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The Effect of MCP on the Quality of Fresh-cut Apples and the Development of MCP Controlled Release Devices

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THE EFFECT OF MCP ON THE QUALITY OF FRESH-CUT APPLES AND THE DEVELOPMENT OF MCP CONTROLLED RELEASE DEVICES

By

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ABSTRACT

THE EFFECT OF MCP ON THE QUALITY OF FRESH-CUT APPLES AND THE DEVELOPMENT OF MCP CONTROLLED RELEASE DEVICES

By

Krittika Tanprasert

1-Methylcyclopropene (MCP), an ethylene antagonist, can be used to extend the storage life and shelf life of horticultural crops. The cultural use of MCP on fruits and vegetables is a single application after harvest. This dissertation relates to two aspects of MCP: first, the potential of MCP-treated apples as a raw material for fresh-cut apples and, second, development of a controlled release device to enable continuous in-package application of MCP.

Fresh-cut apples are increasingly more popular and have the potential to increase the revenue stream of the apple industry. One of the objectives of this study is to evaluate how postharvest treatments such as MCP and controlled atmosphere (CA) storage, individually and in combination, affect the subsequent quality of fresh-cut apples over 9 month storage period. The combination of MCP treatment and CA storage resulted in slices with superior firmness but were highly susceptible to enzymatic browning. The combination treatment resulted in apple slices having a different volatile profile from apples receiving either of the individual treatments. MCP + CA storage apples are suitable as a raw material for fresh-cut apples only when the enzymatic browning can be minimized. When this is not the case, MCP treated apples and CA storage apples are the better choice to use. At 3 and 9 months storage of intact apples, MCP-treated apples

were better than CA-storage apples. At 3 months, MCP treated apples had greater firmness and less susceptibility to enzymatic browning. At 9 months, the firmness of MCP treated apples was greater than the minimum threshold level and the slices were less sensitive to enzymatic browning than CA storage apples. At 5 and 7 month storage, CA storage apples and MCP treated apples resulted in slices with a similar quality.

The other objective of this study was to develop controlled release devices to enable a continuous in-package MCP treatment. Then, the release characteristics of several developed devices were evaluated as a function of temperature and relative humidity. In this study, four controlled release devices, monolithic (LDPE and EVA matrices) and reservoir (LDPE and EVA membrane) were developed. None of the devices released 100% of the available MCP. Among them, the LDPE monolithic device had the most desirable characteristics. The release characteristics of the device depended greatly on temperature and relative humidity. The total amount of MCP released and the release rate increased with increasing temperature. The effect of relative humidity at 22 and 5°C were different. The amount of MCP released and the release rate increased with an increasing RH at 22°C but RH had little effect at 5°C. It is anticipated that the device will to be used as a supplement to the single application after harvest for produce such as tomatoes, apples, and avocados that benefit from repeated or continuous treatment MCP treatment.

This dissertation is dedicated to

My late grandpa, Mr. Preecha Tanprasert,

My late grandma, Mrs. Sirilak Anomasiri

and

the late Dr. Ruben Hernandez

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INTRODUCTION

1-Methylcyclopropene (MCP), an ethylene antagonist, can help to extend the storage life and shelf life of horticulture crops. MCP is available commercially under the trade names EthylBloc® and SmartFresh™. EthylBloc® is approved for treatment on flowers and ornamental crops. SmartFresh™ is approved for uses on apples, melons, tomatoes, pears, avocados, mangoes, papayas, kiwi fruit, peaches, nectarines, plums, apricots, persimmons, bananas, and broccoli. The cultural use of MCP on fruits and vegetables is a single application after harvest. It can be used in place of or in combination with controlled atmosphere storage (CA). When used alone, its effectiveness is similar to that of CA. When used in combination, the effect is additive to the effect of CA. This dissertation relates to MCP in two ways: first, the potential of MCP-treated apples as a raw material for fresh-cut apples and, secondly, development of a delivery device to enable a continuous in-package treatment of MCP.

Fresh-cut apples are increasingly more popular and have potential to increase the revenue stream for the apple industry. The product is available in supermarkets and quick serve restaurants. Unlike other apple products, fresh-cut apples have a shorter shelf life than the raw material, i.e whole apples. Therefore, fresh-cut apples need to be processed at the time when the apple slices are required to be in the market. In order to have this product available year round, apples must be preserved using the appropriate postharvest

treatment. One of the objectives of this research is to evaluate how the postharvest treatments of MCP treatment and CA storage, individually and in combination, over a period of 9 months storage, affects the subsequent quality of fresh-cut apple slices.

Several published research papers have described an additional benefit of repeated and continuous MCP treatment of produce such as apples, tomatoes, and avocados. Therefore, several attempts have been made to develop a method to continuously deliver MCP. Most devices are reservoir devices that contain an active component (MCP) within a rate controlling membrane. MCP is supplied as a gas, contained within a molecular encapsulated complex, or in a solvent. To a lesser extent, monolithic devices containing MCP gas or a molecular encapsulation complex are being developed. Thus, the other objective of this research is to develop MCP controlled release devices and to evaluate their release characteristics as a function of temperature and relative humidity.

1 LITERATURE REVIEW

1.1 Introduction

Ethylene is a plant hormone produced by higher plants that regulates the growth and development of fruits and vegetables. Its major postharvest cultural use is to induce uniform ripening and improved eating quality. Ethylene synthesis is also implicated in some defense mechanisms to prevent disorders and microbial spoilage. Despite its beneficial roles, ethylene also has detrimental effects that shorten the storage life and shelf life of produce by promoting senescence (Watkins 2002).

The effect of ethylene can be induced by endogenous and exogenous ethylene. Endogenous ethylene is produced by the produce itself and the amount depends on the biology and stage of development of the produce. The ethylene biosynthesis pathway can be found in elsewhere (Watkins, 2002). Exogenous ethylene is produced by biotic and abiotic sources external to the effected plant material. This ethylene can come from several sources in the produce distribution chain. Wholesale markets typically have a low level of exogenous ethylene (0.06 $\mu L\ L^{-1}$) while distribution centers can have a level of ethylene high have an ethylene level of 0.6-1.4 $\mu L\ L^{-1}$, which is enough to be physiologically active. Supermarket stores have the lowest ethylene level (0.02-0.04 $\mu L\ L^{-1}$) particularly in the display area. Domestic refrigerators have a tendency to have high ethylene concentration (0.01-0.6 $\mu L\ L^{-1}$). The major

sources of ethylene in domestic refrigerators are from other ripened climacteric fruits. To a lesser extent, trucks and gas-powered forklift vehicles operating in the distribution environment can produce some ethylene adding 0.001 – 0.005 μL L^{-1} to the normal ethylene levels (Wills and others 2000). In order to extend the postharvest life of produce, the negative effects of endogenous and exogenous ethylene have to be controlled. To achieve this, the distribution chain should be designed so that exposure to exogenous ethylene is minimized. An alternative is to use an ethylene antagonist, which can counteract the effects of both endogenous and exogenous ethylene.

Several compounds are known to be ethylene antagonists but not all of them are suitable for commercial use. One of the most effective ethylene inhibitors is a silver ion, usually applied as silver thiosulfate (STS). It inhibits ethylene action in a non-competitive manner (Veen 1983). However, due to the heavy metal content, it cannot be used for edible plant products (Sisler and Serek 1997).

Sisler and his co-workers (Sisler and Serek 1999) have worked to find compounds that can inhibit ethylene activity. They have found several ethylene antagonists including 2,5-norbornadiene (NBD) , trans-cyclooctene, diazocyclopentadiene (DACP), light-irradiated DACP, 3,3-dimethylcyclopropene (DMCP), cyclopropene, and 1-substituted cyclopropenes. All compounds have competitive kinetics for ethylene receptors but some, such as NBD and trans-cyclooctene, requires continuous exposure because they have a short dissociation time (Sisler and Serek 1999).

Among the ethylene inhibitors mentioned, cyclopropene and 1-substituted cyclopropenes are among the most effective. Cyclopropene is not as stable as the 1-substituted cyclopropene (Sisler and Serek 1997). 1-Methylcyclopropene (MCP) is the most studied compound and is commercially applied to several types of produce worldwide. 1-ethylcyclopropene (ECP), 1-propylcyclopropene (PCP) and MCP cause a similar response on avocado but ECP and PCP require higher concentrations to obtain the maximal ethylene inhibition effect (Feng and others 2004). In bananas, the concentration necessary to keep the banana peel green increases as the size of the substitution group increases up to 3 carbons. Conversely, the necessary concentration decreases as the size of the substitution group is increased to 4 carbons or more. The necessary concentration of 1-substituted cyclopropene with a substitution group of 5 or more carbons is less than that of MCP. However, at the concentration necessary to keep banana peel green, 1-nonylcyclopropene and 1-decylcylopropene do not prevent softening of bananas, which may be a result of low permeation of these compounds through the banana peel. Another drawback of 1-substituted cyclopropene with a large substitution group is the significantly longer required treatment time (Sisler and others 2003).

While companies and scientists are interested in other substituted cyclopropenes, they are not likely to pursue approval of new compounds. MCP shows the most commercial potential because of its approval for use with several plant products. Therefore, the next section focuses only on MCP.

1.2 1-Methylcyclopropene

1-Methylcyclopropene (MCP) is effectively inhibiting ethylene action by competing for its receptor. Like ethylene, MCP probably binds to a metal in the receptor. As currently envisioned, ethylene binds to the receptor causing electrons to be withdrawn, and resulting in a trans positioned ligand moving away from the metal. Another ligand consequently moves toward the metal (Figure 1.1). As this happens, ethylene diffuses away from the receptor and the active complex, which is responsible for several ethylene response, is formed. MCP is thought to remain bound for a longer period; thus the active complex is not formed (Sisler and Serek 1997). The effect of MCP is not permanent, as ethylene response resumes after a certain period of time. This may occurs as a result of the synthesis of new ethylene receptors or MCP may slowly diffuse from the ethylene receptors (Cameron and Reid 2001).

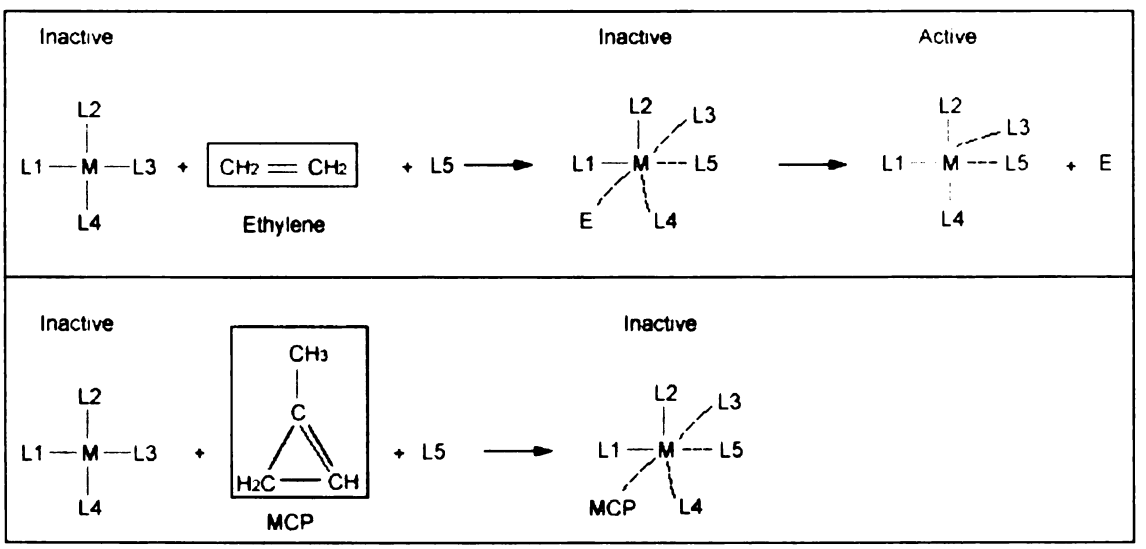

Figure 1.1 Proposed model for ethylene and MCP action on the ethylene receptor. M represents metal, L1-5 represent ligand of unknown structure, E represents ethylene (modified from Sisler and Serek 1997)

The efficacy of MCP depends on several factors. Factors that have been identified include MCP concentration, crop type, maturation stage and treatment duration, temperature, and frequency of treatment. In several crops, research has shown that the efficacy of MCP increases with increasing MCP concentration up to a certain level. At a concentration higher than this, no additional MCP benefit is observed (Jiang and others 1999a; Serek and Sisler 2001; Dong and others 2002). This concentration level has been established for several crops and is referred to in this review as "the optimum concentration". At this concentration, the amount of MCP present is sufficient to saturate the response (Cameron and Reid 2001). Different crops have different optimum concentrations. The required MCP also depends on the treatment duration and temperature. Lower concentration requires a longer duration (Sisler and others 2003). Treatment at low temperature requires higher concentration, likely because the binding rate of MCP to the receptors is low. However, at low temperature, MCP remains effective longer because new receptors are generated at a lower rate than at high temperature (Sisler and Serek 1997). Table 1.1 contains a summary of the concentration, treatment duration and temperature that provides beneficial effects in fruits and vegetables.

Table 1.1 Summary of listing MCP concentration and treatment duration and temperature that provide beneficial effect to fruits and vegetables (modified from Blankenship and Dole, 2003)

Scientific name	Common name	Treatment		
		Conc., µl/l	Temp, °C	Time, hour
Anamas comosus	Pineapple	0.1	20	18
Anmona squamosa x Annoma cheimola[*1]	Custard apple	25	20	14
Arabidopsis	-	0.0022	-	-
Brassica oleracea	Broccoli	1, 12	5, 10, 20	6, 12, 16
B. Rapa var. Chinesis[*2]	Pak choy	12	10	16
B. Juncea var. foliosa[*2]	Chinese mustard	12	10	16
B rapa var. parachinensis[*2]	Choy sum	12	10	16
B. Rapa var. nipposinica	Mibuna and mizuna	12	10	16
B rapa. Var. rosularis	Tatsoi	12	10	16
Carica papaya[*3]	Papaya	25	20	14
Coriandrum sativum	Coriander	0.05	20	24
Cucumis melo (plants)	Melon	0.1	-	0.17
Citrullus lanatus	Watermelon	0.5	20	18
Citrus paradise	Grapefruit	-	25	16 (twice)
Citrus spp.	Orange	0.1 (fruit), 50 (petioles)	25	6, 12
Daucus carota	Carrot	1	20	4

Table 1.1 (continued)

Scientific name	Common name	Treatment		
		Conc., µl/l	Temp, °C	Time, hour
Diospyros kaki	-	0.3	20	3
Fragaria x ananassa	Strawberry	0.005-0.015, 0.25-0.5, 2	20	2-18
Hanconia speciosa		90	31	Continuous
Lactuca sativa	Lettuce	1, 0.1	6	4
Lycopersicon esculentum	Tomato	0.005-0.007, 0.01-0.02, 0.15, 20	20	2-24
Lycopersicon esculentum (plants)	Tomato	4 mg EthylBloc powder/L	Growing temperature	Overnight
Malus domestica 'Anna', 'Fuji', 'Golden Delicious', 'Red Delicious', 'Rome', 'Gala', 'McIntosh', 'Granny Smith', 'Ginger Gold', 'Jonagold', 'Empire', 'Law Rome'	Apple	0.6-2	0, 5, 10, 15, 20-25	7 to 20
Mangifera indica[*4]	Mango	250	20	14
Musa sp., AAA group, Cavendish subgroup	Banana	0.005-0.5, 0.1, 45	20-24	6-24
Nicotiana attenuate (plants)	Tobacco	0.03, 1.6-18 g, EthylBloc powder/L	Growing temperature	6
Persea Americana	Avocado	0.05-0.3, 0.45, 25	3, 5, 20, 22	6-48
Pisum sativa (seedlings)	Pea	40	-	24
Prunus armeniaca	Apricot	1	20	4, 20

Table 1.1 (continued)

Scientific name	Common	Treatment		
		Conc., µl/l	Temp, °C	Time, hour
Prunus persica[*5]	Peach and nectarine	0.02, 0.1, 500	20-24	4, 18, 24
Prunus salicina	Plum	1, 13, 26, 39	20	6, 20, 24
Pyrus communis	Pear	2, 4	2	16
Vignaradiata (leaves)	Mung bean	0.06	Ambient	24

[*1] MCP treatment increases decay.
[*2] MCP is effective only when exogenous ethylene is present.
[*3] MCP increases blemish
[*4] MCP increases stem rots
[*5] MCP increases internal browning and reduces juice

1.3 The effect of MCP on fresh fruits and vegetables

The effect of MCP has been studied in several crops in order to maximize the storage life of produce as well as to understand the role of ethylene in ripening of fruits and vegetables. Some examples follow in this section.

1.3.1 Apple (*Malus Pumila*)

Apple is the first crop to which MCP could be applied and then sold for human consumption. The effect of MCP on this crop has been widely studied. Most of the studies have focused on how MCP and treatment parameters affect apples in terms of internal ethylene content, respiration rate, firmness, titratable acidity, total soluble solids, volatile production and storage disorders. All of the studies have shown the potential of MCP to delay apple ripening and prolong storage life. Apples studied include 'McIntosh,' 'Empire,' 'Delicious,' 'Law Rome,'

'Granny Smith,' 'Red Delicious,' 'Fuji,' 'Ginger Gold,' 'Jonagold,' 'Gala,' 'Braeburn,' 'York Imperial,' 'Cortland' and 'Anna'.

MCP suppresses ethylene production and loss of tissue firmness in apples (Fan and others 1999a; Fan and others 1999b; Watkins and others 2000; Reed 2002; Lu and Toivonen 2003). The reduction of firmness loss is probably through inhibiting changes in cell wall degrading enzymes (Rupasinghe and others 2000). MCP inhibits the increase of failure strain and the reduction of failure stress, toughness, modulus and shock wave speed, which are characteristics of texture changes associated with ripening.

The effect of MCP on respiration rate, starch content, total soluble solids and titratable acidity has been investigated but to a lesser extent than internal ethylene content and firmness. Young fruits have higher starch content and titratable acidity than more mature fruits. During maturation, titratable acidity decreases while starch is converted to sugar, thus increasing the total soluble solids content. MCP reduced the respiration rate and starch loss rate of 'Delicious' but did not influence the change in starch of 'Ginger Gold,' 'Gala' and 'Jonagold' (Fan and others 1999a). MCP slowed down the reduction in titratable acidity in most cultivars evaluated (Fan and others 1999a; Fan and others 1999b; Watkins and others 2000; Reed 2002; Lu and Toivonen 2003) with the exception of 'McIntosh,' 'Empire,' 'Delicious,' 'Law Rome' (Watkins and others 2000) and 'Braeburn' (Reed 2002) during 30-40 weeks in controlled atmosphere (CA) storage and 'Gala' during 28 weeks in normal air storage (Mir and others 2001). The effect of MCP on the total soluble solids is inconclusive because there have

been reports that MCP decreases (Watkins and others 2000), increases (Fan and others 1999a; Fan and others 1999b) or has no effect (Rupasinghe and others 2000; DeEll and others 2002; Reed 2002) on the total soluble solids of even the same cultivars.

Apple aroma is an indicator of eating quality and can be assessed by gas chromatography or sensory evaluation. Based on the analytical analysis, MCP treatment reduces the production of ester compounds, which are major components of apple aroma, but does not change the proportion of the 3 main ester compounds (butyl acetate, 2-methylbutyl acetate and hexyl acetate) (Lurie and others 2002). MCP treatment and low oxygen controlled atmosphere storage are very similar in their effect on volatile production except MCP induces the suppression of volatile production at a faster rate (Mattheis and others 2001). Many researchers have hypothesized the mechanism for MCP suppression of the production of ester volatiles. Research with 'Fuji' apples by Fan and Mattheis (1999) indicates that MCP inhibits either alcohol production or conversion of alcohols to esters (Fan and Mattheis 1999). Lurie et al. (2002) observed that MCP inhibits the conversion of alcohol to esters because the alcohol detected in MCP treated 'Anna' apples was higher than in non-treated MCP apples. The reduced volatile production may also be due to a reduced respiration rate and apparent limiting of acetyl-CoA, a common precursor of fatty acid biosynthesis, in treated fruits (Rupasinghe and others 2000).

With regard to sensory evaluation, only one publication was found which described the effect of MCP on sensory characteristics of 'Anna' apples. The

sensory evaluation of apples during ripening before and after storage was performed on various intensities of aroma using a trained panel. Non-treated and 0.1 $\mu L\ L^{-1}$ MCP treated apples had greater fruity, ripe and overall aromas but the preference was toward 1 $\mu L\ L^{-1}$ MCP treated apples with a less ripe aroma (Lurie and others 2002). The preference toward apples with higher MCP concentration treatment may also be a result of retention of apple's high acidity.

In addition to preserving the eating quality, MCP also helps to retain the peel color. It maintains the brightness of the red color associated with 'Delicious' and 'Gala' and suppresses the loss of chlorophyll in 'Granny Smith' and 'Golden Delicious' (Mattheis and others 2001; Saftner and others 2003).

MCP influences the development of physiological disorders in stored apples. The occurrence of superficial scald, induced by conjugated trienes (autooxidation products of α-farnesene) (Fan and others 1999b) is lower in MCP treated 'Law Rome,' 'Delicious,' Granny Smith,' 'Fuji' and 'Cortland' apples because MCP delays and reduces α-farnesene production (Fan and Mattheis 1999; Fan and others 1999b; Watkins and others 2000; DeEll and others 2002; Reed 2002). In addition, MCP also reduces soft scald, greasiness and core flush in 'Fuji' apples (Fan and others 1999b). Regardless of its beneficial effect, MCP can increase the incidence of internal browning relating to induced carbon dioxide injury in 'Golden Delicious,' (Mattheis and others 2001) 'Braeburn' (Mattheis and others 2001, Reed 2002) and 'York imperial' (Reed 2002). Increasing the time between harvest and MCP treatment may help reduce the risk of internal browning (Mattheis and others 2001).

The effectiveness of MCP on apples depends on the maturity of the fruit as well as the treatment parameters. The effect of MCP is greater when applied to fruits at the pre-climacteric stage than the climacteric stage (Watkins and others 2000; Reed 2002). MCP concentration (0.5 – 2 $\mu L\ L^{-1}$) affects ethylene production of some cultivars, such as 'Law Rome' and 'Delicious', but not in others, such as 'McIntosh' and 'Empire' (Watkins and others 2000). In 'Anna' apples, MCP treatments of 0.1 $\mu L\ L^{-1}$ for 20 hours at 20°C did not reduce ethylene production, while treating with 1 $\mu L\ L^{-1}$ reduced internal ethylene content by 95% (Lurie and others 2002). The optimum MCP concentration has been established for 'McIntosh' and 'Delicious' to be 1 $\mu L\ L^{-1}$ for 12-18 hours at 20°C (Fan and others 1999a; Rupasinghe and others 2000). The treatment temperature influences the required treatment time to obtain the maximum effect. Six hours is required for a treatment temperature of 13 and 23°C, while nine hours are required when the treatment is applied at 3°C (DeEll and others 2002). The storage temperature affects the impact of treatment frequency. At low temperature, the treatment frequency does not change the MCP response. As the temperature increases, the beneficial impact from treatment frequency increases (Mir and others 2001).

There are other postharvest technologies used to extend the storage life of apples. MCP has the potential to replace or be combined with existing technologies. Controlled atmosphere storage is a widely used method to extend the storage life of apples. MCP and controlled atmosphere storage have a similar effect. Cultivars that respond favorably to controlled atmosphere will

respond positively to MCP (Mattheis and others 2001). The combination of MCP and CA storage resulted in greater inhibition than either treatment alone (Watkins and others 2000; Reed 2002; Lu and Toivonen 2003).

Methyl jasmonate is a plant growth regulator that can affect climacteric fruit ripening and volatile production. The ability of MJ to reduce ethylene production is enhanced when combined with MCP. Both compounds inhibit volatile production by inhibiting both alcohol production and ester formation but they affect individual alcohols and esters differently. The inhibition of volatile production by MCP is a result of inhibition of ethylene production but the MJ inhibitory mechanism is still unknown.

1.3.2 Apricot (*Prunus armeniaca*)

MCP did not produce satisfactorily results with 'Patterson' and 'Canonin' apricots when treated prior to storage. It had no effect on delaying the increase in soluble solids, reduction of titrable acidity or brown rot development (Dong and others 2002; Palou and Crisosto 2003). Although MCP slightly delayed the softening process in an ethylene-free environment, it adversely affected the 'Patterson' apricot texture when ethylene was present (Palou and Crisosto 2003). In addition, it caused an increased incidence of internal browning of 'Canino' apricots (Dong and others 2002).

Although the use of MCP to extend the storage life of apricots was not successful in 'Canino' apricots, the application of MCP to extend the post storage shelf life is promising. When MCP is applied after storage, it delays fruit softening and reduces internal browning and decay. When MCP is applied after

5 day cold storage, it reduces ethylene production and respiration of apricot during ripening period at room temperature. In contrast, it enhances ethylene production and does not affect the respiration rate when applied after a long-term cold storage (30 days) (Dong and others 2002)..

The optimum concentration has not been established for apricots but a treatment of 1 $\mu L\ L^{-1}$ MCP at 20°C for 20 hours resulted in fruit with better firmness and less internal browning and decay than treatment at a lower concentration (Dong and others 2002).

1.3.3 Avocado (*Persea americana*)

MCP delays avocado ripening but renders it more susceptible to decay. It increases the number of days to ripen in 'Haas' avocado (Hofman and others 2001) and increases the retention of green color in 'Simmonds' avocado (Jeong and others 2002). Softening in several cultivars of avocado including 'Simmonds,' 'Haas,' 'Etinger,' 'Reed' and 'Fuerte' was delayed by MCP treatment through the suppression of enzymes associated with the softening process, including C_x-cellulase and polygalacturonase (Feng and others 2000; Jeong and others 2002). MCP slightly increases the decay sensitivity of avocado (Hofman and others 2001).

Chilling injury, expressed as mesocarp browning, can be reduced by MCP treatment. Browning is the result of oxidation of o-diphenols to o-quinones by polyphenol oxidase resulting in the formation of a brown pigment. Chilling injury is more pronounced in the presence of exogenous ethylene and it is ethylene concentration-dependent. MCP reduces this problem by suppressing polyphenol

oxidase activity while exogenous ethylene induces the activity of this enzyme (Pesis and others 2002).

MCP treatment parameters influences how MCP affects avocado. At a treatment concentration of 0.45 $\mu L\ L^{-1}$, an increasing treatment time from 6 to 24 hours resulted in increased MCP effectiveness on 'Simmonds' avocado (Jeong and others 2002). Similar results were also found for 'Haas' avocado at concentrations of 0.1 and 0.3 $\mu L\ L^{-1}$ when the treatment time increased from 24 to 48 hours. Repeating the treatment after 10 days enhanced the MCP effect (Pesis and others 2002) because the effect of the first treatment lasts about 2 weeks; the treated fruits then resume normal ripening (Feng and others 2000).

1.3.4 Banana (*Musa paradisiacal*)

MCP treatment of bananas can affect ethylene and respiration climacteric, volatile production, skin color, and pulp softening. Without the presence of exogenous ethylene, MCP delays the onset of respiration and ethylene climacteric. In the presence of exogenous ethylene, MCP does not affect the onset of the climacteric stage, but MCP-treated fruit produces less ethylene and has a lower respiration rate (Golding and others 1998). It delays and reduces volatile production (Golding and others 1998; Golding and others 1999) by disruption of the ester formation process. The other undesirable consequence of MCP treatment is the uneven degreening when MCP treated bananas ripen (Golding and others 1998; Jiang and others 1999a).

As with other fruits, the efficacy of MCP depends on MCP concentration and treatment duration. The optimum concentration for a 12 hour treatment at

20°C was 0.05 μL L^{-1}. For shorter treatment duration, a higher concentration is required to obtain a similar effect, i.e. treatment with 0.1 μL L^{-1} MCP for 12 hours gave the same result as 1 μL L^{-1} MCP for 1 hour (Jiang and others 1999b). An optimum concentration of 0.5 μL L^{-1} was reported for treatment in 0.03 mm thick low density polyethylene (LDPE) bags for 24 hours at 20°C (Jiang and others 1999a). The higher MCP concentration needed is due to the loss of MCP through the bag due to permeation.

The banana maturation stage plays an important role in successful extension of its storage life when treated with MCP. Treatment during the preclimacteric stage, or up to 12 hours after climacteric onset delays the start of ethylene and respiration climacteric and skin color change. MCP application after 24 hours of the climacteric onset is too late to stop the ripening process (Golding and others 1998).

The timing of the MCP treatment relative to the timing of the exposure to exogenous ethylene is of prime importance. In banana, application of exogenous ethylene is used to induce ripening to attain desirable qualities such as peel color (bright yellow), a firm pulp texture and a good flavor (Kerbel 2002). The effect of ethylene on MCP treated fruits improves when the time between MCP treatment and subsequent ethylene treatment increases (Pathak and others 2003). However, exposure to exogenous ethylene an improper time causes reduction in banana storage life. MCP can delay the undesirable effect of exogenous ethylene if applied no later than 1 day after bananas are subjected to exogenous ethylene (Jiang and others 1999b).

MCP, when combined with other treatments such as modified atmosphere packaging and controlled atmosphere storage, gives synergistic effects. The combination of MCP and modified atmosphere packaging slows the softening process and color change, thus extending the storage life of banana more than either treatment alone. Fruits which underwent the combination treatment ripened normally without uneven degreening (Jiang and others 1999a). The effect of MCP on reducing softening rate is also found when MCP is applied together with controlled atmosphere storage (60 and 100% oxygen content) or high temperature storage (Jiang and others 2001a; Jiang and Joyce 2003).

1.3.5 Broccoli (*Brassica oleracea*)

MCP extends the shelf life of broccoli by delaying the yellowing process, in part by reducing peroxidase and chlorophyllase activities (Gong and Mattheis 2003). In addition, MCP slows down the respiration rate (Fan and Mattheis 2000). It also protects broccoli against exogenous ethylene. The benefit of MCP treatment is similar to the benefit achieved in low temperature storage (Able and others 2002). This has practical value in distributing broccoli due to the reduced low temperature requirement.

MCP treatment of broccoli is effective over a wide range of treatment parameters and storage conditions, but the efficiency depends on several factors including the temperature at which MCP is applied, frequency of treatment and MCP concentration. Treatment at high temperature is more effective than at low temperature because MCP can better attach to ethylene receptor site at high temperature (Ku and Wills 1999). However, exposure to high temperature can

shorten the shelf life of broccoli and causes physiological damage such as abscission and rotting (Able and others 2002).

Treatment frequency is another factor that influences the shelf life of broccoli. A second application (12 $\mu L\ L^{-1}$ for 6 hours daily) does not increase the shelf life of broccoli when compared to a single application at the time of harvest. More than four additional applications can cause harmful side effects such as wilting and physiological damage. However, continuous application (12 $\mu L\ L^{-1}$, 20 hours daily) helps prolong the shelf life (Able and others 2002).

The effectiveness of MCP treatment is concentration-dependent. The shelf life of broccoli increases when MCP concentration increases. The optimum concentration of MCP was reported to be between 1-14 $\mu L\ L^{-1}$. Ku and Wills (1999) found that the optimum concentration is 1 $\mu L\ L^{-1}$ (6 hours at 20°C). In contrast, Fan and Mattheis found no difference in the yellowing process in the concentration range of 0.01 - 1$\mu L\ L^{-1}$ when treated for 12 hours at 10°C (Fan and Mattheis 2000). However, too high concentration can have negative effet. MCP concentration greater than 25 $\mu L\ L^{-1}$results in red-brown coloring on the florets (Able and others 2002).

1.3.6 Cherry (*Prunus avium*)

An MCP concentration of 0.1 – 10 $\mu L\ L^{-1}$ does not have any effect, beneficial or adversarial, on cherries, a non-climacteric fruit. Treated and non-treated 'Bing' and 'Rainier' have approximately the same color, firmness, respiration rate, and stem browning disorder (only when not exposed to

exogenous ethylene) but the treated fruits had higher ethylene production (Gong and others 2002). Since ethylene production in non-climacteric is inhibited by ethylene, MCP promotes ethylene formation by decreasing ethylene action.

1.3.7 Coriander (*Coriandrum sativum*)

Coriander can benefit from MCP treatment particularly when exposed to less than ideal storage conditions (high temperature or high exogenous ethylene concentration). Retaining the chlorophyll and protein content in coriander was affected by MCP during 6 days storage at 15 and 20°C but not at 5 and 10°C because coriander has low ethylene sensitivity at the low temperature. MCP treatment also reduces the accumulation of free amino acids, ion leakage and ethylene production, but does not affect the respiration rate. The optimum concentration of MCP for coriander is 0.05 $\mu L\ L^{-1}$ when treated for 24 hours at 20°C (Jiang and others 2002).

1.3.8 Custard apple (*Annona cherimola*)

MCP can delay the ripening of 'African Pride' custard apples, both in the presence or absence of ethylene. However, total soluble solids and titratable acidity remains unaffected. The effective MCP treatment to delay the ripening process is 25 $\mu L\ L^{-1}$ MCP for 14 hours at 20°C. However, at this concentration the amount of black tips, grey flesh, internal black discoloration and core rot increases (Hofman and others 2001).

1.3.9 Mango (*Mangifera indica*)

The influence of MCP on total soluble solids and titratable acidity of mango depends on stage of maturation and cultivars. Total soluble solids for 'Espada' and 'Jasmin' varieties in the mature green stage (1-25% non-green surface) is not affected by MCP treatment while that of pre-climacteric (51-75% non-green surface) mangoes is influenced by MCP treatment. 0.1 $\mu L\ L^{-1}$ MCP on preclimacteric mangoes reduced the maximum total soluble solids in 'Jasmin' and 'Rosa' while increasing these components in 'Espada' (Silva and others 2004). MCP treated 'Espada' and 'Jasmin' maintained higher acidity than non-treated fruits (Silva and others 2004). The total soluble solids and titratable acidity of 'Kensington Pride' are not affected by MCP treatment (Hofman and others 2001).

Skin color, a good indication of ripening, is maintained by MCP treatment. MCP maintained skin color and external appearance of 'Jasmin', 'Espada' and 'Rosa' because it prevents oxidation of skin pigments, which can result in dulling of skin color (Silva and others 2004). A desirable effect on skin color change is also found in 'Zihua' mangoes. The treatment of MCP prior to passive modified atmosphere packaging (polyethylene bag) delays ripening for an additional 10 days at 20°C when compared to mangoes in polyethylene bags with no MCP treatment (Jiang and Joyce 2000). A desirable effect on skin color was observed only before the ripening started. Once fruits undergo ripening, the peel color of treated and untreated fruits are the same (Jiang and Joyce 2000; Silva and

others 2004). In contrast, MCP treated 'Kensington Pride' mangoes undergo skin darkening (Hofman and others 2001).

MCP treatment of mangoes can affect the acceleration of ripening by exogenous ethylene, a common commercial practice. In 'Kensington Pride,' MCP had the same effect when applied alone or immediately prior to ethylene treatment (Hofman and others 2001). This may be desirable as MCP can protect mangoes from the deleterious effect of exogenous ethylene. However, the fruit may not have the same quality as non-treated fruit, and the commercial ethylene ripening process may have to be altered. The duration between MCP treatment and exogenous ethylene treatment is critical. A longer duration results in faster ethylene-induced ripening of MCP treated fruits. The more time between the two treatments is presumed to allow more ethylene binding sites to be synthesized, and the fruits to regain ethylene sensitivity (Jiang and Joyce 2000).

Mangoes are sensitive to mechanical injury such as impact stress as a result of improper harvesting or handling. This can accelerate ethylene production and impair color development. MCP treatment following mechanical injury slowed down the senescence process in mature green 'Rosa' mango by reducing internal browning, but not in preclimacteric fruit. Preclimacteric MCP treated fruits that are mechanically injured have a high percentage of internal browning, fungi infection and water soaked areas, resulting in a fruit condition which is not acceptable to consumers (Santos and others 2004).

Regardless of the benefits of MCP, its draw back is an increased sensitivity to storage disorders of treated mangoes. It increases the rot

sensitivity in 'Kensington Pride'. This effect is greater when fruits are treated with ethylene after MCP treatment (Hofman and others 2001).

MCP concentration and treatment duration are critical factors in the successful application of MCP. The optimum concentration is 100 $\mu L\ L^{-1}$ for a 12 hour treatment time or 50 $\mu L\ L^{-1}$ for 24 hours for 'Zihua' mangoes. (Jiang and Joyce 2000) Other concentrations that have desirable effects on mangoes were 25 $\mu L\ L^{-1}$ and 14 hours for 'Kensington Pride' (Hofman and others 2001) and 0.1 $\mu L\ L^{-1}$ and 24 hours for 'Jasmin', 'Espada', and 'Rosa' (Silva and others 2004) at room temperature (20-23°C). The latter two concentrations may not represent the optimum concentration.

1.3.10 Nectarine (*Prunus persica*)

MCP retards firmness loss in 'Flavortop' (both ripening after harvest and ripening after storage), but it caused increased storage disorders during 30 days in cold storage. This is believed to be a result of ethylene action inhibition. As a result, pectinesterase and polygalacturonase gene expression are low and normal cell wall breakdown is slowed down, causing the retardation of loss of firmness as well as increased storage problems. This suggests that MCP is not suitable for extension of the storage life of nectarines but has potential to extend the shelf life of fruits placed in the market directly after harvest (Dong and others 2001).

1.3.11 Orange (*Citrus sinensis*)

MCP has little desirable effect on 'Shamouti' oranges. The partial inhibition of the degreening process at a concentration of 0.025 $\mu L\ L^{-1}$ and total inhibition of this process above that concentration is beneficial. However, the use of MCP to arrest degreening has to be done with care because MCP can increase chilling injury and render oranges more susceptible to decay such as stem-end rot, caused by *Diplodia natalensis*, and mold rot, caused by *Penicillium digitatum*. It can also increase the accumulation of acetaldehyde and ethyl acetate in the juice headspace and ethanol in the fruit internal atmosphere. MCP has no effect on weight loss, firmness, total soluble solids, acid content and ethylene production (Porat and others 1999).

1.3.12 Papaya (*Carica papaya*)

MCP can effectively increase the time to ripen for papaya by approximately 3-fold with the treatment of 25 $\mu L\ L^{-1}$ for 14 hours at 20°C. However, it increases the sensitivity to postharvest disorders including external blemishes, stem black rots, body black rots, and anthracnose (Hofman and others 2001).

1.3.13 Pear (*Pyrus communis*)

The effect of MCP on pears is mainly on their texture and ethylene production. MCP slows down the softening process in 'Barlett' pears that have started to ripen and completely inhibits this process in 'D'Anjou' pears. It also retards change in mechanical properties of both pears tissues (Baritelle and

others 2001). In 'La France' pears, MCP treatment prior to climacteric onset inhibits the climacteric peak and softening process. When treated after the climacteric onset, MCP suppressed ethylene production and loss of firmness (Hiwasa and others 2003).

The effect of MCP concentration on pear responses has not been published. Treatment concentrations that have beneficial effects are 2 $\mu L\ L^{-1}$ for 16 hours for 'Barlett' and 'd'Anjou' (Baritelle and others 2001) and 20 $\mu L\ L^{-1}$ for 12 hours for 'La France' at 20°C (Hiwasa and others 2003).

1.3.14 Persimmon (*Dispyros kaki*)

MCP does not alter the ethylene production and respiration of persimmon fruit during cold storage (15°C) and at room temperature after removal from cold storage. However, it slows the softening process in both conditions. Another beneficial effect of MCP on persimmon is that it reduces the production of off-flavor compounds, acetaldehyde and ethanol. The MCP concentration that has a significant impact on storage and shelf life of persimmons is 1 $\mu L\ L^{-1}$ or 0.5 $\mu L\ L^{-1}$ twice (at the time of harvest and after 20 days in cold storage) at 15°C for 24 hours (Salvador and others 2004).

1.3.15 Pineapple (*Ananas comosus*)

Although MCP stimulates ethylene production in cold stored pineapples, it extended the storage life of 'Queen' pineapples at a concentration of 0.1 $\mu L\ L^{-1}$. It completely eliminates internal browning, a major physiological disorder in the first two weeks of cold storage. Although internal browning occurs after that, the

percent occurrence is reduced and the extent of browning is less than in non-treated pineapples. MCP also delays shell ripening and the loss rate of ascorbic acid, total soluble solids and weight (Selvarajah and others 2001).

1.3.16 Plum (*Prunus domestica*)

The effect of MCP on plums was studied in both climacteric ('Gulfruby', 'Beauty', 'Royal Zee', 'Laetitia', 'Santa Rosa' and 'President') and suppressed climacteric cultivars ('Shiro' and 'RedRuby'). Suppressed climacteric or very slow-ripening cultivars produce much less ethylene and have a longer shelf life than climacteric cultivars (Lelievre and others 1997). Both types of plum response to propylene (ethylene analog) and MCP differently. MCP-treated suppressed climacteric cultivars over-ripened and rotted after treatment without any aroma or ethylene production, but exogenous ethylene treatment can restore ethylene and aroma production (Abdi and others 1998).

MCP has a more beneficial effect on climacteric cultivars. It delays ethylene and respiratory climacteric when applied to harvested plums before storage (Abdi and others 1998; Dong and others 2002; Argenta and others 2003; Salvador and others 2003) and after cold storage (Dong and others 2002; Argenta and others 2003; Salvador and others 2003; Valero and others 2004). The effect of MCP on maximal ethylene production and respiration rate varies between cultivars. MCP increased maximal ethylene production and respiration rate in 'Beauty' and 'Gulfruby' at a concentration of 26 $\mu L\ L^{-1}$ (Abdi and others 1998) and 'Royal Zee' at a concentration of 1 $\mu L\ L^{-1}$ (Dong and others 2002). However, it reduced ethylene production and respiration rate in 'Laetitia' at a

concentration about 0.5 μL L^{-1} (Argenta and others 2003). In 'Santa Rosa', 0.5 and 0.75 μL L^{-1} of MCP delayed ethylene and the respiration climacteric peak and reduced the maximum amount of ethylene produced, but did not impact respiration rate (Salvador and others 2003).

Aroma production in MCP treated 'Gulfruby' and 'Beauty' plums is arrested by MCP but could be restored by propylene treatment (Abdi and others 1998). MCP also reduces the production of off-flavor compounds such as ethanol and acetaldehyde (Salvador and others 2003).

MCP delays the change in skin color, softening, and reduction in titratable acidity in 'Royal Zee' (Dong and others 2002), 'Laetitia' (Argenta and others 2003), 'Santa Rosa' (Salvador and others 2003) and 'President' (Valero and others 2004) plums. It also prevents texture defects such as "gummy and corklike" in 'Santa Rosa' but did not affect their sugar content (Salvador and others 2003). In contrast, the sugar content in 'President' plums is affected by MCP (Valero and others 2004).

The effect of MCP in plums is concentration-dependent. In 'Laetitia', 'Santa Rosa' and 'President' plums, the optimum concentration is 0.5 μL L^{-1} when treated at 1°C for 24 hours (Argenta and others 2003; Salvador and others 2003; Valero and others 2004). For 'Beauty' and 'Gulfruby', the optimum concentration is 13 μL L^{-1} at 20°C for 24 hours, which was the minimum concentration tested. The actual optimum concentration may be lower than 13 μL L^{-1} (Abdi and others 1998).

The mode of MCP application plays a role in the efficiency of MCP. For the same concentration, MCP was found to be more effective when applied after 'President' plums were packaged in a perforated carton, a well aerated package, than when treated in bulk. This may be due to the greater fruit accessibility of MCP in the well aerated package (Valero and others 2004).

1.3.17 Rambutan (*Nephelium lappaceum*)

MCP extends the shelf life of Rambutan at a concentration of 0.1 $\mu L\ L^{-1}$. It enhanced the respiration rate, decreased the ethylene production rate, and slowed down the loss of titratable acidity and change in lightness (L* value) of the skin (U-ae and others, 2002).

1.3.18 Strawberry (*Fragaria spp.*)

The potential use of MCP in extending the shelf life of strawberries, a non climacteric fruit that can be affected by exogenous ethylene, is very limited because it only has a favorable effect on a few varieties and the range of useful concentration is very narrow. MCP caused reduction in the shelf life of 'Tioga', 'Seascape' and 'Parker' stored at 20°C, due to rotting. For 'Selva', 0.005-0.015 $\mu L\ L^{-1}$ MCP increased the storage life but greater concentration shortened the shelf life due to decay (Ku and others 1999). Similar results were found for 'Everest' strawberry but at a higher concentration (0.1-0.25 $\mu L\ L^{-1}$). The higher concentration resulted in retention of fruit firmness and color, but shortened the shelf life due to accelerated leak rot, a major disease of this cultivar (Jiang and others 2001b). It is believed that MCP interferes with strawberry's natural

defense system (Ku and others 1999) as the experiment resulted in a reduction of phenylalanine ammonia lyase (PAL) activity and phenolic content (Jiang and others 2001b).

1.3.19 Tomato (*Lycopersicon esculentum*)

The shelf life of tomatoes can be extended by MCP treatment, and its effectiveness depends on several variables. Those that have been studied include tomato maturation, treatment temperature, MCP concentration, and frequency of treatment. Based on the delay of color change and firmness of the flesh, the most effective treatment is the application of MCP to tomatoes at the mature green stage (Lee 2003; Mir and others 2004). After MCP-treated tomato is ripened, the taste and aroma are not altered, but the locular gel changes color much slower than in non-treated fruits (Mir and others 2004).

Treatment parameters have a great influence on MCP effectiveness. The combination of low temperature and MCP treatment extends the storage life the most (Lee 2003). The effect of MCP is concentration dependent. The maximum response is obtained at the concentration of 1 $\mu L\ L^{-1}$ for a single treatment, which was the highest concentration tested (Mir and others 2004). Multiple treatment (once a day) and continuous treatment are more effective than a single treatment (Lee 2003; Mir and others 2004).

1.4 The effect of MCP on fresh-cut produce

MCP research on fresh-cut produce (apples) started in 2002. The number of publications in this area has risen greatly and expanded to other fresh-cut produce such as pineapples, tomato, lettuce, and watermelon. The effect of MCP on fresh-cut produce, arranged alphabetically by produce type is reviewed in this section.

1.4.1 Fresh-cut apples

Most, if not all, the factors that influence how MCP affects intact fruit play an important role in how MCP affects fresh-cut apples. In addition, the timing of MCP treatment relative to the cutting process is important. The quality of fresh-cut apples also depends on processing conditions such as temperature, the sharpness of the cutter, and the use of antibrowning and antimicrobial agents. As a result of these factors, the effect of MCP on fresh-cut apples varies. The differences may be due to the different cultivars and from differences in processing.

The timing of MCP treatment influences the effect of MCP on fresh-cut apples. A treatment of 10 $\mu L\ L^{-1}$ MCP on 'Golden delicious' apples prior to cutting was more effective in delaying deterioration of fresh-cut apples than a 1 $\mu L\ L^{-1}$ MCP applied to apple slices (Jiang and Joyce 2002). MCP application on intact fruits was more practical and simpler than its application to fresh-cut apples because of the stricter sanitation requirements for fresh-cut produce.

When treatment is applied immediately after harvest of 'Gala' and 'Braeburn' apples, the treated apples (before processing) had lower ethylene

content. However, during the shelf life of fresh-cut apples, the ethylene content increased to approximately the same level as from non-treated apples. MCP did not affect the respiration rate of 'Gala' fresh-cut apples and minimally affected the respiration rate of 'Braeburn', which suggests that wound induced respiration may not be ethylene-dependent. MCP treated apples are firmer before processing and retain their firmness better after processing. The effect on flesh color is different in the two cultivars. MCP had a beneficial effect on 'Braeburn' but negative impact on 'Gala'. The magnitude of the difference is much less in 'Braeburn' than in 'Gala'. In 'Gala' the large reduction in L* value is attributed to secondary browning due to mold growth because MCP may have impaired the defense mechanism. In contrast, MCP did not affect decay in fresh-cut 'Braeburn' apples. MCP did not have any effect on titratable acidity of intact 'Braeburn' but did have a positive effect on titratable acidity retention of the slices. Despite the benefits of MCP, a drawback is reduction of aroma production (Perera and others 2003), which also happens in treated intact apples.

The storage time between harvest and MCP treatment and between MCP treatment and processing influences the quality of fresh-cut apples. As storage time of intact apples increased, the difference in respiration rate of MCP treated and non MCP treated Fresh-cut 'Gala' increased. However, after processing, the respiration rate of slices from MCP treated apples increased at a faster rate. The flesh color of non-treated apples is better than that of MCP treated apples regardless of the storage time. As the storage time of intact apples increases,

however, the difference in the flesh color is lessened (Bai and others 2004). The storage time between harvest and MCP treatment is a critical factor. MCP had a more positive effect on 'Braeburn' slices from apples, which received MCP treatment right after harvest, than 'Pacific Rose' slices from apples which received MCP treatment after 3 months storage (Perera and others 2003).

1.4.2 Fresh-cut lettuce

MCP has a beneficial effect on minimally-processed lettuce. When treated before processing, it reduces ascorbic acid loss, leaf yellowing, russet spotting, respiration rate and ethylene production. The beneficial impact is greater than that for application of calcium alginate edible coating (a promising method to extend the shelf life of fresh cut produce). MCP treated and non-treated lettuce yields fresh cut lettuce with a similar texture while coating lettuce with calcium alginate can maintain the crispness of cut lettuce better. The beneficial effect of MCP was achieved by treating lettuce with 0.5 $\mu L\ L^{-1}$ MCP for 4 hours at 20°C prior to processing (Tay and Perera 2004).

1.4.3 Fresh-cut pineapples

Fresh-cut pineapple is another product that can benefit from MCP treatment. Treatment of intact pineapple fruits reduces the respiration rate and flesh browning and results in the retention of more ascorbic acid in minimally processed pineapples, but does not affect firmness or microbial growth. The greater retention of ascorbic acid is hypothesized to be a reason for reduction in browning of fresh-cut pineapples. MCP treatment increases the electrolyte

leakage but addition of ascorbic acid to the pineapple slices helps reduce the leakage. The optimum MCP concentration was found to be 1 $\mu L\ L^{-1}$ (Budu and Joyce 2003).

1.4.4 Fresh-cut tomato

MCP treatment can benefit fresh-cut tomatoes. Texture retention is improved by MCP treatment of the sliced tomato (1 $\mu L\ L^{-1}$ for 24 hours). Factors influencing its impact include tomato maturity and treatment temperature. The treatment is more effective in retaining firmness and reducing the incidence of water soaking when tomato slices are less ripened. The effect is greater when MCP treatment is performed at 5°C. Wound induced ethylene production is also greater in MCP treated slices at 5°C but this does not happen when MCP is applied at 10 and 15°C. The respiration of slices is not affected by MCP treatment (Jeong and others 2004).

1.4.5 Fresh-cut watermelon

MCP treatment (10 $\mu L\ L^{-1}$ for 18 hours) of intact watermelon before cutting did not improve the texture retention of fresh-cut watermelon. Dipping of the slices in calcium chloride is a better texture preservation method. However, this treatment activates lipolytic enzymes, such as phospholipase C, phospholipase D and lipoxygenases, which are associated with membrane lipid degradation. The use of MCP treatment together with calcium chloride can inhibit this activation by shutting down the Ca^{2+}-activation system of lipolytic enzymes (Mao and others 2004).

1.5 MCP commercialization

Commercialization of MCP has been accomplished by Florallife, Inc. (Waterboro, SC) under the trade name EthylBloc® for ornamental crops. The product was approved by the United States Environmental Protection Agency (EPA) in 1999 (Blankenship and Dole 2003). Most MCP treatment of flowers is done at the bouquet preparation step, but treatments during trucking and by the wholesaler are increasing as reflected by the increase in sales in those market segments (Daly and Schluter 2001). AgroFresh, Inc., a subsidiary of Rohm and Haas (Spring House, PA), sells MCP under the trade name SmartFresh™ (Blankenship and Dole 2003) for edible crops. The crops that are approved for MCP treatments are apples, melons, tomatoes, pears, avocados, mangoes, papayas, kiwi fruit, peaches, nectarines, plums, apricots, persimmons, bananas, and broccoli.

1.6 MCP delivery system

MCP gas is relatively unstable due to its reaction potential and possible explosiveness when compressed. Therefore, it is not safe to commercialize it in gas form. Molecular encapsulation has been used as means of retaining the MCP gas to increase safety. In addition, it provides a convenient way to deliver MCP at a more accurate dosage. Molecular encapsulation agents that can be used include cyclodextrin, a crown ether, a polyoxyalkylene, a prophorine, a polysiloxane, a phosphazene and a zeolite (Daly and Kourelis 2000). In commercial uses MCP (EthylBloc® and SmartFresh™) is encapsulated in α-cyclodextrin. The molecular encapsulation complex can retain MCP for a long

time. MCP is released from α-cyclodextrin by adding a buffer containing potassium hydroxide (Mir and others 2001) or water (Blankenship and Dole 2003). The release rate is relatively high. At standard temperature and pressure, MCP is released from the complex in approximately 20-30 minutes, but may take longer at lower temperatures (Blankenship and Dole 2003). This MCP delivery system is suitable for a one-time MCP treatment.

The disadvantages of powder delivery systems are their dustiness and the inherent difficulty in accurately measuring small amounts of powder. Moreover, the powder release system starts to deliver MCP almost immediately upon contact with a releasing agent. One way to eliminate these disadvantages is the use of pressure agglomeration of the molecular encapsulation complex to form it into tablets, wafers, pellets and similar forms. These forms overcome the potential disadvantages and slow down the release rate when it is first in contact with a releasing agent (Konstansek 2002).

Several attempts have been made to improve MCP release from a molecular encapsulation complex more efficiently as shown in several patents. The addition of water absorbent materials, e.g. sodium polyacrylate and polysaccharide, and/or deliquescent compounds, e.g. calcium chloride, reduces the required amount of water to release MCP. A mixture of all three compounds releases all encapsulated MCP within a day when exposed to high humidity and within 2 hours when the mixture was dipped in water (Kostansek 2002). The addition of carbon dioxide generating agents such as sodium bicarbonate and citric acid to MCP molecular encapsulation complexes results in a much more

efficient release of MCP. Incorporating dextrose, an absorbent material, into this complex does not further improve the release rate, but the addition of benzoic acid or sodium dodecyl sulfate results in the release of all MCP within 2 hours (Kostansek and others 2004).

Another MCP delivery system uses absorbing agents. Silica gel and Tenax-TA (80 mesh) are good absorbing agents. Silica gel has higher MCP absorption capacity than Tenax-TA. Activated carbon (80/100 mesh) and silica gel were studied to determine their MCP release rates. No MCP was released from activated carbon due to its high MCP affinity. Silica gel released MCP faster at higher humidity (Lee 2003).

An alternative to a solid absorbing agent is a solution containing a lithium MCP salt. This is achieved by mixing 3-chloro-2-methylpropene into a lithium diisopropylamide mono(tetrahydrofuran) solution in cyclohexane inside a sealed tube flushed with argon gas. The chemical mixture yields tetrahydrofuran and a cyclohexane solvent based solution containing the lithium salt of MCP (Macnish and others 2004).

The previous MCP forms can be applied to fresh produce in a storage room. However, storage room systems are usually only available at wholesalers and others dealing in bulk quantities (Mir and Beaudry 2001). An alternative to storage room treatment is the treatment in packages. MCP treatment in well-aerated packages is more effective than in a bulk container (Valero and others 2004). Continuous treatment and repetitive treatment have been shown to exhibit beneficial effects and to extend the shelf life/storage life of fruits (Mir and

others 2001; Able and others 2002; Pesis and others 2002). Several controlled release delivery systems has been developed to facilitate in-package treatment and to continuously supply MCP to produce. The controlled release devices found in the published literature are either reservoir or monolithic devices.

The reservoir device consists of an active component (MCP) contained within a polymeric film or other materials. The active component can be in the form of a gas, solvent or powder, as molecular encapsulation complex or absorbed onto an absorbing agent. For MCP in the gaseous state, gas is injected into polymer pouches (Sittipod 2003). The release rate of this reservoir device is the easiest to model. The release rate depends on the transmission rate of MCP through the polymeric materials. With no leakage, the rate depends mainly on the concentration of MCP inside the pouch, the surface area of the pouch, the MCP permeability of the pouch materials, thickness, and environmental conditions (temperature, relative humidity and pressure).

For MCP-absorbing agents, the absorbing agent is placed in a pouch made of Tyvek®, Filter paper, LDPE or polyvinyl acetate (PVA). The Tyvek® and paper pouches containing absorbing agent are exposed to MCP in a closed system. For LDPE and PVA pouches, MCP is directly injected into the pouch. Tyvek® and paper pouches release the maximum MCP amount in less than an hour while LDPE and PVA pouches delay the maximum release to about 5 hours. No release trigger mechanism is required, but humidity in the air enhances the amount of MCP released from the complex. The effect of relative

humidity was greater in Tyvek®, paper and PVA pouches where the water vapor transmission rate was higher (Lee 2003).

The reservoir device containing a molecular encapsulation complex is the most studied because of its commercial availability. Molecular encapsulation complexes need to be in contact with or exposed to a releasing agent. This releasing agent can be either from an external source or incorporated within the same reservoir device (same or different compartment). Devices that use external sources are simpler in construction but their release rate depends on the environmental conditions, which may not always be controllable.

A reservoir device described in a US Patent (US 6,548,448) consists of a molecular encapsulation complex laminated between two layers of film without the presence of release triggering agent. The films used are polyvinyl alcohol (PVOH) and LDPE. The release rate from PVOH was much slower, about $1/20^{th}$ that of LDPE (Konstansek and Edward 2003).

Gas releasing pouches and cartridges are examples of reservoir devices containing a releasing agent in a separate reservoir. In one device, the pouch contains molecular encapsulation complex powder and a thin-walled plastic bubble, containing releasing agent. When the release of MCP is desired, gentle pressure is applied to the pouch to break the bubble, which allows the releasing agent to mix with the powder and release MCP gas. The pouch is made up of two types of polymer, one with high gas permeability and the other one with very low permeability to gas. The permeable side of the pouch is adhered to the produce to channel the released MCP to the fruit directly. The device was shown

to be effective in inhibiting ripening of banana (Mir and Beaudry 2001). The cartridge device uses a similar concept, with a different mechanism, to bring the MCP molecular encapsulation complex into contact with the releasing agent (Lamola and others 2004).

Reservoir devices that have a releasing agent and a molecular encapsulation complex in the same compartment and reservoir devices that contain active agent in the form of MCP solvent are presented in several forms. Rate controlling materials include a silicone rubber septum, clear PVC, natural rubber and LDPE. For the same type of device, the amount of MCP released from 0.09 grams EthylBloc® and 1.8 ml releasing agent (deionised water) was 3-70 times less than the MCP released from 1 ml MCP solvent. Among all the devices, the clear PVC tube (6 mm i.d and 1.5 mm thick) sealed with a glass rod at both ends had the most desirable MCP release characteristics (Macnish and others 2004).

Another type of MCP controlled release system is monolithic device with the active agent distributed throughout the rate controlling matrix. One system uses natural rubber as the rate controlling material and uses MCP gas or MCP solution as an active compound. The device is created by exposing natural rubber to MCP gas or immersing it into an MCP solution. This device did not work well because no MCP was detected (Macnish and others 2004), which could have been due to either too low or too high affinity between the natural rubber and MCP. If the affinity is poor, natural rubber will not absorb MCP, thus

the initial concentration will be very low or zero. If the affinity is high, MCP will be held tightly by the rubber, and in either case, it is not effective.

Other rate controlling matrices that are mentioned in US 6,548,448 include polymeric packaging materials (flexible and rigid), waxes, coated paperbased-materials and adhesive components. The example shown in the patent includes waxy cast film (Parafilm), high density polyethylene (HDPE) and wax paper. The molecular encapsulation complex is mixed into the parafilm solution before the casting process. The device contains 0.5 gram of the encapsulation complex and establishes an MCP concentration of greater than 1 $\mu L\ L^{-1}$ in a 36 liter chamber in less than 1 hour. For HDPE and the wax paper matrix, the materials are exposed to a MCP gas concentration of 2206 $\mu L\ L^{-1}$ for 2 and 5 hours. The release rate from HDPE is approximately 11 times higher than the rate from wax paper (Konstansek and Edward 2003).

The only efficacy study of the controlled release devices was done using reservoir devices (PVC tube). The test was conducted in a carton of Geraldton waxflower. The device established and maintained a concentration above 0.03 $\mu L\ L^{-1}$ in a 21 L carton for at least 6 days with the maximum concentration of 1 and 2.5 $\mu L\ L^{-1}$ for cartons without and with Geraldton waxflowers, respectively. However, no MCP was detected when this device was placed in the carton in an export handling environment for 4.5 days. Two to three devices per carton were required to reduce weight loss and abscission of floral organ and leaves during export handling. The greater the number of devices used, the greater was the MCP protection capacity against exogenous ethylene. The protection offered

against exogenous ethylene for 2-3 controlled release devices was comparable to that of a pulse STS treatment and better than that of a MCP fumigation treatment prior to export handling. The prevention of floral organ and leaf abscission by the MCP fumigation treatment was superior to that of the controlled release devices (Macnish and others 2004).

Placing controlled release devices in packages is less controllable than using storage rooms. The controlled release devices were less effective in the carton lined with LDPE than with newsprint because LDPE film is less permeable to gas and moisture which may have caused higher ethylene accumulation inside the carton (Macnish and others 2004).

1.7 Conclusion

Researchers have strived to find an ethylene antagonist to slow the maturation of fresh produce. To date, the most promising ethylene antagonists are substituted cyclopropenes. MCP is a compound in this category that is being used because of its commercial availability. It can be used with fresh and minimally processed produce to reduce the effect of ethylene. An undesirable result for some produce is the compromising of the produce's defense mechanism against some microorganisms for some produce. MCP is currently commercially available in a molecular encapsulation complex powder. Several attempts have been made to provide an alternative delivery method to facilitate continuous and in-package MCP treatment.

2 THE EFFECT OF POSTHARVEST CONDITIONS ON SUBSEQUENT QUALITY OF FRESH-CUT APPLES

2.1 Introduction

Fresh-cut produce has become one of the most popular commodities in grocery stores over the past 10 years (Garrett 2002). Fresh-cut vegetables such as pre-packaged salads and shredded carrots are very popular with consumers, owing to their convenience and flexibility of use. The market for fresh-cut fruits has been slower to develop, which may be attributable to two reasons: first, fruits are more perishable than vegetables, causing them to have a shorter shelf life (Warren 2005); and secondly, consumer perception of quality is different for fresh-cut fruits and vegetables. The desirable flavor of fresh-cut vegetables usually comes from an accompaniment, such as a salad dressing, while consumers expect the inherent flavor and textural quality of fresh-cut fruits to be self standing (Beaulieu and Baldwin 2002). Most research in fresh-cut fruits has focused on the reduction in browning and not as much on texture and flavor. Thus, consumers are still apprehensive about buying fresh-cut fruits. This hesitation contributes to slow market growth of fresh-cut fruits (Kader 2002).

Sales for fresh-cut produce are expected to rise to $15 billion by the end of 2005, from $10 - $12 billion in 2002 – 2003. Despite its slow market development in the past, fresh-cut fruits are expected to be a significant contributor to this growth (Harte and others 2004). Sales of fresh cut fruits were $719 million in 2004 and are expected to reach the $1 billion level in the near future (Warren 2005).

Fresh-cut apples are increasingly more popular and have potential to increase the revenue stream for the apple industry. Local supermarkets have started to carry more fresh-cut apple products. They are mostly from a third party and carry their own SKUs, rather than being processed in-house. Large quick serve restaurants such as McDonald have included fresh-cut apples in their menu. Although fresh-cut apples are becoming more available, a survey has shown that the purchase of apple slices would not replace the whole apple purchased (Novak 2004). This indicates that fresh-cut apples will create a new marketing opportunity for the apple industry.

Due to their longer shelf life, apple products such as applesauce or apple juice can be processed when whole apples are in the stage that results in the best product. However, this is not the case with minimally processed apples. Because of their short shelf life, they need to be processed at the time when they are required to be in the market. In order to have this product available year round, the whole apples (prior to slicing) must be preserved using appropriate postharvest treatments.

Controlled atmosphere storage (CA) is a well-established and widely used postharvest practice to prolong the storage life of whole apples. Lower oxygen (1-3%) and higher carbon dioxide (0 – 3%) content in CA storage extend the storage life of apples by inhibiting ethylene action as well as reducing the respiratory rate. CA also affects other biological processes that are associated with produce quality (Beaudry 1999). Recently, 1-methylcyclopropene (MCP), an ethylene action inhibitor, has been commercially used to prolong the storage life

of apples. Like CA, it has a beneficial effect in extending the storage life of several cultivars of apples. MCP suppresses the loss of firmness (Fan and others 1999a; Fan and others 1999c; Rupasinghe and others 2000; Watkins and others 2000; Lu and Toivonen 2003), reduces the rate of starch content reduction (Watkins and others 2000) and helps to maintain the titratable acidity in some apple cultivars (Fan and others 1999a; Fan and others 1999c; Lu and Toivonen 2003). Despite these beneficial effects, both CA and MCP cause reduction of aroma volatiles that are produced by apples (Plotto and others 2000; Lurie and others 2002) (Perera and others 2003; Tay and Perera 2004). Despite this, sensory evaluation indicates preference toward MCP-treated apples over non-MCP-treated apples (Lurie and others 2002).

Fresh-cut processing is considered to be minimal processing; thus, the quality of fresh-cut apples relies mainly on the intact apples. However, most of the research with fresh-cut apples has been concerned with selecting the right preservation technique. Only a limited number of studies have evaluated the effect of postharvest handling on the subsequent quality of apple slices. Massey and McLellan (1985) observed that apples, upon immediate removal from CA storage, may not be optimum for processing either in terms of yield or quality of the finished product (Massey and McLellan 1985). Delay in placing fruits in CA worsens the yield and firmness of fresh-cut apples, particularly when the apples are harvested late (McLellan and others 1990). The oxygen content in the storage atmosphere affects apples in terms of anaerobic volatile production, flesh color, and firmness. Apple slices from intact apples in 1 kPa oxygen undergo

less browning but lose firmness more quickly than slices from intact apples in 100 kPa O_2 atmosphere. However, high oxygen pressure in the storage atmosphere results in less formation of products associated with off-flavors (Lu and Toivonen 2000).

The first research on the use of MCP with fresh-cut produce started in 2002. Publications in this area, to-date, include apples (Jiang and Joyce 2002; Perera and others 2003; Bai and others 2004; Calderon-Lopez and others 2005), pineapples (Budu and Joyce 2003), tomato (Jeong and others 2004), lettuce (Tay and Perera 2004) and watermelon (Mao and others 2004). The effect of MCP on on the subsequent quality of fresh-cut apples is similar in terms of firmness retention and reduction of volatile production (Perera and others 2003; Bai and others 2004; Calderon-Lopez and others 2005). The effect on flesh browning is inconsistent between cultivars. This may be partly due to the difference in the maturity of fruits at the time of harvest as well as other processing parameters. The maturity of apple fruits can influence the extent of enzymatic browning (Prabha and Patwardhan 1985; Lozano and others 1994).

The objective of this study is to determine how MCP treatment and CA storage, individually and in combination, with storage time affect the quality of 'Jonagold' apples both as whole fruits and the subsequent quality (flesh color, texture and volatile production) of fresh-cut apples.

2.2 Materials and Methods

2.2.1 Plant materials

'Jonagold' apples were harvested in late September of 2002. At harvest, the average internal ethylene content of the apples was approximately 0.24 μL L^{-1} with an average weight of 175 gram/fruit and 60% redness of the skin. The apples had a firmness of 81 N, a starch index of 5.7 and 14.5° Brix. Apples were then subjected to 4 different postharvest processes: non-MCP treatment in normal air storage (air or control apples), MCP treatment in normal air storage (Air + MCP apples), non-MCP treatment in CA storage (CA apples) and MCP treatment in CA storage (CA + MCP apples). Description of each of these postharvest treatments is presented in 2.2.2.

2.2.2 MCP treatment and storage conditions

Apples were placed in plastic mesh bags (50 apples/bag). Four bags were placed in a plastic barrel. Prior to tightly sealing the barrel, a small plastic container with ~ 0.18 g of SmartFresh™ and water was placed in the barrel to release sufficient MCP to achieve approximately 1 μL L^{-1} MCP gas in the 30 gallon barrel headspace. The calculation of the required amount of SmartFresh™ is presented in Appendix D. The barrel remained sealed for 16 hours at ambient temperature (~20°C). This concentration and storage time were expected to be sufficient to saturate the ethylene response in the apples (Fan and others 1999b; Rupasinghe and others 2000). Another four bags of apples were treated in the same manner but without exposure to MCP gas. After 16 hours, apples were removed from the barrel and placed in a ventilated 5

gallon plastic container (25 apples/container) and stored at 0°C for 10 days. After 10 days, half of the MCP-treated and non-MCP-treated apples were removed from normal air storage to CA storage of 1.5% O_2 and 3% CO_2. The other half remained in air storage. The fruits were then removed at 3, 5, 7 and 9 months for evaluation and processing into fresh-cut slices. Whole apple evaluation included internal ethylene content, total soluble solids, flesh color, and firmness.

2.2.3 Internal ethylene content

Internal ethylene content (IEC) of intact apples was evaluated by drawing 1 mL of gas from the interior of the apples as described by Mir and others (2001).

2.2.4 Total soluble solids

The total soluble solids in apple juice were measured using a standard handheld refractometer. The °Brix was recorded.

2.2.5 Firmness

Apple firmness was measured using a drill-stand-mounted Effegi penetrometer (FT-327; McCormick Fruit Tree Inc., Yakima, WA) with an 11-mm-diameter probe. Two skin discs of approximately 2.5 cm diameter were removed from opposite sides of each fruit prior to pressing the probe into a cut surface to a depth of approximately 8-9 mm. The force required to press the probe into the apple flesh was recorded as an index of flesh firmness.

2.2.6 Flesh color measurement

The flesh color of intact apples was measured immediately after the whole apples were cut open. The flesh color was measured using a HunterLab ColorQuest 45°/0° spectrophotometer (Reston, VA) in 45°/0° geometry. Immediately after cutting apples in half, the apple flesh was placed over a 1 cm opening and the L*, a* and b* measurements were recorded. These three values together serve to define the location of any color in the uniform color space. L* indicates the lightness co-ordinate and it ranges from 0 to 100 with 0 indicating black and 100 indicating white. a* is the red/green opponent co-ordinates. A positive value indicates redness while a negative value indicates greenness. b* is the yellow/blue opponent co-ordinate with a positive value representing yellowness and a negative value representing blueness (MacDougall 2002).

2.2.7 Fresh-cut apple preparation

Apples taken out of storage were kept at 5°C in air for 24 hours prior to processing at room temperature. Apples were sliced into 8 wedges and the core materials of each piece were removed using a sharp knife. The apple slices were dipped in a 3% commercial antibrowning agent (NatureSeal™; Mantrose-Haeuser Co., Inc., Westport, CT), whose active ingredient is calcium ascorbate or deionized water for 15 seconds and pad-dried using paper towel.

2.2.8 The effect of postharvest condition on flesh color of fresh-cut apples

After dipping and pad-drying the slices, the flesh color of the cut surface was measured using the procedure described in 2.2.6. The slices were then placed on a plastic tray and packaged in resealable LDPE bags, each bag

containing 4 slices. The bags were stored at 5°C. Slices were removed from each bag and flesh color was measured again after 2, 4, 6 and 12 hours and 1, 2, 4, 6, 10 and 14 days or until microbial spoilage was visually observed. After each measurement the slices were returned to the packages. The experiment was performed in random order. Four replicates were used for each postharvest condition. In addition to the the three measurements (L*, a*, and b*), the total color difference between flesh color at time t and time = 0 (ΔE^*) was calculated according to the following equation (MacDougall 2002):

$$\Delta E^* = \sqrt{(L^*_0 - L^*_t)^2 + (a^*_0 - a^*_t)^2 + (b^*_0 - b^*_t)^2}$$

where subscript 0 represents the value at time = 0 and the subscript t represents the value at any time t.

2.2.9 The effect of postharvest condition on texture of fresh-cut apples

After dipping and pad-drying, the slices from the same fruit were packed together in resealable LDPE bags and kept at 5°C. One slice was taken out of the bag at 1 hour, and then at 7 and 14 days for texture evaluation using a Texture Management System equipped with a thin blade shear-compression cell (TMS-90; Food Technology Corporation; VA). Apple slices with known weight were placed in the chamber of the compression cell. The cell moved downward at a constant speed of 0.15 cm/s. The work to move the shear press through the slice was recorded in N-cm. The value was normalized using the weight of the apple slice in grams. This weight-normalized work is reported in N-cm g^{-1} as an indication of texture. The higher the value, the greater the firmness. The

experiment was performed in random order. Four replications were used for each postharvest treatment.

2.2.10 The effect of postharvest condition on volatile production by apple slices

This experiment was performed only with slices dipped in the antibrowning agent. The volatile compounds were analyzed as individual volatiles and total volatiles. Selected compounds were analyzed using GC-MS and the total volatiles using an electronic nose. For both analyses, four replicates were used. To measure a selected volatile, four slices from the same fruit were packed together in a resealable LDPE bag. An extra heat-seal was set in place below the resealable seal. This was to ensure an air tight seal. The headspace volatiles in the bag were collected at 0.5, 7 and 14 days during the holding period of fresh-cut slices at 3°C using a solid-phase microextraction fiber with 100 μm polydimethylsiloxane coating (Supelco, PA). The fiber was inserted into the bag through a silicon septum and to collect volatiles in headspace for 4 minutes at 3°C. The volatiles were desorbed for 3 minutes into a gas chromatograph (Hewlett-Packard, Agilent, CA) equipped with a time of flight mass spectrophotometer (FCD-650, LECO Corp, St. Joseph, MI) for detection and identification of volatiles. Column temperature was initially set at 40°C and then increased at a rate of 70°C/min to 250°C. The temperature was held constant at 250°C for 2.5 minutes. The hexyl acetate peak areas were recorded as an index of the amount of volatile ester present.

The effect of postharvest treatment on total volatiles was compared using an electronic nose system (Fox 3000, Alpha-MOS, Toulouse, France). A 1 cm diameter and 0.5 cm thick disc was cut from an apple slice and sealed in a 10 mL headspace vial. The vial was placed on a sample tray. The headspace volatiles were generated for 10 minutes in a 35°C oven having an agitation speed of 500. A headspace sample of 2.5 mL was taken with an automatic sampler and injected into a sensor chamber, containing12 metal oxide sensors. The sensor responses were recorded for 5 minutes. A delay of 5 minutes between each injection was used to ensure that the sensors had returned to their baseline. The sensor responses were optimized and analyzed by the acquisition software (Alpha SOFT version 8.0, Alpha-MOS, Toulouse, France). The electronic nose was used to measure the total volatiles twice during a 14-day holding period (3°C), at the beginning and at the end. Both analyses used apple discs from the same fruits as those used for individual volatile compound analysis.

2.2.11 Statistical analysis

The condition of the apples upon removal from storage was analyzed by two-way analysis of variance (ANOVA) using a "proc mixed" procedure in SAS (version 8.0, SAS Institute, Inc., Cary, NC). The independent variables were MCP treatment, storage atmosphere and their interactions. The data were analyzed separately for each storage time.

The effect of postharvest condition on flesh color and texture of fresh-cut slices was analyzed by repeated measure design using the "proc mixed" procedure in SAS. The independent variables were MCP treatment, storage

atmosphere, antibrowning treatment, storage time of fresh-cut slices and their interactions. The data from each storage time (3, 5, 7 and 9 months) were analyzed separately. The effect of postharvest conditions on individual volatiles was analyzed using the same method as for flesh color and texture, but the independent variables did not include the antibrowning agent. The SAS codes for two-way ANOVA and repeated measurement are presented in Appendix A.

Data from optimized electronic nose sensor responses obtained from 0 and 14 days holding period of apple slices were analyzed using multivariate analysis: principal component analysis (PCA), which is an unsupervised learning technique, and canonical discriminant analysis (CDA) which is a supervised learning technique.

2.3 Results and Discussion

2.3.1 Condition of apples before fresh-cut apple processing

2.3.1.1 Internal ethylene content (IEC)

Internal ethylene content (IEC) of intact apples was affected by both MCP treatment and the storage atmosphere (Figure 2.1). A statistical analysis was performed on Ln (IEC) to minimize the difference in variance of untransformed IEC data. Control apples had the highest IEC and MCP-treated apples in CA storage had the lowest IEC throughout 9 months storage. The combination of MCP treatment and CA storage had an additive effect. This agrees with the published results on stored 'McIntosh,' 'Law Rome,' and 'Delicious' apple fruits (Watkins and others 2000). MCP-treated apples had lower ethylene than CA

storage apple after 3 and 5 month storage. After 7 months storage, the IEC of these apples were comparable. Similar results were also found in 'Golden Delicious' up to 5 months storage (Saftner and others 2003) and in 'McIntosh,' 'Law Rome,' and 'Delicious' up to 6.5-7 months storage (Watkins and others 2000). Between 7 and 9 months in air storage, the IEC of MCP apples increased greatly while IEC of both CA and CA + MCP apples remained low.

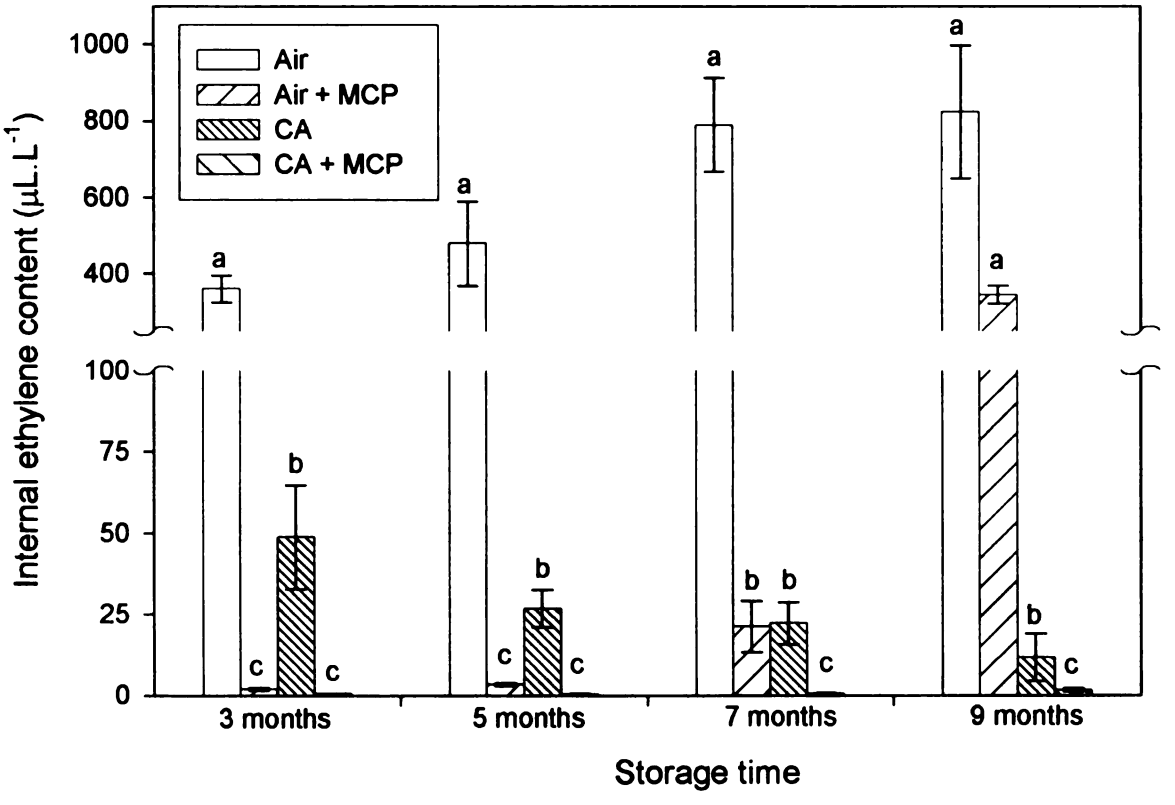

Figure 2.1. Internal ethylene content of MCP treated and untreated intact apples stored in air and controlled atmosphere for 3, 5, 7 and 9 month at 0°C (n=5). Error bars are ± standard error. For each storage time, the same letter indicates no significant difference between postharvest treatments within samples from the same storage time (p-value > 0.05).

MCP treatment and CA storage inhibits ethylene biosynthesis by influencing 1-aminocyclopropane-1-carboxylic acid synthase (ACS) and 1-aminocyclopropane-1-carboxylic acid oxidase (ACO). MCP blocks autocatalytic ethylene production (Watkins 2002), which is accomplished by binding to ethylene receptor sites. This inhibits both ACS and ACO activities (Lu and Toivonen 2003). The ability of CA storage to suppress ethylene inhibition may be due to the low oxygen level. Ethylene biosynthesis is oxygen-dependent (Mir and Beaudry 2002) because ACO requires oxygen as one of its substrates (Watkins 2002). Thus, the reduced oxygen concentration suppresses the activity of ACO. The sharp rise in IEC of MCP-treated apples in 9 months air storage may be a result of the diffusion of MCP away from the ethylene receptors or the formation of new ethylene receptors (Cameron and Reid 2001). This causes ethylene production to resume. A sharp rise in IEC did not occur in MCP-treated or untreated apples in CA storage because they were continuously being exposed to a low oxygen level.

Another interesting observation that can be made from the data shown in Figure 2.1 is, as the storage time increased, the IEC of CA apples decreased while the IEC of CA + MCP apples stayed relatively the same. The high IEC of CA apples at 3 month storage than at other storage times may be due to the delayed placement of apples in CA storage at the beginning of the experiment. This was also observed in previous research (McLellan and others 1990). For CA + MCP apples, ethylene production was suppressed by MCP treatment when the placement of apples in CA storage was delayed.

2.3.1.2 Total soluble solids

Total soluble solids, as indicated by °Brix, is a quality index. Since sugar is the main component in fruit juice, % soluble solids is used as an indication of the sweetness of fruits (Kitinoja and Kader 2002). Fruits with higher total soluble solids content are sweeter. MCP treatment and storage atmosphere have an effect on °Brix but the effect was different for each storage time (Figure 2.2). When compared with the value at harvest, °Brix in control apples stayed relatively the same at 3 months and slightly declined after that. Apples subjected

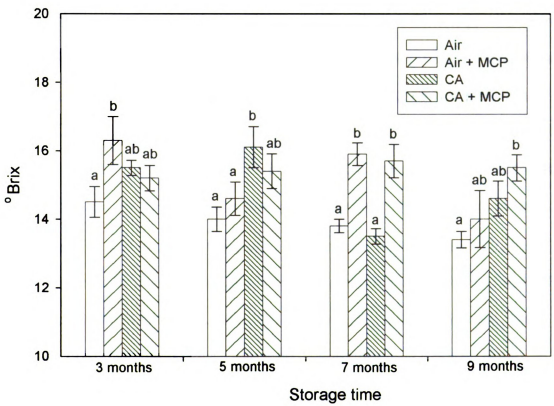

Figure 2.2. Total soluble solid, as represented by °Brix, of MCP treated and untreated intact apples stored in air and controlled atmosphere for 3, 5, 7 and 9 months at 0°C (n=5). Error bars are ± standard error. For each storage time, the same letter indicates no significant difference between postharvest treatments within samples from the same storage time (p-value > 0.05).

to at least one of the postharvest treatments had equal or greater °Brix than the control apples of the same storage time. The individual treatment of MCP or CA storage either increased or had no effect on the total soluble solids. Several publications had reported that MCP decreases (Watkins and others 2000), increases (Fan and others 1999a; Fan and others 1999c) or has no effect (Rupasinghe and others 2000; DeEll and others 2002; Reed 2002) on total soluble solid of even the same cultivars.

2.3.1.3 Firmness

Firmness is a quality index of apples. Reduction in firmness is an indication of softening, which, if excessive is undesirable. Firmness was strongly influenced by MCP treatment and storage atmosphere (Figure 2.3). In general, firmness decreased with storage time. The firmness of control apples was reduced to approximately the minimum threshold of 53.4 N (12 lb.), as set by the Washington tree fruit industry (Mir and others 2001), after 3 months storage at 0°C, and below the threshold with further storage time. The firmness of MCP-treated apples and apples in CA storage was similar for all storage durations. Combination of MCP treatment and CA storage had the strongest inhibitory effect on loss of firmness throughout storage. For up to 9 months of storage, the firmness of apples that received either MCP treatment, CA storage, or the combination of the two was always higher than the threshold level of 53.4 N.

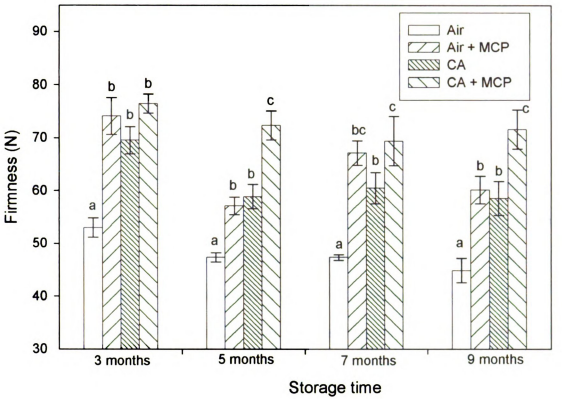

Figure 2.3. Firmness of MCP treated and untreated intact apples stored in air and controlled atmosphere for 3, 5, 7 and 9 months at 0°C (n=5). Error bars are ± standard error. For each storage time, the same letter indicates no significant difference between postharvest treatments within samples from the same storage time (p-value > 0.05).

The relationship of firmness to the logarithm of IEC was analyzed using the Pearson correlation to determine the strength and direction of the relationship. The Pearson correlation coefficient can range from -1 to +1. The larger the absolute value, the greater the correlation, while the mathematical sign indicates whether the two data are proportional or inversely proportional. From this analysis (Table 2.1) the only significant relationship was found with control apples. The coefficients suggest that the relationship between firmness and the

logarithm of IEC was inversely proportional which agrees with the results in other studies (Watkins and others 2000). However, the lack of significance with the other treatments disagrees with previous work done by Watkins et al. (2000), which showed a significant inverse relationship between IEC and firmness of air and CA storage apples.

The lack of significant relationship between log (IEC) and firmness in 'Jonagold' apples receiving at least one of the postharvest treatments may be due to small changes in IEC and firmness during storage. The data were again analyzed to look for a correlation between all apples in air storage and in CA storage. The correlation coefficients were -0.76 (p-value < 0.0001) and -0.49 (p-value = 0.001) for apples in air and CA storage, respectively. The relationship was stronger in apples in air storage, which is consistent with Watkin et al (2000). Another analysis was performed on MCP-treated and non MCP-treated apples and the correlation coefficients were -0.45 (p-value = 0.004) and -0.68 (p-value < 0.0001), respectively. This indicates a strong relationship between IEC and firmness in non-MCP treated apples.

Table 2.1. Pearson correlation coefficients and p-values of correlation evaluation between flesh firmness (N) and log IEC for untreated 'Jonagold' apples in air and CA storage and MCP treated apples in air and CA storage for 9 month storage.

Postharvest condition	*Pearson correlation coefficient*	*p-value*
Air (control)	-0.50	0.025
Air + MCP	-0.34	0.154
CA	0.06	0.784
CA + MCP	0.05	0.845

2.3.1.4 Flesh color

Flesh color of apples removed from storage after 3, 5, 7 and 9 month storage was represented by L*, a* and b*. At each storage time, apples had similar lightness (L^*) (Figure 2.4). When a difference was detected, control apples had the lightest flesh color while MCP-treated apples in CA storage had the darkest color. In order to determine whether this difference was visually detectable, a normalized difference in lightness for each storage time was calculated by $(\Delta L/L_0) \times 100$ where ΔL is the difference in the average lightness between apples receiving postharvest treatments and control apples from the same storage time. L_o is the average lightness of control apples. For apples, the detectable limit of difference is 2.5. Browning is described as "slight browning" but the apples are still acceptable when the normalized difference is 4.0. Apples that undergo serious browning will have a normalized difference of about 15 (Laurila and others 1998). The normalized differences of 'Jonagold' were less than the detectable limit except for MCP-treated apples stored in CA atmosphere for 7 months, whose flesh was described as slightly brown but still acceptable (Table 2.2).

Apple flesh color can be described as being between the green and red co-ordinates with slightly more green component because it has a low negative number for a* (Figure 2.5). The yellow-blue opponents coordinates (b*) indicated that the flesh was more yellow due to its large positive b* number (Figure 2.6). Both a* and b* values had greater variation than lightness. No significant

Table 2.2. Normalized difference in lightness of apples after 3, 5, 7 and 9 months in storage for untreated 'Jonagold' apples in air and CA storage and MCP treated apples in air and CA storage.

Storage time,	Normalized difference in lightness			
months	Air (control)	Air + MCP	CA	CA + MCP
3	0.0	0.8	0.6	1.3
5	0.0	0.4	0.5	2.3
7	0.0	1.5	0.4	3.6
9	0.0	0.6	0.1	0.2

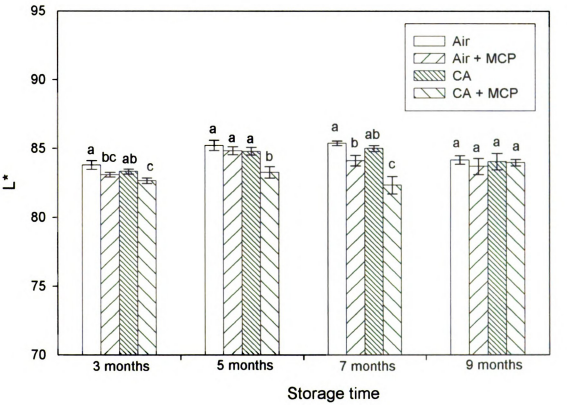

Figure 2.4. Lightness (L*) of apple flesh from MCP treated and untreated apples stored in air and controlled atmosphere for 3, 5, 7 and 9 months at 0°C (n=5). Error bars are ± standard error. For each storage time, the same letter indicates no significant difference between postharvest treatments within samples from the same storage time (p-value > 0.05).

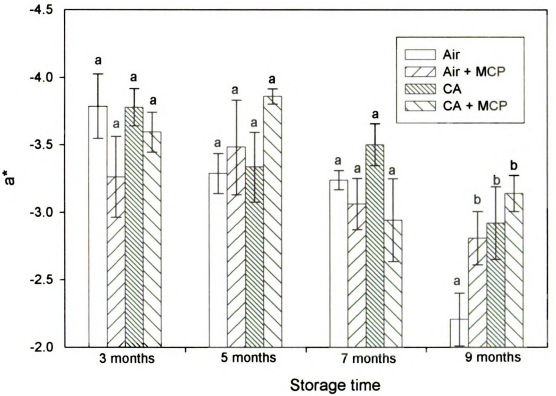

Figure 2.5. a*-value of apple flesh from MCP treated and untreated apples stored in air and controlled atmosphere for 3, 5, 7 and 9 months at 0°C (n=5). Error bars are ± standard error. For each storage time, the same letter indicates no significant difference between postharvest treatments within samples from the same storage time (p-value > 0.05).

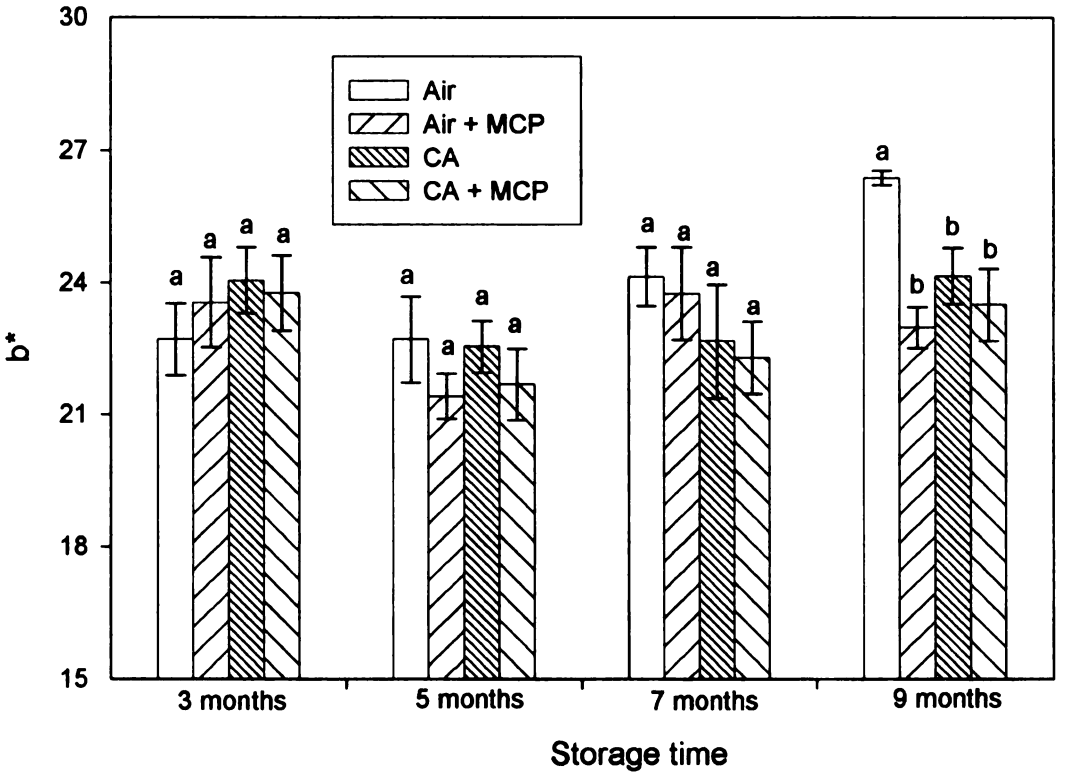

Figure 2.6. b*-value of apple flesh from MCP treated and untreated apples stored in air and controlled atmosphere for 3, 5, 7 and 9 months at 0°C (n=5). Error bars are ± standard error. For each storage time, the same letter indicates no significant difference between postharvest treatments within samples from the same storage time (p-value > 0.05).

difference was observed between treatments and the control, or among the treatments after 3, 5, and 7 months in storage. However, after 9 months in storage, the flesh (control apples) had significantly more red and yellow components than the flesh of other apples. The increase in redness and yellowness is an indication of flesh browning (Lozano and others 1994).

2.3.2 The effect of postharvest condition on flesh color of fresh-cut apples

The flesh color at the cut surface of fresh-cut slices changed during storage to a brown color as indicated by a reduced L*(lightness) and an increased a* (redness) and b* (yellowness) values (Lozano and others 1994). Due to the change in these measurements, ΔE at the cut surface also increased. This was observed in all apple slices to some extent, depending on the apple storage time before processing as well as the postharvest treatment. Figures 2.7 – 2.22 presents values of L*, a*, b* and ΔE of the cut surface of fresh-cut slices during a 14-day holding period at 5°C for apples from 3, 5, 7, and 9 months. The lines connecting the data points do not represent a browning rate model; They are only used to increase the ease of differentiating between each treatment. The statistical analysis and the pairwise comparison are presented in Appendix B.

From the four parameters used to describe color, the effect of MCP and CA storage on L*, a* and ΔE values were similar (with some slight differences) while this b* value (yellowness) trend was inconsistent. Therefore, the change in b* values was not considered in the following discussion.

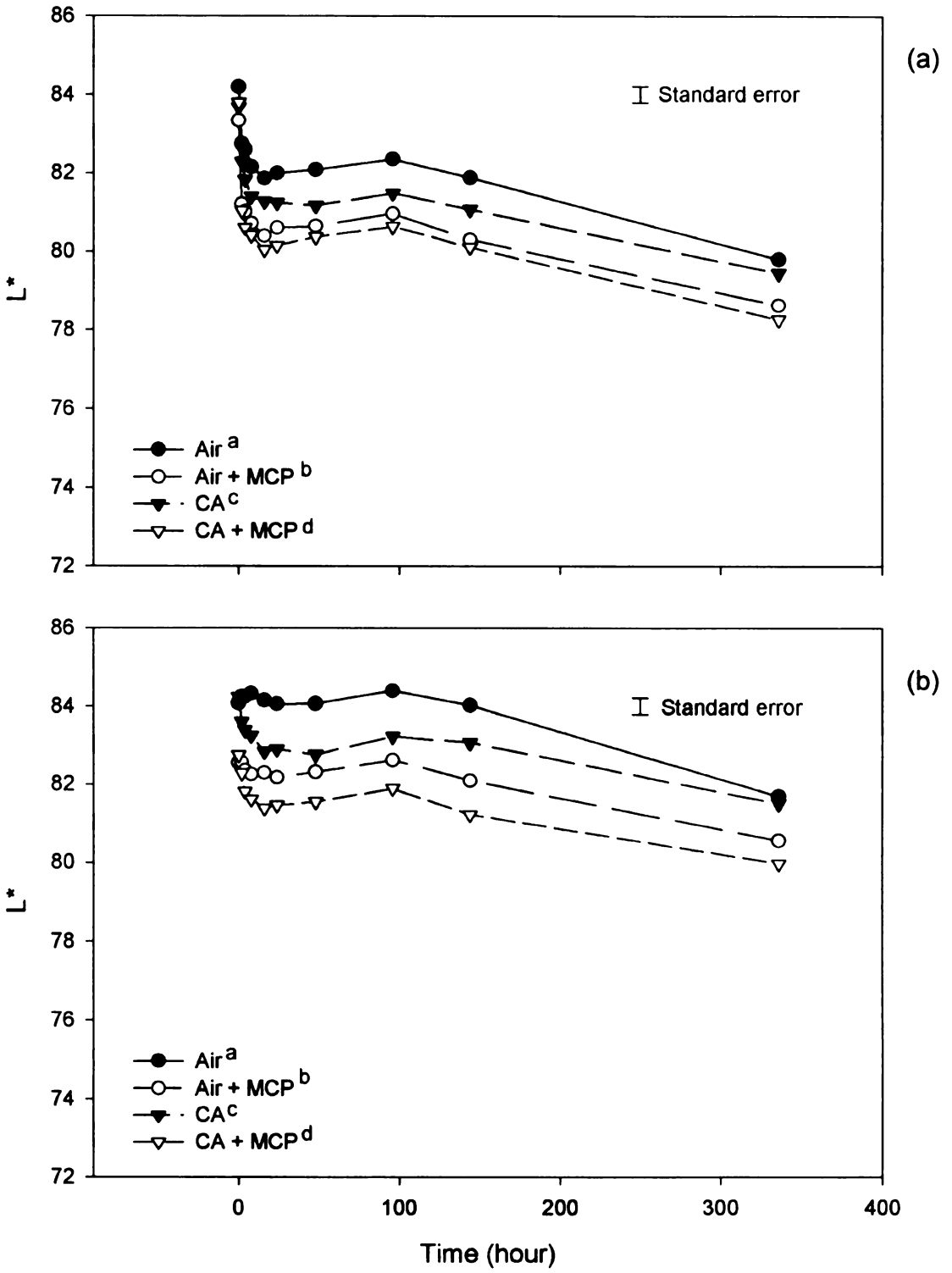

Figure 2.7. Effect of postharvest treatments after 3 months storage on lightness (L*) of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

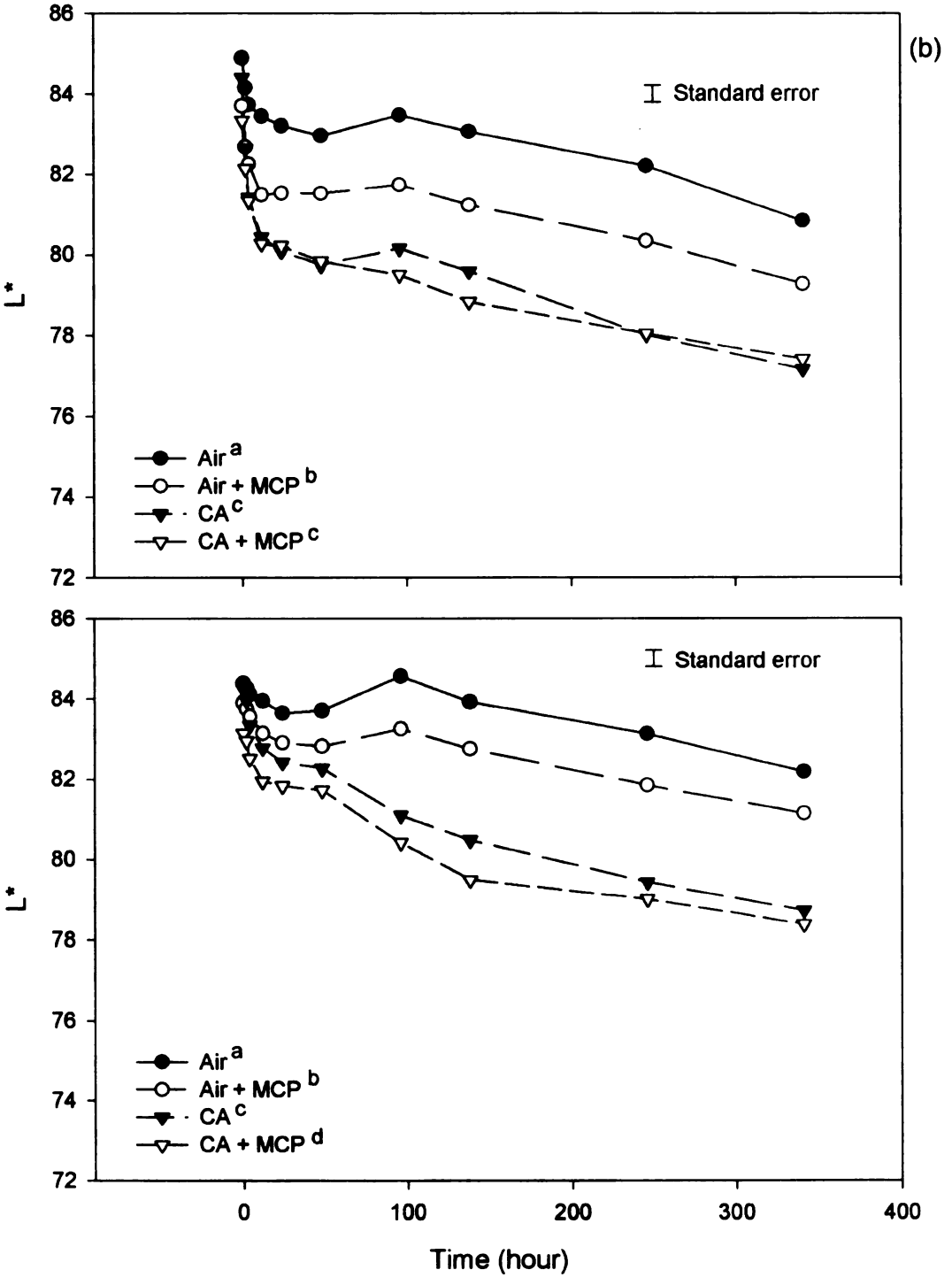

Figure 2.8. Effect of postharvest treatments after 5 months storage on lightness (L*) of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

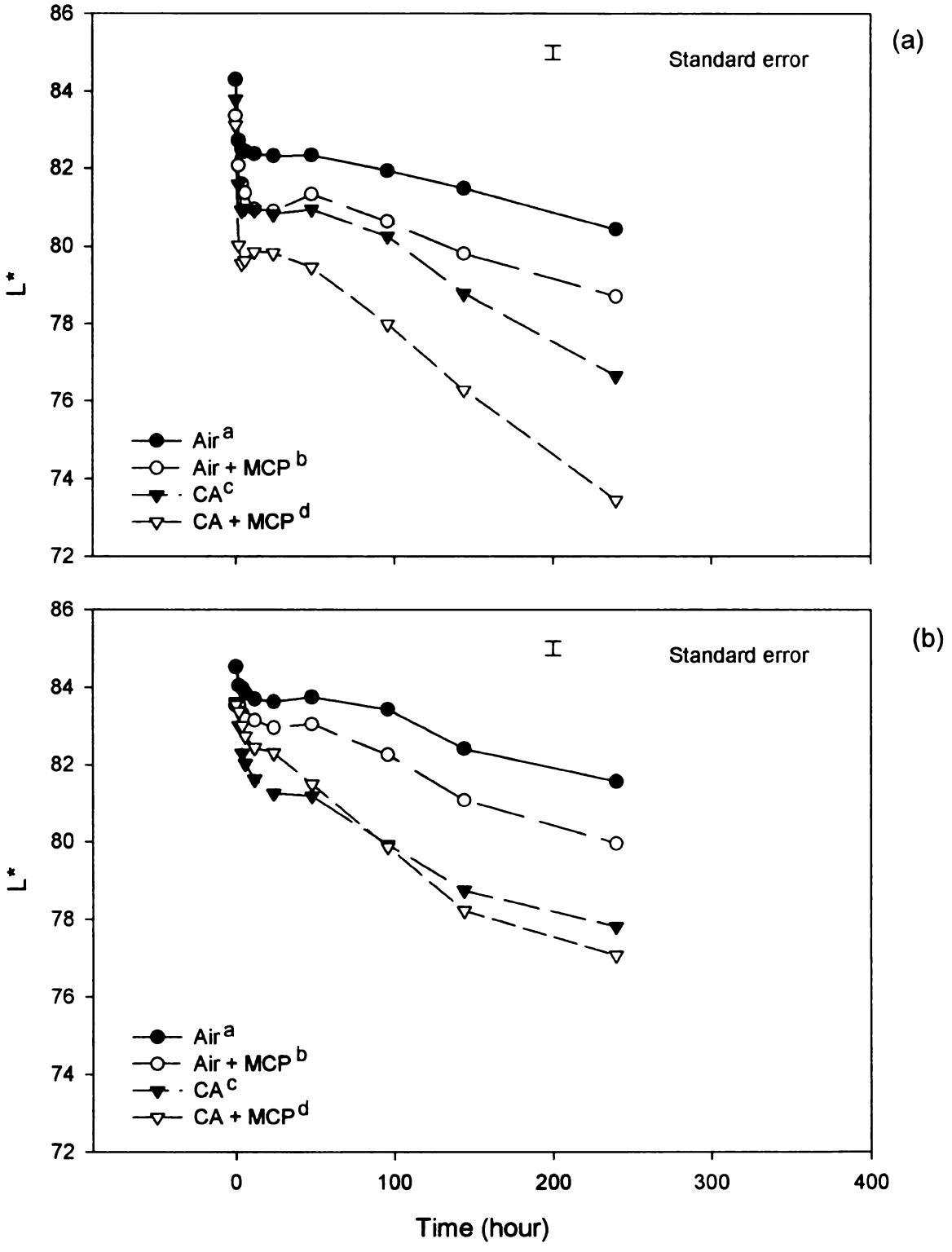

Figure 2.9. Effect of postharvest treatments after 7 months storage on lightness (L*) of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

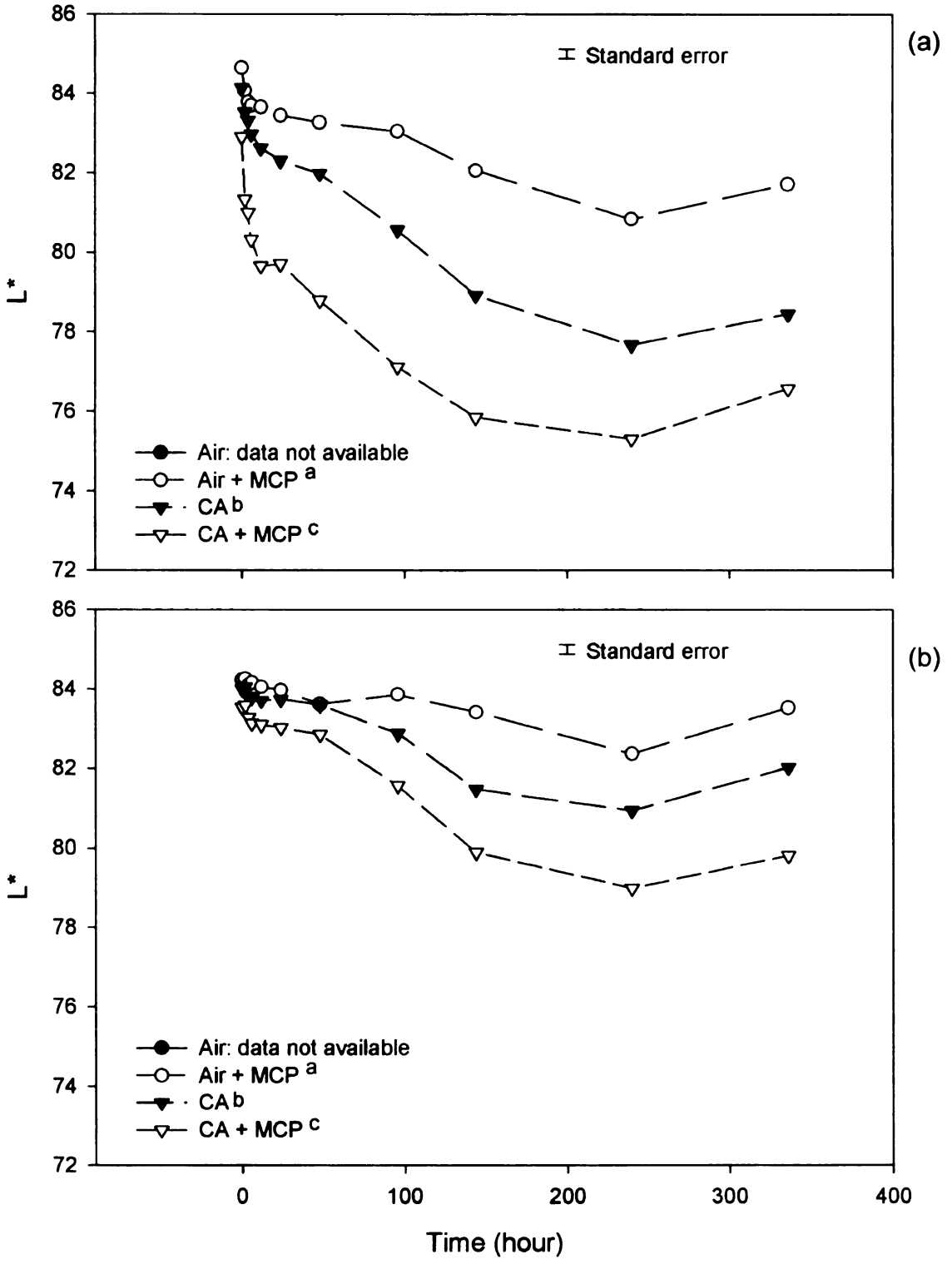

Figure 2.10. Effect of postharvest treatments after 9 months storage on lightness (L*) of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4 The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

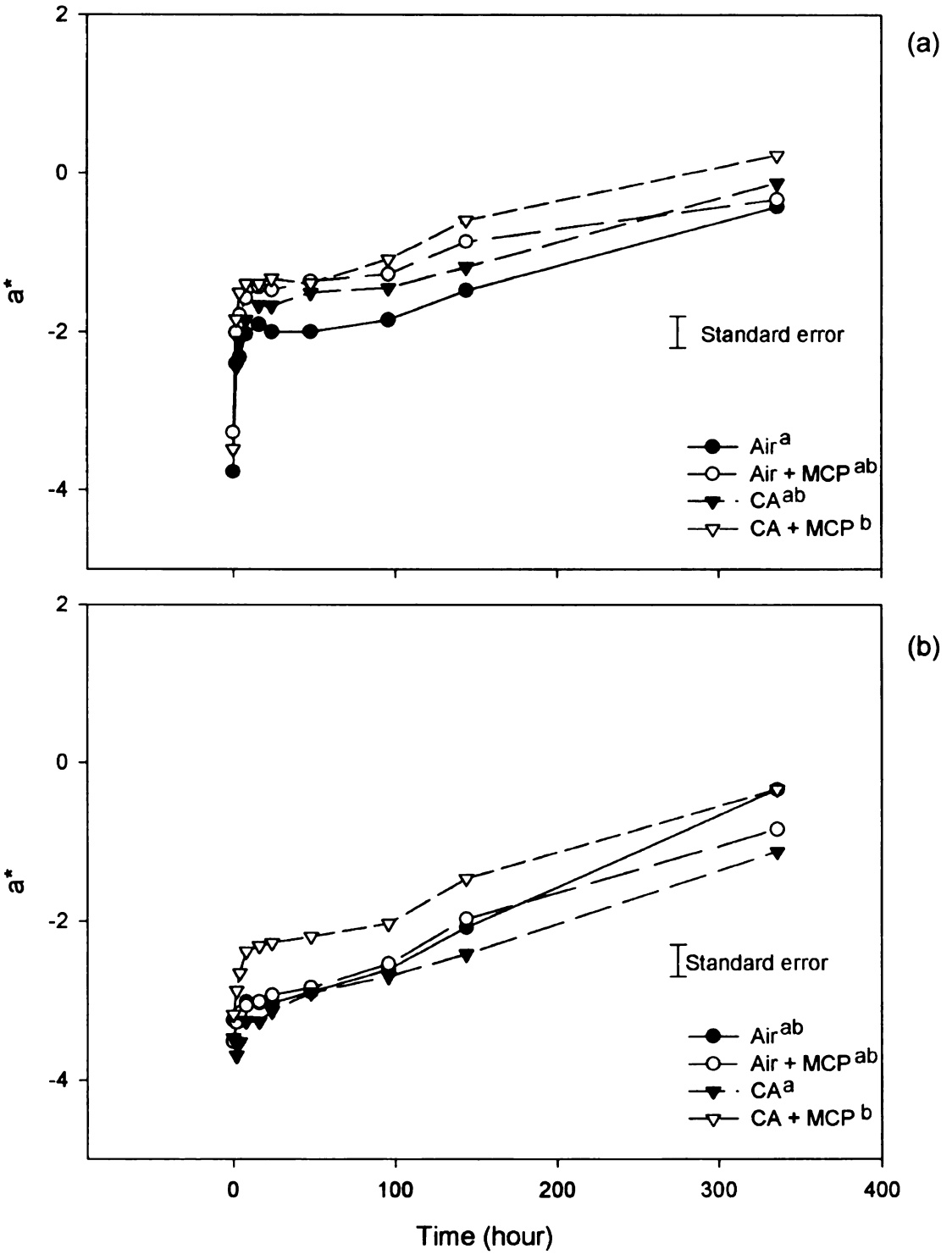

Figure 2.11. Effect of postharvest treatments after 3 months storage on a* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

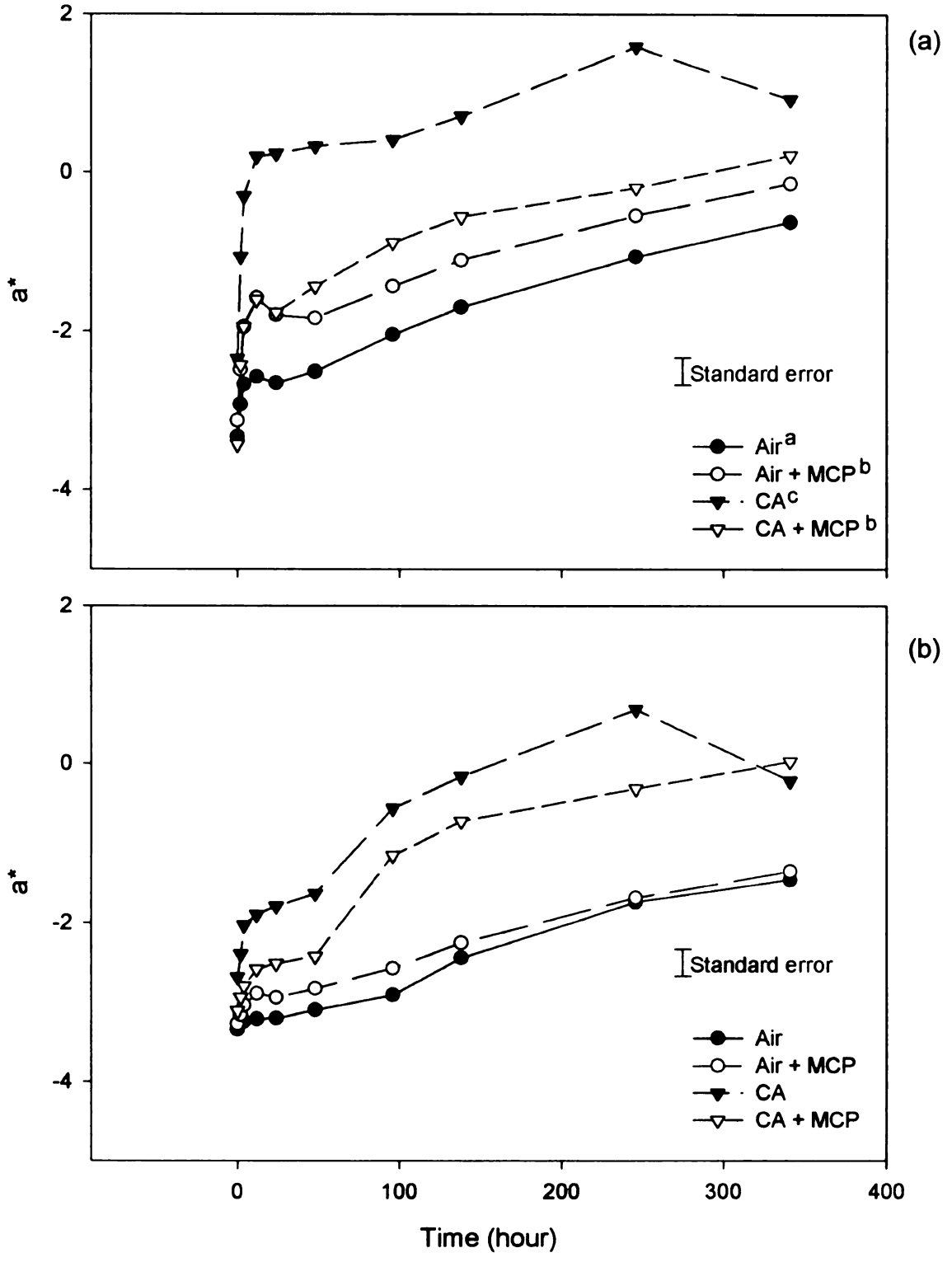

Figure 2.12. Effect of postharvest treatments after 5 months storage on a* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

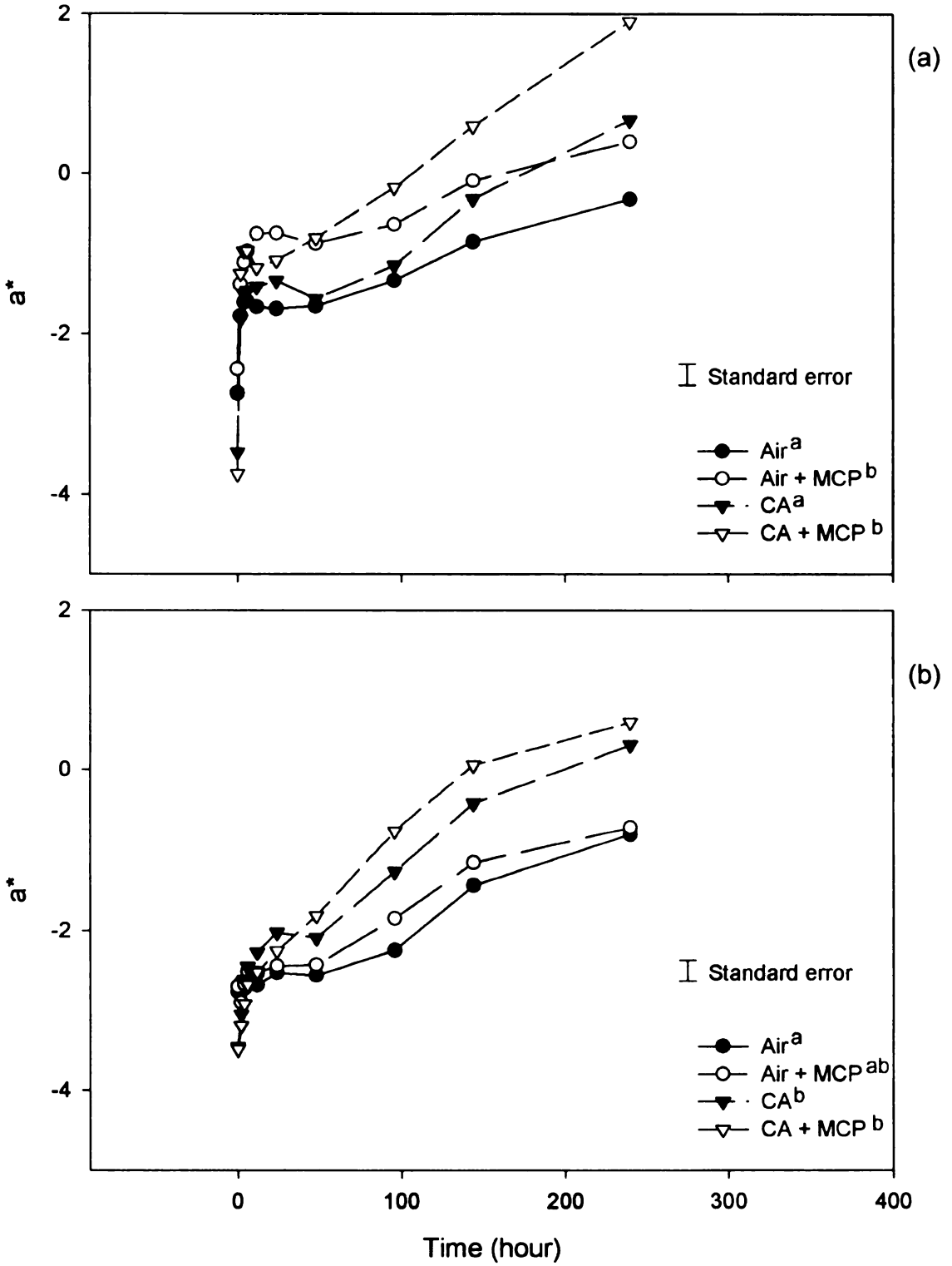

Figure 2.13. Effect of postharvest treatments after 7 months storage on a* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

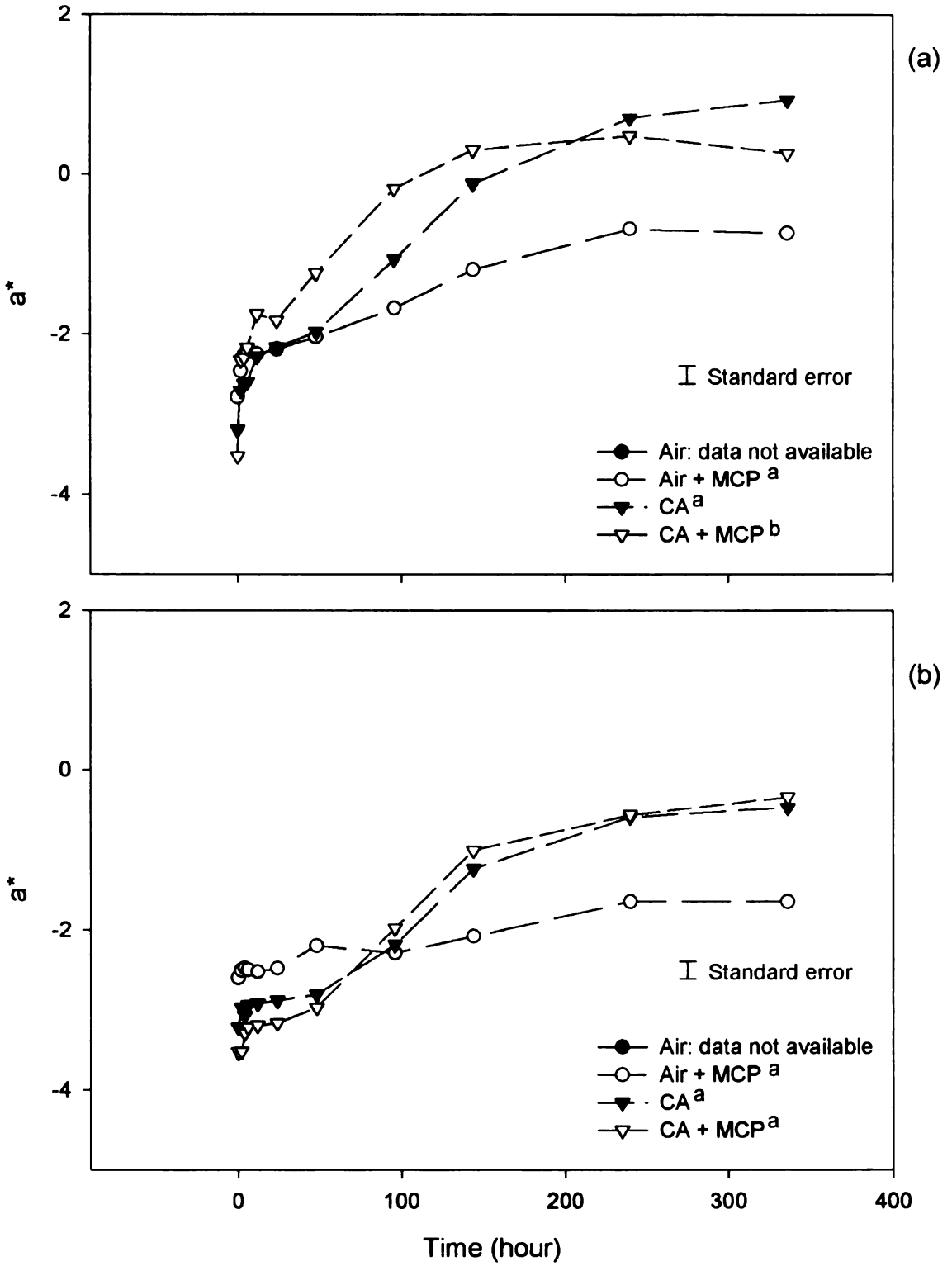

Figure 2.14. Effect of postharvest treatments after 9 months storage on a* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

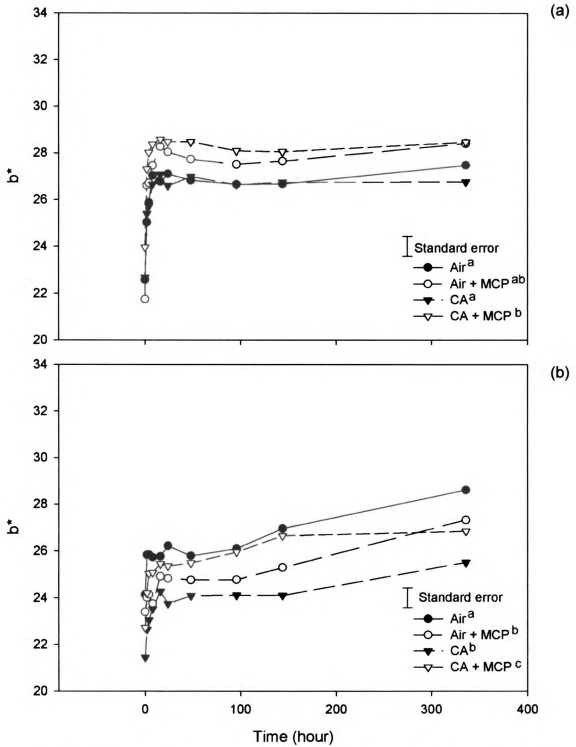

Figure 2.15. Effect of postharvest treatments after 3 months storage on b* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

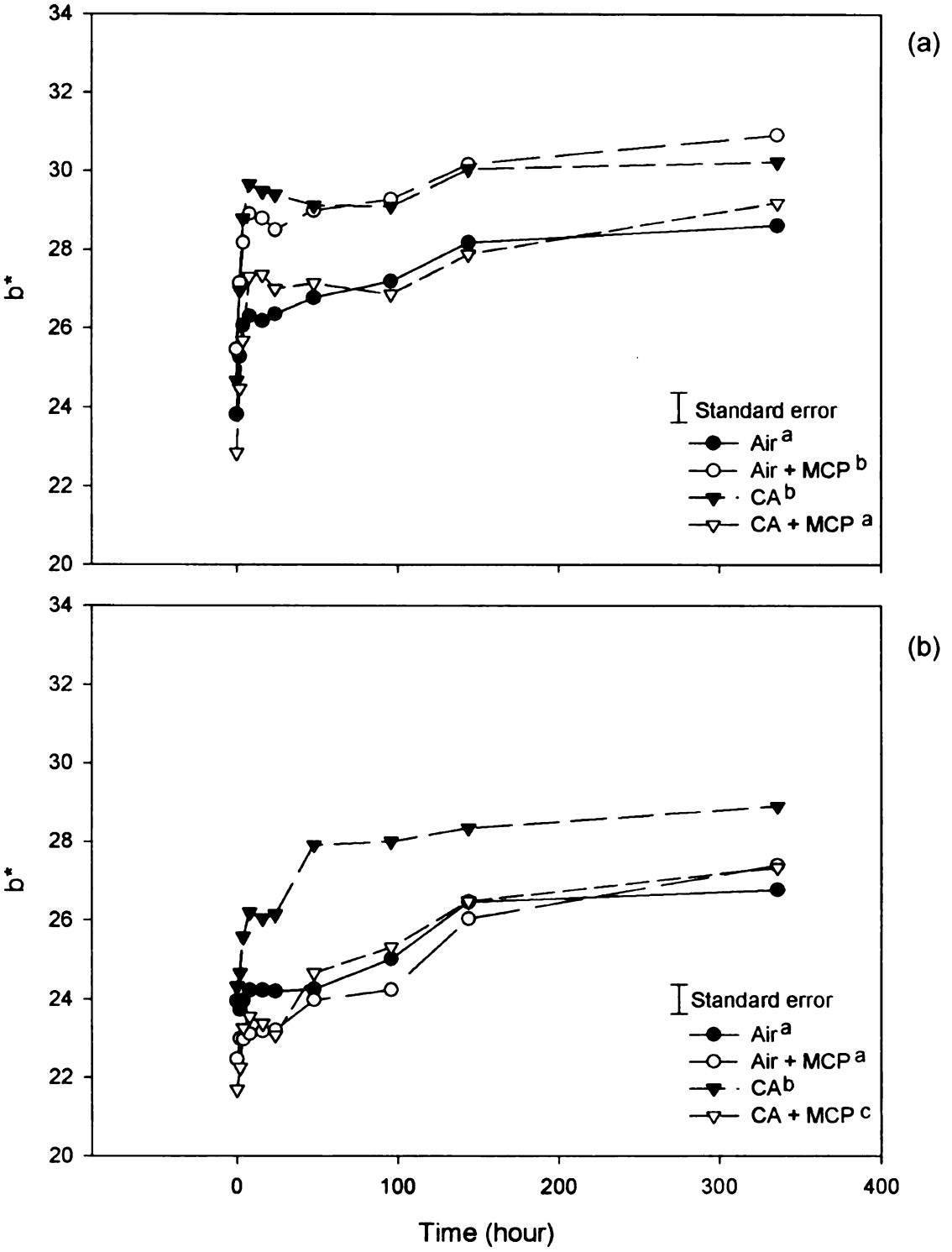

Figure 2.16. Effect of postharvest treatments after 5 months storage on b* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

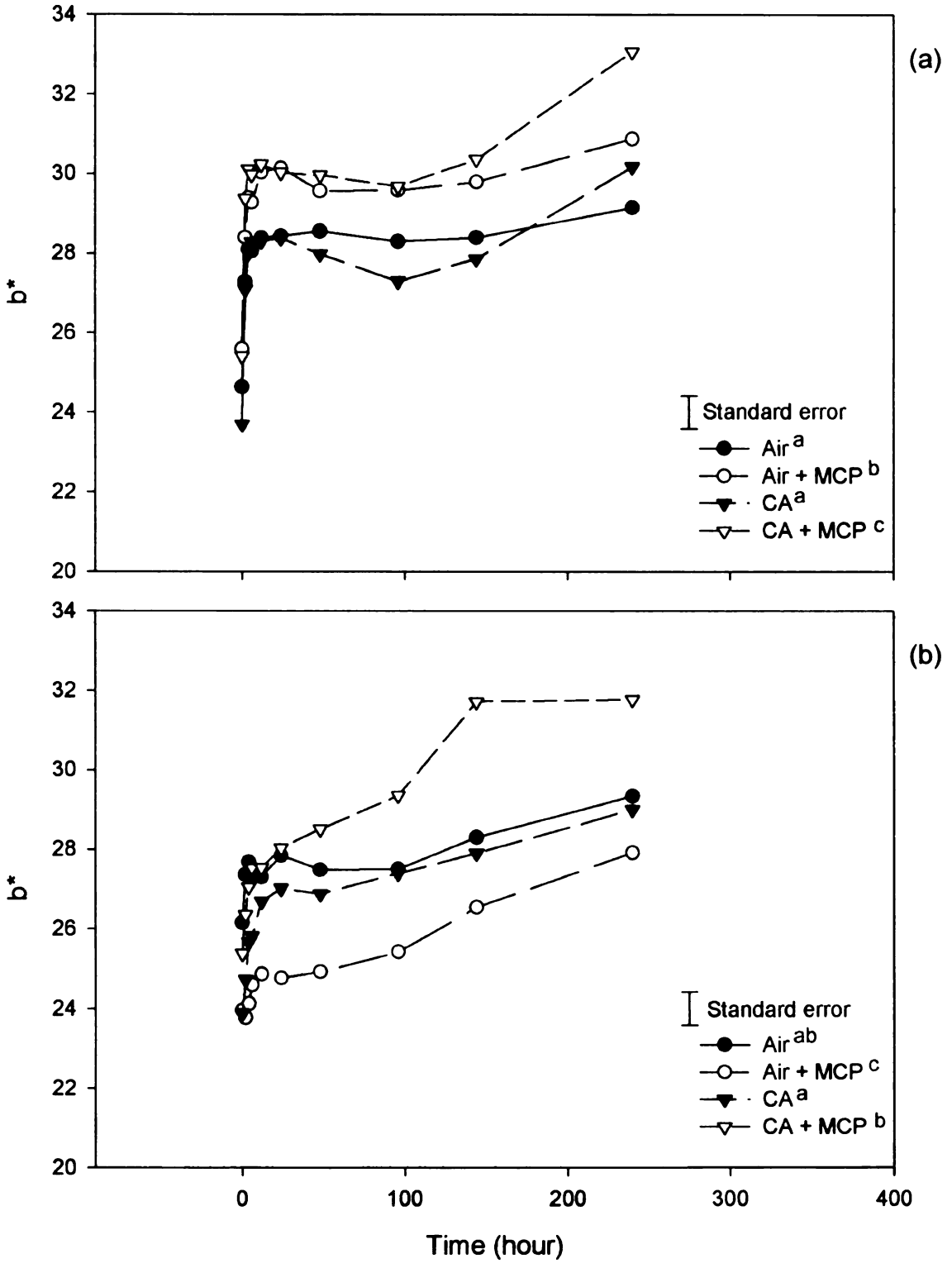

Figure 2.17. Effect of postharvest treatments after 7 months storage on b* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

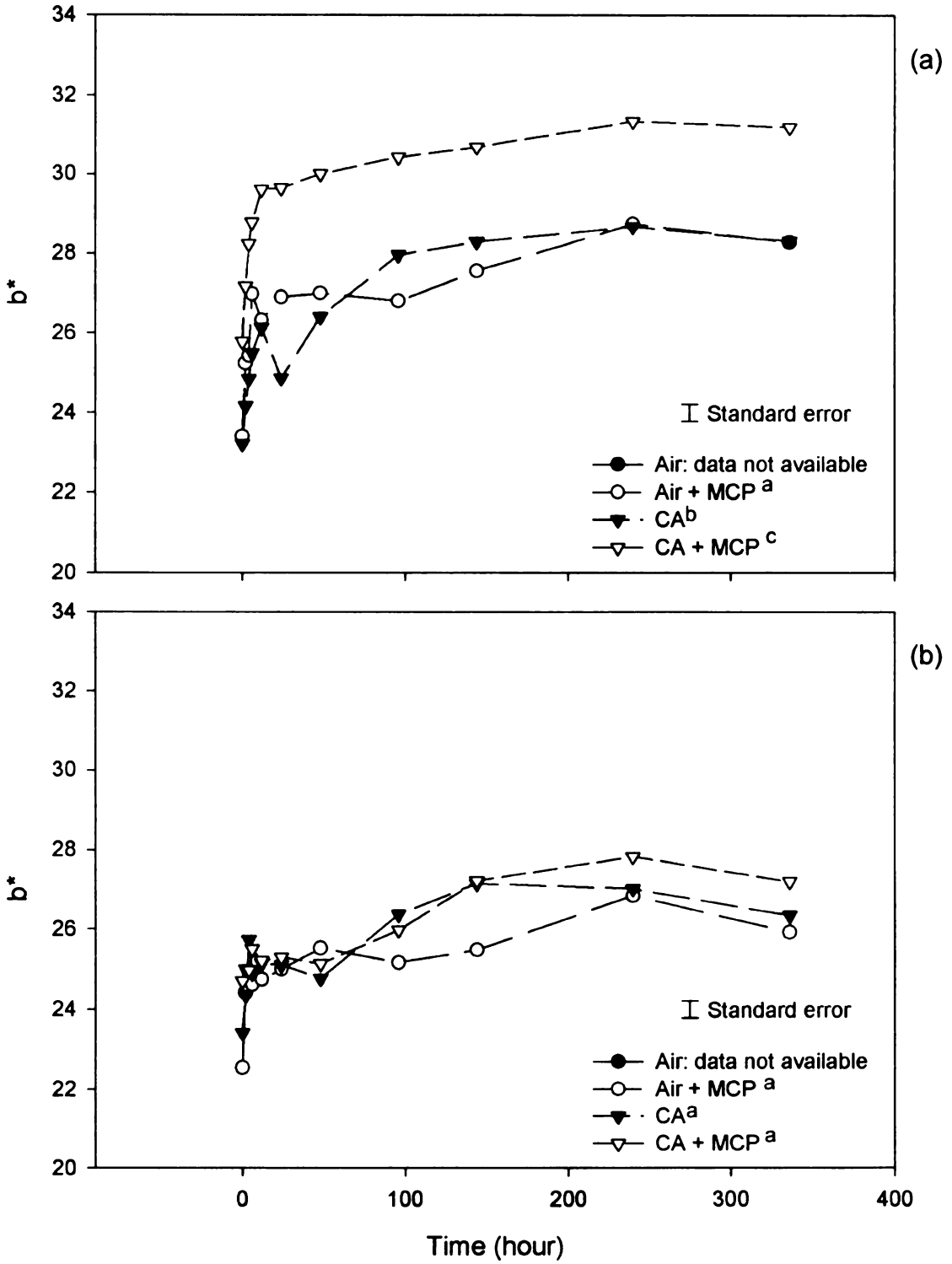

Figure 2.18. Effect of postharvest treatments after 9 months storage on b* value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

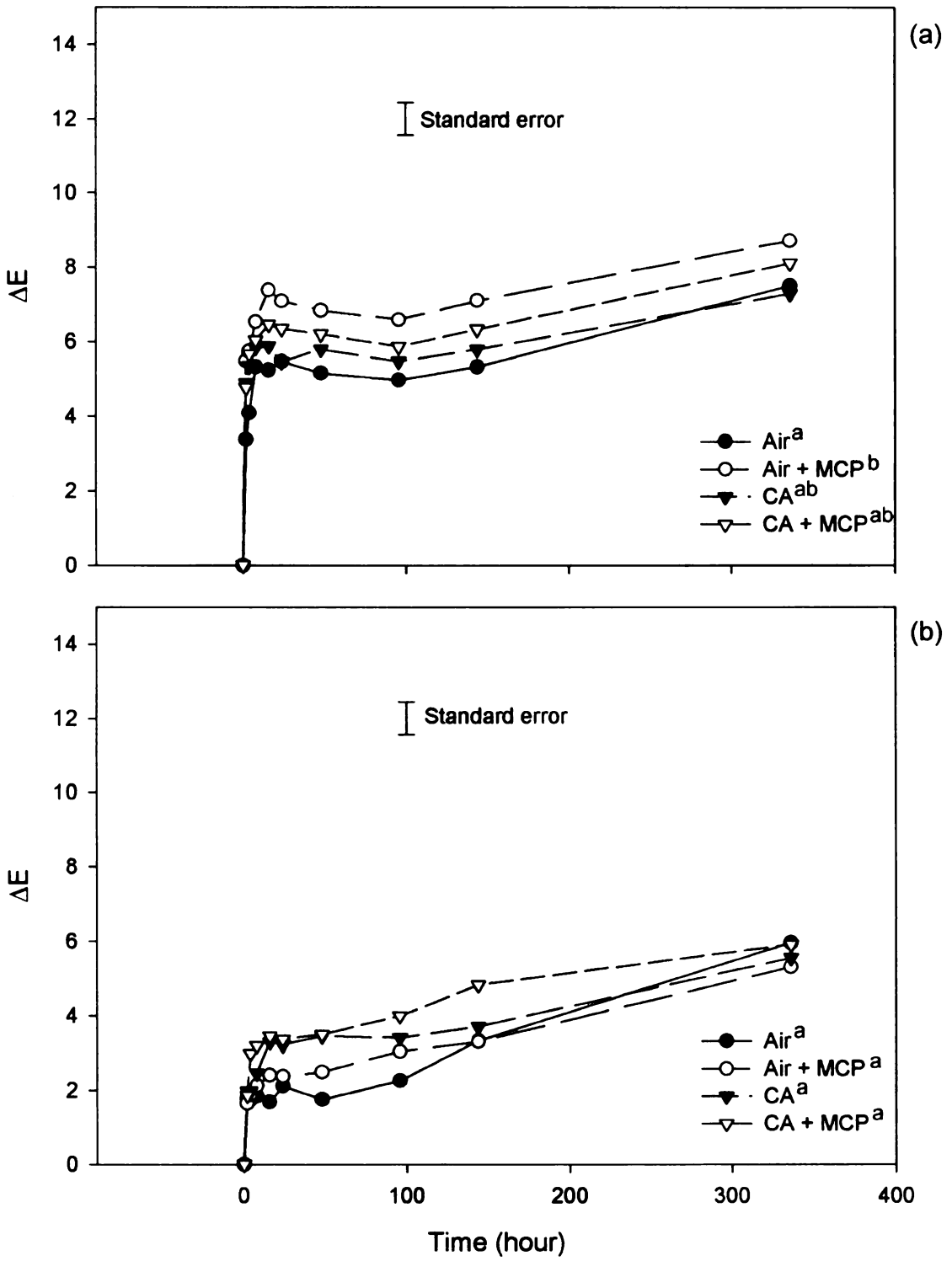

Figure 2.19. Effect of postharvest treatments after 3 months storage on ΔE value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

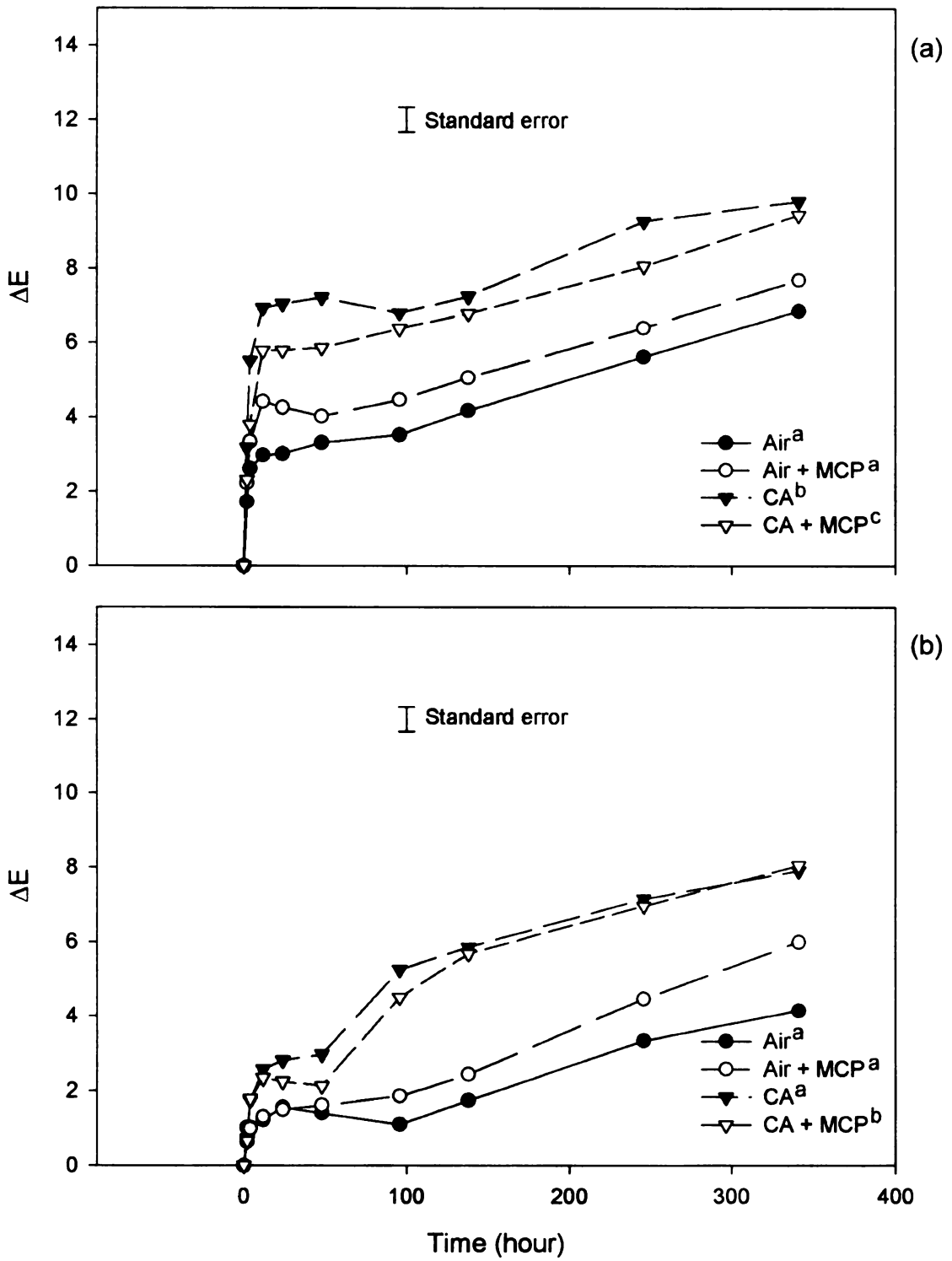

Figure 2.20. Effect of postharvest treatments after 5 months storage on ΔE value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

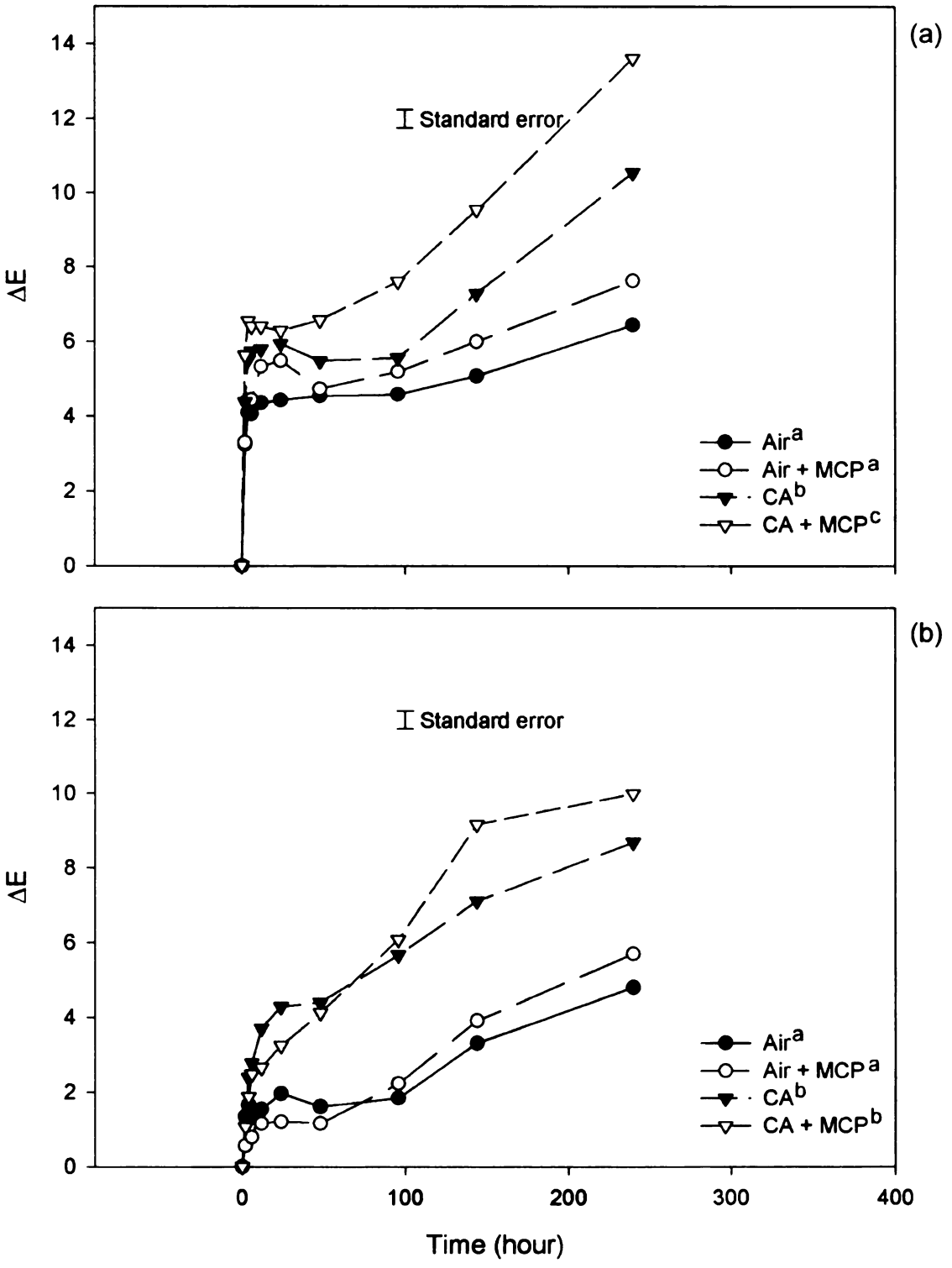

Figure 2.21. Effect of postharvest treatments after 7 months storage on ΔE value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

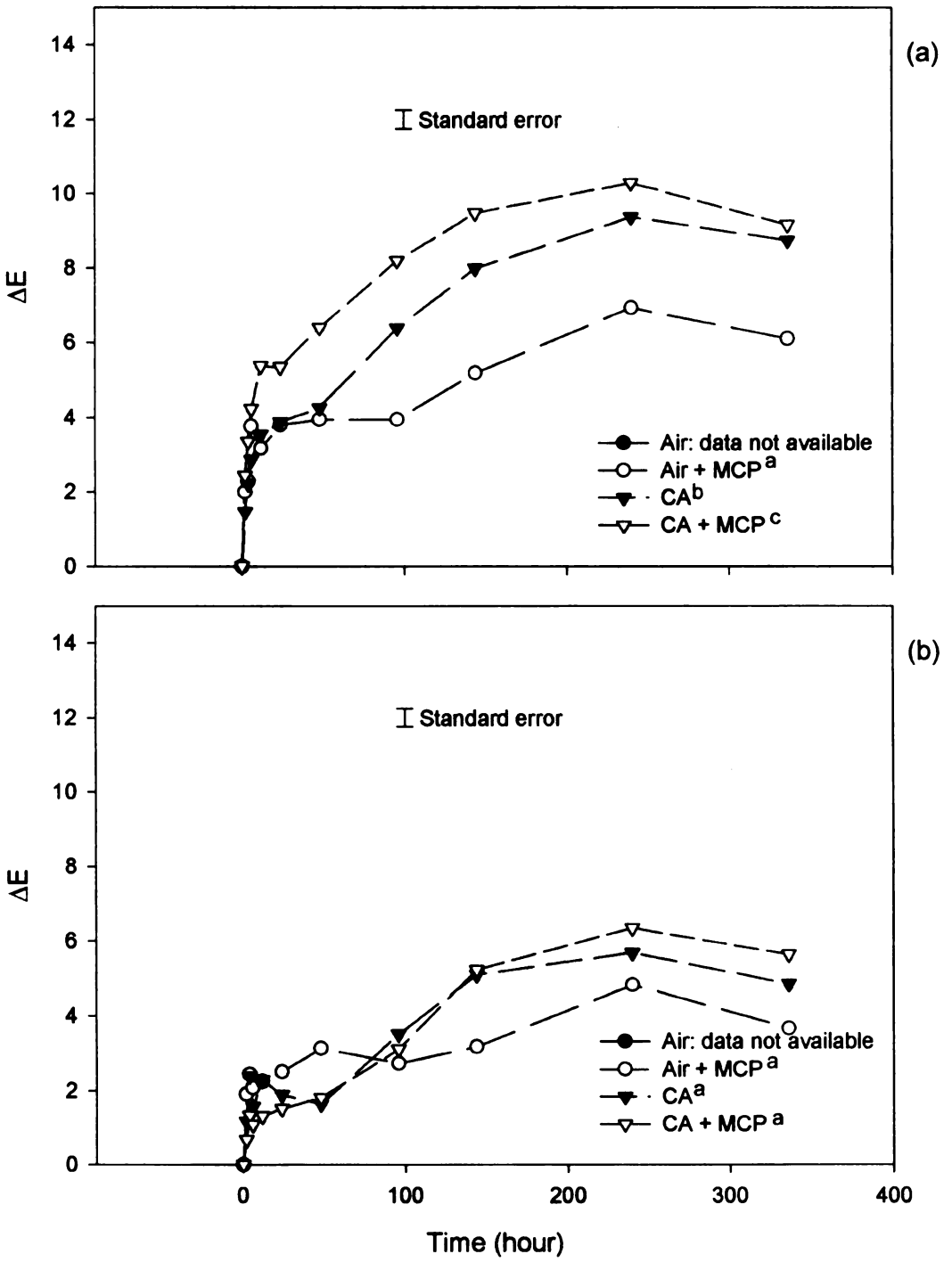

Figure 2.22. Effect of postharvest treatments after 9 months storage on ΔE value of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

The major cause of discoloration on the cut surface was enzymatic browning, particularly during the early stages of the fresh-cut slice holding period. During this period, the rate of color change was very fast and was reduced greatly by the addition of antibrowning agent. During the latter part of the storage, color change occurred at a slower rate and the magnitude of change with and without antibrowning agent was approximately the same. The change in color during this period may have been partly due to enzymatic browning but was probably also affected by desiccation and/or microbial growth.

After 3 months storage, fresh-cut slices from non MCP-treated apples (control and CA) experienced less discoloration than MCP-treated apples (MCP and CA + MCP). This was observed regardless of whether antibrowning agent was used. The effect of MCP on L*, a*, and ΔE values was less for slices receiving antibrowning agent.

For apples stored for 5 months, fresh-cut slices with antibrowning agent which showed the least to the most discoloration were as follows: control, then air + MCP and CA + MCP. The slices with the most discoloration were those from CA apples. This was also observed in slices without antibrowning agent, except that the flesh colors of slices from control and MCP apples were not significantly different.

For apples stored for 7 months, slices from control apples experienced the least discoloration, then air + MCP and CA. The slices with the most browning. were from CA + MCP apples. This trend was noticed in slices with and without

antibrowning agent but the difference for apple receiving antibrowning agent was much less.

After 9 months storage of whole apples, slices with antibrowning agent that suffered the least to the most discoloration were slices from air + MCP < CA < CA + MCP. For slices without antibrowning agent, the trend was the same, but no significant differences were detected between treatments.

Overall, slices from apples in CA storage (MCP-treated and non-MCP-treated) were more susceptible to discoloration than slices from apples in air storage except for apples from 3 months storage. Control apples yielded slices that were the least susceptible to discoloration. For apples from 3 months storage, MCP-treated apples in air and CA storage were more susceptible than non MCP-treated apples in the same storage condition.

In general, slices from more ripe fruit underwent less color change than fruit that received postharvest treatments that reduced ripening. This agrees with Lozano (1994) who found that overripe 'Golden Delicious' apples underwent the least discoloration when compared to green and mature apples, which had lower IEC (Lozano and others 1994). Vamos-Vigyazo et al. (1985) observed a 65% reduction in enzymatic browning after 6 months in storage, where the IEC of apples increased (Vamos-Vigyazo and others 1985). The lower browning may be attributed to the reduced PPO activity and total phenolic content in the apples during ripening. This was found to be the case for 'Golden Delicious' and 'Aumburi' pulp whose PPO activity and total phenolic content were reduced by 50% and 10%, respectively, as the apples fully ripened (Prabha and Patwardhan

1985). Apples in CA storage were more susceptible to browning than apples in air storage upon cutting into slices. This was also found in fresh-cut 'Gala' after 3 month in 1.4% CO_2 and 3% O_2 for both slices treated with and without antibrowning agent (Beaulieu and Baldwin 2002).

Slices from CA storage and MCP treatment were more susceptible to enzymatic browning because they were less ripe than apples from air storage. They were also firmer; therefore, more cellwall may have been broken during apple slice preparation. Greater discoloration in slices from MCP-treated apples was found in fresh-cut 'Gala' but the authors attributed the discoloration to microbial spoilage (Perera and others 2003). Contradictory results were found in fresh-cut 'Bareburn' from MCP-treated apples, whose flesh color was not affected by MCP treatment (Bai and others 2004). This may be a result of the use of an antibrowning agent and good low temperature maintenance, which could greatly inhibit enzymatic browning.

2.3.3 The effect of postharvest condition on texture of fresh-cut apples

CA and MCP treatment, individually and in combination, improved the firmness of intact apples prior to processing. The length of time slices were held at 5°C did not significantly affect the firmness (Figure 2.23 – 2.26). This result agrees with that of fresh-cut slices from other cultivars (Calderon-Lopez and others 2005). The results of statistical analysis are presented in Appendix B. Apple slice firmness showed the same trend as the intact apple firmness, but the difference between treatments was more pronounced in the slices.

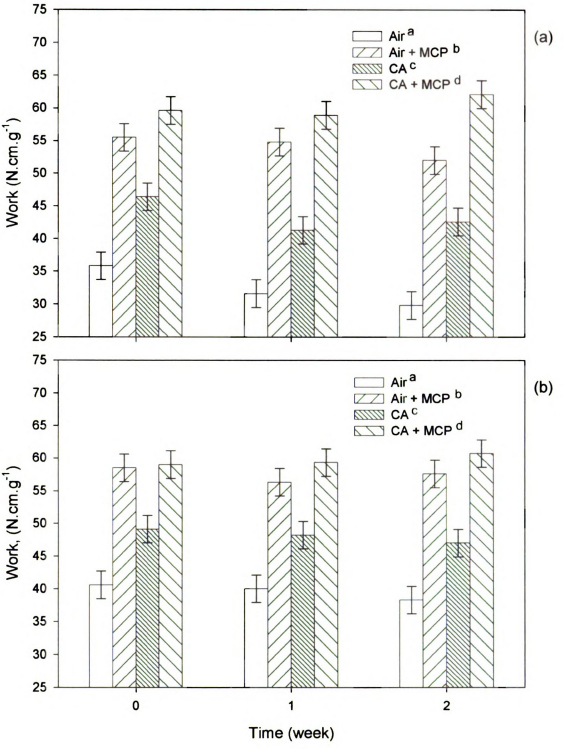

Figure 2.23. Effect of postharvest treatments after 3 months storage on the texture of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). Error bars are ± standard errors. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

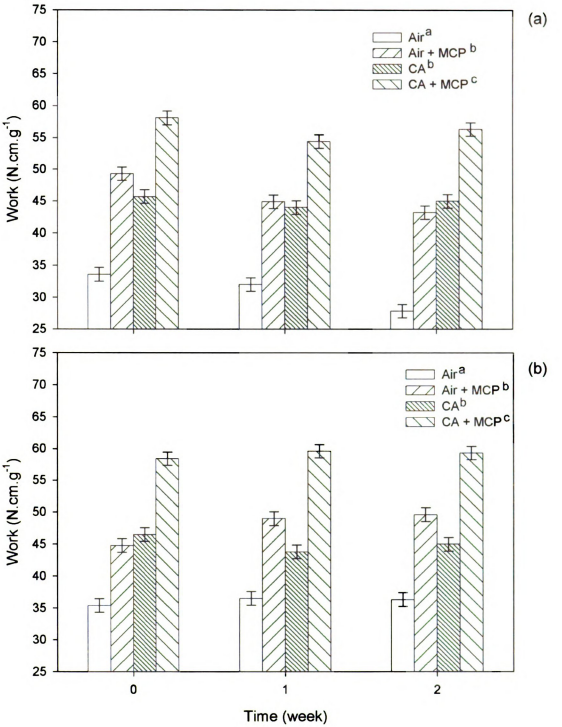

Figure 2.24. Effect of postharvest treatments after 5 months storage on the texture of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). Error bars are ± standard errors. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

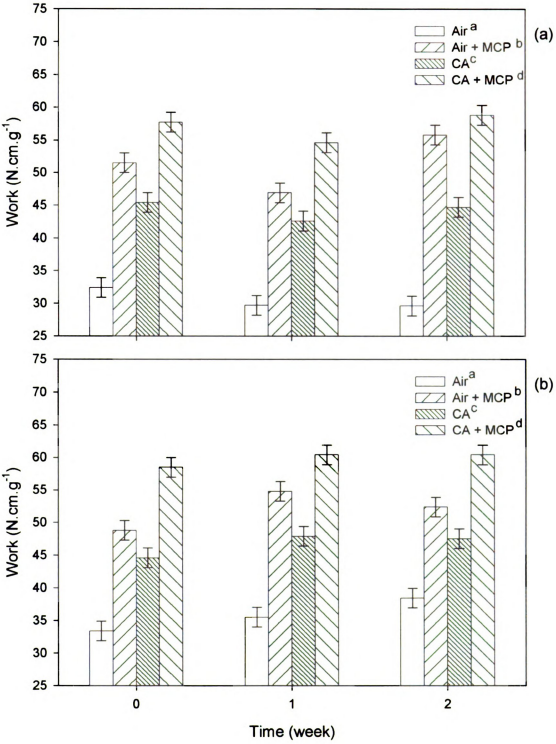

Figure 2.25. Effect of postharvest treatments after 7 months storage on the texture of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). Error bars are ± standard errors. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

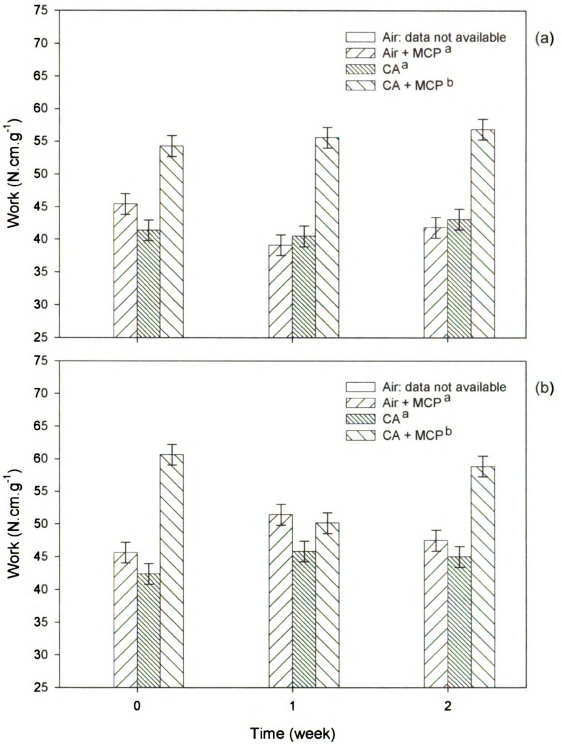

Figure 2.26. Effect of postharvest treatments after 3 months storage on the texture of flesh of apple slices without antibrowning agent (a) and with antibrowning agent (b) during the holding period at 5°C (n=4). Error bars are ± standard errors. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

Slices from MCP-treated apples had greater firmness than slices from non MCP-treated apples. This agrees with the results for firmness of whole fruit following MCP treatment of 'Bareburn,' 'Pacific Rose,' (Perera and others 2003) 'Gala,' (Bai and others 2004) 'Golden Delicious,' (Jiang and Joyce 2002) 'Empire,' 'Delicious,' 'Idared,' 'Mutsu,' and 'Law Rome' (Calderon-Lopez and others 2005).

Comparison between individual postharvest treatments showed that slices from MCP apples had better texture than CA apples up to 7 months storage. Slices from MCP and CA apples taken from 9 month storage had similar firmness although the IEC of intact MCP apples was much higher. The combination of MCP and CA storage had an additive effect in preserving the texture of apples. Slices from CA + MCP apples had greater firmness than slices from other apples. In addition to the postharvest treatments, the antibrowning agent also affected the texture. A significant difference was found only for slices with low firmness. These slices also had the least enzymatic browning at the cut surface. The effect of the antibrowning agent on firmness may be attributed to its calcium content. This was also previously observed in fresh-cut 'Golden Delicious' slices because calcium can prevent the softening process (Lee and Smith 1995).

2.3.4 The effect of postharvest condition on volatiles of fresh-cut apples

Hexyl Acetate

Hexyl acetate is a compound that contributes to the aroma of apples and, after 5, 7 and 9 months storage, it had the highest concentration among compounds detected in the package headspace of fresh-cut 'Jonagold' apples.

In addition, hexyl acetate is responsible for fruity flavor of apples. Because of these results, hexyl acetate was selected as the target compound. The area response from GC-MS chromatograms of hexyl acetate (HA) are presented in Figure 2.27 – 2.30 for fresh-cut slices from apples that had been stored for 3, 5, 7, and 9 months, respectively. The statistical analyses are presented in Appendix B. The results show that, during the 14 day shelf life of fresh-cut slices, HA increased after 1 week. It then either leveled off or declined during the second week of the holding period. This agrees with the volatiles results for 'Gala' slices (Bett and others 2000). The effect of postharvest treatment depended on the storage time of the intact apples. For 3 and 5 months storage, the effect of MCP treatment and CA storage was not clear. For 3 months storage, the HA concentration in the package headspace of slices from air + MCP, CA, CA + MCP apples were the same at both 0 and 1 week shelf life. This concentration was lower than that of slices from control apples at 0 week but the same at 1 week shelf life. At 5 months storage, no postharvest treatment or time in the holding period effect on the concentration of HA in the headspace except for fresh-cut slices from CA storage, where the HA concentration increased during the first week but fell back to the same level the second week.

For intact apples stored for 7 and 9 months, postharvest treatments had greater effect on the HA content than at 3 and 5 months storage. At 7 months, slices from apples in CA storage (both MCP and non-MCP-treated) produced more HA than those from apples in normal air storage. The concentration of HA in the headspace was relatively constant during the 14 days holding period

except for CA + MCP apples, whose HA concentration slightly declined. At 9 months storage, MCP-treated apples in air had a greater HA concentration. The concentration increased slightly during the first week storage but decreased during the second week. Fresh-cut slices from CA apples had a high concentration initially, but the concentration decreased to the same level as that of slices from CA + MCP apples.

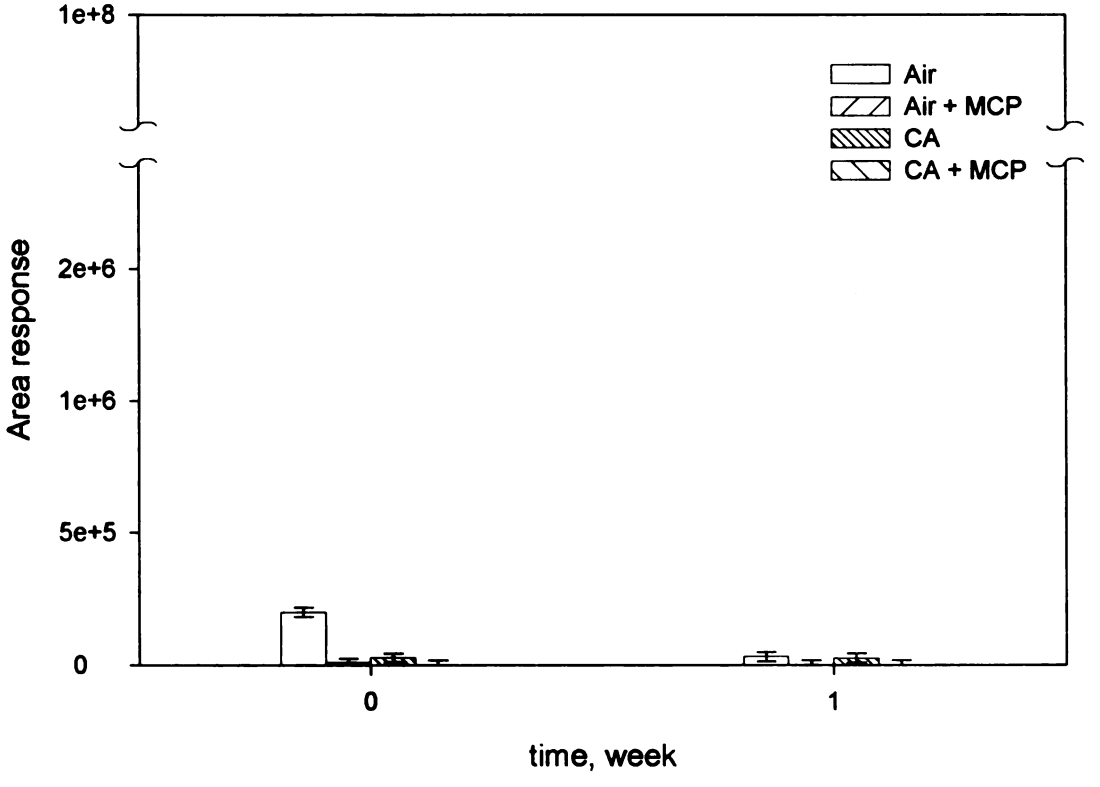

Figure 2.27. Effect of postharvest treatments after 3 months storage on area response from GC-MS of hexyl acetate in the headspace of apple slice packages during the holding period at 3°C (n=4). Error bars are ±standard error. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

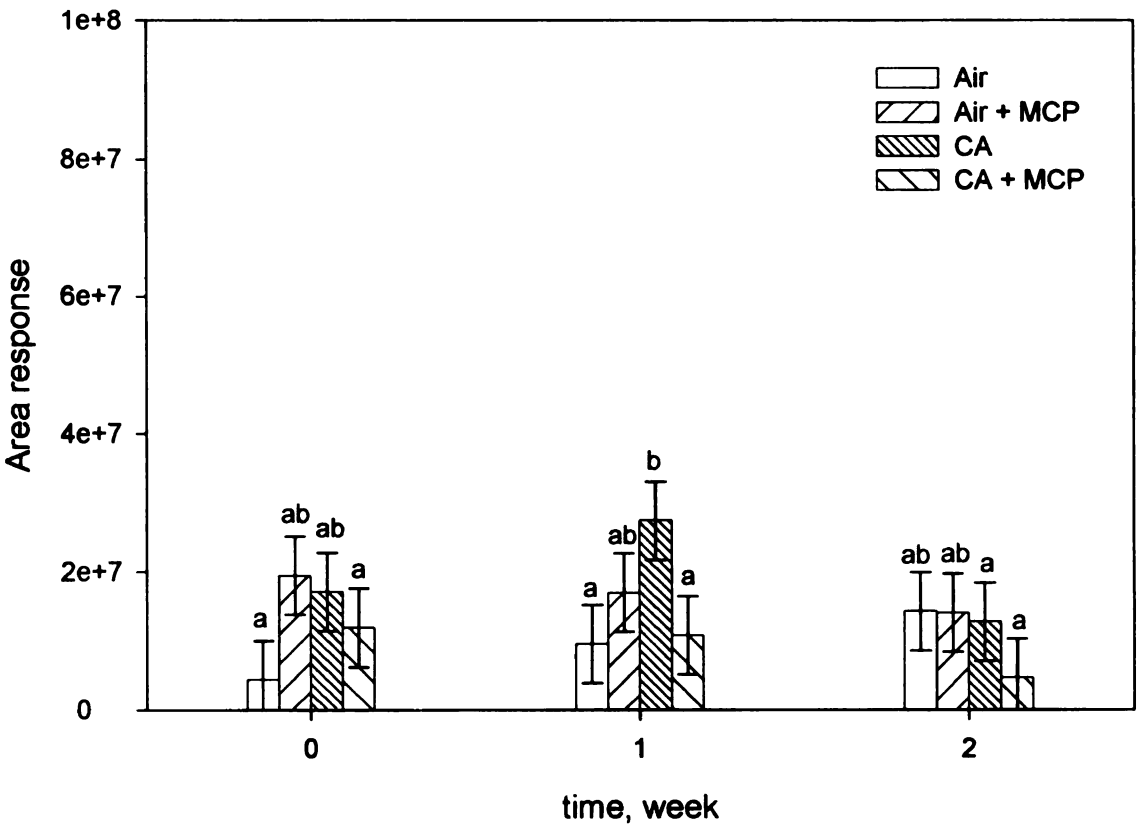

Figure 2.28. Effect of postharvest treatments after 5 months storage on area response from GC-MS of hexyl acetate in the headspace of apple slice packages during the holding period at 3°C (n=4). Error bars are ±standard error. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

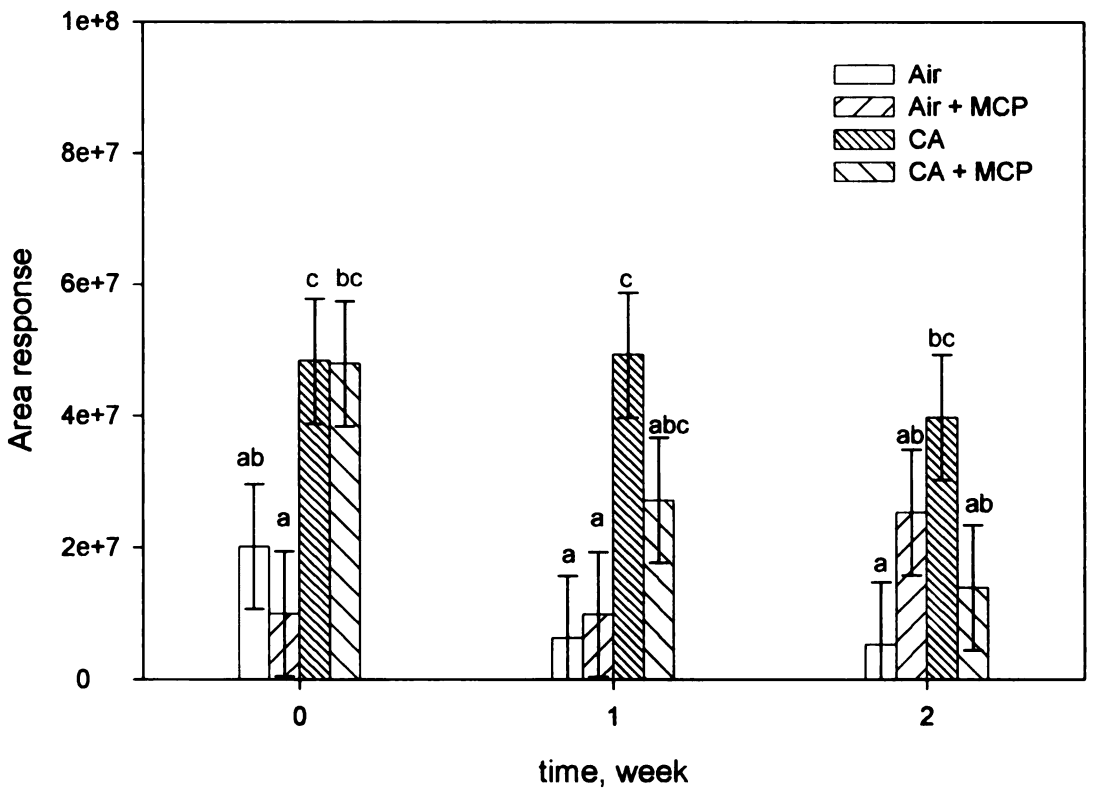

Figure 2.29. Effect of postharvest treatments after 7 months storage on area response from GC-MS of hexyl acetate in the headspace of apple slice packages during the holding period at 3°C (n=4). Error bars are ±standard error. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

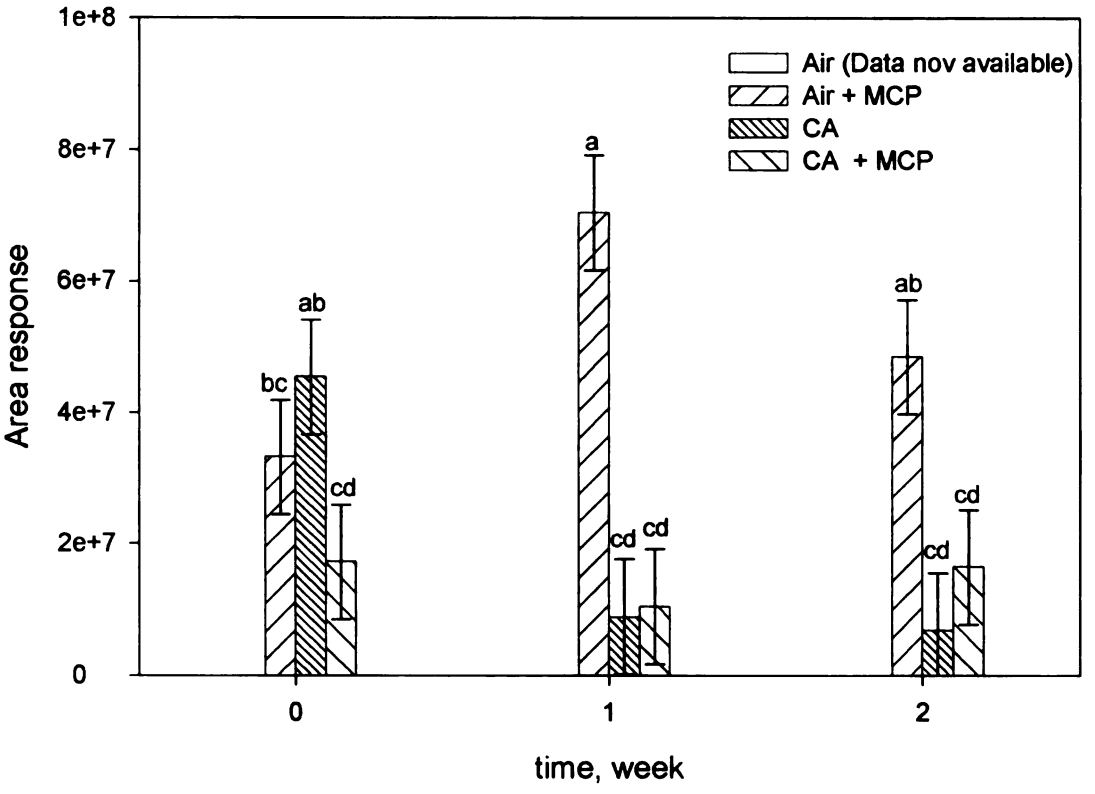

Figure 2.30. Effect of postharvest treatments after 9 months storage on area response from GC-MS of hexyl acetate in the headspace of apple slice packages during the holding period at 3°C (n=4). Error bars are ±standard error. The same letter indicates no significant difference between postharvest treatments (p-value > 0.05).

Total volatiles

The total volatiles generated from fresh-cut slices were analyzed using the electronic nose. This instrument utilizes an array of sensors with partial specificity and an appropriate pattern recognition system to analyze the volatile profile without separating volatiles into individual components. Electronic nose responses together with multivariate analysis has the potential to differentiate aroma from produce of different cultivars, of differing maturity, harvest date and defects (Young and others 1999; Echeverria and others 2004; Saevels and others 2004; Berna and others 2005; Tan and others 2005).

Optimized electronic nose sensor responses were analyzed using principle component analysis (PCA) and canonical discriminant analysis (CDA). PCA, an unsupervised learning technique, analyzes a set of data without their corresponding descriptors (Gardner and Bartlett 1992) to identify a set of variables called principle components (PC) that can explain all or nearly all of the total data variation. CDA is a supervised learning technique that analyzes a set of data, for which descriptors are known, to identify the factor that can be used to distinguish the predefined groups (Silver and Stam 1994).

Figure 3.21 – 3.28 are the PCA and CDA plots of data for slices at 0 and 14 days after processing from apples subjected to postharvest treatment that has been stored for 3, 5, 7 and 9 months. For all 4 storage times, the combination of the first and second principal component (PC1 and PC2) was able to explain more than 95% of the total variation in data. The combination of the first and

second discriminant functions (DF1 and DF2) was able to explain more than 95% of the variation between postharvest treatments.

For slices from 3 month storage apples at 0 week holding period (Figure 2.31a), the response from control and CA + MCP apples clustered within its own group while the data from MCP and CA apples clustered together. According to the distance between each cluster, the volatiles from MCP and CA apples were more similar to the volatiles from CA + MCP apples than to those from control apples. From CDA, DF1 accounted for the variation between slices from the combination of CA + MCP and the rest. DF2 were accounted for the variation between slices from the control apple slices and CA or MCP apple slices. After the slices had been held for 17 days (Figure 2.32), electronic nose responses to all postharvest treatment clustered within its own group.

After 5 months storage of intact apples (Figure 2.33-2.34), the headspace volatile of CA + MCP apples were completely separated from the other postharvest treatments by PC1 and DF1. This was observed at both 0 and 14 days apple slice holding period. The control, air + MCP, and CA apple partially clustered together at 0 day holding period along PC2 and DF2. They totally clustered together at 14 day holding period.

For intact apples stored for 7 months, slices from the individual treatment (MCP or CA storage) apples were similar but differentiable in PC2. At 0 weeks, the enose response from this group showed a clear difference from the volatile from the control and CA + MCP (Figure 2.35a). After 2 weeks in storage, the enose response from individual treatment with MCP and CA storage clustered

together more (Figure 2.35b). This group could be separated from CA + MCP apple slices by PC1 and DF1 and could be separated from control apple by PC2 and DF1.

After 9 months storage, the volatiles profiles in the slices from all apples receiving postharvest treatment were clearly distinguishable on both PCA and CDA plots (Figure 2.37-2.38). The enose response from MCP treated apples and CA storage apples were more similar at 0 week storage than the response from apples receiving the combination treatment of MCP and CA storage. MCP and CA storage influences were less pronounced after a 2-week holding period of apple slices. Each group, however, was still separated from each other and the separation could mostly be explained by PC1 and DF1.

The difference between enose response after 2 week storage for the different treatments was less than the difference at the beginning of the holding period. For most of the intact apple storage time, the enose responses from control apple slices and CA + MCP were differentiable from slices from MCP and/or CA storage. This is because MCP treatment and CA storage reduced apples volatile production(Plotto and others 2000; Lurie and others 2002; Perera and others 2003; Tay and Perera 2004; Mattheis and others 2001). Fresh-cut slices from MCP and CA apples had similar overall production of volatiles up to 7 months storage of intact apples. At 9 month storage, the IEC of air + MCP increased tremendously resulting in a greater difference in enose response between Air + MCP and CA apples. The combination of MCP treatment and CA storage had greater effect in slowing down ripening process, thus, the combined

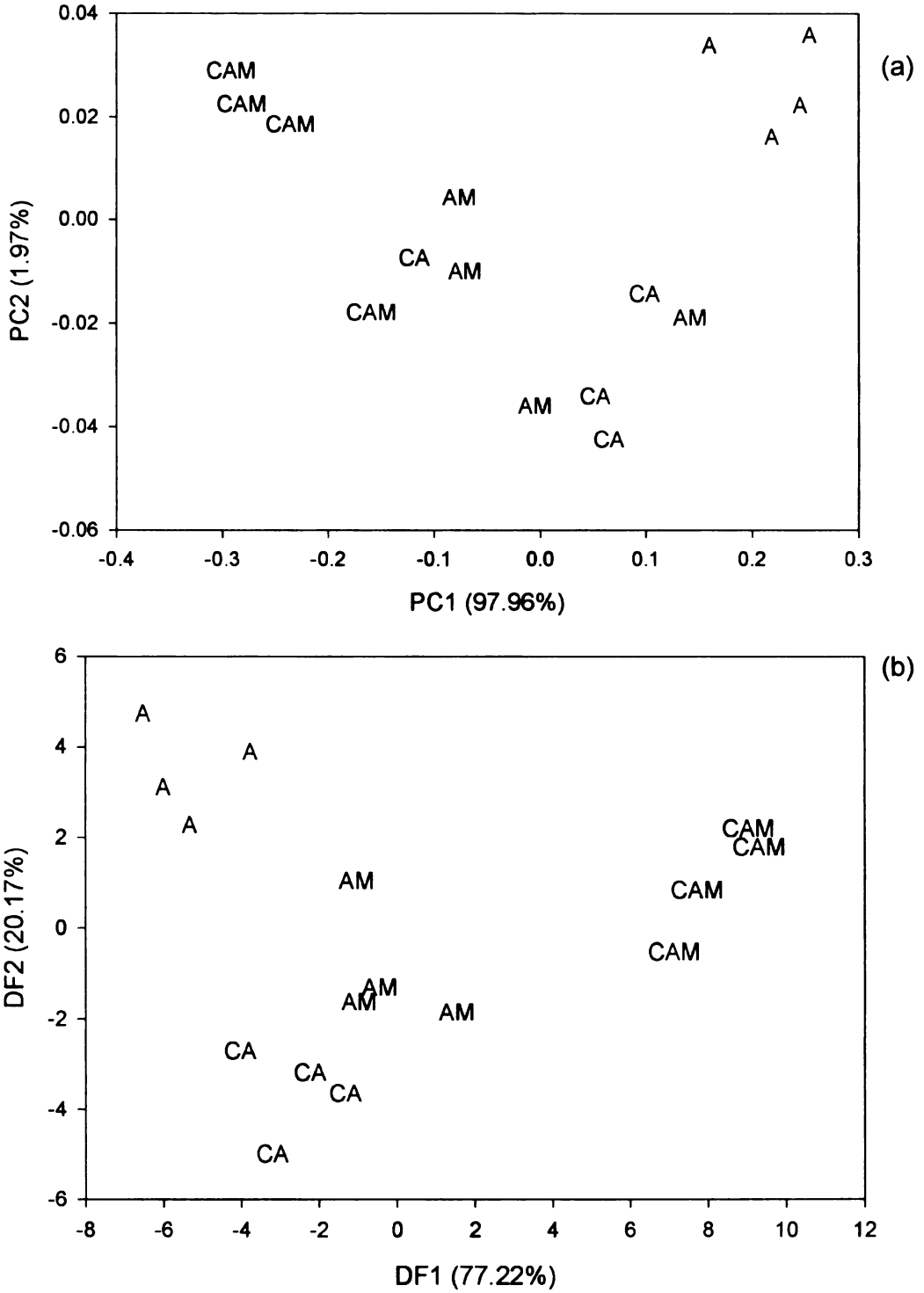

Figure 2.31. Principal component analysis (a) and canonical discriminant analysis (b) of 0 week holding period of slices from intact apple stored for 3 months subjected to the following postharvest treatments: Air storage or control (A), MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

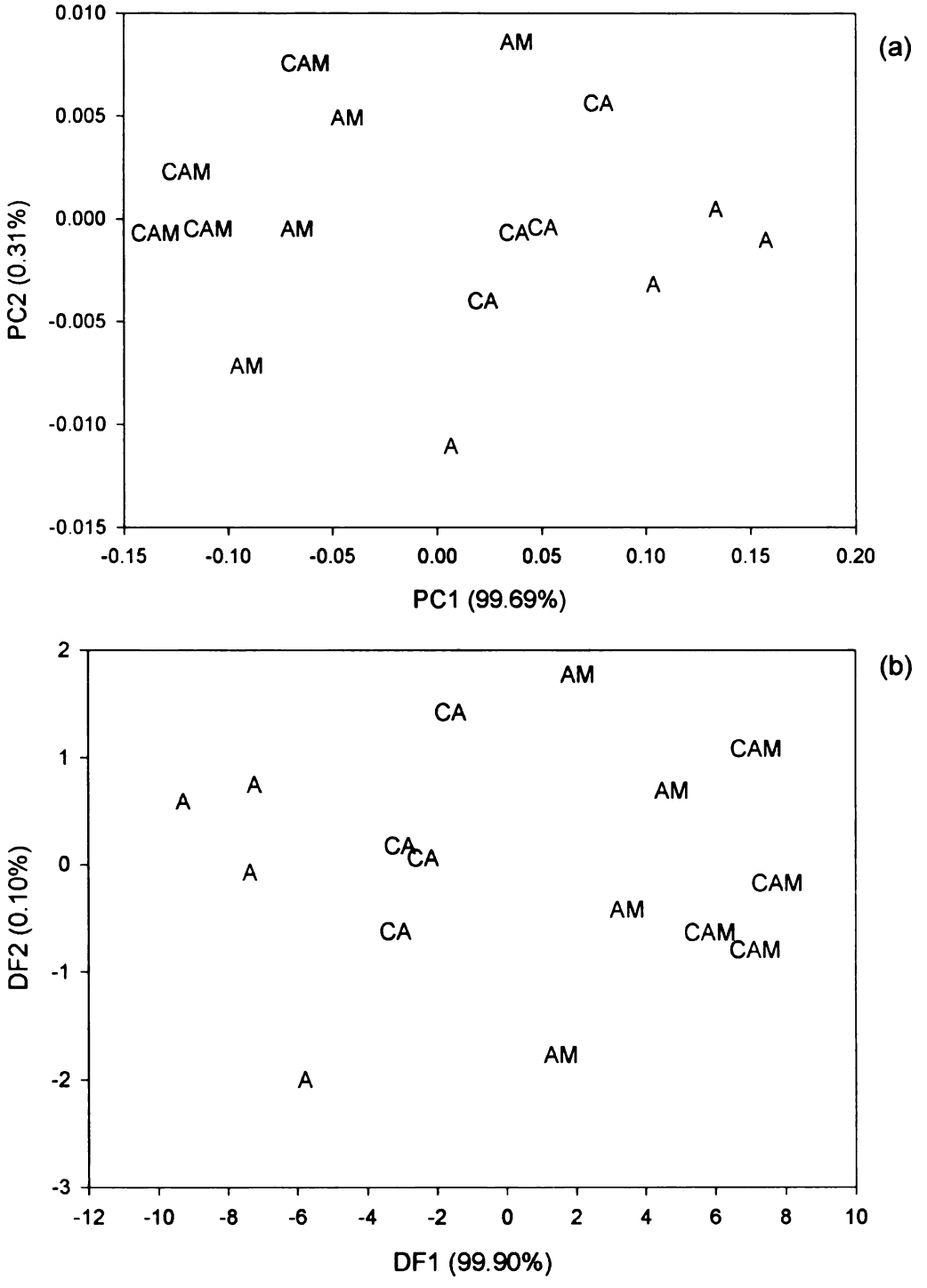

Figure 2.32. Principal component analysis (a) and canonical discriminant analysis (b) of 2 week holding period of slices from intact apple stored for 3 months subjected to the following postharvest treatments: Air storage or control (A), MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

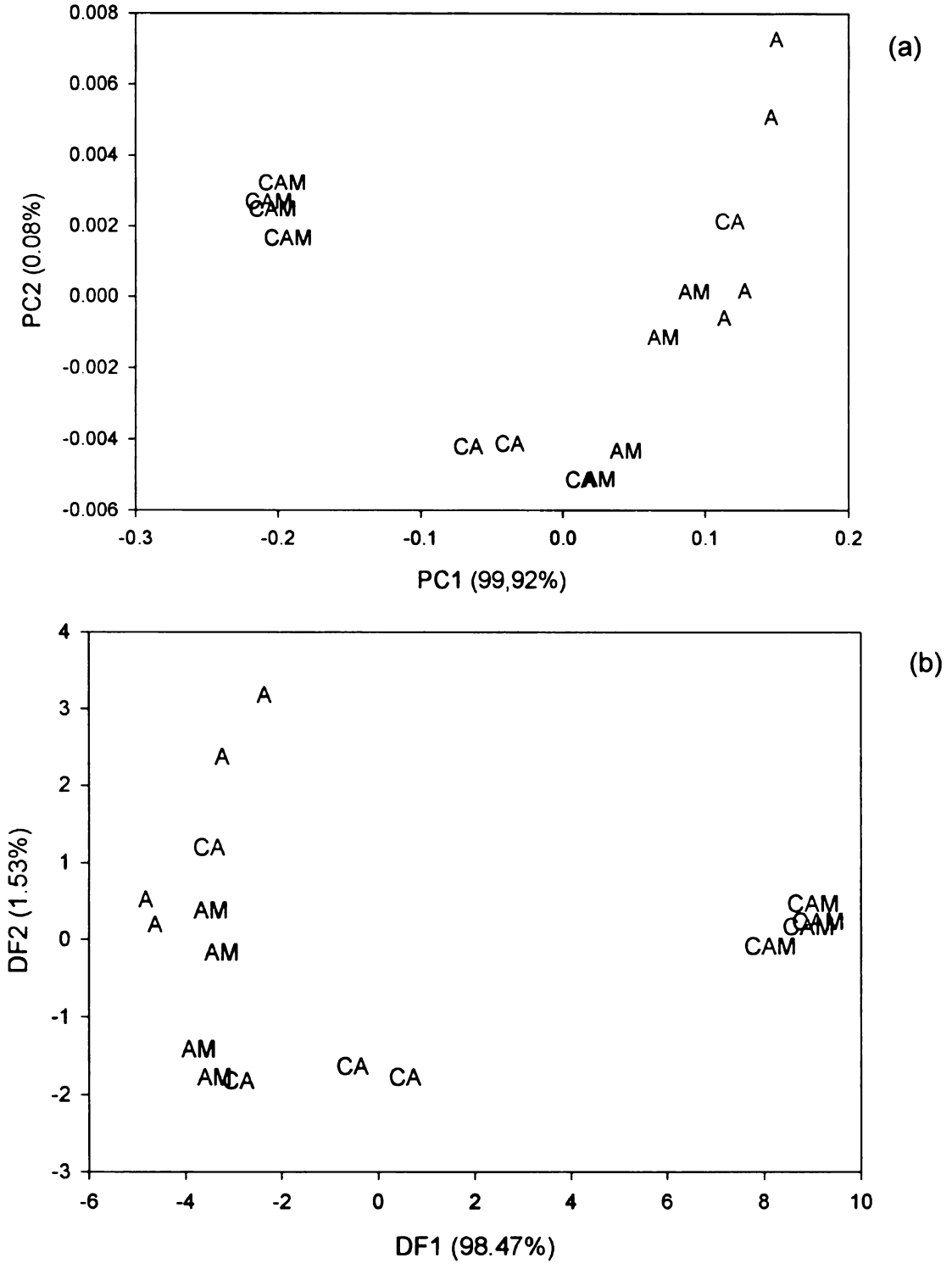

Figure 2.33. Principal component analysis (a) and canonical discriminant analysis (b) of 0 week holding period of slices from intact apple stored for 5 months subjected to the following postharvest treatments: Air storage or control (A), MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

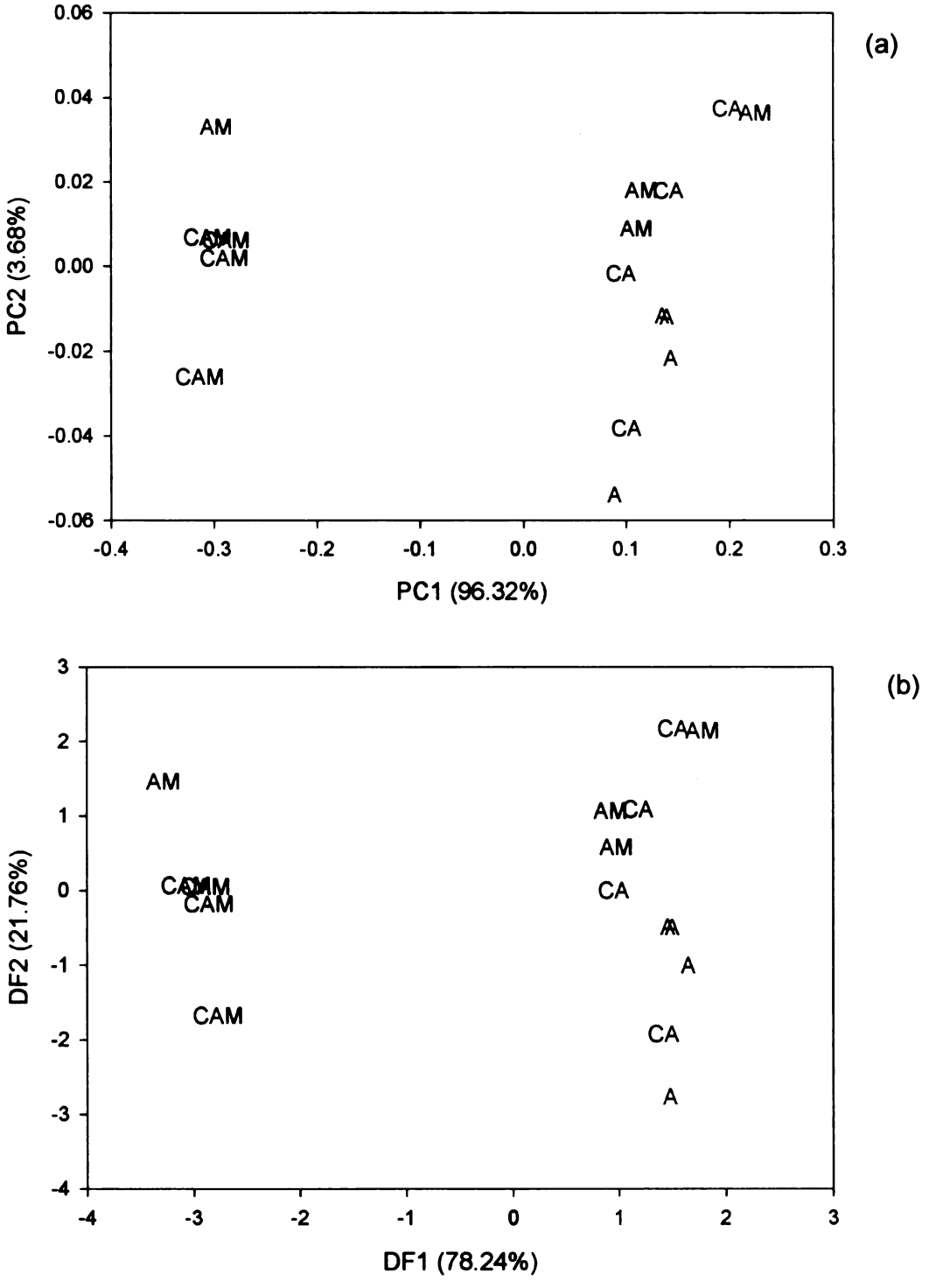

Figure 2.34. Principal component analysis (a) and canonical discriminant analysis (b) of 2 week holding period of slices from intact apple stored for 5 months subjected to the following postharvest treatments: Air storage or control (A), MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

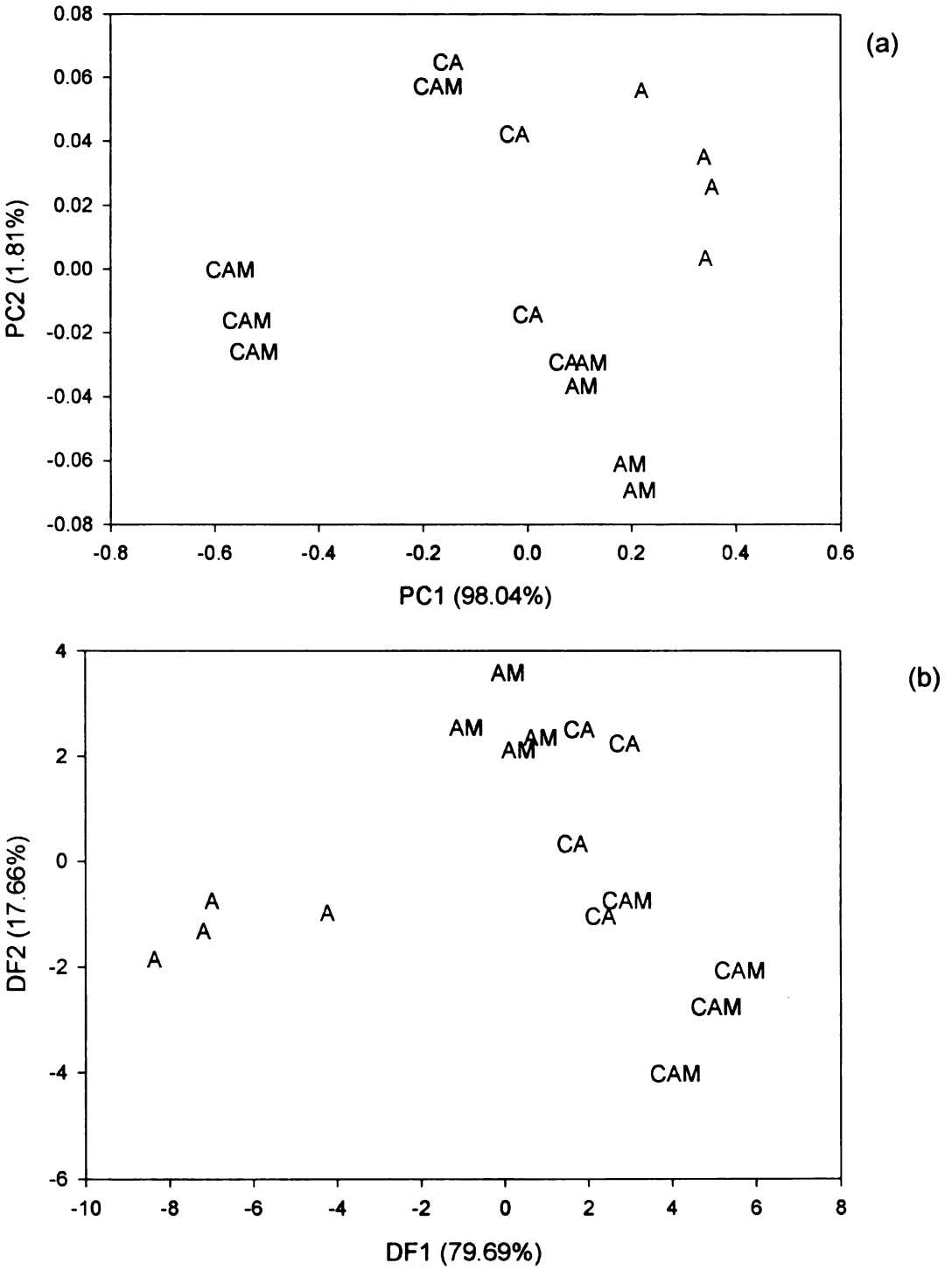

Figure 2.35. Principal component analysis (a) and canonical discriminant analysis (b) of 0 week holding period of slices from intact apple stored for 7 months subjected to the following postharvest treatments: Air storage or control (A), MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

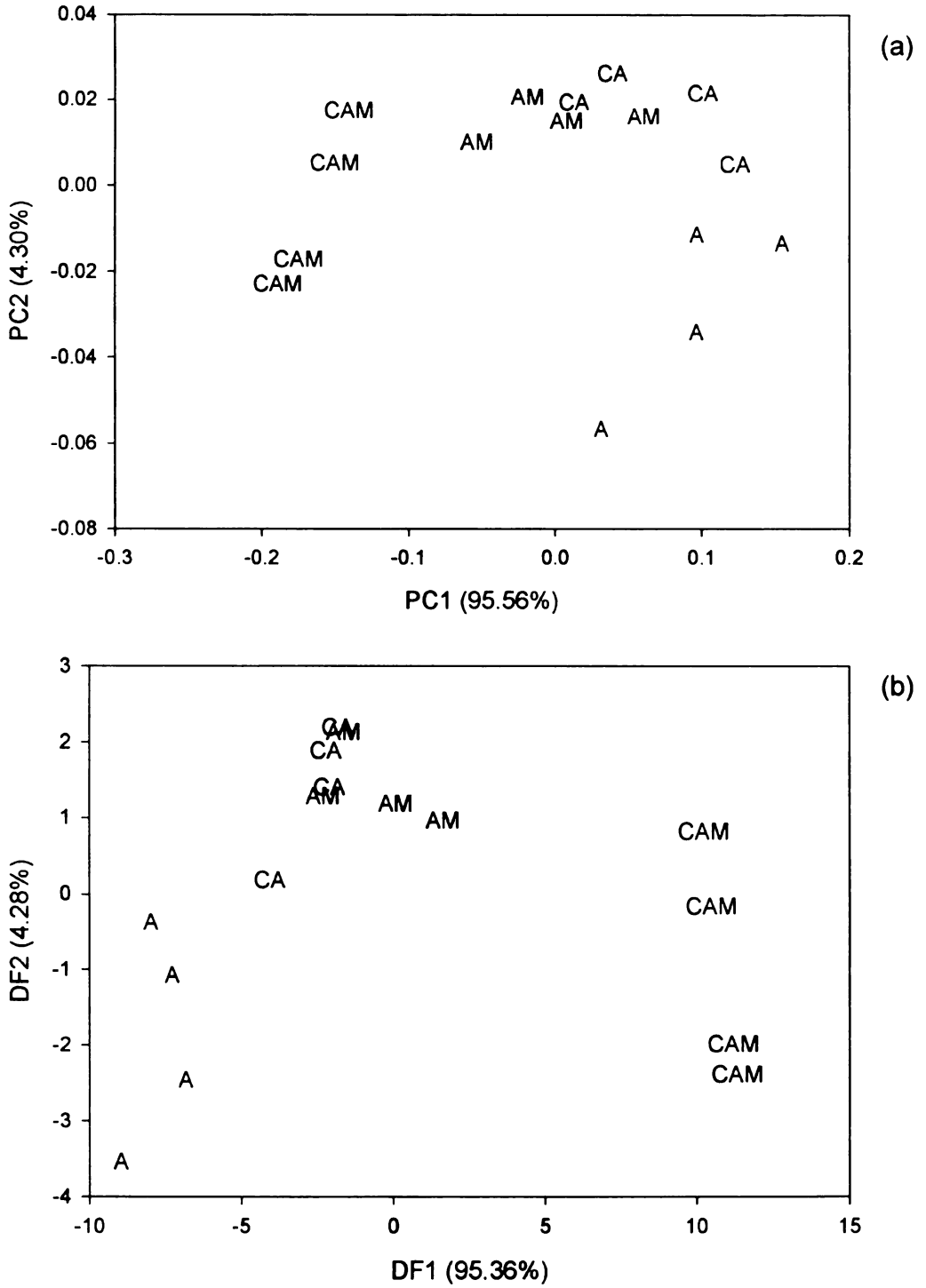

Figure 2.36. Principal component analysis (a) and canonical discriminant analysis (b) of 2 week holding period of slices from intact apple stored for 7 months subjected to the following postharvest treatments: Air storage or control (A), MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

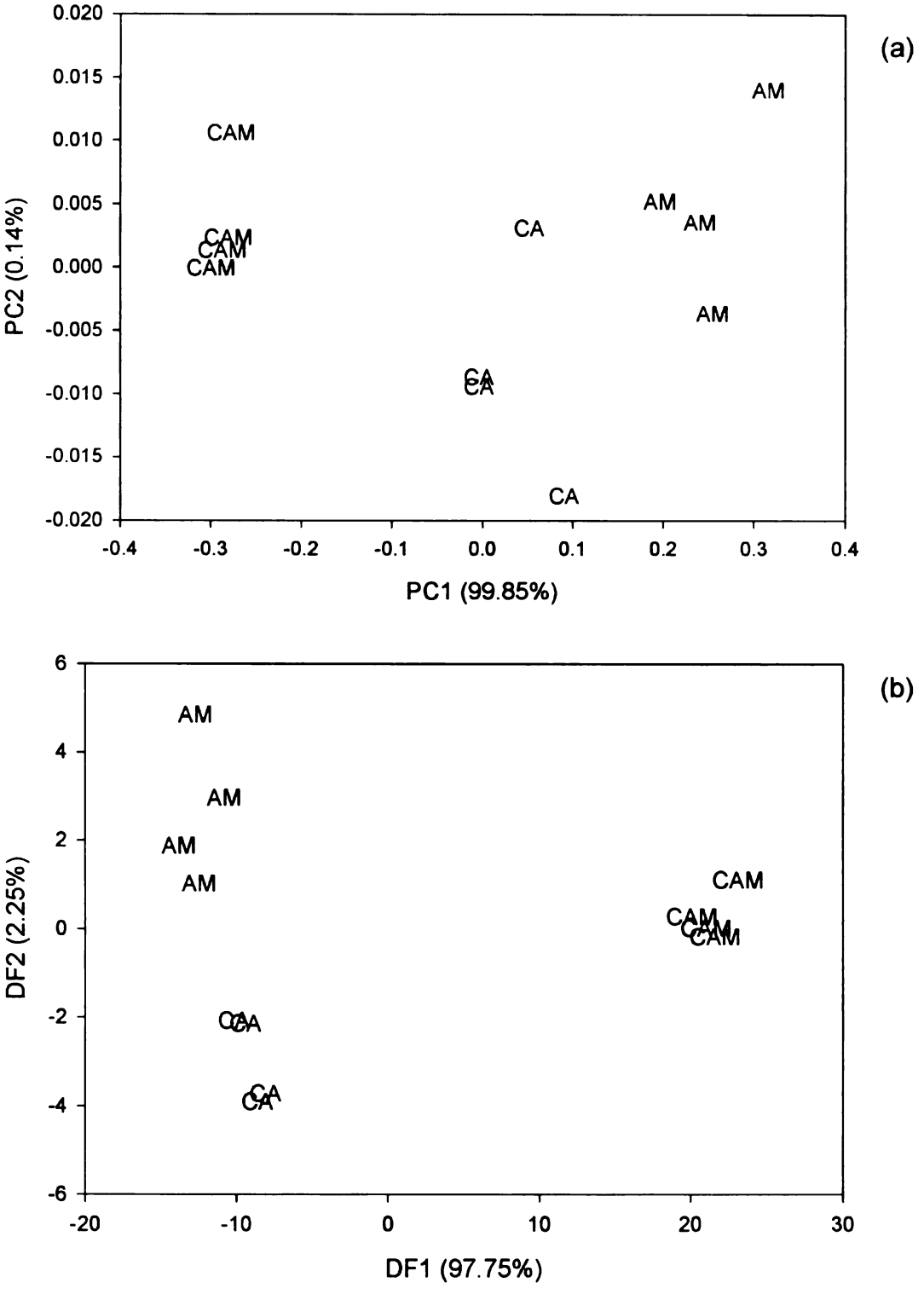

Figure 2.37. Principal component analysis (a) and canonical discriminant analysis (b) of 0 week holding period of slices from intact apple stored for 9 months subjected to the following postharvest treatments: MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

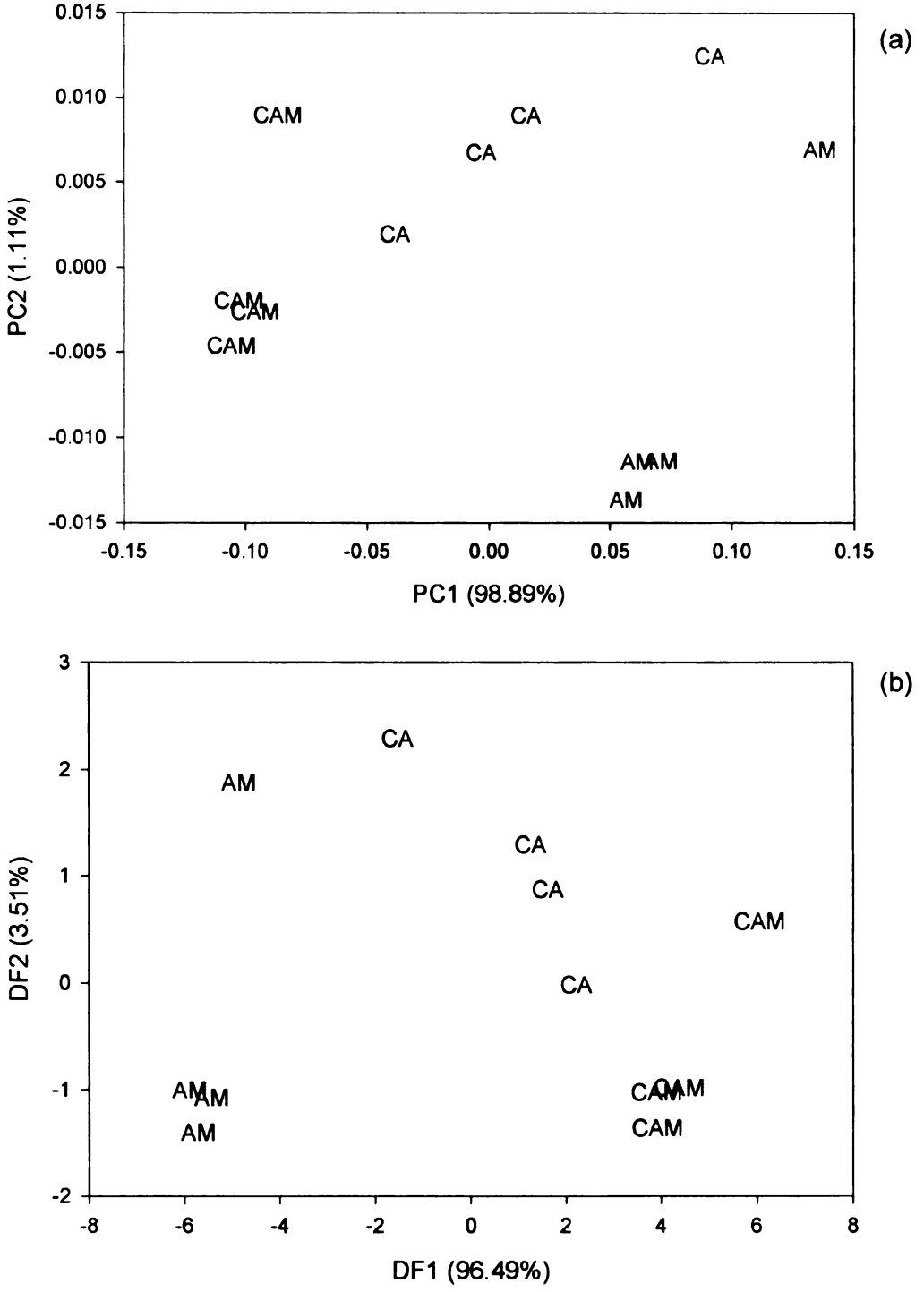

Figure 2.38. Principal component analysis (a) and canonical discriminant analysis (b) of 2 week holding period of slices from intact apple stored for 9 months subjected to the following postharvest treatments: MCP treatment (AM), CA storage (CA) and MCP treatment + CA storage (CAM).

The combined treatment was expected to suppressed volatile production in the intact apples more than each individual treatment does. Therefore, the volatiles production in fresh-cut slices from MCP treated apples in CA storage was different from apples receiving only one of the individual treatments.

2.4 Summary and Conclusion

MCP treatment and CA storage, individually or in combination, impacted the quality of intact 'Jonagold' apples as well as the subsequent quality of fresh-cut apple slices. Either MCP treatment or CA storage suppressed ethylene production similarly up to 7 months. After that ethylene production in MCP treated apples increased while that of CA apples remained suppressed. None of the postharvest treatments adversely affected the flesh color of apples at the time of slice preparation.

The subsequent quality of fresh-cut slices was affected by the postharvest treatments. Apples subjected to postharvest treatment (MCP, CA, CA + MCP) were more susceptible to enzymatic browning due to their immaturity. The firmness of fresh-cut slices depends solely on the firmness of apples at the time of processing, which was influenced by postharvest treatment. The use of antibrowning agent significantly reduced flesh discoloration and. The effect of antibrowning agent was observed only for slices with very low firmness. The electronic nose response to the volatiles of the slices from MCP apples and CA apples was very similar. These responses were differentiable from CA + MCP and control apple slices except for apples stored for 5 months.

Postharvest treatments are a significant contributor to the character of intact apple and the quality of fresh-cut slices. The storage time also interacts with these treatments. At 3 month storage of intact apples, MCP treatment was the best among the three treatments for fresh-cut apple processing. MCP treated apples had the most firmness, while their susceptibility to enzymatic browning and volatile production were similar to the apples in CA storage. At 5-7 month storage, MCP-treated apples and apples in CA storage had similar characteristics and either one of them could be used as the raw material for fresh-cut apples. At 9 months storage, MCP treatment was the most suitable treatment again because the firmness of MCP-treated apples was still greater than the minimum threshold (53.4 N) and they were less susceptible to enzymatic browning than slices from the other apples. The combination treatment of MCP and CA always resulted in apples having more firmness than other apples. However, greater susceptibility to enzymatic browning and the compromised volatile production made it not suitable for fresh-cut apples unless the effective means to prevent enzymatic browning is implemented.

3 DEVELOPMENT OF 1-METHYLCYCLOPROPENE CONTROLLED RELEASE DELIVERY DEVICE

3.1 Introduction

1-Methylcyclopropene (MCP) is a very effective ethylene action inhibitor that maintains quality and extends the shelf life and storage life of several varieties of produce by delaying physico-chemical changes related to the ripening process (Blankenship and Dole 2003). Some varieties of produce that benefit from MCP treatment are apples (Fan and others 1999; Fan and Mattheis 1999; Watkins and others 2000; Baritelle and others 2001; Crouch 2001; Selvarajah and others 2001; DeEll and others 2002; Lurie and others 2002), apricots (Dong and others 2002), avocados (Feng and others 2000; Hofman and others 2001), bananas (Jiang and others 1999; Jiang and others 2001; Mir and Beaudry 2001), broccoli (Ku and Wills 1999; Fan and Mattheis 2000; Gong and Mattheis 2003), coriander (Jiang and others 2002), custard apples (Hofman and others 2001), mangoes (Jiang and Joyce 2000; Hofman and others 2001), nectarines (Dong and others 2001), oranges (Porat and others 1999), papayas (Hofman and others 2001), pears (Baritelle and others 2001; Hiwasa and others 2003), persimmons (Salvador and others 2004), pineapples (Selvarajah and others 2001), plums (Abdi and others 1998; Argenta and others 2003; Salvador and others 2003), rambutans (U-ae and others 2002) and tomatoes (Lee 2003; Mir and others 2004). Commercial MCP treatment is usually a single application following harvest of the produce and prior to handling and packing. Due to the explosive nature of MCP gas, MCP is commercially available in a molecular

encapsulation complex using α-cyclodextrin as a molecular encapsulation agent. MCP gas is released from the complex by adding a buffer containing potassium hydroxide (Mir and others 2001) or water (Blankenship and Dole 2003).

Recent research indicates the potential of continuous and repeated MCP treatment (Mir and others 2004). The storage rooms used for single bulk treatment are typically only available at the wholesaler level or other dealing in bulk quantities (Mir and Beaudry 2001). When such storage rooms are not available, a sealed package can provide a mean to contain MCP gas. Packaging can also create a modified atmosphere around the packaged produce. The combination of modified atmosphere packaging and in-package MCP treatment increased the shelf life of bananas (Jiang and others 1999). The in-package treatment can also provide a continuous exposure of the packaged item. Repeated and continuous MCP treatments have an additional benefit versus a single MCP treatment because the MCP effect is not permanent. Produce becomes sensitive to ethylene again after a certain period of time has elapsed. Apples, tomatoes and avocados can benefit from a repeated and/or continuous treatment. The storage life of apples was extended with MCP repeated treatment (once a week) at storage temperatures of 5, 10, 15 and 20°C (Mir and others 2001). Sequential and continuous treatment reduced the loss of firmness and color change more than a single application, particularly at an early stage (Lee 2003; Mir and others 2004). After 10 days in cold storage, a repeated MCP treatment was found to preserve the firmness of avocado through its shelf life (Pesis and others 2002).

The current commercial MCP delivery system employs a molecular encapsulation technique to sustain MCP gas in a powder form. The encapsulation agent is α-cyclodextrin (Blankenship and Dole 2003). The complex releases all MCP within a very short time once in contact with the triggering agent (water or potassium hydroxide buffer). This makes it suitable for a single treatment as in the current commercial practice.

Several controlled release delivery devices have been developed in order to facilitate in-package and/or continuous MCP treatment. These devices are either a reservoir (active component contained within a rate controlling membrane (Zeoli and Kydonieus 1983)) or a monolithic (active component distributed throughout a rate controlling membrane (Zeoli and Kydonieus 1983)) types. The active component in reservoir device is in the form of a gas (Sittipod 2003), molecular encapsulation complex (Mir and Beaudry 2001; Macnish and others 2004), sorbed on an absorbing agent (Lee 2003) or in a solvent form (Macnish and others 2004). The rate limiting membranes include commonly used polymeric packaging materials (low density polyethylene, polyvinyl acetate, Tyvek®, PVC), silicon and natural rubber. The active component in monolithic device is in the form of a gas (Konstansek and Edward 2003; Macnish and others 2004), molecular encapsulation complexes (Konstansek and Edward 2003) and solvent (Macnish and others 2004). The rate limiting membranes include natural rubber, polymeric packaging materials, wax paper and waxy cast film.

The release characteristics of monolithic and reservoir devices are different. In a reservoir device, the release is essentially a permeability process

and the release rate is a zero order function (Christie and others 1997). This is true as long as the concentration of the active component is constant. The release rates of monolithic devices depend on diffusion and, in some cases, solubility coefficients. The release rates are inversely proportional to $\sqrt{\text{time}}$. However, if the active component is dissolved in the polymer matrix, this relationship is only valid up to the time when the device releases 60% of the active component. The release rates beyond that point and the release rate of reservoir devices when the concentration of the active agent is not constant are first order(Zeoli and Kydonieus 1983).

The amount or ratio of active ingredient released from the controlled release device can be described as a function of time either by an empirical or theoretical relationship. Sinclair and Peppas proposed using a simplified exponential relationship for slabs, cylinders and spheres (Sinclair and Peppas 1984). Al-Zahrani proposed a modified hyperbola and exponential rise to maximum functions to describe his monolithic device for release of several fertilizers from paraffin and polyethylene wax. Modified hyperbola provided the best fit for his controlled release device (Al-Zahrani 2000).

The objectives of this study are to develop a device that effectively controls release of MCP from a molecular encapsulation complex and then to evaluate the effect of temperature and relative humidity on its release of MCP.

3.2 Materials and Methods

3.2.1 Polymer matrices

Low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) were used as polymer matrices for the controlled release device. Low density polyethylene (MN 722-00, Equistar, Houston, TX) was provided in a powder form of 50 mesh irregular particles. Ethylene vinyl acetate (MU 760-00, Equistar, Houston, TX), a copolymer of polyethylene and 20% vinyl acetate, was provided in a powder form of 35 mesh irregular particles.

3.2.2 Active compound

The active compound, MCP, was bound in an encapsulation agent. The MCP molecular encapsulation complex is commercially available in powder form under the trade name SmartFresh™ (Rohm and Haas Company, Philadelphia, PA). The encapsulation agent used in SmartFresh™ is α-cyclodextrin. SmartFresh™ is referred to as the molecular encapsulation complex throughout the study.

3.2.3 Thermal analysis

Differential scanning calorimetry

The polymer matrix melting temperature was determined by differential scanning calorimeter (DSC) according to ASTM D3418-03 (ASTM 2003). The thermogram was analyzed using Universal Analysis Software (TA Instruments, New Castle, DE) to determine melting temperature.

Thermogravimetric analysis

The thermal degradation of polymer matrices, and the molecular encapsulation complex was studied using a Thermogravimetric analyzer (TGA 2950, TA Instruments, New Castle, DE) according to ASTM D3850-94 (ASTM 2002). The thermogram obtained was analyzed using Universal Analysis Software (TA Instruments, New Castle, DE) to determine the degradation temperature.

3.2.4 MCP analysis

MCP gas was analyzed using a gas chromatograph equipped with a flame ionization detector (HP 6890, Hewlett Packard Co., Wilmington, DE) and a 30 m x 0.32 mm x 0.25 μm HP-5 column. The column temperature was kept at isothermal at 80°C. The run time was 4 minutes. The area responses were integrated by using Empower software (Waters Inc., Milford, MA). A standard curve was prepared using 1-butene due to its similarity in chemical structure to MCP. The procedure for construction of the calibration curve and the actual calibration curve are presented in Appendix C.

3.2.5 Barrier properties

The barrier properties of LDPE and EVA films to moisture and MCP were determined. Test specimens were created by compression molding a plastic sheet (according to the method for processing blank monolithic devices described in Section 3.2.6). Two plastic sheets were placed on top of each other and compressed between two metal plates at 110°C for 1 minute and then

allowed to cool for 5 minutes before the pressure was released. The sample thickness was 61 ± 3 μm. The test specimens were conditioned at 23°C, 50% RH for at least 24 hours prior to testing.

Moisture barrier

Moisture barrier of the test specimens was determined at 10, 20 and 30°C, 90% RH using a Permatran W3/31 (Mocon, Minneapolis, MN). The test samples were conditioned for 2 hours in the test cell at the test condition prior to testing. The test was terminated when steady state was obtained. The average water vapor transmission rate (WVTR) during the steady state period was used to calculate the water vapor permeability coefficient (P_{water}) using the following equation;

$$P_{water} = WVTR \times \frac{\ell}{\Delta p}$$

where Δp is the partial pressure difference between the opposite sides of the permeation cell and ℓ is the thickness of the test specimen. Using the permeability coefficients at the three temperatures, the activation energy of the water vapor permeation process was obtained using the Arrhenius equation (Hernandez and others 2000).

$$P_T = P_0 \cdot e^{-E_p/RT}$$

MCP barrier

MCP barrier properties were tested at 21°C and 5°C at 0% RH using a quasi-isostatic method (Hernandez and others 2000). The permeation cell is shown in Figure 3.1. Three ml of MCP stock gas of approximately 2000 $\mu L\ L^{-1}$ was introduced into the high concentration side. The MCP concentration in the high concentration side was quantified using gas chromatography, as described in Section 3.2.5. At predetermined intervals, 200 μL aliquots were drawn from the low concentration cell and quantified in the same manner. For LDPE and EVA, the sampling intervals were 30 and 10 minutes, respectively. The experiment was terminated when the difference in concentration between the two sides of the film was at approximately 10%. The MCP which permeated through the test specimen was plotted as a function of time (example in Figure 3.2). The slope (F_{ss}) of this plot was used to calculate the MCP permeability (P_{MCP}) using the following equation:

$$P_{MCP} = F_{SS} \times \frac{\ell}{A \cdot \Delta p}$$

where A is the surface area of the test specimen exposed to the MCP gas, ℓ is the thickness of film specimen, and Δp is the partial pressure difference between both sides of test specimen. The MCP diffusion coefficient (D_{MCP}) was calculated as follows (Hernandez and others 2000):

$$D_{MCP} = \frac{\ell^2}{6 \cdot \theta}$$

where θ is the lag time which is the point where the steady state portion extends to intersect with the time axis (x-axis). The MCP solubility coefficients (S_{MCP}) were calculated from the following equation (Hernandez and others 2000).

$$S_{MCP} = \frac{P_{MCP}}{D_{MCP}}$$

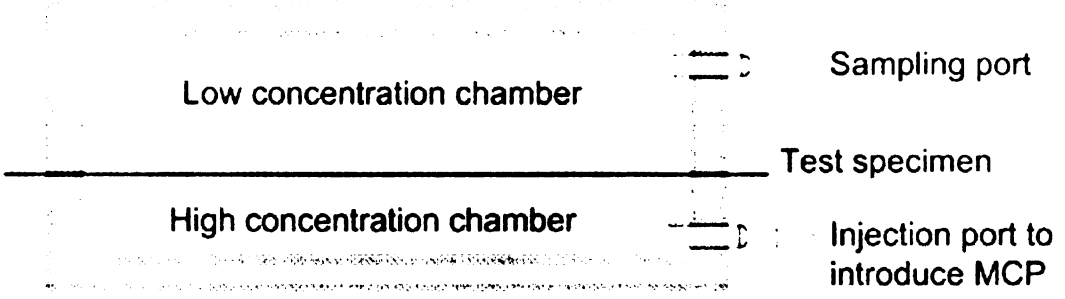

Figure 3.1. The quasi-isostatic technique used for determining MCP barrier properties

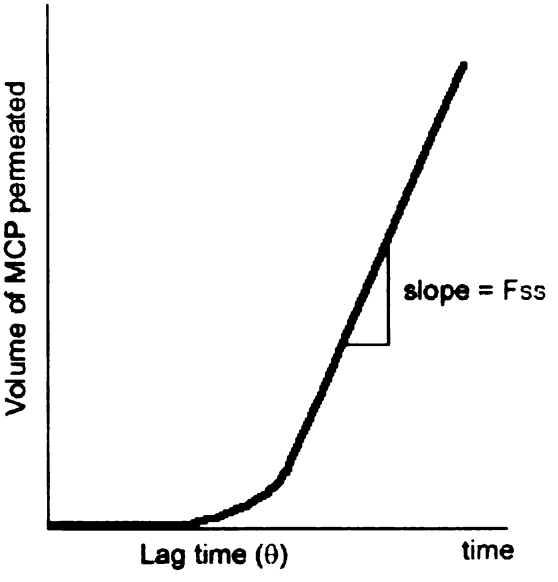

Figure 3.2. An example of typical amount of MCP vs. time plot from quasi-isostatic permeability experiment

3.2.6 MCP controlled release devices

The monolithic device was a plastic sheet that had SmartFresh™ powder dispersed in it. It was made by mixing approximately 180 mg of polymer matrix with 30 mg of SmartFresh™ powder. This mixture was placed in a mold which consisted of 3 metal sheets (Figure 3.3) stacked on top of each other. The middle sheet had 22 mm circular openings into which the polymer matrix – active compound mixture was placed. The two outer sheets were lined with thin aluminum foil. The mold containing the mixture was compressed at a pressure and temperature of 10,000 psi and 110°C for 5 minutes using a Carver laboratory press (Model M, Carver, Inc., Wabash, IN). The mold was allowed to cool for 5 minutes to approximately 50°C before the pressure was released. The monolithic device was made in the same manner in the absence of the SmartFresh™ powder.

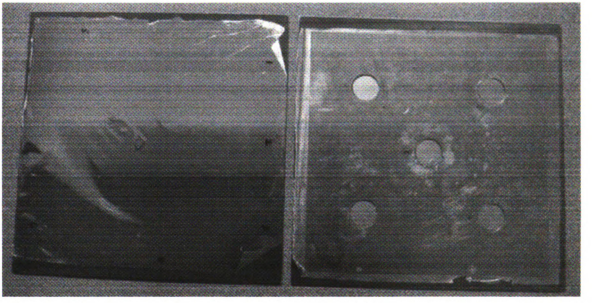

Figure 3.3. The mold used for processing of monolithic devices

The reservoir device was the two plastic sheets laminated together with the SmartFresh™ powder in the middle. The two plastic sheets were made in the same manner as the blank monolithic device. Approximately 30 mg of SmartFresh™ were placed between the two sheets. The sheets were placed between two metal sheets lined with aluminum foil and a pressure and temperature of 2000 psi and 80°C for 50 seconds was applied using the Carver laboratory press. The blank specimen for this device was made in the same manner in the absence of the SmartFresh™ powder.

The monolithic and reservoir devices developed were formed in the shape of a round disc with different thicknesses and diameter (Figure 3.4). Monolithic LDPE and EVA devices had the same diameter of 22 mm and thickness of 550 ±5 μm. The reservoir device (LDPE membrane) diameter was 25 mm and its thickness was 912±6 μm. The reservoir device (EVA membrane) diameter was 33 mm and its thickness was 624±6 μm. The other difference in the reservoir device was that the molecular encapsulation powder in the EVA device was broken up into several small groups while the powder in the LDPE device was continuous. The thickness across the surface was constant. This indicates that the thickness of the LDPE and EVA membrane over the location of the powder was less than 456 and 312 μm (half of the thickness of the reservoir device), respectively.

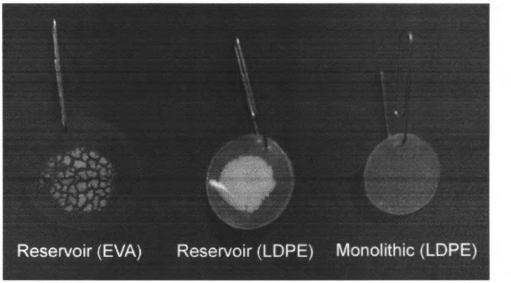

Figure 3.4. Monolithic and reservoir devices for MCP release study

3.2.7 Release of MCP

Release of MCP from the controlled release devices or the molecular encapsulation complex was studied by subjecting them to a controlled temperature and relative humidity (RH) in a 920 mL glass jar with a sampling port (Figure 3.5). The controlled RH was achieved using a 100 mL saturated salt solution or deionized water. The salt solution and the relative humidity are shown in Table 3.1. The jar was placed in a controlled temperature chamber (5 or 22°C). A 250 μL aliquot was withdrawn from the glass jar and analyzed as described in 3.2.4. The blank was also tested in the same manner as the sample. The fraction of MCP released (Q_t) was calculated as:

$$Q_t = \frac{\text{volume of MCP released}}{\text{expected volume of MCP to be released}}$$

The expected MCP volume is the amount of MCP released at equilibrium (the state where the volume of MCP in the headspace does not change with time)

from the molecular encapsulation complex subjected to the test temperature and relative humidity.

Table 3.1. Salt solutions used in the study of MCP release and the expected relative humidity they created at 4 and 22°C

Salt Solution	% RH	
	4°C	22°C
Lithium chloride	n/a	11
Magnesium chloride	n/a	36
Magnesium nitrate	n/a	53
Sodium chloride	n/a	75
Ammonium sulfate	79	81
Potassium chloride	87	85
Potassium nitrate	97	93
Deionized water	~100	~100

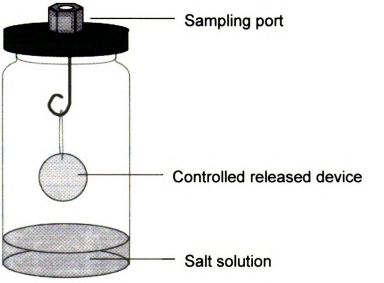

Figure 3.5. The setup of 920 mL glass jar containing salt solution or water described in Table 3.1 used for the MCP release study.

The release profile is constructed by plotting the fraction of MCP released or the volume or fraction of MCP released as a function of time. Each point on the release profile is the average of 3 data points and the error bar represents a standard error. The line graph on a release profile represents the predicted fraction or volume of MCP released based on the empirical models (described in Section 3.2.8).

3.2.8 The effect of MCP delivery devices on the MCP release characteristics

The amount of MCP released from the monolithic devices (LDPE and EVA matrices), reservoir devices (LDPE and EVA membranes), and the molecular encapsulation complex was monitored at 22°C at a relative humidity of approximately 100% by using water in place of a salt solution. The release profiles were fitted with 3 empirical equations (Table 3.2). Q_t is fraction of MCP released, t is time (day) and *a* and *b* are regression coefficients. The regression analyses were performed using SigmaPlot 2000 (Version 6.10, Systat Software Inc., Point Richmond, CA)

Table 3.2. Empirical equation used to describe the release profiles of MCP delivery devices

Name	*Equation*
Power function	$Q_t = a \cdot t^b$
Modified hyperbola	$Q_t = \frac{a \cdot t}{1 + b \cdot t}$
Exponential rise to maximum	$Q_t = a \cdot (1 - e^{-bt})$

All three functions, power, modified hyperbola and exponential rise to maximum, had two regression coefficients. The coefficient *a* is a magnification factor and increases when the Q_t at the equilibrium (constant MCP concentration in the headspace) increases. The shape of the graph depends mainly on the coefficient *b*. In the power function, for time less than 1 unit, the greater the *b* value, the lower the release rate. For time greater than 1 unit, the release rate increases with increase in *b*. One disadvantage of this equation is that it does not approach a maximum level, thus, it is not suitable for describing a release profile that includes the equilibrium portion (equilibrium state is defined as the time that the concentration of MCP in the headspace is considered constant). The modified hyperbola function is described by a first order reaction at the low t-value and by a zero order reaction as the t-value increases (Al-Zahrani 2000). As *b* increases, the change from the first to zero order release occurs at lower t values and the change is more abrupt. When parameter *a* is constant, an increasing *b* value indicates that the release rate and amount of MCP released will decrease. In the exponential rise to maximum, an increasing *b* value indicates a greater release rate.

3.2.9 The effect of temperature on the release of MCP

The amount of MCP released from the monolithic device (LDPE matrix), reservoir device (LDPE membrane) and molecular encapsulation complex were monitored at 5 and 22°C at approximately 100% RH by using deionized water. The release profiles were fitted with 3 empirical equations as described in section 3.2.8.

3.2.10 The effect of relative humidity on the release of MCP

The amount of MCP released from the monolithic device, reservoir device and molecular encapsulation complex was monitored at 5 and 22°C and various RH (Table 3.3). The release profiles of the monolithic device were fitted with modified hyperbola functions while the release profiles of the reservoir device and the molecular encapsulation complex were fitted with an exponential rise to maximum function. Since the expected volume was different for the different relative humidities, both volume of MCP released and fraction of MCP released were considered.

Table 3.3. Experiments performed to evaluate the effect of relative humidity on the MCP release from the MCP delivery devices

Exp.	*Delivery device*	*Polymer*	*T, °C*	*% RH*
1	Monolithic	LDPE	22	11, 36, 53, 75, 85, 93, ~100
2	Monolithic	EVA	22	11, 36, 53, 75, ~100
3	Reservoir	EVA	22	85, 93 and ~100
4	Molec. encapsulation	-	22	11, 36, 53, 75, 81, 85, 95, ~100
5	Monolithic	LDPE	5	87, 97 and ~100
6	Molec. encapsulation	-	5	87, 97 and ~100

3.3 Results and Discussion

3.3.1 Thermal analysis

Differential scanning calorimetry

The DSC thermogram (Figure 3.6) indicates that the theoretical onset temperatures, according to ASTM D3418-03, were 103 and 84°C for LDPE and

EVA, respectively. Below this onset temperature, some melting had taken places. The melting temperatures, which are the temperatures at the peak of the DSC thermograms of LDPE and EVA, were 110 and 94°C, respectively. These data can be useful to determine the minimum processing temperature for controlled release devices.

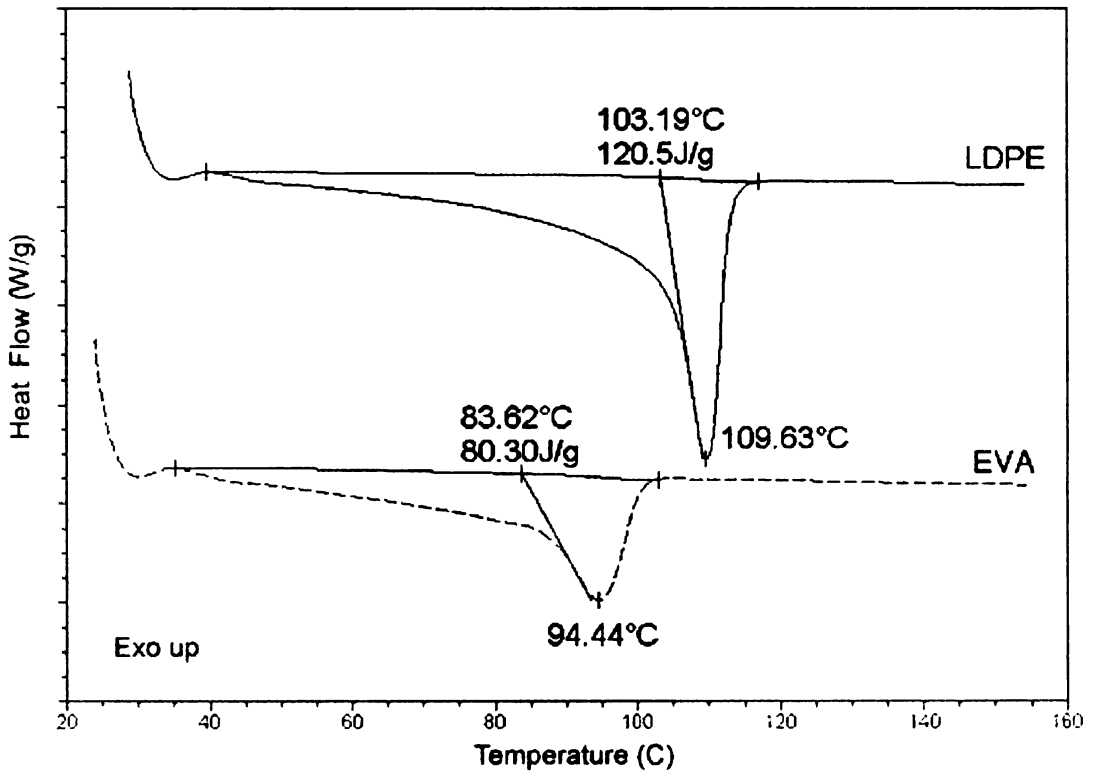

Figure 3.6. Differntial scanning calorimetric thermogram of low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) powder.

Thermal Gravimetric Analysis

The TGA thermogram (Figure 3.7) shows the weight change of the sample as a function of temperature, which indicates the thermal stability of the sample. The threshold for thermal degradation of LDPE and EVA powder occurred at 377°C and 319°C, respectively. Above these temperatures, the respective polymers are expected to undergo thermal degradation. For the molecular encapsulation complex, two weight loss events occurred at 209°C and 275°C. The degradation temperature of α-cyclodextrin is in the range of 250-300°C (Huang and others 1998). Degradation at 209°C is not in this range; therefore, it is probably degradation of an additive in the SmartFresh™ product. Degradation at 275°C is the degradation of cyclodextrin. The remaining mass of approximately 20% (w/w) is a char that forms as a result of cyclodextrin degradation (Trotta and others 2000).

The lower degradation temperature (200°C) is used to set the maximum processing temperature for the controlled release devices. The processing condition chosen was based on the DSC results for the polymer. It was set below this temperature so it could safely be used for the MCP controlled release device.

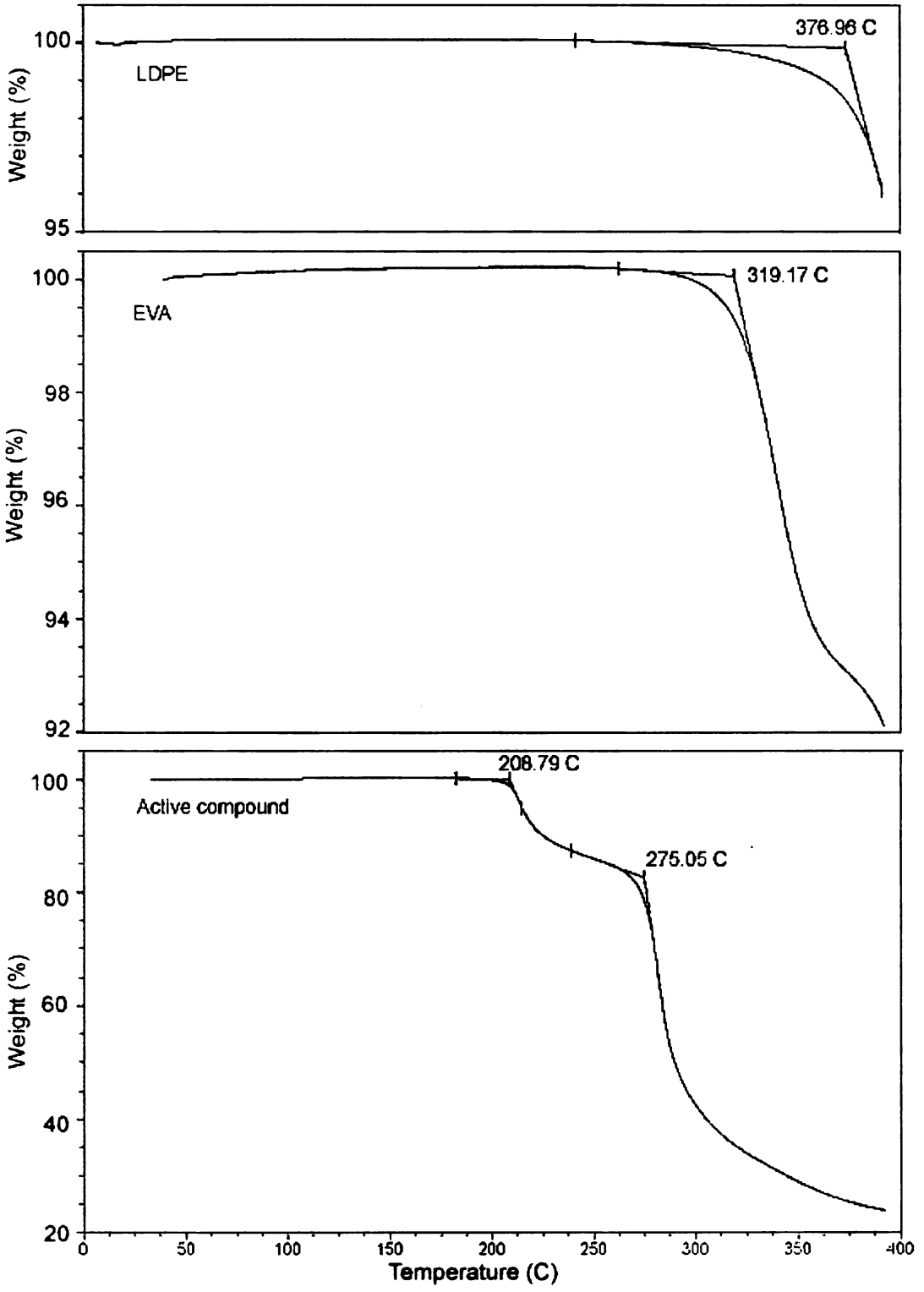

Figure 3.7. Thermogravimetric analysis thermogram for low density polyethylene (LDPE), ethylene vinyl acetate (EVA) and the molecular encapsulation complex

3.3.2 Barrier properties

Moisture barrier

Water vapor permeability coefficients of LDPE and EVA at 10, 20 and 30°C and the activation energy of the permeation process are presented in Table 3.4. The Arrhenius plots of the two polymers are presented in Figure 3.8. The Arrhenius equation for LDPE was:

$$P_{water} = 4.27\times10^{-13}\ \frac{kg\cdot m}{m^2\cdot s\cdot Pa}\cdot e^{-\frac{2119.2\ kJ/mole}{T}}$$

The Arrhenius equation of EVA was:

$$P_{water} = 5.49\times10^{-12}\ \frac{kg\cdot m}{m^2\cdot s\cdot Pa}\cdot e^{-\frac{2348.2\ kJ/mole}{T}}$$

From the Arrhenius equation, the water vapor permeability coefficients of the two polymers at 5 and 22°C were calculated (Table 3.5). Although 5°C is outside the range of temperature used in the determination of water vapor barrier, the Arrhenius relationship was assumed to be valid because 5°C is well above the glass transition temperature of both LDPE and EVA.

The water vapor diffusion (D_{water}) and solubility (S_{water}) coefficients were not experimentally determined. A previous study has found that the water diffusion coefficient of EVA was less than that of LDPE (Marias and others 1998; Devallencourt and others 2002). Since the water vapor permeability coefficient of EVA was much greater than that of LDPE, it can be deduced that water solubility coefficient of EVA is substantially greater than that of LDPE.

Table 3.4. Water vapor permeability coefficient of low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) at 10, 20, and 30°C and activation energy of the permeation process (E_p) at a relative humidity of approximately 90%

Polymer	P_{water}, x 10^{16} kg.m.m^{-2}.s^{-1}.Pa^{-1},			E_p, kJ.mol^{-1}
	10°C	20°C	30°C	
LDPE	2.45 ± 0.05	2.93 ± 0.04	4.03 ± 0.09	17.6 ± 1.1
EVA	13.5 ± 0.2	18.6 ± 0.1	23.4 ± 0.6	19.5 ± 1.8

Note: The error term associated with the water vapor permeability coefficient is the standard error (n=2) and the error term associated with the activation energy is the propagated error from the standard error of the slope of the Arrhenius plot.

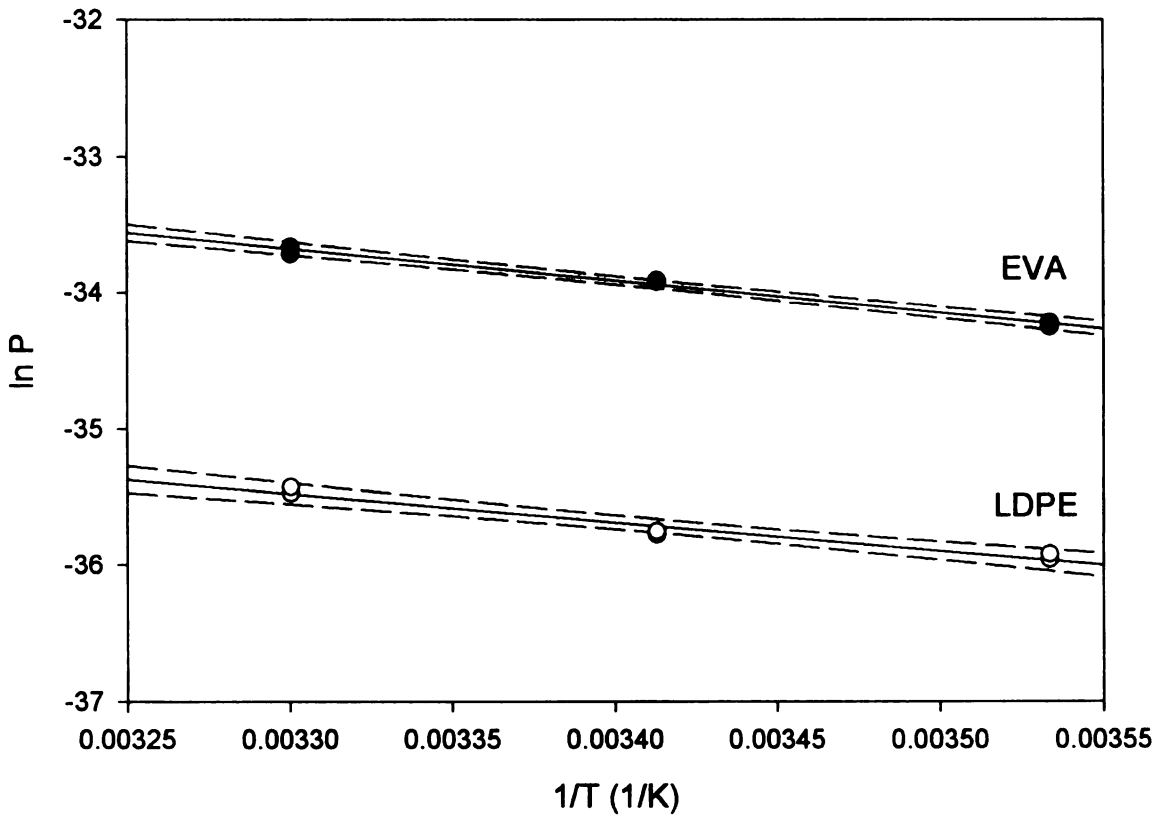

Figure 3.8. Arrhenius plot of water vapor permeability for low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) in the temperature range of 10-30°C . The solid lines represent the predicted values and the dash lines represent the confidence interval.

MCP barrier

The volume of MCP which permeated through the LDPE films for both test temperatures are presented in Figure 3.9. The MCP permeability, diffusion and solubility coefficients of LDPE at 5 and 22°C are presented in Table 3.6. All three coefficients increased with increasing temperature. The permeability of MCP at 23°C was previously determined, also by a quasi-isostatic method (with slightly different setup), by two other researchers to be 1.31 x 10^{-10} cc (at 23°C).m.m^{-2}.s^{-1}.Pa^{-1} (Lee 2003) and 1.77 x 10^{-10} cc (at 23°C).m.m^{-2}.s^{-1}.Pa^{-1} (Sittipod 2003). Despite the similarity in the permeability coefficient, the diffusion and solubility coefficients, determined in previous research (Lee 2003), were quite different from the values obtained in this experiment. This may be due to a difference in the base resin.

The MCP permeability of EVA could not be determined by the quasi-isostatic method employed in this experiment because EVA absorbed MCP. A significant decrease in MCP concentration in the high concentration side was observed as the experiment proceeded. Thus, the MCP partial pressure difference between the two sides of the film was not constant. This occurred because EVA has a high MCP solubility coefficient. The solubility coefficient of polymer containing vinyl acetate monomer was about 26 times higher than the solubility coefficient of LDPE (Lee 2003). Lee also reported the MCP permeability of EVA to be 1.56 x 10^{-10} cc (at 23°C).m.m^{-2}.s^{-1}.Pa^{-1}, which is very similar to that of LDPE, and the diffusion coefficient to be 5.98 x 10^{-14} m^2.s^{-1}, which is less than that of LDPE.

Table 3.5. Calculated water vapor permeability coefficient of low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) at 5 and 22°C

Polymer	Calculated P_{water}, x 10^{16} kg.m.m^{-2}.s^{-1}.Pa^{-1},	
	5°C	22°C
LDPE	2.09	3.24
EVA	11.8	19.7

Table 3.6. MCP permeability (P_{MCP}), diffusion (D_{MCP}) and solubility (S_{MCP}) coefficient of low density polyethylene at 5 and 22°C

Temperature, °C	P_{MCP}, x 10^{10} cc.m.m^{-2}.s^{-1}.Pa^{-1}	D_{MCP}, x 10^{12}.m^2.s^{-1}	S_{MCP}, cc.m^{-3}.Pa^{-1}
5	0.41 ± 0.02	2.7 ± 0.16	15.4 ± 1.5
22	2.1 ± 0.18	5.7 ± 0.27	37.5 ± 2.0

Note: The error term is the standard error (n=3)

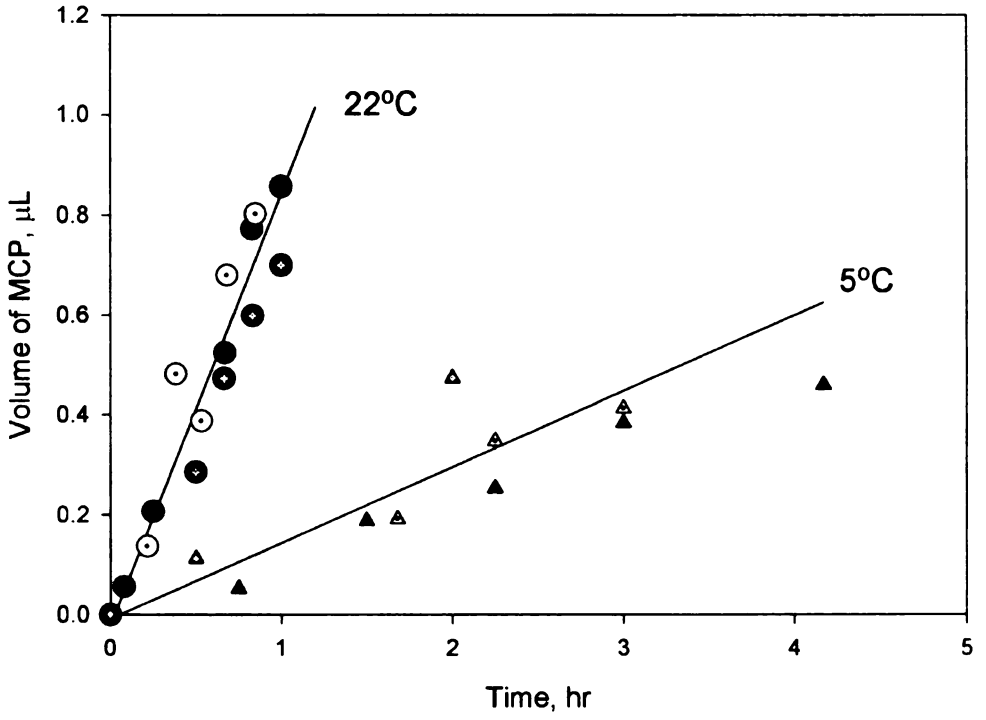

Figure 3.9. The volume of MCP gas permeated through LDPE film during the MCP barrier property testing at 4 and 22°C.

3.3.3 The effect of MCP delivery devices on the MCP release characteristics

The fraction of MCP released (Q_t) of the controlled release devices, monitored as a function of time, was fitted with three functions (listed in Table 3.2). All equations can be used to describe the release profiles with an adjusted r^2 in the range of 0.7 – 0.8 (Table 3.7). However, these functions are not suitable to describe the fraction of MCP released from the molecular encapsulation complex because some of the regression coefficients were not significant (Table 3.8). The reason was because the complex released MCP rapidly. The profile was better described by two linear equations. The first equation described the release during 0-3 hours where Q_t increased from 0 to 1 with the equation Q_t = 8t. The second linear equation (Q_t = 1) described the fraction of MCP during steady state. The experimental and the predicted values were used to construct MCP release profiles (Figure 3.10 – 3.14). The functions that best described each profile (the highest adjusted r^2) were used to compare release of MCP from each device (Figure 3.15).

The MCP delivery devices significantly affected the MCP release characteristics. Enclosing the molecular encapsulation complex in polymer matrix/membrane significantly reduced the MCP release rate (Figure 3.15). The effect of polymer on the release rate has been shown in other applications with fertilizers (Al-Zahrani 2000) and drugs (Burgos and others 2002).

Table 3.7. The regression coefficients and the adjusted r^2 of the release profile for MCP delivery devices for power, modified hyperbola and exponential rise to maximum functions at 22°C and ~100% RH.

Model	Regression analysis	Monolithic		Reservoir	
		LDPE	EVA	LDPE	EVA
Power	a	0.44 ± 0.08	0.39 ± 0.03	0.06 ± 0.02	0.35 ± 0.04
	b	0.21 ± 0.04	0.34 ± 0.05	0.51 ± 0.11	0.39 ± 0.07
	Adj. r^2	0.7268	0.7476	0.8007	0.7284
Mod.	a	2.02 ± 0.05	1.15 ± 0.3	0.04 ± 0.02	0.49 ± 0.13
Hyperbola	b	2.96 ± 0.83	1.64 ± 0.49	0.10 ± 0.07[+]	0.51 ± 0.18
	Adj. r^2	0.7800	0.7709	0.7288	0.7786
Exp. rise	a	0.62 ± 0.03	0.61 ± 0.04	0.34 ± 0.10	0.80 ± 0.60
to max.	b	2.34 ± 0.49	1.34 ± 0.29	0.09 ± 0.05[+]	0.47 ± 0.11
	Adj. r^2	0.7666	0.7616	0.7099	0.7906

[+] indicates that the regression coefficients was not significant

Table 3.8. The regression coefficients and the adjusted r^2 of the MCP release profile for the molecular encapsulated for power, modified hyperbola and exponential rise to maximum functions at 5 and 22°C, ~100% RH.

Model	Regression analysis	Temperature	
		5°C	22°C
Power	a	0.83 ± 0.05	1.01 ± 0.02
	b	0.16 ± 0.04	0.00 ± 0.02[+]
	Adj. r^2	0.7125	0.9647
Mod. Hyperbola	a	6.45 ± 1.64	255824 ± 70964101[+]
	b	6.01 ± 1.71	255969 ± 71032297[+]
	Adj. r^2	0.8326	0.9649
Exp. rise to max.	a	1.01 ± 0.04	1.00 ± 0.02
	b	3.98 ± 0.67	2240 ± 3635410[+]
	Adj. r^2	0.8746	0.9649

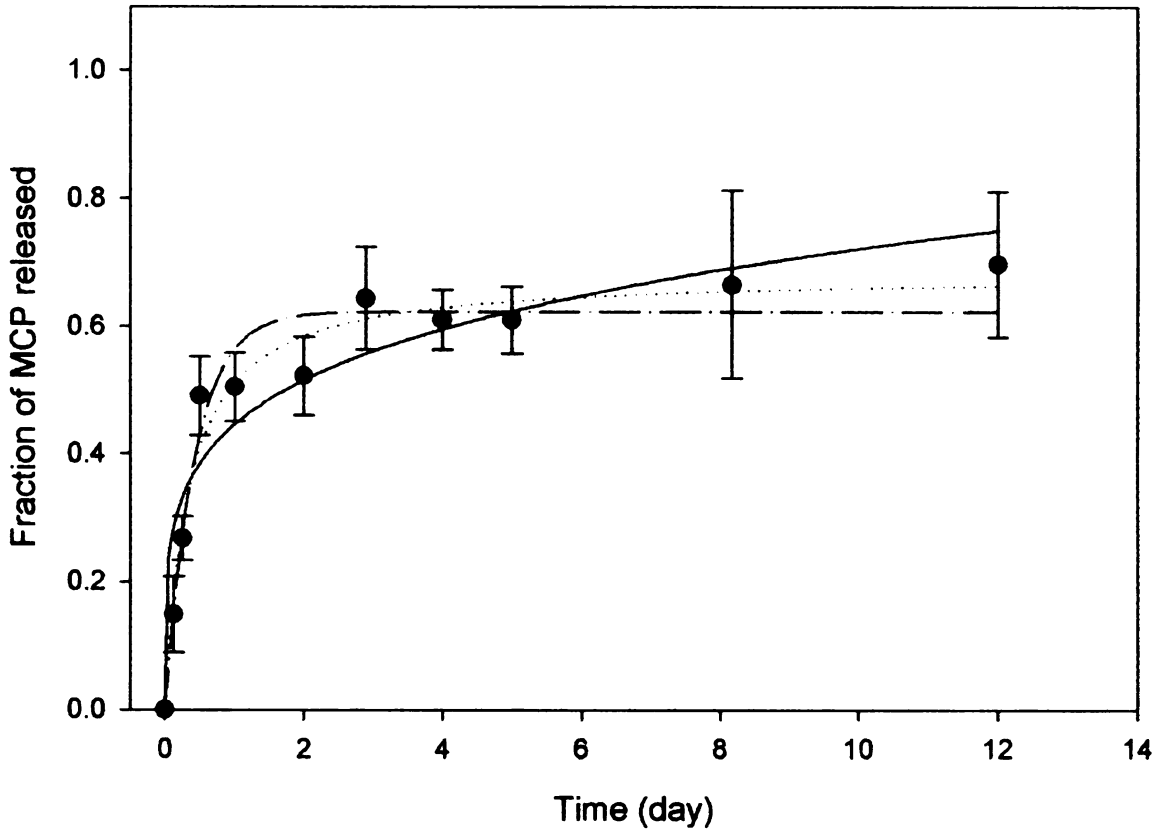

Figure 3.10. The experimental release profiles of monolithic devices (LDPE matrix) when subjected to 22°C and ~100% RH (circle) and the predicted fraction of MCP released using the power function (solid line), the modified hyperbola function (dotted line) and the exponential rise to maximum function (dash-dotted line). The error bar represents standard error.

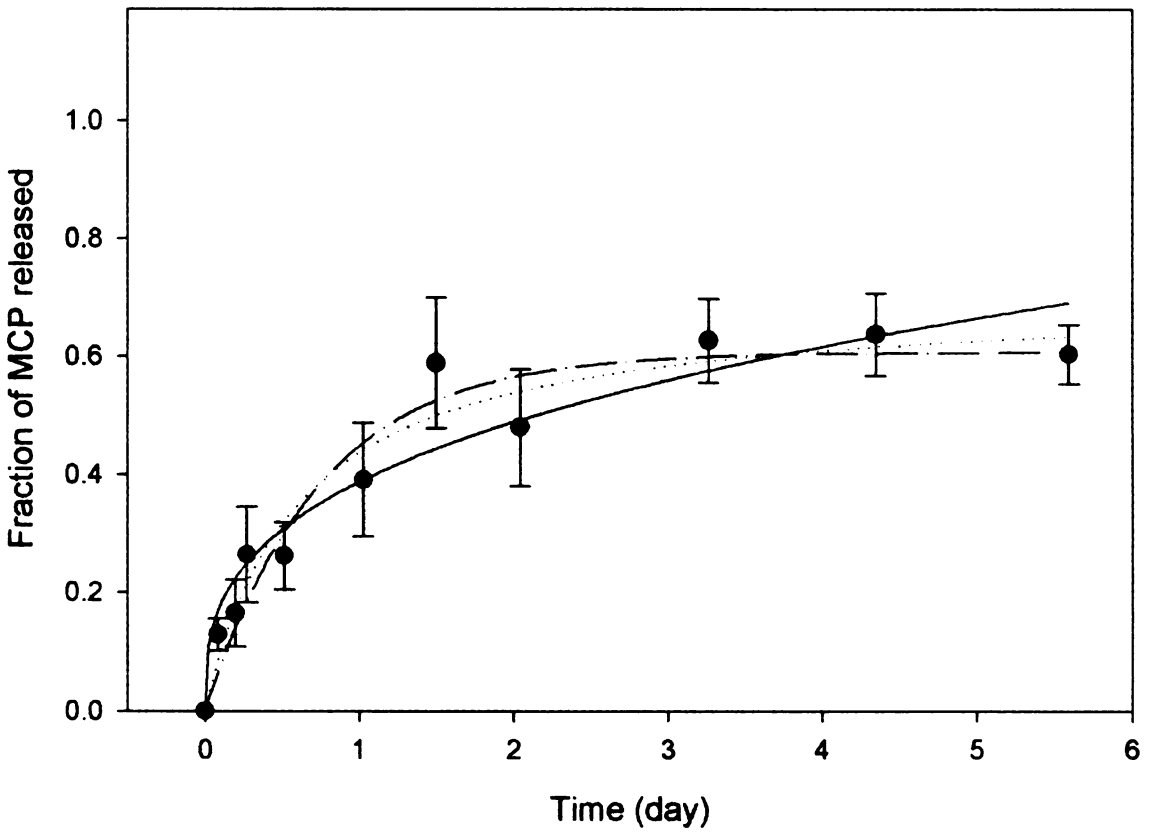

Figure 3.11. The experimental release profiles of monolithic devices (EVA matrix) when subjected to 22°C and ~100% RH (circle) and the predicted fraction of MCP released using the power function (solid line), the modified hyperbola function (dotted line) and the exponential rise to maximum function (dash-dotted line). The error bar represents standard error.

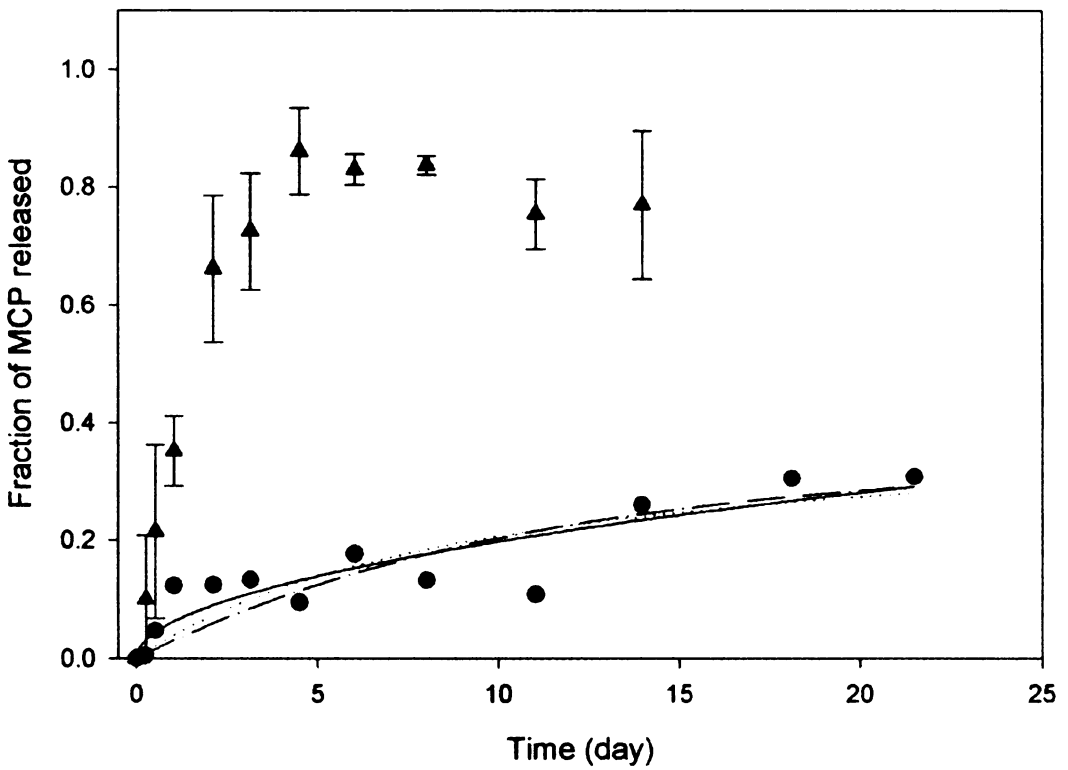

Figure 3.12. The experimental release profiles of reservoir devices (LDPE membrane) when subjected to 22°C and ~100% RH (circle for the intact devices and triangle for the devices with compromised integrity) and the predicted fraction of MCP released from the intact device using the power function (solid line), the modified hyperbola function (dotted line) and the exponential rise to maximum function (dash-dotted line). The error bar represents standard error.

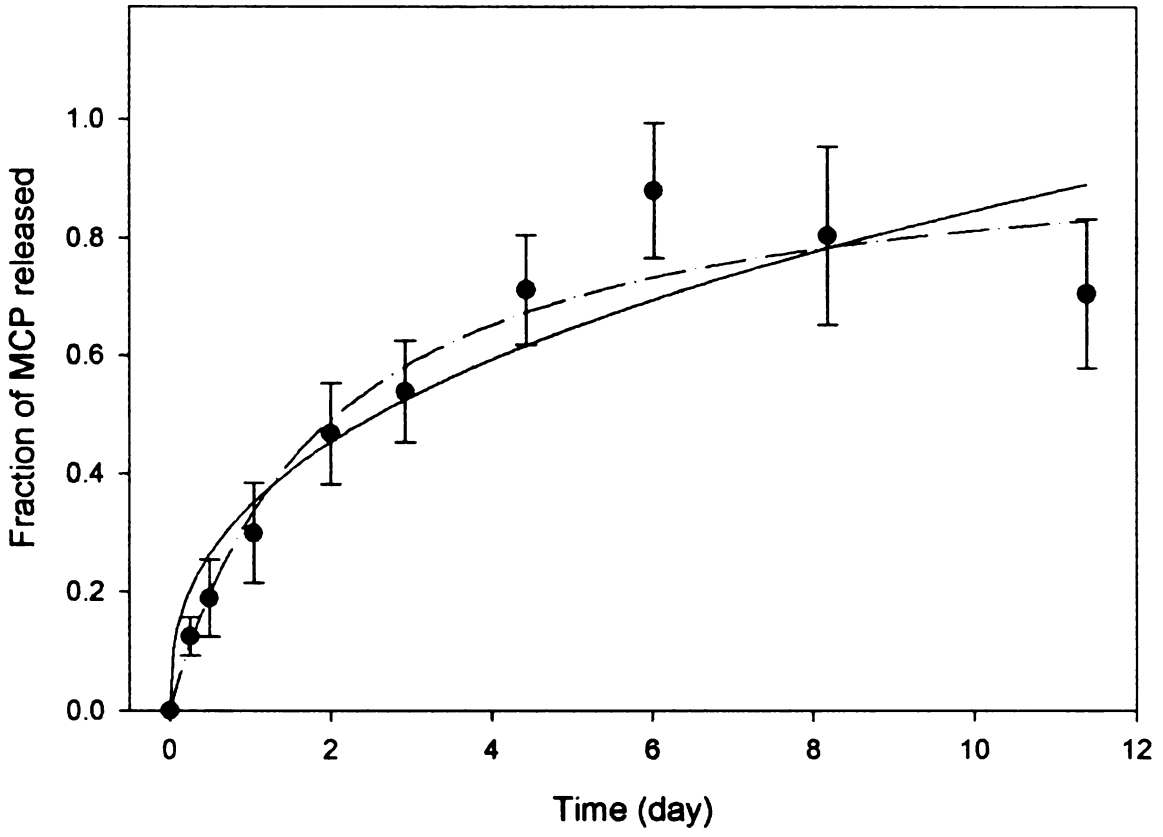

Figure 3.13. The experimental release profiles of reservoir devices (EVA membrane) when subjected to 22°C and ~100% RH (circle) and the predicted fraction of fraction of MCP released using power function (solid line), modified hyperbola function (dotted line) and exponential rise to maximum function (dash-dotted line). The error bar represents standard error.

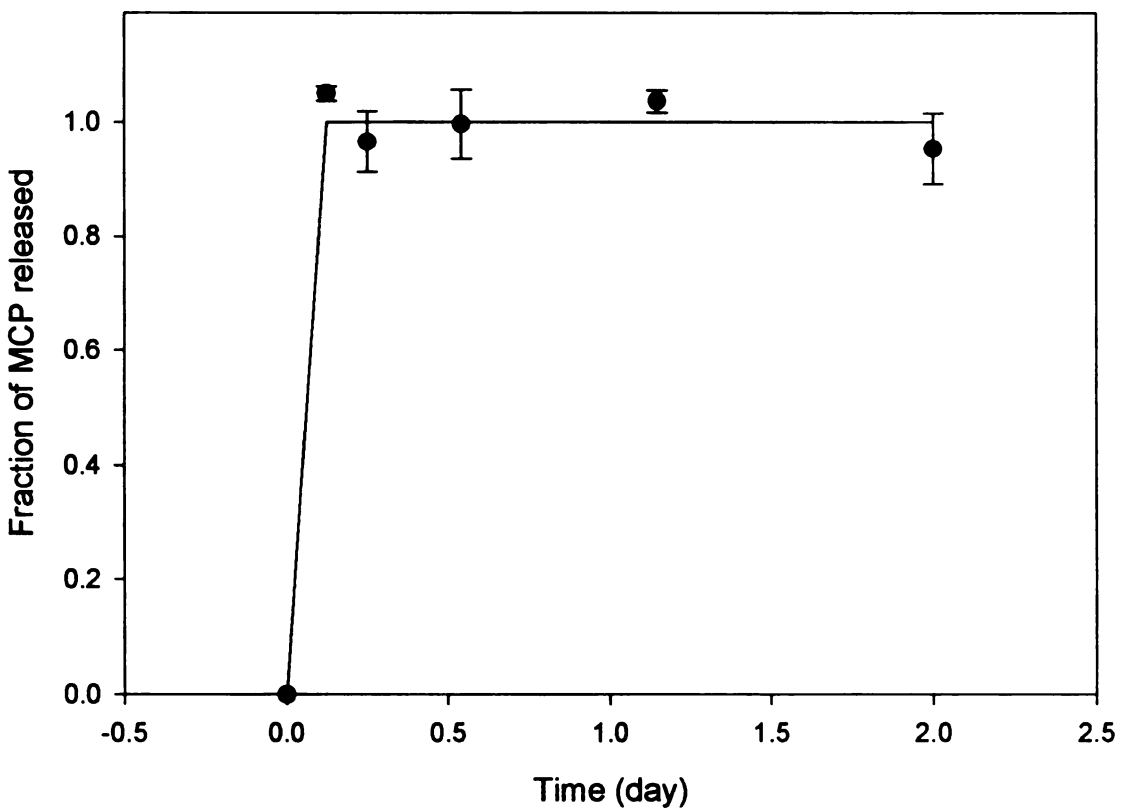

Figure 3.14. The experimental release profiles of molecular encapsulation complex when subjected to 22°C and ~100% RH (circle) and the predicted values of fraction of MCP released during equilibrium using a linear equation (solid line). The error bar represents standard error.

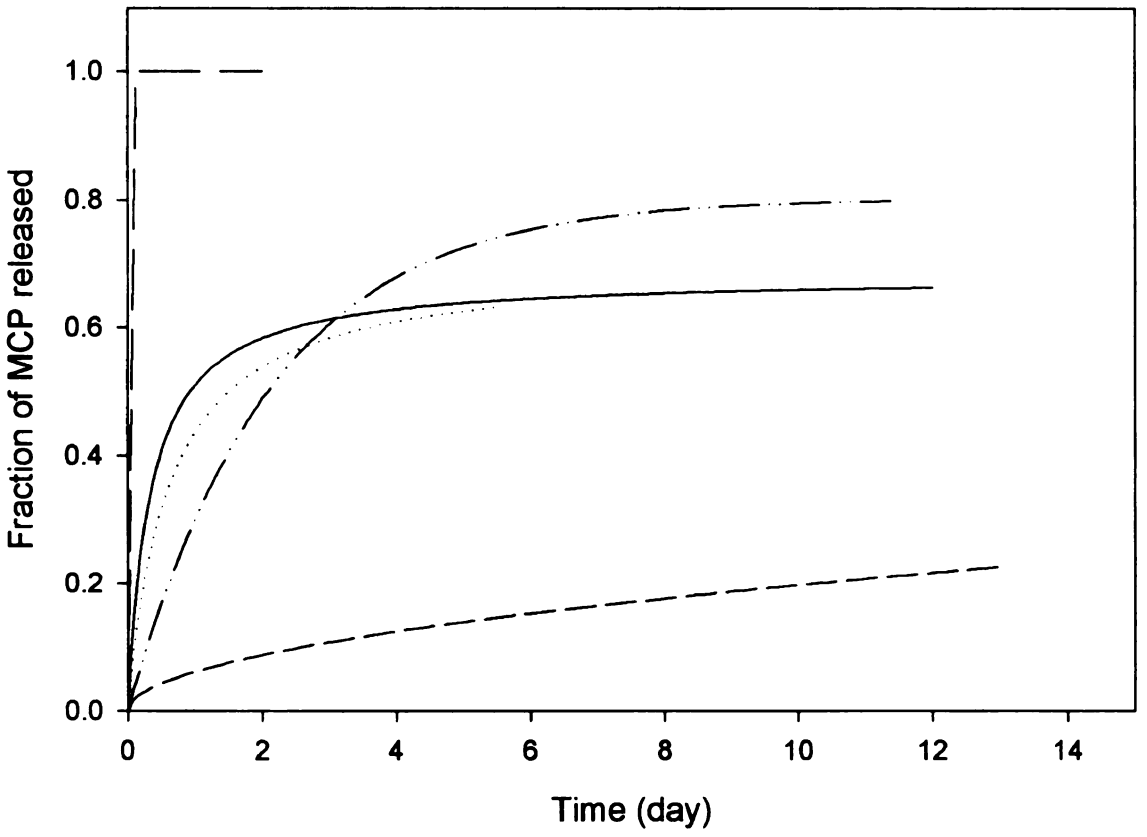

Figure 3.15. Comparison of predicted MCP delivery system: molecular encapsulation complex (long dash), monolithic devices with LDPE matrix (solid line) and EVA matrix (dotted line) and reservoir devices with LDPE membrane (medium dash) and with EVA membrane (dash-dotted line).

The release in monolithic device depends on diffusion and, in some cases, solution of active ingredient in the polymer (Zeoli and Kydonieus 1983). The monolithic device in this study is slightly different because it involves the diffusion and solution of triggering agent. The proposed model of MCP release from the monolithic device in this study follows these steps:

1. Sorption of water into the surface of the polymer with subsequent diffusion within the polymer matrix. Desorption from the polymer then occurs at the interface of the matrix and the molecular encapsulation complex. The interface can be anywhere in the polymer matrix.
2. Absorption of water molecules by the encapsulation complex.
3. Release of MCP from the encapsulation complex.
4. Sorption of MCP into the polymer at the matrix/encapsulation complex interface with subsequent diffusion within the polymer matrix and desorption into the atmosphere in the release cell.

The release profiles of LDPE and EVA monolithic devices (Figure 3.15) were best described by the modified hyperbola function. This equation was also found to best describe the release profile of nitrogen phosphate and potash, monoamonium phosphate, diammonim phosphate and granular triplesuperphosphate fertilizer in polyethylene and paraffin wax matrices. (Al-Zahrani 2000) The other two functions, experimental rise to maximum and power function, can also be used to described the release profile with slightly lower adjusted r^2. All three functions showed that the LDPE matrix device had higher regression coefficient *b* but only the modified hyperbola had a higher

coefficient *a* for the LDPE matrix device. This indicates that the LDPE device released MCP faster than the EVA matrix device (based on all three functions) but the release amount at equilibrium was similar (based on the power and exponential rise to maximum functions). This was unexpected because EVA had a greater permeability to both water vapor and MCP. The slower release rate may be attributable to the fact that EVA absorbs MCP.

The proposed model for MCP release from the reservoir device is the same as the model for the monolithic device except that the polymer/molecular encapsulation complex interface is located between two polymer sheets. Therefore, the water vapor and MCP molecules have to diffuse across the thickness of the polymer sheet instead of some distance within the polymer.

The release profiles of LDPE reservoir devices were divided into two groups according to their release rates (Figure 3.12). The first group included those that released MCP very fast and the other group those that released only a little MCP. After examining the devices, it was found that the two polymer sheets in the first group could be easily peeled apart. This may have allowed the water vapor and the released MCP to pass through some voids created by the compromised integrity of the device. Therefore, only data from the second group was used in determining the function that best described the MCP release profile. MCP released from this device very slowly and did not reach equilibrium for more than 20 days. This release profile was best described by the power function.

The EVA reservoir device released MCP at a much greater rate (Figure 3.13) than the LDPE reservoir device and released up to 80% of the expected

amount. This release profile was best described by the exponential rise to maximum function. The release rate from the reservoir (EVA membrane) was significantly greater than that of the LDPE membrane device. The release rate of the reservoir devices depends on permeation of both active compound and the release triggering agent (water). Both water and MCP need to permeate across the polymer sheet in order for the release to happen. The MCP permeability coefficient for EVA was slightly greater than that of LDPE, according to Lee (2003) by the factor of 1.2 times. The water vapor permeability coefficient of LDPE was 16% of the water vapor permeability coefficient of EVA. Based on the total thickness of the device, the thickness of LDPE can be at least 1.5 times greater than the thickness of EVA membrane. With thickness correction, the transmission rate of MCP and water vapor across LDPE was 57% and 11% of the rates across EVA membrane. This indicates that both MCP and water vapor transmission across polymer sheets had influence on the slower MCP release from the LDPE device but water vapor permeability had greater impact.

Over time, the surface of the monolithic devices changed from smooth to rough, while the surface of the EVA membrane reservoir device was smooth but its thickness increased significantly in the presence of the molecular encapsulation complex. Neither smoothness nor thickness changes were detected in the reservoir (LDPE matrix), which only released a small amount of MCP. The increase in the roughness of the monolithic device and the thickness of the reservoir device (EVA membrane) was not a result of change in polymer

dimensions but a result of the moisture absorption by the molecular encapsulation powder, which caused the powder to swell and then liquefy.

When LDPE reservoir and monolithic devices containing LDPE were compared, it was found that the monolithic device released more MCP and at a higher rate. The rate limiting factor should be the amount of water that reached the molecular encapsulation complex. In the monolithic devices, the polymer/encapsulation complex interfaces are located throughout the polymer and, thus, can start releasing MCP faster. In the reservoir device, it can take a very long time for the molecular encapsulation to receive enough moisture to cause the release of MCP due to the moisture barrier of the LDPE.

When the reservoir and monolithic devices containing EVA were compared, the reservoir device released more MCP but at a slower rate than the monolithic device. The greater release rate in the monolithic device can be explained by the existence of the interface between the polymer and the encapsulation complex like in the LDPE devices. The lower amount released from the monolithic device may be attributable to absorption of MCP by EVA, as observed in the MCP permeability experiment. The other possibility might be that, the moisture absorption of molecular encapsulation complex in the monolithic device located closer to the surface retarded the movement water vapor to the inner part of the device and/or the movement of MCP from the inner part of the device.

3.3.4 The effect of temperature on the release of MCP

The effect of temperature on the release rate was studied in the molecular encapsulation complex and in the LDPE monolithic and reservoir devices at a relative humidity of ~100%. The amount of MCP released from the molecular encapsulation complex at 5 and 22°C was not significantly different (p-value = 0.10) (Figure 3.16) but the release rate was quite different. As explained in 3.3.4 the release rate of the molecular encapsulation complex at 22°C was very fast and was described by two linear equations as described in 3.3.4. The fraction of MCP released from the encapsulation complex at 5°C was slower and was well described with the exponential rise to maximum function (Table 3.8). The molecular encapsulation powder at both temperatures became liquefied at the end of the evaluation period. The slower release rate could be due to the slower water absorption rate at a low temperature condition.

Temperature had a significant effect on the release rate of monolithic (LDPE matrix) devices. The device at both temperatures had a rough surface at the end of the release evaluation period. Figure 3.17 shows that the devices held at 5°C released less MCP and at a slower rate. This was also shown in the regression coefficients *a* and *b* for all 3 functions, power, modified hyperbola and exponential rise to maximum (Table 3.9).

The release amount and the release rate of reservoir devices with the LDPE membrane held at 5 and 22°C were very low (Figure 3.18) and no change in either the thickness or surface was detected. The regression coefficients (Table 3.9) suggested that none of the three functions can be used to describe

the release profile of the device at 5°C because the device released a very low amount of MCP and reached equilibrium in a short time. The power function was the only function of the three used that could describe the release profile of the device at 22°C.

Higher temperature resulted in a higher release amount of MCP as well as a higher release rate in both monolithic and reservoir. The greater release rate was due to the enhanced MCP and water vapor permeation at higher temperature and the greater water absorption rate of the molecular encapsulation complex at higher temperature. The reduced amount of MCP released at lower temperature may have been the result of reduced water vapor permeation rate; Thus, less water vapor are available for the molecular encapsulation complex to absorb.

Table 3.9. The regression coefficients and the adjusted r^2 of the release profile for MCP controlled release devices for power, modified hyperbola and exponential rise to maximum functions at 5 and 22°C, ~100% RH.

Model	Regression analysis	Monolithic (LDPE)		Reservoir (LDPE)	
		5°C	22°C	5°C	22°C
Power	a	0.14 ± 0.01	0.35 ± 0.02	0.09 ± 0.02	0.06 ± 0.02
	b	0.22 ± 0.03	0.19 ± 0.02	0.13 ± 0.08[+]	0.51 ± 0.11
	Adj. r^2	0.8193	0.8678	0.1982	0.8007
Mod. Hyperbola	a	0.40 ± 0.07	1.27 ± 0.24	0.28 ± 0.20[+]	0.04 ± 0.02
	b	1.64 ± 0.33	2.33 ± 0.51	2.17 ± 1.75[+]	0.10 ± 0.07[+]
	Adj. r^2	0.8739	0.8439	0.2348	0.7288
Exp. rise to max.	a	0.22 ± 0.01	0.50 ± 0.02	0.12 ± 0.01	0.34 ± 0.10
	b	1.15 ± 0.18	1.59 ± 0.28	1.21 ± 0.68[+]	0.09 ± 0.05[+]
	Adj. r^2	0.8558	0.7846	0.2348	0.7099

[+] indicates that the regression coefficient was not significant

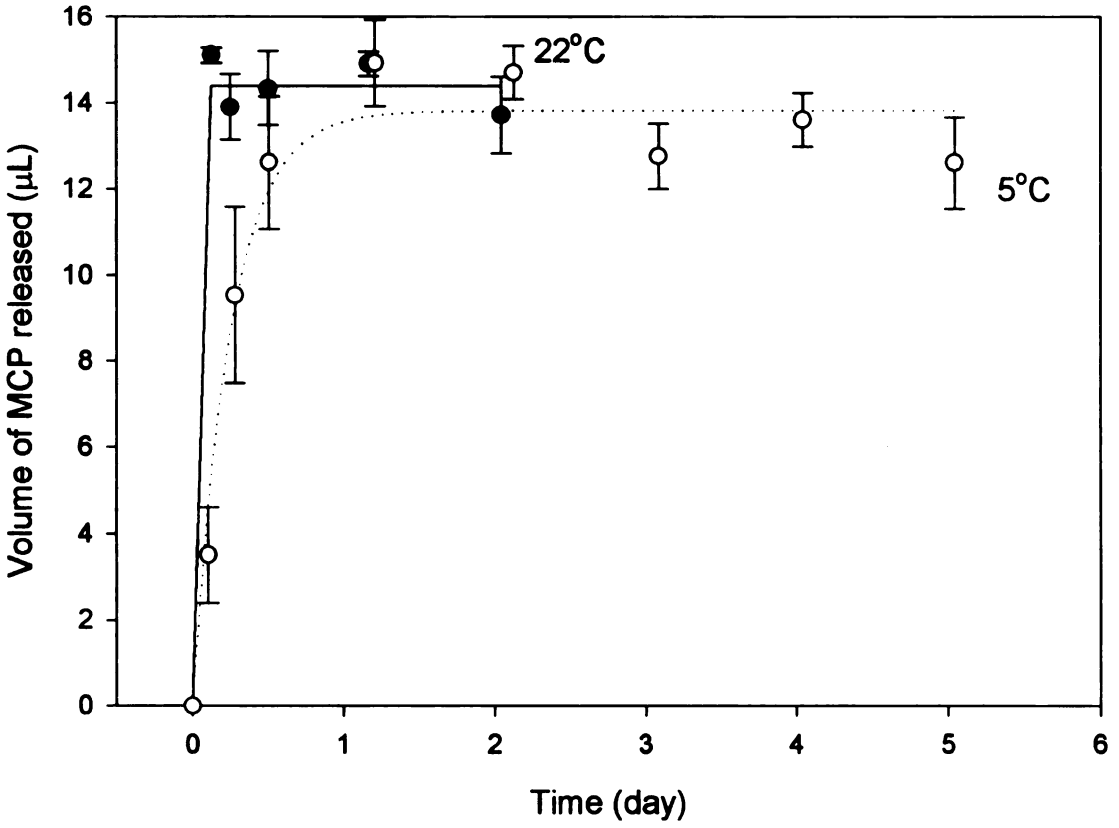

Figure 3.16. Volume of MCP released from approximately 30 mg of the molecular encapsulation complex at 5 and 22°C, ~100% RH. The error bar represents standard error.

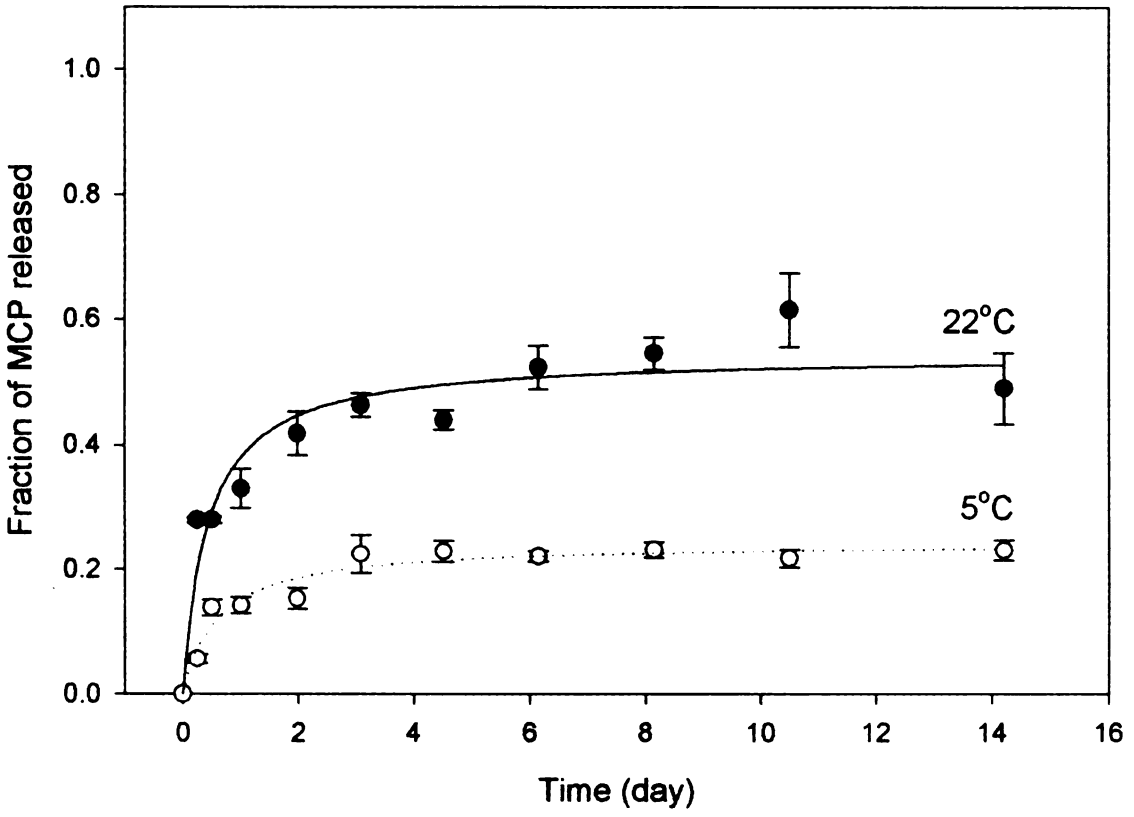

Figure 3.17. The experimental MCP release profiles of monolithic devices at 5°C (white circle) and at 22°C (black circle) and the predicted values of MCP release using the modified hyperbola function at 5°C (dotted line) and 22°C (solid line). The error bar represents standard error.

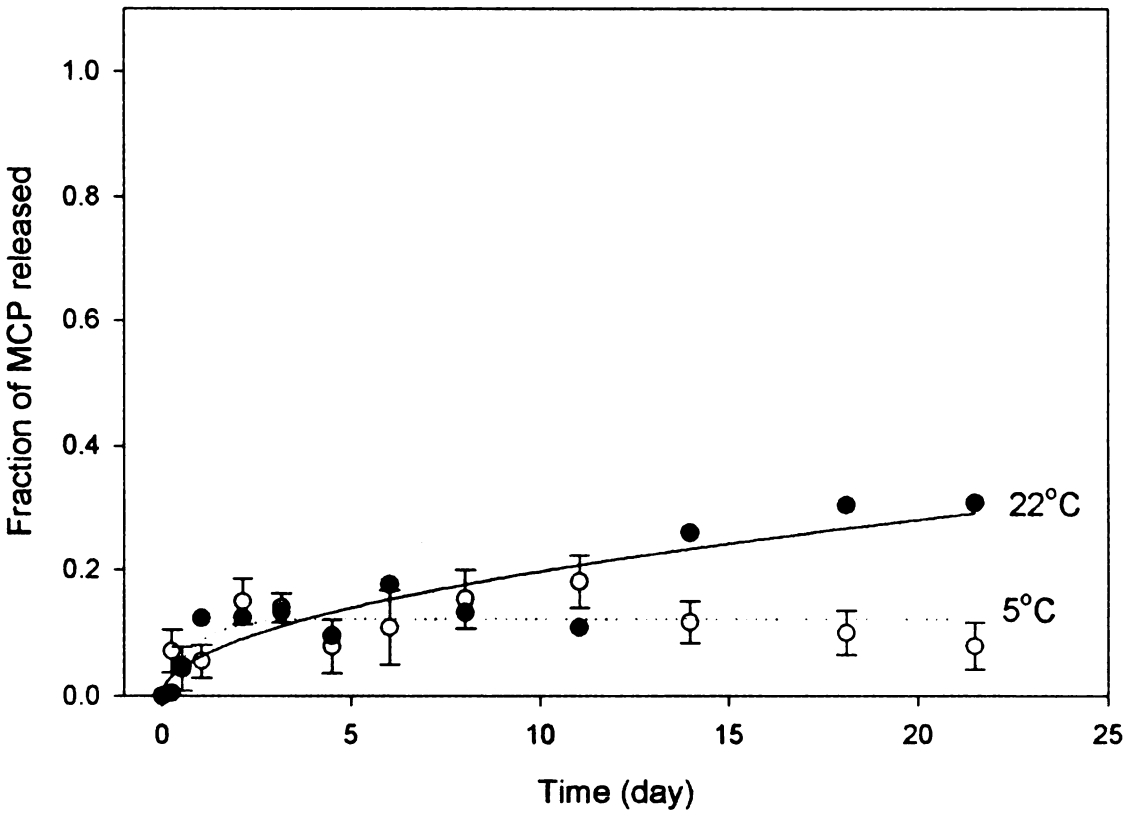

Figure 3.18. The experimental MCP release profiles of reservoir devices at 5°C (white circle) and at 22°C (black circle) and the predicted values of MCP release using the modified hyperbola function at 5°C (dotted line) and 22°C (solid line). The error bar represents standard error.

3.3.5 The effect of relative humidity on the release of MCP at 22°C

The effect of relative humidity was studied on monolithic (LDPE and EVA matrices) and reservoir (EVA membrane) devices and the molecular encapsulation complex. The release profiles were then compared to the release profile of the molecular encapsulation complex at the same temperature and relative humidity, represented as the fraction of MCP released.

MCP molecular encapsulation complex

Relative humidity has a significant impact on the volume of MCP released from the molecular encapsulation complex (Figure 3.19). The complex did not release MCP when subjected to RH of 75% or less. MCP began to desorb at 81% RH but the volume of MCP released was quite low. The powder was completely liquefied only when subjected to 93 and 100% RH. At 81 and 85%, the powder absorbed enough moisture to cause caking. No difference in appearance of the powder was observed at the other relative humidity levels.

The effect of relative humidity (81% to ~100%) was analyzed by fitting the release profile (based on the volume of MCP released) with the exponential rise to maximum function, which was previously found to best describe the release profile. The regression coefficients (Table 3.10) indicate that when the relative humidity increased, the amount of MCP released increased (higher coefficient *a*). The release rates at 81 and 85% relative humidity, as indicated by parameter b, were not significantly different but they were both less than at 93% RH. The release rate at ~100% was the highest.

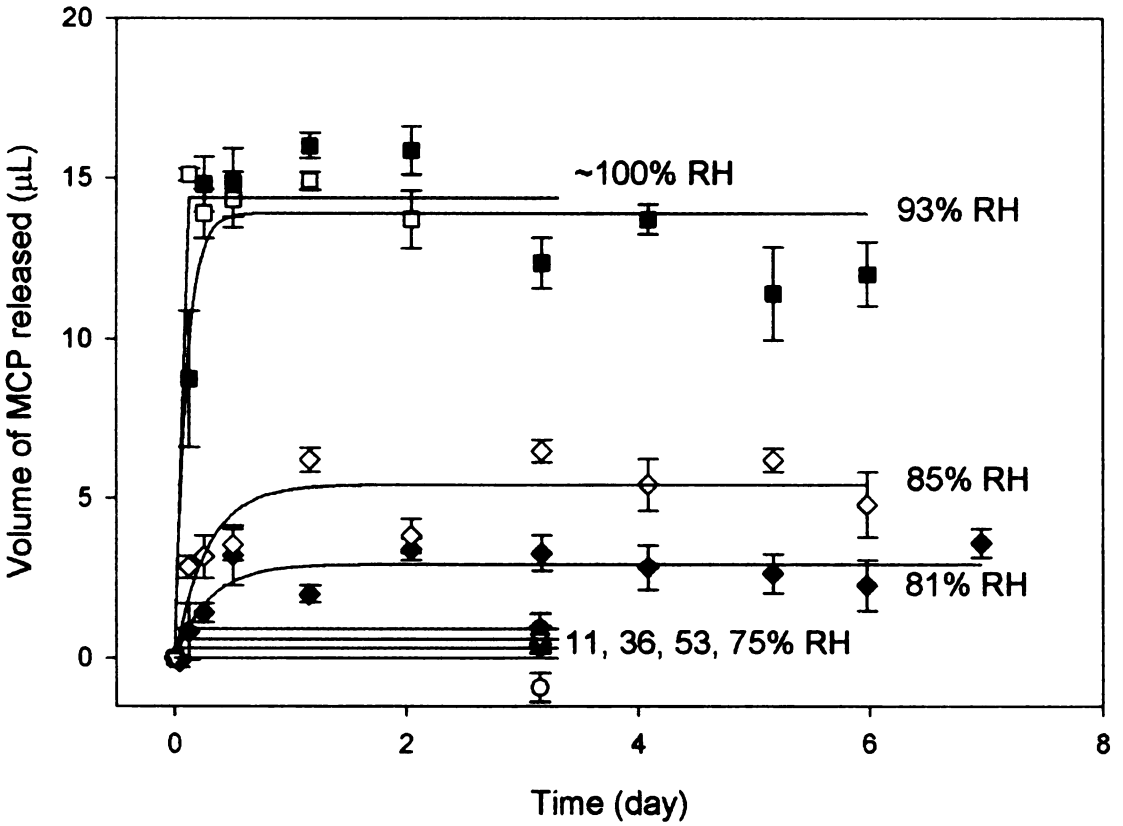

Figure 3.19. The experimental data for MCP volume released from the molecular encapsulation complex at 22°C when subjected to 11% RH (closed circle), 36% RH (open circle), 53% RH (closed triangle), 75% RH (open triangle), 81% RH (closed diamond), 85% RH (open diamond), 93% RH (closed square) and ~100% RH (open square). The predicted data based on linear function (11, 36, 53, 75 and ~100% RH) and exponential rise to maximum function (81, 85, 93% RH) are presented as a solid line. The error bar represents standard error.

Table 3.10. The regression coefficients and the adjusted r^2 of the volume of MCP released from the molecular encapsulation complex for an exponential rise to maximum function at 22°C.

Relative humidity	MCP Volume released		
	a	b	Adj. r^2
81%	2.94 ± 0.22	3.34 ± 1.22	0.5764
85%	5.42 ± 0.05	3.59 ± 0.90	0.6723
93%	13.90 ± 0.04	10.13 ± 2.54	0.7756
~100%	14.39 ± 0.27	2109 ± 3635410[+]	0.9649

[+] indicates that the regression coefficients was not significant

Monolithic device (EVA and LDPE matrices)

Relative humidity had a similar effect on the monolithic devices for both EVA and LDPE matrices (Figure 3.20 and 3.21). No MCP was released when either polymer matrix was subjected to a relative humidity of 75% or less. Change in surface roughness of the device was found at 85% RH but to a much lesser extent than at 93 and ~100% RH. The release profile at higher relative humidity was described by the modified hyperbola function, which was found to best describe the release profile of the monolithic device in a section 3.3.4. For devices with an EVA matrix, the only relative humidity tested was at ~100%. At this relative humidity, the device released MCP and the release profile based on the volume and ratio of MCP released was described by the following equations:

$$V_t = \frac{(16.86 \pm 4.08)\cdot t}{1+(1.64 \pm 0.50)\cdot t}$$

$$Q_t = \frac{(1.15 \pm 0.27)\cdot t}{1+(1.64 \pm 0.49)\cdot t}$$

The adjusted r^2 values for the V_t and Q_t equations were 0.7631 and 0.7786, respectively. All regression coefficients were significant. The fraction of MCP released as a function of time was presented in Figure 3.11.

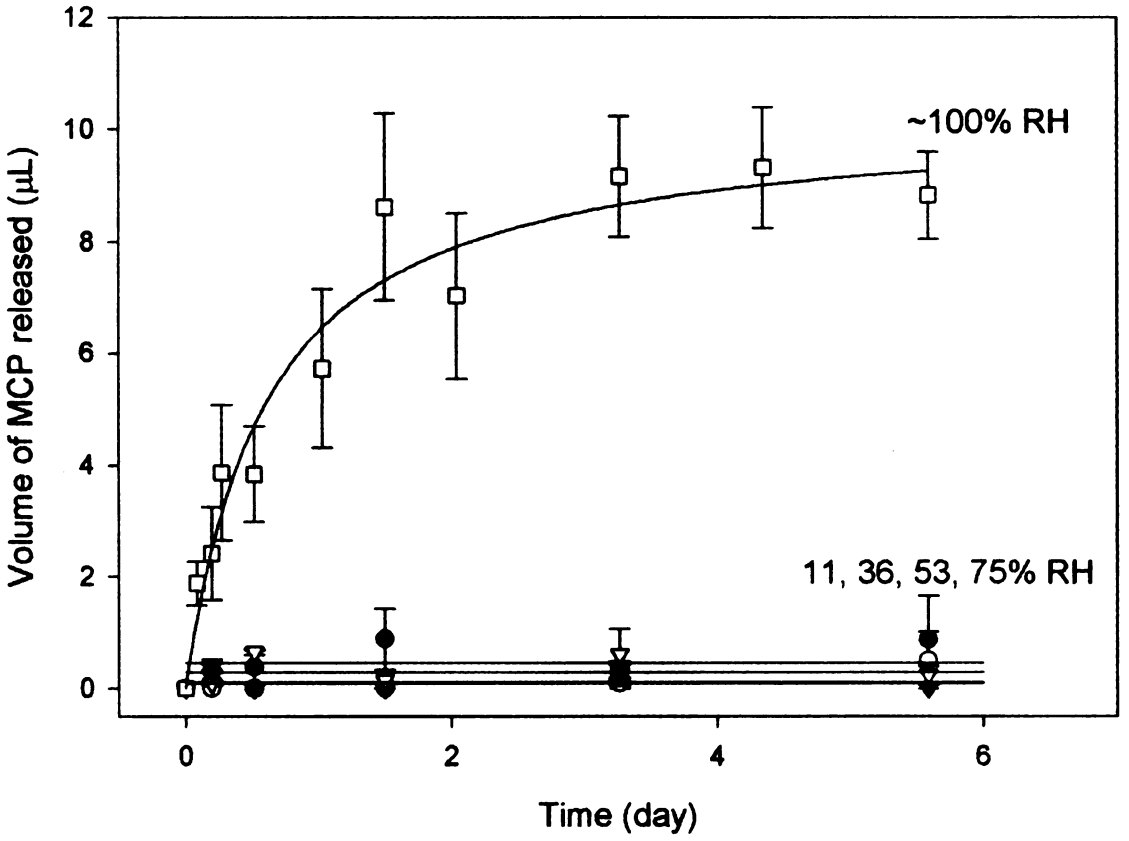

Figure 3.20. The experimental data for MCP volume released from the monolithic (EVA matrix) devices at 22°C when subjected to 11% RH (closed circle), 36% RH (open circle), 53% RH (closed triangle), 75% RH (open triangle) and ~100% RH (open square). The predicted data are based on linear function (11, 36, 53, 75) and modified hyperbola (100% RH) and are presented as a solid line. The error bar represents standard error.

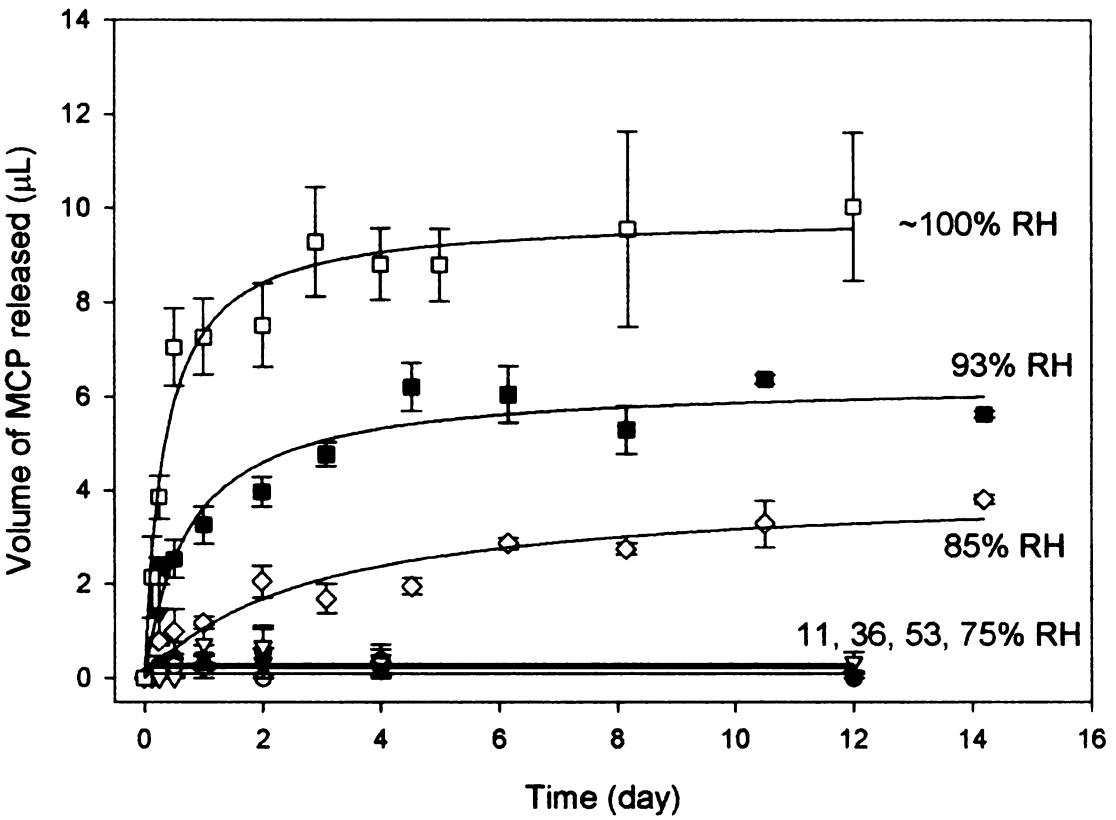

Figure 3.21. The experimental data for MCP volume released from the monolithic devices (LDPE matrix) at 22°C when subjected to 11% RH (closed circle), 36% RH (open circle), 53% RH (closed triangle), 75% RH (open triangle), 85% RH (open diamond), 93% RH (closed square) and ~100% RH (open square). The predicted data based on a linear function (11, 36, 53 and 75% RH) and modified hyperbola (85, 93 and 100% RH) are presented as a solid line. The error bar represents standard error.

Table 3.11. The regression coefficients and the adjusted r^2 of the MCP released from the monolithic devices (LDPE matrix) for a modified hyperbola function at 22°C.

RH	Volume of MCP released			Ratio of MCP released		
	a	b	Adj. r^2	a	b	Adj. r^2
85%	1.45 ± 0.29	0.36 ± 0.1	0.808	0.26 ± 0.05	0.35 ± 0.10	0.8150
93%	8.50 ± 1.46	1.35 ± 0.27	0.8685	0.63 ± 0.11	1.34 ± 0.27	0.8720
~100%	29.12 ± 7.12	2.96 ± 0.82	0.7848	2.02 ± 0.50	2.96 ± 0.83	0.7800

The relationship of the MCP released (based on the volume and fraction of MCP released) as a function of time for LDPE matrix device was also described by a modified hyperbola function (Table 3.11). Both regression coefficient *a* and *b* increased significantly with an increasing relative humidity (Table 3.11). The amount of MCP released was greater and the rate was higher at a higher relative humidity. The release rate based on fraction of MCP (Figure 3.22) followed the same pattern as the release profile based on the volume of MCP released. However, the device at 85% RH released a higher fraction of MCP than the device at 93 and ~100% RH.

Reservoir devices (EVA membrane)

EVA membrane reservoir devices were studied at 85, 93 and ~100%. These were the conditions that provided sufficient moisture to release MCP from the molecular encapsulation complex and the monolithic devices. Change in thickness at the location of the powder agglomeration was observed at 93 and 100% RH. The reservoir device released MCP under all three conditions. As

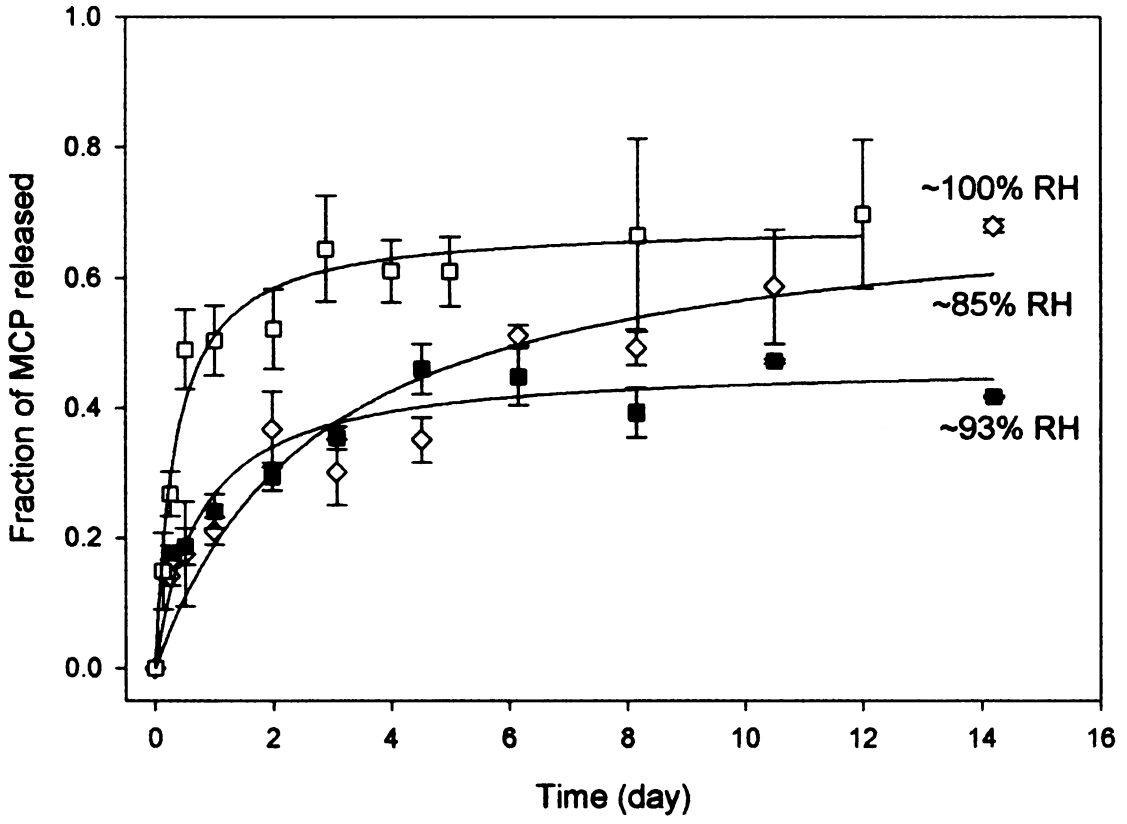

Figure 3.22. The experimental data for fraction of MCP released from the monolithic devices (LDPE matrix) at 22°C when subjected to 85% RH (open diamond), 93% RH (closed square) and ~100% RH (open square). The predicted data based on modified hyperbola are presented in a solid line. The error bar represents standard error.

time progressed up to 8 days, the volume of MCP in the test container increased but between 8 and 16 days, the volume of MCP in the test container decreased. This decrease after 8 days was not observed for any devices containing LDPE polymer. The reduction of the MCP concentration in the headspace of the test container is attributed to MCP absorption by EVA, as observed in the permeability experiment.

Only the release rate (both fraction and volume) up to 8 days was used to determine the regression coefficients of the exponential rise to maximum function. Table 3.12 shows that the regression coefficients for devices at 93 and ~100% RH were not significantly different. Coefficient *a* at these two RH levels was greater than that of the device at 85% RH based on the volume of MCP released and significantly less than that of the device at 85% RH based on fraction of MCP released. Coefficient *b* at 85% RH was not significantly different from that at ~100% RH but slightly less than that at 93% RH. This indicates that RH affected the volume of MCP released but did not have as much effect on the rate at which it was released. The effect of relative humidity on the volume of MCP released diminished at RH greater than 93%.

The fraction of MCP released as a function of time (Figure 3.24) shows that the devices at 93 and ~100% RH released approximately 80% of the expected MCP at these relative humidity levels. At 85% RH, the fraction of MCP released was higher than at other relative humidities and the value was greater than 1. This was also found in the monolithic device (LDPE matrix) where the fraction of MCP released at 85% was higher than at 93%. This may be a result

Table 3.12. The regression coefficients and the adjusted r2 of the MCP released from the reservoir devices (EVA membrane) for an exponential rise to maximum function at 22°C.

RH	Volume of MCP released			Ratio of MCP released		
	a	b	Adj. r^2	A	b	Adj. r^2
85%	8.30 ± 1.48	0.24 ± 0.08	0.8293	1.50 ± 0.27	0.24 ± 0.09	0.8189
93%	10.67 ± 0.85	0.60 ± 0.15	0.8474	0.78 ± 0.06	0.62 ± 0.16	0.8363
~100%	12.24 ± 1.24	0.38 ± 0.10	0.8222	0.88 ± 0.09	0.38 ±0.1	0.8218

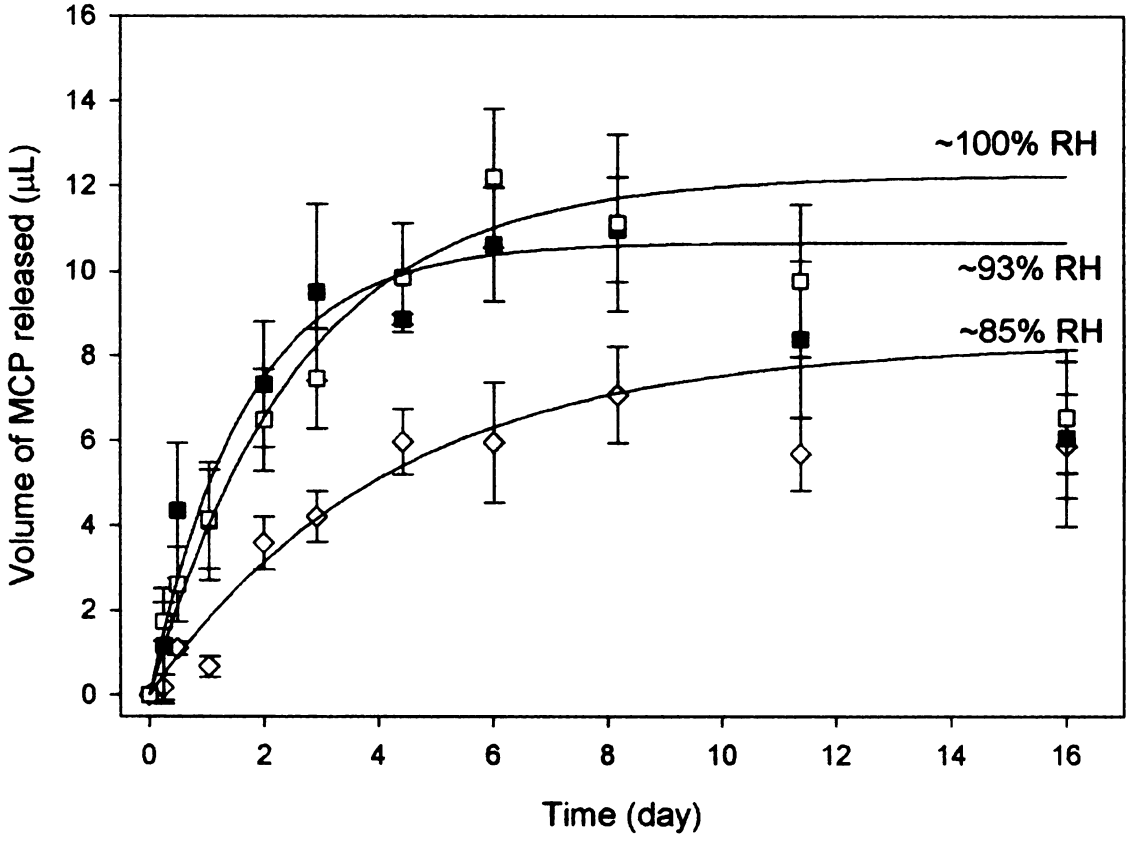

Figure 3.23. The experimental data for MCP volume released from the reservoir devices (EVA membrane) at 22°C when subjected to 85% RH (open diamond), 93% RH (closed square) and ~100% RH (open square). The predicted data based on a modified hyperbola are presented as a solid line. The error bar represents standard error.

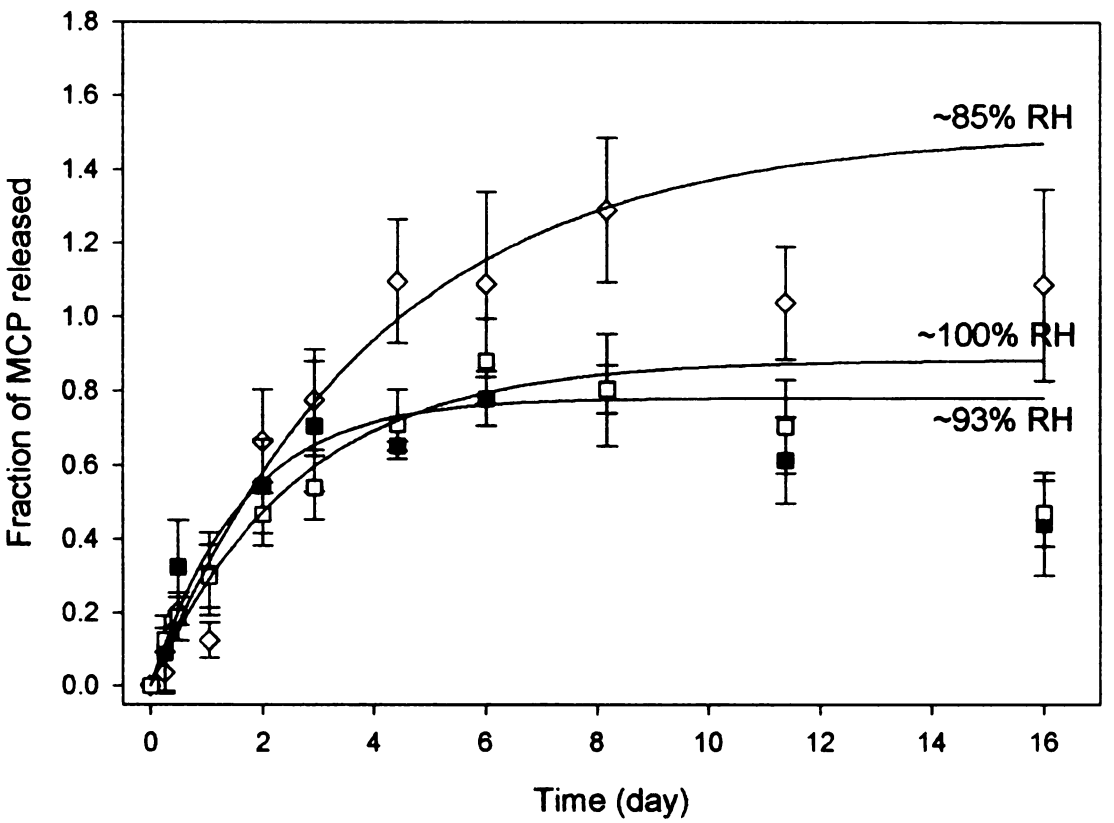

Figure 3.24. The experimental data for fraction of MCP released from the reservoir devices (EVA membrane) at 22°C when subjected to 85% RH (open diamond), 93% RH (closed square) and ~100% RH (open square). The predicted data based on a modified hyperbola are presented as a solid line. The error bar represents standard error.

of an underestimation of MCP released from the molecular encapsulation complex at 85% RH, which was used as the expected volume when calculate Q_t at 85% RH.

According to these results, EVA is not an appropriate polymer for use in MCP controlled release devices because it absorbs MCP. Although LDPE has higher MCP and water barrier, it is a better choice due to its low interaction with MCP. The LDPE monolithic device released more MCP at a faster rate than the reservoir device. Therefore, the release rate of the monolithic device (LDPE matrix) was chosen to further study the effect of relative humidity at 5°C.

3.3.6 The effect of relative humidity on the release of MCP at 5°C

MCP molecular encapsulation

The release rate of the molecular encapsulation complex at 5°C was studied at 79, 87, 97 and 100% RH. In this range, the relative humidity affected the release amount and the rate of MCP released from the complex (Figure 3.25). The exponential rise to maximum function was used to describe the release profile. The regression coefficients are presented in Table 3.13. This model described the release at 87, 97 and 100% RH satisfactorily. At 79% RH, the atmospheric moisture was not enough to release a significant amount of MCP from the complex. Because the coefficient *b* of exponential rise to maximum function at 79% RH was large but not significant, this function was reduced to a linear function of Q = a, which is a linear function. Both regression coefficients (*a* and *b*) at 87% RH were less than at 97 and ~100% RH. This

Table 3.13. The regression coefficients and the adjusted r^2 of the MCP released from the molecular encapsulation complex for an exponential rise to maximum function at 5°C.

RH	Volume of MCP released		
	a	b	Adj. r^2
79%	1.07 ± 0.15	9.43 ± 8.93[+]	0.2153
87%	10.12 ± 0.34	1.88 ± 0.26	0.9135
97%	13.08 ± 0.45	4.69 ± 0.78	0.8757
~100%	13.81 ± 0.49	3.98 ± 0.67	0.8746

[+] indicates that the regression coefficients was not significant

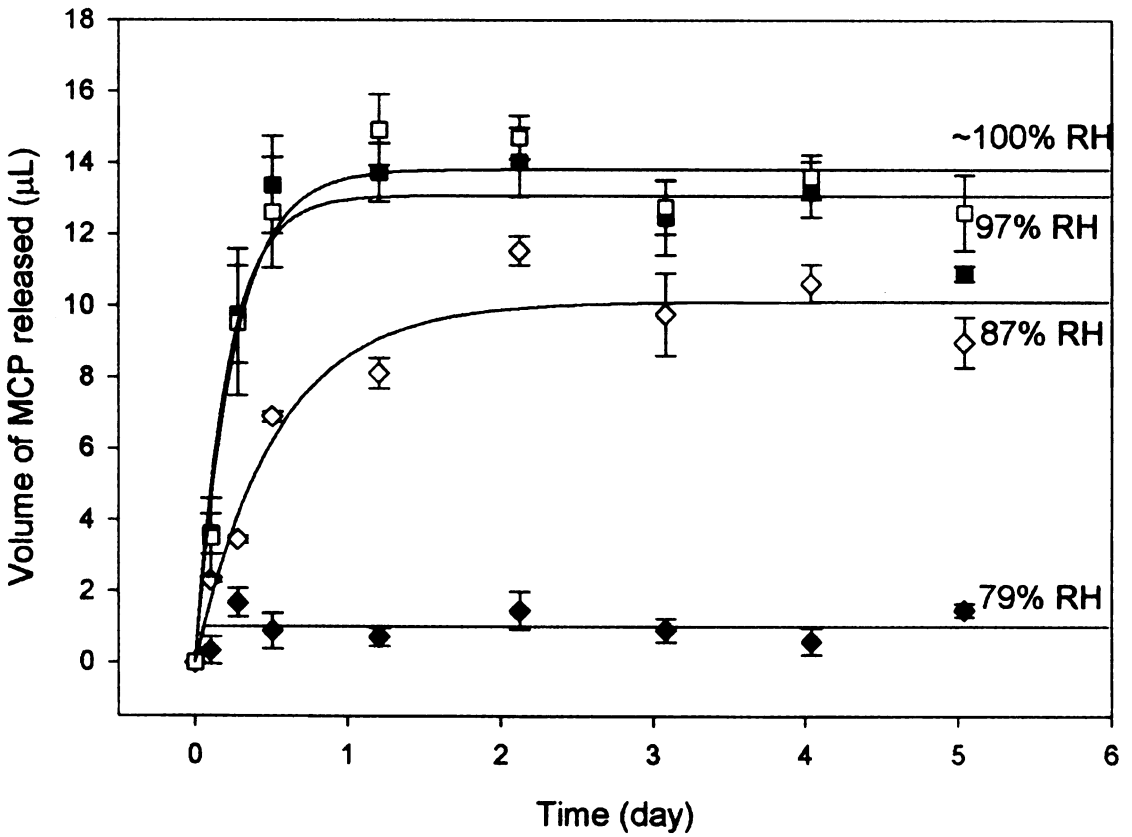

Figure 3.25. The experimental data for volume of MCP released from the molecular encapsulation complex at 5°C when subjected to 79% RH (closed diamond), 87% RH (open diamond), 97% RH (closed square) and ~100% RH (open square). The predicted data based on an exponential rise to maximum function are presented as a solid line.

indicates that at 87% RH, less MCP was released from the complex than at 97 and ~100% RH and at a slower rate.

Monolithic devices (LDPE matrix)

The release of MCP from the monolithic device (LDPE matrix) was studied at 87, 97 and ~100% RH. The release profiles (Figure 3.26) were fitted with a modified hyperbola function. The regression parameters are presented in Table 3.14. The volume of MCP released from the devices at 87 and 97% RH was very low and could not be described satisfactorily by the modified hyperbola function as indicated by the insignificance of coefficients *a* and *b*. The fraction of MCP released and the release rate at 87 and 97% relative humidity were very similar (Figure 3.27). At these relative humidity levels, the device only released about 10% of the amount of MCP expected to be released while at ~100% RH, about 20% was released. Although 87 and 97% RH provided sufficient moisture to result in the release of MCP from the molecular encapsulation, the low water vapor permeability at this temperature prevented sufficient water from permeating into the polymer. Thus, not enough moisture was available to release MCP from the molecular complex.

Table 3.14. The regression coefficients and the adjusted r^2 of the MCP released from the monolithic device (LDPE matrix) for an exponential rise to maximum function at 22°C.

RH	Volume of MCP released			Ratio of MCP released		
	A	b	Adj. r^2	a	b	Adj. r^2
87%	2.80 ± 3.98$^+$	2.92 ± 4.61$^+$	0.0815	0.28 ± 0.40$^+$	2.91 ± 4.65$^+$	0.0623
97%	1.04 ± 0.52$^+$	0.59 ± 0.38$^+$	0.1318	0.08 ± 0.04$^+$	0.56 ± 0.14$^+$	0.4953
~100%	5.52 ± 1.03	1.64 ± 0.35	0.8602	0.40 ± 0.07	1.64 ± 0.33	0.8739

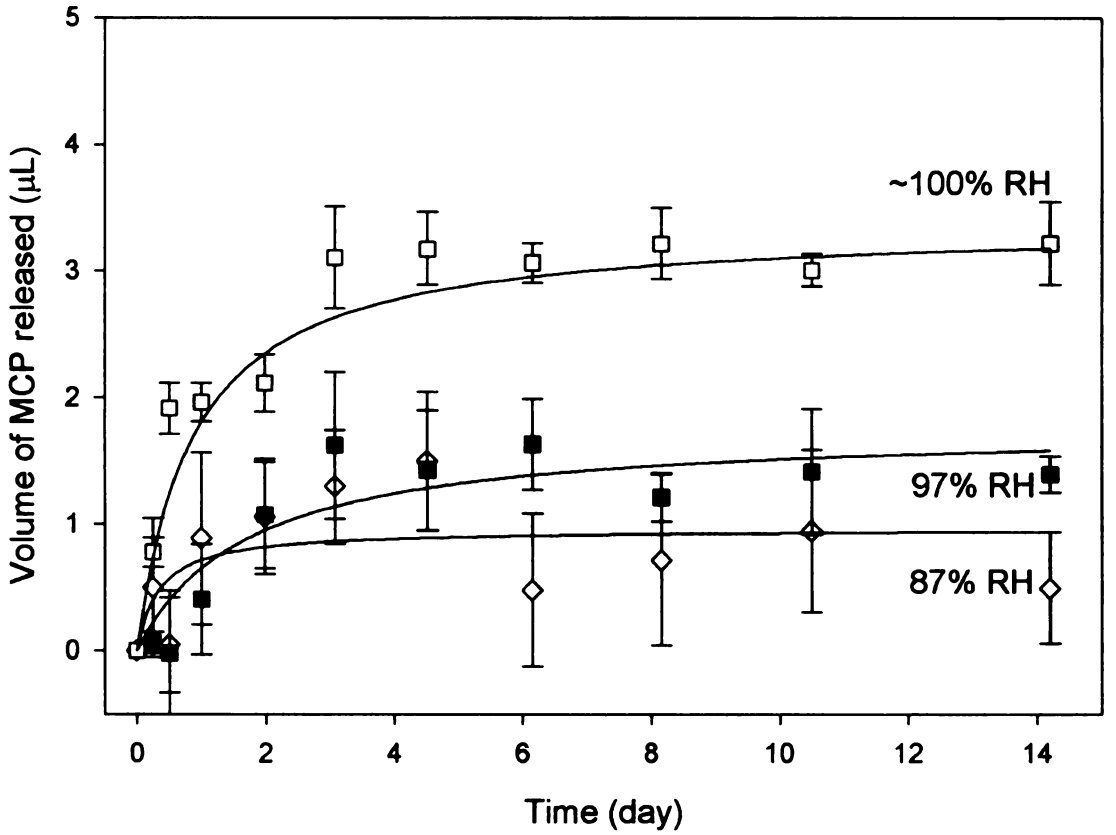

Figure 3.26. The experimental data for volume of MCP released from the monolithic device (LDPE matrix) at 5°C when subjected to 85% RH (open diamond), 93% RH (closed square) and 100% RH (open square). The predicted data based on an exponential rise to maximum are presented as a solid line.

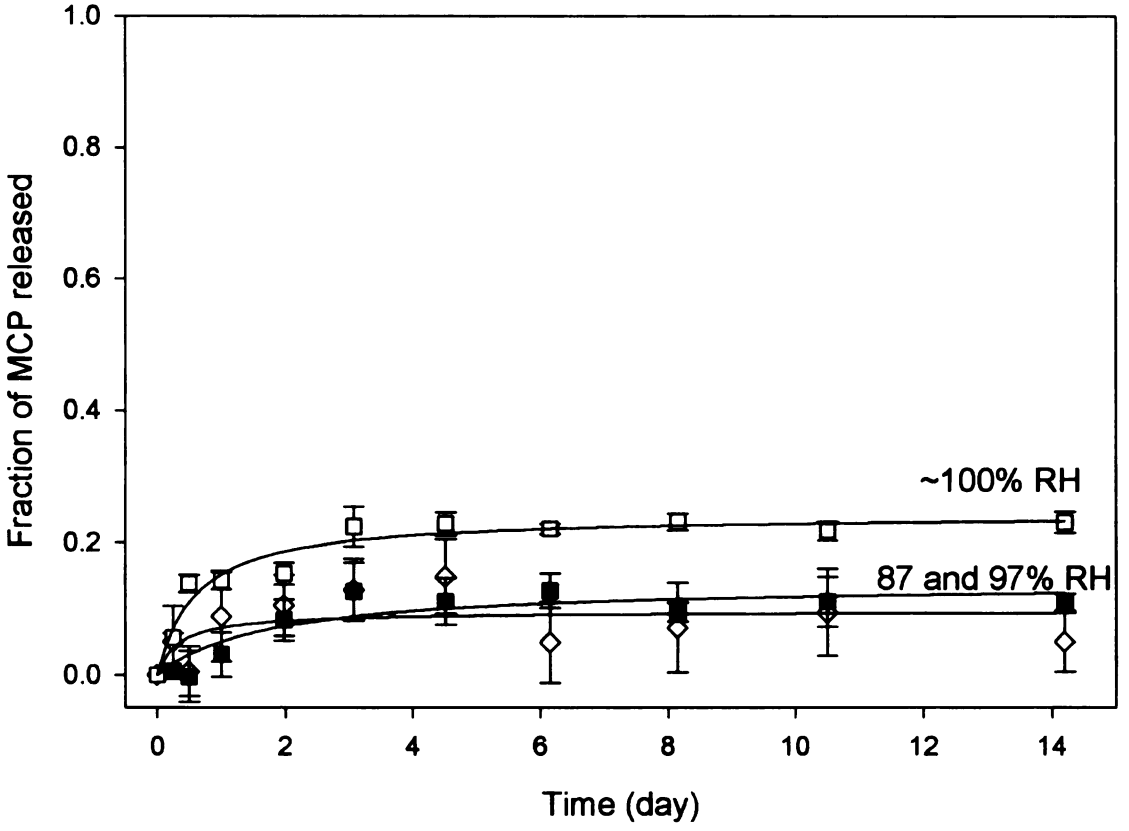

Figure 3.27. The experimental data for fraction of MCP released from the monolithic device (LDPE matrix) at 5°C when subjected to 85% RH (open diamond), 93% RH (closed square) and 100% RH (open square). The predicted data based on an exponential rise to maximum are presented as a solid line.

Of the two rate controlling polymers evaluated, LDPE was the more suitable for use in the controlled release device. The main reason was that it did not interact with (absorb) MCP. Of the two devices (LDPE matrix) the monolithic device had a more desirable release rate because the reservoir device only released a small amount of MCP even at the highest temperature and relative humidity tested. The monolithic device also has several advantages over the reservoir device. To make this device is a simpler process and can be accomplished in one continuous step in large scale production. The molecular encapsulation complex is also contained within the polymer matrix and, therefore, it is not likely to disintegrate and prematurely release MCP immediately when exposed to humid air. It would also prevent contamination of the product with the encapsulation powder if the device disintegrated.

The controlled release device could be used for MCP treatment for any produce that can benefit from repeated or continuous treatments such as tomatoes, apples and avocados. The device is not intended to replace a single treatment at the time of harvest because the release rate would be too slow to achieve the right MCP concentration. The anticipated use is as an additional treatment to prevent produce from regaining its sensitivity to ethylene. The controlled release device allows in-package treatment by including this device in a sealed package. When designing the in-package treatment, serious consideration must be given to the packaging material used. The packaging materials must have the following properties

- Heat sealable to prevent MCP escaping through pores or channels

- High MCP barrier to reduce the loss of MCP through permeation
- High water vapor barrier to retain moisture from respiration of the produce and to create an atmosphere with sufficient RH to cause release of MCP
- Oxygen and carbon dioxide permeability should be appropriate to create an optimum modified atmosphere condition and not cause anaerobic respiration

Once the packaging system is decided, the number of device can be determined according to the amount of produce in the package and MCP transmission rate across the packages. The MCP mass transfer occurring in the package is envisioned in Figure 3.28. MCP released from the device could be absorbed by the produce, remain in headspace or permeate out from the package.

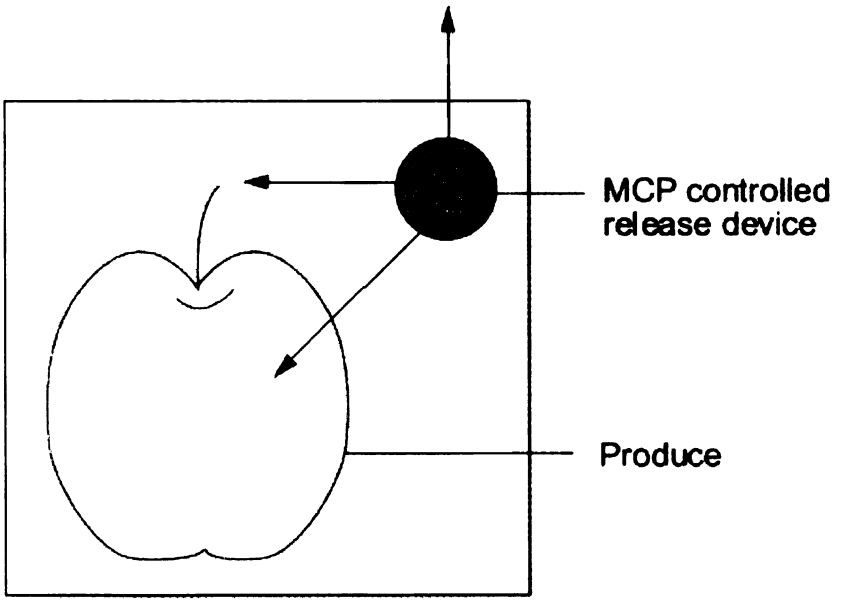

Figure 3.28. The envisioned MCP mass transfer activity in produce – package system containing MCP controlled release devices

The model for the amount of MCP absorbed by produce, MCP in the package headspace, and MCP permeated out from the package is proposed with the following assumption:

1. The fraction of MCP absorbed by produce is not concentration dependent.
2. The permeability of packaging material is not concentration dependent.
3. The permeation process of MCP in packaging material is at steady-state.
4. The headspace in the package is constant.

Based on these assumptions, the numerical model for MCP mass distribution for a certain period of time is proposed to be:

$$n \cdot \left(V_{t\,n+1} - V_{t\,n}\right) = \left[x \cdot W \cdot \Delta t\right] + \left[V_{MCP}\right] + \left[\frac{P}{\ell} \cdot A\left(\frac{V_{MCP}}{V_{HS}} \cdot P_{atm}\right) \cdot \Delta t\right]$$

where n is number of devices in the package, V_t is the volume of MCP released from device at time t, x is fraction of MCP absorbed by produce (= volume of MCP/weight of fruits), W is weight of fruit, Δt is $t_{n+1} - t_n$, V_{MCP} is volume of MCP in the headspace, P is permeability of packaging material, ℓ is thickness of packaging material, A is surface are of the package, V_{HS} is headspace volume, and P_{atm} is atmospheric pressure.

3.4 Summary and Conclusion

Four controlled release devices, monolithic (LDPE and EVA matrices) and reservoir (LDPE and EVA membrane), were developed and their release rates were determined. The two polymer matrices of monolithic devices had similar

release profiles but EVA was found to absorb MCP which caused a reduction in MCP concentration. The reservoir device released MCP at a slower rate than did the monolithic device. Release from reservoir device depends largely on the polymer membrane. The LDPE device released MCP very slowly while EVA released a greater amount of MCP at a higher rate.

The storage conditions, i.e. temperature and relative humidity, had a significant effect on MCP release from the device. The amount of MCP released and the release rate were greater at higher temperature because both MCP and water vapor permeation processes are enhanced. Relative humidity had a great effect on the release rate. The minimum relative humidity that triggered the release of MCP from the molecular encapsulation complex was 81% and 87% RH at 22 and 5°C, respectively. The release rate and release volume increased with increasing RH for the monolithic device (LDPE matrix) at 22°C but at 5°C the device only released a significant amount of MCP at ~100% RH. For the EVA reservoir device, the increased RH resulted in an increased volume of MCP released but did not affect the release rate.

The LDPE monolithic device has the most desirable characteristics both in that it does not react with MCP and will not cause a safety concern in case device disintegrates. The anticipated use of the device is as an in-package treatment as a supplement to the single application following harvest of the produce. It would be ideal for produce such as tomatoes, apples and avocados that benefit from repeated and/or continuous exposure to MCP.

CONCLUSION

The objectives of this research were to evaluate MCP-treated apples as a potential raw material for fresh-cut apples and, second, to develop of a device to enable continuous in-package application of MCP.

The combination of MCP treatment and CA storage resulted in intact apples with more firmness than intact apples subjected to the individual treatment. This resulted in apple slices with greater firmness. However, slices from apples subjected to the combination treatment had high susceptibility to enzymatic browning, and thus, had the most flesh discoloration. In addition, they had different volatile profiles from slices. Apples from the combination treatment are suitable as the raw material of fresh-cut apples only when the enzymatic browning can be minimized by controlling external factors through use of higher concentration of antibrowning agent, well controlled cold chain distribution and reduced oxygen atmosphere. When the external factors can not be tightly controlled, MCP treated apples or CA storage apples are the better choice as raw materials. At 3 months storage of intact apples, MCP-treated apples were better than CA storage apples because they had the greatest firmness while their susceptibility to enzymatic browning and the volatiles production were similar to apples in CA storage. At 9 months storage, MCP treatment was the most suitable treatment although the slice firmness had declined significantly. The firmness was still greater than the minimum threshold (53.4 N). MCP treated apple slices produced more hexyl acetate and were less sensitive to enzymatic

browning than slices from other apples. At 5 and 7 months storage, CA storage apple and MCP treated apple slices had similar quality.

Four controlled release devices, monolithic (LDPE and EVA matrices) and reservoir (LDPE and EVA membrane) were developed. The release profiles for the four devices were similar but the amount of MCP released and the release rate. Among them, the LDPE monolithic device had the most desirable characteristics in that it did not react with MCP and for safety reason in the case where the device may disintegrate. The release characteristics of the LDPE monolithic device depended largely on temperature and relative humidity. The amount of MCP released and the release rate from the device increased with increasing temperature. The effects of relative humidity at 22 and 5°C were different. The amount of MCP released and the release rate increased with an increasing RH at 22°C but had very little effect at 5°C. The anticipated use of the device as an in-package treatment would likely be to supplement the single application after harvest for produce such as tomatoes, apples, and avocados that benefit from repeated or continuous treatment MCP treatment.

APPENDICES

APPENDIX A

SAS CODES FOR STATISTICAL ANALYSIS OF APPLES CONDITION AND FRESH-CUT APPLES QUALITY

SAS code for two-way analysis of variance used for analyzing the effect of MCP treatment and storage atmosphere on the quality of apples before fresh-cut apple processing

```
************************************************
proc mixed data=Initialapple;
by month;
class storage MCP;
model a=storage MCP storage*MCP;
lsmeans storage*MCP/diff;
run;
/a is a response, storage is storage atmosphere,
MCP is MCP treatment/
************************************************
```

SAS code for repeated measurement analysis for analyzing the effect of postharvest condition on flesh color and texture of fresh-cut apples during 14 days storage

```
************************************************
proc mixed data=freshcut color;
by time;
class Storage MCP NS day apple;
model a= Storage|MCP|NS|day/ddfm=satterth;
repeated day/type=ar(1)
subject=apple(storage*MCP*NS*day);
lsmeans Storage*MCP*NS/diff;
run;
/a is a response, storage is storage atmosphere,
MCP is MCP treatment, NS is antibrowning agent,
day is storage time of fresh-cut apple/
************************************************
```

SAS code for repeated measurement analysis for analyzing the effect of postharvest condition on individually selected volatile compound during 14 day storage.

```
*****************************************************
proc mixed data=volatiles;
by time;
class Storage MCP day apple;
model EA= Storage|MCP|day/ddfm=satterth;
repeated day/type=ar(1) subject=apple(storage*day);
lsmeans Storage*MCP*day/diff;
MAKE 'diffs' OUT=diff;
MAKE 'lsmeans' OUT=means;
run;
/a is a response, storage is storage atmosphere,
MCP is MCP treatment, day is storage time of fresh-
cut apple/
*****************************************************
```

APPENDIX B

STATISTICAL ANALYSIS OF THE EFFECT OF POSTHARVEST TREATMENTS ON THE SUBSEQUENT QUALITY OF FRES-CUT APPLES

B1. The effect of postharvest treatment on the condition of intact apples before processing

Table B1. p-value for main effect and interaction of storage condition (storage) and MCP treatments (MCP) of IEC, °Brix, firmness, L*, a* and b* after 3, 5, 7 and 9 month storage

Response	Factor	Storage time, month			
		3	5	7	9
Ln (IEC)	Storage	0.0070	<0.0001	<0.0001	<0.0001
	MCP	<0.0001	<0.0001	<0.0001	ns
	Storage * MCP	ns	ns	ns	ns
°Brix	Storage	ns	0.0098	ns	0.0239
	MCP	ns	ns	< 0.0001	ns
	Storage * MCP	0.0397	ns	ns	ns
Firmness	Storage	0.0017	0.0001	0.0211	0.0010
	MCP	< 0.0001	0.0001	0.0002	0.0004
	Storage * MCP	0.0125	ns	ns	ns
L*	Storage	ns	0.0099	0.0150	ns
	MCP	0.0080	0.0132	0.0001	ns
	Storage * MCP	ns	ns	ns	ns
a*	Storage	ns	ns	ns	0.0208
	MCP	ns	ns	ns	ns
	Storage * MCP	ns	ns	ns	ns
b*	Storage	ns	ns	ns	ns
	MCP	ns	ns	ns	0.0208
	Storage * MCP	ns	ns	ns	0.0295

ns = not significant different (p-value > 0.05)

Table B2. Pairwise comparison of Ln (IEC) between 4 postharvest treatments at 3, 5, 7 and 9 month storage

Storage time		Air	Air + MCP	CA	CA + MCP
3 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*		*	
5 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*	*	*	
7 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*	*	*	
9 months	Air				
	Air + MCP				
	CA	*	*		
	CA + MCP	*	*	*	

* denotes the statistically significant difference (p-value < 0.05)

Table B3. Pairwise comparison of °Brix between 4 postharvest treatments at 3, 5, 7 and 9 month storage

Storage time		Air	Air + MCP	CA	CA + MCP
3 months	Air				
	Air + MCP	*			
	CA				
	CA + MCP				
5 months	Air				
	Air + MCP				
	CA	*	*		
	CA + MCP				
7 months	Air				
	Air + MCP	*			
	CA		*		
	CA + MCP	*		*	
9 months	Air				
	Air + MCP				
	CA				
	CA + MCP	*			

* denotes the statistically significant difference (p-value < 0.05)

Table B4. Pairwise comparison of firmness between 4 postharvest treatments at 3, 5, 7 and 9 month storage

Storage time		Air	Air + MCP	CA	CA + MCP
3 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*			
5 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*	*	*	
7 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*		*	
9 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*	*	*	

* denotes the statistically significant difference (p-value < 0.05)

Table B5. Pairwise comparison of L*-value between 4 postharvest treatments at 3, 5, 7 and 9 month storage

Storage time		Air	Air + MCP	CA	CA + MCP
3 months	Air				
	Air + MCP	*			
	CA				
	CA + MCP	*		*	
5 months	Air				
	Air + MCP				
	CA				
	CA + MCP	*	*	*	
7 months	Air				
	Air + MCP	*			
	CA				
	CA + MCP	*	*	*	
9 months	Air				
	Air + MCP				
	CA				
	CA + MCP				

* denotes the statistically significant difference (p-value < 0.05)

Table B6. Pairwise comparison of a*-value between 4 postharvest treatments at 3, 5, 7 and 9 month storage

Storage time		Air	Air + MCP	CA	CA + MCP
3 months	Air				
	Air + MCP				
	CA				
	CA + MCP				
5 months	Air				
	Air + MCP				
	CA				
	CA + MCP				
7 months	Air				
	Air + MCP				
	CA				
	CA + MCP				
9 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*			

* denotes the statistically significant difference (p-value < 0.05)

Table B7. Pairwise comparison of b*-value between 4 postharvest treatments at 3, 5, 7 and 9 month storage

Storage time		Air	Air + MCP	CA	CA + MCP
3 months	Air				
	Air + MCP				
	CA				
	CA + MCP				
5 months	Air				
	Air + MCP				
	CA				
	CA + MCP				
7 months	Air				
	Air + MCP				
	CA				
	CA + MCP				
9 months	Air				
	Air + MCP	*			
	CA	*			
	CA + MCP	*			

* denotes the statistically significant difference (p-value < 0.05)

B2. The effect of postharvest treatment on the flesh color of FC apples

Table B8. p-value for main effect and interaction of storage condition (storage) and MCP treatments (MCP), antibrowning treatment (AB) and shelf life (time) of L*, a*, b* and ΔE of FC apples from apples after 3, 5, 7 and 9 month storage

Response	Factor	Storage time of intact apples, month			
		3	5	7	9
L*-value	Storage	<0.0001	0.0001	<0.0001	<0.0001
	MCP	<0.0001	0.0001	<0.0001	<0.0001
	Storage * MCP	ns	0.0116	ns	-
	AB	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * AB	ns	ns	ns	<0.0001
	MCP * AB	ns	ns	<0.0001	<0.0001
	Storage * MCP * AB	ns	0.0417	0.0023	-
	Time	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * time	ns	<0.0001	<0.0001	<0.0001
	MCP * time	ns	ns	ns	ns
	Storage * MCP * time	ns	ns	ns	-
	AB * time	ns	ns	ns	<0.0001
	Storage * AB * time	ns	ns	ns	ns
	MCP * AB * time	ns	ns	ns	ns
	Storage * MCP * AB *time	ns	ns	ns	ns
a*-value	Storage	ns	<0.0001	0.0109	ns
	MCP	0.0065	0.0102	0.0002	ns
	Storage * MCP	ns	<0.0001	ns	-
	AB	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * AB	ns	ns	ns	0.0017
	MCP * AB	ns	ns	0.0035	
	Storage * MCP * AB	ns	0.0079	ns	-
	Time	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * time	ns	ns	<0.0001	<0.0001
	MCP * time	ns	ns	ns	ns
	Storage * MCP * time	ns	ns	ns	ns
	AB * time	ns	ns	ns	ns
	Storage * AB * time	ns	ns	ns	ns
	MCP * AB * time	ns	ns	ns	ns
	Storage * MCP * AB *time	ns	ns	ns	ns

Table B8. (continued)

Response	Factor	Storage time of intact apples, month			
		3	5	7	9
b*-value	Storage	ns	0.0291	0.0395	<0.0001
	MCP	0.0490	0.0020	0.0207	0.0130
	Storage * MCP	0.0054	<0.0001	<0.0001	-
	AB	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * AB	ns	ns	ns	<0.0001
	MCP * AB	0.1092	0.0022	0.0005	0.0008
	Storage * MCP * AB	ns	0.0152	0.0025	-
	Time	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * time	ns	ns	ns	0.0002
	MCP * time	ns	ns	ns	ns
	Storage * MCP * time	ns	ns	ns	-
	AB * time	ns	ns	ns	<0.0001
	Storage * AB * time	ns	ns	ns	ns
	MCP * AB * time	ns	ns	ns	ns
	Storage * MCP * AB *time	ns	ns	ns	-
ΔE	Storage	ns	<0.0001	<0.0001	<0.0001
	MCP	0.0418	ns	0.0156	0.0130
	Storage * MCP	ns	0.0092	ns	-
	AB	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * AB	ns	ns	ns	<0.0001
	MCP * AB	ns	ns	0.0053	0.0008
	Storage * MCP * AB	ns	ns	ns	-
	Time	<0.0001	<0.0001	<0.0001	<0.0001
	Storage * time	ns	ns	<0.0001	0.0002
	MCP * time	ns	ns	ns	ns
	Storage * MCP * time	ns	ns	ns	-
	AB * time	ns	ns	ns	<0.0001
	Storage * AB * time	ns	ns	ns	ns
	MCP * AB * time	ns	ns	ns	ns
	Storage * MCP * AB *time	ns	ns	ns	-

ns = not significant different (p-value > 0.05)

Table B9. Pairwise comparison of L*-value between 4 postharvest treatments A (air), AM (Air + MCP), CA (controlled atmosphere storage) and CAM (CA + MCP) with and without antibrowning agent (AB) at 3, 5, 7 and 9 month storage

Storage time		A	A/AB	AM	AM/AB	CA	CA/AB	CAM	CAM/AB
3 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB		*	*					
	CA	*	*	*	*				
	CA/AB	*	*	*	*	*			
	CAM	*	*		*	*	*		
	CAM/AB	*	*	*	*		*	*	
5 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB		*	*					
	CA	*	*	*	*				
	CA/AB	*	*		*	*			
	CAM	*	*	*	*		*		
	CAM/AB	*	*		*	*	*	*	
7 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB		*	*					
	CA	*	*	*	*				
	CA/AB	*	*		*	*			
	CAM	*	*	*	*	*	*		
	CAM/AB	*	*		*	*		*	
9 mo.	A								
	A/AB	-							
	AM	-	-						
	AM/AB	-	-	*					
	CA	-	-	*	*				
	CA/AB	-	-		*	*			
	CAM	-	-	*	*	*	*		
	CAM/AB	-	-	*	*	*	*	*	

* denotes the statistically significant difference (p-value < 0.05)

Table B10. Pairwise comparison of a*-value between 4 postharvest treatments A (air), AM (Air + MCP), CA (controlled atmosphere storage) and CAM (CA + MCP) with and without antibrowning agent (AB) at 3, 5, 7 and 9 month storage

Storage time		A	A/AB	AM	AM/AB	CA	CA/AB	CAM	CAM/AB
3 mo.	A								
	A/AB	*							
	AM		*						
	AM/AB	*		*					
	CA		*		*				
	CA/AB	*		*		*			
	CAM	*	*		*		*		
	CAM/AB			*			*	*	
5 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB			*					
	CA	*	*	*	*				
	CA/AB	*	*		*	*			
	CAM	*	*		*	*			
	CAM/AB		*		*	*	*		
7 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB	*		*					
	CA		*	*	*				
	CA/AB	*	*	*		*			
	CAM	*	*		*	*	*		
	CAM/AB	*	*	*		*			
9 mo.	A								
	A/AB	-							
	AM	-	-						
	AM/AB	-	-	*					
	CA	-	-		*				
	CA/AB	-	-	*		*			
	CAM	-	-	*	*	*	*		
	CAM/AB	-	-	*				*	

* denotes the statistically significant difference (p-value < 0.05)

Table B11. Pairwise comparison of b*-value between 4 postharvest treatments A (air), AM (Air + MCP), CA (controlled atmosphere storage) and CAM (CA + MCP) with and without antibrowning agent (AB) at 3, 5, 7 and 9 month storage

Storage time		A	A/AB	AM	AM/AB	CA	CA/AB	CAM	CAM/AB
3 mo.	A								
	A/AB								
	AM								
	AM/AB	*	*	*					
	CA				*				
	CA/AB	*	*	*		*			
	CAM	*	*		*	*	*		
	CAM/AB			*			*	*	
5 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB	*		*					
	CA	*	*		*				
	CA/AB		*	*	*	*			
	CAM		*	*	*	*			
	CAM/AB	*		*		*	*	*	
7 mo.	A								
	A/AB								
	AM	*	*						
	AM/AB	*	*	*					
	CA			*	*				
	CA/AB	*		*	*	*			
	CAM	*	*		*	*	*		
	CAM/AB				*		*	*	
9 mo.	A								
	A/AB	-							
	AM	-	-						
	AM/AB	-	-	*					
	CA	-	-	*	*				
	CA/AB	-	-	*		*			
	CAM	-	-	*	*	*	*		
	CAM/AB	-	-	*		*		*	

* denotes the statistically significant difference (p-value < 0.05)

Table B12. Pairwise comparison of ΔE between 4 postharvest treatments A (air), AM (Air + MCP), CA (controlled atmosphere storage) and CAM (CA + MCP) with and without antibrowning agent (AB) at 3, 5, 7 and 9 month storage

Storage time		A	A/AB	AM	AM/AB	CA	CA/AB	CAM	CAM/AB
3 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB			*					
	CA		*		*				
	CA/AB	*		*		*			
	CAM		*		*		*		
	CAM/AB	*		*		*		*	
5 mo.	A								
	A/AB	*							
	AM		*						
	AM/AB	*		*					
	CA	*	*	*	*				
	CA/AB		*		*	*			
	CAM	*	*	*	*	*	*		
	CAM/AB		*		*	*		*	
7 mo.	A								
	A/AB	*							
	AM		*						
	AM/AB	*		*					
	CA	*	*	*	*				
	CA/AB		*		*	*			
	CAM	*	*	*	*	*	*		
	CAM/AB		*		*	*		*	
9 mo.	A								
	A/AB	-							
	AM	-	-						
	AM/AB	-	-	*					
	CA	-	-	*	*				
	CA/AB	-	-	*		*			
	CAM	-	-	*	*	*	*		
	CAM/AB	-	-	*		*		*	

* denotes the statistically significant difference (p-value < 0.05)

B3. The effect of postharvest treatment on the texture of FC apples

Table B13. p-value for main effect and interaction of storage condition (storage) and MCP treatments (MCP), antibrowning treatment (AB) and shelf life (time) of texture of FC apples from apples after 3, 5, 7 and 9 month storage

Factor	Storage time of intact apples, month			
	3	5	7	9
Storage	<0.0001	<0.0001	<0.0001	<0.0001
MCP	<0.0001	<0.0001	<0.0001	<0.0001
Storage * MCP	ns	ns	0.0108	-
AB	0.0178	0.0015	0.0118	<0.0001
Storage * AB	ns	ns	ns	ns
MCP * AB	ns	ns	ns	ns
Storage * MCP * AB	ns	ns	ns	-
Time	ns	ns	ns	ns
Storage * time	ns	ns	ns	ns
MCP * time	ns	ns	ns	ns
Storage * MCP * time	ns	ns	ns	-
AB * time	ns	ns	ns	ns
Storage * AB * time	ns	ns	ns	ns
MCP * AB * time	ns	ns	ns	ns
Storage * MCP * AB *time	ns	ns	ns	-

ns = not significant different (p-value > 0.05)

Table B14. Pairwise comparison of texture between 4 postharvest treatments A (air), AM (Air + MCP), CA (controlled atmosphere storage) and CAM (CA + MCP) with and without antibrowning agent (AB) at 3, 5, 7 and 9 month storage

Storage time		A	A/AB	AM	AM/AB	CA	CA/AB	CAM	CAM/AB
3 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB	*	*						
	CA	*		*	*				
	CA/AB	*	*		*				
	CAM	*	*	*		*	*		
	CAM/AB	*	*			*	*		
5 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB	*	*						
	CA	*	*						
	CA/AB	*	*						
	CAM	*	*	*	*	*	*		
	CAM/AB	*	*	*	*	*	*		
7 mo.	A								
	A/AB	*							
	AM	*	*						
	AM/AB	*	*						
	CA	*	*	*	*				
	CA/AB	*	*	*	*				
	CAM	*	*	*	*	*	*		
	CAM/AB	*	*	*	*	*	*		
9 mo.	A								
	A/AB	-							
	AM	-	-						
	AM/AB	-	-	*					
	CA	-	-		*				
	CA/AB	-	-						
	CAM	-	-	*	*	*	*		
	CAM/AB	-	-	*	*	*	*		

* denotes the statistically significant difference (p-value < 0.05)

B4. The effect of postharvest treatment on the hexyl acetate concentration of FC apples

Table B15. p-value for main effect and interaction of storage condition (storage) and MCP treatments (MCP) and shelf life (time) of hexyl acetate area response apples from apples after 3, 5, 7 and 9 month storage

Factor	Storage time of intact apples, month			
	3	5	7	9
Storage	0.0020	ns	0.0001	0.0001
MCP	<0.0001	ns	ns	ns
Storage * MCP	0.0039	0.0089	ns	ns
Time	0.0027	ns	ns	ns
Storage * time	0.0030	ns	ns	ns
MCP * time	0.0053	ns	ns	ns
Storage * MCP * time	0.0060	ns	ns	ns

ns = not significant different (p-value > 0.05)

Table B16. Pairwise comparison of hexyl acetate concentration in the package headspace of FC apples at the shelf life of 0, 1 and 2 weeks from intact apples that received 4 postharvest treatments A (air), AM (Air + MCP), CA (controlled atmosphere storage) and CAM (CA + MCP) at 3, 5, 7 and 9 month storage

Storage time		A0	A1	A2	AM0	AM1	AM2	CA0	CA1	CA2	CAM0	CAM1	CAM2
3 mo.	A0												
	A1	*											
	A2	-	-										
	AM0	*		-									
	AM1	*		-									
	AM2	-	-	-	-	-							
	CA0	*		-			-						
	CA1	*		-			-						
	CA2	-	-	-	-	-	-	-	-				
	CAM0	*		-			-			-			
	CAM1	*		-			-			-			
	CAM2	-	-	-	-	-	-	-	-	-	-	-	
5 mo.	A0												
	A1	*											
	A2												
	AM0		*										
	AM1												
	AM2												
	CA0		*										
	CA1												
	CA2												
	CAM1		*	*									
	CAM2		*	*		*							
	CAM3		*	*		*							
7 mo.	A0												
	A1												
	A2												
	AM0												
	AM1	*	*	*	*								
	AM2	*	*	*	*								
	CA0					*	*						
	CA1					*							
	CA2					*	*						
	CAM1					*	*						
	CAM2					*							
	CAM3					*	*						
9 mo.	A0												
	A1	-											
	A2	-	-										
	AM0	-	-	-									
	AM1	-	-	-									
	AM2	-	-	-	*								
	CA0	-	-	-			*						
	CA1	-	-	-			*						
	CA2	-	-	-			*						
	CAM1	-	-	-			*						
	CAM2	-	-	-			*						
	CAM3	-	-	-			*						

* denotes the statistically significant difference (p-value < 0.05)

APPENDIX C

MCP CALIBRATION CURVE

Since the known concentration of MCP gas was not available, 1-butadiene was selected for construction of MCP calibration curve due to their similarity in their chemical structure. 1-Butadiene was injected into a glass jar with a known volume to give a concentration of 1.5, 6, 33.3 and 100 $\mu L\ L^{-1}$ in the headspace. The volume of 50, 100, 200, 300, 400 and 500 μL of the headspace were withdrawn using the airtight syringe and injected into a gas chromatography equipped with a flame ionization detector. The calibration curve is presented in Figure C1. The statistical analysis were presented in Table C1-C2.

MCP calibration curve prepared using 1-Butadiene is a linear relationship in the range of 0 – 0.06 μL of MCP. The calibration equation is:

Area response = (6012408 * volume of 1-butadiene) + 3575.01

This equation is adequately describe the relationship of the area response from gas chromatography and volume of 1-butadiene injected (p-value < 0.0001). Both the slope and the intercept of the models are significant (both p-values < 0.0001). The intercept represents the area response when injected blank (air without 1-butadiene). Thus, when use the calibration equation to calculate the concentration of MCP, the area response of the blank for that particular day was subtracted from the area response of the sample. Then, only the slope was used to calculate the concentration as in the following equation:

$$\text{volume of MCP} = \frac{\text{Corrected area response}}{6012408}$$

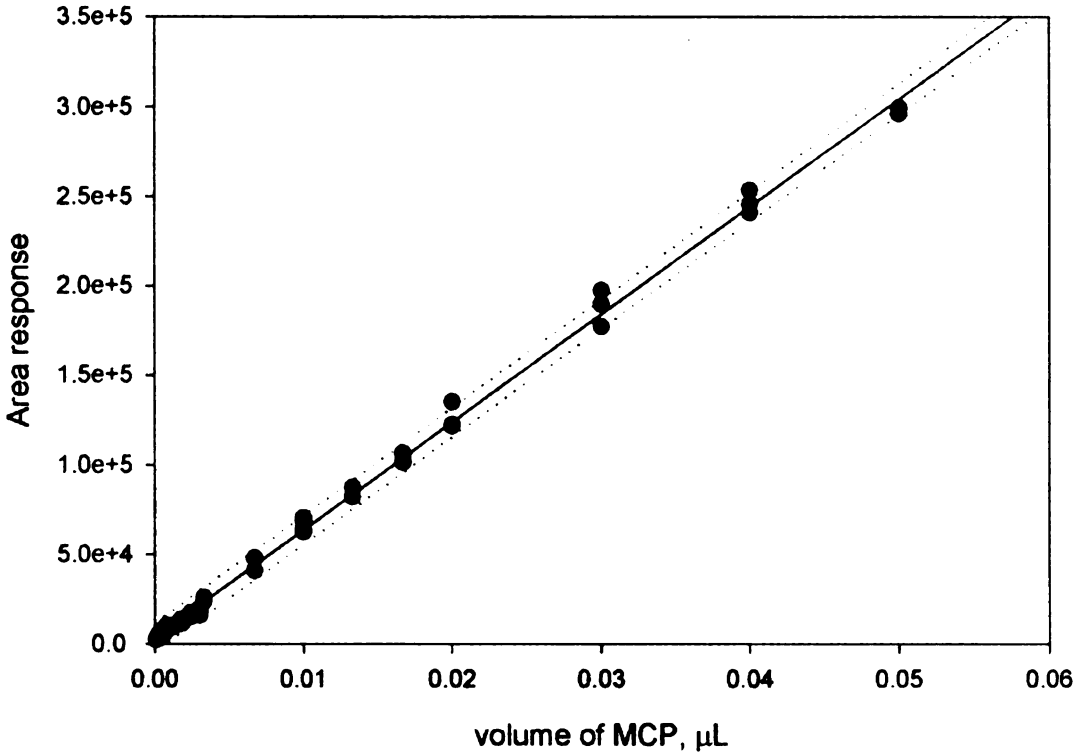

Figure C0.1. MCP calibration curve prepared using 1-butadiene. The solid line represents the predicted value and the dotted lines represent the prediction interval.

Table C1. Analysis of variance for calibration equation

	df	SS	MS	F	Significance F
Regression	1	4.44E+11	4.44E+11	27054.53	8.53E-86
Residual	64	1.05E+09	16413459		
Total	65	4.45E+11			

Table C2. t-test results for regression parameters of calibration equation

	Coefficients	Standard Error	t Stat	P-value
Intercept	3575.01	610.292	5.86	1.77E-07
Slope	6012408	36553.45	164.48	8.53E-86

APPENDIX D

CALCULATION OF THE REQUIRED AMOUNT OF SMARTFRESH™

Example of the calculation of the amount of SmartFresh™ required to established a desired concentration of MCP (X $\mu L.L^{-1}$) in a treatment chamber with volume = V liter.

1) Volume of MCP in a treatment chamber = V_{MCP} (mL) = $X.V \times 10^{-3}$
2) Weight of MCP in a treatment chamber, w (g) is calculated based on the Ideal gas Law.

$$P \cdot V = \frac{w}{MW} \cdot R \cdot T$$

Where P is pressure (atm)

MW is molecular weight of MCP (54 g)

R is gas constant (82.06 $atm.mL.mole^{-1}.K^{-1}$)

T is temperature (K)

3) Amount of SmartFresh™ required = $\frac{100 \cdot w}{\%\text{ active ingredient of SmartFresh}}$

To determine the amount of SmartFresh™ required to established 1 $\mu L\ L^{-1}$ of MCP in 30 gallon (113.56 L) barrel, used in Chapter 2, are shown as an example.

Volume of MCP in a treatment chamber = V_{MCP} = $1 \times 113.56 \times 10^{-3}$ mL

Weight of MCP in a treatment chamber, w (g) is calculated based on the Ideal gas Law.

$$1\ \text{atm} \times 113.56 \times 10^{-3}\ \text{mL} = \frac{w}{54\ \text{g}} \cdot 82.06 \frac{\text{atm} \cdot \text{mL}}{\text{mole K}} \cdot (273 + 20)$$

$$w = 0.00026\ \text{g}$$

$$\text{Amount of SmartFresh}^{\text{TM}}\ \text{required} = \frac{100 \times 0.00026\ \text{g}}{0.14} = 0.18\ \text{g}$$

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