# Characterization of the emissions of volatile organic compounds from polymer-based consumer products: towards a realistic exposure assessment

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by
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1st Reviewer: Prof. Dr. Dr. Andreas Luch

2nd Reviewer: Prof. Dr. Daniel Klinger

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# Erklärung

Hiermit versichere ich, dass ich die vorliegende Dissertation mit dem Titel “ Characterization of the emissions of volatile organic compounds from polymer-based consumer products: towards a realistic exposure assessment” ohne Benutzung anderer als der zugelassenen Hilfsmittel selbstständig angefertigt zu haben.

Alle angeführten Zitate sind als solche kenntlich gemacht. Die vorliegende Arbeit wurde in keinem früheren Promotionsverfahren angenommen oder als ungenügend beurteilt.

Berlin, den 15. Juni 2021

Morgane Even

Die Dissertation wurde in englischer Sprache verfasst.

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## Abstract

While technological improvements enable the production of a myriad of new products, assuring consumer safety has become an essential preoccupation for authorities. Indeed, consumers are potentially exposed to chemical risks with health consequences upon product usage. Polymer-based products have proliferated around the globe in the last decades and are appreciated for their cheap and flexible usage. However, they also often release hazardous substances that may be ingested, dermally absorbed or inhaled. This thesis focuses on the emissions of volatile organic compounds (VOCs) from plastic-based and wooden consumer products such as toys. Exposure data to apprehend the risks arising from such articles are scarce although the affected consumer group of children represent a vulnerable population.

This data gap on exposure assessment is largely due to a lack of adequate analytical methods. Strategies existing for emission measurements from construction products are unsuitable for consumer products: Large emission test chambers (50 L to 20 $m^3$) are not adapted to consumer product size. Alternative and more economical methods such as dynamic headspace (DHS, 20 mL or 1 L), microchambers (44 or 114 mL), glass chambers (24 L) and the flask method were investigated in this thesis. DHS sampling allowed semi-quantitative emission results and was further used for sample pre-selection. Both microchambers and 24 L glass chambers provided results that correlate with bigger emission test chambers: These devices would be suitable for market surveillance. The standardized flask method for formaldehyde emissions from wooden toys was not appropriate for exposure assessment.

Furthermore, an assessment of the potential exposures from polymer-based consumer products was carried out. First, the samples were selected via DHS sampling and the constituting polymers were characterized. Then, the high-emitting samples were studied in conventional emission test chambers, 24 L glass chambers or microchambers. An exposure assessment was performed considering indoor air scenarios for short-term (a few hours) to long-term (28 days) exposure. Results were compared to existing toxicologically based guideline values. Emitted concentrations from single products do not typically exceed thresholds. However, scenarios with numerous products or smaller breathing zones are more concerning. Indeed, the cyclohexanone guideline value was exceeded during the study of the exposure from costume masks investigated with a doll’s head setup.

This work is the first to systematically examine strategies for inhalation exposure assessment in official control laboratories. The exposure assessment data generated in the frame of this thesis give insights in the possible health risks associated with the use of polymer-based consumer products.

# Zusammenfassung

Während die Herstellung einer Vielzahl neuer Produkte durch technologische Entwicklungen ermöglicht werden, ist die Gewährleistung der Verbrauchersicherheit zu einem wesentlichen Anliegen für die Behörden geworden, da Verbraucher bei der Verwendung des Produkts potenziell chemischen Risiken mit gesundheitlichen Folgen ausgesetzt sind. Produkte auf Polymerbasis haben sich in den letzten Jahrzehnten weltweit verbreitet und sind wegen ihrer kostengünstigen Herstellung und flexiblen Verwendung beliebt. Sie setzen jedoch häufig gefährliche Substanzen frei, die über den Mund, die Haut oder die Atemwege aufgenommen werden können. Diese Arbeit legt den Fokus auf die Emissionen flüchtiger organischer Verbindungen (VOCs) aus Bedarfsgegenständen auf Kunststoff- und Holzbasis wie Spielzeug. Die betroffene Verbrauchergruppe der Produkte, Kinder, sind gegenüber den gesundheitlichen Risiken dieser Emissionen besonders empfindlich. Dennoch existieren für diese Artikel kaum Expositionsdaten, aus denen sich eine Risikobewertung ableiten lässt.

Diese Datenlücke ist größtenteils auf den Mangel an geeigneten Analysemethoden zurückzuführen. Die bestehenden Strategien für die Emissionsmessungen aus Bauprodukten sind für Bedarfsgegenstände ungeeignet: Große Emissionsprüfkammern (50 L bis 20 m$^3$) sind nicht an die Größe der Verbraucherprodukten angepasst. In dieser Arbeit wurden alternative und wirtschaftlichere Methoden wie die dynamische Headspace-Technik (DHS, 20 mL oder 1 L), Mikrokammern (44 oder 114 mL), Glaskammern (24 L) und die Flaschen-Methode untersucht. Die DHS-Technik ermöglichte semi-quantitative Emissionsergebnisse und wurde daher für die Probenvorauswahl verwendet. Sowohl die Mikrokammern als auch die 24-L-Glaskammern lieferten Ergebnisse, die mit größeren Emissionsprüfkammern korrelieren: Diese Geräte sind für die Marktüberwachung geeignet. Die standardisierte Flaschen-Methode für die Untersuchung von Formaldehydemissionen aus Holzspielzeug erwies sich als ungeeignet für die Expositionsabschätzung.

Darüber hinaus wurde eine gesundheitliche Bewertung der potenziellen Expositionen gegenüber Bedarfsgegenständen auf Polymerbasis durchgeführt. Zunächst wurden die Proben mittels DHS-Probenahme ausgewählt und die konstituierenden Polymere charakterisiert. Anschließend wurden die hochemittierenden Proben in Standard-Emissionsprüfkammern, 24 L-Glaskammern oder Mikrokammern untersucht. Eine Expositionsabschätzung wurde unter Berücksichtigung von Raumluftszenarien für eine kurzzeitige (einige Stunden) bis langzeitige (28 Tage) Exposition durchgeführt. Die Ergebnisse wurden mit bestehenden toxikologisch begründeten Richtwerten verglichen. Die von einzelnen Produkten emittierten Konzentrationen überschreiten unter den meisten Bedingungen nicht die Richtwerte. Szenarien mit mehreren Produkten oder kleineren Atemzonen sind jedoch besorgniserregend. Der Cyclohexanon-Richtwert wurde während der Untersuchung der Exposition aus Faschingsmasken, die mit einem neuentwickelten Puppenkopfaufbau untersucht wurden, überschritten.

Diese Arbeit ist die erste, die systematisch Strategien zur Bewertung der Inhalationsexposition durch Untersuchungsämter untersucht. Die im Rahmen dieser Arbeit generierten Expositionsdaten geben Einblicke in die potenziellen Gesundheitsrisiken, die mit der Verwendung von Bedarfsgegenständen auf Polymerbasis verbunden sind.

## Abbreviations

| | |
|---|---|
| AIR | German Committee on Indoor Guide Values (German: Ausschuss für Innenraumrichtwerte) |
| AgBB | German Committee for the Health-related Evaluation of Construction Products (German: Ausschuss zur gesundheitlichen Bewertung von Bauprodukten) |
| BfR | Federal Institute for Risk Assessment (German: Bundesinstitut für Risikobewertung) |
| BHT | butylated hydroxytoluene |
| CE | European Conformity (French: Conformité européenne) |
| CMR | carcinogenic, mutagenic or toxic for reproduction |
| COPD | chronic obstructive pulmonary disease |
| DEHP | diethylhexylphthalate/ bis(2-ethylhexyl)phthalate |
| DHS | dynamic headspace |
| DNA | deoxyribonucleic acid |
| DNEL | derived no-effect level |
| DNPH | 2,4-dinitrophenylhydrazine |
| EC | European Commission |
| ECHA | European Chemicals Agency |
| EN | European Standard (German: Europäische Norm) |
| EPHECT | Emissions, Exposure Patterns and Health Effects of Consumer Products in the EU |
| EU | European Union |
| FTIR | Fourier transform infrared spectroscopy |
| GC/MS | gas chromatography coupled to mass spectrometry |
| GC/O | gas chromatography with olfactometry detection |
| HPLC/UV | high-performance liquid chromatography with ultraviolet detection |
| ISO | International Organization for Standardization |
| LCI | lowest concentration of interest |
| LFGB | German food and feed code (German: Lebensmittel-, Bedarfsgegenstände- und Futtermittelgesetzbuch) |
| MAK | maximale Arbeitsplatz Konzentration (German maximum workplace concentration) |
| MOHs | mineral oil hydrocarbons |
| Mw | molar mass |
| MRL | minimal risk level |
| NIAS | non-intentionally added substances |
| NIK | niedrigste interessierende Konzentration (German LCI) |
| OCLs | official control laboratories |
| OEL | occupational exposure limit |
| PE | polyethylene |
| POPs | persistent organic pollutants |
| Pow | octanol-water partition coefficient |
| PP | polypropylene |
| PS | polystyrene |
| PTR-MS | proton-transfer-reaction mass spectrometry |
| PVC | polyvinyl chloride |

| | |
|---|---|
| REACH | registration, evaluation, authorisation and restriction of chemicals |
| RNA | ribonucleic acid |
| RW | guideline value (German: Richtwert) |
| SAFE | solvent-assisted flavor evaporation |
| SBS | poly(styrene-butadiene-styrene) |
| SCHEER | Scientific Committee on Health, Environmental and Emerging Risk |
| $SER_A$ | area-specific emission rate |
| SIFT-MS | selected-ion flow-tube mass spectrometry |
| SPME | solid phase microextraction |
| SVHC | substance of very high concern |
| SVOCs | semi-volatile organic compounds |
| $T_B$ | boiling point |
| TD | thermal desorption |
| TDI | tolerable daily intake |
| TDU | thermal desorption unit |
| TLV | threshold limit value |
| TXIB | 2,2,4-trimethyl-1,3-pentanediol diisobutyrate |
| VOCs | volatile organic compounds |
| VVOCs | very volatile organic compounds |
| WHO | World Health Organization |

# 1. Introduction

## 1.1. Organic compounds in polymer-based consumer products

Volatile organic compounds (VOCs) are among the chemicals which may enter the human body via the inhalation exposure route. These compounds can be released inter alia by consumer products.

### 1.1.1. Consumer products

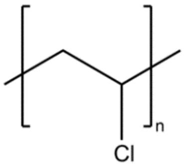
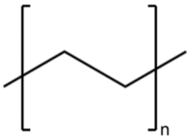
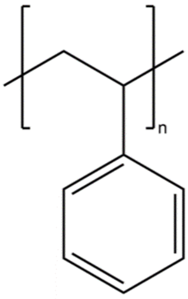
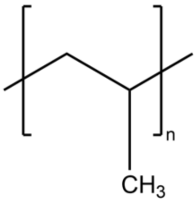
Consumer products or consumer goods are products that people buy for their own use [1], i.e., for personal, family or other non-business use. It includes for example food contact materials, furniture, health care and household articles, decorations or toys. This work looked at non-food polymer-based consumer products, hence excluding food packaging but including wooden products.

The majority of the samples considered in this work were toys because they are omnipresent in our society and they often come in very close contact with children; a population which deserves special attention. Indeed, younger generations represent a sensitive and vulnerable group due to their low body weight, immature metabolism and growing body functions [2]. The toy industry has increased its production in the last years and represented a market of 94.7 billion dollars in 2020 [3]. The toy sector is nowadays a global market; most toys used in the European Union (EU) are imported from Asia to reduce production costs. The EU imported 9.1 billion euros worth of toys from around the world in 2016 [4]. China is the world's largest exporter of toys with more than 86% of worldwide exports, the EU follows with 4.6% [5].

### 1.1.2. Polymers and characterization techniques

This work focused on polymer-based consumer products. A polymer is a macromolecule composed of chains or rings of chemically linked repeating subunits. It is composed of amorphous regions where chains are randomly arranged and eventually of a crystalline structure. There are three main types of synthetic polymers: elastomers, thermosetting polymers and thermoplastics [6]. Elastomers (commonly called rubber) are deformable at ambient temperature. Indeed, their long linear chains can be stressed as they are only linked to one another with weak intermolecular interactions. Their properties are necessary to manufacture rubber bands or adhesives. They can typically be irreversibly hardened at high temperature (vulcanization). Thermosetting polymers (also called resins) irreversibly harden during manufacturing too because they are formed of a three-dimensional cross-linked covalent bond network. They are mostly used in the car industry or for household appliances. Most commodity polymers are thermoplastics for which the chains are linked by weak bonds (Van der Waals). At elevated temperature, bonds are broken, and the polymer becomes malleable, which is very convenient to design a high variety of toys or decoration products. For this reason, thermoplastics are also often recyclable. Examples of synthetic thermoplastics used for consumer product manufacturing are referenced in **Table 1**.

**Table 1**: Examples of thermoplastics used for consumer product manufacturing [6].

| **Name** | **Abbreviation** | **Structure** |
|---|---|---|
| **Polyvinyl chloride** | PVC |  |
| **Polyethylene** | PE |  |
| **Polystyrene** | PS |  |
| **Polypropylene** | PP |  |

A polymer can also be a combination of different monomers, called copolymer. Combining different monomers broadens the range of application. Styrene-butadiene-styrene (SBS) is for example a thermoplastic elastomer which presents the advantages of both elastomers and thermoplastics: It can be stretched at ambient temperature and becomes malleable upon elevated temperature.

Wood is a natural product made of polymers, mainly lignin, cellulose and various hemicelluloses [7]. It is considered in this work because wooden toys may also release hazardous substances.

The chemical structure of the main synthetic polymers constituting the investigated products can be identified using different techniques. Online-pyrolysis-GC/MS (gas chromatography/mass spectrometry) is used to determine the material composition. It enables the identification of the polymer structure via a thermal degradation and identification of the degradation products. It does not require extensive sample preparation as it is directly applied to the material of interest. A very small piece of the sample is placed in a tube which is brought in contact with a pyrolysis filament. The pyrolysis was performed in a previous work at 700°C to decompose the polymer [8]. The degradation products are then cryofocused, released and separated, they can be identified based on their mass spectra. The identification of unique substances, or substance clusters in the decomposition pattern enables the attribution to a certain polymer [9]. Fourier transform infrared (FTIR) spectroscopy is also used as a complementary technique for structure identification [8], but it is less precise as polymers are identified by comparison of spectra with a data bank and not by identification of specific components. The Beilstein test allows the confirmation of polyvinyl chloride (PVC) samples. If the applied flame turns green after having brought in contact with copper, it is indicative for a halogen presence. As the organic emissions from a product are usually linked with the constituting polymer (e.g., degradation products, additives), it is useful to characterize the polymer structure of the investigated products to better identify and understand emission patterns.

### 1.1.3. Additives and non-intentionally added substances in polymeric articles

Besides the primary polymeric structure, polymeric articles are composed of many constituents. It is necessary to differentiate between intentionally added substances (additives) and non-intentionally added substances (NIAS). Additives are used to enhance the material properties. Examples of polymer additives are plasticizers, antioxidants, heat stabilizers, slip agents [10] but also coloring agents or flame retardants [11]. NIAS are substances such as leftovers from the production (e.g., solvents, monomers, contaminants and impurities) and degradation products of the material or its additives [8]. Commercialized wood contains additives such as preservatives, adhesives or coatings [12] and also their degradation products. Both additives and NIAS can present a risk to human health. Data on exposure to these substances is often missing and is necessary to better protect consumers via regulation.

### 1.1.4. Regulation in the European Union and in Germany

Regulations from different areas apply to polymeric articles and the organic compounds they contain. In Europe, articles should comply with the Regulation concerning the registration, evaluation, authorisation and restriction of chemicals (REACH) [13] if no other more specific regulation exists. It regulates chemicals with toxicological relevance such as persistent organic pollutants (POPs) or substances of very high concern (SVHC) like certain phthalates. The German Product Safety Law (Produktsicherheitsgesetz) is derived from the European Directive 2001/95/EC [14]. It affirms that products should not be marketed if they endanger safety or health [15]. The German Food and Feed Code (LFGB Lebensmittel-, Bedarfsgegenstände- und Futtermittelgesetzbuch) [16] states that a material or article ("Bedarfsgegenstand") should be manufactured in a way that it is not harmful to health under the foreseeable conditions of use.

Particular care should be taken for products coming into contact with children. For this reason, the European Toy Safety Directive 2009/48/EC sets specific recommendations for this product type [17]. It states that "toys, including the chemicals they contain, shall not jeopardize the safety or health of users or third parties when they are used as intended or in a foreseeable way, bearing in mind the behavior of children" [17]. The manufacturer, distributor or importer is responsible for the compliance. Besides safety specifications on physical and mechanical properties, electrical properties, flammability, hygiene and radioactivity, it sets requirements for chemical properties.

According to the Toy Safety Directive, "substances that are classified as carcinogenic, mutagenic or toxic for reproduction (CMR) of category 1A, 1B or 2 under Regulation (EC) No 1272/2008 [18] shall not be used in toys, in components of toys or in micro-structurally distinct parts of toys" [17]. Derogations exist depending on the CMR categories with maximum weight percentages of 0.1% to 3%. Specific requirements apply for nitrosamines and nitrosable substances, allergenic fragrances (with lists of prohibited substances and substances that should be listed when concentrations exceed 100 mg/kg) and for elements (migration limits). The analysis of allergenic fragrances was studied extensively in a previous work [19].

Since 2009, different amendments to the Toy Safety Directive were published: Specific limit values were set for chemicals used in toys designed for use by children under three years or in other toys expected to be placed in the mouth. Five of them concerned VOCs. In 2015, an emission limit was set for formamide. The emission of formamide from foam toy materials into the air was limited to 20 $\mu g/m^3$ measured after a maximum of 28 days from beginning of the emission testing, following a test method in accordance with the ISO 16000-6 [20] and 16000-9 [21] standards (see 1.2.2) [22]. In 2017, a limit of 10 mg/kg was set for phenol in toys [23]. An amendment was also adopted in 2019 to regulate the emissions of formaldehyde from wooden toys [24]. An emission limit of 0.1 $mL/m^3$ was set when using the emission test chamber standard method EN 717-1 [25] (see 1.2.2.1). This last amendment which applied from May 2021 is discussed extensively in the Chapter 2.4. Recently, citronellol, atranol and chloroatranol were added to the lists of allergenic substances [26, 27].

The part 9 of the European standard on toy safety EN 71-9 from 2007 sets more practical requirements concerning organic chemical compounds in toys [28]. It includes content, migration and inhalation (see 1.3.2) thresholds for different substances from multiple toy materials. The sample preparation and analysis methods necessary to comply with EN 71-9 are presented in EN 71-10 [29] and EN 71-11 [30] (see 1.2.1). However, these standards do not have a legal value: They cannot be used to prove the conformity of toys with the European Toy Safety Directive.

In practice, the CE sign requires that the toy article complies with the Toy Safety Directive: “Manufacturers shall, before placing a toy on the market, carry out an analysis of the chemical, physical, mechanical, electrical, flammability, hygiene and radioactivity hazards that the toy may present, as well as an assessment of the potential exposure to such hazards” [17]. A declaration of conformity is necessary. Products without CE sign cannot be made available in the EU and the manufacturer is responsible for placing the CE sign. Member States are in charge of the organization and the implementation of the market surveillance of toys. In Germany the surveillance is carried out in the federal states by the official control laboratories (OCLs, “Untersuchungsämter”). A common European rapid alert system for dangerous non-food products (Safety Gate Rapid Information Exchange System [31]) exists to share knowledge on irregularities, recall and withdrawals. In 2019, toys represented 29% of all notified products and chemical risks acquainted for 23% of all notifications [32]. About half of the products concerned originated from China. This is not a surprise as China is the first toy importer for the EU.

### 1.1.5. Volatile organic compounds and their emissions

Among the chemicals present in consumer products, VOCs represent a relevant group for the inhalation exposure. Indeed, VOCs are compounds that can vaporize at ambient conditions and be found in the vapor phase. Common VOCs chemical structures are presented in **Figure 1**. In synthetic polymeric articles, they can be either additives (e.g., fragrances) or NIAS (e.g., residual solvents and degradation products). There are several ways to define the VOC group:

- According to their boiling point: According to the World Health Organization (WHO), VOCs are substances with a boiling point between 50-100°C and 240-260°C [33].
- According to their vapor pressure: US scientists often defined VOCs as compounds having a vapor pressure above 0.1 Torr (13.3 Pa) at 25°C and atmospheric pressure [34].
- Chromatographically: According to ISO 16000-6 and EN 16516, VOCs are compounds eluting between *n*-hexane and *n*-hexadecane on a non-polar GC column (e.g., 5% phenyl / 95% methyl-polysiloxane) [20, 35].

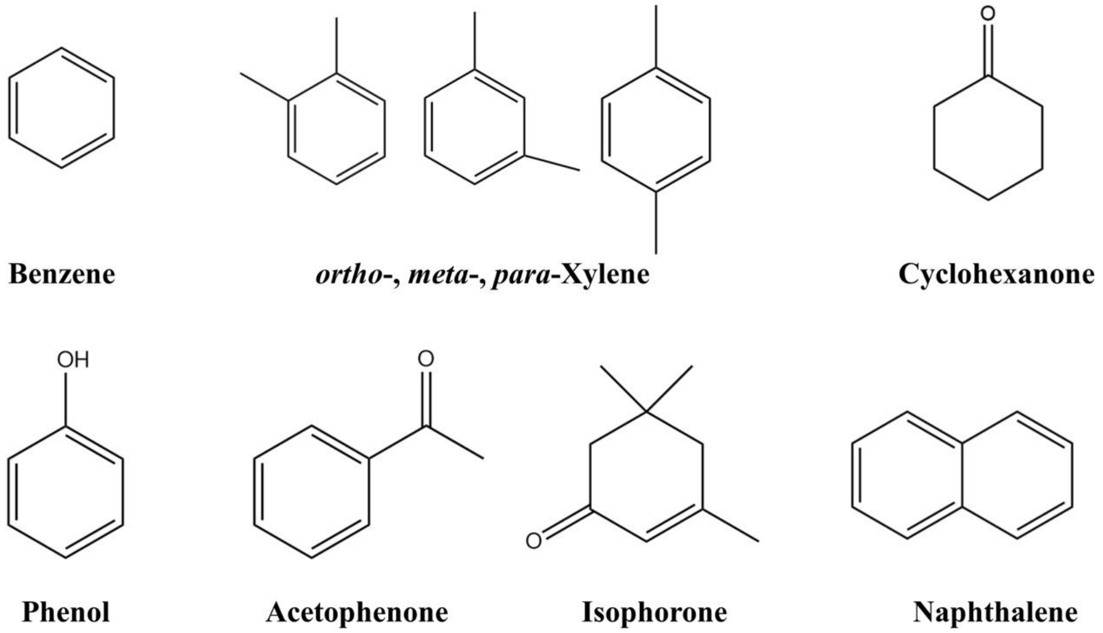


***Figure 1**: Common VOCs chemical structures.*

In this work, 24 substances (including 19 VOCs under the WHO definition) were considered. Substances that are more volatile are called very volatile organic compounds (VVOCs) and less volatile substances are called semi-volatile organic compounds (SVOCs). The compounds summarized in **Table 2** were chosen either because they had been detected in polymer-based consumer products by the OCLs or because they were analyzed with high GC/MS signal intensities in real samples during the frame of this work.

***Table 2 :*** *Chemical properties of substances considered in this work [36]. It is indicated whether or not they were present in a polyurethane reference material (see Chapter 2.1, 2.2, 2.3 and 2.6.1) and if they are analyzed by liquid chromatography (LC) or gas chromatography (GC);* $T_B$*: boiling point; Mw: molar mass; P: octanol-water partition coefficient; *: very volatile organic compound (VVOC);* $^{\dagger}$*: semi-volatile organic compounds (SVOCs); BHT: Butylated hydroxytoluene; TXIB: 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate.*

| Name | CAS | Molecular formula | $T_B$ (°C) | Mw (g/mol) | Log P | Reference material | LC | GC |
|---|---|---|---|---|---|---|---|---|
| **Formaldehyde*** | 50-00-0 | $CH_2O$ | -19 | 30 | 0.35 | | x | |
| **Benzene** | 71-43-2 | $C_6H_6$ | 80 | 78 | 2.13 | x | | x |
| **Toluene** | 108-88-3 | $C_7H_8$ | 111 | 92 | 2.73 | x | | x |
| ***n*-Butylacetate** | 123-86-4 | $C_6H_{12}O_2$ | 126 | 116 | 1.78 | | | x |
| **Ethylbenzene** | 100-41-4 | $C_8H_{10}$ | 136 | 106 | 3.15 | | | x |
| ***p*-Xylene** | 106-42-3 | $C_8H_{10}$ | 138 | 106 | 3.15 | x | | x |
| ***m*-Xylene** | 108-38-3 | $C_8H_{10}$ | 139 | 106 | 3.2 | x | | x |
| ***o*-Xylene** | 95-47-6 | $C_8H_{10}$ | 144 | 106 | 3.12 | x | | x |
| **Dimethylformamide** | 68-12-2 | $C_3H_7NO$ | 153 | 73 | -1.01 | x | | x |
| **Cyclohexanone** | 108-94-1 | $C_6H_{10}O$ | 156 | 98 | 0.81 | x | | x |
| **Octanal** | 124-13-0 | $C_8H_{16}O$ | 171 | 128 | 3.5 | | | x |
| **Phenol** | 108-95-2 | $C_6H_6O$ | 182 | 94 | 1.46 | x | | x |
| **2-Ethylhexanol** | 104-76-7 | $C_8H_{18}O$ | 185 | 130 | 2.73 | | | x |
| **Acetophenone** | 98-86-2 | $C_8H_8O$ | 202 | 120 | 1.58 | x | | x |
| **2-Phenyl-2-propanol** | 617-94-7 | $C_9H_{12}O$ | 202 | 136 | 1.8 | x | | x |
| **Isophorone** | 78-59-1 | $C_9H_{14}O$ | 215 | 138 | 1.7 | x | | x |
| **Dodecane** | 112-40-3 | $C_{12}H_{26}$ | 216 | 170 | 6.1 | | | x |
| **Naphthalene** | 91-20-3 | $C_{10}H_8$ | 218 | 128 | 3.3 | x | | x |
| **Formamide** | 75-12-7 | $CH_3NO$ | 220 | 45 | -1.51 | x | | x |
| **1-Dodecanol** | 112-53-8 | $C_{12}H_{26}O$ | 259 | 186 | 5.13 | x | | x |
| **BHT**$^{\dagger}$ | 128-37-0 | $C_{15}H_{24}O$ | 265 | 220 | 5.1 | | | x |
| **Dimethyl phtalate**$^{\dagger}$ | 131-11-3 | $C_{10}H_{10}O_4$ | 284 | 194 | 1.6 | | | x |
| **Eicosane**$^{\dagger}$ | 112-95-8 | $C_{20}H_{42}$ | 343 | 282 | 10.16 | | | x |
| **TXIB**$^{\dagger}$ | 6846-50-0 | $C_{16}H_{30}O_4$ | 380 | 286 | 4.91 | | | x |

Among these compounds, several are included on priority lists for indoor air chemicals that were established for example in the European Union (formaldehyde, benzene, naphthalene, toluene and xylenes) [37] or in the state of Washington in the USA in the context of a Children’s Safe Product act (formaldehyde) [38].

Two main mechanisms take part in the VOCs’ emission process:

- The VOCs diffuse through the material to the surface. The diffusion rate depends on material properties, VOC properties and concentration gradients [39], as well as the ambient temperature and humidity. The influence of material properties was further studied in this work (see Chapter 2.6.1).
- The VOCs partition between the material surface and the surrounding air. The partition rate mainly depends on the VOC properties, the air flow rate at the material surface but also on the ambient temperature and humidity.

The emission rate is the parameter that is commonly used to quantify VOC releases [21]. It refers to the quantity of a single substance that is released from the material per unit of time. Increased diffusion and partition behaviors will result in increased emission rates. The establishment of standardized analytical methods is necessary to reliably determine the emissions of VOCs.

## 1.2. Analytical methods

To better regulate the emissions of VOCs from consumer products, the assessment of the inhalation exposure with reliable analytical methods is needed.

### 1.2.1. Shortcomings of current standard methods

The methods used at the moment in the OCLs to analyze VOCs from polymer-based consumer products do not allow a realistic exposure assessment:

- Most studied polymer-based samples in the OCLs are extracted with a solvent (e.g., toluene) [40] and analyzed via GC/MS or HPLC/UV (high-performance liquid chromatography with ultraviolet detection). This method allows the determination of the whole VOC content of a sample for which limit values exist. However, no difference is made between the compounds that stay in the core of the material and those that rapidly emit from the surface.

- For gas phase analyses, sample pieces are placed in a vial (usually 20 mL), heated and their headspace is analyzed via adsorption on fiber material (SPME: solid phase microextraction) or by syringe sampling, for example at 90°C for 45 min for solvents according to EN 71-11 [30]. VOCs in toys can also be analyzed via direct thermal desorption (TD) according to EN 71-11 [30]: In this method, the compounds emitted from the sample piece incubated at 40°C for 15 min are focused on a cold trap and directly desorbed in the GC/MS.

- The flask method, which has been developed for building materials (EN 717-3 [41]), is also routinely used to study formaldehyde emissions from wooden toys. As shown in **Figure 2**, the sample is hung in a 500 mL bottle filled with 50 mL water and the formaldehyde content in water is determined after three to 24 hours. This method is however highly criticized as it does not correlate with other emission measurement methods [42].

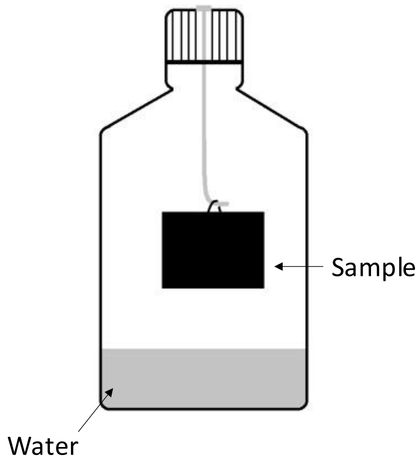


***Figure 2***: *Schematic representation of the flask method.*

These methods all force the VOCs to diffuse in the sample and partition with the ambient air by using extraction, high temperature or humidity. Moreover, none of these procedures involves an air exchange around the sample although this is a determining parameter for VOC emissions as it governs the partition between the materials and the surrounding air. Consequently, those methods which do not implement realistic conditions are not suitable for a reliable exposure assessment. However, other analytical methods exist to generate realistic exposure data.

### 1.2.2. Standardized methods for building material emission measurements

#### *1.2.2.1. Emission test chambers*

An emission test chamber is a device with an inner chamber made of an inert material with no inherent emission and low adsorption (glass or stainless steel) where the environmental parameters (temperature, relative humidity and air exchange) are regulated to simulate an indoor environment. The sample is placed inside the chamber and there is a possibility to sample air (directly from the chamber or at its outlet) to study its possible emissions. This device allows the study of emissions from an item under realistic indoor conditions. A schematic picture of an emission test chamber is presented in **Figure 3**.

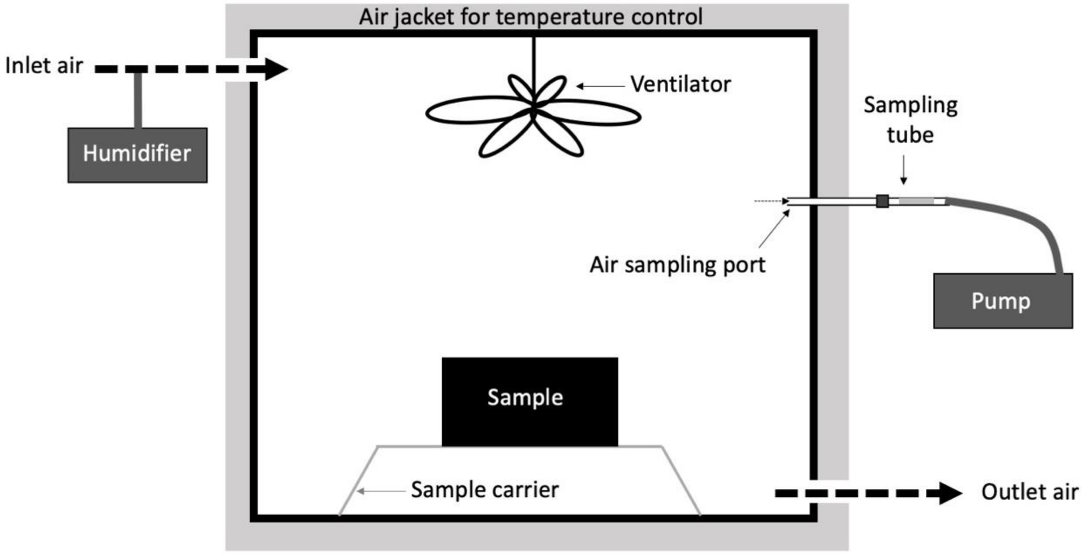


***Figure 3**: Schematic representation of an emission test chamber.*

Conventional emission test chambers feature different sizes, from a few liters to the size of a room. In this study, 24 L glass chambers built from desiccators as well as 203 L and 1000 L stainless steel chambers were used. Standard methods such as ISO 16000-9 [21], EN 16516 [35] and EN 717-1 [25] define parameters for emission measurements from construction materials. The air change rate is regulated via the inlet and outlet flow and the homogeneity is preserved with a ventilator. The relative humidity is adjusted with a humidifier: Part of the dry inlet air flow passes through a water reservoir and humid and dry air are mixed to achieve the desired humidity. The temperature is regulated with an air jacket surrounding the chamber or via controlling the temperature in the room where the chamber is placed. The loading of the chamber (ratio of exposed surface to chamber volume) is also an important parameter, which can be varied for different sample types [35].

Such standardized procedures are not available for polymer-based consumer products. But emission test chambers have already been used in a few studies before this work. VOCs from polymer-based scented toys [39], "squishy toys" [43] or a polymer-based personal care item [44] have been studied in the past using emission test chambers. Important parameters describing emission test chamber measurements and results are the area-specific air flow rate and the area-specific emission rate.

$$q = \frac{n_{CH}}{L} = \frac{n_{CH} * V_{CH}}{A} \qquad (1)$$

with:
q: area-specific air flow rate ($m^3/(h \cdot m^2)$)
$n_{CH}$: chamber air change rate (/h)
L: chamber loading ($m^2/m^3$)
$V_{CH}$: chamber volume ($m^3$)
A: sample surface area ($m^2$)

$$SER_A = \frac{C_{CH} * n_{CH} * V_{CH}}{A} \qquad (2)$$

with:
$SER_A$: area-specific emission rate ($mg/h \cdot m^2$)
$C_{CH}$: chamber concentration ($mg/m^3$)

#### *1.2.2.2. Air sampling and analysis*

After the material has been placed in the emission test chamber, air samples can be taken and analyzed at different time points. A differentiation is made between the analysis of high volatile carbonyl compounds and the other VOCs.

For carbonyl compounds ($C_1$-$C_4$), the air sampling and analysis can be performed according to ISO 16000-3 [45]. Such analysis can be divided into three phases:

1) The air from the chamber is sampled with a sampling pump with a flow of ca. 1 L/min on cartridges coated with DNPH (2,4-dinitrophenylhydrazine).
2) The cartridges are then eluted with acetonitrile as organic solvent.
3) The resulting solution is analyzed for DNPH-derivates of carbonyl compounds using HPLC with ultraviolet detection at 365 nm. Quantification is performed via external calibration with commercial solutions containing carbonyl derivates.

Alternatively, the air coming from the chamber can be trapped in water, derivatized with acetyl acetone and analyzed via photometry [25].

For the other VOCs, the procedure is also divided into three phases, following ISO 16000-6 [20]:

1) The chamber air is sampled with a sampling pump and a flow of 50-200 mL/min on glass or metal tubes filled with Tenax® TA (Poly(2,6-diphenylphenylene oxide)).
2) The tubes are then desorbed thermally with an automatic device (e.g., thermal desorption unit, TDU) to release the analytes directly into the GC/MS.

3) Finally, a GC/MS analysis is used to allow qualitative and quantitative determination of the analytes.

For quantification purposes, small amounts of solutions containing internal standards or the calibration levels of the target analytes are spiked onto desorption tubes. The tubes are flushed with clean air or nitrogen. In this work, ethyl acetate was preferred to the usual methanol as a solvent for those standard solutions to avoid quantification mistakes. Indeed, 1,1-dimethoxy-cyclohexane may form from cyclohexanone in methanolic solutions [46].

### 1.2.3. Alternative methods

Emission test chambers provide reliable results for exposure assessment, but standard test procedures are highly expensive and not adapted to the common size of consumer products. Indeed, the standard procedures require testing over 28 days [47] which are linked with high costs. The OCLs cannot afford such expensive tests for the small and cheap consumer products they have to inspect. Moreover, the size of commercial emission test chambers (up to 20 $m^3$) is not suited to most polymer-based consumer products such as small toys or figurines. A single small product in a huge chamber would lead to hardly detectable VOC concentrations. For these reasons, alternative cost-effective methods were tested in this work for their reliability and comparability to emission test chambers.

#### *1.2.3.1. Dynamic headspace (DHS)*

Unlike the headspace methods mentioned in 1.2.1, the DHS technique involves an air exchange around the sample. The automated device allows the septum of the vial to be perforated by two needles. As illustrated in **Figure 4,** the longer needle conducts the inlet air with a defined flow rate through the glass 20 mL vial, while the shorter needle samples the exiting air. The VOCs present in the exiting air can then be adsorbed on a Tenax® TA tube and analyzed automatically via TD-GC/MS following ISO 16000-6 [20]. The vial temperature is controlled via the vial container but there is no apparatus to control the relative humidity of inlet air. Moreover, dry nitrogen is usually used as inlet gas instead of synthetic air which will necessitate elaborate filtering as for the common emission test chambers.

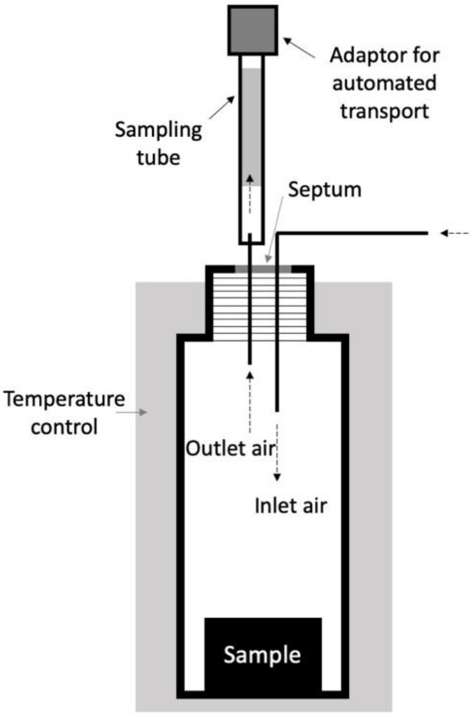


***Figure 4:*** *Schematic representation of the dynamic headspace (DHS) apparatus.*

This technique which exists since 2007 [48] has been used in the past for the study of VOCs emitting from scented toys [49], but no comparison of the emission results with other analytical techniques was performed. Additionally, a large-volume dynamic headspace device using stainless steel containers with volumes from 125 mL to 1 L was introduced in 2016 [50] and allows the study of bigger samples. This large-volume technique was used in the past to sample carbonyl emissions from wooden products including children's toys on DNPH cartridges [51], but the elution and analysis steps following ISO 16000-3 [45] could not be automated yet. Moreover, the use of a dry inlet gas would in this case be prone to errors as carbonyl emissions depend on the humidity rate. Usually, this technique is used for the single analysis of the headspace from a sample. However, this only allows the detection of the most volatile substances if the system is used at ambient temperature. To mimic an emission test chamber, DHS can be also used continuously during several hours/days by sampling the emissions on several tubes and ventilating the vial in the meantime. A comparison of the DHS with emission test chamber measurements is still lacking. The main drawback of such a setup is that the GC/MS analytical device is monopolized by one single experiment during this time frame. The analysis of other sampling tubes (e.g., from an external emission test chamber) is not possible in the meantime.

### 1.2.3.2. Microchambers

Contrary to the DHS technique, microchambers are stand-alone stainless steel devices that do not allow an automated analysis. However, they make it possible to perform emission measurements over several days (e.g., 28 days [47]). Moreover, they enable the continuous parallel analysis of several samples (four to six) at the same time and do not monopolize the GC/MS analytical device.

**Figure 5** presents a schematic representation of the microchamber device. Two commercial models are available: six chambers of 44 mL volume or four chambers of 114 mL volume. Both instruments were used in this work. All chambers are operated in parallel. They have a common inlet flow which can be humidified and a common air jacket for heating. It is possible to shut off some chambers, but every running chamber will be operated with the same parameters (i.e., flow, temperature and relative humidity). The chamber volume can be used as a whole (left chamber in **Figure 5**; bulk measurement in Chapter 2.3, 2.4 and 2.6) or be reduced via sample carriers, usually for surface emission measurements (right chamber in **Figure 5**; Chapter 2.5).

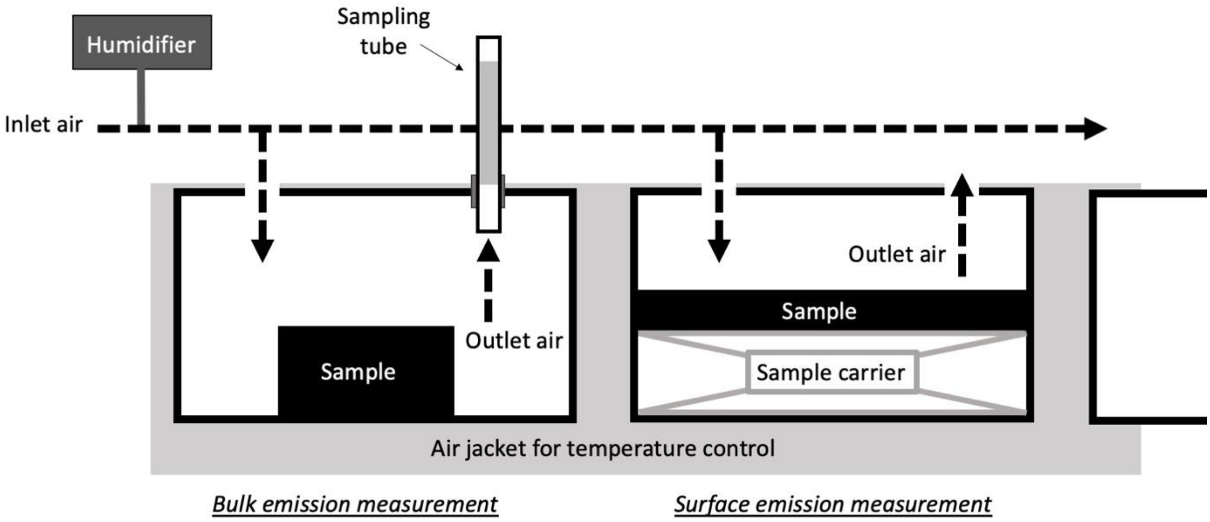


***Figure 5:*** *Schematic representation of the microchamber device.*

Microchambers have been used in research works in the past. Schripp *et al.* introduced the device in 2007 [52], Nohr *et al.* used it to develop an emission reference material [53] and Marc *et al.* performed emission tests from small polymer toys (however under forced conditions such as high temperature [54]). Yet, no study had been carried out on the comparability of those miniaturized emission test chambers with the standard large-volume chambers. The standard

ISO 16000-25 [55] is a microchamber method for the determination of the emission of SVOCs from building products. The measurements are divided into two steps: the emission step (typically over 24 hours) and the desorption step of the SVOCs adsorbed on chamber's wall at 220-240°C. The standard is originally written for a chamber volume of 630 mL but the microchambers presented here (44 and 114 mL) are the only commercial devices available. This method does not follow the emissions in real-time but accelerates them, which is necessary for SVOCs which emit over a long period of time.

The OCLs need methods which give reliable results while being cost-effective and allowing high sample throughput. The space needed for the device installation is also an important criterion for OCLs as the installation of big chambers would for example necessitate new rooms. The advantages and disadvantages of the different methods are summarized in **Table 3**. Results on the comparability of the different procedures are extensively presented and discussed in the result part of this work (Chapter 2.1, 2.3, 2.4 and 2.5).

***Table 3:*** *Overview of methods for the exposure assessment of VOCs from polymer-based consumer products towards the use in OCLs.*

| | **Advantages** | **Drawbacks** |
|---|---|---|
| **Methods currently used in OCLs (e.g., solvent extraction, headspace, flask method)** | - Cost-effective | - No exposure assessment, only determination of VOC contents |
| **Emission test chambers** | - Realistic exposure results | - Expensive, space demanding<br>- Low sample throughput |
| **Dynamic headspace** | - Automated sampling and analysis<br>- High sample throughput if used for single headspace analysis of the sample | - GC/MS analytical device monopolized during the whole emission measurement<br>- Low sample throughput if one sample used continuously<br>- Only small samples or sample pieces<br>- Inlet gas is not humidified |
| **Microchambers** | - Easy to install, little space needed<br>- High sample throughput | - Only small samples or sample pieces<br>- Same parameters (flow, temperature, relative humidity) for all chambers |

### 1.2.4. Sensory tests

The most natural detector we possess is the human nose as it can detect inhaled odorous VOCs. Its ability to recognize VOCs and the link between odors and emissions should be investigated. The sensory methods are usually implemented to develop products with a pleasant smell in the industry but are also interesting from a regulatory point of view. Indeed, many consumers experience unpleasant odors coming from plastic articles, sometimes associated with headache or nausea, and wonder if it could have further health consequences.

The first olfactory method is the human-sensory evaluation and aims at describing the odor of a product. The products are presented to a panel comprising trained sensory specialists. The panelists first name attributes describing the product's odor, examples of attributes are "rubber-like", "sweet" or "moldy" [56]. The intensity of the most named attributes is then rated together with the overall intensity of the product and its hedonic (i.e., pleasant or unpleasant odor).

***Figure 6:*** *Human sensory evaluation, panelists open the lid and immediately smell the samples to record their odor impressions; odorous pens with standard substances are used to help the rating of single attributes.*

The second olfactory method enables the identification of the individual substances causing the odor via sensory analytics. It uses GC with olfactometry detection (GC/O) instruments, i.e., the combination of instrumental and sensory analytics. The compounds will be separated on the GC column as usual. However, a special detector port where the user smells the separated compounds is attached. It allows a clear distinction between odorous and non-odorous substances. The odorous compounds are also given attributes like in the first method. It gives insights into the characterization of the constituents of the overall odor. The panel test is always carried out at ambient conditions while the typical sample extraction via solvent-assisted flavor evaporation (SAFE) [56-58] or thermal extraction [59] would also release fewer volatile substances that are not emitted at ambient temperature. To allow a direct comparison between emissions and odors, it makes more sense to use DHS as sample preparation technique [60]. These olfactory methods had been used for polymer-based consumer products in the past [56, 58, 59] but no correlation was sought between realistic emission analyses and their odors.

## 1.3. Assessment of the inhalation exposure for consumers

Humans will be exposed to VOCs from consumer products, mostly via indoor air, if they happen to be in the surroundings of the product. The three routes of exposure (oral, dermal and inhalation) may be considered for these compounds. The oral and dermal VOC exposures are likely to occur by direct contact of the consumer and the product (i.e., via mouthing or holding), but the main route for such compounds is the inhalation. Indeed, the surrounding air will be breathed in by the consumers and it will cause the VOCs diluted in the inhaled air to concentrate in the human body if they are absorbed.

### 1.3.1. Health risks related to VOC inhalation

This work focused on the inhalation exposure assessment. It is necessary to differentiate between short-term and long-term exposures as well as between acute and chronic effects. The ECHA (European Chemical Agency) guidance on information requirements and chemical safety assessment Chapter R.8 [61] considers as short-term inhalation exposure periods shorter than 15 minutes. Besides the analyses, toxicological knowledge is necessary to provide a thorough risk assessment.

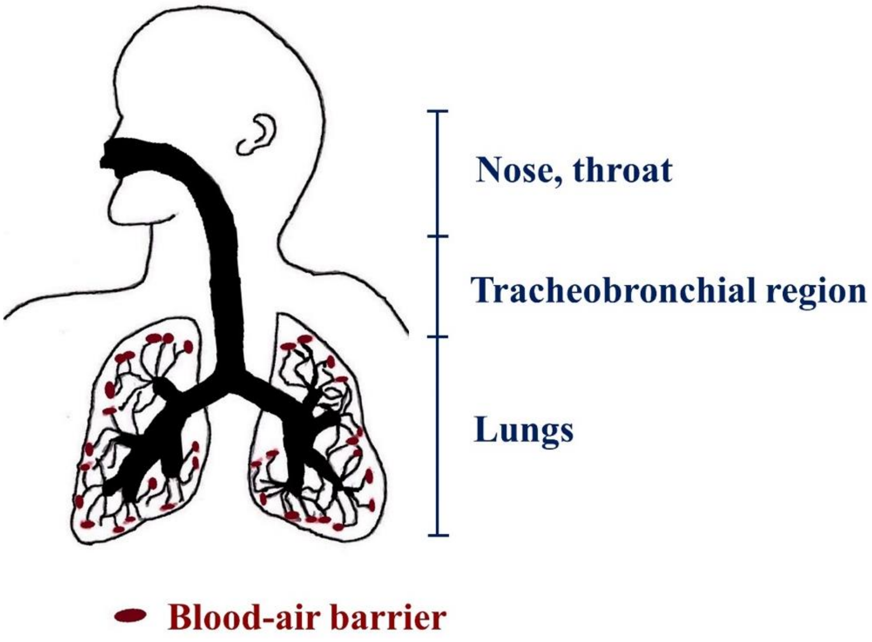


***Figure** 7: Simplified scheme of the respiratory tract.*

VOCs typically enter the body by breathing through nose and mouth. Their water solubility and thermodynamic properties control the effects in the respiratory tract. Unlike particles, they would not be filtered by the nose hair due to their very small size, but some polar VOCs will be affected by the nose and mouth humidity. They can already lead to irritation when coming in contact with tissues in the nose or the throat (and even via direct contact between ambient air and eyes). This is a typical acute effect, induced for example by formaldehyde [62]. In the tracheobronchial region, VOCs can induce allergenic reactions and constrictions that may induce long-term effects such as asthma or chronic bronchitis [63]. If VOCs further enter the respiratory tract, they reach the lungs, where they may also further pass the blood-air barrier via the alveoli. Once in the blood, they are able to reach the other tissues and organs. In all tissues, they can be recognized by receptors, either at the cell surface or in the cell. They may be metabolized by enzymes and the VOC or its metabolites can induce structural or functional alterations by binding to proteins or DNA/RNA (deoxyribonucleic acid/ribonucleic acid). Those alterations mainly taking place in the lungs typically result in chronic effects such as edema or emphysema [63]. COPD (chronic obstructive pulmonary disease), which is mainly caused by smoking, is characterized by both chronic bronchitis and emphysema [64]. Depending on their mode of action, the toxic compounds are for example classified by the European Commission and the ECHA as CMR, endocrine disruptors or sensitizers [18, 65]. The classification of the substances considered in this work are summarized in **Table 4**.

In vitro and in vivo studies are carried out to investigate the compounds' toxicities [66-69]. Their results are applied to relate the analytical data (exposure assessment) with the toxicity data (hazard assessment) and thus determine the risk of the investigated products.

***Table 4 :** VOCs considered in this work, together with their toxicological properties (1A: known effect, 1B: may cause the effect, 2: suspicion of the effect, Ss: skin sensitizer, ED*: under assessment as endocrine disruptor [18, 65]) and their gas-phase concentration guideline values: EN 71-9 inhalation [28], DNEL (derived no-effect level) for long-term inhalation exposure for the general population and systemic effects [65], NIK (Niedrigste Interessierende Konzentration, [47]), EU-LCI (European Lowest Concentration of Interest, [70]), AIR values (German Committee on Indoor Air Guide Values,[71]); BHT: Butylated hydroxytoluene ; TXIB: 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate.*

| | **Regulation (EC) No 1272/2008** | | | | **EN 71-9** | **DNEL** | **NIK** | **EU-LCI** | **AIR** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **(all in mg/m$^3$)** | | | | | |
| **Name** | **C** | **M** | **R** | **Other** | | | | | **I** | **II** |
| **Formaldehyde** | 1B | 2 | | Ss. | | 3.2 | 0.10 | 0.10 | 0.1 | |
| **Benzene** | 1A | 1B | | | | - | | | | |
| **Toluene** | | | 2 | | 0.26 | 56.5 | 2.9 | 2.9 | 0.3 | 3 |
| ***n*-Butylacetate** | | | | | | 12 | 4.8 | 4.8 | | |
| **Ethylbenzene** | | | | | 5.0 | 15 | 0.85 | 0.85 | 0.2 | 2 |
| ***p*-Xylene** | | | | | 0.87 | 65.3 | 0.50 | 0.50 | 0.1 | 0.8 |
| ***m*-Xylene** | | | | | | 65.3 | | | | |
| ***o*-Xylene** | | | | | | 65.3 | | | | |
| **Dimethylformamide** | | | 1B | | | 15 | 0.015 | | | |
| **Cyclohexanone** | | | | | 0.136 | 10 | 0.41 | 0.41 | | |
| **Octanal** | | | | | | 0.32 | 0.90 | 0.90 | 0.1 | 2 |
| **Phenol** | | 2 | | | | 1.32 | 0.070 | 0.070 | 0.02 | 0.2 |
| **2-Ethylhexanol** | | | | | | 2.3 | 0.30 | 0.30 | 0.1 | 1 |
| **Acetophenone** | | | | | | 5.4 | 0.49 | 0.49 | | |
| **2-Phenyl-2-propanol** | | | | | | - | | | | |
| **Isophorone** | 2 | | | ED* | | 0.7 | | | | |
| **Dodecane** | | | | | | - | 6.0 | 6.0 | | |
| **Naphthalene** | 2 | | | | | - | 0.010 | 0.010 | 0.01 | 0.03 |
| **Formamide** | | | 1B | | | - | | | | |
| **1-Dodecanol** | | | | | | 77 | | | | |
| **BHT** | | | | ED* | | 0.86 | 0.10 | 0.10 | | |
| **Dimethyl phtalate** | | | | | | 16.3 | | | | |
| **Eicosane** | | | | | | - | | | | |
| **TXIB** | | | | | | 4.35 | 0.45 | 1.3 | | |

### 1.3.2. Toxicologically based guideline values for VOC air concentrations

To interpret the measured exposure concentrations and provide a reliable risk assessment, the comparison of experimental results with toxicological data is imperative. Measured inhalation concentrations can be directly compared with toxicologically based gas-phase concentration guideline values. The guideline values are usually derived from animal studies under consideration of assessment factors, mainly for intraspecies variability, interspecies variability and depending on the duration of exposure [37, 61].

Different guideline values were considered in this work:

- In most cases, the VOCs released from consumer products will result in increased indoor air concentrations. The German Committee on Indoor Guide Values (AIR, Ausschuss für Innenraumrichtwerte) sets guideline values (RWI and RWII) for indoor air concentrations, they are derived based on current toxicological and epidemiological knowledge. RWII is an effect-base value while RWI is a lower precautionary value. They correspond to levels at which no health impairment is expected, even after a life-long exposure [71]. The WHO also implemented indoor air quality guideline values for certain chemicals including benzene, formaldehyde or naphthalene [72].
- The Committee for the Health-related Evaluation of Construction Products (AgBB, Ausschuss zur gesundheitlichen Bewertung von Bauprodukten) defined a scheme to interpret results from emission test chamber studies of single construction products [47]. The emitted concentrations after 3 or 28 days in an emission test chamber are compared to the lowest concentration of interest (European LCI, Lowest Concentration of Interest [70], or corresponding German NIK, Niedrigste Interessierende Konzentration [47]).
- The DNEL (derived no-effect level) values are defined by the ECHA as recommended exposure levels above which humans should not be exposed. The DNEL values are published on the European Chemicals Agency (ECHA) website [65]. But unlike AIR or LCI values, they are established by the manufacturer or importer (registrant) of the substance following the ECHA Guidance Chapter R.8 [61]. Different values may be derived for workers and for the general population, values for the general population were considered in this work as the emissions from consumer products were assessed. Additionally, distinction is made between short-term and long-term exposures.

The European standard EN 71-9 also included inhalation limits in Table 2F but specifies that a measurement method still needs to be validated [28]. The recent amendment of the European Toy Safety Directive indicates a limit value of 0.1 mL/m$^3$ for formaldehyde when following EN 717-1 ([24, 28] and see also Chapter 2.4 for discussion). Other guideline values such as the

American Reference Exposure Levels (REL) might be used but this work focused on guideline values used in Germany and the EU.

The different guideline values considered in this work are summarized in **Table 4**. Differences are obvious and plausibly result from the consideration of different toxicological studies and assessment factors. Occupational exposure limits (e.g., OEL or MAK – occupational exposure Limit/maximale Arbeitsplatzkonzentration, TLV – threshold limit value, MRL – minimal risk level), are also derived from toxicological studies for indoor environments. However, they are not applicable in this work because they should be used for healthy adult populations and shorter exposure scenarios (8 hours per day).

### 1.3.3. Indoor air scenario

As indoor environments present much poorer air exchange than outdoor environments and human beings spend nowadays on average 90% of their time indoors and 65% at home [73], this work focused on indoor air scenarios. Higher pollution levels are expected in indoor air than in outdoor air [74, 75]. Recent studies investigated the burden of disease (i.e., the financial cost impact of a health problem) due to indoor air pollution for Europe [76] and France [77] combining field studies and toxicological knowledge. A cost of €20 billion per year, representing 1% of the French gross domestic product was evaluated considering six indoor air pollutants including the VOCs benzene and trichloroethylene. A more recent study also identified VOCs such as benzene as important contributors to the burden of disease in China where VOC concentrations are higher than in Europe [78]. Those studies are subject to many uncertainties, but they show that indoor air pollution is a serious societal issue. A better regulation of chemicals emitted from consumer products is necessary to tackle the problem.

Exposure assessment aims to determine the amounts of VOCs that would become available to consumers via inhalation. As with construction materials, an ideal indoor environment similar to an emission chamber with an air change rate of 0.5 $h^{-1}$, which is typical for residences, and a perfect air distribution (provided by the ventilator in the emission test chamber), can be considered [35]. A room size of 30 $m^3$ [35] and an exposure scenario with one sample in a room are useful to interpret exposures caused by single products. The values measured in the emission test chamber need to be extrapolated (dilution) to find the VOC indoor concentration caused by one single sample. This scenario depicted in **Figure 8** enables direct comparison with indoor air guideline values.

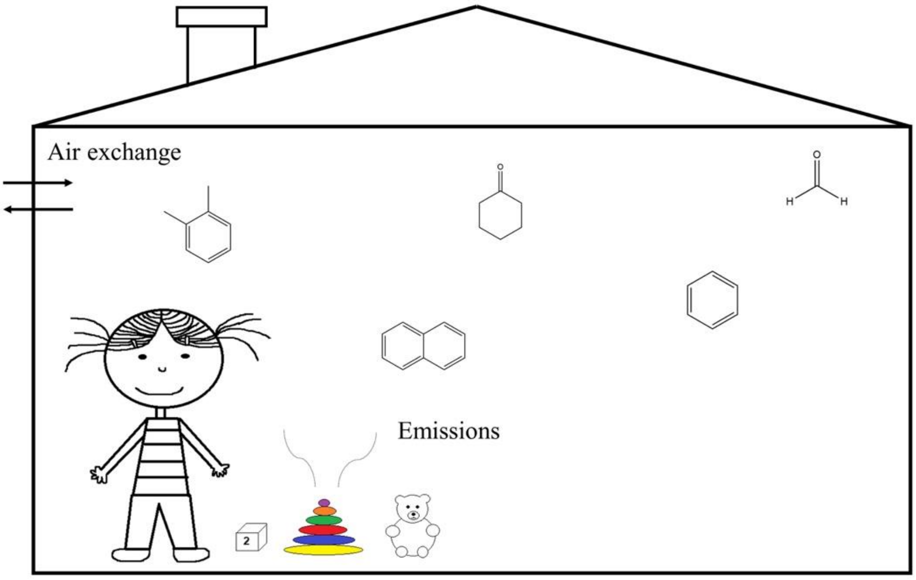


***Figure 8****: Schematic representation of the indoor air exposure scenario from one single product.*

If an air change rate higher than 0.5 h$^{-1}$ is applied for emission testing (Chapter 2.3, 2.4 and 2.6.2), a conversion based on the area-specific emission rate (see 1.2.2.1) needs to be performed to calculate the corresponding indoor air concentration:

$$C_{indoor} = \frac{SER_A * A}{V_{room} * n_{room}} = C_{CH} * \frac{V_{CH} * n_{CH}}{V_{room} * n_{room}} \tag{3}$$

with:
$SER_A$: area-specific emission rate (mg/h·m$^2$)
$C_{CH}$: chamber concentration (mg/m$^3$)
$V_{CH}$: chamber volume (m$^3$)
$n_{CH}$: chamber air change rate (/h)
A: sample surface area (m$^2$)
$C_{indoor}$: indoor air concentration (mg/m$^3$)
$V_{room}$: room volume (m$^3$)
$n_{room}$: room air change rate (0.5 /h)

### 1.3.4. Complex exposure scenario

Besides the indoor air scenario with a single product, other more conservative scenarios should be considered. If a child occupying a room is further considered, possible scenarios leading to higher exposure concentrations were described in the literature. It is often the case that more than one toy is present in the room (e. g. 40 toys [43]). It is also possible that the child plays very close to the emission source in a poorly ventilated room. This scenario causes the VOCs to be concentrated in the child's breathing zone (e.g., breathing zone of 1 $m^3$ [39]). Moreover, special products lead to distinctive exposure scenarios being considered: This was the case in this work with costume face masks for which the emitted VOCs are concentrated in the small volume between the mask and the human head (Chapter 2.5).

### 1.3.5. Risk assessment

Risk is a function of exposure and hazard. Once the exposure was assessed, the values were compiled with known hazard data, in this work with toxicologically based guideline values for gas-phase concentrations (see 1.3.2), to assess the potential risk. A risk is possible when the estimated exposure exceeds the corresponding guideline values. This topic will be discussed in more detail in Chapter 3.3.2.

## 1.4. Objectives

In the recent years, polymer-based consumer products have become increasingly popular around the globe. These products may contain potentially harmful substances. The risk does not necessarily originate from their presence alone but from their capacity to leave the material. They may for example volatize and ultimately enter the human body via inhalation and be harmful to health. Yet, current legislation in Europe is too permissive for this route of exposure compared to the potential burden, mostly because appropriate methods and exposure data are lacking for market surveillance.

The first objective of this work was to establish analytical methods based on GC/MS to characterize the emissions of VOCs from polymer-based consumer products. Furthermore, another aim of this thesis was the assessment of the inhalation exposure of consumers to those substances. Both the comparison of different emission test methods and the determination of the inhalation exposure towards risk assessment were the key elements.

**Method comparison to find practicable methods for market surveillance**

A central aim of this work was to compare emission test methods to determine which one would be appropriate for market surveillance. These methods should be adapted to the consumer product size, affordable, reliable and should enable a high sample throughput. Until now, comprehensive studies on emission test chamber comparisons are missing, especially on the comparison with modern miniaturized or automated devices. The key aspect of this subproject was to select the appropriate parameters and descriptor (area-specific air flow rate and area-specific emission rates, see Chapter 1.2.2.1) to allow a direct comparison. Different types of emission test chambers were investigated on a spiked polyurethane reference plate (Chapter 2.1 and 2.3) or, along with the flask method, on wooden samples (Chapter 2.4). The goal of these experiments was to seek functioning analysis methods for the determination of VOC emissions from consumer products in OCLs. Miniaturized chambers were then used to generate other meaningful results on the influence of sample properties on emission results (Chapter 2.6.1) or for exposure assessment (Chapter 2.3, 2.4 and 2.6.2).

### Determination of the inhalation exposure towards risk assessment

A second objective of this thesis was to provide an overview on the VOC inhalation exposure from the polymer-based consumer products from the German market (local or online shops). Over 70 samples (Chapter 2.2, 2.4, 2.5 and 2.6.2) were investigated in the following way:

1) Characterization of the constituting polymer (except for wooden toys)
2) Pre-selection of samples with high emissions (via DHS or flask method)
3) Evaluation of the emission over time with emission test chambers, determination of the emission rates
4) Exposure assessment, considering different exposure scenarios
5) Assessment of the potential risk by correlation of this exposure data with toxicological data

Another subproject was also carried out to provide a correlation between VOC emissions and perceived odors via sensory tests.

The results obtained in this work should facilitate the implementation of test methods and regulations for VOC emissions from polymer-based consumer products. The ultimate goal would be to provide OCLs with a standardized procedure. This would allow them to verify quickly and reliably if a product is likely to be harmful to health.

## 2. Results

The results of this thesis are divided in six chapters including four published articles. The aim of all these sub-projects was to provide a realistic exposure assessment from the measurement of the emissions of VOCs from polymer-based consumer products.

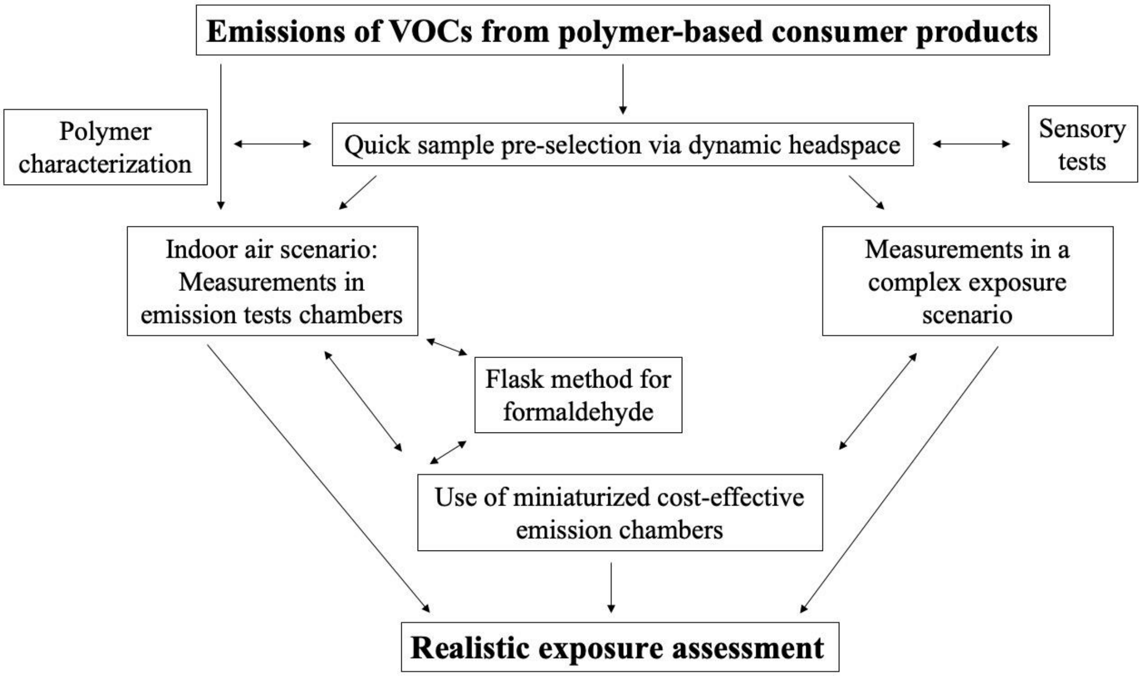


***Figure 9:** Overview of this work*

## 2.1. Preliminary results: Use of dynamic headspace (DHS) in automated emission testing

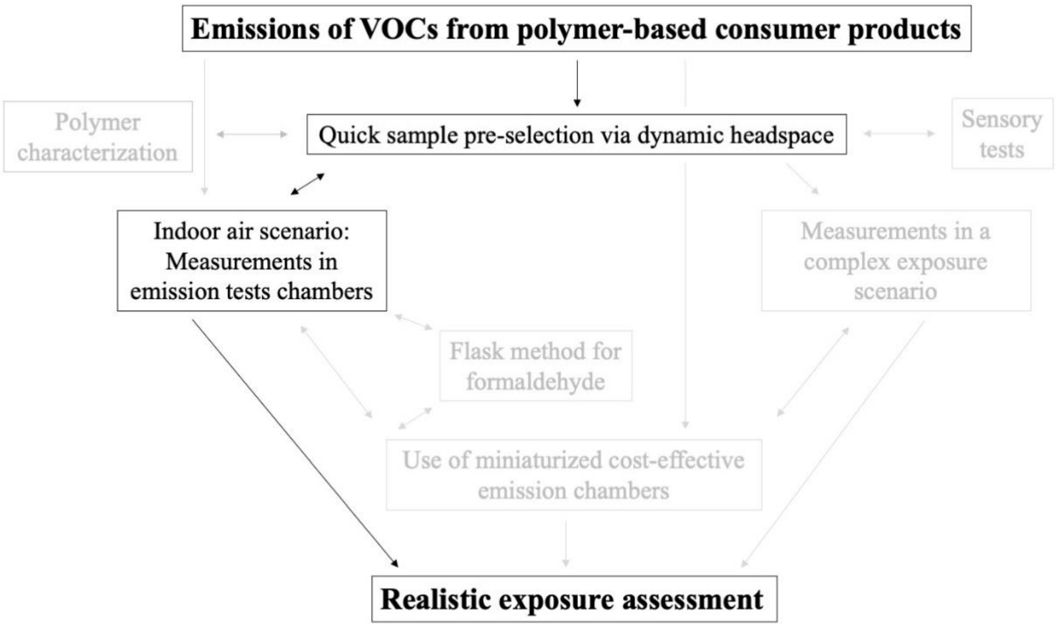


***Figure 10***: *Overview of this work, focus on preliminary DHS experiments 2.1.*

### *Introduction*

As introduced in Chapter 1.2.3.1, the DHS can be used continuously during several hours/days to mimic an emission test chamber. This study aimed at examining the correlation between results from a standard emission test chamber (203 L) and the DHS. Both the vial (20 mL) and large-volume container (1 L) options of the DHS were considered.

### *Methods*

A polymer reference material was employed in this work to compare emission measurements with different methods (see also Chapter 2.3 and 2.6.1). The use of a reference material allows the homogeneous dispersion of pre-defined substances in the sample. Polyurethane was used as material to manufacture these plates because it allows a synthesis at ambient temperature (cold casting system) and therefore a minimal loss of the volatiles spiked and homogenized during polymer synthesis. The material was synthesized by Polymaterials AG (Kaufbeuren, Germany) with a concentration of 1 mg/g of each VOC. The initial 14 compounds (see **Table 2** in 1.1.5) present in the polyurethane reference material were chosen because they had been detected in polymer-based consumer products by the OCLs and because they represented a wide range of physicochemical properties.

The continuous use of both 20 mL vial and 1 L container was tested and compared with a 203 L emission test chamber. The temperature was set to 23°C for both systems. The emission test chamber was operated with humidified synthetic air while the DHS used dry nitrogen as inlet gas. The surface-specific air flow rate was kept constant between both systems (see Chapter 1.2.2.1 and 2.3). The analytical procedure (air sampling and TD-GC/MS analysis) is described in Chapter 2.3. Further details to these experiments are also summarized in **Annex I** (poster).

### *Results*

Due to the monopolization of the analytical device during a continuous DHS experiment (see Chapter 1.2.3.1), these studies were limited to a few hours. The emission profiles depicted as area-specific emission rates (see Chapter 1.2.2.1) are shown in **Figure 11**.

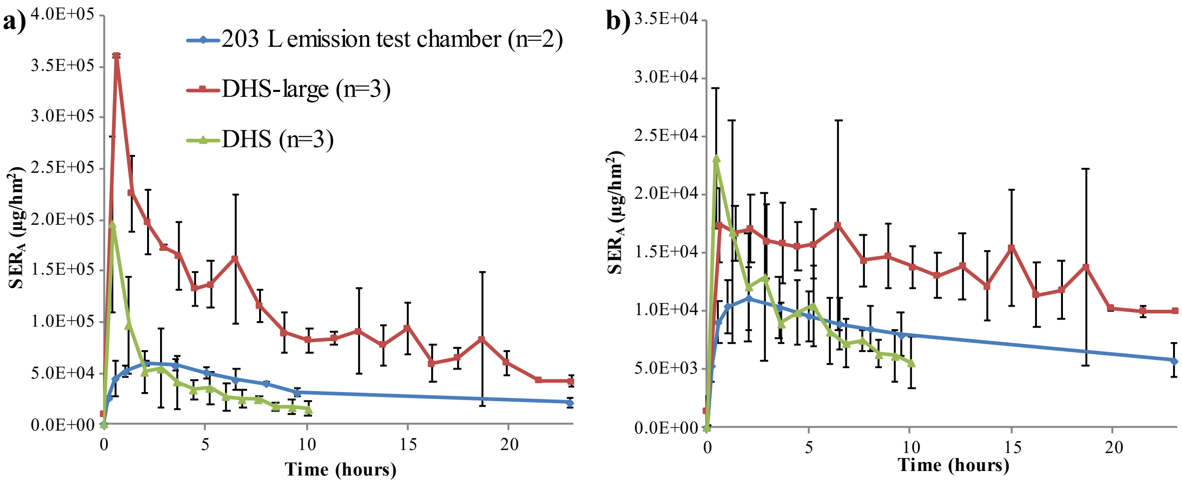


***Figure 11:*** *Results of the comparison between dynamic headspace (DHS; 20 mL vial; 10 hours), large-volume DHS (1 L container; 24 hours) and a 203 L emission test chamber (24 hours) for benzene (a) and acetophenone (b) emission measurements from a reference polyurethane material; repeated twice.*

As displayed in **Figure 11** for benzene (a) and acetophenone (b), the emissions in the DHS apparatus and the emission test chamber were in the same order of magnitude. The DHS results were slightly higher at first. With the higher air change rate in the DHS experiments, the concentrations sampled at the exit are at the beginning higher concentrated than in the emission test chambers. However, the decay was much faster in the 20 mL DHS vial than in the large-volume container or in the emission test chamber. This is probably due to the regular perforation of the vial septum, leading to an air leak which is more prominent for the 20 mL smaller vial.

For this reason, the study with the 20 mL vial was limited to 10 hours. Therefore, additionally to the fact that it monopolizes the analytical device, this setup is not adapted to long-term emission testing. Moreover, the standard deviation was found to be very high between repetitions, especially for the less volatile compounds. The use of DHS was sufficient for sample pre-selection as the emissions were in the correct order of magnitude. But the integration of a flowmeter in the sampling device would enable to verify possible reasons (flow variations) for the high deviations. This could not be achieved in the frame of this work.

### *Conclusion*

Based on the results obtained in this experiment, the DHS was further used for sample pre-selection (see Chapter 2.2, 2.5 and 2.6.2).

## 2.2. Emissions of VOCs From Polymer-Based Consumer Products: From Emission Data of Real Samples to the Assessment of Inhalation Exposure

Morgane Even, Mathilde Girard, Anna Rich, Christoph Hutzler and Andreas Luch, Frontiers in Public Health, 2019, 7:202.

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Involvement of the author within this publication: Project planning: 70%, project execution: 70%, data analysis: 85%, writing of the manuscript: 90%
Supplementary material: Annex II

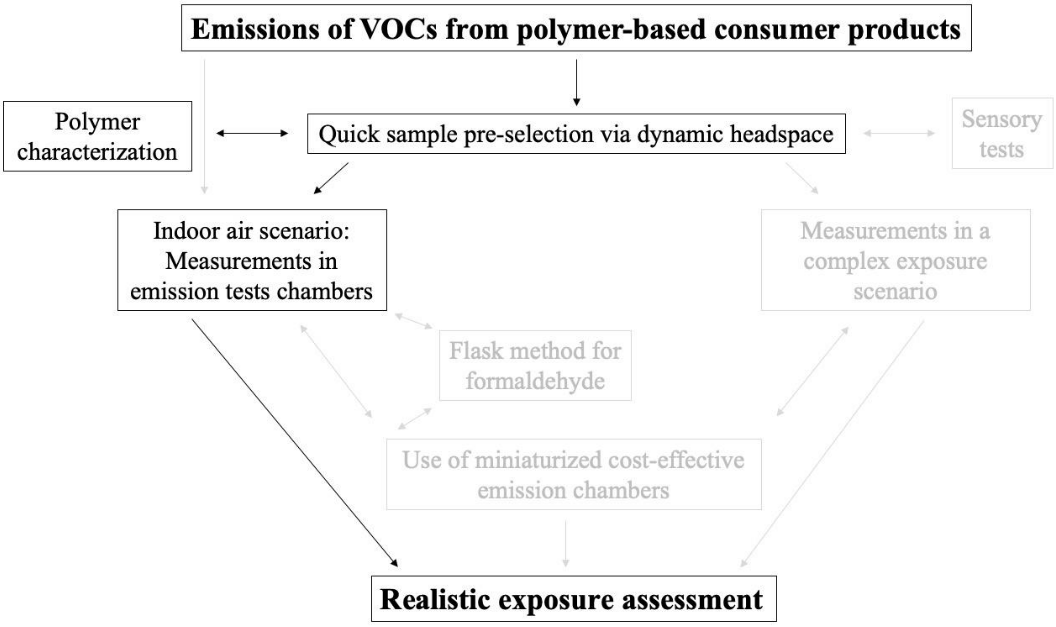

***Figure 12**: Overview of this work, focus on publication 2.2.*

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# Emissions of VOCs From Polymer-Based Consumer Products: From Emission Data of Real Samples to the Assessment of Inhalation Exposure

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The development of consumerism led to an increase in toy production. Such consumer products may contain non-intentionally added toxic substances that can emit from the product and may be inhaled by the consumer. Little data is available on the inhalation exposure of humans to volatile organic compounds (VOCs) from consumer products, so a reliable exposure assessment is needed. Only the emission chamber technique developed for building material emissions can provide solid estimations as it allows the products to be studied under real room conditions. This paper proposes a strategy to interpret emission experiment results from consumer products and assess the corresponding potential risk. It focuses on 14 common VOCs. The identification of the polymer type of 41 plastic articles was first performed by pyrolysis coupled online to gas chromatography with mass spectrometric detection (pyr-GC/MS). Their VOC profile was also determined by Dynamic Headspace-GC/MS (DHS-GC/MS). Softer polymers caused higher and broader emission profiles. Four specific toy samples were selected to be studied in a 203 l emission chamber and their emissions were compared to a reference material. A rapid decrease in the emissions was observed for each product and VOC. Based on these emission curves over time, the corresponding indoor air concentration could be calculated for the target VOCs for short-term or long-term exposures. The indoor air levels obtained were at least 35 times lower than the levels according to conventional indoor air guidelines. Guideline values were only exceeded using very conservative exposure scenarios.

**Keywords: emission, VOCs, toys, polymers, consumer, exposure**

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## INTRODUCTION

Today, we are living in a globalized world, with an economy that facilitates the global exchange of goods and people. The development of easier transportation means led to the establishment of multinational companies that export goods worldwide. The total revenue of the global toy market has significantly increased over the past decade (1). This competitiveness prompts manufacturers to produce more attractive and cheaper products, sometimes at the expense of quality. Moreover, it becomes more and more difficult to control goods entering the national market, as a significant part of the products is ordered directly by the client via the internet from one country to another.

Consumer products can contain harmful substances, such as residual solvents, monomers, or additives (2). Consumer complaints about strong and unpleasant odors from toys were registered and several studies addressed the identification of off-odorants in toys (3–5). These odors are linked to emissions of volatile organic compounds (VOCs) from the products that may also release other non-odorous but harmful substances. The emitted substances will end up in the indoor air and may negatively influence the occupants' health. Indoor air quality is a growing concern as humans are nowadays spending 65% of their time at home (6) and also staying indoors when they work or commute. The air change rates are decreasing because of enhanced insulation techniques (7). The overall exposure control can often be instituted by small individual actions (8) as the most important sources of pollution are small and close to the person (9). Main sources of short term emission of VOCs indoors are personal care and cleaning products or cooking. Furniture and building material emissions (10) are considered as important emission sources too as they result in long term emissions.

The emissions of VOCs from building materials have been studied in detail for some time (11). This resulted in the development of standardized analytical methods and health-related indoor air guidelines [AIR or LCI values (12, 13)]. However, consumer products (e.g., toys, water toys, decoration products) may also emit harmful substances that can be inhaled by the occupants. So far, the results on the evaluation of inhalation exposure due to consumer products are insufficient for an adequate exposure assessment, which is required for reliable risk assessment. Much work on the emissions of VOCs from similar products has been carried out with headspace techniques, with a syringe (14), Solid-Phase-Micro-Extraction-GC/MS (SPME-GC/MS) (15) or DHS-GC/MS (16). While such experiments provide results on emitted compounds, they give no claim regarding possible risks from product use (14). In fact, it does not allow the description of emission kinetics under consumer-relevant conditions and a realistic exposure assessment. No standard method exists to determine the inhalation exposure to consumer products. There is a need for more data to provide a realistic evaluation of the inhalation exposure of consumers.

The emission test chamber method (17) can be used for this purpose. It was developed to determine the emission of VOCs from building products and furniture under indoor air conditions. Air samples can be collected on sorbent materials and analyzed via GC/MS (18). This method has already been used for such products: The emissions of allergenic fragrances from scented toys were studied in a 1,000 l emission chamber over 28 days (19) while the emissions of VOCs from "squishy toys" were characterized in a 113 l emission chamber (20) after 1 h or 3 days. The present work focuses on pre-selected non-scented products and non-intentionally added substances (NIAS) and presents 28 day emission profiles and a varied range of samples while describing a method for exposure assessment.

This work focuses on 14 substances which are summarized in **Table 1**. These compounds depict a broad range of physico-chemical properties (volatility, molecular weight, or polarity) and were all found in toy or consumer product samples by the German enforcement laboratories. Most of them are also described in the literature (3, 5, 16, 20) and some of them like benzene have carcinogenic, mutagenic, or reprotoxic properties (22) (**Table 1**). To evaluate the viability of reference materials to depict reliable emission profiles, a polyurethane material was spiked with the 14 substances in order to compare their emission profiles to real samples.

As 28 day tests are costly and long, a sample pre-selection was carried out. First, the polymer structure of 41 plastic consumer products was characterized via Pyrolysis-GC/MS. In parallel, their VOC profile was determined via DHS-GC/MS. Four samples with high emissions of target compounds were then successively placed in the 203 l emission chamber. Air samples were taken regularly to follow the emission kinetics and therefore provide a complete estimation of the inhalation exposure over 28 days. The exposure was assessed by calculating indoor air concentrations and comparing them to indoor air guideline values (**Table 1**). The goal of this work was to introduce an effective strategy for sample selection and interpretation of emission testing results to provide solid estimations of the inhalation exposure to VOCs in consumer products.

# MATERIALS AND METHODS

## Chemicals

The VOC ingredients under consideration are summarized in **Table 1** and were supplied from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, USA). Ethyl acetate of analytical grade was obtained from Merck and used as organic solvent for all solutions.

## Materials

Standard material and real samples were studied. The standard plasticized polyurethane reference material plates were spiked with 12 different VOCs. The three xylene isomers were spiked as a single substance. Polyurethane was chosen because it can be synthesized at low temperature to prevent the loss of the VOCs spiked during the synthesis. It was doped at a target concentration of 1 mg/g, which enables the observation of all substances' emissions while still being realistic for material contamination, and custom synthesized by Polymaterials AG (Kaufbeuren, Germany). The plates had DIN A4 dimensions (21.0 × 29.7 cm) with a thickness of 6 ± 0.2 mm and a hardness of shore 70. Pieces of 12 × 10 cm were cut from the plate with a precision knife from NT cutter (Osaka, Japan) and placed in the emission chamber. Cutting metal utensils were cleaned twice with ethyl acetate and dried in the lab 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.

Forty-one plastic toys or decoration products were bought from local shops and kept in gas-tight bags made of aluminum composite-layer film at room concentration until usage. Four specific samples were used further for emission experiments, their properties are summarized in **Table 2**.

**TABLE 1 |** Target VOCs with associated CAS number, boiling points ($T_B$), molecular weights (MW), octanol-water partition coefficient (LogPow) (21), carcinogenic, mutagenic, reprotoxic (CMR) properties (22), and indoor air concentration guidelines ($mg/m^3$) (12, 13, 23).

| Name | CAS | $T_B$(°C) | MW | LogPow | C | M | R | AIR RWI | RWII | EU-LCI | NIK | DNEL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Benzene | 71-43-2 | 80 | 78 | 2.1 | 1A | 1B | – | – | – | – | – | – |
| Toluene | 108-88-3 | 111 | 92 | 2.7 | – | – | 2 | 0.3 | 3 | 2.9 | 1.9 | 192 |
| m-Xylene | 108-38-3 | 139 | 106 | 3.2 | – | – | – | 0.1 | 0.8 | 0.5 | 2.2 | 221 |
| 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 | – | – | 1B | – | – | – | 0.015 | 15 |
| Cyclohexanone | 108-94-1 | 156 | 98 | 0.8 | – | – | – | – | – | 0.41 | 0.41 | 40 |
| Phenol | 108-95-2 | 182 | 94 | 1.5 | – | 2 | – | 0.02 | 0.2 | – | 0.01 | 8 |
| Acetophenone | 98-86-2 | 202 | 120 | 1.6 | – | – | – | – | – | 0.49 | 0.49 | 22 |
| 2–Phenyl–2–propanol | 617-94-7 | 202 | 136 | 1.8 | – | – | – | – | – | – | – | – |
| Formamide | 75-12-7 | 210 | 45 | −0.8 | – | – | 1B | – | – | – | – | 6.6 |
| Isophorone | 78-59-1 | 215 | 138 | 1.6 | 2 | – | – | – | – | – | – | 11 |
| Naphthalene | 91-20-3 | 218 | 128 | 3.3 | 2 | – | – | 0.01 | 0.03 | – | 0.05 | 25 |
| Dodecanol | 112-53-8 | 259 | 186 | 5.1 | – | – | – | – | – | – | – | – |

**TABLE 2 |** Overview of the four selected samples for emission chamber experiments.

| No | Description | Dimensions per piece ($cm^3$) | Manufacturer/ importer | Country of origin | Identified polymer |
|---|---|---|---|---|---|
| #1 | 2 water wings turtle | 13.6 × 13.9 × 14.4 | I | China | PVC |
| #2 | Plopper animal figurine | 13.8 × 7.8 × 8.8 | II | China | PVC |
| #3 | Plopper penguin figurine | 14.6 × 8.5 × 8.1 | II | Not given | PVC |
| #4 | 10 piece puzzle play mat | 32.2 × 32.2 × 1.0 | III | Not given | PE |

## Pyr-GC/MS

Pyr-GC/MS enables the identification of the polymer structure via a thermal degradation of the polymer and the identification of the degradation products. A pyrolysis filament mounted on a Pyrolyzer Module was localized in a thermal desorption unit (TDU). It was connected to a cooled Injection System (CIS) equipped with liquid nitrogen cooling and a MultiPurpose Sampler (MPS2-XL; all items from Gerstel, Mülheim an der Ruhr, Germany). The CIS was installed into a gas chromatograph coupled with the mass selective detector 7890A-5975C GC/MSD System (Agilent, Santa Clara, CA). Pyrolysis of a polystyrene solution was performed regularly at 500°C for 0.33 min to assure a reliable performance of the system by evaluating the signal intensity for styrene oligomers. A constant ratio of the monomer-signal to the trimer-signal was used as quality requirement: a value of 3.9 ± 0.6 was indicative of an appropriate pyrolysis. Pieces of the polymers were cut as small as possible and placed directly into pyrolysis tubes (Gerstel) above a glass wool piece. A solvent vent method was applied: 60 ml/min helium (purity ≥99.999%, Linde, Pullach, Germany) passed into the Pyr-TDU-CIS complex using a pneumatic gas regulator (Gerstel) and a vent pressure of 30 kPa was applied. The pyrolysis took place subsequently at a temperature of 700°C to decompose the polymer (24). A lead time of 0.10 min, an initial time of 0.33 min and a follow-up time of 1.00 min were used. The TDU temperature was initially set at 50°C, followed by a ramp at 720°C/min up to 320°C and a final hold for 1.43 min. The CIS initial temperature was held at −120°C using cryo cooling to capture the volatile pyrolysis products for 4 min and was followed by a ramp of 12°C/min up to 320°C and a final hold for further 3.0 min.

Chromatographic separation was performed using an HP-5MS GC column (30 × 0.25 mm i.d., 0.25 μm df, Agilent) equipped with a pre-column (10 × 0.25 mm i.d., Phenomenex, Aschaffenburg, Germany). Helium gas (purity ≥99.999%) from Linde was used as a carrier gas at a constant flow of 1.0 ml/min. The GC oven was heated at 50°C for 6 min, ramped with 10°C/min to 320°C and held for an additional 3 min. MS analyses were carried out by collecting total ion chromatograms in the full scan mode and the mass range of 30–500 amu. Data were processed with the Chemstation E.02.02 software from Agilent. The degradation products were identified utilizing the NIST 11 mass library with the spectral search program version 2.0 distributed by Agilent.

## Dynamic Headspace

DHS was used to provide a quick determination of the VOC profile of the 41 samples. It does not lead to a direct exposure assessment, but the existence of an air exchange allows the comparison of samples under realistic conditions. Pieces of 0.13–3.03 g were cut with baked metal scissors to fill approximately half of 20 ml glass headspace vials tightly closed with magnetic

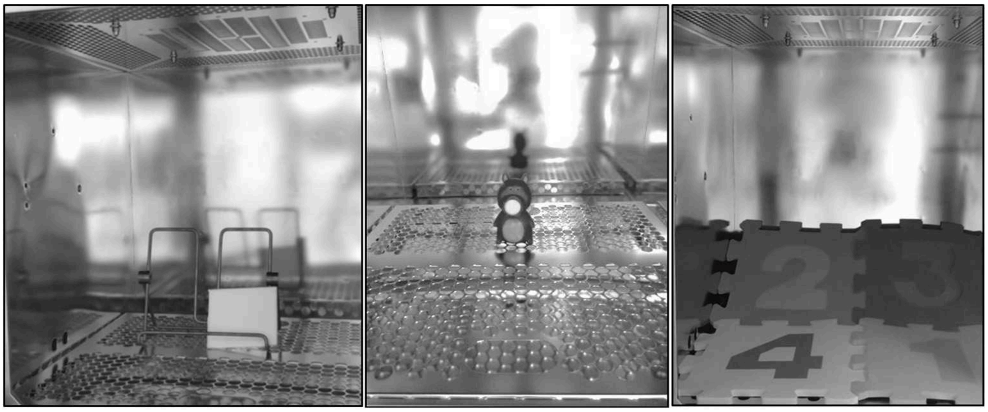

**FIGURE 1 |** Placement of the standard polyurethane plate (left), sample #2 (middle), and sample #4 (right) in the emission chamber.

silicon/PTFE caps. After a few hours of equilibration at room temperature, the headspace was purged with 600 ml nitrogen (purity ≥99.999%, Linde) with a flow rate of 15 ml/min. Analytes were trapped at 23°C on glass desorption tubes (6 × 0.4 cm i.d. × 0.6 cm o.d.) from Gerstel filled with Tenax TA®. The transfer heater between the vial and the desorption tube was held constant at 50°C. A conditioned desorption tube was used for each sample vial (procedure described in section Air Sampling From the Emission Chamber). The DHS apparatus was cleaned between each run: an empty glass vial was flushed with 1,000 ml at a flowrate of 100 ml/min at 70°C while the transfer heater was held at 70°C.

A DHS score was calculated for each target analyte and each sample. The signal area ($A_{\text{sample}}$) was normalized with the IS (internal standard) signal area, corrected with the blank and normalized with the sample weight so that the results are comparable:

$$\text{DHS score} = \frac{\frac{A_{\text{sample}}}{A_{\text{IS sample}}} - \frac{A_{\text{blank}}}{A_{\text{IS blank}}}}{\text{Sample weight}}$$

## Emission Chamber

In experiments of this kind, the test sample is placed in an emission chamber which consists of a material with low adsorption and desorption characteristics. The environmental parameters in the chamber are regulated to mimic an indoor environment. A 203 l VOC emission test chamber model VCE 200 from Vötsch Industrietechnik (Balingen-Frommern, Germany) was used for emission testing. It had an inner chamber made of electro-polished stainless steel and a ventilator to ensure homogeneous air distribution. The standard plate pieces were placed on an easel while the toy samples were placed on the metal grid positioned at the bottom of the chamber (see **Figure 1**). Four samples with high emissions were pre-selected: The whole figurine for sample #2 and #3, one water wing for sample #1 and four puzzle pieces for sample #4 were loaded in the chamber. The parameters were set up in line with ISO 16000-9 (17) to a temperature of 23 ± 2°C, 50 ± 5% relative humidity and an air change rate of 0.5/h.

## Air Sampling From the Emission Chamber

Active air sampling was performed following ISO 16000-6 (18) using glass desorption tubes (6 × 0.4 cm i.d. × 0.6 cm o.d.) from Gerstel filled with Tenax TA®. Active sampling of 500 or 600 ml was carried out using a Gillian Dual Mode Low Flow Sample pump (Sensidyne, FL, USA) with an airflow of 100 ml/min. Blank samples were taken before the emission chamber was loaded to ensure low blank values of the chamber. Different air samples were regularly collected over 28 days after sample loading. For the reference plate, the whole experiment was repeated while for the toys, two air samples were collected successively for each time point. Prior to sampling, tubes were conditioned over 3 h with a nitrogen flow of 75 ml/min at 300°C. p-Xylol-$d_{10}$ at 1 ng/μl or cyclodecane at 50 or 500 ng/μl in ethyl acetate were used as internal standard solutions in the different tests and stored in a freezer (−18°C). One microliter of internal standard solution was manually spiked with a rinsed 1 μl microvolume syringe (Trajan, Victoria, Australia) onto the desorption tubes. It was dried with 100 ml lab air or nitrogen at a flow rate of 100 ml/min. The tubes were stored in tight plastic storage containers from Gerstel at room temperature and subsequently loaded and analyzed within 1 week.

## Analysis of Air Samples (DHS and Emission Chamber)

The analysis was also carried out following ISO 16000-6 (18). Thermal desorption was performed in a TDU from Gerstel that had been connected to an Agilent 6890 gas chromatograph coupled with an Agilent 5975 mass selective detector. A helium gas flow and the following temperature program were used: 25°C for 0.2 min, then increase at 700°C/min to 280°C and final hold for further 2 min. During thermal desorption, analytes were cryotrapped with liquid nitrogen from Linde at −150°C in the 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 min. Analysis from air samples was adapted from splitless to split 1:400 to allow every analyte to be quantified in its linear range.

**TABLE 3 |** Analytical parameters: Retention time (RT), quantifier and qualifier ions.

| Name | RT (min) | Quantifier | Qualifier 1 | Qualifier 2 |
|---|---|---|---|---|
| Benzene | 6.5 | 78 | 52 | 77 |
| Toluene | 8.0 | 91 | 92 | – |
| m/p-Xylene | 9.7 | 91 | 106 | – |
| o-Xylene | 10.2 | 91 | 106 | – |
| Dimethylformamide | 8.1 | 73 | 44 | – |
| Cyclohexanone | 10.2 | 55 | 98 | 69 |
| Phenol | 11.1 | 94 | 66 | 65 |
| Acetophenone | 12.8 | 105 | 77 | 120 |
| 2–Phenyl–2–propanol | 13.0 | 121 | 77 | 43 |
| Formamide | 6.8 | 45 | 44 | 43 |
| Isophorone | 13.6 | 82 | 138 | – |
| Naphthalene | 14.8 | 128 | 127 | 102 |
| Dodecanol | 19.3 | 55 | 69 | 83 |

The gas chromatograph (GC) was equipped with a DB-5MS column (60 m × 0.32 mm i.d., 1.00 µm df) (J & W Scientific, Folsom, CA, USA). 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 min, was heated up to 200°C at 12°C/min, held for 5 min then heated up to 280°C at 20°C/min and held for 10 min.

The temperatures of the transfer line, quadrupole, and ion source were 295, 150, and 230°C, respectively. The mass spectrometer was used in combined SIM-Scan mode. The mass range in full scan was 40–450 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 target compound and internal standard. One quantifier and one or two qualifier ions were used (see **Table 3**), with dwell times of 10 ms.

## Quantitative Analysis of VOC Emissions

Analytes were quantified by internal calibration. Cleaned desorption tubes were first spiked with internal standards as described in section Air Sampling From the Emission Chamber. One microliter of the prepared solution in ethyl acetate, stored in a freezer (−18°C), was then also spiked with a rinsed 1 µl microvolume syringe (Trajan).The tubes were then dried, depending on the sampling volume, with 500 or 600 ml lab air or nitrogen at 100 ml/min. Subsequently, desorption tubes for calibration were analyzed as described in section Analysis of Air Samples (DHS and Emission Chamber).

Data processing was performed with the Mass Hunter Quant Software (B.05.00) from Agilent. The results were calculated as piece-specific emission rate according to the ISO (International Organization for Standardization) norm 16000-9 (17) and extrapolated for sample #1 and #4 to the whole sample:

$$\mathrm{SERpiece} = \frac{\mathrm{Cchamber}*\mathrm{Vchamber}*n}{F}$$

with $\mathrm{SER}_{\mathrm{piece}}$: Piece-specific emission rate (µg/h)
$\mathrm{C}_{\mathrm{chamber}}$: Analyte concentration in the chamber (µg/m$^3$)
$\mathrm{V}_{\mathrm{chamber}}$: Volume of the chamber (m$^3$)
n: Air change rate (/h)
F: Fraction of the whole sample placed in the chamber

The dispersion of values is displayed with the standard deviation of two measurements.

## Exposure Assessment

The room concentration is calculated for a 30 m$^3$ room according to EN 16516:2017 (24) and compared to indoor air guideline values. The German Committee on Indoor Guide Values derives limit values (AIR-values, RWI, and RWII) that are based on current toxicological and epidemiological knowledge and correspond to levels where no health impairment is expected, even with a life-long exposition (12). The European LCI (lowest concentration of interest) values or the corresponding German NIK values (13) are usually compared to the emissions of building materials determined after 28 days of testing in the emission chamber. Unlike building materials, toys may be used directly after unpacking, so their emissions for the first hours were here compared to EU-LCI guideline values. The DNEL (Derived No-Effect Level) (23) values are defined by the German social accident insurance as derived exposure levels above which workers should not be exposed. The different values for the target analytes are shown in **Table 1**. AIR and LCI/NIK values are therefore chronic values while the DNEL is an acute level. For consumer products, lower DNEL values should be considered as they can affect more sensible groups (e.g., children), but those values were not available.

# RESULTS

## Material Characterization

To characterize the polymer structure, chromatograms obtained upon pyrolysis of the consumer product samples were analyzed. The degradation products were identified and the peak list of each sample was compared to model chromatograms found in reference literature (25). Among 41 samples, 26 were identified as polyvinylchloride (PVC), 4 as polyethylene (PE), 4 as methyl methacrylate-butadiene-styrene copolymer, 3 as styrene-butadiene-styrene copolymer, 2 as polystyrene, 1 as polydimethylsiloxane, and 1 as polypropylene. The regular pattern of alkene chains surrounded by their corresponding diene and alkane analogous compounds is for example characteristic of polyethylene degradation. In all PVC samples, the presence of halogen could be confirmed via the Beilstein test: when the samples were brought in contact with copper, an applied flame turned green.

## VOC Profile

The VOC profile was characterized by application of DHS-GC/MS to all 41 samples.

$$\text{DHS score} = \frac{\frac{A_{\text{sample}}}{A_{\text{IS sample}}} - \frac{A_{\text{blank}}}{A_{\text{IS blank}}}}{\text{Sample weight}}$$

In **Figure 2**, the sum of the mean analyte DHS score is depicted for each polymer type. The highest scores were found for cyclohexanone, toluene and 2-phenyl-2-propanol. It

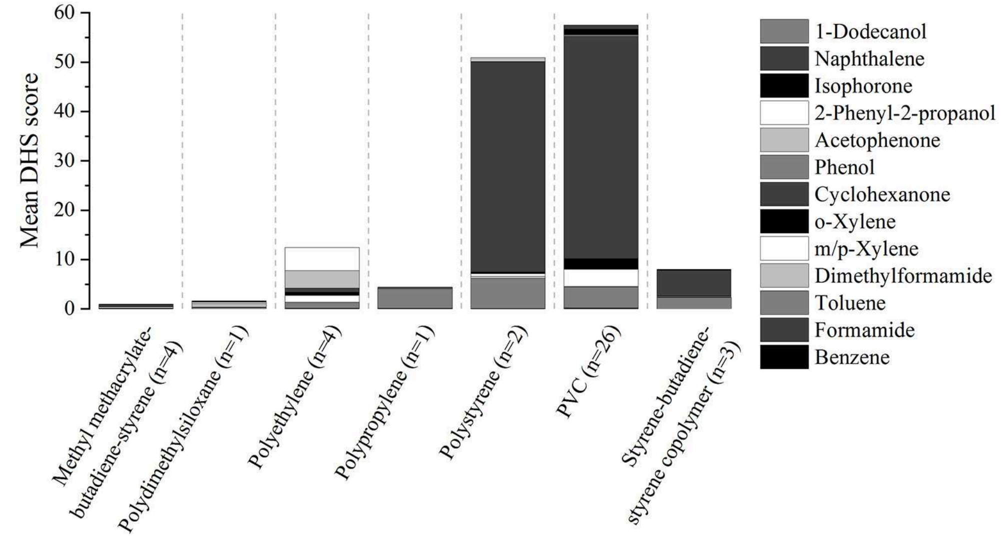

**FIGURE 2 |** Sum of mean analyte DHS score for each type of polymer.

could be observed that softer plastics like PVC, polystyrene or PE emit larger quantities compared to hard ones like polydimethylsiloxane or methyl methacrylate-butadiene-styrene copolymer. This was probably due to the polymer structure: More porous polymer may contain and emit more VOCs because of more inner free space and easier diffusion processes.

Three PVC samples and one PE sample were selected for subsequent emission testing (**Table 2**) because they led to relative high scores of different target analytes and the remaining sample quantity was representative and big enough for the emission chamber. An example for Pyr-GC/MS and DHS-GC/MS chromatograms is shown in **Supplementary Figure 1** for sample #4.

## Quantification of Emissions

A piece of the reference material plate and four real samples were studied in the 203 l emission chamber for 28 days each. Six target analytes (m- or p-xylene were considered as one analyte as they cannot be separated completely by the chromatographic method used) could be detected in the toys' emissions. The total emitted amounts per toy or material plate, calculated by taking the area under the emission curve, are displayed in **Figure 3** using a logarithmic scale. The standard reference plate spiked with 1 mg/g emitted much higher quantities compared to the four real samples. The most similar emission value was found for 2-phenyl-2-propanol from sample #4 with values only three times lower than from the polyurethane reference material. o-Xylene from the reference material showed much lower total emission values compared to the other target substances because only one isomer (m- or p-xylene) was spiked with 1 mg/g while the two others were impurities of the spiked substance.

The piece-specific emission rate ($SER_{piece}$) profiles of four analytes emitted from the toy samples are shown in black on **Figure 4**. In gray, the curves obtained for the same analytes from the standard polyurethane plate were normalized to result in the same maximal emission rate.

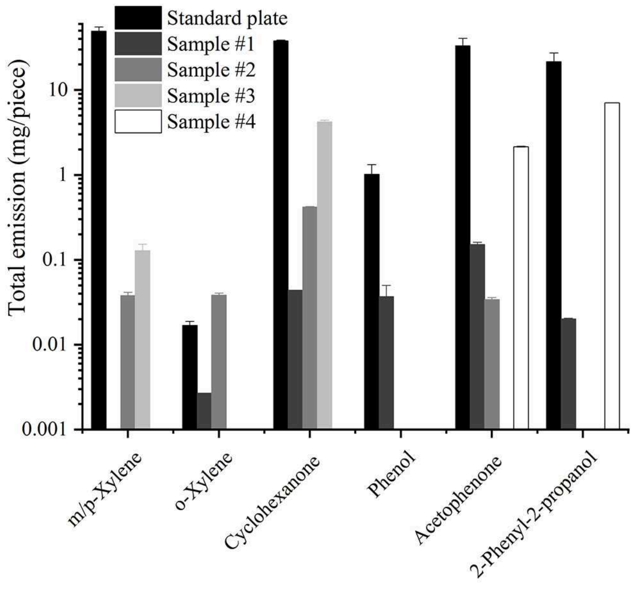

**FIGURE 3 |** Total emission values during 28 days for 6 substances from the reference plate and the toy samples.

## Exposure Assessment

VOC concentrations found in the 203 l emission chambers can be diluted to look into the influence of the sample emissions on the room concentrations. The new European standard (26) suggests 30 $m^3$ as the volume for a reference room. In **Figure 5**, the calculated room concentration of analytes for which indoor air concentration guidelines exist are depicted for each toy sample on a logarithmic scale and compared to guidelines. No indoor air guideline values exist for substances such as 2-phenyl-2-propanol, which was emitted at high concentrations from the play mat. The monitoring of VOC emissions over a month

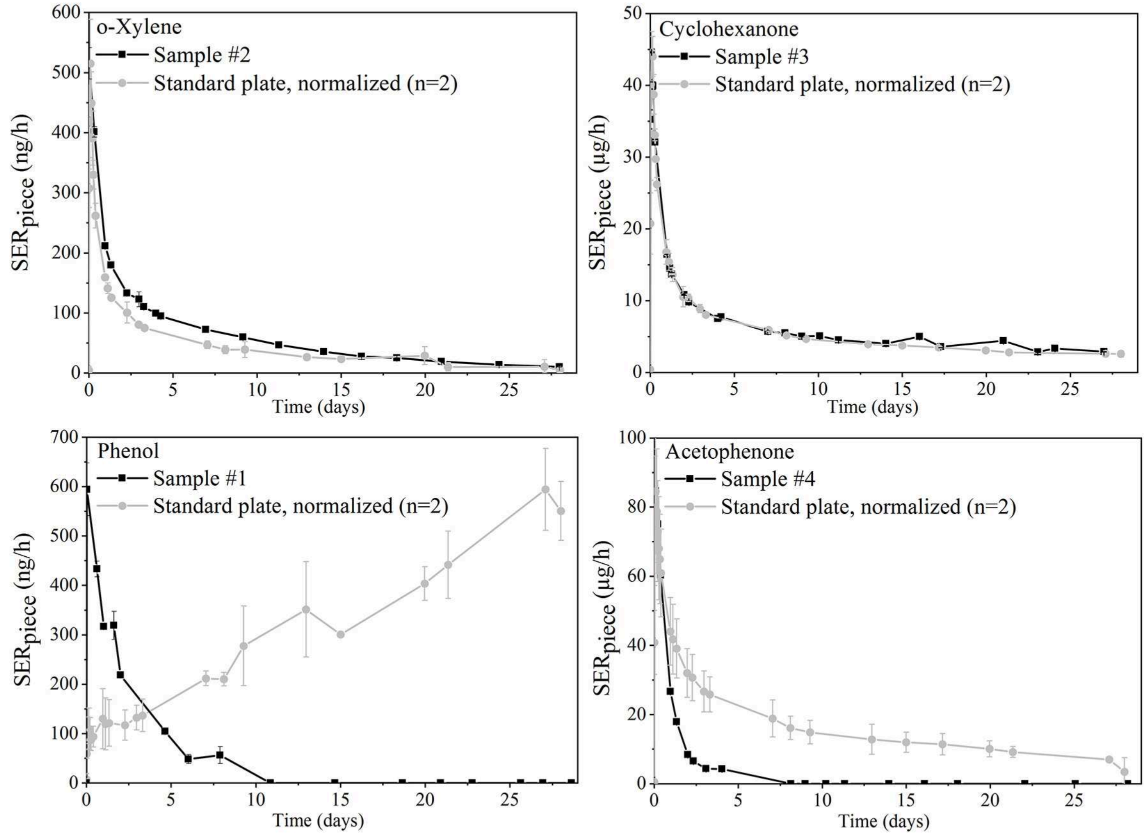

**FIGURE 4 |** Emission profiles of four selected analytes from toy samples and comparison to normalized curves of the polyurethane plate (same maximum concentration).

enables the study of different exposure cases: The maximum detected concentration (always after a few hours), the mean concentration in the first hours (from 7.1 for sample #3 to 14.9 h for sample #1 depending on sampling points) and the mean concentration over 28 days are shown. They, respectively, correspond to a peak exposure (child shortly playing at maximum concentration), a short-term exposure (child playing for a few hours or sleeping with the toy) and a long-term exposure (the toy stays a month in the child's room). Room concentrations induced by single samples were much lower compared to guideline values. The closest one was the maximum acetophenone concentration from a play mat which was 35 times lower than the EU-LCI value mentioned in (13).

# DISCUSSION

## Interpretation of the DHS Experiments

For the DHS experiments, only a score based on the sum of the target substances was presented in the result part. Data were analyzed statistically to establish whether or not the polymer type correlates with the emission profile. For this purpose, it is possible to use Principal Component Analysis (PCA). A 3D plot of a PCA with three principle components was considered. No grouping based on the polymer structure could be determined when 29 target substances were considered.

## Emission Profiles

**Figure 4** displays different emission profile shapes. They were compared between the standard plate and the toy samples for the different analytes of interest: For o-xylene from sample #3 and cyclohexanone from sample #2, the toy and plate profiles were very similar: The spiked reference material was in this case a good model to mimic real sample emission profiles.

However, the results can differ when the analyte depicts chemical properties that may interact with specific materials. Phenol emissions from the standard plate increased for example over 28 days while the phenol emission curve from sample #1 decreased. The synthesis of the polyurethane plates was conducted by reaction of an isocyanate and a polyol. It might be a reasonable explanation that part of the isocyanate functions also bound to the hydroxyl groups of the available VOCs. They were therefore released much more slowly than the other substances with the same volatility. Differences in emission profiles may also come from specific properties of the material itself. Acetophenone emissions decreased for example much more quickly from the play mat compared to the polyurethane standard material. This was probably

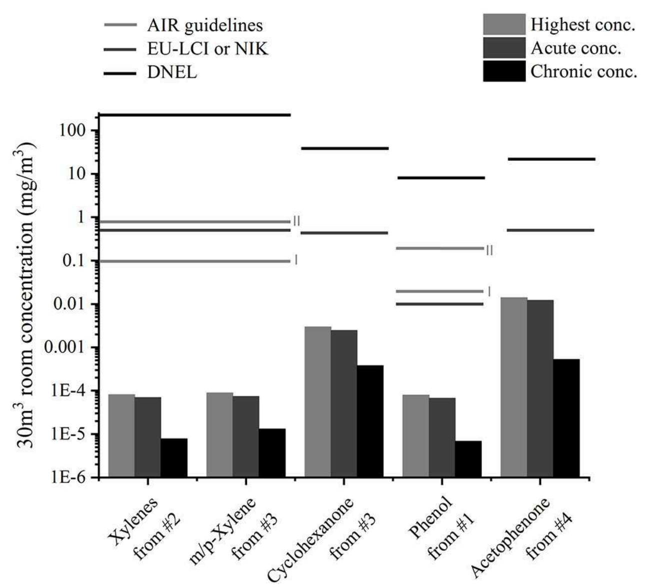

**FIGURE 5 |** Calculated highest, acute (mean over first hours) and chronic (mean over 28 days) room concentrations of analytes from the four samples and comparison to indoor air concentration guideline values (12, 13, 23).

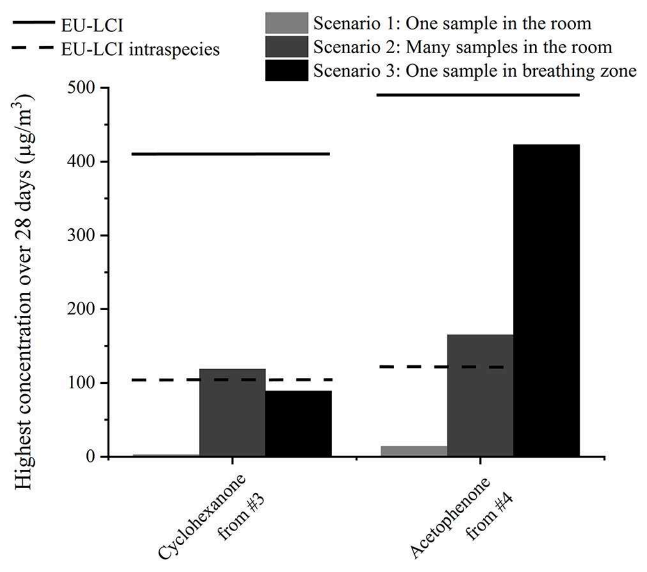

**FIGURE 6 |** Calculated highest concentrations of two substances from two samples depending on the exposure scenario and comparison to the EU-LCI guidelines (13).

caused by the fact that the play mat is made of foam which allows much faster internal diffusion compared to a polyurethane plate.

For all four toy samples, a quick decrease of the VOC emissions is observed in the first hours or days after unpacking. If we only take these compounds into account, a good advice would be to let the toy outside for a few days before use. However, other chemicals like semi-volatile organic compounds are not considered here and could result in persistent high exposure over longer time frames.

## Exposure Scenarios

First assessments led to acceptable values for single substances from one product, but the realistic exposure scenario is more complex. Products often emit mixtures of substances that may trigger the same toxicological end point and therefore induce a cumulative effect. Moreover, children's toys only represent an additional source to human activities such as cooking, and other material emissions from building materials or furniture. Furthermore, other exposure scenarios different from the one used in section Exposure Assessment which considers only one sample in one 30 m$^3$ room could be taken into account. In **Figure 6**, the highest emitted concentrations for two other scenarios are shown for cyclohexanone from sample #3 and acetophenone from sample #4. In the second scenario, not only one but several samples are present in the 30 m$^3$ room: The floor of the model room (12 m$^2$) is carpeted with the play mat or 40 figurines [as suggested in (20)] are present in the room. As the air distribution and ventilation may not be as good in a real room compared to the emission chamber, the air volume around the object may contain higher emission concentrations compared to the rest of the room. In the third scenario, a breathing zone of 1 m$^3$ around the sample, as used in Masuck et al. (19), was considered. Those results were compared to the EU-LCI guidelines. As described in (20), an intra-species factor of four can be considered for a child, as it is more vulnerable than an adult. Only with this consideration did the emission concentrations exceed the guidelines for cyclohexanone from #3 in the first scenario and for acetophenone from #4 in both scenarios.

## CONCLUSION

This study was carried out to fill the data gap necessary for the exposure assessment of VOC emissions from consumer products made of polymers. It was first shown, based on 41 samples and DHS experiments, that softer polymers emit broader and higher VOC profiles than harder plastics. Four specific samples were selected to be studied in an emission chamber over 28 days and their emissions compared to those of a reference polyurethane plate spiked with 14 VOCs. The real samples led to lower total emitted quantities than the reference material spiked at 1 mg/g, but the emission curves could result in similar shapes depending on the analyte and material properties. The room concentrations derived from the emissions of each single sample in a 30 m$^3$ room were lower than existing indoor air guidelines. However, when other scenarios with more samples in the room or a smaller breathing zone were considered, the highest emitted concentrations exceeded the EU-LCI guideline corrected with an intra-species factor for children. Those first estimations are of low concern as the EU-LCI is a guideline for chronic concentrations and it was only exceeded by the peak concentrations in extreme scenarios. It was demonstrated that the experimental approaches used and the strategy for calculating exposure scenarios for VOCs emitted from consumer products is feasible for risk assessment. To our best knowledge, this is the first study to give a full characterization of the polymer type and the VOC profile of consumer product samples as well as complete emission curves from reference materials or real samples and results on the inhalation exposure assessment. It should always be considered that consumer products may represent an additional source of VOC emissions beside well-known sources, such as building products. More data regarding emissions from consumer products will be necessary in the future to provide a better overview on the current market and make it possible to exclude health risks for consumers. Standardized methods will also be required to support the routing work of official control labs.

## DATA AVAILABILITY

The datasets generated for this study are available on request to the corresponding author.

## AUTHOR CONTRIBUTIONS

Each author has participated in the work intellectually or practically and takes responsibility for the content of this article. ME, MG, and AR carried out the practical work and data analysis. ME, CH, and AL designed the study, interpreted the results, and contributed to the manuscript. The final version was approved by all authors.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fpubh.2019.00202/full#supplementary-material

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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

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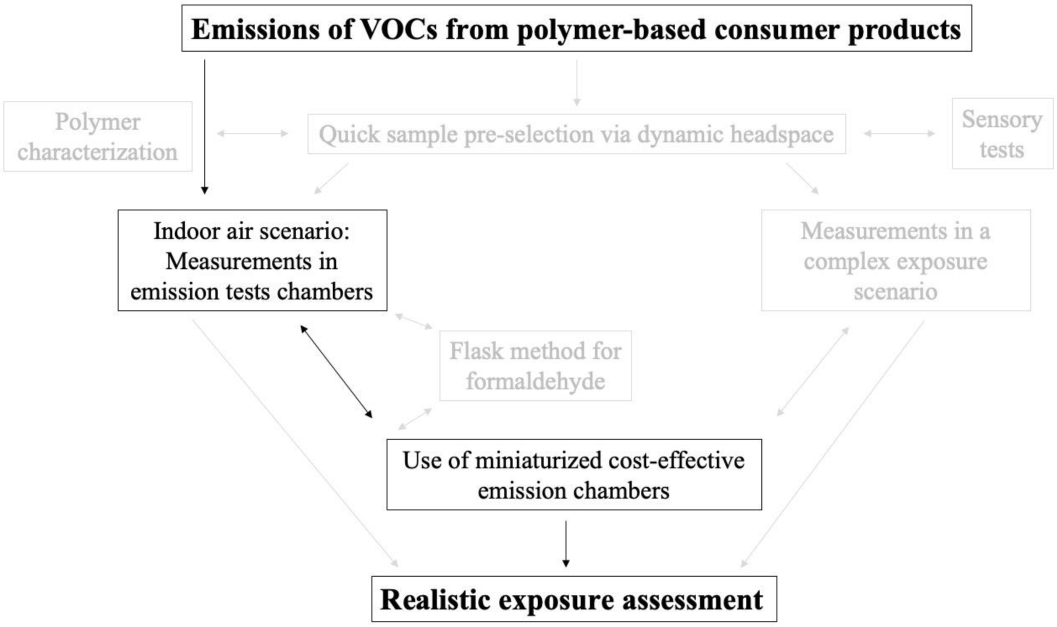

***Figure 13**: Overview of this work, focus on publication 2.3.*

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ORIGINAL ARTICLE

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

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## 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 |

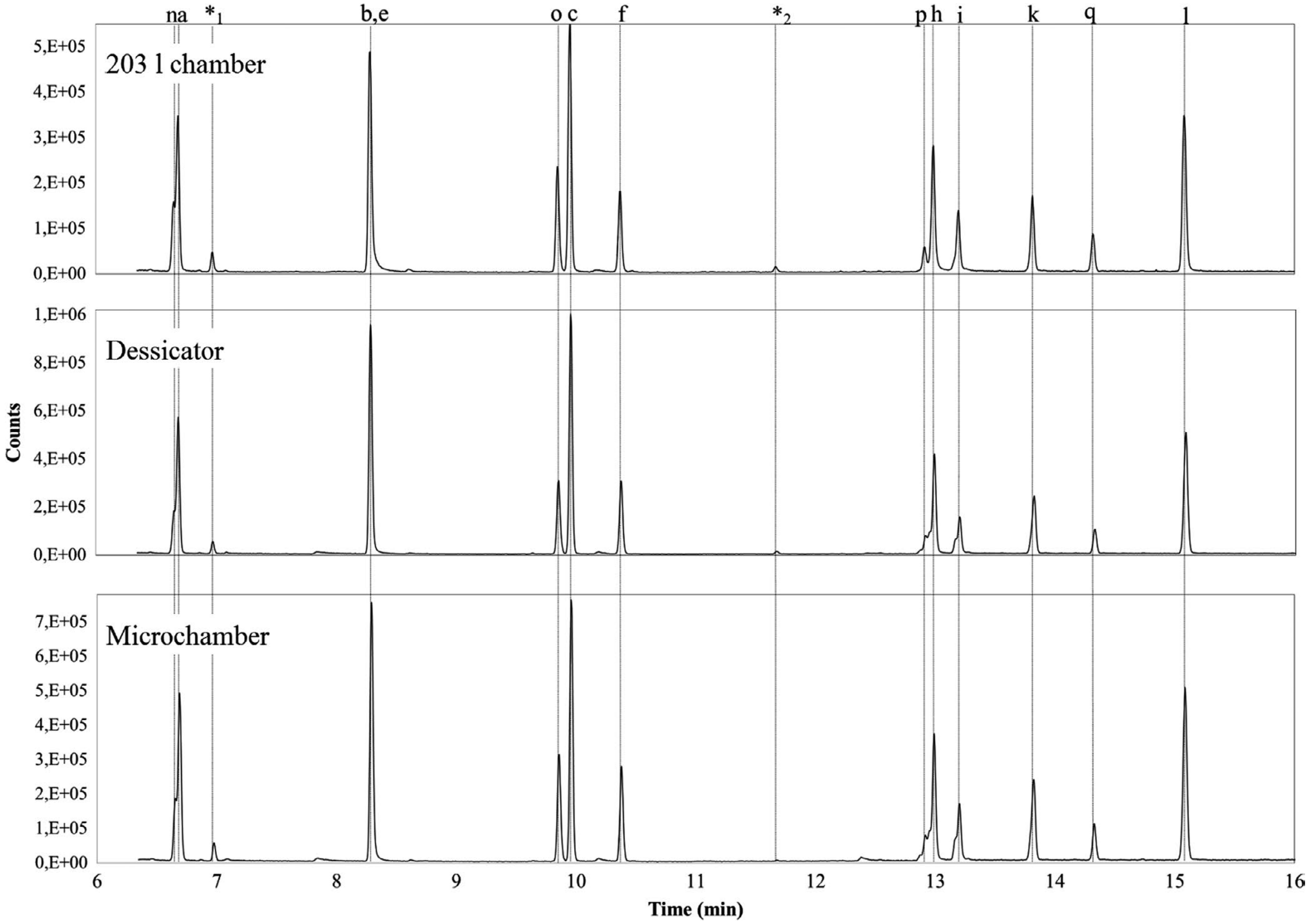

**FIGURE 1** GC/MS chromatograms in scan mode (split: 1:400). Above: sampling from 203 L emission chamber after 32.1 h; middle: sampling from the 24 L desiccator after 31.2 h; below: sampling from the 44 mL microchamber after 31.6 h; $*_1$:1-ethoxy-butane; $*_2$: α-methylstyrene

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

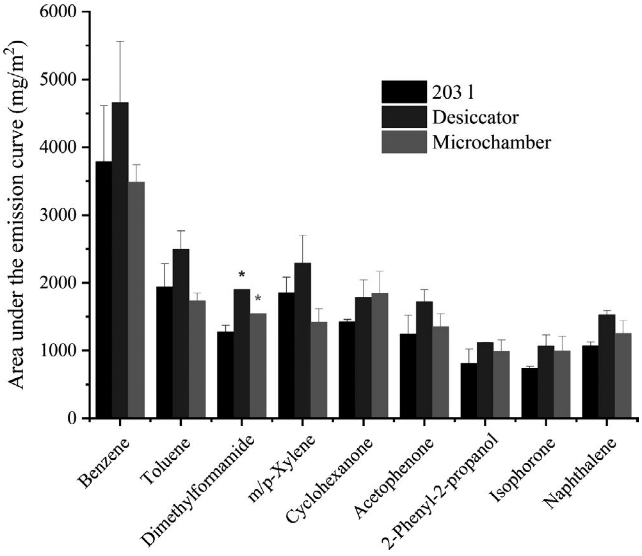

**FIGURE 2** Total emission values during 28 d (area under the emission curve); repeated once, *: single measurements

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.

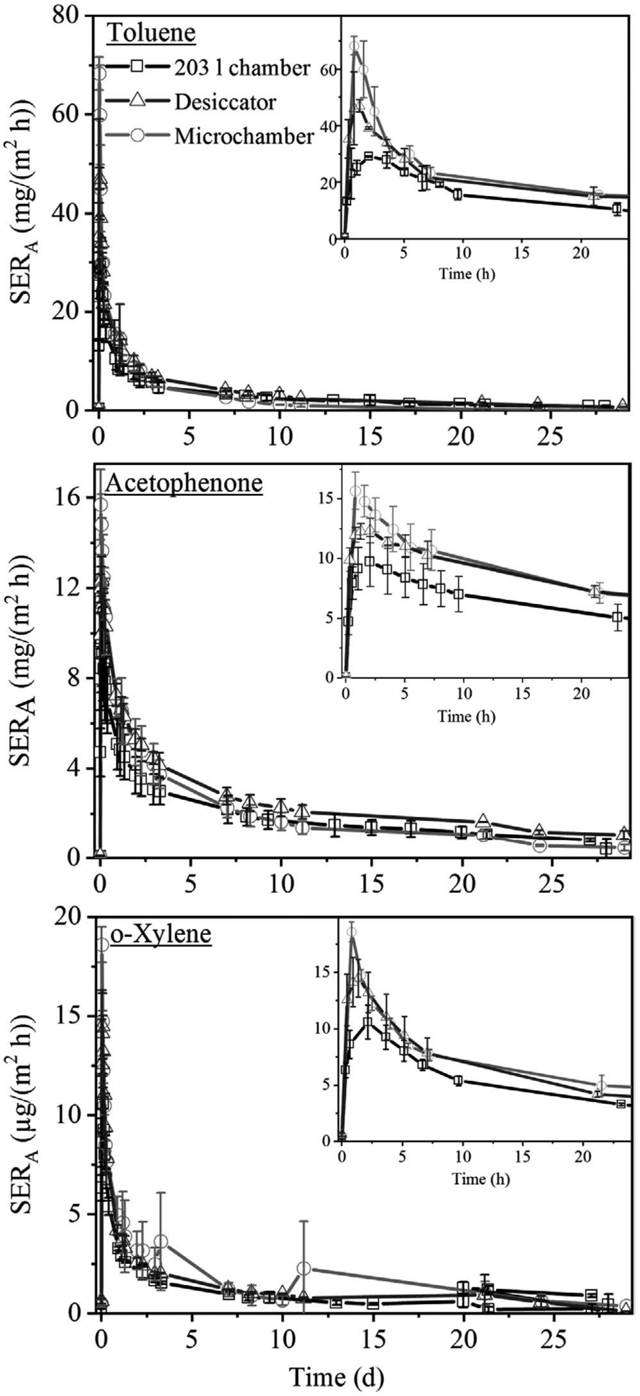

**FIGURE 3** Emission profiles of three selected analytes from the polyurethane plate obtained in three different emission chambers; bigger frame: 28 d profile; smaller frame: 24 h profile; repeated once

## 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/

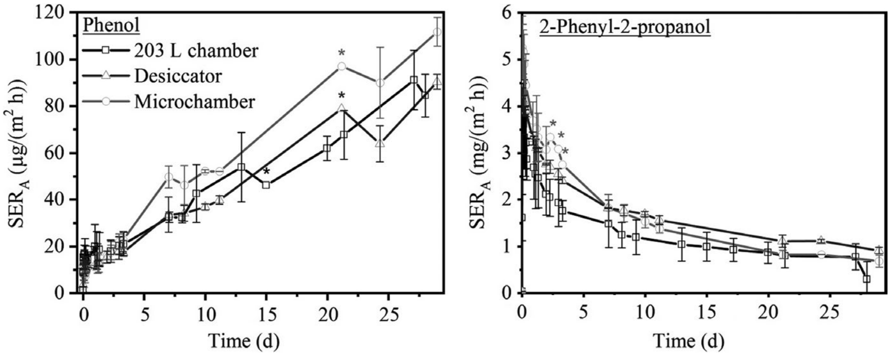

**FIGURE 4** Twenty-eight d emission profiles of two substances containing a hydroxyl group each. Profiles were obtained from the polyurethane plates in three different emission chambers (repeated once, or *: single measurements)

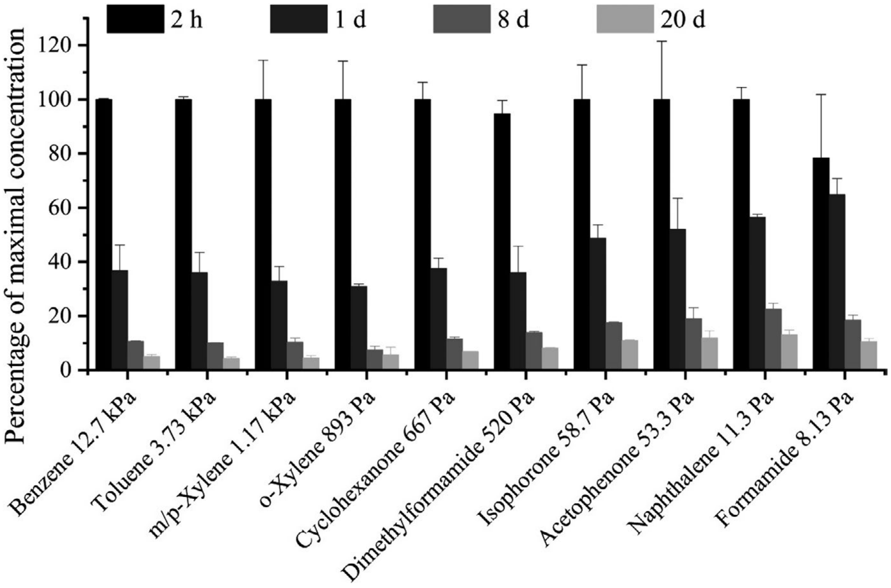

**FIGURE 5** Percentage of maximal concentration obtained for selected analytes with various vapor pressures from the polyurethane plate at different time points in the 203 L chamber; repeated once

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

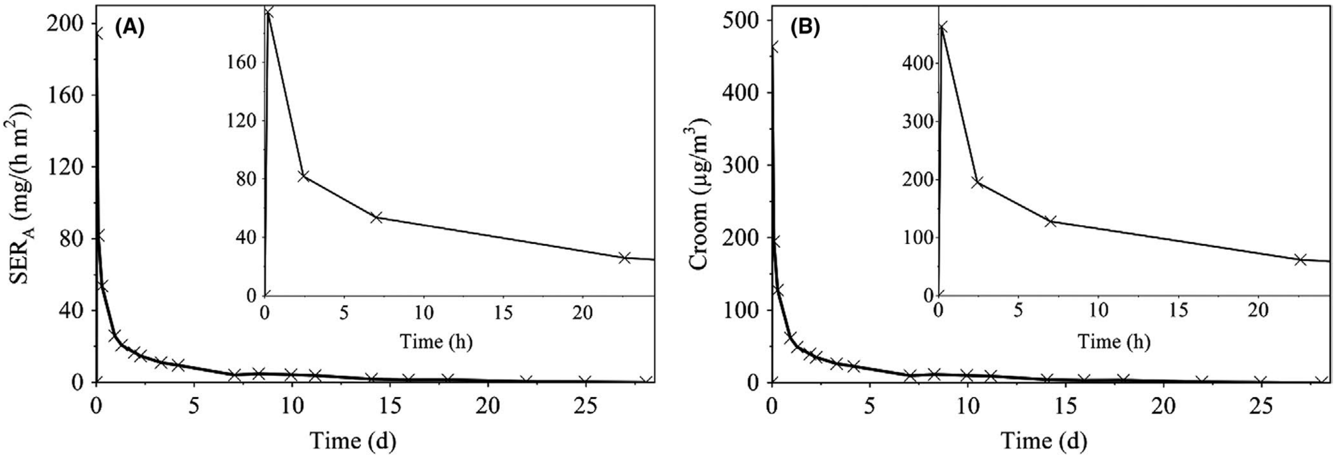

**FIGURE 6** Area-specific emission rate of cyclohexanone from a 12 mm diameter piece from a PVC toy figurine placed in a 44 mL microchamber (A) and resulting calculated air concentration for the whole figurine in a 30 m$^3$ room (B); bigger frame: 28 d profile; smaller frame: 24 h profile

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.

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## 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

## 2.4. Formaldehyde Emissions from Wooden Toys: Comparison of Different Measurement Methods and Assessment of Exposure

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Supplementary material: Annex IV

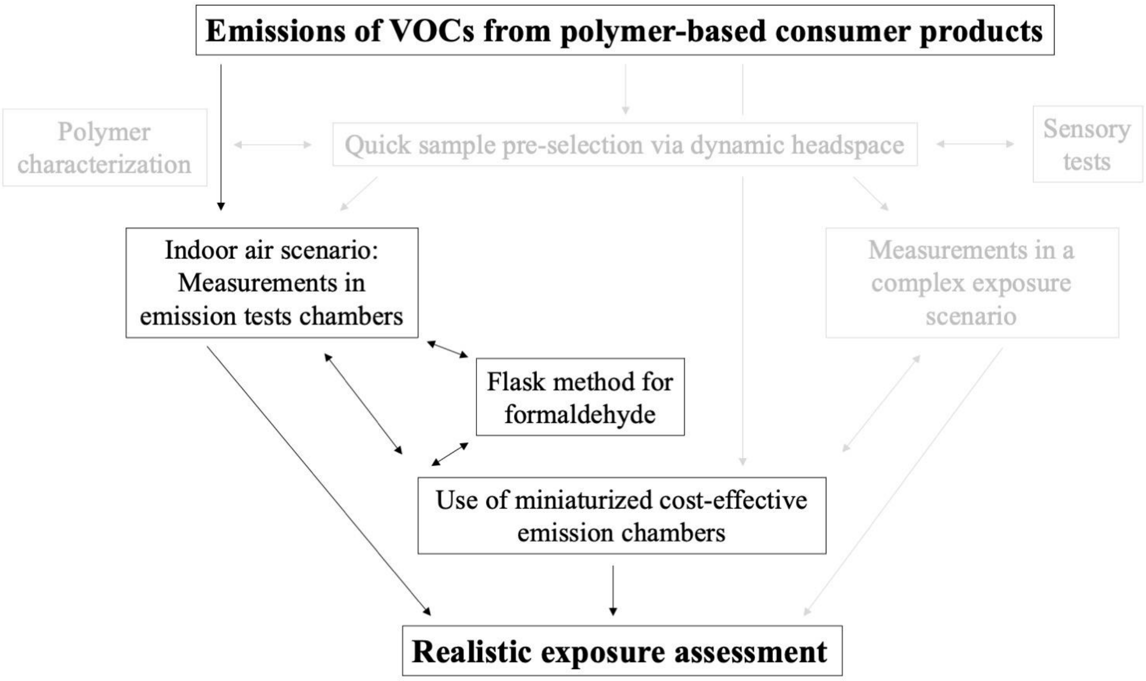

***Figure 14**: Overview of this work, focus on publication 2.4.*

materials

MDPI

*Article*

# Formaldehyde Emissions from Wooden Toys: Comparison of Different Measurement Methods and Assessment of Exposure

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**Abstract:** Formaldehyde is considered as carcinogenic and is emitted from particleboards and plywood used in toy manufacturing. Currently, the flask method is frequently used in Europe for market surveillance purposes to assess formaldehyde release from toys, but its concordance to levels measured in emission test chambers is poor. Surveillance laboratories are unable to afford laborious and expensive emission chamber testing to comply with a new amendment of the European Toy Directive; they need an alternative method that can provide reliable results. Therefore, the application of miniaturised emission test chambers was tested. Comparisons between a 1 $m^3$ emission test chamber and 44 mL microchambers with two particleboards over 28 days and between a 24 L desiccator chamber and the microchambers with three puzzle samples over 10 days resulted in a correlation coefficient $r^2$ of 0.834 for formaldehyde at steady state. The correlation between the results obtained in microchambers vs. flask showed a high variability over 10 samples ($r^2$: 0.145), thereby demonstrating the error-proneness of the flask method in comparison to methods carried out under ambient parameters. An exposure assessment was also performed for three toy puzzles: indoor formaldehyde concentrations caused by puzzles were not negligible (up to 8 $\mu g/m^3$), especially when more conservative exposure scenarios were considered.

**Keywords:** formaldehyde; wooden toys; emission test chamber; flask method; EN 717-3; microchamber

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## 1. Introduction

Formaldehyde, the simplest aldehyde (HCHO), is colourless and detectable in the gas phase at ambient temperature. It is mainly used in the production of industrial resins, adhesives, and coatings. Since it was demonstrated to induce tumours in the nasopharynx of rodents [1], it has been classified as a carcinogen of category 1B since 2016 [2]. Formaldehyde scored highly as one of the top chemicals for both exposure and toxicity in Washington, USA [3], and in the European Union [4].

The German committee on indoor guideline values determined a guideline value of 100 $\mu g/m^3$ based on toxicological data [5], which is in line with the WHO guideline [6]. An initial German survey in the years 1985–1986 revealed indoor formaldehyde concentrations of up to 309 $\mu g/m^3$, with a mean concentration of 59 $\mu g/m^3$ from 329 measurements [7]. In the following years, great efforts were made to reduce the formaldehyde sources and lower indoor air concentrations were measured, with a maximum of 68.9 $\mu g/m^3$ during 2003–2006, for example [8]. A recent statistical review analysis from 2019 indicates that average concentrations of formaldehyde are within the range of 20–30 $\mu g/m^3$ for European households under typical residential conditions [9].

Wood-based materials made of urea-formaldehyde resins may emit high formaldehyde concentrations [10,11]. They are mainly used as building materials or in the manufacturing of furniture, which caused 70% of formaldehyde indoor air concentrations in newly built timber-frame houses [12]. Urea-formaldehyde adhesives have poor water resistance: the presence of water causes hydrolysis and, consequently, the release of formaldehyde [13]. The European standard EN 717-1 suggests determining the release of formaldehyde from wood-based panels through the emission test chamber method [14]. The test chamber method is regarded as the method of choice for emission measurements as it mimics a real indoor environment (air exchange, temperature and humidity). Since 2017, the new standard method EN 16516 is in place in Europe: it describes emission testing with lower air change rate, higher relative humidity and higher chamber loading factor than EN 717-1 [15]. Since January 2020, the German national chemicals prohibition ordinance sets stricter requirements as EN 16516 must now be used instead of EN 717-1 to comply with the concentration limit of 0.1 ppm (corresponding to 124 $\mu g/m^3$) for formaldehyde [16]. For the same chamber loading, EN 16516 leads to measured concentrations being a factor of 1.6 higher compared to EN 717-1 [10]. With a higher chamber loading of 1.8 $m^2/m^3$ instead of 1.0 $m^2/m^3$, a factor of 2 could be expected. According to EN 717-1, the air samples from test chamber measurements are analysed by photometry after reaction with acetylacetone or with liquid chromatography (HPLC) after derivatisation with 2,4-dinitrophenylhydrazine (DNPH), following ISO 16000-3 [17].

Toys made of wood-based panels may also emit formaldehyde. However, their origin and quality are not typically controlled in the same way as particleboards because they are usually directly imported from distant countries. The European Toy Safety Directive 2009/48/EC [18] specifies a general maximum level of 0.1% (1000 $mg/kg_{toy}$) for carcinogenic compounds such as formaldehyde; however, this represents only a content limit and does not account for its emission behaviour. As formaldehyde is usually present in a chemically bound form and only emitted after hydrolysis, a content analysis for formaldehyde does not give any indications on the inhalation exposure assessment.

The so-called flask method is widely used by official control laboratories (OCLs) which are responsible for the toy market surveillance in the EU member states to measure formaldehyde emission of products [19]. It was developed by Roffael in the 1970s [20] and adapted into the European standard EN 717-3 [21]. The tested material is placed into the headspace of a 500 mL bottle filled with 50 mL water. After the incubation period of 3 h at 40 °C, the amount of formaldehyde dissolved in the water is determined by photometry. The method is still in use for wooden toys because of a lack of alternative methods, although it has been proven that the correlation to emission chamber testing is poor [22]. Moreover, different limits are used in the practice: EN 71-9 stipulates a maximum level of 80 $mg/kg_{toy}$ if EN 717-3 is used (3 h experiment) [23], whereas the former German Federal Health Agency (BGA) recommended a limit of 110 $mg/kg_{toy}$ for a 24 h flask experiment [24]. Using different materials, a study demonstrated that the values obtained by the flask method remained linear over time for at least 30 h [22], meaning that the two different limits are not comparable. The same study also suggested using an emission chamber test for more realistic results. There were several discussions at the subcommittees of analytics and toys related to the BfR's committee for consumer products where German OCLs asked for advice and developments of reliable measurement methods for formaldehyde in wooden toys with respect to children's safety [25].

In November 2019, a new European directive was adopted, amending 2009/48/EC for the purpose of specific limit values for chemicals used in certain toys [26]: here, in compliance with the German Chemicals Prohibition Ordinance [27], an emission limit of 0.1 ppm was stipulated for formaldehyde from resin-bonded material, starting from May 2021. In addition, the working group recommended emission testing by following EN 717-1 (i.e., a standardised method for wood-based panels) [14]. However, the OCLs will not be able to afford emission chamber testing for every toy and are therefore in need of an alternative method which provides reliable results. Smaller test chambers are cheaper, adapted to the typical size of toys and enable a higher sample capacity; their comparability to the standard chambers should be assessed considering the results obtained by the flask method.

Several studies have compared methods for determining formaldehyde emissions in the past. Firstly, the Field and Laboratory Emission Cell (FLEC) was compared to a standard 1 $m^3$ emission chamber and provided good correlation [28]. Unfortunately, this method cannot be used for toys, which do in most cases do not have flat surfaces. In another study, most standard methods were compared and showed sample-dependent results [29]. This may have been influenced by the fact that test conditions also vary between different standards. Three environmental chambers of different sizes were also compared for formaldehyde emissions from carpets [30]. In this case, the test conditions (temperature, humidity, air change rate and loading factor) were kept constant but considerable differences in formaldehyde emissions could still be observed. These previous studies did not consider the use of microchambers (μ-CTE) which allow cheaper measurements of small products in replicates and already showed good correlation for VOC emissions from a polymeric material [31]. The μ-CTE is a device with six 44 mL (or four 114 mL) miniaturised emission test chambers where the temperature, humidity and air change rate are controlled: the air can be sampled at the chamber outlet [32]. To our knowledge, microchambers have so far never been compared to large and regular emission chambers in terms of formaldehyde emission testing. The so-called "Dynamic microchambers" (DMC) were used on particleboards by Hemmilä et al. (2018) [11] and compared with a 1 $m^3$ emission test chamber and the perforator method (ISO 12460-5 [33]). However, DMC have a much higher volume (44 L) than the microchambers used in this study and are therefore linked with higher operating costs. Another micro-scaled chamber (1 L) that allowed process automation was tested for formaldehyde emission. However, no correlation with standard emission chambers could be demonstrated [34].

A standard cost-effective routine method usable for formaldehyde emission testing of toys and other consumer products in OCLs still needs to be established. Thus, we tested the comparability of formaldehyde emissions from wooden products in emission test chambers of different sizes and with the flask method: we demonstrated that microchambers can be used as a good alternative to the existing methods. Finally, we estimated the corresponding inhalative exposure against formaldehyde from wooden toys and showed that it was not negligible.

## 2. Materials and Methods

### 2.1. Samples

An overview of the samples used is given in Table 1, the exact dimensions are provided in Table S1. Two particleboards were initially studied. They were bought from a local do-it-yourself store and had already shown relatively high formaldehyde emissions during previous tests two years earlier [10]. Eight different wooden toys were also investigated. They were bought in local stores and had shown (except for Sample #9) flask method values (40 °C, 24 h) beyond the limit of 110 $mg/kg_{toy}$ recommended by the former German Federal Health Agency (BGA) [24] during market surveillance (see Table S2 for the exact values). Their country of origin was always China if it could be identified, meaning that the initial wood-based materials had not necessarily been controlled according to European standards [14,15]. Until usage, the samples were kept at room temperature in their original packaging or covered with aluminium foil. Pictures of the samples are provided in Figure S1.

**Table 1.** Overview and dimensions of the samples studied; ¥: the puzzle pieces were cut to fit in the microchambers, open edges were partly (#1 and #2) or entirely (#5, #6, #8 and #10) covered.

| No. | Description | Origin | Sample Surface Area ($cm^2$) | | | |
|---|---|---|---|---|---|---|
| | | | **Microchambers** | **1 $m^3$ Chamber** | | |
| #1 | Particleboard | E.U. | 16.0 ¥ | 9300 | | |
| #2 | Particleboard | E.U. | | | | |
| #3 | Block set | China | 34.4 | **Desiccator** | | **Number of Pieces Per Set** |
| #4 | Hammer and nail set | unknown | 28.9 | **Plate** | **Pieces** | |
| #5 | Puzzle birds | China | 19.7 ¥ | 1456 | 651 | 12 |
| #6 | Puzzle fish | China | 12.6 ¥ | | | |
| #7 | Puzzle shapes | unknown | 24.0 | 1426 | 711 | 12 |
| #8 | Play set meal | China | 23.9 ¥ | 1475 | 828 | 5 |
| #9 | Puzzle numbers | unknown | 29.0 | | | |
| #10 | Plug set garden | unknown | 16.9 ¥ | | | |

### 2.2. Emission Test Chambers

Three different types of emission test chambers (1 $m^3$, 24 L, and 44 mL) were used for emission testing, along with a clean air supply system. The 1 $m^3$ chamber was the standard VOC emission test chamber model from Heraeus-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 chambers were desiccators made of glass and equipped with a ventilator from the BAM (Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany). They were used instead of the 1 $m^3$ test chambers as standard chambers for the wooden puzzles because some samples were too small to obtain meaningful concentrations in the bigger chambers. The 44 mL chambers were part of a micro-chamber/thermal extractor device (µCTE®) produced by Markes (Llantrisant, UK).

The edges of the particleboard pieces (two plates of 0.5 m × 0.5 m and 0.43 m × 0.5 m in the 1 $m^3$ chamber and 1 piece of 2 cm × 4 cm in the microchambers) were covered with an emission-free aluminium-coated tape according to EN 717-1 [14]. The ratio between the open edge and the total surface was adjusted to 1.5 $m/m^2$. Some toy samples had to be cut with a saw to fit into the microchambers (#5, #6, #8 and #10). In this case, the freshly cut edges were covered completely with tape; indeed, the non-geometrical form of the toy makes it difficult to cover a defined ratio of the edges.

The two particleboards were placed upright in the 1 $m^3$ chamber. The puzzle and toy pieces were placed on metal carriers in the desiccators and on small plastic carriers in the microchamber if air would not otherwise circulate under the sample. Pictures of chamber loading are presented in Figures S2 and S3. Replicates were used for the microchambers: two or three chambers were always loaded with similar pieces of the same sample.

The systems were set to a temperature of 23 ± 1 °C and 50 ± 5% relative humidity. The microchambers were operated at a flow of 23.1–29.3 mL/min, while the desiccators were operated with 1.80 and 1.88 L/min. Similar to our previous work [31], the air change rate in the 1 $m^3$ chamber was adapted to the chamber loading to obtain a similar area-specific airflow rate (ratio of air change rate to loading) as applied for the microchamber, resulting in a flow of 14.5 L/min. Evidently, this represents a crucial parameter for such studies [35] and should be kept as constant as possible. Despite the maximum possible loading of the desiccator (all the puzzle pieces with the exception of the one placed in the microchambers), the area-specific air flow for chamber comparison was lower in the microchamber but still in the same order of magnitude. The area-specific values for air flow used during chamber comparisons are summarised in Table 2. To compensate the discrepancies, the results of method comparisons are presented as surface area specific.

**Table 2.** Sample area-specific air flow ($m^3/m^2 \cdot h$) values for chamber comparisons (n.u., not used; −, range due to flow fluctuation).

| No. | Microchamber | Desiccator | 1 $m^3$ Chamber |
|---|---|---|---|
| #1 | 0.97−1.06 | n.u. | 0.94 |
| #2 | 0.95−1.03 | n.u. | 0.94 |
| #5 | 0.72−0.79 | 1.73 | n.u. |
| #7 | 0.61−0.63 | 1.59 | n.u. |
| #8 | 0.68−0.74 | 1.36 | n.u. |

### *2.3. Air Sampling and Analysis of Air Samples*

Air sampling was performed using DNPH cartridges (Supelco, St. Louis, MO, USA). The DNPH method [17] was preferred to the photometry method [14] for sample analysis because it was already widely used and validated in our laboratory. Active sampling was carried out for the 1 $m^3$ chamber and desiccators following ISO 16000-3 [17] using an air check 3000 sample pump (SKC Ltd., Dorset, UK) at 1 L/min for 30 min. Two samples were collected simultaneously for each time point in the 1 $m^3$ chamber: a self-designed sampling pump was used for the second sample. For the microchambers, the sampling lasted 20 h at the outlet to allow a sampling volume of around 30 l. Several samples were taken before the actual measurements started to control for blank values of the chambers and the DNPH cartridges. Air samples were regularly collected over 28 or 10 days after loading of the chambers.

The cartridges were refrigerated before and after sampling and eluted with 2 mL acetonitrile within two weeks after sampling. The solutions were analysed using HPLC (HP1100 from Hewlett-Packard, Waldbronn, Germany) in accordance with ISO 16000-3 [17]. An UltraSep ES ALD column (125 mm × 2.0 mm) and a pre-column (10 mm × 2 mm) from SepServ (Berlin, Germany) were used. The gradient of acetonitrile to water + 6% tetrahydrofuran varied between 30% and 83% (30% hold for 5 min, to 32% in 5 min and hold for 20 min, to 83% in 25 min). The mobile phase flow was 0.5–0.6 mL/min and the Diode Array Detector was used at 365 nm. Formaldehyde was quantified via external calibration with a commercial solution of its derivative from Sigma-Aldrich (Darmstadt, Germany) with a maximum concentration of 50 ng/µL. Samples were diluted if they did not fit into the calibration range. Data was processed using the OpenLab Data Analysis A.01.02 software from Agilent (Waldbronn, Germany). The results are provided as area-specific emission rates ($SER_A$), weight-specific emission rates ($SER_W$) or indoor air concentrations ($C_{indoor}$):

$$SER_A = \frac{C_{CH} * V_{CH} * n_{CH}}{A} \tag{1}$$

where $SER_A$ is the area-specific emission rate ($mg/h \cdot m^2$); $C_{CH}$ is the chamber concentration ($mg/m^3$); $V_{CH}$ is the chamber volume ($m^3$); $n_{CH}$ is the chamber air change rate (/h); and A is the sample surface area ($m^2$).

$$SER_W = \frac{C_{CH} * V_{CH} * n_{CH}}{m} \tag{2}$$

where $SER_W$ is the weight-specific emission rate ($mg/h \cdot g$); and m is the sample weight (g).

$$C_{indoor} = \frac{SER_A * A}{V_{room} * n_{room}} = C_{CH} * \frac{V_{CH} * n_{CH}}{V_{room} * n_{room}} \tag{3}$$

where $C_{indoor}$ is the indoor air concentration ($mg/m^3$); $V_{room}$ is the room volume (30 $m^3$ [15]); and $n_{room}$ is the room air change rate (0.5/h [15]).

Surface areas of the samples were determined by approximating their shape to geometrical forms (e.g., ellipse and triangle, see Table S1) if they were not already geometrical. For Sample #1, #2, #5, #7 and #8, all surface areas were determined. For the other samples, only the surface areas of the pieces placed in the microchambers were determined; the last approximation (3.4) with the whole sample surface area was done with the mean surface area of Sample #5, #7 and #8.

When two chambers were compared, an offset was calculated:

$$\text{Offset} = \frac{(\text{Highest SER}_A - \text{Lowest SER}_A)}{\text{Lowest SER}_A}\ (\%) \tag{4}$$

The use of the offset allows a direct comparison of the differences between emission test chambers for different samples.

The linearity of the correlation between $SER_A$ at steady state in different emission test chambers was investigated. The coefficient of determination ($R^2$) and the *p*-values were considered for statistical analysis of the linear regressions. *P*-values were computed with the mean of each data point and were considered statistically significant when < 0.05 and highly statistically significant when < 0.001.

### 2.4. Flask Method

The flask method was carried out the same way as it is done by toy market surveillance [24]: in accordance with EN 717-3 [21] at 40 °C but for 24 h. The results are given in mg formaldehyde released per kg toy ($mg/kg_{toy}$). The linearity of the correlation between the flask method values and the emission rates after 10 or 11 days in the microchamber was investigated.

For Samples #3–#7, the test was conducted again after microchamber testing to study the influence of emission testing on the flask method values.

Except for the samples (particleboards and wooden toys), which are possibly only purchasable for a restricted time frame, and the desiccators which were self-made, all the materials and equipment used in this study are available commercially.

## 3. Results and Discussion

### 3.1. Chamber Comparison Using Particleboards

The 1 $m^3$ chamber and the microchamber were first loaded with pieces from the same particleboards and air samples were collected regularly over 28 days. Area-specific emission rates are depicted in Figure 1.

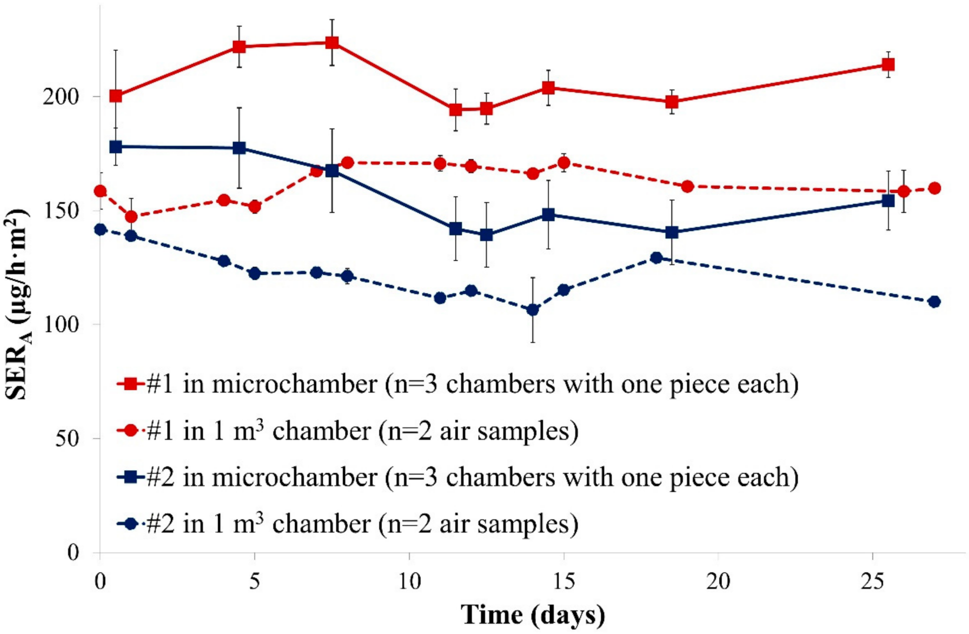

**Figure 1.** Emission profiles of formaldehyde from the two particleboards in two different emission chambers over four weeks ($SER_A$, area-specific emission rate). Error bars represent SD (standard deviation).

Firstly, it was observed that both chamber types led to similar emission profiles for formaldehyde: area-specific emission rates were relatively constant over 28 days, probably due to a year-long storage under chamber climate similar conditions. Emission rates were always used for test chamber comparisons because it is directly related to the indoor air concentration (see Equation (1)) but normalised to the area-specific air flow rate. Secondly, a relatively stable offset was observed between both chamber types: the emission levels measured in the microchamber were in mean about +27% and +28% (offset calculated according to Equation (4)) compared to those of the 1 $m^3$ chamber. A possible reason for the observed discrepancies could be the covering of the open edges with a ratio to the total surface of 1.5 $m/m^2$ as stipulated by EN 717-1 [14]: it represented 2.4 mm of open edges for the 2 cm × 4 cm pieces placed in the microchambers, which is difficult to accurately achieve using tape. Differences in air velocities at the sample's surface could also explain this deviation between both chambers. However, it is not possible to measure the air velocity in the microchambers.

These data still indicate that a good correlation between both chamber sizes was observed under the selected conditions. Thus, small chamber sizes might be a promising alternative for cost-effective emission measurement of formaldehyde from particleboards.

It has been demonstrated in previous work that the flow circulation in the microchamber is heterogeneous [32]. The height of the sample could disturb the air flow and thus would have an influence on the emission. This is of particular importance in the case of specimens that represent one-third of the chamber volume. For this reason, formaldehyde emission was analysed for different positions of both Samples #1 and #2 in the microchamber. The results are provided in Figure 2.

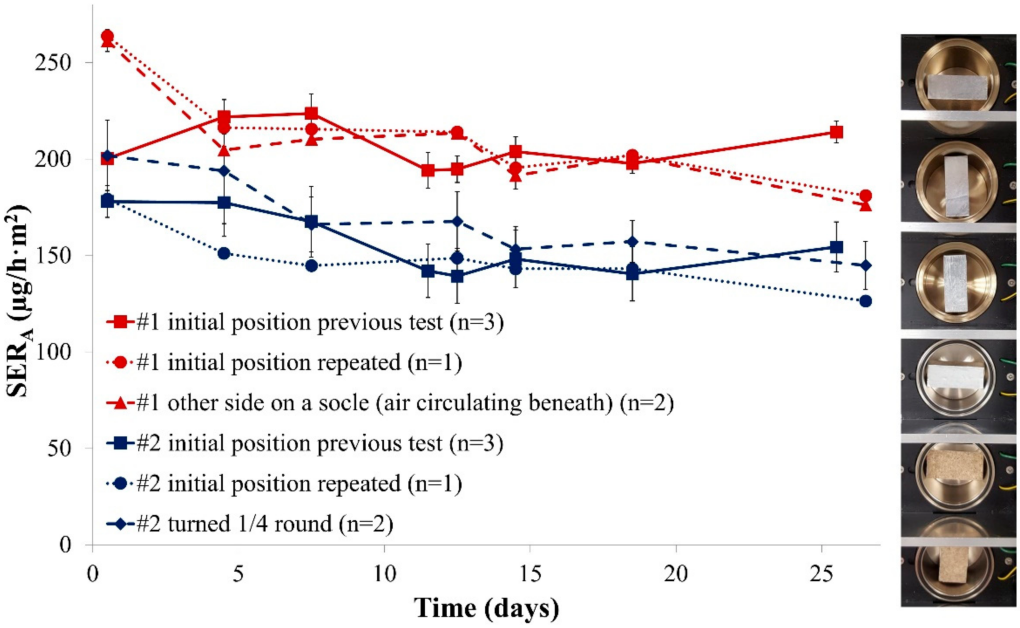

**Figure 2.** (**Left**) Emission profiles of formaldehyde released from two particleboards for different sample positions in the microchamber ($SER_A$, area-specific emission rate); and (**Right**) picture of the different testing positions. Error bars represent SD.

This experiment revealed that the position of the sample in the microchamber is only of low importance: irrespective of the exact position, the area-specific emission rate was similar (same position repeated or new position tested). This is an important result as it means that the exact position of the sample in the emission chamber would not be a crucial parameter in market control experiments. Furthermore, Figures 1 and 2 both show that an emission rate equilibrium is reached very quickly. For this reason and to allow fast and efficient investigations the following experiments were limited to 10 days.

### 3.2. Chamber Comparison for Toy Samples

A similar experiment to the one presented in Section 3.1 was conducted using wooden puzzles. Most puzzle pieces fit into the microchamber or easily fit when cut, and the cutting edge was covered by aluminium tape. Puzzle or play set pieces were chosen for this comparison; one piece was loaded into the microchamber while all other available pieces (8–18) of the same sample were loaded into a desiccator chamber, resulting in area-specific air flow rates that were slightly higher in the desiccator (see Table 2) compared to the microchamber. Three samples were studied over 10 days. The formaldehyde emission results are shown in Figure 3.

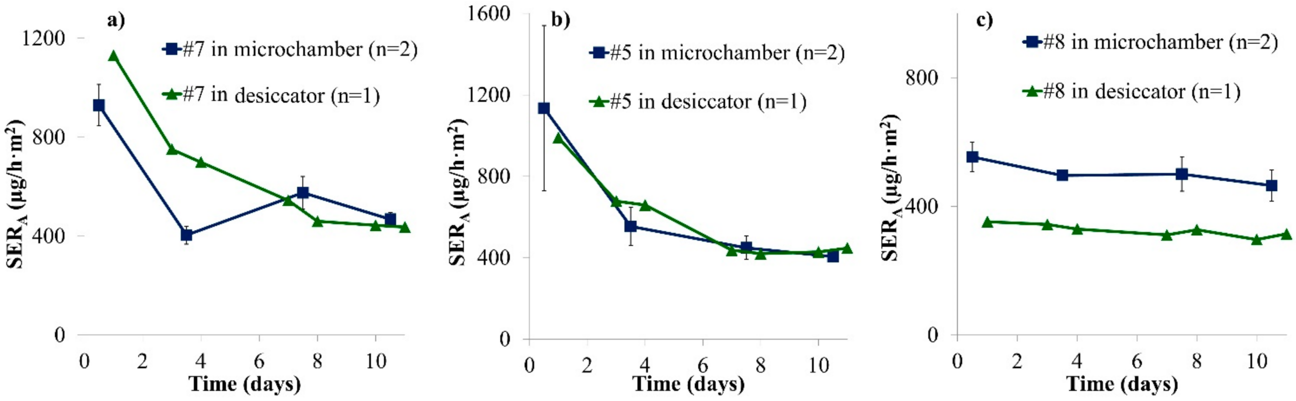

**Figure 3.** Emission profiles of formaldehyde from puzzle pieces in two different emission chambers over 10 days ($SER_A$, area-specific emission rate). (**a**) Sample #7; (**b**) Sample #5; (**c**) Sample #8. Error bars represent SD.

Formaldehyde concentrations were found to be fairly constant after seven days. Over the course of 10 days, the area-specific emission rates were similar in both chambers for all three samples. For Samples #5 and #7, there was no significant offset between both chamber results in contrast to Figure 1. For Sample #8, the average offset between microchamber and desiccator results was +53%, slightly higher than for Samples #1 and #2. For Sample #8, the area-specific air flow rate was only 1.9 times higher in the desiccator than in the microchamber while the ratio between both chambers was 2.3 and 2.6 for Samples #5 and #7, respectively (see Table 1). This finding may contribute to the fact that Sample #8 behaved similarly to Samples #1 and #2 (for which the area-specific air flow was constant between chambers). Moreover, the shape of the pieces from Sample #8 (play set) were thicker and approached the shape of Samples #1 and #2 more than the puzzle pieces from Samples #5 and #7. This may lead to differences in air velocities at sample surface. Additionally, for Samples #5 and #7, a decrease of the formaldehyde emission rate is observed over the first few days. Such a decrease was not observed for Sample #8 or for the particleboards in Figure 1. These differences can be due to more consistent conditions during storage or to the fact that Samples #5 and #7 were coloured with stickers while Sample #8 was painted (see Figure S1). Stickers could emit high formaldehyde concentrations during the first hours. The decrease was also observed for Sample #6 (see Figure S4). Hemmilä et al. (2018) also observed that the formaldehyde profile before steady state depended on the sample: no linear correlation was found between DMC results at Days 1 and 7 for different samples [11].

The results obtained from the microchamber and the desiccator experiments are similar, especially after 10 days. Again, the microchamber seems to provide reliable and comparable formaldehyde emission results. When using the microchamber, temperature and humidity are regulated according to EN 717-1 [14], but the chamber loading factor and the air change rate are higher to achieve similar area-specific air flows (see Table 2). In consequence, this leads to the conclusion that the standard method cannot be applied word by word. Furthermore, it will be difficult in practice to comply with the standard

EN 717-1 [14] as it requires that sample edges should be partly covered by a special ratio and that a certain loading factor should be used. This is much more complicated for toy samples than for large and rectangular wood-based panels. A practical suggestion would be to completely cover cut edges with tape before sample loading.

The linear correlation between the emission rates measured at steady state in the emission test chambers and the microchambers is shown in Figure 4. For Samples #1, #2 and #8, the whole measurement period was considered as steady state. For Samples #5 and #7, only the measurements at Days 7 and 10 were considered.

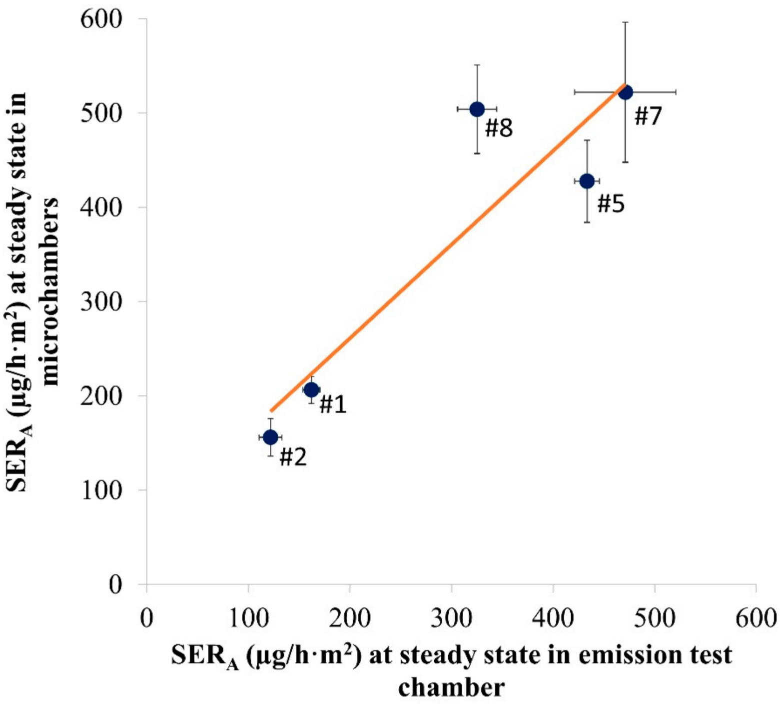

**Figure 4.** Study of the linearity between the area-specific emission rate (SER$_A$ in µg/h·m$^2$) in the emission test chamber and in the microchambers for Samples #1, #2, #5, #7 and #8. R$^2$: 0.834; *p*-value: 0.0304 ($n$ = 4–24, depending on the number of air samples during steady state). y = 0.9944x + 62.113. Error bars represent SD.

A good correlation was observed between the microchamber and the test chamber (1 m$^3$ or desiccator) results, with a R$^2$ of 0.834 and a significant *p*-value of 0.0304 (<0.05). A slope of 0.9944 indicates a good matching between chambers of different sizes.

### 3.3. Feasibility of the Flask Method

For all investigated samples, microchamber and flask experiments were carried out using two pieces of the same sample that were as similar as possible. The correlation between the flask method value and the emission rates at Day 10 (or Day 11 for Samples #1 and #2) is presented in Figure 5.

In Figure 5a, both the R$^2$ (0.145) and the *p*-value (0.2775 > 0.05) indicate a poor correlation between flask method values and area-specific emission rates (SER$_A$) of the samples. If Samples #3, #4 and #8 are removed, a R$^2$ of 0.956 is obtained, indicating a good linear correlation with a highly significant *p*-value (0.00014 < 0.001). As observed by Hemmilä et al. (2018) with the perforator method, the correlation between the emission chamber and the flask method result is consistent only for a selection of samples [11]. The results seem to depend on the geometry of the toy. Samples #3 and #8 were the thickest samples (1.4 and 1.8 cm) and yielded the lowest ratios of the flask method value to SER$_A$, while Sample #4, as the thinnest sample (0.3 cm), was found to result in the highest ratio. Hemmilä et al. (2018) also observed a differentiation between samples with varying thickness [11].

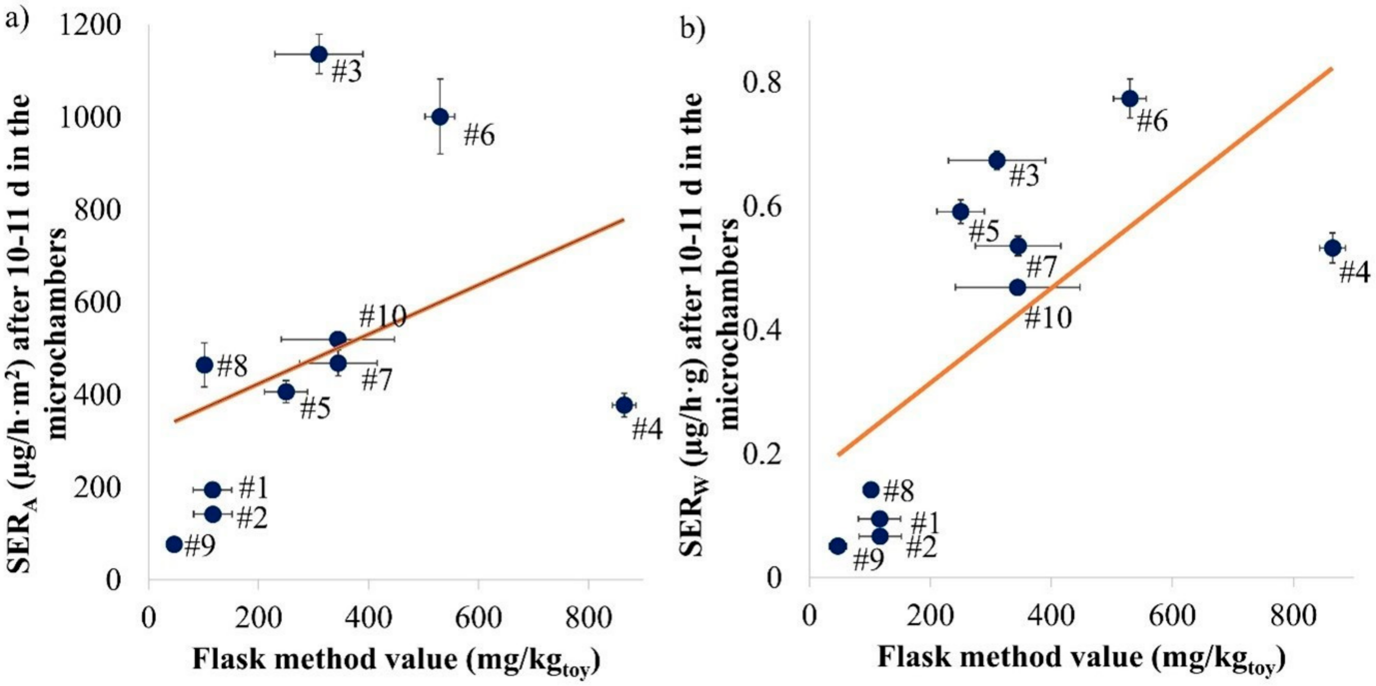

**Figure 5.** Study of the linear correlation between the flask method values and the area-specific ((**a**) $R^2$: 0.145; *p*-value: 0.27775) or weight-specific ((**b**) $R^2$: 0.470; *p*-value: 0.02876) emission rates after 10 or 11 days in the microchamber for each sample investigated. Error bars represent SD (*n* = 2 for microchamber samples, for flask method see Table S2).

$SER_A$ is a common unit for material emission measurements but as the flask method value is based on the weight of the toy, a correlation with the weight-specific emission rate ($SER_W$) was also considered and is presented in Figure 5b. In this case, a better correlation is obtained between the flask method values and the weight-specific emission rate, with a statistically significant correlation (*p*-value: $0.02876 < 0.05$) but a poor $R^2$ (0.470). If only Sample #4 is removed, a $R^2$ of 0.845 and a highly statistically significant *p*-value of 0.0005 (<0.001) are obtained. The correlation between the microchamber and the test chamber (1 $m^3$ or desiccator) results is better ($R^2$: 0.834, see Figure 4). An interesting observation was that Sample #3 seemed to be made of massive wood and still emitted as much formaldehyde (1.4 mg/h·m² at Day 10) as the other samples. Such results have also been observed in the past [36] and may be attributed to the lacquer. The area-specific emission rate curves from the toy samples over 10 days in the microchamber are provided in Figure S4.

Overall, the flask method is not a good way to predict the emission measurements performed under realistic environmental conditions for varying toys. This mirrors the evidence obtained by other studies [22,29]. The flask method also has the significant disadvantage that the sides cannot be covered permanently (the humidity is too high for the tape) if the sample needs to be cut.

Additionally, the influence of the time point of the flask method test on the results was studied. The results presented above consider the flask experiment conducted with samples similar to those used in the microchamber. The flask method was carried out again for some samples that had undergone the microchamber experiment (Samples #3–#7) and the observed values are shown in Table S2 together with those of the similar samples. Generally, no significant difference was observed between both values (margins of error overlap). Significant differences were only observed for Sample #4: this would enhance the correlation with the microchamber results, which will however stay poor ($R^2$: 0.517).

Samples #5 and #6 resulted in similar values in both scenarios: it seemed to be of minor significance whether they had an open edge (following the chamber experiment).

### *3.4. Exposure Assessment from Whole Toy Samples*

As shown in Section 3.2, puzzle or play set pieces were studied in a desiccator for comparison with the formaldehyde emission in the microchamber in which they could often fit without further sample preparation. The puzzle plates can also emit formaldehyde, but they are not investigated by OCLs because they also do not fit in the flask. It may be possible that the plate is the part with the greatest emissions. However, this is not necessarily considered for market surveillance or exposure assessment purposes. An evaluation of the contribution of both sample parts is presented: puzzle plates for each of the three samples (Samples #5, #7 and #8) were also studied in a desiccator for 10 days. The results of the piece-specific emission rates, normalised to one plate or to the number of associated pieces, are presented in Figure 6.

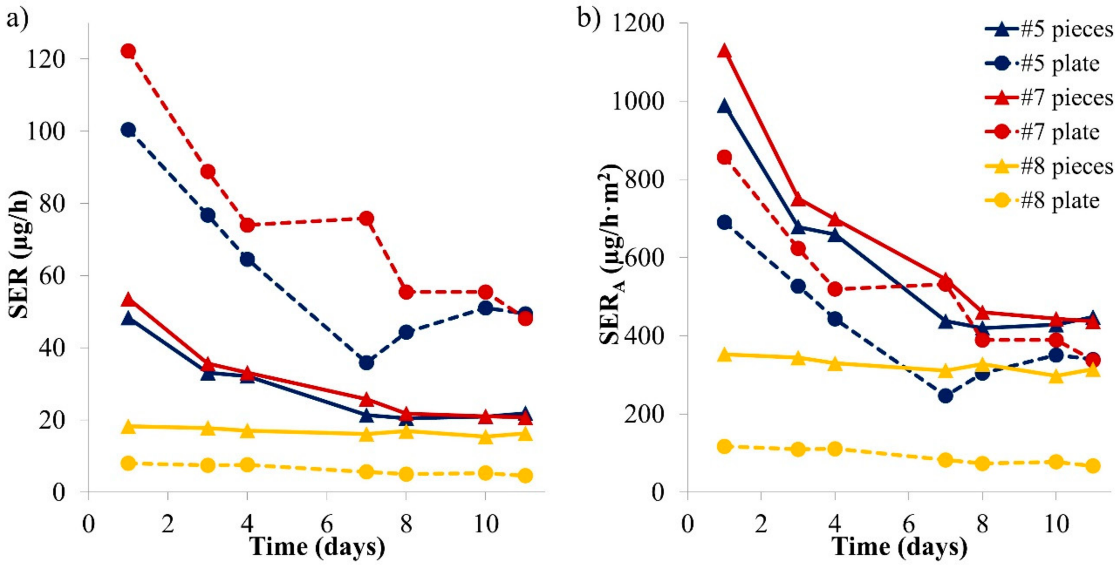

**Figure 6.** Emission rates of formaldehyde from the plate and the pieces of three puzzles: SER (sample-specific emission rate) (**a**); and SER$_A$ (area-specific emission rate (**b**)). The results were obtained with the desiccator method ($n$ = 1).

For Samples #5 and #7, the plate was emitting higher amounts of formaldehyde compared to the puzzle pieces. However, for play set Sample #8, the pieces were emitting more formaldehyde compared to the plate. These differences are likely due to the different geometries of the samples: the play set plate (682 cm$^2$) is smaller compared to the puzzle plates (1426 and 1456 cm$^2$), whereas the sum of the piece surface areas was similar between samples (474–518 cm$^2$). The results in area-specific emission rates are similar for the pieces and the plate for Samples #5 and #7. For Sample #8, pieces emitted much more formaldehyde per surface unit than the plate: this is probably partly due to the fact that they were thicker (typically 1.8 cm) than the plate (0.5 cm). This shows that every part of a toy should be investigated when exposure needs to be assessed.

Furthermore, an exposure assessment of formaldehyde was carried out using the results of the desiccator experiments. The influence of a whole puzzle set (plate and corresponding number of pieces, as a consumer would buy it; see number of pieces in Table 1) on the formaldehyde room concentration has been considered. Evaluating indoor air concentrations allows a direct comparison with the indoor air guideline and therefore a reliable risk assessment [37]. They were calculated as shown in Equation (3), and the results are displayed in Figure 7.

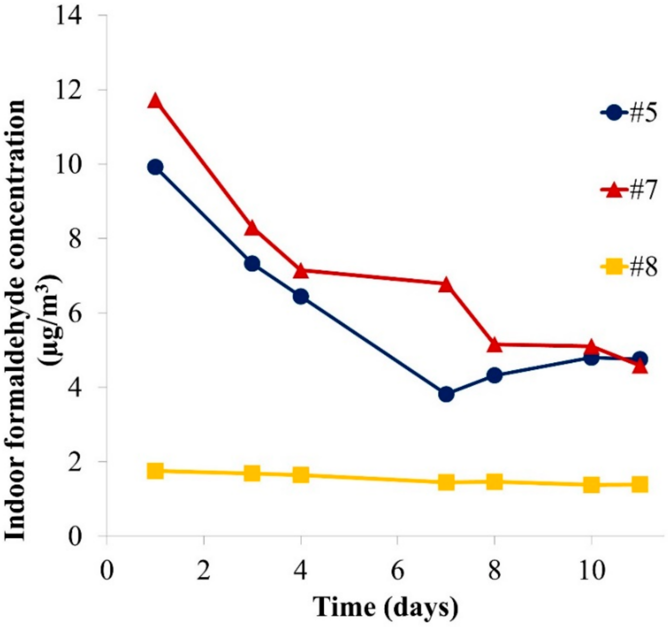

**Figure 7.** Calculated formaldehyde concentration for a 30 $m^3$ room resulting from each puzzle set sample (plate and pieces) ($n$ = 1).

In the indoor air scenario (Figure 7), the influence of one sample on the formaldehyde concentration is considered in a 30 $m^3$ room with an air change rate of 0.5/h [15]. The assessment reveals that whole puzzle samples could induce indoor air concentrations of formaldehyde of up to 12 µg/$m^3$ on the first day and 5 µg/$m^3$ after 10 days. In comparison, the indoor air guideline value [5] is 100 µg/$m^3$. However, the children may play in very close proximity to the product in a poorly ventilated space with a concentration gradient. The concentration in the child's breathing zone will then be higher than the average room concentration. Moreover, there may also be other formaldehyde sources in the indoor air environment, meaning that the contribution of such products cannot be considered negligible. The BfR stated in 2007 that emissions from toys should only contribute to 10% of the overall indoor formaldehyde guideline concentration [38]. As an example, Samples #5, #7 and #8 represent, respectively, 4.8%, 4.6% and 1.7% of the 100 µg/$m^3$ guideline at steady state. An exceedance is easily possible if a room containing several toys and other formaldehyde sources such as furniture or building products is considered. It should also be considered that an increased temperature and/or humidity can enhance formaldehyde emissions drastically [39] and therefore cause even higher exposures. Lower air change rates indoors can also lead to higher VOC concentrations. A reduction of the formaldehyde emission limit is currently under discussion in Europe. Lower limits are already in effect for certain types of samples in the USA [40] and in Japan [41].

A similar exposure assessment for formaldehyde could be carried out directly using the area-specific emission rates from microchamber studies as they correlated with those obtained from bigger emission test chambers. The results from this approximation are shown in Table 3. This would lead to slightly higher concentrations for Samples #3 and #6 than for the previous considerations.

**Table 3.** Room concentration at Day 10 or 11 approximated from microchamber measurements.

| | #3 | #4 | #5 | #6 | #7 | #8 | #9 | #10 |
|---|---|---|---|---|---|---|---|---|
| Approximated $C_{room}$ from microchamber (μg/m$^3$) ($n$ = 2) | 8.27 ±0.31 | 2.75 ±0.18 | 3.29 ±0.18 | 7.29 ±0.59 | 3.71 ±0.20 | 3.71 ±0.35 | 0.56 ±0.01 | 3.78 ±0.12 |
| *$C_{room}$ from desiccator* (μg/m$^3$) | | | *4.78* | | *4.84* | *1.71* | | |
| Percentage of the WHO guideline | 8.3% | 2.7% | 3.3% | 7.3% | 3.7% | 3.5% | 0.6% | 3.8% |

The difference between the approximated formaldehyde concentrations of the desiccator and the microchamber for Sample #8 is due to the plate, which emitted less formaldehyde than the pieces and was not considered in the microchamber approximation. This underlines the fact that representative pieces (e.g., a cut piece of the plate with covered edges) should be analysed if using the microchamber. With this consideration, the microchamber seems to be an appropriate method for market surveillance. The approximation carried out with only pieces of Sample #5 and #7 are close to the values obtained with the desiccator.

## 4. Summary and Conclusions

Formaldehyde emission is a key aspect when ensuring wooden toy safety. The emission test chamber method described in EN 717-1 [14] is not practicably and economically feasible for measurement purposes of toys. There is an urgent need for a standardised measurement method which demonstrates a good correlation to the existing emission test chamber methods whilst being more cost-effective. A possible method was investigated in our present study: the capacity of miniaturised emission test chambers (44 mL) to facilitate the surveillance of formaldehyde emissions from wooden toys was evaluated. It was shown that the emission results obtained (area-specific emission rates) were comparable to those from bigger chambers for both particleboards and wooden toys. In contrast, the currently used flask method showed a bad correlation with emission test chamber results. Its further use for market control of wooden toys is highly questionable. The main drawback in suggesting large-volume emission test chambers for toy market surveillance are higher costs and low sample capacity. Therefore, microchambers represent an affordable alternative for reliable market surveillance by the OCLs. They show a statistically significant correlation with bigger chambers (overtime and at steady state with $p < 0.05$ and $R^2$: 0.834), but further investigations with a larger number of samples and a validation using a homogeneous material are suggested to support these findings before standardisation.

As the sample may be heterogeneous, it is necessary to analyse representative pieces of the toy. Moreover, the standard EN 717-1 [14] is not directly suited to microchamber testing of toys. The air change rate will be higher than 1/h and the toy edges cannot be covered with a specific ratio. In addition, it is impossible to use a defined chamber loading factor for wooden toys due to the variable shapes. In the most recent standard EN 16516, different loading factors are stipulated for different sample types [15]. The new amendment of the toy safety directive [26] could indicate either an area-specific emission limit or a concentration limit per toy piece instead of following EN 717-1 with a defined chamber loading. Additionally, other analytical techniques, such as photometry [14], could be considered for air sample analysis to further reduce measurement costs.

An exposure assessment led to notable indoor air concentration values, indicating that formaldehyde emissions from a single wooden play set could represent up to 8% of the WHO formaldehyde guideline for indoor air. These products should therefore be considered as important emission sources, especially if numerous wooden toys are kept in smaller rooms or if children play with such toys and keep them in close proximity to their breathing zone.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/1996-1944/14/2/262/s1, Figure S1. Representative pictures of the investigated toy samples, Figure S2: Example image of chamber loading for Sample #1 in: the 1 $m^3$ chamber (a); and the microchamber (b), Figure S3: Example image of chamber loading for Sample #7: pieces in the microchamber (a); pieces in the desiccator (b); and plate in the desiccator (c), Figure S4: Emission profiles of formaldehyde from wooden toy pieces in the microchamber over 10 days, Table S1: Dimensions of the samples for chamber studies, Table S2: Flask method values of the samples similar to those studied in the microchamber and of samples after microchamber testing (mg/$kg_{toy}$).

**Author Contributions:** Conceptualisation, M.E., O.W., P.S., and C.H.; methodology, M.E., O.W., S.K., and C.H.; validation, M.E. and S.K.; formal analysis, M.E.; investigation, M.E. and S.K.; resources, P.S.; data curation, M.E.; writing—original draft preparation, M.E.; writing—review and editing, O.W., S.K., P.S., C.H., and A.L.; visualisation, M.E.; supervision, M.E., O.W., P.S., C.H., and A.L.; project administration, M.E. and C.H.; and funding acquisition, O.W., P.S., C.H., and A.L. All authors have read and agreed to the published version of the manuscript.

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## 2.5. Exposure Assessment of Toxicologically Relevant Volatile Organic Compounds Emitted from Polymer-Based Costume Masks

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Supplementary material: Annex V

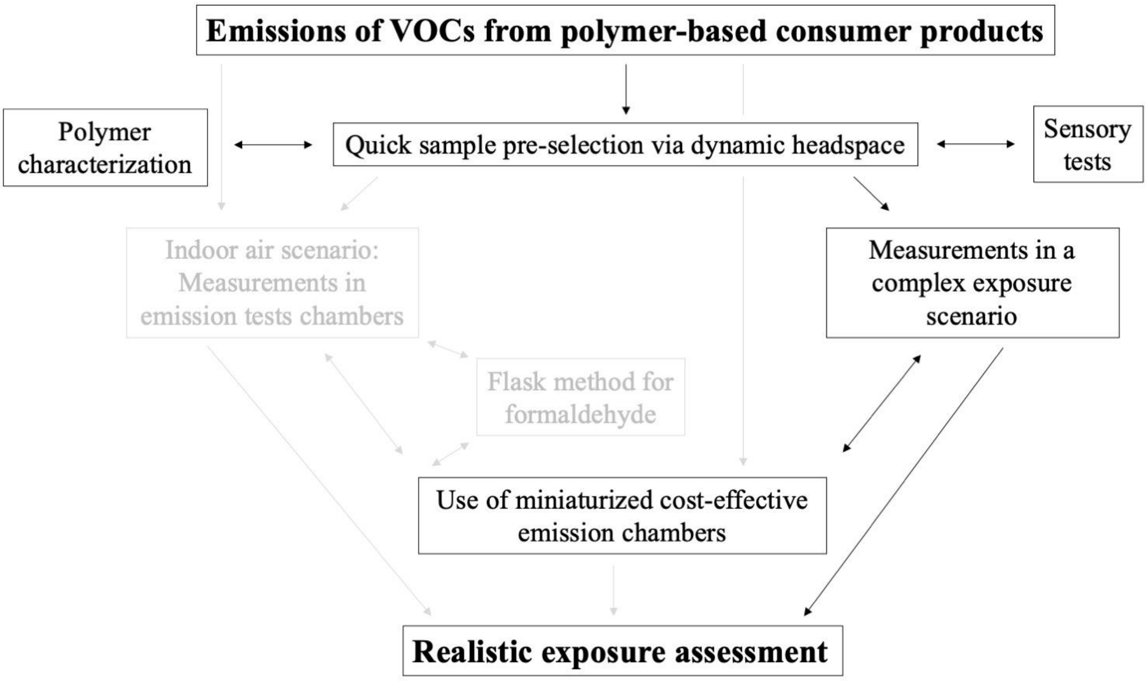

***Figure 15**: Overview of this work, focus on publication 2.5.*

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# Exposure Assessment of Toxicologically Relevant Volatile Organic Compounds Emitted from Polymer-Based Costume Masks

Morgane Even,* Alexander Roloff,* Nils Lüttgert, Jonathan Beauchamp, Daniel Stalter, Agnes Schulte, Christoph Hutzler, and Andreas Luch

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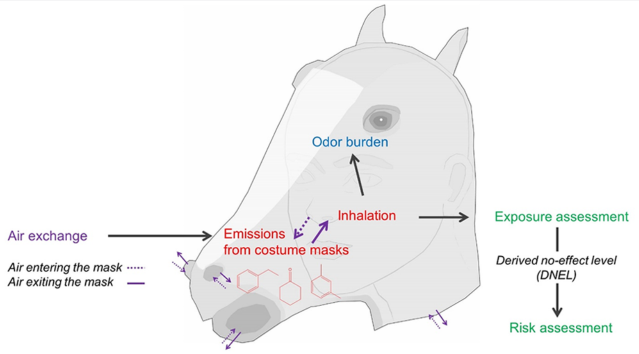
**ABSTRACT:** Plastic costume masks regularly exhibit unpleasant odors that may be associated with the emissions of volatile organic compounds (VOCs). Upon inhalation, VOCs might adversely affect the wearer's health if the exposure exceeds regulatory threshold values. The VOCs emitted from a selection of costume masks ($n = 12$) were characterized semiquantitatively with a screening method based on GC/MS measurements in dynamic headspace sampling mode. Furthermore, odors associated with the masks were evaluated by a sensory panel. Two masks emitted particularly high concentrations of ethylbenzene, xylenes, and cyclohexanone and exhibited the most intense and unpleasant odors, which were described as *rubber-like*, *pungent*, and *leather-like*. To simulate and assess the inhalation exposures for wearers of these masks, an innovative experimental setup based on a doll's head was developed, with sampling of emitted volatiles on adsorption material and subsequent analysis by thermal desorption−GC/MS. The measured inhalable concentrations of cyclohexanone exceeded the derived no-effect level (DNEL) for systemic effects on the general population over several hours of wearing, and also after repeated use. Importantly, the cyclohexanone DNEL was reevaluated in relation to a recent study on inhalation toxicity in rodents and was found to be significantly lower (1.4 $mg \cdot m^{-3}$) compared to the industry-derived values (10−20 $mg \cdot m^{-3}$), thus aggravating the health risks associated with inhalation exposure from some of the costume masks tested. Finally, a comparison of the inhalable concentrations derived from the simulated exposure assessments with those derived from measurements in miniaturized emission test chambers indicate that microchambers represent a useful tool for high-throughput analysis. The influences of temperature and inhalation/exhalation flow rates on VOC exposures were also studied.



## 1. INTRODUCTION

Plastics may contain different chemical additives and impurities that can migrate into and contaminate food, water, soil, and air.[1] Among others, volatile organic compounds (VOCs) in plastic-based materials can be released into the air at ambient temperature on account of their high vapor pressures. If inhaled, some of these compounds potentially elicit adverse health effects. It has recently been demonstrated, for example, that a mixture of aromatic compounds, namely benzene, toluene, ethylbenzene, and *p*-xylene, can disturb the functions of pulmonary surfactants.[2] In another study, the polycyclic aromatic hydrocarbon (PAH) naphthalene was shown to cause acute airway cytotoxicity following inhalation by mice.[3] Other VOCs, such as acetophenone and isophorone, were characterized as local irritants as they stimulated responses in trigeminal neurons in mice.[4]

Emissions of VOCs from polymer-based consumer products, including children's toys, have been studied and quantified in recent years.[5,6] Specialized laboratory equipment, such as emission test chambers, allows samples to be characterized under conditions that mimic indoor environments, and this has recently facilitated realistic inhalation exposure assessments of toys.[7−10] For certain products such as costume masks, however, which are frequently worn during Halloween, cultural carnivals, or other themed parties, very little is known about the wearer's exposure to their constituent VOCs. This deficit is a direct consequence of the complex exposure scenario: while wearing a mask, the emissions source (the mask) and the site(s) of inhalation (nose and/or mouth) are in close proximity and within an almost entirely enclosed space of low volume. The air exchange here is actively driven by the inhalation/exhalation pattern of the wearer, as opposed to a passive exchange with ambient air (see the abstract graphic for

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an exposure schematic). Concentrations derived from measurements in conventional emission test chambers are therefore not expected to be representative of actual exposure.

Previous work has raised concerns about the potential release of VOCs from costume masks. A quantitative analysis commissioned by a German magazine detected the presence of benzene, toluene, xylene, phenol, and cyclohexanone in various specimens, but no emissions measurements were carried out to assess the actual inhalation exposure.[11] Indeed, a systematic screening of the market for products exhibiting potentially hazardous VOC emissions by official control authorities would be desirable but is currently out of reach due to the lack of harmonized analytical methods that combine accurate emissions measurements with a reasonable sample throughput. As a precautionary measure, the German Federal Office of Consumer Protection and Food Safety (BVL) advises consumers to self-check purchased costume masks by assessing how easy it is to breathe when wearing the mask while dancing in a crowded room, and recommends avoiding masks with unpleasant odors.[12]

Indeed, the release of VOCs from consumer products may be accompanied by unpleasant odors that can be associated with symptoms of headache and nausea upon extended exposure. Several studies identified off-odorants in toys using a combination of sensory evaluations by trained panels and gas chromatography coupled to an olfactory detector (GC/O). In such tests, however, while the panel evaluations are typically carried out at ambient conditions, instrumental analysis of odor components usually requires sample extraction. This is commonly achieved at relatively high temperature, e.g., either via solvent-assisted flavor evaporation (SAFE)[13−15] or by thermal extraction.[16] Since sample extraction techniques are typically performed on the sample as a whole, subsequent analyses cannot distinguish between odorous VOCs that are emitted from the surface and those that are enclosed within the polymeric matrix and may not be released into the gas phase under conditions of normal use.

Correlations between odors and VOC emissions have been found in studies on building materials,[17,18] automobile air condition evaporators (applying forced parameters, such as 100% relative humidity),[19] and sewage sludge composting plants,[20] among others. To the best of our knowledge, however, no data have been collected hitherto on the correlation between perceived odors and VOC emissions from plastic consumer products measured under realistic conditions (ambient temperature and humidity). Such knowledge is crucial when estimating human inhalation exposures to VOCs.

In this study, we investigated the correlation between sensory impressions and emission properties of polymer-based costume masks. First, a semiquantitative analysis of the emissions of VOCs was performed, allowing a quick preselection of samples with high VOC emissions.[10] In parallel, sensory analyses were conducted to determine the odor attributes and intensities, together with the hedonic ratings of the samples. Furthermore, we describe an innovative setup based on a doll's head to simulate and assess realistic inhalation exposures while wearing costume masks. This system is inspired by a study on disposable filtering facepiece (FFP) respirators.[21] Finally, we measured VOC emissions from mask sample pieces using a commercial microchamber device (a miniaturized emission test chamber) and compared these data with those obtained from the doll's head setup.

## 2. MATERIALS AND METHODS

**2.1. Chemicals.** Chemicals were supplied from Merck (Darmstadt, Germany), Sigma-Aldrich (Steinheim, Germany), and TCI Chemicals (Zwijndrecht, Belgium). Further details are reported in Table S1. Analytical grade ethyl acetate and dichloromethane were obtained from Merck and used as solvents. Nitrogen ($N_2$) and helium of purity ≥99.999% (5.0) from Linde (Pullach, Germany) were used. All chemicals, including solvents and standard solutions, were handled with appropriate care under a fume hood, minimizing contact to potentially harmful substances.

**2.2. Samples and Polymer Characterization.** Twelve costume masks were bought from local or online shops and kept in gastight, aluminum composite-layer film bags at room temperature until usage. Sample details are summarized in Table 1, and pictures of the samples are presented in Figure S1.

Table 1. Overview of 12 Costume Masks

| no. | name | source[a] | origin |
|---|---|---|---|
| 1 | donkey | l | unknown |
| 2 | panda | l | unknown |
| 3 | sumo | l | unknown |
| 4 | grandpa | l | China |
| 5 | wolf | o | China |
| 6 | dwarf 1 | o | unknown |
| 7 | dwarf 2 | o | unknown |
| 8 | rabbit | o | China |
| 9A, 9B, 9C | horse | o | unknown |
| 10A, 10B | unicorn | o | unknown |
| 11 | zombie | o | China |
| 12 | horror | o | China |

[a] Purchased locally (l) or online (o).

Pyrolysis−GC/MS was used to identify the polymer type of each of the masks via thermal degradation according to the method detailed in our previous work.[10] A Beilstein test was also carried out to confirm the presence of halogens: small pieces (~1 mm$^2$) were placed on a hot copper ring and heated in a flame, whereby a green flame color indicated the presence of halogens.

**2.3. Conditioning of Thermal Desorption Tubes and Internal Standard Spiking.** Glass thermal desorption (TD) tubes (6.0 × 0.4 cm i.d. × 0.6 cm o.d.) filled with Tenax TA (Gerstel GmbH, Mülheim an der Ruhr, Germany) were used to capture VOCs emitted from individual samples. Prior to sampling, tubes were conditioned for 3 h with an $N_2$ flow of ca. 75 mL·min$^{-1}$ at 300 °C. Cyclodecane dissolved in ethyl acetate was used as an internal standard on the tubes, either at 50 ng·$\mu$L$^{-1}$ for dynamic headspace (DHS) sampling or at 500 ng·$\mu$L$^{-1}$ for exposure simulation and microchamber experiments; solutions were stored in a freezer (−18 °C) until use. A 1 $\mu$L aliquot of internal standard solution was spiked onto the TD tubes by using a tube spiking system (Gerstel) equipped with a rinsed 10 $\mu$L microvolume syringe. Afterward, the tubes were dried with 100 mL of $N_2$ at a flow rate of 100 mL·min$^{-1}$. The conditioned and internal standard spiked tubes were stored at room temperature in tight plastic storage containers (Gerstel) and subsequently loaded and analyzed within 3 days.

**2.4. Dynamic Headspace Sampling and Score.** First, a semiquantitative analysis of the emissions of VOCs from 12 masks was performed using DHS sampling coupled online to GC with mass spectrometric detection (GC/MS), as demonstrated in our previous work.[10] Circular sample pieces with a diameter of 8 mm were punched manually from each of the 12 mask samples with a metal punching tool. Samples were placed in 20 mL glass headspace vials with the inner face of the mask pointing upward; the vials were then closed with magnetic caps fitted with silicon/polytetrafluoroethylene (PTFE) septa. After 60 ± 5 min equilibration at room temperature, the headspace was purged with 600 mL of $N_2$ at a flow rate of 15 mL·

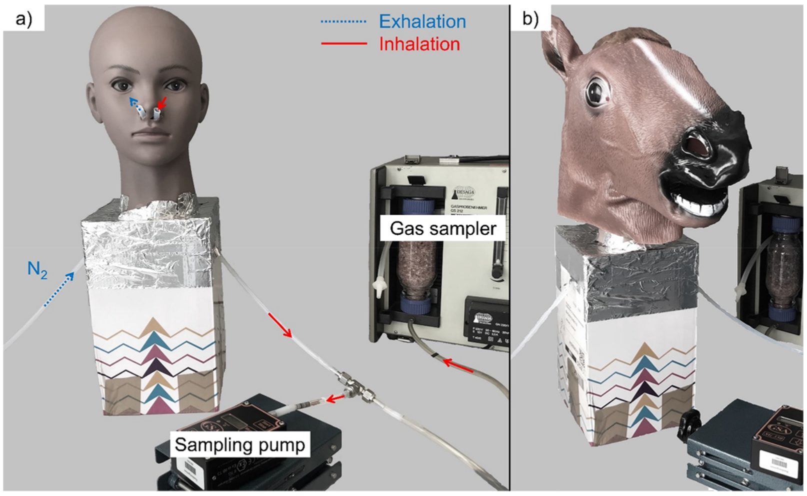

**Figure 1.** Experimental setup for evaluation of simulated exposure of volatiles associated with wearing a costume mask. The doll's head sampling system is shown without mask (a) and in action with sample 9B (b) (see Table 1).

min$^{-1}$. Analytes in the headspace were trapped at 23 °C on conditioned Tenax TA TD tubes spiked with internal standard (described in section 2.3). The transfer heater between the vial and the desorption tube was held at a constant temperature of 50 °C. The DHS system was cleaned between each run: An empty glass vial was flushed with 1 L of $N_2$ at a flow rate of 100 mL·min$^{-1}$ at 70 °C while simultaneously holding the transfer heater at 70 °C. The analyte-loaded TD tubes were analyzed by GC/MS as described in section 2.7.

A "DHS score" was calculated for each target analyte and sample. The signal areas ($A_{\text{sample,analyte}}$) were normalized to the internal standard signal area ($A_{\text{sample,IS}}$) and corrected for the blank values ($A_{\text{blank,analyte}}$ and $A_{\text{blank,IS}}$, respectively):

$$\text{analyte-specific DHS score} = \frac{A_{\text{sample,analyte}}}{A_{\text{sample,IS}}} - \frac{A_{\text{blank,analyte}}}{A_{\text{blank,IS}}} \qquad (1)$$

$$\text{DHS sum score } (n \text{ analytes}) = \sum_{i=1}^{n} \text{analyte-specific DHS score } i \qquad (2)$$

### 2.5. Sensory Evaluations.

Sensory evaluations of samples were carried out by a trained sensory panel (Fraunhofer IVV) exhibiting no signs of any known illness at the time of examination. Training of panel members was accomplished by means of weekly training sessions with selected in-house developed odorant pens containing reference compounds and with a required minimum mean correctness threshold in odor identifications in ensuing tests. Sample pieces of approximately 5 cm diameter were cut from each mask, placed in covered glass jars with the inner face of the mask pointing upward, and presented to the panel. Quantitative descriptive analyses (QDAs), as well as overall odor intensity and hedonic ratings, were performed on each of the 12 masks. Panelists were required to open the lid and then immediately smell the samples and record their odor impressions. In an initial session, six assessors named the odor attributes of each sample, which were subsequently compiled for the most frequent attributes and panel consensus. In a second session, the six trained panelists rated the overall intensity of each attribute for each sample on a scale from 0 (no perception) to 10 (strong perception). A larger panel comprising 13 panelists (six trained and seven untrained) also completed hedonic ratings on a scale from 0 (strong disliking) to 5 (neutral) to 10 (strong liking) as well as ratings of the overall odor intensity on a scale from 0 (no perception) to 10 (strong perception). The mean values of all ratings are reported.

### 2.6. Exposure Assessment through Simulated Use of Masks.

We developed an innovative setup based on a doll's head to simulate and assess realistic exposure while wearing a costume mask. A doll's head intended for cosmetic training (purchased online from Amazon, Luxembourg, Luxembourg) was used for simulated exposure assessments. The dimensions of the head were 21 cm from chin to crown, 20 cm from the tip of the nose to back of the head, and 16 cm between the two ears, resembling a small adult human head. The foam inside the doll's head was removed until the nose was freely accessible from the inside, and it was left to ventilate for 2 months under a laboratory fume hood prior to use. Two holes (approximately 1 cm diameter) were cut into the nose to mimic nostrils, and two PTFE tubes were connected to the nostrils through the inside of the doll's head to simulate exhalation and inhalation. The head was mounted on a stable cardboard base and affixed with low-emission aluminum-coated tape. A picture of the system is presented in Figure 1.

Average at-rest inhalation and exhalation flows for adults are around 6 L·min$^{-1}$.[22] Pure $N_2$ was flushed through the exhalation tube at a rate of 6.00 ± 0.20 or 13.00 ± 0.25 L·min$^{-1}$, with the latter simulating breathing during moderate activity and resembling the maximum flow rate of the pump used to simulate inhalation. The inhalation tube was connected to two pumps via a T-piece. One of the pumps (a gas sampler GS 212, Type 170110, DESAGA GmbH, Heidelberg, Germany) ran continuously at a sampling flow of either 5.90 ± 0.20 or 12.90 ± 0.20 L·min$^{-1}$ to simulate inhalation. The second pump (SG350ex, GSA Messgerätebau GmbH, Ratingen, Germany) ran continuously with a flow rate of 100 mL·min$^{-1}$ and was regularly used for active gas sampling (200 mL, 2 min) to capture any released volatiles on conditioned Tenax TA TD tubes spiked with internal standard (described in section 2.3) according to ISO 16000-6.[23] Blanks were sampled before the masks were placed on the doll's head to ensure low background VOC levels of the system (inhaled concentration of cyclohexanone was below 2.0 mg·m$^{-3}$ for blank samples; blank values were subtracted to obtain background-corrected values).

Ambient temperature $T$ (varying from 20.9 to 25.4 °C) and relative humidity $H$ (varying from 39.5 to 64.8%) were measured directly beside the doll's head immediately before and after each experiment. Exhalation and inhalation flow rates were checked with a gas counter (G 1.6 RF 1, Schlumberger, Amsterdam, The Netherlands) before each experiment.

VOC exposure assessments on the doll's head system were performed on two types of masks, selected on the basis of them exhibiting the highest overall VOC emissions, as determined via DHS analyses (described in section 2.4; results presented in section 3.2). Specifically, samples 9 and 10 were used in these experiments, whereby new batches of the same mask types (9B, 9C, and 10B) were used.

### 2.7. Qualitative and Quantitative Gas Chromatography/Mass Spectrometry Analysis of Gas Samples and Risk

**Assessment.** The Tenax TA TD tubes containing the adsorbed VOCs (either from DHS sampling of mask emissions or from gas sampling from the inhalation tube in the exposure simulation experiments) were analyzed using GC/MS according to ISO 16000-6.[23] Thermal desorption was performed with a thermal desorption unit (TDU; Gerstel) connected to a gas chromatograph 6890 that was coupled to a mass selective detector 5975 (both Agilent, Waldbronn, Germany). The TDU was operated with a helium gas flow of 51.5 mL·min$^{-1}$ and the following temperature program: 25 °C for 0.2 min; heating to 280 °C at 700 °C·min$^{-1}$; 280 °C held for 2 min. During thermal desorption, analytes were cryotrapped at −150 °C with liquid $N_2$ (Linde) in the cold injection system (CIS; Gerstel) equipped with a liner filled with deactivated glass wool (Gerstel). After desorption, the CIS was heated to 285 °C at 12 °C·s$^{-1}$ and then held at 285 °C for 15 min. Injections were carried out either splitless (following DHS sampling) or with a split of 1:400 (1:20 at the CIS and 1:20 at the TDU in exposure simulation and microchamber experiments).

The GC system was equipped with a DB-5MS column (60 m × 0.32 mm i.d., 1.00 μm df, J & W Scientific, Folsom, CA, USA). Helium gas was used as a carrier gas at a constant flow rate of 1.4 mL·min$^{-1}$. The GC oven temperature program commenced with 45 °C for 0.5 min, before being heated to 200 °C at 12 °C·min$^{-1}$, held for 5 min at 200 °C, then heated to 280 °C at 20 °C·min$^{-1}$, and held at 280 °C for 10 min.

The temperatures of the transfer line, quadrupole, and ion source were 295, 150, and 230 °C, respectively. The MS was operated in combined SIM/full-scan mode. The mass range for acquiring full-scan MS data was set to $m/z$ 40−450 and measured at a rate of 3.5 scans·s$^{-1}$ in unit resolution. The target compounds were identified by comparing their retention times and full-scan mass spectra with those of authentic standards. SIM data were acquired with a dwell time of 10 ms per ion and used to quantify target compounds in relation to the internal standard cyclodecane of known concentration. The resolution of the MS was set to low. One quantifier and one or two qualifier ions were assigned to each analyte. SIM parameters are reported in the Table S2.

Analytes were quantified by calibration with authentic standards, applying conditioned and internal standard spiked TD tubes (section 2.3). A volume of 1 μL of the prepared calibration solution in ethyl acetate (stored in a freezer at −18 °C) was added using a tube spiking system (Gerstel) with a rinsed 10 μL microvolume syringe. The tubes were then dried with 500 mL of $N_2$ at a flow rate of 100 mL·min$^{-1}$ and analyzed as described above. A representative calibration curve is presented in Figure S2.

Data were processed by using the MassHunter Quant Software (version B.06.00, Agilent). The results were converted to concentrations in air by dividing the measured amount of analyte by the volume of air that was sampled and compared to the DNEL values published on the European Chemicals Agency (ECHA) website.[24] Inhalation DNELs for the general population are well-suited for a risk assessment based interpretation of the emissions measurement data in an exposure scenario that involves the wearing of costume masks over a few hours. Contrarily, the European lowest concentration of interest (EU-LCI) values, which are commonly used to assess the safety of construction products, refer to emission test chamber measurements with air sampling performed 28 days after chamber loading.[25,26] Similar to DNELs, EU-LCI values are derived toxicologically according to the ECHA guidance Chapter R.8,[27] but the applied assessment factors are specifically adapted to prolonged exposure. Older EU-LCI values were derived from occupational exposure limits (OELs) with conservative considerations for vulnerable populations such as children.[28] Conservative assessment factors make the DNEL also applicable to the general population.[27] Moreover, the ECHA guidance[27] states that, for inhalation exposure periods exceeding 15 min, the long-term (chronic) DNEL should usually be applied. However, an acute/short-term DNEL should be set for acutely toxic substances if peak exposure levels significantly exceed the long-term DNEL. Thus, both acute/short-term and long-term DNELs were considered in this study.

### 2.8. Analysis of Gas Samples by Gas Chromatography/Olfactometry.

GC/O in combination with DHS sampling was used to identify odorous substances. DHS−GC/O avoids the rather laborious SAFE extraction step and allows the sample to be studied online at ambient temperature.[29] DHS sampling prior to GC/O analysis was carried out in a manner similar to the method described in section 2.4, with the following exceptions: the extraction step was carried out at 28 °C because the proximity of the DHS station and the heated olfactometry detector line (250 °C) prevented a lower stable temperature during sampling; furthermore, no internal standard was used because of the qualitative nature of the analyses. Experiments were conducted with samples 9A and 10A in triplicate. Odors were considered when they were detected by the operator in at least two independent DHS−GC/O experiments.

The TD−GC methods resembled those described in section 2.7, albeit using a HP-5MS column (30 m × 0.25 mm i.d., 0.25 μm df, J & W Scientific). The flow rates and capillary length were calculated with the ODP column calculator software (Gerstel). The effluent at the end of the GC column, at a flow rate of 1.47 mL·min$^{-1}$, was split into two equal flows of 0.73 mL·min$^{-1}$ each. A first capillary, with a length of 79 cm heated to 250 °C, led to an olfactory detection port (ODP3, Gerstel) that was held at 250 °C. The same operator smelled all samples from retention times 3.6 to 8.0 min (in a preliminary experiment, no odors were detected beyond these retention times). A second capillary of 51 cm length led through the GC oven to the MS. The MS method is described in section 2.7.

To identify analytes associated with the detected odors, 1 μL of a mixture of authentic reference compounds in dichloromethane (∼25 ng·μL$^{-1}$) was transferred into microvials (Gerstel), placed inside an empty TD tube (Gerstel), and measured as described for Tenax TA-loaded tubes (section 2.7). The analytes were identified by comparing their retention indices[30] and mass spectra with those of the reference compounds. According to the ODP column calculator software, a delay of 0.8 s should be applied between MS and olfactometric detection. This delay was verified experimentally with an odorous model compound (*p*-cresol, 0.7 s).

### 2.9. Surface Emissions Measurements with a Microchamber.

Surface emissions measurements on the costume mask samples were carried out with a miniaturized emission chamber to investigate the potential of such a device for the routine assessment of VOC emissions in complex exposure scenarios. A microchamber/thermal extractor device (μ-CTE250, Markes International, Llantrisant, U.K.) with four chambers, each with a volume of 114 mL, was utilized for these measurements. The microchamber parameters were adapted to approach the area-specific flow rate of the doll's head setup (2.80 mL·cm$^{-2}$·min$^{-1}$): The total area of the inner surface of a mask was estimated by cutting a mask of type 9 (horse) into small geometrical pieces and summing up their individual areas (2141 cm$^2$). The same surface area was assumed for mask 10. The internal volume of the mask (6.0 L) was obtained by measuring the volume of water needed to completely fill the mask after sealing all holes with tape. By subtracting the mean volume of a human head (3.2 L[31]), the gas volume between the head and the mask was calculated to be approximately 2.8 L. As the microchamber has a diameter of 6.4 cm, mask pieces of ca. 32 cm$^2$ were placed inside the chamber (inner side facing upward) for surface emissions measurements (schematic description in Figure S3). The chamber volume was decreased to 42 mL with metal spacers (Markes; height, 1.3 cm) and the $N_2$ flow was set to 88 ± 6 mL·min$^{-1}$, resulting in an area-specific flow rate of 2.74 mL·cm$^{-2}$·min$^{-1}$. The temperature of the chamber (measured with the integrated sensor) was 23 ± 1 °C. The relative humidity, $H$ (measured in one chamber with a HI 9565 sensor from Hanna, Vöhringen, Germany), was 45.4 ± 1.8%.

For comparative measurements, one (sample 9C) or two pieces (sample 10B, in two separate chambers) of 6.4 cm diameter were cut from the neck of the masks with a precision knife (NT cutter, Osaka, Japan) and placed in the microchamber at the same time that the masks (minus the pieces cut from the neck region) were placed on the doll's head. Gas samples were collected at the outlet of the chamber onto conditioned Tenax TA TD tubes spiked with internal standard

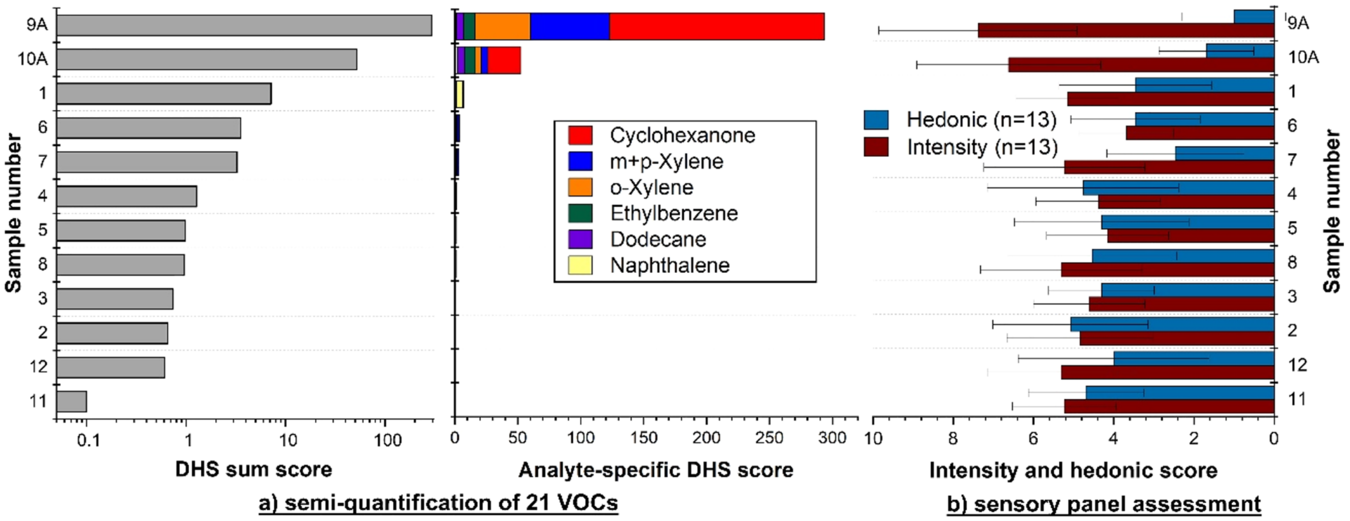

**Figure 2.** DHS sum scores (left, logarithmic *x*-axis scale) and analyte-specific DHS scores (middle, linear *x*-axis scale) of the emitting target analytes (a) and results of the sensory evaluation (right, mean values of hedonic ratings and overall odor intensities, $n = 13$ panelists, error bars represent SDs) (b) of the 12 mask samples.

(sampling time, 2 min 15 s) at the same time that they were collected from the doll's head and analyzed following the protocol described in section 2.7.

To simulate worst-case, real-life conditions for the analyses, the temperature inside mask 11 was measured when it was worn in the sun on a hot summer's day (outside temperature, ca. 35 °C), yielding a temperature of ca. 40 °C. To mimic these conditions, in one experiment the temperature inside the chamber was fixed to 40 ± 1 °C ($H$ = 44.1 ± 0.3%). In a different run, the emissions were measured at $T = 23 \pm 1$ °C and $H = 42.6 \pm 0.1\%$ (sampling time, 1 min 45 s) with a 40% increased area-specific flow rate of 3.85 $\text{mL}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ (resulting from the system's maximum possible flow rate of 124 ± 2 $\text{mL}\cdot\text{min}^{-1}$ when the humidifier was used).

## 3. RESULTS AND DISCUSSION

**3.1. Polymer Characterization.** Pyrolysis−GC/MS analysis of the masks indicated that each mask was at least in part composed of polyvinyl chloride (PVC), as identified through the presence of typical PVC degradation products[32] in each individual sample (two representative pyrograms are presented in Figure S4). In addition, Beilstein tests on samples 9A and 10A yielded the expected green flame that is characteristic of halide-containing polymers, such as PVC. In contrast, all other samples melted without burning (see Figure S5), which can be attributed to the presence of halogen-free flame retardants in their polymeric matrixes.

**3.2. Volatile Profiles and Odor Perception.** The VOC emissions profiles from the mask samples, as determined semiquantitatively via DHS−GC/MS, were compared with the odor profiles evaluated by the sensory panel. A plot of the DHS sum scores for each sample, whereby the scores represent the sum of signal intensities of 21 individual analytes (comprising the compounds with the highest signal intensities), shows that two masks (samples 9A and 10A) exhibited particularly high VOC emissions (Figure 2a, left). Cyclohexanone, xylenes, and ethylbenzene were detected as the most abundant signals in the chromatograms of these two samples (Figure 2a, right; also compare Figure S6). Xylenes are known to be neurotoxic.[33] Furthermore, *o*-xylene and naphthalene, which is classified as possibly carcinogenic to humans[34] and was detected in sample 1, are precursors in the synthesis of phthalic anhydride,[35] a reactant for the production of phthalate-based plasticizers. Their presence as impurities in soft plastics, such as PVC, which frequently contain this class of additives, is therefore explicable. Indeed, bis(2-ethylhexyl) phthalate (DEHP), a regulated phthalate with suspected endocrine disrupting properties, was detected in sample 9A via pyrolysis−GC/MS (see Figure S4). Cyclohexanone, on the other hand, is used as a PVC adhesive and can potentially induce contact dermatitis.[36] Cyclohexanone inhalation also induced hepatotoxicity and nephrotoxicity in rats.[37] This compound was detected in several other studies that investigated emissions and odors from polymer-based products.[7,15,38]

Notably, the sensory panel rated the same two samples featuring the highest DHS sum scores (9A and 10A) as having the highest odor intensities and lowest hedonic ratings (Figure 2b), while samples with lower emissions (low DHS sum scores) were rated with less intense odors and higher hedonic ratings. Although the limited sample size makes it difficult to draw general conclusions, it seems likely that products rated as having a bad smell are of low overall quality, which is reflected in elevated VOC emissions.

**3.3. Odor Profiles.** The sensory profiles from the QDA of the 12 mask samples are depicted in Figure 3. The two masks that exhibited the highest overall odor intensities and emissions (i.e., samples 9A and 10A) feature rather unique profiles: both were characterized as *rubber-like* (reference compound in the odorant pen representing this attribute,

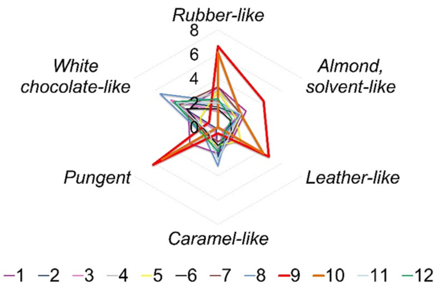

**Figure 3.** Odor profiles of the predominant six attributes of the 12 mask samples that were assigned the highest scores (mean scores of six trained panelists).

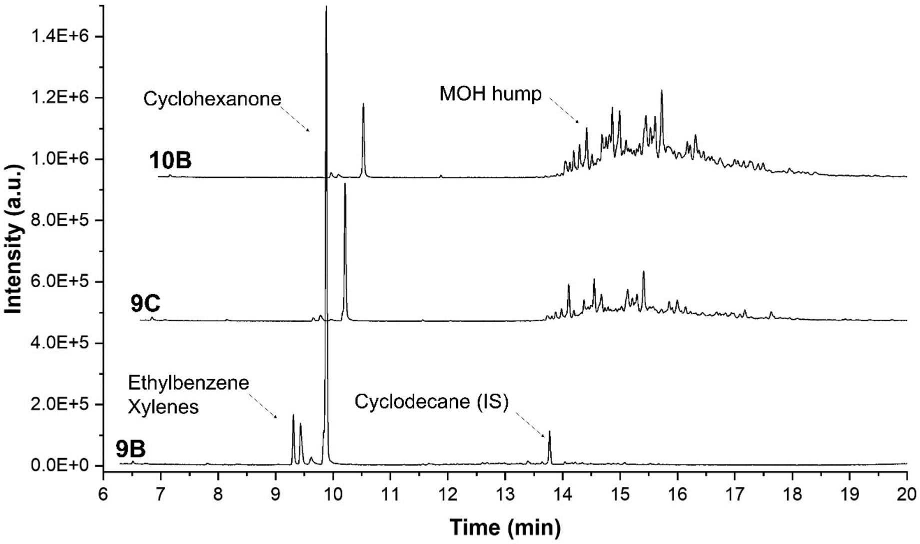

**Figure 4.** GC/MS traces (scan mode) of gas samples taken from the inhalation tube during the first 2 min after placement of the mask on the doll's head during simulated exposure assessments.

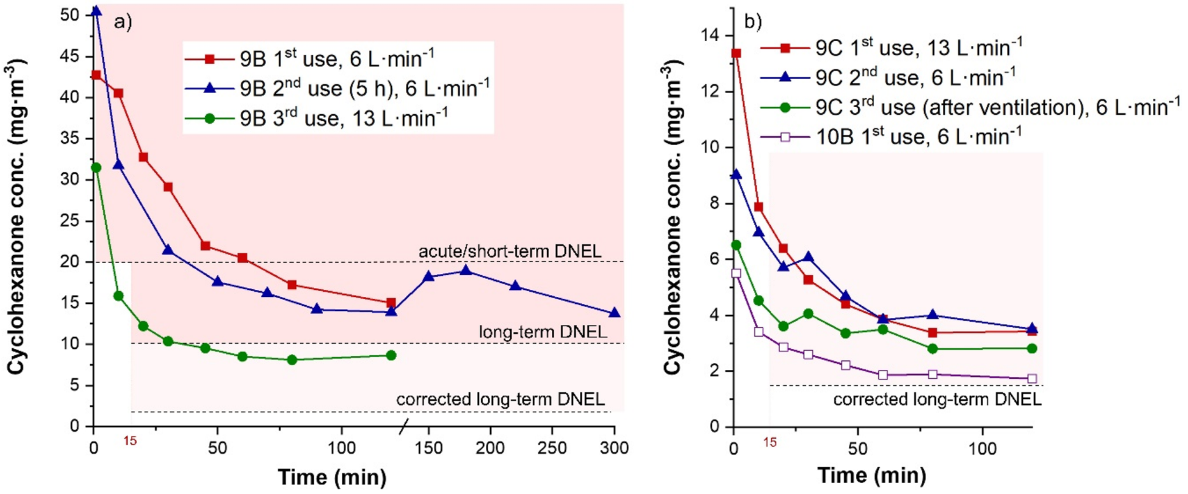

**Figure 5.** Kinetic profiles depicting inhalable concentrations of cyclohexanone while wearing three different costume masks, 9B (a) and 9C and 10B (b), as determined with the doll's head exposure simulation setup. DNEL threshold values, as derived by the industry registrants (acute/short-term, long-term after 15 min) or in this work (corrected long-term), are shown as reference. Long-term DNELs are usually applied for exposures exceeding 15 min.[27] Colored regions indicate regimes where cyclohexanone DNELs were exceeded.

benzothiazole), *pungent* (1-penten-3-one), and *leather-like* (3-methylphenol), which are attributes that are usually perceived as unpleasant. These attributes might therefore explain the very low hedonic scores of these two samples (see Figure 2b). By comparison, the other 10 masks were characterized as exhibiting *white-chocolate-like* (cocoa butter), *caramel-like* (ethyl maltol), or *almond, solvent-like* (acetophenone) odors, which are typically perceived as more pleasant odors and thus explain their higher hedonic ratings. This could imply that those 10 samples were fragranced, although related compounds were not among the highest peaks detected during DHS−GC/MS experiments.

DHS−GC/O−MS analysis of samples 9A and 10A yielded different attributes of the odor-active compounds present in the two samples, as is evident from the list in Table S3, despite their similar descriptive sensory profiles. The substances with the highest emissions in the DHS−GC/MS analyses (see Figure 2a) were largely also identified in the DHS−GC/O−MS analyses, as determined via their chromatographic retention indices (measured with reference compounds) and mass spectra. Interestingly, no odor was perceived for ethylbenzene and the xylenes in DHS−GC/O−MS, despite these compounds exhibiting high DHS scores of up to 9 and 63, respectively, in the DHS−GC/MS analyses. Only cyclohexanone, which had the highest assigned DHS score of 170, was perceived (*flowery, grassy, solvent-like*; RI = 913, see Table S3). Wiedmer and Buettner characterized the odor as *almond-like, inflatable-swimming-aid-like,*[16] but the subjective perception can be different among individual assessors. Overall, the comparison of DHS−GC/MS and DHS−GC/O−MS data sets for the two selected masks revealed that the substances with the highest measured emissions were not necessarily those causing the perceived odors. Notably, the intense odors could also arise from very volatile organic compounds (VVOCs) including solvents, which cannot be measured with the ISO 16000-6 approach.[23]

### 3.4. Emissions Assessments of Masks under Simulated Exposure Conditions.

Figure 4 displays the GC/MS traces depicting the VOCs present in 200 mL of air sampled from the inhalation tube during the first 2 min after the mask was placed on the doll's head. Notably, masks 9 (horse) and 10 (unicorn) revealed very similar chromatograms: those two masks had the same town of origin and were similarly packaged and labeled, indicating a common source. The most abundant peaks corresponded to the same compounds detected in the DHS−GC/MS experiments (see Figure 2a and Figure S6), as expected. However, the chromatograms of samples 9C and 10B featured a hump at later retention times that is characteristic for the volatile fraction of mineral oil hydrocarbons (MOHs). MOHs are sometimes used to soften PVC products.[39] However, they might also have been transferred from printed cardboard packaging during storage. The bioaccumulative and carcinogenic potential of MOHs is under discussion.[40]

Samples 9B and 9C, which were masks of the same type but from different batches, exhibited significant differences in their emitted quantities of specific compounds. The amount of cyclohexanone emitted from mask 9B was approximately 3 times higher than that from sample 9C. Similarly, mask 9C emitted approximately 12 times more MOHs than sample 9B, as quantified by comparison of the integrated peak areas. This indicates a need to characterize many different samples from the same article type to achieve a representative market control.

### 3.5. Exposure Assessments under Simulated Mask Use.

Inhalation exposure estimates require that the inhaled concentrations of specific VOCs emitted from the masks are known as a function of exposure time. The exposure simulation experiments using the doll's head setup revealed kinetic profiles with a slightly faster decrease for compounds with lower boiling points (see Figure S7). The inhalation profiles of cyclohexanone, which was the most abundant compound in both the headspace and doll's head based analyses (see sections 3.2 and 3.5), are depicted in Figure 5.

Different aspects were addressed in these exposure simulation assessments. First, one mask model (sample 9B, horse mask) was studied in three consecutive experiments to investigate the repeated use of a single mask. The inhaled cyclohexanone concentrations during first use of this particular mask exceeded the DNEL for short-term systemic effects on the general population published on the ECHA website[24] (20 $mg \cdot m^{-3}$) by up to 2 times within the first 15 min of simulated wearing. The DNEL for long-term exposure (10 $mg \cdot m^{-3}$) was exceeded over the entire 2 h measurement period (Figure 5a). Concentrations of xylenes and ethylbenzene were below the respective DNEL values; thus related data are not reported here. It is important to note that the DNELs for cyclohexanone were derived by the industry registrants in order to comply with the European REACH Regulation. It was not possible to reproduce how the registrants derived the cyclohexanone DNELs from the reported data on the ECHA website.[24] Considering a recent study on cyclohexanone toxicity upon inhalation in rodents,[37] which was not considered by the registrants, we derived long-term DNELs for workers and the general population of 8.1 and 1.4 $mg \cdot m^{-3}$, respectively (see Table S4 and accompanying text; the latter DNEL is also indicated in Figure 5). The corrected DNEL of 1.4 $mg \cdot m^{-3}$ was exceeded by up to 31-fold during the first few minutes of wearing, and still by more than 10 times after 2 h. As costume masks may be worn repeatedly for several hours, the corrected long-term DNEL is considered more appropriate than the acute DNEL that reflects a single use exposure. Acute DNELs are generally much higher than long-term DNELs as their derivation is based on lethality observed in animal studies. However, for potential hazardous properties of the masks, lethality is not an appropriate end point for consideration. When adjusting the measured cyclohexanone concentrations for shorter daily exposure, as suggested by the ECHA,[41] the long-term DNEL is still significantly exceeded (see the Supporting Information for details). Of note, the EU-LCI threshold value for this substance (410 $\mu g \cdot m^{-3}$)[25] would have been exceeded by up to 128-fold. However, EU-LCI values are intended to cover long-term exposures for substances emitting from building products, for which an initial off-gassing period without direct inhalation exposure is assumed (see section 2.7).

After this first exposure assessment, the mask was repacked in a gastight bag, stored at room temperature for 2 days, and then reassessed for inhalation exposure during second use. The inhaled cyclohexanone concentration reached a maximum of ca. 50 $mg \cdot m^{-3}$ within the first 2 min, which is similar to the first assessment. Two mechanisms contribute to the kinetics of the emissions processes: diffusion of the VOCs within the material along a concentration gradient and partitioning between the material surface and the surrounding air. During the first-use exposure assessment, emissions decreased over time because diffusion was rate-limiting, leading to a steady decrease in the surface concentration of cyclohexanone. While the mask was being stored in the airtight bag, diffusion from the material core resupplied the surface with cyclohexanone that had previously been depleted during the emissions analysis. When the mask was unpackaged and the second measurement started, cyclohexanone was emitted at similar concentrations. Small differences probably result from slight deviations during gas sampling or a slightly different position of the mask on the doll's head. Importantly, cyclohexanone concentrations were also observed to exceed both long-term exposure DNELs for at least 5 h in the second-use exposure assessment. The inhaled amounts of cyclohexanone vapors when wearing this mask are therefore concerning, not only during the first few minutes, but also during repeated or long-term use.

Breathing patterns that are characterized by higher inhalation/exhalation frequencies are typically observed during physical activity or when experiencing strong emotions. As such, the influence of the breathing rate on the cyclohexanone exposure was explored by varying the flow rate from 6 $L \cdot min^{-1}$ (at-rest breathing[22]) in the first two emissions measurements to 13 $L \cdot min^{-1}$ in a third assessment carried out 8 days later. In this scenario, the cyclohexanone concentrations were approximately half of those during the previous measurements. The approximately doubled flow rate dilutes the gas phase concentration of cyclohexanone. Additionally, it is also possible that the surface concentration decreased during the previous two trials, with a lower total concentration of cyclohexanone remaining in the material. However, since the volume of inhaled air per unit of time increases accordingly, the total amount of inhaled VOC remains similar.

The emissions from another specimen of the same mask type (9C, horse mask) were measured to study possible inhomogeneity between similar samples (Figure 5b). In this case, exposure to cyclohexanone was much lower than for sample 9B. Possible reasons for these differences could be the varying amounts of chemicals used during production, as well as different ambient conditions (air change rate, temperature, humidity) that the masks had been exposed to since manufacturing. In these experiments, the first- and second-use assessments were carried out within 2 days, applying flow rates of 13 and 6 L·min$^{-1}$, respectively. The cyclohexanone concentrations were observed to be higher in the first few minutes of the first-use assessment at high flow rate compared to the second-use assessment at low flow rate. Presumably, the lower total amount of cyclohexanone in sample 9C compared to 9B further depleted to a significant extent in the first measurement at high flow.

The third measurement was carried out after venting of the mask under controlled conditions in an emission chamber (203 L, air change rate 0.5 h$^{-1}$, $T$ = 23 °C, $H$ = 50%) for 14 h in order to examine any influence that ventilation might have on emission rates. Two main observations were made. First, ventilation seemingly acted to reduce high initial emissions, whereby the concentrations of cyclohexanone in the first few minutes of the inhalation exposure simulation were lower compared to at the beginning of the previous trial. This likely relates to the air exchange acting to deplete compounds from the material surface compared to packaged storage. On the other hand, the initial concentration is still higher than the concentration measured at the end of the preceding second-use assessment. This highlights that, even under conditions facilitating ventilation, significant amounts of cyclohexanone may accumulate on the mask surface.

The cyclohexanone concentration was determined to be 18.65 ± 0.08 mg·m$^{-3}$ ($n$ = 2) in the 203 L test chamber directly before removing the mask after ventilating it for 14 h. This corresponds to 126 $\mu$g·m$^{-3}$ cyclohexanone in a 30 m$^3$ room, which is 3 times lower than the EU-LCI[25] and 11 times lower than the DNEL derived in Table S4. Items such as costume masks are emissions sources not only while being worn, but also when they are stored indoors. Scenarios with multiple masks—for instance in retail environments—might lead to higher concentrations that ultimately may exceed threshold values. The Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) is currently working on an opinion on toxicological reference values for VOCs (including cyclohexanone) emitted from toys in such scenarios:[42] this was requested after high VOC concentrations were detected in emission chamber testing of squishy toys.[9]

Finally, a comparative analysis with mask 10B (unicorn) revealed that the cyclohexanone inhalation exposure was lowest for this mask yet exhibited kinetic profiles similar to those in masks 9B and 9C (Figure 5b). The PVC-based matrixes of both masks probably govern the release kinetics of cyclohexanone. Of note, the long-term DNEL of 1.4 mg·m$^{-3}$ (derived in Table S4) would be exceeded for all three masks studied (see Figure 5).

It is noteworthy that a combined exposure assessment of all VOCs found in this study may be useful to provide a more comprehensive risk assessment that takes into account possible additive effects. This might add to the concern of VOCs released from costume masks. A thorough mixture assessment would require comparable effect data for all these VOCs in order to determine their individual relative effect potencies. Additionally, a prerequisite for combined additive mixture effects is the same, or a similar, mode of action or at least the same type of effect. Considering the complexity of such an assessment, this was not pursued in the present study. Furthermore, it is emphasized that cyclohexanone was the predominant VOC in this study (see Figure S7) and that it exceeded guideline threshold values even as a single component.

### 3.6. Surface Emissions Measurements with a Microchamber: Toward Facilitating Market Control.

Using a microchamber to investigate surface emissions may be advantageous for control authorities of consumer products, which rely on standardized and cost-effective experimental configurations for a harmonized market control.

Figure 6 displays data from the comparative measurements of cyclohexanone emissions as a function of time for samples 9C and 10B from both the microchamber and exposure simulation configurations. The kinetic profiles obtained from the two analytical experiments were similar. However, although the gas phase concentrations measured in the microchamber are of the same order of magnitude as the inhalable concentrations determined in the exposure simulation measurements, they are significantly higher by a factor of 2.3−7.1 for both masks. When adjusting the area-specific flow rate in the microchamber to reflect the conditions of the doll's head setup (see section 2.9), the inhalation/exhalation flows were considered as being equally distributed in the space between the mask and the doll's head. In reality, however, the area-specific air flow is presumably much higher near the site where the air exits and enters the tubes (i.e., the nostrils) than elsewhere. As such, a smaller surface contributes to the emissions in the more realistic doll's head setup and fewer molecules are emitted per unit surface area. Hence, a sampling time dependent correction factor is needed, which was found to be also analyte- and sample-specific (Figure 7).

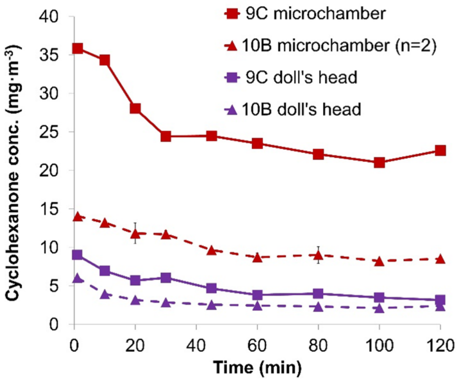

**Figure 6.** Comparison of cyclohexanone concentrations emitted from samples 9C and 10B, as measured simultaneously with the microchamber (representative sample piece) and doll's head exposure simulation setup (rest of the whole mask).

In a final experiment, the emitted cyclohexanone concentrations from different pieces of the same mask were investigated, as were the effects of increased temperature and flow rate (Figure 8).

Comparative, simultaneous emissions measurements of three different pieces of mask 9A in three compartments of the microchamber at 23 °C and a flow rate of 90 mL·min$^{-1}$ indicated a low relative standard deviation (SD), which varied from 3.7 to 12.0% between different sampling time points. The variation was much lower than between different masks of the same type that were measured on the doll's head (see 9B and

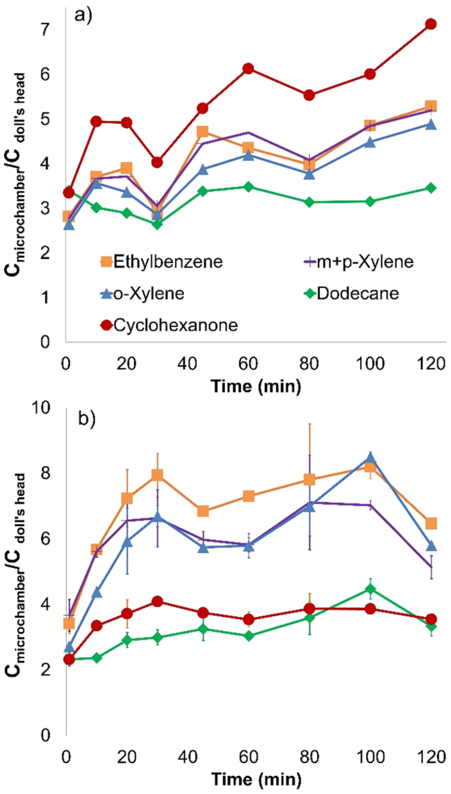

**Figure 7.** Ratio of gas phase concentrations of six analytes measured in the microchamber and with the doll's head exposure simulation setup from sample 9C (a, *n* = 1) and sample 10B (b, *n* = 2). Error bars represent SDs for repeated analyses.

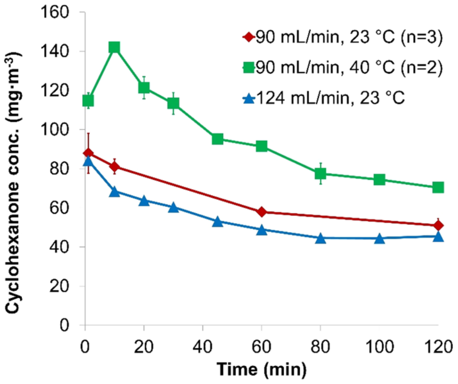

**Figure 8.** Influence of mask homogeneity and increased temperature and flow rate on the cyclohexanone concentrations emitted from sample 9A as measured in the microchamber. Error bars represent SDs for repeated analyses (see figure legend).

9C in Figure 5). This suggests that for a preliminary assessment it would be sufficient to analyze a single piece per mask in the microchamber, facilitating multiplexing.

An increase in temperature inside the chamber from 23 to 40 °C to simulate the temperature beneath the mask on a warm summer's day led to up to a 1.8-fold increase in emissions. This highlights the fact that temperature is an important parameter that must be taken into account in exposure assessments. Of note, the influence of temperature could not be studied conveniently with the doll's head setup because measurements were carried out in a laboratory at room temperature.

Finally, the influence of the air change rates on the emissions profile to simulate higher inhalation/exhalation flows indicated that cyclohexanone emissions decrease with a higher air exchange, as similarly observed for sample 9B in the doll's head setup (see Figure 5a).

## 4. SUMMARY AND OUTLOOK

While standardized methods to assess human exposures of VOC emissions in indoor environments exist,[26,43] knowledge about VOC exposure in more complex emissions scenarios is scarce. In this study, we investigated which gas phase concentrations of VOCs are relevant for a realistic exposure assessment when costume masks are worn. In the particular case of masks, inhalation takes place very close to the emissions source, which increases the probability that harmful substances are inhaled at elevated concentrations and for prolonged periods.

The odors of 12 different polymer-based costume masks were characterized by a sensory panel, which identified two masks as having particularly intense and unpleasant smells. DHS−GC/MS experiments revealed that the same two masks yielded the highest DHS sum scores, which we previously introduced as a measure for the total target VOC emissions.[10] However, DHS−GC/O analysis indicated that the VOCs with the highest detected emissions (cyclohexanone, ethylbenzene, and xylenes) were not necessarily responsible for the unpleasant smell of the masks. Still, in the subset of samples studied, masks with a bad smell seem to be of low overall quality, as represented by their elevated VOC emissions.

Furthermore, we developed an experimental setup that simulates inhalation exposure based on the use of a doll's head. This novel setup enabled simulation of exhalation and inhalation at realistic flow rates and facilitated sampling of the inhaled air containing relevant VOCs that are emitted from worn masks. The data from one mask sample revealed that the inhaled concentration of cyclohexanone exceeded the industry registrants derived no-effect level (DNEL) threshold value for short-term use by a factor of up to 2.5. Although the emissions decreased over time, the DNEL for long-term use was exceeded continuously over 5 h of mask wearing. Based on a recent inhalation toxicity study,[37] we derived a significantly lower DNEL, which was exceeded up to 36-fold. This highlights the relevance of our exposure assessment results. Although the limited sample size makes it difficult to draw general conclusions, it is concerning that cyclohexanone emissions from 2 out of 12 randomly purchased masks exceeded the DNEL. It is also noteworthy that the cyclohexanone exposure was still significant after several uses, even if the mask was left to ventilate overnight. Although it might therefore be advisable to unpack such items outdoors and keep them there for a few days to outgas before use, the implementation of this recommendation cannot be checked. Hence, ventilation before first use is not a sufficient measure to protect consumers. Costume masks—like all other consumer products placed on the market—must meet the legal requirement to not pose a risk to consumers' health. Compliance with this regulation is the responsibility of the manufacturers and importers. Quality control processes during the production steps should be implemented to minimize the contents and release of hazardous VOCs and unpleasant odors to a level as low as reasonably achievable. This is particularly important as such masks may also be used by children.

Surface emissions assessments with a low-volume emission test chamber (microchamber) were investigated as a potential alternative to the doll's head setup. Microchambers are standardized instruments that are lower in cost than large-volume chambers and might provide options for the development of standardized analytical methods to assess VOC emissions from consumer products by official control authorities. For the masks investigated here, both systems yielded similar emissions profiles. However, the implementation of analyte- and sample-specific correlation factors in the range of 2−9 proved necessary to match the chamber-derived VOC concentrations with those from the more realistic doll's head setup. Still, the microchamber allows for a quick and reproducible assessment of VOC emissions and for studying the influence of parameters, such as temperature or exhalation and inhalation flow rates on emission rates.

This work demonstrates that polymer consumer products, such as costume masks, that come into close contact with the consumer can pose a threat to human health due to the release and continuous inhalation exposure of toxicologically relevant volatiles. It remains to be demonstrated whether this is also an issue for other products used in medical and more recently also in public environments (e.g., for surgical and FFP masks intended to prevent airborne infections and for respiratory devices) and during occupational activities (e.g., for personal protective equipment of firefighters[44]). Additionally, less volatile compounds, such as PAHs and certain plasticizers (naphthalene and DEHP were each detected in one mask, respectively), may also need to be considered for long-term exposures during storage, e.g., in retail environments. Tandem chromatography techniques may provide further options to investigate the composition of emitting mineral oil hydrocarbons. Finally, a comprehensive exposure analysis for mask wearers also needs to consider the dermal exposure toward migrating chemicals via skin contact.

The protection of consumers against possible health hazards caused by VOC emissions from products can only be guaranteed if manufacturers, importers, and official control laboratories are aware of this complex topic. It is therefore crucial to develop harmonized analytical methods as well as to correctly interpret the results from a toxicological perspective.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemrestox.0c00414.

> Tables S1 and S2: Details about chemical properties, standards, and analytical parameters; Table S3: results from GC/O experiments; Table S4 and associated text: derivation of corrected DNEL values; Figures S1−S7: mask sample pictures, cyclohexanone calibration curve, schematic diagram of microchamber setup, pyrolysis−GC/MS chromatograms of two samples, picture from sample pieces after Beilstein tests, chromatograms from DHS experiments, kinetic profiles of low-boiling substances in comparison to cyclohexanone (PDF)

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### Author Contributions

Each author has participated in the work intellectually or practically and takes responsibility for the content of this article. M.E. and N.L. carried out the experimental work and data analysis. D.S. and A.S. carried out the assessment and calculation of DNEL values for cyclohexanone. M.E., A.R., C.H., J.B., and A.L. designed the study, analyzed data, interpreted the results, and contributed to the manuscript. The final version was approved by all authors.

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

BVL, German Federal Office of Consumer Protection and Food Safety—Bundesamt für Verbraucherschutz and Lebensmittelsicherheit; CIS, cold injection system; df, film thickness; DEHP, bis(2-ethylhexyl) phthalate; DHS, dynamic headspace; DNEL, derived no-effect level; ECHA, European Chemicals

Agency; EU-LCI, European lowest concentration of interest; FFP, filtering facepiece; GC, gas chromatography; GC/O, gas chromatography/olfactometry; i.d., internal diameter; IS, internal standard; MS, mass spectrometry; MOHs, mineral oil hydrocarbons; $N_2$, nitrogen; ODP, olfactory detection port; o.d., outer diameter; PAH, polycyclic aromatic hydrocarbon; PTFE, polytetrafluoroethylene; PVC, polyvinyl chloride; QDA, quantitative descriptive analysis; REACH, registration, evaluation, authorization, and restriction of chemicals; RI, retention index; SAFE, solvent-assisted flavor evaporation; SCHEER, Scientific Committee on Health, Environmental and Emerging Risks; SD, standard deviation; SIM, selected ion monitoring; TD, thermal desorption; TDU, thermal desorption unit; VOC, volatile organic compound; VVOC, very volatile organic compound

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## 2.6. Additional results: Use of a microchamber to study the influence of the material properties on the emissions and to assess the inhalation exposure to VOCs from plopper toys.

Besides the projects presented in those four publications, other sets of experiments were carried out during the course of this work. The results of two of them are displayed in this chapter because they describe the application of the microchamber emission measurements in the study of the material emission properties and for exposure assessment.

### 2.6.1. Study of the influence of material properties on VOC emissions

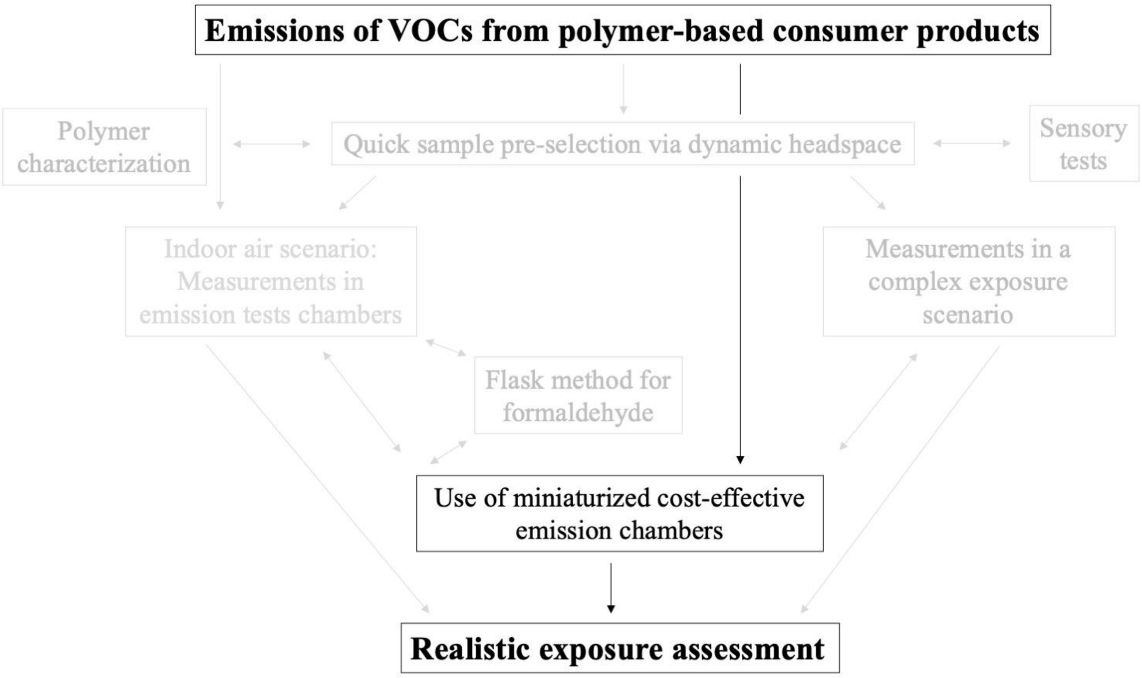

***Figure 16**: Overview of this work, focus on additional microchambers experiments 2.6.1 .*

*Introduction*

The microchambers provide area-specific emission rates comparable to the bigger emission chambers. This was shown in Chapter 2.3 with a polyurethane reference material spiked with 14 VOCs. The polyurethane reference plates used for the comparison studies (Chapter 2.1 and 2.3) were purchased in 2014 and had already been consumed for most of them. To perform further experiments, new plates were purchased in 2017. The goal of this project was to study the influence of the material properties on the emission properties. The influence of the material hardness (Shore A 35 and A 70) and the spiked VOC concentration (0.01 mg/g, 0.1 mg/g and 1 mg/g) were investigated. As the plate manufacturer had modified its synthesis protocol since 2014, it was also possible to study the influence of this change. Such results are important to better understand the material emission properties and could be applied to real samples to predict emission behaviors.

### *Methods*

After the emission test chamber comparison studies (see Chapter 2.1 and 2.3), new standard plasticized polyurethane reference material plates spiked again with the same 14 VOCs were purchased from Polymaterials AG. The plates had DIN A4 dimensions (21.0 cm × 29.7 cm) with a thickness of 6 ± 0.2 mm, a hardness of shore A 35 or A 70 and a concentration of spiked analytes of either 0.01, 0.1 or 1 mg/g (C1, C2 or C3; see **Table 5**). The hardness is measured via the depth of an indentation in the material with a durometer [79]. In comparison to Chapter 2.1 and 2.3, all the analytes were spiked at this target concentration (i.e., the xylene isomers were considered individually and not as a single substance). Pieces with a diameter of 10 mm were cut from the plate and placed in 44 mL microchambers from Markes International Ltd (Pontyclun, U.K.). The flows in the microchambers varied from 22.6 to 26.7 mL/min. Other experimental parameters are detailed in the publication in Chapter 2.3.

***Table 5:*** *Sample properties.*

| Sample | VOC conc. (mg/g) | Shore (Hardness) | Synthesis protocol |
|---|---|---|---|
| **1** | 1 (C3) | A 70 | A (old) |
| **2** | 1 (C3) | A 70 | B (new) |
| **3** | 0.1 (C2) | A 70 | B |
| **4** | 0.01 (C1) | A 70 | B |
| **5** | 0.1 (C2) | A 35 | B |

### *Results*

First, the influence of the spiked analyte concentrations was studied on sample 2, 3 and 4. Two plate pieces per concentration were investigated, each in one microchamber. **Figure 17** shows the emission curves of four representative analytes normalized to the lowest spiked concentration.

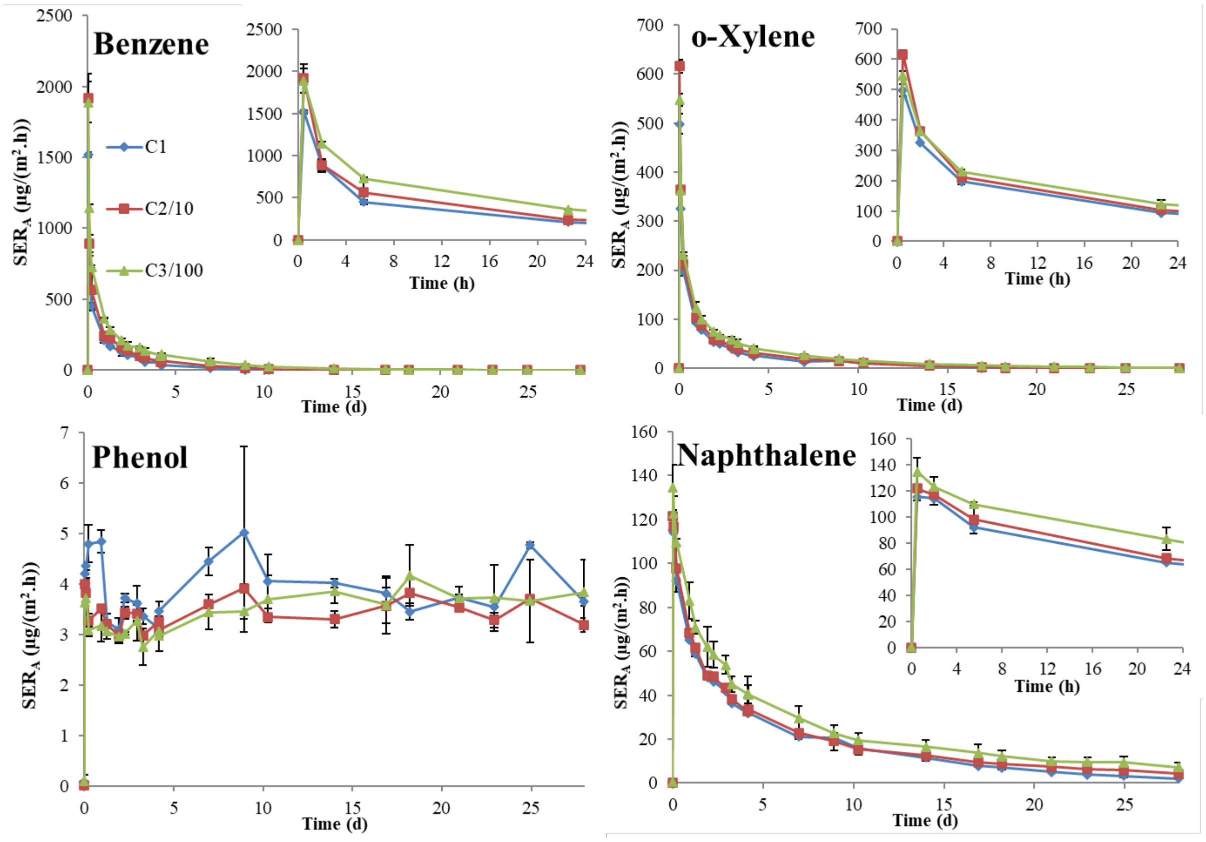

***Figure 17:*** *Emission profiles of four representative analytes from three polyurethane plates with shore 70 A spiked at different concentrations (2,3 and 4 in Table 5) normalized to the lowest one; bigger frame: 28 d profile; smaller frame: 24 h profile; SER$_A$: area-specific emission rate; repeated once (n=2).*

There are no significant differences between normalized emission rates of plates with different concentrations, even when analytes with different emission profiles are considered. The diffusion and partition behaviors seem to depend linearly on the sample concentration, at least at those levels. The distinctive emission profile of phenol is discussed in the publication in Chapter 2.3. Decreases depending on substance volatility are obtained for the other substances (see Chapter 2.3) at every concentration, except for dodecanol and formamide. These two compounds were only detected at very low levels and were not detectable from sample 4.

A second similar experiment was carried out with two plates (sample 3 and 5) with different hardnesses. Three plate pieces of each hardness were investigated, and the results are depicted in **Figure 18**.

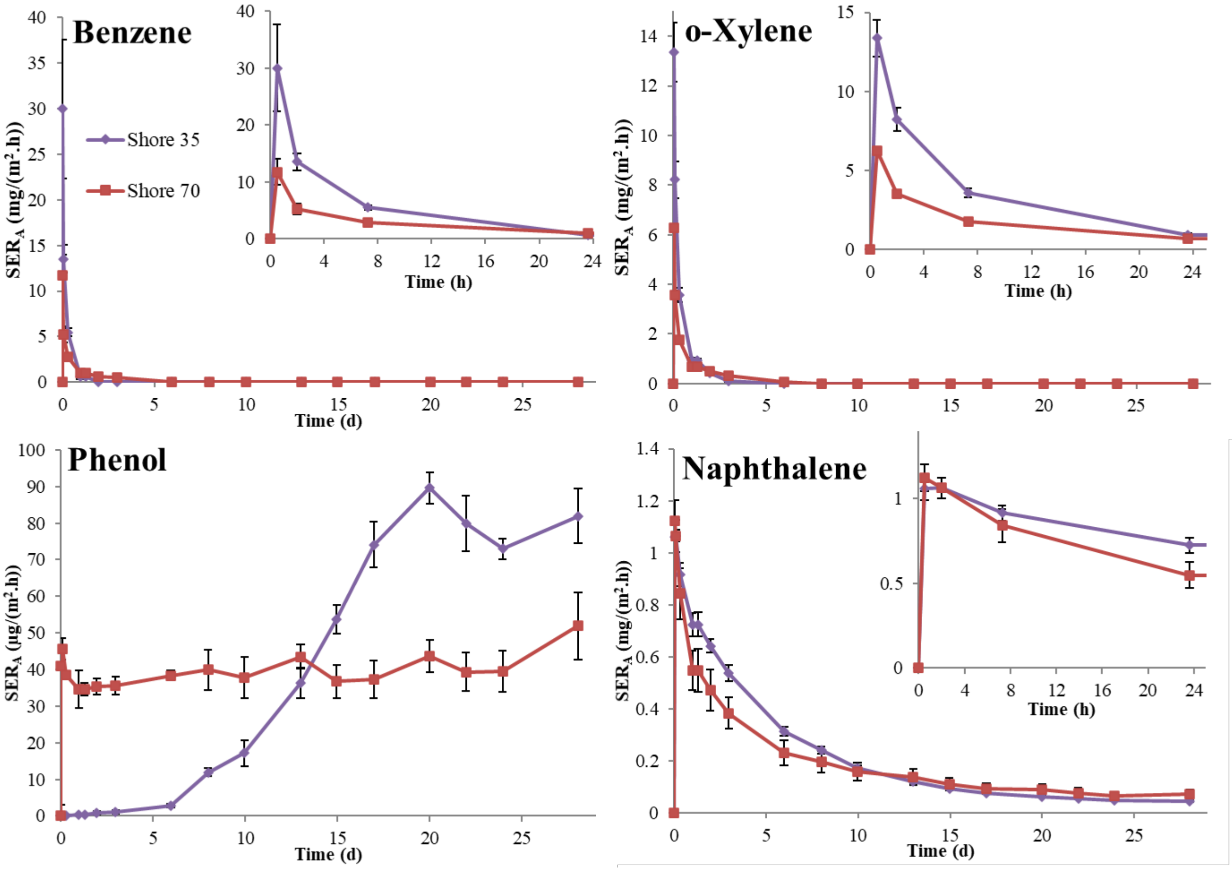

***Figure 18:*** *Emission profiles of four representative analytes from two polyurethane plates with a concentration of 0.1 mg/g and different hardnesses (3 and 5 in Table 5); bigger frame: 28 d profile; smaller frame: 24 h profile; SER$_A$: area-specific emission rate; repeated twice (n=3).*

In this case, the emission profiles depended on the plate hardness. The softer plate led to much faster emissions than the harder one, except for phenol. For the more volatile substances such as benzene ($T_B$: 80°C) or *o*-xylene ($T_B$: 144°C), the emission seems to be determined by the substance diffusion from the beginning. This is due to a facilitated partition of these low-boiling compounds. It led to much higher emission rates for the softer plate in which diffusion is faster. For less volatile substances such as naphthalene ($T_B$: 218°C), partition is probably the determining factor at the beginning as emission rates are similar between both plates in the first hours. Phenol emissions were constant over 28 days for the harder plate while they increased with time until they reached an equilibrium after 20 days for the softer plate. As the specific emission profile of phenol is probably due to a reaction of its hydroxy group with the isocyanate during the material synthesis (see 2.2), a possible explanation for these differences would be that phenol more easily, and probably fully, binds during the synthesis of the softer plate. The release of phenol is then slower than in the harder plate where less covalent bounds need to be broken before phenol emission. At least part of the phenol is freely present at the sample's surface of the harder plate as the substance was emitted from the beginning of the experiment. The total emitted amounts over 28 days were similar.

The differences between the older plates (sample 1) from the publication in 2.3 and the newer one (sample 2) were also investigated by comparing their area-specific emission rates (see **Figure 19**). Here, it was not possible to compare the emissions of the xylene isomers as they were spiked at different concentrations in both samples.

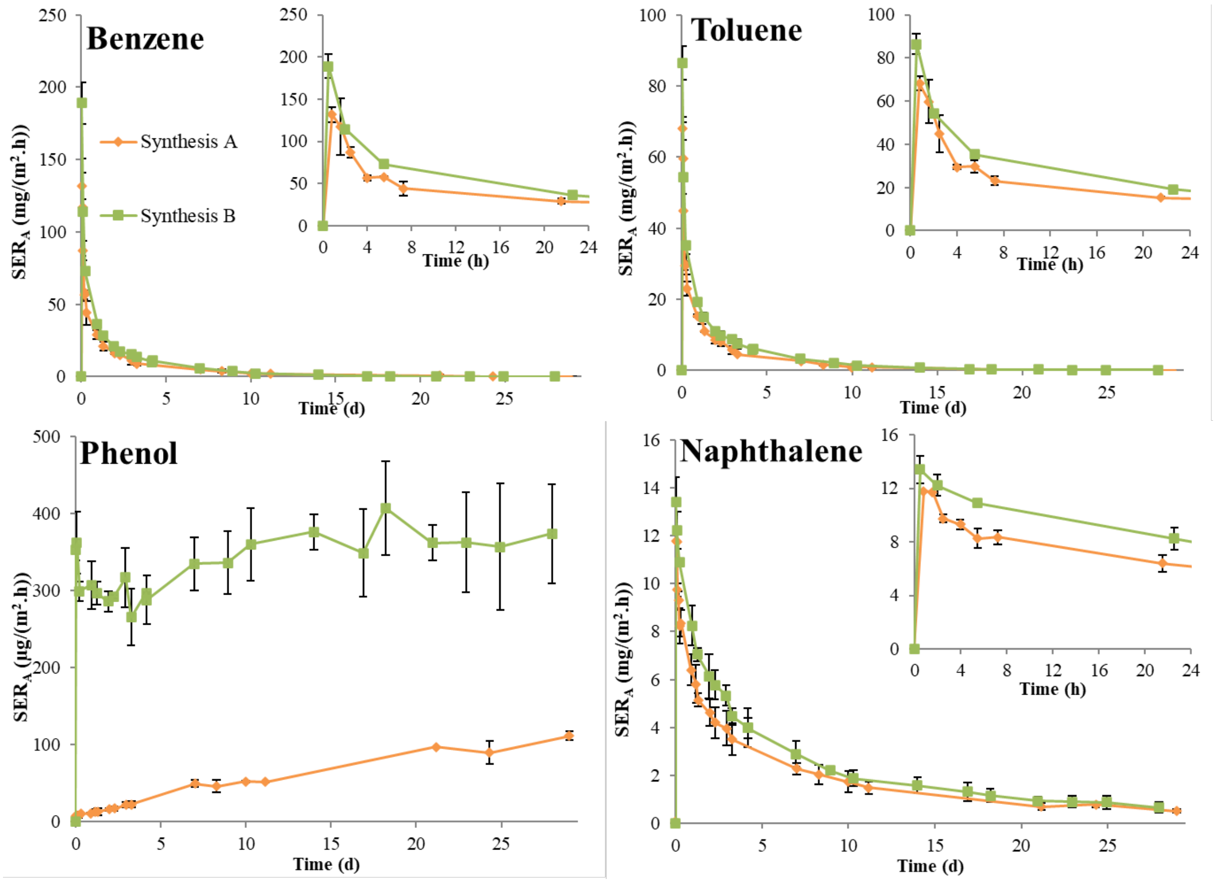

***Figure 19:*** *Emission profiles of four representative analytes from two polyurethane plates with a concentration of 1 mg/g, a shore A 70 and synthesized with different protocols (1 and 2 in Table 5); bigger frame: 28 d profile; smaller frame: 24 h profile;* $SER_A$*: area-specific emission rates; repeated once (n=2, except for the first two air samples of naphthalene with synthesis A).*

For most analytes (here benzene, toluene and naphthalene), the emission profiles obtained with synthesis A and synthesis B are very similar. The emission rates for the older samples are slightly lower. This is probably due to evaporation or degradation during sample storage, even if they were kept refrigerated over years or during the plate manufacturing. For phenol, the emission profiles are very different from one plate to the other. The new plate depicted a constant phenol emission profile with much higher emission rates than the older sample. The different protocols probably lead to different linkage products during the reaction between phenol and the isocyanate during the material synthesis. For example, it could be that different isocyanates were used in both syntheses, leading to differences in phenol release. However, no detailed information was provided about the synthesis.

### *Conclusion and outlook*

These experiments showed that the emissions were proportional to the spiked concentrations for the studied levels and thus that the VOC concentration in the sample had a low influence on the emission profile. On the contrary, a high influence of the plate hardness on the emission profiles could be observed. Softer samples seem to emit the more volatile VOCs faster. It supports the observation made in 2.2 where softer polymers such as PVC emitted higher VOC amounts than harder polymers such as polydimethylsiloxane. This is not only due to the polymer structure but also to the facilitated diffusion in the material. This is a crucial information for real sample exposure assessments as softer plastics used in toys would tend to emit higher acute concentrations. It was also observed that differences in synthesis protocols can also lead to variations in substance emissions. Indeed, certain VOCs can bind to the material structure and result in long-term emissions (see 2.4 for formaldehyde). Further investigations should be carried out with multiple polymers and substances. Emitted concentrations of compounds that do not bind to the polymer structure could then probably be predicted by measuring the VOC concentration in the material (by solvent extraction) and determining the diffusion and partition coefficients [80]. It would allow a faster analysis than emission test chamber measurements. Moreover, even if very similar emission profiles had been observed between the polyurethane reference material and PVC for *o*-xylene and cyclohexanone in Chapter 2.2, it is important to note that polyurethane is a thermosetting polymer while most consumer products are made of thermoplastics: This may lead to differences in emission behaviors.

### 2.6.2. Use of a microchamber to assess the exposure from a set of plopper toys

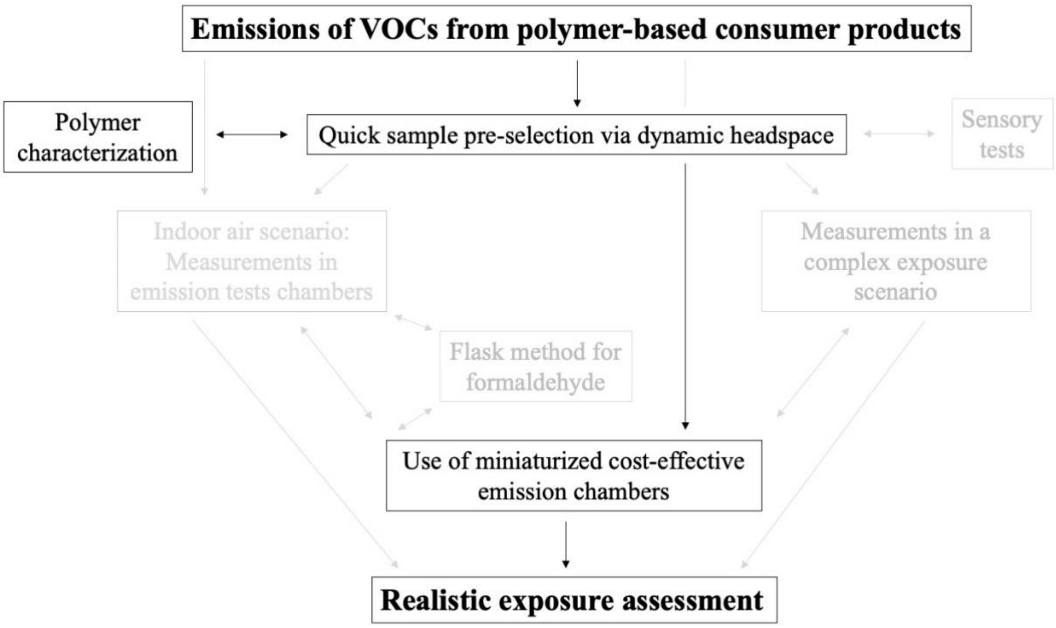

***Figure 20***: *Overview of this work, focus on additional microchamber experiments 2.6.2.*

#### *Introduction*

As it had been demonstrated that microchambers give comparable results to the bigger emission test chambers for a selection of analytes (see 2.3), they were applied to generate emission data for efficient exposure assessments. A first example was given in the last part of the publication presented in 2.3 and the test series included 11 additional samples. Plopper toys are popular 15-20 cm high plastic figurines with a foam ball in the mouth. The ball is ejected by pressing the whole figurine with hands (see **Figure 21**). These toys were selected for this experiment because one article depicted high cyclohexanone emissions during an initial exposure assessment (sample #3 studied with DHS and 203 L chamber in 2.2, here sample S1). With this new experimental setup, emission variations between different articles of one toy type were addressed. Polymer characterization also revealed that they were made of PVC. PVC is a soft polymer for which high emissions can be expected (see 2.2) and a strong odor was perceived from some of the samples.

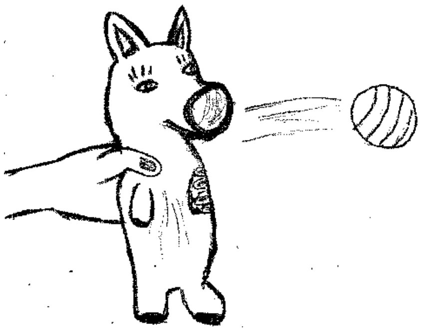

***Figure 21:*** *Illustration of a plopper toy.*

### *Methods*

Sample S1 was bought in a local shop, all the other samples were purchased online. According to the packaging, the samples were from four different manufacturers (A—D, see **Table 6**).

***Table 6:*** *Investigated plopper toy samples from four manufacturers (A—D); investigated with either splitless (SL) or split (SP) thermal desorption analysis after microchamber experiment.*

| | **S1** | **S2** | **S3** | **S4** | **S5** | **S6** | **S7** | **S8** | **S9** | **S10** | **S11** | **S12** | **S13** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Manufacturer** | A | B | B | B | C | B | C | C | B | D | D | D | D |
| **Analysis** | (in 2.2) | SL | SP | SP | SP | SP | SP | SL | SP | SL | SL | SL | SL |

Pyrolysis and DHS experiments were performed according to the protocol detailed in 2.2. Further, the following substances were also considered for calculation of the DHS score (defined in 2.2) because they were detected with high signals: *n*-decane, 2-ethylhexanol and TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate).

Round pieces with a diameter of 12 mm of each sample S2 to S13 were placed each in one 44 ml microchamber and studied over 28 days according to the protocol presented in 2.3. Microchamber flows varied from 22.1 to 26.0 mL/min. Due to significant differences in emitted cyclohexanone quantities, half of the samples were analyzed by TD-GC/MS with split 1:400 (alike for S4 already presented in 2.3.) and the other half splitless (see **Table 6**). Cyclodecane was used as internal standard, at a concentration of 50 (splitless) or 500 (split) ng on tube.

For the estimation of the emissions of the whole toy sample from the emissions of a small piece, information on the whole sample surface is needed (see 1.3.3 and 2.3). The sample surface of two samples was approximated by wrapping them in an aluminum foil and measuring the surface of the folded foil. The mean surface of 357 $m^2$ was used for exposure assessments. The indoor air concentration induced by one toy sample was then calculated according to 1.3.3, considering a room with 30 $m^3$ [35].

The mean concentration over specific time periods was obtained by integrating the emission curves during these periods. Depending on the time period (short-term or long-term exposure), the results were compared either to the DNEL values documented by the ECHA [65] or to the EU-LCI values [70]. A discussion on the criteria for the choice between toxicological reference values is provided in 2.5 and in 3.3.2. To study the combined exposure of different chemicals, an R-score [47] (or risk characterization ratio [43]) was calculated according to the following formula:

$$R = \sum_{i\ emitted\ substances} \frac{c_i}{Toxicological\ reference\ value_i} \tag{4}$$

The guideline values used are shown in **Table 4** in 1.3.2.

### *Results*

**DHS experiment**

Polymers used for all 13 samples were characterized as PVC. The results of the DHS experiments are shown in **Figure 22**. Only the compounds for which at least one sample had a DHS score above 1 are shown.

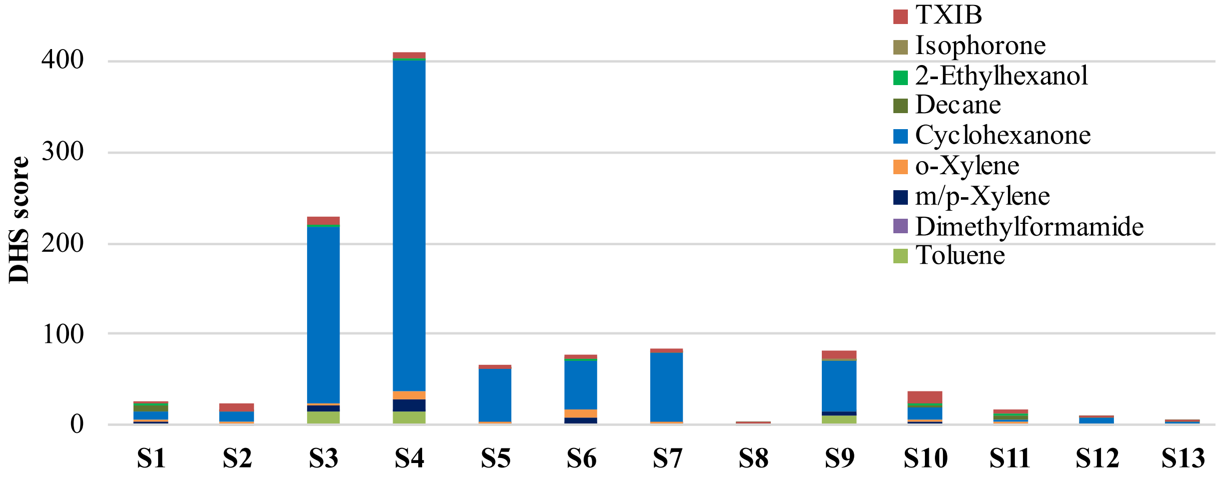

***Figure 22:*** *DHS scores of the 13 plopper toy samples, the 9 highest emitting compounds are shown.*

The highest emitting compound is clearly cyclohexanone, which was highest from S4, S3, S7, S5, S6, and S9. This experiment allowed a first pre-selection of the samples. The air samples emitted from those six samples in microchambers were analyzed in split mode to stay in the linear range of the GC/MS calibration for cyclohexanone. Despite their lower DHS sum scores, the other six samples were analyzed in splitless mode because they presented interesting peaks (e.g., TXIB) in DHS chromatograms. Most of the samples with the highest cyclohexanone DHS scores (S3, S4, S6 and S9) were from the same manufacturer (B, see **Table 6**). Other compounds such as toluene, xylenes or TXIB contributed to the total emissions. Emission profiles of toluene ($T_B$: 111°C) or xylenes ($T_B$: 138–144°C) were expected to decrease fast over measurement time (see 2.2). The plasticizer TXIB, which is used as an alternative to phthalates [81], is much less volatile ($T_B$: 380°C). For such SVOCs, a long-term exposure is expected [82] because diffusion and partition are slower for molecules with higher boiling points.

**Emission measurements**

The estimated indoor air concentrations of cyclohexanone and TXIB induced by the plopper toys over 28 days were calculated according to equation (3) (see 1.3.3) and are depicted in **Figure 23**. For each compound, the samples with the highest emitted concentrations are shown.

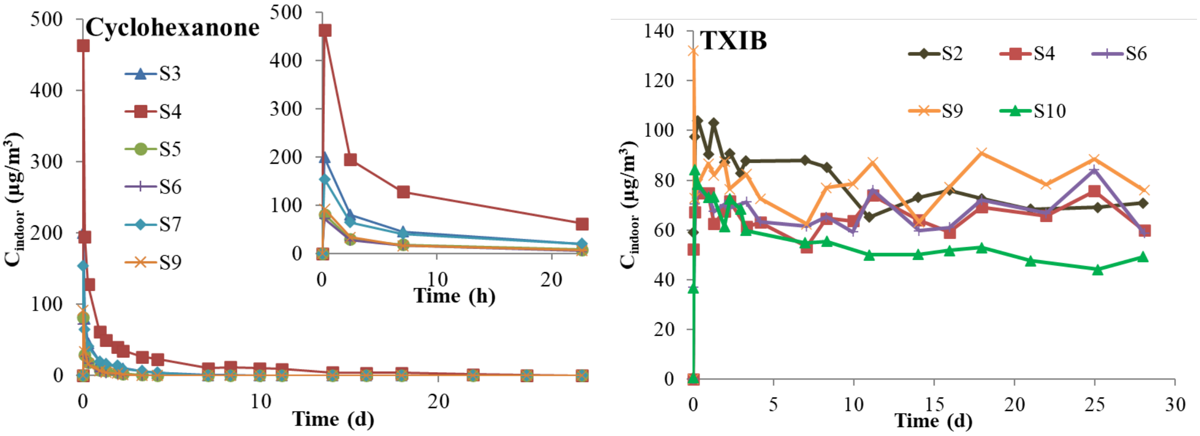

***Figure 23:** Emission profiles of cyclohexanone (left) and TXIB (right) over 28 days, estimated indoor air concentration induced from one sample.*

As expected, the two observed substances led to completely different emission profiles. Cyclohexanone concentrations decreased quickly as observed in 2.2 and 2.3 while TXIB concentrations were almost constant over 28 days. Cyclohexanone is used as PVC additive and seems to have been used in different amounts in the different products, leading to differences in emitted concentrations. On the other hand, TXIB is used as plasticizer and seems to have been added in very similar amounts in the depicted samples, leading to very similar emitted concentrations. The edges from the sample pieces were very thin but were not covered. It means that the emission profiles may be faster here than with the whole samples because VOCs partition does not only occur from the sample surface but also from the sides. Moreover, if a protective layer is applied on the toy surface to prevent or reduce VOC emissions, performing emission testing with open edges might lead to an overestimation of the emitted concentrations. For the herein studied samples, no protective layer could be optically observed. Additionally, it would be a technical challenge to correctly cover open edges from such thin and flexible samples.

**Exposure assessment**

To interpret the emitted concentrations, an exposure assessment was carried out for cyclohexanone and TXIB but also for toluene, *m*/*p*-xylene, 2-ethylhexanol and isophorone which were emitted at significant concentrations from certain samples. The results of the mean indoor air concentration induced by the four samples resulting in the highest emissions are shown in **Figure 24** for three specific time periods. It is important to consider that VOC concentrations during microchamber experiments are probably overestimated in the first hours (see Chapter 2.3). For this reason, a correction factor corresponding to the difference in the mean area-specific emission rates in the 203 L and in the microchamber during the considered time period was employed. The correction factors were determined from experiments with a polyurethane spiked reference material (see Chapter 2.3) and are presented in **Table 7**. As very similar emission profiles had been observed between the polyurethane reference material and PVC at least for *o*-xylene and cyclohexanone in Chapter 2.2, the correction factors were used for the PVC plopper samples. They were applied on the concentrations depicted in **Figure 23**, the resulting exposure assessment is shown in **Figure 24**. For 2-ethylhexanol and TXIB, no factor was considered due to missing data (the reference material in 2.3 did not contain those substances). But the study presented in 2.31.1 indicates that higher correction factors are expected for less volatile substances for which emission profiles in the 203 L emission test chamber and the microchambers were more similar, especially during the first hours.

***Table 7:** Correction factor between the mean area-specific emission rate in the 203 L chamber and in the microchamber as determined in 2.3; *: no available data.*

| | **Toluene** | ***m/p*-Xylene** | **Cyclohexanone** | **2-Ethylhexanol*** | **Isophorone** | **TXIB*** |
|---|---|---|---|---|---|---|
| **2.5 h** | 0.47 | 0.62 | 0.48 | 1 | 0.50 | 1 |
| **1 day** | 0.69 | 0.77 | 0.69 | 1 | 0.62 | 1 |
| **28 days** | 1.13 | 0.81 | 0.98 | 1 | 0.74 | 1 |

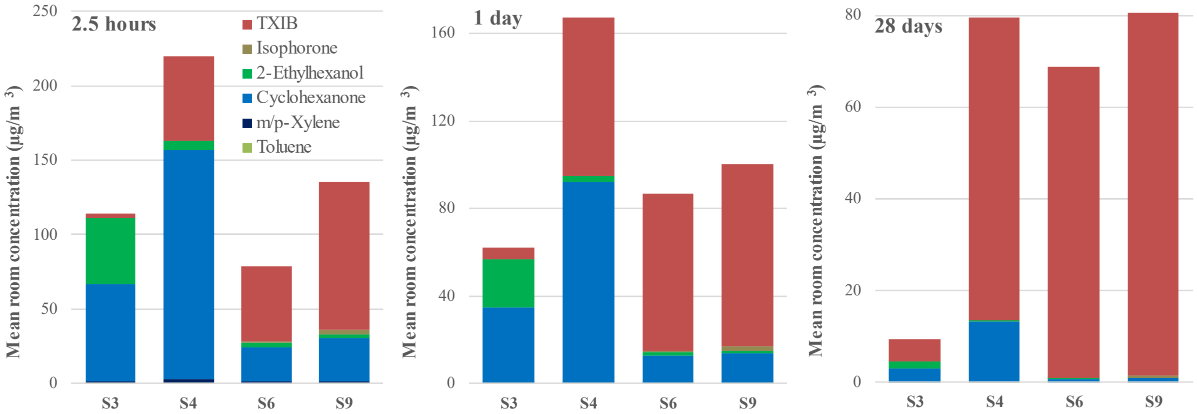

***Figure 24:** Calculated mean room concentrations induced by the four highest emitting samples for three time periods, the six highest emitting compounds are shown. The mean concentrations over a time period are determined by integration of the emission curve.*

In this work, the DNEL value was used to interpret results for short-term exposure (few hours to one day) and the EU-LCI was used for longer-term exposure, as discussed in 3.3.2. The highest cyclohexanone concentrations were emitted from sample S4. 65 such toys would be required in a 30 m$^3$ room to exceed the ECHA DNEL for this substance, if the mean concentration of the first 2.5 hours is considered. If the BfR's derived inhalation DNEL is considered (1.4 mg/m$^3$, see 2.5), the guidance value would be exceeded with only 9 plopper toys in the room. For the same time period, only 2.7 samples would be necessary to exceed the EU-LCI. However, the EU-LCI is a guideline value for long-term emissions and the cyclohexanone concentrations declined very quickly. For long-term exposure, TXIB was the predominant concerning compound. The highest TXIB concentrations were emitted from sample S9. Only 5.4 such samples would be needed to exceed the German NIK for TXIB of 450 µg/m$^3$ (equivalent of EU-LCI, non-harmonized for this compound) and 16.4 for the EU-LCI (1300 µg/m$^3$) if the mean concentration over 28 days is considered. These high TXIB concentrations could be even underestimated as SVOCs typically exhibit sink effect in emission test chambers [55, 82]. All three samples S4, S6 and S9 were from the same manufacturer (B, see **Table 6**), who seems to be using high amounts of TXIB in its products.

For the same four samples with the highest emissions, risk characterization ratios were calculated (see equation (4)) for each time period and are shown in **Table 8**.

***Table 8:*** *Risk characterization ratios of the four highest emitting samples*

| | **2.5 hours** | **1 day** | **28 days** |
|---|---|---|---|
| *Reference value* | *DNEL inhalation* | | *EU-LCI* |
| **S3** | 0.03 | 0.01 | 0.02 |
| **S4** | 0.03 | 0.03 | 0.08 |
| **S6** | 0.02 | 0.02 | 0.05 |
| **S9** | 0.03 | 0.02 | 0.06 |

All ratios were below 1, but the situation would be concerning, especially for long-term exposure, if several toys were kept in the same room (e.g., in collector homes, kindergartens or retail environments). Moreover, a child often plays close to the emission source where the substance concentrations are higher during short-term exposure, especially in poor ventilated rooms. In addition, due to the error-proneness on the sample surface determination, the possible inhomogeneity of the samples and the comparison factor between microchamber and emission test chambers, the depicted concentrations are only estimations. They only give an order of magnitude of VOC emissions from such toys.

### Conclusion

It was observed that even very similar products can lead to significantly different VOC emission profiles. However, the products from one specific manufacturer were depicting the highest VOC emissions. One plopper toy could lead to cyclohexanone room concentrations in the first 2.5 hours of up to 154 µg/m$^3$ in a 30 m$^3$ room. This is concerning if the child plays in close proximity with the toy or if several samples are stored in the same room as the ECHA short-term DNEL for the general population is 10 mg/m$^3$ and the BfR's derived DNEL for long-term exposure is 1.4 mg/m$^3$ (see 2.5). Additionally, a less volatile substance, TXIB, was emitted constantly from several samples over the 28 days. The long-term exposure is concerning for this substance as the mean room concentration over one month could be as high as 79 µg/m$^3$, while the German NIK is 450 µg/m$^3$ (EU-LCI: 1.3 mg/m$^3$). Furthermore, dermal exposure is also an important factor to be considered in order to determine the whole consumer exposure to chemicals from such products as plopper toys are held in the child's hands while playing. This study has limitations as the emitted concentrations are only estimations from microchamber experiments (correction factor, possible inhomogeneity of the sample, uncovered open edges and sink effect on the chamber walls) but it provides useful numbers for exposure assessment.

# 3. Discussion

The method comparison results and exposure data generated within this work open a perspective towards a better market surveillance of VOC emissions from polymer-based consumer products, in particular toys.

## 3.1. Towards practicable methods for market control

This work focuses on market control of single consumer products because the BfR is missioned to develop and provide practicable analytical methods for market surveillance of consumer products with respect to VOCs. Even if we observed that an intense and unpleasant product odor could be an indication for VOC contamination (see Chapter 2.5), an identification and a quantitative assessment of the emissions are necessary to provide a supported decision on the product safety. The conventional emission test chambers were considered as the gold standard for exposure assessment during the course of this work as they apply adapted environmental parameters (temperature, relative humidity and air change rate) to simulate an indoor environment. The results generated here suggest the application of the following methods for market control of VOC emissions from polymer-based consumer products:

- Dynamic headspace: DHS-GC/MS is adapted for a quick sample pre-selection of polymer-based products. However, the substances detected are only the one sampled on the thermal desorption tube (usually filled with Tenax® TA). Thus, it is not directly usable to study carbonyl emissions for which a derivatization step is necessary. The air exchange around the sample allows an approximation of the VOC emissions, even with a single quick analysis. If no VOCs are detected during a first screening of the sample, it is unnecessary to further investigate the product as it is most probably safe. The only example of increasing VOC emissions overtime observed in this work was for phenol from the PU reference material (see Chapter 2.2, 2.3 and 2.6.1). Even if TXIB was released with constant emissions in Chapter 2.6.2, other SVOCs could only be released after a lapse of time and would thus not be detected in DHS analysis at ambient temperature. Limits on parameters such as the analyte-specific and sum DHS scores defined in this work (see Chapter 2.5) should be introduced to decide if the samples need to be further investigated. Future studies should investigate the correlation between conventional emission test chambers and DHS with continuous and controlled inlet flow (see Chapter 2.1). A possible use of this technique for quick and reliable exposure assessment over short time periods could then be feasible. Acquiring a DHS station is practicable for OCLs already owning the adequate analytical basic device.

- Miniaturized emission test chambers: Emissions determined with microchambers show a good correlation with conventional emission test chambers, both for VOCs from a polymeric reference material (Chapter 2.3) and for formaldehyde from wooden products (Chapter 2.4). Correction factors sometimes need to be applied and depend on the substance properties (see Chapter 2.6.2). But the VOC exposure assessment based on data obtained with microchambers seems to be reliable and in the correct order of magnitude. Further investigations should focus on the detailed determination of the correlation factors between miniaturized and conventional emission test chambers for different substances and materials. Moreover, a concept could be developed to predict such factors based on the substance and material properties (e.g., volatility, polarity and hardness). This is of great importance in particular for short-term exposure (first hours) for which the flow steady state is more quickly reached in microchambers with higher air change rates. Moreover, the studies presented in Chapter 2.3 and Chapter 2.4 focused on keeping the area-specific air flow rate as constant as possible between differently sized chambers. It would be useful to investigate the influence of variations of this parameter on the chamber correlations in detail. This device is probably useful for OCLs as it can be easily placed on a conventional laboratory bench with nitrogen or clean air supply. Indeed, it can be implemented for all types of emitted substances (VVOCs, VOCs, SVOCs, carbonyls), provided that the sampling protocol is adapted. For formaldehyde emissions from wooden toys, this would be an alternative to partly comply with the new amendment of the Toy Safety Directive without buying or constructing a conventional emission test chamber [24] (see Chapter 2.4). Moreover, an important parameter to be defined in a reliable standardized method is the sampling time point, this depends on the exposure scenario (peak exposure, short-term, long-term). While VVOC and VOC emissions would be determined after a few minutes or hours, SVOCs exposure should be acquired after several days or at elevated temperature (see Chapter 3.2.2 and 2.6.2). Finally, microchambers are limited to small (chamber volume: 44 or 114 mL) or homogeneous samples.

- Conventional emission test chambers: For bigger samples that do not allow homogeneous subsampling, the use of conventional and bigger emission test chambers seems inevitable for a reliable exposure assessment. Conventional chamber testing is however probably unsuitable for most OCLs as they are expensive, require additional space due to their large volume and allow a very limited sample throughput. Such rare analysis could be performed by other contract laboratories specialized in emission testing of construction products. Additionally, it is more economical to build own glass or stainless steel emission test chambers, for example from 24 L desiccator (see Chapter 2.3 and 2.4).

- Adapted assessment setup: As demonstrated in Chapter 2.5, the use of emission test chambers is not always adequate for the exposure scenario. For complex scenarios such as the wearing of costume masks, an adapted exposure assessment is needed but the DHS and microchamber methods may be used for a first screening of the emissions. These setups should be developed on a case-by-case basis.

Based on the experimental results generated in the present work, the following strategy is suggested for cost-effective and practical market surveillance (see **Figure 25**): DHS-GC/MS may be used for sample pre-selection, except for carbonyl emissions from wooden toys. Considering an indoor air scenario (sample emitting in a whole standard room), samples with high DHS scores can then be studied in microchambers if they are small or homogeneous. For carbonyl emissions, the first sample pre-selection would be preferably directly performed with microchambers as the use of DHS sampling is not adapted to commercial cartridges for formaldehyde sampling [51] and the inlet gas is not humidified. The determination of correction factors depending on the substance and the material properties would be needed for microchamber studies, especially if the exposure in the first hours is considered. The use of bigger emission test chambers is necessary for big inhomogeneous sample. If more complex scenarios are envisaged, adapted setups should be developed for a reliable exposure assessment.

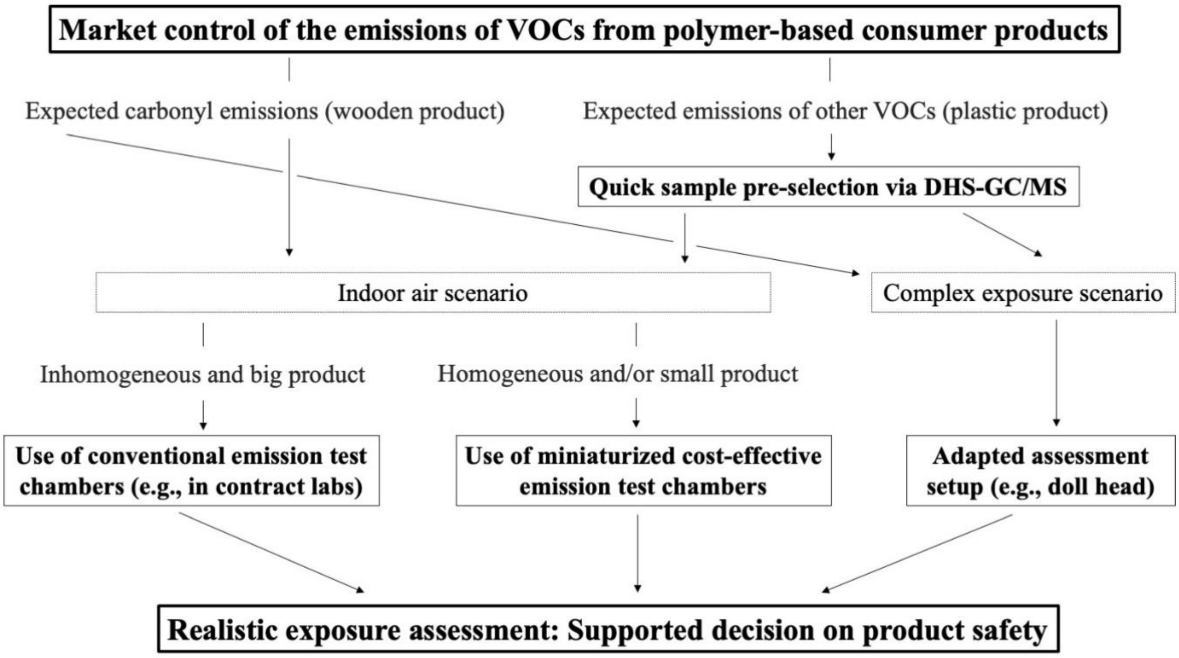

***Figure 25****: Strategy suggested for market control of VOCs emitted from polymer-based consumer products based on the experimental results generated in this work, DHS: dynamic headspace.*

The implementation of these methods would necessitate the acquisition of new devices for OCLs. Provided that they already possess the analytical devices (GC/MS, HLPC-UV), limited additional hardware such as a DHS unit, a microchamber (preferably with volume 114 mL to study bigger samples), a thermal desorption unit as well as sorbent tubes and cartridges is needed to reproduce the methods developed in this work. The biggest challenge probably resides in the choice of the analysis and sampling parameters as well as in the establishment of a standardized procedure to interpret these emission results: This will be discussed in Chapter 3.4.

Other analytical methods could be used for the assessment of VOC emissions from polymer-based consumer products. However, they may not be practicable for market surveillance:

- Real-time analysis with instruments such as PTR-MS (proton-transfer-reaction MS) or SIFT-MS (selected-ion flow-tube MS) could be applied to better understand short-term and peak exposures for which sorbent sampling with sampling times over a few minutes is not adapted. Such instruments were used in the past to determine VOC emission rates of classroom surfaces and other materials and seems complementary to the TD-GC/MS method [83, 84]. However, the implementation of these devices in routine laboratories and OCLs seems difficult in the medium term as it would necessitate the acquirement of new analytical devices and knowledge. Moreover, it is less adapted to multiple sample locations (e.g., emission test chambers in different rooms) as the device is more difficult to transport than sampling tubes.

- Another economical approach would be to keep the current analysis methods with solvent sample extraction and to predict material emissions based on models. This would necessitate an extensive investigation of the VOC emissions (i.e., VOC diffusion and partition coefficients [80]) depending on the substance and material properties such as boiling point, polarity, polymer type and hardness with reference materials (similar to Chapter 2.6.1 but much more comprehensive, with multiple materials). However, extraction is a destructive method and this approach would still at least necessitate the additional identification of the polymer type and measurement of the sample's hardness for each product.

## 3.2. Characterization of further products and emitted chemicals

Even if this thesis includes exposure data for various substances from different samples, aspects such as emissions from recycled or fragranced products, as well as VVOCs or mineral oil hydrocarbon emissions were not addressed experimentally here. They are useful to get a better overview on the health risks generated through emissions from consumer products and to provide practicable methods for their surveillance. While this work focused on polymer-based consumer products and VOCs, the range of products and emitted chemicals that are relevant for consumer protection is broader and is discussed in the present part.

### 3.2.1. Further VOC sources

In this thesis, the main products emitting VOCs were made of PVC (emitting cyclohexanone, xylenes and TXIB) or wood (emitting formaldehyde). Further consumer articles emitting VOCs should be considered to better understand the influence of consumer products on our indoor environments and the related inhalation exposures.

An issue that emerged recently and was not addressed in the present work concerns the emissions from recycled thermoplastics. Indeed, the mixture of polymers with different original sources operated during recycling prevents the tracing of the chemicals from production to consumer use. Recent studies focused on the characterization of odors and the quantification of NIAS including VOCs in recycled products. The overall odor intensity did not improve during the recycling process of plastic film fractions [85]. Additionally, several non-intentionally added VOCs and SVOCs such as acetophenone or diethyl phthalate were detected in recycled polyethylenes [86]. Contamination may cause problems if polymers are planned to be reused in products with equal or higher quality. Indeed, polymers which were developed for a specific regulated application cannot be recycled for applications with a stricter chemical regulation. Methods such as washing, degassing or the use of adsorbents are being developed to tackle the problem of VOC contamination in recycled plastics [87] because contamination restricts the use of recycled products. The identification of undesirable substances is necessary to develop targeted decontamination strategies and increase the share of recycled products on the market. Consumer products made of recycled polymers are controlled like non-recycled products with respect to chemical safety aspects. Their contamination range may be broader due to their multiple origins and the health risks upon use may be higher due to the migration of hazardous substances from the core of the material to its surface.

Additionally, the most investigated VOC emissions from consumer products relate to fragranced products, for example incense, candles, air fresheners and room fragrances as well as cleaning or cosmetic products. These articles are often marketed to be beneficial for indoor air quality. Aromatherapy can be efficient [88] but the addition of compounds also often degrades the air quality. The characterization of the emissions of regulated allergenic fragrances from scented toys was carried out at the BfR between 2008 and 2011 [19]. In the frame of the European EPHECT project (Emissions, Exposure Patterns and Health Effects of Consumer Products in the EU), the use of cleaning agents, air fresheners, personal care products and other fragranced consumer products was investigated in emission test chambers [89]. A health risk assessment was subsequently carried out and revealed that indoor air pollutant concentrations were below the critical exposure levels but could still be considerable, especially for short-term exposure [90]. The study of room fragrances in emission test chambers also revealed high concentrations of solvents such as ethanol or 2-propanol from both passive and active diffusers [91]. 18 of the 26 allergenic substances banned in toys [17] were identified in scented products such as candles or printings [92]. Furthermore, no significant differences can be generally observed between consumer products marketed as “green” (i.e., eco-friendly) and the other products [93]. Besides being a primary source of indoor air pollutants, fragranced consumer products can also contribute to outdoor air pollution [74]. Terpenes such as limonene (the most prevalent fragrance) can induce more toxic secondary chemical emissions after reaction with ozone or nitrogen oxides [94]. In the recent years, extensive analytical and international epidemiological studies of the emissions from fragranced products and their effect on human health were carried out by Steinemann and colleagues. A review summarizing these achievements was published in 2020 [95]. Disabling health effects, loss of workdays and job as well as loss of societal access were found to be associated with the use of fragranced products. Asthmatic and autistic individuals were characterized as sensitive populations. A higher prevalence of the health effects was observed in these groups. Substances are often identified in the emissions although they are not documented on the label. Indeed, fragrances are not required to be fully reported on the product (fewer than 4% of the detected VOCs were actually disclosed in Steinemann *et al.*’s studies). In this field, the exposure assessment knowledge on VOC emissions seems deeper than for toys, but no standardized methods exist for exposure assessment from such products. It would probably be useful to develop similar or combined standardized methods and regulations for VOC emissions from all consumer product types.

### 3.2.2. Analysis of further chemicals

The present work investigated the emissions of various substances such as cyclohexanone, xylenes, formaldehyde and TXIB. However, the analytical chemist should always be aware that we only find what we are looking for. It is not possible to detect the whole range of airborne chemicals with one analytical technique. This work focused on VOCs using mostly the ISO 16000-9, ISO 16000-6 and ISO 16000-3 procedures [20, 21, 45]. The last two methods are typically limited to the study of organic compounds in a volatility range between *n*-hexane ($T_B$: 69°C) and *n*-hexadecane ($T_B$: 287°C) and are also usable for the analysis of SVOCs (up to $C_{30}$, *n*-triacontane with $T_B$: 450°C).

The GC analysis was first limited in the lower boiling range (typically $T_B < 69°C$). VVOCs are substances such as 1,3-butadiene or acrolein that elute before *n*-hexane on an unpolar GC column with the ISO 16000-6 analysis method [96]. Dichloromethane was for example emitted from squishy toys [43]. However, they will typically not be detected when using a solvent such as methanol or ethyl acetate due to masking of the solvent and pre-solvent eluting ranges. Moreover, the Tenax® TA sorbents are often not adapted to this compound range [97]. Research is being carried out to find a suitable analysis method for this compound group [98, 99]. Additionally, these highly volatile compounds could be responsible for the odor, which is thus not necessarily only explained via VOC analyses (see Chapter 2.5).

SVOCs were detected in emissions from PVC plopper toys in this work (Chapter 2.6.2). Also, bis(2-ethylhexyl) phthalate (DEHP) was detected in the pyrolysis-GC/MS chromatograms of the two high-emitting costume masks from Chapter 2.5. SVOCs probably represent the most worrying emissions from such products as they result in long-term emissions. Several studies focused in the recent years on the understanding of SVOCs behavior in indoor air. Due to their lower volatility, SVOCs typically adsorb to airborne particles [100] and distribute on indoor air surfaces such as dust, carpets [101] and clothes [102]. Thus, as mentioned in Chapter 2.6.2, the ISO 16000-9 approach (i.e., emission test chamber measurement at ambient temperature) is not adapted for efficient SVOC exposure assessments. ISO 8124-6 provides a method for the quantification of certain phthalates in toys via extraction in dichloromethane and analysis with GC/MS [103]: Such approaches do not give any indication on emission dynamics (see Chapter 1.2.1). ISO 16000-25 proposes a method to determine the emissions of SVOCs from building products in microchambers with a two-step approach allowing the analysis of both primary and secondary (adsorbed on chamber walls) emissions [55]. Braish applied this method to phthalates and organophosphorus flame retardants in her doctoral thesis [82] to determine the gas-phase concentration of SVOCs in equilibrium with the material surface. Knowledge of this concentration allows the prediction of SVOC emissions and their interaction with airborne particles [104]. In the recent years, attention has been raised to the development of a modular mechanistic framework to predict human exposure to SVOCs [105]. Indeed, toxicological data are also currently missing for most SVOCs. Studies on their bioaccessibility and bioavailability should be carried out to better assess the potential health risks [106]. Kassotis *et al.* even argued for a hazard-based approach, independent of exposure data for endocrine disruptors such as DEHP that are already banned or restricted in toys and products for children in different countries [107].

Moreover, mineral oil hydrocarbons (MOHs) were detected in the emissions of several consumer product samples (Chapter 2.5, also from products in Chapter 2.2). The carcinogenicity of the aromatic fraction of this compound group is under discussion [108]. But they could not be detected individually with the methods used in the frame of this work. A hump comprising a large variety of MOHs was often identified. To separate MOHs, two-dimensional chromatography is necessary. The saturated and aromatic mineral oil fractions can be separated and detected via online coupling of HPLC and GC [109]. As only liquid fractions are analyzed in the first HPLC step, this approach would necessitate the solvent dissolution (e.g., in hexane) of adsorbents containing emission samples. However, two-dimensional GC could be directly applied on TD tubes to elucidate the MOH hump if a thermal desorption unit is used as injector.

Other typical inorganic indoor air contaminants are particles or radon. Radon is not expected to be emitted from polymer-based consumer products as it usually emanates from the soil. However, lead was characterized as a potential toxic element in plastic toys [110]. Particles could also eventually be emitted from specific activities such as 3D printing, partly considered as children's toys [111].

## 3.3. Exposure assessment strategies

### 3.3.1. Exposure scenarios

Besides the influence of a single product on indoor air concentrations and the wearing of costume masks investigated in this thesis, other exposure scenarios may be considered. They include the active use of consumer product via for example heating (electric heating bags [44]), squeezing (squishy toys [43]) or spraying (perfumes [89]) which is usually triggered at the beginning of the emission chamber testing. Lower air change rates than 0.5 /h may also occur in modern well-insulated buildings, for example in children homes in Sweden [112]. This should be taken into account in worst-case scenarios. As mentioned in Chapter 2.2, situations with children playing in close proximity with a toy in a poor ventilated room induce higher exposure concentrations. Masuck introduced a breathing zone of 1 m$^3$ with an air change rate of 0.5 /h with the rest of the room to simulate this scenario [39]. It is only an approximation as real indoor environments are probably better ventilated, but this allows the consideration of a worst-case scenario. Also, scenarios with an emission source presenting a large surface area in the room would be of high interest. For example, playmats may emit SVOC emissions like construction products such as linoleum flooring [113]. For this reason, chamber loading should be adapted to each product type, like for construction materials in the new standard EN 16516 [35].

Besides the exposure of the sensitive population of children, high VOC concentrations emitted from polymer-based consumer products probably reach workers in manufacturing or retail environments. Indeed, they are constantly exposed to freshly manufactured goods. Different studies examined the exposure of workers in shopping and storage area, the latest one investigated 10 retail stores in France [114]. Concerns were expressed about cyclohexanone exposure in such exposure scenarios in Chapter 2.6.2, but cyclohexanone was only detected at low concentrations in the French study (10-50 µg/m$^3$ in toluene equivalents) while formaldehyde and toluene concentrations reached 53 µg/m$^3$ and 252 µg/m$^3$, respectively. However, this is still below occupational guideline values. In 2.6.2, the highest TXIB concentration released from one plopper toy in a 30 m$^3$ room was 76 µg/m . 230 products would be needed to exceed the DNEL for workers (17.62 mg/m [65]), this seems plausible in a retail environment.

Unlike in emission test chambers, VOCs can engender secondary emissions in real environments, mainly when reacting with reactive gases such as ozone [46]. This could have a negative impact on indoor air contamination. Therefore, assessment of single products under standard environmental conditions may help to identify sources and reduce emissions but does not provide comprehensive exposure results.

Indoor VOC concentrations may be reduced via ventilation, photocatalysis [115] or even sorption on indoor surfaces [83]. Treating final polymer-based product VOC contaminations via applying elevated temperatures for a short time would certainly be useful. For baking tins made of silicone, tempering the product at a temperature of 200°C over 4 hours allows the removal of volatile components before use [116]. However, it may also impair product quality for samples like toys which are not engineered to be heated. Moreover, it would not be enough to prevent SVOC contamination. Indeed, harmful additives which are usually linked with necessary product properties (e.g., softness) are often SVOCs and should not be eliminated but replaced by less toxic alternatives. On the other hand, VOCs are mainly unnecessary NIAS (e.g., solvents or degradation products) and their contamination can be reduced by ventilating the product outside for a few days.

### 3.3.2. Exposure interpretation

Once exposure results have been generated with an appropriate exposure scenario, emitted concentrations should be interpreted. In this work, toxicologically based inhalation guideline values including AIR, LCI, NIK, WHO guideline values and DNEL values were used depending on the exposure scenario and the data availability (see **Table 4** in Chapter 1.3.2) to interpret experimental results. As mentioned in Chapter 2.5, SCHEER (Scientific Committee on Health, Environmental and Emerging Risk) recently worked on an opinion on toxicological reference values for VOCs emitted from toys which was published since our last publications [117]. Both EU-LCI and DNEL values were considered, SCHEER does not recommend applying the EU-LCI values as toxicological reference values for inhalation exposure to chemicals from toys. However, their opinion is based on studies considering exposures of up to three days. SCHEER argued that EU-LCI are not to be used as indoor air guideline values because they are intended to assess emissions from construction products during test chamber experiments according to EN 16516. However, EN 16516 specifies a chamber loading factor which is close to real conditions (model room). Therefore, it should not be a contradiction to use EU-LCI for long-term exposure (i.e., 28 days) from toys in a model room. No WHO or AIR indoor air guideline values were mentioned. According to the BfR and SCHEER, toys should only account for 10% of the total emissions [117, 118]. Some limit values already exist for the emissions of VOCs from toys. The Toy Safety Directive specifies emission limits for certain compounds (e.g., formaldehyde [24]) while EN 71-9 also stipulates inhalation limits for certain substances [28]. However, clear or feasible experimental methods to analyze these emissions are missing in both documents. Of note, Masuck interpreted her results by calculating the amount of inhaled fragrances per kg body weight and day [39], which can then be compared with the tolerable daily intake (TDI) if such a value exists.

Additionally, co-exposures from different chemical species may increase health risks. The exposure assessments carried out in this work mainly focused on single compounds while the use of a risk characterization ratio (or R-score) on multiple compounds was introduced in Chapter 2.6.2. Indeed, even if most compound concentrations are below toxicological guideline values, the combination of them might be harmful. This approach is rather conservative as it does not integrate the fact that different compounds and exposure routes only result in combined exposures if they trigger the same toxicological endpoint. In vivo studies sometimes take into account combined exposures (e.g., for benzene, toluene, ethylbenzene and xylenes [119]) but this is not a feasible approach to consider the broad range of possible exposures. A harmonized and consistent approach is currently lacking for mixture risk assessments, but several EU research projects are aiming at filling this knowledge gap [120].

To provide a comprehensive exposure assessment from a single product, the three routes of exposure should be investigated. Dermal chemical exposure from polymer-based consumer products can be assessed with a Franz diffusion cell and is well approximated using an aqueous ethanol simulant for polycyclic aromatic hydrocarbons [8]. For VOCs, a gas-tight diffusion cell would be needed to prevent losses. Additionally, certain phthalates can also be adsorbed via indirect dermal contact with contaminated air [121], dermal uptake is even accelerated by wearing clothes [122]. The oral route of exposure is also to be considered when toys may be ingested or mouthed by children. In this case, a saliva simulant can be used to assess the exposure [49] but it does not take mechanical stress into account.

Combined exposure including multiple sources, chemicals and exposure routes can be derived with mathematical models [123] which however comprise many approximations. These approaches allow the prioritization of chemicals: Aurisano *et al.* identified 126 chemicals of concerns in plastic toys based on estimates, including VOCs such as ethylbenzene [124]. Such models also help prioritizing certain hazardous products and developing databases which are useful for regulators, retailers, manufacturers and the public [125].

## 3.4. Regulating VOC emissions from polymer-based consumer products in practice

Even if the comprehension of the different analytical results, the exposure levels and their interpretation has increased during this work, the way towards the regulation of VOC emissions from polymer-based consumer products is still far. Experimental protocols and data interpretation strategies should be clearly defined and standardized.

On a European level, the Toy Safety Directive [17] and the EN 71-9 to EN 71-11 [28-30] standards should be updated to include a clear experimental protocol for VOC emission measurements and the interpretation of these results. Based on the results generated in this thesis, it is suggested that this procedure could be based on microchamber measurements to provide reliable results while allowing a high sample throughput, an optimized sample size-to-chamber volume ratio and a cost-effective analysis. The following parameters should be defined:

- Measurement parameters: Similar to the ISO 16000-9 standard [21], the temperature and relative humidity would probably be like in a typical indoor environment 23°C and 50%. For microchamber experiments, higher loading factors and air change rates should however be used and defined (see Chapter 2.3 and 2.4). Open edges of toy pieces would be completely covered with an emission-free aluminum tape.
- Sampling time point and analytical strategy: Building on the AgBB scheme for construction products (testing after three and 28 days [47]), sampling time points should be defined. Of note, short-term exposure is expected for consumer products that may be used directly after unpacking while a house with new construction materials is not occupied in the first hours or days. Analytical procedures already exist for the target substances (ISO 16000-3 for carbonyls [45] and ISO 16000-6 for other VOCs and SVOCs [20]).
- Output value: For building materials, air concentrations generated with a defined loading factor are interpreted. This is more difficult for toys which have various shapes. A loading factor range in which the microchamber is usable without influencing the air flow rate should be defined but the output result would probably be either an emission rate (e.g., $SER_A$) or the calculated indoor air concentration engendered by a single product.

A global method harmonization with an update of the ISO 8124 standards for toy safety could also be implemented.

Combining the knowledge about exposure and toxicology is the basis of providing risk assessment and drawing conclusions about the health risks and the protective measures that should be taken to ensure safe use. While the standard methods may be international, the legislation has to be defined in every country or on a European level. The Toy Safety Directive should include a list of different VOCs and SVOCs and their corresponding limit values based on a defined experimental protocol. These limits should rely on established and well-derived guideline values to reliably interpret emission results (see Chapter 3.3.2). Specific assessment factors derived on a case-by-case basis as suggested by SCHEER are not feasible for routine market surveillance [117]. Even if it does not take the different toxicological endpoints into account, the calculation of a risk characterization ratio or R-score (see Chapter 2.6.2) seems the most practicable way to consider combined exposures in market surveillance. A limit on the total VOC concentration (TVOC) defined by AgBB [47] could also be implemented.

Moreover, regulations should be harmonized with other VOC-emitting consumer products such as fragranced products (see Chapter 3.2.1). As mentioned by Goldsmith *et al.* [125], a consumer product database allows laboratories to rely on each other’s data to efficiently perform their own risk assessments and may raise awareness and public information. On a European level, future concerning results on emissions of VOCs from consumer products should be further documented on the Safety Gate platform [31].

# 4. Conclusion and outlook

Polymer-based products are ubiquitous in our modern societies. The possible health-threatening exposures are multiple due to the diversity of contaminants and additives and the different exposure pathways. Legislations and risk assessment strategies are often missing for the inhalation exposure from such products. This work focuses on volatile organic compounds (VOCs) and the inhalation exposure route. According to the objectives established in Chapter 1.41.1, the results of this work include both the correlation of different emission measurement methods and the interpretation of emission results for realistic exposure assessments.

Exposure assessment is challenging because it requires the simulation of emissions under adequate environmental conditions. Conventional emission test chambers are suitable for this purpose as they mimic a typical indoor environment, but they are not adapted to consumer product market control. A major task of this work was to explore cost-effective and suitable alternatives to classical emission test chambers by comparing VOC emission results obtained with different methods. The DHS technique allows a quick and automated study of the sample's VOC emissions. Its correlation with the emission test chamber method could not be established, but it is an efficient tool for consumer product sample pre-selection. For formaldehyde emission measurements from wooden toys, the flask method is still used in some OCLs. It is demonstrated in this thesis that it is not suitable for exposure assessments as it does not correlate with results obtained in emission test chambers. For both formaldehyde from wooden toys and VOCs from plastic products, microchambers (44 mL) present an alternative to bigger emission test chambers (1000 L and 203 L) for market surveillance. The correlation between chamber sizes at ambient temperature and humidity over several days with a polyurethane reference material or wooden products was satisfactory when the area-specific air flow rate was kept constant. Non-commercial glass chambers built from desiccators (24 L) could also be an economical alternative between big emission chambers and microchambers, as their results correlated with both of them. Based on these results, the use of microchambers or 24 L glass chambers, together with bigger emission test chambers for big and inhomogeneous samples, seems suitable for market surveillance and exposure assessments.

Furthermore, the inhalation exposure of consumers to the VOCs was investigated. A characterization of both the polymer material via pyrolysis-GC/MS and VOC emissions with DHS provided a great overview on the emissions expected from different materials. Most high-emitting samples are made of PVC and mainly emit cyclohexanone, xylenes as well as plasticizers. A study of these samples in conventional emission test chambers, smaller glass chambers and microchambers allowed an exposure assessment mimicking typical indoor conditions. The determined gas phase concentrations were compared with toxicologically based guideline values. The guideline values were not exceeded by emissions from single products but scenarios with multiple products or a close proximity between the consumer and the product are more concerning. Indeed, an innovative setup based on a doll's head allowed the assessment of the exposure from costume masks, which emitted much higher inhalable concentrations and exceeded the DNEL value for cyclohexanone. These results are only estimations which can differ from real exposure, especially with microchambers, but they give useful indications for market surveillance. We also showed that intense and unpleasant odors can be an indicator for health-threatening emissions. Moreover, microchambers were employed to study the influence of the material properties on VOC emissions: Hardness plays a crucial role as softer products allow a better diffusion through the material and therefore a faster VOC release. As observed for phenol from the polyurethane reference material, VOCs can also be released slowly if they chemically bind to the polymer structure.

These studies are not representative of the overall consumer product offer, but further data generated by OCLs with adapted routine methods will allow a more comprehensive overview on the market and an improvement of consumer product safety. Future research on the correlation between methods for different materials and environmental parameters could be useful for standardization. Then, the regulation of VOC emissions would necessitate a given list of regulated substances or the implementation of a TVOC (total VOC concentration) concept like for building materials [47]. Defined risk assessment strategies with meaningful measurement output values (e.g., $SER_A$) and appropriate related guideline or limit values are necessary. The mutual implementation of methods and regulations with other VOC-emitting consumer products such as fragranced products should also be considered. The exposure assessment should always be based on the use of the product in an appropriate scenario while the guideline values could remain the same.

Regulation is necessary, as it is more efficient to eliminate risks and injustices than expecting individuals to implement costly consumption changes [126]. Additionally, the environmentally friendly trends of consuming less and favoring second-hand products are partly endorsed by the results of this work as this will eliminate cumulated and acute VOCs exposures. However, second-hand products may become a problem if the product disintegrates and thus new chemicals become available (e.g., via dermal contact).

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# 6. List of publications

## 6.1. Articles integrated in the manuscript

- Even M, Wilke O, Kalus S, Schultes P, Hutzler C, Luch A. Formaldehyde Emissions from Wooden Toys: Comparison of Different Measurement Methods and Assessment of Exposure. Materials. 2021;14;262. doi: 10.3390/ma14020262

- Even M, Roloff A, Lüttgert N, Beauchamp J, Stalter D, Schulte A, Hutzler C, Luch A. Exposure Assessment of Toxicologically Relevant Volatile Organic Compounds Emitted from Polymer-Based Costume Masks. Chem. Res. Toxicol. 2021;34, 1;132-143. doi: 10.1021/acs.chemrestox.0c00414

- 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(1):40-48. doi: 10.1111/ina.12605

- 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 Public Health. 2019;7:202. doi: 10.3389/fpubh.2019.00202.

## 6.2. Talks

- WaBoLu-Innenraumtage, Online, May 2021. Formaldehydemissionen aus Holzspielzeug: Methodenvergleich und Expositionsabschätzung.
- Odours and Emissions of Plastic Materials, Online, March 2021. Formaldehyde emissions from wooden toys: Method comparison and exposure assessment.
- Indoor Air, Online, November 2020. Formaldehyde emissions from wooden toys: Method comparison and exposure assessment.

- WaBoLu-Innenraumtage, Berlin, May 2019. Methodische Entwicklungen und aktuelle Messergebnisse zu Emissionen aus Verbraucherprodukten.
- Odours and Emissions of Plastic Materials, Kassel, March 2019. Investigations on emissions of VOCs from consumer products made of polymers.
- Odours and Emissions of Plastic Materials, Kassel, March 2018. Monitoring of emissions of VOC from consumer products: Influence of the chamber volume.

## 6.3. Posters

- ISES/ISIAQ joint annual meeting, Kaunas (Lithuania), August 2019. Even M., Altemeier M., Lüttgert N., Haffke H., Roloff A., Hutzler C., Luch. A. Exposure assessment of VOC emissions from Halloween masks.
- ISES/ISIAQ joint annual meeting, Kaunas (Lithuania), August 2019. Even M., Girard M., Rich A., Roloff A., Hutzler C., Luch. A. Exposure assessment of VOC emissions from polymer-based consumer products.
- 5th German Pharm-Tox Summit, Stuttgart, February 2019. Even M., Girard M., Rich A., Roloff A., Hutzler C., Luch. A. Exposure Assessment of Volatile Organic Compounds from Consumer Products.
- International Conference on Risk Assessment of Indoor Air Chemicals, Berlin, September 2018. Even M., Girard M., Hutzler C., Vieth B., Luch. A. Investigations on emissions of VOCs from consumer products made of polymers.
- Lebensmittelchemikertag, Berlin, September 2018. Hutzler C., Even M., Wilke O., Luch. A. Safety testing of consumer products: On the use of a microchamber in emission testing of VOCs.
- Indoor Air, Philadelphia (USA), July 2018. Even M., Hutzler C., Wilke O., Vieth B., Luch A. Investigations on emission properties of VOCs from consumer products made of polymers.
- Lebensmittelchemikertag, Würzburg, September 2017. Even M., Hutzler C., Luch A. Safety testing of consumer products: On the use of dynamic headspace coupled to GC-MS in automated emission chamber testing of VOCs. (Annex I)

# Safety testing of consumer products: On the use of dynamic headspace coupled to GC-MS in automated emission chamber testing of VOC

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## 1. Introduction

In modern life, human beings spend 80-90% of their time indoors. Lingering in buildings may lead to relevant exposures against volatile organic compounds (VOC). To estimate the inhalation exposure of humans against VOC, information about the emission of these compounds from relevant materials is needed.

The ISO 16000 standard is regarded as gold standard for emission testing and provides guidelines for VOC emission measurements of building materials [1]. However, also regular consumer products, e.g. toys, may release harmful substances into the indoor air. The existing standard emission procedures for building materials are unsuitable for enforcement laboratories due to the required emission chamber testing resulting in high costs and time consumption. Therefore, there is an urgent need for alternative approaches providing useful emission data for consumer products for realistic exposure assessment.

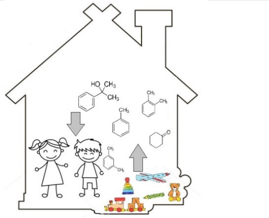
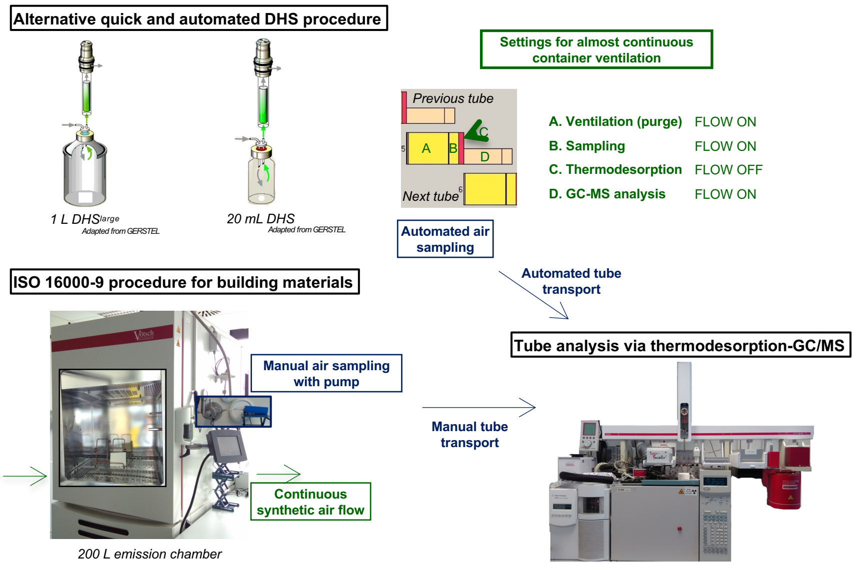


**Figure 1. From consumer products via indoor air to human airways.**

A study comparing the emission chamber testing according to ISO 16000-9 with two less extensive alternative techniques (dynamic headspace (DHS) and large volume dynamic headspace (DHS$^{large}$)) was carried out. The emission kinetics obtained by the faster and less cost intensive alternative methods were compared and correlated to the results obtained by the gold standard method. We focused on 12 single VOC which were indicated as model compounds of practical relevance. A custom synthesized spiked polyurethane (PU) material was used (cf. Table 1) for emission testing to mimic real plastic sample.

## 2. Materials and methods



**Alternative quick and automated DHS procedure**

*1 L DHS$^{large}$*
*Adapted from GERSTEL*

*20 mL DHS*
*Adapted from GERSTEL*

**Settings for almost continuous container ventilation**

| | |
|---|---|
| **A. Ventilation (purge)** | FLOW ON |
| **B. Sampling** | FLOW ON |
| **C. Thermodesorption** | FLOW OFF |
| **D. GC-MS analysis** | FLOW ON |

**Automated air sampling**

**Automated tube transport**

**ISO 16000-9 procedure for building materials**

**Manual air sampling with pump**

**Continuous synthetic air flow**

*200 L emission chamber*

**Manual tube transport**

**Tube analysis via thermodesorption-GC/MS**

**Figure 2. Experimental setup for air sampling from the 200 L chamber or dynamic headspace vessels and subsequent tube analysis.**

**Table 1. VOC present in the PU material (1 mg/g for each) with associated boiling points (BP), molecular weights (MW) and partition coefficients (LogP).**

| Name | BP(°C) | MW | LogP | Name | BP(°C) | MW | LogP |
|---|---|---|---|---|---|---|---|
| Benzene | 80 | 78 | 2.1 | Acetophenone | 202 | 120 | 1.6 |
| Toluene | 111 | 92 | 2.7 | 2-Phenyl-2-propanol | 202 | 136 | 1.9 |
| Xylene (p/o/m) | 139 | 106 | 3.2 | Formamide | 210 | 45 | -1.5 |
| Dimethylformamide | 153 | 73 | -1.0 | Isophorone | 215 | 138 | 2.3 |
| Cyclohexanone | 156 | 98 | 0.81 | Naphtalene | 218 | 128 | 3.3 |
| Phenol | 182 | 94 | 1.5 | Dodecanol | 259 | 186 | 5.1 |

Table 2. Parameters for emission experiments.

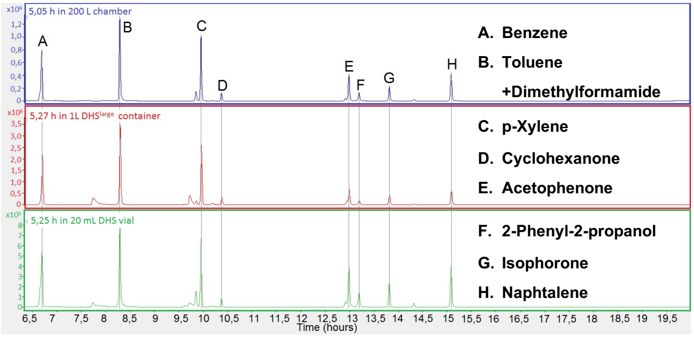
| | ISO 1600-9 procedure | DHS procedures | |
|---|---|---|---|
| | | DHS$^{large}$ | DHS |
| Chamber size | 200 L | 1 L | 20 mL |
| Experiment duration | 28 d | 23 h | 10 h |
| Sampling | 600 mL air on Tenax® TA tubes (spiked with ISTDs) | | |
| Temperature | 23°C | | |
| Relative humidity | 50 %H | Not controlled | |
| Air exchange ($h^{-1}$) | 0.50 | 5.10 | 42.6 |
| Surface-specific air flow ($m^3/(m^2*h)$) | 4.24 | | |

**Table 3. Conditions for the determination of VOCs in air samples by thermodesorption-GC/MS.**

| | |
|---|---|
| Desorption | **Thermal Desorption Unit** (TDU, Gerstel, Mühlheim, Germany)<br>25°C; 700°C/min 280°C – 2 min; splitless |
| Cryo-trapping | **Cold Injection System 4** (Gerstel, Mühlheim, Germany)<br>**Liner:** filled with deactivated glass wool, **Cooling:** -150 °C with liquid $N_2$ , **Heating:** 12 °C/min 285 °C - 15 min; 1:400 or splitless |
| GC/MS | **GC: 6890, MSD: 5975** (both Agilent, Waldbronn, Germany)<br>**Column:** DB-5MS (60 m; 0.320 mm; 1.00 µm); **Flow:** 1.4 ml/min; He; **Oven program:** 45°C-0.5 min, 12 °C/min, 200°C–5 min, 20°C/min, 280°C-10 min; **MS-Modus:** combined SIM-Scan mode, Scan: 40 m/z–450 m/z |

## 3. Results

Chromatograms of air samples taken at similar time points in the different chambers were almost identical and showed very similar peak patterns (cf figure 3).



**A.** **Benzene**
**B.** **Toluene +Dimethylformamide**
**C.** **p-Xylene**
**D.** **Cyclohexanone**
**E.** **Acetophenone**
**F.** **2-Phenyl-2-propanol**
**G.** **Isophorone**
**H.** **Naphtalene**

**Figure 3. GC/MS-chromatograms in scan mode (split: 1:400, air samples taken after 5 h). Above: sampling from 200 L emission chamber; middle: sampling with DHS$^{large}$; below: sampling with DHS.**

After an equilibrium time of about 5h the use of the two DHS devices provided kinetic profiles of area-specific emission rate values (SERa) which were comparable with results obtained with emission chamber testing according to ISO 16000-9. It was observed that a high volatility of the analyte correlates with a rapid decrease in SERa (cf figure 4).

However, a triple determination resulted in higher standard deviations for DHS and DHS$^{large}$ compared to emission chamber testing. There might be several suitable explanations for this observation:

- It might be triggered by the homogeneity of the tested polymer. This influence might be more relevant for smaller sample amounts.
- The environmental parameters, especially humidity, are not as well controlled in the DHS-system when compared to the emission chamber.
- The sink effect may differ between the different containers used for the replicates.

The emissions from the 20 mL-vials decreased compared to the two other devices. A damaged septum was assumed to be the reason. The sampling syringe damages the septum by repeated penetrations which leads to untightness This effect was not observed with DHS$^{large}$ vessels during the first day.

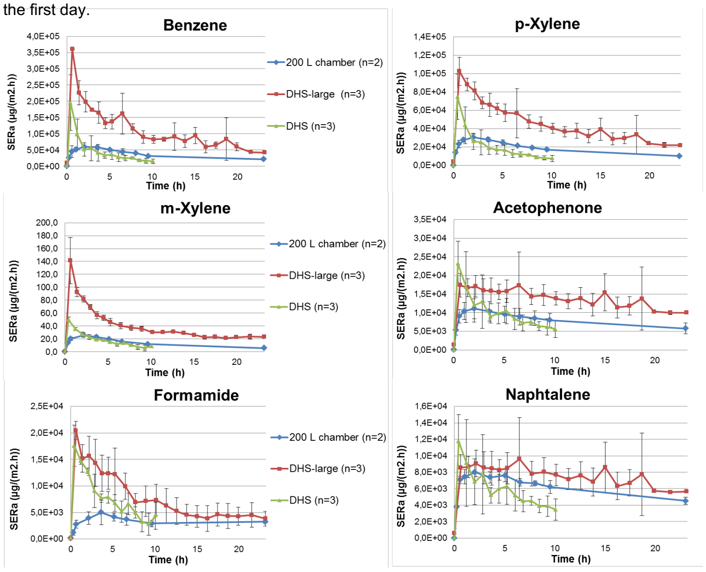


**Figure 4. Emission profiles of 6 selected analytes from the PU plate obtained by emission chamber testing and two DHS techniques.**

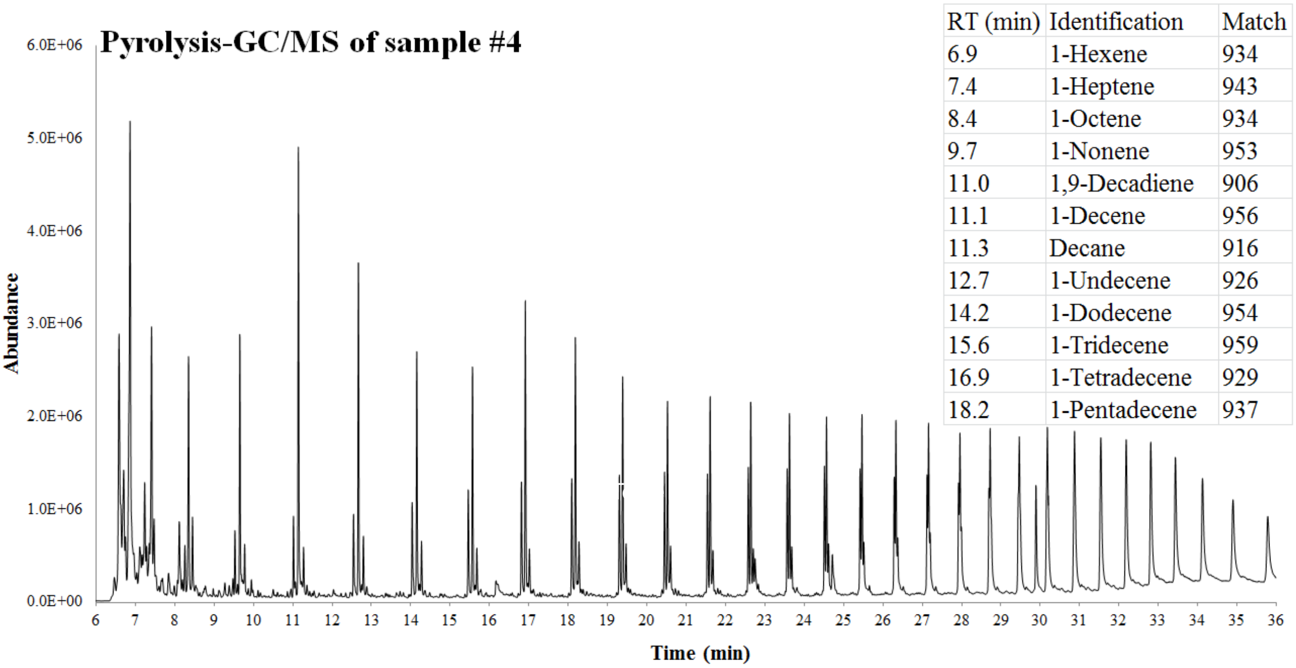
## 4. Summary, Conclusion and Outlook

- The three emission devices (200 L emission chamber, 1 L large DHS and a 20 mL DHS) led to similar chromatograms and emission kinetics after a delay time. For some compounds the standard deviations between replicates were significantly higher for the DHS. This issue along with the influence of the DHS$^{large}$ vessel size (250 mL, 500 mL, 625 mL, 1 L) will be studied in future experiments.
- The use of DHS methods as a valuable tool for the exposure assessment of emissions is a realistic goal. However, there is a need for further optimization and validation of these methods.
- Because of similar emission kinetics in the DHS methods and the emission chamber testing according to ISO 16000-9, DHS methods can be judged suitable for screening emission measurements. This avoids unnecessary time consuming and cost expensive emission chamber testing.

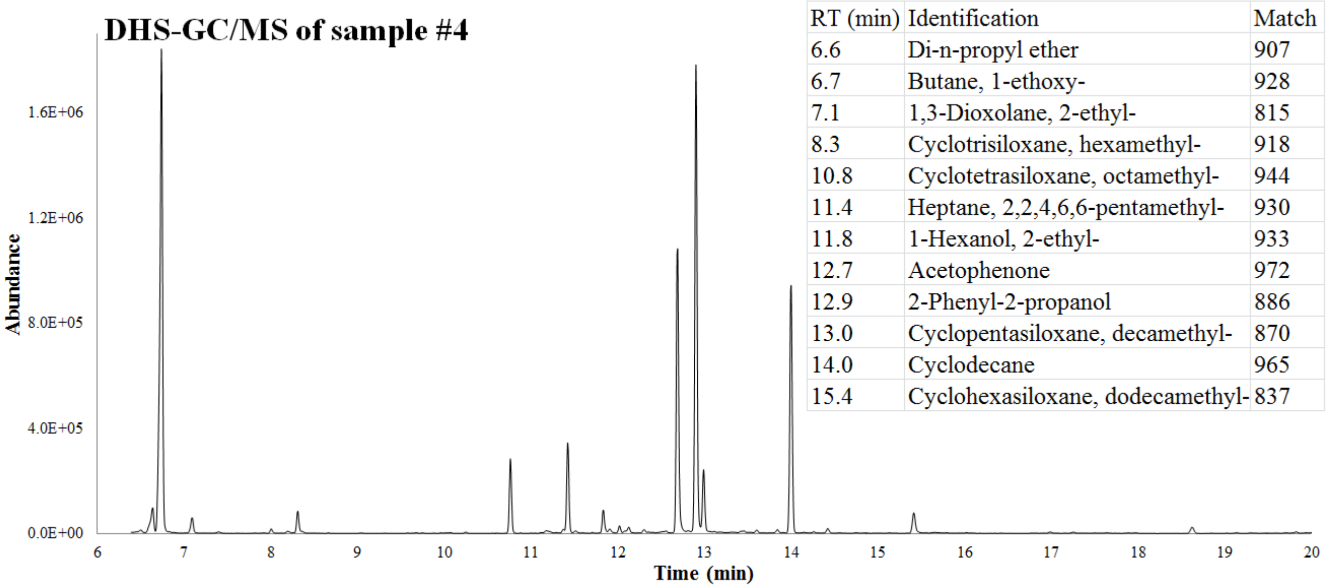
## 5. References

[1] ISO, Indoor Air - Part 9: Determination of the Emission of Volatile Organic Compounds from Building Products and Furnishing - Emission Test Chamber Method (ISO 16000-9:2006), International Organization for Standardization, Beuth, Berlin, 2006.

# *Supplementary Material*



| RT (min) | Identification | Match |
|---|---|---|
| 6.9 | 1-Hexene | 934 |
| 7.4 | 1-Heptene | 943 |
| 8.4 | 1-Octene | 934 |
| 9.7 | 1-Nonene | 953 |
| 11.0 | 1,9-Decadiene | 906 |
| 11.1 | 1-Decene | 956 |
| 11.3 | Decane | 916 |
| 12.7 | 1-Undecene | 926 |
| 14.2 | 1-Dodecene | 954 |
| 15.6 | 1-Tridecene | 959 |
| 16.9 | 1-Tetradecene | 929 |
| 18.2 | 1-Pentadecene | 937 |



| RT (min) | Identification | Match |
|---|---|---|
| 6.6 | Di-n-propyl ether | 907 |
| 6.7 | Butane, 1-ethoxy- | 928 |
| 7.1 | 1,3-Dioxolane, 2-ethyl- | 815 |
| 8.3 | Cyclotrisiloxane, hexamethyl- | 918 |
| 10.8 | Cyclotetrasiloxane, octamethyl- | 944 |
| 11.4 | Heptane, 2,2,4,6,6-pentamethyl- | 930 |
| 11.8 | 1-Hexanol, 2-ethyl- | 933 |
| 12.7 | Acetophenone | 972 |
| 12.9 | 2-Phenyl-2-propanol | 886 |
| 13.0 | Cyclopentasiloxane, decamethyl- | 870 |
| 14.0 | Cyclodecane | 965 |
| 15.4 | Cyclohexasiloxane, dodecamethyl- | 837 |

**Supplementary Figure 1.** GC/MS chromatograms in full scan mode of sample #4. Above: degradation products after pyrolysis at 700°C; below: emitted substances during DHS experiments at 23°C and 15 mL/min. Retention time (RT), NIST library identification and match score (maximum value 1000).

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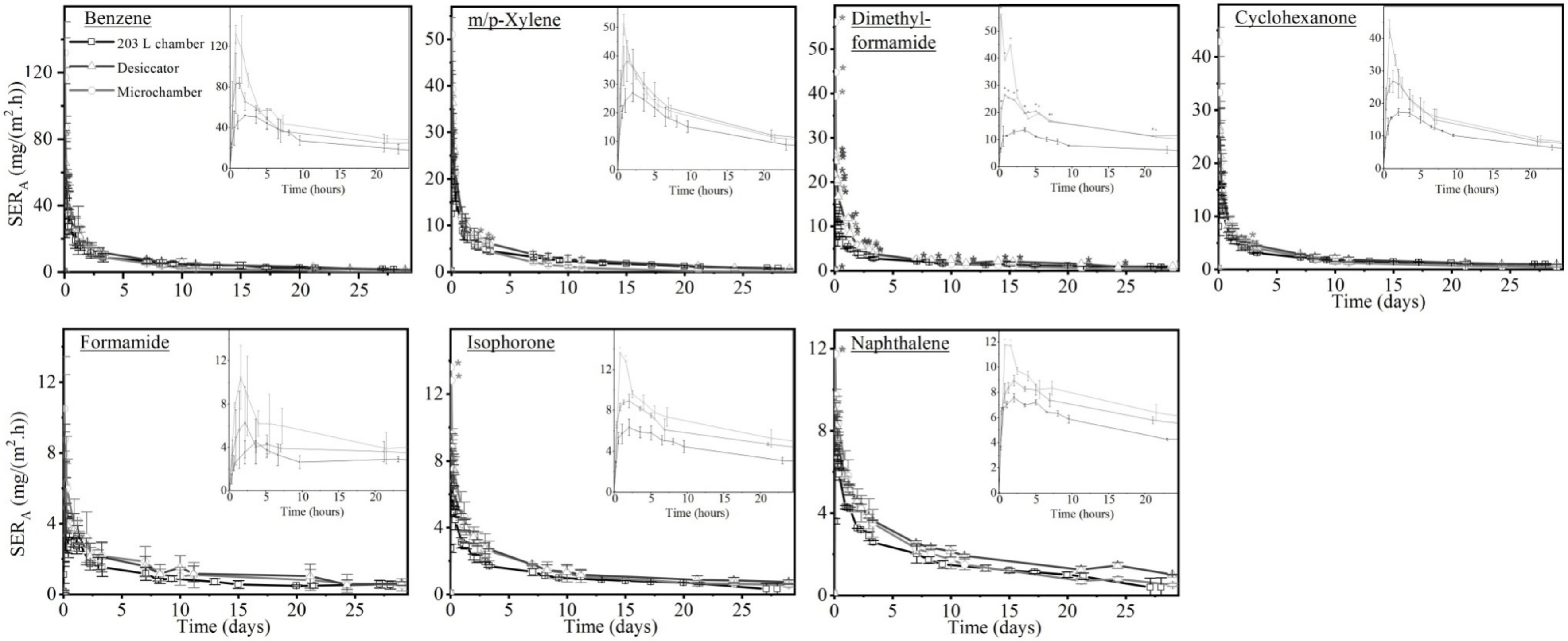
# Emissions of volatile organic compounds from consumer products: comparison of three emission chamber sizes – Supplementary material



**Supplementary material.**

materials

MDPI

*Supplementary Materials*

# Formaldehyde Emissions from Wooden Toys: Comparison of Different Measurement Methods and Assessment of Exposure

**Morgane Even [1,2,3,*], Olaf Wilke [2], Sabine Kalus [2], Petra Schultes [4], Christoph Hutzler [1] and Andreas Luch [1,3]**

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[3] Freie Universität Berlin, Department of Biology, Chemistry, Pharmacy, Institute of Pharmacy, Königin-Luise-Strasse 2-4, 14195 Berlin, Germany
[4] Chemical and Veterinary Analytical Institute Münsterland-Emscher-Lippe (CVUA-MEL), Joseph-König-Str. 40, 48147 Münster, Germany; petra.schultes@cvua-mel.de
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**Figure S1.** Representative pictures of the investigated toy samples.

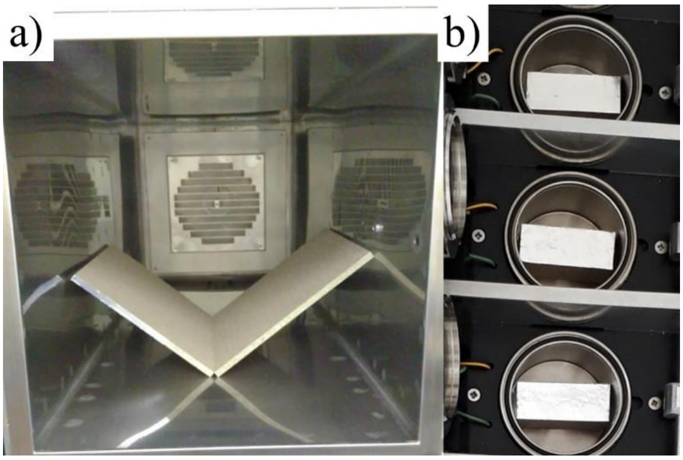

**Figure S2.** Example image of chamber loading for sample #1 in the 1 m³ chamber (**a**) and the microchamber (**b**).

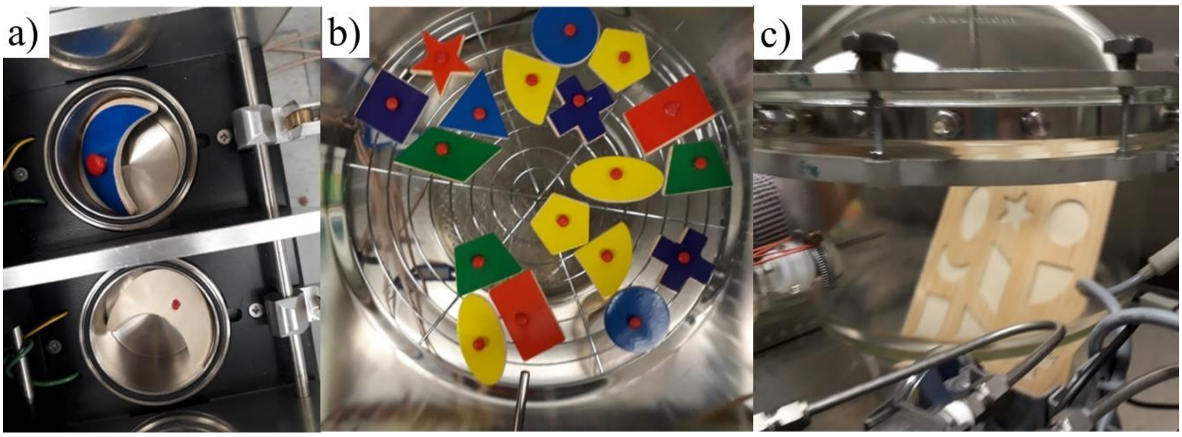

**Figure S3.** Example image of chamber loading for sample #7: Pieces in the microchamber (**a**), pieces in the desiccator (**b**) and plate in the desiccator (**c**).

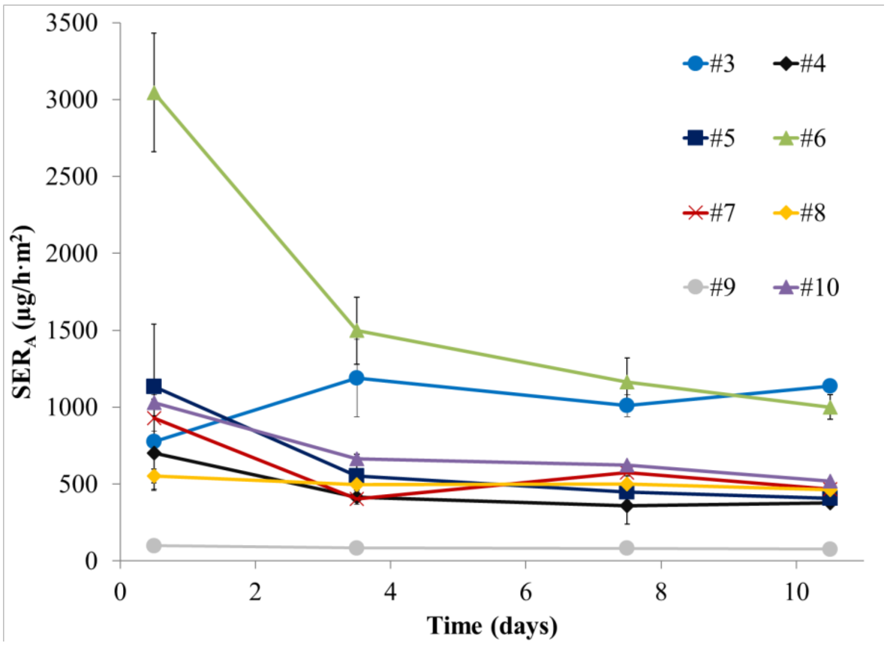

**Figure S4.** Emission profiles of formaldehyde from wooden toy pieces in the microchamber over 10 days (n = 2; SER$_A$, area-specific emission rate). Error bars represent standard deviation (SD).

**Table S1.** Dimensions of the samples for chamber studies; ¥: sample edges were partly covered; *: approximated shape; ellipses, circles: 1st dimension are diameters.

**Microchamber Samples**

| No. | Geometric Shape | 1st Dimension (cm) | 2nd Dimension (cm) | Face Surface Area (cm$^2$) | Perimeter (cm) | Thickness (cm) | Total Surface Sample Surface Area (cm$^2$) | Weight (g) |
|---|---|---|---|---|---|---|---|---|
| **#1¥** | parallelepiped | 4.0 | 2.0 | 8.0 | | 0.16 | 16.0 | 3.2/3.3/3.4 |
| **#2¥** | | | | | | | | 3.3/3.4/3.6 |
| **#3** | parallelepiped | 2.97 | 2.99 | 8.9 | | 1.40 | 34.4 | 5.5/6.2 |
| **#4** | cylinder | 4.03 | | 12.8 | | 0.27 | 28.9 | 1.8/2.3 |
| **#5¥** | half ellipse* | 4.40 | 2.30 | 8.3 | 8.0 | 0.37 | 19.7 | 1.3/1.4 |
| **#6¥** | triangle* | 4.55 | 2.20 | 5.0 | 8.0 | 0.39 | 12.6 | 1.6 |
| **#7** | 2 half ellipses* | 5.00 and 4.20 | 5.00 and 1.80 | 9.0 | 14.3 | 0.41 | 24.0 | 2.1 |
| **#8¥** | quarter circle* | 5.54 | 86° | 5.8 | 6.7 | 1.84 | 23.9 | 8.5 |
| **#9** | ellipse* | 4.07 | 3.50 | 11.2 | 13.8 | 0.48 | 29.0 | 8.3 |
| **#10** | parallelepiped* | 2.98 | 2.04 | 6.1 | 11.4 | 0.48 | 16.9 | 1.9 |

**Dessicator Samples**

| No. | Number of Pieces | Total Pieces Surface Area (cm$^2$) | Number of Plates | Total Plates Surface Area (cm$^2$) |
|---|---|---|---|---|
| **#5** | 16 | 651 | 1 | 1456 |
| **#7** | 18 | 711 | 1 | 1426 |
| **#8** | 8 | 828 | 2 | 1475 |

**1 m$^3$ Chamber Samples**

| No. | Number of Plates | Total Plates Surface Area (cm$^2$) |
|---|---|---|
| **#1¥** | 2 | 0.93 |
| **#2¥** | | |

**Table S2.** Flask method values of the samples similar to those studied in the microchamber and of samples after microchamber testing (mg/kg$_{toy}$); usually, different pieces of the same toy sample were put together in the flask: the values reported here are the mean and standard deviation of the measurement with samples having the same characteristics (in particular color) than the samples studied in the microchambers; *: ±30% SD were estimated from experience of CVUA-MEL because there were no replicates.

| No. | Similar Samples | After Microchamber (n = 1) |
|---|---|---|
| #1 | 116 ± 35* (n = 1) | not measured |
| #2 | 117 ± 35* (n = 1) | not measured |
| #3 | 310 ± 80 (n = 2) | 346 ± 104* |
| #4 | 865 ± 21 (n = 2) | 365 ± 110* |
| #5 | 250 ± 39 (n = 4) | 309 ± 75* |
| #6 | 530 ± 27 (n = 3) | 561 ± 158* |
| #7 | 345 ± 71 (n = 2) | 286 ± 86* |
| #8 | 101 ± 13 (n = 3) | not measured |
| #9 | 47 ± 14* (n = 1) | not measured |
| #10 | 344 ± 103* (n = 1) | not measured |

# Exposure Assessment of Toxicologically Relevant Volatile Organic Compounds Emitted from Polymer-Based Costume Masks

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# Supporting Information

## Table of content

# Samples, Chemicals and Materials

## Costume Masks Investigated in this Study

**Figure S1: Pictures of the 12 costume masks investigated in this study.**

## Doll's head

The doll's head was purchased online from Amazon with the following description: "Ba Sha Afro Head for Wig Display Hat and Glasses with Clip".

## Standards

**Table S1: Chemicals with corresponding CAS number, boiling point (*bp*), supplier and purity.**

| Name | CAS | *bp* (°C) | Supplier | Purity |
|---|---|---|---|---|
| Benzene | 71-43-2 | 80 | Sigma Aldrich | ≥99.9% |
| Toluene | 108-88-3 | 111 | Sigma Aldrich | 99.8% |
| Dimethylformamide | 68-12-2 | 153 | Sigma Aldrich | ≥99.9% |
| *n*-Butylacetate | 123-86-4 | 126 | Sigma Aldrich | ≥99.7% |
| Ethylbenzene | 100-41-4 | 136 | TCI chemicals | ≥99.0% |
| *m*-Xylene | 108-38-3 | 139 | Sigma Aldrich | ≥99.0% |
| *p*-Xylene | 106-42-3 | 138 | Sigma Aldrich | ≥99.0% |
| *o*-Xylene | 95-47-6 | 144 | Sigma Aldrich | ≥99.0% |
| Cyclohexanone | 108-94-1 | 156 | Sigma Aldrich | ≥99.9% |
| Phenol | 108-95-2 | 182 | Sigma Aldrich | 99.5-100.5% |
| Octanal | 124-13-0 | 171 | Sigma Aldrich | 99% |
| 2-Ethylhexanol | 104-76-7 | 185 | Sigma Aldrich | ≥99.6% |
| Acetophenone | 98-86-2 | 202 | Merck | ≥99.5% |
| 2-Phenyl-2-propanol | 617-94-7 | 202 | Sigma Aldrich | 97% |
| Isophorone | 78-59-1 | 215 | Merck | 97% |
| Cyclodecane | 293-96-9 | 201 | Sigma Aldrich | 95 % |
| Dodecane | 122-40-3 | 216 | Sigma Aldrich | ≥99.8% |
| Naphthalene | 91-20-3 | 218 | Merck | ≥99.7% |
| Dimethyl phtalate | 131-11-3 | 284 | Sigma Aldrich | ≥99.5% |
| 1-Dodecanol | 112-53-8 | 259 | Merck | ≥98.0% |
| Butylated hydroxytoluene | 128-37-0 | 265 | Sigma Aldrich | unknown |
| TXIB | 6846-50-0 | 380 | Sigma Aldrich | unknown |
| Eicosane | 112-95-8 | 343 | Sigma Aldrich | ≥99.5% |

## Parameters for MS Detection during GC/MS Analyses in SIM Mode

**Table S2: SIM parameters for GC/MS analyses. Quant: quantifier ion; Qual: qualifier ion; %Qual: Ratio of the qualifier and quantifier peak heights.**

| SIM group | $t_r$ (min) | Name | Quant | Qual 1 | %Qual 1 | Qual 2 | %Qual2 |
|---|---|---|---|---|---|---|---|
| **1**<br>$t_r$ = 6.2-7.5 min | 6.36 | Benzene | 78 | 52 | 18 | 77 | 23 |
| **2**<br>$t_r$ = 7.5-9.0 min | 7.84 | Toluene | 91 | 92 | 63 | | |
| | 7.93 | Dimethylformamide | 73 | 44 | 82 | | |
| | 8.30 | *n*-Butylacetate | 56 | 73 | 45 | 43 | 247 |
| **3**<br>$t_r$ = 9.0-10.5 min | 9.35 | Ethylbenzene | 91 | 106 | 33 | | |
| | 9.45/9.48 | *m*/*p*-Xylene | 91 | 106 | 52 | | |
| | 9.86 | *o*-Xylene | 91 | 106 | 49 | | |
| | 9.92 | Cyclohexanone | 55 | 98 | 52 | 69 | 31 |
| **4**<br>$t_r$ = 10.5-12.3 min | 10.87 | Phenol | 94 | 66 | 39 | 65 | 28 |
| | 11.33 | Octanal | 84 | 57 | 129 | 69 | 64 |
| | 11.69 | 2-Ethylhexanol | 57 | 70 | 24 | 83 | 24 |
| **5**<br>$t_r$ = 12.3-14.3 min | 12.51 | Acetophenone | 105 | 77 | 77 | 120 | 32 |
| | 12.72 | 2-Phenyl-2-propanol | 121 | 77 | 22 | 43 | 102 |
| | 13.34 | Isophorone | 82 | 138 | 23 | | |
| | 13.81 | Cyclodecane | 83 | 70 | 114 | 55 | 163 |
| | 14.06 | Dodecane | 57 | 43 | 78 | 71 | 61 |
| **6**<br>$t_r$ = 14.3-19.5 min | 14.52 | Naphthalene | 128 | 127 | 13 | 102 | 10 |
| | 18.82 | Dimethyl phtalate | 163 | 77 | 19 | 92 | 9 |
| | 18.99 | 1-Dodecanol | 55 | 69 | 84 | 83 | 71 |
| **7**<br>$t_r$ = 19.5 min-end | 19.84 | Butylated hydroxytoluene | 205 | 220 | 24 | 57 | 13 |
| | 21.08 | TXIB | 71 | 56 | 8 | | |
| | 25.74 | Eicosane | 57 | 71 | 73 | 85 | 54 |

# Calibration Curve for Cyclohexanone

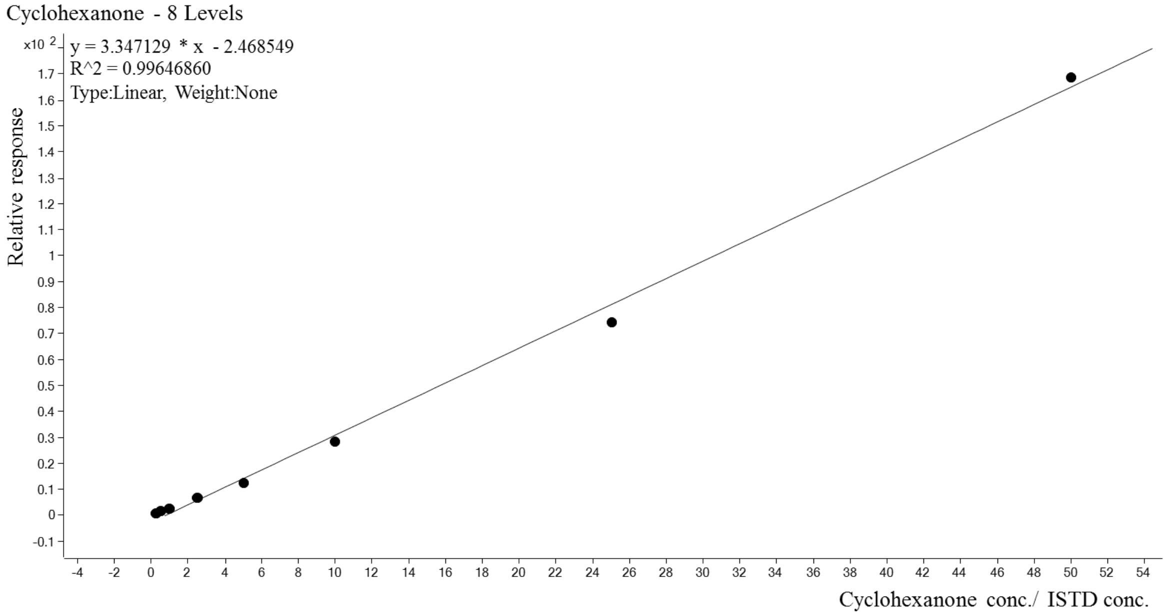


**Figure S2: GC/MS calibration curve for cyclohexanone with equation and correlation coefficient ($R^2$) of the linear regression.**

# Results for DHS-GC/O-MS Analyses of Exemplary Costume Face Mask Samples

**Table S3: Retention indices (RI[1], calculated in relation to a mixture of *n*-alkanes ranging from octane ($C_8H_{18}$) to *n*-tricosane ($C_{23}H_{48}$) in dichloromethane) of odor qualities perceived from two mask samples, as determined by DHS-GC/O-MS on a HP-5MS column.**

| RI | Odor quality | 9A | 10A |
|---|---|---|---|
| <800 | Burnt | | x |
| 875 | Grassy, burnt | | x |
| 895 | Mushroom-like | | x |
| 913 | Flowery, grassy, solvent-like | x | x |
| 934 | Almond-like | x | |
| 981 | Mushroom-like | x | x |
| 992 | Flowery | x | |
| 1026 | Pungent, grassy | x | |
| 1083 | Mushroom-like | x | x |
| 1091 | Burnt | x | x |

## Setups for Simulated Exposure Assessments with a Doll’s Head and Microchamber Measurements

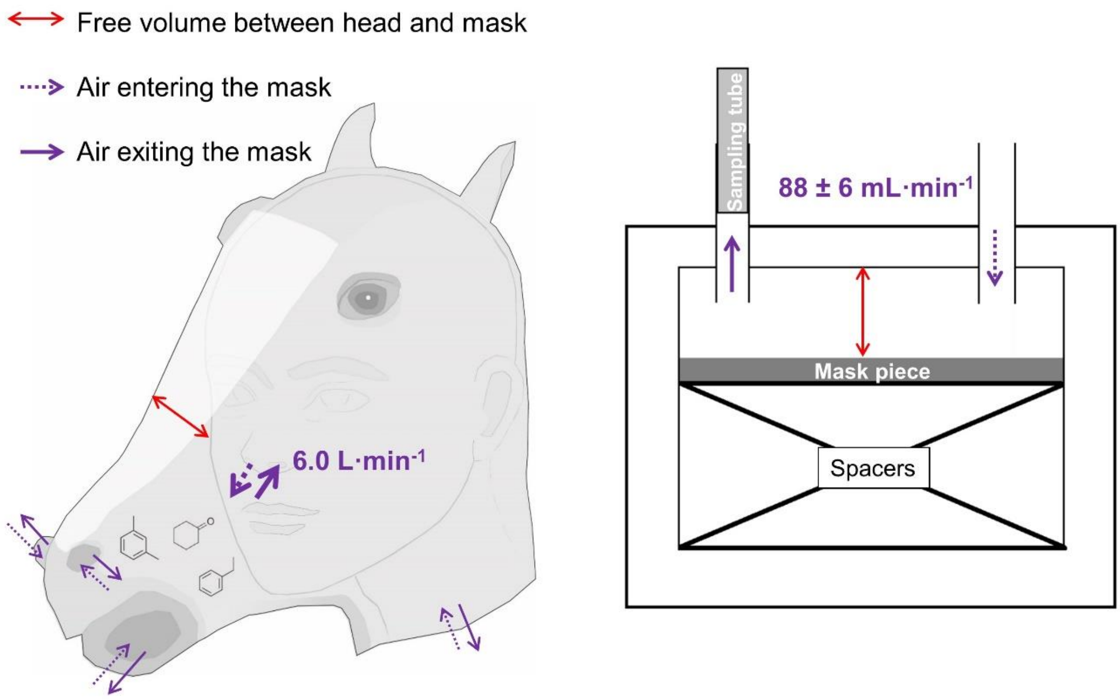
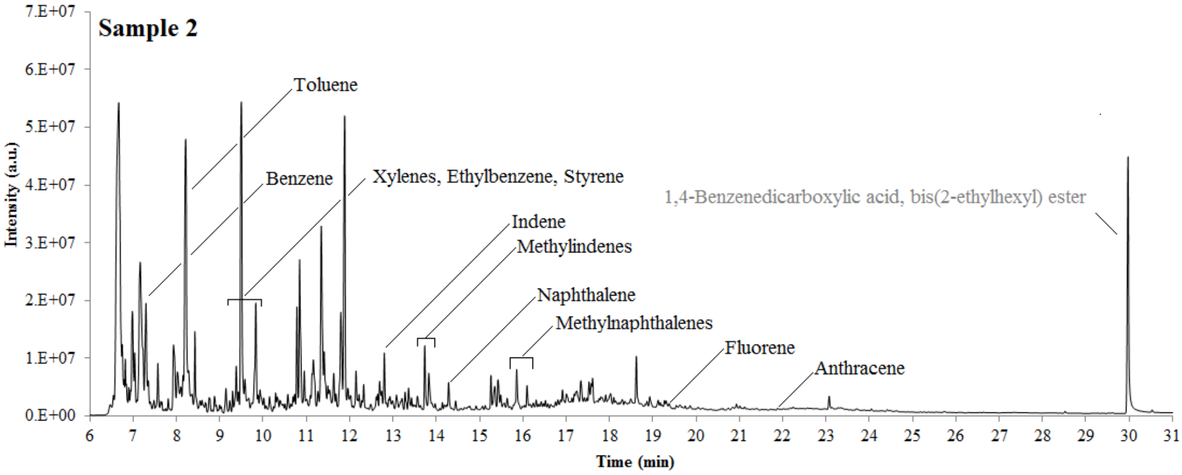


**Figure S3: Schematic diagram of the setup for doll’s head exposure simulation and microchamber measurements.**

# Characterization of the Polymer-Type of Representative Costume Mask Samples



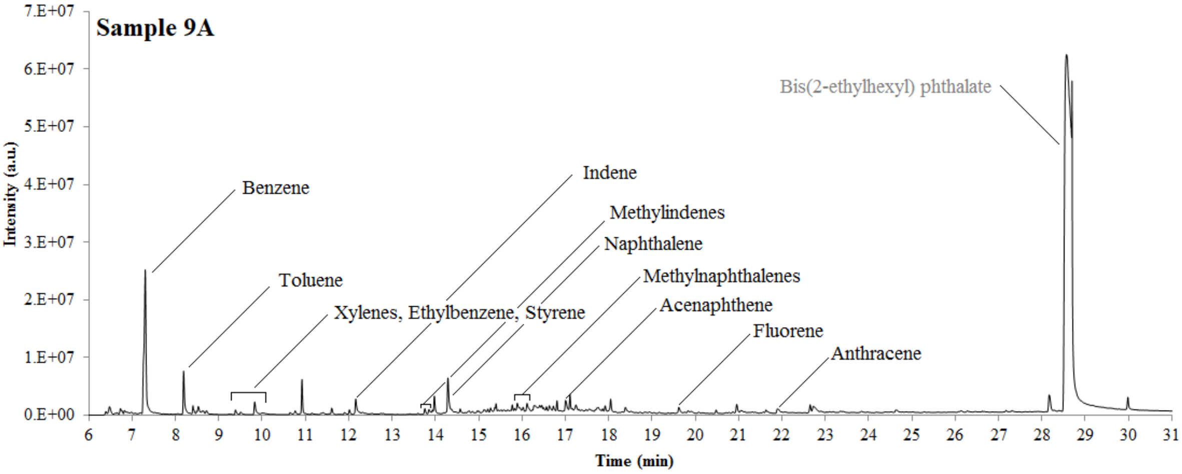


**Figure S4: Pyrolysis-GC/MS pyrograms in full scan mode of the degradation products (all identified PVC degradation products are labeled in black font, additives in grey font) for samples 2 and 9A after pyrolysis at 700°C for 1.43 min. Degradation products were identified by comparison with the NIST library; all typical PVC degradation products[2] were detected, except for hydrochloric acid, which was beyond the MS detection range.**

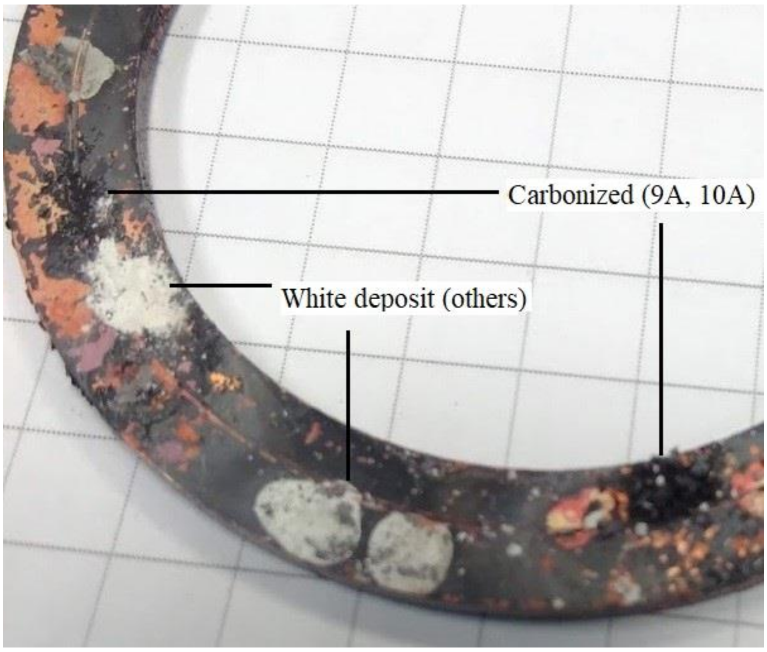


**Figure S5: Image of representative sample pieces heated/burnt on a copper ring during Beilstein tests (tests were positive for samples 9A and 10A and negative for the other samples).**

# DHS-GC/MS Analyses of VOC Emissions from Representative Costume Mask Samples

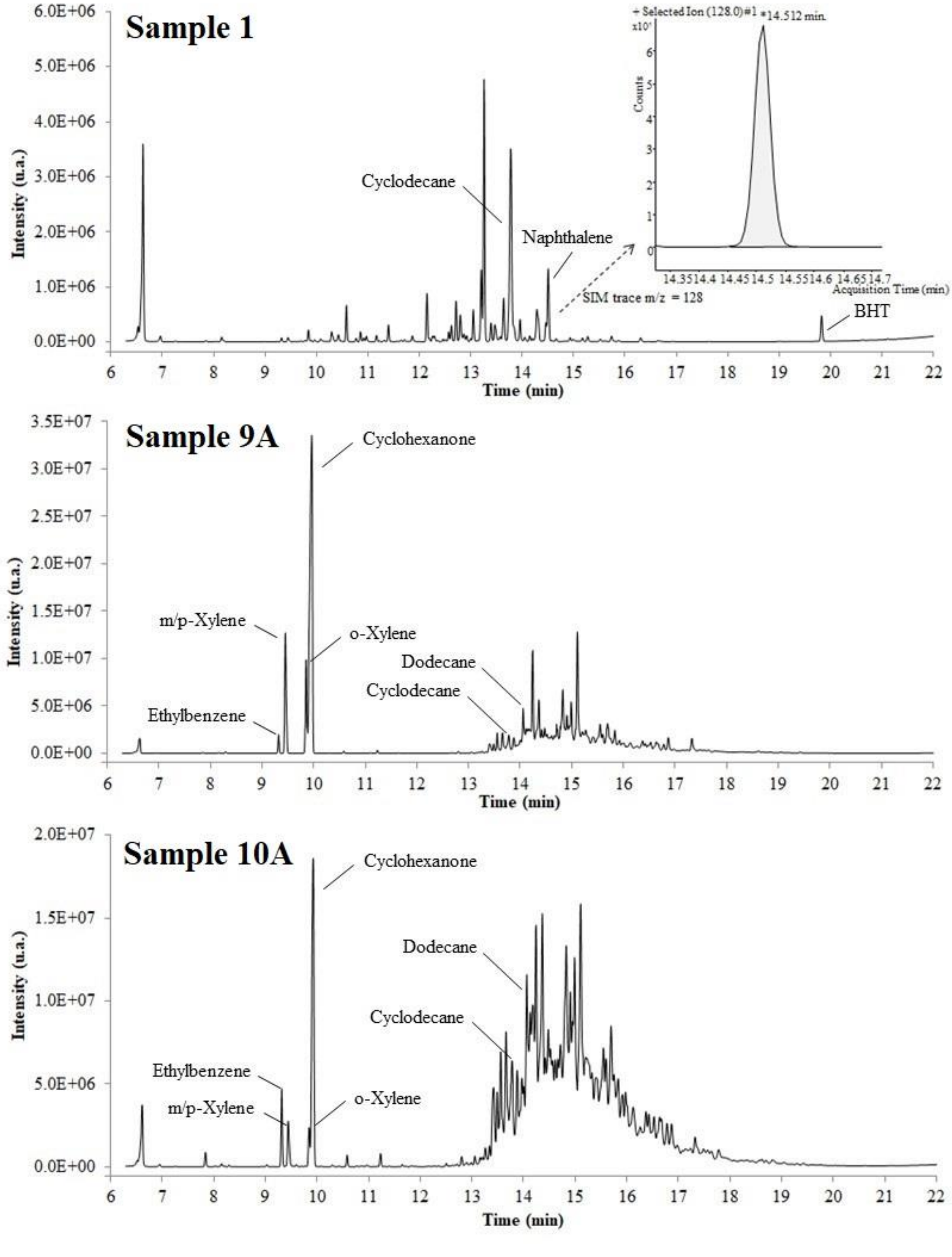


**Figure S6: GC/MS chromatograms in full scan mode of substances emitted during DHS-GC/MS experiments of sample 1, 9A and 10A ($T$ = 23°C, 600 mL air flow at 15 mL·min$^{-1}$). Annotated substances were identified via comparison of their mass spectra with the NIST library and their retention times with those of authentic reference compounds. The integration of naphthalene in SIM mode is presented as an example of integration towards the calculation of analyte-specific DHS scores.**

# Kinetic Emission Profiles for various Analytes Emitting from a Costume Mask

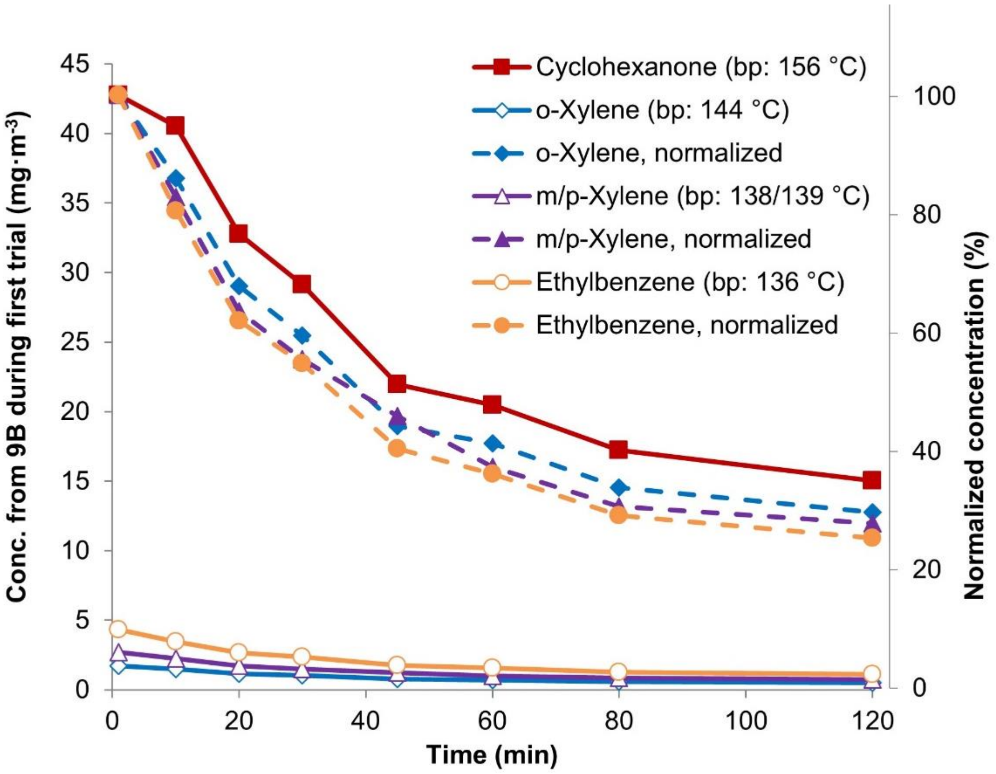


**Figure S7: Kinetic inhalation profiles of the four highest-emitting target analytes while wearing mask 9B (first use) as determined with the doll's head exposure simulation setup; dashed lines represent profiles normalized to the initial inhaled concentration of cyclohexanone; bp: boiling point.**

# Derivation of DNELs for workers and the general population exposed to cyclohexanone by the inhalation route

It was not possible to reproduce how the industry registrants derived the DNELs of 20 $mg \cdot m^{-3}$ (short-term systemic effects) and 10 $mg \cdot m^{-3}$ (long-term exposure systemic effects) from the reported data on the ECHA website[3]. According to the registration dossier, the registrants used a point of departure (POD) for the inhalation DNEL from an older study with daily intravenous injection of the substance over a period of 28 days[4] and an assessment factor of 70 for systemic long-term effects (general population) without clearly specifying how the assessment factor was determined. The resulting DNEL (POD 100 $mg \cdot (kg\ bw)^{-1} \cdot d^{-1}$ divided by 70) would be 1.43 $mg \cdot m^{-3}$, which is significantly lower than the long-term DNEL of 10 $mg \cdot m^{-3}$ that was proposed by the registrants.

A recent study by Lim et al.[5] is more appropriate for deriving a long-term systemic DNEL because the inhalation exposure route was tested: It is more realistic with regards to the expected exposure scenario via costume masks and additional uncertainties from route-to-route extrapolations can be excluded. The authors derived a DNEL for workers that can be retraced. Despite slight differences in the POD correction from rats to humans, the DNEL from Lim et al.[5] is at a similar level as the DNELs derived below (Table S4).

According to the ECHA guidance on information requirements and chemical safety assessment chapter R.15[6], the long-term DNEL for consumers can be adjusted for infrequent exposure (in case exposure days are < 15 $d \cdot a^{-1}$) and shorter daily duration (<< 24 $h \cdot d^{-1}$). However, this adjustment requires a shorter exposure study considering the most relevant route of exposure to derive the point of departure for the DNEL. In case the longer duration studies show relevant effects that are not covered by the shorter studies, the study resulting in the lowest DNEL should be selected. In the absence of relevant short-term (e.g., sub-acute) inhalation exposure studies, the DNEL should not be adjusted for infrequent exposure. Additionally, exposure frequency of ≥ 15 days per year seems possible for costume masks and can be regarded as a realistic worst-case scenario.

The adjustment for shorter duration of exposure during a day can be performed by using modified Haber's Law, as stated in the ECHA guidance[6]. This adjustment should be carried out on the exposure side and hence the exposure concentrations should be divided by the respective adjustment factors to assess a potential risk: exposure by a factor of 4.5 for exposures ≤ 15 $min \cdot d^{-1}$, a factor of 3 for exposures ≤ 1 $h \cdot d^{-1}$, a factor of 2 for exposures ≤ 3 $h \cdot d^{-1}$ and a factor of 1.5 for exposures ≤ 8 $h \cdot d^{-1}$. An exposure time between 1 and 3 $h \cdot d^{-1}$ is plausible and thus an adjustment factor of 2 can be applied, which still results in exposure concentrations exceeding the DNEL for some of the masks.

**Table S4: Overview of derivation of DNELs for workers and general population exposed to cyclohexanone by the inhalation route.**

| **Point of departure for long-term DNEL derivation from Lim et al., 2018[5]** | | |
|---|---|---|
| 90-day whole-body inhalation study, rat (F344), 6h·$d^{-1}$, 5d·$week^{-1}$ | | |
| NOAEC | **401 mg·$m^{-3}$** | |
| Default inhalation absorption | 100% | |
| **Derivation of reference DNELs** | | |
| | WORKERS | GENERAL POPULATION |
| **Assessment Factors** | | |
| Extrapolation LOAEL to NOAEL | - | - |
| Interspecies | 2.5 | 2.5 |
| Intraspecies | 5 | 10 |
| Subchronic to chronic | 2 | 2 |
| **Inhalation** | | |
| Correction for exposure regime (d·$week^{-1}$) | - | 5 / 7 |
| Correction for exposure regime (h·$d^{-1}$) | 6 / 8 | 6 / 24 |
| Breathing rate for workers light activity vs rest | 6.7 / 10 | - |
| Corrected NOAEC (mg·$m^{-3}$) | 201.5 | 71.6 |
| Overall assessment factor (multiplication of assessment factors) | 25 | 50 |
| **Long-term DNEL inhalation (mg·$m^{-3}$)** | **8.1** | **1.4** |

# ABBREVIATIONS

BHT, butylated hydroxytoluene; bp, boiling point; bw, body weight; CAS, Chemical Abstracts Service; DHS, dynamic headspace; DNEL, derived no-effect level; ECHA, European Chemicals Agency; GC, gas chromatography; LOAEL, Low Observed Adverse Effect Level; MS, mass spectrometry; NIST, National Institute of Standards and Technology; NOAEC, No Observed Adverse Effect Concentration; NOAEL, No Observed Adverse Effect Level; POD, point of departure; Qual, qualifier ion; Quant, quantifier ion; RI, retention index; SIM, selected ion monitoring; tr, retention time; TXIB, [2,2,4-trimethyl-3-(2-methylpropanoyloxy)pentyl]-2-methylpropanoate VOC, volatile organic compound

# REFERENCES

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