

Ozone and other photochemical oxidants in ambient and indoor air – properties, sources and concentrations

by Jan Sundell & André Zuber

Physical and chemical properties

Ozone (O_3) occurs naturally in the atmosphere as a result of thunderstorms and photochemical reactions. It is also an air pollutant due to emissions of nitrogen oxides and volatile organic compounds. Ozone and other photochemical oxidants all have the common feature that they react rapidly with organic substances. Examples of other photochemical oxidants are peroxyacetyl nitrate, hydrogen peroxide, and hydrogen peroxy radicals. Ozone is the photochemical oxidant that occurs at the highest concentrations in the atmosphere, and it is that which is the most investigated with respect to its environmental impact.

About 90% of the ozone content of the atmosphere is contained in the stratosphere at an altitude of 10 to 50 km. Stratospheric ozone can be transported to the troposphere during sporadic events, in particular in mountainous regions and in connection with weather fronts. At the earth's surface ozone can increase to high concentrations during such events. The stratospheric ozone plays an important role in screening out harmful ultraviolet radiation from the sun. Ozone is also an important greenhouse gas.

The remainder of the earth's ozone, about 10%, is in the troposphere, from the ground up to about 10 km. Ozone contained between the ground and about 1500 m, the *boundary layer*, determines, to a large extent, the concentration of ground-level ozone. The *free troposphere*, between the boundary layer and the stratosphere, acts as a reservoir of ozone, which in turn supplies the boundary layer with ozone.

Ozone is a triatomic allotrope of oxygen. It is an irritating and corrosive, pale-blue gas and is explosive at high concentrations. The characteristic stale smell has given the gas its name from the Greek *o'zo*, to smell. The odor detection threshold for ozone is about $40 \mu\text{g} \cdot \text{m}^{-3}$ (1). The molecular weight of the gas is $47.8992 \text{ g} \cdot \text{mol}^{-1}$ and, at a pressure of 1013 mbar, the pure gas has a density of $2.144 \text{ g} \cdot \text{l}^{-1}$ at 0°C and a boiling point of -111.3°C . At temperatures above about 100°C ozone rapidly decays to oxygen (O_2). The solubility of ozone in water at 0°C is 1.09 g per liter and this value decreases with increasing temperature, being $0.57 \text{ g} \cdot \text{l}^{-1}$ at 20°C and $0.40 \text{ g} \cdot \text{l}^{-1}$ at 30°C (2). In the liquid phase ozone can react directly with biomolecules or indirectly via the production of reactive oxidative molecules, such as the

hydrogen peroxy radical and hydrogen peroxide. [See also the section on the absorption and metabolic fate of ozone in this issue (3).]

For ozone in ambient air the practical conversion factor for the volume mixing ratio to mass concentration is:

$$1 \text{ ppb} = 2.0 \mu\text{g} \cdot \text{m}^{-3} \text{ (at } 20^\circ\text{C and } 101.3 \text{ kPa).}$$

The general, more precise conversion relationship for other temperatures and pressures is:

$$1 \text{ ppb of ozone} = 1.962 (293/(273+t)) (p/101.3) \mu\text{g} \cdot \text{m}^{-3},$$

where t is the temperature in $^\circ\text{C}$ and p the pressure in kPa.

The temperature at ground level varies within a relatively limited range. Thus temperature has a moderate influence on the conversion factor of 2, about $\pm 10\%$ for a temperature range from -20 to $+35^\circ\text{C}$. However, for sites at high elevation, the reduced pressure must be accounted for. For instance, Mexico City, with an elevation of 2240 m, has a mean pressure that is about 75% of the pressure at sea level, and the conversion factor is therefore close to 1.5. For Albuquerque, New Mexico, at an elevation of 1600 m above sea level, the conversion factor is 1.64 (figure 1).

Formation mechanisms of ozone and photochemical oxidants

Atmospheric ozone is formed primarily through photochemical reactions. Several other processes may also

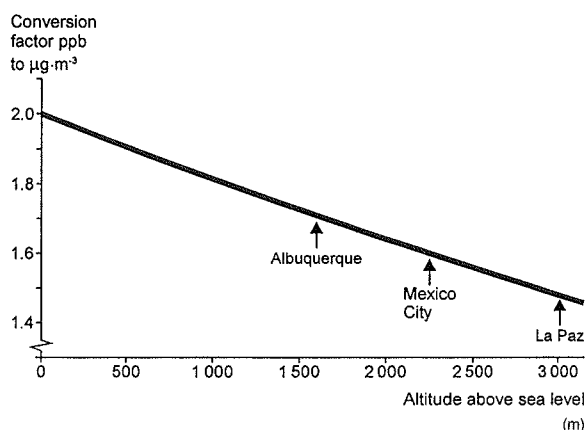
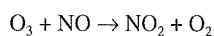
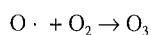
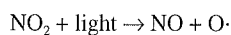


Figure 1. Ozone conversion factor from parts per billion to micrograms per cubic meter as a function of altitude in a standard atmosphere.

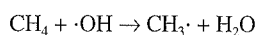
directly create ozone, for instance, electrical discharges and lightning. In the stratosphere ultraviolet solar radiation dissociates molecular oxygen into its atoms, which in turn react with oxygen to form ozone molecules.

Ozone in the troposphere exists, to some extent, due to downward net transport from the stratosphere. However, the major source of tropospheric ozone is the photochemical oxidation of volatile organic compounds in the presence of nitrogen oxides. Volatile organic compounds and nitrogen oxides are *precursors* to photochemical pollution. Oxides of nitrogen play a key role in ozone formation. Nitrogen dioxide (NO_2) is readily dissociated by sunlight, forming nitrogen monoxide (NO) and atomic oxygen (O). The oxygen atom can react with an oxygen molecule to form ozone. However, the ozone molecule can react with nitrogen monoxide, resulting in the destruction of the ozone molecule and the reappearance of nitrogen dioxide:

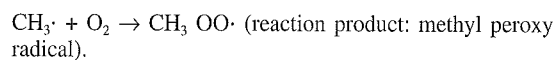


These reactions do not result in net ozone production. In order to obtain net production of ozone, nitrogen monoxide must react with some other oxygen-containing molecule, such as the oxidation intermediates of volatile organic compounds. In particular peroxy radicals react with nitrogen monoxide and compete with ozone for the available nitrogen monoxide. The oxidation of volatile organic compounds often starts with their reaction with hydroxyl radicals, which are formed through photochemical reactions.

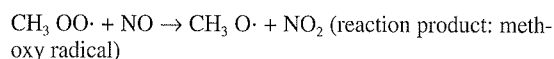
As an example of this reaction mechanism (figure 2), the important steps in methane oxidation are:



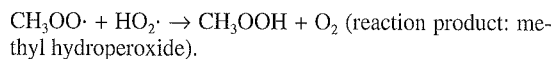
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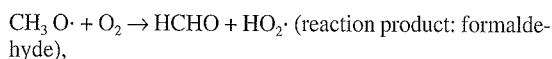
The methyl peroxy radical can react in different ways, the more important of these being:



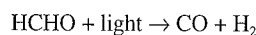
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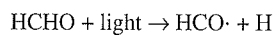
The reaction product from the first of these two reactions, the methoxy radical, reacts to formaldehyde:



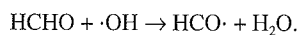
and this reaction is then followed by the following reactions:



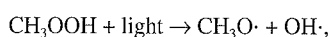
or



or



The hydrocarboxy radical, $\text{HCO} \cdot$, reacts readily with oxygen and also forms carbon monoxide. This carbon monoxide is slowly removed by reaction with the hydroxyl radical and the formation of carbon dioxide. The methyl hydroperoxide is photolyzed:



and the methoxy radical enters into the previously described cycles, or it reacts with hydroxyl radicals:

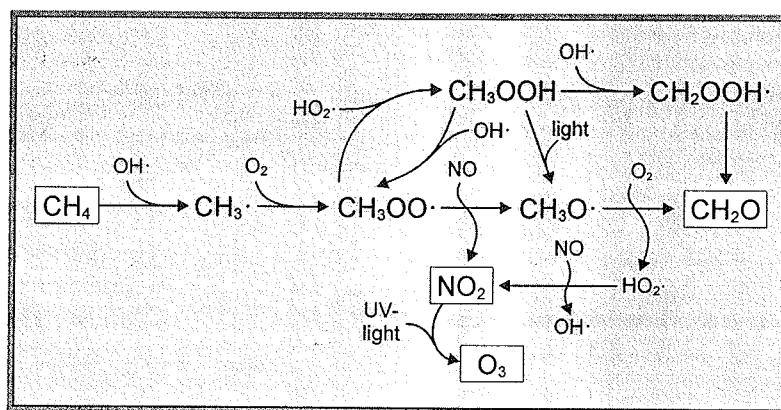
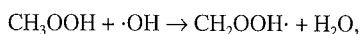
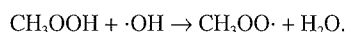
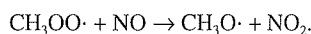


Figure 2. Oxidation cycle of methane as an example of the oxidation of volatile organic compounds and the production of ozone. The compounds in boxes are stable.

where the reaction product undergoes a rapid reaction to formaldehyde. The other important reaction with hydroxyl radicals is:



The reaction scheme for ozone with organic compounds other than methane differs from the one already described, but only in small details. The general characteristic in the oxidation of organic volatile compounds is the production of organic peroxy radicals, $\text{R-CH}_2\text{OO}\cdot$, which act as a supply of oxygen in the reaction with nitrogen monoxide:



The nitrogen dioxide formed is then photolyzed back to nitrogen monoxide and an oxygen atom, the latter rapidly reacting with oxygen to form a new molecule of ozone. The nitrogen monoxide is then freed to react with a new organic peroxy radical and the cycle is repeated.

The number of ozone molecules being formed, as well as the rate of ozone formation, depends strongly on the species of the organic molecule involved in the cycle, the amount of radiation that drives the reactions, the temperature, and, not the least, the amount of nitrogen oxides present.

The general relationship between the concentrations of precursors and the production of photooxidants is not linear. In polluted areas, such as the heavily industrialized areas of northwest Europe, each nitrogen dioxide molecule emitted into the air participates in the generation of 3 to 10 ozone molecules before it is lost from the atmosphere through deposition. Under background conditions, such as those prevailing in remote areas and in the middle troposphere, the concentrations of nitrogen oxides are lower, and each nitrogen oxide molecule emitted into this part of the atmosphere participates in the net generation of 10 to 100 ozone molecules before it is lost from the atmosphere.

However, should the concentration of nitrogen oxides be below about 0.008 to $0.040 \mu\text{g} \cdot \text{m}^{-3}$, the atmospheric chemistry favors a net destruction of ozone. Such low levels of nitrogen oxides are only found over the large oceans and in the upper troposphere.

In the absence of photo-dissociating light, which drives the reactions, ozone formation decreases rapidly.

The major sources of the precursors to photochemical pollution are transport (cars, trucks, air transport and ships), and off-road vehicles and nonroad mobile machinery. In Sweden and other Nordic countries, small-scale wood heating also contributes significantly to the emissions of volatile organic compounds. Emissions of nitrogen monoxide reduce the concentration of ozone in the short-term scale. The rapid reaction, $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$, converts ozone within minutes to nitrogen dioxide. The temporary decrease in ozone concentration that fol-

lows from emissions of nitrogen monoxide is generally found in polluted areas, such as in cities and close to industrial areas.

Occurrence of ozone in urban and rural areas

The local ozone concentration depends on the extent of the emissions, local conditions of terrain and meteorology, temperature, and solar radiation.

On the North American continent episodes of elevated ozone concentration have been a major concern for public health and agriculture since the 1960s. During the last two or three decades summertime ozone episodes have also been a persistent feature in Europe. In Sweden, the levels of the emissions, the temperature, and the sunlight conditions differ strongly from the conditions dominating in southern and central Europe and in the United States (such as the Los Angeles area). Locally produced photochemical smog, with ozone concentrations over $240 \mu\text{g} \cdot \text{m}^{-3}$, does not occur in Sweden. Instead, the occurrence of increased ozone concentrations at ground level is mainly due to long-range transport of the pollutant and its precursors.

The levels of ozone are highest in rural areas and are generally higher in southern Sweden as compared with northern Sweden. In urban areas, the discharges of nitrogen monoxide, primarily from cars, react rapidly with ozone and can thus reduce the levels of ozone somewhat. In the larger city centers (Stockholm, Göteborg, Malmö) the levels of ozone are thus 10% to 40% lower than outside the cities. However, the emissions from the urban areas contribute to ozone formation on a regional scale.

There is a general increase in the relative ozone concentration or mixing ratio with altitude. This increase is due to the ozone in the free troposphere, which acts as a reservoir of the gas. In mountainous areas, such as the Alpine region and the Scandinavian mountains, the ozone levels are therefore higher than at lower altitudes.

Annual and daily variations

The atmospheric levels of ozone are generally higher during summer than winter due to the lower photochemical activity in the absence of sunlight. In addition the uptake of ozone by vegetation and soils is relatively slow in winter, and the levels are therefore similar for nighttime and daytime conditions. In wintertime, the daily (24 h) mean ozone concentrations in rural areas are about $60 \mu\text{g} \cdot \text{m}^{-3}$ in southern Sweden and about $50 \mu\text{g} \cdot \text{m}^{-3}$ in northern Sweden. In cities traffic emissions of nitrogen monoxide react with ozone and form nitrogen dioxide and thus reduce the levels of ozone somewhat, particu-

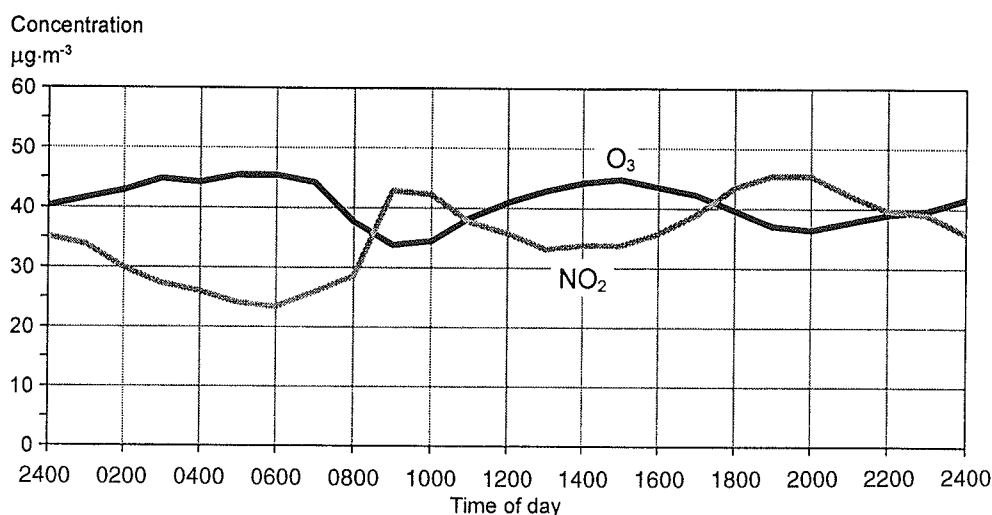


Figure 3. Ozone (O_3) and nitrogen dioxide (NO_2) in central Göteborg. Courtesy of the monitoring network of the Göteborg Municipal Authority.

larly during rush hours. On the average, the nitrogen dioxide concentration in cities is low during the early morning hours, peaks around 0900, decreases somewhat until the evening rush hour sets in, and then peaks again around 1900. In these urban areas the ozone levels may be about 10% to 40% lower than those in the surrounding rural areas (figure 3).

During the summer the increased photochemical production of ozone, increased vertical transport, and increased uptake by vegetation give large differences between daytime and nighttime ozone concentrations. In rural areas of southern Sweden the ozone levels are typically below $50 \mu\text{g} \cdot \text{m}^{-3}$ during nighttime and increase to about 80 to $90 \mu\text{g} \cdot \text{m}^{-3}$ during daytime. In northern Sweden the concentration of ozone is about 10 to $15 \mu\text{g} \cdot \text{m}^{-3}$ lower. In high-concentration episodes during spring and summer the levels can increase to above $180 \mu\text{g} \cdot \text{m}^{-3}$ in southern Sweden during the daytime but stay at relatively low levels during the nighttime. This behavior

during high-concentration episodes reflects the importance of vertical transport, which is stronger during daytime and ceases during nighttime, in particular under the influence of high-pressure weather conditions with clear skies.

Episodes with high concentrations of ozone

Episodes with high concentrations of ground-level ozone occur mainly during the spring and summer. Their main cause is the transport of polluted air containing high concentrations of ozone and ozone precursors from other countries in northwest Europe (4). Ozone concentrations during these episodes can increase to 150 to $200 \mu\text{g} \cdot \text{m}^{-3}$ for a period of several days. In southern and central Sweden, $120 \mu\text{g} \cdot \text{m}^{-3}$ is, on the average, exceeded 130 h per year and $150 \mu\text{g} \cdot \text{m}^{-3}$ is exceeded 12 h per year. In northern Sweden the levels of ozone during ozone episodes are lower, $120 \mu\text{g} \cdot \text{m}^{-3}$ being exceeded 18 h per year on the average (5).

Local meteorological conditions are important for ozone episodes. For instance, in land- and sea-breeze circulation, pollutants such as nitrogen oxides, volatile organic compounds, and ozone can return repeatedly to the area of the emissions and hence accumulate higher and higher concentrations of pollutants. This is one of the causes of the high levels of ozone in the Mediterranean area during the summer, as well as the high levels of Los Angeles photochemical smog (table 1).

Ozone background level

Another aspect of photochemical pollution is the background level of ozone. The background level is somewhat loosely defined as the level excluding the episodic events with high concentrations of ozone. For practical purposes, the long-term average ozone concentration has been used in Sweden to quantify the background levels.

Table 1. Ozone level at the rural monitoring station Aspöreten, 100 km south of Stockholm. The number of hours above ozone concentrations of $120 \mu\text{g} \cdot \text{m}^{-3}$ and $150 \mu\text{g} \cdot \text{m}^{-3}$ and the 24-h average concentrations for summer (April to September) and winter (October to March) are given.

Year	Hours above $120 \mu\text{g} \cdot \text{m}^{-3}$	Hours above $150 \mu\text{g} \cdot \text{m}^{-3}$	Winter mean ($\mu\text{g} \cdot \text{m}^{-3}$)	Summer mean ($\mu\text{g} \cdot \text{m}^{-3}$)
1985	338	98	·	79
1986	1	0	49	53
1987	33	0	52	56
1988	302	23	43	72
1989	189	24	51	73
1990	117	0	49	67
1991	19	0	45	65
1992	153	9	47	72
1993	49	1	52	62
1994	87	7	51	69
Mean 1985— 1994	128	16	49	69

In regions with more frequent episodes, such as southern Europe, the basis for the calculation of the background level may be different.

In Europe, the background level has increased during the last century. Ozone observations made at the Montsouris Observatory outside Paris during the late 19th century showed a background annual mean ozone concentration of about $20 \mu\text{g} \cdot \text{m}^{-3}$. Currently, ozone background levels are above $50 \mu\text{g} \cdot \text{m}^{-3}$ (6). The measurement of ozone in Sweden has a shorter record; ozone levels have been regularly monitored since 1985. Again, the trend is towards higher ozone concentrations (5). For the protection of plants, for example, crops and forests, the average ozone levels during summer days are important, since physiological activities such as gas exchange and photosynthesis are concentrated to this period. The period used to calculate the average concentration of ozone over the vegetation season is also of relevance for the protection of human health since a large portion of our outdoor activities takes place during that season. Over the years 1987 to 1989 the mean ozone concentration during the period April to September, between 0900 and 1600, was about $85 \mu\text{g} \cdot \text{m}^{-3}$ in southern and central Sweden and about $65 \mu\text{g} \cdot \text{m}^{-3}$ in northern Sweden. For the period 1985 to 1990 the trend in ozone levels over the vegetation season varied from unchanged, or even somewhat decreasing levels in the south, to a slowly increasing level in central Sweden. At the Aspvreten station 100 km south of Stockholm the average increase has been 3% to 4% annually since 1985 (5). The elevated levels of ozone during the growing season in central Sweden may be caused by the generally increased emissions of nitrogen oxides in Europe. The relative stability or decreasing trend of ozone levels in southern Sweden may partly be due to a saturation effect in the photochemical ozone production. The saturation effect is expressed as a disproportionately small change in the ozone levels when emissions of ozone precursors are changed. Such saturation effects are known to occur in some parts of northwest Europe, where the concentrations of pollutants are so high that no more or even less ozone is formed close to the emissions (7).

However, due to the short history of ozone monitoring in Sweden, it cannot be ruled out that the trend in ozone levels is due to the interannual variability in weather patterns (5).

Relationship between short- and long-term averages

Levels of air pollutants are monitored during shorter or longer averaging times, and it is possible to derive a frequency distribution from any time series. The conversion between short-term and long-term values is generally expressed as a transfer function. A widely used transfer is the log-normal frequency distribution, which is adequate for pollutants such as nitrogen dioxide but less

useful for ozone. The frequency distribution of ozone concentration in rural areas is closer to a normal frequency function. For ozone, the annual mean value is about $65 \mu\text{g} \cdot \text{m}^{-3}$ in southern and central Sweden, and the mean standard deviation is about $35 \mu\text{g} \cdot \text{m}^{-3}$. For urban areas the distribution is far from normal. To our knowledge, no general transfer functions for short-term and long-term ozone concentrations representative of human exposure currently exist that can convert 1- or 8-h average ozone concentrations to the annual or summertime averages (figure 4).

Ozone indoors

Since human beings spend a large portion of their time indoors, quantitative knowledge on the indoor pollution from ozone is important to assess health impact. In contrast to the major interest regarding ozone in outdoor air, the interest in determining ozone concentrations and related health effects in nonindustrial indoor air has been limited, mainly because the major source of indoor ozone is outdoor ozone and, as ozone quickly reacts with indoor surfaces, indoor concentrations are normally lower than those outdoors (8).

Major sources of indoor ozone, besides outdoor air, are electrical discharges from appliances, such as photo-

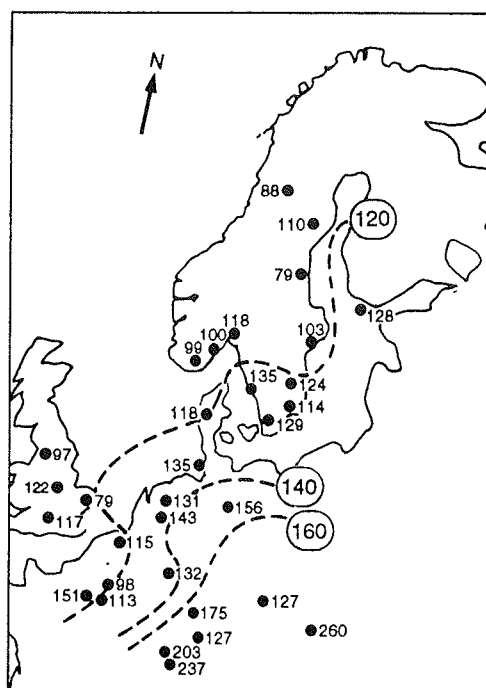


Figure 4. Distribution of ozone above Europe in April to September 1986, 98th percentile for ozone concentration (expressed in micrograms per cubic meter) (3).

copiers, printers, electrical filters, ionizers, and ozonizers. Ultraviolet light is also a source of ozone.

Hansen & Andersen (9) measured the ozone emission from 69 photocopying machines. The source strength, during continuous copying, varied between 0 to $1350 \mu\text{g} \cdot \text{min}^{-1}$, with most ($N = 57$) copiers emitting $< 500 \mu\text{g} \cdot \text{min}^{-1}$. The same laboratory measured ozone emissions from a laser printer. With a new ozone-filter the emission rate was $58 \mu\text{g} \cdot \text{min}^{-1}$, with an old filter it was $292 \mu\text{g} \cdot \text{min}^{-1}$, and without a filter it was $910 \mu\text{g} \cdot \text{min}^{-1}$ (10). In conclusion, they, as well as Olander (11) in a review of the literature, found that, in small rooms with normal ventilation, small printers will hardly cause ozone concentrations to rise above $100 \mu\text{g} \cdot \text{m}^{-3}$.

Wolkoff et al (12) studied human reactions to office machines in climate chambers with 60 recirculations of chamber air per hour and 50% fresh air exchange per hour. Thirty healthy females were exposed in groups of five for 6 h in an office environment with three personal computers, one laser printer, and one photocopier. As a control, the subjects were exposed to an office environment without office machinery. The laser printer chosen had an ozone emission of $113 \mu\text{g} \cdot \text{min}^{-1}$, and that of the copying machine was $215 \mu\text{g} \cdot \text{min}^{-1}$ at continuous operation. The peak ozone levels were $52 \mu\text{g} \cdot \text{m}^{-3}$ in the room containing the office machinery and $< 2 \mu\text{g} \cdot \text{m}^{-3}$ in the control chamber. The mean atmospheric formaldehyde levels were three times higher in the chamber containing the office machinery ($95 \pm 11 \mu\text{g} \cdot \text{m}^{-3}$) than in the control chamber, whereas the concentrations of volatile organic compounds and particulate matter were almost the same. The authors found significantly greater ($P = 0.015$) epithelial damage in the conjunctiva of the eye, as well as subjective eye irritation, and worsened immediate perception of air quality in the presence of the office machinery. The study was not conclusive regarding which agent(s) caused the adverse health effects, but ozone, per se, as well as products from the ozonolysis of volatile organic compounds, were suspected.

Ozone-generating devices are used indoors for deodorization after fires or after hotel room residence by smoking guests, that is, in rooms that are not occupied. However, they are also used in occupied rooms for the modification of room air with focus on the biocidal and deodorizing properties of ozone. The Food and Drug Administration (FDA) in the United States has claimed that, in order to be effective in such respects, the air concentration of ozone has to be much higher than can be safely tolerated by humans, and it labels any device which generates an ozone concentration greater than $100 \mu\text{g} \cdot \text{m}^{-3}$ in room air as "adulterated and misbranded" (13, 14).

Kissel (15) has calculated outlet-air ozone concentrations from ozone generators to be in the range of 400 to

$4000 \mu\text{g} \cdot \text{m}^{-3}$ and resulting room air concentrations to be in the range of 80 to $800 \mu\text{g} \cdot \text{m}^{-3}$, assuming air exchange rates of 30% and 200%, respectively, and ozone half-lives of between 30 and 8 min.

Indoor-outdoor relationships

The half-life of ozone in office rooms is reported to be in the range of 9 to 26 min, and in residences it is between 8 and 21 min (16–19). It depends on the types of surfaces in the room, with high decomposition rates for organic materials such as cotton, wool and neoprene and low rates for inorganic materials such as aluminum and glass (19). Accordingly, the surface-to-volume ratio is also related to the decomposition rate (18). The rate also depends on the humidity of the air, and it increases five-fold over the range of 5% to 55% relative humidity (20).

Extended, simultaneous measurements of ozone indoors and outdoors have been performed by Weschler et al (21) in a telephone switching office in Burbank, California, in the United States. The office had no internal ozone source. During maximum ventilation the concentration of ozone was roughly 65% of the outdoor value, while at minimum ventilation it was typically 30%. Stock & Venso (22) simultaneously measured indoor and outdoor concentrations of ozone in and around six homes in El Paso and four in Houston in the United States. The hourly average indoor ozone concentrations ranged from 2 to $50 \mu\text{g} \cdot \text{m}^{-3}$, the indoor to outdoor ratios being between 0.45 to 0.67 in El Paso and 0.05 to 0.12 in Houston. The variations in ratios were explained by the type of ventilation or cooling used in each dwelling. High ratios (El Paso) were associated with evaporative cooling, using high outdoor airflow rates, and low ratios (Houston) were associated with refrigerative cooling, using low outdoor airflow rates.

If there is no indoor source of ozone, the indoor-to-outdoor ratio is typically reported to be in the range of 0.1 to 0.8 (8, 23), with low values at low ventilation rates and high values at high ventilation rates. The influence of indoor surfaces, surface-to-volume ratio, and the relative humidity of indoor air is, in most studies, not obvious, as the variability of such aspects in most studies is low. Seemingly, as judged from reported continuous measurements, the indoor-to-outdoor ratio is relatively stable during varying outdoor concentrations.

In the case of Sweden, there is a lack of measurements of indoor ozone. However, the ventilation rates are generally in the lower range of the values determined in the United States, which indicate that the indoor-to-outdoor ratio should be low in Swedish dwellings (possibly between 0.1 to 0.5), the lowest values being measured in single family houses and higher values in buildings such as offices or schools (possibly between 0.3 to 0.8), on the assumption that there is no internal sources.

With indoor sources, such as copying machines or laser printers, indoor concentrations can exceed those outdoors.

Personal exposure

Liu et al (24) have simultaneously measured the ozone concentration at stationary ambient monitoring sites in and around 23 homes, as well as the personal exposure of 23 children during 12-h episodes (passive samplers during daytime). The mean concentrations ranged from 21 (indoor, nighttime) to 113 $\mu\text{g} \cdot \text{m}^{-3}$ (outdoor, daytime). The outdoor air concentrations measured at domestic sites and at a stationary ambient monitoring site were highly correlated ($r = 0.81$, $P < 0.01$), even though the concentrations at the domestic sites were, on the average, typically 20% lower than at the stationary ambient monitoring site. In regions with high populations and traffic densities, the outdoor ozone concentrations were lower than in more rural areas. Daytime personal exposure was correlated with both outdoor ($r = 0.41$, $P < 0.01$), at the domestic site, and indoor ($r = 0.55$, $P < 0.01$) concentrations of the gas. There was a highly significant correlation between the indoor and outdoor concentration of ozone at individual domestic sites ($r = 0.56$, $P < 0.01$), the indoor-to-outdoor ratio ranging from 0.07 to 1.16 (mean 0.45, SD 0.23), and there were large differences in this ratio between homes, possibly due to variations in ventilation rates and dissimilar housing materials (walls, furniture, drapes, and books). The variability in personal exposure was explained, to 76%, by exposures indoors and outdoors (at the domestic site) for those persons who stayed at or near their home for at least 95% of the monitoring period ($N = 14$). For the total population ($N = 23$) 40% of the variability in personal exposure could be, at most, explained by the indoor and outdoor domestic concentrations, leaving 60% to be explained by exposure when absent from or near the home.

Monn et al (25) used passive sampling of ozone during four workdays (and nights) to assess the concentrations of ozone indoors and outdoors at the home, as well as the personal exposure. Twenty-six adults were included in the study, which was repeated three times. Over the sampling period, the average outdoor concentration of ozone was 52 (SD 11) $\mu\text{g} \cdot \text{m}^{-3}$, indoor levels were 8 (SD 6) $\mu\text{g} \cdot \text{m}^{-3}$, and the personal exposure was 22 (SD 7.6) $\mu\text{g} \cdot \text{m}^{-3}$. The indoor-to-outdoor ratio was 0.15 (SD 0.12). The personal-to-indoor ratio was 2.75 (SD 2.5) and the personal-to-outdoor ratio was 0.42 (SD 0.33). A high degree of correlation ($r = 0.75$) between the personal exposure and the indoor concentration was found for nonworkers, while the correlation was weaker for part-time ($P = 0.32$) and full-time workers ($P = 0.28$).

Due to the relatively long time spent indoors, total exposure is largely dependent on indoor levels. Variation in indoor ozone concentrations can be large between buildings in the same area, mainly due to differences in ventilation rates. In addition, the variation in personal exposure can be large due to the time spent at home, outdoors, and at work. Thus there are large variations in exposure between people mostly staying at home, such as housewives or small children, and people who spend time in day nurseries, schools, or workplaces, even if they are living in the same building or area. Office workers may have an elevated exposure to ozone from photocopiers or laser printers. Studies involving different categories of people, people living in different types of housing, or people living in different climatic regions (with different ventilation rates) should consider these differences. For instance, it has been shown that buildings in northern Sweden have a mean ventilation rate which is 20% lower than those in southern Sweden, with the same type of ventilation. It is also known that single-family homes have a significantly lower ventilation rate than multi-apartment buildings (26).

Indirect effects of indoor ozone

Ozone can play a role in indoor air chemistry by producing compounds damaging to health, such as aldehydes and free radicals. Thus measurements of ozone concentrations indoors, and without assessment of ozone-related compounds, can underestimate the impact of indoor ozone on human health. Indoor ozone reacts with volatile organic compounds, the result being aldehydes, organic acids, and free radicals (12, 27, 28). Weschler et al (28) measured volatile organic compounds in both the absence and presence of ozone (range 60 to 100 $\mu\text{g} \cdot \text{m}^{-3}$) in a stainless-steel room with fresh carpets. The concentration of carpet emissions, especially unsaturated volatile organic compounds, significantly decreased in the presence of ozone, while concentrations of aldehydes significantly increased. The "loss" of volatile organic compounds, other than aldehydes, possibly due to such reactions, has been significantly associated with an increased prevalence of symptoms of the sick building syndrome. The most important symptoms are the induction of headache, tiredness, perturbations to mucous membrane function, and skin symptoms (12, 29).

Some techniques to determine the concentration of ozone in ambient air

Wet-chemical techniques

Earlier wet-chemical techniques for measuring oxidants suffered from positive interference from other photochemical oxidants, such as peroxyacetyl nitrate, nitrogen

dioxide, and peroxides. The neutrally buffered potassium iodide method suffers also from negative interference from sulfur dioxide. The response to ozone and other interfering gases depends on the type of detector, pretreatment of the sample, and corrections through independent measurements of the interfering gases. The true ozone concentration is generally in the range of 80% to 110% of the total oxidant concentration, as measured with this method. For carefully made measurements, the errors can be substantially lower (30). The improved potassium iodide wet-chemical method acidically buffered with boric acid suffered less from interference from other pollutants.

Optical techniques

Two main techniques are currently being used to determine the concentration of ozone in air at stationary sites such as monitoring stations in urban or rural environments. The *chemiluminescent technique* involves the measurement of light emitted from chemical reactions. For ozone measurements, ethene is added to the sample of air, and the reaction of ozone and ethene generates light which is measured with a light-sensitive detector. The method is sensitive to temperature changes and needs to be re-calibrated often in order to guarantee a high degree of accuracy. The measurement is a point measurement.

The *light absorption technique* exploits the fact that ozone absorbs ultraviolet and visible radiation. Two instruments have been developed using light absorption, the ultraviolet absorption instrument, and the differential optical absorption spectrometer. The ultraviolet absorption instrument measures absorption at a single wavelength. The light source is a small mercury lamp, and the radiation is absorbed by ozone over a distance of 10 to 50 cm in a chamber, which is ventilated with ambient air. This instrument measures the concentration at one point in time. The differential optical absorption spectrometer (DOAS) exploits the fact that ozone has an absorption that varies with wavelength. The instrument consists of a light source that gives continuous radiation in the visible and the ultraviolet spectral areas and a spectrometer for dividing the light into different wavelengths. Measurements are made directly in the atmosphere, over distances ranging from several hundred meters up to about 1 km. The assayed concentration is expressed as the mean concentration along the light path.

Ozone dosimeters

There is a growing need to determine the exposure of humans to ozone as they move in different environments. Passive personal samplers or diffusion samplers are now coming into use to determine the ozone exposure of individual subjects. The advantage of the sampler

is that it follows the individual person as he or she is exposed to different environments. The sampler consists of an impregnated filter that absorbs ozone; the filter is then analyzed with respect to its chemical composition (31–33). Hitherto, such samplers have been used in Sweden to monitor the ozone exposure of workers in relation to paper bleaching with the gas. However, there is substantial interference from other components, for example, hydrogen peroxide. These difficulties are not expected to be encountered in other, less contaminated environments. In ambient air the combined effect of lack of accuracy and lack of precision of the passive samplers gives an uncertainty of 10% to 20%. The sampling time for the passive samplers is generally a few days to a few weeks. Improved samplers with forced flow have reduced the sampling time to only a few hours (31).

Current air quality guidelines and standards

World Health Organization

Several guidelines exist for ozone, depending on the purpose for their implementation. The primary objective of the guidelines is to provide a basis for protecting public health from the adverse effects of ozone in air pollution. The World Health Organization (WHO) has recommended the following guidelines for ozone in ambient air (34): (i) the mean value for 1 h should not exceed 150 to 200 $\mu\text{g} \cdot \text{m}^{-3}$; (ii) the mean value over 8 h should not exceed 100 to 120 $\mu\text{g} \cdot \text{m}^{-3}$. For the protection of vegetation WHO also recommends the following guidelines (34): (i) the mean value for 1 h should not exceed 200 $\mu\text{g} \cdot \text{m}^{-3}$, (ii) the mean value for 24 h should not exceed 65 $\mu\text{g} \cdot \text{m}^{-3}$, and (iii) the mean value over the growing season (100 d) should not exceed 60 $\mu\text{g} \cdot \text{m}^{-3}$. New guidelines for air pollutants have recently been prepared within WHO (35): (i) for ozone the mean value over 8 h should not exceed 120 $\mu\text{g} \cdot \text{m}^{-3}$. It is noted in the WHO document that the new guideline for ozone does not provide a margin of safety for protection from all acute health effects in the most sensitive members of the population.

United Nations Economic Commission for Europe

Within the framework of the Convention on Long-Range Trans-boundary Air Pollutants, held under the auspices of the United Nations Economic Commission for Europe (UNECE), the guidelines for ozone exposure have been related to critical loads and levels (36). The critical levels are based on effects on crops and natural ecosystems, for which there is a scientific basis for determining damage. Below these critical levels no visible damage or growth reduction could be determined on crops (table 2).

In a later review of current data the ECE Working Group on Critical Loads and Levels has proposed the use of cumulative doses above a certain threshold value. The threshold value is $80 \mu\text{g} \cdot \text{m}^{-3}$, and the cumulative dose, calculated as the number of hours times the concentration above the threshold level (in units of micrograms per cubic meter per hour), is then related to the damage. The workshop, held in Bern, in 1993 concluded that (37) (i) for crops cumulative doses of $5200 \mu\text{g} \cdot \text{m}^{-3} \cdot \text{h}$ and $10\,600 \mu\text{g} \cdot \text{m}^{-3} \cdot \text{h}$ give a 5% and 10% relative yield reduction, respectively and (ii) forest trees are less sensitive. A 10% reduction of plant biomass growth was found for oak with a cumulative dose of $12\,000 \mu\text{g} \cdot \text{m}^{-3} \cdot \text{h}$, for birch with a cumulative dose of $18\,000 \mu\text{g} \cdot \text{m}^{-3} \cdot \text{h}$, and for Norway spruce and Scots pine with a cumulative dose of $24\,000 \mu\text{g} \cdot \text{m}^{-3} \cdot \text{h}$. The cumulative doses for forests should not exceed $20\,000 \mu\text{g} \cdot \text{m}^{-3} \cdot \text{h}$.

United States air quality standards

The National Ambient Air Quality Standard for ozone (dating from 1979) is $235 \mu\text{g} \cdot \text{m}^{-3}$ (1-h value) in the United States. A new document on air quality criteria is now under preparation that may result in a new air quality standard for ozone.

European Union

The European Union (EU) has a directive for ozone (38) to inform and warn the public when the levels exceed certain threshold values: (i) a population information threshold of $180 \mu\text{g} \cdot \text{m}^{-3}$ for the mean value over 1 h and (ii) a population warning threshold of $360 \mu\text{g} \cdot \text{m}^{-3}$ for the mean value over 1 h. The EU also recommends a health protection threshold of $110 \mu\text{g} \cdot \text{m}^{-3}$ over 8 h and vegetation protection thresholds of $200 \mu\text{g} \cdot \text{m}^{-3}$ for the mean value over 1 h and $65 \mu\text{g} \cdot \text{m}^{-3}$ for the mean value over 24 h.

Sweden

The Swedish Environmental Protection Agency has guidelines or target values for ozone based on the same criteria documents as those used by the EC, WHO and UNECE (39, 40). In addition, the criteria document by Lindvall has been used. The national targets are (i) the concentration over the growing season (April to September, between 0900 and 1600) should not exceed $50 \mu\text{g} \cdot \text{m}^{-3}$ in order to protect crops and forests, (ii) the 1-h mean value of ozone should not exceed $120 \mu\text{g} \cdot \text{m}^{-3}$ more often than 12 h per year, and $150 \mu\text{g} \cdot \text{m}^{-3}$ should not be exceeded at any time. For work premises the maximum allowed concentration of the gas is related to the time of exposure. The Swedish Board of Occupational Safety and Health requires that the concentration over 8 h must not exceed $200 \mu\text{g} \cdot \text{m}^{-3}$ and that the concentration over any 15-min period during the workday should not exceed $600 \mu\text{g} \cdot \text{m}^{-3}$.

Table 2. Critical concentration levels for ozone with reference to crops (35).

Time (hours)	Concentration ($\mu\text{g} \cdot \text{m}^{-3}$)
0.5	300
1	150
2	110
4	80
8	60
Vegetation season ^a	50

^a The critical concentration for the vegetation or growing season refers to April to September, between 0900 and 1600 daily.

Summary and concluding remarks

Pollution by photochemical oxidants is caused by anthropogenic emissions of nitrogen oxides and volatile organic compounds. Ozone is the most important photochemical oxidant; others are peroxy acetyl nitrate (PAN) and hydrogen peroxide. Photochemical pollution occurs predominantly in summer, during which episodic high levels and elevated background concentrations are encountered. The present Swedish guideline or target value for the protection of human health [$120 \mu\text{g} \cdot \text{m}^{-3}$ (1-h mean) less than 12 h per year] is exceeded about 130 h per year in southern Sweden, but sometimes also in northern Sweden. A complementary guideline (limit value) states that the ozone concentrations should be lower than $150 \mu\text{g} \cdot \text{m}^{-3}$ at all times; this guideline is also exceeded in most parts of Sweden.

The indoor-to-outdoor ratio for the ozone concentration is typically in the range of 0.1 to 0.8, with low values at low ventilation rates and high values at high ventilation rates. Buildings with a low ventilation rate, such as single family homes, can have an indoor-to-outdoor ratio between 0.1 and 0.5, with the lowest values for single family houses and higher values for buildings such as offices or schools (possibly between 0.3 and 0.8). Because of the relatively long periods people spend indoors, total exposure is largely dependent on indoor levels. The variation in personal exposure is largely due to the time spent at home, outdoors, and at work.

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