Received: 4 April 2019 | Revised: 12 August 2019 | Accepted: 18 September 2019

DOI: 10.1111/ina.12605

ORIGINAL ARTICLE

WILEY

Emissions of volatile organic compounds from polymer-based consumer products: Comparison of three emission chamber sizes

Morgane Even[1] | Christoph Hutzler[1] | Olaf Wilke[2] | Andreas Luch[1]

[1]Department of Chemical and Product Safety, German Federal Institute for Risk Assessment (BfR), Berlin, Germany

[2]Division 4.2 – Materials and Air Pollutants, Federal Institute for Materials Research and Testing (BAM), Berlin, Germany

Correspondence
Morgane Even, German Federal Institute for Risk Assessment (BfR), Department of Chemical and Product Safety, Max-Dohrn-Strasse 8-10, 10589 Berlin, Germany.
Email: Morgane.Even@bfr.bund.de

Funding information
Bundesinstitut für Risikobewertung, Grant/Award Number: 1322-559 and 1322-631

Abstract

The ISO 16000 standard series provide guidelines for emission measurements of volatile organic compounds (VOCs) from building materials. However, polymer-based consumer products such as toys may also release harmful substances into indoor air. In such cases, the existing standard procedures are unsuitable for official control laboratories due to high costs for large emission testing chambers. This paper aims at developing and comparing alternative and more competitive methods for the emission testing of consumer products. The influence of the emission chamber size was investigated as smaller chambers are more suited to the common size of consumer products and may help to reduce the costs of testing. Comparison of the performance of a 203 L emission test chamber with two smaller chambers with the capacity of 24 L and 44 mL, respectively, was carried out by using a polyurethane reference material spiked with 14 VOCs during the course of 28 days. The area-specific emission rates obtained in the small chambers were always similar to those of the 203 L reference chamber after a few hours. This implies that smaller chambers can provide at least useful numbers on the extent of polymer-based consumer product emissions into indoor air, thereby supporting meaningful exposure assessments.

KEYWORDS
comparison, consumer products, emission chamber, reference material, size, volatile organic compounds

1 | INTRODUCTION

Indoor pollution levels are often higher than those measured in ambient air.[1] Human beings stay mostly indoors nowadays. We spend 65% of our time at home[2] but also often remain indoors when we work or commute. Air change rates are decreasing because of energy-saving measures and enhanced insulation techniques.[3] This leads to an elevated exposure against VOCs, as the emitted VOCs accumulate in the indoor air and might influence occupants' well-being or health. Construction materials and human activities (eg, cooking, cleaning, and smoking) are regarded as the main sources of indoor VOC pollution. However, complaints about strong and unpleasant odors from polymer-based consumer products point to the need for detailed studies looking into the emissions that arise from these items. Several studies are addressing the identification of off-odorants in toys.[4-6] Such products may release harmful odorants or

non-odorous substances into the indoor air and thus may negatively impact the occupants' health.

The influence of emissions from building materials on indoor air quality has already been studied in detail.[7] So far, the results of the evaluation of inhalation exposure due to polymer-based consumer products (eg, toys and decoration products) are insufficient for the purpose of realistic risk assessments. The emissions of VOCs from consumer products are usually determined with headspace techniques like solid phase micro-extraction-gas chromatography-mass spectrometry (SPME-GC-MS)[8,9] and dynamic headspace-GC-MS (DHS-GC-MS).[10] Nevertheless, data obtained in these studies are not suitable for a proper description of the emission kinetics under consumer-relevant conditions and therefore does not allow a realistic estimation of exposure.

The ISO 16000-9 guideline[11] provides a method for VOC emission measurements from building materials in emission chambers. This document does not give any specifications on chamber sizes, but usually chambers with the volume of 50 to 1000 L are used. The emissions of fragrances from scented toys were studied in the past under ISO 16000-9[11] conditions in a 1000 L chamber.[12] Recently, the emissions of VOCs from "squishy toys" were investigated in 113 L emission chambers[13] while different polymer-based toys were studied in a 203 L chamber,[14] but these chamber volumes are not well adapted to the small size of most consumer products. Moreover, the overall existing standard procedures are unsuitable for market control by official laboratories due to high costs and time consumption. There is therefore a clear need for new methods to perform emission measurements of VOCs from consumer products in an adequate manner.

Currently, there is no sufficient understanding of the correlation between the emission levels measured in chambers of different volumes. Analytical data on VOC emissions from consumer products were published in 2015.[15] Here, variabilities were observed between chambers of different sizes. Similar test conditions (eg, relative humidity) were not rigorously applied between chambers, however, and may also be responsible for the differences observed. In another study, emission concentrations of toluene in three different chambers have been compared.[16] It was shown that results obtained with a 40 mL chamber did not correlate with results obtained in a 30 m^3 or in a 1 m^3 chamber. Again, different area-specific airflow rates were applied which makes comparison difficult. Gunnarsen[17] indeed pointed out the importance of using similar specific airflow rates to be able to compare emission chambers. Other studies observed good correlations between different chamber sizes using constant area-specific airflow: Emission resulting from building materials placed in different emission test chamber was described and compared,[18,19] but only the total VOC and SVOC (semivolatile organic compound) concentrations were reported. In another study,[20] three small chamber test methods for the measurements of VOC emissions from paint were investigated, but the concentrations were only monitored for a relatively short period of time (24 h). Moreover, studies in this research field have been limited to the use of real samples obtained from the market. Yet, the use of a reference material of higher homogeneity should help to ensure more accurate comparisons.

Practical implications

- Besides building materials, children toys and other consumer products can also emit VOCs. The standard emission chambers are not adapted to such product sizes and generate costs that are too high for market control.
- We demonstrate that both 24 L desiccators and 44 mL microchambers can provide useful orientation for exposure assessment, as their results are comparable to those obtained with a regular chamber surrounding a volume of 203 L.
- These smaller chambers can therefore be used to predict and evaluate indoor air concentrations induced by polymer-based consumer products.

This paper presents an approach to compare results from emission experiments in three different test chambers of different sizes. Our systematic emission studies focused on 14 organic substances which are summarized in Table 1. These compounds depict a broad range of physico-chemical properties (volatility, molecular weight, and polarity) and were all detected in polymeric toy or consumer product samples by the official German control laboratories. Most of them were also described in the literature.[4,6,10,13] Experiments were carried out in a standard 203 L emission test chamber and two smaller chambers with volumes of 24 L and 44 mL, respectively, with a spiked reference polyurethane material that contained the 14 substances. The two smaller chambers, widely tested in previous studies,[21-23] would accommodate consumer product sizes much better and should also reduce costs and energy consumption. Moreover,

TABLE 1 VOCs spiked into the polyurethane material (1 mg/g for each) with associated boiling points (T_B), molecular weights (MW), and octanol/water partition coefficients ($LogP_{ow}$)[30]

Name	CAS	T_B(°C)	MW	$LogP_{ow}$
Benzene	71-43-2	80	78	2.1
Toluene	108-88-3	111	92	2.7
m-Xylene	108-38-3	139	106	3.2
p-Xylene	106-42-3	138	106	3.2
o-Xylene	95-47-6	144	106	3.1
Dimethylformamide	68-12-2	153	73	-1.0
Cyclohexanone	108-94-1	156	98	0.8
Phenol	108-95-2	182	94	1.5
Acetophenone	98-86-2	202	120	1.6
2-Phenyl-2-propanol	617-94-7	202	136	1.8
Formamide	75-12-7	210	45	−0.8
Isophorone	78-59-1	215	138	1.6
Naphthalene	91-20-3	218	128	3.3
Dodecanol	112-53-8	259	186	5.1

TABLE 2 Parameters for test chamber experiments

Chamber	Vötsch	Desiccator	Microchamber
Volume (L)	203	24.0	0.0440
Sample-exposed surface (cm^2)	266	60.0	2.67
Loading L (m^2/m^3)	0.131	0.250	6.07
Air change rate n (h^{-1})	0.502	1.01	26.1 → 30.7
Area-specific airflow rate ($m^3/[m^2 \times h]$)	3.83	4.04	4.28 → 5.06

the microchamber device enables to study six 44 mL emission chambers in parallel.

2 | MATERIALS AND METHODS

2.1 | Chemicals

The VOC ingredients under consideration and their physico-chemical properties are listed in Table 1. Compounds were supplied from Merck and Sigma-Aldrich. Ethyl acetate of analytical grade was obtained from Merck and used as an organic solvent for all solutions.

2.2 | Materials

For the characterization of emission profiles, standard plasticized polyurethane reference material plates doped with 12 different VOCs (the three xylene isomers are considered as a single substance) at a target concentration of 1 mg/g were custom synthesized by Polymaterials AG. This concentration is suitable for the characterization of all substances' emissions while still being realistic for highly contaminated materials. Similar VOC concentrations were used in previous studies in a PVC reference material[12] or in a lacquer.[22] The plates had DIN A4 dimensions (21.0 cm × 29.7 cm) with a thickness of 6 ± 0.2 mm and Shore 70. Pieces were cut from the plate to fit to each chamber's size: 12 cm × 10 cm for the 203 L chamber, 6 cm × 4 cm for the 24 L chamber, and Ø 10 mm for the 44 mL microchambers, respectively. Cutting metal utensils were cleaned twice with ethyl acetate and dried in the laboratory air before use. Until usage, the reference materials were kept at −18°C in gas-tight bags made of aluminum composite-layer film. Before starting the measurements, the pieces of reference material were allowed to adapt to room temperature and the bags were opened immediately before loading the chambers.

2.3 | Emission chambers

Three different emission test chamber types (203 L, 24 L, and 44 mL) were used for emission testing, along with a clean air supply system. The 203 L chamber was the standard VOC emission test chamber model VCE 200 from Vötsch Industrietechnik (Balingen-Frommern, Germany) with an inner chamber made of electro-polished stainless steel and a ventilator to ensure homogeneous air distribution. The 24 L chamber

TABLE 3 Analytical parameters: retention times (RT), calibration range, determination coefficient (R^2), internal standards (ISTD), ISTD concentration (C_{ISTD}), split modus, and quantifier and qualifier ions

	Name	RT (min)	Calibration range (ng)	R^2	ISTD		C_{ISTD} (ng/µl)	Split 400	Splitless	Quantifier (m/z)	Qualifier 1 (m/z)	Qualifier 2 (m/z)
a	Benzene	6.70	100-20 000	0.997	*n*	Benzene-d_6	1000	x		78	52	77
b	Toluene	8.29	100-20 000	0.996	*n*	Benzene-d_6	1000	x		91	92	-
c	m/p-Xylene	9.96	50-10 000	0.999	*o*	p-Xylene-d_{10}	500	x		91	106	-
d	o-Xylene	10.18	0.1-20	0.997	*o*	p-Xylene-d_{10}	2		x	91	106	-
e	Dimethylformamide	8.29	50-10 000	0.996	*n*	Benzene-d_6	1000	x		73	44	-
f	Cyclohexanone	10.38	50-10 000	0.999	*n*	p-Xylene-d_{10}	500	x		55	98	69
g	Phenol	11.19	0.2-50	0.988	*o*	Acetophenone-d_8	2		x	94	66	65
h	Acetophenone	12.99	20-5000		*p*	Acetophenone-d_8	200	x	x	105	77	120
i	2-Phenyl-2-propanol	13.20	10-2000	0.999	*p*	Acetophenone-d_8	200	x		121	77	43
j	Formamide	6.74	10-2000	0.999	*n*	Benzene-d_6	100		x	45	44	43
k	Isophorone	13.83	20-5000	0.996	*q*	Cyclodecane	200	x		82	138	-
l	Naphthalene	15.09	20-5000	0.996	*q*	Cyclodecane	200	x		128	127	102
m	Dodecanol	19.54	0.2-50	0.982	*r*	Dodecanol-d_{25}	2		x	55	69	83

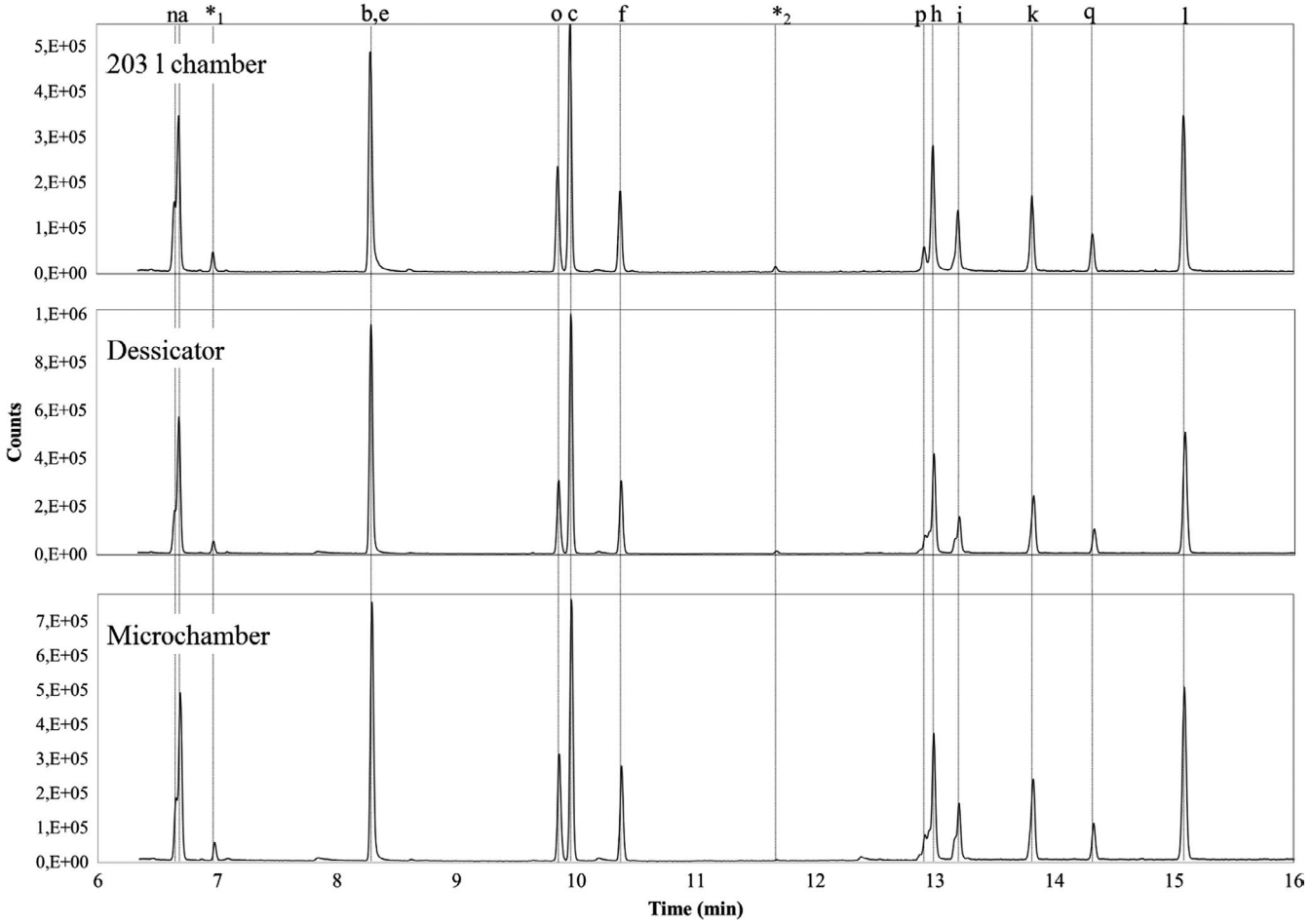

FIGURE 1 GC/MS chromatograms in scan mode (split: 1:400). Above: sampling from 203 L emission chamber after 32.1 h; middle: sampling from the 24 L desiccator after 31.2 h; below: sampling from the 44 mL microchamber after 31.6 h; $*_1$:1-ethoxy-butane; $*_2$: α-methylstyrene

was a homemade desiccator made of glass and equipped with a ventilator. The two 44 mL chambers were part of a micro-Chamber/Thermal Extractor device (μCTE®) from Markes. The samples were placed on metal carriers in the bigger chambers (easel in the 203 L and mesh in the 24 L) while they were placed on the bottom of the microchambers. The whole exposed surface was subsequently considered for area-specific emissions; the edges have a much bigger influence in the microchamber where the material piece is much smaller. The systems were set up in compliance with ISO 16000-9[11] to a temperature of 23°C ± 2°C and 50% ± 5% relative humidity. The air change rate in the 203 L chamber was set to 0.5/h (in line with ISO 16000-9[11]). In the other chambers, the air change rate was adapted to the chamber loading to obtain a similar area-specific airflow rate (ratio of air change rate to loading) in every chamber; detailed parameters can be found in Table 2.

2.4 | Air sampling

Active air sampling was performed using glass tubes (6 × 0.4 cm i.d. × 0.6 cm o.d.) from Gerstel filled with Tenax® TA. Active sampling of 600 mL was carried out for the 203 and 24 L chambers using Gillian Dual Mode Low Flow Sample pump (Sensidyne) with an airflow of 100 mL/min. For the 44 mL microchambers, air was sampled at the outlet for 30 minutes with 19.3 ± 0.3 mL/min for the first trial and 22.3 ± 0.3 mL/min for the second trial; resulting in sampled volumes close to 600 mL. Blank samples were taken before measurements started to ensure low blank values of the chambers. Different air samples were regularly collected over 28 days after loading the chambers. Two samples were collected for each time point, successively in the 203 and 24 L chambers and simultaneously in two identical microchambers. Prior to sampling, tubes were conditioned over 3 hours with a nitrogen flow of 75 mL/min at 300°C. One microliter of internal standard solution in ethyl acetate, stored in a freezer (−18°C), was then manually spiked with a rinsed 1 μL microvolume syringe (Trajan, Victoria, Australia) onto the desorption tubes and dried with 100 mL laboratory air at a flow rate of 100 mL/min. The tubes were stored and transported in tight plastic containers from Gerstel at room temperature and subsequently loaded and analyzed within one week.

2.5 | Analytical conditions

Thermal desorption was performed in a Thermal Desorption Unit (TDU, from Gerstel) connected to an Agilent 6890 gas

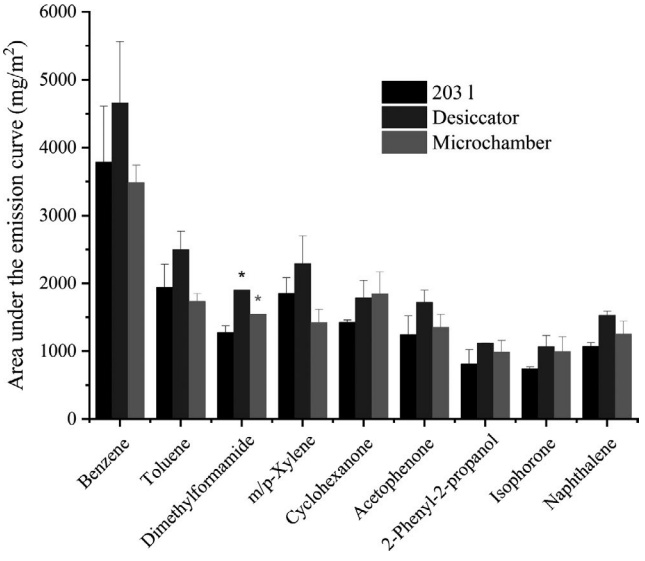

FIGURE 2 Total emission values during 28 d (area under the emission curve); repeated once, *: single measurements

chromatograph (Agilent) coupled with an Agilent 5975 mass selective detector. A helium gas flow of 280 mL/min and the following temperature program were used: 25°C for 0.2 minutes, then increase at 700°C/min to 280°C, and finally held for a further 2 minutes. During thermal desorption, analytes were cryotrapped with liquid nitrogen from Linde at −150°C in the Cold Injection System 4 (CIS) from Gerstel equipped with a liner filled with deactivated glass wool. After desorption, the CIS was heated up to 285°C at 12°C/s and then held for 15 minutes. For each sampling time point, two different methods were used for the two sampled tubes: One tube was analyzed in splitless mode while the other one was analyzed with a split 1:400 at CIS to allow every analyte to be quantified in its linear range (see Table 3).

The gas chromatograph (GC) was equipped with a DB-5MS column, 1.0 µm (60 m × 0.32 mm i.d.) (J & W Scientific). Helium gas (purity ≥ 99.999%) from Linde was used as a carrier gas at a constant flow of 1.4 mL/min. The GC oven temperature started at 45°C for 0.5 minutes, was heated up to 200°C at 12°C/min, held for 5 minutes then heated up to 280°C at 20°C/min and held for 10 minutes.

The temperatures of the transfer line, quadrupole, and ion source were 295, 150, and 230°C, respectively. The mass spectrometer (MS) was used in combined SIM-Scan mode. The mass range in full scan was 40 to 450 m/z with a scan rate of 3.5/s. The target compounds were identified by comparison of their retention times and mass spectra with those of authentic standards. Quantification was done with SIM data for each compound present in the plate and internal standard. One quantifier and one or two qualifier ions were used (see Table 3), with dwell times of 10 ms.

The overall procedure (chamber loadings, air samplings, and analysis) was repeated with another identical polyurethane plate for quality assurance purposes.

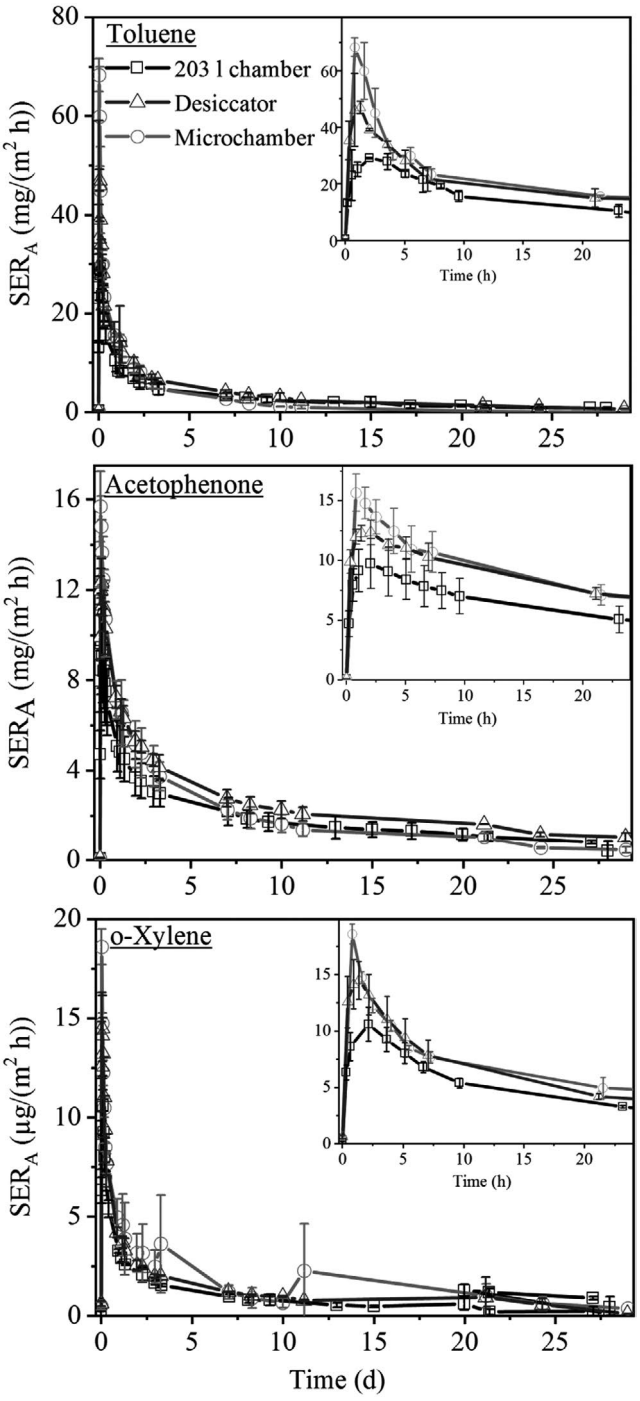

FIGURE 3 Emission profiles of three selected analytes from the polyurethane plate obtained in three different emission chambers; bigger frame: 28 d profile; smaller frame: 24 h profile; repeated once

2.6 | Quantitative analysis of VOC emissions

VOCs emitted from the reference polyurethane plate were quantified by internal calibration. One microliter of the prepared solution in ethyl acetate, stored in a freezer (−18°C), was manually spiked onto the desorption tube with a rinsed 1 µL microvolume syringe from Trajan and then dried with 600 mL laboratory air at 100 mL/

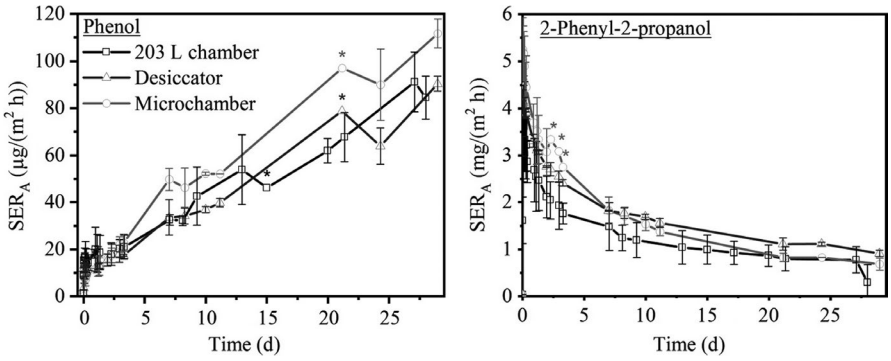

FIGURE 4 Twenty-eight d emission profiles of two substances containing a hydroxyl group each. Profiles were obtained from the polyurethane plates in three different emission chambers (repeated once, or *: single measurements)

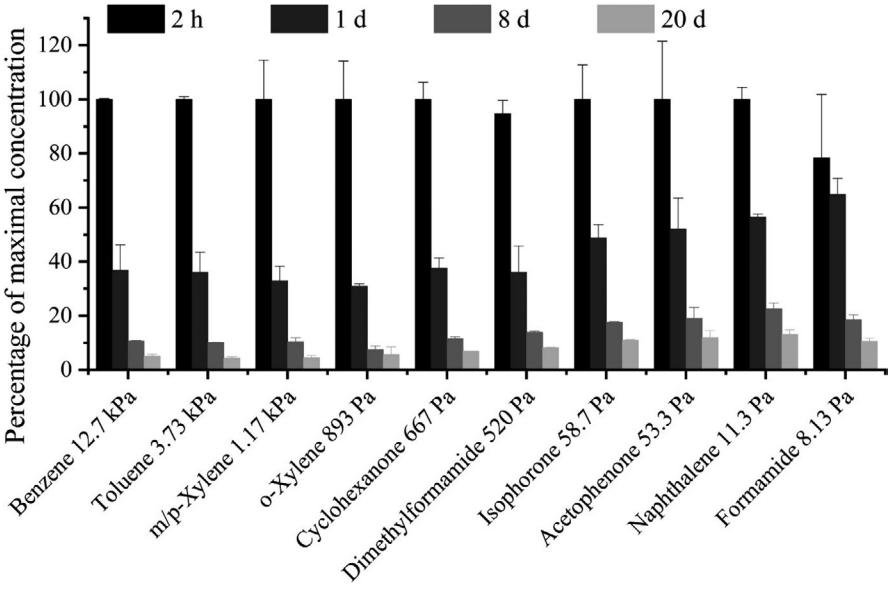

FIGURE 5 Percentage of maximal concentration obtained for selected analytes with various vapor pressures from the polyurethane plate at different time points in the 203 L chamber; repeated once

min. Subsequently, the desorption tubes for calibration were analyzed in the same way as the desorption tubes that contained the collected air samples. Calibration ranges and split modes can be found in Table 3, calibrations were not weighted.

Data were treated with the Mass Hunter Quant Software (B.05.00). To compensate for slight area-specific airflow differences between the chambers, the results are calculated as area-specific emission rates (SER$_A$) in accordance to ISO 16000-9.[11]

3 | RESULTS AND DISCUSSION

3.1 | Chamber comparison

The chromatograms obtained from air samples taken around 31 hours after the chambers were loaded with the reference material are depicted in Figure 1. Similar profiles can be observed in the three chambers where the same peaks were identified with comparable intensities. The sample from the 203 L chamber showed smaller intensities than the samples from the 24 L and 44 mL chambers. Peaks that did not originate from the VOCs in the reference material could be identified in all samples: 1-ethoxy-butane is an impurity arising from ethyl acetate used as solvent for internal standards. It was also found in blank and calibration samples, whereas α-methylstyrene was not found in chamber blanks and, therefore, probably was released from the material itself. α-Methylstyrene is not a common substance for polyurethane, however, but is used to synthesize poly(α-methylstyrene)[24] and may thus arise from contamination during material synthesis.

The total amount emitted per surface unit over 28 days can be calculated from the area under the emission curve. Data for all substances analyzed in split mode can be found in Figure 2: The three chambers led to similar total emission levels for all of these VOCs. It was also noticed that results from the 24 L chamber were always slightly higher. This cannot be explained by a higher sink effect, which is caused by compound-dependent adsorption at the surface of the chamber wall, because the two other chambers consist of stainless steel, which is unknown to have stronger adsorption properties than glass.[25] More likely, this observation was caused from an over-estimation of the airflow in the desiccator as it can, in contrast to the other chambers, only be measured before the experiment and not continuously. The area-specific emission rate could therefore be over-estimated as it is depending on the air change rate.

The emission profiles of three selected analytes from the polyurethane plate obtained in the three emission chambers are shown in Figure 3. Similar area-specific emission rates can be observed from standard material in the three chambers over 28 days. But the emission profile for the 24 L desiccator chamber is always higher

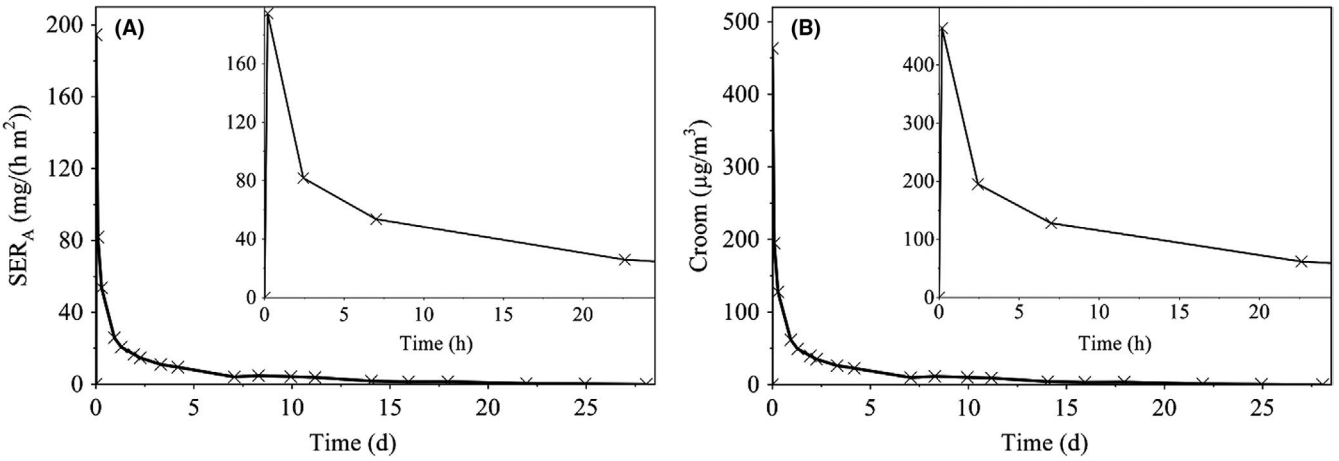

FIGURE 6 Area-specific emission rate of cyclohexanone from a 12 mm diameter piece from a PVC toy figurine placed in a 44 mL microchamber (A) and resulting calculated air concentration for the whole figurine in a 30 m^3 room (B); bigger frame: 28 d profile; smaller frame: 24 h profile

compared with the other chambers. This finding can again be explained by possible over-estimation of the corresponding air change rate. In the first hours, it could be observed that the emission rate was higher for smaller chambers. This observation becomes even more important for more volatile substances like toluene or xylene compared with acetophenone. This probably results from the smaller distance between the sampling location and the source, as well as the higher air change rate in the smaller chambers. The profiles adjust to each other after a few hours of equilibration.

3.2 | Substance-specific emission profiles

Different emission profiles were observed depending on substance properties. Substances containing a hydroxy group led to different emission profiles in comparison with the others. It is shown in Figure 4 that phenol followed a continuous increase while 2-phenyl-2-propanol levels decreased more slowly than the substances shown in Figure 3. The synthesis of the polyurethane plates was based on the reaction of an isocyanate with a polyol. It therefore seems possible that the isocyanate partly bounds to the hydroxyl groups of some VOCs causing a much slower release when compared to other substances of the same volatility. Yet, the emission curves were comparable in all three chambers. Dodecanol is not shown in the figures because it depicted barely detectable emission due to its low volatility. Further emission curves are presented in the Figure S1.

In Figure 2, it can be observed that substances with a higher volatility, such as benzene, were released at total quantities higher when compared to substances with lower volatility like isophorone. It is known that benzene can run through Tenax® (adsorption of only a part of the applied quantity).[26] Preliminary experiments were able to confirm that benzene was the only target analyte that significantly passed Tenax® (eg, 20.5% breakthrough for 100 ng on tube and 1 L air at 100 mL/min). This breakthrough behavior should, however, be compensated by the calibration performed on Tenax® tubes and the fact that an internal standard with close structure (benzene-d_6) was used. Benzene quantities may have been over-estimated, however, because during calibration, the whole quantity is applied at the beginning, possibly leading to a higher breakthrough than during the sampling where the quantity is applied continuously.

While most VOCs reach their maximum levels after 2 hours in the 203 L chamber, the levels of substances tend to decrease with different rates depending on their volatility. The diagram in Figure 5 shows that volatile compounds like toluene decreased more rapidly, with only 4.3% of the maximum concentration remaining after 20 days, compared with less volatile substances like naphthalene (13.2% of maximal concentration after 20 days).

3.3 | Derivation of approximate room concentration from microchamber experiments

As it was shown with a standard material that the microchamber provided similar area-specific emission rates in comparison to the widely used bigger chamber models (except in the first hours of studies), microchambers can be further used for the cost-effective study of the emissions from small or homogeneous consumer products. In such circumstances, the area-specific emission rate from a small piece in the microchamber and a whole toy in a 203 L chamber would be considered equal after a few hours if the area-specific airflow rates are the same. From the value of the area-specific emission rate, the resulting concentrations in a real room with a volume of 30 m^3, for example,[27] can be approximated via the following formula[28]:

$$C = \frac{SERa^*A}{n^*V}$$

With C being the indoor air concentration in µg/m^3, SERa the area-specific emission rate in µg/(h/m^2), A the product surface area in m^2, n the air change rate in h^{-1}, and V the room volume in m^3.

In Figure 6, an example with emissions from a PVC toy figurine is shown: Cylohexanone was the main substance emitted. From the

study of a 12 mm diameter piece of this figurine in the microchamber, it became possible to calculate the resulting indoor air concentration for the whole toy. VOCs usually exhibit low sink effect in emission chambers but for semivolatile compounds (SVOCs), the derivation of an indoor air concentration based on the emission rate in an emission chamber could be incorrect. As for the reference material, a quick decrease of the emission levels is observed directly after chamber loading, which means that the first hours or days after unpacking are of relevance for an exposure assessment of cyclohexanone from such products. This cost-effective approach can also be used for more efficient testing of building or automobile materials if the homogeneity of the material is high enough that the study of one small piece can be representative.

3.4 | Limitations and key points

The standard reference plate spiked with 1 mg/g emitted high VOC concentrations, especially in the first hours (eg, up to 14 mg/m^3 for benzene in the 203 L chamber), raising the question whether the correlation would also be verified with lower emissions. However, on day 3 and 28, where the chamber concentrations are usually compared with guideline values,[28] the levels were already much lower (eg, 2.9 and 0.42 mg/m^3, respectively for benzene). Values were often in the range of the lowest concentration of interest[29] at day 28 (eg, 0.26 mg/m^3 for cyclohexanone). Moreover, a few compounds had much lower emission levels than the majority (eg, maximum chamber concentrations of 0.44 µg/m^3 for o-xylene and 24 µg/m^3 for phenol) and depicted a good correlation in the 3 chambers (Figures 3 and 4). The same plate was also used to compare its emissions with toy samples[14]: The emitted concentrations were much higher compared with emissions of real samples, but the emission profile shapes were very similar to, for example, PVC-based consumer products.

Ultimately, the goal for market control is not only to downscale the emission chamber size, but also to create emission results in shorter periods of time. For this purpose, individual time points obtained after short-term tests and showing a good correlation between chambers should be chosen. A good correlation point for our data set would, for example, be after 3 days: The relative standard deviation between the 3 chambers varied from 5.8% for benzene to 22.9% for 2-phenyl-2-propanol (1-dodecanol was excluded because it was barely detected). Smaller chambers would in this context be very useful to pre-select samples and save capacity of the bigger ones. However, for a complete exposure assessment, a long-term emission profile should be studied to address acute as well as chronic exposure. To this end, the emission profile of phenol from the standard plate should therefore be, for example, studied longer as the emissions were found to be still rising in the last days of the study.

The differences of this study compared with previous emission studies were summarized in the introduction: This study is the first one to compare different emission chamber sizes with a polymer-based reference material which is homogeneous and therefore leads to more reliable results. By using uniform parameters (temperature, humidity, and area-specific airflow rate) for the three chambers, it expands the understanding of correlation between emission chamber sizes as similar area-specific emission rates were observed. However, these results are not valid in any circumstance: In liquid[15] or foam[14] samples, different emission processes are supposed to take place and the correlation is probably different. Also, it should be noticed that the loading of the sample into the chamber should not inhibit the flow circulation, especially in the microchamber where the height of the sample might affect the air stream.[21] The key point to obtain similar results is therefore the use of adequate parameters (eg, temperature, humidity, and area-specific airflow rate) and a solid polymer-based matrix.

4 | CONCLUSION

In this study, the potential of small emission chambers was assessed to provide useful results for exposure assessment of VOCs from polymer-based consumer products. It was shown that comparable emission results can be obtained for VOCs from a polyurethane reference material in three emission chambers with the capacity of 203 L, 24 L, and 44 ml, respectively: The total amounts of VOCs emitted per surface unit as well as the area-specific emission rates over time were similar. Thus, small emission chambers can be used to study the emission of VOCs from small products or to perform meaningful preliminary tests for bigger samples. Such methods would be helpful to effectively generate data regarding the levels of emitted VOCs from consumer products and to provide a better overview on the current market. In case of possible health risks for consumers, official control laboratories will need efficient standardized methods to support their routine work.

ACKNOWLEDGEMENTS

We acknowledge the BfR intramural financial support of our studies (project grants 1322-631 and 1329-559) and thank Karsten Schön and Doris Brödner for excellent technical assistance.

ORCID

Morgane Even https://orcid.org/0000-0002-0241-8860

REFERENCES

1. McDonald BC, de Gouw JA, Gilman JB, et al. Volatile chemical products emerging as largest petrochemical source of urban organic emissions. *Science*. 2018;359(6377):760-764.
2. Brasche S, Bischof W. Daily time spent indoors in German homes-baseline data for the assessment of indoor exposure of German occupants. *Int J Hyg Environ Health*. 2005;208(4):247-253.
3. Hirsch T, Hering M, Bürkner K, et al. House-dust-mite allergen concentrations (Der f 1) and mold spores in apartment bedrooms before and after installation of insulated windows and central heating systems. *Allergy*. 2000;55(1):79-83.

4. Denk P, Velasco-Schon C, Buettner A. Resolving the chemical structures of off-odorants and potentially harmful substances in toys-example of children's swords. *Anal Bioanal Chem*. 2017;409(22):5249-5258.
5. Wiedmer C, Velasco-Schon C, Buettner A. Characterization of off-odours and potentially harmful substances in a fancy dress accessory handbag for children. *Sci Rep*. 2017;7(1):1807.
6. Wiedmer C, Buettner A. Quantification of organic solvents in aquatic toys and swimming learning devices and evaluation of their influence on the smell properties of the corresponding products. *Anal Bioanal Chem*. 2018;410(10):2585-2595.
7. Brown VM, Crump DR, Harrison PT. Assessing and controlling risks from the emission of organic chemicals from construction products into indoor environments. *Environ Sci Process Impacts*. 2013;15(12):2164-2177.
8. Masuck I, Hutzler C, Luch A. Investigations on the emission of fragrance allergens from scented toys by means of headspace solid-phase microextraction gas chromatography-mass spectrometry. *J Chromatogr A*. 2010;1217(18):3136-3143.
9. Lattuati-Derieux A, Bonnassies-Termes S, Lavédrine B. Identification of volatile organic compounds emitted by a naturally aged book using solid-phase microextraction/gas chromatography/mass spectrometry. *J Chromatogr A*. 2004;1026(1–2):9-18.
10. Marc M, Formela K, Klein M, Namiesnik J, Zabiegala B. The emissions of monoaromatic hydrocarbons from small polymeric toys placed in chocolate food products. *Sci Total Environ*. 2015;530–531:290-296.
11. Standardization IOf. Indoor air DIN EN ISO 16000. In. Part 9-Determination of the emission of volatile organic compounds from building products and furnishing - Emission test chamber method (ISO 16000-9:2006); German version EN ISO 16000-9:2006: Beuth Verlag, 10772 Berlin; 2006.
12. Masuck I, Hutzler C, Jann O, Luch A. Inhalation exposure of children to fragrances present in scented toys. *Indoor Air*. 2011;21(6):501-511.
13. Analysis and risk assessment of fragrances and other organic substances in squishy toys. Danish EPA; August 2018.
14. Even M, Girard M, Rich A, Hutzler C, Luch A. Emissions of VOCs from polymer-based consumer products: from emission data of real samples to the assessment of inhalation exposure. *Front Pub Health*. 2019;7:202
15. Bartzis J, Wolkoff P, Stranger M, et al. On organic emissions testing from indoor consumer products' use. *J Hazard Mater*. 2015;285:37-45.
16. Rizk M, Verriele M, Mendez M, et al. Data on comparison between FLEC and CLIMPAQ methods used for fast sorption measurements of VOCs on building materials. *Data Brief*. 2016;7:518-523.
17. Gunnarsen L, Nielsen PA, Wolkoff P. Design and Characterization of the CLIMPAQ, Chamber for Laboratory Investigations of Materials, Pollution and Air Quality*. *Indoor Air*. 1994;4(1):56-62.
18. Jann O, Wilke O, Brödner D.Procedure for the determination and limitation of voc-emissions from furnitures and coated wood based products. Paper presented at: Healthy Buildings/IAQ1997; Washington DC, USA.
19. Wilke O, Jann O, Brodner D. VOC- and SVOC-emissions from adhesives, floor coverings and complete floor structures. *Indoor Air*. 2004;14(Suppl 8):98-107.
20. Afshari A, Lundgren B, Ekberg LE. Comparison of three small chamber test methods for the measurement of VOC emission rates from paint. *Indoor Air*. 2003;13(2):156-165.
21. Schripp T, Nachtwey B, Toelke J, et al. A microscale device for measuring emissions from materials for indoor use. *Anal Bioanal Chem*. 2007;387(5):1907-1919.
22. Nohr M, Horn W, Wiegner K, Richter M, Lorenz W. Development of a material with reproducible emission of selected volatile organic compounds - mu-Chamber study. *Chemosphere*. 2014;107:224-229.
23. Richter M, Mull B, Horn W, Brödner D, Mölders N, Renner M. Reproducibly emitting reference material on thermoplastic polyurethane basis for quality assurance/quality control of emission test chamber measurements. *Build Environ*. 2017;122:230-236.
24. Gies AP, Ellison ST, Vergne MJ, Orndorff RL, Hercules DM. MALDI-TOF/TOF CID study of poly(alpha-methylstyrene) fragmentation reactions. *Anal Bioanal Chem*. 2008;392(4):627-642.
25. Uhde E.Vergleich von Emissionsprüfkammern: Untersuchungen unter dynamischen Bedingungen [Doctoral]. Germany: Naturwissenschaftlichen Fakultät, Technischen Universität Carolo-Wilhelmina zu Braunschweig; 1998.
26. Khan A, Szulejko JE, Kim KH, et al. A comparison of figure of merit (FOM) for various materials in adsorptive removal of benzene under ambient temperature and pressure. *Environ Res*. 2018;168:96-108.
27. DIN. EN 16516:2018 Construction Products - Assessment of Release of Dangerous Substances - Determination of Emissions into Indoor Air. German version EN ISO 16516:2017. Berlin: Beuth Verlag (2018).
28. AgBB - Evaluation procedure for VOC emissions from building products, Part 3 - LCI values. https://www.umweltbundesamt.de/sites/default/files/medien/355/dokumente/agbb_evaluation_scheme_2018.pdf. Published 2018. Accessed July 12th, 2019.
29. EUR 26168 EN Report No 29 of the European Collaborative Action Urban air, indoor environment and human exposure „Harmonisation framework for health based evaluation of indoor air emissions from construction products in the European union using the EU-LCI concept", European union;2013.
30. The PubChem project. https://pubchem.ncbi.nlm.nih.gov/. Accessed July 12th, 2019.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Even M, Hutzler C, Wilke O, Luch A. Emissions of volatile organic compounds from polymer-based consumer products: Comparison of three emission chamber sizes. *Indoor Air*. 2020;30:40–48. https://doi.org/10.1111/ina.12605