

Tracking SVOCs' Transfer from Products to Indoor Air and Settled Dust with Deuterium-Labeled Substances

Vilma Sukiene,^{†,‡} Andreas C. Gerecke,[‡] Yu-Mi Park,[§] Markus Zennegg,[‡] Martine I. Bakker,^{||} Christiaan J. E. Delmaar,^{||} Konrad Hungerbühler,[†] and Natalie von Goetz^{*,†}

[†]Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology (ETH Zurich), Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland

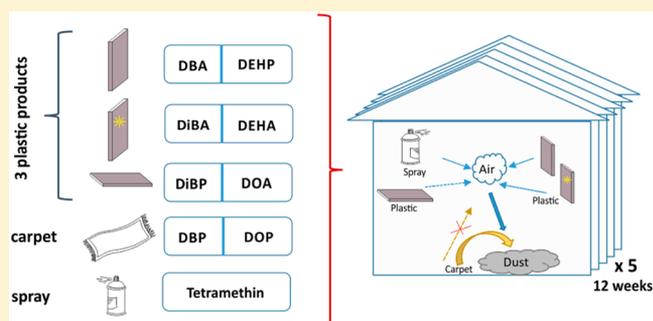
[‡]Swiss Federal Laboratories for Material Science and Technology (EMPA), Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

[§]Environmental Research Complex, National Institute of Environmental Research (NIER), Hwangyong-ro 42, Seo-gu, Incheon 404-708, Republic of Korea

^{||}National Institute for Public Health and the Environment (RIVM), P.O. Box 1, 3720 BA Bilthoven, The Netherlands

S Supporting Information

ABSTRACT: Semivolatile organic compounds (SVOCs) can be released from products and distributed in the indoor environment, including air and dust. However, the mechanisms and the extent of substance transfer into air and dust are not well understood. Therefore, in a small-scale field study the transfer of nine SVOCs was investigated: Four artificial consumer products were doped with eight deuterium-labeled plasticizers (phthalates and adipates) and installed in five homes to investigate the emission processes of evaporation, abrasion, and direct transfer. Intentional release was studied with a commercial spray containing a pyrethroid. During the 12 week study, indoor air and settled dust samples were collected and analyzed. On the basis of our measurement results, we conclude that the octanol-air partitioning coefficient K_{oa} is a major determinant for the substance transfer into either air or dust: A high K_{oa} implies that the substance is more likely to be found in dust than in air. The emission process also plays a role: For spraying, we found higher dust and air concentrations than for evaporation. In contrast, apartment parameters like air exchange rate or temperature had just a minor influence. Another important mechanistic finding was that although transfer from product to dust currently is postulated to be mostly mediated by air, direct transport from product to dust on the product surface was also observed.



1. INTRODUCTION

Semivolatile organic compounds (SVOCs) occur in a variety of consumer products used indoors such as cleaning agents, personal care products, cosmetics, electronics, packaging and building materials. Over time, SVOCs can be released from products and distributed within the indoor environment: they partition between indoor air, airborne particles, settled dust and other indoor surfaces.¹ Given the variety of indoor sources containing SVOCs and the diversity of their usage patterns,² human exposure to SVOCs may take place via different exposure pathways.

In more economically developed countries, people spend most of their time indoors,^{3,4} where they are continuously exposed to dust, which is speculated to be an important secondary source of exposure.^{5,6} In particular, for low-volatile substances released by using consumer products, dust is an important transfer and storage medium.^{7,8} Dust contributes to human exposure to various chemicals such as polybrominated diphenyl ethers (PBDEs),^{6,9–11} other brominated flame retardants (BFRs),^{12,13} polychlorinated biphenyls (PCBs),⁹

insecticides,^{14,15} plasticizers^{7,9,12} and many other substances used in consumer products.

The field studies cited above were conducted with limited control over experimental parameters in home or office settings. In such studies the sources of a substance are not identifiable as the substance detected in air and dust could be emitted from different products present indoors or even have been transferred from outdoors. Moreover, target substances can occur as contaminants of equipment and chemicals used during sample analysis¹² leading to large uncertainties around measured concentrations in dust.

This project aims at experimentally assessing the specific transfer pathway of SVOCs from consumer products to air and dust by using deuterium-labeled substances as tracers. These

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Table 1. Products and Substances Used in the Field Study

Product	Symbol	Abbr.	Substance name	Abbr.	Emission process
Vertical plastic		PV	$^2\text{H}_4$ -dibutyl adipate	DBA	Evaporation
			$^2\text{H}_4$ -di(ethyl-hexyl)-phthalate	DEHP	
Vertical plastic with thermal exposure		PT	$^2\text{H}_4$ -di-isobutyl adipate	DiBA	Evaporation under thermal stress
			$^2\text{H}_4$ -di-(ethylhexyl)-adipate	DEHA	
Horizontal plastic		PH	$^2\text{H}_4$ -diisobutyl phthalate	DiBP	Evaporation and direct diffusion to dust particles
			$^2\text{H}_4$ -di-n-octyl adipate	DOA	
Carpet		C	$^2\text{H}_4$ -dibutyl phthalate	DBP	Evaporation, direct diffusion to dust particles and abrasion
			$^2\text{H}_4$ -di-n-octyl phthalate	DOP	
Spray		S	Tetramethrin	Tetr	Intentional release

tracers cover a range of vapor pressures and are applied to different types of consumer products.

2. MATERIALS AND METHODS

2.1. Materials. Product Description. The transfer of chemicals from consumer products to dust depends strongly on the purpose of the product and, thus, on the product properties. Five products were used to cover four emission processes: intentional release into the air, evaporation, abrasion by mechanical wear and direct transfer.

Intentional release to the air was covered by a spray product. Evaporation was investigated by the use of three plastic products (low density polyethylene, LDPE) and a carpet (polyamide). Two plastic products were vertically installed. One of them was additionally exposed to heat in order to include evaporation under thermal stress. One plastic product was horizontally installed and, together with the carpet, was used to investigate direct diffusive transfer to dust. For the carpet, abrasion was considered as a second process. The list of the products along with the represented emission processes can be found in Table 1.

Substance Selection. For the experiment, substance groups were selected for which physicochemical data are available and which are relevant for human exposure. Thus, plasticizers (phthalates and adipates) were selected, with K_{oa} values between 8 and 12 (subcooled liquid vapor pressures $1\text{--}10^{-5}$ Pa), as well as a synthetic pyrethroid (see Table 1). Because plasticizers are ubiquitous in the indoor environment, in order to reduce the background and enable substance tracking, eight deuterium-labeled plasticizers were synthesized. An insecticide spray containing 0.16 g/100 g tetramethrin was purchased from Martec AG. This substance is not frequently applied indoors, so that background concentrations were always below the detection limit.

Product Preparation. Labeled plasticizers were incorporated into four artificial products: three LDPE products and a polyamide carpet. Into each product two labeled plasticizers were incorporated, one of low and one of high K_{oa} , so that all artificial products contained two unique labeled substances. The LDPE products were installed in the rooms as follows: one product on a horizontal surface (PH), one product vertically hanging on the wall (PV) and one product vertically hanging under thermal stress under a 60 W electric lamp (PT). The plastic products PT, PH and PV contained two, three and four LDPE sheets ($24 \times 18 \times 0.01$ cm), respectively. The sheets

were doped with labeled substances by immersing them for 3 days in an aqueous solution of labeled substances. These aqueous solutions with 5% methanol were prepared to yield 10-fold higher amounts in the artificial products for the less volatile substances ($\log K_{\text{oa}} > 10$) in comparison to the more volatile substances ($\log K_{\text{oa}} < 9$). To keep the solution well mixed, the container with the plastic sheets inside was constantly shaken at 120 rpm. According to the diffusion coefficients for DBP and DOP (2×10^{-12} and 5×10^{-13} cm^2/s),¹⁶ it can be estimated (see the Supporting Information) that the substances entered 10–20% of the material (DBP entered around 10 μm from each side, i.e., around 20% of the 100 μm thick material, DOP around 5 μm , i.e., 10% of the material). The polyamide carpet (57×88 cm) was doped by spraying a solution of DBP and DOP in isooctane on the surface of the carpet. After the application of the solution, the carpet was stored in a closed box for 2 days to allow the substances to diffuse to the fibers of the carpet. Before installation in the apartments, the carpets were kept outside until the carpet had dried.

To mount the plastic products, each plastic sheet was placed on a separate photo frame to keep the plastic sheet straight and ensure the emission of the chemical from the whole plastic surface area.

Product Installation. The same set of five products (three plastic products, a carpet and a spray) was installed in each of the five apartments in Zurich, Switzerland. These households were chosen as sites reflecting the typical parameters of modern apartment environments, e.g., location, size, activity of residents and ventilation patterns.

In all apartments, one frequently used room was selected as the experimental area, where products were installed and samples taken (living rooms, only for apartment 4 a bedroom). The study duration was 12 weeks.

Detailed explanations of sample installation can be found in the Supporting Information.

2.2. Methods. Sampling and Sample Analysis. The sampling campaign was performed between September and December 2013. All the apartments were visited every second week to collect floor dust samples. Passive air samples were taken every 4 weeks. Active air samples were collected before the experiment. Prior to analysis, dust samples were sieved with a 2 mm sieve. Fraction 1 ($F_1 > 2$ mm) and fraction 2 ($F_2 < 2$ mm) were analyzed separately. Dust and air samples were extracted using Soxhlet systems and analyzed using GC/MS. For quality control, background, blank and triplicate samples

Table 2. Log K_{oa} Values and Average Amounts of the Target Substances in the Products

substance	DiBA	DBA	DiBP	DBP	DEHA	DOA	DEHP	DOP	Tetr ^c
product	PT	PV	PH	C	PT	PH	PV	C	S
log K_{oa} ^a	7.9	8.0	8.8	8.9	10.8	10.9	11.7	11.9	12.2
amount in the product before the experiment, mg	15	30	26	80 ^b	190	310	280	800 ^b	160
relative standard deviation before the experiment, %	n.a.	11	8.0	n.a.	n.a.	5.9	15	n.a.	
amount in the products after the experiment, mg	0.0016	0.12	0.59	n.a.	120	240	190	n.a.	0
relative standards deviation after the experiment, %	65	50	118	n.a.	4	14	3	n.a.	28
concentration in the product before the experiment, kg/m ³	1.8	1.8	2.0	0.059 ^b	22	24	16	0.59 ^b	
concentration in the products after the experiment, kg/m ³	$<2.9 \times 10^{-4}$	6.7×10^{-3}	4.5×10^{-2}	n.a.	14	18	11	n.a.	

^aValues from EpiSuite Version 4. ^bAssumed values based on substance amount doped to the carpet (weight, 1.545 kg; density, 1140 kg/m³). ^cOn average, 160 mg of tetramethrin was released in apartments using a commercial spray containing 0.16 g/100 g of tetramethrin; n.a., not applicable (see text).

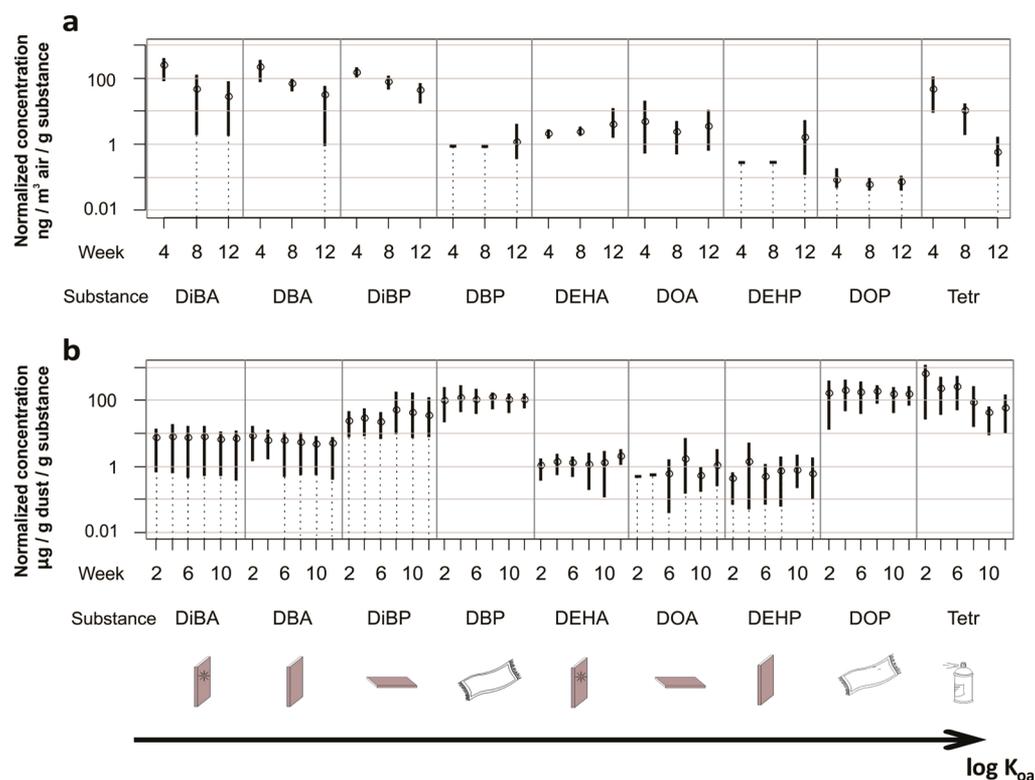


Figure 1. Measured concentrations of target substances in air (a) and floor dust (b) of all five apartments. Lines indicate the range of concentrations in apartments. Dots show the arithmetic mean concentrations. Nondetects were substituted with half the detection limits normalized to the initial strength of the sources. Dotted lines down to 0.01 indicate that samples $< LOD$ were included in the calculation of the mean, horizontal lines, e.g., in the case of DBP in air indicate the LOD and that the substance was detected in none of the apartments.

were analyzed. Background dust and active air samples confirmed that the background concentrations of tetramethrin were below the detection limits (LOD) of 5.7 ng/m³ for air and 0.24 µg/g for dust. For all substances and matrices, the LOD equaled also the limit of quantification in our study. The analysis of blank samples showed the absence of sample contamination. The triplicate samples showed an average relative standard deviation of 20%. Temperature and air exchange rates were continuously measured, the latter based on the carbon dioxide generated by the occupants as a tracer gas. Detailed explanations of sampling procedure, sample preparation, analysis, quality control and air exchange rate measurements can be found in the [Supporting Information](#).

Measured values that were below the corresponding LOD were treated as nondetects. For the derivation of mean values, nondetects were assumed to be half of the corresponding LODs. More sophisticated methods of treating nondetects in

the calculations were not suitable for our purposes because of the small sample number. The uncertainty induced by this procedure is small, as demonstrated exemplarily in chapter 12 in the [Supporting Information](#).

Model for Distribution Dynamics Assessment. On the basis of the model of Weschler and Nazaroff,¹ concentration ratios between product, air and dust samples were calculated to investigate the distribution dynamics between products and the indoor environment (see [Supporting Information](#)). Concentration ratios between organic matter of dust and the gas phase were estimated separately for the three sampling periods (4 weeks each) that correspond to the passive air sampling periods. Floor dust was analyzed every second week and for comparison was averaged over the same three periods. The geometric mean was calculated for air and dust concentrations from all apartments for the three time intervals. Concentration ratios between air and product and between dust and product

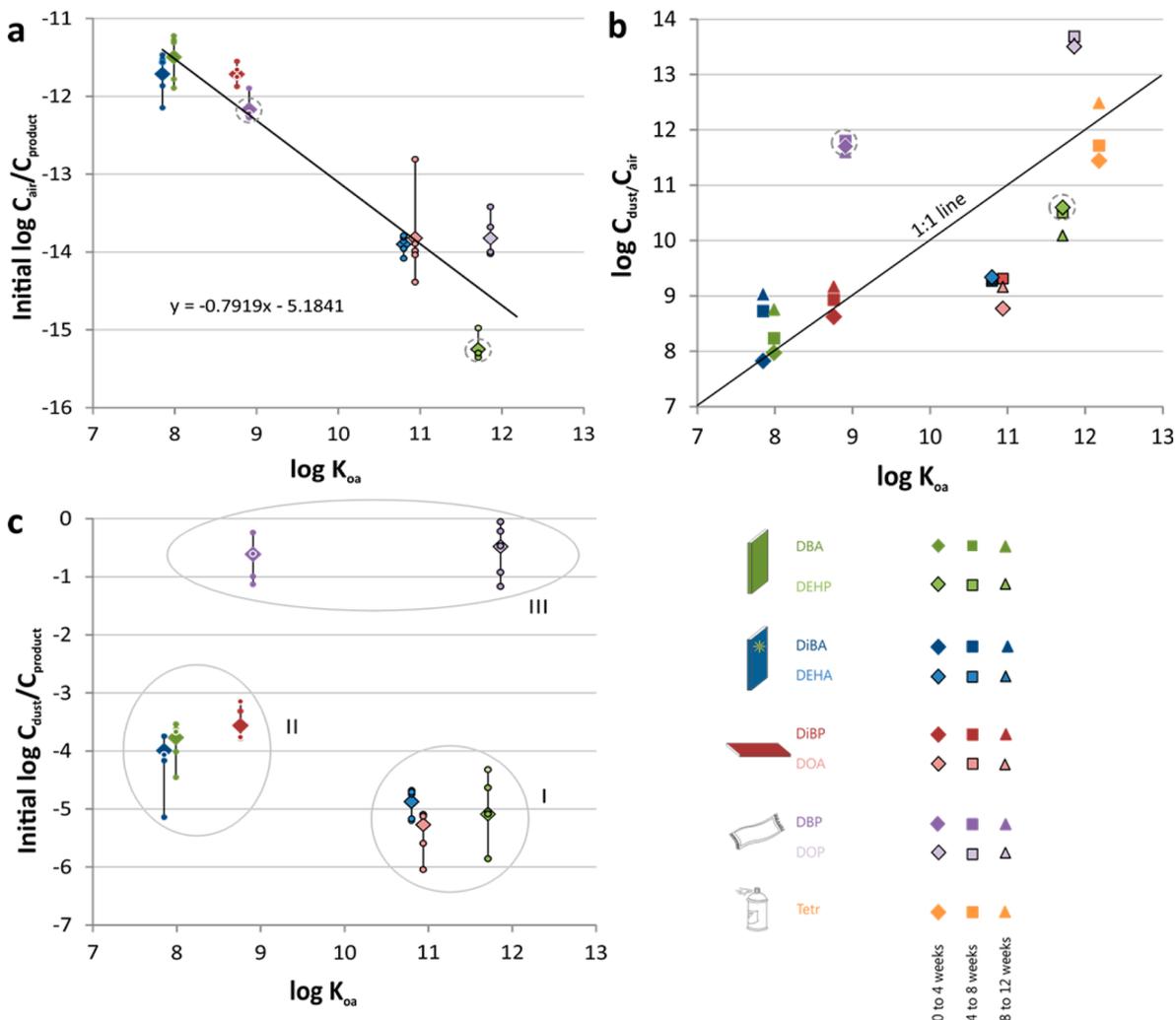


Figure 2. Correlation between $C_{air}/C_{product}$ and $\log K_{oa}$ for the initial phase (a), C_{dust}/C_{air} over time compared to $\log K_{oa}$ (b), $C_{dust}/C_{product}$ for the initial phase compared to $\log K_{oa}$ (c). The error bars represent the variability of concentration ratios in single apartments. Every dot in panels a and c represents one apartment (some overlapping); the larger icon is the geometric mean.

were estimated only for the first sampling period using initial product concentrations.

In calculations of the concentration ratios, we have assumed a dust density of 2000 kg/m³.^{17,18} The average organic matter content of settled dust was measured to be 70% (see Supporting Information). The concentration in the gas phase was calculated from the measured total air concentrations by using the approach of Weschler and Nazaroff^{12,17} (see Supporting Information).

For a full description of the distribution dynamics, the distribution constants between material and air as well as between air and particles, air and dust and air and sink surfaces need to be known. Such data are not available. However, it was shown that for phthalates the ratio of the concentrations in material and air is close to the K_{oa} .¹⁹ Thus, the K_{oa} was used to approximate the partition coefficients between air and material, and air and dust. For all substances in our study, K_{oa} values were available in the literature, but they vary largely for the single substances and different methods. To use a consistent methodology for all substances, we obtained $\log K_{oa}$ values from EpiSuite Version 4 (calculated from the estimated octanol–water partition coefficients (K_{ow}) and Henry’s constants estimated with the bond method) (see Table 2).

The EpiSuite default values for $\log K_{oa}$, which are calculated from either estimated or measured K_{ow} and Henry’s constants, were also considered, but resulted in a less convincing pattern (see the Supporting Information).

3. RESULTS

3.1. Substance Distribution Indoors. Concentrations of target substances in plastic products were measured both before and after the experimental study. For analysis, 12 discs were cut from different locations in each of the products. For the carpet, it was assumed that the complete amount of sprayed substance was equal to the initial amount in the carpet, because the doping technique did not allow homogeneous doping of the carpet (see Materials and Methods).

Table 2 presents total amounts of the deuterium-labeled substances that were installed in each of the apartments and the amounts that remained in the plastic products after the experiment. Relative standard deviations of the amounts in the products before the experiment show the variability between the plastic products produced in different batches (PT products were produced in a single batch). Relative standard deviations of the amounts after the experimental study represent the variability between products in all five apartments. The more

volatile plasticizers (DiBA, DBA and DiBP) had almost completely evaporated from the plastic products over the experimental period (residual 0.01–2.3%). Loss of less volatile substances was lower and varied between 23 and 37% of the initial amounts. However, the absolute released amounts of the less volatile substances were higher due to an order of magnitude higher initial amounts in the products.

Figure 1 shows the ranges and the mean values of the concentrations of all target substances in all apartments over time normalized to the initial concentrations in the sources. One measure of variation among apartments is to calculate the ratio between the maximum and the minimum concentration for one substance (max/min ratio). E.g. for DiBP, the max/min ratios for the five apartments were 3 and 13 on average for air and dust, respectively. For DEHA, the same max/min ratios were 4 in air and 9 in dust (other substances see Supporting Information). The average max/min ratios of all target substances among all apartments were 14 and 17 for air and dust, respectively. Thus, the extremes between apartments did not differ by more than a factor of 20. However, the variability of dust concentrations among apartments on average is larger than of air concentrations.

The variation between substances can be assessed by calculating the ratio between maximum and minimum concentrations (normalized to the averaged initial source strength) for all substances within one apartment. Even though all analyzed substances were SVOCs with $\log K_{oa}$ values between 8 and 12, the average max/min ratios among substances were larger than 2000 for both air and dust (see Supporting Information).

Therefore, substance release into air and dust varied much less between apartments than between substances.

Concentration Patterns in Air. In air, the more volatile substances were detected more frequently (DiBA, DBA, DiBP) and their concentrations were up to 3 orders of magnitude higher than for the less volatile substances (with the exception of tetramethrin). Independent of their vapor pressure, substances from the carpet (DBP and DOP) were not emitted into the air. DBP was detected in only one sample (see Supporting Information). DOP was measured in the air only sporadically and its concentrations in most of the apartments were very low ($<0.1 \text{ ng/m}^3 \text{ air/g substance}$).

Concentration Patterns in Dust. Prior to analysis, the floor dust samples were sieved using a 2 mm sieve. Both fractions ($F1 > 2 \text{ mm}$ and $F2 < 2 \text{ mm}$) were analyzed separately. However, the difference between the two fractions was small and it is possible that the fractions were not separated quantitatively (see Supporting Information). Therefore, we used the mass-weighted average concentrations of both fractions to calculate the ratios for Figure 2.

Normalized concentrations of the less volatile substances in dust (DEHA, DOA and DEHP) were in the order of $1 \mu\text{g/g}$ dust/g substance. The concentrations of more volatile substances in floor dust were higher, presumably due to the sampling method and short study duration. Phthalates that were present in the carpet (DBP and DOP), although of similar K_{oa} as substances in other products, were both detected in all floor dust samples in much higher concentrations (average concentration: $146 \mu\text{g/g}$ dust/g substance). Tetramethrin ($\log K_{oa}$ 12.2) was detected in all dust samples including samples collected after the insecticide application had stopped.

Product Influence on Distribution. Neither the positioning of the product (horizontal or vertical) nor moderate thermal

stress influenced the concentrations of less volatile substances in the air. DEHP (PV) was detected sporadically and in lower concentrations compared to DEHA and DOA, probably due to the higher K_{oa} . In dust, concentrations of DiBA (PT) and DBA (PV) were comparable, but DiBP (PH) was consistently higher. Hence, thermal stress had no influence for more volatile substances in dust, but position might have. Less volatile substances in floor dust were neither influenced by position nor thermal stress.

The concentration patterns of substances over time were consistent between apartments: Concentrations of the less volatile substances in air were stable over time (except for tetramethrin). The concentrations of more volatile plasticizers and tetramethrin decreased in air over time along with the decrease of mass in the products. Concentrations of all plasticizers in dust were stable over time, but tetramethrin in floor dust clearly decreased.

3.2. Distribution Dynamics. On the basis of partitioning theory,^{1,8,17} substances released to the environment partition between air, dust and sorptive surfaces. Predictions of partitioning in the initial emission phase and at equilibrium can be based on the substance's K_{oa} (see the Supporting Information). Using measured initial substance concentrations in products and concentrations in air and floor dust, we explored the relationship between the concentration in sources, and indoor media (see Figure 2). As substance distributions in all studied apartments were comparable, the geometric means of concentration ratios were calculated and compared with predicted values calculated using the model proposed by Weschler and Nazaroff¹ (see the Supporting Information). Even though in our experiment equilibrium was not reached, the dust/air concentration ratios were compared to explore the differences between distribution under conditions of our study and equilibrium. Concentrations in floor dust C_{dust} are the weighted mean in both dust fractions, averaged over two sampling periods (e.g., 2 and 4 weeks). C_{product} represents the initial concentration of substances in the product. Error bars represent the range between lowest and highest concentrations detected in apartments.

$C_{\text{air}}/C_{\text{product}}$ Ratio. Figure 2a shows that for the first time period (4 weeks), there is a negative correlation between the $C_{\text{air}}/C_{\text{product}}$ ratio and the $\log K_{oa}$ of the substances (see eq 4 in the Supporting Information). DEHP and DBP were not detected in the air of any apartment during the first time period. Therefore, their concentration ratios were calculated based on half their detection limits, which leads to larger uncertainties (dotted circles). However, the correlation remains negative regardless of the values used to replace nondetects (see Figure S12 in the Supporting Information).

$C_{\text{dust}}/C_{\text{air}}$ Ratio. Figure 2b shows the ratio between the measured substance concentrations in the organic matter fraction of floor dust and air plotted against the $\log K_{oa}$, because according to literature under equilibrium conditions $C_{\text{dust}}/C_{\text{air}}$ can be estimated by the K_{oa} .¹ The calculated ratios of the more volatile substances in plastic products (DiBA, DBA and DiBP) at the first time point are close to the 1:1 line, but later their concentration ratios exceeded the $\log K_{oa}$ by up to 1 order of magnitude. As expected, the concentrations in dust of less volatile substances (except for DOP) were significantly lower than the theoretical equilibrium concentrations (represented by $\log K_{oa}$). However, independent of the $\log K_{oa}$ values, measured dust/air concentration ratios of the substances

present in the carpet exceeded the $\log K_{oa}$ by up to one and 3 orders of magnitude for DBP and DOP, respectively.

$C_{dust}/C_{product}$ Ratio. In dust samples, concentrations of substances from the carpets (DBP and DOP) were higher than those from plastic products. This phenomenon was observed in all floor dust samples (all apartments and time points).

To obtain insight into the transfer efficiency between product and dust, the ratio of concentrations in dust and product in the initial phase is plotted against $\log K_{oa}$ in Figure 2c. Three types of substance-product combinations can be distinguished therein: The less volatile substances from the plastic products (circle I), the more volatile substances from the plastic products (circle II) and substances from the carpet (circle III). The concentration ratio of the less volatile substances is in the range of 10^{-4} – 10^{-5} . Ratios for more volatile substances are in the range of 10^{-3} – 10^{-4} . The most effectively transferred substances are present in the carpet. Their concentrations in the organic matter of dust are close to the product concentrations.

4. DISCUSSION

4.1. Substance Distribution Indoors. Substance distribution was consistent between apartments. This indicates that apartment parameters in our study had just a minor influence on substance distribution. Previous studies showed that indoor dust composition and substance distribution in the indoor environment differ between countries^{20,21} and regions²¹ (e.g., urban, suburban). Because the adsorption to dust particles is strongest for the organic fraction, partition efficiency depends on the organic matter content of the dust.¹⁷ Regarding substance distribution, in a chamber experiment it was shown that the substance emission rate is strongly and positively correlated with the air exchange rate,²² which varies with region and season.²³

All five apartments investigated in this study were located in the same region. Therefore, it is likely that the dust composition is comparable. The air exchange rates between apartments varied only by a factor of 5 (0.1 – 0.5 h^{-1} , see the Supporting Information) and were lower compared to previously reported values ranging between 0.2 – 2.2 h^{-1} .^{24–27} The behavior of the residents (e.g., not wearing street shoes in the apartments) and parameters such as temperature or relative humidity were also comparable between the apartments.

Concentration Patterns in Air and Dust. The concentrations of a substance in air and dust are highly dependent on the properties of the substance. In agreement with other studies,^{1,12} we have observed that the K_{oa} is a key parameter in determining whether SVOCs are predominantly found in air or in dust.

At equilibrium, assuming the same source strength, concentrations in dust should be larger for less volatile substances compared to more volatile substances.^{7,8} During our experiment we have observed the opposite, indicating that the duration of the field study was too short to reach equilibrium (for a $\log K_{oa}$ of 12 Weschler and Nazaroff,¹ postulate around 1 year for equilibrium to be reached). Also, concentrations of more volatile substances in floor dust samples might be overestimated due to vacuuming as the vacuum cleaner may act as an active air sampler. Moreover, even though the released absolute amounts of less volatile substances were 2–6 times higher due to the higher amounts in the products (see Table 1), the concentrations of less volatile substances (DEHA, DOA and DEHP) in both air and dust are lower than

those of more volatile substances. This means that there must be other sinks in the apartments that were not sampled, e.g., sorptive surfaces,^{1,22,28} and that these sinks are more relevant for substances with $\log K_{oa} > 10$.

The concentrations of tetramethrin in air do not follow the pattern and are relatively high despite its large octanol-air partition coefficient ($\log K_{oa}$ 12.2). It is possible that the selected K_{oa} value is overestimated. However, the $\log K_{oa}$ value calculated from the experimentally measured octanol–water and air–water partitioning coefficients (and suggested as default value in EpiSuite) of 8.9 significantly underestimates the concentrations in the air (see Figure S13b in the Supporting Information). The true value of the K_{oa} may lie between these two values, but the deviation may also result from the fact that equilibrium was not reached during our study, so that the concentration in the dosed medium (here air) is still higher than predicted for equilibrium conditions.

According to our analysis, substances that were incorporated into the carpet were detected in floor dust, but only sporadically in the air, regardless of their vapor pressure. This finding suggests that additional direct transfer processes from product to dust exist, e.g., direct diffusion of substances to dust, or abrasion. When the floor dust samples were collected, the total floor area including the surface of the experimental carpet was vacuumed, which might have induced abrasion of the carpet fibers. Moreover, differing frequency and duration of the floor vacuuming in the apartments might have increased the variability between the floor dust samples. The absence of carpet substances in the air might have been caused by the lower fugacity of the substances in the carpets compared to the plastic products: Comparable amounts of substances were added to both carpet and plastic products, but because the carpet was larger than the plastic products, the concentration of the chemical in carpets was lower, resulting in lower fugacity. Also, the spatial structure of the carpet fibers can reduce the fugacity by acting as sorptive surfaces for molecules emitted from deeper layers of the carpet structure.

The increased concentration of DiBP (PH) in floor dust compared to other more volatile substances may support the hypothesis that a more efficient direct transfer process exists.

Product Influence on Distribution. Concentrations of more volatile phthalates in air were shown to correlate positively with room temperature.⁷ Another study has shown that temperature had a significant impact on phthalate emission from vinyl flooring.²⁹ However, according to our analysis, the heating of the product had no effect on substance emission. It is likely that the duration of thermal exposure (6 h per day) was not long enough or the reached temperature (approximately 30 °C) was not sufficient to significantly enhance the emission.

The concentrations of DiBA, DBA and DiBP in the air decreased over time due to the depletion of the substances from the plastic products. However, the concentrations of these substances in floor dust remained stable over time. This was possibly caused by slower kinetics of uptake into dust and re-emission to the air. The decrease of tetramethrin concentration over time was observed because the spray was applied in the experimental rooms only during the first 5 weeks of the experimental study. Therefore, the source was only partly present in the third dust sampling period, and not any more in the subsequent ones, whereas the plastic products remained in the apartments for the whole experimental period.

It has to be born in mind that the plasticizers were studied in artificial products. Because plasticizers are not chemically

bound to the matrix, the main difference to commercial products is not the structure of the product, but the distribution of the substance within. In commercial products, a homogeneous distribution along the product profile can be expected, whereas in the artificial products a concentration decline toward the center is the result of the doping procedure. This is even more pronounced for the carpet that rather represents surface treatment. Moreover, commercial products (e.g., PVC flooring) may have a cover layer on the surface reducing emission.

4.2. Distribution Dynamics. $C_{\text{air}}/C_{\text{product}}$ Ratio. Our results indicate that $C_{\text{air}}/C_{\text{product}}$ for the initial phase (4 weeks) was negatively correlated with K_{oa} (see Figure 2a). This is in agreement with the model of Weschler and Nazaroff¹ (see Table 2a and the Supporting Information). However, in our experimental study we have collected the first passive air samples 4 weeks after the product installation, so that the pool samples represent average air concentrations over a 4 week-period. To calculate $C_{\text{air}}/C_{\text{product}}$ ratios we have related this value to the initial product concentration (and not to the average product concentration over 4 weeks, which would be the exact match). Thus, because the concentrations in the products decreased over time, the $C_{\text{air}}/C_{\text{product}}$ ratios plotted in the figure are lower than the true ratio. Because this deviation from the real value is more pronounced for more volatile substances, the slope deviates from the slope of 1 that is predicted by Weschler and Nazaroff.¹

$C_{\text{dust}}/C_{\text{air}}$ Ratio. In theory, when the system is at equilibrium, $C_{\text{dust}}/C_{\text{air}}$ is proportional to K_{oa} . The main reason for less volatile substances to have a $C_{\text{dust}}/C_{\text{air}}$ below the predicted value (see Figure 2) is the short duration of the field study (12 weeks), which was not enough to reach equilibrium. Establishing equilibrium under realistic room conditions for SVOCs may take years or it cannot be achieved at all,¹ but this comparison makes clear that transfer of substances to dust does not necessarily occur via air. For the two carpet substances DBP and DOP, the organic matter adjusted concentrations in the floor dust are much higher than the predicted values. The explanation why the measured dust/air concentration ratio is higher than the one predicted for equilibrium may be that these substances were transferred to the dust predominantly by bypassing the gas phase as transfer medium. Such transfer processes can be abrasion or direct transfer from product to dust in direct contact to the source.^{23,28,30}

According to our analysis, the concentration ratios of more volatile substances present in the plastic products (DiBA, DBA and DiBP) at the initial phase (first 4 weeks) seem to match values predicted by the model. However, this match does not indicate that equilibrium was achieved, but is accidentally caused by the depletion of the sources resulting in lower but unknown product concentrations and, consequently, lower air concentrations.

$C_{\text{dust}}/C_{\text{product}}$ Ratio. The larger $C_{\text{dust}}/C_{\text{product}}$ of more volatile substances indicates that more volatile substances are transferred to floor dust faster than less volatile chemicals.

The presence of additional substance transfer processes (other than transfer via air) from product to dust is supported by $C_{\text{dust}}/C_{\text{product}}$ of the substances in the carpet, which are in the range of 0.24–0.4. Compared to ratios of other substances, these values are close to one, meaning that concentrations in product and organic matter of dust are comparable. This cannot be explained by transfer via air alone, because the concentration ratios of substances with similar K_{oa} values that

were doped in plastic products are up to 5 orders of magnitude lower.

Our study indicates that partitioning models based on K_{oa} are suitable to predict initial distributions of SVOCs in indoor air. For dust, however, the partitioning model underpredicts substance concentrations for some substances. We speculate that other primary transfer processes than evaporation (on which the model is based) contribute to substance transfer to dust. Whether these processes are direct transfer from product to dust, abrasion, or others still needs to be studied.

Our study also confirms that even for the more volatile SVOCs dust is a relevant storage medium and should be studied further. The use of labeled substances is a promising procedure to evaluate the distribution of substances emitted from consumer products. Future research could focus on the influence of the type of the product by using the same substances in different product types. Moreover, explicit measurements of the K_{oa} values of SVOCs are important to better understand substance distribution mechanisms.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05906.

Product preparation and installation, sampling, sample preparation, quantitative analyses and quality control descriptions; measured concentrations in indoor air and floor dust in all apartments investigated in the field study; max/min ratios; measurements of the dust organic matter fraction and air exchange rates; apartment parameters; distribution dynamics assessment (PDF).

■ AUTHOR INFORMATION

Corresponding Author

*N. von Goetz. e-mail: natalie.von.goetz@chem.ethz.ch; phone: +41 44 632 09 75.

Notes

The authors declare no competing financial interest.

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