gas-phase mass transfer coefficient (Huang and Haghighat 2002). For laminar flow, there exists (White, 1988)

$$Sh\ = 0.644Sc^{1/3}Re^{1/2}$$ (04)

Where, Sh is Sherwood number ($Sh\ = \frac{k_m}{Dm/Lm}$). Sc is Schmidt number ($Sc\ = \frac{\upsilon}{Dm}$), υ is the kinematic viscosity, m^2/s. Re is Reynolds number ($Re\ = \frac{v \cdot l}{\upsilon}$), v is the velocity of the fluid, m/s, l is the characteristic dimension, m.

The remaining three key parameters (C_{m0}, D_m and K_{ma}) need to be obtained from the emission test data. From Deng's analytical solution of gas-phase concentration (Eq.8), C_{m0} does not affect the shape of concentration curve $C_a(t)$, though it affects the magnitude of $C_a(t)$. So we first estimated the initial value of C_{m0} ($C_{m0,ini}$) by using a first-order evaporation model (Zhang et al, 1999) and then use it in the regression analysis of normalized concentration to estimate D_m and K_{ma}. Since the gas-phase concentration is proportional to C_{m0} for the same D_m and K_{ma}, the final value of C_{m0} can be obtained by:

$$C_{m0} = C_{m0,ini} \frac{\int_0^{t_n} C_{a,data}\, dt}{\int_0^{t_n} C_{a,sim}\, dt} \tag{05}$$

Where, $C_{m0,\,ini}$ is the initial guess of C_{m0}. t_n is the time of the last data point. $C_{a,data}$ is the measured gas-phase concentration from chamber test data. $C_{a,sim}$ is the simulated gas-phase concentration calculated by the analytical solution with D_m and K_{ma} from the regression analysis with initial guess of C_{m0} ($C_{m0,ini}$).

Procedure for the determination of the model parameters

The chamber data are first pre-processed by curve fitting with a power law model, which is then used to generate the data with the same "sampling" time interval. The initial guesses of the three key parameters are obtained from the generated data. To minimize the distortion of normalized curve due to measurement error of maximum concentration, we used the average concentration over the test period ($C_{a,avg}$) to normalize the measured concentrations in the chamber. Then the regression analysis with global minimum algorithm that could find the minimum least square of error in the concentration (target function:$F(D_m, K_{ma}) = \sum(C_{a,estimate}(t) - C_{a,data}(t)\,)^2$) is performed on the normalized data ($C_a/C_{a,avg}$), which is followed by the re-calculation of the C_{m0} by Eq.15. If the results of D_m and K_{ma} are in the range of K_{ma} dominated state (i.e., K_{ma} is so large that there is abundant VOC mass on the surface that the in-material diffusion resistance is inconsequential comparing to the convective mass transfer resistance over the surface), the upper limit of D_m were accepted as final estimation of D_m as the conservative estimate. Otherwise, the results of the regression are used as the parameter estimates.

RESULTS

Verification of the procedure from measured parameters

A reference emissoin test with 840 hours of experimental data for a particlebpard (PB1) obtained by NRC (1999) are used to examine the effect of the elasped time on the regression results. In this test, VOC concentrations were measured at t=94, 120, 168, 240, 336, 504, 672 and 840 hours. The data are well represented by Deng's analytical solution (2001) with the parameters: D_m=7.65 × 10^{-11} m^2/s and K_{ma} = 3289 for toluene (note that the volume of the small-chamber is 50 L, the air change rate is 1 ACH, the loading ratio is 0.729, the thickness of the material is 0.0159 m). We use analytical solution to generate simulated concentration data with a "sampling" interval of 24 hours, which were then used to test the effects of the test period (i.e., the simulated test peiord or elapsted time). The relative error in estimating the three parameters decreases with the increase of the simulated test period. 96 h and 120 h tests would give 150%-200% overestimate of D_m and 30%-20% underestimate of C_{m0}. A test period of longer than 240 h would give reduce the relative error to be less than 1%.

Gas-phase concentration of 94 measured cases (only D_m and K_{ma}) shown in Figure1 were generated by analytical solution. 80% of D_m and 90% of K_{ma} ranged from 20% - 500% that coverd most the compounds in the materials except vinyl flooring from Cox and carpet3 from John Little. All the out of range cases have very small D_m (<1E-12) and K_{ma} ranged from 810 to 450,000. The Dm of these cases converged around 1E-12 m^2/s by the global minimum algorithm with 300 multi-start points, which is one of the local minimum but not the global minimum of target function. 7 of these cases can find the global minimum by increasing the multi-start points to 1000. Genetic algorithm will be tested in the future to increase the speed of convergence to global minimum.

Effects of experimental uncertainty of chamber measured concentration

All the previous discussion or verification of procedure are based on simulated data by analytical solution without any uncertainty of measured chamber concentration which is ideal condition. The experience value of uncertainty in the standard chamber test is 10% from NRC database. To test the effect of uncertainty, 100 cases of PB1 were generated by analytical solution by adding 10% uncertainty which follow the normal distribution on each data points.

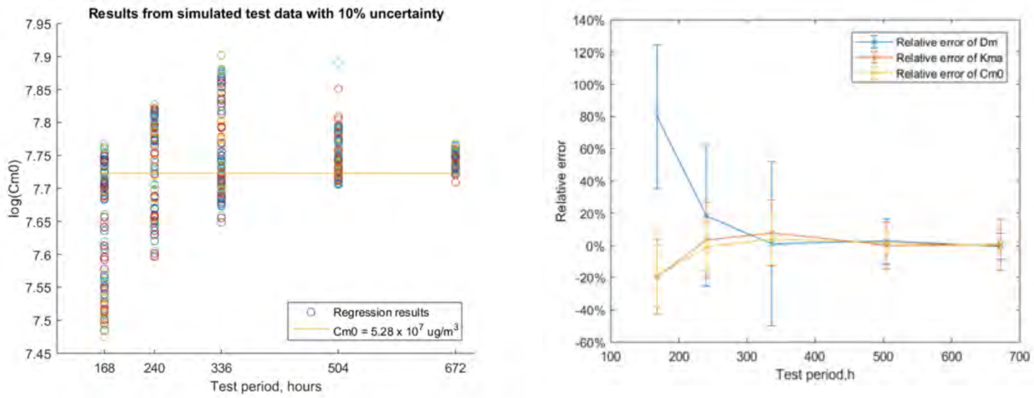


Figure 3 Results of D_m for 1000 cases with 10% uncertainty

From the above figures, the uncertainty of measured data has a significate impact on the results of key parameters for any one case. The statistic results show the similar behavior as discussion of effect of test period. For the above case, the test period less than 120 hours do not have enough data points to eliminate the influence of uncertainty. In other words, the uncertainty has a larger impact to the shorter test period.

The relative error between mean value of 100 cases and given parameters vary with test period. (Figure 4, right). Based on the relative errors of the three key parameters, the prediction of D_m is higher at 168 h and 240 h, but less than 3.02% after 336 h. The prediction of K_{ma} is less than 2.36% with test period longer than 240 h. The prediction of C_{m0} is under 3.72% with the test period longer than 240 h. The standard deviation of the prediction ranged from 54.17% to 2.47% for all the three keys parameters. The procedure can give the same order prediction with test period between 168 h to 240 h and less than 1% +/- 16.01% with 672 h test. Based on the analytical solution (Deng, 2004), the errors in C_{m0} transfer directly into the model prediction errors in C_a and has the largest influence on the model prediction (Wei and Xiong, 2013).

Application of the Procedure on particleboard

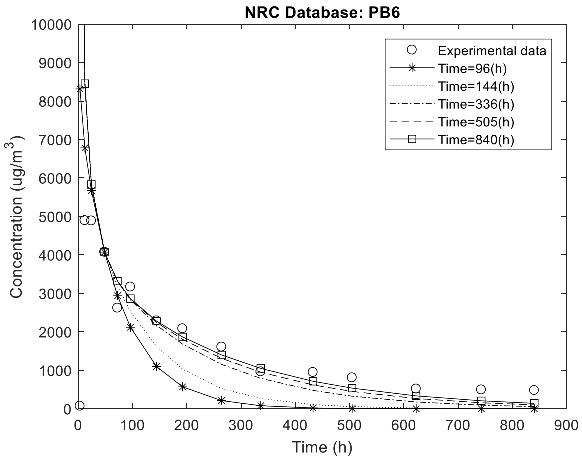


Figure 4 Chamber concentration of PB6

One material (particleboard ID: PB 6) was selected from the NRC database to investigate the application of the procedure. Figure 5 gives the results of PB6 when implement this procedure. For PB6, when the time is longer than 336 h, this procedure gives good result to approach the test data. Using all 840 h data resulted D_m and K_{ma} that gave the best curve fitting for the long-term prediction, but the initial concentration data points were not as well represented.

CONCLUSIONS

Based on the standard chamber test and analytical solution of diffusion model, a procedure has been developed, which can obtain the key parameters of the diffusion model by multi-variance nonlinear regression analysis. The concentration curve generated by estimated key parameters shows a good agreement with the real chamber test data. Uncertainty of measurement affects the accuracy of estimated key parameters very much, but the statistic results show convergence to the true value when applied the procedure to 1000 cases. Further studies will focus on weight factor to enhance the matching of long-term concentration and more efficiency global search algorithm (e.g., genetic algorithm) in the future. Wide applications of the procedure will result in a database of the required emission model parameters for predicting the impact of VOC emissions on IAQ.

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