

OZONE FOR AIR TREATMENT – Basic Principles

Rip G. Rice, Ph.D.

RICE International Consulting Enterprises
1331 Patuxent Drive, Ashton, MD 20861, USA
Tel: 301-924-4224; fax: 301-774-4493; e-mail: RipRice4Ozone@cs.com

Abstract

Ozone is being utilized increasingly for various air treatment applications. Historically, deodorizing exhaust gases from meat processing and sewage treatment plants, pharmaceutical plants and restaurants, to remove smoke odors in bars and hotels, as well as to maintain the cleanliness of HVAC systems has been a foundation for ozone equipment. In recent years, ozone is being used by many fire and flood restoration firms to cope with smoke odors and mildew after flooding of homes and other types of buildings. Additionally, ozone is being commercialized for removal of nitrogen oxides from flue gases. Research studies have shown ozone can be effective for destroying anthrax surrogates, for prolonging the storage life of flowers, and for controlling *Listeria monocytogenes* in Japanese food processing plants. With the recent approval by the US Food & Drug Administration and the US Department of Agriculture of ozone as an antimicrobial agent, many air treatment applications for ozone are being studied and developed in food processing and storage plants.

When considering ozone for air treatment applications, certain basic technical and operating principles must be taken into account. These include the two primary commercial methods of ozone production (UV radiation and corona discharge), the effects of ambient conditions on the generation and efficacy of ozone, safety aspects of workers using ozone, and current government regulations dealing with ozone. These aspects of ozone technologies will be discussed in this paper.

Key Words

Ozone; Air Treatment with Ozone; Fire and Flood Damage; Mold Treatment; Food Storage; Anthrax; Nitrogen Oxides; Air Conditioning; Flower Storage;

Introduction

Ozone was discovered by Schönbein in 1834 (Schönbein, 1840) and was developed as a disinfectant for potable water in the late 1800s. Its first recorded use for treating air was in 1909 at a German meat storage plant (Horváth et al., 1985). Contaminants in air that ozone can destroy or oxidize include microorganisms (bacteria, molds, fungi, mites, yeasts), odorants (sulfidic compounds), and some organics (viruses, smoke, animal odors, volatile organic chemicals from a variety of sources). A most important point to recognize is that not all air contaminants react with ozone at the same rates. A second critical point is that relative humidity plays a crucial role in the treatment of air with ozone.

Unhappily, the practical use of gaseous ozone for treating air preceded knowledge of the safety aspects (to human beings) of ozone in air. Thus early proponents of ozone for air treatment simply recommended applying ozone regardless of whether humans were present or not. Then, after learning that exposure of humans to ozone in the gas phase should not be a recommended procedure, the damage had been done. Since ozone is a regulated air pollutant, and since breathing ozone by humans is bad for their health, public health regulators are opposed to the use of ozone to treat air when it can be breathed by humans.

Over the years, the recommendation to apply ozone when people are present has continued, spurred along by new people coming into the ozone field and not doing their homework. By that is mean not taking the time to learn that applying ozone to treat air in the presence of humans really is the wrong approach and one that raises red flags in the eyes of regulators and public health officials.

One can access the EPA web site to download an EPA Position Paper on ozone for treating air (“Ozone-Generating Air Cleaners and Indoor Air Chemistry” that assumes the addition of ozone to treat air in an enclosed space is to be done with people present.

<http://www.epa.gov/appcdwww/iemb/ozone.htm>

EPA points out that if concentrations of ozone are added that are not toxic to humans, they are so low as to be ineffective for killing microorganisms and for oxidizing volatile organic compounds. Thus, EPA’s position paper is anti-ozone for this purpose.

Instead, the proper approach to air treatment with ozone is to ensure that people will not be present when the appropriate amount of ozone are applied -- and there are several techniques for accomplishing this:

1. Withdrawing contaminated air from the enclosed space, treating the removed air with sufficient ozone to accomplish its purpose(s), destroying excess ozone and returning the treated air to the room;

2. Installing a timing mechanism to turn the ozonation system on at the close of the business day (when people will be absent the room to be treated), then about an hour prior to re-opening, the timer turns off the ozonation system. This approach allows decay of excess ozone prior to people returning to the treated area. Exhaust fans also can be installed to evacuate any residual ozone, if desired.
3. Remove humans, pets, plants sensitive to ozone, etc., from homes/rooms/buildings, add ozone to treat the air, exhaust or destroy excess ozone, and return people and furnishings.

U.S. Government Regulations – Ozone in Air

The following three U.S. Government agencies regulate levels of ozone in air. Their respective values are not identical, for reasons that will become evident – primarily considering the length of time of exposure to specific ozone levels by specific types of individuals.

Occupational Safety and Health Administration (OSHA)

This agency (part of the U.S. Department of Labor) regulates the safety and health of factory workers. These are presumed to be in good health, to enable working 8-hrs per day, 5-days per week. For ozone in plant air, OSHA sets the following limitations:

- ! ***PERMISSIBLE EXPOSURE LEVEL (PEL)***: 0.1 ppm (by weight), time-weighted average over an 8-hr day, 5-days per week.
- ! ***SHORT TERM EXPOSURE LEVEL (STEL)***: 0.3 ppm (by weight) averaged over 15 minutes, not to be exceeded more than twice daily.

NOTE: most humans are able to detect ozone in air at levels of ~ 0.02 ppm

U.S. Food and Drug Administration (FDA)

This agency of the U.S. Department of Health and Human Services regulates levels of ozone in air for the most sensitive humans – those who are either very young, elderly, infirm, confined to rooms, hospitals, nursing homes, etc., or who are immunocompromised. In the early 1970s, FDA determined that ozone levels in air above 0.05 ppm (by wt) are effective for killing most microorganisms, but are also toxic to the sensitive humans cited above (when exposures are 24 hours/day, 7 days/week). On the other hand, ozone concentrations in air below 0.05 ppm (by wt) are not toxic to sensitive humans, but also are not effective for killing microorganisms or oxidizing certain odorants.

Consequently, FDA ruled (US FDA, 1975) that any ozone generator marketed with a medical claim (e.g., “ozone will kill microorganisms in the air”, “ozone makes the air safe to breathe”, etc.) is mis-branded and is illegal to market (in the USA).

U.S. Environmental Protection Agency (EPA)

EPA's Ambient Air Ozone Regulation

EPA's regulatory responsibility for ozone is for the ambient air breathed by all humans, whether healthy or sensitive. On the other hand, if a regulated level of ozone were to be set for healthy individuals, then sensitive individuals could be effected. Consequently EPA has set an ambient ozone level in air of 0.08 ppm (previously 0.12 ppm), not to be exceeded more than three times per year.

We are all aware that this level is exceeded more than three times per year in densely populated urban areas (Los Angeles, Houston, Denver, etc.), and is difficult to enforce. In fact, this ambient ozone level has been challenged in the courts, and its ultimate resolution currently is unknown.

EPA's Ozone Generator Requirements

Pesticide chemicals are regulated by EPA's Office of Pesticide Programs. Since suppliers of ozone generation equipment make pesticidal claims (e.g., "ozone kills microorganisms"), in theory, such claims fall under the regulatory purview of the Federal Insecticide, Fungicide and Rodenticide Act (the FIFRA). However, FIFRA only authorizes EPA to regulate pesticide **chemicals** (meaning solid or liquid or gaseous materials that are packaged, stored, then shipped and delivered to the desired point of application). Since ozone is not packaged, stored, nor shipped to application sites, ozone is not considered by EPA Office of Pesticide Programs as a chemical, but rather as a "device". For information, UV radiation also is considered by EPA as a device, not a pesticidal chemical.

EPA requires that all ozone generators marketed in the USA for which a pesticidal claim is made carry an EPA Establishment Number (EN). Applying for such an EPA EN is fairly simple – contact the nearest EPA Regional Office (Pesticides Branch), or contact Ms. Carol Buckingham at the EPA Office of Compliance, Washington, DC – tel: 202-564-5008; buckingham.carol@epa.gov and request the EN application forms.

EPA's requirements when issuing an Establishment Number are that the device must not bear any false or misleading claims, and that the vendor must keep adequate books and records with respect to manufacture and sale of ozone generators, and be subject to EPA inspections.

U.S. distributors of foreign-made ozone generators imported for sale and distribution within the USA also are required to secure an Establishment Number.

Safety Aspects of Ozone in Air

In case it is not apparent from the regulations on ozone in air discussed above, it should be clear that the best approach for those treating air with ozone in the presence of people, pets and other ozone-sensitive items, is not to have people, pets and other ozone-sensitive items present when ozone is present. Those who do advocate applying ozone when people, etc. are present are skating on very thin ice. In order to be effective, ozone usually must be added in concentrations above which humans are sensitive to ozone. And since there have been all-too-many ozone vendors who have marketed and are marketing ozone in this manner, all regulatory agencies have built up a regulatory prejudice against ozone – based on the assumption that all ozone vendors advocate adding ozone for air treatment when people are present.

Effects of Ozone on Humans

Breathing ozone gas can oxidize epithelial cells in the respiratory system. Nasal, throat and lung tissues can be oxidized. The degree of oxidation is higher the higher the concentration of ozone and/or the longer the exposure time to ozone.

Fortunately, the human body can regenerate the oxidized tissues – unless tissue damage has gone too far. So breathing ozone is a gambling matter – a little ozone will do only small amounts of damage to nasal passages and lungs. If exposure to low ozone levels is ceased early, the body repairs the damages quickly. On the other, continued exposure to ozone at higher levels (which varies with the sensitivity of each affected human being) can overpower the body's ability to repair damage caused by ozone exposure.

EPA's White Paper on Ozone Treatment of Air

EPA's White Paper on ozone can be viewed and downloaded at the following web site:

<http://www.epa.gov/appcdwww/iemb/ozone.htm>

The emphasis in this white paper is to warn people against the dangers of adding ozone to air when people are present. Remember – EPA currently assumes that all vendors of ozone for air treatment advocate applying ozone when people are present. However, about midway through is the statement:

“Can ozone be used in unoccupied spaces?”

“Ozone has been extensively used for water purification, but ozone chemistry in water is not the same as ozone chemistry in air. High concentrations of ozone in air, when people are not present, are sometimes used to help decontaminate an unoccupied space from certain chemical or biological contaminants or odors (e.g., fire restoration). However, little is known about the chemical by-products left behind by these processes (Dunston and Spivak, 1997). While high

concentrations of ozone in air may sometimes be appropriate in these circumstances, conditions should be sufficiently controlled to insure that no person or pet becomes exposed. Ozone can adversely affect indoor plants, and damage materials such as rubber, electrical wire coatings, and fabrics and art work containing susceptible dyes and pigments (U.S. EPA, 1996a)”.

Thus, EPA is effectively stating that even though ozone is to be applied in unoccupied spaces, it can adversely affect items normally encountered in such spaces, and EPA also is concerned about chemical by-products remaining after ozone treatment.

A fair enough position – based on a paucity of credible data and information available to EPA.

An IOA Air Treatment Task Force

What can be done about this? In the experience of this author, the most effective technique to sway a government regulatory agency is to:

- a. meet face to face for discussions on what information is desired by EPA scientists and regulatory personnel,
- b. gather the needed information from vendors currently in the ozone-air treatment business;
- c. if some desired data are not available, determine some efficient method for developing such data, i.e., at academic institutions by professionally recognized (by EPA) academicians, and find some way to fund such programs;
- d. return to EPA with new data/information and request that the White Paper be revised to reflect a positive view toward ozone *when applied properly (in unoccupied spaces)*.

This type of activity can be overseen by an Air Treatment Task Force organized within the IOA. Such a Task Force has been established to oversee and coordinate the specific program cited above – but also to coordinate other ozone air treatment projects to be determined by the Task Force..

Ozone Treatment of Air – General Considerations

There are many considerations when ozone is used to treat air. One of the most fundamental is that the chemistry of ozone in air is not always identical to its chemistry in water. In the literature of the IOA (e.g., Ozone: Science & Engineering; Ozone News; Proceedings of IOA Conferences) and in literature published in other journals, mostly dedicated to treatment of water or wastewaters, there are many articles on the chemistry of ozone in water. One of the best sources is Langlais et al., 1991). On the other hand, the chemistries of ozone as an air pollutant, while known extensively, generally are published in journals such as J. Air Pollution Control Assoc., Environmental Science & Technology and others dedicated to air pollution control. These journals are not widely read by IOA members. That places some ozone vendors at a

disadvantage – understanding aqueous ozone chemistry that is not necessarily applicable to air treatment.

Another important consideration is that reactions of ozone in air usually are much slower than in water, and that increases in relative humidity usually increase ozone gas phase reaction rates significantly. In fact, some studies have shown that ozone inactivation of bacterial spores does not occur at any reasonable rate when the relative humidity is below 50%, and that complete disinfection of such spores is best accomplished above 90% RH (Kim and Yousef, 2002).

Finally – ozone can be generated commercially by either UV radiation or by corona discharge, and both have pros and cons associated with them (see next section).

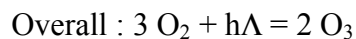
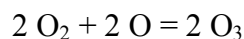
Generation of Ozone

For treatment of air, there are two primary commercial means of generating ozone – by ultraviolet radiation (UV) and by corona discharge (CD).

Ozone Generation by UV Radiation (Photochemically)

An excellent discussion on this topic was published by Dohan and Masschelein (1987), and Masschelein (2002) has discussed the subject further. High energy UV radiation (wavelengths below 200 nm) from the Sun enters the Earth's atmosphere, interacts with oxygen in the Earth's upper atmosphere, and generates ozone – which gives rise to the well-known 'Ozone Layer'. On the other hand, generating ozone from oxygen and UV radiation at ground level is not practical using sunlight, because most of the high energy UV wavelengths already have been absorbed by the Earth's atmosphere. Consequently, special ultraviolet lamps are used to generate ozone at ground level.

The basic reactions for photochemical ozone generation are:



Although nitrogen also is present in the Earth's atmosphere, and in theory, nitrogen molecules can be dissociated at high energies to produce "N" species, and "N" species, if formed, can combine with molecular oxygen to form "NO₂", a type of nitrogen oxide, in practice the energies emitted by UV bulbs at 254 or 185 nm are too low to dissociate more than traces of nitrogen molecules. Consequently, little or no nitrogen oxides are produced during photochemical generation of ozone at ground level using UV bulbs as described above. The disadvantages of

generating nitrogen oxides while generating ozone will be discussed under “Corona Discharge Generation of Ozone”, later.

Basically, with conventional or advanced mercury UV lamp technologies, the generation of ozone relies on 185-nm resonance emission (Masschelein, 2002). Above 200 nm, very little ozone is produced. Furthermore, at 254-nm, ozone is decomposed rapidly, forming a series of short-lived decomposition products, including hydroxyl free radicals in the presence of moisture, which have oxidation potentials sometimes higher than that of molecular ozone itself.

Although UV bulbs emitting at 185-nm are available commercially, many other bulbs are available that emit at both 185- and 254-nm. These bulbs emitting a “combination” of wavelengths, simultaneously produce and destroy molecular ozone. On this subject, Dohan and Masschelein (1987) wrote:

“Seeing that in the present technology with Hg-based UV emission lamps, the 254nm wavelength generally is present simultaneously with the 185 nm radiation, the practical results will always be at least equal to that of a kinetic situation with an obtained balance of ozone generation vs ozone decomposition. The respective absorbances (absorption coefficients) (\log_{10}) are in favor of ozone decomposition : 135 (O_3 at 254 nm) vs $0.1 \text{ atm}^{-1}\text{cm}^{-1}$ (O_2 at 185 nm). Also the relative emission intensity is 5 to 10 times higher at 254 nm compared to the 185 nm wavelength.”

The practical meaning of all this is that to maximize the production of ozone in the gas phase by UV radiation, it is better to employ UV bulbs emitting more 185-nm radiation than 254-nm radiation.

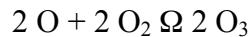
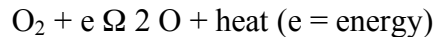
A benefit of employing UV radiation to generate ozone in the gas phase is that very little (traces at best) of nitrogen oxides are generated at the same time as is ozone. On the other hand, the amount of ozone generated per UV bulb, even when only 185-nm radiation is used, is limited. This means that in order to treat large masses of contaminated air, will require an ever-increasing number of ozone-generating UV bulbs would be required in order to build up a concentration of ozone in the air to be treated for a sufficient length of time for the ozone to accomplish its intended purpose(s). At some point in amount of ozone necessary for a particular application, the use of corona discharge ozone will prove to be more economical.

This is not to imply that the use of UV radiation to generate ozone for air treatment is not effective. Quite the contrary. When the amounts of air to be treated are small, and/or when only low levels of ozone are to be maintained in a small enclosure, UV bulbs generating ozone are quite practical and economical.

Still another advantage of ozone generated by UV is that if both 185-nm and 254-nm emission lines are present, much of the O₃ generated is decomposed to short-lived intermediate species, including the hydroxyl free radical when moisture is present in the air being treated. This means first that some air contaminants that are slow to be oxidized by molecular ozone can be oxidized by the reactive intermediates caused by photochemical decomposition of molecular ozone. Second, if the UV radiation is contained in a designed enclosure, the escape of molecular ozone to the surrounding air is minimized. In a food processing plant, for example, minimizing levels of ozone in plant air is a necessity, in order to avoid ozone being breathed by plant personnel.

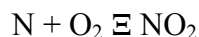
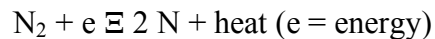
Ozone Generation by Corona Discharge (Langlais et al., 1991, pp. 103-109)

In nature, lightning discharges through air have energies sufficient to dissociate oxygen molecules to produce “O” species, which then combine with oxygen molecules to produce molecular ozone:



Corona discharge ozone generators effectively produce man-made lightning, except that the energy discharges are constant, not intermittent. Consequently, the generation of molecular ozone is constant.

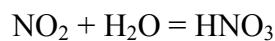
Corona discharges are of sufficient energy (as opposed to UV radiation at 185 nm) to also dissociate some of the nitrogen molecules present in moist air into “N” species that are similar to “O” species. In turn, some “N” species can combine with oxygen molecules to produce “NO₂”, nitrogen dioxide.:



By CD generation techniques, ozone concentrations of up to 4-5 wt% can be obtained if dried air is used as the feed gas to the ozone generator, and up to 14-16 wt% if high purity oxygen is the feed gas. These levels of ozone concentration are significantly higher than those obtainable by UV generation, even if only the 185-nm wavelength is used (ca 1 wt% under ideal conditions). Consequently, if large volumes of air are to be treated with ozone, CD ozone generators usually are more economical than multiple UV bulbs, provided that attention is paid to the quality of gas (air or oxygen or mixtures thereof) fed to the CD ozone generators.

It is of utmost importance that a dry process gas (air) is applied to the CD ozone generator. If air is not properly dried, then two detrimental effects are observed (Langlais et al., 1991):

1. The yield of molecular ozone drops considerably as the dew point of air rises above -60EC.
2. In the presence of moisture, nitrogen oxides are generated by the CD process (when air is used) and these react with ambient moisture to form the corrosive nitric acid. In turn, nitric acid can corrode the ozone generators themselves, as well as downstream equipment. This means frequent downtime for maintenance and/or replacement of parts.



Three methods are available to minimize or eliminate the formation of nitrogen oxides during CD ozone generation (thus minimizing down-time and maintenance due to corrosion) :

1. Dry the air being fed to the CD ozone generator to a dew point of at least -60EC
2. Use high purity oxygen as the feed gas (h.p. oxygen contains little or no nitrogen or moisture)
3. Use an oxygen concentrator prior to the CD ozone generator. Not only does an oxygen concentrator increase the concentration of oxygen and simultaneously minimize the concentration of nitrogen entering the generator, but it also dries the gas produced to about -100EC.

Unfortunately, some vendors of ozone equipment for treating air have not understood the consequences of not drying feed gas air adequately. Although an ambient air ozone generator may provide excellent results during initial operation, before long the buildup of nitric acid spoils the benefits of ozone, resulting in downtime and maintenance, and casting a negative view on ozone for air treatment.

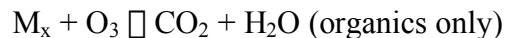
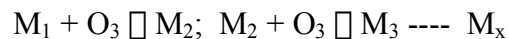
To avoid experiencing such corrosion by nitric acid, some users of ozone for air treatment have retreated to UV generation of ozone, which is free from nitrogen oxide formation. As mentioned earlier, whereas UV generation of ozone is fine for treating relatively small volumes of air, larger volumes are difficult to treat with UV-generated ozone.

Chemical Removal of Air Contaminants With Ozone

When treating air with ozone, it should be appreciated that removal/destruction of contaminants occurs by some oxidation mechanism. Ozone is the most powerful oxidizing agent currently available for air treatment, and the hydroxyl free radical (HO°) is an even stronger oxidant than is molecular ozone. Some contaminants oxidize quickly (sulfides, smoke, many organics, most

microorganisms, molds, fungi), however other contaminants oxidize slowly, if at all (many VOCs – solvents, waxes, and some spore-forming microorganisms, particularly at low relative humidities).

Oxidative processes for the removal/destruction of air contaminants are governed by the rates of reaction (e.g., reaction kinetics) of the many contaminants that may be present. Reaction kinetics are simply mathematical quantifications of the many reaction rates. Knowing the kinetic rate constants for oxidation of specific compounds will indicate how fast oxidation can occur. Mechanisms of organics oxidation involve many stages of oxidative degradation products. Some may exhibit toxicity in early stages, but continued oxidation with ozone usually destroys toxicity effects. Thus time of exposure to ozone becomes important in treating air containing organic contaminants, including microorganisms.



EPA air regulators justifiably are concerned about identity and toxicology of oxidative intermediates (byproducts) of organics produced during ozonation because not all byproducts of all organics are yet identified and tested for toxicological effects. This attitude can be described as the “Fear of the unknown” syndrome.

Oxidation rates in the gas phase depend on a number of factors: oxidation kinetics, temperature, ozone concentration in the gas phase, relative humidity, and the presence of other ozone-demanding materials in the air being treated.

In addition, those treating air in homes/offices should be aware of potentials for collateral damages that can be caused by the presence of ozone, e.g., oxidation of art work, electronic equipment, draperies, carpets, pets, plants, rubber, electrical wire coatings, computer internal parts, etc.

Another significant point is that ozone reactions usually are much slower in air than in water. This means that in air, ozone oxidation rates vary from rapid to very slow or not at all (many VOCs, spore-forming bacteria) to very rapid (sulfides, tobacco smoke odors, many microorganisms, most molds, mites).

Role of Relative Humidity on Ozone Inactivation of *B. subtilis* Spores

One of the most important uses for ozone is the destruction of molds and mold spores in homes and buildings, particularly those that have been damaged by fires and floods. With respect to mold spores, it should be understood that spores of any microorganism have coatings that must be degraded and/or penetrated by the oxidizing agent used to destroy them.

Kim and Yousef (2002) conducted a study on the effects of relative humidity on ozone-inactivation of spores of *Bacillus subtilis*. These investigators found that the optimum relative humidity for maximum inactivation of these bacterial spores is in the range of 90-95% and with ozone concentrations of 0.05 ppm. Furthermore, these investigators also found that below 50% R.H., ozone is ineffective against *B. subtilis* spores. Figure 1 is an electron micrograph showing the deterioration of a *B. subtilis* spore exposed to ozone (Khadre and Yousef, 2001).

Applications of Ozone for Air Treatment

These are many – odor control, fumigation, restoration of homes/buildings that have experienced fires, mildew control, elimination of cat urine odors in homes and automobiles, mold/spore control on stored foodstuffs, packaging of pharmaceuticals, treatment of plastic films prior to lamination (bonding) with aluminum, cleaning surfaces of semiconductors, etc. Several applications are discussed below.

Odor Control

Many odors can be destroyed by ozone – e.g., hydrogen sulfide, odors caused by cigars and cigarettes, many volatile organic compounds (VOCs), perspiration odors, odors in animal rearing facilities, etc. All of these odors can be destroyed by ozone based on its strong oxidation properties. On the other hand, to accomplish odor destruction in a manner that is safe for human beings that may occupy spaces being treated with ozone, and that is also protective of materials contained in these spaces, is another matter entirely.

Consider the addition of ozone to an air space contaminated with odoriferous materials. As long as the level of odoriferous material is greater than the amount of ozone added, there will be no ozone present for human occupants to breathe. However, once sufficient ozone has been added to destroy the odorous material, the level of ozone being added can rapidly rise above the level that is safe for humans to breathe. Usually the odor of ozone becomes apparent, at which point the ozone addition can be decreased. But this becomes a manual control, subject to the sensitivity of the human(s) involved.

A better approach to control ozone would be to install an ambient air ozone monitor, connected to the ozone generator, and preset to turn down the ozone generation, so as to ensure that humans will not breathe more than traces of ozone.

In the early days of the International Ozone Institute (The IOI – founded in 1973 and the predecessor of the current IOA), the primary application for ozone in the USA was odor control (Nebel et al., 1975). Papers by Bollyky (1975), Nash (1975), and many papers included in an early IOI Monograph (Rice and Browning, 1976) contain valuable information on this subject. Primary conclusions of these authors include:

1. Allow sufficient time for ozone gas to be in contact with the odorant(s) to allow oxidative destruction to occur.
2. Recognize that gas-phase oxidations of ozone are relatively slow compared to the same reactions conducted in aqueous solution.
3. Prior to discharge of air/odorant mixtures to the atmosphere, pass the mixtures through an ozone destruction device.
4. Human beings should not be present in contained spaces into which gaseous ozone is passed.

This latter conclusion has led many ozone vendors of odor control equipment to more sophisticated methods of applying gaseous ozone. For example, the technique was quickly developed of drawing odoriferous air from a contained area into an enclosed gas/gas contactor into which ozone is passed, ensuring that sufficient ozone and sufficient gas/gas contact time are provided for complete destruction of the odoriferous compound(s), then discharging the gas mixture through an ozone destruction unit.

For locker rooms, gymnasias and the like, it is customary for the ozone equipment vendor to provide the ozone generator with a timer which can be preset for each user. During the day, when people occupy the facilities, the ozone generator is off. However, the timer turns on the ozone generator after the facility is closed. Then, about an hour or so prior to opening the facility the next day, the timer turns off the ozone generator. This allows any residual ozone in the ambient air to decay before people reenter the facility.

Fumigation of Homes and Buildings

Many companies today offer the service of restoring homes and office buildings damaged by fires (smoke odors) or by floods (molds and mildew). In addition to replacing burned materials and equipment, there usually remain odors associated with burned materials. These odors are pervasive and usually have found their way into draperies, carpets and behind wall paneling. One approach to destroying these fire odors is to evacuate the spaces to be treated for a period of time (sometimes as long as 1-4 days, depending on the extent of fire odors to be treated). When evacuated, the space is taped to make it as gas-tight as is practical, then an ozone generator is placed in the building, turned on, and allowed to run for an appropriate period of time. In this

manner, the ozone gas finds its way into cracks, crevices, nooks and crannies as well as behind wall paneling, and thus destroys the fire-associated odors by oxidation.

For homes or buildings damaged by floods, the undesired contaminants are primarily molds and mildew. The techniques of applying ozone are similar. One U.S. firm (Medallion Healthy Homes) provides equipment to generate ozone for treating mold and odors in “sick” households. Prior to ozone treatment, however, the firm examines the rooms/homes/buildings to be treated using a detailed check list to note particular problems. Arrangements are made for occupants, their pets, sensitive plants, etc. to be away from the home/building during ozone treatment. The area is sealed, and ozone is generated by proprietary UV bulbs (surely emitting at 185-nm). During the several hour treatment (which varies depending on the degree of contamination), ozone levels in the room air rise to 8-12 ppm. After treatment, windows are opened and fans exhaust any excess ozone. Occupants and their pets and ozone-sensitive plants or other possessions are returned.

This technique also shows promise for treating “sick buildings”. These are becoming all the more important in these days of energy conservation, whereby the number of outside air leaks into homes and office buildings is reduced, with fewer provisions for exhausting contaminated air.

Ozone Fumigation of Bedding and Bed Clothes

A recently issued Japanese patent teaches the use of ozone to fumigate bedding and bedclothes (Inui and Ichiyangi, 2001). Ozone is used in conjunction with a negative ion generator and optionally a heater to control mites and ticks.

Packaging of Pharmaceuticals

Many modern U.S. pharmaceutical firms are now packaging many pharmaceutical products in an ozone-containing atmosphere for the purpose of maintaining a sterile packaged product line. Equipment items sterilized in the packaging line include the tubing, process piping, vats, fittings, valves, etc. (L. Kilham, ECO Sensors, Inc., Santa Fe, N.M., Private Communication, May, 2001).

Cleansing of Semiconductor Chips

This is a major application for ozone in the semiconductor industry. When chips are cut, it then becomes critical to clean their surfaces prior to further processing. The major contaminants are organic compounds (hydrocarbons). These are literally burned away from the surfaces by exposure to gas phase ozone at relatively high ozone concentrations (ozone – 12-14% – is generated in high purity oxygen for this purpose).

UV-ozone treatment provides an efficient alternative for the removal of surfactant templates for the routine production of mesoporous silica thin films at low temperatures. This UV-ozone

treatment concomitantly strengthens the silicate phase by fostering the condensation of unreacted silanols leading to mesoporous thin films with well-defined mesoscopic morphologies. The treatment results in (a) complete removal of the surfactant template, (b) strengthening of the inorganic skeleton by fostering silica condensation, and (c) rendering the mesophase thin film surfaces highly hydrophobic (Clark et al., 2000). The UV-ozone combination is created by a UV light bulb generating ozone at a wavelength of 184 nm.

Oxidation of Flue Gas Constituents – To Remove Nitrogen Oxides

In the early 1970s, Mitsubishi ozone specialists developed a process whereby power plant stack gases are treated with ozone to oxidize water-insoluble nitrogen oxides to higher valence state, more water-soluble nitrogen oxides. The oxidized nitrogen oxides now are readily removed from the stack gases by aqueous scrubbing and neutralization. After laboratory and pilot plant testing, the process was demonstrated at a Japanese power plant and found to be successful, from a technical viewpoint. The Japanese government was expected to set nitrogen oxide discharge or air quality standards about 1990; however, such regulations had not been forthcoming as of 1996. Until such regulatory actions are taken, however, this ozonation process was not expected to be adopted in Japan.

German ozone specialists then developed a modification of this process, in which ozone oxidation is followed by aqueous scrubbing of the oxidized nitrogen oxides, followed by addition of ammonia, then evaporation, drying, and pelletizing the ammonium nitrate for sale as a fertilizer material. A large German power plant was designed to utilize this process, but the project ran into problems relating to the ammoniation and subsequent steps. The ozone participant did not believe this project will ever become commercial, since direct catalytic reduction of nitrogen oxides appears to be an inherently cheaper process.

However, in early 2001, BOC Gases introduced the LoTOx™ System – a low temperature oxidation system for NOx control in waste gas streams for end-of-pipe removal of NOx emissions. The LoTOx™ system uses wet or semi-dry scrubbing to remove NOx by addition of ozone as a treatment chemical to increase the solubility of relatively insoluble gaseous NOx. Wet scrubbing follows. The system is said to remove NOx to levels below 0.15 lb NOx/million Btu, and as low as 5 ppm NOx in gas-fired boiler applications.

The chemistry of the LoTOx™ System involves the ozone oxidation of NO to NO₂, ozone oxidation of NO₂ to N₂O₅ (water soluble), ozone oxidation of CO to CO₂ and ozone oxidation of SO₂ to SO₃. After aqueous scrubbing, lime can be added and the solution evaporated, to recover calcium nitrate and sulfate for use as a commercial fertilizer material.

Oxidation of Flue Gas Constituents – To Remove Dioxane

A recently issued Japanese patent teaches the ozone treatment of dioxane-containing incinerator flue gases (Yasuda et al., 2001).

Treatment of Air for Indoor Quality (Air Conditioning Systems)

Gaseous ozone is routinely applied to large scale air conditioning systems (office buildings, hotels, restaurants, casinos, meeting rooms, airport facilities and other public places, etc.). Ozone is applied at the beginning of the air return line and moves through the ducting system. The dosage of ozone is determined qualitatively and adjusted downward so that most, if not all, of the applied ozone decays inside of the air ducting system, thus avoiding exposure of room/building occupants to ozone. Treatment of recirculating air with ozone can reduce the amount of makeup air required, because of the purification provided by the ozone.

An excellent paper by Kilham and Dodd (1999) describes the use of ozone in the air conditioning system of the Imperials Bingo Hall (Renton, Washington, USA) to remove offensive odors and to destroy volatile organic chemicals and smoke. The ozone system designed for this particular system cost the owner \$22,000, replacing an activated carbon system that cost the owner about \$25,000 annually for carbon replacement. This ozone system also has resulted in energy savings of about \$250 per month.

Ozone in Air Uses in Agriculture and Foods

Fumigation

Ozone in the gaseous phase is also being studied for use in agriculture as a potential replacement for the use of methyl bromide. Methyl bromide is very widely used as a soil fumigant to control soil-borne pathogens including fungi, nematodes, and weeds. Its use is being phased out, however, under the terms of the Montreal Protocol (the international treaty mandating reduction of ozone layer depleting substances). Because of its ozone-depletion potential, methyl bromide is scheduled to be completely eliminated by 2005 in developed countries and by 2015 in developing countries. Paradoxically, ozone use as an alternative soil treatment agent has been tested in numerous field trials (Pryor, 2001; Pryor, 1999). In these tests ozone was injected 3-5 inches deep directly into soil through buried drip tubing or drip tape 1 - 5 days prior to planting of the intended crop. At dosages of 50 - 400 lbs ozone per acre delivered at 1 - 3% w/w concentration in air, yield increases in some trials of up to 50 - 75% have been reported for carrots, tomatoes, broccoli, strawberries, cut flowers and orchard replants in soils previously treated with ozone in this manner.

Ozone gas is also being tested as a weed control agent in crops grown on clear plastic-covered soil. Clear plastic is often laid tightly over soil before planting to increase soil temperatures due to the greenhouse effect it produces. This passive process, called solarization, often increases soil temperatures sufficiently over a 30 - 45 day period before planting to be fatal to a variety of plant pests in the soil. However, preplant weed control during solarization is also very unpredictable due to the vagaries of climate and weather. Often, increases in temperature are sufficient to induce seed germination and/or tuber sprouting but insufficient to kill young, rapidly

growing plants -- thus exacerbating the problem. In laboratory tests, daily or every other day dosages of 1% - 5% ozone for as little as 5 minutes a day over a 30 day period have been shown to completely control purple nutsedge, a very pernicious weed plaguing warm weather row crop farmers and arguably the most difficult to control in U.S. agriculture. Laboratory data extrapolated to field conditions indicate good control of purple nutsedge possibly could be achieved for as little as 15-20 lbs of ozone/acre (Pryor et al., 2001). Most other weeds require even lower and less frequent dosages.

Ozone Fumigation of Foodstuffs

Recent studies have shown that continuous or intermittent treatment of stored citrus fruit with gaseous ozone at levels of 0.3 and 1.0 ppm ozone inhibit the normal aerial growth of green and blue molds and greatly reduce sporulation from lesions among infected fruit once lesions have developed (Palou et al., 2001). Earlier studies had reported mixed results – perhaps due to inadequacies of ozone generators and control/analytical procedures of earlier equipment.

Margosan and Smilanick (2000) reported that spores of *Botrytis cinerea*, *Monilinia*, *Penicillium digitatum* and *Rhizopus stolonifer* are significantly inhibited by ozone generated by UV radiation at high relative humidity without damaging the produce tested.

An accepted mode of beneficial ozone action to increase storage life of fresh fruits and other produce (tomatoes) involves ozone's ability to destroy the ethylene that evolves from some stored produce. Gaseous ethylene accelerates the ripening of produce and decreases its storage life. Ozone has been used for many years to retard the ripening of bananas during transit by destroying ethylene.

Ozone for Pest and Fungus Control During Grain Storage

To evaluate the efficacy of ozone for pest and fungus control, Mendez et al. (2003) investigated the flow characteristics of ozone through wheat, and determined the effects of long exposure to a high ozone concentration (50 ppm) on grain quality for end-users of the grain. The flow of ozone through a 3-m column of wheat was shown to have a Phase 1 in which the ozone rapidly degraded as the ozone front moved through the grain, and a Phase 2 in which the ozone moved freely through the grain with little degradation. Increasing the velocity of ozone flow from 0.02 to 0.04 m/s facilitated deeper penetration of wheat in the Phase 1 stage. Treatment of grains with 50 ppm ozone for 30 days had no detrimental effect on popping volume of popcorn, fatty acid and amino acid composition of soybean, wheat, and maize, milling characteristics of wheat and maize, baking characteristics of wheat, and stickiness of rice. These data indicate that if repeated ozone treatments are needed, such treatment should not decrease the quality of grain for end-users.

Chester et al. (2000) describe the use of ozone generated by UV radiation in treating grain as it moves through a grain processing plant on its way to storage and/or packaging. A 75-80%

reduction in plate counts on the ozone/UV-treated grain surfaces was observed in more than 1,000 samples when compared with the former method of grain treatment at a full-scale grain processing plant. The UV+ozone system has been installed at full-scale in this grain processing plant. Although mold counts were not part of this study, Chester et al. (2000) note that visual inspection of equipment and processing lines indicated a similar reduction of mold growth in equipment following ozone/UV treatment.

Ozone to Control *Listeria* in Food Processing Plants (S. Naito, 2002)

In Japanese food processing plants, control of *Listeria monocytogenes* is accomplished with ozone generated by UV (185 nm) radiation. Figure 3 is a schematic diagram of a “kitchen” in which food is processed. The UV bulbs generating ozone are mounted at multiple points on the ceiling. After work hours and after the equipment and floors have been sanitized (note the ozone-water hose at the lower right of the schematic), and after workers have left the room, then the UV bulbs are turned on generating ozone in the gas phase. Since ozone has a higher density than air, it falls slowly from the ceiling, penetrating small cracks in equipment, floor and wall surfaces, where it can attack hidden microorganisms, including *L. monocytogenes*.

Ozone gas is effective at concentrations of 0.5 ppm under wet/moist conditions. *E. coli* dies within 3 days. *Staphylococcus* dies within 15 days. However, at least 5-logs of *L. monocytogenes* can be inactivated within minutes.

Ozone to Cope With Potential Anthrax Attacks

Rice (2002) reviewed available literature that showed that bacterial spores that are surrogates for *Bacillus anthracis* can be destroyed by gas phase ozone, provided that the relative humidity is above 70%. Surrogates tested successfully include *Bacillus globigii* and *B. subtilis*. A detailed study of ozone treatment of *B. globigii* is available (Currier et al., 2001). These spores exhibit a strong tendency to clump together, protecting themselves from attack. This clumping tendency should be recognized when considering this (and perhaps other) application for ozone, in order to provide every opportunity for the applied ozone to come into contact with each and every *B. anthracis* spore possible.

Courier et al. (2001) also showed that under the high humidity conditions (> 70%) and 10-hour exposure to 9,000 ppm of ozone in a simulated business office, there was some collateral damage to computer magnetic media after 16-20 hours of exposure to ozone. This level of ozone may be higher than necessary to cope with anthrax spores, but was the only exposure level reported by Currier et al. (2001).

Ozone to Reduce Losses in the Flower Industry

A recent press release from InterOzone USA, Inc. (www.interozoneuse.com) reports the use of ozone to reduce the number of flowers requiring disposal as a result of various types of spoilage bacteria. Roses were exposed 5 days to ozone in air concentrations of ~ 0.04 ppm, at 85-90% relative humidity and 7EC. Figure 4 shows > 95% reduction in losses of roses.

Conclusions and Recommendations

There are numerous applications for ozone treatment of air. However, not all air contaminants require the same concentrations of ozone nor treatment times.

If ozone is to be used to treat air, humans, pets or other ozone-sensitive items should be removed from the premises to avoid exposure to ozone.

When treating air with ozone, some important factors to keep in mind are adding ozone at appropriate levels and exposure times for the particular contaminants, relative humidity effects, potentials for collateral damages, and understanding the byproducts that can be generated during ozonation, and their possible toxicities when later breathed by occupants.

References

- Bollyky, L.J., "Ozone Systems for Odor Control", in *Proc. First International Symposium on Ozone for Water & Wastewater Treatment* (Stamford, CT: Intl. Ozone Assoc, Pan American Group, 1975), pp. 436-444.
- Chester, T., Graham, D., Schwartz, C., and Sopher, C., "Ozone and UV for Grain Milling Systems", EPRI Final Report, Palo Alto, CA, 2000. 1000591.
- Clark, T., Jr., Ruiz, J.D., Fan, H., Brinker, C.J., Swanson, B.I., and Parikh, A.N., "A New Application of UV-Ozone Treatment in the Preparation of Substrate-Supported, Mesoporous Thin Films", *Chem. Mater.*, 12:3879-3884 (2000).
- Currier, R.P., Torraco, D.J., Cross, J.B., Wagner, G.L., Gladden, P.D., and Vanderberg, L.A., "Deactivation of Clumped and Dirty Spores of *Bacillus globigii*", *Ozone: Sci. & Engrg.* 23(4):285-294 (2001).
- Dohan, J.M., and Masschelein, W.J., "The Photochemical Generation of Ozone: Present State-of-the-Art", *Ozone: Science & Engineering* 9(4):315-334 (1987).
- M. Horváth; L. Bilitzky; J. Huttner, "Fields of utilization of ozone", in *Ozone*, R.J.H. Clark, Ed. (New York, NY: Elsevier Science Publishing Co., Inc., 1985), pp. 257-316.
- Inui, Y. and Ichiyonagi, I., "Ozone Cleaner for Bedding, Bedclothes, etc.", *Japanese Patent* 2001 161797 A2 (Assignee: Yasunaga K.K.), issued 19 June 2001.
- M.A. Khadre; A.E. Yousef, "Sporicidal action of ozone and hydrogen peroxide, a comparative study", *Intl. J. Food Microbiol.* 71:131-138 (2001).
- Kilham, L.B. and Dodd, R.M., "The Application of Ozone for Air Treatment (Case Study of a Bingo Hall HVAC System)", in *Proc. 14th Ozone World Congress, Dearborn, MI, Vol. 2* (Stamford, CT: Intl. Ozone Assoc., Pan American Group, 1999), pp. 49-56.
- J.-G. Kim; A.E. Yousef, "Inactivation kinetics of food-borne spoilage and pathogenic bacteria by ozone", *J. Food Science* 65(3):521-528 (2000).
- Langlais, B., Reckhow, D.A., and Brink, D.R., *Ozone in Water Treatment: Application and Engineering* (Boca Raton, FL: Lewis Publishers, Inc., A CRC Press Company, 1991).

Masschelein, W.J., *Ultraviolet Light in Water and Wastewater Sanitation* (Boca Raton, Florida: Lewis Publishers, A CRC Press Company, 2002), pp. 129-130.

Margosan, D.A. and Smilanick, J.M., "Mortality of Spores of *Botrytis cinerea*, *Monilinia*, *Penicillium digitatum* and *Rhizopus stolonifer* After Exposure to Ozone Gas, and a Survey of the Tolerance of Produce to Sporidicidal Ozone Doses", in *Proc. of Postharvest Integrated Pest Management Meeting, Univ. of California, Davis, CA, August 2000*. Mendez, F., Maier, D.E., Mason, L.J., and Woloshuk, C.P., "Penetration of Ozone into Columns of Stored Grains and Effects on Chemical Composition and Processing Performance", *J. Stored Products Research* 39:33-44 (2003).

Nash, N., "Ozonation and Odor Control in New York City Water Pollution Control Plants", in *Proc. First International Symposium on Ozone for Water & Wastewater Treatment* (Stamford, CT: Intl. Ozone Assoc, Pan American Group, 1975), pp. 450-455.

Nebel, C., Gottschling, R.D., and O'Neill, H.J., "Ozone Treatment of Sewage Plant Odors", in *Proc. First International Symposium on Ozone for Water & Wastewater Treatment* (Stamford, CT: Intl. Ozone Assoc, Pan American Group, 1975), pp. 445-449.

Palou, L., Smilanick, J.M., Crisoto, C.H., and Mansour, M., "Effect of Gaseous Ozone Exposure on the Development of Green and Blue Molds on Cold Stored Citrus Fruit", *Plant Disease* 85(6):632-638 (2001).

Pryor, A., "Ozone as a Gaseous Soil Treatment Agent as an Alternative to Methyl Bromide for Pre-plant Fumigation", Presented at the International Ozone Association PAG Conference, Newport Beach, CA, 2001.

Pryor, A., "Results of Two Years of Field Trials Using Ozone Gas as a Soil Treatment Agent", Presented at the Environmental Protection Agency Methyl Bromide Alternatives, Conference, San Diego, CA, 1999.

Pryor, A., Rocoroni, E., and Bayer, D., "Control of *Cyperus rotundus* (Purple Nutsedge) with Ozone Gas", Presented at the University of California at Davis 45th Annual Weed Day, Davis, CA, 2001.

Rice, R.G., "Ozone and Anthrax – Knowns and Unknowns", *Ozone: Science & Engineering* 24(2):151-158 (2002).

Rice, R.G. and Browning, M.E., editors, *Ozone: Analytical Aspects and Odor Control* (Stamford, CT: Intl. Ozone Assoc, Pan American Group, 1975).

C.F. Schönbein, *Comptes rends Hebd. Scéances Acad. Sci.* 10:706 (1840).

Yasuda, K., Fujimoto, Y., Shinohara, I., Kobayashi, M., Hamano, S., and Nagaya, K., "Treatment of Dioxin-Containing Flue Gases", Japanese Patent 2001 137656 A2 (Assignee: Hitachi Shipbuilding and Engineering Co., Ltd.), issued 22 May 2001.