This is to certify that the

thesis entitled

Modified-Atmosphere Packaging of Raspberry and Strawberry Fruit: Characterizing the Respiratory Response to Reduced O_2, Elevated CO_2, and Changes in Temperature

presented by

Dennis W. Joles

has been accepted towards fulfillment of the requirements for

M.S. degree in Horticulture

Arthur C Cameron
Major professor

Date 11/18/93

MODIFIED-ATMOSPHERE PACKAGING OF RASPBERRY AND STRAWBERRY FRUIT: CHARACTERIZING THE RESPIRATORY RESPONSE TO REDUCED O_2, ELEVATED CO_2, AND CHANGES IN TEMPERATURE

By

Dennis W. Joles

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Horticulture

1993

ABSTRACT

MODIFIED-ATMOSPHERE PACKAGING OF RASPBERRY AND STRAWBERRY FRUIT: CHARACTERIZING THE RESPIRATORY RESPONSE TO REDUCED O_2, ELEVATED CO_2, AND CHANGES IN TEMPERATURE

By

Dennis W. Joles

Modified-atmosphere (MA) packaging has the potential to provide suitable atmospheres to extend the storage life of raspberry and strawberry fruit. To design an effective MA package for raspberry or strawberry the fruit's respiratory response to reduced O_2, elevated CO_2, and temperature should be known. Therefore, experiments were conducted to determine O_2 uptake, CO_2 production, and ethanol content of raspberry and strawberry fruit over a range of O_2 levels, CO_2 levels and temperatures. The lower O_2 limit for aerobic respiration was identified from a breakpoint in the fruit's respiratory quotient (RQ) and ethanol content. Mathematical models were developed to characterize the O_2 uptake and RQ of these fruit. These models and the lower O_2 limit data were used to describe the effect of a change in temperature on package O_2 and CO_2 levels. A system that responds to package ethanol vapor was developed for sensing the induction of anaerobic respiration.

To mom

ACKNOWLEDGMENTS

I would like to thank Dr. Arthur Cameron for giving me the support, guidance and opportunities to learn and improve myself.

I would like to thank Dr. Eric Grulke and, especially, Dr. Randy Beaudry for their advice and assistance during the course of my research.

Thank you also, Dr. Ahmad Shirazi, Dr. Pete Petracek, Dr. P. Chowdary Talasila, Russell Stacy-Ryan, Mark Yelanich, Jane Waldron, and all the basement crew for your help and your time.

Thank you Grandpa for teaching me to work hard and for beginning my interest in horticulture.

Most of all, thank you Jane for your understanding, cooperation, and love.

TABLE OF CONTENTS

CHAPTER 1

MODIFIED-ATMOSPHERE PACKAGING OF 'HERITAGE' RED RASPBERRY 1
Abstract 2
Introduction 4
Materials and Methods 7
Results 13
Discussion 15
List of References 19

CHAPTER 2

MODIFIED-ATMOSPHERE PACKAGING OF STRAWBERRY FRUIT: CHARACTERIZING RESPIRATION AS A FUNCTION OF O_2 AND TEMPERATURE 44
Abstract 45
Introduction 47
Materials and Methods 50
Results 57
Discussion 60
List of References 64

CHAPTER 3

MODIFIED-ATMOSPHERE PACKAGING OF STRAWBERRY AND RASPBERRY FRUIT: MODELING PACKAGE O_2 AND CO_2 OVER A RANGE OF TEMPERATURES 89
Abstract 90
Introduction 91
Model Development 94
Materials and Methods 98
Results and Discussion 98
List of References 106

LIST OF TABLES

Table Page

CHAPTER 1

Table 1. Activation energies (E_a), Arrhenius constants (A_r), and correlation coefficients (r^2) for .00521 and .00766 LDPE film. Values were obtained from linear transformations of the equation: $P = A_r \cdot \exp(-E_a/R \cdot T)$ where P is permeability to O_2 or CO_2 ($mmole \cdot cm \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$); E_a is the energy of activation of O_2 or CO_2 permeation ($kJ \cdot mol^{-1}$); and R is the gas constant (.0083144 $kJ \cdot mol^{-1} \cdot K^{-1}$) (Pauly, 1989). 22

Table 2. Whole package O_2 and CO_2 permeabilities ($P_{O_2} \cdot A/\Delta x$ and $P_{CO_2} \cdot A/\Delta x$, respectively) for the packages used in these experiments at 0, 10 and 20C. Appropriate values were substituted into Eqs. [2] and [3] to calculate O_2 uptake and CO_2 production for fruit at 0, 10, or 20C. 23

Table 3. Constants for Michaelis-Menten (Eq [6]) equation describing the relationship between O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for raspberry fruit sealed in LDPE pouches and stored at various temperatures. The constants of the Michaelis-Menten equation were estimated by non-linear regression analysis. 24

Table 4. Estimated values for Eq. [7], describing the relationship between calculated RQ, steady-state O_2 partial pressure (kPa) and temperature for September-harvested raspberry fruit stored at 0, 10, and 20C. 25

CHAPTER 2

Table 1. Target O_2 partial pressures and the corresponding package dimensions and fruit weights calculated to obtain these partial pressures. The appropriate package dimensions and fruit weights were calculated using Eq. 1 combined with preliminary strawberry O_2 uptake data. The target weights correspond respectively with each target O_2. 66

Table Page

Table 2. Constants for Eq. 9 describing the relationship between O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for 'Honeoye' and 'Allstar' strawberry fruit (Eq. [9]) and shown in Figures 5 and 6. $R_{O2}^{max,0}$ is the maximum rate of O_2 uptake at 0C, Q_{10} is the increase in O_2 uptake for a 10C increase in temperature, $k_{½}$ is the O_2 partial pressure at which the rate of O_2 uptake is half the maximum rate, and P_{O2}^{skin} is a value describing the of the fruit's skin to O_2. These constants were estimated by non-linear regression analysis using SAS. 67

Table 3. Estimated constants for Eq. [10], describing the relationship between calculated RQ, steady-state O_2 partial pressure (kPa) and temperature for 'Honeoye' and 'Allstar' strawberry fruit. The t coefficient in this models is an estimate of aerobic RQ. 68

CHAPTER 3

Table 1. Constants describing the relationship between O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for 'Allstar' strawberry fruit (estimated in Chapter 2). $R_{O2}^{max,0}$ is the maximum rate of O_2 uptake at 0C, Q_{10} is the increase in O_2 uptake for a 10C increase in temperature, $k_{½}$ is the internal O_2 partial pressure at which the rate of O_2 uptake is half the maximum rate, and P_{O2}^{skin} is a value describing the of the fruit's skin to O_2. 104

Table 2. Constants describing the relationship between O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for 'Heritage' raspberry (estimated in Chapter 1). $K_{½}$ is the external (package O_2) O_2 partial pressure at which the rate of O_2 uptake is half the maximum rate. 105

LIST OF FIGURES

Figure Page

CHAPTER 1

Fig. 1. Effect of raspberry fruit weight on steady-state O_2 (circles) and CO_2 (triangles) partial pressures for September (open symbols) and October-harvested (closed symbols) raspberry fruit sealed in LDPE packages where A= 300 cm^2, Δx = .00521 cm for packages at 10 and 20C, and A = 300 cm^2, Δx = .00766 cm for packages stored at 0C. . . 26

Fig. 2. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of O_2 uptake for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages. See Eq. [6] and Table 3 for the equations and constants describing the curves. . . 28

Fig. 3. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of CO_2 production for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages. 29

Fig. 4. Effect of steady-state O_2 partial pressure and storage temperature on the respiratory quotient of September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages. See Eq. [7] and Table 4 for the equations and constants describing the curves. 33

Fig. 5. Interdependent effects of steady-state O_2 partial pressure and storage temperature on headspace ethanol vapor concentration for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages. 34

Fig. 6. Relationship of headspace ethanol vapor concentration and the respiratory quotient measured for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages and stored at 0, 10, and 20C. 35

Fig. 7. Effect of raspberry fruit weight on steady-state O_2 and CO_2 partial pressures in sealed packages with (○) and without CaO(▿) where A = 400 cm^2, Δx = .00521 cm LDPE and held at 20C. 37

Figure Page

Fig. 8. Effect of steady-state O_2 partial pressures on the rate of O_2 uptake for raspberry fruit sealed packages with (○) and without (▿) CaO and matched with a Michaelis-Menten equation. 39
Fig. 9. Effect of steady-state O_2 partial pressures on headspace ethanol vapor concentration for raspberry fruit sealed in packages with (○) and without (▿) CaO. 41

CHAPTER 2

Fig. 1. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state O_2 for 'Honeoye' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C. 69
Fig. 2. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state O_2 for 'Allstar' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C. 70
Fig. 3. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state CO_2 for 'Honeoye' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C. 72
Fig. 4. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state CO_2 for 'Allstar' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C. 74
Fig. 5. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of O_2 uptake for 'Honeoye' strawberry fruit sealed in LDPE packages. See Eq. [9] and Table 2 for the equations and constants describing the curves. 76
Fig. 6. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of O_2 uptake for 'Allstar' strawberry fruit sealed in LDPE packages. See Eq. [9] and Table 2 for the equations and constants describing the curves. 78

Figure Page

Fig. 7. Effect of steady-state O_2 partial pressure and storage temperature on the respiratory quotient of 'Honeoye' strawberry fruit sealed in LDPE packages. See Eq. [10] and Table 3 for the equations and constants describing the curves. . . 80

Fig. 8. Effect of steady-state O_2 partial pressure and storage temperature on the respiratory quotient of 'Allstar' strawberry fruit sealed in LDPE packages. See Eq. [10] and Table 3 for the equations and constants describing the curves. . . 82

Fig. 9. Interdependent effects of steady-state O_2 partial pressure and storage temperature on headspace ethanol vapor concentration for 'Honeoye' strawberry fruit sealed in LDPE packages. 84

Fig. 10. Interdependent effects of steady-state O_2 partial pressure and storage temperature on headspace ethanol vapor concentration for 'Allstar' strawberry fruit sealed in LDPE packages. 86

CHAPTER 3

Fig. 1. Predicted changes in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ as a function of temperature and film permeability characteristics for 'Allstar' strawberry fruit from Eq. [3] and Eq. [8] with constants from Table 1 and Chapter 2. The dotted line on each graph represents the lower O_2 limit for 'Allstar' strawberry fruit as determined by the increase in RQ and ethanol content (Chapter 2). 108

Fig. 2. Predicted changes in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ as a function of temperature and film permeability characteristics for 'Heritage' raspberry fruit from Eq. [3] and Eq. [8] with constants from constants Table 2 and Chapter 1. The dotted line on each graph represents the lower O_2 limit for 'Heritage' raspberry fruit as determined by the increase in RQ and ethanol content (Chapter 1). 109

Figure | Page

Fig. 3. Predicted changes in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ as a function of temperature and film permeability characteristics for 'Heritage' raspberry fruit and 'Allstar' strawberry fruit from Eq. [3] and Eq. [8] with the film permeability characteristic being a E_a of 37 and a permeability ratio of 1.0. 111

Fig. 4. The change in absorbance at 460 nm over time for a ethanol sensing film at 25C exposed to a ethanol vapor partial pressure of .006 kPa and to H_2O vapor. 113

CHAPTER 1

MODIFIED-ATMOSPHERE PACKAGING OF 'HERITAGE' RED RASPBERRY FRUIT: THE RESPIRATORY RESPONSE TO REDUCED OXYGEN, ENHANCED CARBON DIOXIDE AND TEMPERATURE

Abstract. Raspberry (Rubus idaeus L. 'Heritage') fruit were sealed in low density polyethylene packages and stored at 0, 10, and 20C during the Fall of 1990 and 1991. A range of steady-state O_2 and CO_2 partial pressures were achieved by varying fruit weight in packages of a specific surface area and film thickness. Film permeability to O_2 and CO_2 was measured and combined with surface area and film thickness to estimate total package permeability. Rates of O_2 uptake, CO_2 production and RQ were calculated using steady-state O_2 and CO_2 partial pressures, total package permeability, and fruit weight. The rate of O_2 uptake was found to decrease with a decrease in O_2 partial pressure over the range of partial pressure studied. A model was developed for the rate of O_2 uptake as a function of O_2 partial pressure and temperature, using the Michaelis-Menten equation with V_{max} changing exponentially with temperature. Estimated V_{max} values approximately doubled with each 10C increase in temperature and the apparent K_m ($K_{1/2}$) was estimated to be 5.59 kPa O_2 for fruit at 0, 10, and 20C. RQ as a function of O_2 partial pressure and temperature was fitted with an exponential equation. Combining the RQ equation with the Michaelis-Menten equation allows CO_2 production to be predicted over temperature and the range of O_2 partial pressures generated. We found that headspace ethanol increased at RQs above 1.3 to 1.5. Based on RQ, ethanol

production, and taste, we recommend that raspberries be held at O_2 levels above 4 kPa at 0C, 6 kPa at 10C, and 8 kPa at 20C. Steady-state CO_2 partial pressures of 3 to 17 kPa generated after 3 days at 20C had little or no effect on O_2 uptake and headspace ethanol concentrations.

Introduction

Raspberries are a very perishable commodity, in part due to high rates of respiration and transpiration, a morphology that predisposes them to crushing, and susceptibility to gray mold fruit rot. Techniques providing even a relatively short extension of shelf life could have a profound effect on fresh-marketing of raspberry fruit. Exposure to CO_2 levels of 20% or greater has been shown to delay gray mold decay of raspberries and extend shelf life (Goulart et al., 1992; Smith, 1958; Winter et al., 1939). Elevated CO_2 has also been shown to improve firmness of strawberry fruit (Smith, 1992). No research has yet demonstrated a beneficial effect of reduced oxygen for raspberries.

Modified-atmosphere (MA) packaging has the potential to provide suitable atmospheres to extend shelf life of raspberry fruit. In an MA package, steady-state package partial pressures of O_2 ($[O_2]_{pkg}$) and CO_2 ($[CO_2]_{pkg}$) are achieved when the rates of O_2 uptake and CO_2 production by the fruit are equal to the rates of O_2 and CO_2 flux through the film (Beaudry et al., 1992; Cameron et al., 1989).

In MA packaging, $[CO_2]_{pkg}$ cannot be elevated without some reduction in $[O_2]_{pkg}$. The extent of the reduction in O_2 and elevation of CO_2 depends on the rates of O_2 uptake and CO_2 production of the fruit and the permeability of the polymer barrier to O_2 and CO_2. Thus, to design an MA package for raspberries with elevated $[CO_2]_{pkg}$, it is and elevation of CO_2 depends on the rates of O_2 uptake and CO_2 production of the fruit and the permeability of the polymer barrier to O_2 and CO_2. Thus, to design an MA package for raspberries with elevated $[CO_2]_{pkg}$, it is necessary to know the rates of CO_2 production and O_2 uptake as influenced by reduced O_2 and elevated CO_2 partial pressures.

Burton (1978) reported that raspberries stored in 2-3% O_2 developed off-flavors. When O_2 around fruits falls below some critical level, there is a shift from aerobic to anaerobic respiration, with associated ethanol production and eventually off-flavor development (Kader, 1986). The extent of anaerobic metabolism can be measured as an increase in the RQ, since ethanol production involves decarboxylation of pyruvate without uptake of O_2. Beaudry et al. (1992) found that the critical O_2 level for blueberries (defined as the partial pressure of O_2 where an increase in RQ was noted) increased with temperature. Thus, it is important to define a critical lower O_2 limit for raspberries over a range of possible storage temperatures.

Several authors have assumed that elevated $[CO_2]_{pkg}$ can effect the rate of O_2 uptake of fresh produce (Hayakawa et al., 1975; Henig and Gilbert, 1975; Lee et al., 1991; Song et al., 1992), although there is little direct supporting evidence to our knowledge. We addressed this question by generating a range of $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ levels using MA packages (Beaudry et al., 1992; Cameron, 1990) and adding CaO as a CO_2 absorber to a similar group of packages. Thus, it was possible to determine O_2 uptake as a function of $[O_2]_{pkg}$ in the presence and absence of generated CO_2.

The objectives of this study were to use the technique described by Beaudry et al. (1992) to investigate the influence of $[O_2]_{pkg}$, $[CO_2]_{pkg}$ and temperature on the rates of O_2 uptake and CO_2 production and on the O_2 partial pressure at the RQ breakpoint for 'Heritage' red raspberry fruit. Another objective of this study was to compare the respiratory behavior of fruits harvested at different times in the season.

Materials and Methods

Plant material

On 20 Sept. 1990, 15 Oct. 1990, and 9 Sept. 1991, fruit of 'Heritage' red raspberry were hand-harvested from Gibb's Farm in Onondaga, Mich., and spread three to four berries deep in coolers containing ice. A sheet of plastic film was placed over the ice to prevent direct contact. After transportation to Michigan State University, the fruit were sorted and packaged immediately.

Packaging

During Sept. 1990, fruit weights of approximately 5, 7.5, 10, 12.5, 15, 17.5, 22.5, 27.5, 37.5, and 50 g were sealed in packages made of low density polyethylene (LDPE) (Dow Chemical, Midland, Mich.) and placed in 0 and 10C. Fruit weights of approximately 5, 10, 12.5, 15, 17.5, 20, 22.5, 25, 30, 37.5, and 45 g were sealed into packages placed at 20C. For fruit at 10 and 20C, surface area was 300 cm^2 (10 x 15 cm) and film thickness was .00521 cm (2 mil.). For packages placed at 0C, film thickness was .00766 cm (3 mil.) with the same surface area.

In Oct. 1990, fruit weights of approximately 3, 5, 7.5, 10, 12.5, 17.5, 22.5, and 30 g were sealed into packages and placed in 10 and 20C. Surface area and thickness were the same as the September harvest. Five and six replications per target weight were used in the October and September experiments, respectively.

To avoid crushing of the fruit, a rigid support was placed inside each package consisting of a cellulose acetate strip (2.5 cm wide, 30 cm long and .0508 cm thick) and a 3-inch x 5-inch note card. The fruit rested on the note card and the cellulose acetate strip encircled the fruit. Every package had a gas sampling septum attached, consisting of a dab of Dupont Silicone II tub/tiling glue on a short strip of electrical tape (Boylan-Pett, 1986).

For the 1991 experiment, packages were constructed of 2-mil (.00521 cm) LDPE film with a surface area of 400 cm^2 (10 x 20 cm). Target weights were 5.5, 13.5, 18, 28, and 48 g with eight packages at each target weight. A 10 x 12 cm spunbonded polyethylene pouch (Tyvek type 1059B, Dupont, Wilmington, Del.) was constructed containing CaO (98%, Aldrich, Milwaukee, Wis.) as a CO_2 scrubber (1 g CaO per 10 g fruit). A pouch was included in half of the packages at each weight.

Film permeability

Film permeability was measured for three film samples taken from various locations in the 2-mil and 3-mil rolls, using the system described by Beaudry et al. (1992). Each sample was individually sealed in a permeability cell and submerged in a water bath. The permeability cell contained two chambers which were separated by the film sample. A gas mixture of O_2 and CO_2 was directed into one chamber and pure N_2 gas into the other (100 $ml \cdot min^{-1}$). The appearance of O_2 and CO_2 was continuously monitored in the N_2 stream, using a sequential arrangement of O_2 (Ametek S-3A/II with a calcia-zirconia electrochemical detection cell; Ametek Co., Thermox

Instrument Div., Pittsburgh) and CO_2 (ADC 225-Mk3 analytical infrared gas analyzer; Analytical Development Co., Hertfordshire, England) analyzers. By altering water bath temperature, permeabilities were measured at 5C intervals between 0 and 30C. Each film sample was measured over the entire temperature range three to five times.

The Arrhenius equation was used to describe permeation of gases through polymers and can be expressed as:

$$P_i = A_r \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \qquad [1]$$

where P_i is permeability to O_2 or CO_2 ($mmole \cdot cm \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$); E_a is the energy of activation of O_2 or CO_2 permeation ($kJ \cdot mol^{-1}$); and R is the gas constant (.0083144 $kJ \cdot mol^{-1} \cdot K^{-1}$) (Pauly, 1989). Regression analysis was performed on transformed data to estimate values of E_a, the Arrhenius constant A_r and correlation coefficients (Table 1). Appropriate E_a and A_r values were substituted into Eq. [1] to calculate $P_{O_2} \cdot A/\Delta x$ and $P_{CO_2} \cdot A/\Delta x$ at 0, 10, and 20C (Table 2).

Gas analysis and respiration rate calculations

Headspace O_2 and CO_2 partial pressures were determined by withdrawing two 0.5 ml samples from packages using an insulin-type syringe and injecting into a N_2 gas stream (150 to 200 $ml \cdot min^{-1}$ flow rate) which was connected to the sequential O_2 and CO_2 analyzers described above. Response time was 10 s per sample. To avoid sampling errors, a third sample was taken if any difference was noted between the first two samples.

Headspace ethanol concentrations were determined by withdrawing two 0.5-ml samples from the package headspace using a glass syringe (0.5 ml Gastight #1750; Hamilton Co., Reno, Nev.). Gas analysis was performed on a Carle Series 100 gas chromatograph (Hach Co., Loveland, Colo.) equipped with a Haysep 80/100 porous polymer column (Alltech Assoc. Inc., Deerfield, Ill.). Column temperature was 120C and the flow rate of the N_2 carrier gas was 100 $ml \cdot min^{-1}$.

Ethanol analysis of the 1990, September-harvested fruit at 20C showed a large amount variability between replicated packages. To reduce variability in future experiments, the time from sampling to analysis was minimized and needles were checked to ensure that they were not plugged with silicone from the sampling septum.

The time to reach steady-state O_2 and CO_2 levels was estimated by measuring $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ over time in separate packages containing the lowest and highest fruit weights for each storage temperature. When no further change in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ was detected in these packages, gas analysis was performed on all the packages at that temperature. Gas analysis was performed after 12 days at 0C, 7 days at 10C, and 3 days at 20C.

Respiration rates were calculated using the following formulae:

$$R_{O_2} = \frac{\frac{P_{O_2} \cdot A}{\Delta x} ([O_2]_{atm} - [O_2]_{pkg})}{W} \qquad [2]$$

$$R_{CO_2} = \frac{\frac{P_{CO_2} \cdot A}{\Delta x} \left([CO_2]_{pkg} - [CO_2]_{atm}\right)}{W} \qquad [3]$$

where R_{O_2} and R_{CO_2} are the rates of O_2 uptake and CO_2 production ($mmol \cdot kg^{-1} \cdot h^{-1}$), respectively; P_{O_2} and P_{CO_2} are permeability coefficients for O_2 and CO_2 ($mmol \cdot cm^{1} \cdot cm^{-2} hour^{-1} \cdot kPa^{-1}$), respectively; A is film area (cm^2); Δx is film thickness (cm); $[O_2]_{atm}$ and $[O_2]_{pkg}$ are atmospheric and package O_2 partial pressures (kPa), respectively; $[CO_2]_{pkg}$ and $[CO_2]_{atm}$ are package and atmospheric CO_2 partial pressures (kPa), respectively; and W is fruit weight (kg) (Beaudry et al., 1992). The relationship of O_2 uptake to $[O_2]_{pkg}$ and temperature was fitted using the Michaelis-Menten equation:

$$R_{O_2} = \frac{V_{max} \cdot [O_2]_{pkg}}{K_{½} + [O_2]_{pkg}} \qquad [4]$$

$K_{½}$ in this equation was substituted for the standard K_m notation because this estimate is an apparent K_m of the entire fruit which also takes into account skin resistance to gas diffusion.

V_{max} was modeled as a function of T:

$$V_{max} = R_{O_2}^{max,0} \cdot Q_{10}^{\frac{T}{10}} \qquad [5]$$

where $R_{O_2}^{max,0}$ is the maximum rate of O_2 uptake at 0C, Q_{10} is the increase in O_2 uptake for every 10C increase in temperature, and T is temperature in C. Substituting Eq. [5] into Eq. [4]

yielded:

$$R_{O_2} = \frac{(R_{O_2}^{max,0} \cdot Q_{10}^{\frac{T}{10}}) \cdot [O_2]_{pkg}}{K_{½} + [O_2]_{pkg}} \qquad [6]$$

A nonlinear regression analysis to estimate the values of $K_{½}$, a, and b was conducted on SAS (SAS Institute Inc., Cary, NC)

using the data set from the September-harvested fruit at 0, 10, and 20C. $K_{½}$ was originally modeled as a function of temperature but regression analysis revealed that it was constant over the temperatures studied.

The RQ was calculated as R_{CO_2} divided by R_{O_2}. The relationship between RQ, steady-state O_2, and temperature was fitted with the model:

$$RQ = \frac{q \cdot Exp(r \cdot T)}{[O_2]_{pkg}} + 1 \qquad [7]$$

Nonlinear regression analysis was conducted on SAS to estimate the values of q and r.

No postharvest fungicide treatments were used on these fruit. Data was not taken from packages with obvious holes or moldy fruit.

Results

Steady-state O_2, CO_2, and respiration rates

Increasing fruit weight in a package decreased steady-state O_2 and increased steady-state CO_2 at 0, 10, and 20C (Fig. 1). The choice of fruit weights resulted in a range in $[O_2]_{pkg}$ from under 1 to 10 kPa at 0C and 1 to 12 kPa at 10 and 20C. Steady-state $[CO_2]_{pkg}$ ranged from 1 to 8 kPa at 0C, 1 to 10 kPa at 10C, and 1 to 13 kPa at 20C.

$K_{½}$ was found to be 5.59 kPa O_2 at 0, 10, and 20C while V_{max} approximately doubled with each 10C increase in temperature (Table 3). A decrease in $[O_2]_{pkg}$ slowed R_{O_2} (Fig. 2) and R_{CO_2} (Fig. 3) at all temperatures. R_{CO_2} and R_{O_2} of the October-harvested fruit were consistently higher than the September-harvested fruit (Figs. 2 and 3), although the difference were not significant.

The RQ increased gradually as $[O_2]_{pkg}$ decreased from 10 to 6 kPa but climbed more rapidly at lower $[O_2]_{pkg}$ levels (Fig. 4). October-harvested fruit had a slightly higher RQ value at higher $[O_2]_{pkg}$ levels and showed a less definite increase in RQ at lower $[O_2]_{pkg}$ levels. Values for the model (Eq. [7]) describing the relationship of RQ with $[O_2]_{pkg}$ and temperature are presented in Table 4. R_{CO_2} as a function of $[O_2]_{pkg}$, at any of the temperatures and harvests studied, can be calculated by multiplying the equation for RQ (Eq. [7]) by the equation for O_2 uptake (Eq. [6]).

Headspace ethanol concentrations and RQ followed a similar trend with $[O_2]_{pkg}$ at 10 and 20C (Figs. 5 and 6). Headspace ethanol concentrations at 0C were low until $[O_2]_{pkg}$

dropped below ≈3 kPa and then increased sharply. For each harvest and temperature, headspace ethanol was relatively low at RQs below ≈1.3 and increased at RQs greater than 1.3 to 1.5 (Fig. 6). September-harvested fruit at 20C showed a high amount of variability in their headspace ethanol concentrations (Figs. 5 and 6) which may have been due in part to sampling errors (see Materials and Methods).

Packages with and without CaO

In packages containing CaO, $[CO_2]_{pkg}$ was 0.1 kPa or less, while in packages without CaO, $[CO_2]_{pkg}$ ranged from 3 to 17 kPa (Fig. 7). R_{O_2} values were similar for packages with and without CaO (Fig. 8). The $K_{½}$s (O_2 kPa) were 4.09 (SE=±.84) and 4.31 (SE= ±.60) for packages with and without CaO, respectively. V_{max} values (O_2 uptake $mmol \cdot kg^{-1} \cdot h^{-1}$) were 3.09 (SE=±.26) and 3.62 (SE=±.22) for packages with and without CaO, respectively. The 95% confidence intervals showed that these coefficients were not significantly different. Headspace ethanol vapor as a function of $[O_2]_{pkg}$ was similar for packages with and without CaO (Fig. 9).

Discussion

The effect of elevated CO_2 partial pressure on the respiratory rate of a fruit or vegetable is dependent on the commodity and level of CO_2 used (Kidd, 1916; Kubo et al., 1990; Mangin, 1896; Thornton, 1933). Some general models describing O_2 uptake of fresh produce in MA atmospheres have been based in part on the assumption that elevating CO_2 partial pressure to any level will inhibit O_2 uptake (Hayakawa et al., 1975; Henig and Gilbert., 1975; Lee et al., 1991; Song et al., 1992). Elevated CO_2 has been reported to reduce O_2 uptake in some climacteric fruit (Kerbel et al., 1988; Kubo et al., 1990; Young et al., 1962). For raspberries, there was no evidence that CO_2 partial pressures of 3 to 17 kPa altered the rate of O_2 uptake (Fig. 8). The rate of O_2 uptake by blueberries and grapes have been shown to be unaffected by CO_2 partial pressures up to 60 kPa (R.M. Beaudry, in press; Kubo et al., 1990). We found elevated CO_2 partial pressures of 20 to 30 kPa had little if any effect on O_2 uptake by 'Heritage' red raspberries in reduced O_2 atmospheres (D.W. Joles, C. Talasila, and A.C. Cameron, unpublished data). Thus, O_2 uptake by raspberries in our MA packages could be described as a function of O_2 partial pressure and temperature only (Eq. [6] and Table 3).

Beaudry et al. (1992) found for blueberries that an anaerobic RQ breakpoint was sharply defined and on this basis was able to identify lower O_2 levels as a function of temperature. For raspberries, RQ increased gradually with decreasing O_2 which made it difficult to define a clear lower O_2 limit based on RQ breakpoint. In addition, RQ of aerobic fruit at 0C was approximately 1.0 whereas at 10 and 20C, aerobic fruit had an RQ of ≈1.3 (Fig 4). Ethanol production also increased gradually with decreasing O_2 at 10 and 20C with no clear breakpoint (Fig 5). At 0C, ethanol production increased relatively sharply as O_2 fell below 3 kPa. In general, ethanol production did not increase substantially until the RQ rose above 1.3 to 1.5 (Fig 6) which approximately corresponded to O_2 levels of 3 to 4 kPa at 0C, 5 to 6 kPa at 10C, and 6 to 8 kPa at 20C (Fig. 4).

RQ levels above 1.0 without substantial ethanol production may have been due to the utilization of organic acids as the primary respiratory substrate or localized anaerobic respiration combined with partial ethanol metabolism. The correlation between RQ, headspace ethanol, and decreasing O_2 observed at 10 and 20C (Figs. 4, 5, and 6) supports the latter explanation, while at 0C the gradual increase in RQ contrasted with the sharp break in ethanol production (Fig. 5) may indicate that organic acid oxidation results in a RQ increase up to a level of ≈1.3.

In informal taste tests, we noted off-flavors when O_2 levels fell below ≈3 kPa at 0C and ≈5 kPa at 10 and 20C. This approximately correlates with the O_2 partial pressure where RQ exceeded 1.3 to 1.5 at each temperature. We recommend, based on RQ, ethanol production, and taste, that raspberries be held at O_2 levels above 4 kPa at 0C, 6 kPa at 10C, and 8 kPa at 20C, in order to avoid anaerobic induction and the possibility of off-flavor development. It should be noted that raspberries are very sensitive to reduced oxygen levels. For instance, the anaerobic induction point for blueberries at 0C was found to be 0.5 kPa (Beaudry et al., 1992) whereas for raspberries at 0C, it was not less than 3 kPa.

In packages with and without a CO_2 scrubber, headspace ethanol concentrations as a function of O_2 partial pressures were very similar (Fig. 9) which indicates that anaerobic induction was not influenced by the elevated CO_2 levels generated in these packages.

Its been reported that an atmosphere of ≈20 kPa CO_2 retards molds and extends shelf life of raspberry fruit (Goulart et al., 1992; Smith, 1958; Winter et al., 1939). Mold development was retarded for at least a day in packages with CO_2 partial pressures above 15 kPa (data not shown). However, using LDPE, O_2 levels at these CO_2 partial pressures were anaerobic (Figs. 1 and 7). All polymer films have a higher permeability to CO_2 than to O_2 (Pauly, 1989). Thus, by using polymer films, beneficial CO_2 levels (≈20 kPa) cannot be reached without the induction of anaerobic respiration. O_2 diffuses approximately 25% faster than CO_2 in air which infers that the permeability of a perforation to O_2 is 1.3 times higher than the permeability to CO_2. If a package were designed by selection of an appropriately sized perforation to maintain 10 kPa O_2, and if RQ was ≈1.3, then 18.5 kPa CO_2 could be generated at steady-state. However, permeation through a hole changes relatively little with temperature, while O_2 uptake by raspberry fruit approximately doubles with a 10C increase in temperature (Eq. [6] and Table 3). Thus, anaerobic conditions could develop if perforated packages experience an increase in temperature. These are factors which will need to be incorporated into an effective MA package system designed for raspberries.

List of References

Beaudry, R.M., A.C. Cameron, A. Shirazi, and D.L. Dostal-Lange. 1992. Modified atmosphere packaging of blueberry fruit: Effect of temperature on package O_2 and CO_2. J. Amer. Soc. Hort. Sci. 117:436-441.

Boylan-Pett, W. 1986. Design and function of a modified atmosphere package for tomato fruit. MS Thesis, Michigan State Univ., East Lansing.

Burton, W.G. 1978. Biochemical and physiological effects of modified atmospheres and their role in quality maintenance, p. 97. In: H.O. Hultin and M. Milner (eds.). Post-harvest biology and biotechnology. Food and Nutrition Press, Westport, Conn.

Cameron, A.C., W. Boylan-Pett, and J. Lee. 1989. Design of modified atmosphere packaging systems: Modeling oxygen concentrations within sealed packages of tomato fruits. J. Food Sci. 54:1413-1416, 1421.

Cameron, A.C. 1990. Modified atmosphere packaging: A novel approach for optimizing package oxygen and carbon dioxide. Proc. 5th Int'l. CA Conf., Wenatchee, Wash., 14-16 June.

Goulart, B.L., P.E. Hammer, K.B. Evensen, W. Janisiewcz, and F. Takeda. 1992. Pyrrolnitrin, Captan + Benomyl, and high CO_2 enhance raspberry shelf life at 0 or 18C. J. Amer. Soc. Hort. Sci. 117:265-270.

Hayakawa, K., Y.S. Henig, and S.G. Gilbert. 1975. Formulae for predicting gas exchange of fresh produce in polymeric film package. J. Food Sci. 40:186-191.

Henig Y.S. and S.G. Gilbert. 1975. Computer analysis of the variables affecting respiration and quality of produce packaged in polymeric films. J. Food Sci. 40:1033-1036.

Kader, A.A. 1986. Biochemical and physiological basis for effects of controlled and modified-atmospheres on fruits and vegetables. Food Technol. 40(5):99-104

Kerbel, E.L., A.A. Kader, and R.J. Romani. 1988. Effects of elevated CO_2 concentrations on glycolysis in intact 'Bartlett' pear fruit. Plant Physiol. 86:1205-1209.

Kidd, F. 1916. The controlling influence of carbon dioxide. Part III. The retarding effect of carbon dioxide on respiration. Proc. Royal Soc. (London) 89:136-156.

Kubo Y., A. Inaba, and R. Nakamura. 1990. Respiration and C_2H_4 production in various harvested crops held in CO_2-enriched atmospheres. J. Amer. Soc. Hort. Sci. 115:975-978

Lee, D.S., P.E. Haggar, J. Lee, and K.L. Yam. 1991. Model for fresh produce respiration in modified atmospheres based on principles of enzyme kinetics. J. Food Sci. 56(6):1580-1585.

Mangin, L. 1896. Sur la vegetation dans une atmosphere viciee par 1 a respiration. Compt. Rend. Acad. Sci. (Paris) 122:747-749.

Mason, D.T. 1974. Measurement of fruit ripeness and its relation to mechanical harvesting of the red raspberry (Rubus idaeus L.). Hort. Res. 14:21-27.

Pauly, S. 1989. Permeability and diffusion data, p. 435-449. In: Polymer handbook IV. 3rd ed. Wiley, New York.

Robbins, J., T.M. Sjulin, and M. Patterson. 1989. Postharvest storage characteristics and respiration rates in five cultivars of red raspberry. HortScience 24:980-982.

SAS Insitute. 1989. SAS/STAT user's guide. Version 6. Vol. 2. 4th ed. Cary, N.C.

Sjulin, T.M. and J. Robbins. 1987. Effects of maturity, harvest date, and storage time on post-harvest quality of red raspberry fruit. J. Amer. Soc. Hort. Sci. 112:481-487.

Smith, R.B. 1992. Controlled atmosphere storage of 'Redcoat' strawberry fruit. J. Amer. Soc. Hort. Sci. 117:260-264.

Smith, W.H. 1958. The harvesting, precooling, transport, and storage of strawberries and raspberries. Food Invest. Board Misc. Paper 1058.

Song, Y., H.K. Kim, and K.L. Yam. 1992. Respiration rate of blueberry in modified atmosphere at various temperatures. J. Amer. Soc. Hort. Sci. 117:925-929.

Thornton, N.C. 1933. Carbon dioxide storage III. The influence of carbon dioxide on the oxygen uptake by fruits and vegetables. Contrib. Boyce Thompson Inst. 5:371-402.

Winter, J.D., R.H. Landon, and W.H. Alderman. 1939. Use of carbon dioxide to retard the development of decay in strawberries and raspberries. Proc. Amer. Soc. Hort. Sci. 37:583-587.

Table 1. Activation energies (E_a), Arrhenius constants (A_r), and correlation coefficients (r^2) for .00521 and .00766 LDPE film. Values were obtained from linear transformations of the equation: $P = A_r \cdot \exp(-E_a/R \cdot T)$ where P is permeability to O_2 or CO_2 ($mmole \cdot cm \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$); E_a is the energy of activation of O_2 or CO_2 permeation ($kJ \cdot mol^{-1}$); and R is the gas constant (.0083144 $kJ \cdot mol^{-1} \cdot K^{-1}$) (Pauly, 1989).

Film thickness (cm)		E_a	A_r	r^2
.00521	P_{O_2}	38.11	.1312	.945
	P_{CO_2}	35.55	.2183	.957
.00766	P_{O_2}	36.85	.0700	.968
	P_{CO_2}	35.34	.1771	.971

Table 2. Whole package O_2 and CO_2 permeabilities ($P_{O_2} \cdot A/\Delta x$ and $P_{CO_2} \cdot A/\Delta x$, respectively) for the packages used in these experiments at 0, 10 and 20C. Appropriate values were substituted into Eqs. [2] and [3] to calculate O_2 uptake and CO_2 production for fruit at 0, 10, or 20C.

Temp (C)	$P_{O_2} \cdot A/\Delta x$ (mmol·h^{-1}·kPa^{-1})	$P_{CO_2} \cdot A/\Delta x$ (mmol·h^{-1}·kPa^{-1})	P_{CO_2}/P_{O_2}
0	2.443×10^{-4}	1.200×10^{-3}	4.91
10	6.967×10^{-4}	3.444×10^{-3}	4.94
20	12.11×10^{-4}	5.769×10^{-3}	4.76

Table 3. Constants for Michaelis-Menten (Eq [6]) equation describing the relationship between O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for raspberry fruit sealed in LDPE pouches and stored at various temperatures. The constants of the Michaelis-Menten equation were estimated by non-linear regression analysis.

$K_{1/2}$	SE	$R_{O_2}^{max,0}$	SE	Q_{10}	SE
5.59	±.40	.872	±.04	1.92	±.20

Table 4. Estimated values for Eq. [7], describing the relationship between calculated RQ, steady-state O_2 partial pressure (kPa) and temperature for September-harvested raspberry fruit stored at 0, 10, and 20C.

q	SE	r	SE
1.43	±.09	.053	±.002

Fig. 1. Effect of raspberry fruit weight on steady-state O_2 (circles) and CO_2 (triangles) partial pressures for September (open symbols) and October-harvested (closed symbols) raspberry fruit sealed in LDPE packages where A= 300 cm^2, Δx = .00521 cm for packages at 10 and 20C, and A = 300 cm^2, Δx = .00766 cm for packages stored at 0C.

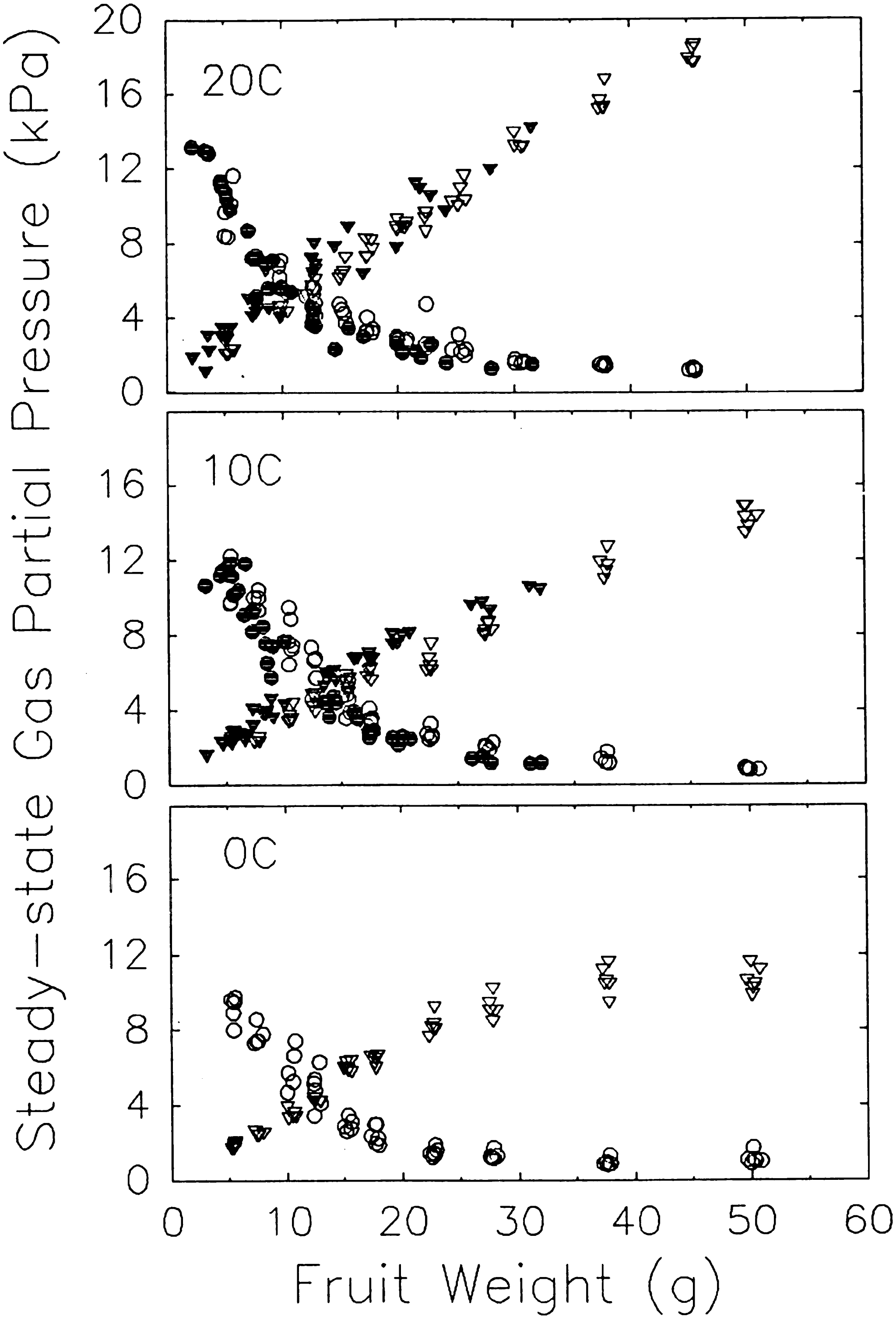

20C
10C
0C
Steady-state Gas Partial Pressure (kPa)
Fruit Weight (g)
0
4
8
12
16
20
0
10
20
30
40
50
60

Fig. 2. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of O_2 uptake for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages. See Eq. [6] and Table 3 for the equations and constants describing the curves.

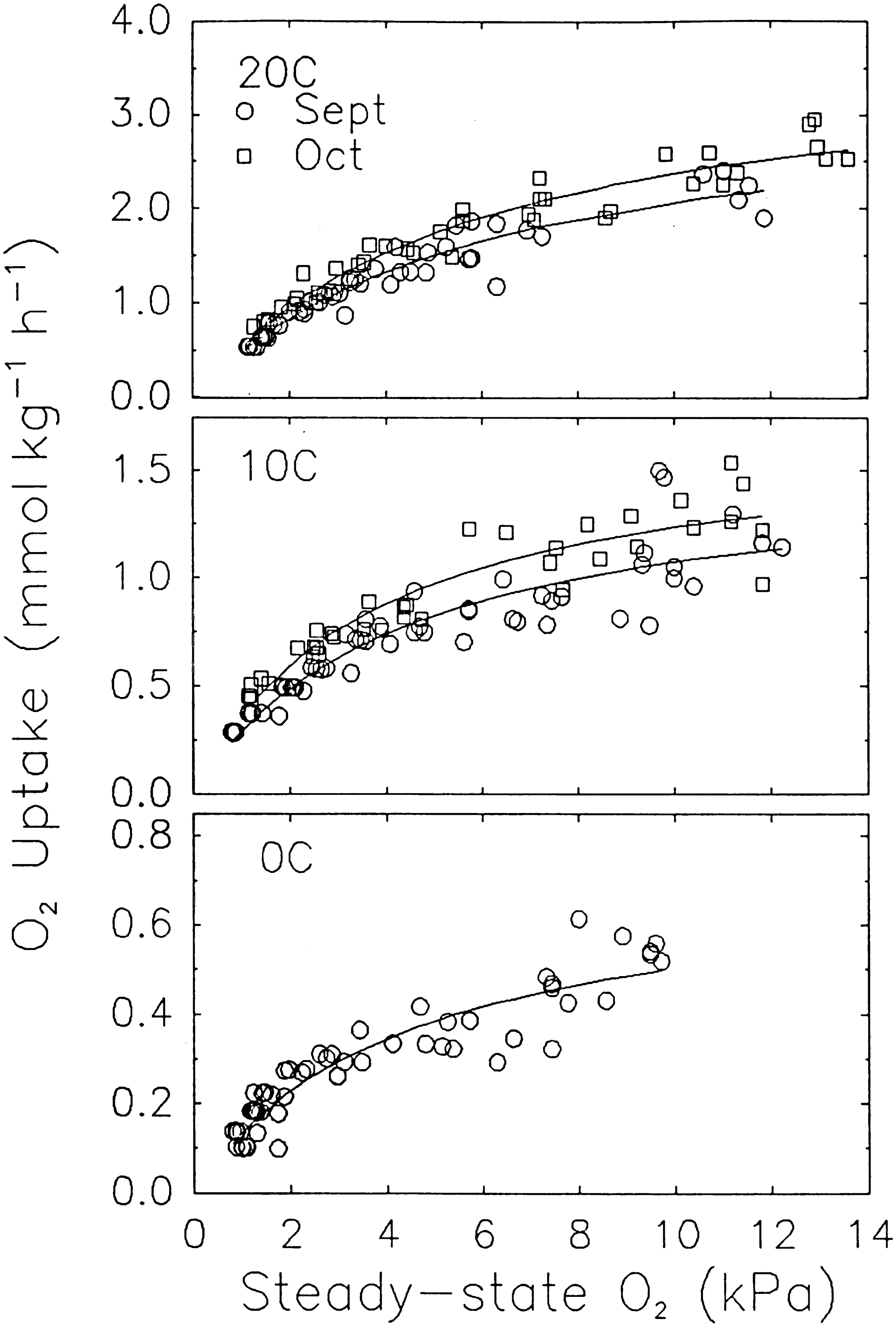
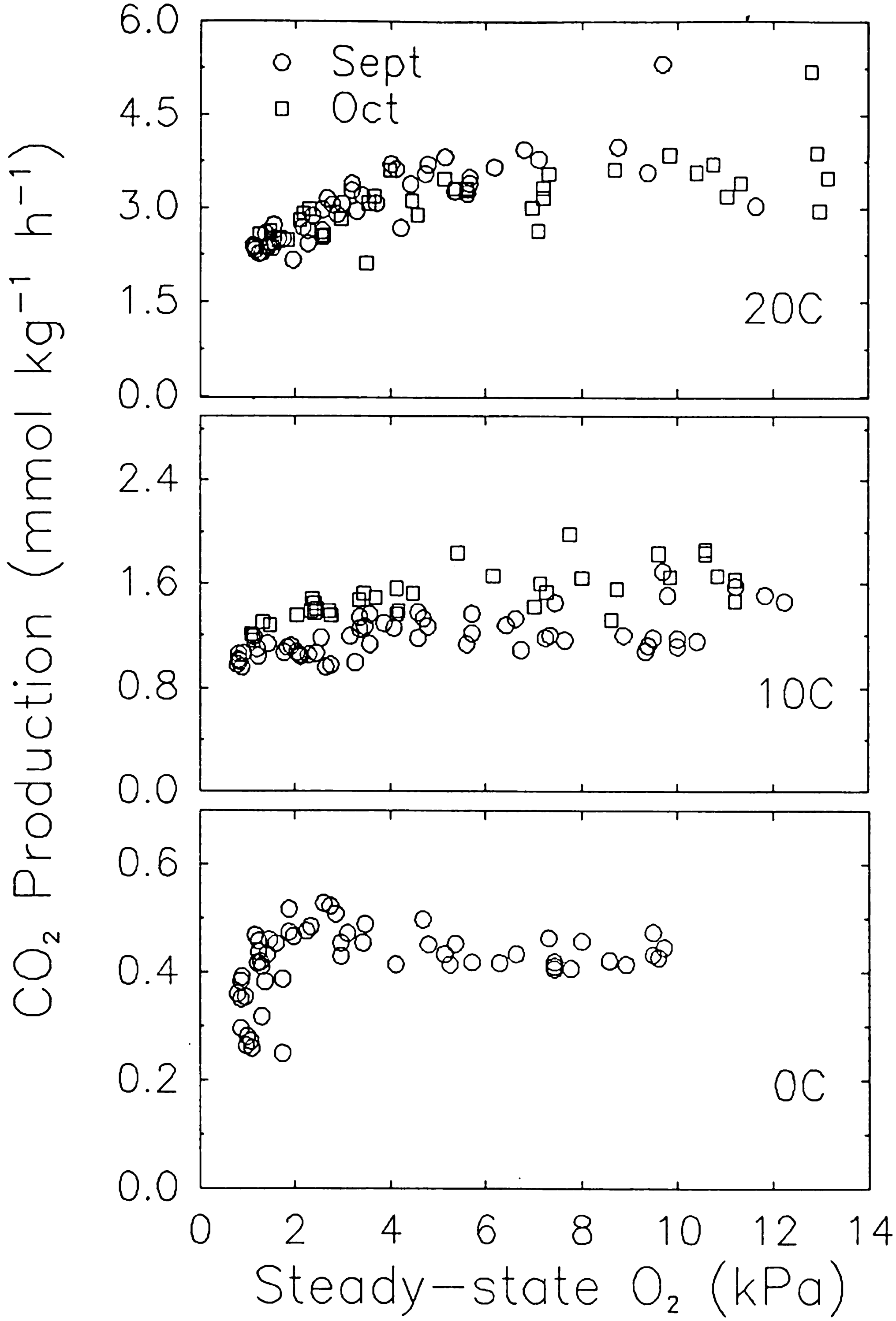
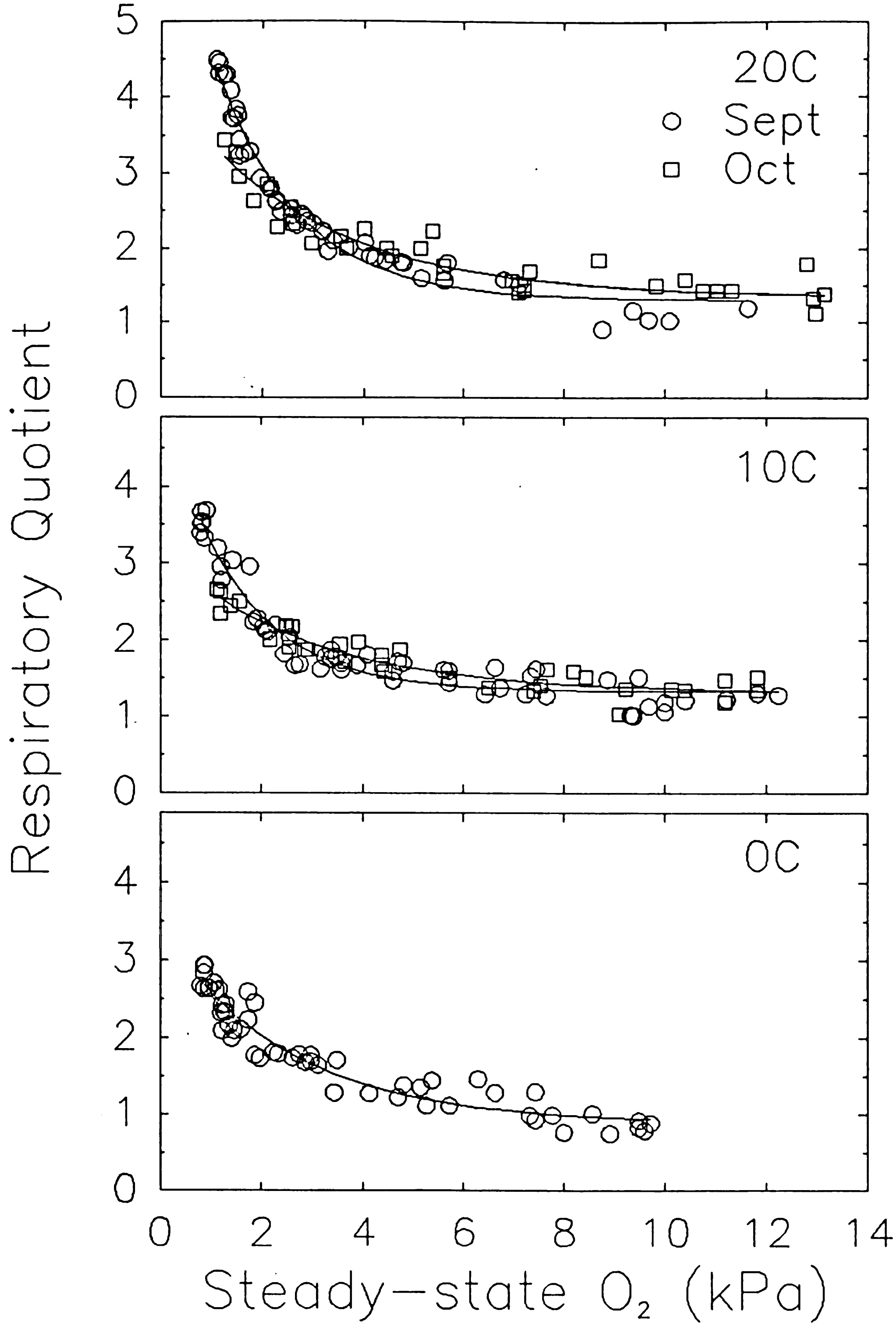

20C
Sept
Oct
10C
0C
4.0
3.0
2.0
1.0
0.0
1.5
1.0
0.5
0.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14
O2 Uptake (mmol kg-1 h-1)
Steady-state O2 (kPa)

Fig. 3. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of CO_2 production for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages.



6.0
4.5
3.0
1.5
0.0
Sept
Oct
20C
2.4
1.6
0.8
0.0
10C
0.6
0.4
0.2
0.0
0C
0
2
4
6
8
10
12
14
CO₂ Production (mmol kg⁻¹ h⁻¹)
Steady-state O₂ (kPa)

Fig. 4. Effect of steady-state O_2 partial pressure and storage temperature on the respiratory quotient of September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages. See Eq. [7] and Table 4 for the equations and constants describing the curves.



20C
Sept
Oct
10C
0C
Respiratory Quotient
Steady-state O_2 (kPa)
0
1
2
3
4
5
0
2
4
6
8
10
12
14

Fig. 5. Interdependent effects of steady-state O_2 partial pressure and storage temperature on headspace ethanol vapor concentration for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages.

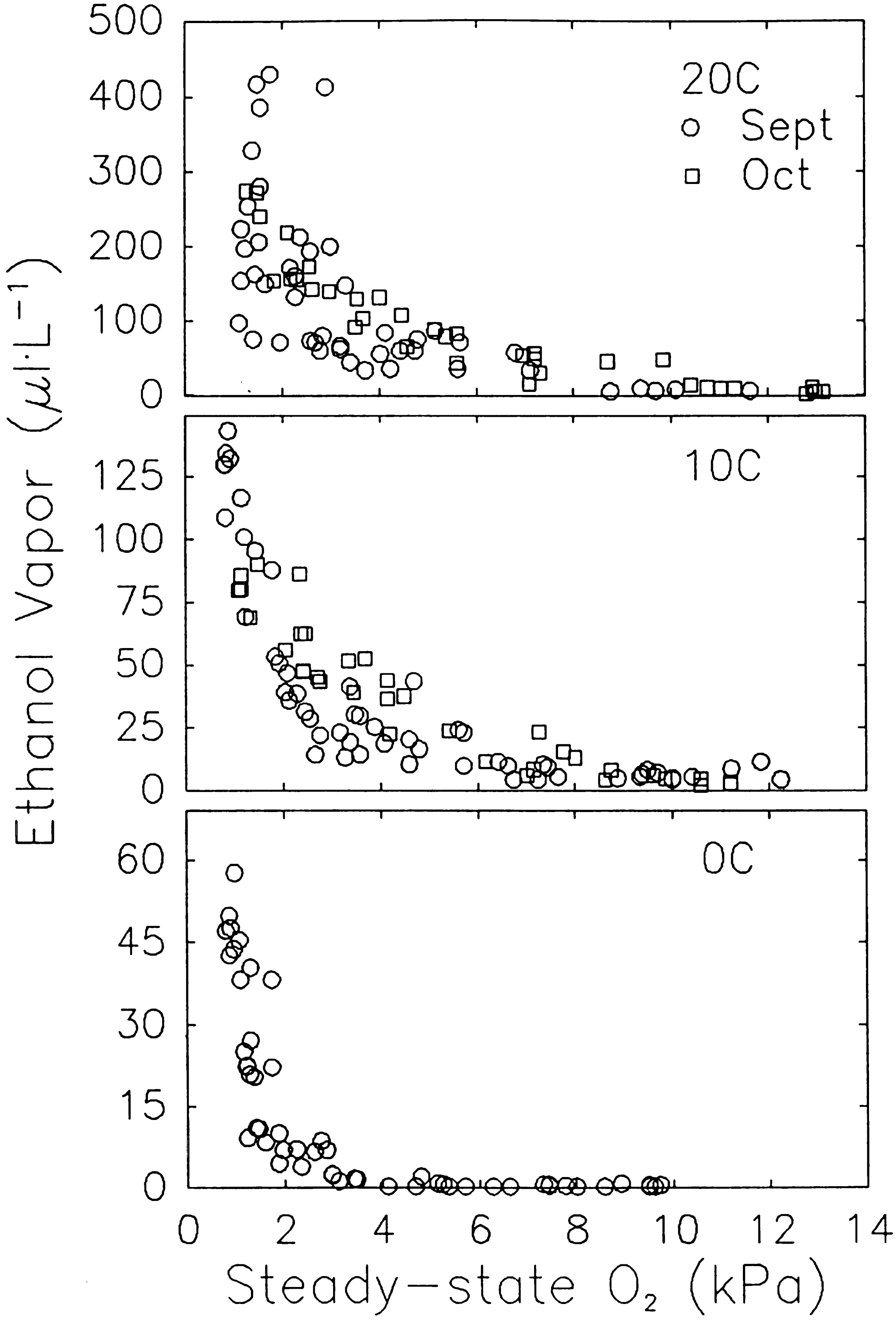
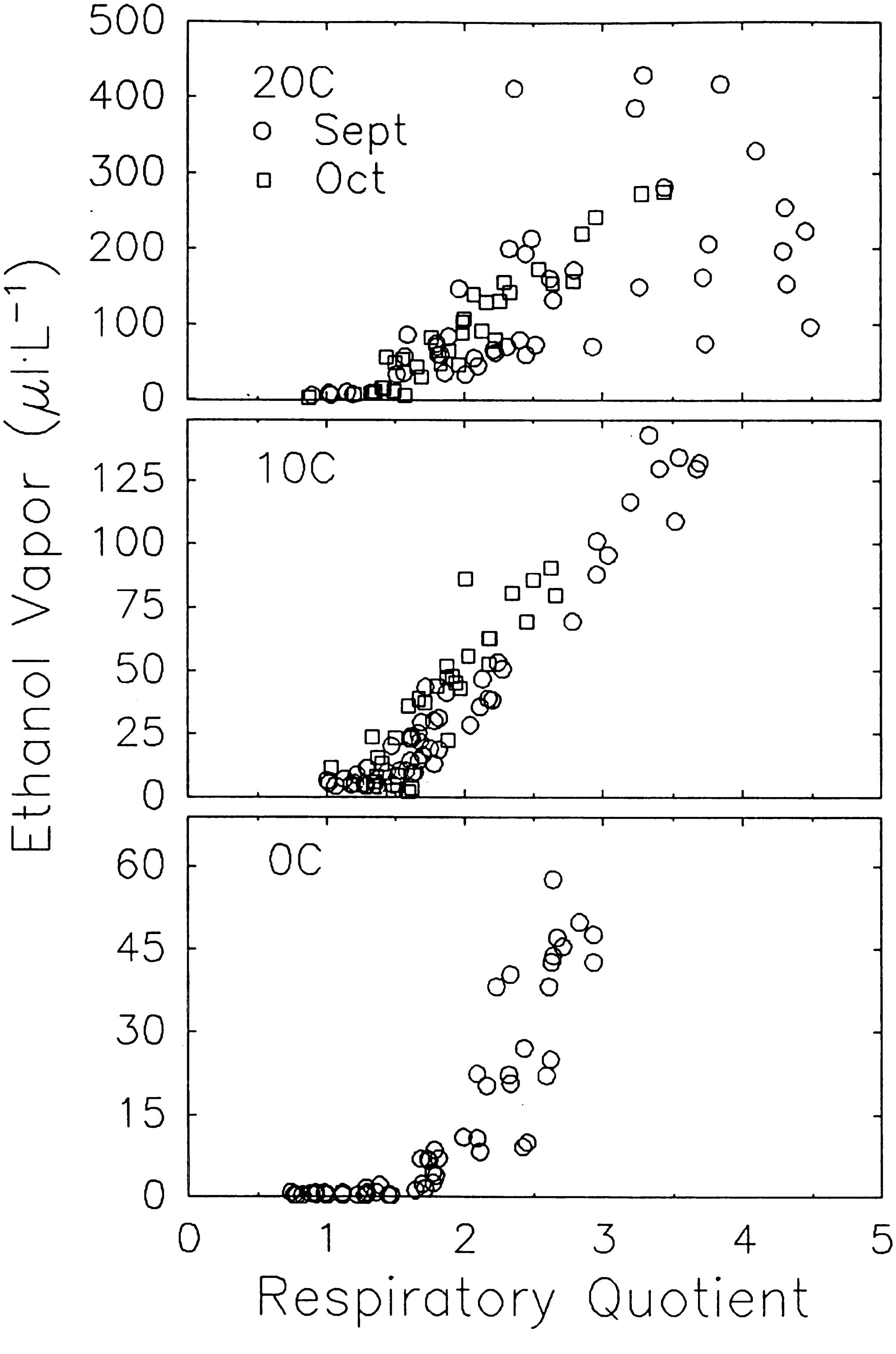
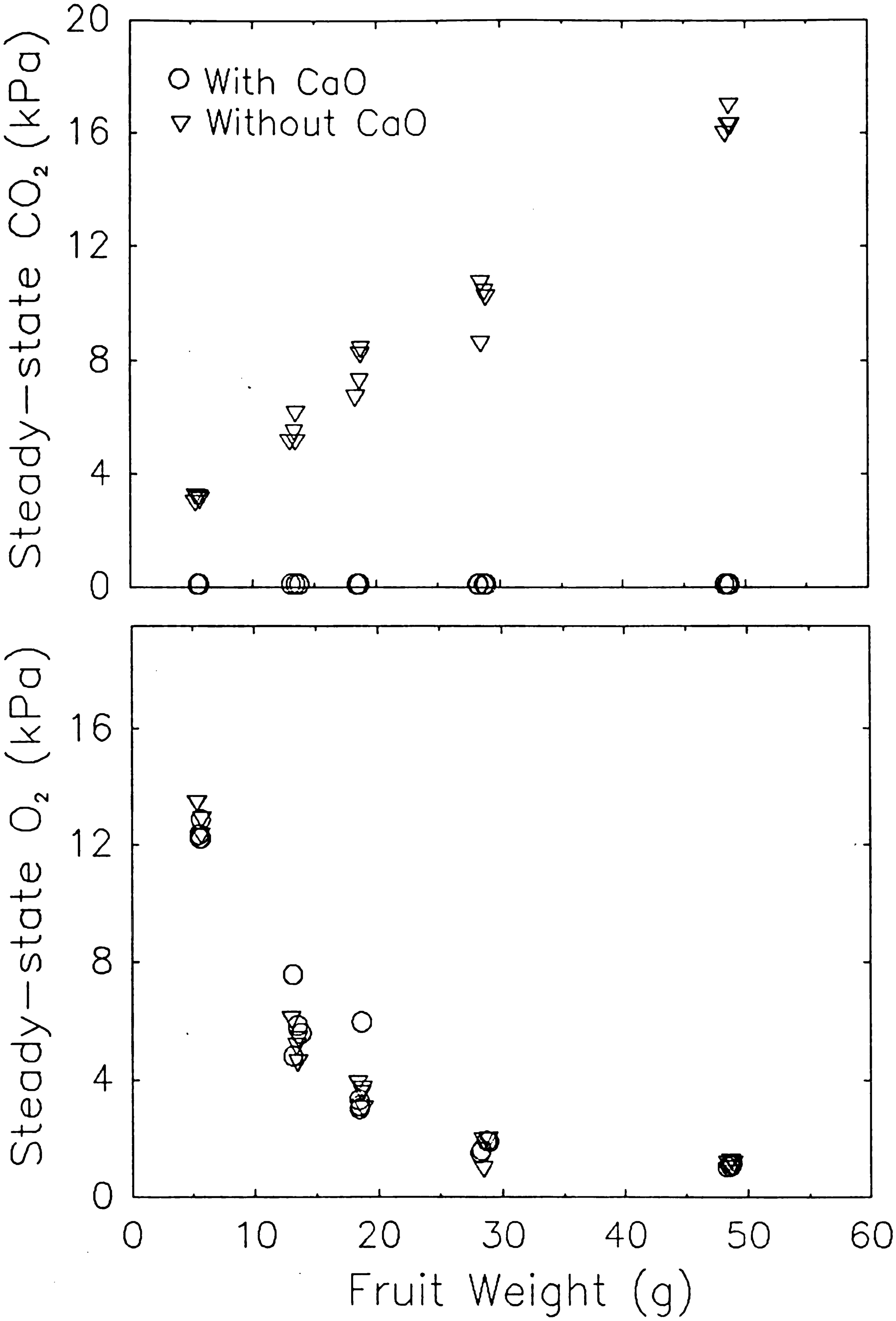

500
400
300
200
100
0
20C
Sept
Oct
125
100
75
50
25
0
10C
60
45
30
15
0
0C
0
2
4
6
8
10
12
14
Ethanol Vapor (μl·L⁻¹)
Steady-state O₂ (kPa)

Fig. 6. Relationship of headspace ethanol vapor concentration and the respiratory quotient measured for September (○) and October-harvested (□) raspberry fruit sealed in LDPE packages and stored at 0, 10, and 20C.



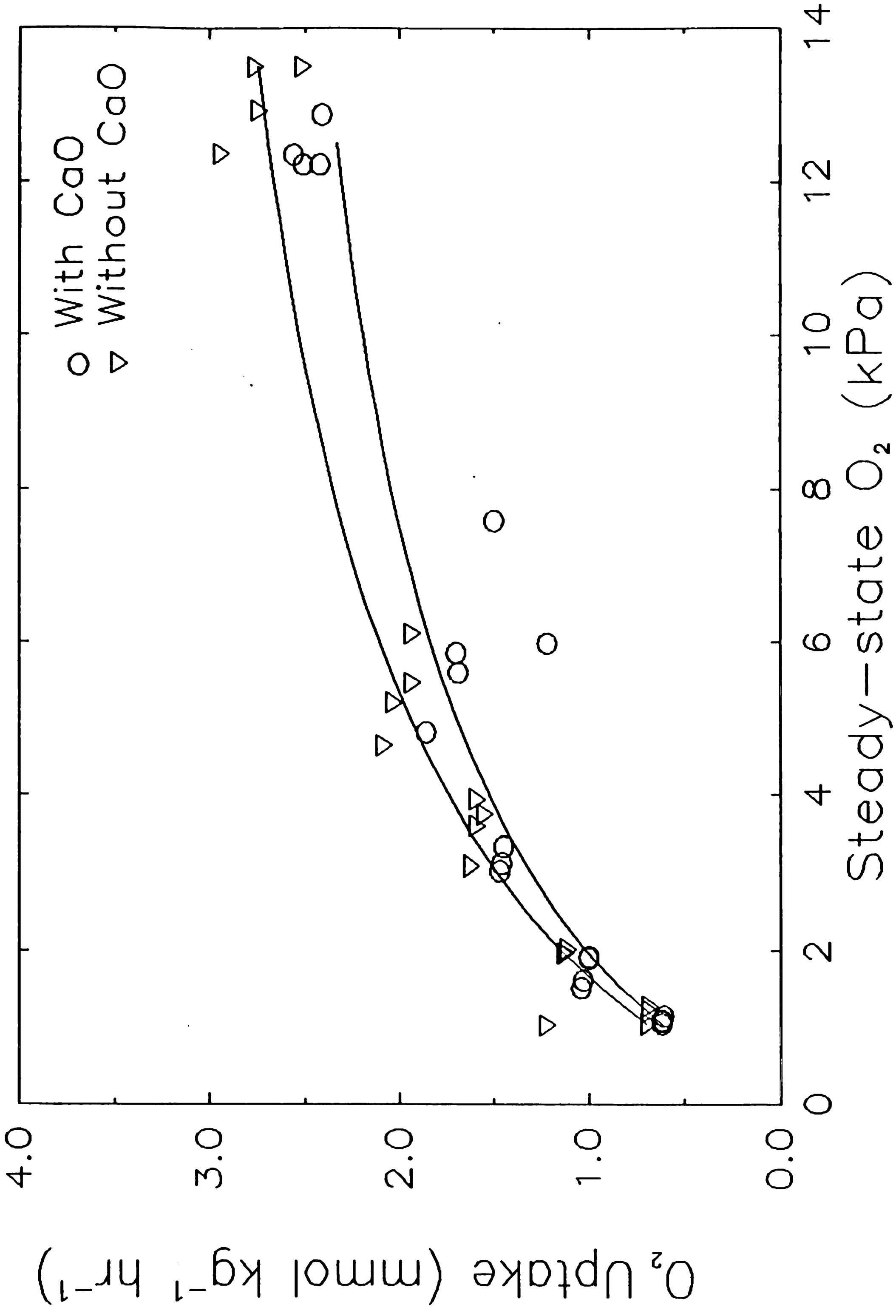
20C
Sept
Oct
10C
0C
Ethanol Vapor (μl·L⁻¹)
Respiratory Quotient
500
400
300
200
100
0
125
100
75
50
25
0
60
45
30
15
0
0
1
2
3
4
5

Fig. 7. Effect of raspberry fruit weight on steady-state O_2 and CO_2 partial pressures in sealed packages with (○) and without CaO(▽) where $A = 400\ cm^2$, $\Delta x = .00521$ cm LDPE and held at 20C.



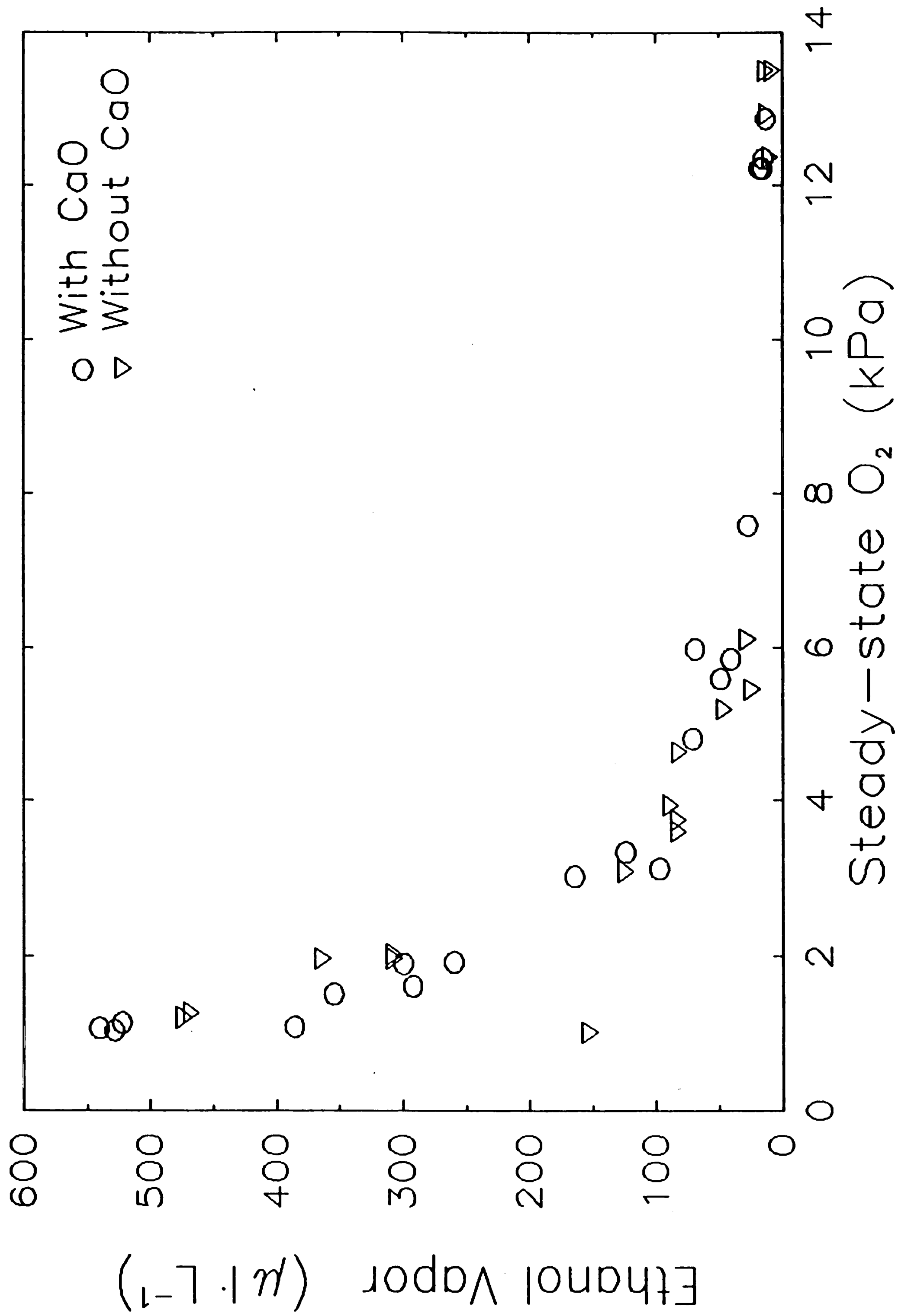
Steady−state CO_2 (kPa)
With CaO
Without CaO
0
4
8
12
16
20
Steady−state O_2 (kPa)
0
4
8
12
16
0
10
20
30
40
50
60
Fruit Weight (g)

Fig. 8. Effect of steady-state O_2 partial pressures on the rate of O_2 uptake for raspberry fruit sealed packages with (○) and without (▿) CaO and matched with a Michaelis-Menten equation.



With CaO
Without CaO
Steady-state O_2 (kPa)
O_2 Uptake (mmol kg^{-1} hr^{-1})
0
2
4
6
8
10
12
14
0.0
1.0
2.0
3.0
4.0

Fig. 9. Effect of steady-state O_2 partial pressures on headspace ethanol vapor concentration for raspberry fruit sealed in packages with (○) and without (▽) CaO.



With CaO
Without CaO
Steady-state O_2 (kPa)
Ethanol Vapor (μl · L^{-1})
0
2
4
6
8
10
12
14
0
100
200
300
400
500
600

CHAPTER 2

MODIFIED-ATMOSPHERE PACKAGING OF STRAWBERRY FRUIT: CHARACTERIZING RESPIRATION AS A FUNCTION OF O_2 AND TEMPERATURE

Abstract. Fruit of two strawberry cultivars (Fragaria x ananassa D. 'Honeoye' and 'Allstar') were sealed in low density polyethylene packages and stored at 0, 5, 10, 15, 20, and 25C. A range of steady-state O_2 (.2 to 16 kPa) and CO_2 partial pressures (30 to 2 kPa) were achieved by varying package surface area, package thickness and fruit weight. Package surface area and thickness were combined with measured permeability coefficients to determine total package permeability. Total package permeability was then used with steady-state O_2 and CO_2 partial pressures and fruit weight to calculate the rates of O_2 uptake, CO_2 production, and respiratory quotient (RQ). A decrease in O_2 partial pressure to ≈5 kPa did not noticeably reduce the O_2 uptake of these fruit. A detailed mathematical model was developed to characterize O_2 uptake as a function of O_2 partial pressure and temperature. This model combined the Michaelis-Menten equation for describing O_2 uptake as a function of internal O_2 and skin permeability to O_2. 'Honeoye' and 'Allstar' fruit had similar O_2 uptake rates although 'Honeoye' O_2 uptake was reduced at slightly higher O_2 levels and had a lower estimated value for skin permeability to O_2. The Q_{10} for O_2 uptake was estimated to be ≈2.4 and the apparent K_m ($k_{½}$) was estimated to be ≈.35 kPa O2 for both cultivars. RQ as a function of O_2 and temperature was fitted with an exponential equation.

Combining this RQ model with the model for O_2 uptake allows estimation of CO_2 production as a function of O_2 and temperature. Based on an increase in RQ and ethanol content, we estimated the lower O_2 limits for safe storage to be approximately 0.4 at 0C, 0.5 at 5C, 0.7 at 10C, .9 at 15C, 1.2 at 20C, and 2.0 at 25C for both cultivars. These estimates are similar to previously reported values.

Introduction

It has been well documented that elevated CO_2 levels (10 to 20%) extends strawberry shelf life (Thornton, 1931; Winter et al., 1940; Anderson and Hardenburg, 1959; Couey and Wells, 1970; Woodward and Topping, 1972; Ben-Yehoshua et al., 1975; El-Goorani and Sommer, 1981; Kader et al., 1989; Smith, 1992). It has also been reported that combining low O_2 levels (1 to 2%) with elevated CO_2 levels (15 to 20%) may help extend strawberry shelf life (Li and Kader, 1989).

Modified-atmosphere (MA) packaging has the potential to provide beneficial elevated CO_2 and low O_2 atmospheres. In fact, recently a California-based company has announced the development of a commercial MA package which utilizes specially microperforated films (Anonymous, Packer, 1990). They claim the use of their package nearly doubles strawberry shelf life although some distributors have noted that mold decay in these packages is still a problem (Anonymous, Packer, 1990).

In an MA package, steady-state package partial pressures of O_2 ($[O_2]_{pkg}$) and CO_2 ($[CO_2]_{pkg}$) are achieved when the rates of O_2 uptake and CO_2 production by the fruit are equal to the rates of O_2 and CO_2 flux through the film or perforation(s) at that temperature (Beaudry et al., 1992; Cameron et al., 1989). Thus, to design an MA package for strawberries which has beneficial $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ levels at a desired storage temperature, the fruit's rate of O_2 uptake and CO_2 production at those O_2 and CO_2 levels and temperature must be known. Once these rates are known, the strategy is to select a film which permits a gas flux equal to these rates.

Couey et al. (1966) reported that off-flavors were present in strawberries treated with O_2 levels of .25% or below at 3C. This was confirmed by Ke et al. (1991) who also showed that off-flavors were positively correlated ethanol content. Exposure of fruit tissue to O_2 levels below their lower tolerance limit induces anaerobic respiration which leads to ethanol production and eventually to off-flavor development (Kader et al., 1989). For raspberries, it was found that at a lower O_2 limit, an increase in ethanol content corresponded with an increase in the fruit's respiratory quotient (Joles et al., 1993). For blueberries, its been reported that the lower O_2 limit for aerobic respiration increased noticeably with temperature (Beaudry et al., 1992). Thus, to avoid off-flavor development in MA packages when temperature increases, the lower O_2 limit must be identified over a range of possible storage temperatures for strawberries.

In an MA package, problems with off-flavor development could also arise from variation in O_2 uptake rate from fruit-to-fruit or from cultivar-to-cultivar. Robbins et al. (1989) found a 39% difference between the CO_2 production rate of some red raspberry cultivars in air. So to determine whether a given MA package designed for one strawberry cultivar will be effective for others, any cultivar differences in respiratory response to reduced O_2 and changes in temperature must be identified.

The first objective of this investigation was to use the techniques described by Beaudry et al. (1992) and Joles et al. (1993) to study the effect of reduced O_2 and changes in temperature on the O_2 uptake, CO_2 production, and ethanol production of 'Honeoye' and 'Allstar' strawberry cultivars. The second objective was to use this information to characterize and compare the respiration of these cultivars and identify their lower O_2 limits.

Materials and Methods

Plant material

On June 21, 22, and 24 of 1993 'Honeoye' strawberry fruit were hand-harvested from Bird's Farm in Haslett, Mich. 'Allstar' strawberry fruit were hand-harvested on June 29, July 2 and 7 from the same location. The harvested fruit were placed into eight-quart flats and transported in an air-conditioned vehicle to Michigan State University. After transportation, fruit with obvious decay or damage were culled. Fruit to be stored at 0 and 5C were harvested on the earliest date while fruit harvested on the last day were stored at 20 and 25C. 'Allstar' fruit to be stored at 25, 20, and 15C were packaged immediately while fruit to stored at 10, 5, and 0C were kept overnight at 0C and packaged the next morning.

Package design

Packages were designed to generate a range of steady-state O_2 levels at temperatures of 0, 5, 10, 15, 20, and 25C. Using unpublished O_2 uptake data for 'Allstar' strawberries collected by R.M. Beaudry (unpublished data), a nonlinear regression model (Joles et al., 1993) was developed which estimated strawberry O_2 uptake over a range of O_2 levels and temperatures. This model was then substituted for R_{O_2} in:

$$\frac{W \cdot \Delta x}{A} = \frac{P_{O_2} \cdot ([O_2]_{atm} - [O_2]_{pkg})}{R_{O_2}} \qquad [1]$$

where W is fruit weight (kg); R_{O_2} is the rate of O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$); P_{O_2} is permeability coefficient for O_2 of low density polyethylene ($mmol \cdot cm^{1} \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$); A is film area ($cm^2$); Δx is film thickness (cm); $[O_2]_{atm}$ and $[O_2]_{pkg}$ is atmospheric and package O_2 partial pressures (kPa), respectively (Cameron, 1990; Beaudry et al., 1992). The O_2 permeability coefficients from Joles et al. (1993) at each desired storage temperature was substituted for P_{O_2} in Eq. 1. Also, 21.0 kPa was substituted for $[O_2]_{atm}$ in Eq. 1. By substituting the desired target steady-state O_2 partial pressures for $[O_2]_{pkg}$ in Eq. 1 and selecting appropriate film thicknesses (Δx), surface areas (A), and fruit weights (W) to balance the equation, package dimensions and fruit weights were chosen to generate a range of O_2 levels at storage temperatures of 0, 5, 10, 15, 20, and 25C.

Packaging

Packages were made of low density polyethylene (LDPE) (Dow Chemical, Midland Mich.) with surface areas of 200, 300, 360, 400, 600, 800 or 1000 cm^2 and film thicknesses of .00254 cm (1 mil.), .00699 cm (2.75 mil.), or .01016 cm (4 mil.). Fruit weights of 10 to 180 g were sealed in these packages. Fruit weights, package area, and film thickness varied depending on target O_2 level and temperature as described above. Table 1 lists the package dimensions and fruit weights which were used at each temperature to try to obtain each target O_2 level. Each target O_2 had a specific fruit weight and each fruit weight was replicated five times.

Each package had a gas sampling septum attached, consisting of a dab of Dupont Silicone II tub/tiling glue on a short strip of electrical tape (Boylan-Pett, 1986).

Gas analysis

Headspace O_2 and CO_2 partial pressures were determined by withdrawing two 0.5 ml samples from packages using an insulin-type syringe and injecting into a N_2 gas stream (9 to 12 $L \cdot h^{-1}$ flow rate) which was connected to the sequential O_2 and CO_2 analyzers described above. Response time was 10 s per sample. To avoid sampling errors, a third sample was taken if any difference was noted between the first two samples.

Headspace ethanol concentrations were determined by withdrawing 0.5 ml samples from the package headspace using a glass syringe (0.5 ml B-D Glaspak; Becton, Dickinson an Company, Rutherford, NJ.). Gas analysis was performed on a Carle Series 100 gas chromatograph (Hach Co., Loveland, Colo.) equipped with a Haysep 80/100 porous polymer column (Alltech Assoc. Inc., Deerfield, Ill.). Column temperature was 120C and the flow rate of the N_2 carrier gas was 6 $L \cdot h^{-1}$. Ethanol peak areas were integrated and headspace ethanol vapor partial pressures calculated (HP3396 Series II Integrator; Hewlett Packard, Avondale, PA.).

The time to reach steady-state O_2 and CO_2 levels was estimated by measuring $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ over time in separate packages containing the lowest and highest fruit weights for each storage temperature. When no further change in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ was detected in these packages, gas analysis was performed on all the packages at that temperature. Gas analysis was performed on the 'Honeoye' strawberries after 20 days at 0C, 14 days at 5C, 9 days at 10C, 7 days at 15C, 4 days at 20C, and 3 days at 25C. Gas analysis was performed on the 'Allstar' strawberries after 18 days at 0C, 13 days at 5C, 9 days at 10C, 5 days at 15C, 4 days at 20C, and 3 days at 25.

Calculation of O_2 uptake and CO_2 production

When steady-state O_2 and CO_2 levels were reached in the package, it was assumed that O_2 and CO_2 flux through the film was equal to flux of O_2 and CO_2 into and out of the fruit (Beaudry et al., 1992; Cameron et al., 1989). On this basis, respiration rates were calculated using the following formulae:

$$R_{O_2} = \frac{\frac{P_{O_2} \cdot A}{\Delta x}\left([O_2]_{atm} - [O_2]_{pkg}\right)}{W} \qquad [2]$$

$$R_{CO_2} = \frac{\frac{P_{CO_2} \cdot A}{\Delta x}\left([CO_2]_{pkg} - [CO_2]_{atm}\right)}{W} \qquad [3]$$

where R_{CO_2} is the rate of CO_2 production ($mmol \cdot kg^{-1} \cdot h^{-1}$); P_{CO_2} is LDPE film permeability coefficient for CO_2 ($mmol \cdot cm^{1} \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$); $[CO_2]_{pkg}$ and $[CO_2]_{atm}$ are package and atmospheric CO_2 partial pressures (kPa), respectively (Cameron, 1990; Beaudry et al., 1992).

Permeability coefficients, for the particular LDPE films used in this experiment, were measured using the method described by Beaudry et al. (1992) (P.C. Talasila and R. Stacy-Ryan, 1993, unpublished data). In brief, 3 replicates were measured at temperatures of 0, 5, 10, 15, and 20C. The data was then transformed into Arrhenius plots and linear regression analysis was performed on SAS (SAS Institute, Cary N.C.) to estimate film activation energies and Arrhenius constants (Beaudry et al. 1992). The r^2 of the regressions was .982 for both O_2 and CO_2 permeability. Substituting the activation energies and Arrhenius constants into the Arrhenius equation yielded:

$$P_{O_2} = .02827 \cdot \exp\left(-\frac{35.63}{.0083144 \cdot (T+273)}\right) \qquad [4]$$

$$P_{CO_2} = .03534 \cdot \exp\left(-\frac{32.00}{.0083144 \cdot (T+273)}\right) \qquad [5]$$

where 35.63 and 32.00 are the energies of activation for O_2 and CO_2 permeation, respectively ($kJ \cdot mol^{-1}$); .0083144 is the gas constant ($kJ \cdot mol^{-1} \cdot K^{-1}$) and T is temperature in C.

Model Development

The relationship of O_2 uptake to internal O_2 partial pressure can be described by the Michaelis-Menten equation:

$$R_{O_2} = \frac{R_{O_2}^{max} \cdot [O_2]_{int}}{k_{1/2} + [O_2]_{int}} \qquad [6]$$

where $R_{O_2}^{max}$ is the maximum rate of O_2 uptake and $[O_2]_{int}$ is the O_2 partial pressure in the internal gas phase of the fruit. $k_{1/2}$ in Eq. 6 was substituted for the standard K_m notation because this estimate is an apparent K_m of the entire fruit, while K_m is a true O_2 substrate concentration available to the oxidase enzymes of the fruit. O_2 uptake as a function of O_2 partial pressure can also be described using a variation of Fick's Law:

$$R_{O_2} = P_{O_2}^{skin} \cdot ([O_2]_{pkg} - [O_2]_{int}) \qquad [7]$$

where $P_{O_2}^{skin}$ is a value describing the ratio of the fruit's O_2 permeability and surface area to its skin thickness and weight ($mmole \cdot kg^{-1} \cdot h^{-1} \cdot kPa^{-1}$). Assuming that Q_{10} is constant from 0 to 25C, $R_{O_2}^{max}$ can be modeled as a function of T:

$$R_{O_2}^{max,T} = R_{O_2}^{max,0} \cdot Q_{10}^{\left(\frac{T}{10}\right)} \qquad [8]$$

where $R_{O_2}^{max,0}$ is the maximum rate of O_2 uptake at 0C, Q_{10} is the increase in O_2 uptake for every 10C increase in temperature, and T is temperature in C. By combining these equations it can be shown that:

$$R_{O_2} = \frac{A - \sqrt{(A)^2 - 4 \cdot \frac{R_{O_2}^{max,T}}{P_{O_2}^{skin}} \cdot [O_2]_{pkg}}}{\frac{2}{P_{O_2}^{skin}}} \qquad [9]$$

Where: $$A = \frac{R_{O_2}^{max,T}}{P_{O_2}^{skin}} + K_{1/2} + [O_2]_{pkg}$$

Nonlinear regression analysis was conducted on SAS to estimate the values of $R_{O_2}^{max,0}$, Q_{10}, $P_{O_2}^{skin}$, and $K_{½}$ using the data set for the 'Honeoye' and 'Allstar' strawberries.

The RQ was calculated as R_{CO_2} divided by R_{O_2}. The relationship between RQ, steady-state O_2, and temperature was fitted with the model:

$$RQ^T = q \cdot Exp(r \cdot T) \cdot Exp([O_2]_{pkg} \cdot s) + t \qquad [10]$$

Nonlinear regression analysis was conducted on SAS to estimate the values of q, r, s, and t.

No postharvest fungicide treatments were used on these fruit. Data was not taken from packages with obvious holes or moldy fruit.

Results

Increasing the ratio of package surface area to film thickness and fruit weight increased the steady-state $[O_2]_{pkg}$ for 'Honeoye' and 'Allstar' strawberries (Figs. 1 and 2). At the lower ratios a break occurred after which the steady-state $[O_2]_{pkg}$ increased at a greater rate per unit increase in the ratio of surface area to thickness and fruit weight. The range in target O_2 levels (from .2 to 16 kPa) was largely obtained but there was some variation in $[O_2]_{pkg}$ level within replicates (Figs. 1 and 2). At temperatures of 10C and above some of the fruit molded or decayed before steady-state was reached and these packages had to be discarded.

Increasing the ratio of package surface area to film thickness and fruit weight decreased the steady-state $[CO_2]_{pkg}$ for 'Honeoye' and 'Allstar' strawberries (Figs. 3 and 4). Steady-state $[CO_2]_{pkg}$ ranged from 30 to 2 kPa and at the lower ratios a break can be seen below which the steady-state $[CO_2]_{pkg}$ increased sharply (Figs. 3 and 4). $[CO_2]_{pkg}$ levels of over 10 kPa were only generated when package surface area to thickness and fruit weight ratios caused $[O_2]_{pkg}$ levels below 1 kPa (Figs. 1, 2, 3, and 4).

'Honeoye' and 'Allstar' strawberry fruit had similar rates of O_2 uptake over the O_2 levels and temperatures studied (Figs. 5 and 6). There was no significant difference between cultivars in the estimates of $R_{O_2}^{max,0}$, Q_{10}, and $k_{½}$ (Table 2). 'Honeoye' fruit had a significantly lower $P_{O_2}^{skin}$ value (Table 2). A decrease in $[O_2]_{pkg}$ from ≈18 to 5 kPa had little effect on the R_{O_2} at any temperature (Figs. 5 and 6). The $[O_2]_{pkg}$ which began limiting R_{O_2} increased with temperature. R_{O_2} began to decrease at O_2 levels above ≈5 kPa at 25C while, at 0C, R_{O_2} dropped noticeably only when $[O_2]_{pkg}$ fell below 3 kPa (Figs 5 and 6). 'Honeoye' O_2 uptake was reduced at slightly higher O_2 levels (Figs. 5, 6, 7, and 8).

'Honeoye' and 'Allstar' headspace ethanol partial pressures and RQs followed a similar trend with $[O_2]_{pkg}$ (Figs. 7, 8, 9, and 10). For all temperatures and both cultivars, ethanol and RQ increased sharply when $[O_2]_{pkg}$ fell below a certain O_2 limit. Lower O_2 limits for aerobic respiration for each cultivar at each temperature were found by identifying the O_2 level at which RQ and ethanol increased and then estimating a lower limit to just above this O_2 level. The approximate which we identified were 0.4 at 0C, 0.5 at 5C, 0.7 at 10C, .9 at 15C, 1.2 at 20C, and 2.0 at 25C for 'Allstar' strawberry fruit (Figs. 7, 8, 9, and 10). The lower O_2 limits for 'Honeoye' fruit were similar except at 15 and 25C where they were slightly higher (Figs. 7, 8, 9, and 10). Ethanol vapor content, in packages with similar O_2 levels, decreased with temperature (Figs. 9 and 10) due to the increase in ethanol solubility at lower temperatures. The coefficients for the curves describing the relationship between strawberry RQ, $[O_2]_{pkg}$, and temperature are given in Table 3. The coefficient t given in Table 3 is an estimate of the aerobic RQ of these fruit

and no significant differences in aerobic RQ was found between the two cultivars studied.

Discussion

Prolonged anaerobic respiration by fruit tissue results in ethanol production and off-flavor development (Kader et al., 1989). By estimating the O_2 which induced an increase in RQ and ethanol content, we identified the lower O_2 limits for aerobic respiration to be approximately 0.4 at 0C, 0.5 at 5C, 0.7 at 10C, .9 at 15C, 1.2 at 20C, and 2.0 at 25C (Figs. 7, 8, 9, and 10). Couey et al. (1966) reported that strawberries treated with O_2 levels of 0.25% at 3C had off-flavors but strawberries treated with O_2 levels of 0.5% did not. This was confirmed by Ke et al. (1991) at 0 and 5C who also showed that off-flavors were positively correlated with ethanol content. Our estimates at 0 and 5C essentially agree with these previous studies.

The lower O_2 limit of strawberries increased with increasing temperature (i.e from 0.4 at 0C to 2.0 at 25C). An MA package designed for strawberries must maintain $[O_2]_{pkg}$ levels above the lower O_2 limit at that storage temperature in order to avoid off-flavor development. An even greater increase in lower O_2 limit with temperature was reported for raspberries (i.e. from 4 kPa at 0C to 8 kPa at 20C) and blueberries (i.e. from 1.8 kPa at 5C to 4.0 kPa at 25C) (Joles et al., 1993; Beaudry et al., 1992). This difference in lower O_2 limit between these fruit could be due to differences in skin permeability or physiology.

CO_2 levels of 10 to 20 kPa prolong strawberry shelf life (Thornton, 1931; Winter et al., 1940; Anderson and Hardenburg, 1959; Couey and Wells, 1970; Woodward and

Topping, 1972; Ben-Yehoshua et al., 1975; El-Goorani and Sommer, 1981; Kader et al., 1989; Smith, 1992). Using a LDPE film like the one utilized in this study, CO_2 levels over 10 kPa cannot be generated unless O_2 drops below 1 kPa and anaerobic respiration is induced (figs. 1, 2, 3, and 4). This is because LDPE is 4 to 5 times more permeable to CO_2 than to O_2. A perforation, however, could have a slightly higher permeability to O_2 than to CO_2 because O_2 diffuses faster in air. Using perforations in MA packaging, would make elevated CO_2 and aerobic O_2 levels (i.e. 15 and 5 kPa) possible (Kader et al., 1989).

In this study, we collected O_2 uptake data over a range of O_2 levels and temperatures (Figs. 5 and 6) and developed a detailed mathematical model to characterize the O_2 uptake of 'Honeoye' and 'Allstar' strawberry fruit as a function of O_2 and temperature (Eq. 9 and Table 2). The fit of this model with the OC data was poor (Figs. 5 and 6) which may be because Q_{10} was not constant over the temperatures studied as was assumed in our model.

This model was used to characterize O_2 uptake in preference to other models (Cameron et al., 1989; Cameron et al, 1993; Joles et al., 1993) because it estimates the fruit's permeability to O_2 and an apparent K_m ($k_{½}$). Thus, O_2 uptake was described as a function of internal O_2 level, which is a better reflection of the substrate [O_2] available to oxidase enzymes. The other models, used for blueberries and raspberries (Cameron et al, 1993; Joles et al., 1993), were based on external O_2 level and because of this the fruit's skin permeability to O_2 was incorporated into their estimate of apparent K_m ($K_{½}$).

We also collected CO_2 production data and combined it with the O_2 uptake data to calculate RQ over a range of O_2 levels and temperatures (Figs 7 and 8). The RQ data was then matched with a mathematical model which estimated RQ as a function of O_2 and temperature (Eq. 10 and Table 3). Since RQ is CO_2 production divided by O_2 uptake, CO_2 production as function of O_2 and temperature can then be estimated by multiplying the model for RQ by the model for O_2 uptake.

In these models, it was assumed that CO_2 had no influence on O_2 uptake. There is some evidence that CO_2 can reduce O_2 uptake of strawberry fruit in flow-through controlled-atmosphere conditions (Li and Kader, 1989). However, in MA packages, CO_2 levels up to 20 kPa had no effect on O_2 uptake of raspberries, cherries, and blueberries (Joles et al., 1993b; Beaudry, 1993). The issue of what affect CO_2 has on O_2 uptake still needs to be resolved. Still, these models can be used to design safe MA packages for strawberries, because even if elevated CO_2 did reduce O_2 uptake, $[O_2]_{pkg}$ would increase which actually would help avoid anaerobic induction.

If an MA package designed for one strawberry cultivar is used for another cultivar with a distinctly higher O_2 uptake rate, anaerobic O_2 levels and off-flavors could result. The cultivars investigated in this study had similar O_2 uptake rates (Figs. 5 and 6). 'Honeoye' O_2

uptake was reduced at slightly higher O_2 levels (Figs. 5, 6, 7, and 8) and this may have be due to their lower $P_{O_2}^{skin}$ (Eq. 9 and Table 2). The aerobic RQs of these cultivars weren't significantly different (Table 3) which suggests that the same target $[CO_2]_{pkg}$ could be obtained for both cultivars in an MA package.

A risk of off-flavor development in an MA package also comes when storage temperature is increased (Kader et al., 1989). The effect of temperature on $[O_2]_{pkg}$ was modeled by Cameron et al. (1993). They showed that the risk of off-flavor development is a major problem for perforated packages because permeation through a perforation changes very little with temperature, while the O_2 uptake of fruit more than doubles per 10C increase in temperature. This risk of developing off-flavors with temperature abuse and fruit-to-fruit variation in respiration rate are important factors that must still be addressed to design safe and effective MA packages for strawberries.

List of References

Anderson, R.E., and R.E. Hardenburg. 1959. Effect of various baskets, film wraps and crate liners on quality of strawberries. Am. Soc. Hort. Sci. 74:394-400.

Anonymous. 1990. FreshHold extends breathable packaging to fresh strawberries. Packer, August 11, XCVII(32):5A.

Beaudry, R.M., A.C. Cameron, A. Shirazi, and D.L. Dostal-Lange. 1992. Modified atmosphere packaging of blueberry fruit: Effect of temperature on package O_2 and CO_2. J. Amer. Soc. Hort. Sci. 117:436-441.

Beaudry, R.M. 1993. Effect of carbon dioxide partial pressure on blueberry fruit respiration and respiratory quotient. Postharvest Biology and Technology, In press.

Ben-Yehoshua, S. 1975. Effects of combined treatments of CO_2 and chain cooling upon the rate of deterioration of strawberries sent by sea or air to Europe. HortScience 10:334.

Boylan-Pett, W. 1986. Design and function of a modified atmosphere package for tomato fruit. MS Thesis, Michigan State Univ., East Lansing.

Cameron, A.C., W. Boylan-Pett, and J. Lee. 1989. Design of modified atmosphere packaging systems: Modeling oxygen concentrations within sealed packages of tomato fruits. J. Food Sci. 54:1413-1416, 1421.

Cameron, A.C. 1990. Modified atmosphere packaging: A novel approach for optimizing package oxygen and carbon dioxide. Proc. 5th Int'l. CA Conf., Wenatchee, Wash., 14-16 June.

Cameron, A.C., R.M. Beaudry, N.H. Banks, and M.V. Yelanich. 1993. Modified-atmosphere packaging of blueberry fruit: Modeling respiration and package oxygen partial pressure at different temperatures. Accepted to J. Amer. Soc. Hort. Sci.

Couey, H.M., Follstad M.N. and M. Uota. 1966. Low oxygen atmospheres for control of postharvest decay of fresh strawberries. Phytopathology 56:1339.

Couey, H.M. and J.M. Wells. 1970. Low oxygen or high carbon dioxide atmospheres to control of postharvest decay of fresh strawberries. Phytopathology 60:47.

El-Goorani, M.A., and N.F. Sommer. 1981. Effects of modified atmospheres on postharvest pathogens of fruits and vegetables. Hortic. Rev. 3:412-461.

Joles, D.W., A.C. Cameron, A. Shirazi, P.D. Petracek, and R.M. Beaudry. 1993. Modified-atmosphere packaging of 'Heritage' red raspberry fruit: The respiratory response to reduced oxygen, enhanced carbon dioxide, and temperature. Accepted: J. Amer. Soc. Hort. Sci. June 1993.

Joles, D.W., P.C. Talasila, and A.C. Cameron. 1993. Modified-atmosphere packaging of small fruits: The influence of CO_2 on O_2 uptake and the lower O_2 limit. HortScience 28(5):511

Kader, A.A., D. Zagory, E.L. Kerbel. 1989. Modified atmosphere packaging of fruits and vegetables. Crit. Rev. Food Sci. Nutrition 28:1-30

Ke, D., L. Goldstein, M. O'Mahony, and A.A. Kader. 1991. Effects of short-term exposure to low O_2 and high CO_2 atmospheres on quality attributes of strawberries. J. Food Sci. 56(1):50-54.

Li, C. and A.A. Kader. 1989. Residual effects of controlled atmospheres on postharvest physiology and quality of strawberries. J. Amer. Soc. Hort. Sci. 114:629-634

Robbins, J., T.M. Sjulin, and M. Patterson. 1989. Postharvest storage characteristics and respiration rates in five cultivars of red raspberry. HortScience 24:980-982.

SAS Institute. 1989. SAS/STAT user's guide. Version 6. Vol. 2. 4th ed. Cary, N.C.

Smith, R.B. 1992. Controlled atmosphere storage of 'Redcoat' strawberry fruit. J. Amer. Soc. Hort. Sci. 117:260-264.

Thornton, N.C. 1933. Carbon dioxide storage III. The influence of carbon dioxide on the oxygen uptake by fruits and vegetables. Contrib. Boyce Thompson Inst. 5:371-402.

Winter, J.D., R.H. Landon, and W.H. Alderman. 1939. Use of carbon dioxide to retard the development of decay in strawberries and raspberries. Proc. Amer. Soc. Hort. Sci. 37:583-587.

Woodward, J.R., and A.J. Topping. 1972. The influence of controlled atmospheres on the respiration rates and storage behavior of strawberry fruits. J. Hort. Sci. 47:547-533.

Table 1. Target O_2 partial pressures and the corresponding package dimensions and fruit weights calculated to obtain these partial pressures. The appropriate package dimensions and fruit weights were calculated using Eq. 1 combined with preliminary strawberry O_2 uptake data. The target weights correspond respectively with each target O_2.

Temp. (C)	Target O_2 (kPa)	Film Thickness (cm)	Area (cm^2)	Target Wt. (g)
0	.2,.25,.5	.01016	400	180,148,82
	1,2	.00699	360	66,44
	4,6,8	.00254	200	44,36,30
	10,12,16	.00254	400	46,38,20
5	.2,.25,.5	.01016	400	135,110,62
	1,2	.00699	360	50,32
	4,6,8	.00254	200	32,26,20
	10,12,16	.00254	400	36,28,15
10	.2,.25	.01016	400	100,80
	.5,1	.00699	360	60,36
	2,4,6	.00254	200	36,24,20
	8,10,12,16	.00254	400	32,28,20,10
15	2,.25,.5	.00699	360	96,78,44
	1,2,4	.00254	200	40,26,18
	6,8	.00254	300	22,18
	10,12,16	.00254	600	28,22,12
20	.2,.25,.5	.00254	200	104,84,48
	1,2	.00254	300	42,28
	4,6,8	.00254	600	38,30,26
	10,12,16	.00254	800	28,22,12
25	.2,.25	.00254	200	74,60
	.5,1	.00254	300	50,30
	2,4	.00254	600	40,20
	6,8,10	.00254	800	30,24,20
	12,16	.00254	1000	20,10

Table 2. Constants for Eq. 9 describing the relationship between O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for 'Honeoye' and 'Allstar' strawberry fruit (Eq. [9]) and shown in Figures 5 and 6. $R_{O_2}^{max,0}$ is the maximum rate of O_2 uptake at 0C, Q_{10} is the increase in O_2 uptake for a 10C increase in temperature, $k_{1/2}$ is the O_2 partial pressure at which the rate of O_2 uptake is half the maximum rate, and $P_{O_2}^{skin}$ is a value describing the of the fruit's skin to O_2. These constants were estimated by non-linear regression analysis using SAS.

	$R_{O_2}^{max,0}$	SE	Q_{10}	SE	$k_{1/2}$	SE	$P_{O_2}^{skin}$	SE
'Honeoye'	.284	±.02	2.38	±.05	.346	±.10	.652	±.05
'Allstar'	.259	±.02	2.48	±.08	.368	±.11	1.11	±.15

Table 3. Estimated constants for Eq. [10], describing the relationship between calculated RQ, steady-state O_2 partial pressure (kPa) and temperature for 'Honeoye' and 'Allstar' strawberry fruit. The t coefficient in this models is an estimate of aerobic RQ.

	q	SE	r	SE	s	SE	t	SE
'Honeoye'	4.83	±.26	.045	±.003	-2.65	±.20	1.60	±.07
'Allstar'	10.9	±.80	.011	±.004	-5.51	±.40	1.74	±.07

Fig. 1. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state O_2 for 'Honeoye' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C.

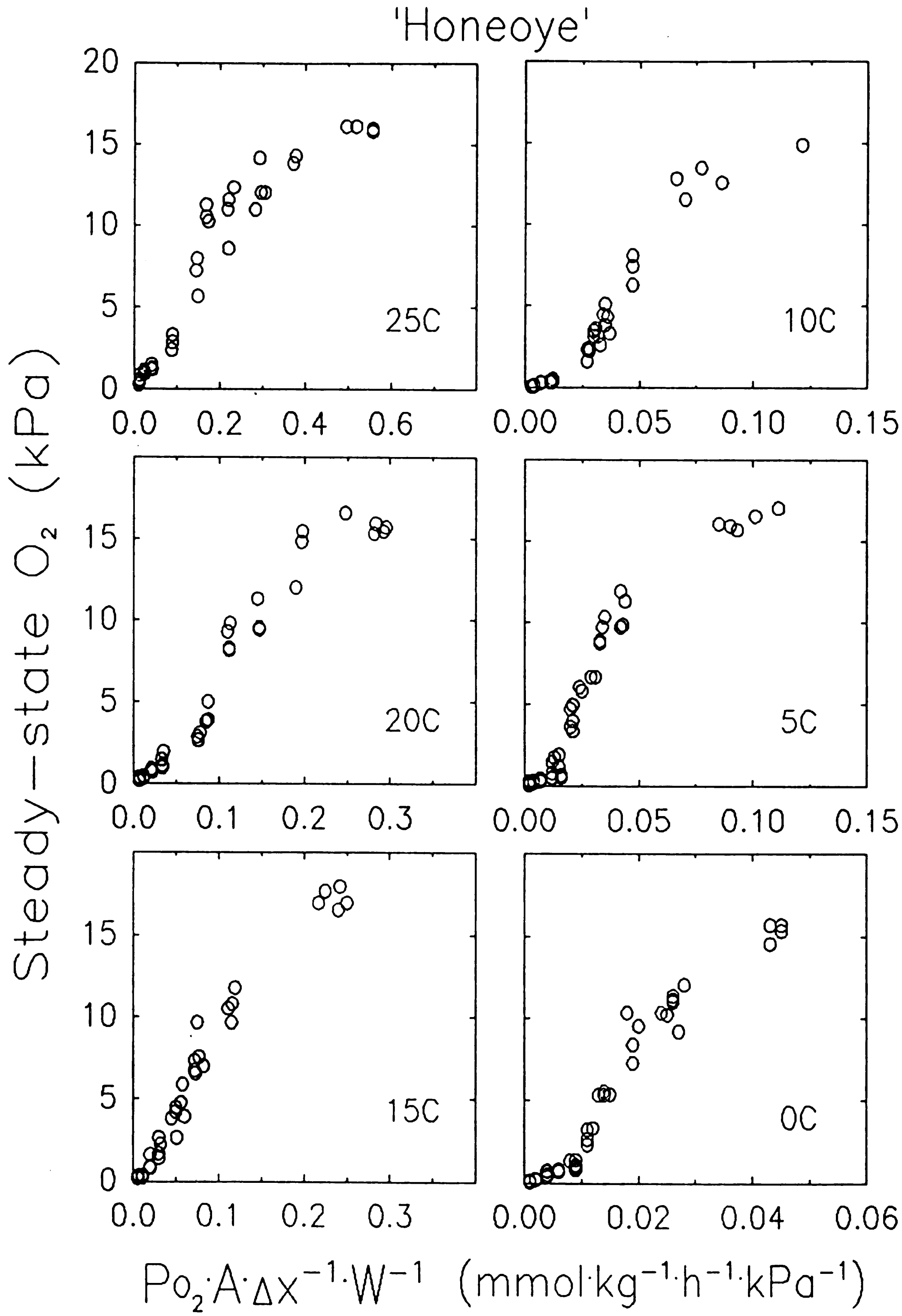

'Honeoye'
Steady—state O_2 (kPa)
25C
10C
20C
5C
15C
0C
$Po_2 \cdot A \cdot \Delta x^{-1} \cdot W^{-1}$ (mmol·kg^{-1}·h^{-1}·kPa^{-1})

Fig. 2. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state O_2 for 'Allstar' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C.

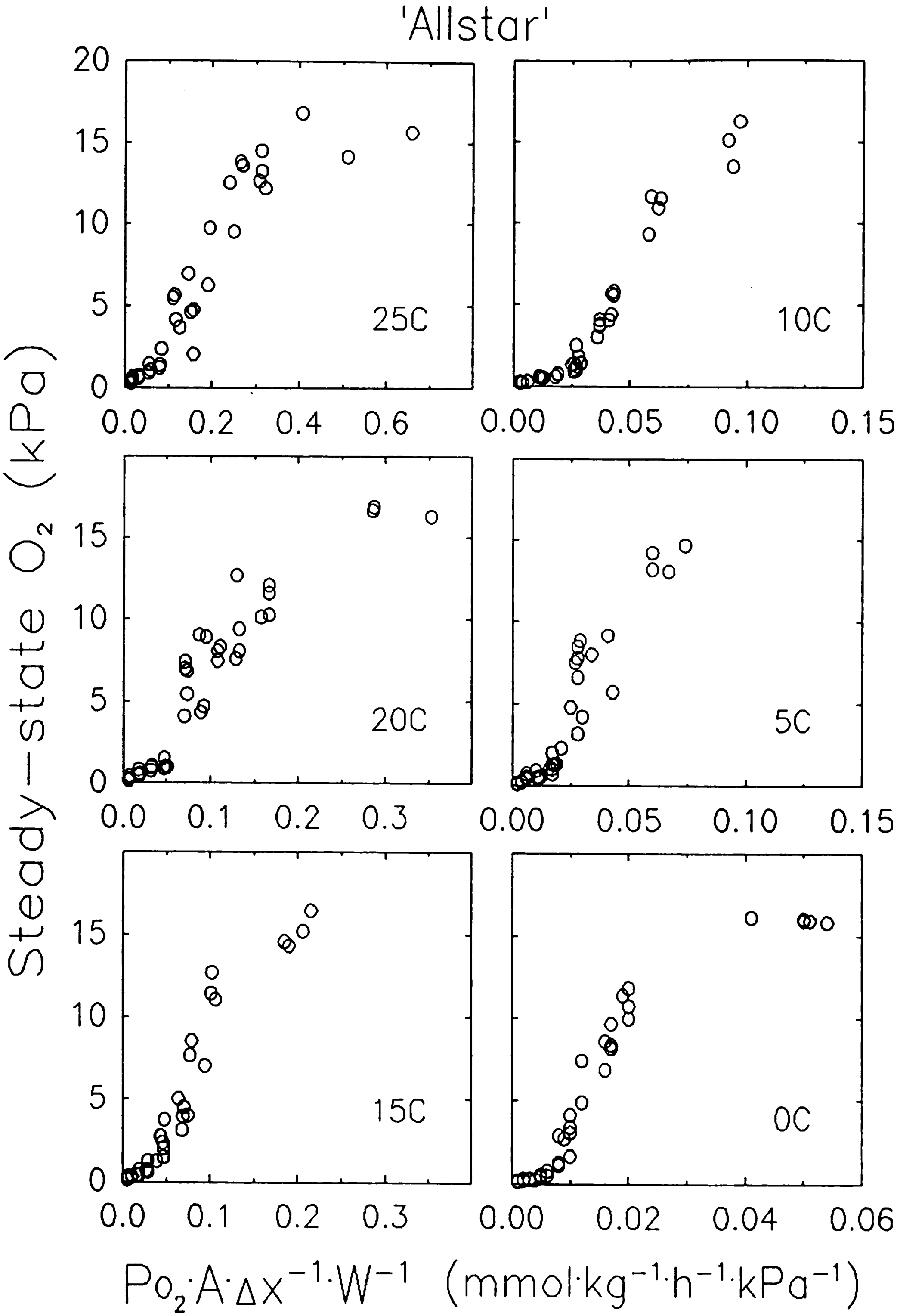

'Allstar'
Steady-state O_2 (kPa)
25C
10C
20C
5C
15C
0C
$Po_2 \cdot A \cdot \Delta x^{-1} \cdot W^{-1}$ (mmol·kg^{-1}·h^{-1}·kPa^{-1})

Fig. 3. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state CO_2 for 'Honeoye' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C.

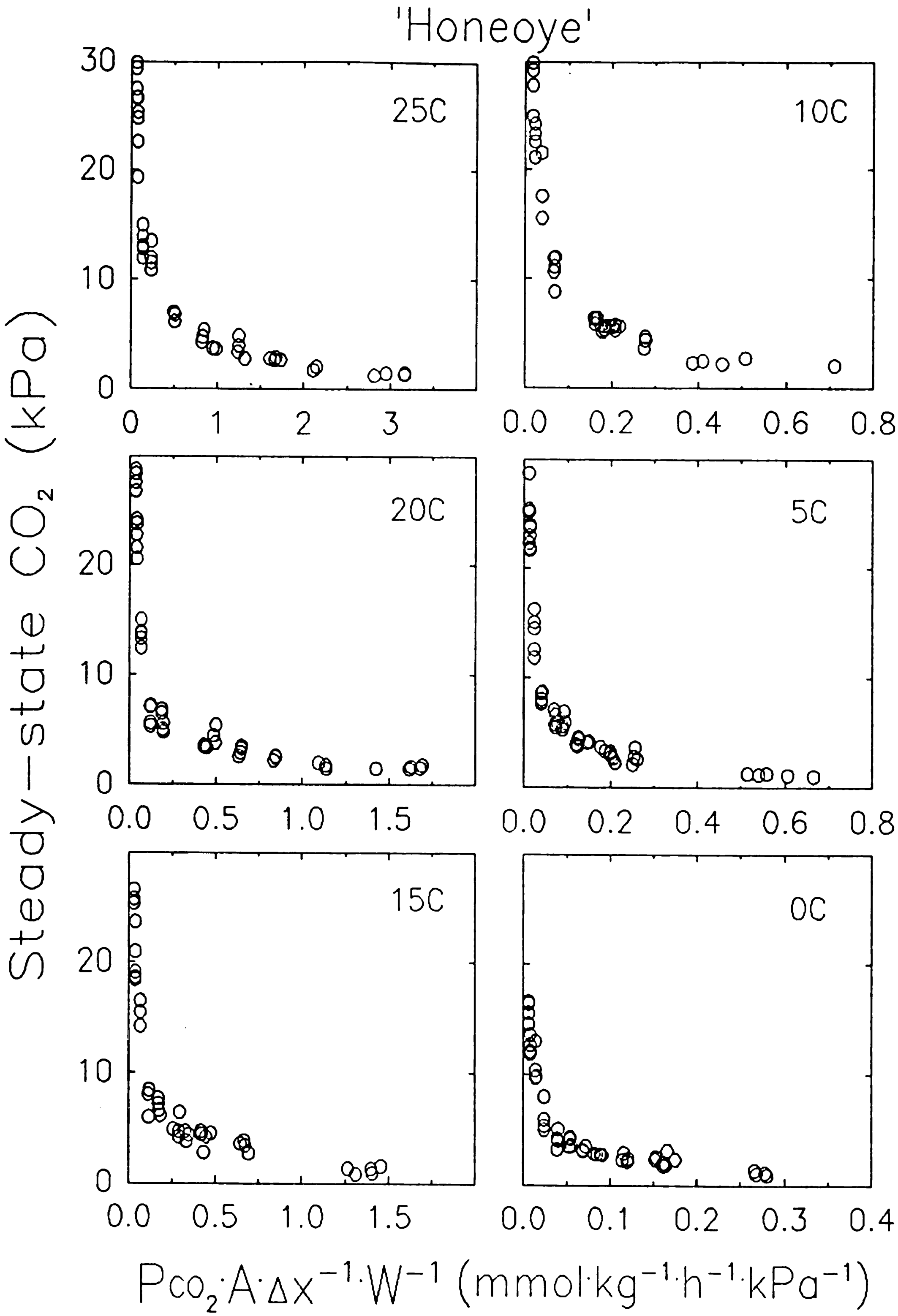

'Honeoye'
Steady-state CO_2 (kPa)
25C
10C
20C
5C
15C
0C
0
10
20
30
0
1
2
3
0.0
0.2
0.4
0.6
0.8
0.0
0.5
1.0
1.5
0.0
0.1
0.2
0.3
0.4
Pco₂·A·Δx⁻¹·W⁻¹ (mmol·kg⁻¹·h⁻¹·kPa⁻¹)

Fig. 4. Effect of changing the ratio of package surface area (cm^2) to film thickness (cm) and fruit weight on steady-state CO_2 for 'Allstar' strawberry stored at temperatures of 25 , 20, 15, 10, 5, and 0C.

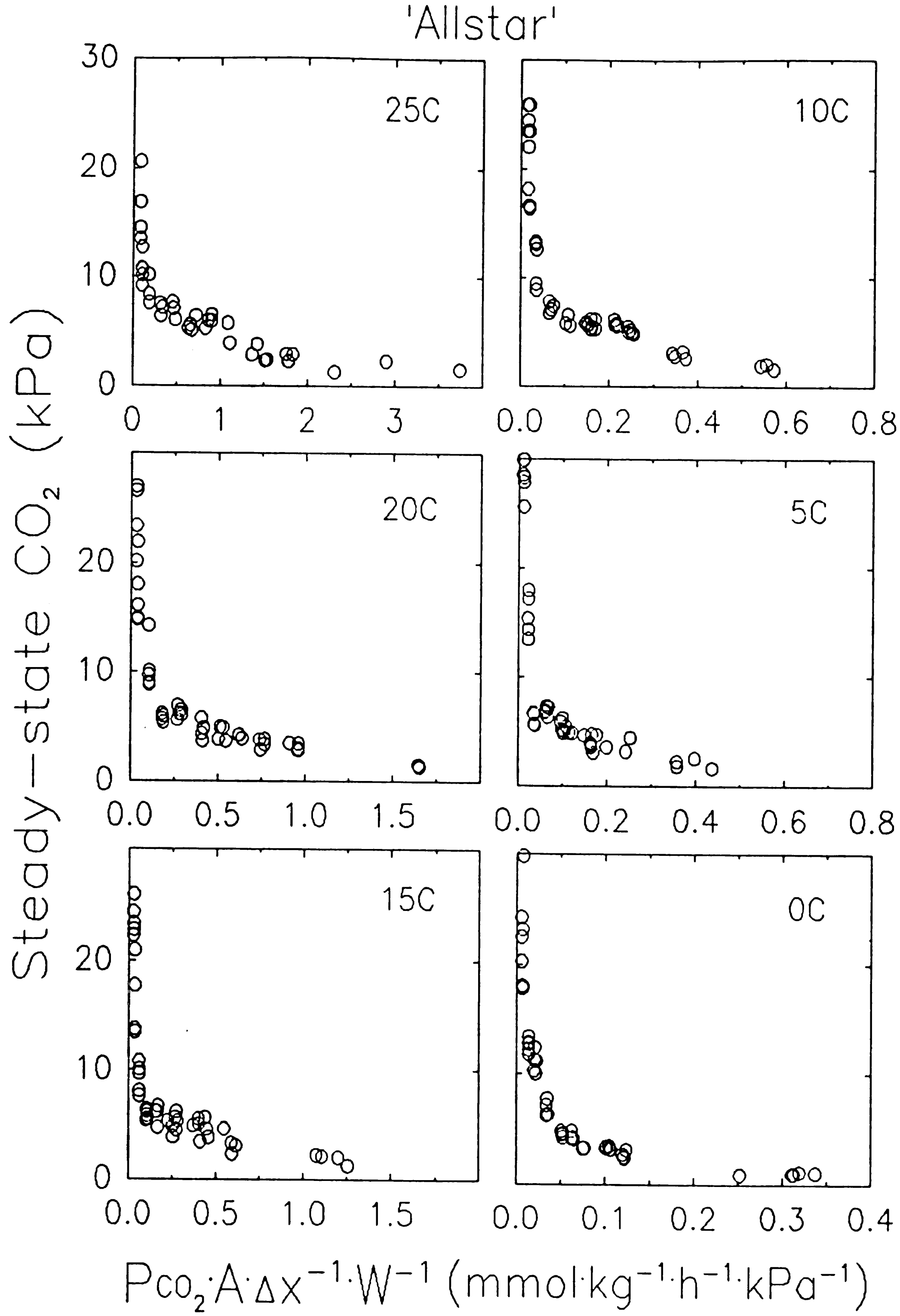

'Allstar'
25C
10C
20C
5C
15C
0C
Steady-state CO_2 (kPa)
$Pco_2 \cdot A \cdot \Delta x^{-1} \cdot W^{-1}$ (mmol·kg^{-1}·h^{-1}·kPa^{-1})

Fig. 5. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of O_2 uptake for 'Honeoye' strawberry fruit sealed in LDPE packages. See Eq. [9] and Table 2 for the equations and constants describing the curves.

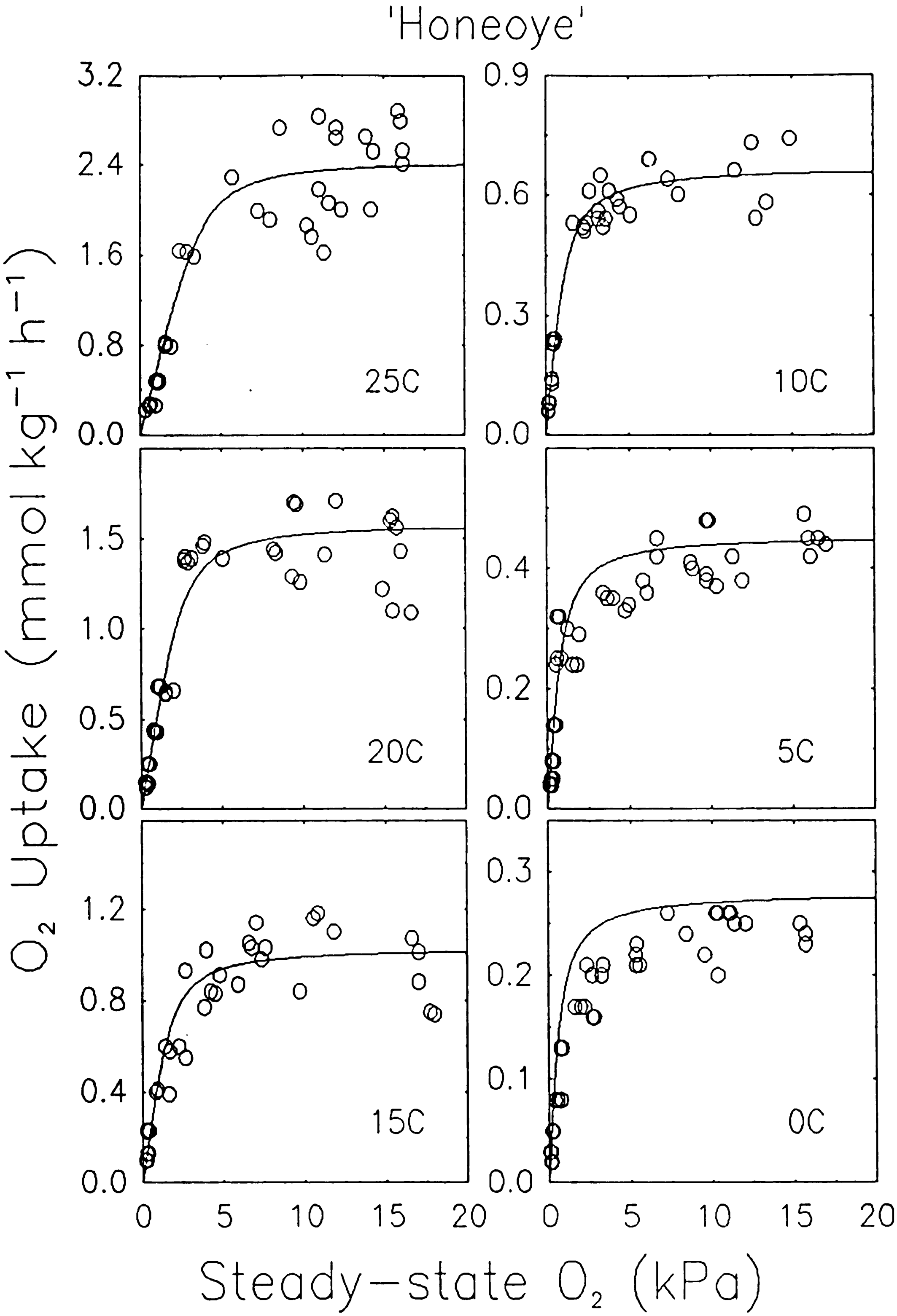

'Honeoye'
O2 Uptake (mmol kg-1 h-1)
Steady-state O2 (kPa)
25C
10C
20C
5C
15C
0C
3.2
2.4
1.6
0.8
0.0
0.9
0.6
0.3
1.5
1.0
0.5
0.4
0.2
1.2
0.3
0.1
0
5
10
15
20

Fig. 6. Interdependent effects of steady-state O_2 partial pressures and storage temperature on the calculated rate of O_2 uptake for 'Allstar' strawberry fruit sealed in LDPE packages. See Eq. [9] and Table 2 for the equations and constants describing the curves.

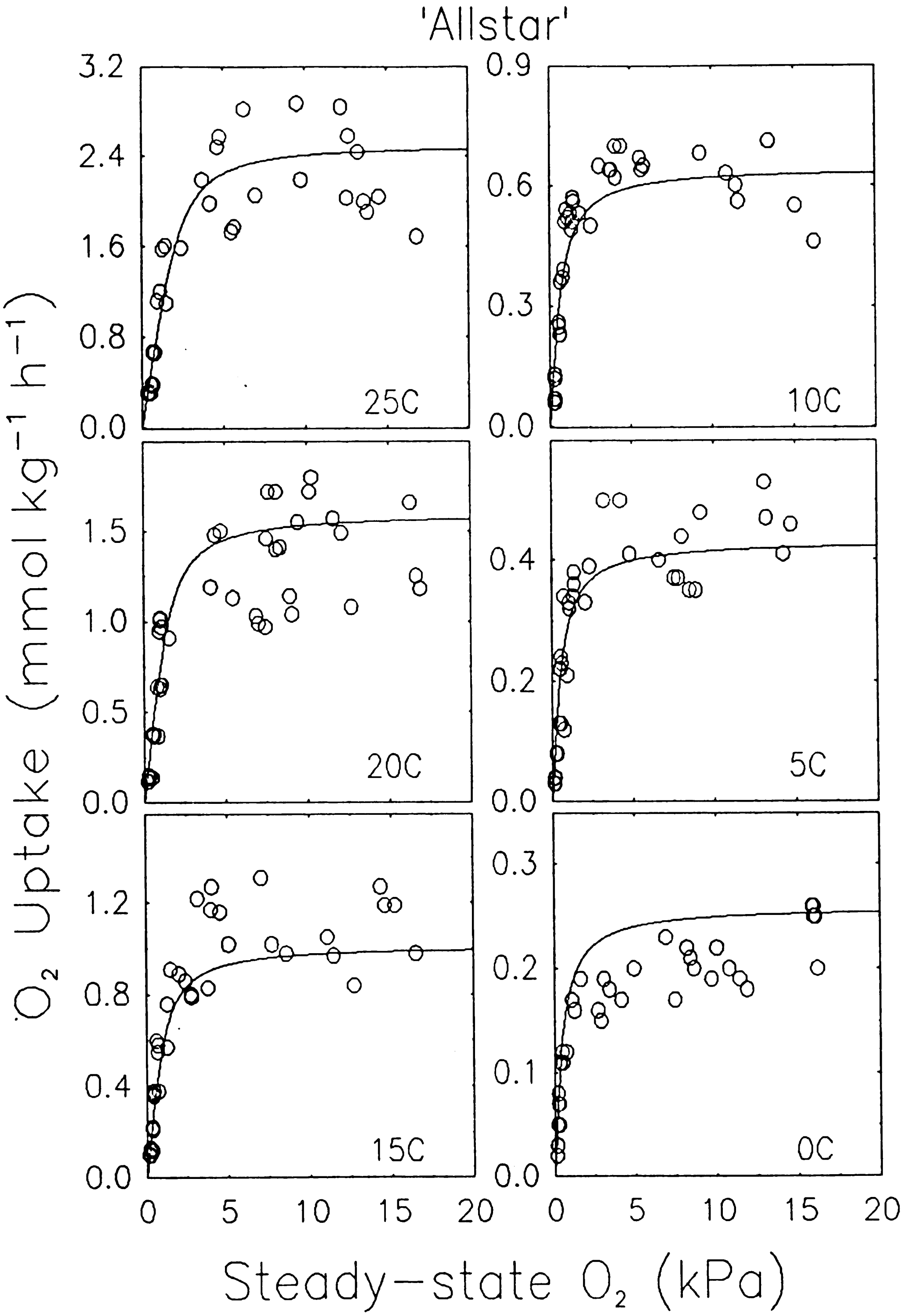

'Allstar'
O2 Uptake (mmol kg-1 h-1)
Steady-state O2 (kPa)
25C
10C
20C
5C
15C
0C

Fig. 7. Effect of steady-state O_2 partial pressure and storage temperature on the respiratory quotient of 'Honeoye' strawberry fruit sealed in LDPE packages. See Eq. [10] and Table 3 for the equations and constants describing the curves.

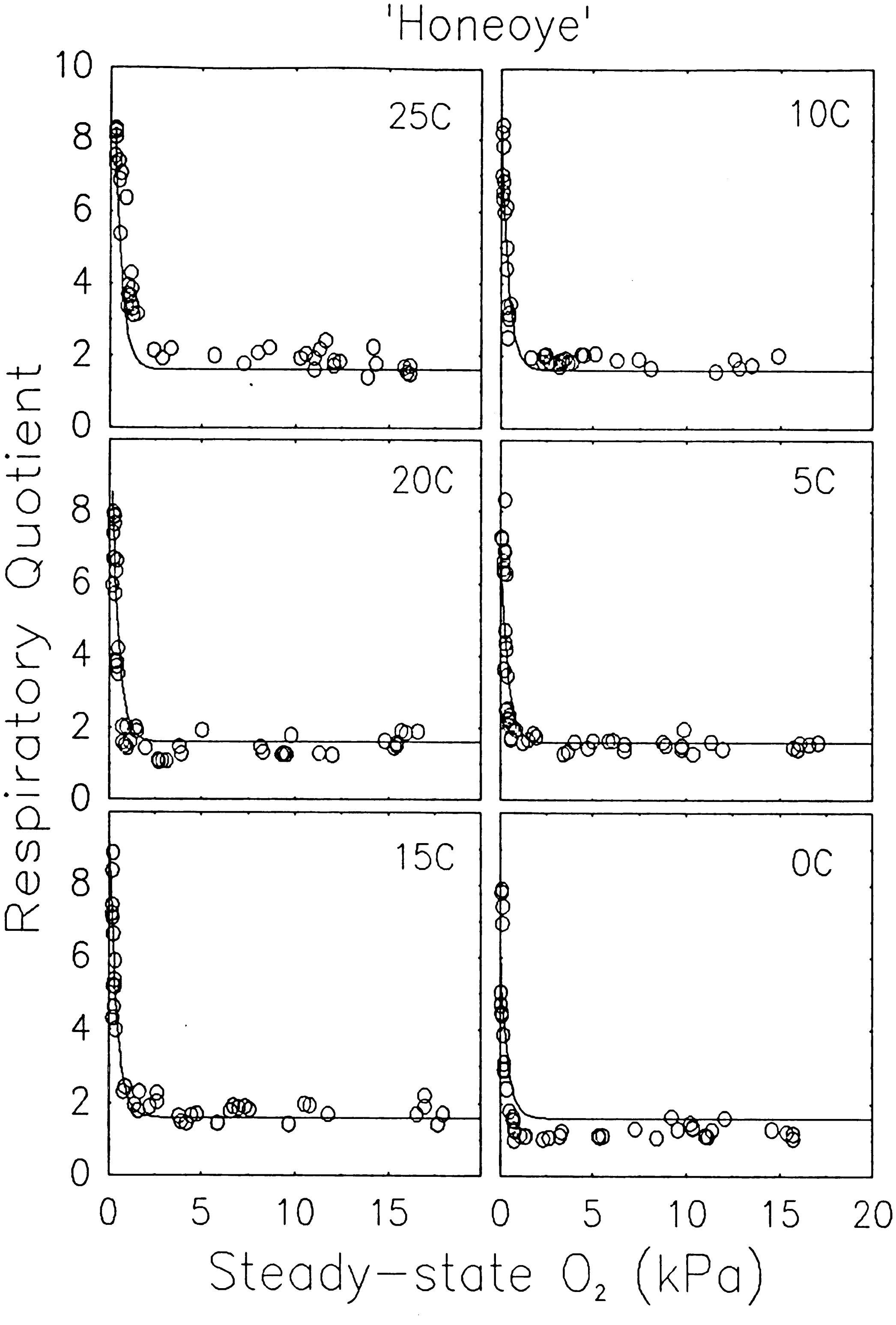

'Honeoye'
25C
10C
20C
5C
15C
0C
Respiratory Quotient
Steady-state O_2 (kPa)
0
2
4
6
8
10
0
5
10
15
20

Fig. 8. Effect of steady-state O_2 partial pressure and storage temperature on the respiratory quotient of 'Allstar' strawberry fruit sealed in LDPE packages. See Eq. [10] and Table 3 for the equations and constants describing the curves.

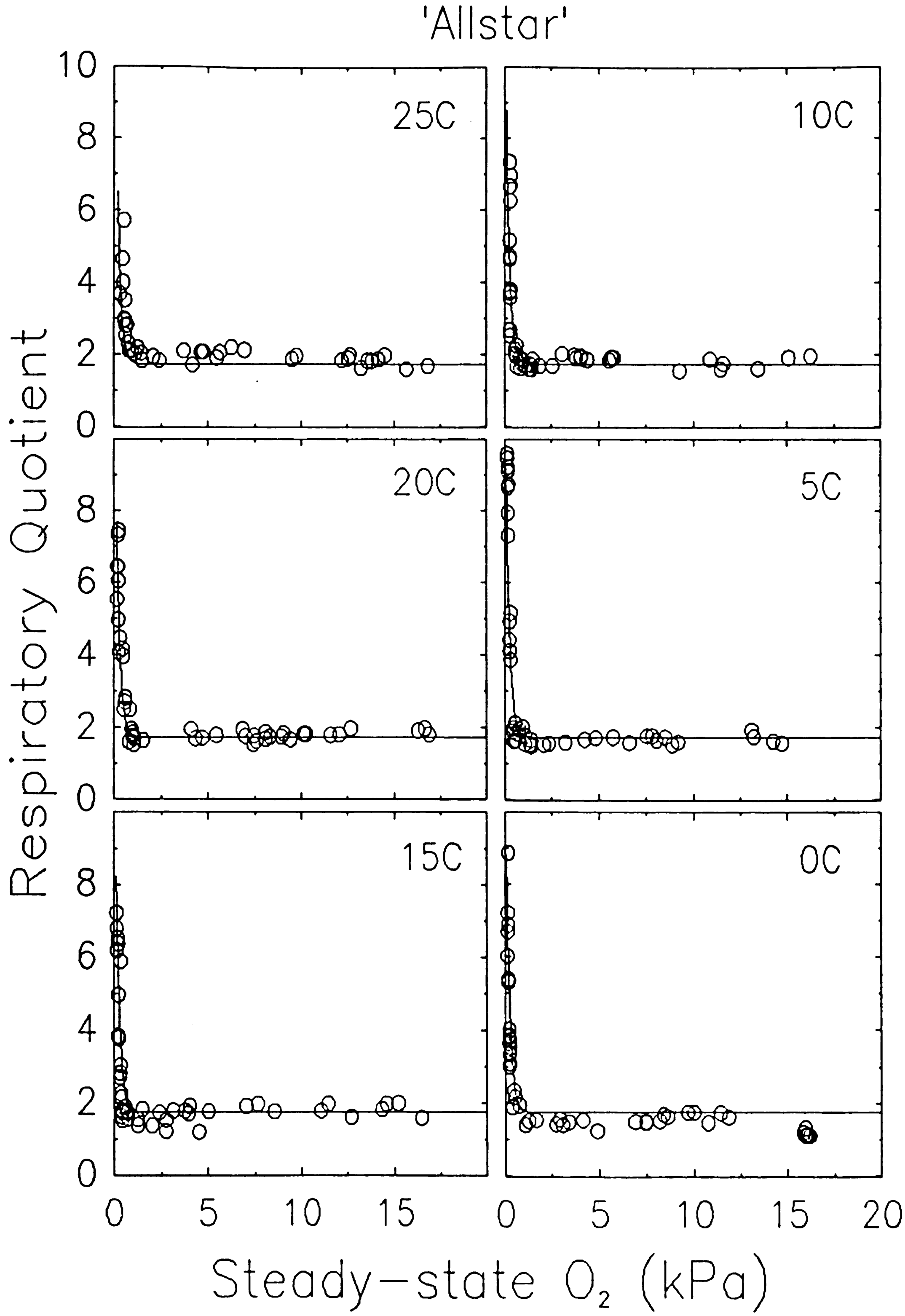

'Allstar'
25C
10C
20C
5C
15C
0C
Respiratory Quotient
Steady-state O2 (kPa)
0
2
4
6
8
10
0
5
10
15
20

Fig. 9. Interdependent effects of steady-state O_2 partial pressure and storage temperature on headspace ethanol vapor concentration for 'Honeoye' strawberry fruit sealed in LDPE packages.

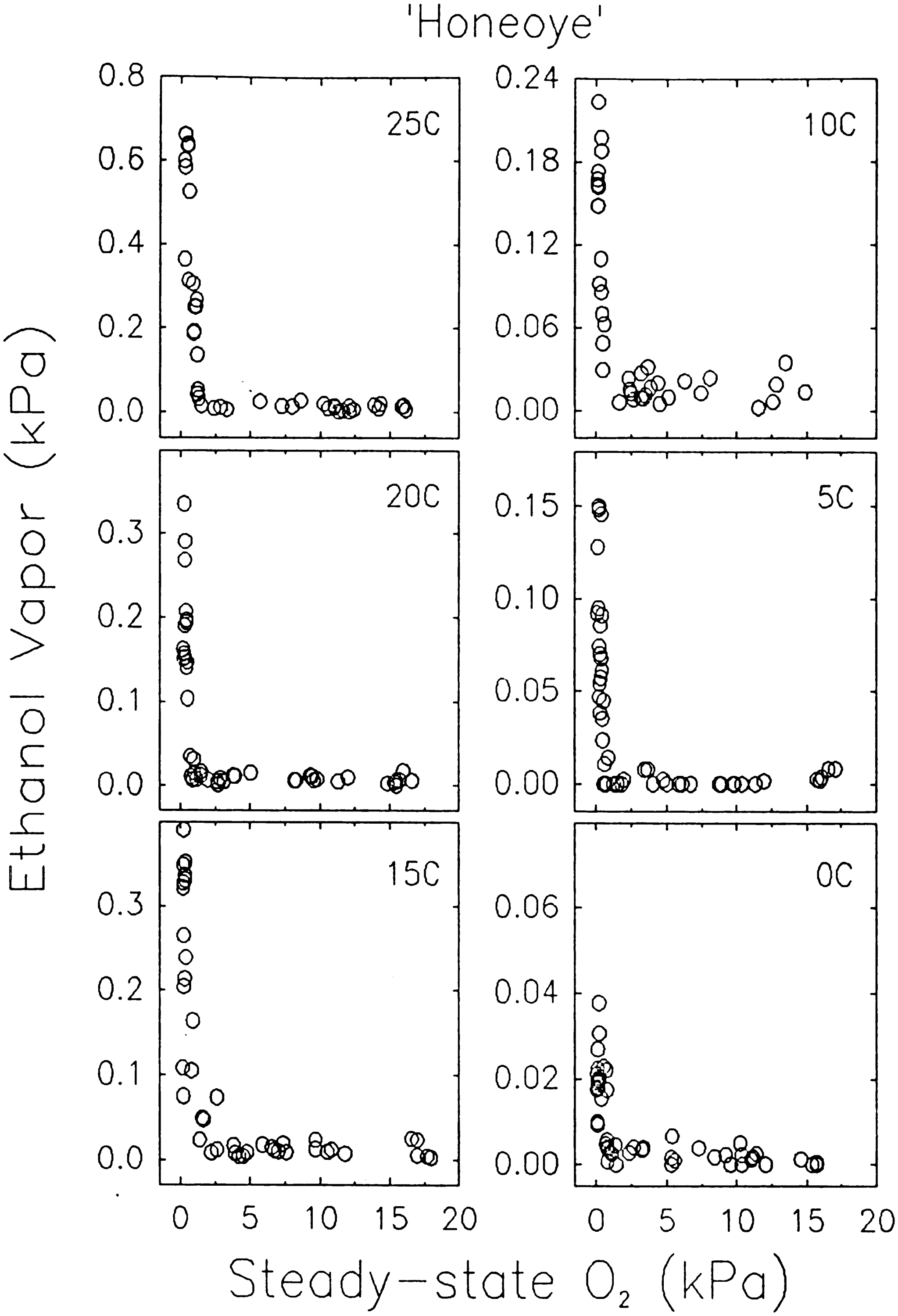
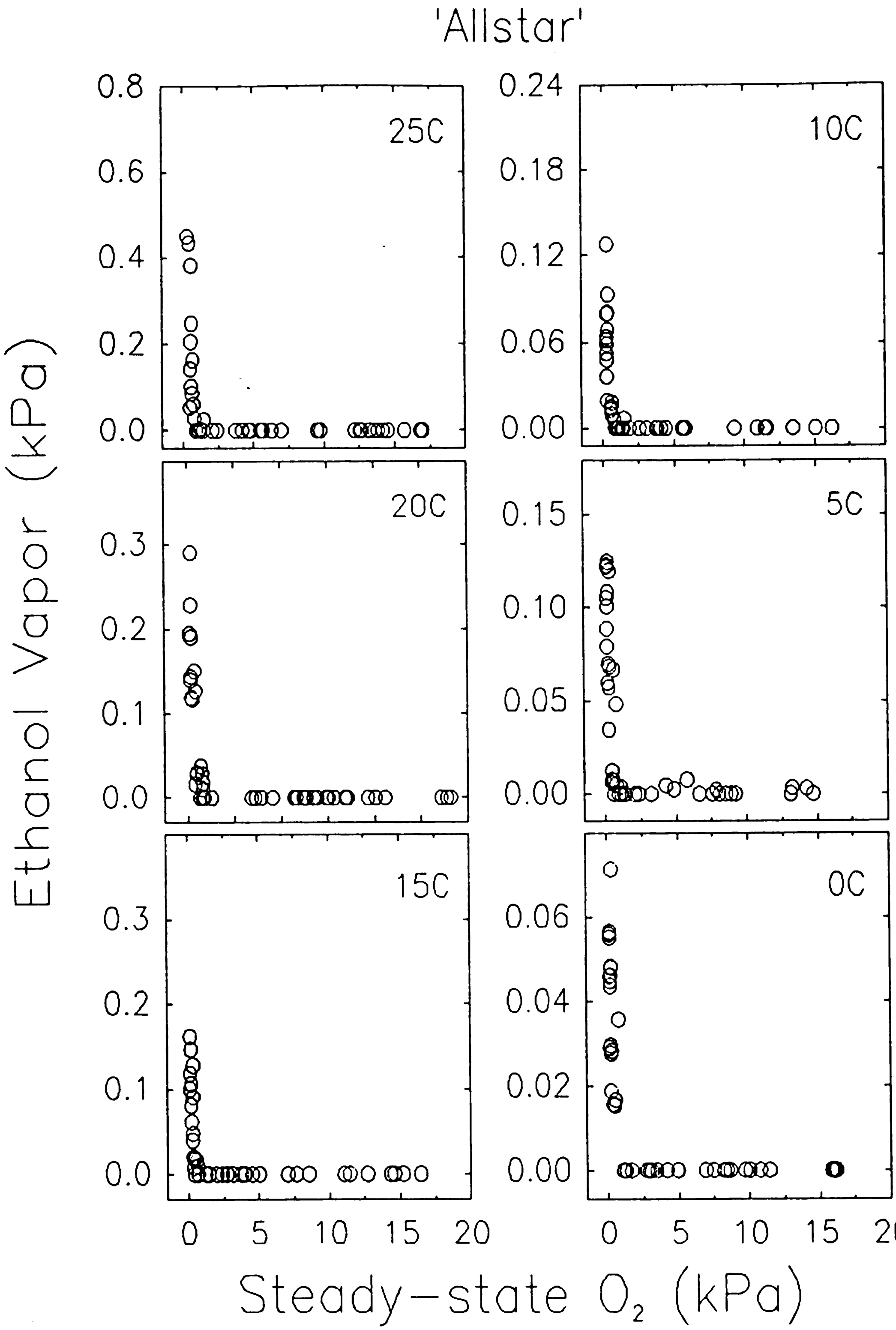

'Honeoye'
Ethanol Vapor (kPa)
Steady-state O_2 (kPa)
25C
10C
20C
5C
15C
0C
0.8
0.6
0.4
0.2
0.0
0.24
0.18
0.12
0.06
0.00
0.3
0.2
0.1
0.0
0.15
0.10
0.05
0.00
0.3
0.2
0.1
0.0
0.06
0.04
0.02
0.00
0
5
10
15
20
0
5
10
15
20

Fig. 10. Interdependent effects of steady-state O_2 partial pressure and storage temperature on headspace ethanol vapor concentration for 'Allstar' strawberry fruit sealed in LDPE packages.


'Allstar'
25C
10C
20C
5C
15C
0C
0.8
0.6
0.4
0.2
0.0
0.24
0.18
0.12
0.06
0.00
0.3
0.2
0.1
0.0
0.15
0.10
0.05
0.00
0.3
0.2
0.1
0.0
0.06
0.04
0.02
0.00
0 5 10 15 20
0 5 10 15 20
Ethanol Vapor (kPa)
Steady-state O2 (kPa)

CHAPTER 3

MODIFIED-ATMOSPHERE PACKAGING OF STRAWBERRY AND RASPBERRY FRUIT: MODELING PACKAGE O_2 AND CO_2 OVER A RANGE OF TEMPERATURES

Abstract. By combining O_2 uptake, RQ, and lower O_2 limit data previously collected for strawberry and raspberry fruit with activation energies for a low density polyethylene film and a perforation, models were developed to characterize the effect of temperature on package O_2 and CO_2 partial pressure. Based on these models it was shown that 1) LDPE film cannot provide beneficial CO_2 package levels and; 2) perforated films can provide beneficial CO_2 levels because of their CO_2 to O_2 permeability ratio but, because of their relatively low activation energy to gas diffusion an increase in temperature can cause package O_2 to fall below the lower O_2 limit. An optimum film for modified-atmosphere packaging of strawberry and raspberry fruit would have a CO_2 to O_2 permeability ratio like that of a perforation but an activation energy like that of a polymer film. A system for sensing low partial pressures of ethanol is also described and its potential use in modified-atmosphere packaging discussed.

Introduction

Mold decay, bruising, and water loss are the main factors which limit strawberry and raspberry fruit shelf life (Smith, 1958). Reducing storage temperature to below 5C reduces mold decay and transpiration. Elevated CO_2 atmospheres (10 to 20 kPa) can have a fungistatic effect on the decay pathogens of strawberries and raspberries (Couey and Wells, 1970; El-Kazzaz et al., 1983; Harris and Harvey, 1973; Harvey, 1982; Sommer et al., 1973; Woodward and Topping, 1972; Goulart et al., 1992; Smith, 1958; Winter et al., 1939). Elevated CO_2 has also been shown to increase firmness of strawberries (Smith and Skog, 1992; Smith, 1992) which could reduce bruising. As has already been pointed out (Kader et al., 1989; Beaudry et al., 1992; Joles et al., 1993), modified-atmosphere (MA) packaging has the potential to provide an elevated CO_2 and a high humidity environment.

In an MA package, CO_2 package level ($[CO_2]_{pkg}$) cannot be elevated without a reduction in O_2 package level ($[O_2]_{pkg}$). The extent $[O_2]_{pkg}$ must be reduced to obtain a beneficial $[CO_2]_{pkg}$ level (10 to 20 kPa) depends upon the packaging films's ratio of CO_2 to O_2 permeability. Recently, a California company has developed an MA package for strawberries that is based on the use of perforated films (Anonymous, Packer, 1993). Perforations or holes were used because they provide a ratio of CO_2 to O_2 permeability under 1.0. Nonperforated polymer films such as low density polyethylene (LDPE) are 4 to 5 times more permeable to CO_2 than to O_2.

In a commercial application of MA packaging there is a good chance that somewhere in the marketing and transportation chain these packages will encounter an increase in storage temperature. When an MA package encounters an increase in temperature, there is a distinct risk that $[O_2]_{pkg}$ could fall below the safe lower limit (Cameron et al., 1993a; Cameron et al, 1993b). It has been shown for strawberry and raspberry fruit that when O_2 falls below the lower limit anaerobic respiration is induced, fruit ethanol content increases, and off-flavors develop (Chapters 2 and 1; Ke et al., 1991; Couey et al., 1966). The decrease in $[O_2]_{pkg}$ with increasing temperature stems from an increase in O_2 uptake rate by the fruit which is larger than the increase in O_2 flux through the packaging film with temperature. The extent to which $[O_2]_{pkg}$ will change with temperature, and consequently the risk of inducing anaerobic respiration will depend upon the packaging film's activation energy (E_a) to O_2 permeation and on the fruit's change in O_2 uptake rate with temperature. For strawberry and raspberry this risk is compounded by the fact that their lower O_2 limit also increases with temperature (Chapters 2 and 1).

For strawberry and raspberry fruit, the change in O_2 uptake and CO_2 production with temperature and O_2, the change in lower O_2 limit with temperature, and the E_a of LDPE to O_2 and CO_2 permeation have been characterized (Chapters 2 and 1). The first objective of this study was to use this information to model the effect of temperature on $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ for strawberry and raspberry fruit in order to identify when anaerobic $[O_2]_{pkg}$ or if beneficial $[CO_2]_{pkg}$ levels are reached in MA packages made with LDPE or perforations.

When induction of anaerobic respiration occurs there is usually a lag phase before the development of off-flavors (Kader et al., 1989; Ke et al., 1991). As fruit go anaerobic, they begin to produce ethanol. If the ethanol produced by a fruit could be sensed and used to increase package permeability, then $[O_2]_{pkg}$ would increase and off-flavors could be avoided. The second objective was to introduce a concept and a technique which may help avoid the development of off-flavors in MA packages by sensing and responding to the ethanol produced by anaerobic fruit.

Model Development

Total O_2 uptake of strawberry and raspberry fruit at steady state conditions can be described by:

$$R_{O_2} = \frac{\frac{P_{O_2} \cdot A}{\Delta x}\left([O_2]_{atm} - [O_2]_{pkg}\right)}{W} \qquad [1]$$

(Chapters 2 and 1) where R_{O_2} is the rate of O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$); P_{O_2} is the packaging film's permeability coefficient for O_2 ($mmol \cdot cm \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$); A is film area ($cm^2$); Δx is film thickness (cm); $[O_2]_{pkg}$ and $[O_2]_{atm}$ are package and atmospheric O_2 partial pressures (kPa), respectively (Chapters 2 and 1; Cameron, 1990; Beaudry et al., 1992). R_{O_2} as a function of $[O_2]_{pkg}$ was also described by the Michaelis-Menten equation:

$$R_{O_2} = \frac{R_{O_2}^{max} \cdot [O_2]_{pkg}}{K_{1/2} + [O_2]_{pkg}} \qquad [2]$$

where $R_{O_2}^{max}$ is the maximum rate of O_2 uptake at that temperature; $K_{1/2}$ is an apparent K_m of the entire fruit which incorporates any resistance of the fruit's skin to O_2 diffusion and thus includes any differences between O_2 diffusion and O_2 uptake as function of temperature (Chapters 2 and 1) . Combining Eq. [1] and [2] yielded:

which was solved for $[O_2]_{pkg}$:

$$[O_2]_{pkg} = \frac{\sqrt{(K_{1/2} + W \frac{\Delta x}{P_{O_2} A} R_{O_2}^{max} - [O_2]_{pkg})^2 + 4 K_{1/2} [O_2]_{atm}}}{2} - \frac{(W \frac{\Delta x}{P_{O_2} A} R_{O_2}^{max} + K_{1/2} - [O_2]_{atm})}{2} \quad [3]$$

(Cameron et al., 1993a). For strawberry and raspberry $R_{O_2}^{max}$ as function of temperature ($R_{O_2}^{max,T}$) has been defined:

$$R_{O_2}^{max,T} = R_{O_2}^{max,0} \cdot Q_{10}^{(\frac{T}{10})} \quad [4]$$

where $R_{O_2}^{max,0}$ is the maximum rate of O_2 uptake at 0C, Q_{10} is the increase in O_2 uptake for every 10C increase in temperature, and T is temperature in C (Chapters 2 and 1). In a previous study, an apparent K_m ($k_{1/2}$) for strawberry fruit was estimated which didn't incorporate skin permeability and was based on fruit internal O_2 partial pressure. Because Eq. [3] uses an apparent K_m which describes a $[O_2]_{pkg}$ partial pressure, the $k_{1/2}$ (an internal O_2 partial pressure) reported for strawberries needed to be converted to a $[O_2]_{pkg}$ partial pressure. This was accomplished using a variation of Fick's Law:

$$R_{O_2} = P_{O_2}^{skin} \cdot ([O_2]_{pkg} - [O_2]_{int}) \quad [5]$$

where $P_{O_2}^{skin}$ is a value describing the ratio of a strawberry fruit's O_2 permeability and surface area to its skin thickness and weight (Chapter 2) ($mmol \cdot kg^{-1} \cdot h^{-1} \cdot kPa^{-1}$); $[O_2]_{int}$

is an internal O_2 partial pressure (kPa). $K_{½}$ at any temperature is by definition an O_2 partial pressure at which R_{O_2} is half of $R_{O_2}^{max}$. Thus, $R_{O_2}^{max}$ divided by 2 is rate of strawberry fruit O_2 uptake at $K_{½}$. Substituting the estimated values for $P_{O_2}^{skin}$, $k_{½}$, and the function defined $R_{O_2}^{max}$ with temperature ($R_{O_2}^{max,T}$) (Chapter 2) into Eq.[5] yielded an equation that calculated $K_{½}$ with temperature ($K_{½}^{T}$):

$$K_{½}^{T} = \frac{R_{O_2}^{max,T}}{2 \cdot P_{O_2}^{skin}} + k_{½} \qquad [6]$$

For raspberry fruit the $K_{½}$ did not change significantly over the temperatures studied (Chapter 1). The constants which were estimated (Chapter 2) to describe 'Allstar' strawberry O_2 uptake ($R_{O_2}^{max,0}$, Q_{10}, $k_{½}$, and $P_{O_2}^{skin}$) are given in Table 1 and the constants estimated (Chapter 1) for 'Heritage' raspberry O_2 uptake ($K_{½}$, $R_{O_2}^{max,0}$, and Q_{10}) are given in Table 2.

Film permeability was assumed to change with temperature as defined by the Arrhenius equation:

$$P_i = A_r \cdot \exp\left(-\frac{E_a}{R \cdot (T+273)}\right) \qquad [7]$$

where P_i is permeability to O_2 or CO_2 ($mmole \cdot cm \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$); A_r is the Arrhenius constant for O_2 or CO_2 permeation; E_a is the energy of activation of O_2 or CO_2 permeation ($kJ \cdot mol^{-1}$); and R is the gas constant (.0083144 $kJ \cdot mol^{-1} \cdot K^{-1}$). The A_r and E_a values for LDPE reported in Chapter 1 were used (A_rs of .07 and .177 for O_2 and CO_2 permeation, respectively; E_as of 36.85 and 35.34 for O_2 and CO_2 permeability, respectively). For perforations it was assumed permeability changed in a manner consistent with the Arrhenius equation but with an E_a similar to that of free diffusion (≈5 kJ mol^{-1}) (Nobel, 1983) and an A_r for CO_2 permeation equal to that of O_2 permeation (i.e. permeability ratio equal to 1.0).

By substituting the equations for a change in permeability with temperature (Eq. [7], the estimated $K_{½}$ values (Eq. [6] or Table 2), and the function defined for $R_{O_2}^{max,T}$ for strawberry and raspberry fruit (Eq. [4]) into Eq. [3] allowed $[O_2]_{pkg}$ to be calculated for strawberry and raspberry fruit over a range of temperatures.

CO_2 production at any temperature and O_2 level can be calculated by multiplying the RQ by the R_{O_2} at that temperature and O_2. Thus, $[CO_2]_{pkg}$ as a function of temperature and O_2 can calculated:

$$[CO_2]_{pkg} = (R_{O_2}^{T} \cdot RQ^{T} \cdot W \cdot \frac{\Delta x}{P_{CO_2}\, A}) + [CO_2]_{atm} \qquad [8]$$

where $R_{O_2}^{T}$ and RQ^{T} are the equations estimated for strawberry and raspberry O_2 uptake and RQ as a function of temperature and O_2 partial pressure (Chapters 2 and 1); P_{CO_2} is film or perforation permeability to CO_2 ($mmol \cdot cm \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$). $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ was calculated for strawberry and raspberry fruit only over the temperature range (0 to 25C and 0 to 20C) where O_2 uptake and RQ have been measured by previous studies (Chapters 2 and 1).

Materials and Methods

Ethanol sensor

The ethanol sensor was based on the enzyme alcohol oxidase which catalyzes the reaction:

$$Ethanol + O_2 \xrightarrow{Alcohol\,Oxidase} H_2O_2 + Acetaldehyde$$

To obtain a color change, the production of H_2O_2 was coupled to another enzyme reaction. The color change reaction was catalyzed by the enzyme peroxidase which used H_2O_2 to oxidize
o-dianisidine and produce a color change in o-diansisidine from white to dark brown. The enzymes and the o-dianisidine were all imbedded into a polyvinyl-alcohol (PVA) film. As o-dianisidine is oxidized the absorbance at 460 nm increases which can be seen visually and quantified spectrophotometrically.

The procedure for preparing the ethanol sensor was to first wash the plasticizer (glycerol) out of the plasticized PVA by simply rinsing it in a water bath for 2 hours. The PVA was then dried. One gram of PVA was dissolved in ≈9 ml H_2O by heating in a microwave. The viscous dissolved solution was then brought to a pH of 7.5 by adding a 50 mM $NaPO_4$ buffer in .1 ml aliquots until the pH was reached. pH measurement was accomplished using indicator strips (Baxter, McGaw Park, IL). Ten mg (4 units) of alcohol oxidase

(Sigma, St. Louis, Mo), 2 mg (100 units) peroxidase (Sigma, St. Louis, MO) and 50 mg o-dianisidine (water insoluble) (Sigma, St. Louis, MO) was added to the viscous solution. The viscous solution was then spread over a glass plate (≈100 cm^2 area) using electrical tape to provide a border. The gel on the plate was then dried overnight under N_2.

To analyze the reaction, a 1 cm^2 piece of the film was cut and put in a high humidity jar for 1 hour. It was then suspended on the inside of a spectrophotometry cuvette in the place at which the beam passes through the cuvette. A small dab of vacuum grease was used to suspend the film. Ethanol solutions were added to the bottom of the cuvette, making sure it did not touch the film. The cuvette was sealed and placed in the spectrophotometer where absorbance at 460 nm was measured at 25C.

Results and Discussion

The lower O_2 limit of strawberry and raspberry fruit (dotted line in Figs. 1 and 2) has been reported to increase with temperature (Chapters 2 and 1). An MA package, using a LDPE film, designed to have a $[O_2]_{pkg}$ above the lower O_2 limit would only generate $[CO_2]$pkg levels of 3 to 8 kPa (top of Figs. 1 and 2) for strawberry and raspberry fruit. $[CO_2]_{pkg}$ levels of below 10 kPa generally do not reduce mold decay (Couey and Wells, 1970; El-Kazzaz et al., 1983; Harris and Harvey, 1973; Harvey, 1982; Sommer et al., 1973) and are less effective in increasing firmness of strawberry fruit (Smith, 1992).

LDPE is 4 to 5 times more permeable to CO_2 than to O_2. This means CO_2 production by a fruit would have to be 4 to 5 times greater than O_2 uptake to raise $[CO_2]_{pkg}$ above 10 kPa. A difference between CO_2 production and O_2 uptake of this magnitude only occurs when fruit are very anaerobic and the risk of off-flavor development is very high. Thus, an LDPE alone cannot be an effective packaging film for strawberry and raspberry fruit. If an LDPE was combined with a in-package CO_2 generating system like that the one developed for meats (Benedict et al., 1975), then beneficial $[CO_2]_{pkg}$ levels could perhaps be generated.

The differential between CO_2 and O_2 permeability for a perforation is under 1.0 (Cameron et al., 1993a). The RQ (ratio of CO_2 production to O_2 uptake) for strawberry and raspberry fruit was found to be over 1.0. Combining the permeability ratio of a perforation with the RQ of the fruit allows beneficial $[CO_2]_{pkg}$ levels (above 10 kPa) to be generated at safe $[O_2]_{pkg}$ levels at optimum low temperatures (middle of Figs. 1 and 2). However, in a perforated package, it is predicted that safe $[O_2]_{pkg}$ levels are not maintained when temperatures increase to above 15C for strawberry (middle of Fig. 1) and above 7C for raspberry (middle of Fig. 2).

An LDPE package was predicted to maintain safe $[O_2]_{pkg}$ levels over the same temperature range (top of Figs. 1 and 2) because its activation energy for O_2 permeation is ≈7 times higher than that for a perforation (36.85 compared to ≈5.0 $kJ \cdot mol^{-1}$) (Chapter 1; Nobel, 1983; Cameron et al., 1993a). A perforated package can be designed to compensate for its low activation energy by having very high initial $[O_2]_{pkg}$ levels at low temperatures but, if this is done, beneficial $[CO_2]_{pkg}$ levels are not generated at the temperatures that are optimum for storage (bottom of Figs. 1 and 2).

A very effective MA package for strawberry and raspberry fruit would be one that had a permeability ratio similar to that of a perforation but had an E_a like that of LDPE. Figure 3 shows that in a package with these characteristics $[CO_2]_{pkg}$ could be maintained at beneficial levels while $[O_2]_{pkg}$ remained at a safe levels as temperature increased. Unfortunately a packaging film with these characteristics is not currently available. So, other ways to avoid the risk of inducing anaerobic respiration in an MA package must be devised.

One concept for avoiding the risk is based on the fact that there is usually a lag phase between induction of anaerobic respiration and the development of off-flavors (Kader et al., 1989; Ke et al., 1991). When fruit go anaerobic, they begin to produce ethanol. If the ethanol produced by a fruit could be sensed and used to increase package permeability, then $[O_2]_{pkg}$ would increase and off-flavors could be avoided.

We are developing a sensing system that will change colors in response to very low partial pressures of ethanol. This system uses an enzyme called alcohol oxidase which is imbedded in a film of polyvinyl-alcohol. This enzyme catalyzes the oxidation of ethanol to acetaldehyde and produces hydrogen peroxide in the process. Currently to sense ethanol vapor and obtain a color change, we are coupling the alcohol oxidase catalyzed reaction to another enzyme reaction. This reaction utilizes the hydrogen peroxide produced by alcohol oxidase to oxidize a compound that changes in absorbance and color as its oxidized. Figure 4 shows the change in absorbance over time which occurs when the ethanol sensor is exposed to an ethanol partial pressure of .006 kPa or to water. There is a lag phase in this reaction that lasts ≈30 minutes but after 50 minutes there is a significant difference in absorbance at 460 nm. After 90 minutes a noticeable change in color was seen (absorbance of ≈.10).

Because some of the chemicals used in our current color change reaction are suspected carcinogens this system is not suitable to be used in commercial MA packaging applications. However, we have shown that our ethanol sensor can produce hydrogen peroxide at very low ethanol partial pressures (Fig. 4). Hydrogen peroxide is a very reactive chemical, so it seems feasible that it could be active enough in small quantities to cause a change in O_2 permeability perhaps, via a free radical reaction or by triggering a electronic detector. We have not yet developed a system to accomplish this but feel its development would be a major breakthrough for MA technology.

Another approach for maintaining safe $[O_2]_{pkg}$ levels with an increase in temperature is to have the package respond to the temperature of the storage environment. This approach was proposed by Patterson and Cameron (1992). Their system is based on the opening of holes in a package when temperature increases beyond a threshold. The holes are originally blocked by hydrocarbons with a specific melting temperature. When the melting temperature of the hydrocarbon is exceeded the hole is opened and consequently O_2 permeability increased.

Because current packaging films do not have the characteristics (i.e. favorable permeability ratio and E_a) to obtain beneficial $[CO_2]_{pkg}$ and safe $[O_2]_{pkg}$ levels for strawberry and raspberry fruit over a range of possible storage temperatures, some type of sense-and-respond technique should be developed to supplement perforation-based MA packaging.

Table 1. Constants describing the relationship between O_2 uptake ($mmol \cdot kg^{-1} \cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for 'Allstar' strawberry fruit (estimated in Chapter 2). $R_{O_2}^{max,0}$ is the maximum rate of O_2 uptake at 0C, Q_{10} is the increase in O_2 uptake for a 10C increase in temperature, $k_{1/2}$ is the internal O_2 partial pressure at which the rate of O_2 uptake is half the maximum rate, and $P_{O_2}^{skin}$ is a value describing the of the fruit's skin to O_2.

$R_{O_2}^{max,0}$	SE	Q_{10}	SE	$k_{1/2}$	SE	$P_{O_2}^{skin}$	SE
.259	±.02	2.48	±.08	.368	±.11	1.11	±.15

Table 2. Constants describing the relationship between O_2 uptake ($mmol\cdot kg^{-1}\cdot h^{-1}$), steady-state O_2 partial pressure (kPa), and temperature for 'Heritage' raspberry (estimated in Chapter 1). $K_{½}$ is the external (package O_2) O_2 partial pressure at which the rate of O_2 uptake is half the maximum rate.

$K_{½}$	SE	$R_{O_2}^{max,0}$	SE	Q_{10}	SE
5.59	±.40	.872	±.04	1.92	±.20

List of References

Anonymous. 1990. FreshHold extends breathable packaging to fresh strawberries. Packer, August 11, XCVII(32):5A.

Beaudry, R.M., A.C. Cameron, A. Shirazi, and D.L. Dostal-Lange. 1992. Modified atmosphere packaging of blueberry fruit: Effect of temperature on package O_2 and CO_2. J. Amer. Soc. Hort. Sci. 117:436-441.

Benedict, R.C., E.D. Strange, S. Palumbo, and C.E. Swift. 1975. Use of in-package controlled atmospheres for extending the shelf life of meat products. J. Agric. Food Chem. 23(6):1208-1212

Cameron, A.C. 1990. Modified atmosphere packaging: A novel approach for optimizing package oxygen and carbon dioxide. Proc. 5th Int'l. CA Conf., Wenatchee, Wash., 14-16 June.

Cameron, A.C., R.M. Beaudry, N.H. Banks, and M.V. Yelanich. 1993a. Modified-atmosphere packaging of blueberry fruit: Modeling respiration and package oxygen partial pressure at different temperatures. Accepted to J. Amer. Soc. Hort. Sci.

Cameron, A.C., B.D. Patterson, P.C. Talasila, and D.W. Joles. 1993b. Modeling the risk in modified-atmosphere packaging: A case for sense-and-respond packaging. Proc. Intl. CA Conf. In Press.

Couey, H.M., Follstad M.N. and M. Uota. 1966. Low oxygen atmospheres for control of postharvest decay of fresh strawberries. Phytopathology 56:1339.

Couey, H.M. and J.M. Wells. 1970. Low oxygen or high carbon dioxide atmospheres to control of postharvest decay of fresh strawberries. Phytopathology 60:47.

El-Kazzaz, M.K., N.F. Sommer, and R.J. Fortage. 1983. Effects of different atmospheres on postharvest decay of strawberries. Phytopathology 73:282.

Goulart, B.L., P.E. Hammer, K.B. Evensen, W. Janisiewcz, and F. Takeda. 1992. Pyrrolnitrin, Captan + Benomyl, and high CO_2 enhance raspberry shelf life at 0 or 18C. J. Amer. Soc. Hort. Sci. 117:265-270.

Harris, C.M. and J.M. Harvey. 1973. Quality and decay of California strawberries stored in CO_2 enriched atmospheres. Plant Dis. Reptr. 57:44.

Harvey, J.M. 1982. CO_2 atmospheres for truck shipment. In Controlled atmospheres for storage and transport of perishable agricultural commodities, D.G. Richardson and M. Meheriuk (Ed.) p 359. Timber Press, Beaverton.

Joles, D.W., A.C. Cameron, A. Shirazi, P.D. Petracek, and R.M. Beaudry. 1993. Modified-atmosphere packaging of 'Heritage' red raspberry fruit: The respiratory response to reduced oxygen, enhanced carbon dioxide, and temperature. Accepted J. Amer. Soc. Hort. Sci. June 1993.

Kader, A.A., D. Zagory, E.L. Kerbel. 1989. Modified atmosphere packaging of fruits and vegetables. Crit. Rev. Food Sci. Nutrition 28:1-30

Ke, D., L. Goldstein, M. O'Mahony, and A.A. Kader. 1991. Effects of short-term exposure to low O_2 and high CO_2 atmospheres on quality attributes of strawberries. J. Food Sci. 56(1):50-54.

Nobel, P.S., 1983. Biophysical plant physiology and ecology. W.H. Freeman, New York, pg. 608.

Patterson, B.D. and A.C. Cameron. 1992. Modified atmosphere packaging. International Patent No. PCT/AU90/00267.

Smith, W.H. 1958. The harvesting, precooling, transport, and storage of strawberries and raspberries. Food Invest. Board Misc. Paper 1058.

Smith, R.B. 1992. Controlled atmosphere storage of 'Redcoat' strawberry fruit. J. Amer. Soc. Hort. Sci. 117:260-264.

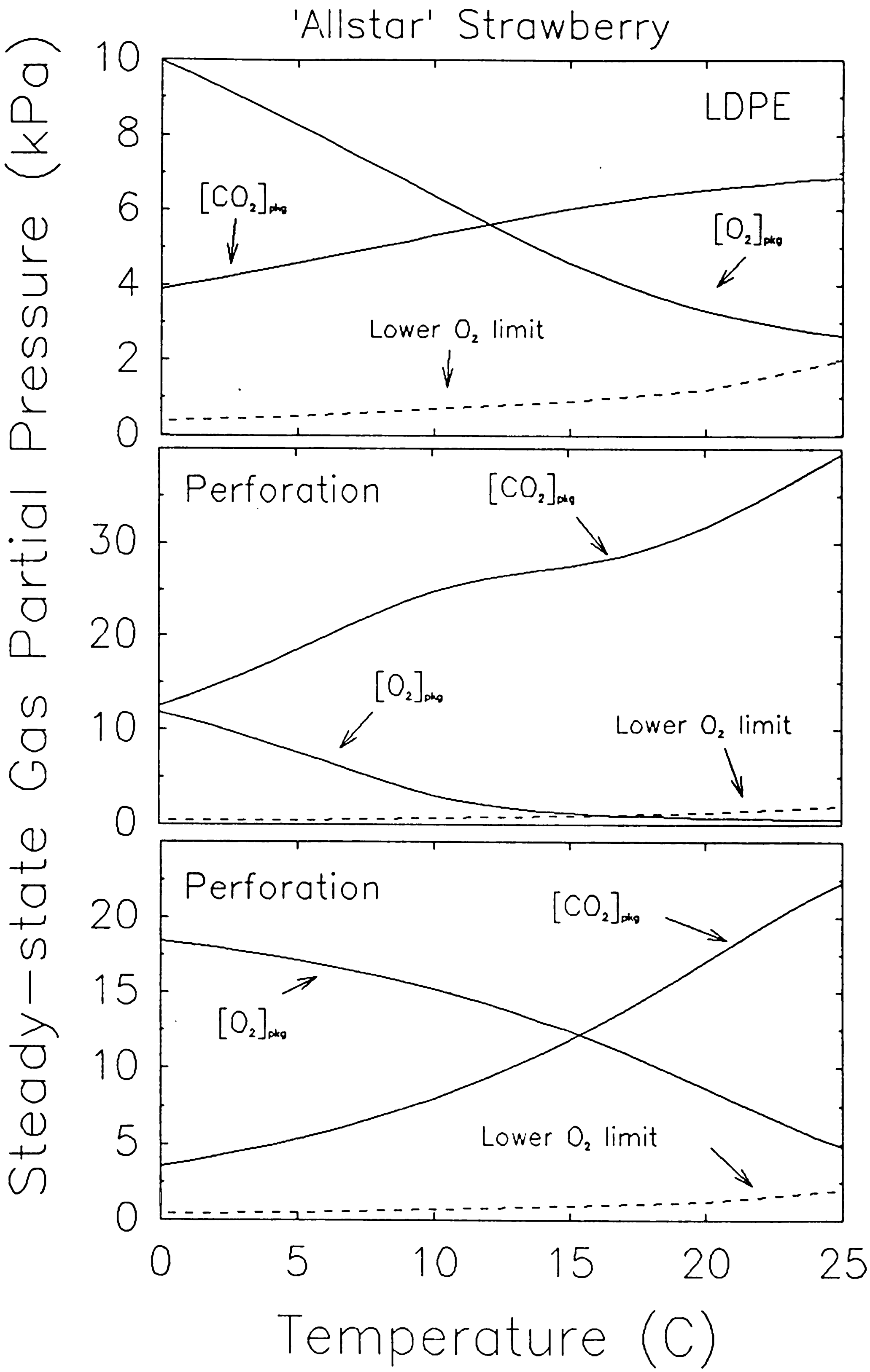
Smith, R.B. and L.J. Skog. 1992. Postharvest carbon dioxide treatment enhances firmness of several cultivars of strawberry. HortScience 27(5):420-421.

Sommer, N.F., R.J. Fortlage, F.G., Mitchell, and E.C. Maxie. 1973. Reduction of postharvest loss of strawberry fruit from grey mold. J. Amer. Soc. Hort. Sci. 98:285.

Winter, J.D., R.H. Landon, and W.H. Alderman. 1939. Use of carbon dioxide to retard the development of decay in strawberries and raspberries. Proc. Amer. Soc. Hort. Sci. 37:583-587.

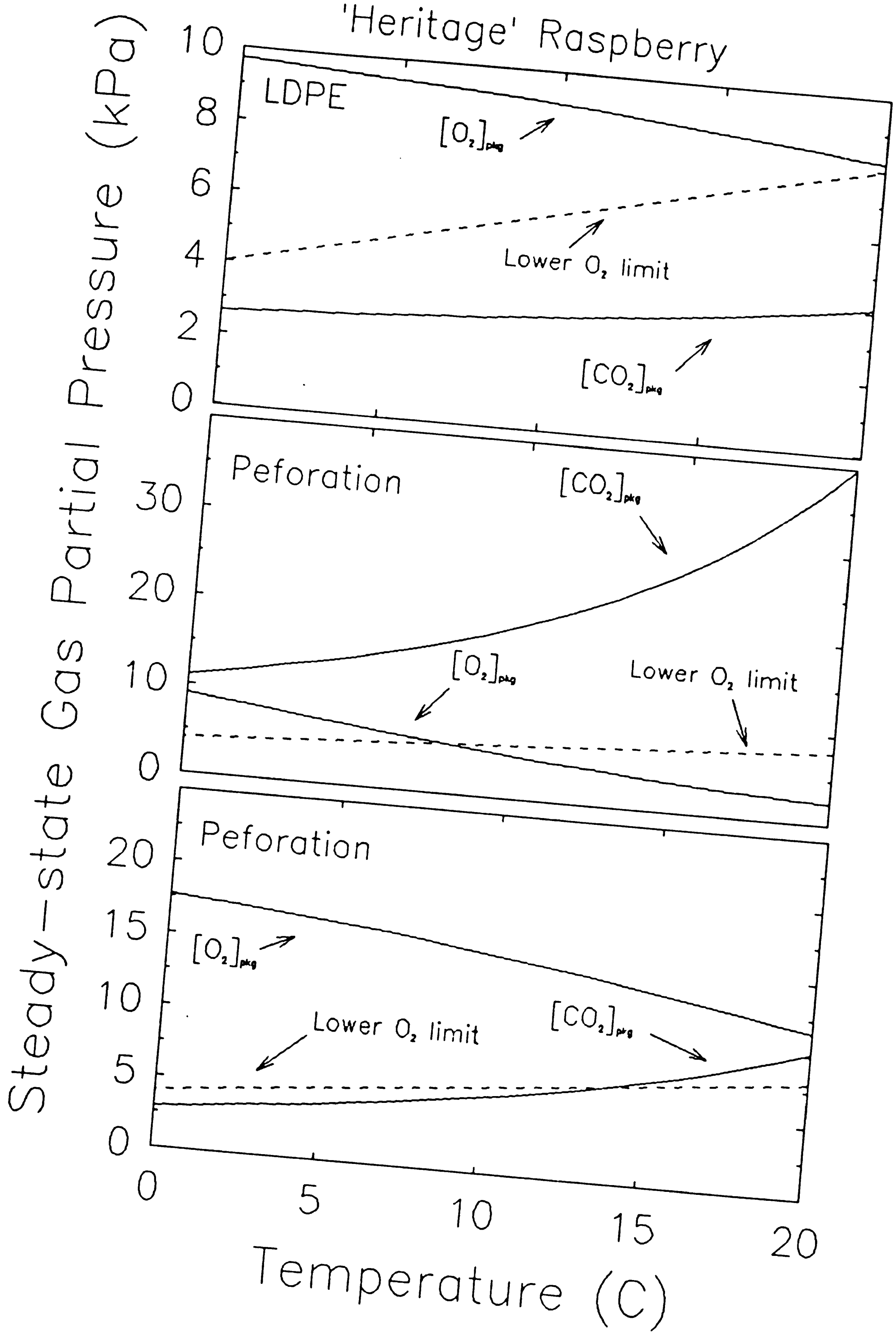
Woodward, J.R., and A.J. Topping. 1972. The influence of controlled atmospheres on the respiration rates and storage behavior of strawberry fruits. J. Hort. Sci. 47:547-533.

Fig. 1. Predicted changes in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ as a function of temperature and film permeability characteristics for 'Allstar' strawberry fruit from Eq. [3] and Eq. [8] with constants from Table 1 and Chapter 2. The dotted line on each graph represents the lower O_2 limit for 'Allstar' strawberry fruit as determined by the increase in RQ and ethanol content (Chapter 2).



'Allstar' Strawberry
LDPE
$[CO_2]_{pkg}$
$[O_2]_{pkg}$
Lower O_2 limit
Perforation
$[CO_2]_{pkg}$
$[O_2]_{pkg}$
Lower O_2 limit
Perforation
$[CO_2]_{pkg}$
$[O_2]_{pkg}$
Lower O_2 limit
Steady-state Gas Partial Pressure (kPa)
Temperature (C)
0
5
10
15
20
25

Fig. 2. Predicted changes in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ as a function of temperature and film permeability characteristics for 'Heritage' raspberry fruit from Eg. [3] and Eq. [8] with constants from constants Table 2 and Chapter 1. The dotted line on each graph represents the lower O_2 limit for 'Heritage' raspberry fruit as determined by the increase in RQ and ethanol content (Chapter 1).



'Heritage' Raspberry
Steady-state Gas Partial Pressure (kPa)
LDPE
[O2]pkg
Lower O2 limit
[CO2]pkg
Peforation
[CO2]pkg
[O2]pkg
Lower O2 limit
Peforation
[O2]pkg
Lower O2 limit
[CO2]pkg
Temperature (C)

Fig. 3. Predicted changes in $[O_2]_{pkg}$ and $[CO_2]_{pkg}$ as a function of temperature and film permeability characteristics for 'Heritage' raspberry fruit and 'Allstar' strawberry fruit from Eq. [3] and Eq. [8] with the film permeability characteristic being a E_a of 37 and a permeability ratio of 1.0.

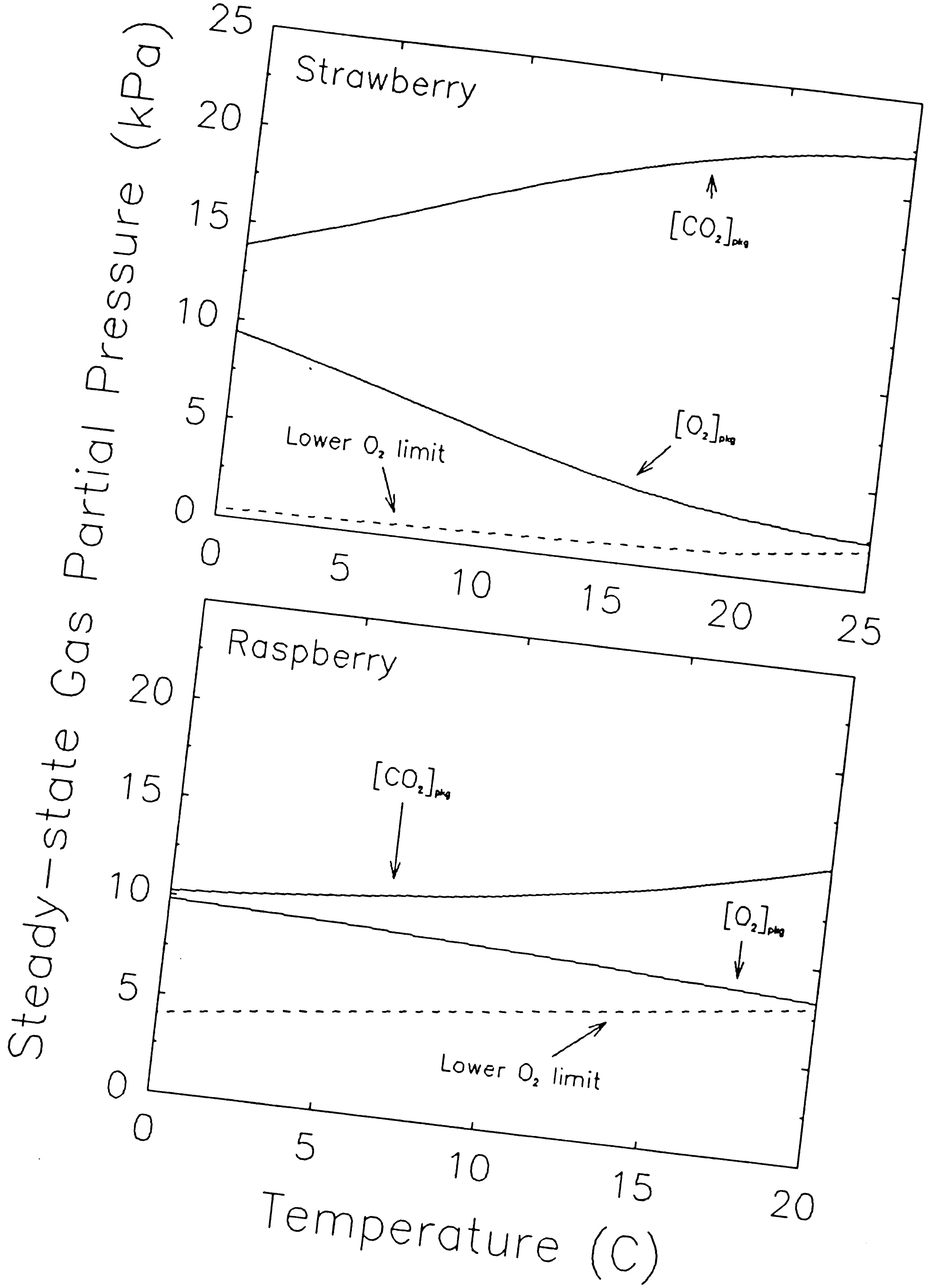
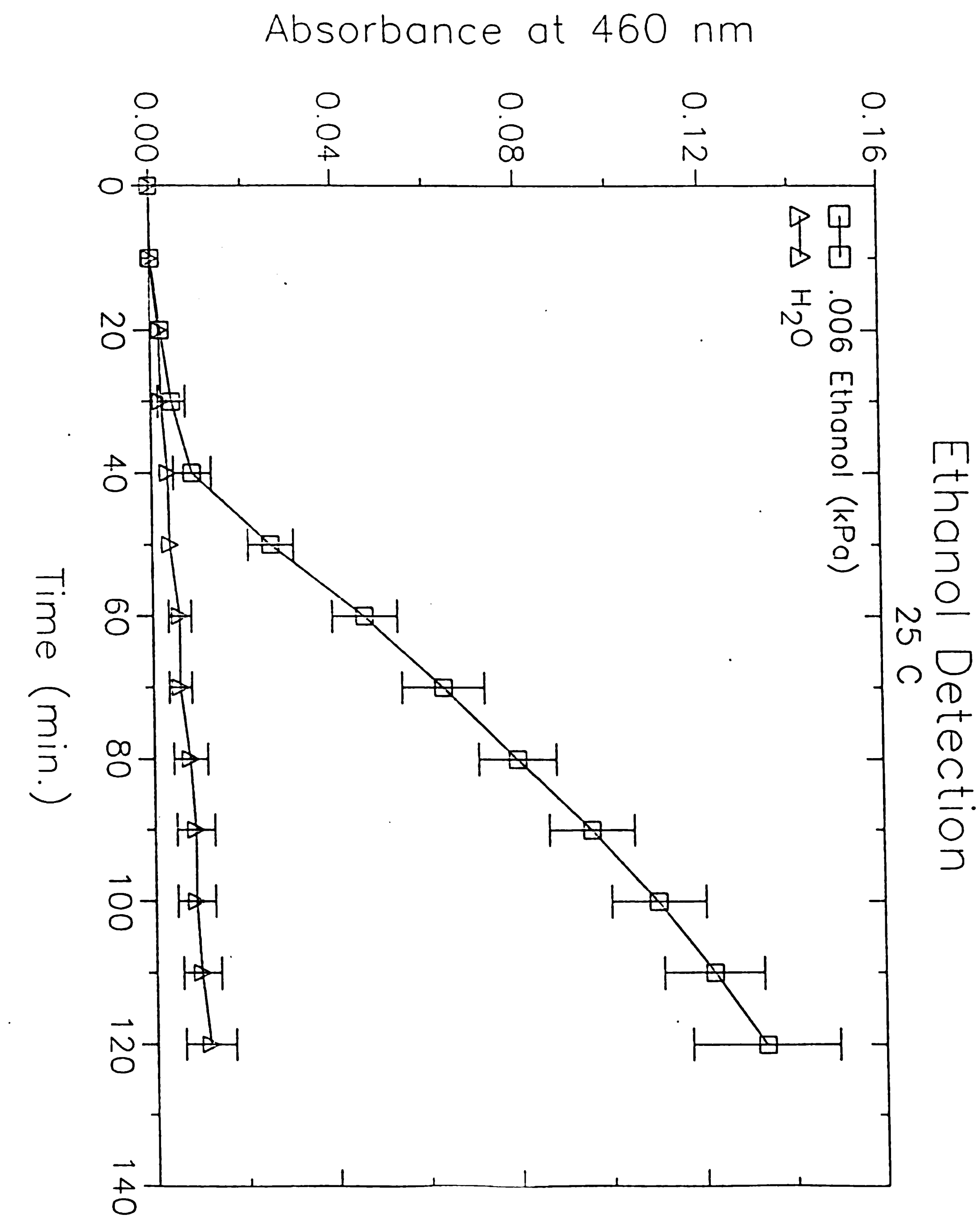

Steady-state Gas Partial Pressure (kPa)
Strawberry
[CO2]pkg
[O2]pkg
Lower O2 limit
Raspberry
[CO2]pkg
[O2]pkg
Lower O2 limit
Temperature (C)

Fig. 4. The change in absorbance at 460 nm over time for a ethanol sensing film at 25C exposed to a ethanol vapor partial pressure of .006 kPa and to H_2O vapor.


Ethanol Detection
25 C
.006 Ethanol (kPa)
H_2O
Absorbance at 460 nm
Time (min.)
0.00
0.04
0.08
0.12
0.16
0
20
40
60
80
100
120
140