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Measurements of VOC Adsorption/Desorption Characteristics of Typical Interior Building Materials

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The adsorption/desorption of volatile organic compounds (VOCs) on interior building material surfaces (i.e., the sink effect) can affect the VOC concentrations in a building, and thus need to be accounted for in an indoor air quality (IAQ) prediction model. In this study, the VOC adsorption/desorption characteristics (sink effect) were measured for four typical interior building materials including carpet, vinyl floor tile, painted drywall, and ceiling tile. The VOCs tested were ethylbenzene, cyclohexanone, 1,4-dichlorobenzene, benzaldehyde, and dodecane. These five VOCs were selected because they are representative of hydrocarbons, aromatics, ketones, aldehydes, and chlorine substituted compounds. The first order reversible adsorption/desorption model based on the Langmuir isotherm was used to analyze the data and to determine the equilibrium constant of each VOC-material combination. It was found that the adsorption/desorption equilibrium constant, which is a measure of the sink capacity, increased linearly with the inverse of the VOC vapor pressure. For each compound, the adsorption/desorption equilibrium constant, and the adsorption rate constant differ significantly among the four materials tested. A detailed characterization of the material structure in the micro-scale would improve the understanding and modeling of the sink effect in the future. The results of this study can be used to estimate the impact of sink effect on the VOC concentrations in buildings.

INTRODUCTION

Interior building materials can act as sinks to adsorb volatile organic compounds (VOCs) from indoor air and re-emit them later. This phenomenon is known as the sink effect, and can affect indoor VOC concentrations significantly. One frequently used model for describing indoor sinks is a first order reversible adsorption/desorption model Langmuir-isotherm (Tichenor et al. 1991 and Levens and Sollinger 1993). This model assumes that at a fixed temperature, the VOC adsorption rate is proportional to the VOC concentration in the bulk air over the material surface while the desorption rate is proportional to the VOC mass adsorbed on the material surface (i.e., first-order). The model is:

$$\frac{dM}{dt} = k_a C - k_d M \quad (1)$$

where M is the VOC mass adsorbed on a unit area of the adsorbent surface, C is the concentration in the bulk air around the surface, and k_a and k_d are adsorption and desorption rate constants, respectively. At equilibrium, the VOC adsorption rate is equal to the VOC desorption rate:

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Figure 1. Schematic of the Dynamic Chamber Test System for Sink Effect Studies

desorption period started immediately after the VOC concentrations in the chamber had become equilibrium. During the desorption period, only the conditioned air was introduced into the chamber. The VOC concentrations in this period decreased with time and eventually became undetectable.

A dynamic chamber test system (Figure 1) was employed for the test. In the sorption period, the VOCs were generated from the VOC permeation tubes inside a temperature-controlled container (C) and carried by dry air (A). The conditioned air from a humidifier (B) was added to the VOCs flow and the total flow was introduced into a test chamber (D). In the desorption period, only conditioned air was introduced into the test chamber. In both periods, the air change rate for the chamber (excluding the volume of the specimen) was constant at $0.5 \pm 0.01 \text{ h}^{-1}$, and the relative humidity and temperature in the chamber were maintained at $50 \pm 2\%$ and $23 \pm 1^\circ\text{C}$, respectively.

It was assumed that the VOCs in the chamber were perfectly mixed and that the mass change of each VOC in the test chamber was described by the mass balance equation (Tichenor et al. 1991):

$$\frac{dC}{dt} = NC_{in} - NC - k_a LC + (k_d/K_e)ML \quad (3)$$

where N and L are the chamber air change rate and the specimen loading ratio, respectively. The NC_{in} term in Equation (3) is the VOC concentration change per unit time due to supply air, while NC is the VOC concentration change per unit time due to the exhaust of air. The $k_a LC$ term in Equation (3) represents the VOC concentration change due to the adsorption on specimen, while the $(k_d/K_e)ML$ term represents the VOC concentration change due to the desorption from specimen. In order to exclude the sink effect of the background materials such as chamber walls, specimen holder, and wax surfaces for specimen edges. Two more terms were added to Equation (3) to account for the VOC mass adsorbed and desorbed on these surfaces. Thus, the mass balance equation is:

Figure 2. Test Materials

Table 1. Detailed Description of Test Specimen

Specimen	Description	Storage	Size, cm × cm	Thickness, cm	Precondition Time, h
Specimen Holder	In-house made, stainless steel, and electro-polished.		20.2 × 45.2	0.08	48
Vinyl Flooring Tile	Commercial vinyl sheet flooring	Stored in the laboratory for over one year	20 × 45	0.3	48
Gypsum Wallboard	Painted with an interior latex paint	Stored in the laboratory for three months after painting	20 × 45	1.0	48
Ceiling Tile	Commercial fiberboard sheet	Stored in the laboratory for over one year	20 × 45	1.4	48
Carpet	Nylon fiber pile bounded with a styrenebutadiene latex to a jute backing	Stored in the laboratory for over one year	20 × 45	0.4 (Fiber) 0.2 (Backing)	48

Figure 3. Comparison of K_e Values Based on Data from Different Test Periods

Table 3. K_e and k_a Values of Five VOCs with Carpet by Three Regression Methods

VOCs	EB	CYH	DCB	BZA	DOD
Sorption Period k_a (mh ⁻¹) K_e (m)	1.62±0.21 1.65±0.04	0.40±0.02 2.08±0.08	0.75±0.04 5.37±0.15	0.94±0.03 8.37±0.11	0.51±0.02 26.03±0.50
Desorption Period k_a (mh ⁻¹) K_e (m)	0.33±0.03 0.64±0.02	0.54±0.04 2.19±0.07	0.49±0.02 3.54±0.08	0.39±0.02 5.51±0.14	0.45±0.02 19.09±0.56
Sorption-Desorption k_a (mh ⁻¹) K_e (m)	0.67±0.17 1.05±0.07	0.44±0.02 2.15±0.05	0.60±0.03 3.79±0.10	0.57±0.04 6.22±0.22	0.42±0.01 22.2±0.5

EXPERIMENTAL RESULTS

Figures 4A through 4E show the measured VOC concentrations for the chamber background and the four test materials. For comparison, the values using the non-sink model [Equation (7)] are also presented. The calculated k_a and K_e values based on the data obtained from the whole adsorption-desorption period for the four materials are shown in Table 4. Table 5 presents the statistic analysis results (coefficient of determination) for the application of linear sink model to the experimental data.

Figure 4B. Test of Vinyl Tile, VOC Concentrations Versus Elapsed Time

Figure 4D. Test of Ceiling Tile, VOC Concentrations Versus Elapsed Time

Table 4. Adsorption/Desorption Equilibrium Constants for Different Test Materials with the Five VOCs

VOCs	EB	CYH	DCB	BZA	DOD
Chamber Background k_a (mh ⁻¹) K_e (m)	0.0046±0.012 0.0041±0.0033	0.0080±0.0047 0.0072±0.0011	0.0080±0.0085 0.020±0.002	0.011±0.004 0.021±0.003	0.010±0.005 0.125±0.006
Vinyl Tile k_a (mh ⁻¹)* K_e (m)*	0.26±0.32 0.095±0.008	0.19±0.05 0.16±0.01	0.25±0.03 0.30±0.01	0.14±0.06 0.25±0.04	0.11±0.02 0.85±0.12
Painted Drywall k_a (mh ⁻¹)* K_e (m)*	0.25±0.28 0.046±0.015	0.076±0.014 0.32±0.05	0.32±0.03 1.13±0.06	0.18±0.01 1.25±0.07	0.076±0.005 2.93±0.25
Ceiling Tile k_a (mh ⁻¹)* K_e (m)*	1.13±0.60 0.31±0.02	1.23±0.04 1.10±0.06	1.40±0.33 1.53±0.07	1.08±0.16 1.38±0.05	0.97±0.14 5.07±0.32
Carpet k_a (mh ⁻¹)* K_e (m)*	0.67±0.17 1.05±0.07	0.44±0.02 2.15±0.05	0.60±0.03 3.79±0.10	0.57±0.04 6.22±0.22	0.42±0.01 22.2±0.5

*The sink effect of the chamber background has been excluded.

Table 5. Coefficient of Determination for Regression Experimental Data with Linear Sink Model

VOCs	EB	CYH	DCB	BZA	DOD
Chamber Background	0.989	0.999	0.994	0.995	0.997
Vinyl Tile	0.990	0.999	0.999	0.992	0.997
Painted Drywall	0.997	0.997	0.996	0.996	0.993
Ceiling Tile	0.995	0.992	0.993	0.997	0.995
Carpet	0.991	0.998	0.996	0.992	0.989

Test of Chamber Background

As shown in Figure 4A, the measured concentrations of ethylbenzene and cyclohexanone were almost identical to that estimated by the non-sink model, indicating that the chamber background did not have any sink effect for the two compounds. A very slight sink effect was observed for 1,4-dichlorobenzene and benzaldehyde, while a small sink effect was observed for dodecane. The results showed that the predicted concentrations using the linear sink model agreed closely with the measured values for these VOCs, while the agreement with the non-sink model was not as close.

The K_e values for 1,4-dichlorobenzene and benzaldehyde were 0.020 m and 0.021 m, respectively. The K_e values for ethylbenzene and cyclohexanone were below 0.01 m. The K_e of dodecane was 0.125 m. These results suggested that sink effect of the chamber background may be ignored if the K_e value is less than 0.1 m.

Test of Vinyl Floor Tile

Figure 4B shows the plots of VOC concentrations vs. time over the surface of vinyl flooring tile. Slight sink effects were observed for cyclohexanone, 1,4-dichlorobenzene, and benzaldehyde, while ethylbenzene displayed a negligible sink effect. The sink effect for dodecane was greater than that for the other VOCs. It is noted that the K_e values of all five VOCs for vinyl

Table 6. Experimental Uncertainty for Individual VOCs

VOCs	Average Concentration, mg/m ³	Standard Deviation	Relative Deviation, %	Sampling Number
EB	1.302	0.0185	1.2	19
CYH	0.745	0.00854	0.6	19
DCB	1.002	0.0108	1.7	19
BZA	0.834	0.0126	1.6	19
DOD	0.98	0.034	0.4	8

Table 7. Comparison of k_a and K_e Values of Dodecane with Carpet (Sorption-Phase Only) Estimated from Different Time Periods

Time (h)	624	487	367	290	199	76
C (mg/m ³)	1.01	0.98	0.94	0.88	0.85	0.64
k_a (mh ⁻¹)	0.51	0.51	0.51	0.52	0.54	0.59
K_e (m)	26.0	26.0	25.9	25.1	23.2	20.2

Adequacy of the Linear Sink Model

In general, the linear sink model was found to be acceptable in fitting the experimental data for K_e values ranged from 0.004 m to 22.2 m. The largest standard deviation was observed for ethylbenzene with chamber, vinyl tile, and painted drywall. In these cases, the K_e values were very small (≤ 0.1 m).

In order to obtain sufficient experimental data for analysis, the test durations for both the sorption period and desorption period in this study were greater than 196 hours. For test of carpet, the total test time was over 1000 hours. Analysis of the test data of carpet with dodecane showed that if the measured concentration were about 90% of the inlet concentration, the K_e value would be about 96% of the real value. Comparison of the K_e and k_a values for different test durations is shown in Table 7. It is noted that the variations of K_e and k_a values for test duration greater than 199 hours were within 11% and 5% of the real value, respectively.

K_e and VOC Vapor Pressure (p_0)

The adsorption/desorption equilibrium constant K_e equals the ratio of the VOC mass adsorbed on a unit surface M_e to VOC concentration in the chamber air at equilibrium C_e . For a given C_e , a large K_e value indicates that more VOC molecules are adsorbed on the surface. In other words, a large K_e value corresponds to a large sink capacity. It was found in this study that K_e apparently depends on surface roughness and VOC vapor pressure. As shown in Figure 5, the K_e values of different materials for individual VOCs increased in the following order:

Chamber background < Vinyl flooring tile < Painted drywall < Ceiling tile < Carpet.

Moreover, the K_e values of different VOCs for the same individual material increased as follows:

Ethylbenzene < Cyclohexanone < 1,4-Dichlorobenzene < Benzaldehyde < Dodecane.

The appropriate relationship between K_e and p_0 was based on fundamental thermodynamics. At a gas-surface equilibrium, the chemical potential $\Delta\mu$ of a VOC in the gas phase is equal to its chemical potential on the adsorption surface (Atkins 1978), given by

and $\log(a_2) = \Delta\mu_{\text{surface}}^0/RT$

and Equation (12) is rewritten as:

$$n/n_s = (a_1/a_2)p/p_0 = ap/p_0 \quad (13)$$

where, $a = a_1/a_2$. Full coverage by monolayer adsorption was assumed. Then n_s is unity and n equals ap/p_0 .

The VOCs in the test chamber were assumed to be ideal gases. Their concentrations at equilibrium can be converted to their pressures by:

$$C_e = pW_{\text{mol}}/(RT) \quad (14)$$

The VOC mass adsorbed on the surface at equilibrium was converted to the VOC adsorbate molar number by

$$n = M_e/W_{\text{mol}} \quad (15)$$

The following equation was established:

$$K_e = M_e/C_e = nW_{\text{mol}}/[pW_{\text{mol}}/(RT)] = aRT/p_0 \quad (16)$$

At a given temperature, RT is constant. The K_e and p_0 are inversely correlated for an individual VOC, based on the Langmuir isotherm and ideal gas conditions. For adsorption processes with VOCs at low concentrations, if no specific interaction exists between material surface and any of the VOCs, the relationship as shown in Equation (16) should apply to each of these VOCs. Moreover, if the standard chemical potentials in air and at the surface are assumed to be identical for all VOCs (i.e., the term a in Equation (16) is independent of p_0), a linear relationship between K_e and $1/p_0$ should be established.

Figure 5 shows that such a linear correlation between K_e and $1/p_0$ does exist for the five VOCs with the five material surfaces. Since the tested five VOCs represented five types of organic compounds (alkanes, ketones, aldehydes, aromatics, and chlorine-substituted compounds), the linear correlation indicated that the type of VOCs may not be the key issue in the sink effect in indoor environment. The actual key issue is the vapor pressure of the VOCs. The equations shown in Figure 5 may be used as a first approximation to Equation (16) under the test condition studied (i.e., 23°C and 50% rh), because $r^2 > 0.9$ does indicate a strong correlation.

As shown in Figure 5, the K_e values for the five material surfaces are quite different. As the measured sample sizes were the same for all these materials, a higher K_e value for an individual VOC indicated a larger effective adsorption surface area (also called specific surface area). The specific surface area of a material is determined by the micro-scale physical structure of the material including both the surface and interior structure. A detailed characterization of the micro-scale structure of the materials tested to determine their specific surface area would improve the understanding of the VOC sorption process.

Adsorption Constant k_a

The k_a values represent the rate of the adsorption on the sink surface. As shown in Table 4 and Figure 6, the average k_a values of the five VOCs increased as: chamber background (0.008 mh^{-1}) < painted drywall (0.18 mh^{-1}) $\approx$ vinyl flooring tile (0.19 mh^{-1}) < carpet (0.54 mh^{-1}) < ceiling tile (1.16 mh^{-1}).

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NOMENCLATURE

A	specimen surface area, m ²
BZA	benzaldehyde
C	VOC concentration (mg/m ³) in chamber at time <i>t</i>
C _e	VOC concentration in chamber at equilibrium, mg/m ³
C _{in}	VOC concentration of supply air, which is constant during sorption period and zero in desorption period
CYH	cyclohexanone
DCB	1,4-dichlorobenzene
DOD	dodecane
EB	ethylbenzene
k _a	adsorption constant, mh ⁻¹
k _d	desorption constant, h ⁻¹
K _e	adsorption/desorption equilibrium constant, which equals k _a /k _d , m
L	specimen-loading ratio, which equals ratio of specimen surface area (m ²) to the net chamber volume (m ³), m ² /m ³
M	VOC mass adsorbed per unit sink surface area, mg/m ²
M _e	VOC mass adsorbed per unit sink surface area at equilibrium, mg/m ²
N	air change rate in the chamber, h ⁻¹
p ₀	VOC saturated vapor pressure, mmHg
R	gas constant (8.314 J K ⁻¹ mol ⁻¹)
rh	relative humidity, %
t	elapsed time, h
V	chamber volume, excluding volume of test specimen, m ³
W _{mol}	VOC relative molecular mass

REFERENCES

- Atkins, P.W. 1978. *Physical Chemistry*. San Francisco: W.H. Freeman and Company.
- Black, M.S., L.M. Work, A.G. Worthan, and W.J. Pearson. 1993. Measuring the TVOC Concentrations of Carpet Using Environmental Chambers. *Indoor Air* 2:401.
- Axley, J.W., and D. Lorenzetti. 1993. Sorption Transport Models for IAQ Analysis. *Modeling of Indoor Air Quality and Exposure*. ASTM STP 1205, p. 105.
- Brown, S.K., M.R. Sim, M.J. Abramson, and C.N. Gray. 1991. Progress Towards National Indoor Air Quality Goals for Volatile Organic Compounds. *A Report to the Air Quality Committee of the National Health and Medical Research Council*.
- Chang, J.C.S., and Z. Guo. 1994. Modeling of Alkane Emissions from a Wood Stain. *Indoor Air* 4:35.
- Chang, J.C.S., and L.E. Sparks. 1997. Evaluation of Sink Effects on VOCs from a Latex Paint. *J. of Air Waste Management* 48(10): 953-958.
- Colombo, A., M. De Bortoli, H. Knoppel, E. Pecchio, and H. Vissers. 1993. Adsorption of Selected Volatile Organic Compounds on a Carpet, a Wall Coating, and a Gypsum Board in a Test Chamber. *Indoor Air*, 3:276.
- Dunn, H.E., and T. Chen. 1993. Critical Evaluation of the Diffusion Hypothesis in the Theory of Porous Media VOC Sources and Sinks. *Modeling of Indoor Air Quality and Exposure*. ASTM STP 1205, p. 64.
- Levsen, K., and S. Sollinger. 1993. Textile-Floor Coverings as Sinks for Indoor Air Pollutants. *Proceedings of Indoor Air* 2:395.
- Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1990. *Handbook of Chemical Property Estimation Methods*. Washington, DC: American Chemical Society.
- Tichenor, B.A., Z. Guo, J.E. Dunn, L.E. Sparks, and M.A. Mason. 1991. The Interaction of Vapor Phase Organic Compounds with Indoor Sinks. *Indoor Air* 1:23.