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Rapid Methods to Estimate Potential Exposure to Semivolatile Organic Compounds in the Indoor Environment

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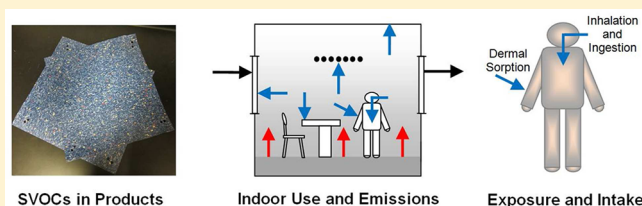
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S Supporting Information

ABSTRACT: A systematic and efficient strategy is needed to assess and manage potential risks to human health that arise from the manufacture and use of thousands of chemicals. Among available tools for rapid assessment of large numbers of chemicals, significant gaps are associated with the capability to evaluate exposures that occur indoors. For semivolatile organic compounds (SVOCs), exposure is strongly influenced by the types of products in which these SVOCs occur. We propose methods for obtaining screening-level estimates for two primary SVOC source classes: additives in products used indoors and ingredients in products sprayed or applied to interior surfaces. Accounting for product use, emission characteristics, and the properties of the SVOCs, we estimate exposure via inhalation of SVOCs in the gas-phase, inhalation of SVOCs sorbed to airborne particles, ingestion of SVOCs sorbed to dust, and dermal sorption of SVOCs from the air into the blood. We also evaluate how exposure to the general public will change if chemical substitutions are made. Further development of a comprehensive set of models including the other SVOC-containing products and the other SVOC exposure pathways, together with appropriate methods for estimating or measuring the key parameters (in particular, the gas-phase concentration in equilibrium with the material-phase concentration of the SVOC in the product, or y_0), is needed. When combined with rapid toxicity estimates, screening-level exposure estimates can contribute to health-risk-based prioritization of a wide range of chemicals of concern.



INTRODUCTION

Potential risks to human health arise from the manufacture and use of thousands of chemicals.^{1,2} A substantial fraction of these chemicals are semivolatile organic compounds (SVOCs), and many of these are found indoors³ where they partition between air, airborne particles, settled dust, and exposed interior surfaces including skin, hair, and clothing.^{4–6} SVOCs have vapor pressures in the range of 10^{-9} to 10 Pa (10^{-14} to 10^{-4} atm).⁶ Indoor SVOCs are of special concern because people spend most of their time inside residences, schools, and occupational buildings.^{7,8} Biomonitoring has shown that humans have body burdens of certain SVOCs^{3,4,6,9,10} that are both ubiquitous and persistent indoors. Associations have been made between adverse health effects and exposure to specific indoor SVOCs, with several categorized as potential endocrine-disrupting compounds.^{6,10}

Although the sources and exposure pathways for many SVOCs are still being elucidated, an understanding of their indoor occurrence and distribution is beginning to emerge.^{5,6,10–16} Products such as building materials, furnis-

ings, household goods, and those used for personal-care contain a vast array of SVOCs. In some cases SVOCs are sprayed as a liquid or applied as a powder. Such applications are the common means by which pesticides, termiticides, herbicides, sealants, stain repellants, and water repellants are introduced to indoor environments. In other cases SVOCs are present as additives or solvents in materials used indoors. These include flame retardants, plasticizers, antioxidants, preservatives, and coalescing agents. In addition to these two primary classes, SVOCs can be generated by incomplete combustion, by high-temperature heating processes, and by chemical processes.⁶ Polycyclic aromatic hydrocarbons are a class of SVOCs that can be emitted indoors by tobacco smoking and from heated cooking oils. Examples of chemical processes include monoesters derived from the hydrolysis of phthalate and

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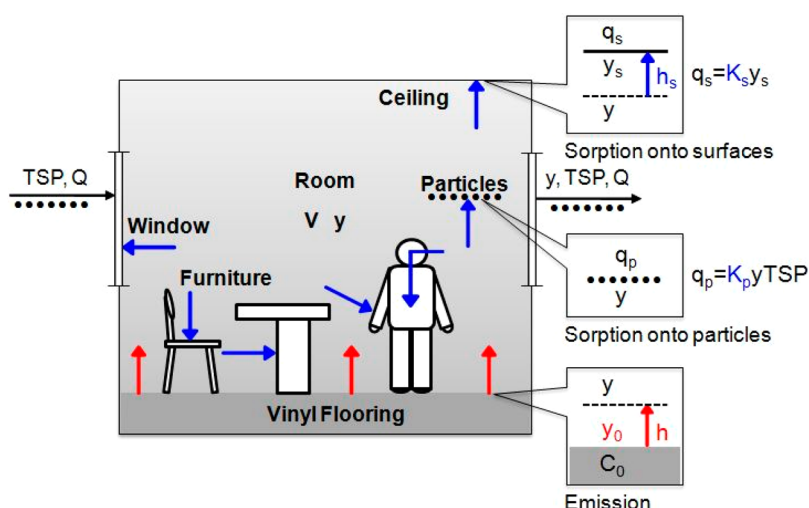


Figure 1. Schematic showing mechanisms governing emissions of SVOCs, present as additives in products, into a room. Because the emphasis is on exposure attributable to indoor sources, we assume that no SVOC enters in the influent air.

phosphate diesters (used as plasticizers and flame retardants) and bisphenol A derived from the degradation of polycarbonate. Bisphenol A is also present in polycarbonate as a residual monomer.

Exposures to manufactured chemicals in the indoor environment are strongly influenced by the types of products in which chemicals occur and the ways in which the products are used. For example, certain phthalates are used as plasticizers in soft polyvinyl chloride (PVC) products, while other phthalates are used as solvents in personal care products such as perfume, eye shadow, moisturizer, and nail polish.¹⁰ Exposure to phthalates in PVC products occurs following emission from the source into air and subsequent migration to different media such as dust^{18,19} or indoor surfaces,¹⁷ while exposure to phthalates present in personal care products is more likely a consequence of dermal absorption or incidental ingestion^{20,21} and therefore largely controlled by human behavior. Phthalates are also found in food as a result of its contact with materials used in processing and packaging.^{21,22} Exposure to certain phthalates appears to be largely controlled by diet.²²

To prioritize testing and to manage risks of industrial chemicals including SVOCs, methods are being developed and applied to rapidly evaluate compounds for their potential hazard. The ToxCast program applies recent advances in high-throughput screening, computational chemistry, and toxicogenomic techniques to profile bioactivity and prioritize toxicity testing for hundreds of chemicals.^{23,24} In addition to toxicological information, there is a compelling need for analogous approaches to rapidly estimate human exposure to large sets of SVOCs. Such screening tools are being developed in the ExpoCast program.²⁵ Combined with high-throughput estimates of toxicity, the development of efficient exposure tools should enable a more complete risk-based prioritization of chemicals in commerce.

Of the roughly 100,000 chemicals catalogued in the Aggregated Computational Toxicology Resource (ACToR) for which there is at least limited toxicity information, some form of exposure information is available for less than 20%. Readily accessible data on concentrations in exposure-related media (air, dust, food) are available for a much smaller proportion.²⁶ Consequently, exposure-based prioritization currently requires the use of simple models to estimate

exposure potential. Multimedia fate and transport models have been developed to evaluate potential exposure and risk resulting from environmental emissions.^{27,28} However, these models are based on persistence outdoors and bioaccumulation in the food chain and do not address exposures that occur indoors. Indeed, because many biotic and abiotic degradation processes that occur in the natural environment do not occur in buildings, the potential for exposure to SVOCs is even higher indoors. Among available tools for rapid assessment of large numbers of chemicals,²⁹ significant gaps are associated with the ability to evaluate indoor exposures.

■ OBJECTIVES

In this paper, we propose rapid methods based on models of mechanistic processes to obtain screening-level estimates of potential indoor exposure of building occupants to SVOCs by considering product use, emission characteristics, and chemical properties. Where possible, we compare predictions to available data to increase our confidence in the reliability of the models. We focus on exposures to SVOCs that are either present as additives in products used indoors or as ingredients in products directly applied to interior surfaces because we judge these two classes to be the major contributors to the broad spectrum of manufactured SVOCs found indoors. We limit our assessment to exposure via inhalation of SVOCs in the gas-phase, exposure via inhalation of SVOCs sorbed to airborne particles, exposure via ingestion of SVOCs sorbed to dust, and exposure via dermal sorption of SVOCs from the air into the blood. Finally, we consider exposure to a single product, exposure to a range of similar products for an entire economy, and evaluate how exposure would change for SVOCs proposed as substitutes in specific products.

■ SIMPLE MODELS TO ESTIMATE SVOC CONCENTRATIONS IN INDOOR AIR

Exposure screening methods should be amenable to rapid implementation for large sets of chemicals. The steady-state models that we propose capture the essential mechanisms driving exposures to SVOCs^{6,13} emitted from products in the indoor environment stressing the relationship between individual sources and potential human intake.

Estimating Gas-Phase Concentration of SVOCs Emitted from Products in which they are Present as Additives. The proposed approach considers the mechanisms governing emissions from a solid material in a room, as illustrated in Figure 1.¹³ Model variables are defined as follows: V is the room volume, A is the surface area of the source, Q is the ventilation rate, and y is the bulk gas-phase concentration of the SVOC. The SVOC in the source, at a material-phase concentration of C_0 , is assumed to be in equilibrium with the SVOC in the air in contact with the source, which has a gas-phase concentration of y_0 . Many SVOCs partition strongly to interior surfaces, and the sorbed SVOC concentration, q_s , on the interior surface, A_s , is assumed to be in equilibrium with y_s , the gas-phase SVOC concentration in the air in contact with the surface. A boundary layer exists between the source and the bulk air in the room, with a mass transfer coefficient, h , and between the bulk air and the interior surface, with a mass transfer coefficient, h_s . The mass concentration of suspended particles in the room is denoted TSP , and a partition coefficient, K_p , describes the equilibrium partitioning of the SVOC between the gas phase and the suspended particles. The dynamic model based on these simple mechanisms is described in more detail in the Supporting Information, and we note that kinetics is included for emissions from and sorption to large-scale interior surfaces but that equilibrium is assumed during interaction with very small suspended particles.⁶

For most SVOCs present as additives (for example, di(2-ethylhexyl) phthalate (DEHP) or di-n-butyl phthalate (DnBP) present as plasticizers in vinyl flooring or 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) present as a flame retardant in polyurethane foam), the depletion of the source can be assumed to occur so slowly that C_0 and hence y_0 are effectively constant. At steady-state, the amount emitted from the source must equal the amount removed from the room, or

$$h \times (y_0 - y) \times A = Q \times y + Q(K_p \times TSP \times y) \quad (1)$$

Solving for the gas phase SVOC concentration, y , yields this result

$$y = \frac{h \times y_0 \times A}{h \times A + Q^*} \quad (2)$$

where

$$Q^* = (1 + K_p \times TSP) \times Q \quad (3)$$

The parameter, Q^* , is an “equivalent” ventilation rate for SVOC removal that includes the species associated with suspended particles in the air. Equation 2 indicates that y is largely determined by y_0 , A , and other parameters that are relatively easy to estimate (h , Q , K_p , and TSP). For example, the convective mass transfer coefficient, h , can be estimated using correlations based on the near surface flow velocity³⁰ with typical values of h indoors available in the literature.^{31,32}

Estimating Gas-Phase Concentration of SVOCs Emitted from Products that are either Sprayed or Applied. A variant of the preceding model is used to estimate the steady state, gas-phase concentration of SVOCs arising from products that are directly sprayed or applied to interior surfaces (for example, an insecticide containing diazinon) or introduced as a powder (for example, chlorpyrifos used as a pesticide). Emissions from such sources can be divided into two stages. First, SVOCs are emitted from the original applied source into air and sorb onto interior surfaces. Then, after the original

applied source is depleted, SVOCs that are sorbed on indoor surfaces desorb, counteracting the decrease in gas-phase concentration.⁶ During the initial phase, a quasi-steady state condition can be obtained from a balance between the rates of emission from the source, sorption to interior surfaces, and removal from the room by ventilation of the SVOC in both the gas phase and associated with airborne particles

$$h \times (y_0 - y) \times A = h_s \times (y - y_s) \times A_s + Q \times y + Q \times (K_p \times TSP \times y) \quad (4)$$

Here y_0 is the gas-phase concentration in equilibrium with the original source. Assuming that y_s is small relative to y , the average gas-phase concentration during this initial phase is estimated as

$$y = \frac{h \times y_0 \times A}{h \times A + h_s \times A_s + Q^*} \quad (5)$$

During the second phase, the surfaces become secondary sources and SVOCs desorb, compensating for the loss due to ventilation. Here we simply assume that y remains approximately constant throughout a depletion period owing to the substantial contributions from desorption. If the only loss of SVOCs from the indoor environment is via ventilation, then the time for the depletion period is estimated on the basis of mass conservation

$$\tau \sim \frac{M_0}{y \times Q^*} = \frac{(h \times A + h_s \times A_s + Q^*) \times M_0}{h \times y_0 \times A \times Q^*} \quad (6)$$

where M_0 is the initial SVOC mass applied. In this case, the indoor concentration, y , and the persistence duration, τ , are largely determined by y_0 , A , and other parameters that are relatively easy to estimate (h , h_s , A_s , Q , K_p , TSP , and M_0).

To illustrate the approach for SVOCs in products that are either sprayed or applied, we use experimental data from US EPA's Indoor Air Quality Test House case study of chlorpyrifos, a pesticide which was used extensively indoors but is no longer registered for residential application.¹⁴ For present purposes, we consider the house to behave like a single well-mixed volume with input parameters reported in Table S.4. Equations 5 and 6 yield an average gas-phase concentration of $0.5 \mu\text{g}/\text{m}^3$ and a persistence duration of about 200 days. These estimates are consistent in magnitude with measurement results in the EPA test house following application of the pesticide. The observed concentration in the treated region was as high as $0.5\text{--}1 \mu\text{g}/\text{m}^3$ in the first few days after application and then decreased to about $0.1\text{--}0.2 \mu\text{g}/\text{m}^3$, persisting for a few months.¹⁴

■ RAPID METHODS TO ESTIMATE EXPOSURE

To estimate the indoor gas-phase concentration resulting from emissions of SVOCs that are present in materials and products as additives, the primary parameters required are y_0 and A . Other necessary parameters are h , Q , K_p , and TSP . To estimate the indoor gas-phase concentration resulting from emissions of SVOCs present in products that are sprayed or applied, the primary parameters required are also y_0 and A . Other necessary parameters are h , h_s , A_s , Q , K_p , and TSP . SVOC persistence is also determined by M_0 , which can generally be estimated from information on product composition or obtained by direct chemical analysis of the product. Because A is almost always

Table 1. Relationships Used to Estimate Exposure to SVOCs in Indoor Environments^a

parameter (units)	equation
particle/air partition coefficient (K_p) ($\text{m}^3/\mu\text{g}$) ⁵	$K_p = f_{\text{om_part}} \times K_{\text{oa}}/\rho_{\text{part}}$
dust/air partition coefficient (K_{dust}) (m^3/mg) ⁵	$K_{\text{dust}} = f_{\text{om_dust}} \times K_{\text{oa}}/\rho_{\text{dust}}$
permeability through stratum corneum of an SVOC when its concentration is measured in water in contact with skin (k_{p_cw}) (cm/s) ³⁸	$\log(k_{p_cw}) = 0.7 \log(K_{\text{ow}}) - 0.0722 \text{ MW}^{2/3} - 5.252$
ratio of stratum corneum permeability to viable epidermis permeability (B) (-) ³⁸	$B = [k_{p_cw} \times (\text{MW})^{0.5}]/2.6$
permeability through stratum corneum/viable epidermis composite of SVOC when its concentration is measured in water in contact with skin (k_{p_w}) (cm/s) ³⁸	$k_{p_w} = k_{p_cw}/(1+B)$
permeability from the boundary layer at the skin surface through the stratum corneum/viable epidermis composite to dermal capillaries (k_{p_b}) (cm/s) ³⁸	$k_{p_b} = k_{p_w} \times K_{\text{wa}}$
overall permeability from bulk air to dermal capillaries (k_{p_g}) (m/d) ³⁸	$k_{p_g} = [(1/\nu_d) + (1/k_{p_b})]^{-1} \times 864$

^aMW is the molecular weight in g/mol units; $f_{\text{om_part}}$ and $f_{\text{om_dust}}$ are volume fraction of organic matter associated with airborne particles and settled dust and estimated to be 0.4 and 0.2, respectively; ρ_{part} and ρ_{dust} are density of airborne particles ($1 \times 10^{12} \mu\text{g}/\text{m}^3$) and settled dust ($2 \times 10^9 \text{ mg}/\text{m}^3$), respectively. k_{p_cw} is expressed in units of cm/h. Units of k_{p_g} are converted from cm/s to m/day by multiplying by 864, while ν_d is the mass-transfer coefficient between the bulk air and the skin surface, with an assumed value of 0.167 cm/s.³⁸

known or readily estimated, only y_0 remains as the primary parameter necessary to estimate SVOC emissions into air.

In some cases, y_0 may be approximated by the vapor pressure of the pure liquid or solid. For example, DEHP plasticizer present in vinyl flooring at a concentration of ~15% by mass tends to behave as a thermodynamically separate liquid phase with a y_0 value that is equal to the vapor pressure.^{33,34} Indeed, it has been suggested that the DEHP in plasticized PVC products spreads out in a very thin liquid layer on the exterior surface of the PVC.³⁵ For chlorpyrifos, which is a pure solid, y_0 is also given by the vapor pressure.

Unfortunately, y_0 is not well approximated by vapor pressure in all cases. Here we briefly consider two examples, which are described in more detail in the Supporting Information. First, in contrast to DEHP, the content of DnBP plasticizer in polymer products is generally so low that it does not behave as a pure liquid. Consequently, y_0 for this compound may be much lower than its vapor pressure. Second, although BDE-47 may sometimes be present at high concentrations in polyurethane foam, it is a solid at room temperature. The material-phase concentration (C_0) of additives such as DnBP and BDE-47 in different products can vary substantially, and the dependence of y_0 on C_0 is presently unknown. Simple linear partitioning is generally only applicable at concentrations below 1% by mass, and Raoult's Law does not apply to polymer solutions owing to the extremely large size of polymer molecules compared to the size of the added SVOC molecules.^{36,37} Therefore, y_0 is not directly available for many SVOCs and the development of methods to measure or estimate y_0 for SVOCs in products used indoors is an area that requires further research.

Estimating Exposure to SVOCs Present in a Single Product. For prioritization purposes, a general estimate of total exposure potential is sufficient. However, the approach proposed here provides further insight into significant exposure pathways based on product characteristics. In addition to inhaling SVOCs in indoor air, exposure via inhalation of airborne particles,^{6,18,19} ingestion of dust,^{5,16,18,19} and dermal absorption^{6,18,19,38,39} may play significant roles, contributing to total human intake rates. For SVOCs present as additives, eq 2 can be used to estimate the gas-phase concentration, with emissions considered to persist for the entire time in which the source is present in the indoor environment. For SVOCs that are sprayed or applied, eq 5 can be used to estimate the gas-phase concentration, and concentrations are considered to persist for the period given by eq 6.

We next illustrate the approach for exposure analysis using three “additives” (DEHP, DnBP, and BDE-47) and one “sprayed or applied” SVOC (chlorpyrifos) as examples. The evidence base is strong for the y_0 values employed for analyzing DEHP and chlorpyrifos. Only crude approximations are possible for the values of y_0 for DnBP and BDE-47, with estimates for y_0 inferred from reported gas-phase concentrations, as described in the Supporting Information. With an estimate of the gas-phase concentration from eq 2 or 5, the particle-phase concentrations and dust-phase concentrations are estimated based on K_p and K_{dust} (i.e., the partition coefficients between particles and air and between dust and air, respectively). A recent study suggests that direct transport of SVOCs from bulk air through skin to dermal capillaries can sometimes be important and, if so, can be modeled considering three mass-transport resistances in series: the resistance from bulk air to air at the skin surface, the resistance through the stratum corneum, and the resistance through the viable epidermis. Therefore, dermal exposure from the gas phase is estimated using an “overall permeability”, k_{p_g} , based on permeabilities through the boundary layer adjacent to skin and through the stratum corneum/viable epidermis composite to dermal capillaries.³⁸ Values for K_p , K_{dust} , and k_{p_g} were obtained using the relationships listed in Table 1, with the required chemical properties for DEHP, DnBP, BDE-47, and chlorpyrifos reported in Tables S.1–S.4. We note here that the relationships that are used to estimate exposure are based on SVOC partition coefficients between octanol and air, K_{oa} , and between octanol and water, K_{ow} , parameters that are readily available or that can be easily estimated for many SVOCs.^{5,6} If both K_{oa} and K_{ow} are known, the water/air partition coefficient, K_{wa} , otherwise known as Henry's constant, is obtained as the ratio of the two. This information was then used to calculate exposure via inhalation, oral ingestion of dust, and dermal absorption from the gas phase for a 3-year old child, as summarized in Tables 2 and 3.

The primary difference between exposure to DEHP and exposure to DnBP (76 and 4.6 ($\mu\text{g}/\text{kg}$)/d, respectively; Table 3) is the volatility of the compounds, with DnBP having a vapor pressure that is 2 orders of magnitude higher than DEHP. The result is that for DEHP, 99% of the exposure occurs through ingestion of dust (due to its low volatility DEHP partitions strongly onto dust and airborne particles), while for DnBP, 55% of the exposure occurs via dermal absorption with 35% via ingestion of dust. In the case of BDE-47, the surface area of the source is somewhat lower (15 m^2), but y_0 (0.0005 $\mu\text{g}/\text{m}^3$) is

Table 2. Parameters Used to Estimate Exposure for a 3-Year Old Child and an Adult⁴⁵

parameter (units)	child	adult
inhalation rate (<i>InhR</i>) (m ³ /kg)/d	0.64	0.20
dust ingestion rate ^a (<i>IngR</i>) (mg/kg)/d	4.3	0.75
skin surface area (<i>SA</i>) (m ²)	0.61	2.1
fraction skin exposed (<i>f_{SA}</i>) (-)	1	1
exposure duration (<i>ED</i>) (-)	0.91	0.80
body weight (<i>BW</i>) (kg)	13.8	80.0

^aDust ingestion rates are uncertain, particularly for adults.

Table 3. Estimated Single Product Exposure ((μg/kg)/d) to DEHP, DnBP, BDE-47, and Chlorpyrifos via Indoor Air and Intake of Particles/Dust for a 3-Year Old Child^a

exposure pathway	DEHP	DnBP	BDE-47	chlorpyrifos	equation
inhalation (air)	0.013	0.34	1.4×10^{-4}	0.32	$y \times InhR \times ED$
inhalation (particles)	0.82	0.02	3.5×10^{-5}	0.01	$y \times K_p \times TSP \times InhR \times ED$
ingestion (dust)	75	1.6	3.2×10^{-3}	0.59	$y \times K_{dust} \times IngR$
dermal absorption (from air)	0.12	2.7	1.0×10^{-5}	0.23	$(y \times k_{p-g} \times SA \times f_{SA} \times ED)/BW$
total ^b	76	4.6	3.5×10^{-3}	1.15	

^aDEHP, DnBP, and BDE-47 exposure persists for as long as the source material is present in the house. Chlorpyrifos exposure persists for ~200 days after application. ^bTotals rounded.

considerably lower than for either DEHP or DnBP. The lower y_0 explains the substantially lower exposure (0.0035 (μg/kg)/d), but the fact that the volatility of BDE-47 is relatively low (falling between DEHP and DnBP) explains why 90% of the exposure occurs through ingestion of dust. For chlorpyrifos, the high y_0 (350 μg/m³) means it is a much stronger source than the others, but the source area is far smaller (0.75 m²). The two effects tend to compensate, with an overall exposure of 1.15 (μg/kg)/d, which is distributed almost equally among inhalation (23%), ingestion of dust (44%), and dermal absorption (31%).

It has been demonstrated that a compound's octanol-air partition coefficient (K_{oa}) is a strong predictor of its abundance in settled dust,⁵ in skin oils on hands,^{6,18,38} and on indoor surfaces.³⁸ However, for SVOCs with high K_{oa} values, the equilibration time scales for sorptive partitioning may be long. As a consequence, exposure via ingestion of dust or direct air-to-skin transfer may be overestimated in the preceding examples for the lower volatility SVOCs such as DEHP and BDE-47. For air/dust partitioning, the limitation may become important for SVOCs with log K_{oa} larger than approximately 8 to 9.^{5,6} Regular cleaning to remove dust may also decrease the opportunity for the dust to reach equilibrium with the lower volatility SVOCs.

Estimating Exposure to SVOCs Present in a Range of Similar Products. In contrast to the idealized illustrative examples for DEHP, DnBP, and BDE-47, there is usually a range of products containing SVOCs in a single indoor environment. As discussed above, y_0 for the additives DnBP and BDE-47 may depend on their content in different polymer products, which can vary greatly. However, evidence indicates that DEHP behaves as a pure liquid in polymer products, and

so y_0 is expected to be essentially constant. One can predict the typical indoor air concentration of DEHP emitted from different polymer products using eq 2 if the exposed surface area of those products is known. Following a recent technical report,⁴⁰ products containing DEHP can be categorized into eight groups with the amount of DEHP used in each group reported for the European Union (EU) (see Table S.5). If one assumes steady state over an entire economy, then the annual production of all plasticized products should equal the annual demand, which should also equal the annual disposal rate of the products. But if we consider a new house that is initially devoid of plasticized products, then the initial demand would be much higher than the initial disposal rate, with plasticized products "accumulating" indoors for the lifetime of the product. With this build up taken into account, one can estimate the mass of plasticized products in an average household. We use this approach to estimate the surface area of plasticized products from which we can estimate emissions and potential exposure concentrations.

Based on this approach, we estimated the average per-capita surface area of each end-product group used indoors in the EU. For example, the amount of DEHP used in flooring is about 30,200 t/y (Table S.5) or 600,000 t during the in-service life of 20 y (multiplying the amount used annually by the in-service life accounts for the accumulation of products to give the average amount present indoors). With an average DEHP content in flooring of 20% w/w, the corresponding mass of flooring produced (which contains the 600,000 t of DEHP) is 3,000,000 t. Assuming that the economy-wide use of DEHP-plasticized flooring is at steady state, and that old flooring is replaced by new flooring at the end of its in-service life, the total amount of flooring in use is also 3,000,000 t, or 6000 g/person (for the EU population of 500 million). Considering an average mass per unit floor area of 2.9 kg/m²,⁴⁰ the surface area of flooring in use is 2.1 m²/person. The surface area of other DEHP-plasticized polymer products is calculated similarly, as shown in Table S.5. Because y_0 for all products is assumed to be the same, the area of all products can be summed to yield a total surface area of 52 m² per person for DEHP-plasticized polymer products. To further calculate the gas-phase concentration of DEHP emitted from these products in a typical indoor environment, it is assumed that 1) the product use data per capita for the EU is also applicable to the US and that 2) all the products are used in residences. Therefore, in an average representative household, with parameters summarized in Table S.6, the gas-phase concentration of DEHP is estimated to be 0.02 μg/m³. This value is reasonably consistent with measured indoor air concentrations reported in the literature,¹⁹ although we note that the use pattern for DEHP is likely to represent the historical situation in Europe because DEHP has been classified as a substance of very high concern and is likely to be phased out. Finally, using our procedure for predicting exposure to SVOCs present as additives, exposure is estimated for both child and adult, with results summarized in Table 4.

We caution that the exposure estimates shown in Table 4 are likely high for three reasons. First, we assumed that all the products are used indoors, and this overestimates the emission surface area. For example, the majority of wires and cables are probably used in the computing and telecommunications industries instead of in residential environments. Second, not all the surface area associated with each product will be in relatively open contact with the indoor air. For example, plasticized sheeting may be folded. Last, and as already

Table 4. Estimated Exposure ($\mu\text{g}/\text{kg}/\text{d}$) to DEHP via Indoor Air and Intake of Particles/Dust in a Typical Household for a Range of Similar Products

	inhalation (air)	inhalation (particles)	ingestion (dust)	dermal absorption (from air)	total
3-year old child	0.01	0.76	70	0.11	71
adult	0.003	0.21	12	0.06	12

mentioned, exposure via ingestion of dust or direct air-to-skin transfer may be overestimated for the lower volatility SVOCs such as DEHP. Nevertheless, we can compare this economy-wide estimate of exposure to values obtained elsewhere. For example, based on an analysis of biomonitoring data, the average total intake of DEHP from all sources was estimated in the US to be $\sim 550 \mu\text{g}/\text{d}$ per person.⁴¹ Another recent study,⁴² also based on urinary excretion of phthalate metabolites, estimated the total daily intake of DEHP in Danish children and adolescents (with ages ranging from 6 to 21 years) at a median of $4 (\mu\text{g}/\text{kg})/\text{d}$ and a maximum of $53 (\mu\text{g}/\text{kg})/\text{d}$. The values shown in Table 4 are equivalent to $71 (\mu\text{g}/\text{kg})/\text{d}$ for a 3-year old child (a total of $980 \mu\text{g}/\text{d}$) and $12 (\mu\text{g}/\text{kg})/\text{d}$ for an adult (a total of $960 \mu\text{g}/\text{d}$). Although the values shown in Table 4 are expected to be high for the indoor exposure pathways assessed, they do not include exposure to food, which is known to be a dominant source of DEHP exposure.^{21,22} The results are nevertheless reassuringly similar to those reported in the other two studies, suggesting that the proposed method can be useful for exposure screening.

Estimating Exposure to SVOCs Proposed as Substitutes in Specific Products. The estimation procedures outlined in the previous sections provide the scientific underpinning for developing a minimal data set required to characterize the potential for humans to be exposed to a given SVOC from product use indoors. Table 5 summarizes the

Table 5. Summary of the Model Parameters Required to Estimate Exposure to SVOCs that are either Present as Additives (ADD) in Products Used Indoors or as Ingredients in Products Directly Applied (DA) to Interior Surfaces

parameters	cases	determination
ventilation rate (Q)	ADD, DA	estimated from room volume and air exchange rate
convective mass-transfer coefficient from emission surface (h)	ADD, DA	estimated by correlation ³⁰
emission surface area (A)	ADD, DA	measured or estimated from use data
gas-phase concentration in contact with the emission surface (y_0)	ADD, DA	may not be available, research need
total suspended particle concentration (TSP)	ADD, DA	measured or estimated ¹⁶
airborne particle/air partition coefficient (K_p)	ADD, DA	estimated (Table 1)
convective mass-transfer coefficient to sorption surface (h_s)	DA	estimated by correlation ³⁰
sorption surface area (A_s)	DA	measured or estimated
initial applied amount (M_0)	DA	measured or estimated
dust/air partition coefficient (K_{dust})	ADD, DA	estimated (Table 1)
overall permeability (k_{p-g})	ADD, DA	estimated (Table 1)

model parameters required to estimate exposure to SVOCs that are either present as additives in products used indoors or as ingredients in products directly applied to interior surfaces – the two dominant contributors for a broad spectrum of manufactured SVOCs found indoors. As shown in Table 5 and Table 1, and with the possible exception of y_0 , exposure to SVOCs can be predicted based on a readily available set of parameters.

The approaches summarized in this paper can be used to gain powerful insights. For example, if a specific SVOC in a material or product is identified as being of high risk, manufacturers might consider replacing the compound with a substitute SVOC. If exposure to the high-risk SVOC is known, or can be estimated using the proposed techniques, then an estimate of the unknown exposure for a substitute SVOC can be estimated. If y_0 is not known, one can assume that y_0 for the high risk SVOC and for its proposed substitute are directly related through their respective vapor pressures, which we believe to be a reasonable approximation. One can then evaluate the ratio of the “unknown” exposure to the “known” exposure for the three indoor exposure pathways: inhalation (of gaseous plus particulate SVOC), ingestion of dustborne SVOC, and dermal absorption from the gas phase. One can do this for either class of SVOCs, i.e., those that are present as additives and those that are directly sprayed or applied to interior surfaces. In the case of SVOCs present as additives, one can simplify the estimation procedure if both SVOCs of interest have a $\log(K_{oa})$ that is less than 9.8, which implies that $Q^* \sim Q$ because sorption to particles is relatively small (see eqs 2 and 3). In this limiting case, the ratio of unknown exposure to known exposure equals $(VP_{unknown}/VP_{known})$ for inhalation, $[(VP_{unknown} \times K_{oa_unknown})/(VP_{known} \times K_{oa_known})]$ for inhalation of particles and ingestion of dust, and $[(VP_{unknown} \times k_{p-g_unknown})/(VP_{known} \times k_{p-g_known})]$ for dermal absorption (see the Supporting Information for derivation of these ratios). Using the properties for DnBP and a hypothetical substitute SVOC shown in Table 6, one can estimate the change in

Table 6. Relevant Properties for DnBP and a Hypothetical Substitute Compound

physical-chemical property	DnBP	substitute
MW (g/mol)	278	260
Log VP (atm, 25 °C)	−8.5	−7.5
Log K_{oa} (−, 25 °C)	9.8	8.8
Log K_{ow} (−, 32 °C)	4.6	3.6
Log K_{wa} (−, 32 °C)	5.0	5.1
k_{p-g} (m/h, 32 °C)	4.8	3.9

exposure that would be experienced by a 3-year old child if such a substitution were made. With all else being equal, and with reference to Table 3, inhalation exposure increases from $0.34 (\mu\text{g}/\text{kg})/\text{d}$ for DnBP to $3.4 (\mu\text{g}/\text{kg})/\text{d}$ for the substitute, while dermal absorption increases from $2.7 (\mu\text{g}/\text{kg})/\text{d}$ for DnBP to $22 (\mu\text{g}/\text{kg})/\text{d}$ for the substitute. Exposure remains the same for the inhalation of particles and the ingestion of dust because the decrease in K_{oa} by a factor of 10 causes a decrease in both K_p and K_{dust} by a factor of 10, while the increase in VP by a factor of 10 causes an increase in the gas-phase concentration by a factor of 10, with the two effects canceling each other. Overall exposure is $27 (\mu\text{g}/\text{kg})/\text{d}$ for the substitute compared to $4.7 (\mu\text{g}/\text{kg})/\text{d}$ for DnBP, with much of the increase attributable to the higher rate of dermal absorption.

Outlook for Estimating Exposure to SVOCs in Products. We envision the approaches outlined here to constitute the kernels of a screening tool that comprises a suite of simple models, each of which incorporates essential aspects of human exposures to SVOCs. Such relatively simple, yet mechanistically sound exposure models can be applied to glean valuable insights concerning exposures to SVOCs that are either present as additives in materials used indoors or as ingredients in products applied to interior surfaces. Further development of a general set of models for the entire range of products containing SVOCs, together with appropriate methods for estimating or measuring the key parameters (in particular, methods to measure or estimate y_0), will facilitate chemical prioritization. In addition, we limited our assessment to exposure via inhalation of SVOCs in the gas-phase, exposure via inhalation of SVOCs sorbed to airborne particles, exposure via ingestion of SVOCs sorbed to dust, and exposure via dermal sorption of SVOCs from the air into the blood. Other exposure pathways including SVOCs in food, dermal sorption of SVOCs in dust, accidental ingestion of SVOCs in personal-care products, SVOCs transferred directly from skin to mouth, and exposure resulting from the friability of products, which might be most important for the extremely low volatility compounds, should be included in the suite of models.

When combined with rapid estimates of hazard potential, methods for obtaining screening-level estimates of human SVOC exposure potential could contribute to risk-based prioritization of a wide range of chemicals of concern. The chemical/product combinations of greatest concern can then be more comprehensively investigated.^{43,44} Because our understanding of the vast number of products remains rudimentary, it is clear that an iterative approach will be required. As the mechanisms and pathways controlling the source-to-dose continuum are more clearly elucidated, improved methods to obtain rapid screening-level exposure estimates should emerge.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The views expressed in this article are those of the authors and do not necessarily reflect the views or policies of the U.S. EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The authors declare no competing financial interest.

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