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Screening-level Estimates of Indoor Exposure to Volatile Organic Compounds Emitted from Building Materials

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Abstract

Knowing the value of the key mass-transfer model parameters is a critical requirement for evaluating volatile organic compound (VOC) emissions from indoor materials. The key parameters are diffusion coefficient (D), partition coefficient (K), and initial material-phase emittable concentration (C_0). Although these parameters can be individually measured in the laboratory, the required time and expense are substantial. A simple method of determining D and C_0 using data from ventilated chamber tests and dimensionless analysis is proposed and then validated using VOC emission data from the material emissions database developed by National Research Council Canada (NRC). The primary application of this method is to provide a rapid screening-level estimate of inhalation exposure to VOCs in building materials. Two standard scenarios using the NRC database are employed to demonstrate the value of the approach to indoor air quality assessment. The method could be a useful screening tool for assessing material emissions or environmental exposures.

Key words: VOC, diffusion coefficient, chamber test, characteristic emission rate

1. Introduction

Contaminants in indoor air are known to adversely affect human comfort and productivity and are considered to be an indoor health risk [1-5]. Considerable work has been done investigating concentrations of volatile organic compounds (VOCs) and formaldehyde (also considered a VOC) and testing emissions of source materials in small and large-scale chambers [6-12]. The results have been used to reduce the adverse consequences of human exposure by developing indoor air quality standards, emissions assessment procedures, and product labeling systems [13-15].

To characterize VOC emissions from building materials, more than 40 analytical or semi-analytical emissions models have been developed during the past two decades [16]. VOC emissions from solid materials are typically controlled by internal diffusion. The three key parameters widely used in analytical models to describe diffusion-controlled VOC emissions are the material-phase diffusion coefficient, D ($\text{m}^2\cdot\text{s}^{-1}$); the material/air partition

coefficient, K ; and the initial material-phase emittable concentration, C_0 ($\mu\text{g}\cdot\text{m}^{-3}$). At present, more than 20 different methods to measure C_0 , D , or K independently or simultaneously have been proposed [16-18]. Although it is more rigorous to obtain the model parameters from independent experimental approaches, physically measuring the mass-transfer parameters for important VOCs in all relevant building materials is not feasible.

A common approach is to estimate one or more of the key parameters (C_0 , D and K) by analyzing data obtained from static or ventilated chamber tests. These methods generally fall into two categories, 1) analytical or numerical multivariate regressions and 2) direct application of a mass-transfer model as a mathematical solution to estimate parameters from pre-designed experiments. Multivariate regressions are frequently applied to fit C_0 , D , and/or K during the early phase of emission model development [19-22]. The main problems associated with fitting are that the solution is not unique or is extremely sensitive to small perturbations [23, 24]. Direct methods that do not require fitting are more robust. The so-called C-history methods can be conducted in static or ventilated chambers following pre-designed experimental procedures [25, 26]. Li [24] proposed another robust method for determining C_0 and D from ventilated chamber data while accounting for experimental estimation errors. These methods commonly only take the first eigenvalue of an analytical model and then derive solutions to estimate C_0 , D and/or K . Although the second category of approach usually works better, the C-history methods require the gas-phase concentrations to reach steady-state before performing the calculations and Li's method requires the sampling interval to be approximately $L^2/100D$ (where L is the thickness of the material, m). In other words, the experiments must be pre-designed to most effectively determine C_0 , D and/or K . In addition, all these methods require solutions to analytical models and are therefore not always convenient in practice.

2. Objectives

In this paper, a simple method of estimating VOC emission model parameters (C_0 and D) is proposed. This method doesn't require solutions to analytical models and can be used to estimate the ranges of D and C_0 (if unknown) using gas-phase VOC concentration data

obtained from ventilated chamber tests that are not necessarily pre-designed for this purpose. If the emission test reaches steady-state, a narrower range of D and C_0 as well as the screening-level exposure to VOCs in indoor environment can be estimated by using only a few data points. Considering the emission period that is insensitive to K , the approach is validated using the Monte-Carlo method and the NRC emissions database [10], which contains gas-phase concentrations, typically measured over 4 – 8 days in a ventilated chamber, for VOCs emitted from ~50 building materials. The application of this method is illustrated by estimating exposure to VOCs in two standard room scenarios.

3. Simple method to estimate D and C_0 from ventilated chamber tests

3.1. Estimating D

Qian et al. (2007) [27] derived a correlation between emission rate and several dimensionless parameters (α , βK , Fo_m , Bi_m/K), or

$$\dot{m}^* = \begin{cases} 1.34\alpha^{8.4 \times 10^{-3}} (\beta K)^{-1.3 \times 10^{-4}} (Bi_m / K)^{0.26} e^{\frac{0.0059}{Fo_m + 0.0038}} & 0 \leq Fo_m \leq 0.01 \\ 0.469\alpha^{0.022} (\beta K)^{-0.021} (Bi_m / K)^{0.021} Fo_m^{-0.48} & 0.01 < Fo_m \leq 0.2 \\ 2.104\alpha^{-7.2 \times 10^{-3}} (\beta K)^{8.5 \times 10^{-3}} (Bi_m / K)^{-7.0 \times 10^{-3}} e^{-2.36 Fo_m} & Fo_m > 0.2 \end{cases} \quad (1)$$

where $\dot{m}^*$ is the dimensionless emission rate; α is the dimensionless air exchange rate; β is the ratio of building material volume to air volume; Fo_m is mass-transfer Fourier number, $Fo_m = D \cdot t / L^2$; and Bi_m is mass-transfer Biot number, $Bi_m = h_m \cdot L / D$, where h_m is the convective mass-transfer coefficient, $m \cdot s^{-1}$.

The correlation is valid for a wide range of building materials and indoor environment conditions. Because the emissions process is approximately complete when $Fo_m = 2.0$ [28], emissions can be divided into three stages, or 1) a peak period when $Fo_m \leq 0.01$; 2) a transition period when $0.1 < Fo_m \leq 0.2$; and 3) a steady-state period when $0.2 < Fo_m \leq 2.0$. Although gas-phase concentrations temporally lag the emission rate, the three-stage classification is still roughly applicable to the gas-phase concentration profile.

For a normal chamber test of a single-layer solid building material, it is common to capture the peak concentration and terminate the experiment when the gas-phase concentration is too low to be measured or reaches steady state. Although there are no simple criteria to determine whether an emission test has reached steady state, especially when experimental and random error is high, one intuitive method is to assume steady state when the concentrations of the last few data points are relative close to each other compared to the first few data points. Assume that t_p is the time of the measured peak gas-phase concentration, t_n is the time of the last sample, and that t_p and t_n are in the peak period and steady-state period, respectively. Then

$$Fo_m(t_p) \leq 0.01 \quad (2a)$$

$$0.2 \leq Fo_m(t_n) \leq 2.0 \quad (2b)$$

and Eq (2) can be arranged to give as Eq (3a) and Eq (3b)

$$D \leq \frac{0.01L^2}{t_p} \quad (3a)$$

$$\frac{0.2L^2}{t_n} \leq D \leq \frac{2L^2}{t_n} \quad (3b)$$

$$\frac{0.01L^2}{t_n} \leq D \leq \frac{2L^2}{t_n} \quad (3c)$$

As t_p is usually less than 10 h for a single layer building material tested at an air change rate (ACH) of $\sim 1 \text{ h}^{-1}$ and the chamber test duration could be several weeks, it is reasonable to assume that the test is sufficiently long to satisfy the condition of $20t_p < t_n$. Hence, the D value range can be derived from Eq (3) and is given by Eq (4a)

$$\begin{cases} \frac{0.2L^2}{t_n} \leq D \leq \frac{0.01L^2}{t_p}, & \text{if } 20t_p \leq t_n \leq 200t_p \\ \frac{0.2L^2}{t_n} \leq D \leq \frac{2.0L^2}{t_n}, & \text{if } t_n > 200t_p \end{cases} \quad (4a)$$

$$\begin{cases} \frac{0.01L^2}{t_n} \leq D \leq \frac{0.01L^2}{t_p}, & \text{if } 20t_p \leq t_n \leq 200t_p \\ \frac{0.01L^2}{t_n} \leq D \leq \frac{2.0L^2}{t_n}, & \text{if } t_n > 200t_p \end{cases} \quad (4b)$$

If the variation of gas-phase concentration during the last sampling interval is still high and thus t_n cannot be considered to be in the steady-state period, $0.01 < Fo_m(t_n) \leq 2.0$ can be used to replace Eq (2b), with Eq (3b) and Eq (4) modified accordingly to Eq (3c) and Eq (4b).

3.2. Interpolation method to estimate C_0

Ideally, C_0 will be known through independent measurement. However, if C_0 is not known, interpolation algorithms can be used to estimate C_0 . Hermite cubic interpolation and cubic spline are common piecewise cubic functions with a continuous derivative and two continuous derivatives, respectively [29]. Cubic spline is the smoother of the two methods. However, Hermite cubic interpolation exhibits less oscillation if the data are not smooth and has the ability to remain monotonous between interpolating intervals, while cubic spline cannot. Theoretically, a VOC concentration profile should be monotonous after a peak concentration. Therefore, Hermite cubic interpolation is preferable.

Fig. 1 demonstrates the PCHIP (piecewise cubic Hermite interpolating polynomial) [30] algorithm to simulate gas-phase VOC concentration profiles using estimates of D described previously. As shown, PCHIP provides an acceptable fit to the true gas-phase concentration profile, especially within the experimental duration ($0 \sim t_n$).

Fig. 1. Using PCHIP algorithm to simulate gas-phase compound concentration profile based on D range estimation.

Because $For_m = 2.0$ is the time when the emission process is approximately complete [28], the gas-phase concentration is also assumed to be zero at $For_m = 2.0$, and the time to “completed emissions” can be calculated as Eq (5)

$$t_U = \frac{2.0L^2}{D_L} \quad (5a)$$

$$t_L = \frac{2.0L^2}{D_U} \quad (5b)$$

where D_L and D_U are the lower and upper limits of D and t_L and t_U are the lower and upper limits of the completed emissions time.

Assume $\{t_1, t_2, \dots, t_n\}$ are the sampling times and that $t_{n+1}(For_m = 2.0)$ is the projected “completed time”. Also assume $\{y_{exp}(t_1), y_{exp}(t_2), \dots, y_{exp}(t_n), y_{exp}(t_{n+1}) = 0\}$ are the corresponding gas-phase compound concentrations. At each sampling interval $I_i = [t_i, t_{i+1}]$ ($i = 1, 2, \dots, n$), we have

$$y_{pchip}(t_i) = y_{exp}(t_i) \quad (i = 1, 2, \dots, n) \quad (6)$$

where $y_{pchip}(t)$ is gas-phase VOC concentration generated by the PCHIP algorithm at any time.

The derivation for $y_{pchip}(t)$ at any time between zero and t_{n+1} except sampling times is proposed by Fritsch and Carlson (1980) [30]. If the gas flow rate through the chamber is constant, the upper limit of C_0 (represented as $C_{0,U}$) is given by Eq (7a)

$$\begin{aligned} C_{0,U} &= \frac{Q}{A \cdot L} \int_0^{t_U} y_{pchip}(t) d(t) = \frac{Q}{A \cdot L} \int_0^{\frac{2L^2}{0.2L^2/t_n}} y_{pchip}(t) d(t) \\ &= \frac{Q}{A \cdot L} \int_0^{10t_n} y_{pchip}(t) d(t) \end{aligned} \quad (7a)$$

$$\begin{aligned} C_{0,U} &= \frac{Q}{A \cdot L} \int_0^{t_U} y_{pchip}(t) d(t) = \frac{Q}{A \cdot L} \int_0^{\frac{2L^2}{0.01L^2/t_n}} y_{pchip}(t) d(t) \\ &= \frac{Q}{A \cdot L} \int_0^{200t_n} y_{pchip}(t) d(t) \end{aligned} \quad (7b)$$

where Q is the airflow rate, $m^3 \cdot s^{-1}$ and A is the exposed surface area of the building material, m^2 . Similarly, the lower limit of C_0 (represented as $C_{0,L}$) is given by

$$C_{0,L} = \begin{cases} \frac{Q}{A \cdot L} \int_0^{200t_p} y_{\text{pchip}}(t) d(t), & \text{if } 20t_p \leq t_n \leq 200t_p \\ \frac{Q}{A \cdot L} \int_0^{t_n} y_{\text{pchip}}(t) d(t), & \text{if } t_n > 200t_p \end{cases} \quad (8)$$

Again, if t_n cannot be considered to be within the steady-state period, Eq (2b) is replaced with $0.01 < Fo_m(t_n) \leq 2.0$ and Eq (7a) is modified accordingly to Eq (7b).

According to this method, although only two data points are critical when estimating D , more data points are needed to determine the peak time and whether the last data point is in the steady-state region. In terms of estimating C_0 , it is always better to have more data. However, some analytical or numerical multivariate regression methods could become applicable when data are sufficient. The simple method has more benefits when only a few data points are available.

It should be pointed out that α and h_m have significant effects on emissions in the early stage and therefore impact the peak concentration of the test. However, this effect can be ignored since only the measured concentration and time matters in terms of estimating D and C_0 .

4. Validation of simple methods to estimate D and C_0

4.1. Region in which emissions are insensitive to K

For dimensionless analysis, α , βK and Bi_m/K are in the range of $[60, 36200]$, $[0.4, 150]$ and $[20, 700]$, respectively, for most building materials in the indoor environment [27], and K is typically between 10^2 and 10^5 [31, 32]. The sensitivity of all the dimensionless parameters, including K , to dimensionless emission rate $\dot{m}^*$ can be derived from Eq (1) and is given by

$$S_\alpha = \frac{\dot{m}^*}{\dot{m}^*(\alpha = 60)} = \begin{cases} \left(\frac{\alpha}{60}\right)^{8.4 \times 10^{-1}}, & 0 \leq Fo_m \leq 0.01 \\ \left(\frac{\alpha}{60}\right)^{0.022}, & 0.01 < Fo_m \leq 0.2 \\ \left(\frac{\alpha}{60}\right)^{-7.2 \times 10^{-1}}, & Fo_m > 0.2 \end{cases} \quad (9a) \quad S_\beta = \frac{\dot{m}^*}{\dot{m}^*(\beta K = 0.4)} = \begin{cases} \left(\frac{\beta K}{0.4}\right)^{-1.3 \times 10^{-1}}, & 0 \leq Fo_m \leq 0.01 \\ \left(\frac{\beta K}{0.4}\right)^{-0.021}, & 0.01 < Fo_m \leq 0.2 \\ \left(\frac{\beta K}{0.4}\right)^{8.5 \times 10^{-1}}, & Fo_m > 0.2 \end{cases} \quad (9b)$$

$$S_B = \frac{n\dot{L}}{n\dot{L}\left(\frac{Bi_m}{K} = 20\right)} = \begin{cases} \left(\frac{Bi_m}{20K}\right)^{0.26}, & 0 \leq Fo_m \leq 0.01 \\ \left(\frac{Bi_m}{20K}\right)^{0.021}, & 0.01 < Fo_m \leq 0.2 \\ \left(\frac{Bi_m}{20K}\right)^{-7.0 \times 10^{-3}}, & Fo_m > 0.2 \end{cases} \quad (9c) \quad S_K = \frac{n\dot{L}}{n\dot{L}(K=1)} = \begin{cases} K^{-0.2601}, & 0 \leq Fo_m \leq 0.01 \\ K^{-0.042}, & 0.01 < Fo_m \leq 0.2 \\ K^{0.0155}, & Fo_m > 0.2 \end{cases} \quad (9d)$$

where S_α , S_β , S_B , S_K are the sensitivities of α , βK , Bi_m/K and K to dimensionless emission rate $n\dot{L}$. In each case, only one dimensionless parameter was examined. In the case of analysis for α , βK and Bi_m/K , the lower range of the dimensionless parameter is considered as a baseline and the ideal limit for a K baseline was considered to be for $K=1$. The sensitivity analysis results are shown in Fig. 2.

Fig. 2. Sensitivity analysis for dimensionless parameters.

Fig. 2(a) and Fig. 2(b) show that the effect of α or βK on dimensionless emission rate $n\dot{L}$ is less than 15% regardless of emissions period. The only two significant effects on dimensionless emission rate are Bi_m/K and K when the emission time is still in the peak period

($Fo_m \leq 0.01$). In this period, different Bi_m/K and K values can vary the dimensionless emission rate by 250% and 95% for each baseline case. Similar results for other baselines can be obtained providing further evidence that h_m may have a significant influence on emissions during the very beginning of the emission process [33]. Moreover, $Fo_m \geq 0.01$ can be considered the insensitive region to K for emissions and $Fo_m \geq (0.05 \sim 0.2)$ can be considered the insensitive region to K for gas-phase VOC concentration, due to the delay effect.

Fig. 3. Demonstration of region insensitive to K .

Fig. 3 demonstrates the region insensitive to K using Yang's (1999) [34] chamber test data. The two curves were predicted by Little et al.'s (1994) [35] analytical emissions model except in one dataset K is set equal to 1. After $Fo_m \sim 0.05$, both curves merge, indicating insensitivity to K .

4.2. Monte-Carlo method to examine C_0 interpolating estimation

To simulate realistic experimental data, additive, uncorrelated, and normally distributed random errors can be assumed for each gas-phase concentration measurement, or

$$y_{\text{exp}}(t_i) = y_{\text{mdl}}(t_i) + \delta_i \quad (10)$$

where $y_{\text{mdl}}(t_i)$ represents the true value of the gas-phase VOC concentration, in this case, determined by Little et al.'s model; and δ_i is the random error for each simulated sampling.

δ_i lies within the range of $[-2.576\sigma, 2.576\sigma]$ with 99% confidence level, where the standard deviation σ is given by [20]

$$\sigma = \beta \cdot y_{\text{exp,max}} \quad (11)$$

where $y_{\text{exp,max}}$ is maximum simulated errorless compound concentration; and β is a fraction that is equal to either 0.05 or 0.01.

Typically we can find C_0 , D and K ranges of $(10^5 \sim 10^8) \mu\text{g}\cdot\text{m}^{-3}$, $(10^{-10} \sim 10^{-13}) \text{m}^2\cdot\text{s}^{-1}$ and $10^2 \sim 10^5$, respectively, for solid indoor materials [18, 31, 36]. Because C_0 is not coupled with D and K in Little et al.'s model, C_0 is assumed to be $10^5 \mu\text{g}\cdot\text{m}^{-3}$. The Monte-Carlo method [37] was applied for each D and K magnitude order combination and each combination was repeated 200 times. The sampling times and chamber configurations were the same as in Fig.1 which were the testing conditions for one carpet emission test (material ID: CRP7) in the NRC database [10]. For each combination, the interpolation estimate of C_0 (represented as C_0') was calculated by the PCHIP algorithm using only 10 simulated sampling times and data (within first 300 h) generated by Little et al.'s model using randomly chosen C_0 , D , and K plus random errors. The error between errorless C_0 and the estimated C_0' was also examined. The results are shown in Table 1 and Table 2. $\bar{X}$ and S are the average error and standard deviation for each combination, respectively.

Table 1

Validation of C_0 interpolating estimation by Monte-Carlo method ($\sigma=0.01 y_{\text{exp,max}}$).

$C_0 = 10^5 \mu\text{g}\cdot\text{m}^{-3}$		Magnitude orders of K							
Magnitude orders of D		10^2		10^3		10^4		10^5	
$\text{m}^2\cdot\text{s}^{-1}$		$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
10^{-10}		7%	6%	2%	3%	-19%	13%	-79%	12%
10^{-11}		5%	15%	2%	14%	-15%	16%	-69%	17%
10^{-12}		83%	99%	75%	96%	56%	72%	-12%	39%
10^{-13}		318%	264%	291%	250%	306%	235%	195%	166%

Table 2

Validation of C_0 interpolating estimation by Monte-Carlo method ($\sigma=0.05 y_{\text{exp,max}}$).

$C_0 = 10^5 \mu\text{g}\cdot\text{m}^{-3}$		Magnitude orders of K		
Magnitude orders of D	10^2	10^3	10^4	10^5

$\text{m}^2\cdot\text{s}^{-1}$	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
10^{-10}	33%	27%	14%	15%	-17%	15%	-79%	12%
10^{-11}	17%	44%	7%	27%	-10%	30%	-71%	17%
10^{-12}	141%	193%	133%	177%	102%	146%	16%	94%
10^{-13}	470%	463%	501%	504%	483%	499%	310%	323%

Results summarized in Table 1 and Table 2 show the overall magnitude order of D has a greater influence on the accuracy of the interpolation estimate of C_0 compared to the magnitude order of K . The most uncertain part of the interpolation is between t_n and t_{n+1} , and within this region the gas-phase concentration can be overestimated if D is small enough to cause $t_n < t$ ($Fo_m = 0.2$) (in this particular case, when D is smaller than 10^{-11} , the variation of C_0 becomes large) and the PCHIP algorithm would tend to create a gentle curve after t_n rather than a dramatically decreasing curve, resulting in an overestimate of C_0 . Similarly, if D is sufficiently large to cause $t_n \geq t$ ($Fo_m = 2.0$), C_0 would be underestimated by PCHIP. In terms of K , usually the higher the K , the longer the duration of the emission process, and vice versa. However, for certain C_0 and D combinations, the interpolation can be acceptably accurate within a wide range of magnitude orders of K if t_n is in the steady-state period. This is due to the existence of a region insensitive to K . Above all, the condition t ($Fo_m = 0.2$) $\leq t_n < t$ ($Fo_m = 2.0$) is a requirement for using interpolation to estimate C_0 by PCHIP. If the last sampling time is still within the transitional period or the peak period, i.e., $t_n < t$ ($Fo_m = 0.2$), the uncertainty of the estimation will increase considerably.

4.3. Validation of the overall D and C_0 estimation method

When using the simple method to estimate D and C_0 , ranges for both D and C_0 can be obtained. Because the upper limit of C_0 is correlated with the lower limit of D , and the lower limit of C_0 is correlated with the upper limit of D , two gas-phase VOC concentration profiles can be generated by analytical models. In addition, it is likely, although not certain, that the true gas-phase VOC concentration profile is within these two previously described emission curves, especially in the period between t_n and t_{n+1} .

One material (carpet, ID: CRP7) was selected from the NRC database [10] to investigate the accuracy of the simple D and C_0 estimation method. The D and C_0 ranges for all 36 VOCs detected in the material were estimated by this method with results summarized in Fig. 4.

Fig. 4. D and C_0 ranges for a single solid building material (CRP7) from the NRC database.

In Fig. 4, each bar represents one VOC emitted from that specific material. VOCs that have similar molecular weight result in overlapping bars. The colored area represents ranges determined by the assumption of $Fo_m(t_n) \geq 0.2$, while the shaded area represents ranges for $Fo_m(t_n) < 0.2$, in case the previous assumption cannot be satisfied. The greater the true D value of a VOC, the more likely the true value of D and C_0 would be in the colored area as well. Compared to the typical D and C_0 ranges for building materials in the indoor environment, the simple method can provide relatively narrow ranges of D and C_0 for VOC emission models. If the measured concentrations reach steady state for most of the VOCs during a chamber test, the predicted ranges of the emission parameters are even smaller.

Based on estimated values of D and C_0 for each compound, the gas-phase concentrations for 36 VOCs were predicted using Little et al.'s model. Because the parameter estimation method cannot provide estimates of K , it was assumed to be equal to 1. Fig. 5 shows the comparison of predicted and measured concentration data.

(a) C_0 : upper limit, D : lower limit, all data included

(b) C_0 : lower limit, D : upper limit, all data included

(c) C_0 : upper limit, D : lower limit, data in regions insensitive to K included

(d) C_0 : lower limit, D : upper limit, data in regions insensitive to K included

Fig. 5. Comparison of predicted and experimental concentration data.

It is true that the variation range of D can influence the estimation of C_0 and therefore influence the exposure estimation. Unfortunately, there is no easy way to provide an estimation of error because there is variation in the C_0 interpolation method due to limited data as well. However, Fig. 5 demonstrated that the overall estimation of exposure could be reasonable. Fig. 5(a) and Fig. 5(b) show that the agreements between predicted and experimental data for both limit-pair emissions are relatively good. More than 95% of the predicted data points had a difference within one magnitude order compared to the corresponding experimental data. The correlation coefficient r was greater than 0.86 for both the C_0 -upper-limit with D -lower-limit pair and the C_0 -lower-limit with D -upper-limit pair with the latter being slightly better than the former. However, greater uncertainties in the prediction of the C_0 -lower-limit with D -upper-limit pair emissions resulted because the requirement of $t_n < t$ ($For_m = 0.2$) was not met. This is because the test duration was within 300 h and in some cases VOC emissions from solid building materials can occur over a time

period that is more than ten times longer. Because all the predictions were based on the assumption $K=1$, the comparison of data in the regions insensitive to K is more appropriate. The comparison of data from the regions insensitive to K in Fig. 5(c) and Fig. 5(d) shows better agreements than those in Fig. 5(a) and Fig. 5(b); the correlation coefficients are greater than 0.89 in both Fig. 5(c) and Fig. 5(d).

A solid indoor material almost always contains more than one VOC. A disadvantage of the simple method is that when two VOCs have an identical gas-phase concentration peak at the same time and were detected in the last sample in a test, the estimated D ranges for these two VOCs would be the same. Examples can be found in Fig. 4(a). Techniques that are more robust can be applied to determine the true values for each VOC if precise estimates of D and C_0 are of interest.

5. Estimate screening-level exposure to VOCs in indoor environment

5.1. Estimation of the gas-phase VOC concentrations using characteristic emission rate

As previously described, for emissions from single solid materials we consider $For_m = 2.0$ is the time when the emission process is approximately completed [28] and, therefore, we assume $\hat{t}$ is the characteristic time, where

$$\hat{t} = \frac{For_m L^2}{D} = \frac{2L^2}{D} \quad (12)$$

Then, the characteristic emission factor $\hat{F}$ and characteristic emission rate $\hat{E}$ are given by

$$\hat{F} = \frac{M / A}{\hat{t}} = \frac{C_0 L}{2L^2/D} = \frac{C_0 D}{2L} \quad (13)$$

and

$$\hat{E} = \frac{M}{\hat{t}} = \frac{C_0 D A}{2L} \quad (14)$$

where M is the total initial emittable material-phase compound mass, μg .

If both D and C_0 are known, the characteristic emission rate and characteristic emission time can be obtained directly. D and C_0 ranges can also be estimated by the simple estimation method. According to Fig. 1, if $C_{0,U} = a C_{0,L}$ and $t_U = b t_L$, the characteristic emission rate for both limit-pair combinations is given by

$$\begin{cases} \hat{E}_1 = \frac{C_{0,L}AL}{t_L} = \frac{C_{0,L}AL}{Fo_m(t_L)L^2/D_U} = \frac{C_{0,L}D_UA}{2L} = \frac{bC_{0,U}AL}{at_U} \\ \hat{E}_2 = \frac{C_{0,U}AL}{t_U} = \frac{C_{0,U}D_LA}{2L} \end{cases} \quad (15)$$

where $\hat{E}_1$ and $\hat{E}_2$ are the characteristic emission rate for the C_0 -upper-limit with D -lower-limit pair and the C_0 -lower-limit with D -upper-limit pair estimations, in $\mu\text{g}\cdot\text{h}^{-1}$, respectively. The compound concentration gradient between the material surface and the chamber or building air, which is assumed to be well-mixed, would be much lower after t_n than before t_n . Basically, the gas-phase concentrations would be much lower than the concentrations during the peak period or eventually close to zero after t_n , leading to $b \geq a$ or $\hat{E}_1 > \hat{E}_2$. Furthermore, taking Fig. 1 as an example, the greater the b ratio, the greater the b/a ratio might be. It is not rigorous to assume $\hat{E}_1 > \hat{E}_2$ is always true possibly due to unpredictable experimental errors and errors caused by the PCHIP algorithm. However, for most cases, we can use $\hat{E}_1$ and $\hat{E}_2$ as the upper and lower limits of the characteristic emission rate, respectively, for single-layer solid building materials.

One material (acoustical ceiling tile, ID: ACT2) was selected from the NRC database [10] to illustrate the characteristic emission rate, emission factor, and emission time for all the emitted VOCs.

Fig. 6. Characteristic emission rate, emission factor and emission time for 35 VOCs in ACT2.

In Fig. 6, each colored data point represents one VOC detected from ACT2 and only the assumption of $For_m(t_n) \geq 0.2$ was employed to provide a clear illustration. The x and y error bars, indicating the range of characteristic emission rate (or emission factor) and characteristic emission time, show that the range of characteristic emission rate or emission factor is small compared to the range of characteristic emission time for a particular VOC. Overall the range of magnitude orders for characteristic emission rate, emission factor and emission time are about $10^{-4} \sim 1 \mu\text{g}\cdot\text{h}^{-1}$, $10^{-3} \sim 10 \mu\text{g}\cdot\text{m}^2\cdot\text{h}^{-1}$ and $10^3 \sim 10^4 \text{ h}$, respectively. In addition, we also analyzed 28 solid building materials selected from the NRC database. Most of these materials were single-layer. The rest were an assembly of materials that can be treated as single-layer. All the characteristic emission rates, emission factors and emission times were in the range of $10^{-5} \sim 10^1 \mu\text{g}\cdot\text{h}^{-1}$, $10^{-4} \sim 10^2 \mu\text{g}\cdot\text{m}^2\cdot\text{h}^{-1}$ and $10^3 \sim 10^5 \text{ h}$, respectively. All 28 materials had about 10^{-2} m^2 of exposed surface area and 10^{-2} m thickness.

Fig. 6 shows a screening-level estimation of the gas-phase VOC concentrations expected to result from this material. The VOCs that appear in the upper right corner, phenol and decane in this case, have high concentrations and long emission durations while the VOCs shown in the bottom left corner, such as benzene and ethylebenzene, exhibit relatively low concentrations over a short emission duration.

The characteristic emission rate and characteristic emission time for VOCs and solid materials detected in the NRC database were from small pieces of building materials that were tested in small-scale chambers. If the actual thickness of the material is different from the material in the database, the characteristic emission rate should be recalculated because the characteristic emission time changes with thickness. On the other hand, if the exposed surface area of a material varies from the material in the database, a proportional estimation can be made to adjust the predicted concentration

$$\hat{E}' = \frac{A'}{A} \hat{E} = A' \hat{F} \quad (16)$$

where $\hat{E}'$ is the characteristic emission rate of the new material, $\mu\text{g}\cdot\text{h}^{-1}$, and A' is the exposed surface area of the new material, m^2 .

5.2. Exposure scenarios

Two standard scenarios, a reference living room in Beijing [38] and a typical private office in the United States [15], were analyzed to predict VOC concentrations using the characteristic emission rates. The floor plan for both scenarios was assumed to be square. All building materials including furniture were selected from the NRC database [10] with the same thickness assumed in the model. The upper limit of the characteristic emission rate ($\hat{E}_1$) was used to calculate VOC concentrations. Because to some extent, characteristic emission rate represents long-term VOC emissions, CRELs (chronic reference exposure levels) [14] were taken as the maximum allowable VOC concentrations. We also assumed an ACH for both scenarios of 1.0 h^{-1} with the amount of VOCs emitted to indoor air calculated on an hourly basis. The standard room configuration and ten selected VOCs are shown in Table 3 and Table 4 respectively. For a majority of materials in the NRC database, gas chromatography/mass spectrometry (GC/MS) analysis was used to measure VOC concentrations. For a small number of materials, aldehyde measurements using high-performance liquid chromatography (HPLC) were also made [39]. Therefore, aldehyde compounds that are usually measured with HPLC (e.g., formaldehyde) might be under-represented in the scenario analysis.

Table 3

Room configurations for two standard exposure scenarios.

	Reference living room in Beijing	Typical private office in the US
Volume (m^3)	57.2	65.2
Loading ratio (m^2 / m^3)	0.23	0.38
Air change rate (h^{-1})	1.0	1.0
Ceiling surface area (m^2)	22.0	26.1
Ceiling material and NRC ID	Acoustical ceiling tile (ID: ACT2)	Acoustical ceiling tile (ID: ACT2)
Flooring surface area (m^2)	22.0	26.1
Flooring material and NRC ID	Linoleum tile (ID: LIN1)	Commercial nylon carpet (ID: CRP7)
Wall surface area (m^2)	48.8	53.1
Wall material and NRC ID	Gypsum wallboard (ID: GB1)	Gypsum wallboard (ID: GB3)

Furniture surface area (m ²)	13.2	24.8
Furniture materials and NRC IDs	Medium density fiberboard (ID: MDF2) with solid pine (ID: PIN1)	Medium density fiberboard (ID: MDF2) with plywood (ID: PLY3)

Table 4

Ten target VOC exposure levels and thresholds ($\mu\text{g}\cdot\text{m}^{-3}$).

CAS	VOC	CREL	Reference living room in Beijing	Typical private office in US
50-00-0	formaldehyde	16	22.60	36.39
71-43-2	benzene	30	0.30	0.13
79-01-6	1,1,2-trichloroethene	300	0.06	0
91-20-3	naphthalene	4.5	0	0.02
100-41-4	ethylbenzene	1000	0.12	0.15
100-42-5	styrene	450	0	0.01
106-46-7	1,4-dichlorobenzene	400	0.89	0.17
108-38-3	1,3-dimethylbenzene	350	0.56	0.53
108-88-3	toluene	150	0.94	0.48
108-95-2	phenol	100	8.03	7.61

For both scenarios, the target VOCs had relatively low gas-phase concentrations, when compared to the corresponding CRELs, except for formaldehyde. Of the selected compounds, formaldehyde had the highest gas-phase concentration in both scenarios, although aldehydes such as formaldehyde were under-represented in the database. This suggests that an ACH of 1.0 h^{-1} is not sufficient for both rooms to maintain the formaldehyde level below CREL. Naphthalene and styrene were not detectable in the reference living room and 1,1,2-trichloroethene was not detectable in the office due to different material usage. Overall, both scenarios suggest measures need to be introduced for formaldehyde, which might still be underestimated. The scenario analysis shows how the estimated parameters D and C_0 can be used to understand long-term indoor air concentrations for various VOCs.

The procedure for estimating screening-level exposure to VOCs emitted from building materials is summarized as follows:

- 1) Estimate D and C_0 ranges for selected VOCs from a ventilated chamber emission test;
- 2) Calculate characteristic emission rates using C_0 -upper-limit with D -lower-limit pair and C_0 -lower-limit with D -upper-limit pair, set all K equal to 1 or other reasonable values;

- 3) Two characteristic emission rates can therefore be obtained. Choose the higher of the two as the characteristic emission rate;
- 4) If the dimension of the building material applied to the room that is to be assessed is different from the one tested in the chamber, the characteristic emission rate can be corrected according to the emission area and thickness of the material;
- 5) The characteristic gas-phase VOC concentration in the indoor environment can be determined by Eq (17)

$$\hat{C} = \frac{\hat{E}}{V \cdot ACH} \quad (17)$$

where $\hat{C}$ is the characteristic gas-phase concentration of a specific VOC, $\mu\text{g}\cdot\text{h}^{-1}$; V is the volume of the room, m^3 ; and ACH is the air change rate of the room, h^{-1} .

6. Conclusions

A simple and rapid method to obtain screening-level VOC exposure caused by emissions from solid building materials in the indoor environment is proposed. The main feature of this simple method is the ability to estimate D ranges for compounds/materials based on dimensionless analysis of data obtained from ventilated chamber tests that were not necessarily pre-designed for this purpose. Although C_0 should be determined by independent measurement, C_0 ranges can be obtained using an interpolating algorithm called PCHIP if C_0 is not known. The required assumption of this method is that the measured peak gas-phase concentration and the last sample are in the peak period and steady-state period of the emissions profile, respectively. If the second part of the assumption cannot be fulfilled, greater uncertainties are introduced and a wider range of D and C_0 can be obtained. This simple method was validated by Monte-Carlo method and using VOC emission data from the NRC database.

The primary application of the proposed parameter estimation methods is to provide a screening-level VOC exposure estimate, which can be quickly obtained for real indoor environments, based on D and C_0 . Emissions from single-layer, solid building materials can be characterized using characteristic emission rate, emission factor, and emission time. Two

standard scenarios demonstrate the usefulness of the application using actual chamber data in the NRC database. Although the simple method does not estimate K , it could be a useful screening tool for assessing material emissions and environmental exposures.

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