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DIFFUSION CHANNELS FOR BROCCOLI STORAGE

by

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A Thesis submitted to the
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ABSTRACT

Mariyappa Ramachandra **M.Sc.(Agrl. Engg.)**

Diffusion Channels for Broccoli Storage

Vegetables are highly perishable products due to continuing metabolism activities in the post-harvest phase. Since respiration rate can be reduced by creating a low-oxygen and, to a lesser extent, increased carbon dioxide atmosphere, storage systems that lead to such atmospheres, known as Controlled Atmospheres (CA), are effective in extending the storage life and post-storage quality of fresh produce. While semi-permeable membranes have proved to be an effective method for passive establishment of controlled atmosphere conditions, a more flexible and less expensive solution based on the diffusion through inert-walled channels of various length and cross section could make CA even more attractive.

This thesis focuses on diffusion channel design for broccoli storage, an important cash crop and consumer commodity in Canada. Experiments were first conducted to determine the respiration rate of broccoli in modified atmosphere conditions created by the produce metabolic activity inside closed chambers, at four different temperatures in the cold room of 3, 7, 13, and 24°C. The respiration rate decreased with a reduction of O_2 concentration inside the chamber. A model to predict the respiration rate of broccoli as a function of O_2 concentration at different temperatures was developed. Experiments were then carried out to determine the cross sectional area and length of diffusion channel leading to various final O_2 (steady-state) concentrations during the storage of broccoli. Combinations of cross sectional area of 0.04, 0.18, and 1.15 cm^2 and length of 0.6, 3, 7, 12, 18, and 25 cm were tested. The carbon dioxide produced through respiratory process was absorbed by placing hydrated lime inside the chambers such that the two-component molecular diffusion model by Ratti et al. (1993) could be evaluated. The length and cross sectional area of diffusion channel have a significant effect on the final level of O_2 (steady-state) concentration. The Ratti model then served as a basis for a modified model for predicting the length of diffusion channel required to obtain a given O_2 concentration as a function of the mass of stored broccoli and the cross sectional area of the diffusion channel.

Although organoleptic, mechanical and color characteristics of the broccoli were measured, no statistically significant relationships between these and O_2 concentrations were observed, probably due to the fact that CO_2 was scrubbed for the purpose of testing the model, whereas CO_2 accumulation to a certain level is known to have a beneficial effect on the storage of many horticultural commodities stored under reduced O_2 conditions.

RÉSUMÉ

Mariyappa Ramachandra **M.Sc.(Génie rural)**

Entreposage du Brocoli par Canaux de Diffusion

Les légumes frais sont rapidement périssables car leurs activités métaboliques restent élevées, même après la cueillette. Leurs activités respiratoires peuvent être réduites à l'aide d'un environnement à faible taux d'O_2 et à haut taux de CO_2, que l'on peut créer avec différents systèmes d'entreposage sous atmosphère contrôlée (AC). Reconnue apte à augmenter la qualité post-récolte et le temps d'entreposage, la méthode des membranes semi-perméables a, par le passé, démontrée qu'elle obtient et maintient un environnement AC de façon efficace et économique. Aujourd'hui, une nouvelle méthode, plus facilement adaptable et plus économique, basée sur la théorie de la diffusion des gaz via des tubes de longueur et diamètre spécifiques, promet de nouveaux développements dans l'entreposage en AC de produits maraîchers.

Le présent document discute de la conception d'un système AC par canaux de diffusion pour l'entreposage du brocoli. Les expériences ont débuté par la détermination du taux de respiration du brocoli sous AC dans des contenants hermétiques à des températures de 3, 7, 13 et 24°C. Les résultats ont démontré que le taux de respiration diminue avec une réduction d'O_2. C'est à partir de ces résultats qu'un modèle fut développé exprimant le taux de respiration en fonction du taux d'O_2 à différentes températures. Des tests furent ensuite conduits afin d'établir la longueur et le diamètre des canaux de diffusion permettant un contrôle approprié pour l'entreposage AC du brocoli. Des surfaces de 0.04, 0.18 et 1.15 cm^2 et des longueurs de 0.6, 3, 7, 12, 18 et 25 cm ont été combinées. Le CO_2 produit dans les chambres AC a été absorbé par de la chaux hydratée granulée, afin d'être conforme au modèle proposé par Ratti *et al.* (1993). Il a été établi que la longueur et la surface des canaux de diffusion ont un effet significatif sur la concentration en O_2 des chambres d'entreposage. Les résultats obtenus furent utilisés avec le modèle Ratti afin d'obtenir un modèle pour la prédiction des dimensions des canaux de diffusion pour une concentration d'O_2 et une masse de brocoli données.

Les propriétés mécaniques, la couleur, de même que les qualités organoleptiques des brocolis ont été mesurées. Aucune différence significative n'a été trouvée en fonction du taux d'O_2. Ceci est probablement dû au fait que le CO_2 a été lessivé, alors que la plupart des produits maraîchers bénéficient de la présence d'un haut taux de CO_2 dans des conditions de faible taux d'O_2.

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LIST OF SYMBOLS

Symbols

a:	color characteristic - hue
a_1, a_2:	regression parameters
$a_1..a_5$:	constants
a, b, c, d, e, f, o, p & q:	regression parameters
A_c:	cross sectional area of the diffusion channel, (cm^2)
b:	color characteristic - chroma
c:	total gas concentration, (mol. cm^{-3})
$[CO_2]$:	CO_2 concentration (%)
C_{O_2}:	concentration of O_2,
C_{CO_2}:	concentration of CO_2,
$D_{O_2-N_2}$:	diffusivity coefficient of O_2 in N_2, (cm^2. min^{-1})
k_1, k_2, k_3:	kinetic constants
K_i:	inhibition constant ($\%O_2$)
K_m:	Michaelis-Menten constant ($\%O_2$)
L:	length of the diffusion channel, (cm)
L:	color characteristic - value
m_s:	mass of produce stored, (kg)
$m_{O_2(t)}$:	the mass of O_2 at time t
$m_{O_2(t+\Delta t)}$:	the mass of O_2 at time $t+\Delta t$,
$m_{CO_2(t)}$:	the mass of CO_2 at time t
$m_{CO_2(t+\Delta t)}$:	the mass of CO_2 at time $t+\Delta t$,
n_{O_2}:	oxygen mass flux, (g. cm^{-2}. h^{-1})
N_2:	nitrogen

O_2:	oxygen
$[O_2]$:	O_2 concentration (%)
Q_{10}:	(rate of deterioration at T+10°C) / (rate of deterioration at T)
r:	RR (ml. or mg. kg^{-1}. h^{-1})
R_x:	rate of respiration in cc of CO_2. kg^{-1}. h^{-1}
$R_{y,x}$:	is the RR cc of CO_2 or O_2. kg^{-1}.h^{-1}
T:	temperature, (°C)
t:	time, (sec, min, or hr)
V:	the free or void volume in the chamber,
V_m:	maximum RR (ml kg^{-1}. h^{-1} or mg kg^{-1}. h^{-1})
$V_{O_2(t)}$:	the volume of O_2 at time t
$V_{O_2(t+\Delta t)}$:	the volume of O_2 at time $t+\Delta t$,
$V_{CO_2(t)}$:	the volume of CO_2 at time t
$V_{CO_2(t+\Delta t)}$:	the volume of CO_2 at time $t+\Delta t$
y:	volumetric concentration of O_2
y_{O_2}:	oxygen mole fraction
z:	volumetric concentration of CO_2
z:	spatial coordinate, (cm)

I INTRODUCTION

Consumers prefer fresh vegetables to processed vegetables because of their freshness, flavor, texture, and color. In a survey conducted in the U.S.A. during 1989 (Powrie and Skura, 1991), 96 % of respondents indicated that they selected fresh fruits and vegetables on the basis of ripeness, freshness, taste, and appearance. The survey also indicated that around 31% of the consumers increased their yearly consumption of fresh vegetables and about 41% increased their consumption of fresh fruits, compared to the last year. In a similar survey in Canada in 1988, the Canadians gave preference to 'freshness' and 'taste' of the produce for consumption.

Fruits and vegetables are highly perishable materials. Post harvest losses have been estimated to be more than 40 to 50% in the tropics and subtropics (Salunkhe and Desai, 1984). It is estimated that about 25% of the harvested produce in the world does not reach consumers because of spoilage (Brecht, 1980). Studies were made at New York and Chicago markets to determine the losses of some fruits and vegetables at wholesale, retail, and consumer levels (Powrie and Skura, 1991). The study indicated that the wholesale loss was 6 to 14%, the retail loss was about 5%, and the consumer loss was 18 to 22% in case of fruits; and 4 to 6%, 2 to 15%, and 7 to 14% respectively in case of vegetables. The reduction of postharvest losses could save millions of dollars to producers, distributors and retailers.

Controlled Atmosphere (CA) or Modified Atmosphere (MA) storage has been shown to be a viable option in improving supplies of certain fresh fruits and vegetables in regions where year-round production is either not possible due to climate constraints or too expensive as in the case of greenhouse production in northern climates. The best examples of the success of CA in Canada are in application to apple and cabbage storage. Both of these commodities may be marketed in fresh or near-fresh condition for periods of 4 months and more due to implementation of CA or MA storage techniques. The advantages of being able to keep fresh produce for extended periods without spoilage are threefold: 1) producers may increase production and market over

a longer period of time so as to take advantage of higher winter and early spring prices, 2) consumer demand can be met by such local supplies so as to reduce the need for imported substitutes, and 3) consumers, distributors and retailers can all benefit from improved storage in that the reduction of losses lowers handling costs and lower prices may be transmitted to the consumer. This third point also applies to imported goods. On the other hand, these advantages are only available where the total costs of production, storage and distribution are competitive with imported commodities, which essentially restricts the range of products to which these advantages apply.

One very popular vegetable that fits into the category of commodities that would benefit from CA/MA storage is broccoli. Although popular for its taste and decorative qualities, it is consumed at moderate rates, unlike items such as potatoes and carrots. It is also quite perishable under refrigeration, usually losing its colour and exhibiting floret rot within two to three weeks after harvest (Hardenburg, 1990). Thus, even at the time of local harvest, broccoli does not have a high immediate demand, but has a moderate demand for a long period. All of these factors are reflected in broccoli consumption and price trends in late fall and early winter. The retail price typically doubles or triples, and sometimes, as in 1994-95, quadruples when the imports come in to Montreal. This is followed by decreased demand and greater potential for losses at the marketing nodes. There is clearly an opportunity for CA storage technology to even out these peaks and incite understandably reticent producers to increase local production of this interesting commodity.

Although various types of systems for establishing and maintaining a CA of desired gas composition (usually reduced O_2 and increased CO_2 relative to ambient) have been developed, this thesis is concerned with CA storage of broccoli in a passive system based on the concept of diffusion channels. The appeal of passive systems in general, as opposed to active systems, is the potential for much lower operating costs, since the only energy input required in a purely passive system is that for refrigeration. The appeal of the diffusion channel over better-known passive systems such as the semi-permeable membrane, is due to its extreme structural simplicity which provides

great flexibility in storage chamber design. Furthermore, since diffusion channels do not operate on the principle of selective diffusion through semi-permeable membranes, materials are considerably less expensive.

The main parameters that influence gas composition in a storage chamber fitted with a diffusion channel are the length and cross-sectional area of the diffusion channel, and, as is the case with membrane systems, the respiration characteristics of the produce stored in quasi-steady-state modified atmosphere conditions. It was therefore proposed to carry out a study of diffusion channels for broccoli storage.

II OBJECTIVES

1) To measure and model the respiration rate of broccoli at different storage temperatures and gas compositions.
2) To assess the effect of the length and cross sectional area of diffusion channel on the steady state concentration of O_2 (CO_2 to be scrubbed) in the storage chambers of broccoli.
3) To develop a model for predicting the length of the diffusion channel for obtaining desired level of O_2 concentration for a given mass of stored broccoli.
4) To assess the keeping quality of broccoli in a CA storage environment created by using the diffusion channel system.

III REVIEW OF LITERATURE

3.1 Introduction

The beneficial effect of CA storage in maintaining the quality of certain varieties of apples was first reported by Kidd and West in 1927. Since then efforts have been made to apply the CA technology to various fruits and vegetables in general (Raghavan et al., 1984, 1982, 1980; El-Goorani and Sommer, 1981; Kader, 1980; Singh et al., 1972). This chapter reviews the factors influencing the storage life of vegetables and fruits, and the various technologies, particularly CA, developed to improve storage life and keeping qualities of fresh horticultural commodities.

3.2 Long term storage of vegetables

Storage is the preservation of commodities after harvest, either temporarily or for long term depending upon the commodity, time of harvest, marketing, demand, rate, etc. Proper storage prolongs the shelf life of fresh fruits and vegetables, prevents gluts on the market and also improves the quality of some commodities as in the case of potatoes (Salunkhe et al., 1991).

Horticultural commodities need storage systems different than those used for grains or seeds because they are often stored for short times till they are distributed to the retailers or are stored for longer periods to make them available all through the year.

The major causes of spoilage of vegetables are water loss and decay. After harvest, the loss of moisture in the vegetables leads to rapid shrivelling and wilting. This causes changes in color, crispness, and palatability, and makes the vegetable tissue tougher and inedible. Moisture loss as low as 5 % causes the vegetable to shrivel. In dry and warm conditions leafy vegetables can spoil within a few hours. On the other hand, the wetting of the produce to reduce water loss may result in the growth of decaying and rotting organisms. The maintenance of a proper relative humidity (RH) in the storage atmosphere is very important to preserve the quality of the vegetables.

3.3 Storage considerations

The factors to be considered for proper storage are the temperature, relative humidity, atmospheric composition, light, and other factors such as the use of herbicides, fungicides, pesticides and growth regulators during crop production (Salunke et al., 1991; Shewfelt, 1986). The following subsections are devoted to the first three factors which are of major importance.

3.3.1 Effect of temperature

Temperature plays an important role in the storage life of vegetables and fruits. Respiration rate of the commodity depends largely upon the temperature at which it is stored. The lower the temperature, the lower the respiration rate. But some commodities are liable to chilling or freezing injuries and cannot be stored at very low temperatures, eg. tomato, banana, etc. Temperatures above the optimum range also reduce the storage life. The rate of deterioration increases by two-to-threefold (Table 3.1) for a rise of every 10°C above the optimum (Hardenburg, 1990; Kader, 1992).

Table 3.1. Effect of temperature on deterioration rate of a nonchilling sensitive commodity (Kader, 1992).

Temperature (°F)	Temperature (°C)	Assumed Q_{10}	Relative velocity of deterioration	Relative shelf life	Loss per day (%)
32	0		1.0	100	1
50	10	3.0	3.0	33	3
68	20	2.5	7.5	13	8
86	30	2.0	15.0	7	14
104	40	1.5	22.5	4	25

Field heat removal or harvesting at cooler temperature increases the shelf life. A proper refrigeration system maintains the temperature within the storage room.

3.3.2 Effect of relative humidity:

Most vegetables and fruits need relative humidity (RH) nearing saturation (Hardenburg, 1990; Raghavan et al., 1980). The commodity suffers water loss when stored below its optimum RH, which causes shrivelling and limping. High RH, above its optimum, may cause growth of microorganisms and hence, precautions are to be taken. The rate of water loss depends upon the vapor pressure deficit between the commodity and the surrounding ambient air, which depends upon the temperature and RH. Water loss at a given humidity increases with the increase in temperature (Kader, 1992). A loss of 5 to 10% of mass of the produce reduces the marketability of the produce (Salunke et al., 1991).

3.3.3 Effect of atmospheric gas composition:

The gas composition of storage air plays an important role in the preservation of the produce since it affects, and can be controlled to regulate, metabolic activity. The respiration rate (RR) of the produce can be reduced by reducing the O_2 level and/or increasing the CO_2 level in the storage room atmosphere, but is primarily controlled by lowering the O_2 level (Smock, 1979; Lipton et al., 1975). Adjustment or control of these gases may be done by several methods as will be discussed in section 3.9. Ethylene is another gas which affects metabolism and must be taken into consideration. Ethylene is in fact thought of as a ripening hormone by some, and can cause leafy vegetables to turn yellow, fruit vegetables to ripen, root vegetables and tubers to sprout, asparagus and beans to toughen, carrots to turn bitter, and lettuce to develop reddish spots (russet spotting) (AVRDC, 1990). This trace gas should therefore be removed from the storage atmosphere.

3.4 Respiration

Vegetables are living organisms which undergo biological processes associated with life. To sustain the activities, vegetables draw energy through respiration from the starch, sugars and other products of photosynthesis. The substances used for respiration

are continually replaced through photosynthesis when they are still attached to the plant. Once the vegetables are harvested, photosynthesis ceases and there is no replacement for the lost reserves; the biological process that keep the cell alive slows down and the cell structure breaks down. In other words, respiration is the process by which organisms convert matter into energy (Ryall and Lipton, 1979). It is a process of oxidative breakdown of organic matter present in cells such as starch, sugars, acids, fats, proteins, into simpler molecules such as CO_2 and H_2O along with the concurrent production of energy and other molecules which can be used by the cell for synthetic reactions (Wills et al., 1989). Though respiration is necessary to maintain tissue vigor it hastens senescence. Vegetable quality and food value deteriorates followed by death of cells. The RR increases with the rate of deterioration. Hence RR is a good index of the potential postharvest life of the vegetable.

Respiration occurring in the presence of oxygen is termed aerobic respiration and in the absence of oxygen is termed anaerobic respiration. The normal substrate for respiration is glucose, and the chemical reaction is given by the equation (Wills et al., 1989):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy \qquad (3.1)$$

In individual plant cells, this reaction is followed by a series of subreactions each of which result in the breakdown of more complex to simpler molecules using specific enzymes as catalyzers. The extent of respiration is measured by determining the amount of substrate loss, O_2 consumed, CO_2 liberated, heat produced, and energy evolved (Pantastico, 1975).

Anaerobic respiration occurs when the availability of O_2 is limited and insufficient to maintain full aerobic metabolism (Figure 3.1), resulting in the conversion of glucose into either lactic acid or acetaldehyde and ethanol, a process termed as fermentation. The O_2 concentration at which anaerobic respiration commences is known as the extinction point and varies between tissues. Anaerobic conditions result in a high respiratory quotient (Wills et al., 1989). Anaerobic respiration gives off an

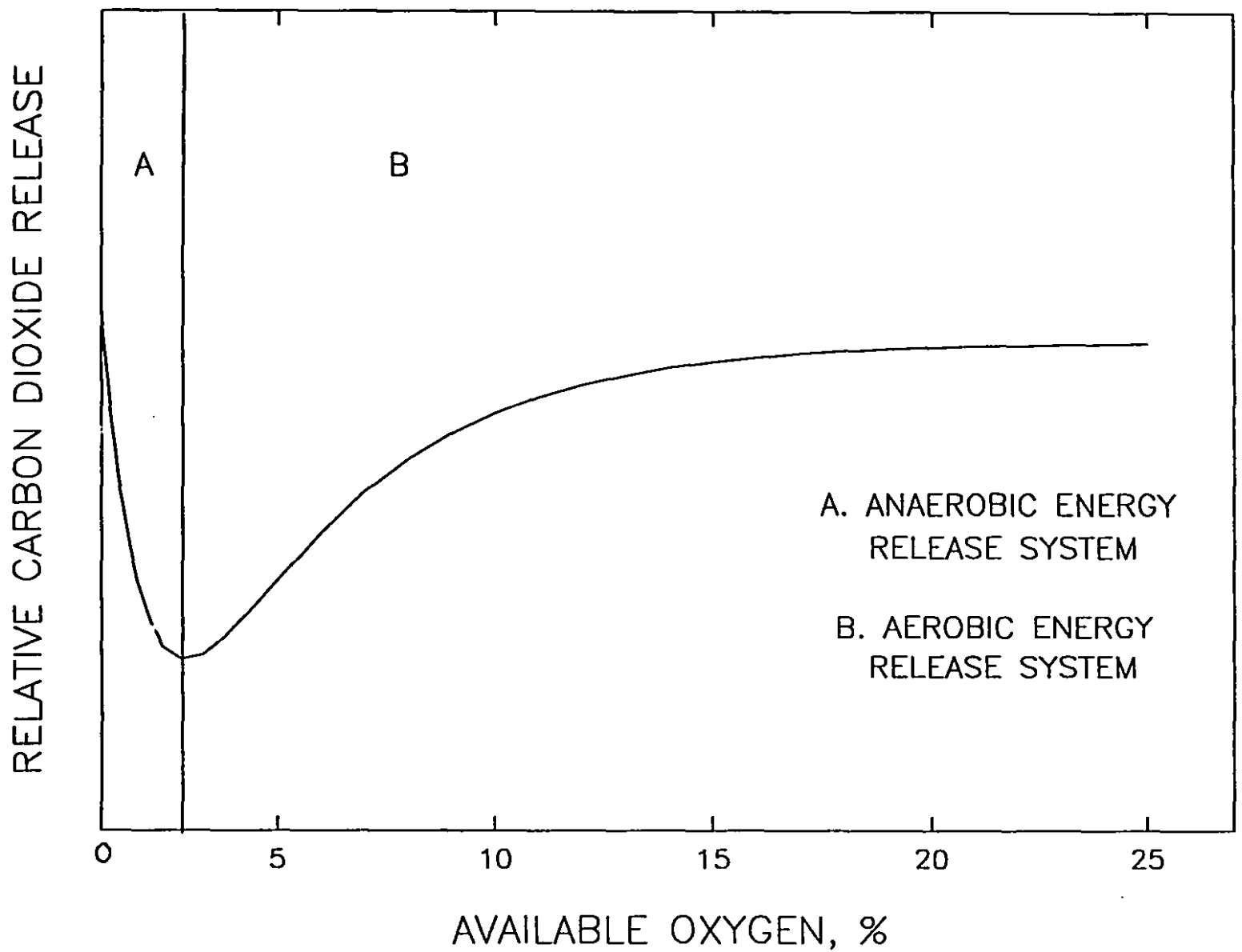

Figure 3.1. Relative amount of CO_2 produced as a function of the available O_2 Concentration (Gariepy, 1989).

alcoholic odor and an off-flavor to vegetables (Gariépy, 1988; and AVRDC, 1990).

3.4.1 Respiration Rate and Respiratory Quotient

The Respiration Rate (RR) is the mass or volume of CO_2 produced per unit of fresh weight/volume for an unit of time (mg or ml CO_2. kg^{-1}. h^{-1}). It may also be expressed in terms of O_2 consumption (mg or ml CO_2. kg^{-1}. h^{-1}), or heat liberated per unit weight of the produce in a given time (kcal. ton^{-1} (produce). day^{-1})[1] (Ryall and Lipton, 1979). Though, higher RR means faster quality deterioration, some commodities having the same RR have different storage life.

The condition of the respiratory reaction of the produce can well be explained by the Respiratory Quotient (RQ) value which is the ratio of CO_2 liberated to O_2 consumed (equation 3.2) during the respiration process (Wills et al., 1989).

The RQ is useful in determining the nature of the substrate used in respiration, completeness of the respiratory reaction, and degree of aerobic or anaerobic process (Pantastico, 1975). The RQ is close to unity when carbohydrate is the predominant substrate utilized for respiration. The RQ is above 1 (unity) when compounds that are partly oxidized, such as organic acids, are the substrate; and the RQ is less than 1, when fats, proteins or other highly reduced compounds are oxidized. Other conditions may cause large changes in RQ. High RQ may be the result of fermentation in a tissue; whereas a low RQ may be the result of partial oxidation of a substrate consuming O_2, producing substantial amount of energy but not releasing any CO_2. Retention of CO_2 or O_2 in the plant tissues could also result in misleading RQ values (Gariépy, 1988).

3.4.2 Factors affecting aerobic respiration

Because respiration is essentially a biochemical process, it depends on the following factors:

A. Primary:

---

[1] 1 mg CO_2. kg^{-1}. h^{-1} = 0.00255 kcal. kg^{-1}. h^{-1} = 61.2 kcal. ton^{-1}. day^{-1}

(1) Temperature:

The RR increases with the increases in temperature.

(2) Commodity:

Different commodities have different RR.

(3) Variety:

Different varieties of the same commodity may have different RR.

(4) Maturity:

The RR is high in the tender stage and gradually reduces as the plant matures.

(5) Nature of the substrate:

Oxygenated substrates such as organic acids require less O_2 (RQ > 1) whereas long chain fatty acids require more O_2 (RQ < 1) to be oxidized.

(6) Presence of CO_2:

High CO_2 levels suppress respiration.

(7) Availability of O_2:

O_2 levels above 20% do not increase the RR while levels below 20% decrease the RR; O_2 levels below the extinction point (minimum level for aerobic respiration, 2-3% for many vegetables) cause anaerobic respiration.

B. Secondary:

(1) Ethylene:

Ethylene even in trace amounts has great influence on the RR and ripening. It causes serious disorders in leafy vegetables and flowers even at very low concentrations (Ryall and Lipton, 1979). Climacteric fruits respire high and produce more ethylene at the time of ripening than the

non-climacteric fruits.

(2) Growth regulators:

Commodities sprayed with growth regulators may have increased RR but have longer storage lives than the non-sprayed ones.

(3) Others:

Stresses, injuries, infection etc., which cause damage to the tissue, increases physiological activity resulting in the loss of quality.

3.5 Storage Methods

Storage methods are broadly classified as natural and artificial (Raghavan and Gariépy, 1985; and Pantastico et al., 1975). In the natural method the product is left in the field as long as possible to mature by delaying harvest. In the artificial method the product is stored in favourable conditions so that the quality is maintained for a longer period. By modifying the temperature, relative humidity and gas composition, storage life of vegetables can be prolonged (Gariépy and Raghavan, 1985).

The artificial storage methods can be further classified as (Raghavan and Gariépy, 1985):

(1) Air-cooled storage,

(2) Mechanically refrigerated storage,

(3) High relative humidity storage,

(4) Controlled atmosphere storage.

The first three methods are referred to as conventional methods and have in common the limitation that respiration rates are reduced only to levels possible by temperature reduction. CA storage can reduce metabolic activity even further at a given temperature, even at the 'best' low temperature. The advantages of CA are discussed below.

3.6 Controlled Atmosphere Storage system

3.6.1 Introduction

The CA storage is considered to be the most important innovation in fruit and vegetable storage since the introduction of mechanical refrigeration (Salunkhe et al., 1991). Controlled Atmosphere (CA) storage is a technique of providing an atmosphere surrounding the produce which assists in maintaining the freshness and eating quality of the produce for significantly longer period than that stored in atmospheric air at the same temperature (Isenberg, 1979). Modified Atmosphere (MA) refers to the initial changes made in gas composition consistent with the expected requirements (Wolfe, 1980).

3.6.2 Controlled Atmospheres

CA consists of altering the atmospheric gas composition around the commodity, different from that of air (78.08% N_2, 20.95% O_2, 0.03% CO_2), normally decreased O_2 and increased CO_2, with low temperature and high RH, suitable to the commodity stored. Carbon monoxide (CO) is introduced, to a limited extent, for slowing down discoloration and controlling decay (Kader, 1992). The advantages of CA storage can be summarised as (Ratti et al., 1993; Gariépy, 1988; Smock, 1979; Lipton et al., 1975): (1) reduction of produce RR, (2) reduction of transpiration rate, (3) reduction of acidity losses, (4) preservation of chlorophyll levels, (5) retardation of pectic hydrolytic changes, (6) reduction of production of volatiles, and (7) reduction of fungal and bacterial infections.

However, progress in the utilization of CA for vegetables was slow due to the following reasons (Wills et.al., 1989; Isenberg, 1979; and Smock, 1979):

1) vegetables belong to a wide variety of plant structures with differing characteristics,
2) the metabolism of each plant structure differs under CA,
3) differences between cultivars, growing locations and conditions have critical effects on the usefulness of CA.

3.7 Storage of Vegetables in Controlled Atmosphere

CA storage is found effective in the storage of many vegetables and it generally results in reduced RR until O_2 and CO_2 levels are within the limits of tolerance of the produce (Barth, 1993; Gariépy and Raghavan, 1991, 1986, 1985; Kader 1986; Aharoni et al., 1985; Hudson and Lachance, 1985). The benefits derived from CA are longer duration of freshness and eating quality; retention of green color and other organoleptic characteristics; and reduction in losses from microbial or other disorders (Reeleder et al., 1989; Smith and Reyes, 1988; Smittle, 1988; Wang and Ji, 1988; Lipton and Mackey, 1987; Gariépy et al., 1984a, 1984b; Isenberg, 1979; Smock, 1979; Burton, 1974).

Kader (1986) notes that the effects of decreased O_2 and increased CO_2 on RR are additive i.e., an addition of 10% of CO_2 to the atmosphere has the same effect as a 2% of O_2 in the atmosphere on the respiratory metabolism and the combination of 2% O_2 + 10% CO_2 has approximately twice the effect. When O_2 levels are below 8% vegetables and fruits reduce their production as well as sensitivity to ethylene. Potatoes kept in 5% O_2 or more than 10% CO_2 are found to have reduced suberization and periderm formation (Lipton, 1975). The optimum conditions of CA storage are influenced by factors such as type of commodity, crop cultivation methods, cultivar, growing conditions, maturity, quality, temperature, relative humidity, and storage duration (Saltveit, 1985). The recommended CA conditions of some of the vegetables are given in Table 3.2.

When vegetables and fruits are exposed to O_2 levels below or CO_2 levels above their tolerance limits various physiological disorders are observed including impaired ripening in climacteric fruits such as tomato, melons, and plum; internal browning in lettuce, celery, cabbage, apple, pear, peach, and other commodities; external brown discoloration in tomato skin, pepper, and lettuce; and surface pitting in cucumber, mushroom, apple, and pear (Kader, 1986). CA is not recommended for garlic and horseradish (Saltveit, 1985) and some conflict exists about CA use for carrots.

Table 3.2. Recommended CA conditions during storage of selected vegetables (Kader, 1992)

Commodity	Temp. range (°C)	CA		Remarks
		% O_2	% CO_2	
Artichokes	0-5	2-3	2-3	No commercial use
Asparagus	0-5	air	5-10	Limited commercial use
Beans, snap	5-10	2-3	4-7	Potential for use by processors
Beets	0-5	None		98-100% rh is best
Broccoli	0-5	1-2	5-10	Limited commercial use
Brussels sprouts	0-5	1-2	5-7	No commercial use
Cabbage	0-5	2-3	3-6	Some commercial use for long-term storage of certain cultivars
Cantaloupes	3-7	3-5	10-15	Limited commercial use
Carrots	0-5	None		98-100% rh is best
Cauliflower	0-5	2-3	2-5	No commercial use
Celery	0-5	1-4	0-5	Limited commercial use in mixed loads with lettuce
Corn, sweet	0-5	2-4	5-10	Limited commercial use
Cucumbers	8-12	3-5	0	No commercial use
Honeydews	10-12	3-5	0	No commercial use
Leeks	0-5	1-2	3-5	No commercial use
Lettuce	0-5	1-3	0	Some commercial use with 2-3% CO added
Mushrooms	0-5	air	10-15	Limited commercial use
Okra	8-12	3-5	0	No commercial use; 5-10% CO_2 is beneficial at 5-8°C
Onions, dry	0-5	1-2	0-5	No commercial use; 75% rh
Onions, green	0-5	1-2	10-20	Limited commercial use
Peppers, bell	8-12	3-5	0	Limited commercial use
Peppers, chili	8-12	3-5	0	No commercial use; 10-15% CO_2 is beneficial at 5-8°C
Potatoes	4-12	None		No commercial use
Radish	0-5	None		98-100% rh is best
Spinach	0-5	air	10-20	No commercial use
Tomatoes,				
mature-green	12-20	3-5	0-3	Limited commercial use
partially ripe	8-12	3-5	0-5	Limited commercial use

3.8 Storage of Broccoli in Controlled Atmosphere

Broccoli (*Brassica oleracea L.*, Italica group) is a floral organ; the head consists of a mass of floral buds having deep green color. They are harvested when the floral buds have not opened, the stalk is tender, they are mild in flavor, and free of fibre (Isenberg, 1979). The RR of freshly harvested broccoli is very high, hence field heat removal is essential after the harvest. The RR of broccoli is 278-320 mg CO_2. $kg^{-1}.h^{-1}$ at 20-21°C and 19-21 mg CO_2. kg^{-1}. h^{-1} at 0°C. It has a storage life of 10-14 days at 0°C and 95-100% RH (Hardenburg, 1990). Fresh and good quality broccoli can be stored by adequate air circulation and spacing between containers, which are filled with crushed ice during transportation. As broccoli is a highly perishable product storage conditions greatly contribute to the visual and organoleptic qualities. Storage disorders which affect the market quality are discoloring of leaves, yellowing of inflorescences, opening and dropping of buds, toughening of stems, development of undesirable odors, soft rot, and mold (Ryall and Lipton, 1979; Makhlouf, 1989b). Yellowing is the major factor limiting the storage and shelf life of broccoli after harvest (Wang, 1979).

Modifying the atmosphere (CA/MA) decreases the RR of broccoli (Barth et al., 1993; Lee et al., 1991; Forney, et al., 1989; Lebermann et al., 1968). Lebermann et al. (1968) reported that RR was reduced by progressive increase in CO_2 and decrease in O_2 levels. An atmosphere of 20% CO_2 & 21% of O_2 had the same effect on RR as one of 0% CO_2 & 2% O_2. O_2 consumption and CO_2 production were reduced by 30 to 40% in CA (Forney, 1989).

Lipton and Harris (1974) reported that O_2 at 1% or less inhibited yellowing of broccoli curds during storage at 5 or 7.5°C, and the effect persisted during their subsequent aeration at 10°C. Similar results were observed by Wang (1979).

It has been found that a CA of 10% CO_2 and/or 1% O_2 can increase the shelf life of good quality broccoli held above 5°C (Hardenburg, 1990). An atmosphere with CO_2 of 10% retards yellowing and toughening; 15% CO_2 has the same effect but induces persistent off-odours. An atmosphere of 1% O_2 retards yellowing, but 0.1 to 0.25% O_2 causes severe injury and result in off-flavours in cooked broccoli (Lipton and

Harris, 1976; Kasmire, et al., 1974)

Better retention of color and chlorophyll was observed by Lebermann et al. (1968) after 16 days of storage at 7°C, with increased CO_2 and lowered O_2. Bastrash et al. (1993) observed enhanced respiration of broccoli florets compared to the heads throughout the storage period; CA of 6% CO_2 & 2% O_2 was satisfactory for preservation of florets at 4°C, which helped in chlorophyll retention, delay of mold & undesirable odors, and reduced yellowing after florets were returned to air at 20°C.

Makhlouf (1989a) reported that the RR of broccoli increased gradually during senescence in air, reaching a maximum after 2 days and declining thereafter. Broccoli placed under 10% CO_2 & 20% O_2 showed the same climacteric-like increase, but was delayed by 1 day and was lower. Low O_2 of 2.5% in the absence of CO_2 considerably reduced the RR.

Makhlouf (1989b) found that a ratio of 6% CO_2 & 2.5% O_2 was good for maintaining the visual quality of broccoli beyond 4 weeks of storage at 1°C, which did not produce any unpleasant odors and disorders. An atmosphere containing 10% CO_2 was found good for an intermediate storage period, independent of O_2 level.

3.9 Atmosphere-Modification Techniques

Basically, CA consists of maintaining the optimum levels of O_2 and CO_2 suitable to the commodity. Several methods are available to reduce the O_2 level and increase the CO_2 level (Bartsch, 1992; Raghavan and Gariépy, 1985). O_2 concentrations can be reduced by purging with nitrogen, burning, using catalytic converters. Water, lime, and molecular sieves are used for scrubbing CO_2. Dry ice or pressurized cylinders are used for addition of CO_2. The above are known as active modification techniques, the advantage being the rapid establishment of the desired atmosphere. The passive or commodity-generated technique consists of allowing an appropriate atmosphere to evolve within closed chambers by the respiration of the produce and maintaining that atmosphere by selective permeability of the gases through membranes or by diffusion of gases through channels (Ratti et al., 1993; Zagory and Kader, 1988).

In the following sections some of the prominent CA storage systems will be described briefly.

3.10 Hypobaric storage:

Hypobaric storage or low pressure storage is a system in which pressure, air temperature, and humidity are precisely controlled; and the rate of air change in the storage environment is closely regulated. The principle of hypobaric storage is that the level of O_2 is directly proportional to the pressure inside the chamber. If a chamber is operated at one-tenth of an atmosphere (76mm of Hg), the partial pressure of O_2 is approximately 1/10 of normal. At lower chamber pressures, the partial pressure of water vapor makes up a larger percentage of the total pressure. The lower O_2 content helps in reducing the RR of the produce (Jamieson, 1980). The system consists of a reinforced, airtight, refrigerated room in which air is continuously removed by a vacuum pump. Depending upon the produce and the temperature, the system will operate at a constant pressure, usually in the range of 10 to 80 mm Hg (Raghavan and Gariépy, 1985). After obtaining the desired sub-atmospheric pressure, fresh humid air is admitted into the cold room at a rate of one to four air changes per hour.

The advantages of the system are:

(a) O_2 and RH levels can be maintained easily;

(b) Removal of by-products of metabolism such as CO_2, C_2H_4, and other volatiles;

(c) Can be used as a vacuum cooler; and

(d) Able to store non-compatible products.

The disadvantages are:

(a) The high cost of constructing an airtight chamber;

(b) Poor flavor of the stored produce;

(c) Unsatisfactory ripening after storage; and

(d) The impossibility to operate at functional levels of CO_2.

3.11 Membrane system

This system makes use of the differential gas permeability properties of certain polymers to allow the selective passage of gases at different rates (Plasse, 1987). The silicone membrane (Figure 3.2), which is the basis of the systems to be described in the below subsections, consists of a fine nylon fabric (52 to 54 g/m^2) covered with a thin and uniform layer (about 90 microns, $80g/m^2$) of silicone rubber compound: dimethyl-polysiloxane (Gariépy et al., 1988). The silicone coating regulates the gas permeability whereas the nylon net provides the mechanical strength to the membrane. Its permeability to CO_2 at one atmosphere is 1750 L d^{-1} m^{-2} Atm^{-1} with CO_2 :O_2 and CO_2 :N_2 selectivity ratios of 6 and 13, respectively (Gariépy, 1988).

3.11.1 The Pallet Packaging System:

Marcellin developed the first commercial silicone membrane system called as "The Pallet Package System" for long term storage of fresh produce (Raghavan and Gariépy, 1982). It consists of a pallet box wrapped in a heavy gauge polyethylene bag on which a silicone membrane window was fixed to regulate the gas exchange.

The advantages of the system are:

(a) Ease of manipulation of the gases;

(b) No necessity of construction of special chambers and special equipments to create controlled atmosphere; and

(c) The possibility to market the produce progressively without affecting the CA within the remaining pallet boxes.

The disadvantages are:

(a) Pallets wrapped with the plastic and membrane are to be spaced apart to obtain the full advantage, thereby reducing the storage capacity of the cold room;

(b) Amount of time required to wrap and unwrap each pallet; and

(c) Special care required to handle the pallet boxes.

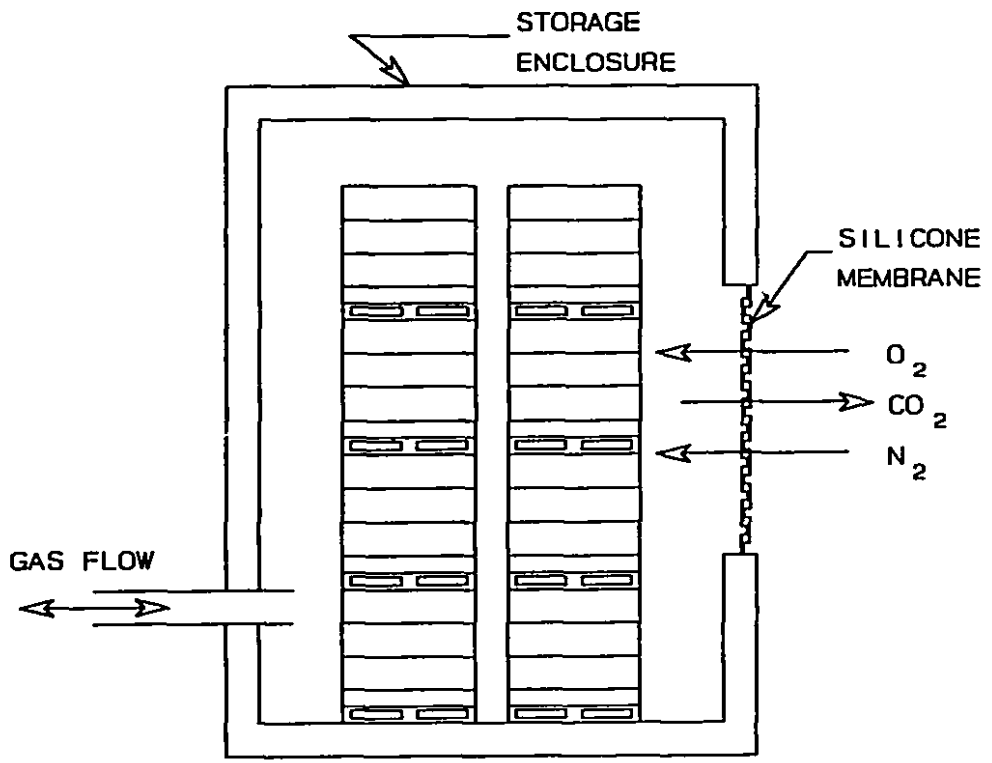

Figure 3.2. Schematic of a Membrane CA storage system.

3.11.2 The Marcellin System:

In this system CA condition in storage room is created by using a series of rectangular bags of silicone rubber connected in parallel (Figure 3.3). The number of bags used in the system depend on the capacity of storage room, the temperature and the nature of the produce stored. The units can be installed inside or outside the CA room. When the unit is exposed to the ambient air, the CA circulates inside the silicone rubber bags. Number of silicone bags to be added or removed can be determined by analyzing the gas composition. To create a CA of 3% O_2 and 3% CO_2, 50 m^2 of silicone membrane is required per 100t of fruit at a bulk density of 200 to 250 kg/m^3 (Gariépy et al., 1988).

3.11.3 The Atmolysair System:

A modified version of the Marcellin system was developed by Atmolysair in Canada (Figure 3.4). The unit consists of gas diffusion panels enclosed in an airtight metallic container with two separate air flow paths and a control panel (Gariépy, 1988; Raghavan, et al., 1984). The gas diffusion panels are made of square frames on which the silicone membrane is fixed. The stacks are so placed side by side in an airtight arrangement that the outside air and the CA flow on opposite sides of the membrane without direct mixing. Two centrifugal blowers operated by a timer circulate the CA and outside air separately. Analysis of the gas composition guides the time of operation of the blowers.

The advantages of this system are:

(a) Ease of operation;

(b) Better gas exchange due to the control of both air streams and its potential for complete automation.

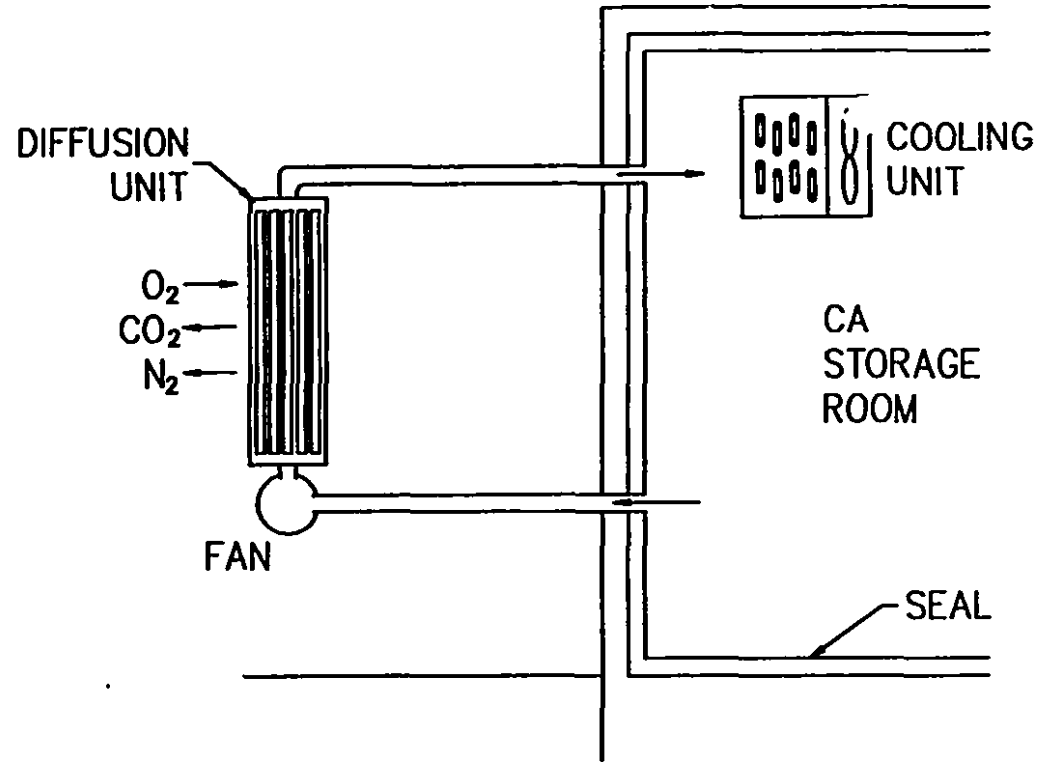

Figure 3.3. Schematic of Marcellin System installed outside CA storage room.

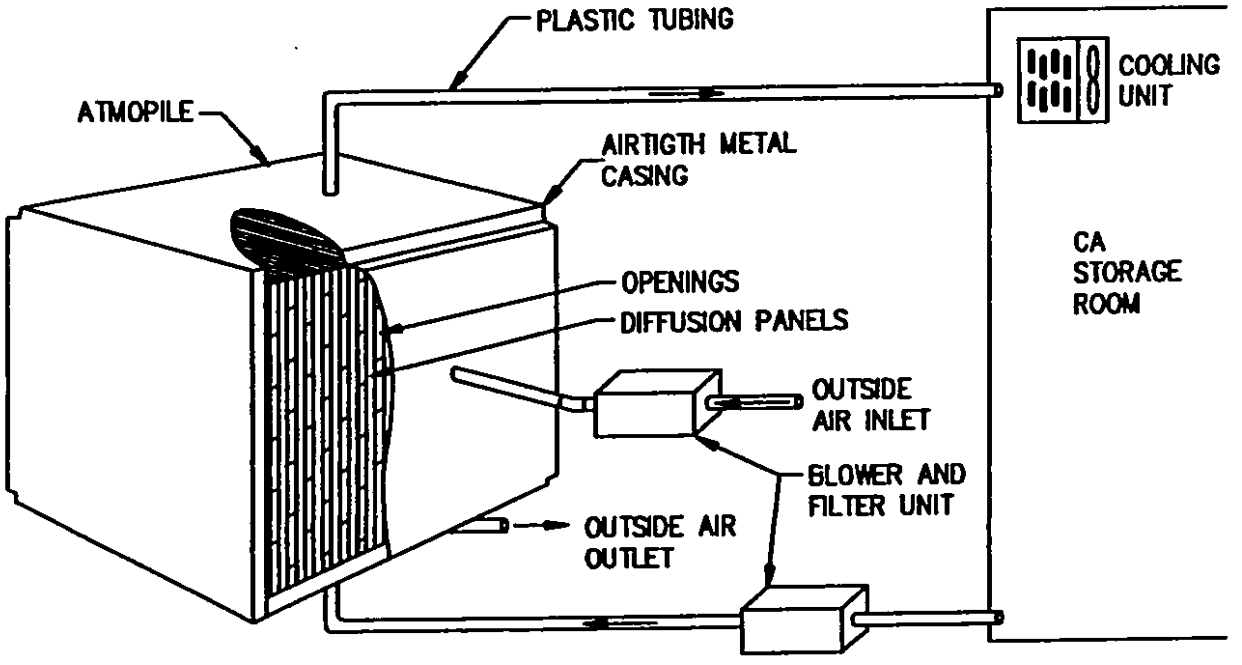

Figure 3.4. Schematic of Atmolysair System for CA storage (Raghavan and Gariépy, 1982).

3.12 Diffusion Channel System

This system is based on the principle of diffusion of gases through channels. Fick's first law of diffusion states that a species of gas diffuses in the direction of decreasing mole fraction of the same gas, just as heat flows by conduction in the direction of decreasing temperature (Bird, 1960).

The commodity is stored in a closed chamber which is connected to ambient air through a hollow channel (or tube), which is termed as "diffusion channel". During the respiration of the commodity, O_2 is consumed and CO_2 is liberated, resulting in a change of concentration of O_2 and CO_2 inside the chamber. The concentration of O_2 decreases and that of CO_2 increases with respect to ambient air at rates depending on the RR and RQ of the produce. This creates concentration gradients through the channel such that O_2 diffuses from outside the chamber to inside, and CO_2 diffuses from the chamber to the outside through the channel (Figure 3.5). The maintenance of required steady-state concentration levels of gases inside the chamber depend upon the mass of the commodity stored, RR, RQ, and the rate of diffusion of the gases. The rate of diffusion depends upon the length and cross-sectional area of the channel and the difference in concentration of O_2 and CO_2 between the chamber and the ambient air as created by metabolic activity of the produce.

Baugerod (1980) has shown that in rooms which are sufficiently airtight, the necessary exchange of CO_2 and O_2 can be achieved by fibre-filled channels of varying cross-sectional area through the walls of the room and connecting the room with a vessel containing a CO_2-absorbing material. He was able to maintain a gas composition of 1 to 2% O_2 and 10% CO_2 for several weeks without adjustments and stated that it was insensitive to changes in barometric pressure and cyclic fluctuations of the temperature in the storage room.

Emond et al., (1991) studied the gas exchanges through a perforation (which can be considered as channel of zero length) and developed a model to predict the gas exchanges through the perforation. Ratti et al. (1994) studied the influence of channel lengths on the final O_2 concentration in the storage chamber.

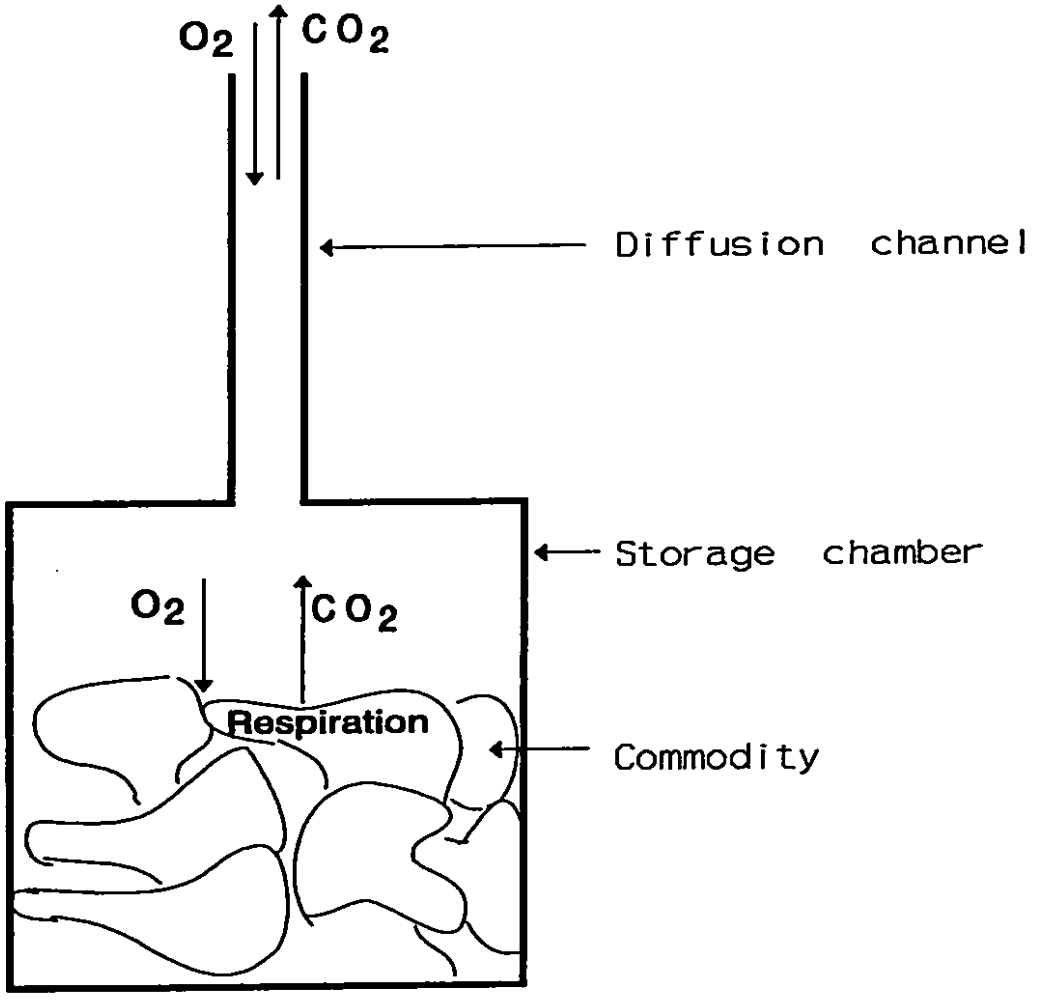

Figure 3.5. Schematic of diffusion of gases through Diffusion Channel during vegetable storage.

The advantages of this system of gas control are:

(i) the channels can be made of any impermeable membrane and maintenance is minimum,

(ii) the concentration level of O_2 can be maintained at the desired level,

(iii) desired levels of CO_2 can be achieved by appropriate scrubbing scheme.

Further research is needed in this field to establish, for particular commodity, the length and cross sectional area of the channel; or the number of channels required; the placing of the channels with consideration of the storage space, type of produce stored, mass, RR, temperature and other parameters.

IV THEORY AND MODELLING

4.1 Introduction

Respiration is a complex process involving a series of enzymatic reactions. Modelling this process involving all the factors would be difficult (Lee et al., 1991; and Zagory and Kader, 1988). Nevertheless, a number of simplified models of gas exchange have been developed and found to be useful even for a complex biological system (Emond et al., 1991; Cameron et al., 1989; Henig and Gilbert, 1975; Hayakawa et al., 1975).

4.2 Modelling the Respiration Rate

A mathematical model was developed for simulating the gas exchange of a fresh produce package by Hayakawa et al. (1975). The model takes into account the effect of atmospheric CO_2 and O_2 concentrations on the post-climacteric respiration rates of both O_2 consumption and CO_2 evolution by fresh produce. Changes in RR were approximated with the combination of two linear equations developed to determine RR.

Rate of O_2 consumption:

$$R_{y_i} = o_i\, y + p_i\, z + q_i \qquad (4.1)$$

Rate of CO_2 evolution:

$$R_{z_i} = d_i\, y + e_i\, z + f_i \qquad (4.2)$$

for which,

$y_{i+1} < y < y_i$;

$z_i < z < z_{i+1}$; $\quad (i = 0, 1, 2, \ldots\ldots, n)$, and

where,

$R_{y,z}$ = RR, (cc (CO_2 or O_2). $kg^{-1}.h^{-1}$)

y = volumetric concentration of O_2

z = volumetric concentration of CO_2, and

d, e, f, o, p & q = regression parameters for the approximation curves.

Hayakawa et al. (1975) derived analytical formulae for estimating transient and steady-state gas concentrations in a fresh produce package from the above equations.

Kok and Raghavan (1984) proposed a model for the rate of generation of CO_2 for apples as a function of temperature and of the partial pressures of O_2 and CO_2. The general form of the model was:

$$R_x = (a_1 + a_2 * y - a_3 * x) * (a_4 + a_5 * T) \quad (4.3)$$

where,

R_x = RR, (cc (CO_2). kg^{-1}. h^{-1})

T = temperature, (°C)

$a_1 ... a_5$ = constants

The values for the constants a_1 to a_5 were obtained using data from the literature. The rate of O_2 consumed by the product was assumed to be equal to the rate of production of CO_2 (i.e., RQ = 1) (Gariépy, 1988).

Plasse (1987) developed a statistical respiration model based on experimental data for celery, cabbage, rutabaga and leeks stored under different CA compositions.

Lee et al. (1991) developed a semi-empirical model to describe the RR of a produce as a function of O_2 and CO_2 concentrations based on the principles of enzyme kinetics. They used a Michaelis-Menten equation to model the RR. In the absence of CO_2, the dependence of respiration on O_2 concentration was modelled as:

$$r = \frac{V_m [O_2]}{K_m + [O_2]} \quad (4.4)$$

The dependence of respiration on CO_2 concentration was:

$$r = \frac{V_m [O_2]}{K_m + (1 + [CO_2] / K_i) [O_2]} \quad (4.5)$$

where,

r = RR (ml kg^{-1}. h^{-1} or mg kg^{-1}. h^{-1})

$[O_2]$ = O_2 concentration (%)

$[CO_2]$ = CO_2 concentration (%)

V_m = maximum RR (ml or mg kg^{-1}. h^{-1})

K_m = Michaelis-Menten constant (%O_2)

K_i = inhibition constant (%O_2)

Equation 4.5 is assumed to be valid as long as aerobic respiration takes place, i.e., sufficient O_2 is available to act as substrate.

Following the idea of the previous model Ratti et al. (1993) represented the respiration rate of cauliflower as a function of concentrations and temperature. The model developed was:

$$r = \frac{k_1 C_{o_2}}{[k_2 + (1 + k_3 C_{co_2}) C_{o_2}]} \quad (4.6)$$

where,

r = RR, (mg Kg^{-1}. h^{-1})

C_{O_2} = concentration of O_2, (mg/l)

C_{CO_2} = concentration of CO_2, (mg/l)

k_1, k_2, k_3 = constants (function of the temperature of reaction).

The effects of temperature were taken into account using an Arrhenius relationship. The functionality of the constants was expressed as:

$$k_i = k_{i\infty} \exp\left(-\frac{\Delta H_{ri}}{R\,T_r}\right) \tag{4.7}$$

where,

k_i = kinetic constants (i = 1, 2, 3)

ΔH_{ri} = activation energy of reaction (i = 1, 2, 3), (J. mol^{-1})

R = universal gas constant, (J. K mol^{-1})

T_r = temperature of reaction, (°C)

4.3 Modelling Diffusion of Oxygen through the Channel

Diffusion of the oxygen through the channel has been modelled by Ratti et al. (1994) from the molecular diffusion theory.

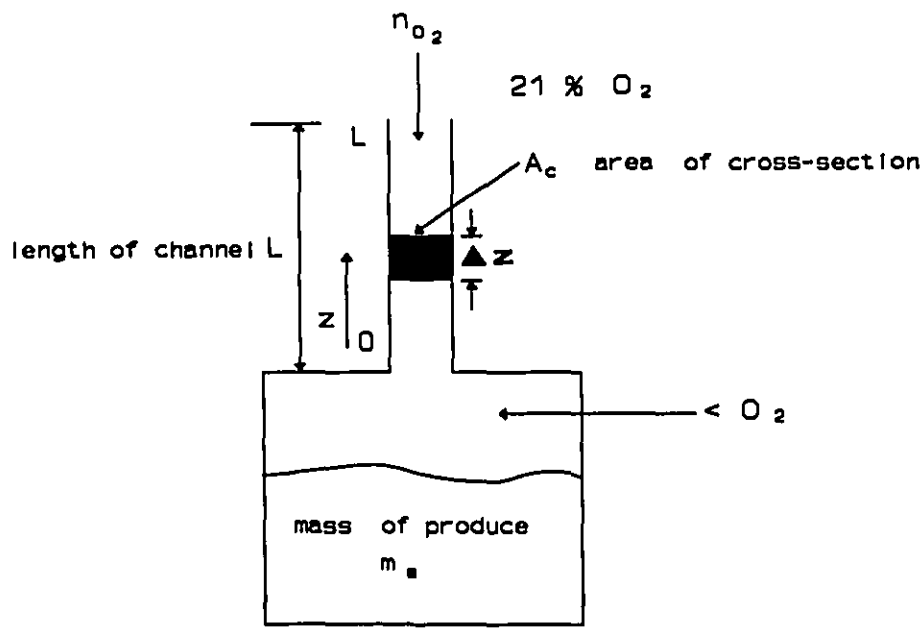

Figure 4.1. Schematic of diffusion process.

This model takes into account the functionality between the final O_2 concentration level in the storage chamber, the diffusion channel length, its cross sectional area and the mass of the produce.While modelling the process the following key assumptions have been made:

(a) The total pressure is constant at 1 atm.

(b) The temperature is constant.

(c) The oxygen concentration in the chamber is uniform at any time.

(d) The system is binary (only oxygen and nitrogen are diffusing; the CO_2 produced by the respiration of the commodity is chemically scrubbed).

(e) Diffusion is one-dimensional.

(f) The diffusivity of O_2 in nitrogen is constant.

The Fick's law of diffusion which gives the flux of a diffusing substance (O_2) in a stagnant gas (N_2), can be stated as:

$$n_{o_2} = - c\, D_{o_2\text{-}N_2} * \frac{dy_{o_2}}{dz} + y_{o_2}\, n_{o_2} \qquad (4.8)$$

where,

n_{O_2} = oxygen mass flux, (g. cm^{-2}. h^{-1})

c = total gas concentration, (mol. cm^{-3})

$D_{O_2\text{-}N_2}$ = diffusivity coefficient of O_2 in N_2, (cm^2. min^{-1})

y_{O_2} = oxygen mole fraction

z = spatial coordinate, (cm)

O_2 = oxygen

N_2 = nitrogen

The O_2 mass balance in an unsteady state in the control volume is given by:

$$\frac{\partial y_{O_2}}{\partial t} = D_{O_2 - N_2} * \frac{\partial^2 y_{O_2}}{\partial z^2} \tag{4.9}$$

The initial and boundary conditions are (Figure 4.1):

$$t = 0 \qquad y_{O_2} = (y_{O_2})_0 \tag{4.10}$$

$$z = L \qquad y_{O_2} = (y_{O_2})_{air} \tag{4.11}$$

$$z = 0 \qquad y_{O_2} = (y_{O_2})_{chamber} \tag{4.12}$$

In steady state conditions the time partial given in equation 4.9 becomes negligible.

The flux of O_2 given in equation 4.8 is then constant and its value can be obtained by its integration.

$$n_{O_2} * dz = -c \frac{D_{O_2-N_2}}{(1-y_{O_2})} * dy_{O_2} \tag{4.13}$$

Integrating between limits,

$$n_{O_2} \int_0^L dz = -c * D_{O_2-N_2} \int_{y_{O_2chamber}}^{y_{O_2air}} \frac{dy_{O_2}}{(1-y_{O_2})} \tag{4.14}$$

$$n_{O_2} = c * \frac{D_{O_2-N_2}}{L} * \ln \left[\frac{(1-y_{O_2air})}{(1-y_{O_2chamber})}\right] \tag{4.15}$$

Under steady-state conditions, the oxygen consumed by the commodity is equal to the oxygen diffusing through the channel, i.e.,

$$z = 0 \qquad n_{O_2} = \frac{r * m_s}{A_c} \tag{4.16}$$

where,

r = respiration rate, (mg O_2. kg^{-1}. h^{-1})

m_s = mass of produce stored, (kg)

A_c = cross sectional area of the diffusion channel, (cm^2)

Equating Equations 4.15 and 4.16, the Equation that gives the length as a function of concentration of oxygen, area of cross section, respiration rate and mass of the produce is obtained.

$$L = A_c * c * \frac{D_{O_2\text{-}N_2}}{r * m_s} * \ln\left[\frac{(1-y_{O_2,air})}{(1-y_{O_2,chamber})}\right] \quad (4.17)$$

The RR of a commodity as a function of O_2 concentration and temperature can be represented from Equation 4.6. When the effect of concentration of CO_2 was negligible, the RR was modelled by Ratti et al. (1993) as:

$$r = \frac{k_1 * C_{O_2}}{k_2 + C_{O_2}} \quad (4.18)$$

At steady-state,

$$y_{O_2} = \frac{C_{O_2}}{c} \quad (4.19)$$

where,

C_{O_2} = concentration of O_2 (mol. cm^{-3})

c = total gas concentration (mol. cm^{-3})

y_{O_2} = oxygen mole fraction

Equation 4.17 can be written as:

$$L = \frac{A_c}{m_s} * \frac{D_{O_2\text{-}N_2} * c\,[(k_2/c) + y_{O_2}]}{(k_1 * y_{O_2})} * \ln\left[\frac{(1-y_{O_2,air})}{(1-y_{O_2,chamber})}\right] \quad (4.20)$$

Replacing,

$$\frac{D_{O_2\text{-}N_2} * c}{k_1} = a_1 \tag{4.21}$$

$$\frac{k_2}{c} = a_2 \tag{4.22}$$

the constants a_1 and a_2 can be obtained through non-linear regression with experimental data.

The model to predict the length of diffusion channel is:

$$L = \frac{A_c}{m_s} * \frac{a_1 (a_2 + y_{O_2})}{y_{O_2}} * \ln \left[\frac{(1-y_{O_2 air})}{(1-y_{O_2 chamber})}\right] \tag{4.23}$$

where,

L = length of the diffusion channel, (cm)

A_c = cross sectional area of the diffusion channel, (cm^2)

m_s = mass of produce stored, (kg)

y_{O_2} = oxygen mole fraction

a_1, a_2 = constants.

V MATERIALS AND METHODS

5.1 Introduction

The experiments were conducted in two parts. The first part consisted of measuring the RR of broccoli stored in modified atmospheres at four temperatures ranging from 3 to 24°C, in order to determine the relationships between RR, temperature and concentrations of O_2 and CO_2. The temperatures selected would cover the range over which broccoli is likely to be exposed after harvest. The experimental results were to be used to provide parameters for the mathematical model.

The second part consisted of determining diffusion of O_2 through channels of different sizes and lengths into the storage chambers containing broccoli and study the steady-state levels of O_2 attained during the storage period. The results will be used to test the model (Equation 4.23) so as to predict the length or cross sectional area of the diffusion channel to obtain the desired O_2 gas concentration for a given mass of stored broccoli. The quality of broccoli in terms of moisture content, mass, color and mechanical properties was to be assessed before and after the storage.

5.2 Respiration Rate of Broccoli at Different Temperatures.

The experiment was conducted at temperatures of 3, 7, 13 and 24°C and performed in triplicate. The broccoli grown in Quebec was bought from a wholesale dealer. It was transported in cardboard boxes packed with crushed ice, was fresh and disease free and were stored in a cold room (2°C). Broccoli heads of relatively uniform in size were selected and trimmed by removing the loose leaves and cutting the stalk edges. The density of broccoli was determined by the method described by Stroshine and Hamann (1994).

A walk-in cold room of 4.5 X 3 m was used for the experiments. The temperature of the room could be maintained at the required level. Broccoli was allowed to reach the required storage temperature before starting the experiment.

5.2.1 Experimental Chambers.

The experiments were conducted by storing broccoli in experimental chambers. The chambers were made from sections of PVC pipe 500 mm long and 250 mm in diameter (Figure 5.1). The thickness of the pipe wall was 9.5 mm. The top and bottom ends of each chamber were closed with square lids of clear plexiglass of 6 mm thickness. The plexiglass allows visual inspection of the product inside the chamber at any time. They were held together by 6 threaded rods of 6 mm diameter. Neoprene gaskets were used on both ends of the chamber to provide an airtight enclosure. Two septa were located on the top lid with silicon paste to facilitate the withdrawal of gas sample from the chamber for analysis. The advantages of this design are ease of construction and durability. They provide near perfect airtightness allowing quick and easy opening and closing procedures as well as providing easy stacking and visibility to assess the product during storage.

All the experimental chambers were washed with chlorinated water (500 ppm) and tested for air tightness to detect any leaks before starting the experiment. The air tightness testing procedure was to increase the air pressure inside the chamber using an air pump. A pressure difference of 5 kPa was maintained between the outside and inside of the chamber for 15 minutes. The chamber was considered as air tight when there was no pressure drop during the test period. Pressures inside the chambers were measured with DPI 601 DIGITAL PRESSURE INDICATOR with a resolution of 0.05% in the range 1 to 3500 kPa.

Broccoli was weighed and stored in the chambers. The mass and volume of broccoli stored and the free (void) volume left in each chamber are given in Table 5.1. The chambers were closed by top lids and secured tightly by fastening nuts on the threaded rods. The temperature of the cold room was maintained constant throughout the experimentation period. The experiment ended when the O_2 levels decreased below 2%. The final pressure inside each chamber was measured at the end of the experiment.

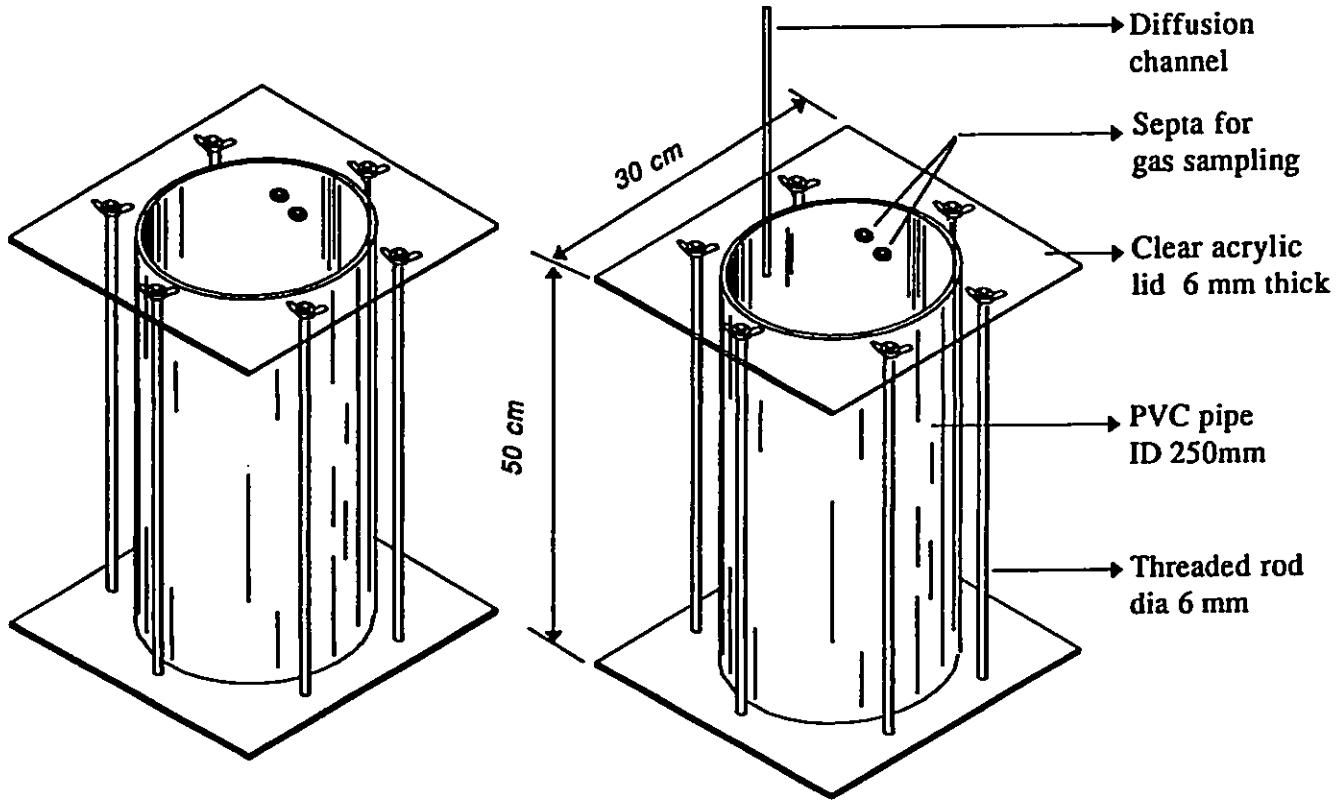

Figure 5.1. Schematic diagram of the experimental chambers with and without diffusion channel.

Table 5.1. Mass and volume of broccoli stored and free volume in the chambers.

Temp, °C	Chamber nos.	Broccoli		Free volume in the chamber, l^*
		Mass, g	Vol, l	
3	1	1871.03	2.02	22.35
	2	2069.59	2.24	22.13
	3	2000.26	2.16	22.21
7	1	2564.91	2.77	21.60
	2	2973.99	3.22	21.15
	3	3038.68	3.29	21.08
13	1	3806.47	4.12	20.25
	2	3794.55	4.11	20.26
	3	4109.28	4.44	19.93
24	1	1866.54	2.02	22.35
	2	1894.33	2.05	22.32
	3	1958.91	2.12	22.25

* Total volume of the experimental chamber, 24.37 litres.

Three gas samples of 0.5 cc were drawn periodically from each chamber through the rubber septa using syringes. The gas samples were analyzed for CO_2 and O_2 concentration using a gas chromotograph.

5.2.2 Gas Chromatograph

Gas analysis was done in an SRI 8610A Gas Chromatograph (SRI Instruments, US) equipped with thermal conductivity detector and operating at an oven temperature of 45°C and detector temperature of 100°C using helium as the carrier gas. Calculations of the concentrations of the gases were made with the 'Peak Simple'

software. Output from the detector was recorded with the SRI instrument 'Peak Simple' data system.

5.2.3 Determination of Respiration Rate

The parameters quantified to determine the RR and RQ are:

1. the mass of the stored product, m_s
2. the free or void volume in the chamber, V
3. the partial pressure inside the chamber at time t and $t+\Delta t$ (to calculate the mass of the gases)
4. the volume of O_2 & CO_2 at time t and $t+\Delta t$; $V_{O_2(t)}$, $V_{O_2(t+\Delta t)}$, $V_{CO_2(t)}$ and $V_{CO_2(t+\Delta t)}$
5. the mass of O_2 & CO_2 at time t and $t+\Delta t$; $m_{O_2(t)}$, $m_{CO_2(t)}$, $m_{CO_2(t+\Delta t)}$ and $m_{CO_2(t+\Delta t)}$.

The RR of the stored product based on the mass and volume of O_2 consumed or CO_2 evolved can be calculated using the following Equations (Gariépy and Raghavan, 1985):

$$RR_{O_2 mass} = \frac{-(m_{O_2(t+\Delta t)} - m_{O_2(t)})}{\Delta t * m_s} \quad (5.1)$$

$$RR_{O_2 vol} = \frac{-(V_{O_2(t+\Delta t)} - V_{O_2(t)})}{\Delta t * m_s} \quad (5.2)$$

$$RR_{CO_2 mass} = \frac{m_{CO_2(t+\Delta t)} - m_{CO_2(t)}}{\Delta t * m_s} \quad (5.3)$$

$$RR_{CO_2 vol} = \frac{V_{CO_2(t+\Delta t)} - V_{CO_2(t)}}{\Delta t * m_s} \quad (5.4)$$

Alternatively, the RR can be obtained by the concentrations of CO_2 or O_2 with time when the commodity is placed in a closed chamber:

$$r = \frac{dC_{O_2}}{dt}\frac{V}{m_s} = -\frac{dC_{CO_2}}{dt}\frac{V}{m_s} \quad (5.5)$$

where,

r = RR, (mg. kg^{-1}. h^{-1})

C_{O_2} = O_2 concentration inside the chamber, (mg/l)

C_{CO_2} = CO_2 concentration inside the chamber, (mg/l)

t = time, (h)

V = free volume of the chamber, (l)

m_s = mass of the stored product (kg)

5.2.4 Determination of Respiration Quotient

The RQ can be calculated using the Equation (Gariépy and Raghavan, 1985):

$$RQ = \frac{RR_{CO_2 vol}}{RR_{O_2 vol}} \quad (5.6)$$

5.3 Diffusion of O_2 through Channels

The experiment was conducted by storing broccoli in chambers having diffusion channels of different lengths and cross sectional areas, at 0°C. The channels consisted of three different cross sectional areas and six lengths, a total of 18 combinations (Table 5.2).

The experimental chambers used were similar to the earlier experiment except for the diffusion channels fitted to the top lid (Figure 5.1). The channels were prepared by cutting tubes of inner diameters 0.226, 0.478 and 1.21 cm and thereby obtaining three cross sectional areas of 0.04, 0.18, and 1.15 cm^2. The lengths of the channels were 3.0, 7.0, 12.0, 18.0, and 25.0 cm. The channels were rigidly fixed to the top lids of the chambers. Three lids were drilled with holes of above diameters which served as the channels of 0.6 cm long, 0.6 cm being the thickness of the lid.

Broccoli, grown in Quebec, was procured from a local wholesale dealer and prepared for storage as explained in the earlier experiment. Moisture content, color, and mechanical properties were measured at the beginning of the experiment. Moisture content of broccoli was determined by hot air oven method (Stroshine and Hamann, 1994).

3 kg (varied from 3.01 - 3.16 kg) of broccoli was placed in each chamber. To achieve a fast pull-down of O_2 inside the chamber, it was flushed with nitrogen (N_2) until the O_2 level was brought down to 2.5-3.5%. 250 g of hydrated lime was placed in each chamber to absorb the CO_2 released during the experimental period. The chambers were covered with the lids holding the diffusion channels and secured tightly. The length and cross sectional area of diffusion channel and mass of broccoli stored in each chamber is presented in Table 5.2.

Three gas samples from each chamber were analyzed daily. The experiment was conducted for six weeks, which is thrice the recommended storage period.

Table 5.2. Lengths and cross sectional areas of the diffusion channels fitted to the experimental storage chambers and mass of broccoli stored in each chamber.

Chamber	Area of cross section, cm^2	Length of channel, cm	Mass of broccoli, kg
1	0.04	0.6	3.15
2	0.04	3.0	3.09
3	0.04	7.0	3.09
4	0.04	12.0	3.07
5	0.04	18.0	3.12
6	0.04	25.0	3.07
7	0.18	0.6	3.16
8	0.18	3.0	3.11
9	0.18	7.0	3.13
10	0.18	12.0	3.14
11	0.18	18.0	3.01
12	0.18	25.0	3.05
13	1.15	0.6	3.07
14	1.15	3.0	3.01
15	1.15	7.0	3.01
16	1.15	12.0	3.10
17	1.15	18.0	3.06
18	1.15	25.0	3.06

5.4 Storage Quality

5.4.1 Mechanical Properties

Mechanical properties were determined with the Instron Universal Testing Instrument, Model 4502. A puncture test was performed with a probe of 11.3 mm dia at a loading arm speed of 25 mm/min. The test method was defined in the Instron Series IX software which is the data acquisition, control and analysis software for material testing. It is a comprehensive software package for use on MS-DOS compatible computers in combination with the Instron Testing Instrument. The test was performed on the stalk, one cm below the branching of limbs of flower head. The measurements were made before storage, as well as after storage, on four samples from each chamber.

5.4.2 Color Characteristics

Color was measured using the Minolta Chroma Meter CR-200b (Minolta Canada Inc., Canada) tristimulus color analyzer, to measure chromaticity in L, a, and b coordinates. L, a, and b represents the color characteristic value, hue, and chroma. The calibration of the Chroma Meter was done according to the manufacturer's recommendations, against a standard calibration plate with a white surface, with L, a and b values adjusted to 94.4, 0.313 and 0.320 respectively. The measurements were made on broccoli before storage, as well as at the end of the experiment, on three samples from each chamber, both at flower head and stalk portion.

5.4.3 Quality Evaluation

The mass of broccoli in each chamber was determined at the end of the experiment. Moisture content was determined. Visual observations were made to evaluate the quality of the broccoli taking into account softening and yellowing of flower head, and presence of microorganisms. A quality index (QI) ranging from 9 (highest quality) to 1 (lowest quality) was used to assess the product (Table 5.3)(Gariépy and Raghavan, 1986).

Table 5.3. Quality Index used to asses the overall quality of CA stored broccoli.

Quality Index	Quality Description	Visual Observations
9	Excellent	Field fresh dark green appearance; flower head and stalks firm & free from defects; minimal trimming required for marketing purposes.
7	Good	Presence of minor defects; slightly chlorotic and pale; light trimming required to improve appearance.
5	Fair	Moderate defects present on the flower heads and stalks; could be brought to acceptable condition with moderate trimming.
3	Poor	Rot and/or other serious defects; could be brought to acceptable condition with heavy trimming.
1	Unsaleable	Rot, mold and/or other serious defects; flower head and stalks soft and flappy; could not be brought to acceptable condition even with heavy trimming.

5.5 Modelling

The Equation 4.6 (section 4.2) was used for modelling the RR. In this case RR was calculated using the Equation 5.5. The mass of CO_2 evolved (inside the closed chamber) during the respiratory activity was determined and plotted as a function of time. Curve fitting was done using polynomial equations on Sigma Plot software. The fitted polynomial was differentiated to determine the numerical derivative present in the Equation 5.5. The RR was calculated in terms of mg CO_2. kg^{-1}. h^{-1} and the reaction at anaerobic conditions was not considered. The RR was plotted as a function of concentration of O_2. The model was then fitted to the data. The constants k_1, k_2, and k_3 were determined by non-linear regression with experimental data, using the Levenberg-Marquardt procedure for non-linear least squares as implemented in Sigma Plot (Jandel Corporation, 1992).

The Equation 4.3 (section 4.3) was used for modelling diffusion of O_2 through the channel. The constants a_1 and a_2 were determined through non-linear regression.

VI RESULTS AND DISCUSSION

6.1 Introduction

The results of progression of O_2 and CO_2 concentration inside the chambers as well as the RR and RQ of broccoli are discussed in section 6.2. The diffusion of O_2 through the channels is discussed in section 6.4. The modelling aspects of RR and diffusion are discussed in sections 6.3 and 6.5 respectively. Additionally, the quality aspects are discussed in section 6.6.

6.2 Respiration Rate of Broccoli at Different Temperatures.

The experiments were conducted at temperatures of 3, 7, 13, and 24°C. The variations of temperature in the storage room was ± 0.5°C. The RH levels inside the storage chambers were close to saturation as evidenced by the occurrence of condensation in all the chambers. The results are presented in the order of the designed temperatures; the average values of three replicates of each temperature are presented in Figures 6.1 - 6.6, whereas the values of each chamber are presented in the Appendix, Figures A.1-A.44.

6.2.1 CA progression in the Experimental Chambers

The gas composition in the storage chambers was analyzed periodically by gas chromatograph. The progression of O_2 and CO_2 concentration as a function of time is presented in Figures 6.1 and 6.2.

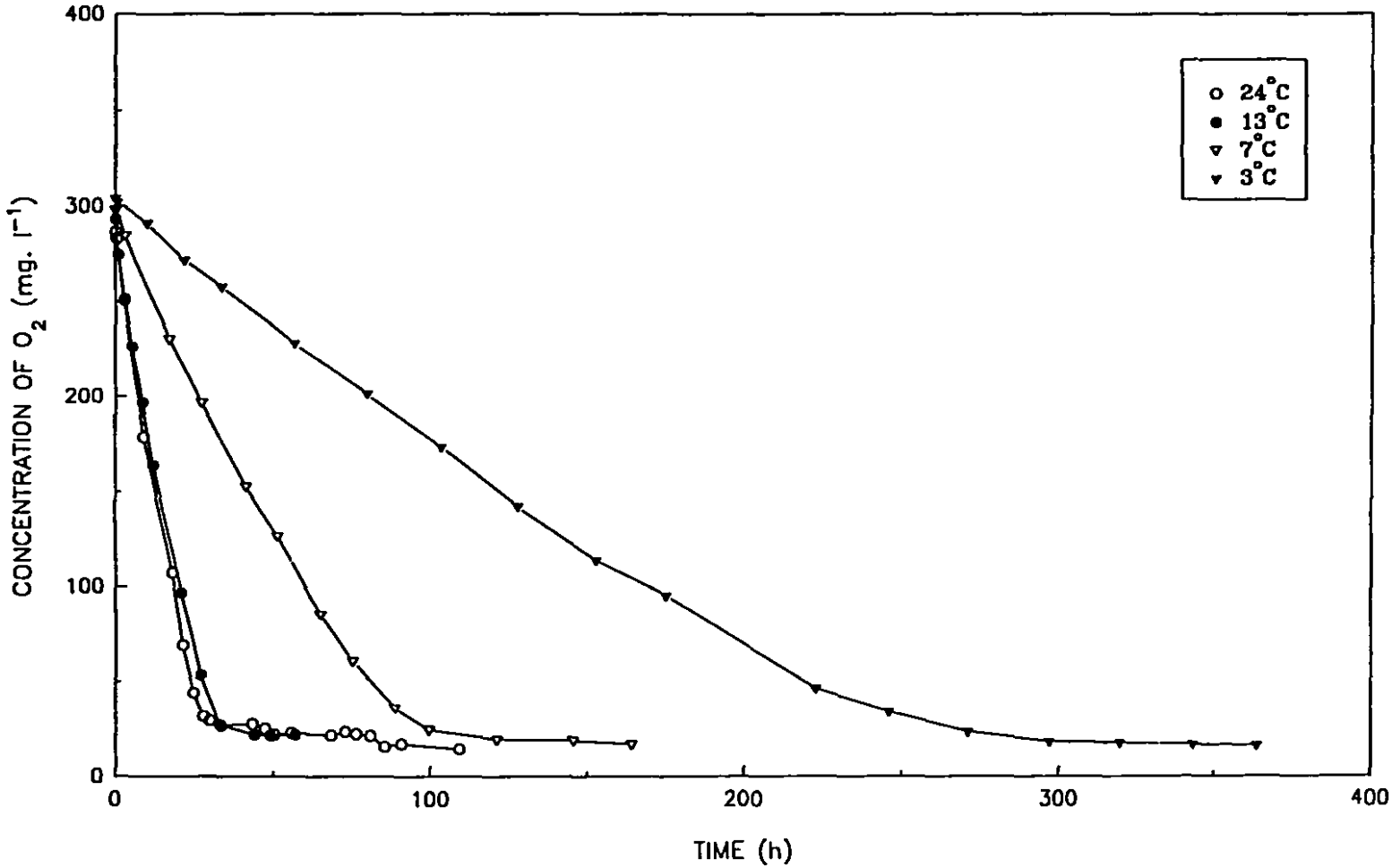

Figure 6.1. Progression of O_2 Concentration as a function of time in sealed chambers containing broccoli at specified temperatures.

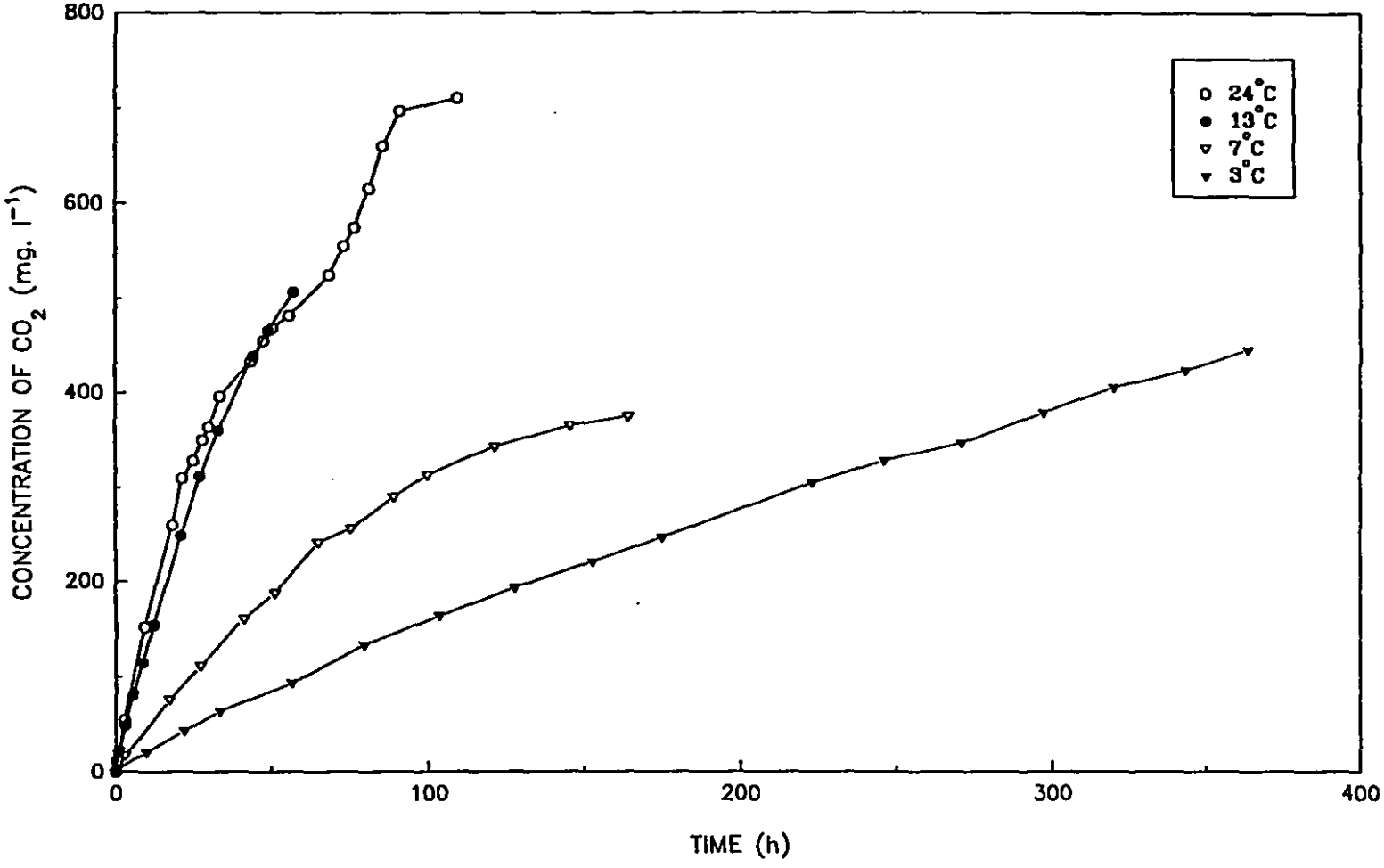

Figure 6.2. Progression of CO_2 Concentration as a function of time in sealed chambers containing broccoli at specified temperatures.

Experimental results clearly indicate the high rate of respiration at high temperature causing faster depletion of O_2 and increase of CO_2 inside the closed chambers which agrees well with the published literature. The data shows that the respiratory reactions were low at low temperature and hence the changes in gas composition inside the chambers were also slow. As observed in Figure 6.1 the consumption of O_2 was high at 24°C compared with the other temperatures; the concentration of O_2 dropped from 300 mg. l^{-1} (21%) to 25 mg. l^{-1} (2%) within 28 hours at 24°C and 33 hours at 13°C, whereas it took 100 and 260 hours to drop to the same level at 7 and 3°C respectively. The consumption of O_2 was almost constant when the O_2 concentration was below 2%, indicating that conditions were near anaerobic inside the chambers. This behaviour was observed at all temperatures. As shown in Figure 6.2, the evolution of CO_2 was high at higher temperatures as expected; the CO_2 concentration reached 370 mg. l^{-1} (20%) from the initial zero level within 30 hours at 24°C and 48 hours at 13°C, whereas it took 165 and 340 hours to reach the same level at temperatures of 7 and 3°C respectively.

6.2.2 RR and RQ progression in the chambers

The results clearly indicate the influence of temperature on RR (Fig 6.3). The RR was high at higher temperatures which is in conformity with the published literature. The results also demonstrate the beneficial effects of CA; the RR decreased with the environment of modified atmosphere (increasing CO_2 and decreasing O_2) which agrees with the findings of Barth, (1993), Lee et al. (1991), Singh et al. (1972). The changes in the RR (mg CO_2. kg^{-1}. h^{-1}) of broccoli as a function of time are presented in Figure 6.3. At 24°C, the RR decreased from 340 to 60 mg CO_2. kg^{-1}. h^{-1} in 25 hours, demonstrating the fast rate of change of gas composition inside the chambers and the creation of a CA condition which reduced the respiratory reactions. At 13°C, the RR reduced from 115 to 60 mg CO_2. kg^{-1}. h^{-1} in 8 hours and gradually reduced to 25 mg CO_2. kg^{-1}. h^{-1} in the next 48 hours. It took about 100 hours to reduce from 40 to 10 mg CO_2. kg^{-1}. h^{-1} in the case of 7 and 3°C.

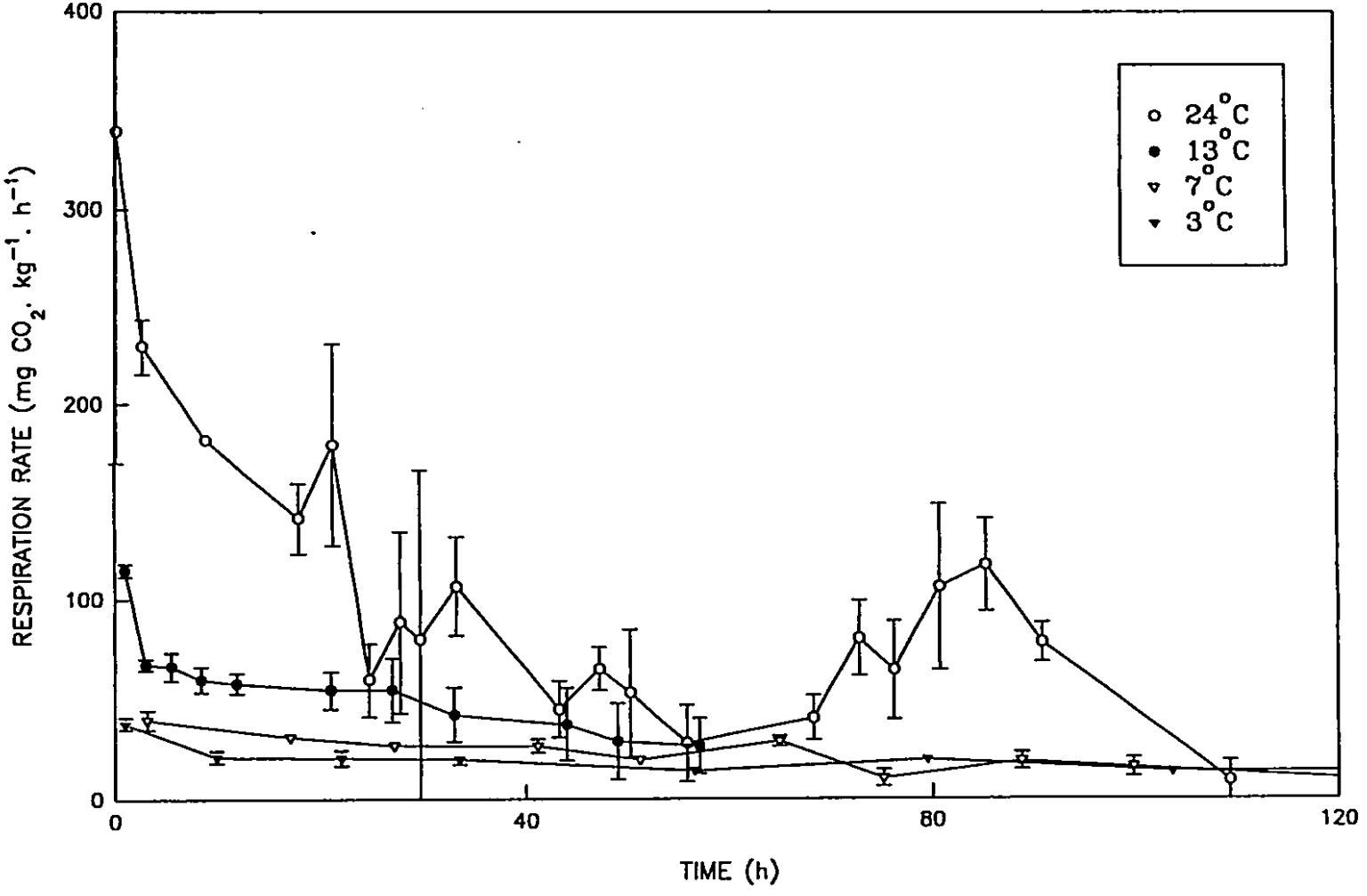

Figure 6.3. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at specified temperatures.

The results also indicate the effect of temperature on RR. The RR was 40% lower at 13°C than at 24°C. Similarly, it was 30% lower at 7°C than at 13°C, 45% lower at 3°C than at 7°C. This also agrees with the published literature (Kader, 1986). The results indicate the importance of creating the CA/MA environment around the produce at the beginning of storage, which helps in the fast reduction of RR, the main criteria in extending the shelf life of fresh produce.

Although the trend of decreasing RR with time (because of the changes in gas composition inside the chambers) was visible, fluctuations in RR were observed (Figure 6.3). The reasons may be that the RR and the metabolic pathway of respiration are subject to both internal and external influences (section 3.4.2) and the RR is sensitive to changes in O_2 concentration below about 8% and CO_2 above about 1% (Zagory and Kader, 1988). The results presented in Figure 6.3 reflect the sensitivity of RR to temperature. The standard deviations are high at 24°C whereas the deviations decrease in dimension at low temperatures.

RR as a function of concentration of O_2 and CO_2 are shown in Figures 6.4 and 6.5. RR decreased with the decrease of O_2 concentration. The shape of the curve represents the enzymatic reaction of respiration. The RR was maximum at high O_2 concentration and fairly constant over a wide range of concentration and decreased towards zero at low O_2 concentration. RR decreased with the increase of CO_2 concentration (Figure 6.5). Large fluctuations in RR were observed towards the end of the experiment in case of broccoli stored at 24°C. This is attributed, as mentioned earlier, to the development of anaerobic conditions when the O_2 level is reduced or CO_2 level increased beyond the tolerance levels of the commodity.

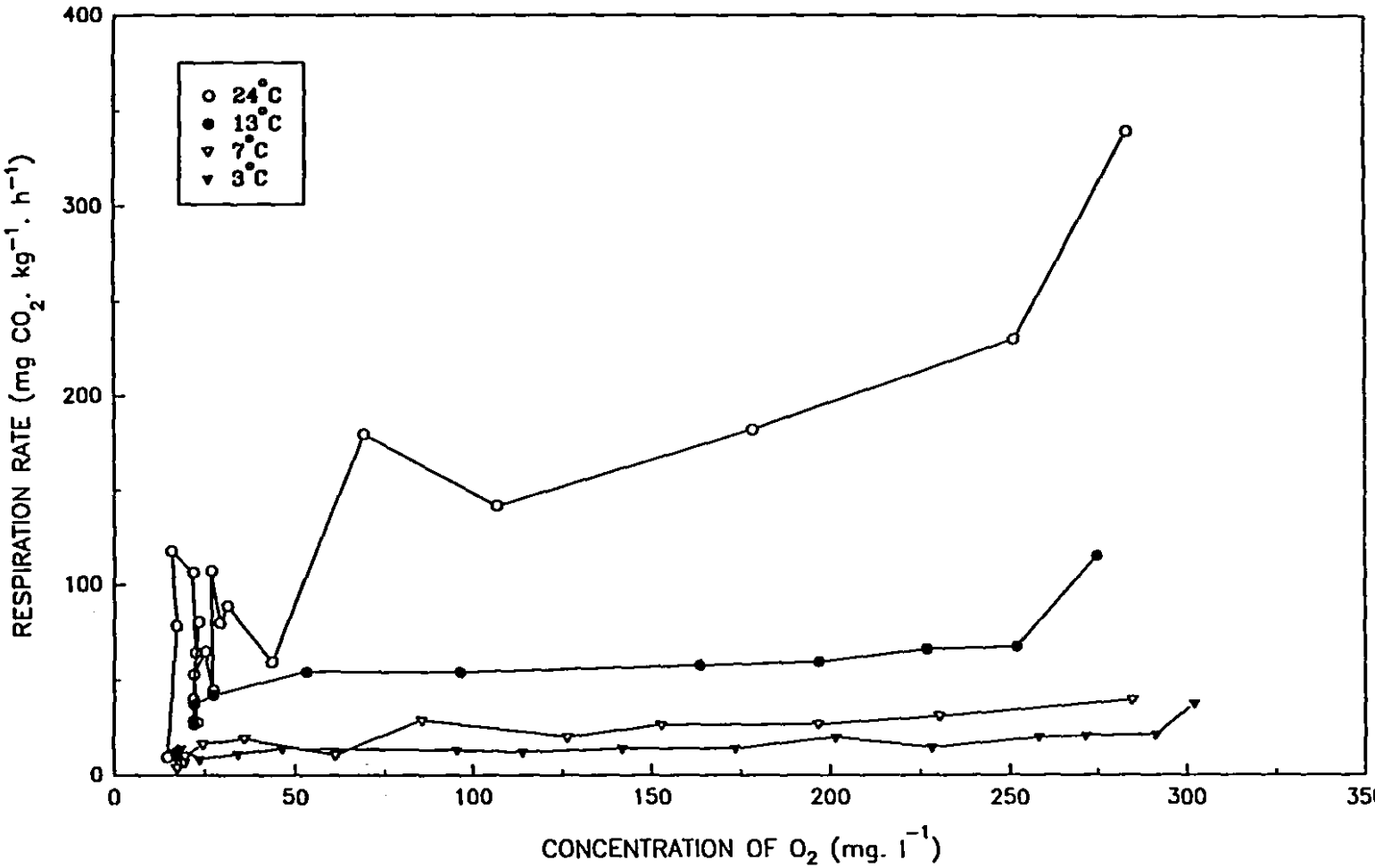

Figure 6.4. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at specified temperatures.

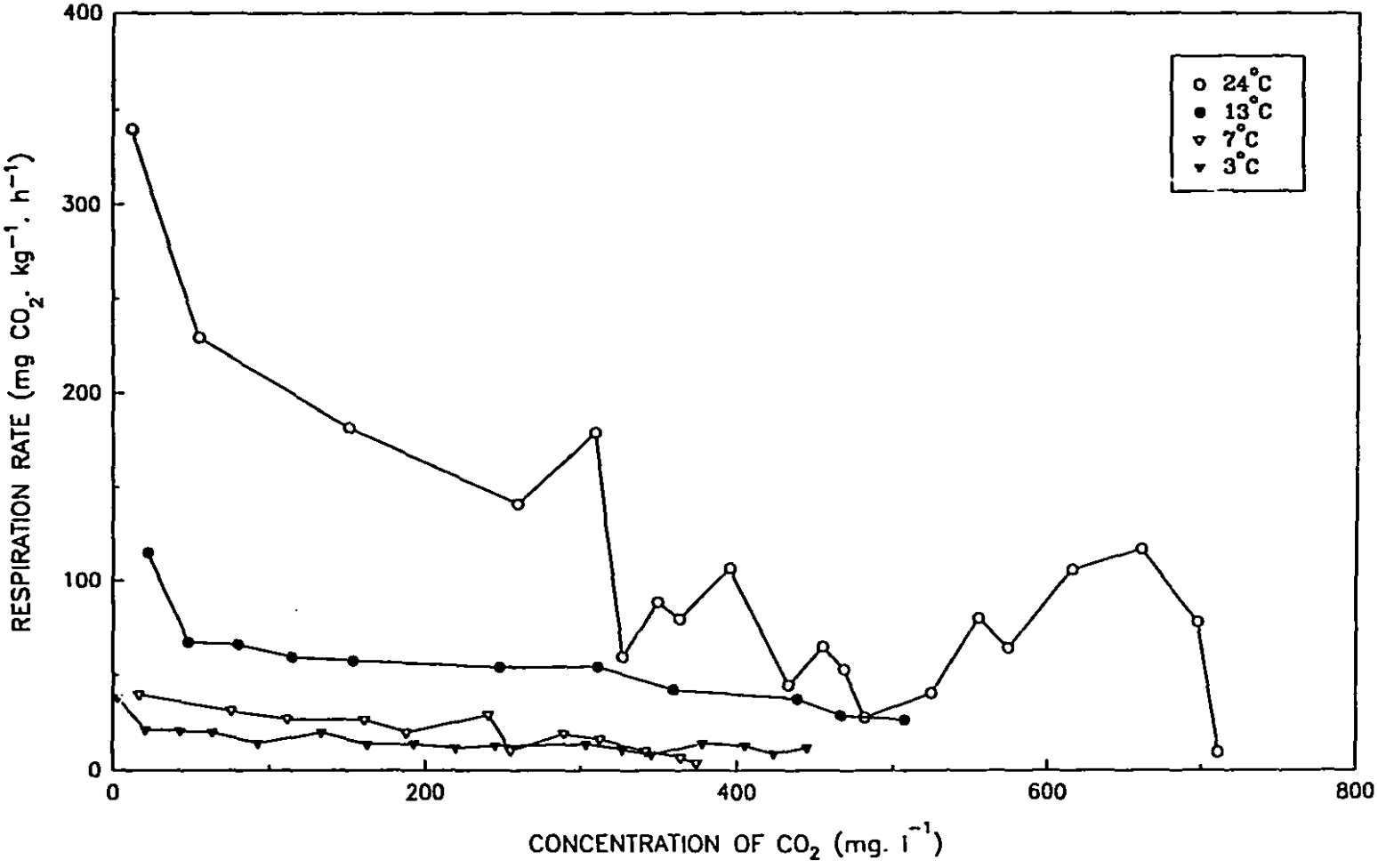

Figure 6.5. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at specified temperatures.

The progression of RQ as a function of concentration of O_2 is presented in Figure 6.6. The average RQ was found to be 1.0, 0.8, 0.8, and 1.0 at the storage temperatures of 3, 7, 13, and 24°C respectively, till the concentration of O_2 reached a level of about 50 mg. l^{-1}. These are similar to values reported by Zagory and Kader, 1988. Abnormal behaviour was observed at all temperatures for O_2 levels below 50 mg. l^{-1}. This behaviour may be attributed to the fermentation of broccoli tissues or retention of O_2 or CO_2 in the tissues (Gariépy, 1988) during the anaerobic conditions created inside the chambers. The RQ is found to be affected by the MA conditions of reduced O_2 and high CO_2 levels; and changes in RQ in turn affect the atmosphere created through respiration.

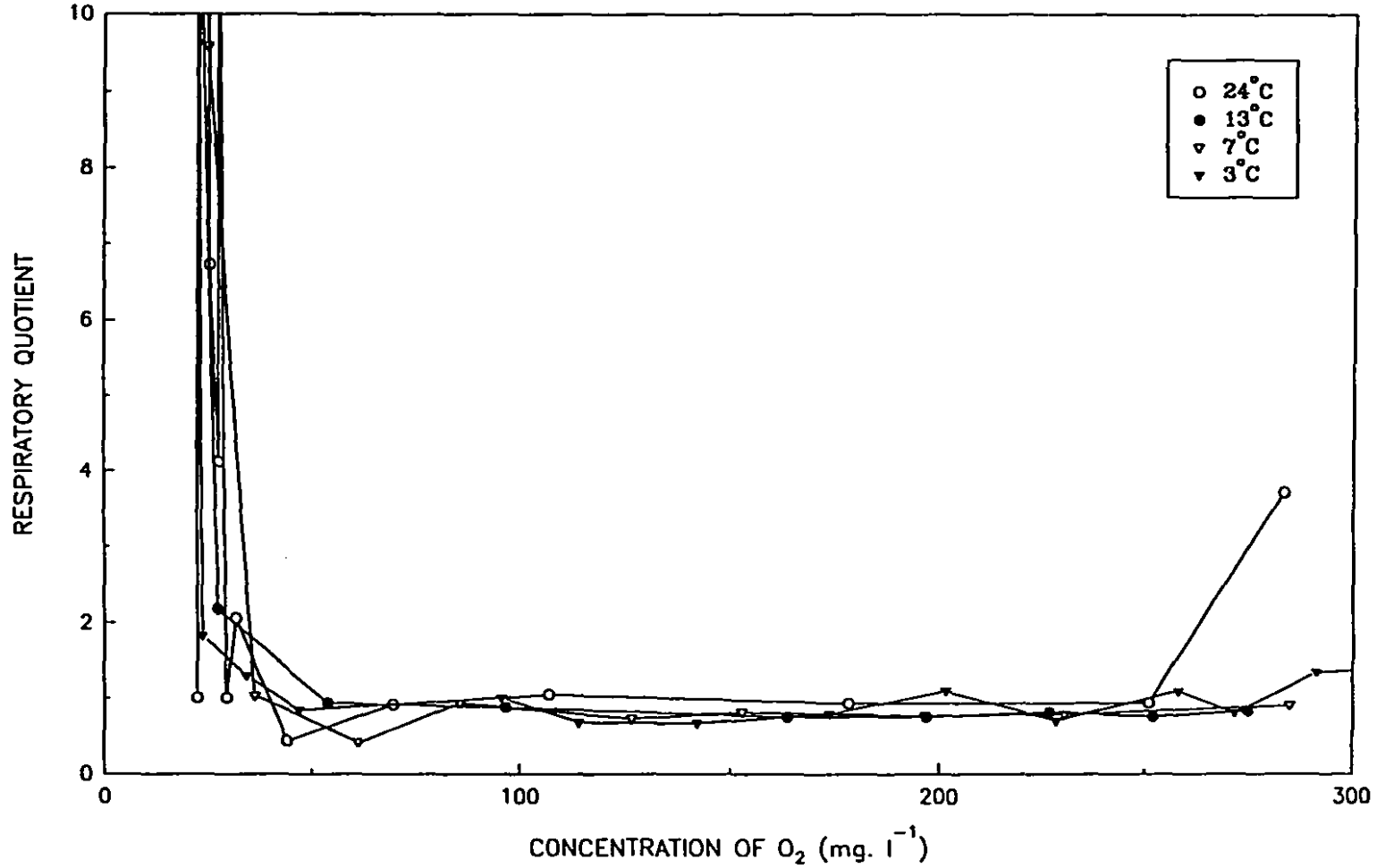

Figure 6.6. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at specified temperatures.

6.3 Modelling of Respiration Rate

The Equation 4.6 was fitted to the experimental data. The constants k_1, k_2, and k_3 determined by non-linear regression are presented in Table 6.1.

Table 6.1 Respiration rate model constants k_1, k_2, and k_3 derived from the experimental data for temperatures 3, 7, 13, and 24°C.

Temp, °C	k_1	k_2	k_3
3	45.67	319.07	~0.00
7	58.33	165.65	~0.00
13	83.12	64.13	~0.00
24	153.32	12.44	~0.00

The value of k_3 was almost zero which indicates that the influence of the concentration of CO_2 on RR was negligible and therefore that the RR of broccoli is mainly a function of O_2 concentration. The results confirm the earlier reports found in literature that the RR of fresh fruits and vegetables is reduced when CO_2 concentration levels are about 20% or higher (Kader, 1986). Similar results were obtained by Ratti et al. (1993) in case of RR of cauliflower.

The modified model is:

$$r = \frac{k_1 C_{O_2}}{[k_2 + C_{O_2}]} \qquad (6.1)$$

The predicted results as well as the experimental results are presented in Figure 6.7. There is a very good agreement between the experimental and predicted results. The small variations observed at low concentrations of O_2 may be due to the nearing anaerobic conditions created inside the chambers and which must be prevented during storage. The proposed model provides an accurate and rapid predictions of RR of broccoli in modified atmospheres at different temperatures.

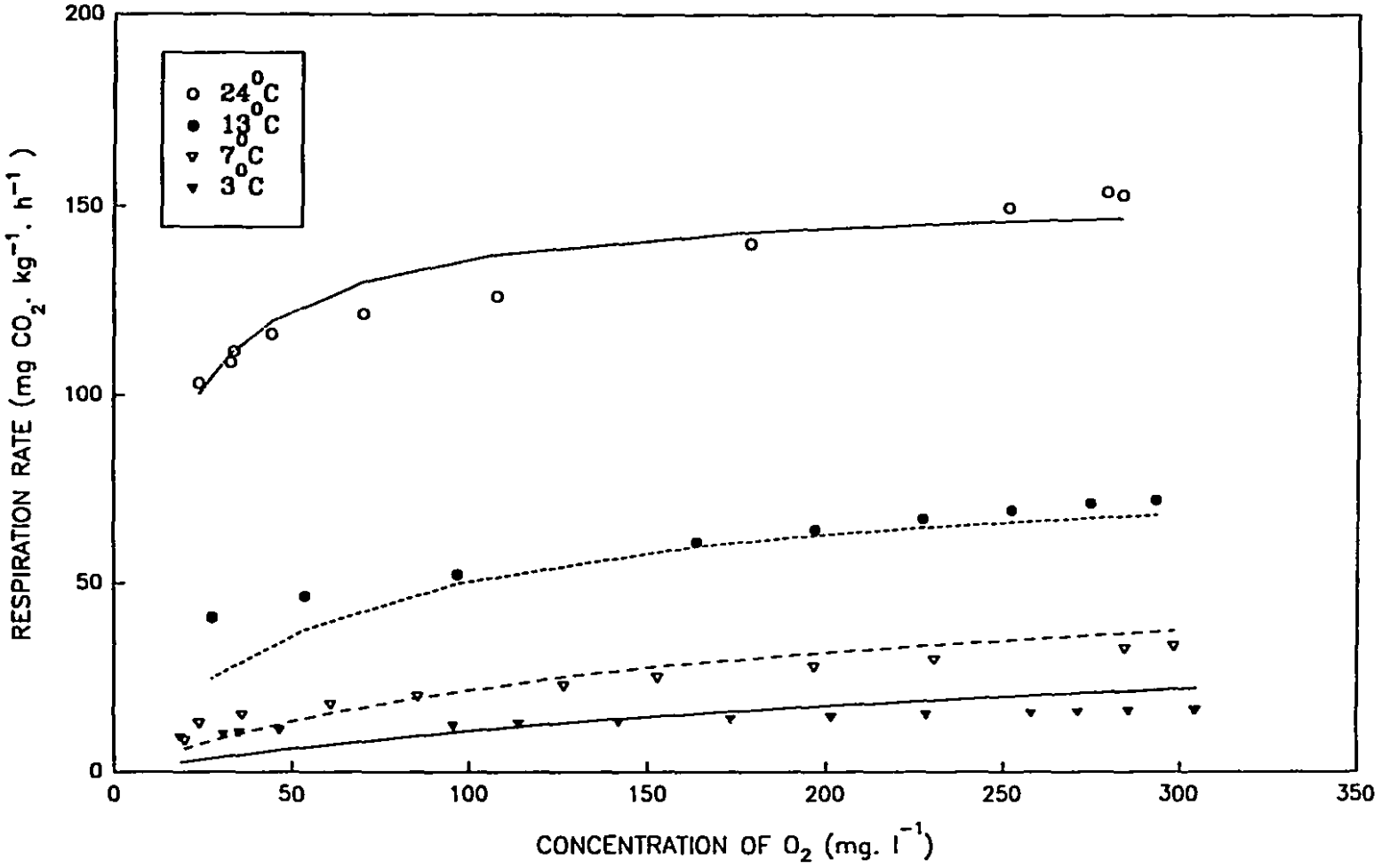

Figure 6.7. Observed and Predicted Respiration Rate (RR) of broccoli as a function of Concentration of O_2 in sealed chambers at specified temperatures.

6.4 Diffusion of O_2 through Diffusion Channels

The experiment was carried out for 44 days in the cold room maintained at 0°C. The variation in temperature was ±0.5°C. The results clearly indicate the effect of length and cross sectional area of channels on the diffusivity of O_2 into the storage chambers. They demonstrate the possibility of maintaining the desired steady-state levels of O_2 concentration inside the storage chambers.

Figures 6.8, 6.9, and 6.10 show the diffusion and the steady-state level of O_2 maintained in the chambers by the diffusion channels of cross sectional area 0.04, 0.18, and 1.15 cm^2 respectively for lengths of 0.6, 3.0, 7.0, 12.0, 18.0, and 25.0 cm.

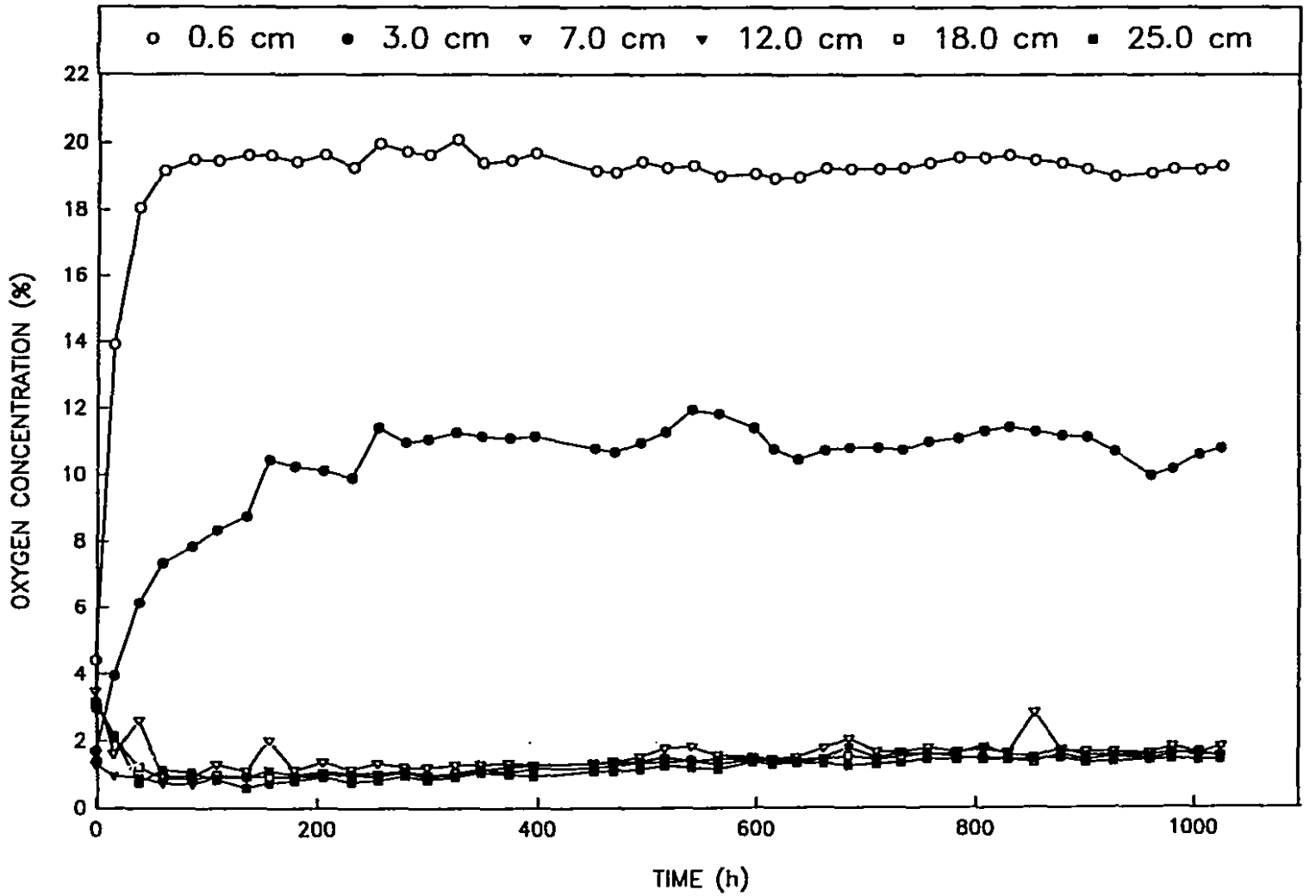

Figure 6.8. Diffusion of O_2 as a function of time through Diffusion Channels of cross sectional area 0.04 cm^2 and specified lengths, after initial nitrogen flushing, into chambers containing broccoli at 0°C.

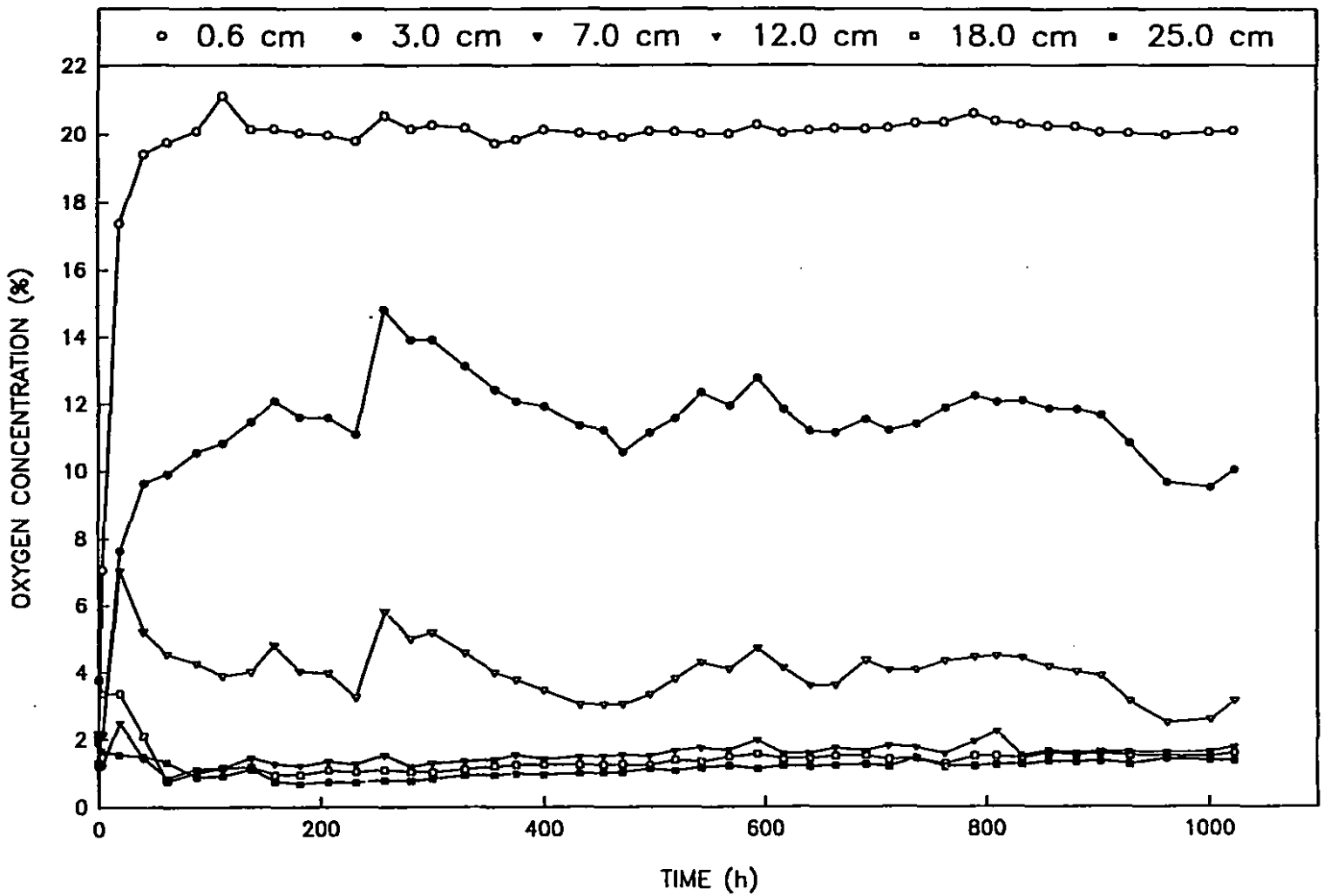

Figure 6.9. Diffusion of O_2 as a function of time through Diffusion Channels of cross sectional area 0.18 cm^2 and specified lengths, after initial nitrogen flushing, into chambers containing broccoli at 0°C.

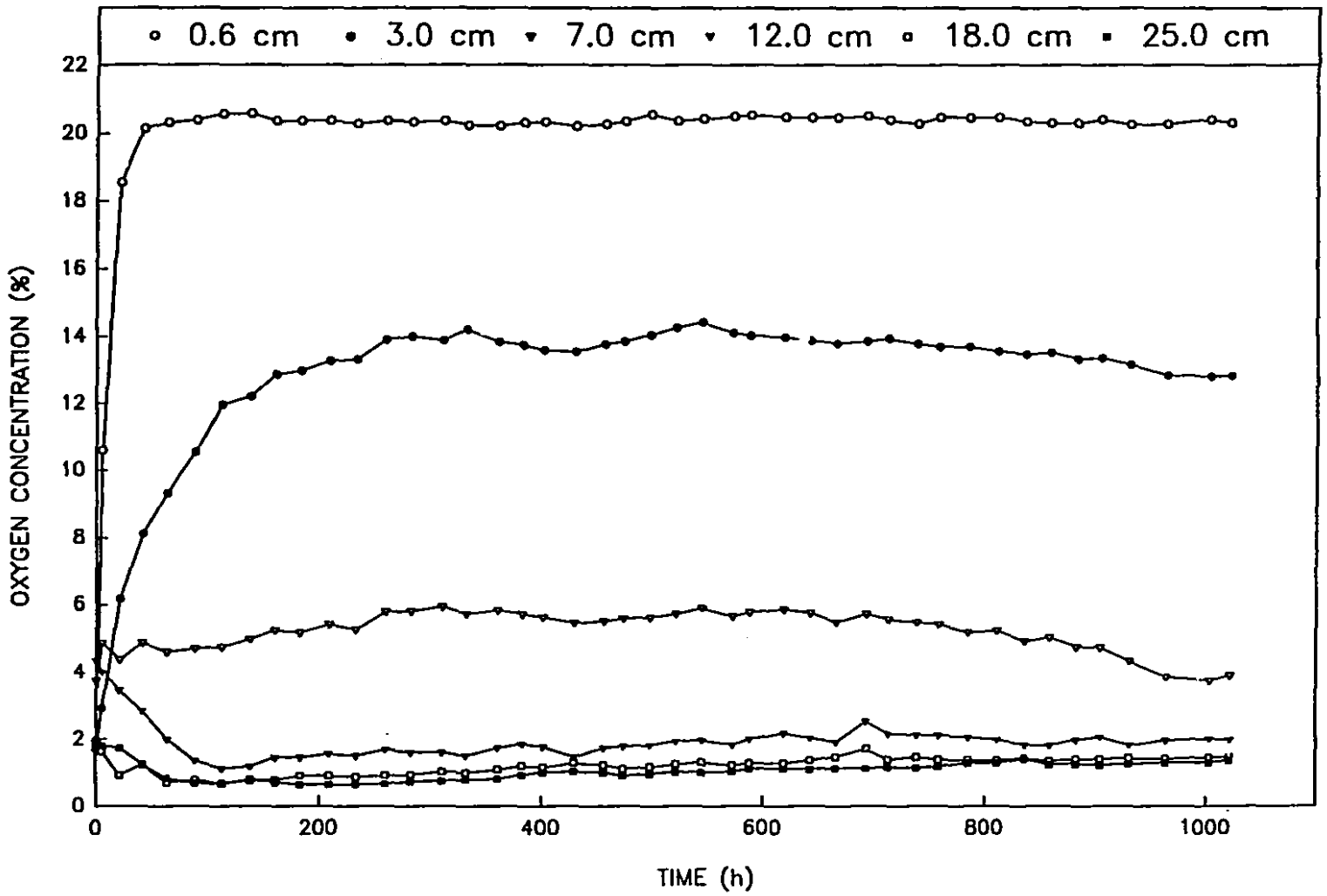

Figure 6.10. Diffusion of O_2 as a function of time through Diffusion Channels of cross sectional area 1.15 cm^2 and specified lengths, after initial nitrogen flushing, into chambers containing broccoli at 0°C.

The results indicate that for lengths more than 7 cm irrespective of the cross sectional area, the O_2 levels dipped down from the initial levels of 3-4% to about 1%, and then increased to slightly higher levels which were almost steady during the experimental period. For lengths less than 7 cm, the O_2 level went on increasing until reaching steady-state levels, except in the case of 7 cm channel of the lowest cross sectional area, in which case it decreased and maintained a lower level.

The results presented in Figure 6.11 (three dimensionally), show the effect of length and cross sectional area on the O_2 concentration. By increasing the length of channel from 0.6 to 3.0 cm (an increase of 500%) the oxygen level decreased by 40%; further increase in channel length to 7 cm resulted in the decrease of oxygen level by 80%. The channels of length 12 cm and more were able to maintain O_2 concentration level below 2%. The channels of 7 cm length maintained O_2 between 1 and 6%, 3 cm between 11 and 14%, and 0.6 cm between 19 and 21%.

The cross sectional area of the channel has an effect on the O_2 concentration level when the length of channels is less than 12 cm. For the same length of channels the O_2 level was maintained at a lower level for lower cross sectional area. For the channels of length 18 cm or more there was not much difference in O_2 levels. The cross section is also found to have an effect on the rate of diffusion of O_2 into the chambers. The rate of diffusion was high with bigger cross sectional area. The O_2 levels stabilised within 40 hours in the case of 1.15 cm^2 cross sectional area, whereas it took 60 and 90 hours in the case of 0.18 and 0.04 cm^2.

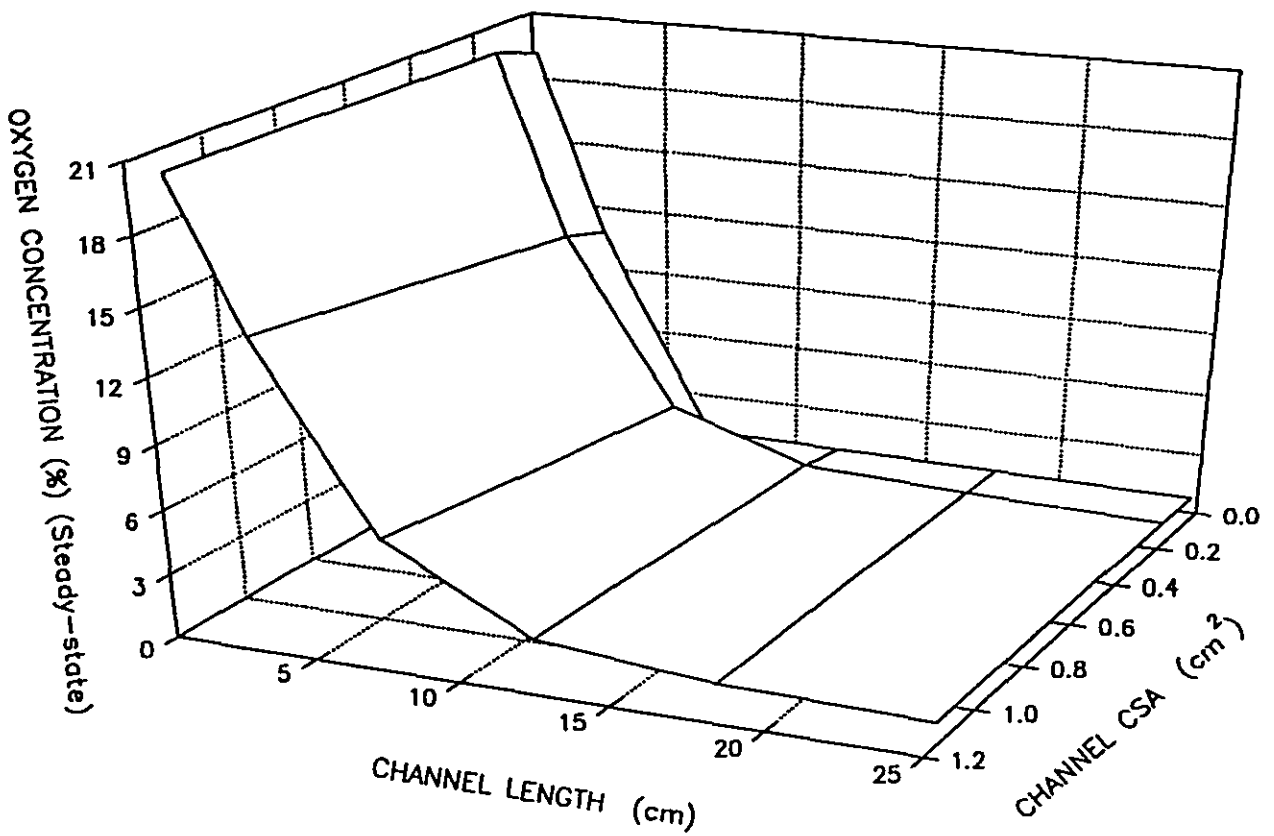

Figure 6.11. Effect of length and cross sectional area of Diffusion Channels on Steady-state Concentration levels of O_2 inside broccoli storage chambers at 0°C.

6.5 Modelling Diffusion of Oxygen through the Channel

The Equation 4.23 was fitted to the experimental data. When the experimental data was fitted to the model, the results obtained were negative in value; since the length cannot be negative the Equation was rewritten as:

$$L = \frac{A_c}{m_s} * \frac{a_1(a_2+y_{O_2})}{y_{O_2}} * \ln[\frac{(1-y_{O_2,chamber})}{(1-y_{O_2,air})}] \qquad (6.2)$$

Prediction using the Equation 6.2 was compared to the experimental data. The constants a_1 and a_2 obtained through non-linear regression with the experimental data were:

$a_1 = 5e^{-8}$

$a_2 = 4e^{+7}$.

The results obtained indicated that the model did not provide a good fit. Analysis was then done for the three cross sectional areas separately and better fits were obtained. The constants a_1 and a_2 obtained were different for each of the three cross sectional areas and are presented in Table 6.2.

Table 6.2 Constants a_1 and a_2 obtained through non-linear regression for the three cross sectional areas.

Area, cm^2	a_1	a_2
0.04	178.07	0.407
0.179	94.97	0.193
1.153	44.67	0.055

After data analysis, the constants were found to have linear relationships with the area. The constant a_2 is related to respiration (section 4.2) and cannot be a function of A_c. Therefore, a_1 was replaced by $(a + b\,A_c)$ and a_2 was replaced by a constant c. The modified model is:

$$L = \frac{(a*A_c + b*A_c^2) * (c+y_{O_2})}{m_s * y_{O_2}} * \ln[\frac{(1-y_{O_2,chamber})}{(1-y_{O_2,air})}] \qquad (6.3)$$

The experimental data was fitted to the new model and after analyzing the results and the model, further corrections were made to improve the predictions. The model was optimised and is given as:

$$L = \frac{(a + b*A_c)^2 * (c+y_{O_2})}{m_s * y_{O_2}} * \ln [\frac{(1-y_{O_2,chamber})}{(1-y_{O_2,air})}] \qquad (6.4)$$

The parameters a, b and c were determined through non-linear regression analysis with the experimental data.

$a = 7.8366$

$b = 1$

$c = 0.0336178$

Since, $b = 1$, the Equation 6.4 can be rewritten as:

$$L = \frac{(a + A_c)^2 * (c+y_{O_2})}{m_s * y_{O_2}} * \ln [\frac{(1-y_{O_2,chamber})}{(1-y_{O_2,air})}] \qquad (6.5)$$

Predictions with the corrected model and the experimental data are presented in Figure 6.12. A good fit is observed between the predicted values and the experimental values. This model can be used to predict the lengths of diffusion channel for different cross sectional areas and steady-state O_2 concentration levels. However the limitation of the model is that it does not take into account the diffusion of CO_2 from inside to outside the chamber through the channel.

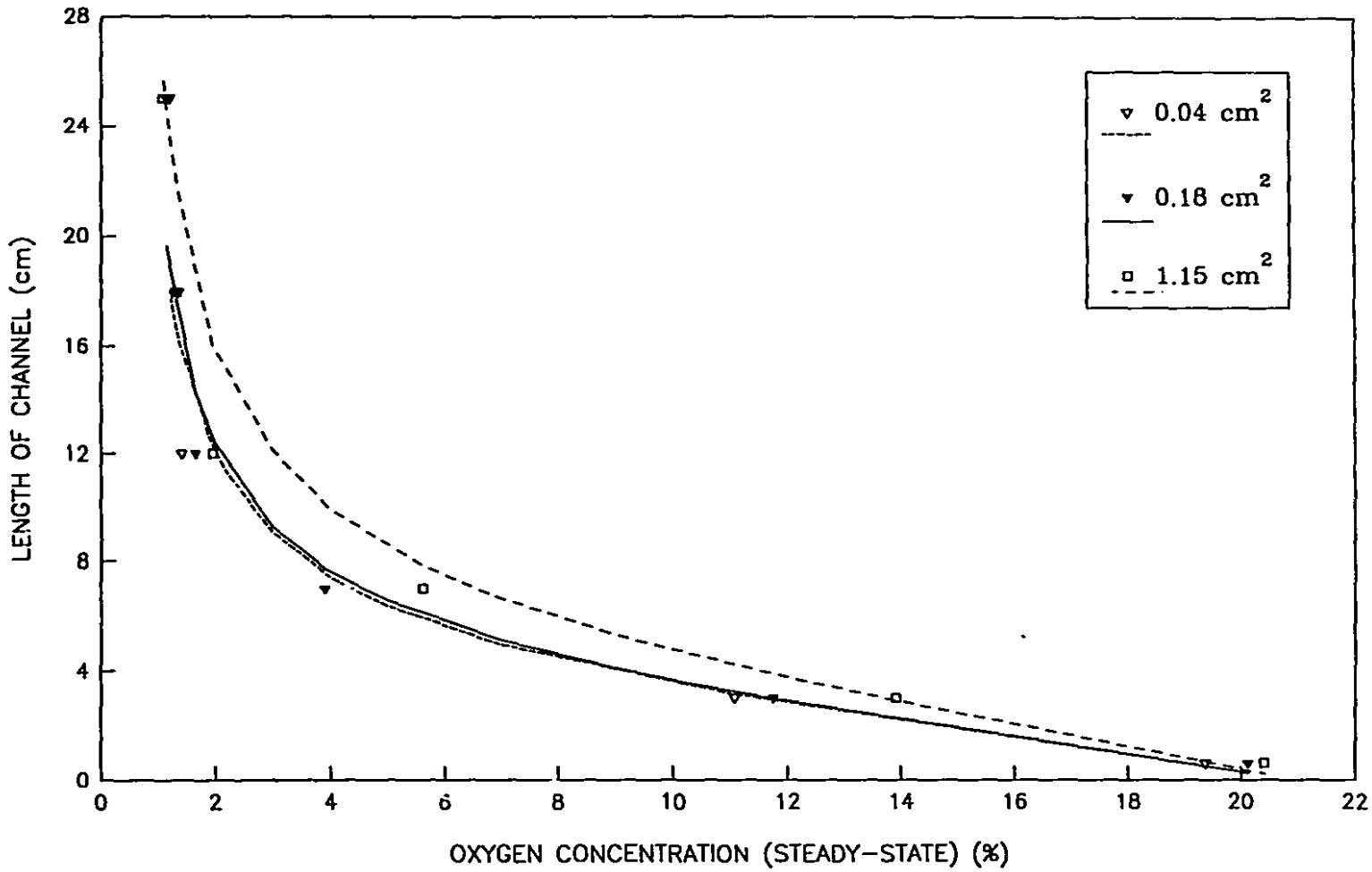

Figure 6.12. Observed and Predicted Diffusion Channel length as a function of O_2 Concentration (Steady-state) inside broccoli storage chambers at 0°C, for specified cross sectional areas.

6.6 QUALITY

It is important to remember here that the recommended CA conditions for storage of broccoli is 1-2% O_2 and 5-10% CO_2 at 0-5°C (Kader, 1992). The present experiment was carried out in the absence of CO_2 (which was scrubbed) in order to model the diffusion of O_2 through the channels rather than to optimize storage conditions for broccoli. Nevertheless, the quality was evaluated for the conditions created.

At the end of the experimental storage period of 44 days, the mass loss, quality index as well as the mechanical properties and color characteristics were determined for each chamber. The quality characteristics before and after the storage period were analyzed.

The relative humidity inside the chambers was near saturation. About 2 to 4 ml of water was found condensed at the bottom of all the chambers. The chambers with less than 2% of O_2 had a higher quality index (Table 6.3). Most of the heads retained green color and appeared fresh, which concurs with the findings of Lipton and Harris (1974). Flowers and stalks were firm. However, it was observed that in each chamber some of the broccoli were attacked by mold and rot. The chambers with the lowest quality index had about 60% mold attack, and the stems and flower portions were soft. Off-flavors and odors were noted when the chambers were opened. This indicates the occurrence of fermentative reactions at low O_2 concentration (Forney, 1991). Kasmire et al. (1974) reported similar off-odors at very low levels of O_2. The fact that some heads were in good condition and others in bad condition in the same chamber indicates that anaerobic conditions might have been created in certain pockets of the chamber or microbial infection. The rotting was found to have started at the cut edges of the stem. In any case, the storage conditions created in these experiments were far from those recommended by Kader (1992) or the CA of 6% CO_2 and 2.5% O_2 (at 1°C) recommended by Makhlouf et al. (1989) to prevent unpleasant odors and disorders.

The mass loss was observed to be less than 3% in all the chambers except one (Table 6.3). The mass loss might be the result of respiration rather than transpiration

because the chambers were near saturation. Broccoli in good condition were selected for determining the mechanical properties. The results are presented in Table 6.4. Mechanical properties in terms of toughness was determined with the Instron Universal Testing Instrument and are presented in Table 6.4. Color characteristics in terms of L, a, and b coordinates representing the value, hue and chroma measured at flower head and stalk portions of broccoli are presented in Table 6.5. Although the analysis of variance showed some differences between treatment means using Duncan's test, closer inspection of the data revealed that neither the mechanical properties data nor the colorimetric data could be quantitatively described by gas concentration. Given the generally poor condition of the broccoli stored in these non-ideal conditions, this is not surprising. Essentially all treatments led to at least some deteriorated broccoli in each chamber, and the observed differences between treatment means could be due to different decay mechanisms occurring at the various gas compositions. However, since the objective was not to determine which decay mechanisms were favored according to the gas compositions, no further analysis was performed.

Table 6.3. Mass loss (%) and Quality Index of broccoli after storage.

Treatment[a] (Chamber No.)	Mass loss, (%)	Q. I.
1	2.62	1.00
2	1.84	1.00
3	2.59	4.00
4	2.54	6.00
5	2.23	7.00
6	2.82	6.00
7	1.87	3.00
8	2.92	5.00
9	2.25	3.00
10	2.34	5.00
11	2.35	7.00
12	2.65	7.00
13	1.98	7.00
14	2.43	7.00
15	2.24	7.00
16	1.76	7.00
17	2.97	5.00
18	5.10	7.00

[a]Details of treatment combinations are presented in Table 5.2

Table 6.4 Results of Instron Mechanical Tests (Toughness) of broccoli before and after storage (mean values of 4 replicates).

Treatment*	Dis. F. max, mm	F. max, mm	Dis. F. break, mm	F. break, kN	Youngs Modulus, MPa	E. break, J	Toughness, MPa
0	9.422[a]	0.115	9.236	0.113	9.194	0.876	0.582
1	5.498[b,c,d]	0.123	8.115	0.098	9.648	0.821	0.546
2	5.966[b,c]	0.122	8.897	0.110	9.538	0.902	0.600
3	4.253[b,c,d]	0.119	8.938	0.092	8.570	0.839	0.558
4	5.305[b,c,d]	0.122	8.275	0.088	9.256	0.771	0.512
5	4.542[b,c,d]	0.115	8.915	0.090	9.470	0.821	0.546
6	3.268[b,c,d]	0.114	8.397	0.081	8.124	0.752	0.500
7	4.802[b,c,d]	0.113	9.263	0.098	8.045	0.843	0.561
8	4.497[b,c,d]	0.118	8.649	0.096	9.566	0.814	0.541
9	2.398[d]	0.129	8.330	0.087	8.959	0.788	0.524
10	3.390[b,c,d]	0.116	8.275	0.081	8.853	0.757	0.503
11	2.857[c,d]	0.119	6.672	0.080	8.543	0.552	0.367
12	2.400[d]	0.106	8.676	0.091	9.002	0.738	0.491

contd.

Table 6.4 (contd.). Results of Instron Mechanical Tests (Toughness) of broccoli before and after storage (mean values of 4 replicates).

Treatment*	Dis. F. max, mm	F. max, mm	Dis. F. break, mm	F. break, kN	Youngs Modulus, MPa	E. break, J	Toughness, MPa
13	4.321[b,c,d]	0.115	8.735	0.101	8.119	0.792	0.527
14	4.934[b,c,d]	0.126	8.783	0.101	8.394	0.832	0.553
15	4.8221[b,c,d]	0.124	8.809	0.111	9.727	0.875	0.582
16	6.369[b]	0.118	8.766	0.109	8.303	0.830	0.552
17	3.689[b,c,d]	0.115	8.987	0.086	9.018	0.761	0.506
18	4.658[b,c,d]	0.127	7.347	0.119	10.328	0.678	0.450

* Means in the same column with the same letter are not significantly different ($P \leq 0.05$).
* Details on combination of variables included in each treatment is presented in Table 5.2.

Table 6.5. Chromaticity in L, a and b coordinates of flower and stem portion of broccoli before and after storage (mean values of 3 replicates).

Treatment*	Flowers			Stem			Moisture content, (%)
	L	a	b	L	a	b	
0	47.20	-13.03	22.67[a]	65.671[a]	-15.47	31.50	91.26
1	45.37	-9.87	22.10[a,b]	45.57[c]	-11.13	24.57	90.60
2	45.50	-9.93	21.93[a,b]	45.70[c]	-10.50	24.00	91.09
3	43.90	-10.67	16.93[a,b,c,d]	57.50[a,b]	-13.33	27.50	91.63
4	47.10	-11.00	20.50[a,b,c]	61.37[a,b]	-11.80	23.37	91.34
5	45.57	-12.03	17.97[a,b,c,d]	61.77[a,b]	-14.97	30.10	90.58
6	43.37	-11.03	15.13[b,c,d]	64.70[a]	-14.90	31.17	92.75
7	46.00	-11.27	17.63[a,b,c,d]	64.10[a]	-15.20	32.53	92.35
8	47.20	-11.60	21.13[a,b,c]	66.03[a]	-13.07	31.07	92.42
9	48.17	-12.83	21.13[a,b,c]	61.87[a,b]	-12.23	29.67	91.92
10	39.73	-9.23	12.37[d]	59.00[a,b]	-13.83	27.70	92.40
11	43.27	-12.03	18.07[a,b,c,d]	53.00[b,c]	-13.17	26.57	92.57
12	43.90	-12.20	20.33[a,b,c]	56.20[a,b]	-13.00	26.47	92.96

contd.

Table 6.5 (contd.). Chromaticity in L, a and b coordinates of flower and stem portion of broccoli before and after storage (mean value of 3 replicates).

Treatment*	Flowers			Stem			Moisture content, (%)
	L	a	b	L	a	b	
13	42.83	-10.23	14.83[b,c,d]	64.47[a]	-14.57	30.63	91.87
14	45.23	-10.80	19.13[a,b,c,d]	58.77[a,b]	-13.10	30.33	82.98
15	44.13	-11.30	19.83[a,b,c]	59.80[a,b]	-13.23	30.17	93.38
16	41.57	-10.33	13.97[c,d]	64.33[a]	-14.67	31.37	92.64
17	43.37	-11.97	18.17[a,b,c,d]	59.50[a,b]	-13.50	27.30	93.27
18	42.27	-10.07	13.87[c,d]	56.27[a,b]	-13.77	27.17	92.88

[a] Means in the same column with the same letter are not significantly different ($P \leq 0.05$).
* Details on combination of variables included in each treatment is presented in Table 5.2.

VII CONCLUSIONS

The conclusions derived from the study were:

i) The respiration rate of broccoli can be controlled by reducing the oxygen concentration level inside the storage chamber.

ii) The model developed to predict the respiration rate of broccoli at different temperatures and MA conditions indicate that the concentration of carbon dioxide has no significant effect on the respiration rate in the range of concentrations observed.

iii) Diffusion channels can be effectively used to maintain the desired oxygen concentration.

iv) Both the length and cross-sectional area of a diffusion channel have significant effects on the final oxygen concentration level. However, the cross sectional area has no significant effect when the length of the channel is more than 18 cm.

v) The model developed to predict the length of channel provides a good estimate of the length when the carbon dioxide produced is scrubbed.

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APPENDIX

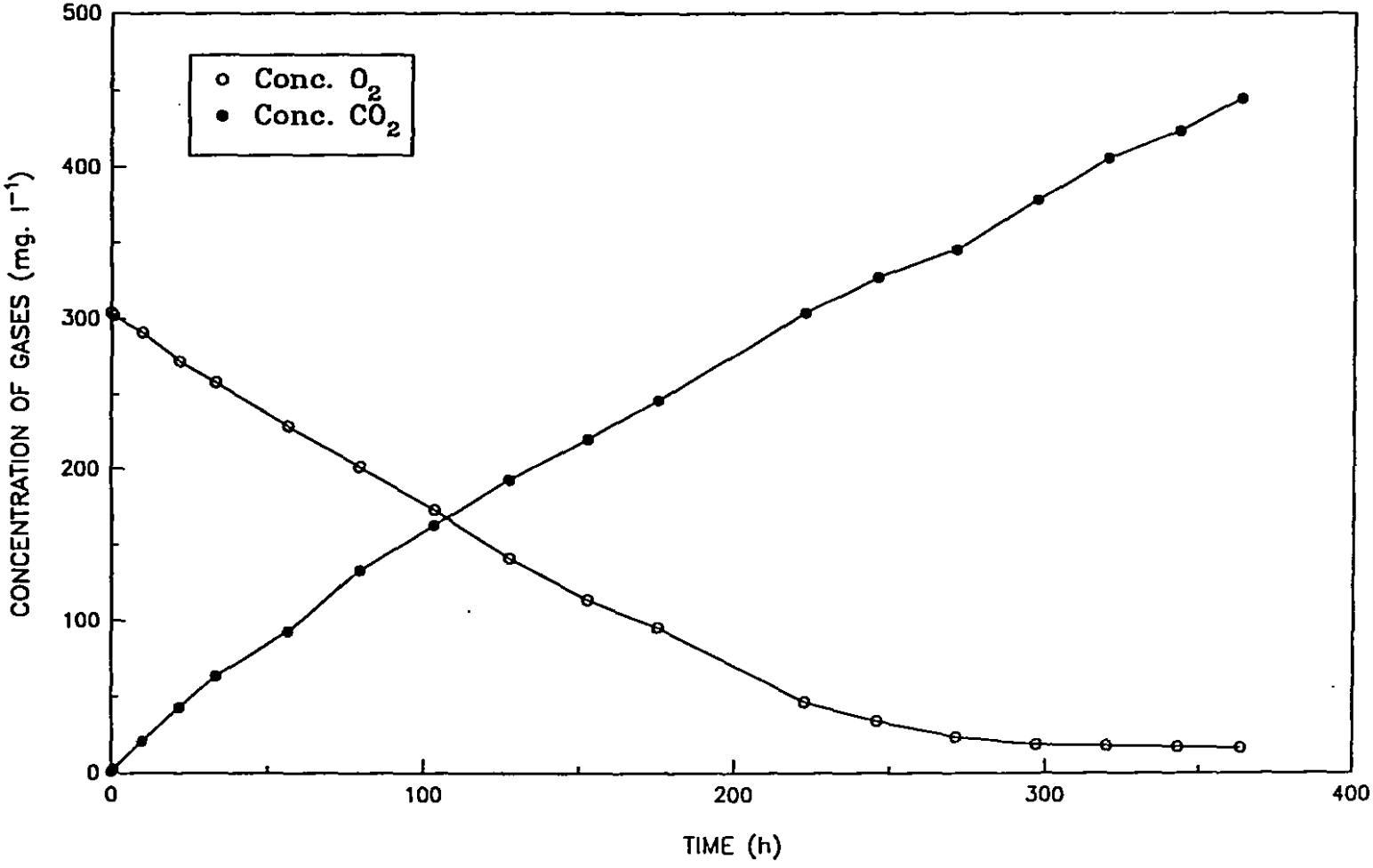

Figure A.1. Progression of O_2 and CO_2 Concentrations as a function of time in sealed chambers containing broccoli at 3°C (mean of 3 replicates).

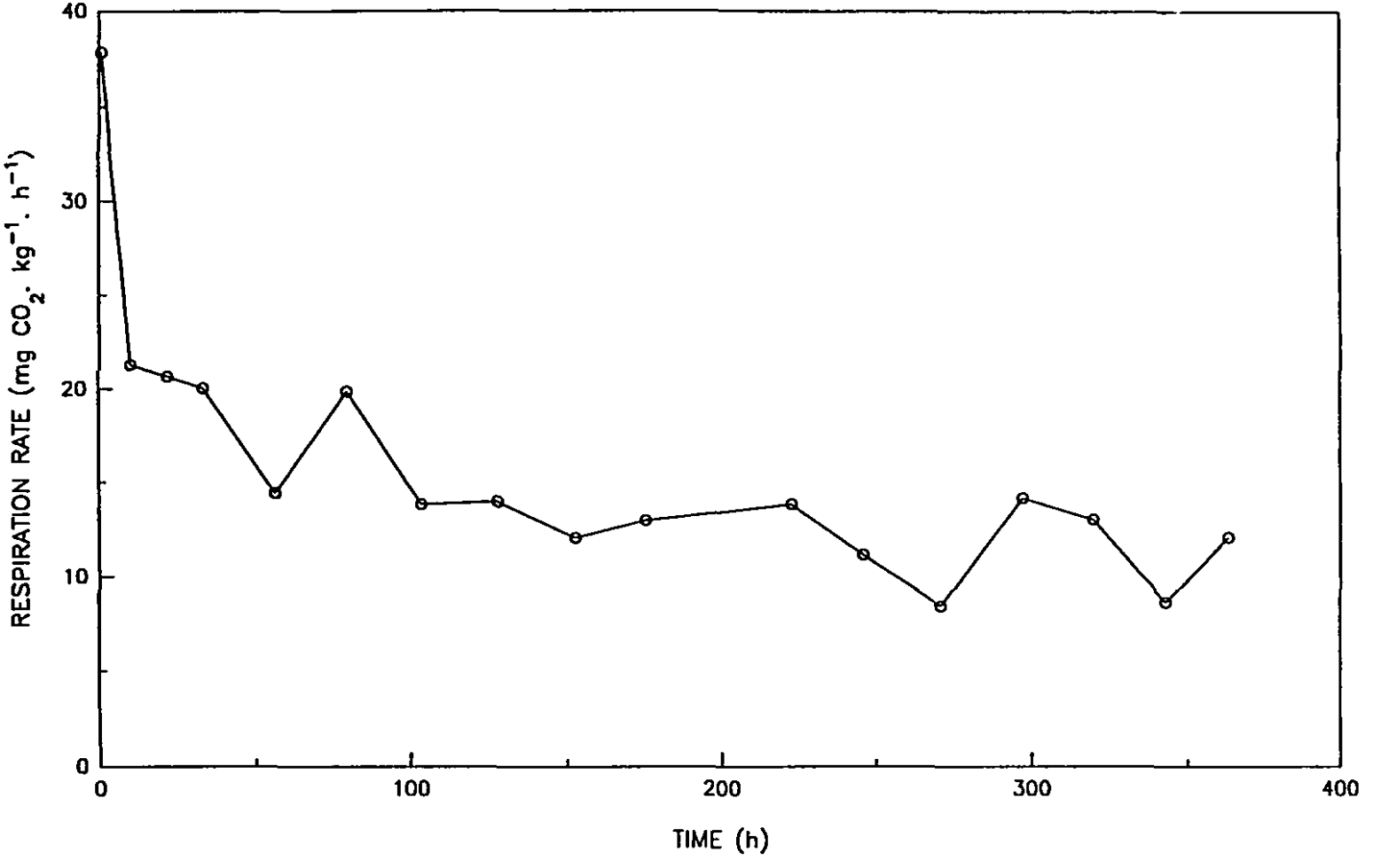

Figure A.2. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 3°C (mean of 3 replicates).

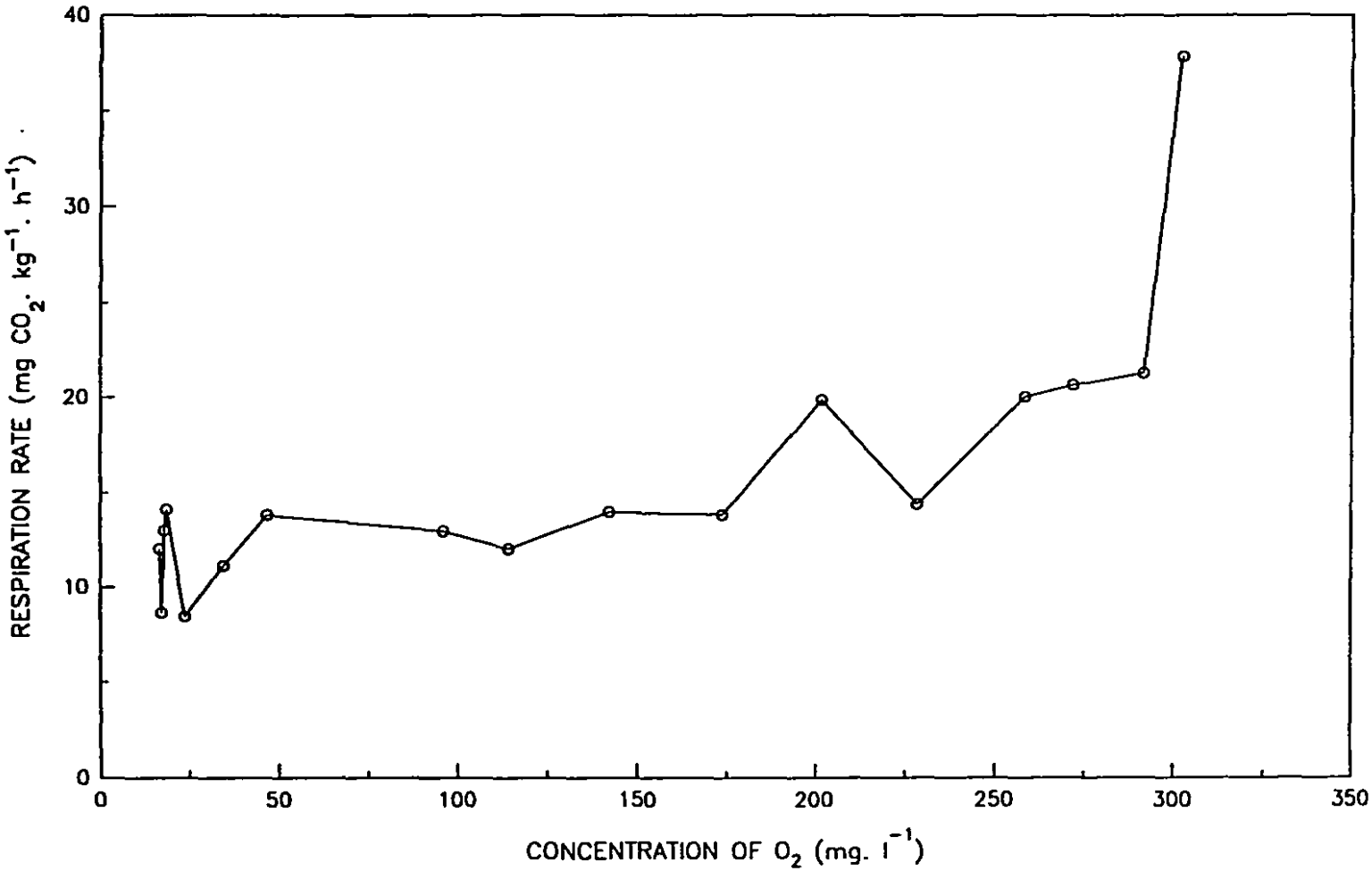

Figure A.3. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 3°C (mean of 3 replicates).

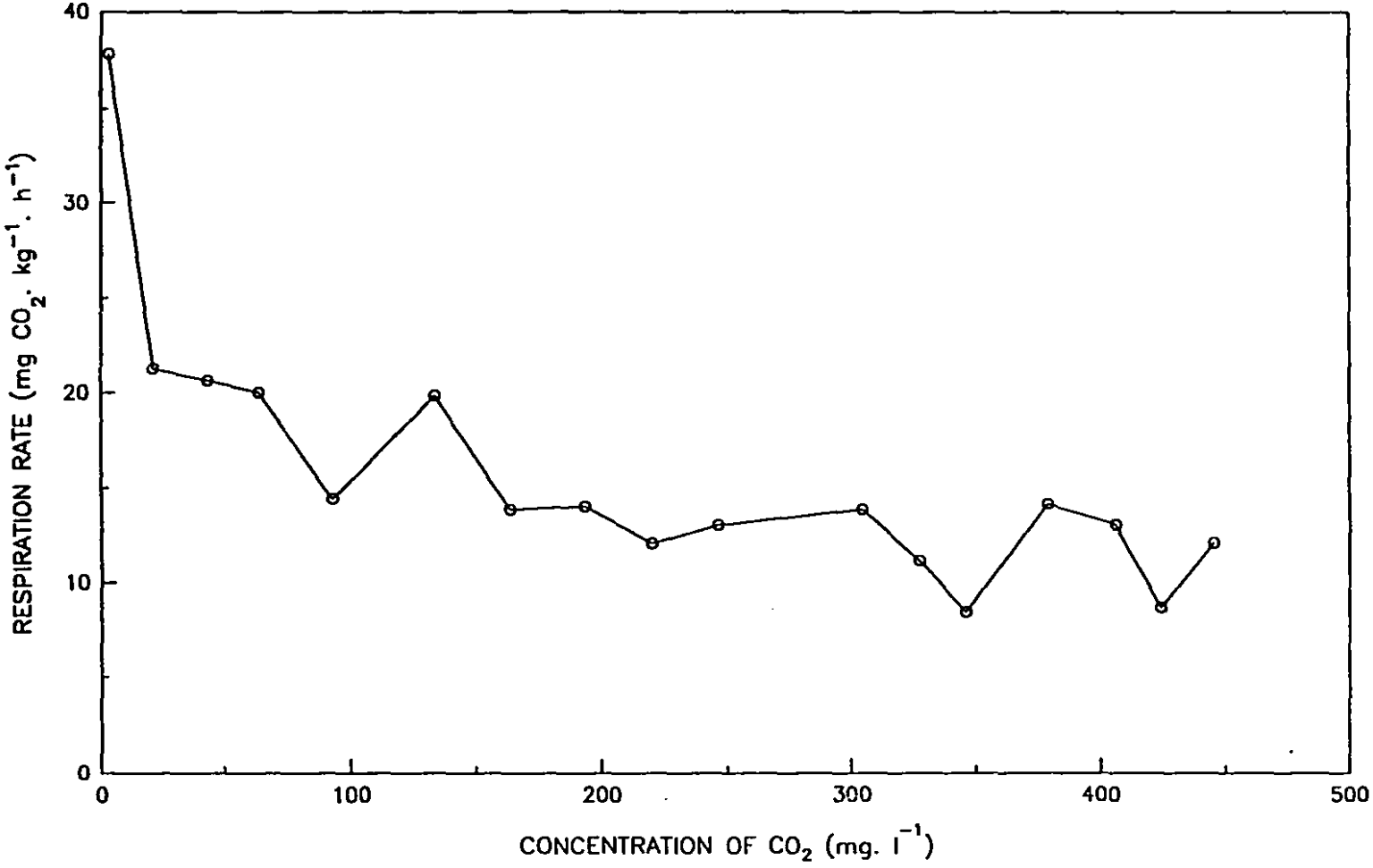

Figure A.4. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 3°C (mean of 3 replicates).

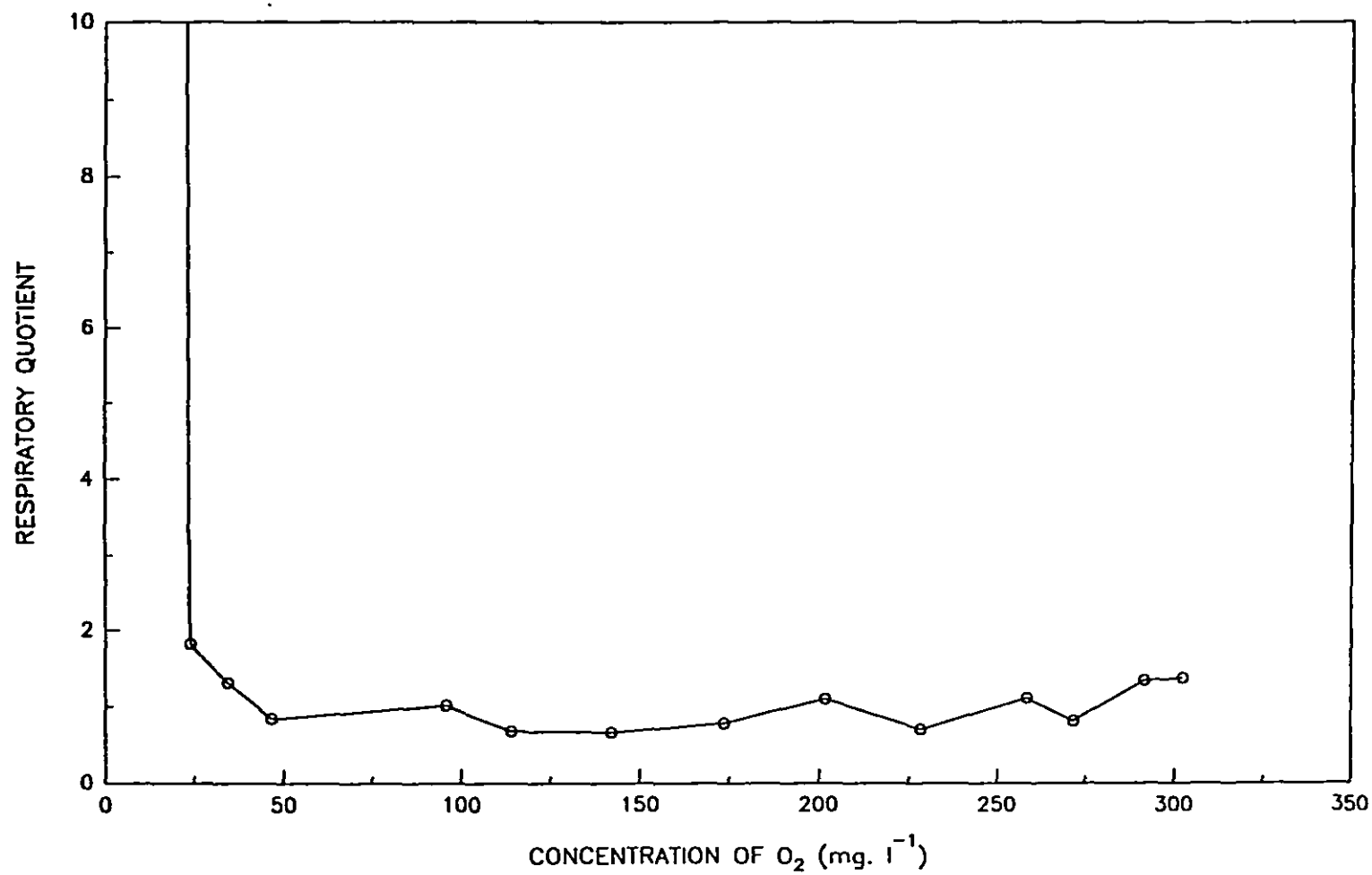

Figure A.5. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 3°C (mean of 3 replicates).

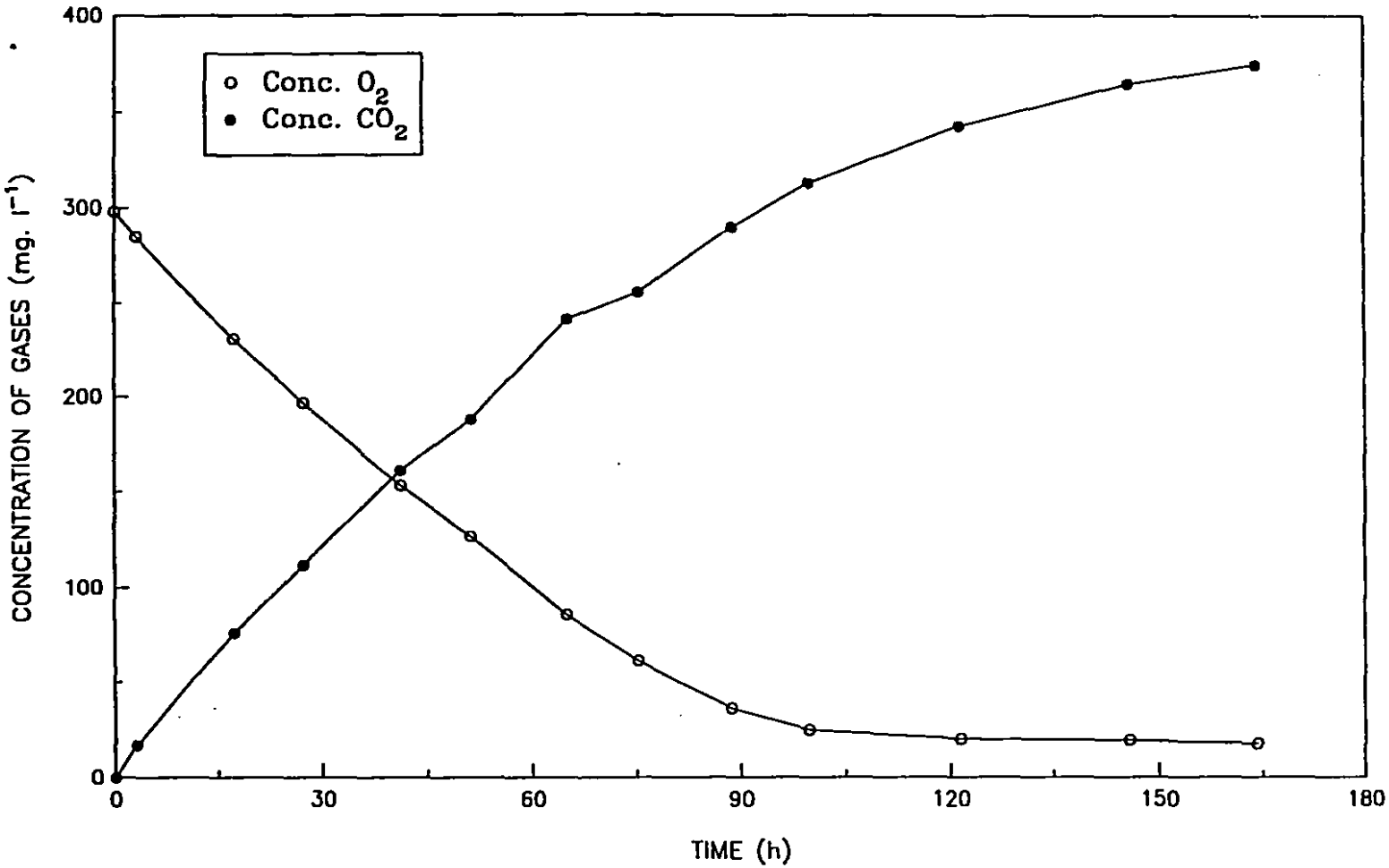

Figure A.6. Progression of O_2 and CO_2 Concentrations as a function of time in sealed chambers containing broccoli at 7°C (mean of 3 replicates).

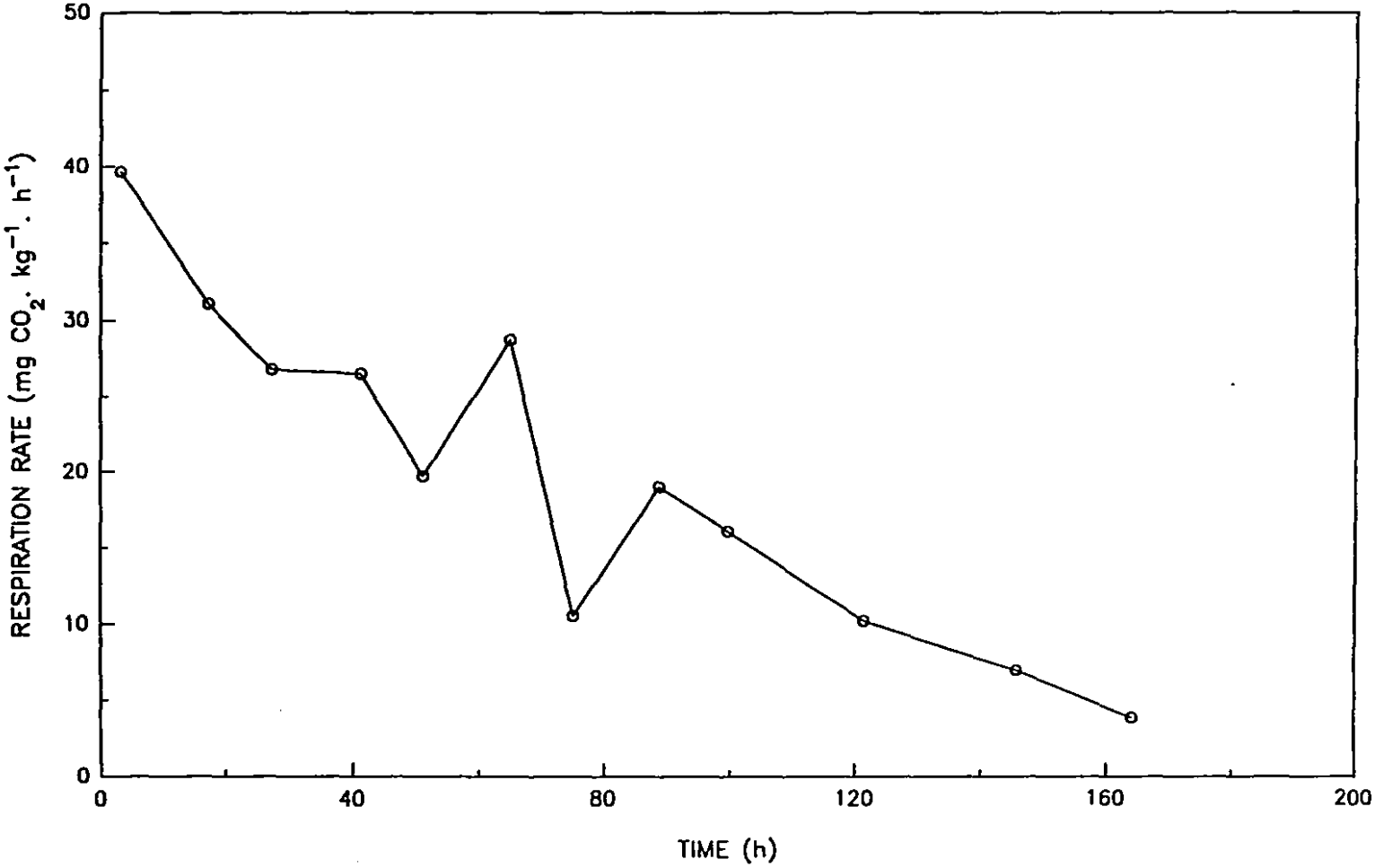

Figure A.7. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 7°C (mean of 3 replicates).

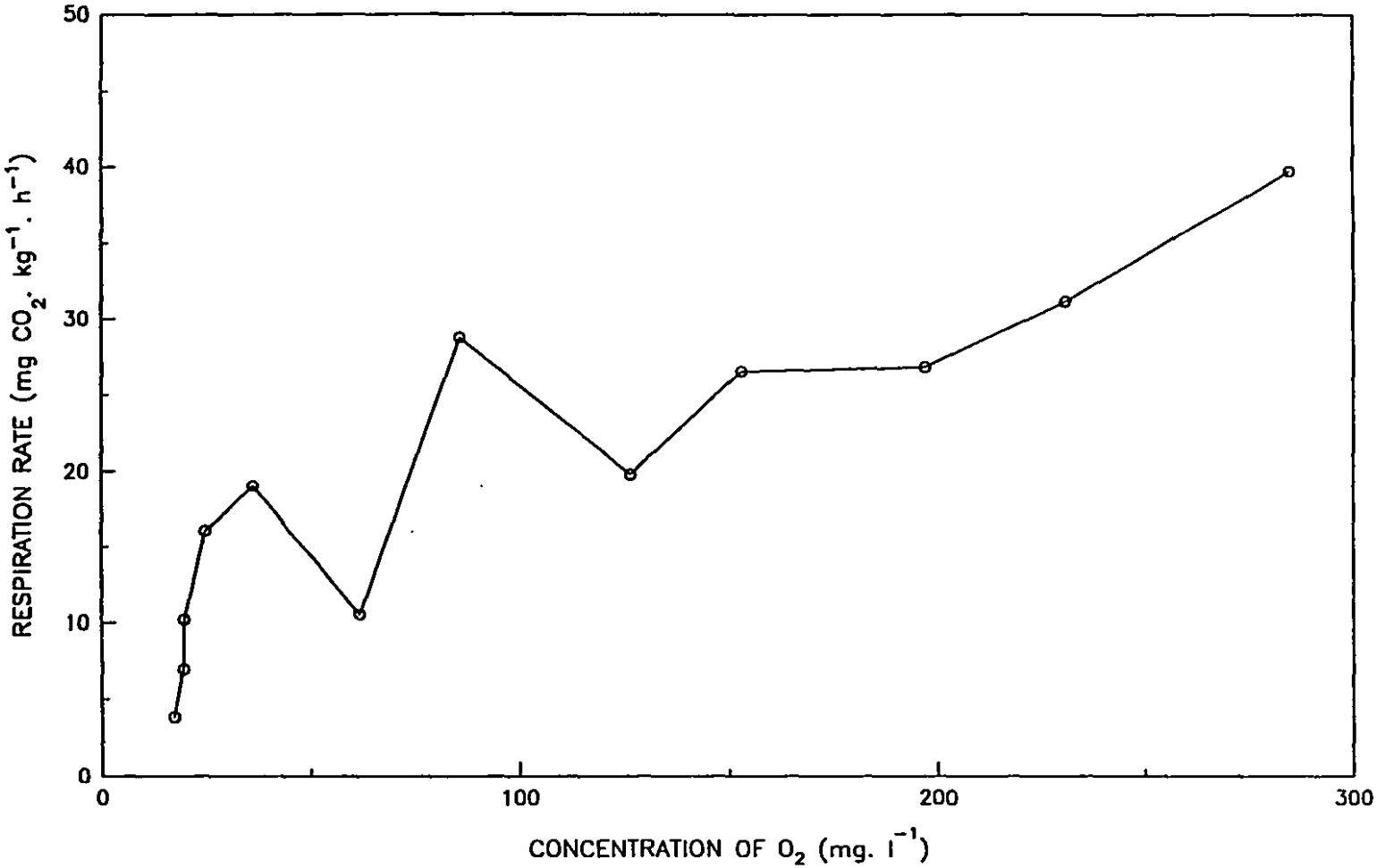

Figure A.8. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 7°C (mean of 3 replicates).

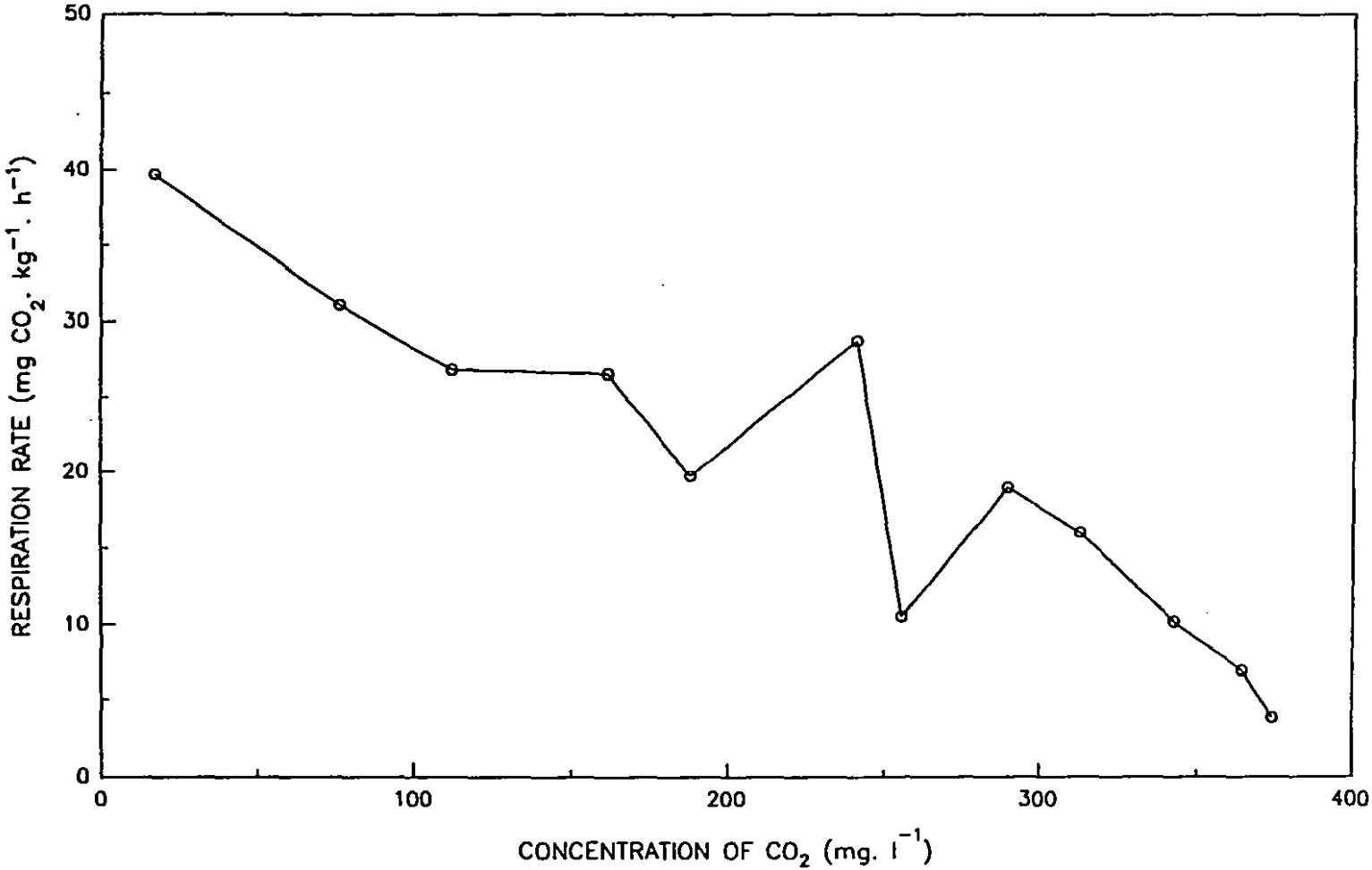

Figure A.9. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 7°C (mean of 3 replicates).

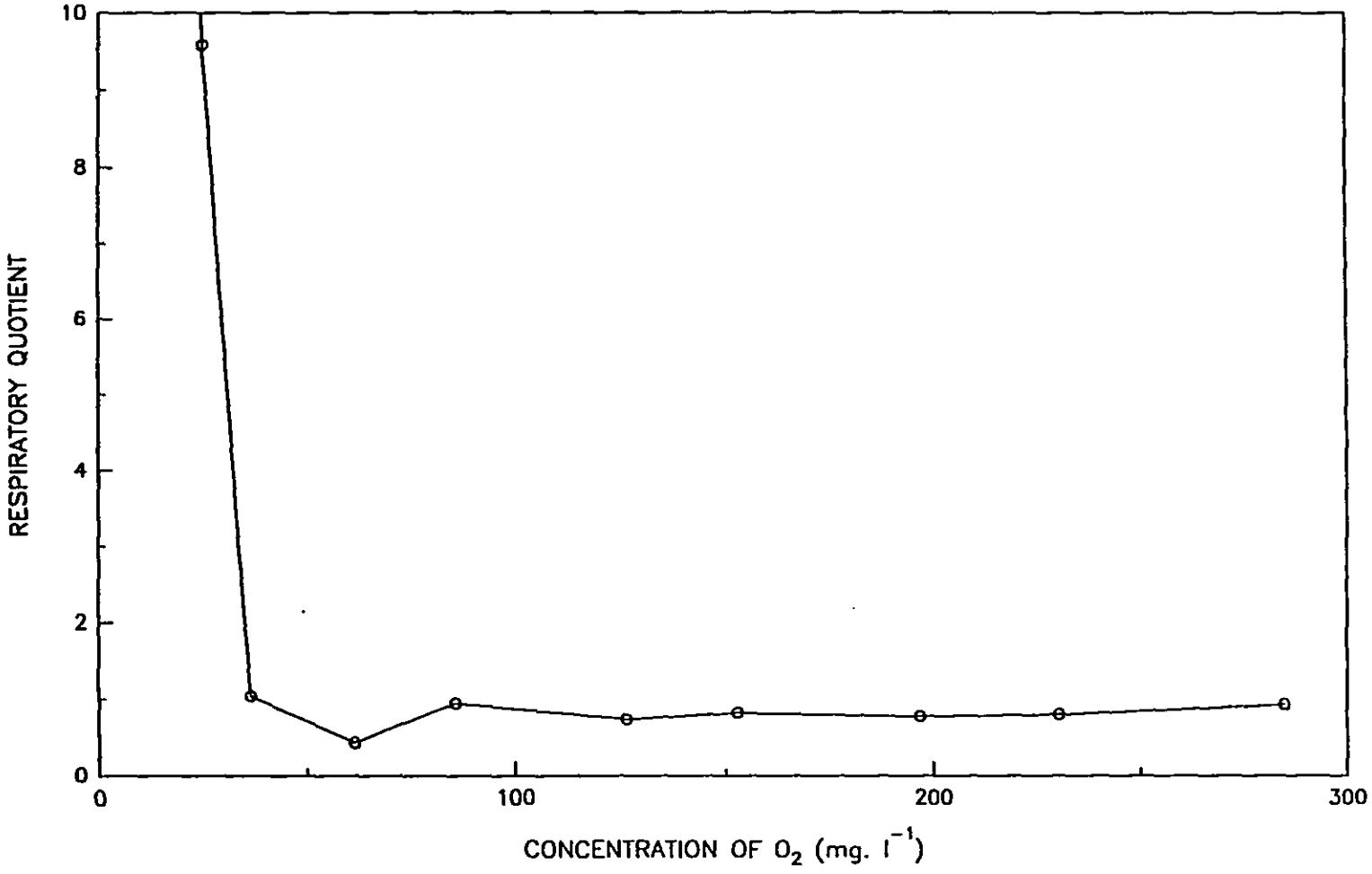

Figure A.10. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 7°C (mean of 3 replicates).

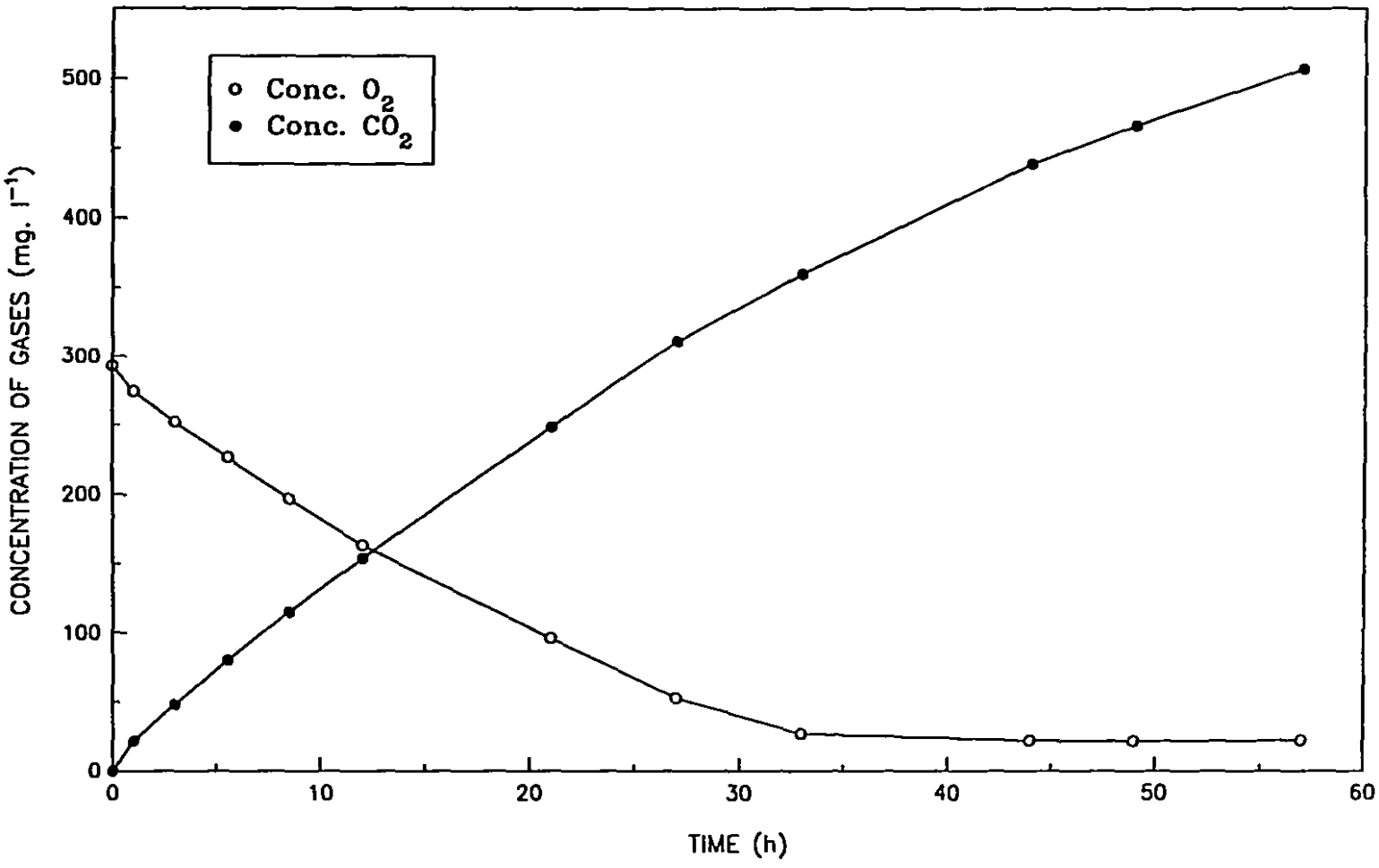

Figure A.11. Progression of O_2 and CO_2 Concentrations as a function of time in sealed chambers containing broccoli at 13°C (mean of 3 replicates).

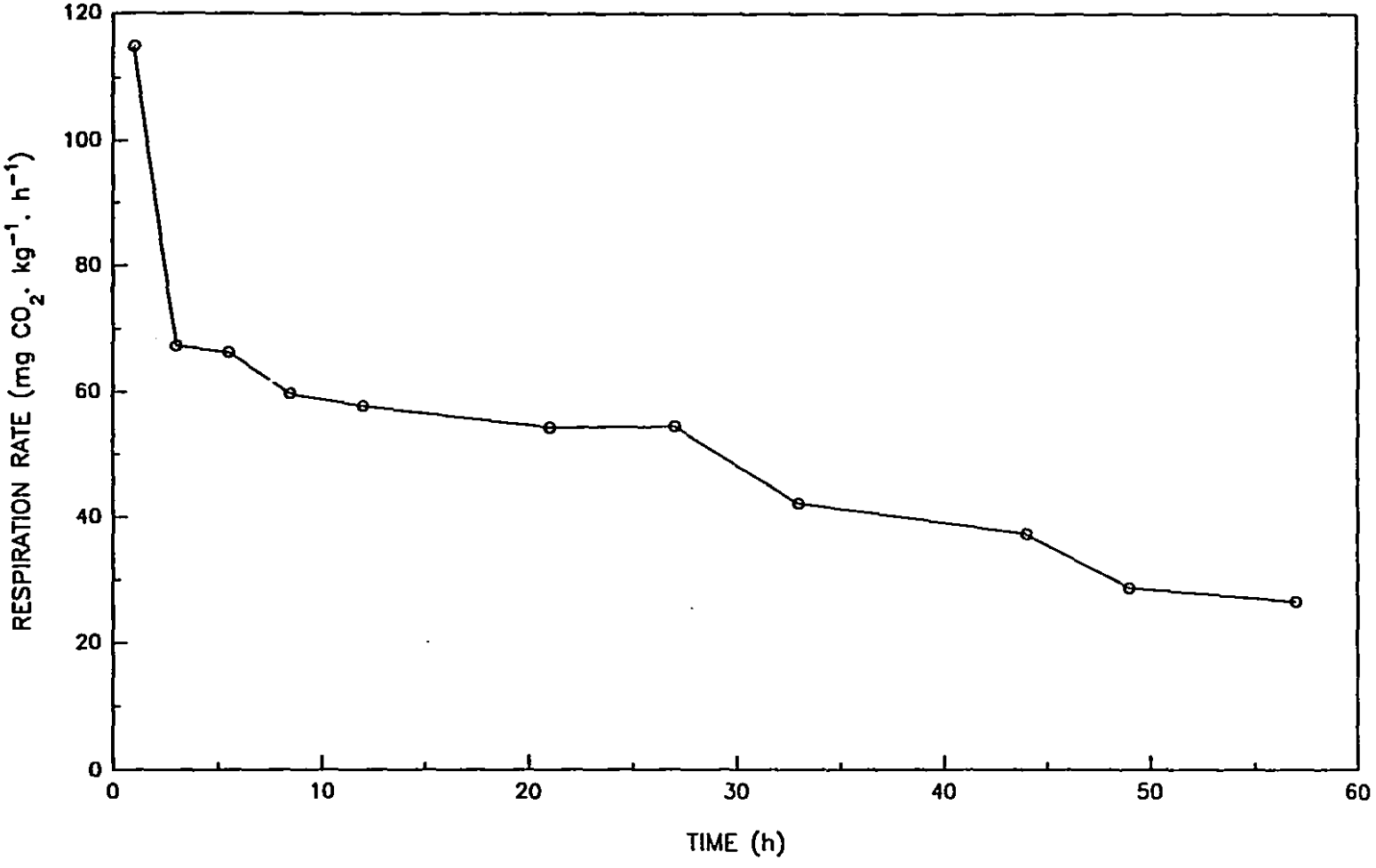

Figure A.12. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 13°C (mean of 3 replicates).

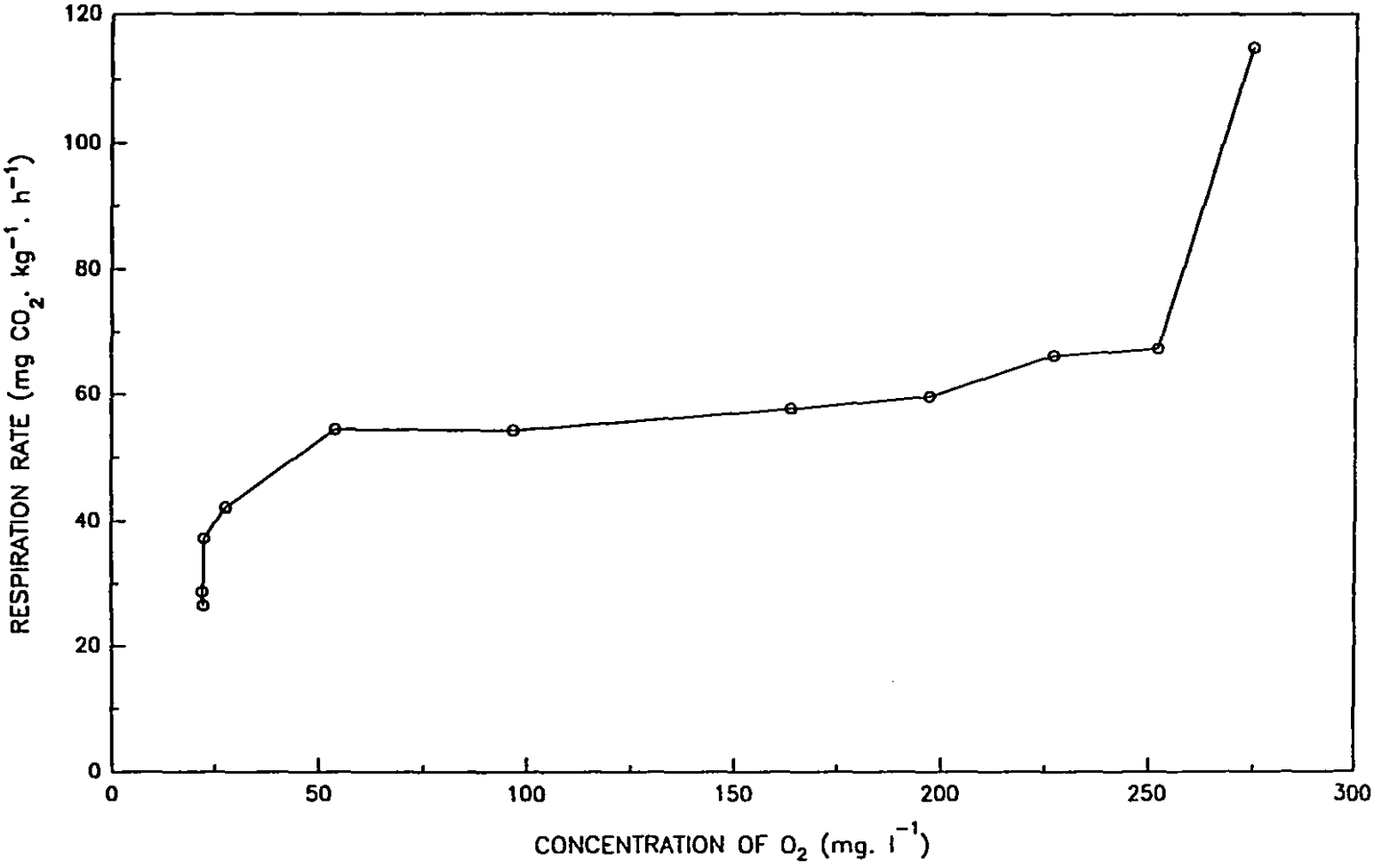

Figure A.13. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 13°C (mean of 3 replicates).

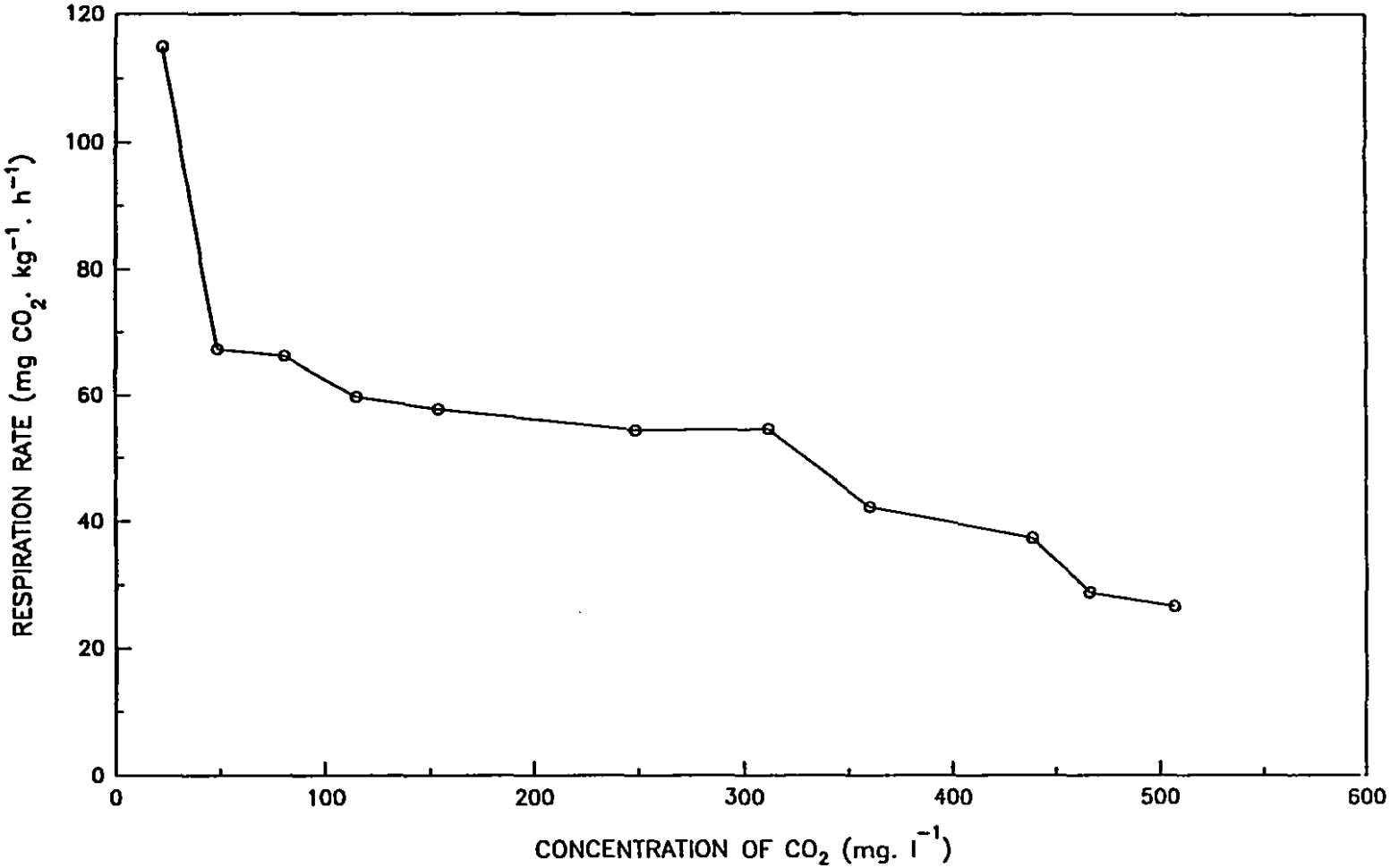

Figure A.14. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 13°C (mean of 3 replicates).

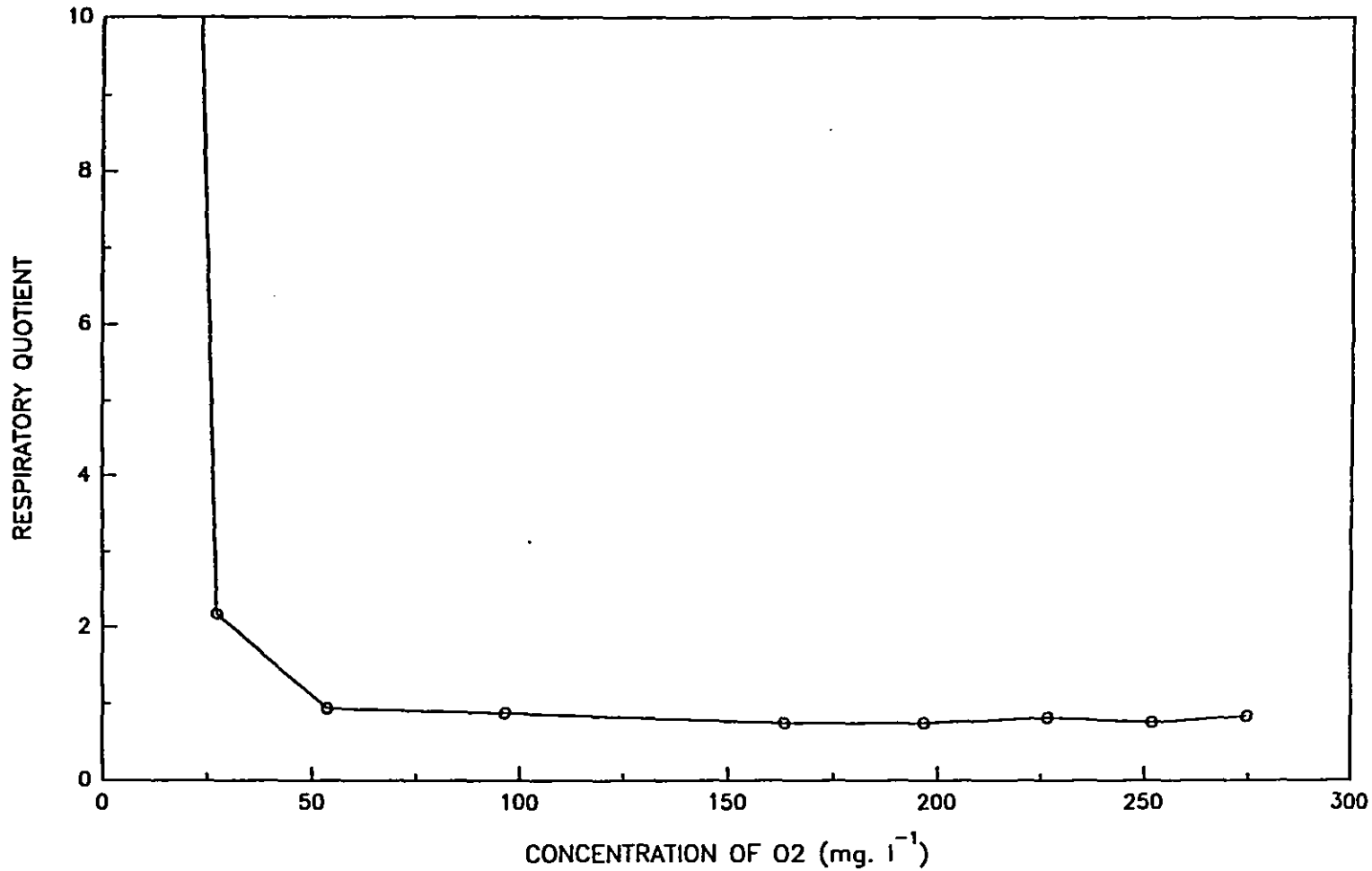

Figure A.15. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 13°C (mean of 3 replicates).

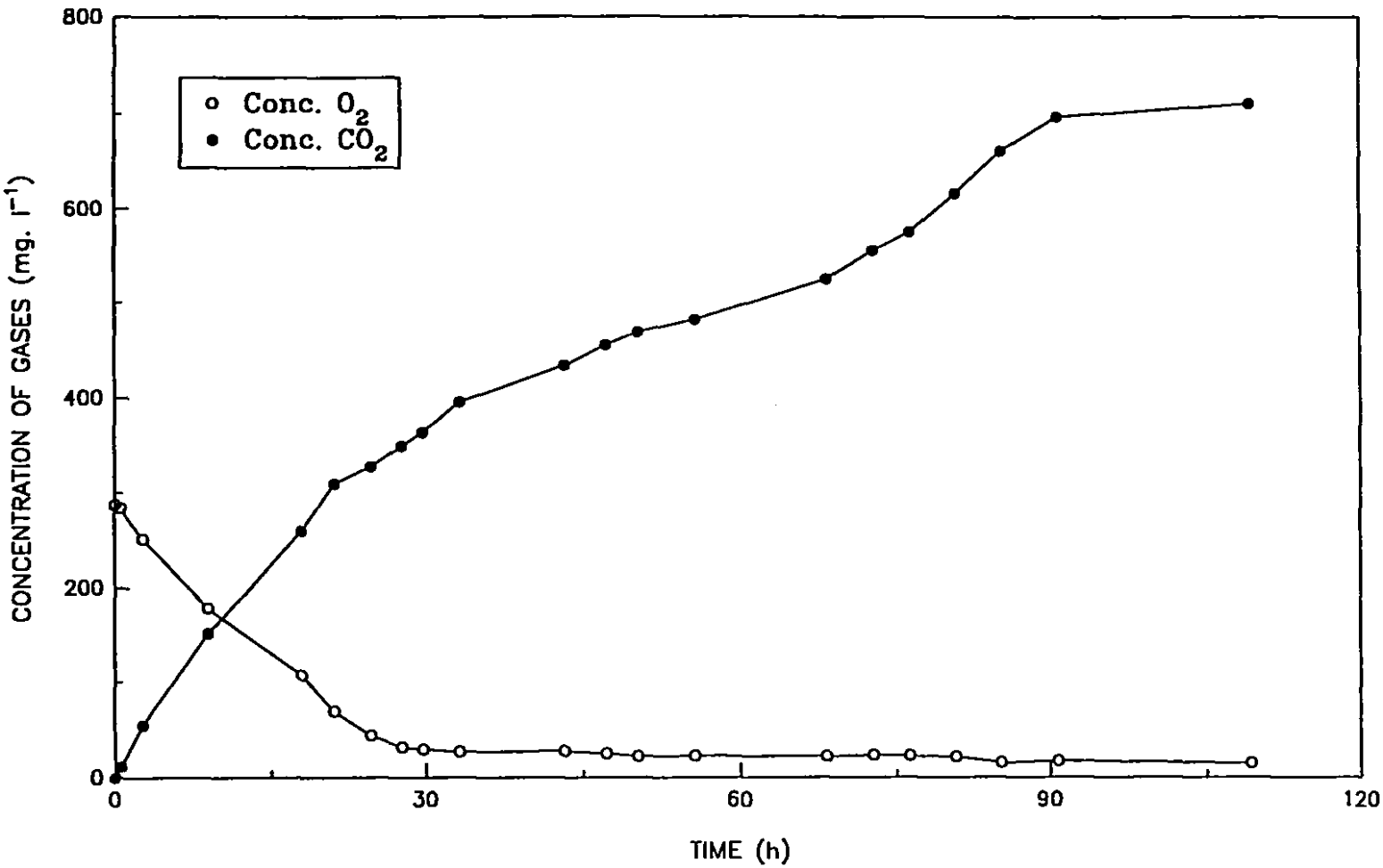

Figure A.16. Progression of O_2 and CO_2 Concentrations as a function of time in sealed chambers containing broccoli at 24°C (mean of 3 replicates).

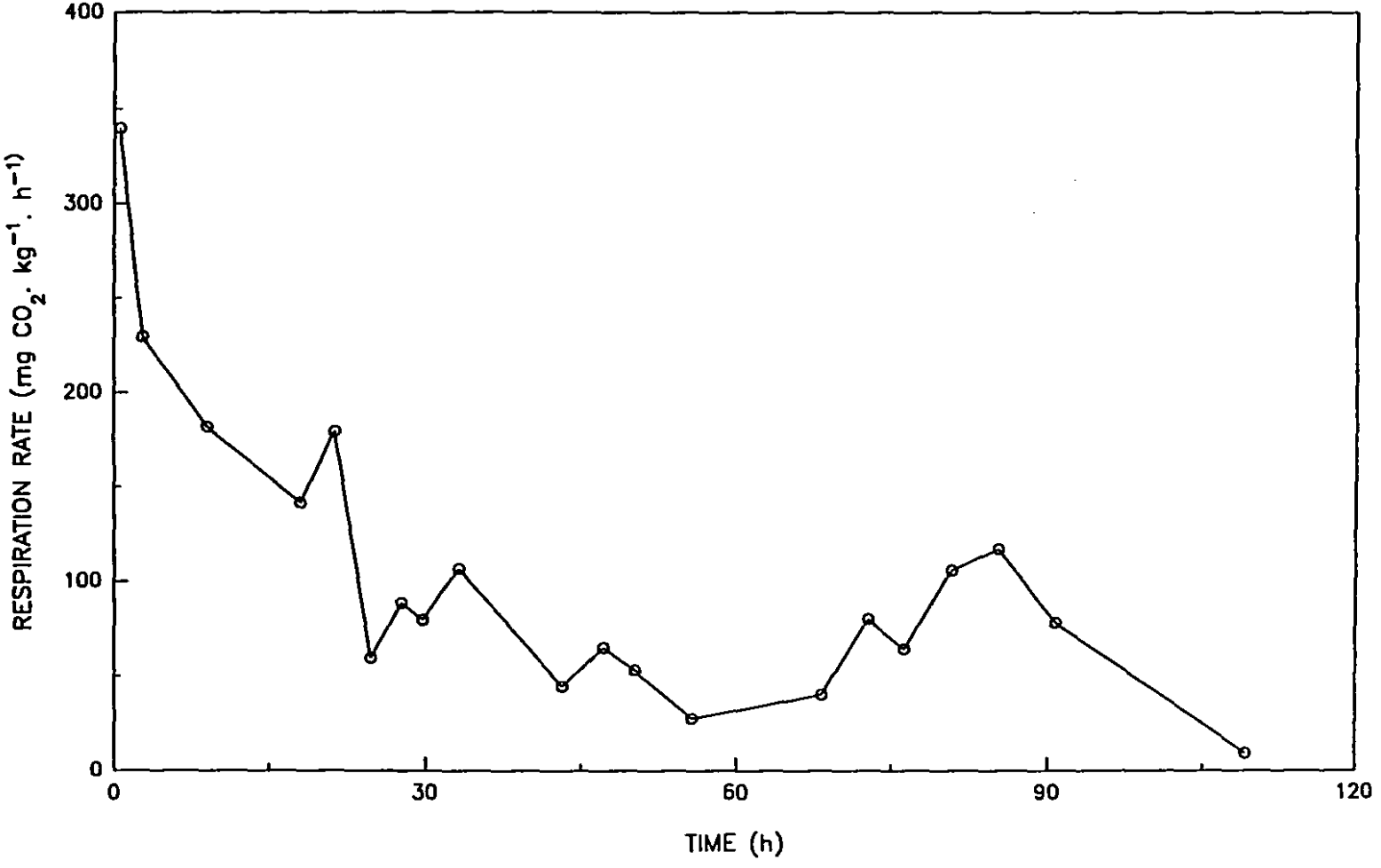

Figure A.17. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 24°C (mean of 3 replicates).

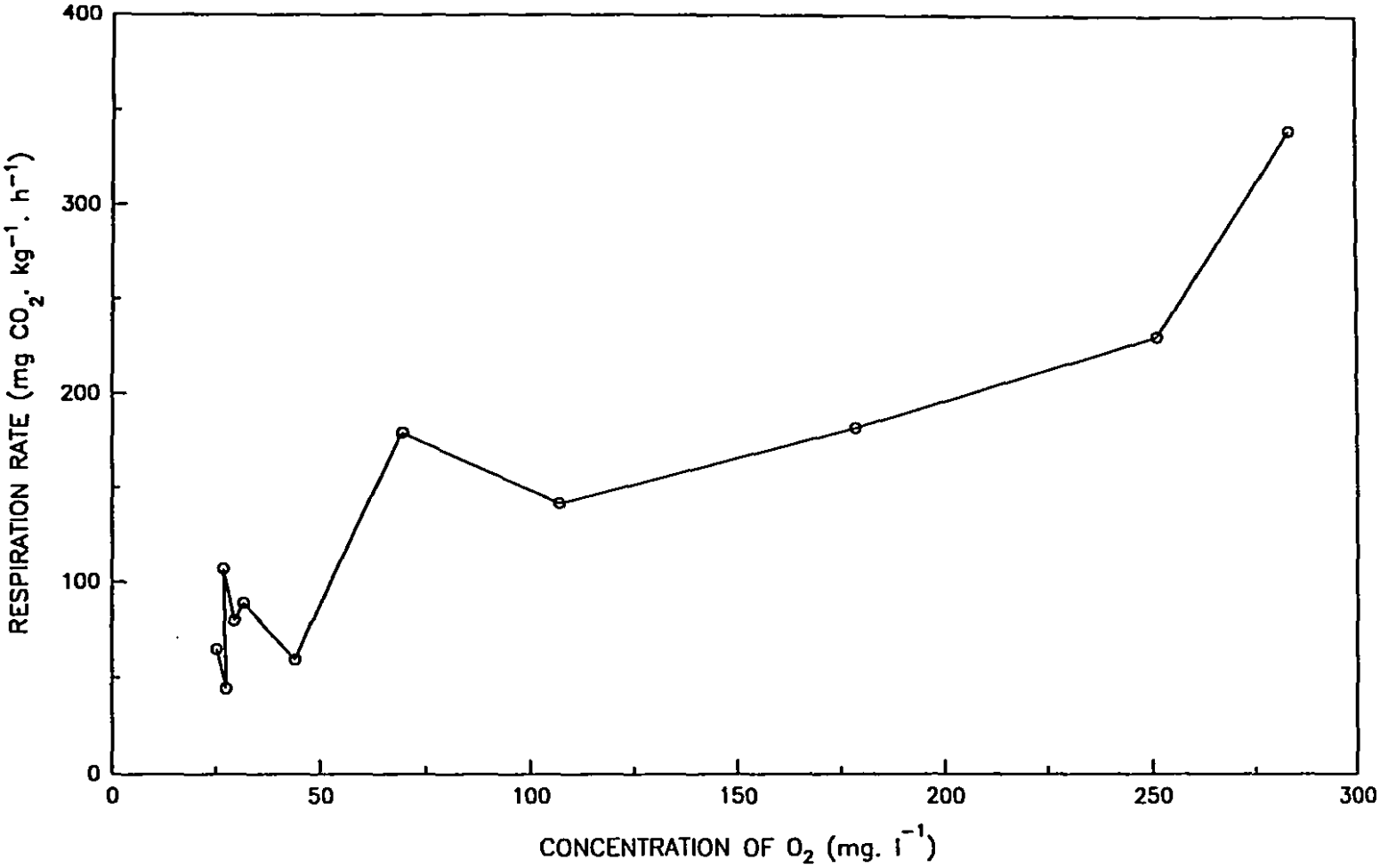

Figure A.18. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 24°C (mean of 3 replicates).

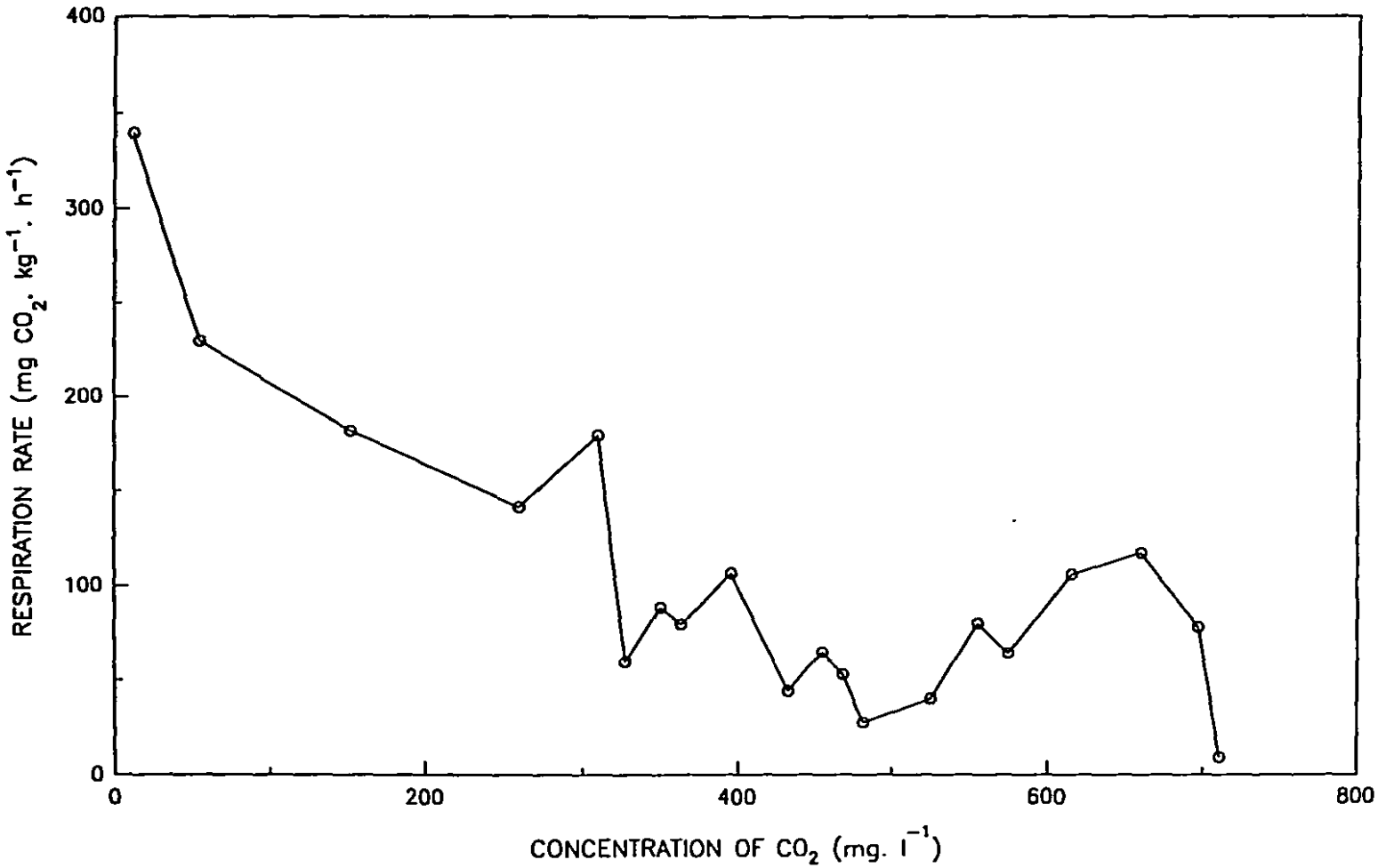

Figure A.19. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 24°C (mean of 3 replicates).

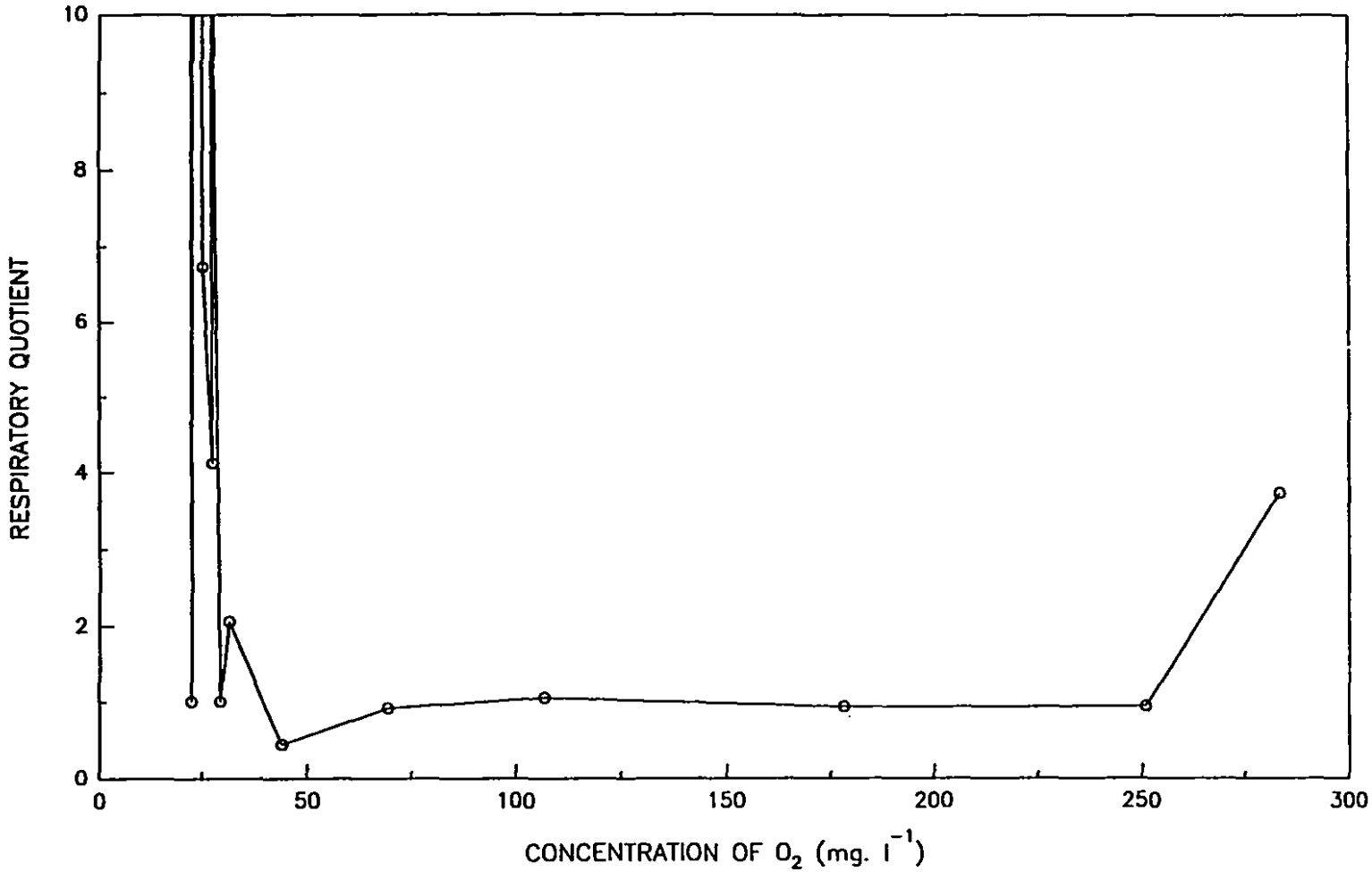

Figure A.20. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 24°C (mean of 3 replicates).

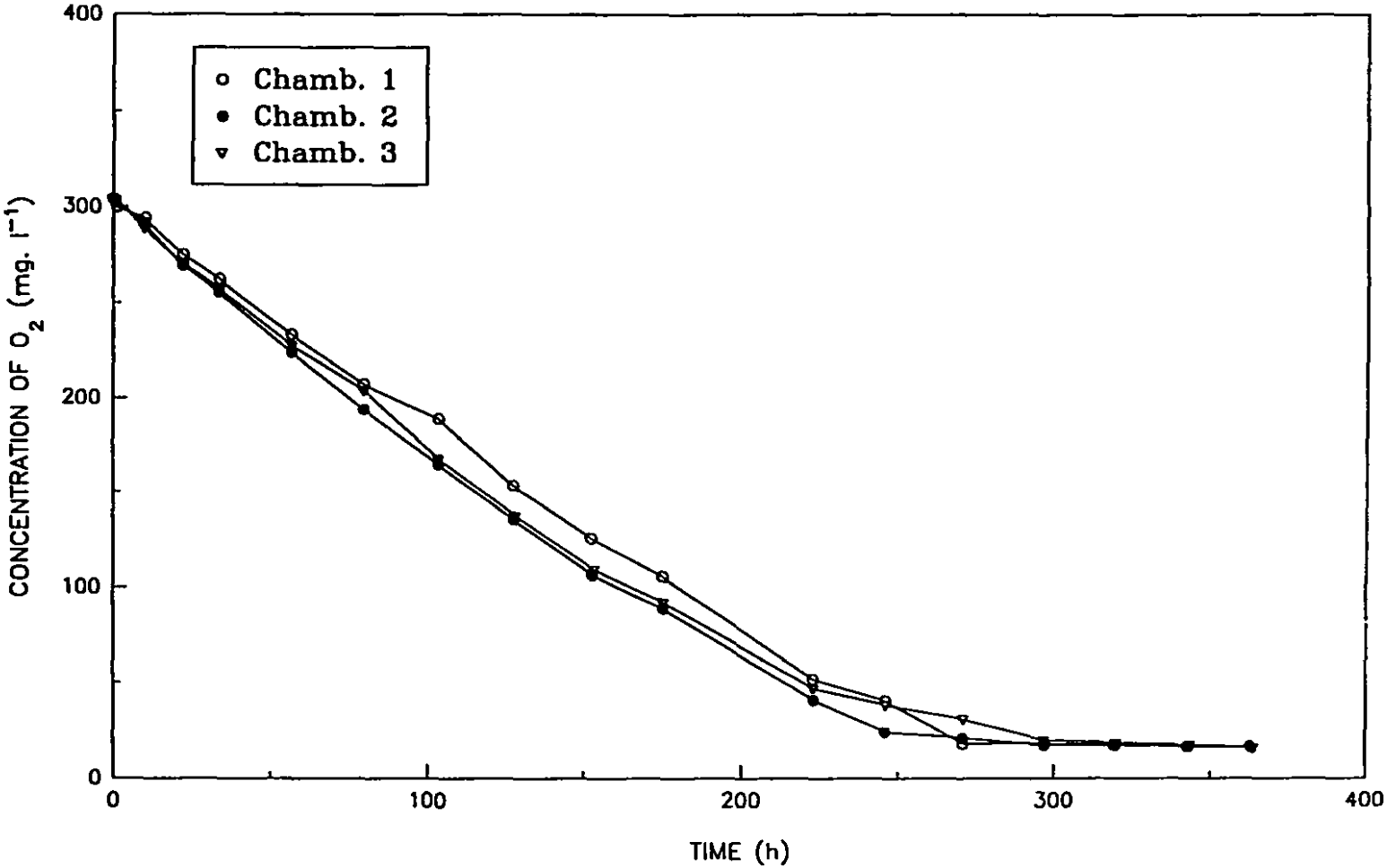

Figure A.21. Progression of O_2 Concentration as a function of time in sealed chambers containing broccoli at 3°C.

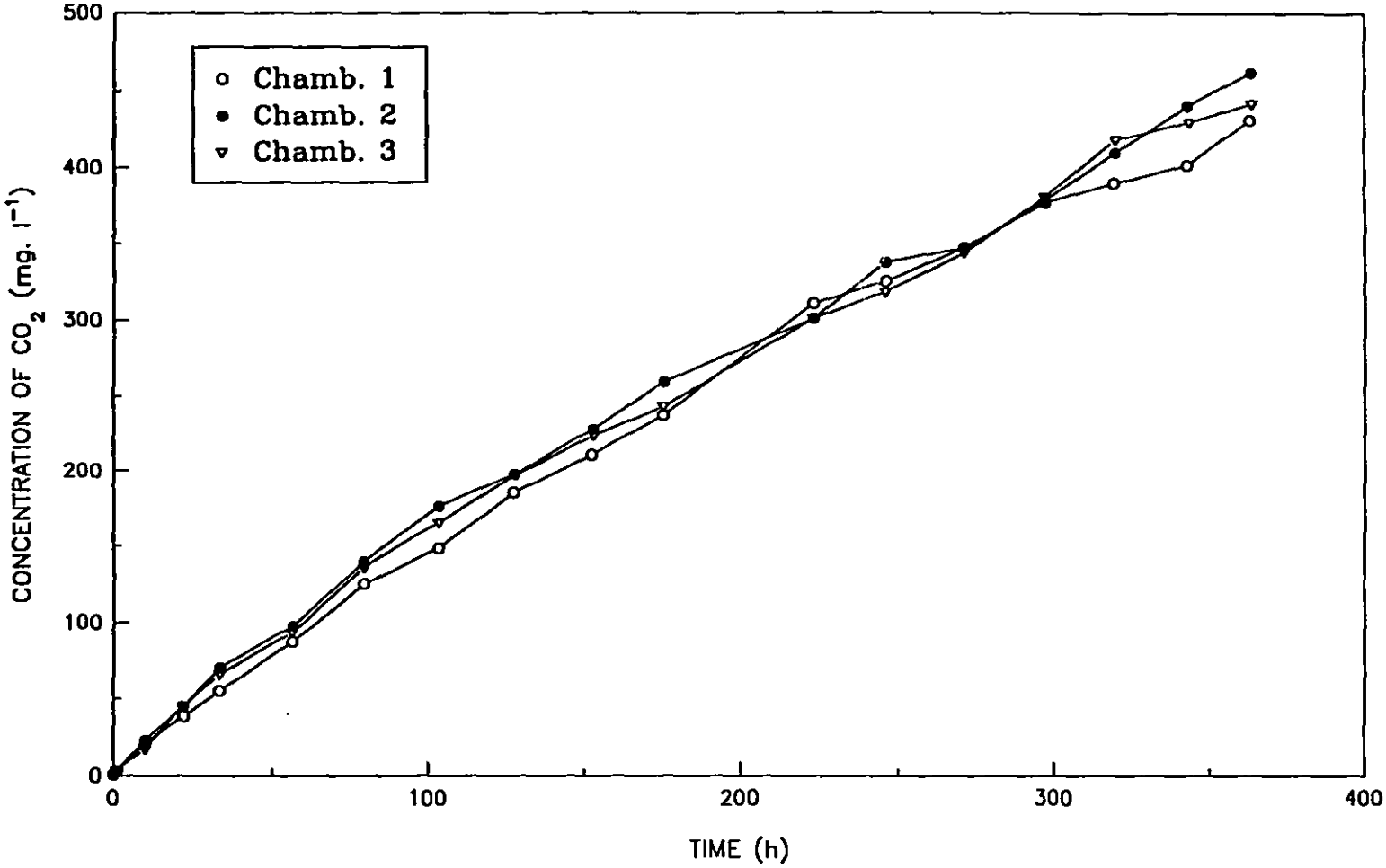

Figure A.22. Progression of CO_2 Concentration as a function of time in sealed chambers containing broccoli at 3°C.

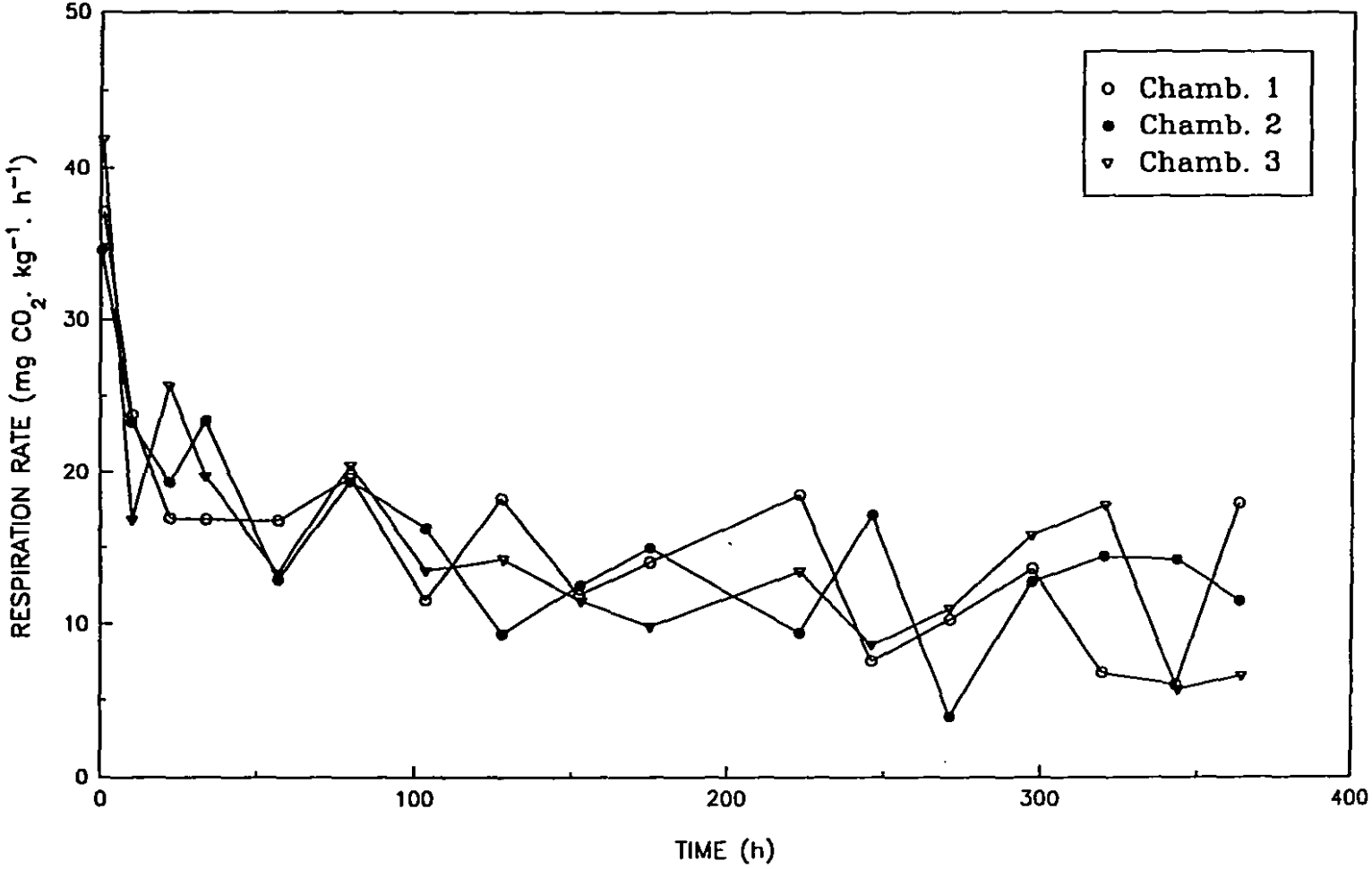

Figure A.23. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 3°C.

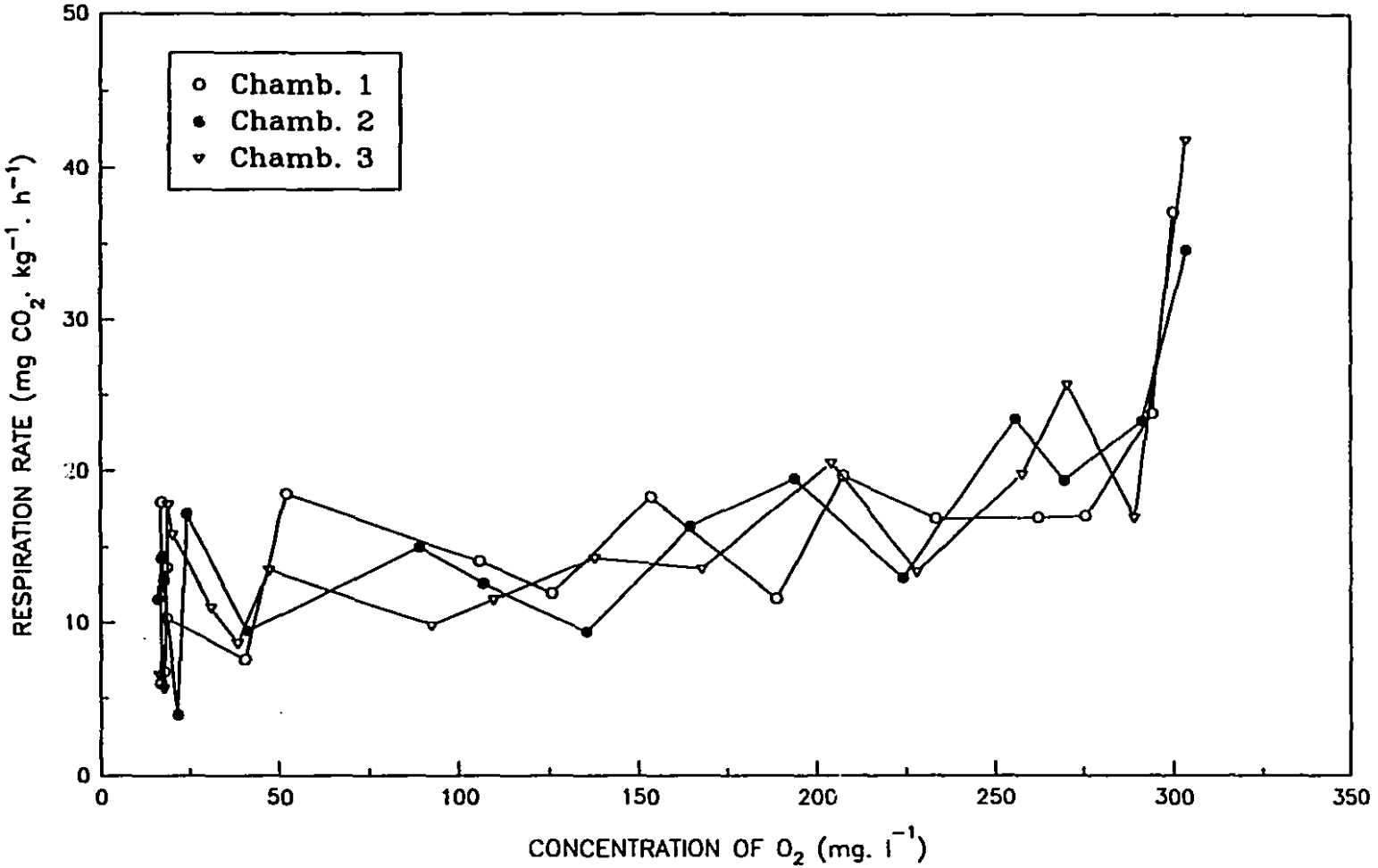

Figure A.24. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 3°C.

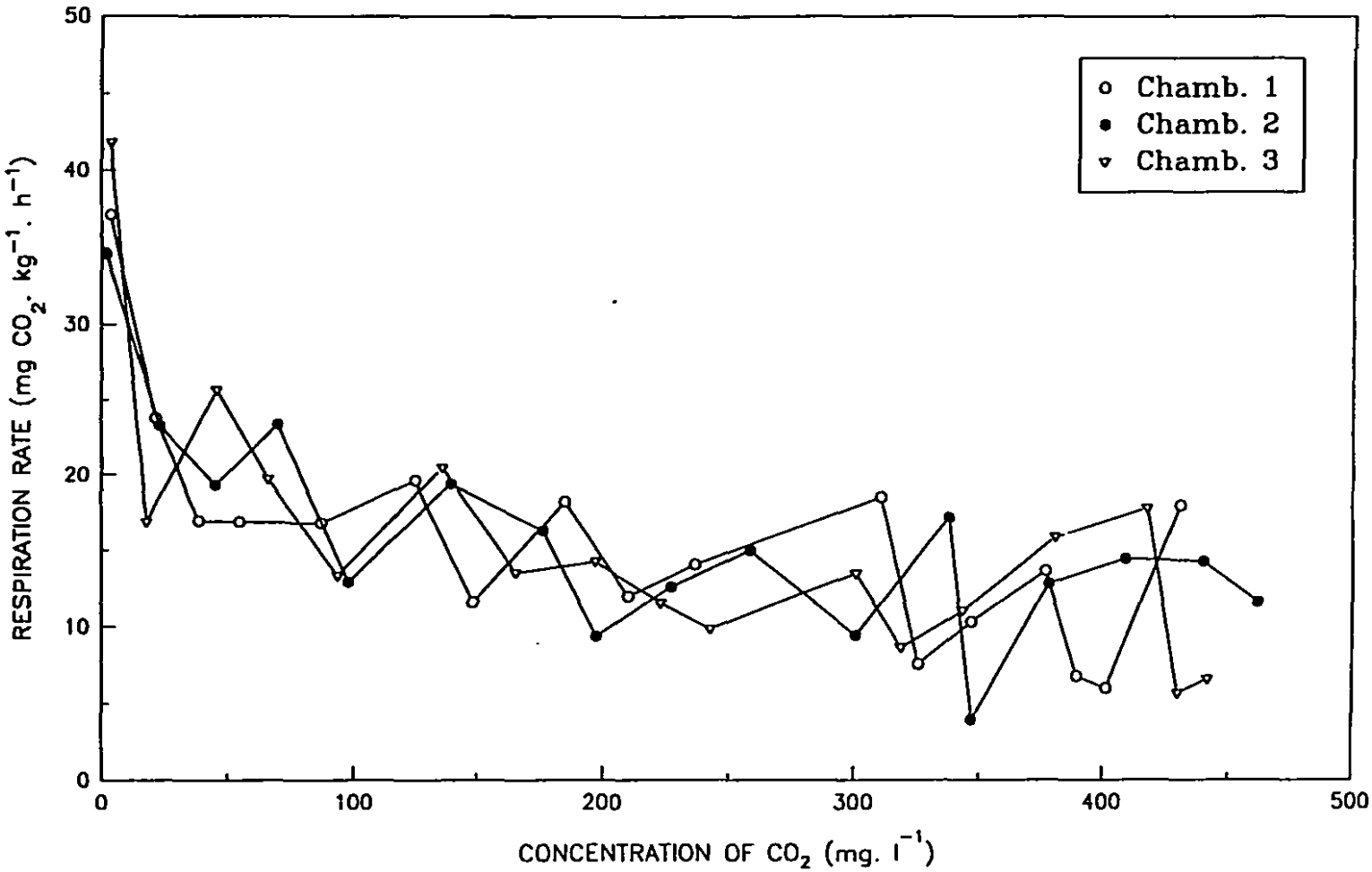

Figure A.25. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 3°C.

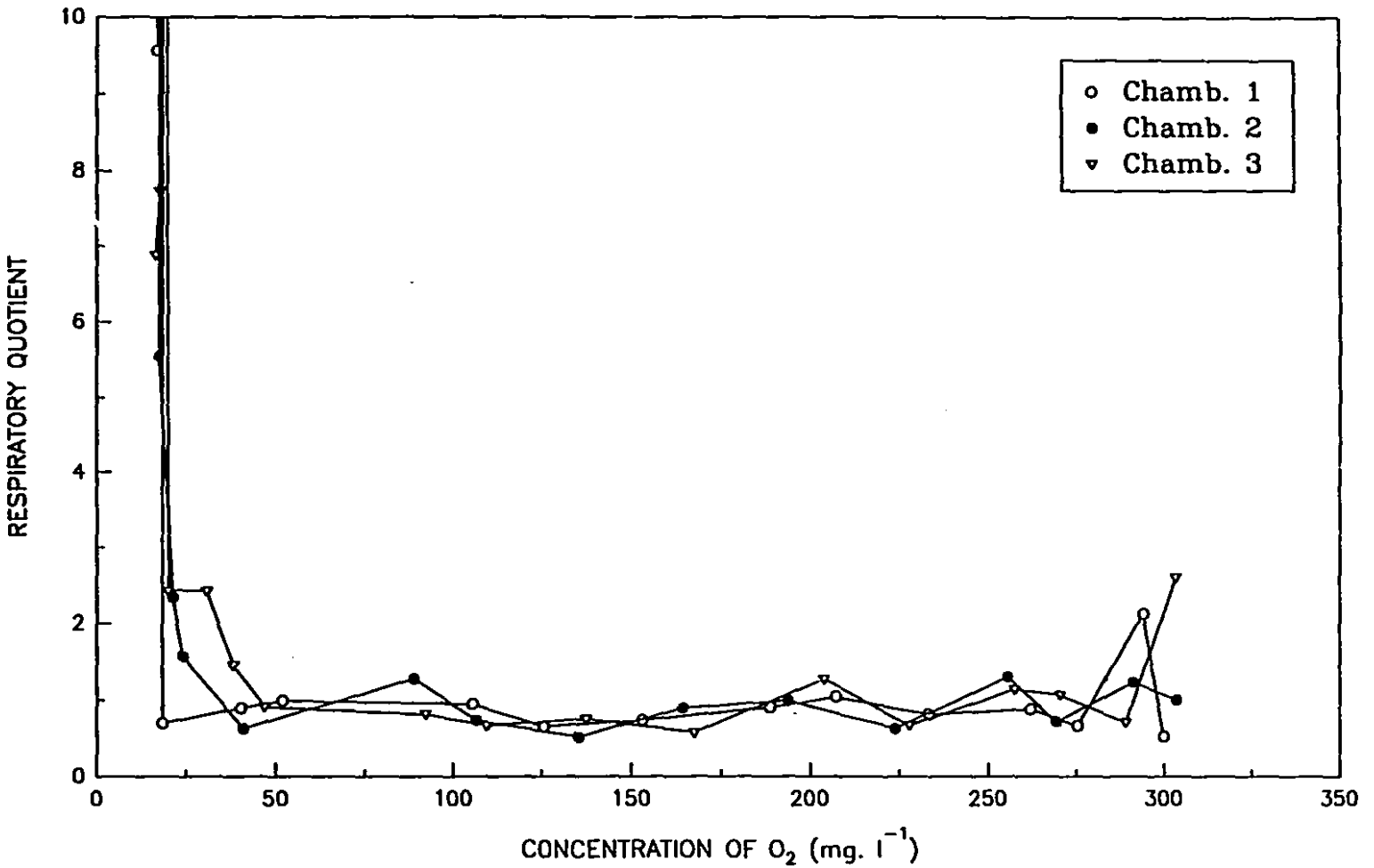

Figure A.26. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 3°C.

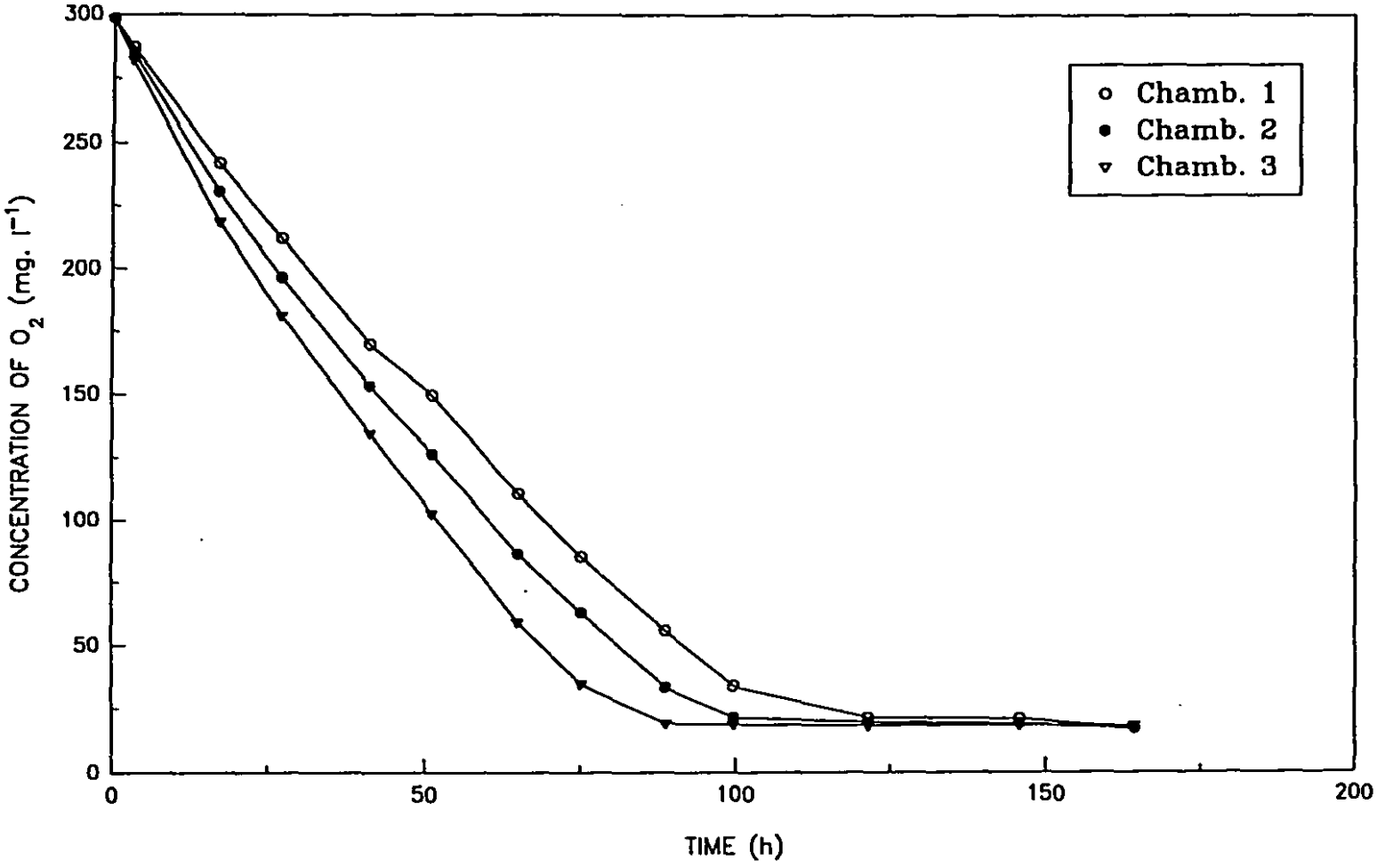

Figure A.27. Progression of O_2 Concentration as a function of time in sealed chambers containing broccoli at 7°C.

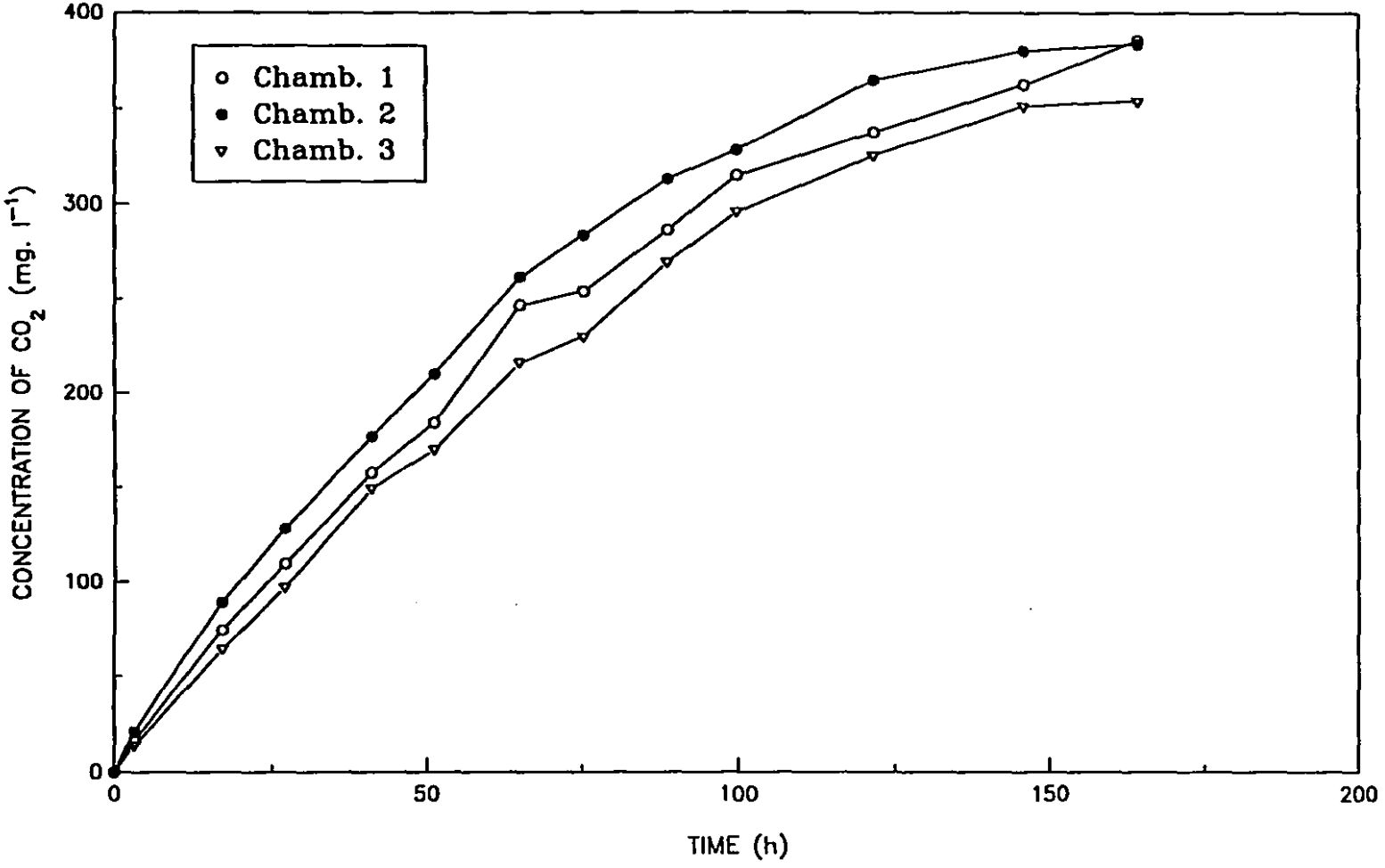

Figure A.28. Progression of CO_2 Concentration as a function of time in sealed chambers containing broccoli at 7°C.

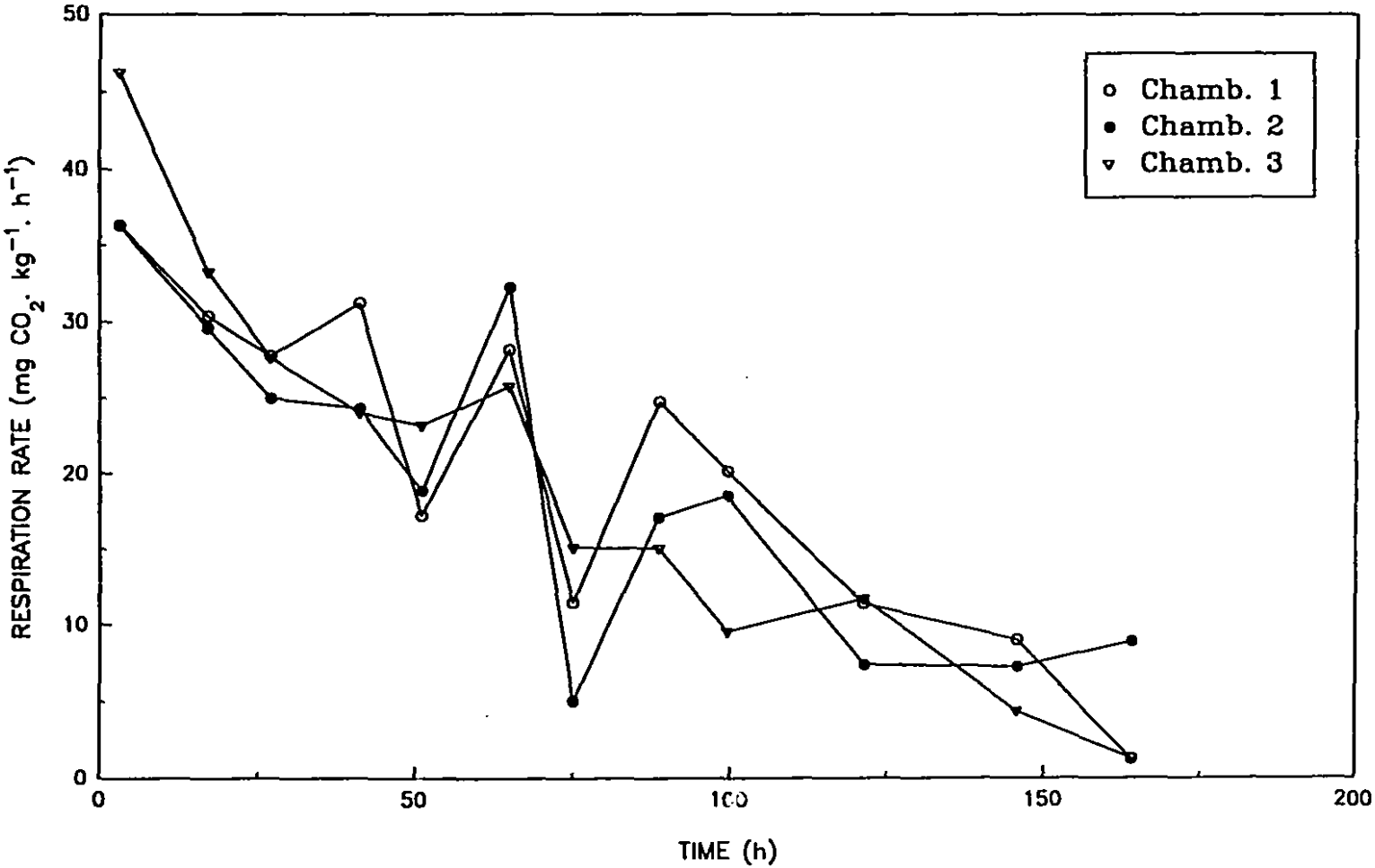

Figure A.29. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 7°C.

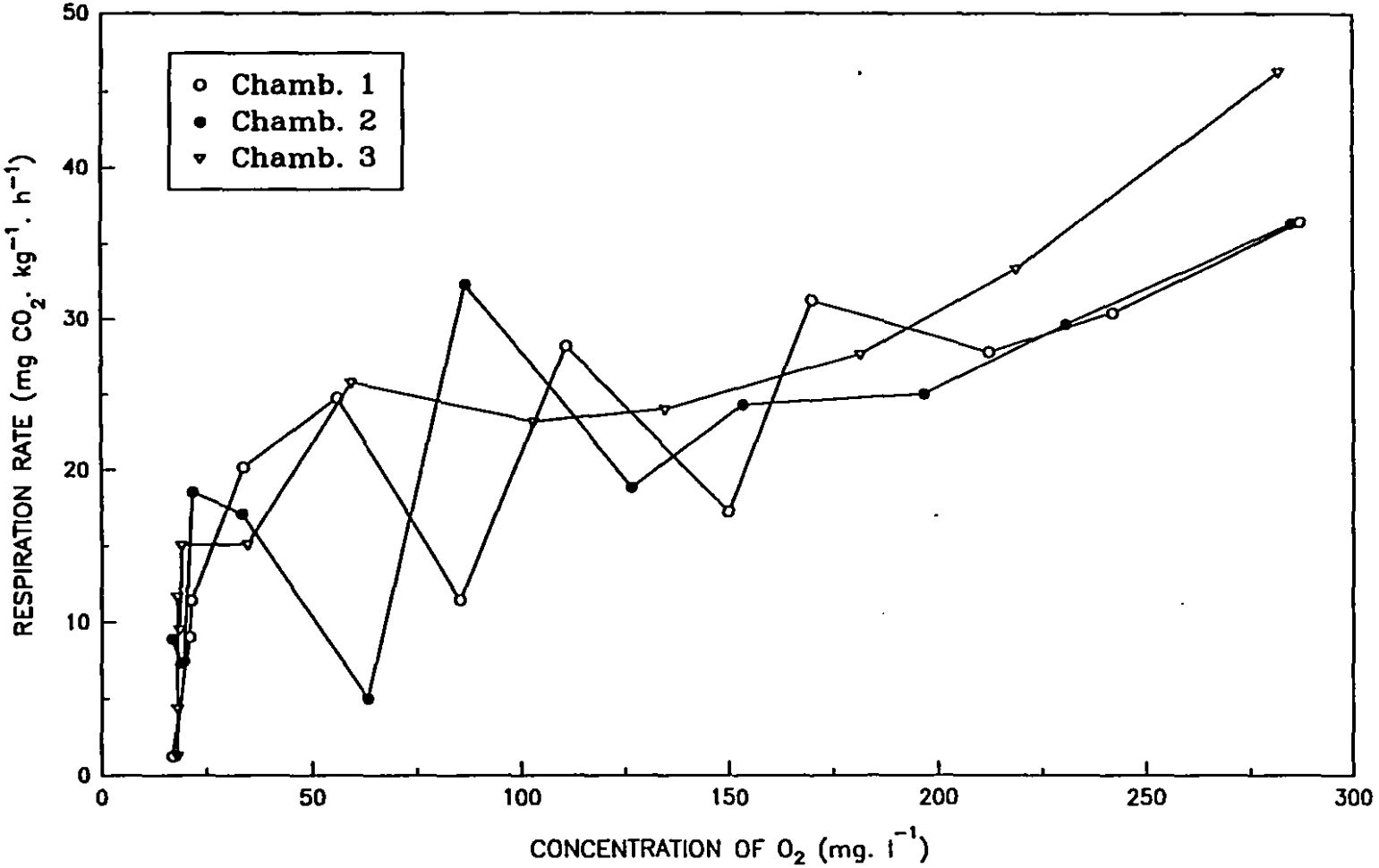

Figure A.30. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 7°C.

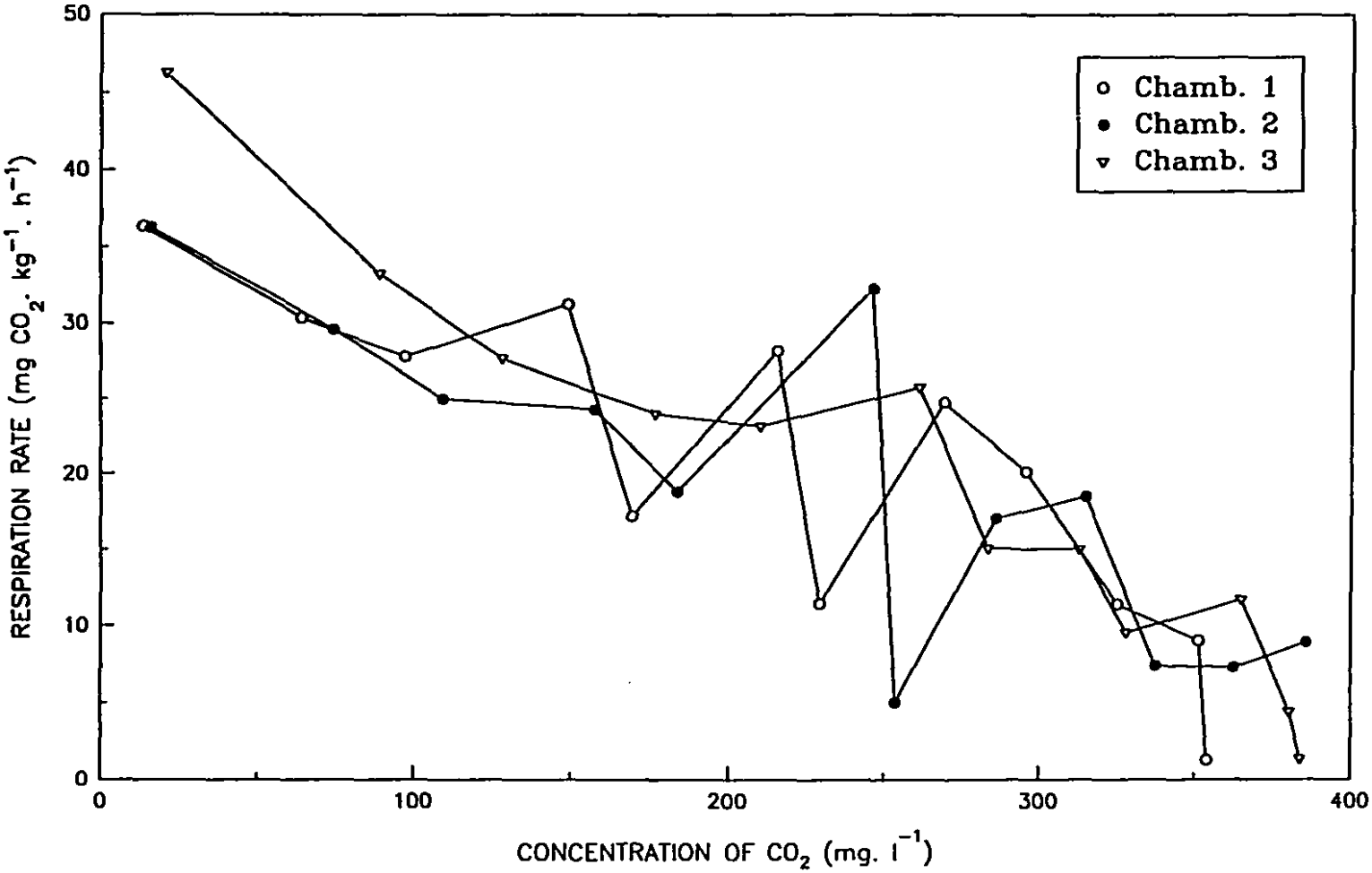

Figure A.31. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 7°C.

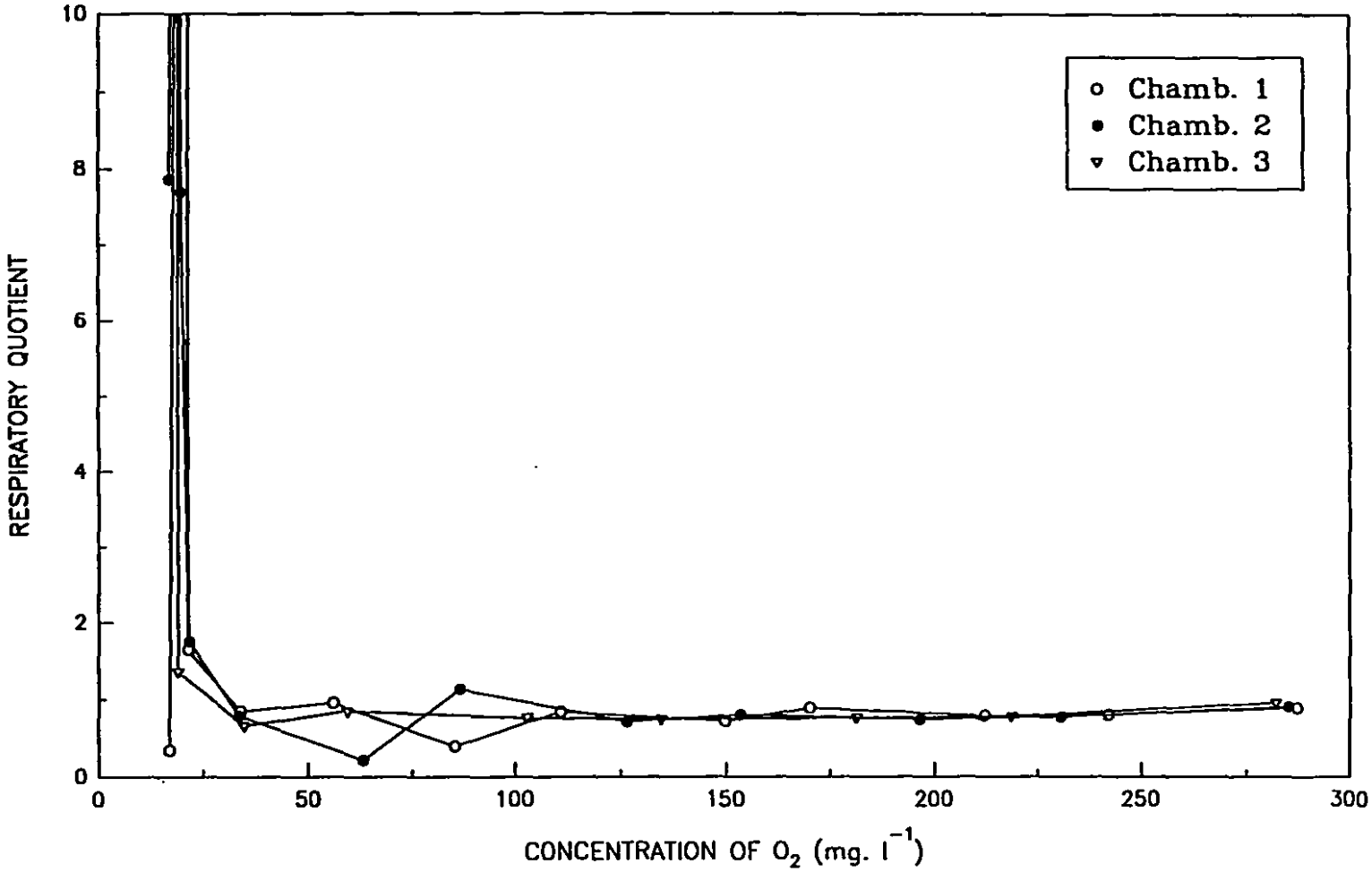

Figure A.32. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 7°C.

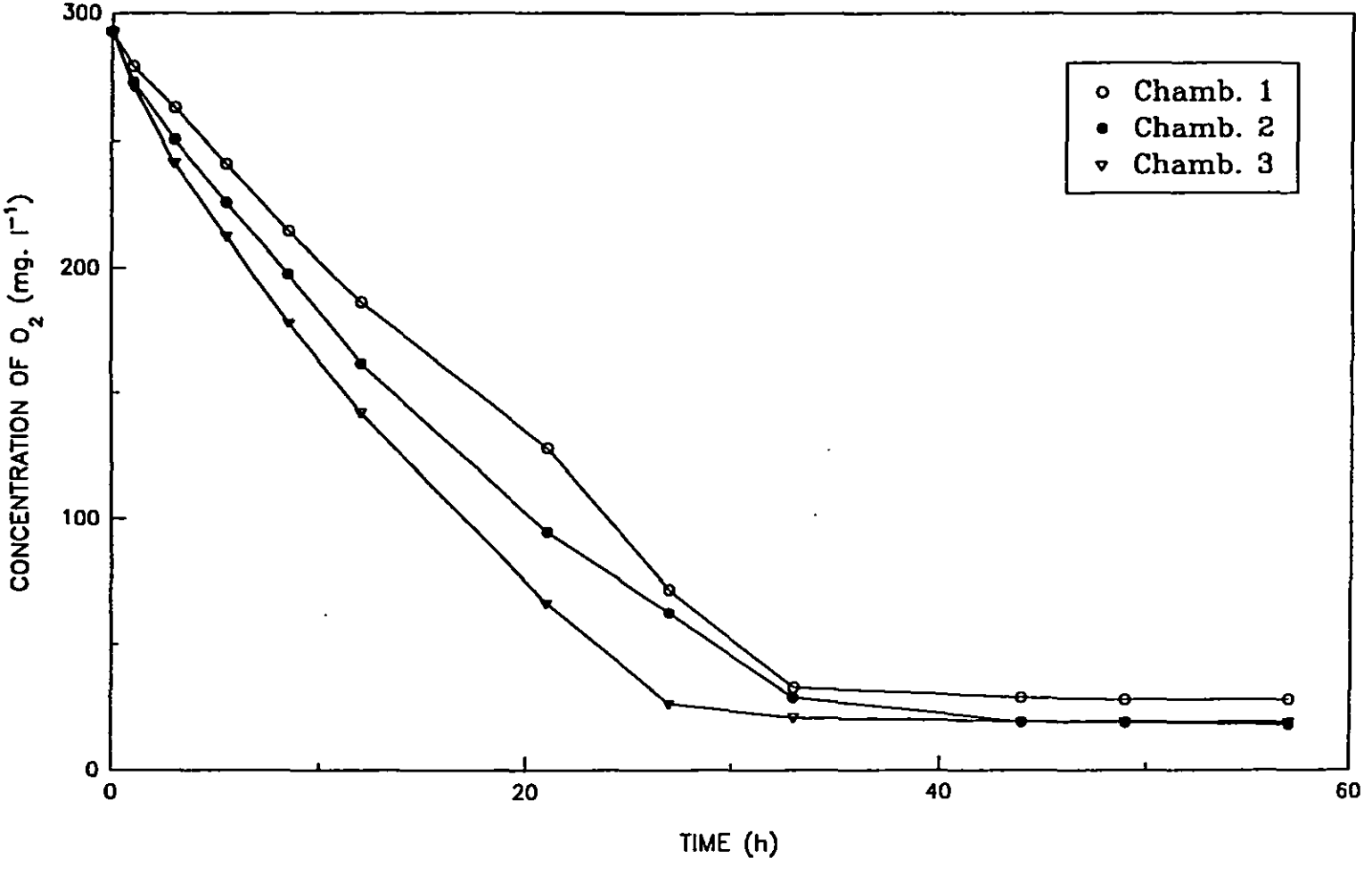

Figure A.33. Progression of O_2 Concentration as a function of time in sealed chambers containing broccoli at 13°C.

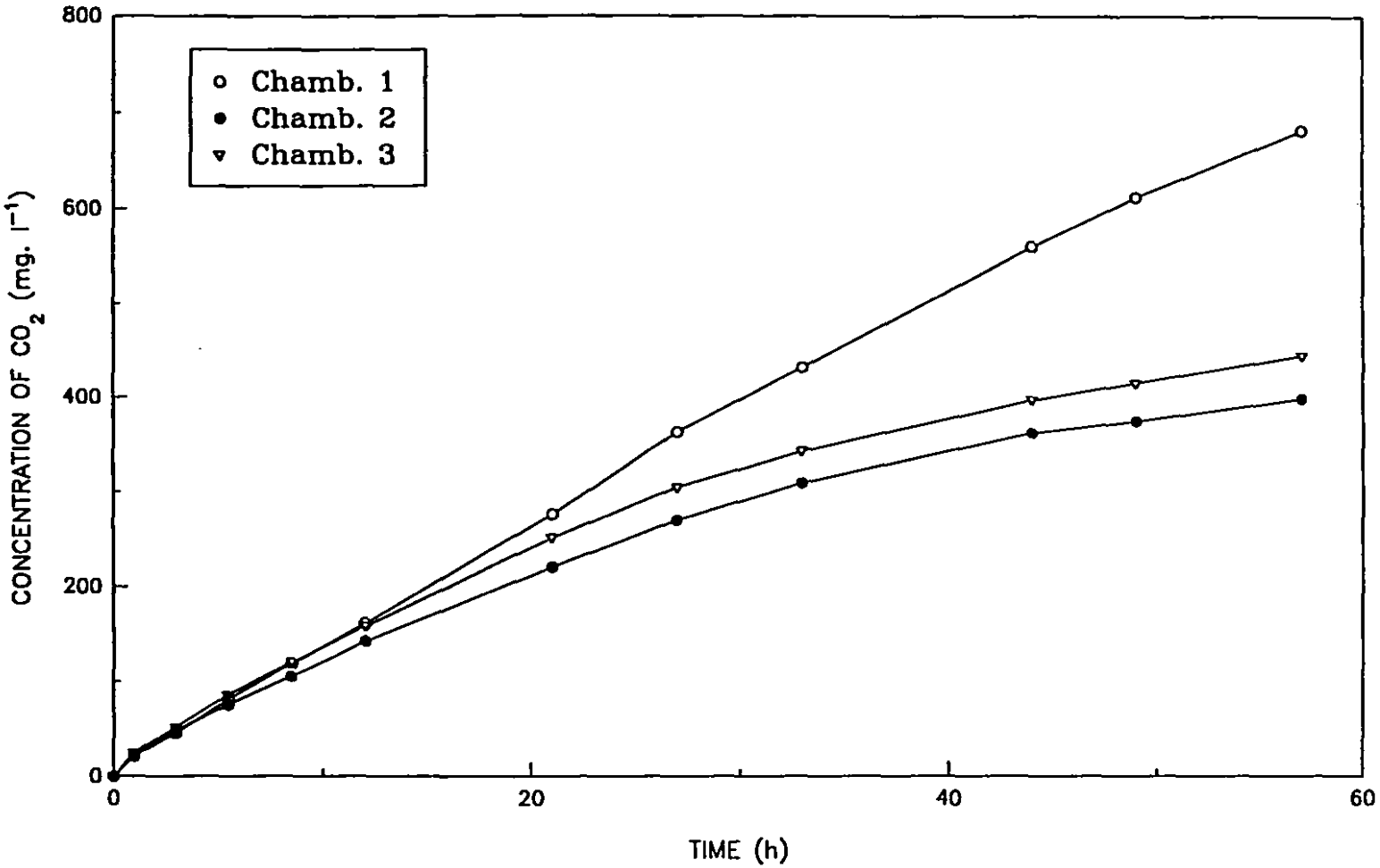

Figure A.34. Progression of CO_2 Concentration as a function of time in sealed chambers containing broccoli at 13°C.

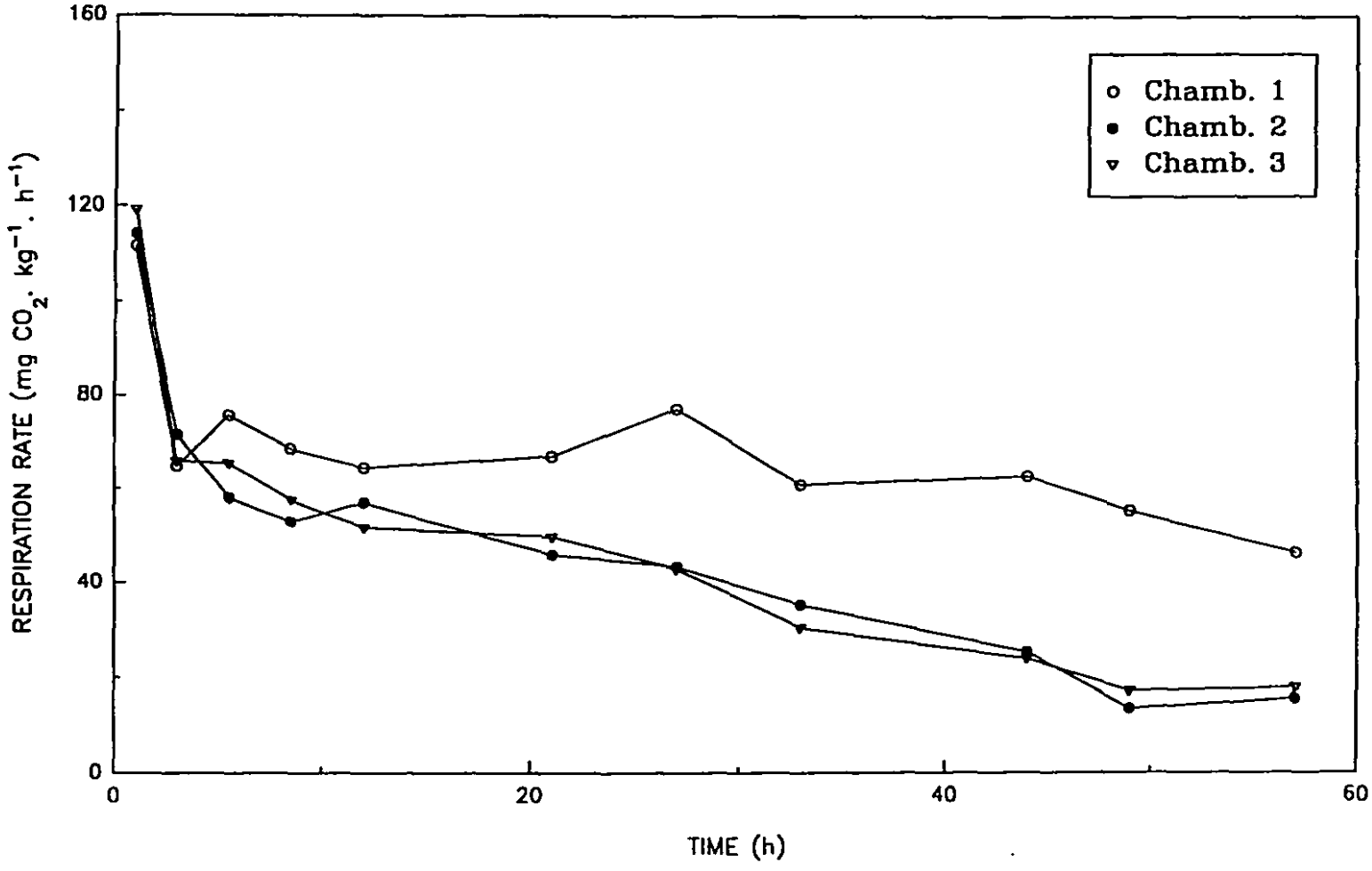

Figure A.35. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 13°C.

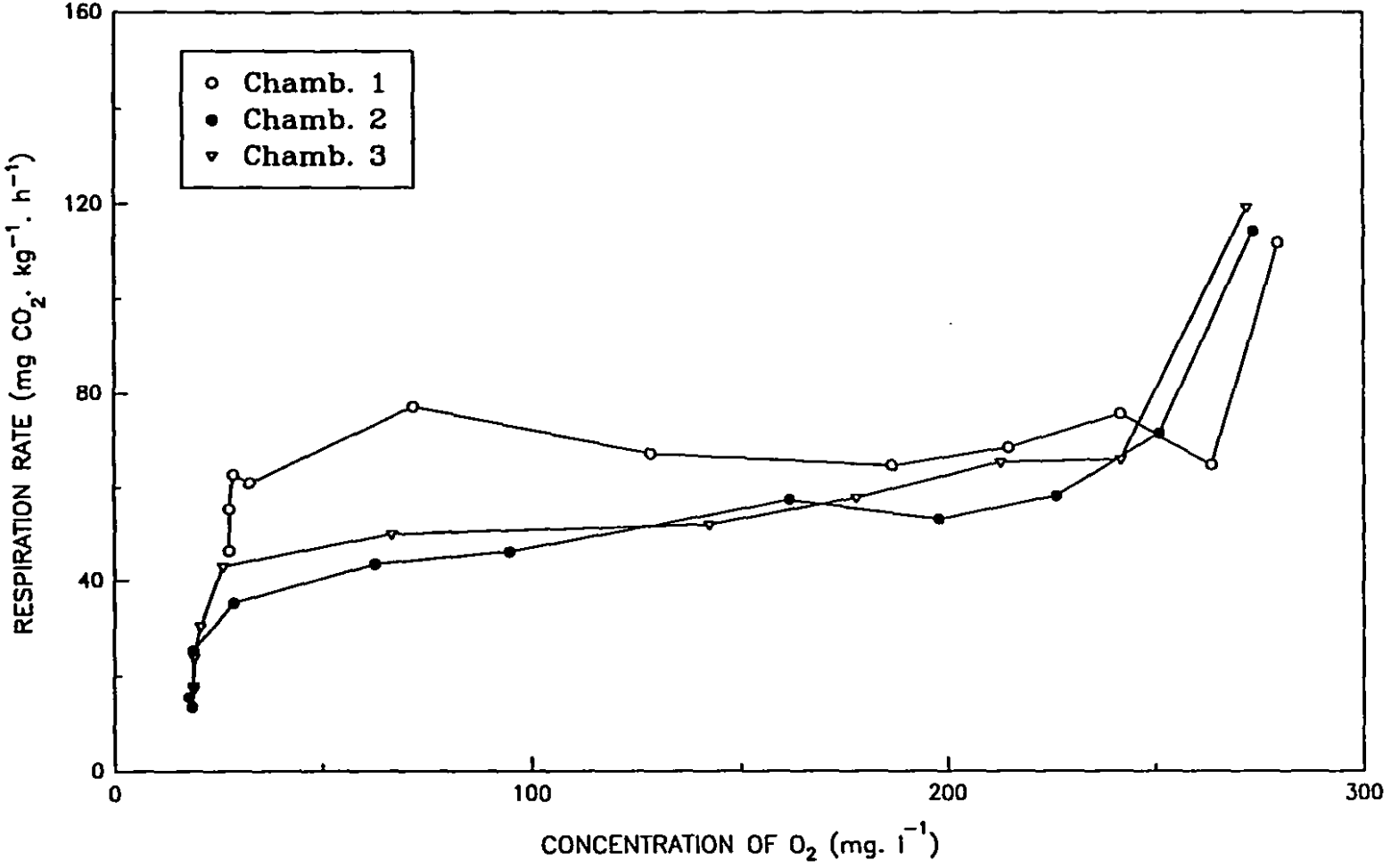

Figure A.36. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 3°C.

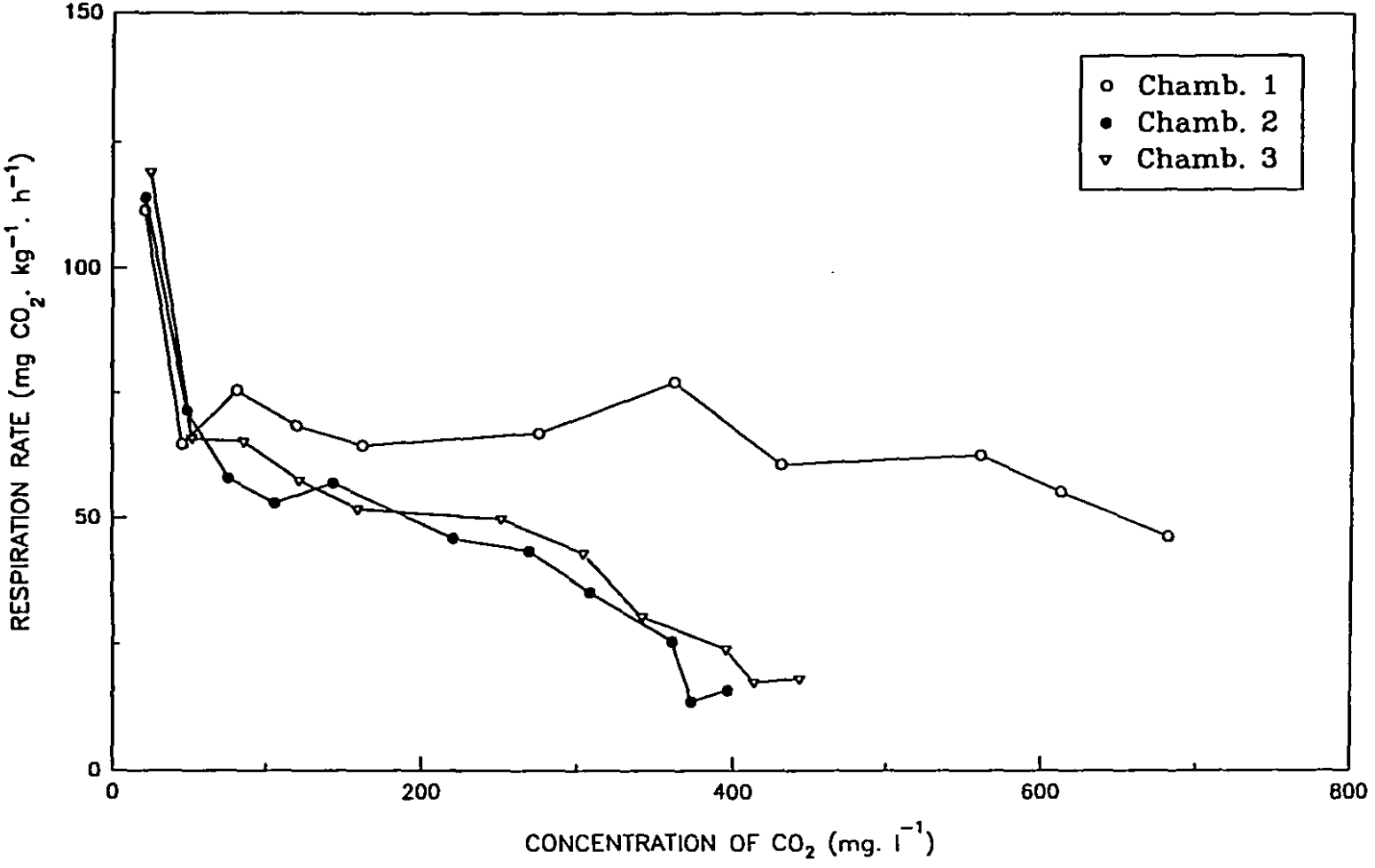

Figure A.37. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 13°C.

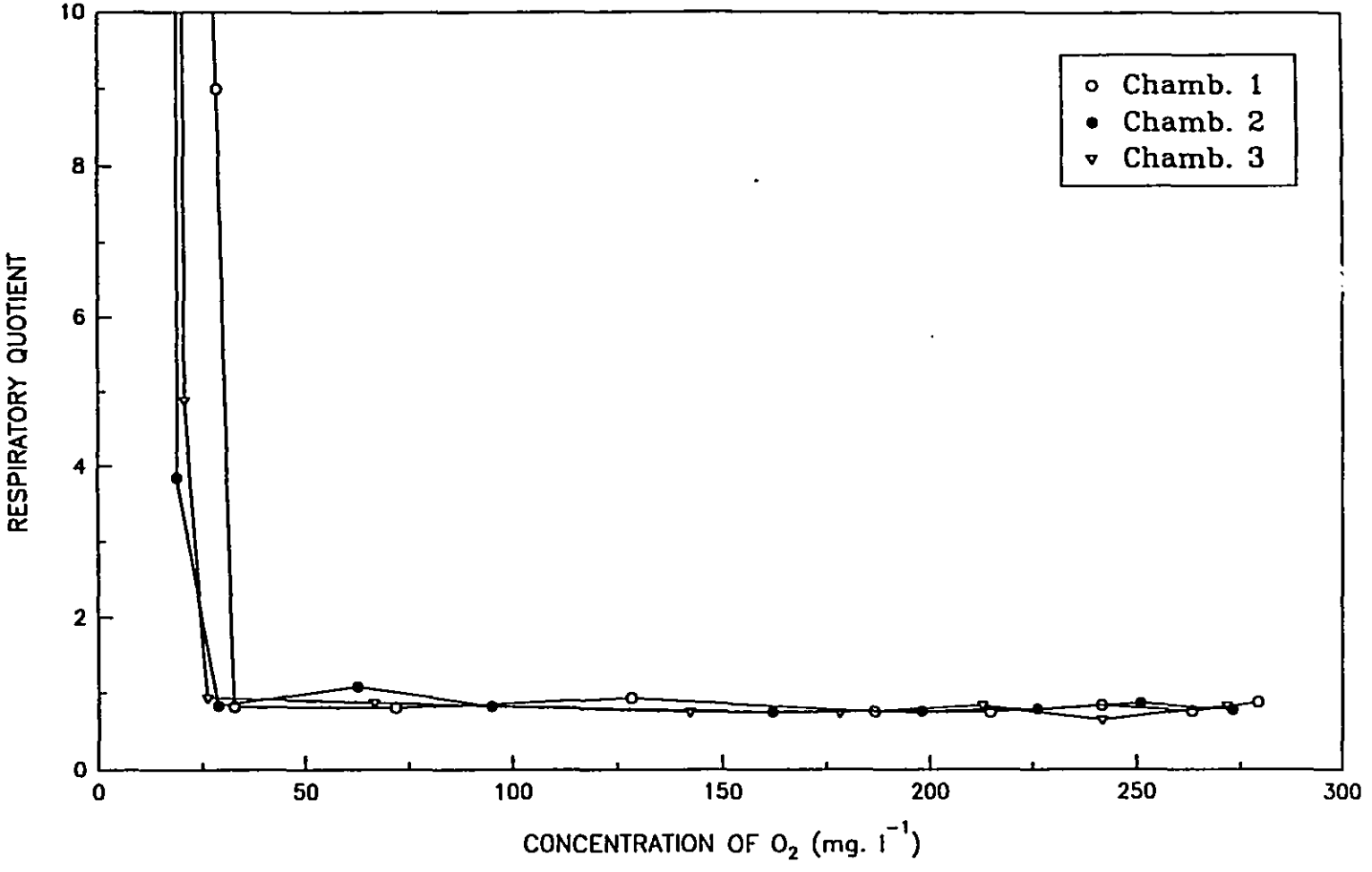

Figure A.38. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 13°C.

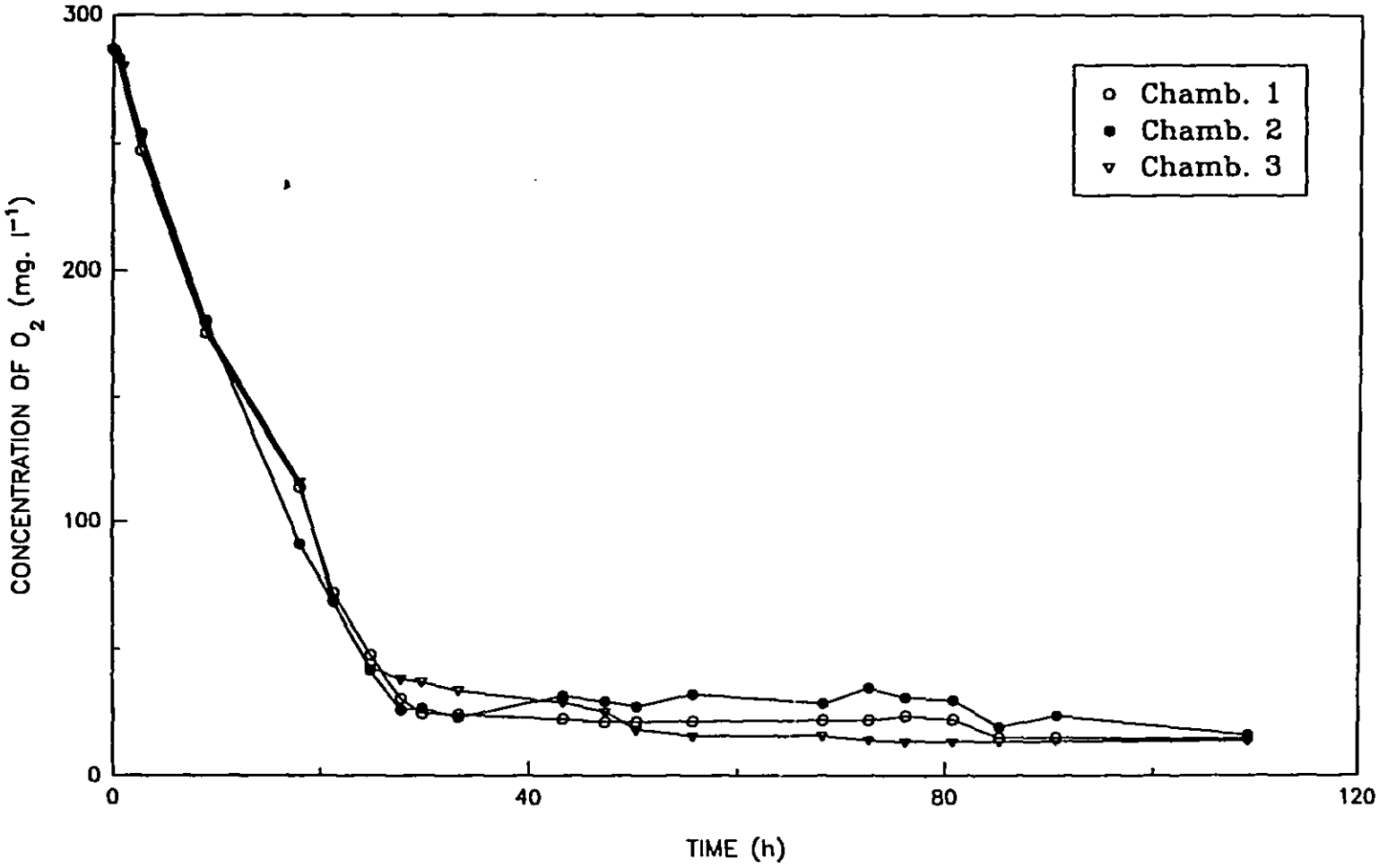

Figure A.39. Progression of O_2 Concentration as a function of time in sealed chambers containing broccoli at 24°C.

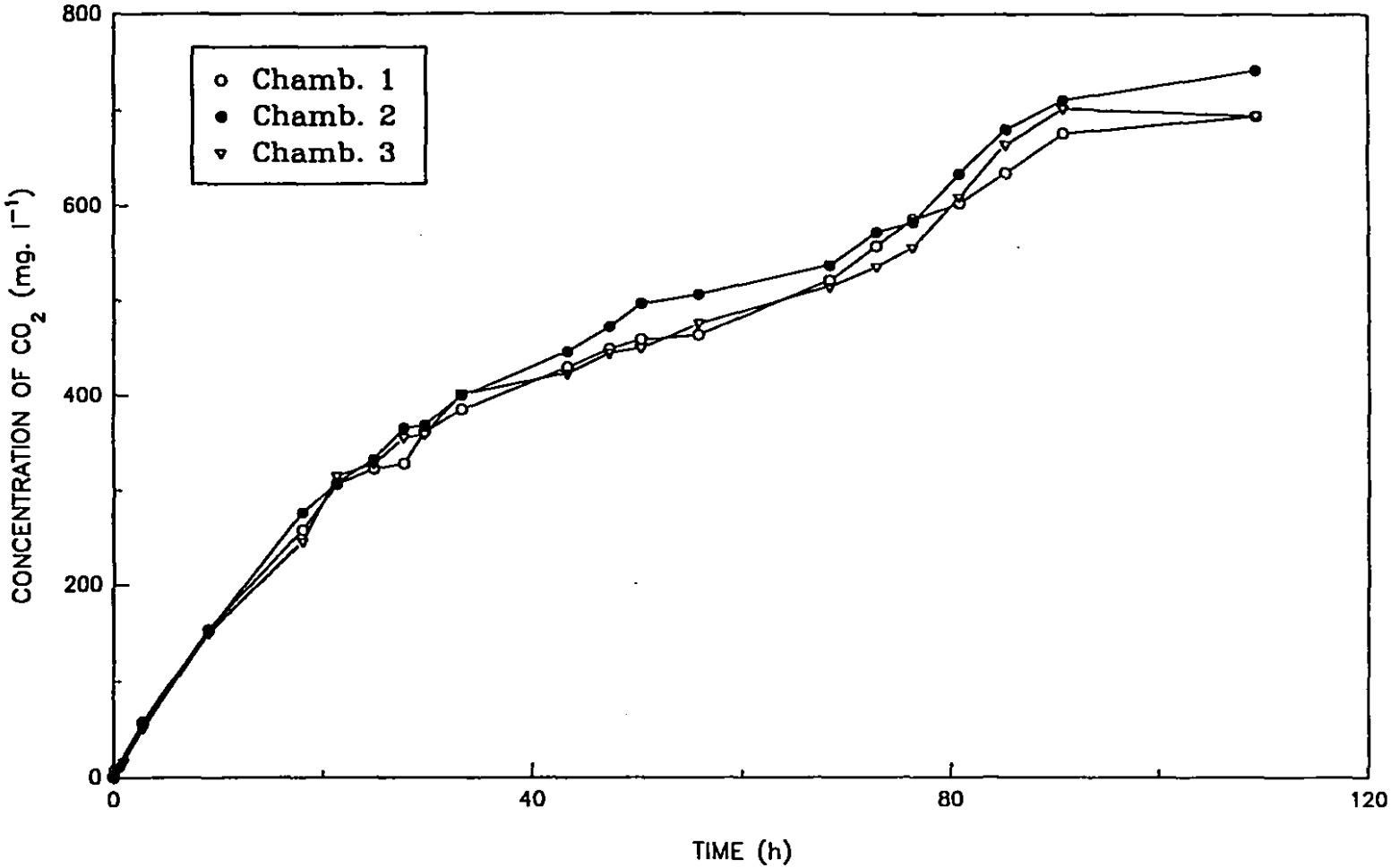

Figure A.40. Progression of CO_2 Concentration as a function of time in sealed chambers containing broccoli at 24°C.

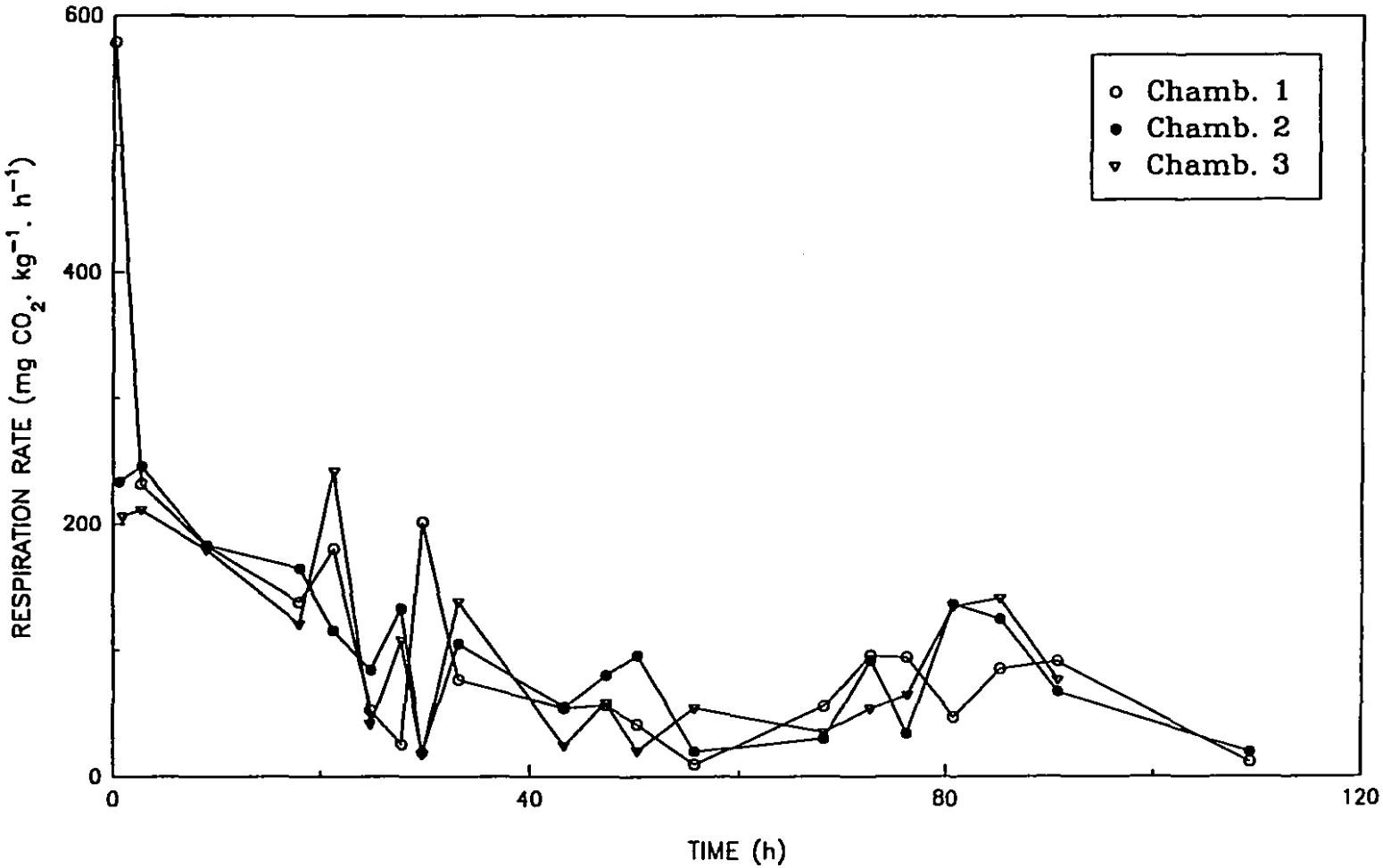

Figure A.41. Progression of Respiration Rate as a function of time in sealed chambers containing broccoli at 24°C.

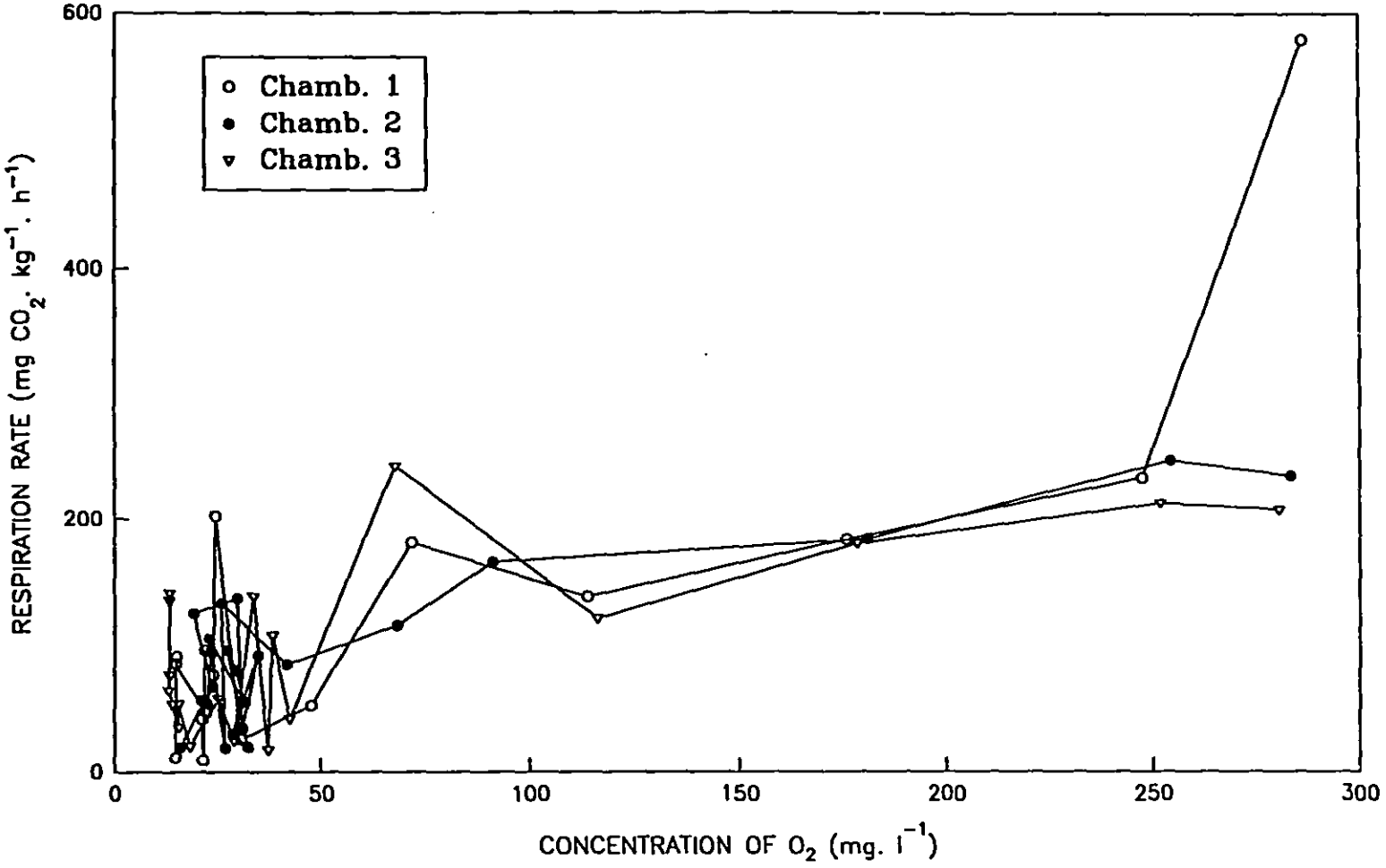

Figure A.42. Progression of Respiration Rate as a function of Concentration of O_2 in sealed chambers containing broccoli at 24°C.

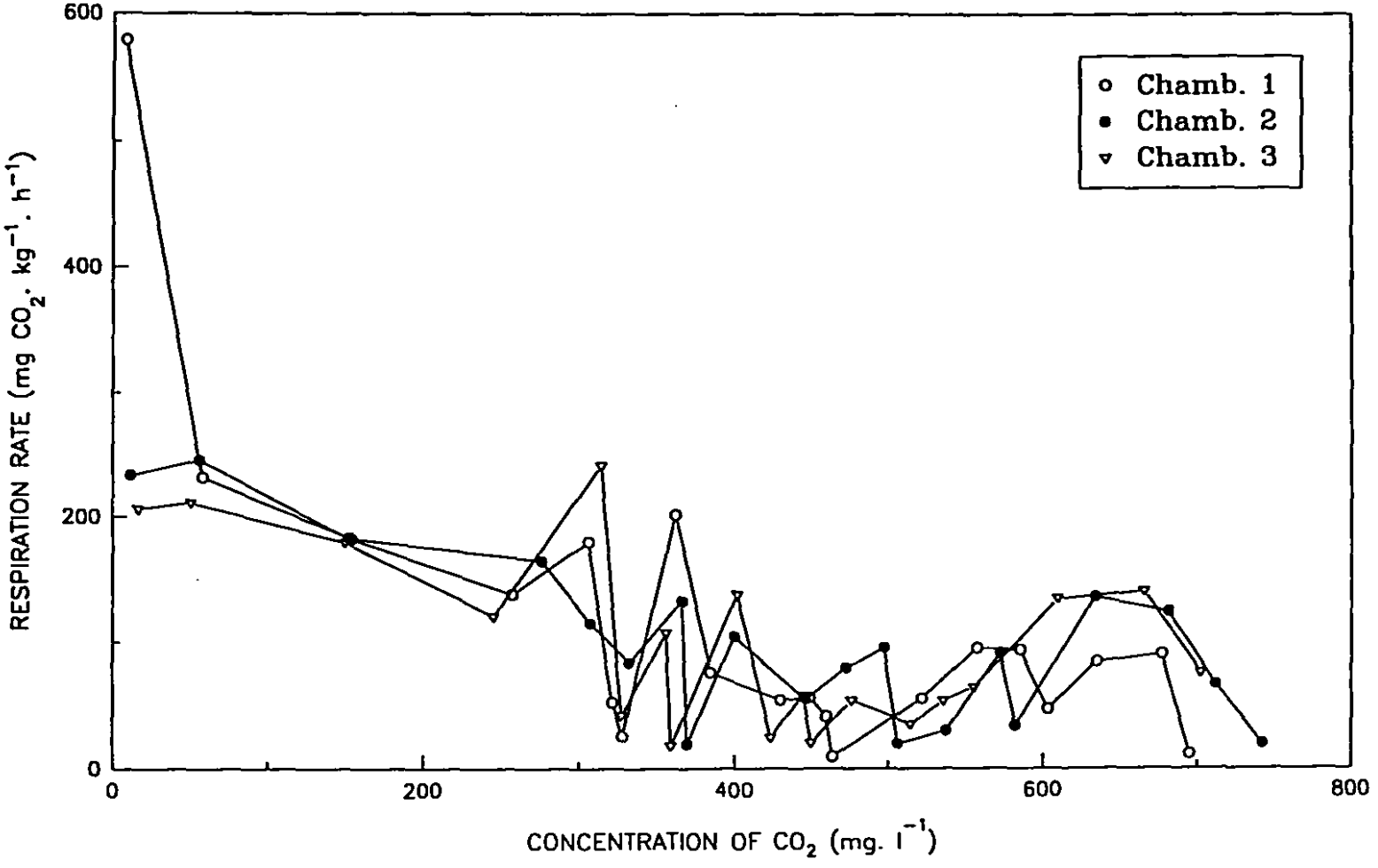

Figure A.43. Progression of Respiration Rate as a function of Concentration of CO_2 in sealed chambers containing broccoli at 24°C.

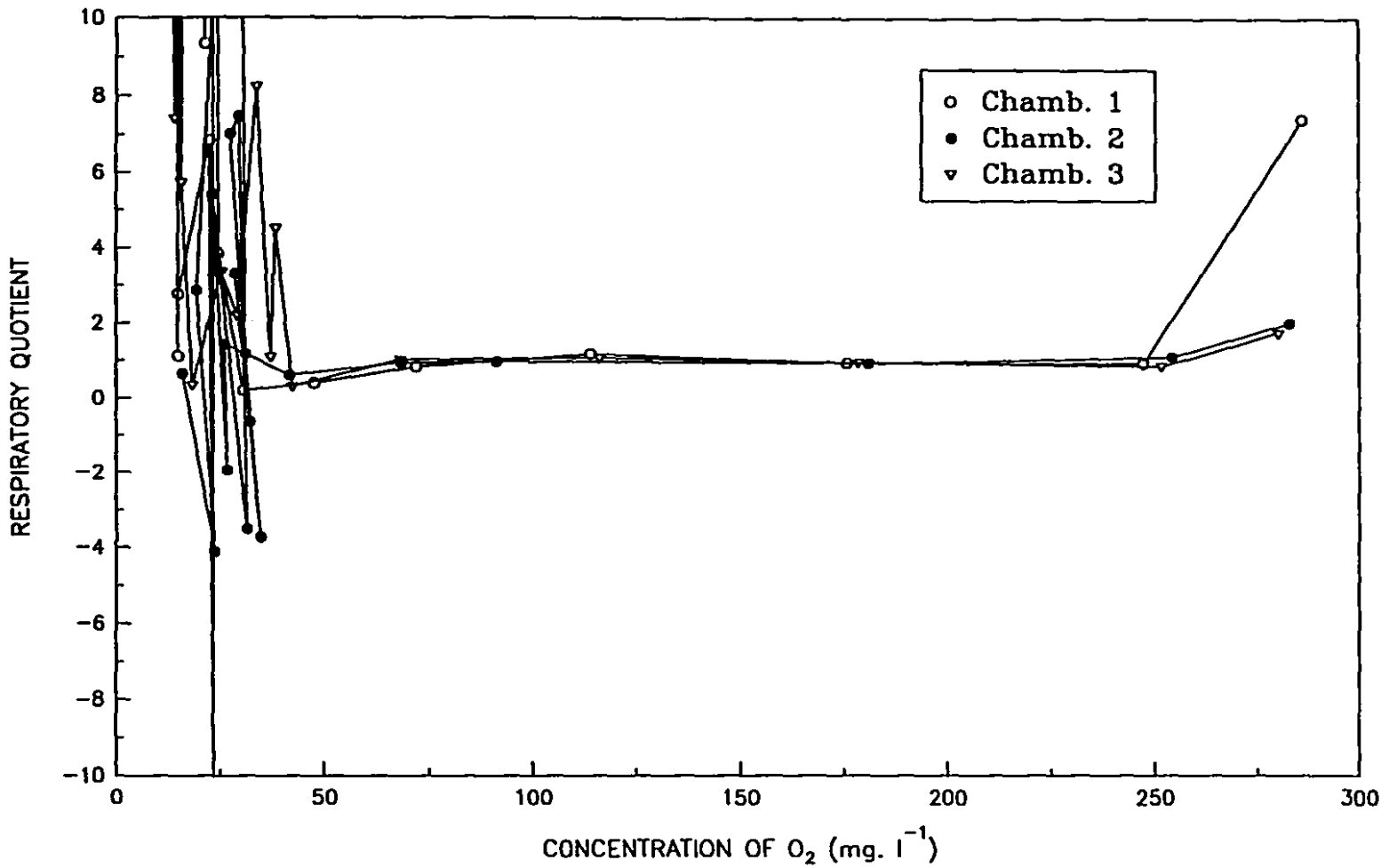

Figure A.44. Progression of Respiratory Quotient (RQ) as a function of Concentration of O_2 in sealed chambers containing broccoli at 24°C.