Abstract
In order to evaluate the impacts of volatile organic compounds (VOCs) emissions from building materials on the 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 was developed for estimating the model parameters by using VOC emission data from standard small chamber tests. In the procedure, initial values of the model parameters were refined by multivariate regression analysis of the measured emission data. To verify the procedure and estimate its uncertainty, simulated chamber test data were generated by adding 10% experimental uncertainties on the theoretical curve from the analytical solution to a mechanistic emission model. Then the procedure was applied to the generated data to estimate the model parameters. Results indicated that estimates converged to the original parameter values used for the data generation and the error of estimated parameters $D_m$, $C_{m0}$ and $K_{ma}$ were within ±10%, ±23%, and ±25% of the true values, respectively. The procedure was further demonstrated by applying it to estimate the model parameters from real chamber test data. Wide application of the procedure would result in a database of mechanistic source model parameters for assessing the impact of VOC emissions on indoor pollution load, which are essential input data for evaluating the effectiveness of various indoor air quality (IAQ) design and control strategies as well as the energy required for meeting given IAQ requirements.

Keywords
- building materials
- volatile organic compounds (VOCs)
- emission source model
- indoor air quality
- building energy efficiency

Article History
Received: 17 November 2019
Revised: 08 January 2020
Accepted: 02 February 2020
© Tsinghua University Press and Springer-Verlag GmbH Germany, part of Springer Nature 2020

1 Introduction
Indoor air quality (IAQ) plays an important role in human health because people typically spend 80%-90% of their time indoors. Many pollutants such as volatile organic compounds (VOCs) have higher concentrations indoors than outdoors due to indoor emission sources. In order to estimate the impact of the VOC pollution on IAQ and the energy required to ventilate the space to meet given IAQ criteria, it is necessary to determine the VOC pollution load in buildings, which is one of the objectives of Subtask 2 of the IEA-Annex-68 IAQ Design and Operation Strategies for Low-Energy Residential Buildings (Rode et al. 2016). Existing approach to characterize the VOC pollution loads in buildings has largely relied on the standard chamber testing of the material emission rate under standard test conditions (23 °C, 50% RH) and the empirical correlation models determined from the emission test results. While this approach is valid for comparing different material selection options in design stage, it fails to facilitate the prediction of the VOC concentrations in real environment, where the conditions vary with time and often differ significantly from the standard conditions. A
mechanistic model with model parameters determined for the various materials is needed. The objective of the present study is to develop a reliable method and 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 analyze and predict the long-term emissions from dry building materials and their impact on indoor air quality as well as the energy required for ventilation to meet given IAQ requirements.

**Mass transfer model.** In order to evaluate the effects of VOC emissions from building materials, a physical mechanistic model was developed by Little et al. (1994) assuming equilibrium condition at the air-material interface and Fick’s diffusion inside the material. They derived the analytical solution by neglecting the convective mass transfer resistance across the air boundary layer over the material surface, which led to an overestimation of the concentration in the air at the early-stage of the material emissions. Huang and Haghighat (2002) considered the convective mass transfer resistance and obtained an analytical solution to the resulting model by neglecting the concentration in the air because of its low value relative to the concentration in the material, and they used this method to predict the long-term emission rate. Zhang and Xu (2003) presented an improved mass transfer model that considered the concentration in the air. However, the concentrations in the material and in the air must be solved simultaneously with the finite difference technique. Yang et al. (2001) developed a numerical simulation model for dry building materials, which can be used for more complex boundary conditions in general. Deng and Kim (2004) successfully derived the analytical solution to the model by considering the convective mass transfer resistance across the boundary layer and the gas phase concentration. In theory, the model can be used to evaluate and predict the emissions of VOC 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 \( C_{m0} \), the in-material diffusion coefficient \( D_m \), the partition coefficient \( K_{ma} \), and the convective mass transfer coefficient \( k_m \).

**Measurement.** Little et al. (1994) also performed a series of emission tests for four kinds of carpets. Their experimental data were used for verifying the mathematical model and analytical solution that did not consider the convective mass transfer in the boundary layer. Bodalal (1999) developed an experimental method to directly measure the \( D_m \) and \( K_{ma} \). They tested three types of VOC through typical dry materials (carpet, plywood, particleboard, vinyl floor, gypsum board, sub-floor tile and OSB). The correlations for predicting \( D_m \) and \( K_{ma} \) based on molecular weight and vapor pressure were developed for each product and type of VOC. These correlations were later verified and improved by Zhang et al. (2003) in sorption and desorption experiments. Xu and Zhang (2011) implemented a dual-chamber test that can measure \( D_m \) and \( K_{ma} \) directly. Xu and Zhang used their data 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. Eighty-seven sets of reported data \( D_m \) and \( K_{ma} \) were found in the previous studies (Table A1, which is in the Electronic Supplementary Material (ESM) of the online version of this paper). The \( D_m \) ranged across four orders of magnitudes from \( 1 \times 10^{-14} \) to \( 1 \times 10^{-8} \) m²/s, and \( K_{ma} \) ranged from 1 to 450,000 depending on the Media (materials)-Environment (\( T \) and \( RH \))-Species (VOC) combinations (Fig. 1).

**Estimation.** Yang et al. (2001) also developed a procedure to obtain \( D_m \), \( K_{ma} \), and \( C_{m0} \). Only \( D_m \) was obtained by curve fitting between the normalized experiment data and numerical solution of standard emission chamber test in Yang’s procedure. \( K_{ma} \) was pre-determined by the correlation

![Summary of \( D_m \) and \( K_{ma} \) value from literature](image.png)
of $K_{ma}$ and vapor pressure from Bodalal’s work (Bodalal 1999). $C_{m0}$ was calculated by correcting the initial value with the ratio between the measured peak concentration and that predicted by the model with the estimated $D_m$ and $K_{ma}$. The accuracy of this correction method, however, is very sensitive to the error of the peak value measured and predicted. He et al. (He and Yang 2005; He et al. 2005) developed a non-linear regression procedure to obtain $D_m$, $K_{ma}$ and $C_{m0}$ based on chamber emission test data and tested the performance of the method. In their procedure, Little’s model (Little et al. 1994) was used which ignores the effect of convective mass transfer through the boundary layer. Xiong et al. (2011, 2012, 2013) developed a method to estimate $D_m$ and $K_{ma}$ by linear regression of the analytical solution of the sorption process in an air-tight chamber and wet coating material emission process. The $K_{ma}$ and $C_m$ was determined by the mass conservation of VOC inside of the chamber and the definition of $K_{ma}=C_{ma}/Ca_{eq}$. The linear regression of the analytical solution only works for the one root of the transcendental equation, which works well in the sorption process solution in the air-tight chamber and wet coating material emission process solution, but it does not work well in the emission process of dry building materials (which will be discussed later in this paper). Zhou et al. (2018) designed an experiment to obtain $K_{ma}$ and $C_{m0}$ by linear regression of equilibrium state gas phase concentrations under several cycles of air-tight and ventilated conditions. The experimental method can reduce the test period to 48 hours. That is a much shorter time than many of the standard chamber test periods, but the emission process involved in Zhou et al.’s test (Zhou et al. 2018) is presumably in a thin layer below the surface.

2 Method and procedure

2.1 The mass transfer model

A schematic of the emission test of dry material in a ventilated chamber is shown in Fig. 2. Assuming that (1) the material is homogeneous with a uniform initial concentration; (2) the diffusion process is one dimensional in the material; (3) the pollutant in the chamber air is perfectly mixed; and (4) the interactions between different VOC are negligible; The in-material diffusion process for a VOC of interest can be described by Eqs. (1)–(6) as described in several previous studies (Bodalal 1999; Deng and Kim 2004; Huang and Haghighat 2002; Little et al. 1994; Yang et al. 2001; Zhang and Xu 2003).

In-material diffusion process:

$$\frac{\partial C_m}{\partial t} = D_m \frac{\partial^2 C_m}{\partial y^2}$$  \hspace{1cm} (1)

where,

$C_m$ is the concentration of the VOC in the material ($\mu g/m^3$);
$D_m$ is the diffusion coefficient of the VOC in the material and is assumed to be constant ($m^2/s$);
$t$ is the elapsed time (s);
y is the vertical coordinate from the bottom to the top surface of the material (m).

The initial condition of Eq. (1) is given as follows:

$$C_m(y,0) = C_{m0} \hspace{0.5cm} 0 \leq y \leq L_m$$  \hspace{1cm} (2)

where,
$C_{m0}$ is the initial concentration of the VOC in the material ($\mu g/m^3$);
$L_m$ is the thickness of the material (m).

The boundary conditions of Eq. (1) are:

$$\frac{\partial C_m}{\partial y} = 0 \hspace{0.5cm} \text{at} \hspace{0.5cm} y = 0$$  \hspace{1cm} (3)

$$-D_m \frac{\partial C_m}{\partial y} = k_m \left( \frac{C_m}{K_{ma}} - C_a \right) \hspace{0.5cm} \text{at} \hspace{0.5cm} y = L_m$$  \hspace{1cm} (4)

where,
$C_a$ is the concentration of VOC in the chamber air ($\mu g/m^3$);
$K_{m}$ is the partition coefficient; 
$k_m$ is the convective mass transfer coefficient of VOC through the top surface (m/s).

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

$$V \cdot \frac{dC_a}{dt} = -Q C_a - AD_m \frac{\partial C_a}{\partial y}$$  \hspace{1cm} (5)

Initial condition:

$$C_a = 0 \text{ at } t = 0$$  \hspace{1cm} (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).

2.2 Analytical solution

Deng and Kim (2004) derived an analytical solution to the above model as follows:

Concentration in the material:

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

Concentration in the air:

$$C_a(t) = 2C_m \sum_{n=1}^{\infty} \frac{q_n \alpha \sin(q_n)}{A_n} e^{-D_m L_m^2 q_n^2 t}$$  \hspace{1cm} (8)

$$A_n = (K_m \beta + (\alpha - q_n^2)K_m B_{m}^{-1} + 2q_n^2 \cos q_n + q_n \sin q_n)(K_m \beta + (\alpha - 3q_n^2)K_m B_{m}^{-1} + \alpha - q_n^2)$$

$$B_{m} = \frac{k_m L_m}{D_m}$$

$$\alpha = \frac{N L_m}{D_m}$$

$$\beta = \frac{L \cdot L_m}{D_m}$$

where,

$B_{m}$ is termed as the Biot number for mass transfer, which represents the ratio of in-material to on-surface mass transfer resistance;
$\alpha$ is the dimensionless air exchange rate, representing the ratio of dilution rate in the chamber air to the in-material diffusion rate;
$L$ is the loading ratio, surface area of the material divided by the volume of the chamber;
$\beta$ is the ratio of the volume of the chamber to the volume of the material.
$q_n$ are the positive roots of:

$$q_n \tan q_n = \frac{\alpha - q_n^2}{K_m \beta + (\alpha - q_n^2)K_m B_{m}^{-1}}$$  \hspace{1cm} (9)

To obtain the accurate solution of Eqs. (7) and (8), we analyzed the effect of the number of the roots. As shown in Fig. 3, $n = 50$ gives the same $C_a(t)$ curve as $n = 200$. In Table 1, we showed the influence of model parameter selection on the required number of $q_n$ roots. For the listed cases of five different levels of $D_m$ and $K_m$, numbers of roots are sensitive to the value of $D_m$ which affects the term of $B_{m}$ in Eq. (9). These cases are not sensitive to $K_m$. To insure all the cases have sufficient accuracy and consistent analysis procedure, we used 200 roots in all the calculations presented in this paper, which appears to be sufficient for dry materials reported.

2.3 Approach to the determination of the model parameters

The present model has four key parameters: $k_m$, $K_m$, $D_m$, and $C_m$. The latter three will be determined by the regression analysis procedure developed in this study. 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 two 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

![Number of the roots of transcendental equation Eq. (9)](image)

Table 1  Required number of roots for five levels of $D_m$ and $K_m$  

| $D_m$ (m$^2$/s) | $K_m$ | $C_m$ (μg/m$^3$) | Minimum number of roots |
|----------------|-------|------------------|------------------------|
| $7.56 \times 10^{-10}$ | 3289 | $5.28 \times 10^2$ | 20                     |
| $7.56 \times 10^{-11}$ | 3289 | $5.28 \times 10^2$ | 30                     |
| $7.56 \times 10^{-12}$ | 3289 | $5.28 \times 10^2$ | 50                     |
| $7.56 \times 10^{-12}$ | 328.9 | $5.28 \times 10^2$ | 50                     |
| $7.56 \times 10^{-12}$ | 32890 | $5.28 \times 10^2$ | 50                     |
relations were also adopted for the gas-phase mass transfer coefficient (Huang and Haghighat 2002). For laminar flow, there exists (White 1988):

\[
Sh = 0.644 Sc^\frac{3}{2} Re^3
\]

where,

\[
Sh \text{ is Sherwood number } (Sh = \frac{k_m}{D_m / L_m});
\]

\[
Sc \text{ is Schmidt number } (Sc = \frac{v}{D_m}), \text{ } v \text{ is the kinematic viscosity (m}^2\text{/s});
\]

\[
Re \text{ is Reynolds number } (Re = \frac{v \cdot l}{v}), \text{ } v \text{ is the velocity of the fluid (m/s)};
\]

\[
l \text{ is the characteristic dimension (m)}.
\]

Therefore, the gas-phase mass transfer coefficient \(k_m\) for the small chamber test can be estimated independently from the chamber’s test condition. When the mechanistic model is applied to a full-scale environmental condition, the mass transfer coefficient for the full-scale condition should be used together with the \(K_{ma}, D_m\), and \(C_{m0}\) determined by the small-scale chamber test data. Such an approach was verified in the study of material emissions from wet coating materials where the VOC emission rate was more sensitive to \(k_m\) than to dry materials (Zhang et al. 1999).

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 the concentration curve \((C_a(t))\), even though it affects the magnitude of \(C_a(t)\). So, we used the normalized curve, \(C_a(t) = C_a(t)/C_{av}\) to estimate \(D_m\) and \(K_{ma}\) first. Logically, the maximum measured concentration \((C_{a,max,data})\) could be used to normalize the concentration data. But due to the relatively large sampling time interval, the actual maximum concentration in the chamber may be missed in the standard emission test. So, using the measured maximum concentration could distort the shape of the curve. To minimize such distortion, we used the average measured concentration over the test period \((C_{a,avg})\) to normalize the measured concentrations in the chamber.

The \(C_{m0}\) can be re-calculated by Eq. (11)

\[
C_{m0,estimated} = C_{m0,initial} \cdot \frac{\int_0^t C_{a,data}(t)dt}{\int_0^t C_{a,estimated}(t)dt}
\]

where,

\(C_{a,estimated}(t)\) is the gas phase concentration generated by the initial guess of \(C_{m0,initial} K_{ma}\) with the estimated \(D_m\) and \(K_{ma}\) from the regression analysis;

\(C_{a,data}(t)\) is the measured gas phase concentration;

\(t_n\) is the time of the last data point.

The detail of the procedure will be discussed in next section.

3 Procedure for the determination of the model parameters

3.1 Overview of the procedure

We first provide an overview of the procedure and then discuss the key issues involved in it. As shown in Figs. 4, 5, and 6. The procedure has four main steps.

(1) Data pre-processing, generating the data with an even time interval.

Step1: Data pre-processing

Input: Raw chamber test data

Power law model to represent \(C(t)\) after 24 hours

Stop Step1 Continue on Step2

Output: Even time interval data

Generate even time interval (24 hours) data points

---

Fig. 4 Flow diagram of the procedure Step 1

Step2: Initial guess and lower&upper limit of the key parameters

Calculate the relative difference between last two data points

Input: Even time interval data, Raw chamber test data

First order exponential model to represent first 24 hour raw data points

Calculate initial guess of \(K_{ma}\) and \(C_{m0}\) by curve fitting

Obtain \(C_{m0}(0), k_m, k_a\) by curve fitting

Integrate \(C(t)\) to obtain the lower limit of \(C_{m0}\) and \(K_{ma}\)

\[
C_{all} = \frac{Q}{V_m} \cdot \int_0^{t_e} C_a(t)dt
\]

\[
C_{all} + C_{a(max)} = \frac{Q}{V_m} \cdot \int_0^{t_e} C_a(t)dt
\]

---

Fig. 5 Flow diagram of the procedure Step 2
Fig. 6 Flow diagram of the procedure Step 3 and Step 4

(2) Initial guessing as well as the lower and upper limits of model parameters.
(3) Doing a regression analysis to determine $D_m$ and $K_{ma}$
(4) Re-calculating $C_{m0}$.

3.2 Data preprocessing

**Power-law curve fitting.** Due to the different test conditions, the real chamber test data from different labs or previous studies may have different sampling time intervals. In order to implement the procedure consistently and minimize the effect of sampling interval on the regression results, we adopted an even sampling approach in which the raw chamber data were first fitted with a power-law model and then “sampled” in an equal interval to generate the data for the regression analysis. The power-law model was found to represent the data well after the first 24–96 hours for several dry building materials, as verified by Zhang et al. (1999). We tested the power-law model for the particleboard test (PB1) from NRC’s chamber test (Zhang et al. 1999) whose test period took as long as 840 hours to verify the power-law model under long-term emission tests (Fig. 7). From the results, using 24–96 hours as data points to do the power-law curve fitting gives the same trend, but it overestimates the long-term concentration. If the entire test data are used for curve fitting, the power-law model gives an accurate representation of concentration but still slightly overestimates the long-term concentration due to the higher concentration or emission factor from initial period. To solve this problem, the logarithm weighting factor was used to increase the weight of long-term concentrations. The power-law model obtained by the logarithm weighting factor represents the raw data very well but overestimates the concentration from initial period. Since the long-term prediction is more important in revealing the in-material diffusion process, the logarithm weighting factor was adopted in the procedure.

**Effect of chamber test period (elapsed time).** Based on the literature review, chamber test period (i.e., the elapsed time) varied from 96 to 840 hours in the previous studies. A reference emission test with 840 hours of experimental data for a particleboard obtained by NRC (Zhu et al. 1999) was used to examine the effect of the elapsed time on the regression results. In this reference emission test, VOC concentrations were measured at $t = 94, 120, 168, 240, 336, 504, 672,$ and 840 hours (Fig. 8). The data were well represented by Deng’s analytical solution with the parameters $D_m = 7.56 \times 10^{-11}$ m$^2$/s, $K_{ma} = 3289$ for TVOCs (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, and $k_m$ is 1/3600 m/s). We used the Deng and Kim (2004)’s analytical solution to generate simulated concentration data with the same “sampling” time as the real chamber test. And the data points with a sampling interval of 24 hours were generated by power-law curve fitting as discussed previously, which were then used to test the effects of the test period (i.e., the simulated test period...
or elapsed time). As shown in Fig. 8, the relative error in estimating the three parameters decreases with the increase of the simulated test period. A test period of 96 hours and 120 hours would give a 1.5–2 times greater estimation of $D_m$ due to insufficient data to capture the behavior. A test period of longer than 240 hours (10 days) test would reduce the relative error to be less than 1%.

3.3 Initial estimate of $D_m$, $K_{ma}$, and $C_{m0}$

Proper initial guesses and limits of the model parameters are necessary to avoid unrealistic regression results and improve the convergence of the nonlinear regression analysis to the correct model parameters.

**Initial guess of $D_m$.** To obtain the initial guess of $D_m$, we applied the correlation between the emission rate and the four dimensionless parameters ($\alpha$, $\beta$, $K_{ma}$, $F_o$, and $Bi_m/K_{ma}$) derived by Qian et al. (2007). The mass-transfer Fourier number ($F_o = \frac{D_m \cdot t}{K_{ma}^2}$), representing the ratio between the emission time and the time-scale of the in-material diffusion process (i.e., a dimensionless time with the in-material diffusion time scale as the reference), could be used to divide the total emission period into three stages, as shown in Fig. 9: (1) $0 \leq F_o < 0.01$, a peak period or initial period (evaporation-controlled emission period); (2) $0.01 \leq F_o < 0.2$, a transition period; and (3) $0.2 \leq F_o \leq 2$, a quasi-steady-state period (i.e., the slow decay period, internal diffusion-controlled emission period).

The emission process was approximately complete (over 99% of VOC is emitted from the material) when $F_o = 2.0$ with $Bi_m/K_{ma}$ in the range of 6–8189. The range covered all the chamber emission test cases, except acetaldehyde of Carpet 3 from Little et al. (1994). From Little’s research, they did not have the data of air concentration in the storage bag of Carpet 3. Therefore, they could not calculate $K_{ma}$ independently as they did with Carpet 1 and 4, which create more uncertainty when they estimated the parameter $D_m$ and $K_{ma}$. The acetaldehyde of Carpet 3 gave the lowest $K_{ma}$ ($K_{ma} = 1$) among all the cases reviewed. Xu and Zhang (2011) used a dual-chamber test to measure the value of $D_m$ and $K_{ma}$ which was different between the emission test and sorption test. All of Xu and Zhang’s tests of calcium silicate were with $Bi_m/K_{ma}$ ranging from 1.07 to 2.87. Therefore, we can accept at least 95% of VOC has already emitted from the dry materials with $Bi_m/K_{ma}$ ranged from 6 to 8189 when $F_o = 2.0$ (i.e., $t = F_o \cdot \frac{F_o^2}{D_m} = 2 \frac{F_o^2}{D_m}$).

For a standard chamber test, there are no simple criteria to determine whether an emission process reaches the quasi-steady state or the concentration is too low to be detected. We used a 10% relative difference as the criteria, which is the same as the typical uncertainty level of the standard emission tests. If the air concentration profile satisfies the above criteria, we assume that the emission process reaches the quasi-steady state. i.e.,

\[
0.2 \leq F_o \left( \frac{t_n}{t_n} \right) \leq 2
\]

where, $t_n$ is the time of the last data point.

The lower and upper limit of $D_m$ can be solved by Eq. (12), and the results are shown as Eq. (13)

\[
D_{m,L} = \frac{0.2L_m^2}{t_n} \leq D_m \leq D_{m,U} = \frac{2L_m^2}{t_n}
\]
where,

\[ D_{m,L} \] is the lower limit of \( D_m \)
\[ D_{m,U} \] is the upper limit of \( D_m \)
\[ D_{m,0} \] was also used as the initial guess of the \( D_m \).

**Initial guess of \( K_{ma} \) and \( C_{m0} \)**: From the analytical solution of gas-phase concentration, \( C_{m0} \) only affects the magnitude of the concentration profile, and the shape was controlled by \( D_m \) and \( K_{ma} \). So, \( C_{m0} \) is re-calculated by Eq. (11) after obtaining \( D_m \) and \( K_{ma} \) by the regression analysis with normalized gas-phase concentration curve. Therefore, the initial guess of \( C_{m0} \) can be assumed as an arbitrary value. The short-term emissions of dry material are not sensitive to the value of \( K_{ma} \) within a certain range (e.g. 1–1000), and the long-term emissions are independent of \( K_{ma} \) (Yang et al. 2001). These allow us to develop a way to estimate the initial guesses of \( C_{m0} \) and \( K_{ma} \) with some approximations. We assumed a first-order decay emission rate during the initial emission period (first 24 hours), adopting the approach used in establishing a semi-empirical emission model for wet coating materials (Zhang and Shaw 1997):

\[
E(t) = k_m \left[ C_i (0) \cdot e^{-kt} - C_i (t) \right]
\]

where,

\( C_i \) is the concentration on the emitting surface (\( \mu g/m^3 \));
\( k_i \) is the convective mass transfer coefficient (m/h);
\( k_s \) is the first-order constant for the VOC concentration on the surface (h\(^{-1}\)).

Using Eq. (14) as the source term, the mass balance equation for the concentration in the test chamber with air change rate \( N \) can be solved to obtain Eq. (15) (Zhang and Shaw 1997).

\[
C_i (t) = \frac{C_i (0) \cdot L \cdot k_m}{L \cdot k_m + N \cdot k_s} \left[ e^{-k_m t} - e^{-\left(1-K_{ma} + N\right) t} \right]
\]

\( C_i (0), K_{ma}, \) and \( k_s \) can be determined by non-linear regression analysis from the gas-phase concentration test data of the first 24 hours for using Eq. (15). From the definition of \( K_{ma} \), \( K_m \) can be expressed as \( K_m = C_{m0} / C_i (0) \). Integrating \( C_i (t) \) in Eq. (15) from initial time point to the time when the gas-phase concentration reaches the peak value can obtain the mass of VOC \( (\Delta M) \) emitted during this period. Assuming an equilibrium condition between the solid material and gas-phase concentration at the peak value of the concentration of chamber air, \( K_m \) can be expressed as \( K_m = \frac{C_{m0} \cdot \Delta M}{V_m} \).

The initial guesses of \( K_{ma} \) and \( C_{m0} \) were calculated from the above two equations of \( K_{ma} \) and \( C_{m0} \).

The range of \( C_{m0} \) does not affect the regression analysis results. The limit of \( C_{m0} \) was considered as double checking for the procedure. The lower limit of \( C_{m0} \) can be determined by integrating the gas-phase concentration from the initial time to the end time of the test.

\[
C_{m0,L} = \frac{Q}{V_m} \int_0^t C_i (t) dt
\]

If the final \( C_{m0} \) obtained from the procedure was less than the lower limit of \( C_{m0} \), that means a major mistake such as wrong implementation of the procedure has happened in the procedure.

**3.4 Implementation of the regression results**

Weighting factor for regression analysis. In this study, the regression analysis results without applying a weighting factor and two different strategies of applying a weighting factor have been compared. As implied by the power-law model, a logarithmic scale would enhance the impact of long-term data points. Relative weighting factor approach (i.e., using the relative deviation as opposed to the absolute deviation between the predicted and the measured data) would give even weight for each data point. For the PB1 case, all the three weighting factor strategies resulted in the same values for the model parameters when no uncertainties were imposed on the data (\( D_m = 7.56 \times 10^{-11} \text{m}^2/\text{s}, K_{ma} = 3289 \) and \( C_{m0} = 5.28 \times 10^7 \mu g/m^3 \)).

The regression results obtained by the different weighting factors showed no significant difference, even when the ratio between the peak and lowest concentrations was about 10 times. If the mean value of concentration is used as the reference value to normalize the curve, the number of data points with the concentrations lower than the mean value (i.e., during the later slow decay period when the level of concentration does not change quickly) is more than that with the concentrations higher than the mean value during the initial period if the elapsed time is longer than 10 days. The mean value is only two times of the lowest value, which also means most of the data points are during the slow decay period, which is an indication of the internal diffusion-controlled process which the mechanistic model intents capture. For the cases with 10% imposed uncertainties in the simulated test data, the different weighting factor methods also gave similar regression results. As shown in Fig. 10, the residuals of the logarithm scale method decrease faster than the other two methods over time, which means the logarithm weighting factor method matches the slow decay period better than the early period. We finally chose logarithm weighting factor because the emission rate from dry materials have been shown to follow approximately the power-law model, and so does the chamber concentration in later time points (Zhang et al. 2006; Zhu et al. 2001).
Sensitivity analysis. To better interpret the experimental results analyzed by the diffusion model, a sensitivity study was performed. The simulated cases for the sensitivity study were created by the analytical solution for the same standard small-chamber test condition. The total elapsed time was 672 hours (28 days) which is the common elapsed time in Europe emission tests for most dry building materials (ISO 2011). Based on the range from the literature, seven levels (49 sets) of $D_m$ ($m^2/s$) and $K_{ma}$ are selected as shown in Table 2.

The overall rate of emission is either dominated by the internal diffusion process (controlled by $D_m$) or the surface emission process (controlled by $k_m$ and $K_{ma}$). According to the sensitivity study, as shown in Figs. 11 to 14, when the value of $D_m$ is over $1 \times 10^{-9}$ m$^2$/s, surface emission process

### Table 2: Sensitivity study with seven levels of parameter values

| $D_m$ ($m^2/s$) | $10^{-14}$ | $10^{-13}$ | $10^{-12}$ | $10^{-11}$ | $10^{-10}$ | $10^{-9}$ | $10^{-8}$ |
|-----------------|------------|------------|------------|------------|------------|------------|------------|
| $K_{ma}$ (m/$s$)| 10         | 100        | 1000       | 5000       | 10,000     | 100,000    | 1,000,000  |

*All combination for all the $D_m$ and $K_{ma}$

![Fig. 10 Residuals distribution for different weighting factors](image)

![Fig. 11 Sensitivity study of effect of $D_m$ under different levels of $K_{ma}$](image)

![Fig. 12 Sensitivity study of effect of $D_m$ under different levels of $K_{ma}$](image)
is the rate controlling process. As a result, $D_m$ cannot be obtained from the nonlinear regression process since $D_m = 1 \times 10^{-9}$ m$^2$/s and $D_m = 1 \times 10^{-8}$ m$^2$/s may not be distinguished from the concentration curve under any value of $K_{ma}$. In other words, the emission data does not contain sufficient information about the in-material diffusion in these cases. When the value of $K_{ma} < 1000$, the concentration profile was not sensitive to the value of $K_{ma}$ as the controlling factor is the in-material diffusion resistance. The diffusion coefficient $D_m$ discussed above is applied with the assumption that the material is homogeneous, and the diffusion is driven by the total concentration (i.e., the sorbed phase plus the free gas phase VOC) gradient in the material. However, many building materials are better represented as porous media in which the VOC diffusion is driven by the free gas phase concentration gradient in the pore air with the pore diffusion coefficient, $D_p = D_m \cdot K_{ma}$. This means the concentration in the chamber air represents the combined effects of $D_m$ and $K_{ma}$ on the VOC emission rates. We define the validated region as the ranges of $K_{ma}$ and $D_m$ with a relative error less than 10%. As shown in Fig. 15, the validated region (dark grey) covered 52.3% of the literature reviewed cases (black points). For the literature cases outside the validated region, the gas-phase concentrations in the test period were also very well represented with a residual less than 4% (Fig. 18), although the estimated $K_{ma}$ and $D_m$ had larger than 10% error. The error of the estimated emission factor for all the literature cases (both inside and outside the validated region) was less than 10% with the test period.

Method of regression analysis. For the method of regression analysis, the least square of target function (Eq. (17)) and trust-region have been applied in this study. The regression analysis process will minimize the target function (Eq. (17)) to find the best curve fitting result.

$$F(D_m, K_{ma}) = \sum (C_{\text{estimated}} - C_{\text{data}})^2$$

(17)
The process of the $k$th iteration has the form:

- Check for stopping criteria: $|F(D_m^k, K_{ma}^k)| < 1 \times 10^{-6}$ or $|F(D_m^k, K_{ma}^k) - F(D_m^{k-1}, K_{ma}^{k-1})| < 1 \times 10^{-6}$ or $k > 1000$
- If not, determine a $\delta D_m(\delta K_{ma})$ such that

\[ F(D_m^{k+1}, \delta D_m K_{ma}^k) < F(D_m^k, K_{ma}^k) \quad \text{or} \quad F(D_m^k, K_{ma}^k + \delta K_{ma}) < F(D_m^k, K_{ma}^k). \]

- Let the new $D_m^{k+1} = D_m^k + \delta D_m$ and $K_{ma}^{k+1} = K_{ma}^k + \delta K_{ma}$.

The trust region is the algorithm to determine the value of $\delta D_m$ or $\delta K_{ma}$ for each iteration step. Trust region means the $\delta D_m$ or $\delta K_{ma}$ of target function in an iteration is believed adequately small enough to apply the Taylor expansion model:

\[ F(D_m + \delta D_m, K_{ma}) = F(D_m, K_{ma}) + \frac{\partial F}{\partial D_m} \delta D_m + \frac{1}{2} \frac{\partial^2 F}{\partial D_m^2} \delta D_m^2 \]

(18)

From the structure of the iteration, this method can finally find out the minimum value of the target function or lead to a local minimum result for multiple solution problems. The key parameters of the final iteration are the case that matches the modified chamber test data best or one of the best for multiple solutions. To figure out whether the target function has multiple solutions or not, the target function distribution for two cases which $D_m$ with two orders of magnitude difference ($1 \times 10^{-11}$ and $1 \times 10^{-13}$) were calculated and shown in Figs. 16 and 17. Both figures show multiple solutions exist in this kind of nonlinear regression analysis problems. The multi-starting global minimum strategy was applied to find the global minimum of the target function in this study.

4 Verification of Procedure

4.1 Literature review cases

Gas-phase concentrations of measured cases (only $D_m$ and $K_{ma}$) from literature shown in Appendix Table A1, which is in the Electronic Supplementary Material (ESM) of the online version of this paper, are generated by the analytical solution (set $C_{m0} = 5.28 \times 10^7 \, \mu g/m^3$) for all the cases since $C_{m0}$ were not provided in literature, test period = 672 hours). All the cases had good convergence with the overall residuals shown in Fig. 18. The worst case was less than 4% normalized residual based on the magnitude of the concentration profile. The estimations of $C_{m0}$ and $D_m$ are shown in Fig. 19. Left $y$-axis and $x$-axis show the bar chart of the ascending sorted relative error of $C_{m0}$ which is the ratio between error and correct number. The right $y$-axis shows the logarithm scale of $D_m$ value. The relative error of estimated $C_{m0}$ was less than ±10% in 62.5% cases that covered all the cases in the validated region (Fig. 15). The other 37.5% cases are good regression analysis results, as discussed in the sensitivity study. These cases had low $D_m$ and high $K_{ma}$ values (except acetaldehyde from Carpet 3 of Little et al. (1994)) which means high in-material diffusion resistance and adequate VOC on the top surface of the material. Therefore, the reason for the underestimation of $C_{m0}$ and overestimation of $D_m$ is that only a thin layer of material participates in emission within the limit test period. As discussed in the sensitivity analysis, the information of in-material diffusion was insufficient in these cases, giving a large relative error. However, considering the implementation of the procedure, we focus on the emission factor to evaluate the IAQ. The error of the emission factor was less than 10% in reproducing the measured emission factor data.
4.2 Effects of experimental uncertainty in the data on the regression results

All the previous discussion or verification of the procedure are based on simulated data by the analytical solution without any uncertainty of measured chamber concentration, which is the ideal condition. From the NRC database (Magee et al. 1999), the estimated value of uncertainty in the measured condition is 10%. To test the effect of uncertainty, 100 uncertainty test cases of PB1 were generated by adding 10% normally distributed uncertainty on each data points which calculated by the analytical solution. From the results, the uncertainty of measured data has a significant impact on the estimation of key parameters for any single case. The statistic results show similar behaviors as the discussion of the effect of the test period. The uncertainty has a larger impact on the early period than the slow decay period. In other words, uncertainty has a larger impact on the shorter test period. Figure 20 shows how the estimation of $D_m$ had an opposed influence on the estimation of $C_{m0}$ of PB1. The higher in-material diffusion rate and lower surface resistance can also let the calculated air concentration with lower in-material concentration match the measured data well. Since $C_{m0}$ was re-calculated after the regression analysis, the accuracy of estimating $C_{m0}$ was affected by the estimation of other parameters. Based on the relative errors of the three key parameters, the relative error of $D_m$ is high at 168 hours and 240 hours, but is less than 4% if the test period is 336 hours or longer. The error of $K_{ma}$ is less than 3% with test period longer than 240 hours. The error of $C_{m0}$ is less than 4% with the test period longer than 672 hours. The standard deviation of the prediction error ranged from 54.17% to 2.47% for all the three key parameters. The procedure can give the same order of magnitude prediction when the test period between 168 hours and 240 hours. And the error was less than 4%±16% with 672 hours elapsed time.

5 Application of procedure on NRC database

One material (particleboard ID: PB 6) was selected from the NRC database to investigate the application of the procedure. Figure 21 shows the results of PB6 with the procedure implemented. We tested the time used for regression analysis that time = 144, 336, and 840 hours. The results show that all the regression analysis results represent the measured data in the test period very well. However, the concentration curve obtained with the model parameters that were estimated from 840 hours test data points was slight lower than the measured concentration in the initial emission period. This was because the procedure fits the evenly generated “sampling” data points from the power-law model which slightly underestimated the concentration curve in the initial emission period. More data points will give a more
accurate estimation, which agrees with the study of elapsed time. So 840 hours data points gives the best regression analysis result.

6 Conclusion

Based on the material emission test in the ventilated chamber and the analytical solution of the diffusion model, this paper developed a procedure which can obtain key parameters (diffusion coefficient, partition coefficient, initial concentration, convective mass transfer coefficient) for dry material. The procedure was suggested using in the validated region ($1 \times 10^{-13} < D_m < 1 \times 10^{-9} \text{ m}^2/\text{s}$, $1000 < K_{ma} < 100,000$).

Applying the procedure to literature cases, all the regression analysis had good convergence with residual less than 4%. 67.5% of the cases had the estimation errors for $D_m$, $C_{m0}$, and $K_{ma}$ within ±10%, ±22.7%, and ±25%, respectively. When the procedure was applied to all the cases collected from the literature, the error in reproducing the measured emission factor data was less than 10%. Uncertainty of measurement affects the accuracy of estimated key parameters very much, but the statistic results show good convergence to the true value when the developed procedure was applied to 100 cases. The good agreement between the simulated results based on the measured parameters and the estimation data validates the effectiveness of the procedure. The procedure can be used to obtain the model parameters with known accuracy based on the emission data from standard small chamber tests. Its adoption for data analysis will result in a database of mechanistic model parameters for evaluating the impact of material emissions on indoor pollution load and IAQ. The procedure also needs to be further validated by applying it to more chamber test data.

Electronic Supplementary Material (ESM): supplementary material is available in the online version of this article at https://doi.org/10.1007/s12273-020-0616-3.

References

Bodalal A (1999). Fundamental mass transfer modeling of emission of volatile organic compounds from building materials. PhD Thesis, Carleton University, USA.

Cox SS, Zhao D, Little JC (2001). Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring. Atmospheric Environment, 35: 3823–3830.

Deng B, Kim CN (2004). An analytical model for VOCs emission from dry building materials. Atmospheric Environment, 38: 1173–1180.

He G, Yang X (2005). On regression method to obtain emission parameters of building materials. Building and Environment, 40: 1282–1287.

He G, Yang X, Shaw CY (2005). Material emission parameters obtained through regression. Indoor and Built Environment, 14: 59–68.

Huang H, Haghifat F (2002). Modelling of volatile organic compounds emission from dry building materials. Building and Environment, 37: 1349–1360.

ISO (2011). Indoor Air—Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID, Standard. Geneva: International Organization for Standardization.

Little JC, Hodgson AT, Gadgil AJ (1994). Modeling emissions of volatile organic compounds from new carpets. Atmospheric Environment, 28: 227–234.
Magee R, Zhu J, Zhang J, Shaw C (1999). A small chamber test method for measuring volatile organic compound emission from "dry" building materials. Final report 1.2 of consortium for material emission and IAQ modelling (CMEIAQ) 1999, Institute for Research in Construction, NRC, Canada.

Qian K, Zhang Y, Little JC, Wang X (2007). Dimensionless correlations to predict VOC emissions from dry building materials. *Atmospheric Environment*, 41: 352–359.

Rode C, Abadie M, Qin M, Grunewald J, Kolarik J, Laverge J (2016). IEA project on indoor air quality design and control in low energy residential buildings. In: Proceedings of the 12th REHVA World Congress.

White F (1988). *Heat and Mass Transfer*, Reading, MA: Addison-Wesley.

Xiong J, Yao Y, Zhang Y (2011). C-history method: rapid measurement of the initial emittable concentration, diffusion and partition coefficients for formaldehyde and VOCs in building materials. *Environmental Science & Technology*, 45: 3584–3590.

Xiong J, Huang S, Zhang Y (2012). A novel method for measuring the diffusion, partition and convective mass transfer coefficients of formaldehyde and VOC in building materials. *PLoS One*, 7: e49342.

Xiong J, Wang L, Bai Y, Zhang Y (2013). Measuring the characteristic parameters of VOC emission from paints. *Building and Environment*, 66: 65–71.

Xu J, Zhang JS (2011). An experimental study of relative humidity effect on VOCs’ effective diffusion coefficient and partition coefficient in a porous medium. *Building and Environment*, 46: 1785–1796.

Yang X, Chen Q, Zhang J, Magee R, Zeng J, Shaw C (2001). Numerical simulation of VOC emissions from dry materials. *Building and Environment*, 36: 1099–1107.

Zhang JS, Shaw C (1997). Modelling of volatile organic compound (VOC) emissions from building materials/furnishings: A literature review. *IRC/NRC Internal Research Report*. National Research Council of Canada.

Zhang JS, Zhu JP, Shaw CY, Zeng J, Plett EG, Bodalal A, Chen Q, Yang X (1999). Development of standard small chamber test methods.

Zhang Y, Xu Y (2003). Characteristics and correlations of VOC emissions from building materials. *International Journal of Heat and Mass Transfer*, 46: 4877–4883.

Zhang J, Zhang JS, Chen Q (2003). Effects of Environmental Conditions on the Sorption of VOCs on Building Materials—Part II : Model Evaluation. *ASHRAE Transactions*, 109(1): 167–178.

Zhang J, Li H, Zhang Z, Salovaara M (2006). On the power-law model for predicting the VOC emissions from office workstation systems. In: Proceedings of the A and WMA Indoor Environmental Quality: Problems, Research and Solutions Conference, Durham, NC, USA.

Zhou X, Liu Y, Liu J (2018). Alternately airtight/ventilated emission method: A universal experimental method for determining the VOC emission characteristic parameters of building materials. *Building and Environment*, 130: 179–189.

Zhu J, Magee R, Lusztyk E, Zhang J, Shaw C (1999). Material emission data for typical building materials: Small environmental chamber test. Final report 4.1 of consortium for material emission and IAQ modelling (CMEIAQ) 1999, Institute for Research in Construction, NRC, Canada.

Zhu J, Zhang J, Shaw C (2001). Comparison of models for describing measured VOC emissions from wood-based panels under dynamic chamber test condition. *Chemosphere*, 44: 1253–1257.