Basics of Ozone Applications for Postharvest Treatment of Fresh Produce

Introduction

Three primary events have stimulated an even higher level of interest in postharvest applications of ozone for decay control and as a sanitizer against human pathogens.

1. Broader consumer demand for enhanced availability of fresh-consumed produce of the highest standard in quality, nutritional value, and safety.
2. Concern, borne of media and therefore public attention to known or potential human health and negative environmental impacts of chlorinated disinfectant by-products.
3. Regulatory acceptance that ozone has been affirmed to qualify for Generally Recognized As Safe (GRAS) status as a food-processing aide. In addition, ozone has been listed as compliant (no restrictions or concerns) with EPA Disinfection by Products Rule.

Although much of stimulation of interest in ozone as an antimicrobial and general shelf-life extending treatment has been based on empirical information and testimonials, an increasing body of recent scientific literature has better defined the benefits and limitations of gaseous and aqueous ozonation in postharvest applications. These will be briefly reviewed below.

This publication provides an introductory overview of the properties, applications, known efficacy, and worker exposure and safety consideration of ozone in the postharvest environment.

Regulatory Status

In a lengthy self-affirmation and extensive petition process, an expert advisory panel asserted the determination that ozone qualified for listing as a GRAS material. On June 26, 2001, the U.S. Food and Drug Administration (FDA) released an official acceptance (in reality, the action was to abandon a challenge of this assertion) of this determination (21 CFR Part 173.368) on the permissible use of ozone as an antimicrobial agent for the treatment, storage and processing of foods in gas and aqueous phases in direct contact with foods, including raw and minimally processed fruits and vegetables.

Ozone-based treatments of fresh vegetables and fruits had been used within the postharvest handling industry for decades. Relatively few produce handlers and processors have used ozone for water disinfection, surface sanitation, cold room air treatment, and other postharvest applications such as final rinses of whole, trimmed-in-the-field, peeled, or minimally processed produce. Until GRAS status was affirmed, however, the legality of ozone contact with food was always within an area of regulatory uncertainty.

By regulation, ozonation treatment of fresh produce and all related handling and applications must be conducted in a manner consistent with Good Manufacturing Practices (GMP). Specifically, ozone has been approved for use under GMP, meaning "exposure of foods to sufficient ozone (concentrations and times of exposure) to accomplish its intended purpose." This translates to the minimum exposure of fruits and vegetables to that dose of ozone necessary to provide the target antimicrobial benefits on specific edible horticultural commodities. Unlike other common water disinfectants and produce surface sanitizers (ex. chlorine gas, calcium hypochlorite, sodium hypochlorite, peroxyacetic acid), no postharvest uses of ozone in contact with produce are currently registered by the U.S. Environmental Protection Agency (EPA) or California Department of Pesticide Registration (DPR). Rather, due to the on-site generation of ozone, each ozone generator unit is required to have an EPA establishment number and a device registration number. Registration is conducted under the approved testing protocols conducted by NSF International: Nonfood Compounds Registration Program (http://www.nsf.org/usda).

Properties of Ozone (O_3)

Ozone is a very pungent, naturally-occurring gas with strong (highly reactive) oxidizing properties. Ozone has a very long history of safe use in disinfection of municipal water, process water, bottled drinking water, and swimming pools. More recent applications include treatment of wastewater, dairy and swine effluent, cooling towers, hospital water systems and equipment, aquariums and aquaculture, water theme parks, and public and in-home spas.

In clean, potable water free of organic debris and soil particulates, ozone is a highly effective sanitizer at concentrations of 0.5 to 2 ppm (1 mg/L = 1 ppm). Ozone is almost insoluble in water (0.00003g/100mL at 20^{o}C [68^{o}F] and effective dispersal is essential for antimicrobial activity. Ozone's disinfectant activity is only marginally affected at a water pH from 6 to 8.5. Ozone is highly corrosive to equipment and lethal to humans with prolonged exposure at concentrations above 4 ppm. Ozone is readily detectable by human smell at 0.01 to 0.04 ppm. OSHA limits of exposure specify a 0.1ppm threshold for continuous exposure during an 8hr period and 0.3ppm for a 15 min period. At 1 ppm ozone has a pungent disagreeable odor and is irritating to eyes and throat.

The need for degassing and off-gas containment in an open process line would have to be carefully evaluated for each planned use but current experience would not forecast a serious problem for line workers.

Ozone is also highly unstable in water and decomposes to oxygen in a very short time. Less than half the activity remains after 20 minutes in pure water and may only have a residual of 2 to 3 minutes in more complex, potable water. In postharvest packing water or fresh cut processing water, with suspended soil and organic matter, the half-life of ozone activity may be less than one minute. Lower water temperatures extend the half-life of ozone. Specific water quality constituents; increasing alkalinity, soluble iron and manganese content, hydrogen sulfide, humic acids, and soluble organic compounds will delay the build-up of detectable ozone residuals in the water and reduce the apparent half-life of ozone.

As a consequence of the low stability, maintaining effective concentrations of dissolved ozone for microbial disinfection by using remote ozone generation and injection into a centralized water system, as is done with chlorine and chlorine dioxide, has proved difficult or impractical. This low stability, however, is one of the perceived benefits of ozone as a disinfectant. When ozone breaks down it forms oxygen (discussed below) and has not been identified as creating undesirable disinfection-by-products. With increased practical use in postharvest handling of fresh vegetables and fruits these obstacles will very likely be overcome. In some applications, a reduced (lower than if used as the sole oxidizing agent) amount of hypochlorite or other more stable disinfectant is added to water to provide a residual effect downstream of the primary ozone injection.

How is ozone formed?
Ozone is formed by a high energy input splitting the O_2 (oxygen) molecule. Single O rapidly combines with available O_2 to form the very reactive O_3.

In nature, ozone is formed by UV irradiation (185nm) from the sun and during lightning discharge. Ozone may also be formed by a variety of commonly used equipment such as photocopiers, laser printers, and other electrical devices. Commercially, UV-based generators pass ambient air (20% O_2) or oxygen-enriched air across an UV light source, typically less than 210nm. These systems have a lower cost but also have a more limited output than corona discharge systems. Corona discharge generators pass dry O_2 enriched air or highly purified oxygen across a high electric voltage (>5,000 V) or corona; similar to a spark plug. Ozone may be pumped into a contained postharvest air volume or pulled into a water stream under the negative pressure created by a Venturi injection system. Bubbling the generated ozone into an assimilation water-tower through an air stone is used in some situations but is deemed far less efficient. Excess O_3 not dispersed in water must be captured and destroyed to prevent corrosion and personal injury. One method of destruction is by UV light at a longer wavelength, 254nm, combined with the use of a catalytic agent or granular activated charcoal.

Measuring and Monitoring Ozone

Effective but safe concentrations are difficult to maintain in typical postharvest uses because automated detection systems have not been highly reliable in complex process water. Due to this uncertainty of reported ozone injection values, past research is often difficult to evaluate and reproduce with reported concentrations of delivered ozone in an experimental or commercial system. Newer electrode probes that measure oxidation-reduction potential (ORP) of the water or colorimetric kits based on indigo blue (indigo trisulfonate) are being used to monitor ozone concentrations more accurately but problems in practical application still exist.

Dissolved ozone monitors, though more accurate and predictive of the residual ozone in process water, are too expensive for most practical situations. Currently, ORP sensors are used to measure the disinfection potential of the treated water and monitor ozone generation demand in a continuous feedback system. In our experience, these values are most useful in monitoring the generator output immediately downstream from the injector. The relation between mass of generated ozone dissolved in water and ORP in mV is not a constant linear relationship. ORP does, nonetheless, reasonably reflect both the build-up of an ozone residual and the antimicrobial oxidative status of the water. Other monitoring test kits, based on DPD, are available and depend on oxidative dye quenching. These are the same substrate used in many rapid chlorine titration kits and, therefore, subject to interference by any other oxidative species (for instance hypochlorous acid or chlorine dioxide).

How does water quality impact effectiveness?

Dissolved and suspended organic and inorganic substances react quickly with ozone and interfere with a desired antimicrobial action. Similar to chlorine, water quality has an important impact on "ozone demand" and stability in water. In particular, dissolved iron, manganese, copper, nickel, hydrogen sulfide, and ammonia will increase the concentration and contact time needed for maximum lethality to microorganisms. Complexes of suspended organics and inorganics have been shown to provide a protective effect for microbes against the action of ozone. High suspended-solids (or insufficient contact time in flumes or drench tanks) are often cited as the responsible factor for lower than expected reductions in viable microbial counts from treated water, often no more than a 10 fold (1 log) decrease. For this reason, an appropriate series of screens and filtration of source water may be needed. Filtration is essential for any use of ozone in re-circulated water systems (i.e. flumes and hydrocoolers). With adequately filtered systems, a 3-4 log (up to 99.99%) reduction may be expected with short treatment exposure and as high as 5 log reductions (99.99% kill) have been reported in pilot trials.

Well water will generally have lower organic and higher inorganic loads than surface water. With deep wells hydrogen sulfide may be a problem and ozone is actually used to deodorize the water. Recirculating process water will have a higher microbial load, higher suspended organic solids, and, potentially, pesticide residues and other organic chemicals. Because of ozone's reactivity with organics, its use may actually assist filtration devices in clarifying recirculating process or cooling water. Ozone treatment will oxidize a wide array of organic contaminants and improve the efficiency of water clarification by flocculation and biological degradation.

How is ozone applied to water?

The ozone generator supply line interfaces with the process water supply or return line at a Venturi-type injection disperser unit. Adequate mixing and sensitive process monitoring are essential for uniform treatment with the low concentrations applied to water for most postharvest uses. Chilling the water and lowering pH increases the solubility. Typical use rates for disinfection of postharvest water are 2-3 ppm. Maximizing ozone output increase mass transfer efficiency and modern injection systems can easily achieve 6 ppm or greater. Protection of equipment and worker safety must always be paramount in system design and operations.

How does Ozone compare to Chlorine?

Ozone is reported to have 1.5 times the oxidizing potential of chlorine and 3,000 times the potential of hypochlorous acid (HOCl). Contact times for antimicrobial action are typically 4-5 times less than chlorine. Ozone rapidly attacks bacterial cell walls and is more effective against the thick-walled spores of plant pathogens and animal parasites than chlorine, at practical and safe concentrations.

In comparison to the potential negative effects of residues and organic reaction products formed with chlorine applications, ozone does not form deleterious chlorinated hydrocarbons, trihalomethanes (such as chloroform) and other chlorinated disinfection by-products. Oxidized products with potentially deleterious properties may form by oxidation (i.e. oxidized bromide ion may further react with water constituents to form a type of trihalomethane or mildly toxic bromate ion)or by breakdown of complex organic materials to simpler forms. Concern has been raised, by a few, for the unknown consequences of pesticide oxidation in water or on produce. We are unaware of any reported health or environmental risk from discharge of ozonated wash, cooling, or produce processing water. More typically, significant savings in wastewater disposal charges and overall net cost of disinfection are ascribed to switching from chlorine-based systems to ozone applications. Partial oxidation of organic contaminants or constituents of wastewater, by ozonation, has been shown to accelerate biological conversion. Presumably, ozonation of discharge water makes these recalcitrant nutrient sources more available. Naturally, in some environmental water systems, into which process water may be released, this elevated microbial growth may be undesirable and subsequent treatments or other water quality protection steps may be need

Has ozone been tried for other postharvest uses?

Ozone has been evaluated for postharvest disease control and other storage uses for many years. Some commercial use has occurred with commodities such as apples, cherries, carrots, garlic, kiwi, onions, and peach, plum, potatoes, and table grapes. There is increasing interest and a great deal of empirical activity in the evaluation of ozone for a diversity of water treatment and air treatment (fumigation) uses in postharvest quality management. Examples include ethylene degradation (within a confined reactor), odor elimination for mixed storage, disinfection of humidification systems and cold storage room surfaces (including retail super markets), fungal spore elimination in storage room aerosols, and treatment of superficial mold after long-distance shipping of onions. Both effective disease control and phytotoxicity of ozonated air have been experienced for table grapes (fruit and rachis damage), carrots (bleaching) and tomatoes (calyx and vine/cluster desiccation and browning).

Gaseous ozone introduction to postharvest storage facilities or refrigerated shipping and temporary storage containers is reported to be optimal at cooler temperatures and higher relative humidity (85< <95%). The most reproducible benefits to storage are in the substantial reduction of spore production on the surface of infected produce and the exclusion of secondary spread from infected produce to adjacent product (various fruit and tubers have been the subject of most evaluations). As compared to laboratory inoculation studies, gaseous ozonation of commercial storage rooms or containers has not been reliable in reducing net decay from natural infections acquired in the field or during harvest handling. These infections are generally within or beneath the plant surface and ozone, as with any currently used disinfectant, does not penetrate natural openings or wounds efficiently or reacts rapidly with exposed oxidizable plant materials rather than pathogen cell walls. Greater success in wound penetration by chlorine dioxide, in comparison to gaseous ozone, has been reported, but substantiation in practice remains to be evaluated.

In general, ozone treatments in postharvest storage have greatest economic benefit when stored produce will be sorted prior to shipment or re-packed following distribution and short-term storage to remove decayed product. For sizing considerations, the impact of wood surfaces, urethane insulation, fiberboard, and other corrugated materials in the storage facility will create an additional demand on ozone application that may reduce the effective delivered dose.

The benefits of ozone treatment to cold storage rooms or facilities may be direct and indirect. Ozone destruction of ethylene in air filtration systems has been linked to extended storage life of diverse ethylene sensitive commodities. Injection of gaseous ozone, at non-hazardous levels, into the common air of a cold storage room has not been effective as compared to forced circulation (high air exchange) of conditioned air through a reaction chamber. In addition, ozone treatment has been reported to induce natural plant defense response compounds thought to be involved in postharvest decay resistance. Excessive exposure to ozone may injury plant tissue and effectively reduce storage or sensory life.

Has ozone been evaluated for uses in food safety?

Applications for decay and spoilage control have been closely paralleled, more recently, by investigations of human pathogen disinfection in water and on equipment, packing surfaces, returnable plastic containers and bins, and transport vehicle sanitizing. As with postharvest plant pathogens, eliminating bacterial pathogens, such as *Salmonella* spp., *E. coli* O157:H7 and *Shigella* spp. is relatively easy in 'clean' water and becomes increasingly more difficult in water of complex quality, on the surface of produce, or with more tolerant spore-forming or parasitic pathogens.

Gaseous ozone treatment of cold rooms has been reported to be effective in significantly reducing *Listeria monocytogenes*.

Additional research is needed to define the potential and limits of effective use of ozone for postharvest treatment s for quality and safety of whole and minimally-processed vegetables and fruits.

Currently, ozone is not registered by the California DPR as a postharvest treatment for direct contact with produce. The recent determination by the FDA supporting petition for GRAS classification of ozone as a disinfectant for foods has opened the door for the produce industry to explore its many potential benefits, when applied in a manner consistent with good manufacturing practices.

The information contained within this bulletin should not be viewed as an authoritative source for current registration status or legal use recommendations of any product. For more information contact the California Department of Pesticide Registration Information Center at (916) 324-0399

Relative Antimicrobial Disinfection Efficiency

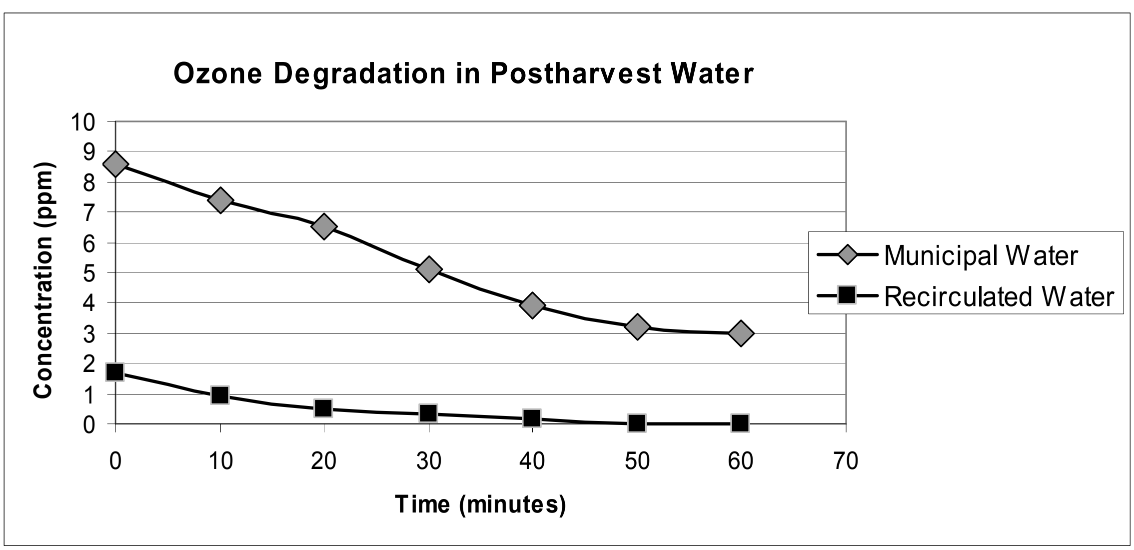
$$OCl < HOCl < ClO_2 < O_3$$

Efficacy Impacted By pH

$HOCl$	O_3	ClO_2
Strong	**Moderate**	**Low**

Relative Corrosive Potential

$$ClO_2 < HOCl < Cl_2 < O_3$$



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See also Postharvest Chlorination Basics
DANR Publication #8003

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