Characterizing Exposure to Indoor VOCs and SVOCs using Simple Mass-Transfer Models

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Characterizing Sources

- Too many materials and products for emissions to be individually measured
- Develop mechanistic mass-transfer models for generic source types
- Independently measure model parameters
- Collect experimental data in small chambers to validate models
- Develop correlation equations to predict model parameters based on compound properties (molecular weight and vapor pressure)
- Use models to predict exposure
Three Generic Source Models

- Liquid Source $\rightarrow$ VOC – Nonane in Coating Materials (Guo et al., 1999)
- Solid Source $\rightarrow$ VOC – Phenol in Vinyl Flooring (Cox et al., 2002)
- Solid Source $\rightarrow$ SVOC – DEHP in Vinyl Flooring (Xu and Little, 2006)
Liquid Source $\rightarrow$ VOC

\[ y_{in} = 0, Q \]

\[ q = K_{s}y \]

\[ y(t) \]

\[ P_i = x_i P_{i}^{vap} \]

\[ h \]

Solvent Mixture
Model Validation
(Nonane in Coating Material)

![Graph showing nonane concentration over time with Guo's Model prediction and experimental data.](image)
"Solid" Source $\rightarrow$ VOC

$y_{in} = 0, Q$

$q = K_s y$

$V y(t)$

$C_{(x=L)} = K y_0$

$x = L$

$x = 0$

$D$

$y(t), Q$

$x$

$C_0$
Model Validation
(Pentadecane in Vinyl Flooring)

Gas-phase Concentration  Material-phase Concentration

![Graph showing gas-phase concentration over time and normalized concentration against depth.](image-url)
"Solid" Source → SVOC

\[ y_{in} = 0, Q \]

\[
q = K_s y
\]

\[
V \ y(t)
\]

\[
C_0 = K y_0
\]

\[
x = 0
\]

\[
x = L
\]
Model Validation
(DEHP in VF)

![Graph showing Model Predicted vs Experiment for Gas Phase Concentration over Time]

- **X-axis**: Time (days)
- **Y-axis**: Gas phase concentration (μg/m³)

Key:
- Red circles: Experiment
- Blue line: Model predicted

The graph illustrates the comparison between the experimental data and the model predictions for gas phase concentration over time. The concentration values range from approximately 0.1 to 0.8 μg/m³, with the model predictions showing a good fit to the experimental data.
Comparison of Three Models (nonane, phenol, and DEHP)

![Graph showing gas phase concentration over time for different VOC sources. The graph includes data for VOC from Coating Materials, VOC from Vinyl Flooring, and SVOC from Vinyl Flooring. The x-axis represents time in hours, with markers indicating hours, months, and years. The y-axis represents gas phase concentration in µg/m³, with a range from 1 µg/m³ to 500 mg/m³.](image-url)
Mechanistic Insights

- Gas-phase concentration is proportional to material-phase concentration, so $x_i$ and $C_0$ are the most important parameters.

- External mass-transfer coefficient ($h$) can be estimated.

- Diffusion coefficient ($D$) correlates with molecular weight, while partition coefficients ($K$ and $K_s$) correlate with vapor pressure. Once values are known for a few compounds, can develop correlations and predict others.

- Because of strong surface sorption, emission and transport of SVOCs depend more on specific residential environment than for VOCs.
Example of SVOC Emissions

- Di-ethylhexyl phthalate (DEHP) used as plasticizer in vinyl flooring.
- Emits slowly, but over very long period.
- Toxicity of phthalates is of concern.
- Extend model validated for small chamber to predict emissions and exposure in residential environment.
- Account for sorption of DEHP by airborne particles as well as interior surfaces.
Effect of Airborne Particles

VOCs

SVOCs
DEHP Emissions + Airborne Particles

\[ y_{in} = 0, \ TSP, \ Q \]

\[ q = K_s y \]

\[ q_p = K_p y_{TSP} \]

\[ V \ y(t) \]

\[ C_0 = K y_0 \]

\[ x = L \]

\[ x = 0 \]

\[ y(t), \ TSP, \ Q\]
Making model more representative of real indoor environment
Two-Room Model

Room 1
- Particles
- Ceiling
- Glass window
- Vinyl Flooring
- $y_1$, TSP, $Q$

Room 2
- Particles
- Ceiling
- Wall
- Glass window
- Wood furniture
- Carpet
- $y_2$, TSP, $Q$

$V_1$, $V_2$
Sorption of DEHP to Interior Surfaces and Dust

• **EPA CTEPP study**
  – 300 homes and day care centers in NC and OH
  – 50 pollutants
  – air, house dust, interior surfaces, and dermal wipe samples

• **Top three high surface conc.**
  – BBP, benzyl butyl phthalate
  – DBP, dibutyl phthalate
  – BPA, bisphenol-A
  – No DEHP data
CTEPP Data

I: hardwood floor surface
II: transferable residues from carpet
III: hand wipe of children
IV: hand wipe of adults
Linear regression to obtain $K_s$ for DBP

- $C_{\text{hard floor}} = 21.1 \, \text{y}$
  - $R^2 = 0.76$, $p$-value $= 6.68e-3$

- $C_{\text{surf}} = 44.9 \, \text{y}$
  - $R^2 = 0.61$, $p$-value $< 2e-16$

- $C_{\text{dust}} = 44.9 \, \text{y}$
  - $R^2 = 0.61$, $p$-value $< 2e-16$

- $C_{\text{dust}} = 21.9 \, \text{y}$
  - $R^2 = 0.68$, $p$-value $< 2e-16$
Correlation of partition coefficient with $V_p$

**Hard floor surface**

$log K_{surf} = -0.779 \log V_p - 1.93$

$R^2 = 0.76$

**Transfer residue from carpet**

$log K_{surf} = -0.627 \log V_p - 1.08$

$R^2 = 0.70$

**Skin**

$log K_{surf} = -1.06 \log V_p - 3.30$

$R^2 = 0.97$

**Dust**

$log K_{p, dust} = -1.27 \log V_p - 4.37$

$R^2 = 1$
Residential Environment
Residential Environment

Source
Vinyl flooring

Sinks
Particles
Walls and Ceilings
Carpets
Wood floors

Bathroom
$y_b$, $V_b$

Main House
$y_a$, $V_a$

Kitchen
$y_k$, $V_k$

$Q_{oa}$, $Q_{ao}$

$Q_{ob}$, $Q_{bo}$

$Q_{oa}$

$Q_{ba}$

$Q_{k}o$

$Q_{ok}$
# Residential Environment

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Main house</th>
<th>Kitchen</th>
<th>Bathroom</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume</strong></td>
<td>128</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td><strong>Flowrate</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$Q_{oa}$</td>
<td>44</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>$Q_{aa}$</td>
<td>65</td>
<td>12</td>
<td>1.1</td>
</tr>
<tr>
<td>$Q_{ko}$</td>
<td>32</td>
<td>34</td>
<td>2.1</td>
</tr>
<tr>
<td>$Q_{ak}$</td>
<td>44</td>
<td>44</td>
<td>14</td>
</tr>
<tr>
<td>$Q_{ka}$</td>
<td>24</td>
<td>24</td>
<td>13</td>
</tr>
<tr>
<td><strong>Surface area</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinyl flooring</td>
<td>19.2</td>
<td>14.4</td>
<td>6.20</td>
</tr>
<tr>
<td>Walls &amp; Ceilings</td>
<td>124</td>
<td>34.0</td>
<td>23.3</td>
</tr>
<tr>
<td>Carpet</td>
<td>35.8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Wood floor</td>
<td>32.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Hard surface furniture</td>
<td>61.4</td>
<td>12.6</td>
<td>5.40</td>
</tr>
<tr>
<td>Windows &amp; mirrors</td>
<td>5.12</td>
<td>1.75</td>
<td>1.05</td>
</tr>
<tr>
<td>Tile &amp; ceramic fixtures</td>
<td>5.12</td>
<td>3.50</td>
<td>16.5</td>
</tr>
<tr>
<td>TSP</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>
Model results

![Graph showing concentration and emission rate over time for Bathroom, Kitchen, and Main house]
## Model results

<table>
<thead>
<tr>
<th>DEHP</th>
<th>References</th>
<th>n</th>
<th>Mean</th>
<th>Max</th>
<th>Our study</th>
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</thead>
<tbody>
<tr>
<td><strong>Gas phase Conc.</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(μg/m³)</td>
<td>Bauch, 1991</td>
<td>40</td>
<td>0.4</td>
<td>1.6</td>
<td>0.1~0.18</td>
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<tr>
<td></td>
<td>Sheldon et al., 1994</td>
<td>125</td>
<td>0.14</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rudel et al., 2003</td>
<td>102</td>
<td>0.07</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fromme et al., 2004</td>
<td>59</td>
<td>0.19</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td><strong>Dust phase Conc.</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(μg/g)</td>
<td>Bauch, 1991</td>
<td>12</td>
<td>950</td>
<td>3100</td>
<td>2000~3500</td>
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<td></td>
<td>Mattulat et al., 2002</td>
<td>600</td>
<td>1200</td>
<td>3500</td>
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<tr>
<td></td>
<td>Rudel et al., 2003</td>
<td>101</td>
<td>340</td>
<td>7700</td>
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</tr>
<tr>
<td></td>
<td>Fromme et al., 2004</td>
<td>30</td>
<td>780</td>
<td>1800</td>
<td>25</td>
</tr>
</tbody>
</table>
Exposure in Residential Environment

Exposure pathways:
- Inhalation of vapor and particles
- Dermal absorption of DEHP from air
- Oral ingestion of household dust

![Graph showing exposure levels over time for children and adults, with inhalation, dermal, and oral exposure pathways, and an RfD value marker.](image-url)
# Sensitivity Analysis

<table>
<thead>
<tr>
<th>Variables</th>
<th>Baseline Value</th>
<th>Exposure pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inhalation</td>
</tr>
<tr>
<td>DEHP concentration in vinyl floor (C₀, µg/m³)</td>
<td>2.55×10¹¹</td>
<td>1.00</td>
</tr>
<tr>
<td>Vinyl floor thickness (L, mm)</td>
<td>2</td>
<td>0.00</td>
</tr>
<tr>
<td>Partition coefficient (K_{vinyl/air})</td>
<td>2.3×10¹¹</td>
<td>-0.50</td>
</tr>
<tr>
<td>Mass transfer coefficient for flat surfaces (h, cm/s)</td>
<td>0.1</td>
<td>0.82</td>
</tr>
<tr>
<td>Total suspended particle concentration (TSP, µg/m³)</td>
<td>20</td>
<td>0.07</td>
</tr>
<tr>
<td>Partition coefficient (K_{particle/air}, m³/µg)</td>
<td>0.25</td>
<td>0.07</td>
</tr>
<tr>
<td>Mass transfer coefficient for particles (h_p, cm/s)</td>
<td>14</td>
<td>0.00</td>
</tr>
<tr>
<td>Partition coefficient (K_{dust/air}, m³/g)</td>
<td>21100</td>
<td>0.00</td>
</tr>
<tr>
<td>Inhalation rate (IR, m³/day)</td>
<td>6.8</td>
<td>1.00</td>
</tr>
<tr>
<td>Exposure duration in kitchen (ED₁, hr/day)</td>
<td>1</td>
<td>0.07</td>
</tr>
<tr>
<td>Exposure duration in bathroom (ED₂, hr/day)</td>
<td>0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>Exposure duration in main house (ED₃, hr/day)</td>
<td>16.5</td>
<td>0.88</td>
</tr>
<tr>
<td>Skin surface area (SA, m²)</td>
<td>0.59</td>
<td>0.00</td>
</tr>
<tr>
<td>Overall skin permeability coefficient of gases (P, cm/hr)</td>
<td>580</td>
<td>0.00</td>
</tr>
<tr>
<td>Daily intake rate of dust (DIR, mg/kg/day)</td>
<td>10.3</td>
<td>0.00</td>
</tr>
<tr>
<td>Body weight (kg)</td>
<td>11</td>
<td>-0.50</td>
</tr>
<tr>
<td>Air exchange rate for three compartments</td>
<td>0.5</td>
<td>-0.46</td>
</tr>
</tbody>
</table>
# Uncertainty Analysis

<table>
<thead>
<tr>
<th>Variables</th>
<th>Min</th>
<th>Max</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEHP concentration in vinyl floor (C₀, µg/m³)</td>
<td>2.25×10¹¹</td>
<td>6.0×10¹¹</td>
<td>Clausen et al., 2004; Deisinger et al., 1998</td>
</tr>
<tr>
<td>Partition coefficient (K_{vinyl/air})</td>
<td>2.05×10¹¹</td>
<td>5.45×10¹¹</td>
<td>--</td>
</tr>
<tr>
<td>Mass transfer coefficient for flat surfaces (h, cm/s)</td>
<td>0.03</td>
<td>0.29</td>
<td>Huang et al., 2004; Lin et al., 2004; Carmeliet et al., 2003</td>
</tr>
<tr>
<td>Total suspended particle concentration (TSP, µg/m³)</td>
<td>12</td>
<td>66</td>
<td>Weschler et al. 2007</td>
</tr>
<tr>
<td>Partition coefficient (K_{particle/air}, m³/µg)</td>
<td>0.215</td>
<td>0.28</td>
<td>Naumova et al. 2003</td>
</tr>
<tr>
<td>Partition coefficient (K_{dust/air}, m³/g)</td>
<td>2000</td>
<td>4×10⁴</td>
<td>Rudel et al. 2001; Weschler et al. 2007</td>
</tr>
<tr>
<td>Inhalation rate (IR, m³/day)</td>
<td>5</td>
<td>14.5</td>
<td>Pastenbach, 2000</td>
</tr>
<tr>
<td>Exposure duration in main house (ED₃, hr/day)</td>
<td>12.6</td>
<td>18.1</td>
<td>Hubal et al., 2000</td>
</tr>
<tr>
<td>Skin surface area (SA, m²)</td>
<td>0.59</td>
<td>1.7</td>
<td>EPA, 1997</td>
</tr>
<tr>
<td>Overall skin permeability coefficient of gases (P, cm/hr)</td>
<td>56</td>
<td>1035</td>
<td>De Dear et al. 1997</td>
</tr>
<tr>
<td>Daily intake rate of dust (DIR, mg/kg/day)</td>
<td>1.03</td>
<td>10.3</td>
<td>Wensing et al., 2005</td>
</tr>
<tr>
<td>Body weight (kg)</td>
<td>9.15</td>
<td>62.2</td>
<td>EPA, 1997</td>
</tr>
<tr>
<td>Air exchange rate for three compartments</td>
<td>0.1</td>
<td>1.1</td>
<td>Wallace et al., 2002</td>
</tr>
<tr>
<td>Vinyl flooring area in kitchen (A₁_{vinyl}, m²)</td>
<td>11.9</td>
<td>47.6</td>
<td>Hodgson et al., 2004</td>
</tr>
<tr>
<td>Vinyl flooring area in bathroom (A₂_{vinyl}, m²)</td>
<td>5.1</td>
<td>20.4</td>
<td>Hodgson et al., 2004</td>
</tr>
<tr>
<td>Vinyl flooring area in main house (A₃_{vinyl}, m²)</td>
<td>2.56</td>
<td>44.8</td>
<td>Hodgson et al., 2004</td>
</tr>
</tbody>
</table>
Uncertainty Analysis

![Graph showing cumulative frequency vs. exposure (μg/kg/d) for different routes of exposure: Inhalation, Dermal, Oral, and Total.]
Concluding Remarks

- Several generic models have been developed and rigorously validated.
- Initial material-phase concentration is most important model parameter.
- Other parameters are either not so important or could be quickly estimated once a few values are known.
- Procedures to measure model parameters are available or are being developed.
- With some investment, this approach could be applied to rapidly estimate screening-level exposure to wide range of compounds in many materials and products.
- Couple with screening-level toxicity estimates from ToxCast to estimate risk and prioritize further action.
Key References

Financial Support

• Little, J. C. Mass Transfer Modeling of Volatile Organic Emissions from Building Materials, National Science Foundation – CAREER Award, 7/15/96 – 6/30/02, BES 9624488.

• Little, J. C. Designing Panelized Systems to Minimize Impact on Indoor Air Quality in Tightly-Sealed Buildings, National Science Foundation – PATH Award, 9/15/01 – 2/28/06, CMS 0122165.

• Little, J. C. and Marr, L. C. Emission of Phthalates from Vinyl Flooring and Interaction with Fine Particles, National Science Foundation, 9/01/05 – 8/31/08, BES 0504167.

• Little, J. C. and Marand, E. Developing Barrier Layers to Minimize Volatile Emissions from Structural Insulated Panels, National Science Foundation, 4/01/06 – 3/31/09, CMS 0600090.