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VOCs and formaldehyde emissions from cleaning products and air fresheners

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SUMMARY
Human indoor exposure to Volatile Organic Compounds (VOCs) may be associated with the use of household products. However little is known about their emissions and to what extent they contribute to indoor air pollution. The French Agency for Environmental and Occupational Health Safety (Afsset) conducted tests in order to characterize VOCs emissions from 32 consumer products: air fresheners, glass cleaners, furniture polishes, toilet products, carpet and floor cleaning products. All experiments were conducted by the Scientific and Technical Centre for Building (CSTB) in realistic conditions of use (in emission test chamber or in an experimental house). Results show that the use of consumer products can lead to high indoor VOCs concentrations. Some of them are toxic airborne contaminants. The link between formaldehyde emissions and product compositions is discussed. Finally, formaldehyde concentrations are compared to the indoor air quality guideline value proposed by Afsset.

KEYWORDS
Formaldehyde, Volatile organic compounds, Household products, Exposure

INTRODUCTION

Most indoor air pollutants come from the use of cleaning products, air fresheners, pesticides or materials related to furniture and construction. Some of them may trigger adverse health effects such as nasal irritation, respiratory disorders and even asthma (Zock et al., 2007). Respiratory conditions including asthma in children have also been correlated to formaldehyde concentrations indoors (Mendell, 2007).

Little is known about chemical emissions resulting from the use of cleaning products and air fresheners and until now, few regulatory frameworks is in place to define the safety of these products.

In June 2004, the French government set up a National Environmental Health Action Plan (NEHAP) which intends to improve indoor air quality (French Ministries, 2004-2008). In this framework, the French Agency for Environmental and Occupational Health Safety (Afsset) was mandated by the Ministries of Health, Environment and Labour to assess health risks associated with formaldehyde and other Volatile Organic Compounds (VOCs) indoors. In this request, Afsset has to identify everyday life products emitting or containing formaldehyde and analyse and quantify associated human exposure by direct and indirect sources.

In this paper, we report on experimental results of emission tests and measurements of indoor formaldehyde and VOCs concentrations associated with the use of various cleaning products and air fresheners. In order to assess the exposure level of consumers to formaldehyde and VOCs, these tests were conducted in realistic conditions of use and ventilation. The composition of some products is also presented and gives the opportunity to make assumptions about a possible relationship between formaldehyde emissions and formaldehyde or releasing-formaldehyde compounds composition (direct or indirect sources).

METHODS

Product selection

32 consumer products from 16 categories were chosen by Afsset among a list of multiple products compositions registered in the national consumer products library (*Base Nationale des Produits et Compositions - BNPC)* managed by the French Poison Control Centre in Nancy. The selected categories are expected to contain VOCs or formaldehyde. Once the categories were defined, the more and the less expensive product in each category were bought in supermarkets and department stores. Categories of tested products are briefly presented in Table 1.

Formaldehyde and VOCs emissions

Application protocols

The tests presented in this paper were carried out by the CSTB (Building Technical and Scientific Centre) in realistic conditions of use and ventilation. Laboratory measurements were conducted in emission test chambers or in the CSTB experimental house MARIA (Mechanised house for Advanced Research on Indoor Air), depending on the category of products. Experimental protocols were carried out in the test room in MARIA for air fresheners, furniture polishes, glass cleaners and glass wipes, in the toilets in MARIA for toilet blocks and gels and in emission test chambers for carpet cleaners, stain removers for carpets, floor cleaners and wipes. These scenarios are described in Table 1.

Table 1. Categories of the 32 tested products.

Product category		Conditions of use	Scenario: number of samples (S) and duration between samples
A1/A2[(1)]	incense	Burning duration: 60 min* / 25 min	S1 : 60 min /25 min; post-combustion S2-S3-S4 : 60 min
B1/B2	electric diffuser	Use during 120 min	S1-S2 : 60 min; post-use S3-S4-S5 : 60 min
C1/C2	liquid air freshener with a wick	Use during 120 min	S1-S2 : 60 min; post-use S3-S4-S5 : 60 min
D1/D2	scented candle	Use during 180 min	S1-S2-S3 : 60 min; post-use S4-S5 : 60 min
E1/E2	spray	Continuous spray during 10 sec**	Post-use S1-S2-S3-S4 : 30 min
F1/F2	air freshener for vacuum cleaners	Use in a vacuum cleaner in function during 5 min	S1 : 5 min, post-use S2-S3-S4: 30 min
G1/G2	glass cleaner	9 trigger pulls on the test room glass, no wipe step	Post-use S1-S2-S3-S4 : 30 min
H1/H2	glass wipes	Use of 4 wipes for the test room window	Post-use S1-S2-S3-S4 : 30 min
I1/I2	furniture polish	Sprays on a laminated table dried up	Post-use S1-S2-S3-S4 : 30 min

Product category		Conditions of use	Scenario: number of samples (S) and duration between samples
J1/J2	toilet block	Blocks installed the day before test, 4 flushes every 30 min	Post-use S1-S2-S3-S4 : 30 min
K1/K2	toilet gel	Application during 15 minutes, 3 flushes every 30 min	Post-use S1 : 15min, S2-S3-S4 : 30 min
L1/L2	carpet cleaner	Application on 100% of a carpet tile[(2)] area	Post-use S1-S2-S3-S4 : 30 min
M1/M2	stain remover for carpet	Application on 10% of a carpet tile area	Post-use S1-S2-S3-S4 : 30 min
N1/N2	floor cleaner***	Application on a glass sheet, no drying	Post-use S1-S2-S3-S4 : 30 min
O1/O2	floor cleaner containing *savon de Marseille****	Application on a glass sheet, no drying	Post-use S1-S2-S3-S4 : 30 min
P1/P2	wipes for floor cleaning	2 applications of 1 wipe, no drying	Post-use S1-S2-S3-S4 : 30 min

* min: minute; ** sec: second; *** following the recommendations of use, floor cleaners were either tested diluted or pure
(1) A1/A2, B1/B2…: the less expensive / the more expensive product per category
(2) the carpet tile corresponds to the carpet tile B, tested in Rousselle *et al.* (2008)

Experimental house MARIA

The CSTB experimental house MARIA is dedicated to study pollutants transfers, test ventilation systems, settle field investigations methods and validate computational models. It is composed with five main rooms equipped with various ventilation systems (natural draught ducts, extract ventilation and combined extract and input ventilation) and heating systems (convectors, water heated floors) (Ribéron and O'Kelly, 2002).

The tests were conducted in the bedroom and the toilets, without any piece of furniture except for the emission test for the furniture polishes (laminated table in the centre of the room). VOCs and formaldehyde were sampled directly from the air extraction system. Measured concentrations are therefore globally representative of the pollutant level in the test room, even if in some cases, the distribution of indoor concentrations can be heterogeneous (e.g. in case of combustion processes, use of sprays etc.).

Parameters such as relative humidity, temperature and air exchange rate were registered during the whole period of the tests. Ventilation conditions were controlled by mechanical extraction during the experiment. The characteristics of the test room and the toilets in MARIA are summarized in Table 2.

Table 2. MARIA test rooms characteristics.

Item	Test room (bedroom)	Toilets
Volume (m^3)	32.3	4.7
Window area (m²)	1.5	-
Temperature (°C)	20 ± 2	-
Air exchange rate (h^{-1})	0.6	3.7

Emission test chambers
The emission test chamber method is described in EN ISO 16000-9 (Determination of the emission of volatile organic compounds from building products and furnishing – Emission test chamber method). The characteristics are summarized in
Table 3.

Table 3. Summary of emission test chamber characteristics.

Item	Contents
Volume (m^3)	0.0509
Temperature	23 +/- 2
Relative humidity (%)	50 +/- 5
Specific ventilation rate qc ($m^3/h/m^2$)	1.25

Sampling and analytical methods
VOCs were sampled on Tenax-TA and analysed using TD/GC/MSD/FID according to ISO 16000-6. The TVOC was calculated as toluene equivalents from the total integrated FID signal between hexane and hexadecane. The detection limit is in the range of 1 to 10 $\mu g.m^{-3}$ depending on the compounds. Formaldehyde has been sampled on DNPH cartridges and analysed using HPLC according to ISO 16000-3. Formaldehyde detection limit is 0.3 $\mu g.m^{-3}$.

RESULTS
The results presented herein do not represent the diversity of marketed cleaning products and air fresheners in France.

VOCs emissions
TVOC and VOCs concentrations are presented in Table 4 (corresponding to the maximal concentrations measured during the whole period of tests). Only some tested products are herein presented with the TVOC and VOCs of concern concentrations (carcinogenic compounds such as benzene, terpenes, high concentrations…).

Table 4. TVOC and specific VOCs concentrations for a selection of tested products.

Tested product	TVOC* ($\mu g.m^{-3}$)	VOCs of concern ($\mu g.m^{-3}$)	Formaldehyde ($\mu g.m^{-3}$)
Electric diffuser B1	216	Octanal: 22	< 0.3 (limit of quantification)
Air freshener for vacuum cleaner F2	1737	Limonene: 39 Eucalyptol: 275 Linalool: 98 Alpha-pinene: 143 Beta-pinene: 40 Camphene: 99	< 0.3
Glass cleaner G1	2662	Trichloroethylene: 14 1-butoxy-2-propanol: 1478 1,1-diethoxyethane: 1121	4
Furniture polish J1	17487	Benzene: 1 Nonane: 1488 Decane: 2350 Undecane: 757	11
Furniture polish J2	17531	Nonane: 2741 Decane: 1077	5
Carpet cleaner M2	523712	1-methoxy-2-propanol: 108924 p-cymene: 1127	10

Tested product	TVOC* ($\mu g.m^{-3}$)	VOCs of concern ($\mu g.m^{-3}$)	Formaldehyde ($\mu g.m^{-3}$)
		Isoparaffine C10-C11: 397215	
Carpet stain remover L2	348853	Trichloroethylene: 31 1-propoxy-2-propanol: 348574	7
Floor wipes P1	103	Benzene : 1 Trichloroethylene: 55	1249
Floor wipes P2	49790	Trichloroethylene:30 1-(1-methylethoxy)-2-propanol: 45927 Terpineol: 14	6

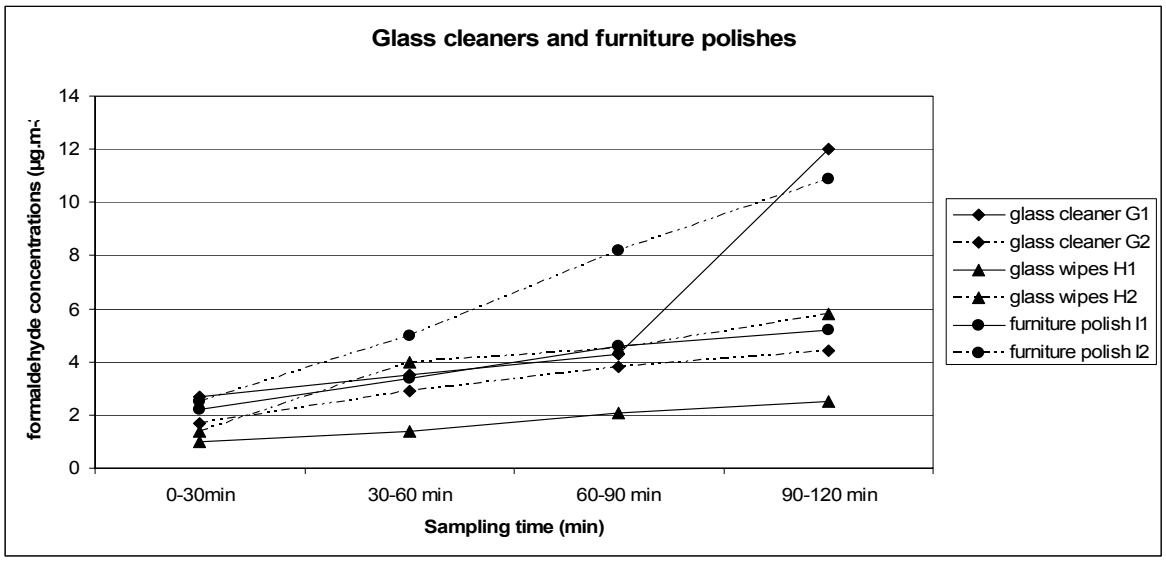
- The TVOC was calculated as toluene equivalents

VOCs levels cover a large range of concentrations and vary widely between different types of products or even between two products from the same category.
For a majority of products, high concentrations of very volatile organic compounds (VVOCs) were measured but the analytical methods used in this study are not suitable for VVOCs quantification.

Over the 32 TVOC concentrations, 37% were below 100 $\mu g.m^{-3}$, 19% were between 100 and 500 and 44% were above 500, with maximum levels above 500000 $\mu g.m^{-3}$ (carpet cleaner M2). Sorption of gas-phase analytes including terpene alcohols to chamber surfaces may also contribute to the persistence of elevated concentrations (Singer et al., 2006).

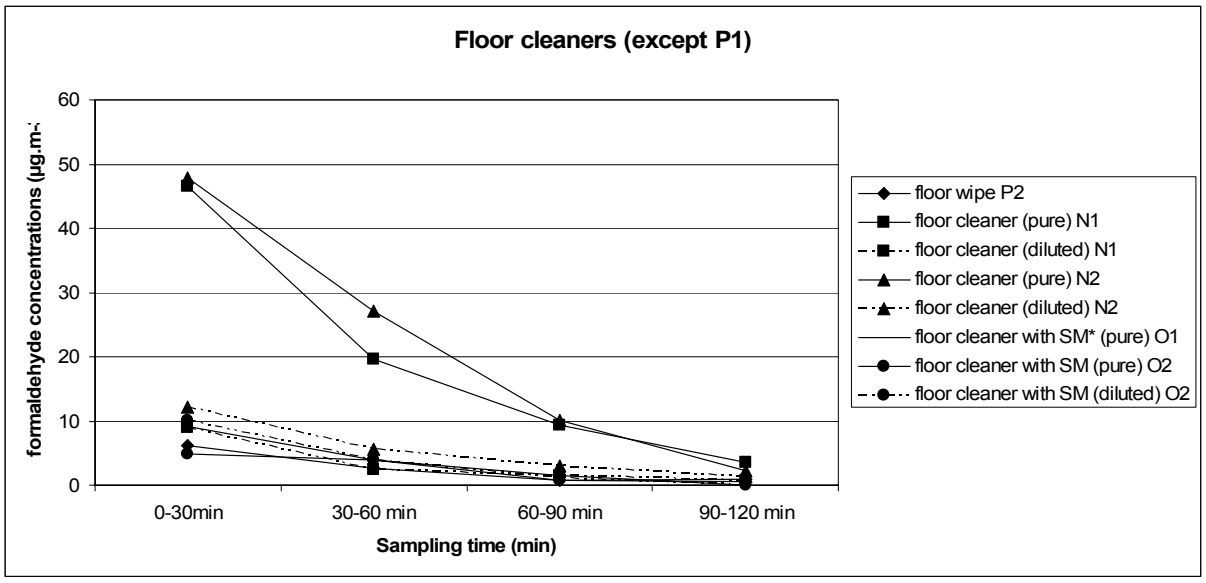
Formaldehyde emissions
For all tested air fresheners, formaldehyde concentrations are generally lower than 10 $\mu g.m^{-3}$ after use and then decrease progressively, reflecting pollutant removal by the ventilation system. Concerning burning devices i.e. incense sticks and scented candles, formaldehyde emission is rather related to combustion than to the composition.
For glass cleaners and furniture polishes, the formaldehyde emission profile is presented in Figure 1. While formaldehyde concentrations remain below 10 $\mu g.m^{-3}$ just after use, emission profiles then increase although the overall product volatilization rate is declining. This may result from varying volatilization, chemical reactions between airborne pollutants or sorption behaviour among the constituents.

Figure 1. Formaldehyde concentrations for glass cleaners and furniture polishes.



For both categories of toilet products, formaldehyde concentrations are increasing with successive flushes, leading to a formaldehyde concentration above 10 µg.m^{-3} for the toilet block J1. For both carpet cleaners and carpet stain removers, formaldehyde concentrations remain steady after use below 10 µg.m^{-3}. Except for the pure use of floor cleaners N1 and N2, formaldehyde concentrations for all floor cleaners are around or below 10 µg.m^{-3} as showed on Figure 2. This trend remains steady after use. The presence of *Savon de Marseille* does not influence formaldehyde emissions, whether these floor cleaners are diluted or pure. On the contrary, the dilution of the other floor cleaners decreases the formaldehyde concentrations. In this product category, the formaldehyde concentrations for floor wipe P1 are the highest among all the tested products: from 1249 µg.m^{-3} (0-30 min) to 128 µg.m^{-3} (not illustrated on Figure 2). This may be explained by the presence of formaldehyde or formaldehyde releasers within the product ("anti-bacterial" wipes).

Figure 2. Formaldehyde concentrations for floor cleaners except floor wipe P1.



* SM : *Savon de Marseille*

DISCUSSION

This work shows that the use of some consumer cleaning products and air fresheners may lead to the emission of high levels of VOCs and formaldehyde.

Human exposure to VOCs occurs through inhalation or skin contact. Consumer products (household products, cosmetics, paints…) represent individually minor sources of VOCs emissions but considered together, they all make a significant contribution to the total load of VOCs indoors.

Information regarding the 32 tested products composition was transmitted *via* the consultation of the *BNPC*, to try to explain emission profiles. This confidential database registers industrial compositions of various types of products that could be implied in human intoxications. They are declared to the *BNPC* on a voluntary basis by manufacturers. By using the specific reference of the 32 tested products, the *BNPC* analysis was performed to investigate the presence of formaldehyde, formaldehyde releasers or other VOCs (terpenes, aldehydes, alcanes) in the tested products. Formaldehyde releasers such as imidazolidinyl urea, diazolidinyl urea, sodium hydroxymethyl glycinate and benzylhemiformal may be used in consumer products as preservatives instead of formaldehyde. The products containing these

compounds may release the formaldehyde they contain when dissolved in aqueous or polar solvents. There is little information on the stability of these formaldehyde releasers in consumer products, as well as their safety profile. None of the 32 tested products were declared to contain formaldehyde. For 7 products, a formaldehyde releaser was declared in the composition but for 5 of them, the highest measured concentrations of formaldehyde are below 10 $\mu g.m^{-3}$. One floor cleaning product (N1) and one floor wipe (P1) were declared to contain a formaldehyde releaser and the associated maximal concentrations of formaldehyde emitted are quite high: 48 $\mu g.m^{-3}$ for N1 and 1249 $\mu g.m^{-3}$ for P1. The possible relationship between formaldehyde emission and the presence of formaldehyde releasers in the composition is not confirmed. Other formaldehyde releasers may not be identified yet such as methylisothiazolinone compounds

Chemical reactivity can occur by photochemistry under the influence of sun rays and heat, converting VOCs into so-called "secondary" pollutants such as aldehydes, ketones, organic acids... (BEUC, 2005). Some studies show that reactive chemistry between terpenes and ozone produces formaldehyde (Destaillats et al., 2006; Fan et al., 2003; Singer et al., 2006). Moreover, specific VOCs are reacting with ozone at a higher rate than others (Destaillats et al., 2006). The effects of these secondary pollutants are still discussed (Nöjgaard et al., 2005) in particular in what extent they contribute to indoor pollution.

For 12 of the 32 tested products, the TVOC concentrations exceeded 1000 $\mu g.m^{-3}$, the maximum limit value in indoor air proposed in the Afsset protocol for qualification of solid building materials (Afsset, 2006; Rousselle et al., 2008). However adverse health effects cannot be assessed specifically on the basis of these values since human exposure and associated risks can only be quantified for each individual compound. Therefore TVOCs concentrations may only be considered as an indicator of significant emissions.

Formaldehyde is identified as a major issue, classified by the International Agency for Research on Cancer (IARC) as a human carcinogenic compound since June 2004, on the basis of observed nasopharyngeal carcinoma in workers (IARC, 2006). In this framework, in 2007, a working group in Afsset proposed formaldehyde Indoor Air Quality guideline values to protect from ocular and nasal irritation. These values will also protect against the occurrence of local carcinogenic effects (nasopharyngeal carcinoma) as nasal irritation is a key-event occurring at lower doses than cytotoxicity (Afsset, 2007; Mandin et al., 2008). The indoor air quality guideline value for short term exposure is 50 $\mu g.m^{-3}$ over 2 hours. In this study, some measured formaldehyde concentrations exceed this guideline value which may lead to irritative symptoms in the consumers. However the cancer risk of formaldehyde at these non-cytotoxic concentrations is likely to be negligible.

CONCLUSIONS

The use of cleaning products and air fresheners can lead to emissions of primary or secondary pollutants indoors. Starting from analytical methods designed for building products and air fresheners, realistic experimental protocols were defined in order to characterise formaldehyde and VOCs emissions of various types of products in order to assess consumers' exposure.

Emissions vary widely depending on the type of products. For some of them, formaldehyde concentrations remained steady or increased after use. This trend may be explained by chemical reactivity between terpenes and ozone but these reaction pathways are still not well

characterized. A majority of products released high concentrations of VVOCs that could not be quantified with the analytical methods used in this study.

Even if this study is not representative of emissions from all the consumer products on the French market, it shows that such emissions can really influence indoor air quality and that further studies are necessary to better understand the contribution of these emissions to human exposure to chemicals.

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