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Cleaning products and air fresheners: exposure to primary and secondary air pollutants

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Abstract

Building occupants, including cleaning personnel, are exposed to a wide variety of airborne chemicals when cleaning agents and air fresheners are used in buildings. Certain of these chemicals are listed by the state of California as toxic air contaminants (TACs) and a subset of these are regulated by the US federal government as hazardous air pollutants (HAPs). California's Proposition 65 list of species recognized as carcinogens or reproductive toxicants also includes constituents of certain cleaning products and air fresheners. In addition, many cleaning agents and air fresheners contain chemicals that can react with other air contaminants to yield potentially harmful secondary products. For example, terpenes can react rapidly with ozone in indoor air generating many secondary pollutants, including TACs such as formaldehyde. Furthermore, ozone–terpene reactions produce the hydroxyl radical, which reacts rapidly with organics, leading to the formation of other potentially toxic air pollutants. Indoor reactive chemistry involving the nitrate radical and cleaning-product constituents is also of concern, since it produces organic nitrates as well as some of the same oxidation products generated by ozone and hydroxyl radicals.

Few studies have directly addressed the indoor concentrations of TACs that might result from primary emissions or secondary pollutant formation following the use of cleaning agents and air fresheners. In this paper, we combine direct empirical evidence with the basic principles of indoor pollutant behavior and with information from relevant studies, to analyze and critically assess air pollutant exposures resulting from the use of cleaning products and air fresheners. Attention is focused on compounds that are listed as HAPs, TACs or Proposition 65 carcinogens/reproductive toxicants and compounds that can readily react to generate secondary pollutants. The toxicity of many of these secondary pollutants has yet to be evaluated. The inhalation intake of airborne organic compounds from cleaning product use is estimated to be of the order of $10\,\mathrm{mg\,d^{-1}\,person^{-1}}$ in California. More than two dozen research articles present evidence of adverse health effects from inhalation exposure associated with cleaning or cleaning products. Exposure to primary and secondary pollutants depends on the complex interplay of many sets of factors and processes, including cleaning product composition, usage, building occupancy, emission dynamics, transport and mixing, building ventilation, sorptive interactions with building surfaces, and reactive chemistry. Current understanding is sufficient to describe the influence of these variables qualitatively in most cases and quantitatively in a few.

Keywords: Indoor air quality; Hazardous air pollutants; Terpenes; Ozone; Hydroxyl radical; Nitrate radical

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1. Introduction

The cleaning of buildings and their contents is a major human activity that aims to promote hygiene, aesthetics, and material preservation. In the United States, out of a total working population of 128 million, three million people are employed as "janitors and cleaners," or as "maids and housekeeping cleaners" (US Department of Labor, 2001). From activity pattern surveys, it is estimated that US adults devote an average of $20-30\,\mathrm{min\,day}^{-1}$ to house cleaning (Wiley et al., 1991). In addition, among California adults, 26% reported that they were near or used cleaning agents on the day on which they were surveyed and 31% reported that they were near or used scented room fresheners (Jenkins et al., 1992).

Despite the large overall effort devoted to these activities, relatively little scientific evidence documents the efficacy of building cleaning practices. Common themes in the literature include the effectiveness of vacuuming and other processes for controlling allergens (Hegarty et al., 1995; Woodfolk et al., 1993; Vaughan et al., 1999) and lead-contaminated dust (Ewers et al., 1994; Lioy et al., 1998). Studies have explored the role of disinfectants in cleaning agents on limiting the spread of infectious disease (Bloomfield and Scott, 1997; Josephson et al., 1997; Rusin et al., 1998). Only a few published studies have considered general cleaning efficacy (Schneider et al., 1994; Franke et al., 1997; Nilsen et al., 2002) or the beneficial attributes of cleaning products (Olson et al., 1994; Jerrim et al., 2001; Jerrim et al., 2002).

While there are substantial perceived benefits of cleaning, there are also risks. One set of concerns arises because cleaning products contain volatile organic compounds (VOCs) that contribute to urban or regional photochemical smog. The California Air Resources Board has adopted regulations to reduce atmospheric emissions from consumer products, including cleaning products and air fresheners (CARB, 2001). Cleaning may also pose risks to cleaners and to building occupants. Wolkoff et al. (1998) have summarized the spectrum of such concerns. These include irritation and other health hazards owing to inhalation exposures to cleaning-product constituents, exposures to dust and other particulate matter suspended during cleaning activities, and the production of secondary pollutants owing to the reaction of unsaturated organic compounds with oxidants such as ozone and nitrogen oxides.

The present paper explores the nature and likely significance of air pollutant exposures among building occupants, including cleaning personnel, resulting from the use of cleaning products and air fresheners in homes and in nonindustrial workplaces. We emphasize chemical exposures resulting from the volatile constituents of cleaning products, considering both primary emissions from the cleaning products themselves and the formation of secondary pollutants caused by the interaction of cleaning product constituents with other reactive species. Our approach involves critically evaluating relevant literature. In doing so, we utilize key principles and tools from the applied physical sciences—mass conservation, reactor models and analysis of kinetic systems—to explore the causal events linking cleaning product use with inhalation exposure to air pollutants.

2. Cleaning products and air pollution

2.1. Emissions and inhalation intake

Because of their potential contributions to urban photochemical smog, product manufacturers and air quality regulators have estimated organic compound emissions from the use of cleaning products. Table 1 presents summary data for California. The total

Table 1
Estimated atmospheric emissions of VOCs from use of household and commercial cleaning products and air fresheners in California, 1997[a]

Product	VOC emissions (tonnes/d)	Per capita VOC emissions ($\mathrm{mg\,d^{-1}\,person^{-1}}$)
Carpet and upholstery care: cleaners and deodorizers	1.07	32
Spot removers	0.64	20
Fabric protectants	0.37	11
Floor care: wax, wax strippers, polish	5.6	170
General purpose cleaners	7.4	220
General purpose degreasers	2.1	64
Glass cleaners	3.4	100
Oven cleaners and metal polishes/cleansers	0.87	26
Bathroom cleaners: toilet bowl, tub, tile, and sink	0.74	22
Furniture waxes and polishes; dusting aids	2.4	71
Air fresheners	7.5	230

[a] *Source*: CARB, 2003; per capita emissions based on 1997 population estimate of 33 million (http://www.dhs.cahwnet.gov/hisp/chs/OHIR/Population/populationindex.htm).

estimated emissions of 32 tonnes d^{-1} corresponds to about 1 g $person^{-1}$ day^{-1} for the entire state's population. Emissions of reactive organic gases (ROG) from the sum of indoor and outdoor sources are estimated to be much larger, about 2400 tonnes d^{-1} for the state (CARB, 2003).

Although cleaning agent use causes a small portion of total organic compound emissions, the health consequences from this usage appear to be out of proportion to the emissions. This reflects the fact that the proportion of emissions inhaled is much higher when those emissions occur in buildings rather than outdoors. The relationship between inhalation and emissions is quantified through the *intake fraction* (Bennett et al., 2002), which is defined as the incremental pollutant mass inhaled per unit pollutant mass emitted. Typical intake fractions for emissions to outdoor air are in the range 10^{-6}–10^{-3}, whereas typical intake fractions for emissions into indoor air are in the range 10^{-3}–10^{-1} (Lai et al., 2000). Thus, the inhalation exposure from the 32 tonnes d^{-1} of organic compounds emitted indoors from cleaning product use may be of similar scale to the inhalation exposure from 2400 tonnes d^{-1} of organic compounds mostly emitted outdoors from all sources.

It is important to appreciate that only a portion of the organic compounds emitted from cleaning products pose direct health concerns because of their toxicity (which varies among species over many orders of magnitude). Given a typical intake fraction of 10^{-2} for airborne contaminant releases in buildings, the emissions of 1 g d^{-1} $person^{-1}$ of organic compounds from cleaning product use would be expected to cause an average mass inhaled of ~10 mg (10 000 μg) d^{-1} $person^{-1}$, provided that most of the release occurs indoors. Depending on species toxicity, this average burden is high enough to be of potential concern. For example, "no significant risk levels" (NSRLs) have been established for inhalation exposure to some chemicals known to cause cancer by the State of California (OEHHA, 2003). These levels are set at a value such that lifetime exposure at that value would increase the estimated risk of cancer by 10^{-5}. Sample NSRLs are 7 μg d^{-1} for benzene, 40 μg d^{-1} for formaldehyde, and 14 μg d^{-1} for tetrachloroethylene. If even a small proportion, i.e. 0.1–1%, of the inhaled mass of organic compounds from cleaning products were as toxic as these compounds, the average exposure would approach levels of concern. Furthermore, inhalation exposures undoubtedly vary broadly across the population, with those who engage in cleaning experiencing larger exposures. This means that the risks to many individuals are likely to be much higher than the average risks throughout the population. In summary, this broad perspective provides some basis for concern about the potential adverse health consequences of inhalation exposure to cleaning agents.

2.2. Inhalation pathways

As summarized in Table 2, the use of cleaning products can influence inhalation exposure to air pollutants by several distinct mechanisms. Volatile constituents of the cleaning products can enter the gas phase during or after use. But nonvolatile constituents can also be inhaled, either because the cleaning process itself releases liquid or solid particulate matter into the air or because residual cleaning materials are later suspended, for example, through abrasion and wear. In addition, secondary pollutants are also of concern: the use of cleaning products can be accompanied by

Table 2
Mechanisms by which use of cleaning products can influence inhalation exposure to air pollutants

Mechanism	Examples
Volatilization	Formaldehyde from wood floor cleaning spray (Akland and Whitaker, 2000; Fig. 4–11); glycol ethers from hard-surface cleaners (Zhu et al., 2001; Gibson et al., 1991)
Production of airborne droplets	Aerosol or pump-spray delivery of surface cleaning products; some spray droplets remain airborne instead of depositing (Fortmann et al., 1999; Roache et al., 2000)
Suspension of powders	Fine particulate matter from carpet freshener (Steiber, 1995); sodium tripolyphosphate from carpet cleaner (Lynch, 2000)
Suspension of wear products	Surfactants, film formers, complexing agents, acids and bases, disinfectants (Wolkoff et al., 1998; Vejrup and Wolkoff, 2002)
Inappropriate mixing	Chloramines from mixing household bleach and ammonia-based cleaners; chlorine gas from mixing bleach with acid-containing cleaner (see Table 3)
Chemical transformations	Chloroform release from chlorine bleach chemistry in laundry applications (Shepherd et al., 1996); terpene hydrocarbons plus ozone form OH radical (Weschler and Shields, 1997a), hydrogen peroxide (Li et al., 2002) and secondary particulate matter (Weschler and Shields, 1999; Wainman et al., 2000)
Altered surfaces	Nicotine release from walls following ammonia cleaner use in smoking environment (Webb et al., 2002); enhanced volatile organic emissions from wet linoleum (Wolkoff et al., 1995)

reactions in water (Shepherd et al., 1996), on surfaces (Webb et al., 2002; Pommer, 2003; Fick, 2003), or in the air (Weschler and Shields, 1999; Wainman et al., 2000), which can affect the indoor concentrations of air pollutants. Although this paper focuses on air pollutants resulting directly or indirectly from the volatile components of cleaning products, the array of exposure routes of potential concern is broader.

3. Direct evidence of health hazards

The medical, occupational, and environmental health literature contains many reports documenting cleaning related inhalation hazards (ingestion or dermal contact hazards are not considered in this review). The reports on inhalation hazards can be divided into those based on the mixing of cleaning products and those focusing on hypersensitivity responses associated with product use. This section summarizes findings from such studies with a view toward gleaning what these studies tell us about the broader issue of inhalation exposure to air pollutants from cleaning products.

3.1. Accidental poisonings associated with inappropriate mixing of cleaning agents

The mixing of certain types of cleaning products can generate hazardous fumes sufficient to cause those exposed to seek medical attention. Table 3 summarizes thirteen reports published during the past four decades documenting such episodes. Common throughout these reports is the use of bleach or other product containing hypochlorite (ClO^-) as an active ingredient. The mixing of bleach with ammonia-based cleaners causes the production of chloramines (NH_2Cl and $NHCl_2$) and possibly gaseous ammonia (NH_3) that can volatilize. In some cases, bleach has been mixed with an acid-based cleaner, which could cause the release of gaseous chlorine (Cl_2) or hypochlorous acid ($HOCl$).

In each of the case reports, one or more subjects sought medical attention for acute respiratory symptoms. Some subjects required no treatment and many others recovered within days. However, in several cases, ongoing respiratory-health impairment resulted from the exposure. One case led to a fatality (Cohle et al., 2001), although the subject had an undiagnosed preexisting condition possibly contributing to the outcome.

In total, this literature makes a compelling case that acute inhalation hazards can result from improper use of cleaning products. Recognizing this, it is common for manufacturers to print labels on cleaning products warning consumers to avoid mixing different products. A recent study suggests that only a small fraction of consumers read cleaning-product labels (Kovacs et al., 1997). The continuing appearance of case reports in the medical literature is clear evidence that the printed warnings have not eliminated the hazard of mixing. Furthermore, the number of total incidents is likely much larger than the published case reports. For example, Mrvos et al. (1993) cite information from the American Association of Poison Control Center's National Data Collection System, which reported more than 7000 exposures to chlorine or chloramine gas in the US in 1990. According to these authors "a large majority are likely to be in-home exposures resulting from the incorrect mixing of cleaning products." Extrapolating from the evidence summarized in Table 3, a plausible concern is that people may experience inhalation exposure to strong acids or bases, or to strong oxidants, owing to even the proper use of cleaning products containing such irritants. For example, reactions between hypochlorite and commonly occurring ppb levels of indoor ammonia may produce low concentrations of chloramines; similarly, reactions between hypochlorite and ppb levels of indoor nitric, hydrochloric or sulfuric acids may produce small amounts of gaseous Cl_2 or hypochlorous acid. However, evidence is lacking to quantify the potential for such chronic, low-level exposures, or to determine their significance.

3.2. Asthma, allergy, and respiratory irritation

A second category of cleaning-related, health-effects literature focuses on occupational asthma, allergy, and/or respiratory irritation as the outcomes of concern. Among the thirteen studies summarized in Table 4 are two main types: case reports and epidemiological investigations. Five of the six case reports identify carpet shampoo or a floor cleaner as the product responsible for the adverse health effect. In several cases a specific chemical agent is identified: ethanolamine, lauryl dimethyl benzyl ammonium chloride, or benzalkonium chloride. In one case, the subject did not directly use the cleaning product. Rather, his occupational asthma was attributed to exposure to a constituent of the floor cleaner used in his office when it was unoccupied (Burge and Richardson, 1994).

Compared with the case reports, epidemiological investigations are not as effective in identifying specific causes, but do provide important information about the size of the affected population. Recent studies in Spain, Finland, Brazil, and several states in the US document an increased prevalence of occupational or work-related asthma among those employed as cleaners.

In contrast to the cases in Table 3, in only a few of the studies in Table 4 are the adverse effects clearly associated with product misuse. Overall, whether owing

Table 3
Documented inhalation toxicity related to mixing of cleaning products

Nature of study	Products mixed	Toxic gas(es)	Outcomes	Ref[a]
Case reports (2)	NaOCl, vinegar, bleach, and detergent; ammonia and NaOCl	Chlorine, ammonia	Acute illness with recovery in days	a
Case report	Ammonia type and hypochlorite cleaners	Ammonia	Acute illness with recovery in days	b
Case report	Bleach (5.25% NaOCl) and powder containing 80% $NaHSO_4$	Chlorine gas	Acute illness with recovery after several days	c
Case report	Several products applied to clear a clogged drain[b]	Uncertain	Severe obstructive airway disease	d
Case reports (2)	NaOCl (5%) and HCl (10%)	Chlorine gas	Acute illness with recovery in several days	e
Case report	Ammonia with household bleach containing hypochlorite	Chloramines	Acute illness with recovery in days	f
Case reports (3)	Aqueous ammonia (5–10%) with bleach (5.25% NaOCl), plus laundry detergent in 2 cases	Chloramines	Life-threatening toxic pneumonitis requiring prolonged hospitalization and residual symptoms	g
Case reports (5 episodes at 2 state hospitals)	Bleach (NaOCl) and phosphoric acid cleaner	Chlorine	Acute poisoning symptoms that abated within hours to days; a few cases required medical treatment	h
Analysis of 216 cases reported to Regional Poison Information Center	Hypochlorite containing product with (a) ammonia (50%), (b) acid (29%), (c) alkali (21%)	Chlorine/ chloramines	Symptom resolution for 93% of patients within 6 h; 33% received medical care; one patient w/preexisting condition required hospital admission for continued respiratory distress	i
Case report	Sequential application of numerous cleaning products to remove a bathtub stain[c]	Hydrofluoric acid	Hemorrhagic alveolitis and adult respiratory distress syndrome; month-long hospital care; residual pulmonary deficit	j
Case reports (2 cases each w/36 soldiers)	Liquid bleach and ammonia mixed in toilet bowls and buckets	Chloramine gas	Acute symptoms; two patients admitted to hospital, one required several days of intensive care observation	k
Case report	Liquid ammonia (3–10% $NH_3(aq)$) and bleach (5% NaOCl)	Chloramine gas	Upper air compromise and pneumonitis requiring emergency tracheostomy and 7 d of hospital care	l
Case report	Bleach and ammonia	Chloramine gas	Death	m

[a] References: a—Faigel (1964), b—Dunn and Ozere (1966), c—Jones (1972), d—Murphy et al. (1976), e—Gapany-Gapanavicius et al. (1982a), f—Gapany-Gapanavicius et al. (1982b), g—Reisz and Gammon (1986), h—Hattis et al. (1991), i—Mrvos et al. (1993), j—Bennion and Franzblau (1997), k—Pascuzzi and Storrow (1998), l—Tanen et al. (1999), m—Cohle et al. (2001).

[b] Products used (selected active ingredients): Liquid Plum-R (NaOCl, 5%; KOH, 2%); Drano (NaOH, 54%; $NaNO_3$, 30%); Clorox (NaOCl, 5%); Sani Flush ($NaHSO_4$, 75%).

[c] Cleaning products used (active ingredient, if reported): cleanser, mildew stain remover (NaOCl, 25–45%), tub and tile cleaner (H_3PO_4, 18%), ammonia cleaner (NaOH, 2–2.5%), bleach (NaOCl, 5.25%), toilet cleaner (HCl, 14.5%), vinegar (CH_3COOH, 5%), rust remover (H_6F_6, 8%). Application of each product was followed by a cold-water rinse.

to misuse or not, the existence of at least 26 papers implicating cleaning or cleaning products as a cause of respiratory health impairment suggests that cleaning product use deserves attention as a cause of air pollutant exposure.

4. Composition, primary emissions, and inhalation exposure

In this section, we explore the causal chain-of-events linking the use of cleaning products with inhalation

Table 4
Documented asthma, allergy associations related to cleaning product use

Key finding	Ref[a]
Dried detergent residue from carpet shampoo "caused respiratory irritation among most employees in an office building and among all staff members and most children in a day-care center."	a
Excessive application of carpet shampoo was associated with widespread, transient, mild respiratory illness among conference attendees.	b
Case report of occupational asthma in a cleaning worker caused by inhalation exposure to ethanolamine from a floor-cleaning detergent.	c
Case report of occupational asthma in a pharmacist attributed to indirect exposure to lauryl dimethyl benzyl ammonium chloride from a floor-cleaning product regularly used in his workplace.	d
Population-based study of occupational asthma revealed that "cleaners" had the fourth highest odds ratio (1.97) for "bronchial hyperresponsiveness and asthma symptoms or medication."	e
Prospective study design indicated increased risk of eye, nose, and throat symptoms, asthma and bronchitis associated with "use of sprayers" among current cleaners as compared with former cleaners.	f
Case report of anaphylactic shock with respiratory failure secondary to carpet cleaning in 42-yr female; hospitalized for 18 d then released.	g
Case reports of female nurses who exhibited occupational asthma following exposure to surfaces cleaned with solutions containing benzalkonium chloride. Cases were also occupationally exposed to this chemical as a disinfectant.	h
Asthma prevalence for indoor cleaners in Spain was 1.7 times the rate for office workers. Risk mainly associated with cleaning of private homes; "may be explained by the use of sprays and other products in kitchen cleaning and furniture polishing."	i
Population study of women in Finland revealed a relative risk of asthma of 1.5 for cleaners as compared with those employed in administrative work.	j
Twelve percent of confirmed cases of work-related asthma in California, Michigan, Massachusetts, and New Jersey were associated with exposure to cleaning products.	k
"Janitors, housekeepers, and cleaners" was the occupational group with the highest number of reported cases of occupational asthma in Sao Paulo, Brazil, and "cleaning products" was the most commonly reported exposure agent.	l
"Cleaning materials" are the most frequently reported agents for work-related reactive airways dysfunction syndrome cases in Michigan, New Jersey, Massachusetts, and California.	m

[a] References: a—Kreiss et al. (1982), b—Robinson et al. (1983), c—Savonius et al. (1994), d—Burge and Richardson (1994), e—Kogevinas et al. (1999), f—Nielsen and Bach (1999), g—Lynch (2000), h—Purohit et al. (2000), i—Zock et al. (2001), j—Karjalainen et al. (2002), k—Rosenman et al. (2003), l—Mendonça et al. (2003), m—Henneberger et al. (2003).

exposure to the primary volatile constituents. The output parameters of interest are species-specific concentration (mass per volume) or mole fraction (moles of species per mole of air), exposure (the time integral of concentration encountered by an exposed person), and intake (species mass inhaled by an exposed person). Broadly, these output parameters depend on three classes of processes: emissions, dynamic behavior, and human factors.

As an illustration of the relationships among these variables, consider the following example. In a cleaning episode, 50 g of a product is used in a single-family residence over a period of 1 h. Assume that 1% of the product is a volatile air contaminant that is completely released at a uniform rate during the hour of use (i.e., the emission rate is 500 mg h^{-1} for 1 h). Furthermore, assume that the residence has a volume of 300 m^3 and a ventilation rate of 0.7 h^{-1}, representative values for the California housing stock (Wilson et al., 1996), and not unusual for the US. Assume that the indoor air mixes rapidly throughout the house so that the species concentration does not vary in space. Also, assume that the contaminant does not sorb or decompose in indoor air, so that the only removal mechanism is ventilation. (Sorption is considered in Section 4.2.) The concentration of the contaminant owing to cleaning product use under these conditions is presented in Fig. 1a. The peak concentration, which occurs at the end of the emission period, is 1200 $\mu g\, m^{-3}$. After use, the concentration decays exponentially with a rate constant equal to the air-exchange rate. For an occupant of the building who is present throughout a 10-h period beginning with product use, the total exposure to the contaminant is represented by the time-integral of the concentration, which is 2380 $\mu g\, m^{-3}$ h. The intake is the time integral of the exposure concentration multiplied by the breathing rate. For a constant breathing rate at a typical value of 0.5 $m^3\, h^{-1}$, the intake would be 1190 μg. The individual intake fraction for this one exposed individual is the intake divided by the mass released, i.e. 0.0024. With n occupants so exposed, the total intake fraction would be 0.0024n.

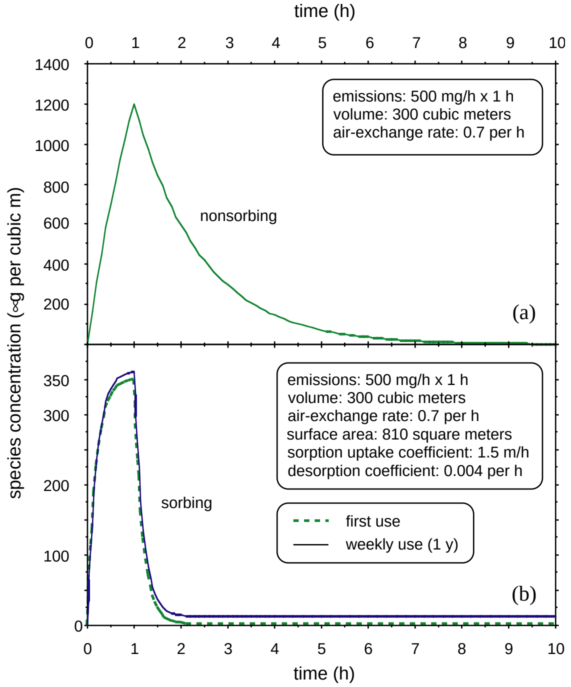

Fig. 1. Hypothetical concentration of an air contaminant resulting from the primary emissions of a volatile constituent of a cleaning product, used in a single-family home. (a) Nonsorbing contaminant. (b) Sorbing contaminant where sorption model follows work of Tichenor et al. (1991), with $k_a = 1.5\,\mathrm{m\,h^{-1}}$ and $k_d = 0.004\,\mathrm{h^{-1}}$, based on the findings of Sparks et al. (1999) for 2-(2-butoxyethoxy)butanol on carpet and gypsum board. The "first use" case assumes no sorbed mass at time $t = 0$. The "weekly use (1 yr)" case presents simulated results for the last of 52 successive weekly applications.

4.1. Emissions

Emissions of primary constituents depend on product composition. Table 5 identifies volatile constituents of cleaning products or air fresheners that are listed by California in Proposition 65 and/or as TACs. Also indicated, where available, are inhalation intake rates or concentration levels that would indicate a threshold of concern for chronic exposure. For those occupationally involved in cleaning, regular repeated exposures could lead to chronic health concerns. Even for less frequent episodic exposures, the time-weighted average exposure concentration over an extended period could be compared with the information presented in Table 5 to make a preliminary evaluation of the potential risk. Regarding the chlorinated organics in this table, it should be noted that they have not been reported as components of cleaning products in papers published since the early 1990s. A review of survey measurements indicates an overall decrease in the indoor concentrations of some chlorinated compounds, which may be associated with provisions of the 1990 Clean Air Act Amendments in the United States (Hodgson and Levin, 2003). Recent studies have reported carbonyls, hydrocarbons, and glycol ethers as toxic ingredients of cleaning products.

The list in Table 5 does not represent all toxic constituents of concern. For example, 4-nonylphenol and nonylphenol ethoxylates are used in disinfecting cleaners, all purpose cleaners and spot removers (Betts, 2003). Reflecting their widespread use, they have recently been reported to be present in the dust and air of each of 120 homes sampled in the Cap Cod region of Massachusetts, with airborne concentrations of 4-nonylphenol ranging from 21 to $420\,\mathrm{ng\,m^{-3}}$ (Rudel et al., 2003). These compounds are of concern because of their ability to mimic female estrogen hormones. However, neither California nor the US EPA has yet to establish exposure guidelines for chemicals based on potential hormonal activity. An attempt to list all such chemicals is beyond the scope of this review. Nonetheless, as is apparent from Table 5, there are numerous constituents identified in the peer-reviewed literature that are a health concern in terms of California's Proposition 65 and TACs list.

A second important factor affecting emissions is the concentration of the volatile constituent in the cleaning product. Some composition and concentration information is available in material safety data sheets (MSDS) from product manufacturers. A few published studies also have reported composition data. For example, Zhu et al. (2001) tested Canadian consumer cleaning products and studied in detail 2-butoxyethanol (BE, $C_6H_{14}O_2$), a glycol ether. For five water-based products, the following percentage concentrations of BE were reported: all-purpose cleaner, 3.72%; glass and surface cleaner (clear), 0.87%; glass and surface cleaner (blue), 0.50%; antibacterial glass and surface cleaner, 0.83%; and lemon fresh and antibacterial spray, 1.28%.

A third factor affecting emissions is the product usage pattern, including the quantity of product used and the frequency of application. These could be considered human factors, and they are discussed in Section 4.3. In addition, the manner of application can influence the timing of emissions, and possibly the total amount emitted. For a single application, product volume times the concentration of the volatile species in the product determines the maximum total release. Depending on the mode of application, all or only part of this mass may be emitted (Wooley et al., 1990). For example, if a floor-cleaning product is diluted in water, applied with a mop, and then the floor is rinsed, some of the volatile constituents may be poured down the drain with the dirty wastewater. In addition to influencing the total amount released, the mode of use along with the physicochemical properties of the volatile constituent

Table 5
Reported volatile constituents of cleaning products listed under California's Proposition 65 and/or as a TAC

Chemical	CAS No.	Guidelines[a]		Cleaning product (reference)
		NSRL	REL	
Glycol ethers				
Ethylene glycol monobutyl ether (2-butoxy ethanol)	111-76-2	—	+	All purpose cleaner, glass and surface cleaners, lemon fresh and antibacterial spray (Zhu et al., 2001); liquid wax (Knöppel and Schauenburg, 1989)
Diethylene glycol monoethyl ether (2-(2-ethoxyethoxy)ethanol)	111-90-0	—	+	Air freshener (Cooper et al., 1995)
Diethylene glycol monobutyl ether (2-(2-butoxyethoxy) ethanol)	112-34-5	—	+	Hard surface cleaners (Gibson et al., 1991); floor-finish stripper, floor cleaner (Zhu et al., 2001); floor polish (Vejrup, 1996)
Hydrocarbons				
Benzene	71-43-2	$7\,\mu g\,d^{-1}$	$60\,\mu g\,m^{-3}$	Liquid detergent, steel wool soap pads, furniture wax (Wallace et al., 1987)
Xylenes	1330-20-7	—	$700\,\mu g\,m^{-3}$	Liquid detergent, steel wool soap pads (Wallace et al., 1987); household cleaners and polishes (Sack et al., 1992)
Toluene	108-88-3	$7\,mg\,d^{-1}$ [b]	$300\,\mu g\,m^{-3}$	Disinfectant bathroom cleaner (Akland and Whitaker, 2000); lemon fresh and antibacterial spray (Zhu et al., 2001); household cleaners and polishes (Sack et al., 1992); paste wax, detergent, liquid floor waxes (Knöppel and Schauenberg, 1989)
Ethylbenzene	100-41-4	—	$2\,mg\,m^{-3}$	Household cleaners and polishes (Sack et al., 1992); paste wax, liquid wax (Knöppel and Schauenberg, 1989); furniture polish (Tichenor and Mason, 1988); steel wool soap pad (Wallace et al., 1987)
Styrene	100-42-5	—	$900\,\mu g\,m^{-3}$	Floor cleaner (Akland and Whitaker, 2000); liquid wax (Knöppel and Schauenberg, 1989)
n-Hexane	110-54-3	—	$7\,mg\,m^{-3}$	Household cleaners and polishes (Sack et al., 1992); paste wax; liquid wax (Knöppel and Schauenberg, 1989)
Carbonyls				
Formaldehyde	50-00-0	$40\,\mu g\,d^{-1}$	$3\,\mu g\,m^{-3}$	Wood-floor cleaning spray (Akland and Whitaker, 2000); liquid floor detergent (Colombo et al., 1991)
Acetaldehyde	75-07-0	$90\,\mu g\,d^{-1}$	$9\,\mu g\,m^{-3}$	Detergent/cleanser, liquid wax (Knöppel and Schauenberg, 1989)
Methyl ethyl ketone (2-Butanone)	78-93-3	—	+	Liquid floor waxes (Knöppel and Schauenberg, 1989); specialized cleaner (Salthammer, 1999)
Chlorinated organics				
Carbon tetrachloride	56-23-5	$5\,\mu g\,d^{-1}$	$40\,\mu g\,m^{-3}$	Household cleaners and polishes (Sack et al., 1992)

Table 5 (*continued*)

Chemical	CAS No.	Guidelines[a]		Cleaning product (reference)
		NSRL	REL	
Dichloromethane (methylene chloride)	75-09-2	200 μg d^{-1}	400 μg m^{-3}	Household cleaners and polishes (Sack et al., 1992)
Tetrachloroethylene (perchloroethylene)	127-18-4	14 μg d^{-1}	35 μg m^{-3}	Household cleaners and polishes (Sack et al., 1992)
1,1,1-Trichloroethane (methyl chloroform)	71-55-6	—	1 mg m^{-3}	Household cleaners and polishes (Sack et al., 1992); chlorine bleach scouring powder (Wallace et al., 1987)
Trichloroethylene	79-01-6	80 μg d^{-1}	600 μg m^{-3}	Household cleaners and polishes (Sack et al., 1992)
Trichloromethane (chloroform)	67-66-3	40 μg d^{-1}	300 μg m^{-3}	Household cleaners and polishes (Sack et al., 1992); chlorine bleach scouring powder (Wallace et al., 1987)
Propylene dichloride (1,2-dichloropropane)	78-87-5	+	+	Paste wax; liquid floor wax (Knöppel and Schauenberg, 1989)
Other				
1,4-Dioxane	123-91-1	30 μg d^{-1}	3 mg m^{-3}	Household cleaners and polishes (Sack et al., 1992)
Acetophenone	98-86-2	—	+	Liquid waxes (Knöppel and Schauenberg, 1989)

[a] NSRL—No significant risk level is the "daily intake level calculated to result in one excess case of cancer in an exposed population of 100,000, assuming lifetime (70-year) exposure at the level in question. REL—Chronic reference exposure levels represent exposure concentrations that would pose no significant health risk to individuals indefinitely exposed to that level. A "+" in either column indicates that the compound is listed as "known to cause cancer" (NSRL) or as a toxic air contaminant (REL), but that the quantitative exposure guideline has not been established. A "—" in either column indicates that the compound has not been listed under the respective program. References for the guideline columns of this table: Proposition 65 chemicals list: http://www.oehha.org/prop65/prop65_list/Newlist.html; Toxic air contaminant list: http://www.arb.ca.gov/toxics/quickref.htm; No-significant risk levels: http://www.oehha.org/prop65/pdf/June2003StatusReport.pdf; Reference exposure levels: http://www.oehha.org/air/chronic_rels/Allchrels.html.

[b] Toluene is listed under Proposition 65 as a reproductive toxicant and the guideline represents the "maximum allowable dose level."

can affect the timing of emissions. Emission studies suggest that glycol ether release from aqueous cleaning products occurs slowly, over periods of hours or even a few days after application (Gibson et al., 1991; Zhu et al., 2001). If generally true, such behavior would have the effect of reducing exposures during cleaning activities, but increasing exposures to building occupants following cleaning.

4.2. Dynamic behavior

Once primary constituents are emitted into indoor air, the resulting concentrations, exposures, and inhalation intake depend on the dynamic behavior of the species in indoor air. Factors influencing the species behavior include ventilation, mixing within a room, mixing between rooms, homogeneous and heterogeneous transformations, sorptive interactions on surfaces, and active air cleaning. This section presents key aspects of most of these factors. Active air cleaning is briefly discussed in Section 4.3, and the role of transformation processes is addressed in Section 5.

Ventilation is a major factor influencing the concentrations of indoor pollutants. Commonly, it is expressed in terms of an air-exchange rate, λ, which is the volume flow rate of air out of a building divided by the volume of air contained within the building. Murray and Burmaster (1995) have analyzed measurements of λ for 2844 US households (not a statistically representative sample). These data are reasonably well described by a lognormal distribution with a geometric mean (GM) of 0.53 h^{-1} and a geometric standard deviation (GSD) of 2.3. Persily (1989) reported on extensive ventilation measurements in 14 office buildings across the US. The time-average values of λ across this sample of buildings are well described as lognormal with a GM of 0.73 h^{-1} and a GSD of 1.8.

In the example presented at the beginning of Section 4, we assumed that indoor air was well mixed. Spatial variability in concentrations can occur, especially when species are emitted from localized sources. One quantitative indicator is the characteristic mixing time, τ, defined as the period required for an instantaneous point release in an unventilated room to disperse such that the relative standard deviation among local concentrations is $<10\%$. Baughman et al. (1994) measured τ in a 31-m^3 room under natural convection flow conditions and found that it varied from ~10 min with strong convection sources to ~90 min under thermally quiescent conditions. Drescher et al. (1995) measured τ to be 2–15 min in the same room for a variety of forced flow conditions. Under conditions where $\tau \ll \lambda^{-1}$ and where the exposure duration is much longer than the release time, the well-mixed approximation should describe exposure conditions reasonably well.

The failure of the well-mixed approximation would be expected to be most acute for estimating peak exposure concentrations for people who are engaged in cleaning activities. Girman et al. (1987) reported on a directly relevant experiment in which a researcher used a paint stripper that contained methylene chloride (CH_2Cl_2) to remove paint from a test panel in a 20 m^3 chamber. The time-dependent CH_2Cl_2 concentration was measured in the breathing zone of the researcher as well as in the center of the chamber during 90 min of activity. At a low air-exchange rate (0.6 h^{-1}), the personal exposure of 2400 ppm-h was very similar to the inferred exposure based on the room-air sampler, 2350 ppm-h. At a high air-exchange rate (3.2 h^{-1}), the personal exposure was about 20% higher than determined from the room air sampler (1120 ppm-h vs. 920 ppm-h); the short-term peak personal-exposure concentration was about 35% higher than the room-air peak (1320 vs. 970 ppm).

Transport between rooms can also affect concentrations and exposures. For people doing cleaning, interzonal transport can reduce concentrations in the room in which they are working, but for occupants of other rooms of the building, it is a vehicle for exposure that might not otherwise occur. Multizone modeling tools have been developed to predict interzonal flows based on information about the ventilation system, interzonal leakage, temperature, and wind conditions (Haghighat and Megri, 1996 and references therein). Although only a limited set of buildings have been examined with these tools, a few generalizations can be made. In residences, open internal doorways and the operation of central-air systems promotes rapid mixing. On the other hand, when the forced air system is off, transport between rooms separated by a closed doorway can be slow. In commercial buildings, air handling systems commonly recirculate ~80–90% of the air flowing through them, promoting mixing throughout the zone served. However, large buildings may be served by multiple air handling units and little is known about the transport of species from one air-handler zone to another. Likewise, little is known about interroom transport in public buildings in which there is no forced recirculating flow, either by design or because the fans are not operating.

The sorptive interactions of cleaning product constituents with indoor surfaces may strongly influence time-dependent concentration fields, and therefore exposures. Species having low or moderate vapor pressure or high polarity may preferentially partition onto the surfaces or into the bulk media of materials found indoors. Sorptive uptake on surfaces has the effect of reducing peak concentrations from episodic uses. To the extent the interactions are reversible, subsequent desorption could serve as a contaminant source after the emissions would otherwise have been purged from the space. Sorptive interactions have emerged as an important indoor air-quality research subject during the past decade. Table 6 catalogs the literature on sorptive interactions involving constituents of concern in cleaning products and materials used indoors. Despite these extensive studies there remain unresolved issues, including the degree to which sorption is reversible vs. irreversible, the extent to which sorption is a surface phenomena vs. one in which internal mass transport may be limiting, and the effects of changing environmental conditions (temperature, humidity) on sorptive uptake or release.

Fig. 1b illustrates the potential significance of sorption in influencing concentration profiles. The conditions are the same as for Fig. 1a: episodic release of 500 mg of a gaseous pollutant during a 1-h cleaning activity in a single-family dwelling. In this case, completely reversible sorption is added to the governing material balance equation. The simulation model follows the pioneering work of Tichenor et al. (1991), and the rate constants for sorptive uptake and desorption are based on data from Sparks et al. (1999) for 2-(2-butoxyethoxy)ethanol interactions with carpet and gypsum board. Results from two simulations are shown. In one, the initial sorbed mass is assumed to be zero, which would correspond to the first use of the cleaning product in the space. In the second, the application cycle is repeated at weekly intervals for one year. The sorbed contaminant mass increases weekly, approaching a steady-state level by the end of the simulated period. The fractional difference between these simulations is small during and shortly after product use. However, the accumulation of sorbed mass in the second simulation leads to a much higher background concentration during the post-cleaning period: the average concentration for days 2–7 is 1.1 $\mu g\,m^{-3}$ in the first case and 12 $\mu g\,m^{-3}$ in the second. Comparing the nonsorbing case (Fig. 1a) with the repeated-cycle sorbing case, there are two large differences. Sorption greatly reduces the peak concentration, so that exposure (the time-integral of concentration)

Table 6
Sorption studies of target cleaning-product chemicals on indoor surface materials

Chemical	CAS No.	Indoor material (reference)[a]
Glycol ethers		
Diethylene glycol monobutyl ether	112-34-5	Gypsum board (f, g, u), carpet (g, u), stainless steel (f)
Ethylene glycol monobutyl ether	111-76-2	Gypsum board (h, p, r, w), carpet (h, p, w), vinyl wallcovering (h, p), wallpaper (p), textile wallcovering (p), acrylic wallcovering (p), PVC flooring (p)
Hydrocarbons		
Benzene	71-43-2	Whole homes (e)
Ethylbenzene	100-41-4	Carpet (a, v, x, y, z), carpet pad (x, z), vinyl flooring (a, b, y, z), gypsum board (a, v, y, z), ceiling tile (a, v, z), plywood (b), pillow (v), glass (v), wood flooring (y, z), fiberglass shower stall (z), upholstery (z)
Styrene	100-42-5	Whole homes (e)
Toluene	108-88-3	Carpet backing (b), carpet (d, l, m, n, p, w, x, y, z), carpet pad (x, z), carpet fibers (k), polyester curtains (d), textiles (j, z), cotton sofa (d), cotton curtains (m), whole homes (e), vinyl flooring (i, m, n, p, y, z), gypsum board (p, r, s, w, y, z), wallpaper (p), textile wallcovering (p), acrylic wallcovering (p), vinyl wallcovering (p), acrylic paint (s), stainless steel (w), wood flooring (y, z), ceiling tile (z), fiberglass shower stall (z)
Xylene	1330-20-7	Whole homes (e), wallpaper (p, q), carpet (p, q, w), acrylic paint on wallpaper (q), PVC (q), aerated concrete (q), gypsum board (p, q, r, w), marble (q), wooden parquet (q), textile wallcovering (p), acrylic wallcovering (p), vinyl wallcovering (p), PVC flooring (p)
Carbonyls		
Formaldehyde	50-00-0	Gypsum wallboard (o)
Methyl ethyl ketone	78-93-3	Acrylic paint (s), gypsum board (s)
Chlorinated organics		
Propylene dichloride	78-87-5	Whole homes (e)
Tetrachloroethylene	127-18-4	Whole homes (e, t), carpet (h, p, t, v, w, x, z), carpet pad (x, z), vinyl wallcovering (h, p), gypsum wallboard (h, p, r, s, v, w, z), wallpaper (p), textile wallcovering (p), acrylic wallcovering (p), PVC flooring (p, z), acrylic paint (s), painted surfaces (t), ceiling tile (v, z), glass (v), pillow (v), wood flooring (z), fiberglass shower stall (z), upholstery (z)
1,1,1-Trichloroethane	71-55-6	Whole homes (e), textiles (j), carpet fibers (k)
Trichloroethylene	79-01-6	Nylon (c), wool (c), polypropylene (c), jute (c), styrene-butadiene rubber (c), glass (c), polyester (c), cotton (c)
Trichloromethane	67-66-3	Whole homes (e)
Alcohols		
Linalool	78-70-6	Wallpaper (p), textile wallcovering (p), acrylic wallcovering (p), vinyl wallcovering (p), PVC flooring (p), gypsum board (p, r), carpet (p)
Terpenes		
Limonene	138-86-3	Carpet (w), gypsum board (w)
α-Pinene	80-56-8	Carpet (h, l, m, n, p), vinyl wallcovering (h, p), gypsum (h, p, r), PVC flooring (m, n, p), cotton curtains (m), wallpaper (p), textile wallcovering (p), acrylic wallcovering (p)
β-Pinene	127-91-3	Wallpaper (p), textile wallcovering (p), acrylic wallcovering (p), vinyl wallcovering (p), PVC flooring (p), gypsum board (p, r), carpet (p)

[a] References: a—An et al. (1999), b—Bodalal et al. (2000), c—Borrazzo et al. (1993), d—Bouhamra and Elkilani (1999a), e—Bouhamra and Elkilani (1999b), f—Chang et al. (1997), g—Chang et al. (1998), h—Colombo et al. (1993), i—Cox et al. (2001), j—Elkilani et al. (2001), k—Elkilani et al. (2003), l—Jørgensen and Bjørseth (1999), m—Jørgensen et al. (1999), n—Jørgensen et al. (2000), o—Matthews et al. (1987), p—Meininghaus et al. (1999), q—Meininghaus et al. (2000), r—Meininghaus and Uhde (2002), s—Popa and Haghighat (2003), t—Sparks et al. (1991), u—Sparks et al. (1999), v—Tichenor et al. (1991), w—van der Wal et al. (1998), x—Won et al. (2000), y—Won et al. (2001a), z—Won et al. (2001b).

during the first 10 h beginning with product use decreases from 2380 $\mu g\,m^{-3}$ h without sorption to 470 $\mu g\,m^{-3}$ h with sorption. However, the persistent background from desorption during the post-cleaning period compensates for this difference: the potential exposure during hours 10–168 is zero without sorption, but 1880 $\mu g\,m^{-3}$ h with sorption. To the extent that effects are related to peak concentrations, sorption may be beneficial overall by reducing peak exposures during cleaning activities. However, if occupancy is much lower during cleaning than at other times, then reversible sorption could cause a much higher population intake of primary pollutants than would occur for a nonsorbing species.

4.3. *Human factors*

Emissions, concentrations, exposures, and intakes of hazardous air pollutants (HAPs) from cleaning product use all depend in part on human factors. One set of human factors influencing emissions is the characteristics of use: frequency, amount, and manner of application. Only a few published studies have looked at cleaning product usage by consumers. Weegels and van Veen (2001) studied the usage of dishwashing liquid, all-purpose cleaner, toilet cleaner, and hair spray in 30 households in The Netherlands. For all-purpose cleaners, they found an average contact frequency of 0.35 per subject per day, a mean duration of 20 min per contact, and an average product usage of 27 g per contact. Kovacs et al. (1997) found that consumers preferred cleaning products with a pleasant scent. They also observed that less of a scented product (either pleasant or unpleasant) was used for cleaning than an unscented product.

A second important human factor linking exposure to intake is breathing rate. Adams (1993) measured breathing rates of 200 individuals across a range of age and activity levels. At rest, average breathing rates were in the range of 0.4–0.6 $m^3\,h^{-1}$, depending on gender, age (child vs. adult), and position (prone, seated, or standing). The average breathing rate for adult females performing housework was 1.0 $m^3\,h^{-1}$. Adult males were not monitored performing this activity. Marty et al. (2002) have estimated that the population mean breathing rate for adults is 0.23 $m^3\,kg^{-1}\,d^{-1}$, which corresponds to 0.67 $m^3\,h^{-1}$ (16 $m^3\,d^{-1}$) for a 70 kg subject.

A third set of human factors addresses the timing of cleaning activities relative to occupancy, how the building is operated during and after cleaning, and the use of protective measures to limit exposure and intake. It should be clear from Fig. 1 that exposure can be affected by the level of occupancy during cleaning. Exposures are minimized by conducting cleaning activities while occupancy is at a minimum, and as far in advance as possible of the next period of heavy occupancy. In addition, it is beneficial to maintain building ventilation, especially during cleaning, but also afterward. In private residences, window opening can be used to increase ventilation rates (Howard-Reed et al., 2002). Enhanced ventilation may incur costs, especially when the ambient temperature is hot or cold. In principle, these costs could be weighed against the benefit of reduced exposures; however, information is inadequate to do so objectively. Finally, both personal respiratory protection measures and indoor air cleaning devices could be used to reduce exposure and intake. Devices commonly used, such as disposable face masks and recirculating air filters, are designed to be effective against particulate matter but not against volatile organic compounds. Activated carbon sorbents are used for personal protection in hazardous material handling. Air cleaning devices that use activated carbon have also been investigated in laboratory studies (VanOsdell et al., 1996). However, we found no evidence of sorbents being used to limit exposure to cleaning product constituents.

5. Reactive chemistry and secondary pollutants

5.1. *Reactions with ozone*

Cleaning product and air freshener constituents can react with oxidants to generate secondary pollutants. Ozone is a common initiator for indoor gas-phase oxidation processes. Reactions of ozone with constituents containing unsaturated carbon–carbon bonds are much faster, and serve as a larger source of secondary pollutants, than reactions with constituents containing only saturated carbon–carbon bonds. Table 7 lists constituents of cleaning products and air fresheners with C=C bonds. Most of these potentially reactive chemicals are terpenes (e.g., α-pinene, *d*-limonene, myrcene) or terpene-related compounds (e.g., linalool, α-terpineol and linalyl acetate). Their inclusion in cleaning products reflects the favorable odor characteristics and solvent properties of terpenoids. Some of the entries in Table 7 have not been explicitly reported but are inferred to be present in cleaning products or air fresheners since they are known constituents of oils or scent formulations used in such products (e.g., α-terpinene found in pine oil; selected sesquiterpenes found in waxes, orange oil and lemon-peel oil). Not only are there differences in ozone reactivity rates between unsaturated constituents (Table 7) and saturated ingredients (most of the compounds listed in Table 5), but also there are substantial differences among the unsaturated constituents themselves. Table 8 lists second-order rate constants for reactions between the compounds in Table 7 and ozone. The compounds are rank-ordered based on their second-order constants

Table 7
Constituents of cleaning products and air fresheners containing C=C bonds

Chemical	CAS No.	Product (reference)
Alcohols		
Citronellol	106-22-9	Major constituent of rose oil (Kirk-Othmer, 1998)
Dicyclopentadiene alcohol	27137-33-3	Liquid floor detergent (Colombo et al., 1991)
Dihydromyrcenol	18479-58-8	Liquid floor detergent (Colombo et al., 1991); one of the principal components of lavender
Geraniol	624-15-7	Constituent of rose oil and citronella oil (Kirk-Othmer, 1998)
Linalool[a]	78-70-6	Air freshener (Cooper et al., 1995; Salthammer, 1999); liquid floor detergent (Colombo et al., 1991); one of the principal components of bergamot
α-Terpineol[a]	98-55-5	Liquid cleaner/disinfectant, liquid floor detergent (Colombo et al., 1991); air freshener (Salthammer, 1999); cleaning agents (Vejrup and Wolkoff, 1994); major component of pine oil
Aldehydes		
Citronellal	106-23-0	Present in balm mint and citronella oil (Kirk-Othmer, 1998)
Geranial	5392-40-05	Present in lemon grass, rose and orange oil (Kirk-Othmer, 1998)
Neral	106-26-3	Present in rose and orange oil (Kirk-Othmer, 1998)
Aromatic hydrocarbon		
Styrene	100-42-5	Floor cleaner (Akland and Whitaker, 2000); liquid wax (Knöppel and Schauenberg, 1989)
Ether		
3-Butenylpropylether		Detergent/cleaner (Knöppel and Schauenberg, 1989)
Esters		
Linalyl acetate[a]	115-95-7	Air freshener (Salthammer, 1999); one of the principal components of bergamot
Methyl methacrylate[b]	80-62-6	Cleaning agents (Wolkoff et al., 1998)
Terpenes		
Camphene	79-92-5	Liquid cleaner/disinfectant (Colombo et al., 1991); antibacterial glass and surface cleaner, all-purpose cleaner (Zhu et al., 2001); cleaning agents (Vejrup and Wolkoff, 1994); air freshener (Cooper et al., 1995)
3-Carene	13466-78-9	Liquid cleaner/disinfectant, floor wax (Colombo et al., 1991); antibacterial glass and surface cleaner (Zhu et al., 2001)
Limonene	138-86-3	Floor wax (Colombo et al., 1991); room freshener (Tichenor and Mason, 1988); detergent/cleaner (Knöppel and Schauenberg, 1989; Maroni et al., 1995); air freshener (Cooper et al., 1995; Salthammer, 1999); cleaning agents (Vejrup and Wolkoff, 1994); all-purpose cleaner, glass and surface cleaner, antibacterial glass and surface cleaner, lemon fresh and antibacterial spray, floor shine cleaner (Zhu et al., 2001)
β-Myrcene	123-35-3	All-purpose cleaner, antibacterial glass and surface cleaner (Zhu et al., 2001); air freshener (Cooper et al., 1995; Salthammer, 1999)
Ocimene	13877-91-3	Air freshener (Zhu et al., 2001; Salthammer, 1999)
α-Phellandrene	99-83-2	Antibacterial glass and surface cleaner (Zhu et al., 2001)
α-Pinene	80-56-8	Liquid cleaner/disinfectant, floor wax (Colombo et al., 1991); antibacterial glass and surface cleaner, lemon fresh and antibacterial spray, floor shine cleaner (Zhu et al., 2001); air freshener (Salthammer, 1999)
β-Pinene	127-91-3	Floor wax, liquid cleaner/disinfectant (Colombo et al., 1991); all-purpose cleaner, antibacterial glass and surface cleaner, lemon fresh and antibacterial spray, floor shine cleaner (Zhu et al., 2001)
α-Terpinolene	586-62-9	Cleaning agents (Vejrup and Wolkoff, 1994)
α-Terpinene	99-86-5	Major constituent of pine oil (Kirk-Othmer, 1998; Hodgson, 2003)
Sesquiterpenes		
Caryophyllene	87-44-5	Wood polishes and waxes (Kirk-Othmer, 1998)
α-Humulene	6753-98-6	Wood polishes and waxes (Kirk-Othmer, 1998)

Table 7 (*continued*)

Chemical	CAS No.	Product (reference)
Longifolene	475-20-7	Wood polishes and waxes; scenting agent (Kirk-Othmer, 1998; Gosselin et al., 1984)
α-Cedrene	469-61-4	Wood polishes and waxes; scenting agent (Kirk-Othmer, 1998; Gosselin et al., 1984)
Fatty acids		
Oleic acid	112-80-1	Wood polishes and waxes (Kirk-Othmer, 1998)
Linoleic acid	60-33-3	Major constituent of linseed oil (Kirk-Othmer, 1998)
Linolenic acid	463-40-1	Major constituent of linseed oil (Kirk-Othmer, 1998)

[a] Compound produced in relatively large amounts, but little published information on reactions with ozone, hydroxyl radicals or nitrate radicals.

[b] Residual monomers from polymers.

Table 8

Reported 2nd order rate constants, k, and calculated pseudo-1st order rate constants, k', for the reactions of selected unsaturated constituents of cleaning products and air fresheners with ozone, hydroxyl radicals and nitrate radicals[a]

Compound	Reaction with O_3			Reaction with OH			Reaction with NO_3		
	k ($ppb^{-1}\,s^{-1}$)	Ref[a]	k' (h^{-1})@20 ppb O_3	k ($ppb^{-1}\,s^{-1}$)	Ref[b]	k' (h^{-1})@5×10^{-6} ppb OH	k ($ppb^{-1}\,s^{-1}$)	Ref[b]	k' (h^{-1}) @10^{-3} ppb NO_3
Camphene	2.2×10^{-8}	d	0.002	1.3	d	0.024	0.016	a	0.06
Longifolene	$<1.7\times10^{-7}$	l	0.01	1.2	m	0.021	0.017	m	0.06
Beta-pinene	3.7×10^{-7}	e	0.03	2.0	b	0.035	0.06	a	0.22
Styrene	4.2×10^{-7}	n	0.03	1.4	c	0.026	0.004	a	0.01
Alpha-cedrene	6.9×10^{-7}	l	0.05	1.6	m	0.030	0.20	m	0.73
Delta-3-carene	9.3×10^{-7}	e	0.07	2.1	b	0.038	0.22	a	0.81
β-Phellandrene	1.2×10^{-6}	k	0.08	4.1	k	0.074	0.20	k	0.71
Cyclohexene	1.8×10^{-6}	h	0.13	1.3	j	0.024	0.013	a	0.05
Alpha-pinene	2.1×10^{-6}	e	0.15	1.3	b	0.024	0.15	a	0.55
Sabinene	2.2×10^{-6}	e	0.16	2.9	d	0.052	0.25	a	0.89
γ-Terpinene	3.4×10^{-6}	e	0.25	3.2	i	0.058	0.72	a	2.6
Copaene	3.9×10^{-6}	l	0.28	2.2	m	0.040	0.39	m	1.4
d-Limonene	5.2×10^{-6}	e	0.37	4.2	b	0.075	0.30	a	1.1
2-Carene	5.9×10^{-6}	e	0.42	2.0	g	0.035	0.46	a	1.7
Linalool	1.1×10^{-5}	f	0.76	3.9	f	0.070	0.28	f	1.0
Myrcene	1.2×10^{-5}	e	0.86	5.2	b	0.094	0.26	a	0.94
Ocimene	1.4×10^{-5}	e	0.99	6.2	b	0.11	0.55	a	2.0
Terpinolene	4.7×10^{-5}	l	3.4	5.5	g	0.10	2.4	a	8.6
α-Phellandrene	7.4×10^{-5}	l	5.3	7.6	b	0.14	2.1	a	7.6
Caryophyllene	3.0×10^{-4}	l	21.0	4.9	m	0.089	0.47	m	1.7
Humulene	2.9×10^{-4}	l	21.0	7.1	m	0.13	0.86	m	3.1
α-Terpinene	5.2×10^{-4}	l	37.0	8.9	b	0.16	4.5	a	16

[a] See text for references supporting the assumed concentrations of O_3, OH and NO_3 used to calculate k'.

[b] References: a—Atkinson (1991), b—Atkinson et al. (1986), c—Atkinson and Aschmann (1988), d—Atkinson et al. (1990a), e—Atkinson et al. (1990b), f—Atkinson et al. (1995), g—Corchnoy and Atkinson (1990), h—Greene and Atkinson (1992), i—Grosjean and Williams (1992), j—Rogers (1989), k—Shorees et al. (1991), l—Shu and Atkinson (1994), m—Shu and Atkinson (1995), n—Tuazon et al. (1993).

for reaction with ozone. These ozone rate constants span more than 4 orders of magnitude.

5.2. Reactions with OH and NO_3

Hydroxyl radicals and nitrate radicals are other oxidants that may be present indoors at sufficient concentrations to produce significant quantities of secondary pollutants. Indoor hydroxyl radicals are derived primarily from ozone/alkene reactions (Nazaroff and Cass, 1986; Weschler and Shields, 1996, 1997a,b; Sarwar et al., 2002b), while indoor nitrate radicals result from the reaction between ozone and nitrogen dioxide (Nazaroff and Cass, 1986; Weschler et al., 1992; Sarwar et al., 2002a). Table 8 also lists the second-order rate constants for OH and NO_3 reactions with the compounds in Table 7. In contrast to the rate constants for reactions with ozone, those for the reactions with OH span a relatively narrow range, approximately an order of magnitude. The rate constants for reactions with NO_3 demonstrate variability that lies between these extremes, spanning approximately 3 orders of magnitude. There are many widely used unsaturated constituents of cleaning products whose rates of reaction with common indoor oxidants have not been reported in the literature. These include α-terpineol, a major constituent of pine oil; linalyl acetate, a common odorant (and a constituent of bergamot); and dihydromyrcenol, another common odorant (and a constituent of lavender).

5.3. Rate comparisons

For a gas-phase reaction between ozone and a cleaning constituent to have a meaningful impact in an indoor environment, the reaction must occur at a rate competitive with air-exchange rates or other removal processes (Weschler and Shields, 2000). Table 8 includes pseudo-first-order rate constants for the reaction of the unsaturated constituents with O_3, OH and NO_3 at oxidant concentrations that are representative of those anticipated to occur near midday during the ozone season in certain indoor settings. These levels are 20 ppb for O_3 (Weschler, 2000), 5×10^{-6} ppb for OH (Sarwar et al., 2002b), and 1×10^{-3} ppb for NO_3 (Sarwar et al., 2002a). Note that the concentration of indoor O_3 is highly variable and depends on both the outdoor ozone level and the air exchange rate; the concentrations of OH and NO_3 are similarly variable since they are derived from reactions initiated by O_3. The reactions of O_3 with most of the compounds in Table 7 are fast enough to be potentially significant in some indoor settings; the exceptions are the very slow reactions with camphene and longifolene. The reactions between O_3 and α-terpinene, terpinolene and the three listed sesquiterpenes are fast enough to have consequences even at air-exchange rates as high as $10\,h^{-1}$. At the OH levels anticipated in indoor settings, reactions between the compounds in Table 7 and OH are expected to be important only at lower air-exchange rates. Even the fastest of these reactions has a pseudo-first-order rate constant of just $0.16\,h^{-1}$ at an OH level of 5×10^{-6} ppb.

Most of the compounds in Table 7 have pseudo-first-order rate constants for reactions with NO_3 that are larger than the analogous rates with OH. Indeed, a number are faster than the analogous rates with O_3. Nitrate radical reactions are anticipated to be particularly important during air pollution episodes with simultaneously elevated NO_2 and O_3. For example, during 14 months of measurements at an office building in Burbank, CA several periods were recorded when indoor NO_2 exceeded 60 ppb while indoor O_3 simultaneously exceeded 30 ppb (Weschler et al., 1994). For similar reasons, NO_3 reactions may also take on added significance in indoor settings with unvented combustion appliances. Of particular note are the reactions of NO_3 with *d*-limonene ($k' = 1.1\,h^{-1}$), linalool ($k' = 1.0\,h^{-1}$), terpinolene ($k' = 8.6\,h^{-1}$), and α-terpinene ($k' = 16\,h^{-1}$).

5.4. Oxidation products

Atkinson and Arey (2003) recently reviewed the kinetics, mechanisms and products of gas-phase reactions between biogenic organic compounds—mostly terpenoids—and the oxidants O_3, OH and NO_3. Much of the reactive chemistry discussed in their paper is relevant to unsaturated cleaning constituents. The major difference is that photochemistry plays an important role in outdoor reactive chemistry, but normally makes only a negligible direct contribution indoors. Table 9 presents the general types of secondary pollutants produced by reactions between unsaturated cleaning compounds or air freshener constituents and O_3, OH and NO_3. These include free radicals, starting with stabilized Criegee biradicals (probably carbonyl oxides; see Kroll et al., 2002). Hydroperoxy and alkyl peroxy radicals warrant special comment. Their lifetimes may be longer indoors than outdoors and their fate indoors may also be altered. Under indoor conditions that produce HO_2 and RO_2, the concentration of NO tends to be extremely low, because the reaction between O_3 and NO is fast, and because negligible NO is produced by indoor photodissociation of NO_2 (Weschler et al., 1994). Hence, the NO destruction pathways of HO_2 and RO_2 are less important indoors than is common outdoors. Modeling studies indicate that indoor HO_2 can easily reach low ppt levels, while indoor CH_3O_2 can exceed 10 ppt (Sarwar et al., 2002a).

Other short-lived, highly reactive species include peroxyhemiacetals and secondary ozonides. Many of the oxidation products are stable compounds with one or more oxygen-containing functional groups ($–C=O$, $–C–OH$, $–COOH$, $–C–NO_2$). As a consequence of these substituent groups, such products absorb radiation in the near-UV range and are susceptible to photodegradation in outdoor air. However, in indoor environments the removal rate by this pathway is small, implying longer lifetimes indoors (especially if the products are sorbed to indoor surfaces). Some of the oxidation products have low vapor pressures and partition between the gas phase and airborne particles, contributing to the growth of secondary organic aerosols (SOA). The increase in the mass concentration of indoor SOA as a consequence of such reactions can be in the range of 10–100 $\mu g\,m^{-3}$ (Weschler, 2003a).

Some of the oxidation products have extremely low odor thresholds (e.g., selected unsaturated aldehydes have thresholds below 50 ppt, while selected aldehydes and carboxylic acids have thresholds in the low ppb

Table 9
Products (reported or inferred for indoor settings) derived from reactions between unsaturated organic compounds and ozone, hydroxyl radicals or nitrate radicals

Product	Product of reaction with			Refs[a]
	O_3	OH	NO_3	
Primary ozonides	✓			a, d
Stabilized Crigee biradicals	✓			d, p, q
Hydroxyl radical	✓			l, o t, u
Alkyl radicals		✓	✓	a, d
Hydroxyalkyl radicals		✓		a
Nitrooxyalkyl radicals			✓	a
Hydroperoxy radical	✓	✓	✓	l, n, v
Alkoxy radicals	✓	✓	✓	a, d, n
Unidentified radical	✓			b
α-Hydroxyhydroperoxides	✓	✓		a, c
Hydrogen Peroxide	✓			h, i
Hydroperoxides	✓			a, h, i, p, q
Peroxy-hemiacetals	✓			p, q
Secondary ozonides	✓			k, p, q
Epoxides	✓			a
Hydroxy carbonyls		✓		a
Dihydroxy carbonyls		✓		a
Hydroxy nitrates			✓	a
Carbonyl nitrates			✓	a
Formaldehyde	✓	✓		a, d
Other aldehydes	✓	✓	✓	a, d
Acetone	✓	✓		a, d
Other ketones	✓	✓	✓	a, d
Formic acid	✓	✓		a
Other carboxylic acids	✓	✓		a
Organic nitrates		✓	✓	a
Multifunctional oxidation products with carbonyl, carboxylate and/or hydroxyl groups	✓	✓	✓	d, e, f, r, x
Secondary organic aerosols via gas/particle partitioning of low volatility products	✓	✓	✓	i, l, s, v, w

[a] References: a—Atkinson and Arey (2003), b—Clausen and Wolkoff (1997), c—Fick et al. (2003), d—Finlayson-Pitts and Pitts (2000), e—Glasius et al. (2000), f—Griffin et al. (1999), g—Jang and Kamens (1999), h—Li (2001), i—Li et al. (2002), j—Long et al. (2000), k—Morrison (1999), l—Nazaroff and Cass (1986), m—Rohr et al. (2003), n—Sarwar et al. (2002a), o—Sarwar et al. (2002b), p—Tobias and Ziemann (2000), q—Tobias et al. (2000), r—Virkkula et al. (1999), s—Wainman et al. (2000), t—Weschler and Shields (1996), u—Weschler and Shields (1997a), v—Weschler and Shields (1997b), w—Weschler and Shields (1999), x—Yu et al. (1998).

range; see Devos et al., 1990). Many products derived from oxidation of the compounds listed in Table 7 are known or anticipated to be irritating (e.g., certain aldehydes, peroxides, hydroperoxides, secondary ozonides, mono- and dicarboxylic acids). Both acrolein and formaldehyde are eye irritants and are listed as California TACs with acute reference exposure levels (RELs) for a 1 h exposure of 0.19 and 94 $\mu g\,m^{-3}$, respectively. In addition, exposure to acetaldehyde, acrolein, formaldehyde and glutaraldehyde pose long-term hazards to the respiratory system and are listed as TACs with chronic RELs of 9, 0.06, 3 and 0.08 $\mu g\,m^{-3}$, respectively. Certain air oxidation products of *d*-limonene have been identified as contact allergens (Karlberg et al., 1992, 1994; Nilsson et al., 1996), and some of these same compounds have been found in the mix of products resulting from ozone initiated oxidation of *d*-limonene (Clausen et al., 2001). Some of the products are suspected carcinogens (e.g., formaldehyde, certain organic nitrates, and SOA). However, for most of the oxidation products, detailed toxicological information is not available; they simply have not been evaluated. Also, many of the reaction products are "stealth pollutants"; i.e., they are difficult to detect and are often overlooked in the sampling and analysis of indoor air (Weschler and Shields, 1997b; Wolkoff and Nielsen, 2001; Carslaw, 2003). This is especially true for free radicals, other short-lived species, thermally labile compounds, and multifunctional products. Atkinson and Arey (2003) specifically mention hydroxy carbonyls, dihydroxy carbonyls, hydroxy nitrates and carbonyl nitrates as known products that are analytically challenging. Over the past ten years there have been advances in derivatizing and detecting higher molecular weight multi-functional products. However, these methods have not been routinely used in indoor air investigations.

Some of the first-generation oxidation products of the compounds in Table 7 contain one or more unsaturated bonds. Examples include 4-acetyl-1-methylcyclohexene (ACM) and 3-isopropenyl-6-oxoheptanal (IPOH or endolim) from the oxidation of limonene and 5-methyl-5-vinyltetrahydrofuran-2-ol (MVT) from the oxidation of linalool. Such compounds tend to react with O_3 at rates slower than their parent compounds, but in some cases still fast enough to contribute to additional "secondary" product formation. Details for specific unsaturated products are further discussed in Calogirou et al. (1999a,b), in the Atkinson/Arey review and in references cited therein. First-generation oxidation products, including those with no unsaturated bonds, can react with OH and NO_3. Hallquist et al. (1997) have reported rate constants for the reaction of OH and NO_3 with pinonaldehyde and caronaldehyde, oxidation products of α-pinene and Δ^3-carene, respectively. However, such kinetic information is not available for most of the first-generation oxidation products of cleaning agent and air freshener constituents.

Reactions with OH and NO_3 also can be significant for primary cleaner or air freshener emissions with no unsaturated bonds. In studies of ozone (40 ppb) and a mixture of 23 volatile organic compounds, including *d*-limonene and α-pinene, the products included compounds that were not directly generated by reactions with ozone, but resulted from secondary reactions between hydroxyl radicals and components of the initial mixture (Fan et al., 2003). Indeed, kinetic modeling of the mixture indicated that OH was responsible for 55–70% of the resulting formaldehyde and 20–30% of the secondary organic aerosol. Such reactions may reduce the airborne concentrations of Proposition 65 and TAC constituents listed in Table 5; however, the products may also be of concern. Reactions of the glycol ethers with OH and NO_3 warrant special comment since they are sometimes the major active ingredient of a cleaning product and are receiving increased scrutiny regarding their potential health effects. Consider, for example, the OH/2-butoxyethanol and NO_3/2-butoxyethanol reactions for which the second-order rate constants are $0.5\,\text{ppb}^{-1}\,\text{s}^{-1}$ (Stemmler et al., 1996) and $<0.004\,\text{ppb}^{-1}\,\text{s}^{-1}$ (Chew et al., 1998), respectively. For the typical indoor OH and NO_3 concentrations reported in Table 8, the resulting pseudo-first-order rate constant for either oxidant is $<0.01\,\text{h}^{-1}$, too slow to be significant in terms of 2-butoxyethanol removal. The significance for product formation is less clear, as even small fractional conversion of 2-butoxyethanol could be of concern if the toxic potency of one or more of the products were high. Such products include ethylene glycol monoformate, butyl formate, propionaldehyde, 3-hydroxybutyl formate, butoxyacetaldehyde, and propyl nitrate (Stemmler et al., 1997). Hydroxyl radicals react up to four times faster with certain other glycol ethers than with 2-butoxyethanol (Aschmann et al., 2001).

5.5. *Reactions on surfaces*

Given their vapor pressures and polarities, many glycol ethers are anticipated to partition between the gas-phase and indoor surfaces (see Section 4.2). Although the gas-phase oxidation of glycol ethers is severely limited by their airborne residence time, there is considerably more time for oxidation if these compounds are sorbed on surfaces. Indeed, oxidation processes initiated by ozone and even dioxygen (i.e., autoxidation) may be important on surfaces. The autoxidation of glycol ethers produces peroxides and hydroperoxides as primary products and alkyl poly(-ethylene glycol) aldehydes, alkyl poly(ethylene glycol) formates, hydroxyaldehydes, and even formaldehyde as secondary products (Bodin et al., 2003). These processes have been the subject of considerable study since some of the products are irritants and skin sensitizers (Bodin et al., 2000, 2001, 2002, 2003).

Surface oxidation also may be important for other constituents of cleaning products and air fresheners. Laboratory studies of the reaction of ozone (Fick et al., 2002) or ozone and nitrogen oxides (Pommer, 2003) with α-pinene, Δ^3-carene and limonene indicate that surface reactions, as well as gas-phase processes, are contributing to the removal of these terpenes; the effect was most pronounced for Δ^3-carene. In buildings with mechanical ventilation systems, the particulate filters present a potentially important site for surface oxidation processes to occur. As these filters load (i.e., collect particulate matter), the resultant surface area of the captured particles can become quite large (Weschler, 2003b). Such filters are typically located downstream of the mixing box, such that the air passing through them is a mixture of recirculated and outdoor air. During a cleaning event the recirculated air may contain high concentrations of compounds from Tables 5 and 7. Such compounds will, to a greater or lesser extent, partition between the airstream and the surface of the loaded filters. The mixed airstream contains a fraction of outside air (typically 10–20%), and ozone in this air can react with sorbed constituents, producing products that subsequently desorb into the supply air over an extended interval. This can further expose building occupants to oxidized constituents of cleaning agents and air fresheners. The importance of oxidation processes on a filter surface is anticipated to grow as a filter loads. Surface oxidation of compounds found in cleaning agents and air fresheners, whether on surfaces within a room or within an HVAC system, is an area that has received little attention and warrants further investigation.

5.6. Influence of reactive chemistry

Reactive chemistry influences the dynamic behavior and fate of selected primary emissions and generates secondary pollutants, many of which would not exist indoors in the absence of such chemical transformations. Fig. 2 illustrates the potential significance of such chemistry on concentration profiles. The conditions are the same as for Fig. 1a: episodic release of 500 mg of a gaseous pollutant during a 1-h cleaning activity in a well mixed, single-family dwelling. In this case, a chemical reaction between the volatile constituent and ozone is added to the governing material balance equation. The assumed indoor concentration of ozone is constant at 20 ppb. The assumed second-order rate constant is $5.2 \times 10^{-6}\,\mathrm{ppb}^{-1}\,\mathrm{s}^{-1}$, similar to the value for the ozone/limonene reaction (Table 8). Fig. 2 depicts both the concentration of the volatile constituent and the concentration of a hypothetical product. The latter has been calculated assuming the stoichiometry is one molecule of product formed per molecule of reactant consumed, and the product is nonsorbing and has the same molecular weight as the reactant. With reactive chemistry, the concentration of the volatile constituent reaches a peak value of $1020\,\mu\mathrm{g\,m}^{-3}$ compared to $1200\,\mu\mathrm{g\,m}^{-3}$ in the nonsorbing, no-chemistry case (Fig. 1a). Whereas this peak occurs at the end of the emission period, the peak value for the hypothetical product ($250\,\mu\mathrm{g\,m}^{-3}$) occurs almost three quarters of an hour after the end of the emission period, 1.7 h after the beginning of the cleaning episode. This lag reflects the time required for reaction coupled with the fact that the volatile constituent continues to react and generate product even after its emission ceases and its concentration begins to decay. Thus, the hypothetical product is more persistent than the volatile constituent. Six hours after the cleaning episode began, and 5 h after the emission of the cleaning constituent ceased, the concentration of the hypothetical product is still at 12% of its maximum value.

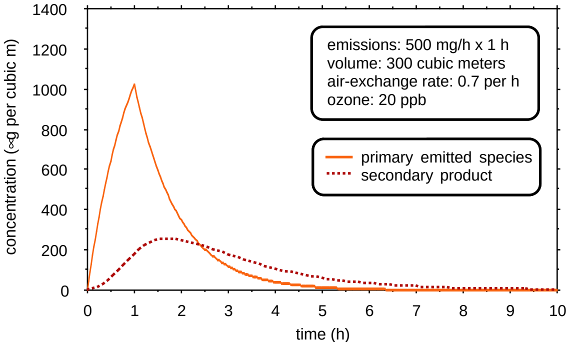

Fig. 2. Hypothetical concentrations of air contaminants resulting from the primary emissions of a reactive volatile constituent of a cleaning product, used in a single-family home. Basic conditions are the same as in Fig. 1. The indoor ozone level is assumed constant at 20 ppb. The second-order rate constant is $k = 5.2 \times 10^{-6}\,\mathrm{ppb}^{-1}\,\mathrm{s}^{-1}$, similar to that for the ozone/limonene reaction (Table 8). The concentration of a hypothetical secondary reaction generated by one-to-one stoichiometry is also shown. Both the reacting contaminant and hypothetical product are assumed to be nonsorbing.

In reality, ozone-initiated chemistry produces multiple products (Table 9), most of which have yields significantly less than unity. Formaldehyde is a known product for the reaction between ozone and several of the constituents listed in Table 7. If the reaction simulated in Fig. 2 had a formaldehyde yield of 10%, similar to that for the ozone/limonene reaction (Grosjean et al., 1993), then this reaction would add $5.6\,\mu\mathrm{g\,m}^{-3}$ of formaldehyde to the room air at its maximum contribution. Secondary organic aerosols (SOA) are also known products for the reaction between ozone and many of the constituents in Table 7. If an SOA yield of 20% is assumed and the average molecular mass of the products contributing to SOA growth is assumed to be $150\,\mathrm{g\,mol}^{-1}$, then the peak value of SOA added to the air as a consequence of this reaction would be $56\,\mu\mathrm{g\,m}^{-3}$. Some cleaners contain 15% pine oil, a mixture of primarily unsaturated terpenoids, some of which react with ozone even faster than limonene (e.g., terpinolene and α-terpinene). Such cleaning products have the potential to generate significantly higher concentrations of secondary pollutants than those shown in Fig. 2.

The causal chain-of-events that links secondary pollutants with inhalation exposure is similar to that for primary pollutants and broadly depends on the same three classes of processes: emissions, dynamic behavior and human factors. However, ventilation and mixing times affect the dynamic behavior and fate of secondary pollutants in an added way since the residence times defined by these factors limit the time available for gas-phase transformation processes (Weschler and Shields, 2000; Sorensen and Weschler, 2002). Also, in considering human factors, it should be noted that some of the short lived, highly reactive compounds (e.g., hydroxyl radicals, hydroperoxy radicals, alkyl peroxyradicals) may be too reactive to penetrate very far within the respiratory tract. On the other hand, for species such as α-terpinene that react with ozone at a relatively fast rate, there is the possibility that an inhaled mixture of ozone and the quickly reacting constituent may produce free radicals as the mixture travels down the respiratory tract towards the lungs. Many of the chemicals generated by O_3, OH or NO_3 initiated oxidation processes are expected to be more irritating than their precursors since oxidized products are more polar, more water soluble, and are often more odorous and acidic. Although the products of nitrate radical chemistry may be of special concern, the current assessment of the role of NO_3 in indoor chemical transformations is based solely on modeling and inference from outdoor nighttime processes.

6. Conclusions

Cleaning generates benefits by improving aesthetics and hygiene, and by preserving objects. Cleaning also generates risks, including the inhalation of volatile constituents of cleaning products or of secondary products formed by reactive chemistry. The benefits of air fresheners are more subjective, while the risks parallel those associated with cleaning. Some specific health problems have occurred as a result of cleaning or because of inhalation exposure to cleaning products. Also, epidemiological studies have identified associations between cleaning activities or exposures to cleaning products and various adverse health outcomes, although causative agents remain to be identified. A better understanding of inhalation exposures to primary and secondary pollutants derived from cleaning agents and air fresheners should ultimately lead to diminished risks while expanding the benefits derived from their use.

To the extent that they occur, inhalation risks from cleaning-product use begin with emissions, and emissions begin with product composition. Challenges arise because some of the desirable attributes of a cleaning-product's active ingredients are also attributes of chemicals that are irritating or otherwise pose health risks. Surfactants, acids, bases, oxidants, complexing agents, and solvents are used in specific cleaning products because they facilitate that product's function. Choices can and have been made to select compounds that are less toxic for these functions. Fragrances are inherent to air fresheners and may improve the aesthetic character of a cleaning product. The challenge is to employ fragrances less likely to produce hazardous secondary products.

In this review, we have synthesized a diverse literature relevant to several key elements of air pollutant exposures associated with cleaning product and air freshener use. We have organized the information into a logical framework stressing the causal relationships among concentrations, exposures, and intake, and the many input variables upon which they depend. As we have demonstrated, there are strong parallels between exposure from cleaning product/air freshener use and the broader concerns of air pollutant exposures from indoor sources. Important data gaps remain to be filled before a fully satisfactory understanding can be gained of inhalation exposures associated with cleaning products and air fresheners. Key data needs include better information on product composition, human factors that affect use and exposure, mechanistic and kinetic details for reactions involving important constituents, and the potential health effects of the secondary pollutants. Although these gaps exist, mass conservation, reaction kinetics and mechanistic reasoning can be used to examine linkages between cleaning product/air freshener use and pollutant exposures.

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