

Article

Volatile Organic Compound (VOC) Emissions from a Personal Care Polymer-Based Item: Simulation of the Inhalation Exposure Scenario Indoors under Actual Conditions of Use

Jolanda Palmisani ^{*}, Alessia Di Gilio ^{*}, Ezia Cisternino, Maria Tutino and Gianluigi de Gennaro 

Department of Biology, University of Bari Aldo Moro, via Orabona 4, 70125 Bari, Italy; ezia.cisternino@gmail.com (E.C.); mariatutino2015@gmail.com (M.T.); gianluigi.degennaro@uniba.it (G.d.G.)

^{*} Correspondence: jolanda.palmisani@uniba.it (J.P.); alessia.digilio@uniba.it (A.D.G.);

Tel.: +39-08-0544-3343 (J.P.)

Received: 19 February 2020; Accepted: 16 March 2020; Published: 25 March 2020



Abstract: Polymer-based items may release Volatile Organic Compounds (VOCs) and odors indoors, contributing to the overall VOC inhalation exposure for end users and building occupants. The main objective of the present study is the evaluation of short-term inhalation exposure to VOCs due to the use of a personal care polymer-based item, namely, one of three electric heating bags, through a strategic methodological approach and the simulation of a ‘near-to-real’ exposure scenario. Seventy two-hour test chamber experiments were first performed to characterize VOC emissions with the items on ‘not-heating mode’ and to derive related emission rates. The polyester bag was revealed to be responsible for the highest emissions both in terms of total VOC and naphthalene emissions (437 and 360 $\mu\text{g}/\text{m}^3$, respectively), compared with the other two bags under investigation. Complementary investigations on ‘heating mode’ and the simulation of the exposure scenario inside a 30 m^3 reference room allowed us to highlight that the use of the polyester bag in the first life-cycle period could determine a naphthalene concentration (42 $\mu\text{g}/\text{m}^3$) higher than the reference Lowest Concentration of Interest (LCI) value (10 $\mu\text{g}/\text{m}^3$) reported in European evaluation schemes. The present study proposes a strategic methodological approach highlighting the need for the simulation of a realistic scenario when potential hazards for human health need to be assessed.

Keywords: VOCs; polymer-based items; indoor air quality; test emission chamber; exposure scenario

1. Introduction

Volatile Organic Compound (VOC) emissions from indoor materials and consumer products have become a subject of concern among indoor air scientists [1–4]. VOCs released into indoor air from a wide range of materials and products may deteriorate Indoor Air Quality (IAQ), resulting in odor annoyance and general discomfort for building occupants as well as adverse effects on human health [5–11]. So far, the interest of indoor air scientists in this issue has been mainly motivated by the need to improve the knowledge regarding sources and their emission characteristics in both private and public settings, to investigate further the physical and chemical interactions of emitted pollutants in indoor air, and to develop innovative methodological approaches for the evaluation of emissions and their potential impacts on human health. Building and interior materials have been widely investigated in terms of VOC emissions, as highlighted by an extensive literature in the field. On the contrary, limited data are available on consumer product emissions and related inhalation exposure for end users. Recently published studies have pointed out that consumer products and polymer-based items may

release VOCs and odors indoors, contributing significantly to the overall VOC exposure of consumers and building occupants [12–17]. Moreover, complaints about odor annoyance from polymer-based consumer products have enhanced the need for in-depth investigations aimed at elucidating emission patterns and characteristics. In this regard, investigations carried out on selected polymer-based items such as plastic utensils and children's toys highlighted that VOC emissions are related to the release of residual solvents and monomers from the material polymeric structure and/or the release of additives (i.e., plasticizers, inks) following surface-applied finishing processes such as coloring and printing [18–21]. VOC emissions from materials and products (i.e., building materials, furnishings, finishing products etc.) are conventionally evaluated by means of test emission chambers according to well-established procedures, standardized by the European Committee for Standardization (CEN) and by the International Organization for Standardization (ISO) [22,23]. More specifically, identification and quantification of VOCs from single or multiple sources requires emission testing inside test chambers, over a defined timescale and with selected micro-environmental parameters (i.e., temperature, relative humidity, air exchange rate) [24]. Small-scale emission testing generally fits investigation purposes when the determination of emission rates from specific materials and products is required, while large-scale experiments are more suitable for simulating realistic inhalation exposure scenarios for building occupants and consumers due to material installation and/or product use. However, some considerations regarding this point are necessary. Although testing procedures are standardized to obtain reliable data on emission characteristics, they may reveal some limitations when applied to consumer products, especially if the evaluation of emissions under actual conditions of use is required. Indeed, it is important to point out that VOC emission characteristics, in terms of the pattern of generated compounds and extent of the emission, may significantly vary during product/item use, particularly if the use involves combustion and/or heating, resulting in exposure scenarios being substantially different [25]. This typology of indoor sources is characterized by short-term emission patterns during the actual use and requires a realistic scenario to be simulated in the test emission chamber. Therefore, in these cases, the integration of conventional procedures (e.g., standardized emission testing) with complementary and innovative methodological approaches can be strategic to answer key questions on VOC emissions under effective conditions of use. The main objective of the present study is the evaluation of VOC emissions from a personal care polymer-based item, an electric heating bag, commonly used to relieve stress and reduce muscle and joint pain. The investigated item must be electrically supplied, therefore emission characteristics may significantly change under conditions of use. For this purpose, the present paper proposes a strategic methodological approach for the estimation of the inhalation exposure to VOCs emitted by the investigated items on 'heating mode' in a real setting, starting from emission data obtained through standardized methods and under controlled conditions. The experimental activity involved test emission chamber and dynamic head-space investigations on three different heating bags, commercially available at the moment of the study and also responsible for odor annoyance at ambient temperature.

Data collected were useful for the estimation of VOC emission rates (ERs) under actual conditions of use and, as a result, for the estimation of the indoor concentrations representative of short-term exposure related to the item use during the first life-cycle period in a realistic setting (e.g., reference room of EU standardized evaluation schemes), allowing the simulation of a near-to-real exposure scenario.

2. Materials and Methods

2.1. Chemicals

Authentic standards of the VOCs under consideration in the present study were included in a customized VOC standard mix in ethanol (Ultra Scientific Analytical Solutions, Italia srl). Ethanol of analytical grade was purchased by Sigma Aldrich and used as a solvent for the preparation of calibration standards.

2.2. Polymer-Based Item Description

The polymeric item under investigation is a portable electric heating bag commonly used for general comfort and/or for therapeutic purposes (i.e., warming during the winter season, reduction of muscle pain and stress). This typology of personal care item has quickly become very popular on the European (EU) market during recent years and received board consensus as it represents a low-cost and easy-to-use version of the conventional warming bag that needed to be filled with hot water to work. Electric heating bags generally appear as small bags made of polymeric material (i.e., polyvinylchloride, polyester) covering the inner bag filled with the heating liquid, provided with a plug base cover and electric cable for heating. They must be electrically supplied to provide their function and, after a few minutes of electrical charge (e.g., 5–10 min), they can be used at high temperature for at least one hour. In the present study, three different heating bags were investigated. They were all manufactured in China, distributed on the EU market and labeled with three different brands (reported as brand A, B and C). More specifically, the first one belonging to brand A was characterized by a printed and colored external coverage made of polyester (labeled in the text and tables as 'polyester-brand A'). The other two bags, belonging to brands B and C, respectively, were instead characterized by an external coverage made of polyvinylchloride (labeled in the text and tables as 'PVC-brand B' and 'PVC-brand C'). The former had an image printed onto the surface of one side, while the latter was only colored. All the investigated bags had the same shape and dimensions with an upper surface area equal to 0.04 m². They were part of a production lot blocked by competent authorities at port customs in a city in the South of Italy (City of Monopoli) after reporting from consumer associations. Due to end user complaints related to strong odor annoyance occurring at a greater extent during the first use events, local competent authorities formally requested the necessary investigations. At the moment of the study, the introduction on the EU market of electric heating bags manufactured in non-EU countries (e.g., China) was allowed with only the CE label ensuring electric safety and conformity in compliance with EU Directive requirements.

2.3. Experimental Design Description

The first investigation level involved 72-hour emission testing inside a small-scale emission chamber under standardized environmental conditions, according to the relevant ISO standards. As a result, emission rates (ERs) for the main detected VOCs were derived, useful for the estimation of indoor concentrations potentially determined by the item in a real setting at ambient temperature (i.e., 'not-heating' mode) and representative of a short-term exposure. This investigation level, although conventionally applied to materials and products for providing data on emission characteristics under simulated indoor conditions, was not exhaustive for the estimation of VOC inhalation exposure levels determined by the item in a real room under the actual conditions of use. In order to derive ERs under heating, non-time-consuming and cost-effective dynamic head-space experiments were performed, placing the investigated items inside customized Nalophan bags. The effect of temperature on VOC emissions from the items was evaluated, and its extent was expressed in terms of the ratio of chromatographic peak areas obtained by GC/MS analysis of the samples collected both at laboratory ambient temperature (approximately 23 °C) and under heating. This second level of investigation allowed us to estimate ERs under heating (starting from ERs derived from 72-hours data inside the chamber) and, as a result, indoor concentrations inside the reference room representative of a realistic short-term exposure scenario for end users.

2.3.1. Test Emission Chamber Experiments

Experiments were carried out inside a small-scale test emission chamber, a hermetically closed glass chemical reactor with a cylindrical shape and with the following dimensions: diameter = 29 cm, height = 61 cm and volume = 0.05 m³. Teflon fans were installed at the top of the chamber to ensure that the air was adequately mixed. The test emission chamber was operated with controlled micro-environmental

parameters, according to the relevant ISO standard. For each experiment, temperature and relative humidity were 23 ± 2 °C and $50 \pm 5\%$, respectively. Air exchange rate (AER) was 0.5 ± 0.1 h⁻¹, which agrees with many European building standards for ventilation in indoor environments [26]. The chamber was supplied with ultrapure compressed air (VOC-free air). Before each experiment, the chamber was cleaned with detergent and rinsed with distilled water, and background samples were taken in order to verify VOC levels. The electric heating bag was introduced inside the chamber, and the test started when the chamber was closed ($t = 0$). Each experiment lasted 72 h and was carried out with the heating bag not electrically supplied ('not-heating mode') as the test chamber configuration was not suitable to carry out the experiments allowing electrical connections between the warming bag (inside the chamber) and outside. The test emission chamber was provided with two outlet ducts to allow chamber air to be monitored by high temporal resolution instrumentation and/or collected onto adsorbent cartridges. In the present study, Total Volatile Organic Compounds (TVOC) concentration was monitored by means of a high temporal resolution photo-ionization detector (PhoCheck[®] Tiger, Ion Science Ltd., UK), over the entire duration of the test, in order to verify the achievement of a steady state concentration inside the test emission chamber. VOCs were sampled in duplicate on suitable adsorbent cartridges by means of calibrated sampling pumps (Pocket pump). Adsorbent cartridges consisted of a cylindrical stainless steel net (100 mesh) containing 350 mg Carbograph 4 (35–50 mesh). Air samples were collected at 72 h after the start of the chamber experiment, with a sampling flow rate of 50 mL/min and a sampling time of 100 min, resulting in a collected air volume of 5 L.

2.3.2. Dynamic Head-Space (DHS) Experiments

Temperature-related effect on VOC emissions from the investigated items under conditions of use was evaluated by performing small-scale dynamic head-space (DHS) experiments inside customized Nalophan bags. Once the item was introduced inside the Nalophan bag, each extremity was tightly closed to avoid any kind of contamination from outside. A pressure-regulator stainless steel line, connected to an ultrapure-grade and VOC-free air cylinder, was introduced through one Nalophan bag extremity, allowing air to enter at constant air flow (50 mL/min). Through the same extremity, the electric cable connected the power outlet to the plug base cover, allowing the item to be electrically supplied. VOCs were sampled through a Teflon tube introduced at the opposite extremity of the Nalophan bag by means of a flow-controlled pump (Pocket Pump) and collected onto Carbograph 4 adsorbent cartridges (35–50 mesh). Two separate experiments were carried out for each investigated item: experiment 1 with the item at ambient temperature (i.e., 'not-heating mode'); experiment 2 with the item electrically supplied (i.e., 'heating mode'), covering the entire heating phase, the achievement of the temperature intended for use and the bag cooling. Experiment 2 involved each item at its first use. The temperature reached by the items once the heating process was completed was on average 55 °C. Air sampling for experiments 1 and 2 was performed with the same sampling flow rate (50 mL/min) and sampling time (100 min). Two sorbent tubes were connected in series in case of VOC breakthrough.

2.3.3. GC/MS Instrumental Analysis Setup

Adsorbent cartridges were thermally desorbed and analyzed on a thermal desorber (UNITY 1[™], Markes International Ltd.) coupled to a gas chromatograph (Agilent GC-6890) and a mass selective detector (Agilent MS-5973N). For quality assurance, adsorbent cartridges were conditioned before each use at 310 °C for 30 min and analyzed to verify the blank level. The chamber air background was also evaluated before each experiment. VOCs were thermally desorbed at 300 °C for 10 min and refocused onto the cold trap at -10 °C. The cold trap was then flash-heated at 300 °C, and VOCs were transferred via the heated transfer line (180 °C) to the GC column. The GC column was a 30 m × 250 µm × 0.25 µm film thickness with (5%-phenyl)-methylpolysiloxane stationary phase (J&W HP5-MS, Agilent Technologies). Carrier gas (helium) flow was controlled by constant pressure mode and equal to 1.3 mL min⁻¹. The GC oven program used for optimal VOC separation was: 40 °C for 1 min, ramp 1: 8 °C min⁻¹ up to 80 °C, ramp 2: 20 °C min⁻¹ up to 270 °C. A mass spectrometer was operated in

electron impact (EI) ionization mode (70eV) in the mass range 25–250 m/z (SCAN acquisition mode, TIC chromatogram). Valves, transfer lines and ion source were kept at 280 °C. Single-target ions were extracted in selected ion monitoring (SIM) mode for compound identification and quantification. One quantifier ion and one qualifier ion were selected for each compound on the basis of their selectivity and abundance (Table 1). Six standard solutions with concentration levels 10, 20, 50, 100, 200 and 400 µg/mL were prepared by successive dilution in ethanol of a certified VOC standard mixture (ULTRA Scientific Italia s.r.l, Bologna, Italy). Six-point calibration curves were constructed by syringe injection of 1 µL of VOC standard solutions onto Carbograph 4 cartridges. Identification of VOCs was based on comparison of the obtained mass spectra with those included in the National Institute of Standards and Technology (NIST) library and considered positive by library search match > 800 for both forward and reverse matching. Further criteria for compound identification were: (i) the matching of relative retention times (t_R) with those of the authentic standards within the allowed deviation of ± 0.05 min; (ii) the matching of ion ratios collected with those of the authentic standards within a tolerance of $\pm 20\%$. Only VOCs of particular concern due to potential adverse effects on human health and with a chamber air concentration approximately equal to or higher than 1 µg/m³ were taken into account for further discussion. The list of VOCs (common for the three different investigated items) and related information (molecular formula, CAS number, quantifier and qualifier ions), as well as the performances of the analytical methodology in terms of Limit of Detection (LOD), Limit of Quantification (LOQ) and correlation coefficients (R^2), are reported in Table 1.

Table 1. Volatile Organic Compounds (VOCs) emitted by the heating bag: molecular formula, CAS number, retention time (t_R), quantifier and qualifier ions (m/z), Limit of Detection (LOD) (µg/m³), Limit of Quantification (LOQ) (µg/m³) and correlation coefficient (R^2).

Compound	Molecular Formula	CAS Number	t_R (min)	Quantifier Ion (m/z)	Qualifier Ion (m/z)	LOD (µg/m ³)	LOQ (µg/m ³)	R^2
1,2-dichloroethane	C ₂ H ₄ Cl ₂	107-06-2	1.64	62	64	0.02	0.07	0.970
Benzene	C ₆ H ₆	71-43-2	1.72	78	52	0.03	0.09	0.994
Toluene	C ₇ H ₈	108-88-3	2.83	91	92	0.02	0.07	0.992
Tetrachloroethene	C ₂ Cl ₄	127-18-4	3.56	166	164/129	0.05	0.15	0.970
Chlorobenzene	C ₆ H ₅ Cl	108-90-7	4.35	112	77	0.03	0.09	0.970
Ethylbenzene	C ₈ H ₁₀	100-41-4	4.72	91	106	0.03	0.09	0.997
m-xylene	C ₈ H ₁₀	108-38-3	4.93	91	106	0.04	0.11	0.996
p-xylene	C ₈ H ₁₀	106-42-3	4.93	91	106	0.04	0.11	0.996
Styrene	C ₈ H ₈	100-42-5	5.51	104	78	0.05	0.16	0.998
o-xylene	C ₈ H ₁₀	95-47-6	5.55	91	106	0.04	0.12	0.997
3-ethyltoluene	C ₉ H ₁₂	620-14-4	7.74	105	120	0.1	0.3	0.998
1,3,5-trimethylbenzene	C ₉ H ₁₂	108-67-8	7.97	105	120	0.1	0.29	0.997
2-ethyltoluene	C ₉ H ₁₂	611-14-3	8.35	105	120	0.1	0.3	0.998
1,2,4-trimethylbenzene	C ₉ H ₁₂	95-63-6	8.83	105	120	0.1	0.29	0.997
1,2,3-trimethylbenzene	C ₉ H ₁₂	526-73-8	9.85	105	120	0.1	0.29	0.997
4-isopropyltoluene	C ₁₀ H ₁₄	99-87-6	10.02	119	134	0.03	0.08	0.939
Acetophenone	C ₈ H ₈ O	98-86-2	11.69	105	77	0.03	0.1	1.000
Naphthalene	C ₁₀ H ₈	91-20-3	15.92	128	127	0.03	0.09	0.999

2.3.4. Test Chamber Experiments: Emission Rates (ERs) and Estimation of Reference Room Indoor Concentrations ($C_{i,ref}$)

The primary objective of emission testing is the determination of VOC specific emission rates (SERs), enabling description of the emission behavior of the material/product regardless of air exchange rate and loading factor. According to ISO standards and most of the existing health-related evaluation schemes at EU level, VOC specific emission rates are calculated at fixed sampling times, e.g., 3 and 28 days after the introduction of the material inside the test emission chamber [27]. The determination of specific emission rates for any individual VOC detected is addressed to model the exposure scenario and to estimate indoor air concentrations that an occupant of a real-scale room could be exposed to. More specifically, VOC specific emission rates derived at 3 days allow the estimation of indoor concentrations representative of short-term exposure. In the present study, the emission rate for

compound i (ER_i) emitted by the electric heating bag at 72 h in the test chamber experiment was calculated on the basis of the mass conservation Equation (1):

$$ER_i = C_i \times V \times n \quad (1)$$

where C_i is the chamber concentration of compound i in the air sampled at 72 h (expressed as $\mu\text{g}/\text{m}^3$ or ng/m^3); V is the chamber volume (m^3); and n is the air exchange rate (h^{-1}). Starting from ER_i , individual VOC indoor concentrations resulting from the presence or use of the investigated item inside the 30 m^3 reference room ($C_{i,ref}$) may be estimated via the following formula:

$$C_{i,ref} = \frac{ER_i}{n \times V} \quad (2)$$

with n and V representing the air exchange rate (0.5 h^{-1}) and volume (30 m^3) of the reference room, respectively.

3. Results and Discussion

3.1. Test Chamber Experiments: Characterization of VOC Emissions and Determination of Emission Rates (ERs)

VOCs reported in Table 2 represent the pattern of gaseous pollutants identified and quantified by test chamber experiments performed under controlled conditions and with the electric bags on ‘not-heating mode’. VOC emission data are expressed as emission rates (ERs) (ng/h) and chamber air concentrations ($\mu\text{g}/\text{m}^3$), with the latter reported as an average value of duplicate measurements corrected for chamber background. If a preliminary comparison among the investigated items is done, emission testing of the heating bag ‘polyester-brand A’ resulted in the highest total VOC chamber concentration at 72 h sampling time. More specifically, for ‘polyester-brand A’ the total emission expressed as the sum of concentrations of VOCs (ΣVOCs , $\mu\text{g}/\text{m}^3$) was equal to $437.0 \mu\text{g}/\text{m}^3$, one order of magnitude higher than those obtained for ‘PVC-brand B’ ($21.1 \mu\text{g}/\text{m}^3$) and ‘PVC-brand C’ ($19.6 \mu\text{g}/\text{m}^3$). In detail, VOC chamber concentrations for ‘polyester-brand A’ ranged from $0.7 \mu\text{g}/\text{m}^3$ (benzene) to $360.5 \mu\text{g}/\text{m}^3$ (naphthalene), whilst 1,2-dichloroethane and tetrachloroethene were both below the LOQ of the applied analytical technique. As a result, the emission rates (ERs, ng/h), calculated by equation (1), ranged from $18 \text{ ng}/\text{h}$ to $9013 \text{ ng}/\text{h}$. VOC chamber concentrations and ERs for ‘PVC-brand B’ ranged from $0.6 \mu\text{g}/\text{m}^3$ (benzene) to $6.8 \mu\text{g}/\text{m}^3$ (toluene) and from 15 to $171 \text{ ng}/\text{h}$, respectively. Finally, VOC chamber concentrations for ‘PVC-brand C’ were in the range from $0.7 \mu\text{g}/\text{m}^3$ (i.e., 1,2-dichloroethane and 1,2,3-trimethylbenzene) to $4.8 \mu\text{g}/\text{m}^3$ (toluene) and, as a result, ER values ranged from a minimum value of $16 \text{ ng}/\text{h}$ to a maximum value of $121 \text{ ng}/\text{h}$. For both ‘PVC-brand B’ and ‘PVC-brand C’, 2-ethyltoluene, 3-ethyltoluene, 4-isopropyltoluene and acetophenone were below the LOQ. Additionally, 1,2-dichloroethane and benzene were below the LOQ for ‘PVC-brand B’ and ‘PVC-brand C’, respectively. Therefore, taking into account all the collected data, it is possible to observe that, whilst VOC emissions from PVC items resulted to be comparable in terms of concentration levels (for both the heating bags, chamber concentrations were generally below $10 \mu\text{g}/\text{m}^3$), the most remarkable result was regarding the naphthalene emission from ‘polyester-brand A’, which resulted in a chamber concentration at 72 h equal to $360.5 \mu\text{g}/\text{m}^3$. Previously published studies have already highlighted that materials and consumer products are responsible for naphthalene emissions and may significantly contribute to naphthalene inhalation exposure inside indoor environments [28]. Screening investigations reported by Kang et al. (2012) aimed at the identification of sources revealed that, disregarding specific sources intended to contain pure crystalline naphthalene (e.g., mothballs), interior materials as well as several consumer products may unintentionally emit naphthalene. The aforementioned study also highlighted that, across the interior materials investigated, mats consisting of PVC-coated polyester material showed the highest naphthalene emission factor, confirming that naphthalene is involved in the production and finishing of these polymeric materials. Naphthalene is,

indeed, primarily used as a chemical intermediate for phthalic anhydride and naphthalene sulphonate production, both involved in the industry manufacture of plasticizers, dyes and rubber formulations. Moreover, according to the existing literature, aromatic hydrocarbon release from polymeric materials (PVC, polyester) used as covering for interior materials such as wallpapers and flooring materials as well as polymeric items such as children toys may be mainly explained by taking into account the use of specific solvents in the manufacturing process such as toluene, ethylbenzene, isopropylbenzene and potential related impurities [4,19,29].

Table 2. Test chamber concentrations ($\mu\text{g}/\text{m}^3$) at 72 h and related emission rates (ERs, ng/h) for VOCs emitted by the investigated bags on ‘not-heating mode’.

Compounds	POLYESTER-Brand A		PVC-Brand B		PVC-Brand C	
	Chamber Conc. ($\mu\text{g}/\text{m}^3$)	ER (ng/h)	Chamber Conc. ($\mu\text{g}/\text{m}^3$)	ER (ng/h)	Chamber Conc. ($\mu\text{g}/\text{m}^3$)	ER (ng/h)
1,2-dichloroethane	<LOQ	/	<LOQ	/	0.7	16
Benzene	0.7	18	0.6	15	<LOQ	/
Toluene	19.4	485	6.8	171	4.8	121
Tetrachloroethene	<LOQ	/	/	/	1.3	33
Chlorobenzene	4.5	113	0.9	24	2.7	67
Ethylbenzene	1.5	38	1.2	29	1.5	38
m/p-xylene	1.9	48	1.3	32	1.9	47
Styrene	2.8	70	1.5	38	2.3	57
o-xylene	5.3	133	1.0	24	1.2	29
3-ethyltoluene	4.8	120	<LOQ	/	<LOQ	/
1,3,5-trimethylbenzene	3.3	83	0.8	19	0.8	19
2-ethyltoluene	2.6	65	<LOQ	/	<LOQ	/
1,2,4-trimethylbenzene	15.2	380	0.9	24	0.8	20
1,2,3-trimethylbenzene	8.4	210	0.8	20	0.7	18
4-isopropyltoluene	2.5	63	<LOQ	/	<LOQ	/
Acetophenone	3.6	90	<LOQ	/	<LOQ	/
Naphthalene	360.5	9013	5.3	133	1.0	10
ΣVOCs	437.0		21.1		19.6	

3.2. Estimation of Emission Rates (ERs) on ‘Heating Mode’

Estimated VOC emission rates from the investigated items on ‘heating mode’ are listed in Table 3. They were estimated starting from the emission rate values derived for ‘not-heating mode’ through 72-hour test chamber experiments and taking into account the GC-MS peak area ratios obtained by dynamic head-space investigations, performed both for ‘not-heating mode’ and ‘heating mode’. Overall, as expected, the high temperature acquired during the heating process affected VOC emissions behavior from all the investigated bags. From a lesser to greater extent, the emission process of the selected VOCs was promoted. With specific regard to the ‘polyester-brand A’ bag, the GC-MS peak area ratios suggest that naphthalene was the most sensitive compound to the temperature change. The estimated naphthalene emission rate when the bag was on ‘heating mode’, indeed, was revealed to be 70 times higher than the calculated emission rate on ‘not-heating mode’, with a variation from 9013 ng/h to 630.9 $\mu\text{g}/\text{h}$. For all the other VOCs, the estimated emission rates ranged from a minimum value of 0.20 $\mu\text{g}/\text{h}$ for benzene to a maximum value of 6.79 $\mu\text{g}/\text{h}$ for toluene. From the comparison of HS experimental data reported in Table 3, it is possible to observe that the estimated emission rates for the VOCs of concern emitted by ‘PVC-brand B’ and ‘PVC-brand C’ were generally lower compared with those estimated for ‘polyester-brand A’. This evidence is not related to temperature because the effect of heating on the emission process is comparable for all the three investigated bags, with peak area ratios of the same order of magnitude. It is, instead, attributable to the starting values of emission rates for ‘PVC-brand B’ and ‘PVC-brand C’ calculated from test chamber experiments being generally

lower than those for 'polyester-brand A'. More specifically, estimated emission rates for 'PVC-brand B' and 'PVC-brand C' on 'heating mode' were in the range 0.11–11.2 $\mu\text{g/h}$ and 0.03–2.9 $\mu\text{g/h}$, respectively. Similarly to 'polyester-brand A', the increase in temperature significantly affected the naphthalene emission from 'PVC-brand B', resulting in an estimated emission rate on 'heating mode' 109 times higher with respect to 'not-heating mode' (with an increase from 113 ng/h to 11.2 $\mu\text{g/h}$). The remarkable effect of the high temperature on the naphthalene emissions observed for both 'polyester-brand A' and 'PVC-brand B' but not for 'PVC-brand C' may be explained by taking into account the different surface treatments. The 'polyester-brand A' and 'PVC-brand B' bags, indeed, had an external coverage characterized by an image applied onto the surface. On the contrary, the coverage of 'PVC-brand C' was only colored. The surface treatment for image application may be responsible for the higher naphthalene emission rates both on 'heating mode' and 'not-heating mode' because it is known, as highlighted above, that naphthalene is used for the production of plasticizers and dyes. Moreover, the use of naphthalene in surface treatment to preserve the items from any kind of deterioration during long-range transport cannot be excluded, i.e., naphthalene used as a repellent for undesired insects or as anti-mold. As regards all the other VOCs, taking into account the peak area ratios representing the effect of the heating process on emission behavior, it is reasonable to make the assumption that the high temperature promoted the diffusion process of compounds through the polymeric bulk and, as a result, the emission from the surface. The emitted VOCs indeed seem to be incorporated in the polymeric structure as residues, and related contaminants of the solvents used in the polymer manufacturing process, unlike naphthalene, seem to be more abundant on the surface layer.

Table 3. Estimation of VOC emission rates (ERs, $\mu\text{g/h}$) for the investigated bags on 'heating mode'.

Compounds	POLYESTER-Brand A			PVC-Brand B			PVC-Brand C		
	ER (ng/h)	Peak Area Ratio	ER ($\mu\text{g/h}$) —Heating	ER (ng/h)	Peak Area Ratio	ER ($\mu\text{g/h}$) —Heating	ER (ng/h)	Peak Area Ratio	ER ($\mu\text{g/h}$) —Heating
1,2-dichloroethane	/	/	/	/	/	/	16	11	0.18
Benzene	18	11	0.20	15	7	0.11	/	/	/
Toluene	485	14	6.79	171	15	2.57	121	9	1.09
Tetrachloroethane	/	/	/	/	/	/	33	8	0.26
Chlorobenzene	113	37	4.18	24	9	0.22	67	43	2.9
Ethylbenzene	38	11	0.42	29	10	0.29	38	25	0.95
m/p-xylene	48	9	0.43	32	9	0.29	47	15	0.71
Styrene	70	10	0.70	38	9	0.34	57	38	2.2
o-xylene	133	12	1.60	24	10	0.24	29	17	0.49
3-ethyltoluene	120	12	1.44	/	/	/	/	/	/
1,3,5-trimethylbenzene	83	18	1.5	19	11	0.21	19	17	0.32
2-ethyltoluene	65	21	1.4	/	/	/	/	/	/
1,2,4-trimethylbenzene	380	19	7.22	24	18	0.43	20	15	0.30
1,2,3-trimethylbenzene	210	30	6.30	20	20	0.40	18	14	0.25
4-isopropyltoluene	63	9	0.57	/	/	/	/	/	/
Acetophenone	90	28	2.5	/	/	/	/	/	/
Naphthalene	9013	70	630.9	133	109	11.2	10	3	0.03

3.3. Simulation of a Short-Term Exposure Scenario: Estimation of Room Reference Concentrations ($C_{i,\text{ref}}$) and Health-Related Evaluation

Once the emission rates for 'heating mode' were estimated, indoor concentrations potentially determined by each single bag under actual conditions of use were derived (Table 4). The exposure scenario taken into account is representative of a short-term inhalation exposure related to the use of the heating bag during the first period of its life-cycle. Moreover, the exposure scenario considers only one bag under heating in a 30 m^3 room resulting in VOC emissions, promoted by high temperature, diluted in the entire volume of the room. For this reason, in the present work, the estimated room reference concentration values that room occupants could be exposed to are low for all the three investigated bags, ranging overall, with the only exception of naphthalene, from 0.01 $\mu\text{g}/\text{m}^3$ (benzene for 'polyester-brand A'; benzene, chlorobenzene, and 1,3,5-trimethylbenzene for 'PVC-brand B'; 1,2-dichloroethane for 'PVC-brand C') to 0.48 $\mu\text{g}/\text{m}^3$ (1,2,4,-trimethylbenzene for 'polyester-brand A'). Attention has to be

paid, instead, to the potential inhalation exposure to naphthalene occurring when the polyester bag is used, according to the selected scenario. On the basis of the obtained results, it may be predicted that, as a consequence of the heating process, the naphthalene indoor concentration determined by the polyester bag in a real setting would be equal to about $42 \mu\text{g}/\text{m}^3$. This evidence is worthy of further discussion as human exposure to naphthalene has been recognized as a public health concern due to demonstrated harmful effects [30]. Naphthalene is indeed classified as a possible human carcinogen (group 2B) by the International Agency for Research on Cancer (IARC) and is included in EU category Carc.2 on the basis of experimental evidence in animals regarding an increased risk of contracting respiratory tract cancer [31,32]. Health-based evaluation of VOC emissions from materials is generally based on the comparison of room reference concentrations for individual compounds with guideline values. In order to assess the potential risks to health arising from inhalation exposure to individual VOCs, most of the existing health-related evaluation schemes at European level are based on the LCI (Lowest Concentration of Interest) approach. The proposed EU-LCI values are health-based reference concentrations for inhalation exposure intended as 'safe' levels where no health impairment is expected, even with a life-long exposure. EU-LCI levels, however, are usually compared to indoor concentrations representative of long-term exposure and based on emission rates derived after 28 days of chamber testing. This basic assumption would apparently limit our discussion, not allowing us to highlight if potential health risks for inhalation exposure could occur in the case of 'polyester-brand A' heating bag use. Therefore, in this regard, clarification is needed. Taking into account the most comprehensive evaluation scheme at EU level, the German AgBB scheme 'Evaluation procedure for VOC emissions from building products', chemicals with potential carcinogenic effects belonging to EU category Carc.2 are also eligible to be checked within the LCI concept at the first step of the evaluation scheme, related to 3-day chamber testing [27]. The room reference concentration estimated for naphthalene ($42 \mu\text{g}/\text{m}^3$), therefore, is eligible to be compared with the LCI value equal to $10 \mu\text{g}/\text{m}^3$. From the comparison, it is possible to state that the actual use of the 'polyester-brand A' heating bag in the first period of its life-cycle could determine a naphthalene concentration inside a 30 m^3 room eight times higher than the reference LCI value. The inhalation exposure to naphthalene emission could represent, therefore, a risk for end users and room occupants. It is also important to point out that the item under investigation is intended to be used very close to the human upper airways, and the resulting exposure may be exacerbated. Moreover, the ventilation inside a real setting may be reduced with respect to the 'ideal' conditions (e.g., 0.5 h^{-1} air exchange rate), leading to higher VOC concentrations in the air volume in proximity with the item, and therefore close to the breathing zone, compared with the rest of the room [33]. Finally, although the most remarkable result has to be attributed to the naphthalene emission from the 'polyester-brand A' bag, it should be noted that both 'polyester-brand A' and 'PVC-brand B' released benzene, recognized as a carcinogen in humans for which no safe level of inhalation exposure can be recommended. In this regard, the World Health Organization pronounced a suggestion to reduce or eliminate the use of materials that are able to release benzene [30].

Table 4. Simulation of a short-term exposure scenario: estimation of room reference concentrations ($C_{i,ref}$, $\mu\text{g}/\text{m}^3$) determined by bags on ‘heating mode’.

Compounds	POLYESTER-Brand A		PVC-Brand B		PVC-Brand C	
	ER Heating ($\mu\text{g}/\text{h}$)	$C_{i,ref}$ ($\mu\text{g}/\text{m}^3$)	ER Heating ($\mu\text{g}/\text{h}$)	$C_{i,ref}$ ($\mu\text{g}/\text{m}^3$)	ER Heating ($\mu\text{g}/\text{h}$)	$C_{i,ref}$ ($\mu\text{g}/\text{m}^3$)
1,2-dichloroethane	/	/	/	/	0.18	0.01
Benzene	0.20	0.01	0.11	0.01	/	/
Toluene	6.79	0.45	2.57	0.17	1.09	0.07
Tetrachloroethene	/	/	/	/	0.26	0.02
Chlorobenzene	4.18	0.28	0.22	0.01	2.9	0.19
Ethylbenzene	0.42	0.03	0.29	0.02	0.95	0.06
m/p-xylene	0.43	0.03	0.29	0.02	0.71	0.05
Styrene	0.70	0.05	0.34	0.02	2.2	0.14
o-xylene	1.60	0.11	0.24	0.02	0.49	0.03
3-ethyltoluene	1.44	0.10	/	/	/	/
1,3,5-trimethylbenzene	1.5	0.10	0.21	0.01	0.32	0.02
2-ethyltoluene	1.4	0.09	/	/	/	/
1,2,4-trimethylbenzene	7.22	0.48	0.43	0.03	0.30	0.02
1,2,3-trimethylbenzene	6.30	0.42	0.40	0.03	0.25	0.02
4-isopropyltoluene	0.57	0.04	/	/	/	/
Acetophenone	2.5	0.17	/	/	/	/
Naphthalene	630.9	42.06	11.2	0.75	0.03	/
ΣVOCs		44.41		1.09		0.64

3.4. Limitations of the Study

In the present study, replicated test chamber experiments under controlled conditions for each investigated bag on ‘not-heating mode’ were not carried out. In addition, investigations after 3 days in order to define VOC emission rate profiles were not performed. The aforementioned lack of data could represent a limitation of the study. However, the authors specified that the main purpose of the study was to evaluate the short-term exposure to VOC emissions resulting from the use of the heating bags during the first life-cycle time, therefore during the first use events. For this purpose, emission data from 3-day test chamber experiments were considered adequate.

4. Conclusions

The present study proposes a methodological approach for the evaluation of short-term inhalation exposure for end users handling three different personal care polymeric items, i.e., electric heating bags. A near-to-real exposure scenario was simulated for each investigated item, taking into account the actual conditions of use (‘heating mode’) during the first period of life-cycle (first use events). Test emission chamber experiments were performed according to the relevant ISO standards, allowing us to derive 72-hour chamber concentrations and emission rates (ERs) for the main identified VOCs. Collected chamber emission data revealed that, under controlled environmental conditions, the item ‘polyester-brand A’ was characterized by the highest VOC emission (expressed as the sum of VOC concentrations) equal to $437 \mu\text{g}/\text{m}^3$, one order of magnitude higher than those of the other two bags, labeled as ‘PVC-brand B’ and ‘PVC-brand C’ (21.1 and $19.6 \mu\text{g}/\text{m}^3$, respectively). A remarkable result was the naphthalene emission from ‘polyester-brand A’, with a chamber concentration equal to $360.5 \mu\text{g}/\text{m}^3$ and an emission rate of about $9 \mu\text{g}/\text{h}$. This investigation level, although conventionally applied for the evaluation of short-term exposure for materials and products, was not exhaustive for the estimation of VOC inhalation exposure levels determined by each investigated item on ‘heating mode’ in a real setting. For this purpose, the effect of the temperature on emission characteristics was evaluated through dynamic head-space experiments and, as a result, VOC emission rates for the ‘heating mode’ were estimated. Indoor concentrations inside a 30 m^3 reference room, representative of short-term exposure related to the item use in a realistic setting, were estimated as well. The simulation of the exposure scenario allowed us to highlight that the use of the ‘polyester-brand A’ heating bag in

the first period of its life-cycle could determine a concentration inside a 30 m³ room equal to 42 µg/m³, eight times higher than the reference value for health effects (LCI value equal to 10 µg/m³) reported in EU evaluation schemes. The inhalation exposure to naphthalene emission from ‘polyester-brand A’ could represent, therefore, a risk for end users and room occupants. Also of concern is the release of benzene, recognized as a carcinogen in humans, for which no safe level of inhalation exposure can be recommended.

Author Contributions: Conceptualization: J.P., G.d.G., M.T.; methodology: J.P., G.d.G., M.T.; investigation: J.P., E.C.; data curation: J.P., E.C., A.D.G.; supervision: G.d.G.; writing—original draft preparation: J.P., A.D.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors acknowledge the Operational Section ‘Pronto Impiego’ of Italian Finance Police placed in the City of Monopoli (Italy) and coordinated by the Company Commander, Luigi Mario Paone. The established collaboration was fruitful and fundamental for the development of the present study.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Salthammer, T. Release of organic compounds and particulate matter from products, materials and electrical devices in the indoor environments. Indoor air Pollution 1–35. In *Indoor Air Pollution*; Springer: Berlin/Heidelberg, Germany, 2014; Volume 64, pp. 1–35. [[CrossRef](#)]
2. De Gennaro, G.; Demarinis Loiotile, A.; Fracchiolla, R.; Palmisani, J.; Saracino, M.R.; Tutino, M. Temporal variation of VOC emission from solvent and water based wood stains. *Atmos. Environ.* **2015**, *115*, 53–61. [[CrossRef](#)]
3. Katsoyiannis, A.; Leva, P.; Barrero-Moreno, J.; Kotzias, D. Building materials. VOC emissions, diffusion behavior and implications from their use. *Environ. Pollut.* **2012**, *169*, 230–234. [[CrossRef](#)]
4. Wilke, O.; Jann, O.; Brödner, D. VOC- and SVOC-emissions from adhesives, floor coverings and complete floor structures. *Indoor Air* **2004**, *14*, 98–107. [[CrossRef](#)] [[PubMed](#)]
5. Peng, Z.; Deng, W.; Tenorio, R. Investigation of Indoor Air Quality and the Identification of Influential Factors at Primary Schools in the North of China. *Sustainability* **2017**, *9*, 1180. [[CrossRef](#)]
6. Śmiełowska, M.; Marć, M.; Zabiegala, B. Indoor air quality in public environments—A review. *Environ. Sci. Pollut. Res.* **2017**, *24*, 11166–11176. [[CrossRef](#)]
7. De Gennaro, G.; Dambruoso, P.R.; Demarinis Loiotile, A.; Di Gilio, A.; Giungato, P.; Tutino, M.; Marzocca, A.; Mazzone, A.; Palmisani, J.; Porcelli, F. Indoor air quality in schools. *Environ. Chem. Lett.* **2014**, *12*, 467–482. [[CrossRef](#)]
8. Campagnolo, D.; Saraga, D.E.; Cattaneo, A.; Spinazzè, A.; Mandin, C.; Mabilia, R.; Perreca, E.; Sakellaris, I.; Canha, N.; Mihucz, V.G.; et al. VOCs and aldehydes source identification in European office buildings—The OFFICAIR study. *Build. Environ.* **2017**, *115*, 18–24. [[CrossRef](#)]
9. Mendell, M.J. Indoor residential chemical emissions as risk factors for respiratory and allergic effects in children: A review. *Indoor Air* **2007**, *17*, 259–277. [[CrossRef](#)] [[PubMed](#)]
10. Wolkoff, P. Indoor air pollutants in office environments: Assessment of comfort, health and performance. *Int. J. Hyg. Environ. Health* **2013**, *216*, 371–394. [[CrossRef](#)]
11. Kotzias, D. Indoor air and human exposure assessment—Needs and approaches. *Exp. Toxicol. Pathol.* **2005**, *57*, 5–7. [[CrossRef](#)]
12. Bartzis, J.; Wolkoff, P.; Stranger, M.; Efthimiou, G.; Tolis, E.I.; Maes, F.; Nørgaard, A.W.; Ventura, G.; Kalimeri, K.K.; Goelen, E.; et al. On organic emissions testing from indoor consumer products’ use. *J. Hazard. Mater.* **2015**, *285*, 37–45. [[CrossRef](#)] [[PubMed](#)]
13. Palmisani, J.; Nørgaard, A.W.; Kofoed-Sørensen, V.; Clausen, P.A.; de Gennaro, G.; Wolkoff, P. Formation of ozone-initiated VOCs and secondary organic aerosol following application of a carpet deodorizer. *Atmos. Environ.* **2020**. [[CrossRef](#)]
14. Kwon, K.-D.; Jo, W.-K.; Lim, H.-J.; Jeong, W.-S. Characterization of emissions composition for selected household products available in Korea. *J. Hazard. Mater.* **2007**, *148*, 192–198. [[CrossRef](#)] [[PubMed](#)]

15. Brattoli, M.; Cisternino, E.; de Gennaro, G.; Giungato, P.; Mazzone, A.; Palmisani, J.; Tutino, M. Gaschromatography analysis with olfactometric detection (GC-O): An innovative approach for chemical characterization of odor active Volatile Organic Compounds (VOCs). *Chem. Eng. Trans.* **2014**, *40*, 121–126. [[CrossRef](#)]
16. 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. [[CrossRef](#)] [[PubMed](#)]
17. Luca, F.-A.; Ciobanu, C.-I.; Andrei, A.G.; Horodnic, A.V. Raising Awareness on Health Impact of the Chemicals Used in Consumer Products: Empirical Evidence from East-Central Europe. *Sustainability* **2018**, *10*, 209. [[CrossRef](#)]
18. Marć, M.; Formela, K.; Klein, M.; Namieśnik, J.; Zabiegala, B. The emissions of monoaromatic hydrocarbons from small polymeric toys placed in chocolate food products. *Sci. Total Environ.* **2015**, *530–531*, 290–296. [[CrossRef](#)]
19. Wiedmer, C.; Velasco-Schön, C.; Buettner, A. Characterization of off-odours and potentially harmful substances in a fancy dress accessory handbag for children. *Sci. Rep.* **2017**, *7*, 1807. [[CrossRef](#)]
20. Abe, Y.; Yamaguchi, M.; Mutsuga, M.; Kawamura, Y.; Akiyama, H. Survey of volatile substances in kitchen utensils made from acrylonitrile–butadiene–styrene and acrylonitrile–styrene resin in Japan. *Food Sci. Nutr.* **2014**, *2*, 236–243. [[CrossRef](#)]
21. 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. [[CrossRef](#)]
22. ISO 16000-9. *Indoor Air—Part 9: Determination of the Emission of Volatile Organic Compounds from Building Products and Furnishing—Emission Test Chamber Method*; ISO: Geneva, Switzerland, 2006.
23. ISO 16000-6. *Indoor Air—Part 6: Determination of Volatile Organic Compounds in Indoor and Test Chamber Air by Active Sampling on Tenax TA Sorbent, Thermal Desorption and Gas Chromatography Using MS/FID*; ISO: Geneva, Switzerland, 2011.
24. Kozicki, M.; Piasecki, M.; Goljan, A.; Deptuła, H.; Niesłochowski, A. Emission of Volatile Organic Compounds (VOCs) from Dispersion and Cementitious Waterproofing Products. *Sustainability* **2018**, *10*, 2178. [[CrossRef](#)]
25. Ahn, J.-H.; Kim, K.-H.; Kim, Y.-H.; Kim, B.-W. Characterization of hazardous and odorous volatiles emitted from scented candles before lighting and when lit. *J. Hazard. Mater.* **2015**, *286*, 242–251. [[CrossRef](#)] [[PubMed](#)]
26. Dimitroulopoulou, C. Ventilation in European dwellings: A review. *Build. Environ.* **2012**, *47*, 109–125. [[CrossRef](#)]
27. AgBB. Requirements for the Indoor Air Quality in Buildings: Health-Related Evaluation Procedure for Emissions of Volatile Organic Compounds Emissions (VVOC, VOC and SVOC) from Building Products. 2018. Available online: https://www.umweltbundesamt.de/sites/default/files/medien/360/dokumente/agbb_evaluation_scheme_2018.pdf (accessed on 27 January 2020).
28. Kang, D.H.; Choi, D.H.; Won, D.; Yang, W.; Schleibinger, H.; David, J. Household materials as emission sources of Naphthalene in Canadian homes and their contribution to indoor air. *Atmos. Environ.* **2012**, *50*, 79–87. [[CrossRef](#)]
29. Lim, J.; Kim, S.; Kim, A.; Lee, W.; Han, J.; Cha, J.-S. Behavior of VOCs and carbonyl compounds emission from different types of wallpapers in Korea. *Int. J. Environ. Res. Public Health* **2014**, *11*, 4326–4339. [[CrossRef](#)]
30. World Health Organization. Selected Pollutants. In *Indoor Air Quality Guidelines*; WHO Regional Office for Europe: Copenhagen, Denmark, 2010.
31. International Agency for Research on Cancer (IARC). Naphthalene, IARC Monograph 1, 367–435. 2001. Available online: <http://monographs.iarc.fr/ENG/Monographs/vol82/mono82-8.pdf> (accessed on 27 January 2020).

32. Regulation (EC) No 1272/2008 on Classification, Labeling and Packaging of Substances and Mixtures, Amending and Repealing Directives 67/548/ECC and 1999/45/ECC and Amending Regulation (EC) No 1907/2006. Available online: https://eur-lex.europa.eu/legal-content/IT/ALL/?uri=uriserv:OJ.L_.2008.353.01.0001.01.ITA (accessed on 27 January 2020).
33. Masuck, I.; Hutzler, C.; Jann, O.; Luch, A. Inhalation exposure of children to fragrances present in scented toys. *Indoor Air* **2011**, *21*, 501–511. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).