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Distribution of five SVOCs in a model room: effect of vacuuming and air cleaning measures†

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With regard to the application of semi-volatile organic compounds (SVOCs) in products for indoor use, a distinct trend towards substitutions can currently be observed. Among the possible phthalate alternatives, in particular the adipic acid esters have gained in market importance. The chemical–physical and thermodynamic properties of the phthalates and adipates allow the conclusion to be drawn that they are distributed between different compartments (gas phase, particle phase, dust, material surfaces) of the indoor space. There are, however, hardly any data in existence which were collected in a real environment over six months and longer. Diisobutyl adipate (DiBA), di-*n*-butyl adipate (DnBA), dipentyl phthalate (DPP), butyl benzyl phthalate (BBzP) and di-2-ethylhexyl adipate (DEHA) were selected as model substances. By means of spiked latex paint and spiked house dust, these SVOCs were introduced into two identically equipped test rooms. One room was cleaned regularly, whilst the reference room was not entered for a 133 day experimental period. The concentrations of the five target substances were determined in the air and in material samples (carpet, vacuum-cleaner bags, filters). During the operation of an air purifier, the air concentration of the target substances in a room could be reduced by more than 50%. In the reference room, a correlation between the logarithmic air concentration and the reciprocal room temperature was found. The results show with great clarity the complexity of the conditions in an indoor room. Models can therefore depict the exposure as a statistical average but not, however, describe the individual case.

Environmental significance

In indoor areas, humans are exposed to widely differing noxious agents *via* the various uptake pathways. Particular attention is thereby directed at semi-volatile organic compounds (SVOCs) which, due to their chemical–physical properties, are distributed between diverse compartments. Model calculations which describe the distribution of a substance between gas phase, airborne particle phase and settled dust phase often presuppose equilibrium conditions which do not occur in a real indoor area. Within the course of this work, the concentration profiles of five SVOCs in the air and on surfaces in the rooms of a test house were recorded over a period of six months. The results provide an insight into the dynamics of these SVOCs under the influence of the outdoor climate and taking into consideration cleaning processes, both with and without human activity.

1 Introduction

Semi-volatile organic compounds, the so-called SVOCs, have the characteristic of distributing themselves in differing ways within the diverse compartments of the indoor area (gas phase, airborne particle phase, sedimented house dust). In 2003 systematic investigations into the occurrence of endocrine-disrupting compounds in indoor air and house dust were published by Rudel *et al.*[1] Indoor measurements by Fromme *et al.*[2] on phthalates revealed high concentrations in the air and low concentrations in dust for substances with high vapor pressure (P_s) and low octanol/air distribution coefficients (K_{OA}). For substances with low vapor pressure and high K_{OA}, the situation was reversed. Following this, further investigations into diverse substance groups such as perfluorinated sulfon-amides,[3] organophosphate esters,[4] pyrethroids,[5] poly-brominated diphenyl ethers[6] and many others[7] were published within a short period of time. A paper by Weschler and Nazaroff[8] summarizes the significant literature up to 2008 and offers theoretical approaches for assessing the distribution of SVOCs between gas phase and particles and between gas phase and sedimented dust. For various phthalates, Weschler *et al.*[9] found, based on the theories of Pankow[10] and Finizio *et al.*,[11] correlations in the data of Fromme *et al.*[2] between the concentrations in airborne particles and in sedimented house dust. A detailed treatise on the distribution of SVOCs between gas phase and sedimented dust was presented by Weschler and Nazaroff[12] in 2010.

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The dynamics of SVOCs between gas phase, particle phase, dust phase, and other surfaces remain the subject of theoretical and practical studies.[13–19] The majority of the investigations have been carried out in test chambers[19–22] or emission cells.[23] In most cases, it is only possible to approximate the actualities of the situation in indoor areas through the use of models. There are diverse reasons for this. As a rule, the models presuppose equilibrium conditions which, however, are scarcely adhered to in reality. In addition to this, the establishment of equilibrium between gas phase and dust phase for SVOCs such as di-2-ethylhexyl phthalate (DEHP) is a process lasting several weeks, which was theoretically predicted by Weschler and Nazaroff[8] and experimentally demonstrated by Schripp et al.[24] The parameters necessary for modelling in accordance with Pankow[10] or Finizio et al.,[11] such as vapor pressure and K_{OA} value, are often only very inaccurately known; this leads to corresponding uncertainties in the results.[25,26] An alternative approach by Goss and Schwarzenbach[27] uses experimentally determined hexadecane/air distribution coefficients; calculated molecular values are, however, also utilized in this model.[28]

Nevertheless, various studies exist in which investigations were carried out on the distribution of SVOCs in residential buildings or test houses. On the basis of a literature study, Wei et al.[29] determined the distribution of gas/particle and gas/dust coefficients for a total of 72 organic compounds. Kolarik et al.[30] investigated phthalates in the house dust of Bulgarian homes in dependence of cleaning habits. Venier et al.[31] compared the distribution of 20 brominated flame retardants between gas phase, dust phase and glass surfaces using measurements recorded in the USA, Canada and the Czech Republic. Sukiene et al.[32,33] marked various SVOCs with deuterium and were thereby able to follow the migration of these compounds within a test house and, in particular, the transfer into house dust. Bi et al.[34] investigated the temperature-dependent distribution of phthalates in a test house between 21 °C and 30 °C and found distinct effects. Wei et al.[35] described the temperature-dependence of distribution coefficients of SVOCs in accordance with the known equations of Van't Hoff and Clausius–Clapeyron.

What has barely been investigated so far are questions concerning the establishment of equilibrium of SVOCs in an indoor area and how the equilibrium reacts to disturbances such as cleaning processes. For this purpose, SVOC-spiked latex paint and SVOC-spiked dust were introduced as emission sources into two identically equipped rooms of a test house. The five selected target SVOCs represent a broad range of well-known physical properties and are expected to be mainly found in the gas phase.[28] Two of the SVOCs were only present in the paint and three were only present in the dust. This experimental design was chosen to study the transfer of the SVOCs between different compartments. In the reference Room 1, no further activities were carried out for a period of 184 days. In the test Room 2, an air purifier was operated in accordance with a defined protocol and parts of the floor were cleaned using a vacuum cleaner. At regular intervals, air and material samples were taken and analyzed. The results enable the description of the dynamics of the air concentration of SVOCs in indoor areas under conditions of use and equilibrium.

2 Material and methods

2.1 Chemical substances

All compounds are commercially available. The purity was checked by gas chromatography, the percentage purity refers to the area under the gas chromatographic signal. Dipentyl phthalate (DPP, CAS no. 131-18-0): ABCR GmbH (99%); butyl-benzyl phthalate (BBzP, CAS no. 85-68-7): Follmann & Co. KG, 99.9%; di-n-butyl adipate (DnBA, CAS no. 105-99-7): Sigma Aldrich, 99.9%; di-iso-butyl adipate (DiBA, CAS no. 141-04-8): ABCR GmbH, 99.9%; di-2-ethylhexyl adipate (DEHA, CAS no. 103-23-1): Sigma-Aldrich, 99.0%.

2.2 Design of the test house experiments

The test house is divided into three rooms (see Fig. 1). Rooms 1 and 2 (7.1 m × 4.7 m × 2.7 m = 90.1 m³) were used for the experiments. The room in the middle was used for the sampling equipment. Rooms 1 and 2 have three windows each (98.5 cm × 137.5 cm) with lacquered wooden frame and one door (honeycomb plate with decorative film) (109 cm × 204 cm). The walls are made of oriented strand board (OSB) and covered with a low-emitting water-based paint. The floor is made of particleboard and covered with textile carpet (synthetic fiber). No adhesive was applied.

The reference Room 1 and the test Room 2 were separately air conditioned by use of radiators (Renkforce Luma 2000 Eco) and humidifiers (Honeywell Ultrastar) (target values: $T = 23$ °C and RH = 50%). The radiators were set up in Room 1 and 2, the humidifiers were in the middle room. An air cleaning device (Philips 3000 Series AC3256/10 air purifier, Clean Air Delivery Rate (CADR) = 393 m³ h⁻¹) was installed in the test Room 2. At certain times vacuum cleaning (Philips FC8726/09) was performed in Room 2. The air cleaner was equipped with a multilayer filter, consisting of prefilter, pollen filter, microfiber, active charcoal filter and HEPA filter. The vacuum cleaner was equipped with a HEPA 13 filter and an active charcoal filter. The reference Room 1 was not entered until day 133 of the experiment.

Latex paint, formulated with 10% BBzP and 10% DEHA (by weight), was applied on aluminum plates (2070 g per 20 m²) and used to deliver these SVOCs into the room air at a constant emission rate (see Schripp et al.[36] for further details).

Sieved house dust from vacuum cleaner bags (<63 μm fraction, density $\rho = 0.75$ g cm⁻³, fraction of organic carbon $f_{OC} = 0.44$, fraction of elemental carbon $f_{EC} = 0.03$) was Soxhlet extracted using acetone/n-hexane to reduce the background concentration of VOCs and SVOCs and the solvents were blown-off in a vacuum. The dust was mixed with 10% DiBA, 10% DnBA, 10% DPP (by weight) and praseodymium (Pr) as internal marker in acetone solution. Then the acetone was blown-off in a vacuum. For dispersing the dried dust, approximately 2 g were placed in a polished stainless steel tube (1000 mm × 10 mm) and blown into the respective room from the middle room
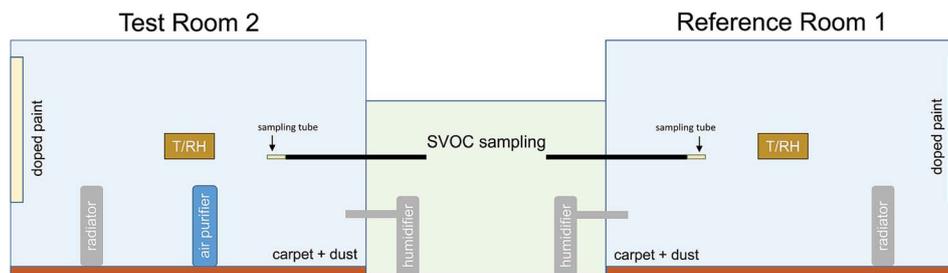
Fig. 1 Design of the test house experiments.

using compressed air. This procedure was repeated at different angles and alignments until the planned amount of dust was introduced (14.95 g in Room 1 and 15.05 g in Room 2). Praseodymium (^{141}Pr) is a stable and comparatively rare lanthanoid (5 ppm in earth's crust), which makes the metal suitable as a marker compound.

The full experimental design is shown in Fig. 1 and the experimental protocol is provided in Table 1. The experiments started on Nov 29, 2017 (introducing paint and dust) and ended on Jun 1, 2018 (after 184 days). After 453 days carpet samples were taken in Rooms 1 and 2. These were analyzed for the five

target compounds and praseodymium. Between day 481 and day 486 the reference Room 1 was vacuumed three times and the particle number concentration was measured. Both rooms were left unchanged between day 184 and day 485 (humidifier and radiator on, air cleaner off).

2.3 Sampling and analysis

Temperature (T) and relative humidity (RH). Rotronic Hygrolog-D data logger at intervals of 20 min.

Air exchange rate (AER). Tracer gas method. The air was spiked with dinitrogen oxide (N_2O) and the concentration *vs.*

Table 1 Protocol of the test house experiments. Temperature and relative humidity were continuously monitored (20 min intervals)

Day	Room 1 (reference room)	Room 2 (test room)
001	Start of experiment (Nov 29, 2017)	Start of experiment (Nov 29, 2017)
084		Air purifier operated for 5 h
096		Filter replaced
		Air purifier operated for 5 h
097		Air purifier operated for 5 h
098		Air purifier operated for 5 h
119		Filter replaced
		Air purifier operated for 5 h
126–128		Air purifier operated for 50 h
132		Filter replaced
		Air purifier operated for 5 h
133	Carpet sample (uncleaned)	Air purifier operated for 5 h
		Carpet sample (uncleaned)
134	Carpet sample (uncleaned)	Air purifier operated for 5 h
		Filter replaced
		Vacuuming (10 min)
		Sampling bag, HEPA 13 filter, charcoal filter replaced
		Carpet sample (cleaned + uncleaned)
167		Air purifier operated for 5 h
168	Carpet sample (uncleaned)	Air purifier operated for 5 h
		Carpet sample (uncleaned)
169	Carpet sample (uncleaned)	Air purifier operated for 5 h
		Filter replaced
		Vacuuming (10 min)
		Sampling bag, HEPA 13 filter, charcoal filter replaced
		Carpet sample (cleaned + uncleaned)
176	Carpet sample (uncleaned)	Carpet sample (cleaned + uncleaned)
		Vacuuming (10 min)
		Sampling bag, HEPA 13 filter, charcoal filter replaced
		Carpet sample (freshly cleaned)
184	End of experiment (Jun 1, 2018)	End of experiment (Jun 1, 2018)
453	Carpet sample (uncleaned)	Carpet sample (cleaned)
481–486	Vacuuming and particles measured	

time curve was recorded with a photoacoustic detector (INNOVA 1412) at 4.5 μm (2215 cm^{-1}). The air exchange was then determined from the N_2O decay curve as described in VDI 4300-7.[37]

Total volatile organic compounds (TVOC$_{PAS}$). Photo acoustic detector (INNOVA 1412) at 3.4 μm (2950 cm^{-1}) with a time resolution of 5 min against the response factor of propane.

Praseodymium. 250 mg of sampled dust were transferred into a digestion vessel. 4 ml nitric acid were added and the material was then digested through microwave irradiation (MLS GmbH). The solution was transferred to a vial, filled to 10 ml and praseodymium was determined by ICP/MS (Agilent ICP-MS 7700x) *versus* a certified standard (He-modus, *m/z* 141). For analysis of the carpet samples the fibers were cut from the carpet back, transferred into a vial and shaken for 30 min after adding 6 ml H_2O and 4 ml nitric acid. Praseodymium was then determined from the filtered solution by ICP/MS.

SVOCs. Air samples were collected using stainless-steel tubes filled with a combination of Tenax TA (Markes Ltd.) and glass wool (flow rate 200 ml min^{-1}; 4–50 l total sampling volume). The tubes were connected to stainless-steel lines and introduced into the respective room through an opening from the middle room. The pump was also located in the middle room (see Fig. 1). The tubes were analyzed *via* thermal desorption (TD100, Markes Ltd.) gas chromatography (7890B, Agilent) mass spectrometry (5977A MSD, Agilent). The GC was equipped with a DB-5 MS column (60 m × 250 μm × 0.25 μm). The MSD was operated in the selected ion monitoring mode (SIM) with ions 129/185 (DiBA), 129/185 (DnBA), 149/237 (DnPP), 104/149 (BBzP), 112/129 (DEHA), 77/326 (TPP), and 152/232 (internal standard). The recovery of the internal standard (a polybrominated biphenyl) had to be between 90% and 110%, otherwise the sample was rejected. All substances were quantified on the basis of original standards. For calibration, the areas under the chromatographic signal of 10 successively diluted solutions of the respective target compound were determined and divided by the areas under the chromatographic signals of the internal standard. In all cases the limit of quantification (LOQ) was <0.05 μg m^{-3}.

House dust and materials (carpet, air purifier filters). 0.5 g dust in 25 ml acetone or 5 g of the respective material in 50 ml acetone were Soxhlet extracted for 16 hours. The extract was concentrated by solvent evaporation, filtered with a 0.2 μm PTFE filter and analyzed with a DB-5 MS UI (30 m × 250 μm × 0.25 μm) using a cold-injection-GC/MS system (7890A/5975C, Agilent). For calibration, the areas under the chromatographic signal of 6 successively diluted solutions of the respective target compound were determined and divided by the areas under the chromatographic signals. In all cases the limit of quantification (LOQ) was <2 μg g^{-1}. The carpet pieces were not pre-cut, but the location of each individual sample was defined before the start of the experiment. Whenever action was required (exchanging filters, vacuuming, taking carpet samples), the respective person entered the room through the door. This person wore a protective suit, gloves, shoe protectors and a breathing mask. Apart from vacuuming, all actions required less than three minutes.

Particles. Fast Mobility Particle Sizer (FMPS, 5.6–560 nm) (TSI, 3091); Optical Particle Sizer (OPS, 0.3–10 μm) (TSI, 3330).

All used materials (unspiked dust, paint, carpet, filters, vacuum cleaner bags, *etc.*) were measured for the five target compounds before the experiment started. In all cases the blank concentrations were below the respective LOQ. The concentrations of DiBA, DnBA, DPP, DEHA, and BBzP in the room air before spiking were also below LOQ.

3 Results and discussion

3.1 Air exchange and climatic parameters

The air exchange rates with all windows and doors closed were determined in Room 1 and Room 2 before and after the investigation period. In all cases the N_2O time *vs.* concentration curves followed a single exponential law. Depending on the outdoor conditions, the AER ranged between 0.2 h^{-1} and 0.3 h^{-1} in both rooms. However, no information is available about air exchange rates during the experimental phase. The profiles for temperature and relative humidity are shown as average daily values in Fig. 2. Although both rooms were air-conditioned using controllable radiators and humidifiers, deviations from the target values (23 °C, 50% RH) were observed. Over the total period of 184 days, the temperature in the reference Room 1 varied between 16.9 °C and 28.7 °C, with an average value of 22.9 °C, and in the test Room 2 between 18.4 °C and 28.6 °C, with an average value of 23.3 °C. The extreme temperature minimum after 93 days was caused by a cold snap with outdoor temperatures of −12 °C. The rising temperatures after 170 days were due to a warm and fair-weather period with maximum values >30 °C and strong global radiation. The average relative humidity was 46% (Room 1) and 44% (Room 2). The short-term deviations from the target value result from the operation of the
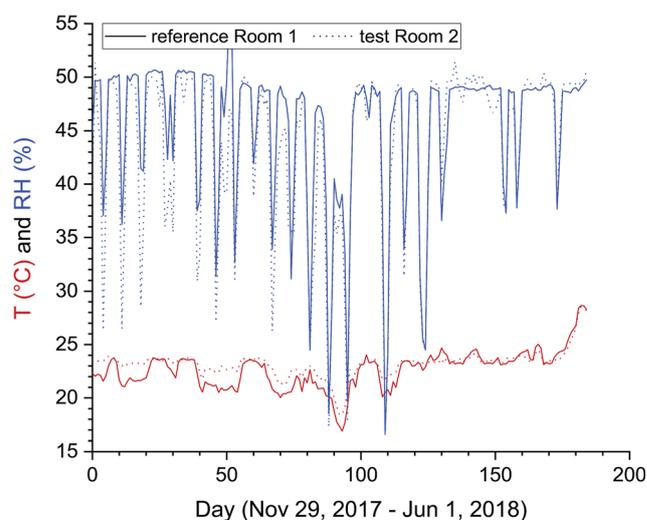

Fig. 2 Temperature and humidity profiles in the reference Room 1 and the test Room 2 between Nov 29, 2017 and Jun 1, 2018 (184 days). The data represent daily averages from recorded 20 min intervals. Temperature, relative humidity and global irradiation in the outdoor air are provided in the ESI.†

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humidifier. The dosage of the quantity of water discharged into the room depends on the fill level of the reservoir.

3.2 SVOCs in the test house air

The chemical properties of the target substances are summarized in Table 2. DiBA and DnBA have similar properties (log K_{OA} ≈ 8, log P_s (Pa) ≈ −1.5). For the other three compounds, K_{OA} and P_s are higher or lower by approx. three orders of magnitude, respectively. All compounds are, however, SVOCs pursuant to the definition in accordance with ISO 16000-6.[38] The ratio of particle and gas phase concentration of the target compound is defined as distribution coefficient K_{ip}. For DiBA, DnBA and DPP, the calculated distribution coefficients between gas phase and airborne particles are $K_{ip} < 10^{-3}$ m³ μg⁻¹. For BBzP K_{ip} is $<10^{-2}$ m³ μg⁻¹ and for DEHA K_{ip} is $<10^{-1}$ m³ μg⁻¹.[28] This means that solely for DEHA it can be expected that a significant proportion (>20%) will accumulate in airborne particles.[28] Measurement of particles was not undertaken for practical reasons during the experimental phase (days 1–184). As the sample was taken from the middle room, sampling lines with a length in excess of 1 m were used, which would have led to major experimental errors due to the assumed organic nature of the particles.[39] Furthermore, the air volumes and volume flows necessary for the determination of PM$_{2.5}$ and PM$_{10}$ would have seriously disrupted the equilibrium in the rooms. However, particle number concentrations were measured at days 481–486.

A typical concentration curve in the test Room 2 is shown in Fig. 3 for the substance DiBA. Following application of the spiked latex paint and the spiked house dust, the initial concentration (day 2) is 20.7 μg m⁻³. Up to day 83 the curve can be fitted to a double exponential function $C(t) = A_1 \times \exp(-k_1 \times t) + A_2 \times \exp(-k_2 \times t) + B$ (OriginPro 2018G, non-linear least squares algorithm). The fast decay process at the beginning of the experiment is expressed by $k_1 = 0.02$ h⁻¹. However, k_1 is significantly smaller than the air exchange, which is due to the constant release of DiBA from the dust. The much smaller kinetic constant $k_2 = 0.001$ h⁻¹ shows that the system is approaching a state of equilibrium, which is attained at day 80. The yellow boxes in Fig. 3 mark the episodes with cold and particularly warm days (see Section 3.1), which are also conspicuous in the concentration profile of DiBA.

Overall, the highest concentrations in the air were measured for DiBA, followed by its isomer DnBA, which has similar properties. The concentrations of the heavier compounds DPP,
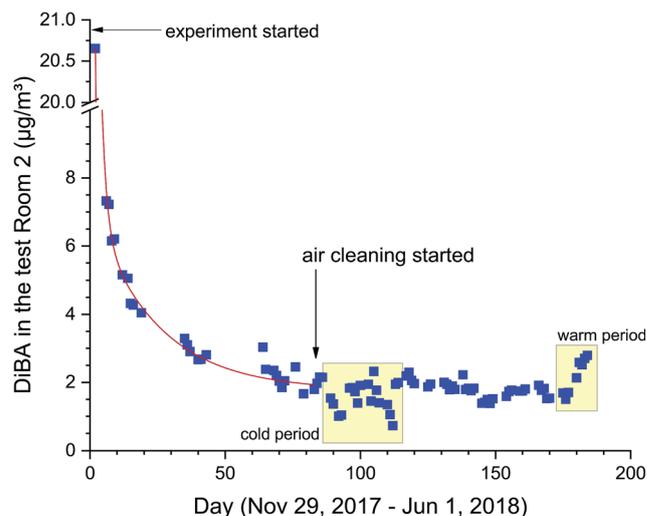

Fig. 3 Concentration *versus* time profile for DiBA in Room 2 between Nov 29, 2017 and Jun 1, 2018 (184 days). The red line represents a double exponential fit to the data between day 2 and day 83. The yellow boxes indicate periods of cold and warm weather, respectively.

BBzP and DEHA were easily measurable but lay consistently below 1 μg m⁻³. The concentration *vs.* time behavior was similar but not identical in Rooms 1 and 2. Surprisingly, the concentrations in the test Room 2 actually scattered slightly less than in the reference Room 1 (see ESI†). In total, approx. 1.5 g DiBA and 1.5 g DnBA were introduced into each room *via* the house dust. The quantities of DPP, BBzP and DEHA applied by means of the latex paint were significantly higher at approx. 200 g per substance and room. In comparison to a further experiment in which di-*n*-butyl phthalate (DnBP, log $K_{OA} = 9.83$, log $P_s = -3.46$ (Pa), calculated using SPARC) was applied as a constituent of latex paint in small and large chambers,[34] the concentrations measured here were considerably lower, despite lower air exchange rates. For DPP, which has similar properties to DnBP, concentrations of significantly less than 1 μg m⁻³ were attained within seven days following the start of the experiment.

A similar experimental design had already been realized at an earlier time by Sukiene *et al.*[32,33] Amongst others, DiBA, DnBA and DEHA were applied as deuterium-marked substances *via* spiked products in test rooms and the concentrations in air and dust were monitored over a period of 12 weeks. The ratio of the air concentrations was analogous to the results described here; the quantities of introduced SVOCs were, however, significantly

Table 2 Chemical properties of the five target compounds

Compound	MW (g mol⁻¹)	bp^a (°C)	Log $P_s{}^a$ (Pa)	Log $K_{OA}{}^a$	$K_{ip}{}^b$ (m³ μg⁻¹)
DiBA	258.4	327.2	−1.35	7.93	1.1×10^{-5}
DnBA	258.4	345.0	−1.53	8.14	2.4×10^{-5}
DEHA	370.6	393.5	−5.07	11.29	2.8×10^{-2}
BBzP	312.4	439.0	−5.43	11.59	1.3×10^{-3}
DPP	306.4	412.0	−4.42	10.72	4.4×10^{-4}

^{a} Data from SPARC On-line Calculator (http://archemcalc.com). ^{b} From Salthammer and Goss.[28] The fraction in the particle phase can be determined from $\Phi = K_{ip} \times [TSP]/(1 + K_{ip} \times [TSP])$, where [TSP] is the concentration of total suspended particulate matter.

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lower. The absolute concentrations of DiBA, DnBA and DEHA were therefore also smaller by approx. one order of magnitude.

The measured TVOC$_{PAS}$ concentrations were of little significance for the experimental design chosen here. Without cleaning measures, the continuously measured concentrations lay within a range of 300 ppb to 500 ppb (relative to propane). Through the operation of the air purifier, the TVOC$_{PAS}$ concentration was reduced by approx. 25–30% (see ESI†). It must, however, be borne in mind that the photo-acoustic method registers in particular small molecules, such as methane, which the device removes from the air only to a small extent. In this respect, the TVOC$_{PAS}$ value is not a criterion for the efficiency of the air-purifying device.

3.3 The effect of cleaning measures

One of the main aspects of this project was the investigation of the influence of cleaning measures on the indoor air concentration of the target substances. The results were comparable for all test conditions and are discussed here using three examples. The air purifier was operated for the first time on day 84 for 5 hours (mode: automatic). The device is conceived for a room area of up to 95 m^2. The Clean Air Delivery Rate (CADR) specifies the quantity of air per time unit which is purified of particles of a certain size under defined test conditions.[40] The stated value of CADR = 393 m^3 h^{-1} for the operated device pertains to cigarette smoke and therefore provides no information concerning the effectiveness as regards the target substances relevant here.

Fig. 4a shows the respective air concentration before, during and following operation of the air purifier. A purifying effect can be clearly observed for DiBA, DnBA and DEHA, but is not evident for DPP and BBzP due to the small concentrations. The effect is, however, only visible during the purifying phase. After switching off the air purifier, the concentration rises back to the original value within 2–3 hours. Fig. 4b shows the results for DiBA from the test protocol between day 126 and day 134. Between day 126 and day 128, the air purifier was operated continuously for 50 hours. On days 132, 133 and 134, the device was switched on for 5 hours per day. Irrespective of the operating time, the concentration of DiBA is reduced from approx. 2 µg m^{-3} to approx. 0.6 µg m^{-3}, which corresponds to a reduction of 70%. However, the effect that the original concentration is swiftly reattained after switching off the device can also be observed here. Fig. 4c once again shows the effect for all target compounds when the air purifier is operated for 5 hours per day on three consecutive days. Here, in contrast to Fig. 4a, the reduction effect can be clearly seen in all cases.

On days 134, 169 and 176, the floor of Room 2 was partially cleaned for a period of 10 minutes using the vacuum cleaner. For this, the room was divided into three equal segments. During each floor cleaning process, a different segment was vacuumed. None of these vacuuming processes has either a short-term or long-term influence on the indoor air concentration of the five target substances. It is, however, known that vacuuming influences the particle concentration in a room.[41]
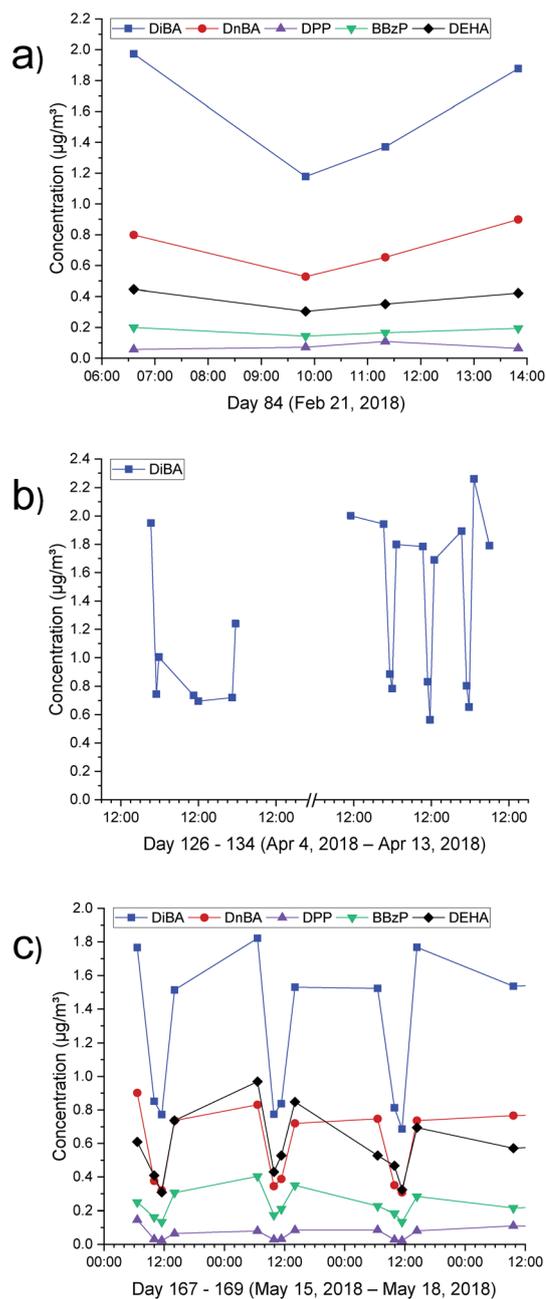

Fig. 4 Effect of cleaning (air purifying) on the air concentration of the target compounds in the test Room 2. (a) The air purifier was continuously operated for 5 h; (b) the air purifier was continuously operated for 50 h between day 126 and day 128 (Apr 4, 2018–Apr 6, 2018). Then the air purifier was continuously operated for five hours per day on days 132, 133 and 134 (Apr 10, 2018–Apr 12, 2018); (c) the air purifier was continuously operated for five hours per day on days 167, 168 and 169 (May 15, 2018–May 18, 2018).

After the end of the experimental phase (day 1–184) both rooms were left unchanged for a certain time (humidifier and radiator on, air cleaner off) and the particle concentrations were continuously measured in Room 1 over five days. During this period the room was vacuumed three times (10 min per event). Without vacuuming activities, the number concentration of

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ultrafine particles (UFP) (5.6–560 nm) was between 5000 # per cm³ and 10 000 # per cm³. Vacuuming significantly increased the UFP level to 15 000–20 000 # per cm³. In case of larger particles (0.3–10 μm) vacuuming had no significant effect on the particle concentration and size distribution. The results are presented in the ESI.† The concentrations of the five target compounds in the room air were not significantly different from the concentrations during the experimental phase (day 80–184).

3.4 SVOCs in materials and house dust

The distribution of an organic compound between gas phase and sedimented dust under equilibrium conditions can be estimated in accordance with Weschler and Nazaroff[12] pursuant to eqn (1).

$$X_{\text{dust,pred}} = \frac{f_{\text{om\_dust}} \times K_{\text{OA}} \times C_{\text{g}}}{\rho_{\text{dust}}} \qquad (1)$$

$X_{\text{dust,pred}}$ is the predicted mass fraction of SVOCs in dust, $f_{\text{om\_dust}}$ is the fraction of organic matter in dust; K_{OA} is the octanol/air distribution coefficient, C_{g} is the concentration of a target compound in the gas phase and ρ_{dust} is the density of the dust.

Although the gas/particle distribution was not measured it can be assumed, on the basis of the published gas/particle distribution coefficients K_{ip} (see Table 2), that more than 90% of DiBA, DnBA, BBzP and DPP are present in the gas phase.[28] For DEHA, with a K_{ip} value of 2.8×10^{-2} m³ μg⁻¹, the fraction in the particle phase Φ may vary within approximately 20% and 60%, depending on the particle concentration.[28] Taking into consideration $f_{\text{OC}} = 0.43$ for the unspiked dust, it can be assumed that the organic proportion $f_{\text{om\_dust}}$ of the spiked dust lies in the range of 0.8–1. With the conservative assumption of a gas phase concentration of $C_{\text{g}} = 0.1$ μg m⁻³ for BBzP, eqn (1) results in $X_{\text{dust,pred}}(\text{BBzP}) = 4 \times 10^4$ μg g⁻¹. Although the calculation of $X_{\text{dust,pred}}$ is subject to errors within an order of magnitude,[26] it becomes clear that the value is considerably higher than the concentrations measured in the collected house dust (see Table 3). This shows that even after several months, the system is still far removed from equilibrium conditions.

Generally, only weak correlations can be observed for the ratio of air to dust concentration.[9,24] The reasons for this lie in the complexity of the indoor conditions and the uncertainty of the analytical procedures. In the experiments performed here, the dust was finely dispersed in the respective room. This, however, in no way guarantees that the distribution across the entire surface of the respective room is homogeneous. Furthermore, as a result of the spiking, the dust exhibits a very high organic content which limits its dispersibility. Areas with higher and lower dust content are therefore to be expected. This assumption is supported by the greatly varying praseodymium values. Moreover, the dust particles might interact with the fibers of the textile floor covering. It can therefore be assumed that the SVOCs migrate from the dust into the floor covering. Carpet fibers are furthermore a strong sink for SVOCs.[42]

A further point concerns the sampling of the floor covering. The extracted pieces had an area of 7 cm × 7 cm. In relation to the total area of the respective room of 33.4 m², this is an area proportion of 1.5×10^{-4}. It is therefore unlikely that the sampled area is representative of the carpet. This is also shown in Table 3. On the whole, the SVOC concentrations of the flooring samples in Rooms 1 and 2 are extremely inconsistent, as are the concentrations of the marker praseodymium (see Table 3). The very highest values for the SVOCs and praseodymium were measured in the sample taken on day 168. Melymuk et al.[43] also monitored SVOCs in different matrices in a residential environment and found that individual dust samples were not necessarily representative of the average room conditions.

Considerably more significant values are obtained through analysis of the contents of the vacuum cleaner bags. In the test Room 2, 5–6 g of dust were collected when 11 m² were cleaned. The concentrations lay between 250 μg g⁻¹ and 800 μg g⁻¹ (DiBA and DnBA), 20 μg g⁻¹ and 50 μg g⁻¹ (DEHA and BBzP) as well as 6000 μg g⁻¹ and 16 000 μg g⁻¹ (DPP). These results are plausible. DiBA and DnBA were constituents of the introduced dust; they are, however, compounds with comparatively high vapor pressures and simultaneously low K_{OA} values. DPP was also added to the dust; the vapor pressure for this substance is, however, three orders of magnitude lower than that of DiBA and DnBA, whilst the K_{OA} value is more than three orders of magnitude higher. DEHA and BBzP were added to the latex paint. Significantly lower concentrations are therefore to be expected for these two compounds, as the enrichment takes place through diffusion via the air pathway.

The experimental activities ended after 184 days but both rooms were left unchanged for another 300 days. Carpet samples (50 cm × 50 cm) were taken on day 453 in both rooms and stripes of 2 cm × 7 cm were analyzed for the five target compounds and praseodymium. The results are presented in the ESI.† Again, high SVOC concentrations roughly correlated with high concentrations of praseodymium. As discussed before, the SVOCs had distributed in the entire room but in case of DPP peak concentrations (43.7 μg g⁻¹, 206.5 mg m⁻²) were only found in Room 1, where no cleaning had occurred. This means that vacuuming is an efficient measure to remove compounds of very low volatility, for which dust provides a reservoir.

3.5 Temperature dependence of the room air concentrations

The mechanism for the release of a substance from a product varies according to the substance and product properties and is correspondingly complex in the case of SVOCs.[44] In general, the temperature dependence of release and distribution processes follows a Van't Hoff approach,[45] which means that the logarithm of the considered value (here: concentration) is, in accordance with eqn (2), proportional to the reciprocal of the temperature.

$$\ln C = A \times \frac{1}{T} + B \qquad (2)$$

Table 3 Results of material and dust analysis

Material	Day	DiBA, µg g^{-1}	DnBA, µg g^{-1}	DEHA, µg g^{-1}	BBzP, µg g^{-1}	DPP, µg g^{-1}	Pr, µg m^{-2}
Room 2 (test room) (air purifier and vacuum cleaner operated)							
Filter air purifier	096	3	4	<LOQ	<LOQ	2	
Filter air purifier	119	5	5	8	3	2	
Filter air purifier	132	21	11	13	2	3	
Filter air purifier	134						
Filter air purifier	169	7	3	12		6	
Sampling bag (dust)	134	288	255	23	24	6533	
Sampling bag (dust)	169						
Sampling bag (dust)	176	646	798	49	47	15 368	
Carpet sample (uncleaned)	133						
Carpet sample (uncleaned)	134	3	2	11	5	7	
Carpet sample (cleaned)	134	3	2	11	6	6	2.3
Carpet sample (uncleaned)	168	29	46	8	7	86	27.6
Carpet sample (uncleaned)	169	4	2	8	7	6	6.0
Carpet sample (cleaned)	169	4	2	8	7	6	6.1
Carpet sample (uncleaned)	176	4	4	16	6	13	
Carpet sample (cleaned)	176	3	<LOQ	7	6	5	
Carpet sample (freshly cleaned)	176	3	<LOQ	9	6	5	
Room 1 (reference room)							
Carpet sample (uncleaned)	133	5	6	3	2	6	
Carpet sample (uncleaned)	134	3	2	7	5	4	
Carpet sample (uncleaned)	168	4	3	22	7	7	3.0
Carpet sample (uncleaned)	169	4	15	12	6	44	8.4
Carpet sample (uncleaned)	176	6	5	7	6	7	

For the five target substances and the reference Room 1, the logarithms of the measured air concentrations against $1/T$ are shown in Fig. 5. In all cases, a distinct temperature dependence can be observed, *i.e.* the concentrations increase with rising temperature. The data can be adjusted in a good approximation through a linear function (see eqn (2)), but in some cases the deviations of individual data from the fit curve were in the range of an order of magnitude. The reasons for this are due to the small temperature window of $\Delta T = 11.8$ K and the analytical error, which increases with lower concentrations.[46] A calculation of the enthalpy, which theoretically results from the linear gradient, was therefore omitted. The linear gradients show that with a temperature increase of 10 K, the air concentration increases by a factor of 3–4. This value lies within the range of the temperature dependence of the thermodynamic variables for the substances examined here.[28] For a substance with the evaporation enthalpy $\Delta H_{vap} = 100$ kJ mol^{-1}, the vapor pressure increases by a factor of 4 when the temperature increases from 291 K to 301 K. This result leads to the conclusion that in this experiment, the distribution processes are controlled by evaporation.

4 Conclusions

The results of the investigations performed here demonstrate the complex dynamic processes within an indoor area, which can only be partially explained by models and predictions.[47] The quantities of SVOCs introduced into the respective rooms of the test house *via* latex paint and house dust were high but not unrealistic, as the proportion of plasticizers in a plastic can certainly amount to 30%.[48] The indoor air concentrations were lower than or comparable to air concentrations in chambers and cells,[25,36,49] higher than in similar experiments carried out by Sukiene *et al.*,[32,33] and within the range of concentrations in real indoor environments.[2,50] Therefore, the measured concentrations can be considered as realistic.

Fundamental conclusions could be drawn from the cleaning activities. The operation of an air-purifying device was efficient
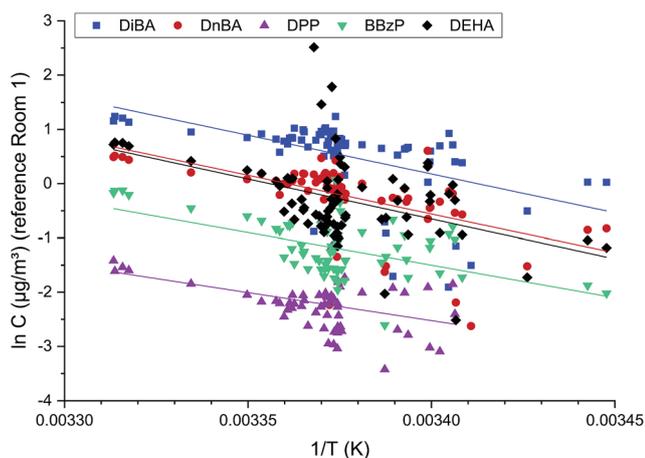

Fig. 5 Plot of the logarithmic air concentration ln C *versus* the reciprocal temperature $1/T$ (in Kelvin) for the five target compounds. The data are taken from the undisturbed reference Room 1 (days 6–184), where no cleaning occurred and were fitted to a straight line.

regarding the five target compounds and reduced their concentrations by approx. 50%. After switching off the device, however, the initial value was reattained within a short time. This shows that the processes leading to the establishment of equilibrium are controlled by evaporation. Vacuum-cleaning of the floor increased the UFP concentration for a short period of time (see ESI†) but did not lead to a reduction of the indoor air concentrations of the target compounds. It must therefore be concluded that the SVOCs had distributed themselves amongst dust, carpet fibers and other surfaces. This also becomes clear from the results of the vacuum cleaner-bag analyses. The DPP added to the dust was still detectable in high concentrations after 176 days, whilst the considerably more volatile compounds DiBA and DnBA were depleted. In this respect, the totality of the room formed the reservoir for the SVOCs after a period of time. However, analysis of the uncleaned (reference Room 1) and cleaned (test Room 2) carpet after 453 days showed that areas of high dust amounts are removed by surface cleaning activities (see Tables SI-1–SI-4†). The losses through air exchange were slight, compared to the quantities introduced. Taking DiBA as an example, the mass removal of this compound through air exchange can be calculated from integration of the data in Fig. 3. When assuming AER = 0.25 h^{-1} (the mean value in the measured range between 0.2 h^{-1} and 0.3 h^{-1}) for the entire experiment over 184 days, the total loss of DiBA is less than 0.5 g.

In summary, the results of the study design provide relevant information on the dynamics of SVOCs in indoor areas with and without disturbance of the equilibrium conditions. Depending on the furnishings and features of the respective room and the activities carried out therein, the substances are subject to diverse distribution processes. As a result, as already demonstrated by Weschler et al.,[9] the attainment of reliable exposure estimates on the basis of models is, for the individual case, difficult to impossible. Reductions of air pollutant concentrations are only possible through increased ventilation or air-purifying measures.

Conflicts of interest

There are no conflicts of interests to declare.

Acknowledgements

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