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Environment International

journal homepage: www.elsevier.com/locate/envint

Ozone-initiated VOC and particle emissions from a cleaning agent and an air freshener: Risk assessment of acute airway effects

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ARTICLE INFO

Article history:

Received 28 January 2014

Accepted 24 March 2014

Available online 24 April 2014

Keywords:

Airway effects
Consumer products
Emissions
Ozone
Particles
Terpenes

ABSTRACT

Emissions of volatile organic compounds and ultrafine particles from a kitchen cleaning agent (cream) and plug-in air freshener were investigated in a 20 m³ walk-in climate chamber at low (~5 ppb) and high ozone (~50 ppb) test concentrations and 0.6 air exchange rate. The products emitted terpenes, inter alia limonene, dihydromyrcenol, geraniol, linalool, and glycol ethers. The ozone-initiated reaction products of these compounds were measured by air sampling on Tenax TA followed by thermal desorption GC–MS and air sampling on DNPH cartridges followed by liquid extraction and HPLC–UV analysis. Particle formation was monitored simultaneously. A number of oxygenated and poly-oxygenated reaction products were identified and risk assessed for acute airway effects: formaldehyde, acetaldehyde, acetone, 4-acetyl-1-methylcyclohexene, 6-methyl-5-heptene-2-one, 3-isopropenyl-6-oxo-heptanal, and 4-oxo-pentanal. These compounds generally increased initially at the high ozone concentration, while the terpenes decayed, concurrent with their consumption of ozone. At high ozone concentration, the plug-in air freshener resulted in concentrations of formaldehyde and 4-oxopentanal that may give rise to concern about sensory irritation and airflow limitation, respectively. At high ozone concentration, the kitchen cleaning agent and air freshener resulted in peak particle mass concentrations at 81 µg/m³ (8.5 × 10⁵ #/cm³) and 24 µg/m³ (2.3 × 10⁴ #/cm³), respectively. At low ozone concentration, the particle concentration peaked at 4 µg/m³ (1.0 × 10⁵ #/cm³) after the application of the kitchen cleaning agent, while no increase was observed for the air freshener. The particles, in view of their organic composition and concentration, are not considered to cause acute airway effects. Testing under realistic conditions that mimic user pattern behavior is warranted to obtain acute and longer-term exposure data at realistic indoor ozone concentrations.

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1. Introduction

Household related consumer products may contain reactive compounds that affect respiratory health among cleaning personal (Zock et al., 2010). Domestic use that results in indoor exposure is also of concern, due to *in-situ* ozone-initiated chemistry with reactive volatile organic compounds (VOCs) (Nazaroff and Weschler, 2004). This is further exacerbated by the advent of stricter energy efficiency measures, i.e. lower air exchange rate (AER) that increases the concentration of ozone-reactive VOCs. Especially, indoor chemistry of terpenes (comprising terpenes and terpenoids), readily undergoes gas-phase and surface reactions to produce a host of complex ozone-initiated reaction products (Walser et al., 2008). Some are gaseous (Atkinson and Arey, 2003; Calogirou et al., 1999) and some have low vapor pressure leading to self-nucleation and formation of secondary organic aerosols (SOA) (Glasius et al., 2000; Koch et al., 2000). These are fine and ultrafine

particles (Wainman et al., 2000; Weschler and Shields, 1999), some of which may condense onto existing particles. For instance, *in situ* production of limonene from orange peeling results in acute formation of SOA (Langer et al., 2008; Vartiainen et al., 2006). The potential health significance of ozone-initiated terpene chemistry was recently reviewed on the basis of *in vitro*, *in vivo*, and human exposure studies (Rohr, 2013).

To our knowledge risk assessment of gas- and particle phase oxidation products from ozone-initiated reactions with household cleaning products has not been carried out. Generally, the main focus has been the SOA size distribution and development upon ozone exposure in various conditions and from surfaces. Few climate chamber studies involving use of consumer products in the presence of ozone have reported the decay of initial compounds and their transformation to oxidation products. For instance, a plug-in air freshener was turned on for 24 h in a large climate chamber (30 m³; AER = 0.55 h⁻¹), then briefly exposed to 74 ppb ozone for 25 min and followed by monitoring of terpenes and the formation of formaldehyde, 4-AMCH (4-acetyl-1-methylcyclohexene), and nopinone (Liu et al., 2004). In another study, the decay of key terpenes from a plug-in air freshener in a 50 m³ chamber (AER = 1 h⁻¹) and 120 ppb inlet ozone was reported after 30 and 90 min of exposure

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(Singer et al., 2006). Further, the formation of acetaldehyde, formaldehyde, acetone, acetic and formic acid, and glycolaldehyde was investigated in a 198 l Teflon bag (AER = 1 or 3 h⁻¹) and 60 to 250 ppb inlet ozone (Destaillets et al., 2006).

One recent and extensive box modeling study with 200 ppb (1.1 mg/m³) limonene and 50 ppb indoor ozone showed formaldehyde to be the key oxidation product at 38 ppb after a cleaning event (AER = 0.76 h⁻¹); other limonene oxidation products were also modeled at about 9 to 5 ppb for IPOH (3-isopropenyl-6-oxo-heptanal) and 4-AMCH, respectively (Carslaw, 2013). The same group expanded the modeling approach to European offices. Peak concentrations of formaldehyde, 4-AMCH, and IPOH, respectively, in the late afternoon after a cleaning event in the morning with a limonene-based product at 0.5 h⁻¹ AER, were 15, 2 and 0.4 ppb, and 75 µg/m³ PM_{2.5} (Terry et al., 2014).

Our objective was to investigate the formation of ozone-initiated reaction products from two selected common household products under near-realistic user conditions in a walk-in climate chamber; further, to apply recently reported thresholds and critical exposure limits for acute airway effects are used for a risk assessment. The selection of the two product types was twofold: first, on the basis of a European market study of consumer product uses and user patterns in four EU regions within the EPHECT (Emission, Exposure Patterns, and Health Effects of Consumer Products in the EU) project resulted in the most used product brands and types (Johnson and Lucica, 2012). Within the EPHECT testing program, two product types out of 16 product categories were identified to emit ozone-reactive VOCs. These were a kitchen cleaning agent (KCA) in a bottle and a plug-in (electric) air freshener (PIAF). These products had 30% and 55% frequency use in ten EU countries.

2. Methods and chemicals

2.1. Chemicals

4-Acetyl-1-methylcyclohexene (4-AMCH) (93%), 6-methyl-5-heptene-2-one (6-MHO) (99%), decane (99%), dihydromyrcenol (99%), di(propylene glycol) monomethyl ether (99%), geraniol (98%), limonene (99%), linalool (97%), methanol (99.8%), pentane (99.9%), α-pinene (98%), α-terpineol (96%), and toluene (99.9%) were obtained from Aldrich-Sigma. 3-isopropenyl-6-oxo-heptanal (IPOH) (97%) and 4-oxo-pentanal (4-OPA) (97%) were synthesized according to Wolinsky and Barker (1960) and Hutton et al. (2003), respectively, by (HM-Chemo Co, Shanghai Branch, CN) and (Shanghai Chempartner Co, CN). For further details about 4-AMCH, IPOH, and 4-OPA, see Wolkoff et al. (2013).

2.2. Qualitative identification of emitted VOCs

Ten most abundant VOCs were analyzed by GC/MS and searched in NIST 2011 library and by use of AMDIS (Ver. 2.7); for analytic details, see below. Identification, in general, was based on inspection and considered positive by library search match >800 for both forward and reverse matching. A further criterion was retention time (t_R) identification with an authentic standard within t_R ± 0.03 min, when applicable.

2.3. Test chamber

Emission testing was carried out in a full scale walk-in steel chamber (20.28 m³) with an ante-chamber (2.72 m³) as inner entrance. Chamber dimensions: height: 2.29 m; length: 3.46 m; width: 2.56 m. Table 1 shows the chamber specification and test conditions for the KCA and PIAF. The chamber was supplied with HEPA filtered outdoor air taken from the roof of the building (low traffic density environment). The chamber could be lit with two fluorescent lamps in the ceiling; however, they were unlit during experiments. Immediately, after the start of the experiment, i.e. outer door closed, three mixing fans were turned on for 60 s. The fans were placed in three corners on the floor and 5 cm from the chamber wall. The AER was 0.6 h⁻¹, in accordance with many European building standards for ventilation of 0.5 h⁻¹ in dwellings (Dimitroulopoulou, 2012). The AER included the chamber exchange rate and the sampling rate of the particle monitor.

Prior to each experiment the chamber was purged by elevation of the air exchange rate (about 15 h⁻¹) for about 24 h. The chamber background was monitored with both Tenax TA (VOCs) and DNPH (carbonyls) sampling, PID (photoionization) detection, and particles before each new experiment, see below. Temperature and relative humidity were measured by Tinytag loggers (Gemini data loggers, West Sussex, UK) placed near the sampling positions and the chamber outlet.

2.4. Products and application

In a series of near-realistic user scenarios KCA (about 40 g) was applied to a clean steel surface (1.0 m²) with a nitrile glove inside the chamber. The steel plate was placed on the floor; the entire operation took less than 2 min. The product container (shaken) and glove were weighed before and after the application. The PIAF was tested in the center of the chamber by inserting it in an electric plug and turning it at maximum setting; it was weighed before and after the end of the experiment. Tests were undertaken without ozone generation (low

Table 1

Test chamber specifications and test conditions for kitchen cleaning agent (KCA) and plug-in air freshener (PIAF).

	Test parameter	KCA	PIAF
Chamber volume, m ³ /chamber floor area, m ²	20.28/8.9		
Surface area, m ²		1.0	
Loading factor, m ² /m ³		0.05	
Air exchange rate, h ⁻¹	0.6 ± 0.1		
Temperature, °C	24 ± 2		
Rel. humidity, %	40 ± 5		
Air velocity, cm/s	0.05 ^a ± 0.01		
Amount applied, g		39.8	
Emission rate, g/h ^b			0.061 (low ozone) 0.052 (high ozone)
Initial ozone concentration, ppb		5; 55	5; 50
Low test; high test ± 5 ppb			
Residual ozone concentration, ppb		5; 14	5; 20
Low test; high test ± 5 ppb			
Other	3 mixing fans turned on for 1 min		
Test duration, min		310	326-360

^a Determined from the exchange rate and chamber geometry.

^b Based on total weight loss within test period at maximum setting.

ozone) and with ozone generation (high ozone). For experimental conditions, see Table 1.

2.5. Ozone generation

Ozone was generated photochemically with a thermostated mercury lamp housing controlled by a high performance variable power supply using air (medical grade) as described previously (Clausen et al., 2001). The ozone generator was adjusted manually to maintain a 50 ± 5 ppb ozone concentration inside the chamber for at least 1 h before the start of the application of KCA or turning on PIAF. The ozone–air mixture with a flow rate of about 0.5 l/min was fed through a ¼" Teflon tube into the chamber via the air inlet of the climate chamber. Ozone was measured with a calibrated API 400 UV ozone monitor (Teledyne API, San Diego, CA).

2.6. Air sampling and analysis

VOCs, carbonyls, and ozone were sampled through a 10 mm stainless steel sampling manifold. The manifold was placed 1.0 m from floor and 1.2 m from the air outlet wall and sampled air 5 cm from the chamber inner wall. Samples for VOCs and carbonyls were taken in duplicate within 30 and 60 min intervals, respectively, starting the first sampling event within the first 3 min after start of the application. After the first 1 to 2 h, five to six more VOC samples were taken at 1-hour intervals. The time of sampling is taken as the midpoint between start and end of each sampling period. VOC and carbonyl data (C1–C4) are reported as mean of duplicates corrected for chamber background air and rounded to nearest integer.

VOCs were sampled on Tenax TA (60–80 mesh) adsorbent tubes (200 mg) at a sampling time of 10 min at 100 mL/min using calibrated pumps (Gillian Gilair 5, Sensidyne, US). The Tenax TA tubes were analyzed on a Perkin Elmer Turbo Matrix 350 thermal desorber (TD) coupled to a Bruker SCION TQ GC–MS system (Bruker Daltonics, Bremen, DE). Tube desorption was carried out at 275 °C for 20 min and the low and high temperatures of the cryo trap were -20 °C and 280 °C, respectively. The GC column was a 30 m \times 0.25 mm with 0.25 μ m film thickness; VF-5MS (Agilent Technologies, Santa Clara, US). The oven program was as follows: 50 °C for 4 min, ramp 1: 4 °C/min to 120 °C, ramp 2: 50 °C/min to 250 °C hold for 2 min. Helium was used as carrier gas at an inlet pressure of 0.97 bar (1.5 mL/min). The mass spectrometer was operated in SIM/Scan mode using electron ionization. Valves, transfer lines and ion source were kept at 270 °C. Six-point calibration was applied ($r^2 > 0.99$) using authentic standards in methanol or pentane for 4-OPA. The detection limit was of the order of 0.5–2 ng/tube, i.e. between 0.5 and 2 μ g/m³ at a 1 L sampling volume. A manganese dioxide scrubber for ozone artefacts was deliberately not applied, because of risk of reduced sampling of VOCs, e.g. for linalool (Singer et al., 2006); furthermore, the short sampling duration was assumed to minimize artifact loss or formation of oxidation products. Glycols and glycol ethers are reported in equivalents of di(propylene glycol) monomethyl ether.

Carbonyls (C1–C4) were sampled (120 L over 60 min) in duplicate on DNPH sampling cartridges (Supelco, LpDNPH S10) with a calibrated pump (Gillian Gilair 5, Sensidyne, US). The cartridges were eluted within 6 h after sampling and analysis initiated within the same day by HPLC (Breeze, Waters, Milford, MA) with UV detection. A dedicated LC column facilitating acetone and acrolein separation was applied (Inertsil acrolein C18, 250 \times 4.6 mm; GL Sciences, CA). Water and acetonitrile were used as solvents A and B, respectively. The elution gradient was as follows: 0–2 min isocratic 55% B, 2–10 min gradient from 55 to 80% B, 10–15 min gradient from 80 to 55% B. The flow was 1.5 mL/min. A standard mix (Supelco, Carbonyl-DNPH Mix 1) was used for six-point calibration ($r^2 > 0.99$). The detection limit was of the order of 1 μ g/m³ for formaldehyde and acetaldehyde at 60 L sampling volume. An ozone scrubber was deliberately not used at this concentration

level, and further to avoid artifact trapping of the carbonyls on the scrubber.

The TVOC concentration was monitored in real-time by use of a PID equipped with a 10.6 eV lamp (ppbRAE, Raesystems, San Jose, CA).

2.7. Particle measurements

Number size distribution measurements were conducted using the TSI Model 3091 Fast Mobility Particle Sizer (TSI, Shoreview, NM). The instrument was operated at 1 second time resolution in the measurement range: 5.6–560 nm; the sampling rate was 10 L/min and with exhaust outside the chamber. Total number concentration was integrated from the number size distribution. Spherical SOA particles with a mean density of 1.2 were assumed for the mass calculations (Bahreini et al., 2005; Saathoff et al., 2009; Turpin and Lim, 2001).

3. Results

3.1. Kitchen cleaning agent

Limonene and dihydromyrcenol were the most abundant reactive VOCs in ratio 3 to 1, while butoxyethoxy ethanol was the second most abundant VOC; other reactive VOCs were also present, but in minor amounts (Table 2).

A maximum limonene concentration about 550 μ g/m³ (99 ppb) was measured within the first 30 min upon application of KCA at the low ozone test concentration (Fig. 1a). This dropped to 350 μ g/m³ (63 ppb) at the high ozone test concentration, which indicates fast ozonolysis and *inter alia* condensation of VOCs on generated SOA (Figs. 1b and 2b). Likewise, the observed difference in 1-(2-butoxyethoxy) ethanol concentration maxima between low and high ozone test conditions may be explained by condensation on SOA. A difference in concentration maxima was also observed for glycol and glycol ethers in PIAF (see below). A reduction of dihydromyrcenol to about one third at the high ozone test concentration was observed relative to the low ozone test condition.

At high ozone test concentration, both formaldehyde and acetaldehyde increased fast for the first 100 min (Fig. 1b). Hereafter, they decreased in line with the consumption of limonene. The high ozone test concentration resulted in poly-oxygenates with peak concentrations of about 17 and 7 μ g/m³, respectively, for IPOH and 6-MHO, key oxidation products of limonene (Atkinson and Arey, 2003; Calogirou et al., 1999) (Fig. 1c). Other poly-oxygenates, 4-AMCH and 4-OPA, only reached peak concentrations of less than 3 μ g/m³. No poly-oxygenated compounds were observed at the low ozone test concentration; however, some formaldehyde and acetaldehyde were emitted from the KCA. The ozone concentration decreased three-fold from about 55 ppb to a minimum of 14 ppb within the first 40 min in the high ozone test concentration, while a decrease from about 10 ppb to < 5 ppb was observed in the case of the low ozone test concentration (Fig. 1d).

Table 2

Qualitative identification (mass spectra library match/reverse match) and area fraction (of total TIC peak area) of ten major VOCs emitted from a kitchen cleaning agent in decreasing order of abundance.

Compound	CAS	Match/R. match	Area fraction (%)
Limonene	5989-27-5	916/916	36
1-(2-butoxyethoxy)ethanol	54446-78-5	926/926	31
Dihydromyrcenol	18479-58-8	831/899	10
o-Cymene	527-84-4	875/926	4
Terpinolene	586-62-9	913/918	3
d-Carvone	2244-16-8	920/955	1
Decanal	112-31-2	922/931	1
Citronellol acetate	150-84-5	908/910	<1
cis-Geraniol	106-25-2	922/924	<1
γ -Terpinene	99-85-4	887/913	<1

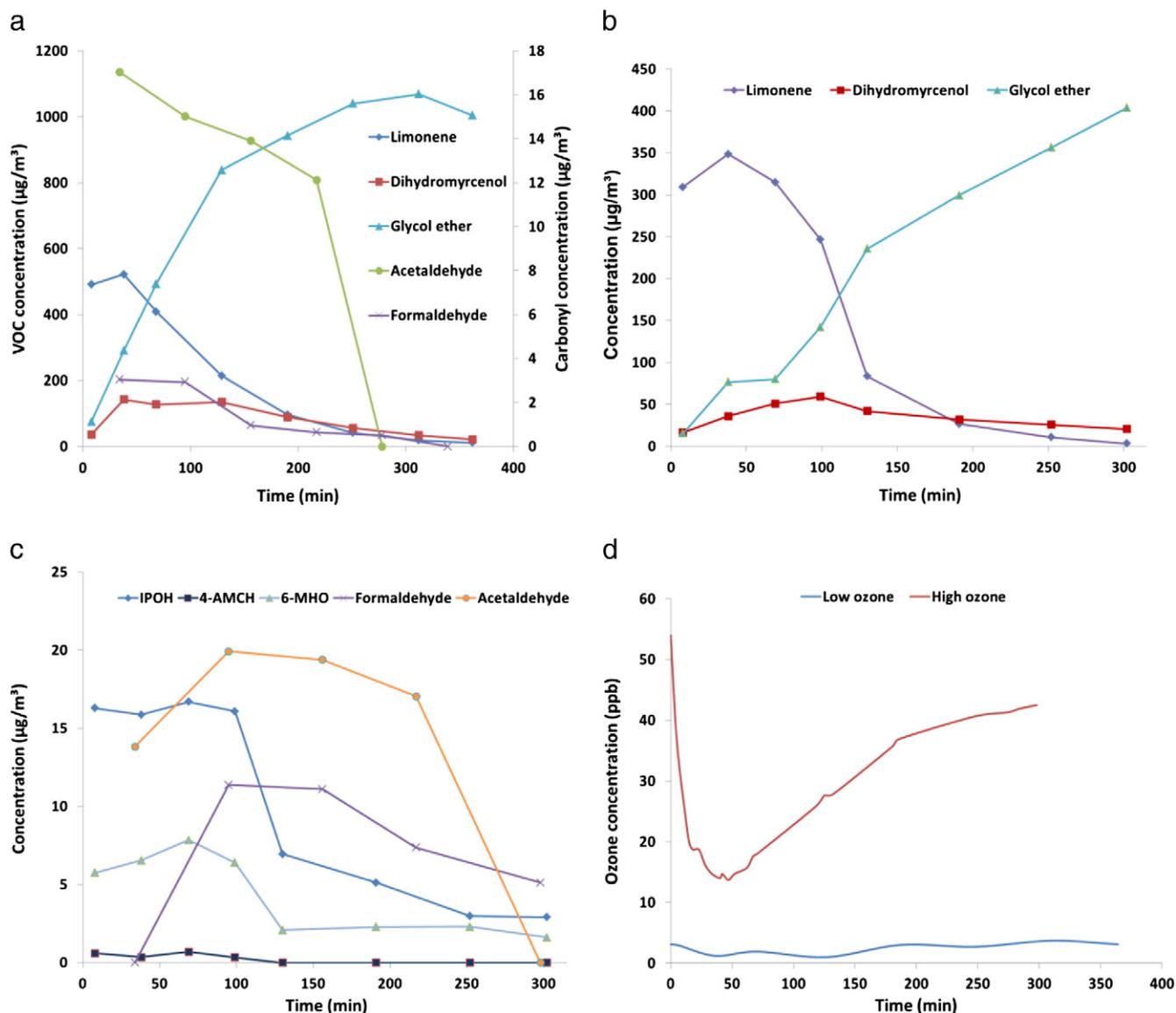


Fig. 1. Gas-phase concentrations of selected VOCs emitted from a kitchen cleaning agent and ozone-initiated reaction products. a) Low ozone test concentration (<5 ppb). b) High ozone test concentration (55 ppb). c) Reaction products at high ozone test concentration. d) Ozone time profiles.

In case of the low ozone test concentration, number concentration increased from around 4×10^3 to 1×10^5 $\#/\text{cm}^3$ within the first 30 min after the application, and with a delayed increase of

the particle mass (Fig. 2a). The mass/time profile showed a low background of $1.2 \mu\text{g}/\text{m}^3$. Mass concentration increased with the number concentration and reached a maximum of $4 \mu\text{g}/\text{m}^3$ after 116 min. The

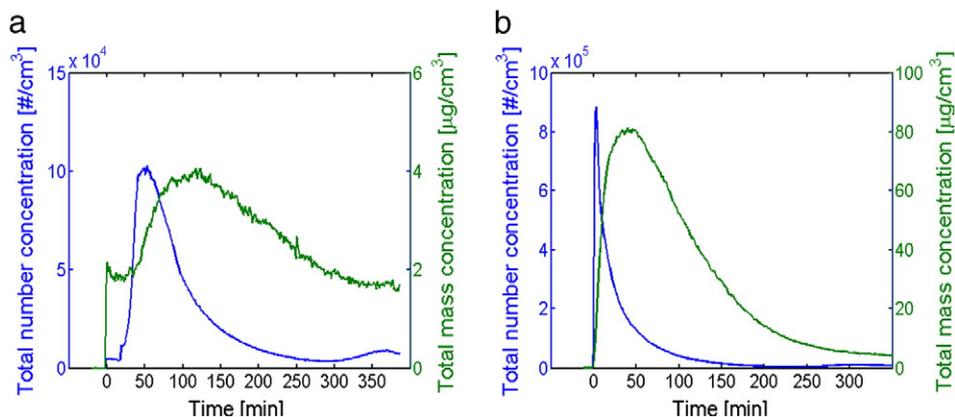


Fig. 2. Ultrafine particle number and mass concentrations from a kitchen cleaning agent at low and high ozone test concentrations. For the ozone time profile, see Fig. 1d. a) Low ozone test concentration (5 ppb). b) High ozone test concentration (55 ppb).

Table 3

Qualitative identification (mass spectra library match/reverse match), and area fraction (of total TIC peak area) of ten major VOCs emitted from a plug-in air freshener, in decreasing order of abundance.

Compound	CAS	Match/R. match	Area fraction (%)
Dipropylene glycol monomethyl ether	20324-32-7	897/907	14
Tripropylene glycol	1638-16-0	807/820	11
Tripropylene glycol monomethyl ether	20324-33-8	789/795	7
α -Terpineol	98-55-5	930/930	6
Linalool	78-70-6	901/905	5
Dihydromyrcenol	18479-58-8	921/921	4
Phenylethyl alcohol	60-12-8	843/890	4
cis-Geraniol	106-25-2	827/863	1
4-Hexen-1-ol	6126-50-7	848/848	1

high ozone test concentration showed an immediate and sharp increase that peaked at $8.5 \times 10^5 \text{ \#}/\text{cm}^3$ about 3 min after the application, and then followed by a sharp decay (Fig. 2b). The mass concentration also increased immediately after application and peaked at $81 \mu\text{g}/\text{m}^3$ after about 40 min.

3.2. Plug-in air freshener

The reactive VOCs were α -terpineol, linalool, dihydromyrcenol, γ -terpineol, geraniol, and 4-hexene-1-ol; however, the major VOCs were two glycol ethers and tripropylene glycol (Table 3).

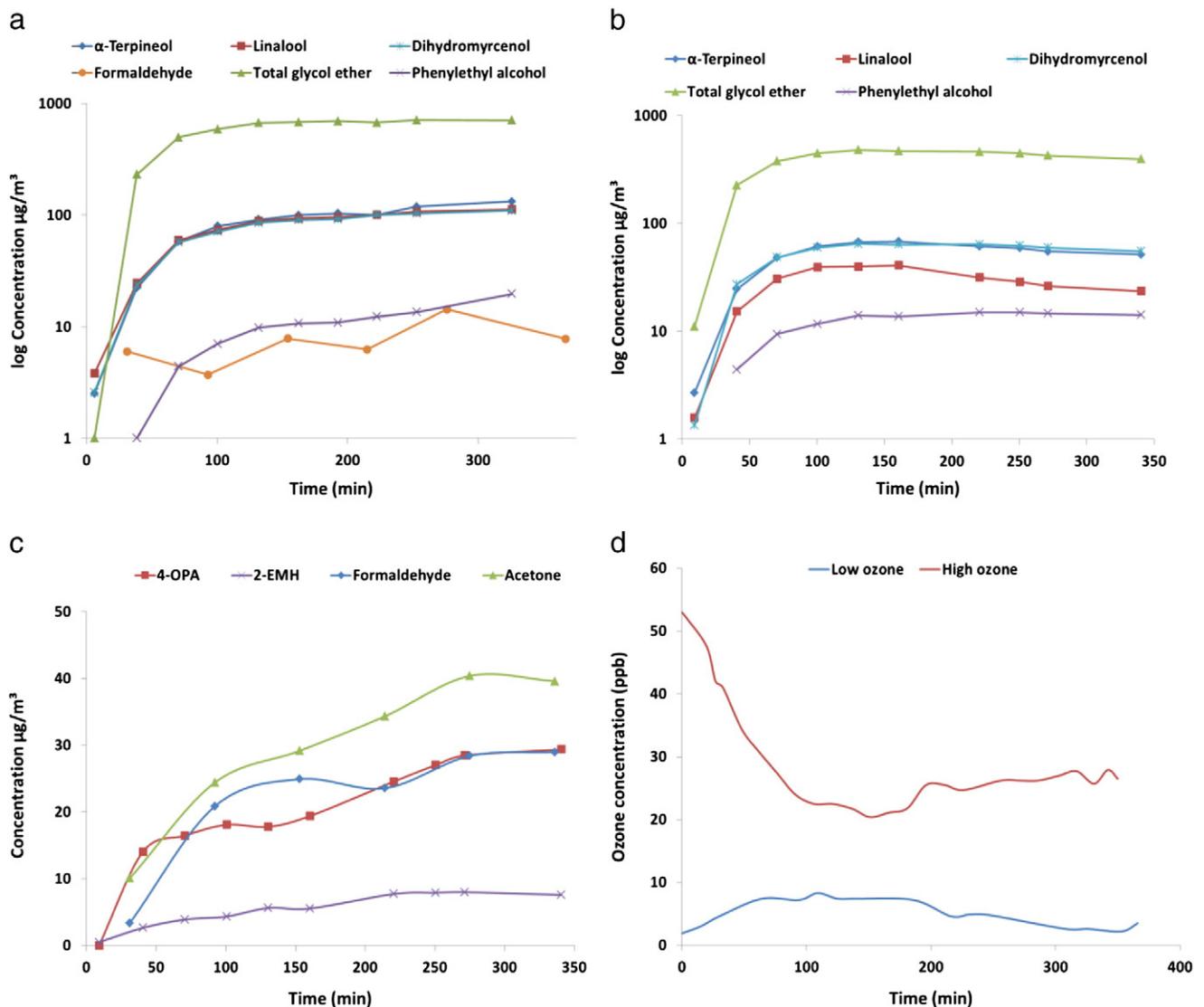


Fig. 3. Gas-phase concentrations of limonene and selected VOCs emitted from a plug-in air freshener and ozone-initiated reaction products. Total glycol ethers include 1-(2-methoxy-1-methylethoxy)-2-propanol, tripropylene glycol and tripropylene glycol monomethyl ether (see Table 3). a) Terpenes at low ozone test concentration (5 ppb). b) Terpenes at high ozone test concentration (50 ppb). c) Major reaction products at high ozone concentration (50 ppb) see Tables 5 a and b. d) Ozone time profiles at low and high test concentrations.

Table 4

Health assessment (acute airway effects: % of threshold values) of peak concentrations from a kitchen cleaning agent at Low (5 ppb) and High (50 ppb) ozone test concentrations in 20 m³ walk-in chamber (AER = 0.6 h⁻¹).

Compound	Thresh µg/m ³	Ozone L,H	Max. conc. µg/m ³	% Max/Thresh
Limonene	90,000 ^a	L	522 ± 24	0.6
		H	349 ± 6	0.4
Dihydromyrcenol	High ^b	L	143 ± 8	–
		H	59 ^h	–
1-(2-Butoxyethoxy) ethanol	16,000 ^c	L	1069 ± 60	7
		H	404 ± 25	3
o-Cymene	9500 ^d	L	26 ± 1 ⁱ	–
		H	15 ± 1 ⁱ	–
Terpinolene	High ^b	L	22 ± 1 ^j	–
		H	2 ± 1 ^j	–
Formaldehyde	100 ^e	L	3 ± 2	3
		H	11 ± 2	11 ^k
Acetaldehyde	7000 ^c	L	17 ± 1	0.2
		H	20 ± 1	0.3
4-AMCH	1130 ^f	L	nd	–
		H	1 ± 1	–
IPOH	1100 ^g	L	nd	–
		H	17 ^h	1.5
6-MHO	1550 ^g	L	nd	–
		H	8 ^h	–
4-OPA	123 ^f	L	nd	–
		H	3 ± 1	–

– = Not considered relevant.

nd = Not detected.

a) Sensory irritation (Carrer et al., 2013).

b) Expected to be in the same order of magnitude as limonene.

c) Sensory irritation (Wolkoff, 2013).

d) Assumed to be of the same order of magnitude as propylbenzene (Wolkoff, 2013).

e) Sensory irritation (Wolkoff and Nielsen, 2010).

f) Airflow limitation (Wolkoff et al., 2013).

g) Sensory irritation (Wolkoff et al., 2013).

h) Only one sample.

i) Quantified in toluene equivalents.

j) Quantified in limonene equivalents.

k) 33% with background adjustment.

After plugging-in glycol ethers, α -terpineol, dihydromyrcenol, and linalool were the major VOCs. The concentrations of the terpenes peaked after about 150–200 min at both low and high ozone test concentrations (Fig. 3a and b). The difference in the total glycol concentration is partly due to 16% lower emission rate at the high ozone concentration (Table 1). Further, condensation of VOCs on the SOA in the high ozone test concentration may also have contributed to this difference.

The concentration of formaldehyde and 4-OPA increased in line with the increase of the reactive VOCs at the high ozone test concentration (Fig. 3b and c). The high ozone test concentration decayed about 60% within the first 2 h from about 50 ppb to about 20 ppb followed by an increase to about 28 ppb. The low ozone concentration varied between 3 ppb and 8 ppb with an increase within the first 100 min (Fig. 3d). In both conditions, the minor variation is due to an increase in the outdoor ozone level during the experiments. Table 5b shows some additionally identified reaction products in agreement with Calogirou et al. (1999) and Kudal (2013).

At low ozone test concentration, the particle number concentration did not change after plugging-in PIAF (Fig. 4a). At high ozone test concentration, a maximum number concentration of 2.3×10^4 #/cm³ was reached after about 33 min, while the mass concentration peaked at about 24 µg/m³ after ca. 270 min (Fig. 4b).

4. Discussion

4.1. Time profiles of oxygenates and poly-oxygenates

Generally, ozone initiates consumption of the terpenes that reduces their concentration, while oxygenates and poly-oxygenates increase

according to their extent of ozonolysis (Atkinson and Arey, 2003; Calogirou et al., 1999; Destailats et al., 2006; Forester and Wells, 2009). For example, the formaldehyde concentration showed a brief increase after the application of KCA. Furthermore, a brief, but substantial, increase of IPOH and 6-MHO was observed; these then decayed in line with the consumption of limonene and the AER. Formation of formaldehyde and 4-OPA was observed for PIAF at the high ozone test concentration. The formation of formaldehyde, 6-MHO, and 4-OPA has been reported in studies that include limonene, geraniol, linalool, and α -terpineol (Bernard et al., 2012; Forester and Wells, 2009; Shu et al., 1997) and modeled in the ozone/limonene system (Carslaw, 2013).

4.2. Oxygenates and poly-oxygenates—risk assessment of acute airway effects

Airway effects (sensory irritation and airflow limitation) on the basis of health based thresholds (human reference values) for limonene, formaldehyde, acetaldehyde, and some poly-oxygenates have previously been discussed by Wolkoff (2013), Wolkoff and Nielsen (2010) and Wolkoff et al. (2013). Limonene was furthermore assessed regarding both acute and long-term airway effects by Carrer et al. (2013). No data was found about airway effects in PubMed and the European Chemicals Agency (ECHA) database for α -terpineol, dihydromyrcenol, geraniol, and linalool. The thresholds for sensory irritation in eyes and the upper airways are expected to be high for terpenes, in general (Carrer et al., 2013; Wolkoff, 2013). One study indicates that α -terpineol and limonene have thresholds for eye irritation similar to butanol, and the authors concluded that they “can probably be ruled out as cause of acute eye irritation indoors” (Mølhave et al., 2000). Based on this, it is assumed that the thresholds for sensory irritation of the identified terpenes are in the same order of magnitude as for limonene. Thus, odor perception is the only effect to be expected from these VOCs (fragrances) in accordance with Gminski et al. (2011).

Since the testing was carried in a semi-realistic scenario and protocol in a walk-in 20 m³ climate chamber it is considered defensible to carry out a tentative health assessment regarding acute airway effects as a first and conservative attempt, well knowing that up-scaling would result in lower room concentrations with the same AER, but higher concentrations at lower AERs reflecting airtight buildings. Such re-scaling, however, requires advanced modeling or alternatively, realistic testing and personal monitoring. Furthermore, the high ozone test concentration may be unrealistically high in certain regions of Europe, thus, leading to less formation of reaction products, for example, see (Morrison et al., 2011; Terry et al., 2014); however, the AER also plays an important role in the reaction probability (Waring, 2014; Weschler and Shields, 2000). Further to this, the presence of people may decrease the ozone room concentration (Fadeyi et al., 2013; Fischer et al., 2013) due to reaction on skin oils and clothing (Coleman et al., 2008; Wisthaler and Weschler, 2010), reaction with unsaturated compounds in dust (Vibenholt et al., in press; Weschler et al., 2011), and catalytic degradation. Fleecy surfaces may act as a sink for the gas-phase terpene concentrations; this, however, may increase the surface ozone-initiated SOA formation, e.g. (Waring and Siegel, 2013). Noteworthy is that some of the reaction products from skin oils are the same as found in this study, see below.

Background levels of formaldehyde and other ozone-initiated reaction products may be added to the measured chamber concentration for a more realistic risk assessment. For instance, an EU mean formaldehyde concentration of 21.5 µg/m³ is considered as a background level in public buildings (Geiss et al., 2011; Kotzias et al., 2009), although higher levels have been reported (Wolkoff and Nielsen, 2010). Downstream 4-OPA concentration of 41 µg/m³ (10 ppb) has been measured from used ozone exposed ventilation filters (Destailats et al., 2011) and concentrations from 8 to 24 µg/m³ have been measured in aircraft cabin and office air (Weschler et al., 2007; Wisthaler and Weschler, 2010); thus, leading to a tentative mean background level of 10 µg/m³ in offices.

Table 5a

Health assessment (acute airway effects: % of threshold value) at peak concentrations from a plug-in air freshener at Low (5 ppb) and High (50 ppb) ozone test concentrations in 20 m³ walk-in chamber (AER = 0.6 h⁻¹), and without and with background level addition.

Compound	Thresh µg/m ³	Ozone L,H	Max. conc. µg/m ³	Max. conc. µg/m ³ + backgr.	% Max/thresh	% Max/thresh + backgr.
Limonene	90,000 ^a	L	5 ± 2		0.0007	–
	9000 ^b	H	5 ± 1	–	0.01	–
Geraniol	High ^c	L	15 ± 1	–	–	–
		H	6 ^j	–	–	–
Linalool	High ^c	L	112 ± 17	–	–	–
		H	41 ± 1	–	–	–
Dihydromyrcenol	High ^c	L	109 ± 21	–	–	–
		H	64 ^j	–	–	–
1-Hexenol	High ^d	L	33 ± 5 ^k	–	–	–
		H	14 ^{j,k}	–	–	–
Phenylethyl alcohol	High ^e	L	20 ± 1 ^k	–	–	–
		H	15 ± 1 ^k	–	–	–
α-Terpineol	High ^c	L	132 ± 12	–	–	–
		H	68 ± 4	–	–	–
Formaldehyde	100 ^f	L	14 ± 5	36	14	36
		H	29 ± 1	50	29	50
Acetone	54,000 ^g	L	14 ± 3	–	0.04	–
		H	40 ± 1	–	0.06	–
4-OPA	123 ^h	L	nd	–	–	–
		H	29 ± 5	39	24	32
6-MHO	1550 ⁱ	L	nd	–	–	–
		H	4 ± 1	8	0.3	0.5
Total glycol ethers	High ^g	L	708 ± 5	–	–	–
		H	478 ^j	–	–	–

nd = Not detected. – = Not considered relevant.

a) Sensory irritation (Carrer et al., 2013).

b) Long-term exposure value/acute effect (Carrer et al., 2013).

c) Assumed to be in the same order of magnitude as limonene.

d) Assumed to be in the same order as 1-octene-3-ol, see Wolkoff (2013).

e) This VOC is significantly less irritating than 2-propanol (Smeets et al., 2002). The threshold (LOAEL) for sensory irritation for 2-propanol is estimated to be >823 mg/m³ on the basis of a RD₅₀ value of >5000 ppm (DeCaurriz et al., 1981) and (Kuwabara et al., 2007).

f) (Wolkoff and Nielsen, 2010).

g) Expected to be high, see Wolkoff (2013).

h) Airflow limitation (Wolkoff et al., 2013).

i) Sensory irritation (Wolkoff et al., 2013).

j) Only one measurement.

k) Quantified in toluene equivalents.

l) Quantified in 6-MHO equivalents.

Indoor concentrations of 6-MHO have been measured from 0.8 ppb in offices (Salonen et al., 2009) to 2.3 ppb in a simulated office (28.5 m³; AER = 1 h⁻¹) with two subjects and an initial ozone concentration of 33 ppb (Wisthaler and Weschler, 2010), and in an occupied and simulated aircraft cabin exposed to ozone (60–70 ppb; AER = 4.4–8.8 h⁻¹) to 3–6 ppb (Weschler et al., 2007). Thus, 4 µg/m³ (1 ppb) is considered a mean background level in offices. To our knowledge measurements of 4-AMCH and IPOH in offices have not been reported.

4.2.1. Kitchen cleaning agent

The maximum/threshold ratios for KIA were all less than 1% with the exception of formaldehyde that amounted to 33% of its threshold value with background addition (Table 4). Thus, acute airway effects are not

expected from this temporary source with the exception of odor perception.

4.2.2. Plug-in air freshener

The PIAF results raise some concern regarding possible acute effects as sensory irritation (eyes and upper airways) by formaldehyde, but also airflow limitation in the conducting airways by 4-OPA, if their tentative background levels are added (Table 5a). This concern is relevant, because the PIAF is a longer-term constant emitting source that produces these reaction products continuously; their abundance depends on the AER, the incoming ozone, and the contribution from other sources (Terry et al., 2014).

Formaldehyde is associated with sampling and analytical difficulties (Chiappini et al., 2011; Herrington and Hays, 2012; Ho et al., 2011;

Table 5b

Additional VOCs identified from a plug-in air freshener exposed to Low (10 ppb) and High (50 ppb) ozone test concentrations in 20 m³ walk-in chamber (AER = 0.6 h⁻¹).

Compound	CAS number	Composition	Ozone L,H	Max. conc. ^c µg/m ³
3-Methylcyclopent-2-enyl-formaldehyde ^a	na	C ₇ H ₁₀ O	L	nd
			H	2 ± 1
2-Ethenyl-2-methyl-5-hydroxy-tetrahydrofuran (2-EMH) ^b	na	C ₇ H ₁₂ O ₂	L	nd
			H	8 ± 1
5-Ethenyldihydro-5-methyl-2(3H)-furanone ^b	1073-11-6	C ₇ H ₁₀ O ₂	L	nd
			H	2 ± 1

na = Not available.

nd = Not detected.

a) Not reported before, identified by GC/MS techniques (Kudal, 2013).

b) Identified by GC/MS and library search.

c) Quantified in 6-MHO equivalents.

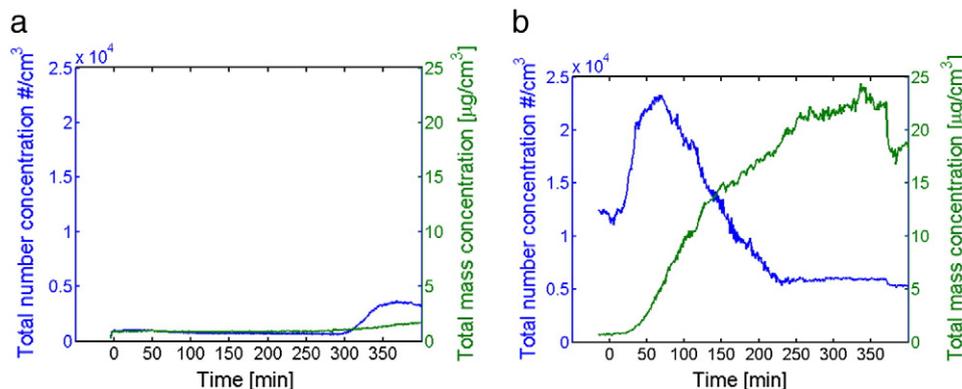


Fig. 4. Ultrafine particle number and mass concentrations from a plug-in air freshener at low and high ozone test concentrations. For ozone time profiles, see Fig. 3d. a) Low ozone test concentration (5 ppb). b) High ozone test concentration (50 ppb).

Salthammer and Mentese, 2008; Wisthaler et al., 2008). Even though, special care was taken to handle the carbonyl cartridges as fast as possible after sampling, it cannot be ruled out that this compound is slightly underestimated, especially in the presence of high ozone. During test of PIAF at high ozone concentration, formaldehyde reached 50% of its threshold for sensory irritation; this includes background level adjustment from other sources and materials. 4-OPA showed that about 30% (background adjusted) of its human reference value for airflow limitation was reached at the high ozone test concentration.

4.3. Ultrafine particles—risk assessment of airway effects

Generally, neither *in vitro* nor *in vivo* studies of ozone-initiated reactions have the gas-phase reaction products been separated from the SOA phase. This issue, however, was investigated in a mouse bioassay by denuding the ozone-initiated reaction mixture of limonene. The denuding process only changed the size distribution slightly towards smaller particle sizes, but without a biological response of the particles themselves regarding sensory effects or airflow limitation (Wolkoff et al., 2008). In another study, F344 rats and ApoE^{-/-} mice were exposed for seven days to denuded α -pinene SOA (200 $\mu\text{g}/\text{m}^3$) derived from UV radiation of a mixture of nitrogen dioxide (+/– sulfur dioxide) and α -pinene (McDonald et al., 2010). Pulmonary inflammation was not observed in either mice or rats and the authors suggested the gaseous products to be of concern. Furthermore, the biological response was mild, also about cardiovascular effects. In general, denuded SOA generated from 1670 $\mu\text{g}/\text{m}^3$ α -pinene and 500 ppb ozone did not show clear pulmonary or systemic responses in rats (Godleski et al., 2011) or *in vivo* oxidative stress (Lemos et al., 2011), see (Rohr, 2013); the only significant finding was a minor increase of the respiratory rate (Diaz et al., 2011), the biological meaning of this finding, however, is not clear.

Human bronchial epithelial cells (BEAS-2b) showed minor elevation of IL-8, among several inflammatory markers, to the exposure of magnetic nanoparticles coated with SOA generated from α -pinene or terpinolene, but not to SOA or the particles alone, or clean air (Jang et al., 2006). Further, the exposure of human lung epithelial cells (A549) to ozone-initiated non-denuded reaction mixtures with α -terpineol or limonene did not show biological effects at levels mimicking indoor air (Anderson et al., 2010, 2013). Thus, the overall, respiratory effects, which included pulmonary inflammation, of SOA in rodents or human airway cells from ozone-initiated terpene reactions appeared not to be significant for those investigated.

The mass concentration of ultrafine particles peaked after 40 min at 81 $\mu\text{g}/\text{m}^3$ from KCA and PIAF at 24 $\mu\text{g}/\text{m}^3$ after about 270 min. The higher particle concentration from KCA is driven by limonene, absent in PIAF, and in agreement with Waring (2014). A NOAEL for ozone-initiated limonene generated SOA of 10 000 $\mu\text{g}/\text{m}^3$ in mice has been

proposed by Wolkoff et al. (2008); this could be translated into a human reference value of 2000 $\mu\text{g}/\text{m}^3$ by applying an assessment factor of five for sensory irritation, see Nielsen et al. (2007). Even applying an additional, but conservative, assessment factor of two for tentatively susceptible people, this would give a reference value of 1000 $\mu\text{g}/\text{m}^3$; this value is about 12 and 42 fold higher than the particle peak concentrations measured for KCA and PIAF, respectively. Furthermore, accumulated effects are not expected from this system (Wolkoff et al., 2012). This indicates that SOA from PIAF would not add to sensory or longer-term airway effects under the assumption that PIAF generated SOA possess similar properties as those generated from the ozone-initiated limonene reaction. Although completely different morphology, the exposure of titanium dioxide generated nanoparticles (90–120 nm) in a similar mouse bioassay at 8000 to 30,000 $\mu\text{g}/\text{m}^3$ for 30 min only showed weak sensory and pulmonary irritation; and, this was further biased by background effects by byproducts (Leppänen et al., 2011). All in all, the generated SOA from KCA or PIAF are not expected to add further to either sensory or lower airway effects; however, long-term effects from continuous exposure are unknown.

5. Conclusion

Near-realistic emission testing of two common consumer products, a kitchen cleaning agent and a plug-in air freshener, in a walk-in climate chamber in the presence of 50 ppb ozone, showed the formation of oxidation products of which some raise concern about possible contribution to acute airway effects, in particular, formation of formaldehyde and 4-OPA from ozonolysis of the PIAF, because it is generally used as a constant source, while in the case of the KCA, the exposure is temporary and short-term. Although, the consumer products investigated cannot be considered as representative of their category, it is recommended to more closely identify the sources and in what conditions formaldehyde and 4-OPA are formed, since they are a result of ozone-initiated reactions with terpenes, common VOCs in fragrances, thus, in a large variety of common consumer products. Further testing under realistic conditions that mimics user pattern behavior is warranted to obtain acute and longer-term exposure data that relate to realistic ozone exposure, people present, and AERs reflecting airtight buildings. Furthermore, toxicological testing of specific airway endpoints of selected reactive VOCs in the presence of ozone is warranted to enable a more integrated health risk assessment. Some of the oxidation products have multiple sources and this should be approached in part by dedicated field measurements during application of common consumer products and also considered in future risk assessment procedures.

Our findings amplify the long-term paradox of testing not only construction products, but particularly fragrance-based consumer and household products in artificially clean air, rather than exposing the test specimen to realistic indoor atmospheres.

Conflict of interest

The authors declare no conflict of interest.

Funding

This project was supported from the projects EPHECT (emission, exposure patterns, and health effects of consumer products in the EU), funded by the European Union, Executive Agency for Health and Consumers under the sub-action: Healthy environments, 2010–2013 and “OFFICAIR” (on the reduction of health effects from combined exposure to indoor air pollutants in modern offices) funded by the European Union 7th Framework (Agreement 265267) under the Theme: ENV. 2010.1.2.2-1.

Acknowledgments

Mr. Brian Hansen is acknowledged for excellent technical assistance.

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