

VOC Sink Behavior on Building Materials – Model Evaluation

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Abstract

The event of 11 September 2001 underscored the need to study the vulnerability of buildings to weapons of mass destruction (WMD), including chemical, biological, physical, and radiological agents. Should these agents be released inside a building, they would interact with interior surfaces, building materials, and furnishings, and could remain for a long period in an indoor environment. In this study, the sink effect was investigated with building materials (e.g. painted gypsum wallboard, vinyl flooring, carpet, mortar) and volatile organic compounds (VOCs), ethylbenzene, 1-butanol, decane, and dodecane, which were used as surrogates of toxic chemicals. It is observed that vinyl flooring has the strongest sink for ethylbenzene and dodecane. The sink experimental data were employed to evaluate the Langmuir-isotherm and diffusion sink models. Test data were also compared to a no-sink model. The sorption and desorption rate constants for the Langmuir-isotherm model were obtained. Mass balance was analyzed. There were strong correlations between equilibrium partition coefficients from the Langmuir-isotherm model and equilibrium partition coefficients and the effective diffusion coefficients from the sink diffusion model. This study provides insights into the sink effect and absorption mechanisms of VOCs in indoor environments.

Keywords

Sink effect, Langmuir-isotherm model, diffusion model, building materials, equilibrium partition coefficients, diffusion coefficients

Nomenclature

A	surface area of solid material, m ²
C	VOC concentration in the chamber air, mg/m ³

C_{in}	gas phase VOC concentration entering the chamber, mg/m^3
C_{d0}	VOC concentration in the chamber air at the end of sorption period and the start of the desorption period, which is assumed to be the steady state concentration, C_e , mg/m^3
C_{dt}	VOC concentration in the chamber air at the end of desorption period, mg/m^3
C_s	VOC concentration in the solid material, mg/m^3
C_i, C_{i+1}	measured VOC concentration in air at time t_i and t_{i+1} , mg/m^3
C_e	VOC concentration in air at steady state, mg/m^3
D	material phase diffusion coefficient, m^2/s
D_e	material phase effective diffusion coefficient, m^2/s
k_a	sorption rate constant, m/h
k_d	desorption rate constant, h^{-1}
K_e	equilibrium partition coefficient in the Langmuir-isotherm model, m
K	material-air equilibrium partition coefficient in the diffusion model (dimensionless)
L	loading ($L=A/V$), m^{-1}
M	mass of the VOC adsorbed on the material surface, mg/m^2
M_e	mass of the VOC adsorbed on the material surface at steady state, mg/m^2
M_t	mass of the VOC adsorbed on the material at time t , mg
M_∞	mass of the VOC adsorbed on the material at steady state, mg
M_{HTC}	mass of the VOC desorbed from high temperature chamber tests, mg
M_{out}	total mass of the VOC leaving the chamber during desorption period, mg
N	air change rate, h^{-1}
Q	air flow rate, m^3/h in the Langmuir-isotherm model and m^3/s in the diffusion model
R	constant emission rate of the chemical generated from the diffusion vial to the chamber, mg/h
t	time, h
t_a	sorption time, h
t_d	desorption time, h
V	chamber volume, m^3
x	distance from the base of the slab of the material, $0 \leq x \leq Z$, m
Z	thickness of the material, m

Introduction

The event of September 11, 2001 underscore the need to study the vulnerability of buildings to weapon of mass destruction (WMD) including chemical, biological, physical, and radiological agents. Should these agents be released inside a building, they would interact with interior surfaces, building materials and furnishings, and could remain for a long period of time in an indoor environment. If a building is being decontaminated after a biological attack, it is necessary to apply an effective dose of the decontaminating agent. A dosing plan that does not properly account for the sink effect will likely under dose the building, resulting in ineffective decontamination. After decontamination is complete, or after a chemical attack, it is necessary to allow sufficient time to remove the chemical agent from the building before personnel re-entry is allowed. This re-entry time may be underestimated if the chemical's sorption/desorption process is not accurately predicted. In order to protect against, and respond to, any future terrorist

attacks, research is needed to develop and extend existing sink effect models and incorporate them into exposure models to predict concentrations of chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) resulting from a terrorist attack or indoor building decontamination and to assess their impact on indoor air quality.

Early studies have shown that the indoor sink effect depends on the properties of incoming pollutants and absorbing materials, as well as environmental conditions. The process involves the sorption/desorption of volatile organic compounds (VOCs) from air phase onto a material surface, and diffusion of VOCs to the material interior. Current methods for characterizing the source/sink behavior of building materials typically employ the dynamic small chamber. The most commonly used and most extensively discussed models for describing indoor sinks include the first order sorption/desorption models [1-5] and diffusion models [6-12].

The Langmuir-isotherm model is the most widely used first-order sorption/desorption model. It assumes that there is a monolayer of molecules on a homogeneous surface and all sorption sites are independent and identical [1]. At the constant temperature, the VOC sorption rate is proportional to the VOC concentration in the air and the desorption rate is proportional to the concentration of VOC adsorbed on the material surface. The sorption rate constants are usually determined by fitting the model to the sorption data from experiments in small environmental chambers. The material to air partition coefficient (K_e) can be estimated by the ratio of the sorption rate constant (k_a) and desorption rate constant (k_d). Examples of k_a and k_d measurements for different materials are found in Tichenor et al., 1991 [1]; Colombo et al., 1993 [2]; Jørgensen et al. 1993 [13]; Chang and Guo, 1994 [14]; De Bortoli et al. 1996 [15]; An et al., 1999 [16]; Jørgensen et al. 1999 [17, 18]; Sparks et al. 1999 [19]; Won et al., 2001 [4]; Popa and Haghighat, 2003 [20]; and Elkilani et al. 2003 [21]. This model does not take into account the diffusion process inside the material, which could be a rate control process of sorption for certain indoor materials. Another drawback of this model is that parameters k_a and k_d are determined statistically. Multiple solutions may be obtained with different initial estimations when the nonlinear regression method is employed to fit experimental data [22].

The diffusion model has been developed for complex surfaces, e.g. porous materials. The diffusion model assumes that the VOCs adsorbed on the material–air interface penetrate to the inside of the material through the rate-determining diffusion process. It applies mass transfer principles based on Fick’s law to mass diffusion in the air and the material. The model parameters, including the initial VOC concentration in the material (C_{s0}), the VOC diffusion coefficient (D) in the material and the VOC partition coefficient between the material and air (K), have well-defined physical meanings and can be determined independently from experiments. Examples of measurement of these parameters (C_{s0} , D , K) are found in Haghighat and Zhang, 1999 [23]; Bodalal et al., 2000 [24]; Bodalal et al., 2001 [25]; Cox et al., 2001a [26];, Cox et al., 2001b [27]; Haghighat et al., 2002 [28]; Zhao et al., 2002 [9]; Kummer and Little, 2003 [10]; Blondeau et al., 2003 [29]; Li and Niu, 2005 [30]; Coris et al., 2007 [31]; Deng et al., 2009 [32]; Xiong et al., 2009 [33]; Xu et al., 2009 [34]; and Farajollahi et al., 2009 [35]. The diffusion model tends to be computationally intensive compared to the Langmuir-isotherm model, but more accurate in describing the solid-phase diffusion mechanism that controls the sorption of certain indoor materials.

Even though there have been reports of sorption isotherms and diffusion coefficients for a large number of VOCs and indoor materials, the existing data base is still limited with respect to model parameters for a wide range of chemicals and materials [31]. If a reasonable correlation between the model parameters and physiochemical properties can be determined for a group of VOCs and reference materials, experimental efforts to determine the parameters involved in the model equations can be reduced and the models applicability can be improved. There have been a number of studies in the literature on developing correlations of diffusion coefficients and partition coefficients in various indoor materials based on physical and chemical properties of the VOCs such as molecular weight, boiling point, and vapor pressure [4, 14, 16, 20, 25, 26, 29, 32, 33, and 35].

Proper validation is required to have a clear view of the applicability conditions for the advanced model development and reliable model application [36]. Such information will prevent the user from misusing the models. To evaluate an established model, the data used for the evaluation process should be independent of the data used to develop the model [37]. However, a few models utilized the same set of experimental data to develop the models and to validate the accuracy of the prediction [8].

In this study, we use VOCs, e.g., ethylbenzene, decane, dodecane, and 1-butanol, as surrogates of CWAs and TICs, and experimentally measure the sink characteristics of selected building materials, including carpeting, wallboard, vinyl flooring, and mortar in small chambers. The purpose is to examine the usefulness of the Langmuir-isotherm model and the diffusion model in predicting the concentrations of potential contaminants. The two models are validated by comparing experimental measurements to the predicted gas-phase concentration in the chamber as a function of time during the chamber experiment using the quantitative criteria recommended by the ASTM D5157-97 [36] and the mass balance of the VOCs introduced in the chamber at steady state. The results presented in this paper will expand the scope of the existing data and knowledge on sink models, address the need of data and flexibility of the models in the sink effect study through the evaluation of the mathematical models using test data, and explore strong correlations between equilibrium partition coefficient in the Langmuir-isotherm model and diffusion and equilibrium partition coefficients in the diffusion model.

To make this model more flexible (i.e., applicable to multi-zonal, and multi-sink environment, and time-varying ventilation rate), it is highly desirable to develop a set of numerical solutions, which can be incorporated more easily into existing indoor air quality models.

Materials and Methods

Test Specimens

Gypsum wallboard, commercial grade carpet, and vinyl flooring used for the present study were purchased from local retailer stores, except the mortar sample which was provided by the authors of ref [31]. The detailed description of each specimen is given in Table 1. They were selected in this study because they represent common interior building material surfaces.

After receipt, the materials were stored in the small chamber laboratory at approximately of 23 °C and 40-45% relative humidity (RH). Gypsum wallboard was painted with latex paint (Table 1) before tests by following ASTM D6803-02 [38]. Test materials were stored in the cleaned dynamic small chamber maintained at 23 °C, 45% RH, and 1 h⁻¹ air change rate (ACH) for at least 48 hours before background samples were collected. These materials were also sent out to University of Texas at Austin and Virginia Tech for the determination of material/air partition coefficients and effective diffusion coefficients by using a dual-volume diffusion chamber and a dynamic microbalance system. The effective diffusion coefficient describes diffusion through the pore space of porous media. The details are in the Reference [31].

Standard Source Generation

Four VOCs, ethylbenzene, decane, 1-butanol, and dodecane, were tested for their sorption and desorption attributes. Gas phase ethylbenzene, decane, and 1-butanol were generated using C or D size diffusion vials (Vici Metronics Inc., Santa Clara, CA) in the 491M Modular Gas Standards Generator (Kin-Tek Laboratories Inc.) and gas phase dodecane was generated using D diffusion vial in Vici Metronic DynaCalibrators, Model MCU gas standards generation system. Nitrogen gas flow to the permeation oven was nominally 210 mL/min. The emission rate of chemicals was determined gravimetrically by periodically weighing the diffusion vial and by measurement via Tenax gas chromatograph mass spectrometer (GC/MS) method for each test. They were in the range of 7 to 11 µg/min. The chemical-N₂ flow together with clean air flow was directed to the inlet of the small chamber. The outlet of the permeation oven was wrapped with heating tape and controlled at 60 °C. Teflon tubing was used to accommodate the air flow system.

Small Chamber Tests

The 53-liter stainless steel environmental chamber is inside the temperature-controlled incubator. In a dynamic chamber test, clean and VOC-free air was supplied to the chamber through a dedicated system consisting of an air compressor, dryer, catalytic oxidizers, and gross particle filters. The RH of the air supply to the chamber was controlled by blending dry air with humidified air from a water vapor generator. All air flows were controlled by mass flow controllers. A small computer fan (1½ inch diameter) operated at 7.5 volt was used in the chamber for air mixing during tests. An OPTO 22 data acquisition system (DAS, OPTO 22, Temecula, CA) continuously recorded mass flow controllers' outputs, temperature, and RH in the chamber and inlet air. A glass sampling manifold was connected to the chamber outlet for the collection of air samples. In addition to the VOC-material tests, empty chamber tests were performed with ethylbenzene and dodecane. A total of 13 tests were conducted whose operation conditions are summarized in Table 2.

The small chamber tests were consistent with the methods described in the ASTM Method D5116-06 [39]. Prior to gypsum board and vinyl flooring tests, each pair of painted gypsum wallboard or vinyl flooring was put together back-to-back (painted sides or vinyl surface exposed). The pieces were vertically placed at the bottom of the chamber in the center, facing the front side to the back end and parallel to the chamber air flow with an aluminum rack held in parallel. For carpet tests, one piece of the carpet sample was placed at the bottom of the chamber

with the carpet fabric side exposed to the air. The empty chamber tests were conducted without substrates for the whole testing period. During the tests, a constant emission rate of VOC was generated and maintained in the standard generation system. They were dosed to the controlled dynamic small chamber where test materials were placed. After dosing for 48 or 144 hours, the VOC flow was disconnected and replaced by clean air flow for 24 hours or longer. The VOC mass introduced into the chamber was calculated by its emission rate and the air flow rate of the test chamber.

High Temperature Chamber Tests

The high temperature chamber (HTC) was made of electro polished stainless steel with the size of 17.8cm (depth) by 2.5cm (height) by 25.4cm (width) (Fig. 1). It was designed to have well-distributed air flow and well-mixed exhaust across a test coupon and to provide heating up to 220 °C. The test coupon rests on the bottom of the chamber. A front drawer is held in place by two cam-activated clamps. The drawer is sealed to the chamber body by a Teflon-encased viton O-ring. The entire unit is encased in an insulated aluminum case. A 122 cm long air heater is at the inlet to the chamber. The line heater heats the incoming air stream independently. Nitrogen gas from a liquid nitrogen tank was used as the clean gas delivery system. The temperature was set and maintained by the control panel of the apparatus at 60 °C or 65 °C for tests. A mass flow controller was used to direct the dry nitrogen flow to the heated chamber to motivate the air flow via OPTO 22 DAS. Relative humidity was not monitored.

During the sink effect tests, VOCs were adsorbed on the surface and then diffused to the interior of test specimen even after the chamber was purged with clean air. The HTC was used to thermally desorb the VOC residues from the specimens that were exposed in the small chamber tests. Before each test, the empty HTC was baked at 60 °C or 65 °C and flushed with 150 mL/min nitrogen for at least 4 hours. Background samples were then collected with the empty chamber. The first sheet faced to the chamber door was taken out from the small chamber right after the sink test and sheared to the size of 15 cm x 20 cm in 10 minutes, and then placed in the HTC for test. All HTC tests were conducted in an air flow of 155 mL/min. During sampling, a pump and a mass flow meter were used to draw a side stream sample through a manifold connected to the outlet of the chamber. The air flow from the oven was passed through a Tenax TA sorbent tube to collect the VOCs. A test could last for several hours to several days depending on test VOC and materials' properties.

Air Sampling and Analysis

VOC samples were collected by approximately 180 mg of Tenax TA (60/80 mesh, Supelco) sorbent tubes and quantitatively analyzed by Agilent 6890/5973 GC/MS system equipped with a Perkin Elmer (PE) 400 automatic thermal desorption (ATD) unit or an Agilent 6890N/5973 GC/MS system with a Unity thermal desorption system (Markes International Ltd.). D₈-toluene gas (50 ppm air balanced, National Specialty Gases, Durham, NC) was used as the internal standard.

Models Description

The Langmuir-isotherm model and the diffusion model are examined in this study. The sink parameters were determined and evaluated by the measured VOC concentrations.

No-Sink Model

If there is no sink effect and the chamber air is well-mixed, the VOC concentration in the chamber air during the sorption period will be

$$C = C_{in} (1 - e^{-Nt_a}) \quad (1)$$

And in the desorption period the VOC gas phase concentration will be

$$C = C_{d0} e^{-Nt_d} \quad (2)$$

Langmuir-isotherm Sink Model

Equations (3) and (4) describe the rate of VOC concentration and sink mass change in the Langmuir-isotherm model [1, 17]. Equation (5) shows the relationship between the material-air partition coefficient and model parameters.

$$\frac{dC}{dt} = \frac{R}{V} - NC - k_a CL + k_d ML \quad (3)$$

$$\frac{dM}{dt} = k_a C - k_d M \quad (4)$$

$$K_e = \frac{k_a}{k_d} = \frac{M_e}{C_e} \quad (5)$$

Using the above equations, the values of the sorption rate constants k_a and k_d can be determined by the least-square fitting method using the sorption data from experiments in the small environmental chambers.

Diffusion Controlled Sorption Model

The diffusion controlled sorption model is governed by the relatively slow diffusion process within the materials [6, 9, and 10]. Transient diffusion through a homogeneous thin slab can be described using Equation 6.

$$\frac{\partial C_s}{\partial t} = D_e \frac{\partial^2 C_s}{\partial x^2} \quad (6)$$

If we assume that there is no flux through the base of the material and the initial VOC concentration in the air and solid material is zero, the VOC concentration C_s in the solid is given by

$$C_s(x,t) = \frac{2Q}{AK} \sum_{n=1}^{\infty} \left\{ \frac{\exp(-D_e q_n^2 t) ((q_n^2) \cos(q_n x))}{[Z(h - k q_n^2)^2 + q_n^2 (Z + k) + h] \cos(q_n Z)} \int_0^t \exp(D_e q_n^2 \tau) K C_{in}(\tau) d\tau \right\} \quad (7)$$

where

$$h = \frac{Q}{AD_e K} \quad (8)$$

$$k = \frac{V}{AK} \quad (9)$$

and q_n values are the positive roots of

$$q_n \tan(q_n x) = h - k q_n^2 \quad (10)$$

For a particular chemical, K is the material-air partition coefficient, which describes the sorption equilibrium [31]:

$$K = \frac{C_s}{C_e} \quad (11)$$

Note that K and K_e have different units and, thus, they are not identical. The effective diffusion coefficient, D_e , is determined by fitting the diffusion model to the experimental sorption and desorption data [10, 31] using equation 12.

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \left[\frac{8}{(2n+1)^2 \pi^2} \exp\left\{ \frac{D_e (2n+1)^2 \pi^2}{4x^2} \right\} \right] \quad (12)$$

The counter n can vary from zero to a large number until the summation converges.

In this work, K and D_e were determined by Corsi, et al. using dual-volume diffusion chamber or dynamic microbalance [31].

Results and Discussion

Summary of Tests

A total of 13 tests were conducted including eleven VOCs tests with building materials and two empty chamber tests. VOC concentrations in chamber air vs. time profiles are shown in Figures 2-5. The sorption time period lasted for 2 or 6 days. The desorption period was 1 to 4 days except

for ethylbenzene-vinyl and dodecane-vinyl flooring tests whose desorption period was extended to 17 days (Fig. 2e) and 92 days (Fig. 3d), respectively.

The sorption/desorption of ethylbenzene and dodecane were tested in the empty stainless steel chamber. The empty chamber sink effect for these two chemicals was assumed to be zero for the calculation of the mass in the high temperature chamber tests. As we can see in Figs. 2a, 2d, and 5a, the measured concentration of ethylbenzene and decane is very close to the prediction of the no-sink model, indicating that there exists minimal sink effect of ethylbenzene on stainless steel chamber (Fig. 2a) and carpet (Fig. 2d) and decane on mortar (Fig. 5a). However, dodecane displayed some level of sorption in the empty chamber experimental system (Fig. 3a).

The high temperature chamber thermal desorption method was first developed using aluminum weighing dishes and then evaluated by the same materials purchased for the small chamber tests but unused in the sink tests. The details of the method are available elsewhere [40]. The high temperature chamber desorption test was not conducted for T2 due to the availability of the HTC at that time. It was noticed that during the material HTC tests, there had been water steam condensation inside the exhausted line from vinyl flooring and painted gypsum board, whose existence can also be confirmed by the difference of RH between inlet and chamber during small chamber tests 2 to 9 shown in Table 2.

Sorption and Desorption Parameters

The parameters for the sink models are usually estimated from a given set of experimental data. Values of the constant k_a and k_d in the Langmuir-isotherm model were determined by the least square fitting of experimental data with Equations 3 and 4 using the SCIENTIST program (MicroMath Scientific Software, PO box 21550, Salt Lake City, Utah 84121). The equilibrium partition coefficient (K_e) was calculated using Equation 5. The equilibrium partition coefficients (K) of the painted gypsum board and carpet in the diffusion model were independently obtained from dual chamber tests and that of vinyl flooring data were acquired from micro chamber tests [31]. The effective diffusion coefficients (D_e) were also independently determined by fitting the diffusion model to the experimental sorption and desorption data [31]. These parameters are summarized in Table 3.

The K_e values of different materials for ethylbenzene and dodecane have the following order: stainless steel chamber < painted gypsum board < carpet < vinyl flooring and for decane it is mortar < painted gypsum board $\approx$ carpet. The equilibrium partition coefficient is a measure of the sorption capacity of a material for a chemical. The higher the values of K_e and K , the more significant the sink effect of chemicals on the materials. The above orders show that vinyl flooring has the greatest sink capacity for the tested chemicals.

The K_e values of 1-butanol with painted gypsum wallboard were larger than those of ethylbenzene and decane, likely due to the polar-polar interactions between 1-butanol and the wallboard. The K_e values of ethylbenzene, decane and dodecane with painted gypsum wallboard and carpet are in an increased order, but their vapor pressure decreases monotonically. The K_e value of ethylbenzene with vinyl flooring is much smaller than that of dodecane with vinyl flooring.

With the available data from this work, correlations between the pair of K_e , K and D_e values for painted gypsum wallboard with different chemicals were examined. Figure 6 shows that the effective diffusion coefficient is inversely proportional to the equilibrium partition coefficient (K_e) for painted gypsum wallboard ($r^2=0.8879$). Figure 7 exhibits that the equilibrium partition coefficient (K) in the diffusion model is strongly correlated with the equilibrium partition coefficient (K_e) obtained from the Langmuir-isotherm model ($r^2 = 0.9925$). Further in-depth studies in the future are needed to comprehend and elucidate these correlations. If confirmed, these relationships will provide a straightforward pathway to reasonably estimate K and D values and to model sorptive interactions for VOCs whose K_e data are available.

Mass Balance

Based on the small chamber experiments described above, the mass of the VOC adsorbed on the material surface at steady state, M_∞ , has been calculated for each test by the following equations

$$M_\infty = M_{out} - (C_e - C_{dt})V + M_{HTC} \quad (13)$$

where, M_{HTC} is applied when data is available and M_{out} is calculated by using the trapezoid rule:

$$M_{out} = \frac{Q}{2} \sum_{i=0}^n \frac{C_{i+1} + C_i}{t_{i+1} - t_i} \quad (14)$$

where $n+1$ is the number of data points.

Shown in Table 4 are the calculation results of mass balance at steady state for each small chamber test and compared to the model predictions whenever data are available. The VOC masses adsorbed on the material as calculated from small chamber tests and predicted by the Langmuir-isotherm and diffusion models are reasonably close to each other.

In Table 4, when data available, the mass desorbed from HTC test coupon was used to calculate the mass balance in the experiments. However, there may exist VOC loss during the preparation of HTC tests, such as the process of moving and cutting the material for HTC tests or even incomplete desorption in the HTC tests, etc. Nevertheless, the HTC data provides the lower bound for the total amount of VOCs absorbed on and in the materials after the purging in the small chamber.

Model Evaluation

In addition to the Langmuir-isotherm model simulation for the small chamber tests, the diffusion model was employed to predict the chamber VOC concentrations with MATLAB[®] (The MathWorks, Inc.), using the diffusion coefficients and equilibrium partition coefficients independently obtained from reference [31]. Fig. 2 to Fig. 5 show the results of experimental data vs. the model results with no sink effect included. It is said that the data used for the model evaluation process should be independent of the data used to develop the model. In this case, the key parameters in the diffusion model (K and D) were independently determined, and, thus, the results shown in Figs 1 to 4 are true predictions. In contrast, the key parameters in the Langmuir-

isotherm model were obtained by fitting the model to the chamber data. Thus, direct comparison of the predictive errors of the two sink models gives an unfair advantage to the Langmuir-isotherm model.

To have an idea how good the agreement would be under our test conditions between the model predictions and the experimental data and to compare the performance of the models for each test, the ASTM method D5157-97 Standard Guide for Statistical Evaluation of Indoor Air Quality Models [37] was applied to evaluate these models. The evaluation includes assessing the general agreement between the predicted and observed concentrations through correlation coefficient (R^2), line of regression, normalized mean square error (NMSE) and assessing bias in the mean or variance of predicted values relative to that for observed values via normalized or fractional bias (FB) of the mean concentrations and a similar index of bias (FS) based on the variance of the concentration. Table 5 presents the statistic analysis results for these models in comparison with the experiment data.

The results in the figures and evaluation statistics indicate that the prediction of the diffusion model was satisfactory for ethylbenzene on painted gypsum wallboard (T2 and T3) and carpet (T4) and decane on carpet (T13). The model is unsatisfactory to predict the sink behavior of dodecane on the gypsum wallboard (T7), carpet (T8) and vinyl flooring (T9), and butanol (T10) and decane (T12) on the gypsum wallboard. Different compounds and materials displayed different discrepancies. The prediction overestimates the adsorption rates of dodecane, butanol, and decane on painted gypsum wall board but underestimates their desorption rates. The reverse is true for dodecane with vinyl flooring and carpet and decane on carpet, that is, the prediction underestimates adsorption rate but overestimates the desorption rates. A larger standard deviation was observed for tests with larger K_e and K values. The parameters (D_e and K) were determined at $24 \pm 2^\circ\text{C}$ in dual chamber or $25.6 \pm 0.3^\circ\text{C}$ in the micro chamber [31]. The test conditions for each small chamber sink test are listed in Table 2. The discrepancy in chamber temperature may be a possible cause of the deviation as discussed in the literature [42]. However, given that the experimental data used by the diffusion model simulation and the obtained model parameters (D_e and K) from the chamber tests in a different laboratory were independent of each other, overall the results are encouraging.

In order to obtain sufficient experimental data for model evaluations, the desorption period was extended to 388 hours for ethylbenzene with vinyl flooring (T5) and over 2208 hours for dodecane with vinyl flooring (T9). Using T9 as an example (Fig. 8), within the first 96 hours of desorption, the equilibrium partition coefficient obtained by fitting the experimental data with the Langmuir-isotherm model is not constant, indicating that the concentration did not reach equilibrium before 96 hours. Therefore, we can not call it as an equilibrium partition coefficient for that time period. This illustrates that the selection of data range plays an important role in the model development and evaluation, especially for indoor sink effect tests that usually last for a much longer period of time.

Under the same conditions, e.g. loading, air change rate, and desorption time period and using the geometric mean of model parameters obtained from the experiments in this study, the mass ratio M_t/M_∞ predicted by the Langmuir-isotherm model and the diffusion model is presented in Fig.9. The figure shows that after 100 hours of desorption, the Langmuir-isotherm model

predicts more than 99% of the mass adsorbed on the sink material was flushed out, whereas the diffusion model predicts that only about 70% was out. This illustrates that the diffusion-sink model often better simulates the longer period of desorption experiments in a longer period of time. However, our experimental results underscore the need for accurately determining the diffusion coefficients and equilibrium partition coefficients and the need of better models that can accurately predict the VOCs sink behavior of indoor materials.

Conclusions

Using VOCs as surrogates of weapons of mass destruction and toxic industrial chemicals, this study assessed the Langmuir-isotherm model and the diffusion model for the sink effect of VOCs on selected building materials. Sorption/desorption rate constants and equilibrium partition coefficients for ethylbenzene, dodecane, butanol, and decane with gypsym wallboard, vinyl flooring, carpet, and mortar were determined by using the Langmuir-isotherm model fitting. Equilibrium partition coefficients and diffusion coefficients of the same VOC-material were applied to the diffusion model. A strong correlation between equilibrium partition coefficients from the Langmuir-isotherm model and that of the diffusion model ($r^2=0.9925$) was observed for painted gypsum wallboard. Our data suggest that there exists likelihood for reasonably estimating K and D_e parameters and simulate sorptive interactions for VOCs whose K_e data are available.

The two models are validated by comparing experimental measurements with the predicted gas-phase concentrations in the chamber as a function of time during the chamber experiment using the ASTM D5157-97 method and the mass balance of the VOCs introduced in the chamber. The statistics results from the present work show that there exist some discrepancies between experimental data and the model results, which underscore the need of accurately determining the equilibrium partition coefficients and effective diffusion coefficients in order to accurately predict the sink effect on indoor air quality. The diffusion model evaluated in this paper calculates the contaminant concentrations in the sink and indoor air with explicit mathematical solutions (Eqs. 7 to 10). To use this model, the following conditions must be met: a single air zone, a single sink material, and a constant ventilation flow rate. Such limitations make it difficult to incorporate this sink model into existing indoor air quality models. To make this model more flexible (i.e., applicable to multi-zonal, and multi-sink environment, and time-varying ventilation rate), it is highly desirable to develop a set of numerical solutions, which can be incorporated more easily into existing indoor air quality models.

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