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# **MATHEMATICAL MODELLING OF MODIFIED ATMOSPHERE PACKAGING SYSTEMS FOR APPLES**

A thesis presented in partial fulfilment of the requirements for the degree of  
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## ABSTRACT

ENZA New Zealand (International) is considering the use of modified atmosphere packaging (MAP) as an adjunct to cool storage for cartons of apples. The objectives of this study were to measure modified atmosphere development in apple cartons and to develop a mathematical model that could be used as a tool for package design and optimization.

Storage trials were carried out with film-lined cartons of 'Braeburn', 'Royal Gala', and 'Granny Smith' apples. Measured package  $O_2$  and  $CO_2$  concentrations showed excellent reproducibility for cartons with heat-sealed liners. Liners closed by folding produced less modified and less consistent package atmospheres, especially for thicker films (40  $\mu m$  versus 25  $\mu m$ ). Macroscopic holes in the liners resulted in almost total loss of atmosphere modification, whereas microscopic holes resulted in smaller changes apparent for  $O_2$  concentrations only. A high incidence of film damage could quickly erode any potential fruit quality benefits imparted by the liners.

Packing of warm rather than pre-cooled fruit resulted in much faster rates of atmosphere modification, without the development of unduly low  $O_2$  or high  $CO_2$  concentrations. The detrimental quality effects of slower cooling rates for film-lined cartons may outweigh any benefits of more rapid modified atmosphere development. Short-term exposures (less than 24 hours) to 20°C resulted in relatively short-lived and non-critical disturbances to package atmospheres. Periods of more than 3 days at 20°C led to a significant risk of anaerobic conditions or harmful  $CO_2$  levels forming within the fruit, especially within the 40  $\mu m$  liners. Folding rather than heat-sealing of liners did not reduce this risk.

The MAP model simulated fruit respiration as a function of temperature and fruit  $O_2$  and  $CO_2$  concentrations;  $O_2$ ,  $CO_2$ ,  $N_2$ , and water vapour exchange between the fruit, package, and external atmospheres; condensation of moisture within the package; and moisture sorption by paper-based packaging materials. Gas concentrations and temperature throughout (i) the fruit and (ii) the package atmosphere were each assumed to be uniform with position. The model can be applied to a wide range of packages under variable-temperature storage regimes. The model closely predicted observed trends in experimental data collected during the MA storage trials, but tended to under-predict  $CO_2$  concentrations and performed less well under conditions of extremely modified atmospheres. Sensitivity analyses showed that this lack of fit was not greater than that which could be explained by uncertainties in respiration and permeability data. It is recommended that future work be aimed at resolving the worst of these uncertainties before a significant amount of effort is directed towards further model development.

The MAP model was considered sufficiently accurate for it to be usefully applied to the design and optimization of MAP systems.

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## ERRATA

- p. x Sub-sections of section 8.2.1 should be numbered 8.2.1.1, 8.2.1.2, and 8.2.1.3.
- p. 13 Second-to-last line of second paragraph. 'Late harvested fruit were used in the trial...' should read 'Late harvested fruit were used in the trial...'.
- p. 33 Eq. 2.7. The symbol  $RQ_m$  should be  $RQ$  (as listed in the definition of symbols on p. 34).
- p. 37 Definition of symbols for Eq. 2.12. Units of  $[i]_{ext}$  and  $[i]_{int}$  should read  $(m^3 \cdot m^{-3})$ .
- p. 96 Eq. 6.14 should read

$$\frac{d(\epsilon V_n C_{O_2,f})}{dt} = k_{O_2} A_n (C_{O_2,p} - C_{O_2,f}) - v M_n$$

- p. 114 Eq. 6.85 should read

$$\frac{d\theta}{dt} = -\alpha(\theta - \theta_e)$$

- p. 121 Throughout Chapter 7, the symbol ' $\epsilon$ ' represents the local error tolerance bound for the numerical solution method. Throughout the rest of the thesis ' $\epsilon$ ' represents the porosity of the fruit flesh  $(m^3 \cdot m^{-3})$ .
- p. 151 Section 8.2.2.1 should be numbered 8.2.1.1.
- p. 155 Section 8.2.2.2 should be numbered 8.2.1.2.
- p. 158 Section 8.2.2.3 should be numbered 8.2.1.3.

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# NOMENCLATURE

This section lists the nomenclature used in the mathematical formulation of the MAP model (Chapter 6). Miscellaneous symbols used locally in Chapters 2, 4, 7, and 8 are defined in the text as necessary.

|                 |                                                                                                     |
|-----------------|-----------------------------------------------------------------------------------------------------|
| $a$             | empirical parameter of the fruit surface area-volume correlation (Eq. 6.17)                         |
| $A_{film}$      | total surface area for gas permeation through the packaging film ( $m^2$ )                          |
| $A_{fruit}$     | total fruit surface area ( $m^2$ )                                                                  |
| $A_{holes}$     | total area of holes in the packaging film ( $m^2$ )                                                 |
| $A_n$           | individual fruit surface area ( $m^2$ )                                                             |
| $A_{pack}$      | average heat transfer area of the packaging materials ( $m^2$ )                                     |
| $A_{tray}$      | effective tray surface area for moisture sorption ( $m^2 \cdot tray^{-1}$ )                         |
| $a_w$           | fruit water activity                                                                                |
| $a_{w, tray}$   | tray water activity                                                                                 |
| $b$             | empirical parameter of the fruit surface area-volume correlation (Eq. 6.17)                         |
| $Bi$            | Biot number for heat transfer                                                                       |
| $Bi'$           | Biot number for mass transfer                                                                       |
| $c_{pa}$        | specific heat capacity of dry air ( $J \cdot kg^{-1} \cdot K^{-1}$ )                                |
| $c_{pf}$        | specific heat capacity of the fruit flesh ( $J \cdot kg^{-1} \cdot K^{-1}$ )                        |
| $c_{pt}$        | specific heat capacity of the dry trays ( $J \cdot kg^{-1} \cdot K^{-1}$ )                          |
| $c_{pv}$        | specific heat capacity of water vapour ( $J \cdot kg^{-1} \cdot K^{-1}$ )                           |
| $c_{pw}$        | specific heat capacity of liquid water ( $J \cdot kg^{-1} \cdot K^{-1}$ )                           |
| $C$             | parameter of the GAB isotherm model (Eq. 2.22)                                                      |
| $C_{CO_2, e}$   | $CO_2$ concentration in the store atmosphere ( $kg \ CO_2 \cdot m^{-3}$ )                           |
| $C_{CO_2, p}$   | $CO_2$ concentration in the package atmosphere ( $kg \ CO_2 \cdot m^{-3}$ )                         |
| $C_{CO_2, f}$   | $CO_2$ concentration in the fruit internal atmosphere ( $kg \ CO_2 \cdot m^{-3}$ )                  |
| $C_{H_2O, p}$   | concentration of water vapour in the package atmosphere ( $kg \ H_2O \cdot m^{-3}$ )                |
| $C_{H_2O, e}$   | concentration of water vapour in the store atmosphere ( $kg \ H_2O \cdot m^{-3}$ )                  |
| $C_i$           | mass concentration of gas species $i$ ( $kg \cdot m^{-3}$ )                                         |
| $C_{i, e}$      | ambient concentration of gas species $i$ ( $kg \cdot m^{-3}$ )                                      |
| $C_{i, p}^0$    | initial package concentration of gas species $i$ ( $kg \cdot m^{-3}$ )                              |
| $C_{i, p}^t$    | package concentration of gas species $i$ at time $t$ ( $kg \cdot m^{-3}$ )                          |
| $C_{N_2, e}$    | $N_2$ concentration in the store atmosphere ( $kg \ N_2 \cdot m^{-3}$ )                             |
| $C_{N_2, p}$    | $N_2$ concentration in the package atmosphere ( $kg \ N_2 \cdot m^{-3}$ )                           |
| $C_{O_2, f}$    | $O_2$ concentration in the fruit internal atmosphere ( $kg \ O_2 \cdot m^{-3}$ )                    |
| $C_{O_2, e}$    | $O_2$ concentration in the store atmosphere ( $kg \ O_2 \cdot m^{-3}$ )                             |
| $C_{O_2, p}$    | $O_2$ concentration in the package atmosphere ( $kg \ O_2 \cdot m^{-3}$ )                           |
| $D$             | mass diffusivity ( $m^2 \cdot s^{-1}$ )                                                             |
| $D_{i, eff}$    | effective diffusivity of gas species $i$ through holes in the packaging film ( $m^2 \cdot s^{-1}$ ) |
| $D_{i, ref}$    | diffusivity of gas species $i$ in air at temperature $T_{ref}$ ( $m^2 \cdot s^{-1}$ )               |
| $D_{i, air}$    | diffusivity of gas species $i$ in air ( $m^2 \cdot s^{-1}$ )                                        |
| $D_{CO_2, eff}$ | effective diffusivity of $CO_2$ through holes in the packaging film ( $m^2 \cdot s^{-1}$ )          |
| $D_{H_2O, eff}$ | effective diffusivity of water vapour through holes in the packaging film ( $m^2 \cdot s^{-1}$ )    |

|                  |                                                                                                                                                                      |
|------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $D_{N_2, eff}$   | effective diffusivity of $N_2$ through holes in the packaging film ( $m^2 \cdot s^{-1}$ )                                                                            |
| $D_{O_2, eff}$   | effective diffusivity of $O_2$ through holes in the packaging film ( $m^2 \cdot s^{-1}$ )                                                                            |
| $E_{a, i}$       | activation energy for permeation of gas species $i$ ( $J \cdot mol^{-1}$ )                                                                                           |
| $h$              | surface heat transfer coefficient ( $W \cdot m^{-2} \cdot K^{-1}$ )                                                                                                  |
| $h_e$            | convective heat transfer coefficient at the external package surface ( $W \cdot m^{-2} \cdot K^{-1}$ )                                                               |
| $h_f$            | convective heat transfer coefficient at the fruit surface ( $W \cdot m^{-2} \cdot K^{-1}$ )                                                                          |
| $h_{fg}$         | latent heat of vaporization of water ( $J \cdot kg^{-1}$ )                                                                                                           |
| $h_p$            | convective heat transfer coefficient at the internal packaging-film surface ( $W \cdot m^{-2} \cdot K^{-1}$ )                                                        |
| $H_p$            | absolute humidity of the package atmosphere ( $kg \cdot kg^{-1}$ )                                                                                                   |
| $k$              | general rate constant (units variable)                                                                                                                               |
| $k_{CO_2}$       | fruit skin permeance to $CO_2$ ( $m \cdot s^{-1}$ )                                                                                                                  |
| $k_{O_2}$        | fruit skin permeance to $O_2$ ( $m \cdot s^{-1}$ )                                                                                                                   |
| $k_{g, skin}$    | fruit skin permeance to water vapour ( $s \cdot m^{-1}$ )                                                                                                            |
| $k_{g, tray}$    | mass transfer coefficient for moisture sorption at the tray surface ( $s \cdot m^{-1}$ )                                                                             |
| $k_{g, fruit}$   | mass transfer coefficient for moisture condensation at the fruit surface ( $s \cdot m^{-1}$ )                                                                        |
| $k_{g, film}$    | mass transfer coefficient for moisture condensation at the inside surface of the packaging film ( $s \cdot m^{-1}$ )                                                 |
| $k_{ic}$         | competitive inhibition constant ( $kg \cdot CO_2 \cdot m^{-3}$ )                                                                                                     |
| $k_{iu}$         | uncompetitive inhibition constant ( $kg \cdot CO_2 \cdot m^{-3}$ )                                                                                                   |
| $k_m$            | half saturation constant ( $kg \cdot O_2 \cdot m^{-3}$ )                                                                                                             |
| $K$              | parameter of the GAB isotherm model (Eq. 2.22)                                                                                                                       |
| $L$              | characteristic dimension (m)                                                                                                                                         |
| $\dot{m}_i$      | net mass flow of gas species $i$ into the package by all mechanisms except bulk flow ( $mol \cdot s^{-1}$ )                                                          |
| $\dot{m}_{CO_2}$ | net mass flow of $CO_2$ into the package through fruit gas exchange, permeation, and diffusion ( $kg \cdot s^{-1}$ )                                                 |
| $\dot{m}_{H_2O}$ | net mass flow of $H_2O$ into the package through fruit moisture loss, permeation, diffusion, condensation/evaporation, and sorption/desorption ( $kg \cdot s^{-1}$ ) |
| $\dot{m}_{N_2}$  | net mass flow of $N_2$ into the package through permeation and diffusion ( $kg \cdot s^{-1}$ )                                                                       |
| $\dot{m}_{O_2}$  | net mass flow of $O_2$ into the package through fruit gas exchange, permeation, and diffusion ( $kg \cdot s^{-1}$ )                                                  |
| $M_{i, p}$       | mass of gas species $i$ in the package atmosphere (kg)                                                                                                               |
| $M_{CO_2, p}$    | mass of $CO_2$ in the package atmosphere (kg)                                                                                                                        |
| $M_{H_2O, p}$    | mass of water vapour in the package atmosphere (kg)                                                                                                                  |
| $M_{N_2, p}$     | mass of $N_2$ in package atmosphere (kg)                                                                                                                             |
| $M_{O_2, p}$     | mass of $O_2$ in package atmosphere (kg)                                                                                                                             |
| $M_{cond, f}$    | mass of condensate on the fruit surface (kg)                                                                                                                         |
| $M_{cond, p}$    | mass of condensate on the inside packaging film surface (kg)                                                                                                         |
| $M_{f, initial}$ | initial total fruit mass (kg)                                                                                                                                        |
| $M_f$            | total fruit mass (kg)                                                                                                                                                |
| $M_n$            | individual fruit mass (kg)                                                                                                                                           |
| $M_p$            | mass of dry air in the package atmosphere (kg)                                                                                                                       |
| $M_{tray}$       | tray dry mass ( $kg \cdot tray^{-1}$ )                                                                                                                               |
| $M_{w, tray}$    | mass of water absorbed by the moulded-pulp trays ( $kg \cdot tray^{-1}$ )                                                                                            |
| $Mr_i$           | molecular mass of gas species $i$ ( $g \cdot mol^{-1}$ )                                                                                                             |
| $Mr_C$           | molar mass of carbon ( $g \cdot mol^{-1}$ )                                                                                                                          |

|                  |                                                                                                                                                                        |
|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $M_{r_{CO_2}}$   | molar mass of $CO_2$ ( $g \cdot mol^{-1}$ )                                                                                                                            |
| $M_{r_{H_2O}}$   | molar mass of water ( $g \cdot mol^{-1}$ )                                                                                                                             |
| $M_{r_{N_2}}$    | molar mass of $N_2$ ( $g \cdot mol^{-1}$ )                                                                                                                             |
| $M_{r_{O_2}}$    | molar mass of $O_2$ ( $g \cdot mol^{-1}$ )                                                                                                                             |
| $\dot{n}_h$      | total molar flow into the package through holes in the packaging film ( $mol \cdot s^{-1}$ )                                                                           |
| $\dot{n}_i$      | net molar flow of gas species $i$ into the package by all mechanisms except bulk flow ( $mol \cdot s^{-1}$ )                                                           |
| $\dot{n}_{CO_2}$ | net molar flow of $CO_2$ into the package through fruit gas exchange, permeation, and diffusion ( $mol \cdot s^{-1}$ )                                                 |
| $\dot{n}_{H_2O}$ | net molar flow of $H_2O$ into the package through fruit moisture loss, permeation, diffusion, condensation/evaporation, and sorption/desorption ( $mol \cdot s^{-1}$ ) |
| $\dot{n}_{N_2}$  | net molar flow of $N_2$ into the package through permeation and diffusion ( $mol \cdot s^{-1}$ )                                                                       |
| $\dot{n}_{O_2}$  | net molar flow of $O_2$ into the package through fruit gas exchange, permeation, and diffusion ( $mol \cdot s^{-1}$ )                                                  |
| $n_{p, tot}$     | total number of moles of gas in the package atmosphere                                                                                                                 |
| $N$              | number of fruit in the package                                                                                                                                         |
| $N_{tray}$       | number of moulded-pulp trays per package                                                                                                                               |
| $p_{sat, tray}$  | saturated vapour pressure of water at the tray temperature (Pa)                                                                                                        |
| $p_{sat, film}$  | saturated vapour pressure of water at the packaging film temperature (Pa)                                                                                              |
| $p_{sat, f}$     | saturated vapour pressure of water at the fruit surface temperature (Pa)                                                                                               |
| $p_{sat, e}$     | saturated vapour pressure of water at the store air temperature (Pa)                                                                                                   |
| $p_{sat, p}$     | saturated vapour pressure of water at the temperature of the package atmosphere (Pa)                                                                                   |
| $p_{w, tray}$    | partial pressure of water vapour at the tray surface (Pa)                                                                                                              |
| $p_{w, f}$       | partial pressure of water vapour beneath the fruit skin (Pa)                                                                                                           |
| $p_{w, e}$       | partial pressure of water vapour in the store atmosphere (Pa)                                                                                                          |
| $p_{w, p}$       | partial pressure of water vapour in the package atmosphere (Pa)                                                                                                        |
| $P$              | pressure (Pa)                                                                                                                                                          |
| $P_{0, i}$       | pre-exponential factor for permeation of gas species $i$ ( $m^2 \cdot s^{-1}$ )                                                                                        |
| $P_{atm}$        | atmospheric pressure (Pa)                                                                                                                                              |
| $P_i$            | permeability of the packaging film to gas species $i$ ( $m^2 \cdot s^{-1}$ )                                                                                           |
| $P_{CO_2}$       | packaging film permeability to $CO_2$ ( $m^2 \cdot s^{-1}$ )                                                                                                           |
| $P_{H_2O}$       | packaging film permeability to water vapour ( $m^2 \cdot s^{-1}$ )                                                                                                     |
| $P_{N_2}$        | packaging film permeability to $N_2$ ( $m^2 \cdot s^{-1}$ )                                                                                                            |
| $P_{O_2}$        | packaging film permeability to $O_2$ ( $m^2 \cdot s^{-1}$ )                                                                                                            |
| $P_p$            | package atmosphere pressure (Pa)                                                                                                                                       |
| $Q$              | cumulative $O_2$ consumption ( $kg \cdot O_2 \cdot kg^{-1}$ )                                                                                                          |
| $Q_{10}$         | temperature coefficient for respiration                                                                                                                                |
| $R$              | gas constant ( $J \cdot mol^{-1} \cdot K^{-1}$ )                                                                                                                       |
| $RH_e$           | relative humidity of the store air (%)                                                                                                                                 |
| $RH_p$           | relative humidity of the package atmosphere (%)                                                                                                                        |
| $RQ_m$           | mass-based respiratory quotient for aerobic respiration ( $kg \cdot kg^{-1}$ )                                                                                         |
| $SA_{corr}$      | empirical correction factor for evaporation of moisture from the fruit surface                                                                                         |
| $t$              | time (s)                                                                                                                                                               |
| $t_{0.5}$        | half cooling or warming time or half life (s)                                                                                                                          |
| $t_h$            | time at which holes in the packaging film are formed (s)                                                                                                               |

|                            |                                                                                                                        |
|----------------------------|------------------------------------------------------------------------------------------------------------------------|
| $T$                        | temperature (K)                                                                                                        |
| $T_{ref}$                  | reference temperature (K)                                                                                              |
| $U_{pack}$                 | overall heat transfer coefficient for the packaging materials ( $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ )       |
| $v$                        | aerobic respiration rate ( $\text{kg O}_2\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ )                                      |
| $v_{max}$                  | maximum aerobic respiration rate at the fruit temperature ( $\text{kg O}_2\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ )     |
| $v_{max,ref}$              | maximum aerobic respiration rate at the reference temperature ( $\text{kg O}_2\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ ) |
| $V_{carton}$               | carton volume ( $\text{m}^3$ )                                                                                         |
| $V_{i,p}$                  | volume of gas species $i$ in the package atmosphere ( $\text{m}^3$ )                                                   |
| $V_{\text{CO}_2,p}$        | volume of $\text{CO}_2$ in the package atmosphere ( $\text{m}^3$ )                                                     |
| $V_{\text{H}_2\text{O},p}$ | volume of water vapour in the package atmosphere ( $\text{m}^3$ )                                                      |
| $V_{\text{N}_2,p}$         | volume of $\text{N}_2$ in the package atmosphere ( $\text{m}^3$ )                                                      |
| $V_{\text{O}_2,p}$         | volume of $\text{O}_2$ in the package atmosphere ( $\text{m}^3$ )                                                      |
| $V_n$                      | individual fruit volume ( $\text{m}^3$ )                                                                               |
| $V_{p,min}$                | minimum package atmosphere volume ( $\text{m}^3$ )                                                                     |
| $V_p$                      | volume of the package atmosphere ( $\text{m}^3$ )                                                                      |
| $V_{p,h}$                  | package atmosphere volume at time $t_h$ ( $\text{m}^3$ )                                                               |
| $W$                        | respiratory heat generation per unit mass of $\text{O}_2$ consumption ( $\text{J}\cdot\text{kg}^{-1}$ )                |
| $x$                        | packaging film thickness (m)                                                                                           |
| $x_i$                      | thickness of the $i^{\text{th}}$ layer of packaging material (m)                                                       |
| $X_i$                      | mole fraction of gas species $i$ in the bulk flow through holes in the packaging film                                  |
| $X_{\text{CO}_2}$          | mole fraction of $\text{CO}_2$ in the flow through holes in the packaging film                                         |
| $X_{\text{H}_2\text{O}}$   | mole fraction of water vapour in the flow through holes in the packaging film                                          |
| $X_{\text{N}_2}$           | mole fraction of $\text{N}_2$ in the flow through holes in the packaging film                                          |
| $X_{\text{O}_2}$           | mole fraction of $\text{O}_2$ in the flow through holes in the packaging film                                          |
| $X_{\text{CO}_2,e}$        | mole fraction of $\text{CO}_2$ in the store air (dry air basis)                                                        |
| $X_{\text{N}_2,e}$         | mole fraction of $\text{N}_2$ in the store air (dry air basis)                                                         |
| $X_{\text{O}_2,e}$         | mole fraction of $\text{O}_2$ in the store air (dry air basis)                                                         |
| $X_m$                      | parameter of the GAB isotherm model (Eq. 2.22)                                                                         |
| $X_{tray}$                 | tray moisture content on a dry solids basis ( $\text{kg}\cdot\text{kg}^{-1}$ )                                         |
| $Y$                        | fractional unaccomplished temperature change                                                                           |
| $Y'_i$                     | fractional unaccomplished concentration change for gas species $i$                                                     |
| $[i]$                      | volume concentration of gas species $i$ ( $\text{m}^3\cdot\text{m}^{-3}$ )                                             |
| $[i]_e$                    | volume concentration of gas species $i$ in the store atmosphere ( $\text{m}^3\cdot\text{m}^{-3}$ )                     |
| $[i]_p$                    | volume concentration of gas species $i$ in the package atmosphere ( $\text{m}^3\cdot\text{m}^{-3}$ )                   |
| $[\text{CO}_2]_e$          | volume concentration of $\text{CO}_2$ in the store atmosphere ( $\text{m}^3\cdot\text{m}^{-3}$ )                       |
| $[\text{H}_2\text{O}]_e$   | volume concentration of water vapour in the store atmosphere ( $\text{m}^3\cdot\text{m}^{-3}$ )                        |
| $[\text{H}_2\text{O}]_p$   | volume concentration of water vapour in the package atmosphere ( $\text{m}^3\cdot\text{m}^{-3}$ )                      |
| $[\text{N}_2]_e$           | volume concentration of $\text{N}_2$ in the store atmosphere ( $\text{m}^3\cdot\text{m}^{-3}$ )                        |
| $[\text{O}_2]_e$           | volume concentration of $\text{O}_2$ in the store atmosphere ( $\text{m}^3\cdot\text{m}^{-3}$ )                        |
| $\alpha$                   | constant in Eq. 6.82 ( $\text{s}^{-1}$ )                                                                               |
| $\gamma$                   | constant in Eq. 6.82                                                                                                   |
| $\varepsilon$              | fruit flesh porosity ( $\text{m}^3\cdot\text{m}^{-3}$ )                                                                |
| $\eta_f$                   | fruit specific enthalpy ( $\text{J}\cdot\text{kg}^{-1}$ )                                                              |
| $\eta_p$                   | specific enthalpy of the package atmosphere (dry air basis) ( $\text{J}\cdot\text{kg}^{-1}$ )                          |
| $\eta_{tray}$              | specific enthalpy of the moulded-pulp fruit trays (dry mass basis) ( $\text{J}\cdot\text{kg}^{-1}$ )                   |

|                     |                                                                                                                            |
|---------------------|----------------------------------------------------------------------------------------------------------------------------|
| $\theta$            | temperature ( $^{\circ}\text{C}$ )                                                                                         |
| $\theta_e$          | store air temperature ( $^{\circ}\text{C}$ )                                                                               |
| $\theta_f$          | fruit temperature ( $^{\circ}\text{C}$ )                                                                                   |
| $\theta_{film}$     | temperature of the packaging film ( $^{\circ}\text{C}$ )                                                                   |
| $\theta_i$          | initial temperature ( $^{\circ}\text{C}$ )                                                                                 |
| $\theta_p$          | temperature of the package atmosphere ( $^{\circ}\text{C}$ )                                                               |
| $\theta_{ref}$      | reference temperature ( $^{\circ}\text{C}$ )                                                                               |
| $\lambda$           | thermal conductivity ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )                                                    |
| $\lambda_i$         | thermal conductivity of the $i^{\text{th}}$ layer of packaging material ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) |
| $\xi$               | empirical correction factor for gas diffusion through holes                                                                |
| $\rho_{f, initial}$ | initial fruit flesh density ( $\text{kg}\cdot\text{m}^{-3}$ )                                                              |
| $\rho_f$            | fruit flesh density ( $\text{kg}\cdot\text{m}^{-3}$ )                                                                      |

# Chapter 1

## INTRODUCTION

New Zealand's economy relies heavily on the export of primary produce such as meat, dairy products, wool, forest products, fish and shellfish, and fresh fruits and vegetables. For the year ending 31 March 1993, fresh horticultural products (fruits, nuts, and vegetables) made up approximately 5.4% of the value of New Zealand exports, making the horticultural industry New Zealand's fifth largest behind dairy, meat, forest products, and fish and shellfish (New Zealand Official Yearbook, 1994).

Fruits and vegetables consist of living tissues in which the metabolic processes essential for cell maintenance continue after harvest. As living structures, fruits and vegetables are susceptible to physical damage, decay, and physiological or pathological disorders. Large economic losses can, and often do, occur between harvest and market as a result of poor storage or handling conditions. According to Wills *et al.* (1989, p. 1), various authorities have estimated that 25 to 80% of total fruit and vegetable production is lost after harvest; Kader (1992a) cites estimated postharvest losses ranging from 5 to 25% in developed countries and 20 to 50% in developing countries. Careful attention to postharvest storage and handling procedures is of paramount importance in minimizing such losses. This entails (a) prevention of mechanical damage, (b) prevention of microbial and pest infestations, and (c) retardation of the natural ripening and senescence processes of the produce. As well as reducing wastage, effective storage technologies extend the storage life of the produce, thereby allowing increased production, supply of the market for a longer period of time, and marketing of a high quality product.

Existing storage technologies that extend the postharvest life of fruits and vegetables by slowing down the natural processes of ripening and senescence are generally based on the control of one or more of three environmental factors: temperature, humidity, and atmospheric composition. Of these, the maintenance of optimum temperature and humidity is widely considered to be of greatest importance (Zagory & Kader, 1988; Kader *et al.*, 1989; Kader, 1992a,b). However, once optimum temperature and humidity have been achieved, modification of the atmosphere surrounding the produce can further aid in maintaining the quality and extending the storage life of some species and cultivars. Modified atmosphere (MA) storage generally involves the direct or indirect control of oxygen and carbon dioxide concentrations in the storage atmosphere and may also involve the removal of organic volatiles, such as the fruit ripening hormone ethylene, from the storage atmosphere. The term 'MA storage' encompasses a range of storage technologies, including modified atmosphere packaging (MAP). MAP involves the use of selected packaging materials to restrict the transport of gases into or out of a package, causing a modified atmosphere to be created and maintained by the metabolism of the packaged produce itself.

ENZA New Zealand (International), the export division of the New Zealand Apple and Pear Marketing Board, is currently investigating the use of plastic film liners in cartons as a means of providing modified atmosphere storage and transport for various apple

varieties. Previous New Zealand research has shown that the packing of apples within film-lined cartons as an adjunct to cool storage can have beneficial effects on the retention of apple quality after harvest (Watkins, 1988; Watkins *et al.*, 1989; Brookfield & Watkins, 1991; Watkins & Cregoe, 1991; Elgar & Watkins, 1992; Frampton & Ahlborn, 1994a; Frampton *et al.*, 1994a). Reported benefits over air-storage of fruit include superior colour and texture; reduced incidence of bitter pit in 'Cox's Orange Pippin'; and reduced incidence of greasiness in 'Gala', 'Royal Gala' and 'Granny Smith'.

Probably the most serious disadvantage inherent in MAP systems is the lack of direct control over package atmospheres: in particular, package oxygen and carbon dioxide concentrations. Under-modification of package atmospheres produces little or no benefit compared to air-stored fruit and therefore represents a low return on investment in terms of the added packaging costs. Conversely, over-modification of package atmospheres can induce physiological injury, with consequent flavour problems or even total fruit breakdown occurring. Accepted "optimum" MA conditions for apples can vary considerably between cultivars. To overcome the inherent lack of control in MAP systems, a good understanding of the factors that affect package atmospheres is essential. To obtain maximum benefit from the use of modified atmosphere liners, it is equally important to develop optimized package designs. Factors that affect package atmospheres include total fruit mass; fruit cultivar and maturity; packaging film surface area, permeability, and thickness; and storage temperature.

To date, the New Zealand work on MA liners has involved the experimental testing of a range of potential package designs. This has provided valuable information on the effects of MAP on the quality and storage potential of various New Zealand apple cultivars. However, for optimization purposes, a purely experimental approach has the disadvantage of being expensive, time consuming, and inflexible. The ability to predict conditions formed inside an MA package as a function of fruit characteristics, packaging characteristics, storage conditions, and time would enable the need for experimental work to be substantially reduced. A predictive model of an MAP system could provide a flexible design tool when used in conjunction with experimental validation, and could be applied to the following areas:

- (a) optimization of package design features;
- (b) investigation of "what if?" questions concerning the effects of proposed changes to package design, coolstore management procedures, or transport and handling procedures;
- (c) rapid identification of fruit attributes and design and environmental factors that significantly affect package atmospheres;
- (d) effective planning of experimental trials to obtain maximum value from a minimum of experimental effort.

The overall objectives of this study were two-fold:

- (1) the experimental investigation of a carton MAP system for apples to gain a better understanding of how modified atmosphere development is influenced by various design and operational factors;
- (2) the development of a mathematical model capable of predicting modified atmosphere conditions as a function of fruit characteristics, packaging characteristics, storage conditions, and time.

## *Chapter 2*

# **MODIFIED ATMOSPHERE PACKAGING OF HORTICULTURAL PRODUCE: A REVIEW OF MODELLING APPROACHES**

## **2.1 PRINCIPLES OF MODIFIED ATMOSPHERE STORAGE**

The effectiveness of any storage technology for harvested horticultural produce is dependent upon the nature and magnitude of its influence on the biochemical and physiological processes occurring within the produce. To understand how a given storage technology brings about its effects, a basic knowledge of these processes is necessary.

### **2.1.1 BACKGROUND TO POSTHARVEST PHYSIOLOGY**

Brief overviews of the physiology and biochemistry of fruits and vegetables, with references to literature containing more detailed information, have been given by Wills *et al.* (1989, pp. 17-38) and Powrie & Skura (1991).

Three major stages are identifiable in the life of any fruit or vegetable, although clear divisions between these stages can seldom be made (Watada *et al.*, 1984; Wills *et al.*, 1989, p. 17). The three stages are growth, maturation and senescence. Growth involves the cell division and cell enlargement that lead to the final physical size of the fruit or vegetable. Maturation, which may commence before growth ceases, involves physiological and biochemical processes that vary widely depending on the commodity. This stage has no clear biochemical or physiological definition, but can be generally described as a phase of transition between growth and senescence. Senescence commences when anabolic (synthetic) biochemical processes give way to catabolic (degradative) processes, culminating in the exhaustion of energy and moisture reserves, cell breakdown and tissue death. For fruits, a stage of ripening is also defined, during which the physico-chemical changes which result in a fruit reaching its optimum eating quality occur. Ripening generally begins during the latter stages of maturation and is considered to be the first stage of senescence. Table 2.1 lists the major changes that occur during fruit ripening.

Respiration is a major metabolic process central to the maintenance of virtually all other processes of cell metabolism. Respiration involves the oxidation of organic compounds such as carbohydrates, organic acids, amino acids and fatty acids to lower molecular weight compounds, coupled to the production of adenosine triphosphate (ATP). ATP is the carrier of free energy in biological systems and is essential for the maintenance of cell metabolism, cellular organization, and cell transport processes (Wills *et al.*, 1989, pp. 29-34; Powrie & Skura, 1991). As well as providing the energy necessary for cell maintenance and growth, the respiratory pathway provides important intermediates for various anabolic processes such as the synthesis of amino acids, fatty acids, aromatic

**Table 2.1** Changes occurring during fruit ripening.<sup>a</sup>

---

|                                                                                                                |
|----------------------------------------------------------------------------------------------------------------|
| Seed maturation                                                                                                |
| Colour changes (e.g. breakdown of chlorophyll, synthesis of carotenoids and anthocyanins)                      |
| Abscission (detachment from parent plant)                                                                      |
| Changes in respiration rate (e.g. increased TCA cycle activity)                                                |
| Changes in rate of ethylene production                                                                         |
| Changes in tissue permeability                                                                                 |
| Softening: changes in composition of pectic substances (e.g. hydrolysis of pectins)                            |
| Changes in carbohydrate composition (e.g. starch hydrolysis, interconversion of sugars)                        |
| Organic acid changes (e.g. organic acid breakdown)                                                             |
| Protein changes (e.g. protein hydrolysis, increased transcription and translation, changes in enzyme activity) |
| Production of flavour volatiles                                                                                |
| Development of wax on skin                                                                                     |

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<sup>a</sup> Adapted from Table 7 of Wills *et al.* (1989) and Table 7.8 of Powrie & Skura (1991).

compounds and pigments. Because of its central role in the maintenance of cell metabolism, measurement of the rate of respiration provides a useful indicator of the overall rate of produce metabolism (Wills *et al.*, 1989, p. 22).

The respiratory process can proceed via either aerobic or anaerobic (fermentative) mechanisms. Aerobic respiration is the predominant mechanism in fruits and vegetables when oxygen is present in sufficient concentrations to sustain the O<sub>2</sub>-consuming reactions of the aerobic pathway. During aerobic respiration, the respiratory substrate is completely oxidized via two biochemical pathways: glycolysis and the tricarboxylic acid (TCA) or Kreb’s cycle. This is coupled to the oxidative phosphorylation of adenosine diphosphate (ADP) to form ATP via the electron transport chain, with molecular oxygen acting as the final electron acceptor. For the complete oxidation of 1 mole of glucose, the equivalent of 36 moles of ATP are produced. This represents a thermodynamic respiratory efficiency of 38% (Stryer, 1981), with the remaining energy released as heat.

Under severe oxygen limiting conditions the energy requirements of the cell are not able to be fulfilled by aerobic respiration alone, and a shift to anaerobic metabolism takes place. During anaerobic respiration, glucose is partially oxidized to pyruvate, a three-carbon molecule, via glycolysis. Further oxidation does not occur and pyruvate is decarboxylated to form acetaldehyde, which is subsequently reduced to form ethanol. Alternatively pyruvate can be directly reduced to form lactate. Via anaerobic respiration, 1 mole of glucose is coupled to the production of only 2 ATP. Prolonged periods of anaerobiosis in fruits and vegetables lead to the development of off-flavours in the tissue due to the build up of acetaldehyde and ethanol. This build up can also induce physiological injury, thereby hastening the onset of senescence.

The volumetric ratio of respiratory CO<sub>2</sub> production to O<sub>2</sub> consumption is termed the respiratory quotient (RQ). The value of RQ depends on both the respiratory substrate and mechanism. The complete oxidation of glucose generates an equal volume of CO<sub>2</sub> to the volume of O<sub>2</sub> consumed, resulting in a respiratory quotient of 1. Organic acids contain a higher proportion of oxygen to carbon than glucose, thus require less O<sub>2</sub> for

oxidation. Fatty acids contain a lower proportion of oxygen to carbon than glucose and require more  $O_2$  for oxidation. The RQ for the complete oxidation of malate, for example, is 1.3, while the RQ for oxidation of stearic acid is 0.7 (Wills *et al.*, 1989, pp. 32-33). Thus, the value of RQ can provide some indication of the respiratory substrate. During anaerobic respiration, no  $O_2$  is consumed, and thus RQ rises sharply as the transition from aerobic to anaerobic respiration occurs.

Respiration rates of fruits and vegetables vary with maturity, being at their highest during the immature stage and thereafter declining steadily with age (Wills *et al.*, 1989, pp. 22-23). For fruits, two basic types of respiratory pattern exist, climacteric and non-climacteric. The respiratory pattern of climacteric fruits is characterized by a pronounced but temporary increase in respiration rate coincident with ripening. Non-climacteric fruits exhibit no respiratory climacteric. Climacteric and non-climacteric fruits can be further distinguished by their responses to, and production of, ethylene, an important plant ripening hormone (Wills *et al.*, 1989, pp. 25-27). While all fruits produce small amounts of ethylene during development, climacteric fruits exhibit a marked increase in ethylene production coinciding with the respiratory climacteric. External application of ethylene to pre-climacteric fruits can, if applied at sufficiently high concentrations, irreversibly induce the respiratory climacteric. However, the magnitude of the climacteric is independent of the ethylene concentration applied. Non-climacteric fruits also show increased respiration in response to applied ethylene, but in this case the effect is reversible and repeatable, and its magnitude is proportional to the applied concentration.

Generally speaking, the postharvest life of any fruit or vegetable is inversely proportional to the rates of the metabolic processes associated with ripening and senescence. It follows, therefore, that the storage life of harvested produce can be increased by slowing down these processes.

### 2.1.2 TECHNOLOGIES FOR EXTENDING POSTHARVEST STORAGE LIFE

Cultivar selection, growing conditions, harvest at optimum maturity, prevention of mechanical damage and prevention of microbial and pest infestations are of primary importance in the production of high quality fruits and vegetables (Zagory & Kader, 1988; Kader *et al.*, 1989; Day, 1993). To maintain this quality during the postharvest life of the produce, efficient storage techniques aimed at slowing the processes of respiration and ripening, and thereby the onset of senescence, are needed.

The most important factor in the postharvest storage of fruits and vegetables is the maintenance of optimum temperature and humidity conditions (Zagory & Kader, 1988; Kader *et al.*, 1989; Kader, 1992a,b).

Temperature has a large effect on the rates of many reactions, including those involved in the processes of respiration and ripening. For biological systems within the physiological range of temperatures, rates of reaction have been found to increase exponentially with temperature such that a  $10^\circ\text{C}$  increase in temperature produces a two to three fold increase in reaction rate (Wills *et al.*, 1989, p. 39). Thus, reducing the temperature can dramatically reduce the rates of biological processes. However, limits

exist with respect to the storage of fruits and vegetables. Many tropical and subtropical fruits and some vegetables are susceptible to a physiological disorder known as chilling injury when cooled below a certain temperature. This temperature can be as high as 12-15°C. Chilling injury is thought to be due to physical changes in membrane lipids affecting membrane function and structural changes in enzymes and other proteins (Wills *et al.*, 1989, pp. 73-78; Powrie & Skura, 1991). For fruits and vegetables that are not prone to chilling injury, there is nevertheless a lower temperature limit of -2 to 0°C, since freezing of plant tissue occurs in this range. When fruit or vegetable tissue freezes, ice crystal formation causes cellular dehydration and permanent structural damage (Wills *et al.*, 1989, p. 40).

The maintenance of optimum humidity during storage is important with respect to the control of moisture loss and microbial spoilage. Moisture loss in fruits and vegetables is undesirable because it represents a loss of saleable weight. In addition, excessive moisture loss results in visible wilting or shrivelling and loss of textural quality (Wills *et al.*, 1989, p. 53; Day, 1993). High store humidities reduce the rate of moisture loss, but can favour the growth of spoilage organisms. The optimum storage humidity for a particular crop is therefore a compromise between these conflicting effects.

Once optimum temperature and humidity conditions have been achieved, modification of the atmosphere surrounding the produce can further help to maintain the quality of the produce and extend its storage life (Do & Salunkhe, 1975; Burton, 1978; Zagory & Kader, 1988; Kader *et al.*, 1989; Kader, 1992a,b). Modified atmosphere (MA) storage refers to the storage of food products under atmospheric compositions that, due to the addition or removal of gases, differ from the normal composition of air. Controlled atmosphere (CA) storage and modified atmosphere packaging (MAP) are common means of applying MA to the storage of horticultural produce. CA storage involves the use of mechanical means (for example, carbon dioxide scrubbers, oxygen burners, gas generators, pressure swing adsorption systems, or hollow fibre membrane systems) to create a modified atmosphere environment (generally reduced O<sub>2</sub> and/or enriched CO<sub>2</sub> levels) (Dewey, 1983; Bishop, 1990). Gas concentrations can be precisely controlled at set levels. MAP involves the use of packaging materials to restrict the transport of gases, thereby causing a similar, although usually less severely altered, environment to be created and maintained by the metabolism of the produce itself. Unlike CA storage, there is no direct control of the levels of specific gases. The advantage of MAP is that it does not incur the large capital costs involved with CA.

The historical development of the use of MA for horticultural and agricultural produce has been discussed by authors such as Dilley (1990) and Bishop (1990). The preservation of fresh produce in caves, enclosed in suitable wrappings underground, or enclosed in sealed vessels with grass and leaves, was well practised by early civilizations and can be dated back at least as far as 8th century China (Dilley, 1990; Wang, 1990). There is even evidence to suggest that ancient Egyptians and Samaritans in the second century BC stored portions of their crops in sealed limestone crypts to prolong storage life (Bishop, 1990). While some scientific studies on CA storage were carried out in the 1800's, it was the 1920's work of Kidd and West on the influences of temperature, carbon dioxide, and oxygen on fruit ripening and respiration that led to the commercial application of CA technology (Wills *et al.*, 1989, p. 62; Dilley, 1990).

Since this work, more than 4000 research reports, many dealing with the determination of optimum MA conditions for various fruits and vegetables, have been published (Kader, 1986; Kader *et al.*, 1989). A list of references to this large body of literature has been compiled by Morris *et al.* (1971), Murr *et al.* (1974), Kader & Morris (1977, 1981), Kader (1985), and Zagory & Kader (1989a).

The physiological and biochemical effects of MA storage have been reviewed by various authors (e.g. Burton, 1974; Do & Salunkhe, 1975; Ulrich, 1975; Burton, 1978; Metlitskii *et al.*, 1983; Kader, 1986; Zagory & Kader, 1989b; Wang, 1990; Knee, 1991). These effects can be beneficial or detrimental, depending on whether or not the gas levels used exceed the tolerance limits of the commodity.

### 2.1.2.1 POTENTIAL BENEFICIAL EFFECTS OF MODIFIED ATMOSPHERES

The application of appropriate MA storage conditions can slow rates of respiration and ripening, and delay the onset of senescence in many commodities. The major beneficial effects that have been observed in fruits and vegetables stored under modified atmospheres are as follows:

- (i) *Reduced rate of respiration.* The rate of aerobic respiratory metabolism is reduced at lowered O<sub>2</sub> and elevated CO<sub>2</sub> concentrations. The effect of lowered O<sub>2</sub> concentration on respiratory rate is thought to be due to a reduction in the activity of various low affinity oxidases. The main mediator of aerobic metabolism, cytochrome-c oxidase, has a high O<sub>2</sub> affinity and would therefore not be significantly affected until physiologically harmful O<sub>2</sub> concentrations had been reached (Burton, 1974, 1978; Kader, 1986; Zagory & Kader, 1989b; Knee, 1991). Elevated CO<sub>2</sub> concentrations reduce the rate of respiration independently of the effect of O<sub>2</sub> and the effects of these two gases acting simultaneously are additive (Kader, 1986). In climacteric fruits, low O<sub>2</sub> and high CO<sub>2</sub> concentrations can also retard the onset of the climacteric peak. The reduction in respiration rate under MA results in a related reduction in respiratory heat generation and thus a lowering of the heat load on refrigeration equipment. The heat load of various commodities under CA, including apples, has been estimated as 30% of that in air (Wang, 1990; Powrie & Skura, 1991).
- (ii) *Reduced ethylene production and sensitivity.* Ethylene is produced in significant quantities by ripening fruit, especially climacteric varieties, and is of physiological importance as a ripening hormone (Burton, 1974). O<sub>2</sub> is required for both ethylene production and action (Knee, 1991). Various studies have shown that ethylene production and sensitivity to ethylene are reduced at levels of O<sub>2</sub> below 8 mol % (Kader, 1986, 1992b). CO<sub>2</sub> levels above approximately 1 mol % have also been found to reduce sensitivity to ethylene (Kader, 1992b), conceivably by competing with ethylene for binding sites (competitive inhibition), or by a feed-back inhibition mechanism (Ulrich, 1975; Metlitskii *et al.*, 1983; Kader, 1986; Wang, 1990). The effects of elevated CO<sub>2</sub> levels on ethylene production are variable, depending on the commodity and the concentration. Wang (1990) notes that inhibition of ethylene production by

CO<sub>2</sub> occurs primarily in fruits, whereas stimulation of ethylene production is observed mainly in photosynthetic vegetative tissues.

- (iii) *Retarded colour development.* Colour development during fruit ripening is due to the degradation of chlorophyll (loss of green colour) and the synthesis and/or revelation of carotenoids (yellow and orange pigments) and anthocyanins (red and blue pigments) (Wills *et al.*, 1989, p. 34). Loss of chlorophyll and biosynthesis of carotenoids and anthocyanins have been shown to be delayed by high CO<sub>2</sub> and/or low O<sub>2</sub> atmospheres (Do & Salunkhe, 1975; Ulrich, 1975; Kader, 1986; Zagory & Kader, 1989b).
- (iv) *Retarded flavour development.* Flavour development in fruits and vegetables can be attributed to compositional changes in carbohydrates, organic acids, proteins, amino acids, lipids and phenolic compounds (Kader, 1986). These changes can be slowed by reduced O<sub>2</sub> and increased CO<sub>2</sub> levels (e.g. reduced starch conversion, reduced loss of sugars, reduced loss of organic acids and reduced loss of amino acids) (Zagory & Kader, 1989b).
- (v) *Retarded softening.* Softening of fruit can be attributed in part to changes in cell wall structure, such as the enzymatic breakdown of insoluble pectins (Zagory & Kader, 1989b). Softening due to loss of cell wall structure can be retarded by increased CO<sub>2</sub> levels and low O<sub>2</sub> levels (Burton, 1974; Ulrich, 1975; Zagory & Kader, 1989b).
- (vi) *Inhibition of tissue browning.* The discolouration observed at cut surfaces of fruit or vegetable tissue is largely due to the enzymatic oxidation of phenolic substances (Burton, 1974; Kader, 1986; Wang, 1990). Reduced O<sub>2</sub> and high CO<sub>2</sub> concentrations can significantly reduce the browning of cut or injured tissue (Burton, 1974, 1978; Wang, 1990).
- (vii) *Reduced moisture loss.* The sealed or packaged conditions needed to produce modified O<sub>2</sub> and CO<sub>2</sub> levels generally lead to high relative humidities in the atmosphere around the produce, and hence reduced water loss (Dewey, 1983).
- (viii) *Reduced incidence of physiological disorders.* Superficial scald in apples appears to be caused by the oxidation products of  $\alpha$ -farnesene, a volatile organic compound found in high concentrations in fruit susceptible to or affected by this disorder (Burton, 1974; Wang, 1990). The incidence of scald can be considerably reduced by maintaining low O<sub>2</sub> levels (Knee, 1991). Chilling injury in some commodities (e.g. avocado), bitter-pit in some apple cultivars, and ethylene-induced disorders such as russet spotting in lettuce, can also be alleviated by MA conditions (Kader, 1986; Wills *et al.*, 1989, p. 76; Wang, 1990; Knee, 1991).
- (ix) *Reduced susceptibility to microbial infection.* In general, undamaged fruits and vegetables exhibit considerable resistance to infection by pathogenic microorganisms. This resistance decreases with the onset of senescence (Kader, 1986). Favourable modified atmospheres delay the onset of senescence and

thus reduce the susceptibility of fruits and vegetables to microbial attack. High CO<sub>2</sub> and/or low O<sub>2</sub> levels can have inhibitory effects on many spoilage organisms, for example, CO<sub>2</sub> levels of about 50 mol % are lethal to many fungi and aerobic bacteria. Although most produce cannot tolerate this level of CO<sub>2</sub>, some control of rots is still observed at lower levels (8-15 mol %) (Burton, 1974, 1978; Dewey, 1983; Kader *et al.*, 1989). Low O<sub>2</sub> levels can exercise some control but generally only at concentrations that would induce anaerobiosis in the commodity. MA can also play a role with respect to insect control in some commodities (Kader, 1992b).

### 2.1.2.2 POTENTIAL DETRIMENTAL EFFECTS OF MODIFIED ATMOSPHERES

In spite of the beneficial effects discussed above, inappropriate MA conditions and some factors inherent in MA storage can produce detrimental effects with respect to the storage life or quality of a particular commodity:

- (i) *Flavour development problems.* Over-modification of the storage atmosphere with respect to CO<sub>2</sub> and/or O<sub>2</sub> can initiate anaerobic respiration and the subsequent development of off-flavours due to the production of acetaldehyde and ethanol (Blanke, 1991; Knee, 1991; Day, 1993). As discussed in section 2.1.1, the build up of these substances can also cause physiological damage and premature onset of senescence. O<sub>2</sub> concentrations must be kept at levels sufficient to avoid a long-term shift to anaerobic metabolism. This imposes a lower O<sub>2</sub> limit of 1-3 mol %, depending on the commodity (Ulrich, 1975; Kader, 1986). Various studies have shown that prolonged exposure to MA can suppress normal flavour or aroma development once the produce has been returned to air storage (Zagory & Kader, 1989b; Wang, 1990). This has been attributed by some researchers to decreased ethylene sensitivity or deficiencies in normal ester development (Wang, 1990).
- (ii) *Physiological injury.* Prolonged exposure to CO<sub>2</sub> concentrations above the tolerance limits of a particular commodity can result in a physiological disorder known as CO<sub>2</sub> injury. In apples, this condition leads to the development of sharply defined brown areas in the flesh, for example, the conditions known as brown heart or core flush (Burton, 1974; Ulrich, 1975; Wills *et al.*, 1989, p. 84; Wang, 1990).
- (iii) *Accumulation of organic volatiles.* The sealed or packaged conditions necessary for MA or CA storage can lead to the accumulation of high concentrations of volatile organic substances, in particular ethylene (Kader, 1986, 1992b; Knee, 1991). Build up of ethylene counteracts the beneficial effects imparted by MA with respect to ethylene production and action, especially during long-term storage (Kader, 1992b).
- (iv) *Development of conditions favourable to microbial growth.* Inappropriate MA conditions can cause physiological injury, thereby hastening senescence and increasing susceptibility to microbial infection (Kader, 1986; Zagory & Kader, 1988; Kader, 1992b). The high humidities typical of MA environments, as well

as the possible condensation of moisture induced by such high humidities, can also create conditions favourable to microbial growth (Ulrich, 1975; Zagory & Kader, 1988; Wills *et al.*, 1989, pp. 53, 57-58).

### 2.1.3 MODIFIED ATMOSPHERE PACKAGING SYSTEMS

To date, the greatest application of modified atmosphere technology to the storage of fresh fruit and vegetables has been the CA storage of apples and pears (Zagory & Kader, 1988; Knee, 1991). Although modern CA technology enables precise and accurate control of gas concentrations at specified levels, significant capital and operating costs are associated with the gas generating and control equipment, and the construction and maintenance of gas-tight storage facilities.

Recent advances in the design and manufacture of polymeric films with a wide range of gas permeabilities and other properties have stimulated interest in the development and use of modified atmosphere packaging for a wide range of food products (Kader *et al.*, 1989; Church, 1994). Types of products to which MAP has been applied include meat, poultry and fish; bakery and dairy products; fresh fruits and vegetables; and convenience foods (Ooraikul & Stiles, 1991). For non-respiring products, MAP often involves flushing packages with the desired storage gas-mixture during the packing operation. However, with respiring produce the package atmosphere can also be modified "passively" through the metabolism of the produce itself (Day, 1993; Church, 1994).

The high capital and operating costs of CA storage, and the potential for applying MAP to retail-display packages, make the development of MAP systems for fruits and vegetables an attractive alternative. To overcome the inherent lack of control of gas levels in MAP, and to avoid the problems of MA storage discussed in the previous section, careful design of such packaging systems is essential.

## 2.2 MODIFIED ATMOSPHERE PACKAGING OF NEW ZEALAND APPLES

ENZA New Zealand (International) is currently investigating the use of plastic film box liners as a means of providing modified atmosphere storage and transport for various apple varieties. Research in New Zealand has shown that the packing of apples within film-lined cartons as an adjunct to cool storage can have definite beneficial effects on the retention of apple quality after harvest (Watkins, 1988; Watkins *et al.*, 1989; Brookfield & Watkins, 1991; Watkins & Cregoe, 1991; Elgar & Watkins, 1992; Frampton & Ahlborn, 1994a; Frampton *et al.*, 1994a).

The New Zealand work on MA liners grew out of work that was initially aimed at examining the use of microperforated-film carton-liners to reduce bitter pit in, and maintain the fruit quality of, 'Cox's Orange Pippin' apples (Watkins *et al.*, 1986; Watkins & Thompson, 1987; Watkins, 1988). Watkins *et al.* (1986) investigated the effects of storage temperature, storage time, and delays at ambient temperature on

'Cox's Orange Pippin' apples packed with and without microperforated liners (plastic liners with 50 holes of 1 mm diameter). The trials also compared the use of microperforated and macroperforated liners (plastic liners with a gusset containing 24 holes of 9 mm diameter). Fruit were stored at 0 or 3°C for 6 or 12 weeks, and were evaluated after a 7 day simulated shelf life at ambient temperatures. Microperforated liners reduced the incidence of bitter pit and produced greener and firmer fruit under all the storage conditions tested. Microperforated liners also had a beneficial effect on some aspects of fruit quality where delays of 1 to 5 days at ambient temperatures occurred before cool storage. However, the incidence of superficial scald was significantly higher in fruit from the microperforated liners than in fruit from the macroperforated liners or fruit stored with no liner.

The work on microperforated liners was extended over the following two seasons (Watkins & Thompson, 1987; Watkins, 1988). As well as the factors investigated earlier, the effects of growing district and maturity at harvest were examined in this work. The beneficial effects of microperforated liners on fruit colour, fruit firmness, and incidence of bitter pit were confirmed. However, the problems with increased incidence of superficial scald remained, especially in early harvested fruit. To overcome this problem, Watkins & Thompson (1987) recommended that an antioxidant such as diphenylamine (DPA) be used with early harvested fruit, or that the use of microperforated liners be restricted to fruit from the last third of the harvest period. Watkins & Thompson (1987) also carried out gas analysis work on the atmospheres formed within macroperforated and microperforated liners. Atmospheres inside the microperforated liners were somewhat modified at 16-17 mol % O<sub>2</sub>, 4-5 mol % CO<sub>2</sub>, and 220-370 ppm ethylene; atmospheres inside the macroperforated liners were less modified at 18-20 mol % O<sub>2</sub>, about 1 mol % CO<sub>2</sub>, and 60-90 ppm ethylene. Work during the 1988 season evaluated a semi-commercial trial of 'Cox's Orange Pippin' sent to Europe in microperforated liners. Late harvested fruit were used in the trial and by doing this the problems with superficial scald were alleviated (Watkins, 1988).

During the 1988 season, storage trials were also set up using newly available, non-perforated, polymeric-film liners (Watkins, 1988). Three film thicknesses were assessed for 'Cox's Orange Pippin' fruit: 22 µm, 28 µm and 40 µm. Rubber rings were used to hold the liners closed over the fruit during storage. All three film thicknesses produced firmer and greener fruit than microperforated or macroperforated liners, this being especially so for the 40 µm film. No problems with storage disorders were encountered, and although no measurements of package atmosphere composition were reported, no evidence of anaerobiosis was detected from any of the films. An untrained taste panel found that fruit from the non-perforated liners had significantly better texture, flavour, and overall acceptability than fruit from the other treatments.

As a result of these findings, subsequent work concentrated on the further evaluation of non-perforated liners, both for 'Cox's Orange Pippin' and for various other cultivars (Watkins *et al.*, 1989; Brookfield & Watkins, 1991; Watkins & Cregoe, 1991; Elgar & Watkins, 1992; Frampton & Ahlborn, 1994a; Frampton *et al.*, 1994a).

Watkins *et al.* (1989) assessed the effect of two thicknesses of non-perforated liner (25 µm and 50 µm) on the storage quality of 'Cox's Orange Pippin', 'Gala', 'Royal

Gala', 'Red Delicious', 'Braeburn', and 'Granny Smith' apples. In these and all subsequent trials, liners were closed over the fruit by folding down the corners of the open end and tucking the end into the side of the carton. Fruit were stored for 8 to 20 weeks depending on cultivar, and were assessed after 1 and 7 days at ambient temperature. In general, fruit from the non-perforated liners were firmer and greener than fruit from microperforated liners, which in turn tended to be firmer and greener than fruit from the macroperforated liners or fruit stored with no liner. No significant storage effect on soluble solids was noted. Alcoholic off-flavours were detected during informal tasting of 'Cox's Orange Pippin', 'Gala', and 'Royal Gala' from the 50  $\mu\text{m}$  liners, although for 'Gala' and 'Royal Gala' these were slight. Increased levels of superficial scald were evident in early harvested 'Cox's Orange Pippin' from the 25  $\mu\text{m}$  liners, but these levels were much less severe than those found in the microperforated liners. The beneficial effects of MA liners on colour and fruit firmness were most noticeable for 'Cox's Orange Pippin', 'Royal Gala', and 'Red Delicious', and less marked for 'Gala', 'Braeburn', and 'Granny Smith'. The 'Gala', 'Royal Gala', and 'Granny Smith' cultivars, normally susceptible to the development of greasiness during storage, showed a marked reduction in greasiness when stored in the non-perforated liners. Informal tasting indicated that fruit from non-perforated liners were generally more crisp and juicy than fruit from other treatments. Gas analysis of package atmospheres showed an increasing degree of atmosphere modification in the following order: macroperforated liners, microperforated liners, 25  $\mu\text{m}$  non-perforated liners, and 50  $\mu\text{m}$  non-perforated liners (Table 2.2).

Brookfield & Watkins (1991) extended the work on non-perforated liners for 'Royal Gala', 'Red Delicious', 'Braeburn', and 'Granny Smith' apples with trials using 25  $\mu\text{m}$ , 40  $\mu\text{m}$ , and 50  $\mu\text{m}$  films. Fruit were stored at 0.5°C for 11 to 16 weeks, depending on cultivar. On removal from cool storage, liners in half the cartons for each cultivar were opened, while liners in the other half were left closed for a further 7 days. All fruit were assessed after 7 days at ambient temperatures. 'Royal Gala' were stored in 40 and 50  $\mu\text{m}$  films. These gave similar results, producing greener and firmer fruit than storage with no polyliner. Greasiness was also reduced. Storage of 'Red Delicious' apples in 40  $\mu\text{m}$  liners had no significant effect on flesh firmness. Colour was not assessed for this cultivar, but greasiness was significantly reduced. Slightly higher levels of superficial scald were noted, although incidence of the disorder was variable between different cartons of fruit. Storage of 'Braeburn' apples in 25  $\mu\text{m}$  liners produced greener

**Table 2.2** Gas concentrations measured inside film-lined apple cartons during the 1989 season.<sup>a</sup>

| Film type        | O <sub>2</sub><br>(mol %) | CO <sub>2</sub><br>(mol %) | Ethylene<br>(ppm) |
|------------------|---------------------------|----------------------------|-------------------|
| Macroperforated  | 18-21                     | 0.1-0.7                    | 0-30              |
| Microperforated  | 11-18                     | 2-4                        | 10-230            |
| 25 $\mu\text{m}$ | 4-17                      | 2-5                        | 40-430            |
| 50 $\mu\text{m}$ | 1-13                      | 2-5                        | 10-460            |

<sup>a</sup> Developed from the results of Watkins *et al.* (1989). Ranges given cover results for all six cultivars tested.

and slightly firmer fruit, and reduced greasiness in late harvest fruit. 'Granny Smith' apples stored in 40  $\mu\text{m}$  liners were greener, firmer, and less greasy than fruit stored without liners, with no disorders or off-flavours noted. Keeping liners closed after removal from cool storage had some beneficial effects on colour ('Royal Gala', 'Braeburn'), flesh firmness ('Royal Gala', 'Braeburn') and greasiness ('Royal Gala', 'Granny Smith'). No disadvantageous effects were noted.

Further work was carried out during the 1991 season to evaluate four newly developed films (Watkins & Cregoe, 1991). These films were tested for 'Red Delicious' apples held at tropical temperatures (35°C) for 7 days after cool-storage, and for 'Red Delicious', 'Royal Gala', 'Braeburn', and 'Granny Smith' apples held at normal ambient conditions (20°C) for 7 days after cool-storage. The films proved unsuitable for use at high temperatures, with fruit condition being too poor for assessment after holding at 35°C for 7 days. None of the new films were particularly promising, with two tending to over-modify the atmosphere and the remaining two not modifying the atmosphere enough to have a significant effect on storage quality. No quantitative information on film properties was reported.

Elgar & Watkins (1992) carried out work with 'Cox's Orange Pippin', 'Royal Gala', 'Golden Delicious', and 'Fuji' stored in liners of the original MA-film. For 'Cox's Orange Pippin' and 'Royal Gala', they investigated the effects of growing district (Canterbury, Nelson, Hastings) and harvest date (early, mid, late) on fruit storage quality. Although there were differences between some of the quality attributes of fruit from different growing districts, district and harvest date generally had no significant effect on the response to MA. 'Cox's Orange Pippin' stored in 25  $\mu\text{m}$  liners for up to 20 weeks at 3°C were greener and firmer than fruit stored in macroperforated liners, although differences in firmness between the two treatments tended to become insignificant after long storage periods (> 12 weeks) or after a period of 7 days at 20°C at the end of storage. Core flush, senescent breakdown, and low levels of superficial scald were noted after 16 to 20 weeks storage in both the 25  $\mu\text{m}$  liners and the macroperforated liners, but incidences of core flush and senescent breakdown tended to be higher in the 25  $\mu\text{m}$  liners, while incidences of scald were higher in the macroperforated liners. 'Royal Gala' stored in 40  $\mu\text{m}$  liners for up to 20 weeks at 0°C were greener, less greasy, and slightly firmer than fruit stored in air. Incidences of storage disorders were very low for both MA and air-stored 'Royal Gala'.

'Golden Delicious' and 'Fuji' apples were stored at 0°C in 25  $\mu\text{m}$  liners, 40  $\mu\text{m}$  liners, macroperforated liners, or air for 12 and 18 weeks respectively. For both cultivars, fruit from the 25 and 40  $\mu\text{m}$  liners were greener than fruit from the macroperforated liners or fruit stored in air. Fruit from the 40  $\mu\text{m}$  liners were also firmer than fruit from the other treatments. Informal tasting indicated that 'Golden Delicious' from the 25 and 40  $\mu\text{m}$  liners were crisper, juicier, firmer, but also blander than fruit from the macroperforated liners or air storage, which were soft and mealy. 'Fuji' from the 25 and 40  $\mu\text{m}$  liners were also crisper and blander than fruit from the macroperforated liners or air storage. After a period of 7 days at 20°C at the end of storage, 'Fuji' from the 25 and 40  $\mu\text{m}$  liners were less greasy than fruit from the macroperforated liners or air storage. Incidences of core browning were found in 'Fuji' from all the treatments, but were highest in fruit from the macroperforated liners (66%) and lowest in fruit from

the 40  $\mu\text{m}$  liners (1%). Low incidences of brown heart (<1%) were found in 'Fuji' from the 25 and 40  $\mu\text{m}$  liners.

Elgar & Watkins (1992) also evaluated the effects of six new types of microperforated film on the quality of 'Granny Smith' apples stored at 0°C for 14 weeks. No details of the new microperforated films (e.g. film thickness, number of holes per bag, or hole diameter) were published. Trials were also run with 25  $\mu\text{m}$  liners of the 'standard' MA-film. No significant effects on colour or firmness were noted for any of the films, but after a final storage period of 7 days at 20°C, fruit stored in the films were less greasy than fruit stored in air. Slight core flush was observed in 25-50% of fruit after 14 weeks cool storage, and slight to moderate core flush was observed in 40-60% of fruit after another 7 days at 20°C. However, the different films had no consistent effect on the incidence of core flush.

Elgar & Watkins (1992) measured package  $\text{O}_2$ ,  $\text{CO}_2$ , and ethylene concentrations at the end of cool-storage for each of the 1992 trials. These data are summarized in Table 2.3.

Frampton & Ahlborn (1994a) assessed the performance of another two new films. Both of these films were 30  $\mu\text{m}$  thick and non-perforated, and one of the films contained an ethylene absorber. In storage trials with 'Royal Gala' fruit, the performance of the new films was compared with that of macroperforated liners and with that of 40  $\mu\text{m}$  liners of the standard MA-film. All three non-perforated films produced similar package atmospheres (12-15 mol %  $\text{O}_2$ , 2.2-3.5 mol %  $\text{CO}_2$ , and 110-150 ppm ethylene after 14 weeks cool-storage), with the film containing the ethylene absorber having no significant effect on package ethylene concentrations. As in previous work, the macroperforated liners produced virtually no atmosphere modification. Fruit from the non-perforated liners lost less weight, were less greasy, and were slightly firmer and greener than fruit from the macroperforated liners or fruit stored with no liner. However, there were no significant differences between fruit from the three different types of non-perforated liner. Fruit from the macroperforated liners lost less weight than air-stored fruit, but the macroperforated liners had no significant effect on any other measured quality attribute.

Frampton *et al.* (1994a), assessed the quality of 'Royal Gala' fruit shipped to the UK in macroperforated liners or in 40  $\mu\text{m}$  liners of the standard MA-film. Again, fruit from the non-perforated liners lost less weight and were less greasy than fruit from the macroperforated liners. However, when fruit were removed from cool-storage and left at ambient temperatures for up to 14 days (with the liners opened), the greasiness of fruit from the non-perforated liners increased rapidly. After 14 days at ambient temperatures, there was no difference in the greasiness of fruit from the macroperforated and non-perforated liners. A similar effect was noted for background colour. Liner type had no effect on soluble solids content or flesh firmness.

The storage trials carried out to date have shown that non-perforated liners can reduce weight loss, retard the development of greasiness, and produce fruit that are firmer and greener than fruit from microperforated liners, macroperforated liners, or storage with no liner. Non-perforated liners also appear to reduce the incidence of bitter pit in cultivars such as 'Cox's Orange Pippin', without inducing the severely increased incidences of superficial scald observed for some of the trials with microperforated

**Table 2.3** Gas concentrations measured inside film-lined apple cartons during the 1992 season<sup>a</sup>.

| Cultivar/film type                                                                                                                                                                                                                        | After cool-storage        |                            |                   | After 7 days at 20°C      |                            |                   |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------|----------------------------|-------------------|---------------------------|----------------------------|-------------------|
|                                                                                                                                                                                                                                           | O <sub>2</sub><br>(mol %) | CO <sub>2</sub><br>(mol %) | Ethylene<br>(ppm) | O <sub>2</sub><br>(mol %) | CO <sub>2</sub><br>(mol %) | Ethylene<br>(ppm) |
| 'Cox's Orange Pippin'<br>macroperforated<br>25 µm                                                                                                                                                                                         | 20-21                     | < 0.3                      | 1-12              | – <sup>b</sup>            | – <sup>b</sup>             | – <sup>b</sup>    |
|                                                                                                                                                                                                                                           | 6-11                      | 3-4                        | 160-350           | – <sup>b</sup>            | – <sup>b</sup>             | – <sup>b</sup>    |
| 'Royal Gala'<br>40 µm                                                                                                                                                                                                                     | 6-12                      | 2-4                        | 90-360            | – <sup>b</sup>            | – <sup>b</sup>             | – <sup>b</sup>    |
|                                                                                                                                                                                                                                           |                           |                            |                   |                           |                            |                   |
| 'Golden Delicious'<br>macroperforated<br>25 µm<br>40 µm                                                                                                                                                                                   | 20                        | 0.1                        | 8                 | 19                        | 1.2                        | 150               |
|                                                                                                                                                                                                                                           | 10                        | 2.4                        | 550               | 6                         | 3.9                        | 370               |
|                                                                                                                                                                                                                                           | 7                         | 3.3                        | 780               | 4                         | 4.7                        | 300               |
| 'Fuji'<br>macroperforated<br>25 µm<br>40 µm                                                                                                                                                                                               | 21                        | 0.1                        | 2                 | 20                        | 0.3                        | 14                |
|                                                                                                                                                                                                                                           | 16                        | 1.6                        | 130               | 8                         | 4.0                        | 230               |
|                                                                                                                                                                                                                                           | 12                        | 2.4                        | 130               | 5                         | 4.8                        | 90                |
| 'Granny Smith'<br>microperforated L1 <sup>c</sup><br>microperforated L2 <sup>c</sup><br>microperforated L3 <sup>c</sup><br>microperforated E1 <sup>c</sup><br>microperforated E2 <sup>c</sup><br>microperforated E3 <sup>c</sup><br>25 µm | 19                        | 1.9                        | 100               | 12                        | 9                          | 380               |
|                                                                                                                                                                                                                                           | 19                        | 2.4                        | 130               | 11                        | 10                         | 460               |
|                                                                                                                                                                                                                                           | 18                        | 3.0                        | 170               | 9                         | 10                         | 340               |
|                                                                                                                                                                                                                                           | 18                        | 1.7                        | 110               | 13                        | 7                          | 460               |
|                                                                                                                                                                                                                                           | 19                        | 1.8                        | 100               | 12                        | 8                          | 390               |
|                                                                                                                                                                                                                                           | 18                        | 2.8                        | 180               | 9                         | 8                          | 460               |
|                                                                                                                                                                                                                                           | 14                        | 1.8                        | 210               | 8                         | 4                          | 310               |
|                                                                                                                                                                                                                                           |                           |                            |                   |                           |                            |                   |

<sup>a</sup> Developed from the results of Elgar & Watkins (1992).<sup>b</sup> Not determined.<sup>c</sup> Codes given to 6 different microperforated films.

liners. Thus, although MA-liners are not seen as a replacement for CA storage, they could be used to help maintain the quality of fruit normally exported from New Zealand under air-storage. At present, the reduction of weight loss and greasiness are of particular interest to ENZA, as the effects on firmness and colour have tended to be less significant and more variable.

Use of MA-liners would also reduce the need for high-humidity cool-stores. Lower humidity stores could significantly reduce the uptake of moisture by cardboard packaging materials, thus improving the strength of cartons and reducing the incidence of fruit damage due to carton failure.

Despite the apparent benefits, there are some problems with the large-scale use of MA liners. Although MA-liners are less costly than CA storage, the additional packaging costs involved are still significant when compared to conventional air-storage. During some of the storage trials carried out to date, MA-liners have been associated with

alcoholic off-flavours, bland-tasting fruit, low levels of superficial scald, and internal browning disorders such as core flush and brown heart. MA packages are generally designed for a specific carton size, fruit cultivar, and fruit weight, and any changes to carton size or contents may necessitate respecification of the MA-film used in the package.

To date, little work has been directed at investigating the performance of MA-liners from the point of view of the atmospheres formed within them, even though these atmospheres are the basis for the effects of the liners on fruit quality attributes. The variability of package atmospheres from carton to carton, the effects of hermetically sealing the liners rather than folding them closed, the rates at which modified atmospheres develop within the cartons, the effects of temperature on steady-state atmospheres and rates of atmosphere development, the effects of transient storage temperatures on package atmospheres, and the effects of holes or tears on package atmospheres are either unknown or can presently be judged only qualitatively from a consideration of theoretical aspects.

For the application of MA-liners to be cost-effective, it is important that package designs are optimized to provide maximum possible benefits at a minimum risk. In New Zealand, little work has been carried out to optimize package designs. No work has yet been directed at (a) determining the range of package atmospheres achievable with current packaging technology, (b) determining which atmospheres in this range provide the maximum storage benefits for various apple cultivars, or (c) developing methods for designing packages to produce a desired modified atmosphere.

The remainder of this review deals specifically with topics related to the design and optimization of modified atmosphere packaging systems for horticultural produce.

## **2.3 DESIGN AND OPTIMIZATION OF MODIFIED ATMOSPHERE PACKAGING SYSTEMS**

The design and optimization of MAP systems has traditionally been based on a "trial-and-error" approach (Kader *et al.*, 1989; Prince, 1989). This involves the experimental testing of a range of potential packaging designs until a suitable design is found. Although experimental evaluation provides the most reliable evidence of the suitability of a proposed package design, experimental approaches to design and optimization are often time-consuming, inflexible, and expensive.

A mathematical model capable of predicting important package variables as functions of fruit characteristics, packaging-material characteristics, storage conditions, and time would allow a more rational and quantitative approach to design and optimization. Such a model could be used to (a) answer "what if" questions concerning changes to package design or storage conditions, (b) rapidly identify design and environmental factors that significantly affect package variables, and (c) effectively plan experimental trials such that maximum value can be obtained from a given amount of experimental effort. The

flexibility of a modelling approach has led to an increasing interest in the development of mathematical models for fruit and vegetable MAP systems.

The aim of any MAP system is the maintenance of product quality. The quality of fresh produce is affected by the cumulative history of physiological processes occurring over the life of the fruit, both pre- and post-harvest. Postharvest physiology, in turn, is influenced by factors such as growing conditions, storage temperature, humidity, fruit internal atmosphere composition, cultivar, and maturity. An ideal model of a modified atmosphere packaging system would therefore be capable of predicting the physical environment around and within a given commodity as a function of store conditions, the effect of this environment on the commodity's physiology given information on cultivar and maturity, and the cumulative effect of the commodity's physiology on some measure of product quality.

## 2.4 MODELLING OF MODIFIED ATMOSPHERE PACKAGING SYSTEMS

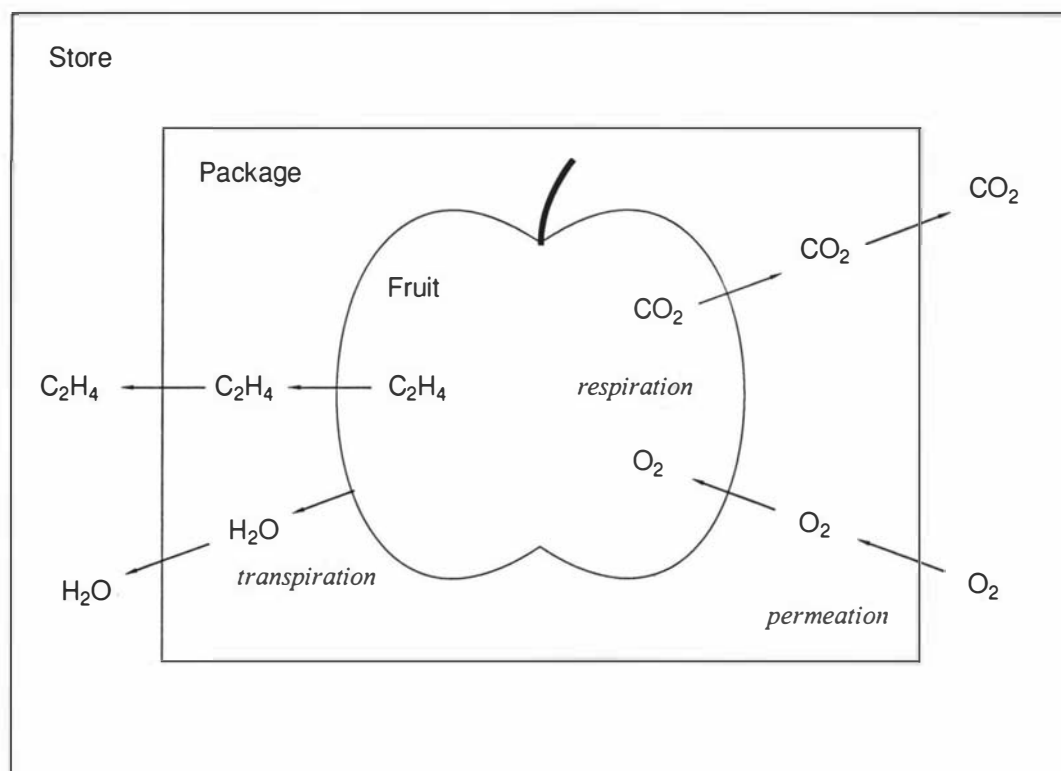
### 2.4.1 DESCRIPTION OF THE PHYSICAL SYSTEM

Figure 2.1 shows a schematic diagram of an MAP system for fresh produce. The produce is enclosed by film packaging, which is usually surrounded by some form of support packaging. The environment external to the package may be either a cool-store environment or normal ambient conditions. During storage, all the metabolic processes involved in cell maintenance and physiological development proceed within the fruit. These processes, together with physical interactions between the produce, the package environment, and the external environment, drive the various transport processes which take place in the MAP system.

#### 2.4.1.1 TRANSPORT OF GASES

The processes of respiration and ripening in fruit give rise to the consumption of oxygen and the production of carbon dioxide, ethylene, and other volatiles. This production and consumption of gases leads to the development of a series of concentration gradients within the MAP system, and the subsequent transport of gases along these gradients.

The mechanisms of gas diffusion within bulky plant organs have been reviewed by various authors, including Burton (1974, 1978), Solomos (1987) and Kader *et al.* (1989). Within the flesh of fruits and vegetables, there is a more or less continuous network of gas-filled intercellular spaces (Burton, 1974, 1978; Woods, 1990). The gases within this intercellular network form what is referred to as the internal atmosphere of the fruit or vegetable. Gas exchange occurs between the internal atmosphere and individual cells, with gas diffusion through the cytoplasm occurring between the cell surface and the centres within the cell where gases are consumed or produced. Within the tissue, gases diffuse mainly through the intercellular spaces, this route being the path of least resistance to gas diffusion (Solomos, 1987; Kader *et al.*, 1989).



**Figure 2.1** Schematic diagram of an MAP system.

The exchange of gases between the internal and package atmospheres can proceed via several pathways: through lenticels or stomata, through the aqueous or waxy layers of the epidermis, or through the pedicel and calyx openings (Solomos, 1987; Kader *et al.*, 1989). Most bulky plant organs have no functional stomata or other active mechanisms for the control of gas exchange, and the diffusivity of  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  in the aqueous phase of the cuticle is about  $10^4$  times less than the diffusivity of these gases in air (Kader *et al.*, 1989). Thus, diffusion through the lenticels and the pedicel and calyx openings offers the path of least resistance. That the majority of gas diffusion in bulky plant organs does indeed occur via these openings has been supported by various studies (Kader *et al.*, 1989).

The resistance to gas diffusion imposed by the skin is generally considered to be significantly larger than the resistance to gas diffusion within the internal tissues. In apples for example, skin resistances 10- to 20-fold higher than flesh resistances have been estimated (Solomos, 1987; Kader *et al.*, 1989). Resistance to gas diffusion within the internal tissues is generally considered to be negligible (Burton, 1974, 1978; Kader *et al.*, 1989), but there are some conflicting data that challenge the validity of this assumption. Burton (1974) cites changes in  $\text{O}_2$  concentration of 0.5 to 1 mol % over a radial distance of about 2 cm in apple flesh, and concentration differences of 0.1 to 0.6 mol % for  $\text{O}_2$  and  $\text{CO}_2$  have been observed between the fruit centre and skin in various apple cultivars (Solomos, 1987). Rajapakse *et al.* (1989a,b, 1990) measured  $\text{O}_2$  concentration differences between the centre and surface of several cultivars of apple, nashi and nectarine. Their results showed  $\text{O}_2$  concentration differences of 0.2-1 mol %

for apples and 1-3 mol % for nashi and nectarines. Dadzie (1992) measured internal O<sub>2</sub> and CO<sub>2</sub> concentrations at the core cavity, calyx end, calyx end shoulder and equatorial regions of fruit from eight apple cultivars. He found that significant concentration differences (up to 9 mol % for O<sub>2</sub> and 3 mol % for CO<sub>2</sub>) can exist between the equator and the calyx end or calyx end shoulder. The magnitudes of these concentration differences varied between cultivars. Much smaller, but still significant, concentration differences were measured between the equator and the core cavity. Such observations suggest that internal resistance to gas diffusion may not be negligible, and that positional variations in skin resistance, intercellular space volume, and respiration rate may exist.

Gas exchange between the fruit internal atmosphere and the package atmosphere changes the composition of the package atmosphere. This, in turn, leads to gas exchange between the package atmosphere and the external atmosphere. In MAP systems, gas exchange between the package and external atmospheres is significantly restricted by the presence of the packaging film. The packaging film may be hermetically sealed so that there is no direct contact between the package and external atmospheres, or the packaging film may be perforated or imperfectly sealed (e.g. folded closed) so that there is a direct path between the package and external atmospheres.

In the former case, gas exchange between the package and external atmospheres occurs solely by gas permeation through the packaging film. Permeation through a non-porous, flawless polymer occurs by three steps: (1) sorption of the penetrant (diffusing gas) into the polymer on the high concentration side; (2) diffusion of the penetrant through the polymer along a concentration gradient; and (3) desorption of the penetrant on the low concentration side of the film (Rogers, 1985; Chao & Rizvi, 1988). In the case of perforated, porous, or imperfectly sealed films, permeation still occurs, but gas exchange by diffusion and flow through holes and pores also becomes important (Chao & Rizvi, 1988).

Within the package or external atmosphere, gas transport occurs by diffusion or by the bulk movement of air currents due to natural or forced convection.

#### **2.4.1.2 TRANSPORT OF WATER AND WATER VAPOUR**

The mechanisms for movement of water and water vapour within fruits and vegetables have been reviewed by Burton (1982, pp. 43-68) and Woods (1990). There are three possible routes for the transport of water within plant tissues: (1) osmotic diffusion from cell to cell via the cytoplasm and plasmodesmata; (2) movement of water through the interfibrillar spaces in the cell walls in response to a hydrostatic pressure gradient; and (3) diffusion of water vapour through the intercellular spaces. The internal atmospheres of fruits and vegetables are generally considered to be almost fully saturated with water vapour. In the absence of temperature gradients throughout the flesh, variations in water vapour pressure throughout the intercellular spaces are therefore minimal, and the driving force for water-vapour diffusion through the intercellular spaces is small (Woods, 1990). Burton (1982, p. 51) cites calculations that estimate the resistance to water movement through the cell walls as being about one-twentieth of the resistance to water movement via osmosis. This suggests that most of the water movement in plant tissues occurs through the cell walls.

The resistance to water movement within plant tissues is generally considered negligible in comparison with the resistance to water vapour diffusion imposed by the skin (Woods, 1990). However, internal resistance to water movement could become significant at very high rates of surface moisture loss, where internal water movement cannot proceed fast enough to replenish the moisture lost from the surface. In such cases surface drying would be observed.

The evaporating surface of plant tissues is generally considered to be the cell walls of the outermost layer of living cells (Burton, 1982, p. 54). In fleshy fruits, the cell-wall surfaces exposed to the ambient air are covered by a waxy cuticle. Although lenticels provide the path of least resistance to gas exchange in fruits, water vapour is thought to preferentially diffuse through the liquid aqueous phase of the cuticle (Kader *et al.*, 1989). Evaporation from fruit surfaces is therefore termed 'cuticular transpiration' (Burton, 1982, p. 54).

Evaporation from plant surfaces occurs when the vapour pressure of water at the evaporating surface is greater than the partial pressure of water in the ambient air. The equilibrium vapour pressure of water at the evaporating surface is dependent on three factors: temperature, the selective permeability of the cell membrane, and the absorptive forces of the cell wall (Burton, 1982, pp. 47-48). Solutes dissolved in the cell sap depress the vapour pressure of the cell sap below that of pure water. However, the cell sap is enclosed by a semi-permeable cell membrane. This membrane is selectively permeable to water vapour, restricting the movement of solutes out of the cell. Thus, the liquid exposed to evaporation has a lower solute concentration, and a higher vapour pressure, than the cell sap (Burton, 1982, p. 48; van den Berg, 1987; Woods, 1990). In addition to solute effects, absorption of water in the interfibrillar spaces of the cell walls tends to further decrease the vapour pressure at the evaporating surface (Burton, 1982, p. 48). In general, the equilibrium vapour pressure at the evaporating surface is expected to lie in the range of 99 to 99.5% of that of pure water at the same temperature (Burton, 1982, p. 48). This agrees with experimental studies on carrots, which neither lost nor gained weight when stored at a relative humidity of about 99.5% (van den Berg, 1987; Woods, 1990).

Transport and exchange of water vapour within and between the package and external atmospheres occur by the same mechanisms as those described for gas transport in section 2.4.1.1. However, one important difference is the possibility of moisture condensation. At any given temperature, there is a maximum amount of water vapour that air can hold (Thompson, 1992). Above this maximum, water vapour condenses to form liquid water. For a given moisture content, the minimum temperature air can be cooled to without water condensing is called the dew point. Condensation of moisture occurs on any surfaces at temperatures below the dew point of the air in contact with them.

#### **2.4.1.3 TRANSPORT OF HEAT ENERGY**

All the various modes of heat transfer - conduction, radiation, forced convection, natural convection, evaporation, and condensation - are identifiable in an MAP system.

In the case of product cooling, heat within the product is transferred to the product surface by conduction (Hallström *et al.*, 1988, p. 105). At the product surface heat may be transferred to the package air by convection, or by the evaporation of moisture. Heat may also be transferred from product to product, or from product to packaging materials, by conduction or radiation (Hallström *et al.*, 1988, p. 85-105). In an unventilated package, natural convection is likely to be the dominant heat transfer mechanism within the package atmosphere. Heat may be transferred to the outer packaging materials by natural convection, conduction, or by the condensation of moisture. Heat is transferred through the layers of the outer packaging materials by conduction, although if air gaps exist within or between these layers (e.g. corrugated cardboard), natural convection may also be important. At the outer surface of the package, heat is transferred to the store air by natural or forced convection, and to other packages or store structures by conduction or radiation.

In the case of product warming, these heat transfer processes are reversed.

## 2.4.2 EXISTING MODIFIED ATMOSPHERE PACKAGING MODELS

Kader *et al.* (1989), Chinnan (1989, 1991), Robertson (1992), and Dessaux (1994) have reviewed developments in the mathematical modelling of MAP systems for fresh produce. Models of MAP systems fall into two broad categories: steady-state models and dynamic models.

### 2.4.2.1 STEADY-STATE MAP MODELS

Tolle (1962) carried out some of the earliest work dealing with the quantitative modelling of modified atmosphere systems. This work involved the development of equations to predict the permeability requirements of films for the packaging of apples. The overall equation proposed by Tolle for the calculation of film permeability requirements was based on the following steady state balance:

$$\left( \begin{array}{c} \text{Rate of } O_2 \text{ or } CO_2 \\ \text{permeation through} \\ \text{packaging film} \end{array} \right) = \left( \begin{array}{c} \text{Rate of respiratory} \\ O_2 \text{ consumption or} \\ CO_2 \text{ production} \end{array} \right) \quad (2.1)$$

Tolle collated respiration data from 82 references covering 20 apple varieties. Carrying out regression analysis on these, he produced equations for estimating respiration rates at storage temperatures of 30 to 40°F (-1.1 to 4.4°C) under normal atmospheric conditions. Tolle multiplied these respiration rates by empirically derived "package-atmosphere" factors to correct for the presence of a modified atmosphere. He then calculated the film permeabilities required for packaging of a bushel-box of graded apples, taking into account film surface area,  $O_2$  and  $CO_2$  partial pressure differences across the film, and a "volume-adjustment" factor. The need for this volume-adjustment factor is unclear, as steady-state package  $O_2$  and  $CO_2$  partial pressures are theoretically not affected by package volume. In his calculations, Tolle assumed a respiratory quotient of one. Tolle also derived an equation to predict the maximum film permeability to water vapour allowable to keep the total water-loss from the fruit over

a storage period of 180 days at less than 2.5% of the fruit's original water content. This equation assumed a package relative humidity of 95%. Tolle did not report any experimental work validating the predictions of his model.

Jurin & Karel (1963) developed a model for predicting the steady state  $O_2$  and  $CO_2$  concentrations in a package of apple fruit. They conducted respiration studies on 'McIntosh' apples to determine respiration rates as a function of package  $O_2$  concentration. Their results indicated that  $CO_2$  concentrations less than about 5-6 mol % had very little effect on respiration rate. At relatively low  $CO_2$  concentrations, respiration rate was therefore assumed to be a function of  $O_2$  concentration only. Their results also showed a respiratory quotient approximately equal to one at  $O_2$  concentrations above 3.5 mol %. Assuming uniform package gas composition and no effect of  $CO_2$  on respiration, Jurin & Karel developed a graphical method for solving the steady state balance given by Eq. 2.1.  $O_2$  consumption and  $O_2$  permeation rates were plotted as functions of package  $O_2$  concentration, with the intersection of these two curves representing the steady-state solution for  $O_2$ . Assuming a respiratory quotient of 1, the rate of  $CO_2$  production was determined, and by setting this equal to the rate of  $CO_2$  permeation, the steady-state package  $CO_2$  concentration was calculated. Jurin & Karel validated their model by comparing model predictions to the results of packaging experiments. Their theoretical predictions agreed well with experimental steady-state gas compositions. Further validation of the model was carried out by Karel & Go (1964), who applied Jurin & Karel's experimental methods and model to the prediction of steady state  $O_2$  and  $CO_2$  concentrations in film packages of preclimacteric bananas. Their experimental and predicted results showed reasonable agreement.

Veeraju & Karel (1966) modelled  $O_2$  and  $CO_2$  concentrations inside fruit containers fitted with windows of two different permeable films. Assuming that gas diffusion through two different film windows occurs in parallel, they solved the steady-state balance given by Eq. 2.1 to produce equations for calculating the film areas required to generate a given modified atmosphere. These equations assumed uniform gas composition and temperature within the containers. Using the respiration data collected by Jurin & Karel (1963), Veeraju & Karel calculated the areas of low density polyethylene and vegetable parchment paper required to produce an atmosphere of 7.6 mol %  $O_2$  and 14 mol %  $CO_2$  inside a container holding 2 kg of 'McIntosh' apples. Steady-state concentrations inside an experimental container fitted with the calculated film areas were 6.7 mol %  $O_2$  and 17.5 mol %  $CO_2$ , somewhat different from the target concentrations. Veeraju & Karel attributed this difference to uncertainties in the respiration data. They therefore back-calculated new respiration data from the observed steady-state gas concentrations, and used these new respiration rates to recalculate the film areas required to produce the desired atmosphere. With these new film areas, steady-state gas concentrations were maintained within 1 mol % of the desired values. Other factors that Veeraju & Karel considered important in terms of the accuracy of their model were changes in respiration rate with time, variations in film thickness, variations in film permeability, and the effect of small changes in room temperature on respiration rates.

Marcellin (1974) formulated equations to describe the equilibrium conditions formed inside each of three types of MA system:

- (i) small, completely sealed polyethylene packages;
- (ii) larger polyethylene bags constructed with windows of silicone film, each bag having a small hole (up to 3 mm diameter, depending on the size of the bag) to allow the equilibration of internal and external pressures;
- (iii) sealed cool-storage rooms equipped with diffusion units (each unit containing 3 m<sup>2</sup> of silicone film) through which room air (for units mounted outside the store) or outside air (for units mounted inside the store) was circulated. Equilibration of internal and external pressures was achieved via a small ventilation tube passing from the inside to the outside of the store.

For system (i), Marcellin's equations were based on the steady-state balance given by Eq. 2.1. For systems (ii) and (iii), an extra term was added to the oxygen balance to account for air flow due to pressure equilibration:

$$\left( \begin{array}{c} \text{Rate of } O_2 \\ \text{permeation through} \\ \text{packaging film} \end{array} \right) + \left( \begin{array}{c} \text{Rate of } O_2 \\ \text{flow through} \\ \text{ventilation hole} \end{array} \right) = \left( \begin{array}{c} \text{Rate of} \\ \text{respiratory } O_2 \\ \text{consumption} \end{array} \right) \quad (2.2)$$

Assuming an O<sub>2</sub>:N<sub>2</sub> ratio of 21:79 in air, Marcellin calculated the second term of Eq. 2.2 as 21/79 times the flow of nitrogen through the ventilation hole. Nitrogen flow was calculated from a steady-state nitrogen balance as follows:

$$\left( \begin{array}{c} \text{Rate of } N_2 \\ \text{flow through} \\ \text{ventilation hole} \end{array} \right) = \left( \begin{array}{c} \text{Rate of } N_2 \\ \text{permeation through} \\ \text{packaging film} \end{array} \right) \quad (2.3)$$

Marcellin used his equations to predict the film surface areas or film thicknesses required for the storage of various fruits and vegetables. In experimental trials with 'Golden Delicious' apples, steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations inside each of the three different MA systems were generally within 1 mol % of the desired values. Data were also collected for various other fruits and vegetables, but comparisons of these data with model predictions were not reported.

Cameron (1989) modelled the steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations formed inside film packages of tomatoes. He combined the steady-state O<sub>2</sub> and CO<sub>2</sub> balances given by Eq. 2.1 with respiration functions derived by Cameron *et al.* (1989) (section 2.4.2.2). These respiration functions applied to respiratory O<sub>2</sub> consumption only, so Cameron assumed a respiratory quotient of one to estimate CO<sub>2</sub> production rates. Predicted O<sub>2</sub> concentrations agreed reasonably well with O<sub>2</sub> concentrations measured inside experimental packages, but predicted CO<sub>2</sub> concentrations were significantly lower than measured CO<sub>2</sub> concentrations. Differences between measured and predicted CO<sub>2</sub> concentrations increased with increasing fruit weight (decreasing O<sub>2</sub> concentration), indicating that anaerobic respiration may have been significant in the heavier packages. By back-calculating O<sub>2</sub> consumption and CO<sub>2</sub> production rates from his experimental O<sub>2</sub>

and CO<sub>2</sub> measurements, Cameron produced a plot of respiratory quotient (RQ) versus steady-state O<sub>2</sub> concentration. This showed a constant RQ of approximately 1.5 for O<sub>2</sub> concentrations greater than 3 mol %, and an exponential increase in RQ at O<sub>2</sub> concentrations below this. As the film permeability values used in his calculations had not been directly measured, Cameron suggested that inaccuracies in these values may have contributed to both the high RQ estimate and model error.

Jeffery *et al.* (1991) modelled steady-state ethylene concentrations within a tray of kiwifruit. Their model considered endogenous ethylene production by the fruit, diffusion of ethylene from the fruit internal atmosphere to the package atmosphere, diffusion of ethylene within the package, and diffusion of ethylene from the package to the store. Jeffery *et al.* modelled transport of ethylene within the tray as a pure diffusion process, treating the package air as immobilized. They assumed that ethylene diffusion within the tray was two-dimensional (i.e. that there were no vertical ethylene gradients), that the ethylene production rate of each individual fruit remained constant, and that temperature throughout the package was uniform. They used finite differences to solve their model numerically. Jeffery *et al.* carried out no formal model validation, but noted that internal ethylene concentrations predicted by the model compared well with values reported in the literature.

Cameron *et al.* (1994) modelled the steady-state O<sub>2</sub> partial pressures formed inside film packages of blueberry fruit. They combined the steady-state O<sub>2</sub> balance given by Eq. 2.1 with temperature-dependent functions for respiration and film permeability. Respiration was modelled as a Michaelis-Menten function of package O<sub>2</sub> partial pressure, with both the maximum respiration rate and the half-saturation constant expressed as exponential functions of temperature. Film permeability to O<sub>2</sub> was expressed as an Arrhenius function of temperature. Cameron *et al.* used their model to investigate the effects of storage temperature on steady-state O<sub>2</sub> partial pressures formed inside film packages having different activation energies for permeation. They did not report any experimental validation of their model.

Various other authors have used equations based on the steady-state balance given by Eq. 2.1 to investigate the O<sub>2</sub> and CO<sub>2</sub> concentrations formed within MA packages of fresh produce. Wade & Graham (1987) investigated the effects of changes in respiratory quotient and film selectivity (the ratio of CO<sub>2</sub> permeability to O<sub>2</sub> permeability) on the relative steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations formed within film packages. Mannapperuma *et al.* (1989) examined the effects of various package design parameters on steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations. Zagory *et al.* (1989) used a steady-state model to design MA packages for broccoli and avocados. Exama *et al.* (1993) investigated the suitability of available packaging films for modified atmosphere packaging of various fruit and vegetable species. Gong & Corey (1994) applied essentially the same approach as Cameron (1989) and Cameron *et al.* (1989) to the modelling of steady-state O<sub>2</sub> concentrations in packages of tomatoes.

### 2.4.2.2 DYNAMIC MAP MODELS

Henig & Gilbert (1975) predicted transient changes in package  $O_2$  and  $CO_2$  concentrations by numerically solving ordinary differential equations based on the following unsteady-state balances:

$$\left( \begin{array}{c} \text{Rate of } O_2 \\ \text{accumulation in} \\ \text{package atmosphere} \end{array} \right) = \left( \begin{array}{c} \text{Rate of } O_2 \\ \text{permeation through} \\ \text{packaging film} \end{array} \right) - \left( \begin{array}{c} \text{Rate of} \\ \text{respiratory } O_2 \\ \text{consumption} \end{array} \right) \quad (2.4)$$

$$\left( \begin{array}{c} \text{Rate of } CO_2 \\ \text{accumulation in} \\ \text{package atmosphere} \end{array} \right) = \left( \begin{array}{c} \text{Rate of} \\ \text{respiratory } CO_2 \\ \text{production} \end{array} \right) - \left( \begin{array}{c} \text{Rate of } CO_2 \\ \text{permeation through} \\ \text{packaging film} \end{array} \right) \quad (2.5)$$

They assumed constant package free volume, perfect mixing of pack air, and a constant, uniform temperature. By fitting piece-wise linear functions to experimental respiration data collected for tomatoes, Henig & Gilbert developed respiration functions expressing respiratory  $O_2$  consumption as a function of package  $O_2$  concentration, and respiratory  $CO_2$  production as a function of package  $CO_2$  concentration. Henig & Gilbert solved their model numerically and compared the resulting predictions to experimental data collected for tomato packages of two different film types. Predicted  $O_2$  concentrations agreed well with experimental data. For the first 12-24 h after packaging, predicted  $CO_2$  concentrations also agreed reasonably well with experimental data. However, predicted steady-state  $CO_2$  concentrations for the two film types were 4 mol % and 9.5 mol % compared to experimental steady-states of 2 mol % and 4 mol % respectively. Henig & Gilbert did not comment on this discrepancy.

Hayakawa *et al.* (1975) developed analytical solutions to the differential equations of Henig & Gilbert (1975). Initially, Hayakawa *et al.* assumed respiration to be dependent on both  $O_2$  and  $CO_2$  concentrations, modelling  $O_2$  consumption and  $CO_2$  production rates as piece-wise linear functions of package  $O_2$  and  $CO_2$  concentrations. They solved the differential equations for package  $O_2$  and  $CO_2$  analytically, assuming a constant package free volume, constant ambient gas concentrations, and a constant, uniform temperature. To provide a second, simplified, set of solutions, Hayakawa *et al.* assumed the rate of  $O_2$  consumption to be independent of package  $CO_2$  concentration and the rate of  $CO_2$  production to be independent of package  $O_2$  concentration. This produced a less cumbersome set of equations than the full solution. Hayakawa *et al.* used this simplified set of equations to predict  $O_2$  and  $CO_2$  concentrations in film packages of tomatoes and bananas, comparing their predictions to experimental data collected by Henig & Gilbert (1975). Predicted steady-state atmospheres and predicted  $O_2$  equilibrium times agreed reasonably well with experimental data. However, predicted  $CO_2$  equilibrium times were generally much shorter than those observed experimentally. Hayakawa *et al.* attributed this to the assumption that  $O_2$  concentrations do not affect  $CO_2$  production and that  $CO_2$  concentrations do not affect  $O_2$  consumption. They showed theoretically that better agreement would be expected if respiration data for the unsimplified solutions could be generated.

Deily & Rizvi (1981) modelled transient  $O_2$  and  $CO_2$  concentrations in packages of peaches. They solved the unsteady-state balances given by Eqs. 2.4 and 2.5 analytically, assuming constant respiration rate, constant temperature, and constant package free-volume. Deily & Rizvi found that peach respiration rates remained constant at  $O_2$  concentrations above 5 mol % and  $CO_2$  concentrations below 20 mol %, and that peach quality was maintained best at 10-15 mol %  $O_2$  and 15-25 mol %  $CO_2$ . They therefore considered their assumption of constant respiration rate valid for the range of gas compositions experienced by the packaged fruit. Deily & Rizvi compared their model predictions with experimental data collected for one package type. They observed close agreement between predicted and experimental results.

Kok & Raghaven (1984) modelled the performance of an MA store similar to the type (iii) storage system modelled by Marcellin (1974) (section 2.4.2.1). Kok & Raghaven assumed a uniform, constant temperature throughout the store, uniform gas concentrations throughout the store, and a constant store pressure equal to atmospheric pressure. They modelled respiration as a linear function of  $O_2$  partial pressure,  $CO_2$  partial pressure, and temperature, assuming a respiratory quotient of one. Kok and Raghaven modelled the diffusion of  $O_2$ ,  $CO_2$ , and  $N_2$  through the membrane within the store's diffusion unit, as well as the air-flow through the vent required to keep the store pressure equal to atmospheric pressure. They solved their model numerically to compare the effect of two different membrane areas on the operation of the store. No experimental model validation was reported.

Mannapperuma & Singh (1987) presented a mathematical formulation for a generic MAP model. This formulation considered (a) exchange of  $O_2$ ,  $CO_2$ , and  $N_2$  between the internal atmosphere of the produce and the package atmosphere, (b) permeation of  $O_2$ ,  $CO_2$ , and  $N_2$  through the packaging film, and (c) convective flow through holes in the packaging film. The formulation was applicable to both rigid and flexible-film packages. Produce respiration rate was expressed as a piece-wise series of linear functions of the commodity's internal  $O_2$  concentration. Mannapperuma & Singh solved their formulated equations analytically for the steady-state case, and gave a brief description of solution procedures for the unsteady-state case. This unsteady-state solution would presumably be numerical. Mannapperuma & Singh did not report any experimental validation of their model.

Yang & Chinnan (1988a) modelled  $O_2$  and  $CO_2$  concentrations within packages of ripening tomatoes. They assumed a constant and uniform package temperature and uniform package gas concentrations. Respiratory  $O_2$  consumption and  $CO_2$  production rates were modelled as polynomial functions of package  $O_2$  concentration, package  $CO_2$  concentration, and storage time (Yang & Chinnan, 1988b). Yang & Chinnan solved their package-atmosphere model iteratively, calculating pseudo-steady-state solutions at set time intervals. This solution method did not allow them to model the initial atmosphere development that occurs immediately after packaging. Model predictions agreed well with experimental data collected for tomatoes packaged in two film types. Yang & Chinnan also compared their model predictions to experimental  $O_2$  and  $CO_2$  concentrations reported by Henig & Gilbert (1975) for packages of tomatoes. For long term storage, Yang & Chinnan's model gave more accurate predictions than Henig & Gilbert's model. Yang & Chinnan combined their package-atmosphere model with a

colour-development model derived by Yang & Chinnan (1987). Predicted times for packaged tomatoes to reach various colour stages compared well with colour changes observed experimentally.

Cameron *et al.* (1989) modelled  $O_2$  concentrations in packages of tomatoes. To estimate respiration data for tomatoes, they measured the rates of  $O_2$  depletion within sealed glass jars containing a single tomato each. By curve-fitting the results of these  $O_2$  depletion runs, Cameron *et al.* developed equations to predict  $O_2$  uptake as a function of fruit external  $O_2$  concentration for tomatoes harvested at three maturity stages. As the  $O_2$  depletion experiments were carried out in the presence of a  $CO_2$  absorbent, the resulting respiration models did not take into account any effect of  $CO_2$  on respiration rate. Cameron *et al.* modelled package  $O_2$  concentrations according to the unsteady-state balance given by Eq. 2.4, assuming a constant, uniform package temperature and a constant package volume. They solved their model analytically to predict steady-state  $O_2$  concentrations, or numerically to predict changes in  $O_2$  concentration with time. Although they did not report any model-validation results, Cameron *et al.* claimed that model predictions agreed well with transient  $O_2$  concentrations measured for experimental packages of tomatoes.

Lee *et al.* (1991) applied a respiration model based on Michaelis-Menten kinetics to the modelling of  $O_2$  and  $CO_2$  concentrations inside film packages. They modelled respiration as a Michaelis-Menten function of package  $O_2$  and  $CO_2$  concentrations, treating  $O_2$  as the rate-limiting substrate and  $CO_2$  as an uncompetitive inhibitor. Lee *et al.* fitted this respiration model to several sets of published respiration data and to their own respiration data for cut broccoli. They further tested the respiration model by combining it with a package-atmosphere model based on the unsteady-state balances given by Eqs. 2.4 and 2.5. They solved the package model numerically, assuming constant temperature and constant package volume. Lee *et al.* validated their model against the respiration and package atmosphere data reported for apples by Jurin & Karel (1963), and against experimental data collected from permeable film packages of cut broccoli. For the apple packages of Jurin & Karel, model predictions agreed reasonably well with experimental  $O_2$  and  $CO_2$  concentrations. For broccoli packages, model predictions agreed well with experimental  $O_2$  and  $CO_2$  concentrations for 4 to 5 hours, but after 6 hours package atmospheres had become anaerobic without equilibrium conditions being reached. Hagger *et al.* (1992) carried out further model validation, again using cut broccoli. Although they ran their package experiments at a lower temperature than those of Lee *et al.* (1991) (13°C rather than 24°C), package atmospheres again became anaerobic within 20 hours.

Emond *et al.* (1991) modelled  $O_2$  and  $CO_2$  concentrations inside packages of non-perforated or perforated films. In experiments with empty perforated-packages, they measured the effective permeabilities of perforations of various sizes (diameters of 6, 8.85 and 11 mm and film thicknesses of 1.59, 7.14 and 12.7 mm) at three package temperatures (274, 284 and 294 K). Analyzing these data by regression, Emond *et al.* produced equations to predict the effective permeability of a perforation as a function of perforation diameter, film thickness, and temperature. They combined these equations with the unsteady-state balances given by Eqs. 2.4 and 2.5 to predict package  $O_2$  and  $CO_2$  concentrations as functions of time. Emond *et al.* solved their model numerically,

**Table 2.4** Summary of steady-state MAP models.

| Reference Number <sup>a</sup>     | 1 | 2 | 3 | 4              | 5 | 6              | 7 |
|-----------------------------------|---|---|---|----------------|---|----------------|---|
| <i>Factors Modelled:</i>          |   |   |   |                |   |                |   |
| O <sub>2</sub>                    | + | + | + | +              | + | -              | + |
| CO <sub>2</sub>                   | + | + | + | +              | + | -              | - |
| N <sub>2</sub>                    | - | - | - | +              | - | -              | - |
| C <sub>2</sub> H <sub>4</sub>     | - | - | - | -              | - | +              | - |
| Moisture loss                     | + | - | - | -              | - | -              | - |
| Heat transfer                     | - | - | - | -              | - | -              | - |
| <i>Respiration:</i>               |   |   |   |                |   |                |   |
| Assumed constant                  | - | - | - | - <sup>b</sup> | - | - <sup>c</sup> | - |
| Function of package atmosphere    | + | + | + | - <sup>b</sup> | + | - <sup>c</sup> | + |
| Function of internal atmosphere   | - | - | - | - <sup>b</sup> | - | - <sup>c</sup> | - |
| Explicit function of temperature  | + | - | - | - <sup>b</sup> | - | - <sup>c</sup> | + |
| Explicit function of storage time | - | - | - | - <sup>b</sup> | - | - <sup>c</sup> | - |
| <i>Solution method:</i>           |   |   |   |                |   |                |   |
| Analytical                        | + | - | + | +              | + | -              | + |
| Graphical                         | - | + | - | -              | - | -              | - |
| Numerical                         | - | - | - | -              | - | +              | - |
| <i>Experimental validation:</i>   |   |   |   |                |   |                |   |
|                                   | - | + | + | +              | + | -              | - |

<sup>a</sup> Key:

- |    |                        |    |                              |
|----|------------------------|----|------------------------------|
| 1. | Tolle (1962)           | 5. | Cameron (1989)               |
| 2. | Jurin & Karel (1963)   | 6. | Jeffery <i>et al.</i> (1991) |
| 3. | Veeraju & Karel (1966) | 7. | Cameron <i>et al.</i> (1994) |
| 4. | Marcellin (1974)       |    |                              |

<sup>b</sup> No specific respiration functions given.

<sup>c</sup> Respiration not modelled in this paper.

assuming a constant, uniform package temperature and constant package volume. They used their model in a trial-and-error manner to determine suitable film properties for MA packages of broccoli and strawberries, but did not report any experimental validation of their model predictions.

Morales-Castro *et al.* (1994*a,b*) modelled O<sub>2</sub> and CO<sub>2</sub> concentrations within glass jars containing sweet corn or lettuce. Each jar was sealed with a screw-top lid fitted with two windows of micro-perforated or non-perforated film. Morales-Castro *et al.* expressed produce O<sub>2</sub>-consumption and CO<sub>2</sub>-production rates as polynomial functions of package O<sub>2</sub> and CO<sub>2</sub> concentrations, storage temperature, and time. They treated gas transport through micro-perforated films in the same manner as permeation through non-perforated films, measuring effective permeabilities for the former. They solved their package model numerically, assuming a constant storage temperature. Morales-Castro *et al.* compared their model predictions with transient O<sub>2</sub> and CO<sub>2</sub> concentrations measured inside experimental packages. Predicted gas concentrations did not always agree well with experimental data. Absolute differences between predicted and experimental O<sub>2</sub> concentrations ranged from 0.5 to 4 mol %, while absolute differences

**Table 2.5** Summary of dynamic MAP models.

| Reference Number <sup>a</sup>     | 1 | 2 | 3 | 4 | 5              | 6 | 7              | 8 | 9 | 10 | 11 |
|-----------------------------------|---|---|---|---|----------------|---|----------------|---|---|----|----|
| <i>Factors Modelled:</i>          |   |   |   |   |                |   |                |   |   |    |    |
| O <sub>2</sub>                    | + | + | + | + | +              | + | +              | + | + | +  | +  |
| CO <sub>2</sub>                   | + | + | + | + | +              | + | -              | + | + | +  | +  |
| N <sub>2</sub>                    | - | - | - | + | +              | - | -              | - | - | -  | +  |
| C <sub>2</sub> H <sub>4</sub>     | - | - | - | - | -              | - | -              | - | - | -  | -  |
| Moisture loss                     | - | - | - | - | -              | - | -              | - | - | -  | -  |
| Heat transfer                     | - | - | - | - | -              | - | -              | - | - | -  | -  |
| <i>Respiration:</i>               |   |   |   |   |                |   |                |   |   |    |    |
| Assumed constant                  | - | - | + | - | -              | - | -              | - | + | -  | -  |
| Function of package atmosphere    | + | + | - | + | -              | + | +              | + | - | +  | +  |
| Function of internal atmosphere   | - | - | - | - | +              | - | -              | - | - | -  | -  |
| Explicit function of temperature  | - | - | - | + | -              | - | -              | - | - | +  | +  |
| Explicit function of storage time | - | - | - | - | -              | + | -              | - | - | +  | -  |
| <i>Respiratory quotient:</i>      |   |   |   |   |                |   |                |   |   |    |    |
| Constant                          | - | - | + | + | +              | - | - <sup>c</sup> | - | + | -  | -  |
| Variable                          | + | + | - | - | -              | + | - <sup>c</sup> | + | - | +  | +  |
| <i>Solution method:</i>           |   |   |   |   |                |   |                |   |   |    |    |
| Analytical                        | - | + | + | - | + <sup>b</sup> | - | + <sup>b</sup> | - | - | -  | -  |
| Numerical                         | + | - | - | + | +              | + | +              | + | + | +  | +  |
| <i>Experimental validation:</i>   |   |   |   |   |                |   |                |   |   |    |    |
|                                   | + | + | + | - | -              | + | +              | + | - | +  | +  |

<sup>a</sup> Key:

- |                                  |                                            |
|----------------------------------|--------------------------------------------|
| 1. Henig & Gilbert (1975)        | 7. Cameron <i>et al.</i> (1989)            |
| 2. Hayakawa <i>et al.</i> (1975) | 8. Lee <i>et al.</i> (1991)                |
| 3. Deily & Rizvi (1981)          | 9. Emond <i>et al.</i> (1991)              |
| 4. Kok & Raghaven (1984)         | 10. Morales-Castro <i>et al.</i> (1994a,b) |
| 5. Mannapperuma & Singh (1987)   | 11. Renault <i>et al.</i> (1994a,b)        |
| 6. Yang & Chinnan (1988a)        |                                            |

<sup>b</sup> For steady-state case only.<sup>c</sup> CO<sub>2</sub> not modelled.

between predicted and experimental CO<sub>2</sub> concentrations ranged from 0.8 to 3 mol %.

Renault *et al.* (1994a,b) modelled the transport of O<sub>2</sub> and CO<sub>2</sub> through microperforated packaging films. Dividing the length of each perforation into a number of nodes, they used finite differences to solve the equations for steady-state gas diffusion and convection through the perforations. Renault *et al.* applied their perforation model to the prediction of transient O<sub>2</sub> and CO<sub>2</sub> concentrations within perforated-film packages of fresh produce. They used the Michaelis-Menten model proposed by Lee *et al.* (1991) to model produce respiration as a function of package O<sub>2</sub> and CO<sub>2</sub> concentrations. In their mass balance for package CO<sub>2</sub>, they also included a term to account for the solution of CO<sub>2</sub> in the cell sap of the produce. Renault *et al.* solved their package-atmosphere model numerically, assuming a constant package temperature and constant

package volume. To validate their model, they compared model predictions with experimental data from (a) empty, perforated-film packages initially flushed with  $N_2$  or  $O_2$ , and (b) perforated-film packages of strawberries. In both cases, model predictions only agreed well with experimental data when the total cross-sectional area of micro-perforations measured for each package was multiplied by a correction factor ranging from 0.2 to 0.8 in the model. Renault *et al.* attributed this need for a correction factor to their assumption that gas concentrations immediately outside the perforations were uniform and equal to the bulk package or external gas concentrations. From their mean correction factor of 0.43, they concluded that about one half of the total resistance to gas transport through micro-perforations may lie external to the microperforations themselves.

#### 2.4.2.3 SUMMARY

Tables 2.4 and 2.5 summarize the major characteristics of the steady-state and dynamic MAP models discussed above.

To date, no fully comprehensive model of a modified atmosphere packaging system has been developed. Most workers have considered package  $O_2$  and  $CO_2$  concentrations, but only a few have attempted to model the transport of  $N_2$ ,  $C_2H_4$ , or water vapour. None of the package models have incorporated the modelling of heat transfer, therefore none can currently be applied to investigating the response of package atmospheres to transient storage temperatures. Only the package model of Mannapperuma & Singh (1987) has incorporated the modelling of gas-exchange between the fruit internal atmosphere and the package atmosphere; all other workers have assumed produce respiration rates to be functions of package gas concentrations. Only Yang & Chinnan (1988a) have attempted to integrate the modelling of package atmospheres with the modelling of fruit quality characteristics.

There is a need for the development of a more comprehensive modified atmosphere packaging model that brings together the various factors considered by the individual models developed thus far. Such a model would need to integrate the modelling of heat and mass transfer with fruit physiological and fruit quality models. The following section gives a brief overview of the modelling of these modified atmosphere packaging components.

### 2.4.3 MODIFIED ATMOSPHERE PACKAGING COMPONENTS

#### 2.4.3.1 FRUIT RESPIRATION

Fruit respiration rate is most frequently modelled as a function of environmental conditions such as atmospheric  $O_2$  and  $CO_2$  concentrations and temperature. Many factors beside environmental conditions influence respiration, including maturity, cultivar, genetic variability, growing conditions, and storage history. However, the effects of these factors are very difficult to quantify, and accounting for them in a mathematical model is therefore equally difficult.

Many respiration models for fresh produce have been based on purely empirical, linear or non-linear functions of one or more of  $O_2$  concentration,  $CO_2$  concentration, storage temperature, or storage time (e.g. Kok & Raghaven, 1984; Yang & Chinnan, 1988a,b; Cameron *et al.*, 1989; Chinnan & Pendalwar, 1990; Beaudry *et al.*, 1992; Drury *et al.*, 1993; Emond *et al.*, 1993; Gran & Beaudry, 1993; Rao *et al.*, 1993; Gong & Corey, 1994; Morales-Castro *et al.*, 1994a,b). Such models are not considered here. Instead, this section discusses some of the more mechanistic approaches that have been applied to the modelling of fruit or vegetable respiration rates.

### *Effects of $O_2$ and $CO_2$ on Respiration Rate*

A number of workers have applied Michaelis-Menten enzyme kinetics to the modelling of aerobic respiration rate as a function of  $O_2$  concentration:

$$r = \frac{r_{max} [O_2]}{k_m + [O_2]} \quad (2.6)$$

where

- $k_m$  = Michaelis-Menten half-saturation constant ( $m^3 O_2 \cdot m^{-3}$ )
- $r$  = aerobic respiration rate ( $m^3 O_2 \cdot kg^{-1} \cdot s^{-1}$  or  $m^3 CO_2 \cdot kg^{-1} \cdot s^{-1}$ )
- $r_{max}$  = maximum aerobic respiration rate ( $m^3 O_2 \cdot kg^{-1} \cdot s^{-1}$  or  $m^3 CO_2 \cdot kg^{-1} \cdot s^{-1}$ )
- $[O_2]$  = oxygen concentration ( $m^3 m^{-3}$ ).

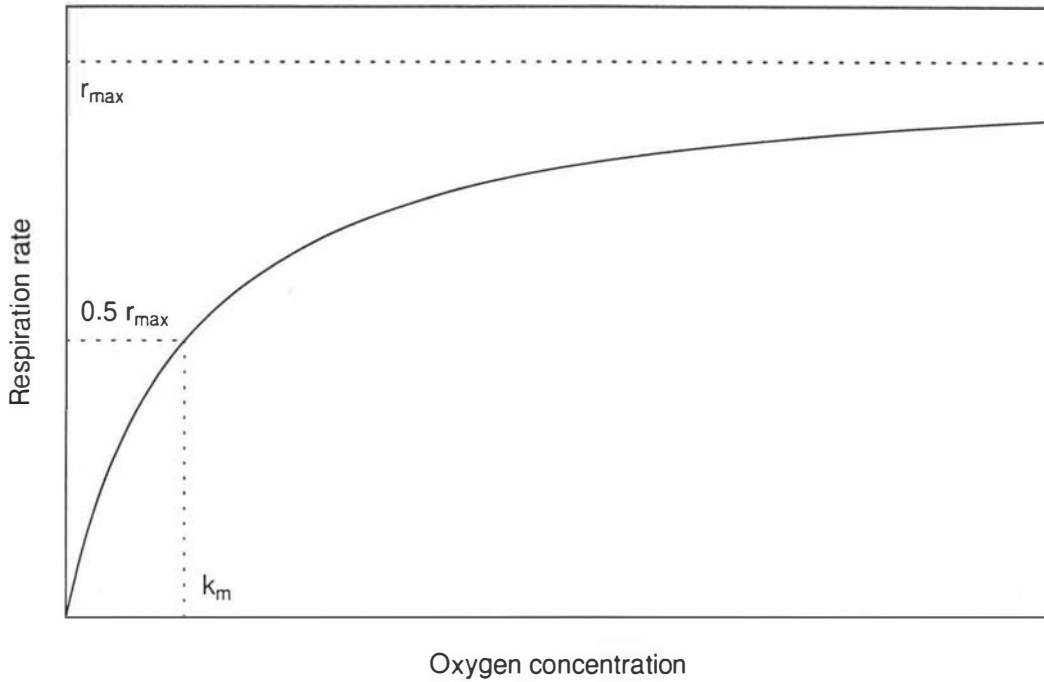
Such a model assumes that the rate of the aerobic respiratory pathway is limited by the rate of a single enzyme-catalysed reaction with  $O_2$  as its rate-limiting substrate. Although this is almost certainly an oversimplification, the model has been successfully applied to a range of fruits and vegetables.

Wade (1974), Lee *et al.* (1991), Cameron *et al.* (1994), and Joles *et al.* (1994) used Eq. 2.6 to model respiration rate as a function of the  $O_2$  concentration external to a given fruit or vegetable. Their studies included work on bananas, apples, tomatoes, broccoli, blueberries, and raspberries. Banks *et al.* (1989, 1993) and Dadzie (1992) used Eq. 2.6 to model the  $O_2$  consumption rate of apples as a function of  $O_2$  concentration in the fruit internal atmosphere. Dadzie (1992) and Banks *et al.* (1993) also modelled  $CO_2$  production rates, adding an empirical term to Eq. 2.6 to account for  $CO_2$  production under anaerobic conditions:

$$r_{CO_2} = RQ_m r_{O_2, max} \left( \frac{[O_2]_{int}}{k_m + [O_2]_{int}} + \frac{10^{-10}}{([O_2]_{int} + a)^b} \right) \quad (2.7)$$

where

- $a, b$  = empirical constants
- $r_{CO_2}$  = rate of respiratory  $CO_2$  consumption ( $m^3 CO_2 \cdot m^{-3} \cdot s^{-1}$ )



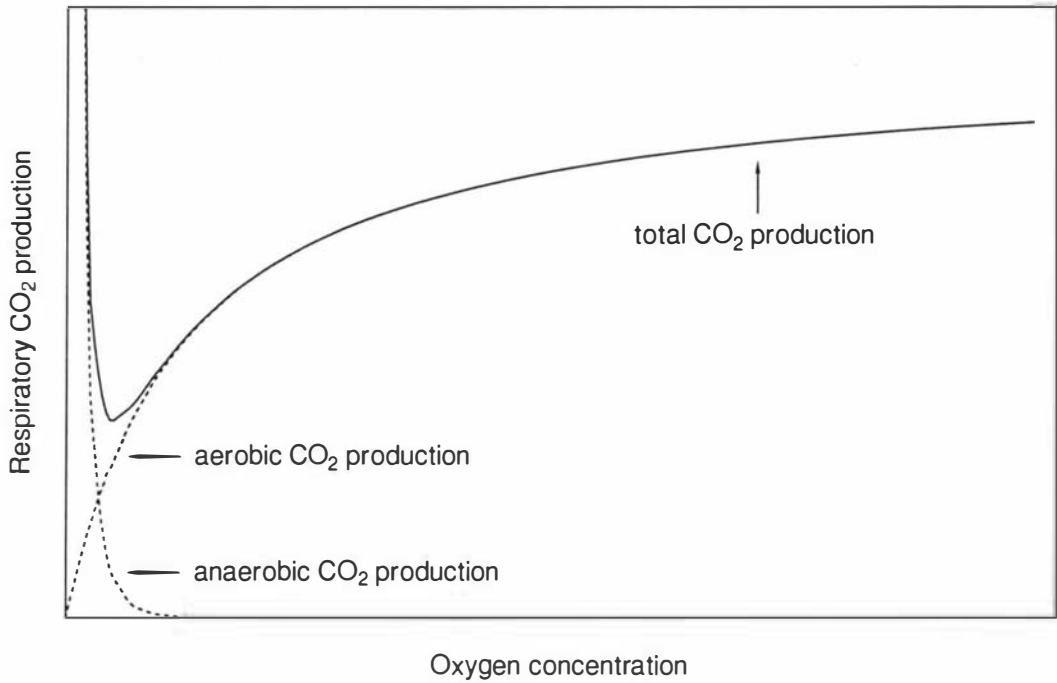
**Figure 2.2** General form of the Michaelis-Menten equation for respiration rate (Eq. 2.6).

- $r_{O_2, max}$  = maximum rate of respiratory  $O_2$  consumption ( $m^3 O_2 \cdot m^{-3} \cdot s^{-1}$ )  
 $RQ$  = respiratory quotient for aerobic respiration  
 $[O_2]_{int}$  = oxygen concentration in the fruit internal atmosphere ( $m^3 \cdot m^{-3}$ ).

Andrich *et al.* (1991) used Eq. 2.6 to model the aerobic respiration rate of apples as a function of  $O_2$  concentration in the cell sap. They did not measure  $O_2$  concentrations in the cell sap directly, but estimated these from  $O_2$  concentrations in the fruit internal atmosphere. They assumed an instantaneous equilibrium between the  $O_2$  concentration in the cell sap and that in the fruit internal atmosphere, and assumed the equilibrium solubility of  $O_2$  in the cell sap to be the same as that in a 0.4 M sucrose solution.

Figures 2.2 and 2.3 illustrate the general forms of Eqs. 2.6 and 2.7.

Lee *et al.* (1991) extended the concept of applying enzyme kinetics to the modelling of produce respiration rates by incorporating the effect of  $CO_2$  as an inhibitor of aerobic respiration. They applied a Michaelis-Menten model with linear, uncompetitive  $CO_2$  inhibition to model respiration rate as a function of  $O_2$  and  $CO_2$  concentrations external to the produce:



**Figure 2.3** General form of the respiration equation proposed by Banks *et al.* (1993) (Eq. 2.7).

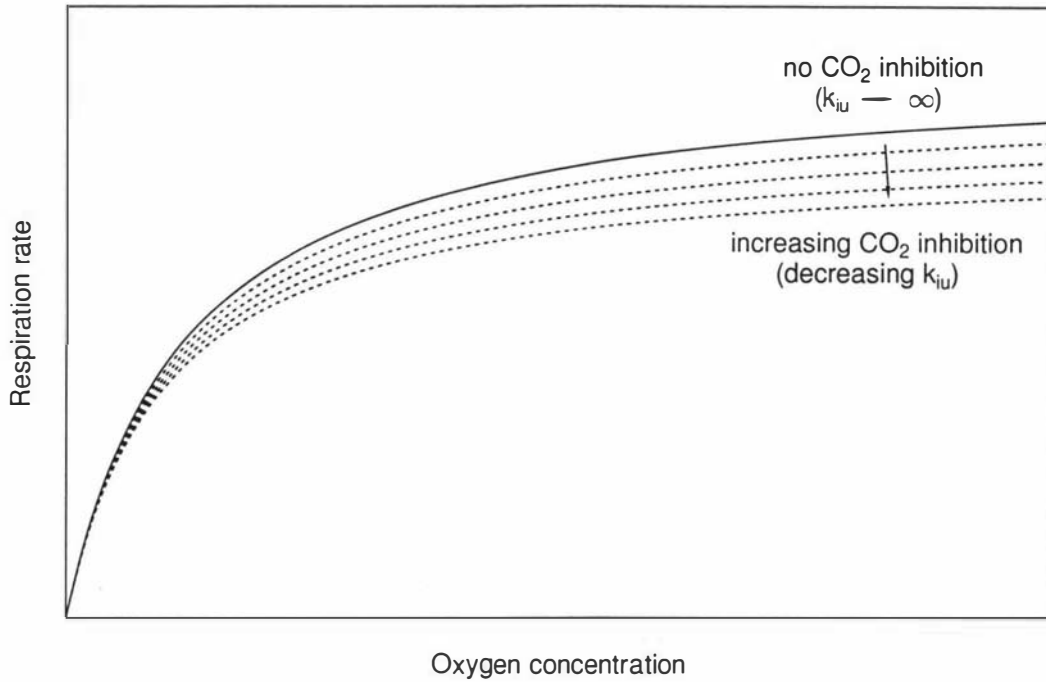
$$r = \frac{r_{max} [O_2]_{ext}}{k_m + \left( 1 + \frac{[CO_2]_{ext}}{k_{iu}} \right) [O_2]_{ext}} \quad (2.8)$$

where

$k_{iu}$  = uncompetitive inhibition constant ( $\text{m}^3 \text{CO}_2 \text{m}^{-3}$ )  
 $[CO_2]_{ext}$  = external carbon dioxide concentration ( $\text{m}^3 \text{m}^{-3}$ )  
 $[O_2]_{ext}$  = external oxygen concentration ( $\text{m}^3 \text{m}^{-3}$ ).

This respiration model assumes that  $CO_2$  and  $O_2$  both affect the same rate-limiting enzyme of the aerobic respiratory pathway, and that  $CO_2$  inhibits this enzyme without affecting the binding of  $O_2$ . Lee *et al.* (1991) fitted Eq. 2.8 to respiration rate data for apples and broccoli. The model has been further applied by Hagger *et al.* (1992) (broccoli), Song *et al.* (1992) (blueberries), and Renault *et al.* (1994a,b) (strawberries).

Figure 2.4 illustrates the effect of  $CO_2$  concentration on respiration rate as predicted by Eq. 2.8.



**Figure 2.4** Effect of uncompetitive  $\text{CO}_2$  inhibition on the Michaelis-Menten equation for respiration rate (Eq. 2.8).

#### *Effect of Temperature on Respiration Rate*

The relationship commonly used to describe changes in reaction rate with temperature for biological systems is

$$r_2 = r_1 Q_{10}^{\left(\frac{\theta_2 - \theta_1}{10}\right)} \quad (2.9)$$

where

- $r_1$  = reaction rate at temperature  $\theta_1$
- $r_2$  = reaction rate at temperature  $\theta_2$
- $Q_{10}$  = temperature quotient
- $\theta_1, \theta_2$  = temperatures in  $^{\circ}\text{C}$  or  $\text{K}$ .

$Q_{10}$  is defined as the ratio of reaction rates at temperatures  $10^{\circ}\text{C}$  apart (Powrie & Skura, 1991). For respiration rates of fresh produce,  $Q_{10}$  generally takes a value of about 2-3 at temperatures between 10 and  $30^{\circ}\text{C}$ , remaining relatively constant within this temperature range. However, between 0 and  $10^{\circ}\text{C}$ ,  $Q_{10}$  can reach values of up to 7 (Wills *et al.*, 1989, p. 39; Powrie & Skura, 1991).

For the Michaelis-Menten respiration models given by Eqs. 2.6 to 2.8, Eq. 2.9 is generally applied to  $r_{\max}$  rather than  $r$  (e.g. Joles *et al.*, 1994; Renault *et al.*, 1994a,b).

The effect of temperature on the rates of chemical reactions (as opposed to biological reactions) is generally modelled by the Arrhenius relationship:

$$r = r_0 \exp\left(\frac{-E_a}{RT}\right) \quad (2.10)$$

where

- $E_a$  = activation energy ( $\text{J}\cdot\text{mol}^{-1}$ )
- $r$  = reaction rate
- $r_0$  = pre-exponential factor
- $R$  = gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
- $T$  = absolute temperature (K).

The Arrhenius relationship has also been used to describe the effect of temperature on respiration. Karel & Go (1964) fitted Eq. 2.10 to respiration rate data for pre-climacteric bananas at 2-37°C. Lee *et al.* (1991) and Hagger *et al.* (1992) applied Eq. 2.10 to respiration rate data for broccoli, and Song *et al.* (1992) applied the relationship to respiration rate data for blueberries. As for the  $Q_{10}$  relationship, Eq. 2.10 is generally applied to  $r_{max}$  for the Michaelis-Menten models given by Eqs. 2.6 to 2.8.

By combining Eqs. 2.9 and 2.10, an approximate relationship between  $Q_{10}$  and  $E_a$  can be derived:

$$\ln Q_{10} \approx \frac{10E_a}{RT^2} \quad (2.11)$$

#### 2.4.3.2 FRUIT GAS EXCHANGE

For bulky plant organs where (a) the skin thickness is small relative to the radius of the organ and (b) the internal atmosphere composition beneath the skin can be considered uniform, gas exchange across the skin can be described by an adaptation of Fick's first law of diffusion (Solomos, 1987; Ben-Yehoshua & Cameron, 1989):

$$N_i = k_i A ([i]_{ext} - [i]_{int}) \quad (2.12)$$

where

- $A$  = surface area of the skin ( $\text{m}^2$ )
- $k_i$  = skin permeance to gas species  $i$  ( $\text{m}\cdot\text{s}^{-1}$ )
- $N_i$  = rate of transfer of gas species  $i$  across the skin ( $\text{m}^3\cdot\text{s}^{-1}$ )
- $[i]_{ext}$  = external concentration of gas species  $i$  ( $\text{m}^3\cdot\text{s}^{-1}$ )
- $[i]_{int}$  = internal concentration of gas species  $i$  ( $\text{m}^3\cdot\text{s}^{-1}$ ).

Eq. 2.12, expressed in various forms, appears to have been universally applied to the modelling of gas exchange in fruits and vegetables. Workers that have applied Eq. 2.12 to study the relationship between the internal and external atmospheres of fruits and vegetables include Burg & Burg (1965), Cameron & Reid (1982), Banks (1985), Banks & Kays (1988), Andrich *et al.* (1989), Banks *et al.* (1989, 1993), Rajapakse *et al.* (1990), Mannapperuma *et al.* (1991), Dadzie (1992), and Park *et al.* (1993).

A number of workers have developed mathematical models to predict fruit internal gas concentrations as functions of external gas concentrations, respiration rate, and gas-exchange characteristics. Banks *et al.* (1989) used Eq. 2.12 to model internal O<sub>2</sub> concentrations in apples, assuming a uniform O<sub>2</sub> concentration throughout the fruit flesh. Mannapperuma *et al.* (1991) modelled steady-state O<sub>2</sub> and CO<sub>2</sub> concentration gradients in apples. They assumed that apple geometry could be approximated by a perfect sphere, that gas-exchange across the fruit skin followed Eq. 2.12, and that gas transport throughout the fruit flesh followed Fick's second law of diffusion. Banks *et al.* (1993) modelled steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations in fruit with wax surface-coatings. They modelled gas-exchange at the fruit surface according to Eq. 2.12, but considered pathways for gas transfer through the fruit cuticle, through pores on the fruit surface, and through the wax coating separately. They assumed uniform gas concentrations throughout the fruit flesh.

#### 2.4.3.3 FRUIT MOISTURE LOSS

The modelling of moisture loss from fresh fruits and vegetables has been reviewed by authors such as Sastry (1986) and Woods (1990). The general equation describing moisture loss from a moist surface is based on Fick's first law of diffusion, and is similar in form to Eq. 2.12 above:

$$N_w = k_g A (p_{w,s} - p_{w,a}) \quad (2.13)$$

where

- $k_g$  = overall mass transfer coefficient at the evaporating surface (s·m<sup>-1</sup>)
- $N_w$  = rate of moisture loss (kg s<sup>-1</sup>)
- $p_{w,s}$  = partial pressure of water vapour at the evaporating surface (Pa)
- $p_{w,a}$  = partial pressure of water vapour in the ambient air (Pa).

As discussed in section 2.4.1.2, the evaporating surface in plant tissues is generally considered to be the cell walls of the outermost layer of living cells. The concept of water activity is used to describe the relationship between the vapour pressure at the evaporating surface and the vapour pressure of pure water at the temperature of the evaporating surface (Sastry, 1986):

$$p_{w,s} = a_w p_{sat,s} \quad (2.14)$$

where

$$p_{sat,s} = f(\theta_s) \quad (2.15)$$

and where

- $a_w$  = water activity of the evaporating surface  
 $p_{sat,s}$  = saturated vapour pressure of water at the temperature of the evaporating surface (Pa)  
 $\theta_s$  = temperature of the evaporating surface (°C).

For respiring and transpiring produce under steady-state conditions,  $\theta_s$  is not necessarily equal to the temperature of the ambient air (Woods, 1990). Rather,  $\theta_s$  depends on the relative rates of heat generation through respiration and heat loss through evaporation. At low rates of moisture-loss,  $\theta_s$  tends to be higher than the temperature of the ambient air; at high rates of moisture loss,  $\theta_s$  tends to be lower than the temperature of the ambient air.

In the case of moisture evaporation from fruits such as apples, the general mass transfer coefficient,  $k_g$ , is referred to as the skin permeance to water vapour,  $k_{g,skin}$ . The inverse of  $k_{g,skin}$  represents the total resistance to mass transfer imposed by the fruit cuticle and by the boundary layer of still air over the fruit surface (Gaffney *et al.*, 1985a; Woods, 1990):

$$\frac{1}{k_{g,skin}} = \frac{1}{k_{g,cut}} + \frac{1}{k_{g,bl}} \quad (2.16)$$

where

- $k_{g,cut}$  = mass transfer coefficient for diffusion of moisture through the fruit cuticle ( $\text{s}\cdot\text{m}^{-1}$ )  
 $k_{g,bl}$  = mass transfer coefficient for diffusion of moisture through the boundary layer ( $\text{s}\cdot\text{m}^{-1}$ ).

The mass transfer coefficient  $k_{g,cut}$  is a property of the fruit, whereas the coefficient  $k_{g,bl}$  is a property of the physical conditions at the fruit surface, for example, air velocities or air-density gradients.

Various models for predicting the moisture loss rates of fruits and vegetables have been developed. All of these are based on Eqs. 2.13 to 2.15 above, although methods for estimating  $k_{g,skin}$  and  $\theta_s$  vary. Examples include the models reported by Hayakawa & Succar (1982), Sastry & Buffington (1983), Chau *et al.* (1985), Gaffney *et al.* (1985a), Romero & Chau (1987), Chau *et al.* (1988), Patel & Sastry (1988), Gan & Woods (1989), Devres (1989), Chau & Gaffney (1990), and Alvarez *et al.* (1994). In general, these models have taken into account respiratory heat generation, evaporative cooling effects, heat conduction, heat convection, radiation, and a variety of product shapes and configurations.

2.4.3.4 FRUIT QUALITY

The quality of fresh produce is determined by an overall evaluation of those characteristics of the produce that are considered important by a given consumer. The perception of produce quality is therefore largely subjective, depending on the consumer and on a large number of mostly qualitative factors. Shewfelt (1990) and Kader (1992*c*) have reviewed the general quality characteristics of fruits and vegetables.

Table 2.6 lists some of the most commonly considered quality attributes of fresh fruits and vegetables. Quantitative measures have been developed to describe several of these attributes, both for research purposes and for use as quality indices in the marketplace. In the case of fruit, for example, skin colour can be measured against graded colour-charts or by chromameter; fruit firmness can be assessed by measuring the force required to penetrate, cut, or shear the fruit flesh; acidity and soluble solids content can be measured by analysis of the juice expressed from the fruit; nutrient content can be measured by chemical analysis; and the extent of starch conversion in some fruits can be assessed by comparing iodine-stained fruit with graded starch-indexes (Wills *et al.*, 1989, pp. 94-100; Kader, 1992*c*).

The quality factors listed in Table 2.6 are the attributes by which fruits and vegetables are ultimately judged in the marketplace. The ability to predict the development of these characteristics as a function of storage conditions and storage time would be extremely desirable from the point of view of providing produce of optimum quality to the market. The difficulty in modelling such quality attributes lies in the number of factors influencing their development, and in the complexity and lack of understanding of the basic mechanisms involved. As a result, models for predicting quality development in fruits and vegetables have so far been largely empirical.

For foods in general, a chemical kinetics approach is often applied to the modelling of quality changes as a function of storage time (Saguy & Karel, 1980; Karel, 1982; Ooraikul, 1991):

$$-\frac{dC_i}{dt} = k \prod_{j=1}^m C_j^{n_j}$$

(2.17)

Table 2.6 Quality attributes of fruits and vegetables.<sup>a</sup>

|                   |                                                                                                  |
|-------------------|--------------------------------------------------------------------------------------------------|
| Appearance        | colour, shape, size, glossiness                                                                  |
| Condition         | absence or presence of pests, moulds, rotting, physiological disorders, bruising, skin punctures |
| Texture           | firmness, crunchiness, crispness, succulence, juiciness, mealiness, smoothness                   |
| Flavour           | sweetness, sourness, bitterness, astringency, aroma                                              |
| Nutritional value | carbohydrates, proteins, lipids, vitamins, minerals                                              |
| Safety            | chemical, microbial                                                                              |

<sup>a</sup> Adapted from Table 7.1 of Powrie & Skura (1991) and Table 20.1 of Kader (1992*c*).

where

- $C_i$  = variable representing the quality attribute of interest  
 $C_j$  = variables representing factors that influence the rate of change of  $C_i$   
 $k$  = reaction rate constant  
 $n_j$  = order of the reaction with respect to  $C_j$   
 $t$  = time.

The temperature dependence of Eq. 2.17 is generally modelled by expressing  $k$  as an Arrhenius function of temperature:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (2.18)$$

where

- $k_0$  = pre-exponential factor.

Chemical kinetics models have been applied to predicting the shelf-life of various food products as a function of storage temperature (e.g. Heldman & Lai, 1983). They have also been applied to predicting losses of vitamins, pigments, acids, and texture as functions of temperature and time (e.g. Singh *et al.*, 1983; Switka & Kruk, 1990).

The chemical kinetics approach has not been widely applied to the modelling of quality changes in fresh fruits. Instead, most workers have chosen to model selected quality characteristics (often colour or firmness) as purely empirical functions of temperature and storage time (e.g. Thorne & Alvarez, 1982; Moreno *et al.*, 1983; Shewfelt *et al.*, 1988; Thai & Shewfelt, 1990; Thai *et al.*, 1990; Thai & Shewfelt, 1991a,b,c; Tijskens & Evelo, 1994). Few workers have attempted to model the effects of atmospheric composition on quality changes. However, one such model was presented by Yang & Chinnan (1987), who developed an empirical equation to predict the colour development of tomatoes as a function of storage time and gaseous environment. Yang & Chinnan applied their model to variable as well as constant gaseous environments by assuming that colour changes during individual storage-periods at constant atmospheres were arithmetically additive and commutative. Yang & Chinnan (1988a) incorporated this colour development model into a modified atmosphere packaging model, described in section 2.4.2.2.

#### 2.4.3.5 GAS PERMEATION THROUGH PACKAGING FILMS

Felder & Huvard (1980) and Rogers (1985) have presented comprehensive overviews of the theory of gas permeation through packaging films.

For polymer-penetrant pairs where sorption of the penetrant by the polymer follows Henry's law and diffusion of the penetrant through the polymer follows Fick's law, the

steady-state permeation rate of the penetrant through a flat membrane of the polymer can be expressed as:

$$N_i = \frac{P_i}{x} A (p_{i,high} - p_{i,low}) \quad (2.19)$$

where

- $A$  = surface area for permeation ( $m^2$ )
- $N_i$  = rate of permeation of gas species  $i$  through the polymer ( $kg \cdot s^{-1}$ )
- $p_{i,high}$  = partial pressure of gas species  $i$  on high-concentration side of film (Pa)
- $p_{i,low}$  = partial pressure of gas species  $i$  on low-concentration side of film (Pa)
- $P_i$  = permeability of the polymer to gas species  $i$  ( $kg \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ )
- $x$  = film thickness (m).

The permeability coefficient,  $P_i$ , is derived from the product of the diffusivity and the solubility of the penetrant in the polymer:

$$P_i = D_i S_i \quad (2.20)$$

where

- $D_i$  = diffusivity of gas species  $i$  in the polymer ( $m^2 \cdot s^{-1}$ )
- $S_i$  = solubility of gas species  $i$  in the polymer ( $kg \cdot m^{-3} \cdot Pa^{-1}$ ).

If there is no interaction between the penetrant and the polymer, then  $P_i$  is a constant for the polymer-penetrant system at a given temperature. However, if the penetrant does interact with the polymer, then sorption may not follow Henry's law and the diffusivity of the penetrant in the polymer may vary with penetrant concentration (e.g. permeation of water vapour through hydrophilic films). In such cases, the permeability coefficient is not constant, and depends on penetrant concentrations and the history of the film (Felder & Huvar, 1980; Rogers, 1985; Pauly, 1989).

The temperature dependence of the permeability coefficient can be represented by the Arrhenius relationship (Pauly, 1989):

$$P_i = P_{i,0} \exp\left(\frac{-E_a}{RT}\right) \quad (2.21)$$

where

- $P_{i,0}$  = pre-exponential factor ( $kg \cdot m \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ ).

Similar expressions can be written to describe the temperature dependence of  $D_i$  and  $S_i$ . For many polymer-penetrant combinations, the activation energy for permeation is a positive value. Thus, film permeability generally increases with increasing temperature.

A number of compilations of permeability data for various polymer-penetrant combinations have been published (e.g. Pauly, 1989).

For fresh fruits and vegetables packaged in relatively thin polymer films, the time taken to establish concentration gradients through the film is generally considered to have a negligible impact on the dynamics of atmosphere development with the package. This assumption appears to have been universally adopted for the modelling of modified atmosphere packaging systems, being implicit in all the MAP models discussed in section 2.4.2.

#### 2.4.3.6 MOISTURE SORPTION BY PAPER-BASED PACKAGING MATERIALS

The concentration of water vapour within a modified atmosphere packaging system is dependent on the rates of transfer of water vapour from moisture sources to moisture sinks within the package. Transpiration from the produce (section 2.4.3.3) is the major moisture-source within an MA package. Permeation of moisture through the packaging film represents one moisture sink, as the water vapour concentration within the package is generally higher than that in the environment surrounding the package. In packages containing paper-based packaging materials (such as the moulded pulp trays that support layers of apples within New Zealand apple cartons), moisture sorption by these materials can represent another major moisture-sink.

Rates of moisture sorption by paper-based packaging materials can be modelled in a similar manner to rates of moisture loss from fresh produce (Eqs. 2.13 to 2.15, section 2.4.3.3). However, in the case of paper-based packaging materials,  $a_w$  cannot be assumed constant, and a relationship expressing water activity at the evaporating surface as a function of moisture content must be found. Equilibrium relationships between moisture content and water activity are known as moisture-sorption isotherms.

Various isotherms have been applied to experimental moisture-sorption data for biological materials (Watt, 1983; van den Berg, 1984; Hallström *et al.*, 1988, pp. 17-18). Two of the most common models are the Brunauer-Emmett-Teller (BET) isotherm and the Guggenheim-Anderson-de Boer (GAB) isotherm. The latter isotherm has been found to provide a good fit to moisture sorption data for a variety of food products at water activities of up to 0.9 (van den Berg & Bruin, 1981; Bizot, 1983; van den Berg, 1984). The GAB isotherm is commonly expressed as

$$\frac{X}{X_m} = \frac{CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \quad (2.22)$$

where

$C, K, X_m$  = model parameters

$X$  = moisture content on a dry weight basis ( $\text{kg} \cdot \text{kg}^{-1}$ ).

The GAB isotherm has a theoretical background, and its three parameters are related to real physical quantities (Bizot, 1983; van den Berg, 1984).  $X_m$  (in  $\text{kg} \cdot \text{kg}^{-1}$ ) represents the moisture content corresponding to the saturation of all primary adsorption sites by one water molecule (sometimes referred to as the moisture content of the monolayer).  $C$  (the Guggenheim constant) and  $K$  are related to the energies of interaction between the first and further sorbed molecules at individual sorption sites. The effects of temperature on moisture sorption can be modelled by expressing  $C$  and  $K$  as Arrhenius-type functions (van den Berg, 1984).

A number of workers (e.g. Weisser & Liebenspacher, 1989, 1991; Eagleton & Marcondes, 1994) have applied the GAB isotherm to moisture sorption data for paper-based packaging systems. Eagleton & Marcondes (1994) found the GAB isotherm to be more appropriate than the BET isotherm for fitting moisture-sorption data for corrugated fibreboard and moulded-pulp trays similar to those used for packaging fresh apples in New Zealand.

#### 2.4.3.7 PACKAGE HEAT TRANSFER

Mathematical descriptions of the basic heat transfer processes can be found in any standard text dealing with the subject of heat transfer. Hallström *et al.* (1988) and Cleland (1990) have presented comprehensive reviews of the modelling of heat transfer in food products, and Gaffney *et al.* (1985b) have reviewed some of the heat transfer models developed specifically for fruits and vegetables, both for individual products and for products stored in bulk.

Heat (and mass) transfer in food products has been the subject of extensive international research, and numerous heat transfer models for food products have been published. Many of these models deal with heat transfer in isolated, individual products. Such models have only limited application to the heat transfer occurring within products that are bulk-packaged, a situation that is complicated by the presence of packaging materials, product-to-product contact, product-to-packaging contact, substantial air-voids within the package, partial ventilation of the package, possible heat generation by the packaged product, evaporation and condensation of moisture within the package, and non-uniform heat-transfer conditions throughout the package.

Heat transfer models fall into three broad categories based on solution methods of increasing complexity (Cleland, 1990, pp. 31-32):

- (1) *Analytical models.* These models are based on analytical solutions of the partial differential equations describing heat conduction within solids under various boundary conditions (Carslaw & Jaeger, 1959). The solutions are applicable to products of homogeneous composition under a limited range of conditions. The boundary condition most generally applicable to heat transfer in food products, known as Newton's law of cooling, assumes that heat transfer at the product surface occurs by convection only, although radiation can be incorporated as pseudo-convection in some cases. Analytical models also

assume constant and uniform external conditions, a uniform initial temperature distribution throughout the product, constant thermal properties, and regular product geometries (sphere, infinite cylinder, infinite slab, or hybrids of these geometries) (Gaffney *et al.*, 1985b; Cleland, 1990, pp. 79-83). Because of these limitations, few purely analytical models have been applied to the modelling of heat transfer in bulk-stored produce (Gaffney *et al.*, 1985b).

- (2) *Empirical extensions to analytical models.* A number of investigators have proposed various empirical or semi-empirical factors to extend the analytical solutions for products of regular geometry to products of irregular geometry (e.g. Earle & Fleming, 1967; Smith *et al.*, 1967; Smith *et al.*, 1968; Fikiin & Fikiina, 1971; Cleland & Earle, 1982; Chuntranuluck *et al.*, 1989; Cuesta *et al.*, 1990; Lin *et al.*, 1993; Jamieson *et al.*, 1993). These models are all based on analyses of the constant half-life (exponential) period that occurs in products of any geometry cooling or warming under constant heat-transfer conditions (Cleland, 1990, p. 84). Other empirical models assume effective thermal properties to model heat transfer in products of heterogeneous composition (e.g. Jamieson *et al.*, 1993). Although empirical models are more broadly applicable than purely analytical models, the assumptions of constant and uniform external conditions and constant thermal properties still apply.
- (3) *Numerical models.* These models are considerably more flexible than analytical or empirical models, but are also far more computationally intensive. Numerical solution methods can be applied to situations of virtually any complexity, including multiple modes of surface heat transfer, varying and non-uniform external conditions, inhomogeneous composition and non-constant thermal properties, temperature-dependent internal heat generation, and irregular product geometry (Cleland, 1990, pp 47-77). Numerical models constitute by far the majority of heat transfer models developed for bulk-stored produce (Gaffney *et al.*, 1985b). Recent examples of numerical models developed for bulk-stored or packaged horticultural produce include models reported by Chau *et al.* (1985), Romero & Chau (1987), Bazan *et al.* (1989), Gan & Woods (1989), Alvarez *et al.* (1994), and Amos (1995).

## *Chapter 3*

### **RESEARCH OBJECTIVES**

As outlined in Chapter 1, the overall objectives of this investigation were two-fold.

Firstly, little is currently known about the extent to which design and operational factors such as fruit size, method of packaging film closure, fruit temperature at packaging, rates of carton cooling, transient storage temperatures, and mechanical damage to the packaging film affect package atmospheres. A better understanding is desirable in view of the lack of direct control over atmospheres formed inside film-lined cartons.

Secondly, careful optimization of package designs is important if maximum benefit is to be obtained from the use of MA liners. To date, various experimental trials have been conducted to gauge the effect of MAP on the quality and storage potential of a number of New Zealand apple cultivars. However, for design and optimization purposes, a purely experimental approach is of limited flexibility. A mathematical model that predicts the conditions formed within an MA package as a function of fruit characteristics, packaging characteristics, storage conditions, and time could provide a flexible design and optimization tool when used in conjunction with experimental validation. Although a number of MA models have been developed by overseas researchers during the last three decades, none have attempted a fully integrated treatment of the major physiological, mass transfer, and heat transfer processes occurring within an MA package. There is need for a more comprehensive MAP model that brings together the various factors considered by individual models developed thus far. Furthermore, an eventual MAP model would need to be fully validated for the New Zealand apple carton MAP system before it could be reliably used for design and optimization.

As discussed in section 2.3, an ideal model of a modified atmosphere packaging system would be capable of predicting the effects of MA environments on the physiological processes of the packaged produce, and the cumulative effects of these processes on selected quality attributes. However, the mechanisms by which fruit storage conditions affect the rates of change of fruit quality attributes are complex and poorly understood. As a consequence, fruit quality models developed to date have been highly empirical. Very few of these models have considered the effects of atmospheric composition on quality changes (section 2.4.3.4). Incorporating models for specific fruit quality attributes in an overall MAP model was therefore considered impractical at this time.

With the above considerations in mind, the following specific objectives for the study were set:

- (1) Experimental measurement of rates of modified atmosphere development inside an apple carton MAP system over a range of different packaging and storage conditions. Factors investigated included the effects of cultivar, fruit size,

package size, film thickness, fruit temperature at packaging, method of film closure, damage to the packaging film, and transient storage temperatures.

- (2) Experimental measurement of apple and package characteristics that influence the formation of modified atmospheres inside a film package and that therefore needed to be quantified as inputs to an eventual MAP model. Such inputs include fruit respiration rate, fruit skin permeance to oxygen and carbon dioxide, packaging film permeability to oxygen and carbon dioxide, and carton cooling rates.
- (3) Formulation of a mathematical model that predicts package atmosphere conditions (oxygen, carbon dioxide, and humidity levels) as a function of fruit attributes (respiration rate; skin permeance), package design factors (fruit weight; film permeability, thickness, and surface area), storage factors (fruit temperature at packing; package cooling rates; storage temperature regime), and storage time. Although designed for apples, the model should be easily adaptable for application to other horticultural products.
- (4) Computer implementation of the formulated model to provide a tool for designing and optimizing modified atmosphere packages.
- (5) Model validation and assessment of model limitations. This involved use of the experimental data collected under objectives (1) and (2) to judge the model's ability to accurately predict modified atmosphere conditions for a range of design and operational factors.

The following chapters describe and discuss the work carried out to meet these objectives.

## Chapter 4

### EXPERIMENTAL METHODS

Experimental data were collected to meet the first and second of the objectives set in Chapter 3:

- (1) *Modified atmosphere development in apple packages.* This objective involved the measurement of MA development over the range of operating conditions that might be encountered in industry. Because the data collected under this objective were also to serve as model validation data, investigation of as wide a range of conditions as possible was desirable.
- (2) *Fruit and package characteristics.* This objective involved the measurement of fruit respiration rates, fruit skin permeances to respiratory gases, carton cooling/warming rates, and packaging film permeability to respiratory gases.

The materials, equipment, and methods used in the collection of experimental data are discussed in the following sections.

#### 4.1 MODIFIED ATMOSPHERE DEVELOPMENT IN APPLE PACKAGES

The effects of the following packaging and storage factors on MA development were investigated:

- (1) fruit cultivar;
- (2) fruit size;
- (3) package size;
- (4) fruit mass:film area ratio;
- (5) method of package sealing;
- (6) fruit temperature at time of packing;
- (7) fruit cooling rates;
- (8) packaging film thickness;
- (9) mechanical damage to the packaging film;
- (10) transient temperature storage regimes.

Four aspects of MA development were chosen for investigation:

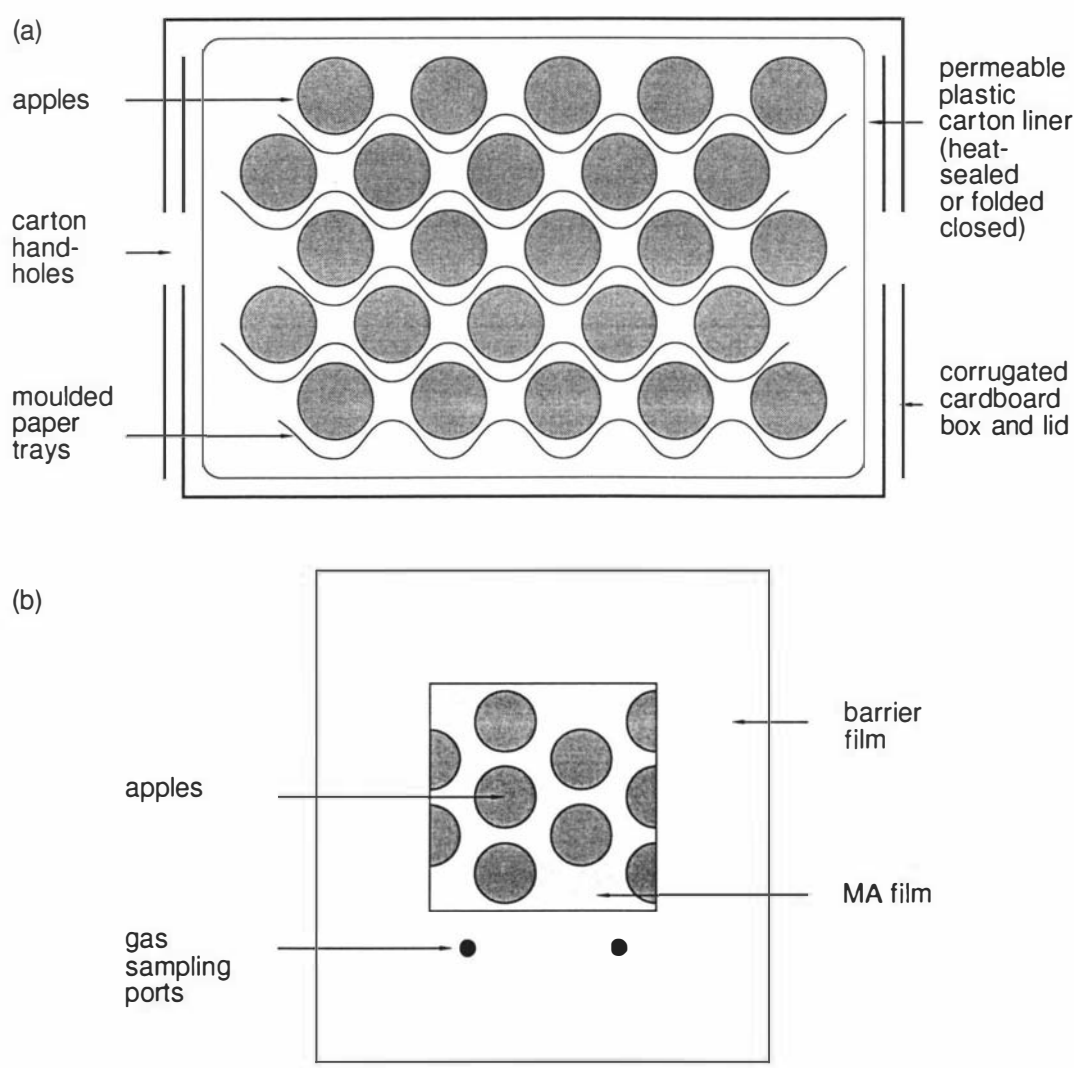
- (1) package atmosphere O<sub>2</sub> and CO<sub>2</sub> concentrations;
- (2) fruit internal atmosphere O<sub>2</sub> and CO<sub>2</sub> concentrations;
- (3) package relative humidity;
- (4) variability of package atmospheres between packages stored under the same conditions.

4.1.1 EXPERIMENTAL DESIGN

Experimental trials were carried out over the 1993 and 1994 New Zealand apple seasons.

Three cultivars of apple (*Malus domestica* Borkh., cultivars ‘Royal Gala’, ‘Braeburn’, and ‘Granny Smith’) were used in the experimental work. In New Zealand, fruit size has traditionally been graded according to the number of fruit of a given size packed into an 18.5 kg (nominal) apple carton. Thus, count 125 fruit (125 apples per 18.5 kg) are smaller than count 80 fruit (80 apples per 18.5 kg). Fruit count sizes of 80, 100, and 125 were used.

Trials were carried out with two package types: (a) standard New Zealand 18.5 kg apple cartons with approximate external dimensions of 520 mm (length) × 320 mm (width) × 300 mm (height) (Figure 4.1a) and (b) small bags (approximately 410 mm × 460 mm)



**Figure 4.1** Packages used in the experimental trials: (a) cartons (side view in cross-section) and (b) bags (plan view).

**Table 4.1** Temperature-time regimes used for the 1994-season MA trials.

| Stage        | Duration     | Nominal storage temperature (°C) |          |          |
|--------------|--------------|----------------------------------|----------|----------|
|              |              | Regime 1                         | Regime 2 | Regime 3 |
| Packaging    | -            | 0                                | 20       | 20       |
| Delay        | 12 hours     | -                                | -        | 20       |
| Cool Storage | 3-4 weeks    | 0                                | 0        | 0        |
| Loading      | 12 hours     | -                                | -        | 20       |
| Shipping     | 3-4 weeks    | -                                | -        | 0        |
| Distribution | up to 1 week | -                                | -        | 20       |

containing five or ten fruit each (Figure 4.1*b*). Cartons were lined with permeable-film liners<sup>1</sup> having a nominal film thickness of 25 or 40  $\mu\text{m}$ . Bags were constructed of a laminated barrier film<sup>2</sup> with a 280 mm  $\times$  280 mm window of permeable film (25 or 40  $\mu\text{m}$ ) heat-sealed into one face. The same type of permeable film (either 25 or 40  $\mu\text{m}$  thickness) was used in all the MA trials. For the carton trials, liners were either folded closed (current industry practice) or heat-sealed (section 4.1.3). All bags were heat-sealed.

During the 1993 season, the majority of trials were carried out at a constant storage temperature of 0°C (nominal). The only exception to this was one set of bag trials for which package atmospheres were allowed to come to equilibrium at 15°C before a step change in storage temperature to 0°C. During the 1994 season, trials were conducted under three different temperature-time regimes, summarized in Table 4.1. Regimes 1 and 2 represented cool-storage at a constant temperature of 0°C, the difference between the two regimes being the fruit temperature at packing (0°C or 20°C). Regime 3 represented a simulated packing, storage, and distribution temperature-time regime. During the two cool-storage stages (representing cool-storage in New Zealand and on-board ship), cartons were left until steady-state package atmospheres had been achieved; in reality the period of time spent in cool-storage before shipping could be much shorter, and the period of time spent in cool-storage on-board ship could vary between two to six weeks.

To investigate the effects of different rates of cooling on atmosphere development, four cartons of 'Braeburn' apples undergoing Regime 2 were insulated on 5 sides each with 100 mm thick expanded polystyrene foam<sup>3</sup>, leaving only one end face of each carton exposed. The purpose of the insulation was to simulate cartons in the middle of a pallet stack, which, in the worst case, are "insulated" on five sides by other cartons in the stack.

<sup>1</sup> Borden Filmpac, Borden (NZ) Ltd, Auckland, New Zealand.

<sup>2</sup> 50  $\mu\text{m}$  linear low density polyethylene - 12  $\mu\text{m}$  metallised polyester - 50  $\mu\text{m}$  linear low density polyethylene: Wrightcel Packaging NZ Ltd, Feilding, New Zealand.

<sup>3</sup> Density 16 kg m<sup>-3</sup>, thermal conductivity 0.036 W m<sup>-1</sup> K<sup>-1</sup>: Landwood Industries Ltd, Palmerston North, New Zealand.

**Table 4.2** Experimental design for the carton trials.

| Cultivar       | Trial code | Fruit count-size | Film thickness (µm) | Method of closure | Storage regime <sup>a</sup> | Number of replicates |
|----------------|------------|------------------|---------------------|-------------------|-----------------------------|----------------------|
| 1993 Season:   |            |                  |                     |                   |                             |                      |
| ‘Braeburn’     | BB93-A     | 125              | 40                  | Fold              | 1                           | 6                    |
|                |            | 125              | 40                  | Seal              | 1                           | 6                    |
|                |            | 125              | 25                  | Seal              | 1                           | 3                    |
|                |            | 80               | 40                  | Seal              | 1                           | 3                    |
|                |            | 80               | 25                  | Seal              | 1                           | 3                    |
| 1994 Season:   |            |                  |                     |                   |                             |                      |
| ‘Royal Gala’   | RG94-A     | 100              | 25                  | Seal              | 1                           | 5                    |
|                |            | 100              | 40                  | Seal              | 1                           | 5                    |
|                | RG94-B     | 100              | 25                  | Seal              | 2                           | 2                    |
|                |            | 100              | 40                  | Seal              | 2                           | 2                    |
|                | RG94-C     | 100              | 25                  | Seal              | 3                           | 4                    |
|                |            | 100              | 40                  | Seal              | 3                           | 4                    |
| ‘Braeburn’     | BB94-A     | 125              | 25                  | Seal              | 2                           | 2                    |
|                |            | 125              | 25                  | Fold              | 2                           | 2                    |
|                |            | 125              | 25                  | Seal              | 2 <sup>b</sup>              | 2                    |
|                |            | 125              | 25                  | Fold              | 2 <sup>b</sup>              | 2                    |
|                | BB94-B     | 125              | 25                  | Seal              | 3                           | 2                    |
|                |            | 125              | 25                  | Fold              | 3                           | 2                    |
|                |            | 125              | 40                  | Seal              | 3                           | 2                    |
|                |            | 125              | 40                  | Fold              | 3                           | 2                    |
| ‘Granny Smith’ | GS94-A     | 125              | 25                  | Seal              | 3                           | 4                    |
|                |            | 125              | 40                  | Seal              | 3                           | 4                    |

<sup>a</sup> See Table 4.1.<sup>b</sup> Insulated cartons.

The experimental designs for trials during the 1993 and 1994 seasons are summarized in Tables 4.2 and 4.3. Note that all temperatures and film thickness stated throughout this chapter are nominal values only. Actual measured values are reported in later results sections (Chapter 8).

## 4.1.2 FRUIT SUPPLY

### 4.1.2.1 1993 SEASON

'Braeburn' apples harvested from a single Hawkes Bay orchard during the first week of the Hawkes Bay commercial harvest were transported to Massey University and stored at 0°C until required for experimental trials (1-3½ months). Before starting the first

**Table 4.3** Experimental design for the bag trials.

| Cultivar     | Trial code   | Fruit count-size | Fruit per bag | Film thickness (μm) | Storage temperature (°C) | Number of replicates |   |
|--------------|--------------|------------------|---------------|---------------------|--------------------------|----------------------|---|
| 1993 Season: |              |                  |               |                     |                          |                      |   |
| Braeburn     | BB93-B       | 125              | 10            | 40                  | 15/0                     | 5                    |   |
|              |              | 125              | 5             | 40                  | 15/0                     | 2                    |   |
|              |              | 80               | 10            | 25                  | 15/0                     | 2                    |   |
|              |              | 80               | 5             | 25                  | 15/0                     | 2                    |   |
|              | BB93-C       | 125              | 10            | 25                  | 0                        | 2                    |   |
|              |              | 125              | 5             | 25                  | 0                        | 2                    |   |
|              |              | 80               | 10            | 40                  | 0                        | 2                    |   |
|              |              | 80               | 5             | 40                  | 0                        | 5                    |   |
|              | 1994 Season: |                  |               |                     |                          |                      |   |
|              | Granny Smith | GS94-B           | 125           | 10                  | 25                       | 0                    | 5 |
|              |              |                  | 125           | 10                  | 40                       | 0                    | 5 |

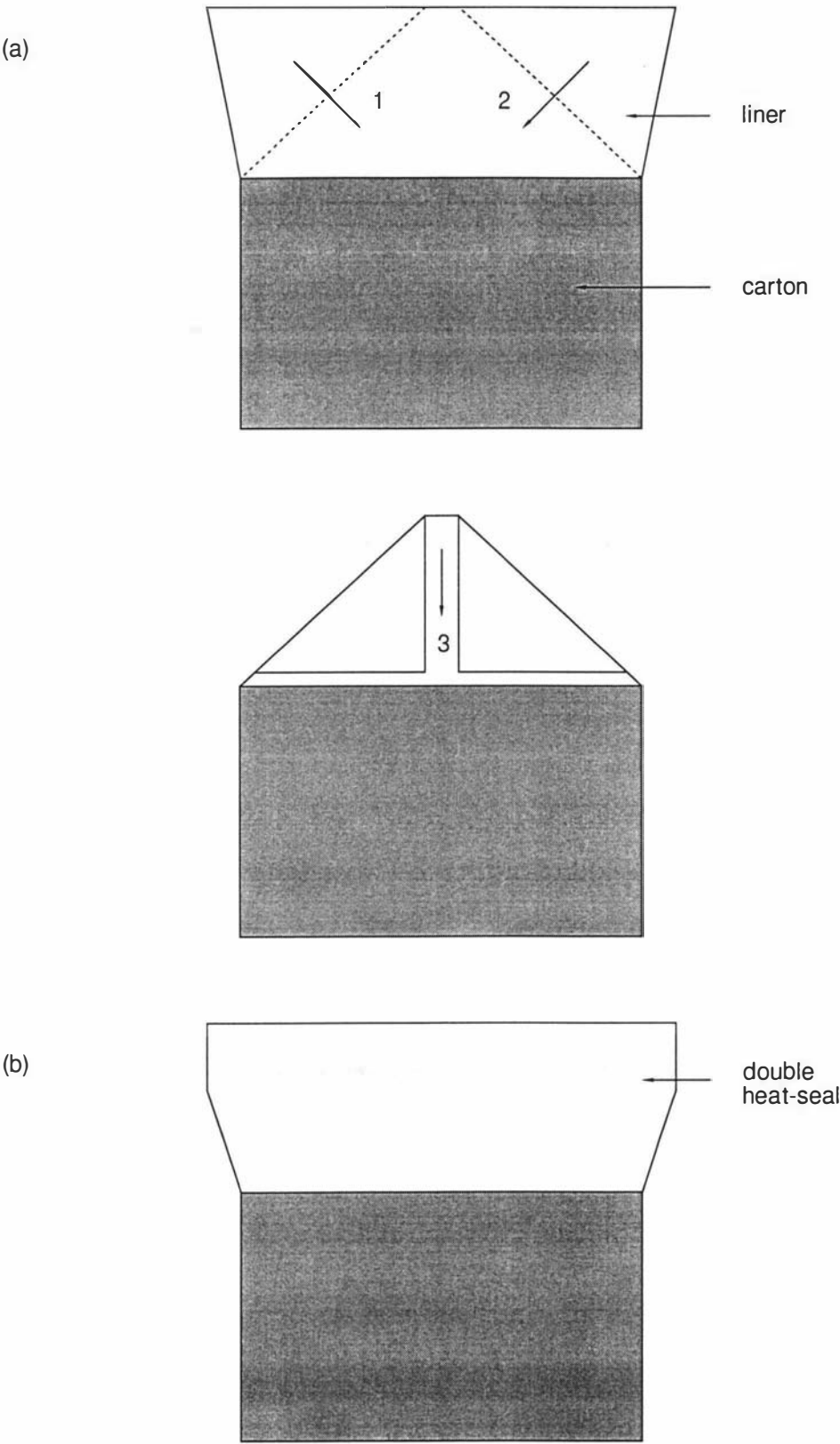
trials, all fruit were treated with 100 ppm ethylene for four days at 0°C to ensure climacteric development.

#### 4.1.2.2 1994 SEASON

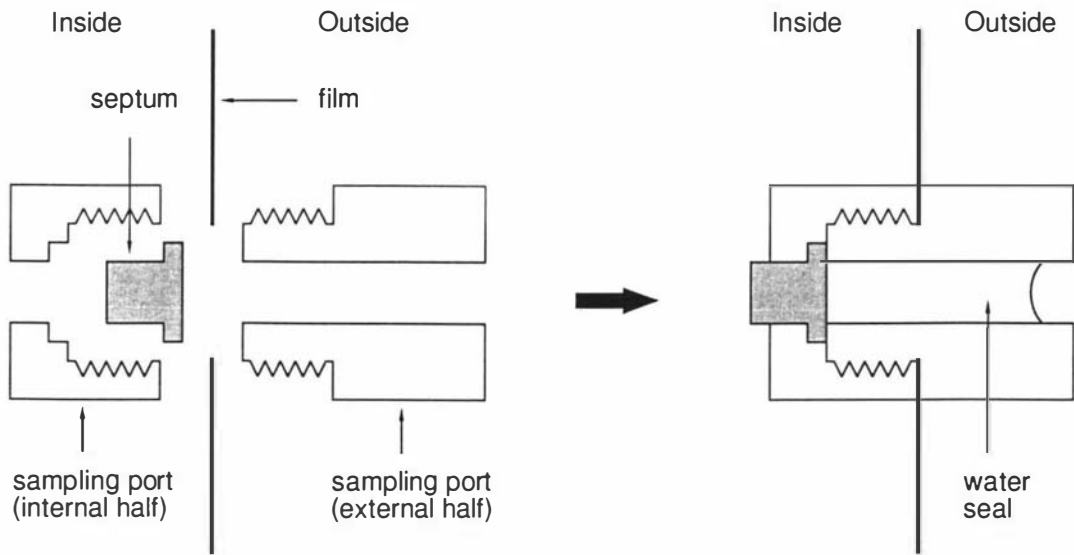
‘Royal Gala’, ‘Braeburn’, and ‘Granny Smith’ apples harvested during the middle of the Hawkes Bay commercial harvest for each cultivar were transported to Massey University and stored at 0°C until required (1-3 weeks, 1½-2 months, and 3 months for ‘Royal Gala’, ‘Braeburn’, and ‘Granny Smith’ respectively). All apples of a single cultivar were harvested from the same Hawkes Bay orchard. 1994 fruit were not treated with ethylene before experimentation. For ‘Royal Gala’, it was therefore possible that the fruit would not all be at the same stage of climacteric development and that this could influence the variability of package atmospheres. The long storage periods before trials commenced with ‘Braeburn’ and ‘Granny Smith’ would almost certainly have resulted in these fruit being post-climacteric.

#### 4.1.3 PACKING AND STORAGE

For each trial, randomly selected fruit were packed and stored according to the experimental designs given in Tables 4.2 and 4.3. Fruit undergoing Regimes 2 or 3 were removed from cool-storage at least 48 h before the start of a trial to allow fruit temperatures to equilibrate to 20°C. Carton liners were either folded closed or sealed with a double heat seal 10-15 cm from the liner opening (Figure 4.2). For cartons with folded liners, folding was performed as shown in Figure 4.2a, with the end of the liner tucked into the side of the carton after folding. Bags were sealed with a double heat seal 2-4 cm from the bag opening.



**Figure 4.2** (a) Closure of carton liners by folding (numbers indicate order of folds). (b) Closure of carton liners by heat sealing.



**Figure 4.3** Septum ports fitted into the packaging film to allow sampling of the package atmosphere (shown in cross-section).

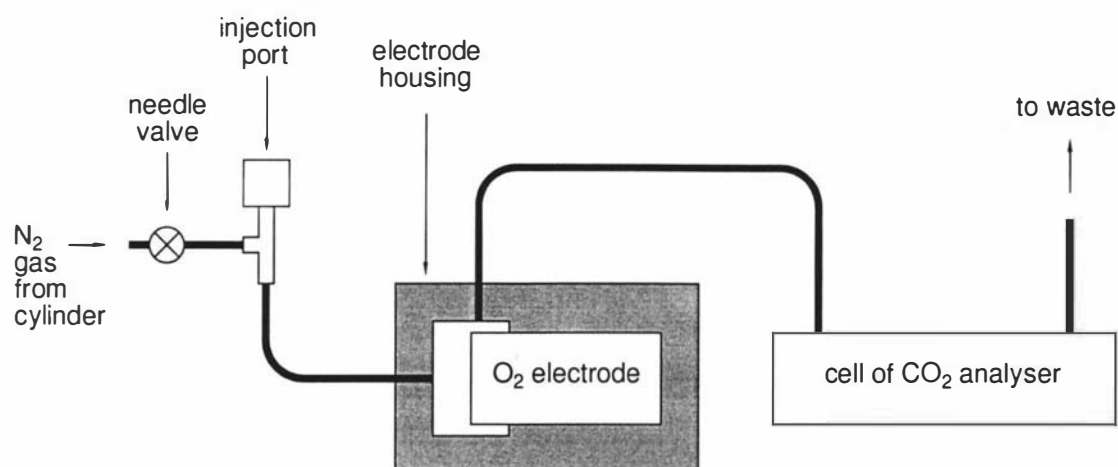
During periods of cool-storage, cartons and bags were stored in a small experimental cool-store (1993 season) or in refrigerated shipping containers (1994 season). During periods at 15 or 20°C, cartons and bags were stored in a small controlled-temperature room (1993 season), in a shipping container set to 20°C (1994 'Royal Gala'), or in a constant-temperature laboratory (1994 'Braeburn' and 'Granny Smith'). Cartons were stacked 4 or 5 high during storage.

Fruit masses in each carton were recorded before packing and again at the end of each trial.

#### 4.1.4 PACKAGE ATMOSPHERE SAMPLING AND GAS ANALYSIS

For gas sampling purposes, each MA carton-liner was fitted with a silicone rubber septum port next to one of the carton hand-holes (Figure 4.3). Each bag was fitted with two such gas-sampling ports set into the barrier film around the edge of the MA-film window (Figure 4.1*b*). The development of modified O<sub>2</sub> and CO<sub>2</sub> levels in each package was monitored by periodic withdrawal of duplicate package-gas samples in 1 ml disposable tuberculin syringes<sup>4</sup>. To prevent atmospheric contamination of samples if pressures inside the MA packages became less than store pressure, the well formed by the central bore of the sampling port was filled with water (Figure 4.3). In this way, water, rather than air, was drawn into the syringe as the needle was removed from the septum. Water was expelled from the syringe before analysis of the gas samples.

<sup>4</sup> Monoject: Sherwood Medical, St Louis, Missouri.



**Figure 4.4** Schematic diagram of the  $O_2/CO_2$  gas analyzer.

#### 4.1.4.1 GAS ANALYSIS SYSTEM

Package atmosphere samples were analyzed for  $O_2$  and  $CO_2$  by injection (0.7 ml) into a stream of  $N_2$  gas<sup>5</sup> (35–40 ml min<sup>-1</sup>) passed over an  $O_2$  electrode<sup>6</sup> and infra-red  $CO_2$  analyzer<sup>7</sup> connected in series.

The use of an  $O_2$  electrode for determining the  $O_2$  content of small gas samples injected into a stream of nitrogen has been described by Banks (1986). Conventional gas chromatography analysis using a molecular sieve column to separate  $O_2$  and  $N_2$  does not allow  $O_2$  to be readily separated from argon (present at 0.93 mol % in air). Analysis of atmospheric gas samples for  $O_2$  by chromatography therefore requires a correction for the presence of argon. At low  $O_2$  concentrations, this could introduce significant uncertainty into the measured  $O_2$  values. The  $O_2$  electrode is not sensitive to argon and therefore has the potential to provide a more accurate method for  $O_2$  analysis, especially at low  $O_2$  concentrations. An infra-red  $CO_2$  analyzer used in series with the  $O_2$  electrode allowed rapid simultaneous analysis of  $O_2$  and  $CO_2$ . Figure 4.4 shows a schematic diagram of the gas analysis system. Similar  $O_2/CO_2$  analysis systems have been used by Banks & Kays (1988), Banks *et al.* (1989), Cameron (1989), Rajapakse *et al.* (1989a; 1989b; 1990), Zagory *et al.* (1989), Ke & Kader (1990), Beaudry *et al.* (1992), and Talasila *et al.* (1994).

Responses of the  $O_2$  electrode (0–13.5 mV) and infra-red  $CO_2$  analyzer (0–10 V) were recorded on a dual-pen, flat-bed chart recorder<sup>8</sup>. A set of 2 or 3 calibration standards was run through the analyzer before and after every 8 to 10 sample injections. Heights of recorded sensor-response peaks were measured manually and sample  $O_2$  and  $CO_2$  concentrations calculated from corresponding standard curves.

<sup>5</sup> Instrument-grade  $N_2$ , gas code 016: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>6</sup> C/S Citicel: City Technology Ltd., London, England.

<sup>7</sup> Model WA470E: Analytical Development Company Ltd, Herts, England.

<sup>8</sup> Model LR 4220: Yokogawa Electric Corporation, Japan.

**Table 4.4** Composition of the calibration standards used in gas analysis

| Volume pure CO <sub>2</sub><br>(ml) | Volume dry air<br>(ml) | CO <sub>2</sub> concentration<br>(mol %) | O <sub>2</sub> concentration<br>(mol %) |
|-------------------------------------|------------------------|------------------------------------------|-----------------------------------------|
| 2.6                                 | 1197.4                 | 0.25                                     | 20.90                                   |
| 5.6                                 | 1194.4                 | 0.50                                     | 20.85                                   |
| 8.6                                 | 1191.4                 | 0.75                                     | 20.80                                   |
| 11.6                                | 1188.4                 | 1.00                                     | 20.74                                   |
| 29.6                                | 1170.4                 | 2.50                                     | 20.43                                   |
| 59.6                                | 1140.4                 | 5.00                                     | 19.91                                   |
| 89.6                                | 1110.4                 | 7.50                                     | 19.38                                   |
| 119.6                               | 1080.4                 | 10.00                                    | 18.86                                   |

#### 4.1.4.2 PREPARATION OF CALIBRATION STANDARDS

Calibration standards were made up in 1050 ml glass jars fitted with metal ring-and-dome lids. Each dome was fitted with two septum ports clamped to the dome and sealed with silicone sealant. Sealing of the jars was aided by a thin layer of silicone grease around the edge of the domes where they were seated onto the jar rims. The amount of gas in each jar was made up to the equivalent of 1200 ml at atmospheric pressure, thereby creating a positive pressure inside the jars to minimize the possibility of atmospheric contamination of the standard samples. Fresh standards were made up every 3-6 days.

Table 4.4 lists the full range of calibration standards used in the experimental work. Standards were made up using pure CO<sub>2</sub><sup>9</sup> and dry air<sup>10</sup>. Volumes of pure CO<sub>2</sub> required to obtain a desired CO<sub>2</sub> concentration were calculated assuming a CO<sub>2</sub> concentration of 0.033 mol % in dry air. O<sub>2</sub> concentrations in each standard were calculated assuming an O<sub>2</sub> concentration of 20.946 mol % in dry air.

#### 4.1.4.3 ANALYZER CALIBRATION

The relationship between sample O<sub>2</sub> concentration and response peak height for an O<sub>2</sub> electrode has been shown to follow a linear relationship for O<sub>2</sub> concentrations between 0 and 21 mol % (Banks, 1986). Sample O<sub>2</sub> peaks were therefore calibrated against the O<sub>2</sub> concentrations listed in Table 4.4 by assuming a linear relationship from 0 to 21 mol % O<sub>2</sub>. Output of the infra-red CO<sub>2</sub> analyzer used in the experimental work was found to be nonlinear for response peaks between 0 and 1 V (corresponding roughly to 0-1 mol % CO<sub>2</sub> in a 0.7 ml injected sample) but linear for response peaks between 1 and 10 V (corresponding roughly to 1-10 mol % CO<sub>2</sub> in a 0.7 ml injected sample). Calibration curves for samples with CO<sub>2</sub> response peaks below 1 V were fitted to a function of the form:

<sup>9</sup> Instrument-grade CO<sub>2</sub>, gas code 013: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>10</sup> Dry air, gas code 108: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

$$y = ax^b \quad (4.1)$$

where

$y$  = response peak height  
 $x$  = CO<sub>2</sub> concentration  
 $a, b$  = fitted constants

Linear calibration (Eq. 4.1 with  $b = 1$ ) was used for samples with CO<sub>2</sub> response peaks above 1 V. Calibration standards for each run were chosen to match the range of CO<sub>2</sub> concentrations in the samples being analyzed.

Analyzer calibration was checked periodically against a certified calibration mixture (2.02 ± 0.04 mol % CO<sub>2</sub>, 5.03 ± 0.10 mol % O<sub>2</sub>, balance N<sub>2</sub>)<sup>11</sup> by running a sample of the calibration mixture through the analyzer in the same manner as other package atmosphere samples. CO<sub>2</sub> and O<sub>2</sub> concentrations (with 95% confidence intervals) measured for the calibration mixture were 2.03 ± 0.03 mol % and 5.24 ± 0.11 mol % respectively (sample size = 5). The calculated CO<sub>2</sub> concentration agreed with the certified value within the bounds of the estimated 95% confidence interval. The calculated O<sub>2</sub> concentration was statistically higher than the certified value, but the magnitude of this error was considered small enough to be acceptable for the purpose of the experimental work.

#### 4.1.5 FRUIT INTERNAL ATMOSPHERE SAMPLING

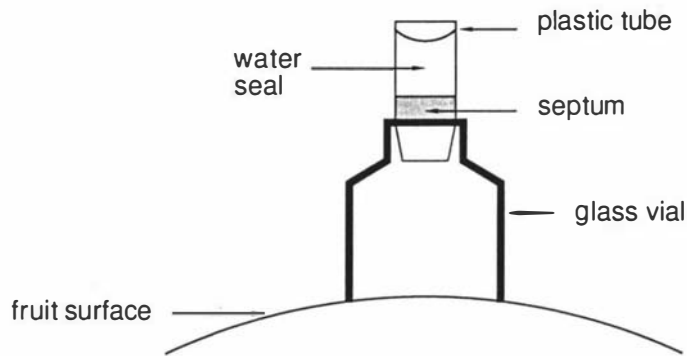
Monitoring the internal atmospheres of fruit inside sealed packages over time required a non-destructive method of fruit internal atmosphere sampling. Methods for sampling the internal atmospheres of plant organs have been reviewed by various authors, including Banks (1983), Solomos (1987), Ben-Yehoshua & Cameron (1989), and Dadzie (1992). These authors describe four common methods:

- (1) Direct sampling of the internal atmosphere of the plant organ with a hypodermic needle;
- (2) Sampling of the atmosphere inside a sealed cavity artificially created inside the plant organ;
- (3) Sampling of the atmosphere inside a small, sealed chamber attached to the surface of the plant organ;
- (4) Collection and sampling of gases removed from the plant organ by vacuum extraction.

Methods (1) and (4) were impractical for application here, as fruit being sampled by these methods would need to be removed from their MA packages. Method (3) was chosen over method (2) because it did not involve any wounding of the fruit and was therefore considered more suitable for fruit undergoing long-term storage. Several

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<sup>11</sup> Beta standard: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.



**Figure 4.5** Chamber for internal atmosphere sampling.

variations of method (3) have been described in the literature. The method described here is closely based on that used by Rajapakse *et al.* (1989a, 1989b, 1990) and Dadzie (1992).

Glass vials<sup>12</sup> were cut horizontally in half with a circular glass-saw and the top halves (approximately 1 ml) used as sampling chambers. Short plastic tubes were cut from the tips of 1 ml tuberculin syringes at about the 0.25 ml graduation mark, and the tapered luer-ends fixed with epoxy resin to the necks of the chambers. The chambers were placed over one or more lenticels on the fruit surface, near the equatorial region, and fixed in place with epoxy resin. After a 24 h period to allow the resin to set, the chambers were sealed by fitting rubber septa (the plunger tips from the 1 ml tuberculin syringes) into the plastic tubes. The wells formed by the plastic tubes were filled with water to prevent leakage of the septa and to prevent atmospheric contamination of gas samples taken from the chambers. Figure 4.5 illustrates the sampling-chamber arrangement.

Chambers were left to equilibrate with the fruit internal atmosphere for 48 h before sampling began (a 48 h equilibration period was measured by Rajapakse *et al.* 1990 for similar chambers sealed onto the surfaces of 'Braeburn' and 'Cox's Orange Pippin' apples). A 100  $\mu$ l gas-tight syringe<sup>13</sup> was used to withdraw gas samples from the chambers. Any dead space in the syringe needle was flushed out with the sample gas before the sample was withdrawn. Before analysis, samples were reduced to 90  $\mu$ l to remove any water drawn into the syringe needle during sampling. Samples were analyzed for O<sub>2</sub> and CO<sub>2</sub> as described in sections 4.1.4.1 to 4.1.4.3.

Poor visibility through the carton hand-holes, combined with the semi-opaque nature of the MA film, made the sampling of internal-atmosphere chambers for fruit in cartons impractical. Fruit internal atmospheres were therefore sampled during the bag trials only. Internal atmospheres were sampled for one apple in each bag: once before packing, every two days initially after packing, and with reducing frequency thereafter.

<sup>12</sup> Alltech Associates, Deerfield, Illinois.

<sup>13</sup> Model 1710 (removable needle): Hamilton Company, Reno, Nevada.

### 4.1.6 PACKAGE RELATIVE HUMIDITY

Changes in package relative humidity (RH) over time were monitored for two cartons of apples: one carton of 'Braeburn' stored at 0°C (folded carton liner) and one carton of 'Granny Smith' stored at 15°C (heat-sealed carton liner).

Relative humidity was measured using two capacitive RH probes<sup>14</sup>: one placed at the centre of the carton during packing and one placed outside the carton to measure store-air relative humidity. The probes were calibrated (at the respective storage temperature for each carton) against the equilibrium relative humidities formed over saturated solutions of  $\text{Mg}(\text{NO}_3)_2$  (55.9% RH at 15°C; Greenspan, 1977), NaCl (75.5% RH at 0°C; Greenspan, 1977), and  $\text{KNO}_3$  (96.3% RH at 0°C and 95.4% RH at 15°C; Greenspan, 1977). Data from the probes were recorded at 30 minute intervals by an electronic data-logger<sup>15</sup>.

Logging of RH data in this manner required that the lead of the probe inside the carton be passed through the liner to be connected to the data-logger exterior to the carton. The bulkiness of the probe itself, and the bulkiness of the lead and plug connected to the probe, caused difficulties in this respect. To pass either the probe or the plug through the liner required a 3-4 cm slit to be made in the liner. The site where the slit was to be made was first reinforced with a patch of adhesive silicone-rubber strip. The lead of the probe was passed through the slit and the weight of the lead supported by a clamp and stand. The slit in the silicone-rubber strip was then sealed with silicone sealant. Silicone sealant was also used to reinforce the adhesion of the silicone-rubber strip to the liner. This arrangement was not entirely satisfactory, as neither the adhesive on the silicone-rubber strip, nor the silicone sealant, bonded firmly to the liner. Hence the effectiveness of the seal around the lead of the RH probe could not be guaranteed.

## 4.2 FRUIT AND PACKAGE CHARACTERISTICS

### 4.2.1 FRUIT RESPIRATION RATES

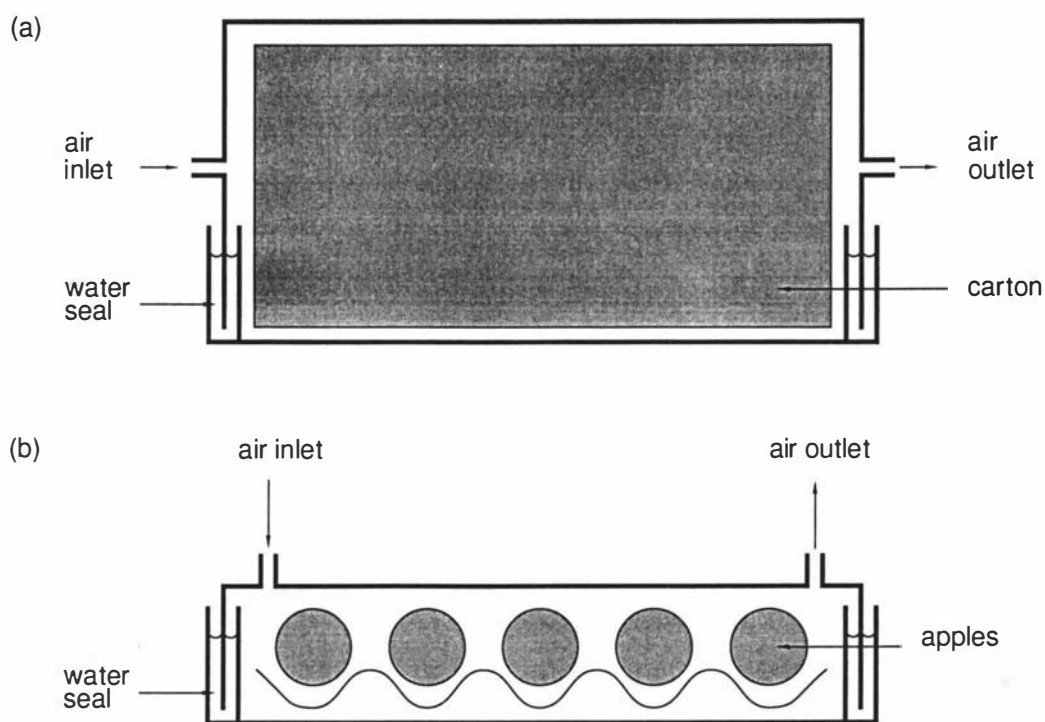
Mathematical modelling of  $\text{O}_2$  and  $\text{CO}_2$  concentrations inside an MA package requires the ability to predict fruit respiration rates as a function of temperature and package (or fruit internal) atmosphere (section 2.4.3.1). The parameters of such a respiration model are usually determined from respiration rate data obtained from the system being studied.

Methods of respiration rate measurement for whole plant organs fall into three categories: closed-system methods, flow-through methods, and permeable-system methods. Closed-system methods involve sealing fruit into a container of known volume and measuring the rate of  $\text{O}_2$  depletion or  $\text{CO}_2$  production inside the container over some interval of time. Flow-through methods involve sealing fruit into a container

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<sup>14</sup> Model VH-L (Vaisala sensor): Grant Instruments (Cambridge) Ltd, Cambridge, England.

<sup>15</sup> Model 1206 Squirrel: Grant Instruments (Cambridge) Ltd, Cambridge, England.



**Figure 4.6** Stainless-steel boxes for respiration rate measurements on (a) whole cartons and (b) single trays of fruit.

through which a measured flow of air (or gas mixture of a specified  $O_2$  and  $CO_2$  concentration) is passed. Respiration rates are estimated from the difference between inlet and outlet concentrations of  $O_2$  or  $CO_2$ . Permeable-system methods involve sealing fruit into a package either partially or wholly constructed of a permeable film of known permeability and film area. Respiration rates are estimated from the rate of modified atmosphere development within the package or from the steady-state atmosphere formed within the package (e.g. Beaudry *et al.*, 1992; Beaudry, 1993; Gran & Beaudry, 1993; Joles *et al.*, 1994; Christie *et al.*, 1995; Lee *et al.*, 1996a). The accuracy of this method of respiration-rate measurement is highly dependent on the accuracy of permeability data available for the packaging film.

A flow-through method was chosen for this work as such a method allowed respiration rates to be measured under steady-state atmospheres, and was independent of any measurements of film permeability.

Respiration rate measurements under different atmospheres were obtained from cartons used in the MA trials described in section 4.1. Respiration rates of cartons of fruit at  $0^\circ C$  were measured in air (before packing) and under the steady-state atmospheres formed inside the  $25\ \mu m$  and  $40\ \mu m$  liners. Respiration rates in air were also measured for single trays of fruit at  $15^\circ C$  (1993 season) and  $20^\circ C$  (1994 season).

For each respiration rate measurement, a carton of fruit was placed inside a stainless steel box consisting of a base edged by a water-filled trough, and a lid fitted with air-inlet and outlet ports at opposite ends (Figure 4.6a). When in place, the sides of the lid

rested in the water-filled trough around the edge of the base, forming a water seal. Air from a cylinder of compressed dry-air<sup>16</sup> was passed through the box at a flow rate of 200-250 ml·min<sup>-1</sup>. To prevent excessive moisture loss from the fruit, the air flow was humidified before it passed into the box by bubbling the flow through water in two 250 ml gas-dispersion jars connected in series. After a 24 h equilibration period, triplicate 1 ml gas samples were collected from the inlet and outlet streams and analyzed for CO<sub>2</sub> as described in sections 4.1.4.1 to 4.1.4.3. Samples were collected in 1 ml disposable tuberculin syringes<sup>17</sup> through septum ports fitted into the inlet and outlet gas lines. The flow rate of air at the inlet to the respiration box was measured with a digital gas-flowmeter<sup>18</sup> before and after each 24 h respiration run.

To minimize the disturbance of package atmospheres during respiration measurements, the flow rate of air passed through the respiration box was chosen to ensure that the concentration of CO<sub>2</sub> in the outlet stream did not exceed 0.5%. For whole cartons of fruit at 15°C or 20°C, this would have entailed excessively high flow rates. Respiration rate measurements at these temperatures were therefore carried out for single trays of fruit (Figure 4.6b).

#### 4.2.2 FRUIT SKIN PERMEANCES TO O<sub>2</sub> AND CO<sub>2</sub>

Mathematical modelling of the relationship between fruit respiration rate and fruit external and internal O<sub>2</sub> and CO<sub>2</sub> concentrations requires knowledge of the fruit skin permeance to O<sub>2</sub> and CO<sub>2</sub> (section 2.4.3.2).

Methods for estimating the permeance of the fruit skin to respiratory gases have been reviewed by authors such as Ben Yehoshua & Cameron (1989) and Dadzie (1992). These methods fall into two categories: steady-state and nonsteady-state methods. Steady-state methods involve the estimation of skin permeances from measurements of fruit internal gas concentrations and steady-state gas-fluxes across the fruit skin. Nonsteady-state methods are based on measurements of the rates of change of internal or external gas concentrations when fruit equilibrated in a given gaseous environment are transferred to an environment of a different gas composition. An example of such a method is the ethane-efflux method described by Cameron & Yang (1982) and Banks (1985).

Because average estimates of fruit skin permeances for each cultivar were considered sufficient for modelling purposes, and because average estimates of steady-state O<sub>2</sub> and CO<sub>2</sub> fluxes could be obtained from the respiration data collected as described in section 4.2.1, a steady-state method was adopted in this work. For this purpose, average internal O<sub>2</sub> and CO<sub>2</sub> concentrations for each cultivar in air at 0°C, 15°C (1993), and 20°C (1994) were obtained from measurements of the internal atmosphere composition of samples of 20 or 25 fruit for each cultivar and temperature.

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<sup>16</sup> Dry air, gas code 108: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>17</sup> Monoject: Sherwood Medical, St Louis, Missouri.

<sup>18</sup> J&W Scientific, Folsom, California.

Of the four common methods listed in section 4.1.5 for sampling the fruit internal atmosphere, the direct sampling method is probably the simplest and quickest. Thus, internal atmosphere samples were obtained by direct sampling from the fruit core cavity. The applicability of this method of gas sampling for estimation of fruit skin permeances is based on the assumption that gas concentration gradients within the fruit flesh can be considered negligible. Some workers have measured significant gas concentration gradients within apples (section 2.4.1.1). However, in this work, a comparison of internal O<sub>2</sub> and CO<sub>2</sub> concentrations measured for 'Braeburn' fruit by direct sampling from the core cavity and by sampling from chambers on the fruit surface suggested no significant concentration gradient between the core and the fruit surface (section 8.1.2). The method of internal atmosphere sampling described here is based on that used by Rajapakse *et al.* (1989a, 1989b, 1990) and Dadzie (1992).

All steps in internal atmosphere sampling were carried out with fruit and syringes submerged in water to prevent atmospheric contamination of the samples. A 1 ml disposable tuberculin syringe<sup>19</sup> fitted with a 50 mm (1 mm internal diameter) canula was flushed out with water to remove air in the dead-space of the syringe and canula. A pin inserted into the canula prevented blockage of the canula as it was inserted through the fruit flesh into the core cavity. A sample of the internal atmosphere in the core cavity was gradually withdrawn, the syringe removed from the canula, and the gas in the syringe immediately sub-sampled with a 100 µl gas-tight syringe<sup>20</sup>. Dead-space in the gas-tight syringe was flushed out with the internal atmosphere sample before the sub-sample was withdrawn. Internal atmosphere samples (90 µl) were analyzed for O<sub>2</sub> and CO<sub>2</sub> as described in sections 4.1.4.1 to 4.1.4.3.

### 4.2.3 CARTON COOLING RATES

Modelling of package atmosphere responses to variable-temperature storage regimes requires information on the cooling (or warming) rates of the packaged fruit. Temperature-time profiles for the centre fruit on the middle tray of a carton were measured for selected cartons during the trials described in section 4.1 (Table 4.2). In addition, temperature-time profiles of selected fruit inside three cartons of 'Granny Smith' apples were measured to compare cooling rates of fruit at three different positions inside a carton, and to compare cooling rates of fruit packaged in cartons with or without an MA-film liner (Table 4.5).

Fruit temperatures were measured with copper-constantan thermocouples (0.5 mm diameter wire) inserted into the centre of the fruit. Gas sampling ports (Figure 4.2) were fitted into the MA-film liners to form exit ports through the film for the thermocouple wires. Thermocouple wires were pushed through the septa in the ports, and silicone sealant was applied around the wires to provide additional sealing. Data from the thermocouples were logged at 5 or 15 minute intervals on a 1200 series Squirrel data-logger<sup>21</sup>.

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<sup>19</sup> Monoject: Sherwood Medical, St Louis, Missouri.

<sup>20</sup> Model 1710 (removable needle): Hamilton Company, Reno, Nevada.

<sup>21</sup> Model 1203 Squirrel: Grant Instruments (Cambridge) Ltd, Cambridge, England.

**Table 4.5** Positions of temperature measurements for ‘Granny Smith’ cartons.

| Carton 1<br>40 µm liner                     | Carton 2<br>25 µm liner   | Carton 3<br>No liner      |
|---------------------------------------------|---------------------------|---------------------------|
| Centre apple, top tray                      |                           |                           |
| Centre apple, middle tray                   | Centre apple, middle tray | Centre apple, middle tray |
| Apple adjacent to hand-hole,<br>middle tray |                           |                           |

**4.2.4 PACKAGING FILM PERMEABILITY**

Mathematical modelling of modified atmosphere packaging systems for horticultural produce requires accurate knowledge of packaging film permeabilities to O<sub>2</sub> and CO<sub>2</sub> over a range of temperature and humidity conditions. Tables of permeability data for a wide range of polymers and penetrants have been published in the literature (e.g. Pauly 1989), and for specific films, manufacturer’s data may be available. However, experimental measurement is often required to obtain accurate permeability data for a given film over a specified range of conditions. The exact composition of the permeable film used in the MA trials was not disclosed by the manufacturer for reasons of commercial sensitivity, and the available permeability data for the film were limited. Experimental measurement of the film’s permeability to O<sub>2</sub> and CO<sub>2</sub> over the range of temperatures and humidities likely to be encountered during fruit storage and transport was therefore necessary.

Felder & Huvard (1980) have presented a detailed review of the experimental methods that have been used to study the permeation, diffusion, and sorption of gases and vapours in polymers. According to these authors, most experimental techniques fall into one of three categories: (1) sorption into or out of a polymer; (2) permeation through a film into (or out of) a closed chamber; and (3) permeation through a film into a flowing stream. Sorption methods are recommended for measurements of equilibrium solubilities, measurements of slow processes, studies of non-Fickian diffusion, high-pressure measurements, and studies of solvent cracking and crazing. They are not recommended for measurements of steady-state permeabilities or for studies of very rapid processes. Methods involving permeation into a closed chamber are recommended for measurements of low permeation rates, penetrants for which accurate calibration standards are difficult to obtain, and measurements of transport rates of easily condensed vapours. Methods involving permeation into a flowing stream are recommended for measurements of moderate to high permeation rates and for membranes susceptible to tearing or distension.

Films for use in MA packaging of fruits and vegetables must possess relatively high O<sub>2</sub> and CO<sub>2</sub> transmission rates to ensure that anaerobic conditions or harmful levels of CO<sub>2</sub> are not formed inside the packages. Thus, a flow-through method was chosen for the permeability measurements. Use of a flow-through method also allowed straightforward establishment of different relative humidities, as the flowing gas streams could be

humidified to desired relative humidities by bubbling the streams through aqueous solutions with corresponding equilibrium humidities.

The flow-through method of film permeability measurement used in this work is described in the following two sections. The method was tested over a number of preliminary runs before the main body of experimental work was carried out.

#### 4.2.4.1 PRELIMINARY MEASUREMENTS

All preliminary runs were carried out at 5°C in a small, experimental cool-store with a specified temperature-control accuracy of  $\pm 0.5^\circ\text{C}$  of set-point. All equipment required for the permeability runs, including the gas-analysis equipment, was held in the cool-store.

A stainless-steel permeability cell<sup>22</sup> (Davis & Huntington, 1977) consisting of two chambers separated from each other by the film sample was used in the preliminary work. The volumes of the top and bottom chambers of the cell were 900 ml and 450 ml respectively, and the internal diameter of the chambers was 0.19 m. The cell was sealed by means of a screw-press mounted over the cell. The sealing edges of the top and bottom halves of the cell were precision-machined to allow a seal to be obtained without the need for rubber O-rings or sealing grease. Film samples were held flat during loading of the cell by clamping the samples into a wooden hoop with a slightly larger diameter than the outer diameter of the cell. Entry and exit ports fitted into opposite sides of both halves of the cell allowed continuous gas flows to be passed through each chamber. Oxygen gas<sup>23</sup> was passed through one chamber and carbon dioxide gas<sup>24</sup> through the other. Gas flow rates ( $10\text{--}45\text{ ml}\cdot\text{min}^{-1}$ ) were set by adjusting a needle valve<sup>25</sup> in each gas line. Permeability measurements were made for both dry and humidified gas streams. For runs with humidified gas streams, humidification was achieved by bubbling each gas stream through water in a 250 ml gas dispersion jar (one jar in each line). Figure 4.7 shows a schematic diagram of the experimental equipment.

The gas flow rate at the inlet of each chamber was measured with a digital gas flowmeter<sup>26</sup> before and after each run. After an equilibration time of 2-3 h, 1 ml gas samples were collected from the outlet stream of each chamber. Samples were collected in 1 ml disposable tuberculin syringes<sup>27</sup> through septum ports fitted into the outlet gas lines. Samples were analyzed on a gas chromatograph<sup>28</sup> fitted with a CTR column<sup>29</sup> and a thermal conductivity detector. Hydrogen gas<sup>30</sup> was used as the carrier gas

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<sup>22</sup> CSIRO Division of Food Research, North Ryde, New South Wales, Australia.

<sup>23</sup> Instrument-grade  $\text{O}_2$ , gas code 018: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>24</sup> Instrument-grade  $\text{CO}_2$ , gas code 013: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>25</sup> Nupro S-series: Swagelok, Willoughby, Ohio.

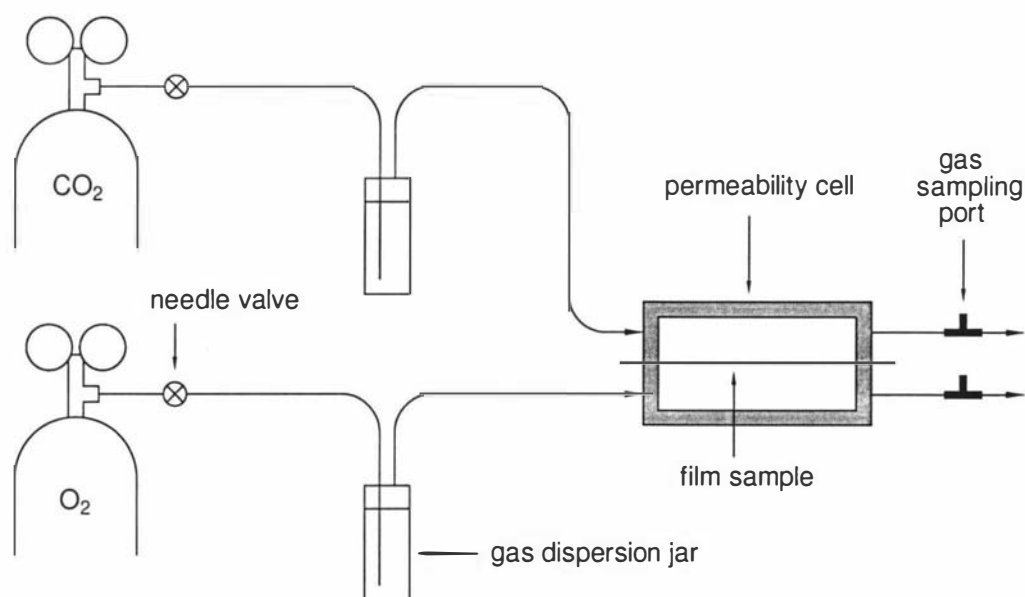
<sup>26</sup> J&W Scientific, Folsom, California.

<sup>27</sup> Monoject: Sherwood Medical, St Louis, Missouri.

<sup>28</sup> SRI 8610 gas chromatograph: Alltech Associates, Deerfield, Illinois.

<sup>29</sup> CTR I: Alltech Associates, Deerfield, Illinois.

<sup>30</sup> Gas code 141: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.



**Figure 4.7** Experimental equipment for the preliminary permeability measurements.

through the column. Detector output was recorded and analyzed by an electronic integrator<sup>31</sup>. Samples of a certified calibration standard ( $2.02 \pm 0.04$  mol % CO<sub>2</sub>,  $5.03 \pm 0.10$  mol % O<sub>2</sub>, balance N<sub>2</sub>)<sup>32</sup> were run through the column before each permeability run to calibrate the integrator for O<sub>2</sub> and CO<sub>2</sub> analysis. Five to six samples from each outlet stream were analyzed during each permeability run. Eight runs under dry conditions and four runs under humidified conditions were carried out.

Results and experience gained from the preliminary work were used in planning further permeability measurements and in refining the flow-through method. Although the method described above was generally satisfactory, long periods were needed for gas concentrations in each chamber of the permeability cell to reach steady-state. To achieve shorter equilibration times, a permeability cell with smaller chamber volumes was designed.

#### 4.2.4.2 MAIN MEASUREMENTS

##### *Experimental Design*

Further permeability measurements were carried out over the range of temperatures and humidities likely to be encountered in modified atmosphere packaging applications. A temperature range of 0 to 30°C was chosen to include cool-storage temperatures as well as the temperatures to which packages might be exposed during periods of removal from cool-storage. At each temperature, permeability measurements were made with dry

<sup>31</sup> Model 3390A: Hewlett Packard, Wilmington, Delaware.

<sup>32</sup> Beta standard: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

**Table 4.6** Experimental design for the main permeability measurements.

| Nominal RH (%) |             | Nominal temperature (°C) |                 |                 |                 |                                   |
|----------------|-------------|--------------------------|-----------------|-----------------|-----------------|-----------------------------------|
| Bottom Chamber | Top Chamber | 0.5                      | 5               | 10              | 20              | 30                                |
| 0              | 0           | 40 <sup>a</sup>          | 25 <sup>a</sup> | 40 <sup>a</sup> | 25 <sup>a</sup> | 25 <sup>a</sup> , 40 <sup>a</sup> |
| 54             | 54          | 40                       | 40              | 40              | 40              | 25                                |
| 85             | 85          | 25                       | 40              | 25              | 40              | 25                                |
| 100            | 100         | 25 <sup>a</sup>          | 40 <sup>a</sup> | 25 <sup>a</sup> | 40 <sup>a</sup> | 25 <sup>a</sup> , 40 <sup>a</sup> |
| 0              | 100         | -                        | -               | -               | 25              | 40                                |
| 100            | 0           | -                        | -               | -               | 25              | 25                                |
| 54             | 100         | -                        | -               | -               | 25              | 40                                |
| 100            | 54          | -                        | -               | -               | 40              | 40                                |
| 85             | 100         | -                        | -               | -               | 25              | 40                                |
| 100            | 85          | -                        | -               | -               | 40              | 40                                |

Key: 40 = 40  $\mu\text{m}$  MA film  
 25 = 25  $\mu\text{m}$  MA film

<sup>a</sup> Replicate runs performed on 3 film samples.

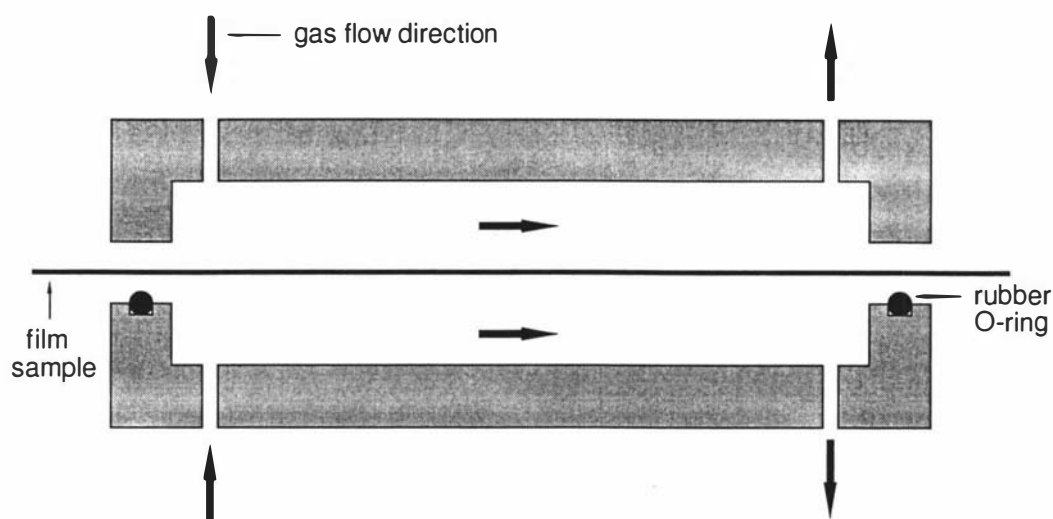
gases and with gases humidified to relative humidities between 50 and 100%. Permeability measurements were made for film thicknesses of 25 and 40  $\mu\text{m}$ , with film thickness randomly selected for each experimental run or set of replicate runs.

Table 4.6 summarizes the experimental design for the main permeability runs. A fully randomized design would have required repeated resetting and re-equilibration of the controlled-temperature rooms in which the permeability runs were carried out. To avoid this, all runs at a given temperature were completed before work at a new temperature was started. The order of temperatures was randomized, as was the order of runs carried out at each temperature.

### *Experimental Method*

The experimental method for the main set of permeability measurements was basically similar to that described in section 4.2.4.1 for the preliminary work. The main differences were equipment related; a permeability cell with smaller chamber volumes was used, and gas analysis was by the O<sub>2</sub> electrode/infra-red CO<sub>2</sub> analyzer described in section 4.1.4.1 rather than by gas chromatography. The O<sub>2</sub>/CO<sub>2</sub> analyzer allowed considerably faster analysis of gas samples than the gas chromatograph used in the preliminary runs.

Permeability runs were carried out in two controlled-temperature rooms (one room for runs at 0 to 20°C and one room for runs at 30°C). Both rooms had a specified temperature-control accuracy of  $\pm 0.5^\circ\text{C}$  of set-point. All experimental equipment except the gas analysis system was held in the controlled-temperature rooms. The gas analysis system was located in a constant-temperature (20°C) laboratory adjacent to the controlled-temperature rooms. Calibration standards were held in the same room as the permeability-cell set-up so that any effects of sample temperature on the response of the



**Figure 4.8** Cross-section of the PVC permeability cell used for the main permeability measurements.

analyzer would be consistent for samples and standards.

Figure 4.8 shows a cross-section of the permeability cell. For ease of machining, the cell was constructed from PVC plastic<sup>33</sup>. Sealing of the cell was achieved by three G-clamps spaced evenly around the circumference of the cell. To ensure complete sealing of the chambers, the edge of the bottom chamber was fitted with a rubber O-ring. Sealing around the edge of the top chamber was aided by a thin layer of silicone grease.

Figure 4.9 shows a schematic diagram of the experimental equipment for the permeability measurements. Nitrogen gas<sup>34</sup> was passed through the top chamber, while carbon dioxide gas<sup>35</sup>, oxygen gas<sup>36</sup>, or a certified mixture of carbon dioxide and oxygen ( $49.9 \pm 0.2$  mol % CO<sub>2</sub>: balance O<sub>2</sub>)<sup>37</sup> was passed through the bottom cell. After an equilibration time of one hour, 1 ml gas samples were collected from the outlet and inlet streams of the top chamber. Samples were collected in a 1 ml gas-tight syringe<sup>38</sup> through septum ports fitted into the inlet and outlet gas lines of the top chamber. To prevent atmospheric contamination of the samples, the dead-space in the needle and head of the syringe was flushed repeatedly with the sample gas before withdrawing each sample. Three samples from the outlet stream and two from the inlet stream were analyzed for each run. To avoid disturbing the equilibrium of the cell, samples from the inlet stream were only taken after all samples from the outlet stream had been analyzed.

<sup>33</sup> Grey PVC: Mulford Plastics, Petone, New Zealand.

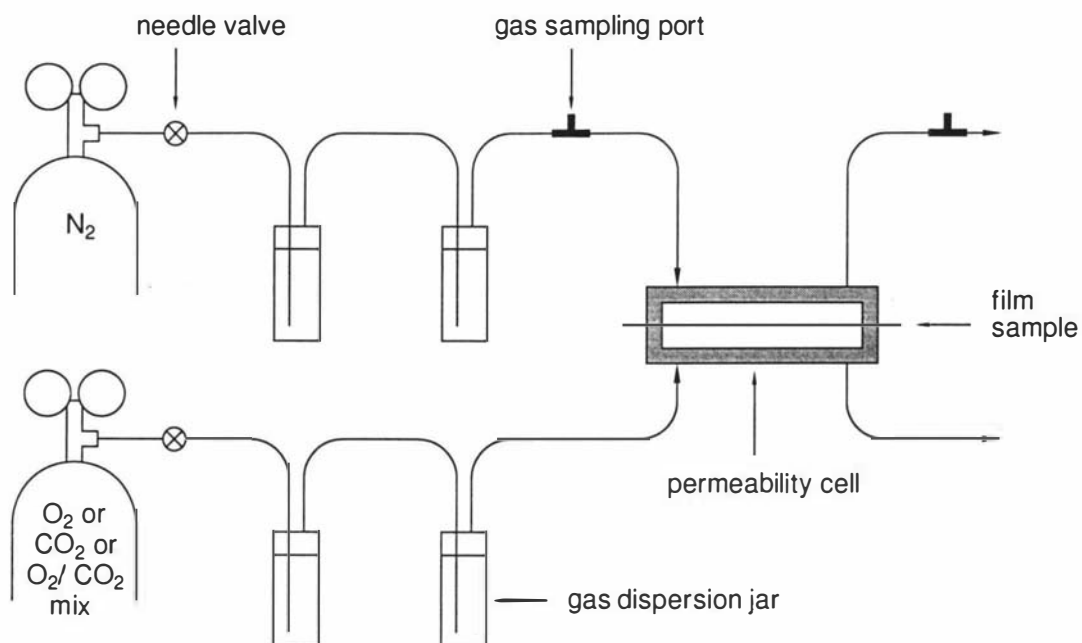
<sup>34</sup> Instrument-grade N<sub>2</sub>, gas code 016: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>35</sup> Instrument-grade CO<sub>2</sub>, gas code 013: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>36</sup> Instrument-grade O<sub>2</sub>, gas code 018: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>37</sup> Beta standard: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>38</sup> Model 1001 (removable needle): Hamilton Company, Reno, Nevada.



**Figure 4.9** Experimental set-up for the main permeability measurements.

Gas samples were analyzed for  $O_2$  and  $CO_2$  by running 0.7 ml sample volumes through the gas analysis system described in section 4.1.4.1. Duplicate samples of two certified calibration standards ( $2.02 \pm 0.04$  mol %  $CO_2$ ,  $0.49 \pm 0.01$  mol %  $O_2$ , balance  $N_2$  and  $4.03 \pm 0.08$  mol %  $CO_2$ ;  $0.99 \pm 0.02$  mol %  $O_2$ , balance  $N_2$ )<sup>39</sup> were run through the gas analyzer before and after each permeability run. Sample  $O_2$  and  $CO_2$  concentrations were calculated from the calibration standards as discussed in section 4.1.4.3.

For runs at temperatures of  $0^\circ C$  to  $10^\circ C$ , pure  $CO_2$  or pure  $O_2$  was passed through the bottom chamber to ensure a large enough  $CO_2$  or  $O_2$  concentration in the  $N_2$  stream for accurate measurement. At these temperatures, two runs were performed for each set of conditions listed in Table 4.6: one run for  $CO_2$  permeability and one run for  $O_2$  permeability. For runs at  $20^\circ C$  or  $30^\circ C$  the  $CO_2/O_2$  mixture was passed through the bottom cell, allowing simultaneous measurement of  $CO_2$  and  $O_2$  permeability.

For runs with humidified gas streams, humidification was achieved by bubbling each gas stream through saturated salt solutions or water in 250 ml gas-dispersion jars (two jars in each line). Relative humidities of the gas streams exiting each salt solution were checked (at  $20^\circ C$ ) with a cooled-mirror dew-point meter<sup>40</sup> (Table 4.7). The discrepancies between published equilibrium humidities and actual measured humidities listed in Table 4.7 indicate that equilibration between the gas flows and the aqueous solutions may not have been achieved (in the case of KCl and water) and that the  $Mg(NO_3)_2$  solution may not have been fully saturated. However, a reasonably wide range of humidities was nevertheless obtained.

<sup>39</sup> Beta standards: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>40</sup> Michell series 3000 dew-point meter: Michell Instruments, Cambridge, England.

**Table 4.7** Theoretical equilibrium humidities and actual measured humidities of gas streams bubbled through aqueous salt-solutions.

| Salt Solution                     | Equilibrium RH at 20°C (%) | Measured RH at 20°C (%) |
|-----------------------------------|----------------------------|-------------------------|
| Mg(NO <sub>3</sub> ) <sub>2</sub> | 54.38 ± 0.23 <sup>a</sup>  | 67.9                    |
| KCl                               | 85.11 ± 0.29 <sup>a</sup>  | 81.9                    |
| Water                             | 100                        | 93.9                    |

<sup>a</sup> Values from Greenspan (1977).

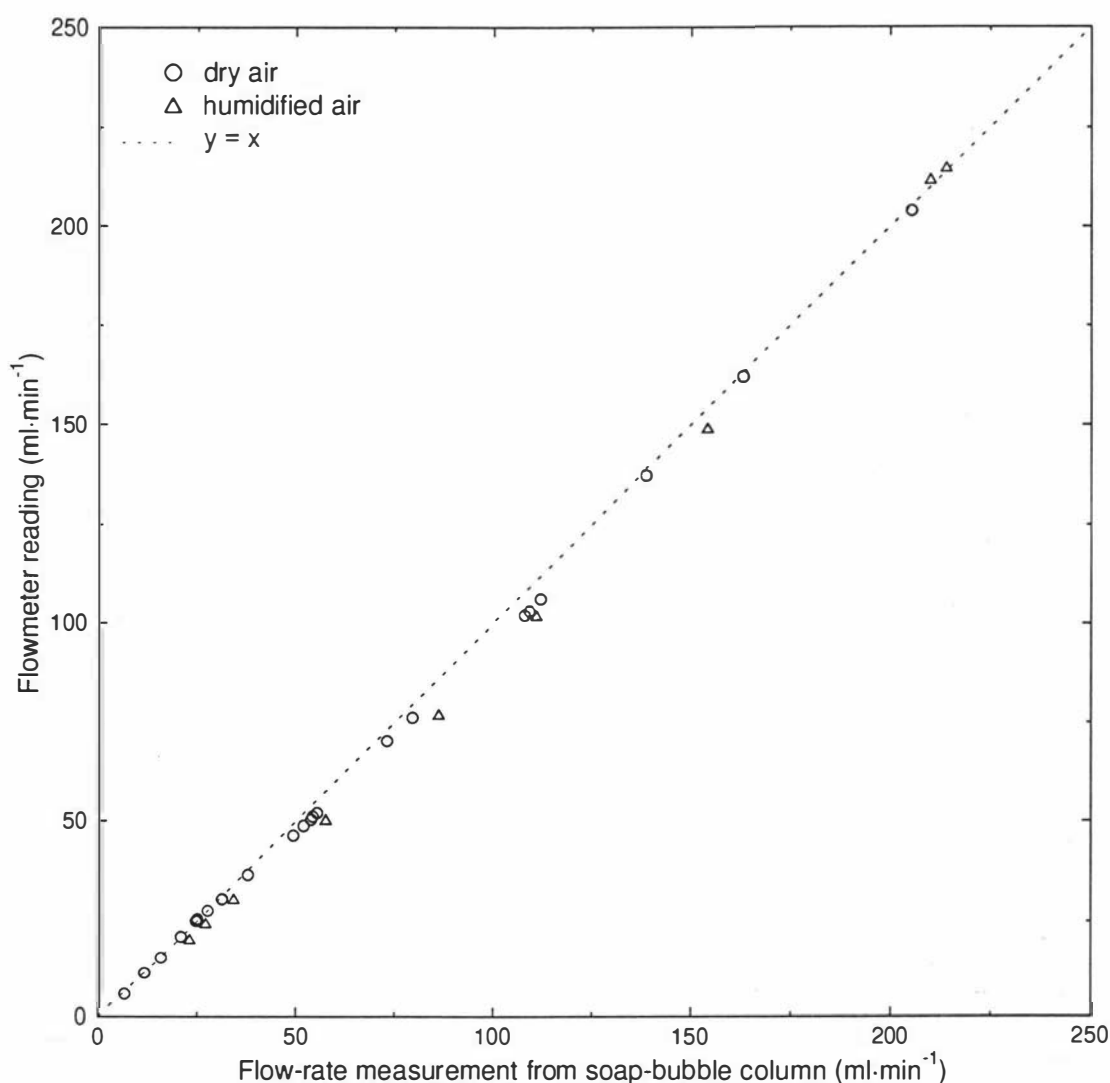
The gas flow rate at the inlet of each chamber of the permeability cell was measured with a digital gas flowmeter<sup>41</sup> before and after each run. For all permeability runs, gas flow rates through both chambers of the permeability cell were set to 20-30 ml·min<sup>-1</sup>. Flowmeter calibration was checked periodically against a soap-bubble column (Figure 4.10). Flowmeter readings for dry gases were accurate between 0 and 40 ml·min<sup>-1</sup>, and above 150 ml·min<sup>-1</sup>, but readings between 40 and 150 ml·min<sup>-1</sup> were up to 6.5% lower than flow measurements from the soap-bubble column. The largest discrepancies occurred between 50 and 100 ml·min<sup>-1</sup>. The flowmeter was also affected by humidity, reading about 10% lower than flow measurements from the soap-bubble column for humidified gas streams in the 20-30 ml·min<sup>-1</sup> range. For the calculation of film permeabilities, a correction factor of +10% was therefore applied to all flow rates measured for humidified gas-streams. Gas species (i.e. O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, or air) did not appear to affect flowmeter readings.

Micrometer callipers were used to measure film thicknesses for five samples of each of the 25 and 40 µm (nominal) films. For each film sample, seven thickness measurements at different positions were taken.

**4.2.4.3 CARTON MEASUREMENTS**

When compared to the actual conditions under which MA carton-liners are used, the experimental conditions described for the film permeability measurements above seem somewhat artificial. Under such experimental conditions, permeabilities are measured for relatively small, well-defined areas of flat, unstressed film. When used to line apple cartons, liners become subject to considerable folding and creasing. Much of the liner surface area comes into contact with the support packaging on the outside or the produce on the inside, and condensation on the inside or outside of the film may be observed for packages moved from one storage temperature to another. To investigate the possible influence of some of these factors on the effective permeabilities of carton liners, a set of permeability measurements was made under conditions designed to more closely resemble a true packaging situation. The method described below is essentially a ‘closed-volume’ method (e.g. Felder & Huvard, 1980; Moyls *et al.*, 1992), with a film-lined, empty apple carton replacing the usual permeability cell.

<sup>41</sup> J&W Scientific, Folsom, California.



**Figure 4.10** Digital gas-flowmeter readings compared with soap-bubble-column flow measurements for dry and humidified gas flows (room temperature).

Four empty apple cartons were lined with 40  $\mu\text{m}$  carton-liners and placed in an experimental cool-store at 0.5°C. Each liner was fitted with a gas sampling port (Figure 4.3) at one of the carton hand-holes. A similar port without a septum was fitted into each liner at the opposite carton hand-hole. 40 to 50 ml water was poured into each liner to create humidified conditions within the packages. The liners were sealed with double heat-seals 13 cm from the liner openings, in the same manner as that employed to seal the liners of cartons filled with apples (Figure 4.2b). After flattening the liners to remove most of the air contained in them, a measured flow of pure  $\text{CO}_2$ <sup>42</sup> was passed into each liner via the ports with no septa. The flow of  $\text{CO}_2$  into the liners was continued until a volume of  $\text{CO}_2$  roughly equal to 5% of the total carton volume had

<sup>42</sup> Instrument grade  $\text{CO}_2$ , gas code 013: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

been delivered. Filling was then continued with pure N<sub>2</sub><sup>43</sup> until the volume of gas inside the liners almost filled the cartons. The sealed ends of the liners were folded over in the same manner as for cartons packed with fruit, and the lids placed on the cartons. The liners were further filled with N<sub>2</sub> until their volumes had expanded to completely fill the cartons. The N<sub>2</sub> flow was discontinued and, after several seconds to allow the pressure inside the liners to equilibrate to atmospheric pressure, the ports used to fill the liners were sealed with silicone-rubber plugs and silicone sealant.

Permeation of O<sub>2</sub> and CO<sub>2</sub> into and out of the liners was monitored by the periodic withdrawal of duplicate package gas samples in 100 µl gas-tight syringes<sup>44</sup>. Gas samples were analyzed as described in sections 4.1.4.1 to 4.1.4.3. Sampling was continued for 90 h, with ten samples taken from each carton during this period.

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<sup>43</sup> Instrument grade N<sub>2</sub>, gas code 016: BOC Gases New Zealand Ltd, Lower Hutt, New Zealand.

<sup>44</sup> Model 1710 (removable needle): Hamilton Company, Reno, Nevada.

## Chapter 5

# MODIFIED ATMOSPHERE DEVELOPMENT IN APPLE CARTONS

This chapter presents a discussion of the effects of various package and storage characteristics on the development of modified atmospheres inside film-lined cartons of apples. The experimental data presented in this chapter were collected according to the methods described in Chapter 4. Much of the material in this chapter has previously been presented to the 19th International Congress of Refrigeration (Merts *et al.*, 1995).

## 5.1 STEADY-STATE PACKAGE ATMOSPHERES

Table 5.1 lists the steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations measured inside cartons with heat-sealed carton-liners. As expected, 40 µm liners produced a greater degree of atmosphere modification than 25 µm liners. For a given film thickness, different cultivars produced only slightly different steady-state atmospheres. However, this does

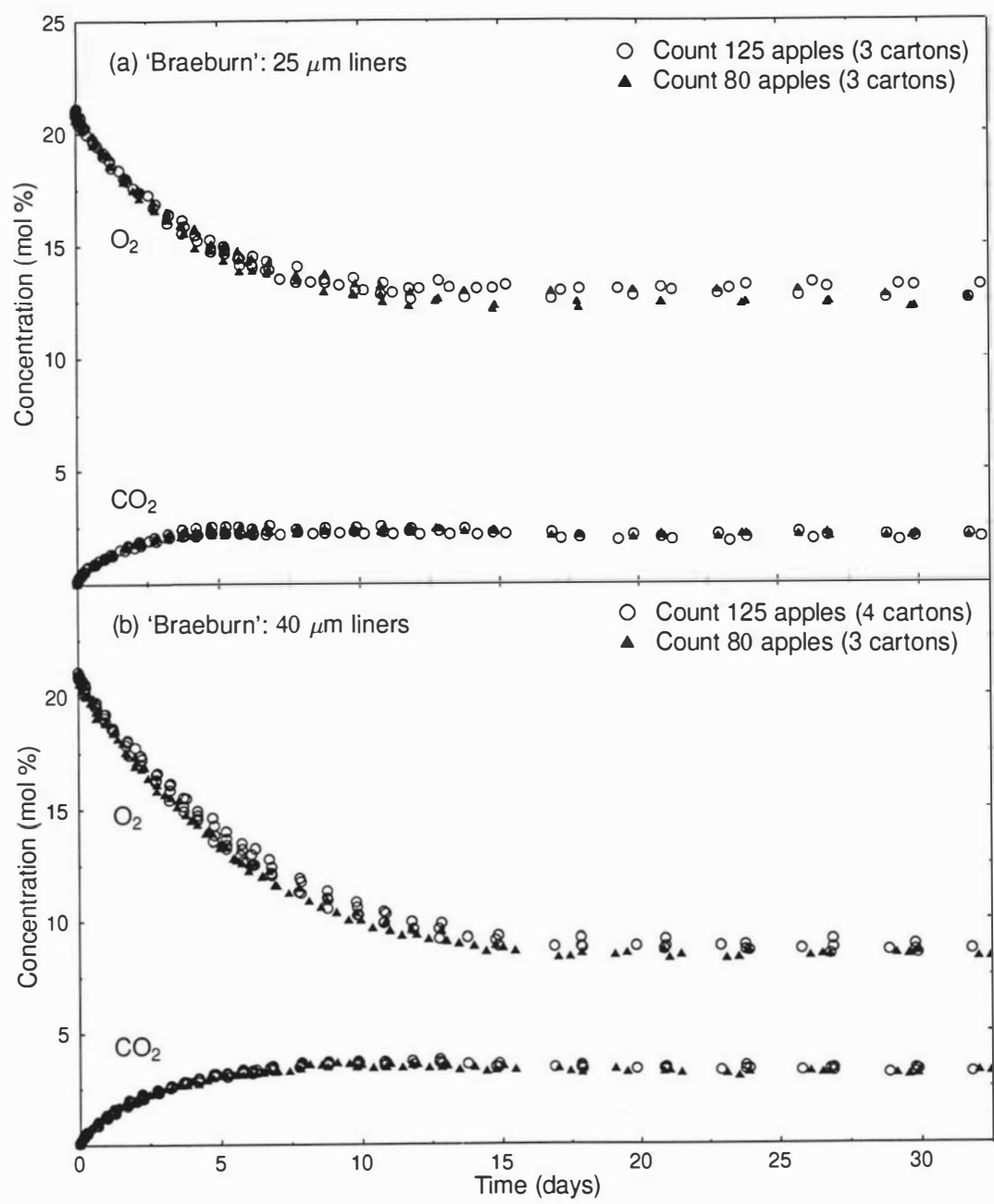
**Table 5.1** Steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations formed within heat-sealed carton-liners.<sup>a</sup>

| Cultivar       | Storage temperature (°C) | Fruit Mass (kg)   | Film thickness (µm) | Package O <sub>2</sub> (mol %) | Package CO <sub>2</sub> (mol %) | n <sup>b</sup> |
|----------------|--------------------------|-------------------|---------------------|--------------------------------|---------------------------------|----------------|
| 1993 Season:   |                          |                   |                     |                                |                                 |                |
| ‘Braeburn’     | 1.6                      | 18.5              | 25                  | 12.8 ± 0.4                     | 2.1 ± 0.1                       | 6              |
|                |                          |                   | 40                  | 8.6 ± 0.2                      | 3.2 ± 0.1                       | 7              |
| 1994 Season:   |                          |                   |                     |                                |                                 |                |
| ‘Royal Gala’   | 1.2                      | 16.8 <sup>c</sup> | 25                  | 14.2 ± 0.3                     | 1.7 ± 0.1                       | 10             |
|                |                          |                   | 40                  | 10.5 ± 0.3                     | 2.5 ± 0.1                       | 11             |
| ‘Braeburn’     | 0.8                      | 18.8              | 25                  | 13.6 ± 0.5                     | 1.8 ± 0.1                       | 6              |
|                |                          |                   | 40                  | 9.7                            | 2.7                             | 2              |
| ‘Granny Smith’ | 0.8                      | 18.6              | 25                  | 13.6 ± 0.5                     | 1.9 ± 0.1                       | 4              |
|                |                          |                   | 40                  | 8.8 ± 0.2                      | 3.0 ± 0.1                       | 4              |

<sup>a</sup> Package O<sub>2</sub> and CO<sub>2</sub> concentrations listed as sample mean ± 95% confidence interval on sample mean.

<sup>b</sup> Sample size (number of cartons).

<sup>c</sup> Whereas 'Braeburn' and 'Granny Smith' apples were passed through commercial grading and packing lines before being transported to Massey University, graded 'Royal Gala' fruit were transported to the University in bulk bins and packed into cartons on arrival. Though smaller than standard count-100 fruit, the apples were packed into available count-100 trays. As a result, 'Royal Gala' cartons used in the MA trials weighed somewhat less than standard New Zealand apple cartons.



**Figure 5.1** Package  $O_2$  and  $CO_2$  concentrations for cartons of count-125 and count-80 'Braeburn' (trial BB93-A).

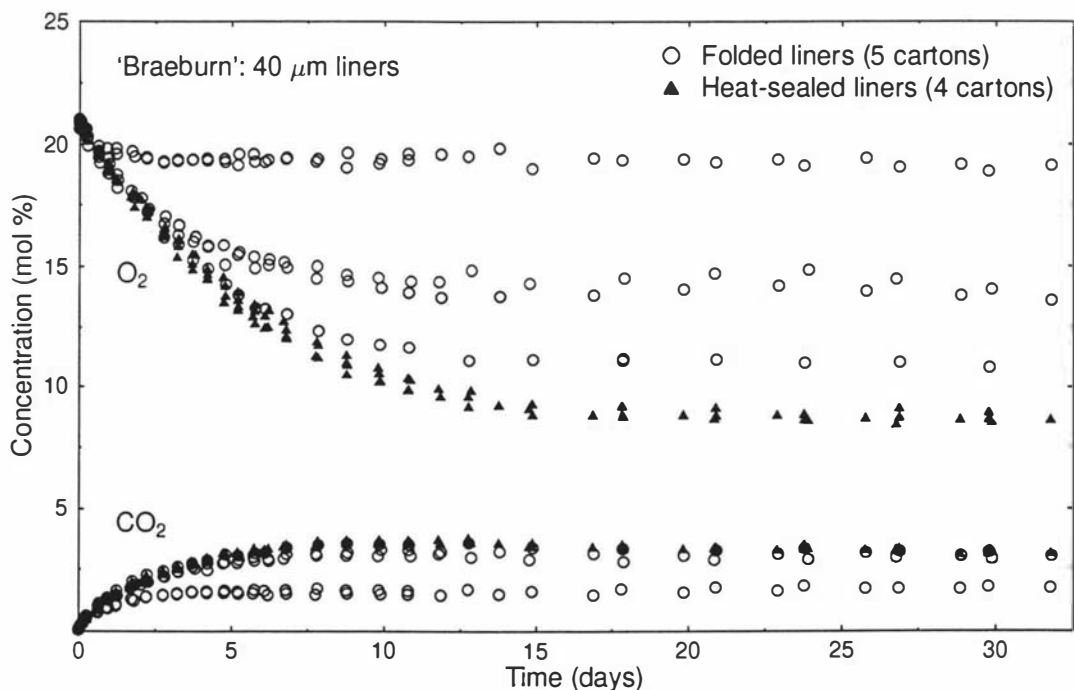
not imply that cultivar is an unimportant factor in the design of MAP systems, as a given MA may have different effects on different apple cultivars (section 2.2).

Fruit count size also had little effect on steady-state package atmospheres, as illustrated in Figure 5.1. Any small difference between the steady-state atmospheres for count 125 and count 80 fruit in Figure 5.1 can probably be attributed to the slight difference between the average weight of cartons of count 125 fruit (18.4 kg) and the average weight of cartons of count 80 fruit (18.8 kg). Steady-state atmospheres for the two count sizes were pooled in Table 5.1.

### 5.1.1 EFFECT OF SEALING METHOD

The current industry practice for packing MA-cartons involves folding the carton-liners closed as described in section 4.1.3. During the MA-trials described in this work, modified atmospheres produced inside folded carton-liners were much more variable than those produced inside heat-sealed liners (Figure 5.2). This was especially pronounced for 40  $\mu\text{m}$  liners, which, being less flexible than 25  $\mu\text{m}$  liners, appeared to form less effective and less consistent folds. In general, folded 25  $\mu\text{m}$  liners produced similar atmospheres to heat-sealed 25  $\mu\text{m}$  liners (as illustrated in Figure 5.7 for 'Braeburn' cartons stored under transient storage temperatures).

Although the results presented here indicate that folding carton liners closed can produce a high carton-to-carton variability, other workers (Frampton & Ahlborn, 1994a; Frampton *et al.*, 1994a; Geeson *et al.*, 1994) have reported reasonably uniform MA

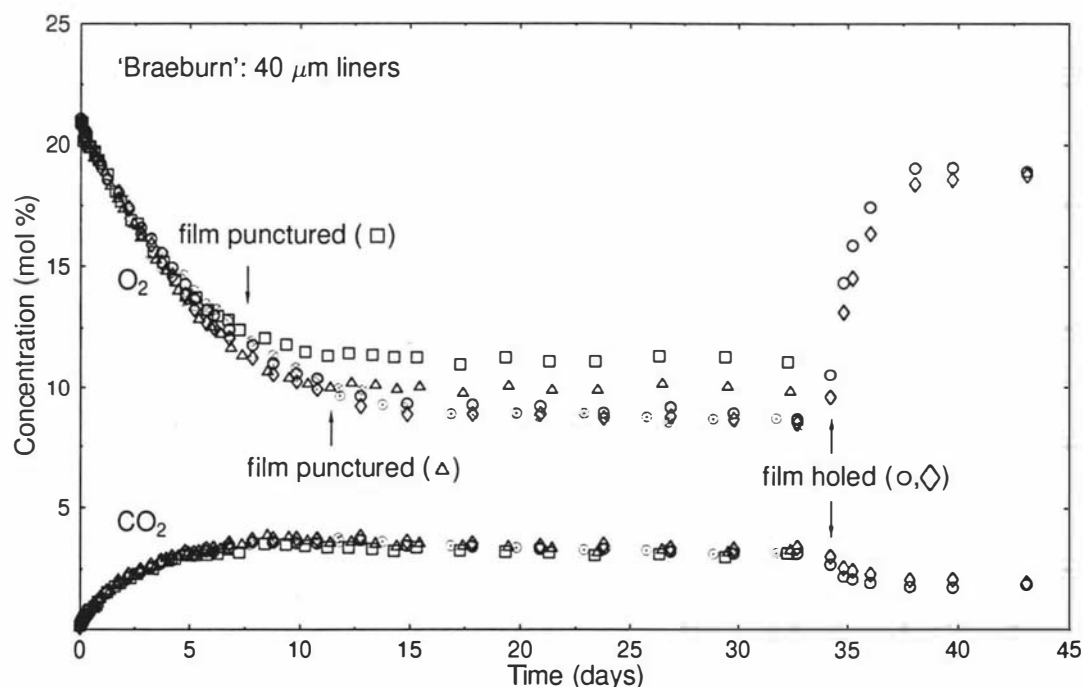


**Figure 5.2** Effect of sealing method on modified atmospheres produced inside cartons with heat-sealed or folded 40  $\mu\text{m}$  carton liners (trial BB93-A).

development inside 30-40  $\mu\text{m}$  liners folded in a similar manner. However, results reported by these workers nevertheless suggest that folding may be less reliable than other methods of sealing. In a trial with 40 cartons of 'Royal Gala' packed in folded 40  $\mu\text{m}$  liners (of the same MA film as that used in the current work), Frampton *et al.* (1994a) found that 2 cartons (a proportion of 5%) failed to establish a modified atmosphere. In trials with 18 kg cartons of 'Bramley's Seedling' apples packed in 30  $\mu\text{m}$  low-density-polyethylene, Geeson *et al.* (1994) found that  $\text{O}_2$  concentrations inside folded liners were 3-4 mol % higher than  $\text{O}_2$  concentrations inside liners sealed by tying the liner openings tightly with string.

### 5.1.2 EFFECT OF MECHANICAL DAMAGE TO THE PACKAGING FILM

Mechanical damage to the packaging film is a possibility throughout the storage, transport, and distribution chain. Figure 5.3 illustrates the effects of two types of film-damage on package atmospheres. On days 7 and 12, the liners of two cartons were accidentally punctured by a syringe needle during sampling of the package atmosphere. Package  $\text{O}_2$  concentrations increased noticeably as a result of these punctures, although the effect on  $\text{CO}_2$  concentrations was barely detectable. At  $0^\circ\text{C}$ , the permeability of the MA film to  $\text{CO}_2$  was about 6 times higher than its permeability to  $\text{O}_2$  (section 8.2.2.1). In contrast, the diffusivity of  $\text{CO}_2$  in air is slightly lower than the diffusivity of  $\text{O}_2$  in air (Treybal, 1980; Rohsenow *et al.*, 1985). Thus, a puncture or hole in the MA film has a larger effect on the overall permeability of the package to  $\text{O}_2$  than on the permeability of the package to  $\text{CO}_2$ . This same effect can also be seen in Figure 5.2 for cartons with folded liners.



**Figure 5.3** Effects of punctures and holes in heat-sealed carton-liners on the atmospheres inside cartons of 'Braeburn' (trial BB93-A).

The holes made by the syringe needle were hardly discernable by eye. When examined under a light microscope the holes appeared oblong in shape with approximate dimensions of 0.03 mm  $\times$  0.44 mm ( $\Delta$  in Figure 5.3) and 0.06 mm  $\times$  1.29 mm ( $\square$  in Figure 5.3).

On day 34, a cork borer was used to make two 8 mm diameter holes in each of two previously undamaged carton-liners. The holes were made at the tops of the cartons, well removed from the gas sampling ports. These large holes resulted in the rapid loss of virtually all atmosphere modification for O<sub>2</sub>, as well as a significant drop in CO<sub>2</sub> concentrations.

Any film-damage occurring during the transport and handling of cartons would most likely take the form of macroscopic tears or punctures rather than microscopic pin-holes. The results presented above suggest that such damage could be expected to result in almost total loss of MA. The risk of film-damage during transport and handling is therefore an important consideration when assessing the suitability of film carton-liners for MA storage during transport and distribution.

## 5.2 TRANSIENT PACKAGE ATMOSPHERES

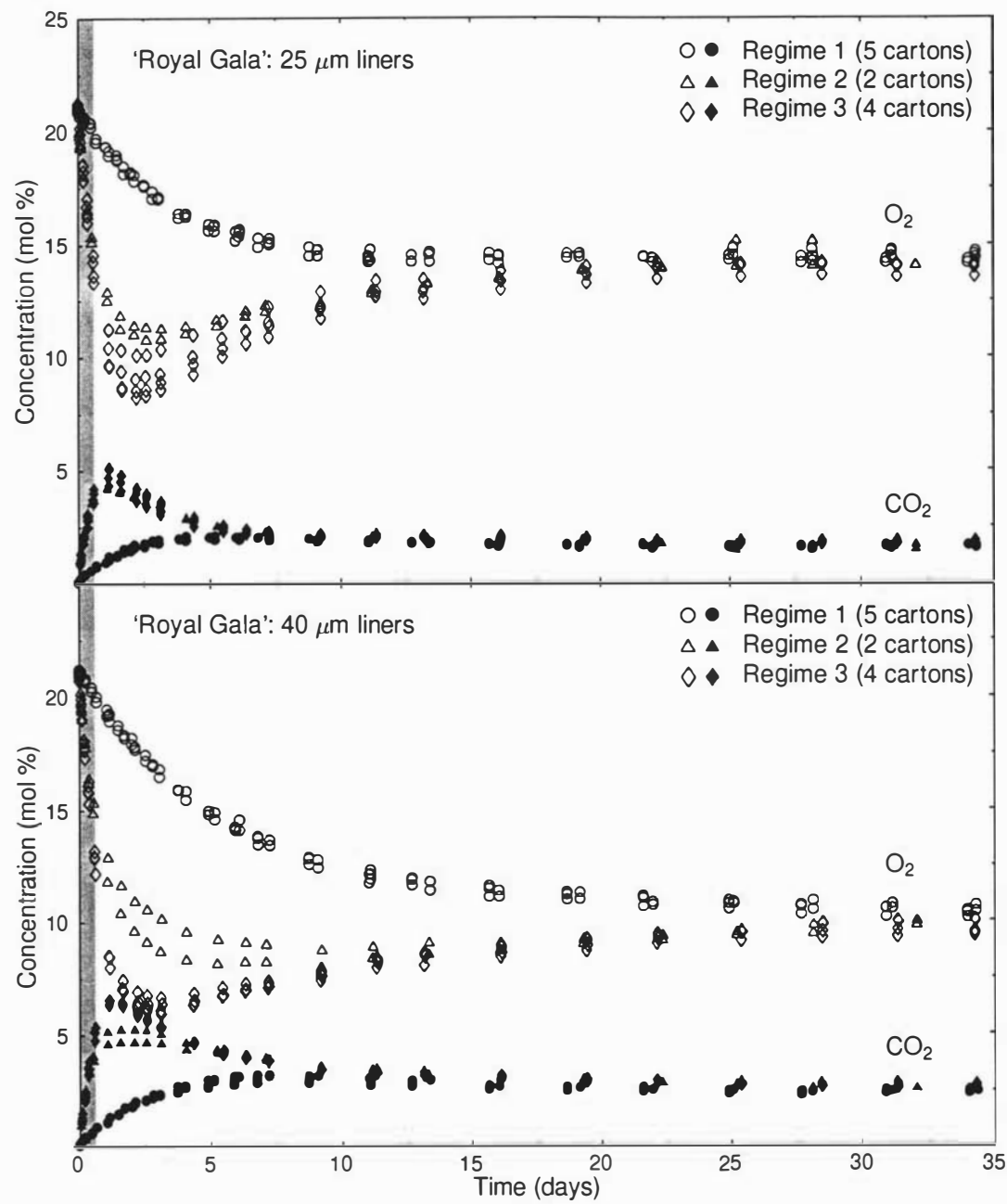
### 5.2.1 EFFECT OF FRUIT TEMPERATURE AT PACKING

Figure 5.4 illustrates the effect of fruit temperature at packing on rates of modified atmosphere development within cartons. Cartons of initially warm fruit showed much faster rates of atmosphere development than cartons of cold fruit, although final steady-state atmospheres, as expected, were the same. Clearly, for a fast pull-down of package O<sub>2</sub> concentrations, packing at elevated temperatures is desirable. Packing at 20°C did not lead to unduly low O<sub>2</sub> or high CO<sub>2</sub> concentrations developing within packages, even with a delay of up to 12 h before cool-storage (Regime 3). However, the rates of atmosphere development achieved under Regimes 2 and 3 indicate that packing warm fruit could incur a significant risk of anaerobic atmospheres developing if the delay before cool-storage became extended beyond 1 or 2 days.

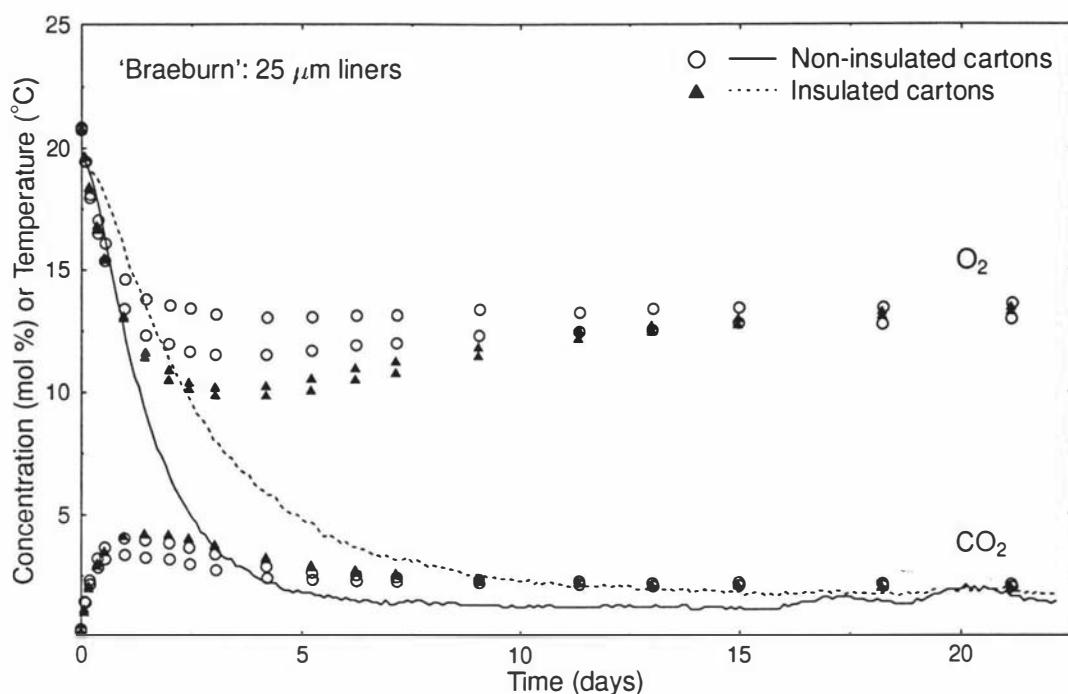
Although the packing of warm fruit resulted in faster rates of atmosphere development than the packing of pre-cooled fruit, cooling rates for packaged fruit are likely to be slower than cooling rates for unpackaged fruit, especially with the MA liners effectively blocking any ventilation through the cartons (section 8.3.1). The beneficial effects of rapid cooling on the maintenance of fruit quality are likely to out-weigh any benefits of rapid modified atmosphere development (Kader, 1992*a,b*).

### 5.2.2 EFFECT OF FRUIT COOLING-RATE

Insulating cartons on 5 sides to simulate cooling at the centre of a pallet stack (trial BB94-A) increased carton half-cooling times from about 23 hours to about 44 hours (section 8.3.1). However, this difference in cooling rates had only a small effect on rates of atmosphere modification, with a slightly more exaggerated depletion of O<sub>2</sub> and



**Figure 5.4** Rates of modified atmosphere development in cartons of 'Royal Gala' packed at 0°C (Regime 1) or 20°C (Regimes 2 and 3). The shaded region indicates the delay at 20°C under Regime 3.



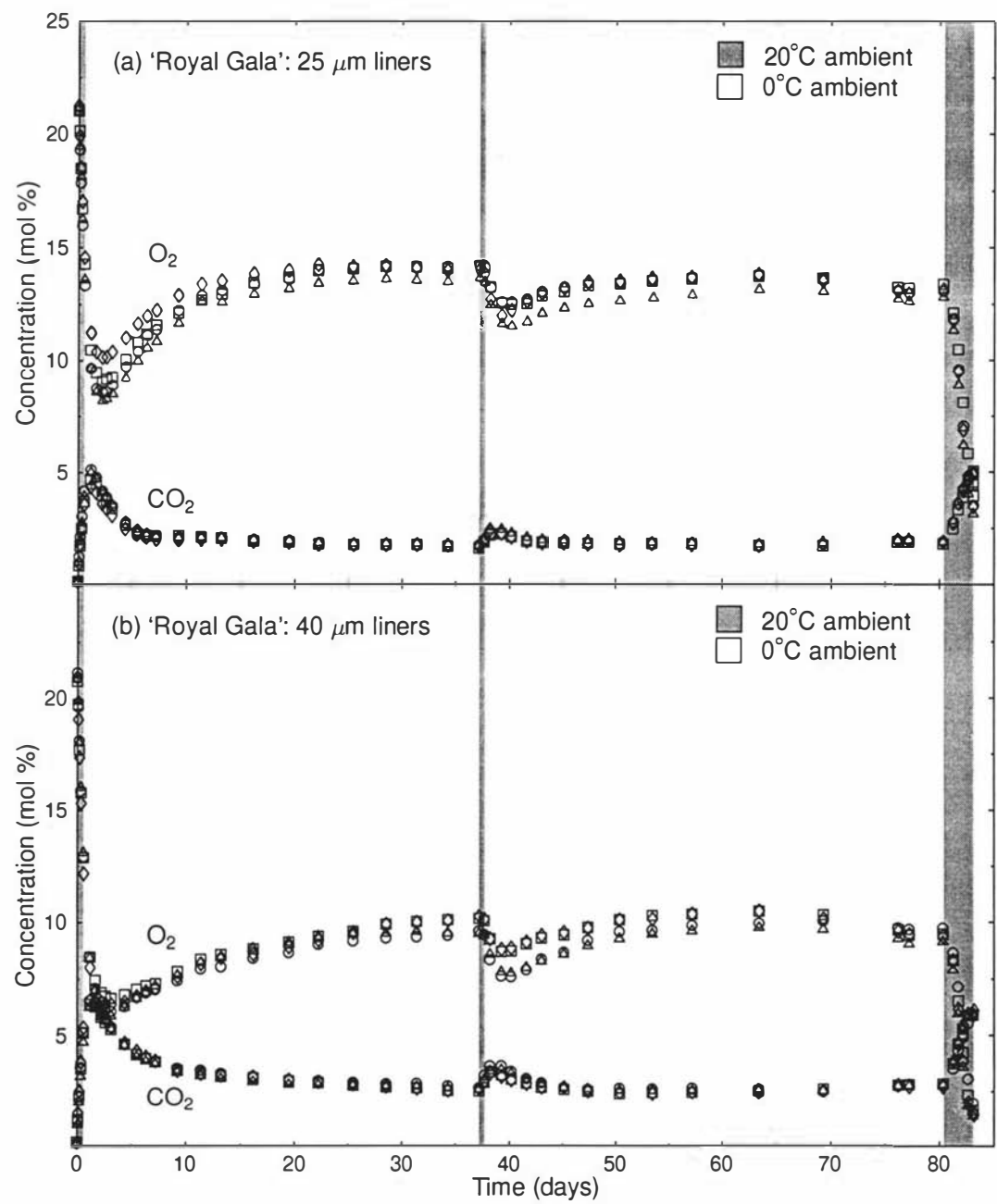
**Figure 5.5** Effect of fruit cooling-rate on modified atmosphere development inside cartons of 'Braeburn' (trial BB94-A). Symbols indicate O<sub>2</sub> and CO<sub>2</sub> concentrations; lines indicate fruit temperature.

a slightly higher peak of CO<sub>2</sub> in the insulated cartons (Figure 5.5). The results in Figure 5.5 indicate that cartons at the centre of a pallet stack, which generally have slower rates of cooling than more exposed cartons, nevertheless have a low risk of developing anaerobic atmospheres during cooling.

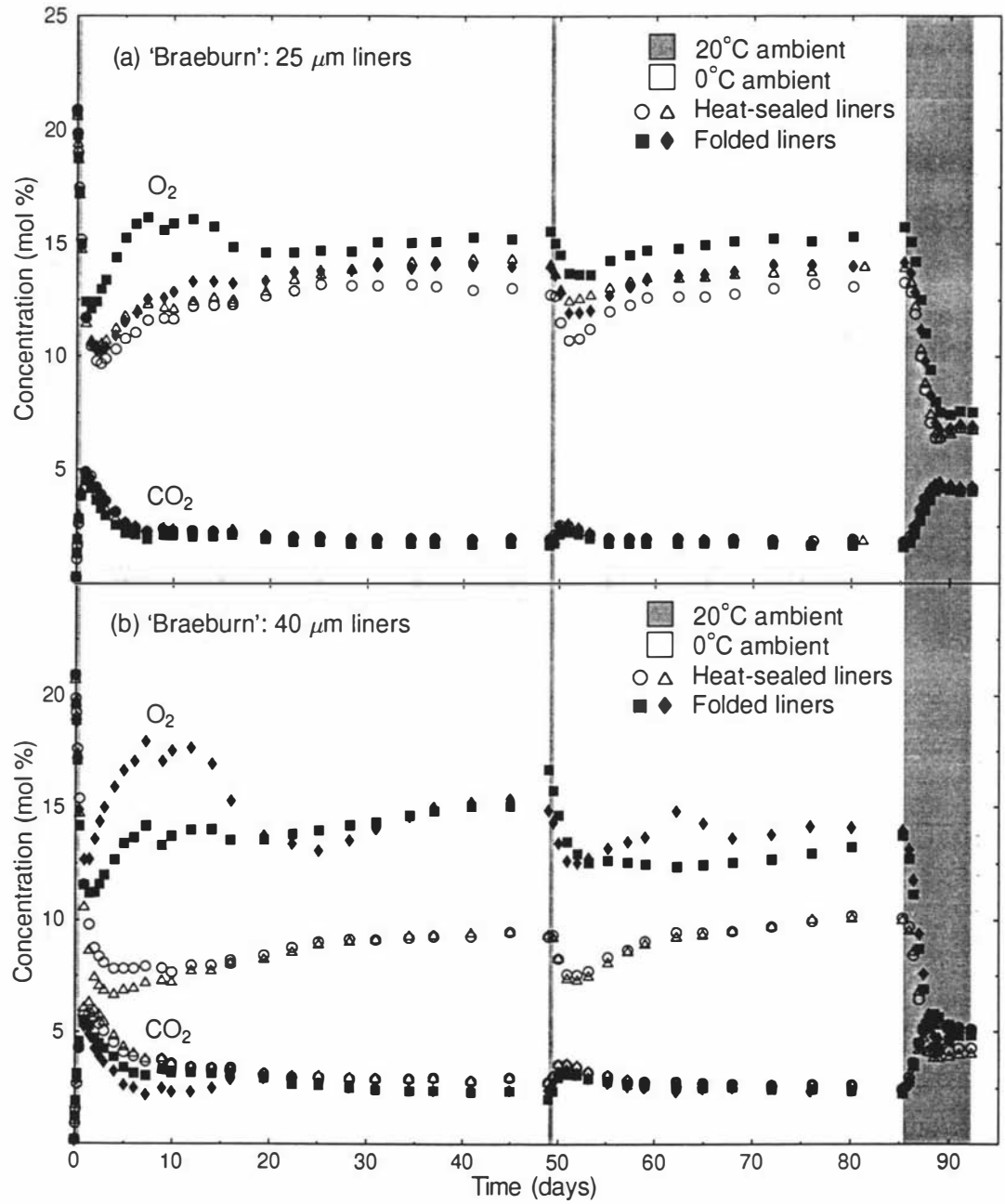
### 5.2.3 EFFECT OF TRANSIENT STORAGE-TEMPERATURE

Figures 5.6 to 5.8 show the transient package atmospheres formed within cartons of 'Royal Gala', 'Braeburn', and 'Granny Smith' apples stored under Regime 3. After an initial rapid pull-down of O<sub>2</sub> concentrations following packing at 20°C, a considerable period of time (20-35 days) was needed for package atmospheres to reach steady-state. The time taken to reach steady-state was longer in 40  $\mu\text{m}$  liners than in 25  $\mu\text{m}$  liners.

The subsequent twelve-hour period at 20°C that simulated loading onto a ship after cool-storage in New Zealand caused a noticeable, but not extreme, disturbance to package atmospheres for both liner thicknesses. Five to ten days were needed for atmospheres to re-equilibrate once cartons had been returned to cool-storage. In Figure 5.6, the slight drop in O<sub>2</sub> concentrations observed between days 70 and 80 was due to an increase in store temperature resulting from a malfunction of the refrigeration system. Twelve to twenty-four hours had elapsed before the fault was detected, and the store temperature had gradually increased to 7°C during this time. While not intentional, this episode indicates that a refrigeration system malfunction during cool-storage should present no great risk to the fruit as long as the problem is diagnosed and rectified promptly.

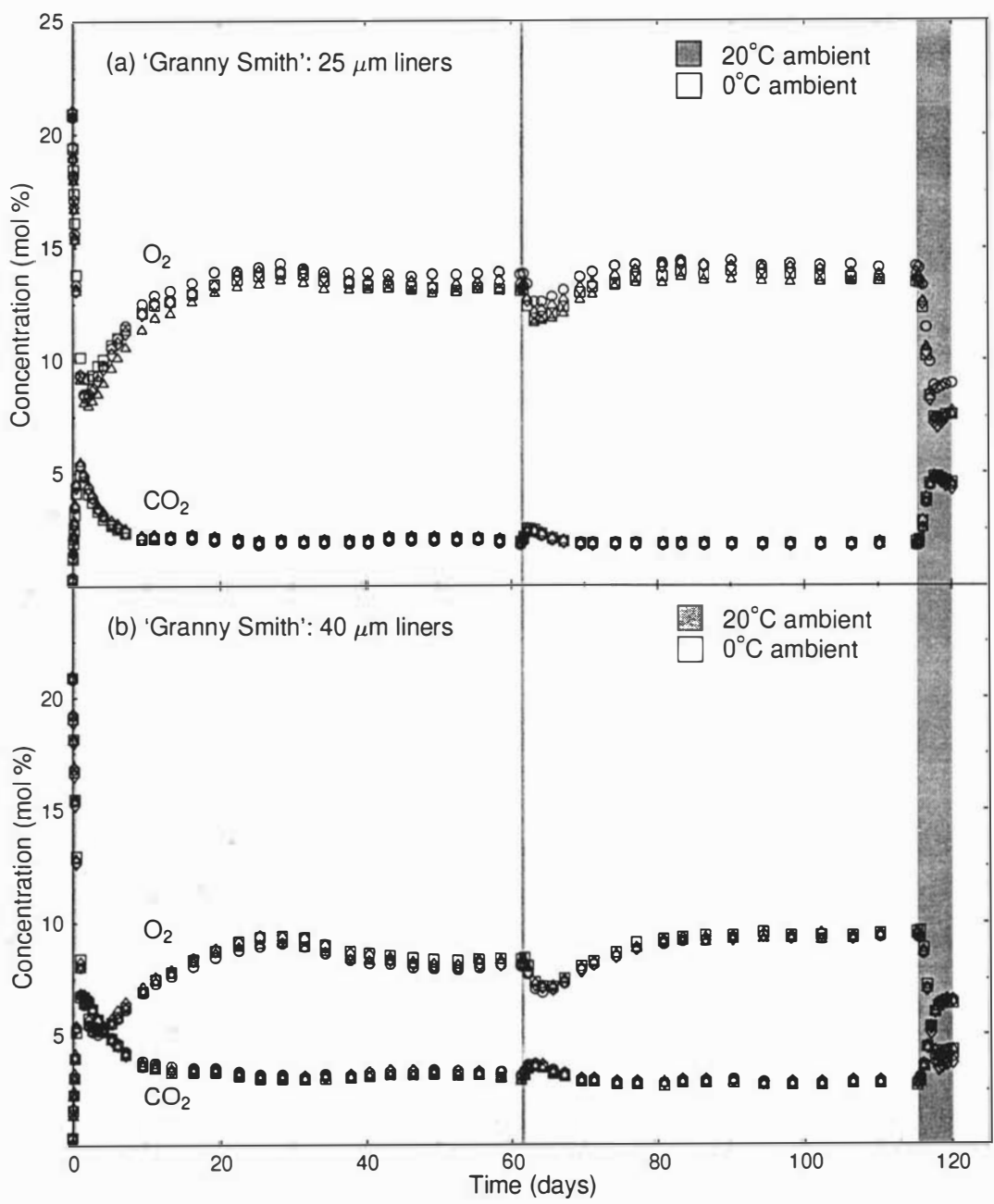


**Figure 5.6** Effect of varying ambient temperature on  $O_2$  and  $CO_2$  concentrations inside cartons of 'Royal Gala' (trial RG94-C). Shaded regions indicate periods at 20°C.



**Figure 5.7**

Effect of varying ambient temperature on  $O_2$  and  $CO_2$  concentrations inside cartons of 'Braeburn' (trial BB94-B). Shaded regions indicate periods at 20°C.



**Figure 5.8** Effect of varying ambient temperature on  $O_2$  and  $CO_2$  concentrations inside cartons of 'Granny Smith' (trial GS94-A). Shaded regions indicate periods at 20°C.

When cartons were removed from cool-storage and left at 20°C for 3-6 days with their liners intact, O<sub>2</sub> concentrations inside the cartons fell rapidly, with corresponding increases in CO<sub>2</sub> concentrations. In cartons with 40 µm liners, O<sub>2</sub> concentrations fell to below 5 mol %, while CO<sub>2</sub> concentrations rose to higher than 5 mol %. Such package O<sub>2</sub> and CO<sub>2</sub> concentrations, when combined with high fruit temperatures and elevated respiration rates, could well produce anaerobic atmospheres or harmful CO<sub>2</sub> concentrations within the fruit internal atmosphere. Thus, allowing cartons under modified atmospheres to remain at significantly elevated temperatures for an extended period of time greatly increases the risk of physiological damage to the fruit. Preferably, cartons should be kept refrigerated at all times, but if long delays at high temperatures are unavoidable then the liners may need to be opened to allow sufficient O<sub>2</sub> into the bag and to prevent the build-up of CO<sub>2</sub>.

Another danger of leaving MAP cartons at elevated temperatures is the increased incidence of fungal growth and rots produced by the combination of high temperature and high package humidity. Whereas no problems with fungal growth and rots were observed in MA packages stored at 0°C (except for some fungal growth on the stalks of very old fruit), 2-3% of fruit in packages left at 20°C for 3-6 days were affected by rots.

Closing carton liners by folding did not appear to reduce the risk of harmful atmospheres developing at high storage temperatures (Figure 5.7). Oxygen concentrations inside folded liners dropped as sharply as those inside sealed liners, to concentrations almost as low as those inside sealed liners.

### 5.3 SUMMARY

Excellent reproducibility was obtained between atmospheres formed inside cartons with undamaged, heat-sealed liners. However, carton liners closed by folding appear to form less modified and less consistent package atmospheres, especially for thicker films. Macroscopic holes or tears in the packaging film are likely to result in almost total loss of MA from a carton; the risk of such damage occurring during transport and handling should therefore be carefully assessed when considering the feasibility of using film carton-liners to provide MA storage during transport and distribution.

Much faster rates of atmosphere modification were achieved by packing warm rather than pre-cooled fruit, with no apparent risk of harmful atmospheres developing during the time taken to cool the cartons after packing. The variations in fruit cooling rate that might be expected throughout a pallet stack did not have a large effect on rates of atmosphere development. Short-term exposures (less than 24 h) of film-lined cartons of apples to ambient temperatures around 20°C do not appear to incur a great risk of anaerobic conditions developing within the packages. However, longer-term exposures could lead to the development of anaerobic conditions within 3 to 4 days. Folding, rather than heat-sealing, of carton liners does not appear to reduce the risk of harmful atmospheres developing at high temperatures.

The results presented in this chapter have important implications for the handling of MA cartons throughout packing, storage, and distribution. However, many questions remain unanswered. For example, will combinations of temperature and time different to those examined in these trials lead to the development of harmful atmospheres? What happens if package weight and dimensions are changed? Will a film suitable for one package size also be suitable for a new package size or fruit weight? What film type or thickness will produce the optimum atmosphere for a given apple cultivar? Is a given film type suitable for MAP applications?

The design of MAP systems is made easier with the availability of a mathematical model that can predict how package atmospheres will change under different storage conditions. Such a model is developed in the following chapters.

## Chapter 6

### MODEL FORMULATION

This chapter presents the mathematical formulation of a comprehensive modified atmosphere packaging model applicable to the simulation of modified atmosphere conditions inside film-lined cartons of apples during storage, transport, and distribution.

#### 6.1 MODEL SCOPE

The physical transport processes that take place within a modified atmosphere packaging system have been described in section 2.4.1. These transport processes are driven by the physiology of the produce within the package and by changes in the physical environment around the package.

As is often the case when modelling complex systems, some of the processes that take place within a modified atmosphere packaging system are too poorly understood to enable anything other than a highly simplified modelling approach. Even for processes that are better understood, a simplified model may be preferable to a more complex, although more fundamentally correct, model if the simplified model is accurate enough to meet the purpose for which the model is required. A model based on a highly complex, although accurate, mathematical formulation is of little practical use if the required input data are unavailable, prohibitively expensive or time consuming to collect, or if the benefits of any increase in prediction accuracy are lost because of input data uncertainties. The choice of an appropriate level of model complexity must be based on the purpose for which the model is required, the current knowledge of the processes to be modelled, and the availability and accuracy of the required input data (Cleland & Cleland, 1989).

The overall aim in formulating the MAP model was to apply the simplest possible models that would adequately describe the observed behaviour of the MAP system. Four areas of primary importance were identified:

- (a) fruit physiology;
- (b) gas transport;
- (c) moisture transport;
- (d) heat transfer.

Table 6.1 summarizes the processes considered in the model formulation. Factors influencing the level of detail chosen for the MAP model are discussed in the following sections.

**Table 6.1** Processes considered in the MAP model formulation.

|                                                                                                                                                                                     |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <i>Fruit Physiology:</i>                                                                                                                                                            |
| Fruit respiratory O <sub>2</sub> consumption and CO <sub>2</sub> production as a function of fruit internal O <sub>2</sub> and CO <sub>2</sub> concentrations and fruit temperature |
| Fruit cumulative O <sub>2</sub> consumption                                                                                                                                         |
| Carbon loss through respiration                                                                                                                                                     |
| <i>Gas Transport:</i>                                                                                                                                                               |
| Exchange of O <sub>2</sub> and CO <sub>2</sub> between the fruit internal atmosphere and the package atmosphere                                                                     |
| Permeation of O <sub>2</sub> , CO <sub>2</sub> , and N <sub>2</sub> through the packaging film                                                                                      |
| Diffusion and flow of O <sub>2</sub> , CO <sub>2</sub> , and N <sub>2</sub> through holes in the packaging film                                                                     |
| <i>Moisture Transport:</i>                                                                                                                                                          |
| Evaporation of moisture from the fruit surface                                                                                                                                      |
| Sorption of moisture by moulded-pulp fruit trays                                                                                                                                    |
| Condensation of moisture on the surface of the fruit and on the internal surface of the packaging film                                                                              |
| Permeation of water vapour through the packaging film                                                                                                                               |
| Diffusion and flow of water vapour through holes in the packaging film                                                                                                              |
| <i>Heat Transfer:</i>                                                                                                                                                               |
| Respiratory heat generation                                                                                                                                                         |
| Evaporative heat loss from the fruit                                                                                                                                                |
| Convection heat transfer at the fruit and packaging surfaces                                                                                                                        |
| Conduction heat transfer through the packaging materials                                                                                                                            |

**6.1.1 FRUIT PHYSIOLOGY**

Oxygen and carbon dioxide are the two gases of primary physiological interest in an MAP system. Their consideration in an MAP model involves the modelling of fruit respiratory O<sub>2</sub> consumption and CO<sub>2</sub> production. At the cellular level, fruit respiration rate is a function of cytoplasmic and mitochondrial dissolved gas concentrations (as well as other factors such as temperature). However, cell gas concentrations are difficult to measure, and fruit respiration data based on cell gas concentrations are scarce, if not non-existent. Modelling of fruit respiration at the cellular level was therefore considered impractical at this time.

The fruit internal atmosphere forms an interface between the cellular environment and the package atmosphere. Respiration data based on fruit internal O<sub>2</sub> concentrations are well documented (e.g. Dadzie, 1992; Banks *et al.*, 1993; Dadzie *et al.*, 1996). Thus, fruit respiration was modelled as a function of the composition of the fruit internal atmosphere and as a function of temperature.

Fruit respiration can proceed by either aerobic or anaerobic pathways (section 2.1.1). However, anaerobic respiration generally becomes significant only at very low fruit internal O<sub>2</sub> concentrations. The development of O<sub>2</sub> concentrations low enough to induce anaerobic respiration in an MA package is undesirable because of the potential for fruit

quality degradation resulting from the significant build up of acetaldehyde and ethanol. Only aerobic respiration was considered in the MAP model.

If gross quality changes due to mechanical damage, microbial and pest infestations, and physiological disorders are disregarded, then fruit quality degradation is related to the natural processes of fruit ripening and senescence. The rates of these processes are related to the overall metabolic rate of the fruit. As the rate of fruit respiration is generally seen as a good indicator of the overall rate of fruit metabolism, a measure such as cumulative respiratory  $O_2$  consumption may serve as a useful indicator of fruit quality degradation during storage. The concept of cumulative  $O_2$  consumption is similar to that of full-history temperature-time indicators for monitoring the quality of chilled or frozen foods (e.g. Wells & Singh, 1992). However, a measure such as cumulative  $O_2$  consumption has the added dimension of accounting for the effects of atmosphere composition as well as the effects of temperature. In an MAP model, cumulative  $O_2$  consumption can be computed at no extra cost in terms of input data requirements.

Fruit cumulative  $O_2$  consumption was modelled in the current work. Although this measure has not as yet been directly related to any specific fruit quality attribute, it may nevertheless provide a useful basis for comparing different storage regimes.

The fruit ripening hormone ethylene is another gas of physiological importance in an MAP system. The presence of ethylene can affect the respiratory behaviour and ripening processes of both climacteric and non-climacteric fruit (section 2.1.1). However, the mechanisms regulating fruit production of and response to ethylene are extremely complex, and no comprehensive mathematical models capable of predicting patterns of ethylene production or responses of fruit respiration and ripening processes to ethylene have been developed. Furthermore, reduced ethylene production and sensitivity have been observed in fruit stored under low  $O_2$ /high  $CO_2$  conditions (section 2.1.2.1). Modelling of ethylene production and action was therefore not attempted in this work.

### 6.1.2 GAS TRANSPORT

Gas exchange in apples is thought to occur predominantly by diffusion through the lenticels or the pedicel and calyx openings (section 2.4.1.1). However, some gas exchange may also occur by permeation through the cuticular layer of the fruit skin. In addition, if the net molar flow due to diffusion and permeation is not zero, a pressure gradient between the fruit internal and external atmospheres could form, causing gases to flow through openings in the fruit skin. In the MAP model, the net effect of all of these mechanisms was accounted for by overall skin permeance values.

Another possible mechanism for fruit gas exchange not accounted for by skin permeance values is the flow of gases due to pressure gradients caused by changes in fruit temperature or changes in external pressure. As this mechanism of gas exchange would only occur during transient periods, any increase in prediction accuracy that might be obtained by modelling gas flow through openings in the fruit skin was not expected to

justify the resulting increase in model complexity. Thus, the flow of gases through openings in the fruit skin was not modelled in this work.

Common MA packaging films have CO<sub>2</sub> permeabilities 3 to 6 times higher than their O<sub>2</sub> permeabilities (Yam & Lee, 1995). In an MAP system, this phenomenon generally results in a higher-than-atmospheric package nitrogen concentration and consequent diffusion of nitrogen out of the package. Three package responses are observed, corresponding to three package-types:

- (1) In a sealed, rigid package, N<sub>2</sub> diffusion out of the package causes the pressure inside the package to decrease.
- (2) In a sealed, flexible-film package, shrinkage of the package volume is observed. The extent of this shrinkage is limited by the spatial arrangement of fruit inside the package. Once the package volume has decreased to its minimum value, a flexible-film package will behave in the same way as a rigid package as long as the seal of the film remains intact.
- (3) In a perforated-film package, any net permeation of gases out of the package is balanced by a bulk flow of gases into the package through perforations. Package pressure and volume remain relatively constant.

Although package N<sub>2</sub> concentration was of no physiological interest in itself, N<sub>2</sub> permeation through the packaging film was modelled in order to predict package volume and pressure changes and the effects of these changes on package O<sub>2</sub> and CO<sub>2</sub> concentrations.

The significance of gas concentration gradients within both the fruit internal atmosphere and the package atmosphere was an important consideration in formulating the MAP model. The likely significance of such gas concentration gradients was judged by a quantitative comparison of external and internal resistances to gas transfer for each case.

Ratios of internal to external transfer resistances are often represented by a dimensionless group known as the Biot number. For mass transfer

$$Bi' = \frac{kL}{D} \quad (6.1)$$

where

- $Bi'$  = Biot number for mass transfer  
 $D$  = mass diffusivity (m<sup>2</sup>·s<sup>-1</sup>)  
 $k$  = surface mass transfer coefficient (m·s<sup>-1</sup>)  
 $L$  = characteristic dimension (m).

If the internal resistance to mass transfer is very much lower than the external resistance to mass transfer, then the latter dominates the transfer process and internal

**Table 6.2** Estimated  $Bi'$  values for gas diffusion in the fruit internal and package atmospheres.

|                              | $T$<br>(K) | $D$<br>( $\text{m}^2\cdot\text{s}^{-1}$ ) | $k$<br>( $\text{m}\cdot\text{s}^{-1}$ ) | $L$<br>(m)         | $Bi'$                |
|------------------------------|------------|-------------------------------------------|-----------------------------------------|--------------------|----------------------|
| Fruit $\text{O}_2$           | 293.0      | $1.2 \times 10^{-7}$ <sup>a</sup>         | $3.6 \times 10^{-7}$ <sup>c</sup>       | 0.013 <sup>g</sup> | $4.0 \times 10^{-2}$ |
| Fruit $\text{CO}_2$          | 293.0      | $1.2 \times 10^{-7}$ <sup>b</sup>         | $4.5 \times 10^{-7}$ <sup>c</sup>       | 0.013 <sup>g</sup> | $5.0 \times 10^{-2}$ |
| Package $\text{O}_2$         | 273.0      | $1.81 \times 10^{-5}$ <sup>c</sup>        | $4.8 \times 10^{-8}$ <sup>f</sup>       | 0.058 <sup>h</sup> | $1.5 \times 10^{-4}$ |
| Package $\text{CO}_2$        | 276.2      | $1.42 \times 10^{-5}$ <sup>d</sup>        | $3.2 \times 10^{-7}$ <sup>f</sup>       | 0.058 <sup>h</sup> | $1.3 \times 10^{-3}$ |
| Package $\text{N}_2$         | 273.0      | $1.85 \times 10^{-5}$ <sup>d</sup>        | $1.3 \times 10^{-8}$ <sup>f</sup>       | 0.058 <sup>h</sup> | $4.1 \times 10^{-5}$ |
| Package $\text{H}_2\text{O}$ | 289.9      | $2.44 \times 10^{-5}$ <sup>d</sup>        | $5.0 \times 10^{-6}$ <sup>f</sup>       | 0.058 <sup>h</sup> | $1.2 \times 10^{-2}$ |

<sup>a</sup> From Rajapakse *et al.* (1990) (for 'Braeburn' apples at 20°C).

<sup>b</sup> Assumed to be the same as for  $\text{O}_2$ .

<sup>c</sup> From Treybal (1980).

<sup>d</sup> From Rohsenow *et al.* (1985).

<sup>e</sup> Skin permeabilities measured for 1994 'Braeburn' at 20°C (section 8.1.2).

<sup>f</sup> Calculated from film permeability data given in section 8.2.1 (25  $\mu\text{m}$  film).

<sup>g</sup> Calculated for an apple radius of 0.04 m (corresponding approximately to count-80 fruit).

<sup>h</sup> Calculated for a carton with internal dimensions of 0.5 m  $\times$  0.3 m  $\times$  0.3 m.

concentrations can be assumed uniform. As a rule of thumb, the error associated with this assumption is usually considered acceptably small when  $Bi \leq 0.1$  (Rohsenow *et al.*, 1985, p. 4/50; Holman, 1986, p. 134; Kreith & Bohn, 1986, p. 95).

For gas diffusion in apples,  $k$  was defined as the fruit skin permeance to  $\text{O}_2$  or  $\text{CO}_2$  and  $D$  as the effective diffusivity of  $\text{O}_2$  or  $\text{CO}_2$  in the fruit flesh. For gas diffusion through the package atmosphere,  $k$  was defined as the packaging-film permeance (permeability divided by film thickness) to  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , or water vapour and  $D$  as the diffusivity of  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , or water vapour in air. Fruit and package characteristic dimensions were obtained by dividing the fruit and package volumes by their respective surface areas (Kreith & Bohn, 1986, p. 95; Holman, 1986, pp. 134-135). Table 6.2 lists the  $Bi'$  values estimated for the fruit and package atmospheres. All the  $Bi'$  values were less than 0.1, indicating that external resistances dominate the diffusion of gases in both the fruit internal atmosphere and the package atmosphere.

Gas concentrations throughout each of the fruit internal atmosphere and the package atmosphere were therefore assumed uniform in the MAP model.

### 6.1.3 MOISTURE TRANSPORT

Fruit moisture loss is important from both a fruit quality and an economic perspective. Prediction of fruit moisture loss in an MAP system requires modelling of package water vapour concentrations. In many ways, this parallels the modelling of package gas transport, but some additional pathways for water vapour transport must also be considered.

Water vapour will condense onto any surface having a temperature below the dew-point of the air in contact with it. In an MAP system, condensation of water vapour onto the

inside surface of the packaging film may occur when the package is moved from a warm temperature to a cooler temperature, and condensation of water vapour onto the fruit may occur when the package is moved from a cool temperature to a warmer temperature. Both of these phenomena were observed during the MA trials where cartons were stored under variable temperature regimes.

Another possible pathway for moisture transport in packaging systems is the sorption of moisture by paper-based packaging materials. New Zealand apple cartons are typically packed with four to six layers of fruit, each layer separated from the layers above and beneath it by a moulded-pulp fruit tray. These trays represent a moisture sink within the packaging system and, with five to eight trays per carton, could significantly affect the dynamics of moisture accumulation in the package atmosphere.

Both condensation and moisture sorption were considered in the MAP model. As in the modelling of package  $O_2$ ,  $CO_2$ , and  $N_2$  concentrations, water vapour concentration was assumed to be uniform throughout the package atmosphere (section 6.1.2, Table 6.2).

#### 6.1.4 HEAT TRANSFER

In New Zealand, most of the apple harvest is packed at ambient temperatures before being transported to land-based cool-storage facilities. From these stores, cartons of apples are transported either to local markets or to ports to be loaded on-board ship for export. In the case of exported apples, a further period of cool-storage takes place on-board ship, followed by unloading, cool-storage in the destination country, and distribution into the market-place.

The experimental results presented in section 5.2.3 show that the changing temperatures that cartons can be exposed to during packing, storage, and distribution can cause marked fluctuations in package  $O_2$  and  $CO_2$  concentrations. In order to model the effect of variable ambient temperature conditions on package atmospheres, modelling of package heat transfer was included in the MAP model formulation.

The simplest method for dealing with package responses to variable-temperature storage regimes would be to assume a step change in fruit temperature for any change in storage temperature. Such an approach might be feasible if the rate of heat transfer within a package was very much faster than the rate of gas transport.

A quantitative analysis of the relative rates of gas transport and heat transfer in cartons was performed by estimating a 'half-life' for each process. Half-cooling times measured for film-lined cartons ranged from 12 to 23 h (section 8.3.1). For gas permeation into or out of an empty, film-lined carton

$$Y_i' = \left( \frac{C_{i,p}^t - C_{i,e}}{C_{i,p}^0 - C_{i,e}} \right) = \exp(-kt) \quad (6.2)$$

where

$$k = \frac{P_i A_{film}}{x V_{carton}} \quad (6.3)$$

and where

- $A_{film}$  = film area ( $\text{m}^2$ )
- $C_{i,e}$  = ambient concentration of gas species  $i$  ( $\text{kg}\cdot\text{m}^{-3}$ )
- $C_{i,p}^t$  = package concentration of gas species  $i$  at time  $t$  ( $\text{kg}\cdot\text{m}^{-3}$ )
- $C_{i,p}^0$  = initial package concentration of gas species  $i$  ( $\text{kg}\cdot\text{m}^{-3}$ )
- $k$  = constant ( $\text{s}^{-1}$ )
- $P_i$  = film permeability to gas species  $i$  ( $\text{m}^2\cdot\text{s}^{-1}$ )
- $t$  = time (s)
- $V_{carton}$  = carton volume ( $\text{m}^3$ )
- $x$  = film thickness (m)
- $Y_i'$  = fractional unaccomplished concentration change for gas species  $i$ .

Eq. 6.2 assumes a constant package volume, a perfectly mixed package atmosphere, and that gas exchange between the package atmosphere and the external atmosphere occurs only by permeation through the packaging film. Half-life values for gas permeation into or out of a carton were calculated from

$$t_{0.5} = \frac{\ln 2}{k} \quad (6.4)$$

where

$$t_{0.5} = \text{half life (s).}$$

Table 6.3 lists the values of  $t_{0.5}$  calculated for  $\text{O}_2$  and  $\text{CO}_2$  permeation at 0 and  $20^\circ\text{C}$ . Comparison of these values with carton half-cooling times of 12 to 23 h suggests that gas transport and heat transfer inside an MA carton occur at roughly similar rates. Thus, a simple assumption of step changes in fruit temperature was considered unrealistic.

**Table 6.3** Values of  $t_{0.5}$  for  $\text{O}_2$  and  $\text{CO}_2$  permeation.<sup>a</sup>

| Gas           | Temperature<br>( $^\circ\text{C}$ ) | $P \times 10^{12}$<br>( $\text{m}^2\cdot\text{s}^{-1}$ ) | $t_{0.5}$<br>(h) |
|---------------|-------------------------------------|----------------------------------------------------------|------------------|
| $\text{O}_2$  | 0                                   | 1.22                                                     | 126.6            |
|               | 20                                  | 4.24                                                     | 36.5             |
| $\text{CO}_2$ | 0                                   | 6.59                                                     | 23.5             |
|               | 20                                  | 21.0                                                     | 7.4              |

<sup>a</sup> Calculated for an empty carton with internal dimensions  $0.5 \text{ m} \times 0.3 \text{ m} \times 0.3 \text{ m}$ , a film area of  $1.4 \text{ m}^2$ , and a film thickness of  $25 \text{ }\mu\text{m}$ .

The likely significance of temperature gradients within an MA carton was assessed in a manner analogous to that described in section 6.1.2 for gas and water vapour transport. Biot numbers for heat transfer within individual fruit and whole cartons were calculated from

$$Bi = \frac{hL}{\lambda} \tag{6.5}$$

where

- Bi* = Biot number for heat transfer
- h* = surface heat transfer coefficient (W·m<sup>-2</sup>·K<sup>-1</sup>)
- λ* = thermal conductivity (W·m<sup>-1</sup>·K<sup>-1</sup>).

Table 6.4 lists the estimated *Bi* values. The value of *Bi* for whole cartons was estimated by using an effective thermal conductivity to approximate heat transfer within a carton as pure heat conduction (Amos, 1995, pp. 82-84). The *Bi* values in Table 6.4 indicate that temperature gradients within the flesh of individual fruit are likely to be small but that the positional variation of temperature within cartons could be significant.

Amos (1995) has recently developed and tested a cooling model specifically for New Zealand apple cartons. This model was designed to predict the positional variation of temperature within an apple carton, and proved capable of reasonably accurate predictions for unventilated cartons. However, the model was complex, dividing the carton into at least 150 interacting zones. Adoption of such a model would have added considerable complexity to the MAP model formulation. Thus, a simpler alternative was sought.

The main aim in modelling heat transfer within an MA package was to predict the effect of fruit cooling or warming rates on changes in the overall rates of O<sub>2</sub> consumption and CO<sub>2</sub> production within the package. For this purpose, average fruit cooling or warming rates were modelled by predicting an average fruit temperature for the package. Although fundamentally less accurate than a model capable of predicting temperature gradients within the package, this approach was favoured in view of its computational simplicity and its greatly reduced data requirements.

**Table 6.4** Estimated *Bi* values for heat transfer.

|                  | $\lambda$<br>(W·m <sup>-1</sup> ·K <sup>-1</sup> ) | $h$<br>(W·m <sup>-2</sup> ·K <sup>-1</sup> ) | $L$<br>(m)         | <i>Bi</i> |
|------------------|----------------------------------------------------|----------------------------------------------|--------------------|-----------|
| Individual fruit | 0.42 <sup>a</sup>                                  | 2.9 <sup>b</sup>                             | 0.013 <sup>c</sup> | 0.09      |
| Whole cartons    | 0.25 <sup>a</sup>                                  | 5 <sup>b</sup>                               | 0.058 <sup>d</sup> | 1.2       |

<sup>a</sup> From Amos (1995), p. 83.  
<sup>b</sup> From section 8.3.2.  
<sup>c</sup> Calculated for an apple radius of 0.04 m (corresponding approximately to count-80 fruit).  
<sup>d</sup> Calculated for a carton with internal dimensions of 0.5 m × 0.3 m × 0.3 m.

Two simple heat-transfer models were included in the MAP model formulation. In order to facilitate the modelling of various moisture transport processes within the package, both models considered fruit and package-atmosphere temperatures separately. However, both models assumed a uniform fruit temperature and a uniform package-atmosphere temperature.

In the first heat-transfer model, heat transfer from the fruit to the external store environment was modelled sequentially: respiratory heat generation within the fruit; evaporation and convection from the fruit surface to the package atmosphere; convection from the package atmosphere to the inside surface of the packaging film; conduction through the packaging materials and trapped air layers; and convection from the outside surface of the package to the store environment. One potential weakness of this model was the dependence of predicted cooling and warming rates on the accuracy of estimated heat transfer coefficients, data that can be difficult to accurately measure or predict. Thus, a second heat transfer model was formulated in which fruit cooling and warming rates were predicted directly from experimental half-cooling times, a measure commonly used in industry.

## 6.2 MODEL EQUATIONS

### 6.2.1 FRUIT RESPIRATION

A number of workers have developed produce respiration models based on Michaelis-Menten enzyme kinetics (section 2.4.3.1). In some cases, these models have incorporated an inhibitory  $\text{CO}_2$  effect, assuming linear, uncompetitive  $\text{CO}_2$  inhibition. However, this assumption has not been justified on a physiological or biochemical basis, and the mechanism by which  $\text{CO}_2$  inhibits the aerobic respiratory pathway appears to be unclear. Despite this lack of justification, the linear inhibition model has proved useful for describing the respiration rates of a number of different fruit and vegetable species.

A general Michaelis-Menten equation with linear  $\text{CO}_2$  inhibition was adopted in this work:

$$v = \frac{v_{max} C_{\text{O}_2, f}}{k_m \left( 1 + \frac{C_{\text{CO}_2, f}}{k_{ic}} \right) + C_{\text{O}_2, f} \left( 1 + \frac{C_{\text{CO}_2, f}}{k_{iu}} \right)} \quad (6.6)$$

where

- $C_{\text{O}_2, f}$  =  $\text{O}_2$  concentration in the fruit internal atmosphere ( $\text{kg O}_2 \cdot \text{m}^{-3}$ )
- $C_{\text{CO}_2, f}$  =  $\text{CO}_2$  concentration in the fruit internal atmosphere ( $\text{kg CO}_2 \cdot \text{m}^{-3}$ )
- $k_{ic}$  = competitive inhibition constant ( $\text{kg CO}_2 \cdot \text{m}^{-3}$ )
- $k_{iu}$  = uncompetitive inhibition constant ( $\text{kg CO}_2 \cdot \text{m}^{-3}$ )

- $k_m$  = half saturation constant ( $\text{kg O}_2 \cdot \text{m}^{-3}$ )  
 $v$  = aerobic respiration rate ( $\text{kg O}_2 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ )  
 $v_{max}$  = maximum aerobic respiration rate at the fruit temperature ( $\text{kg O}_2 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ ).

Eq. 6.6 is the enzyme rate equation for linear, mixed inhibition (Cornish-Bowden & Wharton, 1988). On a purely mathematical basis, all other linear inhibition mechanisms can be viewed as special cases of this expression:  $k_{iu} \rightarrow \infty$  gives the rate equation for competitive inhibition,  $k_{ic} \rightarrow \infty$  gives the rate equation for uncompetitive inhibition, and  $k_{ic} = k_{iu}$  gives the rate equation for non-competitive inhibition. For Michaelis-Menten kinetics with no inhibition,  $k_{ic} \rightarrow \infty$  and  $k_{iu} \rightarrow \infty$ .

A  $Q_{10}$  relationship was used to describe the variation of maximum respiration rate with temperature:

$$v_{max} = v_{max,ref} Q_{10}^{\left(\frac{\theta_f - \theta_{ref}}{10}\right)} \quad (6.7)$$

where

- $Q_{10}$  = temperature coefficient for respiration  
 $v_{max,ref}$  = maximum aerobic respiration rate at the reference temperature ( $\text{kg O}_2 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ )  
 $\theta_f$  = fruit temperature ( $^{\circ}\text{C}$ )  
 $\theta_{ref}$  = reference temperature ( $^{\circ}\text{C}$ ).

The values of  $k_m$ ,  $k_{ic}$ , and  $k_{iu}$  in Eq. 6.6 were assumed to be independent of fruit temperature.

### 6.2.2 FRUIT CUMULATIVE OXYGEN CONSUMPTION

Fruit cumulative oxygen consumption was modelled on an initial fruit mass basis:

$$\frac{d(M_{f,initial} Q)}{dt} = v M_{f,initial} \quad (6.8)$$

which becomes

$$\frac{dQ}{dt} = v \quad (6.9)$$

where

- $M_{f,initial}$  = initial total fruit mass (kg)

- $t$  = time (s)  
 $Q$  = cumulative  $O_2$  consumption ( $kg\ O_2 \cdot kg^{-1}$ ).

### 6.2.3 FRUIT WEIGHT LOSS

Moisture loss through transpiration and carbon loss through respiration were assumed to be the only significant contributions to fruit weight loss.

An unsteady-state mass balance for fruit weight loss was written as

$$\left( \begin{array}{c} \text{Rate of} \\ \text{fruit weight} \\ \text{change} \end{array} \right) = - \left( \begin{array}{c} \text{Rate of moisture} \\ \text{loss from fruit through} \\ \text{transpiration} \end{array} \right) - \left( \begin{array}{c} \text{Rate of carbon} \\ \text{loss from fruit through} \\ \text{respiration} \end{array} \right) \quad (6.10)$$

This balance was converted into the following ordinary differential equation (ODE):

$$\frac{dM_f}{dt} = - k_{g,skin} A_{fruit} (p_{w,f} - p_{w,p}) - RQ_m v M_f \frac{Mr_C}{Mr_{CO_2}} \quad (6.11)$$

where

- $A_{fruit}$  = total fruit surface area ( $m^2$ )  
 $k_{g,skin}$  = fruit skin permeance to water vapour ( $s \cdot m^{-1}$ )  
 $M_f$  = total fruit mass (kg)  
 $Mr_C$  = molar mass of carbon ( $g \cdot mol^{-1}$ )  
 $Mr_{CO_2}$  = molar mass of  $CO_2$  ( $g \cdot mol^{-1}$ )  
 $p_{w,f}$  = partial pressure of water vapour beneath the fruit skin (Pa)  
 $p_{w,p}$  = partial pressure of water vapour in the package atmosphere (Pa)  
 $RQ_m$  = mass-based respiratory quotient for aerobic respiration ( $kg \cdot kg^{-1}$ ).

The partial pressure of water vapour beneath the fruit skin was calculated from

$$p_{w,f} = a_w p_{sat,f} \quad (6.12)$$

where

- $a_w$  = fruit water activity  
 $p_{sat,f}$  = saturated vapour pressure of water at the fruit surface temperature (Pa).

Fruit water activity was assumed to be constant throughout storage.

### 6.2.4 FRUIT OXYGEN CONCENTRATION

An unsteady-state mass balance for fruit internal  $O_2$  was written as

$$\left( \begin{array}{c} \text{Rate of } O_2 \\ \text{accumulation in the fruit} \\ \text{internal atmosphere} \end{array} \right) = \left( \begin{array}{c} \text{Rate of } O_2 \\ \text{transfer across} \\ \text{the fruit skin} \end{array} \right) - \left( \begin{array}{c} \text{Rate of} \\ \text{respiratory } O_2 \\ \text{consumption} \end{array} \right) \quad (6.13)$$

This balance was converted into the following ODE:

$$\frac{d(\varepsilon V_n C_{O_2,f})}{dt} = k_{O_2} A_n (C_{O_2,p} - C_{O_2,f}) - v M_n \quad (6.14)$$

where

- $A_n$  = individual fruit surface area ( $m^2$ )
- $C_{O_2,p}$  =  $O_2$  concentration in the package atmosphere ( $kg\ O_2 \cdot m^{-3}$ )
- $k_{O_2}$  = fruit skin permeance to  $O_2$  ( $m \cdot s^{-1}$ )
- $M_n$  = individual fruit mass ( $kg$ )
- $V_n$  = individual fruit volume ( $m^3$ )
- $\varepsilon$  = fruit flesh porosity ( $m^3 \cdot m^{-3}$ ).

Changes in fruit volume with time were expected to be small as long as no severe weight loss occurs. Thus, fruit volume was assumed constant. Fruit flesh porosity was also assumed constant. In reality, fruit porosity might be expected to change with time as a result of cell structural changes as the fruit mature. Changes in fruit porosity could be especially marked in damaged, diseased, or water-soaked tissue, and in fruit where senescent breakdown occurs. However, for the purpose of this work, changes in the porosity of healthy, non-senescent tissue were assumed to be negligibly small. In accordance with these assumptions, Eq. 6.14 was rewritten as

$$\frac{d(C_{O_2,f})}{dt} = \frac{k_{O_2} A_n (C_{O_2,p} - C_{O_2,f})}{\varepsilon V_n} - \frac{v \rho_f}{\varepsilon} \quad (6.15)$$

where

- $\rho_f$  = fruit flesh density ( $kg \cdot m^{-3}$ ).

Eqs. 6.13 to 6.15 ignore the possibility of  $O_2$  accumulation in the fruit cell sap. If the effect of  $O_2$  solution in the cell sap proves to be significant, then its omission from the model could influence the accuracy of predicted transient  $O_2$  concentrations. However, omission of the solution effect should not affect the accuracy of steady-state predictions.

The value of  $V_n$  was calculated from initial fruit mass and density as follows:

$$V_n = \frac{M_{f,initial}}{N \rho_{f,initial}} \quad (6.16)$$

where

$N$  = number of fruit in the package  
 $\rho_{f, initial}$  = initial fruit flesh density ( $\text{kg} \cdot \text{m}^{-3}$ ).

Fruit surface area is a function of both fruit shape and fruit volume. Clayton *et al.* (1995) have produced correlations between fruit surface area and fruit volume for several New Zealand apple cultivars. These correlations were used to estimate the surface areas of individual fruit as follows:

$$A_n = a V_n^b \quad (6.17)$$

where

$a, b$  = empirical parameters that depend on cultivar.

Individual fruit mass and fruit flesh density were calculated from

$$M_n = \frac{M_f}{N} \quad (6.18)$$

and

$$\rho_f = \frac{M_n}{V_n} \quad (6.19)$$

### 6.2.5 FRUIT CARBON DIOXIDE CONCENTRATION

An unsteady-state mass balance for fruit  $\text{CO}_2$  was written as

$$\left( \begin{array}{c} \text{Rate of } \text{CO}_2 \\ \text{accumulation in the fruit} \\ \text{internal atmosphere} \end{array} \right) = \left( \begin{array}{c} \text{Rate of} \\ \text{respiratory } \text{CO}_2 \\ \text{production} \end{array} \right) - \left( \begin{array}{c} \text{Rate of } \text{CO}_2 \\ \text{transfer across} \\ \text{the fruit skin} \end{array} \right) \quad (6.20)$$

A development similar to that followed for fruit  $\text{O}_2$  yielded the following ODE:

$$\frac{d(C_{CO_2,f})}{dt} = \frac{RQ_m \nu \rho_f}{\varepsilon} - \frac{k_{CO_2} A_n (C_{CO_2,f} - C_{CO_2,p})}{\varepsilon V_n} \quad (6.21)$$

where

$C_{CO_2,p}$  = CO<sub>2</sub> concentration in the package atmosphere (kg CO<sub>2</sub>·m<sup>-3</sup>)  
 $k_{CO_2}$  = fruit skin permeance to CO<sub>2</sub> (m·s<sup>-1</sup>).

$RQ_m$  was assumed to be constant throughout storage. As for O<sub>2</sub>, Eqs. 6.20 and 6.21 ignore the possibility of CO<sub>2</sub> accumulation in the fruit cell sap.

### 6.2.6 PACKAGE OXYGEN CONCENTRATION

An unsteady-state mass balance for package O<sub>2</sub> was written as

$$\begin{aligned} \left( \begin{array}{c} \text{Rate of } O_2 \\ \text{accumulation in the} \\ \text{package atmosphere} \end{array} \right) &= \left( \begin{array}{c} \text{Rate of } O_2 \\ \text{permeation through} \\ \text{the packaging film} \end{array} \right) + \left( \begin{array}{c} \text{Rate of } O_2 \text{ diffusion} \\ \text{through holes in the} \\ \text{packaging film} \end{array} \right) \\ &+ \left( \begin{array}{c} \text{Rate of } O_2 \text{ flow} \\ \text{through holes in the} \\ \text{packaging film} \end{array} \right) - \left( \begin{array}{c} \text{Rate of } O_2 \\ \text{transfer across} \\ \text{the fruit skin} \end{array} \right) \end{aligned} \quad (6.22)$$

This balance was converted into the following ODE:

$$\begin{aligned} \frac{d(M_{O_2,p})}{dt} &= \frac{P_{O_2}}{x} A_{film} (C_{O_2,e} - C_{O_2,p}) + \frac{D_{O_2,eff}}{x} A_{holes} (C_{O_2,e} - C_{O_2,p}) \\ &+ \frac{Mr_{O_2}}{1000} X_{O_2} \dot{n}_h - k_{O_2} A_{fruit} (C_{O_2,p} - C_{O_2,f}) \end{aligned} \quad (6.23)$$

where

$A_{holes}$  = total area of holes in the packaging film (m<sup>2</sup>)  
 $A_{film}$  = total surface area for gas permeation through the packaging film (m<sup>2</sup>)  
 $C_{O_2,e}$  = O<sub>2</sub> concentration in the store atmosphere (kg O<sub>2</sub>·m<sup>-3</sup>)  
 $D_{O_2,eff}$  = effective diffusivity of O<sub>2</sub> through holes in the packaging film (m<sup>2</sup>·s<sup>-1</sup>)  
 $M_{O_2,p}$  = mass of O<sub>2</sub> in package atmosphere (kg)  
 $Mr_{O_2}$  = molar mass of O<sub>2</sub> (g·mol<sup>-1</sup>)  
 $\dot{n}_h$  = total molar flow into the package through holes in the packaging film (mol·s<sup>-1</sup>)  
 $P_{O_2}$  = packaging film permeability to O<sub>2</sub> (m<sup>2</sup>·s<sup>-1</sup>)  
 $x$  = packaging film thickness (m)

$X_{O_2}$  = mole fraction of  $O_2$  in the flow through holes in the packaging film.

The mass concentration of  $O_2$  in the package atmosphere was calculated from

$$C_{O_2,p} = \frac{M_{O_2,p}}{V_p} \quad (6.24)$$

where

$V_p$  = volume of the package atmosphere ( $m^3$ ).

The total molar flow into the package through holes in the packaging film was calculated as described in section 6.2.14.

### 6.2.7 PACKAGE CARBON DIOXIDE CONCENTRATION

An unsteady-state mass balance for package  $CO_2$  was written as

$$\begin{aligned} \left( \begin{array}{c} \text{Rate of } CO_2 \\ \text{accumulation in the} \\ \text{package atmosphere} \end{array} \right) &= \left( \begin{array}{c} \text{Rate of } CO_2 \\ \text{transfer across} \\ \text{the fruit skin} \end{array} \right) + \left( \begin{array}{c} \text{Rate of } CO_2 \text{ flow} \\ \text{through holes in the} \\ \text{packaging film} \end{array} \right) \\ &\quad - \left( \begin{array}{c} \text{Rate of } CO_2 \\ \text{permeation through} \\ \text{the packaging film} \end{array} \right) - \left( \begin{array}{c} \text{Rate of } CO_2 \text{ diffusion} \\ \text{through holes in the} \\ \text{packaging film} \end{array} \right) \end{aligned} \quad (6.25)$$

This balance was converted into the following ODE:

$$\begin{aligned} \frac{d(M_{CO_2,p})}{dt} &= k_{CO_2} A_{fruit} (C_{CO_2,f} - C_{CO_2,p}) + \frac{Mr_{CO_2}}{1000} X_{CO_2} \dot{n}_h \\ &\quad - \frac{P_{CO_2}}{x} A_{film} (C_{CO_2,p} - C_{CO_2,e}) - \frac{D_{CO_2,eff}}{x} A_{holes} (C_{CO_2,p} - C_{CO_2,e}) \end{aligned} \quad (6.26)$$

where

$C_{CO_2,e}$  =  $CO_2$  concentration in the store atmosphere ( $kg\ CO_2\ m^{-3}$ )  
 $D_{CO_2,eff}$  = effective diffusivity of  $CO_2$  through holes in the packaging film ( $m^2\cdot s^{-1}$ )  
 $M_{CO_2,p}$  = mass of  $CO_2$  in the package atmosphere ( $kg$ )  
 $P_{CO_2}$  = packaging film permeability to  $CO_2$  ( $m^2\cdot s^{-1}$ )  
 $X_{CO_2}$  = mole fraction of  $CO_2$  in the flow through holes in the packaging film.

The mass concentration of  $CO_2$  in the package atmosphere was calculated from

$$C_{\text{CO}_2,p} = \frac{M_{\text{CO}_2,p}}{V_p} \quad (6.27)$$

### 6.2.8 PACKAGE NITROGEN CONCENTRATION

An ODE for package  $\text{N}_2$  was derived in a manner analogous to that described for package  $\text{O}_2$  and  $\text{CO}_2$ , but with the term describing fruit gas exchange omitted:

$$\begin{aligned} \frac{d(M_{\text{N}_2,p})}{dt} = & \frac{\text{Mr}_{\text{N}_2}}{1000} X_{\text{N}_2} \dot{n}_h - \frac{P_{\text{N}_2}}{x} A_{\text{film}} (C_{\text{N}_2,p} - C_{\text{N}_2,e}) \\ & - \frac{D_{\text{N}_2,\text{eff}}}{x} A_{\text{holes}} (C_{\text{N}_2,p} - C_{\text{N}_2,e}) \end{aligned} \quad (6.28)$$

where

- $C_{\text{N}_2,e}$  =  $\text{N}_2$  concentration in the store atmosphere ( $\text{kg N}_2 \cdot \text{m}^{-3}$ )
- $C_{\text{N}_2,p}$  =  $\text{N}_2$  concentration in the package atmosphere ( $\text{kg N}_2 \cdot \text{m}^{-3}$ )
- $D_{\text{N}_2,\text{eff}}$  = effective diffusivity of  $\text{N}_2$  through holes in the packaging film ( $\text{m}^2 \cdot \text{s}^{-1}$ )
- $M_{\text{N}_2,p}$  = mass of  $\text{N}_2$  in package atmosphere (kg)
- $\text{Mr}_{\text{N}_2}$  = molar mass of  $\text{N}_2$  ( $\text{g} \cdot \text{mol}^{-1}$ )
- $P_{\text{N}_2}$  = packaging film permeability to  $\text{N}_2$  ( $\text{m}^2 \cdot \text{s}^{-1}$ )
- $X_{\text{N}_2}$  = mole fraction of  $\text{N}_2$  in the flow through holes in the packaging film.

The mass concentration of  $\text{N}_2$  in the package atmosphere was calculated from

$$C_{\text{N}_2,p} = \frac{M_{\text{N}_2,p}}{V_p} \quad (6.29)$$

### 6.2.9 PACKAGE WATER VAPOUR CONCENTRATION

An unsteady-state mass balance for water vapour in the package atmosphere was written as

$$\begin{aligned} \left( \begin{array}{l} \text{Rate of moisture} \\ \text{accumulation in the} \\ \text{package atmosphere} \end{array} \right) = & \left( \begin{array}{l} \text{Rate of} \\ \text{moisture loss} \\ \text{from the fruit} \end{array} \right) + \left( \begin{array}{l} \text{Rate of moisture flow} \\ \text{through holes in the} \\ \text{packaging film} \end{array} \right) \\ & - \left( \begin{array}{l} \text{Rate of moisture} \\ \text{permeation through} \\ \text{the packaging film} \end{array} \right) - \left( \begin{array}{l} \text{Rate of moisture} \\ \text{diffusion through holes} \\ \text{in the packaging film} \end{array} \right) \\ & - \left( \begin{array}{l} \text{Rate of moisture} \\ \text{condensation on} \\ \text{the fruit surface} \end{array} \right) - \left( \begin{array}{l} \text{Rate of moisture} \\ \text{condensation on the inside} \\ \text{packaging film surface} \end{array} \right) \\ & - \left( \begin{array}{l} \text{Rate of moisture sorption} \\ \text{by the moulded-pulp} \\ \text{fruit trays} \end{array} \right) \end{aligned} \quad (6.30)$$

This balance was converted into the following ODE:

$$\begin{aligned}
 \frac{d(M_{H_2O,p})}{dt} = & k_{g,skin} A_{fruit} (p_{w,f} - p_{w,p}) + \frac{Mr_{H_2O}}{1000} X_{H_2O} \dot{n}_h \\
 & - \frac{P_{H_2O}}{x} A_{film} (C_{H_2O,p} - C_{H_2O,e}) - \frac{D_{H_2O,eff}}{x} A_{holes} (C_{H_2O,p} - C_{H_2O,e}) \\
 & - \frac{dM_{cond,f}}{dt} - \frac{dM_{cond,p}}{dt} - N_{tray} \frac{dM_{w,tray}}{dt}
 \end{aligned} \quad (6.31)$$

where

- $C_{H_2O,e}$  = concentration of water vapour in the store atmosphere ( $\text{kg H}_2\text{O} \cdot \text{m}^{-3}$ )
- $C_{H_2O,p}$  = concentration of water vapour in the package atmosphere ( $\text{kg H}_2\text{O} \cdot \text{m}^{-3}$ )
- $D_{H_2O,eff}$  = effective diffusivity of water vapour through holes in the packaging film ( $\text{m}^2 \cdot \text{s}^{-1}$ )
- $M_{cond,f}$  = mass of condensate on the fruit surface (kg)
- $M_{cond,p}$  = mass of condensate on the inside packaging film surface (kg)
- $M_{H_2O,p}$  = mass of water vapour in the package atmosphere (kg)
- $M_{w,tray}$  = mass of water absorbed by the moulded-pulp trays ( $\text{kg} \cdot \text{tray}^{-1}$ )
- $Mr_{H_2O}$  = molar mass of water ( $\text{g} \cdot \text{mol}^{-1}$ )
- $N_{tray}$  = number of moulded-pulp trays per package
- $P_{H_2O}$  = packaging film permeability to water vapour ( $\text{m}^2 \cdot \text{s}^{-1}$ )
- $X_{H_2O}$  = mole fraction of water vapour in the flow through holes in the packaging film.

In reality, evaporative weight loss from the fruit is likely to be dependent on the presence or absence of condensate on the fruit surface. For example, the formation of condensate on the fruit surface could reduce the rate of evaporative weight loss from the fruit. For simplicity, evaporative weight loss from the fruit was treated as being independent of condensation on the fruit surface. As condensation on the fruit surface is likely to occur only when package relative humidity is high and the rate of transpiration therefore low, this treatment was expected to have little effect on the accuracy of model predictions.

The mass concentration and partial pressure of water vapour in the package atmosphere were calculated from

$$C_{H_2O,p} = \frac{M_{H_2O,p}}{V_p} \quad (6.32)$$

$$p_{w,p} = [H_2O]_p P_p \quad (6.33)$$

where

$P_p$  = package atmosphere pressure (Pa)  
 $[H_2O]_p$  = volume concentration of water vapour in the package atmosphere  
 ( $m^3 \cdot m^{-3}$ ).

### 6.2.10 MOISTURE CONDENSATION ON THE FRUIT SURFACE

An unsteady-state mass balance for the mass of condensate on the fruit surface was written as

$$\left( \begin{array}{c} \text{Rate of accumulation} \\ \text{of condensate on} \\ \text{the fruit surface} \end{array} \right) = \left( \begin{array}{c} \text{Rate of condensation} \\ \text{of water vapour onto} \\ \text{the fruit surface} \end{array} \right) \quad (6.34)$$

The resulting ODE depends on whether condensation or evaporation occurs and, if conditions for evaporation exist, on whether there is any condensate present on the fruit surface. If the partial pressure of water vapour in the package atmosphere is greater than the saturated vapour pressure of water at the fruit surface temperature, then condensation of moisture onto the fruit surface occurs:

$$\frac{dM_{cond,f}}{dt} = k_{g,fruit} A_{fruit} (p_{w,p} - p_{sat,f}) \quad \text{for } p_{w,p} \geq p_{sat,f} \quad (6.35)$$

where

$k_{g,fruit}$  = mass transfer coefficient for moisture condensation at the fruit surface  
 ( $s \cdot m^{-1}$ ).

If the partial pressure of water vapour in the package atmosphere is less than the saturated vapour pressure of water at the fruit surface temperature, and if condensate is present on the fruit surface, then evaporation of condensate from the fruit surface occurs:

$$\frac{dM_{cond,f}}{dt} = k_{g,fruit} SA_{corr} A_{fruit} (p_{w,p} - p_{sat,f}) \quad \text{for } \begin{array}{l} M_{cond,f} > 0 \\ p_{w,p} < p_{sat,f} \end{array} \quad (6.36)$$

where

$SA_{corr}$  = empirical correction factor for fruit surface area.

The empirical correction factor in the above equation was included to account for the possible formation of droplets on the fruit surface, a phenomenon that would reduce the surface area available for the evaporation of condensate.

If the partial pressure of water vapour in the package atmosphere is less than the saturated vapour pressure of water at the fruit surface temperature, but if no condensate is present on the fruit surface, then neither evaporation nor condensation occurs:

$$\frac{dM_{cond,f}}{dt} = 0 \quad \text{for} \quad \begin{matrix} M_{cond,f} = 0 \\ p_{w,p} < p_{sat,f} \end{matrix} \quad (6.37)$$

### 6.2.11 MOISTURE CONDENSATION ON THE INSIDE PACKAGING SURFACE

Moisture condensation on the inside surface of the packaging film was modelled in a manner analogous to that described above for moisture condensation on the fruit surface:

$$\frac{dM_{cond,p}}{dt} = k_{g,film} A_{pack} (p_{w,p} - p_{sat,film}) \quad \text{for} \quad p_{w,p} \geq p_{sat,film} \quad (6.38)$$

$$\frac{dM_{cond,p}}{dt} = k_{g,film} SA_{corr} A_{pack} (p_{w,p} - p_{sat,film}) \quad \text{for} \quad \begin{matrix} M_{cond,p} > 0 \\ p_{w,p} < p_{sat,film} \end{matrix} \quad (6.39)$$

$$\frac{dM_{cond,p}}{dt} = 0 \quad \text{for} \quad \begin{matrix} M_{cond,p} = 0 \\ p_{w,p} < p_{sat,film} \end{matrix} \quad (6.40)$$

where

- $A_{pack}$  = average heat transfer area of the packaging materials ( $m^2$ )
- $k_{g,film}$  = mass transfer coefficient for moisture condensation at the inside surface of the packaging film ( $s \cdot m^{-1}$ )
- $p_{sat,film}$  = saturated vapour pressure of water at the packaging film temperature (Pa).

### 6.2.12 MOISTURE SORPTION BY MOULDED-PULP FRUIT TRAYS

An ODE for the mass of water absorbed by the moulded-pulp fruit trays was written as

$$\frac{dM_{w,tray}}{dt} = k_{g,tray} A_{tray} (p_{w,p} - p_{w,tray}) \quad (6.41)$$

where

$$p_{w,tray} = a_{w,tray} p_{sat,tray} \quad (6.42)$$

and where

- $a_{w,tray}$  = tray water activity
- $A_{tray}$  = effective tray surface area for moisture sorption ( $m^2 \cdot tray^{-1}$ )
- $k_{g,tray}$  = mass transfer coefficient for moisture sorption at the tray surface ( $s \cdot m^{-1}$ )
- $p_{w,tray}$  = partial pressure of water vapour at the tray surface (Pa)

$p_{sat, tray}$  = saturated vapour pressure of water at the tray temperature (Pa).

As discussed in section 2.4.3.6, the Guggenheim-Andersen-De Boer (GAB) isotherm for moisture sorption has been successfully fitted to moisture-sorption data for a range of biological materials, including paper-based packaging materials (e.g. Eagleton & Marcondes, 1994; Amos, 1995). The GAB isotherm model was chosen here to describe the moisture-sorption isotherm for moulded-pulp fruit trays. The model was assumed to hold for all values of  $a_{w, tray}$  and the parameters of the model were assumed to be independent of temperature and of whether sorption or desorption occurs. In practice the GAB model is generally recommended for water activities of up to 0.9, and moisture-sorption isotherms are known to vary with temperature and to exhibit hysteresis. Thus, the approach used here can only be regarded as approximate. Nevertheless, the isotherm model was expected to provide meaningful estimates of the effect of tray moisture uptake on package water vapour concentrations.

The expression for the GAB isotherm model given by Eq. 2.22 in section 2.4.3.6 can be rearranged to give

$$X_{tray} = \frac{a_{w, tray}}{\beta_1 a_{w, tray}^2 + \beta_2 a_{w, tray} + \beta_3} \quad (6.43)$$

where

$$\beta_1 = \frac{K}{X_m} \left( \frac{1}{C} - 1 \right) \quad (6.44)$$

$$\beta_2 = \frac{1}{X_m} \left( 1 - \frac{2}{C} \right) \quad (6.45)$$

$$\beta_3 = \frac{1}{X_m CK} \quad (6.46)$$

and where

$C, K, X_m$  = parameters of the GAB isotherm model (section 2.4.3.6)

$X_{tray}$  = tray moisture content on a dry solids basis ( $\text{kg} \cdot \text{kg}^{-1}$ ).

For the purpose of solving Eqs. 6.41 and 6.42, Eq. 6.43 was rearranged to give an expression for  $a_{w, tray}$  as a function of  $X_{tray}$ . Application of the quadratic formula to Eq. 6.43 gives

$$a_{w, tray} = \frac{-(\beta_2 X_{tray} - 1) \pm \sqrt{(\beta_2 X_{tray} - 1)^2 - 4\beta_1 \beta_3 X_{tray}^2}}{2\beta_1 X_{tray}} \quad (6.47)$$

The negative root of the quadratic has no physical meaning and was disregarded in the model calculations.

Tray moisture content was calculated from

$$X_{\text{tray}} = \frac{M_{w,\text{tray}}}{M_{\text{tray}}} \quad (6.48)$$

where

$$M_{\text{tray}} = \text{tray dry mass (kg} \cdot \text{tray}^{-1}\text{)}.$$

### 6.2.13 PACKAGE VOLUME AND PRESSURE

#### 6.2.13.1 PERFECTLY SEALED PACKAGING FILMS

For package atmosphere volumes above a set minimum value, package atmosphere pressure was assumed to remain equal to atmospheric pressure:

$$P_p = P_{\text{atm}} \quad \text{for} \quad V_p > V_{p,\text{min}} \quad (6.49)$$

where

$$\begin{aligned} P_{\text{atm}} &= \text{atmospheric pressure (Pa)} \\ V_{p,\text{min}} &= \text{minimum package atmosphere volume (m}^3\text{)}. \end{aligned}$$

Package atmosphere volume was calculated from

$$V_p = V_{\text{O}_2,p} + V_{\text{CO}_2,p} + V_{\text{N}_2,p} + V_{\text{H}_2\text{O},p} \quad (6.50)$$

where

$$\begin{aligned} V_{\text{CO}_2,p} &= \text{volume of CO}_2 \text{ in the package atmosphere (m}^3\text{)} \\ V_{\text{H}_2\text{O},p} &= \text{volume of water vapour in the package atmosphere (m}^3\text{)} \\ V_{\text{O}_2,p} &= \text{volume of O}_2 \text{ in the package atmosphere (m}^3\text{)} \\ V_{\text{N}_2,p} &= \text{volume of N}_2 \text{ in the package atmosphere (m}^3\text{)}. \end{aligned}$$

Package atmosphere volumes of O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and water vapour were calculated from their corresponding package gas masses as follows:

$$V_{i,p} = \frac{1000 M_{i,p}}{\text{Mr}_i} \frac{R(\theta_p + 273.15)}{P_p} \quad (6.51)$$

where

- $M_{i,p}$  = mass of gas species  $i$  in the package atmosphere (kg)  
 $Mr_i$  = molecular mass of gas species  $i$  ( $\text{g}\cdot\text{mol}^{-1}$ )  
 $R$  = gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )  
 $V_{i,p}$  = volume of gas species  $i$  in the package atmosphere ( $\text{m}^3$ )  
 $\theta_p$  = temperature of the package atmosphere ( $^{\circ}\text{C}$ ).

Where the value of  $V_p$  calculated from Eq. 6.50 was less than the set minimum package atmosphere volume,  $V_p$  and  $P_p$  were recalculated as follows:

$$V_p = V_{p,\min} \quad (6.52)$$

$$P_p = \frac{n_{p,\text{tot}} R (\theta_p + 273.15)}{V_{p,\min}} \quad (6.53)$$

where

$$n_{p,\text{tot}} = \frac{1000 M_{\text{O}_2,p}}{Mr_{\text{O}_2}} + \frac{1000 M_{\text{CO}_2,p}}{Mr_{\text{CO}_2}} + \frac{1000 M_{\text{N}_2,p}}{Mr_{\text{N}_2}} + \frac{1000 M_{\text{H}_2\text{O},p}}{Mr_{\text{H}_2\text{O}}} \quad (6.54)$$

and where

$n_{p,\text{tot}}$  = total number of moles of gas in the package atmosphere.

### 6.2.13.2 PERFORATED PACKAGING FILMS

For perforated films, package atmosphere pressure was assumed to remain equal to atmospheric pressure and package atmosphere volume was assumed to remain constant:

$$P_p = P_{\text{atm}} \quad \text{for} \quad t > t_h \quad (6.55)$$

$$V_p = V_{p,h} \quad \text{for} \quad t > t_h \quad (6.56)$$

where

$t_h$  = time at which holes in the packaging film are formed (s)  
 $V_{p,h}$  = package atmosphere volume at time  $t_h$  ( $\text{m}^3$ ).

### 6.2.14 MOLAR FLOW THROUGH HOLES IN THE PACKAGING FILM

The net molar flow of gases into a perforated package can be split into two parts: bulk flow into the package through holes in the packaging film and flow into the package through all other mechanisms (fruit gas exchange, permeation through the packaging film, diffusion through holes in the packaging film, and evaporation, condensation, and sorption of package moisture). Thus

$$\frac{dn_{p, tot}}{dt} = \dot{n}_h + \dot{n}_{O_2} + \dot{n}_{CO_2} + \dot{n}_{N_2} + \dot{n}_{H_2O} \quad (6.57)$$

where

- $\dot{n}_{CO_2}$  = net molar flow of  $CO_2$  into the package through fruit gas exchange, permeation, and diffusion ( $mol \cdot s^{-1}$ )
- $\dot{n}_{H_2O}$  = net molar flow of  $H_2O$  into the package through fruit moisture loss, permeation, diffusion, condensation/evaporation, and sorption/desorption ( $mol \cdot s^{-1}$ )
- $\dot{n}_{N_2}$  = net molar flow of  $N_2$  into the package through permeation and diffusion ( $mol \cdot s^{-1}$ )
- $\dot{n}_{O_2}$  = net molar flow of  $O_2$  into the package through fruit gas exchange, permeation, and diffusion ( $mol \cdot s^{-1}$ ).

From the ideal gas equation

$$\frac{dn_{p, tot}}{dt} = \frac{1}{R} \frac{d \left( \frac{P_p V_p}{\theta_p + 273.15} \right)}{dt} \quad (6.58)$$

As discussed in section 6.2.13.2, the pressure within a perforated package was assumed to remain equal to atmospheric pressure and the volume of a perforated package was assumed to remain constant. Thus

$$\frac{dn_{p, tot}}{dt} = \frac{P_{atm} V_{p, h}}{R} \frac{d \left( \frac{1}{\theta_p + 273.15} \right)}{dt} \quad \text{for } t > t_h \quad (6.59)$$

A special case that must be considered is the case where a perforation is made in a previously perfectly sealed film at a time when the minimum volume of the package has been reached and the package atmosphere pressure has started to decrease. The assumption that package atmosphere pressure equalizes instantaneously with atmospheric pressure implies that

$$\frac{dn_{p,tot}}{dt} \rightarrow \infty \quad \text{at} \quad t = t_h \quad (6.60)$$

Eq. 6.59 is difficult to apply in practice because of the derivative on the right-hand-side. Thus, in the MAP model, the net molar flows represented by Eqs. 6.59 and 6.60 were approximated by assuming that the package atmosphere pressure equalizes with atmospheric pressure over a small time interval,  $\Delta t$ . The net molar flow into the package was estimated from

$$\frac{dn_{p,tot}}{dt} \approx \frac{\Delta n_{p,tot}}{\Delta t} \quad (6.61)$$

where  $\Delta n_{p,tot}$  was estimated from

$$\Delta n_{p,tot} = \frac{P_{atm} V_{p,h}}{R (\theta_p + 273.15)} - n_{p,tot} \quad (6.62)$$

The first term on the right-hand-side of Eq. 6.62 represents the total number of moles in the package atmosphere under constant pressure and volume, while  $n_{p,tot}$  represents the total number of moles in the package atmosphere as calculated from Eq. 6.54.

Having estimated the net molar flow required to keep the package atmosphere pressure and volume constant, the corresponding molar flow through holes in the packaging film was then calculated by rearranging Eq. 6.57 as follows:

$$\dot{n}_h = \frac{dn_{p,tot}}{dt} - (\dot{n}_{O_2} + \dot{n}_{CO_2} + \dot{n}_{N_2} + \dot{n}_{H_2O}) \quad (6.63)$$

Values of  $\dot{n}_{O_2}$ ,  $\dot{n}_{CO_2}$ ,  $\dot{n}_{N_2}$ , and  $\dot{n}_{H_2O}$  were calculated from

$$\dot{n}_i = \frac{1000}{Mr_i} \dot{m}_i \quad (6.64)$$

where

- $\dot{m}_i$  = net mass flow of gas species  $i$  into the package by all mechanisms except bulk flow ( $\text{mol}\cdot\text{s}^{-1}$ )
- $\dot{n}_i$  = net molar flow of gas species  $i$  into the package by all mechanisms except bulk flow ( $\text{mol}\cdot\text{s}^{-1}$ ).

Values of  $\dot{m}_i$  for each gas species were calculated from

$$\begin{aligned} \dot{m}_{O_2} = & \frac{P_{O_2}}{x} A_{film} (C_{O_2,e} - C_{O_2,p}) + \frac{D_{O_2,eff}}{x} A_{holes} (C_{O_2,e} - C_{O_2,p}) \\ & - k_{O_2} A_{fruit} (C_{O_2,p} - C_{O_2,f}) \end{aligned} \quad (6.65)$$

$$\begin{aligned} \dot{m}_{CO_2} = & k_{CO_2} A_{fruit} (C_{CO_2,f} - C_{CO_2,p}) - \frac{P_{CO_2}}{x} A_{film} (C_{CO_2,p} - C_{CO_2,e}) \\ & - \frac{D_{CO_2,eff}}{x} A_{holes} (C_{CO_2,p} - C_{CO_2,e}) \end{aligned} \quad (6.66)$$

$$\dot{m}_{N_2} = - \frac{P_{N_2}}{x} A_{film} (C_{N_2,p} - C_{N_2,e}) - \frac{D_{N_2,eff}}{x} A_{holes} (C_{N_2,p} - C_{N_2,e}) \quad (6.67)$$

$$\begin{aligned} \dot{m}_{H_2O} = & k_{g,skin} A_{fruit} (p_{w,f} - p_{w,p}) - \frac{P_{H_2O}}{x} A_{film} (C_{H_2O,p} - C_{H_2O,e}) \\ & - \frac{D_{H_2O,eff}}{x} A_{holes} (C_{H_2O,p} - C_{H_2O,e}) - \frac{dM_{cond,f}}{dt} - \frac{dM_{cond,p}}{dt} \\ & - N_{tray} \frac{dM_{w,tray}}{dt} \end{aligned} \quad (6.68)$$

where

- $\dot{m}_{CO_2}$  = net mass flow of  $CO_2$  into the package through fruit gas exchange, permeation, and diffusion ( $kg \cdot s^{-1}$ )
- $\dot{m}_{H_2O}$  = net mass flow of  $H_2O$  into the package through fruit moisture loss, permeation, diffusion, condensation/evaporation, and sorption/desorption ( $kg \cdot s^{-1}$ )
- $\dot{m}_{N_2}$  = net mass flow of  $N_2$  into the package through permeation and diffusion ( $kg \cdot s^{-1}$ )
- $\dot{m}_{O_2}$  = net mass flow of  $O_2$  into the package through fruit gas exchange, permeation, and diffusion ( $kg \cdot s^{-1}$ ).

For a positive value of  $\dot{n}_h$  (bulk flow of air into the package)

$$X_i = [i]_e \quad (6.69)$$

where

- $X_i$  = mole fraction of gas species  $i$  in the bulk flow through holes in the packaging film

$[i]_e$  = volume concentration of gas species  $i$  in the store atmosphere ( $\text{m}^3 \cdot \text{m}^{-3}$ ).

For a negative value of  $\dot{n}_h$  (bulk flow of air out of the package)

$$X_i = [i]_p \quad (6.70)$$

where

$[i]_p$  = volume concentration of gas species  $i$  in the package atmosphere ( $\text{m}^3 \cdot \text{m}^{-3}$ ).

## 6.2.15 HEAT TRANSFER

### 6.2.15.1 SEQUENTIAL HEAT TRANSFER MODEL

#### *Fruit Temperature*

An unsteady-state energy balance for the fruit was written as

$$\left( \begin{array}{c} \text{Rate of energy} \\ \text{accumulation in} \\ \text{the fruit flesh} \end{array} \right) = \left( \begin{array}{c} \text{Rate of} \\ \text{respiratory heat} \\ \text{generation} \end{array} \right) - \left( \begin{array}{c} \text{Rate of convective} \\ \text{heat loss at} \\ \text{the fruit surface} \end{array} \right) \quad (6.71)$$

$$\left( \begin{array}{c} \text{Rate of evaporative} \\ \text{heat loss at} \\ \text{the fruit surface} \end{array} \right)$$

Assuming a uniform fruit temperature, this balance was converted into the following ODE:

$$\frac{d(M_n \eta_f)}{dt} = v M_n W - h_f A_n (\theta_f - \theta_p) - k_{g,skin} A_n (p_{w,f} - p_{w,p}) h_{fg} \quad (6.72)$$

where

- $h_f$  = convective heat transfer coefficient at the fruit surface ( $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ )
- $h_{fg}$  = latent heat of vaporization of water ( $\text{J} \cdot \text{kg}^{-1}$ )
- $W$  = respiratory heat generation per unit mass of  $\text{O}_2$  consumption ( $\text{J} \cdot \text{kg}^{-1}$ )
- $\eta_f$  = fruit specific enthalpy ( $\text{J} \cdot \text{kg}^{-1}$ ).

In strict terms, the derivative on the left-hand-side of Eq. 6.72 should express the accumulation of total energy within the fruit rather than the accumulation of total enthalpy as written. However, when potential and kinetic energy effects are small, the rate of total energy accumulation in a system can be approximated by the rate of internal energy accumulation. For substances with small specific volumes (solids and liquids),

internal energy can be closely approximated by enthalpy. Thus, Eq. 6.72 was written as a total enthalpy balance instead of a total energy balance.

Eqs. 6.71 and 6.72 ignore the possibility of radiative heat transfer at the fruit surface. However, if considered significant, radiation could be accounted for in Eq. 6.72 as pseudo-convection by replacing  $h_f$  with a combined convection and radiation surface heat transfer coefficient. Eqs. 6.71 and 6.72 also ignore the possibility of heat conduction between the fruit and the packaging materials, with the total fruit surface area assumed to be available for convection instead.

Fruit temperature was estimated from fruit total enthalpy as follows:

$$\theta_f = \frac{(M_n \eta_f)}{M_n c_{pf}} \quad (6.73)$$

where

$c_{pf}$  = specific heat capacity of the fruit flesh ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ).

#### *Package Atmosphere Temperature*

An unsteady-state energy balance for the package atmosphere was written as

$$\begin{aligned} \left( \begin{array}{c} \text{Rate of energy} \\ \text{accumulation in the} \\ \text{package atmosphere} \end{array} \right) &= \left( \begin{array}{c} \text{Rate of convective} \\ \text{heat transfer at} \\ \text{the fruit surface} \end{array} \right) + \left( \begin{array}{c} \text{Rate of evaporative} \\ \text{heat loss at the} \\ \text{fruit surface} \end{array} \right) \\ &+ \left( \begin{array}{c} \text{Rate of heat transfer due to} \\ \text{the flow of water vapour through} \\ \text{holes in the packaging film} \end{array} \right) \\ &- \left( \begin{array}{c} \text{Rate of heat} \\ \text{conduction through the} \\ \text{packaging materials} \end{array} \right) \\ &- \left( \begin{array}{c} \text{Rate of heat transfer due to} \\ \text{the permeation of water vapour} \\ \text{through the packaging film} \end{array} \right) \\ &- \left( \begin{array}{c} \text{Rate of heat transfer due to the} \\ \text{diffusion of water vapour through} \\ \text{holes in the packaging film} \end{array} \right) \end{aligned} \quad (6.74)$$

This balance was converted into the following ODE:

$$\begin{aligned}
\frac{d(M_p \eta_p + N_{tray} M_{tray} \eta_{tray})}{dt} = & h_f A_{fruit} (\theta_f - \theta_p) + k_{g,skin} A_{fruit} (p_{w,f} - p_{w,p}) h_{fg} \\
& + \frac{Mr_{H_2O}}{1000} X_{H_2O} \dot{n}_h h_{fg} - U_{pack} A_{pack} (\theta_p - \theta_e) \\
& - \frac{P_{H_2O}}{\chi} A_{film} (C_{H_2O,p} - C_{H_2O,e}) h_{fg} \\
& - \frac{D_{H_2O,eff}}{\chi} A_{holes} (C_{H_2O,p} - C_{H_2O,e}) h_{fg}
\end{aligned} \tag{6.75}$$

where

- $M_p$  = mass of dry air in the package atmosphere (kg)  
 $U_{pack}$  = overall heat transfer coefficient for the packaging materials ( $W \cdot m^{-2} \cdot K^{-1}$ )  
 $\eta_p$  = specific enthalpy of the package atmosphere (dry air basis) ( $J \cdot kg^{-1}$ )  
 $\eta_{tray}$  = specific enthalpy of the moulded-pulp fruit trays (dry mass basis) ( $J \cdot kg^{-1}$ )  
 $\theta_e$  = store air temperature ( $^{\circ}C$ ).

In formulating Eq. 6.75, the moulded-pulp fruit trays and the package atmosphere were assumed to be in thermal equilibrium and their thermal masses were combined. This was found to have no discernable effect on the predicted temperature of the package-atmosphere, but was found to stabilize the numerical solution by increasing the effective thermal mass of the package atmosphere. Heat transfer due to the movement of dry gases into or out of the package atmosphere was assumed negligible, and the sensible heat component of water vapour moving into or out of the package atmosphere was assumed negligible compared to the latent heat component.

As discussed for Eq. 6.72 in the previous section, Eq. 6.75 was written as a total enthalpy balance rather than a total energy balance. Such an approach is less appropriate for gaseous systems than for solid or liquid systems because of the higher specific volumes of gases compared to those of solids or liquids. However, the rate of internal energy accumulation in a gaseous system can be approximated by the rate of enthalpy accumulation in the system as long as the rates of pressure and volume change are reasonably small. Because the thermal mass of the package-atmosphere was combined with that of the fruit-trays in Eq. 6.75, and in view of the simplistic nature of the overall heat transfer model, this approximation was considered unlikely to contribute significant error to the prediction of package atmosphere temperature.

The package overall heat transfer coefficient in Eq. 6.75 was estimated from

$$U_{pack} = \frac{1}{\frac{1}{h_p} + \frac{x_1}{\lambda_1} + \frac{x_2}{\lambda_2} + \dots + \frac{x_i}{\lambda_i} + \frac{1}{h_e}} \tag{6.76}$$

where

- $h_e$  = convective heat transfer coefficient at the external package surface ( $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ )  
 $h_p$  = convective heat transfer coefficient at the internal packaging-film surface ( $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ )  
 $x_i$  = thickness of the  $i^{\text{th}}$  layer of packaging material (m)  
 $\lambda_i$  = thermal conductivity of the  $i^{\text{th}}$  layer of packaging material ( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ).

Package atmosphere temperature was calculated from

$$\theta_p = \frac{(M_p \eta_p + N_{tray} M_{tray} \eta_{tray}) - M_p H_p h_{fg}}{M_p (c_{pa} + H_p c_{pv}) + N_{tray} M_{tray} (c_{pt} + X_{tray} c_{pw})} \quad (6.77)$$

where

$$M_p = M_{\text{O}_2,p} + M_{\text{CO}_2,p} + M_{\text{N}_2,p} \quad (6.78)$$

$$H_p = \frac{M_{\text{H}_2\text{O},p}}{M_p} \quad (6.79)$$

and where

- $c_{pa}$  = specific heat capacity of dry air ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ )  
 $c_{pt}$  = specific heat capacity of the dry trays ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ )  
 $c_{pv}$  = specific heat capacity of water vapour ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ )  
 $c_{pw}$  = specific heat capacity of liquid water ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ )  
 $H_p$  = absolute humidity of the package atmosphere ( $\text{kg} \cdot \text{kg}^{-1}$ ).

Eq. 6.77 assumes that the specific heat capacity of the dry package atmosphere is independent of package atmosphere composition and equal to the specific heat capacity of dry air.

From the assumption of quasi-steady-state heat transfer through the packaging materials

$$h_p A_{pack} (\theta_p - \theta_{film}) = U_{pack} A_{pack} (\theta_p - \theta_e) \quad (6.80)$$

where

- $\theta_{film}$  = temperature of the packaging film ( $^{\circ}\text{C}$ ).

The temperature of the packaging film was estimated from the above equation as follows:

$$\theta_{film} = \theta_p - \frac{U_{pack}(\theta_p - \theta_e)}{h_p} \quad (6.81)$$

### 6.2.15.2 HALF-COOLING-TIME HEAT TRANSFER MODEL

#### *Fruit Temperature*

The exponential cooling or heating of an object under constant ambient conditions can be described by the following relationship:

$$Y = \gamma \exp(-\alpha t) \quad (6.82)$$

where

$$Y = \frac{\theta - \theta_e}{\theta_i - \theta_e} \quad (6.83)$$

and where

- $Y$  = fractional unaccomplished temperature change
- $\alpha$  = constant ( $s^{-1}$ )
- $\gamma$  = constant
- $\theta$  = temperature of the object at time,  $t$  ( $^{\circ}C$ )
- $\theta_e$  = temperature of the environment external to the object ( $^{\circ}C$ )
- $\theta_i$  = initial temperature of the object ( $^{\circ}C$ ).

The "half-life" of an exponential cooling or heating process is defined as the time taken for the fractional unaccomplished temperature change to decrease by half. From this definition,  $\alpha$  can be calculated as

$$\alpha = \frac{\ln 2}{t_{0.5}} \quad (6.84)$$

where

$$t_{0.5} = \text{half cooling or warming time (s).}$$

By differentiating Eqs. 6.82 and 6.83 with respect to time and combining the two results, the following ODE can be derived to describe an object's cooling or heating rate:

$$\frac{d\theta}{dt} = -\alpha(\theta - \theta_e) \quad (6.85)$$

In the half-cooling-time heat transfer model, the expression given by Eq. 6.85 was used to replace the term for convective heat transfer in Eq. 6.72 as follows:

$$\frac{d(M_n \eta_f)}{dt} = v M_n W - M_n c_{pf} \alpha (\theta_f - \theta_e) - k_{g,skin} A_n (p_{w,f} - p_{w,p}) h_{fg} \quad (6.86)$$

The middle term on the right-hand-side of Eq. 6.86 is the dominant term in determining fruit cooling rates. The advantage of Eq. 6.86 over Eq. 6.72 is that fruit cooling rates are now independent of the estimates of  $h_f$  and  $\theta_p$ . Half-cooling-times are commonly used in industry to express product cooling rates, and the value of  $\alpha$  calculated from  $t_{0.5}$  should therefore prove easier to estimate than the value of  $h_f$ . Similarly, the temperature of the storage atmosphere, an input to the MAP model, is likely to be more accurately known than the temperature of the package atmosphere, a dependent variable of the model.

### *Package Atmosphere Temperature*

Package atmosphere temperature was modelled as described previously for the sequential heat-transfer model. Although this requires estimates of  $h_f$  and  $U_{pack}$ , the accuracy of these estimates was now considered less critical than in the sequential heat-transfer model.

## 6.2.16 GENERAL ALGEBRAIC RELATIONS

### 6.2.16.1 STORE ATMOSPHERE

Volume concentrations of water vapour, oxygen, carbon dioxide, and nitrogen in the store atmosphere were calculated from known values of the store relative humidity and the dry-air mole fractions of oxygen and carbon dioxide as follows:

$$p_{w,e} = \frac{RH_e}{100} \times p_{sat,e} \quad (6.87)$$

$$[H_2O]_e = \frac{p_{w,e}}{p_{atm}} \quad (6.88)$$

$$[O_2]_e = X_{O_2,e} (1 - [H_2O]_e) \quad (6.89)$$

$$[CO_2]_e = X_{CO_2,e} (1 - [H_2O]_e) \quad (6.90)$$

$$X_{N_2,e} = 1 - X_{O_2,e} - X_{CO_2,e} \quad (6.91)$$

$$[N_2]_e = X_{N_2,e} (1 - [H_2O]_e) \quad (6.92)$$

where

- $RH_e$  = relative humidity of the store air (%)  
 $p_{sat,e}$  = saturated vapour pressure of water at the store air temperature (Pa)  
 $p_{w,e}$  = partial pressure of water vapour in the store atmosphere (Pa)  
 $X_{O_2,e}$  = mole fraction of  $O_2$  in the store air (dry air basis)  
 $X_{CO_2,e}$  = mole fraction of  $CO_2$  in the store air (dry air basis)  
 $X_{N_2,e}$  = mole fraction of  $N_2$  in the store air (dry air basis)  
 $[CO_2]_e$  = volume concentration of  $CO_2$  in the store atmosphere ( $m^3 \cdot m^{-3}$ )  
 $[H_2O]_e$  = volume concentration of water vapour in the store atmosphere ( $m^3 \cdot m^{-3}$ )  
 $[N_2]_e$  = volume concentration of  $N_2$  in the store atmosphere ( $m^3 \cdot m^{-3}$ )  
 $[O_2]_e$  = volume concentration of  $O_2$  in the store atmosphere ( $m^3 \cdot m^{-3}$ ).

#### 6.2.16.2 CONVERSION OF MASS AND VOLUME CONCENTRATIONS

The mass and volume concentrations of gases in the store, package, and fruit internal atmospheres were converted as necessary by applying the ideal gas law:

$$C_i = \frac{Mr_i}{1000} \frac{P[i]}{R(\theta + 273.15)} \quad (6.93)$$

$$[i] = \frac{1000 C_i}{Mr_i} \frac{R(\theta + 273.15)}{P} \quad (6.94)$$

where

- $C_i$  = mass concentration of gas species  $i$  ( $kg \cdot m^{-3}$ )  
 $P$  = pressure (Pa)  
 $\theta$  = temperature ( $^{\circ}C$ )  
 $[i]$  = volume concentration of gas species  $i$  ( $m^3 \cdot m^{-3}$ ).

#### 6.2.16.3 PACKAGING FILM PERMEABILITY

The dependence of packaging film permeability on temperature was modelled by the Arrhenius relationship:

$$P_i = P_{0,i} \exp \left( \frac{-E_{a,i}}{R(\theta_{film} + 273.15)} \right) \quad (6.95)$$

where

- $E_{a,i}$  = activation energy for permeation of gas species  $i$  ( $\text{J}\cdot\text{mol}^{-1}$ )  
 $P_i$  = permeability of the packaging film to gas species  $i$  ( $\text{m}^2\cdot\text{s}^{-1}$ )  
 $P_{0,i}$  = pre-exponential factor for permeation of gas species  $i$  ( $\text{m}^2\cdot\text{s}^{-1}$ ).

#### 6.2.16.4 RELATIVE HUMIDITY OF THE PACKAGE ATMOSPHERE

The relative humidity of the package atmosphere was calculated from

$$RH_p = \frac{P_{w,p}}{P_{sat,p}} \times 100 \quad (6.96)$$

where

- $P_{sat,p}$  = saturated vapour pressure of water at the temperature of the package atmosphere (Pa)  
 $RH_p$  = relative humidity of the package atmosphere (%).

#### 6.2.16.5 SATURATED WATER VAPOUR PRESSURE

The saturated vapour pressure of water at the fruit, package atmosphere, packaging film, and store temperatures was calculated from Antoine's equation (Reid *et al.*, 1987, p. 208):

$$p_{sat} = \exp\left(23.4795 - \frac{3990.56}{\theta + 233.833}\right) \quad (6.97)$$

#### 6.2.16.6 DIFFUSIVITY OF GASES THROUGH HOLES IN THE PACKAGING FILM

The effective diffusivities of  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and water vapour through holes in the packaging film were calculated from

$$D_{i,eff} = \xi D_{i,air} \quad (6.98)$$

where

- $D_{i,air}$  = diffusivity of gas species  $i$  in air ( $\text{m}^2\cdot\text{s}^{-1}$ )  
 $D_{i,eff}$  = effective diffusivity of gas species  $i$  through holes in the packaging film ( $\text{m}^2\cdot\text{s}^{-1}$ )  
 $\xi$  = empirical correction factor for gas diffusion through holes

In modelling the diffusion of gases through holes in the packaging film, gas concentrations immediately outside the holes were assumed to be uniform and equal to the bulk package or external gas concentrations. The empirical factor,  $\xi$ , was included in the MAP model to correct for this assumption. Renault *et al.* (1994a,b) adopted a similar approach in their model for gas transport through micro-perforations.

The temperature dependence of gas diffusivities in air was modelled according to the following relationship (Liley *et al.*, 1984, pp. 3/285-3/286; Lewis, 1990):

$$D_{i,air} = D_{i,ref} \left( \frac{T}{T_{ref}} \right)^{1.75} \quad (6.99)$$

where

- $D_{i,ref}$  = diffusivity of gas species  $i$  in air at temperature  $T_{ref}$  ( $\text{m}^2 \cdot \text{s}^{-1}$ )  
 $T$  = temperature (K)  
 $T_{ref}$  = reference temperature (K).

## Chapter 7

### MODEL IMPLEMENTATION

This chapter outlines the numerical solution method used to solve the model equations formulated in Chapter 6, and describes the computer software designed to implement the numerical solution.

#### 7.1 NUMERICAL SOLUTION METHOD

Various numerical methods have been developed for the solution of initial value problems such as the ordinary differential equation system formulated in Chapter 6. All of these methods are based on a philosophy of discretizing the independent variable (in this case time,  $t$ ) into  $N$  steps, and estimating the values of the dependent variables at time  $t_{n+1}$  from information at one or more previous times,  $t_n$ ,  $t_{n-1}$ , etc. Detailed descriptions and analyses of the available methods can be found in many of the texts dealing with numerical analysis (e.g. Burden & Faires, 1993; Stoer & Bulirsch, 1993). The methods commonly described by such texts fall into three categories:

- (1) *One-step methods.* These methods use information at only one previous value of the independent variable to estimate values of the dependent variables at  $t_{n+1}$ . The Runge-Kutta methods are included in this category.
- (2) *Multi-step methods.* In contrast to the one-step methods, multi-step methods use information at more than one previous value of the independent variable to estimate values of the dependent variables at  $t_{n+1}$ . Predictor-corrector methods are included in this category.
- (3) *Extrapolation methods.* In these methods, each major step of the independent variable is further divided into sub-steps. Starting at  $t_n$ , a one-step method is used with a range of sub-step sizes to produce a series of estimates of the dependent variable at  $t_{n+1}$ . Extrapolation of this series of estimates is then carried out to estimate the value that would have been obtained for an infinite number of sub-steps. The Bulirsch-Stoer method is included in this category.

In general, the choice of numerical method depends on the problem to which the method is to be applied (Press *et al.*, 1986; Burden & Faires, 1993; Stoer & Bulirsch, 1993). Multi-step methods require the least amount of computation in terms of the number of times the ODE right-hand-side functions must be evaluated (Stoer & Bulirsch, 1993). They are therefore advantageous in cases where the right-hand-side functions are very complicated. Sophisticated predictor-corrector methods can achieve high accuracy. However, they involve large computational expenses in terms of the overhead calculations needed for time-step control, and in terms of storage of prior information. They are also complex to program (Press *et al.*, 1986; Stoer & Bulirsch, 1993).

Press *et al.* (1986) recommend the Bulirsch-Stoer method as an efficient method for situations where high-accuracy solutions are required. However, they state that the method is not suitable for differential equations containing non-smooth functions. For the MAP model, step changes in store conditions, and events such as the opening of a hole in the packaging film, could cause problems in this respect.

Although somewhat unflatteringly termed the 'old workhorse' of ODE integrators by Press *et al.* (1986), Runge-Kutta methods do have the advantage of being less sensitive to discontinuities in the ODE right-hand-side functions, and of being straight-forward to program. Stoer & Bulirsch (1993) recommend a particular class of Runge-Kutta methods, the Runge-Kutta-Fehlberg methods, for situations where very high accuracy is not essential. These methods efficiently calculate two Runge-Kutta solutions at each time-step, one of order  $p$  and one of order  $p+1$ . The difference between the two solutions provides an estimate of the error introduced into the lower order solution at each time step (termed the local error). This error estimate can be used by step-size control procedures to keep the error at each time-step within a specified bound.

With the above considerations in mind, a Runge-Kutta-Fehlberg method was chosen as the solution method for the MAP model. The particular method chosen was the popular 4th/5th order method commonly described in standard numerical analysis texts (e.g. Hoffman, 1992; Atkinson, 1993; Burden & Faires, 1993; Champion, 1993; Rice, 1993). For a single ordinary differential equation

$$\frac{dy}{dt} = f(t, y) \quad (7.1)$$

with the initial condition  $y = y_0$  at  $t = 0$ , the method is defined as follows:

$$\hat{y}'_{n+1} = \hat{y}_n + \frac{16}{135}k_1 + \frac{6656}{12825}k_3 + \frac{28561}{56430}k_4 - \frac{9}{50}k_5 + \frac{2}{55}k_6 \quad (7.2)$$

$$\hat{y}_{n+1} = \hat{y}_n + \frac{25}{216}k_1 + \frac{1408}{2565}k_3 + \frac{2197}{4104}k_4 - \frac{1}{5}k_5 \quad (7.3)$$

where

$$k_1 = \Delta t f(t_n, \hat{y}_n) \quad (7.4)$$

$$k_2 = \Delta t f(t_n + \frac{1}{4}\Delta t, \hat{y}_n + \frac{1}{4}k_1) \quad (7.5)$$

$$k_3 = \Delta t f(t_n + \frac{3}{8}\Delta t, \hat{y}_n + \frac{3}{32}k_1 + \frac{9}{32}k_2) \quad (7.6)$$

$$k_4 = \Delta t f(t_n + \frac{12}{13} \Delta t, \hat{y}_n + \frac{1932}{2197} k_1 - \frac{7200}{2197} k_2 + \frac{7296}{2197} k_3) \quad (7.7)$$

$$k_5 = \Delta t f(t_n + \Delta t, \hat{y}_n + \frac{439}{216} k_1 - 8 k_2 + \frac{3680}{513} k_3 - \frac{845}{4104} k_4) \quad (7.8)$$

$$k_6 = \Delta t f(t_n + \frac{1}{2} \Delta t, \hat{y}_n - \frac{8}{27} k_1 + 2 k_2 - \frac{3544}{2565} k_3 + \frac{1859}{4104} k_4 - \frac{11}{40} k_5) \quad (7.9)$$

and where

$$\begin{aligned} \hat{y}_n &= \text{estimate of } y \text{ at time } t_n \\ \hat{y}'_{n+1} &= \text{fifth order estimate of } y \text{ at time } t_{n+1} \\ \hat{y}_{n+1} &= \text{fourth order estimate of } y \text{ at time } t_{n+1} \\ \Delta t &= \text{step size } (t_{n+1} - t_n). \end{aligned}$$

The difference between the 5th and 4th order solutions is given by

$$\hat{y}'_{n+1} - \hat{y}_{n+1} = \frac{1}{360} k_1 - \frac{128}{4275} k_3 - \frac{2197}{75240} k_4 + \frac{1}{50} k_5 + \frac{2}{55} k_6. \quad (7.10)$$

Although the method above provides an estimate of the error in the 4th order solution, in practice the 5th order solution is often used for further calculations. This is done with the expectation that the error in the 5th order solution will be smaller than that in the 4th order solution (Press *et al.*, 1986; Atkinson, 1993; Rice, 1993). The 5th order solution, extended to a system of ordinary differential equations, was used in solving the MAP model.

Error control was achieved by adjusting the size of the time-step to keep local error estimates within a set tolerance bound,  $\epsilon$ . Stoer & Bulirsch (1993) derive the following general relation for estimating a new step-size at the end of each time-step:

$$\Delta t_{new} = \delta \Delta t \quad (7.11)$$

where  $\delta$  is scale-factor given by

$$\delta = \left( \frac{\epsilon}{|\hat{y}'_{n+1} - \hat{y}_{n+1}|} \right)^{\frac{1}{p+1}} \quad (7.12)$$

They also present a modification of Eq. 7.12, recommended by many authors on the basis of extensive numerical experimentation:

$$\delta = \alpha \left( \frac{\epsilon \Delta t}{|\hat{y}'_{n+1} - \hat{y}_{n+1}|} \right)^{\frac{1}{p}} \quad (7.13)$$

where

$\alpha$  = empirical safety factor ( $\approx 0.9$ ).

This relation has also been recommended by Burden & Faires (1993).

Press *et al.* recommend an alternative modification to Eq. 7.12 as follows:

$$\delta = \alpha \left( \frac{\varepsilon}{|\hat{y}'_{n+1} - \hat{y}_{n+1}|} \right)^{\frac{1}{p+1}} \quad \text{for } \varepsilon \geq |\hat{y}'_{n+1} - \hat{y}_{n+1}| \quad (7.14)$$

and

$$\delta = \alpha \left( \frac{\varepsilon}{|\hat{y}'_{n+1} - \hat{y}_{n+1}|} \right)^{\frac{1}{p}} \quad \text{for } \varepsilon < |\hat{y}'_{n+1} - \hat{y}_{n+1}| \quad (7.15)$$

For the MAP simulation, Eqs. 7.14 and 7.15 were found to perform better than Eq. 7.13. The latter appeared to over-optimistically increase the step-size, resulting in a large percentage of failed iterations. Eqs. 7.14 and 7.15 were thus adopted in the current work, with  $p = 4$  and  $\alpha = 0.84$  (Burden & Faires, 1993).

Values of  $\varepsilon$  for each dependent variable were calculated from a global relative tolerance, *RelTol*, as follows:

$$\varepsilon = RelTol \times (|\hat{y}_n| + \kappa) \quad (7.16)$$

The constant  $\kappa$  prevents  $\varepsilon$  from becoming excessively small or zero when  $\hat{y}_n$  crosses or tends to zero. Values of  $\kappa$  were arbitrarily set one order of magnitude lower than the desired precision of the dependent variable,  $\hat{y}_n$ .

The following additional condition for step-size control was set to eliminate large changes in step size (Burden & Faires, 1993):

$$0.1 \leq \delta \leq 4. \quad (7.17)$$

Newly calculated values of  $\hat{y}'_{n+1}$  were accepted only if

$$\left( \frac{\varepsilon}{|\hat{y}'_{n+1} - \hat{y}_{n+1}|} \right) \geq 1 \quad (7.18)$$

If this condition was not met, the values of  $\hat{y}'_{n+1}$  were rejected and the time step repeated with a new (reduced) step-size calculated from Eq. 7.15. In the MAP simulation, step-size control procedures and acceptance/rejection criteria were based on the minimum value of the ratio

$$\left( \frac{\varepsilon}{|\hat{y}'_{n+1} - \hat{y}_{n+1}|} \right) \quad (7.19)$$

calculated for each dependent variable at each time step.

## 7.2 COMPUTER IMPLEMENTATION

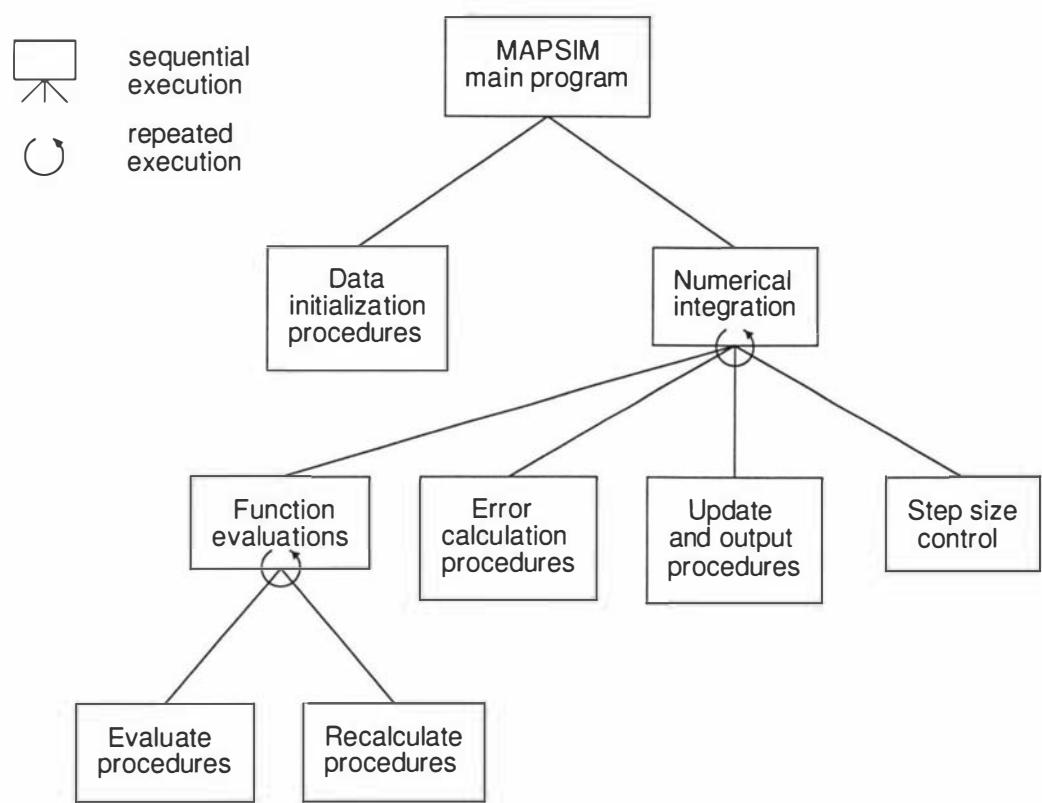
As software design was not central to the main aims of this work, a large expenditure of time and programming effort to produce a highly sophisticated, professional-quality software package was considered unjustified. However, it was considered essential that the implementation meet certain software quality standards, namely:

- (1) *Accuracy.* The overriding aim of the computer implementation was to furnish an accurate solution of the formulated model equations.
- (2) *Clarity.* In the interests of making the code easily understandable, it was desirable that the program be written in a clear, well-structured manner.
- (3) *Ease of use.* Users of the software, although likely to have high levels of technical training, would not necessarily be familiar with the simulation details. As the main user involvement with the simulation concerns data input and program output, it was important that the data entry procedures be flexible and self-explanatory, and that the program output be clearly presented.
- (4) *Robustness.* The program would ideally be free of unexpected causes of failure.

The program (MAPSIM) was developed in the Pascal programming language (Turbo Pascal® Version 7.0 for DOS, Borland International Inc., Scotts Valley, California) and will run on IBM-compatible machines running MS-DOS version 3.3 or higher. Although MAPSIM is executable on machines with an 80386 processor and maths-coprocessor, an 80486 machine or better is recommended to achieve faster execution speeds. The executable file and the full source code for MAPSIM can be found in Appendix A (on diskette). Guidelines for running MAPSIM are given in Appendix B.

### 7.2.1 PROGRAM STRUCTURE

The complete program comprises the main program (MAPSIM) and five program units (GLOBAL, PACKAGE, STORE, DATAIN, and SOLVER). Figure 7.1 shows a



**Figure 7.1** MAPSIM structure diagram.

structure diagram for the overall program. The following sections describe the basic functions of the program units.

**7.2.1.1 UNIT GLOBAL**

This unit makes global constants, data types, procedures, and functions available to the main program and all other program units.

**7.2.1.2 UNITS PACKAGE AND STORE**

Program structure and clarity were enhanced by making use of some of the object-oriented language features provided by Turbo Pascal® Version 7.0.

Simulations of physical systems lend themselves naturally to the object-oriented approach, which seeks to model abstract program data-structures after the real-world objects they represent. Just as the properties and behaviour of real-world objects are inseparably linked, one of the most important tenants of object-oriented programming is the encapsulation of an object’s data together with the code that manipulates that data (Anon., 1992). This concept has been employed in the MAPSIM simulation. The units PACKAGE and STORE contain the MAPSIM object definitions.

For simulation purposes, the modified atmosphere packaging system was divided into four objects: fruit, package atmosphere, packaging materials, and store environment.

These real-world objects were mapped to four corresponding object data types: *TApple*, *TPackAtm*, *TPackage*, and *TStore*. Each of these object data structures consists of two components: the object's data, and the methods that manipulate that data.

Each object's data comprises all the information needed to describe the properties and state of the object as specified by the details of the model formulation. Thus, *TApple* contains all the variables necessary to specify the properties and state of the apples in the MAP system (e.g. fruit temperature, fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations, fruit respiration rate, fruit skin permeances to O<sub>2</sub>, CO<sub>2</sub>, and water vapour, fruit mass, fruit density, fruit volume, fruit surface area, fruit number, etc.). Similarly, *TPackAtm*, *TPackage*, and *TStore* contain all the variables needed to define the properties and states of the package atmosphere, the packaging materials, and the store environment.

Each object's methods define the procedures and functions needed to manipulate the object's data. The MAPSIM object methods were standardized between the four object types, and can be classified as follows:

- (1) *Init* procedures initialize all of an object's data fields at the start of a simulation. The first call to the methods of any object is a call to that object's *Init* procedure.
- (2) *Evaluate* procedures direct the ODE function evaluations corresponding to an object's dependent variables. These procedures are called six times during each time-step (corresponding to the six function evaluations required by the numerical solution method).
- (3) *Recalculate* procedures recalculate the values of those object variables that depend on the value of one or more dependent variables. These procedures are called between each successive call to an *Evaluate* procedure, and also after a failed time step (to reset the variables to their original values at the start of that time step).
- (4) *Update* procedures update the values of all of an object's variables. These procedures are called after each successful time step.
- (5) *WriteOutput* procedures write the values of output variables to a specified output file. These procedures are called at the end of each user-specified output interval.
- (6) *ErrorCalc* procedures calculate the error tolerance values ( $\epsilon$ ) for an object's dependent variables. These procedures are called once every time step.
- (7) *Get* functions pass the value of an object's variable to another object's method or to a program procedure requiring that value.
- (8) *ODE* functions evaluate the ODE right-hand-side functions corresponding to an object's dependent variables. These functions are called only by an object's *Evaluate* procedures.

### 7.2.1.3 UNIT DATAIN

The unit DATAIN contains the code for the procedure *DataInput*. This procedure is responsible for directing the data initialization process.

*DataInput* first prompts the user for a choice of data entry method:

- (1) reading data from an existing data file
- (2) modifying an existing data file, or
- (3) creating a new data file.

*DataInput* then opens a specified input data file (options 1 or 2), prompts the user for new input values (options 2 and 3), writes a new data file (options 2 and 3), opens the new data file (options 2 and 3), and calls object *Init* procedures.

Figure 7.2 shows an example of a MAPSIM input file. A list of definitions of the variable names used to label the data elements in the MAPSIM input files can be found in Appendix A.

### 7.2.1.4 UNIT SOLVER

The unit SOLVER contains the code for two procedures, *Integrate* and *ErrorCalc*. The procedure *ErrorCalc* is private to the unit, as it is only called by the procedure *Integrate*.

The procedure *Integrate* first prompts the user to enter three integration control parameters (total simulation time, maximum time step, and maximum integration error) and the desired output interval. It then prompts the user for output file names, opens the specified output files, and writes the output file headers. The numerical integration loop is then entered.

For each time step, *Integrate* performs six ODE function evaluations (involving six calls to object *Evaluate* procedures, with calls to object *Recalculate* procedures between each evaluation), calls the procedure *ErrorCalc*, and accepts or rejects the time step depending on the result returned by *ErrorCalc*. If the time step is accepted, *Integrate* calls object *Update* procedures, updates the current simulation time, checks whether the end of an output interval has been reached, and calls object *WriteOutput* procedures if necessary. If the time step fails, *Integrate* calls object *Recalculate* procedures to reset object variables back to their original values at the start of the time step. No updating is performed after a failed time step. After accepting or rejecting a time step, *Integrate* calculates a new time step size and checks that this is not smaller than the minimum allowable time step (the program aborts with an error message if this occurs). The timing of discrete events (e.g. output time, change in store conditions, or end of simulation) is checked, and, if the time at which an event occurs is about to be passed, the time step is adjusted to coincide with the event. If the end of the simulation has not been reached, *Integrate* then proceeds with the next iteration.

Once the end of the simulation is reached, *Integrate* leaves the numerical integration

```

Fruit Data Section
RefTemp (°C) : 1.600000000000000E+0000
RefMaxRespRate (kg O2/kg fruit/s) : 7.800000000000000E-0010
Refkm (kg O2/m3) : 1.000000000000000E-0001
RespModel (N, U, or M) : n
Refkic (kg CO2/m3) : 1.000000000000000E+0020
Refkiu (kg CO2/m3) : 1.000000000000000E+0020
Q10 : 3.500000000000000E+0000
RespQuotient (kg CO2/kg O2) : 1.375000000000000E+0000
O2SkinPerm (m/s) : 2.500000000000000E-0007
CO2SkinPerm (m/s) : 2.900000000000000E-0007
H2OSkinPerm (s/m) : 3.000000000000000E-0010
HTModel (H or F) : f
SpecHeatCapacity (J/kg/K) : 3.650000000000000E+0003
RespHeatGen (J/kg O2) : 1.850000000000000E+0007
HalfCoolingTime (hours) : 0.000000000000000E+0000
InitDensity (kg/m3) : 9.049000000000000E+0002
Porosity (m3/m3) : 1.400000000000000E-0001
AreaCoeff : 4.880000000000000E+0000
AreaExp : 6.610000000000000E-0001
FruitWaterAct : 9.800000000000000E-0001
InitFruitTemp (deg C) : 1.600000000000000E+0000
InitFruitO2 (%) : 1.970000000000000E+0001
InitFruitCO2 (%) : 1.400000000000000E+0000
InitFruitMass (kg) : 1.843000000000000E+0001
FruitNo : 125

Packaging Material Data Section
FilmArea (m2) : 1.457000000000000E+0000
FilmThickness (m) : 4.430000000000000E-0005
RefO2Perm (m2/s) : 1.010000000000000E-0004
RefCO2Perm (m2/s) : 1.520000000000000E-0004
RefN2Perm (m2/s) : 9.230000000000000E-0004
RefH2OPerm (m2/s) : 1.370000000000000E-0004
ActEnergyO2 (J/mol) : 4.140000000000000E+0004
ActEnergyCO2 (J/mol) : 3.850000000000000E+0004
ActEnergyN2 (J/mol) : 4.940000000000000E+0004
ActEnergyH2O (J/mol) : 3.350000000000000E+0004
HolesPresent (Y or N) : n
HoleNo : 0
HoleDiameter (m) : 0.000000000000000E+0000
HoleTime (hrs) : 0.000000000000000E+0000
InitTemp (°C) : 1.600000000000000E+0000
OverallHTC (W/m2/K) : 9.700000000000000E-0001
PackArea (m2) : 8.050000000000000E-0001
InitTotVol (m3) : 4.500000000000000E-0002
MinTotVol (m3) : 3.500000000000000E-0002
TrayDryMass (kg/tray) : 8.000000000000000E-0002
TrayArea (m2/tray) : 4.500000000000000E-0001
TrayNo : 6
InitTrayEqRH (%) : 9.000000000000000E+0001
GAB_Xm (kg water/kg dry mass) : 6.537000000000000E-0002
GAB_C : 5.490000000000000E+0004
GAB_k : 7.330000000000000E-0001

Package Atmosphere Data Section
IntHTC (W/m2/K) : 1.900000000000000E+0000
FruitHTC (W/m2/K) : 2.900000000000000E+0000
IntMTC (s/m) : 1.000000000000000E-0008
FruitMTC (s/m) : 1.000000000000000E-0008
TrayMTC (s/m) : 1.000000000000000E-0008
DiffusivityCorrFac : 1.000000000000000E+0000
InitPackO2 (%) : 2.095000000000000E+0001
InitPackCO2 (%) : 3.000000000000000E-0002
InitPackRH (%) : 9.000000000000000E+0001
InitPackTemp (deg C) : 1.600000000000000E+0000

Store Data Section
StageNo : 1
Storage regime :
Time (hrs) Temp (deg C) RH (%) O2 (%) CO2 (%)
0.000000000E+0000 1.600000000E+0000 9.000000000E+0001 2.095000000E+0001 3.000000000E-0002

```

Figure 7.2 Example of a MAPSIM input file.

Run ID: 1993 Braeburn Cartons 1 to 12  
 Input Data Filename: bbctn1.dat

(See end of Table for key to column heading symbols).

| Time<br>(days) | Tf<br>(deg C) | O2f<br>(%) | CO2f<br>(%) | CumO2<br>(kg O2/kg) | WghtLs<br>(%) | MCf<br>(g) |
|----------------|---------------|------------|-------------|---------------------|---------------|------------|
| 0.00           | 1.600         | 19.700     | 1.400       | 0.0000              | 0.0000        | 0.00       |
| 1.00           | 1.757         | 17.355     | 2.932       | 0.0000              | 0.0152        | 0.00       |
| 2.00           | 1.820         | 15.675     | 3.690       | 0.0001              | 0.0287        | 0.00       |
| 3.00           | 1.844         | 14.281     | 3.993       | 0.0001              | 0.0406        | 0.00       |
| 4.00           | 1.850         | 13.112     | 4.073       | 0.0002              | 0.0511        | 0.00       |
| 5.00           | 1.848         | 12.130     | 4.047       | 0.0002              | 0.0605        | 0.00       |
| 6.00           | 1.844         | 11.308     | 3.975       | 0.0003              | 0.0688        | 0.00       |
| 7.00           | 1.839         | 10.626     | 3.887       | 0.0003              | 0.0763        | 0.00       |
| 8.00           | 1.834         | 10.065     | 3.797       | 0.0004              | 0.0830        | 0.00       |
| 9.00           | 1.829         | 9.606      | 3.714       | 0.0004              | 0.0891        | 0.00       |
| 10.00          | 1.825         | 9.234      | 3.639       | 0.0004              | 0.0946        | 0.00       |
| 11.00          | 1.821         | 8.935      | 3.575       | 0.0005              | 0.0997        | 0.00       |
| 12.00          | 1.818         | 8.696      | 3.521       | 0.0005              | 0.1044        | 0.00       |
| 13.00          | 1.815         | 8.506      | 3.476       | 0.0006              | 0.1087        | 0.00       |
| 14.00          | 1.813         | 8.355      | 3.439       | 0.0006              | 0.1127        | 0.00       |
| 15.00          | 1.812         | 8.236      | 3.409       | 0.0006              | 0.1164        | 0.00       |
| 16.00          | 1.810         | 8.143      | 3.384       | 0.0007              | 0.1199        | 0.00       |
| 17.00          | 1.809         | 8.070      | 3.365       | 0.0007              | 0.1233        | 0.00       |
| 18.00          | 1.808         | 8.012      | 3.350       | 0.0007              | 0.1264        | 0.00       |
| 19.00          | 1.808         | 7.968      | 3.338       | 0.0008              | 0.1294        | 0.00       |
| 20.00          | 1.807         | 7.933      | 3.328       | 0.0008              | 0.1322        | 0.00       |
| 21.00          | 1.807         | 7.906      | 3.321       | 0.0009              | 0.1349        | 0.00       |
| 22.00          | 1.807         | 7.886      | 3.315       | 0.0009              | 0.1375        | 0.00       |
| 23.00          | 1.806         | 7.870      | 3.311       | 0.0009              | 0.1400        | 0.00       |
| 24.00          | 1.806         | 7.857      | 3.307       | 0.0010              | 0.1425        | 0.00       |
| 25.00          | 1.806         | 7.848      | 3.304       | 0.0010              | 0.1448        | 0.00       |
| 26.00          | 1.806         | 7.840      | 3.302       | 0.0010              | 0.1471        | 0.00       |
| 27.00          | 1.806         | 7.835      | 3.301       | 0.0011              | 0.1494        | 0.00       |
| 28.00          | 1.806         | 7.831      | 3.299       | 0.0011              | 0.1516        | 0.00       |
| 29.00          | 1.806         | 7.827      | 3.298       | 0.0011              | 0.1537        | 0.00       |
| 30.00          | 1.806         | 7.825      | 3.298       | 0.0012              | 0.1558        | 0.00       |
| 31.00          | 1.806         | 7.823      | 3.297       | 0.0012              | 0.1579        | 0.00       |
| 32.00          | 1.806         | 7.822      | 3.297       | 0.0013              | 0.1600        | 0.00       |

Key:

Tf = fruit temperature  
 O2f = fruit internal O2 concentration  
 CO2f = fruit internal CO2 concentration  
 CumO2 = fruit cumulative O2 consumption  
 WghtLs = fruit weight loss  
 MCf = total mass of condensate on fruit

**Figure 7.3** Example of a MAPSIM fruit-output file.

loop, closes output files, and outputs terminal information to the user screen (minimum and maximum successful time steps, average time step, number of successful iterations, number of failed iterations, percentage of failed iterations, and names of the newly created output files).

The procedure *ErrorCalc* is responsible for providing *Integrate* with a measure of the maximum integration error at the current time step. To do this, *ErrorCalc* calculates local error estimates (the difference between the 4th and 5th order solutions) for each dependent variable, calls object *ErrorCalc* procedures (which return error tolerances for each dependent variable), calculates tolerance/error ratios for each dependent variable, and returns the resulting minimum tolerance/error ratio to *Integrate*.

Figures 7.3 and 7.4 show examples of the MAPSIM output files.

Run ID: 1993 Braeburn Cartons 1 to 12  
 Input Data Filename: bbctn1.dat

(See end of Table for key to column heading symbols).

| Time<br>(days) | Tp<br>(deg C) | O2p<br>(%) | CO2p<br>(%) | RH<br>(%) | Shrinkage<br>(%) | Press<br>(Atm) | MCp<br>(g) | Xt<br>(kg/kg) |
|----------------|---------------|------------|-------------|-----------|------------------|----------------|------------|---------------|
| 0.00           | 1.600         | 20.823     | 0.030       | 90.0      | 0.000            | 1.000          | 0.00       | 0.192         |
| 1.00           | 1.748         | 18.763     | 1.673       | 91.3      | 0.459            | 1.000          | 0.00       | 0.197         |
| 2.00           | 1.802         | 17.071     | 2.422       | 92.3      | 1.646            | 1.000          | 0.00       | 0.202         |
| 3.00           | 1.821         | 15.655     | 2.741       | 93.1      | 3.062            | 1.000          | 0.00       | 0.205         |
| 4.00           | 1.825         | 14.459     | 2.847       | 93.8      | 4.497            | 1.000          | 0.00       | 0.209         |
| 5.00           | 1.823         | 13.449     | 2.851       | 94.4      | 5.857            | 1.000          | 0.00       | 0.212         |
| 6.00           | 1.819         | 12.601     | 2.809       | 94.8      | 7.108            | 1.000          | 0.00       | 0.214         |
| 7.00           | 1.814         | 11.895     | 2.750       | 95.2      | 8.241            | 1.000          | 0.00       | 0.216         |
| 8.00           | 1.809         | 11.311     | 2.686       | 95.6      | 9.265            | 1.000          | 0.00       | 0.218         |
| 9.00           | 1.804         | 10.834     | 2.625       | 95.9      | 10.189           | 1.000          | 0.00       | 0.220         |
| 10.00          | 1.800         | 10.446     | 2.570       | 96.1      | 11.028           | 1.000          | 0.00       | 0.221         |
| 11.00          | 1.796         | 10.133     | 2.522       | 96.3      | 11.795           | 1.000          | 0.00       | 0.222         |
| 12.00          | 1.793         | 9.883      | 2.481       | 96.5      | 12.502           | 1.000          | 0.00       | 0.223         |
| 13.00          | 1.791         | 9.683      | 2.447       | 96.7      | 13.161           | 1.000          | 0.00       | 0.224         |
| 14.00          | 1.789         | 9.525      | 2.419       | 96.9      | 13.779           | 1.000          | 0.00       | 0.225         |
| 15.00          | 1.787         | 9.400      | 2.397       | 97.0      | 14.365           | 1.000          | 0.00       | 0.226         |
| 16.00          | 1.786         | 9.302      | 2.378       | 97.1      | 14.925           | 1.000          | 0.00       | 0.227         |
| 17.00          | 1.785         | 9.225      | 2.364       | 97.2      | 15.465           | 1.000          | 0.00       | 0.227         |
| 18.00          | 1.784         | 9.164      | 2.352       | 97.3      | 15.989           | 1.000          | 0.00       | 0.228         |
| 19.00          | 1.783         | 9.118      | 2.343       | 97.4      | 16.500           | 1.000          | 0.00       | 0.228         |
| 20.00          | 1.782         | 9.081      | 2.336       | 97.4      | 17.001           | 1.000          | 0.00       | 0.229         |
| 21.00          | 1.782         | 9.053      | 2.330       | 97.5      | 17.495           | 1.000          | 0.00       | 0.229         |
| 22.00          | 1.782         | 9.031      | 2.326       | 97.5      | 17.982           | 1.000          | 0.00       | 0.229         |
| 23.00          | 1.781         | 9.014      | 2.322       | 97.6      | 18.465           | 1.000          | 0.00       | 0.230         |
| 24.00          | 1.781         | 9.001      | 2.319       | 97.6      | 18.945           | 1.000          | 0.00       | 0.230         |
| 25.00          | 1.781         | 8.991      | 2.317       | 97.7      | 19.421           | 1.000          | 0.00       | 0.230         |
| 26.00          | 1.781         | 8.983      | 2.316       | 97.7      | 19.895           | 1.000          | 0.00       | 0.230         |
| 27.00          | 1.781         | 8.977      | 2.315       | 97.7      | 20.368           | 1.000          | 0.00       | 0.230         |
| 28.00          | 1.781         | 8.973      | 2.314       | 97.7      | 20.839           | 1.000          | 0.00       | 0.231         |
| 29.00          | 1.781         | 8.969      | 2.313       | 97.8      | 21.310           | 1.000          | 0.00       | 0.231         |
| 30.00          | 1.781         | 8.967      | 2.312       | 97.8      | 21.779           | 1.000          | 0.00       | 0.231         |
| 31.00          | 1.781         | 8.965      | 2.312       | 97.8      | 22.248           | 1.000          | 0.00       | 0.231         |
| 32.00          | 1.781         | 8.963      | 2.311       | 97.8      | 22.717           | 1.000          | 0.00       | 0.231         |

Key:

Tp = package air temperature  
 O2p = package O2 concentration  
 CO2p = package CO2 concentration  
 RH = package relative humidity  
 Shrinkage = package air volume shrinkage  
 Press = package atmosphere pressure  
 MCp = mass of condensate on packaging film inside surface  
 Xt = moisture content of moulded pulp trays (dry solids basis)

**Figure 7.4** Example of a MAPSIM package-output file.

## 7.2.2 PROGRAM TESTING

The accuracy of the MAPSIM program was tested by running the program with various input data set to extreme values, or with some variables held constant, such that an analytical solution to one or more of the model equations could be found. Program output was then compared to results predicted by the appropriate analytical solution. In all cases, program outputs matched the analytical solutions, indicating that the program and the numerical calculation procedure were operating as expected.

Details of the program testing are given in Appendix C.

## Chapter 8

### MODEL INPUT DATA

This chapter presents the input data collected for validation of the MAP model (dealt with in Chapter 9).

Input data for the MAP model were obtained by direct measurement, by experimental estimation, or from literature data. Data obtained by experimental estimation were collected according to the experimental methods described in Chapter 4.

#### 8.1 FRUIT DATA

##### 8.1.1 MASS AND DIMENSIONAL DATA

The MAP model requires inputs of both initial total fruit mass and initial fruit density, as well as values for the parameters of the fruit surface area and volume correlation (Eq. 6.17). Estimates of fruit surface area were also required for calculating fruit skin permeances, as described in section 8.1.2.

Tables 8.1 and 8.2 list the package fruit masses recorded at the start of the carton and bag trials respectively. These masses were used to estimate average individual fruit masses for each cultivar and count size. Average individual fruit volumes were estimated from volume measurements of samples of 40 to 100 fruit for each cultivar and count size. Fruit volumes were measured by water displacement (with the mass of displaced water estimated from the apparent increase in weight of a partially full container of water when fruit were submerged and held steady just beneath the water's

**Table 8.1** Fruit masses for the carton trials.

| Trial  | Fruit count size | Average fruit mass per carton <sup>a</sup> (kg) | n <sup>b</sup> |
|--------|------------------|-------------------------------------------------|----------------|
| BB93-A | 125              | 18.43 ± 0.03                                    | 14             |
|        | 80               | 18.76 ± 0.07                                    | 6              |
| RG94-A | 100              | 16.89 ± 0.06                                    | 10             |
| RG94-B | 100              | 16.71 ± 0.12                                    | 4              |
| RG94-C | 100              | 16.78 ± 0.07                                    | 8              |
| BB94-A | 125              | 19.02 ± 0.26                                    | 8              |
| BB94-B | 125              | 18.67 ± 0.14                                    | 8              |
| GS94-A | 125              | 18.65 ± 0.05                                    | 8              |

<sup>a</sup> Values presented as 'mean ± 95% confidence interval on mean'.

<sup>b</sup> n = sample size (number of cartons).

**Table 8.2** Fruit masses for the bag trials.

| Trial  | Fruit<br>count size | Number of<br>fruit per bag | Average fruit mass<br>per bag <sup>a</sup><br>(kg) | n <sup>b</sup> |
|--------|---------------------|----------------------------|----------------------------------------------------|----------------|
| BB93-B | 125                 | 10                         | 1.433 ± 0.021                                      | 5              |
|        | 125                 | 5                          | 0.715                                              | 2              |
|        | 80                  | 10                         | 2.278                                              | 2              |
|        | 80                  | 5                          | 1.165                                              | 2              |
| BB93-C | 125                 | 10                         | 1.460                                              | 2              |
|        | 125                 | 5                          | 0.725                                              | 2              |
|        | 80                  | 10                         | 2.318                                              | 2              |
|        | 80                  | 5                          | 1.157 ± 0.013                                      | 5              |
| GS94-B | 125                 | 10                         | 1.480 ± 0.014                                      | 10             |

<sup>a</sup> Values presented as ‘mean ± 95% confidence interval on mean’ (for n > 2).

<sup>b</sup> n = sample size (number of bags).

**Table 8.3** Parameters for the fruit surface area and volume correlation <sup>a</sup>.

| Cultivar                 | <i>a</i> | <i>b</i> |
|--------------------------|----------|----------|
| ‘Royal Gala’             | 4.52     | 0.653    |
| ‘Braeburn’               | 4.88     | 0.661    |
| ‘Red Delicious’          | 4.88     | 0.661    |
| ‘Granny Smith’           | 4.87     | 0.663    |
| Above cultivars combined | 4.77     | 0.659    |

<sup>a</sup> From Clayton *et al.* (1995).

**Table 8.4** Fruit density and dimensional data.

| Trial    | Fruit<br>count size | $V_n \times 10^6$<br>(m <sup>3</sup> ) | $A_n \times 10^2$<br>(m <sup>2</sup> ) | $M_{n,initial}$<br>(kg) | $\rho_{f,initial}$<br>(kg·m <sup>-3</sup> ) |
|----------|---------------------|----------------------------------------|----------------------------------------|-------------------------|---------------------------------------------|
| BB93-A   | 125                 | 163.0                                  | 1.530                                  | 0.1475                  | 904.9                                       |
|          | 80                  | 267.5                                  | 2.123                                  | 0.2345                  | 876.6                                       |
| BB93-B/C | 125                 | 163.0                                  | 1.530                                  | 0.1456                  | 893.3                                       |
|          | 80                  | 267.5                                  | 2.123                                  | 0.2316                  | 865.8                                       |
| RG94-A   | 100                 | 195.9                                  | 1.713                                  | 0.1689                  | 862.2                                       |
| RG94-B   | 100                 | 195.9                                  | 1.713                                  | 0.1671                  | 853.0                                       |
| RG94-C   | 100                 | 195.9                                  | 1.713                                  | 0.1678                  | 856.6                                       |
| BB94-A   | 125                 | 167.4                                  | 1.557                                  | 0.1522                  | 909.2                                       |
| BB94-B   | 125                 | 167.4                                  | 1.557                                  | 0.1494                  | 892.5                                       |
| GS94-A   | 125                 | 181.1                                  | 1.609                                  | 0.1492                  | 823.9                                       |
| GS94-B   | 125                 | 181.1                                  | 1.609                                  | 0.1480                  | 817.2                                       |

surface). Initial fruit densities were calculated from average individual fruit masses and volumes. Fruit surface areas for the calculation of fruit skin permeances were estimated from the fruit surface area-volume correlation proposed by Clayton *et al.* (1995) (Eq. 6.17). The parameters for this correlation were taken from Clayton *et al.* (1995) and are given in Table 8.3.

Table 8.4 summarizes the fruit density and dimensional data.

### 8.1.2 SKIN PERMEANCES TO O<sub>2</sub> AND CO<sub>2</sub>

Fruit skin permeances to O<sub>2</sub> and CO<sub>2</sub> were calculated from the steady-state respiration rates and internal atmosphere compositions measured for fruit stored in air (sections 4.2.1 and 4.2.2):

$$k_i = \frac{N_i M_n}{A_n ([i]_{ext} - [i]_{int})} \quad (8.1)$$

where

- $A_n$  = individual fruit surface area (m<sup>2</sup>)
- $k_i$  = fruit skin permeance to gas species  $i$  (m·s<sup>-1</sup>)
- $M_n$  = individual fruit mass (kg)
- $N_i$  = rate of transfer of gas species  $i$  across the fruit skin per unit mass of fruit (m<sup>3</sup>·kg<sup>-1</sup>·s<sup>-1</sup>)
- $[i]_{ext}$  = volume concentration of gas species  $i$  external to the fruit (m<sup>3</sup>·m<sup>-3</sup>)
- $[i]_{int}$  = volume concentration of gas species  $i$  in the fruit internal atmosphere (m<sup>3</sup>·m<sup>-3</sup>).

Values of  $N_{O_2}$  were estimated from measured fruit respiration rates ( $N_{CO_2}$ ) assuming a volumetric respiratory quotient of 1.

Table 8.5 lists the average internal atmosphere compositions measured for the 1993 and 1994 season fruit. Vial and core samples for the 1993 'Braeburn' fruit at 15.3°C did not differ significantly in terms of either O<sub>2</sub> or CO<sub>2</sub> concentration. However, it should be noted that these vial and core samples were not taken from the same sample of fruit and that paired measurements for a more rigorous comparison of vial and core samples were therefore not available.

Table 8.6 lists the average respiration rates measured in air for the 1993 and 1994 season fruit. For the 1993 'Braeburn' fruit, two sets of respiration data measured in air at 1.6°C were available: one set of data measured for cartons at the start of the carton trials and the other set measured for trays of fruit during the bag trials. This second set of data was significantly lower than the first, presumably because of the advanced maturity of fruit used in the bag trials, which were started 2-2½ months later than the carton trials. As the internal atmospheres listed in Table 8.5 were measured for fruit used in the bag trials, the second set of respiration data at 1.6°C was used as the corresponding average respiration rate for skin permeance calculations.

**Table 8.5** Measured internal atmosphere compositions for fruit stored in air.

| Cultivar            | Temperature<br>(°C) | Method       | $[O_2]_{int} \times 10^2$ <sup>a</sup><br>(m <sup>3</sup> m <sup>-3</sup> ) | $[CO_2]_{int} \times 10^2$ <sup>a</sup><br>(m <sup>3</sup> m <sup>-3</sup> ) | n <sup>b</sup> |
|---------------------|---------------------|--------------|-----------------------------------------------------------------------------|------------------------------------------------------------------------------|----------------|
| <i>1993 Season:</i> |                     |              |                                                                             |                                                                              |                |
| 'Braeburn'          | 1.6                 | Vials        | 19.7 ± 0.5                                                                  | 1.4 ± 0.3                                                                    | 11             |
|                     | 15.3                | Vials        | 14.4 ± 1.8                                                                  | 5.1 ± 0.9                                                                    | 11             |
|                     | 15.3                | Core samples | 13.2 ± 0.8                                                                  | 5.1 ± 0.3                                                                    | 19             |
| <i>1994 Season:</i> |                     |              |                                                                             |                                                                              |                |
| 'Royal Gala'        | 1.2                 | Core samples | 20.66 ± 0.05                                                                | 0.34 ± 0.03                                                                  | 20             |
|                     | 19                  | Core samples | 18.92 ± 0.22                                                                | 2.34 ± 0.18                                                                  | 20             |
| 'Braeburn'          | 0.8                 | Core samples | 19.60 ± 0.13                                                                | 1.21 ± 0.09                                                                  | 25             |
|                     | 20                  | Core samples | 12.7 ± 1.0                                                                  | 6.6 ± 0.5                                                                    | 25             |
| 'Granny Smith'      | 0.8                 | Core samples | 19.92 ± 0.16                                                                | 1.16 ± 0.10                                                                  | 25             |
|                     | 20                  | Core samples | 12.0 ± 1.0                                                                  | 6.0 ± 0.3                                                                    | 25             |

<sup>a</sup> Values presented as 'mean ± 95% confidence interval on mean'.<sup>b</sup> n = sample size (number of fruit).**Table 8.6** Measured respiration rates for fruit stored in air.

| Cultivar            | Temperature<br>(°C) | Quantity | $N_{CO_2} \times 10^{10}$ <sup>a</sup><br>(m <sup>3</sup> ·kg <sup>-1</sup> ·s <sup>-1</sup> ) | n <sup>b</sup> |
|---------------------|---------------------|----------|------------------------------------------------------------------------------------------------|----------------|
| <i>1993 Season:</i> |                     |          |                                                                                                |                |
| 'Braeburn'          | 1.6                 | Carton   | 4.06 ± 0.11                                                                                    | 6              |
|                     | 1.6                 | Tray     | 3.18                                                                                           | 2              |
|                     | 15.3                | Tray     | 16.6                                                                                           | 2              |
| <i>1994 Season:</i> |                     |          |                                                                                                |                |
| 'Royal Gala'        | 1.2                 | Carton   | 4.81 ± 0.20                                                                                    | 10             |
|                     | 20                  | Tray     | 38.4                                                                                           | 2              |
| 'Braeburn'          | 1.2                 | Carton   | 4.06 ± 0.12                                                                                    | 16             |
|                     | 20.4                | Tray     | 30.6 ± 2.5                                                                                     | 4              |
| 'Granny Smith'      | 0.8                 | Carton   | 3.97 ± 0.11                                                                                    | 8              |
|                     | 20.4                | Tray     | 35.8 ± 2.4                                                                                     | 5              |

<sup>a</sup> Values presented as 'mean ± 95% confidence interval on mean' (for n > 2).<sup>b</sup> n = sample size (number of cartons or trays).

**Table 8.7** Fruit skin permeances to O<sub>2</sub> and CO<sub>2</sub>.

| Cultivar            | Temperature<br>(°C) | $k_{O_2} \times 10^7$<br>(m·s <sup>-1</sup> ) | $k_{CO_2} \times 10^7$<br>(m·s <sup>-1</sup> ) |
|---------------------|---------------------|-----------------------------------------------|------------------------------------------------|
| <i>1993 Season:</i> |                     |                                               |                                                |
| 'Braeburn'          | 1.6                 | 2.67                                          | 2.45                                           |
|                     | 15.3                | 2.33                                          | 3.37                                           |
| <i>1994 Season:</i> |                     |                                               |                                                |
| 'Royal Gala'        | 1.2                 | 16.7                                          | 15.6                                           |
|                     | 20                  | 18.5                                          | 16.4                                           |
| 'Braeburn'          | 1                   | 2.92                                          | 3.33                                           |
|                     | 20                  | 3.58                                          | 4.50                                           |
| 'Granny Smith'      | 0.8                 | 3.57                                          | 3.26                                           |
|                     | 20                  | 3.71                                          | 5.55                                           |

Table 8.7 lists the average skin permeances to O<sub>2</sub> and CO<sub>2</sub> calculated from the data in Tables 8.5 and 8.6. With the exception of skin permeance to O<sub>2</sub> for the 1993 'Braeburn' fruit, the data suggest that skin permeances tend to increase with temperature. This observation is consistent with the general effect of temperature on mass diffusion processes. However, the variation of skin permeance with temperature appears to be reasonably limited. This is supported by the work of Dadzie (1992), who found no consistent, significant variation of skin permeance with temperature for eight different cultivars between 0 and 30°C. In light of the limited variation of skin permeance with temperature, skin permeance values for the MAP model runs were obtained by averaging the high- and low-temperature values listed in Table 8.7 for each cultivar.

The internal atmosphere compositions, respiration rates, and skin permeances listed in Tables 8.5 to 8.7 are consistent with data reported by Dadzie (1992) for New Zealand grown 'Braeburn', 'Royal Gala', and 'Granny Smith' apples.

### 8.1.3 SKIN PERMEANCE TO WATER VAPOUR

Table 8.8 lists skin permeances to water vapour estimated for 'Braeburn', 'Royal Gala', and 'Granny Smith' apples. These values were calculated from total weight-loss and carbon-loss data reported by Banks (1994) for fruit grown in New Zealand during the 1994 season.

### 8.1.4 RESPIRATION RATE MODELS

An objective in formulating the MAP model was to keep the model general enough to facilitate its possible future application to horticultural products other than apples (Chapter 3). With this in mind, the Michaelis-Menten respiration model (Eq. 6.6) incorporated into the MAP model was kept as general as possible. Rigorous validation

**Table 8.8** Fruit skin permeances to water vapour.

| Cultivar       | $k_{g,skin} \times 10^{10}$<br>(s m <sup>-1</sup> ) |
|----------------|-----------------------------------------------------|
| 'Royal Gala'   | 3.1                                                 |
| 'Braeburn'     | 3.0                                                 |
| 'Granny Smith' | 2.0                                                 |

of Eq. 6.6, and accurate fitting of its four parameters, would require fruit respiration data covering an extensive range of atmosphere compositions and temperatures. In particular, data over a range of independently varied O<sub>2</sub> and CO<sub>2</sub> concentrations would be required to conclusively separate the effects of O<sub>2</sub> and CO<sub>2</sub> on respiration rate.

The respiration data generated from the MA trials described in this work were limited to three atmosphere compositions at cool-storage temperatures (air, steady-state atmospheres formed inside the 25 µm liners, and steady-state atmospheres formed inside the 40 µm liners) and one atmosphere composition (air) at a temperature of 15°C or 20°C. Furthermore, O<sub>2</sub> and CO<sub>2</sub> concentrations in the three different atmospheres were highly correlated, precluding any definitive separation of O<sub>2</sub> and CO<sub>2</sub> effects. In light of these limitations, two simplified respiration models were fitted to the available respiration rate data:

- (a) respiration as a function of temperature and fruit internal O<sub>2</sub> concentration only (no CO<sub>2</sub> inhibition);
- (b) respiration as a function of temperature and fruit internal CO<sub>2</sub> concentration only ( $k_m$  assumed to be zero).

The limited range of atmospheres for which respiration data were available means that the respiration models formulated in the following two sections must not be regarded as mechanistically realistic. Rather, they represent empirical curve-fits valid for predictions within the range of the experimental data only.

In the analysis of respiration rate data, respiration measurements in m<sup>3</sup> CO<sub>2</sub>·kg<sup>-1</sup>·s<sup>-1</sup>, were converted to kg O<sub>2</sub>·kg<sup>-1</sup>·s<sup>-1</sup> by assuming a volumetric respiratory quotient of 1. The fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations corresponding to individual respiration-rate measurements were estimated from respiration rates, skin permeances, and steady-state package atmospheres by rearrangement of Eq. 8.1.

#### 8.1.4.1 RESPIRATION AS A FUNCTION OF FRUIT INTERNAL O<sub>2</sub>

##### *Effect of O<sub>2</sub>*

If CO<sub>2</sub> is assumed to have no inhibitory effect on respiration rate, then Eq. 6.6 reduces to the well known Michaelis-Menten equation:

$$v = \frac{v_{max} C_{O_2,f}}{k_m + C_{O_2,f}} \quad (8.2)$$

where

- $C_{O_2,f}$  =  $O_2$  concentration in the fruit internal atmosphere ( $kg\ O_2 \cdot m^{-3}$ )  
 $k_m$  = half saturation constant ( $kg\ O_2 \cdot m^{-3}$ )  
 $v$  = aerobic respiration rate ( $kg\ O_2 \cdot kg^{-1} \cdot s^{-1}$ )  
 $v_{max}$  = maximum aerobic respiration rate ( $kg\ O_2 \cdot kg^{-1} \cdot s^{-1}$ ).

Transformation of Eq. 8.2 yields the following relationship:

$$\frac{C_{O_2,f}}{v} = \frac{k_m}{v_{max}} + \frac{C_{O_2,f}}{v_{max}} \quad (8.3)$$

Thus, a plot of  $C_{O_2,f}/v$  versus  $C_{O_2,f}$  should yield a straight line with a slope of  $1/v_{max}$  and a y-axis intercept of  $k_m/v_{max}$ . This linearization of the Michaelis-Menten equation was preferred over the more generally known double-reciprocal (Lineweaver-Burk) plot because of the latter's severe distortion of any experimental error in the measured values of  $v$  (Cornish-Bowden & Wharton, 1988, pp. 8-9; Cornish-Bowden, 1976, pp. 25-27).

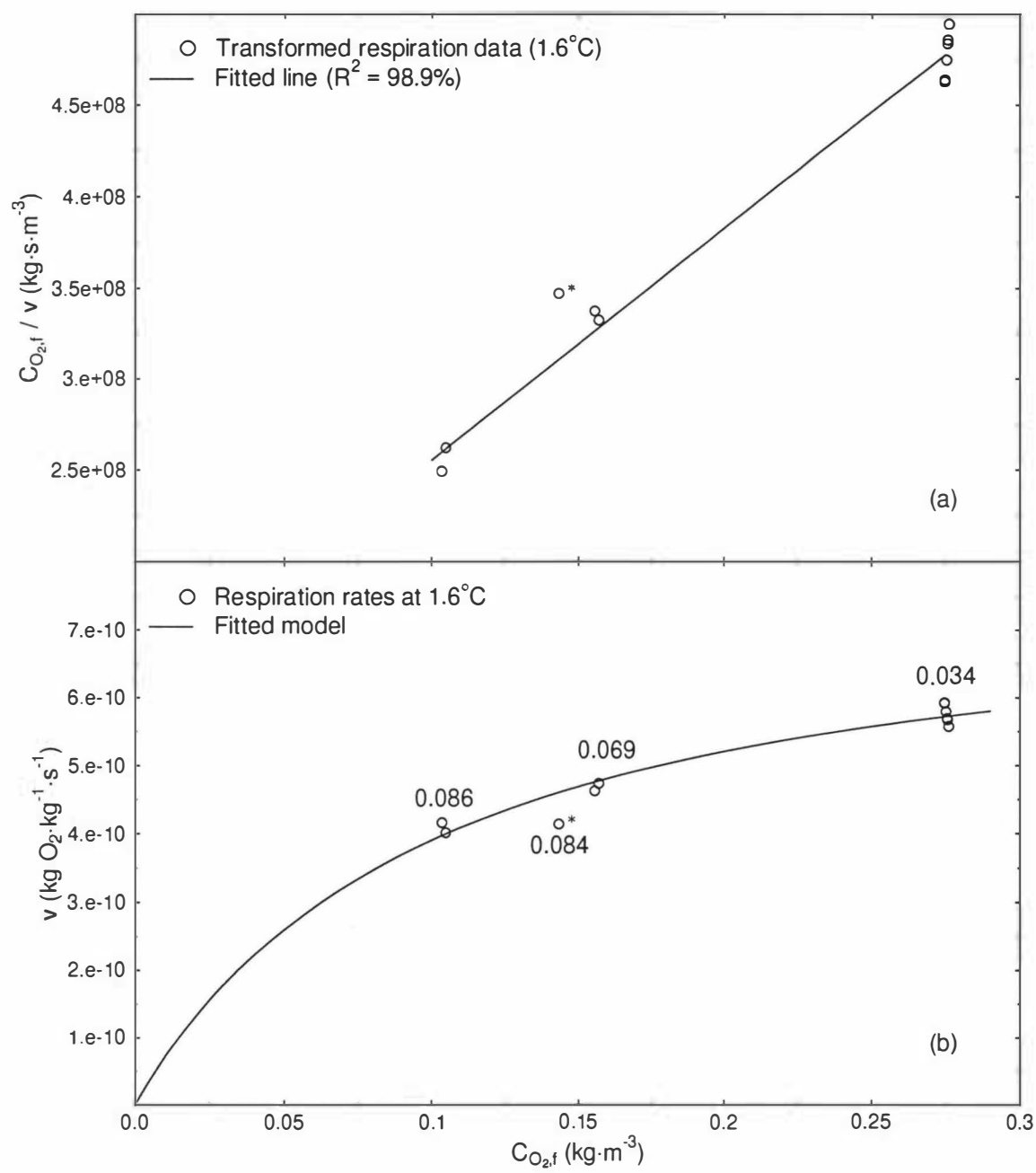
Eq. 8.3 was fitted to respiration rate data for the 1993 and 1994 'Braeburn' and the 1994 'Granny Smith' by least-squares linear regression. Figures 8.1 to 8.3 illustrate the regressions and the resulting fitted respiration models.

With the exception of one anomalous respiration rate measurement, a satisfactory fit was achieved for the 1993 'Braeburn' data (Figure 8.1a). The anomalous data point, omitted from the linear regression, came from a carton of fruit packaged in a 40  $\mu m$  liner that had been punctured once by a syringe needle early in the MA trial. Although the steady-state  $O_2$  concentration within the punctured liner was closer to that typical of 25  $\mu m$  liners, the  $CO_2$  concentration and measured respiration rate were typical of the cartons with intact 40  $\mu m$  liners (Figure 8.1b). Assuming the point represents a valid respiration rate measurement, this suggests that increased  $CO_2$ , rather than decreased  $O_2$ , could be responsible for the depression of respiration rate observed over the range of atmospheres achieved in the MA trials.

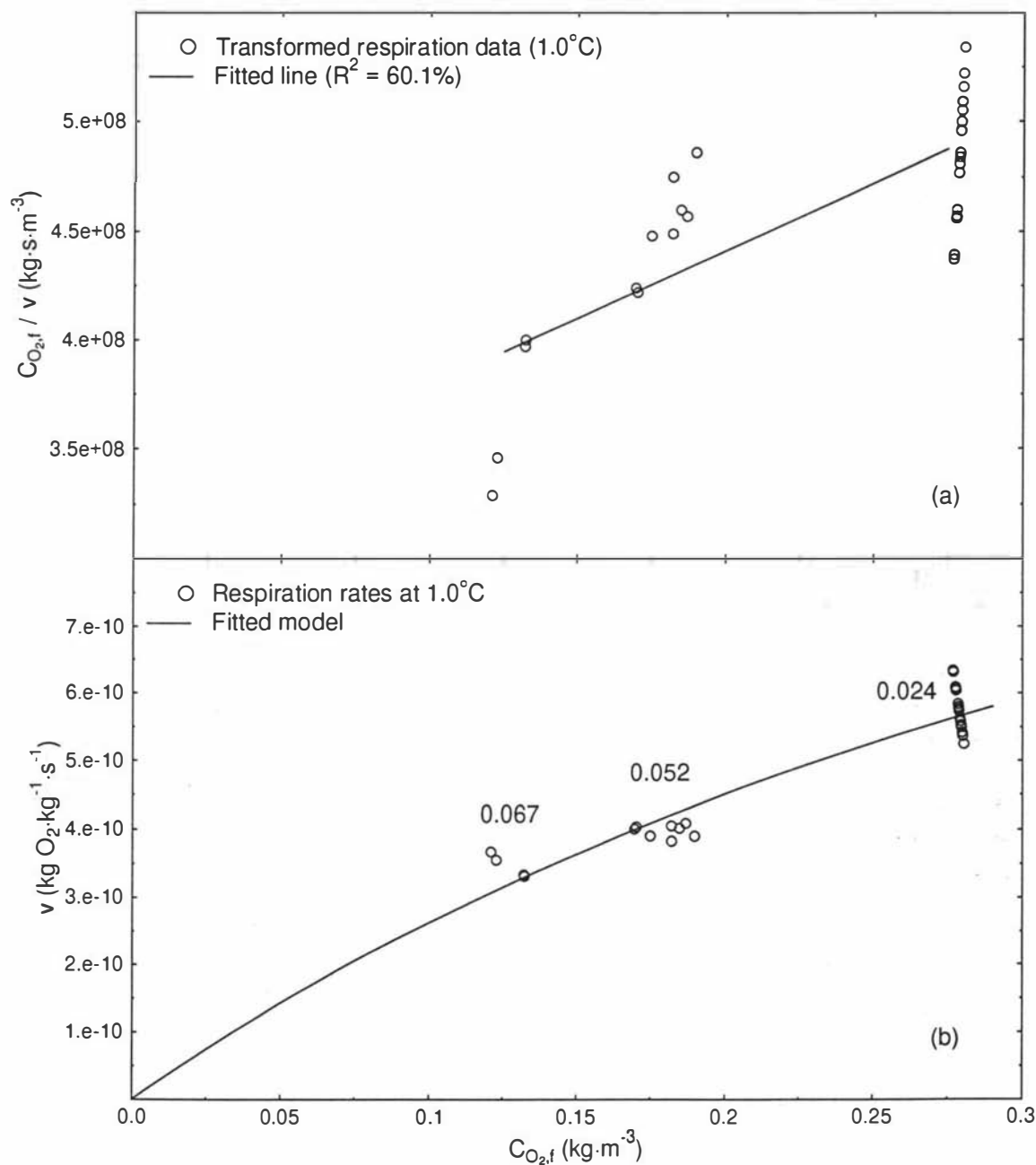
The 1994 'Braeburn' data showed significant lack-of-fit to Eq. 8.3 (Figure 8.2a), indicating the presence of an effect, or effects, not accounted for by a simple Michaelis-Menten model. Again, this raises the possibility of a  $CO_2$  effect on respiration.

A satisfactory fit to Eq. 8.3 was obtained for the 1994 'Granny Smith' data (Figure 8.3a).

Respiration data for the 1994 'Royal Gala' fruit did not exhibit Michaelis-Menten type behaviour over the range of atmospheres for which respiration rates were measured; Eq. 8.3 could not realistically be fitted to these data. To derive a model for 'Royal

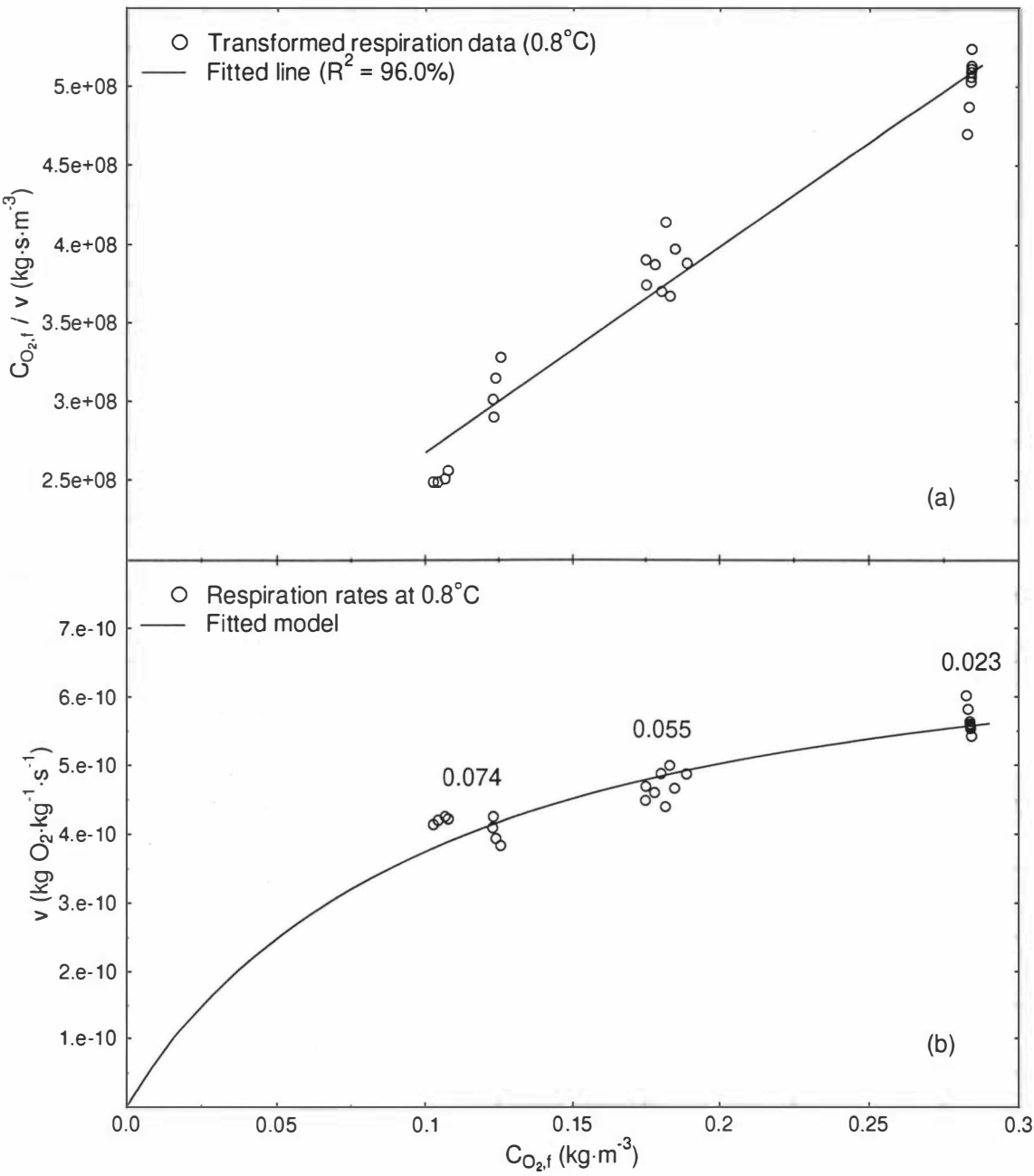


**Figure 8.1** (a) Linear regression of  $C_{O_{2,f}}/v$  versus  $C_{O_{2,f}}$  for 1993 'Braeburn' fruit. The data point marked '\*' was omitted from the regression. (b) Fitted respiration model. Numbers printed on the graph represent average fruit internal CO<sub>2</sub> concentrations ( $\text{kg}\cdot\text{m}^{-3}$ ) for each set of data points.



**Figure 8.2**

(a) Linear regression of  $C_{O_{2,i}}/v$  versus  $C_{O_{2,f}}$  for 1994 'Braeburn' fruit. (b) Fitted respiration model. Numbers printed on the graph represent average fruit internal CO<sub>2</sub> concentrations ( $\text{kg}\cdot\text{m}^{-3}$ ) for each set of data points.



**Figure 8.3** (a) Linear regression of  $C_{O_{2,i}}/v$  versus  $C_{O_{2,i}}$  for 1994 'Granny Smith' fruit. (b) Fitted respiration model. Numbers printed on the graph represent average fruit internal CO<sub>2</sub> concentrations ( $\text{kg}\cdot\text{m}^{-3}$ ) for each set of data points.

Gala' respiration rate as a function of  $O_2$ , a simple first-order kinetic model was fitted to the respiration data:

$$v = k_1 C_{O_2,f} \quad (8.4)$$

where

$$k_1 = \text{first order rate constant (m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}\text{)}.$$

The Michaelis-Menten equation exhibits first order behaviour when  $k_m \gg C_{O_2,f}$ . In this case, Eq. 8.2 simplifies to

$$v \approx \frac{v_{max}}{k_m} C_{O_2,f} \quad (8.5)$$

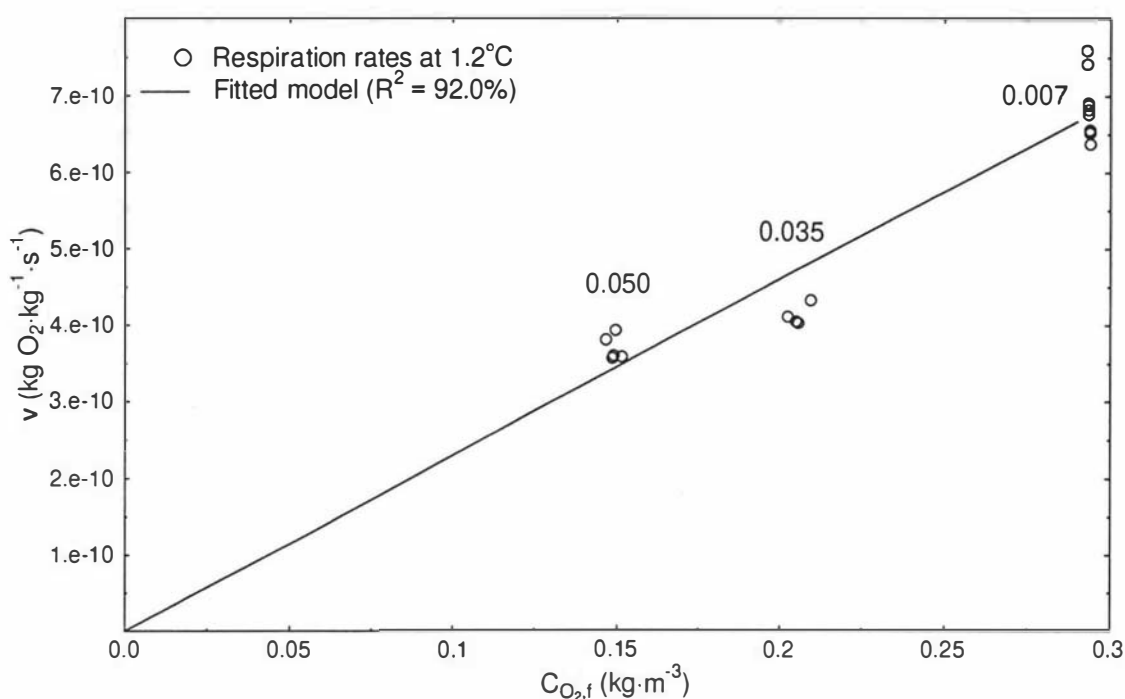
Thus, by choosing a large value of  $k_m$  and a value of  $v_{max}$  such that

$$\frac{v_{max}}{k_m} = k_1 \quad (8.6)$$

first order kinetics can be simulated by the Michaelis-Menten respiration model incorporated in the MAP model.

Figure 8.4 illustrates the first-order model fitted to the 1994 'Royal Gala' data. The model was not entirely satisfactory, showing significant lack of fit for the respiration rate measurements from cartons with 25  $\mu\text{m}$  liners.

Other workers who have fitted first-order models to respiration rate data for apples include Banks *et al.* (1989) (for 'Granny Smith' and 'Gala' apples) and Mannapperuma *et al.* (1991) (for 'Golden Delicious' apples). Banks *et al.* (1989) measured rates of  $O_2$  depletion inside a closed (impermeable) system containing a single apple.  $CO_2$  and  $C_2H_4$  were continuously removed from the atmosphere within the system by circulating the atmosphere through  $CO_2$  and  $C_2H_4$  absorbers. Banks *et al.* estimated respiration rates and fruit internal  $O_2$  concentrations by back-calculating these from the  $O_2$ -depletion curves. For both 'Granny Smith' and 'Gala' apples, they found the relationship between respiration rate and fruit internal  $O_2$  concentration to be almost perfectly linear. However, they noted that respiration rates measured under such transient conditions might well differ from those measured under steady-state conditions where fruit are allowed to come to physiological equilibrium at various  $O_2$  concentrations. Mannapperuma *et al.* (1991) measured their respiration rate data for 'Golden Delicious' apples under steady-state conditions. Although they fitted a first-order relationship to the data, the relationship between respiration rate and fruit internal  $O_2$  concentration did not appear truly first order. In fact, the data showed some evidence of Michaelis-Menten type behaviour.



**Figure 8.4** Fitted respiration model for 1994 'Royal Gala' fruit. Numbers printed on the graph represent average fruit internal  $CO_2$  concentrations ( $kg \cdot m^{-3}$ ) for each set of data points.

Of the four sets of respiration data analyzed in this work, the data for 'Royal Gala' fruit showed the greatest departure from a simple Michaelis-Menten model with respect to fruit internal  $O_2$  concentration. Comparing the average internal  $CO_2$  concentrations given on each of Figures 8.1 to 8.4, it is interesting to note that internal  $CO_2$  concentrations for 'Royal Gala' were significantly lower than those for the other cultivars. In particular, internal  $CO_2$  concentrations for 'Royal Gala' in air were very low, and the respiration rate measurements for this cultivar show a large initial drop between measurements for cartons in air and those for cartons with 25  $\mu m$  liners. This type of behaviour is consistent with the effect of increasing  $CO_2$  predicted by Eq. 6.6, and could therefore be indicative of a  $CO_2$  inhibition effect.

The published literature contains much conflicting evidence regarding the effect of  $CO_2$  on the respiration rate of fresh produce. A number of investigators have suggested that  $CO_2$  directly inhibits the activity of succinate dehydrogenase, an enzyme of the tricarboxylic acid cycle (Blanke, 1991; Peppelenbos & van't Leven, 1996); the resulting accumulation of succinate is thought to further suppress respiration through a feedback inhibition mechanism (Blanke, 1991). Other investigators have demonstrated that  $CO_2$  either directly or indirectly inhibits the activity of phosphofructokinases in the glycolytic pathway (Kerbel *et al.*, 1988, 1990; Peppelenbos & van't Leven, 1996). Some workers have suggested that  $CO_2$  indirectly inhibits the action of more than one respiratory enzyme through its effect on the pH of the cell sap (Peppelenbos & van't Leven, 1996).

In contrast to the above evidence supporting an inhibitory CO<sub>2</sub> effect, various investigators have found CO<sub>2</sub> to have no significant effect on the respiration rate of a range of fruits and vegetables, including satsuma mandarins, lemons, grapes, carrots, dried onions, cauliflower, and cabbage (Kubo *et al.*, 1990), blueberries (Beaudry, 1993), mushrooms (Peppelenbos *et al.*, 1993), and raspberries (Joles *et al.*, 1994).

As discussed in section 2.4.3.1, Michaelis-Menten models with linear, uncompetitive CO<sub>2</sub> inhibition have been fitted to respiration rate data for apples (Lee *et al.*, 1991), broccoli (Lee *et al.*, 1991; Hagger *et al.*, 1992), blueberries (Song *et al.*, 1992), and strawberries (Renault *et al.*, 1994*a,b*). Peppelenbos & van't Leven (1996) have recently examined the applicability of various forms of enzyme inhibition model (competitive, uncompetitive, non-competitive, and mixed) to the respiration of apples, asparagus, broccoli, mungbean sprouts, and cut chicory. They found strong evidence for an inhibitory CO<sub>2</sub> effect on the respiration rates of asparagus, broccoli, mungbean sprouts, and cut chicory, but found no conclusive evidence of a similar CO<sub>2</sub> effect on the respiration rates of 'Golden Delicious' and 'Elstar' apples. The respiration rates of asparagus, broccoli, mungbean sprouts, and cut chicory could be reasonably well described by one or more of the enzyme inhibition models tested.

Michaelis-Menten models with linear CO<sub>2</sub> inhibition (e.g. Eq. 6.6) assume that CO<sub>2</sub> and O<sub>2</sub> both affect the same rate-limiting enzyme of the aerobic respiratory pathway. However, if CO<sub>2</sub> directly inhibits the activity of an enzyme whose rate is not dependent on O<sub>2</sub> concentration (for example, succinate dehydrogenase as discussed above), then the applicability of Eq. 6.6 to modelling the effect of CO<sub>2</sub> on fruit and vegetable respiration is questionable.

If CO<sub>2</sub> and O<sub>2</sub> affect different enzymes in the respiratory pathway, then the observed effect of elevated CO<sub>2</sub> concentration on respiration rate could depend on O<sub>2</sub> concentration. For example, at high O<sub>2</sub> concentrations a reaction inhibited by CO<sub>2</sub> may act as the rate-limiting step in the respiratory pathway. However, at low O<sub>2</sub> concentrations a reaction dependent on O<sub>2</sub> concentration may become the overall rate-limiting step, regardless of whether CO<sub>2</sub> is inhibiting another enzyme in the pathway or not. Some of the respiration data reported in the literature could be supportive of such a scenario. Both Li and Kader (1989) and Talasila *et al.* (1992) found that elevated CO<sub>2</sub> concentrations significantly reduced the respiration rate of strawberries at high O<sub>2</sub> concentrations (about 20 mol %), but not at lower O<sub>2</sub> concentrations (less than 10 mol %). The respiration data reported for 'Golden Delicious' and 'Elstar' apples by Peppelenbos & van't Leven (1996) show some evidence of an inhibitory CO<sub>2</sub> effect at O<sub>2</sub> concentrations above 6 mol %, but no evidence of CO<sub>2</sub> inhibition at O<sub>2</sub> concentrations below this.

Clearly, there is a need for further investigation into the mechanisms by which O<sub>2</sub> and CO<sub>2</sub> affect the respiration of fresh produce. A better understanding of these mechanisms would aid in the derivation of realistic mathematical models to describe respiration rate. The interactions between respiration rate models and the predictions of the overall MAP model are discussed in sections 9.1 and 9.2.

Effect of Temperature

Internal atmosphere compositions and respiration rates measured in air at 15°C or 20°C (Tables 8.5 and 8.6) were used to estimate values of  $v_{max}$  at 15°C or 20°C for each cultivar by rearrangement of Eqs. 8.2 or 8.5. Values of  $k_m$  were assumed constant with temperature. Respiration rates measured in air at 1.6°C for 1993 ‘Braeburn’ fruit used in the bag trials were significantly lower than those measured for the 1993 ‘Braeburn’ used in the carton trials (section 8.1.2, Table 8.6). A separate value of  $v_{max}$  for the fruit used in the bag trials was therefore estimated in the same manner as the values of  $v_{max}$  at higher temperatures (again assuming a constant  $k_m$ ).

$Q_{10}$  values for each cultivar were estimated from

$$Q_{10} = \left( \frac{v_{max,\theta}}{v_{max,ref}} \right)^{\frac{10}{\theta - \theta_{ref}}}$$

(8.7)

where

- $Q_{10}$

=

temperature coefficient of respiration
- $v_{max,ref}$

=

maximum aerobic respiration rate at reference temperature  
(kg O<sub>2</sub>·kg<sup>-1</sup>·s<sup>-1</sup>)
- $v_{max,\theta}$

=

maximum aerobic respiration rate at temperature  $\theta$  (kg O<sub>2</sub>·kg<sup>-1</sup>·s<sup>-1</sup>)
- $\theta$

=

temperature (°C) (15 or 20°C in this instance)
- $\theta_{ref}$

=

reference temperature (°C) (the cool-storage temperature for each trial).

Table 8.9 summarizes the respiration model parameters derived to predict respiration rate as a function of fruit internal O<sub>2</sub> concentration for each cultivar.

**Table 8.9** Respiration model parameters for predicting respiration rates as a function of fruit internal O<sub>2</sub> concentration.<sup>a</sup>

| Cultivar             | $\theta_{ref}$<br>(°C) | $v_{max,ref} \times 10^{10}$<br>(kg O <sub>2</sub> ·kg <sup>-1</sup> ·s <sup>-1</sup> ) | $k_m$<br>(kg O <sub>2</sub> ·m <sup>-3</sup> ) | $k_1 \times 10^9$<br>(m <sup>3</sup> ·kg <sup>-1</sup> ·s <sup>-1</sup> ) | $Q_{10}$ |
|----------------------|------------------------|-----------------------------------------------------------------------------------------|------------------------------------------------|---------------------------------------------------------------------------|----------|
| 1993 Season:         |                        |                                                                                         |                                                |                                                                           |          |
| ‘Braeburn’ (cartons) | 1.6                    | 7.8 ± 0.7                                                                               | 0.100 ± 0.022                                  | -                                                                         | 3.5      |
| ‘Braeburn’ (bags)    | 1.6                    | 6.1                                                                                     | 0.100                                          | -                                                                         | 3.5      |
| 1994 Season:         |                        |                                                                                         |                                                |                                                                           |          |
| ‘Royal Gala’         | 1.2                    | - <sup>b</sup>                                                                          | - <sup>b</sup>                                 | 2.30 ± 0.09 <sup>b</sup>                                                  | 3.2      |
| ‘Braeburn’           | 1.0                    | 16 ± 5                                                                                  | 0.51 ± 0.19                                    | -                                                                         | 3.4      |
| ‘Granny Smith’       | 0.8                    | 7.6 ± 0.7                                                                               | 0.103 ± 0.021                                  | -                                                                         | 3.4      |

<sup>a</sup> Parameters estimated by regression are listed with 95% confidence intervals.  
<sup>b</sup> To run the MAP model for ‘Royal Gala’, an arbitrary value of 1 × 10<sup>9</sup> kg O<sub>2</sub>·m<sup>-3</sup> was chosen for  $k_m$ , with a corresponding  $v_{max,ref}$  of 2.30 kg O<sub>2</sub>·kg<sup>-1</sup>·s<sup>-1</sup> back-calculated from Eq. 8.6.

### 8.1.4.2 RESPIRATION AS A FUNCTION OF FRUIT INTERNAL CO<sub>2</sub>

#### *Effect of CO<sub>2</sub>*

If respiration rate is assumed to be insensitive to O<sub>2</sub> over the range of concentrations for which respiration data were measured, and if the observed depression of respiration rate under modified atmospheres is attributed solely to increased CO<sub>2</sub> concentrations, then Eq. 6.6 reduces to

$$v = \frac{v_{max}}{1 + \frac{C_{CO_2,f}}{k_{iu}}} \quad (8.8)$$

where

$C_{CO_2,f}$  = CO<sub>2</sub> concentration in the fruit internal atmosphere (kg CO<sub>2</sub>·m<sup>-3</sup>)  
 $k_{iu}$  = uncompetitive inhibition constant (kg CO<sub>2</sub>·m<sup>-3</sup>).

Eq. 8.8 can be linearized by taking reciprocals of both sides to give

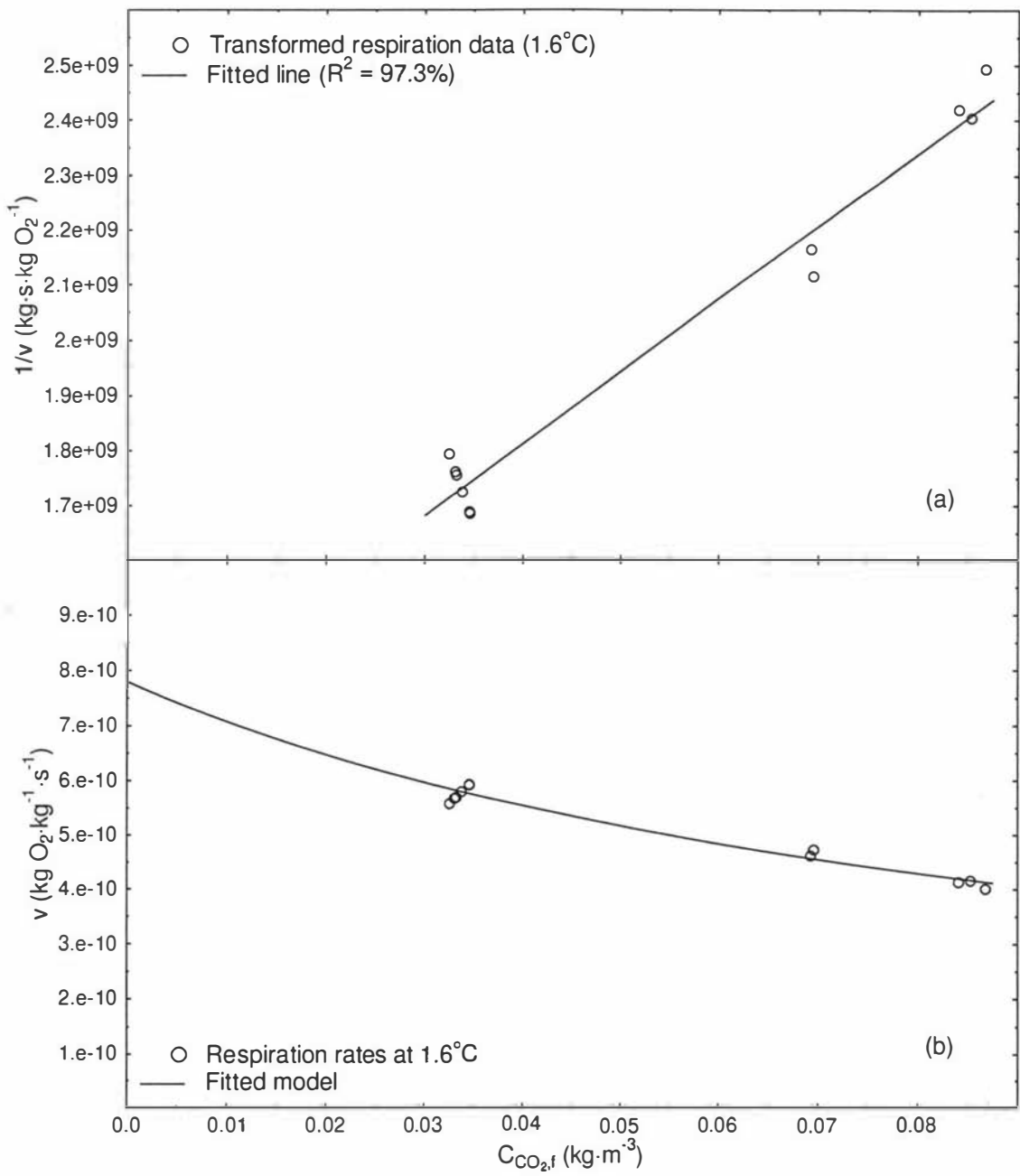
$$\frac{1}{v} = \frac{1}{v_{max}} + \frac{C_{CO_2,f}}{v_{max} k_{iu}} \quad (8.9)$$

Thus, a plot of 1/*v* versus  $C_{CO_2,f}$  should be a straight line with a slope of 1/( $v_{max} k_{iu}$ ) and a y-axis intercept of 1/ $v_{max}$ .

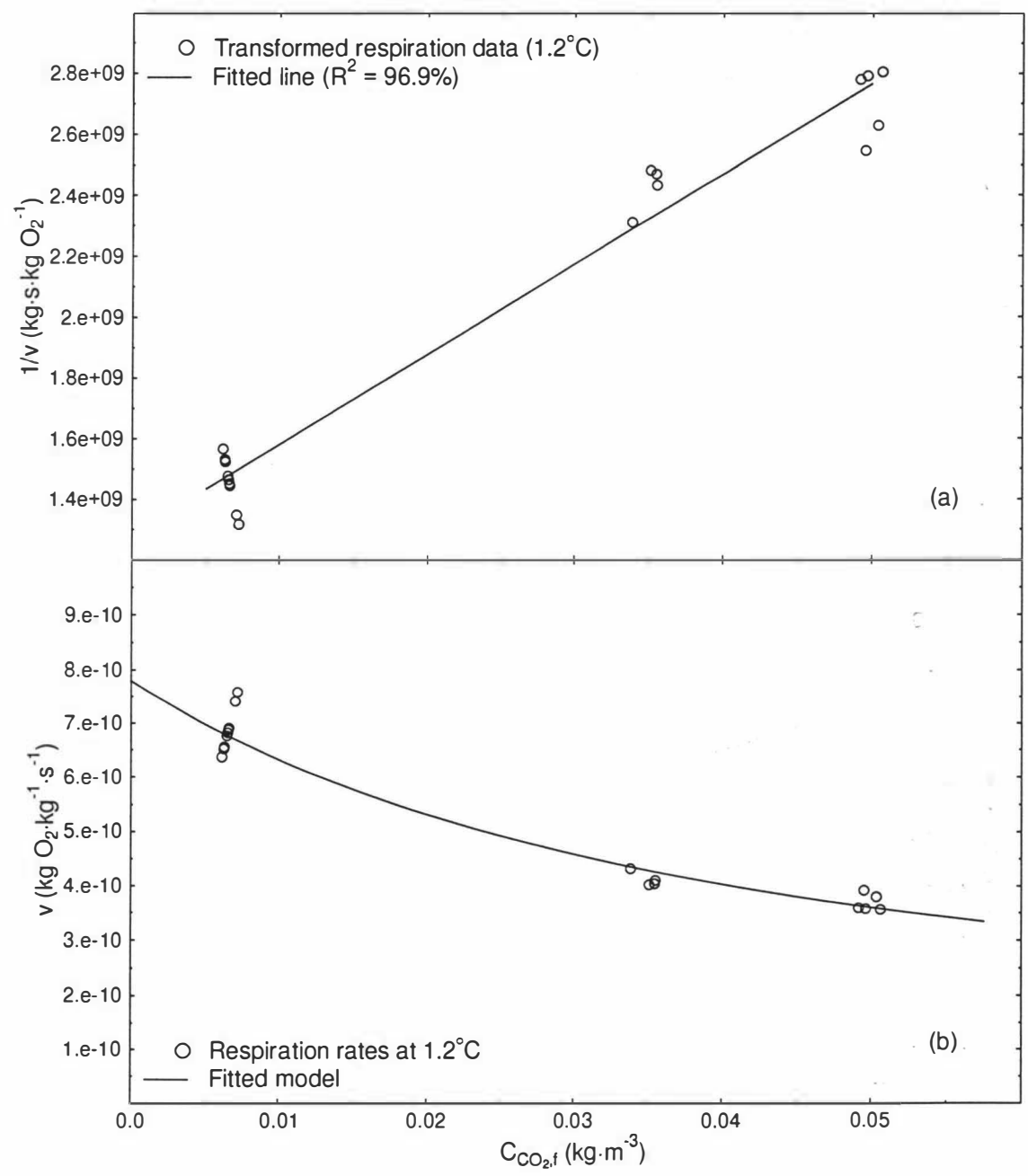
Eq. 8.9 was fitted to respiration rate data for each cultivar by least-squares linear regression. Figures 8.5 to 8.8 illustrate the regressions and the resulting fitted respiration models.

Overall, regression of respiration rate data as a function of internal CO<sub>2</sub> concentration resulted in better fits to the experimental data than the regressions versus O<sub>2</sub> concentration. In particular, fits for the 1994 'Braeburn' and 'Royal Gala' were much improved. For the 1993 'Braeburn', the point omitted in the regression of respiration data versus internal O<sub>2</sub> concentration (Figure 8.1a) showed no lack-of-fit for the regression versus internal CO<sub>2</sub> concentration (Figure 8.5a).

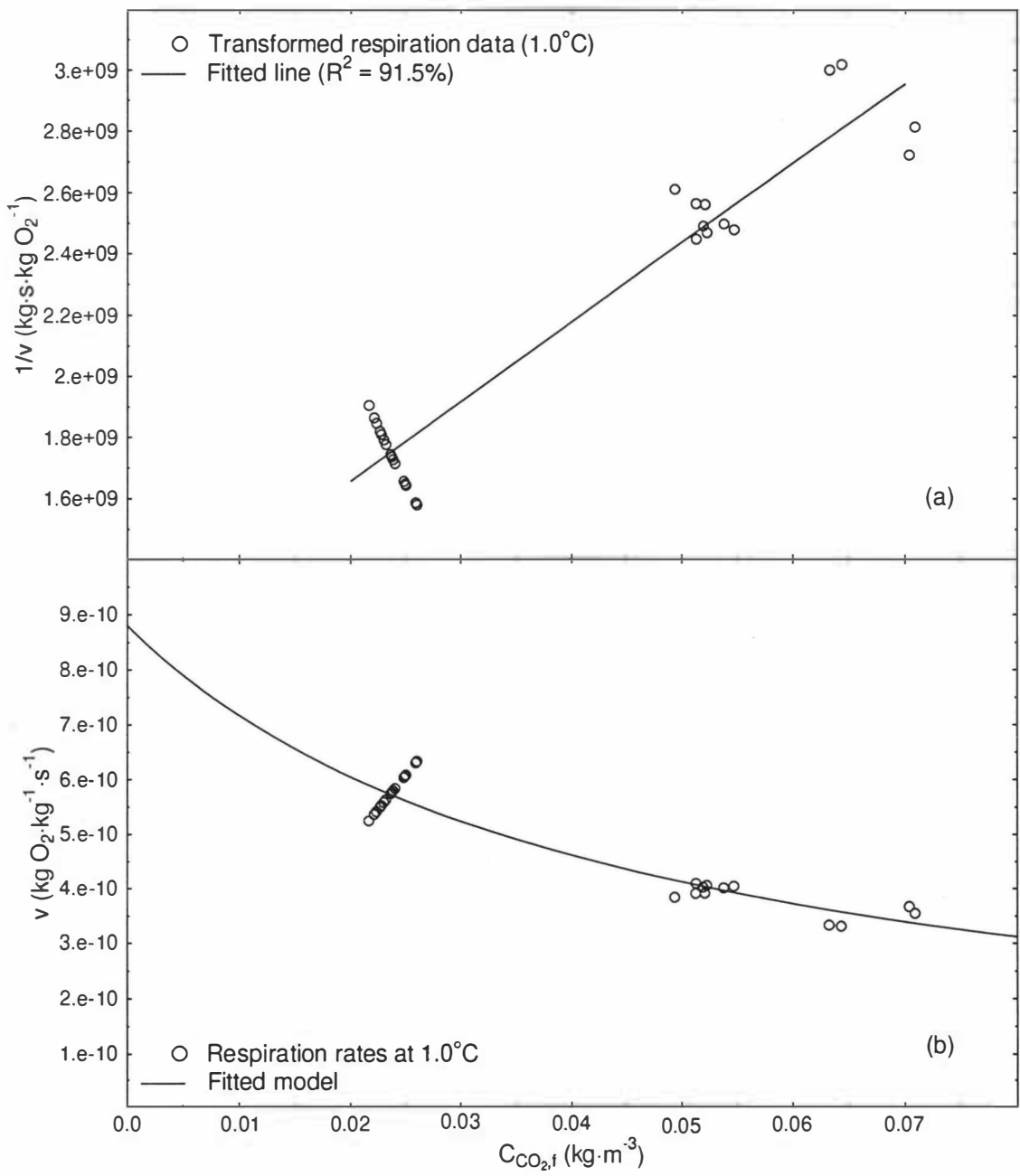
For the relatively high steady-state O<sub>2</sub> concentrations experienced by fruit during the MA trials, the assumption that O<sub>2</sub> concentration does not significantly affect respiration rate seems plausible. However, evidence in the literature leaves little doubt that progressively decreasing O<sub>2</sub> concentrations do depress fruit respiration rates (e.g. Dadzie, 1992; Dadzie *et al.*, 1996; Peppelenbos & van't Leven, 1996). The respiration models in Figures 8.5 to 8.8 are therefore unlikely to hold if extrapolated for modified atmosphere packages having much higher CO<sub>2</sub> concentrations (and consequently much lower O<sub>2</sub> concentrations).



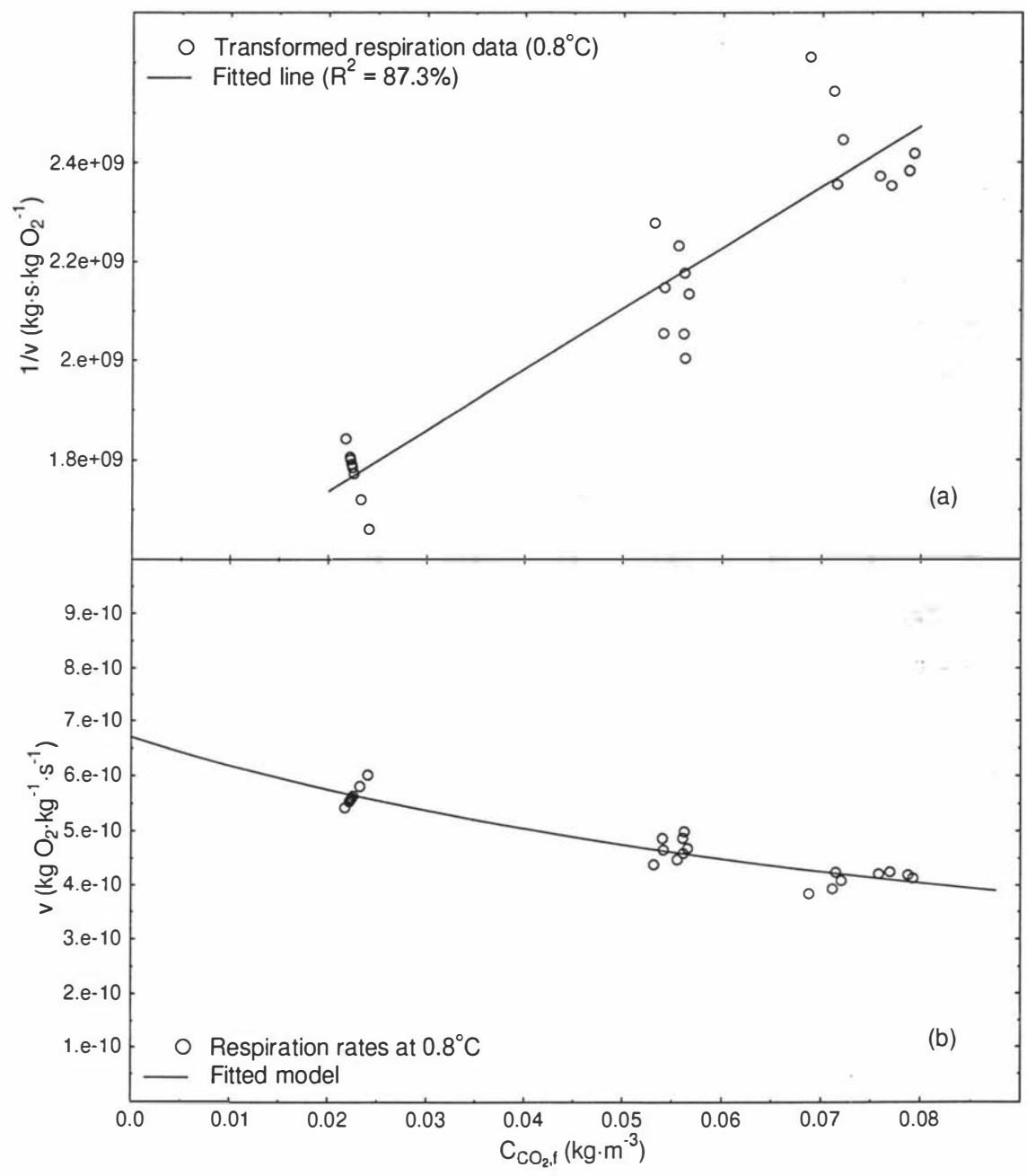
**Figure 8.5** (a) Linear regression of  $1/v$  versus  $C_{CO_2,f}$  for 1993 'Braeburn' fruit. (b) Fitted respiration model.



**Figure 8.6** (a) Linear regression of  $1/v$  versus  $C_{CO_2,f}$  for 1994 'Royal Gala' fruit. (b) Fitted respiration model.



**Figure 8.7** (a) Linear regression of  $1/v$  versus  $C_{CO_2,f}$  for 1994 'Braeburn' fruit. (b) Fitted respiration model.



**Figure 8.8** (a) Linear regression of  $1/v$  versus  $C_{CO_2,f}$  for 1994 'Granny Smith' fruit. (b) Fitted respiration model.

**Table 8.10**      Respiration model parameters for predicting respiration rates as a function of fruit internal CO<sub>2</sub> concentration ( $k_m = 0$  for all cases).<sup>a</sup>

| Cultivar             | $\theta_{ref}$<br>(°C) | $v_{max,ref} \times 10^{10}$<br>(kg O <sub>2</sub> ·kg <sup>-1</sup> ·s <sup>-1</sup> ) | $k_{iu}$<br>(kg CO <sub>2</sub> ·m <sup>-3</sup> ) | $Q_{10}$ |
|----------------------|------------------------|-----------------------------------------------------------------------------------------|----------------------------------------------------|----------|
| <i>1993 Season:</i>  |                        |                                                                                         |                                                    |          |
| ‘Braeburn’ (cartons) | 1.6                    | 7.8 ± 0.6                                                                               | 0.098 ± 0.014                                      | 4.4      |
| ‘Braeburn’ (bags)    | 1.6                    | 5.7                                                                                     | 0.098                                              | 4.4      |
| <i>1994 Season:</i>  |                        |                                                                                         |                                                    |          |
| ‘Royal Gala’         | 1.2                    | 7.8 ± 0.5                                                                               | 0.043 ± 0.005                                      | 3.9      |
| ‘Braeburn’           | 1.0                    | 8.8 ± 1.0                                                                               | 0.044 ± 0.007                                      | 4.5      |
| ‘Granny Smith’       | 0.8                    | 6.7 ± 0.5                                                                               | 0.122 ± 0.022                                      | 3.9      |

<sup>a</sup> Parameters estimated by regression are listed with 95% confidence intervals.

*Effect of Temperature*

$Q_{10}$  values for each cultivar were estimated as described in section 8.1.4.1, but with values of  $v_{max}$  at 15°C or 20°C estimated by rearrangement of Eq. 8.8. The  $Q_{10}$  values estimated for the CO<sub>2</sub>-based respiration models were higher than those estimated for the O<sub>2</sub>-based models. This can probably be attributed to the method used to estimate values of  $v_{max}$  at 15 or 20°C (i.e. back-calculation assuming constant  $k_m$  or  $k_{iu}$ ).

Table 8.10 summarizes the respiration model parameters derived to predict respiration rate as a function of fruit internal CO<sub>2</sub> concentration for each cultivar.

**8.1.5 MISCELLANEOUS FRUIT DATA**

Values for fruit porosity, fruit water activity, specific heat capacity of the fruit flesh, and respiratory heat generation were taken from literature data and are listed in Table 8.11.

**Table 8.11**      Miscellaneous fruit data.

| Parameter                                                      | Symbol     | Value                  | Unit                                |
|----------------------------------------------------------------|------------|------------------------|-------------------------------------|
| Flesh porosity (‘Braeburn’) <sup>a</sup>                       | $\epsilon$ | 0.140                  | m <sup>3</sup> ·m <sup>-3</sup>     |
| Flesh porosity (‘Granny Smith’) <sup>a</sup>                   | $\epsilon$ | 0.166                  | m <sup>3</sup> ·m <sup>-3</sup>     |
| Flesh porosity (‘Royal Gala’) <sup>b</sup>                     | $\epsilon$ | 0.166                  | m <sup>3</sup> ·m <sup>-3</sup>     |
| Fruit water activity <sup>c</sup>                              | $a_w$      | 0.98                   |                                     |
| Specific heat capacity of the fruit flesh <sup>d</sup>         | $c_{pf}$   | 3650                   | J·kg <sup>-1</sup> ·K <sup>-1</sup> |
| Respiratory heat generation per kg O <sub>2</sub> <sup>e</sup> | $\dot{W}$  | 1.85 × 10 <sup>7</sup> | J·kg <sup>-1</sup>                  |

<sup>a</sup> From Rajapakse *et al.* (1989b).  
<sup>b</sup> Assumed to be the same as ‘Granny Smith’.  
<sup>c</sup> From Chirife & Ferro Fontan (1982).  
<sup>d</sup> From Amos (1995, p. 83).  
<sup>e</sup> Estimated from correlations given by Gaffney *et al.* (1985a).

## 8.2 PACKAGING MATERIAL DATA

### 8.2.1 FILM PERMEABILITY DATA

#### 8.2.2.1 FILM PERMEABILITY TO O<sub>2</sub> AND CO<sub>2</sub>

Data on the permeability of the MA-film carton liners to O<sub>2</sub> and CO<sub>2</sub> were obtained from five sources:

- (1) preliminary permeability measurements (section 4.2.4.1);
- (2) main permeability measurements (section 4.2.4.2);
- (3) permeability measurements for whole liners (section 4.2.4.3);
- (4) manufacturer's data supplied by Borden Filmpac (O<sub>2</sub> only);
- (5) independent testing by the Division of Food Processing, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia.

Table 8.12 summarizes the permeability data obtained from all five sources.

#### *Preliminary and Main Runs*

Permeability values for the preliminary and main runs were estimated from

$$P_i = \frac{F_{low} [i]_{low} x}{A_{film} ([i]_{high} - [i]_{low})} \quad (8.10)$$

where

- $A_{film}$  = film area (m<sup>2</sup>)
- $F_{low}$  = flow rate through the low-concentration side of the permeability cell (m<sup>3</sup>·s<sup>-1</sup>)
- $P_i$  = film permeability to gas species  $i$  (m<sup>2</sup>·s<sup>-1</sup>)
- $x$  = film thickness (m)
- $[i]_{high}$  = high concentration of gas species  $i$  (m<sup>3</sup>·m<sup>-3</sup>)
- $[i]_{low}$  = low concentration of gas species  $i$  (m<sup>3</sup>·m<sup>-3</sup>).

O<sub>2</sub> and CO<sub>2</sub> permeabilities measured at relative humidities of approximately 68%, 82%, and 94% during the main permeability runs showed no evidence of a consistent humidity effect. Results from these runs were therefore pooled to give the mean values listed under 'humid' in Table 8.12.

O<sub>2</sub> and CO<sub>2</sub> permeabilities measured under humid conditions during the preliminary runs were significantly lower than those measured under dry conditions. In contrast, results from the main runs showed no significant difference between permeabilities measured under dry or humid conditions. Although permeabilities for 40 µm film samples consistently appeared somewhat lower than those for 25 µm samples, these differences were also not large enough to be considered significant.

**Table 8.12** Permeability of the MA film to O<sub>2</sub> and CO<sub>2</sub>.

| Source              | Temperature<br>(°C) | Conditions | Film<br>thickness<br>(µm) | $P_{O_2} \times 10^{12}{}^a$<br>(m <sup>2</sup> ·s <sup>-1</sup> ) | $P_{CO_2} \times 10^{12}{}^a$<br>(m <sup>2</sup> ·s <sup>-1</sup> ) | n <sup>b</sup> |
|---------------------|---------------------|------------|---------------------------|--------------------------------------------------------------------|---------------------------------------------------------------------|----------------|
| Preliminary runs    | 5                   | Dry        | - <sup>c</sup>            | 2.0 ± 0.3                                                          | 9.4 ± 0.4                                                           | 7              |
|                     |                     | Humid      | - <sup>c</sup>            | 1.3 ± 0.4                                                          | 6.0 ± 1.1                                                           | 4              |
| Main runs           | 0.6                 | Dry        | 40                        | 1.34 ± 0.13                                                        | 8.1 ± 0.3                                                           | 3              |
|                     |                     | Humid      | 25                        | 1.48 ± 0.09                                                        | 8.4 ± 0.9                                                           | 4              |
|                     |                     | Humid      | 40                        | 1.27                                                               | 7.6                                                                 | 1              |
|                     | 4.8                 | Dry        | 25                        | 1.94 ± 0.12                                                        | 10.7 ± 0.9                                                          | 3              |
|                     |                     | Humid      | 40                        | 1.60 ± 0.08                                                        | 9.0 ± 0.3                                                           | 5              |
|                     | 9.7                 | Dry        | 40                        | 2.36 ± 0.20                                                        | 13.41 ± 0.19                                                        | 3              |
|                     |                     | Humid      | 25                        | 2.48 ± 0.24                                                        | 13.6 ± 0.5                                                          | 4              |
|                     |                     | Humid      | 40                        | 2.23                                                               | 13.0                                                                | 1              |
|                     | 19.6                | Dry        | 25                        | 4.82 ± 0.17                                                        | 22.9 ± 0.6                                                          | 6              |
|                     |                     | Humid      | 25                        | 4.5 ± 0.3                                                          | 22.3 ± 0.6                                                          | 7              |
|                     |                     | Humid      | 40                        | 4.03 ± 0.13                                                        | 20.1 ± 0.5                                                          | 14             |
|                     | 30.3                | Dry        | 25                        | 7.81 ± 0.08                                                        | 35.1 ± 0.9                                                          | 3              |
|                     |                     | Dry        | 40                        | 7.5 ± 0.6                                                          | 33.8 ± 1.3                                                          | 3              |
|                     |                     | Humid      | 25                        | 7.5 ± 0.3                                                          | 33.0 ± 1.8                                                          | 6              |
|                     |                     | Humid      | 40                        | 7.12 ± 0.15                                                        | 32.7 ± 0.6                                                          | 8              |
| Carton runs         | 0.9                 | Humid      | 40                        | 1.45 ± 0.04                                                        | 6.43 ± 0.11                                                         | 4              |
| Manufacturer's data | 20                  | Dry        | 25                        | 4.83                                                               | - <sup>d</sup>                                                      | - <sup>e</sup> |
|                     | 23                  | Dry        | 25                        | 5.66                                                               | - <sup>d</sup>                                                      | 1              |
|                     |                     | Humid      | 25                        | 5.47                                                               | - <sup>d</sup>                                                      | 1              |
| CSIRO tests         | 0                   | Dry        | 40                        | 1.8 ± 1.7                                                          | 10 ± 3                                                              | 4              |
|                     |                     | Humid      | 40                        | 1.6 ± 0.7                                                          | 7 ± 3                                                               | 4              |
|                     | 0                   | Humid      | 40                        | 1.10 ± 0.13                                                        | 5.17 ± 0.22                                                         | 16             |

<sup>a</sup> Values presented as ‘mean ± 95% confidence interval on mean’ (for n > 2).  
<sup>b</sup> n = sample size (number of replicate measurements).  
<sup>c</sup> Tests carried out on one sample of 25 µm film and one sample of 40 µm film and results pooled.  
<sup>d</sup> Not measured.  
<sup>e</sup> Not specified.

*Carton Runs*

For a gas species *i* permeating into a sealed, empty package with a perfectly mixed package atmosphere and a constant volume, the theoretical change in package concentration of *i* with time is given by

$$Y'_i = \left( \frac{[i]_t - [i]_e}{[i]_0 - [i]_e} \right) = \exp \left( \frac{-P_i A_{film} t}{x V_p} \right) \quad (8.11)$$

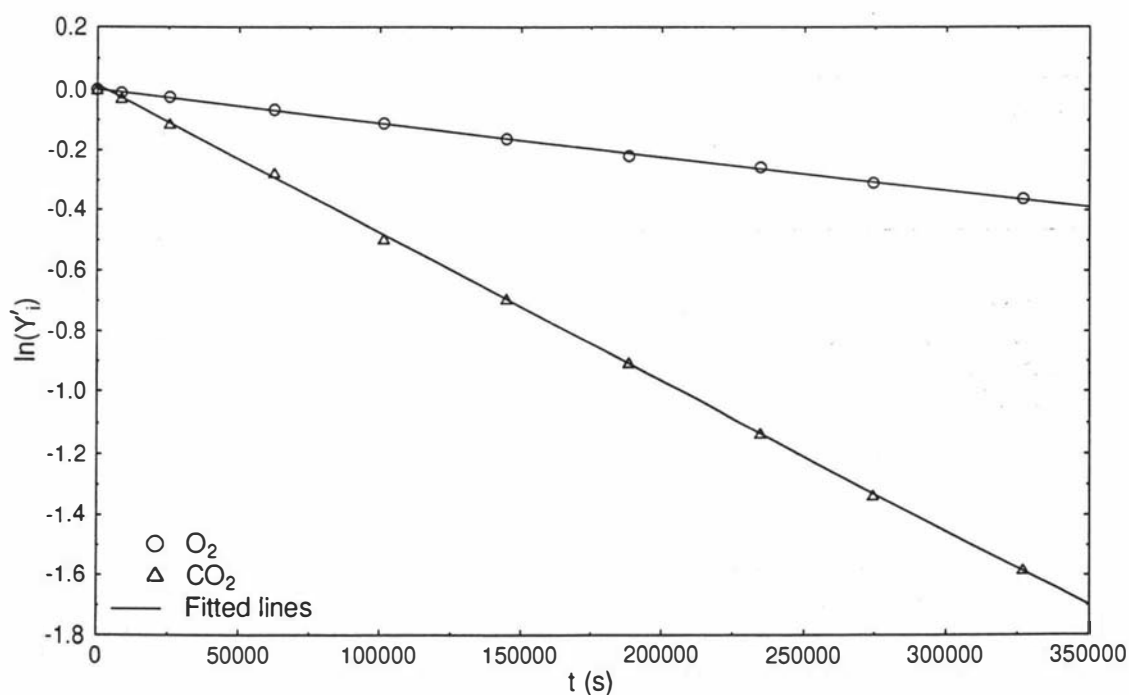
where

- $t$  = time (s)  
 $V_p$  = package volume (m<sup>3</sup>)  
 $Y'_i$  = fractional unaccomplished concentration change for gas species  $i$   
 $[i]_e$  = ambient concentration of gas species  $i$  (m<sup>3</sup>·m<sup>-3</sup>)  
 $[i]_t$  = package concentration of gas species  $i$  at time  $t$  (m<sup>3</sup>·m<sup>-3</sup>)  
 $[i]_0$  = initial package concentration of gas species  $i$  (m<sup>3</sup>·m<sup>-3</sup>).

According to this relationship, a plot of  $\ln(Y'_i)$  versus  $t$  should give a straight line with a slope of  $(-P_i A_{film})/(x V_p)$ .

Values of  $P_{O_2}$  and  $P_{CO_2}$  were estimated by least-squares linear regression of  $\ln(Y'_i)$  versus  $t$  for each of the carton runs. Figure 8.9 shows an example of such a regression for one run. The linearity of the relationship between  $\ln(Y'_i)$  and  $t$  for all of the carton runs indicated that the assumption of constant package volume over the duration of the runs was valid.

$O_2$  permeabilities estimated from the carton runs were consistent with those estimated from the main runs. However,  $CO_2$  permeabilities from the carton runs were significantly lower than those from the main runs (Table 8.12).



**Figure 8.9** Example plot of  $\ln(Y'_i)$  versus  $t$  for one carton run.

*Borden Filmpac and CSIRO Data*

The permeability data reported by Borden Filmpac were measured with a Mocon Ox-Tran 100 instrument used in accordance with standard test method ASTM D 3985-81 (Anon., 1981). Although limited to three values for O<sub>2</sub> permeability, the manufacturer's data appeared consistent with O<sub>2</sub> permeabilities from the main runs.

Permeability values reported by the CSIRO were measured in accordance with the static-cell method reported by Davis & Huntington (1977). Film samples for these tests were taken from the same batch of liners as those used for the main runs and the carton runs.

The first set of CSIRO tests was carried out at 0°C under dry or humidified (95% RH) conditions. The results from these tests were extremely variable (Table 8.12). Although it was suggested that this high variability could have been due to liner-to-liner variations in film permeability, this seems unlikely given the much smaller variability between replicates from each of the other data sets (which also represent film samples taken from different liners) and given the small variability observed between steady-state modified atmospheres measured for replicate cartons during the MA trials.

A repeated set of CSIRO tests was carried out under humidified conditions, this time for film samples taken from only one MA liner. The results from these tests showed much better reproducibility, having a measurement variability consistent with that observed for the other data sets.

O<sub>2</sub> and CO<sub>2</sub> permeabilities from the second set of CSIRO tests were significantly lower than corresponding permeabilities from the main runs and the carton runs.

*Estimation of Model Parameters for Predicting  $P_{O_2}$  and  $P_{CO_2}$  as Functions of Temperature*

Some inconsistencies were apparent between the sets of permeability data obtained from different sources. Firstly, results from the preliminary runs indicated a significant effect of humidity on permeability, but this was not substantiated by results from the other sources. The MA-film was believed to be LDPE-based, and a strong humidity effect would not be expected for a hydrophobic film such as LDPE (Felder & Huvard, 1980; Ashley, 1985; Pauly, 1989). Secondly, CO<sub>2</sub> permeabilities from the carton runs were lower than those from the main runs, and CO<sub>2</sub> permeabilities from the second set of CSIRO tests were lower again. The reasons for these inconsistencies remain unclear. However, as there appeared to be no evidence to credit the validity of one measurement method above any other, data from all five sources were pooled for further analysis.

The Arrhenius relationship for predicting film permeability as a function of temperature (Eq. 6.95, section 6.2.16.3) can be rewritten in terms of a reference temperature and reference permeability as follows:

$$P_i = P_{i,T_{ref}} \exp \left( \frac{-E_{a,i}}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \quad (8.12)$$

where

- $E_{a,i}$  = activation energy for permeation of gas species  $i$  ( $\text{J}\cdot\text{mol}^{-1}$ )
- $P_{i,T_{ref}}$  = film permeability to gas species  $i$  at temperature  $T_{ref}$  ( $\text{m}^2\cdot\text{s}^{-1}$ )
- $R$  = gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
- $T$  = film temperature (K)
- $T_{ref}$  = reference temperature (K).

Transformation of Eq. 8.12 gives

$$\ln P_i = \ln P_{i,T_{ref}} - \frac{E_{a,i}}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (8.13)$$

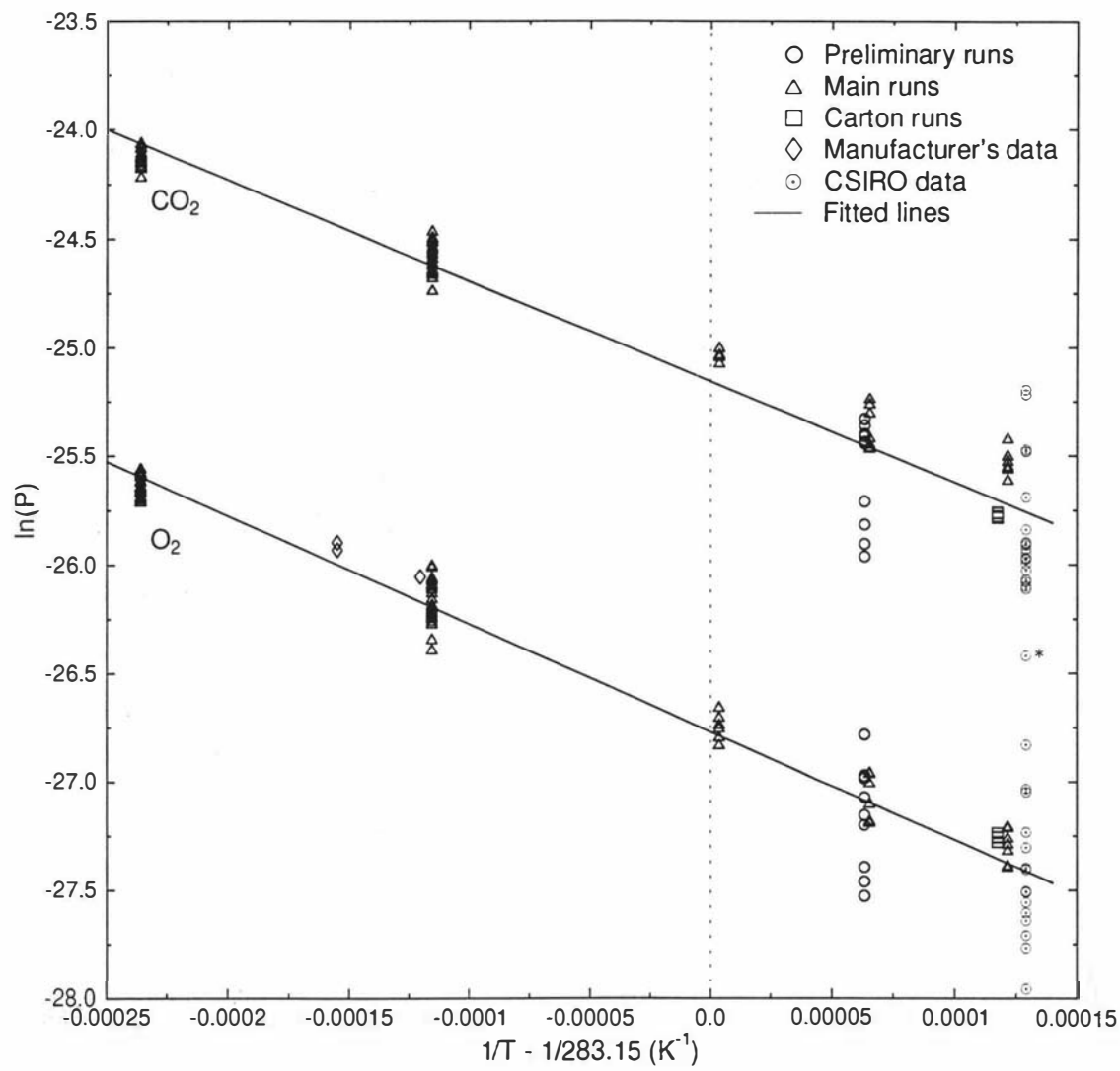
Thus, a plot of  $\ln(P_i)$  versus  $(1/T - 1/T_{ref})$  should give a straight line with a slope of  $-E_{a,i}/R$  and a y-axis intercept of  $\ln(P_{i,T_{ref}})$ . Eq. 8.13 is equivalent to the direct logarithmic transformation of Eq. 6.95, except that the y-axis intercept now represents  $\ln(P_{i,T_{ref}})$  rather than  $\ln(P_0)$ . As  $P_{i,T_{ref}}$  is of more practical interest than  $P_{i,0}$  (which represents the value of  $P$  as  $T \rightarrow \infty$ ), Eq. 8.13 was chosen for analysis and presentation of the permeability data.

Eq. 8.13 was fitted to the permeability data for  $\text{O}_2$  and  $\text{CO}_2$  by least-squares linear regression with  $T_{ref}$  set to 283.15 K ( $10^\circ\text{C}$ ) (Figure 8.10). One extremely high measurement of  $P_{\text{O}_2}$  from the first set of CSIRO data was omitted from the regression for  $\text{O}_2$  because of its large influence on the regression line. Table 8.13 lists the values of  $E_a$  and  $P_{T_{ref}}$  estimated from the regressions, together with the values of  $P_0$  back-calculated from Eq. 6.95. Table 8.14 lists the 95% confidence intervals estimated for predicted values of  $P_{\text{O}_2}$  and  $P_{\text{CO}_2}$  over a range of temperatures.

### 8.2.2.2 FILM PERMEABILITY TO $\text{N}_2$ AND WATER VAPOUR

In terms of input data for the MAP model, the accuracy of film permeability data for  $\text{N}_2$  and water vapour was considered less critical than the accuracy of permeability data for  $\text{O}_2$  and  $\text{CO}_2$ . Values of  $E_a$  and  $P_0$  for  $\text{N}_2$  and water vapour were therefore estimated from literature data rather than by experimental measurement.

Table 8.15 lists the values of  $E_a$  and  $P_0$  given by Pauly (1989) for the permeation of  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and water vapour through low density polyethylene (LDPE). Comparison of the  $E_{a,\text{O}_2}$  and  $E_{a,\text{CO}_2}$  values for LDPE with those estimated for the MA film (Table 8.13) shows that the two sets of data agree within the ranges of the 95% confidence intervals estimated for the MA-film values. Thus, values of  $E_{a,\text{N}_2}$  and  $E_{a,\text{H}_2\text{O}}$  for the MA film were assumed to be equal to those reported by Pauly (1989) for LDPE.



**Figure 8.10** Linear regression of  $\ln(P)$  versus  $(1/T - 1/283.15)$  for pooled permeability data. The data point marked ‘\*’ ( $P_{\text{O}_2}$ ) was omitted from the regression.

Although film permeabilities to gases vary widely depending on gas species and film type, ratios of the permeabilities of two gases are generally relatively constant from film to film (Felder & Huvard, 1980; Ashley, 1985; Pascat, 1986; Day, 1993). Consequently, ratios of the permeabilities of two different films to a given gas species are expected to be relatively constant from gas to gas (Felder & Huvard, 1980; Ashley, 1985). For permeabilities at  $0^\circ\text{C}$  predicted from the parameters in Tables 8.13 and 8.15, the ratios  $P_{\text{O}_2, \text{MA-film}}/P_{\text{O}_2, \text{LDPE}}$  and  $P_{\text{CO}_2, \text{MA-film}}/P_{\text{CO}_2, \text{LDPE}}$  were 2.657 and 2.886 respectively. Assuming similar ratios to hold for  $\text{N}_2$  and water vapour, values of  $P_{\text{N}_2, \text{MA-film}}$  and  $P_{\text{H}_2\text{O}, \text{MA-film}}$  at  $0^\circ\text{C}$  were estimated from

$$P_{i, \text{MA-film}} = 2.77 \times P_{i, \text{LDPE}} \tag{8.14}$$

**Table 8.13** Model parameters for permeation of O<sub>2</sub> and CO<sub>2</sub> through the MA film.

| Gas            | $E_a^a$<br>(J·mol <sup>-1</sup> ) | $P_{T_{ref}} \times 10^{12}{}^{a,b}$<br>(m <sup>2</sup> ·s <sup>-1</sup> ) | $P_0 \times 10^4$<br>(m <sup>2</sup> ·s <sup>-1</sup> ) |
|----------------|-----------------------------------|----------------------------------------------------------------------------|---------------------------------------------------------|
| Oxygen         | 41400 ± 1900                      | 2.37 ± 0.08                                                                | 1.01                                                    |
| Carbon dioxide | 38500 ± 2000                      | 11.9 ± 0.4                                                                 | 1.52                                                    |

<sup>a</sup> Values listed with 95% confidence intervals.<sup>b</sup>  $T_{ref} = 283.15$  K.**Table 8.14** 95% confidence intervals for predicted values of  $P$ .

| $\theta_{film}$<br>(°C) | 95% confidence interval on $P$ (%) |                 |
|-------------------------|------------------------------------|-----------------|
|                         | O <sub>2</sub>                     | CO <sub>2</sub> |
| 0                       | ± 4.7                              | ± 5.1           |
| 5                       | ± 3.7                              | ± 4.0           |
| 10                      | ± 3.2                              | ± 3.5           |
| 15                      | ± 3.3                              | ± 3.6           |
| 20                      | ± 3.9                              | ± 4.3           |
| 25                      | ± 4.8                              | ± 5.3           |
| 30                      | ± 5.8                              | ± 6.5           |

**Table 8.15** Literature values of  $E_a$  and  $P_0$  for low density polyethylene.<sup>a</sup>

| Gas            | $E_a$<br>(J·mol <sup>-1</sup> ) | $P_0 \times 10^5$<br>(m <sup>2</sup> ·s <sup>-1</sup> ) |
|----------------|---------------------------------|---------------------------------------------------------|
| Oxygen         | 42700                           | 6.74                                                    |
| Carbon dioxide | 38900                           | 6.28                                                    |
| Nitrogen       | 49400                           | 33.34                                                   |
| Water vapour   | 33500                           | 4.94                                                    |

<sup>a</sup> From Pauly (1989).**Table 8.16** Model parameters for permeation of N<sub>2</sub> and water vapour through the MA film.

| Gas          | $E_a$<br>(J·mol <sup>-1</sup> ) | $P_0 \times 10^4$<br>(m <sup>2</sup> ·s <sup>-1</sup> ) |
|--------------|---------------------------------|---------------------------------------------------------|
| Nitrogen     | 49400 <sup>a</sup>              | 9.23                                                    |
| Water vapour | 33500 <sup>a</sup>              | 1.37                                                    |

<sup>a</sup> From Pauly (1989).

where

$P_{i, LDPE}$  = permeability of LDPE to gas species  $i$  ( $\text{m}^2 \cdot \text{s}^{-1}$ )  
 $P_{i, MA\text{-}film}$  = permeability of the MA film to gas species  $i$  ( $\text{m}^2 \cdot \text{s}^{-1}$ ).

Values of  $P_0$  for  $\text{N}_2$  and water vapour were back-calculated from Eq. 6.95.

Table 8.16 lists the values of  $E_a$  and  $P_0$  estimated for permeation of  $\text{N}_2$  and water through the MA film.

8.2.2.3 FILM THICKNESS

Average film thicknesses measured for the 25  $\mu\text{m}$  and 40  $\mu\text{m}$  (nominal) films were 28.3  $\mu\text{m}$  and 44.3  $\mu\text{m}$  respectively. Actual rather than nominal film thicknesses were used in all calculations requiring a value for film thickness.

8.2.2 AREA AND VOLUME DATA

Table 8.17 lists the film areas estimated for the carton and bag trials. Film areas for the carton trials were estimated from liner dimensions and the average distances of the heat seals from the ends of the liners. Film areas for the bag trials were estimated from the dimensions of the MA-film windows. For both cartons and bags, the entire area of MA film exposed to the package atmosphere was assumed to be available for permeation. No corrections were made for folds and tucks, contact with the fruit or fruit trays, or condensation on the film.

Tables 8.18 and 8.19 list the package heat-transfer areas and package volumes estimated for the carton and bag trials. In estimating package heat-transfer areas, the total surface area of each package was assumed to be available for convective heat transfer.

**Table 8.17** Film areas for the carton and bag trials.

| Trial          | $A_{film}$<br>( $\text{m}^2$ ) |
|----------------|--------------------------------|
| <i>Cartons</i> |                                |
| BB93-A         | 1.457                          |
| RG94-A/B/C     | 1.426                          |
| BB94-A/B       | 1.403                          |
| GS94-A         | 1.395                          |
| <i>Bags</i>    |                                |
| BB93-B         | $7.928 \times 10^{-2}$         |
| BB93-C         | $7.829 \times 10^{-2}$         |
| GS94-B         | $7.804 \times 10^{-2}$         |

**Table 8.18** Package area and volume data.

| Package                   | $A_{pack}$<br>(m <sup>2</sup> ) | Initial<br>package volume<br>(m <sup>3</sup> ) | Minimum<br>package volume<br>(m <sup>3</sup> ) <sup>a</sup> |
|---------------------------|---------------------------------|------------------------------------------------|-------------------------------------------------------------|
| Cartons                   | 0.805                           | 0.045                                          | 0.035                                                       |
| Bags (5 count 125 fruit)  | 0.377                           | - <sup>a</sup>                                 | $1.573 \times 10^{-3}$                                      |
| Bags (10 count 125 fruit) | 0.377                           | - <sup>a</sup>                                 | $3.146 \times 10^{-3}$                                      |
| Bags (5 count 80 fruit)   | 0.377                           | - <sup>a</sup>                                 | $2.535 \times 10^{-3}$                                      |
| Bags (10 count 80 fruit)  | 0.377                           | - <sup>a</sup>                                 | $5.070 \times 10^{-3}$                                      |

<sup>a</sup> See Table 8.19.**Table 8.19** Package volumes for the bag trials.

| Trial  | Fruit              | Film<br>thickness<br>( $\mu$ m) | Measured final<br>volume ( $\times 10^3$ )<br>(m <sup>3</sup> ) | Estimated initial<br>volume ( $\times 10^3$ )<br>(m <sup>3</sup> ) |
|--------|--------------------|---------------------------------|-----------------------------------------------------------------|--------------------------------------------------------------------|
| BB93-B | 10 $\times$ ct.125 | 40                              | 5.01                                                            | 6.6                                                                |
|        | 5 $\times$ ct.125  | 40                              | 4.85                                                            | 6.1                                                                |
|        | 10 $\times$ ct.80  | 25                              | 5.70                                                            | 7.8                                                                |
|        | 5 $\times$ ct.80   | 25                              | 5.95                                                            | 7.6                                                                |
| BB93-C | 10 $\times$ ct.125 | 25                              | 5.35                                                            | 6.1                                                                |
|        | 5 $\times$ ct.125  | 25                              | 5.25                                                            | 5.7                                                                |
|        | 10 $\times$ ct.80  | 40                              | 6.80                                                            | 7.9                                                                |
|        | 5 $\times$ ct.80   | 40                              | 6.41                                                            | 7.2                                                                |
| GS94-B | 10 $\times$ ct.125 | 25                              | 4.81                                                            | 6.0                                                                |
|        | 10 $\times$ ct.125 | 40                              | 4.89                                                            | 6.0                                                                |

The minimum volumes to which the liners or bags could shrink were estimated from the spatial arrangement of fruit inside the packages.

An initial package volume for the carton trials was estimated from the internal dimensions of the cartons. Bag volumes were measured by water displacement, but to avoid the risk of damaging the bags at the start of the trials, bag volumes were measured at the end of the trials only. Initial bag volumes were estimated from the measured final volumes by first running the MAP model with assumed initial volumes to estimate the shrinkage of the packages over the duration of the trials. New estimates of the initial volumes were then back-calculated from the final volumes and the predicted shrinkages. This procedure was repeated with the newly estimated initial volumes until the estimates converged (one or two iterations).

8.2.3 MOISTURE SORPTION DATA FOR MOULDED-PULP FRUIT TRAYS

Parameters of the Guggenheim-Andersen-De Boer (GAB) isotherm for moisture sorption and desorption by the moulded-pulp fruit trays were taken from the data of Eagleton & Marcondes (1994) (Table 8.20). Eagleton & Marcondes estimated these parameters by curve-fitting equilibrium moisture contents measured over a range of relative humidities from 43% to 96%. Figure 8.11 illustrates the fitted isotherms for sorption and desorption at 1°C and 40°C. Hysteresis and an effect of temperature on moisture sorption and desorption are both apparent. As the MAP model takes no account of either of these effects, GAB isotherm parameters for moisture sorption at 1°C were chosen as model input data.

Table 8.21 lists the tray dry masses and tray areas for the carton and bag trials. Tray areas were estimated by calculating the surface areas of perfectly flat trays and multiplying these areas by an assumed factor of 1.5 to account for the moulded contours of the real trays.

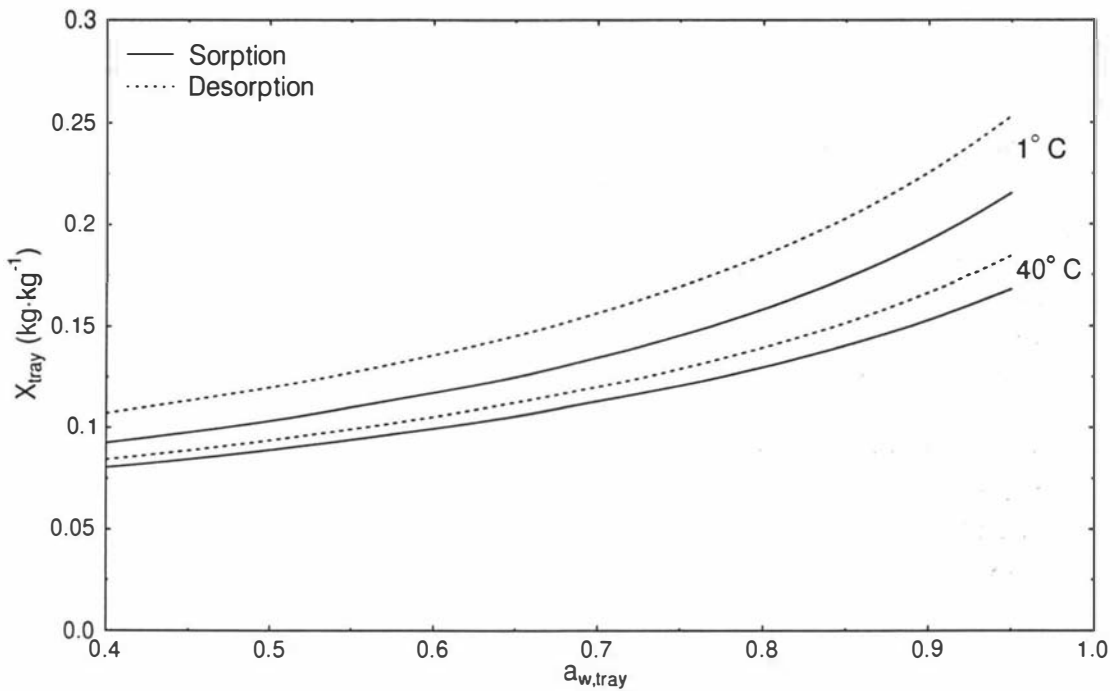
**Table 8.20** GAB model parameters for the moulded-pulp fruit trays.<sup>a</sup>

|                    | $\theta$<br>(°C) | $X_m \times 10^2$<br>(kg·kg <sup>-1</sup> ) | $C$   | $k$   |
|--------------------|------------------|---------------------------------------------|-------|-------|
| <i>Sorption:</i>   | 1                | 6.537                                       | 54900 | 0.733 |
|                    | 10               | 6.155                                       | 18600 | 0.764 |
|                    | 20               | 6.016                                       | 22600 | 0.769 |
|                    | 30               | 5.168                                       | 44600 | 0.792 |
|                    | 40               | 5.849                                       | 2690  | 0.686 |
|                    |                  |                                             |       |       |
| <i>Desorption:</i> | 1                | 7.554                                       | 640   | 0.739 |
|                    | 10               | 7.304                                       | 36.9  | 0.747 |
|                    | 20               | 7.280                                       | 30.7  | 0.734 |
|                    | 30               | 7.443                                       | 13.7  | 0.676 |
|                    | 40               | 6.060                                       | 12900 | 0.706 |
|                    |                  |                                             |       |       |

<sup>a</sup> From Eagleton & Marcondes (1994).

**Table 8.21** Mass and area data for the moulded-pulp fruit trays.

|                           | $M_{tray}$<br>(kg) | $A_{tray}$<br>(m <sup>2</sup> ) | $N_{tray}$ |
|---------------------------|--------------------|---------------------------------|------------|
| Cartons (count 125 fruit) | 0.080              | 0.450                           | 6          |
| Cartons (count 100 fruit) | 0.080              | 0.450                           | 6          |
| Cartons (count 80 fruit)  | 0.080              | 0.450                           | 5          |
| Bags (count 125 fruit)    | 0.032              | 0.180                           | 1          |
| Bags (count 80 fruit)     | 0.040              | 0.225                           | 1          |



**Figure 8.11** Moisture sorption and desorption isotherms at 1°C and 40°C for moulded-pulp fruit trays (from Eagleton & Marcondes, 1994).

## 8.3 HEAT AND MASS TRANSFER DATA

### 8.3.1 CARTON HALF-COOLING TIMES

Transformation of Eq. 6.82 gives

$$\ln Y = \ln \gamma - \alpha t \quad (8.15)$$

where

- $Y$  = fractional unaccomplished temperature change
- $\alpha$  = constant ( $s^{-1}$ )
- $\gamma$  = constant.

For cooling or warming processes, a plot of  $\ln(Y)$  versus  $t$  during the exponential phase should therefore give a straight line with a slope of  $-\alpha$ .

Eq. 8.15 was fitted to the exponential portions of the temperature-time profiles measured for carton cooling. Carton half-cooling times were then estimated from

$$t_{0.5} = \frac{\ln 2}{\alpha} \quad (8.16)$$

where

$t_{0.5}$  = carton half-cooling time (s).

Table 8.22 lists the half-cooling times measured for cartons under different storage and packaging conditions. Storage room and carton arrangement (i.e. single or stacked) had a significant effect on half-cooling times, presumably due to variations in air flow for different rooms and stacking arrangements. The presence of a carton liner significantly increased half-cooling times, especially for cartons cooling under high air-flow conditions (‘Granny Smith’ cartons in the cool-room) where half-cooling times for the

**Table 8.22** Carton half-cooling times.

| Storage                                                          | Package                               | Measurement position                         | $t_{0.5}$<br>(h) |
|------------------------------------------------------------------|---------------------------------------|----------------------------------------------|------------------|
| Shipping container,<br>stacked cartons                           | Lined ‘Royal Gala’<br>carton          | Centre apple, middle<br>tray                 | 22.8             |
|                                                                  | Lined ‘Braeburn’<br>carton            | Centre apple, middle<br>tray                 | 23.1             |
|                                                                  | Lined, insulated<br>‘Braeburn’ carton | Centre apple, middle<br>tray                 | 43.9             |
| Air-conditioned<br>laboratory, single<br>cartons placed on floor | Lined ‘Granny Smith’<br>carton (a)    | Centre apple, top tray                       | 14.4             |
|                                                                  | Lined ‘Granny Smith’<br>carton (a)    | Centre apple, middle<br>tray                 | 15.6             |
|                                                                  | Lined ‘Granny Smith’<br>carton (a)    | Apple adjacent to hand-<br>hole, middle tray | 14.7             |
|                                                                  | Lined ‘Granny Smith’<br>carton (b)    | Centre apple, middle<br>tray                 | 14.6             |
|                                                                  | Unlined ‘Granny Smith’<br>carton      | Centre apple, middle<br>tray                 | 11.5             |
| Cool-room, single<br>cartons on wire racks                       | Lined ‘Granny Smith’<br>carton (a)    | Centre apple, top tray                       | 12.0             |
|                                                                  | Lined ‘Granny Smith’<br>carton (a)    | Centre apple, middle<br>tray                 | 12.7             |
|                                                                  | Lined ‘Granny Smith’<br>carton (a)    | Apple adjacent to hand-<br>hole, middle tray | 11.6             |
|                                                                  | Lined ‘Granny Smith’<br>carton (b)    | Centre apple, middle<br>tray                 | 13.1             |
|                                                                  | Unlined ‘Granny Smith’<br>carton      | Centre apple, middle<br>tray                 | 5.6              |

lined cartons were more than double that of the unlined carton. Under the lower air-flow conditions in the air-conditioned laboratory, warming rates for the lined cartons were about 30% higher than that of the unlined carton. Insulation of lined cartons on five sides (section 4.1.1) also had a significant effect on cooling rate, almost doubling the half-cooling time. Fruit at different positions in one lined 'Granny Smith' carton showed only small differences in half-cooling times.

### 8.3.2 HEAT AND MASS TRANSFER COEFFICIENTS

Heat and mass transfer at the fruit, packaging film, and fruit-tray surfaces were assumed to occur by natural convection only. Heat and mass transfer coefficients at these surfaces were estimated from empirical correlations for natural convection at the surfaces of single spheres (the fruit surface), empty spherical cavities (the packaging film inside surface), and isolated horizontal plates (the fruit trays) (Holman, 1986, pp. 342, 347; Kreith & Bohn, 1986, pp. 262, 265). However, the heat transfer occurring within an apple carton is far removed from the idealized situations to which these correlations apply. In an apple carton, there is significant contact between the fruit and the fruit trays, the fruit and the packaging film, and the fruit trays and the packaging film; radiative heat transfer may also be significant. Thus, the values estimated from the correlations must be considered indicative values only.

Table 8.23 lists the heat transfer coefficients estimated for the cartons and bags. Overall heat transfer coefficients for the packaging materials were estimated from Eq. 6.76 and the data listed in Table 8.24. The overall heat transfer coefficient for insulated cartons was weighted to account for the fact that only five sides of the cartons were insulated (one short end of each carton was left exposed to the store air).

Estimates of the mass transfer coefficients for condensation at the fruit surface and the packaging film inside surface, and for moisture sorption at the fruit tray surfaces, ranged from  $0.5 \times 10^{-8} \text{ s}\cdot\text{m}^{-1}$  to  $1.4 \times 10^{-8} \text{ s}\cdot\text{m}^{-1}$ . Because of the uncertainty associated with these estimates, a global mass transfer coefficient of  $1 \times 10^{-8} \text{ s}\cdot\text{m}^{-1}$  was assumed.

**Table 8.23** Package heat-transfer coefficients.

| Heat transfer coefficient                                | Symbol            | Estimate<br>( $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ ) |
|----------------------------------------------------------|-------------------|----------------------------------------------------------------|
| <i>Convection heat transfer</i>                          |                   |                                                                |
| Fruit surface                                            | $h_f$             | 2.9                                                            |
| Packaging film inside surface                            | $h_p$             | 1.9                                                            |
| Package outer surface                                    | $h_e$             | 5 <sup>a</sup>                                                 |
| <i>Overall heat transfer through packaging materials</i> |                   |                                                                |
| Uninsulated cartons                                      | $U_{\text{pack}}$ | 0.97                                                           |
| Insulated cartons                                        | $U_{\text{pack}}$ | 0.34                                                           |
| Bags                                                     | $U_{\text{pack}}$ | 1.4                                                            |

<sup>a</sup> Assumed.

**Table 8.24** Thermal conductivity data for the calculation of package overall heat-transfer coefficients.

| Material                            | $x_i$<br>(m) | $\lambda_i$<br>(W m <sup>-1</sup> ·K <sup>-1</sup> ) |
|-------------------------------------|--------------|------------------------------------------------------|
| Air gap                             | 0.005        | 0.024 <sup>a</sup>                                   |
| Corrugated cardboard (double layer) | 0.006        | 0.061 <sup>a</sup>                                   |
| Polystyrene insulation              | 0.100        | 0.036 <sup>b</sup>                                   |

<sup>a</sup> From Jamieson *et al.* (1993).

<sup>b</sup> Manufacturer's data.

**Table 8.25** Model constants.

| Quantity                                                                 | Symbol          | Value                   | Unit                                 |
|--------------------------------------------------------------------------|-----------------|-------------------------|--------------------------------------|
| Specific heat capacity of dry air                                        | $C_{pa}$        | 1006                    | J·kg <sup>-1</sup> ·K <sup>-1</sup>  |
| Specific heat capacity of water vapour                                   | $C_{pv}$        | 1870                    | J·kg <sup>-1</sup> ·K <sup>-1</sup>  |
| Specific heat capacity of water                                          | $C_{pw}$        | 4200                    | J·kg <sup>-1</sup> ·K <sup>-1</sup>  |
| Specific heat capacity of dry fruit trays                                | $C_{p, tray}$   | 1340                    | J·kg <sup>-1</sup> ·K <sup>-1</sup>  |
| Latent heat of evaporation of water                                      | $h_{fg}$        | 2500 × 10 <sup>3</sup>  | J·kg <sup>-1</sup>                   |
| Atmospheric pressure                                                     | $P_{atm}$       | 101325                  | Pa                                   |
| Gas constant                                                             | $R$             | 8.314                   | J·mol <sup>-1</sup> ·K <sup>-1</sup> |
| Diffusivity of O <sub>2</sub> in N <sub>2</sub> at 273.15 K <sup>a</sup> | $D_{O_2, ref}$  | 1.81 × 10 <sup>-5</sup> | m <sup>2</sup> ·s <sup>-1</sup>      |
| Diffusivity of CO <sub>2</sub> in air at 276.2 K <sup>b</sup>            | $D_{CO_2, ref}$ | 1.42 × 10 <sup>-5</sup> | m <sup>2</sup> ·s <sup>-1</sup>      |
| Diffusivity of N <sub>2</sub> in N <sub>2</sub> at 273 K <sup>b</sup>    | $D_{N_2, ref}$  | 1.85 × 10 <sup>-5</sup> | m <sup>2</sup> ·s <sup>-1</sup>      |
| Diffusivity of water vapour in air at 289.9 K <sup>b</sup>               | $D_{H_2O, ref}$ | 2.44 × 10 <sup>-5</sup> | m <sup>2</sup> ·s <sup>-1</sup>      |

<sup>a</sup> From Treybal (1980).

<sup>b</sup> From Rohsenow *et al.* (1985).

## 8.4 MODEL CONSTANTS

A number of the physical quantities that appear in the MAP model formulation were treated as universal constants; their values were embedded in the program code rather than allowing them to be specified by the user via data input procedures. Table 8.25 lists the values assumed for these constants.

## Chapter 9

### MODEL VALIDATION

Model validation involves the testing of a proposed model to determine whether it is capable of predicting the behaviour of the real system it represents with a level of accuracy that allows the model to be usefully applied for design, optimization, or investigative purposes. Model validation is therefore best carried out by comparing model predictions with test data collected from the system being modelled.

Disagreement between model predictions and test data can arise from one or more of three sources:

- (1) Shortcomings in the model. Virtually all models are based on assumptions that attempt to simplify the real system being modelled. The effects of these simplifying assumptions show up to a greater or lesser extent as systematic deviations of model predictions from the behaviour of the real system.
- (2) Shortcomings in the test data. All experimental data are subject to a certain amount of error: random, systematic, or both. Random error shows up as 'scatter' in the test data; the magnitude of this error can be estimated if sets of test data collected under replicate conditions are available. Systematic errors are more difficult to detect, as they give rise to systematic differences between model and system behaviour that are difficult to distinguish from the effects of (1) above or (3) below.
- (3) Shortcomings in the model input data. Both random and systematic errors in model input data show up as systematic deviations of model predictions from the behaviour of the real system. Magnitudes of the random errors in model input data can be estimated from the analysis of replicate measurements, and the effects of these errors on model predictions can be characterized. Systematic errors in model input data, again, are difficult to detect.

Assuming that no significant systematic errors go undetected in either the model input data or the test data, model validation should provide answers to the following questions:

- *Taking into account any uncertainties in the test data, does the model accurately predict system behaviour?*
- *If significant differences between model predictions and system behaviour exist, could these be due to uncertainties in system input data, or must they be attributed to shortcomings in the model formulation?*
- *Where could further experimental or model development work be most usefully directed?*
- *Is the model suitable for use as a design or investigative tool?*

The MAP model developed in Chapters 6 and 7 was validated by comparing model predictions with the experimental data collected during the MA trials described in Chapters 4 and 5. The current chapter presents the model validation results in three parts:

- (1) a comparison of the model's predictions with test data from the MA trials;
- (2) a sensitivity analysis to characterize the effects of uncertainties in model input data on the model's predictions;
- (3) an overview of the model's performance in relation to existing MAP models and in relation to the model's application to the design of modified atmosphere packaging systems.

## 9.1 MODEL PREDICTIONS

The model input data presented in Chapter 8 were used to run the MAP model for conditions corresponding to each of the experimental MA trials. Input data files for the model runs are given in Appendix D (on diskette).

### 9.1.1 PACKAGE O<sub>2</sub> AND CO<sub>2</sub> CONCENTRATIONS

Tables 9.1 to 9.4 list the experimental and predicted O<sub>2</sub> and CO<sub>2</sub> concentrations corresponding to the steady-state package atmospheres formed during the carton and bag trials. On average, the model predicted steady-state O<sub>2</sub> concentrations within 1.0 mol %, and steady-state CO<sub>2</sub> concentrations within 0.4 mol % (these averages do not include the model predictions for bags where measured O<sub>2</sub> concentrations dropped below 3 mol %, or predictions made with the CO<sub>2</sub> respiration model for bags at 15°C). Predicted steady-state O<sub>2</sub> concentrations were higher than measured values in some cases and lower in others, but steady-state CO<sub>2</sub> concentrations were consistently under-predicted.

Comparisons between predicted and experimental package atmospheres for each trial are presented graphically in the following four sections, together with a discussion of specific aspects of the model's performance.

#### 9.1.1.1 1993 'BRAEBURN'

##### *Cartons*

Figures 9.1 to 9.8 show the predicted and experimental package O<sub>2</sub> and CO<sub>2</sub> concentrations for the 1993 'Braeburn' carton trial (trial BB93-A).

For cartons with undamaged, heat-sealed liners (Figures 9.1 to 9.4), model predictions for O<sub>2</sub> generally agreed well with experimental data. However, from 3 to 5 days onwards, model predictions for CO<sub>2</sub> were consistently lower than measured CO<sub>2</sub> concentrations, with steady-state CO<sub>2</sub> concentrations under-predicted by 0.3 to 0.9 mol % (Table 9.2).

**Table 9.1** Measured and predicted steady-state package O<sub>2</sub> concentrations (cartons).

| Cultivar          | Film thickness<br>( $\mu\text{m}$ ) | n <sup>a</sup> | Measured <sup>b</sup><br>(mol %) | Predicted <sup>c</sup><br>(mol %) | Predicted <sup>d</sup><br>(mol %) |
|-------------------|-------------------------------------|----------------|----------------------------------|-----------------------------------|-----------------------------------|
| 1993 Braeburn     | 25                                  | 6              | 12.8 $\pm$ 0.4                   | 12.1                              | 11.8                              |
|                   | 40                                  | 7              | 8.6 $\pm$ 0.2                    | 8.9                               | 7.7                               |
| 1994 Royal Gala   | 25                                  | 10             | 14.2 $\pm$ 0.3                   | 13.3                              | 13.1                              |
|                   | 40                                  | 11             | 10.5 $\pm$ 0.3                   | 11.0                              | 10.1                              |
| 1994 Braeburn     | 25                                  | 6              | 13.6 $\pm$ 0.5                   | 12.9                              | 12.4                              |
|                   | 40                                  | 2              | 9.7                              | 10.3                              | 9.0                               |
| 1994 Granny Smith | 25                                  | 4              | 13.6 $\pm$ 0.5                   | 11.6                              | 11.1                              |
|                   | 40                                  | 4              | 8.8 $\pm$ 0.2                    | 8.3                               | 6.7                               |

<sup>a</sup> n = sample size (number of cartons).

<sup>b</sup> Values presented as 'mean  $\pm$  95% confidence interval on mean' (for n > 2).

<sup>c</sup> Values predicted under the O<sub>2</sub> respiration model.

<sup>d</sup> Values predicted under the CO<sub>2</sub> respiration model.

**Table 9.2** Measured and predicted steady-state package CO<sub>2</sub> concentrations (cartons).

| Cultivar          | Film thickness<br>( $\mu\text{m}$ ) | n <sup>a</sup> | Measured <sup>b</sup><br>(mol %) | Predicted <sup>c</sup><br>(mol %) | Predicted <sup>d</sup><br>(mol %) |
|-------------------|-------------------------------------|----------------|----------------------------------|-----------------------------------|-----------------------------------|
| 1993 Braeburn     | 25                                  | 6              | 2.1 $\pm$ 0.1                    | 1.7                               | 1.8                               |
|                   | 40                                  | 7              | 3.2 $\pm$ 0.1                    | 2.3                               | 2.6                               |
| 1994 Royal Gala   | 25                                  | 10             | 1.7 $\pm$ 0.1                    | 1.5                               | 1.5                               |
|                   | 40                                  | 11             | 2.5 $\pm$ 0.1                    | 1.9                               | 2.1                               |
| 1994 Braeburn     | 25                                  | 6              | 1.8 $\pm$ 0.1                    | 1.6                               | 1.7                               |
|                   | 40                                  | 2              | 2.7                              | 2.0                               | 2.3                               |
| 1994 Granny Smith | 25                                  | 4              | 1.9 $\pm$ 0.1                    | 1.8                               | 1.9                               |
|                   | 40                                  | 4              | 3.0 $\pm$ 0.1                    | 2.4                               | 2.7                               |

<sup>a</sup> n = sample size (number of cartons).

<sup>b</sup> Values presented as 'mean  $\pm$  95% confidence interval on mean' (for n > 2).

<sup>c</sup> Values predicted under the O<sub>2</sub> respiration model.

<sup>d</sup> Values predicted under the CO<sub>2</sub> respiration model.

Each of Figures 9.1 to 9.4 shows two sets of model predictions, one for respiration as a function of fruit internal O<sub>2</sub>, and one for respiration as a function of fruit internal CO<sub>2</sub> (section 8.1.4). Although the two respiration models gave similar results overall, the CO<sub>2</sub> respiration model predicted slower rates of atmosphere modification and more modified steady-state atmospheres than the O<sub>2</sub> respiration model. These differences can be explained by considering the nature of each respiration model.

According to the O<sub>2</sub> respiration model, respiration rate decreases with decreasing fruit internal O<sub>2</sub> concentration, gradually at high O<sub>2</sub> concentrations and then more sharply at

**Table 9.3** Measured and predicted steady-state package O<sub>2</sub> concentrations (bags).

| Cultivar      | Fruit       | Film thickness (μm) | θ (°C) | n <sup>a</sup> | Measured <sup>b</sup> (mol %) | Predicted <sup>c</sup> (mol %) | Predicted <sup>d</sup> (mol %) |
|---------------|-------------|---------------------|--------|----------------|-------------------------------|--------------------------------|--------------------------------|
| 1993 Braeburn | 5 × ct.80   | 25                  | 15     | 2              | 8.4                           | 8.6                            | 4.3                            |
|               | 5 × ct.80   | 25                  | 0      | 1              | 12.8                          | 12.9                           | 13.0                           |
|               | 5 × ct.80   | 40                  | 0      | 5              | 8.8 ± 0.8                     | 9.7                            | 9.3                            |
|               | 10 × ct.80  | 25                  | 15     | 2              | 4.4                           | 5.1                            | -                              |
|               | 10 × ct.80  | 25                  | 0      | 2              | 6.2                           | 8.1                            | 7.0                            |
|               | 10 × ct.80  | 40                  | 0      | 2              | 2.3                           | 5.1                            | 0.6                            |
|               | 5 × ct.125  | 25                  | 0      | 2              | 15.3                          | 15.5                           | 15.6                           |
|               | 5 × ct.125  | 40                  | 15     | 2              | 7.9                           | 8.6                            | 4.5                            |
|               | 5 × ct.125  | 40                  | 0      | 2              | 11.4                          | 13.1                           | 13.1                           |
|               | 10 × ct.125 | 25                  | 0      | 2              | 10.9                          | 11.2                           | 11.1                           |
|               | 10 × ct.125 | 40                  | 15     | 5              | 4.2 ± 0.4                     | 4.9                            | -                              |
|               | 10 × ct.125 | 40                  | 0      | 5              | 5.6 ± 0.2                     | 8.1                            | 7.0                            |
|               | 10 × ct.125 | 25                  | 0      | 5              | 9.9 ± 0.6                     | 9.1                            | 8.0                            |
|               | 10 × ct.125 | 40                  | 0      | 5              | 2.5 ± 1.2                     | 6.1                            | 2.5                            |
|               | 10 × ct.125 | 40                  | 0      | 5              | 2.5 ± 1.2                     | 6.1                            | 2.5                            |

<sup>a</sup> n = sample size (number of bags).<sup>b</sup> Values presented as 'mean ± 95% confidence interval on mean' (for n > 2).<sup>c</sup> Values predicted under the O<sub>2</sub> respiration model.<sup>d</sup> Values predicted under the CO<sub>2</sub> respiration model.

lower O<sub>2</sub> concentrations (Figure 8.1). According to the CO<sub>2</sub> respiration model, respiration rate decreases with increasing fruit internal CO<sub>2</sub> concentration, most rapidly at low CO<sub>2</sub> concentrations and more gradually at higher CO<sub>2</sub> concentrations (Figure 8.5). Thus, when incorporated into the MAP model, the CO<sub>2</sub> respiration model depresses respiration rate more significantly early in the simulation, when CO<sub>2</sub> concentrations are low but rising rapidly, whereas the O<sub>2</sub> respiration model depresses respiration rate more significantly later in the simulation, as O<sub>2</sub> concentrations approach the value of  $k_m$ . Hence, the CO<sub>2</sub> respiration model results in slower predicted rates of atmosphere modification than the O<sub>2</sub> respiration model.

At a given temperature, respiration rates predicted by the O<sub>2</sub> and CO<sub>2</sub> respiration rate models are affected only by fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations respectively. If both respiration models fit the respiration data for a given range of atmospheres equally well, then the accuracy with which respiration rates are predicted within the MAP model depends on the accuracy of fruit internal O<sub>2</sub> or CO<sub>2</sub> predictions. In Figures 9.1 to 9.4 package O<sub>2</sub> concentrations are predicted relatively accurately whereas CO<sub>2</sub> concentrations are under-predicted. Assuming that this is also reflected in the predictions of fruit internal O<sub>2</sub> and CO<sub>2</sub>, the steady-state respiration rates predicted by the O<sub>2</sub> respiration model should be close to the experimentally measured respiration rates, whereas the respiration rates predicted by the CO<sub>2</sub> respiration model, because CO<sub>2</sub> concentrations are being under-predicted, would be higher. This explains the differences observed between the two sets of predicted steady-state atmospheres.

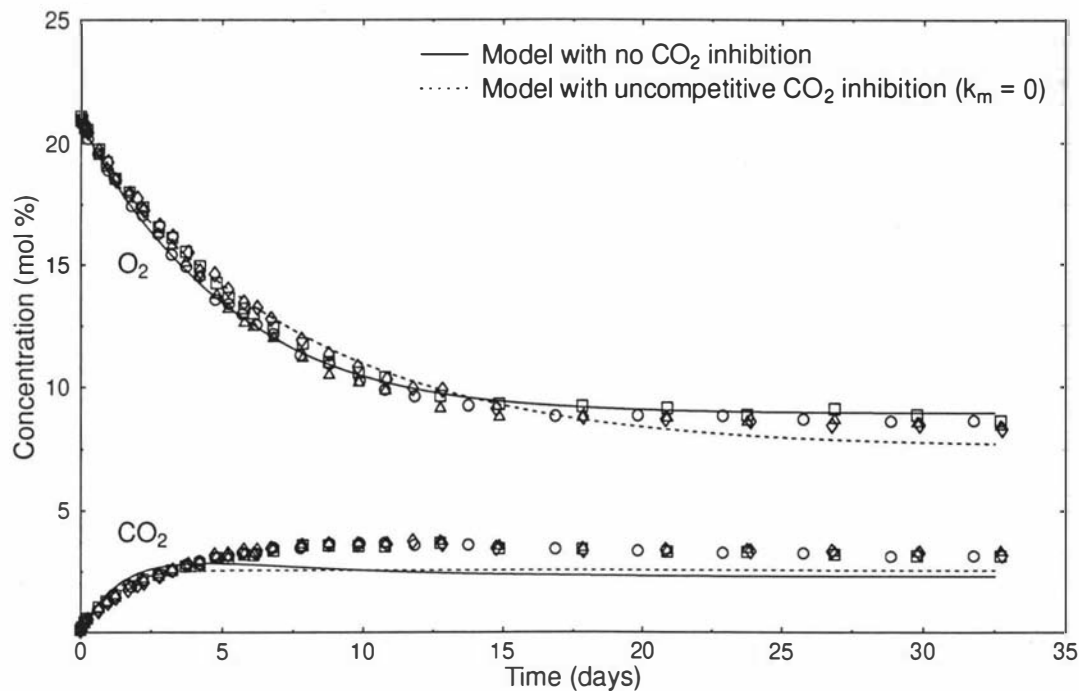
**Table 9.4** Measured and predicted steady-state package CO<sub>2</sub> concentrations (bags).

| Cultivar          | Fruit       | Film thickness (μm) | θ (°C) | n <sup>a</sup> | Measured <sup>b</sup> (mol %) | Predicted <sup>c</sup> (mol %) | Predicted <sup>d</sup> (mol %) |
|-------------------|-------------|---------------------|--------|----------------|-------------------------------|--------------------------------|--------------------------------|
| 1993 Braeburn     | 5 × ct.80   | 25                  | 15     | 2              | 2.9                           | 2.5                            | 3.3                            |
|                   | 5 × ct.80   | 25                  | 0      | 1              | 1.8                           | 1.6                            | 1.6                            |
|                   | 5 × ct.80   | 40                  | 0      | 5              | 2.8 ± 0.2                     | 2.2                            | 2.3                            |
|                   | 10 × ct.80  | 25                  | 15     | 2              | 3.9                           | 3.2                            | 5.8                            |
|                   | 10 × ct.80  | 25                  | 0      | 2              | 3.0                           | 2.5                            | 2.7                            |
|                   | 10 × ct.80  | 40                  | 0      | 2              | 4.4                           | 3.0                            | 3.8                            |
|                   | 5 × ct.125  | 25                  | 0      | 2              | 1.3                           | 1.1                            | 1.1                            |
|                   | 5 × ct.125  | 40                  | 15     | 2              | 3.1                           | 2.5                            | 3.3                            |
|                   | 5 × ct.125  | 40                  | 0      | 2              | 1.9                           | 1.5                            | 1.5                            |
|                   | 10 × ct.125 | 25                  | 0      | 2              | 2.1                           | 1.9                            | 1.9                            |
|                   | 10 × ct.125 | 40                  | 15     | 5              | 4.1 ± 0.1                     | 3.2                            | 5.8                            |
|                   | 10 × ct.125 | 40                  | 0      | 5              | 3.1 ± 0.1                     | 2.4                            | 2.7                            |
| 1994 Granny Smith | 10 × ct.125 | 25                  | 0      | 5              | 2.3 ± 0.1                     | 2.3                            | 2.5                            |
|                   | 10 × ct.125 | 40                  | 0      | 5              | 3.9 ± 0.4                     | 2.8                            | 3.5                            |

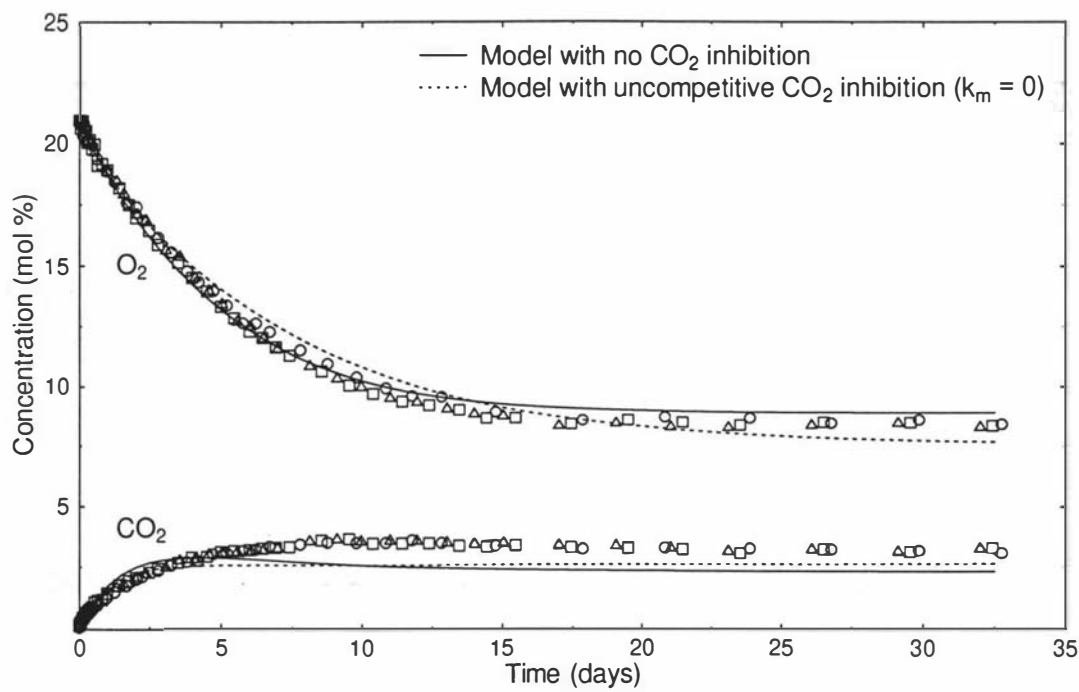
<sup>a</sup> n = sample size (number of bags).<sup>b</sup> Values presented as 'mean ± 95% confidence interval on mean' (for n > 2).<sup>c</sup> Values predicted under the O<sub>2</sub> respiration model.<sup>d</sup> Values predicted under the CO<sub>2</sub> respiration model.

Figure 9.5 shows the same model predictions as Figure 9.1, but this time compared with experimental data collected from cartons with folded liners. Modelling of gas transfer through folds was not considered in formulating the MAP model, and the main value of the MAP model for cartons with folded liners lies in providing an estimate of the maximum expected extent of atmosphere modification. From a risk-analysis perspective, this is the most important extreme that needs to be considered when designing MAP systems. The variability of atmospheres formed inside folded liners (discussed more fully in section 5.1.1) suggests that a stochastic modelling approach could be valuable if the model were to be further developed for such packages.

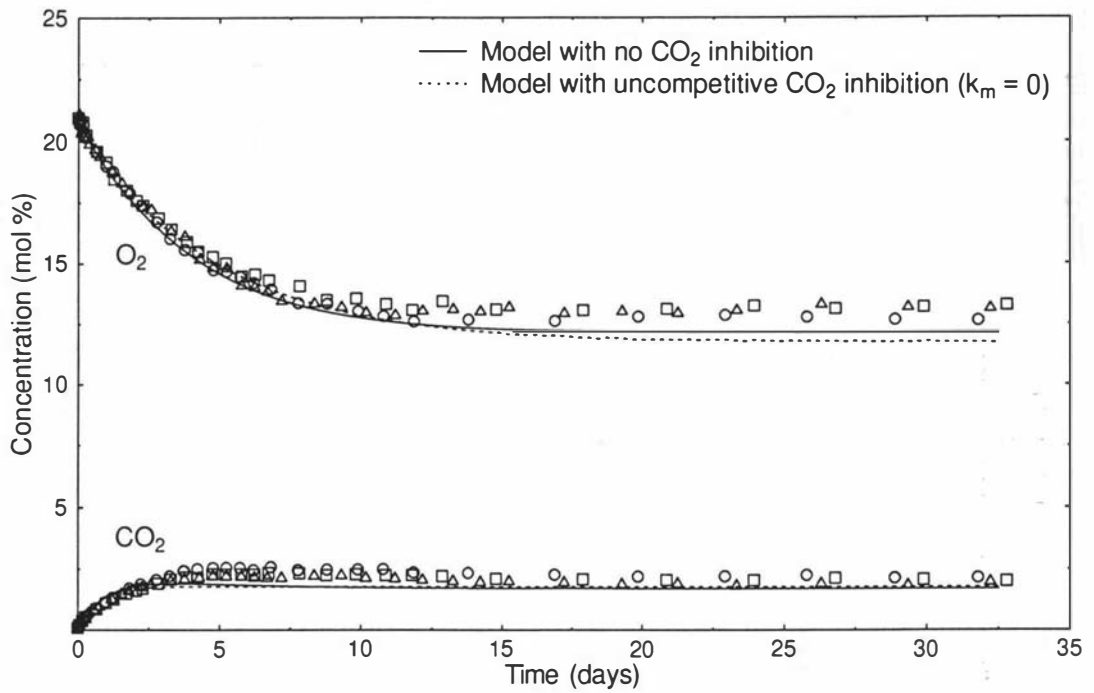
Predicted and experimental package O<sub>2</sub> and CO<sub>2</sub> concentrations for carton liners with holes are shown in Figure 9.6 (1 × 130 μm diameter hole, 40 μm film), Figure 9.7 (1 × 320 μm diameter hole, 40 μm film), and Figure 9.8 (2 × 8 mm diameter holes, 40 μm film) (predictions shown are for respiration with no CO<sub>2</sub> inhibition). Values of the empirical correction factor for gas diffusion through holes (ξ) (section 6.2.16.6) were chosen by running the MAP model with different values of ξ to find a value that gave reasonable predictions for each hole size. This value of ξ decreased as hole diameter increased (ξ ≈ 1 for a hole diameter:film thickness ratio of 3.25; ξ ≈ 0.5 for a hole diameter:film thickness ratio of 8; and ξ ≈ 0.01 for a hole diameter:film thickness ratio of 200).



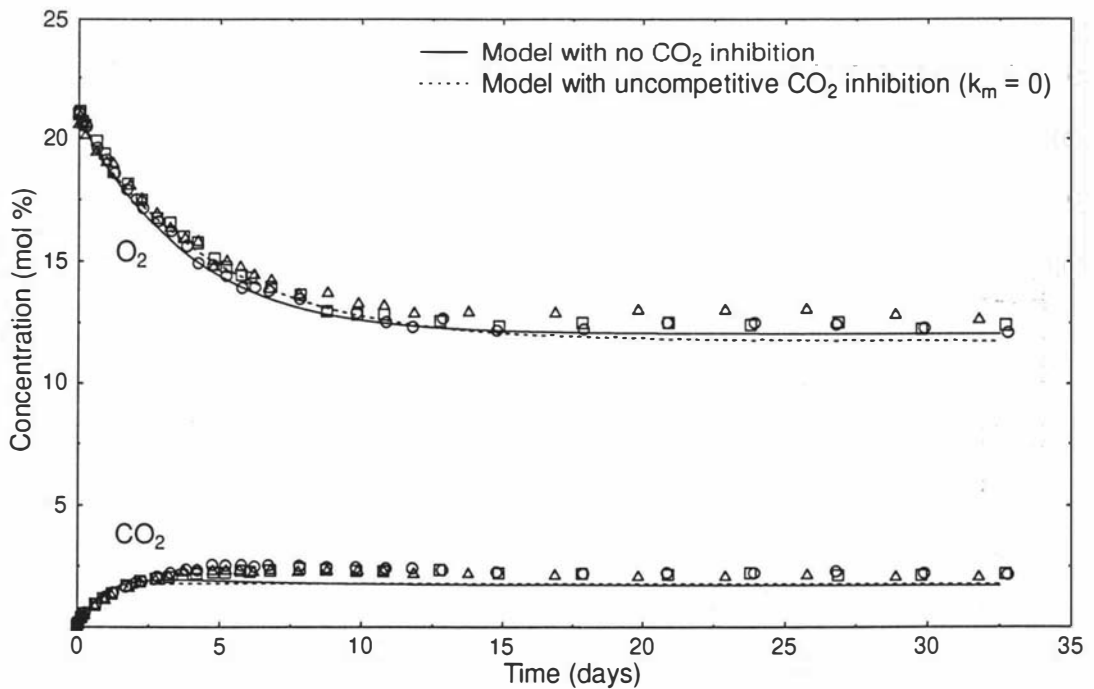
**Figure 9.1** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 'Braeburn' cartons (count 125 fruit, 40 µm film, heat-sealed, trial BB93-A). Experimental data from 4 replicate cartons shown.



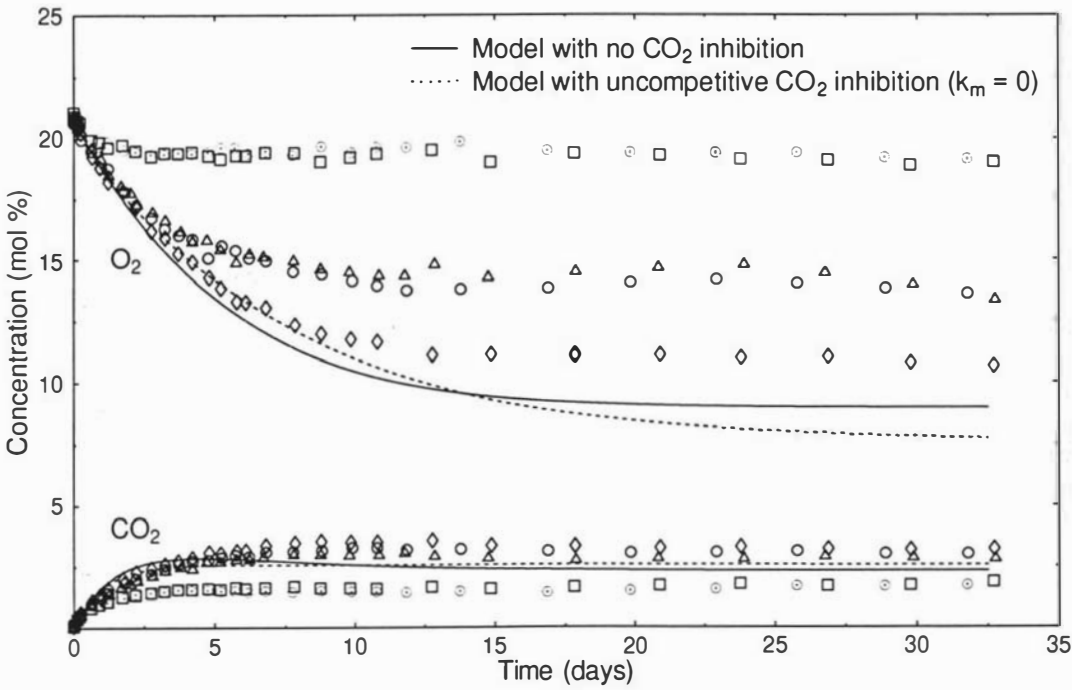
**Figure 9.2** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 'Braeburn' cartons (count 80 fruit, 40 µm film, heat-sealed, trial BB93-A). Experimental data from 3 replicate cartons shown.



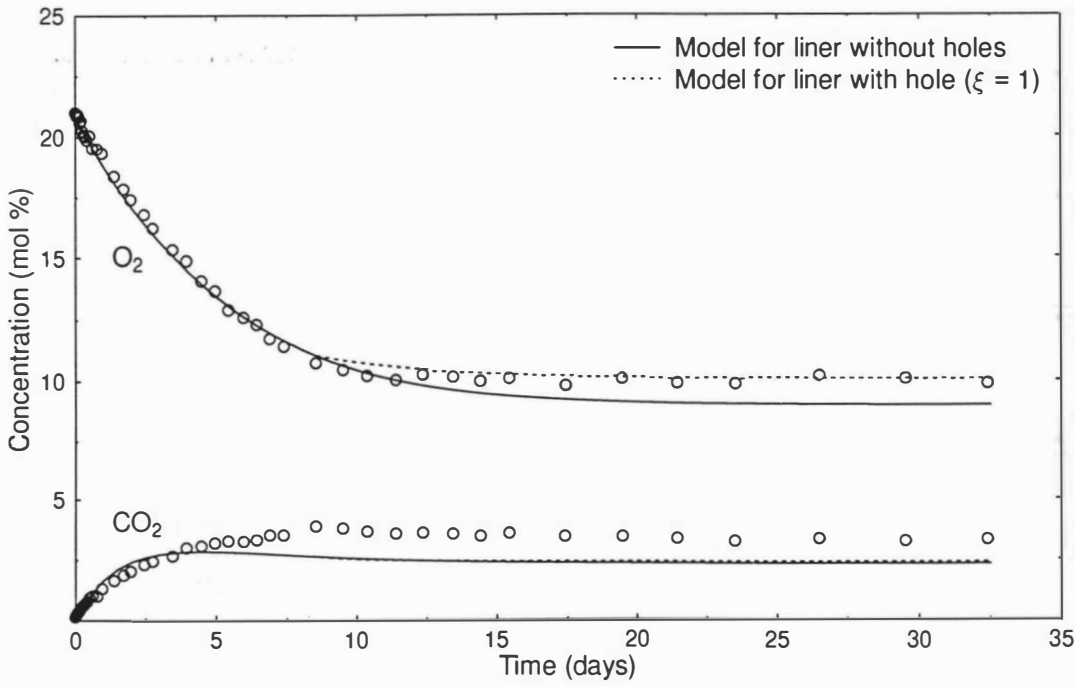
**Figure 9.3** Package  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' cartons (count 125 fruit, 25  $\mu m$  film, heat-sealed, trial BB93-A). Experimental data from 3 replicate cartons shown.



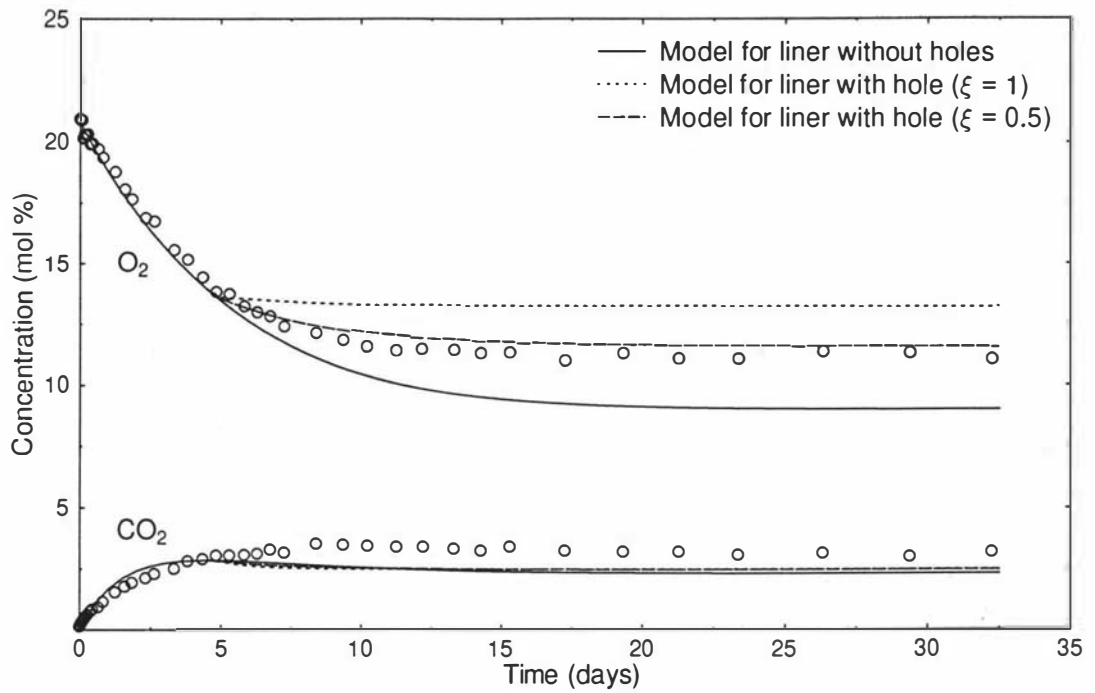
**Figure 9.4** Package  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' cartons (count 80 fruit, 25  $\mu m$  film, heat-sealed, trial BB93-A). Experimental data from 3 replicate cartons shown.



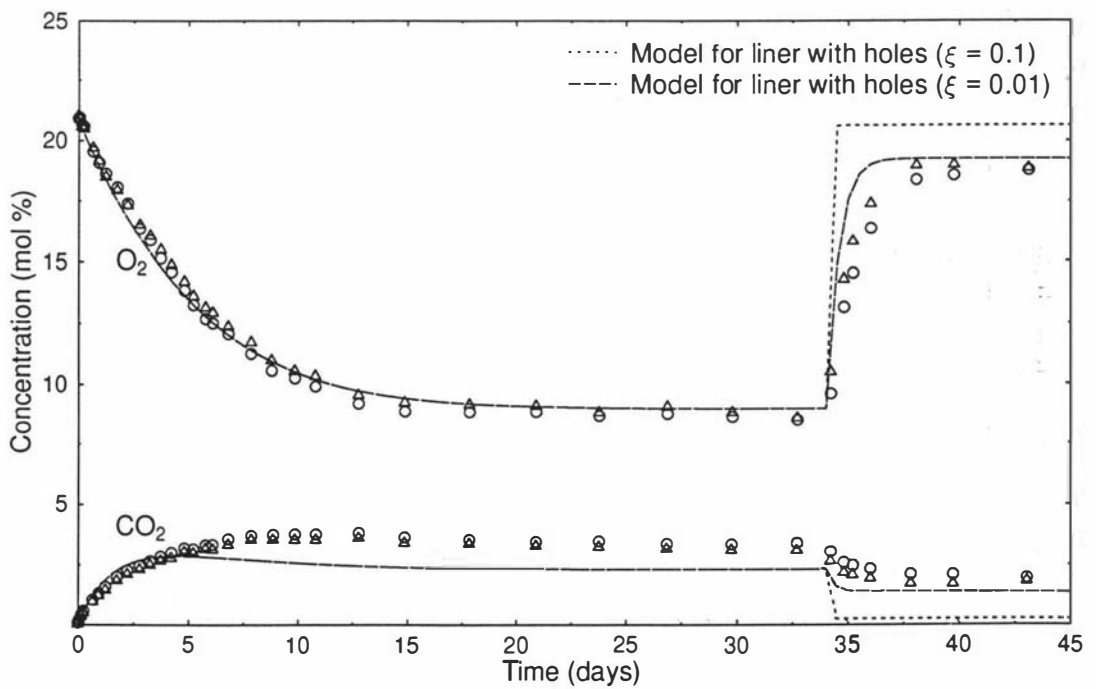
**Figure 9.5** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 'Braeburn' cartons (count 125 fruit, 40  $\mu$ m film, folded, trial BB93-A). Experimental data from 5 replicate cartons shown.



**Figure 9.6** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 'Braeburn' carton with 1 x 130  $\mu$ m diameter hole (count 125 fruit, 40  $\mu$ m film, heat-sealed, trial BB93-A). Predictions shown are for model with no CO<sub>2</sub> inhibition.



**Figure 9.7** Package  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' carton with  $1 \times 320 \mu m$  diameter hole (count 125 fruit,  $40 \mu m$  film, heat-sealed, trial BB93-A). Predictions shown are for model with no  $CO_2$  inhibition.



**Figure 9.8** Package  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' cartons with  $2 \times 8 mm$  diameter holes (count 125 fruit,  $40 \mu m$  film, heat-sealed, trial BB93-A). Predictions shown are for model with no  $CO_2$  inhibition.

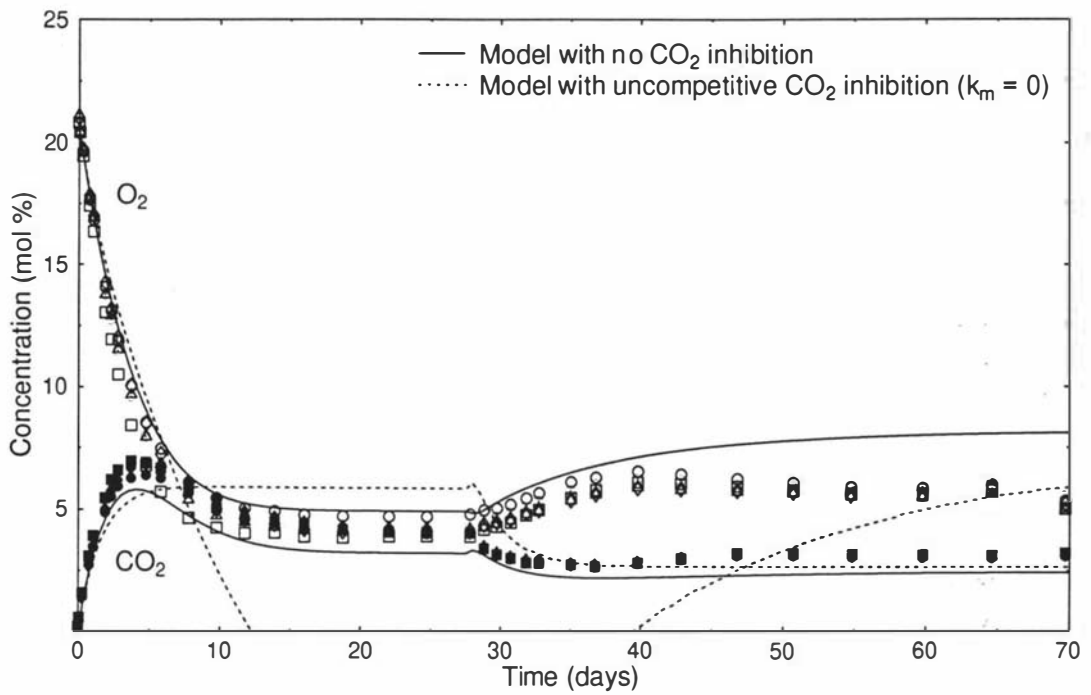
### *Bags*

Predicted and experimental package O<sub>2</sub> and CO<sub>2</sub> concentrations for the 1993 'Braeburn' bag trials are shown in Figures 9.9 to 9.12 (trial BB93-B) and Figures 9.13 to 9.16 (trial BB93-C). Again, each Figure shows two sets of model predictions, one for the O<sub>2</sub> respiration model and one for the CO<sub>2</sub> respiration model.

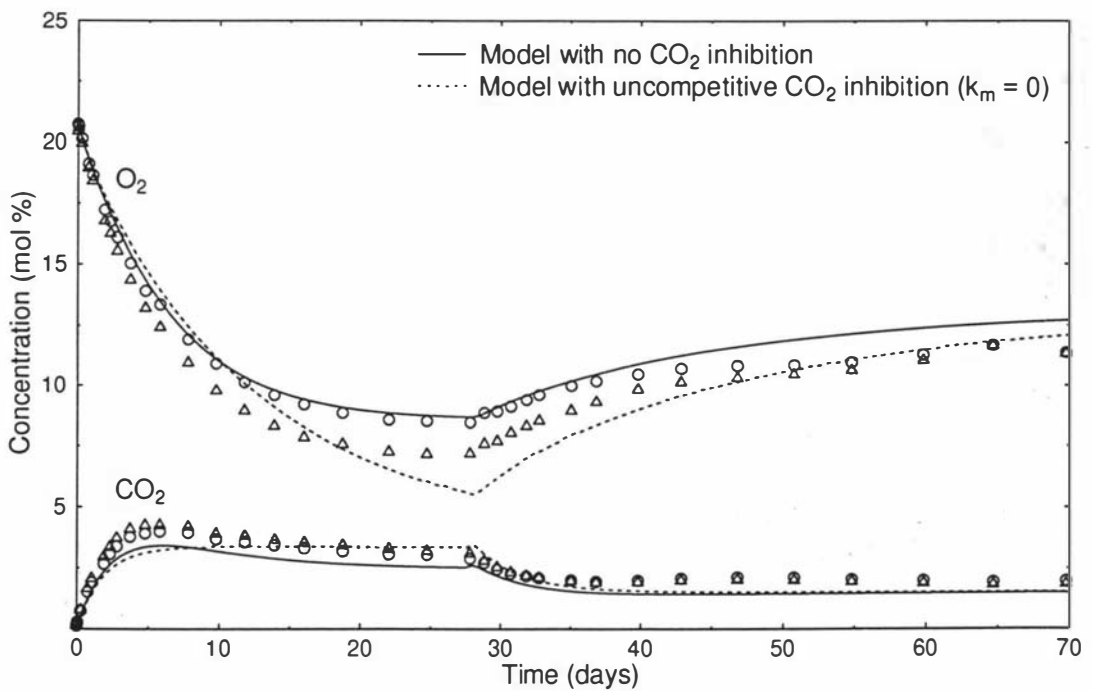
Respiration models for the 1993 'Braeburn' fruit were fitted to respiration data collected during the carton trials. The models were thus fitted for fruit internal O<sub>2</sub> concentrations of 7 to 19 mol % and fruit internal CO<sub>2</sub> concentrations of 1.7 to 4.4 mol %, at a temperature of 1.6°C. Values of  $k_m$  and  $k_{iu}$  were assumed to be independent of temperature. For many of the predictions shown in Figures 9.9 to 9.16, both respiration models were extrapolated well beyond these conditions. For example, the combination of elevated storage temperature and low O<sub>2</sub>/high CO<sub>2</sub> package atmospheres for bags in trial BB93-B during the 15°C storage period (Figures 9.9 to 9.12, days 0 to 28) represents an extrapolation of the respiration models to a higher temperature and to much lower fruit internal O<sub>2</sub> concentrations and higher internal CO<sub>2</sub> concentrations than the ranges for which the models were fitted.

In spite of these limitations, predictions made with the O<sub>2</sub> respiration model generally showed good agreement with experimental data. One exception is shown in Figure 9.15, where predictions failed to reach the very low O<sub>2</sub> concentrations that developed inside the bags. Prediction of respiration rates at such low O<sub>2</sub> concentrations required significant extrapolation of the O<sub>2</sub> respiration model, and the disagreement between the experimental and predicted data suggests a lower  $k_m$  than that fitted for the respiration model.

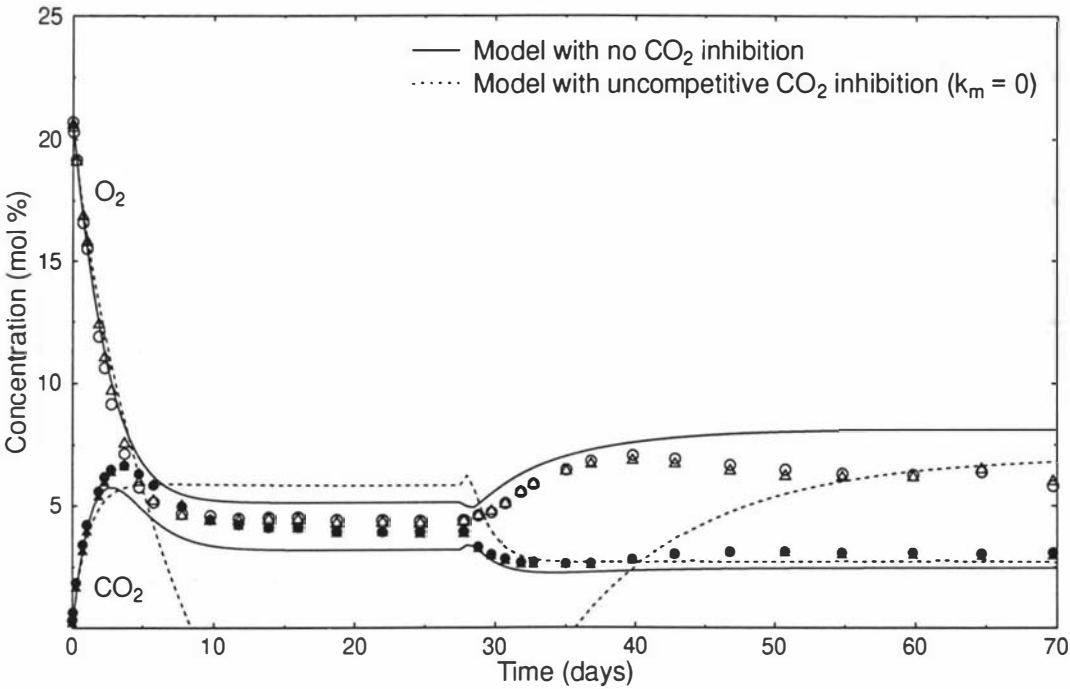
Another significant departure of model predictions from the experimental data can be seen in Figures 9.9 and 9.11, after the transition in storage temperature from 15°C to 1.6°C. During the bag trials in Figures 9.9 to 9.12, package O<sub>2</sub> and CO<sub>2</sub> concentrations rose and fell respectively after the transition as expected. However, in bags containing 10 fruit (Figures 9.9 and 9.11), this initial rise in package O<sub>2</sub> concentration was followed by an unexpected drop. Bags containing only 5 fruit (Figures 9.10 and 9.12) did not exhibit a similar phenomenon. The observed fall in package O<sub>2</sub> concentration suggests some sort of shift in the respiratory behaviour of the fruit. This may have been linked to the physiological age of the fruit at this stage of the trials, although in this case the bags in Figures 9.10 and 9.12 would be expected to show the same behaviour. The fruit in the bags exhibited no signs of internal breakdown at the end of the trials. Mould growth was evident on some of the fruit stalks but, where present, this was slight. One possible explanation for the observed fall in O<sub>2</sub> concentrations is that the respiratory behaviour of the fruit was in some way affected by the prior exposure to low O<sub>2</sub>/high CO<sub>2</sub> atmospheres at an elevated temperature. This could explain why the fall in O<sub>2</sub> concentrations was not exhibited by the packages in Figures 9.10 and 9.12, as these packages, containing fewer fruit, developed less modified atmospheres during the 15°C storage stage. A better understanding of the factors that might cause shifts in respiratory behaviour (e.g. fruit maturity and storage history) would be needed before such effects could be incorporated in an MAP model.



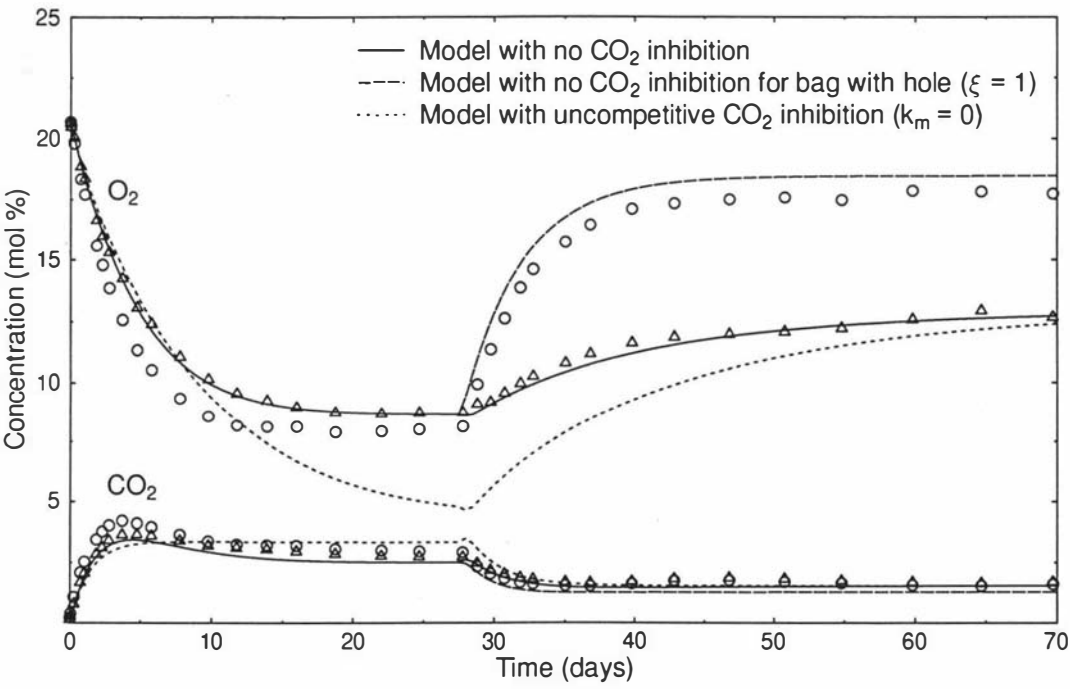
**Figure 9.9** Package  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' bags (10 count 125 fruit, 40  $\mu m$  film, trial BB93-B). Experimental data from 5 replicate bags shown.



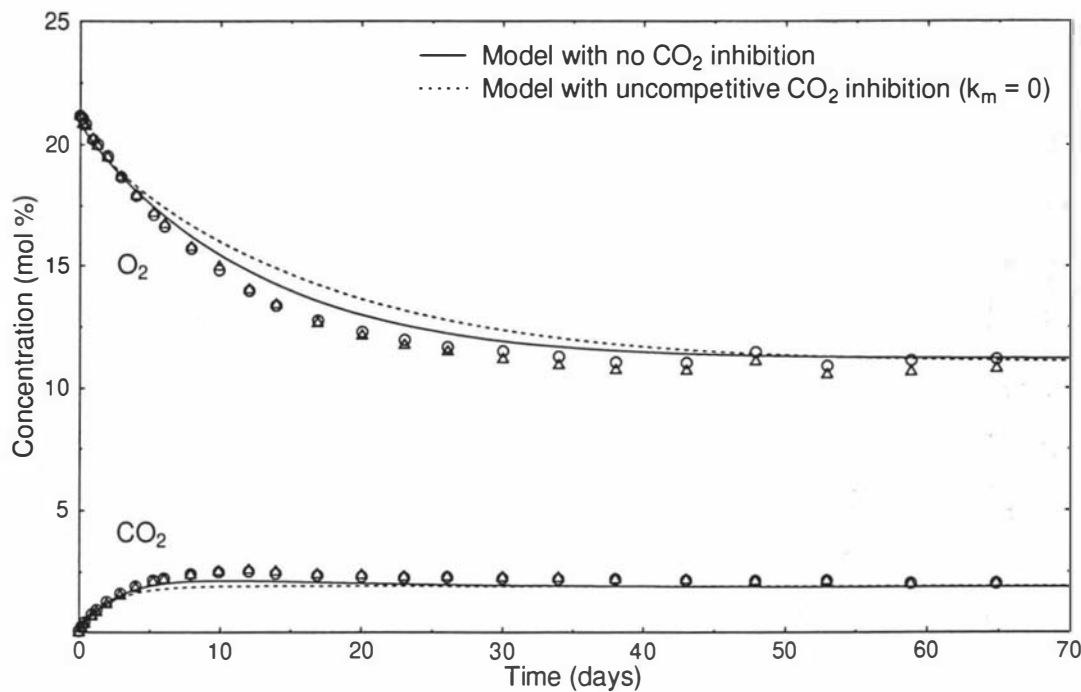
**Figure 9.10** Package  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' bags (5 count 125 fruit, 40  $\mu m$  film, trial BB93-B). Experimental data from 2 replicate bags shown.



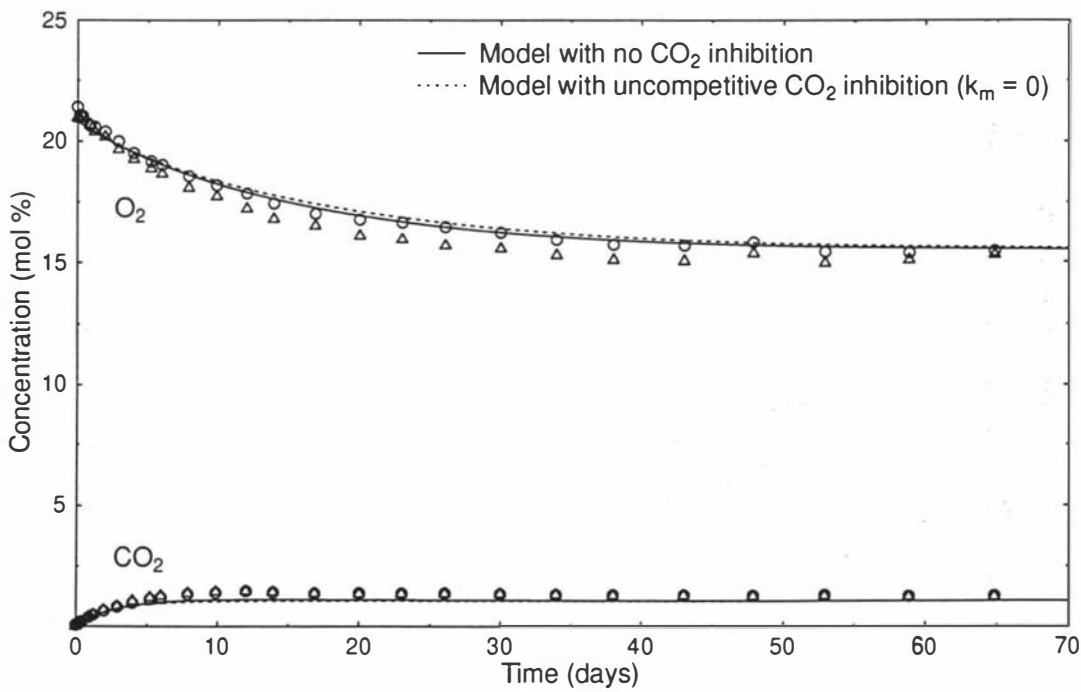
**Figure 9.11** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (10 count 80 fruit, 25 μm film, trial BB93-B). Experimental data from 2 replicate bags shown.



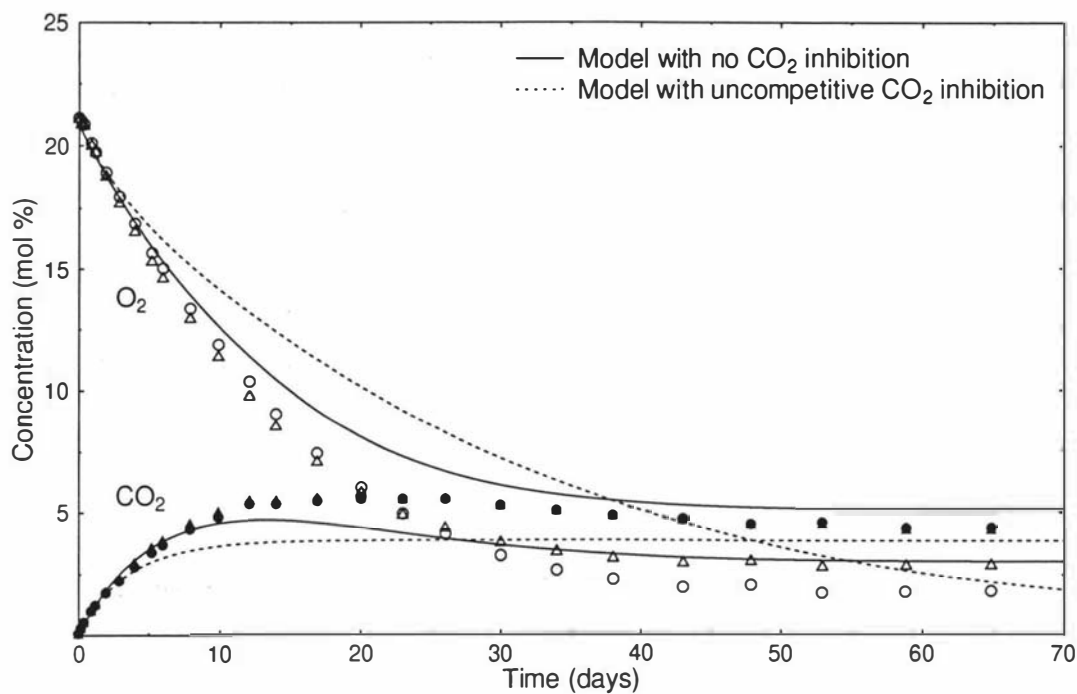
**Figure 9.12** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (5 count 80 fruit, 25 μm film, trial BB93-B). Experimental data from 2 replicate bags shown. 1 × 290 μm hole in bag marked O.



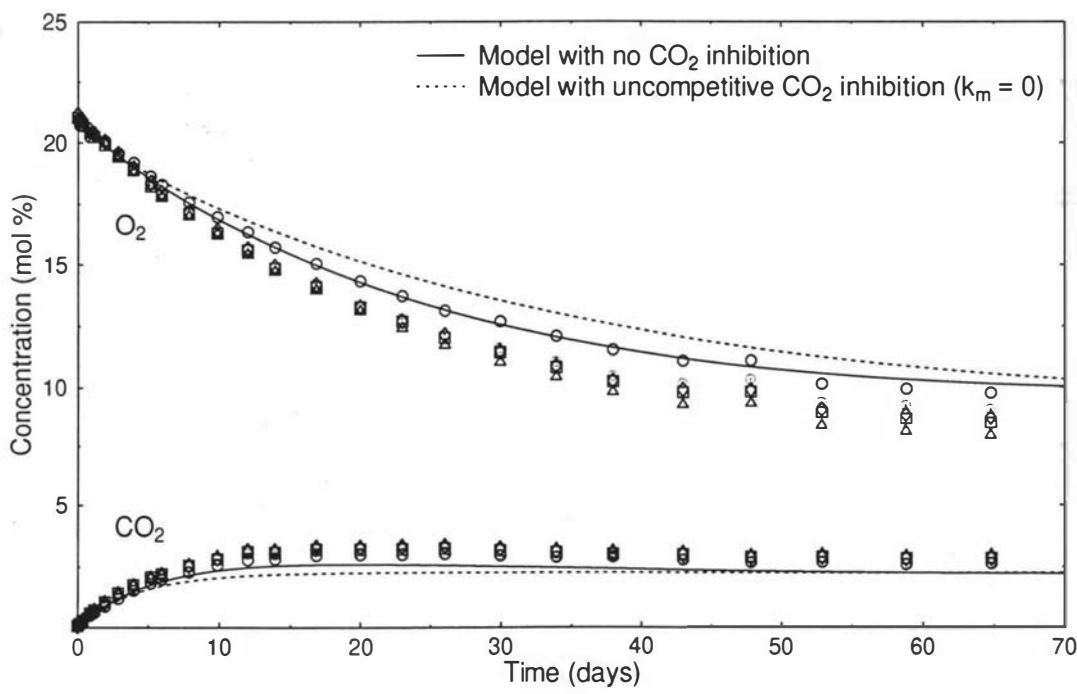
**Figure 9.13** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (10 count 125 fruit, 25 μm film, trial BB93-C). Experimental data from 2 replicate bags shown.



**Figure 9.14** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (5 count 125 fruit, 25 μm film, trial BB93-C). Experimental data from 2 replicate bags shown.



**Figure 9.15** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (10 count 80 fruit, 40 µm film, trial BB93-C). Experimental data from 2 replicate bags shown.



**Figure 9.16** Package O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (5 count 80 fruit, 40 µm film, trial BB93-C). Experimental data from 5 replicate bags shown.

Predictions made with the CO<sub>2</sub> respiration model under low O<sub>2</sub> atmospheres were poor. In Figures 9.9 to 9.12, the CO<sub>2</sub> respiration model failed to predict the CO<sub>2</sub> overshoot observed during the 15°C storage period. This overshoot is characteristic of an O<sub>2</sub> effect on respiration rate, and occurs because of the slower time constant for O<sub>2</sub> permeation into the package than for CO<sub>2</sub> permeation out of the package. The CO<sub>2</sub> respiration model assumes that O<sub>2</sub> has no effect on respiration rate, and consequently it cannot predict the overshoot. For the 15°C storage period, package atmospheres predicted with the CO<sub>2</sub> respiration model were also highly overmodified, so much so that package O<sub>2</sub> concentrations of less than zero were predicted for the bags containing 10 fruit (Figures 9.9 and 9.11). Again, this is likely to be a consequence of ignoring the effect of O<sub>2</sub> on respiration rate when using the CO<sub>2</sub> respiration model outside of its range of applicability.

Figure 9.12 also shows the predicted and experimental O<sub>2</sub> and CO<sub>2</sub> concentrations for a bag that developed a 290 µm diameter hole in the barrier film (112 µm) during the transition from 15 to 1.6°C. Reasonable predictions were obtained for  $\xi = 1$ . This value of  $\xi$ , corresponding to a hole diameter:film thickness ratio of 2.6, is consistent with the values of  $\xi$  estimated for the 1993 'Braeburn' cartons.

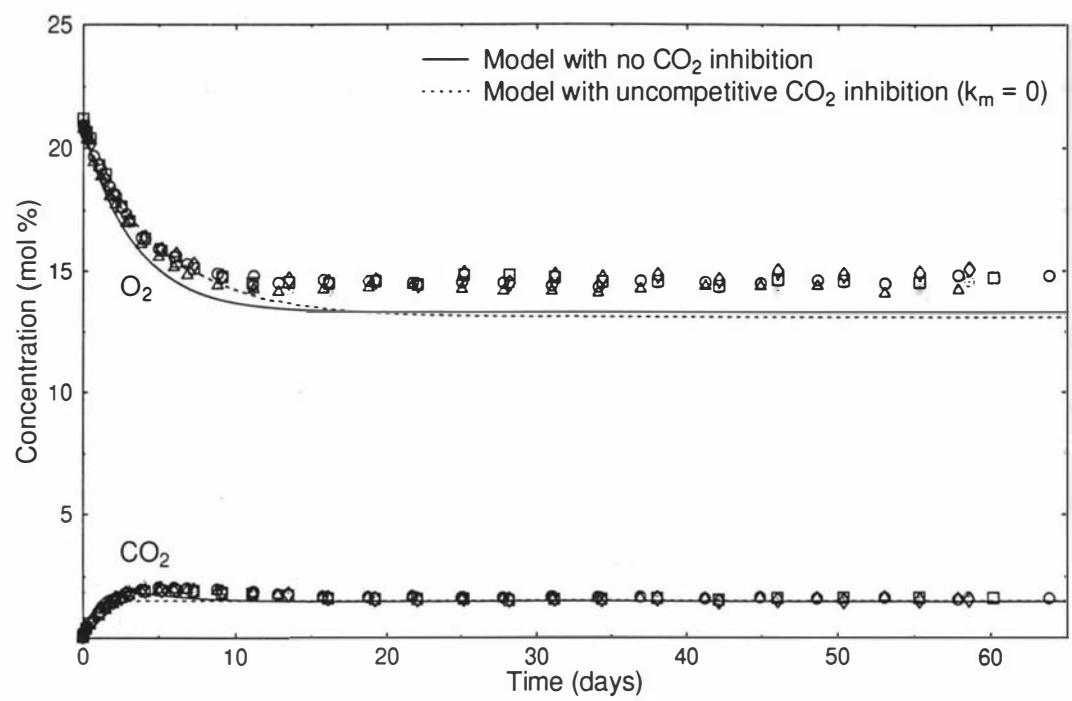
#### 9.1.1.2 1994 'ROYAL GALA'

Predicted and experimental package O<sub>2</sub> and CO<sub>2</sub> concentrations for the 1994 'Royal Gala' trials are shown in Figures 9.17 and 9.18 (trial RG94-A), Figures 9.19 and 9.20 (trial RG94-B), and Figures 9.21 and 9.22 (trial RG94-C). Each Figure shows model predictions for both 'Royal Gala' respiration models (section 8.1.4). For model runs under variable temperature regimes (RG94-B and RG94-C), fruit cooling and warming rates were predicted by the half-cooling-time heat transfer model (section 6.2.15.2).

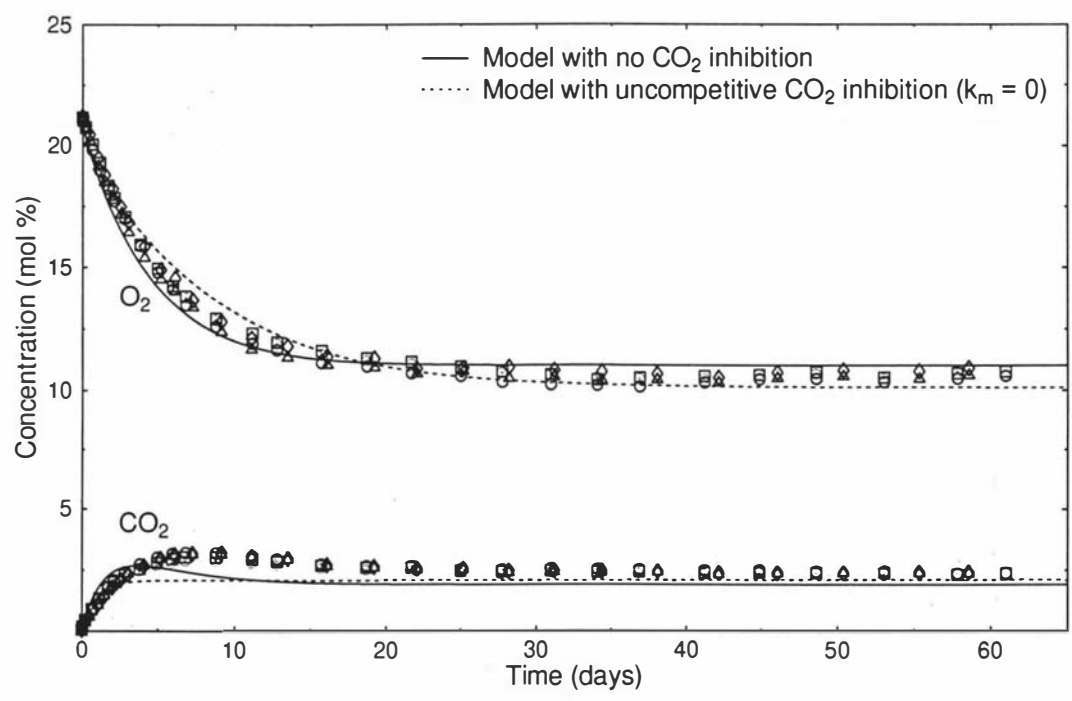
As expected, the model predicted identical steady-state modified atmospheres at 1.2°C for all cartons with liners of the same thickness, regardless of initial fruit temperature or storage regime. However, the fit of model predictions to the experimental data varied somewhat from trial to trial, indicating some variability in the measured steady-state atmospheres. Steady-state modified atmospheres measured during trials RG94-B and RG94-C were slightly more modified than those measured during trial RG94-A ('Royal Gala' respiration rate data were collected from the cartons in trial RG94-A).

With respect to the fit of model predictions to experimental package atmosphere data, general trends were similar to those discussed in section 9.1.1.1 for the 1993 'Braeburn'. Again, the CO<sub>2</sub> respiration model predicted slower rates of atmosphere modification than the O<sub>2</sub> respiration model (Figures 9.17 and 9.18). The MAP model tended to under-predict package CO<sub>2</sub> concentrations, although this was less significant for the 'Royal Gala' trials than for the 1993 'Braeburn'.

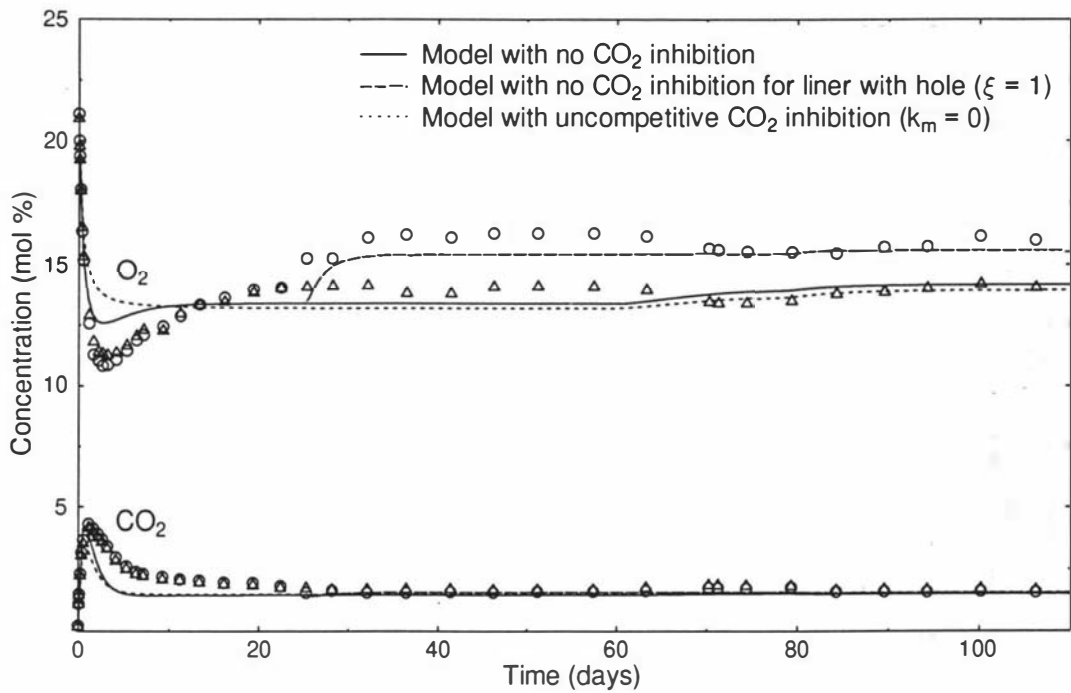
For 'Royal Gala' trials carried out under variable temperature regimes (Figures 9.19 to 9.22), some lack-of-fit was apparent during transient temperature periods. During each initial cooling period, measured package O<sub>2</sub> concentrations decreased rapidly at first, reaching minimum values before rising again to steady-state levels. The pull-down of O<sub>2</sub> concentration predicted by the MAP model was generally less extreme than that



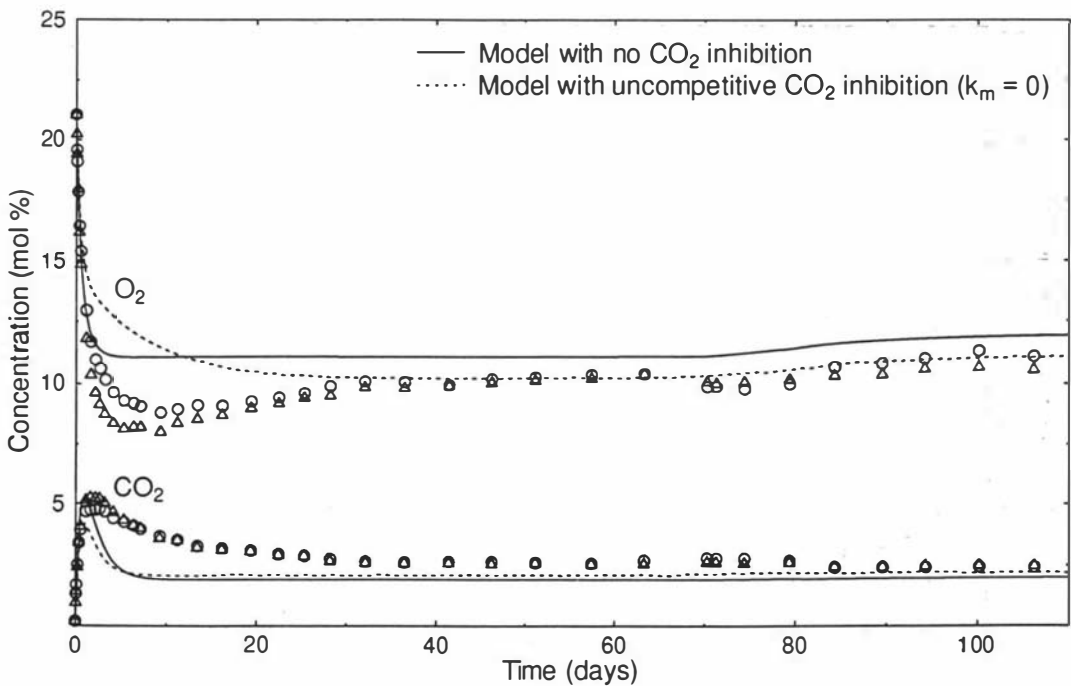
**Figure 9.17** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Royal Gala' cartons (count 100 fruit, 25  $\mu m$  film, heat-sealed, trial RG94-A). Experimental data from 5 replicate cartons shown.



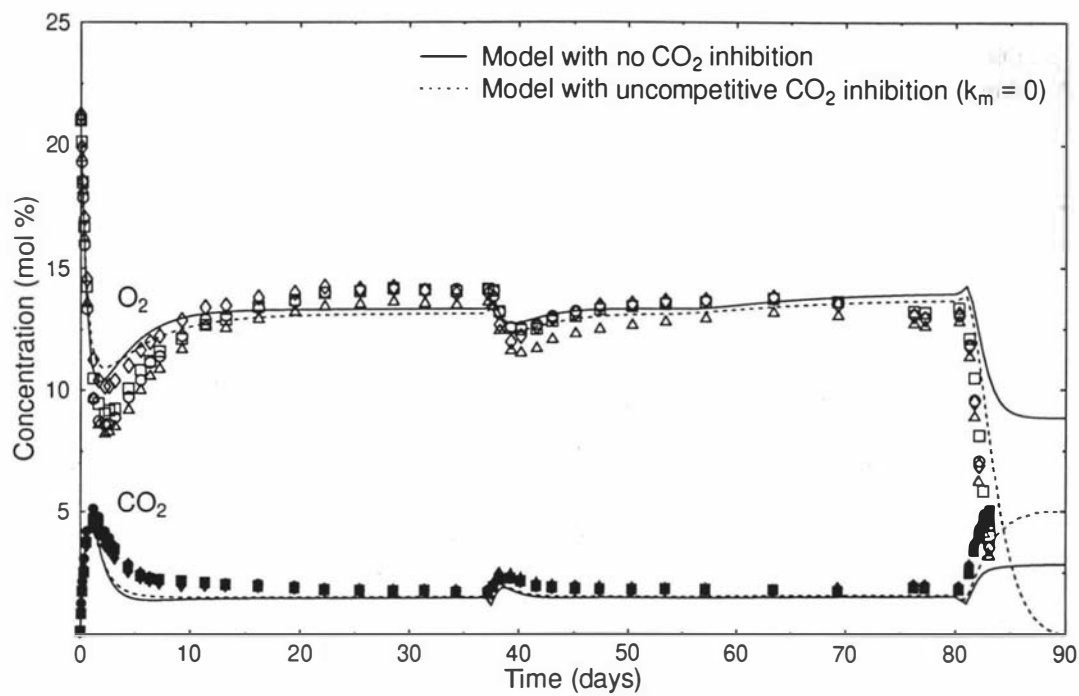
**Figure 9.18** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Royal Gala' cartons (count 100 fruit, 40  $\mu m$  film, heat-sealed, trial RG94-A). Experimental data from 5 replicate cartons shown.



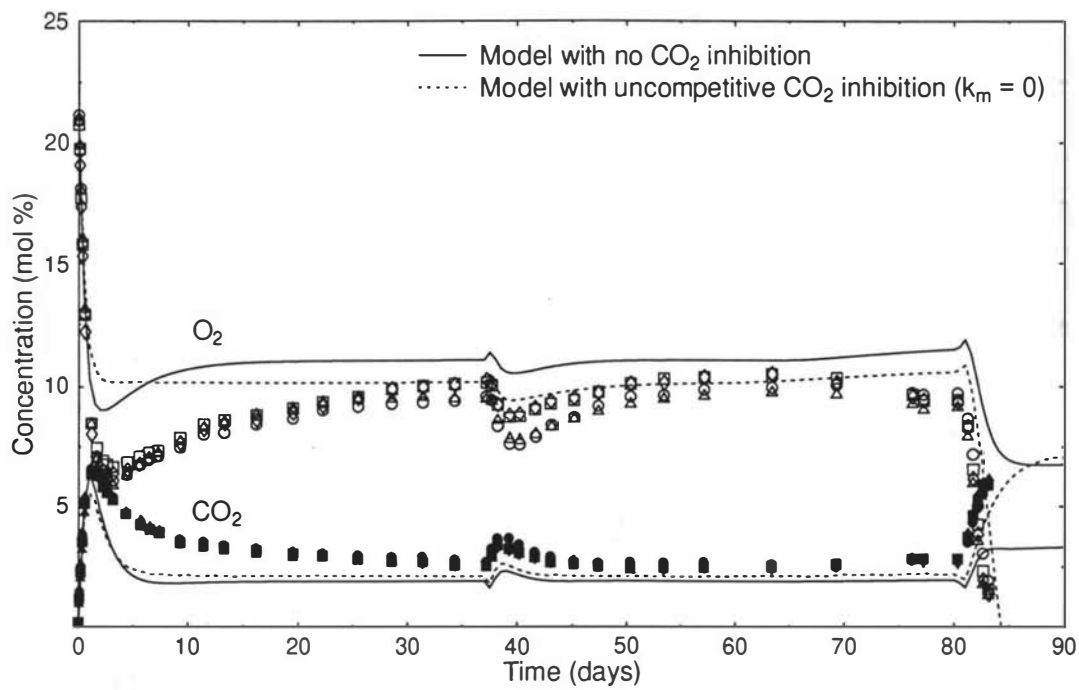
**Figure 9.19** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Royal Gala' cartons (count 100 fruit, 25  $\mu m$  film, heat-sealed, trial RG94-B). Experimental data from 2 replicate cartons shown. 1  $\times$  260  $\mu m$  hole in liner of carton marked O.



**Figure 9.20** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Royal Gala' cartons (count 100 fruit, 40  $\mu m$  film, heat-sealed, trial RG94-B). Experimental data from 2 replicate cartons shown.



**Figure 9.21** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Royal Gala' cartons (count 100 fruit, 25  $\mu m$  film, heat-sealed, trial RG94-C). Experimental data from 4 replicate cartons shown.



**Figure 9.22** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Royal Gala' cartons (count 100 fruit, 40  $\mu m$  film, heat-sealed, trial RG94-C). Experimental data from 4 replicate cartons shown.

observed experimentally, suggesting that predicted respiration rates were depressed too severely during the cooling phase. This may have been due to inaccurate temperature or respiration rate predictions, although the former seems unlikely given that the half-cooling-time model used in the simulations predicted fruit cooling rates accurately (section 9.1.4). Inaccuracies in the respiration models could have arisen from one or more of several sources: the assumption of first order reaction kinetics for the  $O_2$  respiration model; the assumption that the value of  $k_{iu}$  fitted for the  $CO_2$  respiration model at  $1.2^\circ C$  remains constant at higher temperatures; the assumption of constant  $Q_{10}$  values; the assumption that fruit respiration rates respond instantaneously to changes in temperature or fruit internal gas concentrations; or the extrapolation of the respiration models beyond the ranges of atmospheres for which they were fitted. For example, the high package  $CO_2$  concentrations developed during the initial cooling stages lead to correspondingly high fruit internal  $CO_2$  concentrations as the fruit cool. This necessitates extrapolation of the  $CO_2$  respiration model to  $CO_2$  concentrations considerably higher than those for which the model was fitted.

In contrast to the model predictions of the  $O_2$  pull-down, the magnitude of the  $CO_2$  peak during the initial fruit cooling phase was predicted reasonably well. However, once package  $CO_2$  concentrations had peaked, the MAP model predicted a significantly faster  $CO_2$  decline than that observed experimentally. A similar trend was not observed for  $O_2$  (Figure 9.21). These observations might be attributable to  $CO_2$  solution in the fruit cell sap, an effect not accounted for in the model formulation. At  $0^\circ C$ , the solubility of  $CO_2$  in water is more than 45 times that of  $O_2$  (Liley *et al.*, 1984), thus the effect of gas solubility in the cell sap is expected to be more significant for  $CO_2$  than  $O_2$ . If  $CO_2$  solution in the cell sap was significant, then the cell sap, acting as a reservoir for  $CO_2$ , would effectively increase the fruit volume available to  $CO_2$ . This would not affect steady-state  $CO_2$  concentrations, only rates of concentration change. A test of this hypothesis is presented in section 9.2.1.4.

For cartons left to warm to  $20^\circ C$  during the final storage stage in Figures 9.21 and 9.22, the  $O_2$  respiration model depressed respiration rates too severely at low  $O_2$  concentrations, an effect similar to that observed for the 1993 'Braeburn' bag trial in Figure 9.15. The  $CO_2$  respiration model followed the experimental data better, but predicted eventual package  $O_2$  concentrations of less than zero. As discussed for the 1993 'Braeburn' bags stored at  $15^\circ C$  (section 9.1.1.1, Figures 9.9 to 9.12), this seems likely to be a consequence of ignoring the effect of  $O_2$  on respiration rate. Unfortunately, the 'Royal Gala' trials in Figures 9.21 and 9.22 were not carried on long enough to establish steady-state  $O_2$  and  $CO_2$  levels at  $20^\circ C$ . From the negative  $O_2$  concentrations predicted, the  $CO_2$  respiration model would have been expected to over-predict steady-state  $CO_2$  concentrations at  $20^\circ C$ , unless the fruit in the trials had started to respire anaerobically.

For the predictions shown in Figures 9.21 and 9.22, each change in storage temperature from  $1.2^\circ C$  to  $20^\circ C$  resulted in a small initial increase in package  $O_2$  concentration and decrease in package  $CO_2$  concentration before these fell and rose, respectively. This was attributed to the model predicting rapid changes in packaging film temperature relative to changes in fruit temperature, thereby causing package atmospheres to become initially less modified until the increase in fruit respiration rate with temperature became

significant. This effect was not detected in the experimental data, suggesting that the model may be exaggerating any real effect. By arbitrarily increasing the convective heat transfer coefficient at the inside surface of the packaging film (e.g. from 1.9 to 10  $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ ) without changing the overall heat transfer coefficient for the packaging materials, the effect was eliminated from the model predictions.

Figure 9.19 shows the predicted and experimental  $\text{O}_2$  and  $\text{CO}_2$  concentrations for a 25  $\mu\text{m}$  carton liner with one 260  $\mu\text{m}$  diameter hole (a hole diameter:film thickness ratio of 10.4). Model predictions with  $\xi = 1$  fitted the experimental  $\text{O}_2$  and  $\text{CO}_2$  concentrations reasonably well. However, this value of  $\xi$  is somewhat inconsistent with the values of  $\xi$  estimated for the 1993 'Braeburn' cartons and bags.

#### 9.1.1.3 1994 'BRAEBURN'

Predicted and experimental package  $\text{O}_2$  and  $\text{CO}_2$  concentrations for the 1994 'Braeburn' trials are shown in Figures 9.23 and 9.24 (trial BB94-A), and Figures 9.25 and 9.26 (trial BB94-B).

Model predictions for the 1994 'Braeburn' trials showed similar general trends to those discussed in section 9.1.1.2 for 'Royal Gala'. Package  $\text{O}_2$  concentrations during the initial  $\text{O}_2$  pull-down inside cartons packed at 20°C were better predicted for the 1994 'Braeburn' trials than for the corresponding 'Royal Gala' trials. The final storage stage of trial BB94-B (Figures 9.25 and 9.26) was carried on for longer than the same stage of trial RG94-C (Figures 9.21 and 9.22), allowing time for package  $\text{O}_2$  and  $\text{CO}_2$  concentrations to stabilize at 20°C. As observed for 'Royal Gala', the  $\text{O}_2$  respiration model depressed respiration rates too severely at low  $\text{O}_2$  concentrations, whereas the  $\text{CO}_2$  respiration model depressed respiration rates insufficiently at high  $\text{CO}_2$  concentrations.

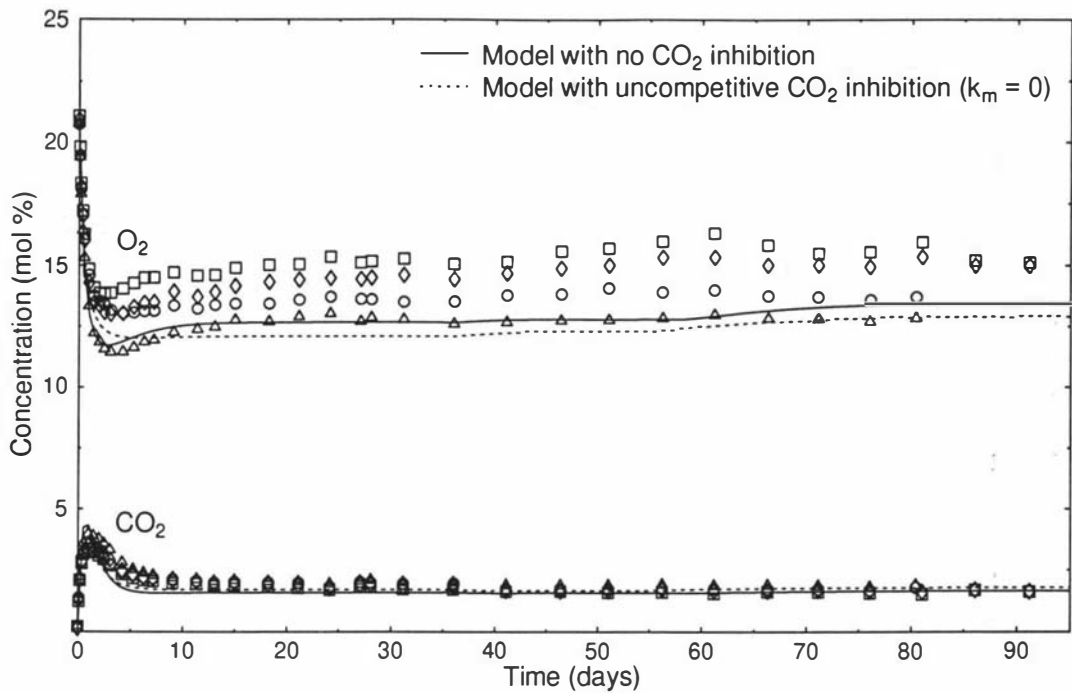
Trials BB94-A and BB94-B both included cartons with folded liners. As for the 1993 'Braeburn' cartons in Figure 9.5,  $\text{O}_2$  concentrations inside the folded liners were higher and less consistent than  $\text{O}_2$  concentrations inside the heat-sealed liners, especially for the 40  $\mu\text{m}$  film (Figure 9.26). As discussed in section 9.1.1.1, the MAP model does not include mechanisms for predicting gas transfer through folds or for predicting the variability between folded liners. For cartons with folded liners, the MAP model predicts the maximum expected extent of atmosphere modification.

#### 9.1.1.4 1994 'GRANNY SMITH'

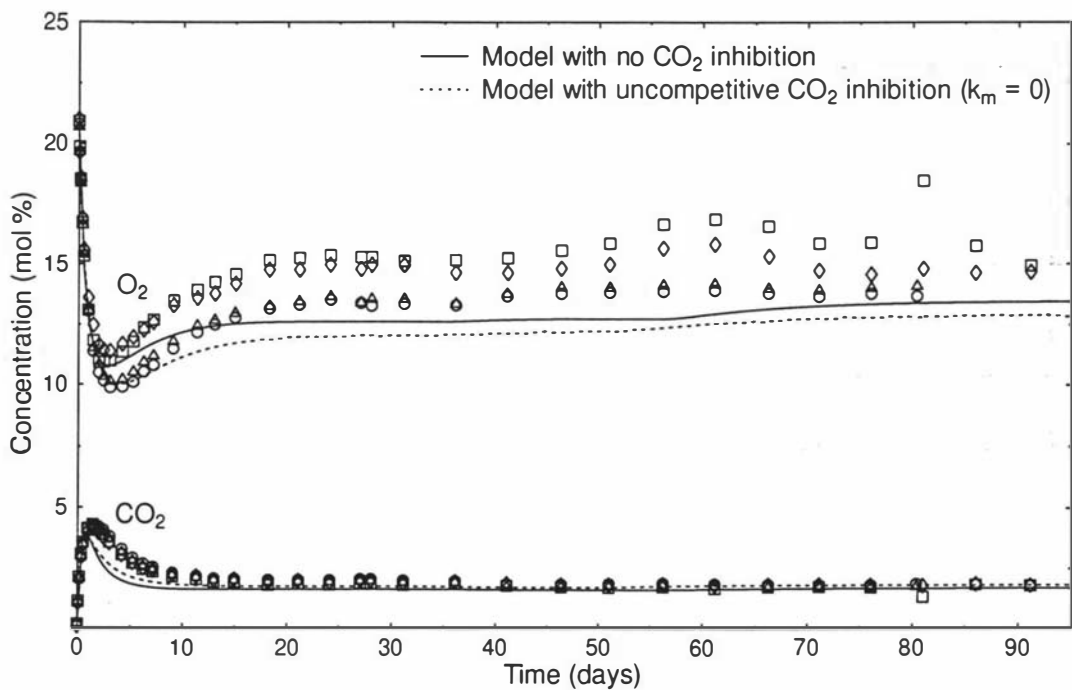
##### *Cartons*

Figures 9.27 and 9.28 show the predicted and experimental package  $\text{O}_2$  and  $\text{CO}_2$  concentrations for the 1994 'Granny Smith' carton trial (trial GS94-A).

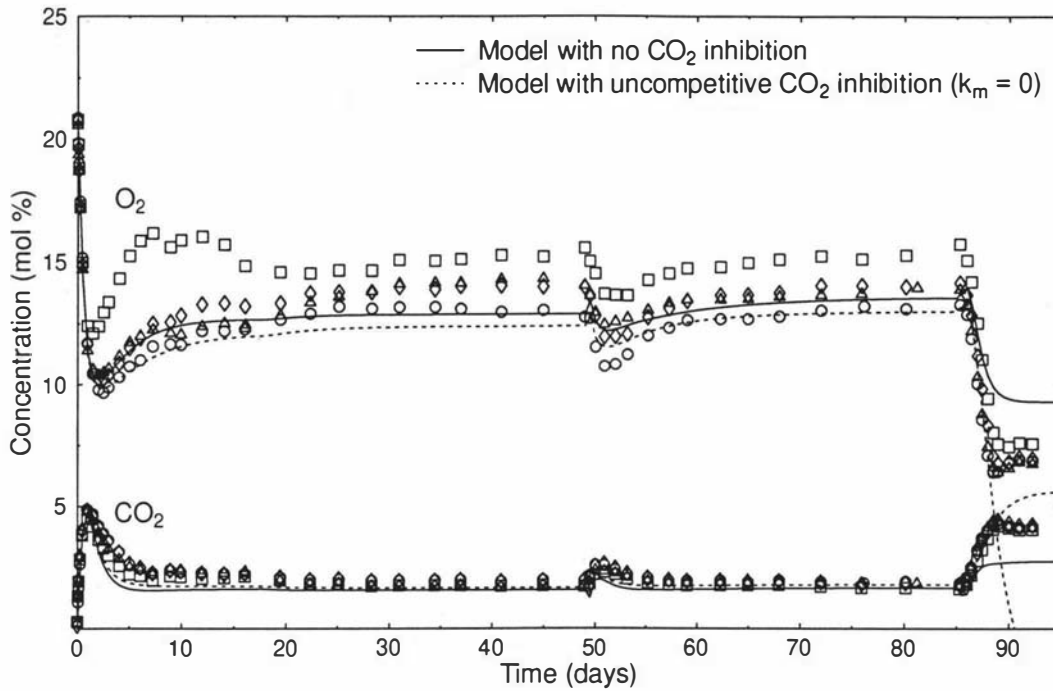
Again, model predictions showed similar general trends to those discussed for the 1994 'Braeburn' (BB94-B) and 'Royal Gala' (RG94-C). The initial  $\text{O}_2$  pull-down predicted for the 'Granny Smith' trials was stronger than that predicted for either the 'Braeburn' or the 'Royal Gala' trials. In Figure 9.27, the  $\text{O}_2$  respiration model closely predicted the drop in package  $\text{O}_2$  concentrations during the final 20°C storage stage, but under-



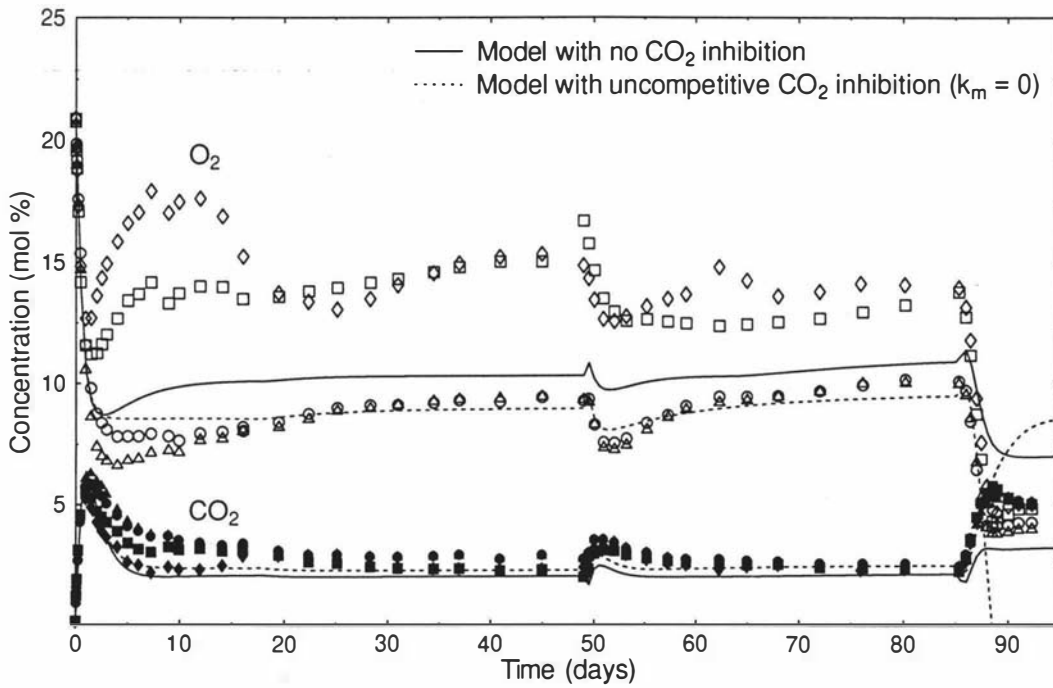
**Figure 9.23** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Braeburn' cartons (count 125 fruit, 25  $\mu\text{m}$  film, non-insulated, trial BB94-A). Experimental data from 2 replicate heat-sealed liners ( $\circ$ ,  $\Delta$ ) and 2 replicate folded liners ( $\square$ ,  $\diamond$ ) shown.



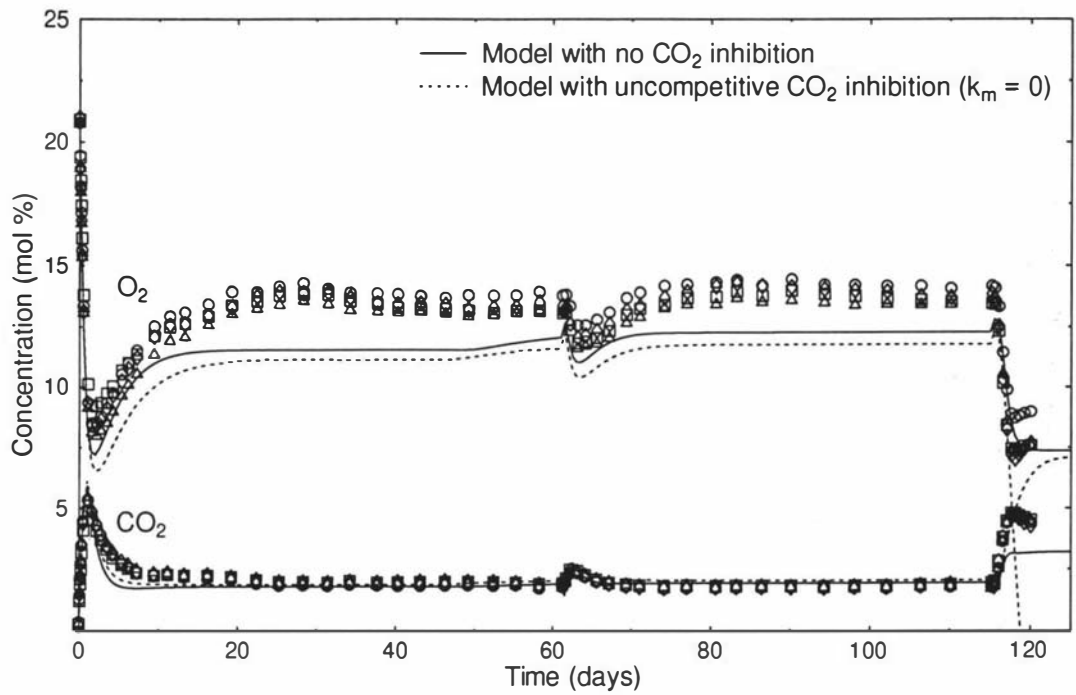
**Figure 9.24** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Braeburn' cartons (count 125 fruit, 25  $\mu\text{m}$  film, insulated, trial BB94-A). Experimental data from 2 replicate heat-sealed liners ( $\circ$ ,  $\Delta$ ) and 2 replicate folded liners ( $\square$ ,  $\diamond$ ) shown.



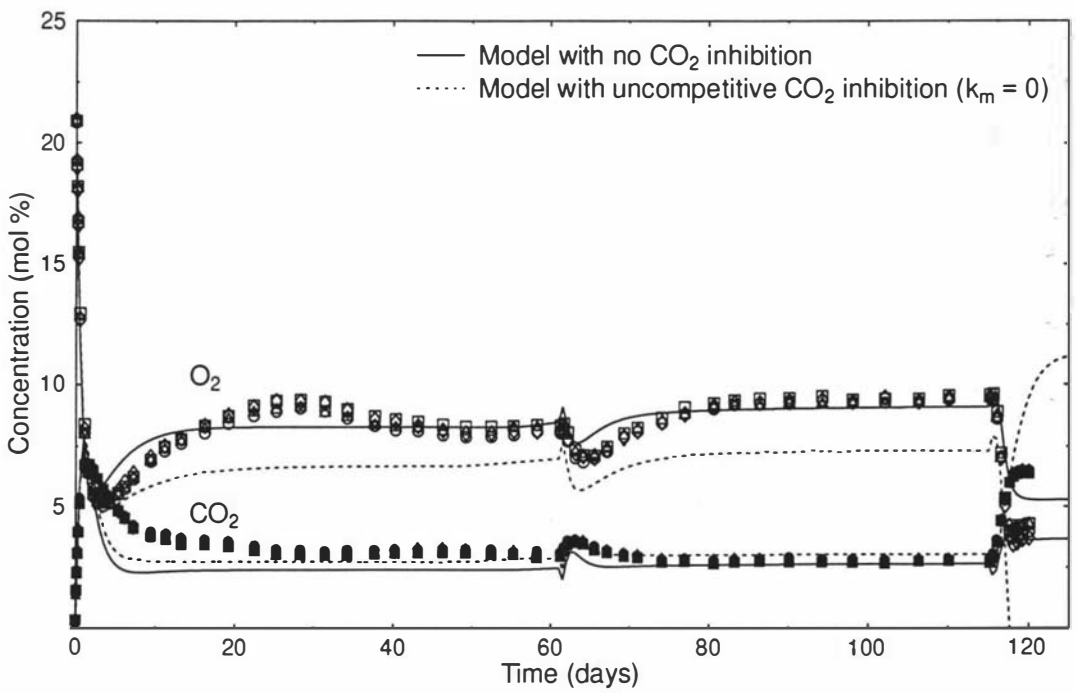
**Figure 9.25** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Braeburn' cartons (count 125 fruit, 25  $\mu m$  film, trial BB94-B). Experimental data from 2 replicate heat-sealed liners ( $\circ$ ,  $\Delta$ ) and 2 replicate folded liners ( $\square$ ,  $\diamond$ ) shown.



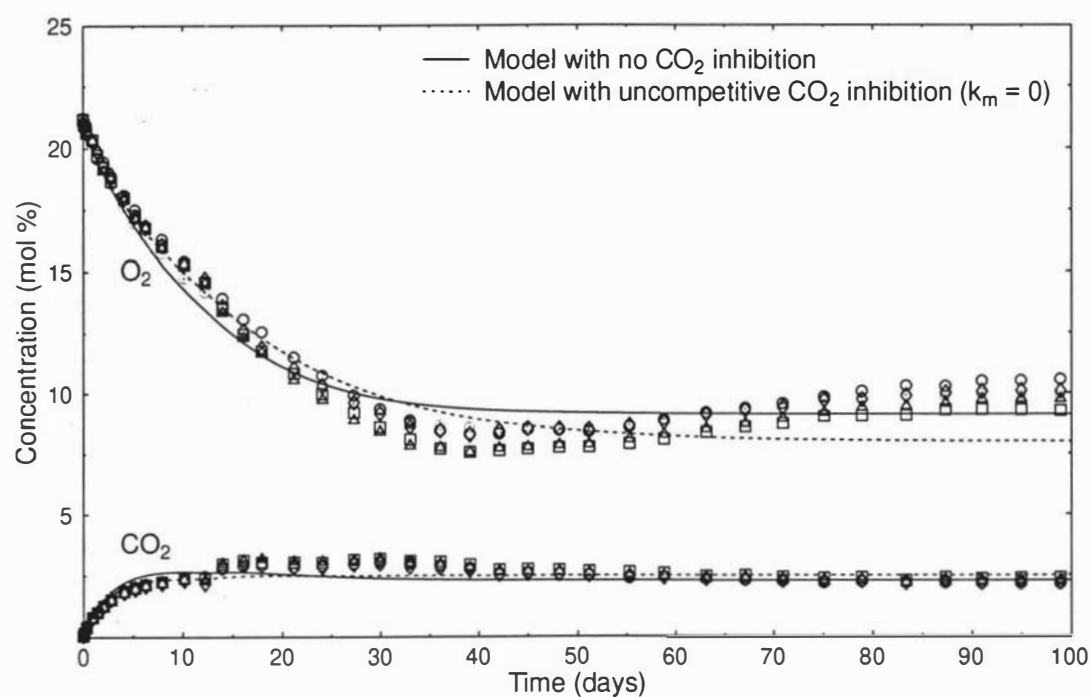
**Figure 9.26** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Braeburn' cartons (count 125 fruit, 40  $\mu m$  film, trial BB94-B). Experimental data from 2 replicate heat-sealed liners ( $\circ$ ,  $\bullet$ ,  $\Delta$ ,  $\blacktriangle$ ) and 2 replicate folded liners ( $\square$ ,  $\blacksquare$ ,  $\diamond$ ,  $\blacklozenge$ ) shown.



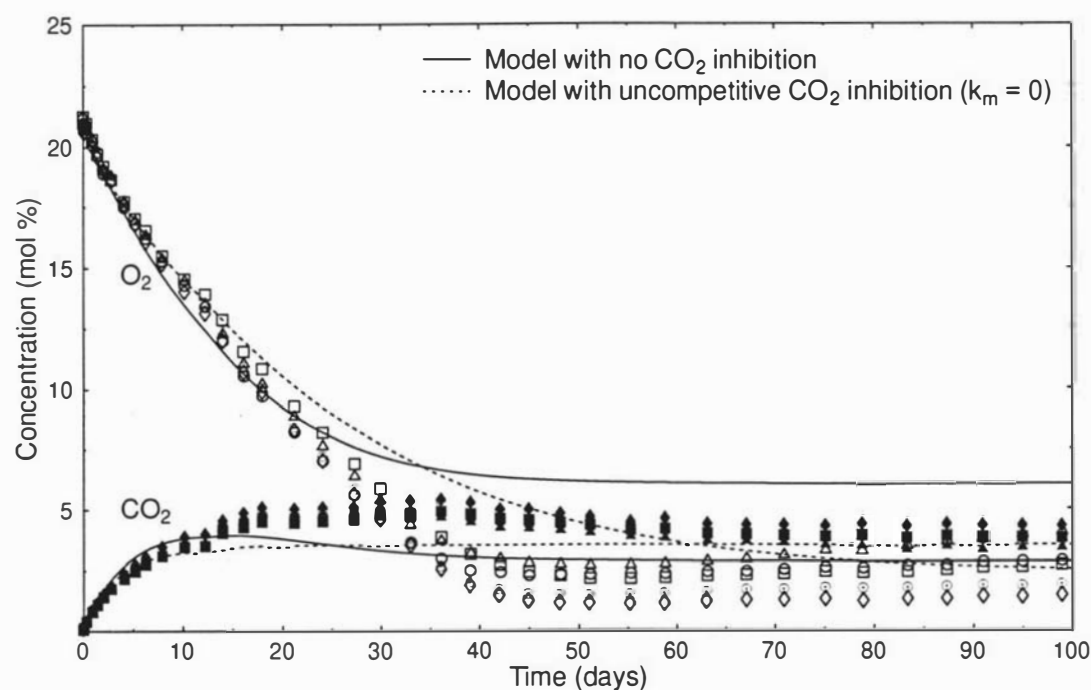
**Figure 9.27** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Granny Smith' cartons (count 125 fruit, 25  $\mu m$  film, heat-sealed, trial GS94-A). Experimental data from 4 replicate cartons shown.



**Figure 9.28** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Granny Smith' cartons (count 125 fruit, 40  $\mu m$  film, heat-sealed, trial GS94-A). Experimental data from 4 replicate cartons shown.



**Figure 9.29** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Granny Smith' bags (10 count 125 fruit, 25  $\mu m$  film, trial GS94-B). Experimental data from 5 replicate bags shown.



**Figure 9.30** Package  $O_2$  and  $CO_2$  concentrations for 1994 'Granny Smith' bags (10 count 125 fruit, 40  $\mu m$  film, trial GS94-B). Experimental data from 5 replicate bags shown.

predicted the corresponding rise in package  $\text{CO}_2$  concentrations. This suggests that anaerobic respiration may have become significant during this stage of the trial. Given that 1 mol %  $\text{O}_2$  in the internal atmosphere of the fruit is thought to be sufficient to avoid fermentation (Yearsley *et al.*, 1996), this explanation would require there to have been a considerable difference between the  $\text{O}_2$  concentrations in the package atmosphere and those in the internal atmosphere of the fruit.

### *Bags*

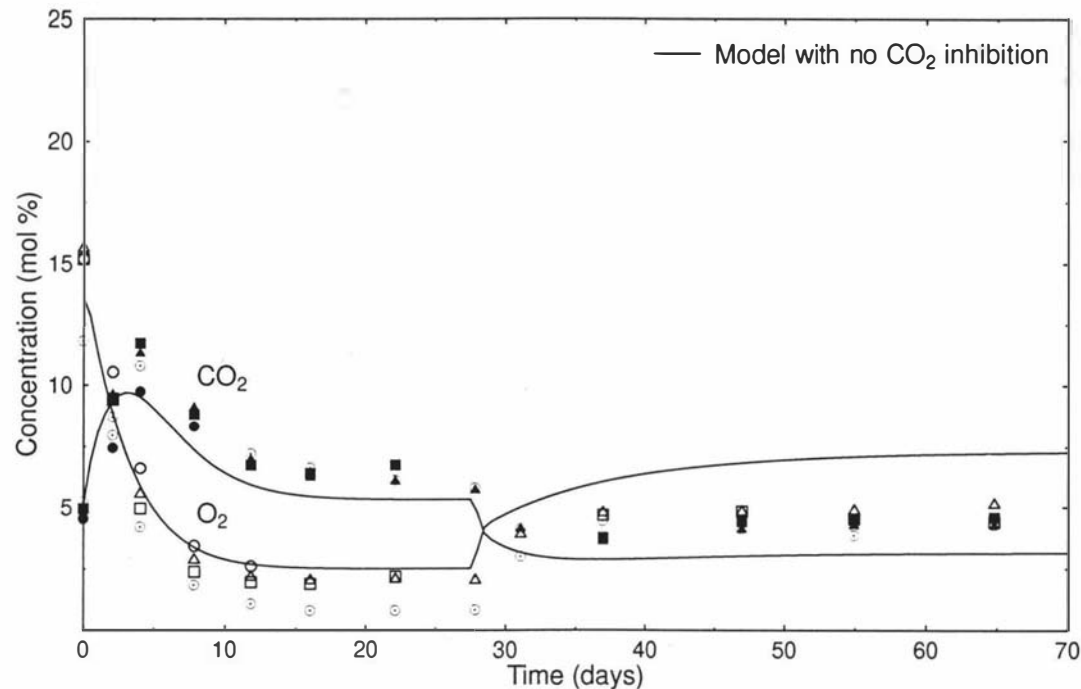
Figures 9.29 and 9.30 show the predicted and experimental package  $\text{O}_2$  and  $\text{CO}_2$  concentrations for the 1994 'Granny Smith' bag trial (trial GS94-B).

The model predictions in Figures 9.29 and 9.30 showed similar trends to those previously discussed for 'Braeburn' and 'Royal Gala' cartons or bags at constant storage temperatures. In particular, predictions for the bags in Figure 9.30 were comparable to those for the 'Braeburn' bags in Figure 9.15. In both cases, the  $\text{O}_2$  respiration model failed to predict the very low  $\text{O}_2$  concentrations developed inside the bags. As discussed for the 1993 'Braeburn' bags, this is likely to have been a consequence of extrapolating the respiration model beyond the range of atmospheres for which it was fitted, and suggests a lower value of  $k_m$  than that fitted to the respiration data. In both Figures 9.15 and 9.30, the  $\text{CO}_2$  respiration model provided better steady-state estimates of package  $\text{O}_2$  and  $\text{CO}_2$  concentrations. However, the general tendency of the  $\text{CO}_2$  model to predict slower rates of atmosphere modification than those observed experimentally was particularly marked in these instances.

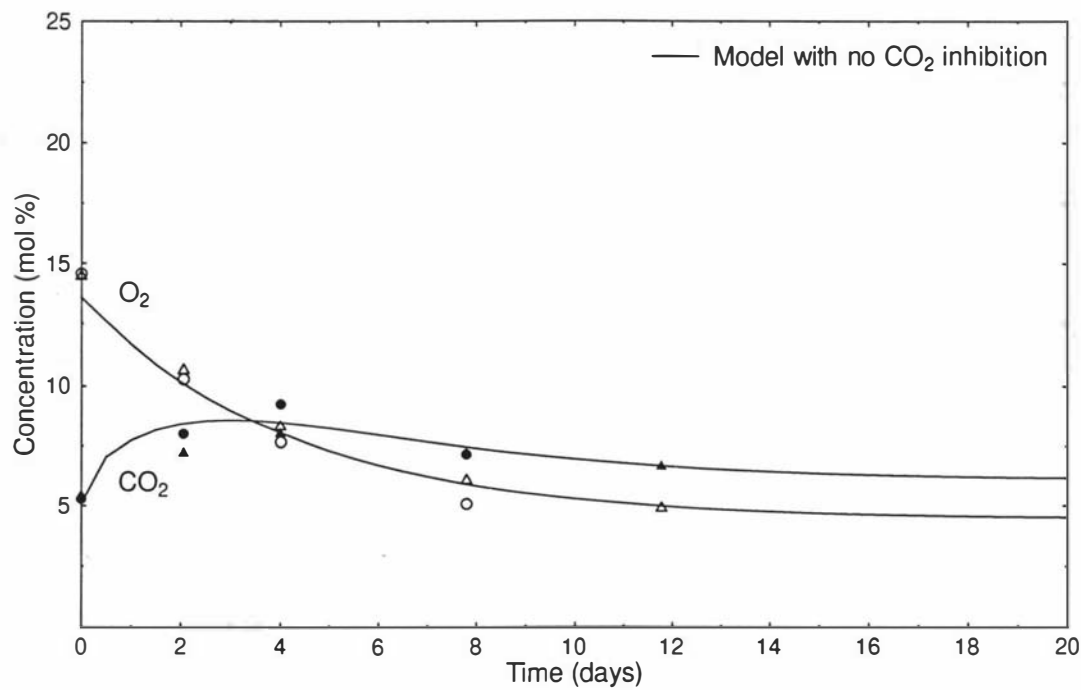
## 9.1.2 FRUIT INTERNAL $\text{O}_2$ AND $\text{CO}_2$ CONCENTRATIONS

Predicted and experimental fruit internal  $\text{O}_2$  and  $\text{CO}_2$  concentrations for the 1993 'Braeburn' and 1994 'Granny Smith' bag trials are shown in Figures 9.31 and 9.32 (trial BB93-B), Figures 9.33 to 9.36 (trial BB93-C), and Figures 9.37 and 9.38 (trial GS94-B). Because of problems with the vials for internal atmosphere sampling coming unstuck from the fruit surface part-way through the trials, internal atmosphere data were not available for the full duration of some trials (Figures 9.32, 9.33, and 9.35). The results from two sets of replicate bags in trial BB93-B have not been shown because of the small number of data points available. In Figures 9.31 and 9.32, model predictions for only the  $\text{O}_2$  respiration model have been given, the  $\text{CO}_2$  respiration model having previously been shown to perform poorly for bags at 15°C (section 9.1.1.1, Figures 9.9 to 9.12).

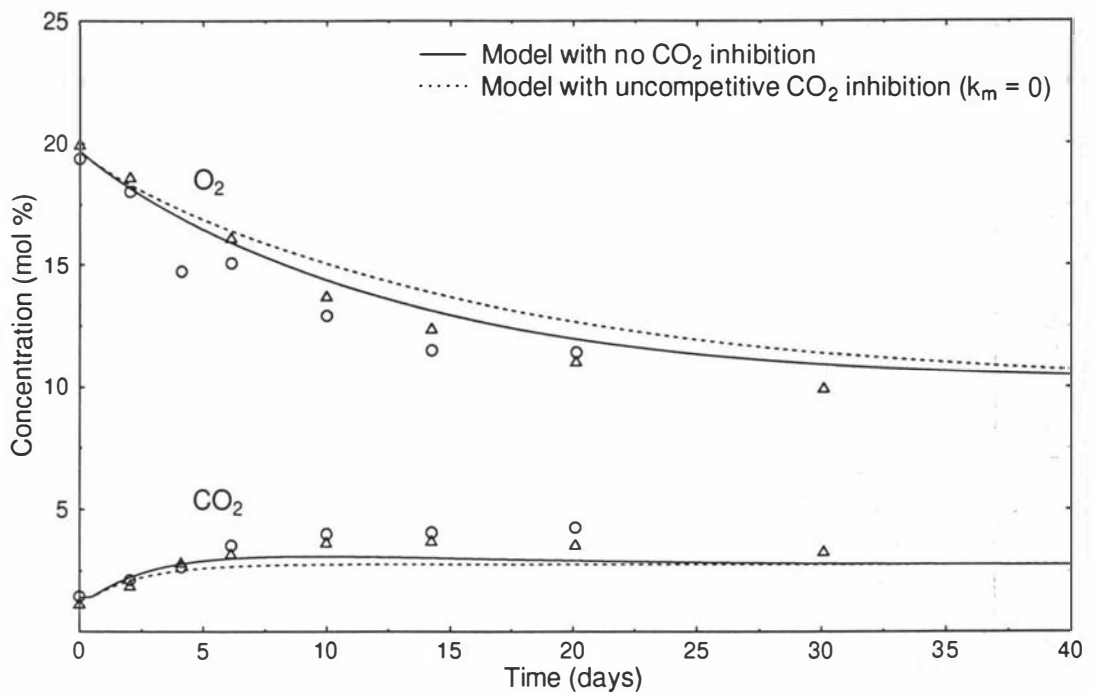
As expected, predicted  $\text{O}_2$  and  $\text{CO}_2$  concentrations for the fruit internal atmospheres reflected the same trends as corresponding predicted  $\text{O}_2$  and  $\text{CO}_2$  concentrations for the package atmospheres. Experimental internal atmosphere data were more variable than package atmosphere data. This is to be expected as the fruit internal atmosphere data represent measurements taken from one apple in each bag. Thus, whereas package atmospheres reflect package-to-package variations in respiration rate, film permeance, and film area, fruit internal atmospheres reflect this variability as well as individual fruit-to-fruit variations in respiration rate and skin permeance.



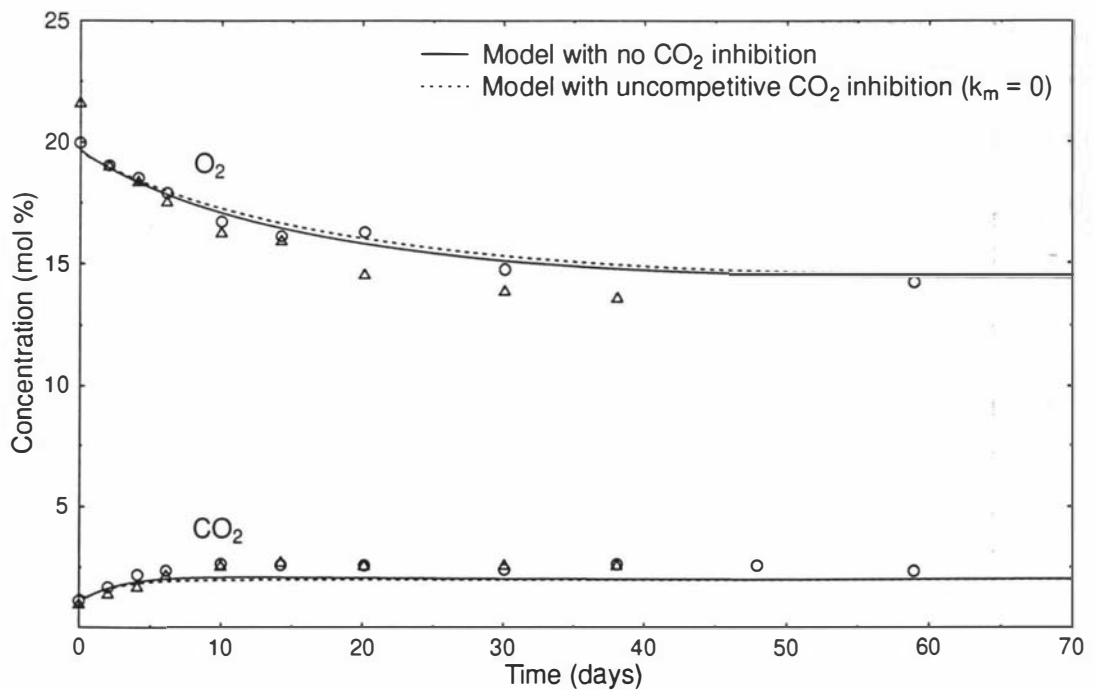
**Figure 9.31** Fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 'Braeburn' bags (10 count 125 fruit, 40 µm film, trial BB93-B). Experimental data from 5 replicate bags shown.



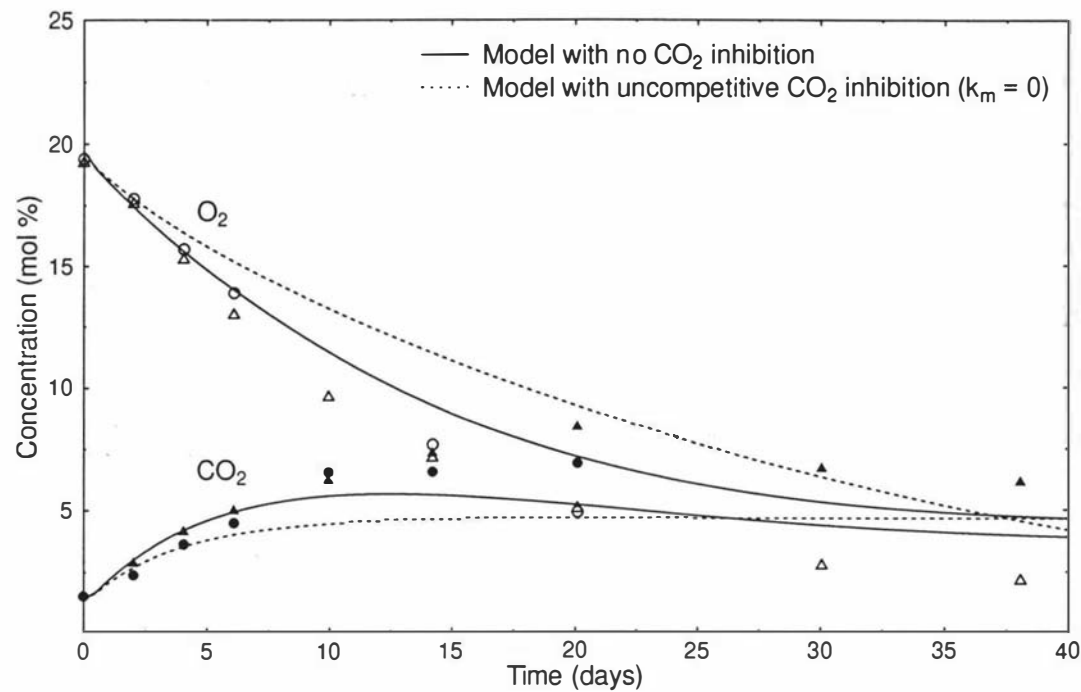
**Figure 9.32** Fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 'Braeburn' bags (5 count 80 fruit, 25 µm film, trial BB93-B). Experimental data from 2 replicate bags shown.



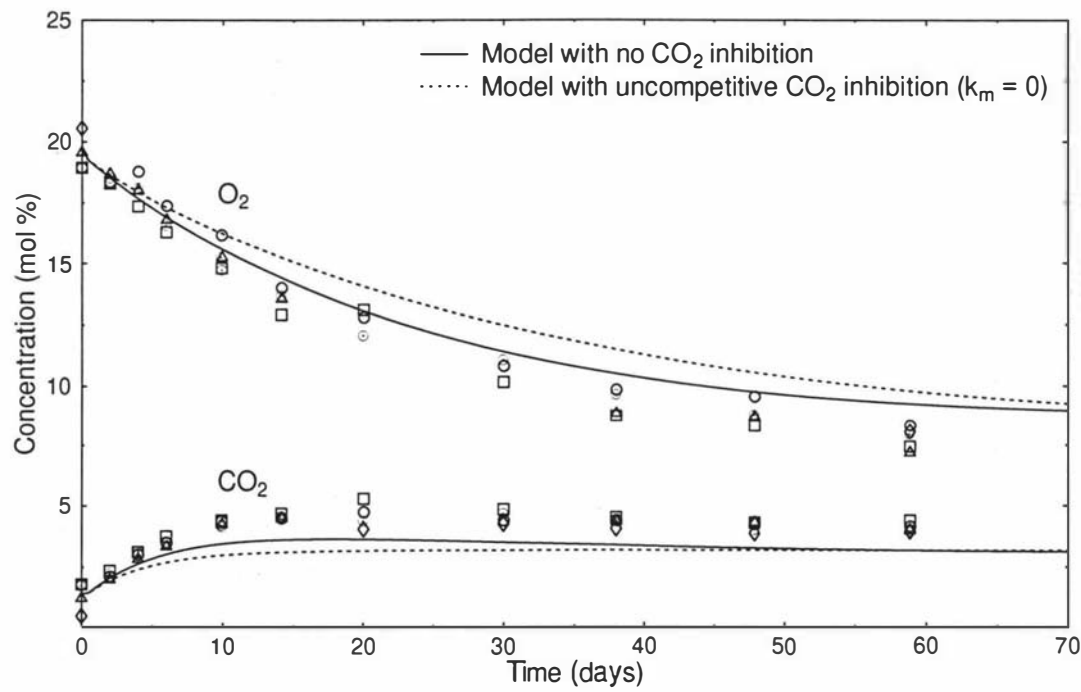
**Figure 9.33** Fruit internal  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' bags (10 count 125 fruit, 25  $\mu m$  film, trial BB93-C). Experimental data from 2 replicate bags shown.



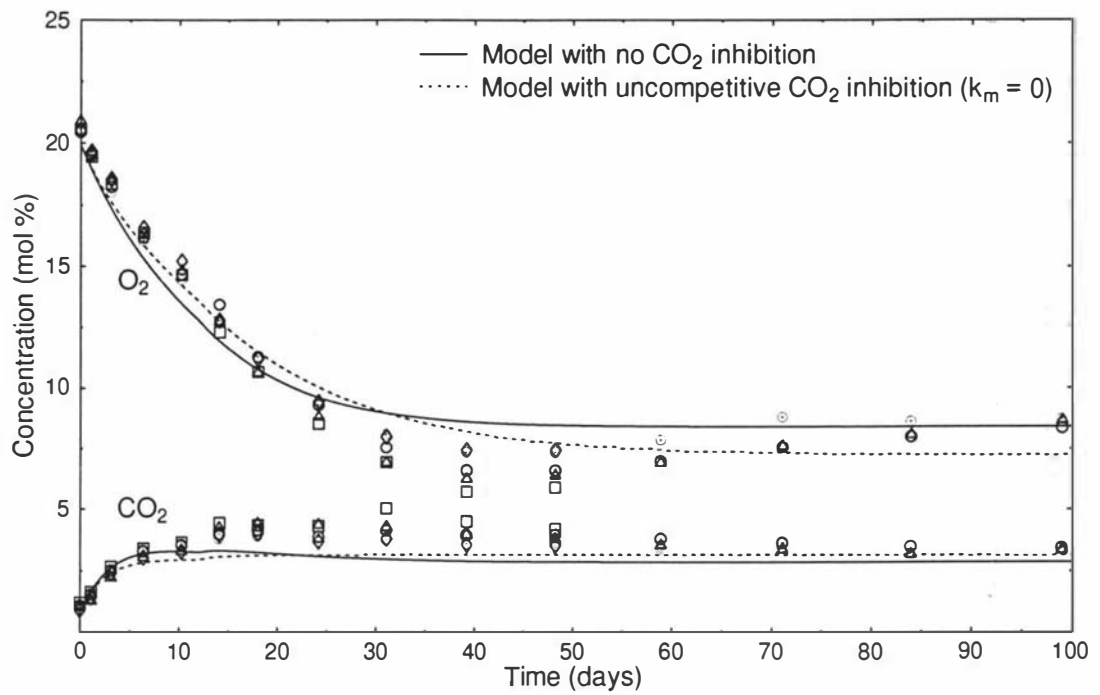
**Figure 9.34** Fruit internal  $O_2$  and  $CO_2$  concentrations for 1993 'Braeburn' bags (5 count 125 fruit, 25  $\mu m$  film, trial BB93-C). Experimental data from 2 replicate bags shown.



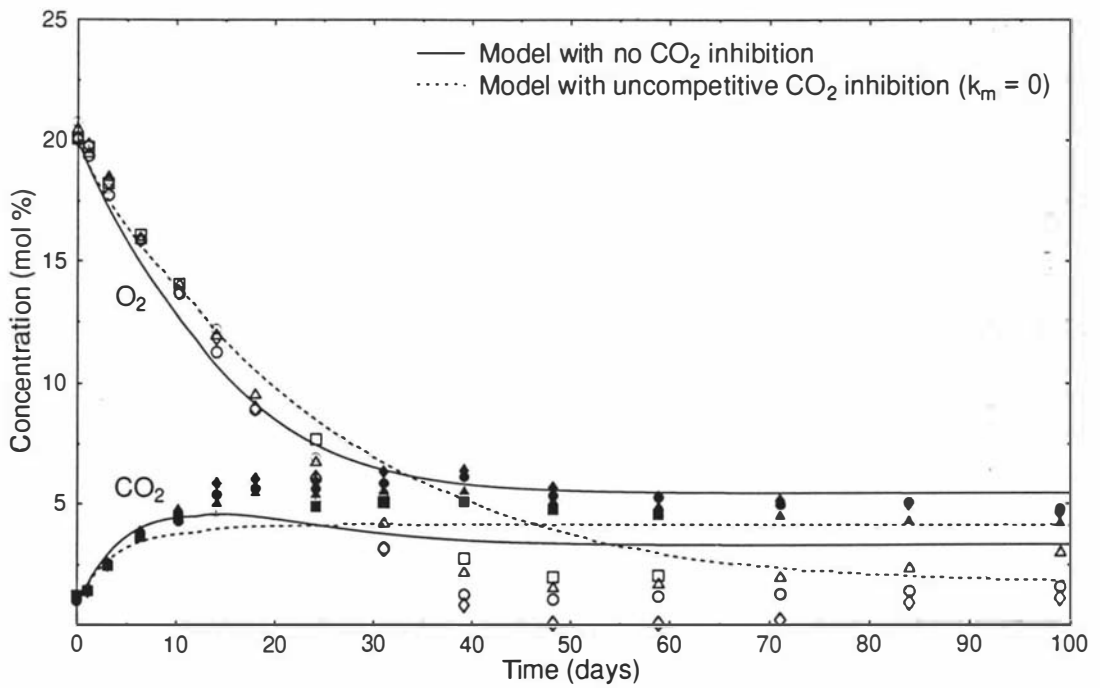
**Figure 9.35** Fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (10 count 80 fruit, 40 μm film, trial BB93-C). Experimental data from 2 replicate bags shown.



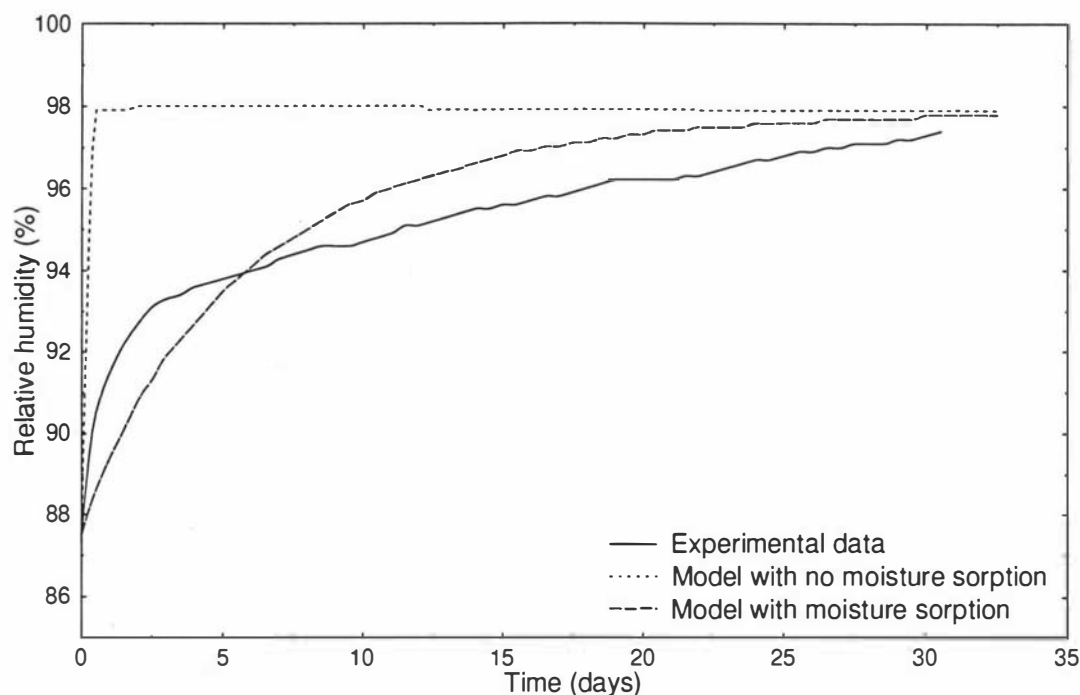
**Figure 9.36** Fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations for 1993 ‘Braeburn’ bags (5 count 80 fruit, 40 μm film, trial BB93-C). Experimental data from 5 replicate bags shown.



**Figure 9.37** Fruit internal  $O_2$  and  $CO_2$  concentrations for 1994 'Granny Smith' bags (10 count 125 fruit, 25  $\mu m$  film, trial GS94-B). Experimental data from 5 replicate bags shown.



**Figure 9.38** Fruit internal  $O_2$  and  $CO_2$  concentrations for 1994 'Granny Smith' bags (10 count 125 fruit, 40  $\mu m$  film, trial GS94-B). Experimental data from 5 replicate bags shown.



**Figure 9.39** Package relative humidity for 1993 'Braeburn' carton (count 125 fruit, 40  $\mu\text{m}$  film, folded, trial BB93-A).

### 9.1.3 PACKAGE RELATIVE HUMIDITY AND FRUIT WEIGHT LOSS

Figure 9.39 shows the predicted and experimental package relative humidities for the 1993 'Braeburn' carton fitted with a relative humidity probe (section 4.1.6). Two sets of predicted relative humidities are shown: one with no moisture sorption by the fruit trays (achieved by setting the number of fruit trays to zero), and one with moisture sorption. The relative humidity versus time profile predicted by the model with moisture sorption showed a much better overall shape than that predicted by the model with no moisture sorption. This indicates that moulded-pulp fruit trays represent a significant moisture sink within the packages. Differences between the model with moisture sorption and the experimental results could well be due to differences between the moisture sorption isotherm used in the model and the true moisture sorption characteristics of the fruit trays, especially at such high relative humidities.

Table 9.5 lists the measured and predicted fruit weight losses for the carton trials. The model predicted slightly different weight losses depending on whether the  $\text{O}_2$  or  $\text{CO}_2$  respiration model was used, presumably because different rates of respiratory heat generation led to slightly different fruit and package temperatures. The weight losses predicted under the  $\text{O}_2$  and  $\text{CO}_2$  respiration models were averaged to give the values listed in Table 9.5. Predicted weight losses were significantly lower than measured values for all except the 1994 'Braeburn' trials. However, trends in the predicted weight losses were similar to those exhibited by the experimental data.

**Table 9.5** Measured and predicted fruit weight losses.

| Trial  | Fruit count size | Film thickness ( $\mu\text{m}$ ) | Trial duration (days) | n <sup>a</sup> | Measured weight loss <sup>b, c</sup> (%) | Predicted weight loss <sup>b</sup> (%) |
|--------|------------------|----------------------------------|-----------------------|----------------|------------------------------------------|----------------------------------------|
| BB93-A | 125              | 40                               | 33                    | 8              | $0.33 \pm 0.04$                          | 0.16                                   |
|        | 125              | 25                               | 33                    | 3              | $0.32 \pm 0.05$                          | 0.17                                   |
|        | 80               | 40                               | 33                    | 3              | $0.30 \pm 0.02$                          | 0.14                                   |
|        | 80               | 25                               | 33                    | 3              | $0.37 \pm 0.28$                          | 0.15                                   |
| RG94-A | 100              | 25                               | 65                    | 5              | $0.58 \pm 0.02$                          | 0.25                                   |
|        | 100              | 40                               | 65                    | 5              | $0.54 \pm 0.02$                          | 0.22                                   |
| RG94-B | 100              | 25                               | 110                   | 2              | 0.68                                     | 0.58                                   |
|        | 100              | 40                               | 110                   | 2              | 0.63                                     | 0.53                                   |
| RG94-C | 100              | 25                               | 85                    | 4              | $0.95 \pm 0.05$                          | 0.57                                   |
|        | 100              | 40                               | 85                    | 4              | $0.86 \pm 0.07$                          | 0.51                                   |
| BB94-A | 125              | 25                               | 95                    | 4              | $0.54 \pm 0.10$                          | 0.49                                   |
|        | 125              | 25                               | 95                    | 4              | $0.58 \pm 0.12^d$                        | 0.53 <sup>d</sup>                      |
| BB94-B | 125              | 25                               | 95                    | 4              | $0.70 \pm 0.05$                          | 0.69                                   |
|        | 125              | 40                               | 95                    | 4              | $0.63 \pm 0.08$                          | 0.60                                   |
| GS94-A | 125              | 25                               | 120                   | 4              | $0.91 \pm 0.13$                          | 0.61                                   |
|        | 125              | 40                               | 120                   | 4              | $0.80 \pm 0.09$                          | 0.55                                   |

<sup>a</sup> n = sample size (number of cartons).

<sup>b</sup> Weight loss calculated on a per carton basis.

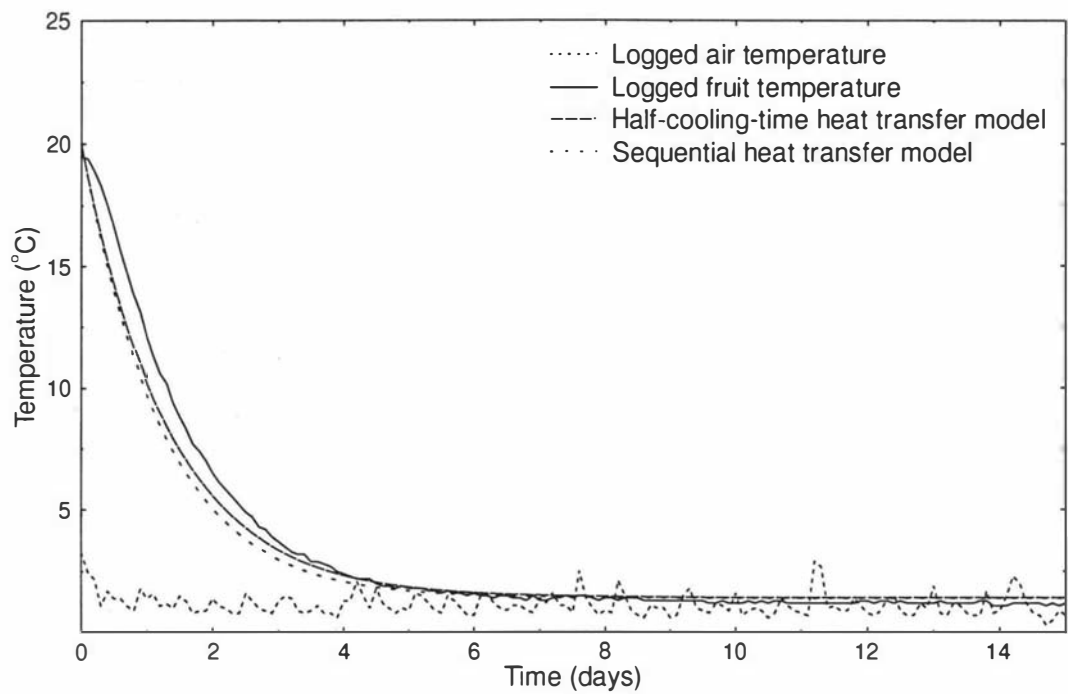
<sup>c</sup> Values presented as 'mean  $\pm$  95% confidence interval on mean' (for n > 2).

<sup>d</sup> Insulated cartons.

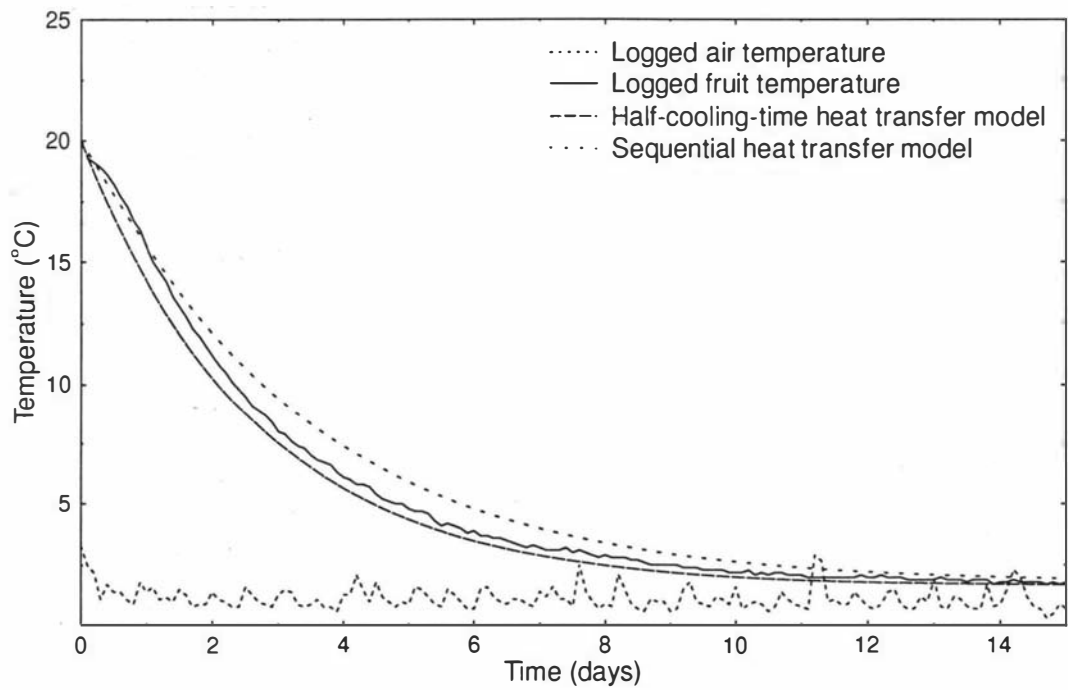
#### 9.1.4 HEAT TRANSFER

Figures 9.40 and 9.41 show the predicted and experimental temperature-time profiles for the uninsulated and insulated 1994 'Braeburn' cartons. Fruit temperatures were measured at the centre of the cartons (section 4.2.3), whereas model predictions represent mass-average temperatures. Hence, the short lag-phase observed at the start of the experimental cooling curves was not seen in the model predictions.

For uninsulated cartons (Figure 9.40), the half-cooling-time and sequential heat transfer models gave very similar predictions, with both models following the measured cooling curve well. For insulated cartons (Figure 9.41), the half-cooling-time model again performed well, while the sequential heat transfer model predicted a slightly slower cooling rate than that observed experimentally. This probably reflects the dependence of the sequential model on the accuracy of estimated heat transfer coefficients.



**Figure 9.40** Temperature-time profiles for uninsulated 1994 'Braeburn' cartons (trial BB94-A).



**Figure 9.41** Temperature-time profiles for insulated 1994 'Braeburn' cartons (trial BB94-A).

## 9.2 SENSITIVITY ANALYSIS

Sensitivity analysis was performed on the MAP model to determine whether input data uncertainties could explain some of the lack-of-fit discussed in previous sections. The analysis concentrated on model predictions of package atmosphere conditions, particularly O<sub>2</sub> and CO<sub>2</sub> concentrations and package relative humidity.

### 9.2.1 PACKAGE O<sub>2</sub> AND CO<sub>2</sub> CONCENTRATIONS

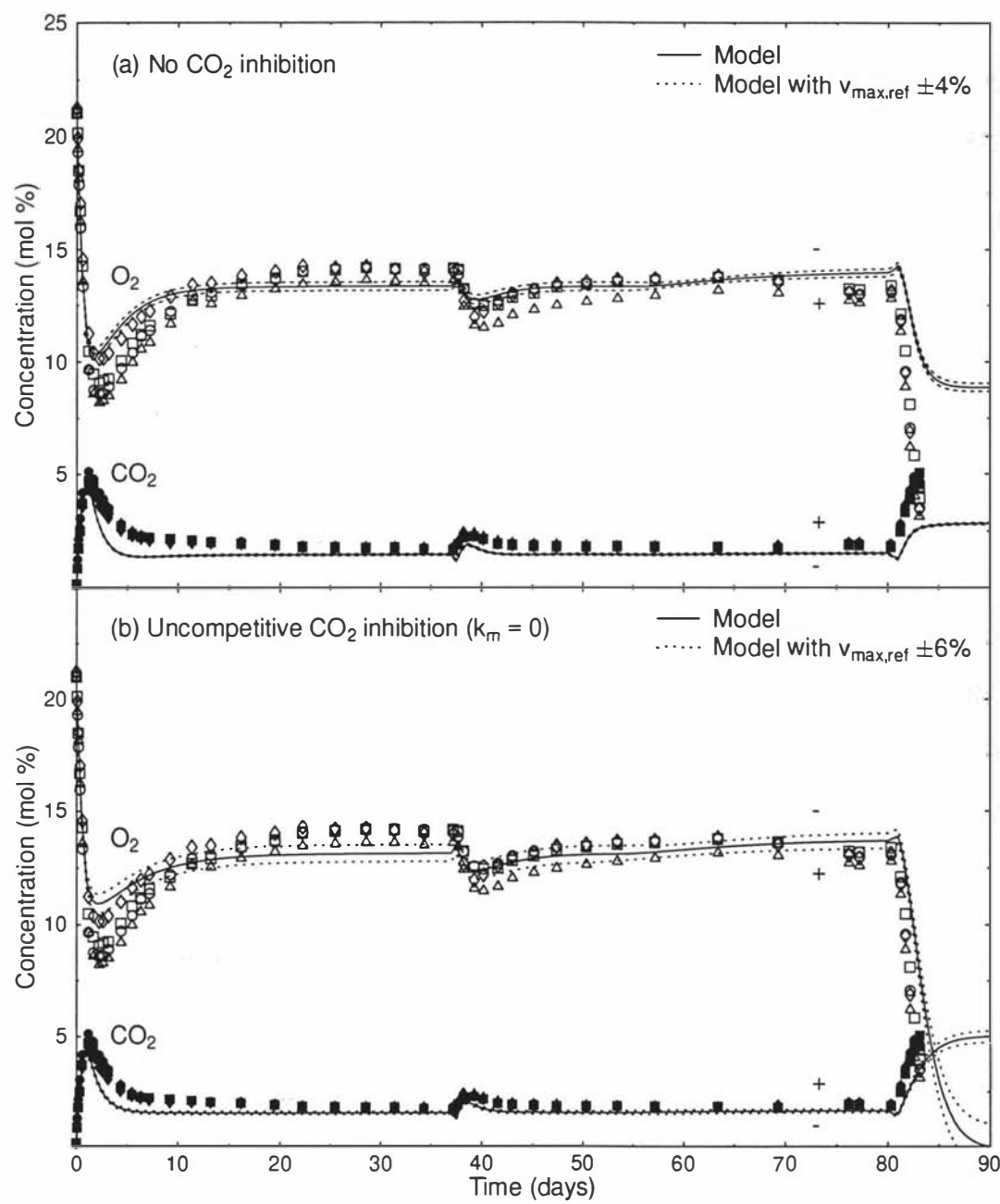
The sensitivity of predicted package O<sub>2</sub> and CO<sub>2</sub> concentrations to fruit respiration rate, fruit skin permeances to O<sub>2</sub> and CO<sub>2</sub>, film permeabilities to O<sub>2</sub> and CO<sub>2</sub>, and CO<sub>2</sub> solubility in the cell sap was investigated. In most cases, sensitivity analysis was performed for two model runs that were considered typical of the overall data set: 1994 'Royal Gala' cartons (25 µm film) from trial RG94-C and 1994 'Braeburn' cartons (40 µm film) from trial BB94-B.

#### 9.2.1.1 SENSITIVITY TO FRUIT RESPIRATION RATE

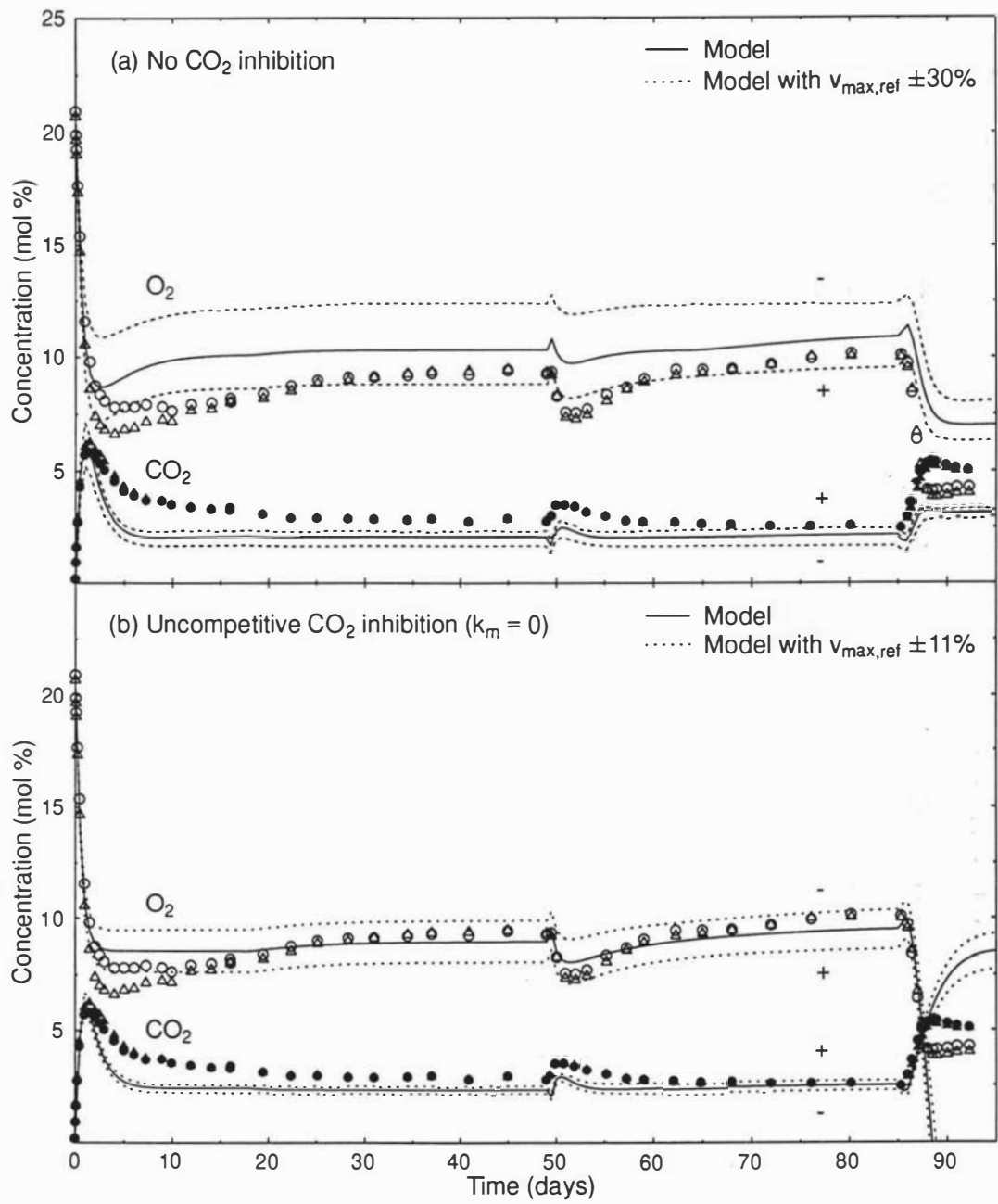
In the MAP model, predicted fruit respiration rates depend on estimated values of  $v_{max,ref}$ ,  $Q_{10}$ ,  $k_m$ ,  $k_{iu}$ , and  $k_{ic}$ . The respiration models derived in section 8.1.4 were restricted to three parameters:  $v_{max,ref}$ ,  $Q_{10}$ , and either  $k_m$  or  $k_{iu}$ . Estimated 95% confidence bounds on  $v_{max,ref}$ ,  $k_m$ , and  $k_{iu}$  (Tables 8.9 and 8.10) were used in the sensitivity analysis for fruit respiration rate.

Figures 9.42 to 9.44 show the effects of uncertainties in  $v_{max,ref}$ ,  $k_m$ , and  $k_{iu}$  on predicted package O<sub>2</sub> and CO<sub>2</sub> concentrations. The large uncertainties in  $v_{max,ref}$  and  $k_m$  for the 1994 'Braeburn' respiration model with no CO<sub>2</sub> inhibition (Figures 9.43a and 9.44a) reflect the poor fit of this model to the 1994 'Braeburn' respiration data (section 8.1.4.1). The effects of uncertainties in either  $v_{max,ref}$ ,  $k_m$ , or  $k_{iu}$  were large enough to account for much of the observed variation between predicted and experimental steady-state O<sub>2</sub> concentrations. However, the sensitivity of predicted CO<sub>2</sub> concentrations to uncertainties in  $v_{max,ref}$ ,  $k_m$ , or  $k_{iu}$  was smaller in absolute terms than that of predicted O<sub>2</sub> concentrations. Even at extreme values of  $v_{max,ref}$ ,  $k_m$ , or  $k_{iu}$ , predicted CO<sub>2</sub> concentrations generally remained lower than the experimental values.

As well as values of the respiration model parameters, the form of the respiration model can significantly affect predicted O<sub>2</sub> and CO<sub>2</sub> concentrations. This was seen in the comparisons between predictions made using the O<sub>2</sub> or CO<sub>2</sub> respiration models in section 9.1. Neither of these respiration models performed well under severely modified atmospheres, and there is evidence that a respiration model with combined O<sub>2</sub> and CO<sub>2</sub> effects would prove more realistic. However, as discussed in section 8.1.4, respiration data collected during the MA trials was too limited to allow valid separation of O<sub>2</sub> and CO<sub>2</sub> effects. For example, when a Michaelis-Menten model with uncompetitive CO<sub>2</sub> inhibition was fitted to the 1994 'Braeburn' respiration data without setting  $k_m$  to zero, the resulting estimate of  $k_m$  was not significantly different from zero, and the estimates of  $v_{max,ref}$  and  $k_{iu}$  were not significantly different from those obtained for the CO<sub>2</sub> respiration model with no O<sub>2</sub> effect.

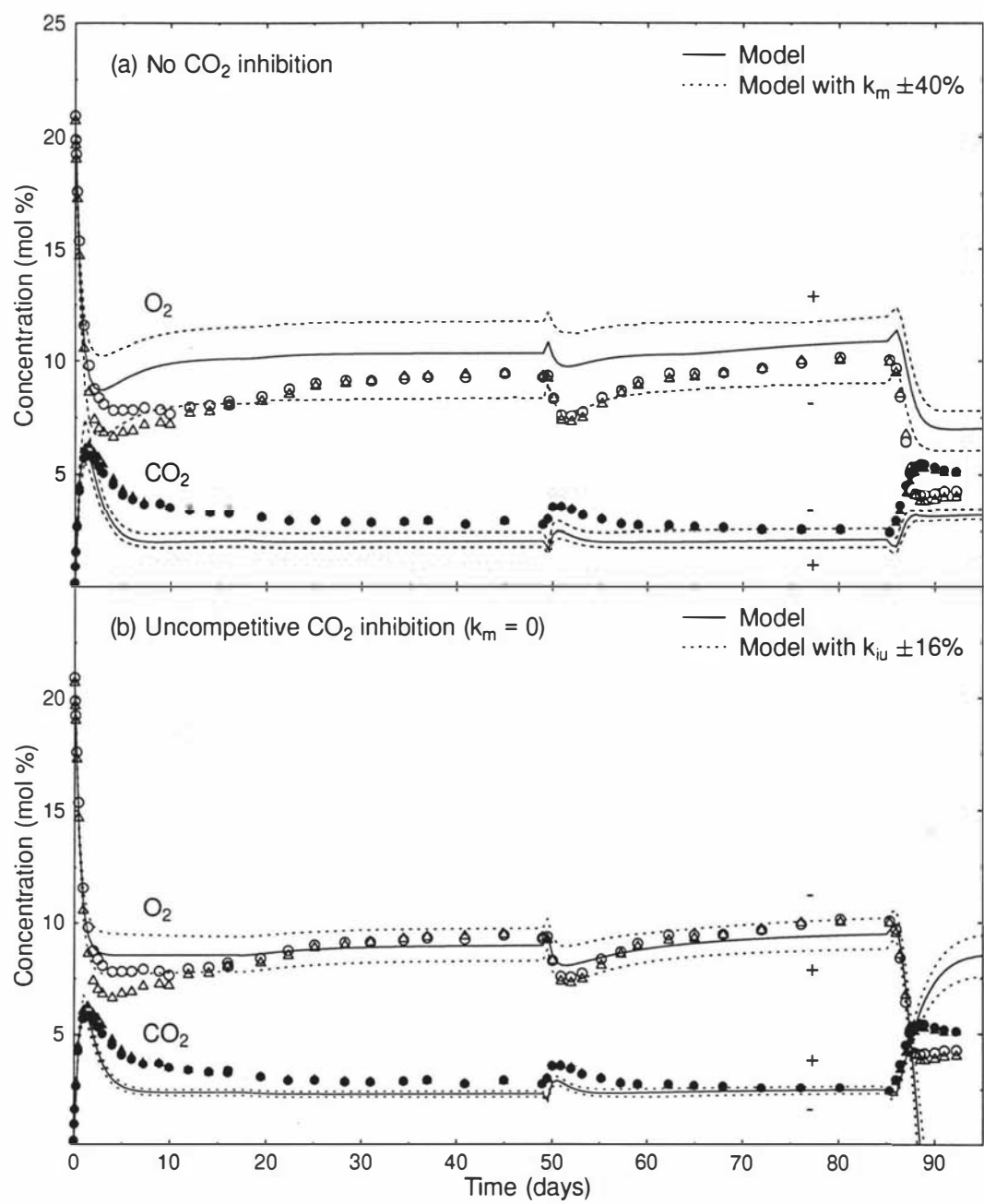


**Figure 9.42** Sensitivity analysis on  $v_{max,ref}$  for 1994 'Royal Gala' cartons (count 100 fruit, 25  $\mu m$  film, heat sealed, trial RG94-C). Experimental data from 4 replicate cartons shown.



**Figure 9.43**

Sensitivity analysis on  $v_{max,ref}$  for 1994 'Braeburn' cartons (count 125 fruit, 40  $\mu\text{m}$  film, heat sealed, trial BB94-B). Experimental data from 2 replicate cartons shown.



**Figure 9.44** Sensitivity analysis on (a)  $k_m$  and (b)  $k_{iu}$  for 1994 'Braeburn' cartons (count 125 fruit, 40  $\mu\text{m}$  film, heat sealed, trial BB94-B). Experimental data from 2 replicate cartons shown.

Dadzie *et al.* (1996) estimated  $k_m$  values ranging from 1.3 kPa O<sub>2</sub> to 3.6 kPa O<sub>2</sub> for 'Cox's Orange Pippin' and 'Granny Smith' apples held at 20°C under various O<sub>2</sub> concentrations. Based on these data, an approximate  $k_m$  of 2.5 kPa O<sub>2</sub> (0.033 kg O<sub>2</sub>·m<sup>-3</sup>) was assumed and a Michaelis-Menten model with uncompetitive CO<sub>2</sub> inhibition refitted to the 1994 'Braeburn' respiration rate data. Resulting estimates of  $v_{max,ref}$ ,  $k_{iu}$ , and  $Q_{10}$  were  $9.2 \times 10^{-10}$  kg O<sub>2</sub>·kg<sup>-1</sup>·s<sup>-1</sup>, 0.047 kg CO<sub>2</sub>·m<sup>-3</sup>, and 4.4 respectively, again not significantly different from the parameters for the CO<sub>2</sub> respiration model with no O<sub>2</sub> effect (Table 8.10). Figures 9.45 and 9.46 show the performance of this combined O<sub>2</sub> and CO<sub>2</sub> respiration model in relation to that of the O<sub>2</sub>-only and CO<sub>2</sub>-only respiration models for Braeburn cartons from trial BB94-B. Predicted package O<sub>2</sub> and CO<sub>2</sub> concentrations under the combined respiration model generally followed those under the CO<sub>2</sub>-only model closely until the final 20°C storage stage. During this stage, predictions under the combined respiration model followed the experimental O<sub>2</sub> and CO<sub>2</sub> data much more closely than those under the O<sub>2</sub> or CO<sub>2</sub> respiration models. Thus, a respiration model with a low  $k_m$ , rather than a model with a high  $k_m$  or a  $k_m$  of zero, appears to better describe the respiratory behaviour of the 1994 'Braeburn' apples under highly modified package (and fruit internal) atmospheres.

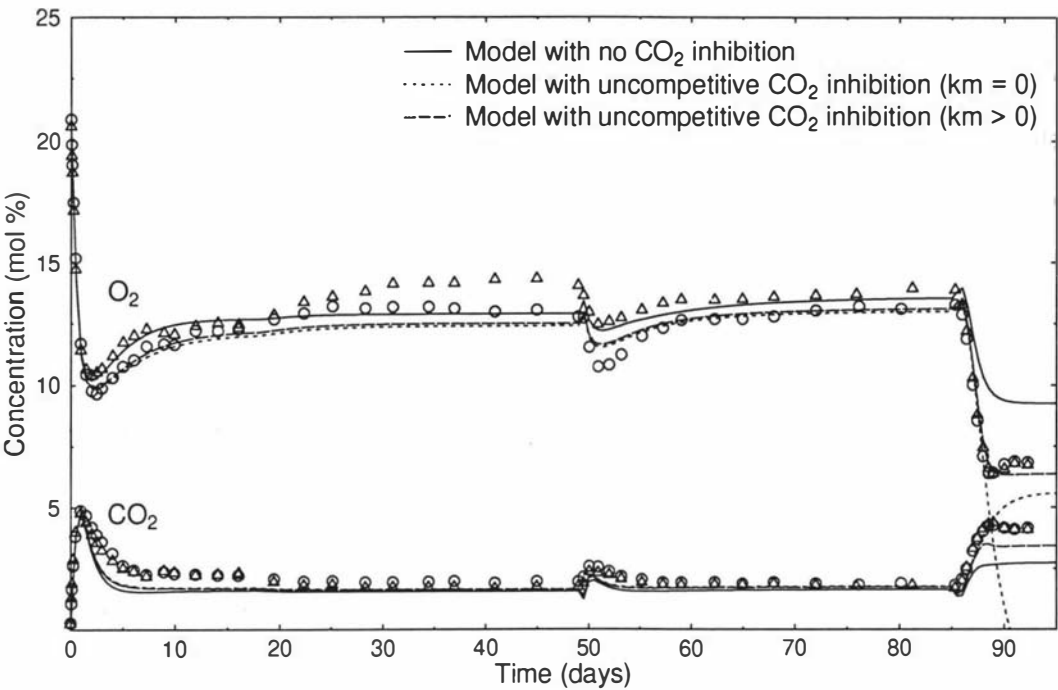
To determine whether a combined respiration model could also improve predictions for some of the bag trials where very low package O<sub>2</sub> concentrations were reached, a Michaelis-Menten model with uncompetitive CO<sub>2</sub> inhibition and a  $k_m$  of 0.033 kg O<sub>2</sub>·m<sup>-3</sup> was also fitted to the 1994 'Granny Smith' respiration data. This gave values for  $v_{max,ref}$ ,  $k_{iu}$ , and  $Q_{10}$  of  $6.9 \times 10^{-10}$  kg O<sub>2</sub>·kg<sup>-1</sup>·s<sup>-1</sup>, 0.189 kg CO<sub>2</sub>·m<sup>-3</sup>, and 3.7 respectively. Only the value for  $k_{iu}$  was significantly different from that for the CO<sub>2</sub> respiration model with no O<sub>2</sub> effect (Table 8.10). Figures 9.47 and 9.48 show the package O<sub>2</sub> and CO<sub>2</sub> concentrations predicted for the 'Granny Smith' bags (trial GS94-B) under the combined respiration model. For bags with 25 µm film windows (Figure 9.47), there was little difference between the three respiration models. For bags with 40 µm film windows (Figure 9.48), differences between the three models were greater, but the combined respiration model did not greatly improve the predicted O<sub>2</sub> and CO<sub>2</sub> concentrations. The shape of the experimental curve for package O<sub>2</sub> concentration in Figure 9.48 suggests a much lower value of  $k_m$  than that assumed in the combined respiration model.

### 9.2.1.2 SENSITIVITY TO FRUIT SKIN PERMEANCES

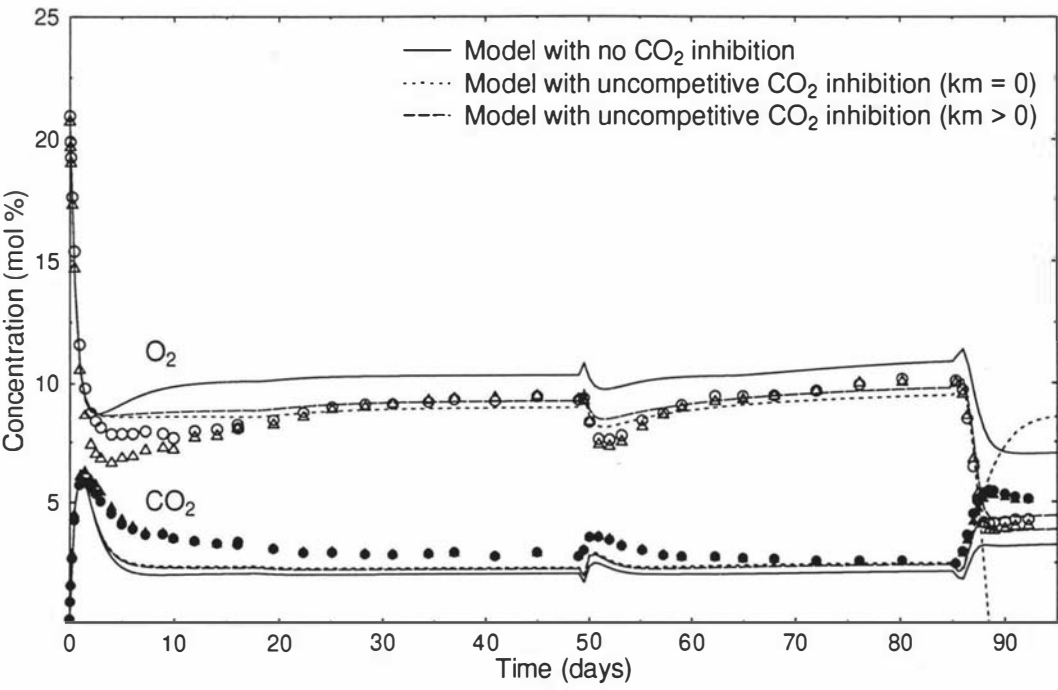
Fruit skin permeances to O<sub>2</sub> and CO<sub>2</sub> affect the relationship between the compositions of the fruit internal and package atmospheres. As the composition of the fruit internal atmosphere affects predicted respiration rates, uncertainties in fruit skin permeances were expected to have an effect on model predictions. However, this effect proved small, with a ±30% assumed uncertainty in skin permeance having very little effect on predicted package O<sub>2</sub> or CO<sub>2</sub> concentrations (Figure 9.49).

### 9.2.1.3 SENSITIVITY TO FILM PERMEABILITY

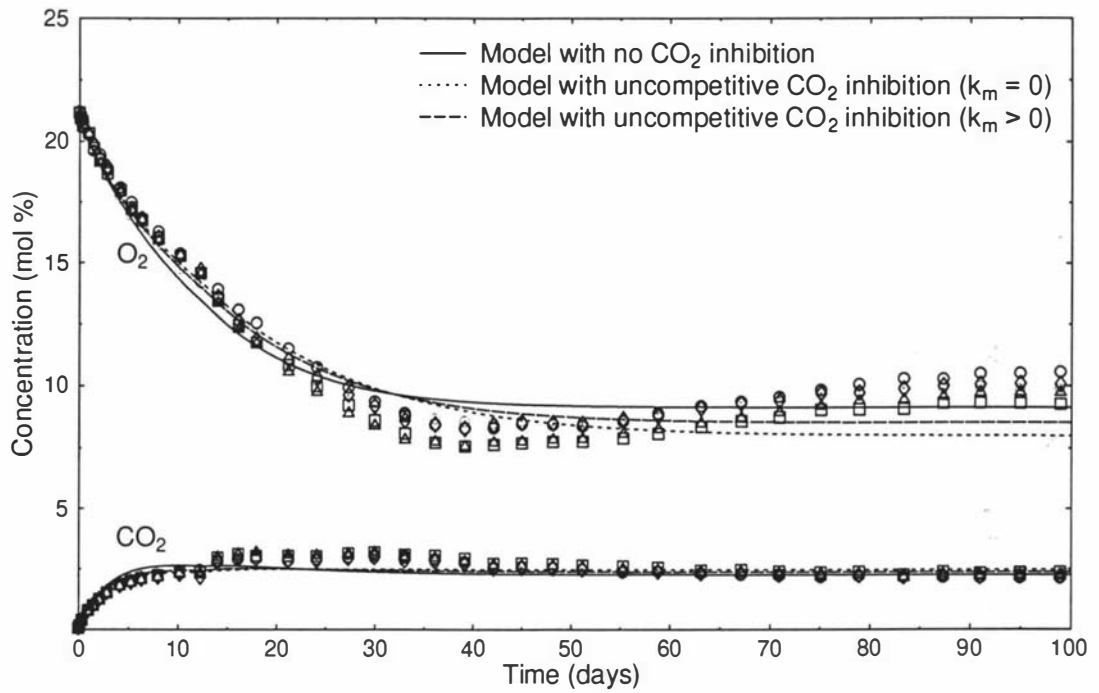
The least-squares linear regression techniques used in section 8.2.2.1 to estimate 95% confidence bounds on predicted O<sub>2</sub> and CO<sub>2</sub> permeabilities (Table 8.14) assume that scatter in the measured data is entirely due to random error. However, the measured film permeabilities presented in Table 8.12 and Figure 8.10 suggest significant



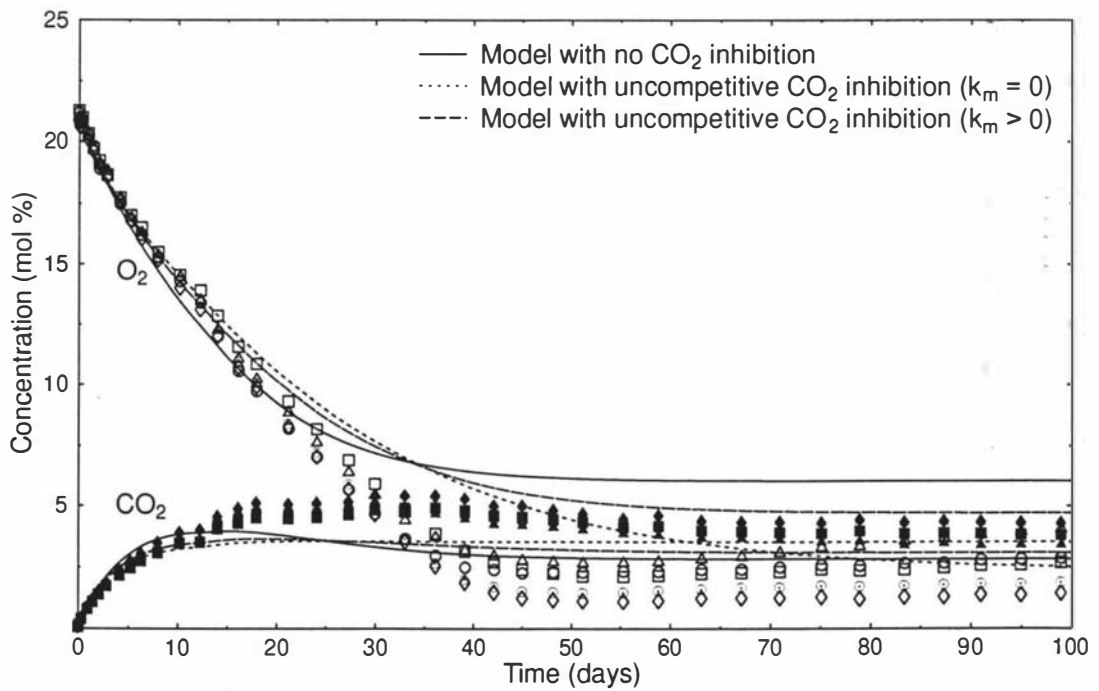
**Figure 9.45** Effect of respiration model on package-atmosphere predictions for 1994 ‘Braeburn’ cartons (count 125 fruit, 25  $\mu m$  film, heat-sealed, trial BB94-B). Experimental data from 2 replicate cartons shown.



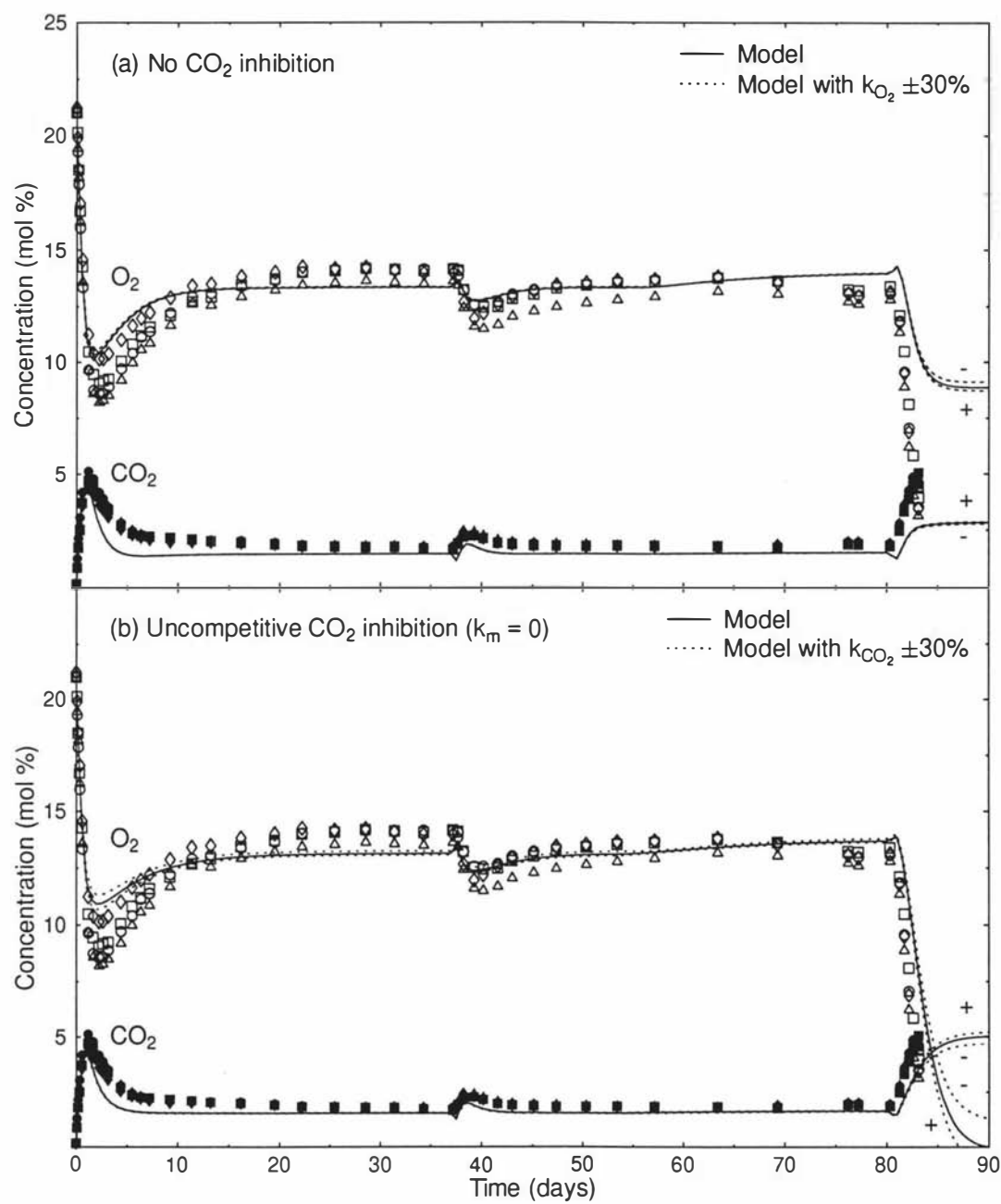
**Figure 9.46** Effect of respiration model on package-atmosphere predictions for 1994 ‘Braeburn’ cartons (count 125 fruit, 40  $\mu m$  film, heat-sealed, trial BB94-B). Experimental data from 2 replicate cartons shown.



**Figure 9.47** Effect of respiration model on package-atmosphere predictions for 1994 'Granny Smith' bags (10 count 125 fruit, 25  $\mu m$  film, trial GS94-B). Experimental data from 5 replicate bags shown.



**Figure 9.48** Effect of respiration model on package-atmosphere predictions for 1994 'Granny Smith' bags (10 count 125 fruit, 40  $\mu m$  film, trial GS94-B). Experimental data from 5 replicate bags shown.



**Figure 9.49** Sensitivity analysis on (a)  $k_{O_2}$  and (b)  $k_{CO_2}$  for 1994 'Royal Gala' cartons (count 100 fruit, 25  $\mu m$  film, heat sealed, trial RG94-C). Experimental data from 4 replicate cartons shown.

differences between the average permeabilities measured by different experimental methods. Thus, predicted film permeabilities may in fact be subject to two sources of uncertainty, one due to random error and one due to method error. While the true uncertainty due to random error is likely to be somewhat smaller than that given by the confidence intervals in Table 8.14, the uncertainty due to method error may be greater than these confidence intervals suggest.

The largest differences between film permeabilities measured by different methods occurred between results from the main permeability runs at 0°C and results from the second set of CSIRO tests (also at 0°C). O<sub>2</sub> and CO<sub>2</sub> permeabilities reported by the CSIRO were 20% and 40% lower, respectively, than those measured during the main runs. Thus, uncertainties due to method error were estimated as  $\pm 10\%$  for O<sub>2</sub> permeability and  $\pm 20\%$  for CO<sub>2</sub> permeability. These estimates, as well as the confidence intervals listed in Table 8.14, were used in the sensitivity analysis for film O<sub>2</sub> and CO<sub>2</sub> permeabilities.

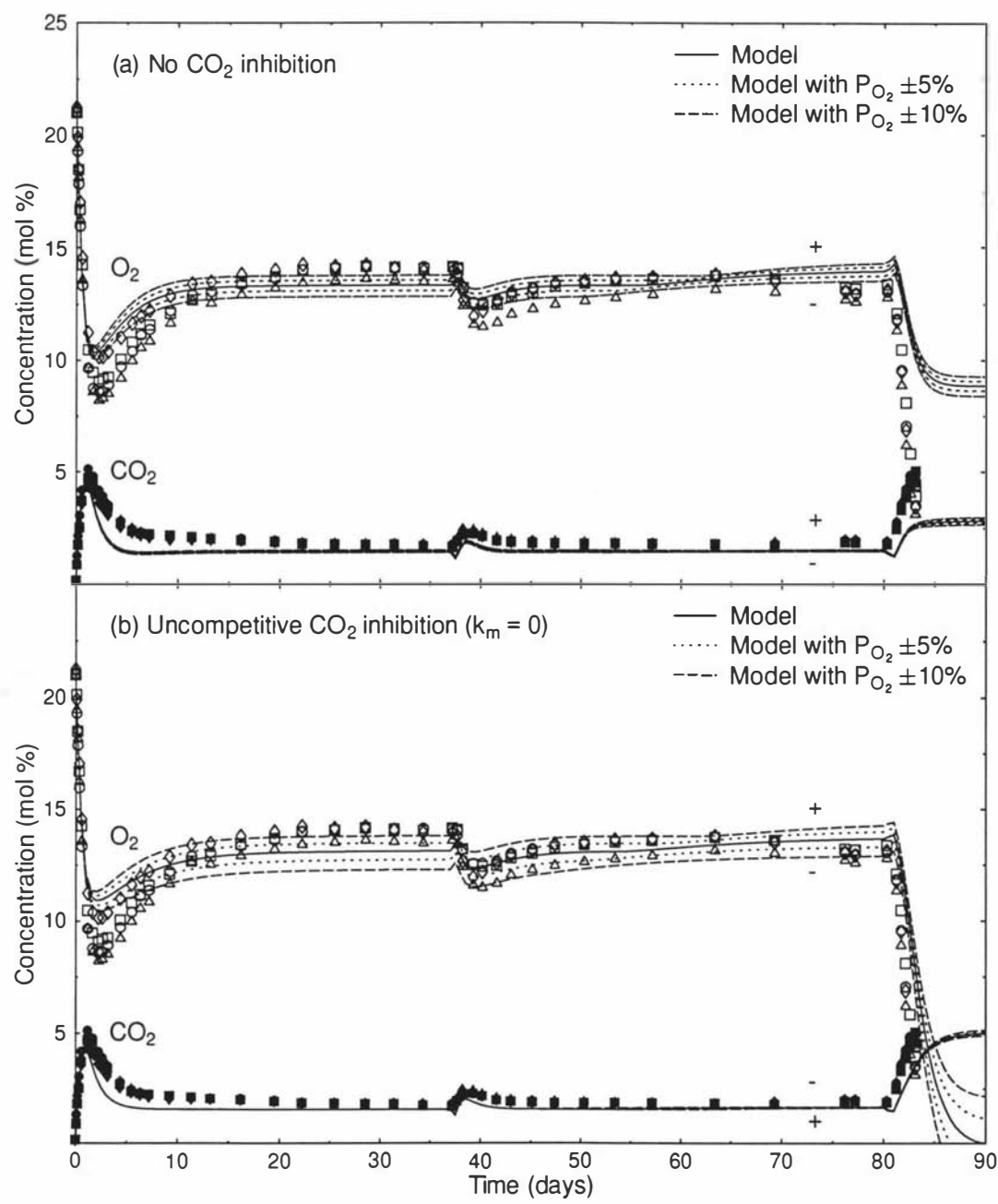
Figures 9.50 to 9.53 show the results of the sensitivity analysis. The effects of random-error uncertainties in O<sub>2</sub> or CO<sub>2</sub> permeability were, in general, not large enough to account for the steady-state differences between predicted and experimental O<sub>2</sub> and CO<sub>2</sub> concentrations. However, these differences could be accounted for by the larger method-error uncertainties.

In the MAP model, film permeabilities to O<sub>2</sub> and CO<sub>2</sub> influence the composition of the package atmosphere and, through this, the composition of the fruit internal atmosphere and the rate of fruit respiration. Depending on the nature of the respiration model, a change in film permeability to either O<sub>2</sub> or CO<sub>2</sub> can therefore affect the predicted package concentrations of both gases simultaneously. This is seen in Figures 9.50a and 9.52a, where changes in O<sub>2</sub> permeability affected O<sub>2</sub> and CO<sub>2</sub> concentrations predicted under the respiration model with no CO<sub>2</sub> inhibition, and in Figures 9.51b and 9.53b, where changes in CO<sub>2</sub> permeability affected O<sub>2</sub> and CO<sub>2</sub> concentrations predicted under the respiration model with uncompetitive CO<sub>2</sub> inhibition.

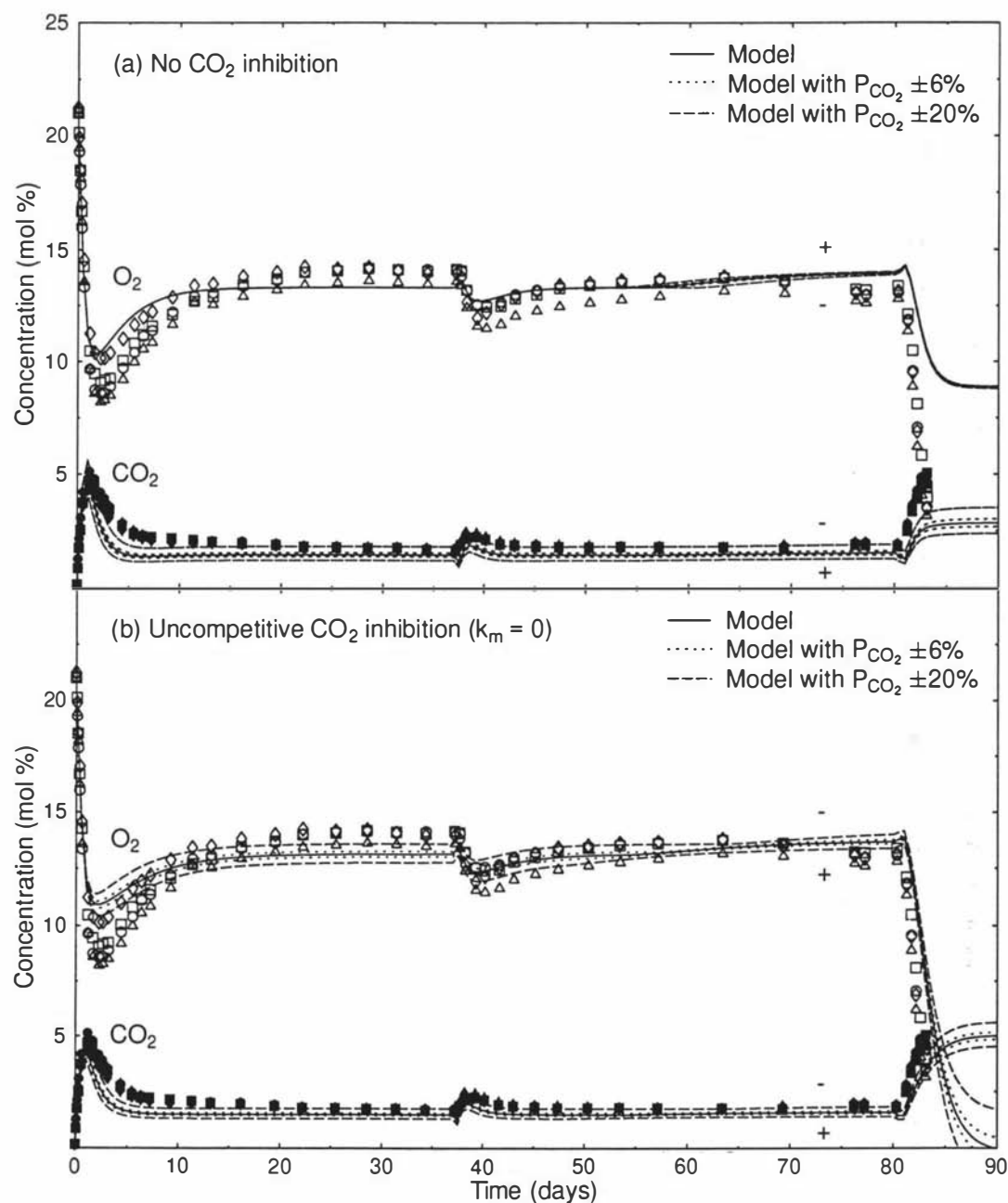
#### 9.2.1.4 SENSITIVITY TO CO<sub>2</sub> SOLUBILITY

CO<sub>2</sub> solution in the fruit cell sap was not included in the MAP model formulation. However, as discussed in section 9.1.1.2, comparisons between predicted and experimental CO<sub>2</sub> concentrations indicated that CO<sub>2</sub> solution in the fruit cell sap may represent a significant effect during periods where CO<sub>2</sub> concentrations change rapidly, particularly at low storage temperatures. To investigate the likely effects of CO<sub>2</sub> solubility on model predictions, the MAP model was run with fruit porosity increased by a factor of 10 in Eq. 6.21. This increased the volume of the fruit internal atmosphere by a factor of 10 for CO<sub>2</sub> only. The factor 10 was estimated from the solubility of CO<sub>2</sub> in water at 0°C (Liley *et al.*, 1984) such that the increase in mass of CO<sub>2</sub> per apple was roughly equal to the mass of CO<sub>2</sub> expected to dissolve in the cell sap.

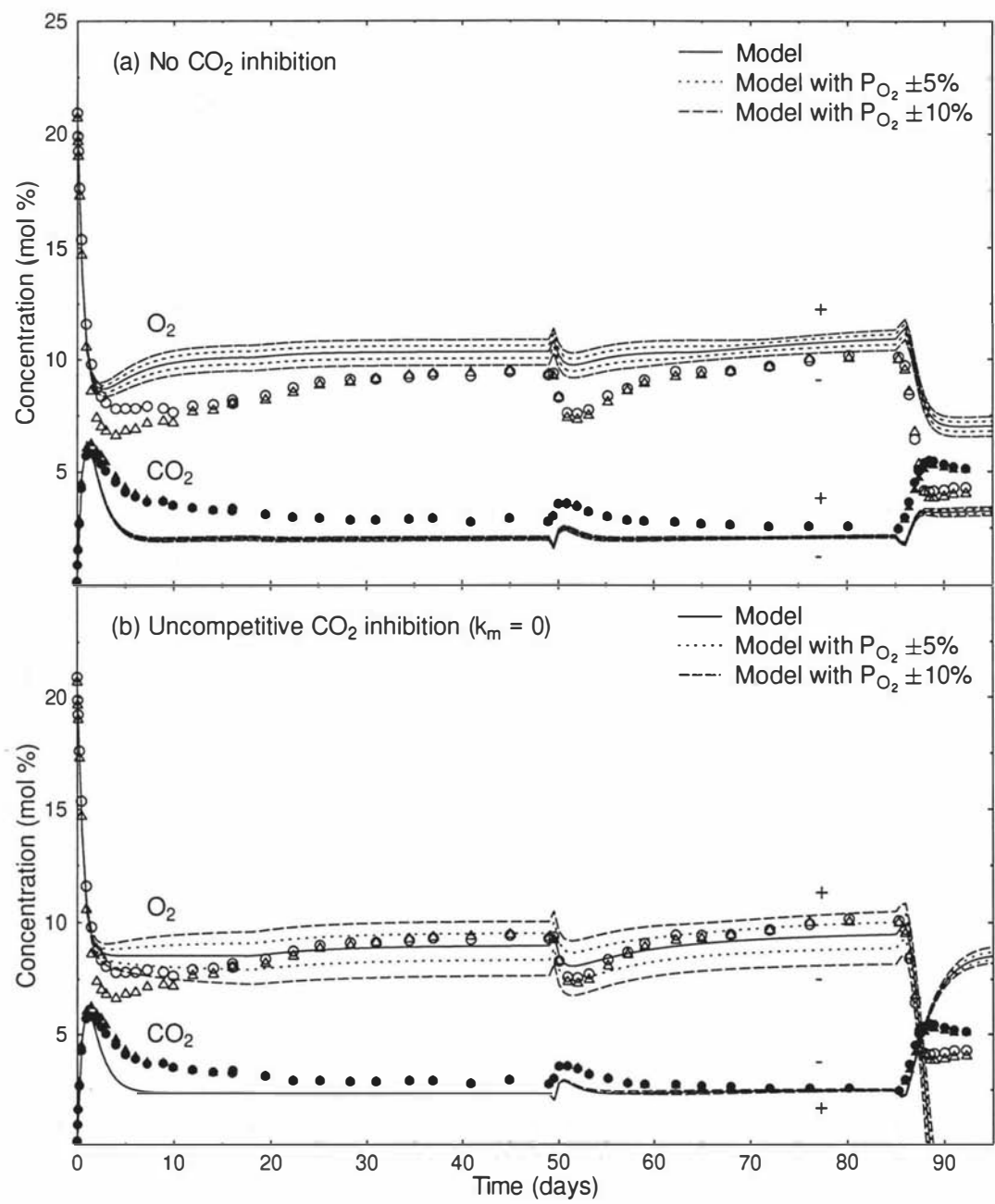
Figures 9.54 and 9.55 show examples of the resulting model predictions. The effects of CO<sub>2</sub> solubility on model predictions were most noticeable during the initial CO<sub>2</sub> peak at the start of the trials; the time axes in Figures 9.54 and 9.55 have therefore been



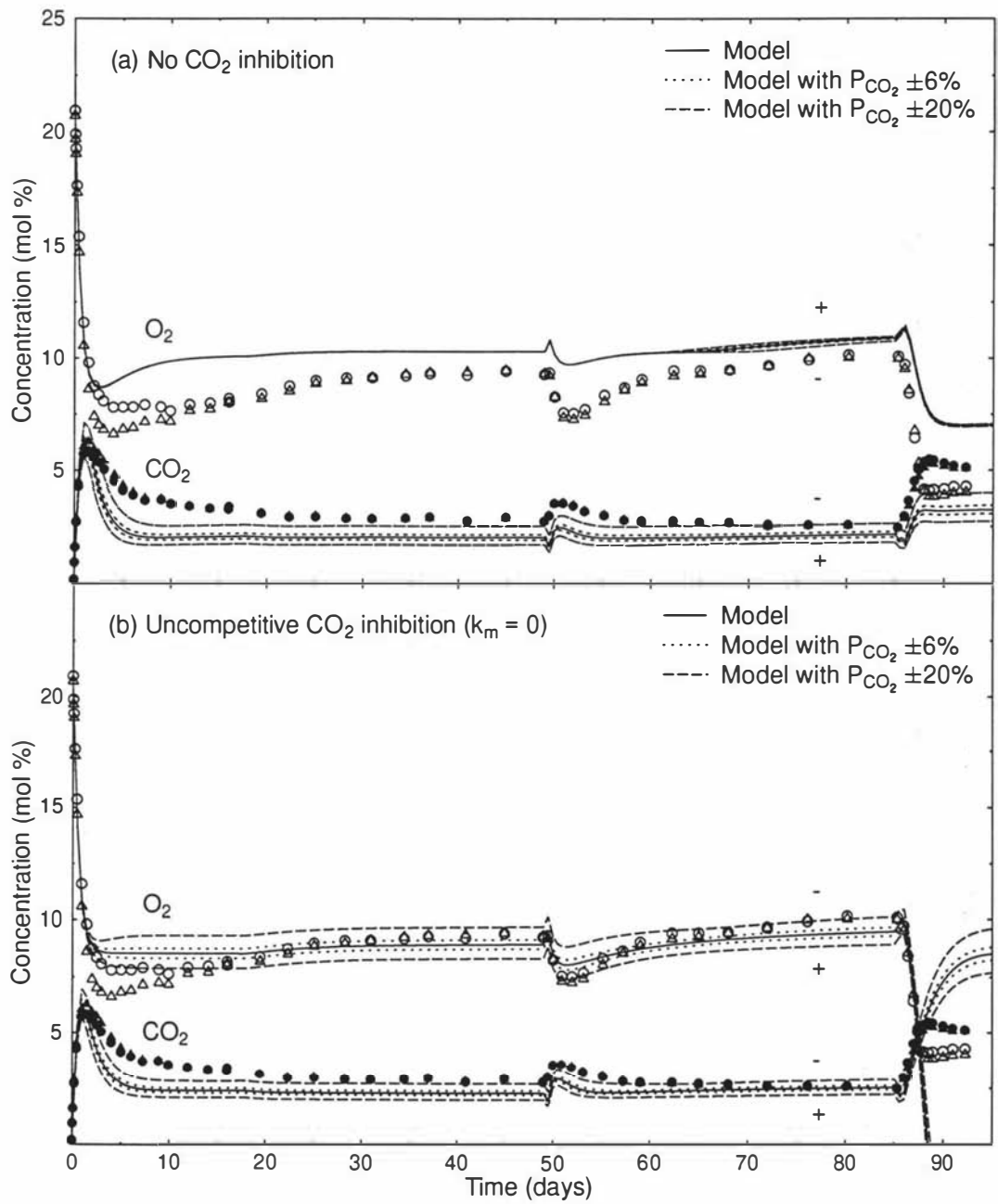
**Figure 9.50** Sensitivity analysis on  $P_{O_2}$  for 1994 ‘Royal Gala’ cartons (count 100 fruit, 25  $\mu$ m film, heat sealed, trial RG94-C). Experimental data from 4 replicate cartons shown.



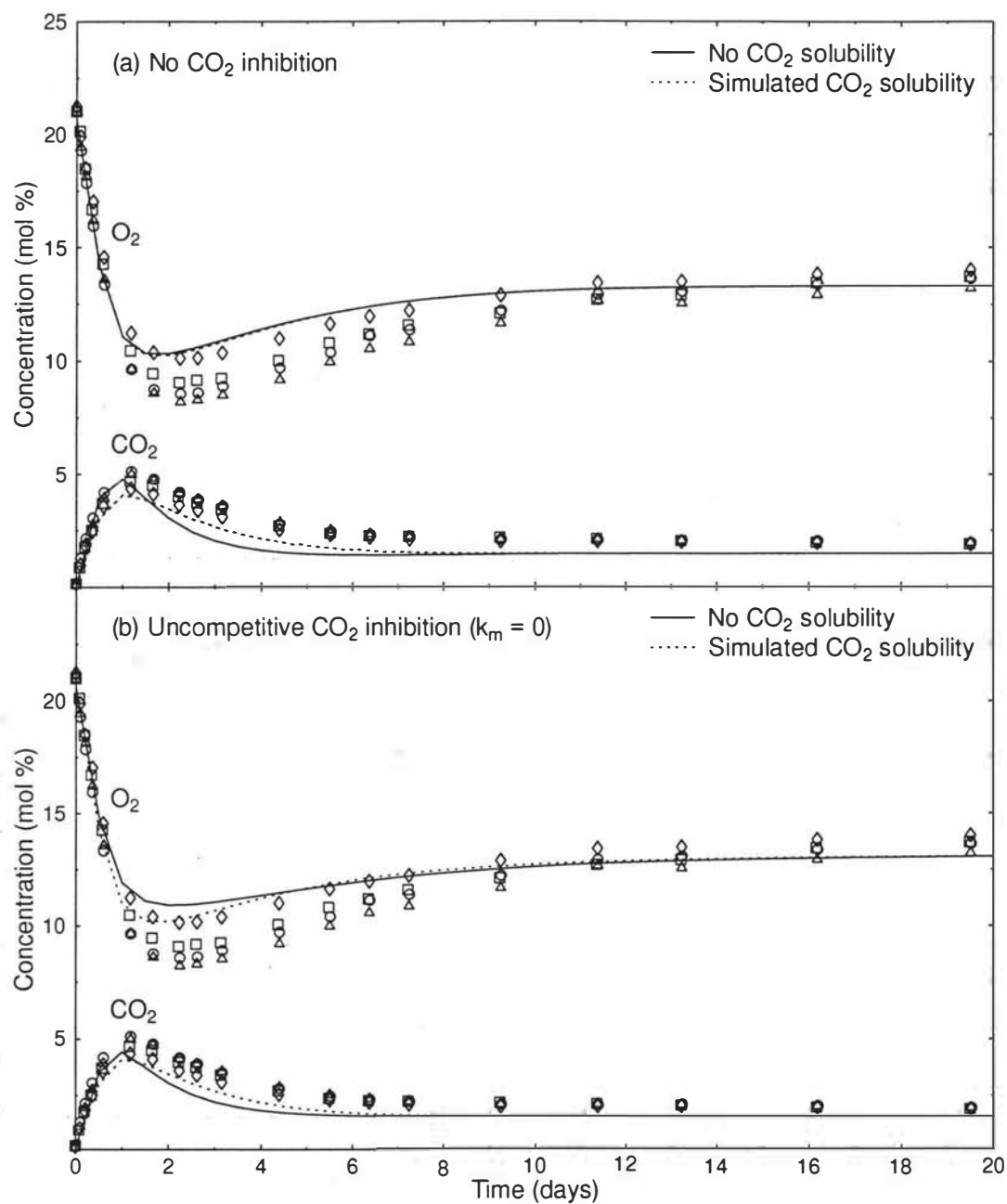
**Figure 9.51** Sensitivity analysis on  $P_{CO_2}$  for 1994 'Royal Gala' cartons (count 100 fruit, 25  $\mu\text{m}$  film, heat sealed, trial RG94-C). Experimental data from 4 replicate cartons shown.



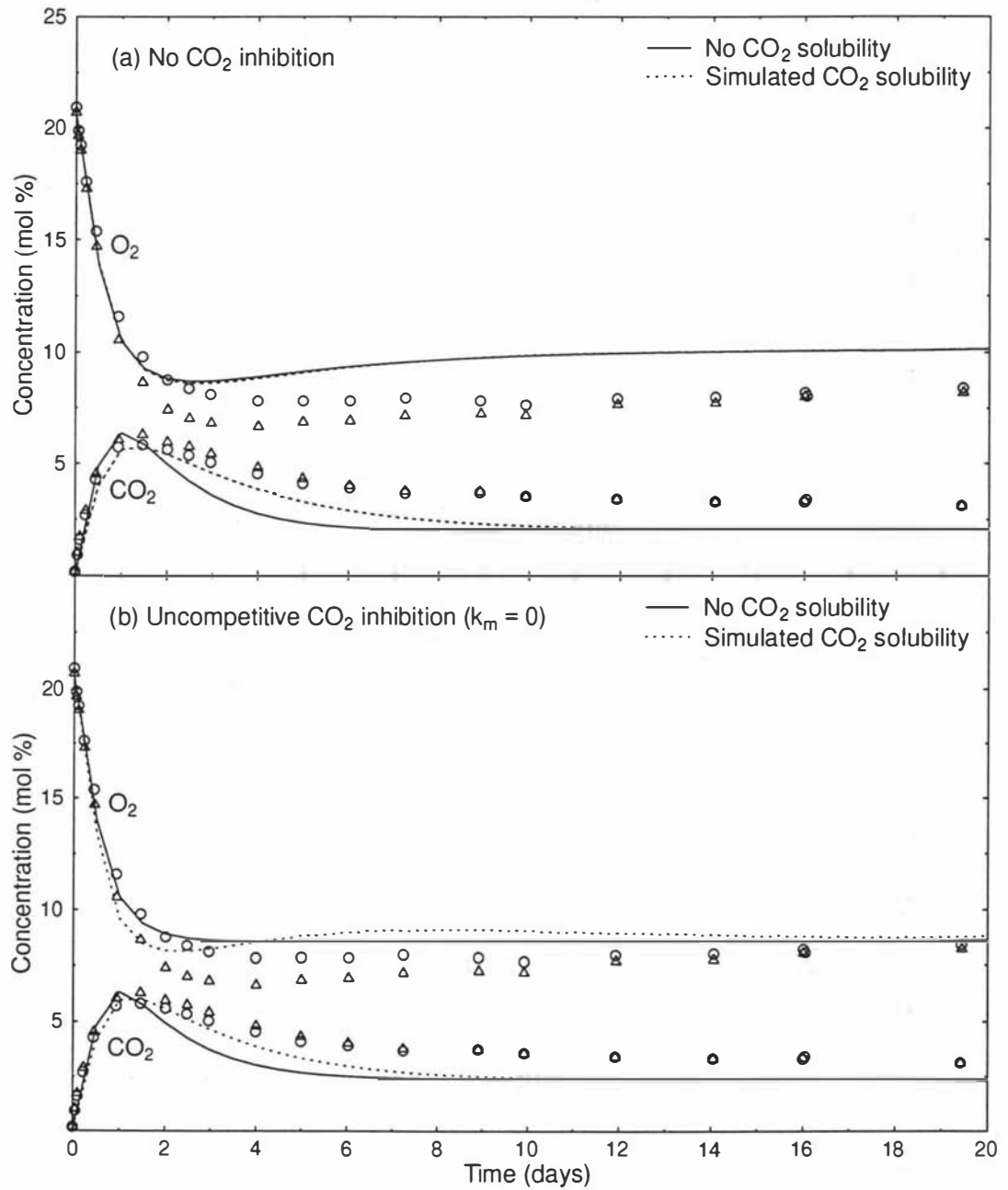
**Figure 9.52** Sensitivity analysis on  $P_{O_2}$  for 1994 'Braeburn' cartons (count 125 fruit, 40  $\mu\text{m}$  film, heat sealed, trial BB94-B). Experimental data from 2 replicate cartons shown.



**Figure 9.53** Sensitivity analysis on  $P_{CO_2}$  for 1994 ‘Braeburn’ cartons (count 125 fruit, 40  $\mu m$  film, heat sealed, trial BB94-B). Experimental data from 2 replicate cartons shown.



**Figure 9.54** Effect of simulated  $CO_2$ -solubility on package-atmosphere predictions for 1994 'Royal Gala' cartons (count 100 fruit, 25  $\mu m$  film, heat-sealed, trial RG94-C). Experimental data from 4 replicate cartons shown.



**Figure 9.55** Effect of simulated  $CO_2$ -solubility on package-atmosphere predictions for 1994 'Braeburn' cartons (count 125 fruit, 40  $\mu m$  film, heat-sealed, trial BB94-B). Experimental data from 2 replicate cartons shown.

expanded to show the first 20 days only. Accounting for  $\text{CO}_2$  solution in the fruit cell sap improved the shape of the predicted  $\text{CO}_2$  peaks. Some lack of fit remained, but this may largely be due to the underprediction of  $\text{CO}_2$  concentrations observed generally. As expected,  $\text{CO}_2$  solubility had no effect on predicted steady-state  $\text{CO}_2$  concentrations.

### 9.2.2 PACKAGE RELATIVE HUMIDITY

Figures 9.56, 9.57, and 9.58 illustrate the sensitivity of predicted package relative humidity to uncertainties in fruit water activity ( $a_w$ ), fruit skin permeance to water vapour ( $k_{g,skin}$ ), and film permeability to water vapour ( $P_{H_2O}$ ) respectively. Values for these parameters were estimated from literature data (sections 8.1.3, 8.1.5, and 8.2.2.2), and thus an estimated uncertainty, rather than a 95% confidence interval, was assigned to each parameter.

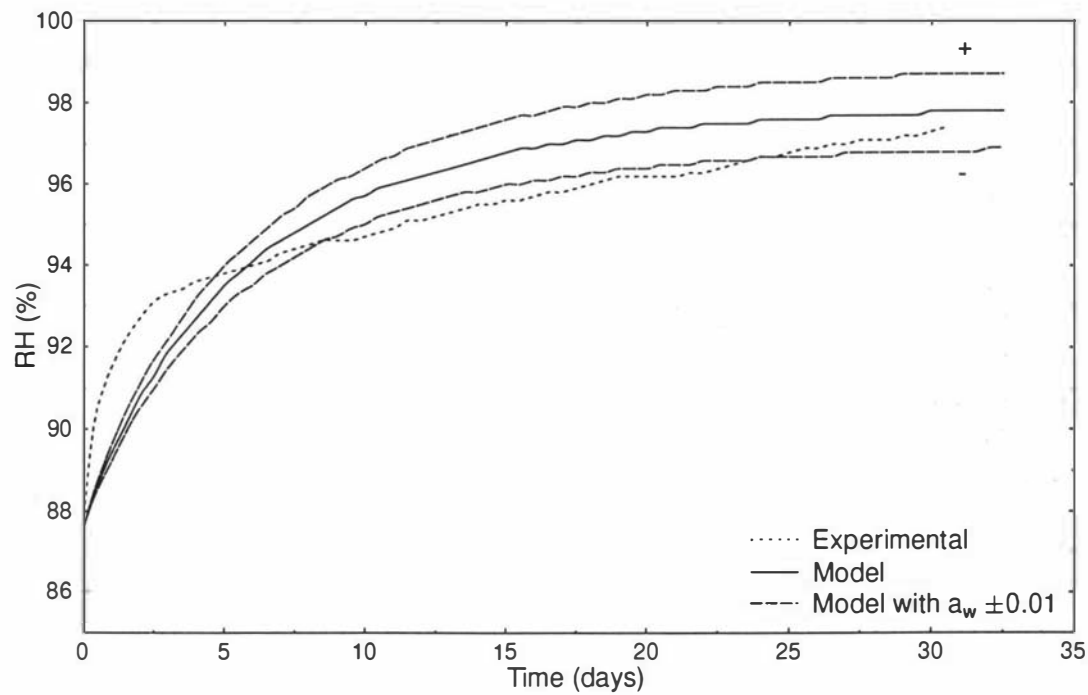
Changes in fruit water activity had a marked effect on predicted equilibrium humidity (Figure 9.56), with the variation in predicted equilibrium humidity equal in magnitude to the input variation in water activity.

Fruit skin permeance to water vapour had a smaller effect on equilibrium humidity, but affected the shape of the predicted humidity-versus-time profile (Figure 9.57). Even so, the uncertainty in  $k_{g,skin}$  could not account for the shape of the experimental humidity-versus-time profile, which was distinctly bi-modal. The shape of the experimental profile is likely to have been strongly influenced by the moisture sorption characteristics of the paper-based fruit trays. In the MAP model, moisture sorption was assumed to follow the GAB isotherm model, with coefficients taken from literature data (section 8.2.3), and with no account taken of differences between sorption and desorption characteristics, or of the effect of temperature on sorption characteristics. Hysteresis and temperature effects are unlikely to have been important for the constant-temperature trial in Figure 9.57. However, uncertainty regarding the true form of the sorption isotherm, especially at very high relative humidity, may have had a major influence.

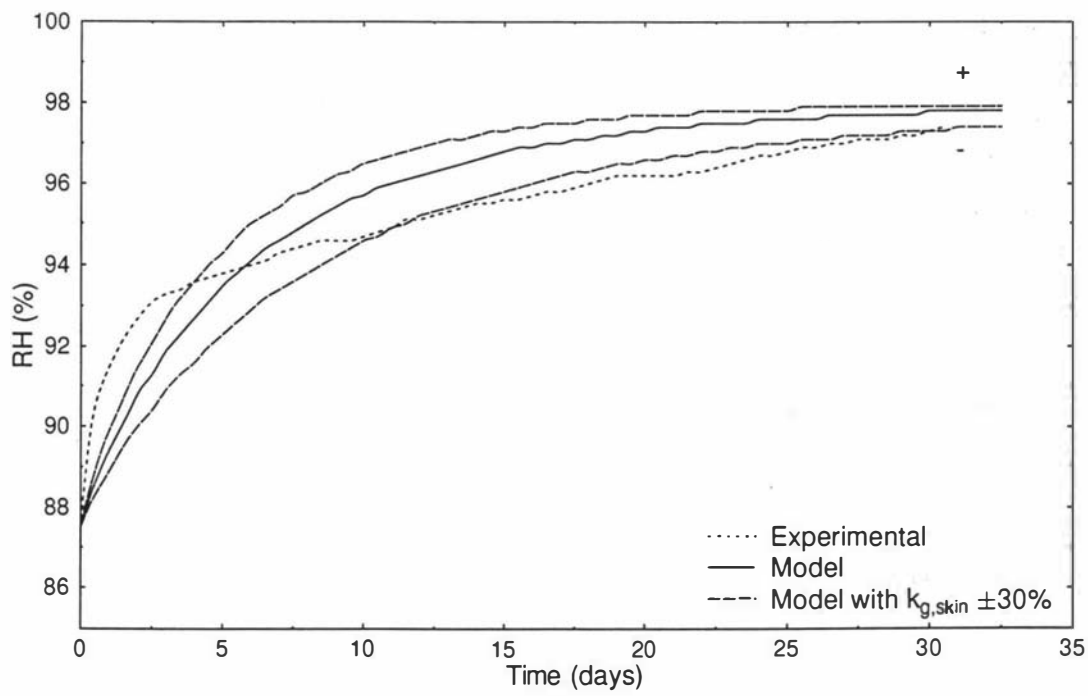
Film permeability had very little effect on predicted RH (Figure 9.58). Thus, the extrapolation of literature data to estimate the water vapour permeability of the MA-film (section 8.2.2.2) is unlikely to have significantly influenced the accuracy of model predictions.

The uncertainties in  $a_w$ ,  $k_{g,skin}$ , and  $P_{H_2O}$  also affected weight-loss predictions, but not significantly enough to account for the differences between predicted and measured weight losses given in Table 9.5. For the 1993 'Braeburn' cartons, the estimated uncertainties in  $a_w$ ,  $k_{g,skin}$ , and  $P_{H_2O}$  produced absolute uncertainties of less than  $\pm 0.02\%$  in predicted fruit weight losses.

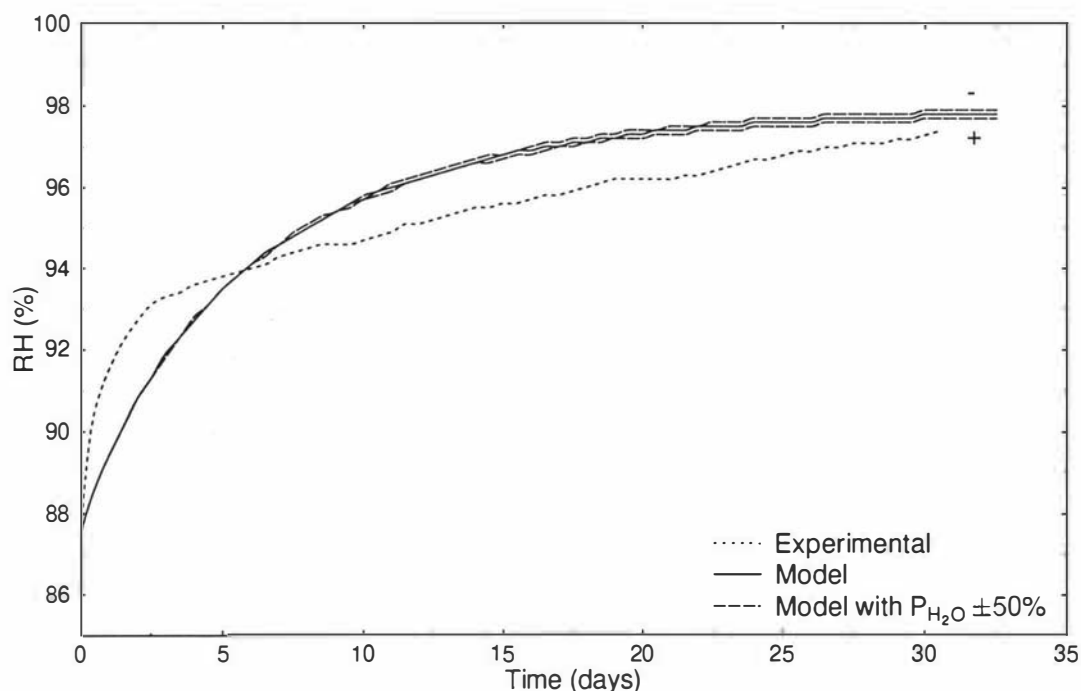
Again, uncertainty regarding the true form of the moisture sorption isotherm may have had a significant effect on weight-loss predictions, especially where periods of changing package RH were long in comparison with the total duration of storage (e.g. trial BB93-A). In some cases, the differences between predicted and measured weight losses in Table 9.5 may be due in part to fruit weights having been recorded 1 or 2 days before the start of a trial, or 1 or 2 days after the sampling of package atmospheres had



**Figure 9.56** Sensitivity analysis on  $a_w$  for 1993 ‘Braeburn’ carton (count 125 fruit, 40  $\mu\text{m}$  film, folded, trial BB93-A).



**Figure 9.57** Sensitivity analysis on  $k_{g,skin}$  for 1993 ‘Braeburn’ carton (count 125 fruit, 40  $\mu\text{m}$  film, folded, trial BB93-A).



**Figure 9.58** Sensitivity analysis on  $P_{H_2O}$  for 1993 'Braeburn' carton (count 125 fruit, 40  $\mu\text{m}$  film, folded, trial BB93-A).

finished. These delays, especially at the end of trials finishing at 20°C, may have contributed to the higher-than-predicted measured weight losses. In addition, the MAP model considers only weight loss due to evaporation (moisture loss) and respiration (carbon loss). The model does not take into account any weight loss due to the production of volatiles (e.g. ethylene). This may also have contributed to differences between measured and predicted weight losses, although a comparison of  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  production rates given by Kader (1992a) suggests that the rate of carbon loss through ethylene production would be at least one order of magnitude lower than the rate of carbon loss through respiration.

## 9.3 DISCUSSION

### 9.3.1 OVERVIEW OF MODEL PERFORMANCE

In general, model predictions agreed reasonably well with the test data collected from the MA trials. For cartons with heat-sealed liners, steady-state package atmospheres were predicted, on average, within 1.0 mol % for  $\text{O}_2$  and 0.4 mol % for  $\text{CO}_2$ . Rates of change in package (or fruit internal)  $\text{O}_2$  and  $\text{CO}_2$  concentrations were generally well predicted. However, some significant deviations between predicted and experimental data were also observed.

Average steady-state deviations between predicted and experimental package atmospheres were larger than would be expected from the estimated uncertainties in

measured package  $O_2$  and  $CO_2$  concentrations (average experimental uncertainties for measured package  $O_2$  and  $CO_2$  concentrations were  $\pm 0.3$  mol % and  $\pm 0.1$  mol % respectively). Also, package  $CO_2$  concentrations were consistently underpredicted. Sensitivity analysis showed that these differences could be largely explained by estimated uncertainties in the respiration and film permeability data used in the model.

Where model simulations required the respiration rate models to be extrapolated significantly beyond the ranges of  $O_2$  and  $CO_2$  for which they were fitted, model predictions agreed less well with experimental data. The limitations of the  $O_2$ -based and  $CO_2$ -based respiration models derived in this work have been discussed in section 8.1.4. Fitting a respiration model with combined  $O_2$  and  $CO_2$  effects to the available respiration data achieved only limited success in improving model predictions under highly modified package atmospheres. However, there is some evidence to support a combined  $O_2$  and  $CO_2$  respiration model. Comparisons between model predictions and experimental data under highly modified atmospheres also suggest that the value of the Michaelis-Menten half-saturation constant for  $O_2$  ( $k_m$ ) may be significantly lower than the values estimated in this work as well as some of the values reported in the literature (e.g. Dadzie *et al.*, 1996).

The MAP model tended to predict faster rates of change in package  $CO_2$  concentrations than those observed experimentally, especially at low storage temperatures. This was not observed for  $O_2$ , which suggests that  $CO_2$  solubility in the fruit cell sap may be a significant effect that is not presently accounted for in the MAP model formulation. Artificial simulation of  $CO_2$  solution in the fruit cell sap (by selectively increasing the internal atmosphere volume of the fruit for  $CO_2$ ) significantly improved the predicted rates of change in package  $CO_2$  concentrations. Although solution of  $CO_2$  in the fruit cell sap affects the prediction of transient  $CO_2$  concentrations, the solubility effect has no influence on predicted steady-state concentrations. Furthermore, periods of transient conditions during apple storage are expected to be relatively short-lived compared to the total duration of the storage period. The current omission of  $CO_2$  solubility from the MAP model formulation is therefore not seen as a major model weakness.

The MAP model consistently underpredicted the total weight losses recorded during the MA trials. Discrepancies between the predicted and measured weight losses could not be explained by the estimated uncertainties in fruit water activity, fruit skin permeance to water vapour, or film permeability to water vapour. However, uncertainty regarding the true form of the moisture sorption isotherm for the moulded-pulp fruit trays may have had a significant influence on predicted changes in package relative humidity and, through this, on predictions of fruit weight loss. It is also possible that delays of several days between weighing the fruit and starting or finishing a trial could have had larger-than-expected effects on measured weight losses, thereby contributing to the differences between predicted and measured values. Predicted and measured weight losses were both small in comparison to the 1 to 4% weight losses reported by Frampton & Ahlborn (1994b) and Frampton *et al.* (1994b) for a number of New Zealand apple cultivars (including 'Royal Gala', 'Braeburn', and 'Granny Smith') stored for 5 to 14 weeks without carton liners.

Application of the MAP model to perforated packages requires the estimation of an empirical correction factor ( $\xi$ ) for the diffusivity of gases through the perforations. This correction factor accounts for the fact that a proportion of the total resistance to gas diffusion through a perforation may actually lie outside the perforation itself (the MAP model assumes that gas concentrations directly outside the perforation are equal to the bulk gas concentrations in the package or external atmospheres, and hence that an airspace of the same thickness as the film represents the total resistance to gas diffusion). The smaller the value of  $\xi$ , the greater the proportion of the total resistance to gas diffusion that lies outside the perforation. In the current work, values of  $\xi$  were estimated by trial and error. The resulting estimates of  $\xi$  ranged from 0.01 to 1, tending to decrease as the ratio of hole diameter to film thickness increased.

For the MAP model to find future application to predicting the gas concentrations formed inside perforated packages, it will first be necessary to find a means of predicting values of  $\xi$  as a function of hole diameter, film thickness, and other possible influential factors such as temperature or the number of perforations per unit area of film. Emond *et al.* (1991) measured the effective permeabilities of holes of various sizes drilled into the covers of rigid plastic boxes. They produced correlations to predict the effective permeability of a perforation as a function of perforation diameter, perforation thickness, and temperature. Analysis of the effective permeabilities reported by Emond *et al.* (1991) produced estimates of  $\xi$  ranging from 0.2 to 3.2. These values of  $\xi$  decreased as the ratio of hole diameter to film thickness increased, a trend consistent with that reported for the current work. Values of  $\xi$  estimated from the data of Emond *et al.* (1991) also increased with increasing temperature and were 20 to 50% higher for CO<sub>2</sub> than for O<sub>2</sub> (in contrast, the MAP model assumes the value of  $\xi$  to be independent of temperature and gas species). Values of  $\xi$  higher than 1 may indicate a significant flow effect in the experiments of Emond *et al.* (1991). In the MAP model, bulk flow through perforations is modelled separately from diffusion. In theory therefore, values of  $\xi$  for the MAP model should not exceed 1.

Theoretically, a similar modelling approach to that used for gas transfer through perforations could also be applied to the modelling of gas transfer through a folded closure. However, if the variability between atmospheres within folded liners is indeed as great as that observed in the current work, such an approach seems unlikely to prove practical. The value of the MAP model for folded liners lies in predicting the maximum expected extent of atmosphere modification.

Overall, the MAP model developed in this work is significantly more advanced than the various MAP models reviewed in Chapter 2. The model is capable of predicting package and fruit internal O<sub>2</sub> and CO<sub>2</sub> concentrations as a function of storage time and as a function of varying storage conditions (temperature, humidity, and external O<sub>2</sub> and CO<sub>2</sub> concentrations). Model predictions of package O<sub>2</sub> and CO<sub>2</sub> concentrations have been validated for commercial, film-lined cartons of apples under storage conditions simulating those likely to be experienced by apples during packing and storage in New Zealand, and during shipment to overseas markets. The model also predicts fruit weight losses and the formation of condensed moisture within packages. Although these aspects of the model are at present only partially validated, the model appears to predict the observed trends well. The modelling of fruit quality attributes has not been

specifically addressed in the current work. However, the model incorporates a measure of the cumulative oxygen consumption of the fruit. In effect, this measure represents a time-temperature-atmosphere indicator for the fruit. In the future, it may prove possible to relate cumulative oxygen consumption to changes in fruit quality attributes during storage, or to incorporate an entirely different fruit quality indicator into the model.

A number of new reports of MAP models have appeared in the literature relatively recently. (These reports were not incorporated into the literature review in Chapter 2, having appeared too recently to influence the direction of the current work.) Some of these reports deal with new applications or minor adaptations of the various models reviewed in Chapter 2 (Fishman *et al.*, 1995; Talasila *et al.*, 1995a; Lee *et al.*, 1996b). However, two models recently published by Talasila & Cameron (1995) and Talasila *et al.* (1995b) represent substantially new approaches.

Talasila & Cameron (1995) combined a steady-state balance for package  $O_2$  with probability density functions for film permeability and product respiration rate to predict the frequency distribution of steady-state  $O_2$  partial pressures inside film packages. Talasila *et al.* (1994) tested the model against experimental data collected for packages of broccoli. For this purpose, they simplified the model by assuming no variation in film permeability to  $O_2$ . Predicted frequency distributions for  $O_2$  partial pressure compared well with the distributions measured for experimental packages.

The model of Talasila & Cameron (1995) can be used to estimate the package  $O_2$  partial pressure that MA packages should be designed for to ensure that a given proportion of packages will develop  $O_2$  partial pressures above a set minimum. A stochastic modelling approach such as this could prove particularly useful for predicting the variability of atmospheres formed inside imperfectly sealed packages (e.g. packages closed by folding or packages with damaged films).

Talasila *et al.* (1995b) developed a dynamic model to predict the atmospheres formed inside rigid packages of strawberries stored under varying temperature conditions. This model appears to have been the first published MAP model to consider heat and mass transfer simultaneously. The heat transfer model developed by Talasila *et al.* (1995b) is of considerably greater complexity than the heat transfer models developed in the current work. Talasila *et al.* applied a finite difference method to modelling temperature gradients within individual strawberries (assumed to be spherical) and across the walls of the package. The temperature of the package atmosphere was assumed to be uniform throughout the package, and product heat-transfer was assumed to be independent of position within the package. Talasila *et al.* tested their model against data collected from experimental packages containing 350 or 800 g of fruit. In these experimental packages, strawberries were laid out evenly on thin plastic trays to form two or three layers of fruit per package. There was no contact between layers nor between individual fruit within layers. The model validation results were variable, with the model tending to underpredict package  $O_2$  concentrations.

The analysis presented in section 6.1.4 of the current work suggests, at least for cartons of apples, that temperature gradients throughout a package are likely to be more

significant than temperature gradients within individual fruit. For an apple carton, the thermal mass of the packaging materials is small compared to the total mass of fruit in the package; the thermal resistance of the packaging materials is therefore likely to be of greater importance than the thermal capacity of these materials. Furthermore, the heat transfer processes occurring within commercial MA packages such as apple cartons are likely to be significantly more complex than the heat transfer processes occurring within the rather idealized experimental packages of Talasila *et al.* (1995b). The simplicity of the heat transfer models developed in the current work is considered justified from the point of view of avoiding large increases in model complexity for what are likely to be only small gains in model accuracy.

### 9.3.2 RECOMMENDATIONS FOR MODEL APPLICATION

The MAP model developed in this work is recommended for use as a research and design tool. Possible applications are listed as follows:

- (a) *Preliminary design of MA packaging systems for horticultural produce.* Although this work has concentrated on the development of a model for the MA storage of apples, the model is general enough to be applied to many other fruits or vegetables for which the basic assumptions of the model hold, and for which the required model input data are available. The model can be used for the preliminary evaluation of proposed package designs, or to estimate the fruit weight, film area, film thickness, or film permeability required to achieve a desired storage atmosphere. Given information on the variability of factors such as respiration rate and film permeability, the model can be used to examine the effects of this variability on transient and steady-state package atmospheres.
- (b) *Evaluation of different storage regimes.* The model can be used to evaluate the responses of package conditions to changes in storage conditions. For example, the model could be used to determine the maximum temperature at which a given package can be stored without risk of harmful package atmospheres developing, or to determine the maximum time for which a package can be exposed to a given temperature before the risk of harmful package atmospheres developing becomes unacceptable.
- (c) *Planning and evaluation of future research.* The model can be used as a tool for designing future trials under MA conditions. It can also be used as a vehicle for testing the outcomes of future research, such as newly developed respiration models or new fruit quality models.

### 9.3.3 RECOMMENDATIONS FOR FURTHER WORK

There is scope for further research work that could improve the accuracy and widen the applicability of the MAP model developed in this work. Possible directions for further investigation are listed as follows:

- (a) *Development of accurate models for fruit respiration.* The analyses presented in sections 9.1 and 9.2 suggest that a better understanding of fruit respiratory behaviour under modified atmospheres could lead to significant improvements in the accuracy of model predictions, especially for packages that develop very low  $O_2$  or high  $CO_2$  atmospheres. The development of realistic respiration models will require the analysis of respiration rate data collected over a wide range of independently varied  $O_2$  and  $CO_2$  concentrations. This will allow the effects of  $O_2$  and  $CO_2$  to be clearly separated. It is also important that respiration rate data be collected for a range of fruit temperatures; as well as having a purely thermal effect on enzyme activity, temperature may further affect respiratory behaviour through changes in the solubilities of  $O_2$  and  $CO_2$  in the fruit cell sap.
- (b) *Comparison of methods for measuring film permeability.* The sensitivity analysis presented in section 9.2 indicates that accurate permeability data and accurate respiration rate data are of equal importance in producing accurate model predictions. However, the permeability data presented in section 8.2.2.1 suggest that different methods for measuring film permeabilities may produce significantly different results. Christie *et al.* (1995) has also reported significant differences between permeability values estimated by different methods. The reasons for these differences have not yet been satisfactorily resolved. Further investigation is therefore required to determine possible reasons for any real differences between permeability values obtained by different experimental methods, and to determine which methods give the most representative estimates for application to MAP systems.
- (c) *Collation of data for the design of MAP systems.* The compilation of a database containing model input parameters for a wide range of produce and packaging materials will facilitate the application of the model as a tool for designing MAP systems. The model input data presented in Chapter 8 form the foundations for such a database; however, the database will need to be extended and updated as the results of new research become available.
- (d) *Modelling the solution of  $CO_2$  in the fruit cell sap.* Incorporating  $CO_2$  solubility into the MAP model formulation is likely to improve the prediction of transient  $CO_2$  concentrations within packages. Although the omission of this effect in the current model is not seen as major model weakness, the effect should be relatively straightforward to incorporate into future updated versions of the model.
- (e) *Further development of the model for gas diffusion through perforations.* Methods for estimating values of the empirical correction factor for gas diffusion through perforations ( $\xi$ ) will need to be developed if the MAP model is to be applied to modelling the atmospheres formed within perforated-film packages.
- (f) *Investigation of the moisture sorption characteristics of paper-based packaging materials.* A better understanding of the moisture sorption characteristics of

paper-based packaging materials such as moulded-pulp fruit trays, particularly under the high relative humidities typical of modified atmosphere packages, may lead to significantly improved predictions of fruit weight loss.

- (g) *Development of models for fruit quality.* As discussed in Chapters 2 and 3, an ideal MAP model would be capable of predicting the effect of MA storage conditions on changes in key fruit quality attributes. One possible avenue for further investigation is the correlation of changes in fruit quality attributes with a measure such as cumulative respiratory O<sub>2</sub> consumption. The development of more mechanistic quality models will require a better understanding of the mechanisms by which fruit storage conditions affect the rates of change of various fruit quality attributes.

At present, the accuracy of the MAP model appears to be limited mainly by input data uncertainties (particularly respiration rates and film permeabilities) rather than by shortcomings in the model itself. It is therefore recommended that future work be aimed at resolving the worst of these uncertainties before a significant amount of effort is directed towards further model development.

## Chapter 10

### CONCLUSIONS

Storage trials with film-lined cartons of 'Braeburn', 'Royal Gala', and 'Granny Smith' apples during the 1993 and 1994 apple seasons have provided important insights into the effects of package characteristics and storage conditions on the dynamics of modified atmosphere development within such packages.

Package O<sub>2</sub> and CO<sub>2</sub> concentrations measured during the trials showed excellent reproducibility between replicate cartons having undamaged, heat-sealed liners. However, the current industry practice of closing liners by folding produced a greater carton-to-carton variability than that observed for heat-sealed liners, especially for thicker packaging films.

Holes of 8 mm diameter made in the liners of two cartons during storage resulted in the loss of virtually all atmosphere modification; microscopic pin-holes in the liners of other cartons resulted in only relatively small increases in package O<sub>2</sub> concentrations and had no observable effect on package CO<sub>2</sub> concentrations. As mechanical damage inflicted during the handling of cartons is likely to be macroscopic rather than microscopic, the potential for such damage to occur needs to be carefully assessed when considering the feasibility of carton liners for modified atmosphere storage. A high risk of film damage could quickly erode any potential fruit quality benefits imparted by the liners.

Packing of warm fruit resulted in much faster rates of atmosphere development than the packing of pre-cooled fruit, but did not lead to the development of unduly low O<sub>2</sub> or high CO<sub>2</sub> concentrations. This was true even when packaged fruit were held at 20°C for up to 12 hours before being transferred to cool storage, or when cartons of fruit were insulated to significantly slow their cooling rates. Cooling rates for packaged fruit are likely to be slower than cooling rates for unpackaged fruit, as carton liners effectively prevent any ventilation through the cartons. The detrimental effects of slower cooling may outweigh any benefits of more rapid modified atmosphere development.

Removal of lined cartons from cool storage conditions to 20°C for periods of 12 hours or longer (simulating periods of removal from cool storage during transport and distribution) produced marked disturbances in package O<sub>2</sub> and CO<sub>2</sub> concentrations. For short-term exposures to 20°C (less than 24 hours), decreases in package O<sub>2</sub> concentrations and corresponding increases in package CO<sub>2</sub> concentrations were relatively short-lived and not extreme. However, exposures to 20°C of 3 days or longer did lead to extreme changes in O<sub>2</sub> and CO<sub>2</sub> concentrations, with package O<sub>2</sub> concentrations falling below 5 mol % and package CO<sub>2</sub> concentrations rising above 5 mol % inside cartons with 40 µm liners. Such package atmosphere compositions, when combined with high fruit temperatures, represent a very real risk of anaerobic conditions or harmful CO<sub>2</sub> levels forming within the fruit. Folding rather than heat-sealing of liners did not reduce this risk. Good management of the refrigerated chain during the transport and distribution of fruit stored under MA is essential if such risks are to be minimized.

A modified atmosphere packaging (MAP) model was developed that should facilitate the future design and optimization of horticultural MAP systems. The model is comprehensive, building on earlier MAP models developed by other workers in the field. It considers fruit respiration as a function of fruit temperature and fruit internal  $O_2$  and  $CO_2$  concentrations;  $O_2$  and  $CO_2$  exchange between the fruit internal atmosphere and the package atmosphere; and  $O_2$ ,  $CO_2$ ,  $N_2$ , and water vapour exchange between the package atmosphere and the external atmosphere. The model also considers water vapour transport within the package, including moisture loss from the fruit, condensation on the fruit and packaging-film surfaces, and moisture sorption by paper-based packaging materials. The model assumes uniform gas concentrations and temperature throughout the fruit, and uniform gas concentrations and temperature throughout the package atmosphere. The model is dynamic and can be applied to sealed, perforated, rigid, or flexible-film packages under constant- or variable-temperature storage regimes.

The MAP model was implemented in a computer program to provide a tool for designing and optimizing modified atmosphere packages. The program has a user interface for data input, and produces tables of predicted values in two output files. The results tables list predicted values of fruit temperature, fruit internal  $O_2$  and  $CO_2$  concentrations, fruit cumulative  $O_2$  consumption, fruit weight loss, mass of condensed moisture on the fruit and packaging film surfaces, package air temperature, package  $O_2$  and  $CO_2$  concentrations, package relative humidity, package atmosphere volume and pressure, and moisture content of paper-based packaging materials within the package.

A full set of model input data corresponding to the MA storage trials conducted during this study was compiled. This data set could be expanded in the future to develop a database of package design data covering a wide range of fruit varieties and packaging materials. Such a resource would be an invaluable aid to future application of the MAP model.

The MAP model was tested by comparing predicted fruit and package  $O_2$  and  $CO_2$  concentrations, fruit weight losses, package relative humidities, and fruit cooling rates with experimental data collected during the MA storage trials. These comparisons showed that the model was capable of closely predicting the observed trends. However, lack of fit of model predictions to experimental data was apparent in some areas. In particular, the model tended to under-predict  $CO_2$  concentrations, and performed less well under conditions of extremely modified fruit internal atmospheres.

Sensitivity analyses performed on the model showed that the observed lack of fit could largely be explained by estimated uncertainties in the current respiration and permeability data. Uncertainties in the respiration data arose mainly from (a) the limited ranges of  $O_2$  and  $CO_2$  concentrations for which measured data were available and the necessity of extrapolating these data in some cases to conditions that fell well outside the experimental ranges, and (b) a lack of conclusive evidence confirming the exact nature of the response of fruit respiration rates to varying  $O_2$  and  $CO_2$  concentrations over a range of temperatures. Uncertainties in the permeability data arose from the significant variability of permeability measurements collected from various sources and by various experimental methods. The causes of this variability have not yet been satisfactorily resolved.

Differences between measured and predicted CO<sub>2</sub> transients suggest that accumulation of CO<sub>2</sub> in the fruit cell sap may significantly affect the rates of change of fruit and package CO<sub>2</sub> concentrations. Solution of CO<sub>2</sub> in the cell sap has no effect on predicted steady-state concentrations, and transient periods are expected to be relatively short-lived compared to the total duration of storage. The current omission of CO<sub>2</sub> solubility from the model formulation is therefore not seen as a major model weakness.

For the carton trials presented in this work, the MAP model was capable of predicting steady-state package O<sub>2</sub> and CO<sub>2</sub> concentrations within 1.0 mol % and 0.4 mol %, respectively, of observed experimental values. This level of accuracy is sufficient for the model to be usefully applied to problems of package design. Possible applications include the preliminary design of packages for new cultivars, new films, or new carton specifications (e.g. carton dimensions and fruit weight), and the specification of cool-chain temperature-time regimes to minimize the risk of harmful atmospheres forming within MA packages during storage and transport. The model should also prove a useful research tool for the planning of future MA trials and for the evaluation of new component models (e.g. for respiration).

At present, the accuracy of the MAP model appears to be limited mainly by input data uncertainties rather than by shortcomings in the model itself. It is recommended that future work be aimed at resolving the worst of these uncertainties before a significant amount of effort is directed towards further model development. Future investigations could include work in the following areas:

- (1) the development of new fruit respiration models based on a better mechanistic understanding of respiratory responses to changing O<sub>2</sub> and CO<sub>2</sub> concentrations;
- (2) a systematic comparison of different methods for measuring the gas permeabilities of highly permeable films typical of MAP applications;
- (3) further investigation of the transport of gases through holes in the packaging film;
- (4) incorporation of CO<sub>2</sub> solution effects into the model formulation;
- (5) the development of models for predicting changes in key fruit-quality attributes as functions of MA storage conditions.

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## Appendix A

### MAPSIM PROGRAM FILES

The MAPSIM program files are given on the diskette at the back of this thesis. The seven program files are

|             |                                                    |
|-------------|----------------------------------------------------|
| MAPSIM.EXE  | Executable program file                            |
| MAPSIM.PAS  | Source code for the main program                   |
| GLOBAL.PAS  | Source code for the unit GLOBAL (section 7.2.1.1)  |
| PACKAGE.PAS | Source code for the unit PACKAGE (section 7.2.1.2) |
| STORE.PAS   | Source code for the unit STORE (section 7.2.1.2)   |
| DATAIN.PAS  | Source code for the unit DATAIN (section 7.2.1.3)  |
| SOLVER.PAS  | Source code for the unit SOLVER (section 7.2.1.4)  |

The following list gives the definitions of the main variable names used in the program source code. Where appropriate, the corresponding nomenclature from Chapter 6 has also been given.

#### *Constants of the unit GLOBAL*

|                   |                                                                                                          |
|-------------------|----------------------------------------------------------------------------------------------------------|
| AtmPress          | atmospheric pressure ( $P_{\text{atm}}$ , Pa)                                                            |
| DryAirSpecHtCap   | specific heat capacity of dry air ( $c_{pa}$ , $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )         |
| DryTraySpecHtCap  | specific heat capacity of dry fruit trays ( $c_{pt}$ , $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ) |
| GasConst          | gas constant ( $R$ , $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )                                  |
| WaterLatHtVap     | latent heat of vaporization of water ( $h_{fg}$ , $\text{J}\cdot\text{kg}^{-1}$ )                        |
| WaterSpecHtCap    | specific heat capacity of water ( $c_{pw}$ , $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )           |
| WaterVapSpecHtCap | specific heat capacity of water vapour ( $c_{pv}$ , $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )    |

#### *Variables of type TApple*

|                  |                                                                                                                                                                  |
|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| AreaCoeff        | parameter $a$ of fruit surface area-volume correlation                                                                                                           |
| AreaExp          | parameter $b$ of fruit surface area-volume correlation                                                                                                           |
| CO2_MTC          | overall mass transfer coefficient for $\text{CO}_2$ exchange through the fruit skin ( $k_{\text{CO}_2}\cdot A_{\text{fruit}}$ , $\text{m}^3\cdot\text{s}^{-1}$ ) |
| CO2SkinPerm      | fruit skin permeance to $\text{CO}_2$ ( $k_{\text{CO}_2}$ , $\text{m}\cdot\text{s}^{-1}$ )                                                                       |
| CondMass         | mass of condensate on the fruit surface ( $M_{\text{cond}, f}$ , kg)                                                                                             |
| CoolingRateConst | cooling rate constant for half-cooling-time model ( $\alpha$ , $\text{s}^{-1}$ )                                                                                 |
| CumO2Consump     | fruit cumulative $\text{O}_2$ consumption ( $Q$ , $\text{kg O}_2\cdot\text{kg}^{-1}$ )                                                                           |
| Density          | fruit flesh density ( $\rho_f$ , $\text{kg}\cdot\text{m}^{-3}$ )                                                                                                 |
| FruitArea        | total fruit surface area ( $A_{\text{fruit}}$ , $\text{m}^2$ )                                                                                                   |
| FruitCO2         | fruit internal $\text{CO}_2$ concentration ( $C_{\text{CO}_2, f}$ , $\text{kg CO}_2\cdot\text{m}^{-3}$ )                                                         |
| FruitMass        | total fruit mass ( $M_f$ , kg)                                                                                                                                   |
| FruitNo          | number of fruit in the package ( $N$ )                                                                                                                           |
| FruitO2          | fruit internal $\text{O}_2$ concentration ( $C_{\text{O}_2, f}$ , $\text{kg O}_2\cdot\text{m}^{-3}$ )                                                            |
| FruitTemp        | fruit temperature ( $\theta_f$ , $^{\circ}\text{C}$ )                                                                                                            |

|                   |                                                                                                                                                            |
|-------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| FruitVol          | total fruit volume ( $\text{m}^3$ )                                                                                                                        |
| FruitWaterAct     | fruit water activity ( $a_w$ )                                                                                                                             |
| H2O_MTC           | overall mass transfer coefficient for evaporation of moisture from the fruit surface ( $k_{g, skin} \cdot A_{fruit}$ , $\text{m} \cdot \text{s}$ )         |
| H2OSkinPerm       | fruit skin permeance to water vapour ( $k_{g, skin}$ , $\text{s} \cdot \text{m}^{-1}$ )                                                                    |
| HalfCoolingTime   | fruit half-cooling time ( $t_{0.5}$ , s)                                                                                                                   |
| HTModel           | heat transfer model (H = half-cooling time model, F = sequential model)                                                                                    |
| InitDensity       | initial fruit flesh density ( $\rho_{f, initial}$ , $\text{kg} \cdot \text{m}^{-3}$ )                                                                      |
| InitFruitCO2      | initial fruit internal $\text{CO}_2$ concentration (mol %)                                                                                                 |
| InitFruitMass     | initial fruit mass ( $M_{f, initial}$ , kg)                                                                                                                |
| InitFruitO2       | initial fruit internal $\text{O}_2$ concentration (mol %)                                                                                                  |
| InitFruitTemp     | initial fruit temperature ( $^{\circ}\text{C}$ )                                                                                                           |
| kic               | competitive inhibition constant ( $k_{ic}$ , $\text{kg CO}_2 \cdot \text{m}^{-3}$ ) (same as Refkic in this version of the program)                        |
| kiu               | uncompetitive inhibition constant ( $k_{iu}$ , $\text{kg CO}_2 \cdot \text{m}^{-3}$ ) (same as Refkiu in this version of the program)                      |
| km                | half saturation constant at reference temperature ( $k_m$ , $\text{kg O}_2 \cdot \text{m}^{-3}$ )                                                          |
| MaxRespRate       | maximum respiration rate at fruit temperature ( $v_{max}$ , $\text{kg O}_2 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ )                                     |
| NodeArea          | individual fruit surface area ( $A_n$ , $\text{m}^2$ )                                                                                                     |
| NodeCumO2         | fruit cumulative $\text{O}_2$ consumption ( $Q$ , $\text{kg O}_2 \cdot \text{kg}^{-1}$ ) (same as CumO2Consump in this version of the program)             |
| NodeVol           | individual fruit volume ( $V_n$ , $\text{m}^3$ )                                                                                                           |
| O2_MTC            | overall mass transfer coefficient for $\text{O}_2$ exchange through the fruit skin ( $k_{\text{O}_2} \cdot A_{fruit}$ , $\text{m}^3 \cdot \text{s}^{-1}$ ) |
| O2SkinPerm        | fruit skin permeance to $\text{O}_2$ ( $k_{\text{O}_2}$ , $\text{m} \cdot \text{s}^{-1}$ )                                                                 |
| Porosity          | fruit flesh porosity ( $\epsilon$ , $\text{m}^3 \cdot \text{m}^{-3}$ )                                                                                     |
| Q10               | temperature coefficient of respiration ( $Q_{10}$ )                                                                                                        |
| Refkic            | competitive inhibition constant at reference temperature ( $k_{ic}$ , $\text{kg CO}_2 \cdot \text{m}^{-3}$ )                                               |
| Refkiu            | uncompetitive inhibition constant at reference temperature ( $k_{iu}$ , $\text{kg CO}_2 \cdot \text{m}^{-3}$ )                                             |
| Refkm             | half saturation constant at reference temperature ( $k_m$ , $\text{kg O}_2 \cdot \text{m}^{-3}$ )                                                          |
| RefMaxRespRate    | maximum respiration rate at reference temperature ( $v_{max, ref}$ , $\text{kg O}_2 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ )                            |
| RefTemp           | reference temperature for respiration rates ( $\theta_{ref}$ , $^{\circ}\text{C}$ )                                                                        |
| RespHeatGen       | respiratory heat generation per unit mass of $\text{O}_2$ consumption ( $W$ , $\text{J} \cdot \text{kg}^{-1}$ )                                            |
| RespModel         | respiration model (N = no $\text{CO}_2$ inhibition, U = uncompetitive $\text{CO}_2$ inhibition, M = mixed $\text{CO}_2$ inhibition)                        |
| RespQuotient      | mass-based respiratory quotient ( $RQ_m$ , $\text{kg} \cdot \text{kg}^{-1}$ )                                                                              |
| RespRate          | respiration rate ( $v$ , $\text{kg O}_2 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ )                                                                        |
| SatWaterVapPress  | saturated vapour pressure of water at the fruit surface temperature ( $p_{sat, fs}$ , Pa)                                                                  |
| SpecHeatCapacity  | specific heat capacity of the fruit flesh ( $c_{pf}$ , $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ )                                               |
| SurfWaterVapPress | partial pressure of water vapour beneath the fruit skin ( $p_{w, fs}$ , Pa)                                                                                |
| TotEnergy         | Fruit total enthalpy ( $M_n \cdot \eta$ , J)                                                                                                               |

WeightLoss                      total fruit weight loss (%)

*Variables of type TPackAtm*

|                     |                                                                                                                                                         |
|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| DiffusivityCorrFac  | empirical correction factor for gas diffusion through holes ( $\xi$ )                                                                                   |
| DryAirMass          | mass of dry air in the package atmosphere ( $M_p$ , kg)                                                                                                 |
| FruitHTC            | convective heat transfer coefficient at the fruit surface<br>( $h_p$ , $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ )                                 |
| FruitMTC            | mass transfer coefficient for moisture condensation at the fruit surface ( $k_{g, \text{fruit}}$ , $\text{s}\cdot\text{m}^{-1}$ )                       |
| InitPackAirEnthalpy | initial enthalpy of the package air (dry air basis) ( $\text{J}\cdot\text{kg}^{-1}$ )                                                                   |
| InitPackAirVol      | initial volume of the package atmosphere ( $\text{m}^3$ )                                                                                               |
| InitPackCO2         | initial package $\text{CO}_2$ concentration (dry air basis) (mol %)                                                                                     |
| InitPackO2          | initial package $\text{O}_2$ concentration (dry air basis) (mol %)                                                                                      |
| InitPackRH          | initial package relative humidity (%)                                                                                                                   |
| InitPackTemp        | initial temperature of the package atmosphere ( $^{\circ}\text{C}$ )                                                                                    |
| IntHTC              | convective heat transfer coefficient at the internal packaging-film surface ( $h_p$ , $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ )                  |
| IntMTC              | mass transfer coefficient for moisture condensation at the inside surface of the packaging film ( $k_{g, \text{film}}$ , $\text{s}\cdot\text{m}^{-1}$ ) |
| MassCO2             | mass of $\text{CO}_2$ in the package atmosphere ( $M_{\text{CO}_2, p}$ , kg)                                                                            |
| MassConcCO2         | mass concentration of $\text{CO}_2$ in the package atmosphere<br>( $C_{\text{CO}_2, p}$ , $\text{kg CO}_2\cdot\text{m}^{-3}$ )                          |
| MassConcH2O         | mass concentration of water vapour in the package atmosphere<br>( $C_{\text{H}_2\text{O}, p}$ , $\text{kg H}_2\text{O}\cdot\text{m}^{-3}$ )             |
| MassConcN2          | mass concentration of $\text{N}_2$ in the package atmosphere<br>( $C_{\text{N}_2, p}$ , $\text{kg N}_2\cdot\text{m}^{-3}$ )                             |
| MassConcO2          | mass concentration of $\text{O}_2$ in the package atmosphere<br>( $C_{\text{O}_2, p}$ , $\text{kg O}_2\cdot\text{m}^{-3}$ )                             |
| MassH2O             | mass of water vapour in the package atmosphere ( $M_{\text{H}_2\text{O}, p}$ , kg)                                                                      |
| MassN2              | mass of $\text{N}_2$ in the package atmosphere ( $M_{\text{N}_2, p}$ , kg)                                                                              |
| MassO2              | mass of $\text{O}_2$ in the package atmosphere ( $M_{\text{O}_2, p}$ , kg)                                                                              |
| MinPackAirVol       | minimum volume to which the package atmosphere can shrink<br>( $V_{p, \text{min}}$ , $\text{m}^3$ )                                                     |
| PackAbsHumidity     | absolute humidity of the package atmosphere ( $H_p$ , $\text{kg}\cdot\text{kg}^{-1}$ )                                                                  |
| PackAirTemp         | temperature of the package atmosphere ( $\theta_p$ , $^{\circ}\text{C}$ )                                                                               |
| PackAirVol          | volume of the package atmosphere ( $V_p$ , $\text{m}^3$ )                                                                                               |
| PackPressure        | package atmosphere pressure ( $P_p$ , Pa)                                                                                                               |
| PackRH              | relative humidity of the package atmosphere ( $RH_p$ , %)                                                                                               |
| PackTotMoles        | total number of moles of gas in the package atmosphere ( $n_{p, \text{tot}}$ )                                                                          |
| PackWaterVapPress   | partial pressure of water vapour in the package atmosphere<br>( $p_{w, p}$ , Pa)                                                                        |
| SatWaterVapPress    | saturated vapour pressure of water at the temperature of the package atmosphere ( $p_{\text{sat}, p}$ , Pa)                                             |
| Shrinkage           | shrinkage of the package atmosphere volume (%)                                                                                                          |
| TotEnergy           | total enthalpy of the package atmosphere plus fruit trays<br>( $M_p \cdot \eta_p + N_{\text{tray}} \cdot M_{\text{tray}} \cdot \eta_{\text{tray}}$ , J) |

|            |                                                                                                                        |
|------------|------------------------------------------------------------------------------------------------------------------------|
| TrayMTC    | mass transfer coefficient for moisture sorption at the surface of the fruit trays ( $k_{g, tray}$ , $s \cdot m^{-1}$ ) |
| VolCO2     | volume of CO <sub>2</sub> in the package atmosphere ( $V_{CO_2, p}$ , $m^3$ )                                          |
| VolConcCO2 | volume concentration of CO <sub>2</sub> in the package atmosphere ( $[CO_2]_p$ , $m^3 \cdot m^{-3}$ )                  |
| VolConcH2O | volume concentration of water vapour in the package atmosphere ( $[H_2O]_p$ , $m^3 \cdot m^{-3}$ )                     |
| VolConcN2  | volume concentration of N <sub>2</sub> in the package atmosphere ( $[N_2]_p$ , $m^3 \cdot m^{-3}$ )                    |
| VolConcO2  | volume concentration of O <sub>2</sub> in the package atmosphere ( $[O_2]_p$ , $m^3 \cdot m^{-3}$ )                    |
| VolH2O     | volume of water vapour in the package atmosphere ( $V_{H_2O, p}$ , $m^3$ )                                             |
| VolN2      | volume of N <sub>2</sub> in the package atmosphere ( $V_{N_2, p}$ , $m^3$ )                                            |
| VolO2      | volume of O <sub>2</sub> in the package atmosphere ( $V_{O_2, p}$ , $m^3$ )                                            |

### *Variables of type TPackage*

|               |                                                                                                                                                             |
|---------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| ActEnergyCO2  | activation energy for permeation of CO <sub>2</sub> through the packaging film ( $E_{a, CO_2}$ , $J \cdot mol^{-1}$ )                                       |
| ActEnergyH2O  | activation energy for permeation of water vapour through the packaging film ( $E_{a, H_2O}$ , $J \cdot mol^{-1}$ )                                          |
| ActEnergyN2   | activation energy for permeation of N <sub>2</sub> through the packaging film ( $E_{a, N_2}$ , $J \cdot mol^{-1}$ )                                         |
| ActEnergyO2   | activation energy for permeation of O <sub>2</sub> through the packaging film ( $E_{a, O_2}$ , $J \cdot mol^{-1}$ )                                         |
| Beta1         | derived parameter of the GAB model ( $\beta_1$ )                                                                                                            |
| Beta2         | derived parameter of the GAB model ( $\beta_2$ )                                                                                                            |
| Beta3         | derived parameter of the GAB model ( $\beta_3$ )                                                                                                            |
| CO2_MTC       | overall mass transfer coefficient for CO <sub>2</sub> permeation through the packaging film ( $P_{CO_2} \cdot A_{film} \cdot x^{-1}$ , $m^3 \cdot s^{-1}$ ) |
| CO2Perm       | film permeability to CO <sub>2</sub> ( $P_{CO_2}$ , $m^2 \cdot s^{-1}$ )                                                                                    |
| CondMass      | mass of condensate on the inside surface of the packaging film ( $M_{cond, p}$ , kg)                                                                        |
| FilmArea      | total surface area for gas permeation through the packaging film ( $A_{film}$ , $m^2$ )                                                                     |
| FilmTemp      | temperature of the packaging film ( $\theta_{film}$ , °C)                                                                                                   |
| FilmThickness | packaging film thickness ( $x$ , m)                                                                                                                         |
| GAB_C         | parameter of the GAB isotherm model ( $C$ )                                                                                                                 |
| GAB_k         | parameter of the GAB isotherm model ( $K$ )                                                                                                                 |
| GAB_Xm        | parameter of the GAB isotherm model ( $X_m$ , $kg \cdot kg^{-1}$ )                                                                                          |
| H2O_MTC       | overall mass transfer coefficient for permeation of water vapour through the packaging film ( $P_{H_2O} \cdot A_{film} \cdot x^{-1}$ , $m^3 \cdot s^{-1}$ ) |
| H2OPerm       | film permeability to water vapour ( $P_{H_2O}$ , $m^2 \cdot s^{-1}$ )                                                                                       |
| HeatFlow      | heat flow through the packaging materials ( $W$ )                                                                                                           |
| HoleArea      | total area of holes in the packaging film ( $A_{holes}$ , $m^2$ )                                                                                           |
| HoleDiameter  | diameter of holes in the packaging film (m)                                                                                                                 |
| HoleNo        | number of holes in the packaging film                                                                                                                       |

|                  |                                                                                                                                                                                     |
|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| HoleNow          | set to 'true' if the current simulation time is greater than the time at which holes in the packaging film are opened                                                               |
| HolesPresent     | holes present at some time during the simulation<br>(Y = yes, N = no)                                                                                                               |
| HoleTime         | time at which holes in the packaging film are opened ( $t_h$ , s)                                                                                                                   |
| InitTemp         | initial temperature of the packaging materials ( $^{\circ}\text{C}$ )                                                                                                               |
| InitTotVol       | initial total volume of the package ( $\text{m}^3$ )                                                                                                                                |
| InitTrayEnthalpy | initial enthalpy of the fruit trays ( $\text{J}\cdot\text{kg}^{-1}$ )                                                                                                               |
| InitTrayEqRH     | initial equilibrium RH of the fruit trays (%)                                                                                                                                       |
| MinTotVol        | minimum total volume to which the package can shrink ( $\text{m}^3$ )                                                                                                               |
| N2_MTC           | overall mass transfer coefficient for $\text{N}_2$ permeation through the packaging film ( $P_{\text{N}_2} \cdot A_{\text{film}} \cdot x^{-1}$ , $\text{m}^3 \cdot \text{s}^{-1}$ ) |
| N2Perm           | film permeability to $\text{N}_2$ ( $P_{\text{N}_2}$ , $\text{m}^2 \cdot \text{s}^{-1}$ )                                                                                           |
| O2_MTC           | overall mass transfer coefficient for $\text{O}_2$ permeation through the packaging film ( $P_{\text{O}_2} \cdot A_{\text{film}} \cdot x^{-1}$ , $\text{m}^3 \cdot \text{s}^{-1}$ ) |
| O2Perm           | film permeability to $\text{O}_2$ ( $P_{\text{O}_2}$ , $\text{m}^2 \cdot \text{s}^{-1}$ )                                                                                           |
| OverallHTC       | overall heat transfer coefficient for the packaging materials<br>( $U_{\text{pack}}$ , $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ )                                             |
| PackArea         | average heat transfer area of the packaging materials ( $A_{\text{pack}}$ , $\text{m}^2$ )                                                                                          |
| Perforated       | set to 'true' if there are holes present at some time during the simulation                                                                                                         |
| RefCO2Perm       | pre-exponential factor for permeation of $\text{CO}_2$ through the packaging film ( $P_{0, \text{CO}_2}$ , $\text{m}^2 \cdot \text{s}^{-1}$ )                                       |
| RefH2OPerm       | pre-exponential factor for permeation of water vapour through the packaging film ( $P_{0, \text{H}_2\text{O}}$ , $\text{m}^2 \cdot \text{s}^{-1}$ )                                 |
| RefN2Perm        | pre-exponential factor for permeation of $\text{N}_2$ through the packaging film ( $P_{0, \text{N}_2}$ , $\text{m}^2 \cdot \text{s}^{-1}$ )                                         |
| RefO2Perm        | pre-exponential factor for permeation of $\text{O}_2$ through the packaging film ( $P_{0, \text{O}_2}$ , $\text{m}^2 \cdot \text{s}^{-1}$ )                                         |
| TrayArea         | effective tray surface area for moisture sorption ( $A_{\text{tray}}$ , $\text{m}^2 \cdot \text{tray}^{-1}$ )                                                                       |
| TrayDryMass      | dry mass of the fruit trays ( $M_{\text{tray}}$ , $\text{kg}\cdot\text{tray}^{-1}$ )                                                                                                |
| TrayMoistContent | tray moisture content on a dry solids basis ( $X_{\text{tray}}$ , $\text{kg}\cdot\text{kg}^{-1}$ )                                                                                  |
| TrayNo           | number of fruit trays per package ( $N_{\text{tray}}$ )                                                                                                                             |
| TrayTemp         | tray temperature ( $^{\circ}\text{C}$ ) (the same as the package atmosphere temperature in this version of the program)                                                             |
| TrayWaterAct     | tray water activity ( $a_{w, \text{tray}}$ )                                                                                                                                        |
| TrayWaterMass    | mass of water absorbed by the fruit trays ( $M_{w, \text{tray}}$ , $\text{kg}\cdot\text{tray}^{-1}$ )                                                                               |

*Variables of type TStore*

|             |                                                                                                                                             |
|-------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| Index       | marks current position in storage regime                                                                                                    |
| MassConcCO2 | mass concentration of $\text{CO}_2$ in the store atmosphere<br>( $C_{\text{CO}_2, e}$ , $\text{kg CO}_2 \cdot \text{m}^{-3}$ )              |
| MassConcH2O | mass concentration of water vapour in the store atmosphere<br>( $C_{\text{H}_2\text{O}, e}$ , $\text{kg H}_2\text{O} \cdot \text{m}^{-3}$ ) |
| MassConcN2  | mass concentration of $\text{N}_2$ in the store atmosphere<br>( $C_{\text{N}_2, e}$ , $\text{kg N}_2 \cdot \text{m}^{-3}$ )                 |

|                    |                                                                                                                                       |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| MassConcO2         | mass concentration of O <sub>2</sub> in the store atmosphere<br>( $C_{O_2, e}$ , kg O <sub>2</sub> ·m <sup>-3</sup> )                 |
| SatWaterVapPress   | saturated vapour pressure of water at the store air temperature<br>( $p_{sat, e}$ , Pa)                                               |
| StageNo            | number of stages in storage regime                                                                                                    |
| StoreRegime        | array of store temperature, store RH, store O <sub>2</sub> concentration, and store CO <sub>2</sub> concentration versus storage time |
| StoreWaterVapPress | partial pressure of water vapour in the store atmosphere<br>( $p_{w, e}$ , Pa)                                                        |
| VolConcCO2         | volume concentration of CO <sub>2</sub> in the store atmosphere<br>( $[CO_2]_e$ , m <sup>3</sup> ·m <sup>-3</sup> )                   |
| VolConcH2O         | volume concentration of water vapour in the store atmosphere<br>( $[H_2O]_e$ , m <sup>3</sup> ·m <sup>-3</sup> )                      |
| VolConcN2          | volume concentration of N <sub>2</sub> in the store atmosphere<br>( $[N_2]_e$ , m <sup>3</sup> ·m <sup>-3</sup> )                     |
| VolConcO2          | volume concentration of O <sub>2</sub> in the store atmosphere<br>( $[O_2]_e$ , m <sup>3</sup> ·m <sup>-3</sup> )                     |

## *Appendix B*

### **GUIDELINES FOR RUNNING MAPSIM**

This Appendix presents some brief guidelines for running the MAPSIM program.

#### **DATA ENTRY**

The program is started from DOS by typing 'mapsim'. You will then be prompted for a choice of one of three data entry options:

- (1) reading data from an existing data file;
- (2) modifying an existing data file; or
- (3) creating a new data file.

Enter 1, 2, or 3, depending on which method you wish to use. (Note that although input data files can be created or modified in any text-file editor, the spacing of the elements in the data files is critical. Use of the MAPSIM program to create or modify data files is therefore recommended to ensure that the files will be read correctly.)

The next step in the program depends on the choice of data entry option.

#### *Reading Data from an Existing Data File*

Under this option, you need only enter the name of the input file you wish to use (enter the path and filename if the file is in a directory other than that from which you are running MAPSIM).

#### *Modifying an Existing Data File*

As before, the first step is to enter the name of the file you wish to modify.

Input files are divided into four sections:

- (1) the fruit data section;
- (2) the packaging material data section;
- (3) the package atmosphere data section; and
- (4) the store data section.

Data in the file to be modified is reviewed section by section. Before starting on each section, you are asked whether you want to change any of the data in that section. If you do not, press 'N' to skip straight to the next section. Otherwise, press 'Y' to start reviewing the data.

For each data element in a section, the current value is displayed and you are asked whether you wish to change that value (press 'Y' or 'N'). Once you have changed a

value, the new value is displayed and you will be asked whether you wish to change this new value. Press 'N' to move on to the next value. (At present, there is no way of going back once you have confirmed a change; if you enter a value incorrectly and confirm it, you will have to complete or skip through the rest of the data entry procedures, abort the run, and start again.)

The following is a list of the data elements in the input file, given in the order in which they are reviewed.

(A) Fruit data section:

- (1) Reference temperature ( $^{\circ}\text{C}$ ) - this is the reference temperature for the fruit respiration rate calculations. Respiration rates at other temperatures are calculated from the maximum respiration rate corresponding to this reference temperature.
- (2) Maximum respiration rate ( $\text{kg O}_2 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ ) - maximum aerobic respiration rate at the reference temperature.
- (3) Michaelis constant ( $\text{kg O}_2 \cdot \text{m}^{-3}$ ) - the Michaelis-Menten half-saturation constant for  $\text{O}_2$ .
- (4) Type of inhibition (none, uncompetitive, or mixed) - choose a respiration model with either no  $\text{CO}_2$  inhibition, uncompetitive  $\text{CO}_2$  inhibition, or mixed  $\text{CO}_2$  inhibition (enter 'N', 'U', or 'M').
- (5) Competitive inhibition constant ( $\text{kg CO}_2 \cdot \text{m}^{-3}$ ) - competitive inhibition constant for linear  $\text{CO}_2$  inhibition (only entered for choice 'M' above).
- (6) Uncompetitive inhibition constant ( $\text{kg CO}_2 \cdot \text{m}^{-3}$ ) - uncompetitive inhibition constant for linear  $\text{CO}_2$  inhibition (only entered for choices 'U' and 'M' above).
- (7) Q10 - temperature coefficient of respiration.
- (8) Respiratory quotient ( $\text{kg} \cdot \text{kg}^{-1}$ ) - mass-based respiratory quotient. (Note that a *volumetric* respiratory quotient of 1 is equivalent to a *mass-based* respiratory quotient of 1.375.)
- (9) Skin permeance to  $\text{O}_2$  ( $\text{m} \cdot \text{s}^{-1}$ ).
- (10) Skin permeance to  $\text{CO}_2$  ( $\text{m} \cdot \text{s}^{-1}$ ).
- (11) Skin permeance to water vapour ( $\text{s} \cdot \text{m}^{-1}$ ) - (note that the units for this value differ to those for skin permeances to  $\text{O}_2$  and  $\text{CO}_2$  above; in the program, skin permeance to water vapour is based on a partial-pressure gradient, whereas skin permeances to  $\text{O}_2$  and  $\text{CO}_2$  are based on concentration gradients).
- (12) Fruit heat-transfer model (half-cooling time or full) - choose a heat-transfer model based on half-cooling times or a model based purely on sequential heat-transfer from the fruit to the package atmosphere and from the package atmosphere to the store atmosphere (the latter model is more sensitive to the accuracy of the heat transfer coefficients entered in sections B and C below) (enter 'H' or 'F').
- (13) Fruit flesh specific heat capacity ( $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ).
- (14) Respiratory heat generation rate ( $\text{J} \cdot \text{kg}^{-1}$ ) - heat generated per unit mass of respiratory  $\text{O}_2$  consumption.
- (15) Half cooling time (h) - only entered if a half-cooling-time model was chosen in (12) above.
- (16) Initial fruit flesh density ( $\text{kg} \cdot \text{m}^{-3}$ ) - fruit flesh density at the start of storage.

- (17) Fruit flesh porosity ( $\text{m}^3 \cdot \text{m}^{-3}$ ).
  - (18) Coefficient of fruit surface area correlation - parameter  $a$  of the surface area/volume correlation proposed by Clayton *et al.* (1995).
  - (19) Exponent of fruit surface area correlation - parameter  $b$  of the surface area/volume correlation proposed by Clayton *et al.* (1995).
  - (20) Fruit water activity - water activity beneath the fruit skin.
  - (21) Initial fruit temperature ( $^{\circ}\text{C}$ ).
  - (22) Initial fruit internal  $\text{O}_2$  (mol %) - fruit internal  $\text{O}_2$  concentration corresponding to the temperature entered in (21) above.
  - (23) Initial fruit internal  $\text{CO}_2$  (mol %) - fruit internal  $\text{CO}_2$  concentration corresponding to the temperature entered in (21) above.
  - (24) Initial total fruit mass (kg) - total mass of fruit per package.
  - (25) Number of fruit per package
- (B) Packaging material data section:
- (1) Packaging film area ( $\text{m}^2$ ) - total area of permeable film available for gas permeation.
  - (2) Packaging film thickness (m).
  - (3) Arrhenius constant for film  $\text{O}_2$  permeability ( $\text{m}^2 \cdot \text{s}^{-1}$ ) - the pre-exponential factor in the Arrhenius equation for  $\text{O}_2$  permeability.
  - (4) Arrhenius constant for film  $\text{CO}_2$  permeability ( $\text{m}^2 \cdot \text{s}^{-1}$ ) - the pre-exponential factor in the Arrhenius equation for  $\text{CO}_2$  permeability.
  - (5) Arrhenius constant for film  $\text{N}_2$  permeability ( $\text{m}^2 \cdot \text{s}^{-1}$ ) - the pre-exponential factor in the Arrhenius equation for  $\text{N}_2$  permeability.
  - (6) Arrhenius constant for film  $\text{H}_2\text{O}$  permeability ( $\text{m}^2 \cdot \text{s}^{-1}$ ) - the pre-exponential factor in the Arrhenius equation for water vapour permeability.
  - (7) Activation energy for  $\text{O}_2$  permeation ( $\text{J} \cdot \text{mol}^{-1}$ ).
  - (8) Activation energy for  $\text{CO}_2$  permeation ( $\text{J} \cdot \text{mol}^{-1}$ ).
  - (9) Activation energy for  $\text{N}_2$  permeation ( $\text{J} \cdot \text{mol}^{-1}$ ).
  - (10) Activation energy for  $\text{H}_2\text{O}$  permeation ( $\text{J} \cdot \text{mol}^{-1}$ ).
  - (11) Perforations in packaging film? - enter 'Y' if perforations will be formed at some time during the simulation, 'N' otherwise.
  - (12) Number of holes in packaging film - only entered for an answer of 'Y' in (11) above.
  - (13) Diameter of holes in packaging film (m) - only entered for an answer of 'Y' in (11) above.
  - (14) Time holes made in packaging film (h) - only entered for an answer of 'Y' in (11) above.
  - (15) Initial packaging temperature ( $^{\circ}\text{C}$ ) - initial temperature of the packaging materials (used to calculate initial film permeabilities).
  - (16) Average overall HTC for package ( $\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ ) - overall heat transfer coefficient for convection at the inside packaging surface, conduction through the packaging materials, and convection at the outside packaging surface.
  - (17) Package area for heat transfer ( $\text{m}^2$ ) - average package surface area available for heat transfer.
  - (18) Initial total package volume ( $\text{m}^3$ ) - the initial total volume enclosed by the packaging film.

- (19) Minimum possible total package volume ( $\text{m}^3$ ) - the minimum volume to which the film package can shrink.
  - (20) Dry mass of fruit trays ( $\text{kg}\cdot\text{tray}^{-1}$ ) - dry mass of the moulded-pulp fruit trays.
  - (21) Effective area of fruit trays ( $\text{m}^2\cdot\text{tray}^{-1}$ ) - surface area for moisture sorption by the trays.
  - (22) Number of fruit trays per package.
  - (23) Initial equilibrium RH of fruit trays (%) - used to calculate the initial moisture content of the trays.
  - (24) GAB isotherm parameter  $X_m$  ( $\text{kg}\cdot\text{kg}^{-1}$ ).
  - (25) GAB isotherm parameter  $C$ .
  - (26) GAB isotherm parameter  $K$ .
- (C) Package atmosphere data section:
- (1) Packaging-film heat transfer coefficient ( $\text{W}\cdot\text{m}^2\cdot\text{K}^{-1}$ ) - convective heat-transfer coefficient at the inside surface of the packaging film.
  - (2) Fruit heat transfer coefficient ( $\text{W}\cdot\text{m}^2\cdot\text{K}^{-1}$ ) - convective heat-transfer coefficient at the fruit surface.
  - (3) Packaging-film mass transfer coefficient ( $\text{s}\cdot\text{m}^{-1}$ ) - mass transfer coefficient for moisture condensation at the inside surface of the packaging film.
  - (4) Fruit mass transfer coefficient ( $\text{s}\cdot\text{m}^{-1}$ ) - mass transfer coefficient for moisture condensation at the fruit surface.
  - (5) Tray mass transfer coefficient ( $\text{s}\cdot\text{m}^{-1}$ ) - mass transfer coefficient for moisture sorption at the fruit-tray surfaces.
  - (6) Empirical correction factor for gas diffusivities - a correction factor applied to gas diffusion through holes in the packaging film. The value of this factor is expected to lie between 0 and 1, but no correlations have yet been developed for predicting this value as a function of hole diameter and film thickness.
  - (7) Initial package  $\text{O}_2$  concentration (mol %).
  - (8) Initial package  $\text{CO}_2$  concentration (mol %).
  - (9) Initial package relative humidity (%).
  - (10) Initial package air temperature ( $^{\circ}\text{C}$ ).
- (D) Store data section:
- (1) Number of storage stages (8 maximum) - a storage regime with up to eight storage stages can be entered. Step changes in store conditions are assumed between one stage and the next. For each storage stage, enter the appropriate values for (2) to (6) below.
  - (2) Time at which stage comes into effect (h).
  - (3) Store temperature ( $^{\circ}\text{C}$ ).
  - (4) Store relative humidity (%).
  - (5) Store  $\text{O}_2$  concentration (mol %).
  - (6) Store  $\text{CO}_2$  concentration (mol %).

Once the input file has been reviewed and modified where necessary, enter the name of the new file.

### *Creating a New Data File*

This option follows a procedure similar to that described above for modifying a data file. Enter the name of the data file to be created, then enter the data values as prompted. Data are entered in the same order as that listed above.

### **SIMULATION PARAMETERS**

Once data entry has been completed, you will be prompted for the parameters needed to control the simulation and output procedures.

First, enter a run-identification label (up to 75 characters). This label will be printed in the header of the output files and can be used to enter descriptive information for later identification of the files.

You are then given a choice of creating one or both of two output files:

- (1) a fruit output file listing
  - storage time
  - fruit temperature
  - fruit internal oxygen and carbon dioxide concentrations
  - fruit cumulative oxygen consumption
  - fruit weight loss
  - mass of condensate on fruit surface;
- (2) a package output file listing
  - storage time
  - package air temperature
  - package oxygen and carbon dioxide concentrations
  - package relative humidity
  - package shrinkage
  - package atmosphere pressure
  - mass of condensate on packaging film inside surface
  - moisture content of fruit trays.

Lastly, enter values for the following simulation parameters:

- (1) Total simulation time (days).
- (2) Maximum time step (s) - this parameter sets the maximum time step the program can take for any one iteration during the numerical calculation. The choice of maximum time step should not affect the accuracy of the integration, as the actual step size is adjusted by error-control procedures. However, the program uses the maximum time step to estimate an initial step size at the start of the simulation. A value between 30 and 300 seconds is recommended.
- (3) Maximum allowable integration error (%) - this parameter is used to control the actual time steps taken throughout the numerical integration. A value of 0.1

or 0.01% is recommended.

- (4) Interval between outputs (h) - this parameter defines how often simulation output is written to the output data files (e.g. every 12 hours, every 24 hours, etc.).

Once these parameters have been entered, the program starts the numerical calculation (you can abort the run before the calculation starts by entering a total simulation time of zero). While the simulation is running, the current simulation time is displayed on the screen to give some indication of how far the simulation has progressed. Once the simulation is finished, the output data files can be imported into other software packages for further analysis.

## Appendix C

### PROGRAM TESTING

This Appendix presents the results of various tests carried out to check the mathematical accuracy of the MAPSIM program.

Each of the tests was based on setting various input data to extreme or constant values so that program output could be compared with the analytical solutions of simplified model equations.

Unless otherwise stated, the nomenclature used throughout this Appendix is defined as in the Nomenclature section and Chapter 6.

#### STEADY STATE O<sub>2</sub> AND CO<sub>2</sub> CONCENTRATIONS

The steady state solutions for Eqs. 6.15, 6.21, 6.23, and 6.26 (for packages with no holes) are as follows:

$$C_{O_2,p} = C_{O_2,e} - \frac{v M_f x}{P_{O_2} A_{film}} \quad (C1)$$

$$C_{CO_2,p} = C_{CO_2,e} - \frac{RQ_m v M_f x}{P_{CO_2} A_{film}} \quad (C2)$$

$$C_{O_2,f} = C_{O_2,p} - \frac{v M_n}{k_{O_2} A_n} \quad (C3)$$

$$C_{CO_2,f} = C_{CO_2,p} - \frac{RQ_m v M_n}{k_{CO_2} A_n} \quad (C4)$$

To simulate a constant respiration rate, the model was run with no CO<sub>2</sub> inhibition and with  $k_m$  set to zero.  $k_{g, skin}$  was set to zero to prevent evaporative weight loss from the fruit. To keep the temperature throughout the package constant, the following conditions were also set:

$$\begin{aligned} W &= 0 \text{ J}\cdot\text{kg}^{-1} \text{ (no respiratory heat generation)} \\ h_f &= 0 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} \text{ (no heat transfer from or to the fruit)} \\ U_{pack} &= 1000 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} \\ h_p &= U_{pack} \text{ (ensures } \theta_{film} = \theta_e \text{).} \end{aligned}$$

The model was run with the following input data:

|                |                                                                            |
|----------------|----------------------------------------------------------------------------|
| $\theta_e$     | = 0, 5, or 10°C                                                            |
| $\theta_f$     | = 0, 5, or 10°C                                                            |
| $\theta_p$     | = 0, 5, or 10°C                                                            |
| $\theta_{ref}$ | = 0°C                                                                      |
| $\rho_f$       | = 1000 kg·m <sup>-3</sup>                                                  |
| $a$            | = 4.88                                                                     |
| $A_{film}$     | = 1.5 m <sup>2</sup>                                                       |
| $b$            | = 0.66                                                                     |
| $E_{a, CO_2}$  | = 40000 J·mol <sup>-1</sup>                                                |
| $E_{a, O_2}$   | = 40000 J·mol <sup>-1</sup>                                                |
| $k_{CO_2}$     | = $3 \times 10^{-7}$ m·s <sup>-1</sup>                                     |
| $k_{g, tray}$  | = 0 s·m <sup>-1</sup>                                                      |
| $k_{O_2}$      | = $3 \times 10^{-7}$ m·s <sup>-1</sup>                                     |
| $M_f$          | = 20 kg                                                                    |
| $N$            | = 100                                                                      |
| $P_{0, O_2}$   | = $1 \times 10^{-4}$ m <sup>2</sup> ·s <sup>-1</sup>                       |
| $P_{0, CO_2}$  | = $1 \times 10^{-4}$ m <sup>2</sup> ·s <sup>-1</sup>                       |
| $Q_{10}$       | = 3.5                                                                      |
| $RH_e$         | = 0%                                                                       |
| $RH_p$         | = 0%                                                                       |
| $RQ_m$         | = 1.375 kg·kg <sup>-1</sup>                                                |
| $v_{max, ref}$ | = $4 \times 10^{-10}$ kg O <sub>2</sub> ·kg <sup>-1</sup> ·s <sup>-1</sup> |
| $x$            | = 25 µm                                                                    |
| $[CO_2]_e$     | = 0.00 m <sup>3</sup> ·m <sup>-3</sup>                                     |
| $[O_2]_e$      | = 0.21 m <sup>3</sup> ·m <sup>-3</sup>                                     |

(Film permeabilities and skin permeances to O<sub>2</sub> were set to the same values as those for CO<sub>2</sub> to prevent shrinkage of the package atmosphere.)

Table C1 lists the model predictions and analytical solutions for three storage temperatures. Slight differences between the model predictions and analytical solutions in the third decimal place are likely to be due to respiratory carbon loss in the model causing small changes in fruit density (carbon loss from the fruit cannot be turned off without either setting respiration rate to zero or altering the program source code).

### FRUIT O<sub>2</sub> AND CO<sub>2</sub> CONCENTRATIONS

If skin permeabilities to O<sub>2</sub> and CO<sub>2</sub> are set to zero, the following solutions can be derived for Eqs. 6.15 and 6.21:

$$k_m \ln \left( \frac{C_{O_2, f}}{C_{O_2, f}^0} \right) - C_{O_2, f} = C_{O_2, f}^0 - \frac{v_{max} \rho_f t}{\epsilon} \quad (C5)$$

$$\frac{(C_{\text{CO}_2,f})^2}{2 k_{iu}} - C_{\text{CO}_2,f} = \frac{(C_{\text{CO}_2,f}^0)^2}{2 k_{iu}} - C_{\text{CO}_2,f}^0 - \frac{RQ_m v_{max} \rho_f t}{\varepsilon} \quad (\text{C6})$$

where

$$\begin{aligned} C_{\text{O}_2,f}^0 &= \text{initial fruit internal O}_2 \text{ concentration (kg}\cdot\text{m}^{-3}\text{)} \\ C_{\text{CO}_2,f}^0 &= \text{initial fruit internal CO}_2 \text{ concentration (kg}\cdot\text{m}^{-3}\text{)}. \end{aligned}$$

A Michaelis-Menten model with no CO<sub>2</sub> inhibition was assumed in the derivation of Eq. C5, and uncompetitive inhibition with no O<sub>2</sub> effect ( $k_m = 0$ ) was assumed in the derivation of Eq. C6. Both Eq. C5 and Eq. C6 are implicit, requiring iterative solutions for  $C_{\text{O}_2,f}$  and  $C_{\text{CO}_2,f}$ .

The model was run with the following input data:

$$\begin{aligned} \varepsilon &= 0.15 \\ \theta_f &= 0^\circ\text{C} \\ \theta_{ref} &= 0^\circ\text{C} \\ \rho_f &= 1000 \text{ kg}\cdot\text{m}^{-3} \\ h_f &= 0 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1} \\ k_{\text{CO}_2} &= 0 \text{ m}\cdot\text{s}^{-1} \\ k_{g, skin} &= 0 \text{ s}\cdot\text{m}^{-1} \\ k_{iu} &= 0.1 \text{ kg CO}_2\cdot\text{m}^{-3} \text{ (for fruit CO}_2 \text{ concentration).} \\ k_m &= 0.1 \text{ kg O}_2\cdot\text{m}^{-3} \text{ (for fruit O}_2 \text{ concentration)} \\ k_{\text{O}_2} &= 0 \text{ m}\cdot\text{s}^{-1} \\ RQ_m &= 1.375 \text{ kg}\cdot\text{kg}^{-1} \\ v_{max, ref} &= 4 \times 10^{-10} \text{ kg O}_2\cdot\text{kg}^{-1}\cdot\text{s}^{-1} \\ W &= 0 \text{ J}\cdot\text{kg}^{-1} \\ [\text{CO}_2]_f^0 &= 0.00 \text{ m}^3\cdot\text{m}^{-3} \\ [\text{O}_2]_f^0 &= 0.21 \text{ m}^3\cdot\text{m}^{-3}. \end{aligned}$$

Table C2 lists the model predictions and analytical solutions. Model predictions agreed exactly with the analytical solutions to 3 decimal places.

### PACKAGE O<sub>2</sub> AND CO<sub>2</sub> CONCENTRATIONS

For a package with no holes, no gas exchange between the fruit internal atmosphere and the package atmosphere, and a constant package volume, the following solution can be derived for both Eq. 6.23 and Eq. 6.26:

$$\left( \frac{C_{i,e} - C_{i,p}}{C_{i,e} - C_{i,p}^0} \right) = \exp \left( \frac{-P_i A_{film} t}{x V_p} \right) \quad (\text{C7})$$

where

- $C_{i,e}$  = concentration of O<sub>2</sub> or CO<sub>2</sub> in the external atmosphere (kg·m<sup>-3</sup>)  
 $C_{i,p}$  = concentration of O<sub>2</sub> or CO<sub>2</sub> in the package atmosphere (kg·m<sup>-3</sup>)  
 $C_{i,p}^0$  = initial concentration of O<sub>2</sub> or CO<sub>2</sub> in the package atmosphere (kg·m<sup>-3</sup>).

Shrinkage of the package atmosphere was prevented by setting  $P_{CO_2}$  equal to  $P_{O_2}$ , setting the initial CO<sub>2</sub> concentration gradient across the film equal (but opposite) to the initial O<sub>2</sub> gradient, turning off all water vapour transport, and by setting heat transfer coefficients to keep the temperature of the package atmosphere constant.

The model was run with the following input data:

- $\theta_e$  = 0°C  
 $\theta_p$  = 0°C  
 $\rho_f$  = 1000 kg·m<sup>-3</sup>  
 $A_{film}$  = 1.5 m<sup>2</sup>  
 $E_{a,O_2}$  = 40000 J·mol<sup>-1</sup>  
 $E_{a,CO_2}$  = 40000 J·mol<sup>-1</sup>  
 $h_f$  = 0 W·m<sup>-2</sup>·K<sup>-1</sup>  
 $h_p$  =  $U_{pack}$  (ensures  $\theta_{film} = \theta_e$ )  
 $k_{CO_2}$  = 0 m·s<sup>-1</sup>  
 $k_{g,ray}$  = 0 s·m<sup>-1</sup>  
 $k_{g,skin}$  = 0 s·m<sup>-1</sup>  
 $k_{O_2}$  = 0 m·s<sup>-1</sup>  
 $M_f$  = 20 kg  
 $P_{0,O_2}$  =  $1 \times 10^{-4}$  m<sup>2</sup>·s<sup>-1</sup>  
 $P_{0,CO_2}$  =  $1 \times 10^{-4}$  m<sup>2</sup>·s<sup>-1</sup>  
 $RH_e$  = 0%  
 $RH_p$  = 0%  
 $U_{pack}$  = 1000 W·m<sup>-2</sup>·K<sup>-1</sup>  
 $V_{carton}$  = 0.045 m<sup>3</sup>  
 $W$  = 0 J·kg<sup>-1</sup>  
 $x$  = 25 μm  
 $[CO_2]_e$  = 0.00 m<sup>3</sup>·m<sup>-3</sup>  
 $[CO_2]_p^0$  = 0.21 m<sup>3</sup>·m<sup>-3</sup>  
 $[O_2]_e$  = 0.21 m<sup>3</sup>·m<sup>-3</sup>  
 $[O_2]_p^0$  = 0.00 m<sup>3</sup>·m<sup>-3</sup>.

Table C3 lists the model predictions and analytical solutions. Model predictions agreed exactly with the analytical solutions to 3 decimal places.

## FRUIT HEAT TRANSFER

If respiratory heat generation and evaporative moisture loss are set to zero, and if the temperature of the package atmosphere remains constant, then the following analytical solution can be derived for Eq. 6.72:

$$\frac{\theta_f - \theta_p}{\theta_f^0 - \theta_p} = \exp\left(\frac{-h_f A_n t}{M_n c_{pf}}\right) \quad (C8)$$

where

$\theta_f^0$  = initial fruit temperature (°C).

The MAP model was run with the following input data (and with the sequential heat transfer model):

|                |                                                          |
|----------------|----------------------------------------------------------|
| $\theta_e$     | = 0°C                                                    |
| $\theta_f^0$   | = 20°C                                                   |
| $\theta_p$     | = 0°C                                                    |
| $\rho_f$       | = 1000 kg·m <sup>-3</sup>                                |
| $a$            | = 4.88                                                   |
| $b$            | = 0.66                                                   |
| $c_{pf}$       | = 3650 J·kg <sup>-1</sup> ·K <sup>-1</sup>               |
| $E_{a, O_2}$   | = 40000 J·mol <sup>-1</sup>                              |
| $E_{a, CO_2}$  | = 40000 J·mol <sup>-1</sup>                              |
| $h_f$          | = 1 W·m <sup>-2</sup> ·K <sup>-1</sup>                   |
| $h_p$          | = $U_{pack}$                                             |
| $k_{CO_2}$     | = $3 \times 10^{-7}$ m·s <sup>-1</sup>                   |
| $k_{g, skin}$  | = 0 s·m <sup>-1</sup>                                    |
| $k_{g, tray}$  | = 0 s·m <sup>-1</sup>                                    |
| $k_{O_2}$      | = $3 \times 10^{-7}$ m·s <sup>-1</sup>                   |
| $M_f$          | = 0.2 kg                                                 |
| $N$            | = 1                                                      |
| $P_{0, O_2}$   | = $1 \times 10^{-4}$ m <sup>2</sup> ·s <sup>-1</sup>     |
| $P_{0, CO_2}$  | = $1 \times 10^{-4}$ m <sup>2</sup> ·s <sup>-1</sup>     |
| $U_{pack}$     | = 1000 W·m <sup>-2</sup> ·K <sup>-1</sup>                |
| $v_{max, ref}$ | = 0 kg O <sub>2</sub> ·kg <sup>-1</sup> ·s <sup>-1</sup> |
| $W$            | = 0 J·kg <sup>-1</sup>                                   |
| $x$            | = 25 μm                                                  |

Table C4 lists the model predictions and analytical solutions. Very slight differences between the model predictions and analytical solutions in the third decimal place are likely to be due to the temperature of the package atmosphere not remaining exactly constant (due to heat transfer from the fruit).

#### PACKAGE HEAT TRANSFER

If heat transfer from the fruit, heat transfer due to moisture transport, and package absolute humidity are set to zero, and if the mass of air in the package atmosphere and the mass of the fruit trays are kept constant, then the following analytical solution can be derived for Eq. 6.75:

$$\frac{\theta_p - \theta_e}{\theta_p^0 - \theta_e} = \exp\left(\frac{-U_{pack} A_{pack} t}{M_{thermal}}\right) \quad (C9)$$

where

$$M_{thermal} = M_p c_{pa} - N_{tray} M_{tray} c_{pt} - N_{tray} M_{tray} X_{tray} c_{pw} \quad (C10)$$

( $X_{tray}$  cannot be set to zero, as it appears in the denominator of Eq. 6.47).

To keep the  $M_{thermal}$  constant, all permeation and moisture transport was turned off.

The model was run with the following input data:

|               |                                        |
|---------------|----------------------------------------|
| $\theta_e$    | = 0°C                                  |
| $\theta_p^0$  | = 20°C                                 |
| $\rho_f$      | = 1000 kg·m <sup>-3</sup>              |
| $A_{pack}$    | = 0.8 m <sup>2</sup>                   |
| $a_{w, tray}$ | = 1                                    |
| $C$           | = 55000                                |
| $h_f$         | = 0 W·m <sup>-2</sup> ·K <sup>-1</sup> |
| $K$           | = 0.7                                  |
| $k_{CO_2}$    | = 0 m·s <sup>-1</sup>                  |
| $k_{g, tray}$ | = 0 s·m <sup>-1</sup>                  |
| $k_{g, skin}$ | = 0 s·m <sup>-1</sup>                  |
| $k_{O_2}$     | = 0 m·s <sup>-1</sup>                  |
| $M_f$         | = 20 kg                                |
| $M_{tray}$    | = 0.1 kg                               |
| $N_{tray}$    | = 5                                    |
| $P_{0, H_2O}$ | = 0 m <sup>2</sup> ·s <sup>-1</sup>    |
| $P_{0, O_2}$  | = 0 m <sup>2</sup> ·s <sup>-1</sup>    |
| $P_{0, N_2}$  | = 0 m <sup>2</sup> ·s <sup>-1</sup>    |
| $P_{0, CO_2}$ | = 0 m <sup>2</sup> ·s <sup>-1</sup>    |
| $RH_p$        | = 0%                                   |
| $U_{pack}$    | = 1 W·m <sup>-2</sup> ·K <sup>-1</sup> |
| $V_{carton}$  | = 0.045 m <sup>3</sup>                 |
| $W$           | = 0 J·kg <sup>-1</sup>                 |
| $X_m$         | = 0.06 kg·kg <sup>-1</sup>             |
| $[CO_2]_p$    | = 0.00 m <sup>3</sup> ·m <sup>-3</sup> |
| $[N_2]_p$     | = 0.79 m <sup>3</sup> ·m <sup>-3</sup> |
| $[O_2]_p$     | = 0.21 m <sup>3</sup> ·m <sup>-3</sup> |

Table C5 lists the model predictions and analytical solutions. Model predictions agreed exactly with the analytical solutions to 3 decimal places.

## NUMERICAL ACCURACY

To test the stability of the numerical solution, the model was run with the maximum allowable local integration error (*RelTol*) set to 0.001, 0.01, 0.1, and 1% (for a normal set of input data from one of the carton trials). At 1%, predicted steady-state values of package RH and mass of condensate on the inside of the packaging film oscillated by up to  $\pm 0.3$  (% or g). This run also had a high percentage of failed iterations (20%). These effects were not observed for the lower values of *RelTol*. Thus, a *RelTol* of 0.1% or less is recommended for running MAPSIM (*RelTol* was set to 0.01% for all the model runs reported in this work).

**Table C1** Steady-state O<sub>2</sub> and CO<sub>2</sub> concentrations (model versus analytical).

|                      | Oxygen (mol %) |            | Carbon dioxide (mol %) |            |
|----------------------|----------------|------------|------------------------|------------|
|                      | Model          | Analytical | Model                  | Analytical |
| <i>0°C storage:</i>  |                |            |                        |            |
| Fruit                | 15.778         | 15.776     | 5.222                  | 5.224      |
| Package              | 16.835         | 16.833     | 4.165                  | 4.167      |
| <i>5°C storage:</i>  |                |            |                        |            |
| Fruit                | 13.204         | 13.202     | 7.796                  | 7.798      |
| Package              | 15.218         | 15.217     | 5.782                  | 5.783      |
| <i>10°C storage:</i> |                |            |                        |            |
| Fruit                | 9.047          | 9.048      | 11.954                 | 11.952     |
| Package              | 12.884         | 12.885     | 8.116                  | 8.115      |

**Table C2** Fruit O<sub>2</sub> and CO<sub>2</sub> concentrations (model versus analytical).

| Time<br>(days) | Oxygen (mol %) |            | Carbon dioxide (mol %) |            |
|----------------|----------------|------------|------------------------|------------|
|                | Model          | Analytical | Model                  | Analytical |
| 0.00           | 21.000         | 21.000     | 0.000                  | 0.000      |
| 0.25           | 18.033         | 18.033     | 3.094                  | 3.094      |
| 0.50           | 15.197         | 15.197     | 5.306                  | 5.306      |
| 0.75           | 12.520         | 12.520     | 7.123                  | 7.123      |
| 1.00           | 10.035         | 10.035     | 8.703                  | 8.703      |
| 1.50           | 5.803          | 5.803      | 11.415                 | 11.415     |
| 2.00           | 2.811          | 2.811      | 13.741                 | 13.741     |
| 3.00           | 0.396          | 0.396      | 17.691                 | 17.691     |

**Table C3** Package O<sub>2</sub> and CO<sub>2</sub> concentrations (model versus analytical).

| Time<br>(days) | Oxygen (mol %) |            | Carbon dioxide (mol %) |            |
|----------------|----------------|------------|------------------------|------------|
|                | Model          | Analytical | Model                  | Analytical |
| 0.0            | 0.000          | 0.000      | 21.000                 | 21.000     |
| 0.5            | 4.354          | 4.354      | 16.646                 | 16.646     |
| 1.0            | 7.806          | 7.806      | 13.194                 | 13.194     |
| 1.5            | 10.542         | 10.542     | 10.458                 | 10.458     |
| 2.0            | 12.710         | 12.710     | 8.290                  | 8.290      |
| 2.5            | 14.429         | 14.429     | 6.571                  | 6.571      |
| 3.0            | 15.792         | 15.792     | 5.208                  | 5.208      |
| 3.5            | 16.872         | 16.872     | 4.128                  | 4.128      |
| 4.0            | 17.728         | 17.728     | 3.272                  | 3.272      |
| 4.5            | 18.406         | 18.406     | 2.594                  | 2.594      |
| 5.0            | 18.944         | 18.944     | 2.056                  | 2.056      |

**Table C4** Fruit temperature (model versus analytical).

| Time<br>(h) | Temperature<br>predicted by<br>model<br>(°C) | Temperature<br>predicted from<br>analytical solution<br>(°C) |
|-------------|----------------------------------------------|--------------------------------------------------------------|
| 0           | 20.000                                       | 20.000                                                       |
| 3           | 15.401                                       | 15.400                                                       |
| 6           | 11.859                                       | 11.859                                                       |
| 9           | 9.132                                        | 9.131                                                        |
| 12          | 7.032                                        | 7.031                                                        |
| 15          | 5.414                                        | 5.414                                                        |
| 18          | 4.169                                        | 4.169                                                        |
| 21          | 3.210                                        | 3.210                                                        |
| 24          | 2.472                                        | 2.472                                                        |
| 27          | 1.904                                        | 1.904                                                        |
| 30          | 1.466                                        | 1.466                                                        |

**Table C5** Package temperature (model versus analytical).

| Time<br>(min) | Temperature<br>predicted by<br>model<br>(°C) | Temperature<br>predicted from<br>analytical solution<br>(°C) |
|---------------|----------------------------------------------|--------------------------------------------------------------|
| 0             | 20.000                                       | 20.000                                                       |
| 5             | 16.143                                       | 16.143                                                       |
| 10            | 13.030                                       | 13.030                                                       |
| 15            | 10.517                                       | 10.517                                                       |
| 20            | 8.488                                        | 8.488                                                        |
| 25            | 6.851                                        | 6.851                                                        |
| 30            | 5.530                                        | 5.530                                                        |
| 35            | 4.464                                        | 4.464                                                        |
| 40            | 3.603                                        | 3.603                                                        |
| 45            | 2.908                                        | 2.908                                                        |
| 50            | 2.347                                        | 2.347                                                        |
| 55            | 1.894                                        | 1.894                                                        |
| 60            | 1.529                                        | 1.529                                                        |

## Appendix D

### INPUT DATA FILES

The MAPSIM input data files corresponding to the model runs reported in section 9.1 are given on the diskette at the back of this thesis. Filenames ending in 'N' indicate files for the respiration models with no CO<sub>2</sub> inhibition; filenames ending in 'U' indicate files for the respiration models with uncompetitive CO<sub>2</sub> inhibition. The following is a list of the input data files and the trials to which the files correspond.

#### 1993 'Braeburn' (subdirectory BB93)

|         |                                                 |
|---------|-------------------------------------------------|
| BBCTN1  | count 125 apples, 40 µm film, trial BB93-A      |
| BBCTN13 | count 125 apples, 25 µm film, trial BB93-A      |
| BBCTN16 | count 80 apples, 40 µm film, trial BB93-A       |
| BBCTN19 | count 80 apples, 25 µm film, trial BB93-A       |
| BBBAG1  | 10 × count 125 apples, 40 µm film, trial BB93-B |
| BBBAG6  | 5 × count 125 apples, 40 µm film, trial BB93-B  |
| BBBAG8  | 10 × count 80 apples, 25 µm film, trial BB93-B  |
| BBBAG10 | 5 × count 80 apples, 25 µm film, trial BB93-B   |
| BBBAG34 | 10 × count 125 apples, 25 µm film, trial BB93-C |
| BBBAG36 | 5 × count 125 apples, 25 µm film, trial BB93-C  |
| BBBAG38 | 10 × count 80 apples, 40 µm film, trial BB93-C  |
| BBBAG40 | 5 × count 80 apples, 40 µm film, trial BB93-C   |

#### 1994 'Braeburn' (subdirectory BB94)

|         |                                                           |
|---------|-----------------------------------------------------------|
| BBCTN22 | count 125 apples, 25 µm film, non-insulated, trial BB94-A |
| BBCTN26 | count 125 apples, 25 µm film, insulated, trial BB94-A     |
| BBCTN30 | count 125 apples, 25 µm film, trial BB94-B                |
| BBCTN34 | count 125 apples, 40 µm film, trial BB94-B                |

#### 1994 'Royal Gala' (subdirectory RG94)

|         |                                            |
|---------|--------------------------------------------|
| RGCTN1  | count 100 apples, 25 µm film, trial RG94-A |
| RGCTN6  | count 100 apples, 40 µm film, trial RG94-A |
| RGCTN11 | count 100 apples, 25 µm film, trial RG94-B |
| RGCTN13 | count 100 apples, 40 µm film, trial RG94-B |
| RGCTN15 | count 100 apples, 25 µm film, trial RG94-C |
| RGCTN19 | count 100 apples, 40 µm film, trial RG94-C |

#### 1994 'Granny Smith' (subdirectory GS94)

|         |                                                 |
|---------|-------------------------------------------------|
| GSCTN25 | count 125 apples, 25 µm film, trial GS94-A      |
| GSCTN29 | count 125 apples, 40 µm film, trial GS94-A      |
| GSBAG15 | 10 × count 125 apples, 25 µm film, trial GS94-B |
| GSBAG20 | 10 × count 125 apples, 40 µm film, trial GS94-B |