MODIFIED ATMOSPHERE PACKAGING OF FRUITS AND VEGETABLES

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I. INTRODUCTION

The primary factors in maintaining quality and extending the postharvest life of fresh fruits and vegetables are harvesting at optimum maturity, minimizing mechanical injuries, using proper sanitation procedures, and providing the optimum temperature and relative humidity during all marketing steps. ¹⁻³ Secondary factors include modification of O₂, CO₂, and/or C₂H₄ concentrations in the atmosphere surrounding the commodity to levels different from those in air. This is referred to as controlled atmosphere (CA) or modified atmosphere (MA). CA implies a greater degree of precision than MA in maintaining specific levels of O₂, CO₂, and other gases.

The beneficial effects of CA in extending the postharvest life of pome fruits were demonstrated about 60 years ago. Since then, more than 4000 research reports on CA and MA have been published and almost half of these reports deal with pome fruits. Most of this research has been aimed at identifying the optimum CA conditions for each commodity and cultivar. 10-13

Current applications of CA and MA technologies include long-term storage of apples, pears, kiwifruits, cabbage, and Chinese cabbage; temporary storage and/or transport of strawberries, bush berries, cherries, bananas, and other commodities; and modified atmosphere packaging (MAP) of some cut or sliced (minimally processed) vegetables such as lettuce, celery, cabbage, and broccoli. MAP facilitates maintenance of the desired atmosphere during the entire postharvest handling time between harvest and use.

Recent advances in the design and manufacturing of polymeric films with a wide range of gas-diffusion characteristics have stimulated renewed interest in MAP of fresh produce. Also, the increased availability of various absorbers and adsorbers of O_2 , CO_2 , C_2H_4 , and water vapor provides possible additional tools for manipulating the microenvironment within MAP units. Such packages can be shipping containers, retail packages containing several intact or sliced commodity units, or retail packages for individual units of the commodity.

This article provides an overview of the responses of fresh fruits and vegetables to MA, implications of MAP other than MA effects, methods of creating and maintaining MA, and current status and future outlook of MAP. This is not intended to be an exhaustive review of every published report dealing with packaging produce in plastic films. Many of these studies were aimed at reducing water loss with atmospheric modification of O_2 , O_2 , and O_2H_4 concentrations as an incidental factor that may or may not have been monitored.

Table 1 CLASSIFICATION OF FRUITS AND VEGETABLES ACCORDING TO THEIR TOLERANCE TO LOW O₂ CONCENTRATIONS

Minimum O ₂ concentration tolerated	
(%)	Commodities
0.5	Tree nuts, dried fruits, and vegetables
1.0	Some cultivars of apples and pears, broccoli, mush- room, garlic, onion, most cut or sliced fruits and vegetables
2.0	Most cultivars of apples and pears, kiwifruit, apricot, cherry, nectarine, peach, plum, strawberry, papaya, pineapple, olive, cantaloupe, sweet corn, green bean, celery, lettuce, cabbage, cauliflower, Brussels sprouts
3.0	Avocado, persimmon, tomato, pepper, cucumber, artichoke
5.0	Citrus fruits, green pea, asparagus, potato, sweet potato

II. RESPONSES OF FRESH FRUITS AND VEGETABLES TO MODIFIED ATMOSPHERES

A. Relative Tolerance to Low O2 and Elevated CO2 Concentrations

The extent of benefits from CA and MA use depends upon the commodity, cultivar, physiological age (maturity stage), initial quality, concentrations of O_2 and CO_2 , temperature, and duration of exposure to such conditions. Subjecting a cultivar of a given commodity to O_2 levels below and/or CO_2 levels above its tolerance limits at a specific temperature-time combination will result in stress to the living plant tissue, which is manifested as various symptoms, such as irregular ripening, initiation and/or aggravation of certain physiological disorders, development of off-flavors, and increased susceptibility to decay. 14-17

Tables 1 and 2 include classifications of fruits and vegetables according to their relative tolerances to low O_2 or elevated CO_2 concentrations when kept at or near their optimum storage temperature and relative humidity. In each case, it is assumed that the other gas is near its normal (air) concentration. Tolerance limits to elevated CO_2 decrease with a reduction in O_2 level and, similarly, the tolerance limits to low O_2 concentrations increase with an increase in CO_2 level. Also, a given commodity may tolerate, for a short duration, higher levels of CO_2 or lower levels of O_2 than those indicated. The limits of tolerance to low O_2 would be higher than those indicated in Table 1 to maintain aerobic respiration if storage temperature and/or duration are increased.

For some commodities, susceptibility to low O_2 and/or high CO_2 stress is influenced by maturity stage. For example, ripe fruits often tolerate higher levels of CO_2 than maturegreen fruits. Minimally processed (cut, sliced, or otherwise prepared) fruits and vegetables have fewer barriers to gas diffusion, and consequently they tolerate higher concentrations of CO_2 and lower O_2 levels than intact commodities.

The effects of stress resulting from exposure to undesirable CA or MA conditions (i.e., levels of O_2 and/or CO_2) can be additive to other stresses (such as chilling injury, wounding, or ionizing radiation) in accelerating the deterioration of fresh produce.

Successful MAP must maintain near optimum O₂ and CO₂ levels to attain the beneficial effects of MA without exceeding the limits of tolerance which may increase the risk of physiological disorders and other detrimental effects.

Table 2 CLASSIFICATION OF FRESH FRUITS AND VEGETABLES ACCORDING TO THEIR TOLERANCE TO ELEVATED CO₂ CONCENTRATIONS

Maximum CO ₂ concentration tolerated	
(%)	Commodities
2	Apple (Golden Delicious), Asian pear, European pear, apricot, grape, olive, tomato, pepper (sweet), lettuce, endive, Chinese cabbage, celery, artichoke, sweet potato
5	Apple (most cultivars), peach, nectarine, plum, or- ange, avocado, banana, mango, papaya, kiwifruit, cranberry, pea, pepper (chili), eggplant, cauliflower, cabbage, Brussels sprouts, radish, carrot
10	Grapefruit, lemon, lime, persimmon, pineapple, cuc- umber, summer squash, snap bean, okra, asparagus, broccoli, parsley, leek, green onion, dry onion, garlic, potato
15	Strawberry, raspberry, blackberry, blueberry, cherry, fig, cantaloupe, sweet corn, mushroom, spinach, kale. Swiss chard

B. Beneficial and Detrimental Effects

The beneficial and detrimental effects of CA and MA on fresh fruits and vegetables have been reviewed by several authors. 14-22 Summaries of optimum CA conditions and their potential benefits for apples, pears, and other-than-pome fruits, and vegetables (prepared by Maheriuk, Richardson, Kader, and Saltveit, respectively) are included in the Proceedings of the Fourth National Controlled Atmospheres Research Conference. 13

Prevention of ripening and associated changes in fruits is one of the main benefits of CA/MA. Oxygen concentration has to be lowered below 8% to have a significant effect on fruit ripening, and the lower the O₂ concentration, the greater the effect. Elevated CO₂ levels (above 1%) also retard fruit ripening and their effects are additive to those of reduced O₂ atmospheres. The effects of CA/MA on delay or inhibition of ripening are greater at higher temperature. Thus, use of CA/MA may allow handling of ripening (climacteric-type) fruits at temperatures higher than their optimum temperature. This is especially beneficial for chilling-sensitive fruits such as tomatoes, melons, avocados, bananas, and mangoes, to avoid their exposure to chilling temperatures.

CA/MA conditions reduce respiration rates as long as the levels of O_2 and CO_2 are within those tolerated by the commodity (Table 3). This, combined with the decreased C_2H_4 production (Table 4) and reduced sensitivity to C_2H_4 action, results in delayed senescence as indicated by retention of chlorophyll (green color), textural quality (e.g., decreased lignification), and sensory quality of non-fruit vegetables. Exposure of fresh fruits and vegetables to O_2 levels below their tolerance limits (Table 1) or to CO_2 levels above their tolerance limits (Table 2) may increase anaerobic respiration and the consequent accumulation of ethanol and acetaldehyde causing off-flavors.

Low O_2 and/or high CO_2 concentrations can reduce the incidence and severity of certain physiological disorders such as those induced by C_2H_4 (scald of apples and pears) and chilling injury of some commodities (e.g., avocado, citrus fruits, chili pepper, and okra). On the other hand, O_2 and CO_2 levels beyond those tolerated by the commodity can induce

Table 3
RESPIRATION RATES OF SOME REPRESENTATIVE FRUITS
AND VEGETABLES AT DIFFERENT TEMPERATURES AND IN
DIFFERENT ATMOSPHERES

Commodity	Cultivar	Atmosphere	Temperature (°C)	Respiration (ml/kg-h)
Apple*	Granny Smith	Air	0	1.0
		15.575	10	3.6
			20	7.4
		2% O ₂ + 2% CO ₂	0	0.1
		T. 000000	10	0.7
			20	1.4
	Cox's Orange	Air	3.3	33.0
	Pippen ^b		7.3	53.0
		10% O ₂	3.3	26.0
			7.3	35.0
		5% O ₂	3.3	21.0
			7.3	30.0
		3% O ₂	3.3	17.0
			7.3	23.0
		$3\% O_2 + 5\% CO_2$	3.3	13.0
			7.3	21.0
		$1.5\% O_2 + 5\% CO_2$	3.3	10.0
			7.3	13.0
Bean, green ^a	Blue Lake	Air	5	17.5
			10	28.3
			20	59.6
		$3\% O_2 + 5\% CO_2$	5	10.8
			10	16.5
			20	28.0
Broccoli ^a	Green Valiant	Air	0	10.0
			5	21.0
			10	85.0
			20	213.0
		1.5% O ₂ + 10% CO ₂	0	7.0
			5	11.0
			10	15.0
727 Digit - 150			20	33.0
Cabbage	Decema	Air	0	1.5
			10	4.0
			20	10.0
		$3\% O_2$	0	1.0
			10	3.0
	INF HOUSEN MOTORS	E-SH-Winnin	20	6.0
Chili pepper	Anaheim	Air	5	3.4
			10	4.8
			12.5	12.8
		$2\% O_2$	5	2.7
			10	3.3
			12.5	6.9
		5% O ₂	5	3.3
			10	3.8
			12.5	10.9
		$Air + 5\% CO_2$	5	3.2
			10	4.5
		1: 1 10% 00	12.5	7.6
		Air + 10% CO ₂	5	4.8
			10	6.0
			12.5	9.8

Table 3 (continued)
RESPIRATION RATES OF SOME REPRESENTATIVE FRUITS
AND VEGETABLES AT DIFFERENT TEMPERATURES AND IN
DIFFERENT ATMOSPHERES

Commodity	Cultivar	Atmosphere	Temperature (°C)	Respiration (ml/kg-h)
Mango	Tommy	Air	10	15.0
	Atkins		15	31.0
			20	61.0
		$4\% O_2 + 7\% CO_2$	10	8.0
			15	14.0
			20	44.0
Tomato ^a	Ace (picked	Air	12.5	9.0
	mature- green)		20	18.0
		Air + 1% CO ₂	12.5	8.0
			20	16.0
		Air + 3% CO ₂	12.5	8.0
			20	15.0
		Air + 5% CO ₂	12.5	7.0
			20	13.0
		Air + 10% CO ₂	12.5	6.0
			20	14.0
	Ace (picked	Air	12.5	10.0
	light-pink)		20	25.0
		Air + 1% CO ₂	12.5	11.0
			20	16.0
		$Air + 3\% CO_2$	12.5	9.0
			20	15.0
		Air $+$ 5% CO ₂	12.5	8.0
			20	15.0
		Air + 10% CO ₂	12.5	8.0
			20	14.0

- ^a Authors' unpublished data.
- b Data from Reference 24.
- Data from Reference 23.

physiological disorders, such as brown stain on lettuce, internal browning and surface pitting of pome fruits, and blackheart of potato. Differences among cultivars in susceptibility to CA/MA-induced physiological disorders may be due to anatomical differences influencing their gas-diffusion characteristics.

Sharples and Johnson²⁶ reported that variations in susceptibility to physiological disorders are influenced by effects of climatic and growing conditions on the structure, mineral composition, and maturity of the fruit when harvested. The incidence and severity of bitter pit on apples is influenced by the effect of storage temperatures and CA on the dynamic balance of minerals in different parts of the fruit.

CA/MA combinations have direct and indirect effects on postharvest pathogens. El-Goorani and Sommer²⁷ pointed out that delaying senescence, including fruit ripening, by CA/MA reduces susceptibility of fruits and vegetables to pathogens. On the other hand, CA conditions unfavorable to a given commodity can induce its physiological breakdown and render it more susceptible to pathogens. Oxygen levels below 1% and/or CO₂ levels above 10% are needed to significantly suppress fungal growth.²⁷ Elevated CO₂ levels (10 to 15%) can be used to provide fungistatic effects on commodities that tolerate such CO₂ levels (Table 2).

Table 4
ETHYLENE PRODUCTION RATES OF SOME
REPRESENTATIVE FRUITS AND VEGETABLES AT
DIFFERENT TEMPERATURES AND IN DIFFERENT
ATMOSPHERES

Commodity	Cultivar	Atmosphere	Temperature (°C)	Ethylene production rate (nl/kg-h)
Apple ^a	Granny Smith	Air	0	472
			10	1,537
			20	4,053
		$2\% O_2 + 2\% CO_2$	0	246
		The state of the s	10	232
			20	312
Chili Pepper ^a	Anaheim	Air	5	33
			10	38
			12.5	553
		2% O ₂	5	23
			10	55
			12.5	198
		5% O ₂	5	33
			10	34
			12.5	186
		Air $+$ 5% CO ₂	5	20
			10	34
			12.5	191
		Air + 10% CO ₂	5	50
			10	36
Dinconnlat	C	1674	12.5	394
Pineapple*	Smooth Cayenne	Air	10	10
			15	30
		11% O ₂	20	150
			10	9
			15	20
Potato ^b	Russet Burbank	Air	20	100
· Olulo	Russet Burbank	All	0	<1
		2.5% O ₂	7.2	1—3
		2.5 % 02	0 7.2	<1
		80% O ₂	0	1-8
		00 % O ₂	7.2	2—20
Tomato ^a	Ace (picked	Air	12.5	1—30 1,220
	mature-green)	12.000.1	20	4,330
	28	Air + 1% CO ₂	12.5	420
			20	1,380
		Air $+$ 3% CO,	12.5	810
		•	20	1,110
		Air + 5 % CO ₂	12.5	520
			20	1,150
		Air + 10% CO ₂	12.5	200
			20	530
	Ace (picked	Air	12.5	6,710
	light-pink)	700-70-70-	20	14,290
		Air + 1% CO ₂	12.5	6,970
		(50)	20	10,260
		Air + 3% CO ₂	12.5	6,200
			20	8,400

Table 4 (continued) ETHYLENE PRODUCTION RATES OF SOME REPRESENTATIVE FRUITS AND VEGETABLES AT DIFFERENT TEMPERATURES AND IN DIFFERENT ATMOSPHERES

Commodity	Cultivar	Atmosphere	Temperature (°C)	Ethylene production rate (nl/kg-h)
		Air + 5% CO ₂	12.5	4,300
			20	7,140
		Air + 10% CO ₂	12.5	4,080
		and a second senate	20	6,880

- a Authors' unpublished data.
- b Data from Reference 25.

Carbon monoxide at 5 to 10% (combined with less than 5% O₂) is an effective fungistat which can be used on commodities that do not tolerate high CO₂ levels. Strict safety procedures must be used if carbon monoxide, which is highly toxic to humans, is added to CA/MA.

C. Biochemical and Physiological Basis

Although much research has been conducted to evaluate the beneficial and detrimental effects of CA and MA on fresh fruits and vegetables, the mode of action of O₂ and CO₂ on these commodities is still not fully understood. Generally, the effect of reduced O₂ and/or elevated CO₂ on reducing the respiration rate has been assumed to be the primary reason for the beneficial effects of CA/MA on fresh produce. Kader²⁸ indicated that postharvest deterioration of fresh produce can be caused by many factors in addition to high respiration rates, including biochemical changes associated with respiratory metabolism, C₂H₄ biosynthesis and action, compositional changes, anatomical changes associated with growth and development, physical injuries, water loss, physiological disorders, and pathological breakdown. These effects are summarized in Table 5.

CA/MA conditions can effectively reduce or inhibit C_2H_4 -induced senescence and physiological disorders in harvested fruits and vegetables. 9.33,34 The direct and indirect effects of CA/MA on postharvest pathogens of fruits and vegetables have been reviewed by El-Goorani and Sommer. 27

The potential benefits of MAP for a given commodity can be predicted from information about the primary cause(s) of deterioration for that commodity and the known effects of MA on those causes as summarized above and in Table 5. Also, the relative tolerance of that commodity to reduced O_2 and elevated CO_2 concentrations (Tables 1 and 2) must be considered. For example, if the primary cause of deterioration is a fungus that can be controlled by a CO_2 -enriched atmosphere, but the host commodity does not tolerate the fungistatic CO_2 concentration, MAP would not be useful for that commodity.

Under CA/MA conditions, it is the concentration of O_2 , CO_2 , and C_2H_4 within the plant tissue that determines the physiological and biochemical responses of that tissue. The internal concentrations of these gases depend on their external concentrations, rates of CO_2 and C_2H_4 production, rate of O_2 consumption, surface area, and resistance of the dermal system to gas diffusion of O_2 , CO_2 , and C_2H_4 (which is much greater than resistance to diffusion of water vapor). Resistance to diffusion within the flesh of fruits increases as they ripen due to the flooding of some of the intercellular spaces with cell sap.

Table 5 BIOCHEMICAL AND PHYSIOLOGICAL BASIS FOR EFFECTS OF MODIFIED ATMOSPHERES ON FRUITS AND VEGETABLES^a

	General effects ^b of		
Cause of deterioration	Reduced O ₂	Elevated CO	
A. Respiratory metabolism			
1. Respiration rate	c	-, 0, or $+$	
2. Shift from aerobic to anaerobic respiration	+ (<1%)	+ (>20%)	
3. Energy produced	_	_ (-20.0)	
B. Ethylene biosynthesis and action			
 Methionine → SAM 	0	?	
2. Synthesis of ACC synthase	0	-	
3. SAM ACC synthase ACC	+	?	
4. Synthesis of EFE	?	-	
5. ACC $\xrightarrow{\text{EFE}}$ C ₂ H ₄	_	- or +	
		OI 1	
6. Ethylene action	122		
C. Compositional changes			
1. Pigments			
a. Chlorophyll degradation	=	-	
b. Anthocyanin development	-	175	
c. Carotenoids biosynthesis	-	-	
2. Phenolics			
a. Phenylalanine ammonia lyase activity	?	+	
b. Total phenolics	?	-	
c. Polyphenoloxidase activity	- (near	177	
	0%)		
3. Cell wall components			
a. Polygalacturonase activity	2	420	
b. Soluble polyuronoides	H-	_	
4. Starch-to-sugar conversion		-	
5. Organic and amino acids			
a. Loss in acidity	-	-	
b. Succinic acid	?	+	
c. Aspartic and glutamic acids	?	_	
d. γ-Amino butyric acid	?	+	
6. Volatile compounds		9.6.9	
a. Characteristic aroma volatiles	-	_	
b. Off-flavors (accumulation of ethanol and acetaldehyde)	+ (<1%)	+ (>20%)	
7. Vitamins	((170)	1 (220%)	
a. Provitamin A (β-carotene) loss	20	_	
b. Vitamin C (ascorbic acid) loss	200	77.7 22.7	
D. Growth and development			
1. Cell division	980 Y	275 65	
2. Cell enlargement	- or +	- or +	
Endogenous growth regulators	- or +	- or +	
Endogenous growth regulators Periderm formation	7	?	
E. Physical injuries	- (<5%)	- (>10%)	
	2010200		
1. Wound healing	See D-4		
2 T: 1	above		
2. Tissue browning	See C-2		
2 6 1 100 100	above		
3. Stress-induced CO ₂ and C ₂ H ₄		-	
F. Transpiration (water loss)			
1. Stomata opening	?	?	
2. Wound healing	See D-4		
	above		

Table 5 (continued) BIOCHEMICAL AND PHYSIOLOGICAL BASIS FOR EFFECTS OF MODIFIED ATMOSPHERES ON FRUITS AND VEGETABLES^a

	General effects ^b of			
Cause of deterioration	Reduced O ₂	Elevated CO ₂		
G. Physiological disorders				
1. Chilling injury	+	- or +		
2. Scald on apples and pears	2 2			
3. C ₂ H ₄ -induced disorders	2,1—2;	- 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		

- " Compiled from Reference 14, 16—19, 27—34.
- Specific O₂ and/or CO₂ concentrations at which these effects are observed depend upon the commodity, cultivar, temperature and duration of storage, and interactions between O₂ and CO₂ levels.
- = decrease or inhibit, O = no effects, + = stimulate or increase, ? = inadequate data for a conclusion.

III. IMPLICATIONS OF PACKAGING PRODUCE IN POLYMERIC FILMS

The beneficial and detrimental effects of packaging fresh produce in polymeric films have been evaluated for more than 25 years.³⁵⁻³⁸ The positive effects of film packaging, other than creation of MA conditions, can include (1) reduction of surface abrasions by avoiding contact between the commodity and the material of the shipping container; (2) improved sanitation by reducing contamination of the commodity during handling; (3) possible exclusion of light, when needed, for commodities such as potatoes and Belgian endive; (4) maintenance of high relative humidity and reduction of water loss; (5) provision of a barrier to the spread of decay from one unit to another; (6) possible carriers of fungicides and scald inhibitors; and (7) facilitation of brand identification.

Plastic films influence the rates of cooling and warming of the commodity and must be considered in selecting the appropriate temperature-management procedures for a packaged commodity. Film-wrapped produce usually requires longer cooling time than unwrapped produce, and the difference can be reduced by perforating the film. Another potential disadvantage of film wrapping is the possible water condensation within the package, which may encourage fungal growth and increase decay problems. Such condensation is likely to occur when the commodity is removed from low storage temperatures to high ambient temperatures during postharvest handling.

Ben-Yehoshua^{38,39} reported that individual seal-packaging may extend shelf life and reduce weight loss, severity of surface blemishes, and chilling-injury symptoms on some commodities, especially citrus fruits, provided they are pretreated against decay. Relatively thin (10 μm) films are used to provide a barrier to water vapor without significant effects on O₂, CO₂, or C₂H₄ diffusion. The water-saturated atmosphere alleviates water stress, encourages wound healing, and helps maintain the skin's resistance to pathogens.

Waxes and other surface coatings provide an artificial barrier to diffusion around the commodity. This may result in reduced O_2 and increased CO_2 concentrations within the commodity, depending on the nature and thickness of the barrier material and how it interacts with temperature and the presence of water. Polymeric films are generally much more effective than waxes in reducing water loss without resulting in an undesirable modification of O_2 , CO_2 , and C_2H_4 concentration.³⁹⁻⁴¹

Both coatings and films can be used to obtain MA in fruit and beneficial effects on quality. However, there is still much to be learned about the basic as well as applied aspects of both coatings and film technology.⁴¹

Hintlian and Hotchkiss⁴² reviewed the safety aspects of MAP, i.e., its effects on food-borne pathogens. Most research so far has been done with meat and fish products. Elevated CO₂ concentrations inhibit some types of bacteria, but has no direct effect on others. Temperature is a very important factor in reducing bacterial growth and it must be kept below 4°C. It is a more critical factor than MA. Lack of refrigeration at any time during a product's life could allow the growth of organisms which had been inhibited by CO₂ during storage at low temperature.²⁰

Because anoxic MA conditions can favor the growth of facultative anaerobes and/or obligate anaerobes over aerobic spoilage organisms, packaging of foods in O₂-excluded MAs could result in a dangerous absence of noxious odors produced by aerobic spoilage organisms. ^{20,42} However, fresh produce, as living tissue, ferments and develops undesirable off-flavors due to the accumulation of ethanol, acetaldehyde, and other volatiles under anaerobic conditions.

Fresh produce should never be packaged in a way that may result in anoxic conditions. This, combined with maintenance of the optimum temperature range throughout postharvest handling, should ensure safety (absence of harmful bacteria) of fresh produce in MAP. Further research is needed to estimate the potential for public health problems and the need for including indicators of temperature abuse and/or anoxic conditions within MAP units of certain commodities. Special attention should be given to minimally processed (e.g., cut, peeled, segmented) vegetables and fruits packed alone or in combination with other ready-to-eat foods, which may increase bacterial contamination.

IV. CREATION AND MAINTENANCE OF ATMOSPHERES

MA within polymeric film packages can be established via active or passive modification or a combination of the two.

A. Active Modification

In the case of active modification, an atmosphere is established by pulling a slight vacuum and replacing the atmosphere of the package with the desired gas mixture (the advantage here is that the atmosphere can be modified immediately after packaging). Additionally, absorbers or adsorbers may be included in the package to scavenge O_2 , CO_2 , or C_2H_4 to control the concentrations of these gases.

1. Oxygen Absorbers

Most commercially available O_2 absorbers use iron powder as the main active ingredient. These products often utilize powdered FeO which becomes Fe_2O_3 , Fe_3O_4 , and their hydroxide forms after absorption of O_2 . It is possible to calculate the right type, size, and amount of FeO needed to lower the concentration of O_2 to approximate desired prechosen values. The lower the temperature, the lower the O_2 absorption speed.

2. Carbon Dioxide Absorbers

Some of the absorbants that are currently being used to remove excess CO_2 from CA storage rooms that could be adapted for their utilization in MAP include (1) lime (freshly hydrated high calcium lime $[Ca(OH)_2]$), (2) activated charcoal, and (3) magnesium oxide.

3. Ethylene Absorbers

Some materials that could be used for C₂H₄ absorption within polymeric film packages are

- Potassium permanganate. Permanganate adsorbed on celite, vermiculite, silica gel, or alumina pellets oxidizes C₂H₄ to CO₂ and H₂O and is a noncorrosive scrubber.
- Builder-clay powder. Its principal component is cristobalite (>87% SO₂, >5% AlO₂, >1% Fe₂O₃), with traces of other crystals. It absorbs ethylene and many other gases and is nontoxic. It may be incorporated into plastic films, but it results in a brownish, cloudy appearance.
- Other compounds like hydrocarbons (squalane, Apiezon) and silicones (phenylmethylsilicone) could be very useful.

An alternative method for quickly developing an MA within a package involves the use of an appropriately sized sachet of ferrous carbonate. The amorphous material oxidizes in moist air, perhaps according to the following equation:

$$FeCO_3 + O_2 + 6H_2O \rightarrow 4Fe(OH)_3 + 6CO_2$$

The reaction, thus, quickly builds up the CO₂ content of the package while reducing the O₂ content somewhat.

Commercially suitable absorbers for any gas should satisfy the following requirements: (1) must be effective and exhibit an appropriate rate of absorption of that gas, (2) must be harmless to humans by direct or indirect contact, (3) must have good storage stability, and (4) must be small in size but have large capacity for gas absorption.

B. Passive Modification

In this case, modification of the atmosphere is attained through respiration of the commodity within the package and depends on the characteristics of the commodity and the packaging film.⁴¹

1. Respiration and Diffusion Characteristics of the Commodity

The exchange of gases between a plant organ and its environment can be considered in four steps as follows: (1) diffusion in the gas phase through the dermal system; (2) diffusion in the gas phase through the intercellular system; (3) exchange of gases between the intercellular atmosphere and the cellular solution (cell sap), which is a function of the distribution of intercellular spaces and respiratory activity; and (4) diffusion in solution within the cell to centers of O_2 consumption or from centers of O_2 and O_2H_4 production.

Carbon dioxide (as a result of respiratory metabolism) and C_2H_4 are produced in the cell sap, and this local increase in concentration will activate diffusion outward toward the cell-wall surface adjacent to the intercellular space. These gases then move into the intercellular space and continue toward regions of lower concentrations until they reach the intercellular space below the dermal system. From there, CO_2 and C_2H_4 diffuse through the openings in the surface of the commodity to the ambient atmosphere. 20,43

The pattern of the gradient that is established for O_2 diffusion is the reverse of that for CO_2 and C_2H_4 . Oxygen diffuses inward from the ambient air into the centers of consumption inside the cells.

Gas diffusion within a fruit or vegetable is determined by: respiration rate, maturity stage, physiological age, commodity mass and volume, pathways and barriers for diffusion, properties of the gas molecule, concentration of gases in the atmosphere surrounding the commodity, magnitude of gas concentration gradient across barriers, and temperature. 44.45

In turn, the respiration rate of a commodity inside a polymeric film package will depend upon: kind of commodity, maturity stage, physical condition, concentrations of O_2 , CO_2 , and C_2H_4 within the package, commodity quantity in the package, temperature, and possibly light.

Theoretically, a gas will diffuse through that pathway which offers least resistance. Gases diffuse mainly through gaseous spaces, i.e., channels filled with air. 43,46-48

Three different routes are available for the exchange of gases between horticultural commodities and their surrounding atmosphere: lenticels and stomata, the cuticle, and the pedicel opening or floral end. In leaves, the resistance of the epidermal layer to gas diffusion is mainly regulated through the stomatal aperture. Extensive research has been conducted to determine exactly how stomatal function is coupled to gas exchange. In bulky plant organs, there is no evidence for the presence of functional stomata or other active controls of gas exchange. These organs have a much lower surface-to-volume ratio than leaves; the distance over which gases must diffuse in the tissues is very large, and respiration, not photosynthesis, accounts for the major metabolic source of CO₂ and sink for O₂. These types of considerations led Devaux⁵² to investigate the internal levels of O₂ and CO₂ in the cavity of pumpkins in order to determine how they differ from air. He suggested that rapid gas exchange must take place even in the largest of bulky plant organs. Studies have shown that the majority of gas diffusion in these organs occurs through the lenticels. The calyx opening of apples for another than the stem scar of tomatoes for the presence of the presence of

While O_2 , CO_2 , and C_2H_4 diffuse mainly through air-filled stomata, lenticels, floral ends, and stem scars, water vapor preferentially diffuses through the liquid aqueous phase of the cuticle. Pieniazek⁶⁰ showed that lenticels accounted for only 8 to 20% of the water vapor flux from apples. Oxygen, CO_2 , and C_2H_4 are constrained from diffusing through the cuticle because their diffusivity in the liquid water phase of the cuticular membrane is about 10,000 times less than that in air.⁶¹

Fick's Law of Diffusion states that the movement or flux of a gas depends on the concentration drop across the barrier involved, the surface area of the barrier, and the resistance of the barrier to diffusion. A simplified version of Fick's Law can be written as follows:

$$J_{gas} \, = \, \frac{A \, \cdot \, \Delta C_{gas}}{R}$$

where $J = \text{total flux of gas } (\text{cm}^3 \cdot \text{sec}^{-1}); A = \text{surface area of the barrier } (\text{cm}^2); \Delta C = \text{concentration gradient across the barrier; and } R = \text{resistance to diffusion of gas } (\text{sec} \cdot \text{cm}^{-1})$

The resistance of plant tissues and organs to diffusion of O_2 , CO_2 , and C_2H_4 has been investigated using the steady-state approach. ^{47,57,62} In this method, the production (consumption) rate of the gas by the organ and the concentration of the gas in the internal and external atmospheres are determined. Then the resistance is calculated as follows:

$$R = \frac{\text{concentration gradient}}{\text{production (consumption) rate}}$$

When using this steady-state approach, one assumes the following: (1) gases are being consumed or produced at a rate equal to their escape from or entry into the organ, (2) the skin is relatively thin relative to the radius of the flesh, and (3) the skin represents the primary barrier to gas diffusion. This method cannot be used to study changes in resistance in systems which involve rapidly changing conditions such as wounded tissue or fruit passing through a climacteric.

Cameron and Yang⁶³ have proposed another method to quantitatively estimate resistance coefficients based on kinetic analysis of the efflux of preloaded gases from plant tissues. The concept is to load a plant organ with a nonphysiological, chemically inert gas and analyze its efflux characteristics. One limitation of this method is that suitable analogs to the gases in question are difficult to find.

There is a need for quantitative determination of the resistances through the various pathways of diffusion for O₂, CO₂, C₂H₄, and water vapor. A majority of studies on gas exchange in plant tissues indicate that the skin represents the main significant barrier to gas diffusion.^{47,64-67} It is the skin barrier that is the primary factor regulating the internal concentrations of gases within a commodity. The effects of waxes and films on diffusion for and resistance to gases moving across the skin are additive.

Researchers have been unable to detect significant gradients of gases in the flesh of orange fruit, ⁶⁶ potato tuber, ⁶⁴ or apple fruit. ⁴⁷ Intercellular spaces are generally thought to facilitate the diffusion of gases within the flesh. ⁶⁸ However, sizeable gradients have been detected in the flesh of avocado fruit. ⁴⁷ Nobel ⁴⁹ pointed out that the apparent gas diffusivity of the apple flesh is only 10- to 20-fold higher than that of the skin, which may create appreciable concentration gradients within the flesh, especially in relatively large fruits. Also, as plant organs advance into the senescence stage, cell walls and membranes begin to breakdown and cell contents fill some of the air spaces. Consequently, the resistance of flesh to gas diffusion may become significant. Different commodities have different total amounts of internal air space, e.g., potatoes have only 1 to 2% internal air space, while tomatoes have 15 to 20% and apples have 25 to 30%. This limited amount of air space could lead to a significant flesh resistance to gas diffusion. The cell wall appears to present some resistance to gas diffusion ^{43,69} and thus a gradient between the cells and the intercellular space may be expected to develop.

Skin resistance to water vapor diffusion has been shown to be much lower than resistance to O₂, CO₂, or C₂H₄ diffusion.⁷⁰ Waxes, and not cutins, seem to be the primary barriers to water vapor diffusion through the skin in leaves and bulky organs.⁷¹⁻⁷³

It has been asserted that CO_2 moves much more readily through the skin than O_2 . $^{30,74-76}$ Burg and Burg⁴⁷ have shown that the resistance to CO_2 and C_2H_4 is very similar in a number of bulky organs.

In those cases in which sufficient data are available, the resistance to the diffusion of CO₂ out of fruits and vegetables has been shown to increase during the maturation period. 66,77 The period of least resistance to gas diffusion appears to be when the fruit is still immature, 76 and generally there is a marked increase in resistance to O₂ and CO₂ diffusion shortly after harvest. 53,78 Resistance to gas diffusion continues to increase during maturation 39 and in some fruits increases further during their postclimacteric. 76,79,80 Changes in the flux of water vapor during maturation of bulky organs have been characterized. Generally, the rates decline during maturation, reaching a minimum, in fruits, about the time of the climacteric and increasing thereafter. 81,82

 Vaz^{83} investigated the effect of internal and external factors on resistance to gas diffusion for a number of fruits and found that, as the fruit ripened, the resistance to CO_2 diffusion increased and the resistance to C_2H_4 diffusion decreased. Larger fruits were more resistant to CO_2 diffusion than smaller ones. Reduced external O_2 levels resulted in lower diffusion resistance to CO_2 and higher resistance to C_2H_4 . Elevated external CO_2 levels increased both the C_2H_4 and CO_2 diffusion resistance.

On the whole, comparison of the published resistance factors and coefficients is extremely difficult since there are no standardized units, and often the shapes and sizes of organs utilized are not given.

2. Film Characteristics and Permeability

Gas diffusion across a film is determined by: film structure, film permeability to specific gases, thickness, area, concentration gradient across the film, temperature, and differences in pressure across the film. Relative humidity may affect diffusion characteristics of some films.

Permeability is defined as transmission of a penetrant through a resisting material. In the

absence of cracks, pinholes, or other flaws, the primary mechanism for gas and water vapor flow through a film or coating is by activated diffusion, i.e., the penetrant dissolves in the film matrix at the high concentration side, diffuses through the film driven by a concentration gradient, and evaporates from the other surface. Differences in the solubility of specific gases in a particular film may determine which gas diffuses more readily across that film.

The second step of the process, i.e., diffusion, depends upon the size, shape, and polarity of the penetrating molecule, crystallinity, degree of cross-linking, and polymer chain segmental motion within the film matrix. Meares⁸⁴ and Kumins and Roteman⁸⁵ have shown that, when there is no interaction between permeant and polymer, the permeability rate decreases with the diameter of the permeant molecule. In most polymeric films, as the degree of cross-linking increases, the diffusion constant decreases.⁸⁶ Plasticizers are additives which decrease the cohesive forces between polymer chains, resulting in increased chain mobility and therefore an increase in permeability by interspersion of plasticizers between polymer chains.⁸⁶

The introduction of unsaturation into a polymer backbone lends greater ease of rotation to the chains, leading to higher diffusivity.⁸⁷ The introduction of methyl groups, on the other hand, decreases the chain flexibility, leading to lower diffusivity.⁸⁸

Other variables that can affect gas permeation into and out of polymeric film packages are free volume inside the package, effectiveness of seal or closure of the package, and air velocity around the package.

Selection of a film that will result in a favorable MA should be based on the expected respiration rate of the commodity at the transit and storage temperature to be used and on the known optimum O₂ and CO₂ concentrations for the commodity.⁸⁹

For most commodities (except those which tolerate high CO_2 levels), a suitable film must be much more permeable to CO_2 than to O_2 . In fact, most commercially available films are indeed more permeable to CO_2 than to O_2 .

The following is a list of the desirable characteristics of plastic films for MAP of fresh produce:

- 1. Required permeabilities for the different gases
- 2. Good transparency and gloss
- 3. Light weight
- 4. High tear strength and elongation
- 5. Low temperature heat-sealability
- 6. Nontoxic
- 7. Nonreactant with produce
- 8. Good thermal and ozone resistance
- Good weatherability
- 10. Commercial suitability
- 11. Ease of handling
- 12. Ease of printing for labeling purposes

3. Equilibrium Gas Concentrations

After a short period of adjustment, steady-state conditions will be established inside an intact polymeric film package once the appropriate relationship among produce and package variables is achieved. Oxygen inside the package is consumed by the produce as it respires and an approximately equal amount of CO₂ is produced. The reduction in O₂ concentration and increase in CO₂ concentration create a gradient causing O₂ to enter and CO₂ to exit the package. Initially, however, the gradient is small and the flux across the package is not sufficient to replace the O₂ that was consumed or to drive out all of the CO₂ that was generated. Thus, inside the package, the O₂ content decreases and the CO₂ content increases.

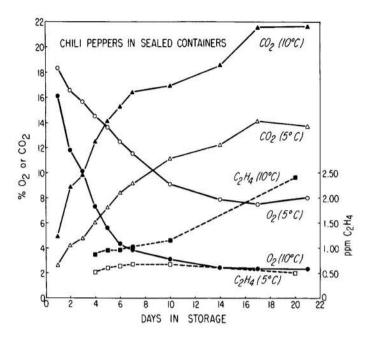


FIGURE 1. Changes in O₂, CO₂, and C₂H₄ concentrations with time within sealed containers of chili peppers kept at 5 or 10°C.

As this MA is created inside the package, respiration rates start to fall in response to the new atmospheres, resulting in elevation of the O₂ content and reduction in the CO₂ content. Thus, new equilibrium concentrations of the gases surrounding the fruit are established. 41.90.91

When O_2 consumption equals O_2 diffusion into the package and CO_2 production equals CO_2 diffusion out of the package, a steady-state equilibrium is achieved. Figure 1 illustrates the establishment of steady-state conditions during MAP of produce. In this case, chili peppers were placed in sealed containers to simulate a gas-tight film package. As expected, the accumulation of CO_2 and C_2H_4 and the depletion of O_2 occurred faster at $10^{\circ}C$ than at $5^{\circ}C$.

4. External Factors

Any change in temperature will affect the rate of respiration and the equilibrium conditions within the package unless the rate of diffusion of gases through the film is changed by temperature to exactly the same extent as respiration. A decrease in the internal concentration of O_2 and an increase in the internal concentration of CO_2 within bulky plant organs in response to an increase in temperature has repeatedly been demonstrated for various commodities including potatoes, oranges, papayas and bananas, and pears. At constant relative humidity, it has been shown that an increase in temperature causes an immediate increase in the transpiration rate of bulky plant organs. On the whole, respiration is roughly doubled or tripled for every rise of 10° C. The permeability of films has been reported to rise from two to five times with every 10° C increase in temperature. Therefore, a film resulting in a favorable atmosphere at a low temperature may result in a harmful atmosphere at higher temperatures.

Solubility of gases in a liquid matrix decreases with increasing temperatures. Thus, changes in temperature will affect gas diffusion between the cell sap and the intercellular spaces and across films.

Films that are available for use in MAP typically have low permeability to water vapor. The high relative humidity formed within packages can cause condensation and favor development of molds/bacteria.

Packets containing chemical compounds that absorb water, such as CaSiO₄, KCl, xylitol, NaCl, and sorbitol, have been used for the control of relative humidity inside polymeric film packages.⁹⁴

The presence of condensed water on the surface of a commodity or on either side of a film may affect the diffusivity (and solubility) of gases across the barriers. Carbon dioxide is more soluble in water than O_2 or C_2H_4 .

The peel of some fruit may shrivel after prolonged exposure to lower water vapor concentrations, and there is evidence that the resistance to diffusion increases. 66.95

Permeability of gases through a film will not necessarily decrease with an increase in relative humidity inside a package (with consequent condensation on the surface of the film). Some materials might actually exhibit a swelling of their structure and cross-link matrix and pores, resulting in higher rates of gas diffusion.

It is important to establish that the total internal pressure of a commodity and that of the ambient atmosphere are reasonably equal since a difference in pressure will generate mass gas flow. The rate of movement of gases through bulky plant organs in response to a pressure gradient has been used to measure diffusion characteristics. 95.96 However, resistance to mass flow and resistance to diffusive flow are not equivalent. 97

V. CURRENT STATUS AND FUTURE OUTLOOK OF MODIFIED ATMOSPHERE PACKAGING

Recent advances in polymeric film design and fabrication have made it possible to create films with specific and differential permeabilities to O₂ and CO₂ ⁹⁸⁻¹⁰¹ (Table 6). Semipermeable films are now used to modify in-package atmospheres as pallet load shrouds, ¹⁰² box liners, ¹⁰³ shipping bags, ¹⁰⁴ consumer packaging, ^{35,105} and individual wrapping. ^{106,107} We can, in principle, specify desired film permeabilities and then find or create a film with those permeabilities. ¹⁰⁸ It should, then, be possible to calculate what the permeabilities of a film are which can be used to passively establish a desired MA around a given commodity knowing the respiration rate of that commodity for the specified atmosphere and temperature.

A. Modeling Atmospheric Modification within a Package

Evaluation of MAP and materials for fresh fruits and vegetables remains a largely empirical, trial-and-error exercise that is time-consuming, subjective, and often without unifying principles to guide the research and development efforts. This empirical approach can lead to long testing times, high development costs, costly overpackaging, and the absence of a mechanism to fine-tune a packaging system once it has been developed. 109

Some attempts have been made to put the design of such packages on a more analytical basis. Tolle¹¹⁰ used regression equations and extrapolation of apple respiration data from 82 references to generate a model of film permeability requirements necessary to generate desired MA in bushel boxes of apples. The model was based on the products of respiration, gas partial pressure differentials, film surface area, and an empirically derived package-volume adjustment factor and package-atmosphere constant. Jurin and Karel¹¹¹ published an empirical method for determining the equilibrium O₂ concentration for a given film and product. The model assumes a respiratory quotient (RQ) equal to one and that the CO₂ concentration within the hypothesized package is too low to effect fruit respiration. They plotted product respiration as a function of O₂ concentration on the same set of coordinates as film permeation. The intersection of the two curves represented the equilibrium O₂ concentration. Veeraju and Karel¹¹² presented an analytical model to design packages using two plastic films of different permeability characteristics in order to independently control the O₂ and CO₂ concentrations in the package. The model required inputs of the rates of O₂ consumption and CO₂ evolution, the areas and thicknesses of the two films, and the permeabilities of

Table 6					
AVAILABLE	POLYMERS	FOR	PLASTIC	FILM	FORMULATION

	Webbar SW STORY			
Film type	0,	CO ₂	CO ₂ /O ₂	MVTR ^b
Polyethylene, low density ^c	3900—13,000	7,700—77,000	2.0—5.9	
Polypropylenec	1,300-6,400	7.700-21,000	3.3 - 5.9	
Polystyrene	2,600-7,700	10,000-26,000	3.4-3.8	
Cellulose acetated	1,814-2,325	13,330-15,500	6.7—7.3	1,163-1,395
Polyvinyl chlorided	620-2,248	4,263-8,138	3.6 - 6.9	140-171
Polyvinylidene chloride ^d	15.5	59	3.8	3.1
Rubber Hydrochloride ^d	589—50,375	4,464—209,250	4.2—7.6	7.8—10.9
Nylon-6 ^d	15.5	31	2.0	126
Polyester	52-130	180-390	3.0-3.5	
Polycarbonate ^d	13,950-14,725	23,250-26,350	1.7-1.8	10.9-17.1
Ethylcellulose ^d	31,000	77,500	2.5	310
Methylcellulose ^d	1,240	6,200	5.0	3,100
Polyvinyl alcohold	near 0	near 0	-	1,240
Polyvinyl fluorided	50	171	3.4	· —
Polychlorotriflour- oethylene ^d	11.8	124	10.5	0.3
Cellulose triacetate ^d	2,325	13,640	5.9	74—93
Vinyl chlorideacetate ^d	233	853	3.7	62

^a Gas transmission rates have been converted so that all are expressed as ml/mil/m²/day @ 1 atm. CO₂/O₂ permeability ratios have been calculated by the authors.

both films to O₂ and CO₂. This model was adequate to design a package to maintain a desired equilibrium atmosphere, but it did not address the processes involved in achieving the equilibrium. Massignan¹¹³ developed a steady-state model to predict package O₂ and CO₂ concentrations for eggplant using an empirically derived linear regression equation to estimate respiration under any set of gas concentrations. The model accurately predicted equilibrium gas concentrations for eggplant wrapped in three films.

All of the above models assume postclimacteric or nonclimacteric fruit, equilibrium conditions, and an RQ equal to one. These assumptions have come under question and later attempts at modeling have addressed some of these issues. Marcellin^{114,115} used estimates of RQ and gas partial pressures to calculate the sizes, thicknesses, and permeabilities of polyethylene bags suitable for wrapping various fruits and vegetables. He extended his model to describe a polyethylene package that contained a silicone rubber window to increase gas permeability. This model assumed equilibrium conditions. Henig and Gilbert¹¹⁶ assumed a variable RQ and transient gas concentrations and used first-order differential equations with numerical solutions to optimize package parameters. However, they assumed that the environmental O₂ concentration had a negligible influence on the rate of CO₂ evolution and that environmental CO₂ had a negligible effect on the rate of O₂ consumption. Available data^{117,118} call these assumptions into question. After examination of available respiration rate data, Hayakawa et al.¹¹⁹ modified this model to reflect the effects of both O₂ and CO₂ concentrations on O₂ consumption and CO₂ evolution. The model of Deily and Rizvi¹²⁰

^b MVTR = moisture vapor transmission rate expressed as ml/day/m²/mil.

Data from Reference 99.

d Data from Reference 98.

assumes that changing O_2 concentrations between 21 and 5% and CO_2 concentrations between 0 and 25% are not reflected in changes in respiration rate. This is an empirical assumption based on their own data for fresh peaches, but it is not clear under what conditions the data were generated. Nevertheless, this empirically derived model was adequate to predict transient and equilibrium gas concentrations for peaches in polymeric packages. Later refinements of this model were based on mass balance of permeating gases with variable produce respiration rates. The resulting model predicted the effects of package headspace, polymer permeability, and product characteristics on internal gas concentrations. ¹²¹ This model was then applied to an apple-packaging system and accurately predicted the time necessary to achieve equilibrium. ¹²²

Most attempts to model the changes in package atmosphere recognize the interaction of respiration by the packaged commodity and the diffusion of respiratory gases through the package. There is general agreement that there is an equilibrium at which O2 is being consumed at the same rate at which it is entering the package and CO2 is being produced at the same rate at which it is exiting the package. Here the agreement ends. It is not clear from the existing literature to what degree the O2 concentration affects the rate of CO3 evolution, or if CO2 concentration affects the rate of O2 consumption. At least part of the problem is methodological. Carbon dioxide evolution is difficult to measure accurately against a high background level of CO₂ (as occurs in MAP) using current technology such as the infrared gas analyzer. Small changes in O2 concentration due to respiratory activity are equally difficult to measure precisely. Paramagnetic, 123 electrochemical (usually based on zirconium oxide galvanic cells), 124 manometric, 125 and polarographic O₂ analyzers 126 may have the necessary sensitivity to measure small changes in O2 against high background levels but they are very sensitive to temperature, pressure, or both and thus are slow and difficult to calibrate and operate. The difficulty of simultaneously and accurately measuring small changes in both O2 and CO2 against high background levels has forced most workers to simply assume an RQ of one and measure either O2 depletion or CO2 production depending on which is at the lowest background level and what instrumentation is available. An RQ equal to one, however, is not the case under some conditions. Even in air, the RQ value for different commodities can be as low as 0.7 or as high as 1.3. 125,127 The condensation of pyruvic acid with CO2 to form oxaloacetic acid results in an RQ value of less than one. When organic acids, in addition to glucose, are being oxidized, the RQ value will be greater than one. 128 When lipids are metabolized, the RQ will be less than one. 127 The RQ may be affected by ambient gas concentrations themselves. That is, as O2 and CO2 concentrations are changing in a package, the ratio of CO2 produced to O2 consumed may itself be changing. 118,129 Henig and Gilbert16 used regression analysis of gas concentration changes for tomatoes in PVC film packages to calculate O2 consumption and CO2 evolution rates under different O2 and CO2 concentrations. They found that RQ values remained constant at about 0.9 in the range 0 to 9% CO₂, then a drop to 0.4 was observed with a later increase to 1.4 as CO₂ concentration increased. This could considerably complicate any effort to model the atmospheric changes taking place within a package, but changes in RO must be accounted for in any generally applicable model. A dearth of germane data makes it impossible to quantitatively address this issue at this time.

The basis of MAP is that a reduced O_2 environment suppresses respiration by the commodity, thereby slowing vital processes and prolonging the maintenance of postharvest quality. A secondary, but potentially important, factor is a concomitant decrease in respiration in response to elevated CO_2 . The degree to which decreased O_2 suppresses respiration is crucial to any attempt to model changes within a film package. Often, a small decrease in O_2 concentration below ambient air has little or no effect on respiration rate. It is not until O_2 falls to 12% or lower that a pronounced decrease in respiration is observed. 116.128 As O_2 concentration falls below 1 to 4%, depending on the commodity, anaerobic respiration begins

to occur, resulting in a reduction in product quality. Therefore, reduced O₂ has a beneficial effect only within a specific range of concentrations, and this range varies with the commodity and even among cultivars of the same commodity (Table 1). There is a great deal of information available for many different commodities, and the effect of reducing O₂ on respiration rate has been successfully incorporated into several models, often through the use of regression equations to simulate changes in respiration over a region of linear changes. ^{116,119,120,130} The possible suppression of respiration by increasing CO₂ has been less well documented. In some cases, such as for bananas, elevated CO₂ may play no role in reducing respiration. ¹²³ Others present evidence that accumulating CO₂ can reduce respiration rates in a variety of commodities. ^{86,111,112,116-119,123,131} Reduced O₂ and elevated CO₂ may act additively to lower the respiration rate below that achieved by modification of either gas concentration alone. ^{118,127} However, few models to date have explicitly incorporated the effect of CO₂ on respiration. This oversight should be rectified but awaits more data on specific elevated CO₂ concentrations combined with reduced O₂ in order to quantitatively combine both O₂ and CO₂ effects on respiration.

B. Flexible Plastic Films for Modified Atmosphere Packaging

The number and types of flexible plastic films available for packaging have proliferated in recent years and new types are constantly under development. These films display a wide range of characteristics in terms of gas permeability, water vapor transmission rates, antifogging properties, strength, and stretch-shrink properties41 (Table 6). It is not possible to describe or even to list all of the flexible plastic films available. Such information is available from a variety of sources. 132 Table 6 presents gas permeability and water vapor transmission properties for a number of plastic polymers currently available for use in the fabrication of flexible plastic films. Because permeability measurements are presented in many different forms, Table 6 presents all figures from the literature converted to units of milliliters per mil per square meter per day at 1 atm. In addition, ratios of CO, to O, permeabilities have been calculated and are presented. The ranges of permeabilities presented for some films are quite broad, reflecting high variability in the measurement of film permeabilities, differing conditions during permeability measurements and variations in fabrication among manufacturers, and even among batches from the same manufacturer, of similar film types. 133.134 In addition, gas permeability is sensitive to changes in temperature and relative humidity. 135 Some of the factors governing the transport of O2 and water vapor through polymeric films have been included in several models of film transport phenomena. 136 As an extreme example, wet cellulose may be thousands of times more permeable to O2 than dry cellulose. 134

Relatively few kinds of polymers are routinely used in the fabrication of flexible films for packaging of fresh produce, with the most important being PVC, polystyrene, polyethylene, and polypropylene. One of the earliest films to be used was a polymer of rubber hydrochloride sold under the name "Pliofilm". This film was quite strong, was an excellent moisture barrier, and could be heat sealed. Is It was also relatively impermeable to gases and could not be used without adequate ventilation. Pliofilm is no longer used and was never suitable for the creation of an MA within a package.

The polyolefins are the predominant plastics used for packaging.¹⁴¹ This group includes polyethylene, polypropylene, and polybutylene as well as their copolymers. Also included are the ionomers, which include sodium or zinc ions to provide cross-linking.¹⁴¹ In general, the polyolefin films are typified by their good water vapor barrier properties, their relatively high gas permeabilities, and their favorable response to heat sealing. Several types of polyethylene films are available and are among those most commonly used in packaging of fresh produce. Polyethylene is generally described as having high, medium, or low density (specific gravity = 0.941 to 0.965, 0.926 to 0.940, 0.910 to 0.925, respectively), which can also be used to describe their water barrier properties. Although not of great tensile

strength, polyethylene displays excellent tear strength, ¹⁴² high resistance to chemical degradation, ¹⁴³ and relatively high gas permeabilities (Table 6). What is of particular importance for MAP is that polyethylene, particularly low-density polyethylene, tends to have a high ratio of CO₂ to O₂ permeability (Table 6). This is of importance in allowing O₂ concentrations to decrease without an associated excessive buildup of CO₂ inside the package. A number of formulations of PVC are also available as flexible films. PVC films typically have moderate levels of water vapor permeability and they can be soft, clear, nonfogging, and durable ^{138,139} (Table 6). Some PVC films can have very high CO₂/O₂ permeability ratios as well, making them well suited for MAP. Some of these films are already in use for overwrapping trays of fresh produce ¹³⁹ and are widely used as shrink film on fresh produce. ¹³⁸

Polystyrene is another polymer with high gas transmission rates and a relatively high CO_2/O_2 permeability ratio. Polystyrene has been used extensively to wrap lettuce and tomatoes and is available as a heat-shrink film. ¹⁴⁴ It is relatively chemically inert and has a high degree of clarity. ¹⁴³

Several polymers are available that may have good strength properties and proper gas permeability ratios for MAP, but their absolute gas transmission rates are too low for them to be suitable for this use. These would include nylon, mylar, polyester, and several variants of polyvinyl (Table 6).

Recent advances in coextrusion technology have made it possible to manufacture materials with designed transmission rates for O₂. ¹⁰⁸ Coextrusion combines several resins in a single step to produce a multilayered polymer. Oxygen transmission rates from 0.1 to 20,000 ml/mil/m²/day at 22°C are available commercially in coextruded films. ¹⁰⁸ The coextruded films found to be most applicable to packaging of fresh produce are those made from blends of low- and medium-density polyethylene with ethyl vinyl acetate. ¹⁰⁸ Orientation of some polymers results in shrinkage of films when heat is applied. ¹³⁷ Biaxial orientation results in shrinkage in both directions. Gas- and moisture-vapor-transmission rates for amorphous polymers are generally not affected by the orientation process, but gas transmission may be reduced 10 to 50% by orientation of crystallizable polymers. ¹³⁷ Moisture vapor permeability may be reduced by orientation of crystalline polymers, particularly at low degrees of crystallization. ¹³⁷ Most of the polyolefin films can be oriented to allow heat shrinkage. Heatshrink films could be of use in MAP because the headspace around the produce can be greatly reduced after the film has been shrunk to fit. This would then result in a more rapid modification of the internal atmosphere.

C. Critical Elements of a Package Model

A model of maximum utility ought to be able to predict the equilibrium atmosphere resulting within a package given the commodity mass and respiration rate and the film size and permeabilities to O₂ and CO₂. It also ought to be able to predict atmospheric changes over time and estimate how long it would take for equilibrium to be established. In order to do so, the model must take into account commodity size and gas-diffusion resistance and the volume of headspace within the package. To work with any fruit or vegetable, the model must be able to assess the following variables:

- 1. The dependence of respiration on O₂ concentration.
- The dependence of respiration on CO₂ concentration. Carbon dioxide may not have the same effect on respiration for all commodities and the model user must have some empirical information with which to guide the model.
- The limiting conditions for each commodity, i.e., minimum concentration of O₂ before injury occurs due to fermentation and the maximum concentration of CO₂ before injury occurs.
- The permeabilities of the plastic films of interest and dependence of permeability on temperature and relative humidity.

- The diffusion resistance of the commodity to O₂, CO₂, and C₂H₄.
- The RQ for a given commodity and any changes in RQ as the atmospheric composition changes.
- 7. The optimal atmosphere for storage of a given commodity.

A model incorporating these parameters and empirical imputs ought to be able to predict equilibrium gas concentrations within a given package as well as how long it will take to establish the equilibrium. Furthermore, such a model would also predict the properties of an optimum film for packaging a given commodity, thereby eliminating a great deal of trial-and-error package-development work. To date, no model of MAP has incorporated all of these factors. For this reason, each model is limited in its utility. It ought to be possible to construct a more generally useful model based on these principles and such a model is being pursued in a number of laboratories around the world.

D. Examples of MAP of Selected Commodities

Many workers have tested MAP with a wide variety of fresh produce. The early work of Tolle¹¹⁰ with apples demonstrated the feasibility of MAP even with the limited packaging materials available at the time. Marcellin^{114,115} put silicone rubber windows in polyethylene bags to increase gas permeability and tested such packages for the storage of artichokes, carrots, turnips, and bell peppers but found that moisture condensation led to decay problems which negated any salutary effects of the MA.

Since apples are known to benefit greatly from CA storage, much early work was devoted to MAP systems for apples. Most workers used polyethylene or polyethylene terephthalate as the packaging materials and studied the effects of package surface area and volume, 111,112 temperature, 145,146 film permeability, 112,145,146 pinholes in the film, 147 and relative humidity 145 on package gas concentrations and/or various quality parameters. Other workers 148 studied the effect of harvest date of apples on subsequent MAP. They found that later-harvested apples developed higher CO₂ and lower O₂ concentrations within the package, apparently due to their higher respiration rates. 148 Only one of these investigations took a conceptual approach when the authors used their own preliminary results to calculate optimum package parameters in subsequent experiments. 112 Much of the other work suffers from being overly empirical in its approach and from the lack of standardization in experimental systems among different investigators.

Citrus has been shipped in plastic packages, although the greatest benefit may be not from modification of O₂ and CO₂ concentrations as from maintenance of high relative humidity, thereby reducing shrinkage. Wrapping citrus in polyethylene films also reduced low O₂ damage to fruit by excluding decaying fruit which respire rapidly and consume more O₂. However, in general, citrus fruits do not respond well to MA^{16,100} so packaging of citrus fruits is not designed to create such atmospheres.

Results with wrapping tomatoes in plastic films have been variable, ¹⁵² perhaps in part because the respiration rate of tomatoes can vary greatly depending on variety, maturity, and the onset of climacteric respiration. ¹¹⁸ Most workers have used polyethylene ¹⁵²⁻¹⁵⁶ or PVC^{37,90,152} films to extend tomato shelf life up to 21 d, although other films have also been tested. ^{90,154,157} Persistent problems with development of adverse flavors or decay have been reported in tomato packages. ⁹⁰ Nevertheless, several types of MAP for tomatoes have been patented. ^{158,159} Geeson et al. ⁹⁰ found that off-flavors and decay developed in films with low gas permeabilities but that such problems did not occur when permeabilities were high enough to allow adequate gas exchange. The value of MAP for tomatoes is not likely to be fully realized until researchers conduct experiments where they assay package gas concentrations and relate them to quality parameters at given temperatures.

Deily and Rizvi¹²⁰ used a model to optimize packaging parameters for peaches in order

to design a retail-size package. Their approach was to calculate the film permeabilities necessary in order to achieve a predetermined package atmosphere based on peach respiration values. They determined respiration rates and resulting package atmospheres experimentally to verify the assumptions behind their calculations. They then measured some of the quality attributes of the packaged and control peaches after various storage durations. Their analytical, integrated approach to MAP could serve as a good example for other workers for developing packages for other types of fresh produce. Other workers have packaged peaches in different films¹⁶⁰ and at various temperatures^{160,161} and have concluded that peaches respond well to MAP. Because of the long distances and time involved in the shipping of tropical fruits to temperate markets, it would be of particular benefit to be able to use MAP to maintain quality and to avoid repackaging at the destination. Some work has focused on the use of MA with tropical fruits. Bananas respond well to MA162.163 and several attempts to devise commercial packages have been encouraging. 162 The benefits to bananas of MA are apparently due to reduced C₂H₄ sensitivity associated with high CO₂ and low O₂. ¹⁶³ Packaging of mangos has met with less success since MA have often been reported to result in the development of off-flavors. 164-166 After being wrapped in various films and stored at appropriate temperatures, the postharvest life of rambutan was extended by 9 d, of carambola by at least 3 weeks, and of sapodilla by up to 3 weeks compared with unwrapped controls. 167

A number of other fruits have been wrapped in films with some success. MAP of avocados greatly reduced their chilling injury at temperatures between 4 and 7.5°C. 131,168 Total storage life of avocados can also be extended through MAP. 169 Wrapping strawberries in sealed PVC film resulted in a considerable improvement in the keeping quality as measured by fruit firmness, weight loss, drying of the calyx, and incidence of Botrytis decay. 170 Strawberries are relatively tolerant of high CO2 which can reduce Botrytis decay during storage, 170-172 and high CO2 atmospheres are used commercially to reduce decay and maintain quality during shipping. 102 Good quality cherries, which are rapidly cooled and humidified, also respond well to elevated (up to 20%) CO₂ levels. 173 High CO₂ atmospheres are created commercially using polyethylene liners within shipping containers. These liners have been shown to reduce water loss and preserve glossiness in cherries. 174 Storing persimmons in high CO₂ conditions results in a reduction in astringency, 175,176 apparently through the resulting production of acetaldehyde and its subsequent polymerization of tannins.¹⁷⁷ Sealing persimmons in polyethylene bags flushed with 100% CO2 resulted in less astringency and less development of ethanol and resulting off-flavors than storage under vacuum or in 100% nitrogen.176

Several vegetables benefit from MAP. Both high CO_2 (5 to 20%) and low O_2 (down to 1%) concentrations retard respiration and senescence of broccoli heads. The Increasing CO_2 seems to be more effective than decreasing O_2 . Broccoli maintained its quality longer in both perforated and sealed polyethylene packages at three temperatures than did nonpackaged controls. The Increasing PVC films with proper gas permeabilities could serve to generate an appropriate equilibrium atmosphere to retard spoilage.

Because of the large surface area of peppers, they are particularly susceptible to water loss and thus are good candidates for film packaging. ¹⁸¹ The results of several studies indicate that packaging with plastic films can extend the postharvest life of peppers but the major benefits appear to be mediated by the maintenance of high relative humidity and not by modification of the atmosphere. ¹⁸¹⁻¹⁸⁴ Shrink wrapping of corn resulted in atmospheric modification that was associated with a threefold increase in postharvest life. ¹⁸⁵ This was attributed in part to atmospheric modification and in part to moisture retention. Seal packing of mushrooms in PVC films was generally associated with reduced respiration and reduced internal browning and, consequently, higher quality. Results varied according to film permeability and number of perforation holes. ^{186,187}

Storage of tulip bulbs in 3 to 5% O_2 increases the time that tulip bulbs can be held at ambient temperatures before planting. MAP was shown to develop and maintain proper atmospheres around tulip bulbs at 20°C with resulting increased quality during storage. Is Fluctuations in temperature did not result in detrimental package atmospheres, probably due to changes in film permeability compensating for changes in respiration rate. Is

E. Future Research Needs

After 25 years of work on MAP of produce, many examples of packaging attempts are available. Nearly all such attempts can be characterized by their narrowness of purpose, namely, to find an appropriate package for a particular commodity. The discipline would benefit from a more comprehensive research approach where studies are based on a rational understanding of principles and processes and where packaging attempts grow logically from a conceptual model of MA. A thorough understanding of the interactions of temperature, O₂ and CO₂ concentrations, film permeabilities, and commodity diffusion resistance, and their effects on quality parameters would lead to a more rational selection of packaging materials and obviate the need for hit-and-miss attempts at packaging that take into account only a few of the salient variables. Before such work can be completed, it will be necessary to generate additional information on several topics, including

- Most data on film permeability are generated at a single temperature and often at very low relative humidity. The responses of film permeability to temperatures between 0 and 20°C and to relative humidities between 85 and 95% must be determined.
- More information on the respiration rates of fresh commodities in MA must also be generated. For many commodities, respiration rates in air and in a single CA are available, but for very few is information available in several CA or MA conditions.
- The additive effects of reduced O₂ and increased CO₂ on respiration and C₂H₄ production merit further investigation to establish some general relationships.
- 4. There is evidence for some fruits and vegetables that exposure to a given atmosphere can affect their respiration and C₂H₄ production rates when subsequently transferred to air or another MA condition. Since MAP will expose a commodity to a continuum of changing atmospheres until equilibrium is achieved, more information is needed on how this residual effect of MA modifies the predicted behavior from steady-state experiments.
- Changes in RQ in response to changing atmospheres could have a great effect on evolving atmospheres inside packages and so should be studied further.
- Additional information is needed on the resistance of fruits and vegetables to diffusion of O₂, CO₂, and C₂H₄ under different atmospheric and temperature conditions.

The advent of new films and manufacturing methods makes possible the production of thinner, more uniform films of greater strength and a greater range of gas permeabilities than ever before. MAP may now be a viable alternative to expensive CA storage facilities and transport vehicles for some commodities and marketing channels. Because it is of the utmost importance that temperature be reduced and atmosphere established as rapidly as possible, it is likely that the future of MAP will include introduction of a desired gas mixture into the package and the subsequent maintenance of the atmosphere by the gas-exchange properties of the film. Such active modification of the package atmosphere may be supplemented through the use of O_2 , CO_2 , and/or C_2H_4 absorbers. Comparisons of the cost/benefit analysis of active vs. passive atmospheric modification are needed for a range of commodities with various degrees of perishability.

However, if MAP of fresh produce is used in the future, it will not be a substitute for adequate temperature management. Even though it may ultimately be possible to manufacture

films that change their gas permeability characteristics in response to temperature changes, thus compensating for concomitant changes in product respiration, the maintenance of quality requires careful handling, avoidance of injury, and good temperature management. Given these caveats, MAP can be a useful supplement in the effort to maintain good quality (appearance, texture, flavor, and nutritive value) of fresh produce throughout the marketing chain.

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