Emissions of Phthalate Plasticizer from Polymeric Building Materials

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ABSTRACT

Modern indoor environments contain a vast array of contaminating sources. Emissions from these sources produce contaminant concentrations that are substantially higher indoors than outside. Because we spend most of our time indoors, exposure to indoor pollutants may be orders-of-magnitude greater than that experienced outdoors. Phthalate esters have been recognized as major indoor pollutants. They are mainly used as plasticizers to enhance the flexibility of polyvinylchloride (PVC) products, as well as in humectants, emollients, and antifoaming agents. Phthalates are found in a wide range of consumer products including floor and wall coverings, car interior trim, floor tiles, gloves, footwear, insulation on wiring, and artificial leather. Because these phthalate additives are not chemically bound to the polymer matrix, slow emission from the products to the surrounding air or other media usually occurs.

Biomonitoring data suggest that over 75% of the U.S. population is exposed to phthalates. The ubiquitous exposure to phthalates is of concern because toxicological investigations have demonstrated considerable adverse health effects of phthalates and their metabolites. Studies have shown that exposure to phthalates results in profound and irreversible changes in the development of the reproductive tract, especially in males, raising the possibility that phthalate exposures could be the leading cause of reproductive disorders in humans. In addition, effects such as increases in prenatal mortality, reduced growth and birth weight, skeletal, visceral, and external malformations are possibly associated with phthalate exposure. Epidemiologic studies in children also show associations between phthalate exposure in the home and the risk of asthma and allergies.

Given the ubiquitous nature of phthalates in the environment and the potential for adverse human health impacts, there is a critical need to understand indoor emissions of phthalates and to identify the most important sources and pathways of exposure.

In this study, a model that integrates the fundamental mechanisms governing emissions of semi-volatile organic compounds (SVOCs) from polymeric materials and their subsequent interaction with indoor surfaces and airborne particles was developed. The emissions model is consistent with analogous mechanistic models that predict emission of volatile organic compounds (VOCs) from building materials. Reasonable agreement between model predictions and gas-phase di-2-ethylhexyl phthalate (DEHP) concentrations was achieved for data collected in a previously published experimental study that measured emissions of DEHP from vinyl flooring in two very different chambers. The analysis showed that while emissions of highly volatile VOCs are subject to "internal" control (through the material-phase diffusion coefficient), emissions of the very low volatility SVOCs are subject to "external" control (through partitioning into the gas phase, the convective mass transfer coefficient, and adsorption onto interior surfaces).

Because of the difficulties associated with sampling and analysis of SVOCs, only a few chamber studies quantifying their emissions from building materials and consumer products are available. To more rigorously validate the SVOCs emission model and more completely understand the mechanisms governing the release of phthalate from polymeric building materials, the emission of DEHP from vinyl flooring was studied for up to 140 days in a specially-designed stainless steel chamber. In the duplicate chamber study, the gas-phase concentration in the chamber increased slowly and reached a steady state level of 0.9 $\mu g/m^3$ after 30 days. By increasing the area of vinyl flooring and decreasing that of the stainless steel surface in the chamber, the time to reach steady state was significantly reduced, compared to the previous study (1 month vs. 5 months). The adsorption isotherm of DEHP on the interior stainless steel chamber surface was explicitly measured using two different methods (solvent extraction and thermal desorption). Strong adsorption of DEHP onto the stainless steel surface was observed and found to follow a simple linear relationship. In addition, parameters measured in the experiments were then applied in the fundamental SVOCs emission model. Good agreement was obtained between the predictions of the model and the gas-phase DEHP chamber concentrations, without resorting to fitting of model parameters.

These chamber studies have shown that the tendency of SVOCs to adsorb strongly to interior surfaces has a very strong influence on the emission rate. Compared to the experimental chamber systems, however, the real indoor environment has many other types of surface that will adsorb phthalates to different extents. The emission rate measured in a test chamber may therefore be quite different to the emission rate from the same material in the indoor environment. For this reason, both a two-room model and a more representative three-compartment model were developed successively to estimate the emission rate of DEHP from vinyl flooring, the evolving gas-phase and adsorbed surface concentrations, and human exposures (via inhalation, dermal absorption and oral ingestion of dust) in a realistic indoor environment. Adsorption isotherms for phthalates and plasticizers on interior surfaces, such as carpet, wood, dust and human skin, were derived from previous field and laboratory studies. A subsequent sensitivity analysis revealed that the vinyl flooring source characteristics, as well as mass-transfer coefficients and ventilation rates, are important variables influencing the steady-state DEHP concentration and resulting exposures. A simple uncertainty analysis suggested that residential exposure to DEHP originating from vinyl flooring may fall somewhere between about 5 μg/kg/d and 180 μg/kg/d. The roughly 40-fold range in exposure reveals the inherent difficulty in using biomonitoring results to identify specific sources of exposure in the general population.

This research represents the first attempt to explicitly elucidate the fundamental mechanisms governing the release of phthalates from polymeric building materials as well as their subsequent interaction with interior surfaces. The mechanistic models developed can most likely be extended to predict concentration and exposure arising from other sources of phthalates, other sources of other semi-volatile organic compounds (such as biocides and flame retardants), as well as emissions into other environmental media (food, water, saliva, and even blood). The results will be of value to architects, governments, manufacturers, and engineers who wish to specify low-emitting green materials for healthy buildings. It will permit health professionals to identify and control health risks associated with many of the SVOCs used in indoor materials and consumer products in a relatively inexpensive way.

ACKNOWLEDGEMENTS

DEDICATION

To my parents, Fengming Xu and Jinzhi Guo and

To my husband, Jian Tu

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Chapter 1: Predicting the Emission Rate of Volatile and Semi-Volatile Organic Compounds from Building Materials and Consumer Products – A Review

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ABSTRACT

Indoor emission source models have been developed and provide a more cost effective and powerful way to characterize emissions of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) from building materials and consumer products. The purpose of this paper is to conceptually review the existing material emission models, and to discuss the methods established for the estimation of model parameters. The models are classified into three categories: VOC emissions from coating materials (wet/VOC); VOC emissions from building materials (dry/VOC); and SVOC emissions from building materials (dry/SVOC). The three models are intimately related, but emissions are controlled by different parameters. Accordingly, the methods available to estimate the critical model parameters are different. Finally, the three types of emission processes are briefly compared.

INTRODUCTION

Modern living exposes us to a vast array of building materials and consumer products, many of which release volatile contaminants into the near-field environment. Sources of volatile organic compounds (VOCs) include adhesives, caulks, sealants, paints, solvents, wood stain, floor wax, carpets, textiles, wallboard, treated wood, urethane coatings, pressed-wood products, and vinyl flooring. Semi-volatile organic compounds (SVOCs),

such as plasticizers, flame retardants, and biocides, are added to many materials and products to enhance performance. For example, phthalate plasticizers are found in toys, medical equipment, paints, inks, vinyl flooring, hair sprays, deodorants, nail polish, perfumes, cling film, and shampoo, while flame retardants are found in computers, electronics, electrical equipment, cables, televisions, textiles, foam furniture, and insulating foams, and biocides are found in shower curtains.

Much progress has been made in developing an understanding of the mechanisms governing the behavior of many of these sources. Reviews of the suite of available models and the methods used to estimate the required model parameters have been published (Guo 2002a; 2002b; Haghighat et al. 2002; 2005). Those reviews focused on both relatively empirical and more fundamental mechanistic models. However, because the emission source models are mainly used for predictions, the usefulness of a model is often judged by whether the parameters can be readily estimated in the absence of experimental data (Guo 2002b). Fortunately, several relatively simple fundamental models that possess this characteristic have now been developed and validated. The present review will focus on these more recently developed physically-based, mass-transfer models, and the methods available to estimate the key model parameters. The models are classified into three categories: models for VOC emissions from "wet" materials (wet/VOC); models for VOC emissions from "dry" materials (dry/VOC); and models for SVOC emissions from "dry" materials (dry/SVOC). Providing mathematical models can be adequately validated, they may provide a more cost effective and powerful way to characterize emissions of VOCs and SVOCs from a wide range of building materials and consumer products.

INDOOR EMISSION SOURCE MODELS

Wet/VOC Model

Two mass transfer models were developed and validated to predict emissions from solvent mixtures and other petroleum-based indoor coatings. One, known as the vapor pressure and boundary layer (VB) model, is for total volatile organic compound (TVOC)

(Tichenor et al. 1993) and the other, known as the VBX model, for individual VOCs (Guo et al. 1998). With reference to Figure 1.1, the transient mass-balance on the VOC in the chamber air is

$$\frac{dy}{dt} \cdot V = AE - Qy \tag{1}$$
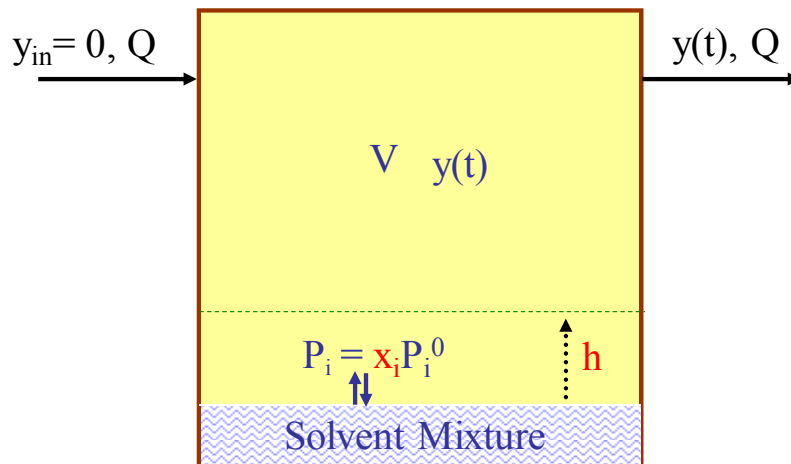
Figure 1.1 Schematic representation of the wet/VOC model

where y is the bulk gas-phase concentration of the VOC, V is the volume of the chamber, Q is the volumetric flow rate of air through the chamber, A is the surface area of the source, E is the emission rate of the specific VOC from the source, and t is time. The emission rate is controlled by mass-transfer through the external convective boundary layer, or

$$E = h(y_0 - y) \tag{2}$$

where y_0 is the gas-phase concentration of the VOC in equilibrium with the surface of the liquid source, and h is the convective mass-transfer coefficient. In the case of the VBX model (Guo et al., 1998) y_0 is equal to the partial pressure of the VOC expressed in terms of gas-phase concentration. It is obtained from Raoult's Law, or

$$P_i = x_i \cdot P_i^{sat} \tag{3}$$

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where for the i-th component of VOC in the liquid, P_i is the partial pressure, x_i is the mole fraction in the liquid, and P_i^{sat} is the vapor pressure of the pure liquid component. Because the various components may be present in the liquid mixture at different concentrations (or mole fractions), and have different liquid vapor pressures, the gas-phase concentration in equilibrium with the liquid (y_0) varies from component to component. This means that the emission rate for the individual components can also vary widely, causing the composition of the liquid mixture to change over time. To keep track of this change, an additional mass-balance equation for each component is employed:

$$\frac{dM}{dt} = -E \qquad (4)$$

where M is the mass of component i in the liquid mixture. Finally, an equation to predict the convective mass-transfer coefficient is required, or

$$h = 0.33 \cdot D_g \cdot L_c^{-(1/3)} \left(\frac{U \rho_g}{\mu_g} \right)^{2/3} \qquad (5)$$

where D_g is the diffusivity of the VOC in gas phase, L_c is the characteristic length of the source (equal to the square root of the source area), U is the air velocity over the source, and ρ_g and μ_g are the density and viscosity of air respectively. Figure 1.2 shows an example of nonane emissions from an alkyd primer, and confirms that the model prediction has excellent accuracy (Guo et al. 1998).
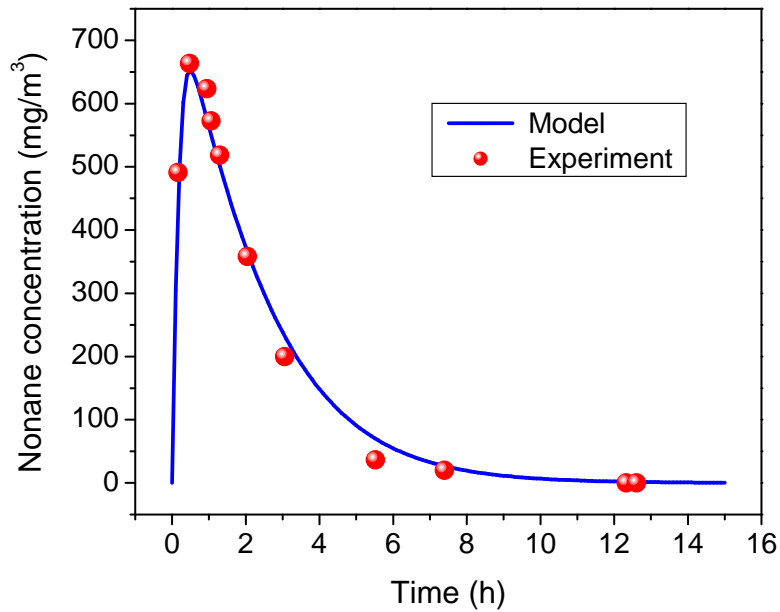
Figure 1.2 Predicted and measured nonane concentration in the alkyd primer test

Dry/VOC Model
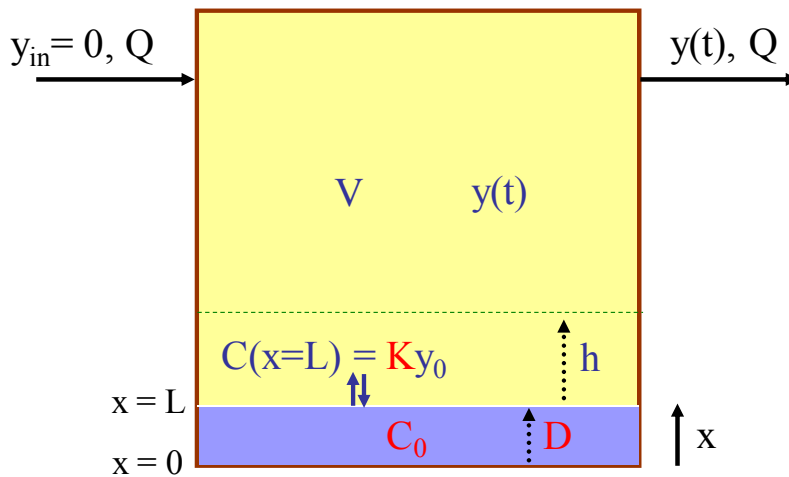
Figure 1.3 Schematic representation of the dry/VOC model

The model describing emissions from a homogeneous, diffusion-controlled source (Cox et al. 2002; Kumar and Little 2003; Little et al. 1994) is briefly reviewed. With reference to Figure 1.3, the transient diffusion equation is

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$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{6}$$

where C is the concentration of a VOC in the slab of material, D is the material-phase concentration-independent diffusion coefficient, t is time, and x is distance from the base of the slab. The initial condition assumes a uniform material-phase concentration of the VOC, C_0. The first boundary condition assumes there is no flux from the base of the slab. The second boundary condition is imposed via a mass balance on the VOC in the chamber air, or

$$\frac{\partial y}{\partial t}V = Q \cdot y_{in} - D \cdot A \left.\frac{\partial C}{\partial x}\right|_{x=L} - Q \cdot y \tag{7}$$

where y_{in} and y are the concentrations of the VOC in the influent and effluent chamber air respectively, Q is the volumetric air flow rate, V is the well-mixed chamber volume, A is the exposed surface area of the slab, and L is the thickness of the slab. A linear and instantaneously reversible equilibrium relationship is assumed to exist between the slab surface and the chamber air, or

$$K = \frac{\left.C\right|_{x=L}}{y} \tag{8}$$

where K is a material/air partition coefficient with units of mass per volume/mass per volume. The instantaneously reversible assumption implies that resistance to mass transfer between the material surface and the bulk chamber air is negligible. Although several subsequent models (Huang and Haghighat 2002; Xu and Zhang 2003; 2004; Yang et al. 2001) considered the resistance, it was found that, for VOCs, mass transfer through boundary layer largely influences only the initial time period of emissions. Combining Equation 7 and 8 and assuming y_{in} is zero, yields

$$\left(\frac{V}{A \cdot K}\right) \cdot \left.\frac{\partial C}{\partial t}\right|_{x=L} + D \cdot \left.\frac{\partial C}{\partial x}\right|_{x=L} + \left(\frac{Q}{A \cdot K}\right) \cdot \left.C\right|_{x=L} = 0 \tag{9}$$

A solution to these equations was given by Little et al. (1994):

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$$C(x,t) = 2C_0 \sum_{n=1}^{\infty} \left\{ \frac{\exp(-Dq_n^2 t)(h - kq_n^2)\cos(q_n x)}{\left[L(h - kq_n^2)^2 + q_n^2(L+k) + h \right]\cos(q_n L)} \right\} \qquad (10)$$

where

$$h = \frac{Q}{ADK} \qquad (11)$$

$$k = \frac{V}{AK} \qquad (12)$$

and the q_ns are the roots of

$$q_n \tan(q_n L) = h - kq_n^2 \qquad (13)$$

An analytical expression for the mass emission rate into the chamber air, E, may be derived from the expression for C(x, t) given in Equation 10, as follows:

$$E(t) = A \cdot J(x,t)\big|_{x=L} = -A \cdot D \cdot \frac{\partial C(x,t)}{\partial x}\bigg|_{x=L} \qquad (14)$$

where J(x, t) is the mass-transfer flux as a function of distance from the base of the slab and time. Figure 1.4 shows a comparison between model prediction and emissions of n-pentadecane from vinyl flooring (Cox et al. 2002).

Dry/SVOC Model

Attention is now turning to semi-volatile organic compounds (SVOCs) such as plasticizers, flame retardants, and biocides. These constituents are added to a variety of products to enhance performance and are often present at considerably higher concentrations than their more volatile counterparts. There are serious health concerns associated with SVOCs in general and phthalate plasticizers in particular. For example, recent research suggests that phthalates, including di-(2-ethylhexyl) phthalate (DEHP), may have a wide range of adverse effects on reproduction and development, including

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decreased fertility, birth defects, hormone disruption, and reproductive malformations, particularly in the male reproductive tract.
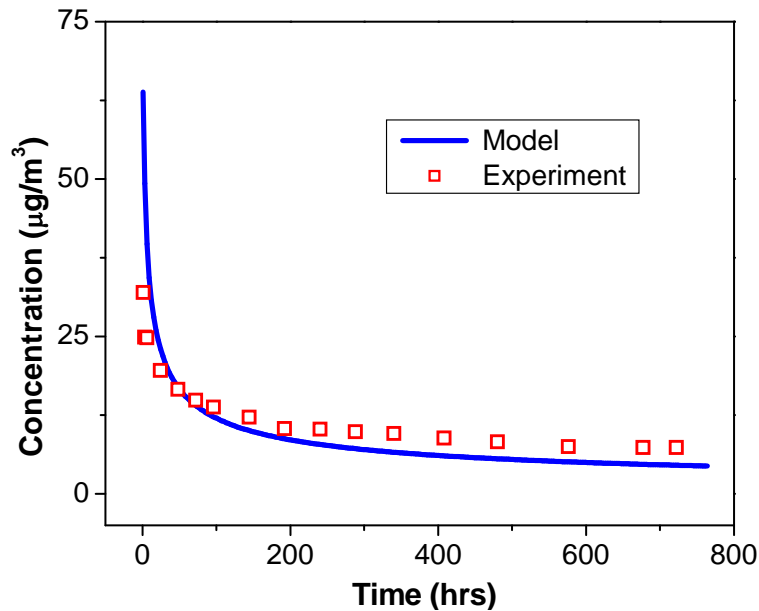
Figure 1.4 Predicted and measured chamber gas-phase n-pentadecane concentration.

The approach used is consistent with that developed previously for emissions of VOCs from building materials. A schematic representation of the idealized material slab placed in a test chamber is shown in Figure 1.5 (Xu and Little 2006). The governing equation describing transient diffusion through the slab is given by Equation 6. The diffusion coefficient D is again assumed to be independent of concentration. The initial condition also assumes that the SVOC is uniformly distributed through the material slab, and the lower boundary condition is a no flux condition. The upper boundary condition is

$$-D\frac{\partial C\,(x,t)}{\partial x} = h\left(y_0(t) - y(t)\right) \qquad \text{for } t>0,\ x=L \tag{15}$$

where h is the convective mass-transfer coefficient, y_0 is the concentration of the SVOC in the air immediately adjacent to the surface, and y is the gas-phase SVOC concentration in the well-
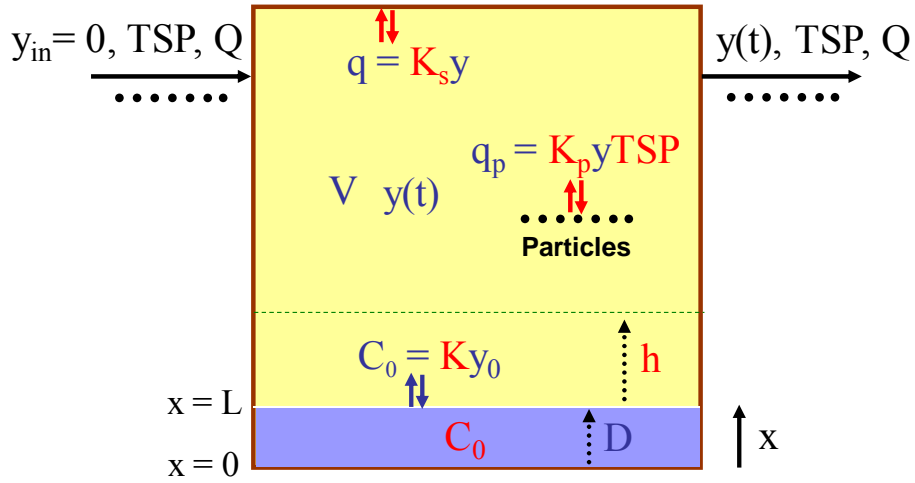
Figure 1.5 Schematic representation of the dry/SVOC model

mixed chamber air. Equilibrium is assumed to exist between the SVOC at the surface of the slab and the air immediately adjacent to the surface, where K is the material/air partition coefficient. K is also assumed to be independent of concentration. Similarly to previous work on VOC emissions modeling (Xu and Zhang 2003), an analytical solution for the emission rate is:

$$C(x,t) = Ky(t) + \sum_{m=1}^{\infty} \frac{\sin(\beta_m L)}{\beta_m} \cdot \frac{2(\beta_m^2 + H^2)}{L(\beta_m^2 + H^2) + H} \cdot \cos(\beta_m x) \cdot$$

$$[(C_0 - Ky(0))e^{-D\beta_m^2 t} + \int_0^t e^{-D\beta_m^2 (t-\tau)} \cdot Kdy(\tau)] \tag{16}$$

where $H = \dfrac{h_m}{KD}$ and β_m (m = 1, 2,…) are the positive roots of

$$\beta_m \cdot \tan(\beta_m L) = H \tag{17}$$

The emission rate per unit area at time t is:

$$\dot{m}(t) = -D \cdot \frac{\partial C(x,t)}{\partial x}\bigg|_{x=L} = D \cdot \sum_{m=1}^{\infty} \sin^2(\beta_m L) \cdot \frac{2(\beta_m^2 + H^2)}{L(\beta_m^2 + H^2) + H} \cdot$$

$$[(C_0 - Ky(0))e^{-D\beta_m^2 t} + \int_0^t e^{-D\beta_m^2 (t-\tau)} \cdot Kdy(\tau)] \tag{18}$$

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A linear and instantaneously reversible equilibrium relationship is assumed to exist between the exposed interior chamber surface area A_i and the chamber air, or

$$q = K_s \cdot y \qquad (19)$$

where q is the adsorbed SVOC surface concentration and K_s is the surface/air partition coefficient. A linear and instantaneously reversible equilibrium relationship is also assumed to exist between the particles and SVOCs in the chamber air, or

$$q_p = K_p \cdot y \cdot TSP \qquad (20)$$

where q_p is the sorbed SVOC particle phase concentration, K_p is the particle/air partition coefficient, and TSP is the total suspended particle concentration. With reference to Figure 5, the accumulation of SVOCs in the chamber obeys the following mass balance:

$$\frac{dy(t)}{dt} \cdot V = Q \cdot y_{in}(t) - A_i \cdot \frac{dq(t)}{dt} - V \cdot \frac{dq_p(t)}{dt} + A_s \cdot \dot{m}(t) - Q \cdot y(t) - Q \cdot q_p(t) \qquad (21)$$

The SVOC emissions model that incorporates interaction with the chamber surfaces and particles present in the air passing through the chamber is obtained by combining equations (18) – (21).

As shown in Figure 1.6, reasonable agreement between model predictions and gas-phase di-2-ethylhexyl phthalate (DEHP) concentrations is achieved for data collected in a previous experimental study that measured emissions of DEHP from vinyl flooring in two very different chambers (Xu and Little 2006; Xu et al. 2009b).

a. CLIMPAQ

(Xu and Little 2006)

b. Specially-designed chamber,

(Xu et al. 2009b)
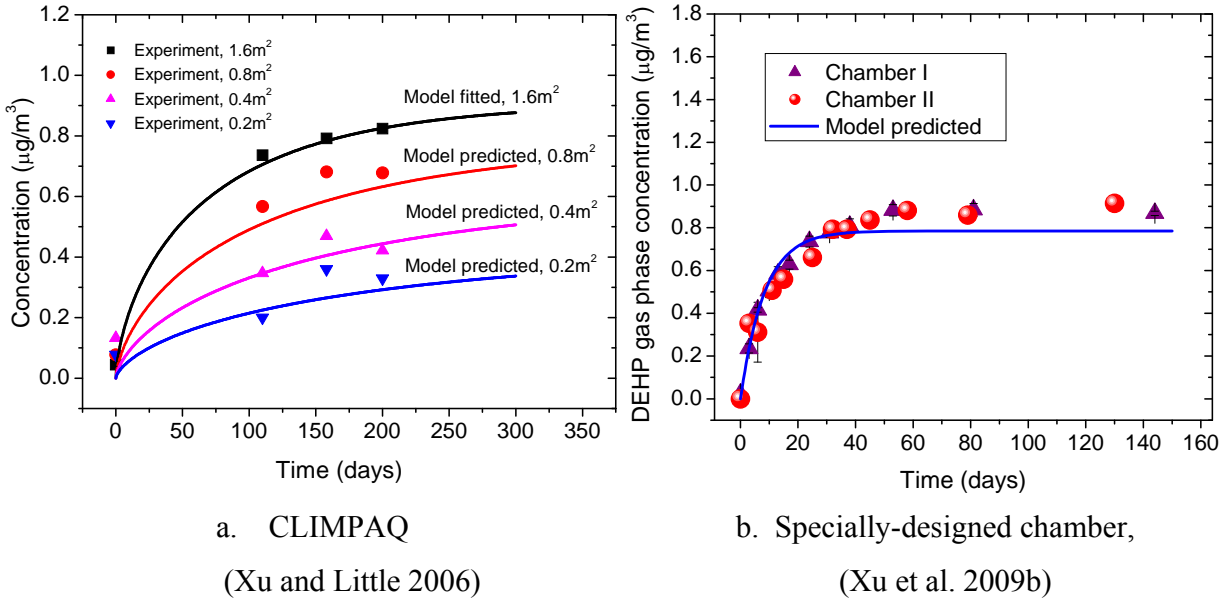
Figure 1.6 Predicted and measured chamber gas-phase DEHP concentration

ESTIMATION OF MODEL PARAMETERS

Wet/VOC Model Parameters

The VB model for TVOCs and the VBX model for individual VOCs are both source models. Combining with two differential equations for TVOCs and an additional two for each individual VOC, room concentrations of VOCs emitted from indoor coating materials can be predicted. Table 1.1 summarizes the model equations and parameters. All the parameters can be readily obtained except P_0, P_i and h (Guo et al. 1998). Methods for estimating P_i and h were proposed in Equation 3 and 5. P_0 can be estimated based on the content of the major VOCs in the solvent. If the behavior of the solvent is close to that of an ideal solution, the total vapor pressure can be estimated from Raoult's law. If the number of VOCs in the mixture is n, then

$$P_0 = \frac{\sum_{i=1}^{n}(P_i\, x_i/m_i)}{\sum_{i=1}^{n}(x_i/m_i)} \tag{22}$$

Table 1.1 Summary of wet/VOC model equations and parameters

Wet/VOCs Model Equations	
TVOCs (VB Model)	$E = h_m \left(1.32 P_0 \dfrac{\overline{m}}{v_m} \dfrac{M_T}{M_{T0}} - C \right);$ $\dfrac{dC}{dt} = \dfrac{SE}{V} - NC; \qquad \dfrac{dM_T}{dt} = -E$
VOCs (VBX Model)	$E_i = h_{mi} \left(1.32 P_i \dfrac{\overline{m}}{v_m} \dfrac{M_i}{M_T} - C_i \right);$ $\dfrac{dC_i}{dt} = \dfrac{SE_i}{V} - NC_i; \qquad \dfrac{dM_i}{dt} = -E_i$

Wet/VOCs Model Parameters			
h_m, h_{mi}	Mass transfer coefficient	C_i	Component i conc. in the bulk air
P_0	Total vapor pressure for TVOC	E	Emission factor for TVOC
P_i	Vapor pressure for individual VOC	E_i	Emission factor for component i
$\overline{m}$	Average molecular weight for TVOC	N	Air exchange rate
v_m	volume of 1 mole gas at 1 atm	V	Room volume
M_T	TVOC amount remaining in the source	S	Source area
M_{T0}	Amount of TVOC applied	x_0	Content of TVOC in product
M_i	Component i amount remaining in the source	x_i	Content of component i in product
C	TVOC concentration in the bulk air	m_i	Molecular weight for component i

Dry/VOCs Model Parameters

In the development of the diffusion-controlled models, the key parameters are the initial concentration in the material phase (C_0), the material/air partition coefficient (K), and the material-phase diffusion coefficient (D). These are shown schematically in Figure 2. The impact of these parameters on VOC emissions from building materials and the associated model predictions have been studied (Huang et al. 2002, Yang et al. 2001). The parameters can be measured independently, or if this is not possible, inferred from chamber test data.

Initial material phase concentration (C_0). Special attention should be paid to C_0 because the gas-phase VOC concentration in the chamber air depends linearly on C_0, and C_0 determines both the short-term and long-term emission characteristics (Yang et al. 2001). An error in the initial concentration estimate will cause a proportional error in prediction results. The effect of a non-uniform distribution of the initial concentration in the material phase on VOC emissions is especially important during the early emission period (Xu and Zhang 2004).

For a single compound, C_0 is defined as the readily emitted mass of compound per unit mass of the material subject to certain environmental conditions. Several methods have been used to obtain C_0 experimentally: solvent extraction; high temperature thermal desorption; direct headspace analysis; low temperature direct thermal desorption and cryogenic milling/fluidized bed desorption. The first three of these methods either use high temperatures or chemical solvents, which can modify the physical structure of polymeric materials and, consequently, affect mass transfer characteristics. The fourth and last method developed avoids these limitations. The benefits of the cryogenic milling/fluidized bed desorption procedure include reduced potential for VOC loss during sample preparation, reduced VOC extraction time, and improved representative sampling of the material phase (Cox et al. 2001a). Using this method as well as low temperature direct thermal desorption method, VOC concentrations in materials can be obtained as shown in Figure 1.7 and Figure 1.8 (Cox et al. 2002).

Diffusion coefficient (D) and material/air partition coefficient (K). The diffusion coefficient (D) determines the rate of diffusion of a VOC through the material and is usually a function of several factors such as material type, compound properties, temperature, as well, in some circumstances, as the material-phase VOC concentration. The material/air partition coefficient (K) describes the equilibrium relationship between the concentration in the gas phase and the concentration in the material phase. The dependence of K and D on concentration is usually ignored since the VOC concentration in the material is usually relatively low.

Several procedures have been used to measure the D and K values of volatile compounds in building materials. These are (1) Cup method: the diffusion coefficient of the test

material is assessed by measuring the weight loss caused by VOC diffusion through a material sample covering a cup containing a liquid VOC at saturation under controlled temperature and humidity conditions. It is the simplest method, but the main drawback is
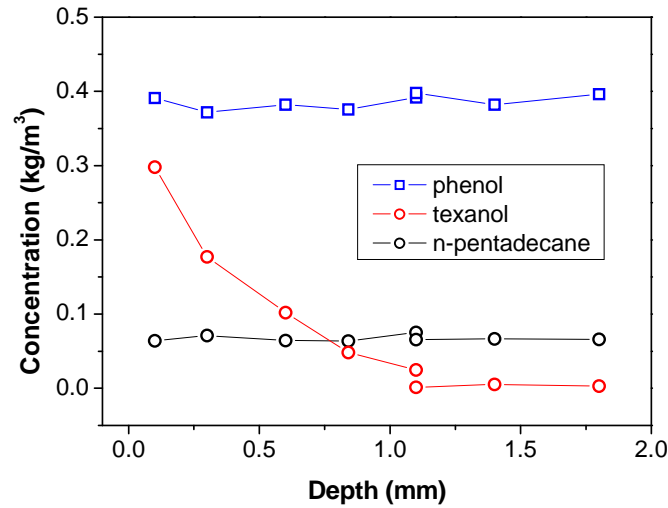
Figure 1.7 VOCs distribution in the material
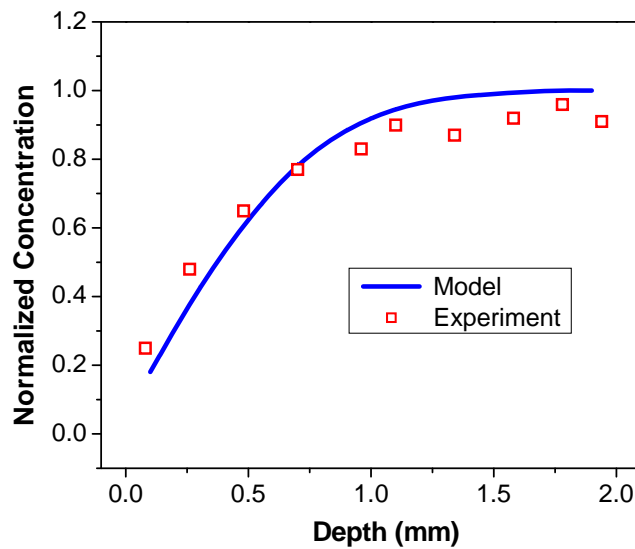
Figure 1.8 Pentadecane distribution in vinyl flooring at the end of emission

that the liquid VOC placed in the cup creates a saturation concentration, which is unrealistically high for indoor air applications. To overcome this, the dry cup method can be used, but it takes a long time (Haghighat et al. 2002). (2) The two-chamber method.

In this method, a sample of building material is installed between two compartments and a particular concentration of compound is introduced into the gas-phase of one compartment while the gas-phase concentration in the other compartment is monitored over time. D and K are then indirectly estimated from the gas-phase concentration data (Haghighat et al. 2002). A complicating feature of this method is that VOC transport between the two chambers may occur by rapid gas-phase diffusion if the material being studied is relatively porous. The two-chamber method can be used to determine K and D under steady state or transient conditions (Bodalal et al. 2000). (3) Porosity test method. This method is only for measuring D and can only be applied to homogeneous and single layer materials. (4) Microbalance method. In this method, the parameters are obtained by weighing a test sample on a microbalance and sweeping the sample chamber with an inert gas containing a known VOC concentration. This simple experimental method can be used for directly measuring the K and D values, and can be applied to diffusion-controlled materials such as VF (Cox et al. 2001b). Through microbalance test, Fig. 1.9 shows sorption and subsequent desorption profiles for phenol with VF at three different gas-phase concentrations. The sorption and desorption profiles are highly symmetrical. It is also evident that the sorption of phenol is completely reversible. Fig. 1.10 shows the equilibrium concentrations of phenol in VF as a function of the imposed gas-phase phenol concentration and confirms the linear relationship assumed in Eq. (8) over the range of concentrations studied. Using the K and D values inferred from the sorption/desorption data given in Figs. 1.9 and 1.10, Fig. 1.11 shows the excellent agreement between the emissions model and experimental data. A recent study extended this method for use in porous materials such as polyurethane foam (Zhao et al. 2004).

When direct experimental measurements are not available, there are two methods that can be used to obtain K and D. The first is to fit the chamber emission data with the emissions model (Yang et al. 1998; Xu and Zhang 2003). Second, since D and K are related to compound properties such as vapor pressure and molecular weight, it is possible to develop correlations between them for various materials. Such correlations for three classes of VOCs: aliphatic hydrocarbons, aromatic hydrocarbons and aromatic hydrocarbons diffusing through various building materials (plywood, particleboard, vinyl floor tile, gypsum board, subfloor tile and oriented strand board) have been developed

(Bodalal et al. 2001). Similarly, relationships between K and vapor pressure and D and the molecular free surface area were used to develop correlation equations for a series of aromatic compounds interacting with polyurethane foam (Zhao et al. 2004).
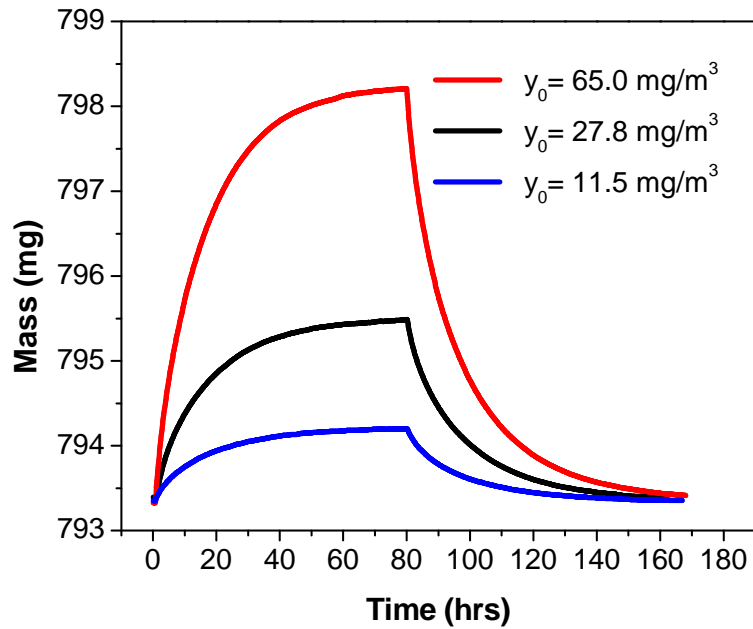
Figure 1.9 Transient mass gain/loss of a VF sample during sorption/desorption of phenol
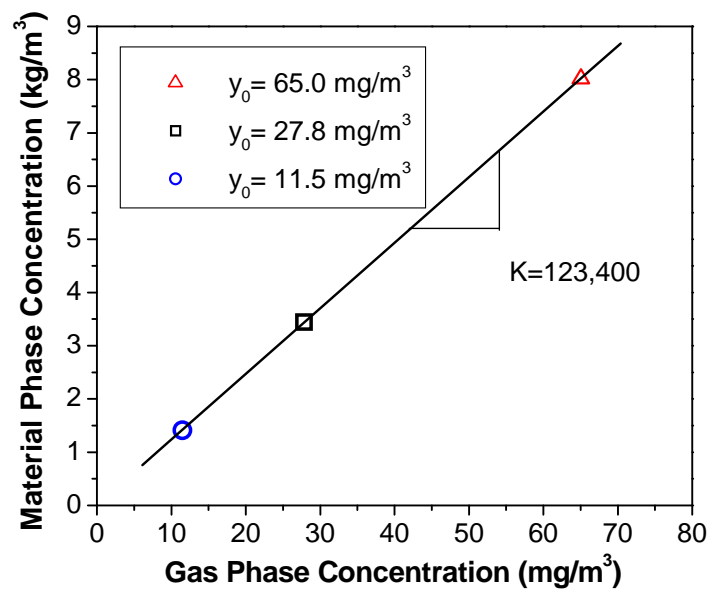
Figure 1.10 Linear sorption isotherm for phenol in VF
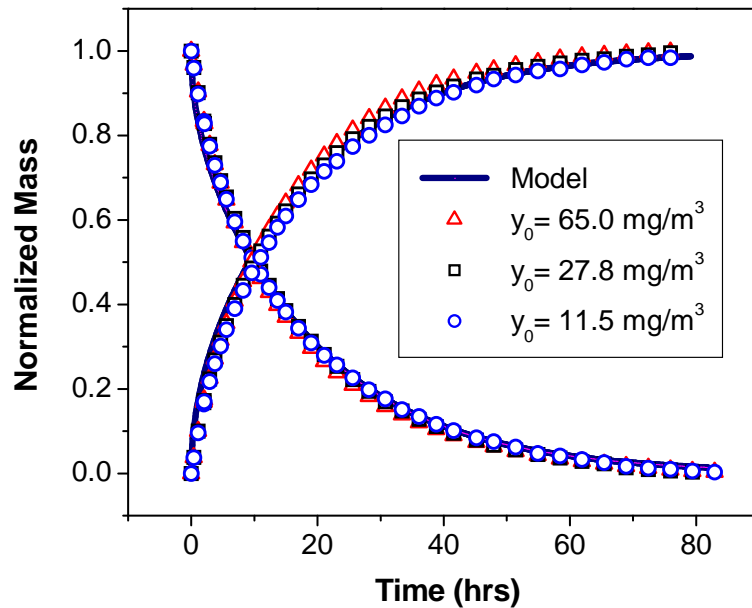
Figure 1.11 Predicted and measured chamber gas-phase phenol concentration

Dry/SVOC Model Parameters

While emissions of highly volatile VOCs are subject to "internal" control (through the material-phase diffusion coefficient), emissions of the very low volatility SVOCs are subject to "external" control through partitioning into the gas phase, convective mass transfer, and adsorption onto interior surfaces (Xu and Little 2006). Therefore, gas phase mass transfer coefficient (h), adsorption isotherm (K_s) initial material phase concentration (C_0) and the material/air partition coefficient (K) are important parameters that determines SVOC emissions.

Gas phase convective mass transfer coefficient (h). The external convective mass-transfer coefficient is denoted h. It is affected by both environmental factors and compound properties and is usually determined by the fluid dynamic conditions of the environment. This is a result of the fact that the coefficient in test chambers can differ from those in indoor environments. Such differences may cause scaling-up problems in the use of chamber-derived emission rates in emissions models. The gas phase mass-transfer coefficient is difficult to determine experimentally. Correlations with the Reynolds and Nusselt numbers can be used to scale the coefficient, as reported in the

literature (Axley 1991; Haghighat and Zhang 1999; Sparks et al. 1996; Zhang and Niu 2003).

Adsorption isotherm (K_s). Strong adsorption of SVOCs onto chamber surfaces, dust and real interior surfaces (e.g. carpet, wood floor, human skin) in residential houses have been observed (Clausen et al. 2004; Xu et al. 2009a; 2009b). K_s can be obtained by relating the surface concentrations with the corresponding gas phase concentrations of SVOCs measured in experiments. Xu et al. (2009b) designed a special stainless steel (SS) chamber to measure K_s for DEHP on stainless steel chamber surfaces. In their design, three SS rods were inserted into the chamber, and were taken out of the chamber during sampling to directly measure the adsorbed DEHP concentration on the rods. Figure 1.12 shows that a simple linear relationship is sufficient to describe the stainless steel surface/air equilibrium for DEHP.

Initial material phase concentration (C_0). Solvent extraction was used to obtain C_0 experimentally for SVOCs. Xu et al. (2009b) extracted vinyl flooring samples (about 30 mg) with methanol using pressurized liquid extraction with a Dionex ASE 200 system. The extraction cell with the sample was preheated to 150 °C for 7 min, followed by a static extraction of 10 min at constant pressure (2000 psi). After the static extraction, the pressure was released and the extract was collected in a 40 ml glass vial. The extraction cycle was repeated three times for exhaustive extraction of both samples and blanks. Figure 1.13 shows the measured DEHP concentration in vinyl flooring. However, using chemical solvents may modify the physical structure of materials and consequently affect mass transfer characteristics. Therefore, further investigation is needed.

Material/air partition coefficient (K). Direct measurement of K for SVOCs has not been developed. Clausen et al. (2004) measured emissions of DEHP from vinyl flooring for up to 472 days in both the FLEC (Field and Laboratory Emission Cell) and the CLIMPAQ (Chamber for Laboratory Investigations of Materials, Pollution, and Air Quality). Based on their experiments, Xu and Little fitted model parameter y_0 (the DEHP concentration in the air immediately adjacent to the material interface). Even though the chamber configurations and operating conditions for the CLIMPAQ and FLEC were

vastly different, the fitted values of y_0, which is related to chemical properties, were within 4%.
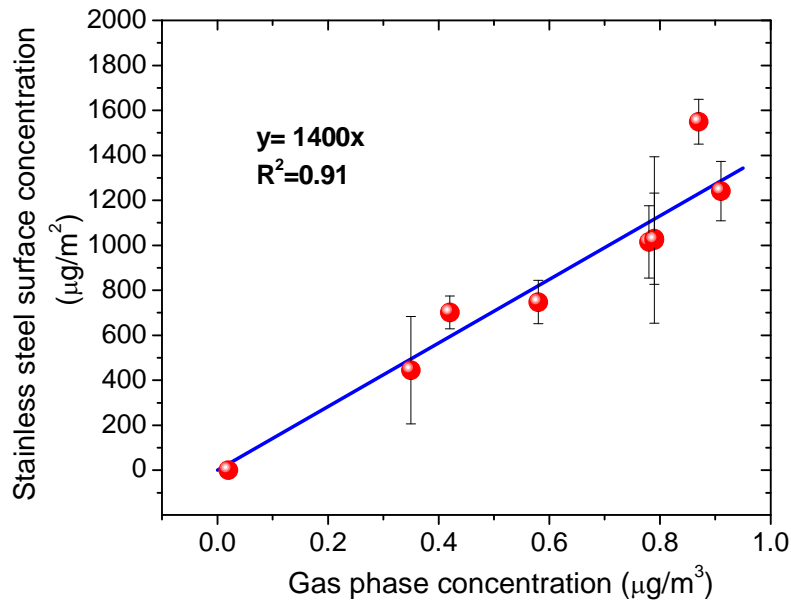
Figure 1.12 Adsorption of DEHP on stainless steel surface
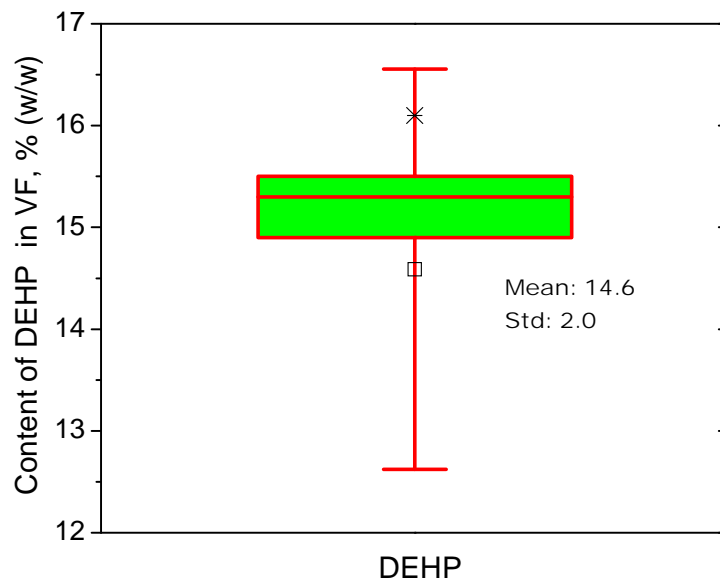
Figure 1.13 DEHP content in vinyl flooring

DISCUSSION AND CONCLUSION

Models to predict the emission rate of VOCs and SVOCs from building materials and consumer products are summarized into three categories: models for VOC emissions from wet materials; models for VOC emissions from dry materials; and models for SVOC emissions from dry materials. These three mass transfer based models are essentially the same. The primary differences arise due to the different mechanisms which control the rate of emissions. As shown in Figure 1.14, for indoor coating materials, VOCs may be released to a peak concentration and disappear within several hours. In contrast, SVOCs emission from dry building materials slowly accumulate until steady state is reached, and may continue for years. VOC emissions from dry building materials fall in between these two extremes.
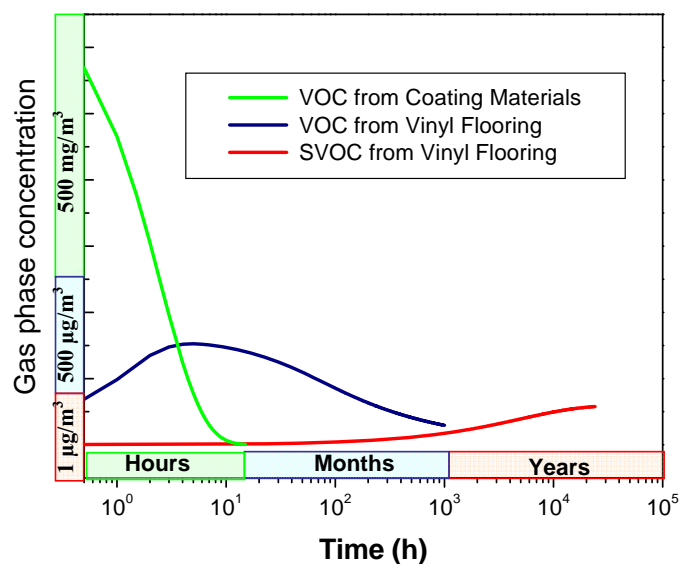
Figure 1.14 Emissions from wet/VOC, dry/VOC and dry/SVOC materials

The usefulness of these models relies on developing simple and effective methods to estimate the model parameters. However, development of these methods has not progressed to the extent that indoor air quality modelers would like (Guo et al. 2001b). Although methods have been developed to estimate model parameters for VOC

emissions, finding ways to determine SVOC emission parameters remains an important task.

ACKNOWLEDGEMENT

REFERENCES

Axley JW. 1991. Adsorption modeling for building contaminant dispersal analysis. . Indoor Air 1: 147-171.

Bodalal A, Zhang JS, Plett EG. 1999. A method for measuring internal diffusion and equilibrium partition coefficients of volatile organic compounds for building materials. Building and Environment 35: 101–110.

Bodalal A, Zhang JS, Plett EG, Shaw CY. 2001. Correlations between the internal diffusion and equilibrium partition coefficients of volatile organic compounds (VOCs) in building materials and the VOC properties. ASHRAE Transactions 107: 789–800.

Clausen P, Hansen V, Gunnarsen L, Afshari A, Wolkoff P. 2004. Emission of Di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. ENVIRONMENTAL SCIENCE & TECHNOLOGY 38: 2531-2537.

Cox SS, Hodgson AT, Little JC. 2001a. Measuring concentrations of volatile organic compounds in vinyl flooring. Journal Air & Waste Management Association 51: 1195–1201.

Cox SS, Little JC, Hodgson AT. 2002. Predicting the emission rate of volatile organic compounds from vinyl flooring. . Environmental Science & Technology 36: 709–714.

Cox SS, Zhao D, Little JC. 2001b. Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring. Atmospheric Environment 35: 3823–3830.

Guo Z. 2002a. Review of indoor emission source models. Part 1. Overview. Environmental Pollution 120: 533-549.

Guo Z. 2002b. Review of indoor emission source models. Part 2. Parameter estimation. Environmental Pollution 120: 551-564.

Guo Z, Sparks LE, Tichenor BA, Chang JCS. 1998. Predicting the emissions of individual VOCs from petroleum-based indoor coatings. Atmospheric Environment 32(231–237).

Haghighat F, Lee C-S, Ghaly WS. 2002. Measurement of diffusion coefficients of VOCs for building materials: review and development of a calculation procedure. Indoor Air 12: 81–91.

Haghighat F, Zhang Y. 1999. Modelling of emission of volatile organic compounds from building materials – Estimation of gas-phase mass transfer coefficient. Building and Environment 34: 377–389.

Huang H, Haghighat F. 2002. Modeling of volatile organic compounds emission from dry building materials. Building and Environment 37: 1127-1138.

Kumar D, Little JC. 2003. A single-layer model to predict the source/sink behavior of diffusion-controlled building materials. Environmental Science & Technology 37: 3821–3827.

Lee C-S, Haghighat F, Huang H. 2005. Modeling Approaches for Indoor Air VOC Emissions from Dry Building Materials--A Review. ASHRAE Transactions Vol. 111(Issue 1): p635-645.

Little JC, Hodgson AT, Gadgil AJ. 1994. Modeling emissions of volatile organic compounds from new carpets. Atmospheric Environment 28: 227–234.

Sparks L, Tichenor B, Chang J, Guo Z. 1996. Gas-phase mass transfer model for predicting volatile organic compound (VOC) emission rates from indoor pollutant sources. Indoor Air 6: 31–40.

Tichenor BA, Guo Z, Sparks LE. 1993. Fundamental mass transfer model for indoor air emissions from surface coatings. Indoor Air 3: 263-268.

Xu Y, Hubal EAC, Clausen PA, Little JC. 2009a. Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – A Mechanistic Analysis. . Environmental Science and Technology Accepted.

Xu Y, Little J. 2006. Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles. ENVIRONMENTAL SCIENCE & TECHNOLOGY 40: 456-461.

Xu Y, Park J, Clausen PA, Kofoed-Sørensen V, Little JC. 2009b. Characterizing Emissions of Phthalate Plasticizer from Vinyl Flooring In a Specially-Designed SVOC Emission Chamber. Submitted.

Xu Y, Zhang Y. 2003. An improved mass transfer based model for analyzing VOC emissions from building materials. ATMOSPHERIC ENVIRONMENT 37: 2497-2505.

Xu Y, Zhang Y. 2004. A general model for analyzing single surface VOC emission characteristics from building materials and its application. ATMOSPHERIC ENVIRONMENT 38: 113-119.

Yang X, Chen Q, Bluyssen PM. 1998. Prediction of short-term and long-term VOC emissions from SRB bitumen-backed carpet under different temperature. ASHRAE Transactions 104 (Part 2): 1297–1308.

Yang X, Chen Q, Zhang JS, An Y, Zeng J, Shaw CY. 2001. A mass transfer model for simulating VOC sorption on building material. Atmospheric Environment 35: 1291–1299.

Zhang LZ, Niu JL. 2003. Laminar fluid flow and mass transfer in a standard field and laboratory emission cell. International Journal of Heat and Mass Transfer 46: 91–100.

Zhao DY, Little JC, Cox SS. 2004. Characterizing polyurethane foam as a sink for or source of VOCs in indoor air. Journal of Environmental Engineering 130: 983–989.

Chapter 2: Predicting Emissions of SVOCs from Polymeric Materials and Their Interaction with Airborne Particles

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ABSTRACT

A model that predicts the emission rate of volatile organic compounds (VOCs) from building materials is extended and used to predict the emission rate of semi-volatile organic compounds (SVOCs) from polymeric materials. Reasonable agreement between model predictions and gas-phase di-2-ethylhexyl phthalate (DEHP) concentrations is achieved for data collected in a previous experimental study that measured emissions of DEHP from vinyl flooring in two very different chambers. While emissions of highly volatile VOCs are subject to "internal" control (through the material-phase diffusion coefficient), emissions of the very low volatility SVOCs are subject to "external" control (through partitioning into the gas phase, the convective mass transfer coefficient, and adsorption onto interior surfaces). The effect of SVOCs partitioning to airborne particles is also examined. The initial DEHP emission rate is unaffected, but the longer term emission rate is increased, especially when partitioning to the airborne particles is strong. Airborne particles may play an important role in inhalation exposure as well as in transporting SVOCs well beyond the source. Although more rigorous validation is needed, the model should help elucidate the mechanisms governing emissions of phthalate plasticizers, brominated flame retardants, biocides, and other SVOCs from a wide range of building materials and consumer products.

INTRODUCTION

Modern indoor environments contain a vast array of contaminating sources. Emissions from these sources produce contaminant concentrations that are substantially higher indoors than outside. Because we spend most of our time indoors, exposure to indoor pollutants may be orders-of-magnitude greater than that experienced outdoors. Volatile emissions are a probable cause of acute health effects and discomfort among building occupants (Andersson et al. 1997) and are known to diminish worker productivity (Bako-Biro et al. 2004). Although emissions from building materials have traditionally been empirically characterized in chambers, we have recently validated a mechanistic model that predicts VOC emissions from vinyl flooring. The approach involves independently measuring C_0 (initial material-phase concentration), D (material-phase diffusion coefficient), K (material/air partition coefficient), and K_s (chamber surface/air partition coefficient), and then predicting the emission rate a priori using a fundamental mass-transfer model (Cox et al. 2001a; 2001b; 2002).

Our attention is now turning to semi-volatile organic compounds (SVOCs) such as plasticizers (Horn et al. 2004), flame retardants (Hites et al. 2004), and biocides (Horn et al. 2003). These constituents are added to a variety of products to enhance performance and are often present at considerably higher concentrations than their more volatile counterparts. There are serious health concerns associated with SVOCs in general and phthalate plasticizers in particular (Adibi et al. 2003). For example, recent research suggests that phthalates, including di-(2-ethylhexyl) phthalate (DEHP), may have a wide range of adverse effects on reproduction and development, including decreased fertility, birth defects, hormone disruption, and reproductive malformations, particularly in the male reproductive tract (Matsumura et al. 2002).

Exposure to phthalates and other SVOCs may be strongly influenced by the presence of airborne particles. SVOCs are expected to sorb strongly to particles that are subsequently inhaled (Weschler 2001), a potentially important yet largely unexamined exposure route. Recent studies suggest that phthalates, within the range of what is normally found indoors, are associated with allergic symptoms in children (Weschler 2001; Bornehag et al. 2004a; 2004b; Øie et al. 1997). An SVOC attached to a particle may lodge deep in the lungs and

exert a more severe health effect. A critical need therefore exists for understanding indoor emissions of SVOCs and their partitioning between gaseous and particulate phases.

In this paper, a model that integrates the fundamental mechanisms governing emissions of SVOCs from polymeric materials and their subsequent interaction with indoor surfaces and airborne particles is developed. The emissions model is consistent with our previously validated model that predicts emission of VOCs from vinyl flooring (Cox et al. 2002). Data collected by Clausen et al. (Clausen et al. 2004), who studied emissions of phthalates from vinyl flooring in small chambers, are used to obtain some model parameters and to provide a preliminary validation of the proposed SVOC emissions model. The model is used to demonstrate the influence of the key parameters on SVOC emissions. To assess the importance of the inhaled particulate exposure pathway, the effect of SVOCs partitioning to airborne particles is examined. By including the influence of particle type, particle concentration, ventilation rate, and particle sorption kinetics, the mechanisms governing emissions of SVOCs from polymeric materials and their subsequent interaction with interior surfaces and airborne particles are clarified.

DEVELOPMENT OF SVOC EMISSIONS MODEL

SVOC Emission Rate
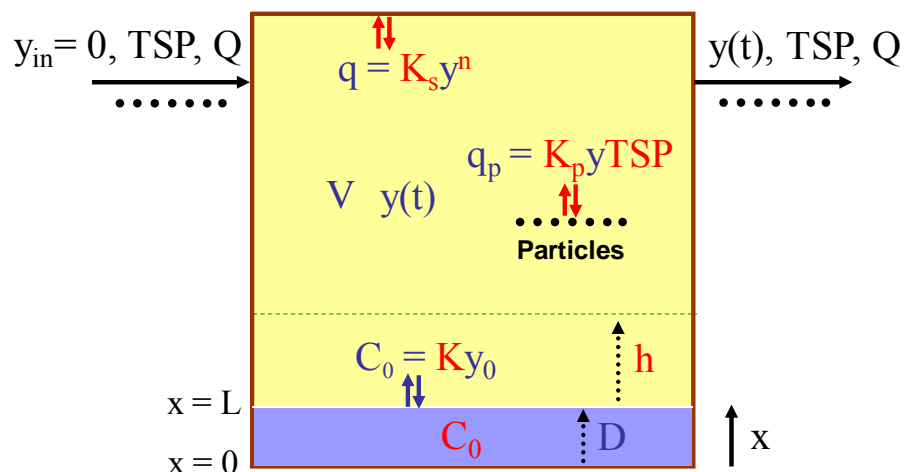
Figure 2.1 Schematic showing vinyl flooring slab in experimental chamber

The approach used is consistent with that developed previously for emissions of VOCs from building materials (Cox et al. 2002; Little et al. 1994; Yang et al. 2001; Kumar and Little 2003; Xu and Zhang 2003; 2004; Deng and Kim 2004; Lee et al. 2005). A schematic representation of the idealized polymeric material slab placed in a test chamber is shown in Figure 2.1. The governing equation describing transient diffusion through the slab is

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{1}$$

where $C(x, t)$ is the material-phase concentration of the SVOC, t is time, and x is distance from the base of the slab. The diffusion coefficient D is assumed to be independent of concentration for the moment. The initial condition assumes that the SVOC is uniformly distributed through the material slab, or

$$C(x,t) = C_0 \quad \text{for} \quad 0 \le x \le L \tag{2}$$

where L is the thickness of the slab, and C_0 is the initial material-phase SVOC concentration. Because the slab is resting on an impermeable surface, the lower boundary condition is

$$\frac{\partial C(x,t)}{\partial x} = 0 \quad \text{for} \quad t > 0, \quad x = 0 \tag{3}$$

The second boundary condition imposed at the upper surface is

$$-D\frac{\partial C(x,t)}{\partial x} = h_m(y_0(t) - y(t)) \quad \text{for} \quad t > 0, \quad x = L \tag{4}$$

where h_m is the convective mass transfer coefficient (Xu and Zhang 2003; Deng and Kim 2004), $y_0(t)$ is the concentration of the SVOC in the air immediately adjacent to the surface, and $y(t)$ is the gas-phase SVOC concentration in the well-mixed chamber air. Equilibrium is assumed to exist between the SVOC in the surface layer of the slab and the air immediately adjacent to the surface, or

$$C(x,t) = Ky_0(t) \quad \text{for} \quad t > 0, \quad x = L \tag{5}$$

where K is the material/air partition coefficient. K is also assumed to be independent of concentration for the moment. Similarly to previous work on VOC emissions modeling

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(Xu and Zhang 2003), an analytical solution for the emission rate (based on equations (1) – (5)) is:

$$C(x,t) = Ky(t) + \sum_{m=1}^{\infty} \frac{\sin(\beta_m L)}{\beta_m} \cdot \frac{2(\beta_m^2 + H^2)}{L(\beta_m^2 + H^2) + H} \cdot \cos(\beta_m x) \cdot$$

$$[(C_0 - Ky(0))e^{-D\beta_m^2 t} + \int_0^t e^{-D\beta_m^2(t-\tau)} \cdot Kdy(\tau)] \tag{6}$$

where $H = \dfrac{h_m}{KD}$ and β_m (m = 1, 2,…) are the positive roots of

$$\beta_m \cdot \tan(\beta_m L) = H \tag{7}$$

The emission rate per unit area at time t is (19):

$$\dot{m}(t) = -D \cdot \frac{\partial C(x,t)}{\partial x}\bigg|_{x=L} = D \cdot \sum_{m=1}^{\infty} \sin^2(\beta_m L) \cdot \frac{2(\beta_m^2 + H^2)}{L(\beta_m^2 + H^2) + H} \cdot$$

$$[(C_0 - Ky(0))e^{-D\beta_m^2 t} + \int_0^t e^{-D\beta_m^2(t-\tau)} \cdot Kdy(\tau)] \tag{8}$$

Chamber Surface Adsorption

A non-linear instantaneously reversible Freundlich equilibrium relationship is assumed to exist between the exposed interior chamber surface area A_i and the chamber air, or

$$q = K_s \cdot y^n \tag{9}$$

where q is the adsorbed SVOC surface concentration and K_s and n are the Freundlich isotherm parameters.

Sorption to Airborne Particles

A linear instantaneously reversible equilibrium relationship is also assumed to exist between the particles and SVOCs in the chamber air (9), or

$$q_p = K_p \cdot y \cdot TSP \tag{10}$$

where q_p is the sorbed SVOC particle phase concentration, K_p is the particle/air partition coefficient, and TSP is the total suspended particle concentration.

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Chamber Mass Balance

With reference to Figure 1, the accumulation of SVOCs in the chamber obeys the following mass balance:

$$\frac{dy(t)}{dt} \cdot V = Q \cdot y_{in}(t) - A_i \cdot \frac{dq(t)}{dt} - V \cdot \frac{dq_p(t)}{dt} + A_s \cdot \dot{m}(t) - Q \cdot y(t) - Q \cdot q_p(t) \quad (11)$$

The SVOC emissions model that incorporates interaction with the chamber surfaces and particles present in the air passing through the chamber is obtained by combining equations (8) – (11).

PARAMETERS ESTIMATION AND MODEL PRELIMINARY VALIDATION

Clausen et al. (2004) measured emissions of di-2-ethylhexyl phthalate (DEHP) from vinyl flooring for up to 472 days in both the FLEC (Field and Laboratory Emission Cell) and the CLIMPAQ (Chamber for Laboratory Investigations of Materials, Pollution, and Air Quality). The loading of vinyl flooring in the CLIMPAQs was varied, but was constant in the FLECs. In addition to these standard emission tests, Clausen et al. (2004) also conducted several sorption/desorption tests. The experimental data used by us involved: (i) joining an empty FLEC to the outlet of a FLEC that contains vinyl flooring and measuring the concentration of DEHP in the gas-phase leaving the second FLEC in the series (the "two FLECs in series" experiment); (ii) quickly removing the vinyl flooring from two replicate experimental FLECs, joining the two "empty" FLECs together, and then monitoring the concentration of DEHP in the gas-phase leaving the combined FLEC (the "double FLEC" experiment); and (iii) quickly removing the vinyl flooring from the CLIMPAQ and then continuing to monitor the concentration of DEHP in the gas-phase leaving the empty chamber (the "empty CLIMPAQ" experiment).

The experimental conditions employed by Clausen et al. (2004) are shown in Table 2.1. The concentration of DEHP in the vinyl flooring was reported to be 17% and this number was used to estimate C_0, the initial material-phase concentration. The value of h_m, the external mass-transfer coefficient, was estimated for the CLIMPAQ using correlation equations (Axley 1991), while for FLEC, due to the laminar flow conditions, h_m was

obtained from equations developed by Zhang and Niu (2003) based on CFD calculations. The material-phase diffusion coefficient, D, was estimated using correlations developed for VOCs in vinyl flooring (Cox et al. 2001b), although D has essentially no influence on the SVOC emissions rate for the circumstances being examined. As shown in Figures 2.2 and 2.3, numerical simulation was then used to obtain the Freundlich isotherm parameters (K_s and n) and the DEHP concentration in the air immediately adjacent to the material interface (y_0). For the CLIMPAQ, only the data obtained for the 1.6 m^2 piece of vinyl flooring were used to obtain these three parameters, while for the FLEC, the duplicate data sets were used simultaneously to obtain the three parameters. Reassuringly, even though the chamber configurations and operating conditions for the CLIMPAQ and FLEC were vastly different (see Table 2.1), the calculated values of y_0 were within 4%, as shown in Table 2.2. The values for the Freundlich isotherm parameters are quite different, although this is most likely due to the difference in materials of chamber construction, with the FLEC made out of stainless steel and the CLIMPAQ being largely glass. The material/air partition coefficient, K, was then estimated from the ratio of C_0 and the average value of y_0 for both chamber systems. Due to the very high initial DEHP concentration in the vinyl flooring, it is reasonable to assume that C(x=L, t) is constant and equal to C_0.

Table 2.1 Test Conditions for CLIMPAQ and FLEC (Clausen et al. 2004)

Parameter	CLIMPAQ	FLEC
temperature (°C)	22	20.1 – 23.6
relative humidity (%)	50	48.0 – 52.0
volume (L)	51	0.035
air flow rate (L min^{-1})	8.3 – 9.4	0.44 – 0.47
air exchange rate (h^{-1})	9.8 – 11	760 – 800
air velocity at test piece surface (m s^{-1})	0.14 – 0.16	0.016
area of test piece (m^2)	0.2 – 1.6	0.018
internal surface area (m^2)	1.6	0.018
chamber surface material	mainly glass	stainless steel
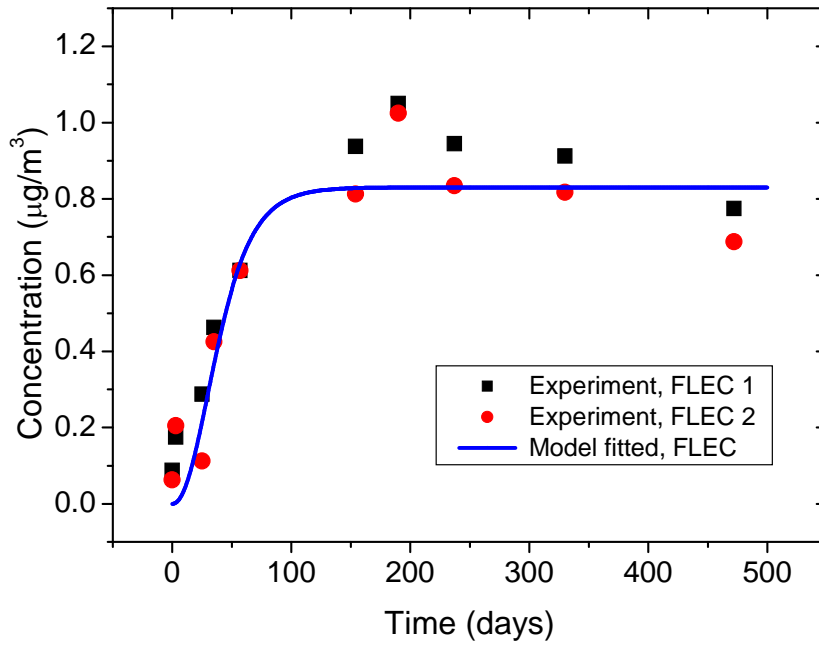
Figure 2.2 Comparison of fitted and predicted gas-phase DEHP concentrations with data measured in CLIMPAQ
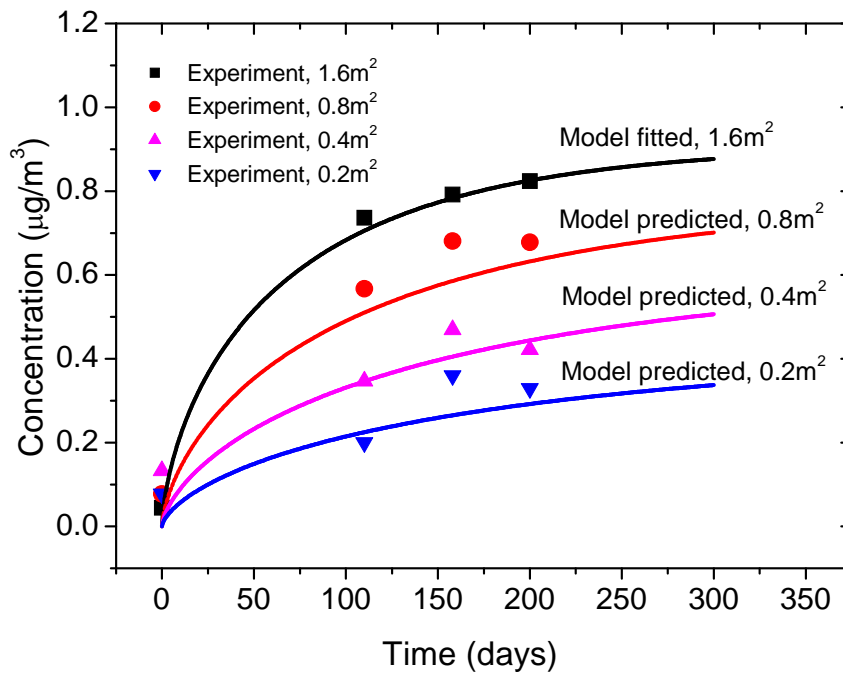
Figure 2.3 Comparison of fitted gas-phase DEHP concentrations with data measured in FLEC

Table 2.2 Model Parameters for DEHP Emissions in CLIMPAQ and FLEC

Parameter	CLIMPAQ	FLEC	Comments
C_0 ($\mu g/m^3$)	2.6×10^{11}	2.6×10^{11}	Known
D (m^2/s)	1.0×10^{-13}	1.0×10^{-13}	Estimated
h_m (m/s)	4.0×10^{-4}	1.4×10^{-3}	Estimated
$K^{\dagger}$ (dimensionless)	2.3×10^{11}	2.3×10^{11}	Calculated
y_0 ($\mu g /m^3$)	1.10	1.06	Fitted
K_s ($\mu g/m^2$)/(($\mu g/m^3$)^n)	3800	6000	Fitted
n (dimensionless)	1.5	0.47	Fitted

†K is calculated using the average value of y_0 for CLIMPAQ and FLEC.

In the development of the SVOC emissions model, the values of both D and K were assumed to be independent of concentration. However, given the very high material-phase DEHP concentration (17 % by weight), it is likely that they would both depend strongly on concentration. Schwope et al. (1989) suggested that D and K are expected to be independent of concentration if the material-phase concentration is below 1 % by weight. Fortunately, for the situation currently being examined, the value of D is irrelevant, and the value of K is effectively constant, because C_0 remains effectively constant. Thus, the two assumptions are valid.

The model parameters for the two chamber systems are summarized in Table 2.2. The three sets of data collected for the remaining experiments carried out in the CLIMPAQ (with vinyl pieces of size 0.8 m^2, 0.4 m^2, and 0.2 m^2) were used to test the predictive ability of the model, as shown in Figure 2.2. Reasonable agreement between the gas-phase DEHP concentrations predicted by the model and the experimental data is obtained.

Preliminary validation of the surface adsorption component of the model was obtained by comparing model predictions to the additional experiments carried out by Clausen et al. (2004). The adsorption data obtained from the "two FLECs in series" experiment are compared to the model predictions in Figure 2.4. The desorption data obtained in the "double FLEC" and "empty CLIMPAQ" experiments also compared fairly well to the model predictions, although the data is not shown here. These three sets of model

predictions suggest that the use of the instantaneously reversible Freundlich isotherm is reasonable in accounting for adsorption to and desorption from the interior chamber surfaces. However, the fact that the gas-phase DEHP concentration is under-predicted in the "two FLECs in series" adsorption experiment (Figure 2.4), and over-predicted in the "double FLEC" desorption experiment (data not shown) suggests that the Freundlich isotherm over-predicts adsorption to the stainless steel surface in the FLEC. Although fewer data were available for the predominantly glass CLIMPAQ, the agreement with the data was better than for the FLEC.
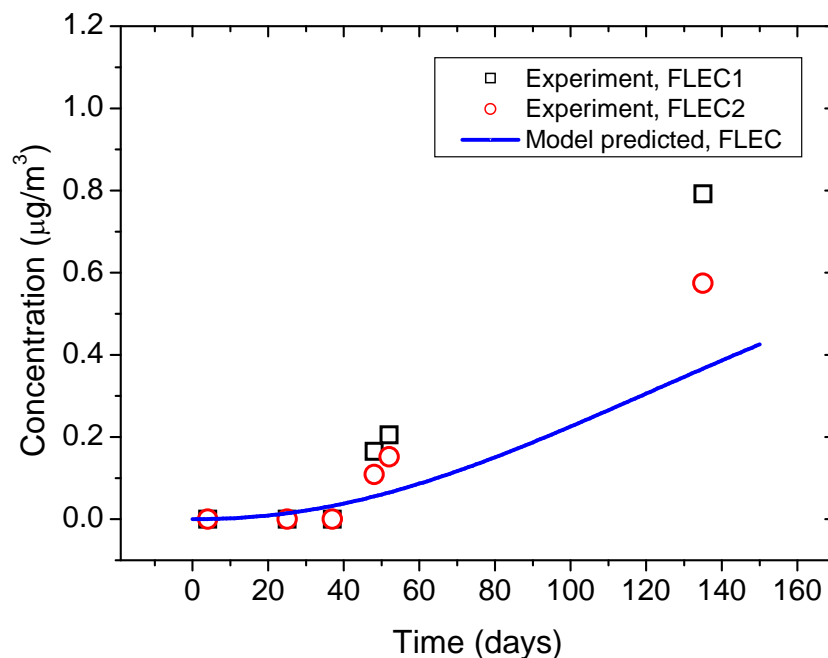
Figure 2.4 Comparison of predicted gas-phase DEHP concentrations with data measured in the Two FLECs in Series experiment

SENSITIVITY TO MODEL PARAMETERS

Here, we examine the sensitivity of SVOC emissions to the material/air partition coefficient (K), the convective mass-transfer coefficient (h_m), the interior chamber surface area (A_i), and the material-phase diffusion coefficient (D). The influence of particles will be discussed in a subsequent section. For the purposes of the sensitivity analysis, we use the model parameters that we obtained from the CLIMPAQ DEHP

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emission experiments (Clausen et al. 2004) because these are roughly representative of conditions in a real room. The analysis assumes a 2-mm thick piece of vinyl flooring with surface area (A_s) of 1.6 m^2 in the CLIMPAQ emission chamber with a volume (V) of 51 L and an air flow rate (Q) of 8.9 L/min. The baseline model parameters are K = 2.4 × 10^{11}; h_m = 4.0 × 10^{-4} m/s; K_s = 3800; n = 1.5; C_0 = 2.6 × 10^{11} μg/m^3; and D = 1 × 10^{-13} m^2/s. We now examine the influence of K, h_m, A_i, and D on the predicted SVOC emission rate and gas-phase concentration in the chamber.

As shown in Figure 2.5, the very high partition coefficient (K) has a strong influence on both the emission rate and the concentration. It plays an important role in controlling emissions during the entire period. Figure 2.6 shows that the convective mass transfer coefficient h_m controls the initial emissions period, and influences the initial emission rate strongly. It therefore has a marked influence on the gas-phase concentration in the chamber. Adsorption to the internal surface area (A_i) also has a significant influence on
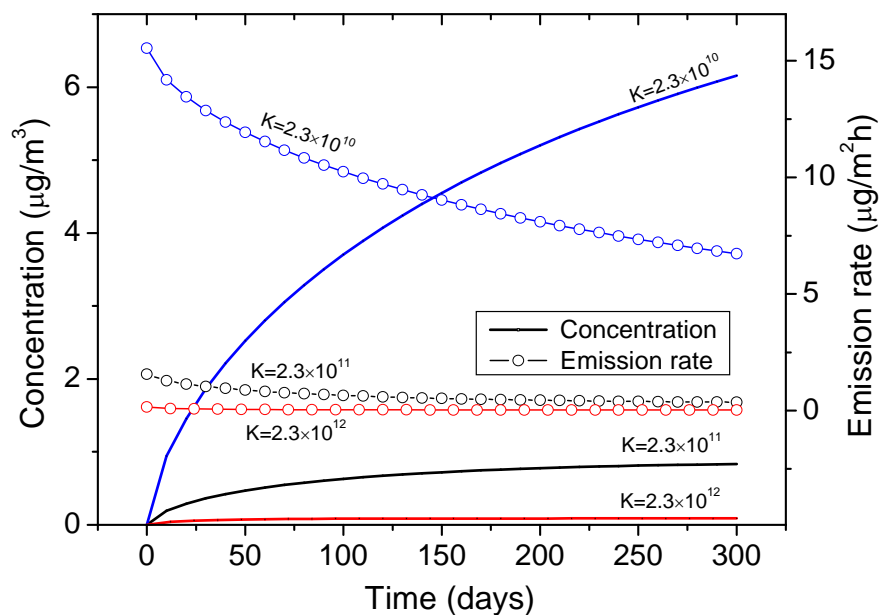
Figure 2.5 The influence of the material/air partition coefficient (K) on SVOC emission rate and gas-phase concentration
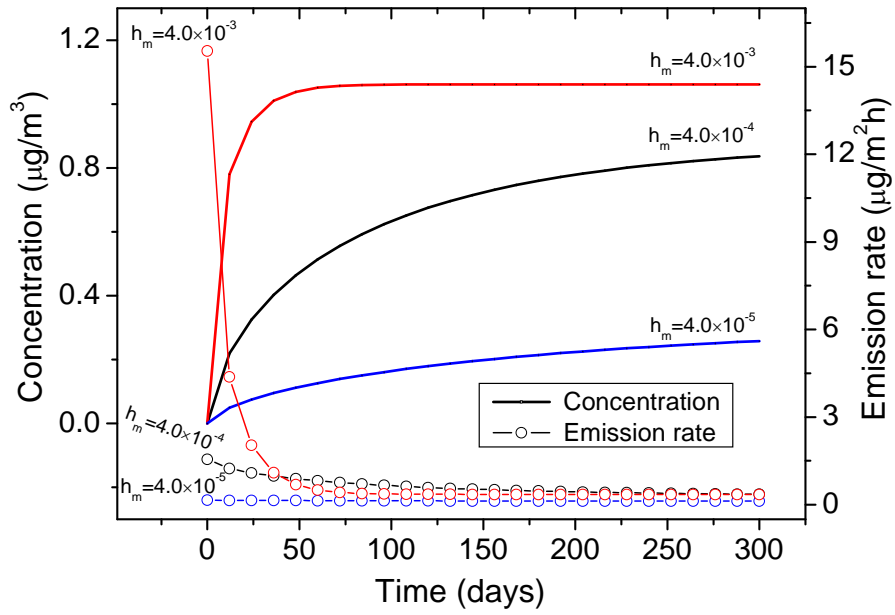
Figure 2.6 The influence of the convective mass transfer coefficient (h_m) on SVOC emission rate and gas-phase concentration
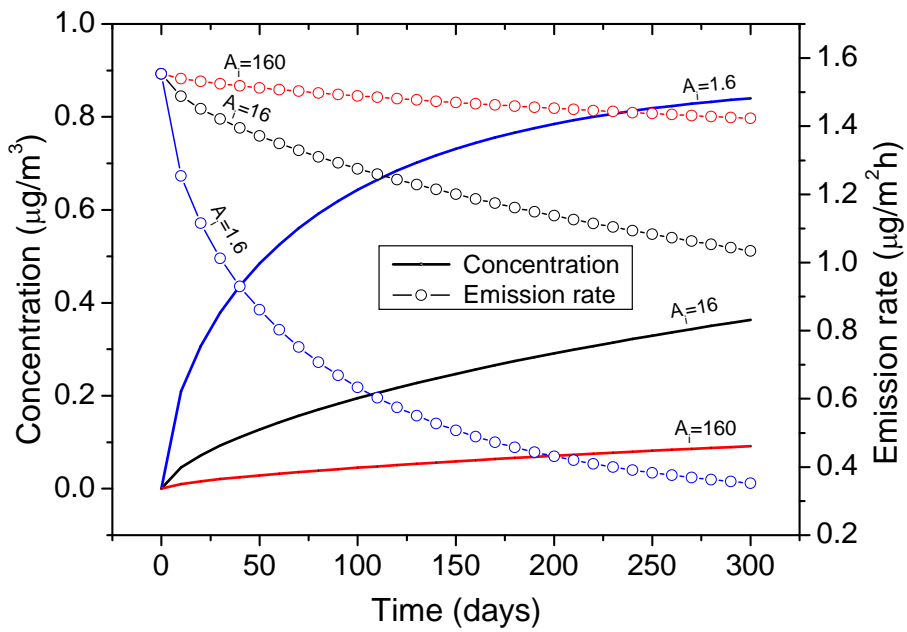
Figure 2.7 The influence of internal surface area (A_i) on SVOC emission rate and gas-phase concentration

SVOC emissions. As shown in Figure 2.7, with A_i increasing, surface adsorption increases and results in a higher SVOC emission rate. The diffusion coefficient for the SVOC in the vinyl flooring (D) has no influence on either chamber air concentration or the emission rate. The calculated results show that the gas-phase chamber concentration and the emission rate both coincide for values of D ranging from 1×10^{-5} to 1×10^{-16} m^2/s. The reason is the very high initial material-phase concentration of 2.6×10^{11} $\mu g/m^3$. The overall loss of DEHP from the vinyl slab is only 0.002 % over the entire duration of the chamber experiment. This means that the material-phase concentration is effectively constant and explains why diffusion is not an important mechanism under these conditions.

This analysis shows that, in contrast to the VOCs which are primarily subject to "internal" control, emissions of SVOCs are primarily subject to "external" control. For highly volatile VOCs, diffusion within the vinyl flooring largely controls emissions, while for very low volatility SVOCs, partitioning into the gas phase, the convective mass transfer coefficient, and adsorption onto interior surfaces, governs the behavior.

IMPACT OF AIRBORNE PARTICLES

It is well known that SVOCs partition strongly into household dust (Clausen et al. 2004). The partioning of SVOCs onto airborne particles has been shown to be important by Weschler (2003), but the impact that this may have on the SVOC emissions process has not been considered. For airborne particles, equilibrium can be achieved relatively fast (within 1 hour) (Odum et al. 1994; Kamens et al. 1995). Therefore, equilibrium partitioning between particles and DEHP can be assumed for air exchange rates on the order of one per hour. Relationships that predict gas/particle partitioning of SVOCs to various particulate phases as a function of vapor pressure have been established by Liang et al. (1997). Using these relationships, and a DEHP vapor pressure of 2.5×10^{-5} Pa (Cousins and Mackay 2000), K_p is 0.28 $m^3/\mu g$ for liquid di-ocotyl phthalate (DOP), 0.091 $m^3/\mu g$ for gasoline secondary organic aerosol (SOA), and 0.035 $m^3/\mu g$ for environmental tobacco smoke (ETS) (Liang et al. 1997). For DOP particles (representing an organic aerosol) and a total suspended particle concentration of 20 $\mu g/m^3$ (Weschler 2003), the

amount of DEHP on the airborne particles is roughly four times greater than that in the gas-phase. The effect that sorption to particles has on the emissions process is shown in Figure 2.8 for the three types of particle. The initial emission rate is largely unaffected, but the longer term emission rate is significantly increased, especially when partitioning is strong. In the case of the DOP particles, the final steady-state emission rate is increased by a factor of five. The particles essentially "scrub" the DEHP out of the system by transporting more DEHP out of the chamber than in the case without particles. If the particle concentration increases, the DEHP emission rate from the material also increases, as shown in Figure 2.9 for DOP particles. It appears that airborne particles may play an important role in distributing SVOCs well beyond the original source, and may substantially increase inhalation exposure.

If the air exchange rate is high, equilibrium between the gas and particles may not be fully achieved before the particles leave the chamber. For high ventilation rates ($\sim$10 h^{-1}), the fractional mass approach to equilibrium, M_t/M_{inf}, ranges between 10% and 70% (M_t/M_{inf} = 1 at equilibrium) (Odum et al. 1994). As shown in Figure 2.10, with an air exchange rate of 10 h^{-1}, even if complete equilibrium is not achieved, the mass of DEHP that sorbs to the particles substantially increases the DEHP emissions rate and decreases the DEHP gas-phase concentration. This is due to the higher flux of airborne particles passing through the chamber at the higher air exchange rate.

FURTHER RESEARCH

In this first mechanistic assessment of the emissions of SVOCs from polymeric materials and their subsequent interaction with both "fixed" and "transient" surfaces (examples of fixed surfaces include interior walls, furniture, carpeting, and dust, while transient surfaces include airborne particles) we have made several simplifying assumptions. Much remains to be done to confirm the overall modeling approach. For example, most studies have assumed a linear relationship for gas/particle partitioning (Weschler 2003; Liang et al. 1997; Bidleman 1998; Rounds and Pankow 1990) as we have done for this
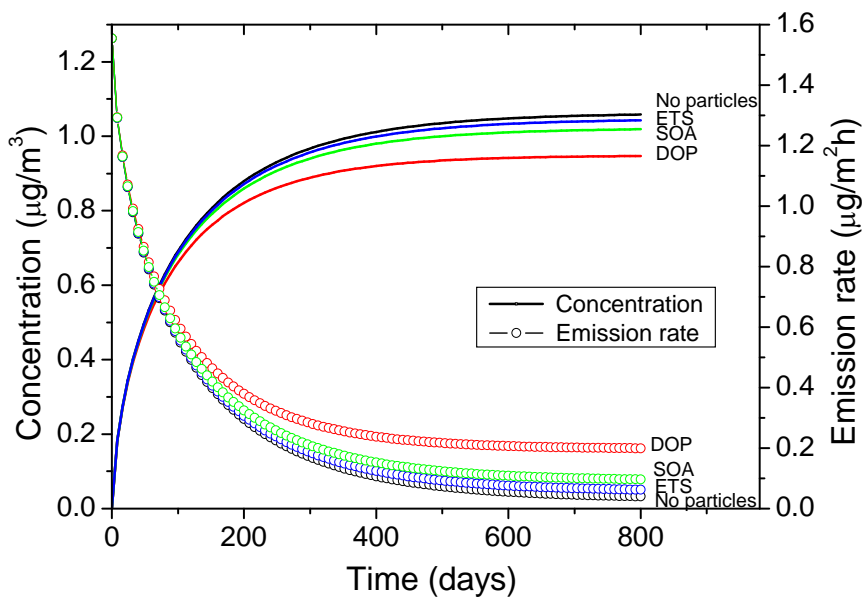
Figure 2.8 The influence of particle type on DEHP emission rate and gas-phase DEHP concentration
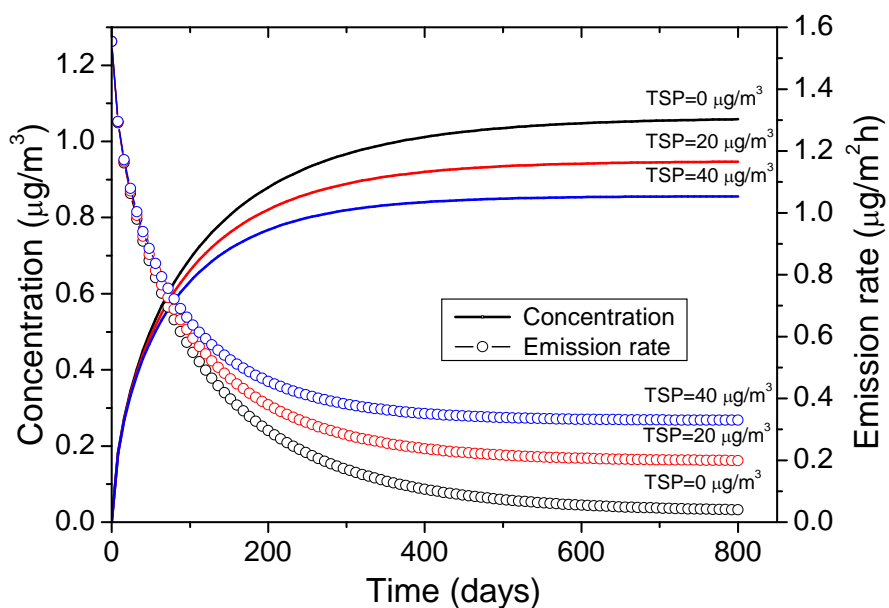
Figure 2.9 The influence of total suspended particle concentration on DEHP emission rate and gas-phase DEHP concentration
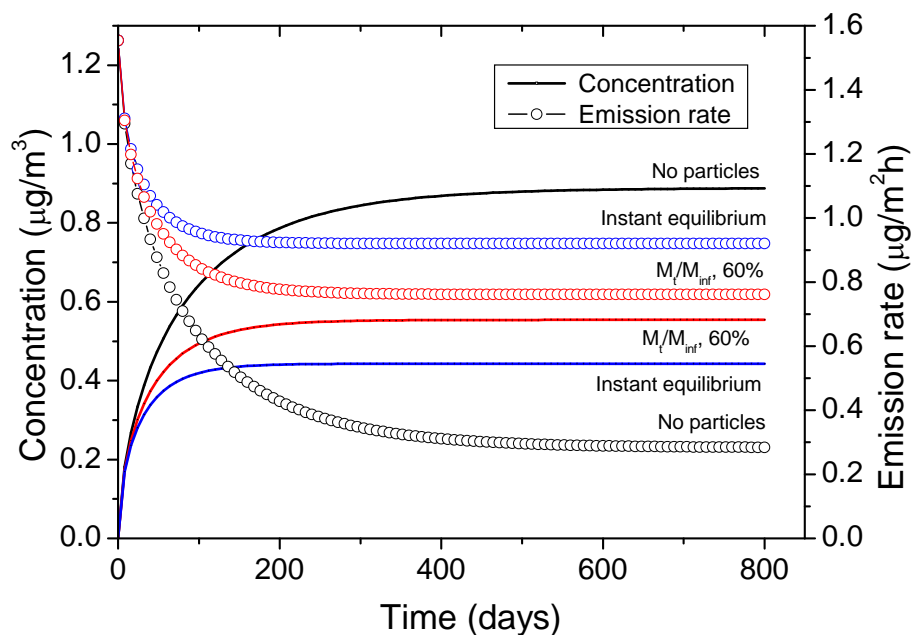
Figure 2.10 The influence of sorption kinetics on DEHP emission rate and gas-phase DEHP concentration at a high air exchange rate

model. However, our analysis of the partitioning between air and the chamber surfaces (glass and stainless steel) shows a non-linear relationship. The same was found for adsorption of nicotine and phenanthrene (also considered SVOCs) on a variety of indoor surfaces (Van Loy et al. 1997; 2001). Research should be done to confirm the equilibrium relationship between low volatility SVOCs and airborne particles, as well as the sorption kinetics. Given that airborne particles may facilitate the transport of SVOCs from the source to surrounding uncontaminated environments, the kinetics of desorption are also of interest. In cases where the initial SVOC material-phase concentration is much lower, the near-surface material could be significantly depleted during the emissions process. Depending on the specific conditions, this might mean that D would become important, and that both D and K would need to be known functions of concentration assuming they remain dependent on concentration. Finally, we note that in the Clausen et al. (2004) experiments, the steady-state gas-phase concentration of DEHP is close to the saturated vapor pressure. This suggests that both D and K are

concentration dependent. Indeed, the "solution" of DEHP in the vinyl flooring (17 % by weight) may well be super-saturated implying that the simple partitioning mechanism cannot be invoked. This must also be evaluated in greater detail.

PHTHALATES, FLAME RETARDANTS, AND OTHER SVOCS

In addition to phthalate plasticizers such as DEHP, other SVOCs (including polybrominated diphenyl ethers (PBDEs) and the phosphate-based flame retardants) are present in building materials and consumer products. For example, phthalates are found in toys, medical equipment, paints, inks, vinyl flooring, hair sprays, deodorants, nail polish, perfumes, cling film, and shampoo (Afshari et al. 2004); while flame retardants are found in computers, electronics, electrical equipment, cables, televisions, textiles, foam furniture, and insulating foams (Birnbaum and Staskal 2004). SVOCs have been found in a range of environmental media including indoor and outdoor air (Wensing et al. 2005; Hartmann et al. 2004), indoor dust (Hartmann et al. 2004), dryer lint, water, and snow. Perhaps because of their widespread use and lipophilicity, PBDEs are also ubiquitous in people (Hites 2004), and the same is probably true of many other SVOCs. For example, the vapor pressure of pentabromodiphenyl ether is 4.7×10^{-5} Pa, which is close to that of DEHP. Depending on their chemical properties, many of these SVOCs may behave in a similar fashion to DEHP, although for the flame retardants, this assumes that they are simple additives and do not react with or irreversibly bond to the material matrix (Birnbaum and Staskal 2004). Although some of the consumer products are liquids, the mechanisms governing emissions are most likely the same as for solid materials like vinyl floori Birnbaum and Staskal 2004ng, because SVOC emissions are probably independent of diffusion within the material itself in many cases. A clear understanding of the mechanisms governing the transfer of SVOCs into indoor air, as well as their subsequent sorption to interior surfaces and airborne particles is needed for reliable exposure and risk assessment. The proposed model will help achieve this goal.

REFERENCES

Adibi JJ, Perera FP, Jedrychowski W, Camann DE, Barr D, Jacek R, et al. 2003. Prenatal exposures to phthalates among women in New York City and Krakow, Poland. Environmental Health Perspectives 111(14): 1719-1722.

Afshari A, Gunnarsen L, Clausen PA, Hansen V. 2004. Emission of phthalates from PVC and other materials. Indoor Air 14(2): 120-128.

Andersson K, Bakke JV, Bjorseth O, Bornehag CG, Clausen G, Hongslo JK, et al. 1997. TVOC and health in non-industrial indoor environments - Report from a Nordic scientific consensus meeting at Langholmen in Stockholm, 1996. Indoor Air 7(2): 78-91.

Axley JW. 1991. Adsorption modeling for building contaminant dispersal analysis. . Indoor Air 1: 147-171.

Bako-Biro Z, Wargocki P, Weschler CJ, Fanger PO. 2004. Effects of pollution from personal computers on perceived air quality, SBS symptoms and productivity in offices. Indoor Air 14(3): 178-187.

Bidleman TF. 1988. Atmospheric processes - wet and dry deposition of organic-compounds are controlled by their vapor particle partitioning. Environmental Science & Technology 22(4): 361-367.

Birnbaum LS, Staskal DF. 2004. Brominated flame retardants: Cause for concern? Environmental Health Perspectives 112(1): 9-17.

Bornehag CG, Sundell J, Sigsgaard T. 2004a. Dampness in buildings and health (DBH): Report from an ongoing epidemiological investigation on the association between indoor environmental factors and health effects among children in Sweden. Indoor Air 14: 59-66.

Bornehag CG, Sundell J, Weschler CJ, Sigsgaard T, Lundgren B, Hasselgren M, et al. 2004b. The association between asthma and allergic symptoms in children and phthalates in house dust: A nested case-control study. Environmental Health Perspectives 112(14): 1393-1397.

Clausen PA, Hansen V, Gunnarsen L, Afshari A, Wolkoff P. 2004. Emission of Di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. Environmental Science & Technology 38(9): 2531-2537.

Cousins I, Mackay D. 2000. Correlating the physical-chemical properties of phthalate esters using the 'three solubility' approach. Chemosphere 41(9): 1389-1399.

Cox SS, Little JC, Hodgson AT. 2001a. Measuring concentrations of volatile organic compounds in vinyl flooring. Journal of the Air & Waste Management Association 51(8): 1195-1201.

Cox SS, Little JC, Hodgson AT. 2002. Predicting the emission rate of volatile organic compounds from vinyl flooring. Environmental Science & Technology 36(4): 709-714.

Cox SS, Zhao DY, Little JC. 2001b. Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring. Atmospheric Environment 35(22): 3823-3830.

Deng BQ, Kim CN. 2004. An analytical model for VOCs emission from dry building materials. Atmospheric Environment 38(8): 1173-1180.

Hartmann PC, Burgi D, Giger W. 2004. Organophosphate flame retardants and plasticizers in indoor air. Chemosphere 57(8): 781-787.

Hites RA. 2004. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. Environmental Science & Technology 38(4): 945-956.

Horn O, Nalli S, Cooper D, Nicell J. 2004. Plasticizer metabolites in the environment. Water Research 38(17): 3693-3698.

Horn W, Jann O, Wilke O. 2003. Suitability of small environmental chambers to test the emission of biocides from treated materials into the air. Atmospheric Environment 37(39-40): 5477-5483.

Kamens R, Odum J, Fan ZH. 1995. Some observations on times to equilibrium for semivolatile polycyclic aromatic-hydrocarbons. Environmental Science & Technology 29(1): 43-50.

Kumar D, Little J. 2003. Single-layer model to predict the source/sink behavior of diffusion-controlled building materials. Environmental Science & Technology 37(17): 3821-3827.

Lee CS, Haghighat F, Ghaly WS. 2005. A study on VOC source and sink behavior in porous building materials - analytical model development and assessment. Indoor Air 15(3): 183-196.

Liang CK, Pankow JF, Odum JR, Seinfeld JH. 1997. Gas/particle partitioning of semivolatile organic compounds to model inorganic, organic, and ambient smog aerosols. Environmental Science & Technology 31(11): 3086-3092.

Little JC, Hodgson AT, Gadgil AJ. 1994. Modeling emissions of volatile organic-compounds from new carpets. Atmospheric Environment 28(2): 227-234.

Matsumura T, Hamada M, Imanaka T. 2002. Development of a microanalysis method of phthalate esters in indoor air and its application to practical measurement. In: Indoor Air 2002. Monterey, CA, 183-187.

Odum JR, Yu JZ, Kamens RM. 1994. Modeling the mass-transfer of semivolatile organics in combustion aerosols. Environmental Science & Technology 28(13): 2278-2285.

Oie L, Hersoug LG, Madsen JO. 1997. Residential exposure to plasticizers and its possible role in the pathogenesis of asthma. Environmental Health Perspectives 105(9): 972-978.

Rounds SA, Pankow JF. 1990. Application of a radial diffusion-model to describe gas particle sorption kinetics. Environmental Science & Technology 24(9): 1378-1386.

Schwope AD, Lyman WJ, Reid RC. 1989. Methods for Assessing Exposure to Chemical Substances.

Van Loy MD, Riley WJ, Daisey JM, Nazaroff WW. 2001. Dynamic behavior of semivolatile organic compounds in indoor air. 2. Nicotine and phenanthrene with carpet and wallboard. Environmental Science & Technology 35(3): 560-567.

VanLoy MD, Lee VC, Gundel LA, Daisey JM, Sextro RG, Nazaroff WW. 1997. Dynamic behavior of semivolatile organic compounds in indoor air .1. Nicotine in a stainless steel chamber. Environmental Science & Technology 31(9): 2554-2561.

Wensing M, Uhde E, Salthammer T. 2005. Plastics additives in the indoor environment - flame retardants and plasticizers. Science of the Total Environment 339(1-3): 19-40.

Weschler CJ. 2003. Indoor/outdoor connections exemplified by processes that depend on an organic compound's saturation vapor pressure. Atmospheric Environment 37(39-40): 5455-5465.

Xu Y, Zhang YP. 2003. An improved mass transfer based model for analyzing VOC emissions from building materials. Atmospheric Environment 37(18): 2497-2505.

Xu Y, Zhang YP. 2004. A general model for analyzing single surface VOC emission characteristics from building materials and its application. Atmospheric Environment 38(1): 113-119.

Yang X, Chen Q, Zhang JS, An Y, Zeng J, Shaw CY. 2001. A mass transfer model for simulating VOC sorption on building materials. Atmospheric Environment 35(7): 1291-1299.

Zhang LZ, Niu JL. 2003. Laminar fluid flow and mass transfer in a standard field and laboratory emission cell. International Journal of Heat and Mass Transfer 46: 91–100.

Zhu LY, Hites RA. 2004. Temporal trends and spatial distributions of brominated flame retardants in archived fishes from the Great Lakes. Environmental Science & Technology 38(10): 2779-2784.

Chapter 3: Characterizing Emissions of Phthalate Plasticizer from Vinyl Flooring In a Specially-Designed SVOC Emission Chamber

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ABSTRACT

The emission of di-2-ethylhexyl phthalate (DEHP) from vinyl flooring was studied in duplicate for up to 140 days in specially-designed stainless steel chambers. In both chamber studies, the gas-phase concentration in the chamber increased slowly and reached a steady state level of 0.9 $\mu g/m^3$ after about 30 days. By increasing the area of vinyl flooring and decreasing that of stainless steel surface in the chamber design, the time to reach steady state was significantly reduced, compared to a previous study (30 days vs. 5 months). The adsorption isotherm of DEHP on stainless steel chamber surfaces was explicitly measured using two different methods (solvent extraction and thermal desorption). Strong adsorptions of DEHP onto the stainless steel surface were observed and found to follow a simple linear relationship. The thermal desorption method was shown to be more reliable than the solvent extraction method due to the higher adsorption isotherm achieved (1400 m vs. 890 m). The content of DEHP in vinyl flooring was investigated through pressurized liquid extraction and was shown to contain about 15% (w/w) of DEHP. In addition, parameters measured in the experiments were then applied in a fundamental emission model. Good agreement was obtained between the predictions of the model and the gas-phase DEHP chamber concentrations, without resorting to fitting of model parameters. This study gave a more complete understanding of the release of DEHP from vinyl flooring. It may also help to elucidate the mechanisms governing emissions of plasticizers, brominated flame retardants, biocides, and other SVOCs from a wide range of building materials and consumer products.

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INTRODUCTION

Phthalate esters have been recognized as major indoor pollutants (CG Bornehag et al. 2005a; Fromme et al. 2004; Wensing et al. 2005). They are mainly used as plasticizers to enhance flexibility of polyvinylchloride (PVC) products, as well as humectants, emollients, and antifoaming agents. Phthalates are found in a wide range of consumer products including floor coverings, wall coverings, car interior trim, floor tiles, gloves, footwear, and artificial leather (Bornehag et al. 2005a). However, because phthalates are not chemically bound in polymers, slow emission from the products to air or other media usually occurs.

There are serious health concerns associated with phthalate esters. When administered orally to pregnant experimental animals, Gray et al. (2000) found that certain phthalate esters have significant effects on the developing male reproductive system. Two studies of male infants suggest that human testicular development may be vulnerable to phthalates (Lottrup et al. 2006). One study shows that phthalate esters may have an etiological association with endometriosis in women (Reddy et al. 2006). In addition to the primary health concerns of various reproductive effects, epidemiological studies shown that there is association between the occurrence of plasticized products indoors such as PVC flooring and allergic symptoms in the airways (e.g. asthma), nose and skin (CG Bornehag et al. 2005a; CG Bornehag et al. 2005b; Jaakkola et al. 2006; Jaakkola et al. 1999; Kolarik et al. 2008; Øie et al. 1997).

Despite these health concerns, only a few chamber studies of phthalate emission characteristics are available (Axley 1991; Clausen et al. 2004; Fujii et al. 2003; Uhde et al. 2001). This is probably due to the difficulties associated with sampling and analysis of SVOCs (Clausen et al. 2004). Clausen et al. (2004) measured emissions of di-2-ethylhexyl phthalate (DEHP) from vinyl flooring for more than a year in both the FLEC (field and laboratory emission cell) and the CLIMPAQ (Chamber for Laboratory Investigations of Materials, Pollution, and Air Quality). In their experiments, they found that about one-half of the emitted DEHP was deposited on the internal surfaces of both the FLEC and the CLIMPAQ. Based on the Clausen et al. (2004) experiments, Xu and Little (2006) developed a model to predict the emission rate of phthalates from polymer

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materials. Their analysis revealed that emissions of the very low volatility semi-volatile organic compounds (SVOCs) (such as DEHP) are subject to "external" control (partitioning into the gas phase, the convective mass-transfer coefficient, and adsorption onto chamber surfaces). Xu et al. (2009a; 2009b) then extended this model and investigated human exposures in residential environment.

The aim of this study is to more completely understand the mechanisms governing the release of DEHP from vinyl flooring in small test chamber, and to more rigorously validate our previous model (Xu and Little 2006). To reduce the time to reach steady-state, a specially designed stainless steel chamber was used. The sorption behavior of DEHP on the stainless steel surface of the chamber wall was investigated, and a more rigorous validation of the previously developed model was obtained.

METHODS AND MATERIALS

Chemicals
DEHP was obtained from Absolute Standards Inc., and methanol (anhydrous, 99.9%) was obtained from VWR International Inc.

Test Piece
A 2-mm thick homogeneous polyurethane reinforced vinyl flooring (VF) was used. The VF contains about 15% (w/w) DEHP as the only plasticizer. It was delivered as a roll wrapped in plastic foil from a merchant in Denmark. A few days after receipt, it was cut into two 0.45m × 0.45m square sheets which were placed in the emission chamber. The specific weight of the VF (~3.9 kg/m^2) was provided by the manufacture.

Emission Chamber
The emission chamber was made of type 304 stainless steel (SS) with electro-polished internal chamber surface. As shown in Figure 3.1, the thin chamber "ring" was positioned between two VF pieces. The two VF test sheets and the internal chamber wall form a short cylindrical-shaped cavity. In this way, we achieved the maximum VF emission area and minimum SS adsorption area. The air flow from the inlet passes

through the chamber and exits at the outlet. Thus, the air velocity over the VF surfaces depends on the chamber airflow rate. The VF itself acts as a good gasket. PTFE sheets (from Fluoro-Plastics Inc.) were used to seal the blank chamber. The air leakage rate was less than 2% of the total flow rate. Three type 304 stainless steel precision-ground rods (3mm diameter × 6cm length), having similar roughness to the interior SS chamber surface, were inserted into the chamber and then periodically removed so that the adsorbed surface concentration could be measured. This allowed us to relate the instantaneous gas-phase concentration to the adsorbed surface concentration at that point in the chamber run and then to establish the equilibrium relationship at the end of the chamber test.
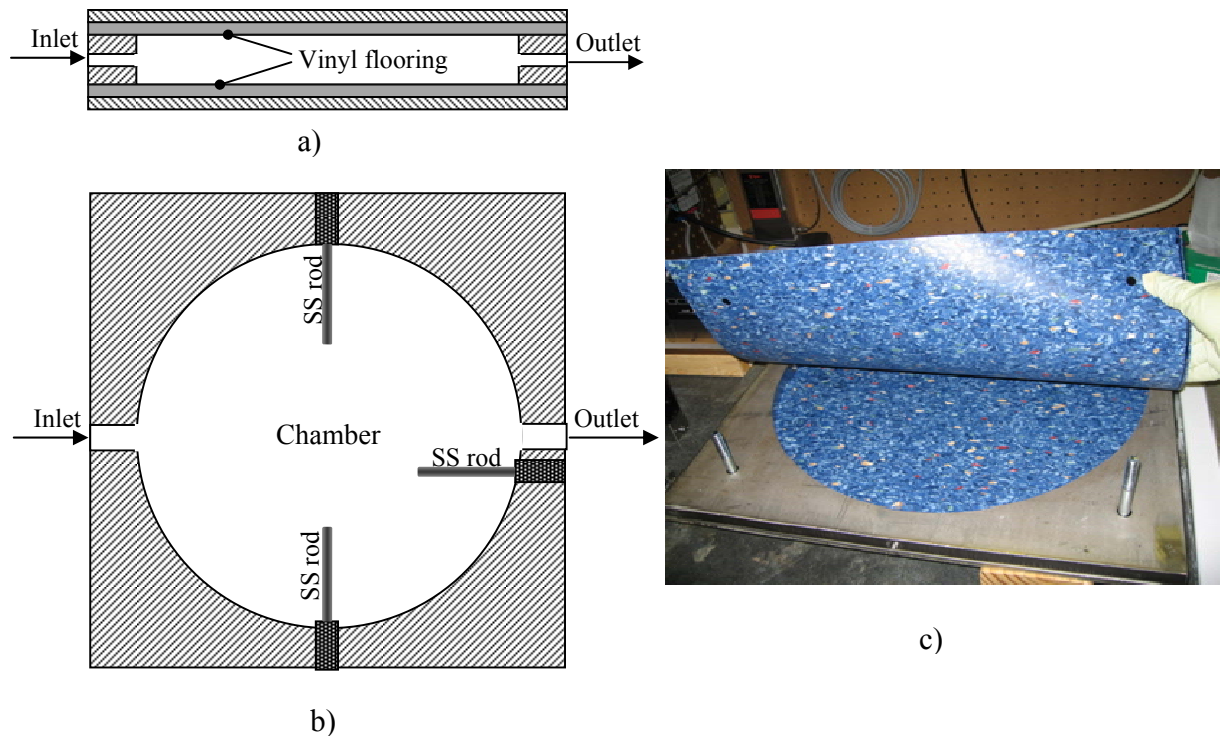
Figure 3.1 Configuration of the chamber. a) Side view, b) Top view, c) Photo.

Emission of DEHP into Air

The first emission test was conducted in one chamber with a separate "empty" chamber as a blank. A duplicate emission test was followed in another identical chamber after the first test was finished. The tests duration were about 150 days with test conditions shown in Table 3.1. The chamber was cleaned, and background measurements were performed before testing. Since humidity does not significantly influence DEHP emission (Clausen et al. 2007), only temperature and airflow rate through the chamber were checked before and after each sampling.

Sorption Experiment

Three SS rods were inserted into the chamber as shown in Figure 3.1. Because the surface of the SS rods is almost identical to the surface of the internal SS chamber, they provide a means to measure the adsorption characteristics of the SS chamber surface. Before use, the SS rods were cleaned with methanol. Two methods, thermal desorption and solvent extraction, were used to measure the adsorbed surface concentration of DEHP.

Thermal desorption. During sampling, the SS rods were taken out of the chamber and quickly put into three stainless steel tubes separately, then sealed until thermal desorption analysis through TD-GC/FID system. All the stainless steel tubes were cleaned with methanol and the empty tube background concentration was checked before use.

Solvent extraction. During sampling, the rods were taken out of the chamber and quickly put into three glass tubes separately, each contained about 10 ml methanol as solvent. The tubes were then sonicated for 15 minutes to ensure that DEHP was exhaustively desorbed from the SS rods and dissolved into the solvent. Next, the extracts were concentrated by gentle blowing with high purified nitrogen gas to evaporate the methanol. Finally, the concentrated extracts (0.2ml) were analyzed by GC-MS system. All glassware used was cleaned with methanol.

Table 3.1 Test conditions

Parameters	
Temperature (°C)	22 ± 0.2
Volume (L)	2
Airflow rate (ml/min)	850 ± 20
Air exchange rate (/h)	25 ± 1
Air velocity at test piece surface (m/s)	0.004[a]
Area of test pieces (m^2)	2 × 0.126
Internal stainless steel surface area (m^2)	0.02
Chamber diameter (cm)	40
Chamber height (cm)	1.6

a. Estimated based on geometry

Sampling of DEHP in the Effluent Air from Chamber

Since the sampling systems were supplied with high purified air from cylinders, we assumed an insignificant amount of particles existed. Therefore, DEHP was sampled directly on Tenax-TA tubes with a pump (SKC 224-PCXR4) calibrated to a nominal flow of 130 ml/min. The sampling time was 24 hours. The sampling system is shown in Figure 3.2. Backup tubes were connected to sample tubes to check for breakthrough. To reduce the loss of DEHP adsorbed onto SS tubing and connection parts, the possible shortest pathway was applied.
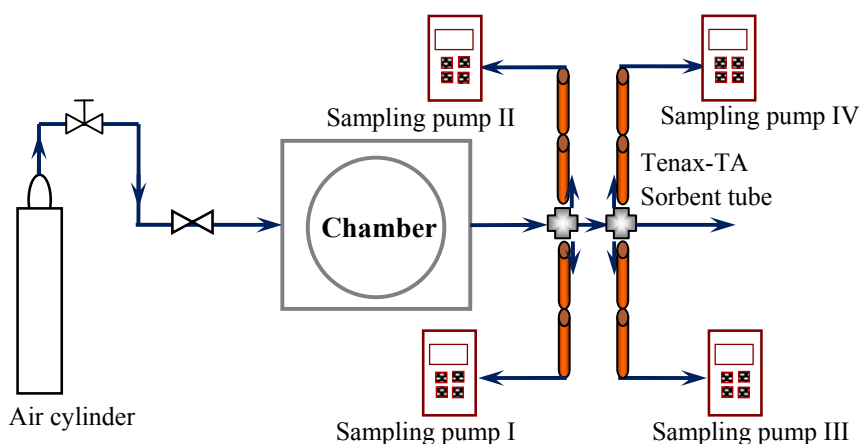
Figure 3.2 Schematic of sampling system

Estimation of DEHP Content in Vinyl Flooring

Ten samples of approximately 30 mg were cut out of the vinyl flooring with a pair of scissors at randomly chosen positions. The samples were extracted with methanol using pressurized liquid extraction with a Dionex ASE 200 system. The extraction cell with the sample was preheated to 150 °C for 7 min, followed by a static extraction of 10 min at constant pressure (2000 psi). After the static extraction, the pressure was released and the extract was collected in a 40 ml glass vial. The extraction cycle was repeated three times for exhaustive extraction of both samples and blanks. 5µl of the extract was injected on Tenax TA tubes, and the tubes analysed with TD-GC-FID.

Analysis of DEHP Samples

TD-GC-FID system. A thermal desorber (TD) (Perkin-Elmer ATD 400) was connected to a gas chromatograph (HP 6890 GC) with flame ionization detector (FID). The sample tubes were desorbed for 30 min at 300 °C, a He flow of 50 ml/min, and a cold trap temperature of -20 °C. The cold trap was narrow bore (Low Flow Trap Tube) packed with a small piece of silylated glass wool. Flash heating of the cold trap to 350 °C transferred the analytes through the valves at 225 °C and the transfer line at 225 °C to the GC. The GC-FID had a constant pressure resulting in a flow of about 10 ml/min at 120 °C and was equipped with 30 m × 0.53 mm i.d. Restek RTX-1 column. The

temperature program was 120 °C, held for 2 min, increased to 300 °C at 15 °C/min, held for 8 min, and finally increased to 320 °C at 20°C/min and held for 4 min. The FID heater temperature was 275°C. The analytical detection limit was 0.01 µg/tube estimated based on evaluation guidelines for air sampling methods utilizing chromatographic analysis (OSHA 1999). The standard solutions in methanol were injected into the Tenax tubes. The calibration curve is shown in Figure 3.3 and 11 standards were used for each point (a total of six different points). All tubes were analyzed by two successive desorptions to ensure complete desorption of both the tube and the TD system. The second desorption of the tubes showed concentrations below the detection limit in all cases. Before use, all tubes were conditioned at 310 °C for one hour with high purified nitrogen gas at 80 ml/min flow rate, and the background concentration of the clean tubes was also checked.
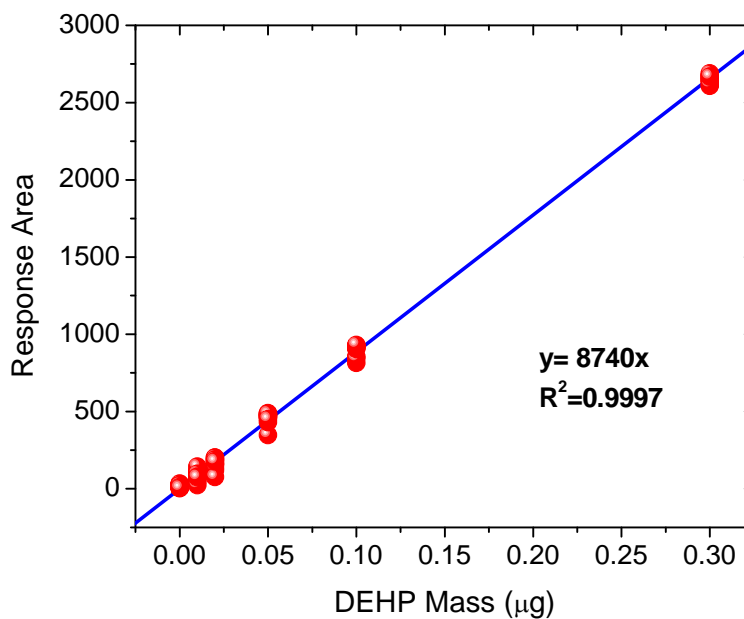
Figure 3.3 Calibration curve

GC-MS system. A GC (Agilent 6890) with mass spectrometric (Agilent 5973 MS) was used to analyze solvent extraction samples. The GC-MS had a constant pressure of (He as carrier gas) about 20 psi with a flow rate of about 1ml/min. It was equipped with 30m

× 0.25 mm i.d. DB-17 column (0.3 μm film thickness). The temperature program was 200 °C, held for 1 minute, increased to 300 °C at 10 °C/min and finally held for 1min. The MS transfer line temperature is 280 °C. The MS was operated in the electron impact ionization mode (EI+, 70 eV) with a source temperature of 230 °C using full-scan mode (m/z 45-550).

RESULTS

Emission of DEHP into Air

There appears to be a good agreement between the two chamber tests shown in Figure 3.4. The concentrations of the blank chamber were about 10 times lower than the corresponding highest measured emission concentrations in the sample chamber with VF (see Figure 3.4). The test conditions were relatively constant over the entire test period (Table 3.1). The DEHP concentration curve increased slowly and reached steady state $(0.8\sim0.9\mu g/m^3)$ at about 30 days. Since the ratio between the VF emission surface and the SS sorption surface was substantially increased by the chamber design compared to the FLEC (Field and Laboratory Emission Cell), the accumulation of DEHP in the gas-phase was much faster and the time to reach steady state was significantly reduced, compared to a previous FLEC study of DEHP emission from VF (Clausen et al. 2004) where it took ~150 days.

Sorption Experiment

Strong adsorption occurred on the stainless steel surfaces. Both solvent extraction and thermal desorption methods show that a simple linear relationship is enough to describe stainless steel surface/air equilibrium for DEHP (Figure 3.5). However, the adsorption isotherm through solvent extraction method is only 65% of the value by thermal desorption. The reason may be loss of DEHP due to adsorption to glassware ('wall memory effect') or when transferring sample between vials and tubes. Therefore, thermal desorption method was considered more reliable to achieve adsorption isotherm for DEHP on SS surfaces.
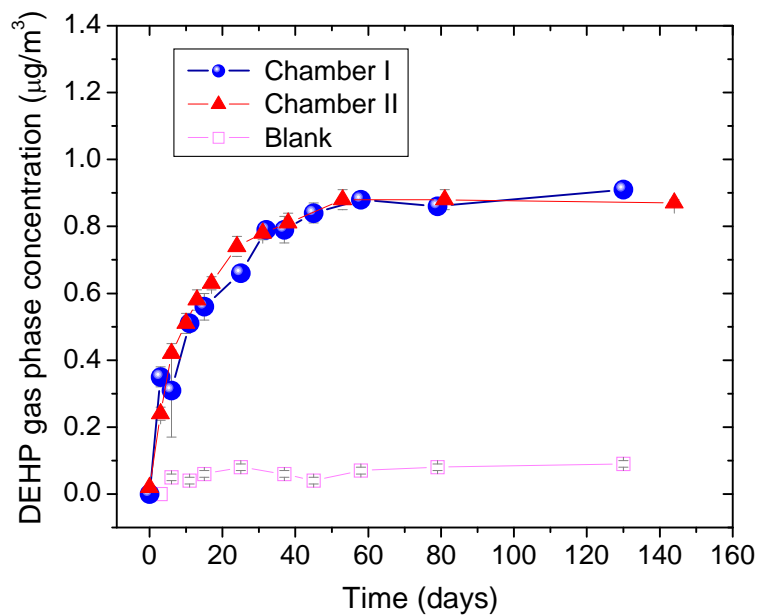
Figure 3.4 Concentrations for emission of DEHP from vinyl flooring

a)   b)
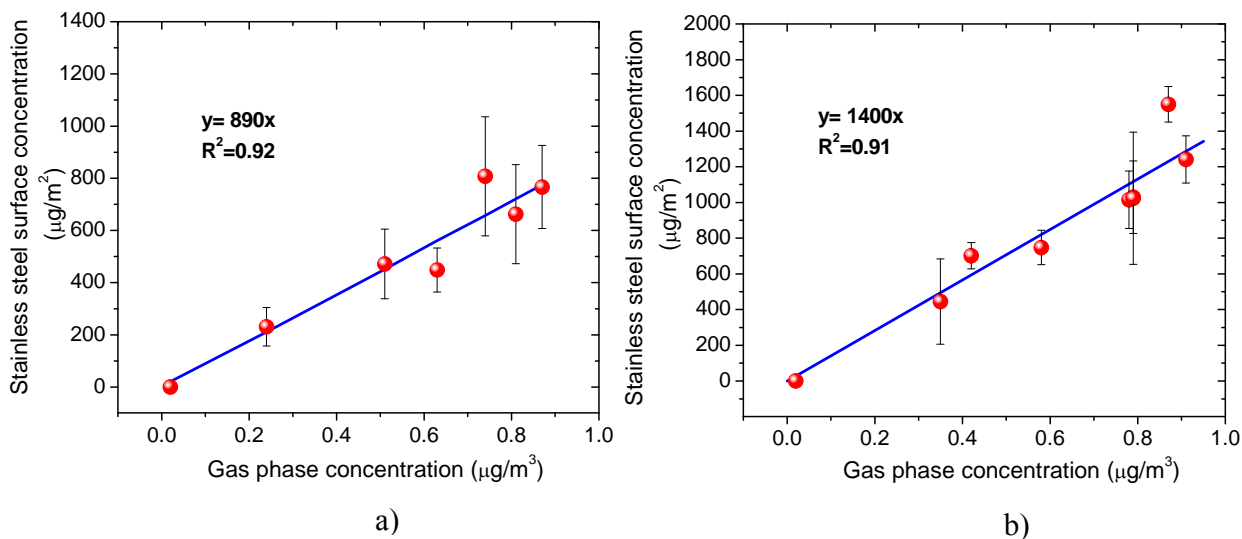
Figure 3.5 Adsorption isotherm of DEHP on SS surface

a) Solvent extraction. b) Thermal desorption

Estimation of DEHP content in vinyl flooring

The results are shown in Figure 3.6. The background level of DEHP in the blank was about 0.5 % of the content of the samples. The results were not blank corrected. Sample

8 appear to be very low. However, we cannot find any errors of the extraction and analysis. Therefore it has not been rejected. The observed variation may be due to inhomogeniety of the distribution of DEHP in the vinyl flooring. Unknown losses of DEHP from the samples may be due to deposition on the scissors during cutting.
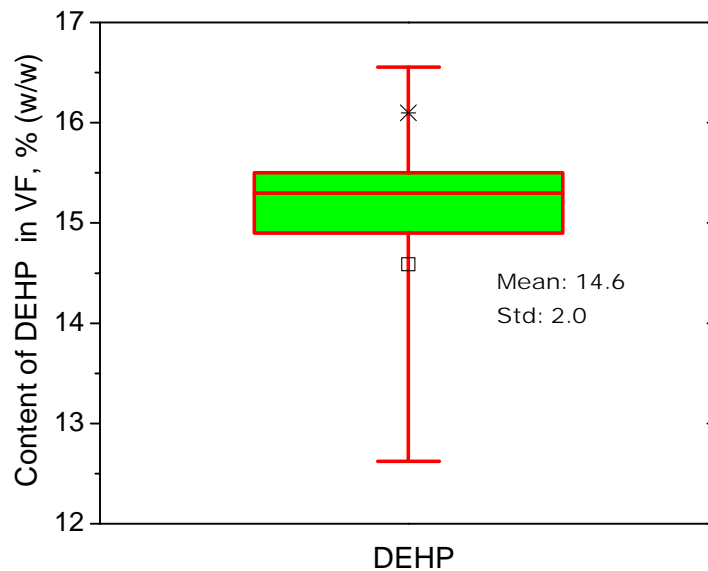
Figure 3.6 DEHP content in vinyl flooring

DISCUSSION

Xu and Little (2006) developed a model to predict the emission rate of phthalates as well as other SVOCs from polymer materials. Their study elucidated the fundamental mechanisms governing the emissions of phthalates. In their analysis, the DEHP emission rate was expressed as:

$$\dot{m}(t) = -D \cdot \frac{\partial C(x,t)}{\partial x}\bigg|_{x=L} = D \cdot \sum_{m=1}^{\infty} \sin^2(\beta_m L) \cdot \frac{2(\beta_m^2 + H^2)}{L(\beta_m^2 + H^2) + H} \cdot$$

$$[(C_0 - Ky(0))e^{-D\beta_m^2 t} + \int_0^t e^{-D\beta_m^2(t-\tau)} \cdot Kdy(\tau)] \qquad (1)$$

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where K is the VF/air partition coefficient, D is the diffusion coefficient within the VF, C_0 is the initial DEHP concentration in the VF, y is the gas phase concentration of the chamber, h_m is the convective mass transfer coefficient across the emission surface, and $H = \dfrac{h_m}{KD}$ and β_m (m = 1, 2,…) are the positive roots of

$$\beta_m \cdot \tan(\beta_m L) = H \tag{2}$$

The linear instantaneously reversible equilibrium relationship between the exposed interior chamber surface area A_i and the chamber air can be expressed as:

$$q = K_s \cdot y \tag{3}$$

where q is the adsorbed DEHP surface concentration and K_s is the partition coefficient. The accumulation of DEHP in the chamber obeys the following mass balance:

$$\frac{dy(t)}{dt} \cdot V = Q \cdot y_{in}(t) - A_i \cdot \frac{dq(t)}{dt} + A_s \cdot \dot{m}(t) - Q \cdot y(t) \tag{4}$$

where Q is the airflow rate and A_s is the emission surface area. The emissions model that incorporates interaction with the chamber surface is obtained by combining equations (1) – (4).

Our previous analysis (Xu and Little 2006) revealed that C_0, K, h_m, and K_s are important parameters that control DEHP emissions. C_0 and K_s are directly measured in this study as shown above. The value of h_m was estimated using correlation equations (Axley 1991), which express h_m as a function of Reynolds number and Schmidt number. The value of K calculated by Xu and Little (2006) was used here. Table 3.2 summarizes the model parameters for the experimental condition. The data collected in the experiments were used to test the predictive ability of the model, as shown in Figure 3.7, with good agreement.

Table 3.2 Summary of model parameters.

Parameters	Value	Comments
C_0 ($\mu g/m^3$)	2.85×10^{11}	Measured, Figure 3.6
D (m^2/s)	1.0×10^{-13}	Estimated, (Xu and Little 2006)
h_m (m/s)	1.0×10^{-4}	Estimated based on mean velocity across VF (Axley 1991)
K	2.3×10^{11}	Calculated, (Xu and Little 2006)
K_s (m)	1400	Measured, Figure 3.5
Q (ml/min)	850	Measured, Table 3.1
A_s (m^2)	0.25	Measured, Table 3.1
A_i (m^2)	0.02	Measured, Table 3.1

An important assumption of Xu and Little's model is that the gas is well mixed within the chamber. Computational fluid dynamics (CFD) method is applied further to investigate the air velocity field in the chamber. A 3-D geometry and mesh is constructed in GAMBIT 2.2.30 in Cartesian coordinate system. Only half of the entire chamber cavity is simulated due to the symmetric structure of the chamber. The circular inlet is simplified to a square for convenience. 34000 grids were employed in the numerical simulation totally. FLUENT 6.3.26 was employed to simulate the velocity field. As shown in Figure 3.8, the air flow is circulated and mixed well within the chamber cavity, which is in accordance with the model assumption.
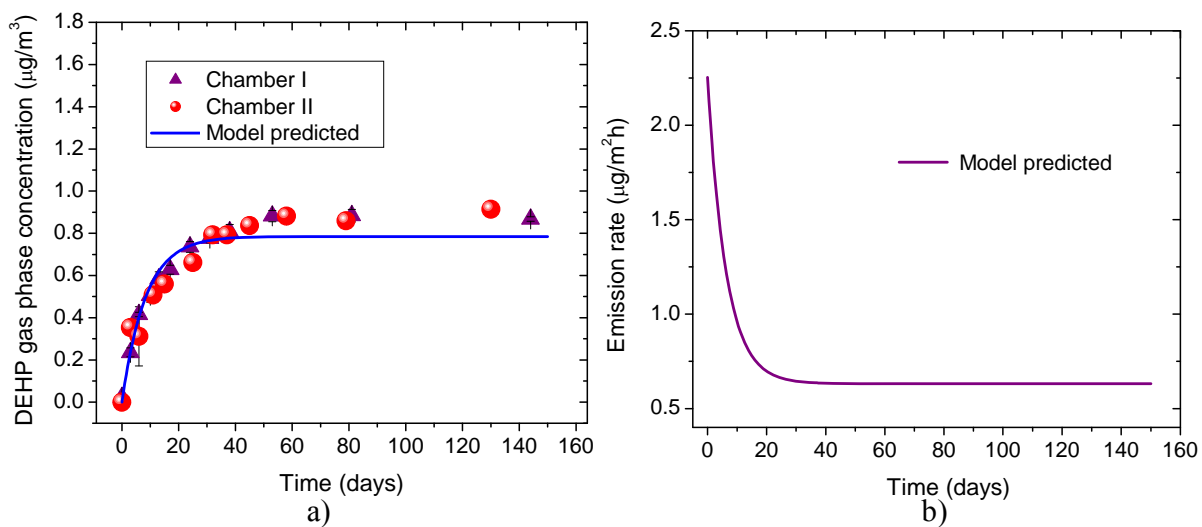
Figure 3.7 a) Comparison of predicted gas-phase DEHP concentrations with data measured in experiment chamber. b) Predicted emission rate.
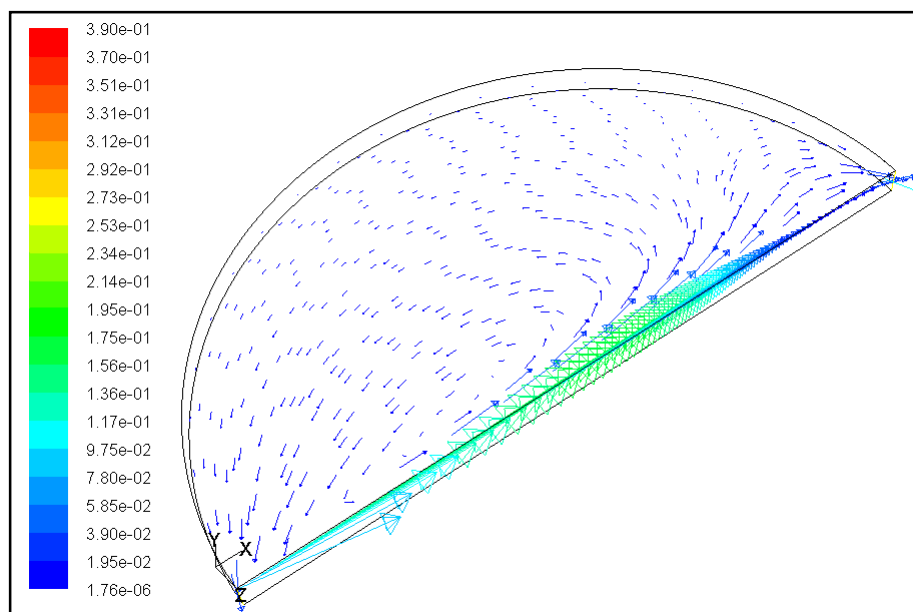
Figure 3.8 Simulation of air velocity field in the chamber
(Velocity vectors coloured by velocity magnitude, m/s)

In this study, a special stainless steel chamber was designed to reduce the time to reach steady-state during testing of the emission of SVOCs from materials. The sorption behavior of DEHP on the stainless steel surface of the chamber wall was investigated, and a more rigorous validation of the previously developed model was obtained. The

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analysis gave a more completely understanding on the release of DEHP from vinyl flooring. It may also help to elucidate the mechanisms governing emissions of plasticizers, brominated flame retardants, biocides, and other SVOCs from a wide range of building materials and consumer products.

ACKNOWLEDGMENTS

REFERENCES

Afshari A, Gunnarsen L, Clausen PA, Hansen V. 2004. Emission of phthalates from PVC and other materials. Indoor Air 14: 120–128.

Axley JW. 1991. Adsorption modeling for building contaminant dispersal analysis. Indoor Air 2: 147-171.

Bornehag CG, Lundgren B, Weschler CJ, Sigsgaard T, Hagerhed-Engman L, Sundell J. 2005a. Phthalates in Indoor Dust and Their Association with Building Characteristics. Environmental Health Perspectives 113(10): 1399-1404.

Bornehag CG, Sundell J, Hagerhed-Engman L, Sigsggard T, Janson S, Aberg N. 2005b. "Dampness"at home and its association with airway, nose and skin symptoms among 10,851 preschool children in Sweden: a cross sectional study. Indoor Air 15(Suppl 10): 48–55.

Clausen P, Hansen V, Gunnarsen L, Afshari A, Wolkoff P. 2004. Emission of Di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. Environmental Science and Technology 38(9): 2531-2537

Clausen PA, Xu Y, Kofoed-Sørensen V, Little JC, Wolkoff P. 2007. The influence of humidity on the emission of di-(2-ethylhexyl) phthalate (DEHP) from vinyl flooring in the emission cell "FLEC". Atmospheric Environment 41: 3217-3224.

Fromme H, Lahrz T, Piloty M, Gebhart H, Oddoy A, Rüden H. 2004. Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). Indoor Air 14: 188–195.

Fujii M, Shinohara N, Lim A, Otake T, Kumagai K, Yanagisawa Y. 2003. A study on emission of phthalate esters from plastic materials using a passive flux sampler. Atmospheric Environment 37: 5495-5504.

Gray LE, Jr. JO, Furr J, Price M, Veeramachaneni DNR, Parks L. 2000. Perinatal Exposure to the Phthalates DEHP, BBP, and DINP, but Not DEP, DMP, or DOTP, Alters Sexual Differentiation of the Male Rat. Toxicological sciences 58: 350-365.

Jaakkola JJ, Ieromnimon A, Jaakkola MS. 2006. Interior surface materials and asthma in adults: a population-based incident casecontrol study. American Journal of Epidemiology 164: 742-749.

Jaakkola JJK, Oie L, Nafstad P, Botten G. 1999. Interior surface materials in the home and the development of bronchial obstruction in young children in oslo, Norway. American Journal of Public Health 89(2): 188-192.

Kolarik B, Bornehag C-G, Naydenov K, Sundell J, Stavova P, Nielsen OF. 2008. The concentrations of phthalates in settled dust in Bulgarian homes in relation to building characteristic and cleaning habits in the family. Atmospheric Environment 42: 8553–8559.

Lottrup G, Andersson A-M, Leffers H, Mortensen GK, Toppari J, Skakkebæk NE, et al. 2006. Possible impact of phthalates on infant reproductive health. International Journal of Andrology 29: 172–180.

Øie L, Hersoug L-G, Madsen JØ. 1997. Residential Exposure to Plasticizers and Its Possible Role in the Pathogenesis of Asthma. Environmental Health Perspectives 105(9): 972-978

OSHA. 1999. Evaluation guidelines for air sampling methods utilizing chromatographic analysis. Available: http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.html. [accessed May 3 2009].

Reddy B, Rozati R, Reddy B, Raman N. 2006. Association of phthalate esters with endometriosis in Indian women. International Journal of Obstetrics and Gynaecology 113: 515–520.

Uhde E, Bednarek M, Fuhrmann F, Salthammer T. 2001. Phthalic Esters in the Indoor Environment –Test chamber studies on PVC-coated wallcoverings. Indoor Air 11: 150-155.

Wensing M, Uhde E, Salthammer T. 2005. Plastics additives in the indoor environment—flame retardants and plasticizers. Science of the Total Environment 339: 19– 40.

Xu Y, Hubal EAC, Clausen PA, Little JC. 2009a. Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – A Mechanistic Analysis. Environmental Science and Technology Accepted.

Xu Y, Hubal EAC, Little JC. 2009b. Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – Sensitivity, Uncertainty, and Implications for Biomonitoring. Submitted.

Xu Y, Little J. 2006. Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles Environmental Science and Technology 40(2): 456-461

Chapter 4: Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – A Mechanistic Analysis

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ABSTRACT

A two-room model is developed to estimate the emission rate of di-2-ethylhexyl phthalate (DEHP) from vinyl flooring and the evolving gas-phase and adsorbed surface concentrations in a realistic indoor environment. Because the DEHP emission rate measured in a test chamber may be quite different from the emission rate from the same material in the indoor environment, the model provides a convenient means to predict emissions and transport in a more realistic setting. Adsorption isotherms for phthalates and plasticizers on interior surfaces, such as carpet, wood, dust and human skin, are derived from previous field and laboratory studies. Log-linear relationships between equilibrium parameters and chemical vapor pressure are obtained. The predicted indoor air DEHP concentration at steady state is 0.15 $\mu g/m^3$. Room 1 reaches steady state within about one year, while the adjacent room reaches steady state about three months later. Ventilation rate has a strong influence on DEHP emission rate while total suspended particle concentration has a substantial impact on gas-phase concentration. Exposure to DEHP via inhalation, dermal absorption and oral ingestion of dust is evaluated. The model clarifies the mechanisms that govern the release of DEHP from vinyl flooring and the subsequent interactions with interior surfaces, airborne particles, dust, and human skin. Although further model development, parameter identification and model

validation is needed, our preliminary model provides a mechanistic framework that elucidates exposure pathways for phthalate plasticizers, and can most likely be adapted to predict emissions and transport of other semi-volatile organic compounds, such as brominated flame retardants and biocides, in a residential environment.

INTRODUCTION

Since the 1930s, phthalates have been used as plasticizers to enhance the flexibility of rigid polyvinylchloride (PVC) products (Latini et al. 2004), with worldwide phthalate production exceeding 3.5 million tons/year (Cadogan and Howick 1996). About 90% of phthalates are used as plasticizers in polymers (e.g., PVC) and are found in a wide range of consumer products including floor- and wall covering, toys, car interior trim, clothing, gloves, footwear, and artificial leather (Bornehag et al. 2005). Di(2-ethylhexyl) phthalate (DEHP) is most widely used and accounts for more than 50% of total phthalate production (Bornehag et al. 2005). The main use of DEHP is in PVC products such as vinyl flooring, where it is typically present at concentrations of ~ 20% – 40% (w/w) (Fromme et al. 2004; Clausen et al. 2004). Other common phthalates are dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP).

Because phthalates are not chemically bound in polymers, slow emission from the products to air or other media usually occurs. Adverse health effects of phthalates are briefly reviewed in the Supplementary Information (SI). Phthalate esters have been recognized as major indoor pollutants (Fromme et al. 2004; Wensing et al. 2005; C-G Bornehag et al. 2005). By sampling in 120 homes and analyzing for 89 organic chemicals, Rudel et al. (2003) revealed that phthalates are one of the most abundant contaminants in indoor air. In the recent EPA-sponsored CTEPP (Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants) study (EPA 2005), concentrations of over 50 target compounds were measured in multimedia samples from the homes and daycare centers of 260 pre-school age children. The two phthalates targeted in the CTEPP study were detected in residential air and house dust, and on interior surfaces and dermal wipe samples. As in Rudel et al.'s study, measured phthalate

concentrations were amongst the highest of any of the targeted compounds, including pesticides, PAHs and PCBs. Despite this, only a few studies of phthalate emission characteristics and exposure are available. Uhde et al. (2001) measured emission of several phthalates from PVC-coated wall-coverings in test chambers under standard room conditions. Clausen et al. (2004) measured emissions of DEHP from vinyl flooring for more than a year in both the FLEC (field and laboratory emission cell) and the CLIMPAQ (chamber for laboratory investigations of materials, pollution, and air quality). In addition, the effect of humidity on the emission of DEHP from vinyl flooring was studied for one year in the FLEC (Clausen et al. 2007), the emission of phthalates from different types of plasticized product was studied for 150 days in the CLIMPAQ (Afshari et al. 2004), and the emission of phthalates from different types of plasticized materials was studied using a passive flux sampler (Fujii et al. 2003).

Based on Clausen et al. (2004) experiments, Xu and Little (2006) developed a model to predict the emission rate of phthalates from polymer materials. Their analysis revealed that emissions of the very low volatility semi-volatile organic compounds (SVOCs) (such as DEHP) are subject to "external" control (partitioning into the gas phase, the convective mass-transfer coefficient, and adsorption onto chamber surfaces). The tendency of phthalates to adsorb strongly to surfaces is most likely similar to other SVOCs. Gebefügi (1989) showed that SVOCs were sorbed by cotton and Van Loy et al. (1997) found that more than 99% of recovered nicotine was adsorbed to the walls of their stainless steel chamber. Compared to these experimental chamber systems, the indoor environment has many other types of surface that will adsorb SVOCs such as DEHP to different extents. The emission rate measured in a test chamber may therefore be quite different to the emission rate from the same material in the indoor environment.

The model developed by Xu and Little (2006) provides a convenient means to estimate the emission rate and gas phase and adsorbed surface concentrations likely to occur in more realistic indoor environments. In this paper we both simplify and extend the Xu and Little model to investigate potential emission and distribution of DEHP in a residential environment. Field data collected in the CTEPP study as well as recent laboratory data are used to parameterize the extended model. The model is then used to

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estimate the emission rate and gas-phase DEHP concentration following the installation of vinyl flooring in a room. Finally, we examine the influence of two key parameters (air exchange rate and airborne particle concentration) on DEHP emissions, and estimate the potential exposure through inhalation, dermal absorption and oral ingestion of dust.

TWO-ROOM MODEL

To better estimate DEHP emissions in a residential environment the SVOC emissions model (Xu and Little 2006) was extended from a one-compartment description of an experimental chamber to a two-compartment representation of two adjacent rooms in a home (Figure 4.1). Vinyl flooring, the only source of DEHP considered, is placed in room 1, while carpet and wooden furniture is arranged in room 2. The room conditions are provided in Table 4.1.

Table 4.1 Conditions for two-room model

	Room 1	Room 2
Volume (m×m×m)	3×3×3	3×3×3
Ventilation rate (m^3/h)	13.3	13.3
Area of vinyl flooring, A_v (m^2)	9	--
Area of carpet, A_c (m^2)	--	9
Area of glass window, A_g (m^2)	1.7[a]	1.7[a]
Area of furniture, A_f (m^2)	--	20.3[a]
Area of ceiling and wall, A_{cw} (m^2)	41	41
Total suspended particles, TSP (μg/m^3)	20[b]	20[b]

a. According to typical surface to volume ratio in residences (Hodgson et al. 2005)

b. Typical TSP in residential environment (Weschler 2003)
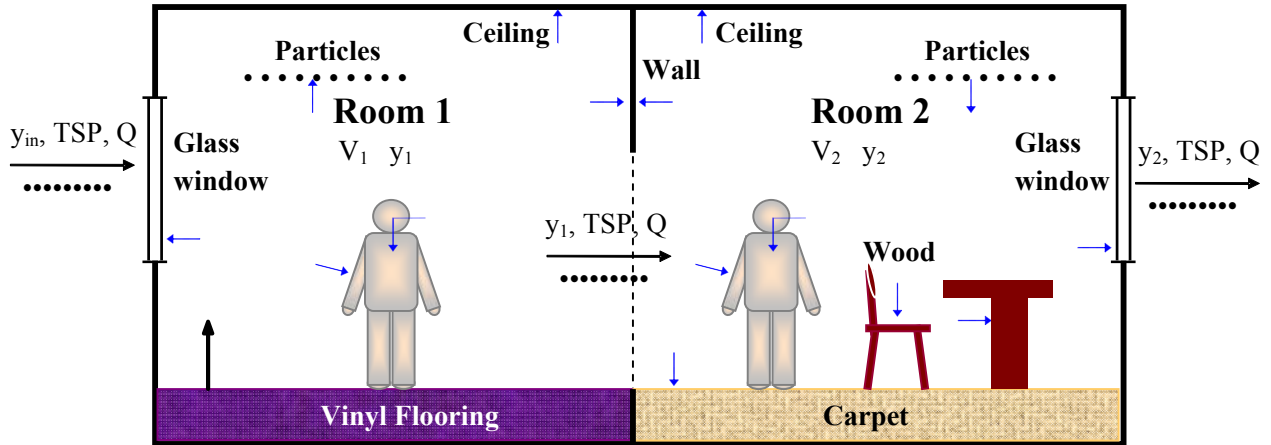
Figure 4.1 Schematic representation of the two-room model

Mass Balance

With reference to Figure 4.1, the accumulation of phthalate in room 1 obeys the following mass balance:

$$\frac{dy_1(t)}{dt} \cdot V_1 = Q \cdot y_{in}(t) - A_g \cdot \frac{dC_g(t)}{dt} - A_{cw} \cdot \frac{dC_{cw}(t)}{dt} - V_1 \cdot \frac{dF_1(t)}{dt} + A_v \cdot \overset{\bullet}{m}(t) - Q \cdot y_1(t) - QF_1(t)$$

(1)

where y_1 ($\mu g/m^3$) is the gas-phase concentration as a function of time, V_1 (m^3) is the room volume, Q (m^3/h) is the ventilation rate, y_{in} ($\mu g/m^3$) is the gas-phase concentration coming in from outside, F_1 ($\mu g/m^3$) is the particle-phase concentration, $\overset{\bullet}{m}$ ($\mu g/m^2 h$) is the vinyl flooring emission rate per unit area, A_v (m^2) is the vinyl flooring surface area, A_g (m^2) and A_{cw} (m^2) are the surface area of glass and ceiling/wall respectively, and C_g ($\mu g/m^2$) and C_{cw} ($\mu g/m^2$) are the corresponding surface concentrations. The accumulation of phthalate in room 2 is given by:

$$\frac{dy_2(t)}{dt} \cdot V_2 = Q \cdot y_1(t) + QF_1(t) - A_g \cdot \frac{dC_g(t)}{dt} - A_{cw} \cdot \frac{dC_{cw}(t)}{dt} - A_c \cdot \frac{dC_c(t)}{dt} - A_f \cdot \frac{dC_f(t)}{dt}$$

$$- V_2 \cdot \frac{dF_2(t)}{dt} - Q \cdot y_2(t) - QF_2(t) \qquad (2)$$

where y_2 ($\mu g/m^3$) is the gas-phase concentration, V_2 (m^3) is the room volume, F_2 ($\mu g/m^3$) is the particle-phase concentration, A_c (m^2) and A_f (m^2) are the surface area of carpet and furniture respectively, and C_c ($\mu g/m^2$) and C_f ($\mu g/m^2$) are the corresponding surface concentrations. The gas-phase and particle-phase concentrations leaving room 1 are the same as those entering room 2, and represent the only source of DEHP in room 2.

DEHP Emission Rate

A detailed description of the mechanisms governing the emissions process is given by Xu and Little (2006). While DEHP is present at a very high concentration in the vinyl flooring, as an SVOC with a very low vapor pressure, it emits very slowly. In fact, calculations show that even after 1 year only 0.003% of the total mass of DEHP has come out of the vinyl flooring. To simplify the model, we therefore assume that the vinyl flooring has an effectively constant DEHP concentration, and ignore the diffusion of DEHP within the vinyl flooring (Figure S1) (Table and Figure numbers preceded by an "S" are in the Supplementary Information for Chapter 4, which is available in Appendix A). Assuming a linear equilibrium relationship exists between the vinyl flooring and the gas phase, and considering the mass transfer within the boundary layer due to the concentration gradient, the emission rate is:

$$\overset{\bullet}{m}(t) = h_m \cdot (y_0 - y) \qquad (3)$$

where $\qquad y_0 = C_0 / K \qquad (4)$

In equations (3) and (4), y ($\mu g/m^3$) is the bulk gas-phase concentration, y_0 ($\mu g/m^3$) is the concentration in the air immediately adjacent to the vinyl flooring surface, h_m (m/h) is the

convective mass-transfer coefficient, K is the DEHP vinyl flooring/air partition coefficient, and C_0 is the constant DEHP concentration in the vinyl flooring.

Surface Adsorption

Although the partitioning behavior of phthalates between air and indoor surfaces is not known, partitioning of VOCs, phenanthrene and nicotine has been studied (Weschler 2003; VanLoy et al. 2001; Won et al. 2001). Assuming a linear equilibrium relationship for phthalates, the ratio of the concentration of a chemical on a surface to its concentration in the gas phase is equal to the surface/air partition coefficient, K_{surf} (m), or

$$K_{surf} = C_{surf} / y_{0, surf} \tag{5}$$

where C_{surf} is the surface concentration ($\mu g/m^2$) and $y_{0, surf}$ ($\mu g/m^3$) is the gas-phase concentration immediately adjacent to the surface (Figure 4.2a). Assuming a boundary layer exists adjacent to the adsorption surfaces, the amount of phthalate accumulated on the surface is equal to the total mass transferred through the boundary layer from the gas phase, or

$$dC_{surf} / dt = h_m (y - y_{0, surf}) \tag{6}$$

Equations (5) and (6) are assumed to apply to phthalate transferring between the bulk air and all exposed interior surfaces, such as carpet, furniture, glass window, ceiling/wall, and even human skin.

Sorption to Airborne Particles

For airborne particles (Figure 4.2b), an equation that has been used successfully to parameterize particle/air partitioning (Pankow 1992) is:

$$K_{p, particle} = (F/TSP)/y_{0p} \tag{7}$$

where $K_{p, particle}$ ($m^3/\mu g$) is the particle/air partition coefficient for a given compound; F and y_{0p} are the particle and gas-phase concentrations ($\mu g/m^3$) of the compound,

respectively; and TSP ($\mu g/m^3$) is the total suspended particulate material concentration. Thus, F/TSP is the fractional concentration of a given organic compound on the particles (e.g., μg of compound per g of particles). It is analogous to the fractional concentration of a compound in dust, in which case $K_{p, dust}$ is the dust/air partition coefficient. Similar to adsorption to the other surfaces, and assuming a boundary layer surrounding each particle, the accumulated particle-phase concentration is equal to the total mass transferred through the boundary layer, or

$$dF/dt = h_{mp} \cdot (y - y_{0p}) \cdot A_p \tag{8}$$

a) Adsorption to interior surfaces b) Adsorption to airborne particles
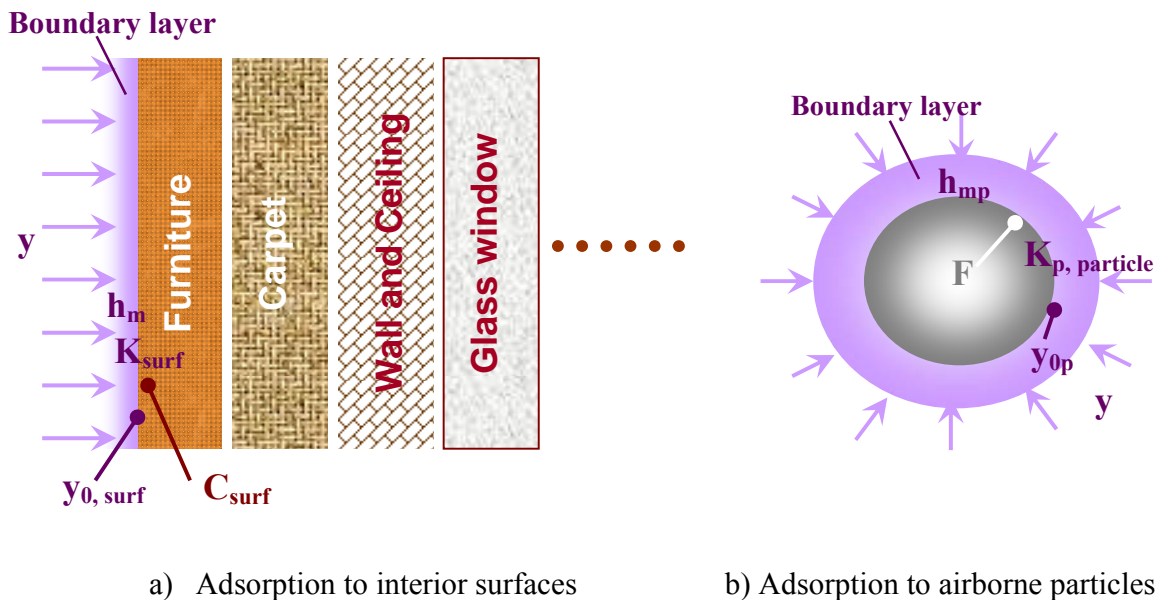
Figure 4.2 Schematic of sorption process

(Note that the four individual materials shown for illustrative purposes in Figure 4.2a do not comprise a layered structure.)

where h_{mp} (m/h) is the mass-transfer coefficient for particles, and A_p is the particle surface area (m^2/m^3 air). Equations (7) and (8) are assumed to apply to phthalate transfer between the bulk air and the airborne particles. The two-room model describing phthalate emissions and subsequent interaction with different interior surfaces and airborne particles is obtained by combining equations 1 through 8. The vinyl flooring

functions as a source only, but all other gas/surface interactions are fully reversible, and embody both equilibrium and kinetic mechanisms.

SORPTION ISOTHERMS FOR DEHP IN RESIDENTIAL ENVIRONMENT

Estimation of Sorption Equilibrium Parameters on Interior Surfaces

To estimate partition coefficients for phthalate and different surfaces, data collected in a residential field study as well as data collected in a laboratory chamber study were used. In the CTEPP field study (EPA 2005), forty-eight hour integrated samples were collected simultaneously at each child's day-care center and at the child's home in either North Carolina or Ohio. The samples were collected from residential air, house dust, interior surfaces and dermal hand-wipes. Only two phthalates (BBP and DBP) were measured in the CTEPP study. We therefore used the top three high-concentration pollutants (BBP, DBP and bisphenol-A (BPA)) in our analysis. BPA is also a semi-volatile organic compound, which is typically present in commercial polycarbonate. Clausen et al. (2004) conducted experiments in three CLIMPAQ chambers to study DEHP uptake by dust on PVC flooring. The DEHP concentrations in the dust and gas-phase will be used in the following analysis of DEHP partitioning between dust and air.

To establish surface/air equilibrium relationships for the three chemicals (BBP, DBP and BPA) and the various indoor surfaces, we plotted the CTEPP data (e.g. DBP on adult skin and dust), as shown in Figure 4.3. Results for the other two chemicals and other surfaces are shown in the SI. The results suggest that simple linear relationships suffice to describe surface/air equilibrium in all cases. The statistical results for the regressions are summarized in Table S1. Based on equation (5), the intercept was set to zero. In all the linear regressions, the p-value was less than 0.05, with 95% confidence that the partition coefficient is different from zero. Furthermore, the p-value of the Shapiro test was larger than 0.05, with 95% confidence that the regression residues are normally distributed.

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a) Adult skin   b) Dust
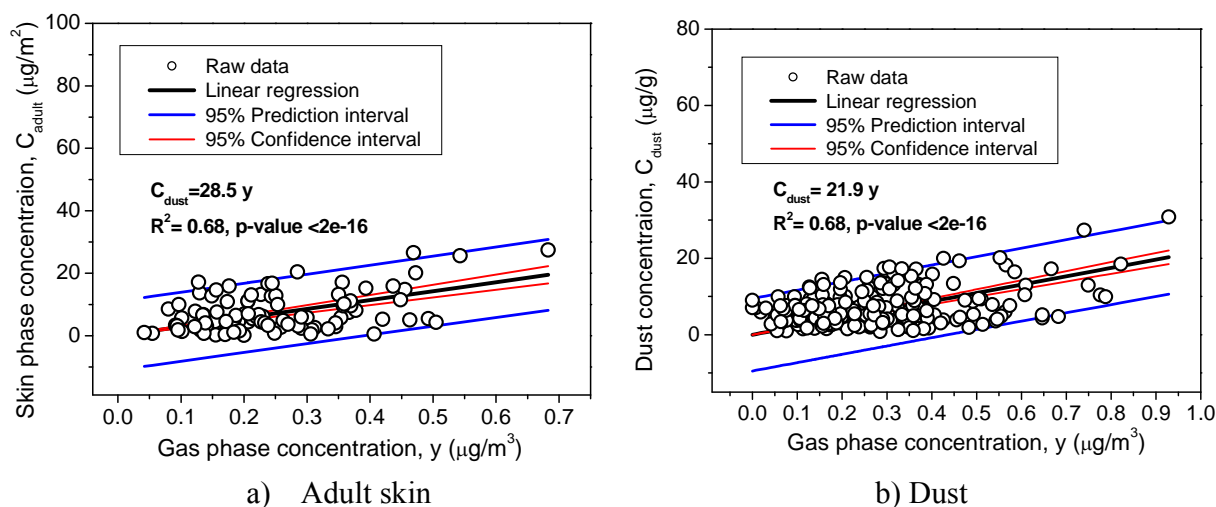
Figure 4.3 Linear regression results for DBP

Unfortunately, according to the sampling method of the CTEPP study, the measured concentrations in the indoor air "y" are actually the total airborne concentrations; that is, the sum of the gas phase and airborne particle concentration "y+F". To obtain a more representative gas/surface partition coefficient, the equilibrium relationships need to be modified, or

$$K_{surf} = K_{surf, \; CTEPP} \cdot (y + F) / y \qquad (9)$$

where $K_{surf, \; CTEPP}$ is the equilibrium coefficient in Table S1 derived from the CTEPP study, and K_{surf} is the desired gas/surface partition coefficient. As discussed in the SI, the modified K_{surf} for each compound is listed in Table S4 in bold. Since K_{surf} is from field study measurement, it already includes the contribution of chemicals sorbed to airborne particles that subsequently deposits on surfaces.

We now have approximate equilibrium relationships for BBP, DBP and BPA between indoor air and various surfaces (hardwood floor, carpet, child skin, adult skin, and dust), as well as the directly measured equilibrium relationship for DEHP between indoor air and dust (Clausen et al. 2004). What we need, however, are the equilibrium relationships between DEHP and hardwood floor, carpet, and human skin. To get these, we developed

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simple correlations between the equilibrium parameters and the vapor pressure of the target chemicals.

Correlation of Equilibrium Parameters with Vapor Pressure

Correlations were obtained between vapor pressure (V_p) and sorption parameters (K_{surf}) for different interior surfaces, including settled dust. Linear relationships between log (V_p) and log (K_{surf}) were found (e.g. human skin and dust) as shown in Figure 4.4. Results for all surfaces are shown in Figure S6. Data for child hand wipe and adult hand wipe were combined to get the relationship between the human skin partition coefficient and vapor pressure. The partition coefficient of BPA for dust did not conform well to this relationship, thus Figure 4.4b only shows the relationship between phthalate vapor pressures and partition coefficients for dust.

a) Human skin   b) Dust
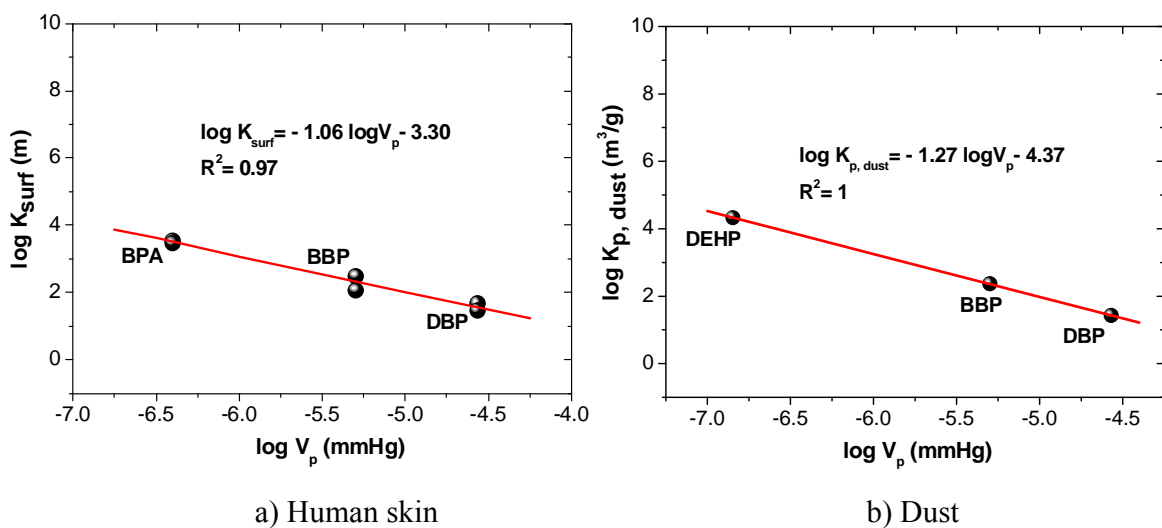
Figure 4.4 Linear regression between log (V_p) and log (K_{surf})

While using only three chemicals does not provide a conclusive relationship, the overall results suggest that it is possible to relate the equilibrium partition coefficients to vapor pressures. Finally, we used the new correlations to obtain the partition coefficient for DEHP on different interior surfaces, as shown in Table 4.2. The isotherm used for glass is based on a previous study (Xu and Little 2006), although the non-linear nature of the

isotherm may have been due to the data fitting procedure. In the SI, the skin/air partition coefficient is checked using a completely different procedure and shown to be acceptable.

Table 4.2 Partition coefficients for DEHP

Surface	Partition coefficient, K	Isotherm exponent, n
Furniture, wall and ceiling [a]	2500 (m)	--
Carpet [b]	1700 (m)	--
Glass [c]	3800 $(\mu g/m^2)/(\mu g/m^3)^n$	1.5
Skin [d]	9500 (m)	--
Airborne particles [e]	0.25 (m^3/ug)	--
Dust [f]	21100 (m^3/g)	--

a. Calculated using $\log K_{surf} = -0.779 \log V_p - 1.93$, figure S6 (a)

b. Calculated using $\log K_{surf} = -0.627 \log V_p - 1.08$, figure S6 (b)

c. Xu and Little (2006) fitted the Freundlich isotherm for glass

d. Calculated using $\log K_{surf} = -1.06 \log V_p - 3.30$, figure 4.4 (a)

e. Calculated using $\log K_{p, particle} = -0.860 \log V_p - 4.67$, equation S3

f. Regression result of Figure S5

Mass transfer coefficient

The value of h_m, the mass-transfer coefficient for the boundary layer adjacent to the various surfaces, was estimated using correlation equations (Axley 1991), which express h_m as a function of Reynolds number and Schmidt number. Huang et al. (Huang et al. 2004) measured air velocities in a typical house in the US. They found velocities with a range of 0.01 m/s – 0.16 m/s and showed that values near the floor are higher than in the center of the room. In the CLIMPAQ chamber (Clausen et al. 2004), which roughly approximates conditions in a real room, the velocity at the test piece surface was estimated to be 0.15 m/s and this value is used to estimate h_m. Odum et al. (1994) measured mass transfer of PAHs and others SVOCs to and from combustion aerosols at 25 ^oC, and their result is used here as h_{mp}, the mass-transfer coefficient for particles.

We now have estimates of all the partition coefficients for DEHP between indoor air and interior surfaces (hardwood floor, carpet, human skin, and particles), as well as the associated mass transfer coefficients. We are therefore able to use the two-room model to estimate the emission rate and evolving gas-phase DEHP concentration following the installation of vinyl flooring in room 1. Note, however, that we do not account for the DEHP on airborne particles that may be deposited on interior surfaces.

Because no other data for DEHP concentrations on real interior surfaces are available, the CTEPP study provides the only available data that we can use to estimate DEHP adsorption isotherms. Even though the values of the partition coefficient for DEHP on interior surfaces can only be considered rough estimates, we showed in a sensitivity analysis (Xu et al. 2009) that they do not have a strong influence on the steady state indoor air DEHP concentration, which is the basis for our exposure analysis (although they do influence the time it takes to reach steady state). We therefore believe that our emissions and transport model represents a reasonable first step.

RESULTS AND DISCUSSION

For baseline conditions (Table 4.1), the indoor air DEHP concentration at steady state is 0.15 $\mu g/m^3$. As shown in Table 4.3, this value is similar to that measured within homes in both the US and Europe, although it should be emphasized that vinyl flooring is the only source of DEHP considered here. Room 1 reaches steady state within about one year, while the adjacent room reaches steady state about three months later. Airborne particles increase the rate at which DEHP is transported between rooms by a factor of 5 relative to gas-phase transport. The boundary layer surrounding the airborne particles is much thinner than the boundary layer adjacent to the other indoor surfaces and the suspended particles reach equilibrium with the gas-phase much more rapidly than the larger surfaces. Suspended particles are therefore very effective at transporting DEHP from one room to another, because DEHP also desorbs very rapidly from the particles.

Table 4.3 Concentration of phthalates in indoor air and household dust samples

DEHP	References	n	Mean	Max	Our study
Gas phase Conc. ($\mu g/m^3$)	(BAUCH 1991)	40	0.48	1.6	0.15
	(Sheldon et al. 1994)	125	0.14	--	
	(Fromme et al. 2004)	102	0.07	1.0	
	(Rudel et al. 2003)	59	0.19	0.4	
Dust phase Conc. ($\mu g/g$)	(BAUCH 1991)	12	950	3100	3000
	(Mattulat 2002)	600	1200	3500	
	(Rudel et al. 2003)	101	340	7700	
	(Fromme et al. 2004; Weschler et al. 2008)	30	776	1542	

In Figure 4.5a, the impact of air exchange rate and total suspended particle concentration on the DEHP emission rate and the DEHP concentration in rooms 1 and 2 is examined. Increasing air exchange rate will increase the DEHP emission rate from the vinyl flooring significantly while an increase in the TSP concentration causes a substantial decrease in the gas-phase concentration in both rooms, but increases the emission rate in Room 1. An increase in the air exchange rate was assumed to double the velocity of the air above the vinyl flooring (from 0.15 to 0.30 m/s) and this higher value was used to calculate the h_m associated with the flooring.

Figure 4.5b shows the predicted DEHP concentration change with time on various interior surfaces in room 2. The predicted DEHP concentration on human skin is 5 to 7 times higher than on the other surfaces due to the high skin/air partition coefficient for DEHP. The skin/air partition coefficient was obtained from hand-wipe samples in the CTEPP study. It is generally believed that these hand-wipe samples are measuring chemicals transferred from indoor surfaces onto the hands directly. However, the fact that the skin/air isotherms determined for both adult and child are almost identical for DBP, BBP, and BPA (see, for example, Figure 4.4a), suggests that SVOCs may be transferring directly from the air to the skin, or that if large amounts are picked up by direct dermal transfer, that some desorbs to re-establish equilibrium with the air. Indeed, in a subsequent paper (Xu et al. 2009), we show that there is a strong correlation between

the concentrations of DBP, BBP, and BPA on skin and those in the gas phase, but almost no correlation with those on interior surfaces. This further suggests that certain SVOCs may reach the skin through the gas phase, and not via dermal transfer as is commonly suspected.

a)   b)
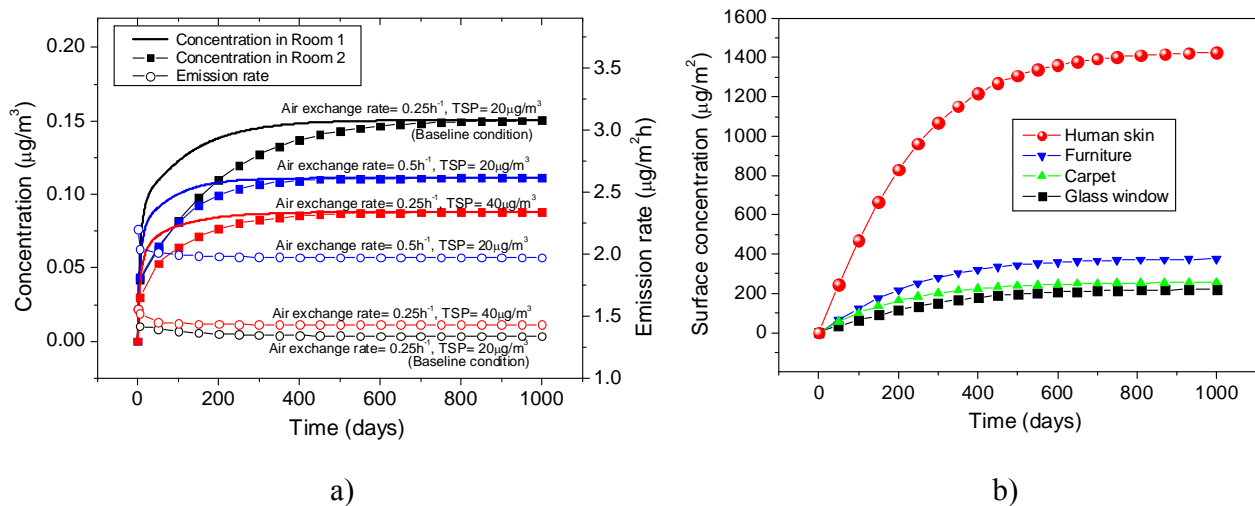
Figure 4.5 a) Effect of air exchange rate and TSP concentration on DEHP concentration and emission rate; b) Predicted DEHP concentration on interior surfaces

ESTIMATING EXPOSURE TO DEHP FROM VINYL FLOORING

Based on the model results, we are interested in evaluating exposure to vapor phase DEHP in air, particle bound DEHP in air, and DEHP in settled dust. The exposure pathways of interest are: inhalation of vapor, inhalation of particles, dermal absorption of DEHP deposited on the skin, and oral ingestion via household dust.

The detailed exposure calculations are shown in the SI. For dermal exposure, the overall skin permeability coefficient, P, is controlled by permeation through the skin ($P_{skin/air}$) as well as by permeation through the air boundary layer adjacent to the skin (P_{air}), or:

$$P = \frac{1}{\frac{1}{P_{skin/air}} + \frac{1}{P_{air}}} \tag{10}$$

where $P_{skin/air}$ (cm/hr) is vapor to skin permeability, and P_{air} (cm/hr) is permeability of the boundary layer. For low volatility compounds, convective mass transfer through the air boundary layer adjacent to the skin may become the rate limiting factor, and this is the case for DEHP. As detailed in the SI, the estimated value of P is 580 cm/hr.

As shown in Table S8, the reference dose (RfD) for DEHP is 20 μg/kg/d according to the U.S. EPA. Airborne particles contribute 80% of the inhalation exposure, although the highest value of total inhalation exposure is less than 0.6 μg/kg/d, which is much lower than the RfD. For infants, exposure through oral intake via dust is 1.6 times higher than the RfD, although the estimate for dust intake rate of 10.3 mg/kg/d (Stubenrauch et al. 1999) may be high. Exposure via these two pathways is similar to other study results (Wensing et al. 2005; Fromme et al. 2007; Wormuth et al. 2006). Dermal absorption of DEHP deposited on skin is greater than that taken up through inhalation. For DEHP, the primary route of exposure is oral ingestion of dust. Overall, children experience two to ten times higher exposure risk than adults based on all exposure pathways.

SUPPORTING INFORMATION AVAILABLE

Further details on the regression results for the CTEPP data, modification of surface partition coefficients, and detailed exposure calculations are available at Appendix A.

REFERENCES

Afshari A, Gunnarsen L, Clausen PA, Hansen V. 2004. Emission of phthalates from PVC and other materials. Indoor Air 14: 120–128.

Axley JW. 1991. Adsorption modeling for building contaminant dispersal analysis. Indoor Air 2: 147-171.

BAUCH. 1991. Analyse und Bewertung der in Raumluft und Hausstaub vorhandenen Konzentrationen der Weichmacherbestandteile Diethylhexylphthalat(DEHP) und Dibutylphthalat (DBP). Sachstandsbericht, Berlin, Eigenverlag.

Bornehag C-G, Lundgren B, Weschler CJ, Sigsgaard T, Hagerhed-Engman L, Sundell J. 2005. Phthalates in Indoor Dust and Their Association with Building Characteristics. Environmental Health Perspectives 113(10): 1399-1404.

Cadogan DF, Howick CJ. 1996. Plasticizers. Kirk-Othmer Encyclopedia of Chemical Technology 19: 258-290.

Clausen P, Hansen V, Gunnarsen L, Afshari A, Wolkoff P. 2004. Emission of Di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. Environmental Science and Technology 38(9): 2531-2537

Clausen PA, Xu Y, Kofoed-Sørensen V, Little JC, Wolkoff P. 2007. The influence of humidity on the emission of di-(2-ethylhexyl) phthalate (DEHP) from vinyl flooring in the emission cell "FLEC". Atmospheric Environment 41: 3217-3224.

EPA US. 2005. A Pilot Study of Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants (CTEPP).

Fromme H, Gruber L, Schlummer M, Wolz G, Böhmer S, Angerer J, et al. 2007. Intake of phthalates and di(2-ethylhexyl)adipate: Results of the Integrated Exposure Assessment Survey based on duplicate diet samples and biomonitoring data. Environment International 33(8): 1012-1020.

Fromme H, Lahrz T, Piloty M, Gebhart H, Oddoy A, Rüden H. 2004. Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). Indoor Air 14: 188–195.

Fujii M, Shinohara N, Lim A, Otake T, Kumagai K, Yanagisawa Y. 2003. A study on emission of phthalate esters from plastic materials using a passive flux sampler. Atmospheric Environment 37: 5495-5504.

Gebefügi I. 1989. Chemical exposure in enclosed environments. Toxicological and Environmental Chemistry 20–21: 121–127.

Hodgson AT, Ming KY, Singer BC. 2005. Quantifying object and material surface areas in residences. Lawrence Berkeley National Laboratory, Paper LBNL-56786.

Huang JM, Chen Q, Ribot B, Rivoalen H. 2004. Modeling contaminant exposure in a singlefamily house. Indoor and Built Environment 13(1): 5-19.

Latini G, Felice CD, Verrotti A. 2004. Plasticizers, infant nutrition and reproductive health. Reproductive Toxicology 19: 27-33.

Mattulat A. 2002. Konzentration von mittel- und schwerflüchtigen organischen Verbindungen in Staub aus Innenräumen - Belastungssituationim.

Odum J, Yu J, Kamens R. 1994. Modeling the mass transfer of semivolatile organics in combustion aerosols. Environ Sci Technol 28: 2278-2285.

Pankow J. 1992. Application of common y-intercept regression parameters for log kp vs1/t for predicting gas particle partitioning in the urban-environment. Atmospheric Environment Part A 26(14): 2489-2497

Rudel R, Camann D, Spengler J, Korn L, Brody J. 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust Environmental Science and Technology 37(20): 4543-4553

Sheldon L, Clayton A, Keever J, Perritt R, Whitaker D. 1994. PTEAM: Monitoring of phthalates and PAHs in indoor and outdoor air. In: Samples in Riverside California Research Note No 94-10: California Environmental Protection Agency, Air Resources Board, Sacramento.

Stubenrauch S, Hempfling R, Doetsch P, Grünhoff D. 1999. Vorschläge zur Charakterisierung und Quantifizierung pfadübergreifender Schadstoffexposition. . Z Umweltchem Ökotoxikol 11: 219-226.

Uhde E, Bednarek M, Fuhrmann F, Salthammer T. 2001. Phthalic Esters in the Indoor Environment –Test chamber studies on PVC-coated wallcoverings. Indoor Air 11: 150-155.

Van Loy MD, Lee VC, Gundel LA, Daisey JM, Sextro RG, Nazaroff WW. 1997. Dynamic behavior of semivolatile organic compounds in indoor air. 1. Nicotine in a stainless steel chamber. Environmental Science and Technology 31: 2554–2561.

VanLoy M, Riley W, Daisey J, Nazaroff W. 2001. Dynamic behavior of semivolatile organic compounds in indoor air. 2. Nicotine and phenanthrene with carpet and wallboard Environmental Science and Technology 35(3): 560-567.

Wensing M, Uhde E, Salthammer T. 2005. Plastics additives in the indoor environment— flame retardants and plasticizers. Science of the Total Environment 339: 19– 40.

Weschler CJ. 2003. Indoor/outdoor connections exemplified by processes that depend on an organic compound's saturation vapor pressure. Atmospheric Environment 37: 5455–5465.

Weschler CJ, Salthammer T, Fromme H. 2008. Partitioning of phthalates among the gas phase, airborne particles and settled dust in indoor environments. Atmospheric Environment 42(7): 1449-1460.

Won D, Corsi RL, Rynes M. 2001. Sorptive Interactions between VOCs and IndoorMaterials. Indoor Air 11: 246–256.

Wormuth M, Scheringer M, Vollenweider M, Hungerbühler K. 2006. What Are the Sources of Exposure to Eight Frequently Used Phthalic Acid Esters in Europeans? Risk Analysis 23(3): 803 - 824.

Xu Y, Hubal EC, Little JC. 2009. Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – Sensitivity, Uncertainty, and Implications for Biomonitoring. Submitted.

Xu Y, Little J. 2006. Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles Environmental Science and Technology 40(2): 456-461

Chapter 5: Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – Sensitivity, Uncertainty, and Implications for Biomonitoring

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ABSTRACT

Given the ubiquitous nature of phthalates in the environment and the potential for adverse human health effects, there is an urgent need to identify the most important sources and pathways of exposure. Using di-2-ethylhexyl phthalate (DEHP) emission from vinyl flooring (VF) as an example, the objective of this study is to illustrate an approach to identify the important sources and pathways of exposure associated with SVOCs used in indoor materials and consumer products. A three-compartment model is developed to estimate the emission rate of DEHP from VF and the evolving exposures (via inhalation, dermal absorption and oral ingestion of dust) in a realistic indoor environment. A sensitivity analysis indicates that the VF source characteristics (surface area and material-phase concentration of DEHP), as well as mass-transfer coefficients and ventilation rate are important variables influencing the steady-state DEHP concentration and resulting exposure. In addition, DEHP adsorbs strongly to interior surfaces, and the interior surface area and surface/air partition coefficients strongly influence the time to steady-state. A simple uncertainty analysis suggests that residential exposure to DEHP originating from VF may fall somewhere between about 5 µg/kg/d and 180 µg/kg/d. The roughly 40-fold range in potential exposure reveals the inherent difficulty in using biomonitoring results to identify specific sources of exposure in the general population.

The relatively simple dependence on source and chemical specific transport parameters suggests that the mechanistic modeling approach could be extended to predict exposure arising from other sources of phthalates, other sources of other semi-volatile organic compounds (SVOCs, such as biocides and flame retardants), as well as emissions into other environmental media (food, water, saliva, and even blood). Although there might be errors resulted from simplification of real residential environment, of human activities indoors and of contaminant emission and adsorption characteristics, the approach could provide a relatively inexpensive way to identify and control health risks associated with many of the SVOCs used in indoor materials and consumer products.

INTRODUCTION

Because of their substantial and widespread use phthalates have become ubiquitous environmental contaminants (Koch et al. 2003; Weschler and Nazaroff 2008; Wormuth et al. 2006). Over 3.5 million tons of phthalates are used worldwide each year primarily as plasticizers in flexible polyvinyl chloride (PVC) products (Cadogan and Howick 1996). Di-2-ethylhexyl phthalate (DEHP) is the most important phthalate and more than two million tons of DEHP are produced globally each year (Lorz et al. 2002). About 90% of phthalates are found in a wide range of consumer products including floor- and wall-covering, car interior trim, clothing, gloves, footwear, insulation on wiring, artificial leather and toys (Afshari et al. 2004; Bornehag et al. 2005; Müller et al. 2003). The main use of DEHP is in PVC products such as vinyl flooring, where it is typically present at concentrations of ~ 20% – 40% (w/w) (Clausen et al. 2004; Deisinger et al. 1998). Since phthalate plasticizers are not chemically bound to the product materials, they emit slowly into the surrounding environment (Müller et al. 2003; Wormuth et al. 2006) and have become widely recognized as major indoor pollutants (Bornehag et al. 2005; Clausen et al. 2003; Fromme et al. 2004; Jaakkola and Knight 2008; Wensing et al. 2005; Weschler et al. 2008; Xu and Little 2006).

The ubiquitous exposure to phthalates is of concern because toxicological studies have demonstrated considerable adverse effects of phthalates and their metabolites to human health (Wormuth et al. 2006). Recently, several review papers were published regarding

toxicities of phthalates and their metabolites (Heudorf et al. 2007; Jaakkola and Knight 2008; Latini et al. 2006; Matsumoto et al. 2008; McKee et al. 2004; Ritter and Arbucklet 2007). These reviews show that exposure to phthalates results in profound and irreversible changes in the development of the reproductive tract, especially in males, raising the possibility that phthalate exposures could be the leading cause of reproductive disorders in humans. In addition, effects such as increases in prenatal mortality, reduced growth and birth weight, skeletal, visceral, and external malformations are possibly associated with phthalate exposure. Epidemiologic studies in children also show associations between phthalate exposure in the home and risk of asthma and allergies.

Given the ubiquitous nature of phthalates in the environment and the potential for adverse human health impacts, there is a need to identify the most important sources and pathways of exposure (NRC, 2006). Levels of phthalate metabolites measured in the general population using biomonitoring methods provide direct evidence of wide-spread human exposure (CDC 2005; Calafat and McKee 2006; Heudorf et al. 2007). Biomonitoring data suggest that over 75% of the U.S. population is exposed to phthalates (Silva et al. 2004). For phthalates with short alkyl chains, monoesters represent the major human metabolites, although in the case of DEHP, DINP, and DIDP, the monoesters are further metabolized. Exposure estimates based on urinary monoester concentrations might underestimate the population's actual exposure to these specific phthalates (Wormuth et al. 2006). When urinary concentrations of secondary metabolites are measured, the estimate increases to 95% (Kato et al. 2004). Results of recent biomonitoring studies in which phthalate metabolites were measured are reviewed by Heudorf et al. (2007). Based on mean body burden of DEHP expressed as urinary excretion of DEHP metabolites, Heudorf et al. estimate that effective intake of DEHP is higher in children than in adults and may occur at levels of significant concern. Note that data are not available for children less than 3 years of age.

Interpretation of biomonitoring data for public health decision making requires contextual information to understand the potential for adverse health impacts and to identify effective interventions (Albertini et al 2006; Bahadari et al 2007). Just as additional information is required to relate a measured concentration of a chemical in a human

tissue or fluid to the administered doses used in animal toxicity studies (Clewell et al 2008), additional information is required to relate biomonitoring data to measures of the parent compound in environmental media (Fromme et al. 2007; Georgopoulos et al. 2008).

Although information on predominant sources, pathways, and routes of exposure is required to protect human health and the environment (NRC 2006), exposure to phthalates is difficult to evaluate because phthalates are so ubiquitous, and also because phthalate concentration measurements are hampered by contamination (Koch et al. 2003). To complicate matters, phthalates adsorb strongly to surfaces, as do other semi-volatile organic compounds (SVOCs, such as biocides and flame retardants) with closely related physical/chemical properties (Weschler and Nazaroff 2008). Even a relatively small gas phase concentration (e.g. 0.1 ppb) is sufficient for meaningful vapor transport of a phthalate ester, and its consequent partitioning between the gas phase and indoor surfaces, including airborne particles and settled dust (Weschler 2003). Adibi et al. (2008) correlated biomonitoring results with concentrations in environmental media by measuring phthalate metabolite concentrations in urine samples from 246 pregnant women and the corresponding indoor air samples, showing that indoor air samples can be used to characterize phthalate exposure in the home. In the recent US Environmental Protection Agency (EPA) CTEPP study (EPA 2005), concentrations of over 50 target compounds were measured in multimedia samples from the homes and daycare centers of 260 pre-school age children. The two phthalates targeted in the CTEPP study were detected in residential air and house dust, and on various interior surfaces and dermal wipe samples. The measured phthalate concentrations were amongst the highest of any of the target compounds, including pesticides, PAHs and PCBs. Based on the CTEPP study, Xu et al. (2009a) developed a model to predict emission and transport of DEHP and estimate the potential exposure through different pathways.

In this study we extend the Xu et al. (2009a) model to predict DEHP emissions and potential exposures via inhalation, dermal absorption and oral ingestion of dust following the installation of vinyl flooring in a three-compartment family residence. We then conduct sensitivity and uncertainty analyses to identify which model parameters have the

greatest influence on exposure, and show why biomonitoring alone cannot be used to identify individual sources of exposure in the general population. Finally, we briefly discuss how the modeling approach could be generalized to include other sources of DEHP, other sources of other SVOCs, as well as emissions, transport and exposure in other environmental media.

Rather than an assessment of exposures to phthalates from vinyl flooring, the objective of this paper is to illustrate an approach to identify the important sources and pathways of exposure associated with SVOCs used in indoor materials and consumer products. Using DEHP emission from vinyl flooring as an example, this paper demonstrates that a mechanistic modeling approach could be extended to predict exposure arising from other sources of phthalates, other sources of other SVOCs, as well as emissions into other environmental media.

MODEL DESCRIPTION AND RESULTS

As shown in Figure 5.1, DEHP is emitted from vinyl flooring (VF) to the air in a typical residence that is divided into three compartments: kitchen, bathroom, and the main house. The emission rate is controlled by partitioning between the VF and the adjacent air, as well as the mass-transfer coefficient within the boundary layer above the VF. The gas phase DEHP is adsorbed on interior surfaces, including walls, ceiling, wood floor, carpet, furniture, windows, tile, ceramic fixtures and particles through partitioning mechanisms. The infiltration/exfiltration rates and ventilation rates between rooms shown in Table 1 were obtained from measurements made by Wilkes and Small (1992) in a five-room house. The interior surface area of furnishing and materials was estimated using typical surface/volume ratios for American houses established by Hodgson et al. (2005), as shown in Table 5.1. There are two different classes of VF; the one for home use is soft and with higher phthalate content than another type which is rigid and used in commercial applications. The VF in the model belong to the later type, whose emission characteristics and DEHP content were completely investigated in previous studies (Clausen et al. 2004; Xu and Little 2006; Xu et al. 2009a; 2009b)
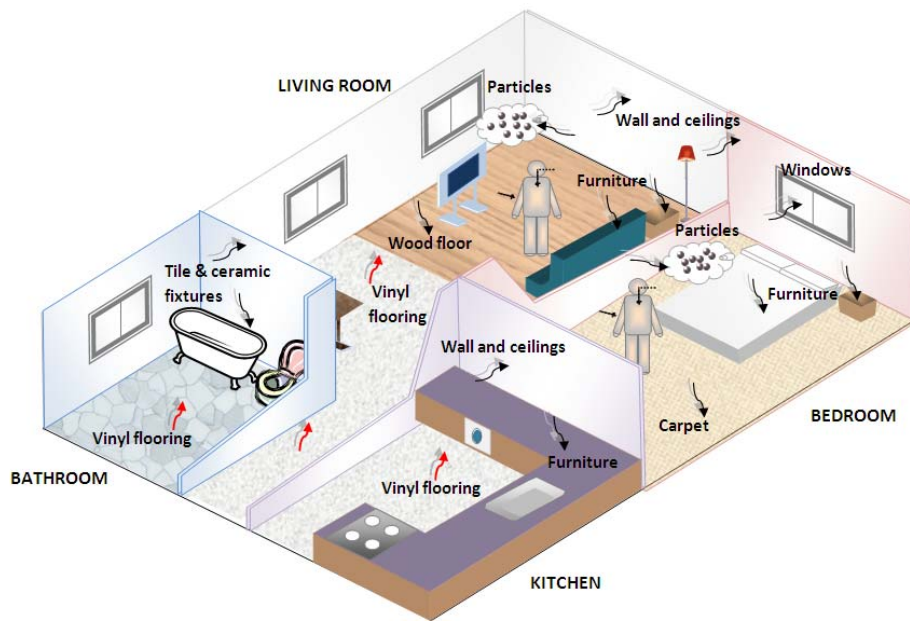
a)
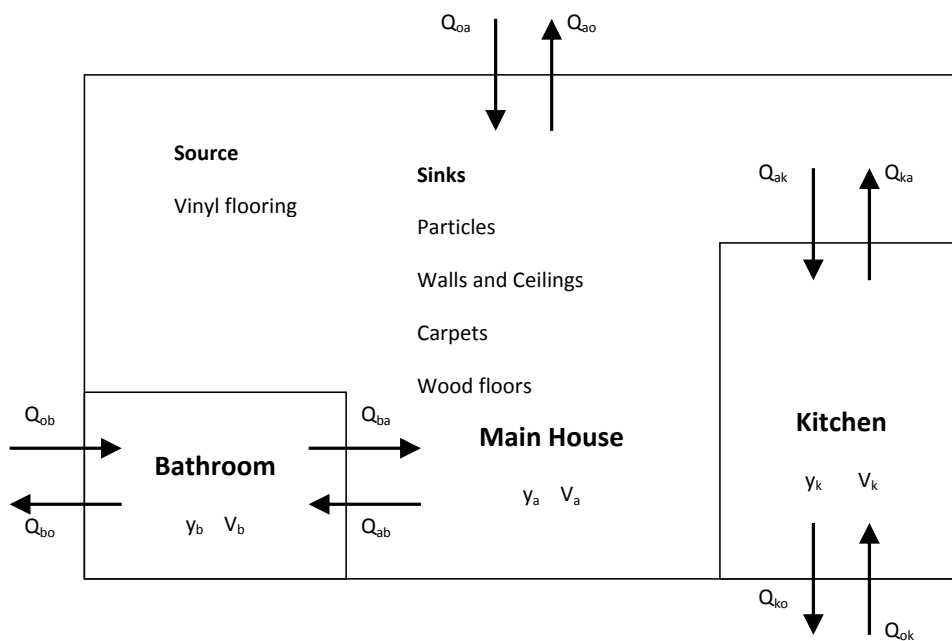
b)

Figure 5.1 Schematic representation of the residential environment model

Table 5.1 The three-compartment residential model conditions

Compartment	Main house		Kitchen		Bathroom	
Volume (m^3)	128		35		15	
Flowrate (m^3/h)	Q_{oa}	65	Q_{ok}	12	Q_{ob}	1.1
	Q_{ao}	44	Q_{ko}	32	Q_{bo}	2.1
			Q_{ak}	44	Q_{ab}	14
			Q_{ka}	24	Q_{ba}	13
Surface area (m^2)						
Vinyl flooring	19.2		14.4		6.20	
Walls & Ceilings	124		34.0		23.3	
Carpet	35.8		--		--	
Wood floor	32.0		--		--	
Hard surface furniture	61.4		12.6		5.40	
Windows & mirrors	5.12		1.75		1.05	
Tile & ceramic fixtures	5.12		3.50		16.5	
TSP (μg/ m^3)	20.0		20.0		20.0	

The parameters used in the model were obtained as described by Xu et al. (2009a).
Adsorption isotherms for phthalates on different interior surfaces were obtained from
data collected in a residential field study and a laboratory chamber study. In the CTEPP
field study (EPA, 2005), forty-eight hour integrated samples were collected
simultaneously at each child's day-care center and at the child's home in either North
Carolina or Ohio. The samples were collected from residential air, house dust, interior
surfaces and via dermal wipe. Clausen et al. (2004) conducted laboratory experiments to
study DEHP uptake by dust on PVC flooring in the CLIMPAQ (chamber for laboratory
investigations of materials, pollution, and air quality). The DEHP concentrations in the
dust and gas-phase were used to determine the DEHP partition coefficient between dust
and air. Log-linear relationships between equilibrium parameters and chemical vapor
pressure were obtained, and the partition coefficients for DEHP on different interior
surfaces were obtained based on the vapor pressure of DEHP (Xu et al. 2009a). The

value of the mass-transfer coefficient for the boundary layer adjacent to the various surfaces was estimated using correlation equations (Axley 1991), which express the mass-transfer coefficient as a function of Reynolds number and Schmidt number.

The model is used to estimate DEHP emission and transport following the installation of VF in the residence (Figure 5.2). The three compartments reach steady state within about one and a half years. The steep initial rise in DEHP concentration occurs because the rate at which it is emitted from the VF is initially faster than the rate at which it is taken up by the many interior sinks. Compared to the other two compartments, the main house has the lowest gas phase concentration due to the larger ratio of sorption surface area (e.g. carpet and furniture) to emission surface area. The lower the gas phase concentration, the higher the concentration gradient in the boundary layer above the VF, and with the highest concentration driving force, the main house experiences the highest emission rate. As shown in Table 5.2, the predicted steady-state results are similar to those measured within homes in both the US and Europe. Given that VF is the only source of DEHP considered here, this suggests that the emission rate from the assumed amount of VF may be roughly equivalent to the average emission rate from the different sources of DEHP in typical residential environments.
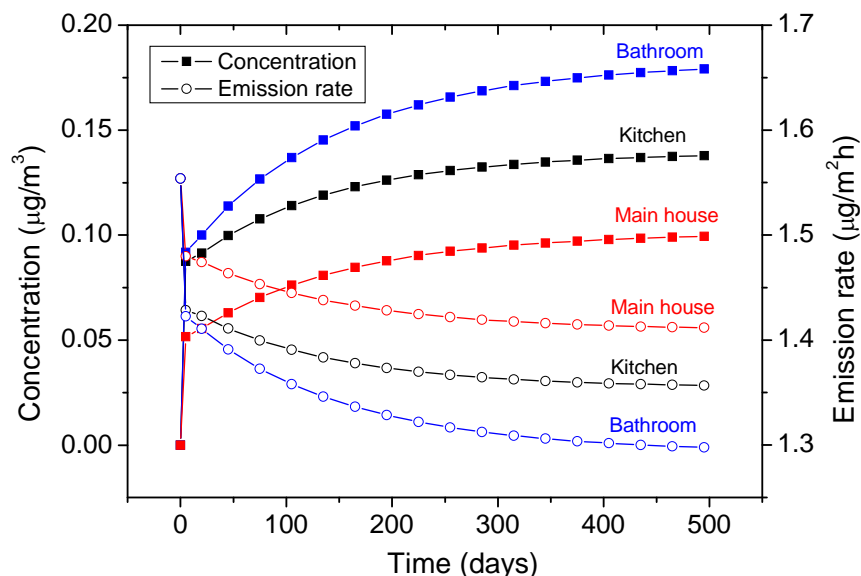
Figure 5.2 Change with time in emission rate and gas-phase concentration of DEHP emitted from vinyl flooring

Table 5.2 Concentration of DEHP in indoor air and dust samples cited in the literature

DEHP	References	n	Mean	Max	Our study
Gas phase Conc. (ug/m^3)	BAUCH 1991	40	0.48	1.6	0.1~0.18
	Sheldon et al. 1994	125	0.14	--	
	Rudel et al. 2003	102	0.07	1.0	
	Fromme et al. 2004	59	0.19	0.4	
Dust phase Conc. (ug/g)	BAUCH 1991	12	950	3100	2000~3500
	Mattulat et al. 2002	600	1200	3500	
	Rudel et al. 2003	101	340	7700	
	Fromme et al. 2004	30	780	1800	
	Weschler et al. 2008	30	776	1542	

Exposure (sometimes referred to as potential dose) is defined as the contact of an individual with an agent of concern (WHO 2004). Based on the above results, we are most interested in evaluating exposures to vapor phase DEHP in air, particle bound DEHP in air, and DEHP in settled dust. The exposure pathways of interest are therefore: inhalation of vapor, inhalation of particles, dermal absorption of DEHP, and oral ingestion via household dust. Both children and adults are considered in this assessment. The magnitude, frequency, duration and time-pattern of contact with DEHP are quantified as in the screening-level assessment presented by Xu et al. (2009a).

The change with time in exposure through inhalation, dermal absorption and oral ingestion via dust for both children (between their first and third year of life) and adults is shown in Figure 5.3. Exposure reaches a steady level after about one and a half years. Children experience two to ten times higher exposure than adults. The results are similar to Heurdorf et al. (2007), who modeled ambient exposure data and concluded that

children may be more highly exposed than adults. The reference dose (RfD) is 20 µg/kg/d according to the U.S. EPA. For children, exposure through oral intake via dust is two times higher than the RfD, although the estimate for dust intake rate of 10.3 mg/kg/d may be high (Xu et al., 2009a). For DEHP, the primary route of exposure is oral ingestion of dust, and inhalation and dermal absorption do not appear to be major exposure pathways, which is consistent with Clark et al (2003).
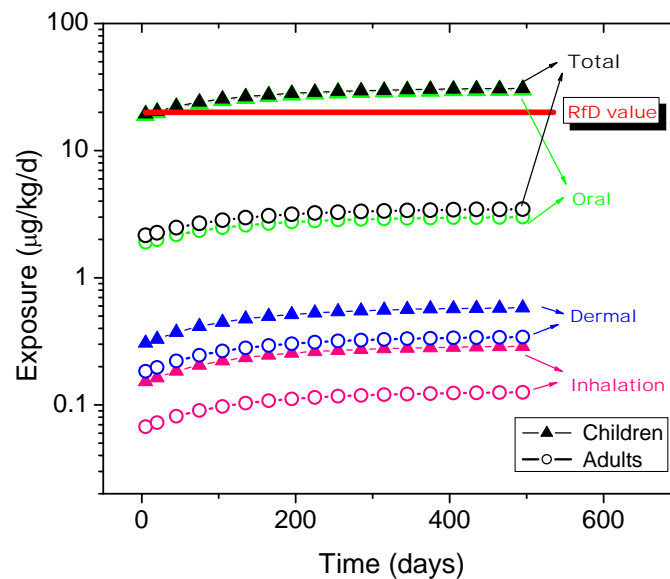
Figure 5.3 Change with time in predicted exposure to DEHP emitted from vinyl flooring through inhalation, dermal sorption and oral ingestion of dust

SENSITIVITY ANALYSIS

A sensitivity analysis was conducted to identify the critical model variables for total exposure as well as for each exposure pathway. In all cases, exposure is computed after each of the three compartments has reached steady state. The sensitivity of model variables is assessed by computing the percent change in exposure per unit increase in an input variable. The baseline conditions are those used for the results shown in Figure 5.3. The results of the sensitivity analysis along with the baseline values of the model variables are provided in Table 5.3.

Table 5.3 Sensitivity of Predicted Steady-State Exposure to Model Parameters

Variables	Baseline value	Exposure pathway			
		Inhalation	Dermal	Oral	Total
DEHP concentration in vinyl floor (C_0, ug/m^3)	2.55×10^{11}	1.00	1.00	1.00	1.00
Partitioning coefficient ($K_{vinyl/air}$)	2.3×10^{11}	-0.50	-0.50	-0.50	-0.50
Mass-transfer coefficient for flat surfaces (h_m, cm/s)	0.1	0.82	0.82	0.79	0.79
Total suspended particle concentration (TSP, μg/m^3)	20	0.07	-0.42	-0.41	-0.41
Partitioning coefficient ($K_{particle/air}$, m^3/ μg)	0.25	0.07	-0.42	-0.41	-0.41
Partitioning coefficient ($K_{dust/air}$, m^3/ g)	21,100	0.00	0.00	1.00	0.97
Inhalation rate (IR,m^3/day)	6.8	1.00	0.00	0.00	0.01
Exposure duration in main house (ED_3, hrs/day)	16.5	0.88	0.88	--	--
Skin surface area (SA, m^2)	0.59	0.00	1.00	0.00	0.02
Overall skin permeability coefficient (P, cm/hr)	580	0.00	1.00	0.00	0.02
Daily intake rate of dust (DIR, mg/kg/day)	10.3	0.00	0.00	1.00	0.97
Body weight (kg)	11	-0.50	-0.50	--	--
Air exchange rate for three compartment	0.5	-0.46	-0.46	-0.46	-0.46
Vinyl flooring area in Kitchen (A_{1vinyl}, m^2)	14.4	0.18	0.18	~0.22	~0.22
Vinyl flooring area in bathroom (A_{2vinyl}, m^2)	6.2	0.13	0.13	~0.25	~0.25
Vinyl flooring area in main house (A_{3vinyl}, m^2)	19.2	0.52	0.52	~0.34	~0.35

The properties affecting the source strength (initial contaminant concentration in VF, partition coefficient between VF and air, and surface area of VF) have a significant effect on all the exposure pathways. Increasing the mass-transfer coefficient (h_m) will increase the emission rate and significantly increase exposure, while increasing the ventilation rate will reduce exposure. Note, however, that the latter assumes an increase in air-exchange rate alone, without increasing the mass-transfer coefficients, which in reality would

increase as ventilation increases. An interesting result is that increasing the total suspended particle concentration (TSP) or increasing the particle/air partition coefficient ($K_{particle/air}$) is equivalent; either of which has a stronger impact on dermal sorption and oral ingestion than on inhalation. The reason is that increasing sorption on particles reduces the gas-phase concentration and both dermal sorption and oral ingestion decrease significantly. However, because particles contribute 80% of the inhalation exposure, the two effects cancel and inhalation exposure increases only slightly. Finally, as expected, exposure duration and body weight also strongly influence the resulting exposure.

UNCERTAINTY ANALYSIS

Model variables can be defined in terms of a Probability Distribution Function (PDF) that is derived from a limited set of observations. A simple Monte Carlo analysis is adopted to account for uncertainty associated with the model parameters as well as natural variability. A PDF for each of the important variables identified in the sensitivity analysis is randomly sampled to obtain a value for the variable. This set of model variables is then used to calculate exposure. The uncertainty analysis consisted of 1000 such exposure computations, which were used to derive a Cumulative Distribution Function (CDF) describing an estimate of the uncertainty in exposure.

As shown in Table 5.4, the ranges in model parameters were developed from data presented in other studies or obtained directly from the literature. Simple uniform distributions were used due to the lack of PDF for each variable. The uncertainty for the individual exposure pathways as well as for total exposure is summarized in Figure 5.4. Overall, exposure varies from about 5 µg/kg/d at the 5th percentile to about 180 µg/kg/d at the 95th percentile, a roughly 40-fold difference. The median value (50th percentile) of about 38 µg/kg/d is almost double the RfD.

Table 5.4 Parameter ranges used in uncertainty analysis

Variables	Min	Max	References
Initial DEHP concentration in vinyl floor (C_0, μg /m^3)	2.25×10^{11}	6.0×10^{11}	Clausen et al. 2004; Deisinger et al. 1998
Partition coefficient ($K_{vinyl/air}$)	2.05×10^{11}	5.45×10^{11}	--
Mass-transfer coefficient for flat surfaces (h_m, cm/s)	0.03	0.29	Huang et al. 2004; Lin et al. 2004
Total suspended particle concentration (TSP, μg/m^3)	12	66	Weschler et al. 2008
Partition coefficient ($K_{particle/air}$, m^3/μg)	0.215	0.28	Naumova et al. 2003
Partition coefficient ($K_{dust/air}$, m^3/g)	2000	4×10^4	Rudel et al. 2003; Weschler et al. 2008
Inhalation rate (IR, m^3/day)	5	14.5	Paustenbach 2000
Exposure duration in main house (ED_3, hr/day)	12.6	18.1	Hubal et al. 2000
Skin surface area (SA, m^2)	0.59	1.7	EPA 1997
Overall skin permeability coefficient (P, cm/hr)	56	1035	De Dear et al. 1997
Daily intake rate of dust (DIR, mg/kg/day)	1.03	10.3	Wensing et al. 2005
Body weight (kg)	9.15	62.2	EPA 1997
Air exchange rate for three compartment (1/hr)	0.1	1.1	Wallace et al. 2002
Vinyl flooring area in Kitchen (A_{1vinyl}, m^2)	11.9	47.6	Hodgson et al. 2005
Vinyl flooring area in bathroom (A_{2vinyl}, m^2)	5.1	20.4	Hodgson et al. 2005
Vinyl flooring area in main house (A_{3vinyl}, m^2)	2.56	44.8	Hodgson et al. 2005
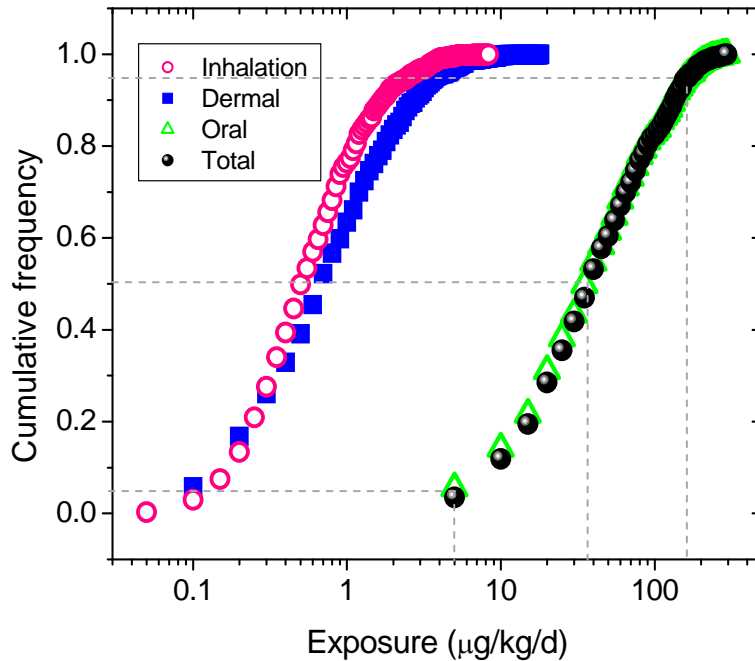
Figure 5.4 Uncertainty in predicted exposure to DEHP emitted from vinyl flooring (VF) via inhalation, dermal sorption and oral ingestion of dust

DISCUSSION

The high surface concentrations of phthalate on human skin observed in the CTEPP study were generally assumed to have been the result of dermal transfer. Hubal et al. (2008) studied the dermal transfer of chemicals from contaminated surfaces (such as floors and furniture) to skin, providing a range of measured transfer efficiencies, all of which were below 100%. Closer examination of the CTEPP data shows that the measured concentrations on skin were almost always higher than the measured concentrations on other surfaces. To investigate if the high dermal loadings are caused by transfer of chemicals from contaminated surfaces or from partitioning with air, a multi-linear regression was conducted. As shown in Table 5.5, the skin concentrations were strongly correlated with the concentration in air, and were not correlated with the hard surface concentrations. This is consistent with our previous finding that strong surface/air equilibrium relationships exist for phthalates on various interior surfaces (Xu et al. 2009a). Since the partition relationships established quickly between surfaces and air, the transfer of phthalate between surfaces (e.g. by touching) may not have great influence on

exposures. Although only ingestion of dust was considered in oral exposure pathway in this study, as the surface concentrations for phthalates are strongly correlated with the concentration in air, once the micro-activity information (e.g. time spent in hand-to-object, hand-to-mouth and object-to-mouth) is collected, it could be easily included in the model.

Table 5.5 Multi-linear regression to establish relationship between skin concentration and both air (x_1) and hard surface concentration (x_2)

Chemicals		K_1 (m), slope for x_1	P-value for K_1	K_2, slope for x_2	P-value for K_2
DBP	Child hand wipe, y	58	0.027	0.07	0.89
	Adult hand wipe, y	79	0.02	0.19	0.82
BBP	Child hand wipe, y	140	0.045	0.03	0.26
	Adult hand wipe, y	55	0.09	0.03	0.04
BPA	Child hand wipe, y	1600	0.005	0.22	0.73
	Adult hand wipe, y	950	0.004	0.31	0.37

In the simple sensitivity analysis described above, only one parameter was varied at a time. However, when the ventilation rate is increased, the mass-transfer coefficients will also increase because of the higher air velocity near the surfaces. As a result, the emission rate of DEHP from vinyl flooring will be stronger and the rate of DEHP adsorption to interior surfaces will be faster. The predicted exposure will therefore only decrease by 25% compared to the decrease of 46% predicted in the simple sensitivity analysis. In addition, the boundary layer of air adjacent to the skin will be thinner and the mass-transfer resistance will be reduced. Because the external gas-phase resistance controls the overall rate of dermal permeation (Xu et al. 2009a), the permeability of DEHP through the skin will be enhanced, meaning that dermal exposure will actually increase by 13%, as opposed to the decrease of 46% found in the simple sensitivity analysis. This rather surprising result suggests that the use of indoor fans could substantially increase the permeation rate of DEHP through the skin.

There are many other interior surfaces (for example, clothing, bedding, rugs, newspapers, books, magazines, human hair, crockery and cutlery) that have not been taken into account in our exposure model. To get a rough idea of the effect of including these additional surfaces, all interior surface areas were nominally increased by a factor of three from the model baseline conditions. In this case, sorption of DEHP to the much higher surface area doubles the time to reach steady state. Direct dermal sorption and ingestion from these other surfaces may increase the risk of DEHP exposure significantly. For example, DEHP would be expected to accumulate in clothes hanging in an open cupboard. When these are worn, dermal sorption could increase substantially. Coensel et al. (2008) studied the chemical contamination of clothes due to their direct or indirect exposure to moth repellent agents, which are similar to SVOCs, and concluded that clothes adsorb high concentrations of contaminants, and that they should be considered as secondary sources of indoor air pollution. Although the surface/air partition coefficient for the interior surfaces did not have a significant effect on the predicted steady-state exposure, it will influence the time to reach steady state. The stronger the partitioning between interior surfaces and air, the longer it will take to reach steady state. For instance, doubling the wall and ceiling/air partition coefficient increases the time to steady state by about 50%.

Other sources, such as food packaging, may be important DEHP exposure pathways (Koch et al. 2003), and young children can additionally be exposed through mouthing of soft PVC toys and teethers (Petersen and Breindahl 2000). In addition to vinyl flooring, there are many other sources of DEHP. For example, plasticized PVC is the most widely used electrical insulation material on wires and cables, which are estimated about 11 million miles in U.S. buildings today (Wilson 2009). By varying the DEHP content, cable manufacturers are able to produce a wide range of sheathing for particular applications (e.g. remain flexible even at low temperatures). These additional sources will result in higher DEHP concentrations in room air and dust and on skin. Indeed, there are many other sources of phthalates. Because the model employs a mechanistic approach to predict exposure media concentrations of DEHP emitted from vinyl flooring, it should be relatively simple to generalize the model to include these other sources. As shown in the sensitivity analysis, the most influential, chemical-specific model

parameters are the various partition coefficients and mass-transfer coefficients. The partition coefficients generally correlate well with vapor pressure while the chemical-specific dependence of the mass-transfer coefficients is provided by the Schmidt number (Xu et al. 2009a). To adjust the mass-transfer coefficient from one compound to another only requires knowledge of the diffusion coefficients of the two compounds in air, which are easy to estimate.

IMPLICATIONS FOR BIOMONITORING

The ability to measure chemicals in humans (biomonitoring) is far outpacing the ability to reliably interpret these data for public health purposes, creating a major knowledge gap (Bahadori et al. 2007). As discussed in the introduction, the use of biomonitoring data to design and evaluate public health interventions for compounds such as phthalates requires additional information on potential sources, temporal and spatial patterns of exposure, as well as a mechanistic understanding of the source-to-outcome continuum. The sensitivity and uncertainty analyses presented above reveal the potential for wide ranges in exposure that would confound the interpretation of cross-sectional biomonitoring results.

In the context of human health risks, Calafat and McKee (2006) outline research needs for using DEHP biomonitoring data to inform exposure assessment. Their recommendations include the need to identify vulnerable segments of the population that may be more highly exposed to phthalates than is the general population, and to identify sources of exposure to these vulnerable groups. The example we present in this paper demonstrates the utility of physically-based models for predicting concentrations of SVOCs as a function of time and space in residential environments. Such an approach combined with traditional scenario-based exposure algorithms facilitates identification of potentially vulnerable groups such as pregnant women and young children. Our example shows that the dependence on source and chemical specific properties is relatively simple, suggesting that the model could be extended to include other sources of phthalates, as well as other characteristics of the indoor environment.

A recent report on phthalates and cumulative risk assessment by the National Academies (NRC 2008) recommends that the US Environmental Protection Agency should: (1) Determine prenatal exposure to phthalates at relevant times during pregnancy; (2) Identify the most important sources of phthalate exposure in the general population; (3) Identify the full spectrum of phthalate metabolites (which are produced when phthalates enter the body) and identify which metabolites can be used to reliably indicate phthalate exposure; (4) Understand the reasons for differences in susceptibility to phthalates based on age, species, and exposure route; and (5) Explore the potential of phthalates to cause synergisms in combination with other antiandrogens. It is clear that biomonitoring alone can not provide answers to recommendations (2) and (4). In contrast, the approach articulated in this paper can be used to identify the most important sources of phthalate exposure, and can explain differences in susceptibility to phthalates based on age, species, and exposure route. Although our example focuses on emissions from a specific source (vinyl flooring) to a specific environmental medium (air), it can most likely be generalized to many other sources (for example, cosmetics, personal-care products, pharmaceuticals, medical devices, children's toys, food packaging, and cleaning and building materials) emitting various SVOCs into a wide range of environmental media (air, food, water, saliva, and even blood). Provided appropriate model development, parameter identification and model validation is undertaken, the approach could provide a relatively inexpensive and efficient way to identify and mitigate potential exposures and health risks associated with many of the SVOCs used in indoor materials and consumer products.

ACKNOWLEDGMENTS

REFERENCES

Adibi JJ, Whyatt RM, Williams PL, Calafat AM, Camann D, Herrick R, et al. 2008. Characterization of Phthalate Exposure among Pregnant Women Assessed by Repeat Air and Urine Samples. Environ Health Perspect 116(4): 467-473.

Afshari A, Gunnarsen L, Clausen PA, Hansen V. 2004. Emission of phthalates from PVC and other materials. Indoor Air 14: 120–128.

Albertini R, Bird M, Doerrer N, Needham L, Robison S, Sheldon L, et al. 2006. The Use of Biomonitoring Data in Exposure and Human Health Risk Assessments. Environ Health Perspect 114(11): 1755-1762.

Axley JW. 1991. Adsorption modeling for building contaminant dispersal analysis. Indoor Air 2: 147-171.

Bahadori T, Phillips RD, Money CD, Quackenboss JJ, Clewell HJ, Bus JS, et al. 2007. Making sense of human biomonitoring data: Findings and recommendations of a workshop. J Expo Sci Environ Epidemiol 17: 308-313.

BAUCH. 1991. Analyse und Bewertung der in Raumluft und Hausstaub vorhandenen Konzentrationen der Weichmacherbestandteile Diethylhexylphthalat(DEHP) und Dibutylphthalat (DBP). Sachstandsbericht, Berlin, Eigenverlag.

Bornehag C-G, Lundgren B, Weschler CJ, Sigsgaard T, Hagerhed-Engman L, Sundell J. 2005. Phthalates in Indoor Dust and Their Association with Building Characteristics. Environ Health Perspect 113(10): 1399-1404.

Bornehag C-G, Sundell J, Weschler CJ, Sigsgaard T, Lundgren B, Hasselgren M, et al. 2004. The Association between Asthma and Allergic Symptoms in Children and Phthalates in House Dust: A Nested Case–Control Study. Environ Health Perspect 112(14): 1393-1397.

Cadogan DF, Howick CJ. 1996. Plasticizers. In: Kirk-Othmer Encyclopedia of Chemical Technology New York: John Wiley and Sons, 258-290.

Calafat A, McKee R. 2006. Integrating biomonitoring exposure data into the risk assessment process: phthalates [diethyl phthalate and di(2-ethylhexyl) phthalate] as a case study. Environ Health Perspect 114: 1783-1789.

CDC. 2005. Third National Report on Human Exposure to Environmental Chemicals. Atlanta:Centers for Disease Control and Prevention. Available: http://www.cdc.gov/exposurereport/ [accessed May 3 2009].

Clark K, Cousins I, MacKay D. 2003. Assessment of critical exposure pathways. In: The Handbook of Environmental Chemistry, 3Q Phthalate Esters (Staples C, ed). New York: Springer, 227-262.

Clausen P, Hansen V, Gunnarsen L, Afshari A, Wolkoff P. 2004. Emission of Di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. Environ Sci Technol 38(9): 2531-2537

Clausen PA, Bille RLL, Nilsson T, Hansen V, Svensmark B, Bøwadt S. 2003. Simultaneous extraction of di(2-ethylhexyl) phthalate and nonionic surfactants from house dust Concentrations in floor dust from 15 Danish schools. J Chromatogr A 986(2): 179–190.

Clewell HJ, Tan YM, Campbell JL, Andersen ME. 2008. Quantitative Interpretation of Human Biomonitoring Data. Toxicol Appl Pharmacol 231(1): 122-133.

Coensel ND, Desmet K, Sandra P, Górecki T. 2008. Domestic sampling: Exposure assessment to moth repellent products using ultrasonic extraction and capillary GC-MS. Chemosphere 71: 711-716.

De Dear RJ, Arens E, Hui Z, Oguro M. 1997. Convective and radiative heat transfer coefficients for individual human body segments. Int J Biometeorol 40: 141–156.

Deisinger PJ, Perry LG, Guest D. 1998. In Vivo Percutaneous Absorption of [14C]DEHP from [14C]DEHP-Plasticized Polyvinyl Chloride Film in Male Fischer 344 Rats. Food Chem Toxicol 36: 521-527.

EPA US. 1997. Exposure Factors Handbook. Available: http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=12464 [accessed May 3 2009].

EPA US. 2005. A Pilot Study of Children's Total Exposure to Persistent Pesticides and Other Persistent Organic Pollutants (CTEPP). Available: http://www.epa.gov/heasd/ctepp/ctepp_report.pdf [accessed May 3 2009].

Fromme H, Albrecht M, Angerer J, Drexler H, Gruber L, Schlummer M, et al. 2007. Integrated Exposure Assessment Survey (INES) Exposure to persistent and bioaccumulative chemicals in Bavaria, Germany. Int J Hyg Environ Health 210: 345-349.

Fromme H, Lahrz T, Piloty M, Gebhart H, Oddoy A, Rüden H. 2004. Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). Indoor Air 14: 188–195.

Georgopoulos PG, Wang S-W, Yang Y-C, Xue J, Zartarian VG, Mccurdy T, et al. 2008. Biologically based modeling of multimedia, multipathway, multiroute population exposures to arsenic. J Expo Sci Environ Epidemiol 18: 462-476.

Heudorf U, Mersch-Sundermann V, Angerer E. 2007. Phthalates: Toxicology and exposure. Int J Hyg Environ Health 210: 623-634.

Hodgson AT, Ming KY, Singer BC. 2005. Quantifying object and material surface areas in residences. Available: http://repositories.cdlib.org/lbnl/LBNL-56786 [accessed May 3 2009].

Huang JM, Chen Q, Ribot B, Rivoalen H. 2004. Modeling contaminant exposure in a singlefamily house. Indoor Built Environ 13(1): 5-19.

Hubal EAC, Nishioka MG, Ivancic WA, Morara M, Egeghy PP. 2008. Comparing surface residue transfer efficiencies to hands using polar and nonpolar fluorescent tracers. Environ Sci Technol 42(3): 934-939.

Hubal EC, Sheldon LS, Burke JM, McCurdy TR, Berry MR, Rigas ML, et al. 2000. Children's Exposure Assessment: A Review of Factors Influencing Children's Exposure, and the Data Available to Characterize and Assess That Exposure. Environ Health Perspect 108(6): 475-486.

Jaakkola JJK, Knight TL. 2008. The Role of Exposure to Phthalates from Polyvinyl Chloride Products in the Development of Asthma and Allergies: A Systematic Review and Meta-Analysis. Environ Health Perspect Vol. 116(7): 845-853.

Jaakkola JJK, Oie L, Nafstad P, Botten G, Samuelsen SO, Magnus P. 1999. Interior surface materials in the home and the development of bronchial obstruction in young children in Oslo, Norway. Am J Public Health 89(2): 188-192.

Kato K, Silva M, Reidy J, Hurtz DI, Malek N, Needham L. 2004. Mono(2-ethyl-5-hydroxyhexyl) phthalate and mono-(2-ethyl-5-oxohexyl) phthalate as biomarkers for human exposure assessment to di-(2-ethylhexyl) phthalate. Environ Health Perspect 112: 327-330.

Koch HM, Drexler H, Angerer J. 2003. An estimation of the daily intake of di(2-ethylhexyl)phthalate (DEHP) and other phthalates in the general population. Int J Hyg Environ Health 206(2): 77-83.

Latini G, Felice CD, Verrotti A. 2004. Plasticizers, infant nutrition and reproductive health. Reprod Toxicol 19: 27-33.

Lin BR, Tan G, Wang P, Song L, Zhu YX, Zhai GK. 2004. Study on the thermal performance of the Chinese traditional vernacular dwellings in summer. Energy Build 36(1): 73-79.

Lorz PM, Towae FK, Enke W, Jackh R, Bhargava N. 2002. Phthalic acid and derivatives. In: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH.

Matsumoto M, Hirata-Koizumi M, Ema M. 2008. Potential adverse effects of phthalic acid esters on human health: A review of recent studies on reproduction. Regul Toxicol Pharmacol 50(1): 37-49.

Mattulat A. 2002. Konzentration von mittel- und schwerflüchtigen organischen Verbindungen in Staub aus Innenräumen - Belastungssituationim.

McKee RH, Butala JH, David RM, Gans G. 2004. NTP center for the evaluation of risks to human reproduction reports on phthalates: addressing the data gaps. Reprod Toxicol 18(1): 1-22.

Müller AK, Nielsen E, Ladefoged O. 2003. Report: Human exposure to selected phthalates in Denmark by the Danish Veterinary and Food Administration.

. Available: http://gl.foedevarestyrelsen.dk/FDir/Publications/2003015/Rapport.pdf [accessed May 3 2009].

Naumova YY, Offenberg JH, Eisenreich SJ. 2003. Gas/particle distribution of polycyclic aromatic hydrocarbons in coupled outdoor/indoor atmospheres. Atmos Environ 37: 703–719.

NRC. 2006. Human Biomonitoring for Environmental Chemicals. Washington, DC: The National Academies Press.

Paustenbach DJ. 2000. The practice of exposure assessment: A state-of-the-art review (Reprinted from Principles and Methods of Toxicology, 4th edition, 2001). J Toxicol Environ Health B Crit Rev 3(3): 179-291.

Petersen JH, Breindahl T. 2000. Plasticizers in total diet samples, baby food and infant formulae. Food Addit Contam 17(2): 133-141.

Ritter L, Arbucklet TE. 2007. Can exposure characterization explain concurrence of discordance between toxicology and epidemiology? Toxicol Sci 97(2): 241-252.

Rudel R, Camann D, Spengler J, Korn L, Brody J. 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust Environ Sci Technol 37(20): 4543-4553

Sheldon L, Clayton A, Keever J, Perritt R, Whitaker D. 1994. PTEAM: Monitoring of phthalates and PAHs in indoor and outdoor air. In: Samples in Riverside California Research Note No 94-10: California Environmental Protection Agency, Air Resources Board, Sacramento.

Silva MJ, Barr DB, Reidy JA, Malek NA, Hodge CC, Caudill SP, et al. 2004. Urinary Levels of Seven Phthalate Metabolites in the U.S. Population from the National Health and Nutrition Examination Survey (NHANES) 1999–2000. Environ Health Perspect 112(3): 331-338.

Wallace LA, Emmerich SJ, Howard-Reed C. 2002. Continuous measurements of air change rates in an occupied house for 1 year: The effect of temperature, wind, fans, and windows. J Expo Sci Environ Epidemiol 12(4): 296-306.

Wensing M, Uhde E, Salthammer T. 2005. Plastics additives in the indoor environment—flame retardants and plasticizers. Sci Total Environ 339: 19– 40.

Weschler CJ. 2003. Indoor/outdoor connections exemplified by processes that depend on an organic compound's saturation vapor pressure. Atmos Environ 37: 5455–5465.

Weschler CJ, Nazaroff WW. 2008. Semivolatile organic compounds in indoor environments. Atmos Environ 42(40): 9018-9040.

Weschler CJ, Salthammer T, Fromme H. 2008. Partitioning of phthalates among the gas phase, airborne particles and settled dust in indoor environments. Atmos Environ 42: 1449-1460.

WHO. 2004. IPCS Risk Assessment Terminology. Harmonization Project Document No. 1, World Health Organization, Geneva. Available:
http://www.who.int/ipcs/methods/harmonization/areas/terminology/en/index.html
[accessed May 3 2009].

Wilkes CR, Small MJ. 1992. Inhalation exposure model for volatile chemicals from indoor uses of water. Atmos Environ 26A(12): 2227-2236.

Wilson A. 2009. Getting Down to the Wire. Available: http://archrecord.construction.com/features/archives/0412feature-1.asp [accessed May 2 2009].

Wormuth M, Scheringer M, Vollenweider M, Hungerbühler K. 2006. What Are the Sources of Exposure to Eight Frequently Used Phthalic Acid Esters in Europeans? Risk Anal 26(3): 803-824.

Xu Y, A.Cohen-Hubal E, Clausen PA, Little JC. 2009a. Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – A Mechanistic Analysis. Environ Sci Technol 43(2374-2380).

Xu Y, Little J. 2006. Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles Environ Sci Technol 40(2): 456-461

Xu Y, Park J, Clausen PA, Kofoed-Sørensen V, Little JC. 2009b. Characterizing Emissions of Phthalate Plasticizer from Vinyl Flooring In a Specially-Designed SVOC Emission Chamber . Submitted.

Appendix A: Supplementary Information for Chapter 4

Predicting Residential Exposure to Phthalate Plasticizer Emitted from Vinyl Flooring – A Mechanistic Analysis

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NOMENCLATURE

A_c surface area of carpet (m^2)

A_{cw} surface area of ceiling/wall (m^2)

A_f surface area of furniture (m^2)

A_g surface area of glass (m^2)

A_p total surface area of suspended particulate material (m^2/m^3 air)

A_v surface area of vinyl flooring (m^2)

BW   body weight (kg)

C_0 constant DEHP concentration in the vinyl flooring ($\mu g/m^3$)

C_c surface concentration of carpet ($\mu g/m^2$)

C_{cw} surface concentration of ceiling/wall ($\mu g/m^2$)

C_f surface concentration of furniture ($\mu g/m^2$)

C_g surface concentration of glass ($\mu g/m^2$)

C_{surf} surface concentration of interior adsorption surface ($\mu g/m^2$)

CF_1 unit conversion factor of 1/24 (d/hr)

CF_2 unit conversion factor of 0.01 (m/cm)

D_{air} diffusivity of chemical in air (cm^2/h)

ED   exposure duration (hr/d)

f_{SA} fraction of skin area in contract with vapor (dimensionless)

F   particle-phase concentration ($\mu g/m^3$)

F_1 particle-phase concentration in room 1 ($\mu g/m^3$)

F_2 particle-phase concentration in room 2 (µg/m^3)

h_c convective heat transfer coefficient (W/m^{2}K)

h_m convective mass-transfer coefficient for surface (m/h)

h_{mp} convective mass-transfer coefficient for particles (m/h)

IR   inhalation rate (m^3/d)

K   DEHP vinyl flooring/air partition coefficient (dimensionless)

$K_{p,\,dust}$ dust/air partition coefficient (m^3/g)

$K_{p,\,particle}$ particle/air partition coefficient (m^3/µg)

K_{surf} surface/air partition coefficient for interior adsorption surface (m)

L   thickness of the boundary layer above skin (cm)

$\dot{m}$ DEHP emission rate from vinyl flooring (µg/m^{2}h)

p_L^o saturation vapor pressure of pure sub-cooled liquid (Pa)

P   overall skin permeability constant of gases (cm/hr)

P_{air} permeability constant through boundary layer (cm/hr)

$P_{skin/air}$ vapor to skin permeability constant (cm/hr)

$P_{skin/neat}$ neat liquid to skin permeability constant (cm/hr)

Q   ventilation rate (m^3/h)

SA   surface area of skin (m^2)

t   time (h)

TSP   concentration of total suspended particulate material (µg/m^3)

V_1 volume of room 1 (m^3)

V_2 volume of room 2 (m^3)

Vp saturation vapor pressure (Pa, mmHg)

y gas-phase concentration ($\mu g/m^3$)

y_0 gas-phase concentration immediately adjacent to the vinyl flooring ($\mu g/m^3$)

$y_{0,p}$ gas-phase concentration immediately adjacent to particle surface ($\mu g/m^3$)

$y_{0,surf}$ gas-phase concentration immediately adjacent to adsorption surface ($\mu g/m^3$)

y_1 gas-phase concentration in room 1 ($\mu g/m^3$)

y_2 gas-phase concentration in room 2 ($\mu g/m^3$)

y_{in} gas-phase concentration coming from outside ($\mu g/m^3$)

ADVERSE HEALTH EFFECT OF DEHP

There are serious health concerns associated with phthalate esters. Hardell et al. (1997) conducted a case-control study of 163 patients in Sweden and observed a surprisingly high risk of testicular cancer associated with occupational exposure to PVC plastics. When administered orally to pregnant experimental animals, Gray et al. (2000) found that certain phthalate esters (DEHP, DBP and BBP) have significant effects on the developing male reproductive system. Two studies of male infants suggest that human testicular development may be vulnerable to phthalates (Lottrup et al. 2006). One study shows that phthalate esters may have an aetiological association with endometriosis in women (Reddy et al. 2006). Besides the primary health concerns of cancer and various reproductive effects, some studies have also shown that inhalation exposure to phthalates adsorbed to suspended particles increases the risk of asthma and is associated with bronchial obstruction in children (Jaakkola et al. 1999; Øie et al. 1997; Bornehag et al. 2004).

SCHEMATIC OF EMISSION PROCESS
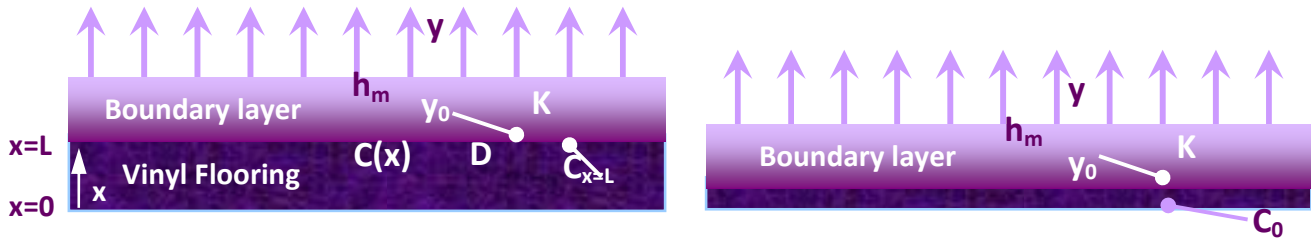
a. Xu and Little Model   b. Simplified Model

Figure S1. Schematic of emission process
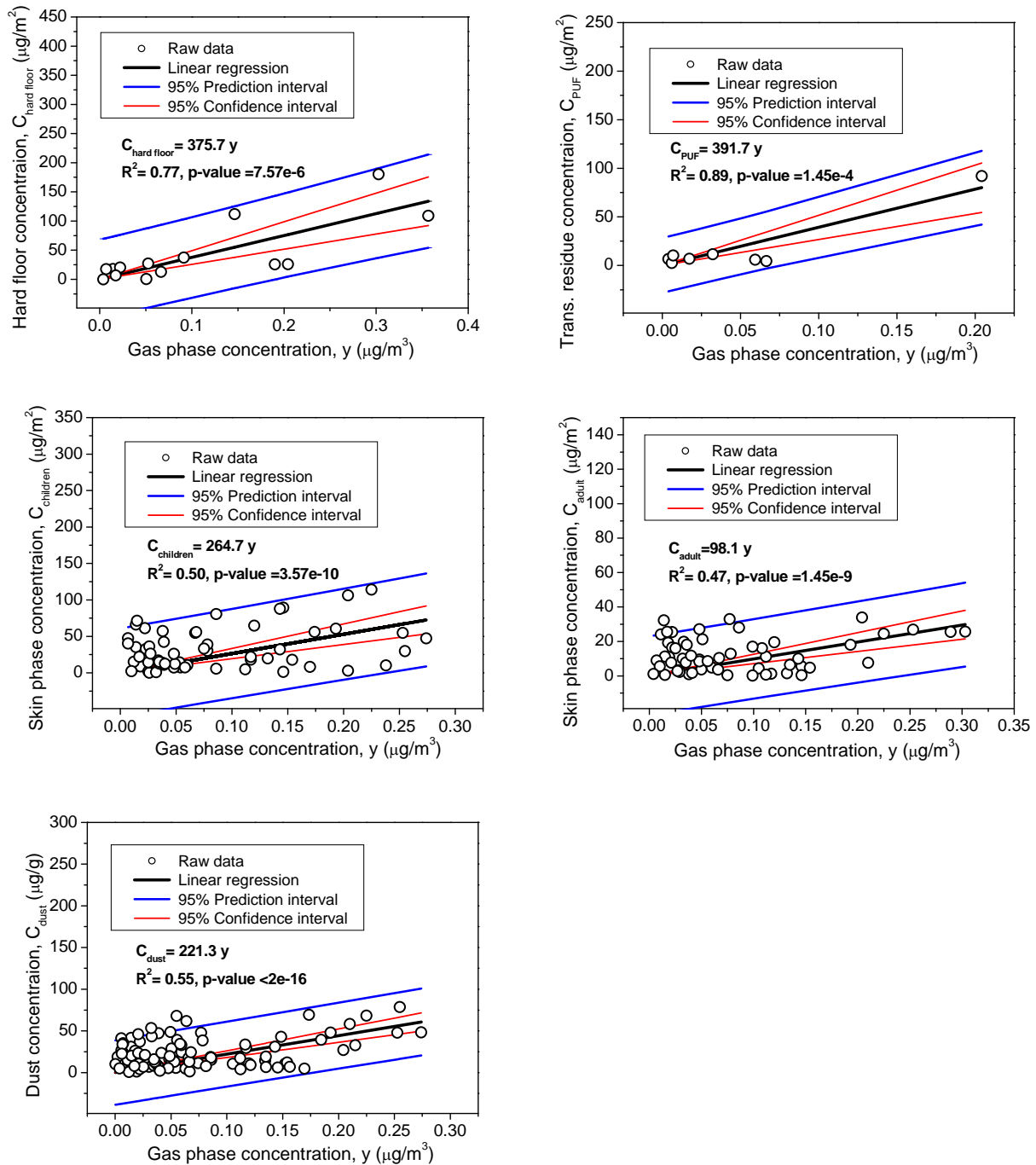
REGRESSION RESULTS
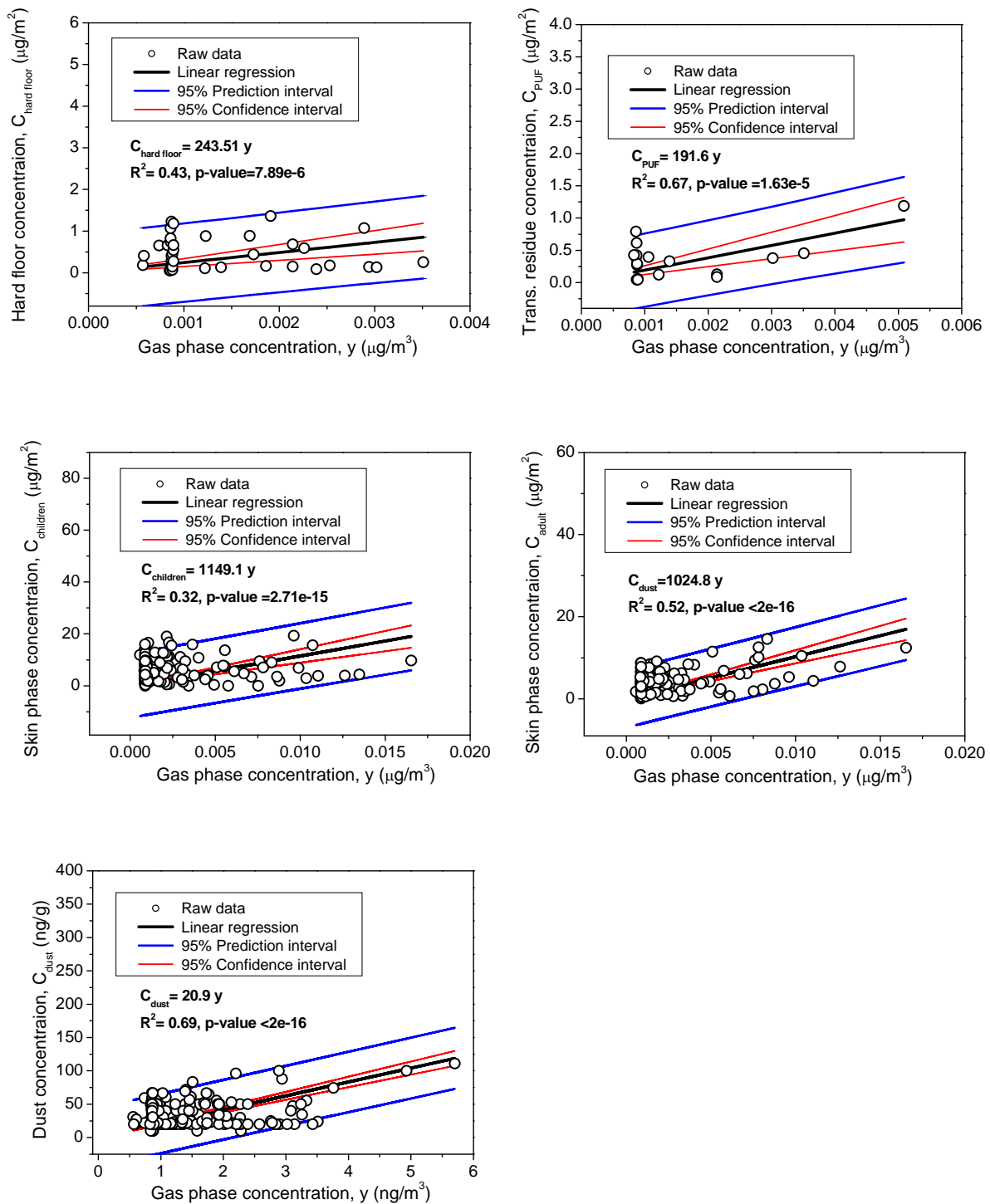

Figure S2. Linear regression results for BBP

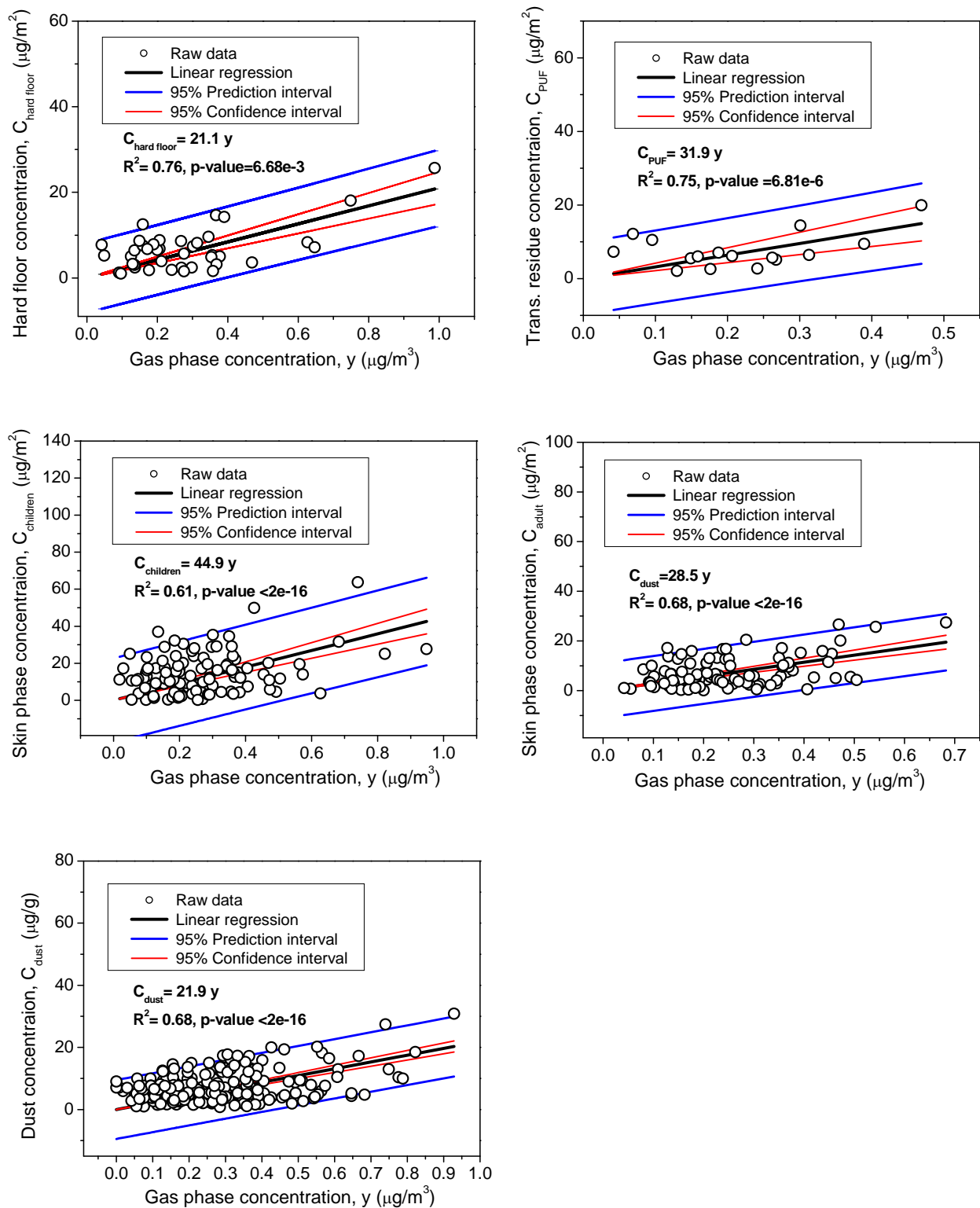Figure S3. Linear regression results for BPA
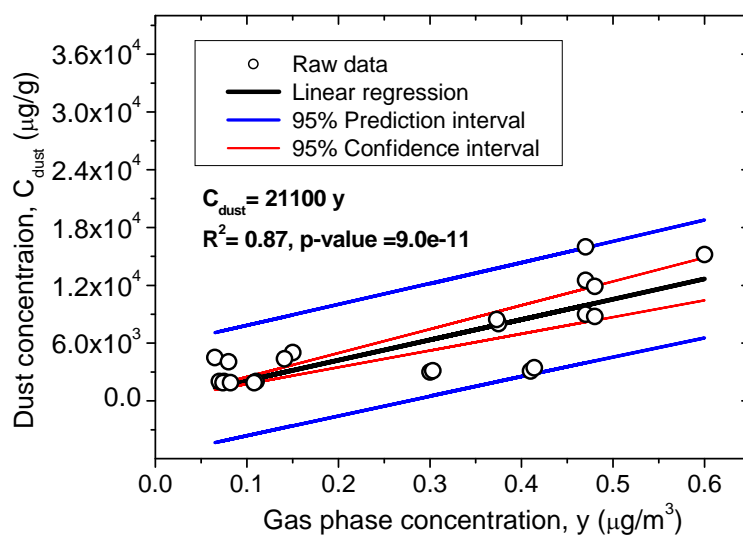
Figure S4. Linear regression results for DBP

Figure S5. Linear regression results for DEHP in dust (Clausen et al. 2004)

Table S1. Linear regression results with indoor gas phase chemical concentration ($\mu g/m^3$) as the independent variable ("Trans. residue concentration" refers to the amount that was transferable from carpets).

	Dependent variable	Sample size	Regression coefficient	Confidence interval (95%)	P-value	R^2	Shapiro test P- value
D B P	**Hard floor surface** ($\mu g/m^2$)	42	21.1 (m)	(17.3, 24.8)	3.81e-14	0.77	0.67
	Trans. residue (PUF) ($\mu g/m^2$)	17	31.9 (m)	(21.8, 42.0)	6.82e-06	0.75	0.12
	Child hand ($\mu g/m^2$)	106	44.9 (m)	(37.9, 51.9)	<2e-16	0.61	0.14
	Adult hand ($\mu g/m^2$)	95	28.5 (m)	(24.5, 32.6)	<2e-16	0.68	0.065
	Dust concentration ($\mu g/g$)	240	21.9 (m^3/g)	(19.9, 23.8)	<2e-16	0.68	0.067
B B P	**Hard floor surface** ($\mu g/m^2$)	16	376 (m)	(256, 493)	7.57e-06	0.77	0.32
	Trans. residue (PUF) ($\mu g/m^2$)	9	392 (m)	(267, 516)	1.45e-04	0.89	0.22
	Child hand ($\mu g/m^2$)	60	265 (m)	(195, 335)	3.57e-10	0.50	0.31
	Adult hand ($\mu g/m^2$)	60	98.1 (m)	(70.8, 126)	1.45e-09	0.47	0.11
	Dust concentration ($\mu g/g$)	101	221 (m^3/g)	(181, 261)	<2e-16	0.55	0.40
B P A	**Hard floor surface** ($\mu g/m^2$)	38	244 (m)	(149, 338)	7.89e-06	0.43	0.44
	Trans. residue (PUF) ($\mu g/m^2$)	19	192 (m)	(124, 260)	1.63e-05	0.67	0.44
	Child hand ($\mu g/m^2$)	163	1150 (m)	(890, 1410)	2.71e-15	0.32	0.069
	Adult hand ($\mu g/m^2$)	153	1030 (m)	(865, 1185)	<2e-16	0.52	0.021
	Dust concentration ($\mu g/g$)	203	20.9 (m)	(18.9, 22.8)	<2e-16	0.69	0.051
D E H P	**Dust concentration** ($\mu g/g$)	22	21100 (m^3/g)	(17400, 24800)	8.98e-11	0.87	0.34

MODIFICATION OF SURFACE PARTITION COEFFICIENTS

Unfortunately, according to the sampling method of the CTEPP study, the measured concentrations in the indoor air "y" are actually the total airborne concentrations; that is, the sum of the gas phase and airborne particle concentration "y+F". To obtain a more representative gas/surface partition coefficient, the equilibrium relationships need to be modified, or

$$K_{surf} = K_{surf, \ CTEPP} \cdot (y + F) / y \qquad (S1)$$

where $K_{surf, \ CTEPP}$ is the equilibrium coefficient in Table S1 derived from the CTEPP study, and K_{surf} is the desired gas/surface partition coefficient. Using equation (7) in the main paper, equation (S1) can be rearranged to give:

$$K_{surf} = K_{surf, \ CTEPP} \cdot (1 + K_{p, \ particle} \cdot TSP) \qquad (S2)$$

As described by Weschler et al. (2008), within a given class of organic compounds, and in some cases even among different classes, the logarithm of $K_{p, \ particle}$ correlates in a linear fashion with the logarithm of the saturation vapor pressure of the pure sub-cooled liquid, p_L^o (Liang et al. 1997; Weschler 2005). The values of $K_{p, \ particle}$ can therefore be calculated using the relationship developed by Naumova et al. (2003) based on over 1800 measured partition coefficients for polycyclic aromatic hydrocarbons (PAHs) derived from indoor and outdoor samples and collected in three US cities:

$$\log K_{p, \ particle} = \text{-0.860} \log p_L^o - 4.67 \qquad (S3)$$

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Since phthalate esters are liquid at room temperature, the problem associated with calculating sub-cooled vapor pressures that are solids at room temperature does not exist (Weschler et al. 2008). Hence, saturation vapor pressure, V_p, will be used. The V_p values as well as other physical properties for the four target chemicals are reported in Table S2. The vapor pressures that are subsequently used for the $K_{p,\,particle}$ calculations as well as in calculations throughout this paper are shown in bold. Table S3 lists $K_{p,\,particle}$ for each target chemical calculated using equation (S3). As TSP was not measured during the CTEPP study, a reasonable mean value for TSP of 20 $\mu g/m^3$ is chosen (Weschler et al. 2008; Weschler 2005), based on numerous studies of non-smoking residences in the United States. Assuming this typical TSP value and using the $K_{p,\,particle}$ reported in Table S3, equation (S2) is used to roughly estimate K_{surf} for each compound, with results listed in Table S4.

Table S2. Compound physical properties

Compound	CAS-No.	MW (g/mol)	m.p. (°C)	b.p. (°C)	Vapor pressure, V_p (mmHg, at 25°C)	Reference
DBP	84-74-2	278	-35	340	8.25E-06	(Howard et al. 1985)
					2.03E-05	(Donovan 1996)
					2.66E-05	(Stephenson and Malanowski 1987)
					2.70E-05	(Staples et al. 1997)
					4.20E-05	(Hinckley et al. 1990)
BBP	85-68-7	312	-35	370	2.67E-06	(Stephenson and Malanowski 1987)
					5.03E-06	(Staples et al. 1997)
					8.18E-06	(Howard et al. 1985)
					8.63E-06	(Petrasek et al. 1983)
					5.99E-05	(Mabey et al. 1982)
DEHP	117-81-7	391	-55	384	1.30E-07	(Chang and Davis 1976)
					1.42E-07	(Hinckley et al. 1990)
					1.43E-07	(Clausen et al. 2002)
					1.45E-07	(Small et al. 1948)
					3.81E-07	(Stephenson and Malanowski 1987)
BPA	80-05-7	228	132	364	4.00E-08	(Howard 1989)
					2.27E-07	EPI Suite
					3.96E-07	(Dow-Europe 1993)
					3.99E-07	(Groshart et al. 2001)

Table S3. Particle-gas partition coefficients $K_{p, particle}$

Compound	V_p (mm Hg, 25°C)	$K_{p, particle}$ (m^3/μg)
DBP	2.70E-05	2.70E-03
BBP	5.03E-06	1.15E-02
DEHP	1.43E-07	2.46E-01
BPA	3.96E-07	1.02E-01

Table S4. Modification of surface partition coefficients

Compound	Surface partition coefficient	Hard floor (m)	Trans. Residue (m)	Child hand (m)	Adult hand (m)	Dust (m^3/g)
DBP	$K_{surf, CTEPP}$	21.1	31.9	44.9	28.5	21.9
	K_{surf}	**22.2**	**33.6**	**47.3**	**30.1**	**26.9**
BBP	$K_{surf, CTEPP}$	376	392	265	98.1	221
	K_{surf}	**462**	**482**	**325**	**121**	**233**
BPA	$K_{surf, CTEPP}$	244	192	1150	1030	--
	K_{surf}	**740**	**583**	**3490**	**3120**	--
DEHP	$K_{p,dust}$	--	--	--	--	**21100**
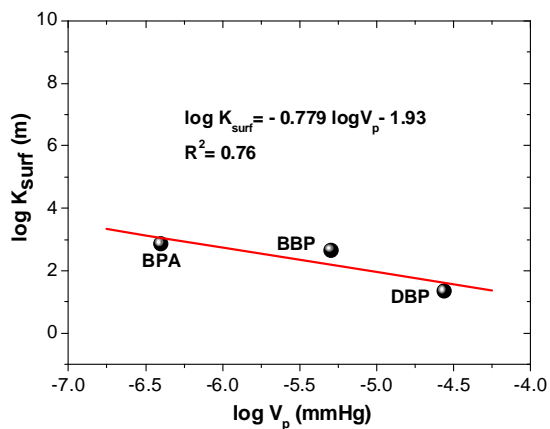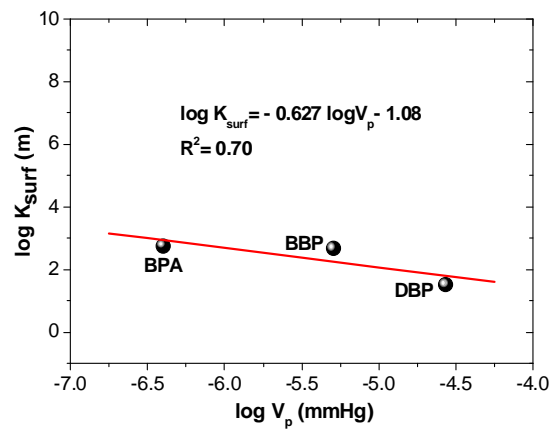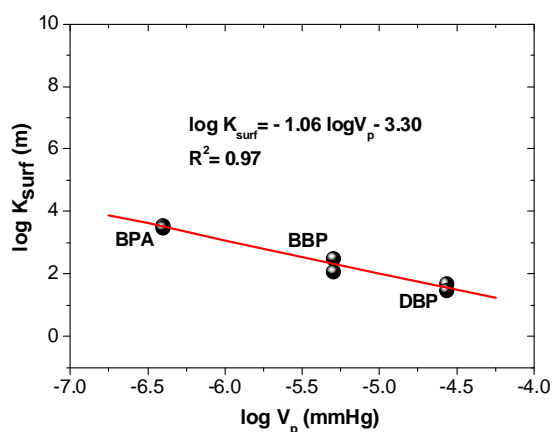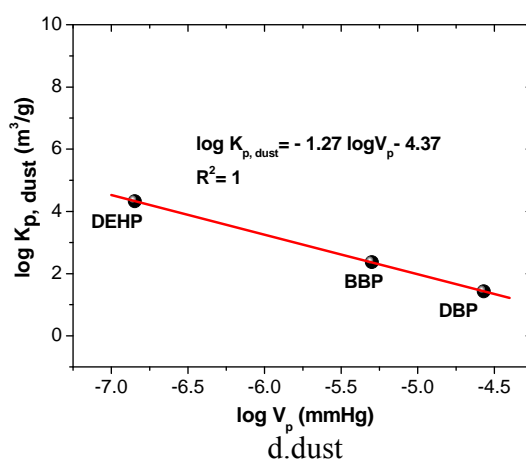
Figure S6. Linear regression between log (V_p) and log (K_{surf})

VALIDITY OF SKIN/AIR PARTITION COEFFICIENT

The skin/air partition coefficient is much higher than for other interior surfaces. To check the validity of this value, we estimated it in another way. Bunge and McDougal (1998) in a study on exposure to chemicals in drinking water obtained the following empirical equation:

$$\log K_{skin/water} = 0.71 \log K_{ow} \qquad (S4)$$

where $K_{skin/water}$ (dimensionless) is the skin/water partition coefficient and K_{ow} (dimensionless) is the octanol/water partition coefficient. The water/air partition coefficient (alternately known as Henry's law constant), K_{wa} (dimensionless) and K_{ow} for DEHP were found through experiments (Cousins and Mackay 2000; Kerstiens 2006). Therefore $K_{skin/air}$ can be estimated from:

$$\log K_{skin/air} = \log K_{skin/water} + \log K_{wa} \qquad (S5)$$

The results are shown in Table S5. Assuming the skin (stratum corneum) has an average thickness of 25 μm (Bunge and McDougal 1998) in order to adjust the units, a dimensionless log value of DEHP skin/air partition coefficient from the main paper is 8.6, which is within the estimated range (8.2 to 10.4) shown in Table S5.

Table S5. Physical-chemical properties for DEHP (25℃)

Reference	Log K_{ow}	Log K_{wa}	Log $K_{skin/water}$ (calculated)	Log $K_{skin/air}$ (calculated)
(Kerstiens 2006)	7.60	4.97	5.40	10.4
(Cousins and Mackay 2000)	7.73	2.80	5.49	8.2

ESTIMATING EXPOSURE TO DEHP FROM VINYL FLOORING

The predicted results were used to develop a screening-level assessment of residential exposure to DEHP from vinyl flooring. Preliminary calculations using default exposure factors (EPA 1992, 1997) indicated that children are more highly exposed than adults by a factor of 3. Children ages 1–6 are the most highly exposed and will be the focus of this assessment. Based on the model results we are most interested in evaluating exposures to vapor phase DEHP in air, particle bound DEHP in air, and DEHP in settled dust. The exposure pathways of interest are therefore: inhalation of vapor, inhalation of particles, dermal absorption of DEHP deposited on the skin, and oral ingestion via household dust.

Exposure through inhalation. Inhalation exposure can be estimated by (29):

$$\text{Inhalation exposure through gas (μg/kg/d)} = \frac{y \cdot IR \cdot ED \cdot CF_1}{BW} \qquad \text{(S6)}$$

where y (μg/m^3) is the contaminant concentration in inhaled air, IR (m^3/d) is the inhalation rate, ED (hr/d) is the exposure duration, CF_1 (d/hr) is the unit conversion factor of 1/24, and BW (kg) is body weight. Inhalation exposure through particles is estimated using the particle phase concentration F (μg/m^3) instead of y.

The steady state DEHP gas-phase concentration of 0.15 μg/m^3 and particle-phase concentration of 0.75 μg/m^3 were used to estimate inhalation exposure. As suggested by EPA (1997), default values for average body weight (people from six months to 21 years

old), exposure duration, and air inhalation rates, are used. As shown in Table S6, exposures due to inhalation of particles are about five times higher than through the gas-phase alone, and children experience three times higher total inhalation exposure than adults.

Table S6. Inhalation exposure assessment

Age (yrs)	Inhalation rate (m^3/d)	Body weight 5thAve. (kg)	Body weight 50thAve. (kg)	Exposure duration (hr/day)	High exposure through vapor (μg/kg/day)	High exposure through particles (μg/kg/day)	High total exposure through inhalation (μg/kg/day)
0.5-1	4.5	7.1	9.2	19.6	0.078	0.39	**0.47**
1-2	6.8	9.2	11.2	19.5	0.090	0.45	**0.54**
2-3	6.8	11.0	13.1	17.8	0.069	0.35	**0.42**
3-6	8.3	14.0	17.1	17.2	0.064	0.32	**0.38**
6-11	10	21.6	27.6	18.0	0.052	0.26	**0.31**
11-16	13.5	36.2	48.6	15.6	0.036	0.18	**0.22**
16-21	14.5	49.3	62.2	15.6	0.029	0.15	**0.17**

Exposure through dermal absorption of deposited DEHP. Because of the high partition coefficient (Table 2), the DEHP surface concentration on human skin is much higher than on other interior surfaces (Figure 5b). Dermal exposure comes from skin contact with contaminants in the air that partition to the skin. The calculation is typically represented by (EPA 1992):

$$\text{Dermal exposure (μg/kg/d)} = \frac{y \cdot SA \cdot f_{SA} \cdot P \cdot ED \cdot CF_2}{BW} \qquad (S7)$$

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where y (μg/m^3) is the gas-phase contaminant concentration, SA (m^2) is the skin surface area, f_{SA} (dimensionless) is the fraction of skin area (SA) in contact with the gas, P (cm/hr) is the overall skin permeability coefficient of gases, and CF$_2$ (m/cm) is the unit conversion factor of 0.01.

The overall skin permeability coefficient, P, is controlled by permeation through the skin as well as permeation through the air boundary layer adjacent to the skin. The estimated value is 580 cm/hr. Dermal exposure is then estimated, as shown in Table S7. Children experience two times higher dermal exposure than adults.

The overall skin permeability coefficient, P, is controlled by permeation through the skin ($P_{skin/air}$) as well as permeation through the air boundary layer adjacent to the skin (P_{air}) or:

$$P = \frac{1}{\dfrac{1}{P_{skin/air}} + \dfrac{1}{P_{air}}} \tag{S8}$$

where $P_{skin/air}$ (cm/hr) is vapor to skin permeability, and P_{air} (cm/hr) is permeability of the boundary layer. For low volatility compounds, convective mass transfer through the air boundary layer adjacent to the skin may become the rate limiting factor (Wilschut and ten Berge 1995), as is often the case for air/water transfer.

Many in vitro studies in both humans and animals have established that skin functions as a membrane (26). Membrane permeability referenced to the air, $P_{skin/air}$, is obtained from permeability referenced to the neat liquid, $P_{skin/neat}$, by multiplying by the neat liquid/air partition coefficient, $K_{neat/air}$ (EPA 1992; Lendzian and Kerstiens 1991), or:

$$P_{skin/air} = P_{skin/neat} \times K_{neat/air} \tag{S9}$$

Only a few studies measuring skin permeability of phthalates are available. In separate in vitro diffusion-cell studies of transdermal permeability of neat DEHP, Scott et al. (1987) and Barber et al. (1992) measured $P_{skin/neat}$ of DEHP through human stratum corneum as 0.57×10^{-5} cm/h and 1.05×10^{-7} cm/h, respectively. The more recent (and lower) value of 1.05×10^{-7} cm/h will be used in the subsequent analysis. The value of $K_{neat/air}$ for DEHP

can be calculated from the vapor pressure using the ideal gas law (Schwarzenbach et al. 2003). Therefore, the permeability of DEHP vapor through human skin, $P_{skin/air}$ is estimated as 3.28×10^4 cm/h. The $P_{skin/air}$ value is also checked using a different approach and found to be reasonable.

The air adjacent to the skin is drawn upward by natural convection associated with dissipated metabolic heat. Assuming a boundary layer is present between the skin surface and room air, the permeation coefficient through this boundary layer (P_{air}, cm/hour) can be estimated by the convective mass transfer coefficient. Dear et al. (1997) measured the air speed around a thermal manikin, and developed an equation suitable for application to both seated and standing postures indoors, or:

$$h_c = 10.3v^{0.6} \tag{S10}$$

where h_c (W/m^{2}K) is the convective heat transfer coefficient, and v (m/s) is the air speed. Based on the Colburn analogy for heat and mass transfer, P_{air} is estimated to be 590 cm/hr. Finally, the overall skin permeability coefficient of DEHP is estimated as 580 cm/hr. Even though the permeability of DEHP vapor through the skin ($P_{skin/air}$) is high, gas-phase resistance through the air boundary layer controls the overall process.

Exposure through oral intake of household dust. The daily intake rate of dust must be known to calculate ingestion exposure. According to Stubenrauch et al. (Wensing et al. 2005; Stubenrauch et al. 1999), the average daily intake rate for adults is 1.03 mg/kg/d, while for infants between their first and third year of life, it is 10.3 mg/kg/d. Using the estimated dust concentration, the oral intake of DEHP is about 32.6 μg/kg/d and 3.3 μg/kg/d for infants and adults, respectively.

Table S7. Dermal exposure assessment

Age (yrs)	Body weight 5th Ave. (kg)	Body weight 50th Ave. (kg)	Skin surface area 5th Ave. (m^2)	Skin surface area 50th Ave. (m^2)	Exposure duration (hr/day)	Medium exposure (μg/kg/day)	High exposure (μg/kg/day)
2-3	11.0	13.1	0.52	0.59	17.8	0.37	**0.78**
3-6	14.0	17.1	0.78	0.72	17.2	0.34	**0.89**
6-11	21.6	27.6	0.86	0.98	18.0	0.30	**0.67**
11-16	36.2	48.6	1.22	1.44	15.6	0.21	**0.49**
16-21	49.3	62.2	1.48	1.70	15.6	0.20	**0.44**

Risk characterization.   As shown in Table S8, the tolerable daily intake (TDI) for DEHP selected by the EU Scientific Committee for Toxicity, Ecotoxicity and the Environment (CSTEE) is 37 μg/kg/d, while the reference dose (RfD) is 20 μg/kg/d according to the U.S. EPA. Airborne particles contribute 80% of the inhalation exposure, and the highest value of total inhalation exposure is less than 0.6 μg/kg/d, which is lower than the RfD. For infants, exposure through oral intake via dust is 1.6 times higher than the RfD, but lower than the TDI. Exposures via these two pathways are close to other study results (Wensing et al. 2005; Fromme et al. 2007; Wormuth et al. 2006). Dermal absorption of DEHP deposited on skin does not appear to be a major exposure pathway. For phthalates like DEHP, the primary route of exposure is oral ingestion of dust. The more volatile, lower molecular weight, phthalates will be inhaled to a greater extent (Koch et al. 2003). Overall, children experience two to ten times higher exposure risk than adults based on all the exposure pathways.

Table S8. High exposure estimates of DEHP and comparison with TDI and RfD values

	Inhalation (µg/kg/day)	Dermal (µg/kg/day)	Oral intake via dust (µg/kg/day)	TDI (µg/kg/day)	RfD (µg/kg/day)
Children	0.54	0.89	32.6	37	20
Adult	0.17	0.44	3.3		

Food may also be a major DEHP exposure pathway (Koch et al. 2003), and young children can additionally be exposed through mouthing of soft PVC toys or teethers (Petersen and Breindahl 2000) as well as via direct dermal transfer, when crawling on vinyl floors or other surfaces that have high concentrations of adsorbed DEHP, for example. In addition to vinyl flooring, there are many other sources of DEHP which will result in a higher DEHP concentration in air and on dust and skin. Although further model development, parameter identification and model validation is clearly required, the simple model developed here provides a mechanistic framework that elucidates exposure pathways for phthalate plasticizers, and can most likely be adapted to predict emissions, transport, exposure and risk associated with emissions of other semi-volatile organic compounds, such as brominated flame retardants and biocides, in a residential environment.

VALIDITY OF DEHP VAPOR PERMEABILITY THROUGH SKIN

Bunge and McDougal (1998) suggested the following empirical equation to estimate permeability referenced to aqueous-phase concentrations:

$$\log P_{SC/W}(cm/h) = -2.72 + 0.71 \cdot \log K_{ow} - 0.006 \cdot MW \qquad (S11)$$

In addition, $\log P_{skin/air} = \log P_{sc/w} + \log K_{wa}$ \qquad (S12)

Equations S11 and S12 were used to calculate the value of log $P_{skin/air}$ as shown in Table S9. The log value of $P_{skin/air}$ from the above calculation is 4.52, which is within the estimated range (3.2 to 5.3) shown in Table S6.

Table S9 $P_{skin/air}$ estimation

Reference	Log K_{ow}	Log K_{wa}	log $P_{sc/w}$	log $P_{skin/air}$
(Kerstiens 2006)	7.60	4.97	0.33	5.3
(Cousins and Mackay 2000)	7.73	2.80	0.43	3.2

REFERENCES (SI)

Barber E, Teetsel NM, Kolberg KF, Guest D. 1992. A Comparative Study of the Rates of in Vitro Percutaneous Absorption of Eight Chemicals Using Rat and Human Skin. Fundamental and Applied Toxicology 19(4): 493-497

Bornehag C-G, Sundell J, Weschler CJ, Sigsgaard T, Lundgren B, Hasselgren M, et al. 2004. The Association between Asthma and Allergic Symptoms in Children and Phthalates in House Dust: A Nested Case–Control Study. Environmental Health Perspectives 112(14): 1393-1397.

Bunge AL, McDougal JN. 1998. In: Exposure to contaminants in Drinking Water (Olin SS, ed): ILSI Press.

Chang R, Davis EJ. 1976. Knudsen aerosol evaporation. J Colloid Interface Sci 54: 352-363.

Clausen P, Hansen V, Gunnarsen L, Afshari A, Wolkoff P. 2004. Emission of Di-2-ethylhexyl phthalate from PVC flooring into air and uptake in dust: Emission and sorption experiments in FLEC and CLIMPAQ. Environmental Science and Technology 38(9): 2531-2537

Clausen PA, Hansen V, Gunnarsen L, Afshari A, Wolkoff P. 2002. Emissions of phthalates from PVC flooring in two very different test chambers. In: Indoor Air 2002:

9th International Conference on Indoor Air Quality and Climate. Santa Cruz, CA, 932-937.

Cousins I, Mackay D. 2000. Correlating the physical-chemical properties of phthalate esters using the `three solubility' approach. Chemosphere 41: 1389-1399.

Dear RJd, Arens E, Hui Z, Oguro M. 1997. Convective and radiative heat transfer coefficients for individual human body segments. Int J Biometeorol 40: 141–156.

Donovan SF. 1996. New method for estimating vapor pressure by the use of gas chromatography. JOURNAL OF CHROMATOGRAPHY A 749(1-2): 123-129.

Dow-Europe. 1993. SIDS ProIile for Bisphenol A. Horgen, Switzerland.

EPA US. 1992. Dermal Exposure Assessment: Principles and Applications. EPA/600/8-91/011B.

EPA US. 1997. Exposure Factors Handbook.

Fromme H, Gruber L, Schlummer M, Wolz G, Böhmer S, Angerer J, et al. 2007. Intake of phthalates and di(2-ethylhexyl)adipate: Results of the Integrated Exposure Assessment Survey based on duplicate diet samples and biomonitoring data. Environment International 33(8): 1012-1020.

Gray LE, Jr. JO, Furr J, Price M, Veeramachaneni DNR, Parks L. 2000. Perinatal Exposure to the Phthalates DEHP, BBP, and DINP, but Not DEP, DMP, or DOTP, Alters Sexual Differentiation of the Male Rat. Toxicological sciences 58: 350-365.

Groshart CP, Okkerman PC, Pijnenburg AMCM. 2001. Chemical study on Bisphenol-A. The Hague, The Netherlands: Nat. Inst. Coast. and Marine Management (RIKZ).

Hardell L, Ohlson C-Gr, Fredrikson M. 1997. Occupational exposure to polyvinyl chloride as a risk factor for testicular cancer evaluated in a case-control study. International Journal of Cancer 73: 828–830.

Hinckley DA, Bidleman TF, Foreman WT. 1990. Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data. J Chem Eng Data 35: 232-237.

Howard PH. 1989. Handbook of Environmental Fate and Exposure Data. Chelsea, MI: Lewis Publishers.

Howard PH, Banerjee s, Robillard KH. 1985. Measurement of water solubilities, octanol/water partition coefficients and vapor pressures of commercial phthalate esters. Environ Toxicol Chem(4): 653-661.

Jaakkola JJK, Oie L, Nafstad P, Botten G. 1999. Interior surface materials in the home and the development of bronchial obstruction in young children in oslo, Norway. American Journal of Public Health 89(2): 188-192.

Kerstiens G. 2006. Parameterization, comparison, and validation of models quantifying relative change of cuticular permeability with physicochemical properties of diffusants. Journal of Experimental Botany 57(11): 2525-2533.

Koch HM, Drexler H, Angerer J. 2003. An estimation of the daily intake of di(2-ethylhexyl)phthalate (DEHP) and other phthalates in the general population. International Journal of Hygiene and Environmental Health 206(2): 77-83.

Lendzian K, Kerstiens G. 1991. Sorption and transport of gases and vapors in plant cuticles. Reviews of Environmental Contamination and Toxicology 121: 65-128.

Liang C, Pankow J, Odum J, Seinfeld J. 1997. Gas/particle partitioning of semivolatile organic compounds to model inorganic, organic and ambient smog aerosols. Environ Sci Technol 31: 3086-3092.

Lottrup G, Andersson A-M, Leffers H, Mortensen GK, Toppari J, Skakkebæk NE, et al. 2006. Possible impact of phthalates on infant reproductive health. International Journal of Andrology 29: 172–180.

Mabey Wr, Smith JH, Podoll Rt, Johnson HL, Mill T, Chou, T.w. G, J., et al. 1982. Aqueous fate process for organic priority pollutants.

Naumova YY, Offenberg JH, Eisenreich SJ. 2003. Gas/particle distribution of polycyclic aromatic hydrocarbons in coupled outdoor/indoor atmospheres. Atmospheric Environment 37: 703–719.

Øie L, Hersoug L-G, Madsen JØ. 1997. Residential Exposure to Plasticizers and Its Possible Role in the Pathogenesis of Asthma. Environmental Health Perspectives 105(9): 972-978

Petersen JH, Breindahl T. 2000. Plasticizers in total diet samples, baby food and infant formulae. Food Additives and Contaminants 17(2): 133-141.

Petrasek AC, Kugeman IJ, Austern BM, Pressley TA, Winslow LA, Wise RH. 1983. Fate of toxic organic compounds in wastewater treatment plants. J Water Pollut Control Fed 55: 286-296.

Reddy B, Rozati R, Reddy B, Raman N. 2006. Association of phthalate esters with endometriosis in Indian women. International Journal of Obstetrics and Gynaecology 113: 515–520.

Schwarzenbach R, Gschwend P, Imboden D. 2003. Environmental organic chemistry 2nd ed ed: Hoboken, N.J. : Wiley.

Scott R, Dugard P, Ramsey J, Rhodes C. 1987. In vitro absorption of some phthalate diesters through human and rat skin. Environmental Health Perspectives 74: 223-227.

Small PA, Small KW, Coeley P. 1948. The vapour pressures of some high boiling esters. Trans Faraday Soc 44: 810-816.

Staples CA, Peterson DR, Pakerton TF, Adams WJ. 1997. The environmental fate of phthalate esters. A literature review. Chemosphere 35(4): 667-749.

Stephenson RM, Malanowski S. 1987. Handbook of the Thermodynamics of Organic Compounds. New York: Elsevier Science Publishing Co., Inc.

Stubenrauch S, Hempfling R, Doetsch P, Grünhoff D. 1999. Vorschläge zur Charakterisierung und Quantifizierung pfadübergreifender Schadstoffexposition. . Z Umweltchem Ökotoxikol 11: 219-226.

Wensing M, Uhde E, Salthammer T. 2005. Plastics additives in the indoor environment—flame retardants and plasticizers. Science of the Total Environment 339: 19– 40.

Weschler C. 2005. Relationships between concentrations of organic compounds in dust and air. Proceedings of Indoor Air 2005: 1636-1640.

Weschler CJ, Salthammer T, Fromme H. 2008. Partitioning of phthalates among the gas phase, airborne particles and settled dust in indoor environments. Atmospheric Environment 42(7): 1449-1460.

Wilschut A, ten Berge WF. 1995. Two mathematical skin permeation models for vapors. In: Fourth International Prediction of Percutaneous Penetration Conference. Cardiff, U.K.: La Grande Motte, STS Publishing.

Wormuth M, Scheringer M, Vollenweider M, Hungerbühler K. 2006. What Are the Sources of Exposure to Eight Frequently Used Phthalic Acid Esters in Europeans? Risk Analysis 23(3): 803 - 824.