Ozone in Indoor Environments: Concentration and Chemistry

CHARLES J. WESCHLER

Abstract The concentration of indoor ozone depends on a number of factors, including the outdoor ozone concentration, air exchange rates, indoor emission rates, surface removal rates, and reactions between ozone and other chemicals in the air. Outdoor ozone concentrations often display strong diurnal variations, and this adds a dynamic excitation to the transport and chemical mechanisms at play. Hence, indoor ozone concentrations can vary significantly from hour-to-hour, day-to-day, and season-to-season, as well as from room-to-room and structure-to-structure. Under normal conditions, the half-life of ozone indoors is between 7 and 10 min and is determined primarily by surface removal and air exchange. Although reactions between ozone and most other indoor pollutants are thermodynamically favorable, in the majority of cases they are quite slow. Rate constants for reactions of ozone with the more commonly identified indoor pollutants are summarized in this article. They show that only a small fraction of the reactions occur at a rate fast enough to compete with air exchange, assuming typical indoor ozone concentrations. In the case of organic compounds, the "fast" reactions involve compounds with unsaturated carbon-carbon bonds. Although such compounds typically comprise less than 10% of indoor pollutants, their reactions with ozone have the potential to be quite significant as sources of indoor free radicals and multifunctional ($-C=O$, $-COOH$, $-OH$) stable compounds that are often quite odorous. The stable compounds are present as both gas phase and condensed phase species, with the latter contributing to the overall concentration of indoor submicron particles. Indeed, ozone/alkene reactions provide a link between outdoor ozone, outdoor particles and indoor particles. Indoor ozone and the products derived from reactions initiated by indoor ozone are potentially damaging to both human health and materials; more detailed explication of these impacts is an area of active investigation.

Key words Ozone; I/O ratio; Indoor chemistry; Aldehydes; Particulates; Free radicals.

Practical Implications
Indoor ozone contributes to total ozone exposures, and reactions driven by indoor ozone produce submicron particles that contribute to total particulate exposures. Indoor ozone concentrations are highly variable, but can be reasonably estimated using available knowledge regarding the factors that influence these concentrations. Although ozone is a powerful oxidizing agent, indoor ozone should not be viewed as a means for eliminating other indoor chemical pollutants. Ozone reacts too slowly with most airborne pollutants for the process to be of practical significance. Ozone does react at a faster rate with a small subset of indoor pollutants, but the oxidation products are themselves potentially irritating to humans and damaging to materials.

Introduction

Ozone is derived from the Greek word "οζειν" or "oz-ein", and was so named on account of its strong smell. (Ironically, ozone can react with common substances, such as unsaturated fatty acids, to produce compounds that are a 1000 times more odorous.) Ozone's odor in the vicinity of electrical discharges was described as early as 1785, but its chemical formula was not established until 1872. Since that time, there have been many misperceptions regarding ozone, especially in the areas of air quality and health.

Whereas the air that surrounds us contains about 20% dioxygen, it contains only trace amounts of ozone (typically 10 to 100 ppb). However, even in trace amounts ozone is potentially deleterious to human health (U.S. EPA, 1996). Around the world various government organizations that are charged with protecting the health of their citizens have established upper limits on the concentration of ozone in the air that people breathe. Examples of such standards are listed in Table 1.

Although outdoor ozone is a major concern and there have been concerted efforts to reduce its concen-

Telcordia Technologies, 331 Newman Springs Rd., Red Bank, NJ 07701, USA, Fax: +1 732 758 2804, e-mail: cweschle@telcordia.com

Table 1 Recommended Limits for Ozone in the United States and Around the World

Standard	Concentration, ppb	Duration, h
US NAAQS[a]	120	1
US NAAQS[b]	80	8
US OSHA[c]	100	8
US FDA[d]	50	e
US NIOSH[f]	100	e
CARB[g]	90	1
WHO[h]	60	8
Japan	60	1

[a] National Ambient Air Quality Standard
[b] In the Dec. 13, 1996 Federal Register (Vol. 61, 65763–65778) the US EPA proposed this new air quality standard for ozone
[c] Occupational Safety and Health Administration, 1989
[d] Food and Drug Administration, 1974
[e] Not to be exceeded at any time
[f] National Institute of Occupational Safety and Health, 1989
[g] California Air Resources Board, 1987
[h] World Health Organization, 1997

tration, this has proven difficult. Comparisons obtained with diverse data sets show an increase in tropospheric ozone levels of between 1 and 2% per year over the last 30 years (Seinfeld and Pandis, p. 94, 1998 and references therein.) Indeed, "... there have been enormous increases in background ozone concentrations over the past half-century" (Graedel and Crutzen, 1993). Projections are that this trend will continue (Lelieveld and Dentener, 2000).

Ozone is a relatively stable molecule; only at high ozone concentrations and/or elevated temperatures does it decompose to oxygen at a significant rate (Cotton and Wilkinson, 1980). At the concentrations that are typically encountered in ambient air such spontaneous decomposition is negligible. Ozone is a very strong oxidizing agent. Just a few species, such as fluorine, the perxenate ion, atomic oxygen and the hydroxyl radical are more powerful oxidants (Cotton and Wilkinson, 1980). However, this fact should not be misconstrued. Although ozone is capable of oxidizing numerous gas phase species, a large fraction of these reactions occur at a slow rate (see below).

In indoor settings, ozone was dismissed as an issue (e.g., Russell, 1988), but that attitude is changing. Indoor exposures to ozone represent a major fraction of total ozone exposures (Weschler et al., 1989). The U.S. EPA includes indoor ozone in its exposure modeling (e.g., pNEM/O_3), addresses indoor ozone in its "Air Quality Criteria Document for Ozone and Related Photochemical Oxidants" (U.S. EPA, 1996) and has funded studies measuring indoor ozone emissions from office equipment (e.g., Leovic et al., 1986). Indoor ozone is not only a health concern, but also adversely affects materials, pigments, and cultural artifacts (Davies et al., 1984; Cass et al., 1988; Brimblecomb, 1990).

Furthermore, ozone is a major driver of indoor chemistry (Weschler and Shields, 1997a). The products of indoor chemistry, initiated by ozone, can be more irritating, odorous, and/or damaging to materials than their precursors. This paper addresses the factors that influence the concentration of indoor ozone and its reactions with other indoor pollutants.

Sources of Ozone
Outdoors
The ozone that is present in outdoor air at ground level reflects a combination of photochemical production and destruction coupled with injection from the stratosphere (Logan, 1985; Danielsen, 1968). The photochemical production of ozone results from a complex set of reactions involving vapor phase organic compounds, nitrogen oxides, carbon monoxide and sunlight. In the United States, as the population density increases the concentrations of vapor phase organic compounds and nitrogen oxides also increases (National Research Council, 1991). Hence, outdoor ozone levels tend to be highest in densely populated areas with abundant sunshine. Areas that experience frequent meteorological inversions have even higher ozone concentrations since inversions trap the air below and allow the concentration of both ozone precursors (i.e., volatile organic compounds and nitrogen oxides) and ozone itself to increase.

Indoors
Several types of office equipment are known to generate ozone including photocopiers and laser printers. Although various photocopying processes produce ozone, most manufacturers incorporate some type of filtration system (e.g., activated carbon filters) to reduce the amount of ozone emitted to the surrounding air. Leovic et al. (1996) have measured ozone emissions from several different dry-process photocopiers. Their work demonstrates that ozone emissions can increase between periods of routine maintenance. For example, ozone emissions from five different photocopiers ranged from 16 to 131 µg/copy before maintenance compared with 1 to 4 µg/copy after maintenance. Emission rates during continuous operation were also recorded. For representative photocopiers from four different vendors, the measured ozone emission rate varied from 1.3 to 7.9 mg/h. More recent measurements by Black and Worthan (1999) are in good agreement; for 5 different dry process photocopiers they measured emission rates ranging from 1.2 to 6.3 mg/h with an average value of 5.2 mg/h. In the same study, they measured emission rates for 12 laser printers

ranging from <0.02 to 6.5 mg/h with an average value of 1.2 mg/h.

Electrostatic air filters and electrostatic precipitators can also generate ozone. The manufacturers of these devices attempt to design them in such a way as to limit ozone production. However, if excessive arcing occurs, these devices can contribute tens of ppb to ozone concentrations in indoor settings.

Numerous commercial ozone generators are advertised to remove airborne contaminants and improve indoor environments. Models are available with emission rates ranging from tens to thousands of milligram per hour (mg/h). One manufacturer in the United States claims to have sold over 2 million ozone generators over the past 12 years (Federal Trade Commission, 1998). Beoniger (1995) has examined the use of ozone generating devices to improve indoor air quality and concludes that "... ozone is not a practical and effective means of improving indoor air quality, especially in light of its potentially serious risk to health". The U.S. EPA (1999) has also assessed the use of ozone generators as air purifiers.

Indoor Ozone Concentrations

Figure 1 shows indoor and outdoor ozone concentrations measured for a 6-day period at a telephone switching office in Burbank, California, USA. Such measurements have been made in numerous types of buildings, including residential, commercial and public structures. In studies conducted by Shair and co-workers at selected California Institute of Technology buildings (Sabersky et al., 1973; Hales et al., 1974; Shair, 1981), the indoor ozone concentrations were found to closely track outdoor concentrations and to be dependent on the air exchange rate. More recent examples of simultaneous indoor and outdoor ozone measurements include multiple locations in a Red Bank, New Jersey, USA office complex (Weschler et al., 1989, 1991, 1992), a telephone office in Burbank, California, USA (Weschler et al., 1994a, b), and six New Jersey homes (Zhang et al., 1994a). Each of these investigations confirmed that indoor ozone concentrations varied in a predictable fashion with outdoor concentrations and the air exchange rate.

For a given site, at a constant air exchange rate and absent varying indoor sources, the indoor ozone concentration divided by the outdoor ozone concentration (I/O ozone) remains relatively constant (Shair and Heitner, 1974; Hales and Shair, 1974; Weschler et al., 1989, 1991, 1992). Table 2 summarizes I/O ozone ratios measured by numerous investigators in a variety of building types. These I/O ratios range from 0.05 in
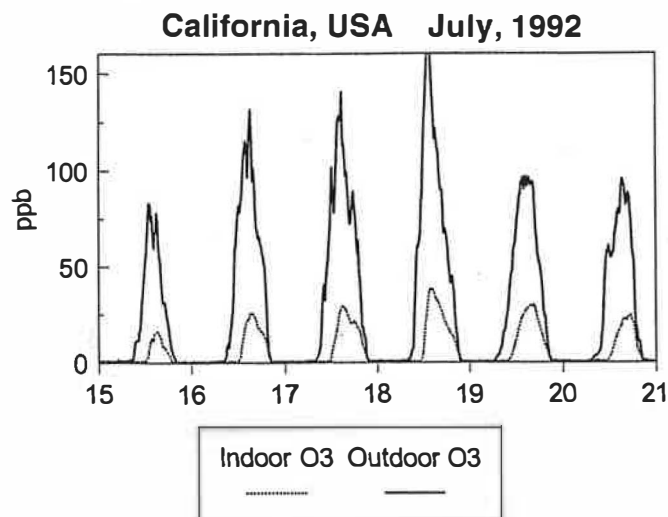

Fig. 1 Outdoor and indoor ozone levels (ppb) at a telephone office in Burbank, California, USA. (Weschler et al., 1994b)

buildings that are tightly sealed or use charcoal filtration to 0.85 in buildings that have very high air exchange rates. Excluding the extremes, the I/O ratio is more often in the range of 0.2 to 0.7. The large number and range of values presented in Table 2 can be systematized with a relatively simple expression (Weschler et al., 1989):

$$I/O = E_x / \{k_d(A/V) + E_x\} \qquad 1$$

where
E_x is the rate at which the indoor air is replaced with outdoor air (air exchange rate), in units of h^{-1}; k_d is the ozone deposition velocity, in units of $m\ h^{-1}$; A is the total surface area within the room, in units of m^2; V is the volume of the room, in units of m^3.

In words, the I/O ratio for ozone can be approximated by the ratio of the air exchange rate to the sum of the air exchange rate and the surface removal rate, $k_d(A/V)$. Equation 1 derives from the fact that dilution and surface removal of ozone are normally much faster than the time variation of the outdoor ozone concentration and, hence, a quasi-steady state situation may be assumed.

Factors that Influence Indoor Ozone Concentrations
Overview
The indoor ozone concentration depends on the outdoor ozone concentration, the rate at which indoor air is exchanged with outdoor air, indoor sources of ozone, the rate at which ozone is removed by indoor surfaces, and reactions between ozone and other chemicals in the air. The relationship between these sources and

Table 2 Indoor/Outdoor (I/O) Ozone Ratios Measured by Various Investigators at Buildings with Negligible Indoor Sources of Ozone

Building	Location	I/O	Notes
Hospital	So. California	0.67	Thompson, 1971
Office/lab	So. California	0.80	Sabersky et al., 1973
Office/lab	So. California	0.65	Ibid.
Home	So. California	0.70	Ibid., natural ventilation
Hospital	So. California	0.5	Thompson et al., 1973
Indoor pool	So. California	0.5	Ibid.
2 Schools	So. California	0.3–0.7	Ibid.
Office/lab	So. California	0.5	Ibid.
Home	So. California	0.6	Ibid., evaporative cooing
2 Offices	So. California	0.66	Shair and Heitner, 1974; maximum ventilation
2 Offices	So. California	0.54	Ibid., minimum ventilation
Office/lab	So. California	0.62	Hales et al., 1974
5 Townhouses	Washington	0.5–0.7	Moschandreas et al., 1978
6 Apartments	Baltimore	0.5–0.7	Ibid.
2 Mobile homes	Denver	0.5–0.7	Ibid.
1 School	Chicago	0.5–0.7	Ibid.
1 Hospital	Pittsburgh	0.5–0.7	Ibid.
Homes	Medford, OR	0.1–0.3	Berk et al., 1981; weatherized homes
10 Homes	Boston, MA	0.2	Moschandreas et al., 1981
2 Offices	Boston, MA	0.3	Ibid.
Art gallery	So. California	0.5	Shaver et al., 1983
2 Museums	So. California	0.1	Ibid; activated carbon air filtration
Art gallery	England	0.7	Davies et al., 1984
41 Homes	Tucson, AZ	0.3	Lebowitz et al., 1984
12 Homes	Houston, TX	<0.1	Stock et al., 1985; conventional air conditioning
Museums	So. California	0.45	Nazaroff and Cass, 1986
2 Museums	So. California	>0.67	Cass et al., 1988; high ventilation
3 Museums	So. California	0.3–0.4	Ibid; conventional air conditioning
2 Museums	So. California	0.1–0.2	Ibid; tight building
4 Museums	So. California	<0.1	Ibid; activated carbon air filtration
Office	New Jersey	0.22	Weschler et al., 1989; 0.6 ach
Office	New Jersey	0.54	Ibid; 4.0 ach
Cleanroom	New Jersey	0.71	Ibid; 8.2 ach
6 Homes	El Paso, TX	0.7	Stock and Venso, 1993; evaporative air cooling
4 Homes	Houston, TX	0.1	Ibid; conventional air conditioning
Office	So. California	0.3	Weschler et al., 1994; 0.3 ach
Office	So. California	0.7	Ibid; 1.9 ach
6 Homes	New Jersey	0.33	Zhang and Lioy, 1994a, Air-Conditioning (AC), windows closed
6 Homes	New Jersey	0.62	Ibid.; windows open, no AC
6 Homes	New Jersey	0.30	Ibid.; windows closed, no AC
40 Homes	Toronto	0.07	Liu et al., 1995, winter
40 Homes	Toronto	0.40	Ibid.; summer
25 Individuals	Greater Vancouver	0.18	Brauer and Brook, 1997; personal to outdoor, 9% of persn. time outdoors
Office	Munich	0.4–0.9	Jacobi and Fabian, 1997, natural vent
Classroom	Munich	0.5–0.8	Ibid.; natural ventilation
Gymnasium	Munich	0.5–0.9	Ibid.; natural ventilation
Home	Munich	0.5–1.0	Ibid.; natural ventilation
126 Homes	So. California	0.37	Avol et al., 1998
145 Homes	Mexico City	0.20	Romieu et al., 1998
3 Schools	Mexico City	0.3–0.4	Ibid.
Physics bldg	Thessaloniki	0.5–0.8	Drakou et al., 1998; natural vent.
Laboratory	Athens	0.2–0.6	Ibid.; mechanically ventilated
40 Homes	Montpellier, France	0.38	Bernard et al., 1999; winter
70 Homes	Montpellier, France	0.50	Ibid.; summer
70 Workplaces	Montpellier, France	0.45	Ibid.; summer

sinks, for a single compartment without filtration, is expressed in Equation 2:

$$d[O_{3\text{-indoors}}]/dt = E_x [O_{3\text{-outdoors}}] + s(t) - [O_{3\text{-indoors}}]\{k_d(A/V) + E_x + \Sigma_i k_i [chem_i]\} \quad (2)$$

where

$[O_{3\text{-indoors}}]$ is the indoor ozone concentration,

in units of ppb; $[O_{3\text{-outdoors}}]$ is the outdoor ozone concentration,

in units of ppb; s(t) is the time-varying rate at which ozone is being generated within the room, in units of $ppb\ h^{-1}$; $[chem_i]$ is the concentration of the ith (1st, 2nd, 3rd, etc.) chemical in the room air that reacts with

ozone, in units of *ppb*; and k_i is the second order rate constant for the reaction between ozone and the *i*th chemical in the room air, in units of $ppb^{-1} \, h^{-1}$.

The specific sources and sinks that influence indoor ozone concentrations are discussed in the following paragraphs. (Detailed presentation of models that can be used to estimate indoor ozone levels can be found in papers by Shair and Heitner, 1974 and Hayes, 1991.)

Outdoor Ozone Concentrations

Figure 2 shows outdoor ozone concentrations measured during 1996 at a relatively clean location, Death Valley National Monument, and a relatively polluted location, Burbank, California, USA (California Environmental Protection Agency, 1997). At the clean location, during winter months, ozone levels tend to be in the range of 30 to 40 ppb, while in summer months the levels are more commonly in the range of 40 to 60 ppb. In contrast to the Death Valley data, the ozone concentrations at Burbank have much larger maxima (mid-afternoon) and much smaller minima (early morning). During the winter months ozone maxima are close to 40 ppb, while in the summer months ozone maxima approach 140 ppb. Since a large fraction of outdoor ozone is derived from photochemical processes, it follows that outdoor ozone concentrations vary with the solar flux. Hence, daytime ozone concentrations tend to be much larger than nighttime levels, and daily ozone levels tend be much higher in the summer months than in the winter months. Furthermore, the difference between summer and winter ozone levels tend to increase as a location's latitude increases. In urban areas located in the northern region of the United States, the summer ozone levels are often five to ten times larger than the winter levels (US EPA, 1998).

The pronounced diurnal variation in Burbank ozone levels (see Figures 1 and 2) is characteristic of urban areas and is due not only to the diurnal variation in solar flux, but also to high emissions of nitric oxide (NO) from motor vehicles (Brace and Peterson, 1998). Ozone and nitric oxide react at a very fast rate (more details will follow). During daylight hours local ozone production is greater than nitric oxide emission rates, with the net result that ozone accumulates in the urban air. During hours of darkness, local ozone production is quite small and there is more than enough nitric oxide to react with the ozone that is present; the net result is that nitric oxide accumulates and the ozone levels are very low. (Note, however, that outdoor ozone levels are not always low at night. Ozone that is pro-

duced during the day can pass over an area downwind of its original source during the night (Wolff et al., 1977). Suburban and rural areas downwind of an urban area with severe photochemical smog might experience their peak ozone levels in the middle of the night if the transport time is on the order of half a day.) Elevated ozone levels are quite common in cities and regions downwind of cities in a large fraction of the United States. More than half of the US population currently lives in areas that exceed the federal ozone standard (US EPA, 1998).

Rate at Which Indoor Air is Exchanged with Outdoor Air

The air exchange rate has a large influence on the I/O ratio for ozone (see Table 2). In the absence of indoor sources, as the air exchange rate increases, the indoor ozone level becomes a larger fraction of the outdoor level. When indoor sources of ozone are present the effect of air exchange on indoor ozone levels depends on the relative magnitude of the indoor source(s) compared with the outdoor ozone level. Regardless, the underlying fact is that the indoor ozone concentration varies with the air exchange rate.

Persily (1989) has made more than 3000 air exchange measurements in 14 mechanically ventilated office buildings over a 1-year period. He found that the air exchange rate was most frequently in the range of 0.5 to 1.2 air changes/h (ach or h^{-1}). Ideally, the ventilation rate increases with the occupant density (ASHRAE, 1989). Hence one would expect larger ventilation rates in conference rooms or auditoriums (on the order of 4 to 6 ach if ASHRAE guidelines are followed) than in less densely occupied offices. Residential air exchange rates vary from a seasonal average of ~ 0.2 ach for tightly constructed housing to as high as 2 ach for loosely constructed housing (ASHRAE, 1997). Based on a statistical analysis of data from 2,844 households, Murray and Burmaster (1995) report a mean air exchange rate of 0.76 ach. Their analysis illustrates the influence of the season on air exchange. During the winter the 25th percentile value was 0.29 ach and the 75th percentile value was 0.67 ach; during the summer the 25th percentile value was 0.53 ach and the 75th percentile value was 1.92 ach. Hence, residential air exchange rates tend to be highest during the season when ozone levels are highest. In residences, ventilation rates tend to be smaller when air conditioning is present and operating, and larger in the absence of air conditioning. As one would expect, ventilation rates are also larger when windows are open (often >5 ach) than when they are closed (Alevantis and Girman,
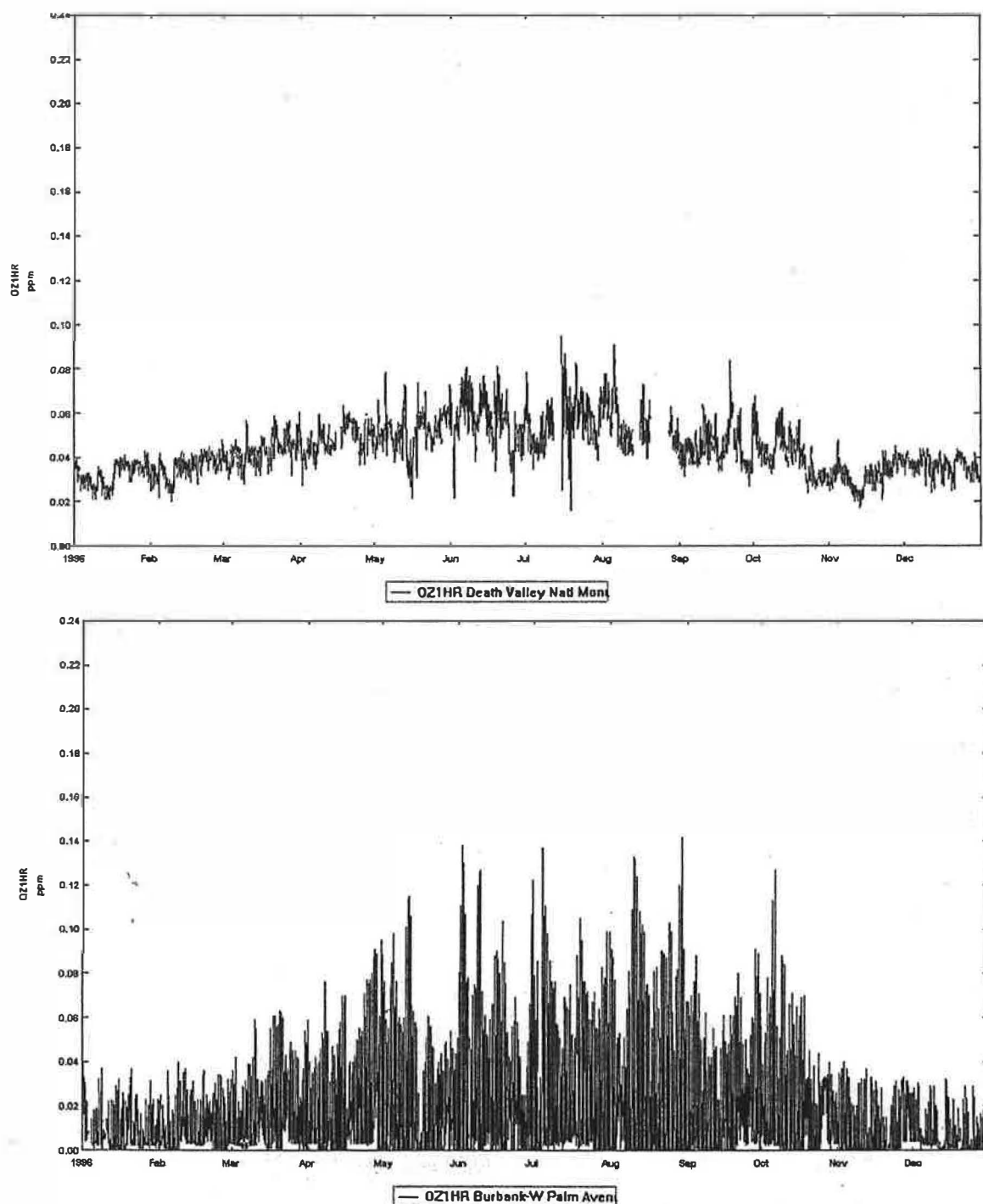
Fig. 2 Ozone levels (ppm) measured at Death Valley National Monument and Burbank, California, USA during 1996 (California Environmental Protection Agency, 1997)

1989). It follows that, in the absence of indoor sources, ozone levels tend to be larger in homes without air conditioning than in homes with, and larger when windows are open than when they are closed. These generalizations are consistent with measurements of indoor ozone levels in 126 Southern California homes (Avol et al., 1998); the investigators found that "... indoor ozone levels were largely determined by outdoor ozone levels and the duration of time that windows were kept open."

Removal by Indoor Surfaces

The product of the deposition velocity and the surface-to-volume ratio defines the first-order rate constant that applies to the removal of ozone by indoor surfaces, $k_d(A/V)$. This sink term for ozone can be directly

274

Table 3 Rate Constants (h^{-1}) for the Removal of Ozone by Surfaces in Different Indoor Environments

Indoor environment	Surface removal rate, $k_d(A/V)$, h^{-1}	Reference
Aluminum Room (11.9 m^3)	3.2	Mueller et al., 1973
Stainless Steel Room (14.9 m^3)	1.4	Ibid.
Bedroom (40.8 m^3)	7.2	Ibid.
Office (55.2 m^3)	4.0	Ibid.
Home (no forced air)	2.9	Sabersky et al., 1973
Home (forced air)	5.4	Ibid.
Department Store	4.3	Thompson et al., 1973
Office (24.1 m^3)	4.0	Allen et al., 1978
Office (20.7 m^3)	4.3	Ibid.
Office/Lab	4.3	Shair and Heitner, 1974
Office/Lab	3.2	Ibid.
Office/Lab	3.6	Ibid.
13 Buildings, 24 Ventilation Systems	3.6	Shair, 1981; assumes $A/V = 2.8$ m^{-1}
Museum	4.3	Nazaroff and Cass, 1986
Museum	4.3	Ibid.
Office/Lab	4.0	Weschler et al., 1989
Office/Lab	3.2	Ibid.
Office	2.5	Ibid.
Lab	2.5	Ibid.
Cleanroom	7.6	Ibid.
Telephone Office	0.8–1.0	Weschler et al., 1994; large office, small A/V
43 Homes	2.8±1.3	Lee et al., 1999

compared with the air exchange rate. In other words, if the surface removal rate constant is 3.5 h^{-1}, the surfaces are removing ozone at a rate equivalent to an air exchange rate of 3.5 h^{-1}. Numerous studies have measured "$k_d(A/V)$". Results from a number of these studies are summarized in Table 3. The values range from 1.4 h^{-1} in a stainless steel chamber to 7.6 h^{-1} in a highly ventilated device fabrication cleanroom. Lee et al. (1999) have measured ozone removal rates in 43 Southern California homes – the most extensive set of measurements in the literature. They report a mean surface removal rate constant of 2.80±1.30 h^{-1}. Earlier measurements in homes and offices are in good agreement with the values reported by Lee and coworkers (see Table 3).

The surface-to-volume ratio, A/V, varies with the indoor dimensions, surface coverings and furnishings. All else being equal, smaller rooms have larger surface-to-volume ratios than larger ones, and ozone removal by indoor surfaces is faster in smaller rooms than in larger ones. Furthermore, fleecy surfaces have more surface area than smooth surfaces. Rooms with fleecy surfaces such as carpeting, drapes and upholstered furniture tend to have larger surface removal rates for ozone than rooms without such appointments (Mueller et al., 1973; Sabersky et al., 1973). Hence the bedroom in Table 3 has a larger surface removal rate constant than offices with similar dimensions.

The deposition velocity, k_d, for ozone varies with the nature of the indoor surface. Sabersky et al. (1973) found that the rate at which ozone deposits to different

common surfaces varied by about a factor of 30. The deposition velocity also varies with indoor airflow conditions. A detailed discussion of ozone deposition velocities is contained in a paper by Nazaroff et al. (1993). Using estimates of the surface-to-volume ratio, the authors calculate ozone deposition velocities, based on studies reported in the literature, that range from 0.015 cm/s in a stainless steel room to 0.075 cm/s in a highly ventilated cleanroom. In typical homes and offices they calculate deposition velocities between 0.025 and 0.062 cm/s. Lee et al. (1999) report an average deposition velocity of 0.049±0.017 cm/s in 43 Southern California homes. Morrison (1999) has developed a general model of reactive gas deposition to indoor surfaces. This model predicts that the area averaged deposition velocity in a typical room would range from 0.02 to 0.06 cm/s. The good agreement among these studies facilitates estimating ozone removal rates when it is not practical to make measurements.

Reactions with Other Indoor Chemicals
A subset of chemicals can react with ozone fast enough to influence its indoor concentration. This will be discussed in detail in the section entitled *Reactions Between Ozone And Various Chemicals Found In Indoor Settings*. The point that is key to the present discussion is that the kind and concentration of indoor chemicals varies from setting to setting. Even within a given setting, the chemicals present vary with time of day, day of week and season reflecting varying sources and varying ventilation rates.

Table 4 Volatile organic compounds commonly found indoors: typical indoor concentrations and rate constants for their reaction with ozone. N. B.: units of concentration are "μg/m³" rather than "ppb", reflecting units used by Brown et al. (1994) in their review of the literature

Common indoor organic	Brown et al., 1994; weighted average[a]	Daisey et al., 1994; geo. mean[b]	Shields et al., 1996; median[c]	Girman et al., 1999; range, median[d]	Rate constant[e]
	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	
Ethanol	50–100	36	–	–	2.46×10^{-10}
Acetone	20–50	10.2	–	7.1–220, 29	2.46×10^{-10}
2-Propanol	–	5.6	–	–	2.46×10^{-10}
Toluene	20–50	9.8	6	1.6–360, 9	3.69×10^{-12}
1,1,1-Trichloroethane	20–50	24.3	–	0.6–450, 3.6	2.46×10^{-11}
m- & p-Xylene	10–20	9.1	5	0.8–96, 5.2	1.48×10^{-11}
Dichloromethane	10–20	1.4	–	0.5–360	2.46×10^{-11}
Decamethylcyclopentasiloxane	–	–	40	–	2.46×10^{-13}
p-Dichlorobenzene	5–10	–	0.2	0.3–85	1.72×10^{-12}
Ethyl acetate	5–10	1.1	–	0.2–65	2.46×10^{-10}
n-Decane	5–10	2.9	6	0.3–50	2.46×10^{-13}
Branched C10	–	–	5	–	2.46×10^{-13}
n-Undecane	1–5	7	9	0.6–58, 3.7	2.46×10^{-13}
n-Dodecane	1–5	10.4	7	0.5–72, 3.5	2.46×10^{-13}
n-Pentadecane	1–5	–	13	–	2.46×10^{-13}
n-Hexadecane	<1	–	11	–	2.46×10^{-13}
n-Tetradecane	1–5	–	11	–	2.46×10^{-13}
1,2,4-Trimethylbenzene	5–10	3.9	5	0.3–25	3.20×10^{-11}
Octamethylcyclotetrasiloxane	–	–	10	–	2.46×10^{-13}
Ethylbenzene	5–10	2.2	2	0.3–30	3.69×10^{-12}
Nonanal	5–10	–	–	1.2–7.9, 3.1	2.46×10^{-10}
2-Butanone	1–5	–	–	0.7–18	2.46×10^{-10}
Benzene	5–10	3.2	–	0.6–17, 3.7	1.72×10^{-12}
Tetrachloroethylene	5–10	2.7	4	0.3–50	2.46×10^{-11}
o-Xylene	5–10	3	2	0.3–38	2.46×10^{-10}
n-Hexane	1–5	1.8	–	0.6–21, 2.9	2.46×10^{-13}
Camphene	10–20	–	–	–	2.21×10^{-8}
1,2-Dichloroethylene	10–20	–	–	–	6.05×10^{-9}
Isoprene	–	–	–	–	2.95×10^{-7}
d-Limonene	20–50	6.7	6	0.3–140, 7.1	5.14×10^{-6}
a-Pinene	1–5	–	0.2	0.3–8.4	2.14×10^{-6}
Styrene	1–5	1.7	1.5	0.2–6.7	5.31×10^{-7}

[a] Based on a summary of fifty studies conducted in over 1200 buildings between 1978 and 1990. For a given VOC, the indoor geometric mean concentrations from multiple studies is summarized as a "weighted average"; of geometric means (WAGM); see the cited article for details

[b] Geometric means of the most frequently identified VOCs in 12 California office buildings, selected without regard to worker complaints. Included are naturally and mechanically ventilated buildings

[c] Based on a study that measured VOCs in 70 U.S. telephone buildings. Listed are the 19 most abundant VOCs identified in the administrative facilities (11 of the 70 buildings) and their median concentrations

[d] Range of indoor concentrations for 21 of the most abundant VOCs identified in the US Environmental Protection Agency BASE (Building Assessment Survey Evaluation) study. For 10 compounds, median concentrations are also reported. The cited database contains measurements from 56 buildings

[e] Rate constants are from the NIST Chemical Kinetics Database (Mallard et al., 1998); Atkinson et al. (1992); and Seinfeld and Pandis (1998)

Additional Factors

Outdoor ozone levels depend on temperature in a nonlinear fashion. There is little correlation for temperatures below 70°F, but a strong correlation for temperatures above 90°F (National Research Council, 1991). Hence, outdoor temperatures indirectly influence indoor ozone concentrations. Temperature also influences indoor ozone levels in at least two other ways. As the difference between indoor and outdoor temperatures increases, the air exchange rate in naturally ventilated buildings increases. This, in turn, increases the outdoor-to-indoor transport of ozone, but dilutes the concentration of ozone generated by indoor sources. To a lesser extent, temperature affects the deposition velocity of ozone. At higher temperatures, the deposition velocity of ozone is slightly larger.

Relative humidity also influences indoor ozone levels. The higher the relative humidity, the larger the deposition velocities of ozone to different surfaces and the larger the surface removal rate. The magnitude of this effect varies with the nature of the surface. The more hydrophilic (water loving) the surface, the larger the effect. However, compared with factors discussed in the preceding paragraphs, the influences of temperature and relative humidity (RH) are relatively small.

Table 5 Half-lives for the reaction of ozone with volatile organic compounds commonly found in indoor air

Common indoor organics	50 ppb O3 half-life	50 ppb O3 half-life	100 ppb O3 half-life	100 ppb O3 half-life
	hours	days	hours	days
Ethanol	15700	650	7850	325
Acetone	15700	650	7850	325
2-Propanol	15700	650	7850	325
Toluene	1040000	43500	522000	21700
1,1,1-Trichloroethane	157000	6500	78300	3250
m-p-Xylene	260840	10868	130420	5434
Dichloromethane	156504	6521	78252	3261
Decamethylcyclopentasiloxane	15700000	652000	7820000	326000
p-Dichlorobenzene	2240000	93000	1120000	46500
Ethyl acetate	15700	650	7850	325
n-Decane	15700000	652000	7820000	326000
Branched C10	15700000	652000	7820000	326000
n-Undecane	15700000	652000	7820000	326000
n-Dodecane	15700000	652000	7820000	326000
n-Pentadecane	15700000	652000	7820000	326000
n-Hexadecane	15700000	652000	7820000	326000
n-Tetradecane	15700000	652000	7820000	326000
1,2,4-Trimethylbenzene	120000	5020	60200	2510
Octamethylcyclotetrasiloxane	15700000	652000	7820000	326000
Ethylbenzene	1040000	44000	520000	22000
Nonanal	15700	650	7850	325
2-Butanone	15700	650	7850	325
Benzene	2230000	93000	1120000	46500
Tetrachloroethylene	157000	6500	78300	3250
o-Xylene	15700	650	7850	325
n-Hexane	15700000	652000	7820000	326000
1,2-Dichloroethylene	636	27	318	13
Camphene	174	7.2	87	3.6
Isoprene	13	0.54	6.5	0.27
d-Limonene	0.75	0.03	0.37	0.02
a-Pinene	1.80	0.08	0.90	0.04
Styrene	7.25	0.30	3.62	0.15

The sum of the sinks for indoor ozone (i.e., the air exchange rate, the surface removal rate and the rate of reaction with other airborne pollutants) determines the 1st order rate constant for ozone decay in a given indoor setting. Absent chemicals that can react with ozone fast enough to influence its indoor concentration, this rate constant lies between 1 and 10 h^{-1}, with values in the range of 4 to 6 h^{-1} most common (see Table 3 and the subsection entitled *Rate at Which Indoor Air is Exchanged With Outdoor Air*). The latter values translate to half-lives between 10 and 7 min.

Variability of Indoor Ozone Levels

Indoor ozone concentrations can vary from hour-to-hour, day-to-day, and season-to-season, as well as from room-to-room and structure-to-structure (Weschler and Hodgson, 1992a). It is not unusual for indoor ozone levels to change 30 or 40 ppb in less than 1 h (see, for example, Figure 1). Given that indoor ozone levels vary with multiple factors including time-of-day, weather conditions, ventilation parameters, geographic location and season, it is not reasonable to speak of a single indoor ozone concentration that is representative of most indoor environments.

Reactions between Ozone and Indoor Pollutants

Factors That Influence Chemical Reactions In Indoor Environments

The claim is sometimes made that ozone can remove other pollutants from indoor air. This statement is misleading. To properly evaluate chemical reactions between ozone and other pollutants in indoor settings, it is necessary to understand the factors that influence indoor air chemistry. These include thermodynamics, kinetics, reactant concentrations and air exchange rates.

Chemical thermodynamics addresses the overall energetics of a reaction – the driving potential. In contrast, chemical kinetics "... deals with the rate of change from initial to final states under non-equilibrium conditions" (Hawley, 1971). Although reactions between ozone and most other compounds are thermody-

namically favorable, in the majority of cases they are quite slow at ambient temperatures and ozone concentrations (for specifics, see below).

The concentrations of the reactants influence the rate at which a chemical transformation occurs. Most indoor reactions are bimolecular processes, and their rates scale linearly with the concentration of each of the reacting species.

For a homogeneous chemical reaction to influence an indoor setting, it must occur at a rate that is comparable to, or faster, than the air exchange rate (Weschler and Shields, 2000). The air exchange rate, coupled with the air change effectiveness (mixing factor), determines the time available for gas-phase indoor pollutants to interact. The air exchange rate also influences the concentration of the reactants (and, hence, the rate at which the reaction occurs – see above). If a reactant has primarily indoor sources, greater air exchange with outdoors reduces its indoor concentration. If a reactant has primarily outdoor sources, greater air exchange increases its indoor concentration.

Volatile Organic Compounds

Volatile organic compounds (VOCs) are so designated because of their boiling points. The lower boiling point range for VOCs is loosely 50–100 °C, while the upper boiling point range is 240–260°C (European Commission, 1997). Numerous investigators have measured volatile organic compounds in indoor settings. Table 4 presents a compilation of the most frequently identified VOCs as reported in four papers that have recently appeared in the peer reviewed literature. Among the VOCs that are listed in Table 4, there are certain compounds that are identified in one of the cited studies but not another. This reflects, in part, the different analytical methods that were used in the various studies. Taken together, columns 2 through 5 in Table 4 provide a reasonable summary of the more commonly identified indoor VOCs.

Reactions between ozone and each of the compounds listed in Table 4 are thermodynamically favorable (i.e., the energetics for these reactions are such that, given sufficient time, they will occur). However, the amount of time required for these reactions to occur varies from compound to compound. The presence of ozone will only significantly alter the concentration of those particular compounds that react with ozone on a time scale comparable to or faster than the air exchange rate. Rate constants for the reaction between ozone and a large number of compounds have been reported in peer reviewed literature and have been summarized in review articles and textbooks (e.g., NIST Standard Reference Database # 17, Mallard et al.,

1998; Seinfeld and Pandis, 1998). The final column in Table 4 lists rate constants for the reaction of ozone with each of the listed VOCs. The overall intent of the tabulation is to evaluate the potential for ozone to alter the concentration of commonly encountered indoor VOCs.

When ozone is present at a concentration significantly larger than that of a given VOC, the half-life of that VOC is independent of its own concentration and depends only on the ozone concentration. Given the rate constants listed in Table 4 it is a simple matter to calculate the half-life for the tabulated VOCs at different ozone concentrations. Table 5 presents such half-lives at indoor ozone concentrations of 50 and 100 ppb. To facilitate comparisons, the half-lives are tabulated in units of both hours and days.

We can also apply the concept of half-lives to air exchange rates. The time required for half of the indoor air to be replaced with ventilation air is referred to as the half-life for a parcel of indoor air. At typical air exchange rates, the half-life for a parcel of indoor air is in the range of 15 min to 3 h. If the half-life for a parcel of indoor air is significantly less than the half-life for a given chemical reaction, that reaction will not have sufficient time to impact the indoor environment in question. It is apparent from Table 5 that the reactions between ozone and most commonly occurring indoor organic compounds are too slow to compete with typical air exchange rates. Indeed, the first twenty-seven compounds listed in Table 5 react with ozone so slowly that it would take more than a year for 50 ppb of ozone to reduce the concentration of any of these compounds by half. To state it even more directly, an indoor ozone concentration of 50 or even 100 ppb will have a negligible effect on the concentrations of most of the VOCs commonly found in indoor air.

There is a subset of VOCs that do react with ozone fast enough to compete with air exchange rates. These compounds have been grouped together at the very bottom of Tables 4 and 5, beginning with 1,2-dichloroethylene and including camphene, isoprene, d-limonene, α-pinene and styrene. The feature that these compounds have in common is that they contain one or more unsaturated carbon-carbon bonds. Ozone reacts with the compounds at these points of unsaturation. The reaction proceeds through an ozonide that rapidly decomposes into one of two possible combinations of a carbonyl and a biradical:

1. $O_3 + R_1R_2C=CR_3R_4 \rightarrow$ ozonide
2a. ozonide $\rightarrow R_1C(O)R_2 + [R_3R_4C \cdot OO \cdot]^*$ or
2b. ozonide $\rightarrow [R_1R_2C \cdot OO \cdot]^* + R_3C(O)R_4$

This is shown schematically as:
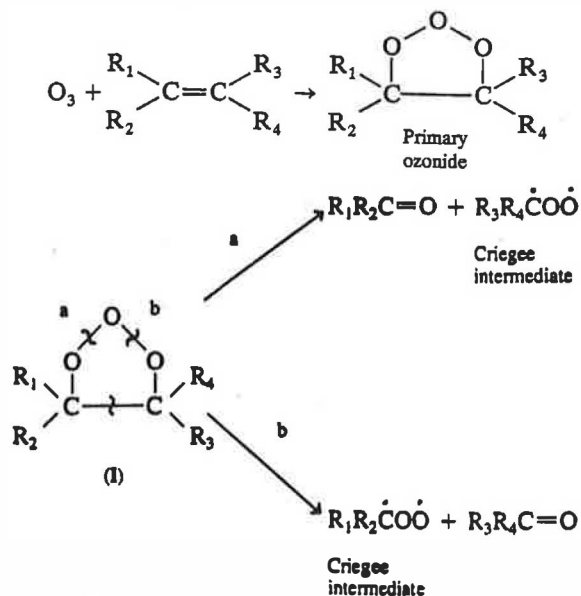
The energy rich biradical ($[R_3R_4C \cdot OO \cdot]^*$ or $[R_1R_2C \cdot OO \cdot]^*$) then rearranges or reacts via several mechanisms (see Atkinson et al., 1995 for details). Intermediate products include highly reactive species such as the hydroxyl, hydroperoxy, and alkylperoxy radicals. Stable products include aldehydes, ketones and organic acids. When ozone reacts with a non-cyclic unsaturated organic compound, the concentration (molar ratio) of the sum of the products is at least twice the initial concentration of the precursor.

A series of recent studies has shown that the reaction between ozone and unsaturated hydrocarbons can lead to hydroxyl radical concentrations in indoor air that are within an order of magnitude of those in outdoor air at midday and higher than the concentration of the hydroxyl radical outdoors at night (Weschler and Shields, 1996b, 1997b). Subsequent reactions between the hydroxyl radical and other indoor pollutants generate still other radicals, as well as stable oxidized compounds containing one or more $-C=O$ (carbonyl), $-COOH$ (carboxylate), and/or $-OH$ (hydroxyl) functional groups.

A major product derived from reactions between ozone and most (those with terminal double bonds) of the unsaturated hydrocarbons found indoors is formaldehyde. Other products include methacrolein and methyl vinyl ketone (from isoprene), 4-acetyl-1-methylcyclohexene (from limonene) and benzaldehyde (from styrene) (Finlayson-Pitts and Pitts, 1986, 2000). Recent detailed studies have identified pinonaldehyde, norpinonaldehyde, pinonic acid, norpinonic acid, pinic acid and C10 hydroxy dicarbonyls as products of the ozone/α-pinene reaction (Yu et al., 1998) and limonic acid, limononic acid, 7-hydroxylimononic acid and 7-

hydroxy-keto-limononic acid as products of the ozone/d-limonene reaction (Glasius et al., 2000). Many of these products are more irritating than their precursors. Karlberg et al. (1992) have noted that some of the oxidation products of d-limonene have greater skin allergenicity than limonene itself. Recent studies by Wolkoff and co-workers (1999, 2000) have demonstrated that the products of selected ozone/terpene (isoprene) reactions are significantly more irritating to mice than either ozone or terpenes (isoprene) alone.

Several studies conducted over the past decade provide results that support the above discussion of reactions between ozone and commonly occurring indoor VOCs. In a 1992 paper, Weschler, Hodgson and Wooley examined the effect that ozone had on VOCs emitted by new carpets that were typical of those used in residences, schools and offices. The different carpets emitted different groupings of saturated and unsaturated VOCs. Hence, the specific compounds that reacted with ozone and the compounds produced from these reactions varied from carpet to carpet. However, the general observations were the same – ozone did not affect the concentrations of the saturated VOCs (with the exception of BHT); ozone did decrease the concentrations of the unsaturated VOCs (including styrene, 4-vinylcyclohexene, and 4-phenylcyclohexene); however, this decrease was accompanied by an increase in the concentration of aldehydes (including formaldehyde, acetaldehyde, benzaldehyde and a series of C5- to C10-aldehydes).

Zhang et al. (1994b) measured indoor and outdoor aldehyde and ozone concentrations at 6 residential homes located in suburban New Jersey. They concluded "... indoor ozone chemistry was believed to play a role in generating several of the measured aldehydes." For the period studied, the indoor exposure of the residents to formaldehyde and total aldehydes was much greater than their outdoor exposure.

Shaughnessy, Weschler and McDaniels (1999) have examined the effect of ozone on the concentrations of VOCs found in environmental tobacco smoke (ETS). Their measurements focused on 18 VOCs, chosen because they represented different types of VOCs and because they were among the most abundant organic constituents of ETS. At moderate ozone concentrations (80–115 ppb), ozone had little effect on the monitored VOCs. At high ozone concentrations (1000–1400 ppb), ozone reduced the concentration of those compounds with unsaturated carbon-carbon bonds. However, based on a comparison of mass concentrations, this reduction was more than matched by an increase in the concentration of a series of aldehydes, including formaldehyde, acetaldehyde and benzaldehyde. At the

lower ozone concentrations, even a very modest ventilation rate (on the order of 0.1 ach) would have produced a greater reduction in the VOCs than that produced by ozone.

It has been previously stated that reactions between ozone and unsaturated hydrocarbons produce both highly reactive free radicals and stable compounds. The stable compounds can be further divided into gas phase and condensed phase species. For example, Grosjean et al. (1992, 1993) have estimated that 22% of the products produced in the ozone/d-limonene reaction occur as aerosols. In a recent study Weschler and Shields (1999) have shown that reactions between ozone and terpenes can be a significant source of indoor sub-micron particles. In a set of experiments conducted in adjacent identical offices, ozone and a terpene (either d-limonene, α-terpinene or a commercial terpene based cleaner containing α-pinene) were deliberately introduced into one office while the other office served as a control. For each terpene examined, particle concentrations were significantly larger in the office with the added ozone (200–300 ppb) than in the control office without the added ozone. This difference was greatest for particles in the 0.1–0.2 micron diameter size range; over time, differences developed in the larger size ranges. The particle production was also greatest when the terpene was d-limonene, although significant particle production was noted for each of the selected terpenes. In the case of d-limonene, the

number concentration of particles in the 0.1–0.2 micron size range was as much as 20 times larger in the office with the added ozone as in the control office (6×10^3 vs. 3×10^2 particle/cm^3). In another set of experiments, d-limonene was deliberately introduced into one of the offices, but ozone was not artificially added to either office. Instead, the indoor ozone concentrations were those that happened to be present as a consequence of outdoor-to-indoor transport – typically between 2 and 40 ppb. In the office that contained supplemental d-limonene, the concentrations of the 0.1–0.2 μm particles tracked those of indoor ozone (the limiting reagent) and were as much as 10 times greater than levels measured in the comparable office that did not contain supplemental d-limonene. At an indoor ozone concentration of 23 to 28 ppb, the mass concentration difference (sub-micron particles) between the two offices was approximately 20 μg/m^3. A subsequent study by Wainman et al. (2000) reaffirms the significant increase in submicron particles that can result from ozone/terpene reactions under typical indoor conditions. Together these studies further illustrate the potential for reactions among commonly occurring indoor pollutants to markedly influence indoor environments. They also demonstrate a coupling between outdoor ozone and indoor submicron particles. Since outdoor submicron particles correlate with outdoor ozone levels, indoor particles generated from ozone/terpene reactions can vary coincidentally with outdoor fine particles. This bears on the epidemiological studies demonstrating an association between incremental changes in outdoor particle concentrations and increases in the rates of morbidity and mortality.

To summarize, at concentrations below 50 ppb ozone does not react with the majority of indoor VOCs (those with saturated carbon-carbon bonds) fast enough to compete with typical ventilation rates. In the case of those VOCs that do react with ozone fast enough to compete with ventilation (a subset of VOCs with unsaturated carbon-carbon bonds), reaction with ozone produces still other contaminants. In some cases the products may be more irritating than their precursors (Karlberg et al., 1992; Wolkoff et al., 1999, 2000).

Very Volatile Organic Compounds and Inorganic Gases

The compounds listed in Table 4 are classified as *volatile organic compounds*. There are other compounds present in indoor air that are even more volatile than these species and are referred to as *very volatile organic compounds* (*VVOCs*). The category of VVOCs includes compounds such as formaldehyde, acetaldehyde and propane. Indoor air also contains inorganic gases such

Table 6 VVOCs and inorganic gases commonly found indoors: typical indoor concentrations and rate constants for their reaction with ozone

VVOCs and inorganic gases	Median indoor concentration[a]	Rate constant[b]
	ppb	ppb^{-1}s^{-1}
Formaldehyde	30	5.17×10^{-14}
Acetaldehyde	5	1.48×10^{-10}
Methane	2000	2.95×10^{-11}
Ethane	2.5	2.46×10^{-13}
Propane	1.5	2.46×10^{-13}
n-Butane	4	2.46×10^{-13}
Ethene	1.5	3.91×10^{-8}
Propene	0.5	2.48×10^{-7}
Isobutene	0.5	2.83×10^{-7}
Nitric Oxide (NO)	0–100	4.43×10^{-4}
Nitrogen Dioxide (NO$_2$)	30	7.87×10^{-7}
Ammonia (NH$_3$)	10	$<2 \times 10^{-10}$
Sulfur Dioxide (SO$_2$)	1	2.46×10^{-12}
Hydrogen Sulfide (H$_2$S)	1	9.91×10^{-6}
Dimethylsulfide (CH$_3$SCH$_3$)	1	1.97×10^{-8}
Carbon Monoxide (CO)	1000	9.84×10^{-15}

[a] Taken from Table 2 in Weschler and Shields, 1996; see footnotes in cited table for original sources
[b] Rate constants are from the NIST Chemical Kinetics Database (Mallard et al., 1998); Atkinson et al. (1992); and Seinfeld and Pandis (1998)

Table 7 Half-lives for the reaction of ozone with VVOCs and inorganic gases commonly found in indoor air

Common indoor VVOCs and inorganic gases	50 ppb O3 half-life	50 ppb O3 half-life	100 ppb O3 half-life	100 ppb O3 half-life
	hours	days	hours	days
Formaldehyde	74500000	3100000	37200000	1550000
Acetaldehyde	26100	1100	13000	550
Methane	130000	5400	65000	2700
Ethane	15700000	652000	7830000	326000
Propane	15700000	652000	7830000	326000
n-Butane	15700000	652000	7830000	326000
Ethene	98.4	4.1	49.2	2.1
Propene	15.5	0.65	7.75	0.32
Isobutene	13.6	0.57	6.8	0.28
Nitric Oxide (NO)	0.0087	0.0004	0.0043	0.0002
Nitrogen Dioxide (NO_2)	4.89	0.20	2.45	0.10
Ammonia (NH_3)	15600	652	7800	326
Sulfur Dioxide (SO_2)	1570000	65000	783000	32500
Hydrogen Sulfide (H_2S)	0.39	0.02	0.19	0.01
Dimethylsulfide (CH_3SCH_3)	196	8.2	98	4.1
Carbon Monoxide (CO)	391000000	16300000	195000000	8150000

as carbon monoxide and the nitrogen oxides. Table 6 lists VVOCs and inorganic gases commonly found in indoor air, as well as typical indoor concentrations, and rate constants for their reaction with ozone. The half-lives for these compounds in the presence of 50 and 100 ppb of ozone are listed in Table 7.

It is apparent from Table 7 that at 50 or 100 ppb, ozone has a negligible effect on the concentration of species such as formaldehyde, acetaldehyde, ammonia, sulfur dioxide and carbon monoxide. Although the reaction between ozone and hydrogen sulfide is relatively fast, the reaction between ozone and dimethylsulfide is much slower – too slow to effectively compete with air exchange.

The fastest reaction listed in Table 6 is that between ozone and nitric oxide. We noted in an earlier section the importance of this reaction in determining the net ozone concentration outdoors. It is also important in determining net ozone levels indoors, both directly and indirectly. Figure 3 shows indoor ozone and nitric oxide concentrations measured during June 1993 at a telephone office in Burbank, California, USA. In this figure indoor ozone and nitric oxide anti-correlate – significant levels of ozone only accumulate when little nitric oxide is present and vice-versa. In indoor settings in which these compounds are present solely as a consequence of outdoor-to-indoor transport, the indoor reaction between ozone and nitric oxide has its greatest impact when "the tide turns" and one of these species shifts from increasing to decreasing in concentration (Axley et al., 1993; Weschler et al., 1994). In the presence of an indoor nitric oxide source (e.g., a gas stove or an unvented kerosene heater), this reaction is important anytime ozone is also present (Zhang et al.,

1994a). Under such conditions, the measured concentration of indoor ozone is a *net* concentration; it is the concentration that remains after any nitric oxide emitted indoors or introduced from outdoors has been titrated. The product of the ozone/nitric oxide reaction is nitrogen dioxide.
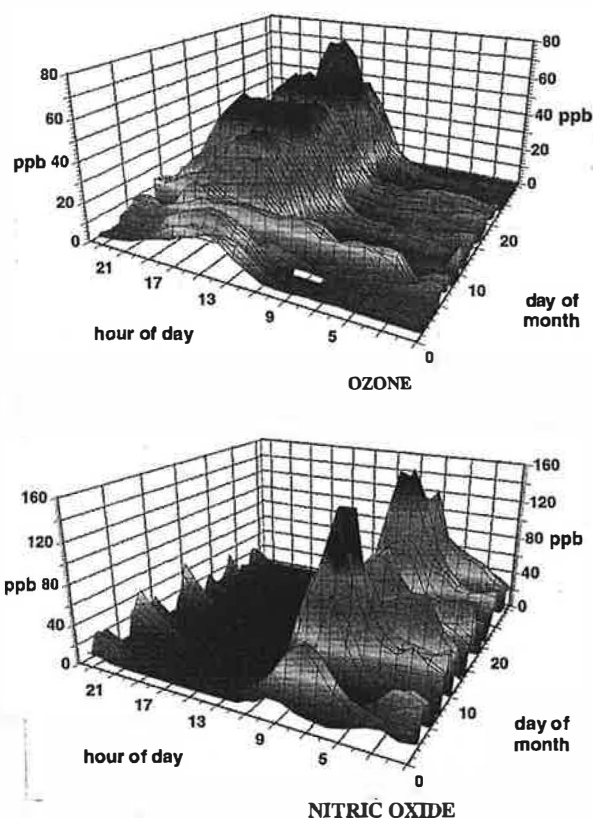

Fig. 3 Indoor levels of ozone (top) and nitric oxide (bottom) for the month of June, 1993 at a telephone office in Burbank, CA (Weschler et al., 1994b).

281

The reaction between ozone and nitrogen dioxide is slower than that with nitric oxide, but still fast enough to compete with moderate air exchange rates. The primary product of the ozone/nitrogen dioxide reaction is the nitrate radical. The nitrate radical is photolytically unstable and does not accumulate outdoors during daylight hours. Indoors, in the absence of direct sunlight, the nitrate radical can accumulate (analogous to outdoors at night). The nitrate radical is very reactive; reaction rates with most indoor organic pollutants are significantly faster than typical air exchange rates (Weschler et al., 1992b; Weschler et al., 1994; Weschler and Shields, 1996a). Given its high reactivity, the nitrate radical is short-lived and is ultimately converted to nitric acid in typical indoor environments.

In summary, for VVOCs and inorganic gases, the situation is similar to that described for VOCs–ozone reacts with only a fraction of these compounds fast enough to compete with average ventilation rates. In the case of those compounds that do react "fast enough", the reactions with ozone produce additional pollutants. (Products that result from the reaction of ozone with compounds listed in Table 7 and not mentioned in the preceding paragraphs include sulfur dioxide from the hydrogen sulfide reaction and formaldehyde from the reaction with ethene, propene or isobutene).

Airborne Particles

Ozone has little effect on the concentration of airborne particles. There are three principal reasons for this: i) most of the constituents of airborne particles react with ozone at rates too slow for the reactions to be of significance indoors; ii) collisions between ozone molecules and airborne particles are much less frequent than collisions between ozone and common VOCs or inorganic gases; and iii) since a particle consists of literally millions of molecules, it takes millions of reactions between ozone molecules and a particle to alter the chemical nature of the particle. The following paragraphs discuss these factors in more detail.

Fine particles (<2.5 μm diameter) are roughly 30–50% water-soluble salts (e.g., ammonium sulfate, ammonium bisulfate, letivocite, ammonium nitrate, sodium chloride), 10–40% carbonaceous material and 5–20% trace elements. Coarse particles (>2.5 μm diameter) are roughly 5–20% water-soluble salts, 5–20% carbonaceous material and 30–60% oxides and minerals (e.g., silicates; calcium, aluminum, and magnesium hydroxides; calcium carbonate; calcium sulfate; iron oxides). The carbonaceous material found in particles is a mixture of elemental and organic carbon. The majority of the organic carbon consists of saturated organic compounds with lesser amounts of unsaturated species. It is only these latter constituents of airborne particles that can react with ozone at a meaningful rate. Typically less than 5% of the constituents of fine particles and less than 3% of the constituents of coarse particles react with ozone fast enough for moderate ozone levels (50 to 100 ppb) to significantly alter their concentrations.

For ozone to react with an airborne particle, a collision must occur between an ozone molecule and a particle. The frequency of such collisions is relatively small compared with the frequency of collisions between ozone and vapors (or gases) commonly found indoors. To fully appreciate this it is useful to compare the number of particles in a cubic centimeter of air with the number of molecules of a given vapor phase compound in the same volume of air. The number of particles in a given volume of air decreases as the size of the particles increase (see Finlayson-Pitts and Pitts, p. 734, 1986; Hinds, p. 277, 1982). For particles in the 0.1–0.2 μm diameter size range, typical indoor concentrations are between 30 and 500 particles/cm^3. For particles in the 0.5–0.6 μm diameter size range, typical indoor concentrations are between 0.03 and 0.5 particles/cm^3. In contrast, in units of molecules per cubic centimeter, a 5 ppb VOC has a concentration of 1×10^{11} molecules/cm^3. The probability of an ozone molecule colliding with a particle is many orders of magnitude less likely than with a VOC.

The *mass accommodation coefficient* is defined as the number of "sticks" per total number of collisions. Tang and Lee (1987) have measured an accommodation coefficient of 5×10^{-4} for ozone striking aqueous surfaces. We are unaware of measurements of accommodation coefficients for collisions between ozone and airborne particles. However, the mass accommodation coefficients are expected to be similar to those measured for sulfur dioxide/particle collisions (Weschler et al., 1992b). The latter are in the range of 10^{-3} to 10^{-4} (Judeikis et al., 1978). When a "stick" occurs in the vicinity of a constituent that contains an unsaturated carbon-carbon bond, there is the potential for ozone altering a molecule associated with the particle. However, even if the collision and "stick" results in the transformation of one of the molecules associated with the particle, it has little effect on the overall composition of the particle. A unit density 0.1-μm diameter particle contains approximately 10^6 molecules; a 0.5-μm diameter particle contains approximately 10^8 molecules. An exceedingly large number of reactions between ozone molecules and an individual particle are necessary before the chemical composition of the particle is altered significantly. The larger the particle, the greater the num-

ber of collisions and subsequent reactions with ozone that are necessary. Yet the larger the particle, the shorter its residence time in air. Hence, ozone is even less effective at altering the composition of coarse particles.

Compounds Associated with Surfaces

In addition to reacting with a small subset of indoor airborne chemicals, ozone can also react with a subset of chemicals that constitute or are adsorbed on indoor surfaces. Examples include natural rubbers and neoprene; compounds associated with latex paint, linoleum and carpet; unsaturated constituents of waxes and polishes; and unsaturated semi-volatile organics (SVOCs) adsorbed on indoor surfaces. Such reactions are referred to as *heterogeneous reactions*, in contrast to gas phase reactions, which are termed *homogeneous reactions*. Heterogeneous reactions involving ozone have a number of undesirable consequences, including cracking of stressed rubber, fading of dyes, damage to photographic materials and deterioration of books (Brimblecombe, 1990). Such reactions can also be a source of volatile, and sometimes highly odorous, aldehydes and ketones, as noted in the following paragraphs.

The section on *Volatile Organic Compounds* discussed a study by Weschler, Hodgson and Wooley (1992c) that examined interactions between ozone and several brands of carpets. In addition to products resulting from the reaction of ozone with selected VOCs emitted by the new carpets, the investigators also identified several higher molecular weight aldehydes (n-C5 to n-C10 aldehydes – pentanal, hexanal, heptanal, octanal, nonanal and decanal) that had no identified gas phase precursors. These compounds were apparently derived from reactions between ozone and unsaturated organic compounds associated with the carpet or carpet backing. Possible precursors included unsaturated fatty acids such as oleic, linoleic or arachidonic acid.

Morrison and Nazaroff (1999) have extended the ozone carpet studies just described. They aged 4 different samples of carpet in a ventilated enclosure for more than a year. The samples were then exposed to 100 ppb of ozone in a 10.5 L chamber for 2 to 5 days. Oxidized organic compounds coming off of the carpets were measured during and after the ozone exposure. One of the carpets – a residential, nylon fiber, cut pile carpet – emitted significant quantities of n-C4 to n-C11 aldehydes, as well as 2-nonenal. The 2-nonenal is especially significant since it has a very low odor threshold – 0.0019 ppb. Even when the ozone exposure ceased, the carpets continued to release the aldehydes. Weschler et al. (1992c) had made similar observations. These com-

pounds apparently sorb to the carpet surface after they have formed, and the carpet becomes a reservoir for the aldehydes, releasing them long after the ozone exposure ends. Using a steady-state model and the measured emission rates, Morrison and Nazaroff estimated that "occupants could smell these compounds for years after installation of this carpet in a typical home". Morrison has further suggested that ozonide intermediates may help to explain the somewhat delayed release of certain oxidation products, such as 2-nonenal, from carpet surfaces (Morrison, 1999). This is an interesting hypothesis with broad implications and warrants further examination.

In a study that was conducted in residences in the greater Boston area, Reiss and co-workers (1995b) found a correlation between the removal of ozone by indoor surfaces and the formation of certain aldehydes, ketones and organic acids. The authors noted that their results were confounded by variations in temperature and relative humidity that occurred during the study. Nonetheless, they concluded, "... ozone reactions may account for a measurable portion of the concentration of polar VOCs (e.g., aldehydes, ketones) found in residential environments."

Paints, especially "low VOC paints", commonly use linseed oil as a drying agent. Linseed oil contains a number of unsaturated fatty acids, including linoleic acid and linolenic acid. Andersson et al. (1996) have demonstrated that when such paints are used indoors in the presence of ozone, a series of aldehydes and organic acids are produced. Major products include propanal, hexanal, propanoic acid, and hexanoic acid, with lesser amounts of formaldehyde, acetaldehyde, pentanal, octanal, and nonanal.

Morrison and Hodgson (1996) exposed various constituents of HVAC systems to 100 ppb of ozone in 10.5-L chambers that were ventilated at 5.7 h^{-1}. They also collected samples of VOCs and aldehydes from the ventilation system of a new building. In general, they found that the contribution of these materials to VOCs and aldehydes in buildings are "... likely to be low". However, they did find that exposures of certain HVAC materials to 100 ppb of ozone resulted in increased concentrations of n-C5 to n-C10 aldehydes. In the case of a new neoprene duct liner they measured a combined n-C5 to n-C10 aldehyde emission rate of approximately 400 $\mu g/m^2h$, large enough to impact the indoor concentrations of these aldehydes under typical conditions.

On a molecular level, the interactions of ozone with surfaces are not as well understood as the interaction of ozone with gas phase species. In the section on airborne particles, *mass accommodation coefficients* (i.e., the

283

number of "sticks" per total number of collisions) were introduced. For surfaces, the mass accommodation coefficient varies with the nature of the surface, compounds adsorbed on the surface, temperature and relative humidity. Typical mass accommodation coefficients for glass, latex paint, and wall paper (vinyl and paper) are in the range of 10^{-5} to 10^{-7} (Reiss et al., 1994). When a "stick" occurs the ozone molecule can react with surface constituents to produce products, including VOCs, or the ozone molecule can decompose through a series of surface assisted steps. For a given VOC, the *VOC formation factor*, κ, is defined as the number of molecules of VOC formed on the surface divided by the total number of "sticks". Different VOCs have different VOC formation factors. Once a VOC is formed on a surface, it can leave the surface and enter the gas phase. Reiss et al. (1995a) determined VOC formation factors for reactions between ozone and various types of interior latex paints. Four different brands of paint were applied to the inside surfaces of glass tubes that served as flow reactors. Air containing ozone (49 to 147 ppb) was passed through the tubes and the concentrations of selected organics were measured upstream and downstream of the tube. The flow of ozone through the tube was too fast for homogeneous chemistry to occur; the only reactions that were possible were heterogeneous reactions. The authors found that, for two of the paints, formaldehyde was produced in significant amounts – the formaldehyde formation factor for these paints ranged from 0.1 to 0.3. The authors hypothesized that the formaldehyde resulted from ozonation of unsaturated residues in the vinyl resins of the paints. Based on these results, they conducted modeling studies that indicated that heterogeneous reactions between ozone and certain latex paints could contribute significant quantities of formaldehyde to indoor settings.

Most of the reported reactions between ozone and surfaces involve constituents or sorbed compounds with unsaturated carbon-carbon bonds. Surfaces that possess only saturated carbon-carbon bonds are not expected to react with ozone or to emit significant quantities of oxidized species as a consequence of such reactions.

Ozone as an "Air Purifying" Agent

Several companies currently offer ozone generators that claim to remove chemical pollutants from indoor air. The devices are promoted as being safe for use indoors, which implies ozone concentrations of 100 ppb or less (see Table 1). However, the preceding sections have presented basic chemical and physical data indicating that ozone concentrations less than 100 ppb will have negligible effects on the majority of gaseous and condensed phase pollutants found in indoor environments. In a 1995 review, Boeniger examined the use of ozone generating devices for the purpose of improving indoor air quality. He concluded that for many of the chemicals found in indoor air it would take months or years for ozone, at 100 ppb, to significantly reduce their concentration. Tables 5 and 7 in the present report – expanded versions of a table presented in the Boeniger review – further illustrate this theme.

As noted above, there are some indoor pollutants that do react with ozone at a meaningful rate – primarily those compounds with unsaturated carbon-carbon bonds. However, these compounds typically represent less than 10% of the total gas phase pollutants (see sections on VOCs and VVOCs and inorganic gases). Furthermore, reductions in the concentration of these unsaturated hydrocarbons are, to a large extent, matched by an increase in the concentration of a series of aldehydes, ketones, organic acids and other oxidized hydrocarbons that are products of the ozone/unsaturated hydrocarbon reactions. In outdoor air, oxidation of an organic often increases its water solubility and hence the rate at which it is removed by rain (Finlayson-Pitts and Pitts, 1986, 2000). In indoor settings, absent precipitation, oxidation accomplishes little in the way of "cleansing". Indeed, the oxidized products are often more irritating than their precursors (Wolkoff et al., 1999, 2000).

Advocates of ozone as an "air purifying" agent attempt to draw parallels between air purification and water purification. However, the concentration of ozone used in water purification is several orders of magnitude larger than an air concentration of 50 or 100 ppb. Additionally, ozone/pollutant reactions in water involve not only the reactants, but also 10 to 20 surrounding water molecules (Mahan, 1965); in air the dominant reactions never involve more than three molecules colliding at the same time. Perhaps most importantly, water provides a solvent cage that surrounds a given ozone/pollutant pair as the reaction proceeds towards completion. In water, when ozone encounters a pollutant, the molecules may collide several hundred times, providing many opportunities for reaction (Mahan, 1965). In air, ozone collides with a pollutant and, if no reaction occurs, the molecules diffuse away from the region where the initial collision occurred. As an illustration of this point, the rate constants for the reaction of ozone with selected alkenes are 100 to 3600 times larger in water than in air (Dowideit and Sonntag, 1998).

For airborne chemical pollutants with primarily indoor sources, a modest increase in ventilation is ex-

pected to produce a greater reduction in pollutant concentrations than the deliberate introduction of 50 to 100 ppb of ozone into a room.

Conclusions

As recently as a 10 to 15 years ago many scientists thought indoor ozone levels were negligible and of little consequence. This misperception persisted despite the pioneering measurements in the early 1970s by Shair and co-workers at Cal Tech and Thompson and co-workers at UC-Riverside. Their studies demonstrated that outdoor to indoor transport of ozone was significant, and that indoor ozone levels were frequently 30% to 70% the corresponding outdoor levels. In the intervening period researchers from around the world have confirmed and extended the original observations of the Shair and Thompson groups regarding outdoor-to-indoor ozone transport. Additionally, during this same period, the indoor sources of ozone have increased – photocopiers, laser printers, electrostatic precipitators and ozone generators (sold as "air purifiers").

Indoor ozone not only directly impacts human health, materials and cultural artifacts, but also plays an important role in indoor chemistry. We now know that ozone/alkene reactions can produce meaningful quantities of hydroxyl radicals indoors (Weschler and Shields, 1996b, 1997b) and that ozone/nitrogen dioxide reactions can produce indoor nitrate radicals (Weschler et al., 1992b). Reactions among hydroxyl (or nitrate radicals) and indoor VOCs generate still other radicals. These free radical processes are driven by ozone, not photochemistry. Ozone/alkene reactions also generate semi-volatile products that can contribute to the growth of submicron particles (Weschler and Shields, 1999; Wainman, 1999; Wainman et al., 2000) and sorb on indoor surfaces (Weschler et al., 1992c; Morrison et al, 1999; Morrison, 1999). Some of the resulting products, especially oxidized products that still contain unsaturated bonds, have very low odor thresholds – less than 10 ppt (see results of Morrison et al., 1999). Such compounds, sorbed on indoor surfaces and offgassing at relatively slow rates, can adversely influence occupant perceptions for extended periods of time.

Indoor ozone chemistry has been somewhat overlooked, in part because most of the analytical tools that have been routinely applied to indoor air have been ill suited to the detection of short lived, highly reactive species or highly polar, multi-functional ($-C=O$, $-OH$, $-COOH$), oxygenated compounds. As techniques are developed that permit the more facile identification of both free radicals and highly polar

oxidized species, we will be in a position to better evaluate the effects of indoor ozone chemistry on ourselves and our surroundings.

References

Alevantis, L.E. and Girman, J.R. (1989) "Occupant-controlled residential ventilation". In: *IAQ '89, The Human Equation: Health and Comfort*, Atlanta, GA, American Society of Heating, Refrigerating, and Air Conditioning Engineers, pp. 184–191.

Allen, R.J., Wadden, R.A. and Ross, E.D. (1978) "Characterization of potential indoor sources of ozone", *American Industrial Hygiene Association Journal*, **39**, 466–471.

Andersson, K., Andersson, B., Nilsson, C.-A. and Sandstrom, M. (1996) "Naturfarger: Indentifiering av de flyktiga amnen som avges nar aggoljetempera torkar", Arbetslivsrapport, ISSN 1401–2928, 12, pp. 1–29.

ASHRAE Standard 62–1989R. (1989) *Ventilation for Acceptable Indoor Air Quality*, Atlanta, GA, American Society of Heating Refrigerating and Air Conditioning Engineers, Inc.

ASHRAE (1997) *1997 ASHRAE Handbook: Fundamentals*, Atlanta, GA, American Society of Heating Refrigerating and Air Conditioning Engineers, Inc., p. 25.14.

Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, J., Kerr, J.A. and Troe, J. (1992) "Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV", *Journal of Physical and Chemical Reference Data*, 21, 1125–1568.

Atkinson, R., Tuazon, E.C. and Aschmann, S.M. (1995) "Products of the gas-phase reactions of O_3 with alkenes", *Environmental Science and Technology*, 29, 1860–1866.

Avol, E.L., Navidi, W.C. and Colome, S.D. (1998) "Modeling ozone levels in and around Southern California homes", *Environmental Science and Technology*, 32, 463–468.

Axley, J.W., Peavey, J.B. and Hartzell, A.L (1993) "Homogeneous and heterogeneous processes in the transport of outdoor air pollutants indoors". In: *Proceedings of IAQ Problems – From Science to Practice*, Warsaw, Poland.

Berk, J.V., Young, R.A., Brown, S.R. and Hollowell, C.D. (1981) "Impact of energy-conserving retrofits on indoor air quality in residential housing", Presented at 74th Annual Meeting of the Air Pollution Control Association, Philadelphia, PA, LBL-12189, Lawrence Berkeley Laboratory.

Bernard, N.L., Gerber, M.J., Astre, C.M. and Saintot, M.J. (1999) "Ozone measurement with passive samplers: validation and use for ozone pollution assessment in Montpell-

ier, France", *Environmental Science and Technology*, 33, 217–222.

Black, M.S. and Worthan, A.W. (1999) "Emissions from office equipment." In: Raw, G., Aizlewood, C. and Warren, P. (eds.) *Indoor Air 99*. Vol. 2, London, Construction Research Communications Ltd, pp. 454–459.

Boeniger, M.F. (1995) "Use of ozone generating devices to improve indoor air quality", *American Industrial Hygiene Association Journal*, 56, 590–598.

Brace, S. and Peterson, D.L. (1998) "Spatial patterns of tropospheric ozone in the Mount Rainer region of the Cascade Mountains, U.S.A.", *Atmospheric Environment*, 32, 3629–3637.

Brauer, M. and Brook, J.R. (1997) "Ozone personal exposures and health effects for selected groups residing in the Fraser Valley", *Atmospheric Environment*, 31, 2113–2121.

Brimblecombe, P. (1990) "The composition of museum atmospheres", *Atmospheric Environment*, 24B, 1–8.

Brown, S.K., Sim, M.R., Abramson, M.J. and Gray, C.N. (1994) "Concentrations of volatile organic compounds in indoor air – a review", *Indoor Air*, 4, 123–134.

CARB (California Air Resources Board) (1987) Ambient air quality standard for ozone. California Codes and Regulation, Title 17, Section 70200.

California Environmental Protection Agency (1997) *California Ambient Air Quality Data*, California Air Resources Board, CD Number: TSD-97-007-CD.

Cass, G.R., Druzik, J.R., Grosjean, D., Nazaroff, W.W., Whitmore, P.M. and Wittman C.L. (1988) *Protection of Works of Art from Photochemical Smog*, Final report submitted to the Getty Conservation Institute, Environmental Quality Laboratory, Pasadena, CA, California Institute of Technology.

Cotton, F.A. and Wilkinson, G. (1980) *Advanced Inorganic Chemistry, 4th Edition*, New York, John Wiley & Sons.

Daisey, J.M., Hodgson, A.T., Fisk, W.J., Mendell, M.J. and Ten Brinke, J. (1994) "Volatile organic compounds in twelve California office buildings: Classes, concentrations and sources", *Atmospheric Environment*, 28, 3557–3562.

Danielsen, E.F. (1968) "Stratospheric-tropospheric exchange based on radioactivity, ozone and potential vorticity", *Journal of Atmospheric Science*, 25, 502–518.

Davies, T.D., Ramer, B., Kaspyzok, G. and Delany, A.C. (1984) "Indoor/outdoor ozone concentrations at a contemporary art gallery", *Journal of Air Pollution Control Association*, 34, 135–137.

Dowideit, P. and von Sonntag, C. (1998) "Reaction of ozone with ethene and its methyl- and chlorine-substituted derivatives in aqueous solution", *Environmental Science and Technology*, 32, 1112–1119.

Drakou, G., Zerefos, C., Ziomas, I. and Voyatzaki, M. (1998) "Measurements and numerical simulations of indoor O_3 and NOx in two different cases", *Atmospheric Environment*, 32, 595–610.

European Commission. (1997) *Total Volatile Organic Compounds (TVOC) in Indoor Air Quality Investigations, Report No 19*, European Collaborative Action: Indoor Air Quality and Its Impact on Man, Luxembourg, Joint Research Center.

Federal Trade Commission (1998) William Converse Position Paper, IAQ Publications, FTC Document 0010371.

Finlayson-Pitts, B.J., and Pitts, J.N. Jr. (1986) *Atmospheric Chemistry*, New York, John Wiley & Sons.

Finlayson-Pitts, B.J. and Pitts, J.N. Jr. (2000) *Chemistry of the Upper and Lower Atmosphere*, Orlando, FL, Academic Press.

Girman, J.R., Hadwen, G.E., Burton, L.E., Womble, S.E. and McCarthy, J.F. (1999) "Individual volatile organic compound prevalence and concentrations in 56 buildings of the Building Assessment and Evaluation (BASE) study". In: Raw, G., Aizlewood, C. and Warren, P. (eds.) *Indoor Air*

99. Vol. 2. London, Construction Research Communications Ltd, pp. 460–465.

Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N.R., Hjorth, J., Kotzias, D. and Larsen, B.R. (2000) "Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone", *Environmental Science and Technology* 34, 1001–1010.

Graedel, T.E. and Crutzen, P.J. (1993) *Atmospheric Change: An Earth System Perspective*, New York, W.H. Freeman and Co.

Grosjean, D., Williams II, E.L. and Seinfeld, J.H. (1992) "Atmospheric oxidation of selected terpenes and related carbonyls: gas-phase carbonyl products", *Environmental Science and Technology*, 26, 1526–1533.

Grosjean, D., Williams II, E.L., Grosjean, E., Andino, J.M. and Seinfeld, J.H. (1993) "Atmospheric oxidation of biogenic hydrocarbons: reactions of ozone with beta-pinene, d-limonene and trans-caryophyllene", *Environmental Science and Technology*, 27, 2754–2758.

Hales C.H., Rollinson, A.M. and Shair, F.H. (1974) "Experimental verification of linear combination model for relating indoor-outdoor pollutant concentrations", *Environmental Science and Technology*, 8, 452.

Hawley, G.G. (1971) *The Condensed Chemical Dictionary*, 8th edition, New York, Van Nostrand Reinhold Company.

Hayes, S.R. (1991) "Use of an indoor air quality model (IAQM) to estimate indoor ozone levels", *Journal of Air and Waste Management Association*, 41, 161–170.

Hinds, W.C. (1982) *Aerosol Technology*, New York, John Wiley & Sons.

Jakobi, G. and Fabian, P. (1997) "Indoor/outdoor concentrations of ozone and peroxyacetyl nitrate (PAN)", *International Journal of Biometeorology*, 40, 162–165.

Judeikis, H.S., Stewart, T.B. and Wren, A.G. (1978) "Laboratory studies of heterogeneous reactions of SO_2", *Atmospheric Environment*, 12, 1633–1638.

Karlberg, A., Magnusson, K. and Nilsson, U. (1992) "Air oxidation of d-limonene (the citrus solvent) creates potent allergens", *Contact Dermatitis*, 26, 332–340.

Lebowitz, M.D., Corman, G., O'Rourke, M.K. and Holberg, C.J. (1984) "Indoor-outdoor air pollution, allergen and meteorological monitoring in an arid southwest area", *Journal of Air Pollution Control Association*, 34, 1035–1040.

Lee, K., Vallarino, J., Dumyahn, T., Ozkaynak, H. and Spengler, J. (1999) "Ozone decay rates in residences", *Journal of Air and Waste Management Association*, 49, 1238–1244.

Lelieveld, J. and Dentener, F.J. (2000) "What controls tropospheric ozone?", *Journal of Geophysical Research*, 105, 3531–3551.

Leovic, K.W., Sheldon, L.S., Whitaker, D.A., Hetes, R.G., Calcagni, J.A. and Baskir, J.N. (1996) "Measurement of indoor air emissions from dry-process photocopy machines", *Journal of Air and Waste Management Association*, 46, 821–829.

Liu, L.-J.S, Koutrakis, P., Leech, J. and Broder, I. (1995) "Assessment of ozone exposures in the greater metropolitan Toronto area", *Journal of Air and Waste Management Association*, 45, 223–234.

Logan, J.A. (1985) "Tropospheric ozone: seasonal behavior, trends and anthropogenic influence", *Journal of Geophysical Research*, 90, 10463–10482.

Mahan, B.H. (1965) *University Chemistry*, Reading, MA, Addison-Wesley.

Mallard, W.G., Westley, F., Herron, J.T., Hampson, R.F. and Frizzell, D.H. (1998) *NIST Chemical Kinetics Database: Windows Version 2Q98*, NIST Standard Reference Database 17, Gaithersburg, MD, U.S. Department of Commerce.

Moschandreas, D.J., Stark, J.W.C., McFadden, J.E. and Morse, S.S. (1978) "Indoor air pollution in the residential environment", Volumes I and II, Final Report, GEO-MET EF-668,

Contract No. 68–08–2294, U.S. Environmental Protection Agency, Environmental Research Center, and U.S. Department of Housing and Urban Development, Office of Policy Development and Research (EPA 600/7–78/229A).

Moschandreas, D.J., Zabransky, J. and Pelton, D.J. (1981) "Comparison of indoor and outdoor air quality", Report EA-1733, Research Project 1309, Palo Alto, CA, Electric Power Research Institute.

Morrison, G.C. and Hodgson, A.T. (1996) "Evaluation of ventilation system materials as sources of volatile organic compounds." In: Yoshizawa, S., Kimura, K., Ikeda, K., Tanabe, S. and Iwata, T. (eds) *Indoor Air '96*, Vol. 3, pp. 585–590.

Morrison, G.C., Nazaroff, W.W., Cano-Ruiz, J.A., Hodgson, A.T. and Modera, M.P. (1998) "Indoor air quality impacts of ventilation ducts: ozone removal and emission of volatile organic compounds", *Journal of Air and Waste Management Association*, 48, 941–952.

Morrison, G.C. and Nazaroff, W.W. (1999) "Emissions of odorous oxidized compounds from carpet after ozone exposure." In: Raw, G., Aizlewood, C., and Warren, P. (eds) *Indoor Air '99*, London, Construction Research Communications Ltd, Vol. 4, pp. 664–669.

Morrison, G.C. (1999) "Ozone-surface interactions: investigation of mechanisms, kinetics, mass transport, and implications for indoor air quality", Ph.D. Dissertation, Engineering – Civil and Environmental Engineering, University of California, Berkeley, California, USA.

Mueller, F.X., Loeb, L. and Mapes, W.H. (1973) "Decomposition rates of ozone in living areas", *Environmental Science and Technology*, 7, 342–346.

Murray, D.M. and Burmaster, D.E. (1995) "Residential air exchange rates in the United States: Empirical and estimated parametric distributions by season and climatic region", *Risk Analysis*, 15, 459–465.

National Research Council (1991) *Rethinking the Ozone Problem in Urban and Regional Air Pollution*, Washington, D.C., National Academy Press.

Nazaroff, W.W. and Cass, G.R. (1986) "Mathematical modeling of chemically reactive pollutants in indoor air", *Environmental Science and Technology*, 20, 924–934.

Nazaroff, W.W., Gadgil, A.J. and Weschler, C.J. (1993) "Critique of the use of deposition velocity in modeling indoor air quality." In: Nagada, N.L. (ed) *ASTM Special Technical Publication: Modeling of Indoor Air Quality and Exposure*, ASTM STP 1205, Philadelphia, PA, American Society for Testing and Materials, pp. 81–104.

Persily, A. (1989) "Ventilation rates in office buildings". In: *IAQ '89, The Human Equation: Health and Comfort*, Atlanta, GA, American Society of Heating, Refrigerating, and Air Conditioning Engineers, pp. 128–136.

Reiss, R., Ryan, P.B. and Koutrakis, P. (1994) "Modeling ozone deposition onto indoor residential surfaces", *Environmental Science and Technology*, 28, 504–513.

Reiss, R., Ryan, P.B., Koutrakis, P. and Tibbetts, S.J. (1995a) "Ozone reactive chemistry on interior latex paint", *Environmental Science and Technology*, 29, 1906–1912.

Reiss, R., Ryan, P.B., Tibbetts, S.J. and Koutrakis, P. (1995b) "Measurements of organic acids, aldehydes, and ketones in residential environments and their relation to ozone", *Journal of Air and Waste Management Association*, 45, 811–822.

Romieu, I., Lugo, M.C., Colome, S., Garcia, A.M., Avila, M.H., Geyh, A., Velasco, S.R. and Rendon, E.P. (1998) "Evaluation of indoor ozone concentration and predictors of indoor-outdoor ratio in Mexico City", *Journal of Air and Waste Management Association*, 48, 327–335.

Russell, M. (1988) "Ozone pollution: the hard choices", *Science*, 241, 1275–1276.

Sabersky, R.H., Sinema, D.A. and Shair, F.H. (1973) "Concentrations, decay rates, and removal of ozone and their relation to establishing clean indoor air", *Environmental Science and Technology*, 7, 347–353.

Seinfeld, J.H. and Pandis, S.N. (1998) *Atmospheric Chemistry and Physics*, New York, John Wiley & Sons.

Shair, F.H. and Heitner, K.L. (1974) "Theoretical model for relating indoor pollutant concentrations to those outside", *Environmental Science and Technology*, 8, 444–451.

Shair, F.H. (1981) "Relating indoor pollutant concentrations of ozone and sulfur dioxide to those outside: economic reduction of indoor ozone through selective filtration of the make-up air", *ASHRAE Transactions*, 87 (Part I), 116–139.

Shaughnessy, R.J., Weschler, C.J. and McDaniels, T. (1999) "Indoor chemistry: ozone and tobacco smoke". In: *Indoor Air 99, Proceedings of the 8th International Conference on Indoor Air Quality and Climate*, London, Construction Research Communications Ltd, Vol. 2, pp. 882–887.

Shaver, C.L., Cass, G.R. and Druzik, J.R. (1983) "Ozone and the deterioration of works of art", *Environmental Science and Technology*, 17, 748–752.

Shields, H.C., Fleischer, D.M. and Weschler, C.J. (1996) "Comparisons among VOCs measured in three types of U.S. commercial buildings with different occupant densities", *Indoor Air*, 6, 2–17.

Stock, T.H., Kotchmar, D.J., Contant, C.F., Buffler, P.A., Holguin, A.H., Gehan, B.M. and Noel, L.M. (1985) "The estimation of personal exposures to air pollutants for a community-based study of health effects in asthmatics – design and results of air monitoring", *Journal of Air Pollution Control Association*, 35, 1266–1273.

Stock, T.H., and Venso, E.A. (1993) "The impact of residential evaporative air cooling on indoor exposure to ozone." In: Jantunen, M., Kalliokoski, P., Kukkonen, E., Saarela, K., Seppanen, O. and Vuorelma, H. (eds) *Indoor Air '93* Vol. 3, pp. 251–256.

Tang, I.N. and Lee, J.H. (1987) "Accommodation coefficients for ozone and sulfur dioxide: implications for SO_2 oxidation in cloudwater", *ACS Symposium Series*, 349, 109–117.

Thompson, C.R. (1971) "Measurement of total oxidant levels at Riverside Community Hospital", *Archieves of Environmental Health*, 22, 514.

Thompson, C.R., Hensel, E.G. and Kats, G. (1973) "Outdoor-indoor levels of six air pollutants", *Journal of Air Pollution Control Association*, 23, 881–886.

U. S. Environmental Protection Agency (1996) *Air Quality Criteria for Ozone and Related Photochemical Oxidants*, Washington, DC, Office of Research and Development (EPA/600/P-93/004aF).

U. S. Environmental Protection Agency (1998) *AIRS Executive Version 2.0*, Research Triangle Park, NC, Office of Air Quality Planning and Standards.

U. S. Environmental Protection Agency (1999) Ozone Generators That Are Sold As Air Cleaners: An Assessment Of Effectiveness And Health Consequences, http://www.epa.gov/iaq/pubs/ozonegen.html, Created: April 16, 1998; Last Modified: March 23, 1999.

Wainman, T. (1999) "Use of a two tiered dynamic chamber to investigate indoor air chemistry", Ph.D. Dissertation, Graduate Program in Environmental Science, Rutgers, The State University of New Jersey, New Brunswick, NJ, USA.

Wainman, T., Zhang, J., Weschler, C.J. and Lioy, P.J. (2000) "Ozone and limonene in indoor air: a source of submicron particle exposure", *Environmental Health Perspectives*, submitted for publication.

Weschler, C.J., Shields, H.C. and Naik, D.V. (1989) "Indoor ozone exposures", *Journal of Air Pollution Control Association*, 39, 1562–1568.

Weschler, C.J., Shields, H.C. and Naik, D.V. (1991) "Indoor-

outdoor ozone measurements." 1988–1991. In: *Proceedings of the 84th Annual Meeting (Vancouver, B.C.)*. Pittsburgh, PA. Air and Waste Management Association.

Weschler, C.J., and Hodgson, A.T. (1992a) "Indoor VOCs: is what you measure on Tuesday night the same as what you measure on Wednesday afternoon?". In: *IAQ'92: Environments For People*, Atlanta, GA, American Society of Heating, Refrigerating and Air-Conditioning Engineers, pp. 213–219.

Weschler, C.J., Brauer, M. and Koutrakis, P. (1992b) "Indoor ozone and nitrogen dioxide: a potential pathway to the generation of nitrate radical, dinitrogen pentaoxide and nitric acid indoors", *Environmental Science and Technology*, **26**, 179–184.

Weschler, C.J., Hodgson, A.T. and Wooley, J.D. (1992c) "Indoor chemistry: ozone, volatile organic compounds and carpets", *Environmental Science and Technology*, **26**, 2371–2377.

Weschler, C.J., Shields, H.C. and Naik, D.V. (1992d) "Indoor ozone: Recent findings". In: Berglund, R. (ed) *Tropospheric ozone and the environment II: Effects, modeling and control*, Pittsburgh, PA, Air and Waste Management Association, pp. 681–700.

Weschler, C.J., Shields, H.C. and Naik, D.V. (1994a) "Indoor chemistry involving O_3, NO and NO_2 as evidenced by 14 months of measurements at a site in Southern Calif", *Environmental Science and Technology*, **28**, 2120–2132.

Weschler, C.J., Shields, H.C. and Naik, D.V. (1994b) "The factors influencing indoor ozone levels at a commercial building in Southern California: More than a year of continuous observations." In: Volstal, J.J. (ed) *Tropospheric Ozone: Critical Issues in the Regulatory Process*, Pittsburgh, PA, Air and Waste Management Association, pp. 236–252.

Weschler, C.J., and Shields, H.C. (1996a) "Chemical transformations of indoor air pollutants". In: Yoshizawa, S., Kimura, K., Ikeda, K., Tanabe, S. and Iwata, T. (eds). *Indoor Air '96*, pp. 919–924, Tokyo, Japan. Organizing Committee of the 7th International Conference of Indoor Air Quality and Climate

Weschler, C.J. and Shields, H.C. (1996b) "Production of the hydroxyl radical in indoor air", *Environmental Science and Technology*, **30**, 3250–3258.

Weschler, C.J. and Shields, H.C. (1997a) "Potential reactions among indoor pollutants", *Atmospheric Environment*, **31**, 3487–3495.

Weschler, C.J. and Shields, H.C. (1997b) "Measurements of the hydroxyl radical in a manipulated but realistic indoor environment", *Environmental Science and Technology*, **31**, 3719–3722.

Weschler, C.J. and Shields, H.C. (1999) "Indoor ozone/terpene reactions as a source of indoor particles", *Atmospheric Environment*, **33**, 2301–2312.

Weschler, C.J. and Shields, H.C. (2000) "The influence of ventilation on reactions among indoor pollutants: modeling and experimental observations", *Indoor Air*, **10**, 92–100.

WHO (World Health Organization) (1997) Air quality guidelines for Europe, 2nd Edition, De Bilt, Netherlands, World Health Organization.

Wolff, G.T., Lioy, P.J., Wight, G.D., Meyers, R.E. and Cederwall, R.T. (1977) "An investigation of long range transport of ozone across the mid western and eastern United States", *Atmospheric Environment*, **11**, 797–802.

Wolkoff, P., Clausen, P.A., Wilkens, C.K., Hougaard, K.S. and Nielsen, G.D. (1999) "Formation of strong airway irritants in a model mixture of (+)-α-pinene/ozone", *Atmospheric Environment*, **33**, 693–698.

Wolkoff, P, Clausen, P.A., Wilkins, C.K. and Nielsen, G.D. (2000) "Formation of strong airway irritants in terpene/ozone mixtures", *Indoor Air*, **10**, 82–91.

Yu, J.R., Flagan, C. and Seinfeld, J. (1998) "Identification of products containing −COOH, −OH, and −C=O in atmospheric oxidation of hydrocarbons", *Environmental Science and Technology*, **32**, 2357–2370.

Zhang, J. and Lioy, P. (1994a) "Ozone in residential air: concentrations, I/O ratios, indoor chemistry, and exposures", *Indoor Air*, **4**, 95–105.

Zhang, J., He, Q. and Lioy, P. (1994b) "Characteristics of aldehydes: concentrations, sources and exposures for indoor and outdoor residential microenvironments", *Environmental Science and Technology*, **28**, 146–152.