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Estimation of the Emission Characteristics of SVOCs from Household Articles Using Group Contribution Methods

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Abstract

The risk to humans from chemicals in consumer products is a function of both hazard and exposure. There is an ongoing effort to quantify chemical exposure due to household articles such as furniture and building materials. Polymers and plastic materials make up a substantial portion of these articles, which may contain chemical additives such as plasticizers. When these additives are not bound to the polymer matrix, they are free to diffuse throughout it and leach or emit from the surface. We have implemented a methodology to predict plasticizer emission from polyvinyl chloride (PVC) products, based on group contribution methods that consider a free volume effect to estimate activity coefficients for chemicals in polymer-solvent solutions. Using the estimated activity coefficients, we calculate steady-state gas phase concentrations for plasticizers in equilibrium with the polymer surface (y_0). The method uses only the structure of the chemical and polymer, the weight fraction, and physical-chemical properties, allowing rapid estimation of y_0 at different weight fractions in PVC. Using the predicted y_0 values and weight fraction data gleaned from public databases, we estimate plasticizer exposures associated with 72 PVC-containing articles using a high-throughput model. We also investigate potential exposures associated with plasticizer substitutions in these products.

Graphical Abstract

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SUPPORTING INFORMATION AVAILABLE

This information is available free of charge via the Internet at <http://pubs.acs.org>.

Supplemental File: Supplement_UNIFACFV.zip. Python code and input data to reproduce activity coefficients as a function of weight fraction for all plasticizers modeled here.

Keywords

plasticizers; phthalates; SVOCs; chemical emission; human exposure modeling; building materials; ExpoCast; exposure assessment

INTRODUCTION

The risks posed to humans due to chemicals are a function of both hazard and exposure. Emission of chemicals from indoor, or “near-field”, sources such as building materials and household articles contribute significantly to exposure. In the U.S., 70% of the average person’s time is spent indoors¹, where outgassed chemicals can accumulate in air and adsorb onto surfaces.^{2, 3} Semivolatile organic compounds (SVOCs) found in near-field sources are of particular concern; due to their high molecular weights and low vapor pressures they are released slowly from materials and can emit from a source for long periods of time without exhaustion. SVOCs that have been measured in indoor air and dust include plasticizers (e.g., phthalates) and flame retardants (e.g., polybrominated diphenyl ethers), among others.⁴ Despite their ubiquity, the actual concentration of SVOCs in consumer articles and building materials is often unknown, since ingredient lists or safety data sheets (SDS) are not required for these products. Recently, voluntary reporting programs for building materials^{5, 6} have provided some quantitative information on SVOC content. However, lack of knowledge of emission processes and mass transfer parameters can impede characterization of SVOC sources and associated exposures even when concentration is known.

Included among SVOCs are phthalate ester plasticizers, which are ubiquitous in the built environment.⁷ Biomonitoring data from the National Health and Nutrition Examination Survey (NHANES) show that people in the United States display biomarkers of exposure to multiple phthalates; for example, 5 different phthalate metabolites measured in NHANES were detected in women of child-bearing age at frequencies greater than 96% in multiple years between 1999-2014.^{8, 9} High molecular weight phthalates are used as plasticizers in food packaging and building materials like vinyl flooring.¹⁰ The archetypal high molecular weight phthalate is diethylhexyl phthalate (DEHP), which is a commonly-used phthalate plasticizer with a high U.S. production volume. The emission^{7, 11-15} and toxicology¹⁶ of DEHP have been well-studied, and it has been found in surveys of urine¹⁷ and breastmilk¹⁸. However, other phthalates having similar uses (and thus exposure pathways) have not been

as extensively characterized. In addition, the last decade has seen the development of phthalate alternatives that have lower toxicity or persistence.¹⁹ However, few studies assessing of the emission of alternative plasticizers exist.²⁰

When the internal diffusion of chemical within a material is not a driving force for emission (as has been shown to be true for plasticizers such as DEHP)²¹, the prediction of emission of a chemical from a material is governed by a single characteristic parameter y_0 , the chemical concentration in the air adjacent to, and in equilibrium with, the material surface. This quantity is usually measured during lengthy emission experiments and is specific to the material-chemical pair as well as chemical concentration, humidity, and temperature. The variation of y_0 with these parameters depends on the nature of the polymer-chemical mixture, for example whether the chemical is bound to the polymer matrix. Plasticizers are not bound and thus a polymer-plasticizer mixture can be approximated as a solution. The simplest approximation that y_0 is equal to the vapor pressure (VP) of the pure chemical is likely to be incorrect in many cases.^{13, 22-26} Recently, Eichler et al.²³ proposed a framework for determining y_0 based on characterizing the partitioning between polymer-plasticizer mixtures and air using Henry's law, a model of solution behavior that assumes a constant extrapolated activity coefficient, which accounts for the nonideal nature of the mixture. In that work, the investigators estimated activity coefficients for two plasticizers and a group coefficient applicable to multiple chemicals from available experimental data. Here, we propose using available models to predict activity coefficient values for plasticizers in polymers for use in estimating y_0 for use in screening level exposure assessments.

Group contribution Quantitative Structure Activity Relationship (QSAR) methods can be applied to estimate activity coefficients in chemical mixtures. Group contribution methods are based on the approximation that molecular interactions can be suitably substituted by the interactions between the functional groups constituting those molecules. The numerous possible overall molecule-molecule combinations are then reduced to a much smaller number of group-group interactions. Since functional groups and not whole molecules are the objects of the theory, no experimental data except for tabulated group parameters (for example, group surface areas or volumes or between-group interaction energies) are necessary inputs to the calculation. If all of its constituent groups are accounted for, in theory any molecule can be represented. These methods are suited to high-throughput applications, where many chemicals must be evaluated with or without experimental exposure data. Group contribution methods have been used to model activity coefficients in plasticizer-solid polymer mixtures^{27, 28}, but they have not been applied for the purpose of characterizing emission.

Here, existing group contribution models are applied to estimate activity coefficients and resulting y_0 values for plasticizers. These methods are then evaluated with existing y_0 data from the literature. Estimated y_0 values from the model with the best performance are used in tandem with an existing screening-level human exposure model to estimate exposures to plasticizers contained in 72 polyvinyl chloride (PVC)-containing building products characterized in a recent voluntary manufacturer reporting program. Additionally, the y_0 predictions are used to both evaluate exposures to plasticizer substitutions in products and to investigate the impact of chemical properties and predicted activity coefficients on exposure.

METHODS

Modeling Activity Coefficients and Steady-State Gas Phase Concentrations

From the thermodynamics of vapor-liquid equilibrium, y_0 for component 1 (e.g., a plasticizer) in a binary mixture with component 2 is given by²⁹

$$y_0 = x_1 \gamma_1 VP_1 \quad (1)$$

where x_1 is the mole fraction of chemical in the mixture, γ_1 is the activity coefficient, and VP_1 is the vapor pressure of pure component 1. The estimation of y_0 then turns into an estimation of γ_1 , if the mole fraction (which can be calculated from weight fraction) and vapor pressure of chemical are known or can be reasonably estimated (e.g., using existing models). This equation can also be formulated in terms of weight fraction WF_1 rather than mole fraction, where γ_1 is replaced by $\hat{\gamma}_1 = \gamma_1 \left(\frac{MW_1}{MW_2} \right)$ where the MW terms are the molecular weights of the two components. The product of x_1 and γ_1 (or WF_1 and $\hat{\gamma}_1$) is the chemical activity, a_1 .

Calculating activity coefficients for phase equilibria is common practice in chemical engineering thermodynamics.³⁰ The introduction of a polymeric component, however, complicates matters since polymers behave differently than normal-sized molecules; various models have been developed to estimate activity coefficients for these non-ideal systems.²⁹ In general, the models consist of terms describing molecular interactions due (1) solely to differences in their size and shape (an entropic or combinatorial term) and (2) to intermolecular forces (an enthalpic or residual term). The first successful attempt at solving this problem is accredited to Flory³¹ and Huggins³² and is therefore known as the Flory-Huggins (FH) equation, which uses statistical lattice theory to estimate the combinatorial term. The Universal Quasichemical (UNIQUAC) model³³ augmented the FH combinatorial term with a correction factor (called the Guggenheim-Staverman correction) and added a residual term quantifying the interaction energies between molecules. The UNIFAC (UNIQUAC Functional-group Activity Coefficients) model³⁴ is an implementation of UNIQUAC that expresses this residual component in terms of interactions between individual functional groups instead of whole molecules, allowing for its empirical calculation for any known molecule based on the sum of interactions among the groups (known as a “solution of groups” approach. Here, we implement and assess two modifications of the UNIFAC model (UNIFAC-FV³⁵ and Entropic-FV^{36,37}) that adjust or replace the UNIFAC combinatorial term to correct for “free-volume” (FV) effects. This correction accounts for additional volume in the matrix due to gaps in entangled polymer chains. The equations for the UNIFAC-FV and Entropic-FV models are given in the Supplemental Information (SI).

Implementation of the Group Contribution Methods for PVC-Plasticizer Systems

The UNIFAC-FV (Equations S1-S8) and Entropic-FV methods (Equations S9-S11) were implemented in custom Python codes. The inputs to the code are the UNIFAC functional group assignments for the plasticizers and for PVC, the UNIFAC functional group parameter values (volume Q , surface area R , and energy interactions A), weight fraction (WF),

polymer and chemical densities (ρ), and temperature, which was assumed equal to 298 K. Assignment of functional groups in a structure to UNIFAC groups for the chemicals modeled herein were obtained from the online group assignment database provided by the Dortmund Data Bank (DDB)³⁸; the published values of the UNIFAC R, Q, and A parameters for all groups were also obtained from the DDB website³⁹ and given in the SI in Table S1. The implementation of the base UNIFAC model was verified against predictions for select binary systems provided by interactive tools at the DDB website; the implementation of the UNIFAC-FV and Entropic-FV models were verified against examples provided in their respective publications. The codes were structured to return predicted γ , $\hat{\gamma}$ (WF-based activity coefficient) and activity (a).

Evaluation of UNIFAC Activity Coefficient Predictions

We evaluated the ability of the base UNIFAC group contribution models to accurately estimate activity coefficients for chemicals via a modeling exercise that compared UNIFAC-based octanol-water partition coefficient (K_{ow}) estimates with those predicted by an independent QSAR model. In terms of the activity coefficient of a chemical in water and octanol⁴⁰, the octanol-water partition coefficient is given by

$$K_{ow} = \frac{MW_w \gamma_w \rho_o}{MW_o \gamma_o \rho_w} \quad (2)$$

where the subscripts w and o represent the water and octanol phases, respectively. In general, the activity coefficient and thus the resulting partition coefficient will be a function of chemical concentration, so we removed this variable by approximating the infinite dilution activity coefficient by calculating γ at very small chemical concentrations ($x = 10^{-10}$). The K_{ow} predictions were compared to K_{ow} values estimated by EPA's OPERA (OPEn saR App) QSAR models and obtained via the EPA CompTox Chemicals Dashboard⁴¹ (<https://comptox.epa.gov/dashboard>).

Estimation and Evaluation of Activity Coefficients for Plasticizers in PVC

The UNIFAC-FV and Entropic-FV models were used to estimate activity coefficients for Di(2-ethylhexyl) phthalate (DEHP) and Bis(2-ethylhexyl) terephthalate (DEHT), the two plasticizers that have been studied broadly over different WF values. These predictions were compared with compiled chemical emission data from an array of published emission chamber studies of these chemicals in a variety of products containing PVC^{12-14, 23, 26, 42-47} (SI Table S2). These data were converted into experimental activity coefficients via Equation 2 using the reported WF, reported measured y_0 , and measured values of VP²³. The model was run using a Monte Carlo algorithm to select values for the input weight fraction and density from a uniform distribution; this allowed for variation in these model inputs. It has been shown that the two models are not very sensitive to the molecular weight of PVC, so it was set as a constant value of 48000 g/mol⁴⁸. However, the models (especially UNIFAC-FV) are sensitive to polymer density, so a uniform distribution spanning experimentally measured and calculated values for PVC (1.37-1.4 g/cm³)⁴⁹ was used. It was often not clear from the published studies if the reported WF was the WF of the plasticizer in the product or in the PVC fraction of the product, so the combined WF of PVC/plasticizer in the product was set

as a uniform distribution 0.7-1.0 (to account for other components in the product). The model was then run using 1000 iterations.

The UNIFAC-FV model (which performed best compared to experimental data as described in the results) was then used to estimate activity coefficients and steady-state gas phase concentrations (y_0) for 30 phthalates and phthalate alternatives (Table 1) as a function of WF in PVC. The list was compiled from published lists from the literature and elsewhere; all chemicals had structural information available via the CompTox Chemicals Dashboard. Chemical densities (required to estimate mole fractions for use in the FV terms of the models) and VP values (required to calculate y_0) were obtained from EPA's Toxicity Estimation Software Tool (TEST)⁵⁰ and OPERA models, respectively (all available via the Dashboard). UNIFAC group assignments for the plasticizers, molecular weights, and densities are provided in the SI in Table S3. Predictions for y_0 were generated for plasticizer weight fractions ranging from 0 to 0.5. Python code for estimating activity coefficients for all the plasticizers modeled here is provided in the Supplemental Information.

High-Throughput Exposure Modeling for Phthalates in Building Materials and Household Articles

We gathered plasticizer and PVC composition data for 72 PVC-containing items in 5 different product categories (resilient flooring, wallcovering, carpet, cabling, and window shades) from publicly available Health Product Declarations (HPDs).⁶ HPD is a voluntary reporting standard for products used in the built environment developed and maintained by a non-profit collaborative of manufacturer and stakeholder members⁶. Chemical names, Chemical Abstract Service Registry Numbers (CASRN) and weight fractions were extracted from the HPDs. We checked the validity of each CASRN via checksum and ensured that chemical weight fractions were plausible ($0 < WF < 1$). To eliminate cases where PVC was a minor component or where it was likely (judging by the WFs) that the plasticizer was not a component within the PVC, only materials that were at least 20% PVC by weight, and products in which the reported plasticizer WF was less than 60% of the reported PVC weight fraction were modeled. We assumed that all reported plasticizer mass was used within the PVC in the product. Ten unique plasticizers were identified in these products. We estimated the WF of the plasticizer in the PVC as the ratio of the product plasticizer midrange WF to the product PVC midrange WF. WF data for all products are given in SI Table S4. The UNFAC-FV model was used to predict the $\hat{\gamma}$, a , and y_0 values associated with the plasticizers each product.

The estimated y_0 values were then used to estimate plasticizer exposures (intakes in $\mu\text{g/kg}$ body weight-day) associated with each product for adults and children using the high-throughput model of Little et al.⁵¹ This simple model takes as input y_0 , chemical properties (VP, K_{ow} , and octanol-air partition coefficient K_{oa}), reasonable estimates of housing parameters (including interior volume, surface area, and air exchange rate), and emission areas. The model yields exposure estimates from four different routes: direct air inhalation, particle inhalation, dust ingestion, and air-to-dermal absorption. The model equations were implemented in a custom R script. For each product modeled, y_0 was estimated via Equation 2 using VP, WF, and median $\hat{\gamma}$ predictions from the UNIFAC-FV model. Emission areas

were assumed for each type of product (SI Table S5); all other model input values were as reported in Little et al. All inputs for the exposure model are provided in SI Table S4.

The analyses described above (estimation of $\hat{\gamma}$, activity, and y_0 using the UNIFAC-FV model, and exposures for the products) were then repeated for each plasticizer that could be modeled (Table 1). This produced exposure estimates associated with 29 potential substitute plasticizers for each product. The WF of plasticizer in each product was assumed to be the same as the original plasticizer.

RESULTS AND DISCUSSION

Group-Contribution Model Predictions for K_{ow}

As a test of the implementation of UNIFAC methods underlying the UNIFAC-FV and Entropic-FV models, octanol-water coefficients (K_{ow}) were estimated for 466 SVOC chemicals, including all the plasticizers modeled in this study. Figure 1 shows the UNIFAC predictions plotted versus the OPERA QSAR values, which were predicted using machine-learning models built with experimental training sets. The agreement between the log of the partition coefficients obtained using the UNIFAC method and OPERA was reasonable ($R^2=0.73$, $p<0.0001$) given that both are predicted values. The agreement for the plasticizers studied here was even higher ($R^2=0.94$, $p<0.0001$). A comparison was also performed directly using measured $\log(K_{ow})$ values that underlie the OPERA model (Supplemental Figure S1.) Fewer chemicals could be compared, but the correlations for all SVOCs ($R^2=0.66$, $N=290$) and plasticizers ($R^2=0.86$, $N=13$) were comparable; the UNIFAC predictions for higher- K_{ow} chemicals compared more favorably to the measured data than to the OPERA predictions. Testing the UNIFAC methodology on available partition coefficient data demonstrates a reasonable estimation of activity coefficients in water and octanol by the UNIFAC, especially for plasticizers used in PVC.

Group-Contribution Model Predictions for Activity Coefficients

Figure 2 shows the weight-fraction-based activity coefficient, $\hat{\gamma}$, predicted by UNIFAC-FV and Entropic-FV for DEHP and DEHT versus experimental values calculated from compiled emission data from consumer articles and building materials. The predictions of UNIFAC-FV are qualitatively similar to the experimental data: they show a basic decreasing trend of $\hat{\gamma}$ with increasing weight fraction DEHP. Entropic-FV did not perform as well. The constant activity coefficient estimated by Eichler et al.²³ ($\hat{\gamma} = 5.12$) based on experimental data for DEHP and DEHT is also shown; the average value of the UNIFAC-FV model predictions over the range of WF values studied by Eichler et al. (WF= 0 - ~0.25) was in close agreement ($\hat{\gamma}=4.88$) with this experimentally estimated value. While the approximation that allows for a constant activity coefficient is valid, it does not capture the qualitative decreasing trend of $\hat{\gamma}$ with increasing WF. The assumption of constant activity coefficient also fails when the weight fraction tends to 1, since in the case of a pure component the activity coefficient approaches 1 as well. According to both models, decreasing the weight fraction of plasticizer increases the activity coefficient $\hat{\gamma}$. Despite this increase in $\hat{\gamma}$, both the product of weight fraction and $\hat{\gamma}$ (the activity, a) and y_0 still decrease with decreasing WF of DEHP.

The uncertainty associated with $\hat{\gamma}$ is illustrated in Figure 2, with the shaded area showing the 95%ile range of the Monte Carlo sampling. The uncertainty is associated with uncertainty in PVC density and in the actual WF of plasticizer in the PVC components of the studied products; the sensitivity of the models to density contributed most to the magnitude of the uncertainty. However, the experimental activity coefficients demonstrate even wider variability. This variability could be due to uncertainties in experimental measurements and corresponding y_0 estimation methods from chamber experiments, uncertainty in the characterization of WF in the products, or variation in activity coefficient from that predicted by the behavior of a binary solution (due to other plasticizers or polymer additives in the PVC).

Based on the reasonable comparison the UNIFAC-FV model with experimental data for DEHP and DEHT, it was used to estimate $\hat{\gamma}$, a , and y_0 (in $\mu\text{g}/\text{m}^3$) for all the plasticizers in Table 1 for WF ranging from 0 to 1. All results are given in SI Table S6; estimates of a for all plasticizers are illustrated in Figure 3. As hypothesized by Eichler et al., the similar structure of phthalates resulted in similar $\hat{\gamma}$ values across individual chemicals. However, some chemicals (notably trimethyl citrate, methyl hexanedioate, and methyl ricinoleate) had predicted activities greater than 1. This resulted when the UNIFAC residual component (which quantifies energy interactions among groups) had a very high positive value. This behavior of the UNIFAC-FV model is not unexpected^{52, 53}, and activity > 0 indicates predicted phase separation of the plasticizer and the polymer. At activity = 1, y_0 equals the pure compound VP. The value of y_0 for these chemicals is predicted to approach VP at very low WF; they are not predicted to be compatible with PVC at higher WF. Additional emission experiments would be required to confirm the predicted y_0 resulting from these interactions.

Exposure Predictions and Plasticizer Substitutions

Exposures ($\mu\text{g}/\text{kg}\cdot\text{day}$) for 72 real products containing plasticizer and PVC were estimated using the model of Little et al.⁵¹ The $\hat{\gamma}$, a , and y_0 values were estimated for the plasticizers using the UNIFAC-FV model as described the Methods. It is relevant to note that the UNIFAC model did not predict phase separation of any of these plasticizer-PVC systems at the real-world WFs (that is, as expected, the model predicted compatibility of the plasticizer with PVC at real WFs). The mean WFs, predicted a , and predicted y_0 values for various products are given in Table 2. All estimates of these parameters and the resulting exposures are given in SI Table S7. Estimates of exposures via inhalation, dermal, and ingestion routes are provided for all products for adults and children.

Exposure generally increased with chemical weight fraction (Figure 4, left), as expected, though the increase appears to level off due to decreasing activity coefficient with weight fraction (activities typically approach 1 and thus y_0 approaches VP). Articles with larger exposed areas (i.e. resilient flooring and wallcoverings) and chemicals with higher VP typically had higher estimated exposures. As expected, given the default exposure factor and body weight inputs for children in the Little model, children had higher exposures than adults. The largest exposures were associated with tributyl citrate in resilient flooring, primarily due to its relatively high vapor pressure (as given by the OPERA models). Other

differences in exposure were driven by partitioning: some exposures for acetyl tributyl citrate were lower in resilient flooring than those for DEHP or DEHT, despite having similar (or higher) weight fractions and higher VP, due to lower K_{oa} values, and thus less exposure via dust ingestion. In these products, some impact of differences in activity coefficients could be observed at low WF. For example, at a WF of 0.12 in resilient flooring, estimated inhalation exposures to acetyl tributyl citrate were lower than that of DEHT despite higher VP due to its lower activity coefficient. However, the effect on total exposure in this case was still dominated by the differences in K_{oa} . For this group of 10 plasticizers in real products, the impact of differences in activity were minor compared to differences associated with chemical properties (VP, K_{oa}).

To quantify the impact of predicted activity coefficient on exposures for individual chemicals, we calculated the deviation in predicted children's exposure that would occur for each chemical-product combination if we assumed the plasticizer-PVC system behaved as an ideal solution ($\hat{\gamma} = 1$). In general, this assumption resulted in a modest underestimation of exposure (Figure 4, right). However, for some chemicals (those with the largest deviations from ideal behavior in PVC), the impacts on exposure could be significant. For example, failing to account for an activity coefficient resulted in an underestimation of exposure to tributyl citrate (77-94-1) in resilient flooring (WF $\approx$ 0.22) by over 600 $\mu\text{g}/\text{kg}\cdot\text{day}$.

To further assess the potential impact of activity coefficient differences across a wider range of plasticizers, the UNIFAC-FV model and the Little et al. exposure model⁵¹ were used to predict the exposures associated with plasticizer substitutions in the 72 products studied here; all 30 plasticizers given in Table 1 were assessed as substitutes. Figure 5 illustrates comparison of the total exposure for adults for the plasticizer substitute compared to that for the original plasticizer in the product (the "baseline exposure") for an example product category (resilient flooring). Note that this comparison makes the assumptions: 1) that the WF of the alternative would be same as the WF of the original plasticizer, and 2) that all alternatives would be appropriate for the application. These assumptions may not be true in all cases (e.g., the functionally relevant WF may vary across plasticizers), but insights can still be gained. VP is the most important parameter impacting alternative exposures. Low VP compounds (e.g., trimellitates) represented by the blue end of the spectrum have lower exposures while the highest exposures are for the chemicals with highest VP (e.g., adipates). These VP differences can result in a difference in exposure for the alternatives of approximately four orders of magnitude. However, in some cases, the impact of activity coefficient differences can be observed. Three example observations are highlighted where relatively high $\hat{\gamma}$ values resulted in exposures for alternatives exceeding those for chemicals with higher vapor pressure. Activity coefficients are more relevant when assessing alternatives having similar VP values (within an order of magnitude). The results indicate that exposures may not be particularly impacted by small differences in estimated activity coefficients, and therefore prediction methods such as UNIFAC-FV, while perhaps uncertain, may be of utility if they can capture the general trend in activity coefficient among different compounds.

The framework of combining the activity coefficient models with a high-throughput exposure model demonstrates the applicability of QSAR predictions for determining the

screening-level exposures associated with chemicals in consumer articles. Since emission studies for non-phthalate plasticizers are scarce, with only DEHT and diisononyl cyclohexane-1,2-dicarboxylate (DINCH) studied in any depth²⁰, this framework can provide some guidance for the development of screening level exposure values for use in alternatives assessments. It also provides some guidance for the design of emission experiments, as it predicts which compounds might have the highest potential for deviation from ideal behavior (as measured by activity coefficient) and exposure. The group contribution models cannot be used to directly model chemicals without unique single structures (i.e., mixtures such as DINCH), but activity predictions for these plasticizers could be estimated using predictions for chemicals similar to their component chemicals. Emission studies on a wider range of plasticizer alternatives could further evaluate the predictability of the UNIFAC-FV model across a range of structural classes. The predictions developed here also assume that the emission of plasticizer from articles is not dependent on the internal diffusion of plasticizer within the polymer matrix. It may be the case that for some plasticizers, this assumption may not be ideal (especially when the concentration of plasticizer in PVC is very low). Further experimental emission studies covering different initial plasticizer concentrations in PVC could aid in quantifying these effects.

From only the “first-principles” of chemical and polymer structure and composition (without emission chamber experiments), we can generate estimates of chemical exposure from consumer articles which can in the future be integrated with exposure estimates from other sources and pathways (e.g., within EPA’s Systematic Empirical Evaluation of Models framework)⁵⁴. While chemical presence, emission, and exposure alone do not indicate risk, these aggregate exposure predictions can be compared with high-throughput hazard information to inform risk-based decision-making (such as the prioritization of chemicals for further study).

Though no emission experiments are required for the application of modeling framework described here, there is still a need for high quality experimental emission data to further evaluate this method and to develop estimates for additional chemical-substrate systems. For example, approaches could be applied to plasticizers in other polymers. However, these group contribution methods can only be applied to chemical/substrate systems that behave as a solution. For chemicals (e.g., flame retardants) that may be bound within the polymer matrix, other modeling approaches would need to be investigated. Further experimental measurement of y_0 values over a range of chemical classes and substrate types could inform the development of data-driven prediction models for emission parameters. Specifically, such data would allow for the development of empirical models for y_0 in terms of chemical properties, structural descriptors, and substrate conditions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

A plot of octanol-water partition coefficients (K_{ow}) for several compounds calculated using the UNIFAC method implementation plotted versus the values from EPA's OPERA QSAR model. The phthalates modeled in this work are shown in blue. The general agreement between the OPERA and UNIFAC-predicted K_{ow} values demonstrates the validity and appropriate implementation of the UNIFAC group contribution models.

Figure 2.

The activity coefficient $\hat{\gamma}$ (top), activity (product of $\hat{\gamma}$ and WF, middle), and y_0 (bottom) for DEHP and DEHT in PVC from experiment and predicted by the UNIFAC-FV and Entropic-FV models. The shaded areas represent the 2.5th–97.5th percentile of 1000 Monte Carlo runs of the model. Note there is one UNIFAC-FV and one Entropic-FV prediction for DEHP and DEHT because they contain identical groups. Experimental values are shown as filled circles and were calculated from emissions data literature. The Henry's law (constant activity coefficient) value estimated by Eichler et al. is also shown. The predictions of UNIFAC-FV generally agree with the available experimental data and show the notable downward trend of $\hat{\gamma}$ as weight fraction increases.

Figure 3.

Predicted activities (ratio of y_0 to VP) for 30 plasticizers (12 phthalates/terephthalates and 18 others). Activities were similar among all phthalates/terephthalates, and were generally less than 1. Other plasticizers exhibited predicted activities greater than 1 (y_0 values greater than pure chemical VP) at some WFs due to energy interactions (positive values of the UNIFAC residual terms). All estimated $\hat{\gamma}$, activity, and y_0 predictions are given in the SI in Table S6.

Figure 4.

Left: Predicted total exposures for children (smaller symbols) and adults (larger symbols) associated with 72 real-world plasticizer containing articles (10 unique plasticizers) using the model of Little et al. Exposure generally increases with chemical weight fraction, as expected, though the increase appears to level off due to decreasing activity coefficient with weight fraction (activities typically approach 1 and thus y_0 approaches VP). Articles with larger exposed areas (i.e. resilient flooring and wallcoverings) and chemicals with higher VP typically display higher exposures. Right: Estimated error in total exposure for children that would result from assuming an ideal solution (activity coefficient =1).

Figure 5.

Exposures for 30 alternative plasticizers in 51 resilient floorings containing PVC. The x axis is the ratio of exposure of the alternatives to that predicted for the baseline (original) plasticizer. The black points indicate that the UNIFAC-FV model predicted phase separation (activity>0) at the WF associated with the original plasticizer in the product. The size of the points indicate the magnitude of the activity coefficient.

Table 1.

Properties of plasticizers considered in this study.

CASRN	Name	Molecular Weight (g/mol)	Density ^a (g/cm ³)	VP ^b (mmHg)	Class
102-76-1	Triacetin	218.21	1.13	2.22e-03	triglyceride
103-23-1	Bis(2-ethylhexyl)hexanedioate (DEHA)	370.57	0.89	1.02e-06	adipates
105-76-0	Dibutyl maleate	228.29	1.00	1.08e-03	maleates
109-43-3	Dibutyl decanedioate	314.47	0.94	5.08e-06	sebacates
117-81-7	Di(2-ethylhexyl) phthalate (DEHP)	390.56	0.96	2.22e-07	phthalates
117-84-0	Di-n-octyl phthalate	390.56	0.97	1.71e-07	phthalates
119-06-2	Ditridecyl phthalate	530.83	0.91	4.18e-08	phthalates
123-79-5	Dioctyl hexanedioate	370.57	0.91	8.90e-07	adipates
141-24-2	Methyl ricinoleate	312.49	0.90	3.14e-07	ricinoleate
14234-82-3	2-Butenedioic acid (ZZ)-, bis(2-methylpropyl) ester	228.29	0.98	5.95e-03	maleates
1587-20-8	1,2,3-Propanetricarboxylic acid, 2-hydroxy-, trimethyl ester (trimethyl citrate)	234.20	1.21	1.26e-04	alkyl citrates
1962-75-0	Dibutyl terephthalate	278.35	1.04	3.35e-05	terephthalates
2459-10-1	Trimethyl benzene-1,2,4-tricarboxylate	252.22	1.22	3.56e-06	trimellitates
3319-31-1	Tris(2-ethylhexyl) trimellitate (TOTM)	546.79	0.95	4.01e-09	trimellitates
3648-20-2	Diundecyl phthalate	474.73	0.93	2.39e-07	phthalates
4654-26-6	Dioctyl terephthalate	390.56	0.97	5.56e-07	phthalates
627-91-8	Methyl hexanedioate	160.17	1.14	5.12e-04	adipates
627-93-0	Dimethyl adipate	174.20	1.05	7.37e-02	adipates
6422-86-2	Bis(2-ethylhexyl) terephthalate (DEHT)	390.56	0.96	6.22e-07	terephthalates
6846-50-0	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	286.41	0.91	4.76e-03	isobutyrate
77-89-4	Acetyltriethyl citrate	318.32	1.16	2.39e-05	alkyl citrates
77-90-7	Acetyl tributyl citrate	402.48	1.07	1.06e-06	alkyl citrates
77-93-0	Triethyl citrate	276.29	1.18	4.86e-04	alkyl citrates
77-94-1	Tributyl citrate	360.45	1.09	2.64e-05	alkyl citrates
84-66-2	Diethyl phthalate	222.24	1.11	2.03e-03	phthalates
84-69-5	Diisobutyl phthalate	278.35	1.03	3.69e-05	phthalates
84-74-2	Dibutyl phthalate (DBP)	278.35	1.05	2.43e-05	phthalates
84-75-3	Dihexyl phthalate	334.46	1.01	1.09e-05	phthalates
84-76-4	Dinonyl phthalate	418.62	0.96	6.46e-07	phthalates
85-68-7	Benzyl butyl phthalate (BzBP)	312.37	1.13	4.47e-06	phthalates

^aEstimated from EPA's Toxicity Estimation Software Tool (TEST)^bEstimated using EPA's OPERA (OPEn saR App) model

Table 2.

Mean WFs, predicted activities, and y_0 values for 10 plasticizers in 72 products containing PVC. Mean a is greater than mean WF for each product type, indicating a positive deviation from ideal behavior (higher y_0 than predicted by the behavior of an ideal solution of plasticizer in PVC).

CASRN	Name	Product Category	N	mean WF	mean a	mean y_0 ($\mu\text{g}/\text{m}^3$)
103-23-1	Bis(2-ethylhexyl)hexanedioate (DEHA)	resilient flooring	6	0.354	0.805	1.64e+00
117-81-7	Di(2-ethylhexyl) phthalate (DEHP)	resilient flooring	10	0.224	0.706	3.30e-01
3319-31-1	Tris(2-ethylhexyl) trimellitate (TOTM)	cabling	1	0.003	0.022	2.59e-04
4654-26-6	Diocetyl terephthalate	resilient flooring	1	0.339	0.838	9.80e-01
6422-86-2	Bis(2-ethylhexyl) terephthalate (DEHT)	cabling	7	0.087	0.191	2.50e-01
6422-86-2	Bis(2-ethylhexyl) terephthalate (DEHT)	resilient flooring	17	0.279	0.758	9.92e-01
6422-86-2	Bis(2-ethylhexyl) terephthalate (DEHT)	wallcovering	7	0.232	0.658	8.60e-01
6422-86-2	Bis(2-ethylhexyl) terephthalate (DEHT)	window shades	2	0.151	0.446	5.83e-01
77-90-7	Acetyl tributyl citrate	resilient flooring	10	0.208	0.450	1.03e+00
77-90-7	Acetyl tributyl citrate	wallcovering	4	0.170	0.520	1.19e+00
77-94-1	Tributyl citrate	resilient flooring	5	0.167	0.459	2.35e+01
84-74-2	Dibutyl phthalate (DBP)	carpet	1	0.071	0.467	1.70e+01
84-75-3	Diethyl phthalate	resilient flooring	1	0.233	0.746	1.47e+01
85-68-7	Benzyl butyl phthalate (BzBP)	resilient flooring	1	0.338	0.859	6.46e+00