Emissions of terpenes from the use of essential-oil-based household products under realisatic condition : impact on indoor air quality

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Emissions of terpenes from the use of essential-oil-based household products

under realistic conditions: *impact on indoor air quality*

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Thesis outline

General introduction

General introduction

Indoor environmental quality (IEQ) refers to the quality of a building environment encompassing several key factors that are directly related to the health, wellbeing, and comfort of occupants and residents. These factors, presented in Figure 1, determining the quality of life in indoor environments involve (i) indoor air contaminant concentrations, (ii) light and acoustic conditions and (iii) building design. [1] In order to implement different strategies for improving IEQ, various efforts in the scientific framework are required to fully characterize the complex interactions between the health of occupants and the indoor spaces they inhabit. [2]
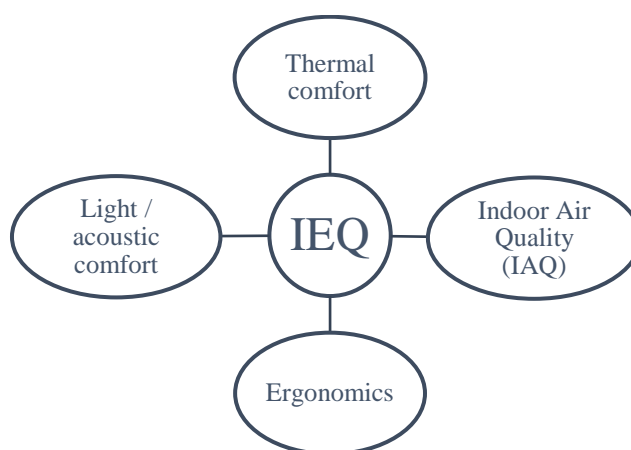
Figure 1. Main key determinants for the assessment of the Indoor Environmental Quality (IEQ)

Major efforts have been made to address indoor air current problematic since the daily activities of the most of the human beings occur in confined environments, representing nearly 90% of the air that people are in contact with. As a consequence of health problems linked to poor indoor air quality, French government spends the substantial amount of 19 billion of euros per year, according to OQAI (Observatoire de la Qualité de l'Air Intérieur). [3]

Among indoor contaminants, people are exposed to a large variety of pollutants from chemical, biological or physical origins. Indeed, confined indoor environments can be considered as an open reactor where the dynamics of the pollutants are driven by various sources and sinks. [4] The attention of the scientific community is chiefly given to chemical pollutants, and among them volatile organic compounds (VOCs). They are defined as organic compounds with lower boiling points ranging from 50 to 100°C and upper boiling points ranging from 240 to 260 °C. [5], [6] The characterization of the sources of these pollutants intends to promote a better understanding of how chemicals are transported and what are their indoor fates in order to evaluate their impact on human health.

Sources of chemical contaminants in confined environments can be divided into three main categories: (i) infiltration from outdoor air, (ii) building materials and furnishing, and (iii) indoor human activities [7] The concentrations of these pollutants can widely vary with time as they are driven by 4 different parameters, known as ***indoor air determinants***. They are: (i) emission rates of primary sources, (ii) air exchange rate between indoor and outdoor environments, (iii) interactions with surfaces, and (iv) homogeneous and heterogeneous reactivity. [8] The fourth determinant should not be ruled out since pollutants can react with other compounds or oxidants, forming secondary species, that otherwise are absent from indoor environments. [9]

The main sources of indoor chemicals are linked to the activities of occupants such as interior renovation or decoration, smoking, cooking, heating, or cleaning activities. [3] Cleaning is an activity done by the population in order to increase hygiene, esthetic, and material preservation. [10] Furthermore, among the thousand products available and marketed, people are tempted to use scented products because a pleasant odor provides the sensation of a cleaner environment. In spite of all the benefits involved in cleaning activities, they present many associated risks. According to literature, household activities might represent nearly 20 % of the indoor pollutant sources. [10]–[12]

Nowadays, as indoor air quality has become a major concern for human health, air purifiers, antibacterial air fresheners and "natural-scented" cleaning products became trend and market leaders among household products. However, based on the ambiguity of the words "*purifying*" and "*natural*", consumer products formulated with essential oils have taken benefits from skillful marketing strategies. Indeed, products containing essential oils take advantages from their so-called "*natural*" or "*green*" formulations to promote an increase of indoor air quality by purifying and reducing synthetic chemical emissions. Nonetheless, Steinemann et al. [13] executed a comparative analysis of volatile emissions from green and conventional fragranced products, including cleaning products and air fresheners. Results evidenced over 550 VOCs emitted from 37 products, where less than 3% were disclosed in the product label, and more than 42 VOCs were classified as toxic pollutant under US federal laws. Moreover, emissions of carcinogenic hazardous air pollutants from "*green*" fragranced products were not significantly different from conventional fragranced products.

Essential oils are known as a group of odorous or fragrant chemicals extracted from plants that might contain a hundred of molecules, mainly belonging to the terpene chemical family: monoterpenes and sesquiterpenes, terpene alcohols and terpenoids. [14] Essential oils promise a decrease of microorganism activities and an increase of indoor air quality due to their anti-bacterial properties. [15]–[20] To that regard, they are widely used in the formulation of household products to (i) naturally scent the products, (ii) enhance purifying performances, (iii) refresh and "*purify*" indoor environments with

a "*natural"* claim. This perception of essential oils as ingredients of natural origins tends to shade the potential impacts of these chemical species on indoor air quality, while they are massively used in different types of consumer products.

The main questions raising from this context are: ***Do essential-oil-based products contribute to indoor air quality by reducing emissions in the air and purifying it? Can essential-oil based products be considered as a passive remediation practice for facing current indoor air problematic?***

This work, as a part of the ESSENTIEL (*EmissionS et TransformationS dEs COV odoraNts Terpéniques : Impact sur la qualitE de L'air intérieur*) Project, funded by CSTB (Centre Scientifique et Technique du Bâtiment), IMT Lille – Douai and ADEME (Agence De l'Environnement et de la Maîtrise de l'Energie) in the frame of the call of projects CORTEA (COnnaissances, Réduction à la source et Traitement des Emissions dans l'Air), aims at answering these questions.

In a first stage, this work provides a literature review of scientific articles published in the last years about primary emissions and indoor reactivity associated to the use of scented household products. An extensive analysis is provided and driven by three main axes:

(i)   The identification of household products composition and use patterns when performing household activities: ***How far cleaning activities lead to a potential exposure?***

(ii)   The identification of primary emissions related to the use of essential-oil-based products: ***Is there a potential exposure risk for consumers related to TerVOCs emitted from household products?***

(iii)   The assessment of indoor air reactivity linked to unsaturated VOCs emitted from essential-oil-based products: ***What is the fate of terpenes once emitted in indoor environment? What about the exposure to indoor concentrations of secondary air pollutants?***

This critical review of the literature allows a better understanding and framing the current issues dealing with the indoor use of essential-oil-based household products. This critical review is presented in Chapter 1.

Thus, the objectives and the positioning of this thesis in the scientific context and regarding ESSENTIEL project is developed in the Chapter 2 of this manuscript. In this same Chapter, a detailed description of the experimental set-ups and the protocols is presented. Subsequently, Chapters 3, 4 and 5 are dedicated to results obtained in the framework of this thesis.

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CHAPTER 1

Does the ubiquitous use of essential-oil-based products promote indoor air quality? A critical literature review

ABSTRACT

Essential oils, as natural fragrances, are frequently used in green and healthy marketed housecleaning products and air fresheners. Nonetheless, they are volatile and reactive chemical species. This review is focused on the impact of essential-oil-based household products on indoor air quality. First, in order to frame the literature review, housecleaning products containing essential oils are explored from a composition point of view while keeping track of existing regulations. A specific insight is provided on terpenes present in fragranced housecleaning products, air fresheners and pure essential oils. Second, experimental methodologies for the monitoring of terpenes are addressed from sampling to experimental chambers and analytical methods. This approach emphasizes the experimental issues to monitor terpenes in indoor air. Third, the temporal dynamics of terpene emissions reported in the literature are discussed. In spite of noteworthy experimental discrepancies, available results evidence essential-oil-based products as significant sources of terpenes in indoor air inducing a high exposure of occupants to terpenes. Finally, the fate of terpenes is explored from a sorptive and a reactive point of view. Beside terpene deposition on surfaces, indoor oxidants may induce homogeneous and heterogeneous reactions. These processes are evidenced as sources of secondary pollutants such as formaldehyde and secondary organic aerosols. This review draw attention to the fact that essential-oil-based products can negatively impact indoor air quality. As a consequence, standard protocols and real scale approaches are expected to explore the indoor physics and chemistry of terpenes from emission to reactivity.

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This chapter aims at critically reviewing and evaluating the literature related to terpene emissions and reactivity from the use of household product. At the same time, it attempts (i) to synthesize the works dealing with the health impact of these materials, (ii) to provide tools to take conscious decisions and (iii) to identify knowledge gaps in the scientific framework.

1. Household product compositions, use patterns and user exposures

1.1 Introduction to household products

In order to frame the approach of the present review, the type of household products considered is defined first. Household products in this work are defined as scented and chemically formulated products used in a non-permanent way in indoor environments for housekeeping and air freshening purposes. Among them, are included: (i) cleaning products, (ii) air fresheners and (iii) air purifiers.

Nazaroff et al. [16] have evidenced that VOC atmospheric emissions per capita from general purpose cleaners and air fresheners are the most contributing in indoor environments with values ranging from 200 to 230 mg per day. Furthermore, typical intake fraction from emissions in indoor air is in the order of 10^{-3} and 10^{-1} while outdoors is in the order of 10^{-6} and 10^{-3}. Intake fraction is defined as the incremental pollutant mass inhaled per unit pollutant mass emitted. [1] This point highlights the fact that the proportion of emissions inhaled is higher when emissions occur indoors rather than outdoors. [2] In order to assess the contribution of household products to indoor pollution, information is required concerning various sets of determinants and processes related to the products and the environments where they are used. Among them, household product composition, usage, consumer use patterns, emission dynamics, transport and mixing, building ventilation, sorptive interactions with building surfaces, and reactive chemistry. [2] The main purpose of this chapter is to define and summarize information regarding: (i) chemical composition of household products, (ii) consumer using patterns and (iii) user exposures. These points are key drivers of primary emissions. This will allow identifying the approaches required to assess and better understand the chemical releases from the use of household product.

1.2 Chemical composition of essential-oil based products

1.2.1 Formulation of cleaning products, air fresheners and purifiers

Cleaning agents are assembled in different product categories according to their technical functions and purposes of use. Moreover, they are typically composed by one or more active components. [3] In order to address that point, six studies are gathered in Table 1, they provide information regarding household products compositions and general formulations. These studies were performed between 1998 and 2013 in various countries. Table 1 discloses this information by mapping the chemical formulations of household products and classifying products according to their categories and diffusion modes.

Table 1. Cleaning products and air fresheners available in the market, classified by application mode and typical active constituents. [2]–[7]

PRODUCT	USE	APPLICATION MODE AVAILABLE	GENERAL FORMULATION	%
General all-purpose cleaner	Floor, soft and hard surfaces, toilets. It can be rinse or non-rinse products.	Trigger spray Foam Liquid Cream Wipes Powder Gel	Water Surfactant (anionic, non-anionic, soap) Solvent (alcohol) and hydrotropes Terpenes	70-95 0.5-15 2-15 ≤ 5
Disinfectant cleaner	Generally to be used on surfaces. Main functionality is to either inhibit growth or to destroy microorganisms.	Trigger spray Liquid Wipes	Water Disinfectant (chlorine releasers) Surfactant (anionic and non-anionic) Base (sodium or potassium hydroxide) Complexing agent Corrosion inhibitor Solvent (alcohol) Terpenes: ≤ 1%	15-95 0.1-10 0.1-25 5-30 1-10 2-10 ≤ 1
Glass (window) cleaner	Glass surfaces, windows and mirrors.	Wipes Liquid Trigger spray	Water Surfactant (anionic and non-anionic) Solvent (alcohol, glycol or glycol ethers) Terpenes	75-95 0-10 5-20 ≤ 5

Floor cleaner	Mainly for floor cleaning and polish. It can be used diluted in water or pure.	Wax Liquid Cream/Gel Wipes	Water Surfactant (anionic, non-anionic, soap) Solvent (alcohol, 2-butoxyethanol, nonoxynol, glycol/glycol ethers, monoethanolamine) Terpenes	70-95 0-30 5-50 ≤ 5
Dishwasher	Clean and remove grease and food left-overs from surfaces	Liquid Powder Cream	Water Surfactant (anionic, non-anionic, amphoteric) Solvent (alcohol) Terpenes	45-80 0-30 3-10 ≤ 5
Sanitary cleaners	Used to clean and sanitize bathroom surfaces. Need of antibacterial active component as bleach (hydrogen peroxide or hypochlorite). Remove organic and inorganic residues.	Gel Liquid Trigger spray Wipes Foam	Water (higher water quantity for spray product) Surfactant (anionic, non-anionic, cationic) Solvent (isopropanol) Terpenes	50-95 0-15 2-15 ≤ 5
Furniture cleaner	Hard and soft surfaces	Aerosol Trigger spray Liquid Wipes	Waxes(not for aerosols) Oils (not for aerosols) Solvent Stearic acid (Only for liquid) Water (Only aerosol) Propellant (Only aerosol) Styrene is contained in liquid wax.	51 22 ≤ 20 7 55-65 ≤ 18
Oven cleaner	Strong degreaser, mainly used on metal surfaces. Products need to soak for some minutes and then rinsed off.	Can spray (aerosol) Trigger spray	Surfactant (anionic, non-anionic). Only liquid) Bases (caustic soda or caustic potash) Solvent (glycol/glycol ethers, monoethanolamine) Terpenes	1-15 1-15 2-30 ≤ 5
Air fresheners	Deodorize or hide any odor in a confined space.	Electric diffuser Plug-in Can spray (Aerosol) Gel (Passive diffuser) Evaporating good sticks (Passive diffuser) Potpourri bag	Mainly contain essential oils and fragrance mixture diluted in a solvent. Air fresheners may contain more than 50 % of fragrance chemicals.	
Air Purifiers		Can Spray		

	Air purifying performance, thus air refreshing.	Passive diffuser (heat diffuser, fan diffuser, nebulization diffuser) Electric diffuser	Contain 100% w/w of essential oils.

A cleaning product is generally constituted by water, solvents, surfactants, preservatives and fragrances. Depending on the usage purpose, other compounds can be included such as disinfectants, acids, bases, bleaching agents, abrasives or enzymes. [4] According to Table 1, surfactants are the main active compound of cleaning products. Their function is to enhance the effect of the cleaning agent by lowering the surface tension of water. On the other hand, acids and bases can be used as active compounds as they enhance the dissolution of specific stains and improve the performance of surfactants by regulating the pH of the solution. [3], [8], [9]

Among cleaning product constituents, water is the compound added in the highest proportion followed by solvents. Both can be present in formulations at mass percentages up to 95 % and 50 %, respectively. Indeed, water is added either for (i) removing the water-soluble deposits of minerals and inorganic salts (ii) dissolving metal ions that can decrease the effect of surfactants or (iii) as an emulsifying agent. [3], [4]

Concerning solvents, they are the most volatile constituents included in cleaning product composition. They have boiling points ranging from 70 to 200 °C. Moreover, these chemicals substances can be present at concentrations ranging from 2 to 50 % w/w. Water-soluble solvents are used to dissolve oil and greases and to increase the "fast-dry effect" on cleaned surfaces. [4]

When a cleaning product emphasizes a disinfectant property, complementary chemicals are added to their formulation to suppress or inhibit microbial activities. Disinfectant substances can be chlorine releasing compounds, alcohols and formaldehyde or formaldehyde releasers. [3], [7]. In the case of "green" cleaning product formulations, essential oil constituents such as geraniol can be considered as active compound, due to its biocide action.

As reported in Table 1, the mass concentrations of main constituents can vary for the same product category. Indeed, the diffusion mode of the product determines the proportion added for the main family of ingredients e.g. solvent, water,

surfactants, etc. For example, regarding all-purpose cleaners in wipes format, the solvent content does not exceed 10 % w/w; while for liquid and spray formats, concentrations can be 1.5 times higher. [4]

1.2.2   Fragrances contained in household products

Fragrance mixtures and essential oils are used in cleaning product formulations either to provide them a pleasant odor, to hide odors from other chemicals used, or to enhance their antibacterial performance. [5], [10] Even though, there is a clear difference between essential oils and fragrance mixtures. Essential oils are natural oils, extracted from plants, while fragrance mixtures represent the combinations of different compounds (synthetized, natural-like or extracted), assembled to replicate a "natural-identical" scent [11], [12]. For instance, household products can be formulated with (i) synthetized fragrances, (ii) pure essential oil or a mixture of them and (iii) mixtures of synthetized fragrances and essential oils, in order to reduce the production costs. Suppliers are required to label substances or mixtures contained in packaging in accordance with the CLP Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures before placing them on the market when the substance is classified as dangerous, or the mixture contains one or more substances classified as dangerous above a certain threshold. However, fragrance mixtures can be confidential, and thus, not labelled on the composition list. [5] [13]

According to Table 1, TerVOCs in cleaning products can achieve mass concentrations up to 5 % w/w. The case of air fresheners and purifiers is completely different. The main purpose of air fresheners and purifiers is to mask or "*eliminate*" unpleasant odors from confined environments. As a consequence, fragrances are their main compounds. Fragrance chemicals contained in air fresheners and purifiers can range from 50 to 100 %, depending whether the product is diluted in an organic solvent or not. The concentration of the organic solvent added to the formulation is directly related to the diffusion mode of the product e.g. aerosol, passive diffuser, etc. [5], [8], [10], [14]

Sarwar et al. [15] reported the quantification of TerVOCs in four different types of household products: (i) pine-scented solid air freshener, (ii) lemon-scented general purpose cleaner, (iii) lime-scented liquid air freshener and (iii) wood floor cleaner). Main detected terpenes were α-pinene, β-pinene, 3-carene, limonene and α-terpinene with individual mass concentrations ranging from 0.2 % w/w to 2 % w/w for individual compounds. Authors confirmed that the total TerVOC contribution in

cleaning products reaches almost 5 % w/w maximum. Concerning air fresheners, limonene contribution is near 50 % w/w while total terpene contribution is practically the entire composition.

Finally, cleaning products and air fresheners present a wide variety of formulations and chemical compositions depending mainly in their usage purpose (general cleaner, disinfectant, floor cleaner, etc.) and their diffusion mode (cream, liquid, spray, etc.) [5]. The diversity of VOCs included in the formulations can result in different temporal emission profiles. Likewise, the chemical composition of household products can influence the kinetic of emissions through (i) the concentration of the cleaning constituents, (ii) the volatility of the constituents and (iii) the chemical affinities develop in-between product components. These parameters will affect the kinetic and the dynamic of the concentrations of the chemicals transferred from the product to the gas phase.

1.2.3   Terpenes in scented household products

A compilation of 14 studies focused on the identification of fragrance chemicals in scented household products is reported in Table 2. Reviewed investigations include natural and synthetic scented products from worldwide markets. Among them, eight studies have been performed along the last decade. Beyond information related to the nature of the fragrance chemicals, Table 2 summarizes their occurrence rates. The frequency of presence is defined as the percentage of products where compounds of interest are detected.

Table 2. Nature and occurrence rate (%) of fragrance chemicals in household products tested worldwide

TerVOCs	United States [8], [10], [16], [17]	CHN [18]	FR [6]	Germany [19]		Europe (*Denmark, Germany, England and Italy*) [5], [20], [21]			NL [14]	Korea [22]–[24]		Mean occurrence rate (%)
Number of products tested	*25*	*21*	*31*	*15*	*54*	*13*	*59*	*15*	*19* [1]	*113*	*59*	*26* [1]	*450* [2]
Limonene	92	72	90	87	43	77	78	100	79	38	44	58	**72**
α-pinene	80	42	74	7	9	62	39	-	-	-	19	31	**40**
β-pinene	80	38	81	13	31	69	37	-	-	-	7	31	**43**
Camphene	36	19	36	-	31	39	37	-	-	-	5	-	**29**

													[2]
α-terpinene	32	14	36	-	31	-	37	-	-	-	-	-	**30**
γ- terpinene	24	29	-	7	31	15	37	-	-	-	2	11	**20**
β-terpinene	-	-	-	-	31	-	37	-	-	-	2	-	**23**
α-terpinolene	-	19	-	7	17	23	37	-	-	-	2	-	**18**
Linalool	28	19	-	47	22	77	61	40	79	46	-	35	**45**
β-phellandrene	24	10	-	-	31		37	-	-	-	-	-	**26**
Citronellol	-	-	-	-	-	-	47	33	53	43	-	-	**44**
Eucalyptol	-	-	-	33	28	39	41	-	-	-	-	-	**35**
Geraniol	-	-	-	-	19	8	41	40	42	54	-	-	**34**
4-Terpineol	-	14	-	47	13	15	51	-	-	-	-	-	**28**
ρ-cymene	40	-	42	27	9	15	37	-	-	-	-	-	**28**
Eugenol	-	-	-	-	-	8	27	20	63	37	-	-	**31**
Myrcene	-	33	-	13	31	69	37	-	-	-	12	27	**32**
Lilial	-	-	-	-	9	-	27	40	55	35	-	-	**33**
Citral	-	14	-	-	-	23	25	27	37	33	-	-	**27**

-: not a target compound in the study for the products tested.

[1]: only air fresheners are tested in this study

[2]: (Total Reviewed Products)

CHN: China; FR: France; NL: The Netherlands

Limonene and linalool are respectively present in 72 % and 45 % of the products reviewed. Limonene was detected at various concentration ranges in 272 out of 450 reviewed products, and linalool was identified in 158 of the 360 products. On the contrary, α-terpinolene, citral, β- and γ-terpinenes were not detected in the majority of products. They are characterized by the lowest mean occurrence with 18, 27 % and 21 %, respectively. On the other hand, Lilial® is a specific compound of European products. It is only identified in 78 out of 260 products. This fragrance substance is synthetized from aromatic aldehydes and is mostly produced and used in European countries. [5], [13], [14], [21], [25]

In sprays, other TerVOCs than limonene and linalool are found in a limited number of products < 20 %. [14], [18] The TerVOC distribution in sprays is very different from other scented products. Regarding air fresheners, Nazaroff et al. [16] confirmed that the four major constituents found are limonene, linalool, dihydromyrcenol, and linalyl acetate. In the same way, Ezendam et al. [14] and Huang et al. [18] confirmed that limonene and linalool are the most frequently used fragrances for electrical room perfumes and scented candles.

Nazaroff et al. [2], [16], Ezendam et al. [14] and Huang et al. [18] established through the analyses of different types of products that the distribution of the most frequently reported fragrances slightly varies from one product to another. Nevertheless, depending on the specifications of the considered household product, specific fragrance chemicals can be

present. These specifications are (i) the scent of the product (lime oil scented products contain limonene as major fragrance compound while pine oil scented products contain pinenes as major compound), (ii) the "*purifying performance*" of the product (products with purification purposes contain essential oils proved to inhibit microbial activity such as eucalyptus oil), (iii) the marketing strategy related to the consumer preferences. [7], [8], [10], [14], [17], [18], [20]

It can be concluded from the reviewed literature that fragrance chemicals included in a household product formulation can differ between manufacturing countries; this point is highlighted by Table 2. Nevertheless, worldwide, most used essential oils in household products formulation are citrus oil, lavender oil, pine oil, eucalyptus oil, tea tree oil and rose oil. [14], [18], [22], [24]

1.2.4   Chemical compositions of pure essential oils

Essential oils are natural oils extracted from plants. They usually contain more than 100 different chemical substances. [13] Their extraction processes can rely either on water vapor distillation, dry distillation, or mechanical extraction methods that do not involve temperature changes. [26] An essential oil is often characterized by major compounds with specific relative abundances that provide the typicality of its smell. Therefore, the characteristic odor of an essential oil directly depends on its chemical composition. [12] Moreover, proportion of chemical constituents in essential oils might vary depending on (i) the sort of the plant, (ii) the place of growth, (iii) the environmental conditions along growth and (iv) parameters set along the extraction process such as pressure and temperature [11], [13], [27].

Preksha [28], in 2018, performed a global analysis to investigate the market size, share and trends of essential oils. The author evidenced that regarding the global production of essential oils, orange oil is the most demanded one with 52.5 kilotons in 2015. The growing demand of orange oil as raw material in cleaning agent industry is the main factor of the production increase. Concerning applications, nearly 20 % of the global production of essential oils corresponds to "cleaning and home". However, food and beverage remains the leading segment with 32.9 %. [28]. Typical mass concentration ranges of seven worldwide common essential oils used in household product formulation are provided in Table 3. It is based on the analysis of eleven studies published between 1994 and 2018. Concentrations are compiled and classified in a decreasing order. Compounds written in bold highlight the major constituents of each essential oil. Note that, only compounds typically present at a mass concentration higher than 2 % are included in Table 3.

Table 3. Typical chemical composition of the most widespread essential oils used in household product formulations: typical concentration ranges

		w/w (%)			w/w (%)
Orange Oil [29]	**Limonene**	**70.0 – 80.0**	Lavender Oil [30] [31]	**Linalyl Acetate**	**40.0 - 50.0**
	β-pinene	2.00 – 11.1 %		**Linalool**	**30.0 - 40.0**
	α-pinene	2.2 – 3.1 %		Camphor	6. 0 - 8.1
	Sabinene	1.0 – 2.8 %		Geraniol	~ 4.0
	Linalool	1.1 – 2.5 %		4-terpineol	1.9 - 2.2
Tea Tree Oil [32] [30] [13]	**4-terpineol**	**40.1 - 41.0**	Pine oil [33]	**α-pinene**	**40.0**
	γ-terpinene	20.0 - 25.0		**Bornyl Acetate[1]**	**≤ 40.0**
	α-terpinene	6.0 - 10.4		Limonene	25.0 - 30.0
	1,8 cineole	5.0 - 5.6		β-pinene[1]	12.5 - 22.0
	Terpinolene	3.0 - 3.1		Camphene	~ 5.5
	Cymene	2.9 - 9.0		Borneol	≤2.0
	α-terpineol	2.4 - 4.0			
	α-pinene	2.0 - 2.6			
Lemon Oil [12], [30], [35]	**Limonene**	**55.0 - 80.0**	Rose Oil [27] [34]	**Citronellol**	**~ 50.0**
	β-pinene	7.0 - 11.1		Geraniol	13.7 - 26.5
	α-phellandrene	~ 9.0		Linalool	≤ 5.0
	γ-terpinene	~ 8.5		Eugenol	0.4 - 2.1
			Eucalyptus Oil [36] [37]	**1,8 cineole[1]**	**19.8 - 63.9**
				α-pinene	3.8 - 4.6
				α-terpineol	0.2 - 5.5
				Cymene	0.5 - 2.4

[1]: Wide composition range due to different extraction methods and different types of leaves.

According to Table 3, oxygenated terpene derivatives are major compounds for lavender oil. More specifically, linalool and linalyl acetate, known as bergamol, represent over 80 % w/w of the composition of lavender oil. At the same time, a higher portion of monoterpenes is identified in pine oil. Indeed, mass concentrations of limonene and α- and β-pinene can achieve up to 92 % of pine oil composition. Regarding tea tree oil, it contains more than 60 % of 4-terpineol, and γ– and α–terpinene, while the major compound of rose oil is citronellol. [12], [31]. Furthermore, tea tree oil presents the largest diversity of terpene molecules in its composition. Indeed, more than 14 different terpenes can be detected in that oil. [32] On the other

hand, citrus oils such as lime, lemon and orange oils tend to have similar fragrance substances but with different mass proportions regarding limonene and $\alpha-$ and $\beta-$pinene for instance. In citrus oils, limonene mass concentration can reach up to 80 % w/w. [12], [29] Additionally, citrus oil is mainly composed by monoterpenes. These molecules are lighter in weight compared to terpene derivates and sesquiterpenes. Rose oil has a specific composition compared to other essential oils. Indeed, rose oil mainly contains long-chain alkanes and alkenes, β-citronellol, geraniol, and nerol. [38] [43] These fragrance substances are less volatile compared to monoterpenes with a boiling point around 230 °C.

Essential oils have specific compositions that provide their distinctive chemical and physical properties and induces their typical odor, color, density, volatility, stability and reactivity. As a consequence, the chemical composition of an essential oil may directly impact its dynamic of volatilization. Therefore, the consequence on indoor air quality related to the use of essential-oil-based household products is directly linked to the chemical composition of the essential oil used. Their impact on indoor air quality is discussed in the next sections of this review.

Whether from natural or synthetic origin, essential oils and fragrance mixture components can be transferred from the liquid phase to the gas phase, thus increasing the inhalation exposure to potential allergenic and toxic air contaminants. Indeed, they can lead to sensitization and subsequent induction of allergic symptoms in the respiratory tract. [21] [5] In spite of the human health concerns related to the used of scented household products, there is no regulation framework to control and define the use of these chemicals in the formulation of products. [38] Thus, in the next section of this review, an analysis is proposed to evaluate current regulations and policies of fragrance chemicals in the European frame.

1.3   Regulations related to household products

Current efforts are focused on establishing restrictions and regulations regarding the use of toxic chemicals in the industry of household products as they exist for food and cosmetic industries. [39] Steinemann [17] aimed at investigating the undisclosed ingredients present in 37 fragranced consumer products. This work evidenced more than 550 VOCs; among these VOCs, less than 3 % were disclosed in the product label. Among the detected VOCs, more than 42 compounds were classified as toxic pollutants under US federal laws. Besides, the content of "*green*" fragranced products regarding hazardous VOCs was not significantly different from conventional products. Likewise, Uhde et al. [19] performed a similar investigation,

aiming at evaluating undisclosed ingredients among 6 non-solid air fresheners. Obtained results evidenced that among the 6 products tested only 18 fragrance chemicals were declared out of 200 detected substances. The mean percentage of labelled fragrance chemicals per product was lower than 10 %. Therefore, the main scope of this section is to review the restrictions and labellings in the formulation of fragranced consumer products, mainly in the European frame.

1.3.1   Regulation and policies for consumer products in the European Union

Cleaning products / The European regulations require manufacturers to make mandatory specific mentions on product labels in order to promote the protection of environment and consumers. However, what is written on product labels is far from being explicit to any citizen. According to the European Regulation N° 907/2006 industries are required to indicate the presence of specific chemicals classified in two categories (i) surfactants and whitening agents and (ii) fragrance allergens. Table 4 presents chemicals considered among mentioned regulation and the concentration restrictions. Note that, regarding allergen substances, terpene compounds are highlighted in bold. [39], [40]

Table 4. Fragrance compounds labelled as allergens in household products in Europe [39], [40]

CLASSIFIED ALLERGENS	SURFACTANTS AND WHITENING AGENTS
Need to be labelled in the ingredient list if their concentration exceeds 0.01 % for products that require to be rinsed after use and 0.001 % for not rinsed products	Required to be mentioned in products labels if their mass concentration exceeds 0.2 %.
Cinnamaldehyde, Amylcinnamyl alcohol, **Lilial (Butylphenyl methylpropional), Cinnamal**, **Isoeugenol**, **Citral**, **Citronellol**, **Coumarine**, **Eugenol**, **Farnesol**, **Geraniol**, Hexyl Cinnamal, **Hydroxycitronellal**, **Limonene**, **Linalool**, Anise alcohol, Benzyl alcohol, Benzyl benzoate, Benzyl cinnamate, Benzyl salicylate, Evernia furfuracea, Evernia Prunasti extract, Lyral, Methyl 2 –octynoate, α-isomethyl ionone.	Hydrocarbons, soap agents, zeolites, phosphates, EDTA (ethylene-diamine-tetra-acetic acid).

Manufacturers are required to label products with the complete list of ingredients and to publish it on a web site to make it available to consumers, it is commonly referred to as material safety data sheet (MSDS). They may also have to comply with the Regulation (EC) No1907/20062 (the REACH Regulation or "REACH"). In the case of mixtures of chemical fragrances, they can be labelled as "Fragrances", in order to guarantee the intellectual property of the mixer proposed by the manufacturer.

Moreover, it is required to visibly identify hazards linked to the product usage. These hazards can be (i) physical risks, such as inflammation, (ii) health risks, such as corrosion, irritation, toxicity, or (iii) environmental risks, such as water or air pollution.

Purifying or biocides products / For (i) air purifying sprays, (ii) antiacarian products, (iii) pesticides and (iv) biocides, special requirements exist. Manufacturers are not forced to publish their product formulation on a web site, or to label the ingredient list on their product packages. However, according to the European regulation n° 528 / 2012, a product containing an active substance that ensures destruction, repelling or neutralization of a microorganism, virus, or parasite needs to be approved before any introduction on the market. Approving procedures include (i) the evaluation of the targeted active substance regarding its performance as biocide and (ii) the evaluation of its hazards to human health and environment. In the case of products with active substances under evaluation, during the evaluation time of the restriction report, there can be introduced to the market without any restriction. Nonetheless, it is required to mention the active compound on the product with its mass contribution expressed in percentage. [41]

In comparison with US regulations and policies, consumer products are generally restricted by the "Consumer Product Safety Act (CPSA)". The CPSA requires manufacturers to include a warning label on their products. For instance, a warning label might be required if a warning is "reasonably necessary to prevent or reduce an unreasonable risk of injury associated with such product", or if voluntary standards would not "eliminate or adequately reduce the risk". Notably, as the European regulations, CPSA does not require disclosure of all ingredients in products, even for chemical species regulated as toxic pollutants under federal laws. [10] Steinemann et al. [42] performed a survey aiming to evaluate knowledge lacks concerning the composition of fragrance products from consumers in the United States. Among surveyed population, 65 % were not aware that fragrance chemicals do not have to be disclosed on the product labels. Furthermore, 73 % were not aware that fragranced products may contain toxic air pollutants, including green and naturally fragranced products.

In spite of the advancement in European regulations regarding household products safety, chemicals in product formulations are exempted from full disclosure. Except for certain chemicals considered as surfactants, whitening agents or allergens are required to be mentioned in the product labels. Although there are regulations restricting or controlling the mass concentrations of toxic substances that may pose a risk of exposure (CLP and REACH regulation), unregulated but potentially

dangerous substances may be present without any indication or control. Consequently, consumers do not have adequate information concerning the potential exposure to risks and a fictitious perception of safety while buying "*natural*" household products. Nevertheless, more restrictive requirements need to be accomplished by household products manufacturers in order to be certified as organic and green products. Generally, the eco-labelling of products is based on the evaluation of the environmental impact of a product during its life cycle and hazards to human health. Current European eco-labels are reviewed in the next section.

1.3.2   European Ecological Certifications

Several labels have been developed in order to ensure quality standards for "*green*" or "*organic*" products. In total, more than 20 different ecological certifications exist for cleaning products in Europe. Main certifications are (i) ECO-Label from the European Union, (ii) ECOCERT, and (iii) NF Environment from France. [43] Among above mentioned certifications, the strictest one is ECOCERT. This label is available for cosmetic, food, and household products. For a product to be certified by ECOCERT, it has to fulfill the following requirements:

1. 95 % w/w of natural ingredients for all type of products. For organic products: minimum 10 % of ingredients from organic agriculture and 100% w/w of natural ingredients.
2. Maximum of 5 % of synthetized ingredients, organic products not included.
3. No compounds targeted as "*hazardous*" for the environment are allowed.
4. For air fresheners containing alcohol: it must be from organic agriculture.

Regarding additives and fragrances, ECOCERT only certifies products containing chemicals from natural sources extracted by physical and chemical processes. No fragrance and additive from petrochemical sources are allowed. On the other hand, ECO-Label is a certification from the European Union developed by the European Parliament. It mainly aims (i) to control and decrease the use of hazardous chemicals in consumer product formulations, (ii) to reduce the impact on aquatic life, (iii) to reduce wastes from packaging, (iv) to promote clearer usage instructions and (v) to promote assessed performances for products. [44] Regarding allergen substances, certification label CA, standing for Controlled Allergens, has been developed by ARCAA (*Association of Clinical Research in Allergology and Asthmology)* for household products. The 26 compounds

recognized as allergens or skin sensitizers by European Regulation are mentioned in Table 4. [39], [45] This certification has been extended from cleaning products to air purifiers.

In conclusion, whether conventional or eco-certified, fragrance products might contain a range of hazardous air pollutants and only few are revealed to the public through product labels. This lack of disclosure does not allow giving society sufficient knowledge to make conscious decision while selecting household products. Additionally, it might inhibit efforts to understand and reduce adverse effects associated to the exposure to harmful compounds. Exposure to hazardous chemicals contained in household products is also driven by the contact time, the quantity of product applied, the frequency of exposure, etc. These influencing parameters are known as *consumer use patterns*.

1.4 Exposure of users to household products: usage patterns

Numerous household products are repetitively used on a daily basis and by a large variety of people. Household products may contain chemical constituents that might affect human health. Reported symptoms are related to respiratory difficulties and allergies attributed to the contact and exposure to hazardous compounds. [9], [13] Exposure is defined as the contact time with a specific concentration of a chemical. It is estimated by several key drivers. Among these key drivers, the contact time with pollutants from household products can be determined by the use patterns and product composition. These two determinants are crucial to answer to the question: ***How far cleaning activities lead to a potential exposure?*** Use patterns include (i) frequency, (ii) duration of use, (iii) diffusion mode of the product e.g. aerosol, concentrated liquid, trigger spray, (iv) application mode e.g. spraying, diluting, or wiping, and (v) ventilation rate while performing household activities. [2], [3]

Little is known about the use patterns of household products from consumers, thus the estimation of exposure levels can turn difficult and inaccurate [46]. Indeed, only four studies [46]–[49] address contact time and usage behaviors of household products by consumers. All studies have been performed in the European Union along the last 17 years. Among them, in France, ECOVER (European Manufacturing Industry of Green Cleaning Products) along with CREDOC (Research Center of Study and Observation of Life Conditions (CREDOC) performed in 2009 a survey of the French population about cleaning

products. Figure 1 exposes the percentage of French population using cleaning products one or several times per day. Results disclosed in Figure 1 are classified by product category. [47]

According to Figure 1, 90 % of the French population reports a daily contact with cleaning products. Among them, 27 % reports using at least 10 different products on a daily basis during their cleaning activities. [47] Therefore, it leads to an increase of inhalation exposure to product constituents. Additionally, 32 % and 11 % of the French population respectively use at least one and three aerosol products. Moreover, only 55 % of the population reads ingredients labelled on products; chemical composition is not part of their purchase criteria. [47]

A similar study was developed in the framework of the European project "Emissions, exposure patterns, and health effects of consumer products" (EPHECT). Its main objective is to evaluate emissions and associated hazards from 15 types of consumer products among the European Market. A survey was conducted about the use of consumer products to enable the identification of behavior patterns across European countries including: France, Germany, United Kingdom, Denmark, Sweden, Italy, Spain, Czech Republic, Hungary, and Poland. Results established that cleaning products and perfumes have the highest market penetration, and women are the most frequent users. According to interviews, the presence of children along household activities does not have any influence in the product use pattern. [48], [49]
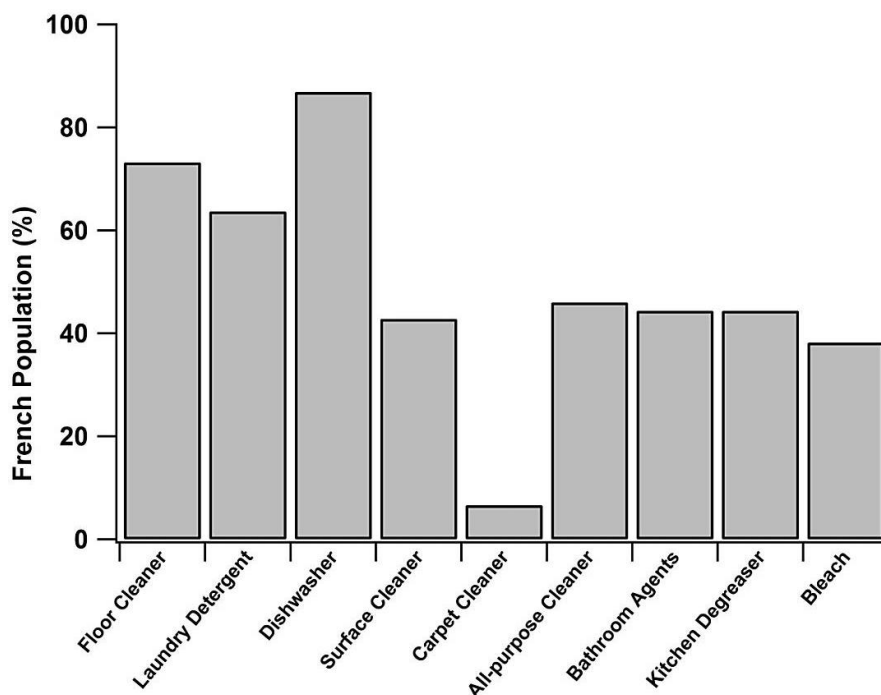
Figure 1. Percentage of the French population using various cleaning products one or several times per day [47]

Regarding the selection of products, EPHECT survey revealed that the price is crucial while buying a household product, followed by the efficiency. This result contrasts with the CREDOC [54] survey which evidenced that among the French population, the efficiency was the main selection criteria reported. Interestingly, according to both studies, other aspects such as the product safety, the chemical composition and the precision of use instructions are not considered by users. [47], [48] In terms of diffusion mode preference, two investigations in the framework of EPHECT project have been reviewed in this paper. Both studies are performed in 2015. Table 5 gathers results for the preferred diffusion modes and quantities applied for commonly used cleaning products by the European population.

Table 5. Preferred diffusion mode and quantity used among population interviewed in the framework of EPHECT project [48] [46]

TYPES OF PRODUCTS	PREFERRED DIFFUSION MODE (EUROPEAN POPULATION)	MOST FREQUENTLY USED QUANTITY	
		Quantity (EPHECT Survey)	Population
All-purpose cleaners	Spray [1] Liquid [2]	2-3 sprayings ≤ 1 cap	49%
Kitchen cleaning agents	Spray	2-3 sprayings	54%
Floor cleaners	Liquid [1] Cream[2]	1 to 2 caps	42%
Glass/Window cleaners	Spray	2-3 sprayings	48%
Bathroom cleaners	Liquid	≤ 1 cap	45%
Furniture polish	Liquid [1] Cream [2]	1 to 2 caps	51%
Floor polish	Liquid	1 to 2 caps	40%
Combustible air fresheners	Candles	1 unit	60%
Air fresheners	Gel (Passive diffuser) [1] Pressurized can [2]	1 unit 3-6 seconds	60% 53%

[1]: First choice;   [2]: Second choice.

The population declared a preference for liquid formats for most of the cleaning products. On the contrary, glass cleaners, window cleaners and furniture polishes are usually used as spray. For air fresheners, the preferences of the population are gel format for a passive diffuser. [46] [48] Regarding the amount of product applied, the most frequently used quantity per application does not exceed 2 caps for liquid and cream products for floor cleaning. Concerning surface and bathroom cleaning the mass applied does not exceed 1 cap. Moreover, mass quantity applied strongly depends on the product dispenser.

Generally, one cap of a liquid cleaning product corresponds to ca. 30 g. On the other hand, while using spray products most of the population does not exceed 3 sprays per cleaning process. Depending in the mechanical system of the spray, distributed mass through one spray can range from 0.39 g per spray to 1.5 g per spray. [8], [22], [55]

In the framework of the project RIVM headed by the *National Institute of Public Health and the Environment* and Delft University of Technology in The Netherlands [46], a survey was performed to identify the duration, the frequency and the amount of products used for different cleaning activities. The main purpose of that survey was to accurately assess the exposure levels regarding 3 classes of cleaning products (i) dishwashers, (ii) all-purpose cleaners and (iii) toilet cleaners. Detailed results data are reported in Table 6. The study revealed a wide variability in results and evidenced that bathroom cleaning duration could overcome 60 minutes being the most intense, followed by all-purpose cleaners and dishwashing, respectively with 20 minutes and 11 minutes in average.

Table 6. Usage patterns by the population in The Netherlands, survey investigation adapted from [46]

PRODUCT	FREQUENCY OF CONTACT/DAY Mean ± SD	DURATION OF CONTACT (min) Mean ± SD	AMOUNT USED (g) Mean ± SD
Dishwashing liquid	0.63 ± 0.79 (n=45)	11 ± 5 (n=45)	5 ± 3 (n=13)
All-purpose cleaner	0.35 ± 0.70 (n=28)	20 ± 22 (n=28)	27 ± 30 (n=12)
Toilet cleaner	0.28 ± 0.55 (n=18)	74 ± 204 (n=28)	-

Concerning ventilation, reported results evidenced that only from 50 to 60 % of European users of cleaning products ventilate their room while undertaking cleaning activities. The most common ventilation way is window opening, followed by internal door opening. Moreover, Dimitroulopoulou et al. [50] performed a literature review to investigate the ventilation rate in European dwellings. The main conclusion of this review is that ventilation poorly operates in European buildings, with an average ventilation rate lower than 0.5 h^{-1}. In spite of the fact that the European commission has given more attention to ventilation requirements through building regulation and policies, in the presence of indoor sources, under-ventilated dwellings result in an increased of indoor pollutant concentrations. Then, exposure levels to these pollutants might increase. [48]

The behavior of consumers is strongly affected by large individual variations in frequency, durations and amounts of products use. Nevertheless, (i) *human behavior* and *(ii) chemical composition of a product* represent main key drivers of inhalation exposure to species contained in cleaning products and air fresheners. Indeed, these determinants have been evidenced as the parameters with the most significant influence on the concentrations of emitted chemicals. Regarding the inhalation exposure risk associated to cleaning products and air fresheners, important information gaps have to be filled before a satisfactory understanding of risks can be observed in the population. It can be suggested that more explicit information on the product composition and human factors should be made available to consumers.

2. Experimental methodologies for the monitoring of TERVOCs emitted from household products

In spite of the potential impact of household products on indoor air quality through VOC emissions, studies have mainly been focused on building material emissions along the last decade because. *Standards have been developed for construction and furniture products by considering the relevant characteristics followed: (1) decreasing of concentration in the time (2) characterizing of emission after 3 and/or 28 days (3) quantifying emissions regarding to specific emission scenario described for reference room. The transposition of these standard to household product must be considering the use of patterns (application mode, mass of products use and or release during the application etc.) and the time scale of the emissions process (minutes or hours).* Therefore, (i) international standard procedures and (ii) normalized sampling techniques on test chambers have been well-established for the assessment of construction material emissions (ISO 16000 - 3, ISO 16000 - 6, ISO 16000 - 9). But what about household products? Do available experimental protocols allow accurate assessments of the emissions and relevant comparisons from one study to another?

A review of 20 studies proposing experimental protocols to assess the impact of fragranced household products on indoor air quality has been performed. Studies have been assembled, summarized and classified in two tables. First, Table 7 reports studies performed in France, while Table 8 reports worldwide studies. Among gathered studies, twelve have been conducted during the last five years, while other eight studies have been performed between 1999 and 2006. Reviewed studies have been compared and classified according to 5 main experimental parameters presented separately in each column of the table.

(i)   ***The volumes of chambers and their operational parameters:*** It includes the volumes of the experimental chambers used and the selected environmental conditions, mainly temperature, humidity and air exchange rate.

(ii)   ***The categories of products tested and their diffusion modes:*** It includes cleaning products and air fresheners with different diffusion modes (if indicated).

(iii)   ***The application methodology of the selected products:*** It includes (i) the amount of product applied and its dilution if required, (ii) the application processes, e.g. rinsed or not rinsed, and the use of cleaning materials, (iii) the loading factor expressed in m^2/m^3, defined as the ratio between cleaned surface and chamber volume, and (iv) the cleaning yield, defined as the surface that can be cleaned with the amount of product applied.

(iv)   ***The sampling protocol of emitted species:*** it mainly refers to the sampling time and frequency. Generally, the duration of the experiment and the sampling frequency are directly dependent on the type of the products used and their expected emission kinetic.

(v)   ***The materials of the chambers:*** It includes construction materials from floor, ceiling and walls that can be present in the test chambers. These surfaces may highly contribute to the fate of species emitted along the household product application. In addition, when experiments have been conducted in real environment (and not standardized emission test chamber) furniture that might be present in the chamber during the emission test are also mentioned.

Table 7. Overview of experimental protocols used in France to assess the emissions of VOCs during the use of household products

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY			SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application	LS m²/m³	Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
ADOQ Project, France [6]										
EXPERIMENTAL HOUSE *MARIA*	Dishwasher *Liquid*	Depending on the surface to clean	Dishes cleaning during 5 min. Diluted in water	NS	Sampling timing of of-line measurements is not specified.	NS	NS	Wood (Parquet Floor)	Common cement walls	Yes.
Room1: 33 m³ Sanitary: 18 m³	Glass cleaner *Spray*	12 - 23 g	10 sprays	0.04						Real scenario application in an
Kitchen: 27 m³	Furniture cleaner *Spray*	NS	Application with a tissue	NS	On-line continuous measurements for:					experimental house
AER 2.2 - 2.5 /h	Kitchen cleaner *Spray*	14 – 37 g	20 sprays	0.06	COV concentration					
	Glass cleaner *Wipes*	Wipe weighted before and after application	1 wipe	0.04						
FOR SUMMER TESTING	Surface cleaner *Wipes*		1 wipe	0.06	Formaldehyde concentration					
Temperature 21 – 34 °C	Floor cleaner *Wipes*		1 wipe	NS	Ozone concentration					
HR 26 - 64%	Kitchen cleaner *Cream*	33 – 112 g	Rinse after application	0.06	Particle matter augmentation and					
FOR WINTER TESTING		67 – 69 g 13 – 25 g	Spray, leave on for few minutes, rinse	1.67 0.08	composition					
Temperature 21 – 34 °C	Sanitary cleaner *Foam*									
HR 26 – 64 %										

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study.

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY			SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application	LS m²/m³	Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
AFSSET France – Solar et al. [51]										
EXPERIMENTAL HOUSE *MARIA*	Incense	1 unit	Placed and lighted in the test room	N/A	25 min after lighting 60 min after complete combustion	1 hour	NS	Uncovered concrete	Common cement walls	Yes. Real scenario application in an experimental house
Test room: 32.3 m³ Bathroom: 4.7 m³	Scented candle				60 min during lighting 60 min after complete combustion	3 hours				
AER 0.6 /h	Air fresheners *Plug-in*	NS			60 min during use 60 min after use	2 hours				
Temperature 20 ± 2 °C	Air fresheners *Passive diffusors Solid/Liquid*				30 minutes after application	30 minutes				
HR ~ 55 %	Air fresheners *Aerosol spray*	1 spray during 10 seconds	Sprayed in the room							
	Glass cleaner *Trigger spray*	9 sprays	Applied on window. No wipe step or rinse	0.05						
	Glass cleaner *Wipes*	4 wipes	Applied on window. No rinse							
	Furniture polish *Trigger spray*	NS	Applied on laminated table	0.06						
	Toilet block *Solid*		Block installed day before the test 4 flushes each 30minutes	N/A						
	Toilet cleaner *Gel*		Application during 15 minutes. 3 flushes every 30 minutes							

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study.

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY			SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application	LS m²/m³	Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
BEUC: The European Consumer Organization, France [38]										
Recent Built rooms. 7 different rooms were tested. Volume of chamber is not specified **Temperature** 21 ± 2 °C **HR** 50 ± 5 % **AER** NS	Scented candles *Solid, combustion.* Air Fresheners: Incense *Combustion* Air fresheners *Plug-in* Air fresheners *Aerosol spray* Air fresheners *Passive diffusors* *Gel/Liquid*	1 unit 1 unit 3 spray with 15 minutes intervals. NS	Product placed/ sprayed in the middle of the rooms	N/A	2 hours after ignition After complete combustion ~1.5 hrs. 2 hours after switching on. 1 minute after last spray 2 hours after opening.	2 hours After complete combustion N/S 2 hours	NS	NS	NS	Empty rooms.
Que Choisir, France – Chesnais et al. [52], [53]										
1 m³ & Chamber Testing 30 m³ **AER** 0.5 /h **HR** 50 % ± 5 % **Temperature** 23 °C ± 2 °C	7 Essential oil based Air purifiers *Spray* 5 Air Fresheners and 3 air purifiers *Diffusion mode has not been specified*	Time and number of sprays tested in each of the chamber were done by following manufacturer instruction	Depending on product recommendations	N/A	0h-after application 1 – 3 h 3 – 5 h 5 – 7 h	THC ≤ 5% C initial	NS	NS	NS	N/A

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study.

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY			SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application	LS m²/m³	Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
ASPA, France – Delmas et al. [26]										
42 m³ (Test room) & 9 m³ (Experimental Chamber)	Air purifier PurEssentielle® (Mixture of 41 essential oils)	**Experimental chamber** 4 sprays **Test Room** 8 Sprays	**Experimental chamber** Sprays inside the chamber **Test Room** 2 Sprays in each corner of the room	N/A	**Experimental chamber** Each 30 seconds **Test Room** 1 - 30 minutes 30 - 60 minutes	**Experimental chamber** 30 minutes **Test Room** 60 minutes	NS	NS	NS	Empty Room
AER 3.38 1/h (Experimental Chamber) Not specified for the test room										
HR 42 % ± 5 % (Test Room)										
Temperature 22.5 °C ± 2 °C (Test room)										

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study.

Table 8. Overview of experimental protocols used worldwide to assess the emissions of VOCs during the use of household products

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY				SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application	LS m²/m³		Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
USA - Nazaroff et al. [16] **, Singer et al.** [54]											
50 m³	Pine oil based surface cleaner	6.4 - 6.5 g	Spray directly onto surface. Rinse and no rinse application	0.020		0 - 10 min 10 - 30 min 30 - 60 min	24 h after application of products	Gypsum wallboard coated with low-VOC paint	Wood framing with plywood underlying.	Gypsum wallboard coated with low-VOC paint	Laminated table (1.16 m²) in the middle of the room
Temperature 21 ± 2 °C	*Spray bottle* All-purpose cleaner	Surface: 5.7-6.6 g	Direct spray onto surface Rinse and no rinse application	0.020		1 – 2 h 4 – 24 h			Subfloor covered with aluminium sheets		
HR 41 – 67 %	*Spray bottle*	Floor: 53, 103, 153 g	Dilution in water (~4l)	0.080							
AER 0.50 ± 0.02 /h	All-purpose cleaner *Liquid*	Surface: 9.9 g Floor: 50 g	Direct spray onto surface No rinse Dilution in water (~4l)	0.020 0.080					3.9 m² portion of floor covered with vinyl for mopping		
	Air freshener *Plug-in*	1.5 g/day	Maximum setting fixed	N/A		Sampling timing NS	3 days				
Denmark - Nørgaard et al. [55]											
Full scale walk-in chamber 20.28 m³	Kitchen cleaner *Cream*	39.8 g	Applied in steel plate. Cleaning for 2 minutes.	0.050		3 min after application	310 minutes	NS	8.9 m² Material: NS	NS	No furniture present
Temperature 24 ± 5°C	Air fresheners *Plug in*	NS	Placed at center of the chamber and plugged in at maximum position	N/A		Sapling: 30 - 60 min intervals respectively	326-360 minutes				
HR 40 ± 5 %											
AER 0.6 ± 0.1 /h											

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study; NM: not measured due to fast evaporation.

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY		LS m²/m³	SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application		Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
Germany - Uhde et al. [19]										
Glass chamber of 1 m³	Air fresheners *Passive diffusers*	NS	Placed in the chamber after package opening	N/A	After product application 30 min 1 hours 2 hours 4 hours 24 hours	1 day	Stainless steel	Stainless steel	Stainless steel	No furniture
	Air fresheners *Electric diffuser*	1 unit								
Stainless steel of 3 m³	Air fresheners *Car diffusers*	18 g								
Temperature	Air fresheners *Automatic spray*	NS	1 spray each 28 minutes at medium intensity							
23 ± 2°C										
HR	Air fresheners *Manual spray*	NS	5 spray with short intervals in-between							
50 ± 2 %	Scented candles	1 unit 450 g	N/A		Candle lighting: 30 minutes Total burning (4h) After burning 30 minutes, 2 h 24 h	28 hours	Glass	Glass	Glass	
AER 0.5 /h	Air fresheners *Potpourri bag*	100 g	Placed with textile bag Removed from the bag and placed in glass petri dish.		5 h 24 h 48 h Same samples were tested at days: 14, 15, and 31.	1 month				
USA - Sarwar et al. [15]										
11 m³	Air freshener *Passive diffuser* *Solid/ Liquid*	1 µl of product was diluted in 1ml methanol	Direct injection in the chamber, not real simulation	N/A	After application Sampling each hour during test lasting	600 – 750 min	Stainless steel	Stainless steel	Stainless steel	N/A
Temperature 23 – 25 ℃										
HR ~ 55 %	All-purpose cleaner *Trigger spray*	1 spray	Sprayed in the chamber			350 min				
AER 0.62 - 0.93 /h	Floor Cleaner *Liquid*	4 sprays								

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study; NM: not measured due to fast evaporation.

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY			SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application	LS m²/m³	Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
USA - Singer et al. [56]										
50 m³	Orange oil degreaser *Aerosol foam*	3.7 and 6.7 g	Sprayed in sheet aluminium Wiped after 1 minute	0.002	*Ozone* 0-30 minutes 30-90 minutes	*Ozone* 90 minutes	Gypsum wallboard coated with low-VOC pain	Wood framing with plywood underlying.	Gypsum wallboard coated with low-VOC paint	Laminated table (1.16 m²) in the middle
Temperature 20.8 – 23.9 °C	Pine oil cleaner *Concentrated liquid*	50 - 52 g	Dilution 1/16 in water Floor mopping	0.080	*No ozone* 0-30 minutes	*No Ozone* 12 h		Subfloor covered with		of the room
HR 36 – 56 %					30-90 minutes 1.5-4h 4-12h			aluminium sheets		
AER ~ 1 /h	Air fresheners *Plug-in*	29 - 45 mg/h	Plugged 2 days before start the testing	N/A	NS	Until Steady state is achieved		*3.9 m² & 7 m²* portion of floor covered by vinyl for mopping		
Italy – Colombo et al. [57]										
~ 4.6 m³	All-purpose cleaner *Liquid*	1.1 g	NS	0.072	NS	25 hours	NS	NS	NS	No furniture
Temperature 23 ± 0.5 °C	Floor Cleaner *Liquid*	4.2 g		0.290						
HR 45 & 50 ± 1 %	Carpet cleaner *Trigger spray*	1.5 g		0.100						
	Furniture polish *Trigger spray*	NM		0.200						
AER 0.5 /h	Floor cleaner *wax*	0.072 g		0.072						

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study; NM: not measured due to fast evaporation.

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY			SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			FURNITURE
		Amount	Application	LS m²/m³	Sampling Timing	Duration of the test	Ceiling	Floor	Walls	
USA – Weschler et al. [58]										
Unoccupied offices 29 m³ **Temperature and HR** Varied through the day; not controlled parameters **AER** 1.9 - 2.9 /h	NS Commercial cleaner with α-pinene as major constituent	NM	NS	NS	Particles counts were measured continuously in diameter range of: 0.1-2.0 µm	2 days	Acoustic ceiling tiles	Carpeted	NS	Furnished offices
Austria – Höllbacher et al. [59]										
30 m³ **Temperature** 23 ± 2 ℃ **HR** 50 ± 5 % **AER** 0.5 /h	All-purpose cleaner *Liquid*	25 g	Dilution in water 1:10. 10 min cleaning	N/S	0 - 30 min (simultaneously with or immediately after the test) 30 min – 1 h 1 - 1,5 h	120 minutes	Wood-base building materials	Wood-base building materials	Wood-base building materials	Yes. Fully furnished; including carpets, curtains, and furniture.

LS: Loading factor (m²/m³); N/A: Do not apply; NS: not specified in the study; NM: not measured due to fast evaporation.

CHAMBER VOLUME/ OPERATIONAL PARAMETERS	PRODUCT TESTED *DIFFUSION MODE*	APPLICATION METHODOLOGY				SAMPLING STRATEGY		MATERIALS OF THE CHAMBER			
		Amount	Application	LS m²/m³	Sampling Timing	Duration of the test	Ceiling	Floor	Walls	FURNITURE
EPHECT European Project [58] [59] [22]											
0.26 m³ 0.92 m³ (VITO) & Full scale chamber 20.24 m³	Kitchen cleaner *Liquid*	Amount used varied depending on cleaned surface	In aluminium surface. No rinse. Added with cotton tissue	0.40	0h-after application 1 - 3 h 3 - 5 h 5 - 7 h	THC ≤ 5 % of C initial	**1 m³** Stainless steel **20.24 m³** Stainless steel	**1 m³** Stainless steel **20.24 m³** Stainless steel with 5 m² of surface	**1 m³** Stainless steel **20.24 m³** Stainless steel	N/A
	Glass cleaner *Liquid*		Glass surface cleaning. No rinse	0.07						
	All-purpose cleaner *Liquid*		Diluted and not diluted application.	0.40						
AER 0.5 /h ± 5 %	Floor cleaner *Liquid*	30 ml dilution of 2.5 L of water	Rinse and not rinse							
HR 50 % ± 5 %		1 cap of product diluted in 2 L of water		0.40						
Temperature 23 °C ± 2 °C	Bathroom cleaner *Liquid*	Sprayed and weighted before and after application	1 m² of stainless steel was sprayed	N/A						
	Furniture polish *Liquid*	-	0.6 m² wooden table distributed with a cotton tissue	0.07						
	Floor polish *Liquid*	½ cap diluted in 4 L of water	5 m² was cleaned with a wet mop	0.40						
	Air freshener Solid/Gel/Liquid *Passive diffuser*	Weight after and before testing. Proportional to the duration of the test	N/A	N/A	0 – 3 h 3 – 4 h 4 – 5 h 5 – 6 h	3h after steady state ~ (6 h)				
	Air freshener *Electrical diffuser*		Spray in 45 ° orientation upward air movement	N/A						

Air freshener	0.5 g per m^2 / if automatic: 1			After spray	THC $\leq$ 5 % of
Spray	spray max position			0 - 1 h	C $_{initial}$
Glass and	Depending on instructions	Direct to window surface/ No		1 – 3 h	
window cleaner	and surface to clean	rinse	0.07	3 – 5 h	
Spray				5 – 7 h	

LS: Loading factor (m^2/m^3); N/A: Do not apply; NS: not specified in the study.

The comparative analyses of the various experimental methodologies reported throughout Table 7 and Table 8 is addressed in 3 stages in the following: (i) operational parameters and experimental chambers, (ii) application methodology of products and (iii) sampling methodology for VOC quantifications.

2.1   Overview of operational parameters and experimental chambers

2.1.1   The question of temperature and relative humidity

For most of studies, temperature and relative humidity parameters are regulated in the same range, typically from 21 °C to 23 °C and ca. 50 ± 10 % RH. These values are relatively closed to standard conditions for emission evaluation products (i.e., 23 ± 2 °C and 50 ± 5 % RH). Studies using chamber where temperature and relative humidity conditions are controlled generally adapted the environmental conditions proposed by the international standards organization (ISO) for the "*Determination of the emissions of volatile organic compounds from building products and furnishing – Emission chamber test method*" (ISO 16000-9). However, two specific investigations are performed in an experimental house without any temperature and humidity regulation : Nicolas et al. [6] and Solal et al. [51]. As a consequence, experimental conditions were directly dependent on outdoor meteorological conditions. The highest temperature reached was 34 °C during summer period, inducing corresponding variations on ambient VOC concentrations. Nevertheless, no investigation has specifically evaluated the influence of temperature and humidity on household product emissions since most of the reviewed studies are performed under regulated and stable temperature and relative humidity conditions. This represents a mismatch between test chambers and reality. Indeed, under real conditions, environmental conditons can vary on a large range. As a consequence, further studies are expected to investigate the emissions of household products under a larger range of temperature and humidity. This approach has been developed for material emissions. Indeed, Haghighat et al. [61] performed a literature review dealing with the influence of temperature and humidity on the emission rates of indoor materials. Results indicated that temperature and humidity have a substantial effect on the emissions from several material including paintings and varnishes. This behavior suggests extensive variations as well regarding household product emissions.

2.1.2   The question of ventilation and air exchange rate

The air renewal rate in indoor environments is an operational parameter that directly affects the concentrations of indoor pollutants. Air exchange rate (AER) is expressed in h^{-1}. Since housecleaning products are mostly transient emission sources, the AER directly affects the decay time of emitted pollutants after the use of the product. During the HealthVent project [62], a review of European regulation for AER showed inconsistent and heterogeneous values. Indeed, the ventilation rates in test cases range from 0.23 to 1.21 h^{-1} in dwellings. Nicolas et al. [19], Delmas et al. [37] and Weschler et al. [64] aimed at investigating emissions under real scenario. Then the air exchange rate was measured during each experiment but not controlled. In this study, the AER was directly dependent on the ventilation system of the room used, reaching as lower value 2.5 h^{-1}. Based on the studies reviewed, AER values are contrasted from one experimental chamber to another, and may considerably differ from real conditions.

It has to be noted that no study report the impact of the AER on VOC emission rates from household products. Again, the parallel with material emissions is informative. Indeed, emissions from indoor materials can be strongly influenced by (i) air exchange rate, (ii) local air velocity and (iii) local turbulence, depending on the considered VOC. [63] Then, fluid mechanic considerations should be combined with physical chemistry investigations for the evaluation of the emissions on closed environments.

Another associated factor influencing indoor pollutants concentration is the mixing time. According to Nazaroff and Weschler, "*It is defined as the period required for an instantaneous point released in an unventilated room to disperse such that the relative standard deviation among local concentration is < 10 %*". [2] Indeed, under natural convection flow conditions, mixing time in a room of 31 m^3 can vary from 10 to 90 min, for quiescent to strong convection sources. Under forced convection, the mixing time can decrease from 15 to 2 min, depending on the type of forced flow conditions. [64], [65] Then, in a non-mixed room, peak exposure concentrations might primary affect people undertaking cleaning activities. Finally, air exchange rate and air mixing factor can determine the residence time of pollutants in the gas phase, showing a direct influence (i) on the exposure level of occupants, and (ii) on the experimental sampling strategies for the evaluation of emissions.

2.1.3   The question of experimental chambers: size and materials

Regarding the volumes of experimental chambers, 11 studies performed experiments in real size rooms with volumes larger than 20 m^3. On the opposite hand, 4 studies executed experiments in test chambers with inner volumes lower than 1 m^3. Among reviewed studies, three investigations from Bartzis et al. [66], Delmas et al. [26], and Chesnais et al. [58] evaluated emissions in two or more chambers with different volumes. The main scope of Delmas et al. [26], and Chesnais et al. [58] was not to address the influence of the size of the experimental chamber on the concentrations of emitted pollutants, in order (i) to perform a secondary selection of targeted products or (ii) to optimize application patterns of tested products i.e. the quantity of applied product and its application mode. In the frame of the European Project EPHEC Bartzis et al. [66] attempted to propose a comparison of VOC emissions between selected consumer products in chambers with various dimensions. Interestingly, this study presents and compares the results obtained in chamber of 0.26, 0.92 and 20.24 m^3 by three different laboratories. Unfortunately, results are not conclusive due to the variability between laboratories and the overall testing set ups. Thus to decrease such variability, further studies are required to develop detailed protocols for a standard evaluation of VOCs emitted from consumer products. Such a protocol does not exist yet.

Experimental chamber materials are generally designed or selected according to two main concerns: (i) the potential interactions of emitted species with the chamber surfaces, and (ii) their operational costs. Harb et al. [67] executed an overview of inner materials commonly used for experimental chambers. Results established that Teflon®, stainless steel, glass, aluminum and low-VOC paint might have minimal sorptive properties regarding emitted VOCs. Regarding the respective costs of the materials reviewed, glass is an expensive material thus limited to small chambers. Worldwide, stainless steel and aluminum are the most widespread materials due to their physicochemical surface properties and their low costs. The materials chosen for experimental chambers in almost 60 % of the studies are stainless steel and glass. It has to be noted that glass has been selected in studies only for chambers smaller than 1 m^3, due to technical constraints and cost. [67] Regarding studies using real rooms, the construction materials generally vary from ceiling, floor, and walls. The most widespread materials used in five real-condition studies [6], [16], [51], [54], [56], [58] are: (i) wood for ceiling and floor and (ii) painted cement or gypsum board for walls. Regarding the presence of furniture in experimental chambers and real rooms, more than 40 % of the studies aimed at evaluating the interactions of indoor surface with emitted VOC. Then, tested products were applied in fully furnished chambers. Indeed, furniture might have an influence on the emission dynamics, on the uptake and on the formation of secondary pollutant. Surfaces can interact by sorptive processes with gas phase species. [16], [58]

Surface phenomena are the result of the sorptive or sink capacity of indoor surfaces have towards indoor pollutants. It means that they have the ability to reduce peak concentrations, but also to extend occupant exposure due to their secondary emissions. [68] Consequently, it can reduce the real emitted concentration affecting the profile of the chemical substance analyzed. In spite of the key role of surfaces in indoor air chemistry, more than 36 % of the reviewed literature does not specify the nature of the materials of the experimental chambers.

2.2   Overview of application methodologies of cleaning products

In terms of application methodologies, the main parameters identified as key drivers of the concentrations of emitted pollutants are: (i) the loading factor, (ii) the application procedure and (iii) the amount of product used.

The loading factor is defined as the ratio between the cleaned surface and the chamber volume. Among studies reported in Table 7 and Table 8, more than 70 % of the studies consider loading factors lower than 0.1 m^2/m^3. Furthermore, the loading factor depends on the purpose of the cleaning product used. Under real cleaning conditions, for surfaces it is lower than 0.1 m^2/m^3, while for floors it is generally higher than 0.1 m^2/m^3. For comparison, in the reference room according to the ISO 16000-9 standard, the loading factor for floors is 0.4 m^2/m^3. It must be highlighted that this parameter is of high importance since the cleaned surface becomes the "emissive surface". It is expected to observe higher quantities of pollutants released in the gas phase if the emissive surface is larger. However, the application procedure and the amount of product used are also parameters of influence. Indeed, the larger the surface to clean, the higher the amount of product to apply. [2]

Regarding cleaning products, in almost 60 % of the reviewed studies, the application process and the product quantity are defined according to instructions specified on the product labelling in order to simulate a realistic scenario. Nevertheless, studies performed in the frame of the European project EPHECT have executed a previous phase of "shelf surveys". This approach aimed at accurately identifying the consumer's preferences or habits concerning the real quantities applied and the effective application procedures. It has been observed that, beyond the instructions, the applied quantity of cleaning products depends on the category of product used, its diffusion mode and the surface to clean. [4], [9], [48], [69]–[71]

The amount of product used determines the maximum total mass of pollutants transferred from applied products to the gas phase. It can be calculated by multiplying the volume of product used by the concentration of volatile species (number of species $= n_1^i$) contained in the product. Depending on the application process, all or part of the applied mass might be emitted. For instance, if a floor cleaning product is diluted in water and, after its application, the floor is rinsed, some of the volatile constituents may be transferred down the drain with the wastewater. The same occurs for kitchen or furniture cleaning products, where a rinsing procedure might be performed. Nazaroff et al. [27] and Singer et al. [60] analyzed the impact of "*leaving the wiping towels*" inside the room. Results confirmed that the cleaning material itself might be an additional source of emissions that can considerably increase the concentrations of pollutants in the room if the towels are not removed or rinsed after cleaning.

The exposure of occupants is directly related to the application patterns of the cleaning products such as (i) rinsing and removing the cleaning materials and surfaces, (ii) using diluted products that increase the product dispensed but decrease the mass fraction of active components and scents, and (iii) reduce the frequency and duration of the cleaning activities.

2.3   Overview of application methodologies for air fresheners and purifiers

The case of air fresheners differs from cleaning products. Indeed, their use does not involve a specific process. Subsequently, the loading factor cannot be defined as for cleaning products since air fresheners are not directly applied onto surfaces. Generally, a loading factor of 1 m^2/m^3 is considered in that cases. Thus, primary emissions are mainly influenced by the dispersed mass and the selected diffusion mode.

Plug-in air freshener / The application modes only depending on the intensity adjusted on the electrical set-up. It can be low, medium or high intensity. Therefore, the amount of dispersed species can vary. The products tested are weighted before and after use in all the studies in order to quantify the mass of product vaporized.

Passive diffuser air freshener / It does not involve an application process, just the positioning of the device in the test chamber. Generally, passive diffusers are used to release continuously odorous chemicals. The products tested are weighted before and after use in all the studies in order to quantify the mass of product vaporized.

Spray aerosols / The application process depends on (i) the amount of product distributed by each spray (user dependent) and (ii) the number of sprays performed. The number of sprays might change depending on the volumes of the experimental chambers. For spray air fresheners, all reviewed studies have followed indications provided by the manufacturer. The amount of product released in one spray can vary from 0.39 to 2.00 g/spray depending on the spray mechanism and the user. [4] Finally, depending on the diffusion mode of air fresheners, dynamic of emissions might vary. Plug in air fresheners and passive diffuser serve as continuous emissive sources, while spray aerosols are a one – time sources. Therefore, sampling strategies i.e. sampling time and test duration are required to be optimized depending on the tested product.

2.4   Overview of sampling and analytical strategies

Sampling strategies primarily refer to (i) the duration of tests, (ii) the duration of the sampling, (iii) the frequency of the sampling, and (iv) the interval of time between samplings. Likewise, analytical strategies mainly refer to the instrumental methodologies for qualitative and quantitative analyses. Both, sampling and analytical strategies, are required to be developed and optimized depending on the species of interest and the emission dynamics. Regarding emissions from essential-oil-based household products, the main chemical compounds targeted are terpenes. Then, depending on chemical and physical properties of terpenes, sampling and analytical strategies have to be adapted.

Considering the analytical methodologies, 95 % of reviewed studies followed international standards for emission tests developed for building and construction materials, i.e. ISO 16000 - 6 and ISO 16017-1. [72], [73] Indeed, for the analysis of TerVOCs, air samples are collected using Tenax TA sorbent tubes. Then, samples are analyzed by thermal desorption and GC/MSD/FID, as established in ISO 16000-6. Nevertheless, Fan et al. [74] selected a different analytical methodology using activated carbon sorbents tubes for sampling, and a subsequent liquid-extraction and filtration. Aliquots of 2 µL of extracted samples were injected into GC/FID system. Irrespectively of the analytical devices and detectors, it is important to mention that all reviewed investigations are operated using *off-line* instrument methodologies for VOC determination.

For the majority of the studies reviewed, the first hour of experiment following the application of the product is covered by a continuous off-line sampling with intervals of 30 min. Then, VOC concentrations are evaluated on longer intervals, due to

expected emission profiles. Sampling strategies are optimized and adapted in most of the reviewed studies depending on the type of product used in order to accurately address the specific emissions profile.

Are experimental protocols adapted to household product testing? From the analysis of the reviewed studies it can be concluded that: wide variations and heterogeneity exist regarding experimental methodologies for the evaluation of primary and secondary pollutant emissions from fragranced household products. Variations are related to several crucial parameters: (i) on the one hand it is linked to products: the quantity of dispersed products and application protocols, (ii) on the second hand it is linked to the environment of test: air exchange rate, temperature, chamber size, and relative humidity. Therefore, the comparison of results from one investigation to another may become difficult and inaccurate. This review suggests that efforts in the scientific framework need to be achieved toward the standard experimental methodologies for the evaluation of household product emissions. Indeed, standardized protocols would allow to decrease the variability between studies and improve the relevance of comparisons and subsequently more advanced conclusions.

3. Emissions from essential-oil-based products

Regarding the evaluation of the emissions from building materials, the materials of interested are set as a fixed object in an experimental chamber under standardized conditions in order to determine and report emissions rates. Moreover, several investigations are executed in order to assess the reproducibility of emission results from the selected materials. As a consequence, in the building material domain, inter-studies variations are minimized to ca. 20 %. [75]–[77] On the other hand, regarding household products, the situation is totally different. Household product emissions generally occur when the product is used, then an application scenario is defined to simulate the use of the product in the test chamber. Depending on the product, applications and emission dynamics might differ from one study to another. For instance, the dynamic of emissions might be either continuous or transient. In spite of identified disparities regarding experimental conditions among reviewed investigations, chamber emission tests allow an exposure approach regarding the diversity of chemical species emitted from household products. In this section the evaluations of emissions from essential-oil-based products in small chambers, large chambers and real size rooms are discussed in order to provide answers to the question: is there a potential exposure risk for consumers related to TerVOCs emitted from household products?

The present section relies on the compilation of 22 studies aiming at exploring the significance of air pollutants released along the use of cleaning products, air fresheners and pure essential oils in homes and non-industrial workplaces. A comparison of experimental methodologies implemented in these studies has been addressed and discussed in the previous chapter. For clarity purpose, the discussion has been classified according to the type of product: (i) emissions from pure essential oils, (ii) emissions from cleaning products and (iii) emissions from air fresheners and purifiers.

3.1   Emissions from pure essential oils

Regarding emissions of VOCs from of pure essential oils, only few studies have been performed. In this section, three investigations aiming at evaluating the impact on indoor air quality from evaporated essential oils are discussed. The three studies reviewed were performed in Taiwan between 2006 and 2012: Chiu et al. [30], Su et al. [35], and Huang et al. [78].

Chiu et al. [30] aimed at identifying the emissions from pure essential oils by thermogravimetric analysis (TGA). Results evidenced the emissions of 52 different VOCs with emission factors ranging from 137 to 173 mg/g. During the evaporation induced by the thermogravimetric analysis procedure with a heating rate of 2 and 15 °C per minute reaching a maximal temperature of 40 °C, recorded total TerVOC concentrations were 88, 75, 113, 116, and 89 ppm respectively for rose oil, lemon oil, rosemary oil, tea tree oil and lavender oil. Thus, regarding their emission abilities, essential oils were ranked as follows: rose ≈ rosemary > tea tree ≈ lemon ≈ lavender. Furthermore, concerning emitted compounds, from 62 to 78 % were cyclic, from 21 to 37 % were paraffin and less than 1.5 % were olefins. It is important to note that there is a deep gap between essential oils vaporized using TGA system compared to their realistic use in an indoor environment i.e. through the use of diffusors in a real scale indoor environments. If the use of TGA allows the evaluation of the terpene emissions, the effective connection between this experimental approach and real indoor issues is far from being straightforward.

Su et al. [35] investigated the effects of evaporating three best-sold essential oils in two different indoor settings characterized by the same volume: 21.6 m^3. Temperature and humidity were not controlled and not specified in this study. Tested essential oils were (i) lavender, (ii) eucalyptus and (iii) tea tree oils. The experimental procedure used was based on the diffusion through a candle diffusor of essential oils diluted in water. The total concentrations of the emitted VOCs were 803, 787, and 855 µg/m^3 corresponding to tea tree, lavender and eucalyptus oil, respectively. More details about the concentrations

monitored are reported in Table 9. It should be noted that the major emitted constituents of the tested essential oils are written in bold. Furthermore, TerVOC emissions during evaporation time mostly occurred during the first 20 minutes for eucalyptus and tea tree oils. Peak concentrations were achieved during the same time span. The case of lavender oil was individual. Indeed, the peak concentration was reached after 30 to 45 minutes. Su et al. [35] attributed this specific behavior to the difference in the chemical composition of lavender oil compared to the other oils tested. Indeed, lavender oil is mainly constituted by terpenes derivatives characterized by lower vapor pressures than monoterpenes. Compared to the study proposed by Chiu et al., this investigation reports TerVOC concentration levels from the evaporation of essential oils under a more realistic scenario and in a real size room.

Table 9. Concentrations of volatile organic compounds during testing periods of 180 min in two different types of indoor environments. [35]

ESSENTIAL OIL Dilution in water: 300 µl/ 50 ml	TerVOCs	CONCENTRATION AFTER 180 min ($\mu g/m^3$)	
		Diffusion through a candle diffuser	
		Office (21.6 m³) AER: 1.3 h^{-1}	*Home* (21.6 m³) AER: 1.8 h^{-1}
Tea Tree (*Melaleuca alternifolia*)	4-terpineol	78	56
	1,8 cineole (Eucalyptol)	16	4
	d- Limonene	108	140
	ρ- cymene	**803**	**754**
	TOTAL TERVOC²	**1005**	**954**
Lavender (*Lavandula angustifolis*)	**Linalool**	**544**	**787**
	d- Limonene	7	81
	4-terpineol	77	112
	TOTAL TERVOC²	**209**	**980**
Eucalyptus (*Eucalyptus globules*)	**1,8 cineole (Eucalyptol)**	**855**	**329**
	d- Limonene	46	19
	ρ- cymene	52	19
	4-terpineol	60	29
	TOTAL TERVOC²	**1013**	**396**

2: Total calculated among the target compounds detected

In the third study, Huang et al. [78] aimed at evaluating the impact of the use of essential oils in aromatherapy environment. Thus, concentrations of TerVOCs were determined before and after the aromatherapy process. One aromatherapy spa was randomly selected from a survey on from main chain stores in Taiwan. Experiments have been performed under realistic scenario: in a spa room of 16.26 m^3. Two essential oils were evaluated, they are identified in the study as aromatherapy #1 and aromatherapy #2. Unfortunately, this study does not reveal the mass and the type of essential oil used which represents a strong limitation. Results evidence that major emitted TerVOCs are α and β pinene. Likewise, detected peak concentration reached 714 and 499 µg/m^3 for the most emitted species from aromatherapy #1 and aromatherapy #2 respectively. In addition, the total concentrations of the five major terpenes monitored reached values as high as 2493 and 1137 µg/m^3 from aromatherapy #1 and aromatherapy #2 respectively.

Based on the reviewed studies, linalool, eucalyptol, limonene, cymene, pinenes, and 4-terpineol are the main TerVOCs monitored from the selected and evaporated essential oils. According to Chiu et al. [30] and Su et al. [35], tea tree oil is evidenced to be one of the most emissive oil among tested ones. Moreover, it clearly appears that the concentrations of evaporated individual terpenes can exceed the exposure limit value defined for long term exposure as established by the European commission through the INDEX Project. [79] Proposed long term exposure limit concentration value is 450 µg/m^3 for limonene and α-pinene, individually. Consequently, the evaporation and diffusion of terpenes from essential oils can be a significant and hidden source in indoor environments and can potentially impact indoor air quality. [30], [35], [78]

3.2 Emissions from Cleaning Products

Regarding the evaluation of cleaning product emissions, 12 studies have been performed, thus providing a larger step back than for pure essential oils. Among them, 7 studies were executed during the last 5 years while 5 others were performed from 1991 to 2006. The reviewed studies have been performed either in Europe or in the United States. For discussion purposes, concentrations have been sorted out by product categories, they are summarized and disclosed in Table 10. Emitted compounds are listed with their maximum concentration values. Concentrations written in bold correspond to the major emitted compound from the considered product.

Three main influential experimental parameters have been considered in Table 10, namely: (i) the chamber volume, (ii) the mass of product dispersed, and (iii) the diffusion mode of the tested product. The main contrast between the studies reviewed relies in the diversity of compounds monitored. The total TerVOC concentrations are calculated as the sum of the concentrations of the targeted compounds emitted. Some studies not only address total emitted TerVOC concentrations but also provide individual identifications and quantifications of TerVOCs. Experimental methodologies were quite heterogeneous from one study to another, then discussions concerning emissions are primarily driven towards the variation of concentration levels and the comparison with other terpenes from indoor sources.

1

2 **Table 10.** Concentrations of TerVOC emission peaks from cleaning products in experimental chambers

3

COMPOUNDS	MAXIMUM CONCENTRATION MEASURED (µg/m^3)					
Floor cleaners						
	EPHECT (EU) [9]	USA [54] [56]	USA [15]	France [6]	Italy [57]	Austria [59]
Chamber Volume	**24 m^3**	**50 m^3 Floor mopping**	**11 m^3**	**0.05 m^3**	**4.5 m^3**	**30 m^3**
(Quantity of product)	**(1 tbsp. = ~ 15g)**	**Diluted (50 g)**	**(~ 2 g)**	**(1.06 g)**	**(4.2 g)**	**25 ml (Diluted)**
Diffusion mode	*Liquid*	*Liquid*	*Liquid*	*Wipes*	*Liquid*	*Liquid*
Limonene	**37**	**1 130**	101	74	-	**726**
Terpinolene	-	1 270	-	-	-	-
Terpineol	-	953	-	**784**	**1 700**	-
β-pinene	-	13	101	-	-	62
Terpinene	-	244	-	-	-	25
p-Cymene	-	174	-	-	-	12
Eucalyptol	-	330	-	-	-	-
Dihydromyrcenol	-	-	-	363	-	25
α-pinene	19	66	30	9	-	86
Citronellol	-	-	-	78		-
Linalool	-	-	-	76		-
Camphene	-	105	-	-	75	-
α-Phellandrene	-	29	-	-	-	-
Camphor	-	-		-	121	-
3-carene	-	-	**190**	-	-	271
TOTAL TERVOC	**56**	**4 314**	**423**	**1 438**	**6 510**	**1 230**

4 1: Constituent of fragrance mix in the European standard series; -: Not a target compound in this study; Tbsp.: tablespoon

5

6

7

8

9

10

11

COMPOUNDS	MAXIMUM CONCENTRATION MEASURED (µg/m³)						

Kitchen cleaners (Spray/ Liquid)

	EPHECT (EU) [9], [66], [70]		USA [54]			Denmark [55]	France [6]
Chamber Volume	**0.92 m³**	**24 m³**		**50 m³**		**20 m³**	**0.05 m³**
Quantity of product	**-**	**3 tbsp.**	**10 g/ Towels removed**	**9.9 g/ Towels remained**	**3.7 g**		**0.42g**
Limonene	**82**	**1 715**	**960**	**1 100**	**5 282**	**522**	44
Terpinolene	-	-	890	1 040	-	22	-
Terpineol	-	-	431	545	-	-	569
β-pinene	-	-	12	14	-	-	-
Terpinene	<1	-	185	225	-	-	-
p-Cymene	1	-	142	172	-	26	-
Eucalyptol	-	-	250	300	-	-	22
Dihydromyrcenol	-	-	-	-	-	143	-
α-pinene	-	≤1	58	74	-	-	-
Citronellol	-	-	-	-	-	-	**1 038**
Linalool	-	-	-	-	-	-	138
Camphene	-	-	87	109	-	-	-
α-Phellandrene	< 1	-	23	29	-	-	-
TOTAL TERVOC	**83**	**1 716**	**3 038**	**3 608**	**5 282**	**713**	**2 443**

12

Surface cleaners

	USA [15]	USA [16]	France [6]	France [80] [6]
Chamber Volume	**11 m³**	**50 m³**	**0.029 m³**	**0.05 m³**
Quantity of product / *Diffusion mode*	**4 sprays / *Trigger Spray***	**(6.6 g) / *Liquid***	**0.42g/ *Powder- Cream***	**0.13 g/ *Foam***
Limonene	**60**	**2 500**	1 230	**374**
Terpinolene	-	-	74	-
Terpineol	-	-	85	137
β-pinene	8	-	27	-
Terpinene	-	-	23	-
ρ-Cymene	-	-	41	-

Eucalyptol	-	-	-	115
Dihydromyrcenol	-	-	-	171
α-pinene	24	-	12	-
Citronellol	-	-	**1 251**	-
Linalool	-	-	61	-
Citral	-	-	64	-
3-carene	18	-	-	-
Geraniol	-	-	464	-
Borneol	-	-	-	61
TOTAL TERVOC	**111**	**2 500**	**3 437**	**858**

13   1: Constituent of fragrance mix in the European standard series; -: Not a target compound in this study; Tbsp.: tablespoon

3.2.1   Variability of the TerVOC primary emissions

As disclosed in Table 10, a total of 19 different fragrance species were detected among evaluated cleaning products. Limonene is evidenced as the most emitted terpene, being detected in 16 out of 17 tested cleaners. In addition, limonene is also the major compound released from 11 cleaning products. Other major terpenes are α-pinene and terpineol, identified in 10 and 8 cleaning products respectively. Fragrance molecules in gas composition after the cleaning activity are widely diverse from one tested product to another. Regarding concentration profiles, maximum levels were detected during the first 60 minutes after the cleaning activity is completed, this behavior is observed for all the studies. The total TerVOC concentrations range from 56 to 6 510 µg/m^3 among the 17 investigated cleaning products, while the concentration of the major emitted species can range from 37 – 5 282 µg/m^3.

Regarding the category of products, the applied mass of product directly depends on the cleaning purpose, i.e. the surface to be cleaned. In the studies reviewed, the mass applied for surface cleaners did not exceed 6.6 g while for floor cleaners and kitchen cleaners the mass of products applied reached 50 g and 10 g, respectively. Nonetheless, all cleaners evidenced similar ranges of total emitted concentrations of fragrance chemicals. The ranking of product regarding their emitted total concentrations of TerVOCs are (i) floor cleaners: from 56 to 6 510 µg/m^3, (ii) kitchen cleaning agents: from 82 to 5 282 µg/m^3, and (iii) surface cleaners: from 111 to 3 437 µg/m^3. Therefore, strongly contrasted concentration levels can be evidenced from the use of one cleaning product or another. Contrasted concentrations can be attributed to: (i) the discrepancies between experimental methods applied in the reviewed studies, (ii) contrasted mass concentrations and high diversity of terpene constituents in the products, (iii) contrasted physicochemical properties of terpenes and (iv) different chemical affinities of terpenes for other species/solvents contained in product formulations.

Three investigations specifically aimed at evaluating the impact of different application methods on IAQ under real conditions. Nazaroff et al. [16] investigated the impact of different use patterns, thus two main experimental protocols were implemented. For surface cleaning, applied methodologies were either "*leaving*" or "*removing*" the cleaning material i.e. wiping towels out of the experimental room. Results evidenced that the fractional emissions of terpenes and solvents can reach overall levels from 35 to 100 % of the amount of product applied when the wiping towels are kept in the room. On the contrary, when towels were removed from the chamber, fractional emissions levels dropped to 20 - 50 %. Singer et al. [54]

evaluated emissions from the use of floor cleaners under realistic conditions. For instance, 50 g of product was diluted in 4.5 L and mopped on 4 m² of a tile-covered portion of floor. The remaining solution was poured into a second bucket within the chamber to simulate disposal. Results confirmed that floor mopping with diluted solution has the lowest emission factor compared to non-diluted countering cleaning. This behavior was attributed to the fact that part of the cleaning solution remained in the bucket and was removed from the chamber at the end of the activity. Instead, fractional emissions of terpene alcohols were in the range of 2 to 5 % whereas monoterpene emissions were in the range of 7 to 12 %. On the other hand, Singer et al. [54] , [56] evidenced a discrepancy regarding emitted concentrations between the terpene hydrocarbons and terpene alcohols. Authors attributed this behavior to a slower volatilization of the alcohols during initial application and a greater partitioning of alcohols into water during scrubbing and rinsing procedures. Consequently, it was evidenced a higher concentration of pollutants if cleaning materials are left in the room, since they will represent an additional source of emission. As a consequence, beyond the cleaning product itself, the application method and the "*human factor*" have a significant influence on the dynamic and level of emissions of TerVOCs.

3.2.2   TerVOCs emissions from cleaning products vs. other indoor sources

Wood-based buildings and furniture materials often contain significant amounts of TerVOCs. Therefore, these materials are identified as additional and substantial sources of TerVOCs in indoor environments. For comparison purposes, Table 11 disclosed maximal detected total terpene concentrations from different building and furniture materials in large volume test chambers.

Table 11. Peak emission concentration of TerVOCs from buildings and furniture materials in large volume chambers

Type of material	TerVOC peak concentration	Test room volume	Reference
Wood-based boards	175 µg/m³	40 m³	Harb et al. [81]
Wood-based walls/floor	70 µg/m³	30 m³	Höllbacher et al. [60]
16-mm pine softwood particleboard	219 µg/m³	33.6 m³	S.K. Brown [82]
Pine board surface (1 m²)	443 µg/m³	56.7 m³	Toftum et al. [83]

Regarding real size test rooms, i.e. with volumes higher than 30 m^3, different categories of wood-based materials have been evaluated as disclosed in Table 11. The contrast among reported concentrations and the diversity of emitted VOCs are expected to be due to the various emissive surfaces tested and different kinds pinewood-based materials used. The maximum concentrations of terpenes ranged from 70 to 443 µg/m^3. The major emitted terpenes from wood-based materials are α and β pinenes. [60], [81]–[83]

Regarding cleaning product emissions evaluated in real size test chambers (30 and 50 m^3), the terpene peak concentrations range from 1 230 to 5 282 µg/m^3. [16], [54], [56], [59] As a consequence, cleaning activities can contribute to TerVOC indoor concentrations by more than one order of magnitude compared to wood-based materials. Nevertheless, it is important to highlight that emissions of cleaning products are characterized by different dynamics compared to indoor material emissions. In fact, they mostly act as punctual or transient sources of pollutants, thus long-term exposure is directly related with cleaning occurrence and human factor, while sources constituted by indoor material mostly act as long term and continuous emission sources.

3.3 Emissions from air fresheners and "purifiers"

Eleven studies focused on the identification of fragrance chemicals emitted along the use of air fresheners and so-called air "*purifiers*" have been identified and are reported in Table 12. Experimental methodologies implemented in these investigations have been assessed and discussed in the previous chapter. Emitted concentrations are assembled by diffusion mode. For aerosol products, the number of sprays and the spraying time-interval for automatic aerosols are indicated in Table 12. It should be noted that values written in bold correspond to major emitted compounds. The experimental chamber volume is specified in Table 12 when indicated in the corresponding study. Furthermore, targeted compounds vary from one study to another, then some information related to emissions of explicit fragrance species may be not specified. The compound named Lilial® is a fragrance mix as defined by European Standards, it has only been detected in investigations performed in Europe. Finally, total TerVOC concentrations are calculated as the sum of the individual concentrations of identified and quantified TerVOCs.

Table 12. Concentrations of TerVOCs emitted by air fresheners in experimental chambers ≥1 m3 and classified by diffusion mode

	MAXIMUM EMISSION CONCENTRATION MEASURED IN µg/m³									
	BEUC (EU) [84] [38]	Germany [19]	France [51]	France [26]	USA [15]	USA [16]	Denmark [55]	EPHECT (EU) [9] [70]		Austria [59]
Chamber Volume	NS *Apartment*	3 m³	32 m³	42 m³	11 m³	50 m³	20 m³	17 / 24 m³	~1m³	30 m³
Plug-in (1 unit of product)										
Limonene	**499**					499	5	**94 / 685**	15	26
Linalool	146					146	112	-	-	**118**
Lilial	41					41	-	-	-	-
Terpinene	-					-	-	LD / 129	22	-
α-pinene	-					-	-	13 / 75	18	10
β-pinene	-					-	-	LD / 132	32	-
3-carene	-					-	-	LD / 22	8	10
α-terpineol	-					-	132	-	652	13
Dihydromyrcenol	-					-	109	-	-	-
Geraniol	-					-	15	-	-	-
Phellandrene	-					-	-	LD / 89	-	-
Camphene	-					-	-	LD / 8	-	-
Citronellol	-					-	-	-	-	-
TOTAL TERVOC	**725**					725	373	107/746	1 139	328
Passive diffusers (Gel/ Liquid) (1 unit of product)										
Limonene	**735**	-	39		1156			**79**	351	
Linalool	37	**560**	98					-		
Lilial	2	-						-		
Terpinene	-	-	-		171			-	137	
α-pinene	-	-	143		942			52	175	
β-pinene	-	-	40		**1 242**			-	276	
3-carene	-	-	-		771			-	29	
Camphene	-	-	99		-			-	68	
Eugenol	16	-						-		
Eucalyptol		-	**275**					-		
Phellandrene	-	-	-		-			-	89	
Cymene	-	-	-		-			-	**591**	
TOTAL TERVOC	888	1 140	694		4 281			131	1 580	
Aerosol spray										
N° of sprays	*3*	*1*		*8*	*1*					
Time-interval	*15min*	*28min*								
Limonene	**2 003**	**12 000**		4 876	**1 930**					

Linalool	750	580	3 123	-
Lilial	310	-	-	-
Terpinene	-	-	962	-
α-pinene	-	-	1 248	119
β-pinene	-	-	851	-
3-carene	-	-	762	920
α-terpineol	-	140	717	-
Hydroxycitronellal	51	-	-	-
Geraniol	40	-	-	-
Coumarine	22	-	-	-
Cymene	-	-	1 010	-
Eucalyptol	-	-	**12 366**	-
Bergamol	-	-	4 505	-
TOTAL TERVOC	**3 176**	**12 720**	**38 972**	**2 969**

- : Not a target compound in this study; NS: not specified in the study; LD: below detection limit

As disclosed in Table 12, among 16 air fresheners, more than 20 fragrance chemicals have been identified. Besides, limonene is detected as the major emitted chemical in 8 out of 17 air fresheners. It is followed by eucalyptol, α-terpineol and linalool being the major emitted compounds in 2 products. Concentration levels from major compounds among tested products reached maximal values of 12 000, 12 366, 652 and 560 µg/m^3, respectively for limonene, eucalyptol, α-terpineol and linalool. Concentrations classified by diffusion modes range from (i) 2 969 to 38 972 µg/m^3 for sprays, (ii) 131 to 4 281 µg/m^3 for passive diffusers and (iii) 107 to 1 139 µg/m^3 for plug-in air fresheners. In spite of the fact that results report higher concentrations for aerosol air fresheners, the mass composition of the fragrance mixture is likely more influential. Indeed, in studies addressing different diffusion modes, results indicated that the composition of the fragrance mixture is the key driver of primary emissions, followed by the type of delivery device. [30], [34], [35] Nevertheless, the main difference regarding the various diffusion modes of air fresheners is that passive and heat diffusers continuously release species to maintain the targeted odor, thus generating a steady state, or long term, concentration of TerVOCs, while aerosols and sprays act as punctual sources of pollutants. [49], [59], [64], [86], [87]

Delmas et al. [26] evaluated a best-sold air purifier spray in France under realistic conditions. The total peak concentration of terpenes almost reached 40 000 µg/m^3. The individual contributions of eucalyptol and limonene were 12 366 and 4 876 µg/m^3, respectively. Furthermore, 3 hours after the product application, limonene concentration was still 70 times higher than typical concentrations reported in French dwellings by OQAI (Indoor Air Quality Observatory). [87], [26], [88] Therefore,

from a VOC point of view, this investigation strongly compromises the "*purifying*" claims of this product since it releases high amounts of volatile compounds that have been specified as allergens by European regulations. Chesnais et al. [52] performed a similar study where a total of 15 products are tested. Among them, seven were essential-oil-based air purifiers and five were odor neutralizers. Results evidenced total VOC concentrations ranging from 475 to 15 790 µg/m^3 for essential-oil-based purifiers and from 514 to 2 717 µg/m^3 for air fresheners claiming for an odor neutralization action. Among 31 VOCs monitored, the majority was terpenes. Limonene and linalool were detected at the highest levels for all tested products. [52], [53]

Air fresheners can produce higher and steady-state concentration levels of terpenes when compared to other indoor terpene sources. Reviewed investigations suggest that the use of air fresheners is responsible of the release of a great variety of fragrance molecules, and suggest an elevation of the health risk of building occupants. As a consequence, it appears that their "*purifying*" or "*odor neutralizer*" claims are highly ambiguous since they mostly correspond to massive emissions of TerVOCs to provide pleasant odors. However, these purifying properties of the essential oils can come from their ability to limit or eliminate the proliferation of microorganisms. [89] Thus, they have an impact on the hygienic quality of the air. But, in return, they are responsible for the emission of many volatile compounds and may considerably contribute to an increase of the exposure of occupants to VOCs.

In the extensive European project *EPHECT* [69], [70] a plug-in diffuser was investigated in two chambers with different volumes : 1 m^3 and 24 m^3, as disclosed in Table 12. Results evidenced that for the plug-in air freshener, the total terpene concentration monitored in the 1 m^3 chamber represents only 14 % of the total concentration found in the 24 m^3 chamber. This result is in agreement with the study of the passive diffuser air freshener tested in the same project where terpene concentrations in the smaller chamber represented only 8 % compared to total concentration detected in 24 m^3 chamber. Therefore, differences in the chamber volumes might have a direct influence on the resulting concentration level as long as realistic scenario are not defined taking into account the chamber volume. This aspect questions the significance of emission tests carried out in various chambers without accurate emission scenario and without transposable environmental conditions such as air renewal rate, temperature and relative humidity. This mismatch praises on the proposal of standard experimental protocols to address the emissions of essential-oil-based products in a relevant way.

3.4   Wrap up on TerVOC emissions

Unexpectedly, the largest contributors of terpenes to indoor air are not sources that are usually recognized, regulated and controlled. Household products have to be seriously envisaged as versatile and high impact sources. Sources of fragrance chemicals in indoor air are chiefly linked to the use of cleaning products, air fresheners and purifiers. These products might release concentration levels of several tens to hundreds of micrograms per cubic meter of TerVOCs, exceeding exposure limits established by the United States. Moreover, these molecules have been classified as allergens responsible to skin irritations, allergic rhinitis, and asthma. [90] Furthermore, one of the main concerns associated to these molecules is related to their chemical structure. Indeed, they are unsaturated volatile organic compounds, thus highly reactive with different indoor air oxidants. To that regard, they can be considered as sources of secondary pollutants such as formaldehyde and organic aerosols. These aspects questions their secondary impact on indoor air quality related to their fate. Indoor air chemistry linked to terpenes might take place under different pathways; homogeneous and heterogeneous reactivity. Next section discuss the fate of terpenes in indoor environments.

4.   The fate of TERVOCs in indoor environment: uptake, reactivity and side – products

"*From a chemical perspective, the indoor environment is a reaction vessel with chemicals continually entering and exiting. Some of these chemicals can react with one another (or themselves) creating reaction products that might otherwise be absent from the indoor setting. Many of the resulting products are more reactive and/or irritating than their precursors*''. Weschler et al. [91] Therefore, the key question is do we address the relevant pollutants ? Wolkoff et al. [92] Indeed, numerous indoor processes modify the concentration and temporal behaviors of air contaminants. These processes include (i) indoor and outdoor air exchange, (ii) non-reactive fate, i.e. sorptive interaction between contaminants and indoor surfaces, and (iii) reactive fate including gas phase and surface reactions. These aspects are fundamentals for the prediction and assessment of exposure risk to indoor pollutants.

Terpenes are known as volatile organic compounds of biogenic origins, being monoterpenes the lighter and more volatile molecules. Chemically, monoterpenes result from the condensation of a penta-carbonate unit with two unsaturated bonds, isoprene (2-methyl-1, 3-butadiene). They are composed of 10 carbon atoms and 16 hydrogen atoms that can be linearly or cyclically arranged according to different isomers. [11] These species might have various degrees of unsaturation, leading to

highly reactive sites in their structures [11], [25]. To that regard, terpenes are highly reactive towards oxidants: (i) ozone, (ii) hydroxyl radicals (HO°) and (iii) nitrate radicals. They are the most common initiators for gas-phase oxidation reactions in indoor and outdoor environment. [93]

As detailed in the previous chapters, the use of household products represents one of the main contributors of indoor terpenes concentrations, nonetheless ***what is the fate of terpenes once emitted in indoor environment?*** Indoor, depending on ventilation conditions, the removal through reactive processes competes with the removal by air exchange rate but also surface uptake. Three main mechanisms associated to the indoor fate of terpenes in indoor air should be considered: (i) homogeneous reactivity, (ii) sorptive interactions and (iii) heterogeneous reactivity, as presented in Figure 2. Therefore, ***what about the exposure to indoor concentrations of secondary air pollutants?***
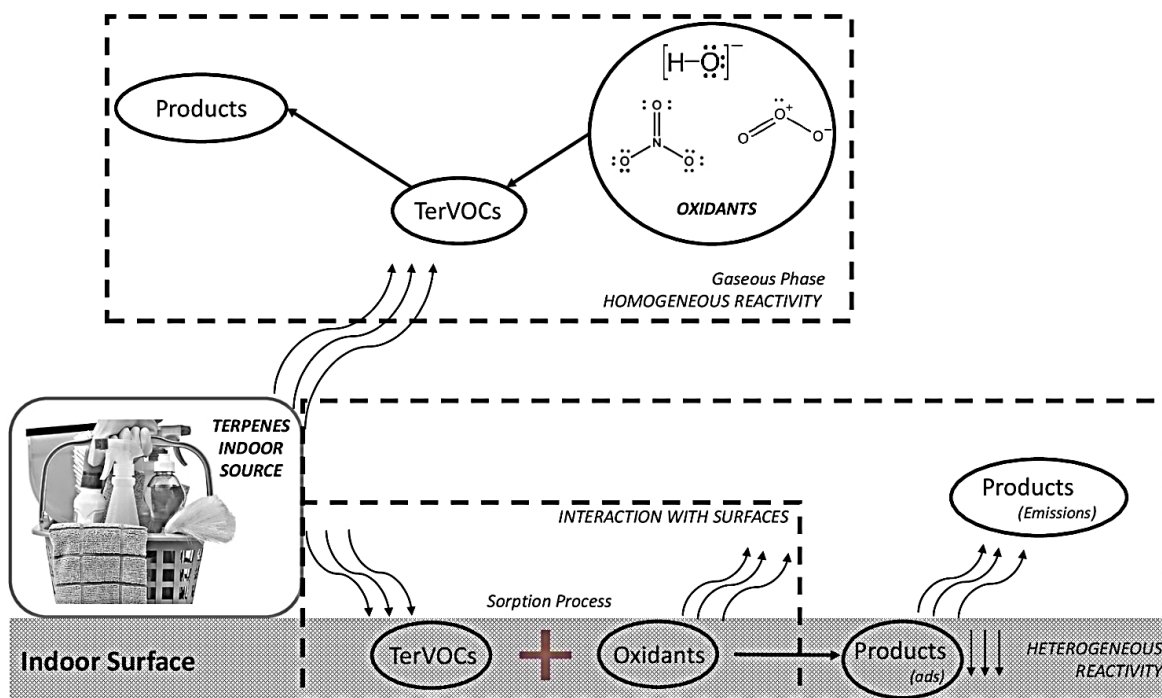

Figure 2. Schema of indoor fate of terpenes and terpenoids

This chapter aims at addressing the fate of terpenes through the analysis and discussion of research works published in the recent years on the subject of indoor fate of TerVOCs emitted by household products. The discussion is driven by five axes:

   (i)   ***Oxidants in indoor air***: analysis of sources and concentrations of potential oxidants;

(ii)   ***Non-reactive fate***: uptake of targeted indoor air contaminants on indoor materials;

(iii)   ***Reactive fate***: evaluation of reaction kinetics and oxidation mechanisms of terpenes;

(iv)   ***Sorptive interactions and heterogeneous reactivity***;

(v)   ***Formation of products:*** assessment from the use of household products under realistic conditions.

4.1   Indoor concentrations and sources of oxidizing agents: HO°, NO₃ and O₃

4.1.1   Ozone in indoor air: sources, concentrations and deposition

Concentration levels of ozone in indoor environments depend on several influential factors. These factors are (i) outdoor concentration levels of ozone, (ii) indoor emission rates and sources, (iii) ventilation rate, (iv) surface removal rates of ozone and (v) homogeneous and heterogeneous reactions involving ozone.

Outdoor concentrations of ozone might widely vary depending on meteorological conditions and environmental pollution, due to its photochemical production. This atmospheric process involves volatile organic compounds, nitrogen oxides, carbon monoxide and sunlight. [16], [94]. During daytime, ozone concentrations are considerably higher and annual maximum peak values are mainly observed during summer season. Weschler et al. [95] recorded ozone concentrations during summer as high as 183 µg/m^3 while during winter the maximum concentration registered was 53 µg/m^3 in an urban location in California, USA. Likewise, the CSTB performed an investigation in their experimental house "MARIA" situated in France, close to Paris [92]. They evidenced the highest outdoor ozone concentrations around 4:00 pm during summer with more than 200 µg/m^3. This result also agrees with Blondeau et al. [96] who revealed maximum ozone concentration of 240 µg/m^3 in the surrounding of French schools in Paris region during August 2003. According to the French forecasting platform PREV'AIR, during summer 2016, a peak concentration of atmospheric ozone increased up to 220-230 µg/m^3 in the northern and eastern regions of France. [97]

Nicolas et al. [92] evidenced that indoor ozone chiefly originates from outdoor and vary in a predictable way according to outdoor concentration variations and air exchange rate. Likewise, indoor and outdoor ozone concentration ratio can vary from 0.2 to 0.7 depending on the outdoor-to-indoor mass flow rate. Additionally, it has been well established that a variation of air exchange rate from 1 to 4 h^{-1} can increase indoor/outdoor ozone ratio from 0.2 to 0.55. [81], [94], [96]

Regarding indoor sources of ozone, Weschler et al. [95], Destaillats et al. [99] and Black et al. [100] have evidenced that the highest indoor contributors of ozone are office equipments such as laser printers, photocopiers, and air purifying devices involving ionization processes. In the case of office equipment, emission rates can reach 7900 µg/h per equipment. Results retrieved from studies aiming at determining ozone emissions from office equipments are reported in Table 13.

Table 13. Ozone emission rates from photocopiers and printers (µg/h) [95], [100]

OFFICE EQUIPMENT	EMISSION RATE (µg/h) PER EQUIPMENT		
	Minimum value	Maximum value	Average value
Photocopiers (Units tested: 9)	1200	7900	5200
Printers (Units tested: 12)	≤ 20	6500	1200

Deposition rates of ozone on surfaces are investigated by a large number of studies. Soft surfaces and gypsum board are the most evaluated materials. [101]–[103] Lee et al. [104] have evaluated the mean decay of ozone in residences, it reaches 2.8 ± 1.3 h^{-1}, with a mean deposition rate of 0.049 ± 0.017 cm/s. From these investigations, decay rate was proved to be the highest in buildings with large surface to volume ratios. Furthermore, Nicolas et al. [105] observed that deposition rates decreases as the ozone concentration increases. This behavior is supported by the hypothesis that potential sites for ozone are limited and determined by the physico-chemical properties of the surface of each material. Then, the higher ozone concentration, the faster potential uptake sites are covered, decreasing the ozone deposition velocity and steady state regime. The deposition of ozone on surfaces definitely impacts ozone concentration in indoor air. Nevertheless, it remains high enough to achieve reactions with unsaturated hydrocarbons under significant reaction rate. [2]

4.1.2   Nitrate radicals (NO$_3^{\circ}$) in indoor air

The main source of indoor nitrate radicals results from the reaction between ozone and nitrogen dioxide. [98] The reaction kinetic between nitrate radicals and unsaturated VOCs present in indoor air might be faster compared to other oxidizing agents like ozone. In spite of the high oxidation ability of NO$_3^{\circ}$, very little experimental work has been performed indoor.

Furthermore, indoor sources of nitrate radical are almost negligible, except for homes with unvented combustion appliances. Typical indoor concentrations of NO_2 are in the range of 13 - 62 µg/m^3. [67]

4.1.3   HO° radical in indoor air

The determination of outdoor concentrations of HO° radical has been recently addressed. It is motivated by its high reaction rates with most of the trace atmospheric constituents. With an outdoor concentration ranging from 10^6 to 10^7 molecules/cm^3 as evidenced by Sarwar et al. [106], HO° drives the lifetimes of many atmospheric compounds. Regarding indoor environments, the principal contributors of HO° radicals are related to chemical interactions between ozone and alkenes as reported by Weschler et al. [107]. Authors performed an evaluation of the main indoor processes contributing to hydroxyl radicals. Results revealed that primarily 13 reactions between indoor alkenes and ozone contribute to an HO° production rate ranging from 2.6 x 10^{-4} to 9.5 x 10^{-8} ppb/s. It should be noted that indoor ozone concentration in this investigation was 20 ppb; information about these investigations are gathered in Table 14. These data clearly evidence that terpenes are characterized by the (i) highest reaction constant and (ii) the highest HO° production rate. [108]

Table 14. Main reactive sources of HO° in indoor environment adapted from [107]

ALKENES + OZONE (O₃ at 20 ppb)	HO° YIELD	HO° PRODUCTION RATE (ppb/s)
α-Terpinene	0.91	$1.2*10^{-4}$
2-methyl-2-butene	0.89	$4.5*10^{-5}$
d-Limonene	0.86	$2.6*10^{-4}$
α-Pinene	0.85	$1.6*10^{-5}$
Isobutene	0.84	$2.3*10^{-6}$
Trans-2-butene	0.64	$1.5*10^{-5}$
Cis-2-butene	0.41	$6.4*10^{-6}$
Styrene	0.37	$1.5*10^{-6}$
Propene	0.33	$9.4*10^{-7}$
Isoprene	0.27	$3.2*10^{-6}$
Camphene	0.15	$1.7*10^{-7}$
Ethene	0.12	$1.5*10^{-7}$
1,3-butadiene	0.08	$9.5*10^{-8}$

Among potential oxidizing agents present in indoor air, ozone is evidenced to be a key reaction initiator due to a strong intake from outdoor leading to significant indoor concentration compared to $NO_3^{°}$ and $HO°$ radicals. Moreover, the structure of terpenes allows a high reactivity toward ozone and such a process can be pointed out as the main source of $HO°$ radicals leading to secondary reactivity. One of the main key driver of the fate of terpenes in indoor environment is suggested to be the reaction with oxidants. In order to evaluate this process, it is important to understand its determinants: (i) thermodynamics, (ii) air exchange rate, (iii) kinetics, and (iv) reactant concentrations.

4.2   Non-reactive fate of terpenes in indoor air: uptake onto surfaces

In contrast to outdoors, indoor conditions combine large surface areas in a relatively small volume, thus the largest surface/volume ratios. Specifically, typical outdoor surface area is estimated to be roughly 10^{-5} cm^2/cm^3 in urban areas while typical indoor surface area might achieve nearly 2.10^{-3} cm^2/cm^3 for a furnished space. [109] Different types of surfaces with various uptake capacities can be present in indoor environments depending on the physical and chemical properties of these materials. Uptake, commonly known as "sink effect", has the potential to reduce gas phase concentrations. Thereafter, the secondary release of compounds taken up onto indoor materials can delay the removal of pollutants by ventilation, thus extending the residence time of pollutants indoors. [68], [110] Five investigations have been carried out to evaluate the interactions between indoor materials and terpenes. Generally, evaluated materials are set is test chambers and exposed to artificially polluted air. Materials are exposed to contaminants either by continuous and known flow of pollutants at a constant concentration, or in a static mode. Static mode experiments operate without any air renewal and a defined amount of VOC is initially introduced.

Meininghaus et al. [111] evaluated the interaction of organic vapors on several indoor materials. Results are presented *via* a permeation factor (PF) calculated in percentage, which characterizes the mass flow through the material. A PF close to 100 % after 1h indicates a low concentration gradient and a low resistance against diffusion. Among 20 investigated VOCs, five terpenes were evaluated in several materials: (i) wall-paper with paste, (ii) simple wall-paper, (iii) acrylic wall cover, (iv) carpet and (v) gypsum board. Results evidence that regarding carpet and acrylic paper, camphor has the highest PF: 79 % and 106 % for both materials respectively. Concerning gypsum board, a significant permeability was detected for volatile compounds or non-polar terpenes, such as α-pinene. Authors verified that materials not in direct contact with indoor air but

covered with permeable materials, might strongly act as sinks. This study characterized the retention capacity of materials (RC) defined as the estimation for the mass of VOCs held back by the material when the species diffused into it. The highest RC values were found for the carpet and gypsum board. Indeed, higher retention capacities were verified with the augmentation of boiling point of molecules and for hydrophilic species. Finally, regarding retention capacities, evaluated materials were ranked as follows: carpet ≥ gypsum board > chipboard ≥ PVC flooring > wallcoverings. In agreement with this study, Thevenet et al. [110] investigated the uptakes of VOCs on gypsum boards, demonstrating that under typical indoor conditions, the hydrophilic properties of gypsum board highly favor the uptake of oxygenated VOCs.

Complementary, Jørgensen et al. [112] evaluated α-pinene and toluene interactions on wool, nylon carpets, PVC coverings and cotton curtain, under realistic indoor concentrations. Results evidenced higher uptake of α-pinene compared to toluene for all tested materials by one order of magnitude. These results agree with Jørgensen et al. [113] who investigated both species on other carpets surface. This study confirms a four times higher uptake capacity of α-pinene on a carpet compared to toluene. Detailed comparison of the uptake of toluene with α-pinene investigations are reported in Table 15.

Table 15. Partitioning coefficient Ke (m) and adsorbed fraction at equilibrium: comparison between toluene and terpenes

Material	Partition coefficient Ke (m)		
	Reference VOC **Toluene**	**α – pinene**	*REFERENCES*
Carpets (2)	0.616 - 0.709	1.670- 1.993	
PVC covering	0.250	0.819	Jørgensen et al. [112]
Cotton curtain	0.074	0.283	
Carpets	0.5 – 0.6	2.300	Jørgensen et al. [113]
Material	Adsorbed mass fraction (%)		
	Reference compound **Toluene**	**β – pinene**	**Limonene**	*REFERENCE*
50-m³ room Painted wallboard, nylon carpet, draperies and wood furnishings.	45 %	51 %	80 %	Singer et al. [114]

These observations are in agreement with those reported by Singer et al. [114] about surface interactions in fully furnished room of 50 m³. VOCs were spiked in the chamber, while gas-phase concentrations were monitored. Results evidenced that the adsorption rates of terpenes, namely limonene and β-pinene, were higher in magnitude compared to toluene. Adsorption

rate were 0.21 h^{-1} and 0.32 h^{-1} for limonene and β-pinene, respectively, while it was 0.15 h^{-1} for toluene. Authors observed that the partitioning of single-ring aromatic hydrocarbons can be related to their molecular mass, suggesting a noteworthy uptake in the absence of ventilation for terpene hydrocarbons. Finally, the uptake of terpenes on typical residential surfaces were identified as a key driver to reduce their gas-phase concentrations on time scales comparable with typical residential ventilation rates. Reviewed studies verified that depending on (i) the molecular structure of the considered species, (ii) the physical and chemical properties of the solid substrate and (iii) the environmental conditions (temperature and humidity), the intensity of the uptake process might vary. Hence, Springs et al. [115] verified that the number of moles of terpenes taken up per unit of surface area tend to decrease with the growth of relative humidity, particularly on glass, suggesting a competitive interactions with water molecules for adsorption sites.
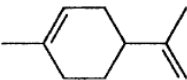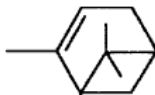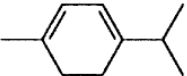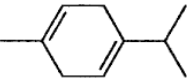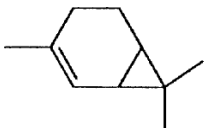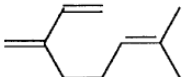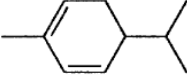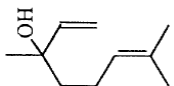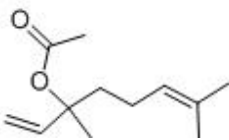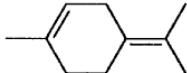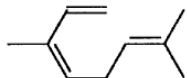
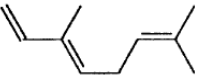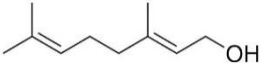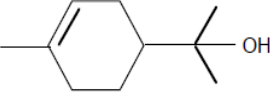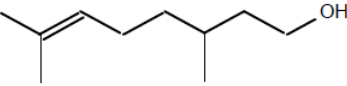## 4.3   Reactive fate of terpenes in indoor air: formation of side products?
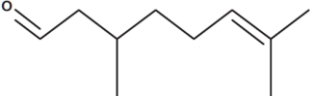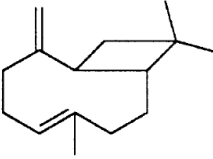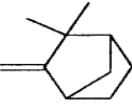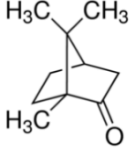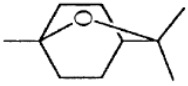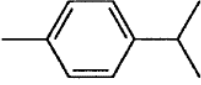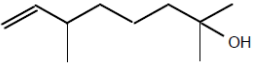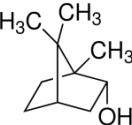
Reaction kinetics and rate constants of terpenes with ozone, hydroxyl radical, and nitrate radical have been extensively assessed, but mostly for open atmosphere purposes and generally in small volume atmospheric simulation chambers. Nonetheless, at the molecular level, the fundamental principles of chemical kinetics and dynamics are similar from outdoors to indoors. Actually, reviewed studies aiming to evaluate bi-molecular rate constants of terpenes and ozone interactions have proceeded in simulation chambers under atmospheric conditions of temperature and humidity. This section attempts to provide a context for the understanding of the reaction kinetics and the formation of secondary products that might be generated due to the indoor reactivity of terpenes in the presence of oxidants. The discussion in this section is addressed by the (i) gas phase reactive interactions, i.e. homogeneous reactivity and (ii) surface chemistry, i.e. heterogeneous chemistry.
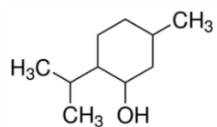
4.3.1   Gas-phase reactions

The chemical structure of the reactants is a key driver of the kinetics. In order to assess the reactivity of indoor terpenes thirteen recent investigations are reviewed in Table 16. These studies evaluate the bimolecular reactions rate constant of 24 terpenes and terpenes derivatives towards ozone, hydroxyl radical, and nitrate radicals at ambient temperature.

Table 16. Chemical structures and reaction rate constants of TerVOCs towards typical oxidants [93], [116]–[127]

TERPENES/ TERPENOIDS	CHEMICAL STRUCTURE	RATE CONSTANTS FOR REACTIONS (cm³/mol *s) REACTION TEMPERATURE AT 298 K		
		HO° (x 10⁻¹¹)	NO₃ (x 10⁻¹⁴)	O₃ (x 10⁻¹⁸)
Limonene $C_{10}H_{16}$		17.1	1220	210
α-pinene $C_{10}H_{16}$		5.4	616	86.6
α-terpinene $C_{10}H_{16}$		36.3	14000	21100
γ-terpinene $C_{10}H_{16}$		17.7	2900	140
2-carene $C_{10}H_{16}$		8	2150	240
β-myrcene $C_{10}H_{16}$		21.5	1100	490
α-phellandrene $C_{10}H_{16}$		31.3	7300	2980
Linalool $C_{10}H_{18}O$		15.9	1120	430
Linalyl Acetate $C_{12}H_{20}O_2$		11.6	NS	431.8
Terpinolene $C_{10}H_{16}$		22.5	9620	1880
Cis-β-Ocimene $C_{10}H_{16}$		25.2	2200	560

Trans-β-Ocimene $C_{10}H_{16}$				
Geraniol $C_{10}H_{18}O$		**23.1**	**1660**	**930**
α-Terpineol $C_{10}H_{18}O$		**19.0**	**NS**	**300**
β-Citronellol $C_{10}H_{20}O$		**17.0**	**1210**	**240**
Citronellal $C_{10}H_{18}O$		**15.0**	**NS**	**350**
β-Caryophyllene $C_{15}H_{24}$		**14.5**	**1900**	**11600**
INERT TERPENES TOWARD OZONE				
Camphene $C_{10}H_{16}$		**5.3**	**66**	**0.9**
Camphor $C_{10}H_{16}O$		**0.38-0.46**	**<0.06**	**<0.07**
1,8 Cineole (Eucalyptol) $C_{10}H_{18}O$		**1.1**	**0.017**	**≤0.15**
ρ-Cymene $C_{10}H_{14}$		**1.5**	**0.099**	**≤0.05**
Dihydromyrcenol $C_{10}H_{20}O$		**380**	**230**	**2.0**
Borneol $C_{10}H_{18}O$		**2.65**	**NS**	**NS**

Menthol $C_{10}H_{20}O$		**1.48**	**NS**	**NS**

NS: Not specified in the literature

In order to have a significant impact on the concentration of indoor terpenes, their gas phase removal has to occur at a rate competitive with indoor removal processes such as air exchange rate. As reported in Table 16, several terpenes are characterized by significantly low reaction rates. Then, the reactive removal of these species with indoor ozone might occur at low reaction rates and these terpenes might be considered as inert. Indeed, compounds species considered as inert TerVOCs are camphene, ρ-cymene, eucalyptol, and camphor. On the contrary, the reaction constants for α-terpinene with ozone is higher by a factor 100 compared to limonene. Considering that α-terpinene has a mean occurrence of 30 % worldwide in household product formulations, the gas phase reactivity of this TerVOC might have a significant impact on (i) its gas phase concentration and (ii) the release side-product formed by its oxidation. [116] [128]

Pommer et al. [129] investigated the main factors influencing the oxidation of monoterpenes under typical indoor conditions. Authors evidenced that (i) an increase in ozone concentration, (ii) an extended reaction time and (iii) a decrease of humidity have a direct impact on the reactivity of α-pinene and 3-carene. For both species, a decrease of the mass fraction of reacted terpenes was induced by an increase in relative humidity. This specific impact of RH cannot be ruled out regarding indoors reactivity of terpenes since humidity variations are generally concomitant with cleaning activities.

On the other hand, indoor reactions between terpenes and oxidants are highly controlled by the residence time lifetime of the species in the indoor environment. Nazaroff et al. [17] and Nicolas et al. [92] evidenced that lifetime might be longer when some of the reactants get adsorbed onto indoor surfaces. To that regard, the interaction with surfaces can be an influencing process.

4.3.2   Heterogeneous reactivity of TerVOCs

Researches on the reactivity of terpenes with ozone are predominantly focused on the homogeneous reactivity. Nonetheless, a substantial fraction of emitted terpenes might be sorbed on indoor materials and surfaces, as discussed in the section 4.2.

The uptake of terpenes onto indoor surfaces do not prevent any reactivity with gas phase oxidants and effective surface reaction rates of terpene oxidation in the adsorbed phase may compete with the homogeneous gas phase kinetics. Indeed, Stokes et al. [130], [131] revealed that surface reaction rate of an adsorbed alkene can be up to 5 orders of magnitude higher than the same reaction in the gas phase. In addition, Destaillats et al. [132] observed that the consumption of ozone in an experimental chamber remained high beyond the removal of TerVOCs by ventilation. Author suggested that terpenes remained on indoor surfaces, promoting heterogeneous consumption of gas phase ozone.

Regarding surface reaction rates, Springs et al. [115] evidenced that the reaction rate of 3-carene and d-limonene adsorbed onto glass and polyvinylchloride (PVC) beads becomes 10 to 100 times higher than homogeneous reaction kinetics. In agreement with this study, Fick et al. [133] reported that among the evaluated terpenes molecules, 3-carene has the highest contribution to heterogeneous interactions on the surfaces of ventilation systems. In addition, Shu et al. [134] determined the surface reaction rate of α-terpineol on 3 usual indoor surfaces: (i) glass, (ii) polyvinyl chloride (PVC) and (iii) latex paint surfaces. For all evaluated surfaces, the heterogeneous reaction probabilities are higher than in the gas phase. More precisely, the highest surface reaction rate was observed for PVC under 50 % of relative humidity, with a factor 25 compared to gas phase kinetics.

Concerning heterogeneous reactions resulting from the application of household products, Nicolas et al. [6] observed that dried residues left on the cleaned surfaces were responsible for an increase in ozone consumption because of reactivity with remaining TerVOCs. In the same way, Palmisani et al. [135] investigated the reactivity of TerVOCs emitted by a carpet deodorizer with indoor surfaces. The main detected terpenoid reactants were dihydromyrcenol and linalool. Other reactive TerVOCs found in lower concentration were: limonene, cymene, and a-terpineol. Experiments were carried out by the direct application of the cleaning products sprayed in an experimental chamber under two condition: (i) empty chamber and (ii) in the present of a carpet covering the complete surface of the floor. Results evidenced the potential of the carpet to significantly remove ozone, promoting the increase of secondary produced aldehydes concentration in the gaseous phase. Indeed, ozone decay was related by authors to reactions occurring on the surface of the carpet. Side products resulting from heterogeneous reactivity were mainly aliphatic aldehydes i.e. nonanal, decanal, and dodecanal.

Based on the five studies reviewed, heterogeneous interactions are suggested by authors to be predominant compared to gaseous phase reactivity: (i) higher heterogeneous reaction rate of ozone compared to homogeneous reactions, (ii) larger surface area vs. volume, typical from indoor environments and (iii) source of emissions due to desorption processes and side-product formation. However, if heterogeneous reactive processes appear as significant sinks of TerVOCs, similarly to homogeneous reactivity they have to be considered as potential sources of secondary pollutants, i.e. side-products, impacting IAQ.

4.3.3   Formation of secondary pollutants: gases and particulate matter

Based on fourteen reviewed studies, Table 17 reports the formation yields of products obtained from the reaction of the three main indoor oxidants with (i) nine monoterpenes, (ii) one sesquiterpenes and (iii) three terpene alcohols. The formation yields of products are generally expressed in moles of reaction product generated per mole of oxidant usually considered as the limiting reactant. Note that NS in the Table 17 corresponds to not reported yield but confirmed secondary product. In the same way, NQ correspond to species with formation yields under the detection limits. Among stable and volatile oxidation products detected and quantified in the studies reviewed to create Table 17, formaldehyde is of particular interest because of its toxicity.

Table 17. Formation yields of gas phase products formed from the reaction between selected terpenes and three oxidizing agents. Adapted from [116]–[122], [122]–[124], [128], [136]–[138].

REACTION PRODUCTS	FORMATION YIELD		
	HO° Radical Reaction	NO₃ Radical Reaction	O₃. Reaction
LIMONENE			
Limona Ketone (4-acetyl-1-methylcyclohexene)	0.20 ± 0.03 0.174 ± 0.028	-	0.02 ~0.01
ENDOLIM – Limonon aldehyde (3-Isopropenyl-6-oxoheptanal)	0.28 0.29 ± 0.06	0.69	0.004^a
Acetone	≤ 0.03	≤ 0.02 ~0.02	-

Formaldehyde	-	-	0.10 0.19
Formic Acid	-	-	0.03-0.10
Hydroxyl Radical	-	-	$0.86^{+0.43}_{-0.29}$
Organic Nitrates	-	0.48	-

α-TERPINENE			
6-Methyl-hepta-2,5-dione	-	-	-
Formaldehyde	**-**	**-**	**-**
Acetone	~0.10		0.03±0.01 ~0.04
Hydroxyl Radical	-		0.38±0.05

α-PINENE			
Pinonaldehyde	From 0.28±0.05 to 0.56±0.04	0.62±0.04 0.69±0.04	From 0.19±0.04 to 0.51±0.06
Acetone	From 0.05±0.02 to 0.15±0.10	-	From 0.03±0.01 to 0.08±0.02
Formaldehyde	0.23±0.09	-	0.22±0.01 0.15±0.04
Formic acid	0.07±0.02	-	0.03-0.20
Organic Nitrates	0.18±0.09	0.14±0.007 0.19	-
α-Pinene oxide	-	0.03±0.005	0.021±0.007
Hydroxyl radical	-	-	From 0.70±0.17 to 0.91±0.23
Pinic Acid	-	-	0.03-0.06
Hydroxypinonaldehyde	-	-	0.019-0.112
Pinonic Acid	-	-	0.022-0.079
Norpinonic Acid/isomers	-	-	0.043-0.126
Norpinonaldehyde	-	-	0.012-0.026
2,2-Dimethyl-cyclobutyl-1,3-dicarboxaldehyde	-	-	0.003-0.016
Hydroxypinonic acid	-	-	0.015-0.037
Carbonyls	-	0.71	-

2-Hydroxypinan-3-nitrate	-	0.05±0.004	-
3-Oxopinan-2-nitrate	-	0.03±0.002	-
β-PINENE			
Nopinone (Pina Ketone)	From 0.25±0.03 to 0.79±0.08	~0.01-0.02	From 0.16±0.04 to 0.40±0.02
Formaldehyde	0.54±0.05 0.45±0.08	-	From 0.42 to 0.76±0.02
Acetone	From 0.02±0.02 to 0.13±0.02	-	0.04-0.07±0.05
Formic Acid	0.02±0.01	-	0.02±0.05
Hydroxyl radical	-	-	$0.35^{+0.18}_{-0.12}$
Pinic Acid	-	-	0.026-0.037
Norpinonic acid/isomers	-	-	0.059-0.165
Hydroxypine-ketones			From 0.073 to 0.15±0.05
3-Oxo-pina-ketones	-	-	0.018-0.077
Organic Nitrates	-	0.61	-
Carbonyls	-	0.14	-
MYRCENE			
Acetone	From 0.36±0.05 to 0.45±0.06		From 0.21±0.03 to 0.29±0.05
Formaldehyde	0.30±0.06		0.26±0.03
Formic Acid	-		0.19±0.03
Hydroxyacetone			
Hydroxyl radical	-	$1.15^{+0.58}_{-0.39}$	0.63±0.09
4-vinyl-4-pentanal	0.19±0.04		0.70±0.13
3- CARENE			
Caronaldehyde	0.31-0.34±0.08	0.02-0.03	From 0.09±0.03 to 0.44±0.03

Acetone	0.15±0.03	-	From 0.10±0.02 to 0.22±0.05
Formaldehyde	0.21±0.04 0.25±0.02	-	0.16
Formic Acid	0.08±0.02 0.11±0.01	-	-
Hydroxyl Radical	-	-	$1.06^{+0.53}_{-0.36}$ 0.86±0.11
3-Caronic Acid	-	-	0.042
Hydroxycaronaldehydes	-	-	0.032
3- Caric acid	-	-	0.019
Pinic Acid	-	-	0.012
Nor-3-caronic acid/isomers	-	-	0.023
Hydroxy-3-caronic acid	-	-	0.012
Organic Nitrates	-	0.66	-
Carbonyls	-	0.29	-

OCIMENE			
Acetone	0.18 0.20±0.15	-	0.21 to 0.24±0.04
4-methyl-3,5-hexadienal	≤0.02	-	0.33±0.06
Hydroxyl radical	-	-	$0.63^{+0.32}_{-0.21}$ 0.55±0.09

β-PHELLANDRENE			
4-Isopropyl-2-cylcohexen-1-one	0.29±0.07	-	0.29±0.06
Hydroxyl radical	-	-	~0.14

TERPINOLENE			
4-methyl-3-cyclohexen-1-one	0.24 to 0.26 ±0.05	-	0.40±0.06
1-methylcyclohexene-4-one	0.08 to 0.10 ±0.02	-	≤0.02
Acetone	0.32 to 0.39 ±0.05 0.44±0.04	-	0.50±0.05 0.44
Formaldehyde	**0.29±0.06**	-	-
Formic Acid	0.08±0.02 0.04±0.04	-	-

Hydroxyl radical	-	-	$1.03^{+0.52}_{-0.35}$
			0.74 ± 0.10

CARYOPHYLLENE (SESQUITERPENES)			
Formaldehyde	-	-	**0.80**
			0.76
3,3-Dimethyl-γ-methylene-2-(3-oxobutyl)-cyclobutanebutanal	-	-	0.08[1]
3,3-Dimethyl-γ-oxo-2-(3-oxobutyl)-cyclobutanebutanal	-	-	0.08[1]
Hydroxyl radical	-	-	$0.06^{+0.03}_{-0.02}$

LINALOOL			
Acetone	0.505±0.047	0.225±0.052	From 0.160 to 0.211±0.024
6-Methyl-5-hepten-2-one	0.068±0.006	-	-
4-Hydroxy-4-methyl-5-hexen-1-al	0.46±0.11	0.191±0.051	0.85+0.14
			0.50±0.09
Formaldehyde	-	-	From 0.34 to 0.36±0.06
Methylglyoxal	-	-	0.11±0.01
5-Ethenyldihydro-5-methyl-2(3H)-furanone	-	-	From 0.110 to 0.126±0.025
Hydroxyl radical			$0.72^{+0.36}_{-0.24}$
			0.66±0.10

α-TERPINEOL			
Acetone	NQ	NS	-
Ethanedial (Glyoxal)	0.014	NS	-
2-oxopropanal (methyl glyoxal)	0.005	NS	0.019
4-Methyl-3-cyclohexen-1-one	0.057	-	-
6-Hydroxyhept-5-en-2-one	0.20	-	0.31
4-oxopentanal	0.022	-	0.006

GERANIOL			
Acetone	NQ	NS	-
Glycolaldehyde	0.29	-	0.31
6-Methylhept-5-en-2-one	0.075	-	0.14
6-Hydroxy-4-methyl-4-hexenal	-	-	0.26
Ethanedial (Glyoxal)	0.005	-	0.006
2-oxopropanal (methyl glyoxal)	-	-	0.065
4-oxopentanal	0.37	-	0.035
5-oxopent-4-enal	-	-	0.10

1: In the absence of an HO° radical scavenger.

Several species displayed in Table 17 correspond to the first generation of oxidation product, i.e. primary reaction intermediates, such as limona ketone and limonon aldehyde formed from limonene oxidation. These primary intermediates are characterized by lower reaction rates with ozone compared to initial terpenes, however they are highly reactive to HO° and NO_3. Thus, along the oxidation pathway of terpenes, several and various oxidant can be involved. Formaldehyde is a major secondary product of terpene oxidation. As reported in Table 17, among monoterpenes, β-pinene shows the highest formation yield with 0.76, followed by myrcene with 0.30. The ability of terpenes to form formaldehyde as side-products of their oxidation represents the main concern in terpene indoor reactivity.

4.3.4   Formaldehyde production from household product reactivity

The formation of formaldehyde related to indoor reactivity involving household product emissions has been specifically evaluated by eight studies. The main results are assembled in Table 18. These investigations were performed along the last 15 years in the Unites States, France and Denmark. Several factors might strongly impact the resulting concentrations of formaldehyde. These factors are (i) ozone inlet concentration, as oxidizing agent, and acting as the limiting reactant, and (ii) the reaction rate of emitted terpenes with oxidants. Reviewed studies were executed under diverse experimental chamber scales, from small size to real size. Likewise, different cleaning products were tested, therefore emitted terpenes might be largely contrasted from one study to another. Moreover, ozone concentration in the reviewed studies ranged from 20 to 250 ppb. Consequently, this section does not allow the direct comparison of formaldehyde concentrations after the household

product application. Nevertheless it is possible to compare the formation yields of formaldehyde, thus the ratios of formaldehyde concentrations before and after ozone introduction (FAO/FBO ratio) for each tested household product.

Table 18. Peak concentration of formaldehyde produced by gas phase reactivity between ozone and terpenes emitted from household products [6], [16], [54], [56], [80], [132], [139], [140]

PRODUCT CATEGORY	FORMALDEHYDE CONCENTRATION BEFORE OZONE INLET (FBO: µg/m³)	FORMALDEHYDE CONCENTRATION AFTER OZONE INLET (FAO: µg/m³)	RATIO FAO/FBO
Bathroom cleaner (Foam)	22.0	33.0	**1.50**
All-purpose cleaner (Powder to cream)	17.0	8.0	**0.47**
Kitchen cleaner (Spray)	7.0	10.0	**1.43**
Glass cleaner (Spray)	9.0	10.0	**1.11**
Air freshener (Plug-in)	**2.5**	**28.2**	**11.28**
Orange degreaser	10.1	29.3	**2.89**
Pine general cleaner	9.0	19.8	**2.19**
Air freshener (Plug-in)	6.7	13.8	**2.07**

Complementarily, Fan et al. [74] evaluated the reactivity of 23 volatile organic compounds with 40 ppb of ozone. In this study, the air exchange rate is set to 1.8 h^{-1} in a 25 m³ experimental chamber. Among the tested VOCs, this study compared the reactivity of two gas mixtures: (i) 21 non-terpenic VOCs typically observed in indoor environments mixed with 40 ppb of ozone; and (ii) 2 terpenes (limonene and α-pinene) mixed with 40 ppb of ozone. Reported reaction products included compounds that are not directly generated by the reaction with ozone, but any reaction product resulting from the oxidation process and possibly involving HO° radicals. Regarding the formation of formaldehyde, after ozone introduction in the presence of the two-terpene mixture, the total formaldehyde concentrations from reactions with ozone exceeds 29 µg/m³. On the contrary, the 21 VOC mixture only produce a total formaldehyde concentration of 2.1 µg/m³. Moreover, in the O$_3$/terpene system, almost 70% of the formaldehyde observed was derived from the reactions of HO° with α-pinene and d-limonene. This study provides a striking evidence that the indoor reactivity of terpenes is a key source of secondary formaldehyde.

As presented in Table 18, Destaillats et al. [132] investigated the formation of secondary pollutants in a 0.13 m³ experimental chamber from the use of 3 household products: (i) a plug-in air freshener, (ii) a pine oil-based general purpose cleaner, and

(iii) an orange oil-based degreaser. Ozone was introduced under different concentrations: (i) low, i.e. 30 ppb, (ii) moderate, i.e. 60 ppb, (iii) high, i.e. from 120 to 130 ppb and (iv) very high, i.e. 250 ppb. Authors evidenced that the yields of formaldehyde were contrasted from one tested product to another: (i) 90 % for the plug-in air freshener, (ii) 20 % for the pine-oil-based cleaner, and (iii) 30 % for the orange-oil-based degreaser. This investigation coincides with Singer et al. [56] who observed a FAO/FBO ratio of 11.28 for a plug-in air freshener, the highest compared to other tested products. Both studies agree on the fact that TerVOCs mass concentration in air fresheners are substantially higher compared to cleaning products. Likewise, an important effect on formaldehyde production was observed and attributed to the longer indoor residence time of TerVOCs from plug-in air freshener, since they act as continuous emission sources.

Regarding the differences in FAB/FBO reported in Table 18, investigations confirmed that the variance in the formation yield of formaldehyde was strongly related to the diversity of molecules contained in the tested household products. Indeed, Destaillats et al. [132] evidenced that after application of a pine oil-based cleaner in the presence of 250 ppb of ozone, up to 90 % of α-terpinene was consumed in comparison with only 30 - 40 % of α-terpinolene and 15 - 20 % of limonene. Results are consistent with the fact that α-terpinene is the most reactive among tested terpene molecule, as discussed in Table 16. Furthermore, Liu et al. [139] investigated the reactivity of TerVOCs from an air freshener. As ozone was introduced in the large scale chamber, rapid decays of limonene, and pinenes were observed. On the contrary, camphene decayed at a lower rate, consistently with its slower reaction rate with ozone.

Overall, for all household products tested, reviewed studies report an increase of the concentration of formaldehyde after the application of products compared to blank concentration levels of formaldehyde. Formaldehyde is clearly pointed out as a major secondary products formed with significant yields from most of the terpenes. The indoor reactive chemistry of emitted terpenes may contribute to an increase of the concentration of formaldehyde and higher exposures of occupants to formaldehyde among other secondary pollutants

Moreover, several primary reaction products observed along the reaction between terpenes and ozone are characterized by high molecular weights, increased polarity, and low vapor pressure, therefore, beyond the formation of gaseous products, nucleation processes might take place and lead to the formation of secondary organic aerosols.

4.3.5   Formation of secondary organic aerosols from household products emissions

The formation of secondary organic aerosols from the use of household products has been assessed by twelve studies, corresponding results are gathered in Table 19. These investigations were performed along the last 15 years in the Unites States, France and Denmark. Table 19 present by column (i) the category and the diffusion mode of the applied product, (ii) the particle number measured in the experimental chamber before introducing ozone, (iii) the particle number formed by the reactivity of TerVOCs and ozone, (iv) formation ratio associated to introduction of ozone. The particle number is expressed in number of particles par cubic centimeter (#.cm^{-3}). As for formaldehyde production, differences in experimental parameters, such as ozone inlet concentration, shows a direct impact on the formation of particles. Subsequently, this section does not directly compare particle numbers between studies but evaluate and discuss the trends in particle number before and after the introduction of ozone through the PAO/PBO ratio, i.e. particle number after ozone introduction / particle number before ozone introduction. Indeed, inlet ozone concentrations in reviewed studies vary from 20 to 250 ppb.

Table 19. Peak particle number (# /cm^3) produced by the reaction of terpenes after ozone inlet and household product application [6], [15], [16], [55], [56], [58], [74], [80], [132], [139], [141], [142]

PRODUCT CATEGORY	PARTICLE NUMBER BEFORE OZONE INLET (PBO: #/m^3)	PARTICLE NUMBER AFTER OZONE INLET (PAO: #/m^3)	PAO/PBO
Bathroom cleaner (Foam)	4 678	87 715	**18.75**
All-purpose cleaner (Powder to cream)	4 999	187 475	**37.50**
All-purpose cleaner (Spray)	5 000	211 000	**42.20**
Kitchen cleaner (Spray)	3 498	10 493	**2.30**
Glass cleaner (Spray)	3 034	13 595	**4.48**
Floor cleaner (Liquid)	8 200	>LD = 670 000	**> 81.71**
Air freshener (Spray)	11 500	>LD = 670 000	**> 58.26**
Air freshener (Solid passive diffuser)	7 300	>LD = 670 000	**> 91.78**
Floor pine-oil cleaner (Diluting + mopping)	1 826	189 881	**103.99**

As reported in Table 19, Long et al. [142], in collaboration with Harvard School of Public Health, examined the formation of particles associated to the use of household products under realistic conditions. Experiments were conducted in four homes located in four different suburban town close to Boston, USA. This study evidenced that during floor mopping with a pine-oil-based cleaner, the peak particle number concentration (#/cm^3) increased by a ratio of 104. During the application of this pine-oil-based product, local ambient concentration of ozone was moderated (from 44 to 48 ppb) and AER was 0.53 h^{-1}. Moreover, a key finding in this study relies in the fact that more than 50 % of generated particles during floor mopping were ultrafine particles with a diameter in the range of 0.02 and 0.1 µm. Similar results were obtained by Weschler et al. [58] by evaluating indoor sources of particles by introducing a popular commercial cleaner in two different furnished offices: (i) a "no-ozone" office, and (ii) an "ozone-added" office with an emission rate of 330 to 2000 µg of ozone per min. Major terpenes detected in the commercial cleaner applied was α-pinene, α-terpinene and limonene. This investigation confirmed that reaction between ozone and TerVOCs can produce a substantial increase in the number and mass concentration of sub-micron organic aerosols. Indeed, under supplemental ozone, the measured net mass concentration of aerosols increases nearly to 95 µg/m^{-3}. In addition, Nicolas et al. [6] evaluated the reactivity of terpenes emitted from 54 household products under realistic scenario. Experiments were performed in the experimental house MARIA, under non controlled temperature and humidity. Results evidenced an augmentation of particle number by ratios of 38 and 19 for foam all-purpose cleaner and a bathroom cleaner, respectively. Similar behaviors are observed for other tested products. This trend is confirmed by Sarwar et al. [15] who experimentally evaluated the potential of secondary organic particle formation and growth from the use of several consumer products in the presence of high concentrations of ozone. Tested products were (i) a solid air freshener, (ii) a plug-in air freshener, (iii) a floor cleaner and (iv) a general-purpose cleaner. For the first three mentioned products, authors evidenced that the particle number strongly increased by a factor higher than 60. Results presented herein clearly indicate that the formation of fine particle and their growth occur concomitantly with the application of terpene-containing household products, in the presence of ozone.

Regarding the growth of produced aerosols, reviewed studies confirms that the particle size distribution of particulate matter shift to higher diameters along the cleaning activities, i.e. during the ageing of aerosols. Weschler et al. [58] noticed that after introducing ozone, the number of particles monitored in the 0.1 µm channel declines concomitantly with the increase in the 0.2, 0.3, and 0.4 µm channels of the particle sizer. Moreover, the Environmental Protection Agency in the United States (US EPA) [139] observed that ultrafine particles were formed with high number concentration right after ozone was introduced

in the experimental chamber in the presence of a plug-in air freshener; followed by (i) an shift of the particle size distribution toward higher diameters and (ii) a decrease of the particle number concentration. Author illustrated that these observations are related to a primary mechanism of particle growth through condensation in the initial reaction process, followed by a gas-to-particle partitioning of oxidation products. As a result, this section illustrate an intense increase of the particle number as soon as the oxidation process of terpenes occurs, then, the size distribution of particles shift to higher diameters.

Generally cleaning activities are performed in order to improve indoor air quality and hygiene. However, the emissions of terpene contained in cleaning products and air fresheners combined with indoor oxidants might produce significant amounts of secondary, i.e. "hidden", air pollutants. Among them, formaldehyde and secondary organic aerosols might be generated in significant amounts and may increase the exposure of occupants, exceeding relevant health standards and guidelines.

5. CONCLUSIONS

The perception of essential oils as ingredients of natural origins tends to shade the potential impacts of these chemical species on indoor air quality while they are massively used in housecleaning products and air fresheners. Essential oils mostly consist in complex mixtures of terpenes and terpenoids. The physical and chemical properties of TerVOCs lead to their direct transfer from the liquid phase to the gas phase, increasing the inhalation exposure to allergens and pollutants. Moreover, TerVOCs can lead to sensitization and subsequent induction of allergic symptoms in the respiratory tract. In spite of the possible health concerns related to the ubiquitous use of scented household products, no specific regulation is proposed. More restrictive requirements have to be satisfied by household products manufacturers in order to be certified as organic and/or green products since the eco-labelling of products is based on the evaluation of its environmental impact and hazards to human health along its life cycle. However, whether conventional or eco-certified, fragranced products might contain a range of hazardous air pollutants and only few are revealed to the public through product labels. **As a consequence, consumers do not have adequate information concerning the potential exposure to risks and a fictitious perception of safety while buying "*natural*" household products is possible**.

The exposure to hazardous chemicals contained in household products is mainly driven by the contact time, the quantity of product applied, and the frequency of exposure. These parameter enable the definition of the consumer use patterns. It has been evidenced that the behavior of consumers is characterized and strongly affected by large individual variations such as

the frequency and durations of use, and the amounts of products applied. Nonetheless, (i) human behavior and (ii) chemical composition of a product are pointed out as the key drivers of inhalation exposure to species contained in cleaning products and air fresheners since they determined the concentrations of emitted chemicals. **Regarding the inhalation exposure risk associated to cleaning products and air fresheners, it is suggested that important information gaps have to be filled before a satisfactory understanding of potential risks can determined**.

Beyond the consumer use patterns, the emissions of TerVOCs from household products can be strongly affected by indoor environmental conditions such as temperature, relative humidity and air exchange rate. Nevertheless, no reviewed investigation has specifically assessed the influence of temperature and/or humidity on household product emissions since most of the investigations are performed under regulated and stable temperature and relative humidity conditions. This observation highlight a first mismatch between test chambers and the reality of indoor air. Similarly, the diversity, and sometimes the ambiguity, of the experimental chambers regarding (i) volumes, (ii) air renewal rates, (iii) inner materials, and (iv) mixing factors make difficult the comparisons from one study to another and question the discrepancies between reviewed investigations and realistic conditions. **As a consequence, in order to decrease such a variability and make further studies compliant with the reality of indoor environments, it is required to develop detailed protocols for a standard evaluation of TerVOCs emitted from consumer products**.

If a standard evaluation protocol is proposed, it should be adapted to each type of products. Indeed, in spite of a significant variability, the reviewed literature still highlight that (i) the category of product used, (ii) its diffusion mode and (iii) the surface to clean are influential factors of TerVOC emissions. The exposure of occupants is directly related to the application patterns of the cleaning products such as (i) rinsing and removing the cleaning materials and surfaces, (ii) using diluted products that increase the product dispensed but decrease the mass fraction of active components and scents, and (iii) reduce the frequency and duration of the cleaning activities. It has been evidenced that the case of air fresheners differs from cleaning products: depending on the diffusion mode of air fresheners, the temporal dynamic of TerVOC emissions considerably differs. Plug-in air fresheners and passive diffuser act as long term emission sources, while spray aerosols are temporary. **Therefore, beyond the definition of standard experimental protocol, the complementary construction of realistic scenarios of use are definitely expected**.

The emissions of TerVOCs from household product can act as continuous or transient sources of VOCs but their intensity is most of the time higher than other sources. It is evidenced that the use of pure essential oils can temporarily dwarf other indoor sources of VOCs since the concentrations of evaporated individual terpenes can easily exceed the exposure limit value defined for long term exposure by the European commission. If TerVOC levels emitted from cleaning products are lower, they are highly variable. Reported concentrations are highly contrasted; this behavior is suggested to be attributed to: (i) the diversity of experimental methodologies used in the reviewed studies, (ii) contrasted mass concentrations and high diversity of terpene constituents in the products, (iii) contrasted physicochemical properties of terpenes and (iv) different chemical affinities of terpenes for other species or solvents contained in the product formulations. Regarding air fresheners, it clearly appears that their "*purifying*" or "*odor neutralizer*" claims are highly ambiguous since they mostly correspond to massive emissions of TerVOCs to provide pleasant odors. They only provide a feeling of sanitization and no purification actions are assessed. On the contrary, their contribution to an increase of the exposure of occupants to VOCs can be clearly pointed out. **The emissions of TerVOCs from essential-oil-based products are not enough considered among indoor emissions sources while their significance can be clearly evidenced. They are not related to the building itself, but dependent on the activities of occupants.**

Beyond their emission, the fate of TerVOCs in indoor environments has to be assessed in order to provide a global and long term overview of their impact on indoor air. **Since indoor environments are characterized by high surface/volume ratios, the uptake of terpenes is likely higher than outdoors.** The deposition of terpenes on typical indoor surfaces and its dependence on environmental parameters has to be deeper investigated and considered. Alike outdoor chemistry, indoor oxidants can initiate oxidation reactions in the gas phase, before any uptake of TerVOCs. **Therefore, in spite of the fact that cleaning activities are performed in order to improve indoor air quality and hygiene, the reaction of terpene with indoor oxidants might produce significant amounts of secondary air pollutants.** Among them, formaldehyde and secondary organic aerosols might be generated in substantial amounts and may increase the exposure of occupants, exceeding relevant health standards and guidelines. Results reported in the literature related to outdoor chemistry provide relevant orientations to understand the homogeneous reactivity of indoor TerVOCs. Nonetheless, the homogeneous reactivity does not preclude that adsorbed terpenes do not react with indoor oxidants. **On the contrary, the formation yields of secondary pollutant are enhanced when TerVOCs are in the adsorbed phase suggesting a predominant impact of heterogeneous**

processes on indoor air quality. The homogeneous and heterogeneous reactive behaviors of TerVOCs in indoor environment evidence further needs to understand their indoor physics and chemistry.

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Chapter 2

Objectives, strategy, and experimental approach

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1.1 Context of the ESSENTIEL project

This project takes place at a key time when the buildings are facing technological changes to meet growing constraints in terms of energy efficiency and health. The reduction of energy costs leads to an increasing of indoor confinement, affecting the air exchange rates. These energy improvements carry with them the risk of worsening the indoor air quality. The awareness of the importance of the health issue is still, at this stage, less pronounced than energy issues. The implementation of good practices in terms of ventilation, cleaning and sanitation of confined environments is currently adopted by a certain fraction of the population who becomes aware of the environmental issues. Nevertheless, some new practices based on the use of essential-oil-based products can be questioned regarding their effective impact on indoor air quality (IAQ).

The project call CORTEA aims at supporting initiatives permitting the improvement of ambient and indoor air quality. **Along the last 20 years, it has clearly been stated that indoor air quality can be improved by (i) optimizing ventilation, (ii) reducing the inner sources of pollutants, and (iii) complementary, in some specific situations, pollutants can be treated by different remediation technologies and devices.** Regarding the last point, in terms of remediation technologies, adsorption and photo-catalysis have been the most investigated and developed processes. In 2009, standards related to these technologies have been proposed. [1]–[3] The risk of by-products formation using these air remediation technologies has been pointed out. [4], [5] Therefore, since 2010, passive remediation technologies have been more and more investigated for indoor applications. [6] In that context of "*air treatment*", "*air purification*" and "*remediation*", the use of so-called "*natural*" air purifiers, such as essential oils, have recently upsurge among consumer products. However, they allow a purifying performance mainly associated to a bacteriological point of view. To that regards, they may create an ambiguous perception among consumer since their "*purifying*" claim is not clearly defined and established. Moreover, there is no warning to consumers regarding the potential toxicity of essential oils released in indoor air and the fate of essential oils constituents after their diffusion in indoor air.

The ESSENTIEL project aims at satisfying two needs:

(i)   To enhance the knowledge related to the emission factors and the characteristics of terpenes released during the use of essential-oil-based household products indoors. To that end, the project proposes a test

methodology involving specific and realistic scenarios allowing the accurate characterization of the emissions related to these new consumer products;

(ii)   To study the fate of terpenes indoors and in particular their interaction with indoor surfaces. The project aims at informing on the contribution of the homogenous and heterogeneous chemistry related to terpenes in indoor environments.

The ESSENTIEL project illustrates one of the collaborations between IMT Lille Douai (SAGE) and CSTB (Health and Confort). It takes place in the frame of several research projects in connection with indoor pollutant source characterizations and their impacts on indoor air quality. The experimental approach is based on the complementarity of skills and knowledge between the two partners. The main strength of this collaboration is the multi-scale methodology to achieve comprehensive results.

1.2 Objectives of this thesis and structure of the manuscript

The scientific outlines of the thesis have been designed to answer to the first need of the ESSENTIEL project: **to investigate the emissions of essential-oil-based household products under real consumer use patterns and to assess their impacts on indoor air quality.**

The following issues emerge from that objective:

(i)   How to define realistic scenarios for the evaluation of emissions from essential oil based products? How to take into account diverse modes of diffusion: from the use of the cleaning products to the direct diffusion of essential oils in indoor environments?

(ii)   Are emission tests using "small volume chambers" representative of real scale and real use pattern experiments?

(iii)   How to determine an accurate, representative and useful emission factor from the monitoring of resulting indoor concentrations of pollutants?

This work aims at providing realistic test protocols allowing the accurate assessment of terpene emissions from the use of essential-oil-based products via the determination of representative emission factors.

To achieve this objective, a multi-scale and integrated approach has been elaborated and split into three work-packages:

- The determination of the concentrations of terpene molecules in the liquid selected household products and their respective gas-transferred concentrations by **micro-chamber testing**;

- The investigation of the primary emissions of terpene molecules from the use of the same selected products under realistic use conditions in a 1m ^{3} **emission test chamber;**

- The comparison of the primary emissions of terpene molecules determined in a 1 m^3 emission chamber with those determined under real use and real scale conditions in the 40 m^3 **experimental room IRINA.**

Therefore, this chapter details (i) the selection of the investigated household products, (ii) the investigation protocol to characterize the content of terpene molecules in the selected liquid essential-oil-based cleaning products, (iii) the experimental set-ups for the evaluation of their emissions in experimental chambers at different scales, and (iii) the experimental strategies including analytical devices for characterizing the emission process from the use of this type of products. Finally, the results obtained from the experimental approach presented in this chapter are discussed in Chapters 3 to 5. Figure 1 describes the experimental results and discussion presented in the following chapters of this manuscript.
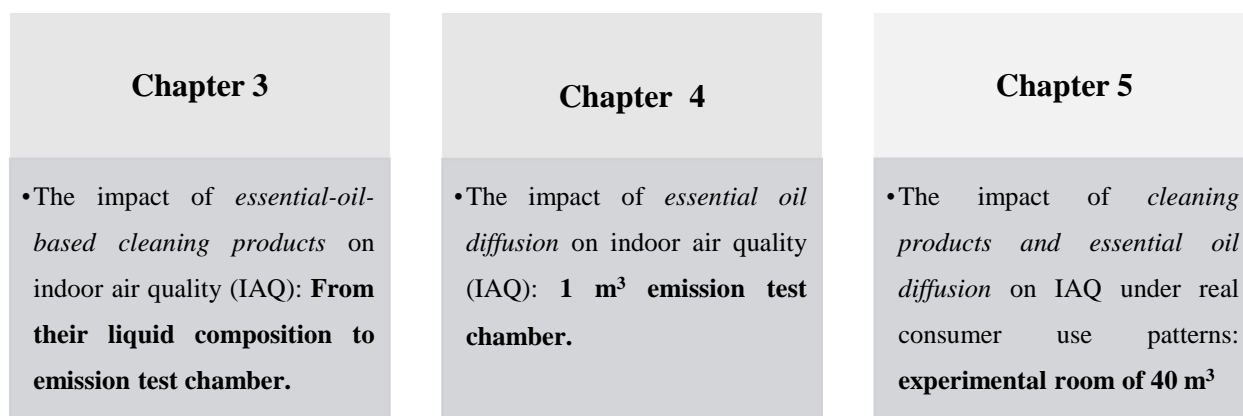
Chapter 3	**Chapter 4**	**Chapter 5**
•The impact of *essential-oil-based cleaning products* on indoor air quality (IAQ): **From their liquid composition to emission test chamber.**	•The impact of *essential oil diffusion* on indoor air quality (IAQ): **1 m^3 emission test chamber.**	•The impact of *cleaning products and essential oil diffusion* on IAQ under real consumer use patterns: **experimental room of 40 m^3**

Figure 1. General description and structure of the investigated proposed in the following chapters.

2. Experimental approach for the evaluation of essential-oil-based products under real consumer use patterns

2.1 Benchmarking of essential-oil-based household products and diffuser devices

In the frame of this project, essential-oil-based household products are defined as naturally scented and organic certified products used in a non-permanent way in indoor environments for housekeeping purposes. They can be classified in two categories of products: (i) essential-oil-based cleaning products and (ii) air purifiers, defined as pure essential oils or

essential oil blends claiming for air cleaning performances and/or toxin-neutralizing activities. For their selection, a benchmark analysis is performed among household products that have been certified as *ecological products* by different European labels. [7]–[9] A total of 108 essential-oil-based household products are identified from various retail-stores in France: 48 cleaning products and 60 air purifiers including 22 pure essential oils. The benchmark analysis also permits to identify a total of 21 different devices allowing the diffusion of essential oil blends under different mechanisms.

Annex 1 reports an exhaustive list of the identified products and their characteristics: use purpose, diffusion mode, brand, retail store, fragrance, and composition indicated by the manufacturer.

Selection criteria of cleaning products / A total of 8 cleaning products are selected in the frame of this project, displayed in Table 1. This selection has been done by considering: (i) the diverse purpose of use and the diversity of application instructions, (ii) the variety of application modes i.e. liquid form, spray, foam cleaners and (iii) the diversity of essential oils used as natural fragrances in the formulations. The product selection intends to be representative of the market and targets the assessment of the impact in indoor air quality of the product formulation, the terpene content and the diffusion mode.

Table 1. Specification on the selected cleaning products.

	Cleaning products					*Type of characterization*			
Selected Product	**Product category**	**Diffusion mode**	**Natural Fragrance[1]**	**Retail store**	**Application instructions**	**Liquid composition**	**Volatile fraction (micro-chamber)**	**Realistic emissions (1m^3 test chamber)**	**Real emission (40 m^3 experimental room)**
KC – 1	Kitchen cleaner	Trigger spray	Lemon oil	*Naturalia*	Rinse-off	X	X		
KC – 2		Trigger spray	Eucalyptus oil	*Bio c'est bon*	Rinse-off	X	X	X	
MC – 1	Multi-use cleaner	Liquid / Dosing cap	Citrus oil	*Carrefour*	*Surface cleaner:* Leave on	X	X	X	X
					Floor cleaner: Rinse-off				*X*

MC – 2		Liquid	Lemon oil	*Naturalia*	Leave on	X	X		
MC – 3		Liquid	Mint and eucalyptus oil	*Carrefour*	Leave on	X	X		
SC – 1	Surface cleaner	Trigger spray	Lavender and sage oil	*Biocoop*	Leave on	X	X	X	X
SC – 2		Wipes	Lavender oil	*Naturalia*	Leave on	X			
GC – 1	Glass cleaner	Trigger spray	Citrus oil	*Naturalia*	Leave on	X	X		

1: *Based on information given by the manufacturer*

Selection criteria of air purifiers / As report in Table 2, 4 representative air purifiers are selected. This selection is done by considering firstly their chemical compositions and their diversity of terpene molecules, secondly their application modes i.e. aerosols, trigger sprays or "to be used with diffuser or not".

Table 2. Specifications on the selected air purifiers.

Air purifiers					*Type of characterization*		
Selected Product	**Diffusion mode**	**Instruction of use**	**Natural Fragrance**[1]	**Retail store**	Liquid composition	Realistic emissions (1m^3 test chamber)	Real emission (40 m^3 experimental room)
AP - 1	Liquid	To be used with a diffuser	Mixture of different essential oils	Nature & Découverte	X		
AP - 2	Liquid	To be used with a diffuser	Tea tree oil	Nature & Découverte	X	X	X
AP - 3	Aerosol	To be directly sprayed	Mixture of different essential oils	Naturalia	X		
AP - 4	Trigger spray	To be directly sprayed	Mixture of different essential oils	Pharmacy	X	X	

Selection criteria of diffuser devices / As presented in Table 3, three contrasted diffusion devices are selected. To frame this study, solely the process of transfer of terpenes from essential oil to the gas phase using a commercial diffuser is investigated. Then, two main points are taken into account (i) devices not requiring water and (ii) devices not involving a candle or flame. Indeed, (i) the emission dynamics through mechanisms involving water might also involve interactions between terpene molecules and water droplets and (ii) diffusion processes involving a candle or flame may also generate secondary products from the combustion process such as combustion gases and particulate matters.

Table 3. Specifications of the selected diffuser devices.

		Diffuser devices			**Type of characterization**	
Device	**Diffusion mechanism**	**Retail store**	**Photo**		**Realistic emissions (1m³ test chamber)**	**Real emission (40 m³ experimental room)**
Nebulizing diffuser	An air flow is forced through a small tube, increasing its velocity while the pressure at the exit point is reduced. That difference of pressure induces a suction causing the essential oil to rise upwards in a separate glass tube. Then, a stream of pressurized air hits the oil surface and creates micro-droplets that get easily evaporated.	*Nature & Découverte*			X	
Ceramic electric heat diffuser	It evaporates essential oil by a soft electric heat gain. A heating resistance maintains a small ceramic receptacle at a constant temperature	*Pharmacy*			X	X
Capillary diffuser	It consists in a wick-based system that combines the action of wicking and evaporation. A stick made of beech wood is screwed on the essential oil flask, the top of this porous stick is exposed to the air, so that the volatile liquid slowly diffuses at the liquid-air interphase.	*Nature & Découverte*			X	X

Regarding the investigation of the emissions from the use of air purifiers and the diffusion of essential oil blends, only the results associated to the diffusion process of tea tree oil are included in this manuscript. The characterization of the

liquid composition of all the selected products (Table 1 and 2) and the evaluation of the emission from AP – 4 in the emission test chamber will be provided to ADEME in the final report of the ESSENTIEL project and published on-line.

2.2 Characterization of the liquid composition of the essential-oil-based household products

The preliminary stage before evaluating the emissions and the indoor fate from the use of essential-oil-based household products is the identification of their chemical compositions. The experimental set-up for the assessment of the terpene content is specific to the type of product evaluated (i) the **8 essential-oil-based cleaning products** and (ii) the **tee-tree oil**.

Cleaning products / Several extraction parameters have been optimized in order to maximize the complete extraction of terpene molecules including (i) the selection of the extraction organic solvent, (ii) the mass ratio of the cleaning product to the solvent, (iii) the contact time between the solvent and the cleaning product to be extracted, and (iv) the number of consecutive extractions. For the evaluation of the terpene content, 60 ± 5 g of aqueous cleaning product samples are extracted with 120 g of diethyl ether or dichloromethane, depending on the performance of the solvent regarding each cleaning product formulation among 4 evaluated organic solvents. Lopez et al. [10] compared the extraction of 5 terpenes into 7 organic solvents. Results evidenced that dichloromethane and diethyl ether were the most efficient solvents regarding the quantification of these aromatic compounds. Details regarding the physical and chemical properties of organic solvents used for the extractions are gathered in Table 4.

Moreover, the tested contact times and product/solvent mass ratios are 20, 40 and 60 minutes and 2:1, 1:2 and 1:1. The optimization results in evidencing that the maximum terpene mass concentrations (µg/g of product) is retrieved from the samples settled 60 minutes under a mass ratio product/solvent of 1:2. The extraction process is repeated three times consecutively to assess the complete extraction. Terpene molecules are identified and quantified from each sample of the consecutive extraction processes.

Table 4. Organic solvents used for the terpene extraction from cleaning products.

Solvent	Molecular formula	Relative molecular mass	Density (kg.L^{-1})	Boiling point (°C)	Water solubility (g.L^{-1})	Viscosity (cP)	Extracted cleaning products
Diethyl ether	$C_4H_{10}O$	74.12	0.713	35	69	0.29	KC – 1 KC – 2 MC – 1 MC – 2 GC – 1
Dichloromethane	CH_2Cl_2	84.93	1.330	40	20	0.55	SC – 1 MC – 3 SC – 2

Subsequently, the extracted samples are analyzed by gas chromatography (GC), using direct liquid injection. The injection volume for each sample is 1 µL. The analysis is performed using a 7890A type instrument from Agilent Technologies equipped with a Restek 10189 chromatographic column (105 m x 530 µm, 3µm film thickness) connected to two different detectors (i) a Flame Ionization Detector (FID) used for quantification, and (ii) a Mass Spectrometer (MS) used for identification from Agilent Technologies 5975C inert MSD. Additionally, 22 high purity standards of terpenes from Sigma-Aldrich®, diluted into methanol and assembled into 3 distinct mixtures are used for analytical developments (compound identification and quantification). Several chromatographic parameters have been optimized including (i) the split flow, (ii) the injection temperature, (iii) the temperature program of the oven. The typical detection limit of this instrument for hydrocarbon VOCs with abovementioned analysis conditions is 0.01 µg/g.

Tee Tree oil / For the composition analysis of the tee tree oil, three samples are prepared at a concentration of 0.7 mg/mL, diluted in methanol. Then, 1 µL of each diluted sample is directly injected in the gas chromatograph (GC). The analytical protocol to quantify terpene concentrations is the same than the one reported for cleaning products.

2.3 Experimental set-ups of different scales: from micro-chamber testing to real-scale room experiments

For the investigation of the indoor emissions from the use of essential-oil-based household products, three experimental chambers of different scales are employed (i) a micro-chamber, (ii) an emission test chamber of 1 m^3, and (iii) an experimental room of 40 m^3 IRINA (*Innovative Room for INdoor Air studies*). In this section, the respective experimental set-ups are detailed.

2.3.1   Micro-chamber-thermal extractor (µCTE) testing set-up

Description of the micro-chamber / The liquid-to-gas transfer capacity of the selected cleaning products is evaluated by employing a micro-chamber-thermal-extractor device of 44 mL volume (M-CTE-120 Markes International®). The micro-chamber device consists of six individual stainless-steel cylindrical micro-chambers (d = 4.5 cm) positioned in a heated block, as reported in Figure 2a. The temperature of the heating blocks can be adjusted from ambient temperature to 120 °C. Moreover, the six micro-chambers are simultaneously supplied with a controlled flow of dry air via a restrictor. The dry air generation is ensured by an air compressor combined with membranes for humidity removal. It is coupled with a mass flow controller. Before entering the micro chamber, the dry air is purified by an activated carbon filter in order to remove particles and trace pollutants. Blank measurements are performed to determine the background levels of VOCs at the chamber outlet before running each set of experiments. Note that mean concentration levels of blank measurements in the micro - chamber did not exceed quantification limits for individual target VOC background concentrations. For each micro-chamber, the air flow can be adjusted by changing the pressure supplied. The device is 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 is used and set at 50 mL/min. The dry air flow enters in each micro-chamber through the lid, as shown in Figure 2b, and is preheated to the temperature of the micro-chamber at 40 °C. A total volume of 50 µL of each selected cleaning products is placed in the micro-chamber, operated under the above mentioned optimized parameters (temperature and air flow). The top of the chamber acts as a door, whereby sealing is done with a silicon gasket for leak control.

Analytical strategy / The TerVOCs emitted from the investigated products inside each micro-chamber are monitored using an off-line device for their identification and quantification. Subsequently, the entire exhaust flow from each micro-chamber is collected on two consecutive sorbent tube (packed with Tenax TA® adsorbent) which are attached to the lid, one after the other, for evaluating whether any breakthrough of the collected VOCs occurs. The sampling time is fixed at 15 minutes and the total collected sample volume from the outlet of the micro-chamber is 750 mL.

Samples are desorbed at 280 °C, under a helium flow of 50 mL/min during 20 minutes by using a PerkinElmer® thermal desorber (Model: Turbo Matrix 350). Then, desorbed compounds are thermally transferred under helium and refocused on a Carbotrap B/C trap at 5 °C with an outlet split flow of 70 mL/min. These set parameters regarding the thermal desorption process are optimized for terpene quantification and identification without any chemical transformation of the analytes: (i) the desorption temperature, time and flow, (ii) the trap cold temperature, and (iii) the split flow are optimized.

The gas chromatographic analyses are performed using a 7890A type 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) a Flame Ionization Detector (FID), and (ii) a Mass Spectrometer (MS) from Agilent Technologies 5975B inert MSD. Several parameters for the gas chromatographic analyses have been optimized including the oven temperature program. The typical detection limit of this instrument for hydrocarbon VOCs with abovementioned sampling and analytical conditions is ca. 0.1 ppb. The individual calibrations of the identified and quantified TerVOCs are achieved by liquid doping of their corresponding high purity and certified standards from Sigma-Aldrich® on adsorbent tubes Tenax TA®. The entire experimental set-up configuration is detailed in Figure 2c.

(a)

(b)

(c)
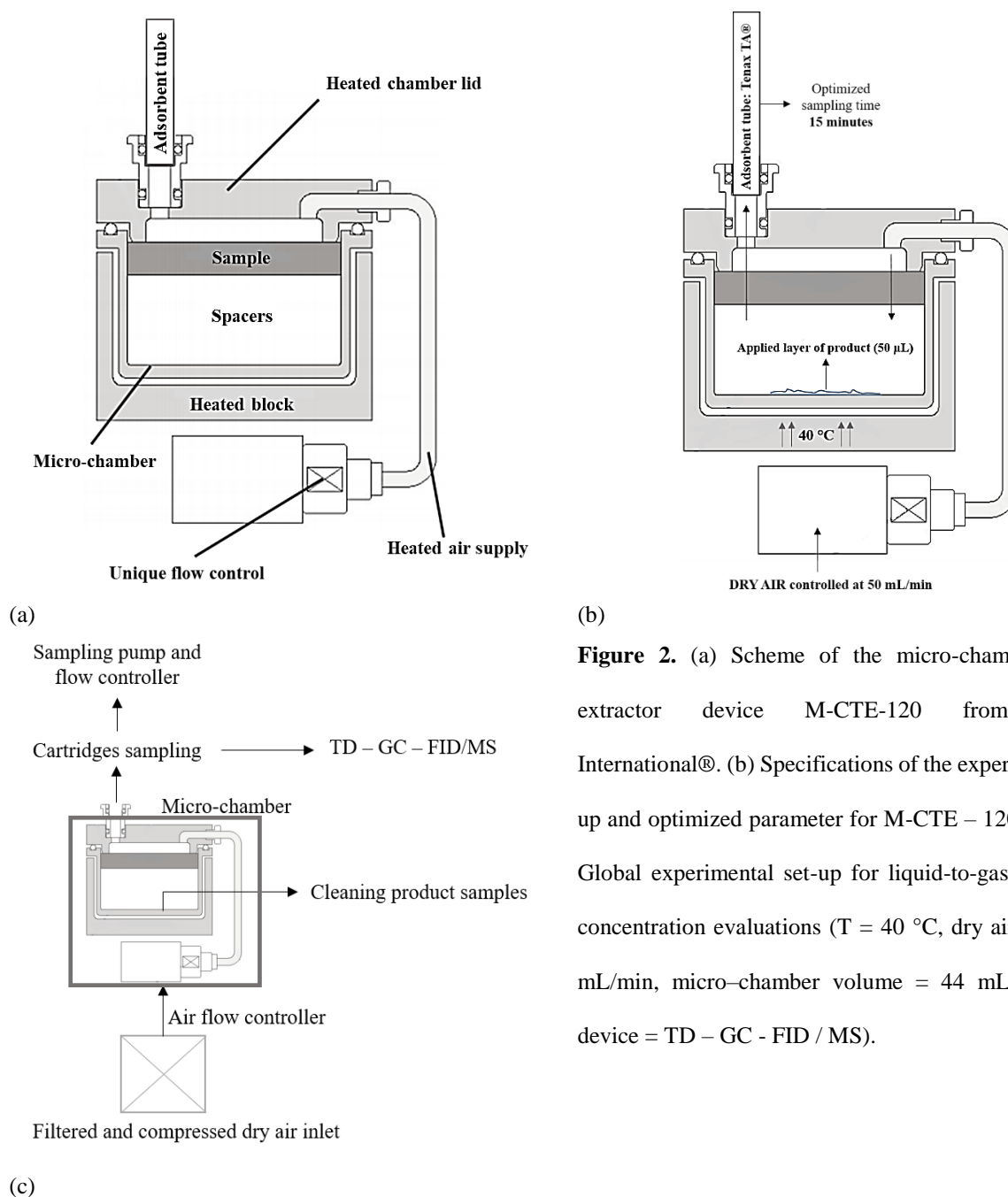
Figure 2. (a) Scheme of the micro-chamber-thermal extractor device M-CTE-120 from Markes International®. (b) Specifications of the experimental set-up and optimized parameter for M-CTE – 120 testing (c) Global experimental set-up for liquid-to-gas transferred concentration evaluations (T = 40 °C, dry air flow = 50 mL/min, micro–chamber volume = 44 mL, analytical device = TD – GC - FID / MS).

2.3.2 The 1 m^3 emission test chamber

Description of the emission test chamber / The investigation of the emissions from essential-oil-based household products are conducted in an emission test chamber of 1 m^3 (Model: Vötsch VCE1000 Classic). This setup complies with the ISO 16000-9 and the ISO 16516 standards. [11] This emission test chamber allows the evaluation of emissions under controlled environmental parameters of (i) temperature, (ii) humidity and (iii) air exchange rate (AER). The emission test chamber compiles: an external box and a 976 L stainless-steel test chamber (inner box) where the experiments are executed, as presented in Figure 3a. The external box acts as a thermal regulating jacket to control the temperature of the stainless steel chamber inside. The dry air generation is ensured by an external air compressor equipped with different filter stages and a mass flow meter controlling the air flow. Before entering the emission test chamber, this air flow is purified by a final activated carbon filter, placed before the inlet air of the chamber, to remove particles and trace pollutants (Figure 3b). Blank measurements are performed to determine background levels of VOCs in the chamber before running each set of experiments. Note that mean concentration levels of blank measurements in the emission test chamber did not exceed standardized values for background concentrations of individual VOCs (according to the recommendations of ISO 16000-6 and NF 16516 standards). [12] The inlet air flow is controlled by a mass flow controller located in the external case of the chamber and introduced through a bulkhead connection. Furthermore, the air inside the emission test chamber is continuously mixed by a magnetic fan, ensuring the homogeneity of the gas phase. The humidity is controlled by the water tank located at the back of the chamber, and it is continuously monitored. Finally, the air inside the chamber is evacuated via a main outlet through a bulkhead connection. It can be sampled thought sorbent tubes via a second controlled outlet flow. In the frame of this work, the above described environmental conditions are set at 23 ± 1 °C, 50 ± 5 % and 0.3 h^{-1} ± 0.05. The values for humidity and temperature are established according to the ISO 16000-9. [11] Concerning the air exchange rate, the established value correspond to the percentile 25 reported in French dwellings by the OQAI (Indoor Air Quality Observatory). [13], [14] The entire experimental set-up for the emission evaluation from essential-oil-based household products in emission test chamber of 1 m^3 is presented in Figure 3b.

(a)
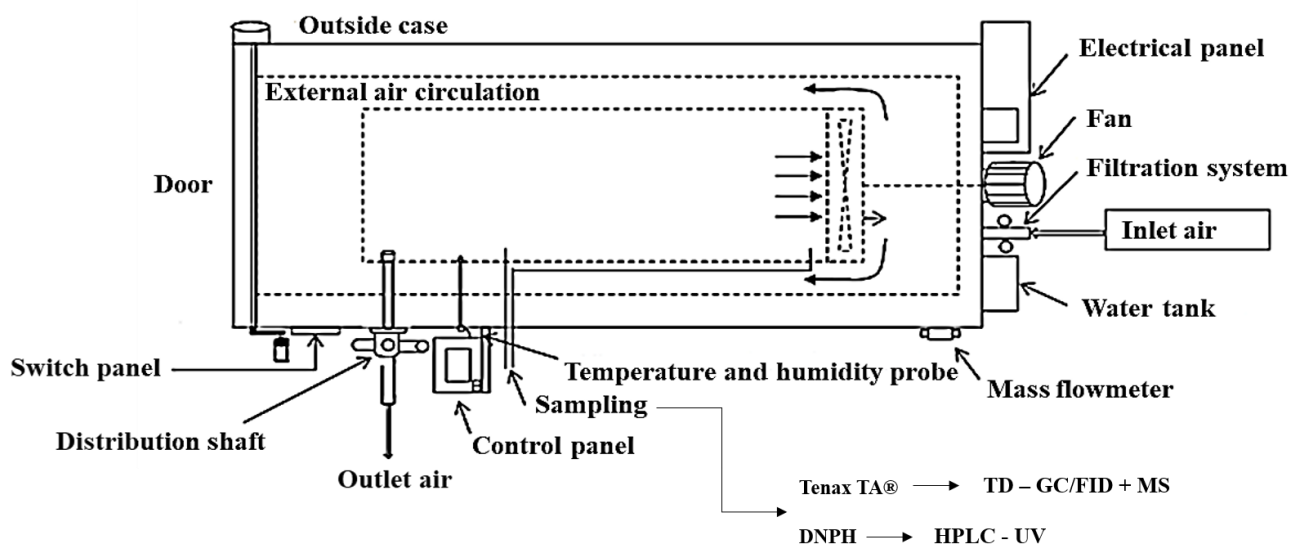
(b)

Figure 3. (a) Internal and external view and (b) Scheme of the 1 m3 emission test chamber Vötsch VCE1000 Classic. [15]

Sampling and analytical strategy of cleaning products / Regarding the analytical methodology, the VOC concentrations inside the emission test chamber are monitored using an off-line device that allows their quantification. Several preliminary sets of experiments are performed in order to explore the duration of the experiment depending on the type of product. From these preliminary results, the duration of a typical emission experiment involving a cleaning product is established at 5 hours. Off-line samplings are performed using Tenax TA® adsorbent tubes and 2, 4-dinitrophenylhydrazine (DNPH) impregnated silica cartridges (Model: Xposure, Waters®) according to ISO 16000-3 and 16000-6. [11], [16] Samplings are performed using a pump (KNF®) connected to a mass flow controller under specifically optimized flow rates and sampling times for each type of product tested, as described in Table 5.

Except regarding the transfer split flow, optimized at 4 mL (outlet split), the analytical protocol to quantify TerVOC concentrations are the same than the one reported in section 2.3.1 for the gas-transferred concentration determination using µ-chambers.

Derivatized carbonyl compounds (OVOCs) are extracted from DNPH cartridges with 3 mL acetonitrile and analyzed with a Thermo Dionex Ultimate U3000 liquid chromatograph. Compounds are eluted on Acclaim RSLC Carbonyl column (2.1 x 150 mm) and detected by RS variable wavelength UV absorption. Calibrations of the carbonyls are achieved using high purity certified standard solutions (Aldehyde/Ketone-DNPH Stock Standard-13). Considering these conditions, the typical detection limit for carbonyl compounds is 0.01 ppb.

Table 5. Optimized experimental parameters for off - line sampling systems for the analysis of essential-oil-based cleaning products.

Evaluation of TerVOCs and OVOCs emission from cleaning products		
Sampling devices	*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
Time intervals (h)* and sampling duration (min)	From 0 to 1 h: sampling of 15 min each : total of 4 samples From 1 h – 5 h: sampling of 60 min each : total of 4 samples	

* Optimized experimental parameters

Sampling and analytical strategy of tee tree oil diffusion / Regarding the analytical methodology, the temporal dynamics of TerVOC concentrations at the outlet of the emission test chamber are determined by off-line and on-line samplings with different temporal resolutions. Details concerning the sampling parameters optimized for tea tree oil diffusion are gathered in Table 6.

Off-line measurements are performed on Tenax TA® sorbent tubes and 2, 4-dinitrophenylhydrazine (DNPH) impregnated silica cartridges according to ISO 16000-3 and 16000-6. [12], [16] Samplings are controlled by a pump connected to a mass flow controller under specifically optimized flow rates and sampling times for tea tree oil diffusion. The parameters for off-line samplings are described in Table 6. Preliminary sets of experiments are performed in order to assess duration of a typical experiment depending on the type of diffuser. From these preliminary results, the duration of an emission involving the diffusion of tea tree oil by electric and nebulizing devices is established at 14 hours. The emission from the diffusion of a capillary device may last for several days; nevertheless the duration of the experiment is restrained at 72h. This duration allows addressing the typical steady-state regime of this type of diffuser. The analytical protocols to quantify TerVOC and OVOC concentrations are the same than those described for cleaning product emission experiments. However, the transfer split flow is optimized depending on the concentration of TerVOCs in the adsorbent tube, then the outlet split is optimized at 20 mL/min.

Table 6. Experimental optimized parameters for off - line sampling systems for tea tree oil diffusion.

Evaluation of TerVOCs and OVOCs emission from tea tree oils diffusion		
	Off-Line	
	Tenax TA® *for TerVOCs*	**DNPH Cartridges** *for OVOCs*
Sampling Flow	0.040 L/min	0.800 L/min
Sampling duration (min) and time intervals (h)	0 – 2 h : 10 min sampling each 30 min 2h – 6h : 10 min sampling each hour	0 – 1 h : continuous sampling each 15 min 1 – 5 h : continuous sampling each hour 8 – 60 h : 1 hour sampling with intervals of 6, 8, and 12 hours

On-line measurements are performed with a compact gas chromatograph system (C-GC/FID) (Model: Global Analyzer Solutions CGC4) with a Restek-VMS column (15m x 0.32 mm ID, 1.8µm film thickness). It is coupled to a Flame Ionization Detector (FID) for the quantification of TerVOCs. Additionally, this on-line device is equipped with an automated sampling system. It samples air at a flow rate of 25 mL.min^{-1} during 4 min, each 15 minutes. Subsequently,

analytes are refocused on a multi-layer sorbent (Model: General Purpose Hydrophobic from Markers Internationals®) and transferred to the column under helium at 280 °C. The oven temperature is constant, and it is set at 100 °C. Several C-GC/FID parameters have been preliminarily optimized by the injection of individual TerVOCs vaporized in a 6 L canister (Model: Silonite® from Entech). Typical detection limits of this instrument for TerVOCs with abovementioned sampling conditions are 0.1 ppb.

Inter-comparison of monitoring methods / Since no gaseous standards are available for the calibration of the considered TerVOCs using C-GC/FID, a specific calibration methodology has been developed. This method relies on the cross-calibration of C-GC/FID with the TD-GC-FID/MS. The TD-GC-FID/MS is preliminarily calibrated off-line using Tenax TA® sorbent tubes doped with liquid TerVOC standard solutions. TerVOCs are identified using the MS detector and quantified using the FID detector. The correlation between the C-GC/FID signal and the TD-GC-FID/MS quantitative response is achieved through simultaneous samplings along the diffusion of terpenes in the emission test chamber. For each TerVOC, the concentration monitored by the quantitative off-line system is plotted as a function of the peak area of the C-GC/FID signal, as reported on Figure 4. For all detected TerVOCs a linear trend is observed with correlation coefficients ranging from 21 to 124. The slopes of the linear regressions are used for the quantitative analysis of TerVOCs by the C-GC/FID.

The off-line sampling is considered as the reference measurement method. However, for discussion purpose, C-GC/FID is preferred since it allows a complete quantitative screening of all TerVOCs under a shorter time of 15 minutes along the emission experiments resolution, if compared to off-line sampling methodology.

Figure 4. Evolution of α-pinene concentration measured by off-line TD-CG-FID/MS as a function of the on-line C-GC/FID peak area of α-pinene with a correlation coefficient value of 85.

2.3.3   IRINA: the 40 m³ experimental room

Description of the 40 m³ experimental room / The set of experiments aiming at evaluating the emissions and impacts on indoor air quality related to the use of essential-oil-based household products in a real scale room and under real consumer use patterns are conducted in the experimental room IRINA. This experimental room has (i) 40 m³ of volume and (ii) 1.59 m⁻¹ of surface/volume ratio. The room is operated in a semi-closed mode with an average air exchange rate of 0.3 ± 0.1 h⁻¹. The inner surfaces of IRINA are fully covered with aluminum foils to minimize VOC sinks or sources from the experimental room walls. A looped air conditioning system (AC - Mitsubishi®) is placed in IRINA to ensure temperature and humidity control as well as air homogenization by the recirculation of the air inside the room. Pamela et al. [17] evaluated the homogeneity of VOC concentration injected in the room by measuring their concentration at three different positions. The obtained results verified that the air inside the room homogenize within 150 seconds. Therefore, the positioning of the table for surface cleaning and diffusers support is not a factor that might impact the measured concentrations. In spite of the rapid homogenization of the experimental room, the table is placed at the center of the experimental room, as presented in Figure 5.

Four sensor arrays are continuously used to monitor temperature, relative humidity and CO_2 concentration inside the room located at different positions. The complete description of the experimental room IRINA is exposed by Harb et al. [17] who performed its experimental validation.

As described in Figure 5, four bulkhead connections allow (i) the injection of VOCs and CO_2 and (ii) the connection of online sampling systems. They are set on the eastern chamber walls at a distance of 5.7 m from the air conditioning and 0.5 m high from the floor. For comparative purpose, the environmental condition parameters set are the same than the parameters of the 1 m³ emission test chamber of. Then, temperature and humidity are respectively set at 23 ± 1 °C and 50 ± 5 %. The air exchange rate is experimentally determined during each set of experiment through the injection of this tracer gas, CO_2.
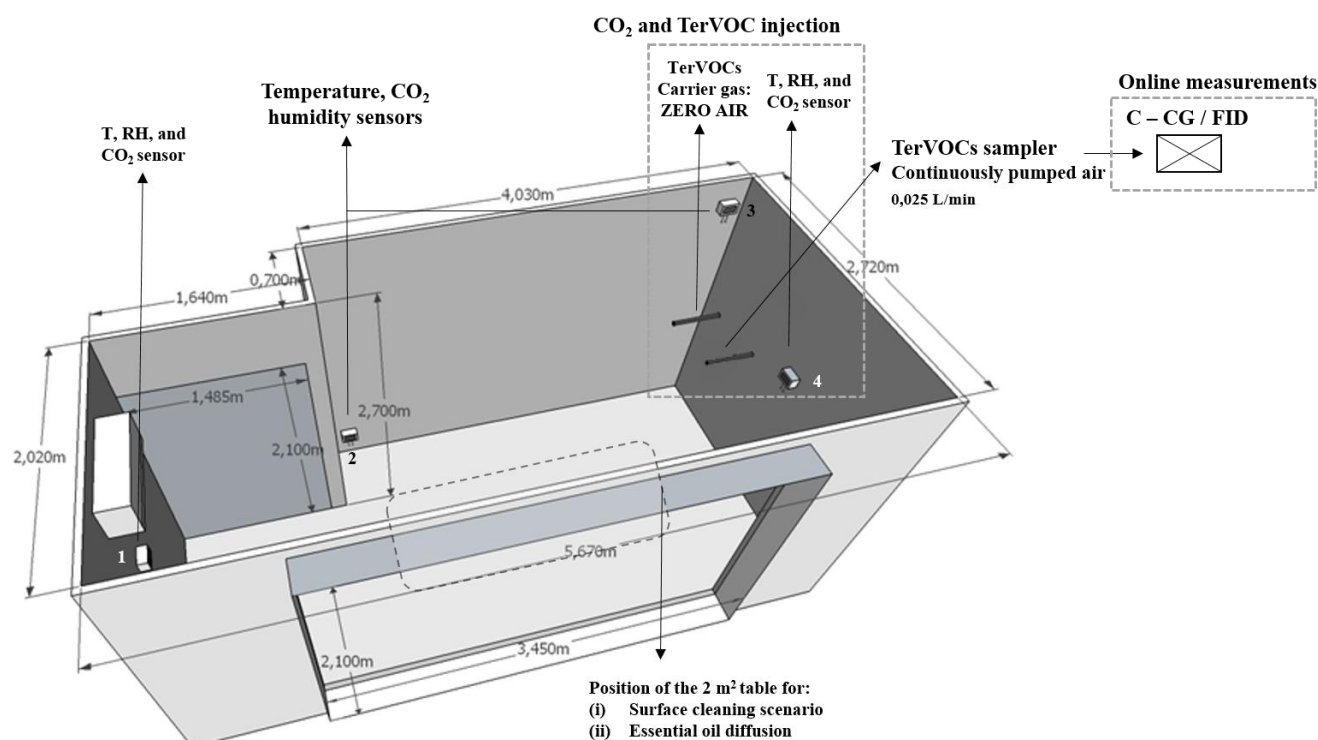
Figure 5. Overview of the 40 m3 experimental room IRINA showing dimensions, air conditioning system, sensors for constant monitoring of temperature, relative humidity and CO2 concentrations in the room, and instrumentation dedicated to injection, sampling and analysis of TerVOCs. [17]

Online measurements with C – GC/FID / TerVOC emitted concentrations from tested products in the experimental room are monitored within a short temporal resolution by employing the compact gas chromatograph system (C-GC/FID) (Model: Global Analyzer Solutions CGC4).

The analytical protocol to quantify and identified TerVOCs emitted in the 40 m³ experimental room is the same than the one reported in section 2.3.2 associated to the evaluation of the emissions from tea tree oil in the emission test chamber

of 1m³. However, the split ratio used for experiments relative to cleaning product differs from the one for essential oil diffusion. Indeed, monitored concentrations vary from one order between cleaning product and essential oil diffusion experiments. Since no gaseous standards for the calibration of terpene molecules are available, the calibration of the C – GC/ FID is performed as well by a cross calibration of C-GC/FID with the TD-GC-FID/MS. The correlation between the C-GC/FID signal and the TD-GC-FID/MS quantitative response is achieved through simultaneous samplings (4 minutes sampling each 11 minutes) along the volatilization of a mixture of 22 high purity standards of terpenes from Sigma-Aldrich® in the 40 m³ experimental room through the VOC injection system. This injection system relies on the heated and pressurized injection of liquid terpenes vaporized in the room. The injector temperature is set at 220 °C in order to volatilize the terpene mixture without any chemical transformation. The carrier gas used to propel the TerVOCs injected in the room is zero air. Subsequently, simultaneous samplings are performed using the online system and the preliminarily calibrated adsorbent tubes Tenax TA®, until the complete evacuation of the volatilized terpenes from the experimental room. It generally takes 6 hours. For each TerVOC, the concentration monitored by the quantitative off-line system is plotted as a function of the peak area of the C-GC/FID signal, as reported in Figure 6. This process is performed in triplicate for each type of product (i) essential-oil-based cleaning products and (ii) essential oil diffusion, since the split flow of the online measurement system is optimized at 1 mL/min and 20 mL/min, respectively, according to the terpene emitted concentrations from the preliminary set of experiments.

For all detected TerVOCs a linear trend is observed with correlation coefficients ranging from 154 to 530 and 25 to 75 respectively for cleaning products and essential oil diffusion. The slopes of the linear regression are used for the quantitative analysis of TerVOCs by the C-GC/FID.

The off-line sampling is considered as the reference measurement method. However, for discussion purpose, C-GC/FID is preferred since it allows a complete quantitative screening of all TerVOCs under a shorter time of 15 minutes along the emission experiments resolution, if compared to off-line sampling methodology.
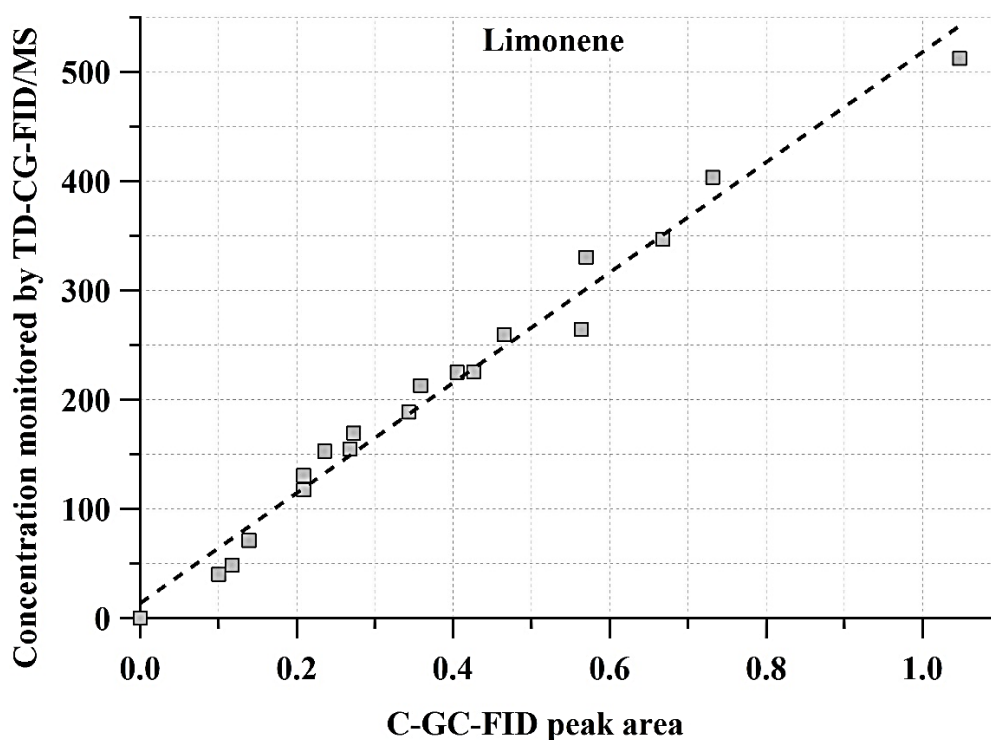
Figure 6. Evolution of limonene concentrations measured by off-line TD-CG-FID/MS as a function of the on-line C-GC/FID peak area of limonene for the calibration process of cleaning product experiments with a correlation coefficient value of 530.

2.4 Application protocols

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

The product application procedure requires to be correlated to a typical consumer use patterns in order to mimic a real application scenario for the evaluation of cleaning product emissions. The key parameters required to be determined in order to define specific product applications are (i) the quantity of product to apply and (ii) the surface to clean. They are estimated from the loading factor and the product yield reference values.

Loading factor / It is defined as the ratio between the emissive surface, i.e. the cleaned area, and the volume of the chamber. For the correlation between the 1 m^3 emission test chamber and the 40 m^3 experimental room, the loading factor is required to be identical. Conventionally, a reference room is used to extrapolate VOC measured concentrations in test chambers with small volumes for assessing the human exposure. The reference room is supposed to be characterized by

a floor area of 12 m^2 and a ceiling height of 2.5 m, and presents a volume of 30 m^3. Nevertheless, in this study, the real scale experimental room IRINA of 40 m^3 is employed for the experiments under real use consumer patterns. Therefore, IRINA, is considered as the reference room for these calculations.

For the surface application scenario in the 40 m^3 experimental room, a typical table area of 2 m^2 is considered, resulting 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 experimental room, the loading factor is required to be identical. Therefore, a *surface cleaning scenario* is defined under the same loading rate, and the surface to clean can be determined for the 1 m^3 emission test chamber, corresponding data are reported in Table 7.

Product yield / It is defined as the mass of product required to clean 1 m^2 of surface considering the loss due to the wiping process, if required. This parameter has been individually estimated for the selected cleaning products. Firstly, the average amount of cleaning product required to clean 1 m^2 of surface is determined from 10 different operators who performed the cleaning activity on the 1 m^2 reference surface. Subsequently, the average mass dispersed by one single spray from each trigger spray mechanism of the selected product is determined for a set of 10 successively sprays performed by the same operator. This two-step procedure allows the estimation of the mean number of sprays required for the surface cleaning scenario in the 1m^3 emission test chamber and in the 40 m^3 experimental room.

Once these key parameters are estimated, the mass to apply can be calculated. These results are detailed in Table 7. Note that the correlation methodology for the application protocol at different scales is only considered for surface cleaning, since floor cleaning is exclusively performed in the experimental room of 40 m^3.

Table 7. Application parameters for the cleaning scenario: reference values for product yield and loading factor, and quantity of product to apply.

Application parameters for defining a realist application scenario				
		EMISSION TEST CHAMBER (*1 m³*)	**REAL ROOM** (*40 m³*)	
Cleaning scenario		*Surface*	*Surface*	*Floor*
SURFACE TO CLEAN		0.05 m²	2 m²	14 m²
LOADING FACTOR (m²/m³)		0.05	0.05	0.35
PRODUCT YIELD	**SC – 1**	8.67 (g.m⁻²)		-
	MC -1	7.21 (g.m⁻²)		12.39 (g.m⁻²)
	KC - 2	12.00 (g.m⁻²)		-
APPLIED MASS QUANTITY	**SC – 1**	3.21 g	18.00 g	-
	MC -1	4.44 g	14.97 g	176.8 g
	KC - 2	2.67 g	24.00 g	-

Floor cleaning in the 40 m³ experimental room / For floor mopping, two full-filled dosing caps of MC – 1 (equivalent to ca. 60 g) are diluted in 5 L of water. The dilution is prepared outside of the experimental room. This solution is prepared outside of the experimental room. Subsequently, the solution is mopped over the tile floor of 14, 27 m² by employing a micro-fiber fabric mop of 10.5 cm x 33 cm. Four mop strokes (back and forth) are performed to apply the solution to each 4 tiles of the floor, equivalent to 0.36 m². Then, the mop is immerged into the solution and squeezed to drain the liquid excess before repeating the cleaning process. The bucket with the cleaning solution and the micro-fiber mop are weighted before and after the application process, in order to determine the amount of solution applied considering the lost related to the mopping. The floor cleaning practice lasted approximately 5 – 6 minutes before removing all the cleaning materials from the room. Time zero of the experiments correspond to the time when the cleaning process is completed and all the materials are removed from the experimental room. A set of three experiments are performed for evaluating the repeatability of the experimental protocol.

Surface cleaning in the experimental room of 40 m³ / For the trigger spray product, the calculated mass is sprayed, respecting the number of sprays previously determined, over the 2 m² glass table and evenly wiped. . , In contrast, for the

surface cleaner in liquid format, the specific mass to apply is weighted outside of the experimental room, then it is evenly drizzled and wiped over the glass table. The wiping material is weighted before and after the cleaning practice for estimating the real mass of product applied by considering the loss due to the wiping process. Once the cleaning activity is completed, the experimental room remains closed during the whole emission monitoring. For each cleaning product, a set of three experiments is performed in order to evaluate the repeatability of the experimental protocol. Additionally, during the experiment, t = 0 corresponds to the time when the application process of the cleaning product is completed inside the room. Figure 7 presents the application scenario for the table cleaning under realistic conditions in the experimental room.
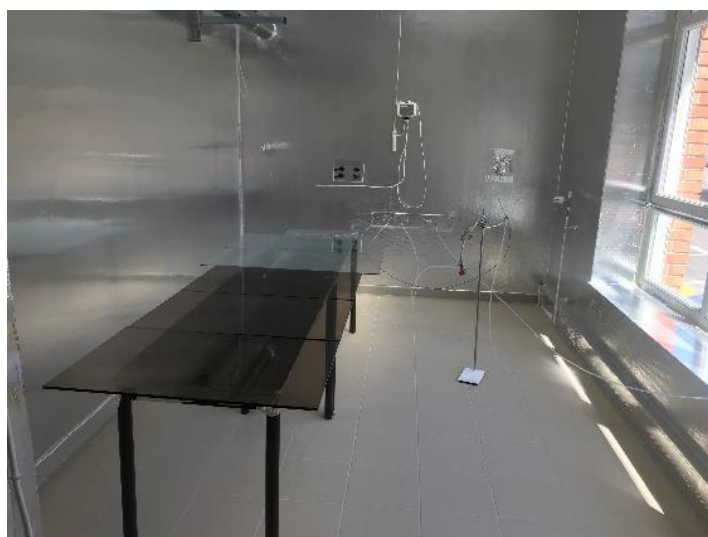
Figure 7. Illustration of the 2 m² surface cleaning under real consumer use patterns in the 40 m3 experimental room (IRINA).

Surface cleaning in the 1 m^3 emission test chamber / For each experiment, the calculated mass of product is evenly drizzled or sprayed on a stainless-steel surface of 0.05 m^2 placed at the center of the 1 m^3 emission test chamber. Once the simulation of the cleaning activity is completed, the chamber remains closed during the whole emission monitoring. For each cleaning product, a set of three experiments is performed in order to evaluate the repeatability of the experimental protocol. Additionally, during the experiment, t = 0 corresponds to the time when the application process of the cleaning product is completed inside the test chamber.

2.4.2   Essential oil diffusion: application protocol at different scales

Regarding the assessment of the emission from the tea tree oil diffusion, identical application protocol are executed for both experimental chambers since it is not possible to adapt the diffusion action to the volume of the considered chamber. Therefore, the real diffusion of essential oil is identically performed in the 1 m^3 and in the 40 m^3 chambers. Note that in the emission test chamber of 1 m^3 three diffusers are investigated, namely the electric device, the nebulizing device and the capillary device; while in the 40 m^3 experimental room only the electric and the capillary devices are tested.

Essential oil diffusers are introduced and placed in the center of the chambers. For the electric and nebulizing diffusers, 20 drops of the tree tea oil are applied according to manufacturer instruction of each diffuser device in order to simulate a realistic usage. In contrast, for the capillary diffuser the entire bottle is placed in the center of the chamber with the diffusion device (support and wood sticks). Time zero of the experiment corresponds to the time when (i) the nebulizing and electric diffusers are switched on and off from the outside of the chambers. They remain closed during the measurement of emissions, (ii) or for capillarity diffuser, when the bottle with the diffusing stick is placed in the center of the chamber. For each diffuser, a set of three experiments are performed in order to evaluate the repeatability of the experimental protocol. Figure 8 illustrates the application protocol in the experimental room IRINA for the evaluation of the emission from the diffusion of essential oils.

Figure 8. Evaluation of the emission from tea tree oil diffusion by employing a diffuser device in the experimental room of 40 m3 IRINA under real consumer use patterns.

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Chapter 3

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

ABSTRACT

Cleaning is an activity done by the population in order to increase hygiene, aesthetic and material preservation. In spite of all the benefits involved in cleaning activities, risks are associated with them since they may contribute to nearly 20 % of the indoor pollutant sources. As indoor air quality has become a major concern for human health, "natural-scented" cleaning products, formulated with essential oils, became trend and market leaders among the household products. However, based on the ambiguity of the words "green" and "natural", these consumer products have taken benefits from skillful marketing strategies. This study aims at assessing the emission of terpene molecules and carbonyl compounds from three essential-oil-based cleaners in an emission test chamber under a realistic scenario. Firstly, results retrieved from the micro-chamber experiments suggest that emission kinetics of terpene molecules are likely to be driven by multiple factors other than the terpene liquid phase concentrations. The characterization of the emission processes studied during a set of 1 m^3 emission test chamber experiments, under realistic scenarios evidences contrasted maximum concentrations of total TerVOCs among investigated products ranging from 150 ppb to 300 ppb. The estimation of the emission rate profiles confirms that the liquid to gas transfer of terpene molecules are driven by (i) the formulation of the product matrix inducing specific chemical affinities between terpenes and the cleaner constituents and subsequent impacts on the emission, (ii) the liquid mass concentration of individual terpene molecules, and (iii) the intrinsic volatility of terpenes themselves. Additionally, regarding the individual emission kinetics of formaldehyde, a specific profile is evidenced, suggesting the presence of a particular source of emission attributed to the presence of formaldehyde-releasers. Consequently, the use of essential-oil-based cleaning products might generate a long term increase of indoor formaldehyde concentrations, and the maximum levels might be reached several hours after the cleaning practices are completed. Thus, essential-oil-based cleaners have to be seriously envisaged as versatile and significant sources of fragrance molecules and formaldehyde, which might induce indoor concentration levels exceeding exposure limits established by the European Union and the United States.

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1. INTRODUCTION

Major efforts have been made to address indoor air current problematic since the daily activities of society are mostly developed in confined environments. Indoors, people are exposed to a large variety of chemical, biological or physical pollutants coming from (i) infiltration from outdoor air, (ii) building materials and furnishing, and (iii) occupants and their indoor activities. [1] [2] Attention of the scientific community is given to chemical pollutants, principally volatile organic compounds (VOC), defined as organic molecules with lower boiling points ranging from 50 to 100°C and upper boiling points ranging from 240 to 260 °C. [3], [4] Among indoor sources of pollutants, the main origins of chemical contaminants are linked to the activities of the occupants such as interior renovation or decoration, smoking, cooking, or housekeeping. [5] Among the thousands of cleaning products available and marketed, people are tempted to use scented products because a pleasant odor provides the sensation of a cleaner environment. Therefore, in spite of all the benefits involved in cleaning activities, such as increasing hygiene, esthetic, and material preservation, raises the question of the chemical and physical pollutant exposure risks. [6] Nazaroff et al. [16] have evidenced that VOC atmospheric emissions per capita from general purpose cleaners and air fresheners are the most contributing in indoor environments with values ranging from 200 to 230 mg per day. The intake fraction is defined as the incremental pollutant mass inhaled per unit of mass of pollutant emitted. [7] Typical intake fraction from emissions in indoor air is in the order of 10^{-3} and 10^{-1} while outdoors is in the order of 10^{-6} and 10^{-3}. This point highlights the fact that the proportion of emissions inhaled is higher when emissions occur indoors rather than outdoors. [8] Unexpectedly, the largest contributors of terpene VOCs to indoor air are not usually recognized, regulated and controlled sources. Indeed, the composition of VOC emitted from household products have been associated to health hazards for indoor occupants. [6], [8]–[12] Nevertheless, limited information is available about composition, quantification and emission dynamics associated to housekeeping activities in confined environments. Available scientific data are for most cases incomparable due to wide variations and heterogeneity in the experimental methodologies for the evaluation of primary and secondary pollutant emissions from fragranced household products. These variations are related to two key parameters: (i) the application protocol (quantity, operation mode) and (ii) the environment of the test (air exchange rate, temperature, chamber size, and relative humidity). [13]–[24] Therefore, the comparison of results from one investigation to another may become difficult and inaccurate.

Fragranced household products can be formulated with (i) synthetized fragrances, (ii) pure essential oils and (iii) mixtures of synthetized fragrances and essential oils, in order to reduce the production costs. Essential oils are used in "naturally" formulated cleaning products either to provide them a pleasant odor, to hide odors from other chemicals used, or to enhance their antibacterial performance. [9], [25] Essential oils are extracted from plants by water vapor distillation, dry

distillation or mechanical extraction methods that do not involve temperature changes. [13] They usually contain more than 100 different chemical substances which provide the typicality of its smell, mainly belonging to the terpene chemical family: monoterpenes and sesquiterpenes, terpene alcohols and terpenoids (TerVOCs). [26], [27] [28]. The characteristic smell of an essential oils is often given by its major compounds; therefore, the typical "scent" of an essential oil directly depend on its chemical composition. [3] In contrast, fragrance mixtures represent the combination of different compounds (synthetized, natural-like or extracted), assembled to replicate a "natural-identical" scent [27], [29].

This work is developed in the frame of the ESSENTIEL project, aiming at characterizing the impact of essential-oil-based products on indoor air quality (IAQ) through the investigation of their realistic emissions and indoor fate. The objective of this work is firstly, to evaluate the correlation between the fragrance chemicals present in cleaning products and their volatile fraction through the determination of the gas-transferred concentration by micro-chamber testing. Secondly, to characterize and assess their emissions in a 1 m^3 experimental chamber by conceiving a realistic application scenario. The proposed experimental approach and the results provided in this work are required (i) to propose harmonized and realistic test protocols, but also (ii) in order to define risk scenarios and to evaluate the human exposure to TerVOCs associated to the use of essential-oil-based cleaning products.

2.   MATERIAL AND METHODS

2.1   *Cleaning product benchmarking*

In order to frame the present study, it is required to define the type of considered cleaning products. Essential-oil-based cleaning products in this work are defined as naturally scented and organic certified products used in a non-permanent way in indoor environments for housekeeping purposes. For their selection, a benchmark analysis is performed among cleaners that have been certified as *ecological products* by different European labels. A total of 108 essential-oil-based products are identified from the European market. Among them, 6 representative cleaning products are selected in the framework of this work and classified by category i.e. use purpose: (i) 2 kitchen degreasers, (ii) 2 general (multi-use) cleaners, (iii) 1 surface cleaner, and (iv) 1 glass cleaner. This selection has been done by considering: (i) the diverse purpose of use in order to assess the effect from different solvent formulations, (ii) the variety of application modes and (iii) the diversity of essential oils used as natural fragrance in the formulation of the cleaning product. It must also be noticed that the solvent matrix composition could vary from one product to another in terms of organic contains (%

ethanol) or presence of texturing agents (gums). The content of fragrance chemicals and their volatile fraction are characterized for the six selected cleaning products, whereas only three products are considered for the $1m^3$ emission test assessment. Table 1 details the characteristics of the six selected products.

Table 1. Specifications on the selected cleaning product.

					Type of characterization		
Product	**Product category**	**Diffusion mode**	**Natural Fragrance**[1]	**General product formulations**[1]	**Liquid composition**	**Volatile fraction (micro-chamber)**	**Realistic emissions ($1m^3$ test chamber)**
KC – 1	Kitchen cleaner	Trigger spray	Lemon oil	< 5% surfactant (anionic and non-anionic), 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 (non-anionic), essential oils (including eucalyptus oil[2]), water, alcohol[2], preservatives, acid correctors	x	x	x
MC – 1	Multi-use cleaner	Liquid	Citrus oil	< 5% surfactant (anionic and non-anionic), water, alcohol, citrus oil[2], citric acid	x	x	x
MC – 2			Lemon oil	< 5% surfactant (anionic and non-anionic), 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 non-anionic), citric acid, essential oils[2] (including eucalyptus oil), amphoteric surfactants	x	x	

1: Based on information given by the manufacturer

2: Certified organically grown

2.2   *Characterization of the liquid composition*

For the evaluation of the terpene content, 60 ± 5 g of aqueous cleaning product samples are extracted with 120 g of diethyl ether or dichloromethane, depending on the performance of the solvent regarding each cleaning product formulation. In agreement with Lopez et al. [30], dichloromethane and diethyl ether are verified to be the most effective organic solvents for the liquid-liquid extraction of TerVOCs, compared to freon-11, ether pentane, ether hexane, pentane and hexane. More details concerning the physical and chemical properties of organic solvents used for the extractions are gathered in Table 2. The extraction process is repeated three times consecutively to maximize the complete extraction of terpene molecules.

Table 2. Organic solvents used for the terpene extraction from cleaning products.

Solvent	Molecular formula	Relative molecular mass	Density $(kg.L^{-1})$	Boiling point (°C)	Water solubility $(g.L^{-1})$	Viscosity (cP)	Extracted cleaning products
Diethyl ether	$C_4H_{10}O$	74.12	0.713	35	69	0.29	KC – 1 KC – 2 MC – 1 MC – 2 GC – 1
Dichloromethane	CH_2Cl_2	84.93	1.330	40	20	0.55	SC – 1

Subsequently, the extracted samples are analyzed by gas chromatography (GC), by direct liquid injection. The injection volume for each sample is 1 µL. The analysis is performed using a 7890A type instrument from Agilent Technologies equipped with a Restek 10189 chromatographic column (105 m x 530 µm, 3µm film thickness) connected to two different detectors (i) a Flame Ionization Detector (FID) used for quantification, and (ii) a Mass Spectrometer (MS) used for identification from Agilent Technologies 5975C inert MSD. Additionally, 22 high purity standards of terpenes from Sigma-Aldrich®, diluted into methanol and gathered into 3 distinct mixtures are used for analytical development (identifying and quantitating compounds). The typical detection limit of this instrument for hydrocarbon VOCs with abovementioned sampling conditions is 0.01 µg/g.

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

The liquid to gas phase transfer capacity, of each terpene identified in the composition of the cleaning products, is defined as the gas-transferred concentration. It is determined by using a stainless-steel micro-chamber of 44 mL volume (M-CTE-120 Markes International®). The top of the chamber acts as a door, whereby sealing is done with a silicon gasket. A total volume of 50 ± 1 µL of each selected fragranced cleaner is introduced into the micro-chamber. Temperature and air flow are set, after optimization, at 40 °C and 50 mL/min, respectively. The detailed characteristics of the micro-chamber are presented in Figure 1a.

Subsequently, two consecutives Tenax TA® cartridges collect volatilized compounds at the outlet flow of the experimental set-up during 15 minutes. The total sampled volume is 0.6 L. Afterward, these samples are desorbed at 280 °C, under a helium flow of 50 mL, using a PerkinElmer® thermal desorber (Model: Turbo Matrix 350). Then, desorbed compounds are thermally transferred under helium and refocused on a Carbotrap B/C trap at 5 °C with an outlet split flow of 70 mL. The gas chromatographic analyses are performed using a 7890A type 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) a Flame Ionization Detector (FID), and (ii) a Mass Spectrometer (MS) from Agilent Technologies 5975B inert MSD. The typical detection limit of this instrument for hydrocarbon VOCs with abovementioned sampling conditions is ca. 0.1 ppb. Calibration of the identified and quantified TerVOCs is achieved by individual liquid doping of their corresponding high purity and certified standards from Sigma-Aldrich®.

2.4 Emission chamber test: Simulation of a real case scenario – Correlation methodology from a real size room

Characteristics of the emission chamber / Experiments reported in this paper are conducted in an experimental chamber of 1 m^3 of volume (Model: Vötsch VCE1000 Classic) that complies the ISO 16000-9 standards. [31] The chamber is operated under controlled temperature, humidity and air exchange rate (AER). These values are set at 23 ± 1 °C, 50 ± 5 % and 0.3 h^{-1} $\pm$ 0.05, respectively. The values for humidity and temperature are established according to the ISO 16000-9. Concerning the air exchange rate, the established value corresponds to the percentile 25 reported in French dwellings by the OQAI (Indoor Air Quality Observatory). [5], [32] The detailed characteristics of the experimental chamber are presented in Figure 1b. Before loading the test chamber with the selected product, blank measurements are performed to determine background levels of TerVOCs and oxygenated volatile organic compounds (OVOCs). Note that

mean concentration level of blank measurements in the experimental chamber did not exceed standardized values for background concentrations concerning individual VOCs.

Table 3. Application parameters for the surface cleaning scenario: reference values for product yield and loading factor, and quantity of product to apply.

		EMISSION TEST CHAMBER $(1\ m^3)$	REAL SIZE ROOM $(40\ m^3)$
*Application parameters to mimic a **2m² surface cleaning***			
SURFACE TO CLEAN		**0.05 m²**	2 m²
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})	
APPLIED MASS QUANTITY	SC – 1	**3.2 g**	18.0 g
	MC -1	**4.4 g**	15.0 g
	KC - 2	**2.7 g**	24.0 g

Application methodology / Emission chamber tests have been focused on surface cleaning scenarios. Therefore, aiming at mimicking a realistic surface cleaning scenario, the product application procedure, namely (i) the quantity of product to apply and (ii) the surface to clean, has been defined based on product yield and loading factor reference values. The *product yield* is defined as the mass (in grams) of product required to clean 1 m² of surface, following the manufacturer instructions by considering: (i) the loss related to the wiping and (ii) the rinsing process, if required. The *loading factor* is defined as the ratio between the emissive surface, i.e. the cleaned surface, and the volume of the chamber. More details about the determination of the reference values for product yield and loading factor are reported in Chapter 2. The considered values and application parameters i.e. the surface to clean and the quantity of product to apply are reminded by Table 3. For each experiment, the calculated mass of product is evenly drizzled or sprayed on a stainless-steel surface of 0.05 m² placed at the center of the 1 m³ experimental chamber. Once the simulation of the cleaning activity is completed, the experimental chamber remains closed during the whole emission monitoring. For each cleaning product, a set of three experiments is performed in order to evaluate the repeatability of the experimental protocol. Additionally,

during the experiment, t = 0 corresponds to the time when the application process of the cleaning product is completed inside the chamber.
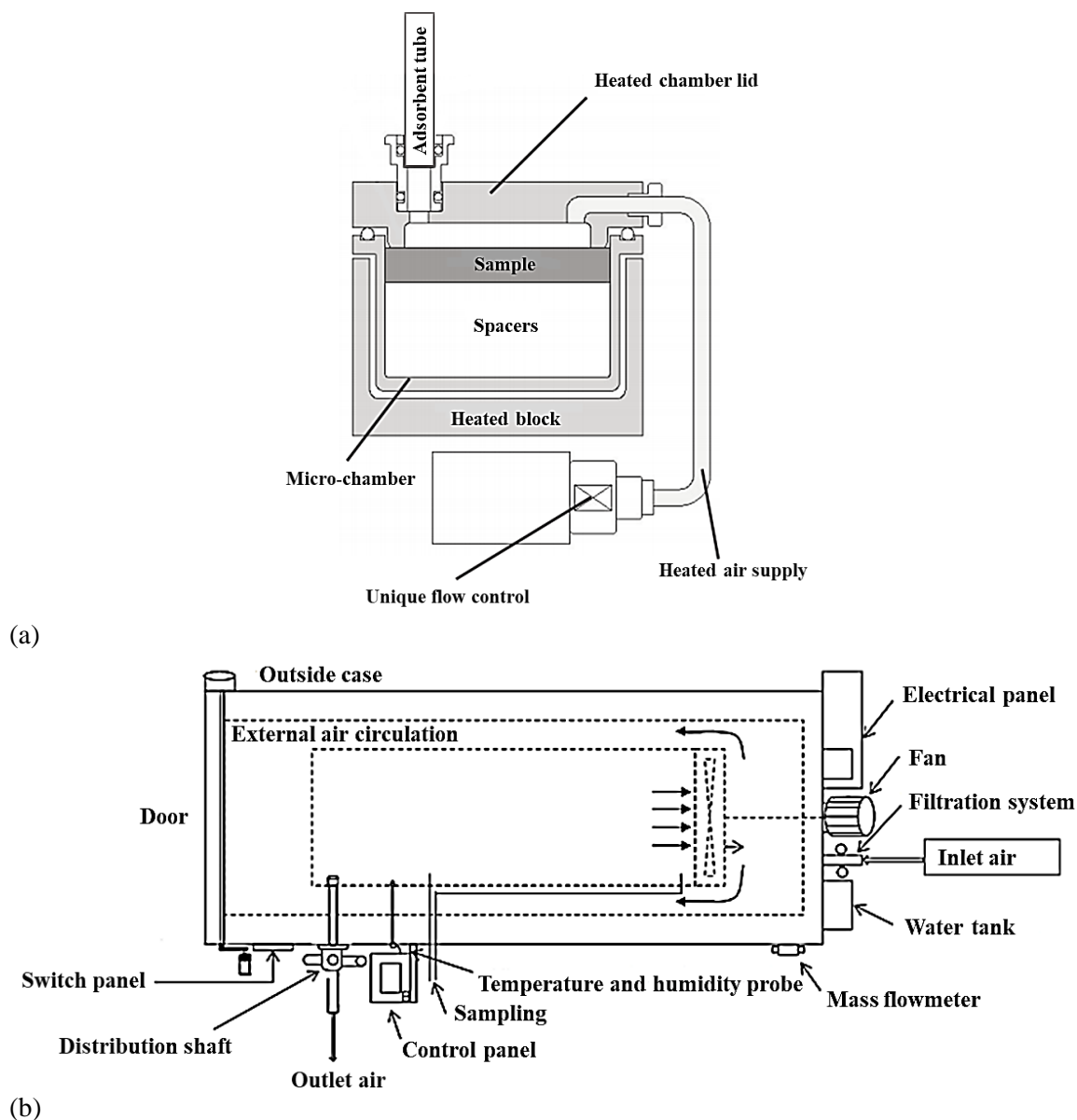
Figure 1. (a) Schema of the micro-chamber M-CTE-120 Markes International®. (b) Scheme of the 1 m^3 emission chamber Vötsch VCE1000 Classic.

Sampling and analytical parameters / Regarding the analytical methodology, the temporal dynamics of TerVOC and OVOC concentrations inside the experimental chamber are monitored using an off-line device that allows their quantification under an long temporal resolution. Several preliminary tests are performed in order to optimize the

experiment duration depending on the involved cleaning product. From these preliminary results, the duration of a typical emission experiment is established at 5 hours.

Off-line samplings are performed using Tenax TA® cartridges and 2, 4-dinitrophenylhydrazine (DNPH) impregnated silica Supelco cartridges (Model: Xposure) according to ISO 16000-3 and 16000-6. Samplings are performed using a pump (KNF®) connected to a mass flow controller under specific flow rates and duration times specifically optimized for each type of cleaning product tested, as described in Table 4.

The analytical protocol to quantify TerVOCs concentrations are the same than the one reported in section 1.3 for the gas-transferred concentration determination. In contrast, derivatized carbonyl compounds (OVOCs) are extracted from DNPH cartridges with 3 mL acetonitrile and analyzed with a Thermo Dionex Ultimate U3000 liquid chromatograph. Compounds are eluted on Acclaim RSLC Carbonyl column (2.1 x 150 mm) and detected by RS variable wavelength UV absorption. Calibration of the carbonyls are achieved using high purity certified standard solutions (Aldehyde/Ketone-DNPH Stock Standard-13). Considering these conditions, the typical detection limit for carbonyl compounds is 0.01 ppb.

Table 4. Experimental protocol and optimized parameters for off - line sampling systems.

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

*Experimental parameters that have been optimized

3.   RESULTS AND DISCUSSION

3.1   *Chemical composition: terpene (TerVOCs) content of natural organic certified cleaning products*

The terpene contents of the six selected cleaning products are reported in Table 5. Note that for the identified compounds, predominant terpenes are written in bold. The most frequently identified terpenes are limonene, linalool, and α-terpineol being present in all the evaluated cleaning products. Compared to the literature, five studies have assessed the presence of fragrance chemicals in cleaning product formulations on the European market. Among 121 cleaning products evaluated, limonene and linalool are reported with the highest occurrence rates: respectively 84.2 % and 60.8 %. [14], [22], [25], [33], [34] Indeed, worldwide, the most used essential oils in household products formulation are citrus oil, lavender oil, pine oil, eucalyptus oil, tea tree oil and rose oil. In contrast, several terpene derivatives, such as camphor and bergamol found in SC-1 and KC-2, are more rarely reported. [35]–[38]

Total TerVOCs / Regarding the total terpene contents in household products, mass concentrations are evidenced to be extremely contrasted, ranging from 37.6 ± 2.5 µg/g (of product) to 3180.7 ± 200.5 µg/g. Nevertheless, these concentrations only account for 0.01 % to 0.17 % w/w of the total composition of selected products, as notice in Table 5. Sarwar et al. [21] reported the quantification of TerVOCs in four different categories of cleaning products, namely floor cleaners and general purpose cleaners. The major detected terpenes were α-pinene, β-pinene, 3-carene, limonene and α-terpinene with individual mass concentrations ranging from 0.2 % w/w to 2.0 % w/w for individual compounds. Indeed, industrial formulations of cleaning products do not exceed 5.0 % w/w of fragrance chemicals. [9], [25], [35], [39]

Individual TerVOCs / Among the selected cleaning products, a total of 27 terpene molecules are detected: (i) 14 monoterpenes, (ii) 8 terpene alcohols, (iii) 4 terpene derivates, and (iv) 1 sesquiterpene. Per product, the diversity of odorous chemicals might vary from 6 to 20 different species. Furthermore, all tested products have evidenced a correlation between the predominant terpene detected and the essential oil indicated by the manufacturer, except for KC – 1. Indeed, this product is specified to be formulated with lemon oil; however, the major terpene is α – terpineol instead than limonene. Comparing the product categories, limonene is verified to be the predominant terpene contained in the multi-use cleaners, both fragranced with citrus oils. While for kitchen cleaners tested, the main detected terpene varied from one product to another: eucalyptol for KC – 2 and α-terpineol for KC – 1. Concerning the mass concentration of terpenes,

the predominant species among the selected products are: limonene, linalool, eucalyptol, and α – terpineol. These molecules are detected at diverse concentrations ranging from 10.0 ± 0.3 µg/g to 2230.8 ± 71.4 µg/g.

Table 5. Liquid composition (expressed in µg of terpene per g of product: µg/g) of the six selected cleaning products, and their occurrence rate from the literature. NB: the mass concentration of the predominant TerVOCs of each cleaning product is written in bold.

Identified Terpenes	Mass of individual TerVOCs (this work) Mass ± SD (µg/g)						Occurrence rate (%) from literature [121 cleaning products] [14], [22], [25], [33]
	MC -1	**MC -2**	**SC - 1**	**KC - 1**	**KC – 2**	**GC - 1**	
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
Others 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**	

In addition, the chemical composition of a cleaning product might widely vary mainly depending on their usage purpose and their diffusion mode. For instance, when a cleaning product emphasizes a disinfectant property, complementary chemicals are added to their formulation to suppress or inhibit microbial activities. Then, in the case of so-called "*green*" cleaning product formulations, specific essential oils might be added in order to increase the concentration of terpene molecules with an antibacterial and antiseptic performance, such as eucalyptol and geraniol. Therefore, no correlation is evidenced between the diffusion mode of the selected cleaning products and their total mass concentration in terpene molecules. This point is suggested to be associated to the intrinsic industrial formulation in order to accomplish a particular performance.

Finally, the contrasted terpene contents point at the question of the intrinsic emission potential of the cleaning products. The diversity in the volatility of the constituents interrogates on the emission dynamic associated to the cleaning activity. Does a high terpene content necessary imply high emission levels? What is eventually the effective amount of terpenes to be transferred to the gas phase? What is the impact of the matrix of the cleaning product on that gas phase transfer? How long is the user impacted by the emission?

Therefore, in order to provide key elements for these questions, a screening of their ability to be transferred from the liquid to the gas phase, defined in the frame of this work as the gas-transferred concentration, is the first insight to understand the emission potential of each cleaning product.

3.2   *Gas-transferred concentration Vs. Liquid composition*

<u>Total gas-transferred concentration /</u> The total gas-transferred concentration of terpenes corresponds to the sum of the concentrations of terpenes, subsequently expressed in $\mu g/m^3$, collected at the outlet flow of the µ-chamber set-up. It assesses the ability of a given cleaning product to release terpenes in the gas phase. Comparing the six selected products, the total gas-transferred concentrations are highly contrasted ranging from 125 ± 15 to $85\,225 \pm 5\,500\ \mu g/m^3$. More precisely, the glass cleaner GC – 1 is evidenced as the less emissive product, with a total gas-transferred concentration of $125 \pm 15\ \mu g/m^3$. While, the gas-transferred concentrations of the surface cleaner SC – 1 and the kitchen cleaner KC – 2 are observed to be higher by 2 orders of magnitude. These two products transferred analogous terpene total concentrations to the gas phase, considering the standard deviation, with $85\,000 \pm 5\,500\ \mu g/m^3$ and $81\,000 \pm 12\,000\ \mu g/m^3$ respectively.

Figure 2 reports the correlation between the total terpene mass concentrations in the liquid phase of the selected products ($\mu g/g$) and their total gas-transferred concentrations of TerVOCs ($\mu g/m^3$). As evidenced in Figure 2, comparing both multi-use cleaners (MC – 1 and MC – 2), volatile concentrations reach equivalent levels ca. $27\,000\ \mu g/m^3$. However, their

total terpene mass concentrations in the liquid phase are highly contrasted with a concentration ratio of 2:1. Additionally, similar observations are done between the surface cleaner SC – 1 and the kitchen cleaner KC – 2. Their gas-transferred concentrations reach analogous values, around 80 000 µg/m³, considering the standard deviation values. Nevertheless, the kitchen cleaner KC – 2 is characterized by a terpene content of 3200 ± 270 µg/g; while the terpene content of the surface cleaner SC – 1 reaches half of this value. In contrast, the two household products (SC – 1 and MC – 1) evidence equivalent terpene mass contents, but lead to a ratio of gas-transferred concentrations of 3. Consequently, no direct correlation is evidenced between the total terpene mass content and the total gas-transferred concentration among the six selected products. Therefore, the estimation of the amount of terpene emitted by a given product cannot be deduced from its liquid content of terpenes and emission tests are required.
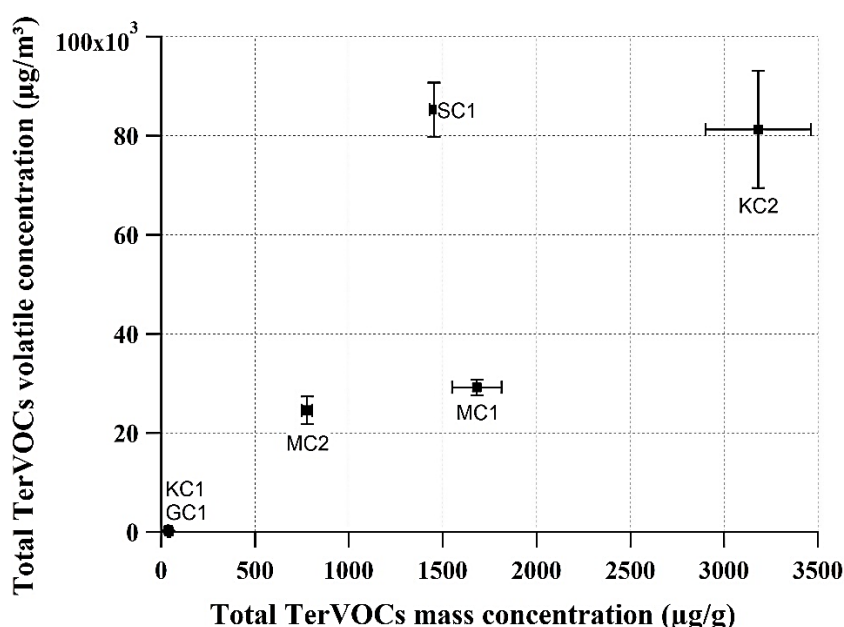

Figure 2. Total TerVOCs gas-transferred concentration from micro–chamber testing (µg/m³) as a function of the total terpene mass concentration in the liquid form (µg/g) for the six selected cleaning products. (T = 40 °C, dry air flow = 50 mL/min, micro–chamber volume = 44 mL).

Individual gas-transferred concentrations / Only 19 terpene molecules from the 27 TerVOCs contained in the cleaning products are identified in the gas phase from micro-chamber evaluation. Nevertheless, the number of emitted terpenes might vary from 1 to 14 per cleaning product. Table 6 gathers information associated to (i) volatile/liquid fraction ratio (V/L) per cleaning product and (ii) various physical and chemical properties of individual terpene molecules. For discussion purposes, in this work, V/L concentration ratio is defined as the ratio among the individual gas-transferred concentration and the mass fraction in the liquid phase per identified terpene. In this regard, when V/L value is higher

than 1 for a compound *X*, it is suggested that the respective molecule present a higher ability to be transferred from liquid to gas phase compared to another molecule with a V/L value lower than 1.

Among physical and chemical properties of TerVOCs, the saturation vapor pressure 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. Vapor pressures (VP) have been experimentally determined in literature for the most of TerVOCs, corresponding values are gathered and displayed in Table 6. Terpenes report highly varied vapor pressures ranging from 0.3 Pa for α-terpineol to 599 Pa for α-pinene.

As shown in Table 6, α-pinene reports a V/L ratio higher than 1, ranging from 1.15 to 1.39, among the cleaning products in where this molecule is detected. That suggests a significant ability of α-pinene to be transferred to the gas phase independently of the solvent matrix composition. This observation could be related to its acute vapor pressure at 599 Pa, verified as the highest value among all identified terpenes. In contrast, for the other compounds, the relation between VPs and V/L ratios is not predictable. Particular behaviors are observed: (i) linalool, attesting a low volatility (VP values lower than 30 Pa), evidences highly contrasted V/L ratios values depending on the cleaning product. These values are ranging from 0.47 for MC – 2 to 1.17 for KC -2 and (ii) β-pinene, which verifies analogous chemical and physical properties from α-pinene, evidences V/L ratios once again with a wide variation from 0.49 for MC – 1 and 2.83 for KC – 1. Thus, for most terpene species, the transfer to the gas phase is not exclusively driven by the intrinsic properties of the pure molecule, but more by the solvent medium properties. It is known that the proportion of organic solvent or the presence of texturing agents in the aqueous media of the cleaning product play a key role in the flavor release. [40] Interactions between flavor compounds and matrix were highly studied in the field of food sciences. [41] The determination of a gas-liquid partition coefficient, determined under equilibrated conditions, specific to each couple VOC/matrix would permit to explain the various observed behaviors. [42]

In consequence, terpene emissions from essential-oil-based household products cannot be directly predicted from their liquid composition. Instead, the released concentrations of TerVOCs species contained in this type of products could be governed by the contribution of three main key drivers: (i) their inherent volatility, (ii) the chemical affinities developed among TerVOCs and other compounds in formulations and (iii) the mass concentration of terpenes at the liquid phase. Finally, micro-chamber tests allowed the screening of major emitted compounds transferred to the gas phase. Nevertheless, this experimental approach does not substitute emission testing using experimental chambers of

conventional size and under realistic conditions of temperature, humidity and air velocity. In the further section, primary emission of three representative cleaning products of each product category among the six selected products is performed.

Table 6. Comparison among total TerVOCs gas-transferred concentrations (T = 40 °C, dry air flow = 50 mL/min, micro-chamber volume = 44 mL) and total TerVOCs mass fractions at their liquid form per cleaning product, individually. NB: Physical and chemical properties of identified terpenes (vapor pressure, 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 literature (Pa) [29]–[34]	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 literature; *: Vapor pressure nearly 0 Pa

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

For the assessment of the primary emissions associated to the application of essential-oil-based products, one representative product from each category is selected. This selection is based on the previously discussed results regarding the correlation between the gas-transferred concentration and the liquid content of TerVOCs. Indeed, the cleaning product of each category attesting the highest ratio between its gas-transferred concentration and its liquid content of TerVOCs are selected. Therefore, products investigated and discussed in this section are (i) the surface cleaner SC – 1, (ii) the multi-

use cleaner MC – 1, and (iii) the kitchen cleaner KC – 2. Regarding the diversity of the species emitted, a total of 7 out of the 22 TerVOCs contained in the three cleaning products are identified in the gas phase (Figure 3b).

Profiles of total TerVOCs / The temporal profiles of the total TerVOC concentrations monitored for SC – 1, KC – 2 and MC – 1, reported in Figure 3a, are characterized by the three typical phases of a transient emission process: (i) a sudden increase of the total TerVOC concentration confirming the rapid transfer of terpenes from the applied cleaning product layer to the gas phase until a peak concentration is reached (< 30 minutes) , (ii) a primary decreasing trend referred to the gradual exhaust of the VOC source and to the removal of VOCs from the experimental chamber, (iii) a final decreasing phase exclusively associated to the evacuation of the gas phase terpenes by the air exchange and the possible deposition on the inner walls of the experimental chamber. Note that along any of the three phases, possible losses of terpenes on walls have to be considered. As observed in Figure 3a, SC – 1 and MC – 1 evidence analogous values of peak total TerVOC concentration at ca. 300 ppb within the first half-hour after application considering their respective standard deviations. Regarding KC – 2, its maximum emitted level of TerVOCs is lower and reaches ca. 160 ppb at analogous peak time than the other two cleaning products. In contrast, considering the total terpene composition in the liquid phase (section 2.1), KC – 2 is characterized by the highest mass concentration of TerVOCs among the three cleaners with 3200 ± 200 µg/g. This results confirms the absence of correlation between the liquid content of terpenes and the resulting concentrations of terpenes in the 1 m^3 emission test chamber. Based on the investigated products, the temporal emission dynamics of essential-oil-based cleaning products cannot be directly predicted from their liquid composition.

In comparison with other indoor sources of terpenes, emission from a wood based building product evaluated by Harb et al. [46] verified that the peak concentration of total TerVOCs detected under real conditions reached ca. 80 ppb. In agreement with this study, S.K. Brown [47] identified similar emitted concentrations from a 16-mm pine softwood particleboard. As a consequence, cleaning activities may transiently exceed wood-based materials regarding the contribution to indoor total concentration of TerVOCs. But emissions from cleaning products are characterized by different temporal dynamics compared to indoor material emissions. Actually, they mostly act as punctual or transient sources of pollutants. Thus, the cumulated exposure to TerVOCs from cleaning products is directly related to the cleaning occurrences and the human factor. This behavior contrasts with sources constituted by wood-based materials which mostly act as long term and continuous emission sources.
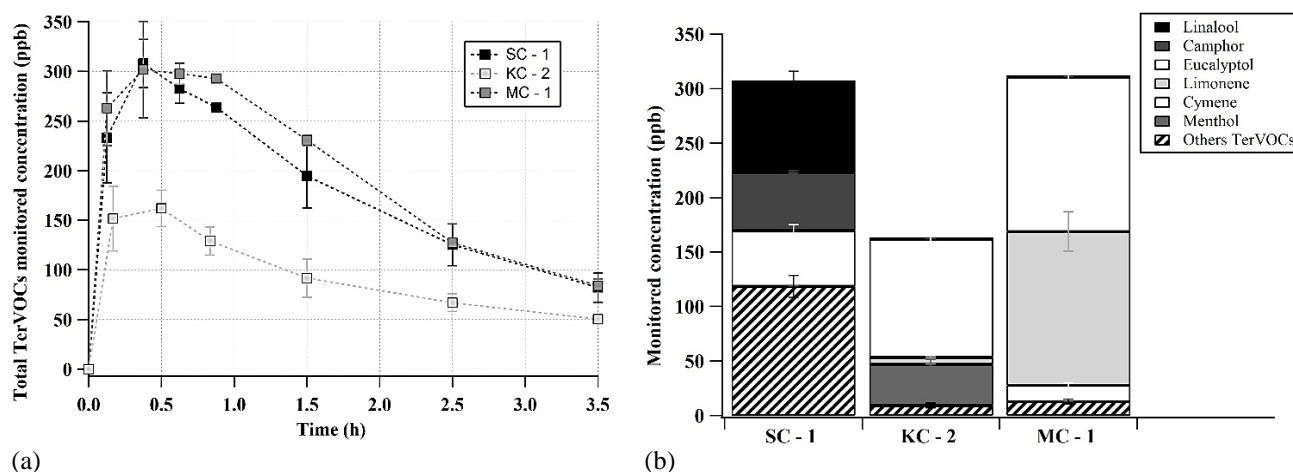
(a)

(b)

Figure 3. (a) Temporal evolutions of the total TerVOC concentrations during the cleaning activity with SC – 1 (black symbols), MC – 2 (dark grey symbols) and KC – 2 (light grey 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.

Individual profiles of TerVOCs / Individual emissions of 9 monoterpenes, 7 terpene alcohols, 1 oxygenated terpene, and 1 sesquiterpene have been quantified. The SC – 1 is confirmed to be characterized by the largest diversity of terpenes since it emits a total of 16 different terpene molecules. Figure 4 reports the individual profiles for the terpene species predominantly emitted. The individual profiles are characterized by the three same phases observed in the emission profiles of total TerVOCs (Figure 3a). Nonetheless, some differences are observed from one tested product to another.

For the surface cleaner SC – 1, the predominantly released terpenes are: linalool, eucalyptol and cymene. Peak concentration levels of these TerVOCs are respectively monitored at 85 ± 10 ppb, 50 ± 5 ppb and 55 ± 5 ppb. In addition, their cumulated concentration values account for 47.6 % of the peak concentration of the total TerVOCs. Interestingly, regarding the emission kinetics, in spite of the fact that these compounds show contrasted physical and chemical properties (Table 6), their peak concentrations are reached at equivalent emission times, i.e. nearly 25 minutes after the cleaning activity is completed (Figure 4a). This observation suggests that other determinants, different from the individual physical and chemical properties of the TerVOCs, are involved in the emission process of TerVOCs during the cleaning activity. For instance, in the liquid composition of the SC – 1, a significant concentration of ethanol has been evidenced at 70 % w/w. In general, surface cleaners contain in their formulation water and various water-miscible solvents i.e. alcohols and

glycols, included for (i) enhancing the "fast-dry effect" and (ii) to dissolve grease in the cleaned surface. [1], [6], [39], [48] The presence of ethanol in the composition of surface cleaner SC – 1 is probably linked to that purpose and may accelerate the emission kinetics of TerVOCs due to the fast drying rate.

Regarding the kitchen cleaner KC – 2, major terpenes emitted are eucalyptol, menthol, and limonene as reported on Figure 4b. Their respective peak concentrations reach up to 110 ± 10 ppb, 38 ± 5 ppb, and 7 ± 1 ppb; contributing to 96 % w/w of the total TerVOCs peak concentration. In the case of the KC – 2, analogous times are observed for the peak concentrations of eucalyptol and limonene at ca. 15 minutes (Figure 4b). Noticeably, the emission profile of eucalyptol is characterized by a sharp increase of its concentration with a subsequent clearly marked maximum concentration at ca. 15 min. The emission kinetic of eucalyptol contrasts with the one of menthol with a peak concentration at ca. 30 minutes after the cleaning product is applied. The lower vapor pressure of menthol at nearly 18 Pa may explain this different behavior.

In the case of the multi-use cleaner MC – 1, limonene, eucalyptol and cymene are the main terpenes identified in the gas phase. As shown in Figure 4c, limonene and eucalyptol are characterized by peak concentrations within the same magnitude at ca. 145 ppb. Nonetheless, besides their similar vapor pressure, several differences can be noticed in the emission profiles of these terpenes. For limonene and eucalyptol, they are characterized by a sharp increase up to their peak concentrations within 8 minutes. For both terpenes, 90 minutes after the cleaning activity is finished, their gas phase concentrations still account for more than 60 % of their peak concentrations. This behavior suggests that beyond the intense emission within the first minutes after the cleaning activity, their emissions may occur on longer time scale. This point can be deepened and evaluated through the determination of individual TerVOC emission rates as a function of time. On the contrary, cymene presents a concentration profile characterized by a broad emission peak attesting of a weakly marked peak concentration, but possibly an emission on longer time scales.

Comparing the emission dynamic of eucalyptol (commonly released among all cleaners), a rapid emission kinetic is observed for MC – 1 reaching its maximum emitted concentration within the first 8 minutes after its application. The peak concentration emitted of eucalyptol from this product (MC – 1) is higher compared to the other tested products, it is observed at 140 ppb; however, eucalyptol is only contained at ca. 424 µg/g in the liquid form. In contrast, in comparison with KC – 2, a slower dynamic of emission for the same terpene molecule, eucalyptol, is noticed. Indeed, the positioning time of its peak concentration is at nearly 23 minutes after the application of the kitchen cleaner. Nevertheless, this product

contain the highest concentration of eucalyptol at its liquid phase at ca. 2230 µg/g but instead its maximum emission concentration is evidenced at only ca. 110 ppb. This observation suggest that the liquid concentration of individual terpene molecule is not the only key factor driving the transfer from the liquid to the gas phase. In order to assess the emission process of individual TerVOCs from each cleaner, the mass emission rate is calculated from the concentration profiles and assess in the further section.
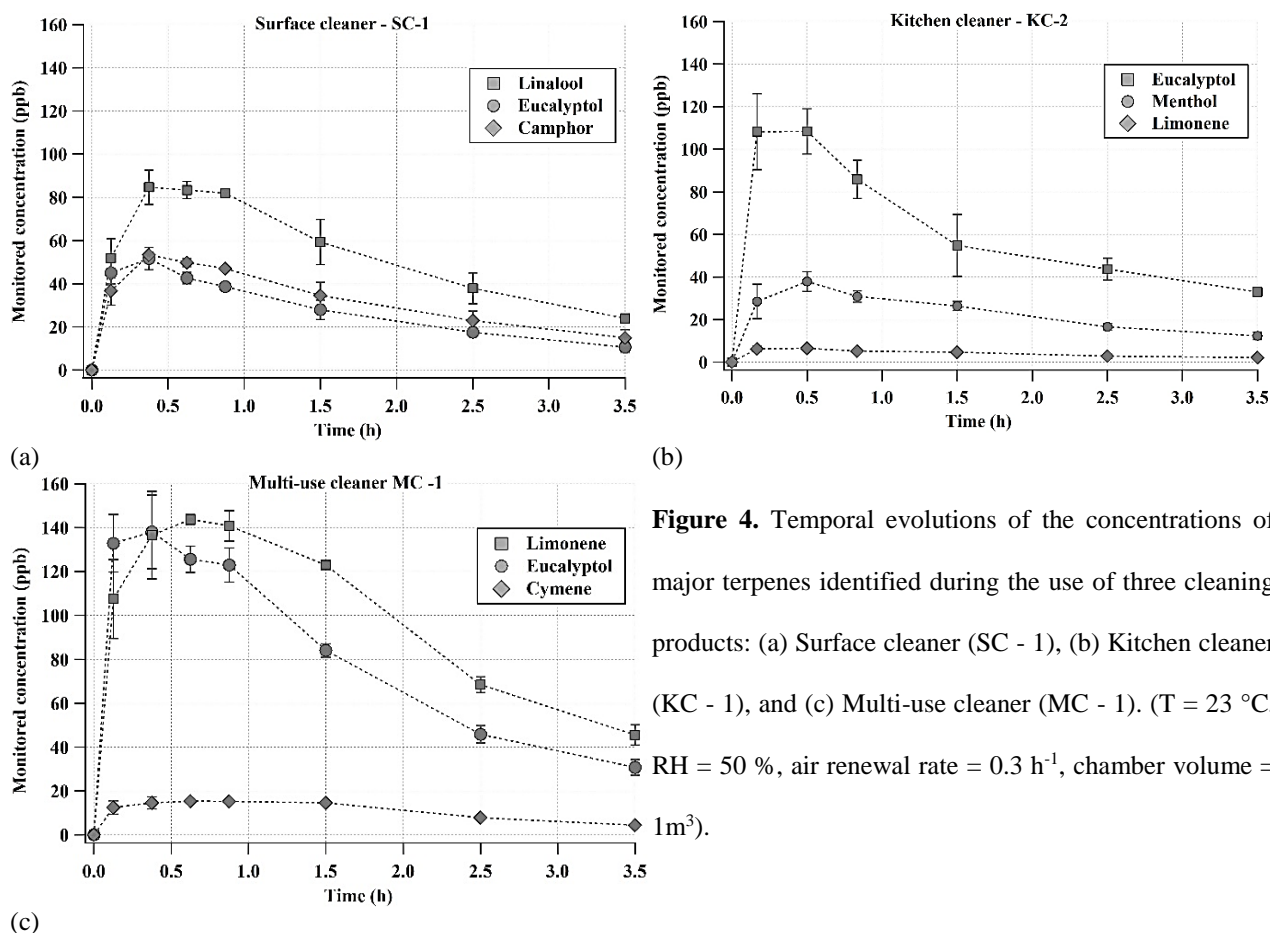

(a)

(b)

(c)

Figure 4. Temporal evolutions 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) Multi-use cleaner (MC - 1). (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1m^3).

3.4 Estimation of TerVOC mass emission rates from their monitored concentration profiles

In this work, the emission rate of a cleaning product is defined as the mass of volatile compound emitted per gram of applied product per time unit at a given time *t* from the beginning of the emission. The estimation of the mass emission rate of a source is of major importance since: (i) it provides key information to understand and describe the emission process of an indoor source of pollutants, (ii) it is a representative parameter that can be extrapolated to real 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, among them ventilation, emission sources, and pollutant transformation such as uptakes or chemical interactions. Same phenomena could be observed in an emission test chamber. Therefore, it is required to address the fate of pollutants considering the contribution of each process distinctively. In a typical indoor environment, the concentration variation of an individual VOC is driven by the mass conservation equation reported in *Eq. 1*.

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

Eq. 1

In controlled environments, such as the emission chamber used for our experiments, several processes encompassed 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 is continuously monitored during experiments; the ozone level remains lower than the detection limit of the ozone analyzer (0.4 ppb) for all experiments, suggesting that the contribution of ozone-induced homogeneous and heterogeneous reactivities can be neglected. Harb et al. [49] and Haghighat et al. [50] evidenced that stainless steel is the most widespread chamber material in reviewed publications due to its inert properties. Indeed, the use of stainless steel avoids surface reaction of deposited TerVOCs with the inner material of the chamber. This is supported by the fact that no other terpenes than the ones monitored in the liquid composition, and no other carbonyls than the one reported in the literature have been evidenced in the gas phase of the experimental chamber. Therefore, surface reactivity on stainless steel is disregarded. Additionally, desorption phenomena are endothermal processes. Then, in a temperature-controlled environment, sorption processes of TerVOCs are suggested to be irreversible and desorption is considered as negligible.

Finally, along the emission experiments involving cleaning products, the resulting TerVOC concentrations in the emission test chamber are predominantly contributed by (i) the air exchange, (ii) the emission rate of the TerVOC sources, and (iii) their loss on the inner walls of the chamber (k_D). Therefore *Eq. 2* can be considered to describe the resulting pollutant concentration [X] in the experimental chamber. It clearly appears that the determination of the TerVOC emission rates from their monitored concentration profiles requires to sort out the contribution of their respective air exchange rates and deposition rates.

$$\boxed{\frac{d[X]}{dt}}_{\substack{\text{Concentration}\\\text{profile}}} = -\boxed{\frac{d[X]_{Out}}{dt}}_{\text{Air Exchange}} + \boxed{\frac{d[X]_E}{dt}}_{\substack{\text{Pollutant}\\\text{source}}} - \boxed{\frac{d[X]_{Dep}}{dt}}_{\substack{\text{Deposition on}\\\text{surfaces}}} \quad Eq.2$$

Air exchange / The air exchange induces the removal of the species X by the air renewal system of the emission test chamber. It is characterized by the air exchange rate k_{AER} expressed in h^{-1}. It can be calculated considering the ventilation flow and the volume of the chamber or experimentally determined using a relevant tracer gas. Based on the inlet ventilation flow of our emission test chamber, k_{AER} is set to 0.3 h^{-1} for all experiments.

$$-\boxed{\frac{d[X]_{Out}}{dt}}_{\text{Air Exchange}} = -k_{AER} \times [X] \quad\quad Eq.3$$

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

$$\boxed{\frac{d[X]_E}{dt}}_{\substack{\text{Pollutant}\\\text{source}}} = \frac{\tau(t) \times V_{chamber}}{m_p} \quad\quad Eq.4$$

Deposition on inner surfaces of the emission test chamber / This phenomenon corresponds to the uptake of gas phase TerVOCs on the surface of the stainless-steel chamber. The non-reactive uptake of TerVOCs on indoor materials can be characterized by the deposition rate k_D expressed in h^{-1}. It is also driven by the concentration of the gas phase species X, as reported in *Eq. 5*. Note that k_D depends on the nature of the material and on the VOC, it has been assessed for each set of experiment in order to provide a comprehensive evaluation of this process in the fate of emitted TerVOCs and its impact on the resulting TerVOC concentrations in the gas phase.

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

Eq.5

As finite sources of TerVOCs, fragrance molecules from cleaning product may get exhausted. Thereafter, the drivers of the TerVOC concentrations in the experimental chamber are only: (i) the air renewal, at a known decay rate (k_{AER}) and (ii) the deposition on walls, at a decay rate (k_D) to be calculated. The corresponding situation is described in *Eq. 6* by the linearized form of Eq 2. The air renewal rate is set to 0.3 h^{-1} in our emission test chamber, therefore it can easily be taken into account. The methodology to determine k_D can be illustrated using the temporal profile of linalool emitted by the surface cleaner SC – 1 recalled in Figure 5a. Beyond 1 hour of emission, the profile of linalool reveals that the emission peak is overcome and experimental data inside the square frame (Figure 5a) correspond to the decay of linalool concentration due to the air exchange and its possible loss on the emission chamber walls. Based on Eq 6 this reduced data series is plotted in Figure 5b as ln ([linalool]) as a function of time (h). The linear form attests of the pseudo-first order of the decay process. The slope of the straight line displayed in Figure 5b is contributed by 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}.

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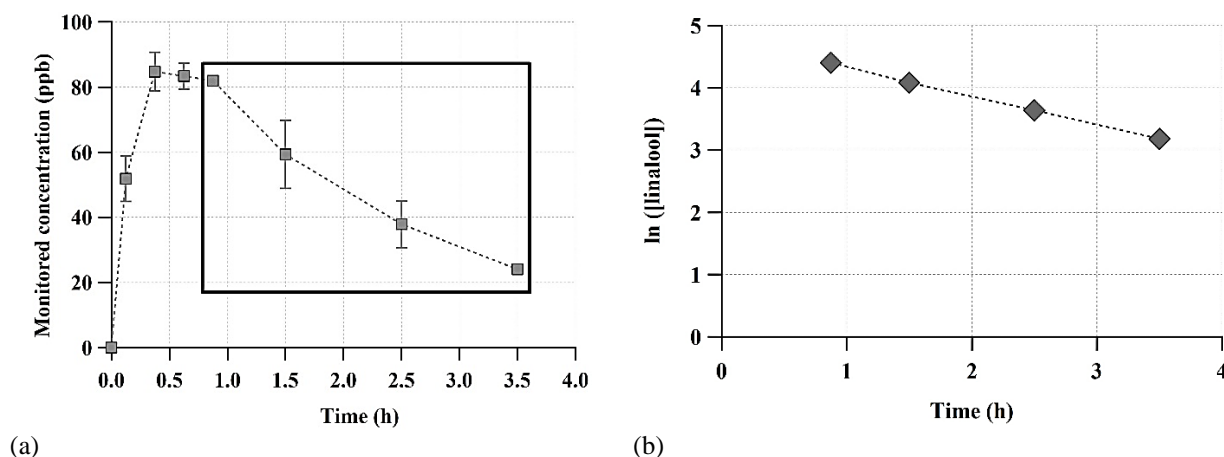

(a)   (b)

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

The deposition rates of the 6 predominantly released TerVOCs have been experimentally determined along the application of the surface cleaner SC – 1, the kitchen cleaner KC – 2, and the multi-use cleaner MC – 2. Table 7 reports the deposition rates (k_D) for these molecules along the cleaning activity with each product. From one terpene to another, the deposition rates range from 0.12 to 0.52 h^{-1}. These values clearly support the fact that the deposition rates of TerVOCs on the chamber walls have to be determined to understand the concentration profiles since they impact the resulting concentrations by the same order of magnitude than the air exchange rate (0.3 h^{-1}).

According to Table 7, it can be pointed out that for the same species, k_D values may differ from one applied product to another. For instance, α-pinene values of k_D are: 0.52, 0.46, and 0.26 h^{-1} respectively for SC – 1, KC – 2, and MC – 1. This behavior is suggested to be associated to the cleaning product formulation. Indeed, among cleaning product constituents, water can be present in formulations at mass percentages ranging from 95 % and 50 %. Subsequently, when a cleaning practice is performed, the relative humidity of the confined environment increases. Springs et al. [51] evidenced that the number of moles of terpenes taken up per unit of surface area tends to decrease with RH, suggesting competitive interactions with water molecules for uptake surfaces. Consequently, the deposition rate (k_D) of fragrance molecules on indoor material could be impacted by the contribution of two main factors (i) the competition for uptake that could be generated among terpenes and cleaning constituents and (ii) the increase of the relative humidity related to the water content of the respective cleaning product. As a consequence, the k_D value for a given terpene might be different from on cleaning product used to another.

Table 7. Comparison of the deposition rate coefficient kD (h^{-1}) of predominant terpenes from the three selected cleaning products (i) the surface cleaner SC – 1, (ii) the kitchen cleaner KC – 2, and (iii) the multi-use 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

Ø = this terpene has not been identified in the chemical composition of the cleaning product at its liquid form

ND: this terpene is not predominantly emitted from the cleaning product; therefore, it is not detected in the gas phase

Determination of the mass emission profiles from the concentration profiles / Finally, the mass conservation equation under our experimental conditions during the cleaning practices is described by *Eq.7, w*here [X] is the concentration of the species X, m_p is the applied mass of 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 the species X related to air renewal and deposition.

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

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. Figure 6 reports the temporal evolutions of (a) linalool emitted from the cleaning activity using the surface cleaner SC – 1 and (b) eucalyptol released from the cleaning activity using the kitchen cleaner KC – 2. The concentrations of linalool and eucalyptol directly monitored in the 1 m^3 emission test chamber are reported using black squares in Figure 6a and Figure 6b. First, this raw profile is corrected by the air renewal rate. It leads to linalool and eucalyptol concentration profiles that would have been monitored if no air exchange was performed in the emission test chamber (light grey square symbols in Figure 6). Second, the latter profiles are corrected by the specific deposition rate of each terpene. The final profiles obtained correspond to the concentration profiles if no linalool and eucalyptol were removed from the chamber gas phase, neither on the chamber walls, nor by air exchange (dark grey circle symbols in Figure 6). As a consequence, the resulting profiles are exclusively contributed by linalool and eucalyptol emissions respectively from SC – 1 and KC – 2. Therefore, the time when terpenes reach steady states indicates the end of their emission processes 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 have been performed for all terpenes detected in the gas phase from the emission along the use of the three cleaners.

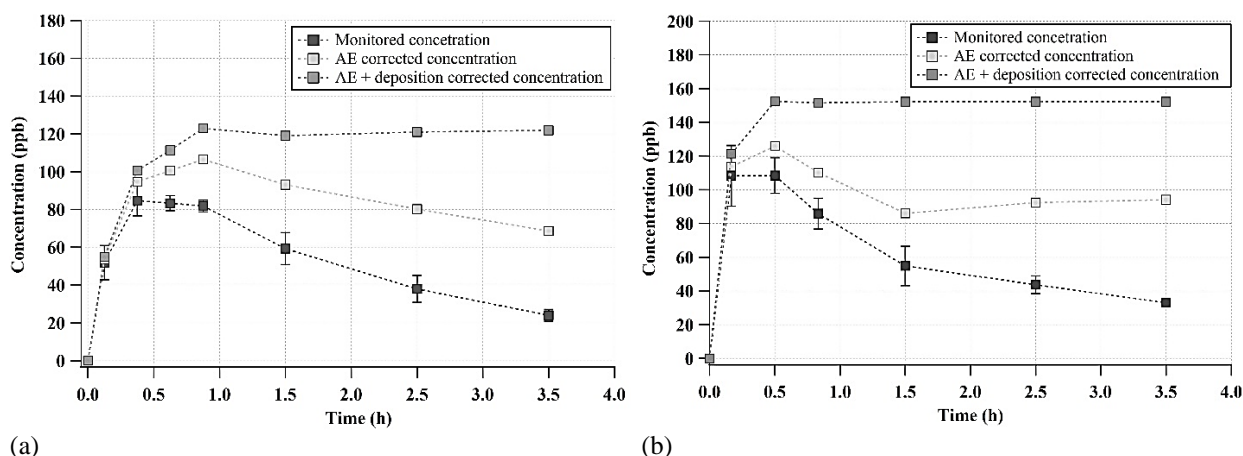$$\tau(t) = \frac{V_{chambre}}{m_{produit}} \times \frac{(C_{i+1} - C_i)}{(t_{i+1} - t_i)} \quad Eq. 8$$

(a)   (b)

Figure 6. (a) Temporal evolutions of linalool (i) monitored concentration (ppb), (ii) air exchange corrected concentration (ppb), and (iii) air exchange + deposition corrected concentration (ppb) during the cleaning activity using the surface cleaner SC – 1. (b) Temporal evolutions of eucalyptol (i) monitored concentration (ppb), (ii) air exchange corrected concentration (ppb), and (iii) air exchange + deposition corrected concentration (ppb) during the cleaning activity using the kitchen cleaner KC – 2. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

<u>Emission rate profiles of individual TerVOCs /</u> Based on *Eq.8* temporal evolutions of the mass emission rates are calculated for each cleaner and for each TerVOC emitted. Figure 7 presents the temporal evolution of the mass emission rates of the three predominant TerVOCs monitored along the use of (a) SC – 1, (b) KC – 2 and (c) MC – 1. The temporal profiles of emission rates allow the determination of (i) the time required to reach the maximum emission rate, (ii) the value of the maximum emission rate, and (iii) the time the emission source is exhausted.

Based on Figure 7, irrespectively of the cleaning product, for a given terpene, the time required to reach the maximum emission rate is analogous: within 8 minutes after the cleaning activity is completed. However, the magnitude of the peak of emission rate of the predominant terpene released is clearly contrasted from one cleaning product to another. This value reaches at 710 ± 15 µg/h of linalool along the use of SC – 1, 1550 ± 90 µg/h of eucalyptol along the use of MC – 1, and 5 000 ± 120 µg/h for eucalyptol along cleaning with KC – 2.

Noticeably, in the case of the kitchen cleaner KC – 2, the emission process is exhausted within 50 minutes for eucalyptol and menthol, and after 30 minutes for limonene. This category of product reports the highest emission rate levels of the three selected products. However, regarding the SC – 1 and MC – 1, both products showed a shorter emission process compared to the kitchen cleaner. Indeed, their total emission process of TerVOCs is evidenced to be completed within only 24 minutes.

Looking at the emission behavior of individual terpenes, eucalyptol is the solely emitted terpene reported for the three tested cleaners. However, its peak emission rates widely vary reaching 620 ± 20 µg/h, $4\,900 \pm 110$ µg/h and 1460 ± 30 µg/h, respectively for the surface cleaner (SC – 1), the kitchen cleaner (KC – 2) and the multi-use cleaner (MC – 1). A similar emission rate variability is observed for limonene identified and emitted from two products: the emission rates are 240 ± 30 µg/h and 1100 ± 80 µg/h respectively for the KC – 2 and the MC – 1.

a)

b)
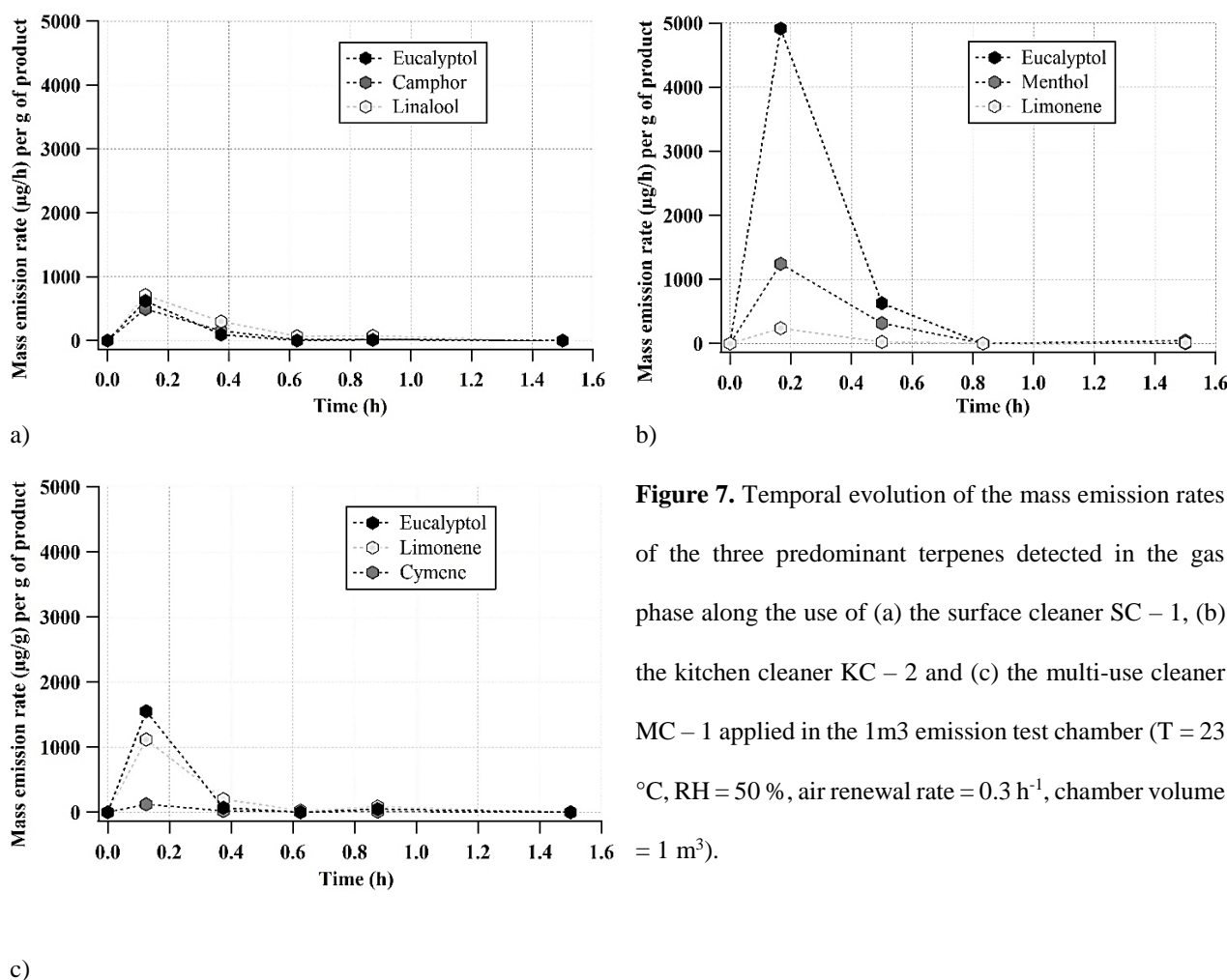
Figure 7. Temporal evolution of the mass emission rates of the three predominant terpenes detected in the gas phase along the use of (a) the surface cleaner SC – 1, (b) the kitchen cleaner KC – 2 and (c) the multi-use cleaner MC – 1 applied in the 1m3 emission test chamber (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

c)

The analysis of the emission rates confirms that, beyond the liquid TerVOC content of the cleaner, the dynamics of the emission process is also driven by (i) the solvent matrix in where fragrance molecules are contained due to chemical affinities that might be generated among species, delaying the emission kinetics, and (ii) the individual volatility of individual terpene molecules itself.

3.5 *Emission of OVOCs from natural cleaning products under realistic application conditions: 1 m³ emission test chamber*

Carbonyl compounds are monitored during each set of emission experiments. Three targeted oxygenated VOCs has been identified and quantified from the application of SC – 1, KC – 2 and MC – 1: formaldehyde, acetaldehyde and acetone. Their individual maximum emitted concentrations vary from one product to another. They range from (i) 6 ± 1 to 18 ± 3 ppb for formaldehyde, (ii) 22 ± 3 to 210 ± 20 ppb for acetaldehyde, and (iii) 18 ± 4 to 108 ± 15 ppb for acetone. Among the identified OVOCs, formaldehyde has been classified in 2016 by the European Regulation as carcinogenic and mutagenic. Additionally, the guideline limit concentration associated to long-term exposures has been established at 9 ppb by the World Health Organization (WHO) in 2010. [3] Consequently, in the frame of this work, formaldehyde is of particular interest because of its toxicity.

Formaldehyde emission profiles from the use of natural cleaning products/ Figure 8 reports the temporal evolution of the emitted concentrations of formaldehyde from the cleaning activities involving SC – 1, KC – 2 and MC – 1. Unlike terpene emission profiles, the temporal evolution of the formaldehyde concentrations observed in Figure 8 are characterized by two particular phases: (i) a marked increase of HCHO concentrations confirming of the rapid transfer of formaldehyde from the product to the gas phase along the first 50 minutes of emission, and (ii) a slower increasing trend for SC – 1 and MC – 1, and a steady state regime for KC – 2. Unlike TerVOC emission profiles, the concentration profiles of formaldehyde do not follow a typical transient emission process. As observed in Figure 8a, the maximum emitted concentration of formaldehyde reach ca. 9 and ca. 16 ppb for the surface cleaner (SC – 1) and for the multi-use cleaner (MC – 1). These values are observed 3.5 hours after the cleaning procedure is finished. In the case of the kitchen cleaner KC – 2, the peak concentration of formaldehyde reaches 6 ppb and it is observed after 0.8 hours; however, this value remains constant in the experimental chamber for at least 3.5 hours after product application. These observations suggest that even after this time span (t = 3.5 h), the emission source of formaldehyde is not exhausted, attesting a delayed emission kinetics which may not solely be related to a primary release of the cleaning product itself. In agreement with literature, Solal et al. [15], [52] assessed the emissions of formaldehyde from 35 consumer products from different categories applied under realistic conditions in the experimental house MARIA. Among 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 have associated to an increase of formaldehyde concentration in the experimental house. The observed concentrations were described by the same two phases attested in Figure 8a (i) a sharp increase of HCHO concentrations confirming of the rapid transfer of formaldehyde from the product to the gas phase and (ii) a slower increasing trend. The maximum concentration levels

reached from 6 to 16 ppb, depending on the category of the product applied. These values were evidenced at 120 minutes after the cleaning procedure was completed.

In order to confirm these suggestions, the emission profile is corrected by the air exchange of the experimental chamber i.e. k_{AER} at 0.3 h^{-1}. The corrected profile is presented in Figure 8b, it leads to the temporal evolution of the concentration of formaldehyde that would have been monitored if no air exchange was performed in the emission test chamber. This corrected profile is solely contributed by the transfer of formaldehyde to the gas phase and the possible uptakes on the inner walls of the experimental chamber. However, the mass emission rate of formaldehyde cannot be calculated by the estimation methodology developed in section 3.4, since the emission source could not be assumed as exhausted and the deposition rate (k_D) cannot be determined. As can be noticed in Figure 8b, the corrected profile of formaldehyde emission from SC – 1, MC – 1 and KC – 2 are characterized once again by two main phases (i) a primary increase of the concentration, suggesting a release linked to a primary emission of potentially contained formaldehyde in the cleaning product and (ii) a linear augmentation of the concentration of formaldehyde. The slope of the linear augmentation of the corrected concentration of formaldehyde is evidenced to vary depending on the cleaning product.

The temporal evolution of the formaldehyde corrected concentration, presented in the Figure 8b, does not correspond to a transitory emission profile but suggests the presence of formaldehyde-releasers in the cleaning product formulation. Therefore, the concentration of formaldehyde might be associated to secondary sources of emission.

The specific concentration dynamics associated to the emission of formaldehyde are suggested to be related with two mechanisms (i) direct (or primary) emission of formaldehyde contained in the cleaning product and, (ii), emission of formaldehyde from formaldehyde-releaser molecules present in the cleaning product formulations. [53] Indeed, formaldehyde-releasers are defined as chemical compounds that decompose to release formaldehyde when dissolved in aqueous solvents. [54]–[56] This process is characterized by an in-situ degradation of non-formaldehyde-containing components, i.e. the self-oxidation of ethoxylated alcohols. Generally, these chemicals are used in consumer products as preservatives, antiseptics, and/or for enhancing their disinfectant performance. The concentration of formaldehyde or formaldehyde-releaser compounds added in product formulations might depend on their use purpose. According to the National Database for Products and Compositions in France (BNPC), it is evidenced that in ca. 78 % of household products, formaldehyde-releasers are included in their formulations as preservative agents, verifying a mass concentration ranging from 0.2 % to 0.3 % w/w. [57]

Groot et al. [56] performed an assessment of formaldehyde and formaldehyde-releaser contained in consumer products of various categories by reviewing the Danish Product Register Database (*PROBAS*). His findings point out that the most important product category containing formaldehyde or formaldehyde releaser are (i) biocide or pesticide, (ii) paints, lacquers and vanishes, and (iii) cleaning and washing agents. Concerning the cleaning and washing agents, 9 different formaldehyde-releaser compounds were identified. Among these chemicals, Bronopol® (*2-brono-2-nitropropane-1, 3-diol*) was evidenced as the most frequently used as formaldehyde-releaser; being detected in 124 out of 275 cleaning products or washing agents. However, the author indicated that a total of 19 out of 42 formaldehyde-releaser compounds could not be found in the *PROBAS*. Similarly, the BNPC in France had evidenced the presence of formaldehyde-releasers in 236 out of 692 cleaning products on the European market. [57]. Additionally, the BNPC published and identified a list of 24 compounds thoroughly confirmed as formaldehyde-releasers, including Bronopol® and Methenamine as the most frequently used among household products. Likewise, Kajimura et al. [55] investigated the formation of HCHO from a common formaldehyde-releaser compound known as Bronopol® from a homemade cosmetic product prepared with ca. 0.1 % w/v of this molecule. This study aimed at correlating the presence of Bronopol® and the respective formation of formaldehyde by head-space analysis. These results verified an increase of formaldehyde concentration with time, reaching at 20 ppm after 10 days, and this level was observed constant over 50 days. Note that this value cannot be compared to our work considering the experimental protocol used.

Regarding the three cleaning products evaluated in this work, the presence of Bronopol® is solely indicated by manufacturers for the multi-use cleaner MC – 1. Its presence may explain the specific emission profile observed for formaldehyde from that product. Nevertheless, according to European legislations for the cleaning product industry, numerous formaldehyde-releasers are not required to be indicated in the product ingredient list. With this lack of information, the link between formaldehyde emission profile observed for the other cleaning products tested and the presence of formaldehyde-releaser in their composition is suggested but has not been confirmed.
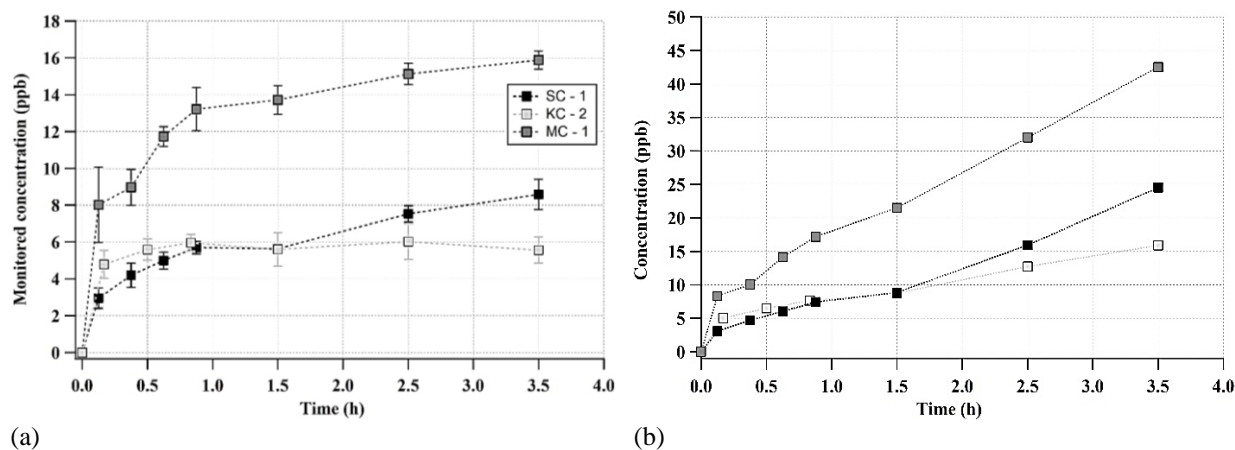
(a)   (b)

Figure 8. (a) Temporal evolution of the concentrations of formaldehyde (ppb) from the use of three cleaning products: (i) Surface cleaner (SC-1), (ii) Kitchen cleaner (KC-1) and (iii) Multi-use cleaner (MC-1). (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3). (b) Temporal evolution of *air exchange corrected* concentrations of formaldehyde (ppb) as a function of time during the cleaning activity along three cleaner (i) SC – 1, (ii) KC – 2, and (iii) MC – 1. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3)

As a consequence, the use of natural cleaning product might generate a continuous augmentation of the indoor formaldehyde concentration; in where the maximum emitted levels might remain in the confined environment for several hours after the cleaning practices are completed. Additionally, formaldehyde-releasers included in consumer product represent a hidden source of formaldehyde of which the consumers might not even be aware, extending its impact on indoor air quality at several tens of ppb.

3.6 *Wrap up on the terpene emissions from cleaning products: From their liquid composition to their mass emission rates*

In this work, TerVOC emissions from the use of 3 cleaners are investigated comparing different scales including their liquid composition, their gas-transferred concentration and their emission under realistic use patterns. This innovative methodology allows the investigation on the emission process of fragrance molecules at different scales for the evaluation of the impact on indoor air quality through an 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 define risk scenarios.

Figure 9 reports the relative abundances, expressed in percentage of the predominant TerVOCs, and in their respective absolute scale regarding (i) the mass concentration detected in the liquid form (μg/g of product), (ii) the volatile fraction associated to the micro-chamber testing (μg/m^3), and (iii) the maximum emission rates per individual terpene (ppb/h per g of product) associated to: (a) the surface cleaner SC – 1, (b) the kitchen cleaner KC – 2, and (c) the multi-use cleaner MC – 1.

If we are interested at first in the absolute values, no correlation can be found between them. As partially commented in the section 3.2, this work confirm that the maximum emission rate of terpene molecules from the use of essential-oil-based cleaning products cannot be directly predicted from their content at the liquid form or from micro-chamber testing. Indeed, micro-chamber results are associated to key general trends, as the predominant emitted terpenes. However, these results should not be considered for realistic emission assessment. Secondly, 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 are conducted under a temperature of 40°C, enhancing the transfer from the liquid to the gas phase.

Thirdly, if we are focusing on specific compounds eucalyptol and limonene, two species with similar vapor pressure (respectively 260 and 219 Pa), substantial differences can be pointed out. In all 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, whatever the solvent matrix of the cleaner. In contrast, for a given cleaning product, limonene contributes (i) in a lower relative abundance to the maximum mass emission rate compared to its content in the liquid phase and (ii) in a higher relative abundance to the volatile fraction if compared to the mass concentration at the liquid form. These observations suggest that the emission of limonene might be more impacted by the solvent matrix included in the cleaning product rather than its volatility (VP = 219 Pa).
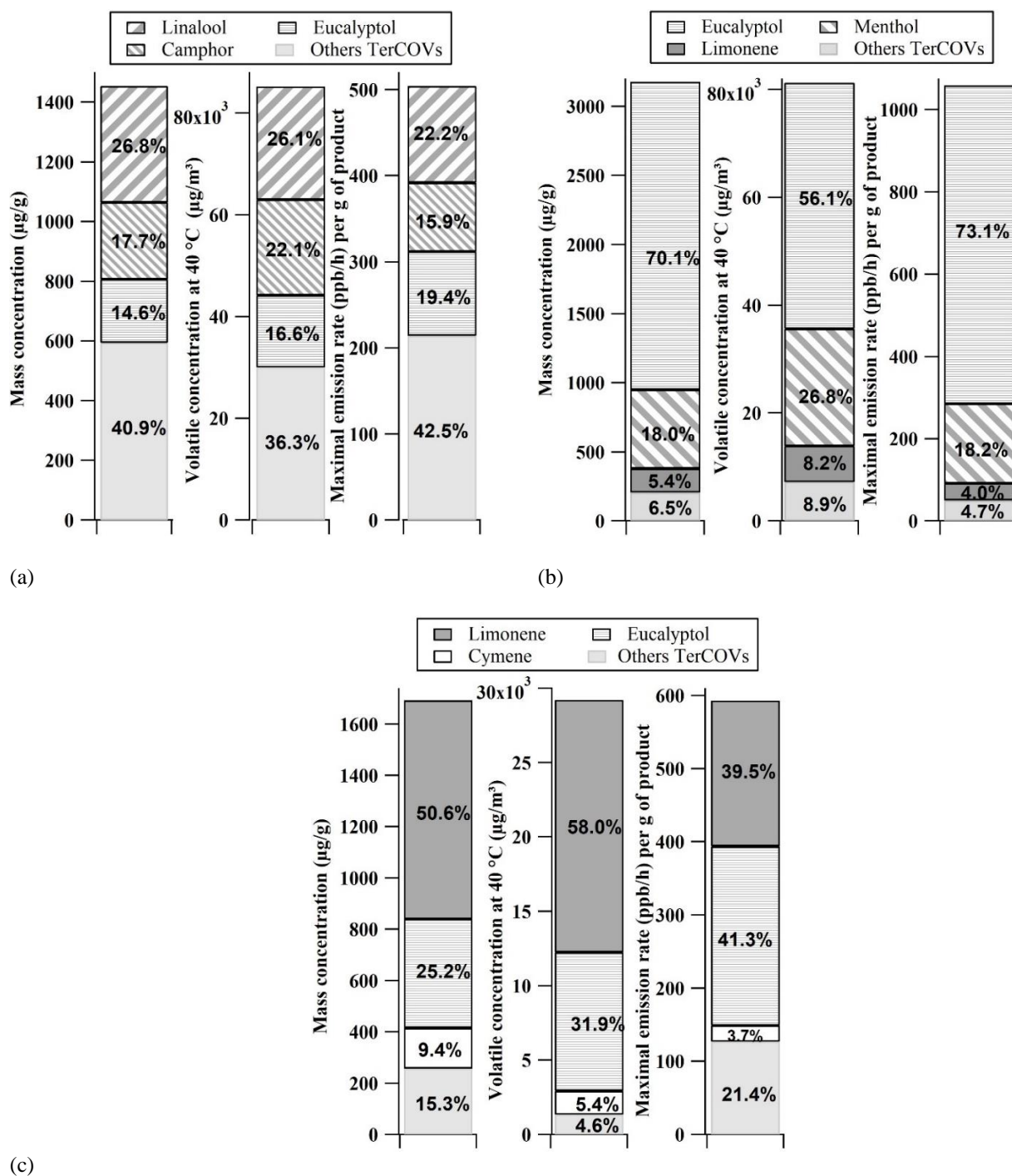
Figure 9. Comparison of the relative abundances among the mass concentration (µg/g) in liquid phase, the volatile concentration (µg/m^3) (T = 40 °C, dry air flow = 50 mL/min, micro – chamber volume = 44 mL) and the maximum emission rate per gram of cleaning product (T = 23 °C, RH = 50 %, air renewal 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 multi-use cleaner MC – 1.

4. CONCLUSIONS AND PERSPECTIVES

This work has evidenced that the largest contributors of terpenes to indoor air are not only recognized, regulated and controlled sources, namely building materials. Indeed, household products have to be seriously envisaged as versatile and high impact sources. These fragrance chemicals classified as allergens responsible of skin irritations, allergic rhinitis, and asthma are primarily associated to the use of cleaning products. [58] Essential-oil-based household products might release concentration levels of several tens to hundreds of ppb of TerVOCs, exceeding exposure limits established by the European Union and the United States [3], [5], [11]. Regarding formaldehyde emissions from the investigated cleaning products, this study has confirmed that these products could represent a hidden source of formaldehyde in confined environments. Indeed, consumers might increase formaldehyde concentration indoors by several ppbs without being aware of it due to the presence of not regulated formaldehyde-releaser compounds contained in these types of products.

Several key factors are confirmed to drive the mass transfer from the liquid to the gas phase of terpene molecules contained in essential-oil-based cleaning products. These key factors are (i) the mass concentration of individual terpenes in the liquid phase, since a correlation between the major contained and the predominantly emitted terpenes is observed for all tested cleaning products, (ii) the solvent matrix included in the cleaning formulation that may generate chemical affinities between terpenes and the cleaner constituents impacting their emission dynamics, and (iii) the volatility of the individual terpene molecules.

Micro-chamber testing does not intend to replace standard emission test chambers, it is a complementary tool that allows the evaluation of the gas-transferred concentrations and to study by fast screening the potentially released TerVOCs from essential-oil-based household products prior to a detailed product emissions characterization. Micro-chamber experiments need to be completed by an evaluation of the effective emissions under realistic conditions in a test chamber, in order to accurately estimate the human exposure to cleaning product constituents and to recommend   application scenarios.

While this study aims to implement realistic scenarios, it is required to recognize that the 1 m^3 chamber exhibit a limitation regarding the application process. Indeed, due to space limitations, real consumer use patterns while performing a cleaning activity could not be faithfully mimic. Without to be wiped, trigger spray products are directly sprayed in the chamber and dispersed by droplets onto the surface and, liquid cleaning products are drizzled in the surface placed at the center of the chamber. The assessment of the TerVOC emissions from essential-oil-based cleaning product under real consumer use patterns in a full-scale room are further investigated. These results are presented and discussed in Chapter 5.

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Chapter 4

Indoor use of essential oils: *Emission rates and impact on air quality*

ABSTRACT

Essential oils have attracted an increasing interest due to their enhanced performance as inhibitor of metabolic functions of microorganisms. Therefore, they have widely been promoted as easy-to-use compounds to improve indoor air quality, and associated to purifying actions. Nonetheless, they are sources of volatile and reactive chemical species. Firstly, this study aims at assessing the emissions of molecules contained in essential oils, in confined environments by employing different diffusion mechanisms under realistic conditions of use using a 1 m³ emission test chamber. Terpenes and carbonyl compounds are typically identified and quantified compounds along the emission of the selected tea tree essential oil. Regarding terpene species, contrasted concentration levels and kinetics are evidenced depending on the mechanism of diffusion, and reported concentration levels can exceed by one order of magnitude the recommended Critical Exposure Level (CEL) established in the frame of the European project EPHEC. Additionally, it is evidenced that the relative contributions of individual terpenes in the gas phase vary all along the diffusion process, for any investigated diffusion device. Therefore, the human exposure to terpene species during the diffusion process of essential oils depends on (i) their volatility, (ii) their liquid mass concentrations, (iii) the physical principle of the diffusion device, and (iv) the advancement of the diffusion process. Then, in order to assess the duration of the impact of essential oil diffusion on indoor air, the mass emission rates of individual terpenes are determined. This study evidences that, depending on the diffusion mechanism, the impact of essential oil diffusion in confined environments varies from 5 hours for electric diffusers up to 60 days for capillarity diffusers. The proposed experimental approach and the results provided in this work are the first insights into the definition of risk scenarios and human exposure to the use of essential oils in indoor environments. The diffusion of essential oil indoors, as a so-called "remediation practice" for facing current indoor problematic, definitely questions the "purifying" nature of this practice form a volatile organic compound point of view.

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1.   INTRODUCTION

The efforts of the scientific community to address indoor air quality challenges considerably increased in the last decade, meanwhile, society has become aware of the health risks related to human contact with hazardous substances in confined environments. Promoted as air "*cleaners*" and "*purifiers*" due to their acknowledged antibacterial, antifungal, antivirus and sedative properties, essential oils have upsurge, as easy-to-implement products to supposedly improve indoor air quality. However, their widespread use and positive perception do not rule out any consequences on indoor gas pollutant levels. Therefore, detailed evaluations of the corresponding emissions under realistic conditions have to be undertaken. [1]–[3].

Essential oils are extracted from plants by water vapor distillation, dry distillation or mechanical extraction methods that do not involve temperature changes [4]. They usually contain more than 100 different chemical substances: mostly odorant and mainly belonging to the terpene chemical family such as monoterpenes, sesquiterpenes, terpene alcohols and terpenoids - hereinafter referred as *TerVOCs* [5], [6]. An essential oil is generally characterized by major compounds with specific relative abundances that provide the typicality of its smell. Therefore, its characteristic odor directly depends on its chemical composition [3]. Nonetheless, the proportions of TerVOCs in essential oils might slightly vary depending on (i) the species of the plant, (ii) the place of growth, (iii) the environmental conditions along growth and (iv) parameters set along the extraction process such as pressure [6], [5], [7].

Depending on their compositions, essential oils can inhibit the metabolic functions of microorganism. Indeed, Inouye et al. [8], [9] exhibited the antimicrobial action of essential oils by gaseous contact. The results suggest that vapor level of 0.1 – 0.9 mg/L in air may suppress the growth of the bacterial pathogens of respiratory infection. Cinnamon bark, lemongrass and thyme oils are evidenced as the most effective. Likewise, tea tree oil (*Melaleuca alternifolia*) has been widely investigated for his acknowledge antimicrobial, anti-inflammatory and antiseptic performances [10]–[13]. Usachev et al. [14] evidenced a strong antiviral efficiency of the vapors of tea tree and eucalyptus oil against two different viruses, praising on the use of essential oils as natural disinfectants for further developments of air treatment technologies and indoor air quality improvement. [15] Tea tree oil is also commonly incorporated to household product, but to our knowledge, no scientific data evidenced its air sanitation action.

Terpene hydrocarbons, presenting low molecular weights and high pressure vapors, are highly volatile molecules that have boiling points ranging from 150 to 260 °C [16]. Monoterpenes result from the condensation of a penta-carbonate unit with two unsaturated bonds, isoprene (2-methyl-1, 3-butadiene). They are composed of 10 carbon atoms and 16 hydrogen atoms that can be linearly or cyclically arranged according to different isomers. These species might have various degrees of unsaturation, leading to highly reactive sites in their structures [6], [17]. To that regard, terpenes are highly reactive towards major oxidants such as ozone, hydroxyl radicals (HO°) and nitrate radicals; being the most common initiators for gas-phase oxidation reactions in indoor and outdoor environments [18]. Consequently, the use of these products in confined environments may contribute to worsening indoor air quality related to the emissions of primary VOCs and the potential formation of secondary products i.e. gas and particulate by-products. In indoor environments, primary VOC emissions have to be addressed first in order to frame the contribution of such sources on indoor air quality.

In spite of these diverse recognized sanitation benefits related to the use of essential oils, several risks associated to their use in indoor environments are still questioned. Can essential oils be considered as a healthy remediation practice for facing current indoor air problematic? The lack of baseline information about the release of hazardous fragrance molecules during dissemination of essential oils in confined environments motivates the present work. To that end, the emission dynamics of TerVOCs related to tea tree oil diffusion have been investigated using three different and widespread diffusers. Then, the consequences of essential oil diffusion on indoor air quality is discussed in terms of diffusion mechanisms, emission rates and duration of impact on indoor air.

2.   EXPERIMENTAL

2.1   Selection of essential oil and diffusers of interest

Essential oil / A benchmark analysis was performed regarding the most widespread essential oils for indoor diffusion. A total of 38 essential oils claiming for air cleaning performances and/or toxin-neutralizing activities were identified. Among them, tea tree oil is selected, not only for its reported sanitation properties, but also for its extensive use and chemical composition. Interestingly predominant terpenes contained in this tea tree essential oils are highly reactive towards indoor oxidants.

Diffusers / Along the benchmark investigation, three contrasted and major diffusion mechanisms have been identified. As a consequence, three representative diffusion devices are selected for this study:

Nebulizing diffuser: it consists in a water-less diffusion device where essential oil is diffused through aerosolized. Hence, an air flow is forced through a small tube, increasing its velocity while the pressure at the exit point is reduced. That difference of pressure induces a suction causing the essential oil to rise upwards in a separate glass tube. Subsequently, a stream of pressurized air hits the oil surface and creates micro-droplets that easily get evaporated. Experiments conducted using that devices are performed at medium nebulization intensity.

Ceramic heat diffuser: this diffuser evaporates essential oil thanks through a soft heat gain. A heating resistance maintains at a small ceramic receptacle a constant and single temperature. In this study, the selected device heats the oil at 68 ± 2 °C. The steady state temperature is reached within 30 minutes after the equipment is turned on. The moderate heating has been evidenced as allowing evaporation of oil, without impacting its chemical composition.

Capillarity diffuser: it consists in a wick-based system that combines the action of wicking and evaporation. In this diffuser, a stick made of beech wood is directly screwed on the essential oil flask, the top of this porous stick is exposed to the air, so that the volatile liquid slowly diffuses from the liquid-air interphase. The dimensions of the stick are L: 6.5 cm x D: 4 cm.

The 3 selected diffusers have been purchased in environmental-friendly retail stores. Note that each diffuser has been operated under technical recommendations indicated on the device. The selection of the presented diffuser is based on the contrasted physical processes of these devices, as a representative selection of the most extensive used diffusers by consumers.

2.2 Characterization of the chemical composition of tea tree essential oil

For the composition analysis of the tea tree essential oil, three samples are diluted in methanol at a concentration of 0.7 mg/mL. Then, 1 µL of each sample is directly injected in a gas chromatograph (GC). The analysis is performed using a 7890A type instrument from Agilent Technologies equipped with a Restek 10189 chromatographic column (105 m x 530 µm, 3µm film thickness) connected to two different detectors (i) a Flame Ionization Detector (FID) used for quantification, and (ii) a Mass Spectrometer (MS) used for identification from Agilent Technologies 5975C inert MSD. Additionally, 22 high purity standards of terpenes from Sigma-Aldrich®, diluted into methanol and gathered into 3 distinct mixtures are used for analytical development (identifying and quantitating compounds). The typical detection limit of this instrument for hydrocarbon VOCs with abovementioned sampling conditions is 0.01 mg/mL.

2.3 Experimental chamber: Simulation of a real case scenario

Emission chamber parameters / Experiments reported in this paper are conducted in an experimental chamber of 1 m^3 of volume (Model: Vötsch VCE1000 Classic) that complies the ISO 16000-9 standards. [19] The chamber is operated under controlled temperature, humidity and air exchange rate (AER). These values are set at 23 ± 1 °C, 50 ± 5 % and 0.3 h^{-1} ± 0.05, respectively. The values for humidity and temperature are established according to the ISO 16000-9. Concerning the air exchange rate, the established value correspond to the percentile 25 reported in French dwellings by the OQAI (Indoor Air Quality Observatory). [20], [21] Detailed characteristics of the experimental chamber are presented in Figure 1. Before loading the test chamber with the selected product, blank measurements are performed to determine background levels of TerVOCs and carbonyl compounds. Note that mean concentration level of blank measurements in the experimental chamber did not exceed standardized values for background concentrations concerning individual VOCs.

For each diffuser, a set of three experiments are performed in order to guarantee the repeatability of the experimental protocol. Essential oil diffusers are introduced and placed in the center of the chamber, 20 drops of the tree tea oil are applied according to manufacturer instruction of each diffuser device in order to simulate a realistic usage. Time zero of the experiment corresponds to the time when (i) the nebulizing and electric diffusers are switched on and off from the outside of the experimental chamber, which remains closed during the measurement campaigns, (ii) or for capillarity diffuser, when the bottle with the diffusing stick is introduced in the center of the chamber. Detailed experimental protocol parameters are described and presented in Table 1.
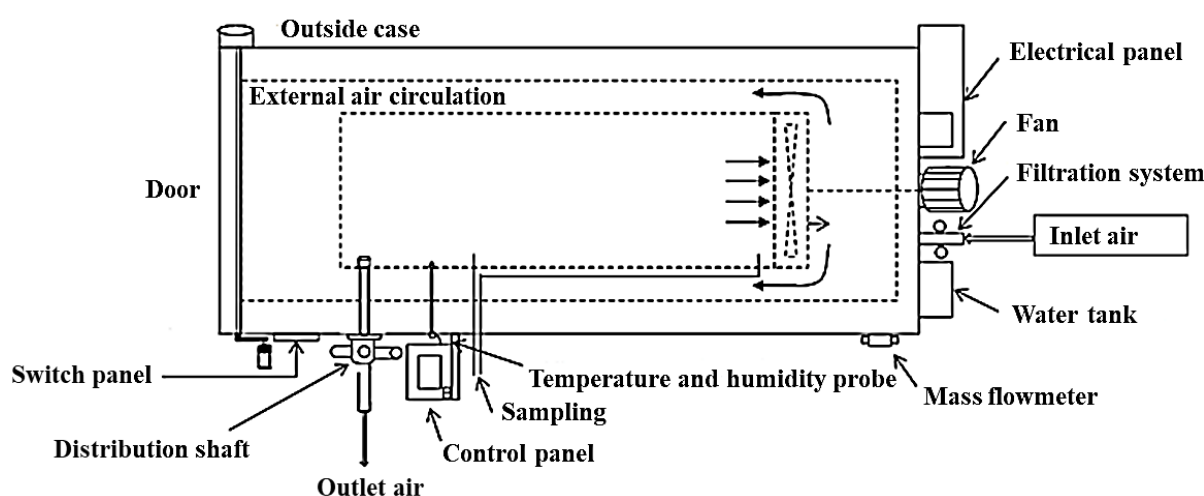

Figure 1. General scheme of the 1 m^3 experimental chamber Vötsch VCE1000 Classic (adapted from [24]).

Sampling and analytical parameters / Regarding the analytical methodology, the temporal dynamic of TerVOCs concentrations at the outlet of the experimental chamber are determined by off-line and on-line samplings with different temporal resolutions. Details concerning the sampling parameter optimized for essential oil diffusion tested are gathered in Table 2.

Off-line measurements are performed on Tenax TA® cartridges and 2, 4-dinitrophenylhydrazine (DNPH) impregnated silica Supelco cartridges according to ISO 16000-3 and 16000-6. [22], [23] Samplings are controlled by a pump connected to a mass flow controller under specific flow rates and duration times specifically optimized for each type of diffuser tested, as described in Table 2.

Sampled Tenax TA® cartridges are desorbed using a PerkinElmer® thermal desorber (Model: Turbo Matrix 350), coupled to a 7890A type instrument from Agilent Technologies Agilent. Desorbed compounds are thermally transferred under helium and refocused on a Carbotrap B/C trap at 5 °C. The gas chromatographic analysis is performed using a Restek 10189 chromatographic column (60 m x 320 µm, 1 µm film thickness) connected to two different detectors (i) a Flame Ionization Detector for quantification, and (ii) a Mass Spectrometer from Agilent Technologies 5975B inert MSD for the identification of compounds. The typical detection limit of this instrument (TD-GC-FID/MS) for VOCs with abovementioned sampling conditions is 0.1 ppb. Calibration is achieved by sorbent tube spiking with home-made diluted mixtures of 27 TerVOCs, individually provided by Sigma-Aldrich®.

Derivatized oxygenated volatile organic compounds (OVOCs) are extracted from DNPH cartridges with 3 mL acetonitrile and analyzed with Thermo Dionex Ultimate U3000. Compounds are eluted on Acclaim RSLC Carbonyl column (2.1 x 150 mm) and detected by RS variable wavelength UV absorption. Calibration of the carbonyls are achieved using high purity certified standard solutions (Aldehyde/Ketone-DNPH Stock Standard-13). Considering these conditions, the typical detection limit for carbonyl compounds is 0.01 ppb.

On-line measurements are performed with a compact gas chromatograph system (C-GC/FID) (Model: Global Analyzer Solutions CGC4) with a Restek-VMS column (15m x 0.32 mm ID, 1.8µm film thickness). It is coupled to a Flame Ionization Detector (FID) for compound quantification. Additionally, this on-line device is equipped with an automated sampling system. It samples air at a flow rate of 0.025 L.min^{-1} during 4 min, each 15 minutes. Subsequently, analytes are refocused on a multi-layer sorbent (Model: General Purpose Hydrophobic from Markers Internationals®) and transferred

to the column under helium at 280 °C. Several C-GC/FID parameters have been preliminarily optimized by the injection of individual TerVOCs vaporized in a 6 L canister (Model: Silonite® from Entech). Typical detection limits of this instrument for TerVOCs with abovementioned sampling conditions are 0.1 ppb.

Table 1. Experimental protocol parameters.

	Experimental Protocol		
	ELECTRIC DIFFUSER	***NEBULIZING DIFFUSER***	***CAPILLARITY DIFFUSER***
Duration of experiment	18 h		65 h
Applied / used mass (average ± standard deviation) N=3	0.79 ± 0.02 g	0.82 ± 0.01 g	0.55 g

Table 2. Sampling parameters for essential oil diffuser tests.

	Sampling parameters		
	Off-Line		***On-line***
	Tenax TA® *for TerVOCs*	***DNPH Cartridges*** *for OVOCs*	
Sampling Flow	0.040 L/min	0.800 L/min	0.025 L/min
Sampling duration (min) and time intervals (h)	Electric and nebulizing diffusers: 0 – 2 h : 10 min sampling each 30 min 2h – 6h : 10 min sampling each hour	0 – 1 h : continuous sampling each 15 min 1 – 5 h : continuous sampling each hour 8 – 60 h : 1 hour sampling with intervals of 6, 8, and 12 hours	4 min each 15 min

Inter-comparison of monitoring methods / Since no gaseous standards are available for the calibration of the considered diverse TerVOCs using C-GC/FID, a specific calibration methodology has been developed. This method relies on the

cross-calibration of C-GC/FID with the TD-GC-FID/MS. The TD-GC-FID/MS is preliminarily calibrated off-line through Tenax TA® sorbent cartridges doping with liquid TerVOC standard solutions. TerVOCs are identified using the MS detector and quantified using the FID detector. The correlation between the C-GC/FID signal and the TD-GC-FID/MS quantitative response is achieved through simultaneous samplings along the diffusion of terpenes in the experimental chamber. For each TerVOC, the concentration monitored by the quantitative off-line system is plotted as a function of the peak area of the C-GC/FID signal, as reported on Figure 2. For all detected TerVOCs a linear trend is observed with correlation coefficients ranging from 21 to 124. The slopes of the linear regression are used for the quantitative analysis of TerVOCs by the C-GC/FID.

Off-line sampling is considered as the reference measurement method, however the characterization of the emission process of essential oil requires a higher temporal resolution. For this reason, in the frame of this paper C-GC/FID is preferred since it allows a complete quantitative screening of all TerVOCs of interest every 15 minutes.
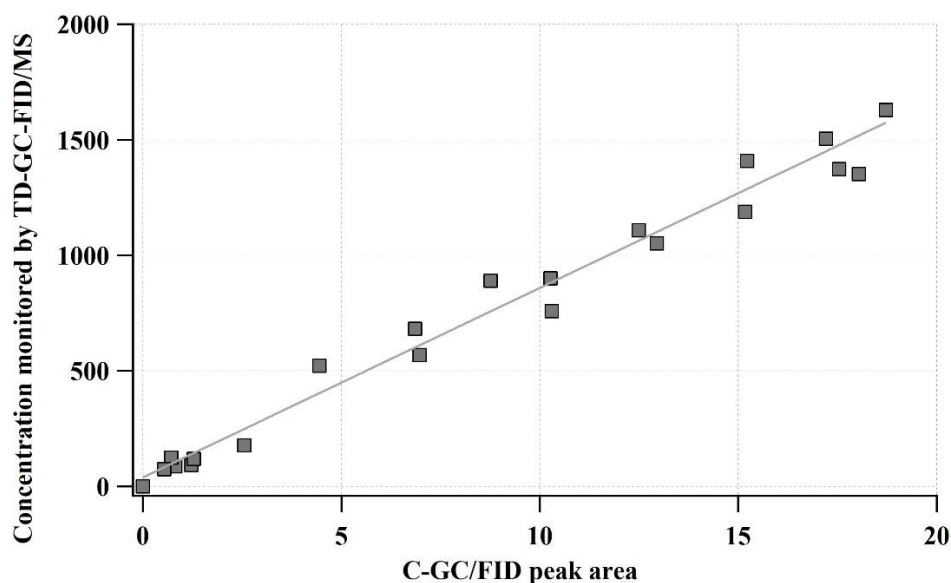

Figure 2. Evolution of α-pinene concentration measured by off-line TD-CG-FID/MS as a function of the on-line C-GC/FID peak area of α-pinene with a correlation coefficient value of 85.

3.   RESULTS AND DISCUSIONS

3.1   Chemical composition of liquid tea tree oil.

The chemical composition determined for the selected tea tree oil is reported in Table 3. The detected TerVOCs are listed by decreasing molar masses and major compounds are written in bold. Note that the results evidence that the total mass concentration of the quantified terpene molecules represent 98.8 % w/w of the injected mass. This point ensures that the developed methodology allows an exhaustive quantitative and qualitative analysis of TerVOCs present in tea tree oil.

Regarding the diversity of TerVOCs, the tea tree oil is mainly composed by 9 monoterpenes, 3 terpene alcohols, and 3 sesquiterpenes. Predominant compounds in tea tree oil are 4-terpineol, γ-terpinene, α-terpinene, eucalyptol and α-terpineol with respective mass concentrations of 42.5, 22.8, 12.8, 3.70 and 3.21 % w/w. These five molecules account for 85.1 % w/w of the total mass concentration. Seven other TerVOCs are detected at trace concentrations below 1.5 % w/w mass concentration, such as α-thujene, β-myrcene, β-pinene, α-phellandrene, d-limonene, varidiflorene, and δ–cadinene. Results obtained for the chemical composition of the tea tree oil are in agreement with the range of mass concentrations of the typical terpenes reported in literature, as reported in Table 3. As an example, Chiu et al. [24] reported the chemical composition of a commercial oil, in which 4-terpineol, γ-terpinene, α-terpinene, eucalyptol and α-terpineol represent 87 % w/w of the total mass concentration (i.e. 43, 19, 7, 6, and 5 % w/w, respectively). Possible variations between tea tree oil mass concentrations can be related to origin, extraction procedure and intrinsic properties of the plant.

Among the physical and chemical properties of TerVOCs, the saturation vapor pressure of pure molecules is one of the key driver governing the emissions. The volatility of an essential oil is directly driven by the abilities of the respective terpenes to transfer from liquid to gas phase since no solvent matrix is present in the chemical composition. The vapor pressures have been experimentally determined for the most of TerVOCs, corresponding values are gathered and displayed in Table 3. Monoterpenes report highly contrasted vapor pressures ranging from 90 to 599 Pa. Nevertheless, concerning the predominant compound in tea tree oil (4-terpineol), its vapor pressure value is among the lowest compared to other TerVOCs such as β-pinene and α-pinene with respective vapor pressures of 572 and 396 Pa.

Table 3. Liquid composition of the selected tea tree essential oil and physical and chemical properties of identified terpenes (vapor pressure, boiling point and molar mass), and comparison with the literature. NB: the three predominant TerVOCs of tea tree oil are written in bold.

	Mass of individual TerVOCs (this work) Mass ± SD (mg/g)	Mass percentages per TerVOCs (this work) (% w/w)	Mass percentages from literature [24]–[27] (% w/w)	Vapor pressure from literature [Reference] (Pa)	Boiling point (° C)	Molar mass (g / mol)
Monoterpenes						
α - thujene	12.0 ± 0.1	1.21	NS	NS	151	136.24
β- myrcene	11.7 ± 0.1	1.18	NS	220, 251, 268 [28]	167	136.24
α - pinene	26.9 ± 0.1	2.72	2.0 – 2.6	589, 599, 529 [29], [30]	156	136.24
α -terpinene	**127.0 ± 0.3**	**12.85**	**6.0 – 10.4**	**222** [31]	**175**	**136.24**
β- pinene	7.1 ± 0.1	0.72	NS	400, 391 [31]–[33]	166	136.24
α – phellandrene	5.1 ± 0.2	0.52	NS	195, 220 [32]	172	136.24
limonene	10.7 ± 0.2	1.09	1.0	189, 192, 213 [32], [34]	176	136.24
γ - terpinene	**226.0 ± 1.5**	**22.88**	**20.0 – 25.0**	**103, 145** [30]	**183**	**136.24**
α - terpinolene	34.5 ± 0.2	3.49	1.5 – 5	90, 99 [30], [32]	187	136.24
Terpene alcohols						
4 -terpineol	**419.3 ± 1.9**	**42.45**	**40.1 – 41.0**	**37, 20** [32]	**209**	**154.25**
α -terpineol	31.7 ± 0.2	3.21	2.4 – 4.0	*	175	154.25
eucalyptol	36.5 ± 0.2	3.70	0 – 5.6	230, 260, 254 [34]	176	154.25
Sesquiterpenes						
aromadendrene	15.9 ± 0.1	1.61	NS	NS	NS	204.36
varidiflorene	12.2 ± 0.3	1.23	NS	2 [29]	NS	204.36
δ - cadinene	11.3 ± 0.2	1.14	NS	NS	NS	204.36

NS: Not specified in literature; *: Vapour pressure nearly 0 Pa;

After the evaluation of the content of the selected essential oil, this work has addressed the impact of its dissemination in indoor environments through the use of above described diffusers. Depending on the devices, and depending on the amount of essential oil involved in the diffuser, temporal emission dynamics might be highly contrasted. Therefore, in this paper, evaluated diffusers are classified as (i) transient diffusers or (ii) continuous diffusers. Transient diffusers are devices in where a limited mass of oil is introduced, typically from one to tens of droplets of oil. As a consequence, it mostly behaves as a punctual emission source. In contrast, diffuser involving the whole flask of essential oil, typically several milliliters, are classified as continuous diffusers; they represent finite but long-term sources. For clarity, the temporal dynamics of selected diffusers are separately assessed according to this classification.

3.2   Transient diffusers: TerVOCs emissions from electric and nebulizing devices

The temporal dynamics of total TerVOCs concentrations from the two transient diffusers evaluated (electric and nebulizing devices) are presented in Figure 3. Among the 15 compounds evidenced and quantified in the liquid chemical composition of the tea tree oil, only 12 are detected in the gas phase along emissions by both transient diffusers. Detailed temporal dynamic of the four predominant TerVOCs monitored in the gas phase are displayed in Figure 4 and results of the complete gas phase composition are provided in Table 4. Results presented are obtained from a set of three distinct experiments in order to evaluate the repeatability of the experimental protocol for each diffuser. The variation coefficients for the various sets of experiments range from 4.1 % to 16.5 %.

Profiles of total TerVOCs / In spite of the fact that electric and nebulizing diffusers are characterized by contrasted emission mechanisms, both transient devices evidenced analogous temporal emission dynamics regarding the total released TerVOCs. The corresponding profile is reported in Figure 3, they are both characterized by three main phases associated to the diffusion process: (i) a sudden increase of the total TerVOCs concentrations attesting of the rapid vaporization of terpenes from the tea tree oil until peak concentrations are reached, (ii) a primary decreasing trend referred to the gradual exhaust of the VOCs source and to the removal of VOCs from the experimental chamber, (iii) a final decreasing stage referred to the evacuation of emitted terpenes by the air exchange and the possible losses on the walls.

Regarding emission levels, the peak concentrations of the total TerVOCs reached up to 17 350 ± 710 ppb and 16 660 ± 630 ppb, respectively for electric and nebulizing diffusers. Considering the standard deviation values, both diffusers are characterized by equivalent maximum concentrations. Additionally, maximum concentrations are reached at ca. 90 minutes after diffusers are turned on. Interestingly, the maximum total TerVOCs concentrations are higher than (i) usual

VOCs concentrations in indoor air by 3 orders of magnitude and (ii) the long-term exposure limit value proposed in the frame of the project INDEX by 200 orders of magnitude. [17], [20] Transiently, the total concentration of TerVOCs emitted by electric or nebulizing diffusers of essential oils totally dwarf other indoor sources of VOCs. Transient diffusers of essential oils may appear as intense sources of VOCs in indoor environment.

Su et al. [16] investigated the effects of evaporating three best-sold essential oils, including tea tree oil, in two different indoor settings characterized by equivalent volumes: 21.6 m^3. In that study, environmental parameters, such as temperature and humidity, were not controlled and not specified. The experimental procedure was based on the diffusion of 300 µL of essential oils diluted in 50 mL of water using a candle diffuser. Note that, the mass of tea tree oil evaporated by Su et al. [16] was 3 orders of magnitude lower than the mass used in this work, and diluted in an aqueous media. Studying the evaporation of tea tree oil, authors evidenced a peak concentration of total TerVOCs of ca. 1400 ppb. Likewise, terpenes emissions during evaporation mostly occurred during the first 20 minutes for eucalyptus and tea tree oils, and peak concentrations were achieved after the same time span. The contrasts in terms of temporal profiles (levels of emitted TerVOCs, positioning of emission peak) from one study to another are suggested to be directly related to: (i) air exchange rate and chamber volume, (ii) mechanism of diffusion, and (iii) quantity of diffused essential oils. Therefore, relevant comparisons from one study to another would be allowed provided typical emission scenario are defined. Nonetheless, irrespectively of the variability of the emission protocols, resulting total concentrations of TerVOCs largely exceed ppm levels.
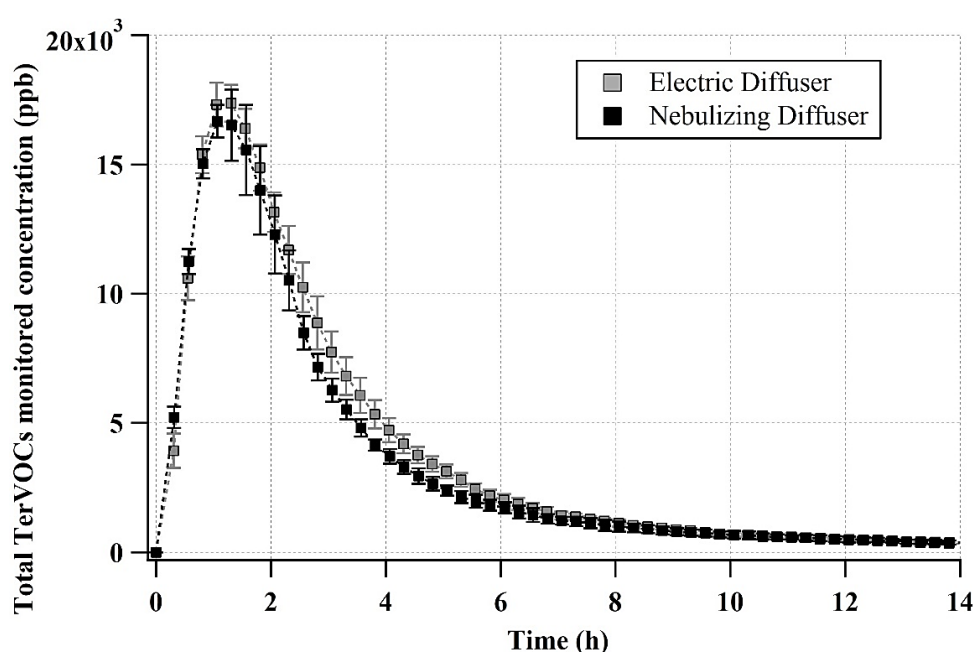

Figure 3. Evolution of TerVOCs total concentrations emitted from electric and nebulizing diffusers as a function of time (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

Individual profiles of TerVOCs / Beyond the global profile addressed through total TerVOCs concentrations, the individual emissions of 9 monoterpenes and 2 terpenes alcohols have been identified and quantified in the gas phase. The main three predominant TerVOCs detected along the electric diffusion of tea tree oil are γ-terpinene, α-terpinene, and α-pinene. Their individual temporal profiles are reported on Figure 4. They are characterized by the same three phases as evidenced on the total TerVOCs concentration profile (Figure 3). Therefore, maximum concentrations can be determined for electric diffusion: 5900 ± 125 ppb for γ-terpinene, 5090 ± 200 ppb for α-terpinene and 1600 ± 80 ppb for α-pinene. Corresponding data are reported in Table 4. In the case of the nebulizing diffuser, similarly, γ-terpinene, α-terpinene, and α-pinene are the major TerVOCs with typical transient temporal profiles. Their maximum concentrations are within the same concentration range than with the electric diffuser as attested by the concentration ratios reported in Table 4.

Highly contrasted emission dynamics are evidenced among individual terpenes. Comparing two molecules with distinct chemical and physical properties, such as α-pinene (Figure 4-c) and 4-terpineol (Figure 4-d), their concentration profiles are highly contrasted. While α-pinene is characterized by a sharp increase of its concentration with a subsequent clearly marked maximum concentration at only 0.56 h; the concentration of 4-terpineol remains negligible within the first minutes of diffusion and is characterized by a broad emission peak leading to a weakly marked maximum concentration after ca. 5 h of diffusion. Additionally, for both diffusion devices, 10 hours after the emission started, the gas phase concentration of 4-terpineol still represent nearly 40 % of the peak concentration, while the gas phase concentration of α-pinene is completely evacuated beyond 4 hours. Consequently, 4-terpineol evidences a particularly slow emission kinetic compared to other predominant molecules. For other major TerVOCs, namely γ-terpinene, α-terpinene and α-terpinolene, analogous concentration dynamics with α-pinene are evidenced. The investigation of the individual concentration profiles suggest that the dynamic of the liquid-to-gas transfer is driven by (i) the intrinsic physical and chemical properties of individual TerVOCs and (ii) the abundance of individual TerVOCs in the pure essential oil.

As can be observed on Figure 4, even if TerVOCs may exhibit contrasted emission profiles, this is only related to the TerVOC itself, but not to the diffusion mechanism. Indeed, for each VOC, profiles observed for electric and nebulizing diffusers overlap. However, a slight difference can be pointed out for the less volatile terpenes such as 4-terpineol (Figure 4-d). It appears that the electric diffuser promotes the maximum concentration of low volatility TerVOCs by 30 % (Table 4). This phenomenon can be associated to the impact that distinct temperatures might have over terpenes with heavier molar mass and low volatility.
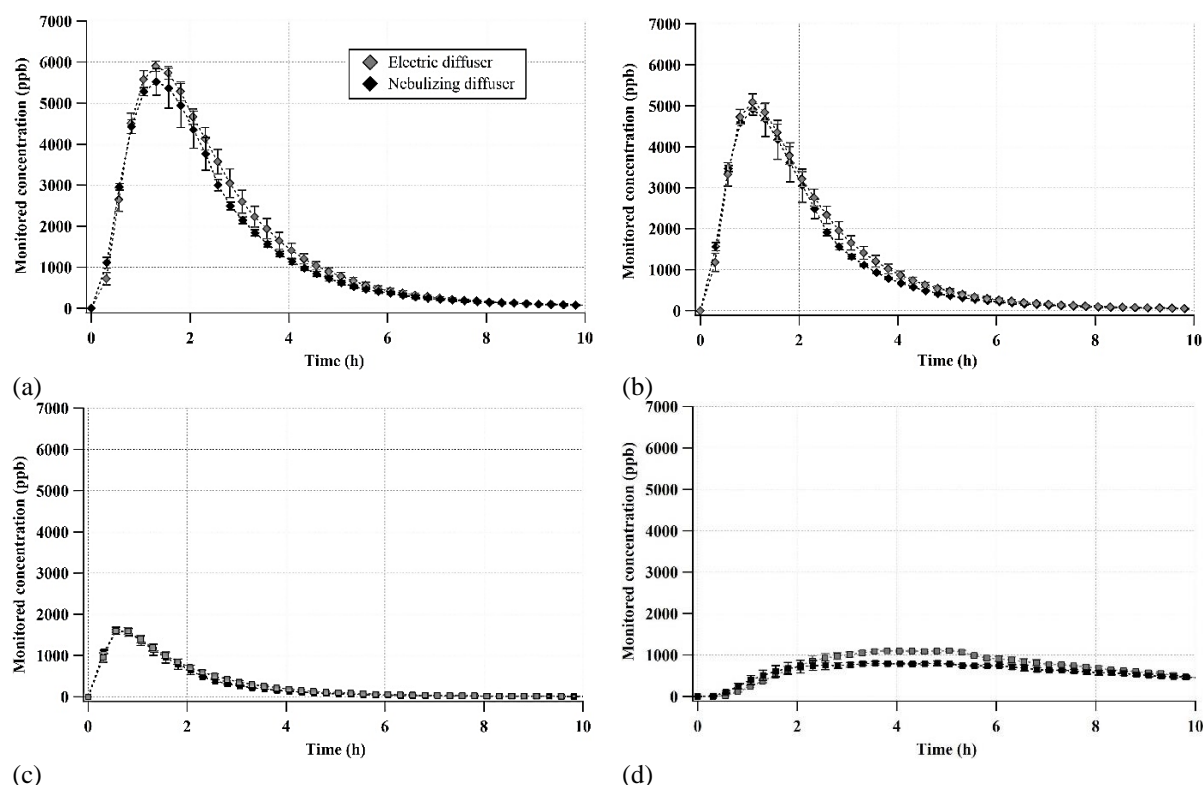
Figure 4. Evolution of (a) γ-terpinene, (b) α-terpinene, (c) α-pinene and (d) 4-terpineol concentrations as a function of time during the diffusion of tea tree oil using and electric diffuser (grey symbols) and a nebulizing diffuser (black symbol) (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

In the frame of the European project EPHEC (Emissions, Exposure Patterns and Health Effects of Consumer Products in the EU) [35], [36] a health risk assessment methodology has been developed for limonene and α-pinene for the estimation of their CEL regarding short and long term exposures. In the EPHEC project, these values have been established at 810 ppb and 1620 ppb for α-pinene and limonene, respectively. Indeed, the results presented in this section confirmed that the diffusion of tea tree oil through transient devices might induce indoor concentration levels higher by one order of magnitude compared to the CEL, if consider α-pinene as the compound of reference.

Table 4. Emission characteristics of the 6 major terpenes emitted along the electric and nebulizing diffusion of tea tree oil (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

	Tea tree oil *Transient diffusers*			
	Maximum Concentration (ppb) ± SD		**Time of maximum concentration (h)**	**k$_D$ Deposition rate (h^{-1})**
MAJOR TERPENES	ELECTRIC / NEBULIZING	CONCENTRATION RATIO ELECTRIC / NEBULIZING	ELECTRIC / NEBULIZING	ELECTRIC / NEBULIZING
γ -terpinene	5900 ± 125 / 5520 ± 330	1.07	1.31 / 1.31	0.31 / 0.31
α -terpinene	5090 ± 200 / 4900 ± 145	1.04	1.06 / 1.06	0.34 / 0.35
α -pinene	1600 ± 80 / 1600 ± 85	1.00	0.56 / 0.56	0.38 / 0.38
α -terpinolene	1530 ± 30 / 1400 ± 100	1.09	1.56 / 1.56	0.26 / 0.23
Eucalyptol	1490 ± 120 / 1340 ± 150	1.11	1.31 / 1.31	0.31 / 0.31
4 -terpineol	1100 ± 20 / 800 ± 45	1.38	5.06 / 4.82	N.D

N.D.: Not determined

Quantitative fingerprint of tea tree essential oil along diffusion / In the frame of this work, the fingerprint of an essential oil is defined as the contribution of each terpene molecule to the TerVOCs gas concentration at a specific time t. Considering that the temporal profiles individual TerVOCs are analogous with electric and nebulizing diffusers, the analysis of the fingerprint is only illustrated with results obtained from the nebulizing diffuser.

The diffusion through nebulizing device initiates at t = 0. At this time, all individual terpenes are in the liquid phase as reported on the left side of Figure 5. In the liquid composition of the tea tree oil, α-pinene is one of the minor compounds, present at 2.78 % w/w and 4-terpineol is the major compound, present at 42.5 % w/w. Nonetheless, nearly 30 minutes after the diffusion process started, the concentration of α-pinene contributes up to 20 % of the total TerVOCs emitted in the gas phase (Figure 5). While at the same time, 4-terpineol, characterized by a lower saturation partial pressure, is still present in the liquid phase and not transferred to the gas phase yet. After 4 hours of diffusion, 4-terpineol contributes up to 16.7 % to the TerVOCs transferred to the gas phase, while α-pinene only accounts for 3.8 % of the total gas phase terpenes. Indeed, at t = 4 h, α-pinene is evidenced to be almost exhausted from the tea tree oil and gradually evacuated from the experimental chamber due to the air renewal or by the deposition on inner surfaces. As a consequence, the contrasted emission dynamics of individual TerVOCs emitted from tea tree oil induces a considerable variation of the gas

phase terpene composition within the diffusion timespan. The fingerprint of the essential oil in the gas phase varies along the emission process as evidenced in Figure 5. This phenomenon has a direct impact on (i) the odor perception and (ii) the exposure of individuals to terpenes while diffusing essential oils indoors.
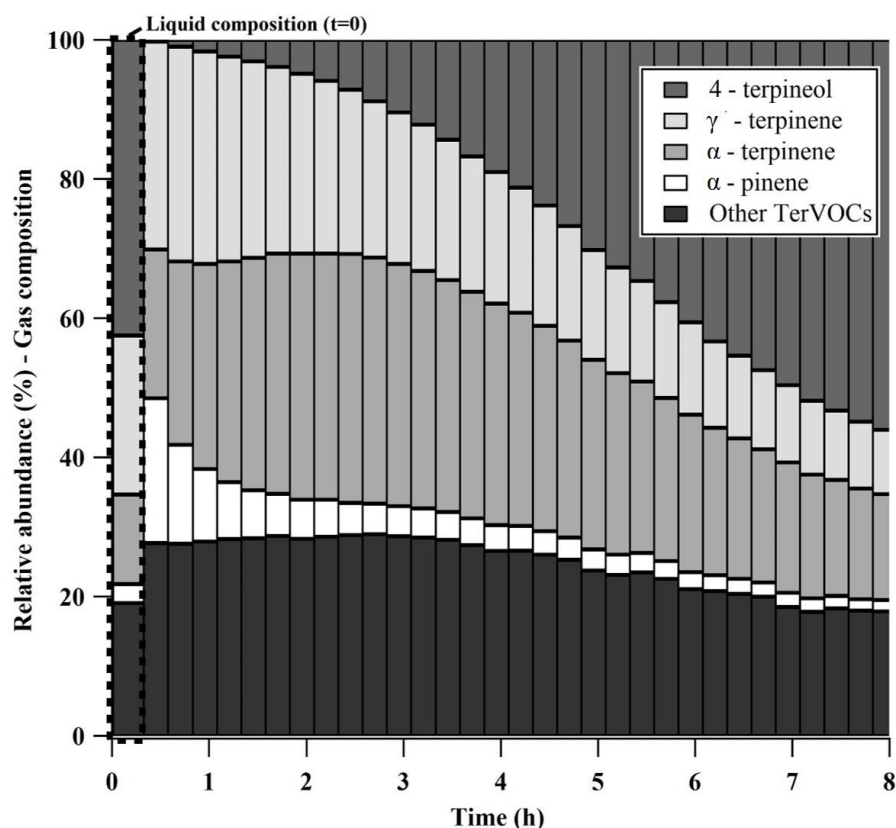

Figure 5. Temporal evolutions of the relative abundances of major TerVOCs transferred to the gas phase along the diffusion of tea tree essential oil using the nebulization device. NB: the relative abundances of major TerVOCs in the liquid phase are reported at t = 0 (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

Individual profiles of oxygenated VOCs (OVOCs) / Additionally, carbonyl compounds have been monitored during every diffusion experiment. Acetone, methylglyoxal, o-tolualdehyde, p-tolualdehyde, glyoxal and 2, 5-dimethyl benzaldehyde have been identified and quantified along the diffusion of tea tree oil using electric diffuser as well as nebulizing diffuser. Concerning the electric diffuser, the three predominant carbonyls monitored in the gas phase are acetone, methylglyoxal, and o-tolualdehyde. Their respective maximum concentration are 840 ± 55, 600 ± 85, and 175 ± 10 ppb, they are observed at 1.1 h for acetone and 0.6 h for methylglyoxal and o-tolualdehyde. The nebulizing device is characterized by the emission of the same major carbonyls with maximum concentrations at analogous times. The maximum concentration levels are in the same order of magnitude as well, confirming that the emission characteristics of electric and nebulizing diffusers are equivalent. In the literature, Chiang et al. [37] have indicated that the distillation of aromatic plants could induce the generation of decomposition products such as acetone, methyl alcohol, low molecular

weight fatty acids, and phenols. Likewise, monitored aldehydes and ketones might originate from the extraction process. Due to the heating system used in the electric diffuser, some OVOCs may be suspected to originate from a possible thermal degradation of terpenes. However, since equivalent emission profiles of aldehydes and ketone are evidenced irrespectively of the diffusion mechanism, i.e. with heating (electric diffuser) or without heating (nebulization diffuser), the formation of the OVOCs cannot be attributed to any thermal decomposition by electric device. Interestingly, it has been evidenced in the literature that among 5 investigated essential oils, the sequence of carbonyl VOC content is: tea tree > lavender > rosemary > lemon = rose. [38]–[40]

3.3   Determination of TerVOCs emission rates from tea tree essential oil using transient diffusers

Mass conservation equation / According to the international standards ISO 16000-9, the emission rate of a source is defined as the "*product specific rate describing the mass of volatile organic compound emitted from a product per time at a given time from the start of the emission*". [19] It must be highlighted that determining the source emission rate is of major importance since: (i) it provides key information to understand and characterize the emission process of an indoor source of pollutant, (ii) it is a representative parameter that can be extrapolated to real 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, among them ventilation, emission sources, and pollutant transformation such as uptakes or chemical interactions. Therefore, it is required to understand the fate of pollutants considering the contribution of each process distinctively. In a typical indoor environment, the concentration variation of an individual VOC is driven by the mass conservation equation reported in *Eq. 1*.

$$\underbrace{\frac{d[X]}{dt}}_{\substack{\text{Concentration} \\ \text{variation}}} = -\underbrace{\frac{d[X]_{Out}}{dt}}_{\substack{\text{Air Exchange}}} + \underbrace{\frac{d[X]_E}{dt}}_{\substack{\text{Pollutant} \\ \text{source}}} - \underbrace{\frac{d[X]_{Dep}}{dt}}_{\substack{\text{Deposition on} \\ \text{surfaces}}} + \underbrace{\frac{d[X]_{Des}}{dt}}_{\substack{\text{Desorption} \\ \text{from surfaces}}} + \underbrace{\frac{d[X]_{Hom}}{dt}}_{\substack{\text{Homogeneous} \\ \text{reactivity}}} + \underbrace{\frac{d[X]_{Het}}{dt}}_{\substack{\text{Heterogeneous} \\ \text{reactivity}}}$$

Eq.1

In controlled environments, such as the experimental chamber used for our experiments, several processes encompassed in *Eq. 1* can be ruled out. First, the concentration of one of the main oxidants in the experimental chamber is continuously monitored during experiments; the ozone level remains lower than the detection limit of the ozone analyzer (0.4 ppb) for

all experiments, suggesting that the contribution of ozone-induced homogeneous and heterogeneous reactivities can be neglected.

Harb et al. [41] and Haghighat et al. [42] evidenced that stainless steel is the most widespread chamber material in reviewed publications due to its inert properties. Indeed, the use of stainless steel avoids surface reaction of deposited TerVOCs with the inner material of the chamber. This is supported by the fact that no other terpenes than the ones monitored in the liquid composition, and no other carbonyls than the one reported in the literature have been evidenced in the gas phase of the experimental chamber. Therefore, surface reactivity on stainless steel is disregarded. Additionally, desorption phenomena are endothermal processes. Then, in temperature-controlled environment, sorption processes of TerVOCs are suggested to be irreversible and desorption is considered as negligible.

Finally, along our essential oils diffusion experiments, the resulting TerVOCs concentrations in the experimental chamber are predominantly contributed by (i) the air exchange, (ii) the emission rate of the pollutant sources, and (iii) the loss of pollutants on inner walls of the chamber (k_D). Therefore *Eq. 2* can be considered to describe the resulting pollutant concentration [X] in the experimental chamber. It clearly appears that the determination of the TerVOCs emission rates from their monitored concentration profiles requires to sort out the contribution of their respective air exchange rates and deposition rates.

$$\underbrace{\frac{d[X]}{dt}}_{\substack{\text{Concentration}\\\text{variation}}} = -\underbrace{\frac{d[X]_{Out}}{dt}}_{\text{Air Exchange}} + \underbrace{\frac{d[X]_E}{dt}}_{\substack{\text{Pollutant}\\\text{source}}} - \underbrace{\frac{d[X]_{Dep}}{dt}}_{\substack{\text{Deposition on}\\\text{surfaces}}} \qquad Eq.2$$

Air exchange / The air exchange induces the removal of the species X by the ventilation system of the chamber. It is characterized by the air exchange rate k_{AER} expressed in h^{-1}. It can be calculated considering the ventilation flow and the volume of the chamber or experimentally determined using a relevant tracer gas. Based on the inlet ventilation flow of our experimental chamber, k_{AER} is set to 0.3 h^{-1} for all experiments.

$$\underbrace{-\frac{d[X]_{Out}}{dt}}_{\text{Air Exchange}} = -k_{AER} \times [X] \qquad Eq.3$$

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Emissions rate / The emission rate of a species X is determined from its release by an emissive device per unit of time. In the case of essential oil diffusion, the mass emission rate is determined using *Eq. 4*, where m_p is the mass of tea tree oil used in the diffuser expressed in g and $V_{chamber}$ corresponds to the volume of the experimental chamber in m^3:

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

Eq.4

Deposition on inner surfaces of the chamber / This phenomenon corresponds to the uptake of gas phase TerVOCs on the surface of the stainless-steel chamber. The non-reactive uptake of TerVOCs on indoor materials can be characterized by the deposition rate k_D expressed in h^{-1}. It is also driven by the concentration of the gas phase species X, as reported in *Eq. 5*. Note that k_D depends on the nature of the material and on the VOC, it has been assessed for each set of experiment in order to provide a comprehensive evaluation of the process in the fate of emitted TerVOCs and its impact on the resulting TerVOCs concentrations in the gas phase.

$$\left. -\frac{d[X]_{Dep}}{dt} \right|_{\substack{\text{Deposition on} \\ \text{surfaces}}} = -k_D \times [X]$$

Eq.5

As finite sources of TerVOCs, transient diffusers of essential oils may get exhausted. Thereafter, the drivers of the TerVOCs concentrations in the experimental chamber are only: (i) the air renewal, at a known decay rate (k_{AER}) and (ii) the deposition on walls, at a decay rate (k_D) to be calculated. The corresponding situation is described in *Eq. 6* by the linearized and simplified form of Eq 2. The air renewal rate is set to 0.3 h^{-1} in our experimental chamber, therefore it can be taken into account. The methodology to determine k_D can be illustrated using the temporal profile of γ-terpinene emitted by the nebulization diffuser recalled in Figure 6-a. Beyond 3 hours of diffusion, the profile of γ-terpinene reveals that the emission peak is overcome and experimental data inside the square frame (Figure 6-a) correspond to the decay of γ-terpinene concentration due to air exchange and loss on the chamber walls. Based on Eq 6 this reduced data series is plotted in Figure 6-b as ln ([γ-terpinene]) as a function of time (h). The linear form attests of the pseudo-first order of the decay process. The slope of the straight line displayed in Figure 6-b is contributed by the sum of k_{AER} and k_D. Since k_{AER}

is a known experimental constant, the deposition rate of γ-terpinene under our experimental conditions can be determined as k_D (*γ-terpinene*) = 0.25 h^{-1}.

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

(a)   (b)
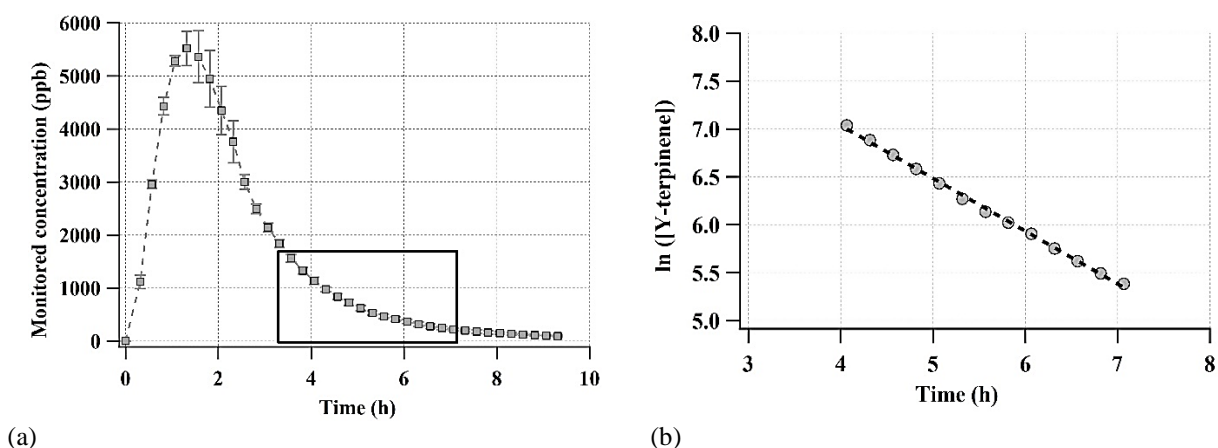
Figure 6. (a) Evolution of γ-terpinene concentration (ppb) as a function of time during the diffusion of tea tree oil using the nebulizing diffuser (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1m^3); data series in the square frame corresponds to γ-terpinene decay beyond exhaustion of its source. (b) Evolution of ln ([γ-terpinene]) as a function of time (h); NB: only data series from the square frame are plotted.

The deposition rate k_D of the 5 major emitted TerVOCs have been experimentally determined along electric diffusion and nebulizing diffusion of tea tree oil. Results are reported in Table 4 for both diffusers. It can be noticed first that, for a given terpene, the type of transient diffuser has no impact on the TerVOC deposition rate. This process only relies on the VOC characteristics and on the nature of the chamber walls. From one terpene to another, the deposition rates range from 0.23 to 0.38 h^{-1}. These values clearly support the fact that the deposition rates of TerVOCs on the chamber walls have to be determined to interpret concentration profiles since they impact the resulting concentrations by the same order of magnitude than the air exchange rate (0.3 h^{-1}). Based on Table 4, it can be pointed out that α-pinene presents the highest affinity to the chamber walls. Several studies have been carried out to evaluate the interactions of terpenes with indoor materials. These investigations evidenced that the intensity of the uptake process can vary depending on (i) the molecular structure of the considered species, (ii) the physical and chemical properties of the solid substrate and (iii) the environmental conditions, mainly temperature and humidity. [43]–[47] For instance, Springs et al. [48] evidenced that the number of moles of terpenes taken up per unit of surface area tends to decrease with RH, suggesting competitive interactions with water molecules for uptake sites.

From concentration profiles to emission profiles / Finally, the mass conservation equation under our experimental conditions during the essential oil emissions using transient diffusers is described by *Eq.7, w*here [X] is the concentration of the species X, m_p is the applied mass of tea tree oil, $V_{chamber}$ corresponds to the volume of the chamber (m^3), and k_{AER} and k_D are the decay rates (h^{-1}) of the species X related to air renewal and deposition.

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

Eq.7

Based on *Eq 7* the emission rate of a given TerVOCs is retrieved from its concentration profile corrected by the air renewal rate and by the depletion rate. Figure 7 reports the temporal evolution of γ-terpinene emitted from tea tree essential oil using the nebulizing diffuser. The concentration of γ-terpinene directly monitored in the experimental chamber is reported using black squares in Figure 7. First, this raw profile is corrected by the air renewal rate. It leads to the γ-terpinene profile that would have been monitored if no VOCs were extracted by ventilation from the chamber (light grey square symbols in Figure 7). Second, the latter profile is corrected by the deposition rate of γ-terpinene. This final profile corresponds to the concentration profile of γ-terpinene if no γ-terpinene were lost on the chamber walls and by air exchange (dark grey circle symbols in Figure 7). As a consequence the resulting profile is solely contributed by γ-terpinene emission. Therefore, the time when γ-terpinene reaches a steady state indicates the end of γ-terpinene emission from the diffused oil. Moreover, this final profile can be used to calculate the emission rate of γ-terpinene according to *Eq 8*.

$$\tau(t) = \frac{V_{chambre}}{m_{produit}} \times \frac{(C_{i+1} - C_i)}{(t_{i+1} - t_i)} \quad Eq. \ 8$$
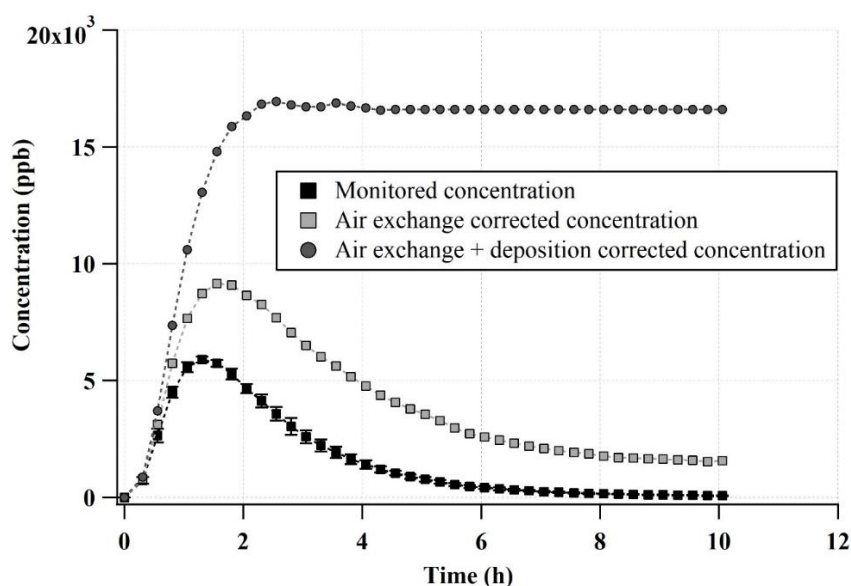
Figure 7. Evolution of γ-terpinene monitored concentration (ppb), air exchange corrected concentration (ppb) and air exchange + deposition corrected concentration (ppb) as a function of time (h) during the diffusion of tea tree oil using a nebulizing device. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1m^3).

Emission rate profiles using transient diffusers / Based on *Eq.8* the temporal evolution of the mass emission rates are calculated for each evaporation device and for each TerVOC emitted. The temporal evolutions of the mass emission rates of the three major TerVOCs (γ-terpinene, α-terpinene and α-pinene) are presented in Figure 8. As reported in Figure 8, transient diffusers evidence equivalent temporal emission rate profiles. The temporal profiles of emission rates allow the determination of (i) the time required to reach the maximum emission rate (ranging from 0.3 to 0.8 for α-pinene, α-terpinene and γ-terpinene), (ii) the value of the maximum emission rate (ranging from ca. 17 to ca. 82 for α-pinene, α-terpinene and γ-terpinene), and (iii) the time the emission source is exhausted (ranging from 1.3 to 2.8 hours for α-pinene, α-terpinene and γ-terpinene). Noticeably, in the case of α-pinene, the emission process is exhausted 2.2 times faster than for γ-terpinene using the same nebulizing diffuser. Such observations confirm that a faster emission dynamic process characterizes monoterpenes with higher vapor pressure and lower molar weight. Nonetheless, whatever the transient diffuser, for a given VOC, the emission rate profile is analogous. Additionally, Table 5 displays the experimentally determined maximal emission rates for the 5 major released terpenes. The first two data series respectively refer to electric and nebulizing devices. Note that the predominantly emitted molecule for each device is written in bold.
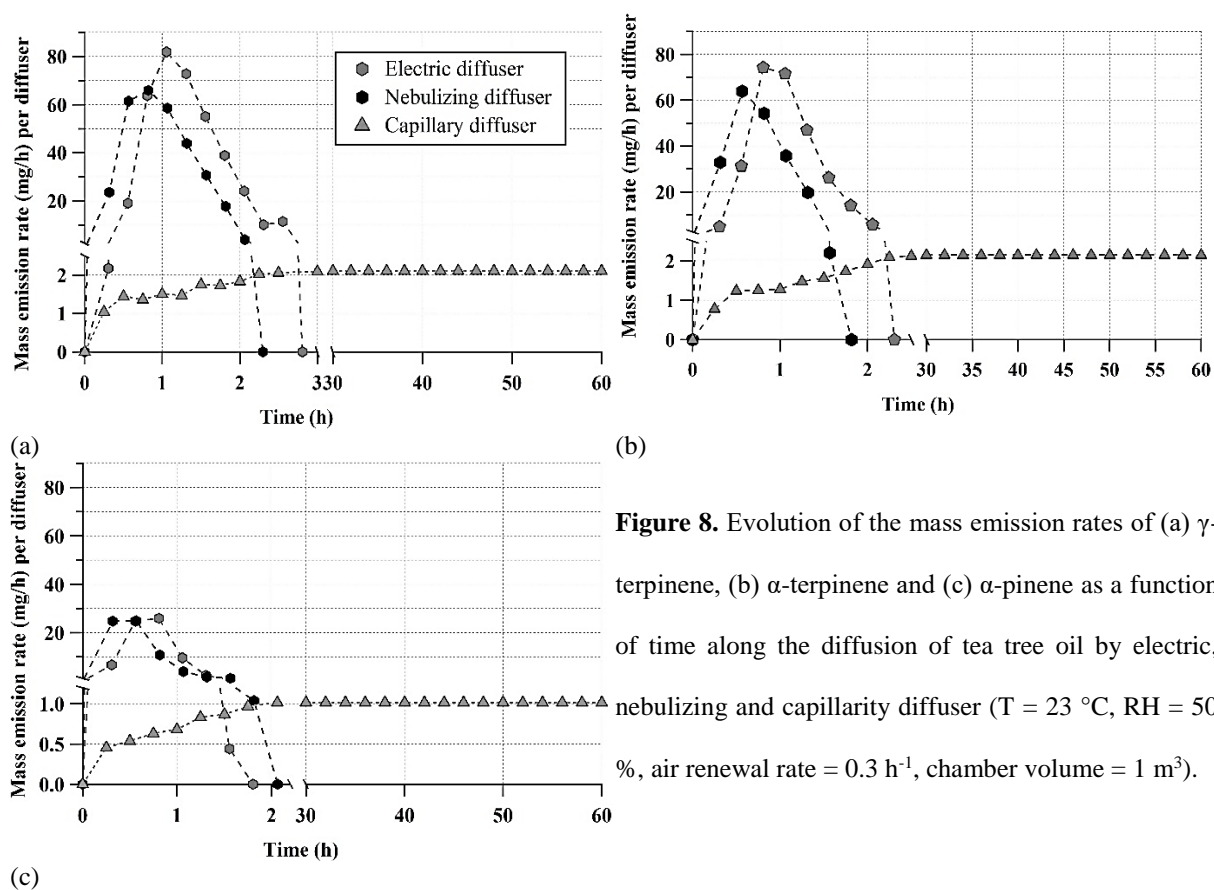
(a)

(b)

(c)

Figure 8. Evolution of the mass emission rates of (a) γ-terpinene, (b) α-terpinene and (c) α-pinene as a function of time along the diffusion of tea tree oil by electric, nebulizing and capillarity diffuser (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

Table 5. Comparison of mass emission rates (mg/h) per gram of tea tree oil diffused through: (i) electric diffuser, (ii) nebulizing diffuser, and (iii) capillarity diffuser.

	Tea tree oil - *Tested diffuser devices*		
	Maximal mass emission rate (mg/h) per g of product		
COMPOUNDS	ELECTRIC DIFFUSER	NEBULIZING DIFFUSER	CAPILLARITY DIFFUSER
γ -Terpinene	**81.8**	**66.0**	3.8
α -Terpinene	74.3	64.0	**3.9**
α -Pinene	26.0	25.0	1.8
α -Terpinolene	19.0	16.4	3.1
Eucalyptol	20.7	17.3	1.0

In the discussed section, a complete assessment regarding the diffusion of tea tree oil by transient diffusers in confined environment is accomplished including (i) the experimentally measured concentration profiles for detected species, (ii)

the calculation methodology for the evaluation of their mass emission rates and (ii) the quantitative fingerprint evolution of the gas phase along the diffusion of tea tree oil. In the further section, the same analysis is driven related to the diffusion of essential oil by a long-term diffusion device.

3.4.   Continuous diffuser: capillarity devices

Using the capillarity diffuser with tea tree oil in the experimental chamber, the same 12 terpenes (9 monoterpenes and 3 terpene alcohols) are detected. Figure 9 displays the total TerVOCs concentration profile as well as the concentration profiles of the four predominant individual TerVOCs, namely γ-terpinene, α-terpinene, 4-terpineol and α-pinene. Using the capillarity diffuser, all emission profiles, total TerVOCs and individual TerVOCs, are characterized by two main phases: (i) an increase of the gas concentration of TerVOCs; (ii) a steady state concentration regime of gas phase TerVOCs inside the experimental chamber. The steady state regimes attest that an equilibrium is reached between: (i) the emissions from the diffusion device, (ii) the removal of diffused terpenes by air renewal rate and (iii) possible losses on the inner walls of the experimental chamber.

For the continuous diffuser, unlike transient diffusers, no peak concentration is observed, but maximum concentrations can be defined from the steady state regimes (Figure 9). Noticeably, one order of magnitude difference is observed between the maximum concentrations reported for transient diffusers and steady state concentrations observed using the continuous diffuser. Another specificity of the TerVOCs profiles using the continuous diffuser (Figure 9) is that the mean time to achieve the steady state regime can exceed 20 hours, while for transient diffusers, the maximum concentrations are reached within only 1 to 4 hours depending on the terpene molecule.

Once the steady state diffusion regime is reached, the 4 major emitted TerVOCs are γ-terpinene, α-terpinene, eucalyptol and 4-terpineol. Their respective concentrations are 610 ± 5, 600 ± 20, 340 ± 5 and 270 ± 10 ppb. At the steady state, these concentration levels account for 23, 21, 16 and 12 % of the total emitted concentration for γ-terpinene, α-terpinene, and eucalyptol, respectively. Indeed, at stable concentrations, these four predominant molecules account for 72 % of the total terpene concentration. Finally, irrespectively of the diffuser, it can be noticed that same two predominant terpenes are detected in the gas concentration i.e. ϒ-terpinene and α-terpinene. The predominance of γ-terpinene, α-terpinene, and eucalyptol can be explained by three key factors: (i) their significant mass contribution in the composition of the liquid tea tree oil (ii) their volatility and (iii) their affinity with the material of the diffuser stick. Nevertheless, a specific behavior

is observed for 4-terpineol. The selected tea tree oil primarily contains 4-terpineol at 42.6 % w/w, however, its steady state concentration only accounts for 12 % of total emitted TerVOCs concentration at stabilization time.
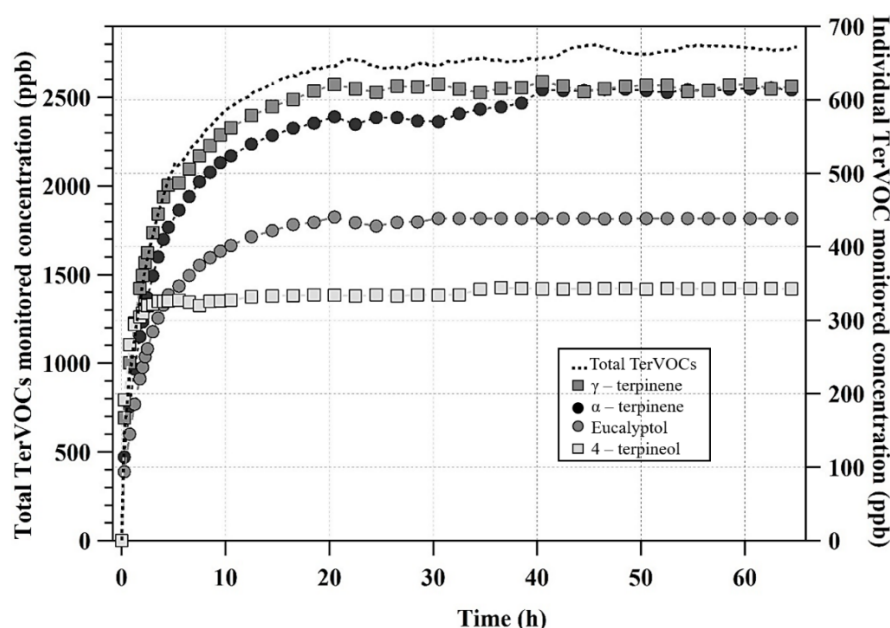

Figure 9. Evolution of γ-terpinene, α-terpinene, eucalyptol, and 4-terpineol and total TerVOCs concentrations as a function of time during the diffusion of tea tree oil using a capillarity diffuser. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3).

Looking at the individual behavior of TerVOCs diffused by capillarity, the time to reach the steady state concentration strongly varies from one molecule to another. Indeed, the stabilization times range from 4 hours for 4-terpineol to 27 hours for eucalyptol. For 4-terpineol, this observation contrasts with its behavior when diffused by transient diffusers because it was characterized by a delayed emission compared to other TerVOCs. In the case of the capillarity diffuser, the very first step of the emission process relies on the capillarity diffusion of liquid TerVOCs in the fibrous beech wood stick. It can be suggested that the specific behavior of 4-terpineol may be associated to its capillarity diffusion ability in the fibrous stick. Once again, the individual physical and chemical properties of TerVOCs directly impact their diffusion and the resulting gas phase concentrations depending on the diffusion mechanisms involved.

Emission rates / Based on the individual concentration profiles, emission rates of each TerVOC are determined for the capillarity diffuser according to the methodology presented in section 2.3. The emission process associated to the use of the continuous diffuser in the experimental chamber is described by the mass conservation equation reported in *Eq.8* and the emission rates are calculated using previously determined parameters.

As reported in Figure 8, for the capillarity diffuser, the emission rates achieve a steady state after 3, 2.5, and 1.7 hours of diffusion respectively for γ-terpinene, α-terpinene and α-pinene. Moreover, at steady state regime, emission rate levels reached equivalent values for γ-terpinene and α-terpinene at. 4 mg/h, and at ca. 2 mg/h for α-pinene. Additionally, long-term diffusion devices maintain a constant emission rate for several days. Indeed, the emission process might be solely limited by the liquid essential oil source itself. Thus, it can be assumed that constant emission rates for capillarity diffusers could be observed on time scales up to several days or weeks under stable environmental conditions, i.e. temperature and humidity, and until the source gets exhausted.

For assessing the duration of impact on indoor air quality from the diffusion of tea tree oil by capillarity, several calculations were performed in order to extrapolate the timespan of the emission process until the source gets exhausted. Based on *Eq 9,* the emitted mass E_{mass} in g can be calculated by employing the determined emission rates ER at the steady state regime per individual terpene *X* (section 2.3) in gram per day, and the time *t* in days.

$$E_{mass_X} = ER_X \times t \qquad Eq.\ 9$$

The total mass contained in the essential oil bottle is identified in order to establish the total boundary mass corresponding to the emission exhaust. This value is represented in Figure 10 by a dashed line. Subsequently, considering the chemical composition determined in section 2.1, this same boundary mass is now identified per individual terpene. These values are assembled in Table 6. Note that when the source exhaust time is reached, the total emitted mass equals the sum of the individual boundary masses.

Table 6. The calculated mass boundary for individual and total TerVOCs contained the tea tree oil bottle.

Compound	Individual boundary mass *(g)*	Emission rate at steady state *(g/day)*	Source exhaust time *(days)*
γ –terpinene	2.98	0.09	32
α –terpinene	1.67	0.09	18
α –pinene	0.35	0.04	8
α –terpinolene	0.45	0.02	19
Eucalyptol	0.48	0.07	7
Others TerVOCs	7.07	0.12	61
TOTAL MASS IN THE TEA TREE OIL BOTTLE	13.01	-	-

The mass of individual terpenes emitted from the capillarity diffuser (E_{massX}) is calculated per day by employing *Eq 9*, until the cumulative emitted masses reach the boundary mass previously established from the liquid content of the essential oil bottle. Figure 10 reports, by bar series in the histogram, the emitted mass of individual TerVOCs per day. Note that when the bar series in Figure 10 turn from full color to stripes, then the source of individual terpenes is considered to be exhausted.

As observed in the Figure 10, it can be evidenced that the contribution of individual TerVOC to the total emitted mass per day might vary along the entire emission process. Indeed, α-pinene and eucalyptol are verified to present higher emission rates compared to the other detected terpenes. Therefore, these molecules are observed to be entirely emitted only after 8 and 9 days of diffusion, respectively. This observation is explained by the acute volatility that characterizes these species associated to their high vapor pressures of 599 and 260 Pa for α-pinene and eucalyptol, respectively. In contrast, other terpene molecules characterized by lower volatilities, such as γ-terpinene, are completely transferred to the gas phase 30 days after the capillarity diffusion is initiated. Note that, at this same time of diffusion (30 days), the emissions of 4 out of 6 terpenes (α-pinene, eucalyptol, α-terpinene and α-terpinolene) presented in Figure 10 are over. Therefore, after 30 days of diffusion by capillarity of tea tree oil, the gas phase composition is only contributed by terpene molecules presenting the lowest vapor pressures, predominantly 4-terpineol. Finally, the total mass contained in the tea tree oil bottle is evidence to be completely transferred to the gas phase after 62 days. Beyond this time period, concentration levels are evacuated from the room. Therefore, when diffusing essential oils in indoor environments through a capillarity device, occupants might be exposed to terpene molecules at concentration levels reaching up to the ppm range and on a timespan from several days to weeks.
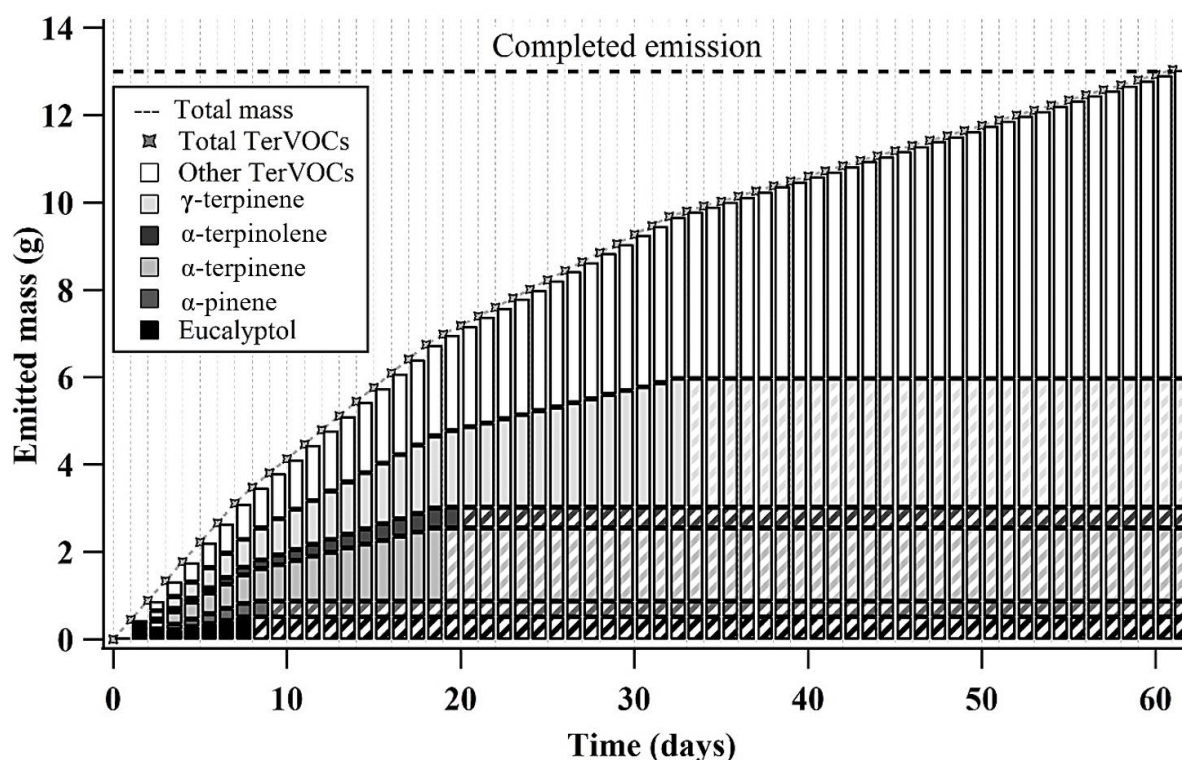
Figure 10. The temporal evolution of the emitted mass per day along the capillarity diffusion from t = 0 until the exhaustion of the mass content in the bottle of tea tree oil.

4.   CONCLUSIONS AND PERSPECTIVES

This study indicates that the use of essential oil diffusers in confined environments represents a massive source of indoor terpene VOCs. The emitted concentration levels observed in the 1 m^3 emission test chamber associated to essential oil diffusions might potentially impact indoor air quality on a time span ranging from 5 hours to 60 days, respectively for transient and continuous devices. On the one hand, regarding the exposure of consumers during the evaporation of essential oils in the 1 m^3 emission test chamber, transient diffusers (electric) are associated to high emission rates, i.e. 100 mg/h per gram of product, during a short period of time, typically in the hour range. On the other hand, continuous diffusion (i.e. capillarity device) releases a lower concentrations of terpenes, with emission rates in the range of 5 mg/h per gram of product, but on much longer time spans, exceeding tens of days. As consequence, the transient diffusers can be associated to acute exposures while the capillarity diffuser induces chronic exposure.

The results provided in this work provides the first quantitative insights into the assessment of emissions associated to the use of essential oils in indoor environments. Further studies are required in order to (i) define risk scenarios, (ii) address human exposure to diffused essential oils and (ii) assess the representativeness of the results in the frame of this work compared to experiments conducted in a real size room under equivalent controlled conditions. Furthermore,

essential oil diffusion, as a source of indoor contaminants, deserves more attention because of its potential formation of formaldehyde and secondary organic aerosols as a consequence of their high reactivity towards indoor oxidants.

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Chapter 5

Real consumer use patterns of essential-oil-based household products: *Emission rate assessment in a real scale 40 m³ room and impact on indoor air quality*

ABSTRACT

In the frame of indoor air quality the use of essential-oil-based household products has upsurge due to their purifying performances from a biological point of view. However, the potential toxicity of essential oils released in indoor air has not been clearly established. The first step is to accurately evaluate the effective levels of VOCs emitted along the use of essential oil based consumer products. This study aims at assessing the corresponding emission processes under real use patterns of (i) essential-oil-based cleaning products and (ii) tea tree oil diffusion in a real scale experimental room, and (iii) to compare these results with the realistic scenario performed in the 1 m³ emission test chamber. Regarding the use of essential-oil-based cleaning products contrasted concentration levels are evidenced for terpene species related to the application process and use purpose of these products. In order to assess the emission process of terpene molecules from the use of cleaning products, the mass emission rate profiles are determined. Specific emission kinetics are noticed and correlated to the product formulation. Indeed, scent retention technologies might delay emission kinetics to prolong odor perception up to several hours. Concerning the indoor diffusion of tea tree oil, contrasted concentration levels and kinetics are evidenced depending on the mechanism of diffusion used and concentration levels can exceed by more than one order of magnitude the recommended Critical Exposure Level (CEL). Additionally, it is noticed that the relative contributions of individual terpenes in the gas phase vary all along the diffusion process, for any investigated diffusion device. Then, in order to assess the duration of the impact of essential oil diffusion on indoor air composition, the mass emission rates of individual terpenes are determined. Results evidence that, depending on the diffusion mechanism, the impact of essential oil diffusion in confined environments varies from 6 hours for electric diffusers up to 51 days for capillarity diffusers. Finally, several limitations are found regarding the evaluation of TerVOC emissions using test chambers with small volumes. Indeed, for the investigated essential-oil-based household products, it is evidenced that the concentration levels of TerVOCs and their emission kinetics are clearly dependent on the chamber volume. Small size emission test chambers may lead to a noticeable underestimation of the TerVOC emissions.

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Until recently, scientific efforts associated to VOC emission tests were mainly focused on building material emissions. Regarding household products, standards for emission evaluations in real scale rooms are currently unavailable. In scientific research projects, the emission characterizations of household products have been performed using various methodologies such as head-space tests, chamber tests of various dimensions and volumes, and even experimental houses. [1]–[6] This chapter aims at (i) characterizing the impact of essential-oil-based products on indoor air quality (IAQ) through the investigation of their emissions and indoor fate under real consumer use patterns in a real-scale experimental room, and (ii) comparing the emission assessments using experimental chambers with contrasted volumes, the 40 m^3 experimental room and the 1 m^3 emission test chamber, presented in chapters 3 and 4.

1. Realistic consumer use patterns of essential-oil-based cleaning products: *emission rate assessment in a 40 m^3 experimental room and impact on indoor air quality*

The impact on indoor air quality related to the use of essential-oil-based cleaning products has been addressed in a 40 m^3 experimental room IRINA under real consumer use patterns. Among the six pre-selected cleaning products investigated in Chapter 3, only 2 cleaners are retained for the assessment of their emissions under real application conditions. For comparison purpose, the experimental protocol implemented for the investigation of the emissions associated to the use of essential-oil-based cleaning products is consistent with the protocol executed in the 1 m^3 emission test chamber. This protocol can be retrieved in details in Chapters 2 and 3.

1.1 Protocol for cleaning product application under real consumer use patterns

The final selection of the cleaners has been done by considering: (i) the category of products allowing the evaluation of different use patterns (ii) the variety of application modes, i.e. liquid and spray format, and (iii) the results discussed in Chapter 3, i.e. the cleaning products characterized by the highest emission rates of terpene molecules in the experimental chamber of 1 m^3. Therefore, the investigated products are: the surface cleaner SC – 1, fragranced with lavender oil; and the multi-use cleaner MC – 1, fragranced with citrus oils. Regard to the multi-use cleaner, it is applied considering the two different scenarios indicated by the manufacturer instructions: (i) floor mopping, and (ii) surface cleaning. Detailed information on the two selected cleaning products is gathered in Table 1. *Note that due to analytical issues the investigation of OVOC emissions from cleaning products did not lead to reliable results. Therefore, it is not presented in this section, and has to be completed by additional sets of experiments.*

Table 1. Detailed information on the selected essential-oil-based cleaning products

Category of product	Diffusion mode	Essential oil	Acronym	Total TerVOC concentration (Mean + SD) (μg/g)	Manufacturer indication of use	Mass of product applied (Mean + SD) (g)
Multi-use cleaner	Liquid	Citrus oil	MC – 1	1682.8 ± 131.3	**Floor cleaning:** *to dilute 1 or 2 dosing cap in 5 L of water and directly applied on the floor*	**Diluted product:** 176.8 ± 9.0 **Pure product:** 3.2 ± 0.1
					Surface cleaning: *to be directly applied on the surface to be cleaned*	**Pure product:** 13.3 ± 1.5
Surface cleaning	Trigger spray	Lavender oil	SC – 1	1453.7 ± 22.6		**Pure product:** 15.3 ± 0.6

For the surface cleaning scenario, both products (SC – 1 and MC – 1) are directly applied on a glass table of 2 m² placed in the center of the experimental room IRINA, and then wiped with a dry cleaning paper. In contrast, for floor mopping, two full-filled dosing caps of MC – 1 (equivalent to ca. 60 g) are diluted in 5 L of water. This solution is prepared outside of the experimental room. Subsequently, the solution is mopped over the tile floor of 14, 27 m² by employing a micro-fiber fabric mop of 10.5 cm x 33 cm. Four mop strokes (back and forth) are performed to apply the solution to each 4 tiles of the floor, equivalent to 0.36 m². Then, the mop is immerged into the solution and squeezed to drain the excess before repeating the cleaning process. The bucket with the cleaning solution and the micro-fiber mop are weighted before and after the application process, in order to determine the amount of solution applied considering the lost related to the mopping. The floor cleaning practice lasted approximately 5 – 6 minutes before removing all the cleaning materials from the room. Time zero of the experiments correspond to the time when the cleaning process is completed and all the materials are removed from the experimental room.

1.2 Terpene emissions from the use of essential-oil based cleaning products under realistic consumer use patterns in the real size room of 40 m³

The temporal dynamics of TerVOC concentrations from the two cleaners evaluated under different cleaning practices (SC – 1 and MC – 1) are presented in Figure 1. In regard to the diversity of molecules detected in the liquid form (Chapter

3), SC – 1 and MC – 1 evidence to contain a total of 20 and 11 terpene species, respectively. Nevertheless, only 8 and 6 terpenes are emitted in the gas phase of the 40 m^3 experimental room with concentrations exceeding the C-GC detection limits along the cleaning practices under real conditions with the products SC – 1 and MC – 1. The results presented are obtained from a set of three distinct experiments, in order to evaluate the repeatability of the experimental protocol for each cleaning product. The variation coefficients on monitored terpene concentrations for the various sets of experiments range from 2.5 % to 17.1 %.

Several studies aiming to investigate the impact on indoor air quality from the use of cleaning products in real size chambers i.e. with volumes higher than 30 m^3 evidenced highly contrasted concentration of total TerVOCs. [7], [8], [9], [10]. Indeed, authors attested that released levels of TerVOCs range from 220 ppb to 770 ppb. However, the variation between observed maximum concentrations of total terpenes are related to (i) the discrepancies between experimental methods applied i.e. air exchange rate, temperature, humidity, and chamber volume, and (ii) the diversity in products formulations. Finally, the comparison of results from these investigations and this work may become difficult and inaccurate. Consequently, standardized protocols would allow decreasing the variability between studies and improve the relevance of comparisons and subsequently more advanced conclusions.

Profile of total TerVOCs / Regarding the maximum concentrations of total terpene molecules monitored in the 40 m^3 chamber after the cleaning activities reach values of 43 ± 2 ppb, 70 ± 2 ppb, and 75 ± 3 ppb respectively for the SC – 1, the MC – 1 as a surface cleaner and the MC – 1 as a floor cleaner.

Comparing the experiments using both cleaners in their undiluted form, the released levels of TerVOCs are highly contrasted verifying a concentration ratio between MC – 1 and SC – 1 of nearly 2. However, their total mass concentrations of TerVOC species in their liquid format evidenced equivalent values (ca.1500 µg/g) considering their respective standard deviations, as reported in Table 1. Additionally, identical mass quantities of SC – 1 and MC – 1 are applied for full surface cleaning. Similarly to the 1 m^3 emission test chamber experiments, differences between the maximum concentrations of terpene molecules from the use of SC – 1 and undiluted MC – 1 are suggested to be related with (i) the intrinsic chemical properties of TerVOCs and (ii) the presence of other chemicals in the product formulation impacting the volatilization process i.e. fast drying alcohols or glycol ethers.

Comparing the experiments using the same cleaner (MC-1) under different cleaning practices i.e. floor mopping with a water diluted solution and surface wiping with undiluted product, both cleaning practices evidence (i) analogous temporal emission dynamics and, unexpectedly, (ii) analogous total released TerVOC levels. The corresponding profiles are

reported in Figure 1b and 1c, they are both characterized by three main phases associated to the emission process: (i) a sharp increase of the total TerVOC concentrations attesting of the rapid vaporization of terpenes from the MC – 1 until their peak concentrations are reached, (ii) a primary decreasing trend referred to the gradual exhaust of the VOC source and to the removal of VOCs from the room, (iii) a final decreasing stage referred to the evacuation of emitted terpenes by the air exchange and their possible losses on the room walls.

Regardless of the analogous values of total emitted terpenes verified for MC – 1 under different application methods, the mass of pure product applied is one order of magnitude higher for surface cleaning i.e. 13.3 g for surface cleaning and 3.2 g for floor cleaning. It is suggested that floor mopping is associated to higher loading factors (m^2/m^3). Therefore, even if the quantity applied of pure product is lower for floor mopping compared to table wiping, its emissive surface is nearly 7 times higher. Moreover, as the product is extended on a larger surface and diluted in water, the film of solution applied is thinner for floor mopping, therefore it might accelerate the drying phase enhancing the volatilization of terpene molecules. Consequently, beyond the cleaning product itself, the application method and the "human factor" could have a significant influence on the level of the emissions of TerVOCs. The application protocol of the product represent a key factor regarding the exposure to terpene molecules contained in cleaning products.

It can be observed in Figures 1b and 1c that equivalent levels associated to the peak concentration of TerVOCs are observed at ca. 70 ppb, whatever the application protocol with MC - 1. Nonetheless, the individual contributions of the emitted terpenes to the maximum TerVOC concentrations differ between floor mopping and surface cleaning, as reported in Figure 1d. It can be pointed out that the contribution of eucalyptol is evidenced to be 2.6 times lower when the product is diluted and mopped compared to when it is applied undiluted under a wiping protocol. Singer et al. [7] aimed at evaluating the impact of different application methods on IAQ under real conditions. The reported results proved that the emitted concentrations of terpene alcohols were lower when the product was used diluted in comparison to full strength application. Authors attributed this behavior to a slower volatilization of the alcohols during initial application and a greater partitioning of alcohols into water during scrubbing and rinsing procedures. [8]

A particular temporal dynamic of TerVOCs concentration is observed along the use of SC – 1, as presented in the Figure 1a. The corresponding profile is characterized by two analogous concentration peaks reaching up to ca. 40 ppb at 0.36 h and 1.6 h. Once the second concentration peak is reached, the emission profile is characterized by the two decreasing phases, as previously described. However, regarding the maximum emitted level reached at 1.6 h, it is mainly contributed

by linalool at ca. 35 % of the total TerVOCs concentration. Indeed, a specific behavior regarding the emission process of linalool is observed.

(a)

(b)

(c)

(d)
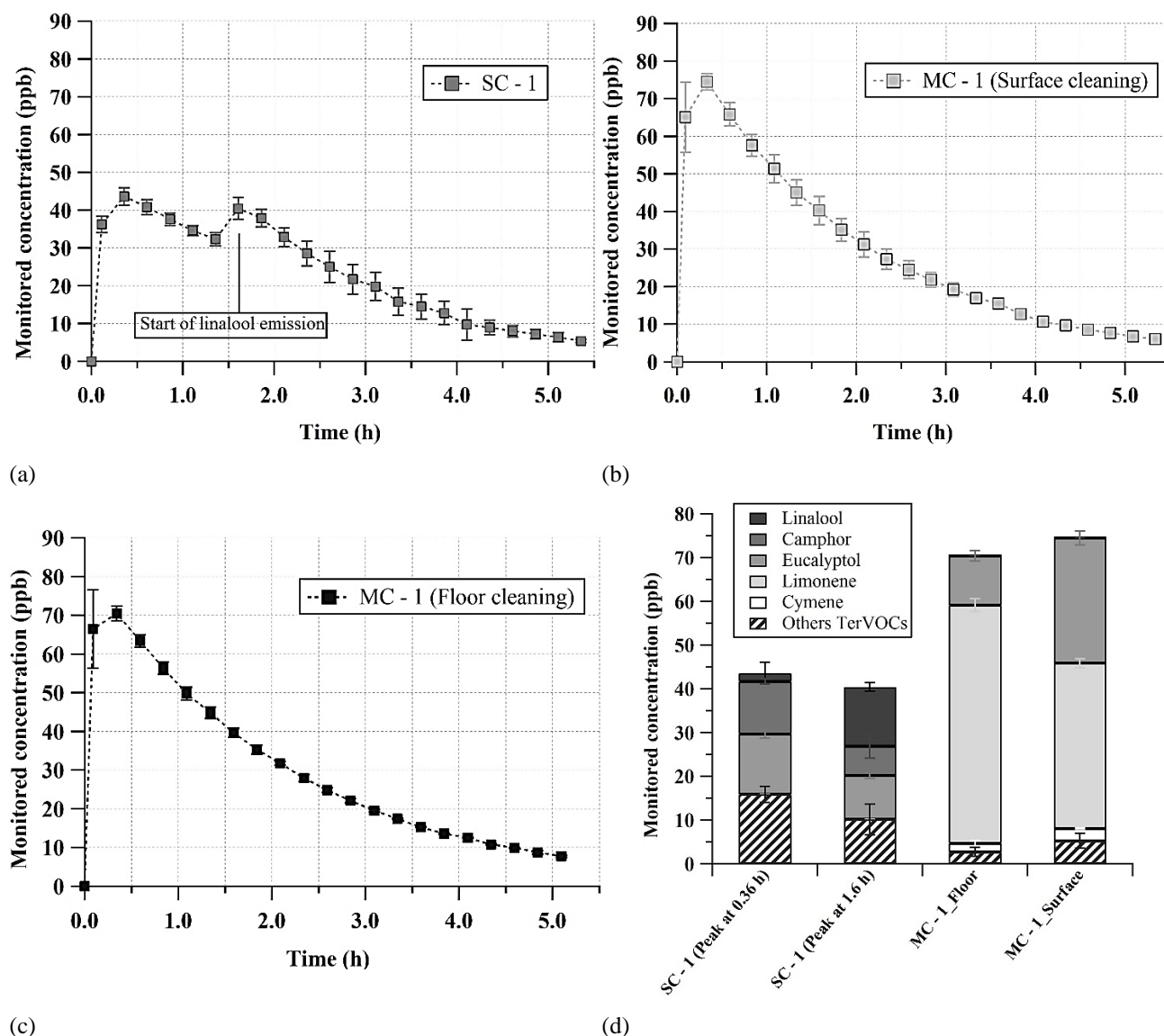
Figure 1. Evolution of total TerVOC concentration as a function of time during the cleaning activity with (a) SC – 1 (dark grey squares), (b) MC – 1 applied as a surface cleaner (light grey squares) and (c) MC – 1 applied as a floor cleaner (black squares) (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m³**) (d) Peak monitored concentration of total TerVOCs and the contribution of the 3 predominant terpenes after the application of SC – 1, MC – 1 (surface cleaner) and MC – 1 (floor cleaner).

Individual profiles of TerVOCs / Beyond the global profile addressed through total TerVOC concentrations, the individual emissions of TerVOCs have been identified and quantified in the gas phase from the cleaning practices with SC – 1 and MC – 1. Figure 2 reports the temporal concentration profiles of the three predominant terpene species emitted for each investigated cleaner.

For the surface cleaner SC – 1, the main released terpenes are linalool, eucalyptol and camphor. Their respective peak concentrations are 14.2 ± 0.5 ppb, 15.2 ± 0.9 ppb and 12.0 ± 0.9 ppb. As observed in Figure 2a, the emission process of linalool is evidenced to be delayed, starting 1.5 hours after the cleaning activity is finished. This behavior is suggested to be related solely to the formulation of the product. Several technologies, such as the nano-encapsulation of fragrance chemicals, are used in the industrial frame for the production of food, perfumes and household products for marketing purpose. [11], [12] The encapsulation of odor chemicals in a mixture of lipid, phospholipid, and polymer matrix might control the release of a scent. The shell of the capsule can act as a diffusion barrier and enhance the retention of the fragrance delaying its emission dynamics. [13], [14] Subsequently, the "clean-scent" that provides to consumers the perception of a cleaner environment might be extended by employing these technologies.

Even if eucalyptol and camphor evidence contrasted vapor pressures, 260 Pa and 28 Pa, their maximum released concentrations are reached at equivalent timespans of 20 minutes after completed cleaning. This observation can be explained by the fact that SC – 1 contains significant concentrations of alcohols, at 73 % w/w, included in the product formulation as a solvent and as an antimicrobial agent. [15]–[18] Therefore, alcohol compounds might enhance the drying process of the layer of product applied over the surface, resulting in an acceleration of the emission process of heavier terpene molecules.

Regarding the multi-use cleaner MC – 1, for both application modes, the predominantly identified terpenes in the gas phase are limonene, eucalyptol, and cymene (Figures 2b and 2c). Their respective peak concentrations are: 54.4 ± 2.3 ppb, 11.3 ± 0.3 ppb, and 2.0 ± 0.1 ppb for floor mopping, and 37.8 ± 1.4 ppb, 28.6 ± 0.3 ppb and 2.7 ± 0.2 ppb for surface cleaning. Moreover, the concentration profiles of limonene and eucalyptol are described by a sharp rise up to their peak concentration within 10 minutes after the cleaning process is finished, for both cleaning protocols. Nevertheless, several differences related to the maximum concentration of individual TerVOCs are noticed between floor moping and surface cleaning. Indeed, the maximum concentrations of eucalyptol are characterized by a ratio of ca. 2.5 if the cleaning action is performed undiluted; while for limonene similar peak concentrations are observed for floor and surface cleanings. This observation can be explained by the fact that some water soluble constituents, such as alcohol, are retained in the solution used during scrub and rinsing procedures. Indeed, Singer et al. [7] observed that when executing a floor cleaning practice with a diluted cleaning product, a dichotomy was noticed between the terpene hydrocarbons and terpene alcohols. These results showed that in the floor mopping scenario, fractional emissions of terpene alcohols were in the range of $2 - 5$ % whereas terpene hydrocarbon emissions were in the rage of $7 - 12$ %. Author attributed this behavior to the greater partition coefficient of terpene alcohols for water, compared to terpene hydrocarbons. Therefore, the released

concentrations of terpene alcohols from cleaning activities involving rinse procedures, scrub, and dilutions are expected to be lower.

Moreover, for all cleaning products tested, the maximum emitted concentrations of individual terpenes are observed to be evacuated from the experimental room around 4 hours after the cleaning activity is finished, except for linalool. Indeed, depending on the formulation of the cleaning products and on the use of technologies for enhancing the odor retention, the dynamics of emissions could be delayed. Therefore, cleaning practices might impact indoor concentration of odor molecules for at least several hours after completed cleaning.

(a)

(b)

(c)
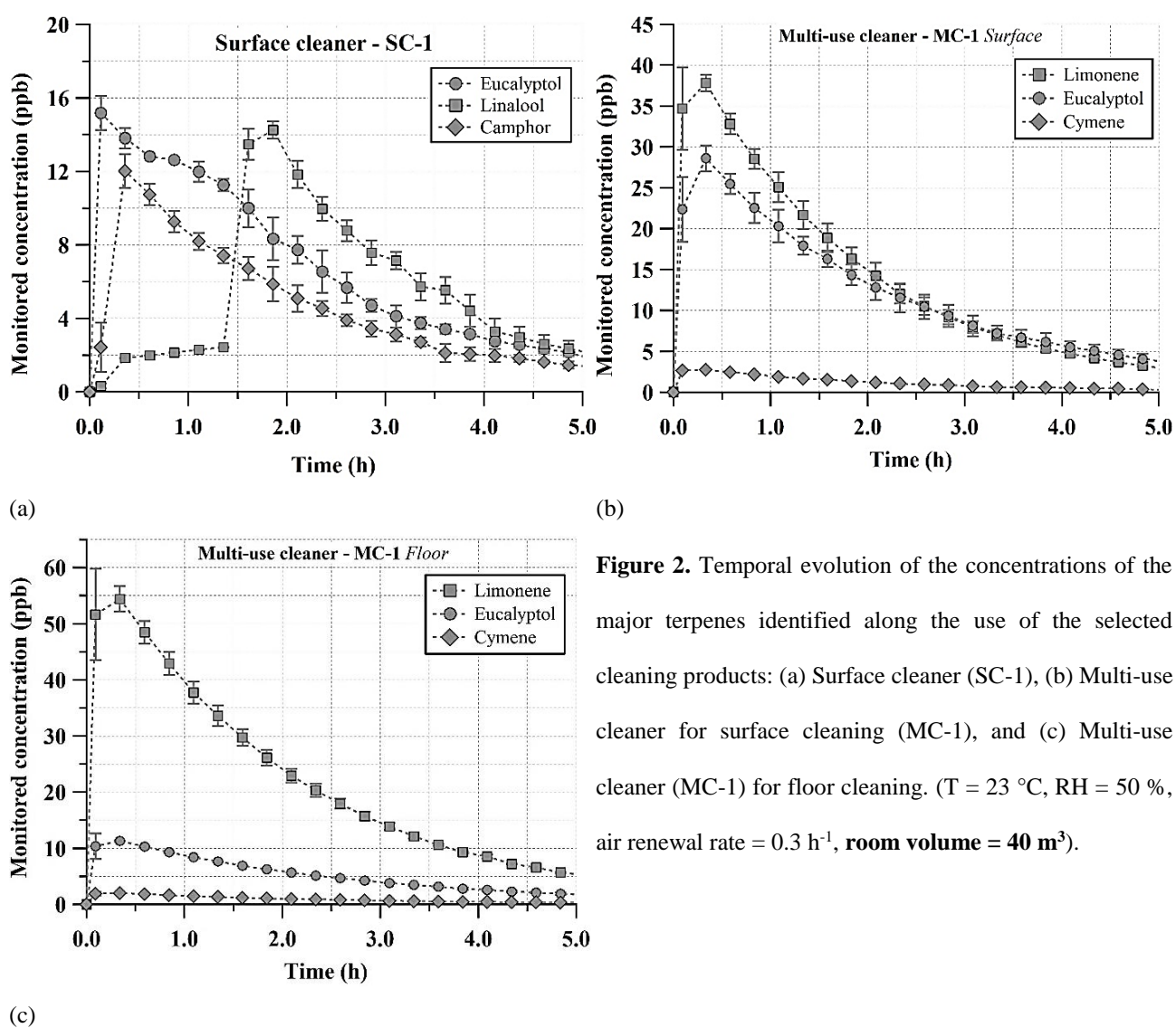
Figure 2. Temporal evolution of the concentrations of the major terpenes identified along the use of the selected cleaning products: (a) Surface cleaner (SC-1), (b) Multi-use cleaner for surface cleaning (MC-1), and (c) Multi-use cleaner (MC-1) for floor cleaning. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m^3**).

1.3 Determination of the mass emission rates of TerVOCs along the use of essential-oil-based cleaning products under real consumer use patterns in the experimental room of 40 m³

The mass emission rates of individual terpenes associated to the use of cleaning products is estimated from their concentration profiles and by employing the estimation methodology previously described in the section 3.4 of chapter 3. Figure 3 reports the temporal evolutions of the monitored concentrations, the air exchange corrected concentration profiles and the air exchange and deposition corrected concentration profiles for (i) eucalyptol emitted along the floor mopping using the MC – 1 and (ii) limonene emitted along the surface cleaning using MC – 1.

(a)   (b)
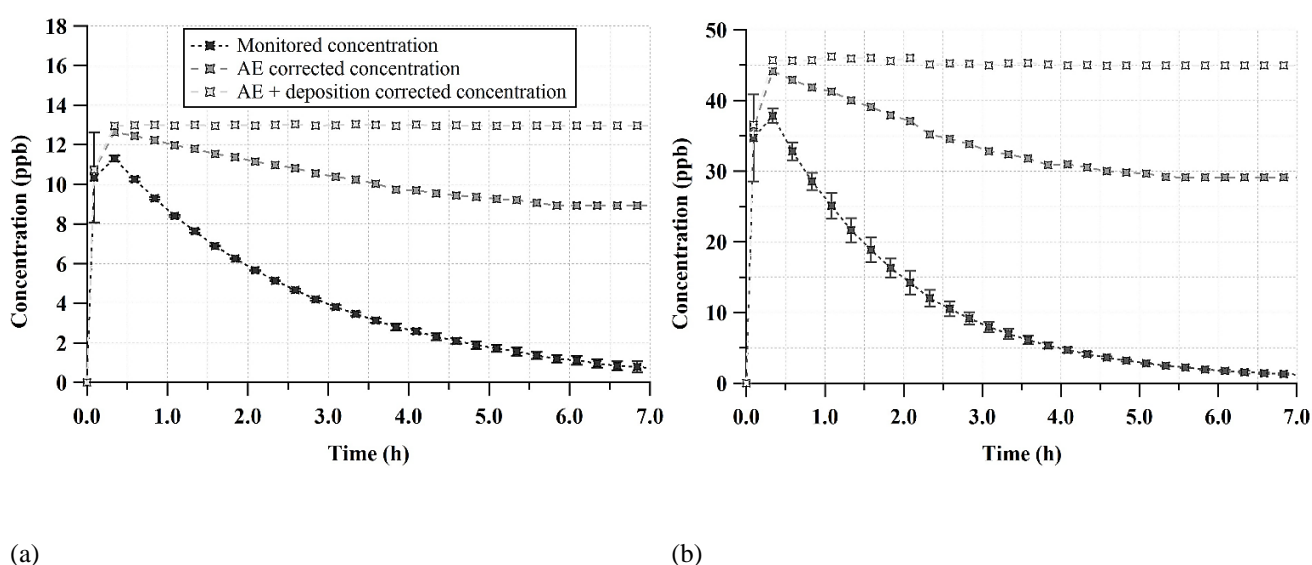
Figure 3. (a) Temporal evolution of eucalyptol directly monitored concentrations (ppb), air exchange (AE) corrected concentrations (ppb) and air exchange (AE) + deposition corrected concentrations (ppb) during the cleaning activity using the multi-use cleaner MC – 1 for floor cleaning. (b) Temporal evolution of limonene directly monitored concentrations (ppb), air exchange (AE) corrected concentrations (ppb) and air exchange (AE) + deposition corrected concentrations (ppb) during the cleaning activity using the multi-use cleaner MC – 1 for surface cleaning. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m³**).

Determination of the individual deposition rates / As can be retrieved from Figure 3, the end of the emission process is identified when the terpene molecules reach their steady state profiles after the air exchange and deposition corrections. Table 2 reports the deposition rate (k_D) experimentally determined along the cleaning practices involving SC – 1 and MC –1 for the 3 predominant terpene molecules. For a given cleaning product, the deposition rates of the predominant emitted terpenes range from 0.04 to 0.20 h^{-1}. These values clearly support the fact that the deposition rates of TerVOCs on the

chamber walls have to be determined to interpret concentration profiles since they impact the resulting concentrations by the same order of magnitude than the air exchange rate (0.3 h^{-1}). Then, the deposition of terpene species on the surfaces of the experimental room are evidenced to be likely competitive with air exchange.

Interestingly, depending the cleaning products employed and their application methods, a same terpene can verify different deposition rates (k$_D$). It can be pointed out that for eucalyptol, its k$_D$ values range from 0.01 h^{-1} to 0.11 h^{-1} from one product to another. This observation is suggested to be associated to the cleaning product formulation and its application method. For floor moping, as the product is used diluted, the relative humidity in the experimental room in observed to increase up to 70 %. Springs et al. [19] evidenced that the number of moles of terpenes taken up per unit of surface area tends to decrease with RH, suggesting competitive interactions with water molecules for uptake on walls. In coherence with these observations, the deposition rates of the three predominant terpenes emitted along the use of MC – 1 are verified to decrease when the product is applied in its diluted form compared to the undiluted surface application.

Table 2. Comparison of the deposition rate coefficients kD (h^{-1}) per terpene from three tested cleaning products (i) the surface cleaner SC – 1, (ii) the multi-use cleaner MC – 1 for floor mopping, and (iii) the multi-use cleaner MC – 1 for surface cleaning

Deposition rate k$_D$ (h^{-1})			
TERPENE	**Cleaning Product**		
	SC – 1	**MC – 1** *Surface cleaning*	**MC – 1** *Floor cleaning*
limonene	Ø	0.18 ± 0.01	0.10 ± 0.02
linalool	0.20 ± 0.04	Ø	Ø
eucalyptol	0.11 ± 0.02	0.07 ± 0.01	0.010 ± 0.002
cymene	Ø	0.10 ± 0.02	ND
camphor	0.04 ± 0.01	Ø	Ø

Ø = this terpene has not been identified in the chemical composition of the cleaning product in its liquid form
ND: no deposition rate is observed or nearly to 0

Moreover, differences in the deposition rate between SC – 1 and MC – 1 (surface cleaning) are related to the product formulation. Indeed, the water content in the composition of a cleaning product is specific to the formulation itself. Then, it is expected that the competition for uptake on walls between water molecules and terpenes might vary depending in the applied product due to disparities related to the water content. In agreement with the literature [20]–[24], these results

suggest that the impact of the uptake process associated to cleaning practices can vary depending on (i) the molecular structure of the considered species, (ii) the physical and chemical properties of the solid surface available for losses, (iii) the cleaning product formulation and its applications method, that could generate competitive interactions for uptake sites, and (iv) the environmental conditions, mainly temperature and humidity.

Mass emission rate profiles of individual TerVOCs / The temporal evolutions of the mass emission rates for the three predominant terpenes emitted along the use of SC – 1 and MC – 1 (surface and floor cleaning) are reported in Figure 4. In the case of the floor cleaning, the mass emission rate is calculated by considering the mass of *pure product* mopped in the 14, 27 m^2 floor, i.e. 3.2 ± 0.1 g.

The maximum mass emission rates are evidenced to be contrasted for a given terpene, mainly depending on the product used and its application mode. These values reach (i) from 6860 ± 500 µg/h to $39\,630 \pm 1780$ µg/h for limonene, (ii) from 2450 ± 200 µg/h to 8920 ± 510 µg/h for eucalyptol, (iii) from 515 ± 40 µg/h to 1405 ± 100 µg/h for cymene, (iv) 760 ± 60 µg/h for camphor, and (v) 2100 ± 160 µg/h for linalool.

Comparing different application modes using the same cleaning product (MC – 1), the maximum emission rates are reached at analogous time, within the first 7 minutes after the cleaning activity is completed for all detected terpenes. Similarly, as reported in Figures 4b and 4c, their respective emission processes are observed to be exhaust after 36 minutes for all TerVOCs. In spite of the similarities associated to the dynamic of their emission process, the mass emission rate levels strongly vary, with ratios between floor and surface cleaning of nearly 6, 2 and 3, respectively for limonene, eucalyptol, and cymene.

Noticeably, in the case of the surface cleaner SC – 1, the emission process is exhausted after 24, 36 and 126 minutes respectively for eucalyptol, camphor and linalool. Likewise, their respective peak mass emission rates are reached at 6, 24 and 96 minutes. Indeed, a particular dynamic is observed for the emission process of terpenes along the use of the surface cleaner SC – 1. The emission process of linalool is verified to be importantly delayed, starting 72 minutes after the product application, probably due to the implementation of encapsulation technologies for this fragrance compounds. In contrast, the mass emission rate of eucalyptol is characterized by a sharp increase within the first 2 minutes. This behavior is expected as eucalyptol presents an important vapor pressure at nearly 260 Pa, being highly volatile if compared to other terpene molecules, as camphor.

To conclude, these results evidence that the mass transfer of fragrance species from the liquid phase of cleaning products to the gas phase of a real scale room are not exclusively governed by their mass concentration in the liquid form but by

the contributions of several key factors : (i) the constituents included in the formulation of the cleaning product that might induce physical and chemical interactions between species modifying the emission kinetics, (ii) the use of technologies intending to enhance and prolong the perception of a "cleaner environment", (iii) the application protocol i.e. rinsing procedure, dilution of the product, amount of product applied, and (iv) the environmental parameters within the environmental room, noticeably the relative humidity.
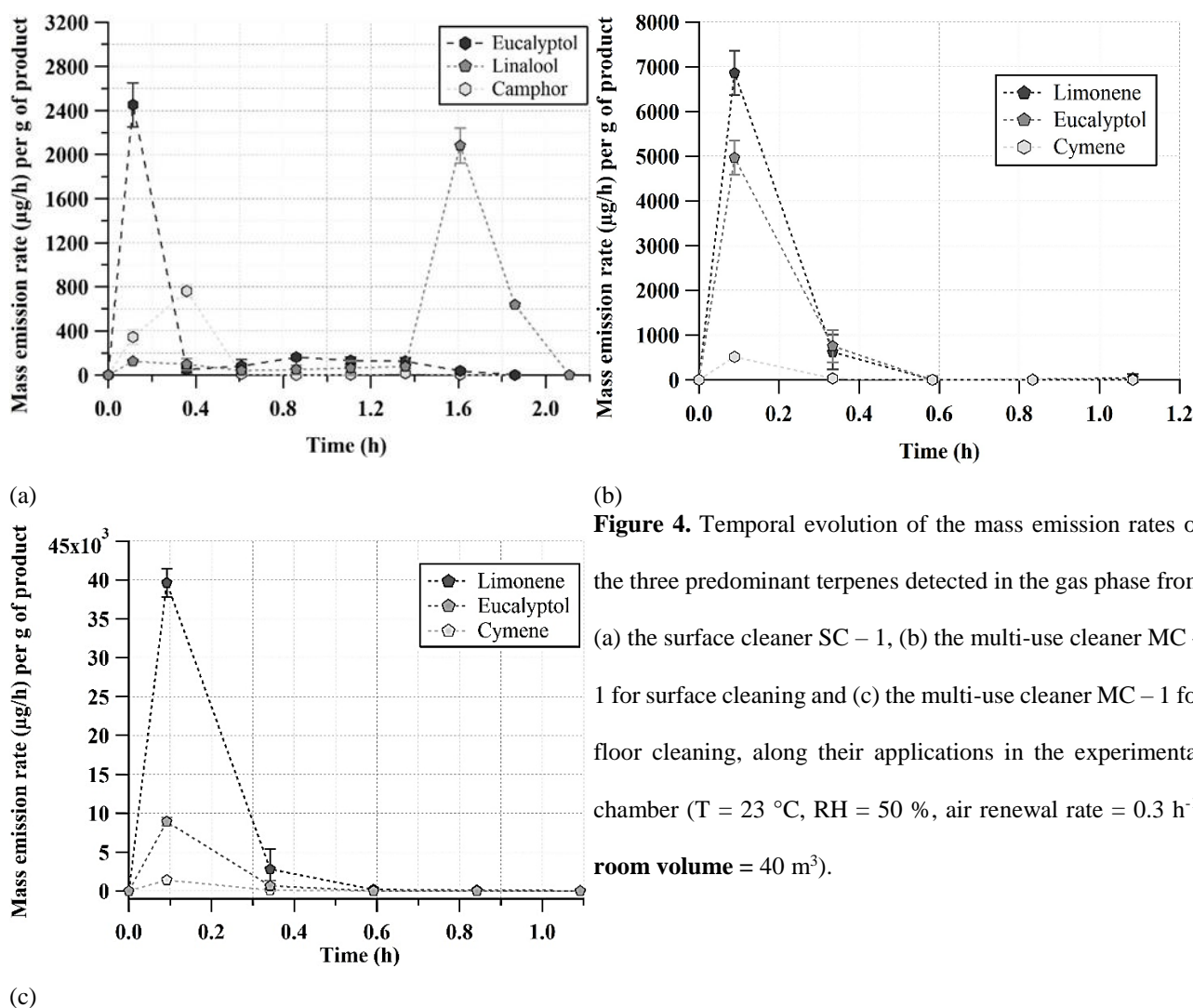
(a)

(b)

(c)

Figure 4. Temporal evolution of the mass emission rates of the three predominant terpenes detected in the gas phase from (a) the surface cleaner SC – 1, (b) the multi-use cleaner MC – 1 for surface cleaning and (c) the multi-use cleaner MC – 1 for floor cleaning, along their applications in the experimental chamber (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m^3**).

1.4 Mass emission rates of TerVOCs along the use of essential-oil-based cleaning products: specific comparison between the 1 m^3 emission test chamber and the 40 m^3 experimental room

This section is addressed at assessing the comparability of the mass emission rates associated to the use of cleaning products under realistic conditions using experimental chambers of different volumes (1 m^3 and 40 m^3). It aims at

providing a specific insight into the possible impact of the volume of the experimental chambers used in the emission assessments and further experimental recommendations.

Surface Cleaner SC – 1 / Figure 5 compares the mass emission rates of the 3 predominant emitted terpenes of SC – 1 between the experimental chamber of 1 m^3 and the experimental room of 40 m^3. As observed in Figure 5, several differences can be noticed for all detected terpenes mainly related to (i) the maximum emission rate levels and (ii) the temporal evolutions of the mass emission rates, i.e. the peak times and the exhaust times of the emission processes. These dissimilarities are discussed in this same order.

Contrasted emission rate levels / For a given terpene, the maximum emission rate is observed to be higher by one order of magnitude along the experiments performed in the real size room (40 m^3) compared to the small chamber (1m^3). Noticeably, when the SC – 1 is applied by spraying and wiping in the real size room, the maximum emission rates of the three predominant terpenes are evidenced to be (i) 4 times higher, at ca. 2400 $\pm$ 150 µg/h, for eucalyptol, (ii) 3 times higher, at ca. 2080 $\pm$ 80 µg/h, for linalool, and (iii) 2 times higher, at 760 $\pm$ 90 µg/h, for camphor. These differences between the emission rate levels during the use of SC – 1 in experimental chambers of different volumes are explained by the contribution of two correlated factors (i) the impact of the "wiping" process and (ii) the intensity of the mass transfer flow in order to achieve the equilibrium between the liquid phase and the gas phase.

Firstly, after performing a cleaning activity, one of the main factors influencing the volatilization of the compounds contained in the cleaner is the "drying-effect" of the product itself. In general, manufacturers include in their formulations light-weight solvents, i.e. alcohol, for enhancing a rapid drying-effect with no spots, stains and streaks over the cleaned surface. [16] When a cleaning product is applied with a wiping procedure, the layer of product is evenly distributed over the entire table. Therefore, the product film on the surface is thinner and the drying process of the product might be accelerated, increasing the mass transfer flow from the liquid film to the gas phase of the cleaner constituents. However, the evaluation of emission from cleaning product in small experimental chambers might present several limitations related to the application process, since no wiping procedure is performed due to the volume restriction. In this case, the product is directly sprayed in the chamber and dispersed as droplets onto the surface. Hence, the applied mass is distributed in a thicker layer distributed in different zones, this aspect may delay and hinder the drying phase and therefore the emission process.

Secondly, during the emission process of a pollutant X an equilibrium tends to be reached between the liquid phase and the gas phase (air) characterized by the liquid-to-air partition coefficient (k_{L-AX}). This coefficient is a temperature

dependent physical parameter that allows the prediction of the behavior of a pollutant *X*, it is described by the ratio between the concentration in the gas phase expressed in µg/m^3 and the concentration in the liquid phase expressed in µg/m^3, both concentrations under equilibrium condition. [25] Independently of the volume of the chamber, the liquid concentration of a terpene *X* diluted in a given cleaner is equivalent at time t = 0. At the start of the emission process, the equilibrium is not achieved yet, it can be described by a transient regime. Under this transient condition, a mass transfer flux from the liquid to the gas phase takes place, tending to balance the gas phase concentration of the TerVOC above the liquid source. When the emission process occurs in a small experimental chamber, the gradient across the concentration in the gas phase at time *t* and the equilibrium concentration is lower since the volume of air to balance is limited to 1 m^3. Then, the equilibrium regime tends to be reached faster in comparison to the real size room of 40 m^3. In contrast, in the 40 m^3 experimental room, the gradient across the concentration in the gas phase at time *t* is maintained stronger because of the larger volume to balance. Consequently, the liquid-to-air mass transfer flux increases in order to equilibrate the 40 m^3 of air of the experimental room. This variability in the intensity of the mass transfer flux along the transient regime from one volume to another is proposed to explain the contrasted values of the mass emission rates of terpenes.

Variations on the temporal dynamic of the emission process / As noticed in Figure 5a, for eucalyptol, equivalent temporal dynamics of the emission rate profiles in both experimental chambers are observed for eucalyptol. The emission rate profile in the real scale chamber (40 m^3) is characterized by a sharp increase of the released mass, reaching the maximum level after only 7 minutes, and completing its emission process after 22 minutes using the SC – 1. Indeed, for both experimental chambers, eucalyptol is noticed to be rapidly volatilized presenting analogous peak times and source exhaustion times. This observation is explained by the acute volatility of eucalyptol. In contrast, for camphor, differences are observed in the temporal emission rate profiles retrieved from both chambers. In the 40 m^3 experimental chamber, the maximum emission rate is reached after 22 minutes after the application of SC – 1, while in the 1 m^3 emission test chamber, the maximum emission rate level is reached only within 8 minutes. However, beyond these differences related to the time positioning of the peak concentrations of camphor, the exhaustion time is identical in both experimental chambers.

Unexpectedly, contrasted mass emission rate profiles are noticed for linalool between the 1 m^3 and the 40 m^3 experimental chambers, as observed in Figure 5. In the 1 m^3 emission test chamber, the emission rate profile of linalool is concomitant with the profiles of other TerVOCs. In the 40 m^3 experimental room, a delayed dynamic of emission is evidenced. In this case, the emission process of linalool is only initiated at nearly 1.5 hours after the application of SC – 1. The delay in the emission process of linalool has been suggested to be associated to the implementation of encapsulation technologies for

prolonging the "clean-scent". The dissimilarities regarding the peak time of linalool emission rates in chambers of different volumes are associated to the drying rate. Indeed, Berger et al. [26] evidenced that regarding encapsulation of fragrance chemicals in consumer products, the drying rate has an strong impact on their retention time. Therefore, considering the experimental differences in the application protocol between both experimental chambers, it is suggested that the different emission rate profiles of linalool are related to the "wiping process" that impacts the drying velocity of the product and the deactivation of the encapsulation barrier.

(a)

(b)

(c)

Figure 5. Comparison of the temporal evolutions of the mass emission rates observed in the experimental room (40 m^3) and the emission test chamber (1 m^3) during the cleaning activity involving the surface cleaner (SC – 1) regarding the three major terpenes emitted. (T = 23 °C, RH = 50 %, and air renewal rate = 0.3 h^{-1}).

Multi-use Cleaner MC – 1 / Figure 6 compares the mass emission rates of the three predominantly emitted terpenes from MC – 1 between the experimental chamber of 1 m^3 and the experimental room of 40 m^3. As observed in Figure 6, analogous temporal evolutions of the mass emission rates are evidenced from all the emitted terpene molecules. Whatever the volume of the chamber, for a given terpene, the maximum emission rate is reached at nearly 5 to 7 minutes and the emission process is noticed to be completed 24 minutes after the application of the MC – 1, for the undiluted application. Nevertheless, significant differences are detected regarding the maximum mass emission levels for the three

predominantly emitted terpenes. Indeed, the maximum emission rates in the real size room are evidenced to be higher than in the small experimental chamber by (i) 7 times, 6860 ± 250 µg/h, for limonene, (ii) 3 times, 5000 ± 310 µg/h, for eucalyptol, and (iii) 5 times, 510 ± 35 µg/h, for cymene. These observations are explained, as previously described for the SC – 1, by the contribution of the key factors: (i) the impact of the "wiping" process and (ii) the intensity of the mass transfer flow in order to achieve the equilibrium between the liquid phase and the gas phase.

Overall, the emission process resulting from the application of essential-oil-based cleaning products evidences strong variations linked to the volume of the experimental chamber. Indeed, the investigation of indoor terpene emissions from the use of essential-oil-based cleaning product might present several limitations if these products are tested in a small, and subsequently non-realistic, experimental chambers. These limitations are mainly related to the application conditions, since small chambers are reduced in space, and therefore, a real-use scenario i.e. rinsing, wiping, or mopping procedures cannot be performed, implying biases in the physical state of the applied product and, as a results, in the effective emissions.
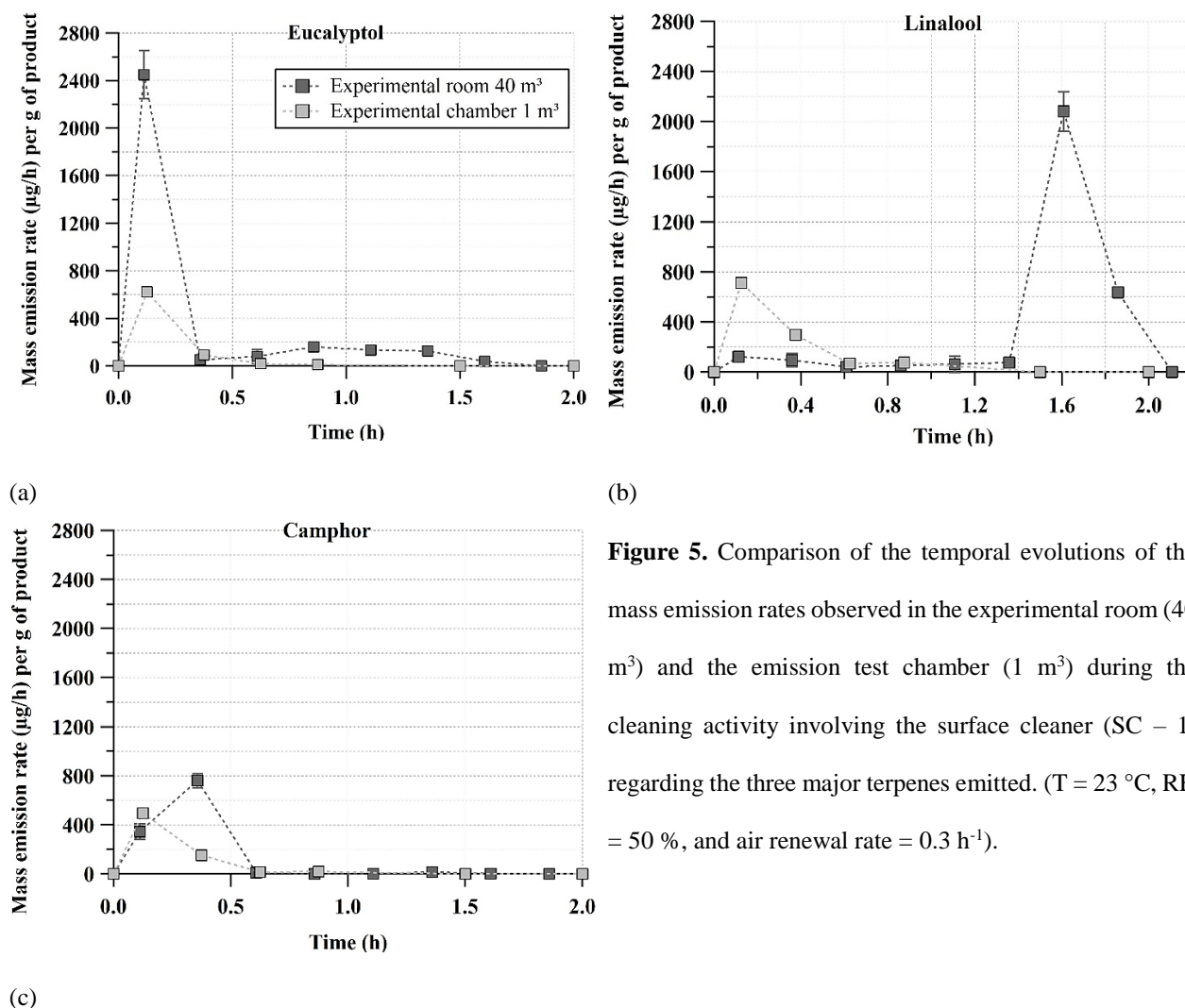

(a)

(b)

(c)
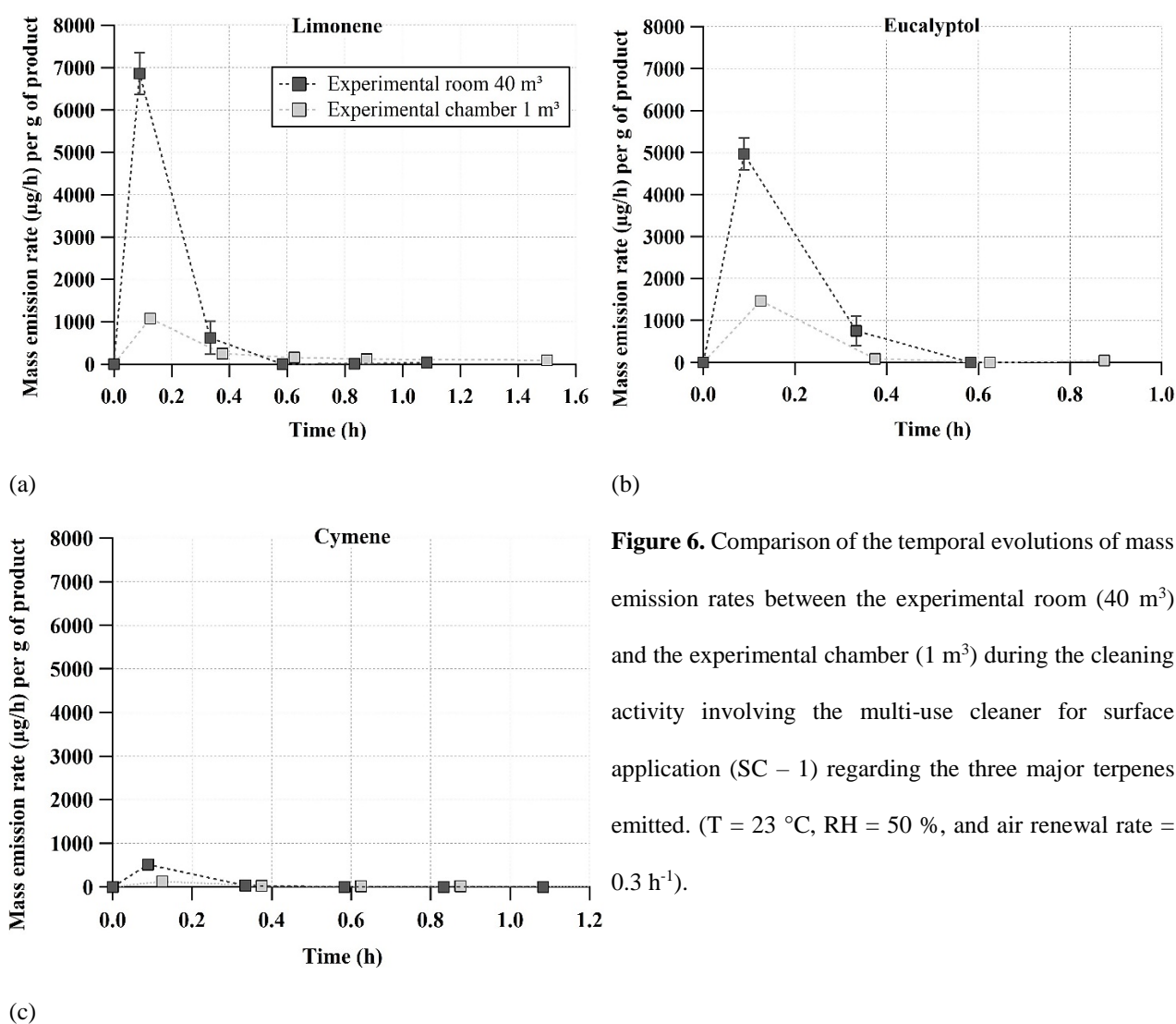
Figure 6. Comparison of the temporal evolutions of mass emission rates between the experimental room (40 m^3) and the experimental chamber (1 m^3) during the cleaning activity involving the multi-use cleaner for surface application (SC – 1) regarding the three major terpenes emitted. (T = 23 °C, RH = 50 %, and air renewal rate = 0.3 h^{-1}).

1.5 Wrap up on the terpene emissions from the use of essential-oil based cleaning products: from liquid composition to realistic consumer use patterns in a real scale room of 40 m³

This section aims at addressing an overall comparison of the mass concentrations of TerVOCs in the liquid form, for SC – 1 and MC – 1, and the evaluation of their emissions at different scales, namely (i) micro-chamber testing, (ii) 1 m³ emission test chamber under realistic condition and (iii) 40 m³ experimental room under real consumer using patterns. Figure 7 reports the mass concentration (µg/g) in liquid phase, the gas-transferred concentration by micro-chamber testing (µg/m³), the maximum emission rate per gram of cleaner in the 1 m³ emission test chamber (ppb/h), and the maximum emission rate per gram of cleaner in the 40 m³ experimental room (ppb/h) with the respective relative abundances of the predominant terpenes.

Beyond the dissimilarities associated to the emission rate profiles of individual terpene molecules in both experimental chamber (1 m³ and 40 m³), discussed in the previous section, strong differences can be noticed concerning the relative abundances of the predominantly emitted terpenes. Indeed, regarding the major terpenes contained in SC – 1, linalool, it can be observed that its mass concentration in the liquid phase corresponds to 26.8 % of the total TerVOCs concentration. However, the peak mass emission rate of this compound is almost negligible for the 1 m³ emission test chamber, but reaches 22.2 % using the 40 m³ experimental room. This difference between both experimental chambers is directly associated to the application protocol, due to the volume limitation that does not allow a wiping process impacting the retention barrier of the fragrance molecule encapsulation. Therefore, if these technologies are employed in the formulation of cleaning product, the evaluation of their emissions in a small experimental chamber induces disparities regarding the concentrations monitored and subsequently biases in the determinations of the mass emission rates, the durations of impact on indoor air quality and the human exposure assessment. Finally, the main advantage of full-scale chamber relies in the real application process that provides accurate information regarding the concentration levels, the mass emission rate for assessing the emission process.

These results indicate that the evaluation of the emissions of TerVOCs from cleaning products in test chambers with small volumes provides key information concerning the general trends of major terpenes emitted. **However, <u>realistic does not necessarily mean real</u>; as a consequence, to accurately assess the impact of consumer products on indoor air quality and the human exposure to emitted chemicals, the investigation of emissions should be executed in a real-scale chambers and employing real application protocols.**

(a)   (b)
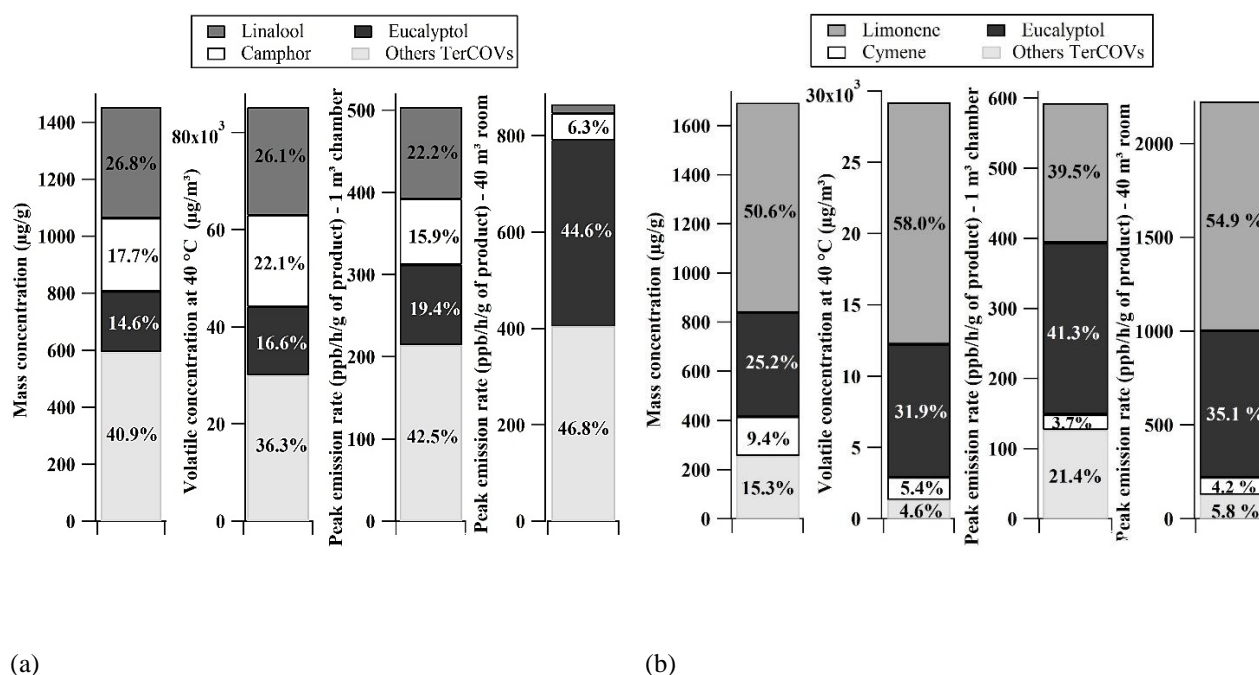
Figure 7. Comparison of the relative abundances of TerVOCs determined as (i) mass concentrations (µg/g) in liquid phase, (ii) gas-transferred concentrations by micro-chamber testing (µg/m^3) (T = 40 °C, RH = 50 %, air flow = 50 ml/min, micro – chamber volume = 40 mL) and, (iii) maximum emission rates expressed per gram of cleaning product using two emission chambers with contrasted volumes   (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, chamber volume = 1 m^3 and **room volume = 40 m^3**) for: (a) the surface cleaner SC – 1, and (b) the multi-use cleaner MC – 1

2. Realistic consumer use patterns of essential oil diffusion: *emission rate assessment in a 40 m^3 experimental room and impact on indoor air quality*

The impact on indoor air quality from the diffusion of tea tree oil has been addressed in the 40 m^3 experimental room IRINA under real consumer use patterns. Two diffusion devices presenting contrasted physical processes of emissions are investigated in this chapter: an electric diffuser and a capillary diffuser. The experimental protocol implemented for the investigation of the emissions associated to the diffusion of tea tree oil is identical to the protocol executed for the emission test chamber of 1 m^3. This protocol can be retrieved in details in Chapter 4. Depending on the diffusion device, and depending on the amount of essential oil involved in the diffuser, temporal emission dynamics might strongly be different. Therefore, the evaluated diffusers are classified as (i) transient diffuser and (ii) continuous diffuser.

Transient diffusers are devices involving a limited mass of oil, typically from 10 to 20 drops of oil. As a consequence, it behaves as a punctual emission source since the low mass of oil can be diffused on short time scales. In contrast, diffusers involving the whole flask of essential oil, typically several milliliters (mL), are classified as continuous diffusers; they

represent finite but long term sources. Moreover, in addition to terpene molecules, oxygenated volatile organic compounds (OVOC) have also been monitored along the diffusion process of tea tree oil. *Note that the emitted concentrations of OVOCs are below the detection limits of the analytical equipment used in this study; therefore, no specific section is dedicated to this type of compounds.*

2.1 Transient diffuser: TerVOC emissions from an electric diffuser in a real scale room of 40 m³

Profile of total TerVOCs / The temporal dynamics of the total TerVOC concentrations emitted from the diffusion of tea tree oil by employing an electric diffuser have been monitored. Results are obtained from a set of three distinct experiments in order to evaluate the repeatability of the emission protocol for each electric diffuser. The variation coefficients of the total concentrations for the various sets of experiments only range from 2.9 % to 15.8 %. The corresponding averaged profile is reported in Figure 8. It is characterized by three main phases associated to the diffusion process: (i) a sharp increase of the total TerVOC concentrations attesting of the rapid vaporization of TerVOCs from the tea tree oil until a maximum total concentration is reached, (ii) a primary decreasing trend referred to the gradual exhaust of the TerVOC source and to the removal of TerVOCs from the gas phase of the experimental room, (iii) a final decreasing stage referred to the evacuation of emitted terpenes by the air exchange and their possible losses on the inner surfaces of the room.

Regarding the emission levels, the peak concentration of total TerVOCs along the use of the electric diffuser is observed at 2140 ± 30 ppb. Additionally, this concentration is reached at ca. 70 minutes after the electric diffuser is turned on. Noticeably, the maximum concentration of total TerVOCs exceeds by 2 orders of magnitude the usual VOC concentration in indoor air and by one order of magnitude the recommended Critical Exposure Level (CEL) for long-term exposures established in the frame of the European projects EPHEC and INDEX. [27]–[29] Furthermore, considering the CEL of α-pinene, i.e. 810 ppb as reference value, the duration of impact on indoor air associated to the emission of terpene molecules along the transient diffusion of tea tree oil in confined environments might exceed 6 hours.

Su et al. [30] investigated the effect of evaporating essential oils in large size rooms, i.e. with volumes higher than 20 m³, under real conditions of use. In this study, environmental parameters, such as temperature and humidity, were unfortunately not controlled and not specified. Nonetheless, studying the evaporation of tea tree oil, Su et al. [30] evidenced a peak concentration of total TerVOCs of ca. 1400 ppb. It is in the same order of magnitude than this study. Consequently, the evaporation and diffusion of terpenes from essential oils can be a transient but intense source of

TerVOCs in indoor environments and can potentially impact indoor air quality exceeding recommended exposure concentrations by one order of magnitude.
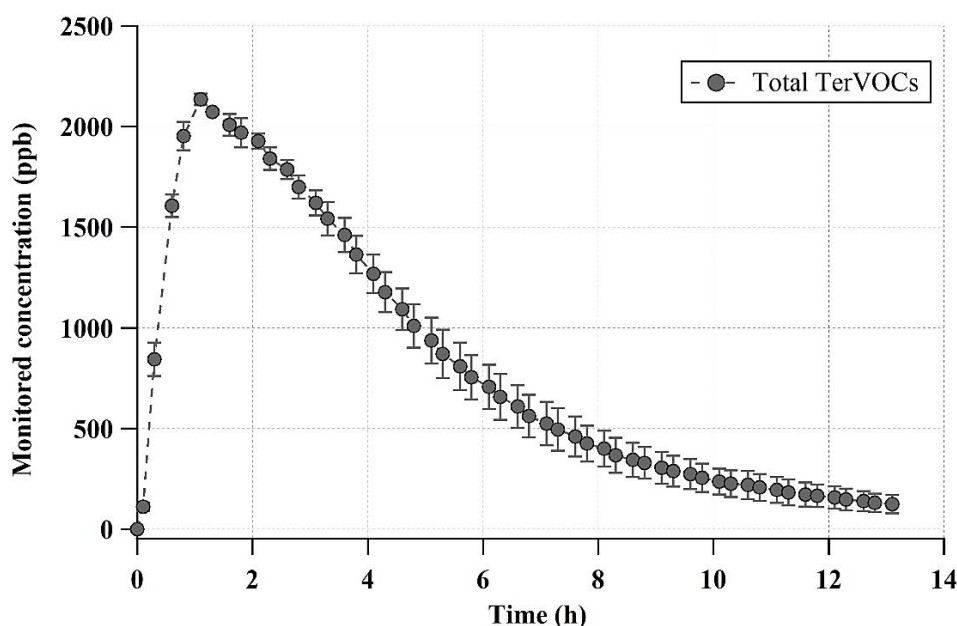
Figure 8. Temporal evolution of TerVOC total concentrations emitted along the diffusion of tea tree essential oil using an electric diffuser (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m³**).

**Individual profiles of TerVOCs ** Among the 15 compounds detected in the liquid chemical composition of the tea tree oil, 9 monoterpenes and 2 terpene alcohols are identified and quantified in the gas phase of the 40 m³ experimental room. The predominant terpene molecules detected along the diffusion of tea tree oil by using an electric device are: 4-terpineol, γ-terpinene, α-terpinene, eucalyptol and α-pinene. Their individual emission profiles are reported in Figure 9 and detailed emission characteristics are displayed in Table 3. Their profiles are characterized by the same three phases observed for the total TerVOC concentration profile (Figure 8).

Regarding the emission levels, the individual maximum concentrations are: 790 ± 17 ppb for 4-terpineol, 685 ± 20 ppb for γ-terpineol, 310 ± 10 ppb for α-terpinene, 110 ± 8 ppb for eucalyptol, and 100 ± 10 ppb for α-pinene. Compared with the mass concentration of individual TerVOCs in the liquid tea tree oil, a correlation is evidenced between the major terpenes detected in the liquid form and the predominant TerVOCs emitted in the gas phase of the 40 m³ room along the diffusion with an electric device under a realistic use pattern, as it can be observed in the left column of Table 3.
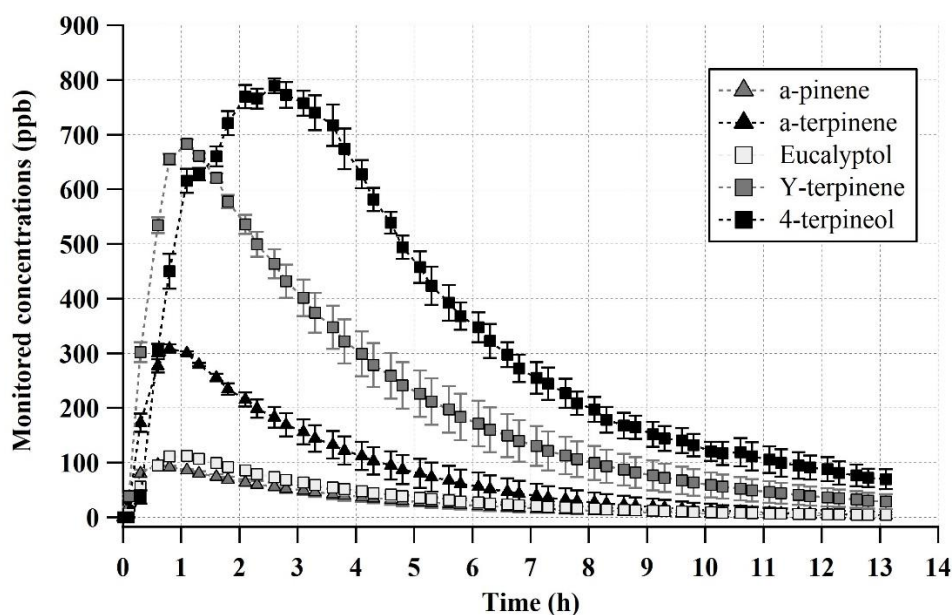
Figure 9. Temporal evolutions of α-pinene, α-terpinene, eucalyptol, γ-terpinene, and 4-terpineol concentrations during the diffusion of tea tree oil using an electric diffuser. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m³**).

Interestingly, several variations are evidenced regarding the dynamics of the emission processes among individual TerVOCs. Indeed, the time positioning of the peak concentration is noticed to differ depending on the terpene molecule (Table 3). As observed in Figure 9, the concentration profile of 4-terpineol is characterized by a broad emission peak spanning from ca. 1 to 4 hours after the diffusion is initiated. Furthermore, the gas phase concentration of 4-terpineol still represents nearly 40 % of the peak concentration 6 hours after the emission process started. Among the emitted TerVOCs, 4-terpineol appears as the terpene with the slowest emission kinetic. This behavior could be correlated with the fact that 4-terpineol is characterized by the lowest vapor pressure, one order of magnitude lower than the one of eucalyptol, α-pinene and α-terpinene. The emission profile of γ-terpinene is typified by a sharp increase of its concentration as soon as the diffusion is initiated. Then, its emission peak is reached nearly 1.1 hours after the diffuser is turned on. Immediately after this time period, the concentration of γ-terpinene decreases, suggesting the rapid exhaustion of that TerVOC and its subsequent evacuation by the air exchange and/or uptakes on the room walls. For other major TerVOCs, namely eucalyptol, α-pinene and α-terpinene, analogous concentration dynamics with γ-terpinene are evidenced; they reach their emission peak within the same time span. Interestingly α-pinene, characterized by the highest saturation partial pressure (599 Pa), is typified by one of the lowest time for emission peak: 0.6 hours. These observations suggest that the transfer of individual terpenes from the essential oil to the gas phase is mainly governed by (i) their intrinsic physical and chemical properties and (ii) the abundances of individual TerVOCs in the pure essential oil.

Table 3. Intrinsic properties and emission characteristics of the 5 major terpenes monitored along the electric diffusion of tea tree oil (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m³**)

	Tea tree oil *- Electric diffuser*				
MAJOR TERPENES	**Peak concentration (ppb) ± SD**	**Time of maximum concentration (h)**	**k_D Deposition rate (h^{-1})**	**Mass concentration at the liquid phase (% w/w)**	**Vapor pressure from literature (Pa)**
4-terpineol	790 ± 15	2.6	-	42.45	37, 20 [31]
γ-terpinene	685 ± 10	1.1	0.01	22.88	103, 145 [32]
α -terpinene	310 ± 8	1.1	0.12	12.85	222 [33]
Eucalyptol	110 ± 5	1.1	0.01	3.70	230, 260, 254 [34]
α-pinene	100 ± 5	0.6	-	2.72	589, 599 [32], [35]

-: no deposition rate evidenced for this TerVOCs

Gas phase fingerprint of tea tree essential oil along electric diffusion / As mentioned in chapter 4, the fingerprint of an essential oil is defined as the contribution of each terpene molecule to the TerVOC gas concentration at a specific time t. The diffusion through the electric device initiates at t = 0. At this time, all individual terpenes are in the liquid phase as reported on the left side of Figure 10.

Considering the chemical composition of the tea tree oil in its liquid form, α-pinene is one of the minor compounds, present at only 2.8 % w/w and 4-terpineol is the major compound, present at 42.5 % w/w. However, nearly 20 minutes after the diffusion process is initiated, the concentration of α-pinene contributes at ca. 15 % of the total TerVOCs released in the gas phase (Figure 10). While at the same time, 4-terpineol, characterized by a lower vapor pressure (ca. 20 Pa), is still mostly present in the liquid phase and not transferred to the gas phase yet. After 1 hour of diffusion, 4-terpineol contributes up to 28.3 % of the TerVOCs transferred to the gas phase, while α-pinene only accounts for ca. 4.3 % of the total terpene concentration. This behavior suggests that at t = 1h, α-pinene may be almost exhausted from the tea tree oil and gradually evacuated from the experimental room due to the air renewal or by the deposition on inner surfaces. Finally, the contrasted emission dynamics of individual TerVOCs emitted from tea tree oil induces a significant variation of the gas phase terpene composition along the diffusion process employing an electric device. **The fingerprint of the essential oil in the gas phase varies all along the emission process**, as it can be observed in Figure 10. This phenomenon has a direct impact on (i) the odor perception and (ii) the exposure to individual terpenes while diffusing essential oils indoors.

It can be pointed out from Figure 10 that from the start of the diffusion process until nearly 4 hours, variations in the contributions of individual TerVOCs in the gas phase are observed. However, the relative abundances from individual terpenes remain at constant values beyond 4 hours of emission. This observation suggests that after this timespan, the emission term of TerVOCs is exhausted and the concentration of individual terpenes in the gas phase is solely related to their evacuation by the air renewal and their deposition on the inner walls of the chamber. In order to confirm this point the mass emission rates need to be calculated. They are discussed in the next section.
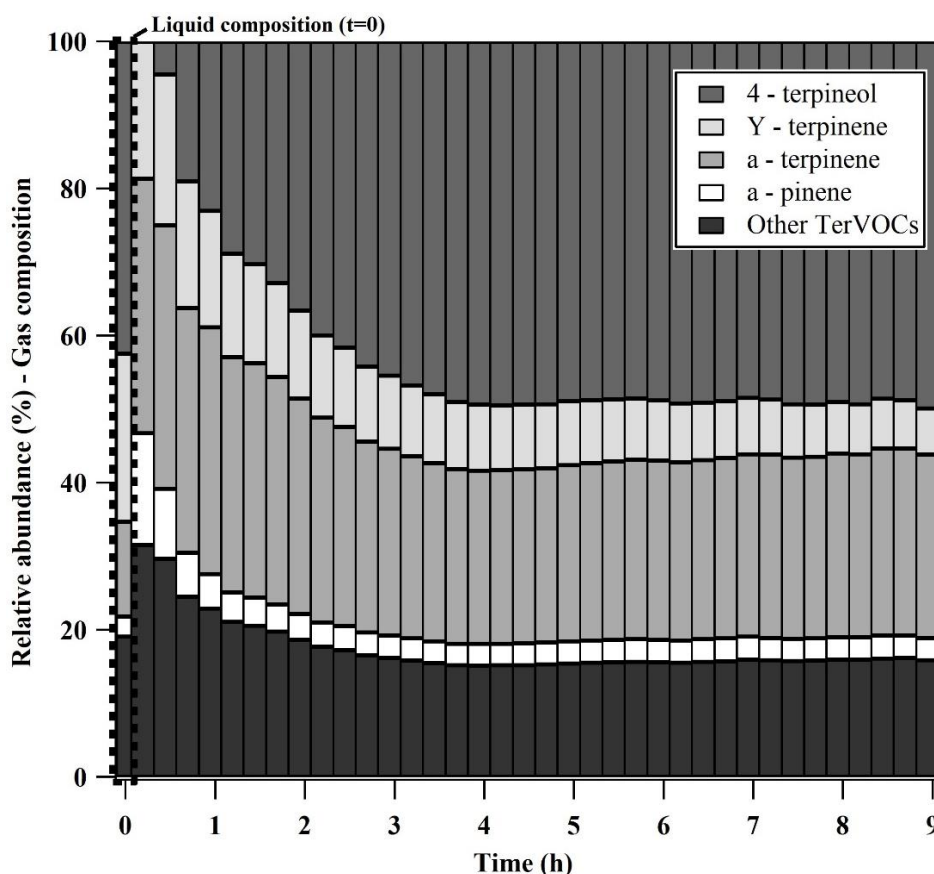
Figure 10. Temporal evolutions of the relative abundances of major TerVOCs transferred to the gas phase along the diffusion of tea tree essential oil using the electric device. NB: the relative abundances of major TerVOCs in the liquid phase are reported at t = 0 (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m³**).

2.2 Determination of the mass emission rates from the transient electric diffusion of essential oils in the real scale experimental room of 40 m³

The assessment of the mass emission rates is of key importance since: (i) it provides crucial information to understand and characterize the emission process of an indoor source of pollutant, (ii) it is a representative parameter that can be extrapolated to several cases leading to the prediction of pollutant emissions in other scenarios, and (iii) it is required for

the evaluation of human exposure and to define risk scenarios. In this section the mass emission rate of individual terpenes is estimated along the electric diffusion of tea tree oil in a real scale experimental room of 40 m^3 from their concentration profiles and by employing the estimation methodology detailed in Chapter 4. The temporal evolutions of the mass emission rates of the four predominant terpenes (γ-terpinene, α-terpinene, α-pinene and eucalyptol) released from the electric diffusion of tea tree oil are gathered in Figure 11.

NB: it has to be noted that the mass emission rates involving essential oil diffusion have been expressed per diffusion device, unlike emission rates of cleaning products expressed per gram of cleaning product. It could have been envisaged to express the mass emission rate related to essential oil diffusion per gram of essential oil, however it would not have been a valuable information, because of the diffusion processes themselves. First, regarding continuous capillarity diffusion, the principle of the diffuser relies on the saturation of a fibrous emissive part by a sufficient amount of essential oil. To that end, the emissive part is partially immersed in liquid essential oil, i.e. directly connected to the flask. Therefore, the emission process is not controlled by the amount of essential oil involved in the device operation, but only by the diffusive device itself. Indeed, doubling the size of the essential flak, would not result in doubling the emission rates of TerVOCs. It may only result in expanding the emission duration, not its intensity. Regarding the transient electric diffuser, similarly, the principle of the diffuser has to be taken into account. The diffusion of essential oils using an electric diffuser is not only and linearly controlled by the amount of essential oil involved in the diffusion. Indeed, the cross section of the heated plate where liquid essential oils are applied, as well as the electrical power of the device to heat essential oils can be considered as controlling and limiting factors of the diffusion. Moreover, in order to allow a direct comparison of both diffusing devices investigated in the 40 m^3 experimental room, mass emission rates have to be expressed in the same unit. As a result, to allow an operational use of this parameter, mass emission rates of essential oil diffuser are expressed in mg of TerVOC emitted per hour and per diffuser: mg/h/diffuser.

Mass emission rate profiles of individual TerVOCs / As can be noticed in Figure 11, γ-terpinene, α-terpinene and eucalyptol observed analogous temporal emission rate profiles, reaching their maximum emission rate levels within the first 20 minutes after the start of the diffusion process. However, their respective peak values of mass emission rate are highly contrasted, reaching 250 ± 20 mg/h per diffuser for γ-terpinene, 150 ± 15 mg/h per diffuser for α-terpinene and 50 ± 5 mg/h per diffuser for eucalyptol. Noticeably, α-pinene, is characterized by a sharp increase of its mass emission rate up to its peak value at ca. 75 ± 5 mg/h per diffuser attesting its rapid volatilization in a short time span of nearly 3 minutes.
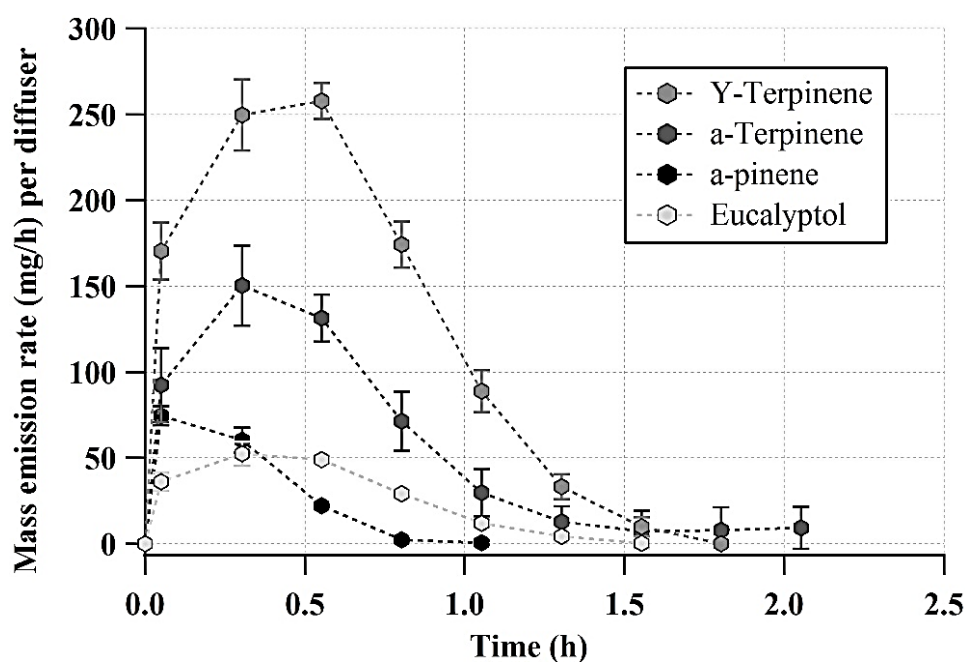
Figure 11. Temporal evolutions of the mass emission rates of, γ-terpinene, α-terpinene, α-pinene, and eucalyptol expressed in mg of essential per hour and per diffuser along the diffusion of tea tree oil by electric diffuser (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m³**).

In addition to the maximum mass emission rate levels and their time positioning, the determination of the emission rate profiles provides key information related to the time of exhaustion of the source. Based on Figure 11, even if acute differences are reported regarding the intensity of the emission rates of individual TerVOCs, it can be pointed out that γ-terpinene, α-terpinene and eucalyptol evidence analogous exhaustion time at ca. 1.5 hours after diffusion process starts. In contrast, α-pinene, characterized by a fast volatilization dynamic associated to its high saturation vapor pressure, exhibits an emission process exhausted after only 0.8 hours. These results confirm that the transfer of terpene species to the gas phase during the diffusion of tea tree oil using an electric device are primarily driven by (i) the mass concentration of individual terpene molecules in the liquid gas, (ii) the intrinsic volatility of the individual TerVOCs, in connection with the temperature of the diffuser i.e. 65 ± 2 °C, which might enhance the mass transfer flux from the liquid oil to the gas phase.

A complete assessment of the diffusion of tea tree oil employing an electric device in a 40 m³ full-scale chamber is accomplished including (i) the experimental determination of concentration profiles of TerVOCs, (ii) the determination of their mass emission rates and (iii) the determination of the relative fingerprint evolution in the gas phase along the diffusion of tea tree oil. The diffusion of tea tree oil in a 40 m³ real scale rooms results in a major increase of indoor

terpene concentrations up to several hundreds of ppb, impacting indoor air quality for nearly 6 hours, considering the CEL of α-pinene. ***Are these real sale results equivalent to the investigation of the transient diffusion of tea tree oil in the smaller emission test chamber of 1 m³?*** In the next section a comparative analysis between the mass emission rates of the main TerVOCs in the 1 m³ emission test chamber and the real-scale room of 40 m³ is performed to address to impact of the chamber volume on the representativeness of the emission investigations.

2.3 Mass emission rates of TerVOCs along the transient electric diffusion of essential oils: comparison between the 1 m³ emission test chamber and the 40 m³ experimental room

This section aims at comparing the mass emission rates associated to the indoor diffusion of essential oils under real conditions of use between experimental chambers of highly contrasted volumes i.e. the real-scale chamber of 40 m³ and the emission test chamber of 1 m³. Figure 12 reports the mass emission rates of the 4 predominantly emitted terpenes from the diffusion of tea tree oil by the electric device in the emission test chamber of 1 m³ and in the real-scale room of 40 m³. For a given terpene, several dissimilarities can be noticed by comparing the mass emission rate profiles retrieved from both chambers; these differences are related to (i) the maximum emission rate levels and (ii) the temporal evolution of the mass emission rates i.e. the temporal positioning of the peak emission rate and the exhaustion time of the emission process.

Contrasted emission rates / Based on Figure 12, for γ-terpinene and α-terpinene, their respective maximum emission rate values are higher by one order of magnitude if the tree tea oil is diffused in the 40 m³ room, reaching 250 ± 20 mg/h/diffuser and 150 ± 10 mg/h/diffuser. While in the 1 m³ emission test chamber, the maximum emission rates of the same TerVOCs only reach 82 ± 7 mg/h/diffuser and 74 ± 9 mg/h/diffuser, respectively for γ-terpinene and α-terpinene. Similarly, for α-pinene and eucalyptol, their respective mass emission rates in the 40 m³ room are evidenced to be (i) 4 times higher, 75 ± 5 mg/h/diffuser and (ii) 3 times higher, 50 ± 5 mg/h/diffuser, compared to the 1 m³ emission test chamber. Figure 12 clearly highlights the fact that, for a given terpene, the maximum emission rate levels are strongly impacted by the volume of the experimental chamber. These discrepancies regarding the mass emission rates during the electric diffusion of tea tree oil in experimental chambers of different volumes are suggested to be explained by the intensity of the mass transfer flow of TerVOCs from the liquid essential oil to the gas phase of the chamber to reach an equilibrated regime between the liquid phase and the gas phase.

Along the emission process of a terpene *X* from the electric diffusion of tea tree oil, an equilibrium between the concentration of *X* in the liquid phase and in the gas phase tends to be reached. However, at the start of the emission

process the equilibrium condition is not achieved yet, it leads to a transient regime. Under this transient condition, a mass transfer flux of TerVOCs from the liquid oil to the gas phase takes place, tending to balance the gas phase concentration of TerVOCs above the liquid source. When the emission process occurs in a small experimental chamber, the gradient across the concentration of X in the gas phase at time t and the equilibrium concentration is lower since the volume of air to be balanced is limited to 1 m^3. Then, the equilibrium regime tends to be reached faster in comparison to the 40 m^3 room. In contrast, in the 40 m^3 experimental room, the concentration gradient of the TerVOC X in the gas phase is maintained stronger because of the larger volume; consequently, the liquid-to-air mass transfer flux increases in order to balance the 40 m^3 of air to equilibrate the experimental room. The variability in of the intensity of the mass transfer flux along the transient regime from one volume to another is proposed to explain the contrasted values of the mass emission rates of terpenes.

Variations in the temporal dynamics of the emission process / Regarding the four predominantly emitted terpenes using the electric diffusion of tea tree oil in the 40 m^3 experimental room, the mass emission rate profiles are characterized by a steep increase within the first three minutes after the diffuser is switched on. Then, their respective maximum mass emission levels are reached. In the 40 m^3 experimental room, the exact time positioning of the mass emission rate peaks appears to be controlled by the individual volatilities of the TerVOCs (33 minutes for ɣ-terpinene, 18 minutes for α-terpinene and eucalyptol, and 3 minutes for α-pinene). Once the peak time is reached, the mass emission rate is characterized by a marked decreasing phase attesting of the gradual exhaust of the emission source; the source exhaustion time ranges from 48 minutes for α-pinene to 108 minutes for ɣ-terpinene.

In contrast, in the emission test chamber of 1 m^3, the emission process is noticed to be slower compared to the real size room. Regarding the four predominantly released terpenes, their mass emission rate profiles are characterized by a more gradual increase within the first minutes of diffusion, until their emission rate peaks are reached. The maximum mass emission rates are reached at 48 minutes for ɣ-terpinene and eucalyptol and 33 minutes for α-terpinene and α-pinene. Subsequently, the mass emission rates slightly decrease for all the predominant terpenes, until the emission process is completed. Moreover, the exhaustion time is observed to diverge depending on the intrinsic volatility of the individual terpenes. The emission processes are noticed to be completed after 73 minutes for α-pinene, 123 minutes of eucalyptol and α-terpinene and 168 minutes for ɣ-terpinene. Furthermore, independently on the volume of the chamber, a linear correlation is noticed between (i) the vapor pressure of the major emitted terpene molecules and (ii) their respective positioning time of the mass emission rate along the diffusion by an electric device.

These results suggest that, whatever the volume of the chamber, the mass transfer flux along the diffusion of tea tree oil by employing an electric device is driven by the liquid content of individual terpene in the oil, and the volatility of each terpene molecule. However, comparing both experimental chambers, significant variations are evidenced regarding the mass emission rate levels and the dynamic of the emission process, being both inferior using the emission test chamber of 1m³. Therefore, the evaluation of the emissions of TerVOCs and their effective impacts on indoor air quality using small volume test chambers might induce several strong limitations and biases, and may lead to a severe under-estimation of the human exposure to these molecules.

(a)   (b)

(c)   (d)
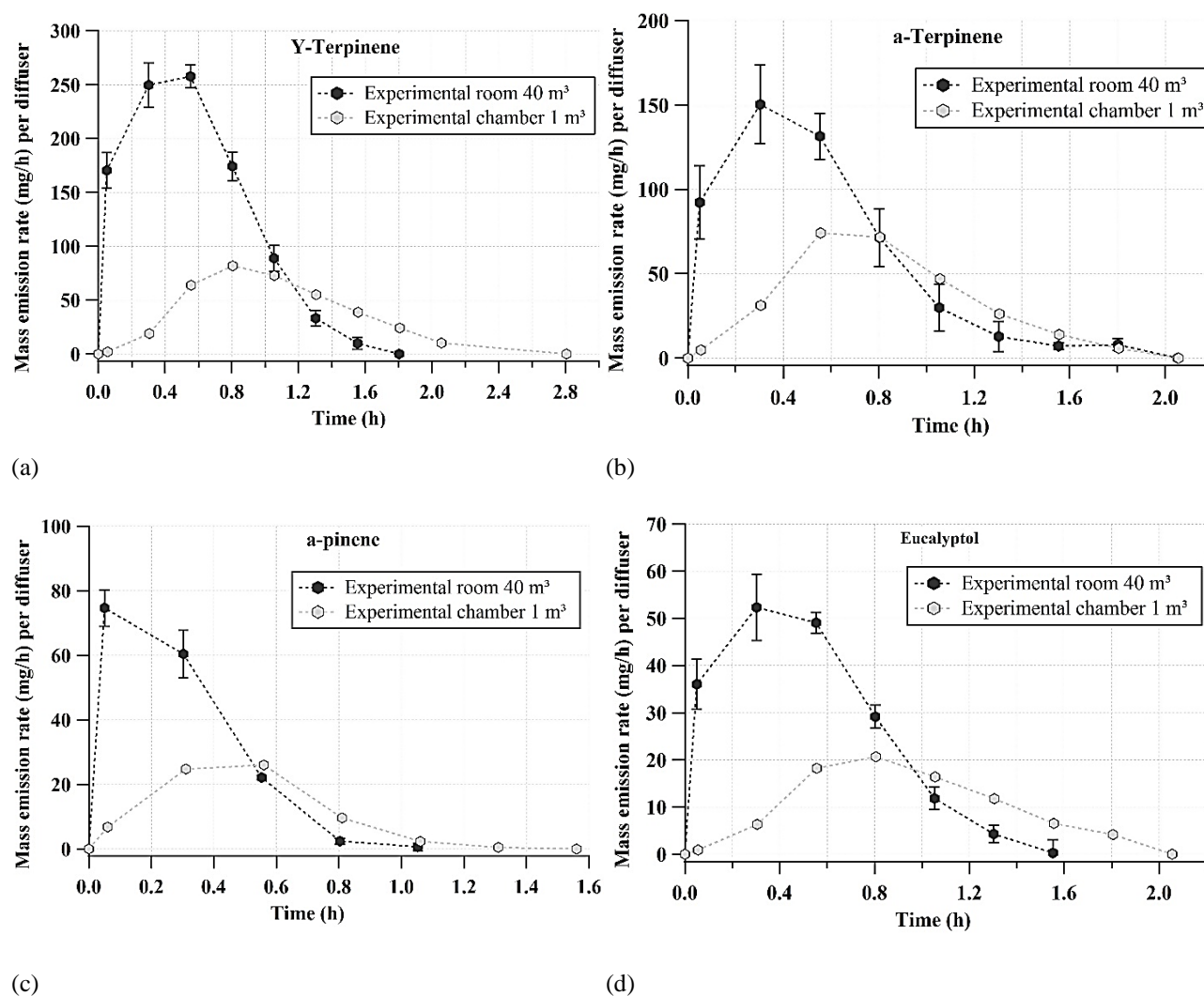
Figure 12. Comparison of the temporal evolutions of the mass emission rates of, γ-terpinene, α-terpinene, α-pinene, and eucalyptol along the diffusion of tea tree oil by an electric device using the experimental room of 40 m³ and the emission test chamber of 1 m³ (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}).

2.4 Continuous diffuser: TerVOC emissions from a capillary diffuser in a real scale room of 40 m³

Along the diffusion of tea tree oil using a continuous diffuser, namely capillary device, in the 40 m³ experimental room the same 11 terpenes than those monitored during the diffusion using an electric device (9 monoterpenes and 2 terpenes alcohols) are identified and quantified. The concentration profiles of the four predominant terpenes (α-terpinene, eucalyptol, γ-terpinene, and 4-terpineol) as well as the total TerVOC profile are displayed in Figure 13. All concentration profiles can be described by two main stages: (i) an increase of the gas concentration of TerVOCs, and (ii) a steady state concentration regime of gas phase TerVOCs inside the 40 m³ experimental room. The steady state regime attests that an equilibrium is reached between sources and sinks or TerVOCs in the 40 m³ room: (i) the emissions of TerVOCs from the continuous diffuser, (ii) the removal of diffused terpenes by air renewal rate and (iii) their possible losses on the inner surfaces of the room. In the case of the continuous diffuser, the maximum concentrations reached by the TerVOCs are not typified by a peak in the concentration profile, but by the steady state regime itself, as reported in Figure 13.

Compared to the electric diffusion, the diffusion of tea tree oil by capillarity leads to a maximum concentration of total TerVOCs, by one order of magnitude lower: 430 ± 10 ppb. Noteworthy, another observed difference between the two diffusion mechanisms relies in the time span to reach the maximum concentration: they are strongly contrasted. Indeed, when using a capillary device in a real size room, the mean time to reach the steady state concentrations might overcome 15 hours; while for the electric diffuser, the maximum concentrations are reached within only 1 to 2 hours, depending on the individual TerVOCs. This difference can be attributed to the heating of essential oils provided by the electric diffuser which definitely enhances the kinetic of the liquid to gas phase transfer.

Regarding the predominantly emitted terpenes by the capillary device, individual TerVOC values reached during the steady state regime are highly contrasted: 140 ± 10 ppb for γ-terpinene, 100 ± 8 ppb for 4-terpineol, 60 ± 5 ppb for α-terpinene and 15 ± 3 ppb for eucalyptol. At the steady state, these concentration levels respectively account for 33, 23, 15 and 6 % of the total emitted concentrations for γ-terpinene, α-terpinene, 4-terpinol and eucalyptol. Likewise, along the steady state emission regime, these four predominant molecules account for 76 % of the total terpene concentration. Unlike the electric device, where the main terpene released is 4-terpineol, the predominantly emitted terpene during diffusion using the capillary device is γ-terpinene. Unexpectedly, no correlation has been evidenced between major emitted terpenes by the capillary diffuser and their respective relative abundances in the liquid phase or their usual liquid-gas physicochemical properties. Therefore, it can be suggested that when diffusing using capillary devices, in addition to

the chemical composition of the liquid tea tree oil and the intrinsic volatility of terpenes, the affinity of TerVOCs to the material of the diffuser stick itself may play a key role in the emission process. Indeed, the emission process by employing a capillary device is primarily initiated and controlled by the diffusion of the liquid TerVOCs in the fibrous beech wood sticks and therefore by the interaction of TerVOCs with that material.
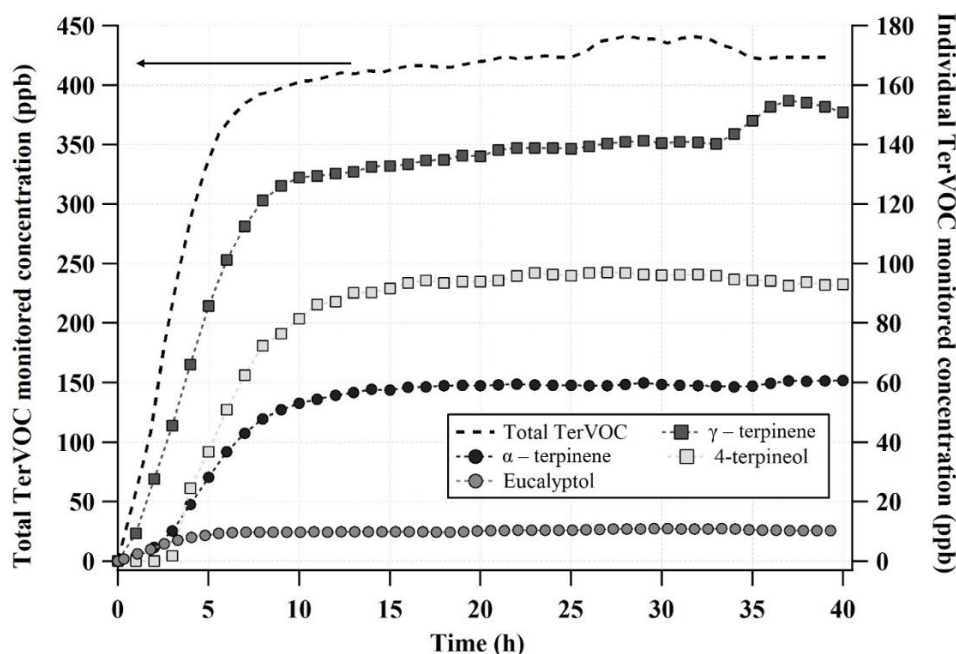
Figure 13. Temporal evolutions of the total TerVOC, α-terpinene, eucalyptol, γ-terpinene, and 4-terpineol during the diffusion of tea tree oil using a capillary diffuser. (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m^3**)

Regarding the dynamic of the emission process, the three predominant terpenes, namely γ-terpinene, α-terpinene, and 4-terpineol, verify the same stabilization times at nearly 10 hours beyond the start of the diffusion process. While for the highly volatile eucalyptol, the steady state is achieved only 5 hours beyond the start of the diffusion. Once the stabilization regime is achieved, the emission process appears to be solely limited by the liquid content of the individual terpenes in the essential oil flask. This aspect is defined in this work as the *individual boundary mass* of the emission process. To assess the duration of impact of the capillary diffusion of tea tree oil on indoor air quality, several calculations were performed in order to determine the timespan of the emission process till the source gets exhausted. Firstly, from the concentration profiles and using the estimation methodology previously introduced in Chapter 4, the mass emission rates are calculated and expressed in g per day and per diffuser (ER$_{day}$) (Table 4). These results are gathered in the left column of Table 4. Secondly, the emitted mass E$_{massX}$ expressed in g is estimated using *Eq 1* and (i) the determined mass emission rates at the steady state ER$_{day}$ per individual TerVOCs *X* and (ii) the time *t* in days.

$$E_{mass\,X} = ER_{dayX} \times t \qquad Eq.\ 1$$

Table 4. Mass emission rates of the five predominantly emitted terpenes along the capillary diffusion of tea tree oil (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h^{-1}, **room volume = 40 m^3**).

	Tea tree oil　*- Capillary diffuser*				
MAJOR TERPENES	**Mass emission rate per diffuser at steady state** *(g/day per diffuser)*	**Steady state time** *(h)*	**Individual boundary mass** *(g)*	**Source exhaustion time** *(h)*	**Vapor pressure** (From Table 3) *(Pa)*
4-terpineol	0.07	11	4.61	51	20 - 37
γ-terpinene	0.10	15	2.98	23	103 - 145
α -terpinene	0.08	13	1.67	16	222
Eucalyptol	0.02	7	0.48	18	230 - 260
α-pinene	0.02	7	0.35	17	529 – 599
Other TerVOCs	**0.03**	-	**2.91**	51	-

In addition to the individual boundary masses established, the total mass contained in the essential oil flask is identified in order to establish the total boundary mass corresponding to the emission exhaustion. This value is represented in Figure 14 by a dashed line. Note that when the source exhaustion time is reached, the total emitted mass equals the sum of the individual boundary masses. These values are assembled in Table 4.

The mass of individual terpenes emitted from the capillary diffuser (E$_{massX}$) is calculated per day by employing *Eq 1,* until the cumulated emitted masses reach the individual boundary mass. Figure 14 reports, using bar series in the histogram, the emitted mass of individual TerVOCs per day. Note that when the bar series in Figure 14 turn from full color to stripes, it indicates that the source of individual terpenes is considered to be exhausted.
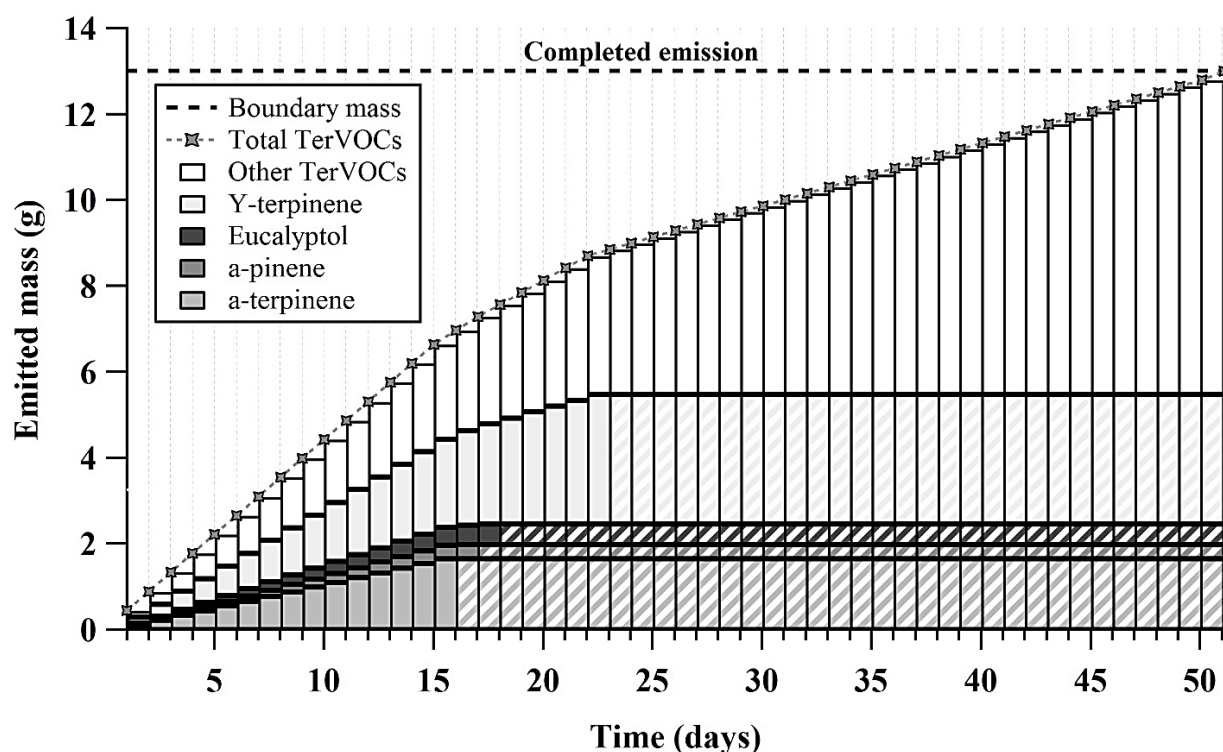
Figure 14. Temporal evolutions of the cumulated and individual masses of TerVOCs emitted per day along the capillary diffusion from t = 0 until the exhaustion of the mass content in the flask of tea tree oil.

It can be pointed out from Figure 14 that the source exhaustion time of individual terpenes are contrasted and range from 16 days for α-terpinene to 50 days for other terpenes including 4-terpineol. Noticeably, α-terpinene evidences the shortest exhaustion time. Indeed, it presents (i) a higher emission rate compared to the other detected terpenes due to its acute volatility, and (ii) a lower individual boundary mass. In contrast, other terpene molecules characterized by lower volatilities, such as γ-terpinene, are completely transferred to the gas phase 23 days after the capillary diffusion is initiated. As observed in Figure 14, at this same day of diffusion (days = 23), the emission of three terpenes (α-pinene, eucalyptol, α-terpinene) is finished. Consequently, after 23 days since the capillary diffusion of tea tree oil is started, the gas phase composition is solely contributed by terpenes attesting lower volatility, as 4-terpineol.

To conclude, the total mass contained in the tea tree oil bottle is determined as being entirely transferred to the gas phase after 51 days when it is diffused by a capillary device in a 40 m³ experimental room. After this time span, a decreasing phase of the individual TerVOC concentrations may occur due to air renewal until they are completely evacuated and possibly taken up on the chamber walls. Regarding the duration of impact on indoor air quality of the diffusion of essential oils in a 40 m³ experimental room, when diffusing essential oils in confined environments through a capillary device, occupants might be exposed to terpene molecules at concentration levels

reaching up to several tens or few hundreds of ppb and on a timespan easily exceeding several days or weeks. *Are these results equivalent to the investigation of the continuous diffusion of tea tree oil in the emission test chamber of 1 m³?*

2.5 Mass emission rates of TerVOCs along the continuous diffusion of essential oils: comparison between the experimental chamber of 1 m³ and the 40 m³ experimental room

The assessment of the mass emission rates of the TerVOCs emitted along the capillary diffusion of tea tree oil has been performed in two experimental chambers with highly contrasted volumes: 1 and 40 m³. Figure 16 reports the temporal profiles of the mass emission rate of the predominantly emitted terpene: ϒ-terpinene, along the diffusion process by capillary device in (i) the emission test chamber of 1m³ and (ii) the experimental IRINA of 40 m³. Regardless of the chamber volume, the mass emission rate profiles can be described in two steps: (i) a transient regime, characterized by an increase of the mass emission rates, and (ii) the steady state regime, where a constant mass emission rate is observed, supposedly until the exhaust of the terpene species contained in the liquid oil flask, assuming unchanging environmental conditions.

However, from one chamber volume to another, both transient regimes are highly different and the steady state regimes are contrasted as well. These dissimilarities between mass emission rate profiles in both experimental chambers (1 m³ and 40 m³) are observed to be equivalent for all the emitted terpenes. Therefore, in this section, only the major terpene released is discussed, namely γ-terpinene. Regarding the emission process in the 40 m³ room, the transient regime is characterized by a slow augmentation of the mass emission rate of ϒ-terpinene from the start of the diffusion to 3 hours after the capillary diffuser is set in the experimental room of 40 m³. After this time span, the slope of the increasing trend upsurges until the equilibrium condition is attained, nearly 12 hours after the emission process initiates. This behavior can be correlated with the gradual impregnation of the diffusive stick by the liquid essential oil. Therefore the emission rates get more and more intense until the saturation and subsequent equilibration of the stick. In contrast, in the experimental chamber of 1m³, the transient regime is shorter, higher emission rates are reached since the very beginning of the diffusion process and the steady state conditions are reached only within 2 hours of diffusion. Noticeably, the steady state concentrations observed for ϒ-terpinene between the 1 m³ and the 40 m³ chambers differ by a factor 2. For the same reason than emission rates of cleaning products are enhanced in a larger volume emission chamber, the magnification of the concentration gradient and the subsequent higher intensity of the mass transfer flux of TerVOCs is suggested to explain the enhancement of the steady state concentration on the 40 m³ room compared to the 1 m³ chamber. **These**

observations evidence that when diffusing an essential oil by a capillary device, the kinetic of the emission process is highly dependent on the volume of the chamber.
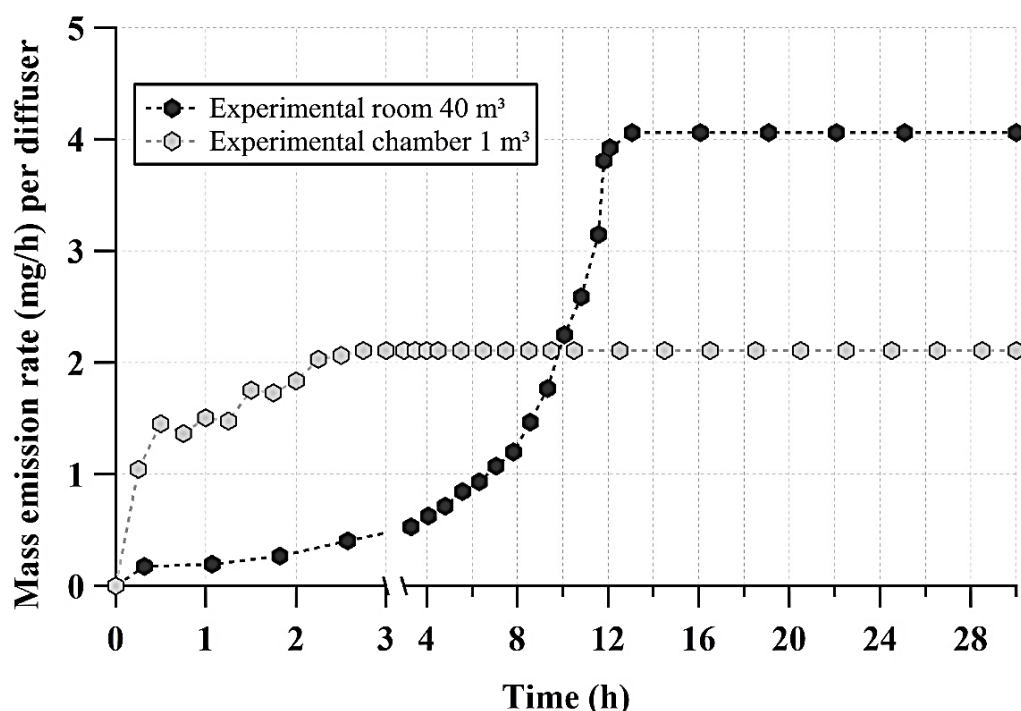
Figure 15. Comparison of the temporal evolutions of the mass emission rates along the diffusion of tea tree oil using a capillary device set in two chamber with contrasted volumes: 40 m³ and 1 m³ for (a) γ-terpinene and (b) α-terpinene (T = 23 °C, RH = 50 %, air renewal rate = 0.3 h⁻¹).

This work answers to the question: *Are these results equivalent to the investigation of the continuous diffusion of tea tree oil in the emission test chamber of 1 m³?* **The emission process of individual terpene molecules from the indoor diffusion of essential oils is confirmed to be dependent of the chamber volume. Indeed, several discrepancies observed between experimental chambers of different dimensions are mainly associated to (i) the concentration levels of released terpenes, (ii) the emission rate profiles including the duration of the emission process, (iii) the duration of impact on indoor air quality. Consequently, for an accurate estimation of the human exposure to released odor chemicals from the indoor diffusion of essential oils and their impact on indoor air quality, experimental protocols should be executed in real-scale rooms and under real conditions of use. The evaluation of the emissions in small size experimental chambers can provide information related to general trends such as major emitted terpenes, but accurate information regarding concentration levels and mass emission rates and exposure evaluation requires real scale room experiments.**

3.   CONCLUSIONS AND PERSPECTIVES

This real scale study confirms that household activities employing essential-oil-based household products, i.e. cleaning product use and essential oil diffusion, represen2t a significant indoor source of terpenes transiently increasing the concentration of these chemicals depending on the product employed. Indeed, exposure concentrations range from several tens to hundreds of ppb for cleaning products and from several hundreds to thousands of ppb for essential oil diffusion.

Among the two investigated cleaners, one has been interestingly employed under two different application modes, evidencing that this parameter is a key factor directly driving the kinetic of the emission process. Strong differences are evidenced when the essential-oil-based cleaning product is wiped or applied in a diluted solution compared to when it is sprayed or drizzled. Moreover, it is confirmed that the duration of impact on indoor air quality of the emitted terpenes and their dynamics of emission are also directly influenced by the product formulations, and noticeably by the addition of releaser agents aiming at prolonging the clean odor perception.

Limitations are evidenced regarding the evaluation of terpene emissions in an experimental chamber with a small volume. First, the limited space available in such emission test chambers does not allow performing a real application of all products. Therefore, depending on the physical state of the product film applied, different drying rates obtained. Second, the volume of gas to equilibrate with emissions impacts the mass transfer flow from the essential oil based product to the gas phase of the experimental chamber. While these biases may appear as a minor contributions, they definitely control the emission process and the resulting concentrations. Indeed, comparing results obtained using the 1 m^3 and the 40 m^3 chambers, emission rates in small chambers are underestimated from 50 % to 88 %, depending on the released compound. These observations highlight the interest of the characterization of the emission processes at real scale. The evaluation of the emission process using a small test chamber provides substantial information concerning general trends of major released terpenes. However, for the accurate estimation of human exposure and the definition of risk scenarios associated to the use of essential-oil-based cleaning products, application protocol under real consumer use patterns are required to be simulated in real scale chambers.

The indoor diffusion of essential oils by an electric diffuser might transiently rise the total terpene concentration up to several hundreds or few thousands of ppb, exceeding the Critical Exposure Levels (CEL) established by the European Project EPHEC. Indeed, the emitted TerVOC concentration levels associated to essential oil diffusion might potentially impact indoor air quality on a time span ranging from 6 hours to 50 days respectively for transient and continuous devices. Regarding the exposure of consumers during the evaporation of essential oils in confined environments, electric diffusers

tested in the 40 m^3 experimental are evidenced to be associated to high emission rates, i.e. 250 mg/h per diffuser, during a short period of time, typically in the hour range. However, the continuous diffusion releases a lower concentration of terpenes, nearly 4 mg/h per diffuser, but on much longer time spans. Therefore, the real scale approach developed in the 40 m^3 experimental room confirms that the transient device is related to an acute exposure while the capillarity device may induce chronic exposure of occupants. Moreover, this work verifies that the emission process of terpene molecules from the diffusion of essential oils relies on the chamber volume; indeed, the evaluation of the emissions of terpenes in small emission test chambers might lead to an under-estimation of the human exposure to these chemicals from 30 % to 75 %, depending on the terpene, compared to the results obtained in the 40 m^3 real scale room. The characterization of the emission processes from these products requires to be executed in real scale experimental rooms, since it is the ***only*** experimental approach that allow to mimic a real consumer use and provide an accurate emission rate assessment that could be extrapolated for the evaluation of other case scenario.

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General conclusions and perspectives

General conclusions and perspectives

Essential oils are intuitively introduced in confined environments, as "*ingredients of natural origin*" and recognized as antibacterial agents: they are perceived by most of consumers as safe and health-friendly. These chemicals are subsequently widely included in the formulation of natural housecleaning products and air fresheners, supposedly as air purifying agents. ***However, do essential-oil-based products contribute to indoor air quality by reducing emissions in the air and purifying it? Can essential-oil based products be considered as a passive remediation practice for facing current indoor air problematic?***

This work clearly evidences that the use of essential oils, as a complex mixture of terpenes and terpenoids (TerVOCs) is a significant indoor source of pollutants. The intrinsic physical and chemical properties of TerVOCs lead to their direct transfer from the liquid phase to the gas phase, increasing the inhalation exposure to allergens and pollutants that might promote allergic symptoms in the respiratory tract, among other possible health concerns. Moreover, this study has evidenced that the accurate investigation of the emission process of TerVOC molecules from consumer products must necessarily rely on real scenarios of use and real scale evaluation.

The main objective of this study is to assess the emission process of terpenes and terpenoids from (i) the use of natural and eco-certified essential-oil-based cleaning products and (ii) the indoor diffusion of essential oils, both at different scales of emission test chambers under realistic and real scenario of use. This section summarizes the results obtained in this thesis, the recommendations and future perspectives for the evaluation of the impact on indoor air quality associated to the use of (i) essential-oil-based cleaning products and (ii) pure essential oils.

1. **Assessment of the emissions of TerVOCs from essential-oil-based cleaning products at different scales: 40 m^3 experimental room, 1 m^3 emission test chamber, and micro-chamber testing.**

This study proposes (i) an innovative methodology that defines a realistic application scenario for the evaluation of essential-oil-based cleaning products from a real use protocol considered as a *reference case* and (ii) an entire assessment that integrates the evaluation of the emissions of TerVOCs at different scales: micro-chamber testing, 1 m^3 emission test chamber, and 40 m^3 experimental room.

The application of cleaning products under real consumer use patterns in the 40 m^3 experimental room enables the fair assessment of the concentrations to which users are exposed. The experimental design proposed in this study allows to

characterize the dynamics of the emission processes by considering several key parameters regarding human exposure levels to TerVOCs and the duration of impact on indoor air quality: (i) the maximum concentration peak and the concentration profiles of individual TerVOCs, (ii) the time span required to evacuate pollutants out of the experimental room and (iii) the emission rate profiles. The emission rate profiles determined in this work are representative parameters since they can be extrapolated to real cases allowing the prediction of pollutant emissions in other scenarios. They are required for the evaluation of human exposure and the design of indoor quality control technologies.

Hereafter, the evaluation of the key parameters describing the emission dynamics points out the role of (i) the product formulation impacting the emission processes of volatile compounds from the cleaning products, and (ii) the effect of consumer use patterns that might impact the product film drying rate, and therefore, the emission kinetics.

The availability of real scale experimental rooms is generally limited, then the correlation with the 1 m^3 emission test chamber has been considered since such small volume setups are more accessible. Subsequently, experiments in the 1 m^3 emission test chamber have been designed following a realistic scenario defined through the correlation with real consumer use patterns. In spite of this methodology, the emission rates deduced from the 1 m^3 chamber experiments differ from those determined using the real scale 40 m^3 experimental room. These variations, evidenced to depend on the chamber volume, are related to (i) the drying velocity of the cleaned surface associated to the application protocol, impacting the mass transfer rate from the liquid to the gas phase and (ii) the intensity of the mass transfer flow in order to achieve the equilibrium between the liquid phase and the gas phase.

Nevertheless, the 1 m^3 emission chamber experiments allowed the identification of as a hidden source of formaldehyde due to the presence of not regulated formaldehyde-releaser compounds contained in the formulation. This type of chambers feed with clean air, free of any carbonyl compounds enable the measurement of lower emission rates of formaldehyde. In contrast, experimental rooms are in interaction with the outdoor environment, and the formaldehyde concentration in the infiltrated air may vary, making the assessment of low formaldehyde emissions more challenging. Finally, the evaluation of the emissions of TerVOCs from cleaning products in test chambers with small volumes solely provides key qualitative information concerning the general trends of major emitted terpenes. In order to ensure an accurate assessment of the impact of consumer products on indoor air quality and on the human exposure to emitted chemicals, the investigation of emissions should be executed in a real-scale chamber and employing real application protocols.

The micro-chamber testing is evidenced as a complementary tool that permits (i) the evaluation of gas-transferred concentration, (ii) the emission screening for assessing the potentially emitted compounds, and (iii) to preliminarily

discriminate products one from another. It can be pointed out that it is a complementary tool and it cannot substitute to real scale emission evaluation neither

2. Assessment of the emissions of TerVOCs from the indoor diffusion of tea tree oil along the use of contrasted diffusion devices at different scales: 1 m³ emission test chamber and 40 m³ experimental room

This study evidences that the diffusion of essential oils potentially induces an increase of the indoor concentrations of terpenes by several hundreds to thousands of ppb. Moreover, depending on the diffusion device, the indoor concentration of terpene molecule might exceed the Critical Exposure Levels (CEL) from 5 hours to 60 days. This work evidences that the diffusion of essential oils by capillary devices induces chronic exposure while transient electric devices can be associated to acute exposure. When compared to the concentrations associated to a typical cleaning activity with essential-oil-based products, the indoor diffusion of essential oils induce a human exposure to terpene molecules higher by one order of magnitude and on a considerably longer timespan.

Regarding the investigation of the diffusion of essential oils, this work evidences a crucial difference related to the emission process of terpenes between both experimental chambers associated to (i) the concentration levels of released terpenes, (ii) their emission rate profiles, (iii) the duration of impact on indoor air quality. Consequently, the indoor diffusion of essential oils is confirmed to be reliant on the chamber volume. This study suggests that the intensity of the mass transfer flow from the liquid essential oil to the gas phase varies according to the chamber volume. For an accurate estimation of the human exposure to released odor chemicals from the indoor diffusion of essential oils and their impact on indoor air quality, experimental protocols have to be executed in real-scale rooms and under real conditions of use. One of the main limitation of the evaluation of essential oil diffusion in small experimental chambers is that the mass correlation of the essential oil from a real scale room cannot be performed. Indeed a minimum mass of essential oil is required for the proper operation of the diffuser device. Finally, the evaluation of the emissions from the diffusion of essential oils in small size experimental chambers can provide information related to general trends such as major emitted terpenes, but accurate information regarding concentration levels, mass emission rates and exposure evaluation require real scale room experiments.

Recommendations associated to the indoor use of essential-oil-based household products

1. It is suggested that future regulations and policies associated to the human exposure to TerVOC molecules while employing essential-oil-based household products must not only be based on the liquid concentration of

TerVOCs but on the characterization of the emission process of individual TerVOCs under real condition of use and using real scale experimental rooms.

2. Considering the levels of the emission rates and the resulting concentrations determined, the use of essential-oil-based household products in confined environments should NOT be recommended (i) for sensitive users, avoiding exposure of young children, elderly people and persons with respiratory disorders, (ii) as an indoor air remediation practice solely considering a biological point of view, and (iii) to be employed in a permanent way but only transiently.

Experimental perspectives

1. The assessment of the indoor diffusion of essential oils should be address under different diffusion mechanisms involving nebulization and candles for evaluating the complex interaction of emitted terpenes with (i) water droplets and (ii) combustion products: ***diffusion mechanisms inducing complex interactions***

2. The evaluation of the influence of (i) air renewal rate, (ii) humidity, and (iii) temperature on the emission process of terpenes from essential-oil-based household products under real application protocols: ***influence of environmental conditions of the emission kinetics from essential-oil-based household products.***

3. The identification of the influence of different diffusion modes on the emission dynamic of terpene molecules while employing an essential-oil-based cleaning product: ***influence of diffusion modes of cleaning products on their emission kinetics.***

Scientific perspectives

1. This study suggests that efforts in the scientific framework should be addressed towards the identification of formaldehyde-releasers included in cleaning product formulation and their release dynamics in order to provide key information associated to their impact on indoor air quality: ***formaldehyde releasers in household products.***

2. The assessment of non-reactive interactions between emitted terpenes from the use of essential-oil-based household products and the surfaces presents in confined environments: ***non-reactive heterogeneous interactions***. This aspect has been addressed in the framework of the ESSENTIEL project and evidenced significant impacts on the indoor fate of terpenes.

3. The evaluation of the reactivity of terpenes emitted along the use of essential-oil-based products concerning (i) homogeneous reactivity between gas phase terpenes and indoor oxidants, and (ii) heterogeneous interactions

between adsorbed terpenes and indoor oxidants: ***reactive interactions between terpenes and oxidants in indoor air (homogenous and heterogeneous phases).***

4. The evaluation of the emission process of scented molecules from household products potentially presenting encapsulation techniques for fragrance retention. This investigation is planned to be assessed in the frame of the Q-Wash project (APR ADEME CORTEA 2019 – IMT et CSTB): ***release kinetics of fragrance molecules retained by encapsulation techniques in household products.***

Annex A

Table 1A. Bench market analysis: essential-oil-based cleaning products identified in the French market. NB: selected cleaning products for this work are written in bold

Category of product	Diffusion mode	Brand	Retail Store	Fragrance	Chemical composition (indicated by the manufacturer)	Essential oils included (indicated by the manufacturer)
Dishwasher	Liquid	Etamine du Lyn	Bio c'est bon	Lemon and mint	5 - 15 % anionic surfactants, ≤ 5 % nonionic surfactants, amphoteric surfactants	*100% Natural fragrance* Essential oils: mint and lemon (Citral, Limonene)
Dishwasher	Liquid	Naturalia	Naturalia	Lemon	≥ 30 % water, 5 - 15 % anionic surfactants, ≤ 5 % nonionic surfactants, amphoteric surfactants	Essential oil: Lemon 0.1% (Linalool)
Multi-use cleaner	Liquid	Naturalia	Naturalia	Orange	≥ 30 % water, 5 – 15 % anionic surfactants, ≤ 5 % nonionic surfactants, amphoteric surfactants	Essential oils: Lemon and orange
Toilet cleaner	Gel	Ecover	Naturalia	Pine	≤ 5 % non-anionic surfactants	Essential oil: Pine oil (Limonene)
Laundry detergent	Liquid	Naturalia	Naturalia	Lavender	≤ 5 % nonanionic surfactants, Marseille soap	Essential oils: 0.5% lavender oil and (Limonene, Linalool)
Stain remover	Solid	Sodasan	Naturalia	Orange	≥ 90 % organic vegetable soap	Essential oils: 2 – 4 % orange oil
Bathroom cleaner	Spray	Etamine du Lys	Naturalia	Orange	≥ 30 % water, ≤ 5 % non-anionic surfactant, palm and sugar, ethanol	≤ 5% *Natural fragrance* Essential oil: orange oil (Limonene, Linalool)
Multi-use cleaner	Solid wax	Sorélia la Pierre	Naturalia	Lemongrass	≥ 30 % soft clay, ≤ 5 % soap, 5 – 15 % water	Essential oil: lemongrass oil
Kitchen cleaner	Spray	Ecover	Naturalia	Flower	≥ 30 % water, ≤ 5 % non-anionic surfactant, citrate, lactic acid	*100% Natural fragrance* Essential oils: *not indicated*
Degreaser	**Spray**	**Kitz**	**Naturalia**	**Lemon**	**< 5 % surfactant (anionic and non-anionic), citrus oil, citric acid, water,**	***100% Natural fragrance***

					methylisothiazolone, 5-Chloro-2-methyl-4-isothiazolin-3-one, Nitrilotriacetic acid trisodium salt monohydrate	**Essential oils: lemon oil and pine oil (Limonene, Citral)**
Glass cleaner	**Spray**	**Lerutan**	**Naturalia**	**Eucalyptus**	**> 30 % water, 5 – 15% alcohol, < 5 % surfactant (anionic and non-anionic), citric acid, essential oils2 (including eucalyptus oil), amphoteric surfactants**	*100% Natural fragrance* **Essential oil: Eucalyptus oil and lemon oil (Limonene)**
Multi-use cleaner	Liquid	Rampal Latour - Savon Noir	Naturalia	Lavender	Water, sodium soap and linen potash, potassium carbonate, glycerin	Essential oil: lavender oil (Linalool)
Floor cleaner	Liquid	Osanis	Naturalia	Citrus	≤5 % non-anionic and anionic surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Limonene)
Floor cleaner	Liquid	Hygios	Naturalia	-	< 5 % anionic surfactants and non-ionic surfactants, lactic acid 1.32 %	*100% Natural fragrance* Essential oils: *not indicated*
Dishwasher	Gel	Osanis	Naturalia	Lemon and citrus	5 – 15 % anionic surfactants, ≤ 5 % nonionic surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Limonene, Citral)
Degreaser	Spray	Osanis	Naturalia	Citrus	≤5% non-anionic and anionic surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Limonene, Citral)
Multi-use cleaner	Wipes	Ecover	Naturalia	-	< 5% non-ionic surfactants, methylisothiazolinone, benzisothiazolinone	*100% Natural fragrance* Essential oils: *not indicated* (Limonene)
Toilet cleaner	Spray	Etamine du Lys	Naturalia	-	> 30 % water, < 5 % non-ionic surfactants (coconut, palm kernel, sugar), < 5 % anionic surfactants (coconut, palm kernel)	*100% Natural fragrance* Essential oil: Eucalyptus oil (Limonene)
Kitchen cleaner	**Spray**	**Etamine du Lys**	**Naturalia**	**Eucalyptus**	**> 30 % water, < 5 % nonionic surfactants (palm, sugar), ethanol,**	*100% Natural fragrance* **Essential oil: Eucalyptus oil**

					menthol, hydroxyethylminodiacetic acid, disodium salt (sequestering agent), citric acid	(Limonene)
Vacuum cleaner	Granulated powder	Etamine du Lys	Naturalia	-	Corn flakes	*100% Natural fragrance* Essential oils: cinnamon oil, cedar oil, clove oil, lavender oil, mint oil and thyme oil
Multi-use cleaner	Liquid	Puryfitoux	Naturalia	Essential oil mixture	Water, cocamidopropyl betaine, thymus vulgaris*, caprylyl, capryl glucoside	*100% Natural fragrance* Essential oils: eucalyptus oil, thyme oil, mint oil and clove oil. (Camphor)
Multi-use cleaner	Liquid	Sonett	Naturalia	Lemongrass	5 – 15 % coconut alcohol sulphate, 5 – 15 % sugar surfactants, 1 - 5 % ethanol	*100% Natural fragrance* Essential oil: > 1 % lemongrass oil
Surface cleaner	**Spray**	**Sonett**	**Naturalia**	**Lavender**	**70 % ethanol, < 1 % lavender oil, < 1 % sage oil, water**	***100% Natural fragrance*** **Essential oils: lavender oil and sage oil (Linalool)**
Multi-use cleaner	**Liquid**	**Ecover**	**Naturalia**	**Essential oil mixture**	**< 5 % surfactant (anionic and non-anionic), water, alcohol, lemon oil, lactic acid, fatty acids, sodium citrate, glyceryl caprylate**	***100% Natural fragrance*** **Essential oil: lemon oil (Limonene)**
Dishwasher	Liquid	Sonett	Naturalia	Lemon	Water, sodium lauryl sulfate, alkyl polyglycoside, sodium chloride, citric acid	*100% Natural fragrance* Essential oils: *not indicated* (Limonene, Citral)
Surface cleaner	Wipes	Sanytol	Carrefour	Grapefruit and lemongrass	< 5 % di-decyldimethyllammonium chloride, anionic surfactants, non-ionic surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Limonene, Linalool, Cinnamal)

Surface cleaner	Wipes	Sanytol	Carrefour	Eucalyptus	< 5 % di-decyldimethyllammonium chloride, anionic surfactants, non-ionic surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Limonene, Eucalyptol)
Kitchen/Bathroom cleaner	Spray	Carolin	Carrefour	Eucalyptus	2-amino ethanol, benzalkonium chloride	*100% Natural fragrance* Essential oil: eucalyptus oil
Surface cleaner	Spray	You By Salveco	Carrefour	-	< 5 % surfactant anionic and non-anionic, water, alcohol, citric acid	*100% Natural fragrance* Essential oils: *not indicated*
Bathroom cleaner	Spray	You By Salveco	Carrefour	-	< 5 % surfactant anionic and non-anionic, water, alcohol, citric acid	*100% Natural fragrance* Essential oils: *not indicated*
Degreaser	Spray	You By Salveco	Carrefour	-	< 5 % surfactant anionic and non-anionic, water, alcohol, citric acid	*100% Natural fragrance* Essential oils: *not indicated*
Glass cleaner	Spray	You By Salveco	Carrefour	-	100% active < 5 % surfactant anionic and non-anionic, water, alcohol, citric acid	*100% Natural fragrance* Essential oils: *not indicated*
Surface cleaner	Liquid	Carolin	Carrefour	Linen	≤ 5 % soap, non-ionic surfactants	*100% Natural fragrance* Essential oils: linen oil (Linalool)
Multi-use cleaner	Liquid	Carolin	Carrefour	Eucalyptus	≥ 30 % water, 5 - 15 % anionic surfactants, ≤ 5 % nonionic surfactants, amphoteric surfactants	*100% Natural fragrance* Essential oil: eucalyptus oils
Multi-use cleaner	**Liquid**	**You By Salveco**	**Carrefour**	**Citrus**	**< 5 % surfactant anionic and non-anionic, water, alcohol, citrus oil, citric acid**	***100% Natural fragrance*** **Essential oil: orange oil (Limonene, Citral)**
Multi-use cleaner	Liquid	You By Salveco	Carrefour	Mint	< 5 % surfactant anionic and non-anionic, water, alcohol, citrus oil, citric acid	*100% Natural fragrance* Essential oils: mint and eucalyptus oils (Limonene, Eucalyptol)
Multi-use cleaner	Liquid	Carrefour ECO-PLANET	Carrefour	Rosemary	With active ingredients of plant origin	*100% Natural fragrance* Essential oils: *not indicated*
Multi-use cleaner	Liquid	Ajax	Carrefour	*Flower festival (yellow)*	≤ 5 % non-anionic and anionic surfactants	*100% Natural fragrance*

						Essential oils: *not indicated* (Cinnamal, Linalool, Citronellol, Limonene)
Multi-use cleaner	Liquid	Ajax	Carrefour	*Flower festival (red)*	≤ 5 % non-anionic and anionic surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Cinnamal, Linalool, Citronellol, Limonene)
Multi-use cleaner	Liquid	Ajax	Carrefour	*Flower festival (green)*	≤ 5 % non-anionic and anionic surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Cinnamal, Linalool, Citronellol, Limonene)
Surface cleaner	Liquid	Ajax	Carrefour	Eucalyptus	≤ 5 % non-anionic and anionic surfactants, lactic acid	*100% Natural fragrance* Essential oil: eucalyptus oils
Bathroom cleaner	Spray	You By Salveco	Carrefour	Essential oil mixture	≤ 5 % non-anionic and anionic surfactants	*100% Natural fragrance* Essential oils: *not indicated*
Toilet cleaner	Gel	WC Net intense	Carrefour	Lemon		*100% Natural fragrance* Essential oils: *not indicated* (2-bromo-2nitropropan-1, 3-diol, methylchloroisothiazolinone)
Laundry detergent	Liquid	Maison Verte	Carrefour	Essential oil mixture	5 – 15 % anionic surfactants, non-anionic surfactants, ≤ 5 % soap, polycarboxylate	*Natural fragrance and synthetized fragrances* Essential oils: *not indicated*
Dishwasher	Gel/Liquid	Maison Verte	Carrefour	Basil and thyme	5 – 15 % anionic surfactants, ≤ 5 % nonionic surfactants, amphoteric surfactants	*Natural fragrance and synthetized fragrances* Essential oils: *not indicated*
Dishwasher	Gel/Liquid	Maison Verte	Carrefour	Lemon	5 – 15 % anionic surfactants, ≤ 5 % nonionic surfactant, amphoteric surfactant	*Natural fragrance and synthetized fragrances* Essential oils: *not indicated*

Dishwasher	Gel/Liquid	You By Salveco	Carrefour	Mint	5 – 15 % anionic surfactants, ≤ 5 % nonionic surfactants, amphoteric surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Limonene)
Dishwasher	Gel/Liquid	WINGO	Carrefour	Citrus	5 – 15 % anionic surfactants, ≤ 5 % nonionic surfactants, amphoteric surfactants	*100% Natural fragrance* Essential oils: *not indicated* (Limonene, Citral)

Table 2A. Bench market analysis: air purifiers, air fresheners and essential oils for diffusion. NB: selected cleaning products for this work are written in bold

Category of product	Diffusion mode	Brand	Retail Store	Essential oils (indicated by the manufacturer)
Air freshener	**Aerosol**	**Phytoramasol**	**Naturalia**	*100% Essential oils* **Lavender and rosemary oil**
Air freshener	Aerosol	Phytoramasol	Naturalia	*100% Essential oils* Pine and eucalyptus oil
Air freshener	Aerosol	Phytoramasol	Naturalia	*100% Essential oils* Bergamot and lemon oil
Air freshener	Aerosol	Phytoramasol	Naturalia	*100% Essential oils* Verbena and Hô wood oil
Air freshener	Aerosol	Phytoramasol	Naturalia	*100% Essential oils* Orange and bitter orange oil
Air purifier	Aerosol	Florame	Naturalia	*100% Essential oils* *Not indicated*
Air freshener	Candle	Air Wick: ESSENTIAL OILS Line	Carrefour	*Essential oils and synthetized fragrances* Coumarin and lemongrass (Citronellol, Limonene, Linalool)
Air freshener	Electric Diffuser	Air Wick: ESSENTIAL OILS Line	Carrefour	*Essential oils and synthetized fragrances* *Not indicated* (Linalool)
Air freshener	Electric Diffuser	Air Wick: ESSENTIAL OILS Line	Carrefour	*Essential oils and synthetized fragrances* *Not indicated* (Citral, Geraniol, Limonene, Pinene, Linalool)
Air freshener	Electric diffuser with battery	Air Wick: ESSENTIAL OILS Line	Carrefour	*Essential oils and synthetized fragrances* *Not indicated*
Air freshener	Electric diffuser with battery	Air Wick: ESSENTIAL OILS Line	Carrefour	*Essential oils and synthetized fragrances* *Not indicated*
Air freshener	Passive diffuser (Wood sticks)	AURA	Carrefour	*Essential oils and synthetized fragrances*

				(R-p-mentha-1,8-dien, ethyl 2,3 -epoxy-3-phenylbutyrate)
Air freshener	Passive diffuser (Wood sticks)	IBA Paris	Carrefour	*Essential oils and synthetized fragrances* 0.144 mg/ml of essential oils
Air freshener	Passive diffuser (Liquid)	IBA Paris	Carrefour	*Essential oils and synthetized fragrances* 9.45 mg/75 ml essential oils (Linalool, Eugenol, Limonene, Coumarin)
Air freshener	Candle	IBA Paris	Carrefour	*Essential oils and synthetized fragrances* 14.4 mg/ 120 g candle of essential oils
Air freshener	Passive diffuser (evaporation for dry flowers)	IBA Paris	Carrefour	*Essential oils and synthetized fragrances* 3.5 g / bottle of essential oils
Air freshener	Automatic aerosol	Air Wick: ESSENTIAL OILS Line	Carrefour	*Essential oils and synthetized fragrances* (Limonene)
Air freshener	Electric Diffuser	Air Wick: ESSENTIAL OILS Line	Carrefour	*Essential oils and synthetized fragrances* Lavender oil (Linalool, Limonene, Coumarin, Eugenol, Pinene, Citronellol, Geraniol)
Air freshener	Passive diffuser (Wood sticks)	AURA	Carrefour	*100% Essential oils* *Not indicated* (Limonene, alcohol FREE)
Air freshener	Candle	Air Wick: ESSENTIAL OILS Line	Carrefour	*100% Essential oils* *Not indicated* (Alpha-hexylcinnamaldehyde, Hexyl salicylate, eugenol, Linalool)
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*6 essential oils:* ylang ylang, ceylon cinnamon, rose geranium, sweet orange, patchouli, sandalwood amyrisl
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*5 essential oils:* pine, peppermint, penny-royal, rosemary, common sage

Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*4 essential oils:* cinnamon, rosewood, atlas cedar, elemi
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*5 Essential oils:* lavender, lavender, Asian rosewood, marjoram, common sage
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*3 essential oils:* pine, cistus rock rose, cypress
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*4 essential oils:* sweet orange, white grapefruit, cinnamon leaves and bark, bitter orange grain
Air purifier	**Spray**	**PurEssentiel**	**Grande Pharmacie de France**	***41 essential oils***
Air purifier for diffusion	**Liquid**	**Nature & Découverte**	**Nature & Découverte**	**Essential oil mixture**
Air freshener	Spray	PurEssentiel	Grande Pharmacie de France	*12 essential oil* : mixture Rest & Relax
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*Essential oil blends*: tea tree, shiu wood, cajuput, cedar, lemon, cypress, eucalyptus, gaultheria, lavender, spearmint, peppermint, niaouli, orange, petit grain bitter, pine, rosemary, savory, thymol
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*18 essential oils:* green anise, tea tree, cajuput, cedar, lemon, cypress, eucalyptus, clove, lavender, lavender, peppermint, niaouli, oregano, pine, ravintsara, rosemary, cineole, common sage, thymol
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*10 essential oils:* shiu wood, cajuput, roman chamomile, lavender, lavender, lavender, marjoram, orange, palmarosa
Essential oil for diffusion	Liquid	PurEssentiel	Grande Pharmacie de France	*4 essential oils:* lemonella, eucalyptus, lavender, lemongrass
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Verbena oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Sweet orange oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Lavender oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Lemon oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Mandarin oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Ylang-ylang oil

Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Roman chamomile oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Geranium rose oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Lemongrass oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Bitter orange oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Patchouli oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Bergamot oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Neroli aurantium oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Marjoram oil
Essential oil for diffusion	**Liquid**	**Nature & Découverte**	**Nature & Découverte**	**Tea tree oil**
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Eucalyptus radiata oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Eucalyptus globulus oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Scots pine oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Red myrtle oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Niaouli oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Thyme oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Cinnamon oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Rosemary oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Lavender oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Citronella oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Ravintsara oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Palmarosa oil
Essential oil for diffusion	Liquid	Nature & Découverte	Nature & Découverte	Cypress oil

Summary

Essential oils, as natural fragrances, are frequently used in *green* marketed housecleaning products and air fresheners. Nonetheless, they contain volatile and reactive chemical species. This thesis investigates the emissions of essential-oil-based household products under real consumer use patterns to assess their impacts on indoor air quality. The experimental approach allows an integrated assessment of the estimations of the terpene emissions from 10 selected essential-oil-based household products in experimental chambers at different scales; from micro-chamber to the 40 m^3 experimental room.

Regarding essential-oil-based cleaning products, contrasted concentration levels are evidenced for terpene species related to the application process and use purpose of these products. Moreover, long term increase of formaldehyde concentrations are noticed after the application of these products that might be related to secondary sources. Concerning the indoor diffusion of tea tree oil, contrasted concentration levels and kinetics are evidenced depending on the mechanism of diffusion used. Concentrations can exceed by more than one order of magnitude the recommended Critical Exposure Level (CEL). It is noticed that the relative contributions of individual terpenes in the gas phase vary all along the diffusion process, for any investigated diffusion device. Finally, essential-oil-based household products have to be seriously envisaged as versatile and significant sources of VOCs since they might induce indoor concentrations of terpenes exceeding exposure limits established by the European Union and the United States.

Résumé

Les huiles essentielles, en tant que parfums naturels, sont fréquemment utilisées dans les produits ménagers et les désodorisants commercialisés comme *verts*. Cependant, elles contiennent des espèces chimiques volatiles et réactives. Ce travail de thèse vise à renseigner les émissions de produits ménagers à base d'huiles essentielles à travers des protocoles de mise en œuvre et d'usages réels afin d'évaluer leurs impacts sur la qualité de l'air intérieur. L'approche expérimentale a permis l'étude des émissions en terpènes de 10 produits à base d'huiles essentielles au sein de chambres expérimentales de différents volumes : depuis les micro-chambres d'émission jusqu'à une pièce expérimentale de 40 m^3.

Concernant les produits de nettoyage à base d'huiles essentielles, des niveaux de concentration contrastés sont mis en évidence pour les terpènes émis en fonction du protocole d'application et de l'usage du produit. Par ailleurs, une augmentation des niveaux de formaldéhyde peut être observée après l'application de certains produits, suggérant des sources secondaires pour ce COV. Concernant la diffusion d'huile essentielle d'arbre à thé, des niveaux de concentrations et des cinétiques d'émissions contrastés ont été mis en évidence en fonction du mécanisme de diffusion utilisé. Les concentrations en terpènes peuvent dépasser de plus d'un ordre de grandeur les niveaux critiques d'exposition recommandés. Il est montré que les contributions individuelles des terpènes émis varient tout au long du processus de diffusion quel que soit le mode de diffusion. Les produits ménagers à base d'huiles essentielles doivent donc être envisagés comme des sources significatives et variables de COV puisqu'ils peuvent induire des concentrations en terpènes en air intérieur dépassant les limites d'exposition établies par les Etats-Unis et l'Union Européenne.