Exponential Decay Model of TVOC Emission from Indoor Building Materials

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Abstract. Total volatile organic compounds (TVOC) are mainly derived from indoor building materials and are one of the main causes of indoor air pollution. This paper presents a research on simulating the TVOC release of building materials in the environmental chamber. In this work, a simple and practical prediction model of exponential decay is established to study the transport and the emission behaviors under the effect of convective mass transfer theory. Based on this theory, the model considers the porous structure of indoor building materials and assumes that concentration of TVOC at the boundary of building material obeys exponential distribution. This paper focuses on two kinds of indoor building materials, interior wall coatings and wood coatings. Numerical simulation and experimental parameters are obtained by environmental chamber method. By modelling the emission of TVOCs, and comparing the present model with the classical model, the validity of the present model can be confirmed. Besides, from the results of the fitting, it can be seen that the new exponential decay prediction model has a better agreement with the experimental data, and which can describe the release characteristics and transmission mechanisms of TVOCs more accurately, and the root mean square error is much less than the classical model.

1. Introduction
As the standard of people's life improving, indoor air pollution attracts more and more attention. In fact, Volatile organic compounds (VOCs) released from building materials is harmful to human health. Some studies have shown that VOCs can stimulate and poison human respiratory and visual systems inducing neurological diseases [1-3]. The release process of VOCs and formaldehyde from building materials has a complicated and long emission period. Therefore, it is necessary to investigate the emission characteristics and transmission mechanisms of VOCs from building materials.

The prediction models of VOCs emission from indoor building materials mainly include empirical model and physical mass transfer model [4-6]. The empirical model is obtained by experimental data and numerical simulation. Besides, the exponential model is one of the classical empirical models which can predict the emissions of VOCs in building materials. The first-order decay model was
discussed by Guo et al. [7]. Although the first-order decay model has a low prediction for long-term emission, it can well fit short-term emissions characteristic [8]. As a matter of fact, the various parameters in the empirical model are empirical parameters, lacking physical meaning, and a large amount of experimental data is required, and the data obtained from the environmental chamber cannot be directly applied to the indoor. However, VOCs emission in building materials is a complex mass transfer process, the physical model based on mass transfer theory can well overcome the shortcomings of empirical models [9]. Therefore, the physical mass transfer model is widely used in VOCs emission researches.

The mass transfer model considers the release characteristics of formaldehyde and VOCs from the following three aspects: 1) VOCs diffuse in building materials; 2) diffusion from the surface of building materials to the air boundary layer; 3) convection and diffusion of air layer. Accordingly, the mass transfer characteristics of pollutants were specifically analyzed. Based on this theory, Fariborz and Huang et al. [10] used different models to predict the emission of VOCs, verified the transition between models, and obtained the relationship between partition coefficient and porosity. Zhang and Xu [11] developed an improved analytical model with the convective mass transfer. Numerical results shown that the fitting results are better than previous model. In addition, Deng and Kim [12] considered the relationship between the concentration of VOCs in air and in building materials, and further studied this model and improved the prediction accuracy. Moreover, a large number of references [13-17] have studied the mass transfer model. The mass transfer model overcomes some shortcomings of the empirical model, and its parameters have practical physical significance. Due to the parameters have to be solved by the model, hence, establishing a simple and practical emission model is very meaningful.

This study aims to develop a simple and practical model to simulate the characteristic of VOCs emission in the environmental chamber by considering the convective mass transfer and mass balance equation in the indoor environment. By fitting the experimental data and comparing the model with the classical model, it can be found that the model has high precision.

2. Model development

The classical empirical model to predict the concentration of TVOCs in the environmental chamber is as follow [18]:

$$C_{av} = at^{-b}$$  \hspace{1cm} (1)

where $C_{av}$ is the concentration of TVOCs in the environmental chamber, $t$ is time, and $a, b$ are both constants.

The model is very suitable in early stage, but the result of fitting is not ideal in the late stage, primarily because this model lacks theoretical basis and limits its use conditions. Therefore, we need to establish a predictive model with better versatility and physical meaning to discuss the emissions of TVOCs in indoor environments.

Considering the diffusion process of TVOCs in the material and the boundary layer, it can be found that the interface between building materials and air has an effect on the emission characteristic of TVOCs. At the material-air interface, the concentration of TVOCs in the material is higher than the TVOCs in the air due to the adsorption of formaldehyde on the material.

The relationship between the concentration of TVOCs in the material and the interface can be expressed by [12]:

$$C_{i,v,d} = K_{mv} C_{a1}$$  \hspace{1cm} (2)

where $C$ is the concentration in the material, $K_{mv}$ is the interface partition coefficient of TVOCs. $C_{a1}$ is the concentration in the interface, $t, d$ is thickness.

The pore structures on the surface of building materials can affect TVOCs emission. For volatile organic compounds are released through the pores on the surface of building materials, the porosity of building material cannot be ignored. At the material-air interface, the mass transfer is modified as follows [19-21]:
The concentration of TVOCs at the boundary of building material is exponentially decay, it can be written as [12]:

$$C\bigg|_{x=\delta} = Ae^{-Bt} + C_\infty.$$  

where $C_\infty$ is the concentration of TVOCs, which comes from chemical reaction, and $A$ and $B$ are constants.

Substituting equations (2)-(3) into equation (4), the equation (4) can be changed to the following form:

$$\frac{dC_{\text{air}}}{dt} + (Lh + N)C_{\text{air}} = \frac{Lh}{K_{\text{ma}}} \left( C - C_{\text{air}} \right).$$  

Substituting equation (6) into equation (7), the equation (7) can be written as:

$$\frac{dC_{\text{air}}}{dt} + (Lh + N)C_{\text{air}} = \frac{Lh}{K_{\text{ma}}} \left( Ae^{-Bt} + C_\infty \right)$$  

We can get

$$C_{\text{air}} = e^{-(Lh+N)t} \left[ \int \frac{Lh}{K_{\text{ma}}} \left( Ae^{-Bt} + C_\infty \right) e^{(Lh+N)\delta t} dt + C_1 \right]$$

$$= C_1 e^{-(Lh+N)t} + \frac{LhC_\infty}{K_{\text{ma}}(Lh + N)} + \frac{ALh}{K_{\text{ma}}(Lh + N - B)} e^{-Bt}$$  

Based on the initial condition, we can obtain

$$C_{\text{air}}(0) = C_1 + \frac{LhC_\infty}{K_{\text{ma}}(Lh + N)} + \frac{ALh}{K_{\text{ma}}(Lh + N - B)} = 0$$
Then,
\[
C_1 = -\frac{LhC_e}{K_m(Lh+N)} - \frac{ALh}{K_m(Lh+N-B)}
\]  

(11)

Hence, the concentration \( C_{air} \) in environmental chamber can be expressed as:
\[
C_{air} = -\left(\frac{LhC_e}{K_m(Lh+N)} + \frac{ALh}{K_m(Lh+N-B)}\right)e^{(Lh+N)y} + \frac{ALh}{K_m(Lh+N-B)} e^{-Rt} + \frac{LhC_e}{K_m(Lh+N)}
\]  

(12)

The final form is as follow:
\[
C_{air} = a_i e^{-b_i t} - (a_i + c_1) e^{-b_2 t} + c_1
\]

(13)

where
\[
a_i = \frac{LhC_e}{K_m(Lh+N)}, \quad b_1 = B, \quad b_2 = -(Lh+N), \quad c_1 = \frac{ALh}{K_m(Lh+N-B)}.
\]

If we ignore the process filling the environmental chamber with TVOCs, without the chemical reaction, equation (13) can be simplified to the following single exponential decay model:
\[
C_{air} = a_i e^{-b_i t}
\]

(14)

3. Results and discussion
The TVOCs emission experiment was carried out in an approximately 1 m\(^3\) environmental chamber. Hainate and VWH-1000 is the brand and model of the chamber in this experiment. Table 1 shown the experimental conditions. The interior wall coating or wood coating was placed in the chamber, and the material parallel to the airflow. 3-methyl-2-benzothiazolinone hydrazone (MBTH) collected TVOCs which emitted into the air. Spectrophotometry was applied to test the concentration every 24 hours until it reached equilibrium.

| Table 1. Experimental parameters. |
|-----------------------------------|
| Temperature (°C)                  | 23±0.5                          |
| Relative humidity (%)             | 45±1                            |
| Air exchange rate (h-1)           | 1±0.01                          |
| Dimensions of the environmental chamber (m × m × m) | 0.80×1.10×1.14 |
| Dimensions of the building material (m × m × m) | 1.00×0.50×0.008 |

The release characteristic of TVOCs for interior wall coating is shown in figure 1. Because the time to fill the chamber is very short, the experimental data at this stage are not considered, only the decay process of TVOCs concentration in the environmental chamber is taken into account. A rapid process filling the environmental chamber with TVOCs is ignored. So the concentration drops slowly from the maximum value, and it has a long-term emission process. The deviation between the present model and the classical model can be seen from figure 1. The classical model has larger error in describing the TVOCs emission, while the present model has high precision. Meanwhile, the fitting parameters and root mean square error (rmse) are shown in table 2, which further verifies the above viewpoints.
Figure 1. Chamber concentration of TVOCs emitted from interior wall coating.

Table 2. Fitting parameters and the root mean square error (rmse).

|                | \(a\) | \(b\) | \(a_1\) | \(b_1\) | rmse |
|----------------|-------|-------|---------|---------|------|
| Present model  | —     | —     | 2.4219  | 0.0025  | 0.0765 |
| Classical model| 11.9674 | 0.4186 | —       | —       | 0.2247 |

Figure 2 shows TVOCs emission of wood coating. It can be found that the TVOCs release characteristic of wood coatings is consistent with that of interior wall coatings. It has a slowly decline process from the peak value of TVOCs concentration. Numerical simulation results show that this model is superior to the classical model in the later release process. The corresponding parameter values and rmse are given in table 3, which further verifies the validity of the single exponential model.

Figure 2. Chamber concentration of TVOCs emitted from wood coating.

Table 3. Fitting parameters and the root mean square error (rmse).

|                | \(a\) | \(b\) | \(a_1\) | \(b_1\) | rmse |
|----------------|-------|-------|---------|---------|------|
| Present model  | —     | —     | 5.6597  | 0.0052  | 0.2606 |
| Classical model| 79.1382 | 0.7164 | —       | —       | 0.5327 |

4. Conclusions
A simple and practical exponential decay empirical model is proposed to describe TVOCs emission in this paper. By modeling the emission of TVOCs for indoor building materials, the fitting results show
that the new exponential decay empirical model shows a great agreement with the experimental data, which can describe the release characteristics of TVOCs more accurately.

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References
[1] Yan M H, Zhai Y B, Shi P T, Hu Y J, Yang H J and Zhao H J 2019 Emission of volatile organic compounds from new furniture products and its impact on human health Hum. Ecol. Risk Assess. 25 1886-1906.
[2] Tuomainen A, Seuri M and Sieppi A 2004 Indoor air quality and health problems associated with damp floor coverings Int. Arch. Occ. Env. Hea. 77 222-226.
[3] Adebayo O J, Abosed O O, Sunday F B, Ayooluwa A A, Adetayo A J, Ademola S J and Alaba A F 2018 Indoor air quality level of total volatile organic compounds (TVOCs) in a university offices (Article) Int. J. Civ. Eng. Technol. 9 2872-2882.
[4] Wang X K, Zhang Y P and Zhao R Y 2011 General analytical mass transfer model for VOC emissions from multi-layer dry building materials with internal chemical reactions Chin. Sci. Bull. 56 222-228.
[5] Sparks L E, Tichenor B A, Chang J and Guo Z 1996 Gas-Phase Mass Transfer Model for Predicting Volatile Organic Compound (VOC) Emission Rates from Indoor Pollutant Sources Indoor Air. 6 31-40.
[6] Xu Y, Zhang Y P and Cheng T B 2003 A New Mass Transfer Based Model of VOC Emissions from Building Materials ASHRAE Trans. 837-843.
[7] Guo Z S 2002 Review of indoor emission source models. Part 1. overview Environ. Pollut. 120 533-533.
[8] Ye W, Won D and Zhang X 2016 Examining the applicability of empirical models using short-term VOC emissions data from building materials to predict long-term emissions Build. Simul. 9 701-7154.
[9] Park H S, Ji C and Hong T 2016 Methodology for assessing human health impacts due to pollutants emitted from building materials Build. Environ. 95 133-144.
[10] Fariborz H, Huang H Y and Chang-Seo Lee 2005 Modeling Approaches for Indoor Air VOC Emissions from Dry Building Materials - A Review ASHRAE Trans. 111 635-645.
[11] Zhang Y P and Xu Y 2003 Characteristics and correlations of VOC emissions from building materials Int. J. Heat Mass Transfer. 46 4877-4883.
[12] Deng B Q and Kim C N 2004 An analytical model for VOCs emission from dry building materials Atmos. Environ. 38 1173-1180.
[13] Bodalal A, Zhang J S, Plett E G and Shaw C Y 2001 Correlations between the internal diffusion and equilibrium partition coefficients of volatile organic compounds (VOCs) in building materials and the VOC properties ASHRAE Trans. 107 789-800.
[14] Hu H P, Zhang Y P, Wang X K and Little J C 2007 An analytical mass transfer model for predicting VOC emissions from multi-layered building materials with convective surfaces on both sides Int. J. Heat Mass Transfer. 50 2069-2077.
[15] Zhou X J, Liu Y F, Song C, Wang X K, Wang F H and Liu J P 2019 Modelling and testing of VOC source suppression effect of building materials modified with adsorbents Build. Environ. 154 122-131.
[16] Weig M, Fürhapper C, Niedermayer S, Habla E, Nohava M, Nagl S and Polleres S 2014 VOC emissions from building materials: results from lab and model room trials Int.Wood Prod. J. 5 136-138.
[17] Haghighal F and Zhang Y 1999 Modelling of emission of VOC from building materials - estimation of gas-phase mass transfer coefficient Build. Environ. 34 377-389.

[18] Liu W W 2013 Research on Some Key Problems in Labeling of VOC Emissions from Furniture. http://kns.cnki.net/kns/detail/detail.aspx?FileName=1015007157.nh&DbName=CDFD2015.

[19] Axley J W 1991 Adsorption Modelling for Building Contaminant Dispersal Analysis Indoor Air. 1 147-171.

[20] Mocho P, Desauziers V, Plaisance H and Sauvat N 2017 Improvement of the performance of a simple box model using CFD modeling to predict indoor air formaldehyde concentration Build. Environ. 124 450-459.

[21] Zhang Y, Jiang J X, Bai Y, Liu J M, Shao H Q, Wu C D and Guo Z B 2019 A fractional mass transfer model for simulating VOC emissions from porous, dry building material Build. Environ. 152 182-191.

[22] Liu W W, Zhang Y P, Yao Y 2013 Labeling of volatile organic compounds emissions from Chinese furniture: consideration and practice Chin. Sci. Bull. 58 3499-3506.