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Indoor use of essential oil-based cleaning products: Emission rate and indoor air quality impact assessment based on a realistic application methodology

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ABSTRACT

Cleaning is performed to increase hygiene, esthetics and material preservation. Despite its benefits, cleaning also poses risks, potentially contributing to nearly 20 % of indoor pollution. As indoor air quality has become a major human health concern, "natural-scented" cleaning products, formulated with essential oils, have become market leaders among household products. However, these consumer products have benefitted from skillful marketing strategies based on the ambiguity of the words "green" and "natural". The characterization of the emission processes studied through 1-m^3 chamber experiments under a realistic scenario suggests variable maximum total terpene concentrations from 150 to 300 ppb. The estimated emission rate profiles confirm that the liquid-to-gas transfer of terpenes is driven by (i) the formulation of the product matrix inducing specific chemical affinities, (ii) the liquid content of individual terpenes, and (iii) the intrinsic volatility of terpenes. A unique formaldehyde emission kinetics profile was observed, suggesting the presence of a unique emission source: formaldehyde-releasers. Consequently, the use of essential-oil-based cleaning products might generate a long-term increase in the indoor formaldehyde concentration, and the maximum levels might be sustained for several hours after cleaning. Thus, essential-oil-based cleaners should be seriously considered as versatile and significant sources of fragrance molecules and formaldehyde.

KEYWORDS: cleaning products; emission rates; indoor air quality; terpenes

ABBREVIATIONS: TerVOCs Terpenic volatile organic compounds; **AER** Air exchange rate; **OVOCs** Oxygenated volatile organic compounds; **VP** Vapor pressure; **PROBAS** Danish Product Register Database; **BNPC** National Database for Products and Compositions

1 INTRODUCTION

Major efforts have been focused on addressing indoor air problems since daily activities mostly occur in confined environments. Indoors, people are exposed to a wide variety of chemical, biological and physical pollutants that (i) infiltrate from outdoor air, (ii) are released from building materials and furnishing, and (iii) are generated by occupants and their indoor activities (Missia et al., 2012; Weschler, 2001). The scientific community has focused on chemical pollutants, principally volatile organic compounds (VOCs), defined as organic molecules with boiling points ranging from 50 to 100 °C on the low end and from 240 to 260 °C on the high end (Brown et al., 1994; World Health Organisation, 2010). Among indoor sources of pollutants, the main origins of chemical contaminants are linked to occupant activities, such as interior renovation or decoration, smoking, cooking, or housekeeping (Kirchner et al., 2001).

Among the thousands of cleaning products available and marketed, people are tempted to use scented products because a pleasant odor is associated with a cleaner environment. Therefore, despite all the benefits of cleaning activities, such as increased hygiene, esthetics, and material preservation, the chemical and physical pollutant exposure risks posed by such activities remain unclear. Previous studies (Nazaroff and Weschler, 2004; Wolkoff et al., 1998) have shown that atmospheric VOC emissions per capita from general purpose cleaners and air fresheners contribute the most to indoor VOC pollution, with values ranging from 200 to 230 mg per day. The intake fraction is defined as the pollutant mass inhaled per unit of pollutant mass emitted (Lai et al., 2000). A typical intake fraction from indoor emissions is on the order of 10^{-3} and 10^{-1}, while that from outdoor emissions is on the order of 10^{-6} and 10^{-3}. These data highlight the fact that the proportion of emissions inhaled is higher when emissions occur indoors rather than outdoors (Nazaroff and Weschler, 2004).

Unexpectedly, the largest indoor sources of terpene VOCs are not usually the recognized, regulated and controlled sources. Indeed, the composition of VOCs emitted from household products has been associated with health hazards to indoor occupants (Dimitroulopoulou et al., 2015; Nazaroff and Weschler, 2004; Steinemann, 2009, 2016; Trantallidi et al., 2015; Wolkoff et al., 1998). Nevertheless, limited information is available about the composition, quantification and emission dynamics associated with housekeeping activities in confined environments. Available scientific data are, in most cases, incomparable due to wide variations and heterogeneity in the experimental methodologies used for the evaluation of primary and secondary pollutant emissions from fragranced household products (Angulo et al., 2020). These variations are related to two key parameters: (i) the application protocol (quantity, mode of operation) and (ii) the test environment (air exchange rate (AER), temperature, chamber size, and relative humidity (RH)) (BEUC, 2005; Chesnais and Marchais, 2014; Colombo et al., 1991; Delmas et al., 2016; Höllbacher et al., 2017; Nicolas and Chiappini, 2013; Norgaard et al., 2014; Sarwar et al., 2004; Singer et al., 2006a, 2006b; Solal et al., 2014; Uhde and Schulz, 2015). Therefore, comparing the results from one investigation to those of another may be difficult and inaccurate.

Fragranced household products can be formulated with (i) synthetic fragrances, (ii) pure essential oils and (iii) mixtures of synthetic fragrances and essential oils to reduce production costs. Essential oils are used in “naturally” formulated cleaning products either to provide them with a pleasant odor, to hide odors from other chemicals in the formulation, or to enhance their antibacterial performance (Rastogi, 2002; Steinemann, 2009). Essential oils are extracted from plants by water vapor distillation, dry distillation or mechanical extraction, which does not involve temperature changes (Delmas et al., 2016). They usually contain more than 100 different

93 chemicals that compose their characteristic smell, and most of these chemicals are terpenes:
94 monoterpenes, sesquiterpenes, terpene alcohols and terpenoids (denoted TerVOCs) (Babu et al.,
95 2002; Lassen et al., 2008; Zuzarte and Salgueiro, 2015). The characteristic smell of an essential
96 oil often originates from its major chemical components; therefore, the typical "scent" of an
97 essential oil directly depends on its chemical composition. In contrast, fragrance mixtures
98 combine differently sourced compounds (synthetic, natural-like or extracted) to replicate a
99 "natural" scent (Teixeira et al., 2013; Zuzarte and Salgueiro, 2015).

100 Although diverse sanitation benefits of essential oil-based cleaning products have been
101 recognized, several risks associated with their use in indoor environments are still questioned. ***Is***
102 ***there a potential exposure risk to consumers posed by TerVOCs emitted from household***
103 ***products?***

104 This study is developed within the framework of the ESSENTIEL research project,
105 aiming to characterize the impact of essential oil-based products on indoor air quality (IAQ)
106 through investigation of their realistic emissions and indoor fate. The objectives of this
107 investigation are to evaluate the correlation between the fragrance chemicals contained in
108 cleaning products and their volatile fraction through determination of the gas-transferred
109 concentration by micro-chamber testing and to characterize and assess their emissions in a 1 m^3
110 experimental chamber reflecting a realistic application scenario. The proposed experimental
111 approach and the results provided in this study are required (i) to propose harmonized and
112 realistic test protocols and (ii) to define risk scenarios and evaluate the human exposure to
113 TerVOCs associated with the use of essential oil-based cleaning products.
114
115

2 MATERIAL AND METHODS

2.1 Cleaning product benchmarking

To frame the approach of the present study, it is necessary to define the type of cleaning products considered. Essential oil-based cleaning products are defined in this work as naturally scented and certified organic products used in a nonpermanent way in indoor environments for housekeeping purposes. For their selection, a benchmark analysis was performed among cleaners certified as *ecological products* by different European labels. A total of 108 essential oil-based products were identified from the European market. Among them, 6 representative cleaning products were selected in the framework of this work and classified by category, i.e., intended use: (i) 2 kitchen degreasers, (ii) 2 general (multiuse) cleaners, (iii) 1 surface cleaner, and (iv) 1 glass cleaner. This selection considered (i) diverse intended uses to assess the effect of different solvent formulations, (ii) a variety of application modes and (iii) a diversity of essential oils used as natural fragrances in the formulation of the cleaning products. The selected cleaning products were purchased from environmentally friendly and ecologically conscious retail stores in France.

Importantly, the solvent matrix composition could vary from one product to another in terms of the organic content (% ethanol) or the presence of texturing agents (gums). The contents of the fragrance chemicals and their volatile fractions were characterized for the six selected cleaning products, whereas only three products were considered for the 1 m^3 emission test. Table 1 details the characteristics of the six selected products.

Table 1. Specifications of the selected cleaning products.

Product	Product category	Diffusion mode	Natural fragrance[1]	General product formulation[2]	Characterization performed		
					Liquid composition	Volatile fraction (micro-chamber)	Realistic emissions (1 m^3 test chamber)
KC – 1	Kitchen cleaner	Trigger spray	Lemon oil	< 5 % surfactant (anionic and nonanionic), citrus oil, citric acid, water, methylisothiazolone, 5-chloro-2-methyl-4-isothiazolin-3-one, nitrilotriacetic acid trisodium salt monohydrate	x	x	
KC – 2			Eucalyptus oil	< 5 % surfactant (nonanionic), essential oils (including eucalyptus oil[2]), water, alcohol[2], preservatives, acid correctors	x	x	x
MC – 1	Multiuse cleaner	Liquid	Citrus oil	< 5 % surfactant (anionic and nonanionic), water, alcohol, citrus oil[2], citric acid	x	x	x
MC – 2			Lemon oil	< 5 % surfactant (anionic and nonanionic), water, alcohol, lemon oil[2], lactic acid, fatty acids, sodium citrate, glyceryl caprylate	x	x	
SC – 1	Surface cleaner	Trigger spray	Lavender oil	70 % ethanol[2], < 1 % lavender oil[2], < 1 % sage oil[2], water	x	x	x
GC – 1	Glass cleaner	Trigger spray	Eucalyptus oil	> 30 % water, 5 – 15 % alcohol[2], < 5 % surfactant (anionic and nonanionic), citric acid, essential oils[2] (including eucalyptus oil), amphoteric surfactants	x	x	

1: Certified organically grown

2: Based on information given by the manufacturer

2.2 Characterization of the liquid composition

Several extraction parameters were optimized to maximize the extraction of terpenes: (i) the organic extraction solvent, (ii) the mass ratio of the cleaning product to the solvent, (iii) the contact time between the solvent and the cleaning product, and (iv) the number of consecutive extractions. The extraction procedure and the analytical methods and parameters are detailed in a supplementary information sile (SI file).

2.3 Determination of the gas-transferred concentration by micro-chamber testing

2.3.1 Micro-chamber description

The liquid-to-gas phase transfer capacity of each terpene identified in the cleaning products is defined as the gas-transferred concentration and was determined by using a stainless steel cylindrical micro-chamber with a 44 mL volume (M-CTE-120 Markes International®). The device was equipped with restrictors allowing the selection of a low-flow range and a high-flow range of 10 – 70 mL/min and 50 – 500 mL/min, respectively. In this work, the low-flow range was used and set at 50 mL/min. The dry air generation is ensured by an air compressor combined with membrane for humidity removal. Before entering the micro chamber, the dry air is purified by an activated carbon filter in order to remove particles and trace pollutants. The top of the chamber acts as a door and is sealed with a silicon gasket for leak control. After optimization, the temperature and air flow were set at 40 °C and 50 mL/min, respectively. Dry air flow enters each micro-chamber through the lid and is preheated to the micro-chamber temperature of 40 °C. A total volume of 50 ± 1 µL of each selected fragranced cleaner was introduced into the micro-chamber. Blank measurements were performed to determine the background levels of VOCs in the chamber outlet before running each set of experiments. Note that the mean concentration of

blank measurements in the micro-chamber did not exceed the quantification limits for the background concentrations of the individual target VOCs. The detailed characteristics of the micro-chamber are presented in Fig. 1a.

(a) (b)

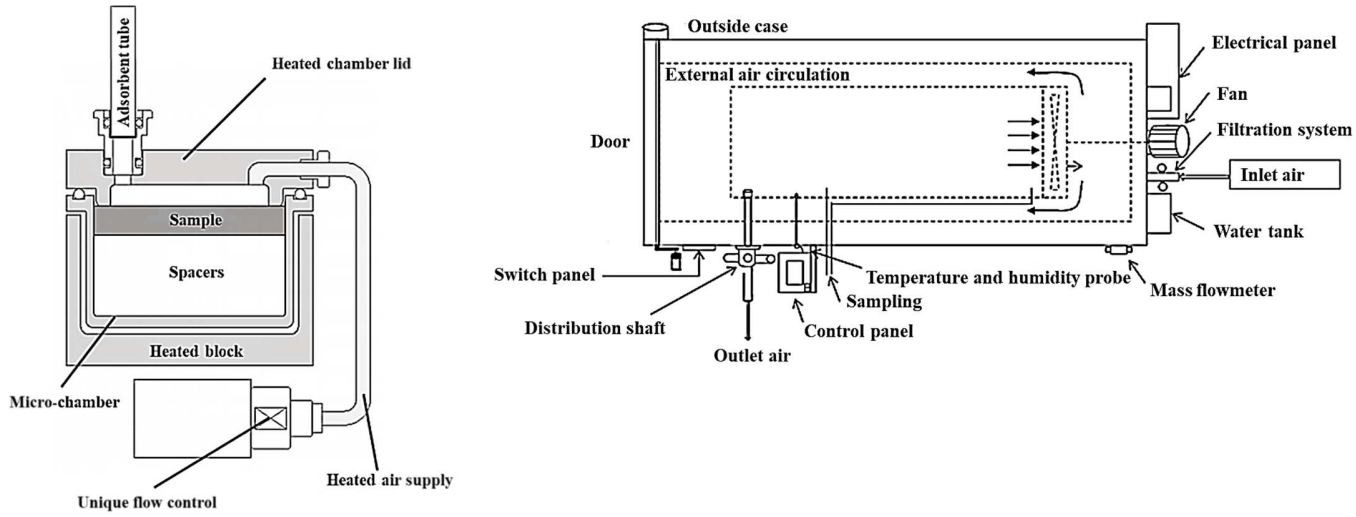


Fig. 1. (a) Schematic of the M-CTE-120 micro-chamber from Markes International®. (b) Schematic of the 1 m^3 emission chamber VCE1000 Classic from Vötsch.

2.3.2 Analytical strategy

The TerVOCs emitted from the investigated products inside each micro-chamber were monitored using an off-line device for their identification and quantification. Subsequently, two consecutive Tenax TA® cartridges collected volatilized compounds at the device outlet for 15 minutes. The total sampled volume was 0.6 L. Afterward, these samples were desorbed at 280 °C under a helium flow of 50 mL/min using a PerkinElmer® thermal desorber (model: Turbo Matrix 350). Then, the desorbed compounds were thermally transferred via the helium flow and refocused on a Carbotrap B/C trap at 5 °C with an outlet split flow of 70 mL/min. The gas

chromatographic analyses were performed using a 7890A instrument from Agilent Technologies equipped with a Restek 10189 chromatographic column (60 m x 320 µm, 1 µm film thickness) connected to two different detectors: (i) an FID and (ii) an MS (5975B inert MSD) from Agilent Technologies. The typical detection limit of this instrument for hydrocarbon VOCs with the abovementioned sampling conditions is 0.5 µg/m^3. Calibration for the identified and quantified TerVOCs was achieved by individual liquid doping of the high-purity certified standards from Sigma-Aldrich® on Tenax TA® absorbent tubes.

2.4 Emission chamber test: simulation of a realistic scenario – correlation method for a realistically sized room

2.4.1 Emission chamber parameters

The experiments reported in this paper were conducted in an experimental chamber with a 1 m^3 volume (Vötsch VCE1000 Classic) that complied with the ISO 16000-9 (2006) standards. The chamber was operated at a controlled temperature, humidity and air exchange rate (AER) of 23 ± 1 °C, 50 ± 5 % and 0.3 h^{-1} ± 0.05, respectively. The humidity and temperature were set according to ISO 16000-9. The established AER corresponds to the 25th percentile reported in French dwellings by the Indoor Air Quality Observatory (OQAI) (Kirchner et al., 2001; Lucas et al., 2009). Detailed characteristics of the experimental chamber are presented in Fig. 1b. Before loading the test chamber with the selected product, blank measurements were performed to determine background levels of TerVOCs and oxygenated volatile organic compounds (OVOCs). Note that the mean concentration determined from blank measurements in the

experimental chamber did not exceed the standardized background concentrations of individual VOCs.

2.4.2 Definition of a realistic scenario for the use of essential oil-based household products

The assessment of TerVOC emissions in the experimental test chamber has been primarily focused on *surface cleaning scenarios*. The product application procedure must be based on the typical consumer use pattern to mimic realistic application in the evaluation of cleaning product emissions. The key parameters required to define a specific and standardized product application procedure are (i) the quantity of product to apply and (ii) the surface to clean. These parameters were estimated from the loading factor and the final application yield of the cleaning product after wiping, called *product yield* is this study.

Loading factor

The loading factor is defined as the ratio between the emissive surface area, i.e., the cleaned area, and the chamber volume. This is the key parameter to transfer the real application scenario at scale 1:1 to the 1m3 test chamber. It has to be keot constant between both chamber volume as reported in Table 2. Conventionally, a reference room is used to extrapolate measured VOC concentrations in test chambers with small volumes when assessing human exposure. The reference room considered for the study is the IRINA experimental room characterized by a floor area of 12 m^2, a ceiling height of 2.5 m and a volume of 40 m^3. (Harb et al., 2016) In regard to the product application for surface cleaning, a typical table area of 2 m^2 was considered in the reference room. It results in a loading factor of 0.05 m^2/m^3. For the correlation between the 1 m^3 emission test chamber and the 40 m^3 reference room, the loading factor must be identical (Table

2). Based on this consideration, the *surface cleaning scenari*o was defined and the surface to clean was determined for the 1 m^3 emission test chamber as reported in Table 2, along with the corresponding masses of cleaning products. Table 2.

Table 2. Application parameters for the surface cleaning scenario: reference values from the 40 m3 room for the product yield and loading factor and subsequent quantities of products to be applied in both chambers 40 m^3 and 1m^3.

Application parameters to mimic a 2 m^2 surface cleaning in a 40 m^3 room to the 1m^3 test chamber			
		(40 m^3) REFERENCE ROOM	*1 m^3 TEST CHAMBER*
SURFACE TO CLEAN		**2 m^2**	*0.05 m^2*
LOADING FACTOR (m^2/m^3)		**0.05**	**0.05**
PRODUCT YIELD	**SC – 1**	8.7 ($g.m^{-2}$)	
	MC -1	7.2 ($g.m^{-2}$)	
	KC - 2	12.0 ($g.m^{-2}$)	
MASS APPLIED	**SC – 1**	**18.0 g**	*3.2 g*
	MC -1	**15.0 g**	*4.4 g*
	KC - 2	**24.0 g**	*2.7 g*

Product yield

The product yield is defined as the effective mass of product remaining on a 1 m^2 surface; it includes the total mass applied balanced by the losses induced by wiping. This parameter was estimated for each selected cleaning product. First, the average amount of cleaning product required to clean 1 m^2 of surface was determined from the cleaning of a 1 m^2 surface by 10 different operators. Subsequently, the average mass of each product dispersed by a single spray from each trigger spray mechanism was determined for a set of 15 successive sprays performed

239 by the same operator. Then the mass of product lost on wipes is determined by weighing. This
240 procedure allows the estimation of the effective mass of product remaining on a 1 m^2 surface.
241 The mass of product required for the *surface cleaning scenario* in the 1 m^3 emission test chamber
242 is determined from this product yield by proportionality.

243 For each experiment, the calculated mass of product was evenly drizzled or sprayed on a
244 0.05 m^2 stainless steel surface placed at the center of the 1 m^3 experimental chamber. Once the
245 simulation of the cleaning activity was completed, the experimental chamber remained closed
246 during the emission monitoring. For each cleaning product, a set of three experiments was
247 performed to evaluate the repeatability of the experimental protocol. Additionally, during the
248 experiment, t = 0 corresponded to the time when the application of the cleaning product was
249 completed inside the chamber.

250 *2.4.3 Sampling and analytical parameters*

251 Regarding the analytical methodology, the temporal dynamics of the TerVOC and OVOC
252 concentrations inside the experimental chamber were monitored using off-line devices that
253 allowed their quantification with high temporal resolution. Several preliminary tests were
254 performed to optimize the experiment duration depending on the cleaning product. On the basis
255 of these preliminary results, the duration of a typical emission experiment was 5 hours.

256 Off-line sampling was performed according to ISO 16000-3 and 16000-6 by using (i)
257 Tenax TA® cartridges for terpene compounds and (ii) 2,4-dinitrophenylhydrazine (DNPH)-
258 impregnated silica cartridges (Sep-Pak DNPH-Silica Plus Short Cartridges, Waters) for carbonyl
259 compounds. Sampling was performed using a pump (KNF®) connected to a mass flow controller
260 with specific flow rates and durations optimized for each cleaning product tested, as described in
261 Table 3.

Table 3. Experimental protocol and optimized parameters for the off-line sampling systems.

Evaluation of emissions from cleaning products		
Sampling device		***Terpenes (TerVOCs):*** Tenax TA® adsorbent ***Carbonyl Compounds (OVOCs):*** DNPH cartridges
Duration of experiment* (h)		5 h
Sampling flow*	*TerVOCs*	0.150 L/min
	Carbonyl compounds	0.800 L/min
Sampling duration (min) and time interval (h)*		From 0 to 1 hour; continuous sampling for 15 minutes; total of 4 samples From 1 – 5 hour; continuous sampling for 60 minutes; total of 4 samples

*Experimental parameters that were optimized

The analytical protocol to quantify TerVOCs was the same as that reported in section 2.3 for the gas-transferred concentration determination. In contrast, derivatized carbonyl compounds (OVOCs) were extracted from DNPH cartridges with 3 mL of acetonitrile and analyzed with a Thermo Dionex Ultimate U3000 liquid chromatograph. Compounds were eluted on an Acclaim RSLC Carbonyl column (2.1 x 150 mm) and detected by RS variable-wavelength UV absorption. The acquisition was performed at 365 nm wavelength. Calibration for the carbonyl compounds was achieved using high-purity certified standard solutions (Aldehyde/Ketone-DNPH Stock Standard-13). Under these conditions, the detection limit for the carbonyl compounds was 0.01 ppb.

3 RESULTS AND DISCUSSION

3.1 Chemical composition: terpene (TerVOC) content of natural, certified organic cleaning products

279 The terpene contents of the six selected cleaning products are listed in Table 4. Note that of the
280 identified compounds, the predominant terpenes are written in bold. The most frequently
281 identified terpenes were limonene, linalool, and α-terpineol, which were present in all the
282 evaluated cleaning products. To date, five studies have assessed the presence of fragrance
283 chemicals in cleaning product formulations on the European market. Among the 121 cleaning
284 products evaluated, limonene and linalool have been reported with the highest occurrence rates:
285 84.2 % and 60.8 %, respectively (Nicolas and Chiappini, 2013; Pors and Fuhlendorff, 2003;
286 Rastogi, 2002; Rastogi et al., 2001; Uhde and Schulz, 2015). Worldwide, the most commonly
287 used essential oils in household product formulations are citrus oil, lavender oil, pine oil,
288 eucalyptus oil, tea tree oil and rose oil. In contrast, several terpene derivatives, such as camphor
289 and bergamol, detected in SC-1 and KC-2, have been more rarely reported (Ezendam et al.,
290 2009; Huang et al., 2011; Jo et al., 2008; Kwon et al., 2007).

291 **Table 4.** Liquid composition (expressed in µg of terpene per g of product: µg/g) of the six
292 selected cleaning products and their occurrence rate in the literature. NB: the mass concentration
293 of the predominant TerVOCs in each cleaning product is written in bold.

	Mass of individual TerVOCs (this work) Mass ± SD (µg/g)						**Occurrence rate (%) in the literature**
Identified Terpenes	**MC -1**	**MC -2**	**SC - 1**	**KC - 1**	**KC – 2**	**GC - 1**	*[121 cleaning products]* (Nicolas and Chiappini, 2013; Rastogi, 2002; Rastogi et al., 2001; Uhde and Schulz, 2015)
Diffusion mode	*Liquid*	*Liquid*	*Spray*	*Spray*	*Spray*	*Spray*	
α-Pinene	24.2 ± 6.2	23.3 ± 4.8	37.6 ± 5.0	-	35.6 ± 3.8	-	36 %
Limonene	**852.9 ± 32.9**	**472.0 ± 8.2**	25.5 ± 0.7	6.3 ± 0.5	173.3 ± 36.1	2.2 ± 0.3	84 %
Linalool	10.2 ± 0.6	6.0 ± 0.9	**390.0 ± 5.0**	6.5 ± 0.5	4.3 ± 0.7	1.5 ± 0.3	61 %

Eucalyptol	424.1 ± 37.0	-	213.4 ± 4.7	-	**2230.8 ± 71.4**	**18.0 ± 1.5**	38 %
Cymene	158.7 ± 23.9	8.5 ± 0.2	-	-	76.2 ± 11.5	-	26 %
Bergamol	-	-	279.0 ± 2.0	-	-	-	NS
Camphor	-	-	256.8 ± 2.5	-	19.3 ± 2.5	-	NS
β-Pinene	69.9 ± 3.6	146.2 ± 5.0	21.8 ± 0.4	3.4 ± 0.4	3.1 ± 1.4	-	40 %
γ-Terpinene	15.9 ± 2.6	61.4 ± 5.7	2.6 ± 0.2	-	7.5 ± 0.5	-	20 %
α-Terpineol	29.7 ± 7.4	2.9 ± 0.8	16.4 ± 0.5	**10.0 ± 0.3**	18.2 ± 0.8	12.8 ± 2.0	NS
Menthol	-	-	-	1.0 ± 0.3	570.9 ± 25.2	3.3 ± 0.7	NS
Other TerVOCs	121.5 ± 15.8	79.1 ± 7.4	247.9 + 6.9	10.3 ± 0.6	77.2 ± 18.5	1.30 ± 0.3	-
TOTAL TerVOCs	**1682.8± 131.3**	**776.0 ± 28.1**	**1453.7 ± 22.6**	**37.6 ± 2.5**	**3180.7 ± 200.5**	**39.1± 4.5**	

294

295 *3.1.1 Total TerVOC mass concentration*

296 Regarding the total terpene content in household products, the mass concentrations varied
297 widely, ranging from 37.6 ± 2.5 to 3180.7 ± 200.5 µg/g (of product). Nevertheless, these
298 concentrations accounted for only 0.01 % to 0.17 % w/w of the total composition of the selected
299 products, as shown in Table 4. Sarwar et al. (2004) reported the quantification of TerVOCs in
300 four different types of cleaning products used as floor cleaners and general purpose cleaners. The
301 main detected terpenes were α-pinene, β-pinene, 3-carene, limonene and α-terpinene, with
302 individual mass concentrations ranging from 0.2 % w/w to 2.0 % w/w. The proportions of
303 fragrance chemicals in industrial formulations of cleaning products do not exceed 5.0 % w/w
304 (Ezendam et al., 2009; Rastogi, 2002; Steinemann, 2009; Steinemann et al., 2011).

305

306 *3.1.2 Individual mass concentration of TerVOCs*

307 Among the selected cleaning products, a total of 27 terpenes were detected: (i) 14 monoterpenes,
308 (ii) 8 terpene alcohols, (iii) 4 terpene derivatives, and (iv) 1 sesquiterpene. Per product, the
309 diversity of odorous chemicals varied from 6 to 20 different species. Furthermore, all tested
310 products, except for KC – 1, showed a correlation between the predominant terpene detected and
311 the essential oil indicated by the manufacturer. KC – 1 was reportedly formulated with lemon oil;
312 however, the major terpene was α-terpineol instead of limonene. In terms of the product
313 categories, limonene was the predominant terpene contained in the multiuse cleaners, both
314 fragranced with citrus oils. In the kitchen cleaners tested, the main detected terpene differed:
315 eucalyptol in KC – 2 and α-terpineol in KC – 1. Concerning the mass concentration of terpenes,
316 the predominant species in the selected products were limonene, linalool, eucalyptol, and α-
317 terpineol, detected at concentrations ranging from 10.0 ± 0.3 µg/g to 2230.8 ± 71.4 µg/g.

318 The chemical composition of a cleaning product might vary widely depending on its
319 usage purpose and diffusion mode. For instance, when a cleaning product emphasizes a
320 disinfecting property, complementary chemicals are added to its formulation to suppress or
321 inhibit microbial activity. In so-called "*green*" cleaning product formulations, specific essential
322 oils might be added to increase the concentration of terpenes with antibacterial and antiseptic
323 activity, such as eucalyptol and geraniol. Therefore, no correlation was evidenced between the
324 diffusion mode of the selected cleaning products and their total terpene mass concentration. This
325 finding is suggested to result from the intrinsic industrial formulations designed to achieve a
326 particular performance.

Finally, the contrasting terpene contents bring up questions about the intrinsic emission potential of the cleaning products. The diversity in the constituent volatility affects the emission dynamics associated with the cleaning activity. *Does a high terpene content necessarily imply high emission levels? What is the effective amount of terpenes eventually transferred to the gas phase? What is the impact of the cleaning product matrix on the gas phase transfer? How long is the user impacted by the emissions?*

To provide key elements needed to answer these questions, a screening of their ability to be transferred from the liquid to the gas phase, defined in this paper as the gas-transferred concentration, was performed to identify the emission potential of each cleaning product.

3.2 Gas-transferred concentration vs. liquid composition

3.2.1 Total gas-transferred concentration

The total gas-transferred concentration of terpenes corresponds to the sum of the concentrations, subsequently expressed in $\mu g/m^3$, of terpenes collected at the outlet of the micro-chamber setup. This concentration can be used to assess the ability of a given cleaning product to release terpenes to the gas phase. Comparison of the six selected products revealed very different total gas-transferred concentrations, ranging from 125 ± 15 to 85 225 ± 5 500 $\mu g/m^3$. The glass cleaner GC – 1 was the least emissive product, with a total gas-transferred concentration of 125 ± 15 $\mu g/m^3$, while the gas-transferred concentrations of the surface cleaner SC – 1 and the kitchen cleaner KC – 2 were higher by 2 orders of magnitude. These two products transferred analogous total terpene concentrations to the gas phase, considering the standard deviation: 85 000 ± 5 500 $\mu g/m^3$ and 81 000 ± 12 000 $\mu g/m^3$, respectively.

Fig. 2 shows the correlation between the total terpene mass concentrations in the liquid phase of the selected products (µg/g of product) and the total gas-transferred concentrations of TerVOCs (µg/m^3) for the same products. For the multiuse cleaners (MC – 1 and MC – 2), the volatile concentrations reached equivalent levels of 27 000 µg/m^3, but their total terpene mass concentrations in the liquid phase differed by a concentration ratio of 2:1. The pattern between the surface cleaner SC – 1 and the kitchen cleaner KC – 2 was similar, with gas-transferred concentrations that both reached approximately 80 000 µg/m^3, considering the standard deviation, but a terpene content of the surface cleaner SC – 1 that was half that of the kitchen cleaner KC – 2 (3200 ± 270 µg/g). In contrast, the two household products SC – 1 and MC – 1 had equivalent terpene mass contents but gas-transferred concentrations that differed by a factor of 3. Consequently, no direct correlation was evidenced between the total terpene mass content and the total gas-transferred concentration among the six selected products. Therefore, the amount of terpenes emitted by a given product cannot be estimated from its liquid terpene content, and emission tests are required.

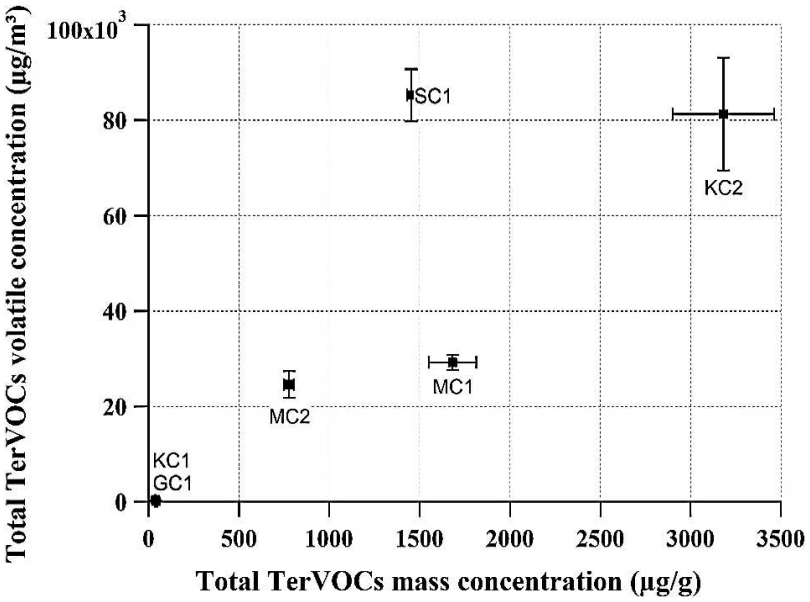


Fig. 2. Total TerVOC gas-transferred concentration from micro-chamber testing (µg/m^3) as a function of the total terpene mass concentration in the liquid form (µg/g) for the six selected cleaning products (T = 40 °C, dry air flow = 50 mL/min, micro-chamber volume = 44 mL).

3.2.2 Individual gas-transferred concentrations

Only 19 terpene molecules from the 27 TerVOCs contained in the cleaning products were identified in the gas phase during the micro-chamber evaluation, and the number of emitted terpenes varied from 1 to 14 per cleaning product. Table 5 lists the (i) volatile/liquid fraction concentration ratio (V/L) of each cleaning product and (ii) various physical and chemical properties of the individual terpene molecules. For discussion purposes, in this paper, the V/L concentration ratio is defined as the ratio of an individual gas-transferred concentration to its mass fraction in the liquid phase for each identified terpene. Higher is the V/L value, greater is the ability of the considered molecule to be transferred from the liquid to the gas phase.

Table 5. Comparison of the total TerVOC gas-transferred concentrations (T = 40 °C, dry air flow = 50 mL/min, micro-chamber volume = 44 mL) with the total TerVOC mass fractions in the liquid form for each cleaning product, individually. NB: The physical and chemical properties of identified terpenes (VP, boiling point and molar mass) from the literature are detailed.

TERPENES	***RATIO* –** Gas-transferred concentration/Mass fraction (V/L) **- (this work)**						**Vapor pressure (VP) from the literature (Pa)***	**Boiling point (°C)**
	MC - 1	**MC -2**	**SC - 1**	**GC – 1**	**KC - 1**	**KC - 2**		
α-Pinene	1.15	1.39	-	-	-	1.27	529- 599,	156
Limonene	1.15	1.02	0.68	-	3.99	1.51	189- 213	176

Linalool	-	0.47	0.97	-	-	1.17	20-27	198
Eucalyptol	1.27	-	1.13	2.17	-	0.80	230- 260	176
Cymene	0.58	0.99	-	-	-	1.73	192-195	177
Bergamol	-	-	1.15	-	-	-	NS	220
Camphor	-	-	1.25	-	-	1.02	28	209
β-Pinene	0.49	1.02	0.53	-	2.83	1.12	391-400	166
γ-Terpinene	0.17	1.19	0.64	-	-	1.99	103-145	183
α-Terpineol	-	-	1.31	-	-	-	**	175
Menthol	-	-	-	-	-	1.49	11-18	212

NS: Not specified in the literature; *: (Harb et al., 2016; ISO 16000-9, 2006; López and Gómez, 2000; Lucas et al., 2009; Rastogi et al., 2001; Teixeira et al., 2013 ; Espinoza et al., 1999; Hoskovec et al., 2005; Štejfa et at., 2014); **Vapor pressure near 0 Pa

Among the physical and chemical properties of TerVOCs, the saturation vapor pressure (VP) of a pure molecule (expressed in Pa) is an inherent property required for the investigation of vapor-liquid equilibrium and a key parameter for emission assessment. It is defined as the pressure exerted by a vapor in equilibrium with its pure condensed phase at a given temperature in a closed system. VPs have been experimentally determined in the literature for most TerVOCs, and the corresponding values are given in Table 5. The reported VPs of terpenes are highly varied, ranging from 0.3 Pa for α-terpineol to 599 Pa for α-pinene.

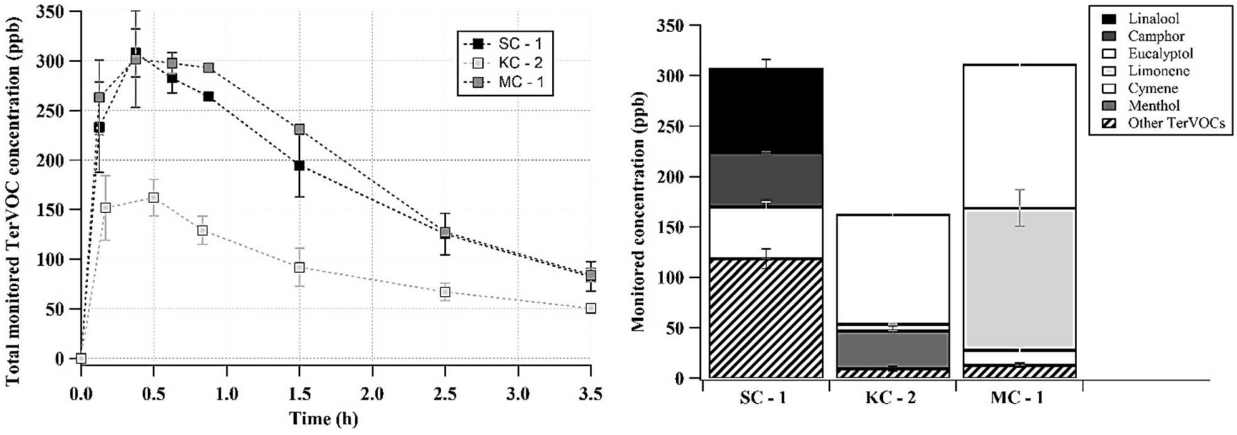
As shown in Table 5, α-pinene had a V/L ratio higher than 1, ranging from 1.15 to 1.39 among the cleaning products in which this molecule was detected. This suggests a significant ability of α-pinene to be transferred to the gas phase independent of the solvent matrix composition and could be related to its high VP of 599 Pa, the highest among all identified terpenes. In contrast, for the other compounds, the relation between the VP and V/L ratio was not predictable. Unique behaviors were observed for different terpenes: (i) the V/L ratio of linalool, with low volatility (VP values below 30 Pa), differed greatly depending on the cleaning product,

399 ranging from 0.47 for MC – 2 to 1.17 for KC – 2, while (ii) V/L ratio of β-pinene, with chemical
400 and physical properties analogous to those of α-pinene, widely varied from 0.49 for MC – 1 and
401 2.83 for KC – 1. Thus, for most terpene species, the transfer to the gas phase is not exclusively
402 driven by the intrinsic properties of the pure molecule but more by the solvent properties. The
403 proportion of organic solvent and the presence of texturing agents in the aqueous media of a
404 cleaning product play key roles in flavor release (Jouquand et al., 2008). Interactions between
405 flavor compounds and a matrix have been extensively studied in the field of food sciences
406 (Guichard, 2002). The determination of the gas-liquid partition coefficient under equilibrated
407 conditions specific to each VOC/matrix pair could be used to explain the various observed
408 behaviors (Ettre et al., 1993).

409 Consequently, terpene emissions from essential oil-based household cleaning products
410 cannot be directly predicted from the liquid composition of the product. Instead, the
411 concentrations of TerVOC species released from such products could be governed by three main
412 factors: (i) the inherent volatility of the TerVOCs, (ii) the chemical affinities between the
413 TerVOCs and other compounds in the formulations and (iii) the mass concentrations of terpenes
414 in the liquid phase. In the micro-chamber tests, the major compounds emitted and transferred to
415 the gas phase were identified, but this experimental approach is not a substitute for emission
416 testing using experimental chambers of conventional size. Moreover, micro-chamber tests are
417 not conducted under realistic conditions of temperature, humidity and air velocity, but under
418 conditions which potentially enhance the transfer from the product to the gas phase. Next,
419 primary emissions were investigated from a representative cleaning product for each of the three
420 product categories of the six selected products.
421

3.3 Emission of TerVOCs under realistic application conditions: 1 m³ emission test chamber

To assess the primary emissions associated with the application of essential oil-based products, one representative product from each category was selected. This selection was based on the previously discussed results regarding the correlation between the gas-transferred concentration and the liquid content of TerVOCs. The cleaning product in each category attesting the highest ratio between its gas-transferred and liquid concentrations (V/L) was selected: (i) the surface cleaner SC – 1, (ii) the multiuse cleaner MC – 1, and (iii) the kitchen cleaner KC – 2. Regarding the diversity of the species emitted, 19 out of the 23 TerVOCs contained in the three liquid cleaners were identified in the gas phase. Fig. 3b shows the contributions of the top three emitted terpenes to the total TerVOC concentration after the separate application of the selected cleaners.



(a) (b)

Fig. 3. (a) Temporal evolution of the total TerVOC concentration during cleaning with SC – 1 (black symbols), MC – 2 (dark gray symbols) and KC – 2 (light gray symbols) (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3). (b) Peak concentration of total TerVOCs and the contributions of the 3 predominant terpenes after the application of SC – 1, MC – 1 and KC – 2.

438

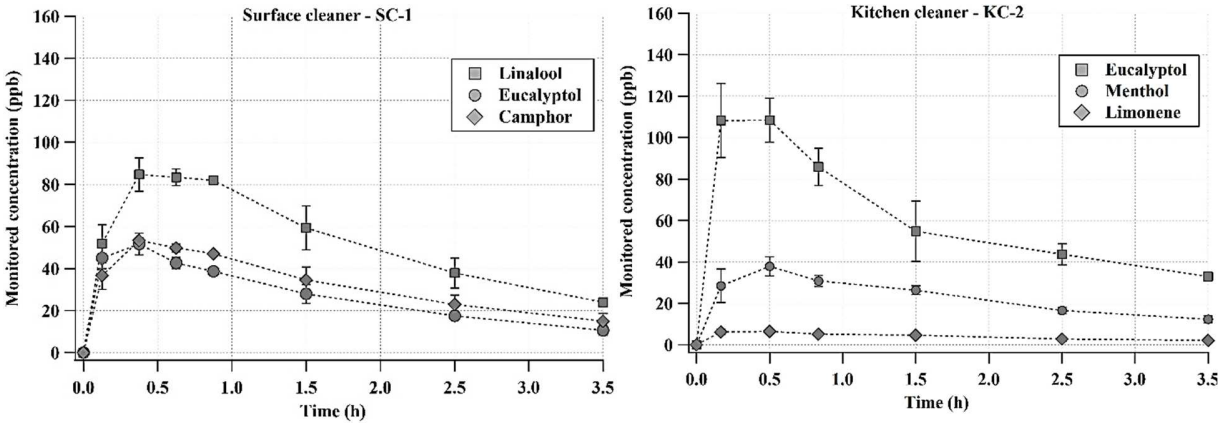
439 *3.3.1 Emission Profile of total TerVOCs*

440 The temporal profiles of the total TerVOC concentrations in SC – 1, KC – 2 and MC – 1,
441 reported in Fig. 3a, are characterized by the three typical phases of transient emission: (i) a
442 sudden increase in the total TerVOC concentration, reflecting the rapid transfer of terpenes from
443 the applied cleaning product layer to the gas phase until a peak concentration is reached (< 30
444 minutes); (ii) a long decrease, corresponding to the gradual depletion of the VOC source and
445 removal of VOCs from the experimental chamber; and (iii) a final decrease exclusively
446 associated with the evacuation of the gas phase terpenes by air exchange and possible deposition
447 on the inner walls of the experimental chamber. Note that in any of the three phases, possible
448 losses of terpenes from deposition on the chamber walls must be considered. As observed in Fig.
449 3a, SC – 1 and MC – 1 had similar, considering their respective standard deviations, peak total
450 TerVOC concentrations of approximately 300 ppb within a half-hour after application. The
451 maximum emitted concentration of TerVOCs KC–2 (160 ppb) was lower than those of the other
452 two cleaning products but was reached at an analogous time. However, considering the total
453 terpene composition in the liquid phase (section 2.1), KC – 2 was characterized by the highest
454 mass concentration of TerVOCs (3200 ± 200 µg/g) among the three cleaners. These results
455 confirm the absence of correlation between the liquid content of terpenes and the resulting
456 concentrations of terpenes in the 1 m^3 emission test chamber. Based on the investigated products,
457 the temporal emission dynamics of essential oil-based cleaning products cannot be directly
458 predicted from their liquid composition.

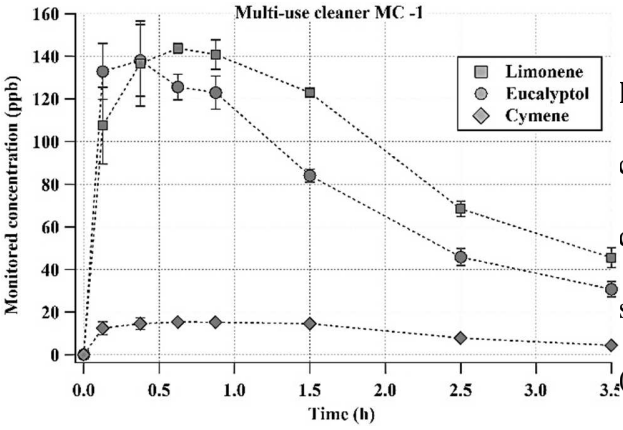
459 In comparison with other indoor terpene sources, primary emissions from a wood-based
460 building product evaluated by Harb et al. (2018) produced a peak concentration of total

TerVOCs of 31 ppb under realistic conditions. Brown (1999) identified similar emitted concentrations from a 16-mm pine softwood particleboard. Thus, the contribution to the indoor total concentration of TerVOCs made by cleaning activities may transiently exceed that made by wood-based materials. However, emissions from cleaning products are characterized by temporal dynamics different from those of indoor material emissions; the former emissions mostly act as punctual or transient sources of pollutants. Thus, the cumulative exposure to TerVOCs from cleaning products is directly related to cleaning frequency and human factors. This behavior contrasts with wood-based materials, which mostly act as long-term and continuous emission sources.

3.3.2 Individual emission profiles of TerVOC



(a) (b)



(c)

Fig. 4. Temporal evolution of the concentrations of major terpenes identified during the use of three cleaning products: (a) surface cleaner (SC - 1), (b) kitchen cleaner (KC - 1), and (c) multiuse cleaner (MC - 1) (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

The individual emissions of 9 monoterpenes, 7 terpene alcohols, 1 oxygenated terpene, and 1 sesquiterpene were quantified. SC – 1 was characterized by the largest diversity of terpenes, since it emitted a total of 16 different terpene molecules. Fig. 4 shows the individual profiles of the predominantly emitted terpene species. The individual profiles were characterized by the same three phases observed in the emission profiles of the total TerVOCs (Fig. 3a). Nonetheless, some differences can be observed among the tested products.

The predominant terpenes released from *surface cleaner SC – 1* were linalool, eucalyptol and cymene, which had peak concentrations of 85 ± 10 ppb, 50 ± 5 ppb and 55 ± 5 ppb, respectively. Their cumulative concentration accounted for 47.6 % of the peak total TerVOC concentration. Interestingly, regarding the emission kinetics, despite these compounds showing contrasting physical and chemical properties (Table 5), their peak concentrations were reached at equivalent emission times, i.e., nearly 25 minutes after the cleaning activity was completed (Fig. 4a). This observation suggests that determinants other than the physical and chemical properties of individual TerVOCs are involved in the emission of TerVOCs during cleaning. For instance, in the liquid composition of SC – 1, a significant concentration of ethanol of 70 % w/w was

487 detected. In general, in their formulations, surface cleaners contain water and various water-
488 miscible solvents, i.e., alcohols and glycols, which are included to (i) enhance the "fast-dry
489 effect" and (ii) dissolve grease on the surface being cleaned (Magnano et al., 2009; Missia et al.,
490 2012; Steinemann et al., 2011; Wolkoff et al., 1998). The ethanol in surface cleaner SC – 1 was
491 probably included for those purposes and may have accelerated the emission kinetics of
492 TerVOCs due to the fast drying rate.

493 The major terpenes emitted from *kitchen cleaner KC – 2* were eucalyptol, menthol, and
494 limonene, as reported in Fig. 4b. Their respective peak concentrations were 110 ± 10 ppb, 38 ± 5
495 ppb, and 7 ± 1 ppb, contributing to 96 % w/w of the total TerVOC peak concentration.
496 Analogous times (15 minutes) were observed for the peak concentrations of eucalyptol and
497 limonene (Fig. 4b). Noticeably, the emission profile of eucalyptol was characterized by a sharp
498 increase in its concentration and a subsequent clearly identifiable maximum concentration ca. 15
499 minutes. The emission kinetics of eucalyptol contrasts with those of menthol, which had a peak
500 concentration at 30 minutes after the cleaning product was applied. The lower VP of menthol of
501 approximately 18 Pa may explain this different behavior.

502 In the case of the *multiuse cleaner* MC – 1, limonene, eucalyptol and cymene were the
503 main terpenes identified in the gas phase. As shown in Fig. 4c, limonene and eucalyptol had peak
504 concentrations of approximately 145 ppb. However, despite their similar VPs, several differences
505 can be noted in the emission profiles of these terpenes. Limonene and eucalyptol were
506 characterized by a sharp increase up to their peak concentrations within 8 minutes, and 90
507 minutes after the cleaning activity was completed, their gas phase concentrations still accounted
508 for more than 60 % of their peak concentrations. This behavior suggests that after the intense
509 emission within the first minutes post cleaning, their emissions may continue over a long time

510 scale. This phenomenon can be evaluated through the determination of individual TerVOC
511 emission rates as a function of time. In contrast, cymene presents a concentration profile
512 characterized by a broad emission peak corresponding to a low peak concentration but possibly
513 emission over a longer time scale.

514 Comparing the emission dynamics of eucalyptol (commonly released from all cleaners),
515 rapid emission kinetics were observed for MC – 1, from which the maximum emitted
516 concentration of eucalyptol was reached within the first 8 minutes after its application. The peak
517 eucalyptol concentration (140 ppb) emitted from this product (MC – 1) was higher than that from
518 the other tested products; however, the liquid form contained only 424 µg/g eucalyptol. In
519 contrast, slower eucalyptol emission dynamics were observed from KC – 2, with the peak
520 concentration occurring nearly 23 minutes after the application of the kitchen cleaner. KC – 2
521 contained the highest concentration (2230 µg/g) of eucalyptol in its liquid phase, but its
522 maximum emitted eucalyptol concentration was only 110 ppb. These observations suggest that
523 the liquid concentration of individual terpene molecules is not the only key factor driving the
524 transfer from the liquid to the gas phase. To assess the emission of individual TerVOCs from
525 each cleaner, the mass emission rate was calculated from the concentration profiles and assessed
526 in the next section.

527

528 ***3.4 Estimation of TerVOC mass emission rates from monitored concentration profiles***

529 In this study, the emission rate of a cleaning product is defined as the mass of volatile compound
530 emitted per gram of applied product per unit time for a given duration *t* from the beginning of the
531 emission. The estimated mass emission rate from a source is of major importance since (i) it
532 provides key information to understand and describe the emission from an indoor source of

pollutants; (ii) it is a representative parameter that can be extrapolated to realistic cases, allowing the prediction of pollutant emissions in other scenarios; and (iii) it is required for the evaluation of human exposure and indoor quality control technologies.

Indoor pollutant concentrations are governed by various processes, including ventilation, pollutant emission, and pollutant transformation, such as uptake or chemical interaction. The same phenomena could be observed in an emission test chamber. Therefore, it is necessary to address the fate of pollutants considering the contribution of each process separately. In a typical indoor environment, the variation in the concentration of an individual VOC is driven by the mass conservation equation shown in *Eq. 1*.

$$\underbrace{\frac{d[X]}{dt}}_{\text{Concentration profile}} = -\underbrace{\frac{d[X]_{Out}}{dt}}_{\text{Air Exchange}} + \underbrace{\frac{d[X]_{E}}{dt}}_{\text{Pollutant source}} - \underbrace{\frac{d[X]_{Dep}}{dt}}_{\text{Deposition on surfaces}} + \underbrace{\frac{d[X]_{Des}}{dt}}_{\text{Desorption from surfaces}} + \underbrace{\frac{d[X]_{Hom}}{dt}}_{\text{Homogeneous reactivity}} + \underbrace{\frac{d[X]_{Het}}{dt}}_{\text{Heterogeneous reactivity}} \quad \textit{Eq. 1}$$

In controlled environments, such as the emission chamber used for our experiments, several processes included in *Eq. 1* can be ruled out because of the design and operation of the chamber. First, the concentration of one of the main oxidants in the experimental chamber was continuously monitored during experiments; the ozone level remained lower than the detection limit of the ozone analyzer (0.4 ppb) during all experiments, suggesting that the contribution of ozone-induced homogeneous and heterogeneous reactions can be neglected. Harb et al. (2016) and Haghighat and De Bellis (1998) evidenced that stainless steel is the most common chamber material in reviewed publications due to its inert properties. The use of stainless steel prevents the reaction of deposited TerVOCs with the inner material surface of the chamber. This is supported by the fact that no terpenes other than those monitored in the liquid composition and no carbonyls other than those reported in the literature were detected in the gas phase in the

554 experimental chamber. Therefore, surface reactivity on stainless steel was disregarded.
555 Additionally, desorption is endothermic. Moreover, in a temperature-controlled environment, the
556 sorption of TerVOCs is suggested to be irreversible, and desorption is considered negligible.

557 Thus, in the emission experiments with the cleaning products, the TerVOC
558 concentrations in the emission test chamber were predominantly controlled by (i) the air
559 exchange, (ii) the emission rate from the TerVOC sources, and (iii) the loss due to sorption to the
560 inner walls of the chamber (k_D). Therefore, *Eq. 2* describes the resulting pollutant concentration
561 [*X*] in the experimental chamber. Determining the TerVOC emission rates from their monitored
562 concentration profiles requires knowledge of the contributions of their respective AERs and
563 deposition rates.

$$\underbrace{\frac{d[X]}{dt}}_{\text{Concentration profile}} = -\underbrace{\frac{d[X]_{Out}}{dt}}_{\text{Air Exchange}} + \underbrace{\frac{d[X]_E}{dt}}_{\text{Pollutant source}} - \underbrace{\frac{d[X]_{Dep}}{dt}}_{\text{Deposition on surfaces}}$$

564 *Eq. 2*

565

566 *3.4.1 Air exchange*

567 Air exchange removes species *X* via the air renewal system of the emission test chamber and is
568 characterized by k_{AER}, expressed in h^{-1}. The air exchange can be calculated considering the
569 ventilation flow and the volume of the chamber or experimentally determined using a relevant
570 tracer gas. Based on the inlet ventilation flow of our emission test chamber, k_{AER} was fixed at 0.3
571 h^{-1} in all sets of experiments.

$$\underbrace{-\frac{d[X]_{Out}}{dt}}_{\text{Air Exchange}} = -k_{AER} \times [X]$$

572 *Eq. 3*

573

574 *3.4.2 Emission rate*

575 The emission rate of species *X* is determined from its release from the mass of applied product
576 per unit of time. For cleaning products, the mass emission rate is determined using *Eq. 4*, where
577 m_p is the mass of cleaner applied over the surface depending on the cleaning purpose, i.e., floor
578 or surface cleaning, and $V_{chamber}$ corresponds to the volume of the experimental chamber.

$$\underbrace{\frac{d[X]_E}{dt}}_{\text{Pollutant source}} = \frac{\tau(t) \times V_{chamber}}{m_p}$$

579 *Eq. 4*

580 *3.4.3 Deposition on the inner surfaces of the emission test chamber*

581 This phenomenon corresponds to the sorption of gas-phase TerVOCs to the surface of the
582 stainless steel chamber. The nonreactive sorption of TerVOCs on indoor materials can be
583 characterized by the deposition rate k_D expressed in h^{-1} and is driven by the concentration of the
584 gas-phase species X, as reported in *Eq. 5*. Note that k_D depends on the nature of the material and
585 the VOC and was assessed for each set of experiments to provide a comprehensive evaluation of
586 the fate of emitted TerVOCs and its impact on the resulting TerVOC concentrations in the gas
587 phase.

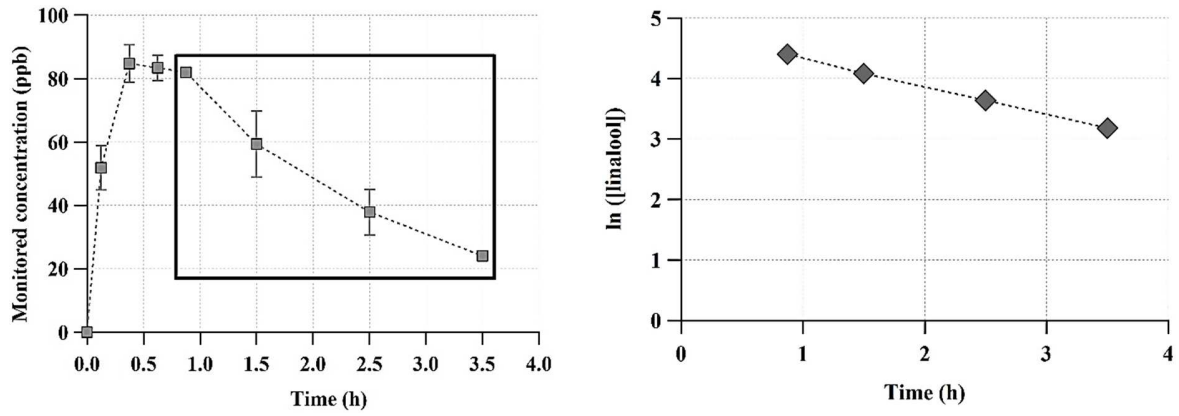
$$\underbrace{-\frac{d[X]_{Dep}}{dt}}_{\text{Deposition on surfaces}} = -k_D \times [X]$$

588 *Eq. 5*

589 As finite sources of TerVOCs, fragrance molecules in cleaning products may become
590 depleted. Thereafter, the drivers of the TerVOC concentrations in the experimental chamber are
591 only (i) the air renewal at a known decay rate (k_{AER}) and (ii) the deposition on walls at a decay
592 rate (k_D). This situation is described in *Eq. 6*, the linearized form of Eq. 2. The air renewal rate
593 was set to 0.3 h^{-1} in our emission test chamber and was therefore easy to account for. The method

to determine k_D is illustrated with the temporal profile of linalool emitted from the surface cleaner SC – 1 in Fig. 5a. After 1 hour of emission, the peak in linalool emission has past, and the experimental data inside the box (Fig. 5a) correspond to a decaying linalool concentration due to air exchange and possible sorption on the emission chamber walls. Based on Eq. 6, this portion of the data series is plotted in Fig. 5b as ln ([linalool]) as a function of time (h). The linear relationship indicates pseudo-first-order decay. The slope of the straight line in Fig. 5b is the sum of k_{AER} and k_D. Since k_{AER} is a known experimental constant, the deposition rate of linalool under our experimental conditions can be determined as k_D (linalool) = 0.16 h^{-1}.

$$\ln\big(X(t)\big) = -(k_{AER} + k_D) \times t + A \qquad (A = constant) \qquad Eq.\ 6$$



(a) (b)

Fig. 5. (a) Temporal evolution of the linalool concentration (ppb) during cleaning using the surface cleaner SC – 1 (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3); the data series in the box corresponds to linalool decay after depletion of its source. (b) Plot of ln ([*linalool*]) as a function of time (h); NB: in b), only the data series within the box in (a) is plotted.

The deposition rates (k_D) of the 6 predominant released TerVOCs were experimentally determined during the application of the surface cleaner SC – 1, the kitchen cleaner KC – 2, and

610 the multiuse cleaner MC – 2 (Table 6) and ranged from 0.12 to 0.52 h^{-1}. These values clearly
611 show that the deposition rates of TerVOCs on the chamber walls have to be determined to
612 interpret the concentration profiles since they impact the resulting concentrations by the same
613 order of magnitude as the AER (0.3 h^{-1}).
614
615 **Table 6.** Comparison of the deposition rate coefficient k_D (h^{-1}) of the predominant terpenes from
616 the three selected cleaning products: (i) the surface cleaner SC – 1, (ii) the kitchen cleaner KC –
617 2, and (iii) the multiuse cleaner MC – 1.

Deposition rate k_D (h^{-1})			
TERPENE	**Cleaning Product**		
	SC – 1	**KC – 2**	**MC – 1**
α-Pinene	0.52	0.46	0.26
Limonene	0.12	0.11	0.24
Linalool	0.16	ND	ND
Eucalyptol	0.19	0.38	0.30
Cymene	Ø	0.22	0.31
Bergamol	0.12	Ø	Ø
Camphor	0.12	ND	Ø
Menthol	Ø	0.08	Ø

618 Ø = This terpene was not identified in a cleaning product in its liquid form.
619 ND: This terpene was not a predominantly emitted terpene from a cleaning product; therefore, it was not detected in
620 the gas phase.

621 According to Table 6, the k_D values for the same species may differ from one applied
622 product to another. For instance, the k_D of α-pinene was 0.52, 0.46, and 0.26 h^{-1} for SC – 1, KC –
623 2, and MC – 1, respectively. These differences are suggested to be associated with the cleaning
624 product formulations. Among cleaning product constituents, water can be present in formulations
625 at mass percentages ranging from 95 % and 50 %. Subsequently, during cleaning, the RH of the

confined environment increases. Springs et al. (2011) evidenced that the number of moles of terpenes taken up per unit of surface area tends to decrease with increasing RH, suggesting competitive interactions with water molecules for uptake surfaces. Consequently, the deposition rate (k_D) of fragrance molecules on indoor materials could be impacted by two main factors: (i) competition for uptake among terpenes and cleaning constituents and (ii) the increase in RH related to the water content of the cleaner. Consequently, the k_D value for a given terpene might differ depending on the cleaning product formulation.

3.4.4 Determination of the mass emission profiles from the concentration profiles

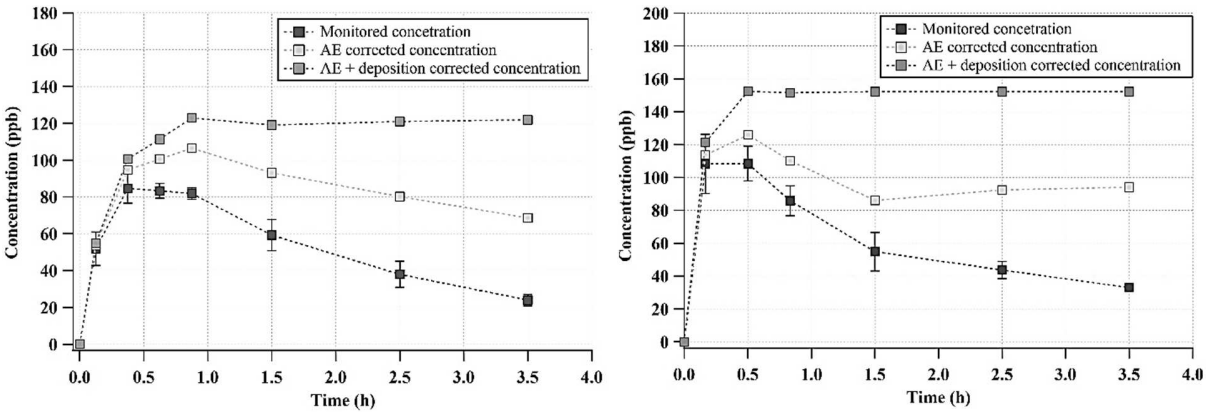
The mass conservation equation under our experimental conditions during cleaning is described by *Eq. 7, w*here [*X*] is the concentration of species X, m_p is the mass of applied cleaning product, $V_{chamber}$ corresponds to the volume of the chamber (m^3), and k_{AER} and k_D are the decay rates (h^{-1}) of species X related to air renewal and deposition.

$$\underbrace{\frac{d[X]}{dt}}_{\text{Concentration profile}} = \underbrace{\frac{\tau(t) \times V_{chamber}}{m_p}}_{\text{Pollutant source}} - \underbrace{(k_D + k_{AER}) \times [X]}_{\text{Concentration of X removed by air exchange and deposition}} \qquad \textit{Eq. 7}$$

Based on *Eq. 7*, the emission rate of a given TerVOC can be retrieved from its concentration profile corrected by the air renewal rate and by the depletion rate. Fig. 6 shows the temporal evolution (a) of linalool emitted during cleaning using the surface cleaner SC – 1 and (b) of eucalyptol released during cleaning using the kitchen cleaner KC – 2. The concentrations of linalool and eucalyptol directly monitored in the 1 m^3 emission test chamber are plotted as black squares in Fig. 6a and b. First, the raw profile was corrected by the air renewal rate, resulting in linalool and eucalyptol concentration profiles that would have been recorded if no air

exchange occurred in the emission test chamber (light gray squares in Fig. 6). Then, these profiles were corrected by the specific deposition rate of each terpene, producing final profiles that correspond to the concentrations if no linalool and eucalyptol had been removed from the gas phase in the chamber, neither by sorption on the chamber walls nor by air exchange (dark gray circles in Fig. 6). The resulting profiles reflect only the linalool and eucalyptol emissions from SC – 1 and KC – 2, respectively. Therefore, the times when these terpenes reach steady state indicates the end of their emission from their respective cleaners. Moreover, this final profile can be used to calculate the emission rate of linalool and eucalyptol according to *Eq. 8*. The same calculations were performed for all terpenes detected in the gas phase during the use of the three cleaners.

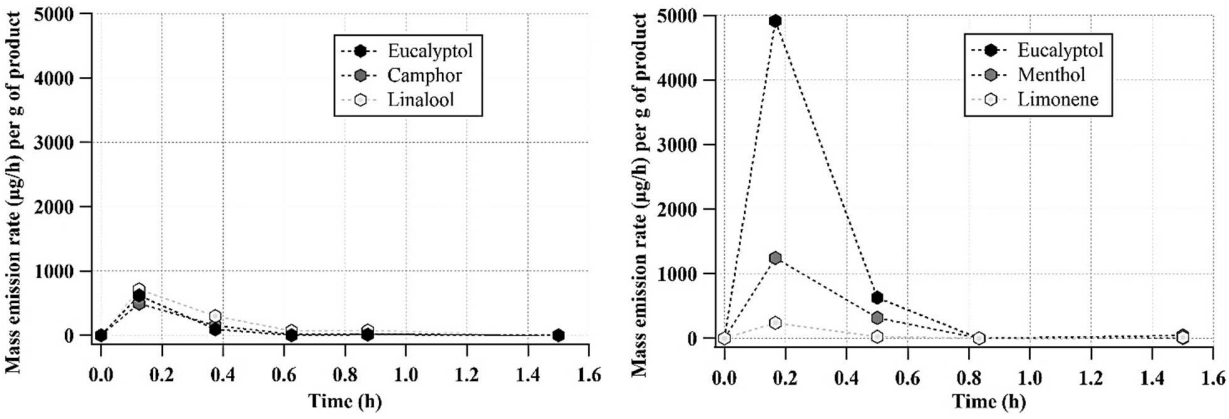
$$\tau(t) = \frac{V_{chambre}}{m_{produit}} \times \frac{(C_{i+1} - C_i)}{(t_{i+1} - t_i)} \qquad \textit{Eq. 8}$$



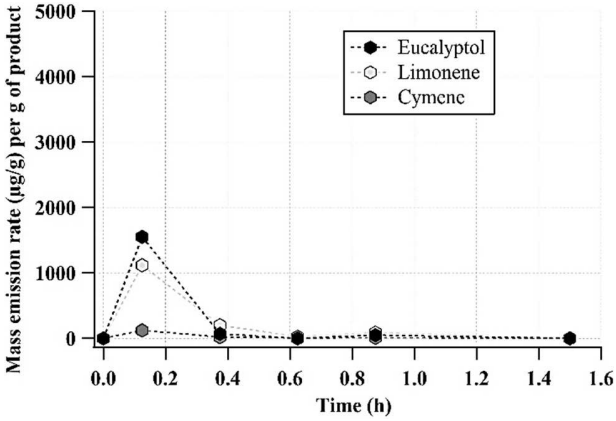
(a) (b)

Fig. 6. (a) Temporal evolution of the (i) monitored concentration (ppb), (ii) air exchange-corrected concentration (ppb), and (iii) air exchange + deposition-corrected concentration (ppb) of linalool during cleaning using the surface cleaner SC – 1. (b) Temporal evolution of the (i) monitored concentration (ppb), (ii) air exchange-corrected concentration (ppb), and (iii) air exchange + deposition-corrected concentration (ppb) of eucalyptol during cleaning using the

663 kitchen cleaner KC – 2 (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1
664 m^3).
665
666 *3.4.5 Emission rate profiles of individual TerVOCs*
667 Based on *Eq. 8*, the temporal evolution of the mass emission rate was calculated for each cleaner
668 and for each TerVOC emitted. Fig. 7 presents the temporal evolution of the mass emission rates
669 of the three predominant TerVOCs monitored during the use of (a) SC – 1, (b) KC – 2 and (c)
670 MC – 1. The temporal profiles of the emission rates allow the determination of (i) the time
671 required to reach the maximum emission rate, (ii) the value of the maximum emission rate, and
672 (iii) the time at which the emission source is depleted.



a) b)



c)

Fig. 7. Temporal evolution of the mass emission rates of the three predominant terpenes detected in the gas phase during the use of (a) the surface cleaner SC – 1, (b) the kitchen cleaner KC – 2 and (c) the multiuse cleaner MC – 1 applied in the 1 m^3 emission test chamber (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

Based on Fig. 7, irrespective of the cleaning product, the time required for a given terpene to reach the maximum emission rate was similar for all monitored terpenes: within 8 minutes after cleaning was completed. However, the magnitude of the peak emission rate of the predominant terpene released clearly differed from one cleaning product to another: (i) 710 ± 15 µg/h linalool from SC – 1, (ii) 1550 ± 90 µg/h eucalyptol from MC – 1, and (iii) 5 000 ± 120 µg/h eucalyptol from KC – 2.

Noticeably, the emission of eucalyptol and menthol from KC – 2 was exhausted within 50 minutes and after 30 minutes for limonene. Of the three selected categories, this product category had the highest emission rates. However, SC – 1 and MC – 1 showed shorter emission durations than KC – 2. Their total TerVOC emissions were exhausted within only 24 minutes, as shown in Fig. 7a and b.

Regarding the emission of individual terpenes, eucalyptol was only terpene emitted from all three tested cleaners. However, its peak emission rate varied widely, reaching 620 ± 20 µg/h, 4 900 ± 110 µg/h and 1460 ± 30 µg/h for the surface cleaner (SC – 1), the kitchen cleaner (KC –

687 2) and the multiuse cleaner (MC – 1), respectively. Similar emission rate variability was
688 observed for the limonene emitted from two products: 240 ± 30 µg/h and 1100 ± 80 µg/h for KC
689 – 2 and MC – 1, respectively.

690 The assessment of the emission rates confirms that in addition to the liquid TerVOC
691 content in the cleaner, the emission dynamics are also driven by (i) the solvent matrix in which
692 the fragrance molecules are contained due to chemical affinities that might be generated among
693 species, delaying the emission kinetics, and (ii) the volatility of individual terpene molecules.

694

695 ***3.5 Emission of OVOCs from natural cleaning products under realistic application conditions:***
696 ***1 m^3 emission test chamber***

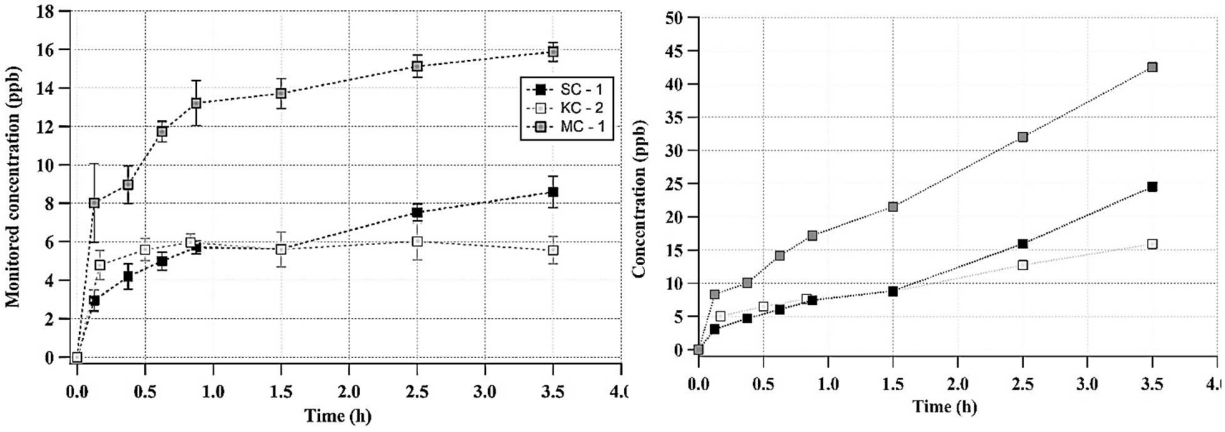
697 Carbonyl compounds were monitored during each set of emission experiments. Three targeted
698 oxygenated VOCs emitted from the application of SC – 1, KC – 2 and MC – 1 were identified
699 and quantified: formaldehyde, acetaldehyde and acetone. Their individual maximum emitted
700 concentrations varied from one cleaning product to another, ranging from (i) 6 ± 1 to 18 ± 3 ppb
701 formaldehyde, (ii) 22 ± 3 to 210 ± 20 ppb acetaldehyde, and (iii) 18 ± 4 to 108 ± 15 ppb acetone.
702 Among the identified OVOCs, formaldehyde was classified in 2016 by the European
703 Commission as carcinogenic (Group 1) and genotoxic (International Agency for Research on
704 Cancer, 1979). Additionally, the long-term exposure limit was established at 9 ppb by the World
705 Health Organisation (2010). Thus, in the framework of this study, formaldehyde is of particular
706 interest because of its toxicity.

707

708 *3.5.1 Formaldehyde emission profiles from the use of natural cleaning products*

Fig. 8a presents the temporal evolution of the concentration of formaldehyde emitted by cleaning with SC – 1, KC – 2 and MC – 1. Unlike the terpene emission profiles, the temporal evolution of the formaldehyde concentration in Fig. 8 is characterized by two phases: (i) a marked increase confirming the rapid transfer of formaldehyde from the product to the gas phase during the first 50 minutes of emission and (ii) either a slow increase for SC – 1 and MC – 1 or steady state for KC – 2. In contrast to the terpene concentration profiles, the emission profiles of formaldehyde do not follow a typical transient emission process. As observed in Fig. 8a, the maximum emitted concentration of formaldehyde was 9 and 16 ppb for the surface cleaner (SC – 1) and for the multiuse cleaner (MC – 1), respectively. These values were observed 3.5 hours after the cleaning was finished. For the kitchen cleaner KC – 2, the concentration of formaldehyde reached 6 ppb at 0.8 hours and then remained constant for at least 3.5 hours after the product application. These observations suggest that even after 3.5 h, the emission source of formaldehyde was not exhausted, reflecting delayed emission kinetics that may not solely be related to a primary release from the cleaning product itself. In agreement with our findings, (CSTB, 2006); Solal et al. (2014) assessed the emissions of formaldehyde from 35 consumer products in different categories applied under realistic conditions in the experimental house MARIA. Among the evaluated products, the uses of (i) 2 vacuum fresheners, (ii) 2 carpet cleaners, (iii) 3 toilet cleaners, (iv) 4 glass cleaners and (v) 2 furniture polishes were associated with increases in the formaldehyde concentration in the experimental house. The observed concentrations were described by the same two phases shown in Fig. 8a: (i) a sharp increase in the HCHO concentration confirming the rapid transfer of formaldehyde from the product to the gas phase and (ii) a slower increase or steady state. The maximum concentrations that arise from the

731 emission were 6 to 16 ppb, depending on the category of product applied. These values were
732 observed at 120 minutes after the cleaning was completed.
733



(a) (b)

734 **Fig. 8.** (a) Temporal evolution of the concentration of formaldehyde (ppb) from the use of three
735 cleaning products: (i) surface cleaner (SC-1), (ii) kitchen cleaner (KC-1) and (iii) multiuse
736 cleaner (MC-1) (T = 23 °C, RH = 50 %, AER = 0.3 h^{-1}). (b) Temporal evolution of the *air*
737 *exchange-corrected* concentration of formaldehyde (ppb) as a function of time during cleaning
738 with the three cleaners: (i) SC – 1, (ii) KC – 2, and (iii) MC – 1 (T = 23 °C, RH = 50 %, AER =
739 0.3 h^{-1}).
740

741 To confirm these observations, the emission profile was corrected by the air exchange in
742 the experimental chamber, i.e., k_{AER} of 0.3 h^{-1}. The corrected profile is presented in Fig. 8b,
743 which depicts the temporal evolution of the concentration of formaldehyde that would have been
744 monitored if no air exchange occurred in the emission test chamber. The concentration variation
745 resulted from only the transfer of formaldehyde to the gas phase and the possible sorption on the
746 inner walls of the experimental chamber. However, the mass emission rate of formaldehyde

747 cannot be calculated by the estimation method in section 3.4 since the emission source could not
748 be assumed to be exhausted and the deposition rate (k_D) could not be determined. As shown in
749 Fig. 8b, the corrected profile of formaldehyde emission from SC – 1, MC – 1 and KC – 2 was
750 characterized by two main phases: (i) a primary increase in the concentration, suggesting a
751 release linked to a primary emission of formaldehyde potentially contained in the cleaning
752 product, and (ii) a linear increase in the concentration of formaldehyde. The slope of the linear
753 relationship of the corrected formaldehyde concentration varied depending on the cleaning
754 product. Therefore, the temporal evolution of the corrected formaldehyde concentration,
755 presented in Fig. 8b, did not correspond to a transient emission profile but suggested the
756 presence of formaldehyde releasers in the cleaning product formulation, in which case, the
757 concentration of formaldehyde might be associated with secondary emission sources.

758 The specific concentration dynamics associated with the emission of formaldehyde are
759 suggested to be related to two mechanisms: (i) direct (or primary) emission of formaldehyde
760 contained in the cleaning product and (ii) emission of formaldehyde from formaldehyde-
761 releasing molecules present in the cleaning product formulations (Pastor-Nieto et al., 2017).
762 Formaldehyde releasers are defined as chemical compounds that decompose to release
763 formaldehyde when dissolved in aqueous solvents (De Groot et al., 2009; Flyvholm and
764 Andersen, 1993; Kajimura et al., 2008). This process is characterized by an in situ degradation of
765 non-formaldehyde-containing components, i.e., the self-oxidation of ethoxylated alcohols.
766 Generally, these chemicals are used in consumer products as preservatives, antiseptics, and/or for
767 enhancing their disinfectant performance. The concentration of formaldehyde or formaldehyde-
768 releasing compounds added in product formulations might depend on their use purpose and
769 manufacturer preferences. According to the National Database for Products and Compositions in

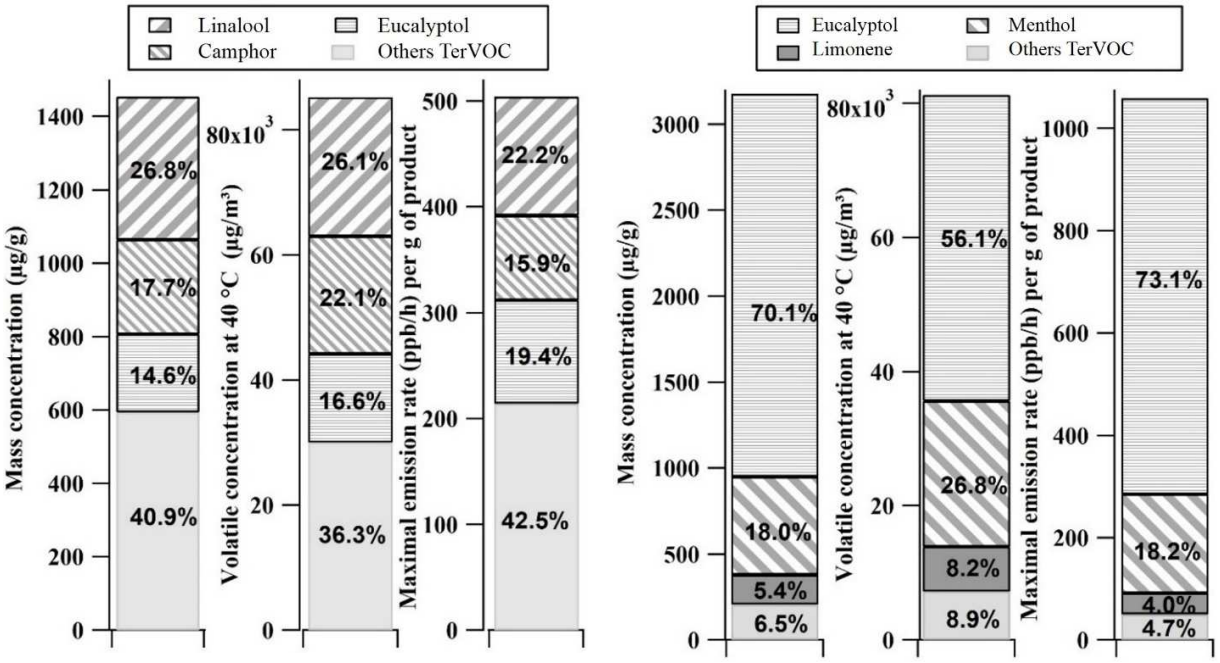
770 France (BNPC), formaldehyde releasers are included in the formulations of 78 % of household
771 products as preservative agents, corresponding to a mass concentration ranging from 0.2 % to 0.3
772 % w/w (Affset, 2009).

773 De Groot et al. (2009) assessed formaldehyde and formaldehyde releasers contained in
774 consumer products in various categories by reviewing the Danish Product Register Database
775 (*PROBAS*). His findings reveal that the most important product categories containing
776 formaldehyde or formaldehyde releaser are (i) biocides or pesticides; (ii) paints, lacquers and
777 varnishes; and (iii) cleaning and washing agents. In the cleaning and washing agents, 9 different
778 formaldehyde-releasing compounds were identified. Among these chemicals, Bronopol® (*2-*
779 *brono-2-nitropropane-1,3-diol*) was the most frequently used formaldehyde releaser, being
780 detected in 124 out of 275 cleaning products or washing agents. However, the authors indicated
781 that a total of 19 out of the 42 detected formaldehyde-releasing compounds were not found in
782 *PROBAS*. Similarly, the BNPC in France reported the presence of formaldehyde releasers in 236
783 out of 692 cleaning products on the European market (Affset, 2009). Additionally, the BNPC
784 published and identified a list of 24 compounds confirmed as formaldehyde releasers, including
785 Bronopol® and Methenamine as the most frequently used among household products. Kajimura
786 et al. (2008) investigated the formation of HCHO from a common formaldehyde-releasing
787 compound known as Bronopol® from a homemade cosmetic product prepared with 0.1 % w/v of
788 this molecule. This study aimed to correlate the presence of Bronopol® and the respective
789 formation of formaldehyde by headspace analysis. Their results verified an increase in
790 formaldehyde concentration over time, reaching 20 ppm after 10 days, and this level was
791 observed to be constant over 50 days. Note that this concentration cannot be compared to our
792 results because of differences in the experimental protocol and approach.

793 Regarding the three cleaning products evaluated in this study, the presence of Bronopol®
794 was listed by manufacturers for only the multiuse cleaner MC – 1. Its presence may explain the
795 unique formaldehyde emission profile observed for that product. However, according to
796 European legislation for the cleaning product industry, numerous formaldehyde releasers are not
797 required to be included in the product ingredient list. With this lack of information, the
798 correlation between the formaldehyde emission profile observed for the tested cleaning products
799 and the presence of formaldehyde releasers in their composition is suggested but has not been
800 confirmed.
801 Therefore, the use of natural cleaning products might generate a continuously increasing
802 indoor formaldehyde concentration, in which the maximum emitted levels might remain in the
803 confined environment for several hours after the cleaning is completed. Additionally,
804 formaldehyde releasers included in consumer products represent a hidden source of
805 formaldehyde, of which consumers might not even be aware, extending its impact on IAQ by
806 several tens of ppb for several hours after household activity is completed.
807
808 ***3.6 Wrap-up of the terpene emissions from cleaning products: from their liquid composition to***
809 ***their mass emission rates***
810 In this work, the TerVOC emissions from the use of 3 cleaners were investigated by comparing
811 different scales, including their liquid composition, their gas-transferred concentration and their
812 emission under realistic use patterns. This innovative methodology allowed the investigation of
813 the emission of fragrance molecules at different scales to evaluate the impact on IAQ through an
814 integrated approach, achieving an accurate assessment of the mass emission rates. These

estimated mass emission rates could be further implemented for the estimation of human exposure to these chemicals and to the definition of risk scenarios.

Fig. 9 shows the relative abundances expressed as percentages of the predominant TerVOCs and as their respective absolute scales for (i) the mass concentration detected in the liquid form (µg/g of product), (ii) the volatile fraction (gas-transferred concentration) associated with the micro-chamber testing (µg/m^3), and (iii) the maximum emission rates per individual terpene (ppb/h per g of product) associated with the use of (a) the surface cleaner SC – 1, (b) the kitchen cleaner KC – 2, and (c) the multiuse cleaner MC – 1.



(a) (b)

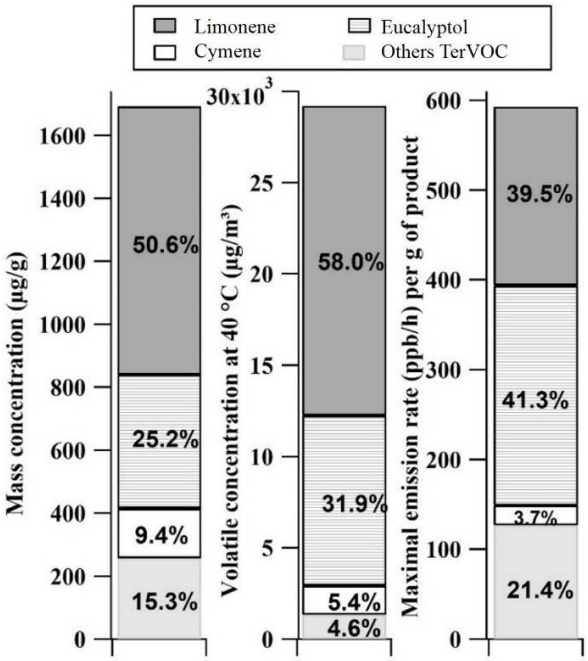


Fig. 9. Comparison of the relative abundances in the mass concentration (µg/g) in the liquid phase, the volatile concentration (µg/m^3) (T = 40 °C, dry air flow = 50 mL/min, micro-chamber volume = 44 mL) and the maximum emission rate per gram of cleaning product (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3) for (a) the surface cleaner SC – 1, (b) the kitchen cleaner KC – 2, and (c) the multiuse cleaner MC – 1.

(c)

In terms of the absolute values, written in bold in Fig. 9, no correlation was found between them. As mentioned in section 3.2, the maximum emission rate of terpene molecules from the use of essential-oil-based cleaning products cannot be directly predicted from their content in the liquid form or from micro-chamber testing. Micro-chamber results can be used to describe key general trends of the predominant emitted terpenes but should not be considered for realistic emission assessment. Moreover, the relative distributions between terpenes for the liquid content and for the maximum emission rate are much closer rather than one for the gas-transferred concentration. That can be explained by the fact that micro-chamber experiments were conducted at a temperature of 40 °C, enhancing the transfer from the liquid to the gas phase.

In regard to the behavior of specific compounds, such as eucalyptol and limonene, two species with similar VPs (260 and 219 Pa, respectively), substantial differences were observed. In all the investigated cleaning products, eucalyptol evidence higher proportions in the maximum mass emission rate if compared to its relative abundance in the liquid form. This observation confirms the ability of eucalyptol to be transferred from the liquid to the gas phase, irrespective of the solvent matrix of the cleaner. In contrast, for a given cleaning product, limonene had (i) a lower relative abundance at the maximum mass emission rate than in the liquid phase and (ii) a higher relative abundance in the volatile fraction than in the liquid form. These observations suggest that the emission of limonene might be more impacted by the solvent matrix in the cleaning product than by its volatility (VP = 219 Pa), and therefore, its mass transfer might be delayed due to chemical affinities to other compounds.

4. CONCLUSIONS AND PERSPECTIVES

This study has shown that the largest contributors of terpenes to indoor air are not only recognized, regulated and controlled sources, namely, building materials, but also “green” household products, which should be seriously considered as versatile and high-impact sources. These fragrance chemicals classified as allergens responsible for skin irritation, allergic rhinitis, and asthma are primarily associated with the use of cleaning products (Wolkoff and Nielsen, 2017). Essential-oil-based household products might release concentrations of several tens to hundreds of ppb TerVOCs, exceeding the exposure limits established by the European Union and the United States (Dimitroulopoulou et al., 2015; Kirchner et al., 2001; World Health Organisation, 2010). Regarding formaldehyde emissions from the investigated cleaning products, this study has confirmed that these products could represent a hidden source of formaldehyde in

858 confined environments. Indeed, consumers might increase the formaldehyde concentration
859 indoors by several ppb without being aware of it due to the presence of non-regulated
860 formaldehyde-releasing compounds contained in these types of products.

861 Several key factors were confirmed to drive the mass transfer from the liquid to the gas
862 phase of terpene molecules contained in essential-oil-based cleaning products: (i) the mass
863 concentration of individual terpenes in the liquid phase, since a correlation between the major
864 contained and the predominantly emitted terpenes was observed for all the tested cleaning
865 products; (ii) the solvent matrix included in the cleaning formulation, which may generate
866 chemical affinities between terpenes and the cleaner constituents, impacting the emission
867 dynamics; and (iii) the volatility of the individual terpene molecules.

868 Micro-chamber testing cannot replace standard emission test chambers but is a
869 complementary tool that allows evaluation of the gas-transferred concentrations and rapid
870 screening of the potentially released TerVOCs from essential-oil-based household products prior
871 to a detailed product emissions characterization. Micro-chamber experiments need to be
872 accompanied by an evaluation of the effective emissions under realistic conditions in a test
873 chamber to accurately estimate the human exposure to cleaning product constituents under
874 recommend application scenarios.

875 While this study aimed to implement realistic scenarios, the 1 m^3 chamber imposes
876 limitations regarding the application process. Due to space limitations, real consumer use
877 patterns while performing a cleaning activity could not be completely reproduced. Without being
878 wiped, trigger spray products were directly sprayed in the chamber and dispersed by droplets
879 onto the surface, and liquid cleaning products were drizzled on the surface placed at the center of

the chamber. Therefore, further assessments of TerVOC emissions from essential-oil-based cleaning products under real consumer use patterns in a full-scale room are highly recommended.

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DECLARATIONS OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

AFFSET, 2009. Formaldéhyde - Rélation Entre Composition et Émission. Rapport ANSES, France, pp. 150-200.

Babu K.G.D., Singh B., Joshi V.P., Singh V., 2002. Essential oil composition of Damask rose (Rosa damascena Mill.) distilled under different pressures and temperatures. Flavour and Fragrance Journal 17, 136-140.

BEUC, 2005. Emission of Chemicals by Air Fresheners. Final Report. ICRT International Consumer Research & Testing, Belgium.

Brown S.K., 1999. Chamber assessment of formaldehyde and VOC emissions from wood-based panels. Indoor Air 9, 209-215.

Brown S.K., Sim M.R., Abramson M.J., Gray C.N., 1994. Concentrations of volatile organic compounds in indoor air – A review. Indoor Air 4, 123-134.

Chesnais E., Marchais M., 2014. Sprays assainissants et désodorisants. Notre Intérieur Dégradé 530, 50-53.

Colombo A., De Bortoli M., Knöppel H., Schauenburg H., Vissers H., 1991. Small chamber tests and headspace analysis of volatile organic compounds emitted from household products. Indoor Air 1, 13-21.

CSTB, 2006. Caractérisation des Émissions de COV et Formaldéhyde par Différents Types de Produits. Rapp. Sci. CSTB SB-06-044.

De Groot A.C., Flyvholm M.A., Lensen G., Menne T., Coenraads P.J., 2009. Formaldehyde-releasers: relationship to formaldehyde contact allergy. Contact allergy to formaldehyde and inventory of formaldehyde-releasers. Contact Dermatitis 61, 63-85.

Delmas C., Weiler A.S., Ortega S., Duong O., Dazy A., Ott M., Schneider C., Moritz R., Leclerc N., Rivière E., De Blay F., 2016. Mesure de la concentration aérienne de COV terpéniques (dont le limonène) selon plusieurs procédures lors de pulvérisations d'un mélange d'huiles essentielles. Revue Française d'Allergologie 56, 357-363.

Dimitroulopoulou C., Trantallidi M., Carrer P., Efthimiou G.C., Bartzis J.G., 2015. EPHECT II: exposure assessment to household consumer products. Science of the Total Environment 536, 890-902.

Espinosa Díaz M.A., Guetachew T., Landy P., Jose J., Voilley A., 1999. Experimental and estimated saturated vapour pressures of aroma compounds. Fluid Phase Equilibria 157, 257-270.

Ettre L.S., Welter C., Kolb B., 1993. Determination of gas-liquid partition coefficients by automatic equilibrium headspace-gas chromatography utilizing the phase ratio variation method. Chromatographia 35, 73-84.

934 Ezendam J., Te Biesebeek J.D., Wijnhoven S.W.P., 2009. The Presence of Fragrance Allergens in
935 Scented Consumer Product. Letter Report 340301002/2009. National Institute of Public Health
936 and the Environment, Netherland.
937 Flyvholm M.A., Andersen P., 1993. Identification of formaldehyde releasers and occurrence of
938 formaldehyde and formaldehyde releasers in registered chemical products. American Journal of
939 Industrial Medicine 24, 533-552.
940 Guichard E., 2002. Interactions between flavor compounds and food ingredients and their influence on
941 flavor perception. Food Reviews International 18, 49-70.
942 Haghighat F., De Bellis L., 1998. Material emission rates: literature review, and the impact of indoor air
943 temperature and relative humidity. Building and Environment 33, 261-277.
944 Harb P., Locoge N., Thevenet F., 2018. Emissions and treatment of VOCs emitted from wood-based
945 construction materials: impact on indoor air quality. Chemical Engineering Journal 354, 641-652.
946 Harb P., Sivachandiran L., Gaudion V., Thevenet F., Locoge N., 2016. The 40m^3 Innovative experimental
947 Room for INdoor Air studies (IRINA): development and validations. Chemical Engineering
948 Journal 306, 568-578.
949 Höllbacher E., Ters T., Rieder-Gradinger C., Srebotnik E., 2017. Emissions of indoor air pollutants from
950 six user scenarios in a model room. Atmospheric Environment 150, 389-394.
951 Hoskovec M., Grygarová D., Cvačka J., Streinz L., Zima J., Verevkin S.P., Koutek B., 2005. Determining
952 the vapour pressures of plant volatiles from gas chromatographic retention data. Journal of
953 Chromatography A 1083, 161-172.
954 Huang Y., Ho S.S.H., Ho K.F., Lee S.C., Gao Y., Cheng Y., Chan C.S., 2011. Characterization of
955 biogenic volatile organic compounds (BVOCs) in cleaning reagents and air fresheners in Hong
956 Kong. Atmospheric Environment 45, 6191-6196.
957 International Agency for Research on Cancer, 1979. IARC Monographs on the Evaluation of the
958 Carcinogenic Risk of Chemicals to Humans. International Agency for Research on Cancer, Lyon,
959 France.
960 ISO 16000-9, 2006. Indoor Air - Part 9: Determination of the Emission of Volatile Organic Compounds
961 from Building Products and Furnishing - Emission Test Chamber Method. BSI, London, UK.
962 Jo W.K., Lee J.H., Kim M.K., 2008. Head-space, small-chamber and in-vehicle tests for volatile organic
963 compounds (VOCs) emitted from air fresheners for the Korean market. Chemosphere 70, 1827-
964 1834.
965 Jouquand C., Aguni Y., Malhiac C., Grisel M., 2008. Influence of chemical composition of
966 polysaccharides on aroma retention. Food Hydrocolloids 22, 1097-1104.

967 Kajimura K., Tagami T., Yamamoto T., Iwagami S., 2008. The release of formaldehyde upon
968 decomposition of 2-Bromo-2-nitropropan-1, 3-diol (Bronopol). Journal of Health Science 54,
969 488-492.
970 Kirchner S., Buchmann A., Cochet C., Dassonville C., Derbez M., Leers Y., Lucas J.P., Mandin C.,
971 Ouattara M., Ramalho O., Riberon J., 2001. Qualité d'Air Intérieur, Qualité de Vie. 10 ans de
972 Recherche Pour Mieux Respirer. CSTB, Paris, France.
973 Kwon K.D., Jo W.K., Lim H.J., Jeong W.S., 2007. Characterization of emissions composition for selected
974 household products available in Korea. Journal of Hazardous Materials 148, 192-198.
975 Lai A.C., Thatcher T.L., Nazaroff W.W., 2000. Inhalation transfer factors for air pollution health risk
976 assessment. Journal of the Air and Waste Management Association 50, 1688-1699.
977 Lassen C., Havelund S., Mikkelsen S., 2008. Health Assessment of Chemical Substances in Essential Oils
978 and Fragrance Oils. Survey No. 92. Danish Environmental Protection Agency (DEPA), Denmark.
979 López E.F., Gómez E.F., 2000. Comparison of solvents for determination of monoterpenes in wine using
980 liquid-liquid extraction. Chromatographia 52, 798-802.
981 Lucas J.P., Ramalho O., Kirchner S., Ribéron J., Intérieurs P., 2009. Etat de la Ventilation Dans le Parc
982 de Logements Français. CSTB DESE/SB-2009-037, Paris, France.
983 Magnano M., Silvani S., Vincenzi C., Nino M., Tosti A., 2009. Contact allergens and irritants in
984 household washing and cleaning products. Contact Dermatitis 61, 337-341.
985 Missia D., Kopanidis T., Bartzis J., Ventura G., De Oliveira Fernandes E., Carrer P., Wolkoff P., Stranger
986 M., Goelen E., 2012. Literature Review on Product Composition, Emitted Compounds and
987 Emissions Rates and Health End Points from Consumer Products. Final Report European Project
988 EPHECT. Executive Agency for Health and Consumers-EAHC, European Union.
989 Nazaroff W.W., Weschler C.J., 2004. Cleaning products and air fresheners: exposure to primary and
990 secondary air pollutants. Atmospheric Environment 38, 2841-2865.
991 Nicolas M., Chiappini L., 2013. Household Products Using and Indoor Air Quality: Emissions, Reactivity
992 and By-products. Final Report ADOQ Project. Centre Scientifique et Technique du Bâtiment
993 (CSTB), INERIS, Paris, France
994 Nicolas M., Karr G., Real E., Maupetit F. Avril 2019. Impact des produits d'entretien sur la qualité de
995 l'air intérieur. PEPS – Définition d'un protocole d'essais simple et harmonisé pour l'évaluation
996 des émissions en composés volatils. Report ADEME. 20 – 162p. www.ademe.fr/mediatheque
997 Norgaard A.W., Kofoed-Sorensen V., Mandin C., Ventura G., Mabilia R., Perreca E., Cattaneo A.,
998 Spinazze A., Mihucz V.G., Szigeti T., De Kluizenaar Y., Cornelissen H.J., Trantallidi M., Carrer
999 P., Sakellaris I., Bartzis J., Wolkoff P., 2014. Ozone-initiated terpene reaction products in five

European offices: replacement of a floor cleaning agent. Environmental Science and Technology 48, 13331-13339.

Pastor-Nieto M.A., Alcántara-Nicolás F., Melgar-Molero V., Pérez-Mesonero R., Vergara-Sánchez A., Martín-Fuentes A., González-Muñoz P., De Eusebio-Murillo E., 2017. Preservatives in personal hygiene and cosmetic products, topical medications, and household cleaners in Spain. Actas Dermo-Sifiliográficas 108, 758-770.

Pors J., Fuhlendorff R., 2003. Mapping of Chemical Substances in Air Fresheners and Other Fragrance Liberating Products. Survey No. 30. Danish Environmental Protection Agency (DEPA), Denmark.

Rastogi S.C., 2002. Contents of Selected Fragrance Materials in Cleaning Products and Other Consumer Products. Survey No. 8. Danish Environmental Protection Agency (DEPA), Denmark.

Rastogi S.C., Heydorn S., Johansen J.D., Basketter D.A., 2001. Fragrance chemicals in domestic and occupational products. Contact Dermatitis 45, 221-225.

Sarwar G., Olson D.A., Corsi R.L., Weschler C.J., 2004. Indoor fine particles: the role of terpene emissions from consumer products. Journal of the Air and Waste Management Association 54, 367-377.

Singer B.C., Coleman B.K., Destaillats H., Hodgson A.T., Lunden M.M., Weschler C.J., Nazaroff W.W., 2006a. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. Atmospheric Environment 40, 6696-6710.

Singer B.C., Destaillats H., Hodgson A.T., Nazaroff W.W., 2006b. Cleaning products and air fresheners: emissions and resulting concentrations of glycol ethers and terpenoids. Indoor Air 16, 179-191.

Solal C., Rousselle C., Mandin C., Manel J., Maupetit F., 2014. VOCs and Formaldehyde Emissions from Cleaning Products and Air Fresheners, Proceedings of the 11th International Conference on Indoor Air Quality and Climate. Technical University of Denmark (DTU), Copenhagen, Denmark, Paper ID: 183.

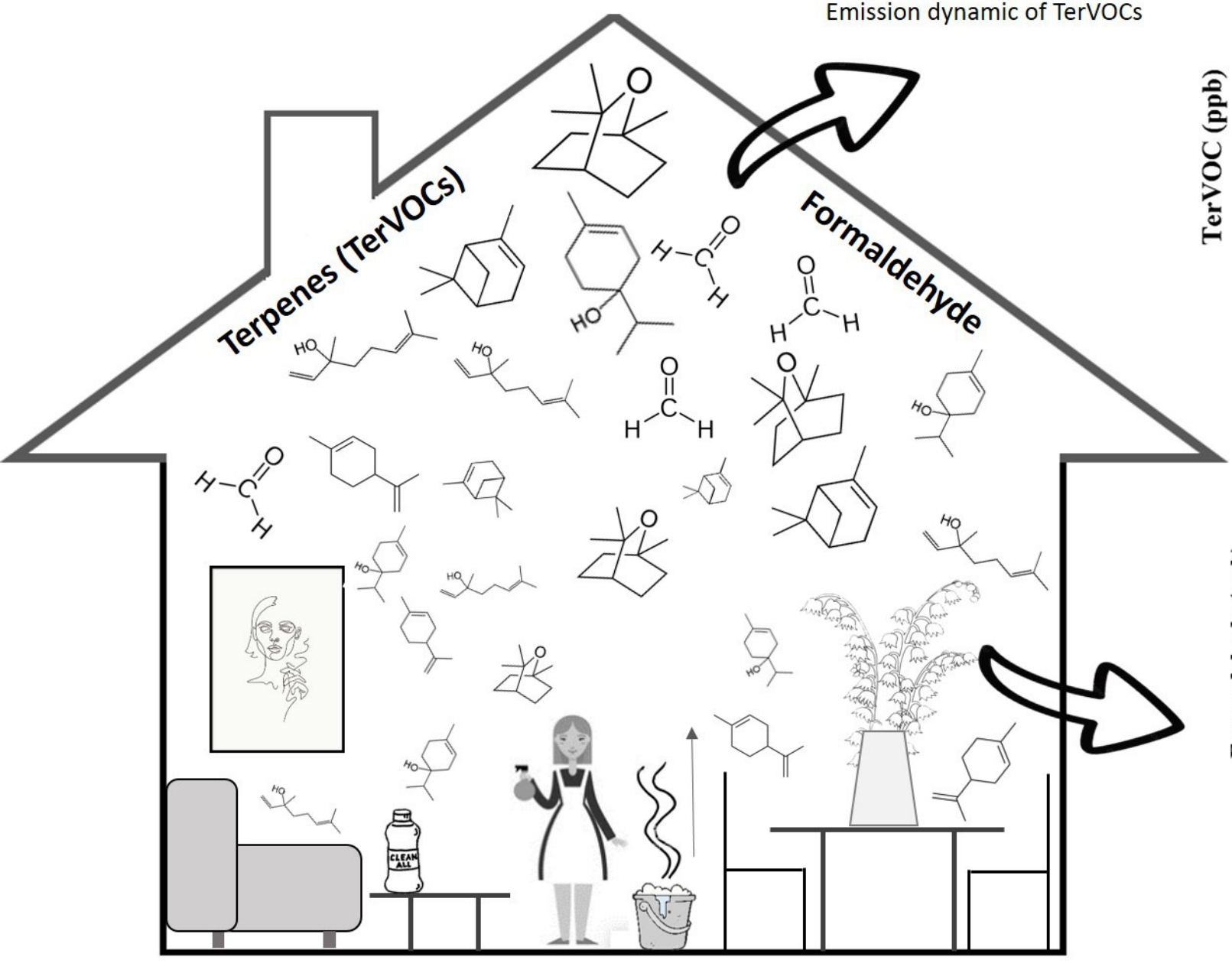
Springs M., Wells J.R., Morrison G.C., 2011. Reaction rates of ozone and terpenes adsorbed to model indoor surfaces. Indoor Air 21, 319-327.

Steinemann A., 2016. Fragranced consumer products: exposures and effects from emissions. Air Quality, Atmosphere and Health 9, 861-866.

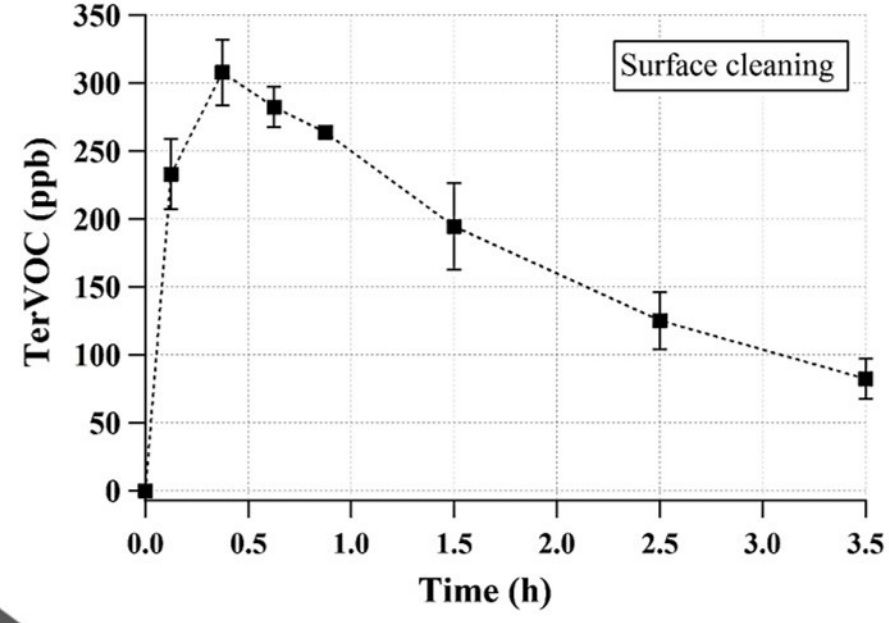
Steinemann A.C., 2009. Fragranced consumer products and undisclosed ingredients. Environmental Impact Assessment Review 29, 32-38.

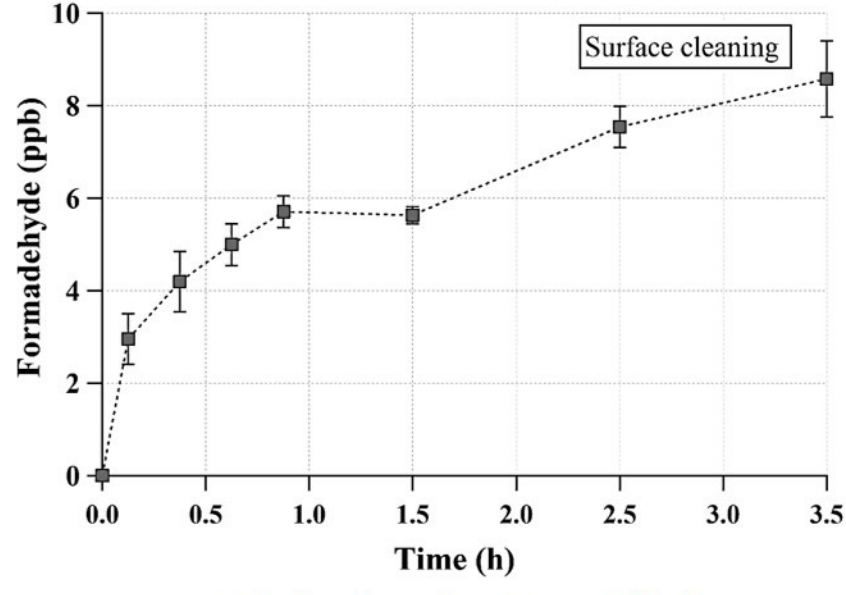
Steinemann A.C., MacGregor I.C., Gordon S.M., Gallagher L.G., Davis A.L., Ribeiro D.S., Wallace L.A., 2011. Fragranced consumer products: chemicals emitted, ingredients unlisted. Environmental Impact Assessment Review 31, 328-333.

1034 Štejfa V., Fulem M., Růžička K., Červinka C., 2014. Thermodynamic study of selected monoterpenes II.
1035 The Journal of Chemical Thermodynamics 79, 272-279.
1036 Teixeira B., Marques A., Ramos C., Neng N.R., Nogueira J.M.F., Saraiva J.A., Nunes M.L., 2013.
1037 Chemical composition and antibacterial and antioxidant properties of commercial essential oils.
1038 Industrial Crops and Products 43, 587-595.
1039 Trantallidi M., Dimitroulopoulou C., Wolkoff P., Kephalopoulos S., Carrer P., 2015. EPHECT III: health
1040 risk assessment of exposure to household consumer products. Science of the Total Environment
1041 536, 903-913.
1042 Uhde E., Schulz N., 2015. Impact of room fragrance products on indoor air quality. Atmospheric
1043 Environment 106, 492-502.
1044 Weschler C.J., 2001. Reactions among indoor pollutants. The Scientific World Journal 1, 443-457.
1045 Wolkoff P., Nielsen G.D., 2017. Effects by inhalation of abundant fragrances in indoor air - An overview.
1046 Environment International 101, 96-107.
1047 Wolkoff P., Schneider T., Kildesø J., Degerth R., Jaroszewski M., Schunk H., 1998. Risk in cleaning:
1048 chemical and physical exposure. Science of the Total Environment 215, 135-156.
1049 World Health Organisation, 2010. WHO Guidelines for Indoor Air Quality. Final Report, 2010. WHO
1050 European Centre for Environment and Health, Copenhagen Ø, Denmark.
1051 Zuzarte M., Salgueiro L., 2015. Essential Oils Chemistry, in: De Sousa, D.P. (Ed.), Bioactive Essential
1052 Oils and Cancer. Springer International Publishing, Cham, pp. 19–61.



Emission dynamic of TerVOCs





Emission dynamic of Formaldehyde