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USE OF OZONE GENERATING DEVICES TO IMPROVE INDOOR AIR QUALITY

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Room ozonization has been in widespread use to "freshen" indoor air for more than 100 years. This use is sometimes promoted with the claim that ozone can oxidize airborne gases, and even particulates, to simple carbon dioxide and water vapor. Aside from whether ozone can improve indoor air quality, the potentially deleterious consequences to public health of overexposure to ozone are of concern. The literature on both allegations is reviewed. It indicates 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 commercial use of ozone for the removal of indoor air contaminants, including odors, evidently was conceived originally more than 100 years ago.[1] The presumption made to promote ozone for this purpose is that it will oxidize organic compounds to the extent that only carbon dioxide and water vapor remain. This theory is shown in Figure 1. In the United States there are several commercial manufacturers of air purifying devices (APDs) that generate ozone. These APDs are sold with the claim that ozone will remove air contaminants from indoor air. Sales of such devices by one leading manufacturer have exceeded 140 000 units.[2] These devices are marketed to homes, schools, businesses, and offices and when used introduce ozone into occupied indoor spaces. Aside from whether the claims of effectiveness are supported, the devices may be capable of producing unhealthy levels of ozone if they are not carefully monitored and controlled.[3]

The focus of this report, in addition to the possible health hazard associated with exposure to ozone, is on the removal of organic contaminants from air by use of ozone. Related issues, which are not reviewed here, include the use of ozone as an effective anti-microbiological agent, use of ozone for odor removal from surfaces (such as after fire damage), and the concurrent use of air ionization. An adequate body of literature exists on these other subjects, and indicates that if provided with high concentrations, while simultaneously providing protection to individuals from exposure to ozone, some control effectiveness may be possible.

To better resolve both the purported effectiveness of ozone for air purification and the health effects of ozone, a literature review was conducted. The primary criterion used for selecting literature was publication in a scientific, preferably peer-reviewed, journal. Also included are the findings and conclusions of widely recognized institutions and public advocacy groups that have studied this subject. There is a large body of anecdotal literature not supported by experimental research and written for promotional purposes. Such literature was not included here.

HEALTH EFFECTS OF OZONE

Ozone is a gas consisting of three oxygen atoms having the molecular formula O_3. The toxicity of ozone to the lung has been studied extensively. Yet most of the research has involved short-term studies ($\leq$1 day).

Above 120 ppb, acute ozone exposure in humans has been associated with a remarkable array of complaints including eye irritation and visual disturbances, headaches, dizziness, dry feeling in the mouth and throat, feeling of tightness and aches in the chest, insomnia, and coughing.[4] After exposure to lower, more environmentally relevant levels (60–120 ppb), ozone induces in healthy individuals measurable loss of lung function with cough and chest pain on deep inhalation, inflammatory response associated with cellular and biochemical changes, and increased airway responsiveness to allergens and irritants.[5–8] There is also evidence that ozone increases the hazard associated with exposure to other environmental pollutants and allergens, increases susceptibility to infection, and impairs clearance of inhaled particles.[7,9–13] Simultaneous exposure to ozone and other respiratory irritants can produce additive or synergistic effects.[14] Finally, both controlled exposure studies and population studies of subjects exposed to ambient pollution indicate substantial differences in response to ozone, suggesting the existence of more susceptible subgroups within the population.[15–18] Significant individual variation in response (i.e., susceptibility) is observed for ozone-induced increases in airway resistance and decreases in lung volumes and flows. Increased airway resistance has been observed in individual adults exposed to measured ozone concentrations of 100 ppb.[19] Children appear to be more susceptible to the effects of ozone; decrements in lung function are suggested for concentrations as low as 60 ppb.[20]

Tolerance to repeated exposure to ozone has been observed,[21] probably resulting from damage to irritant receptor cells in the naive (previously unexposed) animal or person. In the short term this increased tolerance may seem biologically

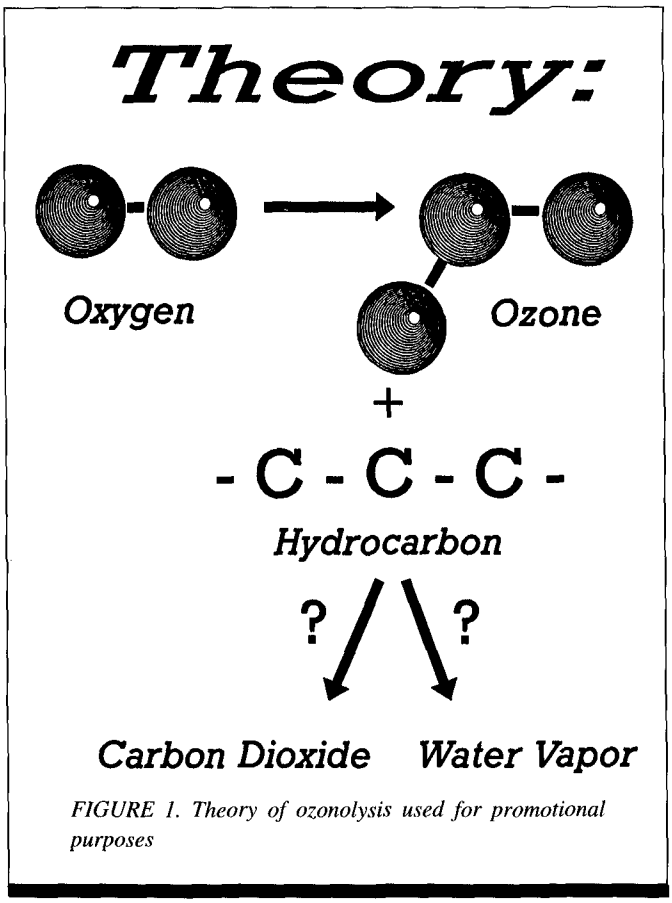

FIGURE 1. Theory of ozonolysis used for promotional purposes

beneficial, since symptoms and decreased lung function are alleviated.[21] However, like the skin's tolerance to chronic exposure to sunlight, which results in thickening and the loss of elasticity, chronic exposure to irritation in the lung also may lead to permanent damage. Hence, chronic exposure of experimental animals to ozone (lasting several months to several years) has been shown to cause irreversible obstructive airway disease. Concentrations as low as 60 ppb have been associated with fibrosis and emphysematous changes.[22–25] The changes observed have been equated with premature aging of the lung.[26] Some epidemiological studies of people chronically exposed to high ambient ozone show functional decrements consistent with the chronic experimental animal studies where cumulative structural changes occurred.[26] Ozone also has increased the incidence of lung tumors in Strain A mice at concentrations of 310 ppb and higher, but there is no evidence that ozone is a lung carcinogen in humans.[27–30]

OCCURRENCE AND EXPOSURE CRITERIA

Ozone occurs naturally at ground level at concentrations of 10 to 25 ppb, but may be as high as 100 to 300 ppb in urban areas as a result of photochemical smog.[31] At present, the U.S. Primary National Ambient Air Quality Standard (NAAQS) for ozone is 120 ppb averaged over 1 hour, not to be exceeded more than once per year.[32] The Occupational Safety and Health Administration (OSHA) permissible exposure level (PEL) standard restricts workplace exposure to no more than 100 ppb ozone, averaged over an 8-hour workday.[33] The Food and Drug Administration decreed that "no device shall produce ozone concentrations in excess of 50 ppb in enclosed spaces intended to be occupied by people for extended periods of time (e.g., homes, hospitals and offices)."[34]

More than half of the U.S. population already lives in areas exceeding the prevailing NAAQS for ozone. In 1991 the American Lung Association (ALA) and several states sued the U.S. Environmental Protection Agency (EPA) to force reevaluation of the adequacy of the current ambient ozone concentration based on post-1988 health effects research. They presented exposure analysis documentation for an 8-hour, 80 ppb level, which is lower than the current EPA level of 120 ppb for 1 hour. If EPA were to adopt the ALA level, an additional 31 million Americans would be classified as living in areas that exceed the NAAQS limit.[35] Being indoors normally provides some protection from the ozone concentrations experienced in outside air, unless of course an ozone generating APD is in use or there are windows open.[36,37]

Given the fact that ozone is a toxic gas and the potentially detrimental health effects that it can cause, it would seem prudent to minimize or eliminate any unnecessary exposure to ozone, such as that generated by air purifiers, unless benefits can be clearly demonstrated.

OLFACTORY DETECTION

The odor of ozone often has been described as unpleasant, pungent, and associated with electrical equipment that has developed a malfunction and caused sparking. The odor threshold for ozone in clean air has been reported by various researchers at between 2 and 100 ppb, although most people can initially detect about 10 to 15 ppb ozone on leaving an uncontaminated area.[38–40] The odor threshold of ozone appears to differ among individuals, and the ability of an individual to sense ozone by its odor may even change from day to day.[41] Rapid olfactory fatigue to ozone has been reported. Henschler et al. found that at 20 ppb ozone, the initial odor among 10 test subjects could no longer be detected after 30 sec to 12 min, and an average of 5 min. At 50 ppb and using 14 test subjects, olfactory perception lasted longer, 2 to 30 min, and on average 13 min. At 110 ppb and using 11 test subjects no odor could be detected after an average 22 min.[38] Wanner and Gilgen reported a definite detection of ozone on entering a room containing 30 ppb but also the rapid disappearance of smell after several min.[42] Thus, the sense of smell when used to warn of the presence of elevated concentrations of ozone appears to be unreliable when exposure is continuous.

GASEOUS-STATE CHEMISTRY OF OZONE

Due primarily to efforts to understand photochemical smog reactions in ambient air, rate constants (k_E) have been determined experimentally for the reaction of ozone with over 100 chemical compounds in air. These rate constants, determined by physical science kineticists, have been determined for compounds that

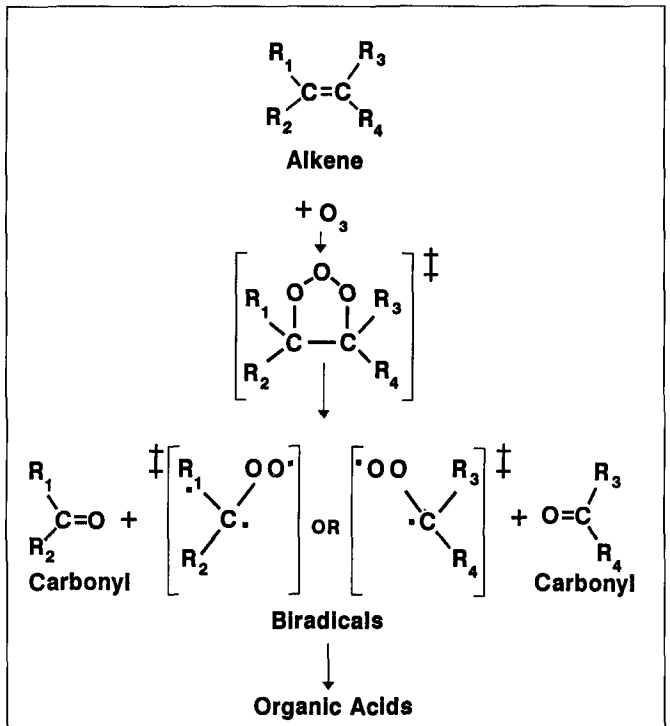

FIGURE 2. Reaction pathway of ozone and alkene compounds leading to formation of an aldehyde or ketone and an organic acid

encompass all major classes of chemicals and can be used to calculate the persistence of an organic compound in the presence of any constant concentration of ozone.[43]

It is important to note for this discussion that the rate of reaction between ozone and any concentration of an organic substrate depends on the ozone concentration. The half-life of a chemical—the time it would require to remove half of the initial concentration of a gaseous compound—is calculated using the formula $\ln 2/k_E[O_3]$, where k_E = reaction rate constant of organic compound with ozone, and $[O_3]$ is the constant concentration of ozone (molecules/cm^3). The half-lives are independent of the initial organic concentration but are directly related to the ozone concentration.[43] For example, a constant concentration of 50 ppb ozone requires twice the time to remove any concentration of an organic compound than would 100 ppb. Ozone may react rapidly with an organic compound or extremely slowly, with rate constants generally ranging from 10^{-15} to 10^{-24} cm^3 molecules^{-1} sec^{-1}, respectively. Theoretically, the time it would take to remove half the amount of an organic compound with a constant concentration of 100 ppb of ozone over the range of reactivities indicated by the above rate constants would range from 10 min to thousands of years. The preponderance of scientific literature indicates that significant reactivity occurs between ozone and only one class of chemical compounds—the unsaturated alkenes. Figure 2 shows the most likely mechanism involving chemical oxidation with alkenes.[43]

The reaction of ozone with an alkene probably occurs by electrophilic attack on the carbon-carbon double bond resulting in a 1,3-dipolar cycloaddition. The dissociation of the cycloaddition compound creates two new compounds, one containing a carbonyl group. If one of the -R moieties on the carbonyl compound is a hydrogen atom, an aldehyde is formed. A ketone is formed if both -R moieties are alkyl groups. The second compound formed as a result of this dissociation is an unstable biradical, as indicated by the ‡ mark in Figure 2. This biradical can react with several common air contaminants. If it reacts with NO, NO_2, or SO_2, another aldehyde or ketone may form while oxidizing the gas with which it reacted.[43] In one experiment, about 0.7 mole of formaldehyde was produced for every mole of ethylene removed.[44] In another experiment the gas-phase reaction products of styrene and ozone were formaldehyde and benzaldehyde, with respective yields of 37% and 41%.[45] The biradical also may react with water vapor to produce an organic acid.[43] The reaction products, if any, formed when ozone reacts with other classes of compounds (e.g., alkanes, aromatics, etc.) are largely unknown, partly because these reactions are so slow.

It is important to note that none of the experimental evidence found in the literature supported the suggestion that any of the gaseous-phase reactions are so extensive at the concentrations of ozone relevant to this discussion as to result in decomposition to carbon dioxide and water vapor. Only when near-explosive (highly exothermal) conditions exist would such decomposition likely take place.[46] Description of results from some actual experiments used to determine the effectiveness of air ozonization are presented in a later section.

Table I shows the calculated half-lives in the presence of ozone of 14 compounds most often found in residential indoor air.[47] The list for the organic pollutants was compiled by a working group of the World Health Organization, and a concentration of 100 ppb of ozone was assumed in calculating the half-life. Although styrene is not usually found in residential and office

TABLE I. Calculated Half-Life of the Most Common Residential Indoor Air Contaminants[A]

Compound	*Rate Constant (cm^3 molecules^{-1} sec^{-1})*	*Half-Life at 100 ppb O_3*
n-Hexane[B]	$\sim 10^{-23}$	>880 years
n-Heptane[B]	$\sim 10^{-23}$	>880 years
Cyclohexane[B]	$\sim 10^{-23}$	>880 years
Methylcyclohexane[B]	$\sim 10^{-23}$	>880 years
Toluene	$<10^{-20}$	>0.9 years
m,p-Xylene	$<10^{-21}$	>9 years
Trichlorethylene[B]	$\sim 10^{-20}$	0.9 years
1,1,1-Trichloroethane	$<10^{-23}$	>880 years
Tetrachloroethylene[B]	$\sim 10^{-23}$	880 years
Isobutanol[B]	$<10^{-20}$	>0.9 years
Formaldehyde	$<2 \times 10^{-24}$	>4400 years
Acetaldehyde	$<10^{-20}$	>0.9 years
n-Hexanal[B]	$<10^{-21}$	>9 years
Styrene	2×10^{-17}	3.9 hours

[A] List compiled for residential homes in report by World Health Organization, *Indoor Air Quality: Organic Pollutants.* (EURO Reports and Studies No. 111). Copenhagen: WHO, Regional Office for Europe, 1989

[B] Estimated rate constant and half-life based on chemical similarities to tested compounds

indoor air, it may be present in various building products and especially if new carpet with padding recently has been installed.[48] The half-lives are on the order of years for all compounds on the list, except styrene—the only alkene compound. Among a more extensive list of 68 volatile chemical compounds frequently detected in indoor air (albeit at exceedingly small concentrations), only six are of the alkene class.[49] These volatile compounds are in themselves generally innocuous and are emitted from pine wood construction and furnishings (e.g., terpenes). However, it will be discussed later how oxidation of the compounds by ozone can increase their toxicity.

The rate constants used in Table I were taken from the literature and typically were experimentally determined in an airtight and inert heavy quartz-glass or stainless steel vessel, where causes of chemical loss, other than chemical interactions in the gaseous state, are negligible.[43] When a specific rate constant for a compound was not found, it was estimated from the rate constants of similar chemicals in that class that had been evaluated. Additional means of chemical loss that might otherwise normally occur in a container without ozone include diffusion through the walls of the container, air leakage, adsorption to the wall, or chemical reactions with the container surface.

REPORTS ON THE USE OF OZONE GENERATORS INDOORS

Potential for Excessive Exposure

In an attempt to demonstrate that ozone generating APDs could produce unacceptably high ozone concentrations, Shaughnessey and Oatman experimented with two different commercially available ozone generators intended for residential and office use.[3] The ozone generators were operated separately inside either a closed unfurnished room with 111 ft^2 of floor space or a typical business office with 350 ft^2 of floor space. The smallest ozone generator elevated the concentration in the closed room to 1000 ppb in about 3 hours, and the concentration continued to increase thereafter. The concentration in the office space equilibrated at 80 or 100 ppb depending on whether the fresh air exchange rate was 1.3 or 0.45 air exchanges per hour. The larger ozone-generating unit, when used in the office space, equilibrated at 300 or 500 ppb with the two different air exchange rates, respectively. Thus it was demonstrated that under these particular test conditions and with the two devices chosen, indoor air concentrations of ozone that exceed the health-based occupational and ambient criteria and standards can be generated by a single unit.

The Consumers Union, publishers of *Consumer Reports* magazine, recently conducted an evaluation of ozone generating devices.[50] Two devices were purchased from different manufacturers. The size of the devices and the output of ozone was selected by consultation with company representatives. Different size chambers, corresponding to rooms $9\frac{1}{2}$ by $20\frac{1}{2}$ ft, 17 by 17 ft, and 37 by 37 ft, with 8-ft ceilings, were either sealed or provided with one air change per hour. The rooms were designed in accordance with specifications of the Association of Home Appliance Manufacturers protocol for evaluating air cleaners. In the unventilated smallest room one APD generated 150 ppb of ozone on the low setting and 2700 ppb on the high setting after 15 hours. With one air change per hour in the room this same APD produced 700 ppb of ozone on its high output setting in 24 hours. The other manufacturer's device provided an adjustment knob to control ozone output according to the size of the room. In the three rooms used in the tests and with the output control set corresponding to manufacturers' recommendations according to room size, ozone levels were below 50 ppb only in the smallest room with one air change per hour. The ozone levels were reported to exceed this level in all other rooms (exact concentrations not reported), both with and without forced air ventilation.

Effectiveness in Removing Air Pollutants

Studies that have attempted to evaluate the effectiveness of ozone to remove air contaminants and odors are summarized in Table II.

Weschler et al. performed studies on the effect of ozone on volatile emission products from new carpets.[51] The authors acknowledged that ozone reacts rapidly with some compounds containing unsaturated carbon-carbon double bonds (i.e., alkenes). The primary volatile organic compounds (VOCs) emitted from new carpets are 4-phenylcyclohexene, styrene, and 4-ethenylcyclohexene, each of which come from the styrene-butadiene rubber latex adhesive commonly used to bind the secondary backing of carpets. These compounds all contain an unsaturated carbon double bond. An environmental test chamber constructed of stainless steel with an interior volume of 20 m^3 was used in the experiments. Four new carpets typical of the types used in residences, school classrooms, and offices were tested.

The experimental protocol for the above study consisted of placing a carpet sample on the floor of the chamber, sealing the chamber, and sampling the air in the chamber for several volatile components in the carpet and possible oxidation products for a period of seven days. On the seventh day the ozone generator was turned on, and the concentration of ozone in the chamber was monitored. Twenty-four hours after ozone was first introduced into the chamber, samples for specific VOCs, total volatile organic compounds (TVOCs), and aldehydes were collected. The ozone generator was then turned off. Sampling for organic compounds was repeated after a period when no ozone was present and when the ozone generator was turned on again. This provided two full test cycles, with and without ozone, for each carpet sample.

The results from the above study showed clear and substantial changes in the concentrations of compounds inside the chamber after ozone was introduced. The primary VOCs emitted from new carpets, such as phenycyclohexene, styrene, and 4-ethenylcyclohexene, were reduced sharply. At the same time, however, a number of new compounds were detected that were not present prior to introducing ozone. The new compounds were primarily linear aldehydes and formaldehyde. However, likely products of reaction of ozone with styrene, including benzaldehyde, benzoic acid, and acetophenone, also attained much higher concentrations when ozone was present. In addition, after ozone was introduced, the TVOC concentration increased about four fold.

TABLE II. Summary of Experimental Studies on the Effectiveness of Ozone to Remove Chemicals and Odors from Air

Experimental Design	*Results*	*Reference*
New carpet samples placed in chambers with and without O_3 and instrumentally monitored	With ozone, only alkene compounds reacted and were converted into aldehydes, organic acids, and ketones. Total volatile organic compound concentration increased.	51
Sewage sludge air treated with ozone in wet scrubbing process	Ozone produced multiple new compounds as determined by UV spectrometry.	52
Formaldehyde concentration monitored in chamber and effect of ozone-generating device evaluated	Ozone was not found to influence disappearance of formaldehyde in air.	53
Panel of odor judges rated intensity of odor before and after ozone was introduced into room	Ozone was not found to decrease odors once ozone dissipated, indicating lack of chemical removal.	54
Concentration of several organic compounds in air monitored in presence of ozone	Ozone did not affect organic compound concentration in air, although ability to smell odorous compounds decreased in the presence of ozone.	55
Tobacco smoke odors instrumentally monitored and panel of judges used to determine odor after ozone was introduced into the test chamber	Ozone was not found to have affectively decreased the odor from tobacco smoke after an overnight exposure.	50

This pattern of decreasing unsaturated carbon compounds with ozone present, followed by a simultaneous increase in aldehydes and total organic compounds, was demonstrated repeatedly with each carpet and during each ozone cycle. It was demonstrated experimentally that the new compounds were not the product of reactions with ozone within the multisorbent samplers, nor were the aldehydes generated by reaction of ozone with the chamber materials. The increase of TVOCs when ozone was present suggested that ozone was reacting directly with relatively nonvolatile substances in the carpet (presumably alkene-type compounds), resulting in an increased production of volatile compounds in the air. It also was found that other VOCs, like the saturated alkyl benzene and saturated alkanes, displayed no unexpected concentration decrease in the presence of ozone. Furthermore, not all compounds with unsaturated carbon double bonds were reduced markedly in the presence of ozone. Vinyl acetate was relatively unaffected by ozone.

The authors concluded that the experiments show how ozone

> reduced the concentrations of some potentially irritating compounds (e.g., 4-phenylcyclohexene, styrene, and 4-ethenylcyclohexene) while at the same time generating a different set of irritants (e.g., formaldehyde and other aldehydes). The evidence suggests that the higher molecular weight aldehydes were generated from the reaction of ozone with relatively nonvolatile substances such as unsaturated fatty acids or unsaturated polymers [in the carpet].

The authors also cautioned that the use of some common household products, such as detergents, waxes, cleaners, and scented "room fresheners" (e.g., terpenes) might contain alkene compounds that could be converted into aldehydes in the presence of ozone.

A related demonstration of the conversion of volatile alkene type compounds from a sewage treatment plant to other compounds was reported by Arnold.[52] Many new compounds resulted from the introduction of ozone into the effluent air stream. However, no identification of either the compounds produced or their toxicity was attempted.

Esswein and Boeniger conducted an experiment intended to replicate, under controlled laboratory conditions, the airborne formaldehyde concentrations during an embalming process.[53] Using embalming solution, which contained approximately 35% formalin, the effect of an ozone-generating APD on the change in formaldehyde concentration over time was monitored. An initial concentration of 2.5 ppm formaldehyde in air was created, which resembles short-term peak levels often encountered in funeral homes. All experiments were run for 90 min, the average duration of most embalmments. One set of test runs was performed without introducing ozone and one set was performed with ozone. Test runs performed each way were done in triplicate. When ozone was introduced, a static concentration of 500 ppb was maintained. The formaldehyde and ozone (when introduced) concentrations were monitored continuously during each test run. The results indicated no effect of ozone, even with the high concentrations used (five-fold excess of the OSHA PEL), in enhancing the natural decline of formaldehyde within the test chamber.

Several studies have been performed to investigate the reduction of odors by ozone, as measured by the sense of smell. Witheridge and Yaglou evaluated the effectiveness of body odor removal by ozone.[54] Using a room occupied by test subjects who produced the odor and judges who entered the room, the ability to affect malodorant intensity by ozone was studied. It was found that only when the odor of ozone was perceptible, was the body odor not detected. Depending on the concentration of each, either the ozone odor or the body odor was detected. To support the evidence that the obliteration of odors was due to masking and not to chemical oxidation, one experiment was

performed where the subjects left the test chamber at the end of an experiment where ozone had been present and where the judges could no longer detect the body odor, but could detect the smell of ozone. With the ozone generator turned off, ozone quickly spontaneously decomposed and could no longer be detected by smell, but the body odor could once again be detected. If ozone had removed the malodorants from air chemically, the effect should have been permanent, and the odor would not have returned. The authors speculated that since body odor may be composed primarily of organic acids, which would be resistant to chemical oxidation by ozone, body odor is not likely to be permanently affected by the presence of ozone. The authors cautioned about the variable amounts of ozone produced due to varying humidity levels, and the lack of control over the resulting ozone concentration. They concluded that "the use of ozone should be discouraged because of its great toxicity."

Erlandsen and Schwartz failed to obtain any demonstrable oxidation by ozone of odorous compounds like hydrogen sulfide, ammonia, trimethylamine, butyric and valeric acids, indol, and skatol, although the odors of these substances were effectively masked.[55]

Consumer Reports magazine also reported their investigation of the ability of ozone-generating devices to remove tobacco odor from a room.[50] They suggested that some odors, like tobacco smoke, may linger long after the smoke has cleared visibly, because the gases may desorb from surfaces over time. To test whether ozone generation was effective in removing the odors of tobacco smoke from air, a room was first heavily contaminated. Using a nonspecific, broad response "odor sensor" sampling device and a team of trained sensory panelists, the odor level of the room was monitored. Thirty minutes after the contaminated room had been treated with ozone, only 13% of the odor was removed with the ozone generator. By comparison, 67% of the odor was removed using a simple table-top air cleaning device that used only air filtration (with no ozone). The following day the panelists reported the room treated by the ozone generator smelled of stale tobacco smoke and the odor of ozone.

While some researchers have concluded that ozone does not remove odors in occupied spaces, others have concluded that ozone, with its own distinct odor, could temporarily mask or disguise the objectionable odors. It has been reported that an irritant such as ozone can immediately diminish and actually block olfaction.[56] When ozonization was discontinued, the original odors were still present. The biological mechanism of blocking is presumably due to interplay between the sensory activity of the trigeminal nerve being activated by the irritant and the sensory activity of the olfactory nerve system. Many modern air deodorizer sprays contain irritants or pungent compounds that perform this same function of camouflage.

DISCUSSION

None of the commercially available ozone generating devices sold for use in the home or business include a means of quantifying of the level of ozone created in the air. Typically, the sense of smell is solely relied on to determine the acceptable ozone concentration in a room. Biological diversity in the human population and conditions affecting the upper respiratory tract would suggest variation in the ability of people to smell ozone. Since olfactory fatigue can occur when continually smelling other compounds, and there is evidence that this could occur with ozone as well, one cannot place reliance on the sense of smell to avoid the potential hazard of excessive exposure.[57,58] Furthermore, the influence of other odors on one's ability to smell ozone (i.e., masking effect) appears not to have been suitably studied.

An additional concern is that room air humidity appreciably affects the generation and persistence of ozone, reducing both when humidity is high. Achievable levels could thus be much higher during dry periods.[54] Unless the ozone generation rate was adjusted to compensate for the change in humidity, there could be an unintentional risk of higher exposure without the smell of ozone being noticed.[54,57]

The presence of varying amounts of air contaminants that might react with ozone also suggests the practical dilemma of adjusting the ozone generation rate in response to varying concentrations of a reactive organic. If a sufficiently reactive organic is present, the ozone may be removed rapidly. When the organic is not present or not reactive, the ozone would not be consumed at the same rate and could accumulate and reach harmful levels.

Reactivity with ozone increases with an increasing number of electron-donating substituents in the organic compound.[43,59] As has been shown previously, interaction of ozone is most likely to occur with aliphatic and aromatic alkene chemicals. In the ambient environment alkene compounds are also very reactive with other atmospheric species, such as the nitrate radical (NO_3^-) and hydroxyl radical (OH^-), and therefore are inherently short-lived. As was previously shown, when ozone reacts with alkene compounds, one common product is an aldehyde. Such compounds are often more toxic, notably allergenic and carcinogenic, than the parent alkene.[60] Haloalkenes (e.g., containing chlorine, fluorine), with their electron withdrawing substituents, are less reactive than nonhalogenated alkenes. Other classes of compounds, such as the amines, aldehydes, ketones, sulfides, and all aliphatic and aromatic alkanes and haloalkanes are much less reactive and would require weeks to many years for half of the original concentration to be removed strictly by reaction with 100 ppb ozone (Table I).

The practical utility of ozone to remove pollutants from indoor air can be put in better perspective when compared to alternative means. For instance, dilution ventilation combined with minimizing the source of pollutants can be very effective in reducing indoor contaminant concentrations. Due to modern construction practices and energy conservation requirements buildings have become increasingly tight. Such structures tend to trap contaminants emitted from building materials and furnishings. Lack of adequate ventilation was found to be the most prominent cause of indoor air quality complaints from occupants of office buildings.[61] With minimal ventilation indoor air contaminants can be effectively reduced. To illustrate this, an opened window can introduce substantial amounts of fresh dilution air, provided that the outside air is less contaminated than the indoor air. The equation $C_t = C_o e^{-kmt}$ for estimating the final concentration of indoor contaminants, can be used to make some rough approximations of how effective simple ventilation can be. The factors

included for calculating the final concentration are C_o = initial concentration, k = a mixing factor, m = air changes per hour, and t = time in hours.[62] For purposes of illustration, the author assumed a single level residence of 1000 ft^2. (Air infiltration through the opened windows was assumed to be 250 linear ft/min due to a slight breeze, convection, and diffusion; the width of window was 2 ft; and mixing inside due primarily to the opened windows such that k = 0.3.) Assuming a very tight building with little infiltration and an initial concentration of contaminant with no new generation, only 3% of indoor air contaminants will be removed in 3 hours (assuming no other source of removal, e.g., adsorption, surface reactivity). If three typical windows are opened 1 inch for 3 hours, there will be a reduction of about 60% in the concentration of indoor contaminants. For most building construction, normal outside air infiltration provides at least this much fresh air change in all but the tightest buildings.[63] Adequate ventilation, plus controlling the sources of indoor air contaminants, are two effective steps that can be taken in the interest of improving indoor air quality.

Among the most common complaints from occupants with indoor air problems are irritation of the eyes, nose, and throat, headache and fatigue. While over 300 different compounds have been found in the air of residential homes, formaldehyde is the most common contaminant and is the most irritating.[47,64] The complaints in general, and specifically for formaldehyde exposure, are quite similar to the symptoms reported with exposure to ozone. The similarity of effects and the potential for additive and perhaps synergistic interactions between typical indoor contaminants and ozone should be of concern. The result of such interactions could worsen the air quality and the discomfort of the occupants, and may cause long-term harm.

In addition to the negative conclusions about the effectiveness of ozone generators drawn in the investigations cited above, others have concluded that such devices have little utility, especially when the toxicity of ozone is considered. *Patty's Industrial Hygiene & Toxicology* states that "ozone-producing devices have been offered for indoor use, but they generate such low concentrations that their effect in controlling malodorants is nil."[65] The London Consumers Association concluded in regard to ozone generators, "inhalation of air enriched with even minute quantities of ozone is useless and could be dangerous."[66] The American Society of Heating, Refrigerating and Air Conditioning Engineers offers in regard to ozone:

> while oxidizing gases such as ozone and chlorine can oxidize odors in water, concentrations required for air deodorization would be so high that they would be toxic to space occupants. The major effect of ozone generators is to reduce sensitivity of the sense of smell, rather than reduce actual odor concentrations.[67]

Various state health departments and the federal Food and Drug Administration have formed similar conclusions.[34,68,69] Recently, *Consumer Reports* magazine concluded after performing tests that they "wouldn't recommend an ozone generator, even as a last resort."[50]

The debate has been active for almost a century over whether ozone generation at low levels is effective in removing indoor air contaminants. It is interesting from a historical perspective that Konrich wrote with obvious frustration in 1913:

> It should be pointed out that the thoroughly negative criticisms of investigators who have been concerned experimentally with air ozonization stand in striking contrast to the fact that ozone machines at the present time are apparently being bought and used in large numbers. Whether this contradiction will ever be resolved remains to be seen. Evaluation from a hygienic standpoint is obliged to base itself on the solid ground of experimental knowledge. If hygienists wanted to leave this ground and align themselves with what practice, based on false assumptions, seems to be teaching, then they would thus be giving up the most effective weapon to which they owe their greatest success, namely scientific experimentation.[1]

CONCLUSION

Introducing ozone in indoor air may present a risk to human health, especially if it is present with other air contaminants. Detrimental effects, primarily to the respiratory system, have been well documented. Health effects from chronic exposure are less well studied, but there is evidence of irreversible damage to the lung.

Despite the long-term and widespread use of these devices, there is a lack of evidence in the scientific literature that would support ozone as effective at low concentrations to remove organic contaminants from indoor air. Rather, scientific evidence exists that implies that low levels of ozone will not effectively remove most indoor air contaminants. Subjective claims of improved air quality may instead be explained by evidence indicating that ozone may act only to mask odors or to convert some odorous compounds to less odorous but potentially more toxic compounds. Anecdotal reports of enhanced mood and subjective perception of better health may be influenced psychologically whereby the known introduction of an "air purification" device, and possibly the odor of ozone, might be equated with improved air quality.

Dilution ventilation with clean air, combined with eliminating or controlling the source of pollutants, are proven means of reducing indoor air contaminants and improving indoor air quality. Compared with the use of ozone these alternative strategies are safer and more effective in removing contaminants from indoor air.

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