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## Atmosphere Modification

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### I. INTRODUCTION AND DEFINITIONS

The terms *controlled atmosphere* (CA) and *modified atmosphere* (MA) refer to atmospheres in which the gas composition surrounding the commodity is different from air (i.e., 78.08% N<sub>2</sub>, 20.95% O<sub>2</sub>, 0.93% argon and 0.03% CO<sub>2</sub>). In practice, CA and MA usually involve reducing oxygen (O<sub>2</sub>) levels below 5% and/or elevating carbon dioxide (CO<sub>2</sub>) levels above 3%. Controlled atmosphere differs from MA only in the degree of precision in controlling the partial pressures of O<sub>2</sub> and CO<sub>2</sub>; the control is more exact in CA than in MA. Other terms used to refer to certain CA storage conditions include *reduced (or low) O<sub>2</sub> storage*, *elevated (or high) CO<sub>2</sub> storage*, and *nitrogen (N<sub>2</sub>) storage*. The last term is meaningless, since N<sub>2</sub> is an inert gas with no physiological effects. Manipulation of O<sub>2</sub> and CO<sub>2</sub> levels was first described as "gas storage" by Kidd and West (1920s); however, this term had unpleasant connotations after World War I and was soon replaced by the presently used terms. Initial work on CA storage of apples by Kidd and West in England and Smock and Allen in the United States preceded the first commercial use of CA in those countries during the 1930s and later throughout the world.

Low-pressure (hypobaric) storage (LPS) is one method used to establish a CA atmosphere. In LPS, the commodity is held under a partial vacuum (e.g., one-tenth atmosphere, 10.1 vs. 101 kPa) and the reduced partial pressures of the gases are similar to a CA environment at normal pressure. For example, 2.1% O<sub>2</sub> at 101 kPa is roughly equivalent to 21% O<sub>2</sub> at 10.1 kPa.

Controlled atmosphere, MA, and LPS are supplements to and not substitutes for proper maintenance of the optimum temperature and relative humidity ranges. Both CA and MA can be used during transport, temporary storage, and/or long-term storage of

horticultural commodities to either prolong storage life and/or to maintain higher quality. Low-pressure storage has very limited commercial application.

## II. BIOLOGICAL BASES OF O<sub>2</sub> AND CO<sub>2</sub> EFFECTS ON POSTHARVEST LIFE OF HORTICULTURAL PERISHABLES

Increasing CO<sub>2</sub> concentrations and/or decreasing O<sub>2</sub> concentrations beyond those tolerated by each commodity (and often each specific cultivar within the species) can contribute to the incidence of physiological disorders and increased susceptibility to decay even though the commodities are kept at optimum temperature and relative humidity. The stresses caused by elevated CO<sub>2</sub> are additive to, and sometimes synergistic with, stresses caused by low O<sub>2</sub> levels, by physical or chemical injuries, and by exposure to temperatures, relative humidities, and/or ethylene concentrations outside the optimum range for the commodity.

Plant tissues have the capacity for recovery from the stresses caused by brief exposure to fungistatic atmospheres (>10% CO<sub>2</sub>) or insecticidal atmospheres (40% to 80% CO<sub>2</sub>). Postclimacteric fruits are less tolerant and have lower capacity for recovery following exposure to reduced O<sub>2</sub> and/or elevated CO<sub>2</sub> levels than preclimacteric fruits. The speed and extent of recovery depend upon the duration and level of stress and underlying metabolically driven cellular repair.

Mild stress concentrations of CO<sub>2</sub> used in CA environments reduce the respiration rate, inhibit ethylene production and action, retard compositional changes, alleviate some physiological disorders, and retard decay development. Elevated CO<sub>2</sub> atmospheres inhibit the activity of ACC synthase (a key regulatory enzyme of ethylene biosynthesis), while ACC oxidase activity is stimulated at low CO<sub>2</sub> levels and inhibited at high CO<sub>2</sub> concentrations and/or low O<sub>2</sub> levels. Elevated CO<sub>2</sub> atmospheres inhibit ethylene action.

Optimum CA environments retard loss of chlorophyll (green color), biosynthesis of carotenoids (yellow, orange, and red colors) and anthocyanins (red and blue colors), and biosynthesis and oxidation of phenolic compounds (brown color). Controlled atmosphere environments slow down the activity of cell wall-degrading enzymes that cause fruit softening, and enzymes involved in lignification that cause toughening of vegetables. Controlled atmosphere environments influence flavor quality by reducing loss of acidity, starch to sugar conversion, interconversion of sugars, and biosynthesis of flavor volatiles. Retention of ascorbic acid (vitamin C) and other vitamins results in better nutritional quality of fruits and vegetables kept in CA environments.

Severe stress CA conditions decrease cytoplasmic pH and ATP levels and reduce pyruvate dehydrogenase activity, while pyruvate decarboxylase, alcohol dehydrogenase, and lactate dehydrogenase are induced or activated. Activation of these enzymes stimulates anaerobic respiration with the accumulation of acetaldehyde, ethanol, ethyl acetate, and/or lactate. These compounds may accumulate to levels detrimental to the quality of the commodity if it is exposed to stress CA conditions beyond its tolerance limits.

An overview of the general effects of elevated CO<sub>2</sub> and reduced O<sub>2</sub> concentrations on causes of deterioration of fresh vegetables is presented in Table 1. Specific concentrations of O<sub>2</sub> and CO<sub>2</sub> at which these general responses occur and their magnitude vary among commodities and cultivars, maturity and ripeness stages, storage temperatures and durations, and, in some cases, ethylene concentrations.

Controlled atmospheres can influence postharvest decay-causing pathogens directly by inhibiting their spore germination and slowing down their growth. The O<sub>2</sub> and CO<sub>2</sub>

**Table 1** An Overview of the General Effects of Oxygen Levels Below 5% and Carbon Dioxide Levels Above 5% on Quality Attributes of Horticultural Perishables

Cause of deterioration	General effects <sup>a</sup>	
	Reduced O <sub>2</sub>	Elevated CO <sub>2</sub>
A. Respiratory metabolism		
1. Respiration rate	- <sup>b</sup>	-, 0, or +
2. Shift from aerobic to anaerobic respiration	+ (<1%)	+ (>20%)
3. Energy produced	-	-
B. Ethylene biosynthesis and action		
1. Methionine → SAM	0	?
2. Synthesis of ACC synthase	-	-
3. ACC synthase activity	0	-
4. Synthesis of ACC oxidase	-	-
5. ACC oxidase activity	-	- or +
6. Ethylene action	-	-
C. Compositional changes		
1. Pigments		
a. Chlorophyll degradation	-	-
b. Anthocyanin development	-	-
c. Carotenoids biosynthesis	-	-
2. Phenolics		
a. Phenylalanine ammonia lyase activity	-	+
b. Total phenolics	-	-
c. Polyphenol oxidase activity	-	-
3. Cell wall components		
a. Polygalacturonase activity	-	-
b. Soluble polyuronides	-	-
4. Starch-to-sugar conversion	-	-
5. Organic and amino acids		
a. Loss in acidity	-	-
b. Succinic acid	-	+
c. Malic acid	+	-
d. Aspartic and glutamic acids	?	-
e. $\gamma$ -Amino butyric acid	?	+
6. Volatile compounds		
a. Characteristic aroma volatiles	-	-
b. Off-flavors (accumulation of ethanol, acetaldehyde, and ethyl acetate)	+ (<1%)	+ (>20%)
7. Vitamins		
a. Provitamin A ( $\beta$ -carotene) loss	-	-
b. Vitamin C (ascorbic acid) loss	-	-
D. Growth and development		
1. Cell division	- or +	- or +
2. Cell enlargement	- or +	- or +
3. Endogenous growth regulators	?	?
4. Periderm formation	- (<5%)	- (>10%)
E. Physical injuries		
1. Wound healing	See D4 above	
2. Tissue browning	See C2 above	
3. Stress-induced CO <sub>2</sub> and C <sub>2</sub> H <sub>4</sub>	-	-

Table 1 Continued

Cause of deterioration	General effects <sup>a</sup>	
	Reduced O <sub>2</sub>	Elevated CO <sub>2</sub>
F. Transpiration (water loss)		
1. Stomata opening	?	?
2. Wound healing	See D4 above	
G. Physiological disorders		
1. Chilling injury	+ <sup>b</sup>	- or +
2. Scald on apples and pears	-	-
3. C <sub>2</sub> H <sub>4</sub> -induced disorders	-	- or +
4. CA-induced disorders	+	+
H. Pathological breakdown		
1. Susceptibility to pathogens	- or +	- or +
2. Fungal growth	- (<1%)	- (>10%)
3. Bacterial growth	- or 0	- or 0

<sup>a</sup> Specific O<sub>2</sub> and/or CO<sub>2</sub> concentrations at which these effects are observed depend upon the commodity, cultivar, temperature and duration of storage, and interactions between O<sub>2</sub> and CO<sub>2</sub> levels.

<sup>b</sup> - = decrease or inhibit, 0 = no effects, + = stimulate or increase, ? = inadequate data for conclusion.

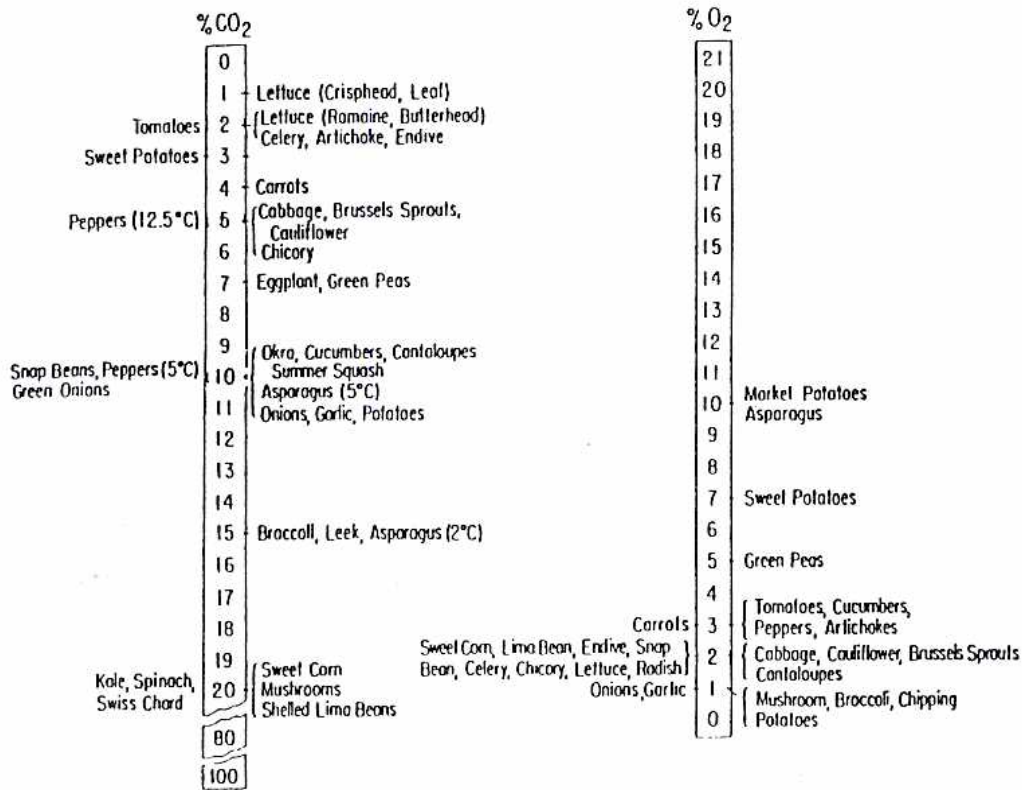
Source: Kader, 1997.

concentrations required to inhibit spore germination and/or growth (fungistatic CA) vary with the species of fungi, but generally O<sub>2</sub> levels below 1% and/or CO<sub>2</sub> levels above 10% are needed to significantly suppress fungal growth. Not all vegetables will tolerate such concentrations of O<sub>2</sub> and CO<sub>2</sub> for more than a few days without physiological injury. The limits of tolerance for each commodity to fungistatic CA depend upon cultivar, maturity stage, temperature, and duration of exposure. Controlled atmospheres can also cause an indirect effect on postharvest decay by retarding senescence and maintaining the health of the host commodity, or by inducing formation of antifungal compounds and maintaining resistance of the host to infection.

### III. RELATIVE TOLERANCE OF VEGETABLES TO REDUCED O<sub>2</sub> AND ELEVATED CO<sub>2</sub> LEVELS

Based on a review of published data, the limits of tolerance of vegetables to elevated CO<sub>2</sub> and reduced O<sub>2</sub> levels are presented in Figure 1. These are not recommended MA or CA conditions but rather levels of CO<sub>2</sub> above which and O<sub>2</sub> below which physiological damage would be expected. In using this information, the following points should be considered:

1. These limits of tolerance can be different at temperatures above or below the recommended temperatures for each commodity. Also, a given commodity may tolerate higher levels of CO<sub>2</sub> or lower levels of O<sub>2</sub> than those indicated for a short duration. The limit of tolerance to low O<sub>2</sub> would be higher as storage temperature and/or duration increases since O<sub>2</sub> requirements for aerobic respiration of the tissue increase with higher temperatures. Depending on the commodity, damage associated with CO<sub>2</sub> may either increase or decrease with an increase in temperature. Production of CO<sub>2</sub> increases with temperature but its solubility decreases. Thus, the CO<sub>2</sub> concentration in the tissue can increase or decrease with an increase in temperature. Further, the physiological effect of CO<sub>2</sub> could be temperature dependent.



**Figure 1** Relative tolerance of vegetables to elevated CO<sub>2</sub> and reduced O<sub>2</sub> levels at recommended storage temperatures. (From Kader and Morris, 1977.)

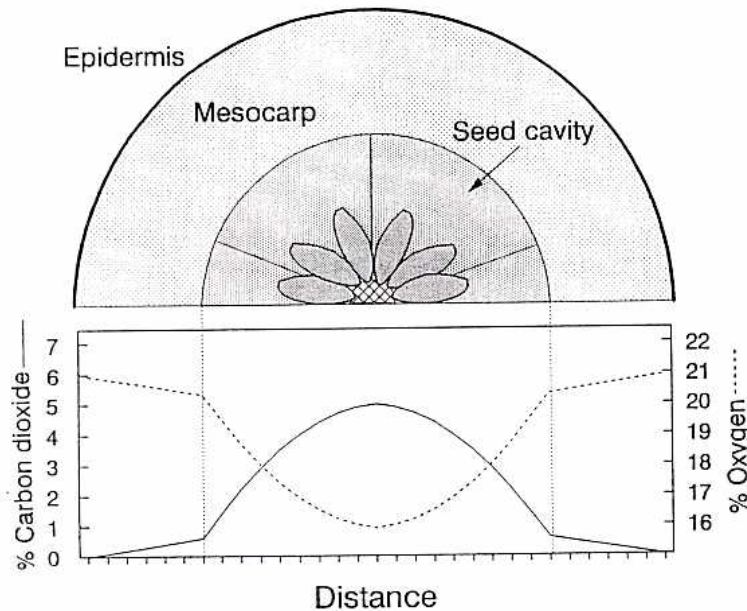
2. The limits of tolerance to either elevated CO<sub>2</sub> or reduced O<sub>2</sub> shown in Figure 1 are based on the assumption that the other component is near its normal (air) concentration. Tolerance limits to elevated CO<sub>2</sub> decrease with a reduction in O<sub>2</sub> level, and similarly the tolerance limits to reduced O<sub>2</sub> increase with an increase in CO<sub>2</sub> level.

3. The possible effects of supplemental gases (CO, SO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, etc.) on modifying the tolerance limits of O<sub>2</sub> and CO<sub>2</sub> should be considered.

4. In some commodities, their physiological age at harvest may influence their susceptibility to elevated CO<sub>2</sub> and/or reduced O<sub>2</sub> damage. For example, ripe fruits may tolerate higher levels of CO<sub>2</sub> than mature-green fruits.

5. The form in which a given commodity is handled can affect its tolerance to elevated CO<sub>2</sub> or reduced O<sub>2</sub>. For example, fresh-cut lettuce (*Lactuca sativa* L.) tolerates much higher levels of CO<sub>2</sub> and/or lower levels of O<sub>2</sub> than intact heads of lettuce.

As shown in Figure 1, about 2% O<sub>2</sub> is the lower limit tolerated by most vegetables. Below this, anaerobic respiration may result in the development of off-flavors and off-odors. Tolerance limits for elevated CO<sub>2</sub> are more variable. Vegetables with a wide variety of botanical structures differ greatly in their CO<sub>2</sub> tolerance. While lettuce is damaged by 1% to 2% CO<sub>2</sub>, spinach (*Spinacia oleracea* L.) tolerates 20% CO<sub>2</sub>. Broccoli (*Brassica oleracea* L. Botrytis group) tolerates 15% CO<sub>2</sub>, but 5% CO<sub>2</sub> damages cauliflower (*B. oleracea* L. Botrytis group).



**Figure 2** Cross section through a vegetable showing how the concentration of  $O_2$  and  $CO_2$  can vary within the tissue due to tissue respiration and internal barriers to gas diffusion.

Differences in susceptibility to elevated  $CO_2$  and/or reduced  $O_2$  levels among commodities, or among cultivars of a given commodity, may be due to structural (anatomical) differences rather than metabolic differences. Natural barriers in the commodity may affect the diffusion coefficients of  $CO_2$  or  $O_2$  (e.g., cuticular resistance, number of stomata and lenticels). Gas diffusion across these barriers and tissue respiration combine to significantly alter gas composition within commodities (Fig. 2). Gas concentrations that are maintained at tolerable levels inside vegetables in an air atmosphere may be so altered when the ambient atmosphere is replaced by CA that they may become damaging. This is especially true in bulky vegetables. For example, whereas a 5% decrease in  $O_2$  or a 5% increase in  $CO_2$  might not be damaging when the commodity is in air, the same change in an environment of 5%  $O_2$  plus 5%  $CO_2$  CA would likely cause internal damage. Differences in gas solubility in the tissue (e.g., solute concentration and cellular and vacuolar pH) should also be considered in studying the relationship between internal and external  $CO_2$  and  $O_2$  concentrations.

#### IV. BENEFITS AND HAZARDS OF ATMOSPHERIC MODIFICATION

##### A. Potential Beneficial Effects

Used properly, CA or MA can supplement proper temperature and relative humidity management and can result in one or more of the following benefits, which translate into reduced quantitative and qualitative losses during postharvest handling and storage of some vegetables:

1. Retardation of senescence (ripening) and associated biochemical and physiological changes—i.e., slowing down respiration and ethylene production rates, softening, and compositional changes.

2. Reduction of the commodity's sensitivity to ethylene action at O<sub>2</sub> levels below about 8% and/or CO<sub>2</sub> levels above 1%.
3. Alleviation of certain physiological disorders, such as chilling injury of various commodities and russet spotting in lettuce.
4. Controlled and modified atmospheres can have direct or indirect effects on post-harvest pathogens and consequently decay incidence and severity.
5. Atmospheres of low O<sub>2</sub> (0.5% or lower) and/or elevated CO<sub>2</sub> (40% or higher) can be useful tools for insect control in some commodities.

## B. Potential Harmful Effects

In most cases, the difference between beneficial and harmful combinations of CA or MA is relatively small. Also, combinations of CA or MA that are necessary to control decay or insects, for example, cannot always be tolerated by the commodity and may result in faster deterioration. Potential hazards of CA or MA to the commodity include the following:

1. Initiation and/or aggravation of certain physiological disorders such as black-heart in potatoes (*Solanum tuberosum* L.) and brown stain on lettuce
2. Irregular ripening of fruits such as melons (*Cucumis melo* L.) and tomato (*Lycopersicon esculentum* Mill.) can result from O<sub>2</sub> levels below 2% or CO<sub>2</sub> levels above 5%
3. Development of "off" flavors and odors at <0.5% O<sub>2</sub> and/or >20% CO<sub>2</sub> as a result of fermentative metabolism
4. Increased susceptibility to decay when the commodity is physiologically injured by excessively low O<sub>2</sub> or high CO<sub>2</sub> concentrations
5. Stimulation of sprouting and retardation of periderm development in some root and tuber vegetables such as potatoes

## V. CA RECOMMENDATIONS FOR SPECIFIC VEGETABLES

A brief summary of the recommended optimum and range for the storage atmosphere and temperature and the potential benefit from using the CA or MA environment are given for 34 selected vegetables (Table 2). Commercial CA storage facilities are used for cabbage (*B. oleracea* L. Capitata group), Chinese cabbage (*B. rapa* L. Pekinensis group), and sweet onion (*Allium cepa* L.) cultivars. CA during transport is used to a limited extent on melons, tomato, asparagus (*Asparagus officinalis* L.), broccoli, lettuce, sweetcorn (*Zea mays* L. var. *rugosa* Bonaf.), and fresh-cut vegetables.

## VI. SUPPLEMENTAL TREATMENTS TO MODIFICATION OF O<sub>2</sub> AND CO<sub>2</sub> LEVELS

### A. Ethylene Removal

Scrubbing ethylene to below 1  $\mu\text{l} \cdot \text{L}^{-1}$  (1 ppm) in the storage atmosphere is recommended for CA or MA storage of vegetables. Ethylene removal from CA storage and transport vehicles was once thought unnecessary because ethylene's effects on vegetative senescence and fruit ripening are diminished at 0 to 5°C and under the low-O<sub>2</sub> and elevated CO<sub>2</sub> levels found in CA and MA environments. However, recent studies indicate that the

**Table 2** A summary of CA and MA Requirements and Recommendations for 34 Selected Harvested Vegetables

Vegetable	Temperature <sup>a</sup>		Atmosphere <sup>b</sup>		Application
	Optimum	Range	O <sub>2</sub>	CO <sub>2</sub>	
Artichokes	0	0-5	2-3	2-3	Moderate
Asparagus	2	1-5	Air	10-14	High
Beans					
Green snap	8	5-10	2-3	4-7	Slight
Processing	8	5-10	8-10	20-30	Moderate
Broccoli	0	0-5	1-2	5-10	High
Brussels sprouts	0	0-5	1-2	5-7	Slight
Cabbage	0	0-5	2-3	3-6	High
Cantaloupes	3	2-7	3-5	10-20	Moderate
Cauliflower	0	0-5	2-3	3-4	Slight
Celeriac	0	0-5	2-4	2-3	Slight
Celery	0	0-5	1-4	3-5	Slight
Chinese cabbage	0	0-5	1-2	0-5	Slight
Cucumbers					
Fresh	12	8-12	1-4	0	Slight
Pickling	4	1-4	3-5	3-5	Slight
Herbs <sup>c</sup>	1	0-5	5-10	4-6	Moderate
Leeks	0	0-5	1-2	2-5	Slight
Lettuce (crisphead)					
Whole	0	0-5	1-3	0	Moderate
Cut or shredded	0	0-5	1-5	5-20	High
Lettuce (leaf)	0	0-5	1-3	0	Moderate
Mushrooms	0	0-5	3-21	5-15	Moderate
Okra	10	7-12	Air	4-10	Slight
Onions					
Bulb	0	0-5	1-2	0-10	Slight
Bunching	0	0-5	2-3	0-5	Slight
Parsley	0	0-5	8-10	8-10	Slight
Pepper					
Bell	8	5-12	2-5	2-5	Slight
Chile	8	5-12	3-5	0-5	Slight
Processing	5	5-10	3-5	10-20	Moderate
Radish (topped)	0	0-5	1-2	2-3	Slight
Spinach	0	0-5	7-10	5-10	Slight
Sugar peas	0	0-10	2-3	2-3	Slight
Sweetcorn	0	0-5	2-4	5-10	Slight
Tomatoes					
Green	12	12-20	3-5	2-3	Slight
Ripe	10	10-15	3-5	3-5	Moderate
Witloff chicory	0	0-5	3-4	4-5	Slight

<sup>a</sup> Optimum and range of usual and/or recommended temperatures. A relative humidity of 90% to 95% is usually recommended.

<sup>b</sup> Specific CA recommendations depend on cultivar, temperature, and duration of storage.

<sup>c</sup> Herbs: chervil, chives, coriander, dill, sorrel, and watercress.

Source: Saltveit, 1977b.



presence of ethylene at concentrations likely to occur in MA and CA conditions can enhance senescence, fruit softening, and germination of fungal spores. Methods to remove  $C_2H_4$  from CA and MA are discussed in Section IX.

### B. Use of Carbon Monoxide (CO)

Carbon monoxide is a colorless, tasteless, odorless, and flammable gas with explosive limits between 12.5% and 74.2% (by volume) in air. It is extremely toxic to humans and adequate safety precautions must be followed if and when it is used. Plant tissues can oxidize CO to  $CO_2$ , which is further metabolized into organic acids and other constituents.

Carbon monoxide has both beneficial and harmful effects on horticultural commodities. Addition of 1% to 5% CO to reduced  $O_2$  atmospheres (2% to 5%  $O_2$ ) inhibits discoloration of mechanically damaged tissue (e.g., lettuce butts). This inhibition of discoloration is lost upon transfer of the commodity to normal air during destination marketing. When added to CA or MA at 5% to 10%, CO inhibits the growth of several important postharvest pathogens and prevents decay development on several vegetables. The fungistatic effects of CO are maximized at  $O_2$  levels below 5%.

Harmful effects of CO include the aggravation of certain physiological disorders. For example, if CO is used in a situation where  $CO_2$  accumulates above 2% during transport of lettuce, it will increase the severity of brown stain (a  $CO_2$ -induced disorder). Carbon monoxide is also known to mimic ethylene effects, including stimulation of fruit ripening and induction of certain physiological disorders, such as russet spotting on lettuce. However, when CO is used in combination with reduced  $O_2$  and/or elevated  $CO_2$ , such effects are minimized.

Because of its extreme toxicity to humans and flammability, the commercial use of CO has been very limited. For example, CO at 5% to 10% has been used to a small extent as a component of MA during transport of whole and cut lettuce.

## VII. MODIFIED ATMOSPHERE PACKAGING (MAP)

The positive effects of film packaging, other than creation of CA or MA conditions, can include (a) maintenance of high relative humidity and reduction of water loss; (b) improved sanitation by reducing contamination of the commodity during handling; (c) minimized surface abrasions by avoiding contact between the commodity and the shipping container; (d) reduced spread of decay from one unit to another; (e) possible exclusion of light, when needed, for commodities such as potato and Belgian endive (*Cichorium intybus* L.); (f) use of the film as carrier of fungicides, sprout inhibitors, or other chemicals; and (g) facilitation of brand identification. The negative effects include slowing down cooling of the packaged commodity and increased potential for water condensation within the package, which may encourage fungal growth. Modified atmospheres can be created either passively by the commodity or actively, as described below.

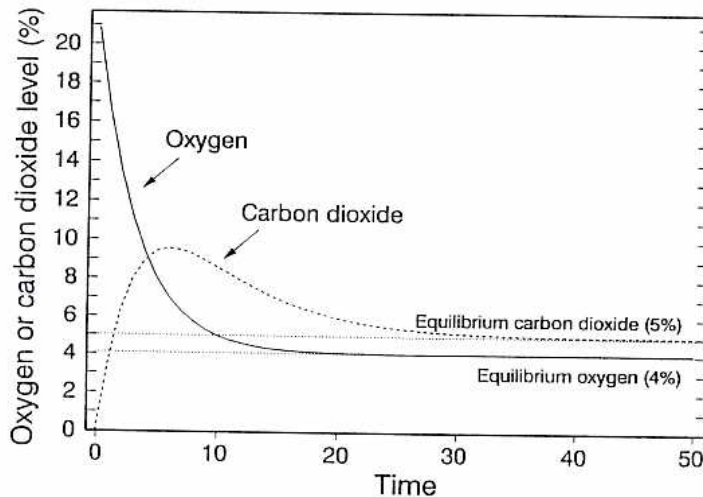
### A. Commodity-Generated or Passive MAP

If the respiratory consumption of  $O_2$  and the production of  $CO_2$  for a commodity (i.e., the respiration rate and mass of product) are properly matched with film permeability characteristics, an appropriate atmosphere can develop within a sealed package through consumption of  $O_2$  and production of  $CO_2$  by respiration and the diffusion of these gases through the film. The gas permeability of the selected film must allow  $O_2$  to enter the

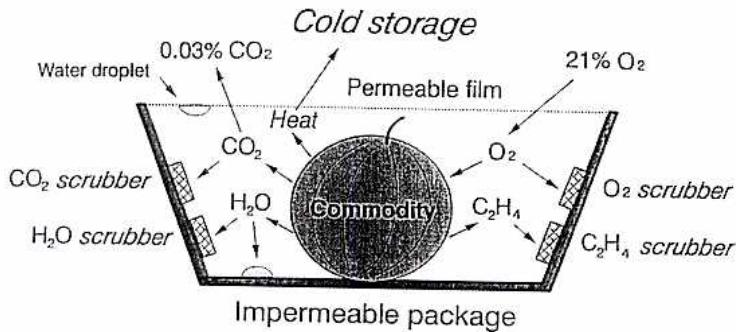
package at a rate offset by the consumption of  $O_2$  by the commodity. Similarly,  $CO_2$  must diffuse from the package at a rate sufficient to offset the production of  $CO_2$  by the commodity. Ideally, the atmosphere should be established rapidly and without creating anoxic conditions or injuriously high levels of  $CO_2$  during the equilibration process. In practice, however, passive MAP systems typically take several days to reach the equilibrium or steady-state atmosphere and can maintain an appropriate atmosphere within only narrow limits of temperature.

Many plastic films are available for packaging, but relatively few have been used to wrap fresh produce and fewer have gas permeabilities that make them suitable to use for MAP. Because  $O_2$  content in MAP is typically reduced from an ambient 21% to between 2% and 5% (a decrease of 19% to 16%), there is a danger that  $CO_2$  could correspondingly increase from an ambient 0.03% to 16% to 19% in the package as the equilibrium  $O_2$  concentration is being established by respiration. This is because there is normally about a one-to-one correspondence (respiratory quotient) between  $O_2$  consumed and  $CO_2$  produced. To avoid such high levels of  $CO_2$  from occurring, an ideal film for MAP must let more  $CO_2$  exit than it lets  $O_2$  enter. The  $CO_2$  permeability should be about three to five times the  $O_2$  permeability for most vegetables, depending upon the desired atmosphere to be produced in the package. Several polymers used in film formulation have desirable  $CO_2/O_2$  permeability characteristics for fresh produce. In the example illustrated in Figure 3, the film, package, and commodity characteristics were selected to produce an equilibrium atmosphere of 4%  $O_2$  plus 5%  $CO_2$ . As can be seen in this example, the equilibrium  $O_2$  concentration would be reached in one-half the time required to reach the equilibrium  $CO_2$  concentration, and the  $CO_2$  concentration would reach close to 10% before equilibrating at 5%.

Low-density polyethylene and polyvinyl chloride are the main films used in packaging fruits and vegetables. Polystyrene has been used, but Saran™ and polyester have such low gas permeabilities that they would be suitable only for commodities with very low



**Figure 3** Changes in the concentrations of  $O_2$  and  $CO_2$  within a modified atmosphere package as the atmospheric composition comes to equilibrium due to commodity respiration and gas diffusion across the film.



**Figure 4** A possible MAP system using adsorbing or absorbing substances in the package to scavenge water, O<sub>2</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> and showing movement of gases and heat across the semipermeable film and movement of gases from the commodity to the various scrubbers.

respiration rates. Recent technological advances have facilitated production of some films with more desirable permeability (higher ratio) of CO<sub>2</sub>/O<sub>2</sub> for fresh produce.

### B. Active MAP

Because of the limited ability to regulate a passively established atmosphere, atmospheres within MA packages may be actively established. This is usually done by pulling a slight vacuum and replacing the package atmosphere with the desired gas mixture. This mixture can be further adjusted and maintained through the use of absorbing or adsorbing substances in the package to scavenge O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, or C<sub>2</sub>H<sub>4</sub> (Fig. 4). This procedure is most suitable for highly perishable commodities. It is sometimes called controlled atmosphere packaging (CAP), a misnomer, since there is no active feedback or control of the package atmosphere comparable to CA storage.

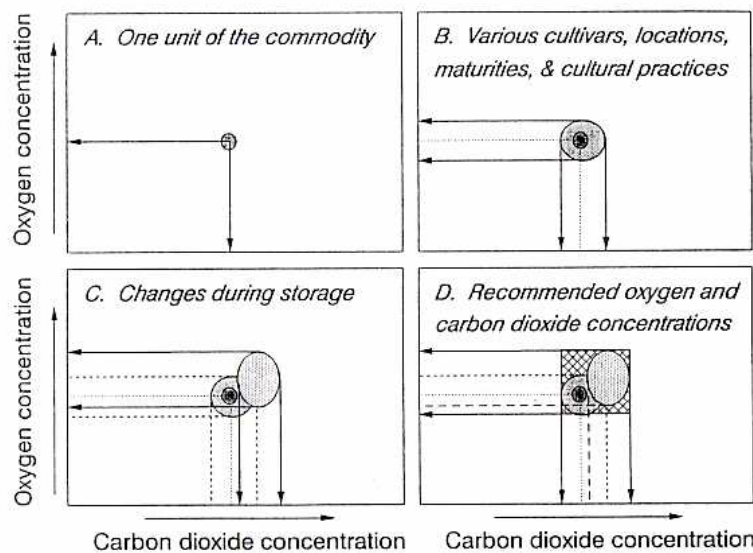
The main advantage of active MAP is that the initial vacuum-flush-seal cycle ensures the rapid establishment of the desired atmosphere in the film package. In-package inserts or sachets are not commonly used, primarily due to negative consumer reactions to "chemicals" in possible contact with fresh produce. However, absorbing or adsorbing substances can potentially address several problems in MAP. For example, CO<sub>2</sub> absorbers can prevent the buildup of CO<sub>2</sub> to injurious levels, which can occur for some commodities during passive modification of the package atmosphere. Oxygen absorbers can help maintain a low O<sub>2</sub> atmosphere when the film has been selected to produce a low CO<sub>2</sub> atmosphere. Packets of chemicals can also be included that help maintain a desirable relative humidity. Excessive water vapor in MAP can condense on the commodity or (more likely) on the inside surface of the package film as the storage temperature oscillates due to normal refrigeration cycles. Too low a relative humidity would cause excessive water loss from the commodity. Ethylene adsorbers can help retard senescence and delay the respiratory climacteric in ripening climacteric fruits.

## VIII. THE FUTURE OF CA AND MA RECOMMENDATIONS

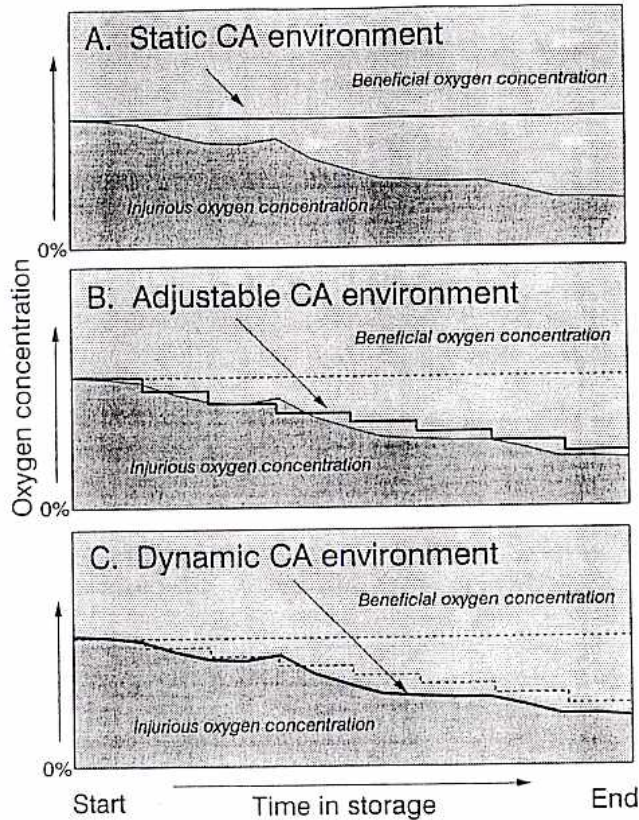
The foremost problem with trying to establish an optimal CA or MA environment for every commodity is the problem inherent with all biological material: variability. The

optimal  $O_2$  and  $CO_2$  levels vary with species and cultivar, with growing conditions (season, regional, location, cultural practices), with harvest maturity and uniformity, with postharvest handling (harvest method, handling, treatments), with packaging, with current and previous biotic and abiotic stresses, and with the developmental stage, ripening, aging, and senescence of the commodity (Fig. 5). While it theoretically should be possible to identify a very narrow range of gas concentrations, temperature, harvest maturity, duration of storage, and postharvest handling that would give the optimal CA or MA storage environment for each combination of variables (Fig. 5A), the combined variability inherent in the commercial storage of harvested vegetables would result in a fuzziness to these recommendations that is necessary to encompass all the prestorage variability (Fig. 5B). Even if all these prestorage sources of variability could be controlled, there exists the variability resulting from changes in the commodity during storage (Fig. 5C). While each permutation of these combined variables should have a clearly defined optimum, grouping them together into larger and larger complexes (as is done in commercial practices when produce originating from different sources is stored together) widens the recommended boundaries to ensure that none of the commodities will be damaged (Fig. 5D). This results in recommendations that are excessively vague and that almost guarantee that none of the commodities will be stored in optimal conditions.

Most CA and MA recommendations are merely snapshots of a dynamic process. Changes that occur in storage (e.g., ripening, cuticular changes, metabolic adjustments to altered gaseous concentrations, etc.) alter both the physical diffusion of gases into and out of the commodity and the physiological response of the commodity to the storage environment. To optimize the storage environment over the duration of the storage period, periodic adjustments may be needed to the  $O_2$  and  $CO_2$  concentration (Fig. 6B) and the temperature; and maybe even to the relative humidity. In other words, an adjustable CA environment will probably be much better than the currently used static approach in which



**Figure 5** Sources and effects of commodity variability on the recommended  $O_2$  and  $CO_2$  concentrations for controlled and modified atmosphere storage. (From Saltveit, 1997a.)



**Figure 6** Comparison of the static, adjustable, and dynamic approaches to regulating the  $O_2$  concentration in a controlled atmosphere storage over time. The two shaded areas represent the  $O_2$  concentrations that are either beneficial or injurious to the commodity. The solid line indicated by the arrow in each panel (the horizontal line in A, the stepped line in B, and the line of the boundary between the beneficial and injurious levels in C) represents the  $O_2$  concentration that is maintained in each type of CA storage. (From Saltveit, 1997a.)

one environment is established and maintained for the duration of the storage period (Fig. 6A). However, if the method used to evaluate the effectiveness of the adjustable approach remains an evaluation of the post-storage quality, then the amount of work needed to assess all the permutations of a recommended CA and MA environment would be formidable. Yet, even this approach may not be optimal if it does not take into account the changing requirements and responses of the stored commodity over some critically short periods of time. Simply adjusting the CA environment in uniform increments from what was optimal at the start of storage to what is optimal at the end of the storage period could produce injurious atmospheres during storage (Fig. 6B). This would not be a problem if the response of the commodity to the CA storage environment was used to indicate how the storage atmosphere should be modified (Fig. 6C). In all of these scenarios, we are assuming that the optimal  $O_2$  concentration occurs at the boundary between the beneficial and injurious  $O_2$  concentrations.

### **A. What Is to Be Optimized?**

Before we attempt to optimize the storage environment, we must first ask ourselves what criteria should be used to evaluate the effectiveness of the storage environment. The criteria could be the retention of quality, or the lowering of respiration, or the lowering of ethylene production or action, or the lowering of the number and extent of disorders. We could also want to have better flavor and aroma, or better color, or better texture, or firmer tissue. It is inconceivable that one storage environment would produce an optimum for all the criteria listed. We need to know which quality criteria are most important to be able to properly designate which parameters of the storage environment are most critical.

### **B. A Dynamic Method to Continually Evaluate Effectiveness of CA Is Needed**

Controlled and modified atmosphere recommendations for constant storage atmospheres (Fig. 6A) cannot be optimal, since they must always be nondamaging. A dynamic system to sense the response of the commodity to the storage atmosphere is the only way to optimize quality retention in CA. The characteristics of a dynamic indicator are that it be continuous, nondestructive, usable at a distance, and capable of automation. A number of physiological parameters could be indicators for the dynamic approach. They include the anaerobic compensation point (ACP), volatile products of anaerobic respiration, the respiratory quotient (RQ), near infrared (NIR) determinations of composition (e.g., sugars), nuclear magnetic resonance (NMR) evaluations of composition, transmission of sound through the tissue or vibration modes to determine changes in texture or external or internal color, fluorescence, or some other measure. Experiments need to be performed to establish which parameter has the consistency and predictability needed.

Some work has been done using the onset of anaerobic respiration (i.e., ethanol production) as the signal to modulate the  $O_2$  concentration in storage. While the ACP appears to be an interesting candidate for an accurate indicator of the "optimum" storage atmosphere with some commodities, much more research is needed to establish if the maintenance of the ACP gas concentration correlates with maximum quality retention in other crops. A complication in using the ACP is that both aerobic and anaerobic respiration occur at the ACP. The question arises as to whether this duality is inherent in plant tissue or whether it is the result of tissue architecture and microsites of anaerobic respiration due to differential barriers to gas diffusion. Another dilemma with using volatiles produced by the stored commodity is the problem of "one bad apple."

### **C. One Bad Apple**

The appearance of ethanol and RQ changes can be used to identify increased anaerobic respiration and the lower limit for  $O_2$ . However, ripening fruit naturally produce ethanol, and diseased tissues produce ethanol and other volatiles, often in great abundance. The possibility could arise in which a few overripe or diseased fruit could cause an erroneous modification of the storage environment because of their production of volatiles. Some method is needed to eliminate this problem.

### **D. What Are the Important Criteria in the Storage Environment?**

We must stop being obsessed with the exact concentrations of  $O_2$  and  $CO_2$  in the storage environment. While they are important to achieve our desired goal, we should really be

concerned with the response of the tissue to the CA environment. We should not use a predetermined recommendation for the "optimum" storage atmosphere but should use the feedback from the tissue to modulate the  $O_2$  level that will be optimal for each specific batch of commodity.

While theoretically this dynamic feedback method could be easily used to modulate the concentration of  $O_2$  in a storage environment once the proper indicator is identified, other biologically important gases, like  $CO_2$  and  $C_2H_4$ , are also often present at active concentrations in the storage environment. Active means are usually employed to exclude  $C_2H_4$  from the storage environment. Over the past 50 years, the recommended  $CO_2$  levels in the CA and MA storage of apples [*Malus sylvestris* (L.) Mill. var. domestica (Borkh.) Mansf.] has been decreased as the recommended  $O_2$  levels have continued to drop to lower and lower levels. The contribution of  $CO_2$  to the maintenance of quality in most commodities may be diminished as the  $O_2$  level is held near the absolute minimum. When  $CO_2$  is needed in the storage atmosphere (e.g., for disease control) a more complex computer program could integrate the response of various indicators and both gases to achieve an optimum storage environment.

The question is not whether a dynamic feedback method should be used to control the CA storage environment but rather what indicator should be used to generate the feedback necessary to control the storage environment.

## IX. METHODS OF ATMOSPHERIC MODIFICATION DURING TRANSPORT AND STORAGE

Atmosphere generators can be used to establish and/or maintain CA environments. The  $O_2$  level can be reduced by oxidizing a combustible gas with either an open flame burner or a catalytic converter. The catalytic converter is preferred because it works at lower temperature and there is no open flame. When oxidation or product respiration are used to reduce the  $O_2$  level, they also increase the  $CO_2$  concentration. Removal of  $CO_2$  is accomplished by using regenerative scrubbers, such as activated charcoal and molecular sieve scrubbers. Nonregenerative scrubbers, such as water, sodium hydroxide, and hydrated lime, can also remove  $CO_2$ . Supplemental  $CO_2$  is usually added from pressurized gas cylinders.

A better and more common method to establish and/or maintain CA environments is to flush the store with  $N_2$  gas. Nitrogen gas can be produced on site with equipment that concentrates  $N_2$  from the air (by either membrane separation or molecular sieve separation), or it can be purchased as a liquid and vaporized as needed.

Carbon monoxide is added from pressurized gas cylinders using a blending system with  $N_2$  to avoid exceeding 10%  $CO$ .

Ethylene is removed by absorbers, oxidation, or ventilation. Use of chemical absorbers may be expensive, and disposal of the spent toxic chemicals can present a problem. Some examples of  $C_2H_4$  absorbers are potassium permanganate (e.g., alkaline  $KMnO_4$  on aluminum silicate or zeolite pellets) or activated and brominated charcoal alone or in combination with  $KMnO_4$ . Catalytic burners and ozone can be used to oxidize ethylene. Ultraviolet light can produce ozone, which reacts with  $C_2H_4$  to produce  $CO_2$ , but since  $O_2$  is needed for ozone production, the effectiveness of this method is reduced in low- $O_2$  storage atmospheres. Also, ozone is phytotoxic and must be removed from the atmosphere before it is recirculated into the storage room.

Ethylene can be removed in LPS by simple ventilation of the storage container with air at reduced pressure. Low pressure systems work in the following way. Reducing the total pressure under a partial vacuum results in reductions of the partial pressures of each individual gas in the atmosphere. This is an effective method for reducing the partial pressure of  $O_2$ , and for accelerating the escape of  $C_2H_4$  and other volatiles from the commodity by increasing the rate of diffusion. However, since the lowered pressure also lowers the relative humidity of the atmosphere, water vapor must be introduced into the low-pressure side of the flowing air stream to prevent desiccating the commodity.

In the case of commodity-generated CA or MA, the respiration of the commodity is used to reduce  $O_2$  and increase  $CO_2$  under restricted air exchange conditions. If elevated  $CO_2$  and/or  $C_2H_4$  levels are not desirable, the  $CO_2$  and/or  $C_2H_4$  scrubbers mentioned above are used. Restriction of air exchange may be achieved by enclosing the commodity in an airtight room, using semipermeable packaging films, or coating the surface of the commodity. Some examples are packaging in film wraps or bags, use of polyethylene liners in shipping containers, use of pallet shrouds, and manipulation of vents in over-the-road, rail, and intermodal marine containers.

Polyethylene pallet covers (or shrouds) are used to cover all shipping containers on a pallet and are sealed by various means (e.g., tape, heat seal, etc.) to establish a gas-tight environment. A partial vacuum is established within the pallet cover and the desired gas mixture is introduced. This method can permit the shipping of commodities that are temperature-compatible but require different MA conditions during transit at the same temperature. Problems with pallet covers are primarily related to loss of seal due to tearing of the pallet cover or imperfect seal of the cover to the base.

Nitrogen flushing is used to establish low- $O_2$  MA in over-the-road, rail, and intermodal marine containers. Atmospheres with elevated  $CO_2$  and/or  $CO$  are established by adding these gases with gas blending manifolds. Gas tightness of the transit vehicle is essential to the maintenance of MA during transit. Carbon dioxide is removed by placing bags of lime in the transit vehicle (the amount of lime depends upon commodity, the quantity of the commodity in the container, and the transit time).

A more active and precise control of gas composition can now be achieved with  $O_2$  and  $CO_2$  sensors linked to on-board computers controlling miniaturized versions of the aforementioned atmosphere-modifying technologies. With these new tools at hand, which are expensive both to install and to operate, it has become more of an economic question than a postharvest physiological question as to how precisely the composition of the atmosphere should be regulated and maintained. These tools offer the opportunity to use a more dynamic and interactive approach to preserving quality in CA and MA than is currently done with generalized recommendations and static atmospheres for the duration of storage or transit.

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