The Interaction of Vapour Phase Organic Compounds with Indoor Sinks

Bruce A. Tichenor, Zhishi Guo, James E. Dunn, Leslie E. Sparks, and Mark A. Mason

Abstract
The interaction of indoor air pollutants with interior surfaces (i.e., sinks) is a well known, but poorly understood, phenomenon. Studies have shown that re-emissions of adsorbed organic vapours can contribute to elevated concentrations of organics in indoor environments. Research is being conducted in small environmental test chambers to develop data for predicting sink behaviour. This paper reports on the development of sink models based on fundamental mass transfer theory. The results of experiments conducted to determine the magnitude and rate of adsorption and desorption of vapour phase organic compounds for several materials are presented. Five materials were evaluated: carpet, painted wallboard, ceiling tile, window glass, and upholstery. Two organic compounds were tested with each material: tetrachloroethylene (a common cleaning solvent) and ethylbenzene (a common constituent of petroleum-based solvents widely used in consumer products). The results of the experimental work are presented showing the relevant sink effect parameters for each material tested and comparing the sorptive behaviour of the two organic compounds evaluated. An indoor air quality (IAQ) model was modified to incorporate adsorption and desorption sink rates. The model was used to predict the temporal history of the concentration of total vapour phase organics in a test house after application of a wood finishing product. The predicted results are presented and compared to measured values. Suggestions for further research on indoor sinks are presented.

KEY WORDS:
Indoor sinks, Vapour phase organics, Adsorption, Desorption, Mass transfer, IAQ models

Introduction
The interaction of indoor air pollutants with interior surfaces (i.e., sinks) is a well known phenomenon. While it is possible that the mass transfer mechanism could be absorption (i.e., for a water soluble compound to a moist surface), this paper assumes that the mechanism is adsorption. Researchers have developed models and data to deal with the adsorption of particles and NO₂ to a variety of indoor surfaces (Nazaroff and Cass, 1989; Yanagisawa et al., 1987) and, for NO₂, the generation of NO from the surface has also been reported (Billick and Nagda, 1987; Spicer et al., 1989). Berglund et al. (1988) presented an extensive review of the literature on adsorption and desorption of vapour phase organic compounds in indoor environments, including data on a ventilation system heat exchanger. The same authors reported that organic compounds adsorbed on building materials in a 7-year-old preschool were re-emitted (i.e., desorbed) when placed in a small environmental test chamber ventilated
with clean air (Berglund et al., 1989). Zsolnay et al. (1987) reported on the transport of lindane vapours between wood and cotton cloth. Gebeufgi and Korte (1989) extended this research to include other fungicides and additional textile materials. The Danish Town Hall Study provided empirical evidence that re-emission of indoor pollutants, including vapour phase organics, from fleecy (i.e., large surface area) materials may contribute to the Sick Building Syndrome (Nielsen, 1987; Nielsen, 1988; Valbjorn and Skov, 1987). Seifert and Schmahol (1987) reported on research to determine the adsorption and desorption behaviour of several organic compounds and several surface materials, but concluded “... no rule can be deduced to predict the sorption behaviour of different VOC with different VOC with different VOC’s”. Dunn and Tichenor (1988) presented data showing the effect of sinks in small environmental test chambers used to determine emission rates of organic compounds for latex caulk and moth repellent, and they illustrated the use of adsorption and desorption rate constants in mass balance models. Tichenor et al. (1988) reported on studies in an IAQ test house where para-dichlorobenzene was measured in significant concentrations several days after the source (moth repellent) was removed. Measurements in the same test house, taken 12 months after additional moth repellent emission tests, showed concentrations of para-dichlorobenzene well above the outdoor concentration, indicating the re-emission of para-dichlorobenzene previously adsorbed on interior surfaces.

In view of the significant impact of sinks on indoor concentrations of vapour phase organic compounds, research is being conducted to develop data for predicting sink behaviour. This paper reports on the development of sink models and the results of experiments conducted to determine the magnitude and rate of adsorption and desorption of vapour phase organic compounds for several materials. In addition, an IAQ model was modified to incorporate adsorption and desorption sink rates, and the model was used to predict the temporal history of the concentration of total vapour phase organics in a test house after application of a wood finishing product. The concentrations predicted by the model are presented and compared to measured values. Finally, suggestions for further research on indoor sinks are presented.

Theory

Adsorption Isotherms

The study of adsorptive/desorptive behaviour of gas molecules with solid surfaces has resulted in several well known adsorption isotherm equations (Daniels and Alberty, 1961).

The Langmuir isotherm assumes a monolayer of molecules on a homogeneous surface with all adsorption sites mutually independent and identical (i.e., all sites require the same energy to adsorb molecules). At equilibrium, the Langmuir isotherm can be represented by:

\[ k_d C_e (1-\theta) = k_d' \theta \]  

(1)

where \( k_d \) is the adsorption rate constant; \( C_e \) is the equilibrium concentration of the adsorbate in the gas phase; \( k_d' \) is a desorption constant; and \( \theta \) is the proportion of available adsorption sites occupied. For the low vapour concentrations of single compounds used in the experiments discussed below, it can be assumed that the occupied sites are a very small fraction of the available sites (i.e., \( \theta << 1 \)). Thus, equation (1) can be simplified to a linear form:

\[ k_d C_e = k_d' \theta \]  

(2)

Since the equilibrium mass per unit area on the sink, \( M_e \), is directly proportional to \( \theta \), it follows that:

\[ k_d C_e = k_d M_e \]  

(3)

where \( k_d \) is the desorption rate constant. For
Applications to Chamber Testing

Dunn and Tichenor (1988) proposed a set of ordinary differential equations to describe the mass balance in a test chamber using the schematic shown in Figure 1:

\[
\begin{align*}
\text{x} &= \text{Mass to chamber over time } t \ [\text{dx/dt} = R(t)] \\
\text{y} &= \text{Mass from chamber over time } t \ [\text{dy/dt} = k_3(x-y-w)] \\
\text{w} &= \text{Mass in the sink} \ [\text{dw/dt} = k_3(x-y-w) - k_4w]
\end{align*}
\]

A sink with an area of A, the mass balance equation is:

\[
k_cC_A = k_dM_A
\]  

(4)

Also, an equilibrium constant, \(k_e\), can be defined as:

\[
k_e = k_d/k_d = M_e/C_e
\]

(5)

The Freundlich isotherm, originally developed as an empirical fit to non-Langmuir isotherms, was later derived by assuming an exponential distribution of adsorption site energies. The Freundlich isotherm can be represented by:

\[
m = kC^a
\]

(6)

where \(m\) is the mass adsorbed per unit of adsorbent and \(k\) and \(a\) are empirical constants.

The BET (Brunauer-Emmett-Teller) isotherm provides for multilayer adsorption. For the low vapour concentrations encountered in indoor environments, it is assumed that the available adsorption sites will not be covered, so the BET isotherm is probably not appropriate.

### Application to Chamber Testing

Dunn and Tichenor (1988) proposed a set of ordinary differential equations to describe the mass balance in a test chamber using the schematic shown in Figure 1:

\[
\begin{align*}
\frac{dx}{dt} &= R(t) \\
\frac{dy}{dt} &= k_3(x-y-w) \\
\frac{dw}{dt} &= k_3(x-y-w) - k_4w
\end{align*}
\]

(7)  

(8)  

(9)

where \(x\) is the mass that enters the chamber over time \(t\); \(y\) is the mass that exits the chamber over time \(t\); \(w\) is the mass in the sink; \(R(t)\) is the input rate to the chamber; \(k_3\) is the air exchange rate, \(N_3\); \(k_3\) is the rate constant to the sink; and \(k_4\) is the rate constant from the sink.

Expressing the sink term in a form consistent with the linear form of Langmuir’s equation gives:

\[
\frac{dw}{dt} = k_3CV - k_4MA
\]

(10)

where the concentration in the chamber, \(C = (x-y-w)/V\); \(V\) is the chamber volume; \(M\) is the mass per unit area in the sink; and \(A\) is the sink area. (Note that \(w = MA\).)

At equilibrium, \(\frac{dw}{dt} = 0\). Thus,

\[
k_3CV = k_4MA
\]

(11)

If a Langmuir adsorption process is assumed, comparison of equations (4) and (11) yields

\[
k_xA = k_3V, \text{ or } k_3 = k_d(A/V) \text{ and } k_4 = k_d.
\]

Since \(CV = x-y-w\),

\[
VdC/dt = dx/dt - dy/dt - dw/dt
\]

(12)
Substitution of equations (7), (8), and (10) and replacing $k_i$ and $k_d$ yield:

$$V\frac{dC}{dt} = R(t) - NC - k_iCA + k_dMA$$  \hspace{1cm} (13)

or

$$\frac{dC}{dt} = \frac{R(t)V - NC - k_iCA}{V} + k_dMA/V$$  \hspace{1cm} (14)

Substituting $L = A/V$ in equation (14) gives:

$$\frac{dC}{dt} = \frac{R(t)V - NC - k_iCL + k_dML}{V}$$  \hspace{1cm} (15)

Appropriate units for equation (15) are:

- $C =$ concentration, mg/m$^3$
- $t =$ time, h
- $R(t) =$ emission rate of source, mg/h
- $V =$ chamber volume, m$^3$
- $N =$ air exchange rate, h$^{-1}$
- $k_i =$ adsorption rate, m/h
- $L =$ ratio of sink area to chamber volume, m$^{-1}$
- $k_d =$ desorption rate, h$^{-1}$
- $M =$ mass per unit area in sink, mg/m$^2$

Substituting for $k_i$ and $k_d$ in equation (10) yields:

$$AdM/dt = Ak_iC - Ak_dM$$  \hspace{1cm} (16)

or simply

$$dM/dt = k_iC - k_dM$$  \hspace{1cm} (17)

Thus, if Langmuir adsorption processes are assumed, equations (15) and (17) describe the rate of change of concentration and mass in the sink, respectively, for small chambers.

### Test Materials and Compounds

Five sink materials were evaluated: (a) carpet - nylon fibre pile bound with a styrenebutadiene latex to a jute backing; (b) wallboard (gypsum drywall) finished with an interior latex paint; (c) ceiling tile - 1.5 cm thick composite material (mineral fibre, starch, clay, gypsum perlite paper fibre, silicate); (d) window glass; and (e) upholstery - throw pillow with 50% polyester/50% cotton fabric covering a polyester fibre fill. Each material was tested with two organic compounds: (a) tetrachloroethylene (perchloroethylene) - a common cleaning solvent and (b) ethylbenzene - a common constituent of petroleum-based solvents widely used in consumer products.

### Test Procedures

A sample of the sink material was placed in a test chamber supplied with clean, humidified air (45% RH, 23 °C) at a nominal rate of 1 air change per hour (ACH). At the start of each test, a portion of the inlet flow was replaced by flow from a constant temperature oven that held a permeation tube containing the test compound. The test compound was added to the chamber inlet flow at a constant rate for 48 hours, then the flow from the permeation oven was shut off and replaced by flow from the clean air system.

The concentration of the test compound was monitored at the outlet of the chamber by gas chromatography. Compounds were identified by retention time and quantified by electronic integration of detector response. Tetrachloroethylene was quantified using an electron capture detector (ECD); ethylbenzene was quantified using a flame ionization detector (FID). Samples were collected using gastight syringes, automated gas sampling valves equipped with fixed volume sample loops, or solid sorbent sampling tubes containing graphitized carbon adsorbents. Syringe and sampling loop samples were injected directly to the packed column of a gas chromatograph equipped with both...
FID and ECD. Sorbent samples were thermally desorbed first to a cryogenic trap and then to a gas chromatograph equipped with a fused silica column and an FID.

Samples were collected as frequently as possible for the first few hours in order to define the rising portion of the concentration vs. time curve (see Figure 2). Once the concentration reached an apparent equilibrium value, the sampling frequency was decreased. Forty-eight hours after the start of the test, the injection of the organic compound was terminated. At this point, the sampling frequency was again increased. Sampling continued until the concentration reached the quantification limit of the method.

**Test Conditions**

A wide variety of test conditions was used. Initial testing was conducted on carpet with tetrachloroethylene to investigate the effect of concentration and temperature on the sorption behaviour. Subsequent tests with the other sink materials and with ethylbenzene were conducted under fewer conditions. Tests to determine the sink behaviour of empty chambers were also carried out. Table 1 summarizes the conditions for all the tests. All tests were conducted at a nominal 1 ACH and a water vapour content equivalent to 45% relative humidity at 23 °C. [Note that trichloroethylene is designated as PCE (perchloroethylene) to avoid confusion with TCE (trichloroethylene).]

**Data Analysis**

Data obtained from the small chamber tests were analysed assuming a Langmuir type adsorption. These analyses yielded values for: $M_s$, the mass per unit area on the sink at equilibrium; $k_a$, the adsorption rate constant; $k_d$, the desorption rate constant; and $k_e$, the equilibrium constant.

**Determination of $M_s$**

Given the experimental procedures described above, the mass in the sink is assumed to be at equilibrium at the time ($t_e$) the flow of the test compound is stopped (see Figure 2). The total mass of the test compound exiting the chamber from time $t_e$ to the end of the test is the sum of (a) the mass of the compound in the chamber air at time $t_e$ and (b) the mass of the compound emitted from the sink. The total mass exiting the chamber from $t_e$ to the end of the test is obtained from the area under the curve (A_e) described by the data points multiplied by the air exchange rate (N) and the chamber volume (V). In this case, the A_e was calculated using the trapezoid rule. The mass of the compound in the
Table 1 Test conditions for sink experiments

<table>
<thead>
<tr>
<th>Material</th>
<th>Compound</th>
<th>Concentration range (mg/m³)</th>
<th>Temperature (°C)</th>
<th>No. of tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpet</td>
<td>PCE</td>
<td>6-50</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>PCE</td>
<td>14-15</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Ethylbenzene</td>
<td>8-9</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>Wallboard</td>
<td>PCE</td>
<td>19-26</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Ethylbenzene</td>
<td>11-13</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>Ceiling</td>
<td>PCE</td>
<td>23-28</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>tile</td>
<td>Ethylbenzene</td>
<td>10-11</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>Window</td>
<td>PCE</td>
<td>19</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>glass</td>
<td>Ethylbenzene</td>
<td>10-11</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>Upholstery</td>
<td>PCE</td>
<td>28-29</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>(pillow)</td>
<td>Ethylbenzene</td>
<td>8-11</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td>Empty</td>
<td>PCE</td>
<td>5-38</td>
<td>23</td>
<td>4</td>
</tr>
<tr>
<td>chamber</td>
<td>Ethylbenzene</td>
<td>12-13</td>
<td>35</td>
<td>2</td>
</tr>
</tbody>
</table>

*Tetrachloroethylene = Perchloroethylene (PCE)*

chamber air is the product of the concentration at equilibrium ($C_e$) and the chamber volume ($V$) - thus:

$$M_e = \frac{(A, NV - C_e V)}{A} \quad (18)$$

where $M_e$ is the equilibrium mass per unit area (mg/m²) in the sink at time $t_e$.

**Determination of $k_e$ and $k_d$**

Equations (15) and (17) can be solved analytically for certain simple cases. If the portion of the concentration vs. time curve from $t_e$ to the end of the curve is considered, the initial conditions are: $t = 0$, $C(0) = C_e$, and $M(0) = M_e = C_e(k_d/k_a)$ [from equation (3)]. For these conditions the solutions for equations (15) and (17) are:

$$C(t) = \frac{C_e[(N-r_2) e^{-t/r_2} - (N-r_1) e^{-t/r_1}]}{r_1 - r_2} \quad (19)$$

$$M(t) = \frac{k_a C_e (r_1 e^{-t/r_1} - r_2 e^{-t/r_2})}{k_d (r_1 - r_2)} \quad (20)$$

where

$$r_{1,2} = \frac{(N + k_d L + k_a) \pm [(N + k_d L + k_a)^2 - 4Nk_d]^1/2}{2} \quad (21)$$

Values for $k_a$ and $k_d$ were obtained by fitting equation (19), where $C_e$ is a known experimental value, to the chamber concentration vs. time data from $t_e$ to the end of the test using a nonlinear regression curve fit routine; in this case, NLIN by SAS (1985). Figures 3 and 4 show the data and the fitted Langmuir adsorption curve for two of the experimental runs (ethylbenzene/wallboard and tetrachloroethylene/carpet); the theoretical “no-sink” curve, defined by $C(t) = C_e e^{-kt}$, is also shown.

**Results**

The experimental results, including values for $C_e$, $M_e$, $k_a$, $k_d$, and $k_e$, are presented in Tables 2 - 5. The relative standard deviations of the estimates for $k_a$ and $k_d$ ranged from 7% to 20%, with an average of 14%. Table 2 provides the results for carpet tested with tetra-
Table 2 Experimental results – tetrachloroethylene (test compound) and carpet (sink material)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Sample area (m²)</th>
<th>ACH</th>
<th>C₀ (mg/m³)</th>
<th>M₀ (mg/m³)</th>
<th>k₁ (m/h)</th>
<th>k₀₁ (h⁻¹)</th>
<th>k₅ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.12</td>
<td>1.03</td>
<td>5.8</td>
<td>5.7</td>
<td>0.14</td>
<td>0.14</td>
<td>0.99</td>
</tr>
<tr>
<td>23</td>
<td>0.14</td>
<td>1.02</td>
<td>10.4</td>
<td>8.7</td>
<td>0.11</td>
<td>0.13</td>
<td>0.84</td>
</tr>
<tr>
<td>23</td>
<td>0.14</td>
<td>1.03</td>
<td>11.1</td>
<td>10.2</td>
<td>0.18</td>
<td>0.19</td>
<td>0.93</td>
</tr>
<tr>
<td>23</td>
<td>0.14</td>
<td>1.03</td>
<td>19.3</td>
<td>21.6</td>
<td>0.10</td>
<td>0.09</td>
<td>1.1</td>
</tr>
<tr>
<td>23</td>
<td>0.14</td>
<td>1.00</td>
<td>19.5</td>
<td>17.5</td>
<td>0.11</td>
<td>0.13</td>
<td>0.90</td>
</tr>
<tr>
<td>23</td>
<td>0.14</td>
<td>1.00</td>
<td>19.8</td>
<td>21.2</td>
<td>0.11</td>
<td>0.10</td>
<td>1.1</td>
</tr>
<tr>
<td>23</td>
<td>0.14</td>
<td>1.03</td>
<td>21.9</td>
<td>19.8</td>
<td>0.11</td>
<td>0.12</td>
<td>0.90</td>
</tr>
<tr>
<td>23</td>
<td>0.12</td>
<td>1.00</td>
<td>35.4</td>
<td>36.5</td>
<td>0.14</td>
<td>0.14</td>
<td>1.0</td>
</tr>
<tr>
<td>23</td>
<td>0.14</td>
<td>1.03</td>
<td>48.8</td>
<td>42.5</td>
<td>0.10</td>
<td>0.12</td>
<td>0.87</td>
</tr>
<tr>
<td>23</td>
<td>0.12</td>
<td>1.02</td>
<td>49.5</td>
<td>51.5</td>
<td>0.18</td>
<td>0.17</td>
<td>1.0</td>
</tr>
<tr>
<td>35</td>
<td>0.14</td>
<td>1.03</td>
<td>13.7</td>
<td>7.3</td>
<td>0.29</td>
<td>0.55</td>
<td>0.53</td>
</tr>
<tr>
<td>35</td>
<td>0.14</td>
<td>1.04</td>
<td>14.5</td>
<td>7.3</td>
<td>0.32</td>
<td>0.63</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Note: The effective chamber volume (V) for all carpet tests was 0.051 m³.
Table 3 Experimental results – tetrachloroethylene and wallboard, ceiling tile, and pillow

<table>
<thead>
<tr>
<th>Sink material</th>
<th>ACH</th>
<th>C_e (mg/m³)</th>
<th>M_e (mg/m³)</th>
<th>k_e (m/h)</th>
<th>k_f (h⁻¹)</th>
<th>k_s (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wallboard</td>
<td>0.982</td>
<td>19.2</td>
<td>2.67</td>
<td>0.22</td>
<td>1.6</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>0.994</td>
<td>25.8</td>
<td>3.79</td>
<td>0.20</td>
<td>1.4</td>
<td>0.15</td>
</tr>
<tr>
<td>Ceiling tile</td>
<td>1.03</td>
<td>22.6</td>
<td>3.68</td>
<td>0.09</td>
<td>0.54</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>1.03</td>
<td>28.4</td>
<td>4.61</td>
<td>0.11</td>
<td>0.69</td>
<td>0.16</td>
</tr>
<tr>
<td>Pillow</td>
<td>0.923</td>
<td>28.4</td>
<td>6.32</td>
<td>0.02</td>
<td>0.09</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>0.925</td>
<td>28.6</td>
<td>8.17</td>
<td>0.03</td>
<td>0.11</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Notes:
1) The sample area (A) for the wallboard and ceiling tile was 0.14 m²; for the pillow, 0.266 m².
2) The effective chamber volume (V) for the wallboard and ceiling tile tests was 0.051 m³; for the pillow, 0.046 m³.

Table 4 Experimental results – ethylbenzene and carpet, wallboard, ceiling tile, and pillow

<table>
<thead>
<tr>
<th>Sink material</th>
<th>ACH</th>
<th>C_e (mg/m³)</th>
<th>M_e (mg/m³)</th>
<th>k_e (m/h)</th>
<th>k_f (h⁻¹)</th>
<th>k_s (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carpet</td>
<td>0.945</td>
<td>8.2</td>
<td>7.79</td>
<td>0.07</td>
<td>0.08</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>0.982</td>
<td>8.6</td>
<td>8.29</td>
<td>0.08</td>
<td>0.08</td>
<td>0.96</td>
</tr>
<tr>
<td>Wallboard</td>
<td>0.975</td>
<td>11.4</td>
<td>3.40</td>
<td>0.58</td>
<td>1.9</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>0.949</td>
<td>12.7</td>
<td>3.83</td>
<td>0.32</td>
<td>1.1</td>
<td>0.30</td>
</tr>
<tr>
<td>Ceiling tile</td>
<td>0.971</td>
<td>9.8</td>
<td>4.30</td>
<td>0.25</td>
<td>0.58</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>0.988</td>
<td>11.2</td>
<td>4.26</td>
<td>0.23</td>
<td>0.60</td>
<td>0.38</td>
</tr>
<tr>
<td>Pillow</td>
<td>0.956</td>
<td>7.6</td>
<td>1.73</td>
<td>0.004</td>
<td>0.018</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>0.991</td>
<td>10.7</td>
<td>3.41</td>
<td>0.005</td>
<td>0.015</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Notes:
1) The sample area (A) for the carpet, wallboard, and ceiling tile was 0.14 m²; for the pillow, 0.266 m².
2) The effective chamber volume (V) for the carpet, wallboard, and ceiling tile tests was 0.051 m³; for the pillow, 0.046 m³.

Table 5 Average adsorption and desorption rate constants and equilibrium constants – Langmuir isotherm model

<table>
<thead>
<tr>
<th></th>
<th>Rate constant</th>
<th>Carpet</th>
<th>Carpet (35 °C)</th>
<th>Wallboard</th>
<th>Ceiling tile</th>
<th>Pillow</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE*</td>
<td>k_e (m/h)</td>
<td>0.13</td>
<td>0.30</td>
<td>0.21</td>
<td>0.10</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>k_f (h⁻¹)</td>
<td>0.13</td>
<td>0.59</td>
<td>1.5</td>
<td>0.61</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>k_s (m)</td>
<td>0.97</td>
<td>0.52</td>
<td>0.14</td>
<td>0.16</td>
<td>0.25</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>k_e (m/h)</td>
<td>0.08</td>
<td>—</td>
<td>0.45</td>
<td>0.24</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>k_f (h⁻¹)</td>
<td>0.08</td>
<td>—</td>
<td>1.5</td>
<td>0.59</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>k_s (m)</td>
<td>0.95</td>
<td>—</td>
<td>0.30</td>
<td>0.41</td>
<td>0.27</td>
</tr>
</tbody>
</table>

*Tetrachloroethylene = Perchloroethylene (PCE)

Note: All tests were conducted at 23 °C, except where noted.
chloroethylene; Table 3 presents the results for the remainder of the tetrachloroethylene experiments; Table 4 provides information on the experiments conducted with ethylbenzene; Table 5 presents a summary of the Langmuir rate constants for all the tests. Note that the tests conducted on the empty chamber and on window glass showed no sink effect, so no results are presented for these experiments.

Discussion

Applicability of Langmuir Isotherm

Figure 5 presents a least squares plot of $M_e$ vs. $C_e$ for tetrachloroethylene and carpet at 23 °C. The plot shows a linear relationship with a slope of 0.97 and an $r^2$ correlation of 0.97. This linearity confirms the applicability of the Langmuir equilibrium at low concentrations represented by equations (3) and (5) [i.e., $M_e = (k_c/k_d)C_e = k_eC_e$], with the slope of the line equal to the average $k_e$ value for the 10 tests (see Table 5).

Fitting the kinetic data (i.e., C vs. t) using equations (19) and (21) to obtain $k_c$ and $k_d$ values based on a Langmuir sorption process shows a good fit for ceiling tile and wallboard (see Figure 3). On the other hand, the fit of the data for the pillow and carpet data indicates that the desorption process for these materials deviates from the Langmuir assumptions (see Figure 4). Thus, it appears that Langmuir kinetics apply to relatively flat, smooth surfaces (e.g., ceiling tile, wallboard), but may be inappropriate for more complex surfaces (e.g., carpet and upholstery). In spite of the relatively poor fit of the kinetic data for carpet and pillow, it is felt that the values of $k_{eq}$, $k_{d0}$, and $k_c$ for these materials can be used to compare their sorption behaviour with other materials and to compare the sink effects of different compounds.

Sink Strength

The capability of a sink material to adsorb indoor air pollutants is represented by $k_e$; the higher the $k_e$ value, the greater the mass adsorbed on the sink at a given concentration (i.e., the stronger the sink). An analysis of variance (AOV) of the $k_e$ values in Tables 2 - 4 shows a significant ($p = 0.06$) COMPOUND X MATERIAL interaction (i.e., the differences in the $k_e$ values among the materials depend on the compound). Carpet was a significantly stronger sink ($p < 0.01$) than the other three materials for both compounds, while no significant differences in $k_e$ were detectable ($p = 0.01$) among the other three materials for either compound. As stated previously, glass was not a sink for either compound.
The sink strengths of the two compounds tested are also different. Ceiling tile adsorbed significantly more (p < 0.01) ethylbenzene than tetrachloroethylene. A similar trend (p = 0.05) was evident for wallboard. For carpet and pillow, no differences (p = 0.79 and p = 0.80, respectively) in sink strength were observed between the two compounds.

**Adsorption and Desorption Rates**

Values for $k_s$ and $k_d$ were analysed to determine differences in adsorption and desorption rates for the materials and compounds tested. An AOV indicated a significant MATERIAL X COMPOUND interaction for $k_s$ (p < 0.01), but not for $k_d$ (p = 0.99). Other findings include:

- wallboard and ceiling tile adsorbed ethylbenzene at significantly higher rates (p < 0.01) than carpet and pillow. Ethylbenzene adsorption by wallboard was faster than by ceiling tile; the adsorption rates for carpet and pillow were not significantly different;
- wallboard adsorbed tetrachloroethylene at significantly higher rates (p < 0.01) than the pillow, with carpet and ceiling tile representing intermediate, but indistinguishable, values;
- ethylbenzene adsorbed at a significantly higher rate than tetrachloroethylene on the wallboard (p < 0.01) and ceiling tile (p < 0.01). There were no significant differences in the adsorption rates for the two compounds for carpet (p = 0.22) and pillow (p = 0.68);
- wallboard desorbed at a significantly higher rate (p < 0.01) than the other three materials. Ceiling tile desorbed at a significantly higher rate (p < 0.01) than carpet and pillow, which are indistinguishable;
- there was no significant difference (p = 0.56) in the desorption rates for ethylbenzene and tetrachloroethylene for any of the sink materials.

**Effect of Temperature**

Only limited data were collected to investigate the effect of temperature. Based on thermodynamics, both the adsorption and desorption rates should be higher at elevated temperatures. The values for $k_s$ and $k_d$ for the tetrachloroethylene/carpet tests conducted at 35 °C indeed show significantly higher values (p < 0.001) than those observed at 23 °C. The significantly lower value of $k_s$ at 35 °C occurred because the desorption rate was elevated more than the adsorption rate.

**Practical Implications**

The data presented herein, while limited, do confirm that common indoor materials absorb and subsequently re-emit vapour phase organic compounds. The type of material and compound affects the rates of adsorption and desorption as well as the amount of material adsorbed.

Recent experiments conducted at an indoor air quality (IAQ) test house (Jackson et al, 1987) provide further confirmation of the importance of indoor sinks. A wood stain was applied to a bare oak floor, and the concentration of total vapour phase organics (based on sampling with Tenax/charcoal and analysis with gas chromatograph/flame ionization detector) was followed over time as shown in Figure 6.

An IAQ model (Sparks, 1988) was used to evaluate the data. The emission rate of total organics from the stain was calculated from:

$$ ER_{tot} = ER_{app} + ER_{s} e^{-kt} $$

where, $ER_{tot}$ is the total emission rate (mg/m²-h); $ER_{app}$ is the emission rate during the application of the product (mg/m²-h); $ER_{s}$ is the initial emission rate of the drying phase (mg/m²-h); $k$ is the decay constant for the emission rate during drying (h⁻¹); and $t$ is the time (h). The following values were used: $ER_{app} = 15,000$ mg/m²-h for the first 0.4 hours; $ER_{s} = 17,000$ mg/m²-h; $k = 0.4$ h⁻¹.
The value for ER_{app} was developed from ongoing experiments; the values for ER, and k were obtained from chamber tests (Tichenor and Guo, 1988).

Figure 6 shows the results of the model runs for three cases: (a) assuming no sink effect; (b) assuming Langmuir type sinks; and (c) assuming re-emitting sinks are non-Langmuir (noted as “Best Fit”). Note that the prediction assuming “no sink” fails to account for the increased concentration due to the re-emitting sinks after the first few hours of the test.

The curve labelled “Langmuir sink” was predicted by the model with the sink behaviour described by equation (17) and using the chamber derived values for k_s and k_i based on the ethylbenzene tests. The test house carpet values (k_s = 0.08 m/h; k_i = 0.08 h^{-1}) were taken directly from the chamber data. Single values for all wall and ceiling surfaces (k_s = 0.35 m/h; k_i = 1.0 h^{-1}) were based on averages of the wallboard and ceiling tile chamber data. The “Langmuir sink” curve does indicate re-emissions from the sinks, but it does not adequately predict the time history of these re-emissions. The failure of the Langmuir isotherm data to accurately predict the sink behaviour could be caused by several factors:

- the ethylbenzene data do not properly account for the sink behaviour of the complex petroleum-based solvent emitted from the stain;
- the test house sink surfaces are different and more complex than the surfaces evaluated in the chambers; and
- the desorption behaviour is not adequately defined by a Langmuir process. (Note the previous discussion of the poor fit of the chamber kinetic data for carpet and pillow.)

The curve labelled “Best Fit” was predicted by the model assuming all sink surfaces behaved according to a Langmuir adsorption process and a non-Langmuir desorption process. The rate of change of mass in the sink was described by:

\[
\frac{dM}{dt} = k_s C_A - k_d (M_i)^n A
\] 

(23)

where, k_s and A have been previously defined; C_A is the concentration at time t (mg/m^3); k_d is the desorption rate constant; M_i is the mass in the sink at time t (mg/m^2); and n is an empirical constant. Note that the desorption portion of this equation is analogous to a Freundlich isotherm described previously [see equation (6)]. The following
values, obtained from analyses of the chamber data for ethylbenzene/carpet, were used in the IAQ model: \( k_a = 0.1 \text{ m/h}; k_d^* = 0.004; \) and \( n = 1.5. \) The fit of the model (see the “Best Fit” line) is quite good for the sink behaviour described by equation (23). The theoretical basis for this equation is weak, and further research is required to refine this approach.

**Conclusions**

Experiments conducted to examine the behaviour of indoor sinks vis-à-vis vapour phase organic compounds have clearly shown adsorption to and re-emission from common indoor materials for two typical indoor air pollutants. Of the five materials tested, only window glass had no measurable sink effect. Both the type of material and the type of organic compound affect the rates of adsorption and desorption, as well as the equilibrium mass in the sink. Higher temperatures increase both the adsorption and desorption rate constants. Fundamental Langmuir adsorption theory appears adequate to describe the behaviour of smooth materials, such as wallboard and ceiling tile. The desorption kinetics of rough, complex materials, such as carpet and upholstery, appear to be governed by non-Langmuir processes. Experiments conducted in an IAQ test house confirm the importance of sinks in controlling the levels of vapour phase organics over extended periods. If appropriate adjustments are made to account for non-Langmuir desorption processes, IAQ models can adequately predict the impact of sinks on the concentration/time history in full scale (i.e., test house) environments.

**Research Needs**

Further research is needed to increase understanding of the behaviour of indoor sinks with respect to vapour phase organic compounds:

- examination of the equilibrium and kinetic behaviour of additional sink materials and additional organic compounds, including mixtures of vapour phase organics;
- evaluation of the behaviour of sinks under a wider range of conditions (i.e., temperature, humidity, concentration);
- examination of the behaviour of sinks exposed to dynamic, non-steady source emissions;
- development of sink models that account for non-Langmuir desorption processes. Such models should be capable of predicting re-emissions from sinks over long periods (e.g., for weeks or months);
- incorporation of sink models into IAQ models and validation in full-scale indoor environments. Methods for simplifying complex, multiple sinks and for dealing with vapour phase organic mixtures are needed.

*A preliminary version of this paper was presented at the Fifth International Conference on Indoor Air Quality and Comfort, Toronto, Canada, July 1990.*
References


